ALLENYLPHOSPHONATES-UTILITY IN C-C AND C-X (X = N, O) BOND FORMING REACTIONS

AND

REACTIVITY OF PHOSHORUS (IIIJ COMPOUNDS WITH ACTIVATED ALKYNES, ALKENES AND ALLENES

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

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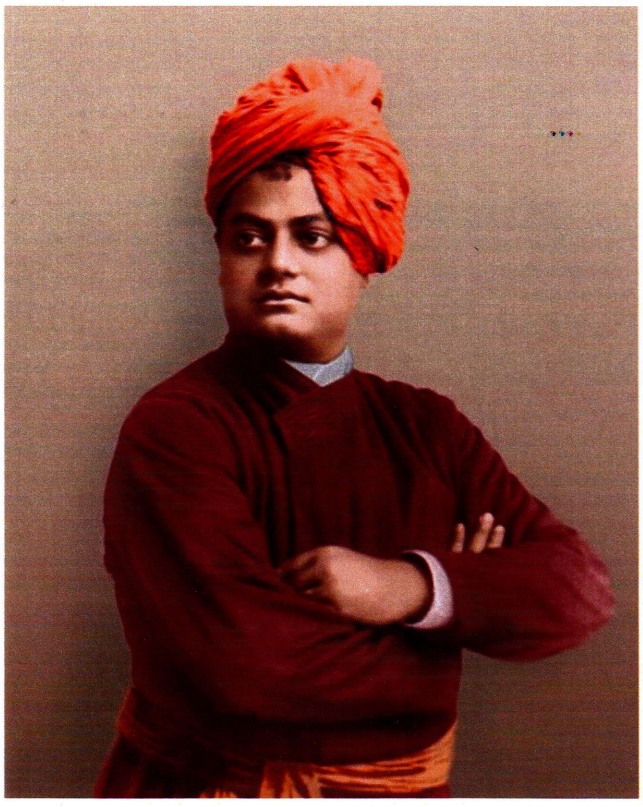

All power is within you;
you can do anything and everything.
Believe in that,
do not believe that you are weak.
Stand up and express the divinity within you.

- Swami Vivekananda

Dedicated to my family

CONTENTS

PART B

REACTIVITY OF PHOSHORUS(III) COMPOUNDS WITH ACTIVATED ALKYNES, ALKENES AND ALLENES

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, Hyderabad, under the supervision of Prof. K. C. Kumara Swamy.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

Hyderabad

November 2008

N. N. Bhuvan Kumar

CERTIFICATE

This is to certify that the work described in this thesis entitled "*Allenylphosphonates-Utility in C–C and C–X (X = N, O) Bond Forming Reactions and Reactivity of Phosphorus(III) Compounds with Activated Alkynes, Alkenes and Allenes*" has been carried out by Mr. N. N. Bhuvan Kumar, under my supervision and the same has not been submitted elsewhere for any degree.

Hyderabad

November 2008

Prof. K. C. Kumara Swamy

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Dean

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LIST OF PUBLICATIONS

1. Further Characterization of Mitsunobu-Type Intermediates in the Reaction of Dialkyl Azodicarboxylates with P(III) Compounds
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N. N. Bhuvan Kumar, Manab Chakravarty, N. Satish Kumar, K. V. Sajna and K. C. Kumara Swamy
J. Chem. Sci. (*accepted*).

9. Mitsunobu and Related Reactions: Advances and Applications
K. C. Kumara Swamy, **N. N. Bhuvan Kumar**, E. Balaraman and K. V. P. Pavan Kumar (Submitted).

10. Base catalysed reactions of salicylaldehydes with allenylphosphonates
N. N. Bhuvan Kumar, M. N. Reddy and K. C. Kumara Swamy (*to be communicated*).

11. Synthesis of phosphono-vinyl and phosphono-allyl ethers in base catalyzed reactions and synthesis *trans*-1,3-butadiene
N. N. Bhuvan Kumar and K. C. Kumara Swamy (*to be communicated*).

12. Lewis acid catalyzed Stereoselective allylation of activated aromatics
N. N. Bhuvan Kumar, K. Ramesh and K. C. Kumara Swamy (*to be communicated*).

13. Synthesis of tetracyclic rings from Diels-Alder reaction of allylphosphonates
N. N. Bhuvan Kumar, K. V. Sajna and K. C. Kumara Swamy (*to be communicated*).

Papers presented in symposia

1. Towards Chiral Cyclotriphosphazenes
N. Satish Kumar, **N. N. Bhuvan Kumar** and K. C. Kumara Swamy
MTIC-X, IIT Bombay, INDIA, Dec 2003.

2. Reaction of Phosphorus(III) Compounds with Activated Acetylenes and Dialkyl Azodicarboxylates
K. C. Kumara Swamy and **N. N. Bhuvan Kumar**
8th National Symposium in Chemistry (CRSI), IIT Bombay, INDIA, Feb 2006.

3. Allenylphosphonates–Versatile Precursors for the Carbon-Carbon and Carbon-Heteroatom Bond Forming Reactions
N. N. Bhuvan Kumar and K. C. Kumara Swamy
Chemfest-2008, School of Chemistry, University of Hyderabad, March-2008 (**Oral Presentation**).

Synopsis

This thesis divided into two parts: Part-A and Part-B. Part-A deals with the synthesis of various new phosphorus based allenes and their utility in C-C and C-X (X = N, O) bond forming reactions. Part-B involves the reactions of various phosphorus(III) compounds with activated alkynes, alkenes and allenes in an effort to isolate and characterize compounds analogous to the intermediates proposed in phosphine-catalyzed reactions.

Each part is subdivided into three chapters: (a) Introduction (literature survey), (b) Results and Discussion and (c) Experimental. The compounds obtained in the present study are characterized by Mp, IR and NMR (^{1}H, ^{13}C & ^{31}P) techniques followed by elemental analysis (of representative compounds). Wherever feasible, X-ray crystal structures are determined. References are compiled at the end of each part.

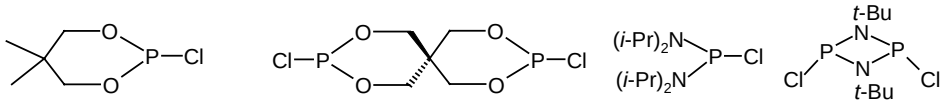
PART-A

In the Chapter 1, a review of literature on aspects relevant to this part is presented. Chapter 2 describes the results obtained on the above-mentioned aspects. The experimental details are presented in Chapter 3. Important results are outlined below.

(i) Phosphorus(III) precursors and allenes/allenylphosphonates

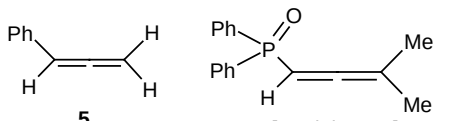
The phosphorus(III) precursors **1-4** and the allenes **5**, **6**, **7a-k**, **8a-b** and **9** used in the present study are shown in Charts 1 and 2. Among these, **7e-h**, **7j**, **7k**, **8a-b** and **9** are new [*Note*: The numbering of compounds given here is different from that in the main part of the thesis].

Chart 1



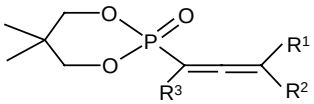
1 [b.p. 40°C/ 1mm, δ(P): 145.8] **2** [δ(P): 206.5] **3** [δ(P): 148.9] **4** [δ(P): 206.5]

Chart 2

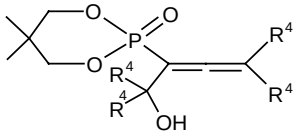


5

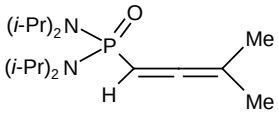
[**6**, δ(P): 26.0]



7a-k



R^4 = H [**8a**, δ(P): 10.1, 17% isolated yield; X-ray][a]
R^4 = Me [**8b**, δ(P): 10.9, 75%][a]



[**9**, δ(P):19.6, 80%][a]

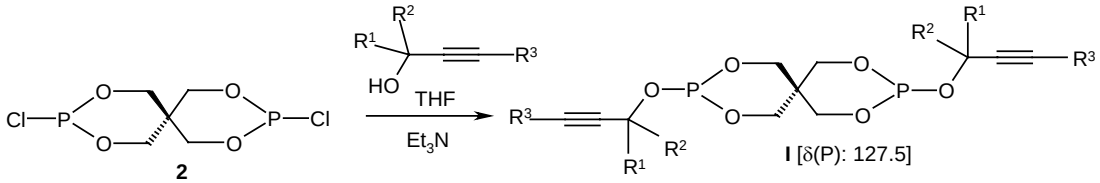
$R^1 = R^2 = R^3 = H$	[**7a**, δ(P): 7.4]
$R^1 = R^3 = H$ $R^2 = Me$	[**7b,** δ(P): 7.9]
$R^1 = R^2 = Me$, $R^3 = H$	[**7c**, δ(P): 8.5]
$R^1 = Me$, $R^2 = Et$, $R^3 = H$	[**7d**, δ(P): 9.3]
$R^1 = R^2 = H$, $R^3 = Phenyl$	[**7e**, δ(P): 6.6, 80%][a]
$R^1 = R^2 = H$, $R^3 = 4$- tolyl	[**7f**, δ(P): 7.8, 80%][a]
$R^1 = R^2 = H$, $R^3 = 4$ - anisyl	[**7g**, δ(P): 7.5, 80%][a]
$R^1 = H$, $R^2 = (CH=CHMe)$, $R^3 = Ph$	[**7h**, δ(P): 6.7, 70%][a]
$R^1 = R^2 = H$, $R^3 = Me$	[**7i**, δ(P): 12.2, 90%]
$R^1 = Pentyl$, $R^2 = R^3 = H$	[**7j**, δ(P): 11.3, 80%][a]
$R^1 = Hexyl$, $R^2 = R^3 = H$	[**7k**, δ(P): 11.2, 78%][a]

[a] New phosphorus-based allenes synthesized in this study

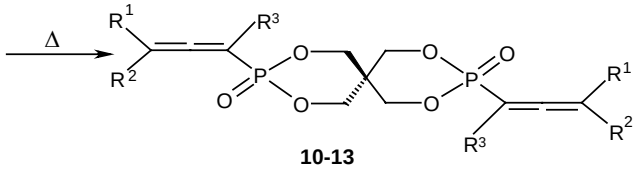
(ii) Synthesis of new bis(allenyl)phosphonates, *cis*- and *trans*-bis(allenyl)cylclodiphosph(V)azanes and a bis(allyl)cyclodiphosph(V)azane

Compounds **10**-**13** that also contain the 1,3,2-dioxaphosphorinane ring with two reactive allene residues have been prepared in good yields by slightly modifying the procedure adapted for the synthesis allenylphosphonate **7e**, using $[ClP(OCH_2)_2]_2C$ (**2**) and the appropriate propargyl alcohol (Scheme 1). The structure of the compound **10** was confirmed by X-ray crystallography.

Scheme 1



2 **I** [δ(P): 127.5]



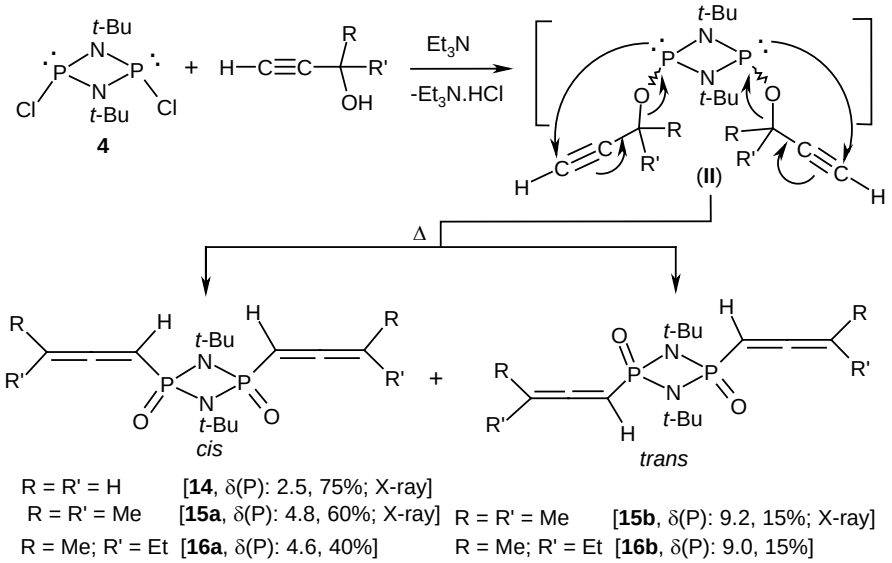
10-13

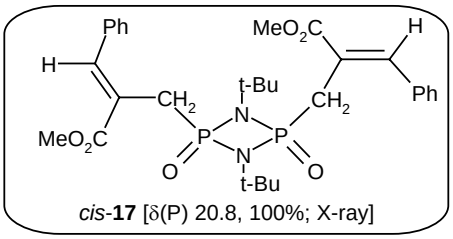
$R^1 = R^2 = R^3 =$ H [**10**, δ(P): 11.4, 79%; X-ray]
$R^1 =$ Et, $R^2 =$ Me, $R^3 =$ H [**11**, δ(P): 13.0, 74%]
$R^1 = R^2 =$ Me, $R^3 =$ H [**12**, δ(P): 12.6, 76%]
$R^1 = R^2 =$ H, $R^3 =$ Ph [**13**, δ(P): 10.6, 74%]

Compounds **14**, **15a-b** and **16a-b** were synthesized by treating *cis*-$[ClP(\mu\text{-N-}t\text{-Bu})]_2$ (**4**) with the corresponding propargyl alcohol in the presence of triethylamine

(Scheme 2). The reaction using the unsubstituted propargyl alcohol HC≡CCH$_2$OH gave essentially the *cis* isomer **14** and only traces of the *trans* isomer. In contrast, substituted propargyl alcohols HC≡CC(Me)(R)OH (R= Me, Et) afforded both *cis*- and *trans*-products **15a-b** and **16a-b**. The bis(allyl)cyclodi*phosph(V)*azane **17** was prepared similarly using **4** and the corresponding Baylis-Hillman alcohol. The X-ray structures of *cis*- and *trans*- isomers **15a-b** are shown in Fig. 1**.**

Scheme 2





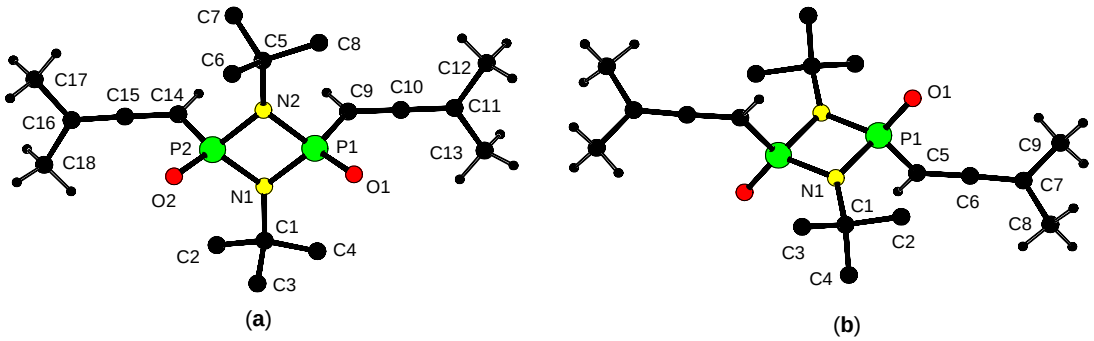


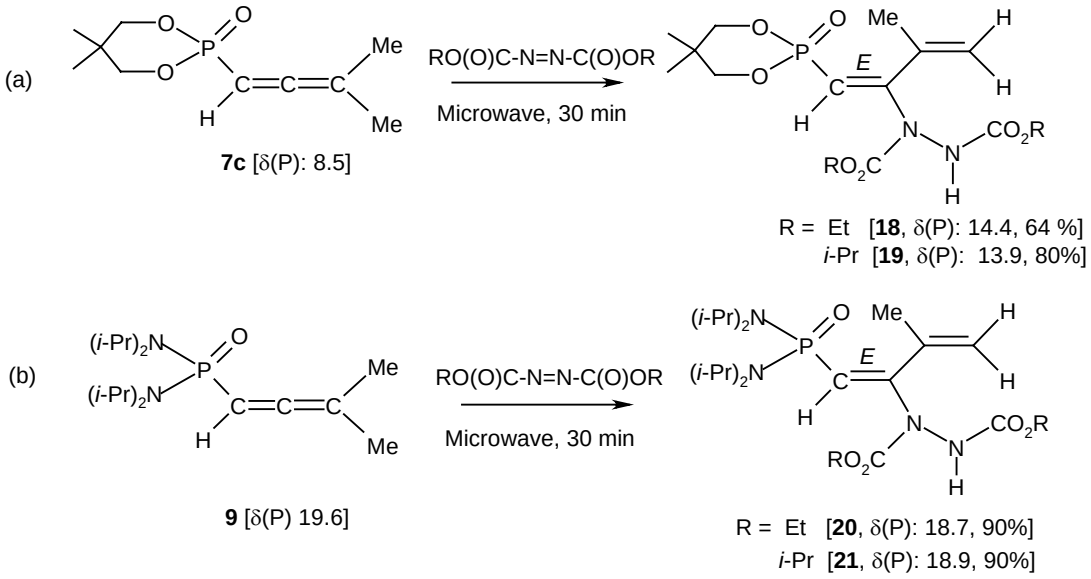
Fig. 1. Molecular structures of (a) **15a** and (b) **15b**.

(iii) Reactions of allenyl phosphonates/ phosphoramidates with dialkyl azodicarboxylates

(a) Synthesis of phosphonyl substituted trans-1,3-butadienes (18-21)

Heating allenylphosphonate **7a** or **7b** with diethyl azodicarboxylate (DEAD) or diisopropyl azodicarboxylate (DIAD) under MW conditions (160 W; ~ 180 ^{o}C) for about 30 min afforded a mixture of products. However, treatment of **7c** with DEAD or DIAD gave stable 1,3-butadiene products **18-19** *regio- and stereo-specifically* in ≥60% yield (Scheme 3a). This feature appears to be general for =CMe_2 terminal allenes since we could isolate analogous butadienes **20-21** (Scheme 3b) starting from the allene **9**.

Scheme 3



7c [δ(P): 8.5]

R = Et [**18**, δ(P): 14.4, 64 %]
i-Pr [**19**, δ(P): 13.9, 80%]

9 [δ(P) 19.6]

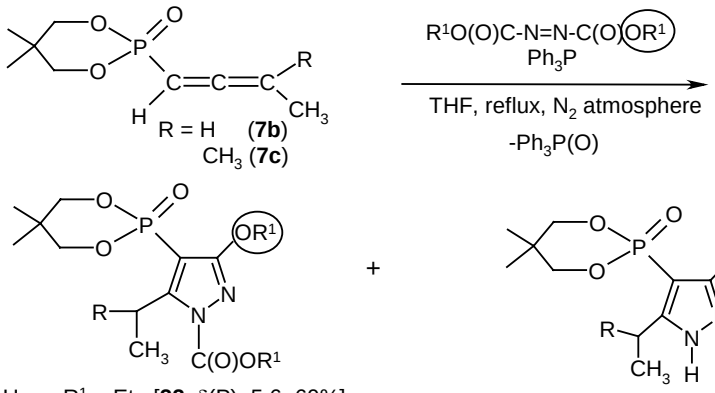
R = Et [**20**, δ(P): 18.7, 90%]
i-Pr [**21**, δ(P): 18.9, 90%]

(b) Synthesis of phosphonopyrazoles

We have performed the above reaction of allenylphosphonates (**7a-d)** with DEAD/DIAD in the presence of Ph_3P. The rationale for this comes from the fact that the phosphine reacts with DIAD/DEAD to give the reactive zwitterion Ph_3P^{+}-$N(CO_2R)$-$N^{-}(CO_2R)$ that should result in products other than **18-21**. Although the =CH_2 terminal allene **7a** when treated with DIAD in the presence of PPh_3 rearranged to give the acetylene $(OCH_2CMe_2CH_2O)P(O)C{\equiv}CMe$, allenylphosphonates **7b-c** readily reacted with Ph_3P-DEAD/DIAD to afford the phosphono-pyrazoles **22-24** and **25** (Scheme 4)**.**

Mechanistic pathways leading to these novel pyrazoles are discussed. Allene **7d** did not react appreciably under these conditions.

Scheme 4

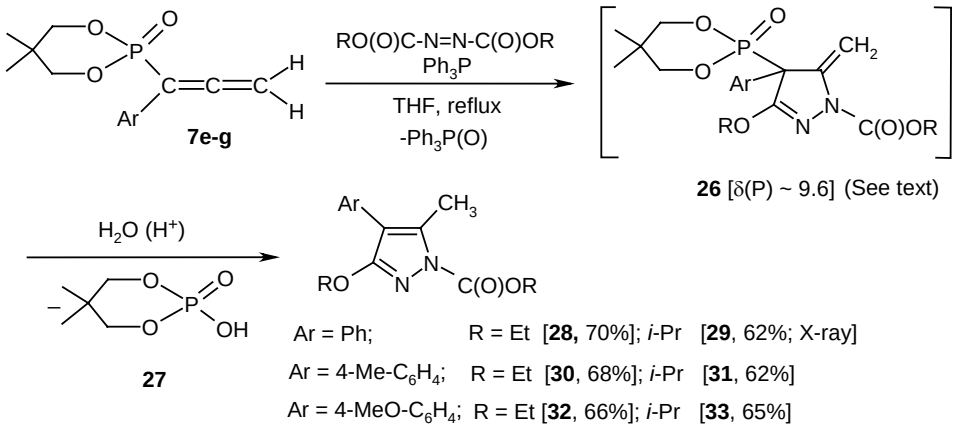


R = H, R^1 = Et [**22**, δ(P): 5.6, 60%]
R = H, R^1 = *i*-Pr [**23**, δ(P): 6.3, 70%]
R = CH_3, R^1 = *i*-Pr [**24**, δ(P): 6.7, 50%; X-ray] R = CH_3, R^1 = *i*-Pr [**25**, δ(P): 10.7, 20%; X-ay]

(c) Novel P-C bond cleavage in phosphono-pyrazolines leading to tetra substituted pyrazoles

In contrast to the above, reaction of allenylphosphonates **7e-g** with Ph_3P-DIAD/DEAD afforded tetrasubstituted pyrazoles **28**-**33** by a facile P-C bond cleavage reaction *via* the phosphono-pyrazoline intermediate **26** (Scheme 5). Species **26**, where R = *i*-Pr; Ar = Ph was identified by ^1H and ^{31}P NMR spectroscopy; in other cases the evidence was from ^{31}P NMR [δ(P) ~ 9] only. The structure of the compound **29** was confirmed by X-ray crystallography. This type of P-C bond cleavage is unique and unprecedented. The phenylallene **5** did not react with DIAD under these conditions.

Scheme 5

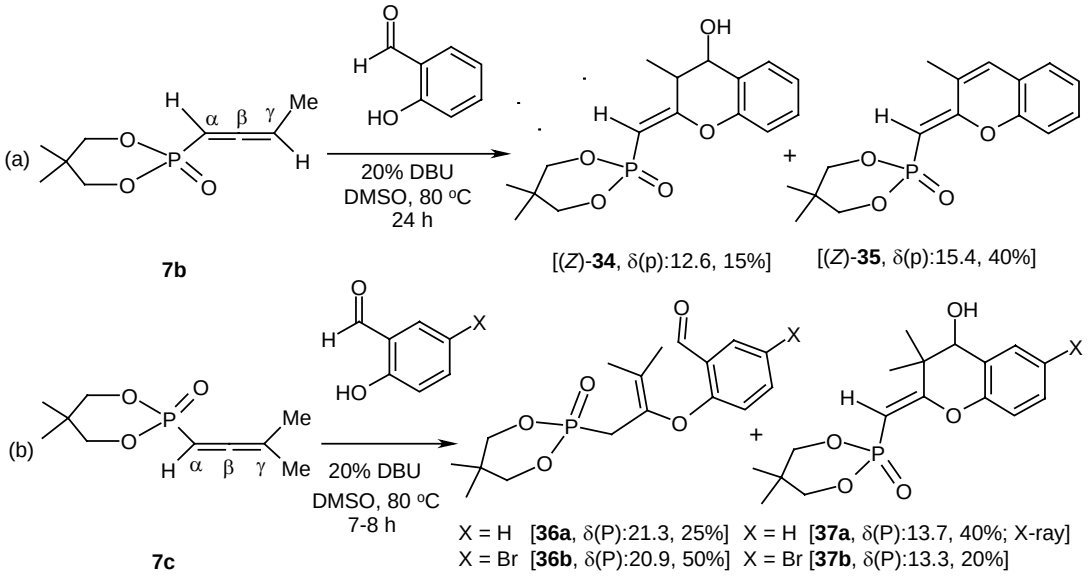


(iv) Base catalyzed reactions of allenylphosphonates with substituted salicylaldehydes

(a) Reaction of allenylphosphonates 7a-c with salicylaldehydes

The reaction of salicylaldehydes with allenylphosphonates in the presence of a base can lead to a variety of phosphono-chromenes and allylic phosphonates. In the present work, the reaction conditions were optimized by using **7e** which is discussed below. Allenylphosphonate **7a** upon treatment with salicylaldehyde in the presence of DBU rearranged to isomeric acetylene $(OCH_2CMe_2CH_2O)P(O)C{\equiv}CMe$. In the case of **7b**, we isolated the phosphono-chromenes (*Z*)-**34** and (*Z*)-**35** (Scheme 6a), but the yields were low. By contrast, the reaction using allenylphosphonate **7c** led to the allylic phosphonates **36a-b** and phosphono-chromenes **37a-b** (Scheme 6b). The geometry of (*Z*)-**37a** was confirmed by X-ray crystallography.

Scheme 6



(b) Reactions of allenylphosphonate 7e with salicylaldehydes and 2-hydroxy aceto-/benzo-phenone

We treated the allenylphosphonate **7e** with salicylaldehyde in the presence of various bases and in different solvents to optimize the reaction conditions. It was found that this reaction led exclusively [^{31}P NMR evidence] to phosphono-chromene **38** using DBU as the base and dimethyl sulfoxide (DMSO) as the solvent. Under the standardized conditions, we have conducted the reactions of a variety salicylaldehydes and 2-hydroxy aceto-/benzo-phenone with allenylphosphonate **7e** for the synthesis of different phosphono-chromenes and also to check the scope and limitations of the reaction (Scheme 7). The overall (combined) isolated yields of the two (*E*/*Z*) isomers **38-44** are moderate to good (Table 1). We have also separated individual isomers in all cases except in **43** (only *E*-isomer isolated); since the R_f values are too close this separation was a bit more tedious and only small quantities of pure isomers were isolated. For compound **40**, structures of both *E* and *Z* isomers were confirmed by X-ray crystallography. Interestingly, interconversion of *E* and *Z* isomers takes place readily in these compounds. Possible rationalization of these results is presented in the thesis.

Scheme 7

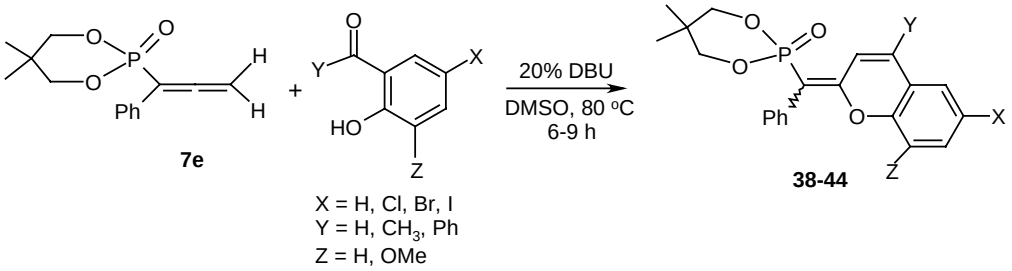


Table 1. ^{31}P NMR data and isolated yields of the compounds **38-44**

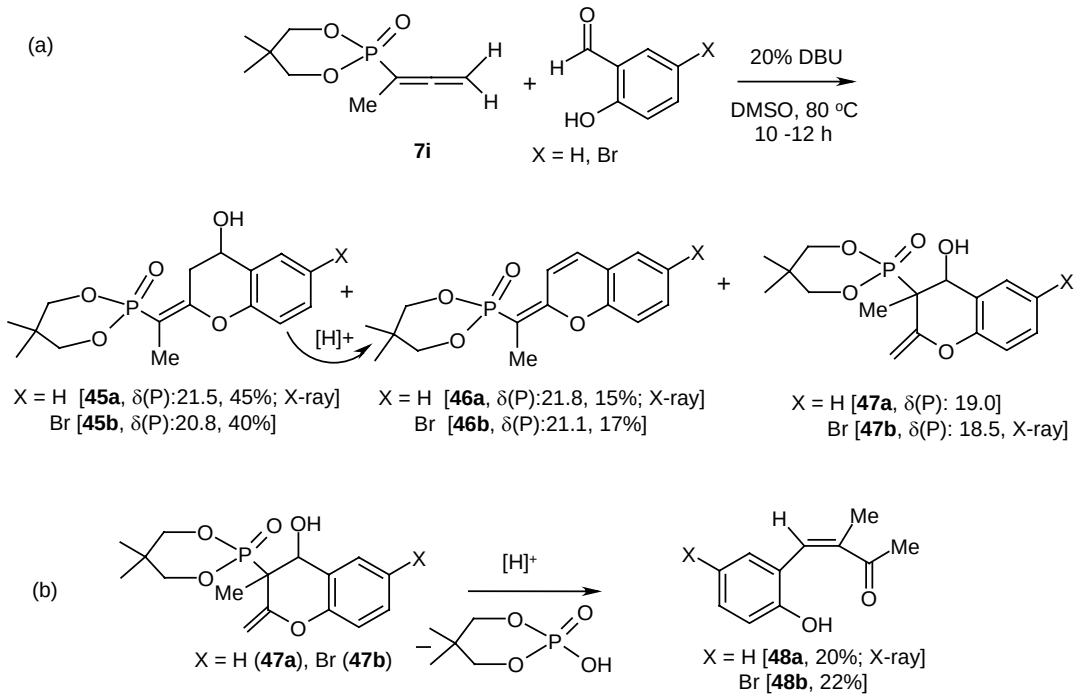
Entry	Compound	δ(P)		Yield (%)(*E*:*Z*)[a]
		(*E*)	(*Z*)	
1	**38**	15.3	12.2	91(1.0:0.6)
2	**39**	12.6	10.8	70(1.0:1.1)
3	**40**	12.5	9.2	84(1.0:1.3)
4	**41**	14.8	11.4	60(1.0:1.2)
5	**42**	15.5	12.0	70(1.0:0.8)
6	**43**	16.4	-	80(1.0:0.8)
7	**44**	15.9	12.5	59(1.0:1.4)

[a]Isolated yields of the pure compounds (combined yields of *E* and *Z* isomers)

(c) Reactions of allenylphosphonate 7i with salicylaldehydes and 2-hydroxy acetophenone

In place of the *α*-phenyl compound **7e**, use of the allenylphosphonate **7i** in the above reaction under similar conditions as for the preparation of **38** led to different types of phosphonochromenes **45-47** (Scheme 8a). However, compounds **45a-b** were converted to **46a-b** in the presence of the base at high temperature (> 80 ^{o}C) or in the presence of 2M HCl at room temperature. The compounds **47a-b** were rather unstable towards moisture [^{1}H NMR evidence]. They underwent novel P-C bond cleavage to give 4-(2-hydroxy aryl)-3-mehtyl buten-2-ones **48a-b** (Scheme 8b).

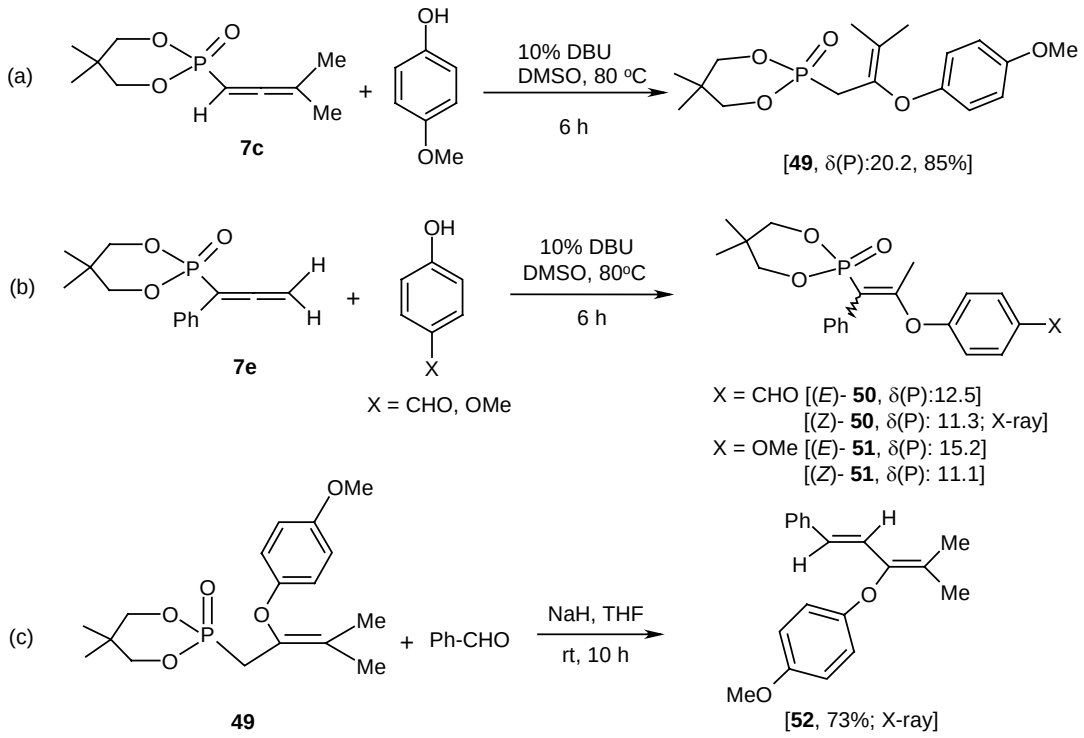
Scheme 8



(v) Reactions of allenylphosphonates 7c and 7e with phenols: Synthetic utility of the product in HWE reaction

In continuation of the above reactions, we wanted to check the reactivity of the phenols with allenylphosphonates in the presence of a base that could help in understanding the first step in the reaction with salicylaldehydes. Thus the reaction between **7c** with 4-hydroxy anisole in the presence of 10 mol% of DBU gave only allylic phosphonyl ether **49** (Scheme 9a) in good yields. In contrast, the allenyl phosphonate **7e** reacted with 4-hydroxy benzaldehye/anisole in the presence of DBU to give vinylic phosphonates **50/51** (Scheme 9b). The isolated yields of the both *E* and *Z* isomers are ≥90% for **50**-**51**. The compound **49** underwent Horner-Wadsworth-Emmons (HWE) reaction with benzaldehyde in the presence of NaH in THF to give the *trans*-1,3-butadiene **52** as shown in the Scheme 9c.

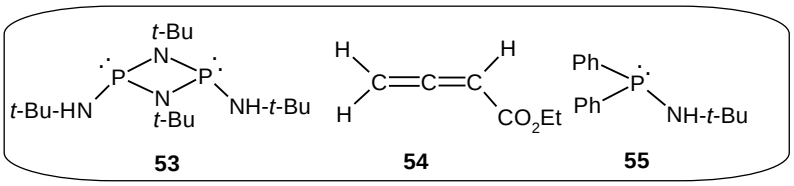
Scheme 9



PART-B

Chapter 4 focuses on literature survey on formation of zwitterions from the reactions of various phosphorus(III) compounds with unsaturated systems like alkenes, alkynes and allenes in the context of phosphine catalyzed reactions. In Chapter 5, the results obtained on the above aspects are discussed. Chapter 6 deals with the experimental details. Important results are outlined below.

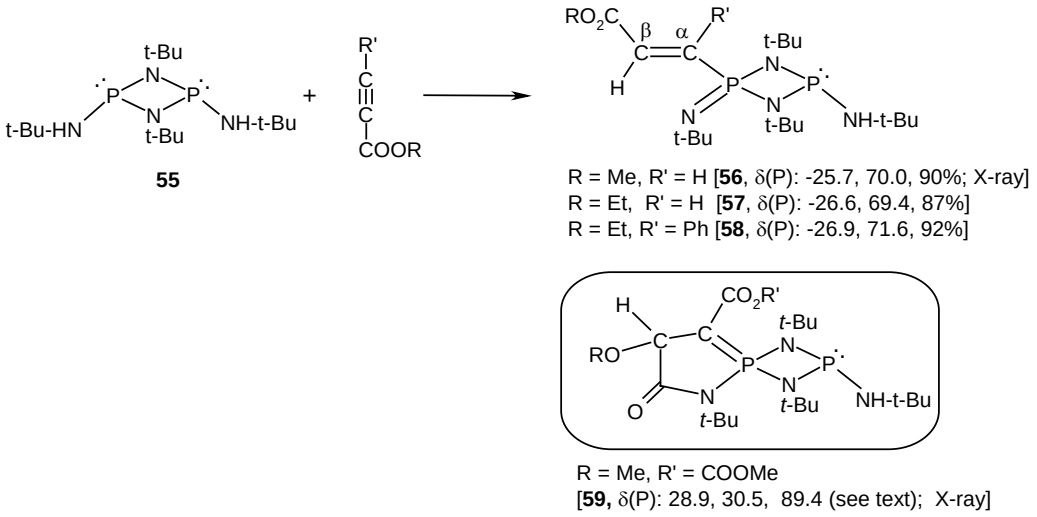
The P^{III} precursors **53, 55** and the allene **54** were obtained by using literature procedures.



(vi) Reactions of cyclodiphosphazane 53 with activated alkynes

The reaction of **53** with activated alkynes (methyl propiolate, ethyl propiolate and ethyl phenylpropiolate) led to compounds **56-58** (Scheme 10) in which the NH proton of the N*H*-*t*-Bu group has moved to the *β*–carbon of alkyne residue. In contrast to above, the reaction of **53** with dimethyl acetylenedicarboxylate (DMAD) led to the novel heterocycle **59**. The initial reaction mixture, when **53** was treated with DMAD, showed major peaks (85%) at δ 72.2 (br), -25.0 (br), -35.3 (br), with the combined intensity of the peaks at δ -25.0 and -35.3 [P^V region] nearly the same as the one at δ 72.2 [P^{III} region]. These are clearly different from those for the final product **59**, but the peaks at δ 72.2 and -25.0 are close to that for **56** and clearly show that formation of **59** occurs *via* a species similar to **56**.

Scheme 10

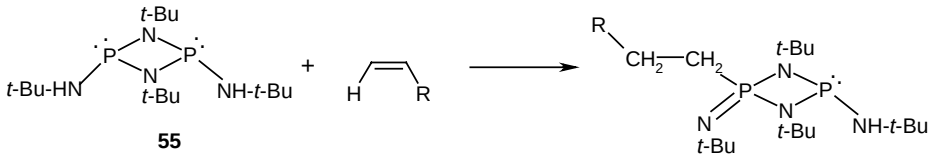


(vii) Reactions of cyclodiphosphazane 53 with activated alkenes

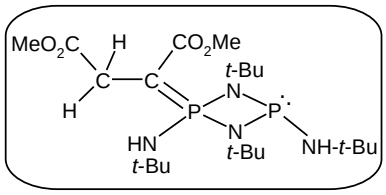
We treated **53** with unsymmetrical activated alkenes CH_2=CHR [R = CO_2R, CN, SO_2Et] and obtained compounds **60-64** (Scheme 11) that are analogous to those with ethyl propiolate discussed above. We also treated **53** with dimethyl maleate and obtained a stable ylide **65,** which is different from **60-64.** From these results, it appears that the reactivity of the P^{III} with activated symmetrical alkenes and alkynes

(dicarboxylates) are different from those of unsymmetrical ones. Compound **65** is close to the first step intermediate in phosphine catalyzed Morita-Baylis-Hillman (MBH) reaction.

Scheme 11



R = CN [**60**, δ(P): -12.2, 73.0, 90%; X-ray]
R = CO_2Me [**61**, δ(P): -6.4, 72.3, 87%]
R = CO_2Et [**62**, δ(P): -6.2, 72.8, 90%]
R = CO_2-*t*-Bu [**63**, δ(P): -3.4, 72.1, 87%]
R = SO_2Et [**64**, δ(P): -10.4, 72.8, 82%]

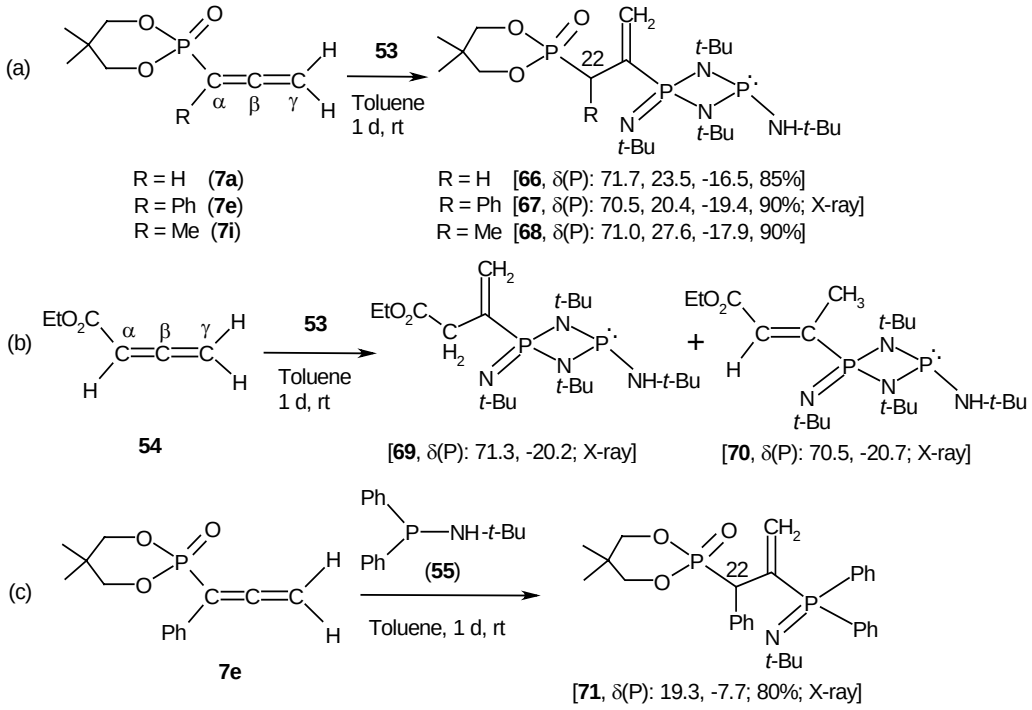


65, δ(P): 23.7, 78.9, 90%; X-ray

(viii) Reactions of phosphorus(III) compounds 53 and 55 with activated allenes

Cyclophosphazane **53** reacts with allenes **7a, 7e** and **7i** to lead to compounds **66-68** shown in the Scheme 12a. In contrast, in the reaction using the ester allene **56**, we obtained the rearranged product **70** by keeping the initially formed product **69** in solution over a period of 2 d (Scheme 12b). Thus the allenylphosphonates and ester allene **54** differ marginally as regards the nature of the final product. We have also shown in Scheme 12c that the aminophosphine Ph_2P(NH-*t*-Bu) (**55**) leads to the product **71** that is similar to **66** which suggests that the reaction is more general for compounds with a P-NH-*t*-Bu group. Confirmatory structural proof for **67** (*R* and *S* forms), **69-70** and **71** is given by single crystal X-ray crystallography.

Scheme 12



(ix) Spontaneous resolution

It may be noted that in compounds **67** and **71**, a chiral center is generated at C(22) in each case. Interestingly, in both of these cases, the compounds crystallized in the chiral space groups, *Pna2₁* and *P2(1)2(1)2(1)* respectively. The absolute configurations at the chiral center as suggested by *checkcif* are *S* and *R*, respectively. In the case of **67**, we checked the structures of several crystals and were able to obtain the structures of both the *S* and the *R* enantiomers (Fig. 2).

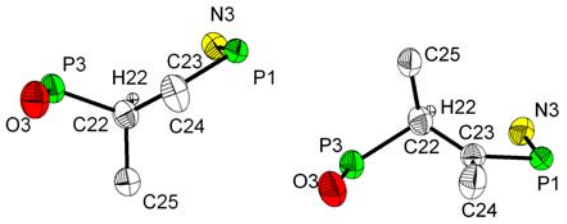


Fig. 2. A picture showing the *R* (left) and *S* (right) configurations at C(22) in the two different crystals of **67**.

PART A

ALLENYLPHOSPHONATES-UTILITY IN C–C AND C–X (X = N, O) BOND FORMING REACTIONS

Chapter 1

INTRODUCTION

1.1 General Introduction: Importance of allenes in C-C and C-X (X = N, O) bond formation reactions

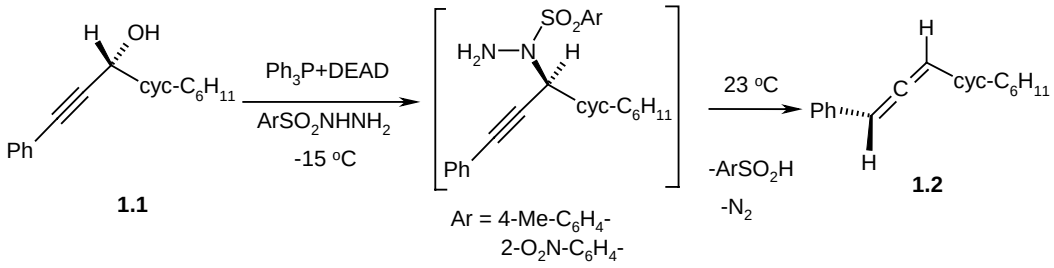
Reactions involving carbon-carbon and carbon-hetero bond formation are central to organic synthesis.[1] In the last decade, metal/nucleophile catalyzed C-C and C-X (X = N, O) bond forming reactions have become important for the preparation of hetrocycles in both academic and pharmaceutical laboratories.[2] In this context, allenes, with two cumulative and orthogonal double bonds, are very versatile precursors for the synthesis of valuable biologically active heterocycles such as furanones, γ- and δ- lactones, functionalized di-hydrofurans, benzofurans, pyrazoles, chromenes, and many more.[3] Allenes also exist in many natural products with interesting biological activities.[3a,b] In the past decade, many highly selective and novel reactions of allenes, which can usually be tuned by electronic/ steric effects and the nature of catalysts involved, have been discovered.[3c-f] Synthetic potential of allenes arises from their substituent-loading capability, axial chirality and three reactive carbon sites. If one of the sustituents on allene is the $-P(O)(OR)_2$ moiety, the resulting compounds are allenylphosphonates (phosphorylated allenes). In the following sections, a brief literature survey on the synthesis and utility of allenes/allenylphosphonates in organic synthesis will be presented. Wherever possible, comparison will be made between the reactivity of allenylphosphonates and other allenes.

1.2 Allenylphosphosphonates (phosphorylated allenes)- Synthesis

Allenylphosphonates are valuable precursors in organic synthesis for various organic transformations due to their ready availability, stability and low cost of preparation. A variety of phosphorus heterocycles, tetra-substituted vinyl phosphonates, allylic phosphonates, *β*-keto- and *β*-amino-phosphonates can be easily synthesized from allenylphosphonates.[4]

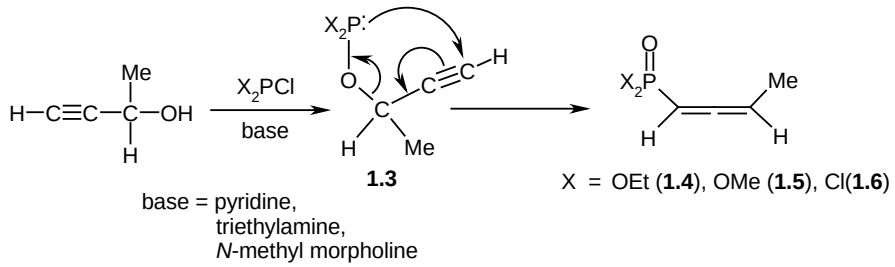
For the synthesis of non-phosphorylated allenes, umpteen methods are available in the literature. A good reference is the book by Brandsma published in the year 2004.[5] There are several other interesting routes to these allenes. In one of these, an activated hydrazine nucleophile is utilized in the Mitsunobu reaction as shown in Scheme 1.1.[6] This route provides access to a wide range of optically active allenes (**1.2**) since a large number of optically active propargyl alcohols (**1.1**) are available. Our interest in this study is mostly on allenylphosphonates and hence more details on the synthesis of this class of compounds are described below.

Scheme 1.1



(i) A convenient method involves the treatment of trivalent phosphorus chlorides X_2PCl with the propargyl alcohols [e.g. Me(H)C(OH)C≡CH] in the presence of a base such as pyridine, triethylamine or *N*-methyl morpholine in a suitable solvent like ether, THF or toluene. The intermediate **1.3** undergoes a pseudo-Claisen type rearrangement, usually at ambient temperature or below, to afford allenylphosphonates **1.4**–**1.6** (Scheme 1.2).[7]

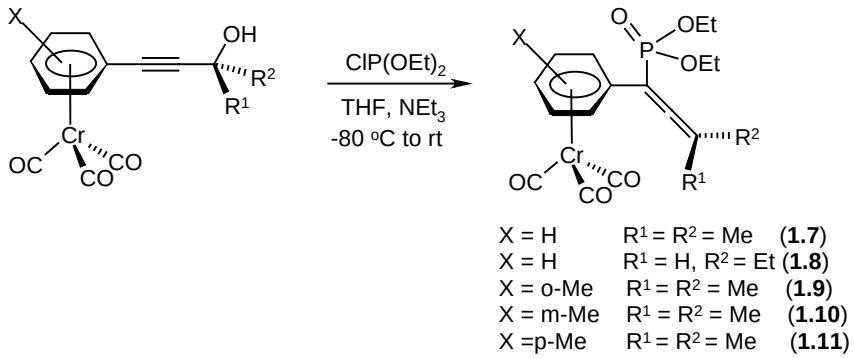
Scheme 1.2



(ii) Allenylphosphonates **1.7**-**1.11** with an α-substituted arene-$Cr(CO)_3$ complex structure have been prepared in good yields (68-80%) from the reaction of

(chloro)diethylphosphite with the corresponding propargyl alcohol in the presence of triethylamine as shown in Scheme 1.3.[8]

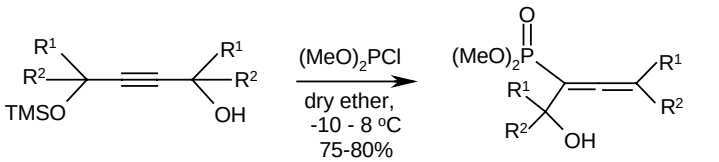
Scheme 1.3



X = H $R^1 = R^2$ = Me (**1.7**)
X = H R^1 = H, R^2 = Et (**1.8**)
X = o-Me $R^1 = R^2$ = Me (**1.9**)
X = m-Me $R^1 = R^2$ = Me (**1.10**)
X =p-Me $R^1 = R^2$ = Me (**1.11**)

(iii) (Hydroxy)allenylphosphonates **1.12-1.14** have been synthesized easily by treating propargyl alcohols with an equimolar amount of appropriate dialkylchlorophosphite in dry ether (Scheme 1.4). Yields were in the range 75–80%.[9] The additional –OH group in these compounds may be of use in annulation reactions later.

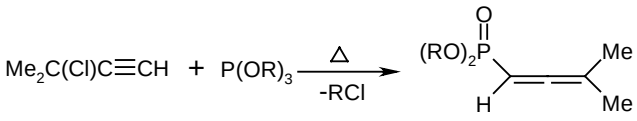
Scheme 1.4



$R^1 = R^2$ = Me (**1.12**)
$R^1 = R^2$ = H (**1.13**)
R^1 = Me, R^2 = H (**1.14**)

(iv) Trialkylphosphites upon heating with 3-chloro-3-methyl-1-butyne lead to allenylphosphonates **1.15-1.16** in moderate to good yields (Scheme 1.5).[10] This method is restricted to the use of terminal alkynes.

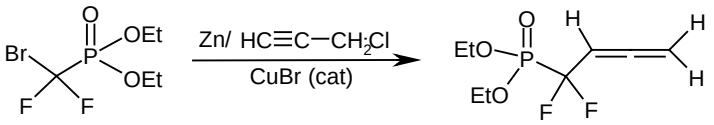
Scheme 1.5



R = Me (**1.15**), Et (**1.16**)

(v) There are other non-conventional routes to specific allenylphosphonates. For example, allenylphosphonate **1.18** can be obtained by alkylation of diethyl bromodifluorophosphonate **1.17** with zinc and propynyl chloride (Scheme 1.6).[11] However, this route has only limited scope because of the only a few α-bromophosphonates are readily accessible.

Scheme 1.6



1.17 **1.18**

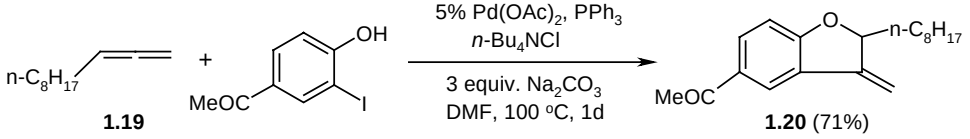
1.3 Transition metal-catalyzed cross coupling and annulation reactions of allenes

Allenes have hybrid character of an olefin and acetylene, and are shown to be reactive toward wide range transition metals (Pd, Pt, Ru, Rh, Cu, Ag, and Au); the resulting species are useful as catalysts/procatalysts.[3b] Among these, palladium compounds are probably the most versatile and widely used catalysts for the synthesis of heterocycles and natural products. They tolerate a variety of functional groups and lead to high stereo- and regio-selectivity. The use of gold compounds in homogeneous catalysis is a relatively new field, but has already witnessed spectacular achievements.[12a-b] By virtue of their unique ability to activate carbon-carbon double and triple bonds as soft, carbophilic Lewis acids, gold salts are highly efficient catalysts for the formation of C-C and C-X (X= N, O, S) bonds.

1.31 *Coupling/cyclization reactions of allenes- Some selected examples*

Larock and co-workers reported the Pd-catalyzed heteroannulations of allenes using functionally substituted aryl halides. The treatment of allene **1.19** with functionalized iodophenol in the presence of $Pd(OAc)_2/PPh_3/(n\text{-}Bu)_4NCl/Na_2CO_3$ at 100 ^oC in DMF afforded benzofuran derivative **1.20** in 71 % yield (Scheme 1.7).[13]

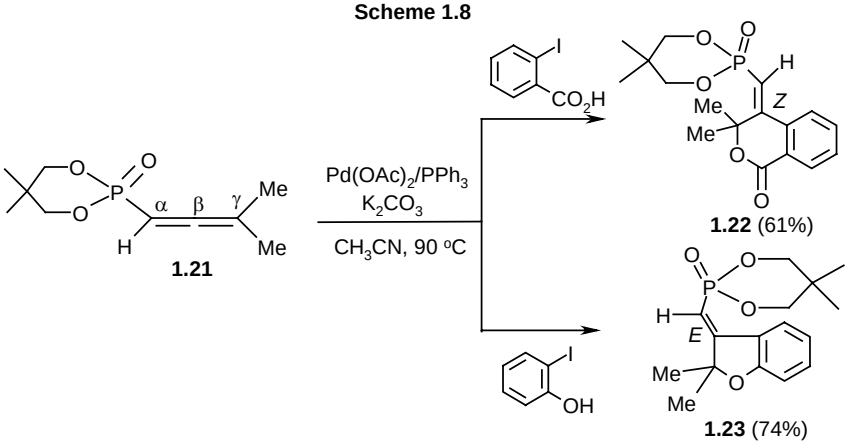
Scheme 1.7



1.19 **1.20** (71%)

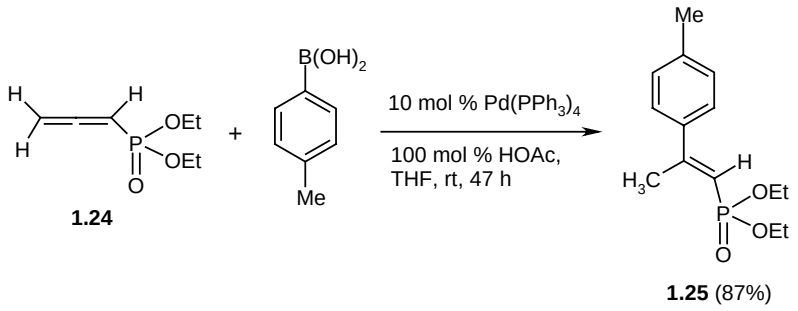
From our laboratory, coupling reactions of various allenylphosphonates with functionalized iodo-aromatics in the presence of Pd^{II}/PPh_3 to give diverse phosphono-benzofurans and phosphono-isocoumarins in good yields have been reported (Scheme 1.8).[14] For example, allenylphosphonate **1.21** reacts stereo-selectively with iodobenzoic acid or iodophenol in the presence of Pd^{II}/PPh_3 and K_2CO_3 to give the corresponding (*Z*)-phosphono-isocoumarin **1.22** or (*E*)-phosphono-benzofurans **1.23**, respectively, in good yields. Unlike the reactions of non-phosphorylated allenes which led to only two types of furans, allenylphosphonates afforded at least four different types of phospho-benzofurans. It was also observed that the use of K_2CO_3 or Ag_2CO_3 as the base afforded entirely different products in the reaction with iodobenzene; while the former underwent a *β*-attack, the latter led to the *α*-attack product.

Scheme 1.8



Ma et al. reported the coupling reaction of 1,2-allenylphosphonate **1.24** with *p*-tolylboronic acid in the presence of $Pd(PPh_3)_4$/AcOH gave highly regio- and stereoselective tri- or tetra-substituted 1(*E*)-alkenylphosphonates **1.25** (Scheme 1.9).[4h] The stereoselectivity was much higher when compared to organic allenes.[15] It can be noted that these arene addition products are different from normal substitution derivatives.

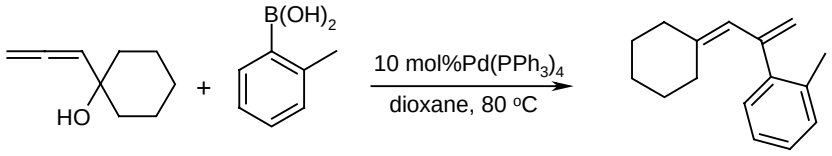
Scheme 1.9



1.24 **1.25** (87%)

Yoshida and co-workers developed a palladium-catalyzed coupling reaction of allenic alcohols with aryl and alkenyl boronic acids, which led to aryl and alkenyl substituted dienes in high yields.[16] Thus 2-methyl-phenylboronic acid upon treatment with allenic alcohol **1.26** in the presence of $Pd(PPh_3)_4$ in dioxane at 80 ^oC gave the diene **1.27** in excellent yield (Scheme 1.10).

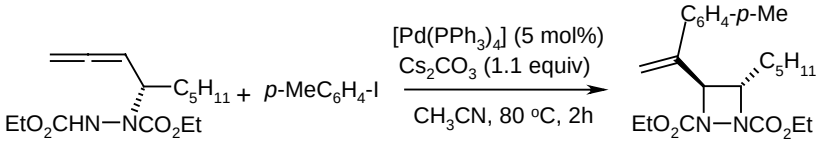
Scheme 1.10



1.26 **1.27** (99%)

Very recently, Ma and co-workers reported arylation-cum-cyclization of enantiomerically enriched 2,3-allenyl hydrazine **1.28** under mild conditions using $Pd(PPh_3)_4/Cs_2CO_3$ to give optically active vinylic 1,2-diazetidine **1.29** in good yields (74%) and high *enantiomeric excess* (99.4%) (Scheme 1.11).[17]

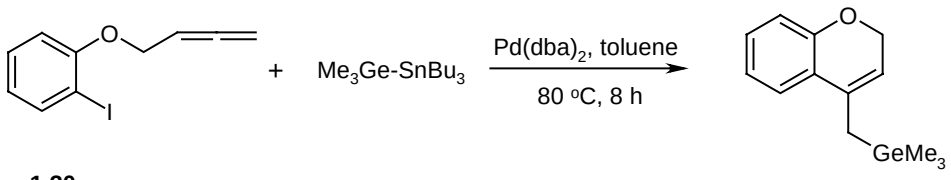
Scheme 1.11



1.28 (3S-4S)-**1.29** (74%)

Jeganmohan et al. developed a phosphine-free $Pd(dba)_2$-catalyzed three-component assembly of allene aryl iodide and stannylgermane for the highly regio-, stereo- and chemo-selective synthesis of allylgermanes.[18] They used same strategy for the synthesis of germanyl chromene **1.31** using the allene **1.30** in good yields (Scheme 1.12).

Scheme 1.12

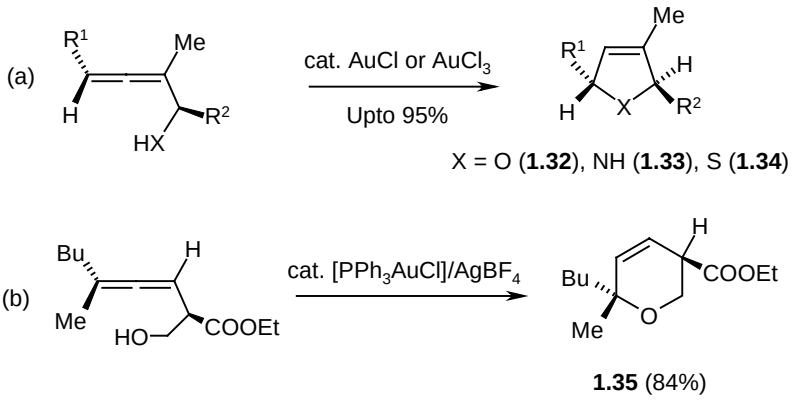


1.30 **1.31** (78%)

1.32 *Cycloisomerization reactions of allenes*

Allenes bearing a pro-nucleophile (nitrogen, oxygen, sulfur or carbon) can be cyclized on treatment with a wide variety of transition metal catalysts and reagents to give products containing various ring sizes. Thus Krause and co-workers reported gold(I)- or gold(III)-catalyzed endo-cycloisomerisation of α- or β-hydroxyallenes to give the corresponding 2,5-dihydrofurans (**1.32**)[19a] or dihydropyrans (**1.35**)[19b] in good yield with complete transfer of chirality in most cases (Scheme 1.13). The method was extended to α-aminoallenes/α-thioallenes giving rise to the corresponding pyrrolines (**1.33**)/2,5-dihydrothiophenes (**1.34**).[19c-d]

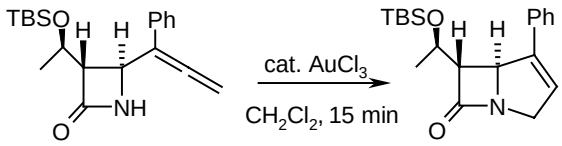
Scheme 1.13



1.35 (84%)

2-Azetidinone is the central building block of β-lactam antibiotics, so functionalization of the 2-azetidinone-framework is pivotal for the development of new β-lactam antibiotics. Thus Lee and co-workers treated 4-(1-substituted allenyl)-2-azetidinone **1.36** with 5 mol% $AuCl_3$ in DCM (dichloromethane) to obtain the bicyclic β-lactam **1.37** in good yields (Scheme 1.14).[20]

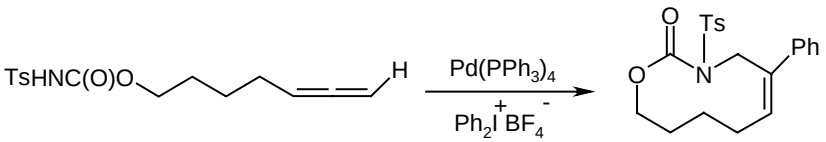
Scheme 1.14



1.36 **1.37** (85%)

Kang et al. developed palladium $Pd(PPh_3)_4$-catalyzed coupling reaction of allenyl *N*-tosylcarbamates with hypervalent iodonium salts to obtain the cyclized *trans-5-substituted* oxazolidinones, 3-oxazin-2-ones, and higher membered carbamates under mild conditions in moderate yields.[21] As an example, allenyl *N*-tosylcarbamate **1.38** treated under conditions as shown in Scheme 1.15 afforded the ten membered ring heterocycle **1.39** in 44% yield.

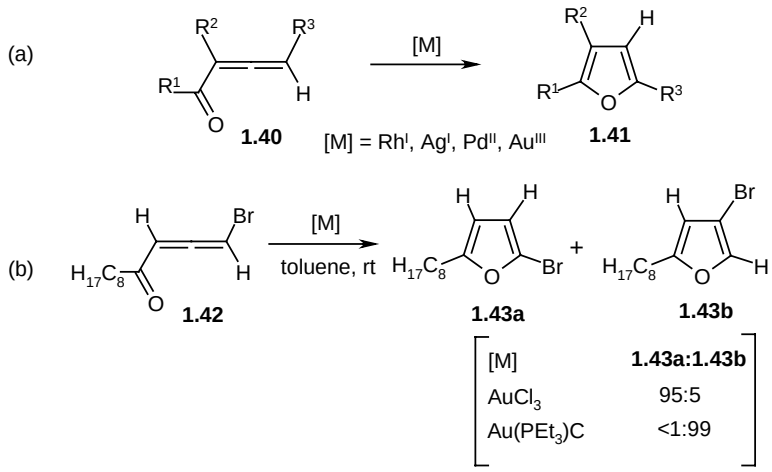
Scheme 1.15



1.38 **1.39** (44%)

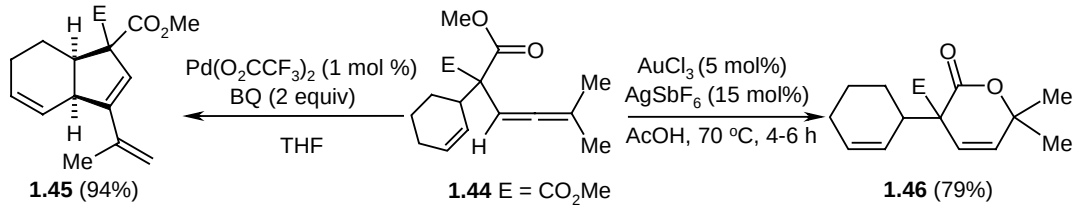
Furans are among the most prominent class of heterocyclic compounds that can be found in many natural products. One of the important methods to synthesize furans (**1.41**) is the transition metal catalyzed cyclization of allenyl ketones (**1.40**) (Scheme 1.16a).[22a-d] Sormek et al. reported that haloallenyl ketone **1.42** treated with Au^{III} or Au^{I} gave regiodivergent halofurans **1.43a** and **1.43b** depending on the catalyst used (Scheme 1.16b).[22e]

Scheme 1.16



Bäckvall and co-workers reported oxidative carbocyclization of allene **1.44** in the presence of a catalytic amount of Pd^{II} and stoichiometric oxidant *p*-benzoquinone (BQ) to afford the bicyclic product **1.45**.[23a] When they treated the same allene with $AuCl_3$-$AgSbF_6$ combination, *β,γ*-unsaturated *δ*-lactones **1.46** was obtained (Scheme 1.17).[23b] Here, nucleophilic attack by an ester oxygen on a C=C bond coordinated to the metal has taken place. This is a good example to illustrate that allenes having different functional groups can lead to a diversity of products in the presence of different catalysts.

Scheme 1.17

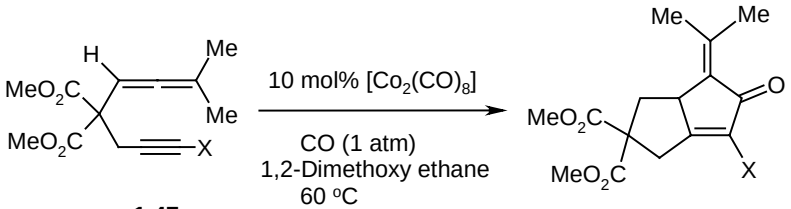


1.33 *Allene-alkyne cyclization reactions*

Allenes undergo various types of allene-alkyne cyclization reactions in the presence of various transition metals or radical initiators (*via* diradicals) to give products with different ring sizes. Pauson-Khand reaction is a formal [2+2+1] cycloaddition involving an alkene, an alkyne and carbon monoxide.[24] Instead of alkene one can use allene in these reactions because of their unique reactivity and synthetic utility of the final products. Livinghouse and co-workers noticed that

(methylthio)alkynes were superior substrates than unsubstituted alkynes for thermally promoted, $[Co_2(CO)_8]$-catalyzed Pauson-Khand reactions of allenynes, providing cyclopentenones in higher yields. Thus allenyne **1.47** was converted to cyclopentenone derivatives **1.48-1.49** (X = H, SMe) in the presence of $[Co_2(CO)_8]$/CO (1 atm) at 60 ^oC in good yields (Scheme 1.18).[25]

Scheme 1.18

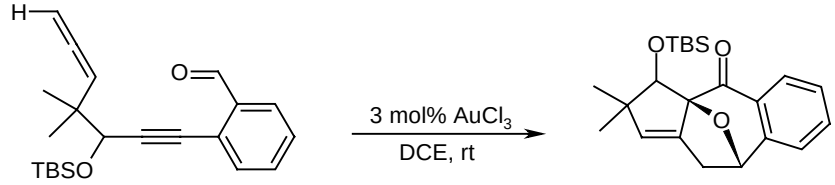


1.47

X = H (**1.48**) (38%)
X = SMe (**1.49**) (70%)

Gupta et al. reported that 1,6-allenynebenzaldehyde **1.50** when treated with $AuCl_3$ or gold nanoparticles underwent intramolecular tandem cycloaddition–cyclization to give fused polycyclic ring product **1.51** in good yields (69%) (Scheme 1.19).[26]

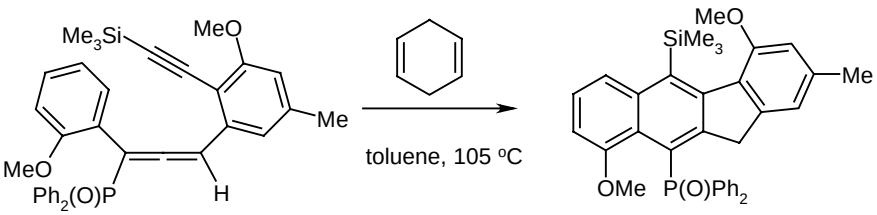
Scheme 1.19



1.50 **1.51** (69%)

As mentioned above, allene-alkyne cyclization takes place *via* diradical intemediate. Echavarren and co-workers demonstrated that the intramolecular cyclization of trimethylsilyl substituted alkynes with allenes (e.g. **1.52**) in the presence of excess 1,4-cyclohexadiene in toluene under reflux proceeded through a diradical pathway.[27] A [4+2] cycloaddition took place to form the tetracyclic derivative **1.53** (Scheme 1.20). This cycloaddition can be applied for the ready construction of benzo[b]fluorenes.

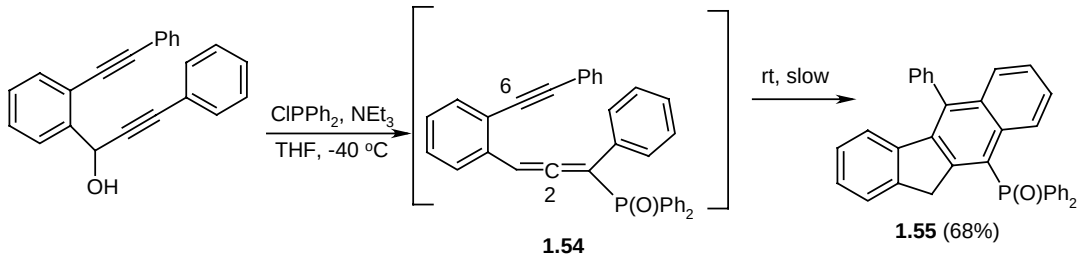
Scheme 1.20



1.52 **1.53** (38%)

Schmittel and co-workers reported a new type of thermal cyclization of the *in situ* prepared 3-(*o*-(1-alkyl)phenyl)allenylphosphine oxide **1.54** *via* diradical pathway to give the tetracyclic derivative **1.55** in moderate yields (Scheme 1.21).[28] It should be noted here that the C-C bond was formed between the C2 and C6 atoms during the cyclization reaction.

Scheme 1.21



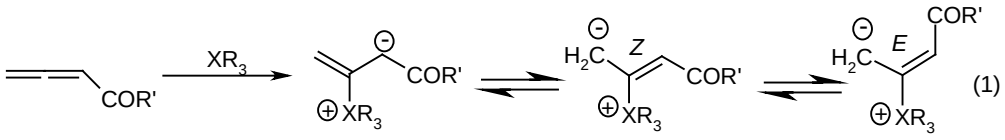
1.54 **1.55** (68%)

1.4 Lewis base catalyzed/promoted reactions of allenes with various functional groups (aldehyde, imine etc.)

We have been working on palladium catalyzed and nucleophilic addition reactions of allenylphosphonates during the past few years.[14,75,77] However, base catalyzed reaction of allenylphosphonates was not investigated on these substrates to any significant extent. Since this aspect forms a part of the work reported here, a brief literature survey on Lewis base catalyzed/promoted reactions of allenes with electrophiles such as aldehydes, aldimines, salicylaldehydes etc. are presented in the following paragraphs.

Catalysis employing phosphines and amines as nucleophilic triggers has emerged as a rapidly growing area of synthetic organic chemistry. In particular, phosphine and amine catalysis of allenoates has proven to be useful for the development of new annulation reactions providing various carbo- and hetero-cycles. Zwitterionic species (e.g. **1.57**, **1.58** and **1.59** in eq. 1) can be generated by

addition of nucleophile to elecrophilic π systems (allenoates). The stability of the zwitterions depends on the nature of the nucleophile and the solvent. These zwitterions react with various functional groups like aldehydes, α,β-unsaturated ketones, imines, activated alkenes, salicylaldehydes etc. to give diverse products depending on the nature of nucleophile and the substituent on the allenoate.



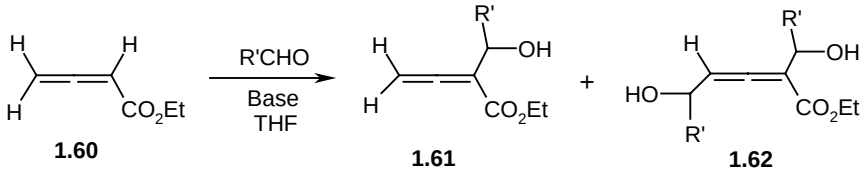
1.56 **1.57** **1.58** **1.59**

X = N, P

1.41 *Reactions with aldehydes*

Tsuboi et al. have reported that ethyl 2,3-butadienoate **1.60** reacted with aliphatic aldehydes in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO, catalyst) at -6 to 25 ^{o}C to give the corresponding 3-hydroxy-2-vinylidenealkanoate **1.61** in 41-54% yield. When they used *n*-BuLi (at -105 to -70 ^{o}C) instead of DABCO, the reaction afforded a higher yield (56-67%) of the products. In some cases in the presence of *n*-BuLi, disubstituted products of type **1.62** were also obtained in low yields (Scheme 1.22).[29a] Very recently, Hammond and co-workers reported that γ-disubstituted allenoates (2,3-butadienoates) when reacted with aromatic aldehydes in the presence of *n*-Bu_4NF (TBAF) at 0 ^{o}C afforded the corresponding α-carbinol allenoates in satisfactory yields (66-69%).[29b]

Scheme 1.22



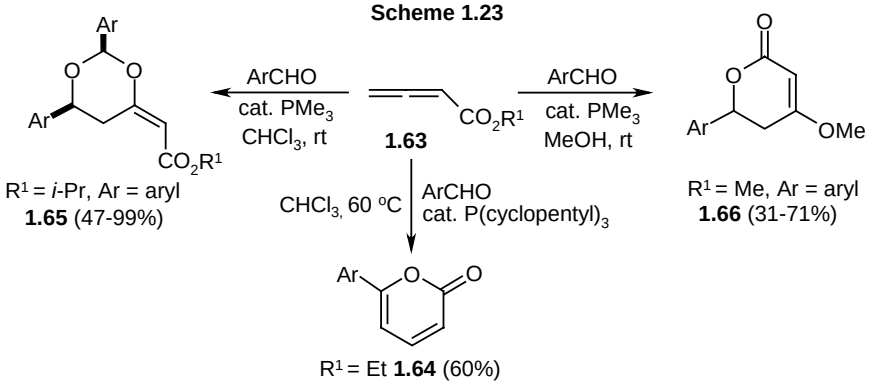
1.60 **1.61** **1.62**

R' = aliph. or Ar

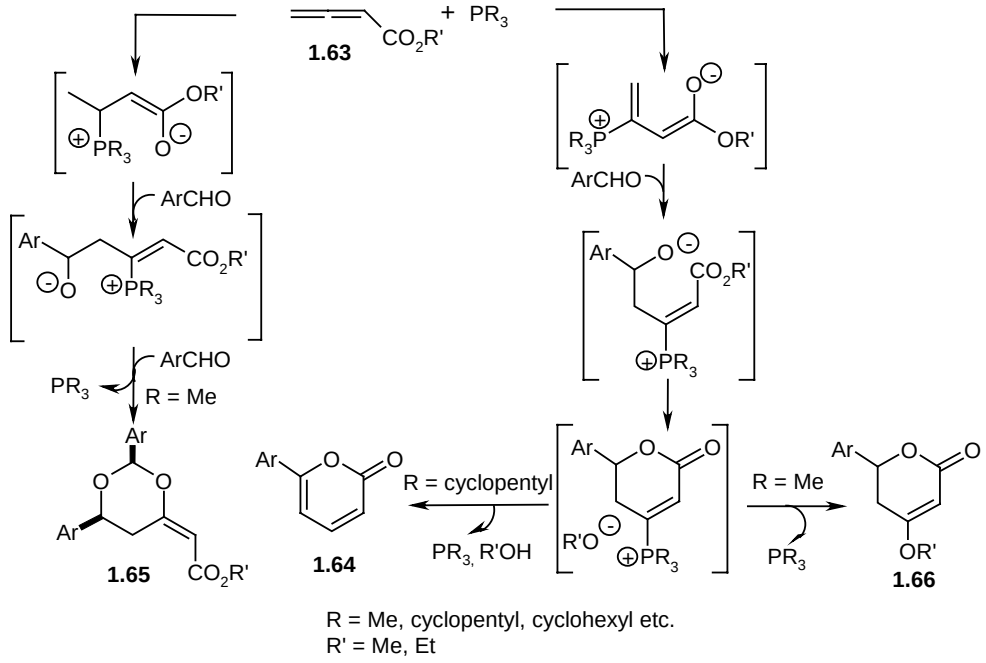
Kwon and co-workers illustrated that allenoates **1.63** reacted with aromatic aldehydes in the presence of sterically demanding trialkylphosphines [e.g. P(cyclopentyl)$_3$] to form 6-substituted 2-pyrones **1.64** *via* zwitterionic species of type **1.59**.[30b] In contrast, the same reaction when carried out in the presence of less

bulky trialkylphosphine PMe_3 gave 2,6-diaryl-[1,3]dioxan-4-ylidene-acetates **1.65** *via* zwitterionic species analogous to **1.58**.[30a] In a protic solvent like methanol, 6-aryl-4-methoxy-5,6-dihydro-2-pyrones **1.66** were formed in good yields as shown in Scheme 1.23. They used *n*-BuLi (1 equiv) to suppress side products.[30c] A possible mechanism for this reaction is illustrated in Scheme 1.24.

Scheme 1.23



Scheme 1.24

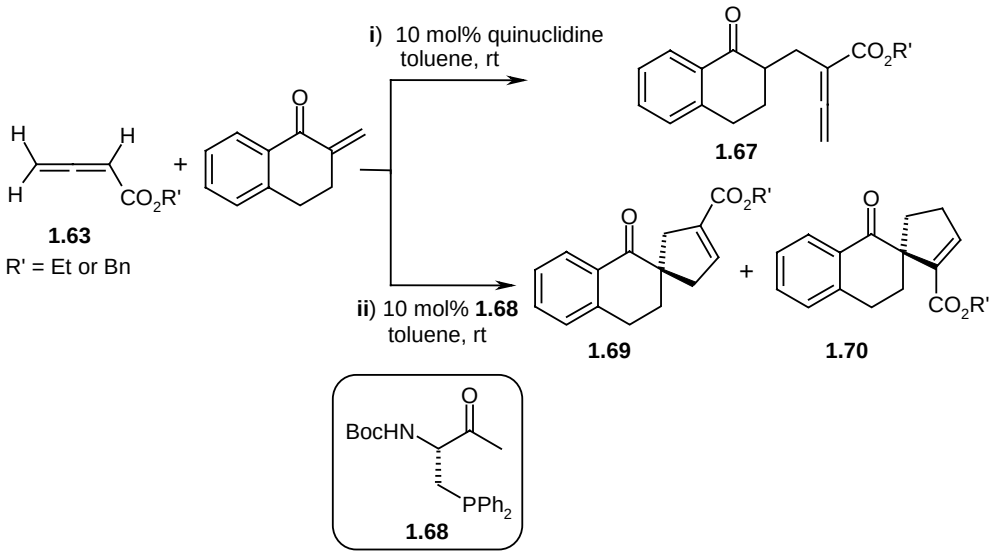


1.42 *Reactions with α,β-unsaturated ketones*

Miller and co-workers found that allenoate **1.63** when treated with *α,β*-unsaturated ketones in the presence of quinuclidine as the catalyst underwent conjugate addition to afford **1.67** in good yields (Scheme 1.25).[31a] In the presence of of phosphine catalyst **1.68**, however, [3+2] cycloaddition took place to afford **1.69**

and **1.70** (**1.69**:**1.70** = 99:1) in 95 % overall yield.[31b] This is a nice paradigm of divergent reactivity exhibited by the allenes in the presence of different nucleophilic catalysts. Notably, significant progress has been reported with chiral phosphines as catalysts by different groups like those of Zhang,[31c] Fu,[31d] and Wallace.[31e]

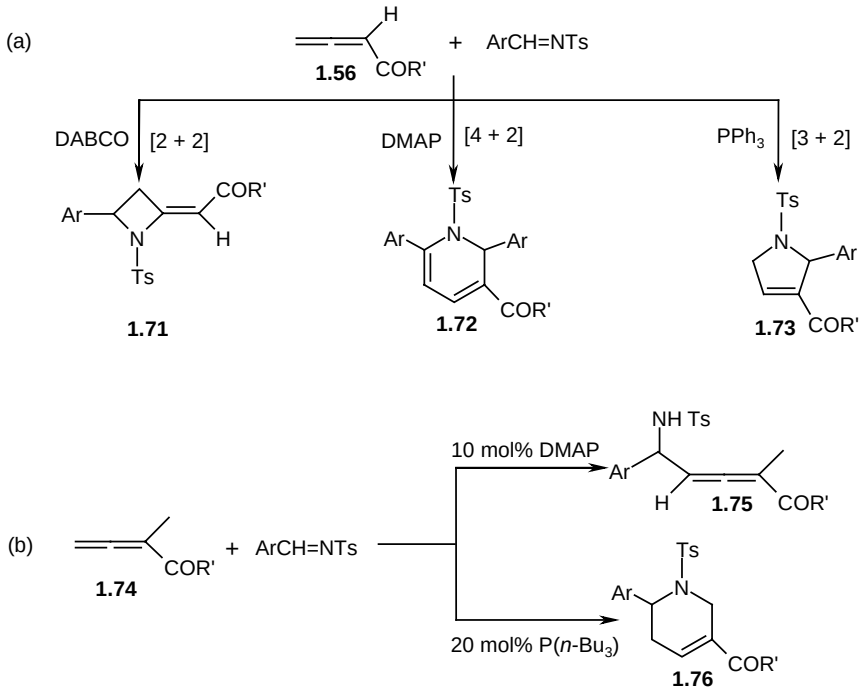
Scheme 1.25



1.43 *Reactions with imines*

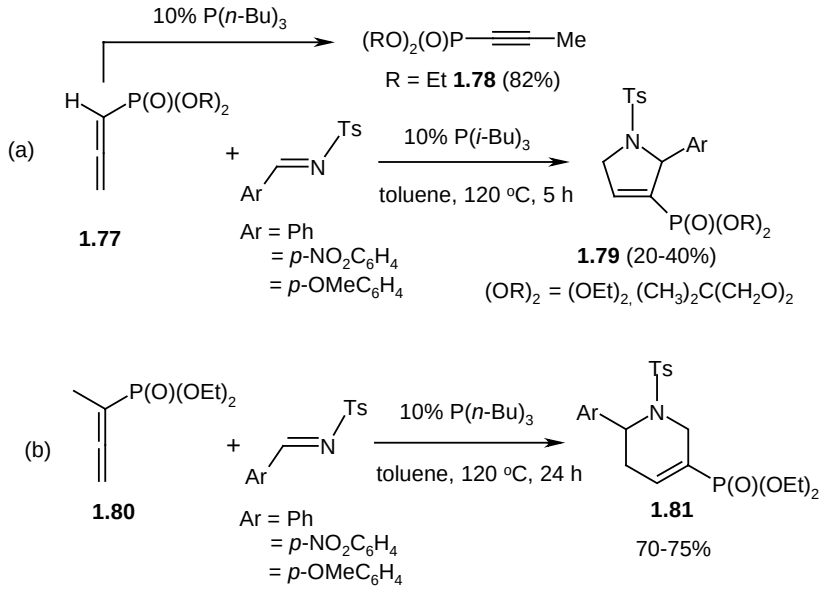
Allenes on reaction with *N*-tosylated imines give various types of products depending on the catalyst used and the substituents on the allene (Scheme 1.26a-b). For example, Shi et al. reported that under DABCO catalysis, *N*-tosylated imines undergo [2+2] cycloaddition with ethyl 2,3-butadienoate or 3,4-pentadien-2-one to afford azetidine derivatives (**1.71)** in good yields. When 4-dimethylaminopyridine (DMAP) was used as a catalyst, the allenoate reacted with two molecules of *N*-tosylated imine to give dihydropyridine **1.72** with the liberation of tosylamine.[32a] Lu and co-workers found that triphenylphosphine catalyzed reaction of methyl 2,3-butadienoate with *N*-tosylated imines led to pyrrolidine derivative **1.73** *via* [3+2] cycloaddition in excellent yield.[32b] If the allene **1.74** had α-methyl group then treatment with *N*-tosylated imines in the presence of the catalyst DMAP in DMSO afforded the corresponding Baylis-Hillman adduct **1.75**.[32c] When the same reaction was performed in the presence of tributylphosphine (P(n-Bu)$_3$), [4+2] cycloaddition took place to give tetrahydropyridine derivatives (**1.76**) in excellent yields with complete regioselectivity.[32d]

Scheme 1.26



Very recently, Panossian et al. accomplished the synthesis of phosphono-pyrroline and phosphono-tetrahydropyridine from the reaction of allenylphosphonates with *N*-tosylated imines in the presence of various trialkylphosphines.[4i] Allenylphosphonate **1.77** isomerized to the corresponding acetylene **1.78** in the presence of P(*n*-Bu)$_3$ at room temperature (Scheme 1.27a). When they changed the catalyst to P(*i*-Bu)$_3$, the desired phosphono-pyrrolidine derivatives **1.79** were obtained in moderate yields (Scheme 1.27a). When a similar reaction was performed using α-methyl substituted allenylphosphonate **1.80**, phosphono-tetrahydropyridine **1.81** was obtained in good yields (Scheme 1.27b). If the aromatic group on the imines had electron-withdrawing groups, the yields were very low or in some cases there was no reaction.[4i] Also, allenylphosphonates were less reactive when compared to allenyl esters.

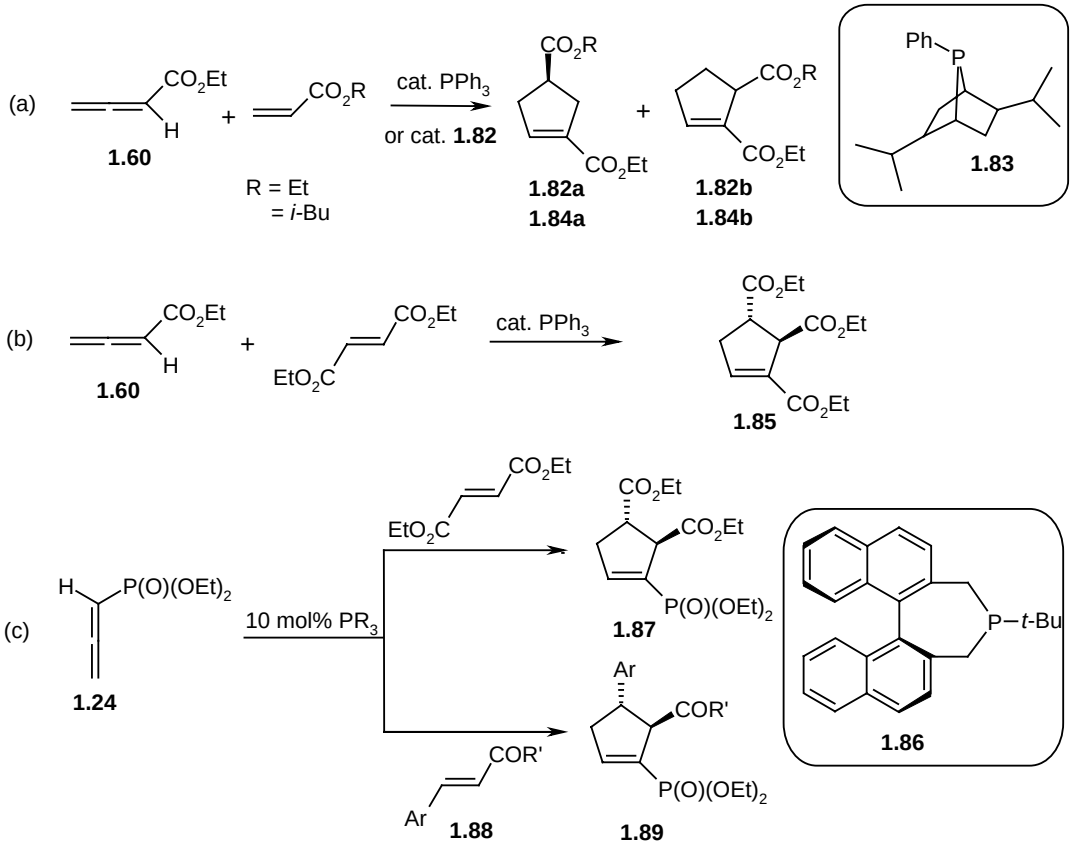
Scheme 1.27



1.44 *Reactions with activated alkenes*

Allenes react with activated alkenes in the presence of catalytic amount of phosphines to give the corresponding cyclopentene derivatives through [3+2] cycloaddition. Lu and co-workers first reported that ethyl 2,3-butadienoate **1.60** and ethyl acrylate in the presence of 10 mol % of PPh_3 gave the cylopentadiene derivatives **1.82a** and **1.82b** (3:1 ratio) in 76% overall yield (Scheme 1.28a).[33a] When P(*n*-Bu)$_3$ replaced PPh_3 as the catalyst, the reaction took place more rapidly, but gave slightly lower yield (66%). Later, Zhang et al. used several chiral catalysts and found that phosphine catalyst **1.83** was the best one. Thus ethyl 2,3-butadienoate **1.60** when treated with isobutyl acrylate along with **1.83** gave only one isomer **1.84a** in good yields (88 %) and high optical purity (93 % *ee*; Scheme 1.28a).[33b] Similarly, **1.60** reacted with diethyl fumarate to yield (*trans*)-**1.85** as a single product**,** implying that the stereochemistry remained unchanged during the cycloaddition reaction (Scheme 1.28b).[33a] Marinetti and co-workers also used allenylphosphonates as precursors for the synthesis of cyclopentene phosphonates using chiral phosphine ligands.[4i] Thus the allenylphosphonate **1.24**, when treated with diethyl fumarate in the presence of chiral phosphine catalyst **1.86**, gave (*trans*)-**1.87** in moderate yields (55 %) and good *ee* (91%). Similar annulation between **1.24** and the aryl enones **1.88** in the presence of **1.86** led to (*trans*)-**1.89** (Scheme 1.28c) with *ee* of up to 89%.

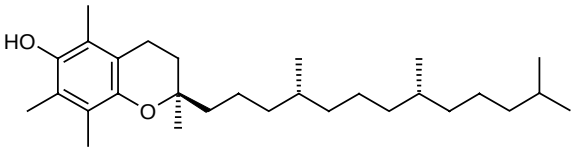
Scheme 1.28



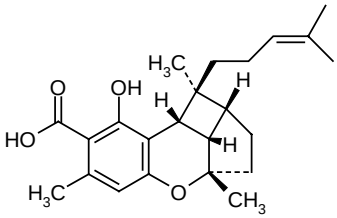
1.45 *Reaction with substituted salicylaldehydes: Synthesis of chromenes*

Chromenes constiute an important class of oxygenated heterocyclic compounds. They are widespread in natural products and have attracted much attention in diverse areas including physical chemistry (photochromism) and medicinal chemistry (anti HIV, anticancer, antioxidant, inhibitory effect on histamine release, antihypertensive and antiviral activity) and hence a number of research groups have developed different methodologies to synthesize these compounds. Some representative examples (**1.90-1.97**) are shown in Chart 1.[34] In this section, we discuss synthesis of functionalized chromenes, mainly from allenes.

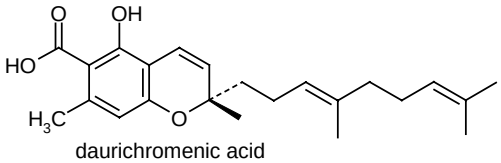
Chart 1



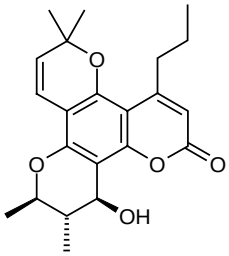
α-tocopherol
antioxidant in tissues
1.90



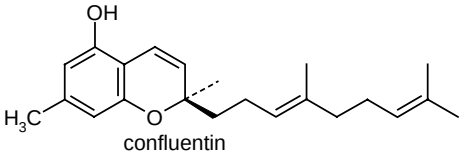
rhododaurichromanic acid A
Potent anti-HIV
1.91



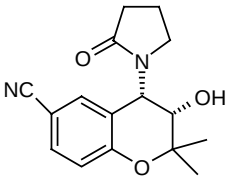
daurichromenic acid
Potent anti-HIV
1.92



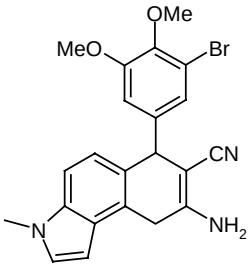
Calanolide A
Potent anti-HIV
1.94



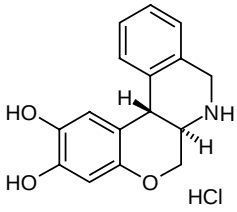
confluentin
inhibitory effect on histamine release
1.93



levcromakalim
antihypertensive
1.95



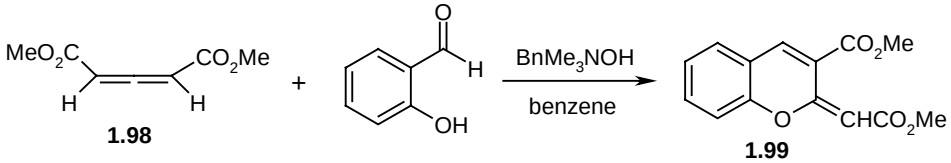
(2-Amino-4-(3-bromo-4,5-dimethoxyphenyl)
-3-cyno-7-methyl-4*H*-pyrrolo[2,3-*h*]chromene
anticancer
1.96



doxanthrine
D1-selective full agonist
dihydrexidine
1.97

Since the pioneering work of Nixon and Scheinmann, dimethyl penta-2,3-dienedinoate **1.98** is known to react with salicylaldehydes in the presence of (benzyl)trimethylammonium hydroxide to give the corresponding chromene **1.99** in good yields (Scheme 1.29).[35]

Scheme 1.29

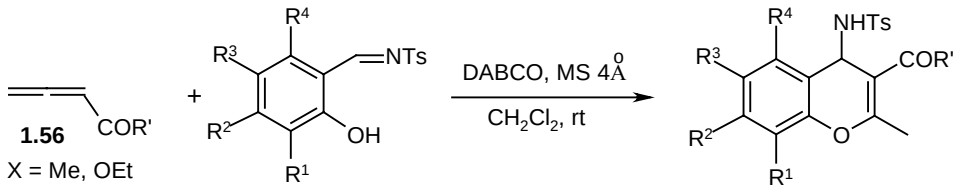


1.98

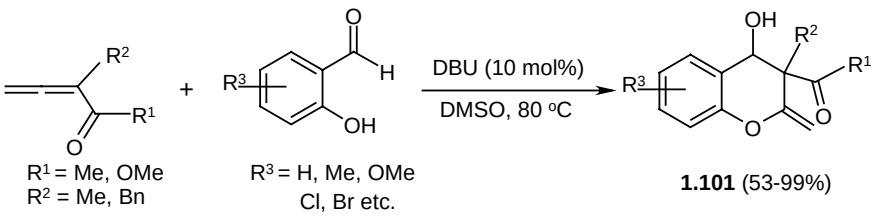
1.99
Yield 69%

Shi and co-workers explored the reactions of salicylaldehydes with different allenes in the presence of various catalysts (phosphines, amines and inorganic bases) and obtained different types of chromenes. In all of these, tertiary amines [DABCO or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene)] or inorganic bases (K_2CO_3 or Na_2CO_3) gave better results than phosphines. First, they treated salicyl-*N*-tosylimines with ethyl 2,3-butadienoate or penta-3,4-dien-2-one using DABCO as the catalyst to obtain the corresponding chromenes (**1.100**) in good to excellent yields (Scheme 1.30).[36a] They examined phosphine catalysts like PPh_3 or PPh_2Me also, but in those cases obtained dihydropyrrole derivatives *via* [3+2] cycloaddition. Later, they performed the reactions of salicylaldehydes with 3-methyl or 3-benzyl substituted penta-3,4-dien-2-one as well as ethyl 2-methylbuta-2,3-dienoate, catalyzed by DBU. Functionalized 2*H*-1-chromenes **1.101** were thus obtained diastereoselectively in good yields in some cases (Scheme 1.31). They screened several bases/solvents, among which DBU-DMSO combination was shown to be the best.[36b]

Scheme 1.30



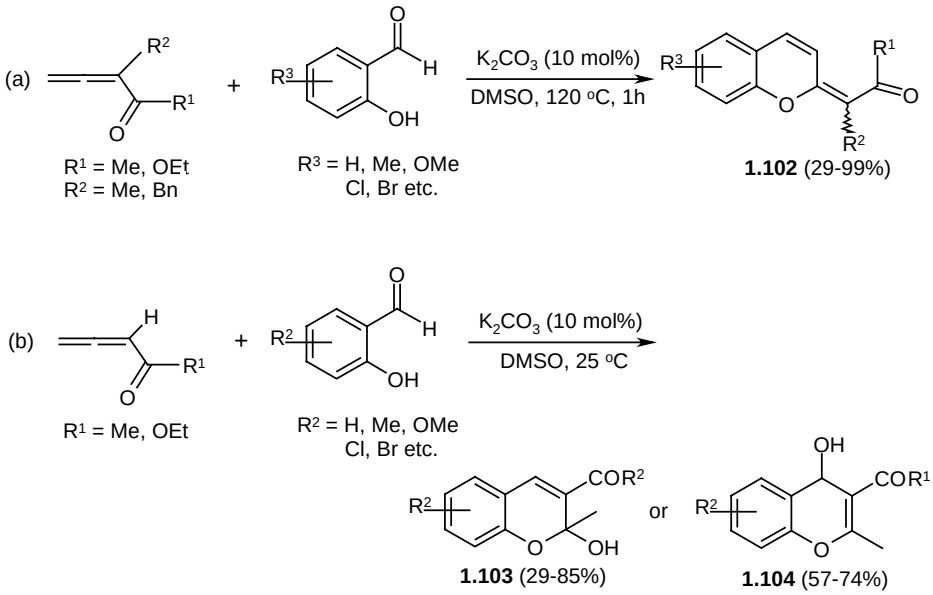
Scheme 1.31



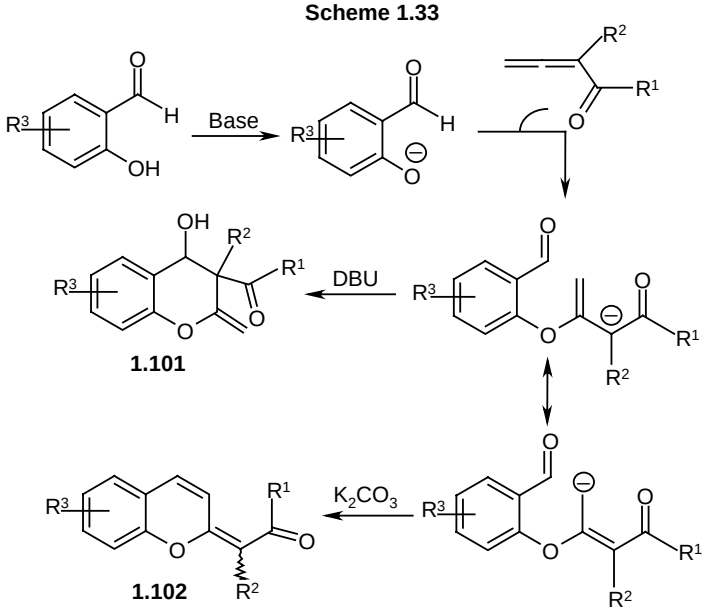
In continuation of their work on the synthesis of functionalized chromenes, Shi and co-workers carried out the above reactions in the presence of K_2CO_3 at high temperature (120 ^oC), but in these cases they obtained chromenes (**1.102**) with a different structure (Scheme 1.32a).[36c] In a similar way, they have conducted reactions between unsubstituted allenes and salicylaldehydes at 25 ^oC in the presence of K_2CO_3 in DMSO or EtOH that afforded the corresponding chromenes

(**1.103** and **1.104**).[36d] Chromene **1.104** was converted to chromene **1.103** under acidic or neat conditions (Scheme 1.32b). This is also a good example to show that the substituents on the allene and the base/nucleophile are playing a role in these reactions. A possible mechanism for the formation of these chromenes is depicted in Scheme 1.33.[36e]

Scheme 1.32



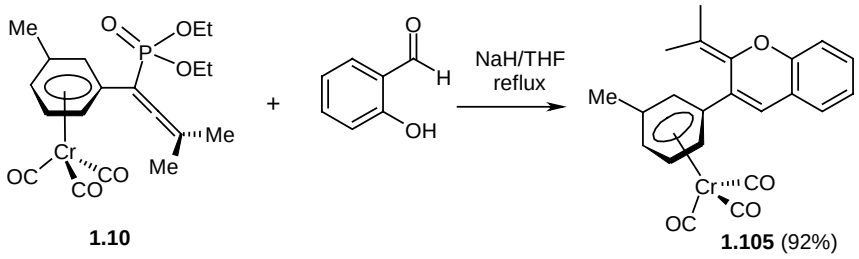
Scheme 1.33



The allenylphosphonate complex **1.10** (see above) reacts smoothly with a number of 1,2- and 1,3-difunctional carbonyl compounds like salicylaldehyde in the

presence of sodium hydride to give arene-$Cr(CO)_3$ substituted heterocycle **1.105** in good yields as a crystalline solid.[8]

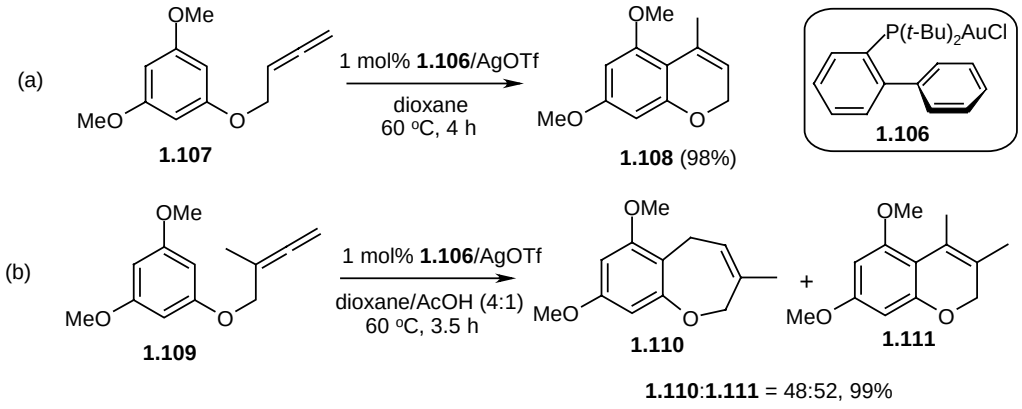
Scheme 1.34



1.46 *Intramolecular annulation using allenes leading to chromenes*

Watanabe et al. have developed a novel and efficient route for the synthesis of chromenes from allenic compounds by means of gold-catalyzed intramolecular hydroarylation.[37] The allenic compound **1.107** is converted to chromene **1.108** in excellent yields in the presence of the catalyst **1.106**/AgOTf (Scheme 1.35a). When they used substituted allene **1.109** in similar conditions, seven-member ring compound **1.110** along with chromene **1.111** was obtained, albeit in low yields (Scheme 1.35b). However, when the solvent system was changed from dioxane to dioxane-acetic acid (4:1) mixture, excellent yields (overall 99%) were obtained.

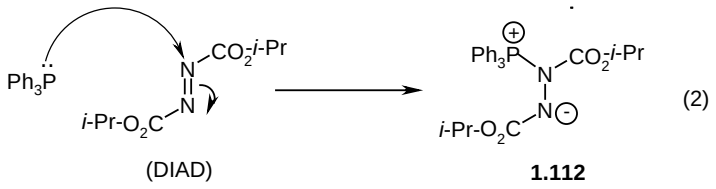
Scheme 1.35



In addition to the above, there are several other routes that do not involve allenes.[36-43] Since this part is not directly relevant to the theme of the present study, these reactions are not discussed here.

1.5 Reaction of dialkyl azodicarboxylates with phosphorus(III) compounds- Utility of the intermediates

The reaction of triphenylphosphine and dialkyl azodicarboxylate leading to the formation of zwitterion **1.112** [also called Morrison-Brunn-Huisgen intermediate/betaine] has been known from the work of Huisgen.[44a-c] It is the key and primary intermediate in the well known Mitsunobu reaction (eq. 2). Apart from Mitsunobu reaction, one can construct C-C and C-X (X = N, O) bonds very easily under mild conditions using this zwitterion. It reacts with compounds containing various functional groups like aldehydes, ketones, 2-hydroxy benzaldehydes, benzoquinones, *N*-alkyl substituted isatins, activated acetylenes/allenes, chalcones and 2-acylaziridines to afford various products depending upon the type of reactants. Our research group has also been working on the characterization of Mitsunobu-type intermediates and has been successful to some degree.[44d-f] With the readily available and inexpensive allenylphosphonates in our hands,[4a] we wanted to check how they react with Morrison-Brunn-Huisgen betaine. A part of this thesis deals with the reactivity of selected P^{III} compounds with unsaturated systems and hence a brief literature survey on relevant topics is presented in the next few sections.

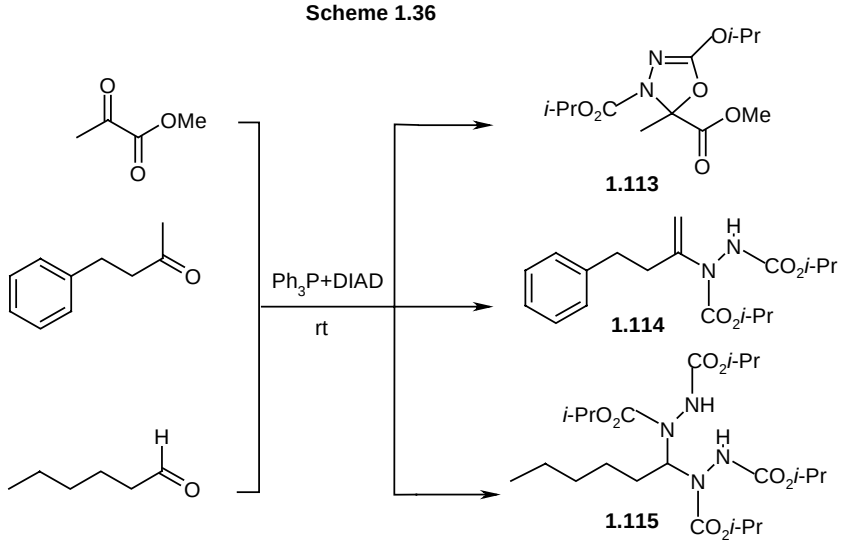


(2)

1.51 *Reactivity of Morrison-Brunn-Huisgen intermediate towards carbonyl compounds*

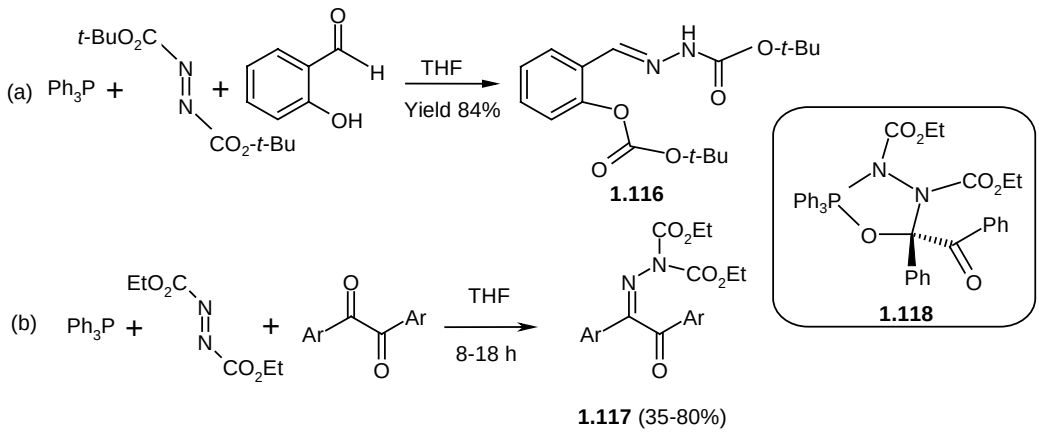
The Morrison-Brunn-Huisgen intermediate **1.112** showed excellent reactivity towards carbonyl compounds to generate a variety of products (e.g. **1.113-1.115**) depending on the substituents present on the carbonyl carbon (Scheme 1.36).[45a] Products analogous to **1.114** were observed previously by Liu et al. when ketones were treated with P(*n*-Bu)$_3$ and dimethyl azodicarboxylate.[45b]

Scheme 1.36



In reactions using 2-hydroxy benzaldehydes, Ph_3P+di-*t*-butylazodicarboxylate (DTBAD) combination and alcohols, hydrazones (**1.116**) are formed as major products rather than the expected alkyl aryl ethers (Scheme 1.37a).[46a] The reaction of diaryl-1,2-diones with Ph_3P+diethyl azodicarboxylate (DEAD) afforded *N*,*N*-dicarboethoxymonohydrazones (**1.117)** by a novel *nitrogen to nitrogen migration* of a carboethoxy group (Scheme 1.37b).[46b] It is proposed that this reaction took place *via* the Morrison-Brunn-Huisgen betaine of type **1.112** and the pentacoordinate intermediate **1.118**. This reaction may be contrasted with that of Otte et al. and Liu et al. wherein other types of products were obtained with aldehydes, ketones or keto-esters (cf. Scheme 1.36 above).[45]

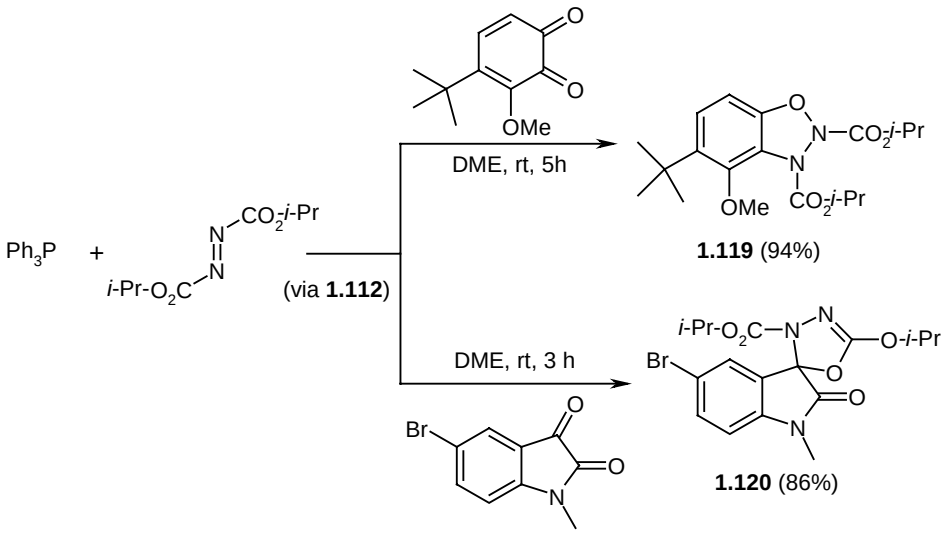
Scheme 1.37



Nair et al. reported that Morrison-Brunn-Huisgen betaine **1.112** [prepared from Ph_3P+diisopropyl azodicarboxylate (DIAD)] reacted with 3-methoxy-5-*t*-butyl-

1,2-benzoquinone to give a tetrahedral intermediate which led to dihydro-1,2,3-benzoxadiazole derivative **1.119** in excellent yields. This reaction is different from those discussed above. They also treated *N*-methyl-isatin in a similar way with Ph_3P+DIAD in dry dimethoxyethane (DME) at room temperature and obtained spirooxadiazoline **1.120** in 86 % yield (Scheme 1.38).[47]

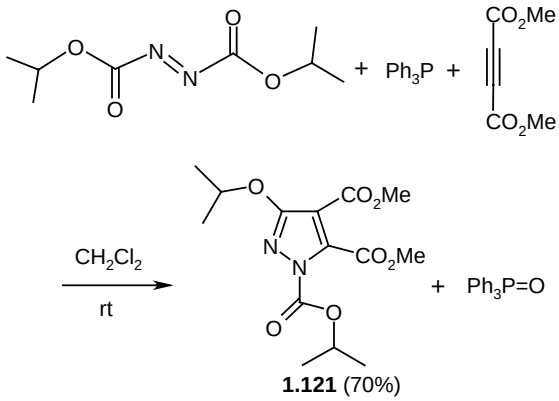
Scheme 1.38



1.52 *Synthesis of pyrazole and pyrazoline derivatives*

Pyrazoles and their derivatives exist in various natural products and possess a variety of biological activities.[48] Limited routes are available for the synthesis of these compounds and hence developing new synthetic routes and methodologies are of some interest. The reaction shown in Scheme 1.39 leading to pyrazole **1.121** is an important one because if one uses substrates containing activated alkynes in the Mitsunobu reaction, it is possible that products (like pyrazoles) other than the expected ones may form by just utilizing the acetylenic functionality.[49] As can be seen from the Scheme 1.39, the phosphine can pick up the oxygen from the azodicarboxylate (instead of an alcohol) to form the phosphine oxide.

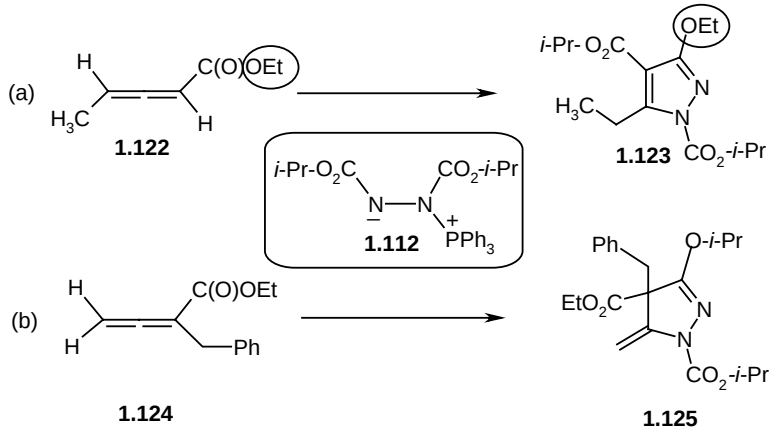
Scheme 1.39



1.121 (70%)

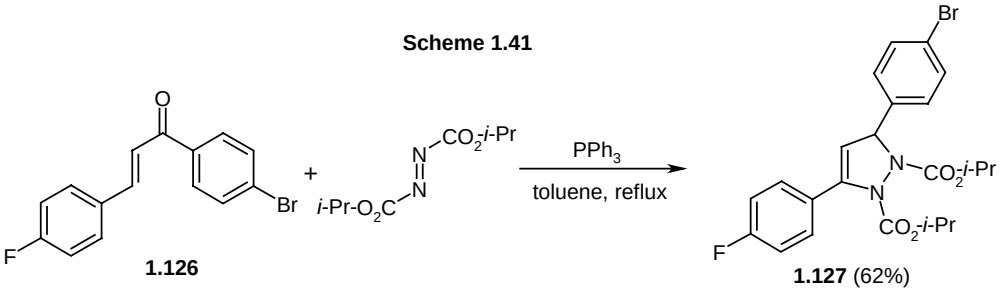
Nair and co-workers used the above strategy for activated allenes and prepared highly functionalized pyrazolines and fully substituted pyrazoles in moderate to good yields. When they treated allene **1.122** with Morrison-Brunn-Huisgen betaine **1.112** in DME at room temperature, fully substituted pyrazole derivative **1.123** was obtained in good yields (Scheme 1.40a).[50] This reaction took place *via* a novel rearrangement involving the nitrogen-carbon migration of the carboalkoxy group. When they treated α-substituted allene **1.124** with the zwitterion **1.112**, functionalized pyrazoline **1.125** was obtained (Scheme 1.40b).

Scheme 1.40



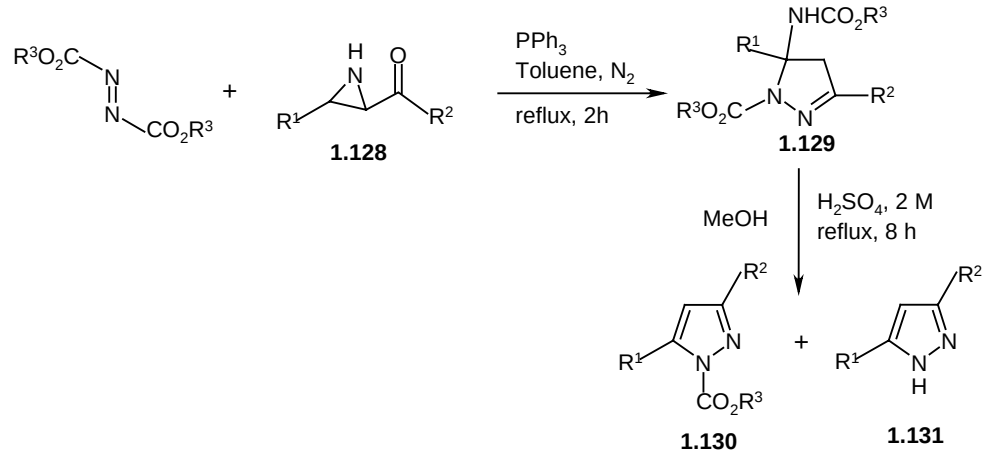
Surprisingly, treatment of the chalcone **1.126** with Ph_3P+DIAD gave pyrazoline derivative **1.127** instead of oxadiazoline (Scheme 1.41).[51] This reaction is general with respect to various substituted chalcones for the synthesis of functionalized pyrazoline derivatives. In a similar way, benzilidene tetralone reacted with Ph_3P+DIAD to afford a tricyclic pyrazoline derivative, thus opening up a new route to polycylic pyrazolines.

Scheme 1.41



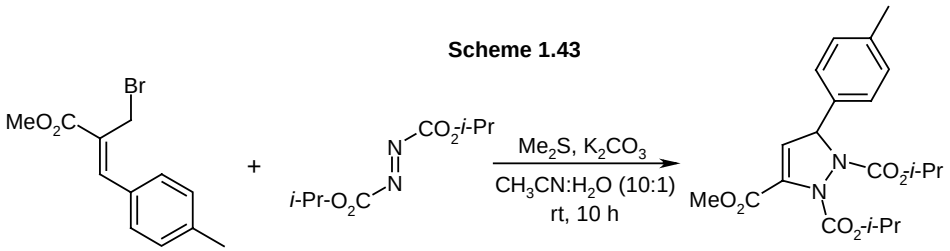
Very recently, Cui et al. reported that 2-acylaziridines **1.128** react with dialkyl azodicarboxylates in the presence of triphenylphosphine to give pyrazoline derivatives **1.129** in excellent yields in toluene; benzene also could be used but yields were lower (Scheme 1.42). These pyrazoline derivatives could be easily transformed into pyrazole derivatives **1.130** and **1.131** by heating them with 2 M H_2SO_4 in MeOH. This method is very useful for the synthesis of pyrazoline derivatives and pyrazole derivatives.[52]

Scheme 1.42



Pyrazoline derivative **1.133** can be synthesized very readily from Baylis-Hillman bromide **1.132**, as reported recently by Basavaiah and co-workers.[53] The bromide **1.132** reacts with dimethyl sulfide to give sulfur ylide or 1,3-dipolarophile in the presence of base (K_2CO_3) that will undergo cycloaddition with dialkyl azodicarboxylates to give pyrazoline derivatives in good yields (Scheme 1.43). This is a better procedure as compared to earlier ones because these reactions are not moisture sensitive and one can get a variety of substituted pyrazolines in one-pot.

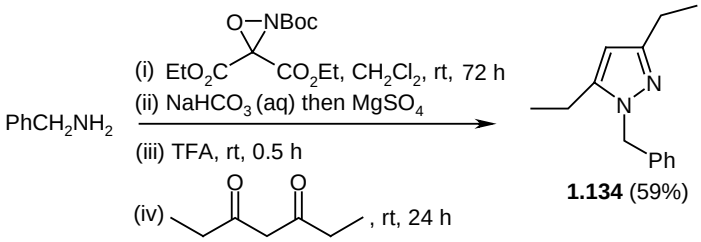
Scheme 1.43



1.132 **1.133**

In addition to the above phosphine-catalyzed routes, there are a few other methods for the synthesis of pyrazoles.[54] A few examples are discussed below for the sake of comparison. Thus one-pot synthesis of 1,3,5-trisubstituted pyrazoles **1.134** by starting with primary aliphatic/ aromatic amines has been reported by Armstrong and co-workers (Scheme 1.44).[55a] Thus primary amines when treated with diethylketomalonate derived from oxaziridine afford the corresponding hydrazines in dichloromethane; the aqueous layer was removed by pipette before sequential addition of solid $MgSO_4$, TFA and 1,3-diketone to obtain the product. Pyrazoles can also be prepared in one-pot from hydrazines and diketones [*in situ* generated from ketones and acid chlorides in the presence of lithium bis(trimethylsilyl)amide (LiHMDS)] in good to excellent yields.[55b] This method is extremely fast, general, and chemoselective, thus allowing the synthesis of previously inaccessible pyrazoles and synthetically demanding pyrazole containing fused rings.

Scheme 1.44

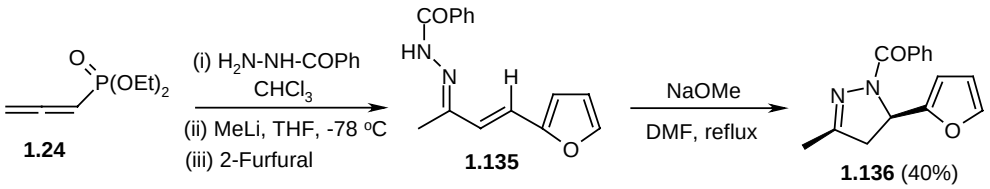


1.134 (59%)

Allenylphosphonate **1.24** reacts with benzhydrazide in refluxing chloroform to lead to phosphonyl *β*-hydrazone. This hydrazone when treated with 2-furfural in the presence of strong base MeLi at –78°C yields the corresponding 1-azadiene with high *E*-selectivity. Formation of *N*-benzoyl-2-pyrazoline **1.136** takes place by

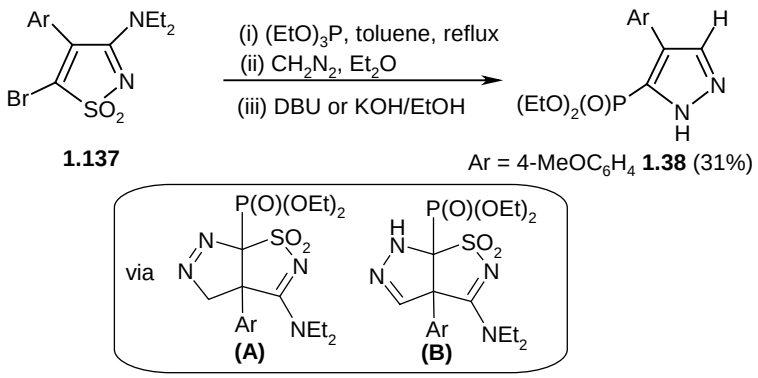
heating hydrazone **1.135** in refluxing DMF in the presence of NaOMe (Scheme 1.45).[56]

Scheme 1.45



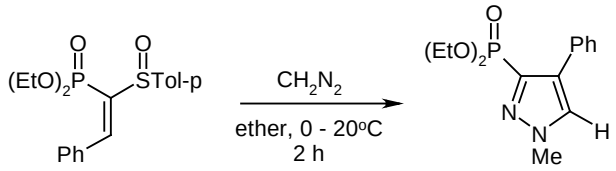
Phosphono-pyrazoles can be prepared from 3-amino-5-bromo-isothiazole dioxide under mild conditions but this route involves many steps. Thus 3-amino-5-bromo-isothiazole dioxide **1.137** when treated with triethylphosphite afforded isothiazolylphosphonate, which could be reacted with diazomethane to give 1- and 2-pyrazolines [**A**+**B**]. These pyazoline derivatives are converted to phosphono-pyrazole **1.138** in moderate yields upon heating with bases like ethanolic KOH or DBU (Scheme 1.46).[57]

Scheme 1.46



α,*β*-Unsaturated sulfoxides are valuable building blocks for a variety of biologically active compounds. The *α*-(phosphono)vinyl sulfoxide **1.139** undergoes 1,3-dipolar addition with diazomethane to give pyrazoline cycloadduct which eliminates sulfenic acid to give isopyrazole. This undergoes rapid tautomerization to 3-phosphonopyrazole **1.140** as the final product in excellent yield (Scheme 1.47).[58]

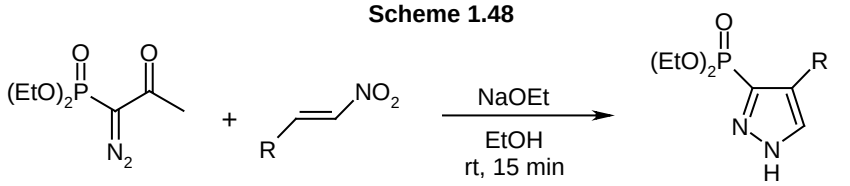
Scheme 1.47



1.139 **1.140** (98%)

Very recently, Muruganantham *et al* reported the synthesis of phosphono-pyrazoles utilizing diethyl 1-diazo-2-oxopropylphosphonate **1.141** as a precursor.[59] Thus compound **1.141** in the presence of NaOEt gave diethyl 1-diazomethylphosphonate anion that reacted with nitroalkenes *via* 1,3-dipolar addition affording phosphono-pyrazoles **1.142** in moderate to good yields (Scheme 1.48). These reactions were carried out using different bases and solvents, and it was found that NaOEt-EtOH combination gave the best results.

Scheme 1.48

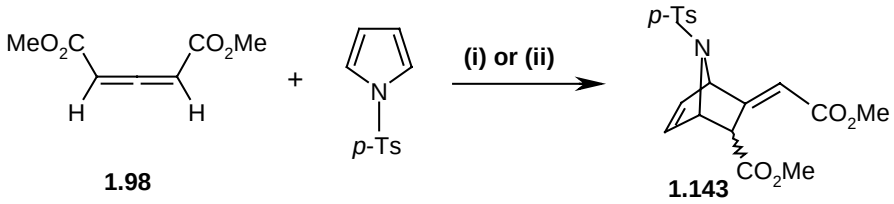


1.141 R = aryl, NMe_2 **1.142** (49-77%)

1.6 Diels-Alder reaction involving allenes

The Diels-Alder reaction is the addition of an alkene to a diene to form a cyclohexene. It is a [4π+2π] cycloaddition. Activated allenes can participate in Diels-Alder in the presence of Lewis acid or under thermal conditions. Allenic esters are highly reactive towards *N*-substituted pyrroles under thermal conditions or *via* Lewis acid ($AlCl_3$) assistance. Thus dimethyl penta-2,3-dienedinoate **1.98** reacted with *N*-tosyl pyrrole as shown in Scheme 1.49 and gave only the endo adduct **1.143** in good yields.[60] It may be noted that Friedel-Crafts reaction was also possible in the presence of the Lewis acid $AlCl_3$, but Diels-Alder reaction took place preferentially.

Scheme 1.49

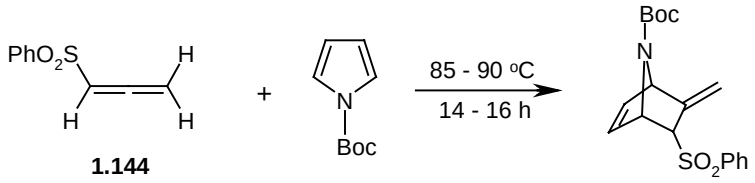


1.98 **1.143**

(i) : $AlCl_3$ (1.2 equiv.) added in DCM at -78 °C Yield 62%
(ii) : The mixture heated at 90 °C in toluene Yield 70 %

Benzenesulfonyl allene **1.144** also undergoes cycloaddition with *N*-protected pyrroles to produce 7-azabicyclo[2.2.1]heptene **1.145** in moderate yields (Scheme 1.50).[61a] This product and its analogues serve as potential precursors for the synthesis of *epibatidine* (Potent agonist of the nicotinic acetyl choline receptor).[61b,c]**.**

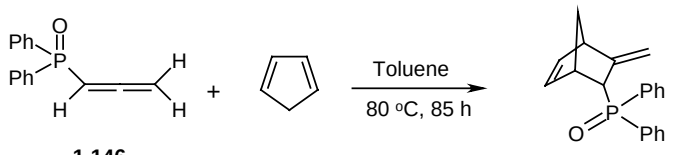
Scheme 1.50



1.144 **1.145** (45%)

Diphenyl(1,2-propadienyl)phosphine oxide **1.146** reacts with cyclopentadiene to provide the endo bicyclic adduct **1.147** (Scheme 1.51).[62] To our knowledge, this is the only report on Diels-Alder reaction using phosphorylated allenes.

Scheme 1.51

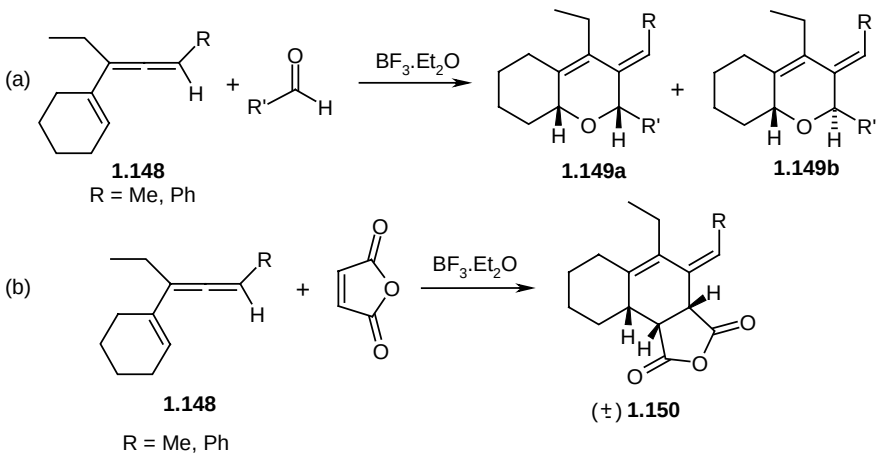


1.146 **1.147** (64%)

The vinyl-allene **1.148** acts as a diene and reacts with aldehyde as the heterodienophile in the presence of Lewis acid ($BF_3.Et_2O$) to give compound **1.149a** as the major product. A *cis* stereochemistry has been assigned to this and is consistent with an endo approach of the heterodienophile to the dienic portion of the molecule. The minor compound **1.149b** was assigned the *trans* stereochemistry,

which indicated an exo approach of the aldehyde (Scheme 1.52a).[63] Vinyl allene **1.148** is also highly reactive towards a dienophiles such as maleic anhydride and gives the endo adduct **1.150** in more than 90% yield (Scheme 1.52b).

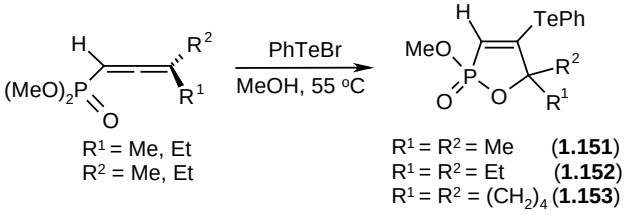
Scheme 1.52



1.7 Electrophilic addition reactions of allenes

The electrophilic addition of a reagent to allenic derivatives can occur, as it does for simple olefins. There are some earlier examples that lead to phosphono-heterocycles.[64-66] Recently, Yuan et al. have developed a PhTeBr-induced electophilic tellurolactonization of allenylphosphonates affording 4-(phenyltelluro)-1,2-oxaphosphol-3-ene 2-oxides (**1.151**-**1.53**) in good yields (62-92%) (Scheme 1.53).[67] No reaction occurred in the case of PhTeCl. Elemental bromine readily reacts with allenes and several reports have appeared in the past,[64,68-71] but there does not appear to be any recent publication.

Scheme 1.53

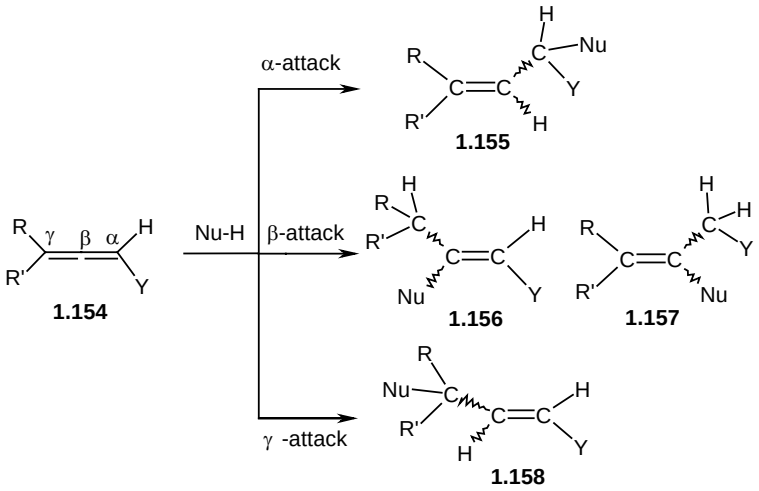


1.8 Nucleophilic addition reactions of allenes/allenylphosphonates

Nucleophilic addition forms an important class of reactions allowing the conversion of C=C moiety into a range of important functional groups. Since allene (**1.154**) is an unsaturated hydrocarbon having two cumulative double bonds, the coming nucleophile can attack any one of the three sp^2 carbon atoms (Scheme 1.54).

If one of the substituents on the allene is electron-withdrawing (e.g. ester or phosphonate), the nucleophile attacks at central carbon atom with only very limited exceptions. Simple addition reactions of allenylphosphonates with nucleophiles like alcohols, phenols, amines, azides or thiols lead to vinyl- or allyl-phosphonates (**1.155**–**1.158**). Intramolecular nucleophilic addition reactions were discussed in an earlier section (section 1.32).

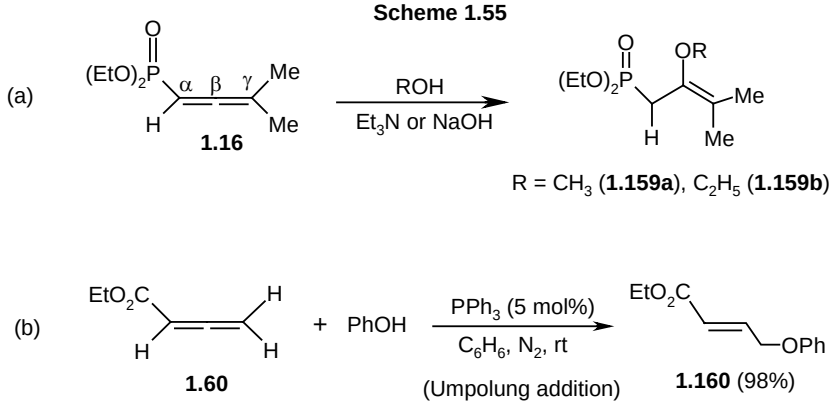
Scheme 1.54



1.81 *Addition of alcohols, phenols or thiols*

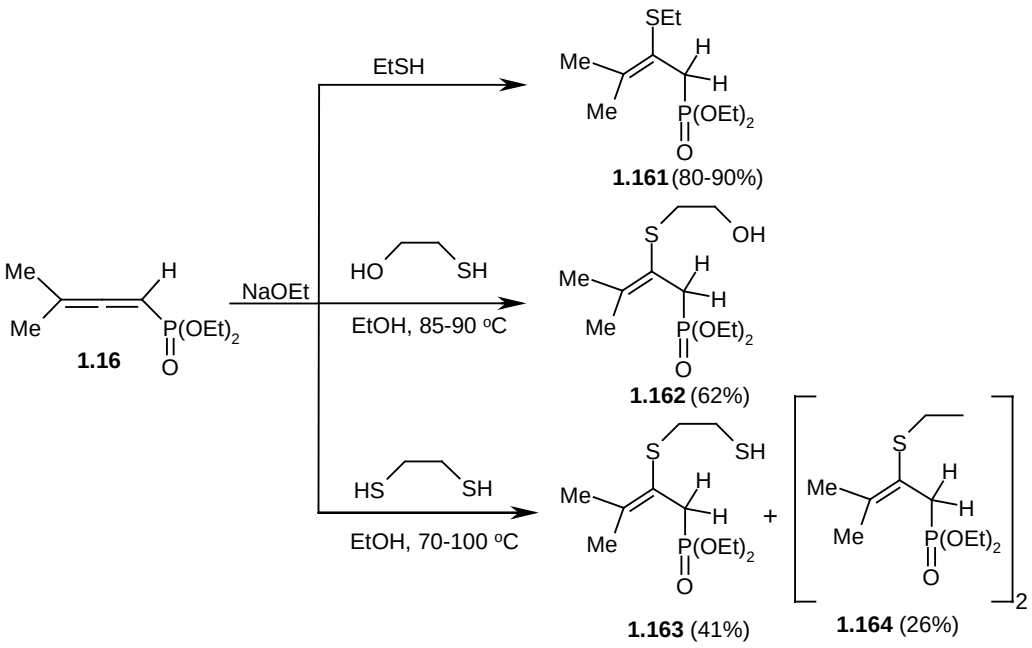
Allenylphosphonate **1.16** reacts with alcohols in the presence of NaOH or triethylamine to produce enol ethers **1.159a-b** (Scheme 1.55a).[72] In contrast, phenol attacks the *γ*-carbon of allenyl ester **1.60** (umpolung addition) under phosphine catalyzed reactions and produces **1.160** in 98 % yield (Scheme 1.55b).[73]

Scheme 1.55



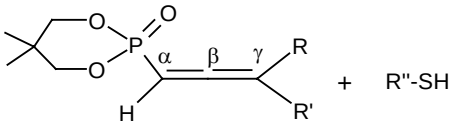
Reaction of phosphorylated allene **1.16** with ethanethiol in the presence of NaOEt leads to the *β*-addition product **1.161**.[74] Similarly, 2-mercaptoethanol and ethane-1,2-dithiol give *β*-addition products **1.162** and **1.163**, respectively, but in the latter case the double-addition product **1.164** is also isolated (Scheme 1.56).[74b-c]

Scheme 1.56



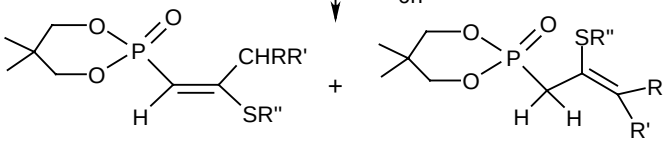
Our research group has recently reported that allenylphosphonates (**1.165a-b** and **1.21**) react with various thiophenols under neat conditions to give allyl- and vinyl-phosphonates (**1.166-1.170**) in good yields (Scheme 1.57a); one of the allylphosphonates (**1.169**) thus obtained is utilized for constructing C-C bonds *via* HWE reaction to give thionyl dienes (**1.171-1.172**) (Scheme 1.57b).[75] Interestingly, these reactions did not require the addition of a base.

Scheme 1.57a



R, R'= H (**1.165a**)
R= Me, R'= H (**1.165b**)
R, R'= Me (**1.21**)

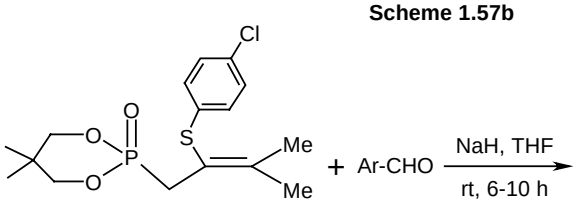
Neat, 110°C
6h



R, R' = H, R'' = 4-Cl-C_6H_4 [**1.166a**]
R = Me, R' = H, R'' = 4-Cl-C_6H_4 [**1.166b**]
R, R'= H, R''= C_6H_{11} [**1.168**]

R, R' = H, R'' = 4-Cl-C_6H_4 [**1.167a**]
R = Me, R' = H, R'' = 4-Cl-C_6H_4 [**1.167b**]
R, R'= Me, R''= 4-Cl-C_6H_4 [**1.169**]
R, R'= Me, R''= CH_2CH_2OH [**1.170**]

Scheme 1.57b



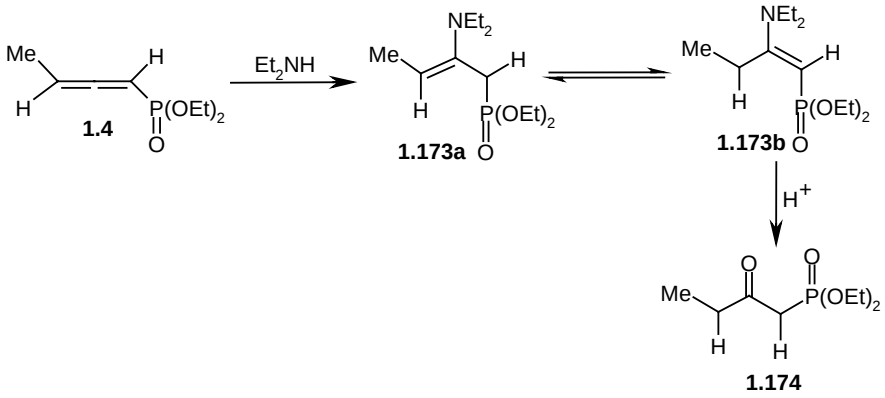
1.169

Ar = 4-Me-C_6H_4 (**1.171**, 76%)
= 4-MeO-C_6H_4 (**1.172**, 73%)

1.82 *Addition of amines*

Nucleophilic addition of diethylamine to allenylphosphonate **1.4** produces enamines **1.173a** and **1.173b** that are in equilibrium with each other; these enamines upon subsequent acid hydrolysis lead to the *β*-ketophosphonate **1.174** (Scheme 1.58).[76]

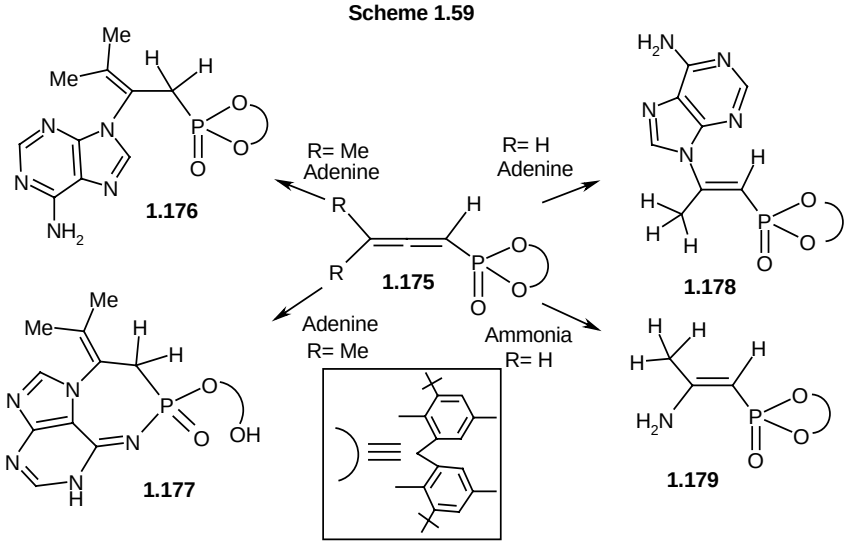
Scheme 1.58



1.4 **1.173a** **1.173b** **1.174**

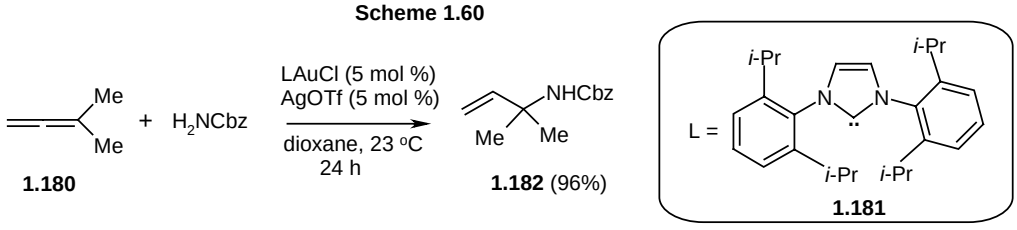
Recently from our laboratory, the reaction of allenylphosphonate **1.175** with nucleobases as well as gaseous ammonia leading to various allylic and vinylic phosphonates has been reported.[77] The nucleobases gave both (*E*)-vinyl and allyl products **1.176-1.178,** whereas in the case of ammonia the (*Z*)-vinylphosphonate **1.179** is preferentially formed (Scheme 1.59). The latter result was attributed to hydrogen bonding effects. It is interesting to note that both the N(9) [**1.176**] and N(7) addition products [**1.177**] are isolated and in the formation of **1.177**, a novel cyclization has occurred after the cleavage of the dioxaphosphocin ring.

Scheme 1.59



Allylic amines are components of many naturally occurring and biologically active molecules and are versatile building blocks for the synthesis of complex nitrogen-containing molecules. Very recently, Widenhoefer and co-workers developed, gold(I)-catalyzed protocol for the intermolecular hydroamination of allenes.[78] For example, treatment of allene **1.180** with benzyl carbamate catalyzed by a 1:1 mixture of LAuCl (L = *N*-heterocyclic carbine) (**1.181**) and AgOTf gave single regio- and diastereo-isomer of **1.182** in good yields (Scheme 1.60).

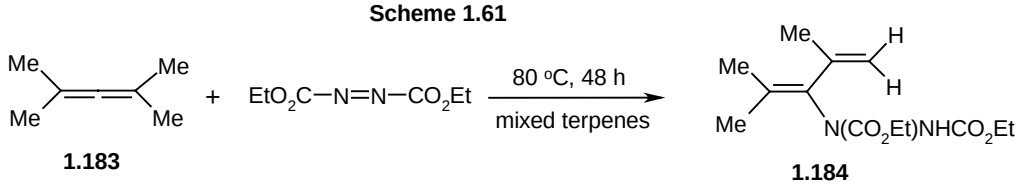
Scheme 1.60



1.83 *Addition of dialkyl azodicarboxylates*

Tetramethyl allene **1.183** reacts with diethyl azodicarboxylate at 80 °C/40 h in the presence of mixed terpene (polymerization inhibitor) to produce the 1,3-butadiene **1.184** (Scheme 1.61).[79] Here, a proton from the terminal CH_3 group migrates to the nitrogen of the azodicaboxylate residue and the nucleophilic attack occurs at the central carbon of the allene, as expected.

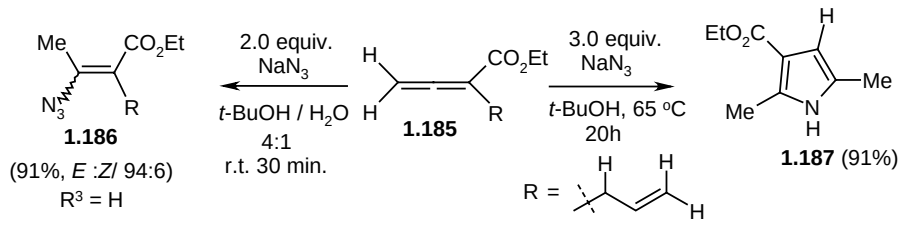
Scheme 1.61



1.84 *Addition of azides*

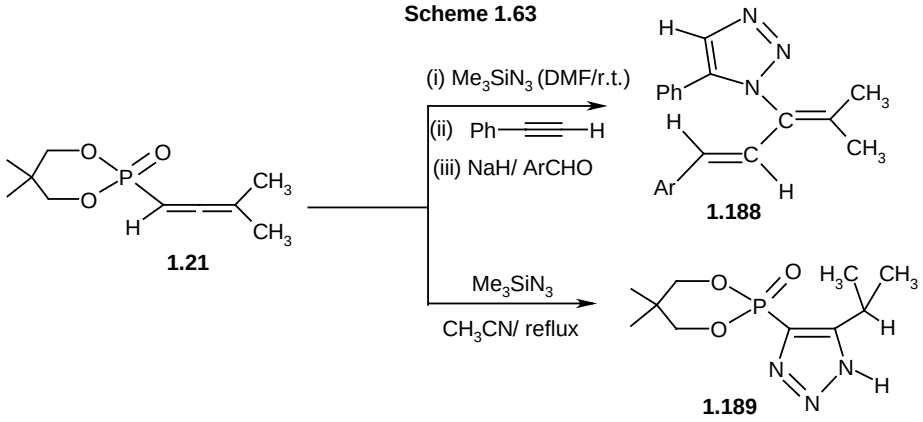
Nucleophilic addition of sodium azide to ester allene **1.185** at room temperature generates vinyl azides **1.186** in excellent yields with excellent regio- and stereoselectivities.[80] Moreover, pyrrole **1.187** were synthesized using allyl-substituted ester allene **1.185** [R = allyl] as substrate in *t*-BuOH at 65 °C (Scheme 1.62).

Scheme 1.62



Very recently our research group reported the reaction of allene **1.21** with trimethylsilyl azide affording the non-cyclized azide product, which underwent 1,3-dipolar cycloaddition with activated acetylenes to give 1,2,3-triazoles and subsequently to diverse *N*-substituted-1,2,3-triazoles **1.188** *via* Horner-Wadsworth-Emmons reaction (Scheme 1.63).[81] The same allenylphosphonate reacted with trimethylsilyl azide in CH_3CN under reflux conditions to give the triazole **1.189** in moderate yields.

Scheme 1.63

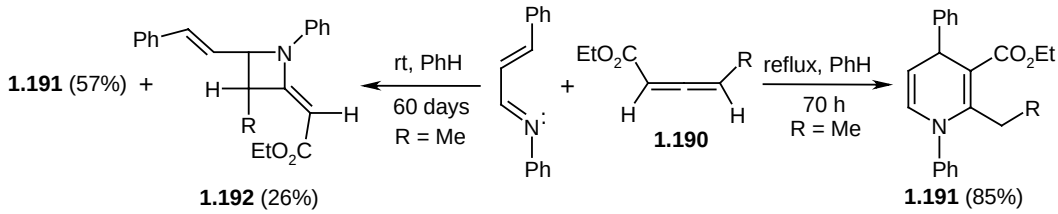


1.21 **1.188** **1.189**

1.85 *Addition of aza-dienes*

Ishar et al. reported that allenic esters **1.190** undergo facile, regioselective [4+2] cycloaddition with 1-aryl-4-phenyl-1-azadienes to afford novel 2-alkyl-1-phenyl-3-ethoxycarbonyl-4-phenyl-1,4-dihydropyridine **1.191** in good yields. However, when the reaction was carried at room temperature, besides the [4+2] addition, [2+2] mode of addition also took place resulting in *N*-aryl-2-ethoxy-carbonyl-methylidene-4-styrylazetidine **1.192** in 26% yield (Scheme 1.64).[82]

Scheme 1.64



1.192 (26%) **1.190** **1.191** (85%)

OBJECTIVES OF THE PRESENT WORK-PART A

The objectives of this part of the work were the following:

(i) To synthesize new allenylphosphonates and to find their utility in C-C and C-X (X = O, N) bond forming reactions,

(ii) To synthesize bis(allenyl)phosphonates and bis(allenyl)cylclodiphosph(V)azanes for possible use in polymer synthesis,

(iii) To explore the reactivity of allenylphosphonates with dialkyl azodicarboxylates in the absence/presence of triphenylphosphine,

(iv) To explore base catalyzed reactions of allenylphosphonates with salicylaldehydes and phenols,

(v) To find the utility of above synthesized products in Horner-Wadsworth-Emmons (HWE) reaction, and

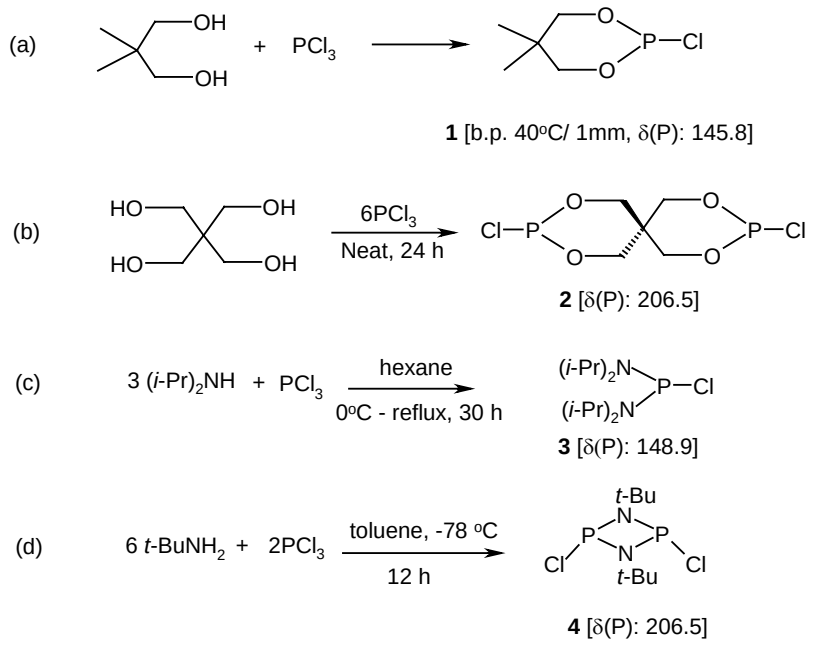
(vi) To check the cycloaddition reactions of allenylphosphonates.

RESULTS AND DISCUSSION

2.1 Synthesis of phosphorus(III) precursors

This part of the present work is essentially based on the key precursor $(OCH_2CMe_2CH_2O)PCl$ (**1**) which has a six-membered 1,3,2-dioxaphosphorinane ring.[83] In the present study, compound **1** was prepared by treating the diol with phosphorus trichloride under neat conditions (Scheme 1a). The precursor $C[(OCH_2)_2PCl]_2$ (**2**) was obtained by a procedure similar to that for **1** using pentaerythritol and PCl_3 (Scheme 1b).[84] The chlorophosphoramidite $[(i\text{-}Pr)_2N]_2PCl$ (**3**) was synthesized by the reaction of PCl_3 with diisopropylamine in hexane and was purified by crystallization from hexane (Scheme 1c).[85] In a similar manner, the cyclodiphosph(III)azane $[ClPN\text{-}t\text{-}Bu]_2$ (**4**) was prepared by using *t*-butylamine and PCl_3 and purified by vacuum distillation (110°C/ 3 mm of Hg) (Scheme 1d).[86]

Scheme 1

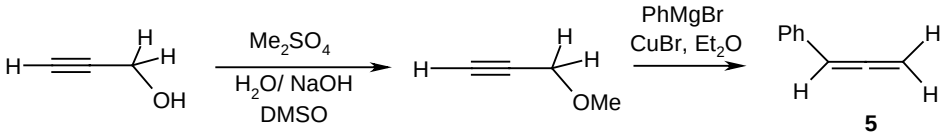


2.2 Synthesis of allenes

2.21 *Phenylallene PhCH=C=CH$_2$ (5)*

Phenylallene **5** was prepared by treating methyl propargylic ether with PhMgBr in the presence of CuBr as a catalyst (Scheme 2)[5] [Caution: dimethyl sulfate is carcinogenic]. In the second step the role of the solvent was crucial; when THF was used in place of diethyl ether, the ether PhCH=CHCH$_2$OMe was preferentially formed.[87]

Scheme 2



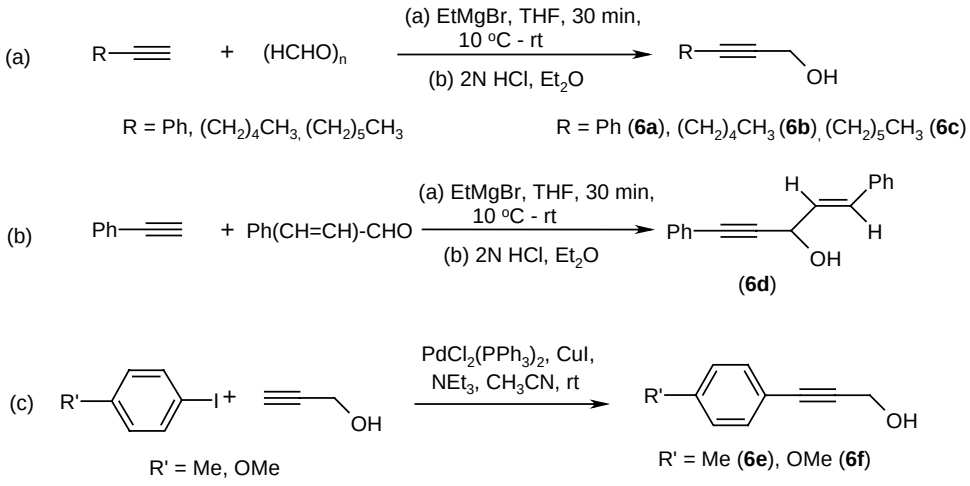
2.22 *Allenylphosphonates 7a-k, phosphonate-allenols 8a-b and the diene 9*

Synthesis of allenylphosphonates and phosphonate-allenols was more straightforward when compared to that of allenyl esters and keto-allenes.[4a,9] However, only a few references dealing with allenylphosphonates are available in the literature. In the following sections we will discuss the synthesis and stability of different types of phosphorus-based allenes.

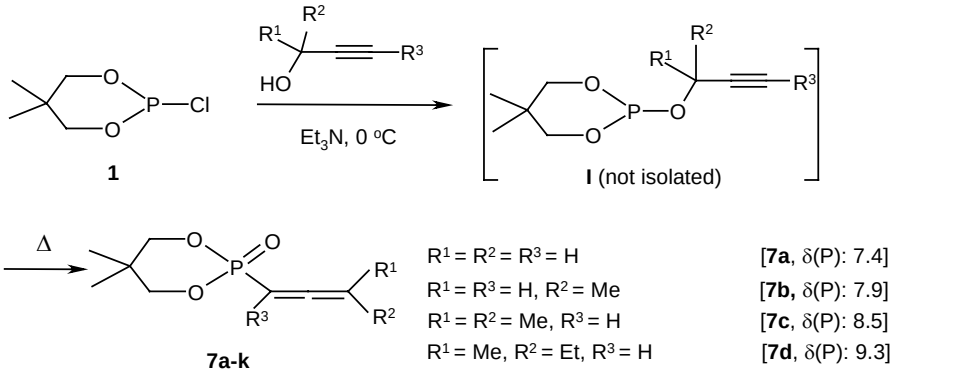
Allenylphosphonates 7a-k

The propargyl alcohols corresponding to the compounds **7a-d** and **7i** were commercially available; the remaining alcohols (**6a-f**) were prepared by using literature procedures (Scheme 3a-c).[88-89] These alcohols were purified by distillation or by using column chromatography. Subsequent reaction of (OCH$_2$CMe$_2$CH$_2$O)PCl (**1**) with the appropriate propargyl alcohol in the presence of a base (NEt$_3$) led to the allenylphosphonates (**7a-k**) after rearrangement of the initially formed P^{III} intermediate **I** (Scheme 4).[4a,7a] Compounds **7e-h** and **7j-k** are new.

Scheme 3



Scheme 4



$R^1 = R^2 = R^3 = H$	[**7a**, δ(P): 7.4]
$R^1 = R^3 = H$, $R^2 = Me$	[**7b,** δ(P): 7.9]
$R^1 = R^2 = Me$, $R^3 = H$	[**7c**, δ(P): 8.5]
$R^1 = Me$, $R^2 = Et$, $R^3 = H$	[**7d**, δ(P): 9.3]
$R^1 = R^2 = H$, $R^3 =$ Phenyl	[**7e**, δ(P): 6.6, 80%]
$R^1 = R^2 = H$, $R^3 =$ 4- tolyl	[**7f**, δ(P): 7.8, 80%]
$R^1 = R^2 = H$, $R^3 =$ 4 - anisyl	[**7g**, δ(P): 7.5, 80%]
$R^1 = H$, $R^2 =$ (CH=CHMe), $R^3 =$ Ph	[**7h**, δ(P): 6.7, 70%]
$R^1 = R^2 = H$, $R^3 = Me$	[**7i**, δ(P): 12.2, 90%]
$R^1 =$ Pentyl, $R^2 = R^3 = H$	[**7j**, δ(P): 11.3, 80%]
$R^1 =$ Hexyl, $R^2 = R^3 = H$	[**7k**, δ(P): 11.2, 78%]

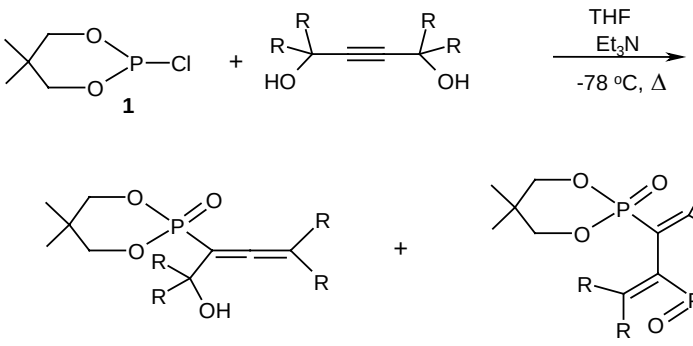
All the allenylphosphonates are crystalline solids and stable under nitrogen. We could preserve them under these conditions for several months. The allenylphosphonates **7e-k** show a characteristic strong band in the range 1927-1962 cm^{-1} due to υ(C=C=C) stretch.[90] The ^{31}P NMR spectra show a single peak in the range δ 6.6-7.8 for the α-aryl allenylphosphonates (**7e-h**) and in the range δ 11.3-12.2 for *α*-alkyl allenylphosphonates (**7i-k**). The ^{13}C NMR spectra are also quite useful for the identification of these compounds. The P*C* signal in the ^{13}C NMR spectra appears as a doublet at δ ~95 for **7e-h** and at δ 87-92 for **7i-k**, all with ^{1}J(P-

C) ~ 180 Hz. The PC=*C* signal for these compounds also appears as a doublet at δ 211-212 [^2J(P-C) ~ 4.0-6.0 Hz].

Phosphonate-allenols 8a-b and phosphonate butadiene 9: X-ray structure of 8a

The phosphonate-allenol **8a** was prepared by a slightly modified procedure compared to that for allenes **7e**. The reason for this modification was the fact that we had to avoid the formation of the butadiene [$(OCH_2CMe_2CH_2O)(O)P\text{-}C(=CH_2)]_2$ (**9**). A local excess of the precursor $(OCH_2CMe_2CH_2O)PCl$ (**1**) had to be avoided, since the butadiene has two phosphorus atoms per diol residue. Hence compound **1** in THF was added slowly to a solution of the diol and NEt_3 in THF at -78 ^oC, and later the reaction mixture was refluxed for 15 h. Yield of **8a** was 80% on the basis of ^{31}P NMR of reaction mixture; the remaining material was the 1,3-butadiene **9** (Scheme 5). Therefore, the product **8a** had to be crystallized carefully. Hence the isolated yield was low. A chromatographic separation was rendered difficult because of similar polarities of **8a** and **9**. We isolated **9** also quantitatively by using 2:1 stoichiometry of **1** and the diol.[91a] Since there are a couple of compounds analogous to **9**[91], and since this compound did not react with dimethyl acetylenedicarboxylate (DMAD) or diisopropyl azodicarboxylate (DIAD), we did not explore its chemistry in detail. Compound **8b** was prepared by the same procedure used for the synthesis of **7e**, but here the butadiene formation was not a problem and the isolated yield was very good.

Scheme 5



R = H [**8a**, δ(P): 10.1, X-ray]
Yield: 80% (NMR); 17% (isolated)

R = Me [**8b**, δ(P): 10.9; 75%]

R = H [**9,** δ(P): 9.0]
Yield: 10% (NMR, along with **8a**); 5% (isolated)
Quantitative (using 2:1 stoichiometry)

In the IR spectra, compounds **8a** and **8b** showed the ν(OH) stretch at 3304 and 3412 cm^{-1} and ν(C=C=C) band at 1968 and 1956 cm^{-1}, respectively. In ^{13}C NMR spectra, the P*C* signal appeared as a doublet at δ 92.9 [^{1}J(P-C) = 183.0 H] and δ 99.4 [^{1}J(P-C) = 179.9 Hz] for **8a** and **8b**, respectively. The ^{1}H NMR spectrum of the **9** is interesting. The two alkene protons show doublets with different coupling constants at δ 6.27 [=CH_AH$_B$ *cis* to P with ^{3}J(P-H) = 20.1 Hz] and δ 6.56 [=CH$_A$$H_B$, *trans* to P with ^{3}J(P-H) = 44.9 Hz]. These ^{3}J(P-H) values between P and H located *cis* and *trans* to each other are nearly double that of ^{3}J(H-H) values observed in normal alkenes. The structure of compound **8a** was confirmed by X-ray crystallography (Fig. 1, left). As expected, hydrogen bonding between the phosphoryl oxygen and the -OH group is present here. This leads to a chain structure (Fig. 1, right).

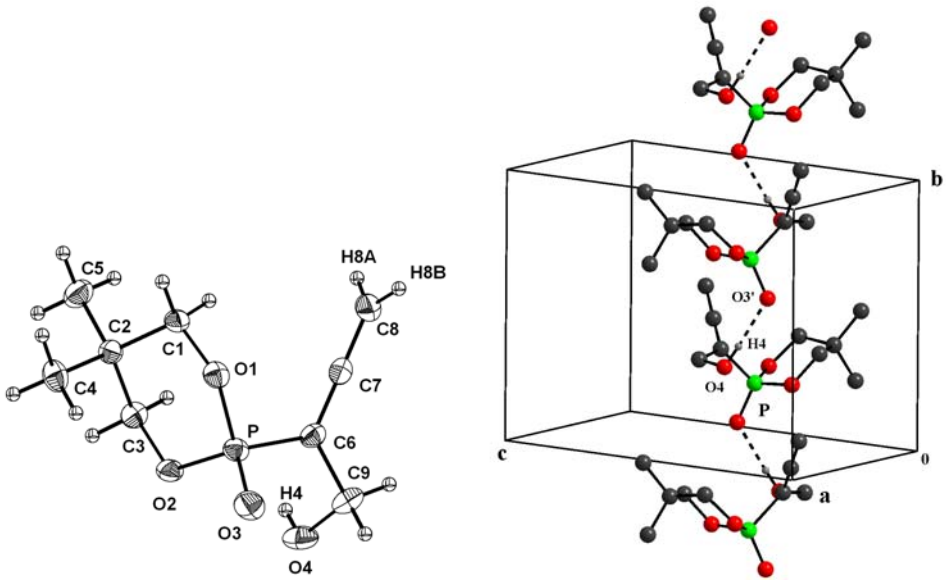


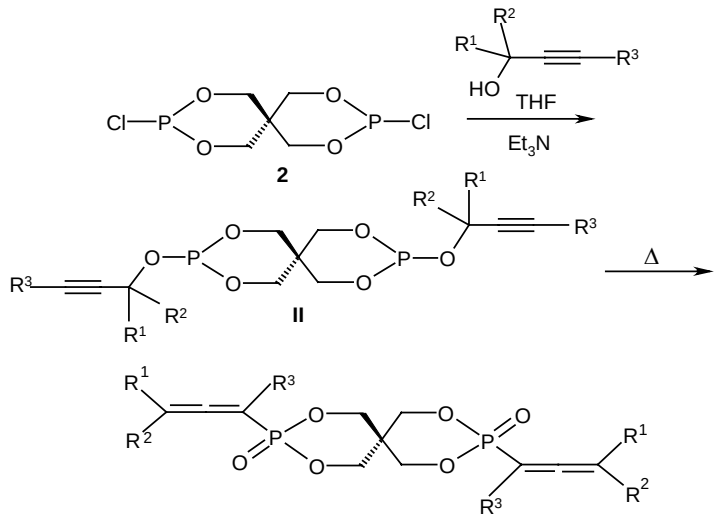
Fig. 1. Left: The ORTEP diagram of **8a**. Right: hydrogen bonding in **8a** [O(4)-H(4)...O(3') 0.82, 1.95, 2.764(2) Å, 174.7 °. Symmetry code: 1.5-x, 0.5+y, 0.5-z].

2.23 *Bis(allenyl)phosphonates 10-13: X-ray structure of 10*

Compounds **10-13** that also contain the 1,3,2-dioxaphosphorinane ring but with two reactive allene residues have been prepared in good yields by slightly modifying the procedure adapted for the synthesis allenylphosphonate **7e**, using [ClP(OCH$_2$)$_2$]$_2$C (**2**) and the appropriate propargyl alcohol (Scheme 6). Although in the reaction using **1** we could not detect the P^{III} intermediate alkoxide **I**, we could do so in that using **2**; the species **II** [R^1 = R^2 = H] was clearly identified by the ^{31}P

NMR [δ(P) 125.7] spectrum as essentially a single component prior to refluxing.[92] The product **10** was obtained as a crystalline material from methanol; it had low solubility in normal organic solvents like toluene, dichloromethane etc.. All these allenylphosphonates (**10**-**13**) could be handled in air, but over a period of ca 15 d, turned into liquids. Our attempts to analyze/ separate the components of these liquids (column chromatography/ NMR) were not successful.

Scheme 6



$R^1 = R^2 = R^3 =$ H [**10**, δ(P): 11.4; 79%, X-ray]
R^1 = Et, R^2 = Me, R^3 = H [**11**, δ(P): 13.0; 74%]
$R^1 = R^2$ = Me, R^3 = H [**12**, δ(P): 12.6; 76%]
$R^1 = R^2$ = H, R^3 = Ph [**13**, δ(P): 10.6; 74%]

Compounds **10**-**13** show a band in range of 1939-1964 cm^{-1} in the IR spectra corresponding to the (C=C=C) stretch. In the ^{13}C NMR spectra, the P-*C* carbon for the compounds **11**, **12** and **13** appears as a doublet at δ 77.3 [^1J(P-C) = 199.1 Hz], 75.4 [^1J(P-C) = 199.1 Hz] and 94.8 [^1J(P-C) = 185.2 Hz], respectively. The structure of **10** was further confirmed by X-ray crystallography (Fig. 2). There are weak C-H...O interactions between the O*CH*$_2$ protons of the six-membered phosphorinane ring and the phosphoryl oxygen as shown in Fig. 2 (right). Thus each oxygen atom has close contacts with the protons of different methylene groups in the extended structure.

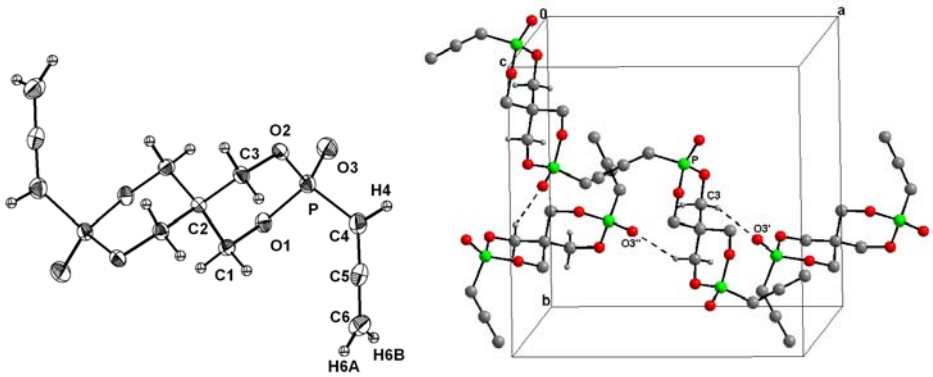


Fig. 2. Left: The ORTEP diagram of **10** (only half of the molecule is present in the asymmetric unit). Right: hydrogen bonding in **10** [C(3)-H(3A)...O(3') 0.97, 2.41, 3.286(4) Å, 150.3°. Symmetry code: (i) 3/4+y, 3/4-x, -1/4+z)].

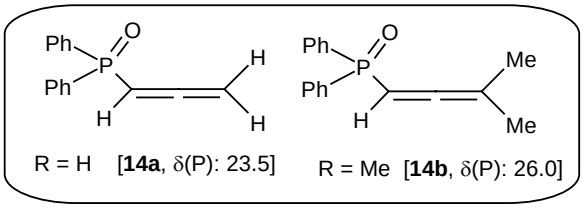
Selected bond parameters for **8a** and **10** are given in Table 1. The P-O (ring), P=O and P-C distances are in the normal range expected for these compounds.[93a-b] In contrast to many previously reported structures,[93b-e] the two adjacent C=C bonds of the allenyl group are much closer in length, a feature similar to that reported by Angelov et al [1.296(4) and 1.299(4) Å].[93a] The C=C=C unit is essentially linear with a deviation of only ~ 1.1° from 180°. The dihedral angle between the planes containing (i) H(8A), H(8B), C(8) and C(7), and (ii) P, C(6), C(7) and C(9) in compound **8a** is 83(1)° which is significantly different from the expected orthogonality. In **10**, this dihedral angle is 87(1)°. The six-membered 1,3,2-dioxaphosphorinane ring has a chair conformation in these structures. Compound **10** has a spirocyclic carbon center; the angles at this center are within 2° of the ones required for tetrahedral geometry.

Table 1. Selected bond parameters for **8a** and **10** (Å, °)

Parameter	**8a**	**10**
P-O(ring)	1.565(2)	1.569(1)
P-O(ring)	1.573(2)	1.568(1)
P=O	1.456(2)	1.466(1)
P-C	1.771(2)	1.779(2)
C(P)=C	1.288(3)	1.302(2)
$C=CH_2$	1.280(4)	1.290(3)
C=C=C	179.1(2)	178.8(2)

2.24 *Allenyl phosphinates 14a-b*

The allenylphosphinates $Ph_2P(O)CH=C=C(R)_2$ [R = H (**14a**, δ(P) 23.5[4f]), R = Me (**14b**, δ(P) 26.0[93e])] were prepared by a procedure similar to that for **7e** using $(Ph)_2PCl$ and corresponding propargyl alcohol. These are known compounds.[4f,93e]

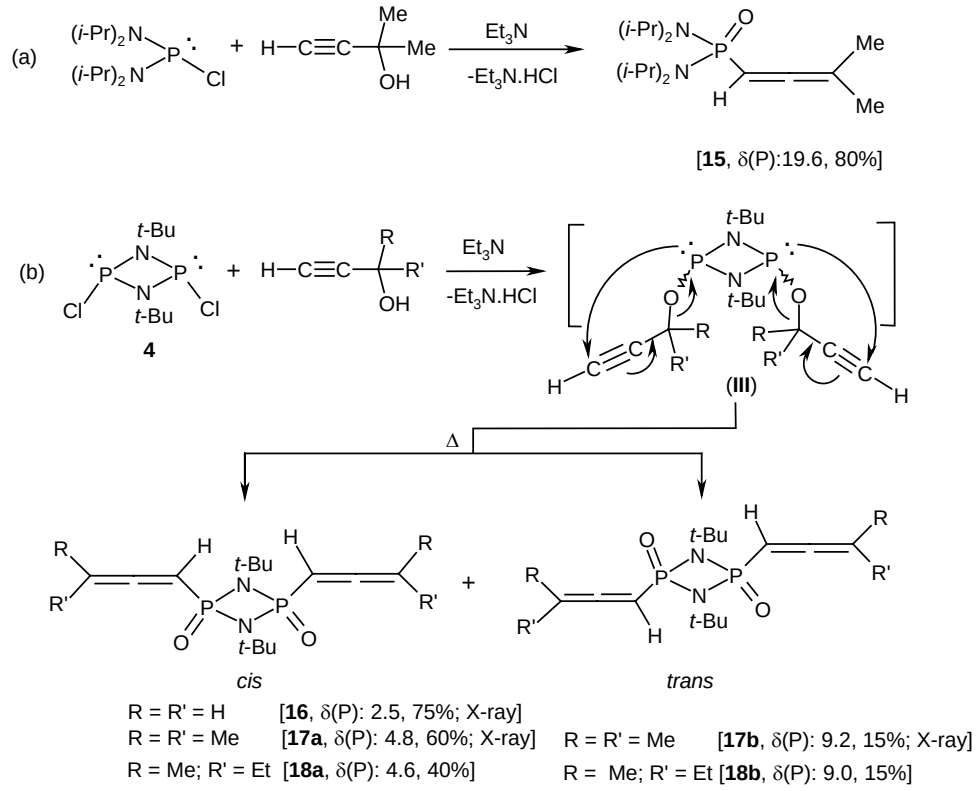


2.25 *Allenylphosphoramidate 15 and bis(allenyl)cylclodiphosph(V)azanes 16-18*

In the previous section, we discussed the synthesis, structures and stability of different types of allenylphosphonates. These allenylphosphonates are electron deficient. In this context, we were interested in modifying the phosphorus center by means of electron-rich amino groups and to study the accompanying changes in the reactivity and structure. Thus the compound $((i\text{-}Pr)_2N)_2P(O)CH=C=C(CH_3)_2$ (**15**) was prepared by a procedure similar to that for **7e**, using $((i\text{-}Pr)_2N)_2PCl$ (**3**) and $HC\equiv CC(CH_3)_2(OH)$ (Scheme 7a). This allene shows a characteristic band at 1966 cm^{-1} in IR spectrum due to υ(C=C=C). The carbon *α* to phosphorus appears as a doublet at δ 86.7 [^1J(P-C) = 148.8 Hz] in the ^{13}C NMR spectrum. Compounds **16**, **17a-b** and **18a-b** were synthesized by treating *cis*-$[ClP(\mu\text{-N-}t\text{-Bu})]_2$ (**4**) with the corresponding propargyl alcohol in the presence of triethylamine as shown in Scheme 7b. The initially formed (alkoxy)cyclodi*phosph(III)*azanes **III** underwent thermal rearrangement to give rise to the (allenyl)cyclodi*phosph(V)*azane products. The reaction using the unsubstituted propargyl alcohol $HC\equiv CCH_2OH$ gave essentially the *cis* isomer **16** and only traces of the *trans* isomer. In contrast, substituted propargyl alcohols HC≡CC(Me)(R)OH (R= Me, Et) afforded both *cis*- and *trans*- isomeric products **17a-b** and **18a-b** in decent yields. These two isomers were readily distinguishable by their ^{31}P NMR chemical shifts with the *trans* isomer appearing downfield by ~4.5 ppm. Although this feature is similar to that of P^{III} derivatives (Δδ ~52 ppm) [94], the Δδ values between the two isomers are smaller for **17a-b** and **18a-b**. The ^{13}C NMR spectra show a characteristic doublet [^1J(P-C) = 156-164 Hz] for the P-*C* carbon at δ 84-87. The signal for the *trans* isomer appears at lower field with a lower ^1J(P-C) value compared to that of the *cis* isomer. The IR

stretch for the allenic moiety appears at 1950-1960 cm^{-1} with that for the *trans* isomer appearing at slightly lower wave number.

Scheme 7



Since the starting material **4** has a *cis*-disposition of the two P-Cl groups, one may expect the reaction to lead to only *cis*-isomer of the P^{III} alkoxide **III** as long as the phosphazane ring remains intact during the reaction. This may not be the case when lithium or sodium alkoxides/aryloxides are used, but is more likely when alcohol/triethylamine system is used.[95] If only *cis*-P^{III} alkoxide is formed, it may be expected that rearrangement to the allenyl phosphoramidates **16-18** lead only to the corresponding *cis*-isomer. We made an attempt to identify the P^{III} intermediate **III** in the case of **17a-b** by performing the reaction at $-15^{o}C$ (ca ~ 1h) in THF and recording the ^{31}P NMR spectrum immediately (<1 h). However, the reaction mixture showed essentially the P^{V} products **17a-b**, indicating that the rearrangement is very facile under these conditions. Even the partially rearranged products with P^{III}-N-P^{V} system were not observed. The *cis*-compound **17a** was stable up to $180^{o}C$/ 2h and no perceptible conversion to the *trans* form was noticed [^{31}P NMR]. Also, the *trans* P^{V} compound **17b** did not appear to convert to the *cis* form upon heating. Thus, once formed, **17a** and **17b** do not isomerize. Several investigations suggest that if sodium

or lithium alkoxide/aryloxide is treated with **4**, *trans* product is formed initially in larger quantities; over a period of time or upon heating more of the *cis*-product is obtained.[94] We also tried to see if use of the lithium salt of the corresponding propargyl alcohol could increase the yield of the *trans* isomer **17b**. Although the reaction mixture showed more of the *trans* product, there were many other peaks that hampered a complete analysis. Preliminary theoretical calculations (using coordinates from X-ray structure and optimizing the geometry) done at B3LYP/6-31G** level suggest that the *cis* isomer **17a** is marginally more stable than the *trans* isomer **17b** by ~ 6.5 kJmol^{-1} in the gas phase. The geometry and structure of the compounds **16** and **17a-b** are confirmed by X-ray crystallography (Figures 3 and 4). Selected geometrical parameters are given in Table 2. We also obtained the X-ray structure for the compound **17c** (allenylcylclodiphosph(V)azane) accidentally while picking up the crystal of **17b**, but in the bulk only **17b** was present and hence spectroscopic data for **17c** were not recorded. Its molecular structure is shown in Figure 5. Compounds **16**, **17a-b**, **18a-b** as well as **10-13** could be useful precursors in polymer synthesis. This aspect is studied further in the laboratory.

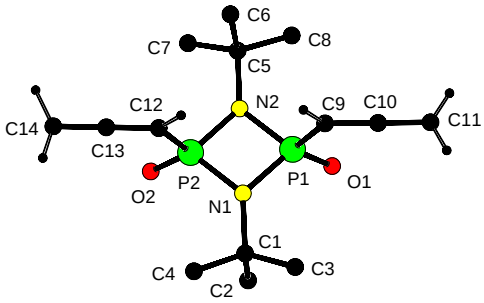


Fig. 3. Molecular structure of **16**

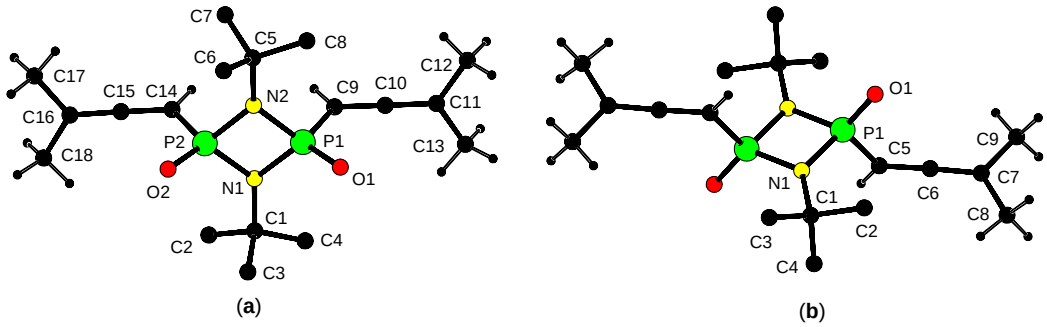


Fig. 4. Molecular structures of (a) **17a** and (b) **17b** (only half of the molecule is present in the asymmetric unit).

Table 2. Selected bond lengths (Å) and bond angles (°) for **16** and **17a-b** with esd's

Compound **16**		Compound **17a**		Compound **17b**	
P(1)-N(1)	1.675(2)	P(1)-N(1)	1.678(3)	P(1)-N(1)	1.674(3)
P(1)-N(2)	1.677(2)	P(1)-N(2)	1.673(3)	P(1)-N(1')	1.668(3)
P(2)-N(1)	1.672(2)	P(2)-N(1)	1.683(3)	P(1)-C(5)	1.768(4)
P(2)-N(2)	1.659(2)	P(2)-N(2)	1.678(3)	C(5)-C(6)	1.294(5)
P(1)-C(9)	1.775(2)	P(1)-C(9)	1.764(4)	C(6)-C(7)	1.304(5)
P(2)-C(12)	1.778(2)	P(2)-C(14)	1.768(4)		
C(9)-C(10)	1.293(3)	C(9)-C(10)	1.290(5)		
C(10)-C(11)	1.283(3)	C(10)-C(11)	1.308(5)		
C(12)-C(13)	1.286(3)	C(14)-C(15)	1.303(5)		
C(13)-C(14)	1.297(4)	C(15)-C(16)	1.302(5)		
N(1)-P(1)-N(2)	83.8(1)	N(1)-P(1)-N(2)	84.4(3)	N(1)-P(1)-N(1')	83.8(2)
N(1)-P(2)-N(2)	84.48(9)	N(1)-P(2)-N(2)	84.1(2)	P(1)-N(1)-P(1')	96.2(2)
P(1)-N(1)-P(2)	95.6(1)	P(1)-N(1)-P(2)	95.5(2)		
P(1)-N(2)-P(2)	96.1(1)	P(1)-N(2)-P(2)	95.9(2)		

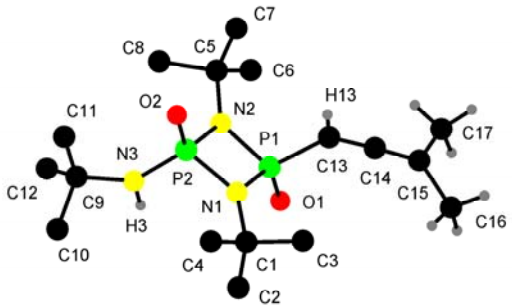
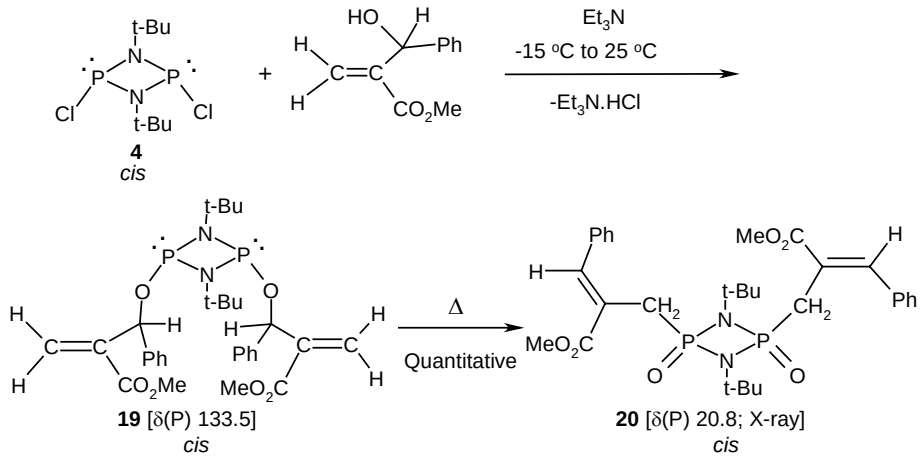


Fig. 5. Molecular structure of **17c** Selected bond lengths [Å] with esd's in parentheses. P(1)-N(1) 1.670(3), P(1)-N(2) 1.658(3), P(1)-C(13) 1.781(4), P(2)-N(1) 1.675(3), P(2)-N(2) 1.706(3), C(13)-C(14) 1.308(5), C(14)-C(15) 1.292(5), N(2)-P(1)-N(1) 84.53(13), N(1)-P(2)-N(2) 82.90(13), P(1)-N(1)-P(2) 96.63(14), P(1)-N(2)-P(2) 95.90(13)° [Hydrogen bond parameters: N(3)-H(3)**…**O(1) 0.83(4), 2.19(4), 3.007(4) Å, 165(3) °; symmetry code: 1-x, 2-y, -z].

2.3 Synthesis of the bis(allyl)cyclodiphosph(V)azane 20: Identification of P^{III} intermediate 19

Since it is known that allyloxy products of P^{III} derivatives can also rearrange to their respective P^{V} phosphonates,[96a,b] we wanted to check the feasibility of identifying the intermediates in these cases for comparison. Thus we treated the Baylis-Hillman alcohol (a substituted allyl alcohol) $PhCH(OH)C(CO_2Me)=CH_2$[96c] with $[ClP(\mu\text{-N-}t\text{-Bu})]_2$ (**4**) (Scheme 8). In this case, we could observe mainly the *cis*-alkoxy P^{III} product **19** *prior to rearrangement* by ^{31}P NMR [Fig. 6(a); δ(P) 133.5]. The assignment of a *cis* structure to **19** is based upon comparison of its δ(P) value with those available in the literature for other compounds.[94-95] The same mixture after one day at 25 °C, showed a complete absence of **19** and the peak corresponding to **20** started developing [Fig. 6(b); δ(P) 20.8]. Upon heating the original reaction mixture at 150 °C for 20 min, only the *cis* isomer **20** is formed quantitatively [Fig. 6(c)]. Interestingly, in the initial reaction mixture, there is a P^{V} product exhibiting two close peaks at δ(P) 24.3 and 24.4 ascribable to the *trans*-isomer of **20** (further isomerism is possible at the site of the C=C bond which may be the reason for two closely spaced peaks). Another peak at δ ~101.6 is unassigned. None of these intermediates is seen after heating the original reaction mixture at 150 °C [Fig. 6(c)]. The structure of the compound **20**.H_2O was further confirmed by X-ray crystallography (Fig. 7); the water of crystallization had entered during the crystallization process.

Scheme 8



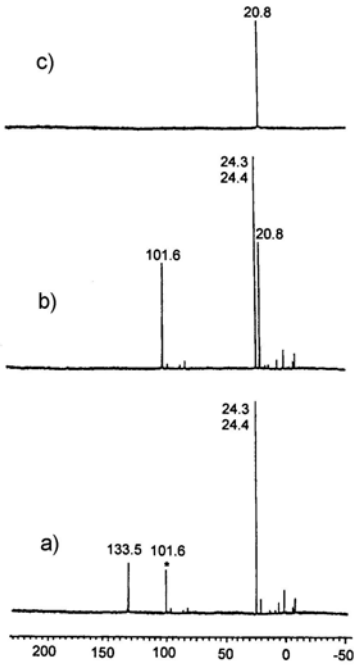


Fig. 6. The ^{31}P NMR spectra of (a) the reaction mixture of **4** with $PhCH(OH)C(CO_2Me)=CH_2/Et_3N$/ 0- 25 ^oC in $CDCl_3$ after 5 h, (b) the solution in (a) after 24 h and, (c) the reaction mixture after heating at 150 ^oC for 20 min and then dissolved in $CDCl_3$.

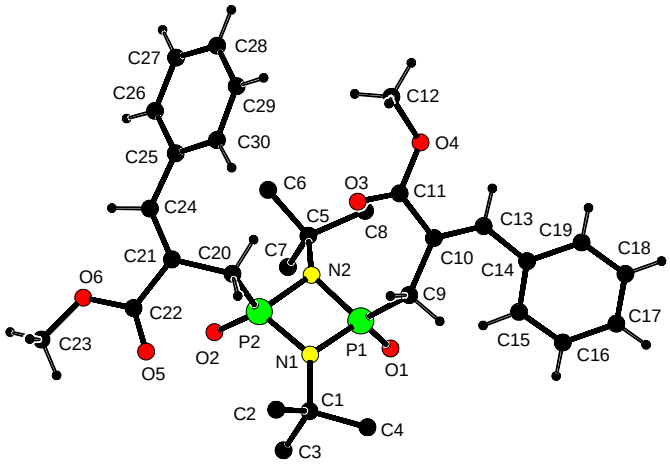


Fig. 7. Molecular structure of **20**.H_2O; solvate water and *t*-butyl hydrogen atoms are not shown. Selected bond parameters with esd's in parentheses: P(1)-N(1) 1.670(2), P(1)-N(2) 1.666(2), P(1)-C(9) 1.817(3), P(2)-N(1) 1.676(2), P(2)-N(2) 1.690(2), P(2)-C(20) 1.814(3)Å; N(2)-P(1)-N(1) 85.10(12), N(1)-P(2)-N(2) 84.18(11), P(1)-N(1)-P(2) 95.37(13), P(1)-N(2)-P(2) 94.99(12)^o.

Comparison of X-ray Structures of 16, 17a-c and 20.H_2O

The molecular structures of **16**, **17a-c** and **20.H_2O** are shown above in Figures 3-5 and 7. Selected geometrical parameters for **16** and **17a-b** are also given in Table 2 above; data for **17c** and **20.**H_2O are given in Figures 5 and 7 respectively. Since phosphorus atoms in **16** and **17a-b** are chemically equivalent, the endocyclic P-N distances to a particular phosphorus atom are nearly equal. These P-N distances [1.660-1.680 Å] are clearly shorter than those found for several other cyclodiphosph(III)azanes (1.71-1.74 Å)[97] or the apical P-N bonds in pentacoordinate phosphoranes.[98] Although the allenic C=C bonds in **16** appear to be slightly shorter than those found in **17a-b**, the variations are within the three times the esd's and hence a definite conclusion cannot be given. The P-C bond distance in all the three compounds is in the expected range.[93a-b] The ring nitrogen atoms are essentially planar with the sum of the bond angles at nitrogen in the range 356-360°. This feature is unlike that in the P^{III} compound $Et_2C[CH_2OP(\mu\text{-N-}t\text{-Bu})_2PNH\text{-}t\text{-Bu}]_2$ wherein the ring nitrogen atoms are non-planar [ΣN = 347-348°].[97] The $[NP]_2$ rings in all the three compounds are essentially planar with the maximum deviation of 0.02 Å found for **17a**.

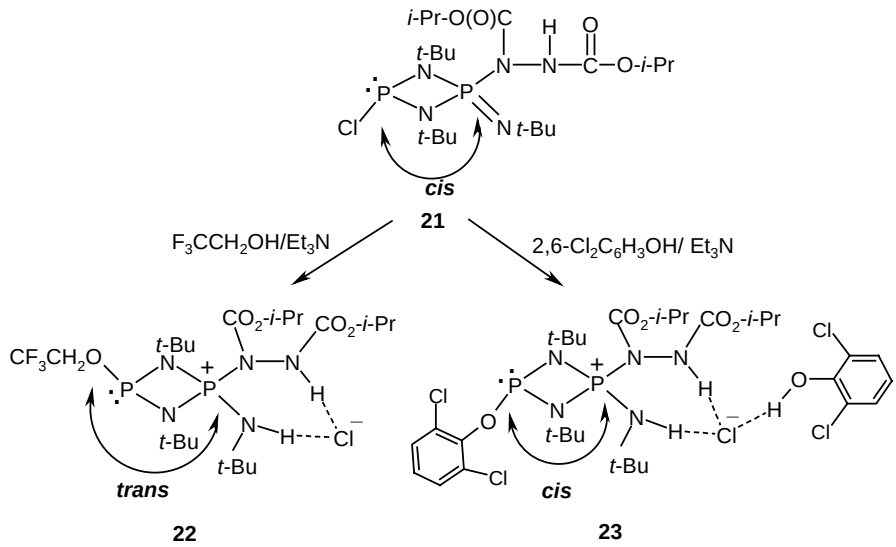
The *cis*-stereochemistry in **20**.H_2O is also clearly revealed by X-ray crystallography (Fig. 7). The P-N distances are similar to those observed in **16** and **17a-b**, but the P-C bonds (mean 1.815Å) are slightly longer. The $[NP]_2$ ring is slightly distorted with the mean deviation of the fitted atoms from the mean plane of the ring being ~0.03Å. The ring nitrogen atoms are more pyramidal [ΣN(1) = 358.3; ΣN(2) = 352.2°] than those in **16** and **17a-b**. The solvate water molecule is hydrogen bonded to the phosphoryl oxygen atoms, but since this was not the interest in the present study, we have not probed this aspect further.[99] In compound **17c** (cf. Fig. 5), although one may expect the P(2)-N(1) and P(2)-N(2) distances to be close, the X-ray structure shows them to be significantly different; a similar difference but of lesser magnitude is found for P(1)-N(1) and P(1)-N(2) bonds.

Cis-trans isomerism in cyclodiphosph(V)azanes

X-ray structures of many *cis*- and *trans*-$[RNHP(S)NR]_2$ are reported in the literature, but such data for both the isomers with the same R group is not available.[100] These compounds were obtained by sulfur-oxidation of the respective

aminocyclodiphosph(III)azanes. In the reaction of compound **21** with 2,2,2-trifluoroethanol and 2,6-dichlorophenol in the presence of Et_3N, we have previously reported that the stereochemistry of P^{III}-N-P^{V} products obtained is different.[101,102] While the former gave the *trans*-product **22**, the latter afforded the *cis*-product **23** (Scheme 9). This feature revealed that the incoming nucleophile also has a role to play in determining the *cis*- or *trans*- stereochemistry in the final products. The reactive site in these cases is the same P^{III}-Cl bond in **21** which is *cis* to the P=N(*t*-Bu) group at the other phosphorus. Based on these observations and the fact that we did not observe the isomerization of pure *cis*-**17a** or *trans*-**17b**, we think that the formation of *cis*-and *trans*- isomeric pairs **17a-b** and **18a-b** took place *via* thermal rearrangement of the corresponding *cis* and *trans* P^{III} alkoxy intermediates of type **III** shown in Scheme 7. In the formation of **20**.H_2O that contains sterically more demanding substituents, however, it is possible that the rearranged P^{V} *trans* product [δ(P) 24.3, 24.4] isomerizes to the *cis*- form [δ(P) 20.8]. This proposition needs further confirmation since there is also a possibility of monomer (phosphazene)-dimer (diphosphazane) equilibrium in this system.[103]

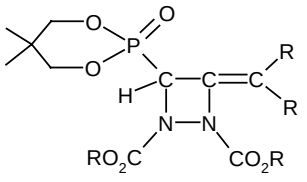
Scheme 9



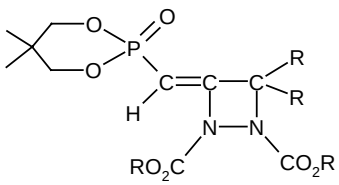
2.4 Reactions of allenyl phosphonates/phosphinates/phosphoramidates with dialkyl azodicarboxylates

2.41 *Synthesis of phosphonyl substituted trans-1,3-butadienes 24-28*

It is possible for allenylphosphonates **7a-c** to undergo [2+2] cycloaddition reaction[104] with dialkylazodicarobxylates to lead to four-membered ring containing products such as (**IV**)-(**IV**'). Such products are formed with non-phosphorylated allenes.[105] However, heating the allenylphosphonate **7a** or **7b** with diethyl azodicarboxylate (DEAD) or diisopropyl azodicarboxylate (DIAD) under MW conditions (160 W; ~ 180 ^{o}C) for about 1/2 h afforded only a mixture of products. By contrast, treatment of **7c** with DEAD or DIAD gave stable 1,3-butadiene products **24**-**25** *regio- and stereo-specifically* in >60% yield (Scheme 10a). This feature appears to be general for =CMe_2 terminal allenes since we could isolate analogous butadienes **26**-**28** starting from the allenes **14b** and **15** (Scheme 10b). Once formed, *they did not cyclize* to give the pyrazoles even upon prolonged heating. Interestingly, formation of similar substituted hydrazine derivatives in the reaction of Morrison-Brunn-Huisgen betaine with ketones has been reported recently by Lee and co-workers, as discussed in section 1.61.[45a] It is also interesting to note that compound **29** that is similar to **25** was prepared by reacting **7c** and $MeO_2CC{\equiv}CCO_2Me$ (DMAD) by one of my colleagues in the laboratory nearly at the same time.[87]

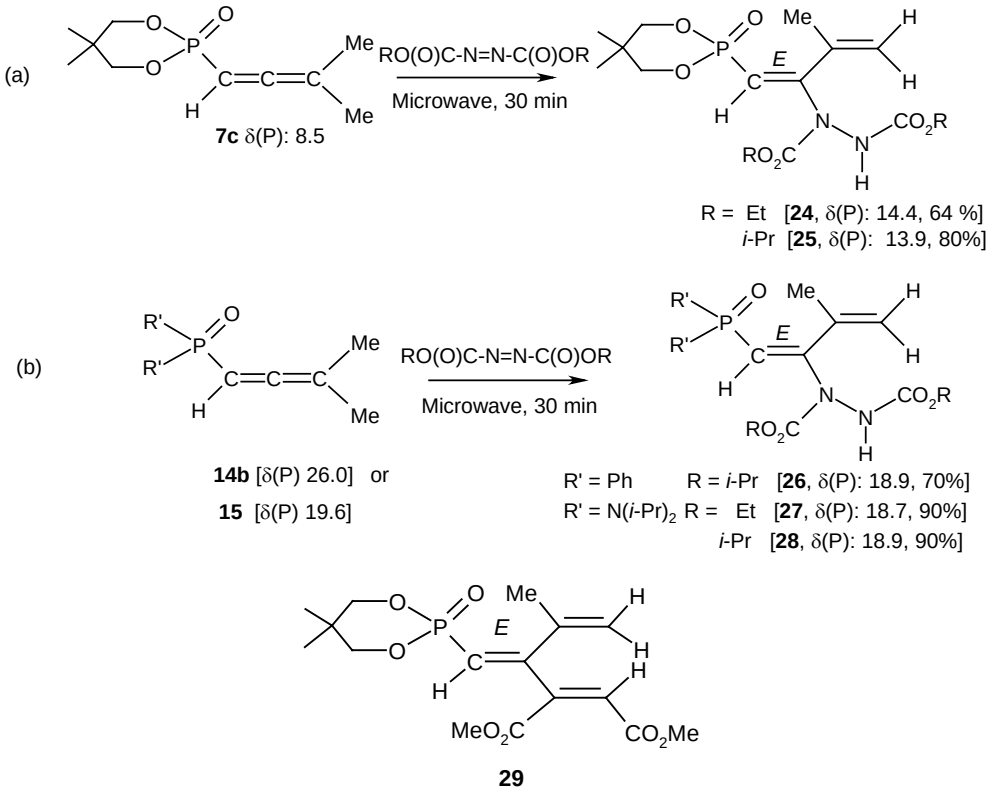


(IV)



(IV')

Scheme 10



29

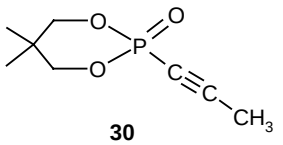
Compounds **24-28** were characterized by spectroscopic and analytical data. They show a band at 3150-3196 cm^{-1} in the IR spectra due to the υ(NH) stretch. The ^{13}C NMR spectra exhibit a characteristic doublet [^{1}J(P-C) = 107-194 Hz] for the P-*C* carbon at δ 98-115, but the ^{1}J(P-C) value changes drastically depending upon the substituents on phosphorus [106.7 Hz for **26**, 146.7 Hz for **28** and 194.1 Hz for **25**].

The reaction of allenylphosphonate $(OCH_2CMe_2CH_2O)P(O)C(Ph)=C=CH_2$ (**7e**) with DIAD under similar conditions gave a major signal at δ(P) 10.8 (> 95%) along with that due to starting material [δ(P) ~ 6.6; ~5%] in the ^{31}P NMR spectrum. Since a butadiene similar to **24-25** cannot be formed in this case, we tried to isolate this compound by using column chromatography, but it decomposed to give a mixture of products.

2.42 *Synthesis of phosphono-pyrazoles and tetra-substituted pyrazoles*

The reactions described in the previous section were done in the absence of triphenylphosphine (PPh_3). We have also performed the above reaction of allenylphosphonates (**7a-g)** and allenylphosphoramidates (**15**) with DEAD/DIAD in the presence of Ph_3P. The $=CH_2$ terminal allene **7a** when treated with DIAD in the presence of PPh_3, rearranged to give the acetylene **30**, as observed elsewhere.[14]

Compound **7b** readily reacted with DEAD/DIAD to afford the phosphono-pyrazoles **31/32** (Scheme 11a). Among the three solvents (DME, THF and dichloroethane) checked, THF worked better. Although the isolated yields are moderate, the ease of isolation of the products makes these reactions quite attractive. The characteristic peak for the P-*C* carbon in the ^{13}C NMR spectra appears as a doublet at δ 96.8 [^{1}J(P-C) = 217.2 Hz] and δ 98.2 [^{1}J(P-C) = 216.2 Hz] for compounds **31** and **32**, respectively. The reaction of allenylphosphonate **7c** with DIAD in the presence of PPh_3 gave two phosphono-pyrazoles, **33** and **34** (Scheme 11b). In the IR spectra, pyrazole **33** shows the C=O stretch at 1752 cm^{-1}, which is absent in the spectrum of **34**. The latter compound shows the -NH stretch at 3181 cm^{-1}. In ^{13}C NMR spectra, the P*C* signal appears as a doublet at δ 97.0 [^{1}J(P-C) = 213.0 Hz] and δ 87.1 [^{1}J(P-C) = 226.8 Hz] for **33** and **34**, respectively. The structures of compounds **33** and **34** were further confirmed by X-ray crystallography (Fig. 8 and Fig. 9). The bond parameters are normal, but in the case of **34**, intermolecular hydrogen bonding involving N*H* and P=*O* is present. Allene **7d** did not react appreciably under the above conditions.



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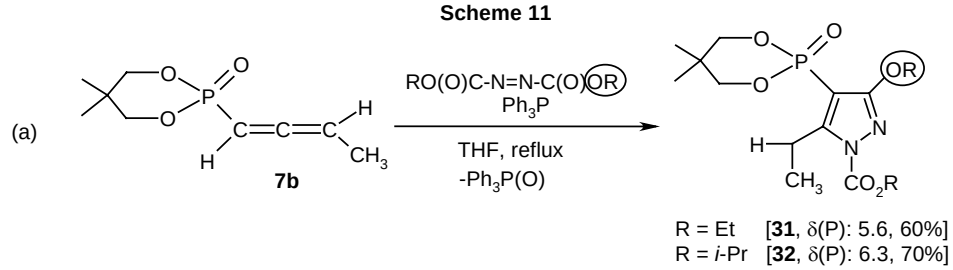
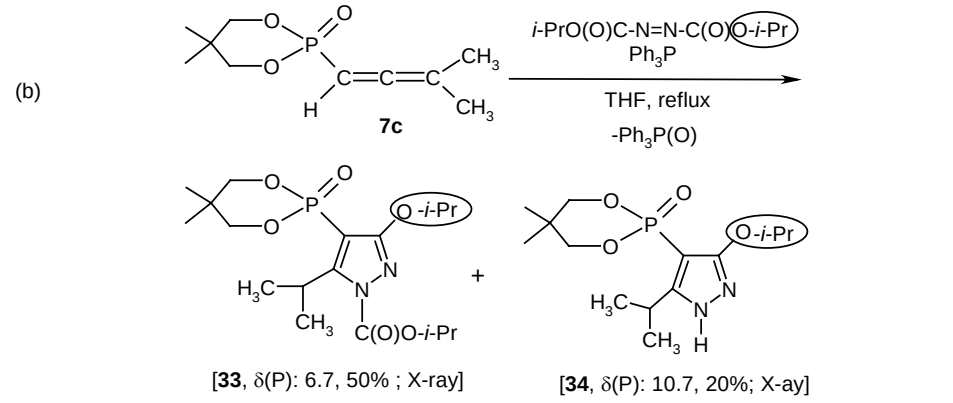
Scheme 11





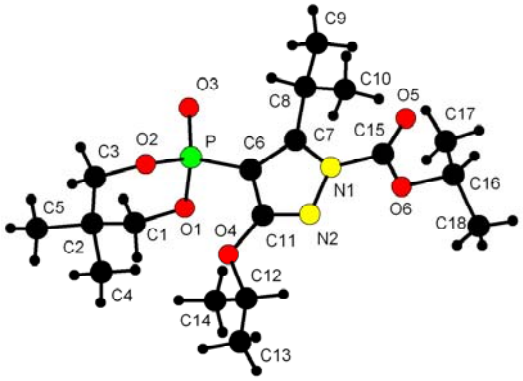


Fig. 8. Molecular structure of compound **33**. Selected bond lengths with esd's in parentheses: P-C(6) 1.770(3), C(6)-C(7) 1.371(5), N(1)-C(7) 1.378(4), N(1)-N(2) 1.382(4), O(4)-C(11) 1.340(4) Å.

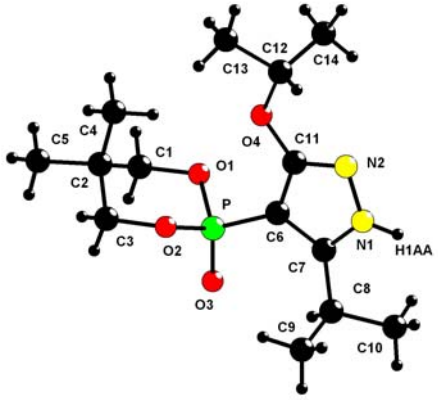


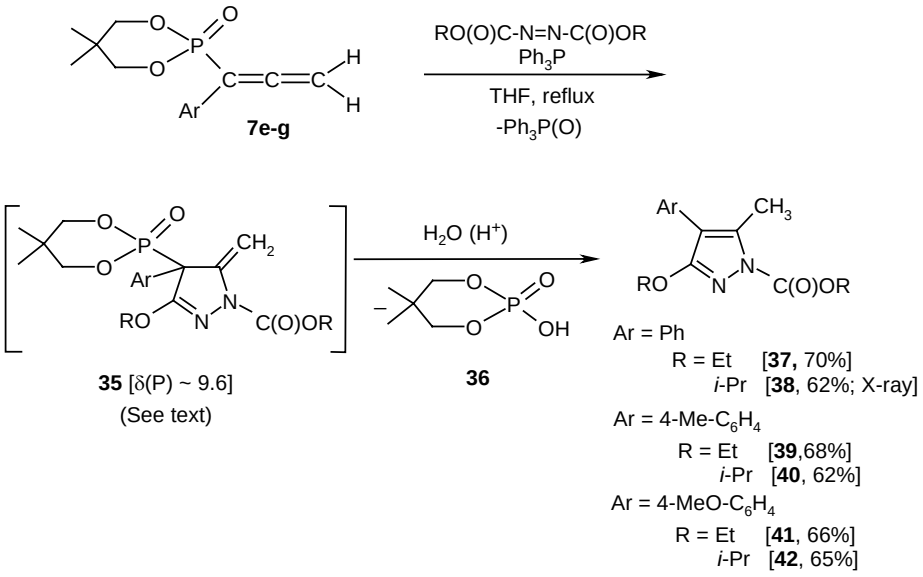
Fig. 9. Molecular structure of compound **34**. Selected bond lengths [Å] with esd's in parentheses: P-C(6) 1.7401(17), C(6)-C(7) 1.396(2), N(1)-C(7) 1.331(2), N(1)-N(2) 1.371(2), O(4)-C(11) 1.348(2). [Hydrogen bond parameters: N(1)-H1AA**...**O(3) 0.91(2) 1.88(3) 2.768(2) Å, 163(2)^{o}; symmetry code: 1-x, 1/2+y, 1/2-z].

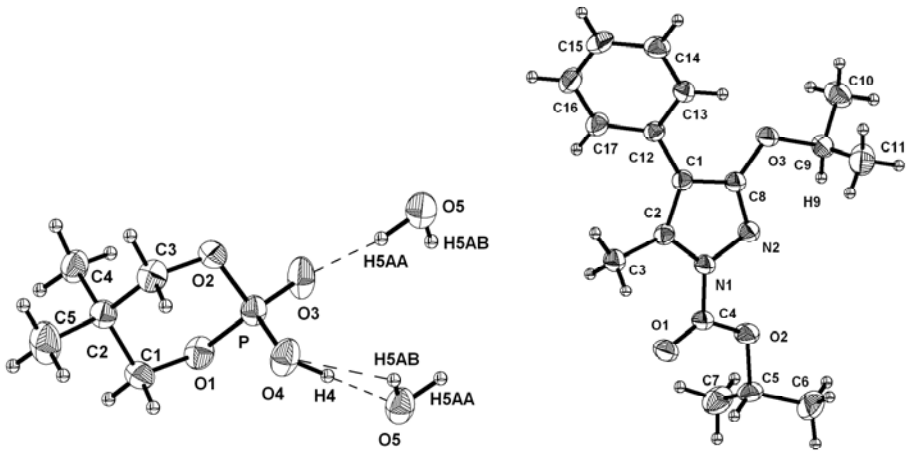
It can be noted that pyrazole **34** is analogous to **33**, except that NCO_2-*i*-Pr group gets hydrolyzed to -NH (in the former) during column chromatography. In the reported reaction using non-phosphorylated allenes, a product of type **34** was not isolated.[50] Thus our results may be gainfully employed in further synthetic work.

Perhaps more interesting is the reaction using allenylphosphonates **7e-g** shown in Scheme 12 wherein tetrasubstituted pyrazoles **37-42** are generated by a facile P-C bond cleavage reaction *via* the phosphono-pyrazoline intermediate **35**. The intermediate species **35**, where R = *i*-Pr and Ar = Ph, was readily identified by ^{1}H and ^{31}P NMR spectroscopy; in other cases the evidence was from ^{31}P NMR [δ(P)

~ 9] only. The ^{1}H NMR spectrum of this intermediate shows the alkenic [=CH_2] protons at δ 5.02 and 5.90 which are close to the values reported for similar non-phosphorylated pyrazoles;[50] the precursor **7e** gives two closely spaced singlets at δ 5.36 and 5.38 for the allenic =CH_2 protons. Further characterization of intermediates of type **35** was rendered difficult due to their hydrolytic instability. The cleavage of the P-C bond subsequently leads to the isolation of the cyclic phosphate **36.**H_2O and the novel pyrazoles **37-42** (cf. Scheme 12). Compound **36.**H_2O has been isolated as a crystalline material and is characterized by ^{1}H and ^{31}P NMR spectroscopy. Interestingly, in our attempts to obtain for crystals of **35**, we found a crystalline form for **36**.H_2O which is different from that reported.[106] Molecular structure of this polymorph of compound **36.**H_2O is depicted in the Figure 10a while that of pyrazole **38** is shown in Figure 10b.

Scheme 12





(**a**) (**b**)

Fig. 10. ORTEP diagrams for the compounds (a) **36.**H_2O and (b) **38.** Selected bond lengths [Å] with esd's in parentheses follow. Compound **36.**H_2O: P(1)-O(1) 1.5531(19), P(1)-O(2) 1.5579(17), P(1)-O(3) 1.4654(18), P(1)-O(4) 1.5270(18), O(4)-H(4) 0.93(5). [Hydrogen bond parameters: O(5)-H(5AA)...O(3) 0.96(6), 1.81(6), 2.730(3) Å, 161(5)^o; symmetry code:1/2+x, 1/2-y, -z, O(5)-H(5AB)...O(3) 0.75(3), 2.45(4), 2.712(3) Å, 102(3)^o; symmetry code:1+x, y, z,O(4)-H(4)...O(5) 0.93(5), 1.55(6), 2.457(3) Å, 165(5)^o; symmetry code: x, y, z]. Compound **38**: [C(1)-C(2) 1.370(2), C(2)-C(3) 1.491(2), N(1)-N(2) 1.3805(18), N(1) C(2) 1.384(2) Å].

We think that the type of reaction leading to **37**-**42** as shown in Scheme 12 is unprecedented. It provides a novel entry into aryl-substituted pyrazoles. This reaction works for α-aryl allenylphosphonates and separation of pyrazoles is very easily accomplished. These compounds show the following characteristic spectral features: (i) ester carbonyl C=O stretch at ~1735 cm^{-1} in the IR spectra, (ii) methyl group on the pyrazole as a singlet at δ ~2.5 in ^{1}H NMR spectra and (iii) the ester carbonyl at δ ~161.4 in the ^{13}C NMR spectra. The structure of compound **38** was confirmed by X-ray crystallography (Fig. 10b). Thus a variety of aryl substituted pyrazoles are accessible since a large number of allenes $(RO)_2PC(Ar)C=C=CH_2$ can be obtained readily *via* the propargyl alcohols $ArC\equiv CCH_2OH$.

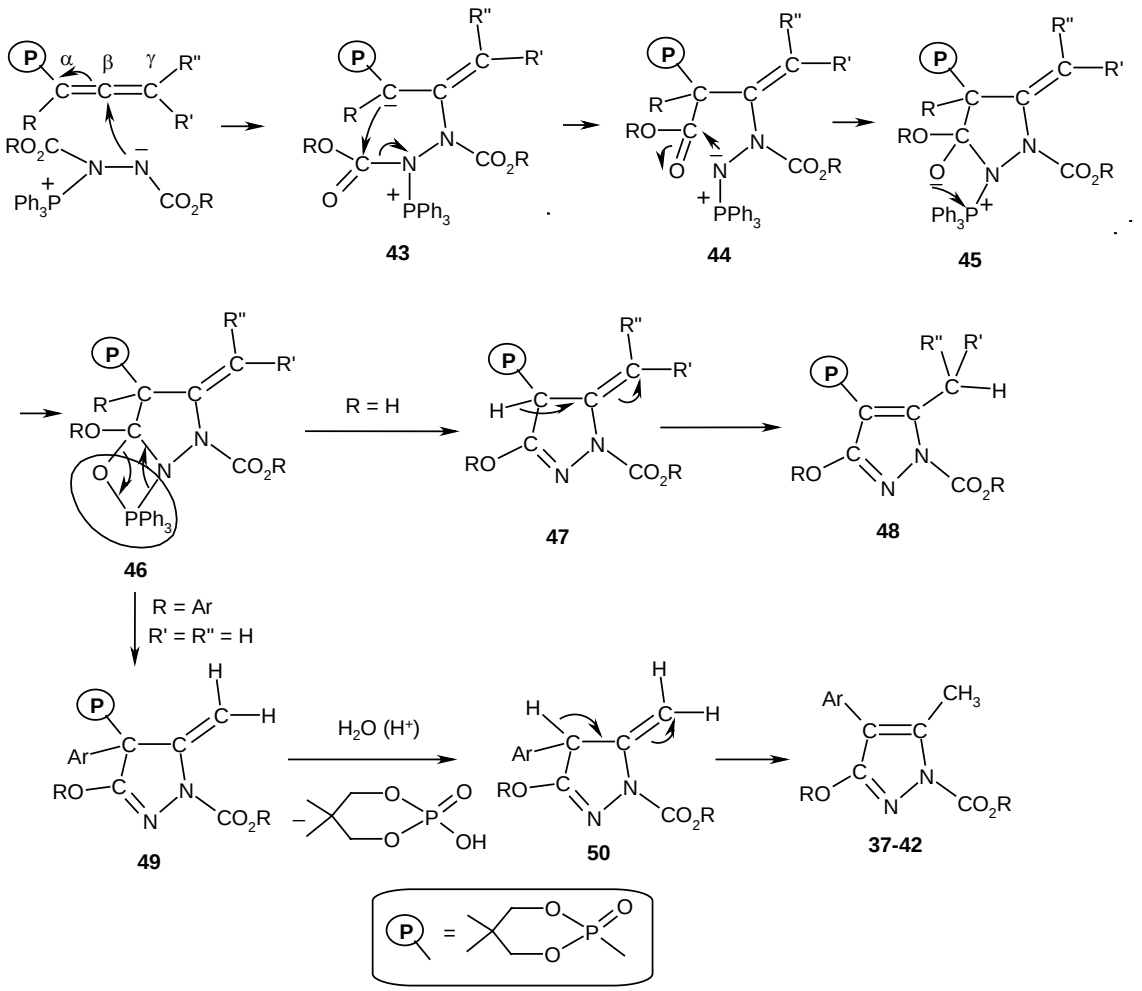
Based on the available literature,[50] the mechanistic pathway for phosphono-pyrazole (**48**) formation is shown in Scheme 13. We note the following:

(i) The carbanion is formed at the carbon atom α to phosphorus (cf. **43**) leading to substituted pyrazoles.

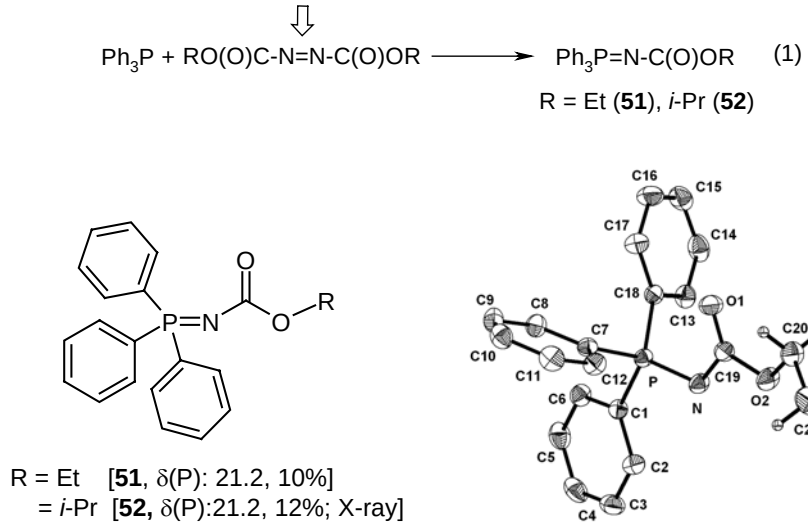
(ii) The -OR group on the pyrazole group is derived from the DIAD/DEAD residue and *not from the allene*.

(iii) The cleavage of P-C bond is very facile and subsequent separation of pyrazoles is very easy. For Ar = Ph and R = -*i*-Pr, the crystalline compound **38** could be characterized by X-ray crystallography [Fig. 10b above].

Scheme 13



In above reactions involving **7e-g**, we have also isolated the iminophosphoranes **51** and **52**, albeit in low yields, along with pyrazoles. Although both of these compounds have been reported in the literature, their synthesis involved the reaction of Ph_3P, DEAD and $H_2NC(O)OR$ [R= Et, *i*-Pr].[107] Compounds **51** and **52** were characterized by spectral and analytical data. The structure of compound **52** was further confirmed by X-ray crystallography (Fig. 11). Thus our results show that under reflux conditions, just Ph_3P and DEAD or DIAD can also lead to iminophosphoranes by the symmetrical cleavage of DEAD/DIAD, as shown in eq. 1. The moral from this result is that such a possibility also needs to be kept in mind in case one intends to conduct the Mitsunobu reaction[108] at high temperatures.



(**a**) (**b**)

Fig. 11. (a) Chemical diagram for the compounds **51** and **52**. (b) An ORTEP drawing of compound **52**. Selected bond lengths [Å] with esd's in parentheses. P(1)-C(1) 1.7991(14), P(1)-C(7) 1.8066(14), P(1)-C(13) 1.8086(14), P(1)-N(1) 1.6022(12), N(1)-C(19) 1.3582(19).

The reactions using the allenylphosphonates **7i-k** were very sluggish with only 10 % starting material reacted [^{31}P NMR evidence]. The phenylallene **5** and the electron-rich allene **15** did not react with DIAD under these conditions.

2.43 Comparison of the reactivity of allenylphosphonates and ester allenes with dialkyl azodicarboxylates

The major difference between allenylphosphonates **7b-c** and ester allenes of type $EtO_2CC(H)=C=CR_2$ is the following. In the reaction of ester allene shown in Scheme 1.40a [Section1.52], the -OEt group on the pyrazole should come from *allene* while in the reaction of **7b-c** (Scheme 11), the O-*i*-Pr substituent at the same position in pyrazoles **32-34** arises from the *DIAD residue*. In the case of α-benzyl ester allenes [Scheme 1.40b, Section1.52] and α-aryl allenylphosphonates **7e-g** (Scheme 12), the -OR substitution on the pyrazoles comes from DEAD/DIAD, but in the latter case the phosphono pyrazoline **49** underwent facile P-C bond cleave to give tetra-substituted pyrazoles **37-42** (Scheme 13). Phenylallene **5** did not react with dialkyl azodicaboxylates under these conditions.

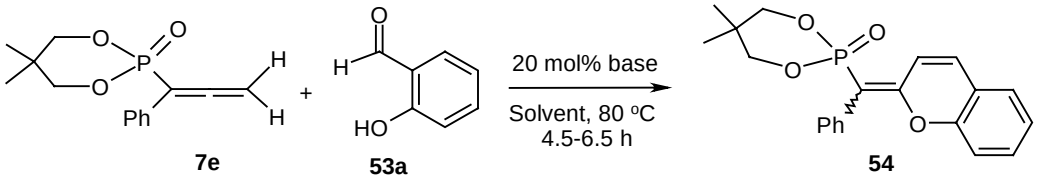
2.5 Base catalyzed reactions of allenylphosphonates with substituted salicylaldehydes

The reaction of salicylaldehydes with allenylphosphonates in the presence of a base can lead to a variety of phosphono-chromenes and allylic phosphonates. In order to check the role of phenolic oxygen, we have studied the reactions of **7c** and **7e** with phenol also. This section deals with the reaction of several allenylphosphonates with substituted salicylaldehydes and phenols under base catalyzed conditions. The experimental conditions were standardized by using the allenylphosphonate **7e**, because the products could be characterized more readily. We have then used the allenes**7a-c** and **7i**, which will be discussed later. The choice of these substrates was dictated by the ease of their synthesis.

2.51 *Reactions of α-phenyl substituted allenylphosphonate 7e with salicylaldehydes and 2-hydroxy aceto/benzo-phenones*

We treated the allenylphosphonate **7e** with salicylaldehyde **53a** in the presence of various bases and in different solvents (Scheme 14) to optimize the reaction conditions. The results are summarized in the Tables 3 and 4. It was found that this reaction led exclusively [^{31}P NMR evidence] to phosphono-chromene **54** using DBU as the base and dimethyl sulfoxide (DMSO) as the solvent. Use of K_2CO_3 also gave excellent yields based on the ^{31}P NMR spectra of the reaction mixtures; however, we faced difficulties in extracting the product. Hence we used DBU as a base in all the reactions. As a solvent, DMSO gave better results (Table 4); PEG-400 also gave good results, but the yields were lower than that in DMSO.

Scheme 14



7e **53a** **54**

Table 3. Details on the yields of compound **54** (*E*:*Z*) in the presence of different bases

Entry	BASE	Time (h)	Yield (%),(*E*:*Z*)[a]
1	DBU	6	100 (1.0:0.4)
2	K_2CO_3	4	100 (1.0:1.2)
3	Na_2CO_3	4.5	90 (1.0:1.5)
4	NEt_3	4	24 (1.0:0.5)
5	PPh_3	6	20 (1.0:0.8)
6	CsF	6	59 (1.0:0.8)
7	DABCO	6.5	40 (1.0:0.6)
8	DMAP	6	46 (1.0:1.5)

[a]Yields are based on ^{31}P NMR spectra of the reaction mixtures.

Table 4. Details on the yields of compound **54** (*E*:*Z*) isomers in different solvents

Entry	Solvent	Temp. (^{o}C)	Yield (%), (*E*/*Z*)[a]
1	DMSO	80	100 (1.0:0.4)
2	DMF	80	95 (1.0:0.9)
3	Acetonitrile	80	13 (1.0:0.8)
4	Dichloroethane	80	23 (1.0:1.1)
5	Ethanol	80	14 (1.0:2.4)
6	Toluene	80	54 (1.0:0.7)
7	THF	80	41 (1.0:1.4)
8	Chloroform	80	30 (1.0:1.1)
9	PEG-400	80	89(1.0:1.1)
10	H_2O	80	24 (1.0:1.9)

[a] Yields were based on ^{31}P NMR spectra of the reaction mixtures.

Under optimized conditions, we have conducted the reactions of a variety of substituted salicylaldehydes and 2-hydroxy aceto-/benzo-phenone with allenylphosphonate **7e** for the synthesis of different phosphono-chromenes and also

for checking the scope and limitations of the reaction (Scheme 15). The yields and *E*/*Z* ratio of the compounds based on the ^{31}P NMR spectra of the reaction mixtures are given in Table 5. We have also separated individual isomers in all cases except in **59** (only *E*-isomer isolated); since the R_f values are too close, this separation was tedious and only small quantities of pure isomers were isolated. The overall (combined) isolated yields of the two isomers are moderate to good (Table 6). Electron withdrawing groups, rather than electron donating groups, on salicylaldehyde led to better results. This is possibly because in the presence of electron-withdrawing group the phenolate anion is more readily formed and thus can lead to higher yields of the products.

Scheme 15

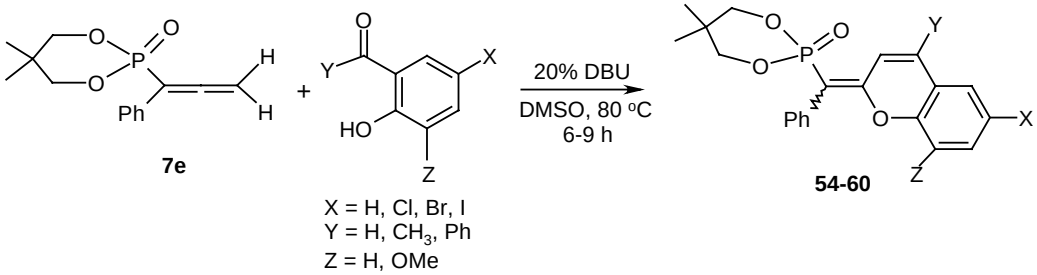


Table 5. Details on the yields of compounds **54-60**

Entry	Compd	X	Y	Z	Yield (%) (*E*:*Z*)[a]
1	**54**	H	H	H	100 (1.0:0.4)
2	**55**	Cl	H	H	77 (1.0:1.3)
3	**56**	Br	H	H	94 (1.0:1.6)
4	**57**	I	H	H	67 (1.0:1.3)
5	**58**	**H**	H	OMe	74 (1.0:0.7)
6	**59**	H	CH_3	H	95 (1.0:0.6)
7	**60**	H	Ph	H	65 (1.0:1.6)

[a]Yields are based on ^{31}P NMR spectra of the reaction mixtures. The *E*/*Z* ratios of the compounds are in the parentheses.

Table 6. ^{31}P NMR data and yields of the compounds **54-60**

Entry	Compd	δ(P)		Yield (%)(*E*:*Z*)[a]
		(*E*)	(*Z*)	
1	**54**	15.3	12.2	91 (1.0:0.6)
2	**55**	12.6	10.8	70 (1.0:1.1)
3	**56**	12.5	9.2	84 (1.0:1.3)
4	**57**	14.8	11.4	60 (1.0:1.2)
5	**58**	**15.5**	12.0	70 (1.0:0.8)
6	**59**	16.4	-	80 (1.0:0.8)
7	**60**	15.9	12.5	59 (1.0:1.4)

[a]Isolated yields of the pure compounds = combined yield of *E* + *Z* isomers.

The structures of *E* and *Z* isomers of **56** were confirmed by X-ray crystallography (Fig. 12). Based on these data, we could assign the ^{31}P NMR chemical shifts for all the other compounds. The signal for the *E*-isomer [δ(P) = 12.5] appears downfield compared to that of the *Z*-isomer [δ(P) = 9.2]. For the identification of *E*- and *Z*-isomers, ^{13}C NMR and ^{1}H NMR spectra were also quite useful. In the ^{13}C NMR, the ^{1}J(P-C) value for the *E*-isomer [~ 201.0 Hz] is higher than that for the *Z*-isomer [~ 180.7 Hz]. In the ^{13}C NMR spectra, the signal for PC(Ph)=*C* carbon of *E*-isomer appears as a doublet at δ 159.0 [^{2}J(P-C) = 35.0 Hz] but in the case of *Z*-isomer, it is almost a singlet at δ 158.1 [low ^{2}J(P-C)]. The ^{13}C NMR spectra of the *E*- and *Z*- isomers of **56** are shown in Fig. 13 and Fig. 14, respectively. In the ^{1}H NMR, the (Ph)C=C-C*H*= proton signal appears as a doublet and is downfield [δ(H) ~ 7.96] in the *E*-isomer when compared to the *Z*-isomer [δ(H) ~ 6.31]. In some cases it is a doublet of doublet with low ^{4}J(P-H) of ~ 1.7 Hz. The assignment of the peaks in the ^{1}H NMR spectra is based on the available data for the *E*- and *Z*- isomers of **56**.

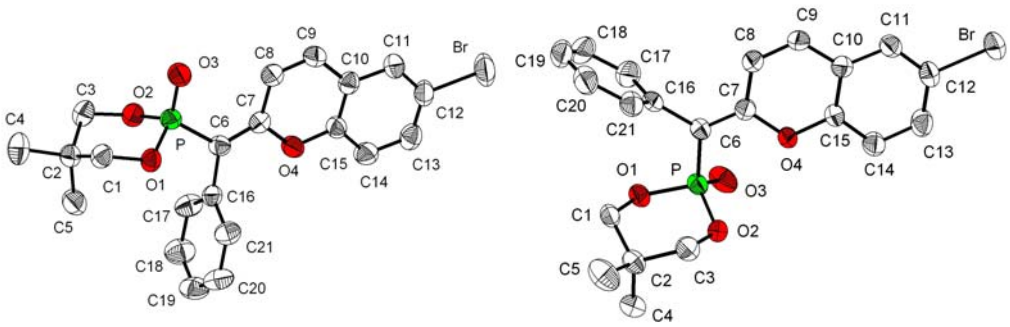


Fig. 12. ORTEP diagrams for the compounds (a) (*E*)-**56** isomer (b) (*Z*)-**56** isomer. Selected bond lengths [Å] with esd's in parentheses follow. Compound (*E*)-**56:** P-C(6) 1.776(4), C(6)-C(7) 1.342(5), C(8)-C(9) 1.337(5), O(4)-C(7) 1.379(4). Compound (*Z*)-**56:** P-C(6) 1.790(3), C(6)-C(7) 1.349(4), C(8)-C(9) 1.333(4), O(4)-C(7) 1.381(3).

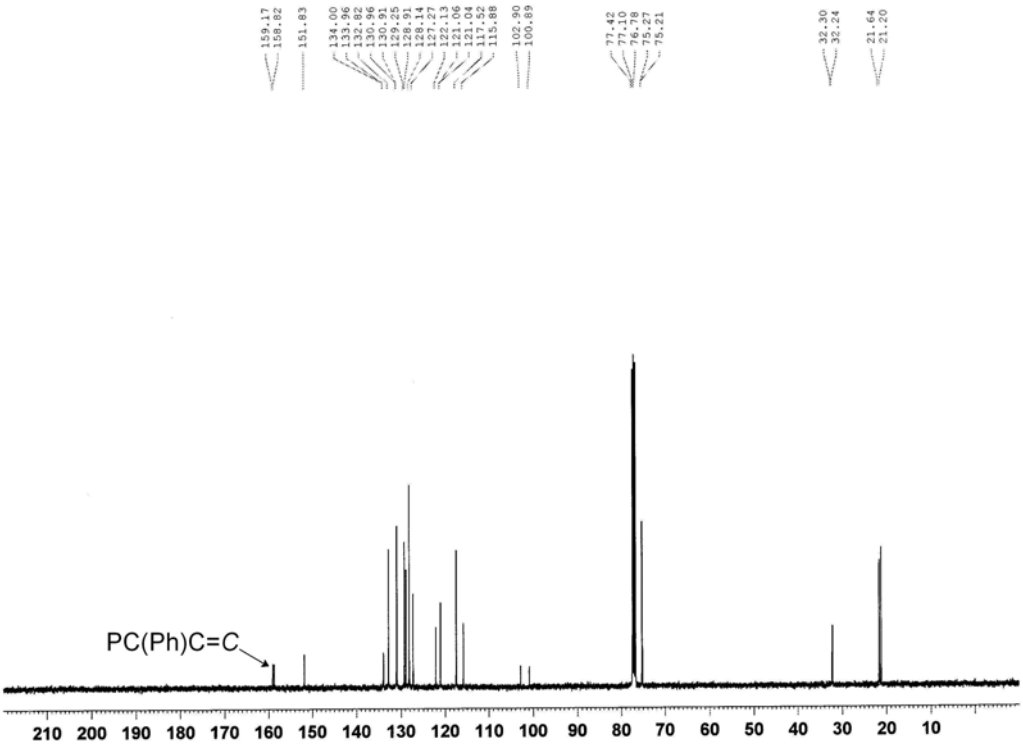


Fig. 13. ^{13}C NMR spectrum for the compound (*E*)-**56**

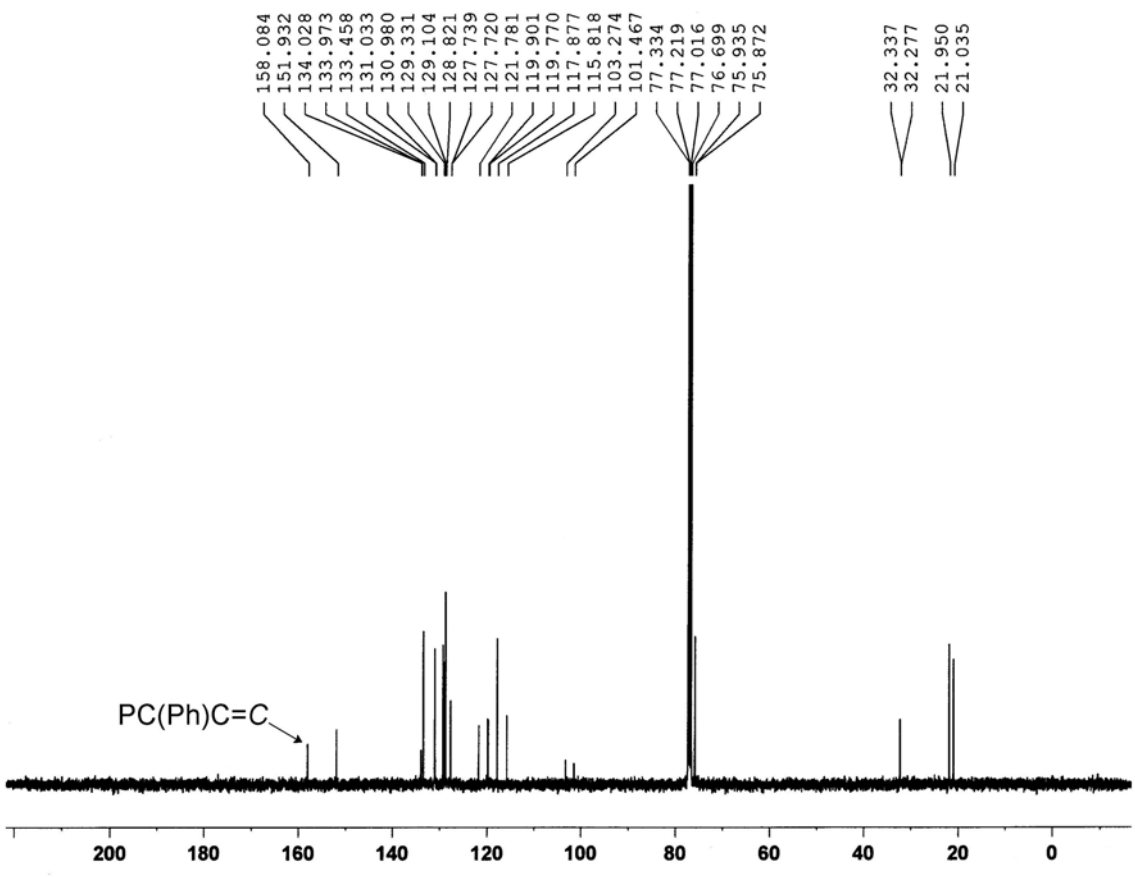
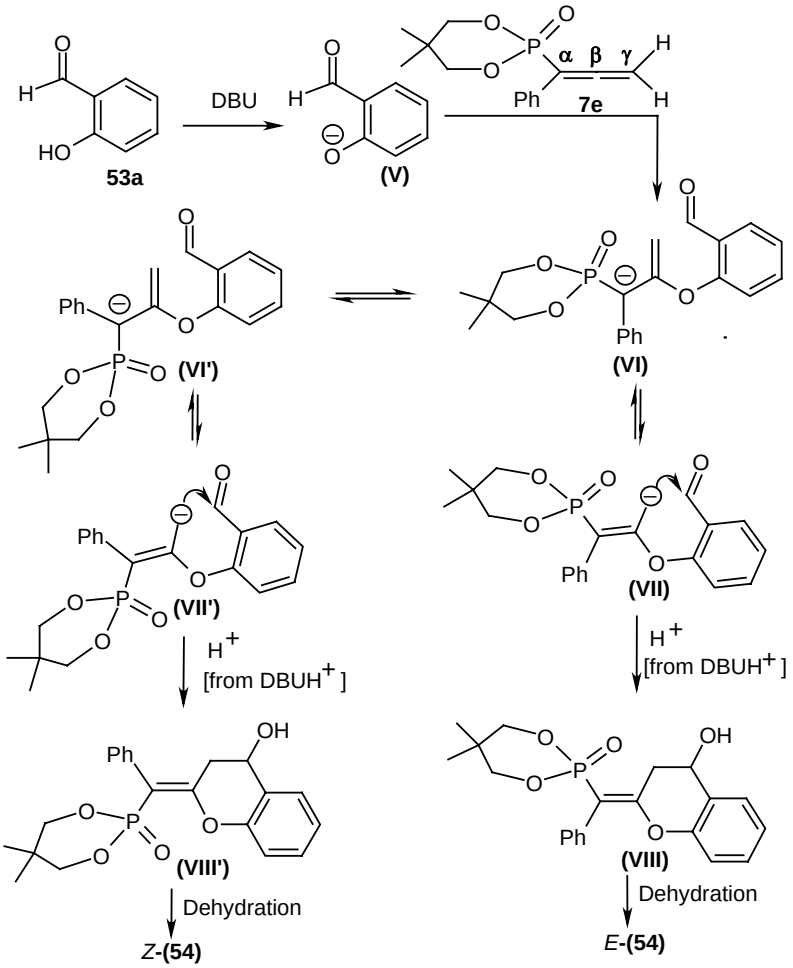


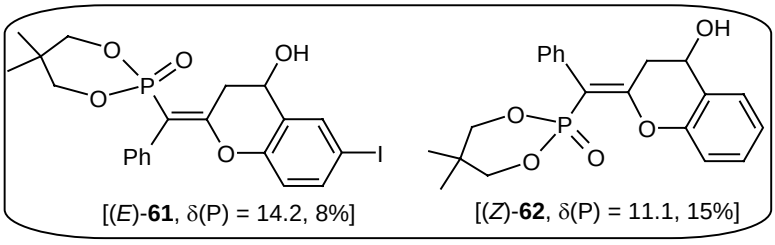
Fig. 14. ^{13}C NMR spectrum for the compound (*Z*)-**56**.

A plausible mechanism for the reaction based on the available literature[36c] is shown in Scheme 16. First, the base (DBU) abstracts proton from salicylaldehyde (**53a**) and generates oxy-anionic intermediate **V** which reacts with allenylphosphonate **7e** at *β*- position to give **VI.** Species **VI** is in equilibrium with **VI'**. Both of these can give rise to **VII** or **VII'**, because *γ*-addition is preferred at elevated temperatures.[36c] Intermediates **VII** and **VII'** undergo intramolecular aldol reaction followed by proton abstraction to afford **VIII** and **VIII'**. Dehydration in the following step leads to the final products *E* and (*Z*)-**54**.

Scheme 16



We have also isolated two phosphono-chromenes (*E*)-**61** and (*Z*)-**62** with structures analogous to **VIII** and **VIII'** shown in Scheme 16**.** Compound (*E*)-**61** is isolated along with **57** in the reaction of iodosalicylaldehyde with allenyl phosphonate **7e**. Compound (*Z*)-**62** is isolated in PPh_3 catalyzed reaction of salicylaldehyde with allenylphosphonate **7e**. The stereochemistry for these compounds was assigned based on ^{13}C NMR spectra; the P-C=*C* signal for (*E*)-**61** is a doublet [^2J(P-C) = 33.8 Hz] and for (*Z*)-**62** is a singlet [low ^2J(P-C) value].



Interconversion of E and Z isomers

Normally, interconversion of *E* and *Z* isomers is not expected to take place readily. We have recorded ^{31}P NMR spectra of isomer (*E*)-**54** at room temperature in $CDCl_3$ at different intervals of time (Fig. 15). Originally, compound (*E*)-**54** showed a peak at δ 15.5. Slowly the peak due to (*Z*)-**54** [δ 12.2] started appearing. After four days, the ratio of the intensities of the signals for *E* and *Z* isomers was nearly 3:2. After fifteen days, the corresponding ratio was nearly 8:7. These are shown in Fig. 15. We also heated the compound (*E*)-**54** at 80 ^{o}C in DMSO for one day; the conversion was faster as expected and the ratio of the signals was ~8:7. Similar *Z* to *E* conversion was also seen but it was slower. In the case of (*Z*)-**58** also conversion to (*E*)-**58** took place but the ratio of the intensities after 15 days was 2:1. A possible pathway for the interconversion of these *E*- and *Z*- isomers is shown in Scheme 17.

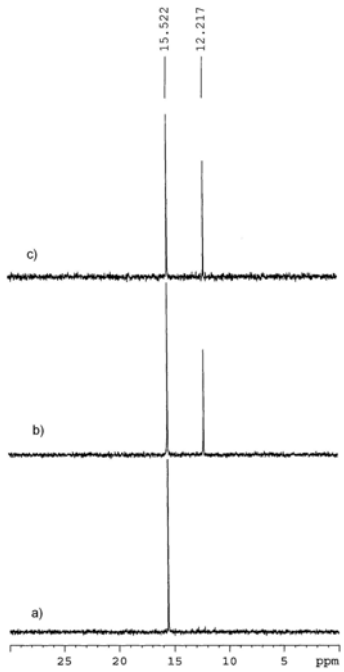
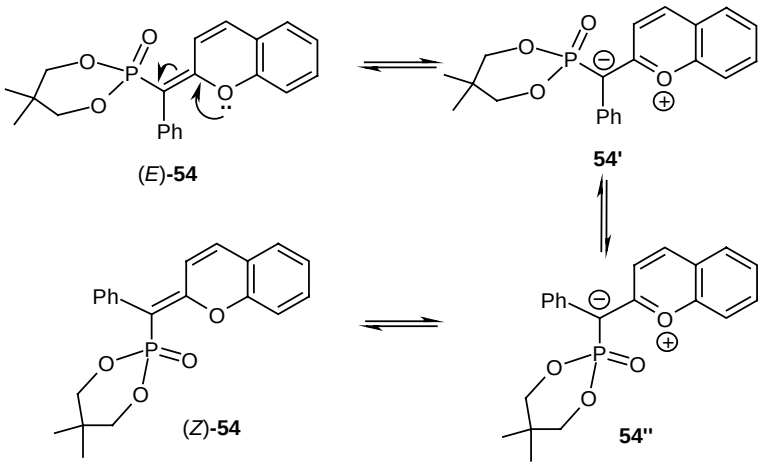


Fig. 15. ^{31}P NMR (162.0 MHz) spectra in $CDCl_3$ recorded over a period of time illustrating the conversion of (*E*)-**54** to (*Z*)-**54** at (a) t (time) = 0, (b) t = 4 d, (C) t = 15 d.

Scheme 17



Synthesis of phosphono-chromenes under a greener protocol

After establishing the above reaction, we wanted to check an environmentally more benign solvent system like PEG-400. In this context, we treated allenylphosphonate **7e** with various salicylaldehydes and 2-hydroxy aceto-/benzo-phenone in the presence of DBU in PEG-400 (Scheme 18). The yields were moderate to good, but not as high as that in DMSO. The results are summarized in the Table 7.

Scheme 18

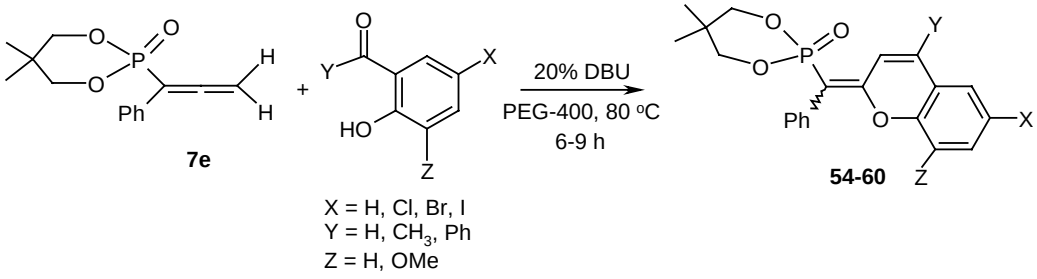


Table 7. Details on the yields of compounds **54-60** in PEG-400

Entry	Compd	X	Y	Z	Yield (%) (*E*:*Z*)[a]
1	**54**	H	H	H	89(1.0:1.1)
2	**55**	Cl	H	H	60(1.0:1.6)
3	**56**	Br	H	H	84 (1.0:1.1)
4	**57**	I	H	H	66 (1.0:0.7)
5	**58**	H	H	OMe	34 (1.0:0.8)
6	**59**	H	CH_3	H	53 (1.0:1.4)
7	**60**	H	Ph	H	37 (1.0:0.7)

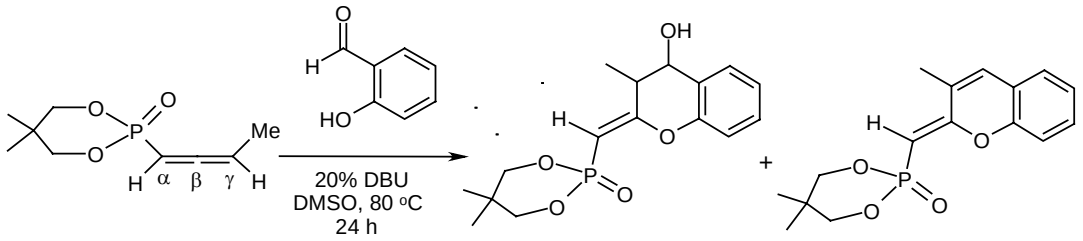
[a]Yields are based on ^{31}P NMR spectra of the reaction mixtures.

2.52 *Reactions of allenylphosphonates 7a-c with salicylaldehydes*

After checking up the reactions with the key precursor **7e** as above, we treated allenylphosphonate **7a** with salicylaldehyde (**53a**) in the presence of DBU at 80 ^{o}C, but this allene rearranged to isomeric acetylene 30 as observed elsewhere.[14] Then we performed the reaction using CsF as the base under similar conditions,[109] this also gave the same rearranged acetylene.

Treatment of the allenylphosphonate **7b** with salicylaldehyde afforded two products (*Z*)-**63** and (*Z*)-**64** in the ratio 3:8 with an overall yield of ~55% (Scheme 19). It can be readily seen that (*Z*)-**64** is a dehydration product of (*Z*)-**63**. Compound (*Z*)-**63** shows the OH stretch at 3364 cm^{-1} in the IR spectrum. Only one olefinic proton with a ^{2}J(P-H) of 10.8 Hz is seen in the ^{1}H NMR spectrum; ^{13}C NMR shows the P-C carbon at δ 90.3 [^{1}J(P-C) = 185.0 Hz]. In compound (*Z*)-**64**, there are two olefinic protons that appear at δ 4.63 [d, ^{2}J(P-H) = 8.8 Hz] and 6.83 in the ^{1}H NMR spectrum. In the ^{13}C NMR, the carbon α to phosphorus appears as a doublet at δ 81.1 with ^{1}J(P-C) value of 195.0 Hz. In both of these compounds, the expected integrated intensities are observed for the ^{1}H NMR signals. The structure of (*Z*)-**64** is similar to (*Z*)-**56** for which solid-state X-ray structure is available. Thus, these data are consistent with the structure as proposed. Further confirmation of the structure and stereochemistry is provided by the X-ray structure of a similar compound in the reaction using **7c**, which is discussed below.

Scheme 19

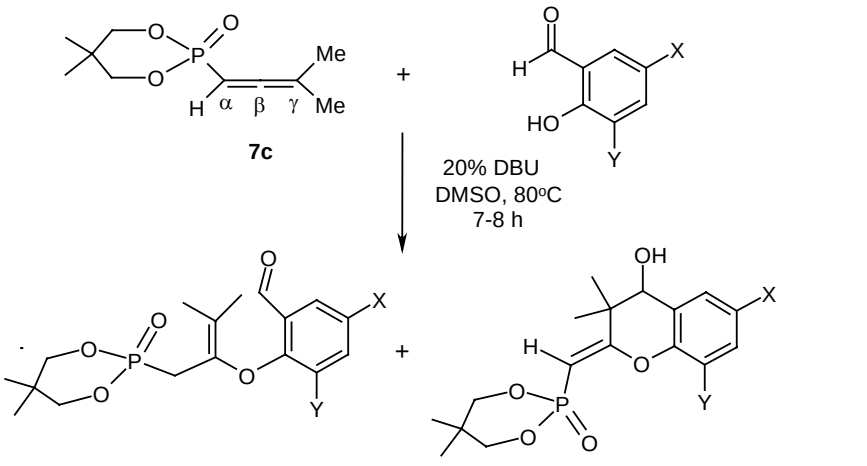


7b [(*Z*)-**63**, δ(p):12.6, 15%] [(*Z*)-**64**, δ(p):15.4, 40%]

Next, we treated allenylphosphonate **7c** with substituted salicylaldehydes in the presence of DBU to obtain the allylic phosphonates **65a-b** and phosphono-chromenes **66a-c** (Scheme 20). In both the cases, this reaction proceeds via attack of phenolate anion on *β*-carbon in the first step as discussed above. This is followed by addition of proton at the *α*-carbon to give the allylic phosphonates **65a-b**. In the

formation of phosphono-chromenes (*Z*)-**66a**, the carbanion attacks the carbonyl carbon (cf. Scheme 16); this compound is the major product and allylic phosphonate **65a** is the minor product. In contrast, use of 5-bromo-salicylaldehyde affords allylic phosphonate **65b** as the major product. In the case of vanillin, the reaction was sluggish with most of starting material remaining, but we were able to isolate compound **66c** in 15% yield. The allylic product **65a** exhibits a doublet at δ 2.90 [^2J(P-H) = 21.4 Hz] in the ^{1}H NMR and δ 26.4 [^1J(P-C) = 139.0 Hz] in the ^{13}C NMR due to PCH_2 group. For the compound (*Z*)-**66a**, the PCH= moiety is appears as a doublet at δ 4.75 [^2J(P-H) = 8.0 Hz] in the ^{1}H NMR; ^{13}C NMR spectrum also shows a doublet at δ 87.9 [^1J(P-C) = 184.3 Hz, PC]. We have confirmed the structure of (*Z*)-**66a** by X-ray crystallography (Fig. 16); this also gives credence to the structural assignment of (*Z*)-**63**. Confirmation of the assigned structures for **65b** and **66b-c** was then possible by comparing their spectroscopic data with those of **65a** and **66a**.

Scheme 20



X = Y = H [**65a**, δ(P):21.3, 25%]
X= Br, Y = H [**65b**, δ(P):20.9, 50%]

X = Y = H [**66a**, δ(P):13.7, 40%; X-ray]
X = Br, Y = H [**66b**, δ(P):13.3, 20%]
X = H, Y = OMe [**66c**, δ(P):11.9, 20%]

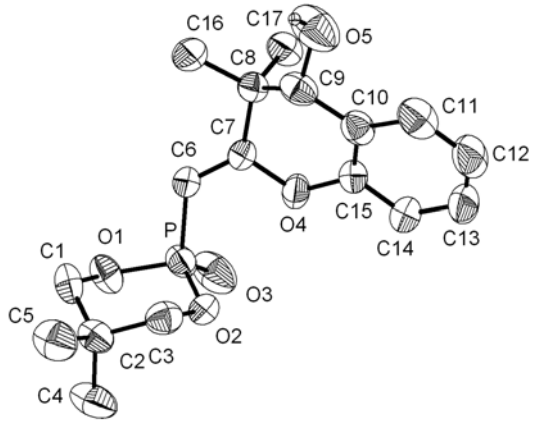
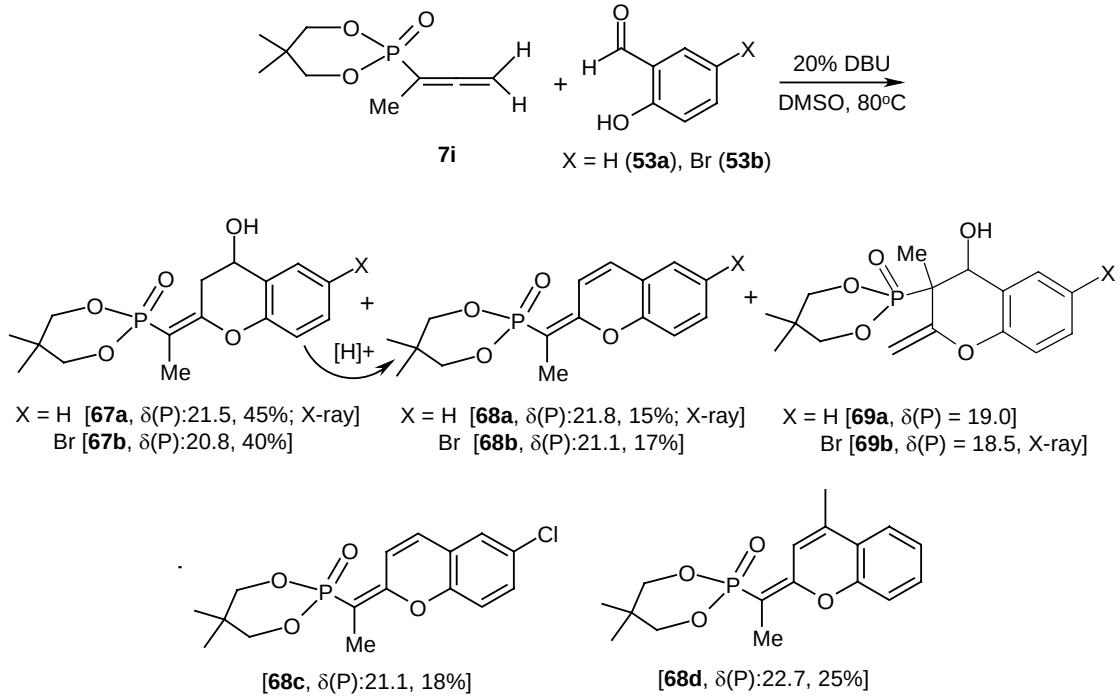


Fig. 16. ORTEP diagram for the compound (*Z*)-**66a**. Selected bond lengths [Å] with esd's in parentheses. P-C(6) 1.768(3), C(6)-C(7) 1.324(4), C(8)-C(9) 1.555(5), O(4)-C(7) 1.369(4). [Hydrogen bond parameters: O(5)-H(5)**…**O(3) 0.82, 1.86, 2.679(5) Å, 178.4 ^{o}; symmetry code: x, 1/2-y, -1/2+z].

2.53 *Reactions of α-methyl substituted allenylphosphonate 7i with salicylaldehydes and 2-hydroxy acetophenone*

In place of the *α*-phenyl allene **7e**, use of the α-methyl allenylphosphonate **7i** in the above reaction, under similar conditions as for the preparation of **54**, led to different types of phosphono-chromenes **67-69** (Scheme 21). We checked different reaction conditions using the bases DMAP, PPh_3 and DBU. Among these, DBU gave good results and in the other cases the reaction was very sluggish. Compounds **67a-b** were the major products. However, they were dehydrated to **68a-b** in the presence of the base at high temperature (> 80 ^{o}C) or in the presence of 2M HCl at room temperature. In the reactions using 5-chlorosalicylaldehyde and 2-hydroxy acetophenone, although reaction mixture showed products similar to **67** as the major components, we were able to isolate only **68c-d**, probably because of the ease of dehydration.

Scheme 21



7i X = H (**53a**), Br (**53b**)

[**68c**, δ(P):21.1, 18%] [**68d**, δ(P):22.7, 25%]

The structures of the above compounds are assigned based on NMR spectra. Alkenic protons of the six-membered pyran ring in **68a-b** appear at δ ~6.8 and ~7.8 in the ^{1}H NMR; these are absent in **67a-b**. The CH_2 protons of **67a-b** appear at δ ~3.4. Also, compounds **67a-b** show a band at 3250-3260 cm^{-1} in the IR spectra corresponding to the OH stretch; these are absent in **68a-b**. The signals for =CH_2 protons in compounds **69a-b** are seen at δ 4.9 and 5.1. Compounds **67a-b** and **68a-b** show ^{1}J(P-C) of ~ 200 Hz while this value for **69b** is ~ 125 Hz (^{13}C NMR spectrum of pure **69a** was not recorded due to its moisture-instability). In general, ^{1}J(P-C) for sp^2-hybridized carbon is expected to be higher than that for sp^3 hybridized carbon.[110] Distinction between *E* and *Z* isomers is somewhat difficult, although comparison of the spectra of **68a-b** with those of *E* and *Z* isomers of **56** suggest that these are *E*-isomers. Thus the signal for PC(Me)=*C* carbon is a doublet with ^{2}J(P-C) ~ 35.5 Hz for both **67a-b** and **68a-b**; this is similar to that observed for (*E*)-**56**. The ^{31}P NMR signals are distinct for the three sets of compounds, but assignment of geometry is difficult on this basis.

To prove the identity and geometrical disposition of these compounds, we have determined the structures of **67a, 68a** and **69b** by X-ray crystallography (Fig. 17). The C6-C7 distance [1.335(3)Å] in **67a** and C5-C6 distance in **68a** [1.353(4)Å] clearly show the location of a double bond while the C6-C7 distance in **69b**

[1.531(6)Å] shows that this is a single bond. The oxygen atoms O4 in **67a** and O3 in **68a** are clearly *trans* to phosphorus, and hence prove the (*E*) stereochemistry in these two cases. The presence of hydrogen bonding involving the hydroxyl [O5-H] group in **67a** and **69b** also confirms that in these two cases dehydration has not taken place. While **63a** forms a dimer, **69b** forms a tetramer [Fig. 18].

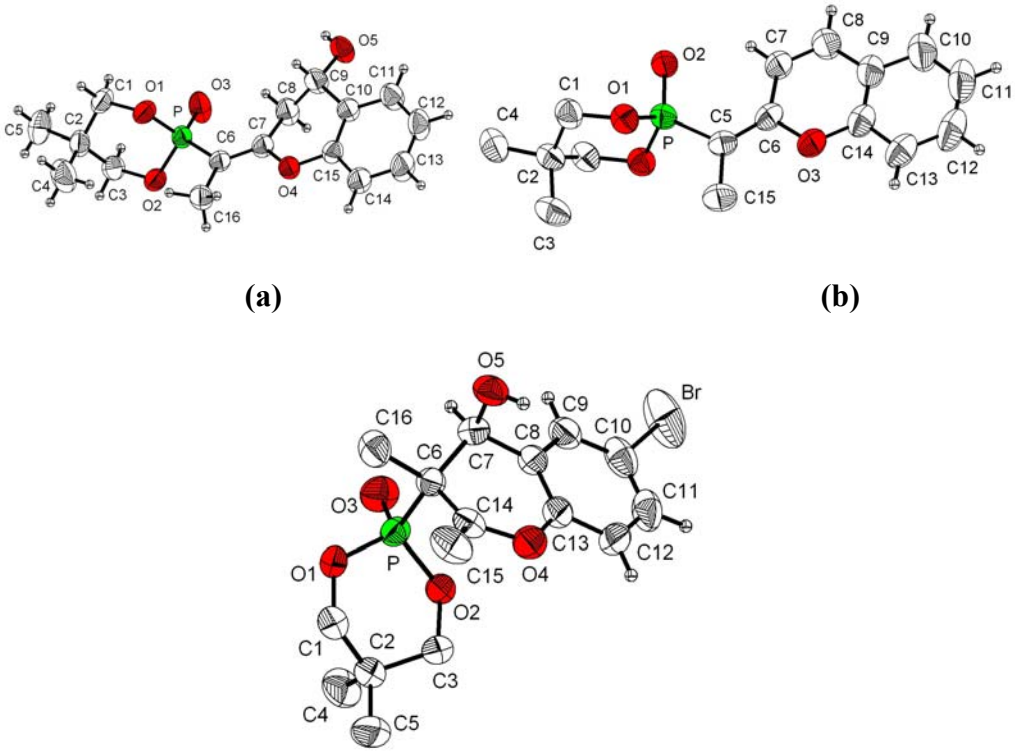


Fig. 17. ORTEP diagrams for the compounds (a) (*E*)-**67a**, (b) (*E*)-**68a** and (c) *trans*-**69b.** Selected bond lengths [Å] with esd's in parentheses follow. Compound (*E*)-**67a:** P-C(6) 1.760(2), C(6)-C(7) 1.335(3), C(8)-C(9) 1.478(4), O(4)-C(7) 1.377(3). [Hydrogen bond parameters: O(5)-H(5)**…**O(3') 0.82, 1.88, 2.698(2) Å, 175.3°; symmetry code: 1/2-x, 1/2-y, 1-z].Compound (*E*)-**68a:** P-C(5) 1.760(3), C(5)-C(6) 1.353(4), C(7)-C(8) 1.325(4), O(3)-C(6) 1.376(3). Compound *trans*-**69b:** P-C(6) 1.852(4), C(6)-C(7) 1.531(6), C(6)-C(14) 1.518(6), O(4)-C(14) 1.412(6). [Hydrogen bond parameters: O(5)-H(5)**...**O(3) 0.64(7), 2.34(7), 2.895(6) Å 146(8)°; symmetry code: 2-y, x, -z].

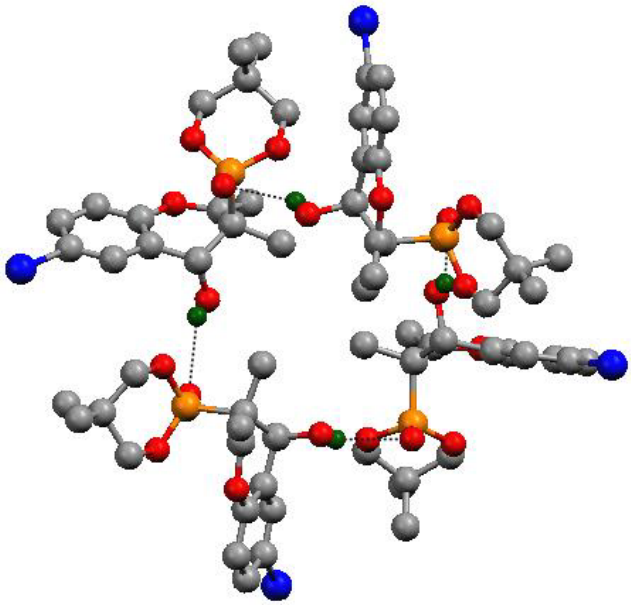
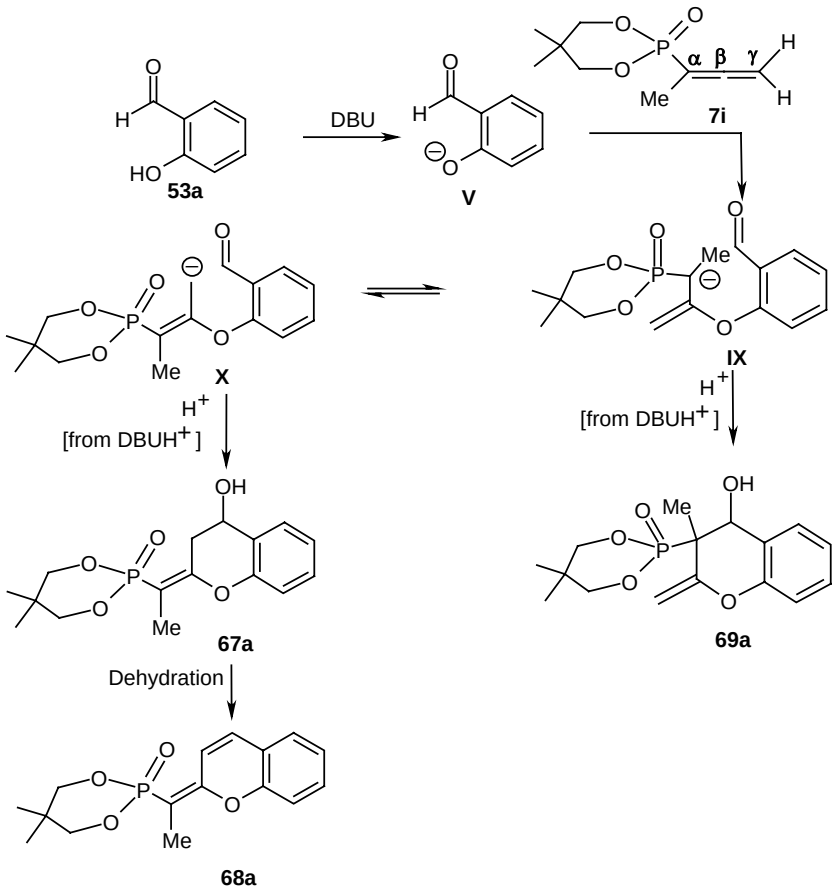


Fig. 18. Hydrogen bonding showing tetrameric formulation in **69b** (yellow = P, red = O, blue = Br, grey = C, green = H); all hydrogen atoms except the ones involved in H-bonding are omitted for clarity. [Hydrogen bond parameters: O(5)-H(5)**...** O(3) 0.64(7), 2.34(7), 2.895(6) Å 146(8)^{o}; symmetry code: 2-y, x, -z].

The above reaction proceeds most likely through a domino oxo-Michael addition followed by aldol condensation. Here two possibilities exist: (β,α)-attack and (β,γ)-attack (Scheme 22). The first one leads to the kinetically controlled product (**69a**) and the second one leads to thermodynamically controlled product (**67a**).[36c] The oxy-anionic intermediate **V** attacks at β-position of allene and generates **IX** that rearranges to **X.** Formation of **67a** and **68a** is analogous to that of **54**. Formation of **69a** occurs *via* **IX** without the rearrangement of carbanion.

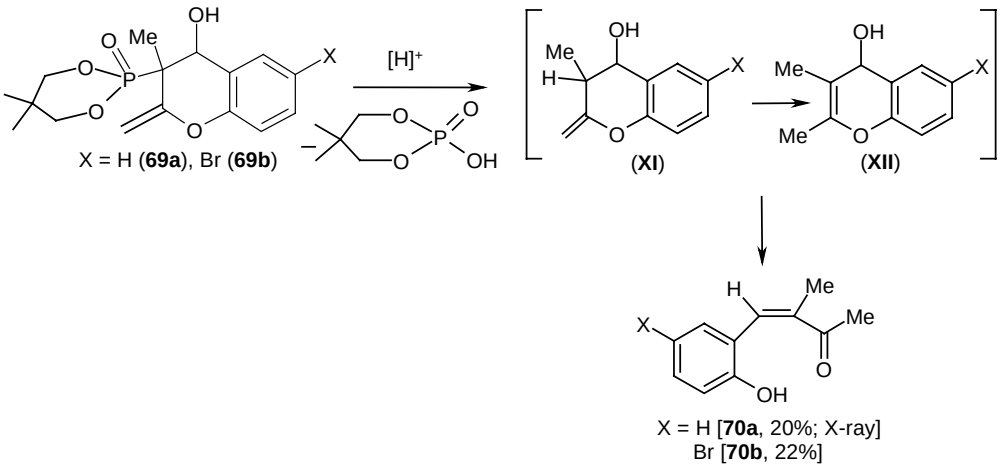
Scheme 22



Novel P-C bond cleavage in phosphono-chromenes

As mentioned above, compounds **69a-b** were rather unstable towards moisture [^{1}H NMR evidence]. They underwent novel P-C bond cleavage to give 4-(2-hydroxy aryl)-3-methylbuten-2-ones **70a-b** (Scheme 23). The structure of compound **70a** was confirmed by X-ray crystallography (Fig. 19). The second step in the proposed mechanism for the formation of **70a-b** is based on an earlier report on species of type XII.[111] This type of cleavage was also observed in the case of phosphono-pyrazoles as discussed in Section 2.42 (Scheme 12).

Scheme 23



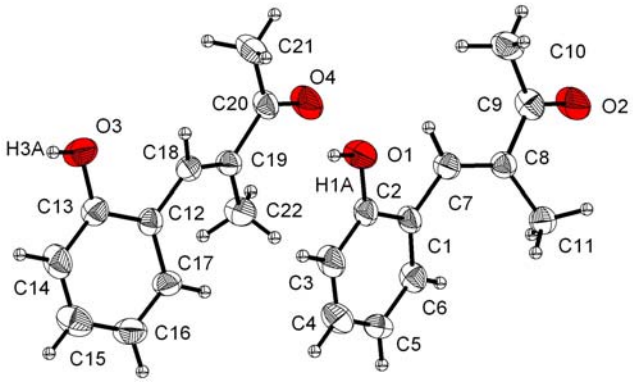


Fig. 19. ORTEP diagram for the compound **70a** (two molecules present in the asymmetric unit)**.** Selected bond lengths [Å] with esd's in parentheses: O(1)-C(2) 1.3503, C(7)-C(8) 1.345(5), O(2)-C(9) 1.225(4), O(3)-C(13) 1.350(5), C(18)-C(19) 1.348(6), O(4)-C(20) 1.213(5). [Hydrogen bond parameters: O(1)-H(1A)**…**O(2) 0.82, 2.01, 2.7904(12) Å, 159.3^{o}; symmetry code: -1/2+x, 1/2-y, z, O(3)-H(3A)**…**O(4) 0.82, 2.03, 2.829(4) Å, 164.0^{o}; symmetry code: -1/2+x, 1/2-y, z].

2.54 *Comparison of the reactivity of allenylphosphonates with other allenes*

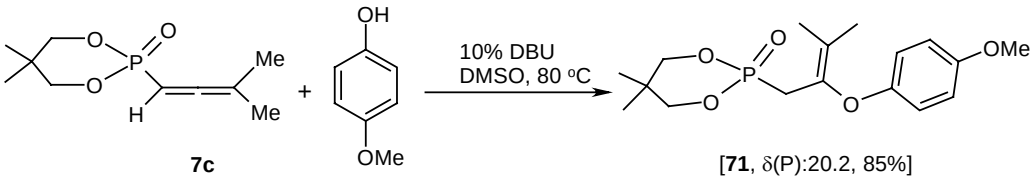
Under base catalyzed reactions, the reactivity of allenylphosphonates with salicylaldehyde is lower (and different) when compared those with ester or keto allenes but higher when compared with phenyl allene **5**.[36] For comparable yields, the reaction of allenylphosphonates with salicylaldehyde in the presence 10 mol% DBU took longer time (more than 24 h) whereas it is reported that ester allenes took 6-15 h under similar conditions. The allenylphosphonate **7a** isomerized to acetylene **30** (i.e. it did not react with salicylaldehyde) in the presence of a base but ester or keto

allenes gave chromenes (Chapter 1, Scheme1.32b). In the case of α-substituted allenylphosphonates (**7e** and **7i**), (β,γ)-attack is favored (Scheme 16 and Scheme 22) whereas in the case of ester or keto allenes (β,α)-attack is favored (Chapter 1, Scheme1.31). The allenylphosphonate (**7c**) gave phenol-addition product allylic phosphonate (**65**) and (β,γ)-attack afforded the phosphono-chromene (**66**). Phenyl allene **5** did not react with salicylaldehyde under these conditions.

2.6 Reactions of allenylphosphonates 7c and 7e with activated phenols: Synthetic utility of the products in HWE reaction

In continuation of the above reactions, we wanted to check the reactivity of the phenols with allenylphosphonates in the presence of a base that could help in understanding the first step in the reaction with salicylaldehydes. Surprisingly, we got very good selectivity here. Thus the reaction between **7c** with 4-hydroxy anisole in the presence of 10 mol% of DBU gave only allylicphosphono ether **71** (Scheme 24). In the ^{1}H NMR, the PCH_2 protons exhibit a characteristic doublet at 2.87 [^2J(P-H)= 21.2 Hz]. The corresponding carbon shows a characteristic doublet at 26.3 [^1J(P-C) = 137.0 Hz] in the ^{13}C NMR. Here, the product is formed by phenoxide attack at β-position followed by proton addition at the α-carbon.

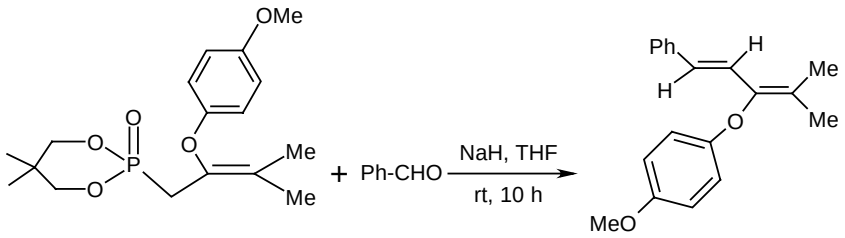
Scheme 24



7c [**71**, δ(P):20.2, 85%]

In general, phosphonates having PCH_2 group undergo HWE reaction easily with aldehydes in the presence of suitable base to afford 1,3-butadienes. In the present work, we utilized allylic phosphonyl ether **71** as a precursor in HWE reaction. The compound **71** reacted with benzaldehyde in the presence of NaH at room temperature in THF to give *trans*-1,3-butadiene **72** as shown in the Scheme 25. The ^{1}H NMR shows *trans* coupling ^3J(H-H) = 15.6 Hz for the alkenic protons; the structure of compound **72** was further confirmed by X-ray crystallography (Fig. 20). Thus these phosphonates offer a convenient route to substituted butadienes.

Scheme 25



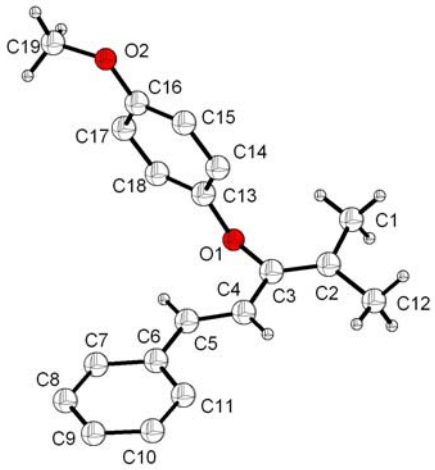


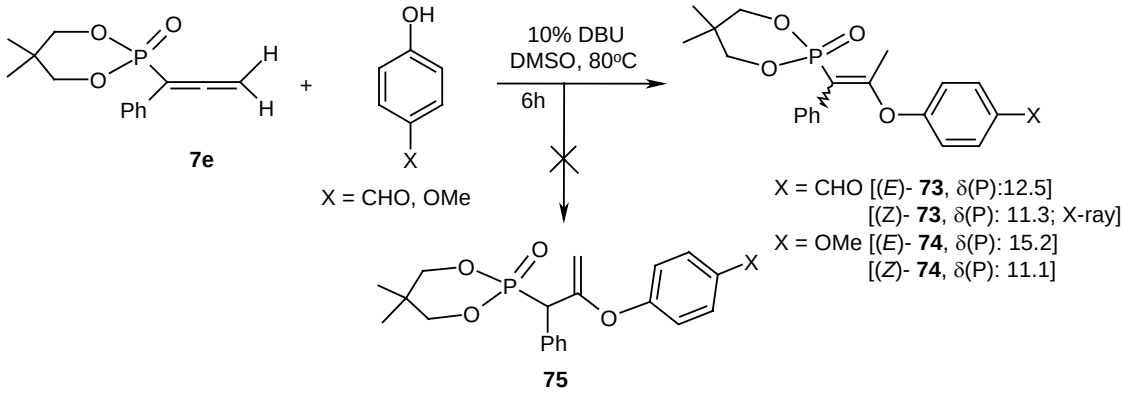
Fig. 20. Molecular structure for the compound (*E*)-**72.** Selected bond lengths [Å] with esd's in parentheses. C(1)-C(2) 1.504(5), C(2)-C(3) 1.336(4), C(3)-C(4) 1.445(5), C(4)-C(5) 1.335(4), O(1)-C(3) 1.407(4).

The allenyl phosphonate **7e** reacted with 4-hydroxy benzaldehye or anisole in the presence of DBU to give vinylic phosphonates **73** or**74**, respectively, in yields of >95% based on ^{31}P NMR of the reaction mixture (Scheme 26). The ^{31}P NMR spectrum of the reaction mixture showed that the *E*/*Z* isomeric ratio was ~1:1; this was the case even in the presence of 10 mol% PPh_3 as a base. Allylic phosphonate **75** was absent. Thus, this reaction proceeded through the phenol attack at *β*-position followed by proton addition at *γ*-position. Thus the reactivity of phenols with ester allene and allenylphosphonate **7e** in the presence of PPh_3 are entirely different. The phenol attacked at *γ*-position in the case ester allene [generally termed as umpolung addition],[112] whereas in the case of **7e**, the phenol attacked at *β*-position and gave vinylicphosphonate ethers (**73-74**). The combined isolated yields of the *E*+*Z* isomers are ≥90% for **73-74**.

The ^{13}C NMR spectra are quite useful for identification of *E*- and *Z*- isomers. As observed in phosphono-chromenes, the ^{1}J(P-C) value for *E*-isomer is greater than

that for the *Z* isomer. Thus, (*E*)-**73** shows ^{1}J(P-C) of 187.1 Hz while (*Z*)-**73** exhibits ^{1}J(P-C) of 176.1 Hz. The corresponding values for (*E*)-**74** and (*Z*)-**74** are, respectively, 194.4 and 177.0 Hz. The PC(Ph)=*C* carbon signal for *E*-isomer is a doublet with a coupling constant ^{2}J(P-C) ~ 32.1 Hz but in the case of *Z*-isomer it is almost a singlet [low ^{2}J(P-C)]. The structure of (*Z*)-**73** is confirmed by X-ray crystallography (Fig. 21).

Scheme 26



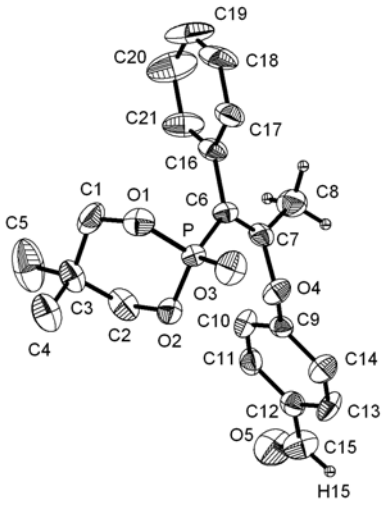
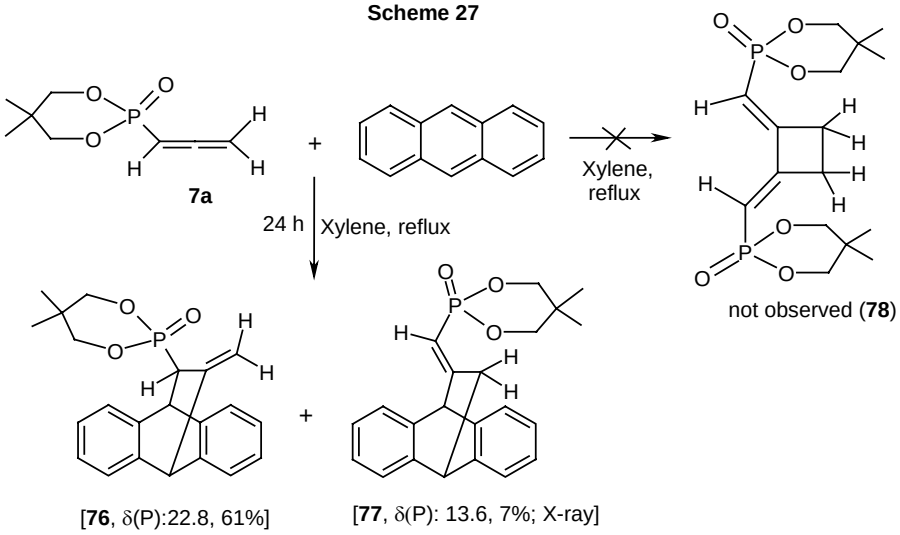


Fig. 21. ORTEP diagram for the compound (*Z*)-**73.** Selected bond lengths [Å] with esd's in parentheses: P-C(6) 1.794(3), C(6)-C(7) 1.330(4), O(4)-C(7) 1.381(3).

2.7 Reactions of allenylphosphonates/ allenylphosphinates with dienes

Allenes can be versatile precursors in Diels-Alder reaction {[4+2] cycloaddition} because either of the double bonds can act as a dienophile in reactions with a diene. Allenylphosphonates can also undergo homo-coupling {[2+2] cycloaddition} in xylene or in the presence of anthracene.[113] In the present study, we treated various allenylphosphonates (**7a**, **7c**, and **7h)** and allenylphosphinate (**14a**) with *N*-tosyl-pyrrole under different conditions (reflux in xylene/neat at high temperature at 140 ^{o}C), but no reaction occurred. These results show that reactivity of allenylphosphonates with substituted pyrroles was lower when compared with ester or sulfonated allenes.[61] Later, we heated several allenylphosphonates (**7a-b**, **7f**, **7g** and **7k**) with anthracene at 180 ^{o}C for one day. The ^{31}P NMR spectra of reaction mixtures in the case of **7a-b** and **7k** showed several peaks at δ(P) ~ 22.0. We were not successful in isolating any of these products. However, when we heated **7a** with anthracene in xylene under reflux conditions, we obtained the [4+2] cycloaddition products **76** and **77** and not the homo-coupled product **78** as shown in Scheme 27. The latter type of homo-coupled product was obtained in the case of **7c** earlier from our laboratory.[113b] The ^{31}P NMR spectrum of the reaction mixture showed mainly three peaks at δ ~ 22.7 (**76**, major ~75%), 13.6 (**77**, 10%) and 8.4. Compounds **76** and **77** had the same R_f values, but we could isolate them by hand-picking after crystallization from dichloromethane-hexane mixture. Only compound **77** gave crystals suitable (separated using microscope) for X-ray work. We could distinguish the two compounds from ^{1}H and ^{13}C NMR spectra. The PC*H* doublet in the ^{1}H NMR spectrum appeared at δ 3.15 [^{2}J(P-H) = 23.2 Hz] for **76** and at δ 5.78 [^{2}J(P-H) = 19.6 Hz] for **77**. The P*C* doublet was also characteristic at δ 43.0 [^{1}J(P-C) = 138.3 Hz] for **76** and δ 106.4 [^{1}J(P-C) = 187.3 Hz] for **77**. These two products are (*β*,*α*) and (*β*,*γ*)-addition products. The *endo* stereochemistry of compound **77** is established by X-ray crystallography (Fig. 22). More details on the mechanistic pathways should come only through additional studies, which are under progress in our laboratory.

Scheme 27



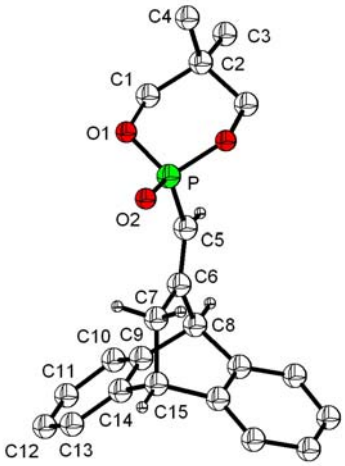


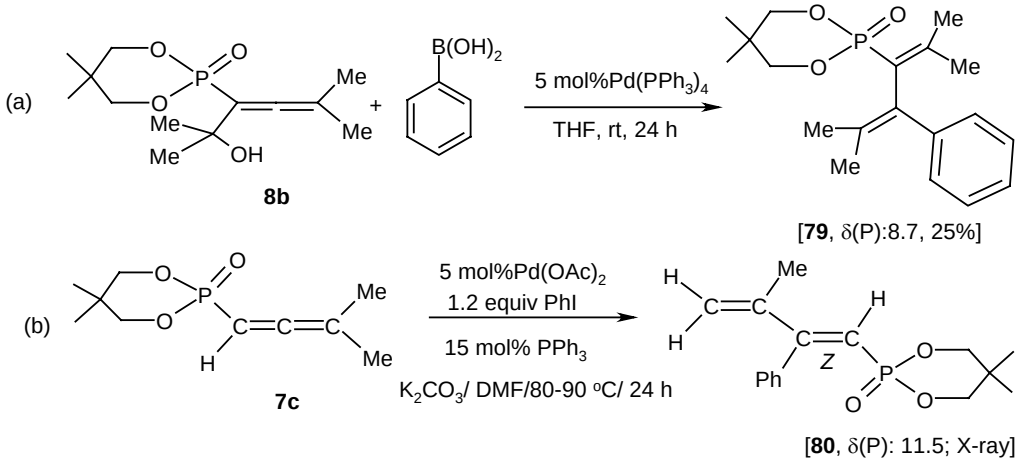
Fig. 22. ORTEP diagrams for the compound **77.** Selected bond lengths [Å] with esd's in parentheses: P-C(5) 1.777(4), C(5)-C(6) 1.336(5), C(6)-C(7) 1.518(5), C(6)-C(8) 1.526(5).

2.8 Pd-catalyzed arylation of phosphonate-allenol 8b

Allenols are good precursors for the preparation of various cyclic products like dihydrofurans, dihydropyrans as well as acylic products like dienes using transition metal (Pd, Au, Pt, etc.) or base catalyzed reactions. In the present work, we wanted to explore the reaction phosphonate allenol **8b** in Pd-catalyzed arylation and compare it with the Heck-type coupling reported by our group using the allene **7c**.[14] Thus treatment of **8b** with phenylboronic acid in the presence of $Pd(PPh_3)_4$ afforded phosphonyl *trans*-1,3-butadiene (**79**) in only moderate yield (25%, Scheme 28a). Here the butadiene was formed by the arylation at *β*-carbon along with

elimination of $B(OH)_3$. Interestingly, Heck type coupling of **7c** with iodobenzene also gave a butadiene with structure **80** as reported from our laboratory before,[14] this product was formed by the arylation at the *β*-carbon with elimination of HI and double bond shift (Scheme 28b). The ^{13}C NMR spectrum of **79** showed a doublet at δ 129.9 [^1J(P-C) = 183.7 Hz] due to P*C*= moiety. Since the yield of **79** was lower than the reported yields (63-99%) of the products using many non-phosphorylated allenols,[16] we did not proceed further.

Scheme 28



SUMMARY - PART A

(1) Several readily accessible and fairly stable new allenylphosphonates **7e-h, 7j-k** and phosphonate-allenols **8a-b** that are versatile candidates for exploring allene chemistry have been synthesized. Bis-allenylphosphonates **10-13** and bis-allenylcyclodiphosphazanes **16**, **17a-b** and **18a-b**, that may be useful precursors for polymerization, are reported. Although the precursor $[ClP(\mu\text{-N-}t\text{-Bu})]_2$ (**4**) has a *cis*-geometry, its reaction with propargyl alcohols leads to both the *cis* and *trans* allenic products. A possible rationalization for this result is presented.

(2) In the absence of PPh_3, the $=CMe_2$ terminal allenes **7c**, **14b** and **15** react with DEAD/DIAD to afford phosphono-1,3-butadienes (**24-28**) in nearly quantitative yields. By contrast, the reaction of allenylphosphonate **7b-c** with DEAD/ DIAD in the presence of PPh_3, leads directly to phosphono-pyrazoles **31-34**. More importantly, a novel P-C bond cleavage leading to tetra-substituted pyrazoles **37-42** in the reaction of α-aryl allenylphosphonates **7e-g** with DEAD/DIAD in the presence of PPh_3 has been discovered.

(3) The reaction of salicylaldehydes with allenylphosphonates in the presence of a base leads to a variety of phosphono-chromenes and allylic phosphonates. Optimization of reaction conditions reveal that DBU (base) in DMSO (solvent) is the best combination. PEG-400 also gives good results, but the yields are lower than that in DMSO. Interconversion of *E* and *Z* isomers of phosphono-chromenes is demonstrated by ^{31}P NMR spectroscopy. In continuation of this study, allenylphosphonates have been treated with activated phenols in the presence of base to selectively afford either allylic phosphonyl ethers or vinylic phosphonyl ethers depending on the substituents on the allenylphosphonate. Utilization of allylic phosphonyl ether in HWE reaction to afford *trans*-1,3-butadiene in good yields is described.

(4) The allenylphosphonate **7a** undergoes Diels-Alder {[4+2] cycloaddition} reaction with anthracene to lead to (β,α) and (β,γ)-addition products. The latter compound is an endo adduct, as shown by X-ray crystallography.

EXPERIMENTAL SECTION

General: Chemicals and solvents were procured from Aldrich/ Fluka or local manufacturers. Further purification was done according to standard procedures wherever required.[114] All operations, unless otherwise specified, were carried out under dry nitrogen atmosphere using standard vacuum line techniques.[115]

Melting points: Melting points were determined using a SUPERFIT hot stage apparatus and are uncorrected.

Elemental analyses: Elemental analyses were carried out on a Perkin- Elmer 240C CHN or Thermo Finnigan EA1112 CHNS analyzer.

Infrared spectroscopy: IR spectra were recorded on a JASCO FT/IR 5300 spectrophotometer.

NMR spectroscopy: ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using 5 mm tubes on a Bruker 200 MHz or 400 MHz NMR spectrometer in $CDCl_3$ solution (unless specified otherwise) with shifts referenced to $SiMe_4$ (^{1}H, ^{13}C: $\delta = 0$) or ext. 85% H_3PO_4 (^{31}P: $\delta = 0$) respectively; *J* values are in Hz.

LC-MS and GC-MS: LC-MS 2010A or GC-MS-QP2010 equipment were used to record mass spectra for isolated compounds where appropriate. LC-MS data were obtained using electrospray ionization (positive mode) on a C-18 column at a flow rate 0.2 mL/ min using MeOH/water (90:10) as eluent. GC-MS data were obtained on EI mode using ZB-1 column.

Optical rotation: The optical rotations were measured by using an AUTOPOL^{TM} II automatic polarimeter (readability ± 0.01).

CD spectra: Circular dichroism (CD) spectra for the crystals were recorded on Jasco-J810 spectropolarimeter.

Representative ^{13}C NMR spectra are illustrated as appropriate.

3.1 Synthesis of P^{III} compounds 1-4, allene 5 and propargyl alcohols 6a-f

General Note: Most of these precursors are in use in our laboratory and some of them are previously known. However, the procedures have been modified and hence are given here along with the spectroscopic data some of which were not reported previously. Compounds $(OCH_2CMe_2CH_2O)PCl$ [**1**; δ(P) 145.8],[83] $C[(CH_2O)_2PCl]_2$,[84] [**2**; ^{1}H NMR: δ 3.62–3.68 (m, 2 H, OC*H*$_2$), 4.23-4.27 (m, 2 H, OC*H*$_2$), 4.49-4.60 (m, 4 H, OC*H*$_2$); ^{31}P NMR: δ 148.9 [lit.146.0[116]], $[((CH_3)_2CH)_2N]_2PCl$ [**3**; δ(P): 140.8][85] and $[ClP(\mu\text{-N-}t\text{-Bu})]_2$ [**4**; δ(P): 206.5][86] were prepared by using literature methods. Allene Ph-CH=C=CH$_2$ (**5**)[5] and the propargyl alcohols **6a-f** were prepared by literature procedure.[88-89]

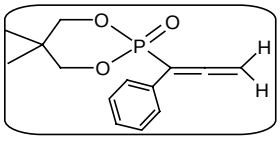
3.2 Synthesis of allenylphosphonates 7a-k

Allenylphosphonates **7a-d** and were prepared by following a literature procedure.[4a,7a] Compounds **7e-h** and **7j-k** are new. General procedure for the synthesis of these compounds is given below.

$(OCH_2CMe_2CH_2O)P(CR^3=C=CR^1R^2)$ (7e-k)

To a solution of substituted propargyl alcohol $R^3C{\equiv}CCR^1R^2OH$ (23.5 mmol) in dry THF (50 mL) was added triethylamine (2.47 g, 3.40 mL, 23.5 mmol), the mixture stirred for 5 min, and then $(OCH_2CMe_2CH_2O)PCl$ (**1**) (4.11 g, 3.37 mL, 23.5 mmol) in THF (20 mL) was added drop-wise (~ 0.5 h) at 0^o C. The contents were brought to room temperature, stirred further for 1 h, and then refluxed for 16 h. Triethylamine hydrochloride formed was filtered off and solvent removed *in vacuo* from the filtrate. Allenes **7e-k** were purified by column chromatography (silica gel; ethyl acetate-hexane 2:3).

(a) $(OCH_2CMe_2CH_2O)PC(C_6H_5)=C=CH_2$ (7e)



Yield: 4.96 g (80 %; using 23.5 mmol of **1**).

Mp: 110-114 ^{o}C.

IR (KBr): 3059, 2976, 2892, 1962, 1933, 1707, 1489, 1271 cm^{-1}.

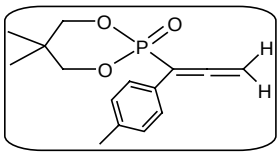
^{1}H NMR: δ 0.88 and 1.29 (2 s, 6 H, C(CH_3)$_2$), 3.92–3.99 (m, 4 H, OCH_2), 5.35 and 5.38 (2 s, 2 H, =CH_2; they may also be a part of closely space AB quartet, but is not investigated further), 7.26-7.60 (m, 5 H, Ar-*H*).

^{13}C NMR: δ 20.8 and 21.9 (2 s, C(*C*H$_3$)$_2$), 32.6 (d, ^{3}J(P-C) = 7.0 Hz, *C*(CH$_3$)$_2$), 77.3 and 78.7 (2 s, 2 O*C*H$_2$), 78.9 (s, =*C*H$_2$), 95.2 (d, ^{1}J(P-C) = 181.0 Hz, P*C*), 127.6, 127.7, 128.0, 128.8, 130.5, 130.6, 212.9 (d, ^{2}J(P-C) = 5.0 Hz, PC*C*).

^{31}P NMR: δ 6.6.

Anal. Calc. for $C_{14}H_{17}O_3P$: C, 63.63; H, 6.48. Found: C, 63.68; H, 6.42.

(b) (OCH$_2$CMe$_2$CH$_2$O)PC(4-Me-C$_6$H$_5$)=C=CH$_2$ (7f)



Yield: 5.23 g (80 %; using 23.5 mmol of **1**).

Mp: 138–140 ^{o}C.

IR (KBr): 3059, 2975, 2886, 1935, 1715, 1481, 1264 cm^{-1}.

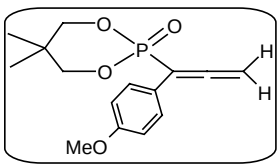
^{1}H NMR: δ 0.89 and 1.30 (2 s, 6 H, C(CH_3)$_2$), 2.34 (s, 3 H, Ar-CH_3), 3.92–4.00 (m, 4 H, OCH_2), 5.33 and 5.36 (m, 2 H, =CH_2), 7.15-7.50 (m, 4 H, Ar-*H*).

^{13}C NMR: δ 20.8 (s, Ar-CH_3), 21.2, 21.9 (2 s, C(*C*H$_3$)$_2$), 32.6 (d, ^{3}J(P-C) = 7.0 Hz, *C*(CH$_3$)$_2$), 77.3 and 77.4 (2 s, 2 O*C*H$_2$), 78.7 (d, ^{3}J(P-C) = 14.0 Hz, =*C*H$_2$), 95.2 (d, ^{1}J(P-C) = 181.0 Hz, P*C*), 127.4, 127.5, 128.5, 129.5, 137.9, 212.7 (d, ^{2}J(P-C) = 4.0 Hz, PC*C*).

^{31}P NMR: δ 7.8.

Anal. Calc. for $C_{15}H_{19}O_3P$: C, 64.74; H, 6.88. Found: C, 64.82; H, 6.87.

(c) (OCH$_2$CMe$_2$CH$_2$O)PC(4-MeO-C$_6$H$_5$)=C=CH$_2$ (7g)



Yield: 5.53 g (80 %; using 23.5 mmol of **1**).

Mp: 105-108 ^{o}C.

IR (KBr): 3061, 2959, 2895, 1937, 1607, 1512, 1458, 1441, 1258, 1057 cm^{-1}.

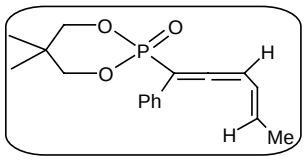
^1H NMR: δ 0.89 and 1.30 (2 s, 6 H, $C(CH_3)_2$), 3.80 (s, 3 H, OCH_3), 3.92–3.99 (m, 4 H, OCH_2), 5.33-5.36 (m, 2 H, $=CH_2$), 6.87-7.54 (m, 4 H, Ar-*H*).

^{13}C NMR: δ 20.6 and 21.8 (2 s, $C(CH_3)_2$), 32.5 (d, ^3J(P-C) = 7.0 Hz, $C(CH_3)_2$), 55.2 (s, OCH_3), 77.2$_7$ and 77.3$_4$ (2 s, 2 OCH_2), 78.8 (d, ^3J(P-C) = 14.0 Hz, $=CH_2$), 94.8 (d, ^1J(P-C) = 180.0 Hz, P*C*), 114.2, 122.4, 122.5, 128.8, 128.9, 159.4, 212.3 (d, ^2J(P-C) = 4.0 Hz, PC*C*).

^{31}P NMR: δ 7.5.

Anal. Calc. for $C_{15}H_{19}O_4P$: C, 61.22; H, 6.51. Found: C, 61.25; H, 6.52.

(d) ($OCH_2CMe_2CH_2O$)PC(Ph)=C=CH(CH=CHMe) (7h)



Yield: 5.01 g (70 % using 23.5 mmol of **1**).

Mp: 122-124 °C.

IR (KBr): 2961, 2926, 1927, 1815, 1597, 1491, 1476, 1456, 1267, 1055, 1003 cm^{-1}.

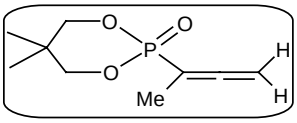
^1H NMR: δ 0.91 and 1.33 (2 s, 6 H, $C(CH_3)_2$), 1.85 (dd, ^3J(H-H) = 5.3 Hz, ^4J(H-H) = 3.5 Hz, 3 H, CH_3), 3.96–4.02 (m, 4 H, OCH_2), 5.92-5.97 (m, 2 H, C*H*=C*H*-CH_3), 6.44 (dd, ^4J(P-H) ~ 12.0 Hz, ^3J(H-H) ~6.0 Hz, 1 H, C=C=C*H*), 7.28-7.63 (m, 5 H, Ar-*H*).

^{13}C NMR: δ 18.5 (s, =C(H)CH_3), 20.9 and 22.0 (2 s, $C(CH_3)_2$), 32.6 (d, ^3J(P-C) = 7.0 Hz, $C(CH_3)_2$), 77.2 and 77.6 (2 d, ^2J(P-C) = 7.0 Hz, OCH_2), 97.7 (d, ^3J(P-C) = 16.0 Hz, C=C=*C*H), 97.3 (d, ^1J(P-C) = 181.0 Hz, P*C*), 122.8 (d, ^4J(P-C) = 10.0 Hz, C=C=CH-*C*H), 127.8, 127.9, 128.1, 128.8, 131.2$_6$, 131.3$_4$ (Ar*C*), 132.0 (d, ^5J(P-C) = 5.0 Hz, CH=*C*H(Me)), 212.8 (d, ^2J(P-C) = 3.0 Hz, PC*C*).

^{31}P NMR: δ 6.7.

Anal. Calc. for $C_{17}H_{21}O_3P$: C, 67.09; H, 6.96. Found: C, 67.05; H, 6.96.

(e) $(OCH_2CMe_2CH_2O)PC(CH_3)=C=CH_2$ (7i)



Yield: 4.27 g (90 %).

Mp: 85-87 ^oC [lit. 102 ^oC[9b]]

IR (KBr): 3073, 2981, 2928, 1944, 1771, 1472, 1404, 1366, 1258, 1132, 1047, 992 cm^{-1}.

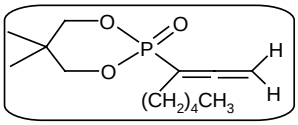
^1H NMR: δ 0.98 and 1.20 (2 s, 6 H, $C(CH_3)_2$), 1.88-1.93 (m, 3 H, $PC(CH_3)$), 3.93–4.08 (m, 4 H, OCH_2), 4.97-5.02 (m, 2 H, $=CH_2$).

^{13}C NMR: δ 14.4 (d, ^2J(P-C) = 4.9 Hz, $PCCH_3$), 20.9 and 21.7 (2 s, $C(CH_3)_2$), 32.5 (d, ^3J(P-C) = 7.3 Hz, $C(CH_3)_2$), 76.0 (d, ^3J(P-C) = 14.6 Hz, $=CH_2$), 76.7 and 76.8 (2 s, OCH_2), 86.7 (d, ^1J(P-C) = 183.1 Hz, PC), 211.9 (d, ^2J(P-C) = 6.1 Hz, PCC).

^{31}P NMR: δ 12.2. [lit. 12.4[9b]]

Anal. Calc. for $C_9H_{15}O_3P$: C, 53.46; H, 7.48. Found: C, 53.45; H, 7.44.

(f) $(OCH_2CMe_2CH_2O)PC[(CH_2)_4CH_3]=C=CH_2$ (7j)



Yield: 4.87 g (80 %; using 23.5 mmol of **1**).

Mp: 57-60 ^oC.

IR (KBr): 3071, 2928, 2855, 1944, 1769, 1470, 1372, 1258, 1047, 993 cm^{-1}.

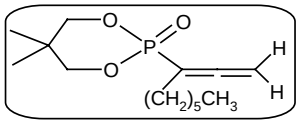
^1H NMR: δ 0.90 (t, ^3J(H-H) = 6.8 Hz, 3 H, CH_2CH_3), 0.99 and 1.20 (2 s, 6 H, $C(CH_3)_2$), 1.33-1.35 (m, 4 H, $CH_2CH_2CH_3$), 1.52-1.56 (m, 2 H, $PCCCH_2$), 2.16-2.23 (m, 2 H, $PCCH_2$), 3.93–4.09 (m, 4 H, OCH_2), 5.04 (td, ^4J(P-H) = 13.6 Hz, ^5J(H-H) ~ 3.1 Hz, 2 H, $=CH_2$).

^{13}C NMR: δ 14.0 (s, CH_2CH_3), 21.0 and 21.7 (2 s, $C(CH_3)_2$), 22.3 (s, CH_2CH_3), 27.6 (d, ^4J(P-C) = 6.1 Hz, $CH_2CH_2CH_3$), 27.8 (d, ^3J(P-C) = 6.1 Hz, $PCCH_2CH_2$), 31.2 [s (^2J(P-C) <2.0 Hz), $PCCH_2$], 32.6 (d, ^3J(P-C) = 7.3 Hz, $C(CH_3)_2$), 76.7 (s, 2 OCH_2), 77.3 (s, $=CH_2$), 92.0 (d, ^1J(P-C) = 180.7 Hz, PC), 211.5 (d, ^2J(P-C) = 6.1 Hz, PCC) [the assignment of the alkyl carbons is tentative].

^{31}P NMR: δ 11.3.

LC/MS *m/z* 259 $[M+1]^+$.

(g) $(OCH_2CMe_2CH_2O)PC[(CH_2)_5CH_3]=C=CH_2$ (7k)



Yield: 4.99 g (78 % using 23.5 mmol of **1**).

Mp: 58-61 ^oC.

IR (KBr): 3075, 2926, 2857, 1943, 1773, 1470, 1372, 1258, 1047, 997 cm^{-1}.

^{1}H NMR: δ 0.89 (t, ^3J(H-H) ~ 6.8 Hz, 3 H, CH_2CH_3), 0.99 and 1.19 (2 s, 6 H, $C(CH_3)_2$), 1.30-1.37 (m, 6 H, $CH_2CH_2CH_2CH_3$), 1.50-1.55 (m, 2 H, $PCCCH_2$), 2.16-2.21 (m, 2 H, $PCCH_2$), 3.92–4.09 (m, 4 H, OCH_2), 5.04 (d, ^4J(P-H) = 13.6 Hz, 2 H, $=CH_2$).

^{13}C NMR: δ 14.0 (s, CH_2CH_3), 21.0 and 21.7 (2 s, $C(CH_3)_2$), 22.5 (s, CH_2CH_3), 27.7$_7$, 27.8$_3$, 28.7 and 31.5 (4 s, $PCCH_2CH_2CH_2CH_2CH_2CH_3$), 32.5 (d, ^3J(P-C) = 6.6 Hz, $C(CH_3)_2$), 76.6 and 76.7 (2 s, OCH_2), 77.2 (d, ^3J(P-C) = 15.8 Hz, $=CH_2$), 92.0 (d, ^1J(P-C) = 181.3 Hz, PC), 211.5 (d, ^2J(P-C) = 5.9 Hz, PCC).

^{31}P NMR: δ 12.2.

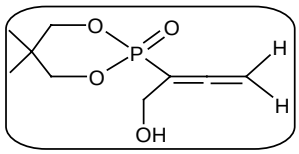
Anal. Calc. for $C_{14}H_{25}O_3P$: C, 61.75; H, 9.25. Found: C, 61.76; H, 9.23.

3.3 Synthesis of phosphonate-allenols $C(CH_2O)_2\{P(O)C[CH_2(OH)]=C=CH_2\}$ (8a), $C(CH_2O)_2\{P(O)C[CMe_2(OH)]=C=CMe_2\}$ (8b) and the butadiene $[(OCH_2CMe_2CH_2O)(O)P\text{-}C(=CH_2)]_2$ (9)

(a) Compounds 8a and 9

To a solution of diol (4.60 g, 53.4 mmol) and triethylamine (5.41 g, 7.45 mL, 53.4 mmol) in THF (135 mL), $(OCH_2CMe_2CH_2O)PCl$ (**1**) (9.00 g, 7.40 mL, 53.4 mmol) in THF (25 mL) was added drop-wise at -78 ^oC, the mixture stirred for 2 h, brought to room temperature and was then heated under reflux for 15-18 h. Triethylamine hydrochloride formed was filtered off and the solvent was removed *in vacuo*. Yield was 80% on the basis of ^{31}P NMR; the remaining material was the 1,3-butadiene $[(OCH_2CMe_2CH_2O)(O)P\text{-}C(=CH_2)]_2$ (**9**). Pure compound **8a** (isolated

yield 2.0 g; low yield because of the other product) was obtained by crystallization from THF.



Yield: 2.01 g (17%).

Mp: 134–138 ^{o}C.

IR (KBr): 3304, 3069, 2975, 2938, 1968, 1939, 1827, 1719, 1472, 1238, 1061, 1009, 839 cm^{-1}.

^{1}H NMR: δ 0.99 and 1.19 (2 s, 6 H, C(C*H*$_3$)$_2$), 2.50 (br, 1 H, O*H*), 4.00-4.12 (m, 4 H, OC*H*$_2$), 4.33 (td, ^{3}J(P-H) = 14.0 Hz, ^{5}J(H-H) = 2.0 Hz, 2 H, C*H*$_2$OH), 5.15 (td, ^{4}J(P-H) = 12.8 Hz, ^{5}J(H-H) = 2.0 Hz, 2 H, C=C*H*$_2$).

^{13}C NMR: δ 20.9 and 21.7 (2 s, C(*C*H$_3$)$_2$), 32.5 (d, ^{3}J(P-C) = 7.0 Hz, *C*(CH$_3$)$_2$), 60.3 (d, ^{2}J(P-C) = 8.0 Hz, *C*H$_2$OH), 77.1 (d, ^{2}J(P-C) = 6.0 Hz, 2 PO*C*H$_2$), 78.0 (d, ^{3}J(P-C) = 14.0 Hz, C=*C*H$_2$), 92.9 (d, ^{1}J(P-C) = 183.0 Hz, P*C*), 211.3 (d, ^{2}J(P-C) = 6.0 Hz, PC=*C*) [*cf.* Fig. 23].

^{31}P NMR: δ 10.1.

Anal. Calc. for $C_9H_{15}O_4P$: C, 49.54; H, 6.93. Found: C, 49.47; H, 7.02.

X-ray structural analysis was performed on this sample.

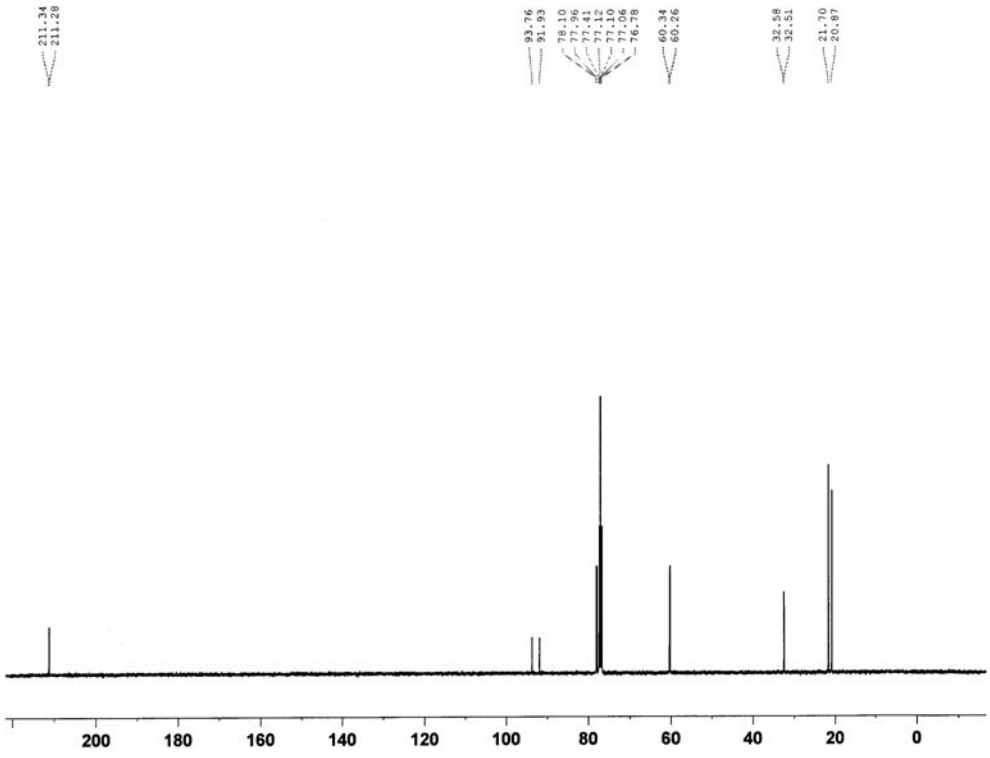
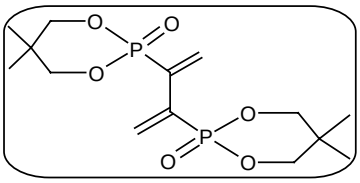


Fig. 23. ^{13}C NMR spectrum of compound **8a**

Compound 9: This was isolated from the same reaction, but a *quantitative* yield could be obtained by using 1:2 molar reaction of propargyl alcohol to **1**.



Yield: 0.93 g (5%).

Mp: 182-186 ^{o}C.

IR (KBr): 2973, 2888, 1931, 1578, 1478, 1265, 1055, 1005, 957 cm^{-1}.

^{1}H NMR: δ 0.96 and 1.24 (2 s, 12 H, C(CH_3)$_2$), 3.98–4.11 (m, 8 H, OCH_2), 6.27 (d, ^{3}J(P-H) = 20.1 Hz, 2 H, =CH_AH$_B$, *cis* to P), 6.56 (d, ^{3}J(P-H) = 44.9 Hz, 2 H, =CH$_A$$H_B$, *trans* to P).

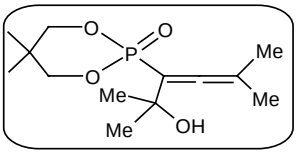
^{13}C NMR: δ 21.1, 21.9 (2 s, C(*C*H$_3$)$_2$), 32.5 (d with virtual coupling (?), ^{3}J(P-C) ~ 6.0 Hz, *C*(CH_3)$_2$), 76.9 (d with virtual coupling (?), ^{2}J(PC) ~ 6.0 Hz, O*C*H$_2$), 132.1 (d, ^{1}J(P-C) = 182.0 Hz, P*C*), 134.2 (d with virtual coupling (?), ^{2}J(P-C) ~ 12.0 Hz, PC=*C*).

^{31}P NMR: δ 9.0.

Anal. Calc. for $C_{14}H_{24}O_6P_2$: C, 48.00; H, 6.91. Found: C, 47.97; H, 6.93.

(b) $C(CH_2O)_2\{P(O)C[CMe_2(OH)]=C=CMe_2\}$ (8b)

Compound **8b** was prepared by a procedure similar to that for **7a** using $(OCH_2CMe_2CH_2O)PCl$ (**1**) (4.11 g, 3.37 mL, 23.5 mmol), diol (3.34 g, 1.35 mmol) and Et_3N (2.47 g, 3.40 mL, 23.5 mmol). It was purified by column chromatography (EtOAc/hexane = 1/1, silica gel).



Yield: 4.83 g (75%).

Mp: 120–122 ^{o}C.

IR (KBr): 3412, 2970, 1956, 1809, 1470, 1364, 1248, 1184, 1063, 1009, 957 cm^{-1}.

^{1}H NMR: δ 0.95 and 1.20 (2 s, 6 H, $C(CH_3)_2$), 1.44 and 1.50 (2 s, 6 H, $OC(CH_3)_2$), 1.81 and 1.83 (2 s, 6 H, $C=C(CH_3)_2$), 3.93-4.09 (m, 4 H, OCH_2).

^{13}C NMR: δ 19.7, 19.8, 21.0 and 21.9 (4 s, $C(CH_3)_2$ + $C=C(CH_3)_2$), 30.0$_9$ and 30.1$_3$ (2 s, $OC(CH_3)_2$), 32.6 (d, ^{3}J(P-C) = 6.8 Hz, $C(CH_3)_2$), 71.7 (d, ^{2}J(P-C) = 7.7 Hz, $C(CH_3)_2OH$), 76.8 and 76.9 (2 s, OCH_2), 99.5 (d, ^{3}J(P-C) = 15.9 Hz, $C=C(CH_3)_2$), 99.4 (d, ^{1}J(P-C) = 179.9 Hz, P*C*), 204.1 (s, PC=*C*).

^{31}P NMR: δ 10.9.

Anal. Calc. for $C_{13}H_{23}O_4P$: C, 56.92; H, 8.45. Found: C, 56.83; H, 8.46.

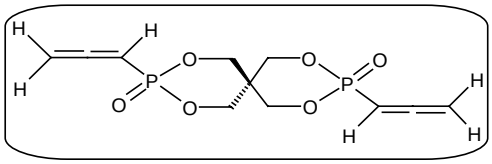
3.4 Synthesis of bis(allenyl)phosphonates $[R^1R^2C=C=C(R^3)P(O)(OCH_2)_2]_2C$ (10-13): Typical procedure for 10

To a solution of **2** (2.04 g, 7.4 mmol) and triethylamine (1.49 g, 14.8 mmol) in dry THF (30 mL) at 0 ^{o}C, the appropriate propargyl alcohol (14.8 mmol) was added at 0 ^{o}C with continuous stirring. The reaction mixture was brought to room temperature, stirred for 3 h and filtered. The tricoordinate species **II** [>90% by ^{31}P NMR] was characterized by ^{1}H and ^{31}P NMR spectra [^{1}H NMR: 2.43 (s, 2 H,

C≡C*H*), 3.30-3.35 and 3.92-3.96 (m each, 2+2 H, OCH_2-C≡CH; the two groups are in slightly different environments), 4.20-4.46 (m, 8 H, CH_2OP). ^{31}P NMR: 125.7]. In the ^{1}H NMR spectrum taken at this stage, solvent peaks (THF: δ 1.80 and 3.70) were also observed. The filtrate was heated under reflux for 15-18 h and the solvent removed in vacuo. Compound **10** (1.72 g, 79%) was purified by crystallization from methanol.

Compounds **11** and **12** were purified using column chromatography (ethyl acetate). Compound **13** was purified by column chromatography using hexane-ethyl acetate (1:1) mixture. Yields were above 95% using the *same* molar quantities for all these compounds [^{31}P NMR]; isolated yields are given below.

(a) C(CH$_2$O)$_4${P(O)C(H)=C=CH}$_2$ (10)



Yield: 1.72 g (79%).

Mp: 199-201 ^{o}C.

IR (KBr): 3069, 2984, 2915, 1944, 1474, 1279, 1237, 1194, 1156, 1024, 843 cm^{-1}.

^{1}H NMR: δ 4.17-4.27 and 4.42-4.52 (2 m, 8 H, OCH_2), 5.16-5.21 (m, 4 H, C=CH_2), 5.40-5.42 (m, 2 H, PC*H*).

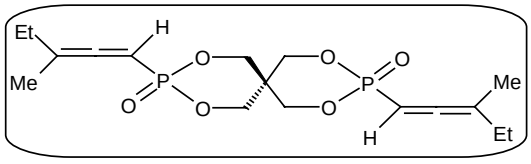
This compound had a poor solubility and hence ^{13}C NMR spectrum was not recorded.

^{31}P NMR: δ 11.36.

Anal. Calc. $C_{11}H_{14}O_6P_2$: C, 43.44; H, 4.64. Found: C, 43.42; H, 4.69.

X-ray structural analysis was performed on this sample.

(b) C(CH$_2$O)$_4${P(O)C(H)=C=CMeEt}$_2$ (11)



Yield: 2.11 g (74%).

Mp: 106-110 ^{o}C.

IR (KBr): 2972, 2915, 1962, 1698, 1458, 1370, 1269, 1200, 1150, 1020, 828 cm^{-1}.

^{1}H NMR: δ 1.07 (t, ^{3}J(H-H) = 7.2 Hz, 6 H, CH_2CH_3), 1.80-1.83 (m, 6 H, C=CCH_3), 2.04-2.13 (m, 4 H, CH_2CH_3), 4.16-4.48 (m, 8 H, OCH_2), 5.30-5.35 (m, 2 H, PC*H*).

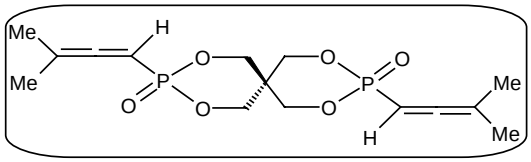
^{13}C NMR: δ 11.9 (s, CH_2CH_3), 17.5 and 17.6 (2 s, CH_2CH_3), 26.0 and 26.1 (2 s, C=CCH_3), 37.3 (t, ^{3}J(P-C) = 6.0 Hz, OCH_2C), 67.5, 67.6, 67.7 and 67.9 (4 d, ^{2}J(P-C) ~ 6.0 Hz, OCH_2), 77.3 (d, ^{1}J(P-C) = 199.1 Hz, P*C*), 104.5 (d, ^{3}J(P-C) = 17.4 Hz, P-C=C=*C*(Me)(Et)), 211.8 (s, PC=*C*).

^{31}P NMR: δ 13.0.

LC/MS: *m/z* 389 $[M+1]^{+}$.

Diastereomers may be expected in this case, but we did not get evidence for the presence of these in our studies.

(c) $C(CH_2O)_4\{P(O)C(H)=C=CMe_2\}_2$ (12)



Yield: 1.98 g (76%).

Mp: 140-144 ^{o}C.

IR (KBr): 2986, 2907, 1964, 1682, 1364, 1269, 1200, 1152, 1020, 820 cm^{-1}.

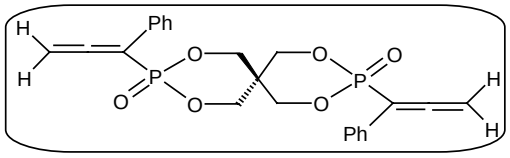
^{1}H NMR: δ 1.80–1.88 (m, 12 H, C=C(CH_3)$_2$), 4.09–4.50 (m, 8 H, OCH_2), 5.22–5.25 (m, 2 H, PC*H*).

^{13}C NMR: δ 19.0 and 19.1 (2 s, C=C(CH_3)$_2$), 37.2 (s, OCH_2C), 67.7 and 67.9 (2 d, ^{2}J(P-C) = 6.5 Hz, OCH_2), 75.4 (d, ^{1}J(P-C) = 199.1 Hz, P*C*), 98.6 (d, ^{3}J(P-C) = 17.2 Hz, C=CMe_2), 212.3 (s, PC=*C*).

^{31}P NMR: δ 12.6.

LC/MS: *m/z* 361 $[M+1]^{+}$.

(d) $[H_2C=C=C(Ph)P(O)(OCH_2)_2]_2C$ (13)



Yield: 2.59 g (74%).

Mp: >300 ^oC.

IR (KBr): 3059, 2982, 1939, 1595, 1493, 1269, 1155, 1076, 1020, 938 cm^{-1}.

^1H NMR: δ 3.99-4.04, 4.22-4.33 and 4.58-4.65 (three groups of m, 8 H, OCH_2), 5.42 (d, 4 H, ^4J(P-H) = 13.2 Hz, $=CH_2$), 7.26-7.55 (m, 10 H, Ar-*H*).

^{13}C NMR: δ 37.5 (t, ^3J(P-C) = 5.7 Hz, OCH_2C), 68.5 and 68.9 (2 d, ^2J(P-C) = 7.0 Hz each, OCH_2), 79.5 (d, ^3J(P-C) = 15.1 Hz, $C=CH_2$), 94.8 (d, ^1J(P-C) = 185.2 Hz, P*C*), 127.7, 127.8, 128.5, 129.0, 129.9, 130.0 (Ar*C*), 213.5 (d, ^2J(P-C) ~ 4.6 Hz, C=*C*=C).

^{31}P NMR: δ 10.6.

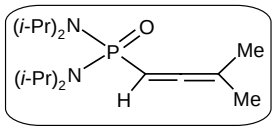
LC/MS: *m/z* 457 $[M+1]^+$.

3.5 Allenyl phosphinates $Ph_2P(O)CH=C=C(R)_2$ [R = H (14a), R = Me (14b)]

Allenes $Ph_2P(O)CH=C=C(R)_2$ [R = H (**14a**, δ(P) 23.5[4f]), R = Me (**14b**, δ(P) 26.0[93e])] were prepared by a procedure similar to that for **7e** using $(Ph)_2PCl$ and corresponding propargyl alcohol. These are known compounds.[4f,93e]

3.6 Allenylphosphoramidate $(((CH_3)_2CH)_2N)_2P(O)CH=C=C(CH_3)_2$ (15)

This compound was prepared by a procedure similar to that for **7e** using $[((CH_3)_2CH)_2N]_2PCl$ (**3**) (3.60 g, 1.35 mmol), $HC\equiv CC(CH_3)_2(OH)$ (1.14 g, 1.31 mL, 1.35 mmol) and NEt_3 (1.37 g, 1.88 mL, 1.35 mmol). Compound **15** was purified by column chromatography (EtOAc/hexane = 1/1, silica gel).



Yield: 3.31 g (80%).

Mp: 52–54 ^oC.

IR (KBr): 2971, 2872, 1966, 1647, 1456, 1401, 1366, 1223, 984 cm^{-1}.

^{1}H NMR: δ 1.19–1.31 (2 d, 24 H, N(CH(CH_3)$_2$)$_2$), 1.70 (d, ^{5}J(P-H) ~ 4.0 Hz, 3 H, =CCH_3), 1.71 (d, ^{5}J(P-H)~ 3.0 Hz, 3 H, =CCH_3), 3.48–3.56 (m, 4 H, N(CH(CH$_3$)$_2$)$_2$), 5.22–5.29 (br m, 1 H, PCH).

^{13}C NMR: δ 18.7$_0$, 18.7$_2$, 18.9, 21.9, 22.6$_7$, 22.6$_8$, 23.0$_5$, 23.0$_6$, 23.7, 45.4, 45.5, 46.8 and 47.3 (4 s, N(CH(CH$_3$)$_2$)$_2$), 86.7 (d, ^{1}J(P-C) = 148.8 Hz, PC), 96.0 (d, ^{3}J(P-C) = 14.4 Hz, PCCC), 208.5 (s, PCC).

^{31}P NMR: δ 19.6.

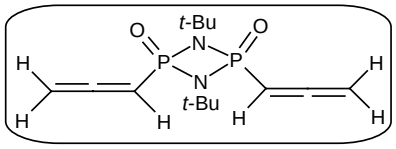
Anal. Calc. for $C_{17}H_{35}N_2OP$: C, 64.93; H, 11.22; N, 8.91. Found: C, 64.80; H, 11.21; N, 8.98.

3.7 Synthesis of *cis*- and *trans*- bis(allenyl)cylclodiphosph(V)azanes [(R'R"C=C=CH)(O)P(*μ*-*N*-*t*-Bu)]$_2$ (16, 17a-b and 18a-b): Typical procedure for 16

To a solution of **4** (2.04 g, 7.4 mmol) in dry THF (30 mL) was added triethylamine (1.49 g, 14.8 mmol) at 0 ^{o}C, the mixture stirred for 5 min, and then the required substituted propargyl alcohol HC≡CCR'R"(OH) (14.8 mmol) was added at 0 ^{o}C. The reaction mixture was stirred for 3 h at room temperature and triethylamine hydrochloride was filtered off. The filtrate was heated under reflux for 15-18 h and the solvent removed *in vacuo*. Compound **16** was purified by crystallization from THF. The geometrical isomers of **17** or **18** were separated using column chromatography (15% ethyl acetate in hexane).

Analogous reaction of **4** with the alcohols HC≡CCH(Me)(OH) and HC≡CC(Ph)(Me)(OH) also gave essentially a single product ascribable to the *cis*-isomer in each case [δ(P) 3.1 and 2.4 respectively] but we did not make attempts to isolate them.

(a) *Cis*-[H$_2$C=C=CHP(O)(*μ*-*N*-*t*-Bu)]$_2$ (16)



Yield: 1.76 g (75%).

Mp: 159-161 ^{o}C.

IR (KBr): 3059, 2971, 1962, 1937, 1464, 1370, 1256, 1086 cm^{-1}.

^{1}H NMR: δ 1.48 (s, 18 H, C(CH_3)$_3$), 5.09-5.14 (m, 4 H, C=CH_2), 5.45-5.50 (m, 2 H, PC*H*).

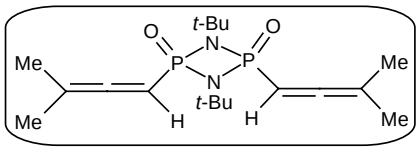
^{13}C NMR (50 MHz): δ 30.9 (s, C(*C*H$_3$)$_3$), 55.5 (s, *C*(CH$_3$)$_3$), 76.8 (d, ^{3}J(P-C) ~ 8.5 Hz, C=*C*H$_2$), 85.0 (dd, ^{1}J(P-C) ~161.9 Hz, ^{3}J(P-C) = 6.1 Hz P*C*), 215.9 (s, PC=*C*).

^{31}P NMR: δ 2.5.

Anal. Calc. for $C_{14}H_{24}N_2O_2P_2$: C, 53.5; H, 7.7; N, 8.9. Found: C, 53.7; H, 7.7; N, 8.9.

X-ray structural analysis was performed for this sample.

(b) *Cis*-[Me$_2$C=C=CHP(O)(*μ*-*N*-*t*-Bu)]$_2$ (17a)



Yield: 1.65 g (60%).

Mp: 160-164 ^{o}C.

IR (KBr): 2971, 1960, 1750, 1373, 1260, 1225, 1088 cm^{-1}.

^{1}H NMR: δ 1.43 and 1.44 (2s, 18 H, C(CH_3)$_3$), 1.78 (m, 12 H, C=C(CH_3)$_2$), 5.25 (br m, 2 H, PC*H*).

^{13}C NMR (50 MHz): δ 18.8 (s, C=C(*C*H$_3$)$_2$), 31.1 (s, NC(*C*H$_3$)$_3$), 55.2 (s, N*C*(CH$_3$)$_3$), 83.5 (dd, ^{1}J(P-C) ~163.8 Hz, ^{3}J(P-C) = 7.3 Hz, P*C*), 97.8 (dd → t, $^{3,5}J$(P-C) ~ 8.5 Hz, C=*C*(CH$_3$)$_2$), 211.8 (s, PC=*C*) [*cf.* Fig. 24].

^{31}P NMR: δ 4.9.

Anal. Calc. for $C_{18}H_{32}N_2O_2P_2$: C, 58.4; H, 8.7; N, 7.6. Found: C, 58.4; H, 8.7; N, 7.6.

X-ray structural analysis was performed for this sample.

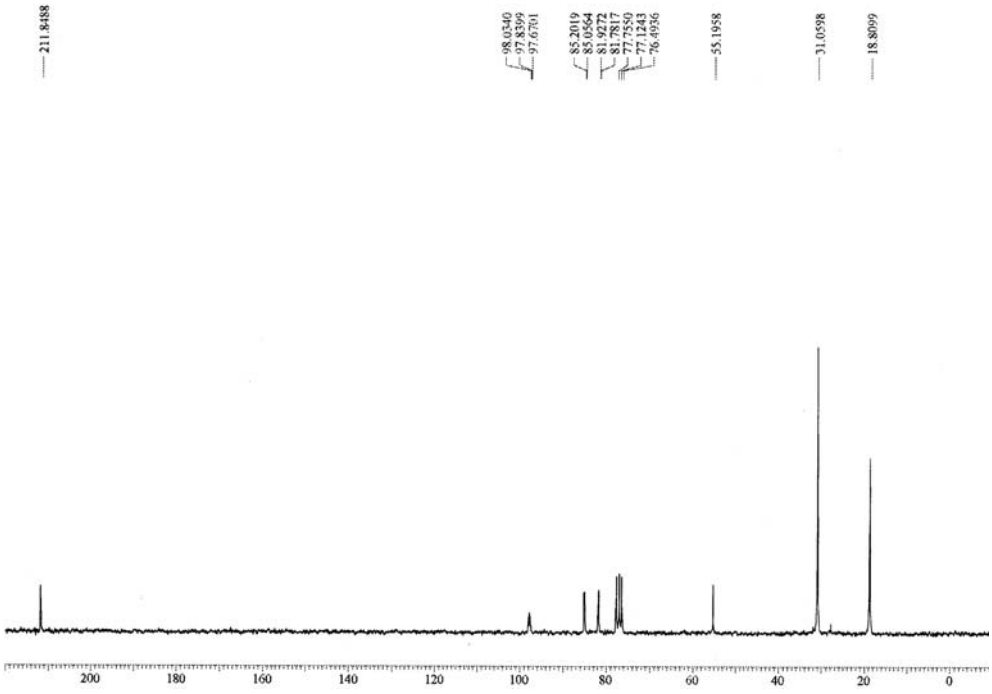
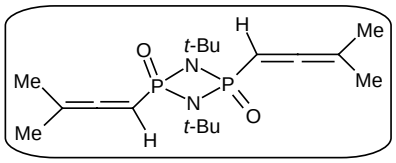


Fig. 24. ^{13}C NMR spectrum of compound **17a**

(c) *Trans*-[Me_2C=C=CHP(O)(μ-N-*t*-Bu)]$_2$ (17b)



Yield: 0.41 g (15%).

Mp: 212-216 ^{o}C.

IR (KBr): 2971, 1958, 1474, 1354, 1262, 1082, 912 cm^{-1}.

^{1}H NMR: δ 1.39, 1.41 and 1.44 (3 s, 18 H, C(CH_3)$_3$), 1.77-1.80 (m, 12 H, C=C(CH_3)$_2$), 5.46 (br, 2 H, PC*H*).

^{13}C NMR (50 MHz): δ 18.8 (s, C=C(*C*H$_3$)$_3$), 30.9 and 32.0 (2 s in 2:1 ratio, NC(*C*H$_3$)$_3$), 54.8 (s, N*C*(CH$_3$)$_3$), 85.5 (d, ^{1}J(P-C) = 156.5 Hz, P*C*), 98.0 (s, C=*C*(CH$_3$)$_2$), 212.5 (s, PC=*C*) [*cf.* Fig. 25].

^{31}P NMR: δ 9.2.

Anal. Calc. for $C_{18}H_{32}N_2O_2P_2$: C, 58.4; H, 8.7; N, 7.6. Found: C, 58.3; H, 8.7; N, 7.8.

X-ray structural analysis was performed for this sample.

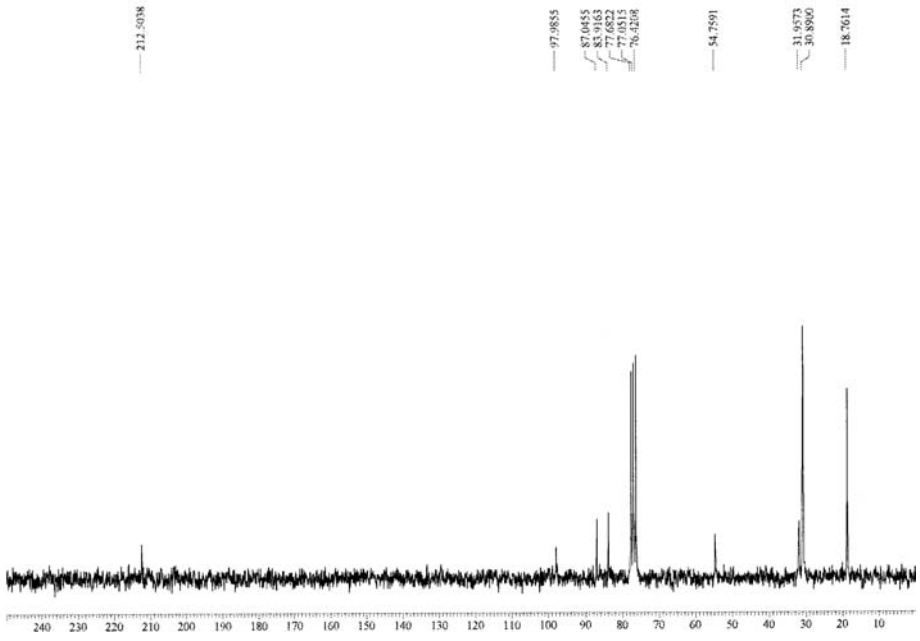
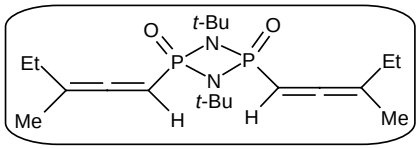


Fig. 25. ^{13}C NMR spectrum of compound **17b**

(d) *Cis*-[(Me)(Et)C=C=CHP(O)(*μ*-N-*t*-Bu)]$_2$ (18a)



Yield: 1.17 g (40%).

Mp: 148-152 ^{o}C.

IR (KBr): 2967, 1958, 1458, 1368, 1260, 1225 cm^{-1}.

^{1}H NMR: δ 1.07 (t, 6 H, ^{3}J(H-H) ~ 7.3 Hz, CH_2CH_3) 1.45 (s, 18 H, $C(CH_3)_3$), 1.76-1.79 (m, 6 H, $C{=}CCH_3$), 2.08 (br m, 4 H, CH_2CH_3), 5.29 (br, 2 H, PC*H*).

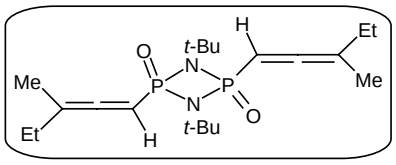
^{13}C NMR (50 MHz): δ 12.0 (s, CH_2CH_3), 17.3 (s, CH_2CH_3), 26.4 (s, $C{=}CCH_3$), 31.1 (s, $NC(CH_3)_3$), 55.2 (s, $NC(CH_3)_3$), 85.2 (dd, ^{1}J(P-C) ~ 162.6 Hz, ^{3}J(P-C) = 7.3 Hz, P*C*), 104.1 (d, ^{3}J(P-C) ~ 8.5 Hz, $C{=}C(CH_3)(Et)$), 211.8 (s, $PC{=}C$).

^{31}P NMR: δ 4.6.

Anal. Calc. for $C_{20}H_{36}N_2O_2P_2$: C, 60.3; H, 9.1; N, 7.0. Found: C, 60.3; H, 9.1; N, 7.2.

(e) *Trans*-[(Me)(Et)C=C=CHP(O)(μ-N-*t*-Bu)]$_2$ (18b)

This was crystallized from dichloromethane.



Yield: 0.44 g (15%).

Mp: 198-200 ^{o}C.

IR (KBr): 2969, 1950, 1456, 1368, 1262, 1235 cm^{-1}.

^{1}H NMR: δ 1.09 (t, 6 H, ^{3}J(H-H) ~ 7.3 Hz, CH_2CH_3), 1.43 (s, 18 H, $C(CH_3)_3$), 1.80 (s, 6 H, $C{=}CCH_3$), 2.12 (br m, 4 H, CH_2CH_3), 5.58 (br, 2 H, PC*H*).

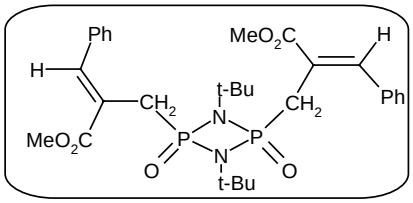
^{13}C NMR: δ 12.1 (s, CH_2CH_3), 17.2 (s, CH_2CH_3), 26.4 (s, $C{=}CH_3$), 30.9 (br s, $NC(CH_3)_3$), 53.4 and 54.7 (2 s, $NC(CH_3)_3$), 87.1 (d, ^{1}J(P-C) = 157.7 Hz, P*C*), 104.1 (s, C=*C*(Me)(Et)), 212.1 (s, PC=*C*).

^{31}P NMR: δ 9.0.

Anal. Calc. for $C_{20}H_{36}N_2O_2P_2$: C, 60.3; H, 9.1; N, 7.0. Found: C, 60.3; H, 9.2; N, 7.0.

3.8 Synthesis of *cis*-bis(allyl)cyclodiphosph(V)azane [((Ph)HC=C(CO_2Me)-CH_2)(O)P-μ-N-*t*-Bu]$_2$.H_2O (20.H_2O) [and identification of 19]

This compound was prepared by treating **4** (2.20 g, 8 mmol) in dry THF (30 mL) with the Baylis-Hillman alcohol PhCH(OH)C(CO_2Me)=CH_2[96c] (3.08 g, 16 mmol) in the presence of Et_3N (1.70 g, 16.8 mmol) at 0^{o}C. The reaction mixture was stirred for 5 h at room temperature and triethylamine hydrochloride was filtered off. In this case, we could observe the *cis*-alkoxy P^{III} product **19** *prior to rearrangement* by ^{31}P NMR [δ(P) 133.5]. The solvent was removed *in vacuo* and the reaction mixture heated at 150 ^{o}C for 20 min to afford **20** in quantitative yields [^{31}P NMR evidence]; it was purified by passing through a short silica-gel column (eluent: hexane-ethyl acetate). Crystallization (dichloromethane + hexane) in open air led to **20**.H_2O.



Yield: 4.70 g (quantitative).

Mp: 117-119 ^{o}C.

IR (KBr): 2973, 1701, 1451, 1372, 1267, 1065 cm^{-1}.

^{1}H NMR: δ 1.29 and 1.30 (2 s, 18 H, C(C*H*$_3$)$_3$), 3.64 (d, 4 H, ^{2}J(P-H) = 18.0 Hz, PC*H*$_2$), 3.85, 3.86 (2 s, 6 H, 2 OC*H*$_3$), 7.36–7.80 (m, 12 H, 2 C=C*H* + Ar-*H*). This sample showed a peak at δ ~1.67 (close to water of $CDCl_3$) in addition to the other peaks.

^{13}C NMR: δ 30.8, 30.8$_8$ and 30.9$_2$ (3 s, NC(*C*H$_3$)$_3$), 32.8 (dd, ^{1}J(P-C) = 108.4 Hz, ^{3}J(P-C) = 6.6 Hz, P*C*), 52.4 (s, COO*C*H$_3$), 56.1 (s, N*C*(CH$_3$)$_3$), 124.8 (d, ^{2}J(P-C) = 11.6 Hz, PC*C*), 128.7, 129.1, 129.6, 134.8 (Ar*C*), 141.3 (d, ^{3}J(P-C) = 12.1 Hz, C=*C*(Ph)), 168.2 (s, *C*OOCH$_3$).

^{31}P NMR: δ 20.8.

Anal. Calc. for $C_{30}H_{42}N_2O_7P_2$: C, 59.6; H, 7.0; N, 4.6. Found: C, 59.6; H, 7.0; N, 4.6.

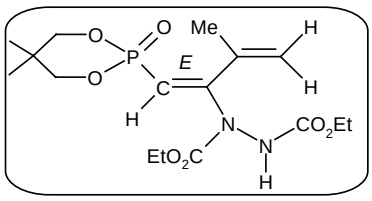
X-ray structural analysis was performed for this sample.

3.9 Reactions of allenyl phosphonates/ phosphinates/ phosphoramidates with dialkyl azodicarboxylates

3.91 *Synthesis of phosphono-trans-1,3-butadienes 24-28*

***(a) Reaction of allene 7c with DEAD: Synthesis of* (OCH$_2$CMe$_2$CH$_2$O)P(O)CH=C[N(CO$_2$Et)-NH(CO$_2$Et)]C(Me)=CH$_2$ (24)**

Allene **7c** (0.17 g, 0.77 mmol) and DEAD (0.77 mmol) were taken in 10 mL conical flask and heated in microwave reactor for 30 min [180 ^{o}C; 160W]. Compound **24** was isolated using column chromatography (EtOAc:hexane = 2:3, silica gel).



Yield: Quantitative (^{31}P NMR); isolated yield 0.19 g (64%).

Mp: 126-128 ^{o}C.

IR (KBr): 3196, 2990, 1750, 1593, 1316, 1238, 1057, 1003 cm^{-1}.

^{1}H NMR: δ 0.88 and 1.18 (2 s, 6 H, C(CH_3)$_2$), 1.28 (t, ^{2}J(H-H)= 6.4 Hz, 6 H, CH_2CH_3), 1.99 (s, 3 H, =CCH_3), 3.85–3.90 (br m, 4 H, 2 OCH_2), 4.17–4.24 (m, 4 H, OCH_2CH$_3$), 5.26 (s, 1 H, =CH_2), 5.49 (s, 1 H, =CH_2), 5.53 (d, ^{2}J(P-H) ~ 12.0 Hz, 1 H, PC*H*), 8.13 (br, 1 H, N*H*).

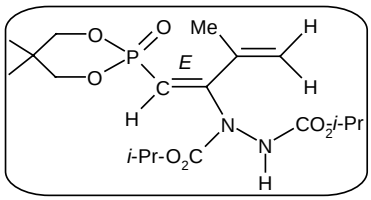
^{13}C NMR: δ 14.1and 14.4 (2 s, OCH$_2$*C*H$_3$), 20.8 and 21.7 (2 s, C(*C*H$_3$)$_2$), 32.3 (d, ^{3}J(P-C) = 6.1 Hz, *C*(CH$_3$)$_2$), 61.9 and 63.2 (2s, O*C*H$_2$CH$_3$), 76.2 (br, O*C*H$_2$C), 98.3 (d, ^{1}J(P-C) = 190.4 Hz, PC), 120.7, 139.1, 153.2, 155.4, 159.2, 159.6.

^{31}P NMR: δ 14.4.

Anal. Calc. for $C_{16}H_{27}O_7N_2P$: C, 49.22; H, 6.97; N, 7.17. Found: C, 49.29; H, 6.95; N, 7.12.

***(b) Reaction of allene 7c with DIAD: Synthesis of* (OCH$_2$CMe$_2$CH$_2$O)P(O)CH=C[N(CO$_2$*i*-Pr)-NH(CO$_2$*i*-Pr)]C(Me)=CH$_2$ (25)**

The procedure was similar to that for **24** using the allene **7c** (0.17 g, 0.77 mmol) and DIAD (0.77 mmol).



Yield: Yield >95% (MW route; ^{31}P NMR); isolated yield 0.23 g (80%)

Mp: 138–141 ^{o}C.

IR (KBr): 3150, 2976, 1736, 1595, 1541, 1472, 1279, 1107, 1057, 1005 cm^{-1}.

^{1}H NMR: δ 0.91 and 1.18 (2 s, 6 H, C(CH_3)$_2$), 1.28 (d, ^{2}J(H-H) = 1.7 Hz, 6 H, CH(CH_3)$_2$), 1.29 (d, ^{2}J(H-H) = 1.7 Hz, 6 H, CH(CH_3)$_2$), 2.00 (s, 3 H, =CCH_3), 3.84–3.96 (m, br, 4 H, 2 C*H*(CH$_3$)$_2$ + OCH_2), 4.95–4.99 (br m, 2 H, OCH_2), 5.28 (s, 1 H, =CH_2), 5.50 (s, 1 H, =CH_2), 5.61 (d, ^{2}J(P-H) = 12.4 Hz, 1 H, PC*H*), 7.38 (br, 1 H, N*H*).

^{13}C NMR(50 MHz): δ 20.9, 21.0, 21.7 and 21.9 (4 s, C(*C*H$_3$)$_2$ + CH(*C*H$_3$)$_2$), 32.3 (d, ^{3}J(P-C)= 6.1 Hz, C(*C*H$_3$)$_2$), 69.9 (s, O*C*H(CH$_3$)$_2$), 71.7 (s, O*C*H(CH$_3$)$_2$), 76.2 (br, O*C*H$_2$), 98.6 (d, ^{1}J(P-C)= 194.1 Hz, P*C*),

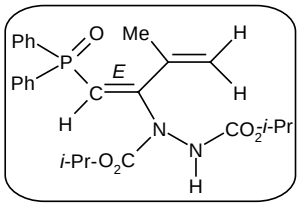
120.7, 139.3, 152.8, 155.1, 159.3, 159.7.

^{31}P NMR: δ 13.9.

Anal. Calc. for $C_{18}H_{31}O_7N_2P$: C, 51.67; H, 7.47; N, 6.69. Found: C, 51.66; H, 7.44; N, 6.64.

***(c) Reaction of allene 14b with DIAD: Synthesis of* (Ph)$_2$P(O)CH=C[N(CO$_2$*i*-Pr)-NH(CO$_2$*i*-Pr)]C(Me)=CH$_2$ (26)**

The procedure was similar to that for **24** using the allene **14b** (0.20 g, 0.75 mmol) and DIAD (0.15 g, 0.75 mmol).



Yield: 0.25 g (70%).

Mp: 170-174 ^{o}C.

IR (KBr): 3152, 2973, 1748, 1727, 1595, 1541, 1474, 1273,1211, 981 cm^{-1}.

^{1}H NMR: δ 1.28 (d, 6 H, ^{2}J(H-H) = 2.1 Hz, CH(C*H*$_3$)$_2$), 1.30 (d, 6 H, ^{2}J(H-H) = 1.9 Hz, CH(C*H*$_3$)$_2$), 1.76 (s, 3 H, =CC*H*$_3$), 5.00–5.03 (m, br, 3 H, OC*H*(CH$_3$)$_2$ + =C*H*$_2$), 5.53 (s, 1 H, =C*H*$_2$), 6.30 (d, ^{2}J(P-H) = 15.9 Hz, 1 H, PC*H*), 7.21 (br, 1 H, N*H*), 7.41–7.81 (m, 10 H, Ar-*H*).

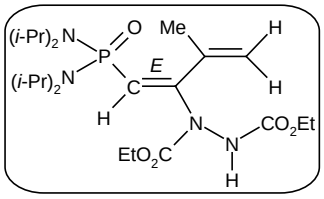
^{13}C NMR: δ 20.3 (s, C(*C*H$_3$)=CH$_2$), 21.9 and 22.0 (2s, CH(*C*H$_3$)$_2$), 70.1 and 71.6 (2s, O*C*H(CH$_3$)$_2$), 109.6 (d, ^{1}J(P-C) = 106.7 Hz, P*C*), 123.1, 128.1, 128.3, 131.1, 131.2, 134.1, 136.2, 138.7, 153.2, 155.3, 158.8.

^{31}P NMR: δ 18.9.

Anal. Calc. for $C_{25}H_{31}N_2O_5P$: C, 63.8; H, 6.6; N, 6.0. Found: C, 63.8; H, 6.6; N, 6.1.

***(d) Reaction of allene 15 with DEAD: Synthesis of* (((CH$_3$)$_2$CH)$_2$N)$_2$P(O)CH=C[N(CO$_2$Et)-NH(CO$_2$Et)]C(Me)=CH$_2$ (27)**

The procedure was similar to that for **24** using the allene **15** (0.224 g, 0.72 mmol).



Yield: 0.31 g (90%).

Mp: 150–153 ^{o}C.

IR (KBr): 3152, 2975, 1748, 1726, 1595, 1541, 1474, 1370, 1304, 1273, 1211, 982 cm^{-1}.

^{1}H NMR: δ 1.22–1.29 (m, 30 H, OCH_2CH_3 + $NCH(CH_3)_2$), 2.08 (s, 3 H, $=CCH_3$), 3.52–3.59 (br m, 4 H, $NCH(CH_3)_2$), 4.20–4.24 (br m, 4 H, OCH_2CH_3), 5.15 and 5.20 (2 s, 2 H, $=CH_2$), 5.88 (br, 1 H, PCH), 6.78 (br, 1 H, NH).

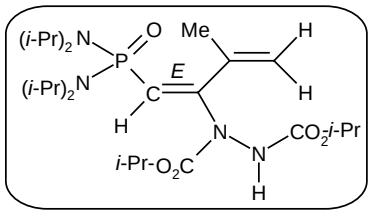
^{13}C NMR(50 MHz): δ 14.2 and 14.3 (2 s, OCH_2CH_3), 22.7 and 23.3 (2 s, $NCH(CH_3)_2$), 45.4 and 45.5 (2 s, $NCH(CH_3)_2$), 61.9 and 62.7 (2 s, OCH_2CH_3), 115.5 (d, ^{1}J(P-C) = 146.8 Hz, PC), 117.8, 140.1, 150.0, 150.3, 154.3, 156.1.

^{31}P NMR: δ 18.7.

Anal. Calc. for $C_{23}H_{45}N_4O_5P$: C, 56.54; H, 9.28; N, 11.47. Found: C, 56.50; H, 9.18; N, 11.70.

***(e) Reaction of allene 15 with DIAD: Synthesis of* (((CH$_3$)$_2$CH)$_2$N)$_2$P(O)CH=C[N(CO$_2$*i*-Pr)-NH(CO$_2$*i*-Pr)]C(Me)=CH$_2$ (28)**

The procedure was similar to that for **24** using the allene **15** (0.20 g, 0.66 mmol).



Yield: 0.29 g (90%).

Mp: 136–138 ^{o}C.

IR (KBr): 3158, 2980, 1739, 1591, 1531, 1472, 1373, 1300, 1269, 1107, 984 cm^{-1}.

^{1}H NMR: δ 1.21–1.29 (m, 36 H, $OCH(CH_3)_2$ + $NCH(CH_3)_2$), 2.10 (s, 3 H, $=CCH_3$), 3.50–3.60 (br m, 4 H, $NCH(CH_3)_2$), 4.96–5.02 (br m, 2 H, $OCH(CH_3)_2$), 5.18 (s, 2 H, $=CH_2$), 5.88 (br d, ^{2}J(P-H) = 8.5 Hz, 1 H, PCH), 6.74 (br, 1 H, NH).

^{13}C NMR: δ 21.8$_6$, 21.9$_0$, 22.8 and 23.4 (4 s, NCH(CH$_3$)$_2$ + CH(CH_3)$_2$), 45.4$_9$, 45.5$_4$ (2 s, NCH(CH$_3$)$_2$), 70.0 and 71.1 (2 s, CH(CH$_3$)$_2$), 115.4 (d, ^1J(P-C) = 146.7 Hz, PC), 117.7, 140.6, 150.3, 150.5, 154.0, 155.8

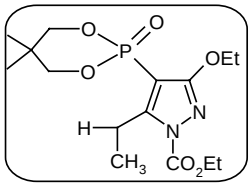
^{31}P NMR: δ 18.9.

Anal. Calc. for $C_{25}H_{49}N_4O_5P$: C, 58.12; H, 9.56 N, 10.84. Found: C, 58.02; H, 9.59; N, 10.53.

3.92 *Synthesis of phosphono-pyrazoles (31-34)*

***(a) Compound* (OCH$_2$CMe$_2$CH$_2$O)P(O)[C=C(CH$_2$CH$_3$)-N(CO$_2$Et)-N=C(OEt)-] (31)**

To a stirred solution of allenylphosphonates **7b** (0.30 g, 1.5 mmol) in anhydrous THF (10 mL) under N_2 atmosphere, DEAD (0.31 g, 0.28 mL, 1.8 mmol) was added and the reaction mixture stirred under reflux. To this, triphenylphosphine (0.47 g, 1.8 mmol) in THF (10 mL) was added through addition funnel in three portions. The reaction mixture was kept stirring under reflux for 24 h, cooled, solvent removed on a rotary evaporator, and the residue was column chromatographed on silica gel using 15% ethyl acetate-hexane to obtain **31**.



Yield: 0.32 g (60%).

Mp: 100–102 ^{o}C.

IR (KBr): 2984, 2936, 1752, 1566, 1509, 1439, 1385, 1314, 1249, 1179, 1053, 995 cm^{-1}.

^{1}H NMR: δ 1.12, 1.15 (2 s, 6 H, C(CH_3)$_2$), 1.25 (t, ^2J(H-H) ~ 7.4 Hz, 3 H, =CCH$_2$CH_3), 1.39–1.46 (m, 6 H, OCH$_2$CH_3), 3.31 (q, 2 H, ^2J (H-H) = 7.2 Hz, =CCH_2CH$_3$), 4.01 (t, ^3J(H-H) = 11.2 Hz, 2 H, OCH_2), 4.17 (t, ^3J(H-H) = 10.8 Hz, 2 H, OCH_2), 4.38 (q, ^2J(H-H) ~ 7.2 Hz, 2 H, OCH_2CH$_3$), 4.48 (q, ^2J(H-H) ~ 7.2 Hz, 2 H, OCH_2CH$_3$).

^{13}C NMR: δ 13.8, 14.1 and 14.5 (3 s, CH$_2$$CH_3$ + OCH$_2$$CH_3$), 20.4, 21.5 and 21.9 (3 s, C(CH$_3$)$_2$ + =CCH$_2$CH$_3$), 32.5 (d, ^3J(P-C) = 6.5 Hz, C(CH$_3$)$_2$), 64.1 and 65.3 (2 s, OCH$_2$CH$_3$), 75.8 and 75.9 (2 s,OCH$_2$), 96.8 (d,

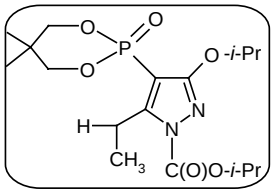
^{1}J(P-C) = 217.2 Hz, P*C*), 149.4 (s, PC*C*O), 160.0 (d, ^{2}J(P-C) = 26.0 Hz, PC*C*), 163.1, 163.2.

^{31}P NMR: δ 5.6.

Anal. Calc. for $C_{15}H_{25}N_2O_6P$: C, 50.00; H, 6.99; N, 7.77. Found: C, 50.11; H, 7.03; N, 7.81.

***(b) Compound* (OCH$_2$CMe$_2$CH$_2$O)P(O)[C=C(CH$_2$CH$_3$)-N(CO$_2$*i*-Pr)-N=C(O*i*-Pr)-] (32)**

In a procedure similar to that for **31**, allenylphosphonate **7b** (1.15 g, 5.7 mmol), DIAD (1.38 g, 1.35 mL, 6.8 mmol) and triphenylphosphine (1.79 g, 6.8 mmol) were used. Compound **32** was purified by column chromatography using ethyl acetate-hexane (1:3) as eluent.



Yield: 1.54 g (70%).

Mp: 62-64 ^{o}C.

IR (KBr): 2976, 1750, 1561, 1509, 1373, 1306, 1231, 1183, 1107, 1049, 995 cm^{-1}.

^{1}H NMR: δ 1.09 and 1.19 (2 s, 6 H, C(C*H*$_3$)$_2$), 1.23–1.45 (m, 15 H, OCH(C*H*$_3$)$_2$ + CH$_2$C*H*$_3$), 3.29 (br q, ^{2}J(H-H) ~ 7.0 Hz, 2 H, =CCH$_2$C*H*$_3$), 4.03–4.16 (m, 4 H, OC*H*$_2$), 5.13 and 5.23 (2 m, 2 H, OC*H*(CH$_3$)$_2$).

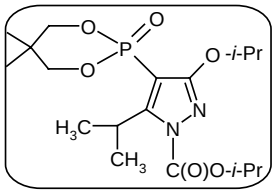
^{13}C NMR: δ 13.9 (s, CH$_2$*C*H$_3$), 20.6, 21.5, 21.7 and 22.0 (4 s, C(*C*H$_3$)$_2$ + OCH(*C*H$_3$)$_2$ + COOCH(*C*H$_3$)$_2$ + *C*H$_2$CH$_3$), 32.5 (d, ^{3}J(P-C) = 6.6 Hz, *C*(CH$_3$)$_2$), 72.8 and 73.0 (2 s, O*C*H(CH$_3$)$_2$), 75.9 and 76.0 (2 s,O*C*H$_2$), 98.2 (d, ^{1}J(P-C) = 216.2 Hz, P*C*), 148.9 (s, PC*C*O), 159.2 (d, ^{2}J(P-C) = 26.1 Hz, PC*C*), 162.3, 162.4.

^{31}P NMR: δ 6.3.

Anal. Calc. for $C_{17}H_{29}N_2O_6P$: C, 52.57; H, 7.52; N, 7.21. Found: C, 52.64; H, 7.54; N, 7.17.

(c) Compounds **($OCH_2CMe_2CH_2O$)P(O)[C=C($CH(CH_3)_2$)-N(CO_2*i*-Pr)-N=C(O*i*-Pr)-] (33) and ($OCH_2CMe_2CH_2O$)P(O)[C=C($CH(CH_3)_2$)-N(H)-N=C(O*i*-Pr)-] (34)**

In a procedure similar to that for **31**, allenylphosphonate **7c** (0.82 g, 3.8 mmol), DIAD (0.92 g, 0.90 mL, 4.5 mmol) and triphenylphosphine (1.20 g, 4.5 mmol) were used. Column chromatography afforded **33** (ethyl acetate-hexane 1:3), followed by **34** (ethyl acetate-hexane 1:1). Crystals of **33** and **34** were obtained from dichloromethane-hexane mixture.



Yield: 0.76 g (50%).

Mp: 72–76 ^{o}C.

IR (KBr): 2976, 2880, 1752, 1566, 1472, 1431, 1375, 1316, 1244, 1183, 1105, 1049, 993 cm^{-1}.

^{1}H NMR: δ 1.02 and 1.23 (2 s, 6 H, C(CH_3)$_2$), 1.37–1.46 (m, 18 H, =CCH(CH_3)$_2$ + OCH(CH_3)$_2$ + COOCH(CH_3)$_2$), 4.00–4.15 (m, 5 H, OCH_2 + =C*CH*), 5.09-5.12 (m, 1 H, O*CH*(CH_3)$_2$), 5.18–5.21 (m, 1 H, COO*CH*(CH_3)$_2$).

^{13}C NMR: δ 19.5, 21.4, 21.7, 22.0 and 22.1 (5s, C(CH_3)$_2$ + CH(CH_3)$_2$ + OCH(CH_3)$_2$ + COOCH(CH_3)$_2$), 27.0 (s, *C*H(CH_3)$_2$), 32.5 (d, ^{3}J(P-C) ~ 7.0 Hz, *C*(CH_3)$_2$), 72.5, 73.1, 76.1 and 76.2 (4s, O*C*H(CH_3)$_2$ + COO*C*H(CH_3)$_2$, 2 O*C*H$_2$), 97.0 (d, ^{1}J(P-C) ~ 213.0 Hz, P*C*), 149.3 (s, PC*C*O), 161.9, 162.1, 162.2 [*cf.* Fig. 26].

^{31}P NMR: δ 6.7.

Anal. Calc. for $C_{18}H_{31}N_2O_6P$: C, 53.72; H, 7.76; N, 6.96. Found: C, 53.70; H, 7.75; N, 6.92.

X-ray structure was determined for this compound.

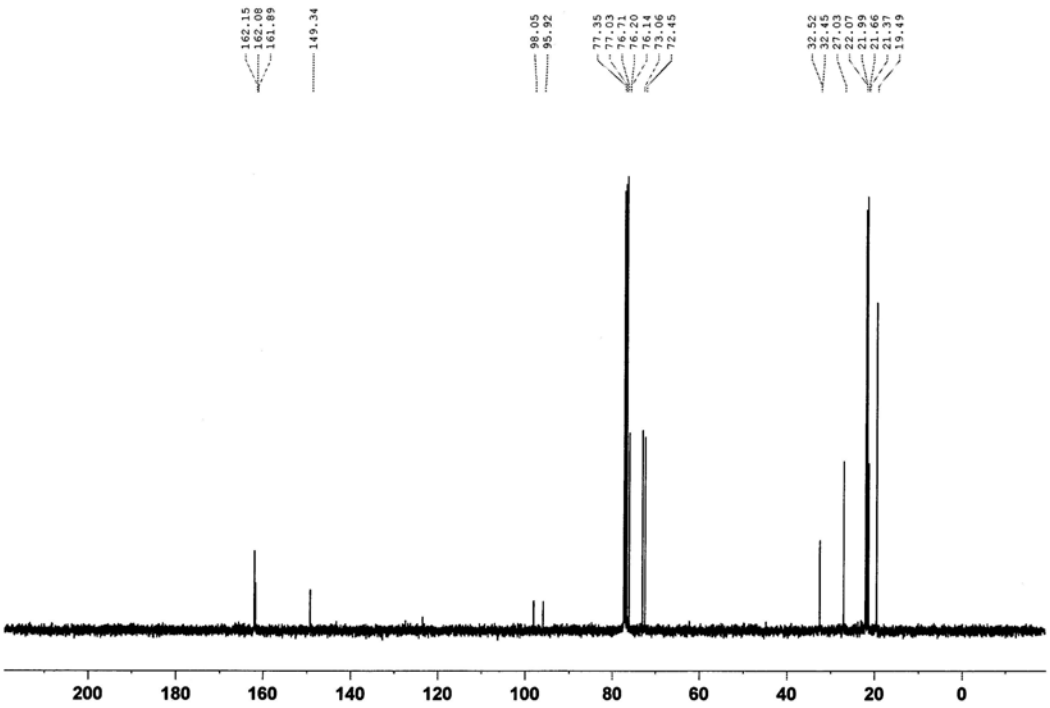
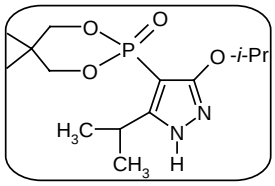


Fig. 26. ^{13}C NMR spectrum of compound **33**

(d) (OCH$_2$CMe$_2$CH$_2$O)P(O)[C=C(CH(CH$_3$)$_2$)-N(H)-N=C(O*i*-Pr)-] (34)



Yield: 0.24 g (20 %).

Mp: 216–218 ^{o}C.

IR (KBr): 3181, 3088, 3046, 1557, 1510, 1470, 1327, 1227, 1186, 1129, 1053, 1003 cm^{-1}.

^{1}H NMR: δ 1.10 and 1.21 (2 s, 6 H, C(C*H*$_3$)$_2$), 1.31 (d, ^{2}J(H-H) = 7.0 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.37 (d, ^{2}J(H-H) = 6.1 Hz, 6 H, OCH(C*H*$_3$)$_2$), 3.66–3.69 (br m, 1 H, C*H*(CH$_3$)$_2$), 4.00 (t, ^{3}J(H-H) = 12.6 Hz, 2 H, OC*H*$_2$), 4.23 (t, ^{3}J(H-H) = 10.5 Hz, 2 H, OC*H*$_2$), 4.94–4.98 (br m, 1 H, OC*H*(CH$_3$)$_2$), 10.18 (br, 1 H, N*H*).

^{13}C NMR: δ 21.8 and 22.2 (2 s, C(*C*H$_3$)$_2$ + OCH(*C*H$_3$)$_2$ + =CCH(*C*H$_3$)$_2$), 25.6 (s, =C*C*H(CH$_3$)$_2$, 32.6 (s, C*C*(CH$_3$)$_2$), 71.9 (s, O*C*H(CH$_3$)$_2$), 75.3 and

75.4 (2s,O*C*H_2), 87.1 (d, ^1J(P-C) = 226.8 Hz, P*C*), 158.1 (d, ^2J(P-C) = 26.7 Hz, PC*C*O), 163.6 (d, ^2J(P-C) = 8.5 Hz, PC*C*).

^{31}P NMR: δ 10.7.

Anal. Calc. for $C_{14}H_{25}N_2O_4P$: C, 53.16; H, 7.97; N, 8.86. Found: C, 53.26; H, 8.09; N, 8.88.

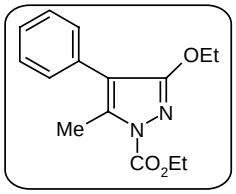
X-ray structure was determined for this compound.

3.93 *Synthesis of the intermediate 35, the byproduct 36.H_2O and pyrazoles 37-42*

Compounds **35** and **36** were obtained along with **38** and details on these are given together.

(a) Tetra-substituted pyrazole **[C(Ph)=C(CH_3)-N(CO_2Et)-N=C(OEt)-] (37)**

In a procedure similar to that for **31**, allenylphosphonate **7e** (0.40 g, 1.6 mmol), DEAD (0.33 g, 0.30 mL, 1.9 mmol) and triphenylphosphine (0.50 g, 1.9 mmol) were used. The residue was taken in THF (5 mL) and treated with 6 N HCl (5 mL) for 24 h. Extraction with diethyl ether and purification by column chromatography (ethyl acetate-hexane 2:98) gave **37**.



Yield: 0.31 g (70%).

Mp: 61–63 °C.

IR (KBr): 2981, 1958, 1898, 1761, 1613, 1593, 1522, 1373, 1325, 1258, 1181, 1063, 1003 cm^{-1}.

^{1}H NMR: δ 1.40 and 1.48 (2 t, ^3J(H-H) = 7.1 Hz, 6 H, OCH_2CH_3), 2.59 (s, 3 H, NCCH_3), 4.42 and 4.51 (2 q, ^3J(H-H) ~ 7.1 Hz, 4 H, OCH_2CH_3), 7.34–7.46 (m, 5 H, Ar-*H*).

^{13}C NMR: δ 13.5 (s, NC*C*H_3), 14.4 and14.6 (2 s, OCH_2*C*H_3), 63.7 and 64.8 (2 s, O*C*H_2CH$_3$), 112.9 (s, NC=*C*Ph), 127.1, 128.4, 129.5, 130.4, 141.9 (s, N=*C*OEt), 150.7 (s, N*C*=CPh), 162.2 (s, *C*OO) [*cf.* Fig. 27].

Anal. Calc. for $C_{15}H_{18}N_2O_3$: C, 65.68; H, 6.61; N, 10.21. Found: C, 65.64; H, 6.65; N, 10.63.

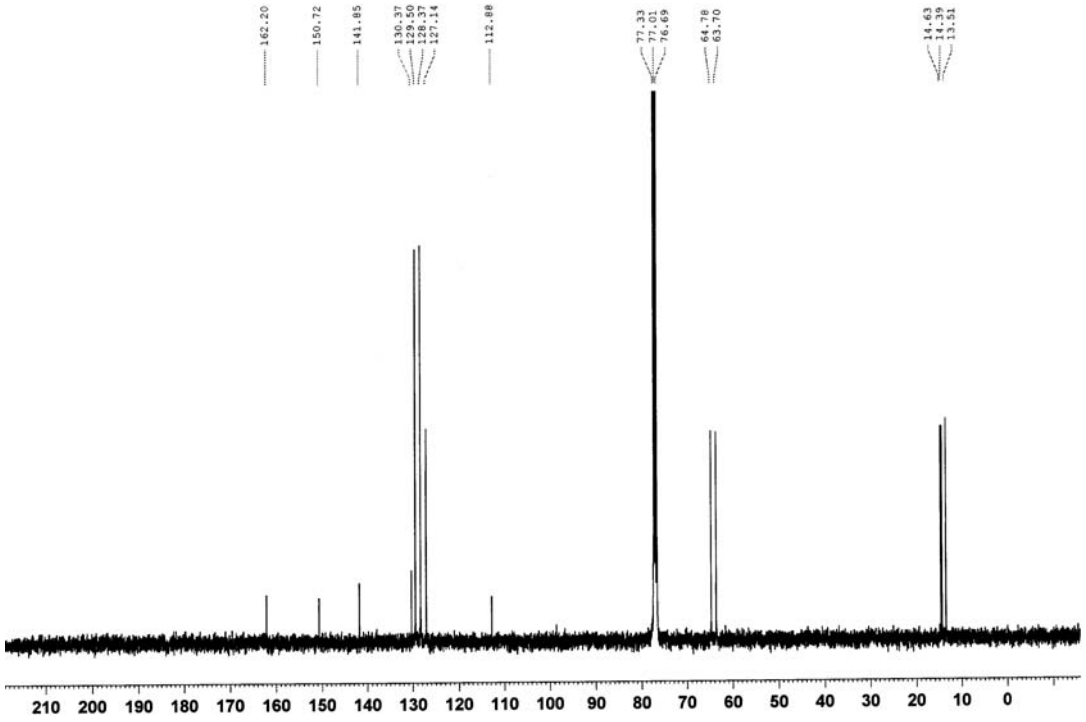


Fig. 27. ^{13}C NMR spectrum for compound **37**

***(b) Compounds* 35, 36.**H_2O ***and the pyrazole* 38**

In a procedure similar to that for **37**, allenylphosphonate **7e** (1.52 g, 6.0 mmol), DIAD (1.46 g, 1.43 mL, 7.2 mmol) and triphenylphosphine (1.90 g, 7.2 mmol) were used. Simple crystallization of **35** in air afforded **38** after separation of the phosphate $(OCH_2CMe_2CH_2O)P(O)OH$ (**36.**H_2O) (less soluble).[12] In a separate experiment, the intermediate phosphonate $(OCH_2CMe_2CH_2O)P(O)CH(Ph)$[C-N($CO_2$*i*-Pr)-N=C(O*i*-Pr)-CH=] (**35**; >93% purity, the rest was **7e**) could be identified prior to hydrolysis but after separation of $Ph_3P(O)$ and Ph_3P. Compound **38** could also be readily obtained by treating the reaction mixture with 6 N HCl.

$(OCH_2CMe_2CH_2O)P(O)CH(Ph)$[C-N($CO_2$*i*-Pr)-N=C(O*i*-Pr)-CH=] (35)

^{1}H NMR: δ 0.99 and 1.17 (2 s, 6 H, C(CH_3)$_2$), 1.26–1.42 (m, 12 H, OCH(CH_3)$_2$), 3.97–4.25 (m, 4 H, OCH_2), 5.02 (d, ^2J(P-H) ~ 6.0 Hz, 1 H, PC*H*), 5.09–5.19 (m, 2 H, OC*H*(CH_3)$_2$), 5.89 (br, 1 H, =C*H*), 7.28–7.69 (m, 5 H, Ar-*H*).

^{31}P NMR: δ 9.5.

This compound was not hydrolytically stable.

$(OCH_2CMe_2CH_2O)P(O)(OH).(H_2O)$ (36.H_2O)

Mp: 150-153 ^oC.

IR (KBr): 3343, 2976, 1738, 1611, 1377, 1088, 851, 777 cm^{-1}.

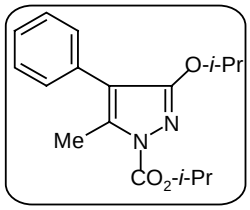
^1H NMR: δ 1.08 (s, 6 H, $C(CH_3)_2$), 4.04 and 4.07 (2s, 4 H, OCH_2), 5.02 (s, 3 H, $POH + H_2O$).

^{31}P NMR: δ -4.3.[118]

Anal. Calc. for $C_5H_{13}O_5P$: C, 32.6; H, 7.1. Found: C, 32.5; H, 7.2.

X-ray structure was determined for this compound.

[C(Ph)=C(CH_3)-N(CO_2-*i*-Pr)-N=C(O-*i*-Pr)-] (38)



Yield: 1.12 g (62%).

Mp: 61-63 ^oC.

IR (KBr): 2984, 1738, 1611, 1591, 1512, 1375, 1314, 1264, 1181, 1109, 1088, 918 cm^{-1}.

^1H NMR: δ 1.38 and 1.46 (2 d, ^2J(H-H) = 6.0 Hz, 12 H, $OCH(CH_3)_2$), 2.55 (s, 3 H, $NCCH_3$), 5.16-5.19 and 5.22-5.26 (m, 2 H, $OCH(CH_3)_2$), 7.33–7.45 (m, 5 H, Ar-*H*).

^{13}C NMR: δ 13.7 (s, $NCCH_3$), 21.9 and 22.1 (2s, $OCH(CH_3)_2$ + $COOCH(CH_3)_2$), 71.8 and 71.9 (2s, $OCH(CH_3)_2$ + $COOCH(CH_3)_2$), 113.2, 127.0, 128.3, 129.6, 130.7, 141.2, 150.3, 161.4 (s, *C*OO).

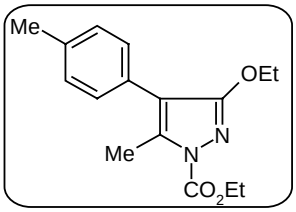
Anal. Calc. for $C_{17}H_{22}N_2O_3$: C, 67.53; H, 7.33; N, 9.26. Found: C, 67.51; H, 7.30; N, 9.20.

X-ray structure was determined for this compound.

***(c) Pyrazole* [C(4-CH_3-C_6H_4)=C(CH_3)-N(CO_2Et)-N=C(OEt)-] (39)**

In a procedure similar to that for **37**, allenylphosphonate **7f** (0.46 g, 1.7 mmol), DEAD (0.39 g, 0.35 mL, 2.3 mmol) and triphenylphosphine (0.59 g, 2.3

mmol) were used. Extraction with diethyl ether and purification by column chromatography (ethyl acetate-hexane 2:98) readily gave **39**.



Yield: 0.34 g (68%).

Mp: 67-69 °C.

IR (KBr): 2984, 2919, 1749, 1603, 1526, 1379, 1344, 1265, 1096, 899 cm^{-1}.

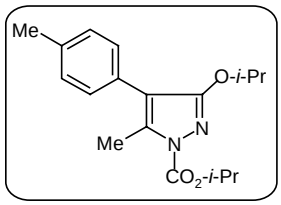
^1H NMR: δ 1.37 and 1.45 (2 t, ^3J(H-H) = 7.2 Hz, 6 H, OCH_2CH_3), 2.38 (s, 3 H, $ArCH_3$), 2.55 (s, 3 H, $NCCH_3$), 4.38 and 4.47 (2 q, ^3J(H-H) ~ 7.2 Hz, 4 H, OCH_2CH_3), 7.21–7.28 (m, 4 H, Ar-*H*).

^{13}C NMR: δ 13.5 (s, $NCCH_3$), 14.4 and 14.6 (2 s, OCH_2CH_3), 21.2 (s, $ArCH_3$), 63.7 and 64.7 (2 s, OCH_2CH_3), 112.8, 127.3, 129.1, 129.4, 136.9, 141.6, 150.7, 162.3 (s, *C*OO).

Anal. Calc. for $C_{16}H_{20}N_2O_3$: C, 66.65; H, 6.99; N, 9.72. Found: C, 66.59; H, 6.94; N, 9.79.

***(d) Pyrazole* [C(4-CH_3-C_6H_4)=C(CH_3)-N(CO_2-*i*-Pr)-N=C(O-*i*-Pr)-] (40)**

In a procedure similar to that for **37**, allenylphosphonate **7f** (0.72 g, 2.6 mmol), DIAD (0.71 g, 0.35 mL, 3.5 mmol) and triphenylphosphine (0.91 g, 3.5 mmol) were used.



Yield: 0.53 g (62%).

Mp: 57-59 °C.

IR (KBr): 2978, 1738, 1607, 1503, 1455, 1379, 1327, 1264, 1200, 1084, 920 cm^{-1}.

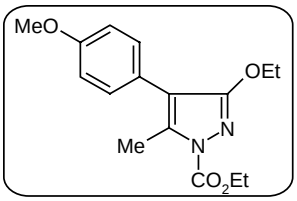
^1H NMR: δ 1.35 and 1.44 (2 d, ^2J(H-H) = 6.2 Hz, 12 H, $OCH(CH_3)_2$), 2.38(s, 3 H, $ArCH_3$), 2.52 (s, 3 H, $NCCH_3$), 5.14-5.18 and 5.20-5.25 (2 m, 2 H, $OCH(CH_3)_2$), 7.20–7.27 (m, 4 H, Ar-*H*).

^{13}C NMR: δ 13.7 (s, NC*C*H$_3$), 21.3 and 22.0 (2 s, OCH(*C*H$_3$)$_2$ + COOCH(*C*H$_3$)$_2$), 22.1 (Ar*C*H$_3$), 71.8 (br s, O*C*H(CH$_3$)$_2$ + COO*C*H(CH$_3$)$_2$), 113.3, 127.7, 129.1, 129.5, 136.8, 141.0, 150.4, 161.5 (s, *C*OO).

Anal. Calc. for $C_{18}H_{24}N_2O_3$: C, 68.33; H, 7.65; N, 8.85. Found: C, 68.22; H, 7.62; N, 8.82.

***(e) Pyrazole* [C(4-OCH$_3$-C$_6$H$_4$)=C(CH$_3$)-N(CO$_2$Et)-N=C(OEt)-] (41)**

In a procedure similar to that for **37**, allenylphosphonate **7g** (0.33 g, 1.1 mmol), DEAD (0.25 g, 0.23 mL, 1.4 mmol) and triphenylphosphine (0.38 g, 1.4 mmol) were used. Extraction with diethyl ether and purification by column chromatography (ethyl acetate-hexane) readily gave **41**.



Yield: 0.22 g (66%).

Mp: 58-60 ^{o}C.

IR (KBr): 2982, 2935, 1755, 1597, 1528, 1373, 1323, 1258, 1098, 1005 cm^{-1}.

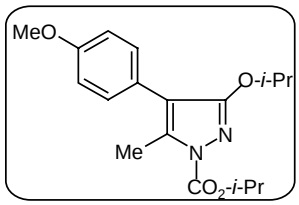
^{1}H NMR: δ 1.38, 1.45 (2 t, ^{3}J(H-H) ~ 7.0 Hz, 6 H, OCH$_2$C*H*$_3$), 2.55 (s, 3 H, NCC*H*$_3$), 3.83 (s, 3 H, OC*H*$_3$), 4.39 and 4.47 (2 q, ^{3}J(H-H) ~ 7.0 Hz, 4 H, OC*H*$_2$CH$_3$), 6.94–7.31 (m, 4 H, Ar-*H*).

^{13}C NMR: δ 13.6 (s, NC*C*H$_3$), 14.5 and 14.7 (2 s, OCH$_2$*C*H$_3$), 55.4 (s, OC*H*$_3$), 63.7 and 64.8 (2 s, O*C*H$_2$CH$_3$), 112.7, 114.0, 122.7, 130.7, 141.5, 150.8, 158.9, 162.4 (s, *C*OO).

Anal. Calc. for $C_{16}H_{20}N_2O_4$: C, 63.14; H, 6.62; N, 9.20. Found: C, 63.25; H, 6.52; N, 9.38.

***(f) Pyrazole* [C(4-OCH$_3$-C$_6$H$_4$)=C(CH$_3$)-N(CO$_2$-*i*-Pr)-N=C(O-*i*-Pr)-] (42)**

In a procedure similar to that for **37**, allenylphosphonate **7g** (0.32 g, 1.1 mmol), DIAD (0.29 g, 0.28 mL, 1.4 mmol) and triphenylphosphine (0.37 g, 1.4 mmol) were used.



Yield: 0.24 g (65%).

Mp: 59-62 ^{o}C.

IR (KBr): 2980, 2936, 1734, 1599, 1503, 1455, 1378, 1321, 1262, 1090, 922 cm^{-1}.

^{1}H NMR: δ 1.35 and 1.44 (2 d, ^{2}J(H-H) = 4.0 Hz, 12 H, OCH(CH_3)$_2$), 2.50 (s, 3 H, NCCH_3), 3.84 (s, 3 H, OCH_3), 5.13-5.17 and 5.18-5.23 (2 m, 2 H, OCH(CH_3)$_2$), 6.94–7.30 (m, 4 H, Ar-*H*).

^{13}C NMR: δ 13.7 (s, NCCH_3), 21.9 and 22.1 (2 s, OCH(CH_3)$_2$ + COOCH(CH_3)$_2$), 55.3 (s, OCH_3), 71.7 and 71.8 (2 s, OCH(CH$_3$)$_2$ + COOCH(CH$_3$)$_2$), 112.9, 113.8, 123.0, 129.7, 130.7, 140.7, 150.3, 150.4, 158.6, 161.5 (s, *C*OO).

Anal. Calc. for $C_{18}H_{24}N_2O_4$: C, 65.04; H, 7.28; N, 8.43. Found: C, 65.01; H, 7.26; N, 8.65.

(g) Compounds 51-52 (Note: compounds 43-50 are proposed intermediates in the mechanistic picture)

Compounds **51** and **52** were formed along with pyrazoles **37-42** in the reaction of allenylphosphonates **7e-g** with DEAD or DIAD. We isolated **51-52** in the reactions using **7g.**

Ph_3P=NCO_2Et (51)

Yield: 0.037 g (10%).

Mp: 133-136 ^{o}C. [lit. 134-136 ^{o}C[117a]]

IR (KBr): 3058, 2982, 1734, 1632, 1485, 1437, 1366, 1265, 1093, 884 cm^{-1}.

^{1}H NMR: δ 1.24 (t, 3 H, ^{2}J(H-H) = 6.9 Hz, CH_2CH_3), 4.07 (q, 2 H, ^{2}J(H-H) ~ 7.0 Hz, OCH_2CH$_3$), 7.48–7.81 (m, 15 H, Ar-*H*).

^{13}C NMR: δ 14.7 (s, OCH$_2$CH_3), 61.2 (d, ^{4}J(P-C) = 3.3 Hz, OCH_2CH$_3$), 127.7, 128.5, 128.7, 132.3$_0$,132.3$_1$, 133.1, and 133.2 (Ar*C*), 162.3 (s, *C*OO)

^{31}P NMR: δ 21.2.

Anal. Calc. for $C_{21}H_{20}NO_2P$: C, 72.2; H, 5.8; N, 4.0. Found: C, 72.3; H, 5.8; N, 4.0.

$Ph_3P{=}NCO_2$-i-Pr (52)

Yield: 0.047 g (12%).

Mp: 102-110 ^oC. [lit. 34-35 ^oC[117b]]

IR (KBr): 3457, 2976, 2926, 1734, 1618, 1437, 1364, 1269, 1113, 895 cm^{-1}.

^1H NMR: δ 1.19 and 1.20 (2s, 6 H, $OCH(CH_3)_2$), 4.82 (m, 1 H, $OCH(CH_3)_2$), 7.45–7.80 (m, 15 H, Ar-*H*).

^{13}C NMR: δ 22.2 (s, $OCH(CH_3)_2$), 67.9 (s, $OCH(CH_3)_2$), 128.4, 128.7, 132.2, 133.0 and 133.2 (Ar*C*), 161.7 (s, *C*OO).

^{31}P NMR: δ 21.2.

Anal. Calc. for $C_{22}H_{22}NO_2P$: C, 72.7; H, 6.1; N, 3.9. Found: C, 72.9; H, 6.1; N, 3.8.

X-ray structure was determined for this compound.

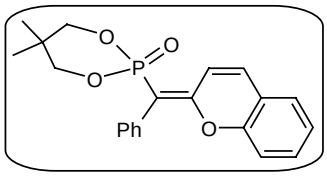
3.10 Reactions of allenylphosphonates with salicylaldehydes

(a) Reaction of allenylphosphonate 7e with salicylaldehydes and 2-hydroxy aceto/benzophenone- Synthesis of phosphono-chromenes 54-60 and chromenols 61-62 (Note: Compounds 53a-b are salicylaldehydes)

To a solution of allenylphosphonate **7e** (0.422 g, 1.67 mmol) and salicylaldehyde (2.51 mmol) in DMSO (4 mL) was added a 10% solution of DBU in DMSO (0.5 mL, corresponds to 0.05 g of DBU, 0.33 mmol), and the mixture heated at 80 ^oC for 6-9 h. The contents were washed with water (2 x 10 mL) and extracted with DCM (dichloromethane) (2 x 25 mL). The solvent was removed and the products were isolated by column chromatography using ethyl acetate and hexane mixture (2:3). In all cases except **59**, we separated the *E* and *Z* isomers. Use of K_2CO_3 also gave excellent yields based on the ^{31}P NMR of reaction mixture; however, we faced difficulties in extracting the compound and hence DBU was used in subsequent reactions.

Compound 54

(i) *E*- isomer



Yield (*E*+*Z*): 0.56 g (91%).

Mp: 160–161 ^{o}C.

IR (KBr): 2967, 2888, 1630, 1568, 1545, 1453, 1406, 1264, 1229, 1055, 1003 cm^{-1}.

^{1}H NMR: δ 0.64 and 0.93 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.55-3.62 (m, 2 H, OC*H*$_2$), 4.08-4.13 (m, 2 H, OC*H*$_2$), 6.74 (d, ^{3}*J*(H-H) = 7.8 Hz, 1 H, Ar-*H*), 6.94 (d, ^{3}*J*(H-H) = 9.8 Hz, 1 H, (Ph)C=C-C=C*H*), 7.03-7.38 (m, 8 H, Ar-*H*), 7.90 (d, ^{3}*J*(H-H) = 9.8 Hz, 1 H, (Ph)C=C-C*H*=).

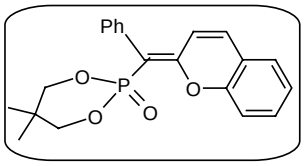
^{13}C NMR: δ 21.2 and 21.7 (2 s, C(*C*H$_3$)$_2$), 32.3 (d, ^{3}*J*(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 75.1$_6$ and 75.2$_2$ (2 s, O*C*H$_2$), 100.4 (d, ^{1}*J*(P-C) = 202.0 Hz, P*C*), 115.8, 119.8, 120.4, 123.6, 126.9, 127.1, 128.1, 130.3, 130.4, 131.0$_8$ 131.1$_3$, 134.3, 134.4, 152.9, 159.7 (d, ^{2}*J*(P-C) = 34.0 Hz, PC(Ph)=*C*).

^{31}P NMR: δ 15.3.

LC-MS: *m/z* 369 $[M+1]^{+}$

Anal. Calc. for $C_{21}H_{21}O_4P$: C, 68.47; H, 5.75. Found: C, 68.44; H, 5.74.

(ii) *Z*-isomer



Yield (*E*+*Z*): 0.56 g (91%).

Mp: 155–157 ^{o}C.

IR (KBr): 3058, 2963, 1719, 1628, 1572, 1549, 1453, 1402, 1244, 1059, 1007 cm^{-1}.

^{1}H NMR: δ 0.76 and 1.16 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.68-3.86 (m, 4 H, OC*H*$_2$), 6.25 (dd, ^{3}*J*(H-H) = 9.9 Hz, ^{4}*J*(P-H) = 1.2 Hz, 1 H, (Ph)C=C-C*H*), 6.72 (dd, ^{3}*J*(H-H) = 9.9 Hz, ^{5}*J*(P-H) = 3.2 Hz, 1 H, (Ph)C=C-C=C*H*), 7.00-7.35 (m, 9 H, Ar-*H*).

^{13}C NMR: δ 21.0 and 22.0 (2 s, C(*C*H$_3$)$_2$), 32.2 (d, ^{3}*J*(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 75.8 and 75.9 (2 s, O*C*H$_2$), 100.7 (d, ^{1}*J*(P-C) = 180.0 Hz, P*C*), 116.1, 118.4, 118.6, 120.0, 123.5, 127.0, 127.5, 128.7, 130.6, 130.8, 131.0, 131.1, 134.2$_5$, 134.2$_9$, 152.9, 158.7 (PC(Ph) = *C*).

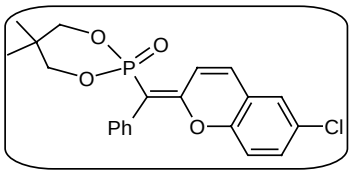
^{31}P NMR: δ 12.2.

LC-MS: *m/z* 369 $[M+1]^{+}$.

Anal. Calc. for $C_{21}H_{21}O_4P$: C, 68.47; H, 5.75. Found: C, 68.48; H, 5.67.

Compound 55

(i) *E*- isomer



Yield (*E*+*Z*): 0.47 g (70%).

Mp: 201–203 ^{o}C.

IR (KBr): 3108, 2965, 2886, 1782, 1634, 1570, 1476, 1428, 1285, 1223, 1049, 997 cm^{-1}.

^{1}H NMR: δ 0.63 and 0.92 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.55-3.61 and 4.01-4.14 (2 m, 4 H, OC*H*$_2$), 6.67 (d,^{3}*J*(H-H) = 8.7 Hz, 1 H, Ar-*H*), 6.85 (d, ^{3}*J*(H-H) = 10.2 Hz, (Ph)C=C-C=C*H*), 7.10-7.40 (m, 7 H, Ar-*H*), 7.97 (d, ^{3}*J*(H-H) = 10.2 Hz, (Ph)C=C-C*H*=).

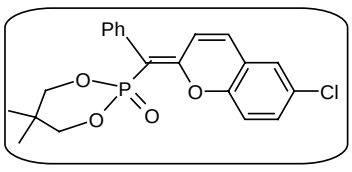
^{13}C NMR: δ 21.1 and 21.6 (2 s, C(*C*H$_3$)$_2$), 32.2 (d, ^{3}*J*(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 75.1$_6$ and 75.2$_2$ (2 s, O*C*H$_2$), 101.9 (d, ^{1}*J*(P-C) = 201.5 Hz, P*C*), 117.1, 120.9$_7$, 121.0, 121.6, 126.2, 127.1$_9$, 127.2, 128.1, 128.5, 128.8, 129.0, 129.3, 129.9, 130.8$_7$, 130.9, 151.3, 159.0 (d, ^{2}*J*(P-C) = 34.8 Hz, PC(Ph)=*C*).

^{31}P NMR: δ 12.6.

LC-MS: *m/z* 403 [M]$^{+}$, 405 [M+2]$^{+}$.

Anal. Calc. for $C_{21}H_{20}O_4PCl$: C, 62.62; H, 5.00. Found: C, 62.59; H, 5.08.

(ii) *Z*-isomer (isomer purity 95%)



Yield (*E*+*Z*): 0.47 g(70%).

Mp: 172–174 ^{o}C.

IR (KBr): 3057, 2957, 2888, 1626, 1572, 1480, 1426, 1244, 1213, 1057, 1009 cm^{-1}.

^{1}H NMR: δ 0.79 and 1.18 (2 s, 6 H, C(CH_3)$_2$), 3.68-3.92 (m, 4 H, OCH_2), 6.32 (dd, ^{3}J(H-H) = 9.9 Hz, ^{4}J(P-H) = 1.7 Hz, 1 H, (Ph)C=C-C*H*=), 6.66 (dd, ^{3}J(H-H) = 9.9 Hz, ^{5}J(P-H) = 3.5 Hz, 1 H, (Ph)C=C-C=C*H*), 7.11-7.38 (m, 8 H, Ar-*H*).

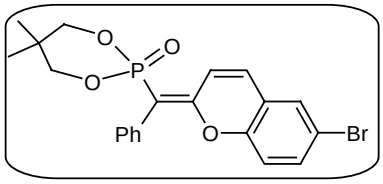
^{13}C NMR: δ 21.1 and 22.0 (2 s, C(*C*H$_3$)$_2$), 32.4 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 75.9 and 76.0 (2 s, O*C*H$_2$), 102.3 (d, ^{1}J(P-C) = 181.0 Hz, P*C*), 117.6, 119.9, 120.0, 121.3, 126.5, 127.0, 127.8, 128.2, 128.6, 128.9, 129.4, 130.7, 131.0$_8$, 131.1$_3$, 134.0$_6$, 134.1$_1$, 151.5, 158.3 (PC(Ph) = *C*).

^{31}P NMR: δ 10.8.

Anal. Calc. for $C_{21}H_{20}O_4PCl$: C, 62.62; H, 5.00. Found: C, 62.59; H, 5.03.

Compound 56

(i) *E*- isomer



Yield (*E*+*Z*): 0.63 g (84%).

Mp: 192–194 ^{o}C.

IR (KBr): 3108, 2965, 2886, 1781, 1632, 1566, 1476, 1426, 1285, 1221, 1049, 995 cm^{-1}.

^{1}H NMR: δ 0.63 and 0.92 (2 s, 6 H, C(CH_3)$_2$), 3.55-3.61 and 4.09–4.14 (2 m, 4 H, OCH_2), 6.61 (d, ^{3}J(H-H) = 8.7 Hz, 1 H, Ar-*H*), 6.84 (d, ^{3}J(H-H) = 10.1 Hz, 1 H, (Ph)C=C-C=C*H*), 7.25-7.40 (m, 7 H, Ar-*H*), 7.96 (d, ^{3}J(H-H) = 10.1 Hz, 1 H, (Ph)C=C-C*H*=).

^{13}C NMR: δ 21.2 and 21.6 (2 s, C(*C*H$_3$)$_2$), 32.3 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 75.2 and 75.3 (2 s, O*C*H$_2$), 101.9 (d, ^{1}J(P-C) = 201.0 Hz, P*C*), 115.9, 117.5, 121.0, 121.1, 122.1, 127.3, 128.1, 128.9, 129.3, 130.9, 131.0, 132.8, 133.9$_6$, 134.0, 151.8, 159.0 (d, ^{2}J(P-C) = 35.0 Hz, PC(Ph)=*C*).

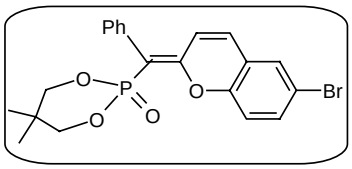
^{31}P NMR: δ 12.5.

LC-MS: *m/z* 447 [M]$^{+}$, 449 [M+2]$^{+}$.

Anal. Calc. for $C_{21}H_{20}O_4PBr$: C, 56.39; H, 4.51. Found: C, 56.33; H, 4.52.

X-ray structure was determined for this compound.

(ii) *Z*-isomer



Yield (*E*+*Z*): 0.63 g (84%).

Mp: 182–185 ^{o}C.

IR (KBr): 2967, 2924, 1883, 1748, 1628, 1570, 1476, 1422, 1254, 1213, 1057, 1005 cm^{-1}.

^{1}H NMR: δ 0.79 and 1.18 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.68–3.92 (m, 4 H, OC*H*$_2$), 6.31 (d, ^{3}*J*(H-H) = 10.0 Hz, 1 H, (Ph)C=C-C*H*=), 6.65 (dd, ^{3}*J*(H-H) = 10.0 Hz, ^{5}*J*(P-H) = 3.1 Hz, 1 H, (Ph)C=C-C=C*H*), 7.07-7.41 (m, 8 H, Ar-*H*).

^{13}C NMR: δ 21.0 and 22.0 (2 s, C(*C*H$_3$)$_2$), 32.3 (d, ^{3}*J*(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 75.8$_7$ and 75.9$_4$ (2 s, O*C*H$_2$), 101.9 (d, ^{1}*J*(P-C) = 180.7 Hz, P*C*), 115.8, 117.9, 119.8, 119.9, 121.8, 127.7$_2$, 127.7$_4$, 128.8, 129.1, 129.3, 130.9$_8$, 131.0, 133.5, 133.9$_7$, 134.0, 151.9, 158.1 (PC(Ph) = *C*).

^{31}P NMR: δ 9.2.

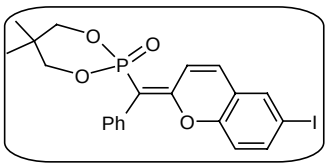
LC-MS: *m/z* 447 [M]$^{+}$, 449 [M+2]$^{+}$.

Anal. Calc. for $C_{21}H_{20}O_4PBr$: C, 56.39; H, 4.51. Found: C, 56.44; H, 4.52.

X-ray structure was determined for this compound.

Compound 57

(i) *E*- isomer (isomer purity ~95%)



Yield (*E*+*Z*): 0.50 g(60%).

Mp: 172–174 ^{o}C.

IR (KBr): 3104, 2959, 2884, 1773, 1632, 1563, 1474, 1422, 1285, 1221, 1049, 995 cm^{-1}.

^{1}H NMR: δ 0.63 and 0.92 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.55-4.14 (m, 4 H, OC*H*$_2$), 6.50 (d, ^{3}*J*(H-H) = 8.7 Hz, 1 H, Ar-*H*), 6.82 (d, ^{3}*J*(H-H) ~ 10.2 Hz, 1 H,

(Ph)C=C-C=C*H*), 7.26-7.49 (m, 7 H, Ar-*H*), 7.94 (d, ^{3}J(H-H) ~ 10.2 Hz, 1 H, (Ph)C=C-C*H*=).

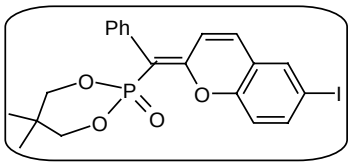
^{13}C NMR: δ 21.2 and 21.6 (2 s, C(*C*H$_3$)$_2$), 32.2 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 75.1$_5$ and 75.2$_1$ (2 s, O*C*H$_2$), 101.8 (d, ^{1}J(P-C) = 201.0 Hz, P*C*), 117.8, 120.8, 122.6, 127.2, 128.1, 128.7, 130.9, 133.9, 135.2, 138.7,152.6 (*C*H = CH + CH = *C*H + Ar*C*), 159.0 (d, ^{2}J(P-C) = 34.0 Hz, PC(Ph)=*C*).

^{31}P NMR: δ 14.8.

LC-MS: *m/z* 495 $[M+1]^{+}$.

Anal. Calc. for $C_{21}H_{20}O_4PI$: C, 51.03; H, 4.08. Found: C, 51.43; H, 4.10.

(ii) *Z*-isomer



Yield (*E*+*Z*): 0.50 g (60%).

Mp: 177–179 ^{o}C.

IR (KBr): 3057, 2967, 1624, 1593, 1566, 1476, 1420, 1244, 1211, 1057, 1005 cm^{-1}.

^{1}H NMR: δ 0.80 and 1.19 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.69-3.93 (m, 4 H, OC*H*$_2$), 6.30 (d, ^{3}J(H-H) = 8.0 Hz, 1 H, (Ph)C=C-C*H*=), 6.65 (dd, ^{3}J(H-H) = 8.0 Hz, ^{5}J(P-H) = 4.0 Hz, 1 H, (Ph)C=C-C=C*H*), 6.95-7.60 (m, 8 H, Ar-*H*).

^{13}C NMR: δ 21.1 and 21.6 (2 s, C(*C*H$_3$)$_2$), 32.3 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 75.8 and 75.9 (2 s, O*C*H$_2$), 102.3 (d, ^{1}J(P-C) = 180.0 Hz, P*C*), 118.2, 119.6, 122.3, 126.4, 128.9, 129.3, , 131.0, 134.0, 135.3, 139.4, 152.7, 158.0 (PC(Ph)=*C*).

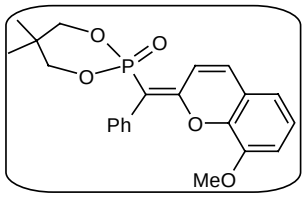
^{31}P NMR: δ 11.4.

LC-MS: *m/z* 495 $[M+1]^{+}$.

Anal. Calc. for $C_{21}H_{20}O_4PI$: C, 51.03; H, 4.08. Found: C, 51.43; H, 4.10.

Compound 58

(i) *E*- isomer



Yield (*E*+*Z*): 0.47 g (70%).

Mp: 132–134 ^{o}C.

IR (KBr): 3042, 2961, 1632, 1578, 1553, 1474, 1412, 1260, 1231, 1096, 1061, 1003 cm^{-1}.

^{1}H NMR: δ 0.65 and 0.94 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.48 (s, 3 H, OC*H*$_3$), 3.58-3.64 and 4.08–4.13 (2 m, 4 H, OC*H*$_2$), 6.81 (d, ^{3}J (H-H) = 7.6 Hz, 1 H, Ar-*H*), 6.92 (m, ^{3}J(H-H) ~ 10.0 Hz, 1 H, (Ph)C=C-C=C*H*), 7.26-7.45 (m, 7 H, Ar-*H*), 7.88 (d, ^{3}J(H-H) = 9.6 Hz, 1 H, (Ph)C=C-C*H*=).

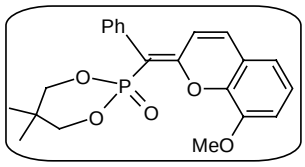
^{13}C NMR: δ 21.2 and 21.7 (2 s, C(*C*H$_3$)$_2$), 32.3 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 57.4 (s, O*C*H$_3$), 75.2 and 75.3 (2 s, O*C*H$_2$), 100.4 (d, ^{1}J(P-C) = 202.0 Hz, P*C*), 116.2, 119.6, 119.8, 119.9, 121.2, 123.4, 127.1, 128.1, 130.6, 131.0$_6$, 131.1$_2$, 134.3, 143.3, 147.1, 159.5 (d, ^{2}J(P-C) = 35.0 Hz, PC(Ph)=*C*).

^{31}P NMR: δ 15.5.

LC-MS: *m/z* 399 [M+1]$^{+}$.

Anal. Calc. for $C_{22}H_{23}O_5P$: C, 66.33; H, 5.82. Found: C, 66.39; H, 5.82.

(ii) *Z*-isomer



Yield (*E*+*Z*): 0.47 g (70%).

Mp: 151–154 ^{o}C.

IR (KBr): 3067, 2961, 1630, 1580, 1476, 1441, 1402, 1248, 1092, 1059, 1009, 986 cm^{-1}.

^{1}H NMR: δ 0.78 and 1.21 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.79-3.94 (m, 4 H, 2 OC*H*$_2$), 3.95 (s, 3 H, OC*H*$_3$), 6.26 (d, ^{3}J(H-H) = 9.6 Hz, 1 H, (Ph)C=C-C*H*=),

6.70-6.77 (m, 2 H, (Ph)C=C-C=C*H* + Ar-*H*), 6.93-7.39 (m, 7 H, Ar-*H*).

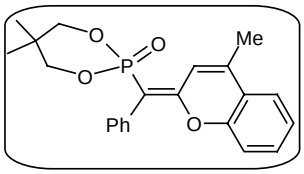
^{13}C NMR: δ 21.0 and 22.2 (2 s, C(*C*H$_3$)$_2$), 32.2 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 57.4 (s, O*C*H$_3$), 75.9 and 76.0 (2 s, O*C*H$_2$), 100.8 (d, ^{1}J(P-C)= 181.0 Hz, P*C*), 115.6, 118.9, 119.1, 119.4, 120.9, 123.3, 127.5, 128.0, 128.8, 130.5, 131.1$_6$, 131.2$_1$, 134.5$_5$, 134.6$_1$, 143.0, 147.6, 158.1 (s, PC(Ph)=*C*).

^{31}P NMR: δ 12.0.

LC-MS: *m/z* 399 [M+1]$^{+}$.

Anal. Calc. for $C_{22}H_{23}O_5P$: C, 66.33; H, 5.82. Found: C, 66.42; H, 5.75.

Compound 59 (*E*- isomer)



Yield (*E*+*Z*): 0.51 g (80%).

Mp: 165–167 ^{o}C.

IR (KBr): 3077, 2961, 2882, 1634, 1597, 1557, 1476, 1447, 1383, 1289, 1221, 1051, 997 cm^{-1}.

^{1}H NMR: δ 0.66 and 0.94 (2 s, 6 H, C(C*H*$_3$)$_2$), 2.29 (s, 3 H, CH$_3$), 3.60 (dd, ^{3}J(P-H) = 16.0 Hz, ^{2}J(H-H) ~ 11.1 Hz, 2 H, OC*H*$_2$), 4.08-4.13 (dd→t, ^{3}J(P-H) = ^{2}J(H-H) ~ 11.1 Hz, 2 H, OC*H*$_2$), 6.75 -7.39 (m, 9 H, Ar-*H*), 7.77 (s, 1 H, C=C-C*H*=).

^{13}C NMR: δ 18.5 (s, C=C(*C*H$_3$)), 21.2 and 21.7 (2 s, C(*C*H$_3$)$_2$), 32.3 (d, ^{3}J(P-C) = 5.9 Hz, *C*(CH$_3$)$_2$), 75.1 and 75.2 (2 s, O*C*H$_2$), 98.1 (d, ^{1}J(P-C) = 202.7 Hz, P*C*), 115.9, 117.8, 117.8$_3$, 121.6, 123.4, 123.7,126.9, 128.0,131.2$_7$,131.3$_2$ 134.4, 134.5, 138.3, 152.6, 159.9 (d, ^{2}J(P-C) = 34.5 Hz, PC(Ph)=*C*).

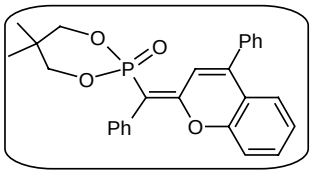
^{31}P NMR: δ 16.4.

LC-MS: *m/z* 383 [M+1]$^{+}$.

The other isomer [δ(P): 13.0] was there in the reaction mixture but we did not succeed in isolating it in a pure state.

Compound 60

(i) *E*- isomer



Yield (*E*+*Z*): 0.44 g (59%).

Mp: 201–203 ^{o}C.

IR (KBr): 3077, 2963, 1626, 1595, 1572, 1555, 1445, 1370, 1285, 1221, 1055, 1005 cm^{-1}.

^{1}H NMR: δ 0.66 and 0.92 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.57-3.63 and 4.06-4.11 (2 m, 4 H, OC*H*$_2$), 6.82-7.46 (m, 14 H, Ar-*H*), 7.89 (s, 1 H, C=C-C*H*=).

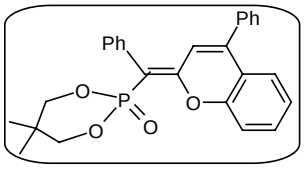
^{13}C NMR: δ 21.2 and 21.6 (2 s, C(*C*H$_3$)$_2$), 32.3 (d, ^{3}(P-C) = 5.0 Hz, *C*(CH$_3$)$_2$), 75.1 and 75.2 (2 s, O*C*H$_2$), 100.4 (d, ^{1}*J*(P-C) = 202.0 Hz, P*C*), 116.2, 118.8, 120.4, 123.3, 125.9, 127.0, 128.0, 128.5, 128.6, 128.7, 128.8, 131.0, 134.3, 136.6, 142.5, 153.1, 159.6 (d, ^{2}*J*(P-C) = 35.0 Hz, PC(Ph)=*C*).

^{31}P NMR: δ 15.9.

LC-MS: *m/z* 445 [M+1]$^{+}$.

Anal. Calc. for $C_{27}H_{25}O_4P$: C, 72.96; H, 5.67. Found: C, 72.87; H, 5.68.

(ii) *Z*-isomer



Yield (*E*+*Z*): 0.44 g (59%).

Mp: 167–169 ^{o}C.

IR (KBr): 3057, 2975, 2878, 1620, 1595, 1566, 1441, 1364, 1265, 1057, 1005, 988, 945 cm^{-1}.

^{1}H NMR: δ 0.80 and 1.21 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.73–3.91 (m, 4 H, OC*H*$_2$), 6.26 (s, 1 H, C=C-C*H*=), 6.99-7.42 (m, 14 H, Ar-*H*).

^{13}C NMR: δ 21.1 and 22.1 (2 s, C(*C*H$_3$)$_2$), 32.4 (d, ^{3}*J*(P-C) ~ 6.0 Hz, *C*(CH$_3$)$_2$), 75.9$_5$ and 76.0$_1$ (2 s, O*C*H$_2$), 100.7 (d, ^{1}*J*(P-C) = 181.1 Hz, P*C*),

116.6, 117.4, 117.5, 120.3, 123.3, 126.0, 127.5, 128.5, 128.7, 128.8, 131.0, 131.1, 131.2, 134.4, 134.5, 136.4, 142.8, 153.3, 158.7 (s, PC(Ph)=*C*).

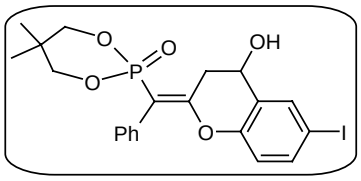
^{31}P NMR: δ 12.5.

LC-MS: *m/z* 445 $[M+1]^+$.

Anal. Calc. for $C_{27}H_{25}O_4P$: C, 72.96; H, 5.67. Found: C, 72.87; H, 5.69.

Compound 61 (*E*-isomer)

This compound isolated along with **57** from the reaction of allene **7e** with 5-iodo salicylaldehyde.



Yield: 0.07 g (8%).

Mp: 214-216 ^{o}C.

IR (KBr): 3279, 3059, 2920, 1640, 1595, 1472, 1406, 1225, 1053, 1003 cm^{-1}.

^{1}H NMR: δ 0.62 and 0.96 (2 s, 6 H, C(C*H*$_3$)$_2$), 2.85 (br, 1 H, O*H*), 3.29-3.33 (m, 1 H, =CC*H*$_A$H$_B$), 3.56-3.66 (m, 2 H, OC*H*$_2$), 3.78-3.83 (m, 1 H, =CC*H*$_A$H$_B$), 4.05 (m, 2 H, OC*H*$_2$), 4.90-4.93 (m, 1 H, C*H*(OH)), 6.48-7.69 (m, 8 H, Ar-*H*).

^{13}C NMR: δ 21.1 and 21.8 (2 s, C(*C*H$_3$)$_2$), 32.5 (d, ^{3}*J*(P-C) = 6.3 Hz, *C*(CH$_3$)$_2$), 33.5 (s, *C*H$_2$), 62.9 (s, *C*H(OH)), 75.6 and 75.7 (2 s, O*C*H$_2$), 118.9, 127.4, 128.0, 128.1, 130.7, 130.8, 133.5, 133.9, 134.0, 151.3, (Ar-*C*), 160.1 (d, ^{2}*J*(P-C) = 33.8 Hz, PC(Ph)=*C*). The spectrum was very noisy, probably because of dehydration during recording. Hence the position of P-C carbon was not identified.

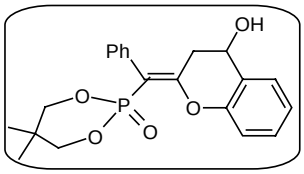
^{31}P NMR: δ 14.2.

LC-MS: *m/z* 512 $[M]^+$.

Anal. Calc. for $C_{21}H_{23}O_5P$: C, 49.24; H, 4.33. Found: C, 49.21; H, 4.25.

Compound 62 (*Z*-isomer)

The procedure was similar to **54** but here we used 20 mol% of PPh_3 as a catalyst.



Yield: 0.10 g (15%).

Mp: 201-203 ^{o}C.

IR (KBr): 3351, 3059, 2949, 1642, 1607, 1485, 1352, 1225, 1059, 1005, 945 cm^{-1}.

^{1}H NMR: δ 0.77 and 1.19 (2 s, 6 H, C(CH_3)$_2$), 2.57 (br d, ^{2}J(H-H) = 14.8 Hz, ^{3}J(H-H) <2.0 Hz, 1 H, =CCH_AH$_B$), 2.84 (dd, ^{2}J(H-H) = 14.8 Hz, ^{3}J(H-H) = 5.6 Hz, 1 H, =CCH$_A$$H_B$), 3.70-3.84 (m, 5 H, 2 OCH_2 + O*H*), 4.70 (br, C*H*(OH) 1 H), 6.99-7.35 (m, 9 H, Ar-*H*).

^{13}C NMR: δ 21.0 and 22.1 (2 s, C(*C*H$_3$)$_2$), 32.3 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 33.2 (d, ^{3}J(P-C) = 10.0 Hz *C*H$_2$), 63.3 (s, *C*H(OH)), 76.1 and 76.2 (2 d, ^{2}J(P-C) ~ 7.0 Hz, O*C*H$_2$), 108.8 (d, ^{1}J(P-C) = 172.0 Hz, P*C*), 116.9, 123.1, 124.9, 127.7, 128.1, 128.7, 130.1, 130.8, 130.9, 133.9, 134.0, 151.3, 160.5 (PC(Ph)=*C*).

^{31}P NMR: δ 11.1.

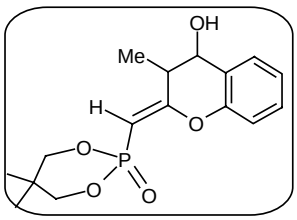
LC-MS: *m/z* 387 $[M+1]^{+}$.

Anal. Calc. for $C_{21}H_{23}O_5P$: C, 65.28; H, 6.00. Found: C, 65.30; H, 5.99.

(b) Reaction of the allene 7b with salicylaldehydes- Synthesis of phosphono-chromenes 63 and 64

The procedure was similar to that described for **54**, using allene **7b** (0.53 g, 2.48 mmol) and salicylaldehyde (3.73 mmol). Compounds **63** and **64** were purified by column chromatography using ethyl acetate and hexane (2:3 v/v).

Compound 63



Yield: 0.12 g (15%).

Mp: Semisolid.

IR (KBr): 3364, 2984, 2882, 2361, 1696, 1647, 1509, 1217, 1055, 1008, 822 cm^{-1}.

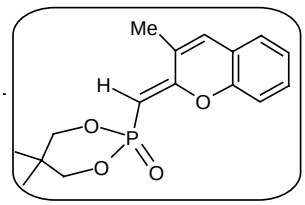
^1H NMR: δ 1.00 and 1.07 (2 s, 6 H, $C(CH_3)_2$), 1.19 (s, 3 H, CH_3), 2.75 (s, 1 H, $CHCH_3$), 3.94–4.05 (m, 4 H, OCH_2), 4.39 (s, 1 H, CH(OH)), 4.80 (d, ^2J(P-H) = 10.8 Hz, 1 H, PCH), 7.04-7.33 (m, 4 H, Ar-H).

^{13}C NMR: δ 15.5 (s, C=C-$C(CH_3)$), 21.4 and 22.0 (2 s, $C(CH_3)_2$), 32.6 (d, ^3J(P-C) = 6.0 Hz, $C(CH_3)_2$), 40.9 (d, ^3J(P-C) = 14.0 Hz, $CH(OH)C(CH_3)$), 68.9 (s, CH(OH)), 76.0 and 76.1 (2 s, OCH_2), 90.2 (d, ^1J(P-C) = 185.0 Hz, PC), 116.5, 123.4$_7$, 123.5$_1$, 129.0, 130.1, 150.4 (Ar-C), 168.8 (s, PC(H)=C).

^{31}P NMR: δ 12.6.

LC-MS: *m/z* 325 $[M+1]^+$.

Compound 64



Yield: 0.30 g (40%).

Mp: 153–155 °C.

IR (KBr): 2928, 1825, 1636, 1568, 1462, 1256, 1055, 1007, 872 cm^{-1}.

^1H NMR: δ 1.13 and 1.17 (2 s, 6 H, $C(CH_3)_2$), 2.03 (s, 3 H, CH_3), 3.92-4.20 (m, 4 H, OCH_2), 4.63 (d, ^2J(P-H) = 8.8 Hz, 1 H, PCH), 6.83 (s, 1 H, CH=$C(CH_3)$), 7.06-7.31 (m, 4 H, Ar-H).

^{13}C NMR: δ 18.8 (s, C=$C(CH_3)$), 21.7$_7$ and 21.8$_4$ (2 s, $C(CH_3)_2$), 32.7 (d, ^3J(P-C) = 6.0 Hz, $C(CH_3)_2$), 75.6 and 75.7 (2 s, OCH_2), 81.3 (d, ^1J(P-C) = 195.0 Hz, PC), 127.1 (d, ^3J(P-C) = 16.0 Hz, C=$C(CH_3)$), 115.7, 120.2, 123.4, 123.7, 126.6, 127.0, ,129.5, 130.0, 152.2, 163.5 (PC(H)=C) [*cf.* Fig. 28].

^{31}P NMR: δ 15.4.

LC-MS: *m/z* 307 $[M+1]^+$.

Anal. Calc. for $C_{16}H_{19}O_4P$: C, 62.74; H, 6.25. Found: C, 62.64; H, 6.25$_1$.

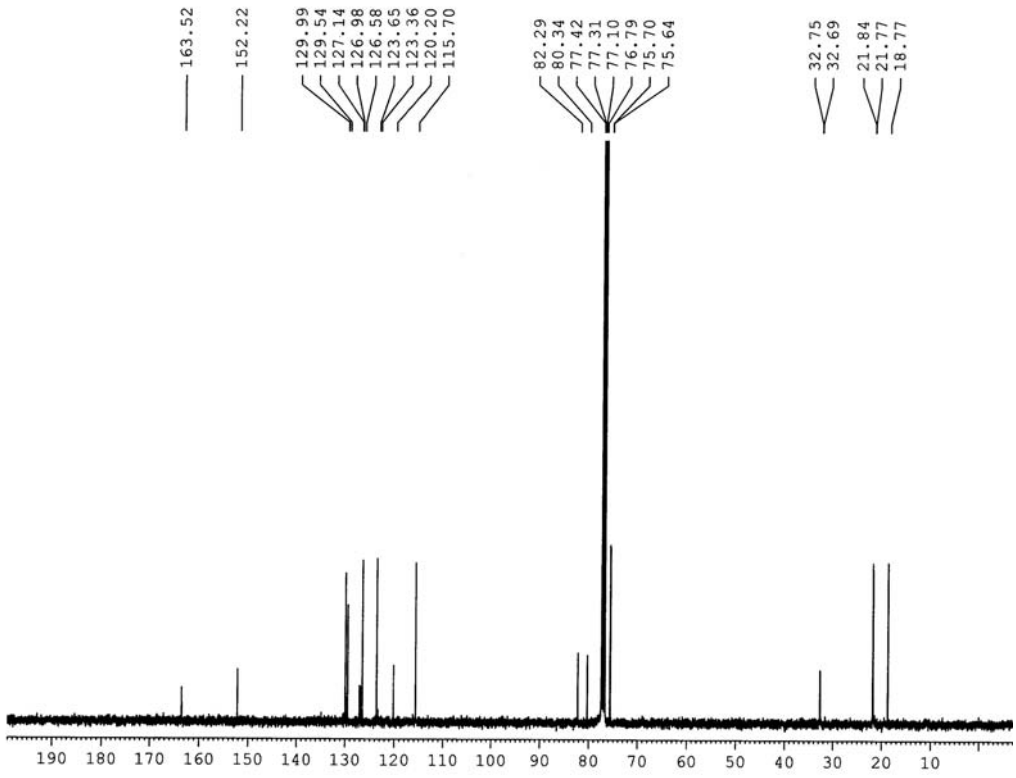
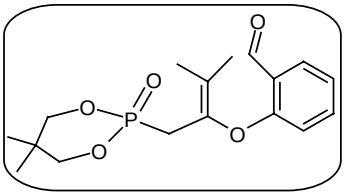


Fig. 28. ^{13}C NMR spectrum of compound (*Z*)**-64**

(*c*) ***Reaction of the allene 7c with salicylaldehydes- Synthesis of allylic phosphonates 65a-b and phosphono-chromenes 66a-c***

The procedure was similar to that described for **54**, using allene **7c** (0.463 g, 2.14 mmol) and 3.21 mmol of salicylaldehydes. In these cases, the phenol addition products (**65a-b**) and the aldehyde addition products (**66a-b**) only were obtained. In the case of *o*-vanillin, we isolated aldehyde addition product **66c**.

Compound 65a



Yield: 0.18 g (25%).

Mp: 106–108 ^{o}C.

IR (KBr): 2975, 2915, 1690, 1599, 1478, 1458, 1400, 1273, 1225, 1059, 1013 cm^{-1}.

^{1}H NMR: δ 0.97 and 1.08 (2 s, 6 H, C(CH_3)$_2$), 1.72 (d, ^{5}J(P-H) = 6.2 Hz, 3 H, C=C(CH_3)$_2$(A)), 1.87 (d, ^{5}J(P-H) = 4.8 Hz, 3 H, C=C(CH_3)$_2$(B)), 2.90 (d, ^{2}J(P-H) = 21.4 Hz, 2 H, PCH_2), 3.74–4.26 (m, 4 H, OCH_2), 6.84-7.89 (m, 4 H, Ar-*H)*, 10.52 (s, 1 H, C*H*O).

^{13}C NMR: δ 17.7 (d, ^{4}J(P-C) = 4.0 Hz, C=C(*C*H$_3$)$_2$(A)), 19.2 (d, ^{4}J(P-C) = 3.0 Hz, C=C(*C*H$_3$)$_2$(B)), 21.2 and 21.3 (2 s, C(*C*H$_3$)$_2$), 26.4 (d, ^{1}J(P-C) = 139.0 Hz, P*C*), 32.5 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 75.1 and 75.2 (2 s, O*C*H$_2$), 125.1 (d, ^{3}J(P-C) = 11.0 Hz, C=*C*(CH$_3$)$_2$), 134.2 (d, ^{2}J(P-C) = 15.0 Hz, *C*=C(CH$_3$)$_2$), 114.5, 122.0, 125.6, 128.5, 135.7, 158.5 (d, ^{4}J(P-C) = 3.0 Hz, Ar*C*O), 189.7 (s, *C*HO) [*cf.* Fig. 29].

^{31}P NMR: δ 21.3.

LC-MS: *m/z* 339 [M+1]$^{+}$.

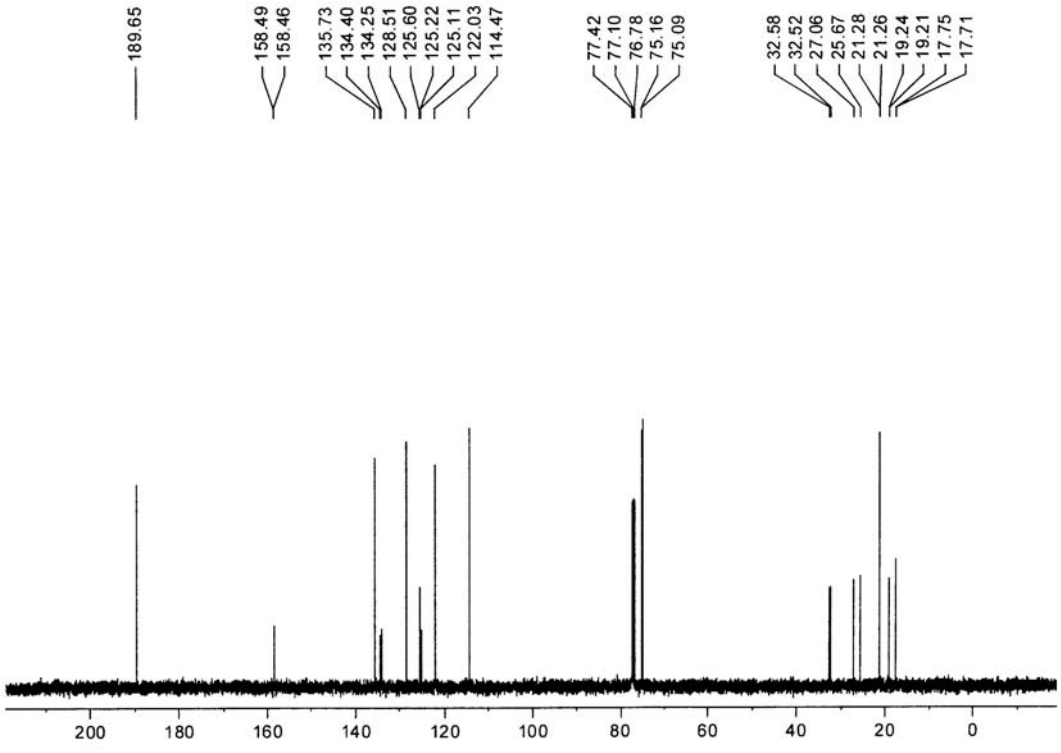
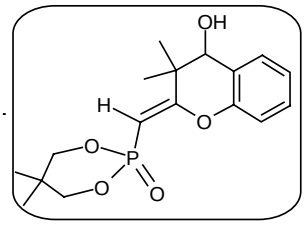


Fig. 29. ^{13}C NMR spectrum of compound **65a**

Compound 66a

(*Z*-isomer)



Yield: 0.29 g (40%).

Mp: 167–169 ^{o}C.

IR (KBr): 3343, 2971, 2880, 1638, 1605, 1456, 1385, 1235, 1094, 1057, 1005, 818 cm^{-1}.

^{1}H NMR: δ 0.84 and 0.94 (2 s, 6 H, C(C*H*$_3$)$_2$), 1.03 and 1.06 (2 s, 6 H, C(OH)C(C*H*$_3$)$_2$), 3.74–3.92 (m, 4 H, OC*H*$_2$), 4.12 (s, 1 H, C*H*(OH), 4.75 (d, ^{2}*J*(P-H) = 8.0 Hz, 1 H, PC*H*), 6.83-7.13 (m, 4 H, Ar-*H*).

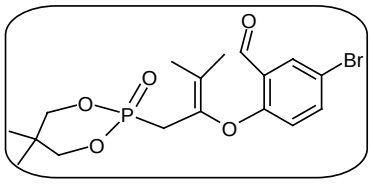
^{13}C NMR: δ 21.2 and 21.3 (2 s, C(*C*H$_3$)$_2$), 21.9 and 24.1 (2 s, CH(OH)C(*C*H$_3$)$_2$), 32.5 (d, ^{3}*J*(P-C) = 6.1 Hz, CH$_2$*C*(CH$_3$)$_2$), 39.9 (d, ^{3}*J*(P-C) = 12.1, CH(OH)*C*(CH$_3$)$_2$), 71.7 (s, *C*H(OH)), 75.9 and 76.0 (2 s, O*C*H$_2$), 87.9 (d, ^{1}*J*(P-C) = 184.3 Hz, P*C*), 115.7, 123.2, 124.3, 128.6, 129.6, 150.1, 173.4 (d, ^{2}*J*(P-C) = 3.9 Hz, PC(H)=*C*).

^{31}P NMR: δ 13.7.

LC-MS: *m/z* 339 [M+1]$^{+}$.

X-ray structure was determined for this compound.

Compound 65b



Yield: 0.45 g (50%).

Mp: Semisolid. After several washings with ether also, we could not get this as a well-defined solid.

IR (KBr): 2968, 2886, 1715, 1684, 1591, 1470, 1393, 1223, 1142, 1061 cm^{-1}.

^{1}H NMR: δ 0.97 and 1.09 (2 s, 6 H, C(C*H*$_3$)$_2$), 1.71 (d, ^{5}*J*(P-H) = 6.0 Hz, 3 H, C=C(C*H*$_3$)$_2$(A)), 1.87 (d, ^{5}*J*(P-H)= 4.8 Hz, 3 H, C=C(C*H*$_3$)$_2$(B)), 2.89

(d, ^{2}J(P-H)= 21.2 Hz, 2 H, PCH_2), 3.73-4.23 (m, 4 H, OCH_2), 6.78-7.97 (m, 3 H, Ar-*H*), 10.43 (s, 1 H, C*H*O).

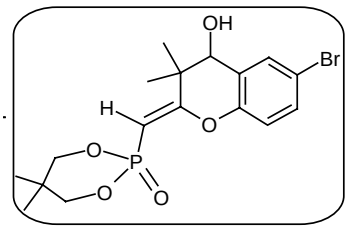
^{13}C NMR: δ 17.8 (d, ^{4}J(P-C) = 3.2 Hz, C=C(*C*H$_3$)$_2$), 19.3 (d, ^{4}J(P-C) = 2.9 Hz, C=C(*C*H$_3$)$_2$), 21.2 and 21.4 (2 s, C(*C*H$_3$)$_2$), 26.4 (d, ^{1}J(P-C) = 139.1 Hz, P*C*H$_2$), 32.6 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 75.0 and 75.1 (2 s, O*C*H$_2$), 125.7 (d, ^{3}J(P-C) = 11.5 Hz, C=*C*(CH$_3$)$_2$), 134.2 (d, ^{2}J(P-C) = 14.7 Hz, *C*=C(CH$_3$)$_2$), 114.9, 116.6, 126.8, 131.1, 138.2, 157.5 (d, ^{4}J(P-C) = 2.4 Hz, Ar*C*O), 188.3 (s, *C*HO).

^{31}P NMR: δ 20.9.

LC-MS: *m/z* 417 [M]$^{+}$, 419 [M+2]$^{+}$.

Anal. Calc. for $C_{27}H_{25}O_4P$: C, 48.94; H, 5.31. Found: C, 49.05; H, 5.28.

Compound 66b



Yield: 0.18 g (20%).

Mp: 167–169 ^{o}C.

IR (KBr): 3364, 2973, 2880, 1638, 1601, 1476, 1238, 1059, 1007, 870 cm^{-1}.

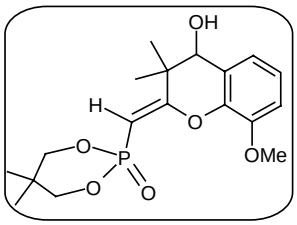
^{1}H NMR: δ 1.01, 1.12, 1.18 and 1.20 (4 s, 12 H, C(C*H*$_3$)$_2$ + CH(OH)C(C*H*$_3$)$_2$), 3.87–4.12 (m, 4 H, OCH_2), 4.25 (s, 1 H, C*H*(OH)), 4.95 (d, ^{2}J(P-H) = 12.0 Hz, 1 H, PC*H*), 6.86-7.43 (m, 3 H, Ar-*H*).

^{13}C NMR: δ 20.9, 21.3, 21.8 and 23.8 (4 s, C(*C*H$_3$)$_2$ + CH(OH)C(*C*H$_3$)$_2$), 32.6 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 39.7 (d, ^{3}J(P-C) = 12.0 Hz, CH(OH)*C*(CH$_3$)$_2$), 70.8 (s, *C*H(OH)), 76.0 and 76.1 (2 d, ^{2}J(P-C) = 7.0 Hz, O*C*H$_2$), 88.4 (d, ^{1}J(P-C) = 184.0 Hz, P*C*), 115.5, 117.5, 126.7, 131.1, 132.3, 149.1, 173.5 (s, PC(H)=*C*).

^{31}P NMR: δ 13.3.

LC-MS: *m/z* 417 [M]$^{+}$, 419 [M+2]$^{+}$.

Compound 66c



Yield: 0. 16 g (20 %).

Mp: 197–199 ^{o}C.

IR (KBr): 3337, 2965, 2874, 1634, 1607, 1485, 1258, 1059, 1007, 872 cm^{-1}.

^{1}H NMR: δ 1.00, 1.13, 1.23 and 1.32 (4 s, 12 H, C(C*H*$_3$)$_2$ + C(OH)C(C*H*$_3$)$_2$), 3.88 (s, OC*H*$_3$), 4.04–4.09 (m, 4 H, OC*H*$_2$), 4.29 (s, 1 H, C*H*(OH)), 5.04 (d, ^{2}*J*(P-H) = 9.2 Hz, 1 H, PC*H*), 6.91-7.02 (m, 3 H, Ar-*H*).

^{13}C NMR: δ 21.3, 21.7, 22.2 and 24.3 (4 s, C(*C*H$_3$)$_2$ + CH(OH)C(*C*H$_3$)$_2$), 32.6 (d, ^{3}*J*(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 39.8 (d, ^{3}*J*(P-C) = 12.0 Hz, CH(OH)*C*(CH$_3$)$_2$), 56.8 (s, O*C*H$_3$), 72.4 (s, *C*H(OH)), 76.1$_5$ and 76.2$_1$ (2 s, O*C*H$_2$), 88.7 (d, ^{1}*J*(P-C) = 186.0 Hz, P*C*), 113.7, 120.5, 123.2, 125.0, 140.0, 147.3, 171.9 (PC(H)=*C*).

^{31}P NMR: δ 11.9.

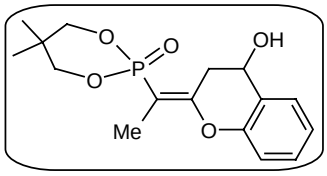
LC-MS: *m/z* 369 [M+1]$^{+}$.

Anal. Calc. for $C_{27}H_{25}O_4P$: C, 58.69; H, 6.84. Found: C, 58.57; H, 6.81.

(*d*) *Reaction of allene 7i with salicylaldehydes and 2-hydroxyacetophenone: Synthesis of phosphono-chromenes (67a-b, 68a-d and 69a-b)*

General procedure: To a solution of allene **7i** (0.420 g, 2.08 mmol) and salicylaldehyde (3.12 mmol) in DMSO (4 mL) was added a 10% solution of DBU in DMSO (0.6 mL, corresponds to 0.06 g of DBU, 0.42 mmol), and the mixture heated at 80 ^{o}C for 10-12 h. The contents were washed with water (2 x 10 mL) and extracted with DCM (2 x 25 mL). The solvent was removed and the products **67-69** were isolated by column chromatography using ethyl acetate and hexane (3:7). Compounds **67a-b** could be converted quantitatively to **68a-b** in the presence of 2M HCl at room temperature.

Compound 67a



Yield: 0.30 g (45%).

Mp: 139–141 ^{o}C.

IR (KBr): 3262, 2959, 1645, 1607, 1470, 1370, 1254, 1196, 1057, 1003, 911 cm^{-1}.

^{1}H NMR: δ 1.00 and 1.22 (2 s, 6 H, C(CH_3)$_2$), 2.03 (d, ^{3}J(P-H) = 13.7 Hz, 3 H, PCCH_3), 3.15-3.19 (m, 1 H, =CCH_AH$_B$), 3.39 (br, 1 H, O*H*), 3.67-3.77 (m, 1 H, =CCH_AH$_B$),3.77-3.88 (m, 2 H, OCH_2), 4.27-4.32 (m, 2 H, OCH_2), 4.88 (br, 1 H, C*H*(OH)), 7.03-7.41 (m, 4 H, Ar-*H*).

^{13}C NMR: δ 11.9 (d, ^{2}J(P-C) = 5.3 Hz, PC*C*H$_3$), 21.6 and 22.1 (2 s, C(*C*H$_3$)$_2$), 32.6 (d, ^{3}J(P-C) = 5.3 Hz, *C*(CH$_3$)$_2$), 33.6 (s, *C*H$_2$), 63.4 (s, *C*H(OH)), 74.6$_7$ and 74.7$_2$ (2 merged d, ^{3}J(P-C) ~ 5.3 Hz, O*C*H$_2$), 100.4 (d, ^{1}J(P-C) = 198.3 Hz, P*C*), 116.5, 122.9, 125.4, 128.0, 129.8, 151.4, 160.4 (^{2}J(P-C) = 35.0 Hz, PC(Me)=*C*).

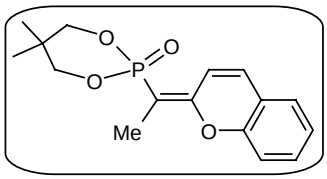
^{31}P NMR: δ 21.5.

LC-MS: *m/z* 307 [M-18]$^{+}$.

Anal. Calc. for $C_{16}H_{21}O_5P$: C, 59.26; H, 6.53. Found: C, 59.38; H, 6.54.

X-ray structure was determined for this compound.

Compound 68a



Yield: 0.10 g (15%).

Mp: 155–157 ^{o}C.

IR (KBr): 2930, 2886, 1634, 1578, 1454, 1285, 1231, 1206, 1051, 993 cm^{-1}.

^{1}H NMR: δ 0.97 and 1.26 (2 s, 6 H, C(CH_3)$_2$), 2.01 (d, ^{3}J(P-H) = 14.1 Hz, 3 H, PCCH_3), 3.75-4.38 (m, 4 H, OCH_2), 6.77 (d, ^{3}J(H-H) = 10.0 Hz, 1 H, (Me)C=C-C=C*H*), 7.04-7.38 (m, 4 H, Ar-*H*), 7.76 (d, ^{3}J(H-H) = 10.0

Hz, 1 H, (Me)C=C-C*H*=).

^{13}C NMR: δ 12.0 (d, ^{2}J(P-C) = 3.6 Hz, PC*C*H$_3$), 21.5 and 22.2 (2 s, C(*C*H$_3$)$_2$), 32.5 (d, ^{3}J(P-C) = 6.1 Hz, *C*(CH$_3$)$_2$), 74.4 and 74.5 (2 s, O*C*H$_2$), 92.7 (d, ^{1}J(P-C) = 203.8 Hz, P*C*), 115.4, 119.9, 120.5, 123.5, 126.9, 128.2, 130.0, 153.1, 159.6 (d, ^{2}J(P-C) = 36.4 Hz, P-C=*C*).

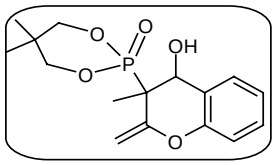
^{31}P NMR: δ 21.8.

LC-MS: *m/z* 307 $[M+1]^+$.

Anal. Calc. for $C_{21}H_{21}O_4P$: C, 62.74; H, 6.25. Found: C, 62.87; H, 6.24.

X-ray structure was determined for this compound.

Compound 69a

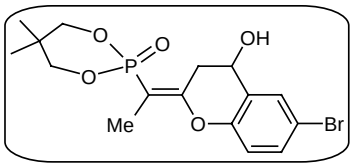


^{1}H NMR: δ 0.98 and 1.03 (2 s, 6 H, C(C*H*$_3$)$_2$), 1.72 (d, ^{3}J(P-H) = 15.6 Hz, 3 H, PCC*H*$_3$), 3.81-4.15 (m, 4 H, OC*H*$_2$), 4.73 (d, ^{3}J(H-H) = 3.4 Hz, 1 H, C*H*(OH)), 4.95 (s, 1 H, =C*H*$_a$H$_b$), 5.09 (m, 1 H, =CH$_a$*H*$_b$), 6.92-7.35 (m, 4 H, Ar-*H*).

^{31}P NMR: δ 18.5.

Because of the moisture sensitivity of this compound, other data were not recorded.

Compound (*E*)**-67b**



Yield: 0.34 g (40 %).

Mp: 178–182 ^{o}C.

IR (KBr): 3252, 2957, 1644, 1601, 1472, 1370, 1256, 1188, 1051, 910 cm^{-1}.

^{1}H NMR: δ 0.97 and 1.21 (2 s, 6 H, C(C*H*$_3$)$_2$), 1.99 (d, ^{3}J(P-H) = 13.6 Hz, 3 H, PCC*H*$_3$), 3.37-3.43 (br m, 3 H, =CC*H*$_2$ + O*H*), 3.78-4.30 (m, 4 H, OC*H*$_2$), 4.81-4.84 (m, 1 H, C(H)O*H*), 6.88-7.55 (m, 3 H, Ar-*H*).

^{13}C NMR: δ 11.9 (d, ^{2}J(P-C) = 5.3 Hz, PC*C*H$_3$), 21.6 and 22.2 (2 s, C(*C*H$_3$)$_2$), 32.6 (d, ^{3}J(P-C) = 5.3 Hz, *C*(CH$_3$)$_2$), 33.5 (s, *C*H$_2$), 62.9 (s, *C*H(OH)),

74.7 and 74.8 (2 d, ^{3}J(P-C) = 5.3 Hz, O*C*H$_2$), 100.5 (d, ^{1}J(P-C) = 198.8 Hz, P*C*), 115.3, 118.1, 128.2, 130.5, 132.3, 150.4, 160.4 (d, ^{2}J(P-C) = 35.3 Hz, PC(Me)=*C*) [*cf.* Fig. 30].

^{31}P NMR: δ 20.8.

LC-MS: *m/z* 385 $[M-18]^+$, 387 $[M-16]^+$.

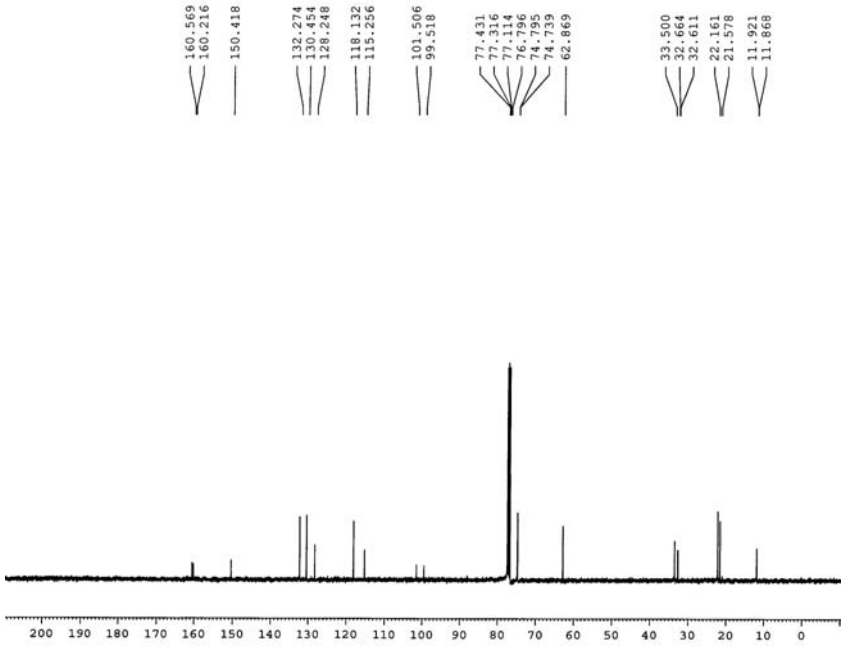
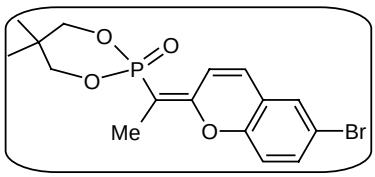


Fig. 30. ^{13}C NMR spectrum of compound (*E*)-**67b**

Compound (*E*)-**68b**



Yield: 0.14 g (17%).

Mp: 172–174 ^{o}C.

IR (KBr): 3100, 2874, 1630, 1574, 1474, 1422, 1283, 1231, 1055, 1001 cm^{-1}.

^{1}H NMR: δ 0.96 and 1.27 (2 s, 6 H, C(C*H*$_3$)$_2$), 2.00 (d, ^{3}J(P-H) = 14.2 Hz, 3 H, PCC*H*$_3$), 3.78 (dd, ^{2}J(H-H) = 10.8 Hz, ^{3}J(P-H) = 17.8 Hz, 2 H, OC*H*$_2$), 4.36 (dd, ^{2}J(H-H) = 10.8 Hz, ^{3}J(P-H) = 5.5 Hz, 2 H, OC*H*$_2$), 6.67 (d, ^{3}J(H-H) = 10.2 Hz, 1 H, (Me)C=C-CH=C*H*), 6.93-7.37 (m, 3 H, Ar-*H*), 7.81 (d, ^{3}J(H-H) = 10.2 Hz, 1 H, (Me)C=C-C*H*=CH).

^{13}C NMR (50 MHz): δ 12.0 (d, ^{2}J(P-C) = 4.9 Hz, PC*C*H$_3$), 21.5 and 22.3 (2 s,

C(CH$_3$)$_2$), 32.5 (d, ^3J(P-C) = 4.9 Hz, C(CH$_3$)$_2$), 74.4 and 74.5 (2 s, OCH$_2$), 94.4 (d, ^1J(P-C) = 202.6 Hz, PC), 115.7, 117.2, 121.2, 122.3, 126.8, 129.3, 132.6, 152.1, 159.6 (d, ^2J(P-C) = 36.4 Hz, PC=C) [*cf.* Fig. 31].

^{31}P NMR: δ 21.1.

LC-MS: *m/z* 385 $[M]^+$, 387 $[M+2]^+$.

Anal. Calc. for $C_{16}H_{18}O_4PBr$: C, 49.89; H, 4.71. Found: C, 49.87; H, 4.71.

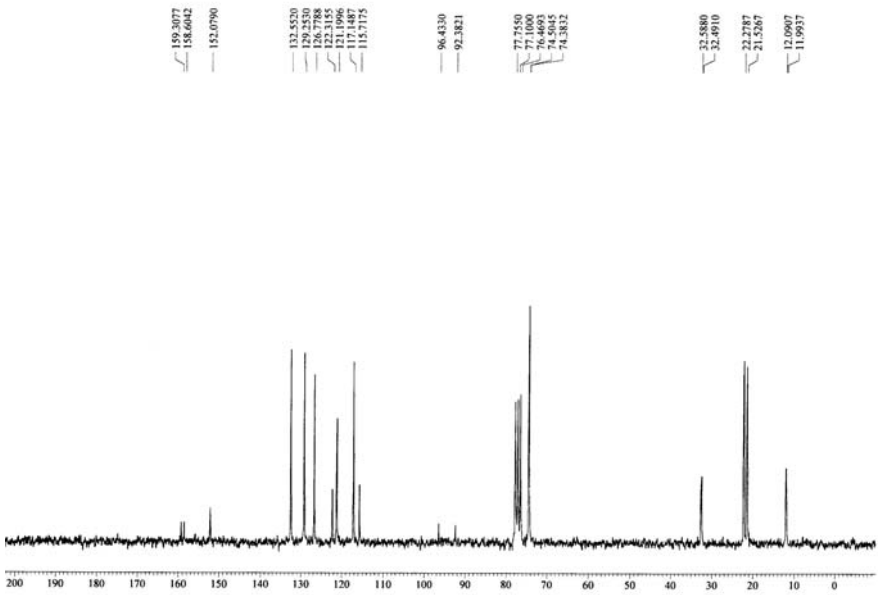
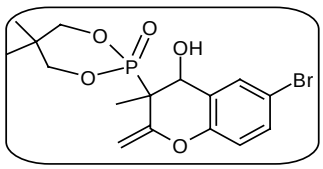


Fig. 31. ^{13}C NMR spectrum of compound (*E*)-**68b**

Compound 69b



Mp: 160-164 ^{o}C.

IR (KBr): 3376, 2963, 1655, 1601, 1480, 1423, 1248, 1190, 1055, 1011, 872 cm^{-1}.

^{1}H NMR: δ 1.02 (s, 6 H, C(CH_3)$_2$), 1.70 (d, ^3J(P-H) = 15.0 Hz, 3 H, PCCH_3), 2.35 (s, 1 H, OH), 3.81-4.15 (m, 4 H, OCH_2), 4.74-4.76 (m, 1 H,

C*H*(OH)), 4.91 (br s, 1 H, =CH_2), 5.07-5.08 (br m, 1 H, =CH_2), 6.81 (d, ^3J(H-H) = 8.7 Hz, 1 H, Ar-*H*), 7.28-7.46 (m, 2 H, Ar-*H*).

^{13}C NMR (50 MHz): δ 16.6 (s, PC(CH$_3$)), 21.5 and 21.7 (2 s, C(CH$_3$)$_2$), 32.7 (d, ^3J(P-C) = 6.0 Hz, C(CH$_3$)$_2$), 44.5 (d, ^1J(P-C) = 125.0 Hz, P*C*), 63.4 (s, *C*H(OH)), ~ 76.6 (OCH$_2$, merged with signals due to CDCl$_3$), 96.7 (d, ^3J(P-C) = 8.5 Hz, =*C*H$_2$), 114.1, 117.4, 124.9, 132.0, 133.3, 151.5, 160.1 (d, ^2J(P-C) = 9.7 Hz, *C*=CH$_2$).

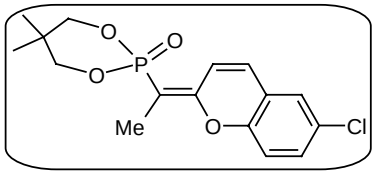
^{31}P NMR: δ 19.0.

LC-MS: *m/z* 403 $[M]^+$, 405 $[M+2]^+$.

Anal. Calc. for $C_{16}H_{20}O_5PBr$: C, 47.66; H, 5.00. Found: C, 47.62; H, 5.03.

X-ray structure was determined for this compound.

Compound 68c



Yield: 0.13 g (18%).

Mp: 168–172 ^{o}C.

IR (KBr): 3104, 2930, 1630, 1574, 1474, 1422, 1283, 1233, 1055, 1001, 820 cm^{-1}.

^{1}H NMR: δ 0.95 and 1.26 (2 s, 6 H, C(CH_3)$_2$), 2.00 (d, ^3J(P-H) = 13.9 Hz, 3 H, PCCH_3), 3.74-4.36 (m, 4 H, OCH_2), 6.67 (d, ^3J(H-H) = 9.1 Hz, 1 H, (Me)C=C-C=C*H*), 6.97-7.29 (m, 3 H, Ar-*H*), 7.80 (d, ^3J(H-H) = 9.1 Hz, 1 H, (Me)C=C-C*H*=).

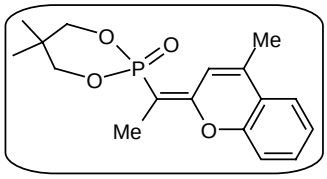
^{13}C NMR: δ 12.0 (d, ^2J(P-C) = 4.0 Hz, PCCH$_3$), 21.5 and 22.2 (2 s, C(CH$_3$)$_2$), 32.5 (d, ^3J(P-C) = 6.0 Hz, C(CH$_3$)$_2$), 74.3$_7$ and 74.4$_3$ (2 s, OCH$_2$), 94.2 (d, ^1J(P-C) = 203.0 Hz, P*C*), 116.7, 117.2, 121.1, 121.7, 126.2, 126.9, 128.3, 129.6, 151.6, 159.0 (d, ^2J(P-C) = 36.0 Hz, PC=*C*).

^{31}P NMR: δ 21.1.

LC-MS: *m/z* 341 $[M]^+$, 343 $[M+2]^+$.

Anal. Calc. for $C_{16}H_{18}O_4PCl$: C, 56.40; H, 5.32. Found: C, 56.41; H, 5.39.

Compound 68d



Yield: 0.17 g (25%).

Mp: 168–170 ^{o}C.

IR (KBr): 3069, 2922, 1640, 1578, 1474, 1368, 1287, 1223, 1055, 1007, 816 cm^{-1}.

^{1}H NMR: δ 0.97 and 1.27 (2 s, 6 H, C(C*H*$_3$)$_2$), 2.00 (d, ^{3}J(P-H) = 14.0 Hz, 3 H, PCC*H*$_3$), 2.22 (s, 3 H, C=C(C*H*$_3$)), 3.74-4.37 (m, 2 H, OC*H*$_2$), 7.08-7.64 (m, 5 H, C*H*=C + Ar-*H*).

^{13}C NMR: δ 11.8 (d, ^{2}J(P-C) = 5.0 Hz, PC*C*H$_3$), 18.3 (s, C=C(*C*H$_3$)), 21.6 and 22.3 (2 s, C(*C*H$_3$)$_2$), 32.5 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 74.3$_5$ and 74.4$_0$ (2 s, O*C*H$_2$), 90.2 (d, ^{1}J(P-C) = 206.0 Hz, P*C*), 115.5, 118.0, 121.7, 123.3, 123.7, 129.9, 135.8, 152.9, 160.0 (d, ^{2}J(P-C) = 36.0 Hz, PC(CH$_3$)=*C*).

^{31}P NMR: δ 22.7.

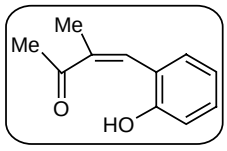
LC-MS: *m/z* 321 [M+1]$^{+}$.

Anal. Calc. for $C_{17}H_{21}O_4P$: C, 63.74; H, 6.61. Found: C, 63.69; H, 6.62.

(e) Synthesis of 4-(2-hydroxy phenyl)-3-methyl buten-2-ones 70a-b

Compounds **69a-b** were moisture sensitive and eliminate phosphate to give the products **70a-b**; the conversion was faster in the presence of 2 M HCl (5 mL per 0.5 g of the material).

(a) Compound 70a



Yield: 0.10 g (20%).

Mp: 120–122 ^{o}C. [lit.124.6-126.0 ^{o}C[119]]

IR (KBr): 3337, 1638, 1603, 1456, 1364, 1306, 1258, 1107, 1003, 893 cm^{-1}.

^{1}H NMR: δ 1.99 (s, 3 H, =C(C*H*$_3$)), 2.50 (s, 3 H, OC(C*H*$_3$)), 5.87 (s, 1 H, C*H*=CMe), 6.90-7.30 (m, 4 H, Ar-*H*), 7.70 (s, 1 H, OH).

^{13}C NMR: δ 13.2 (s, =C(*C*H$_3$)), 26.0 (s, CO(*C*H$_3$)), 115.9, 120.5, 123.0, 130.2$_5$, 130.3$_4$, 135.7, 138.5, 154.0 (s, C(O)*C*Me), 201.5 (s, *C*=O) [*cf.* Fig. 32].

LC-MS: *m/z* 159 $[M+1]^+$.

X-ray structure was determined for this compound.

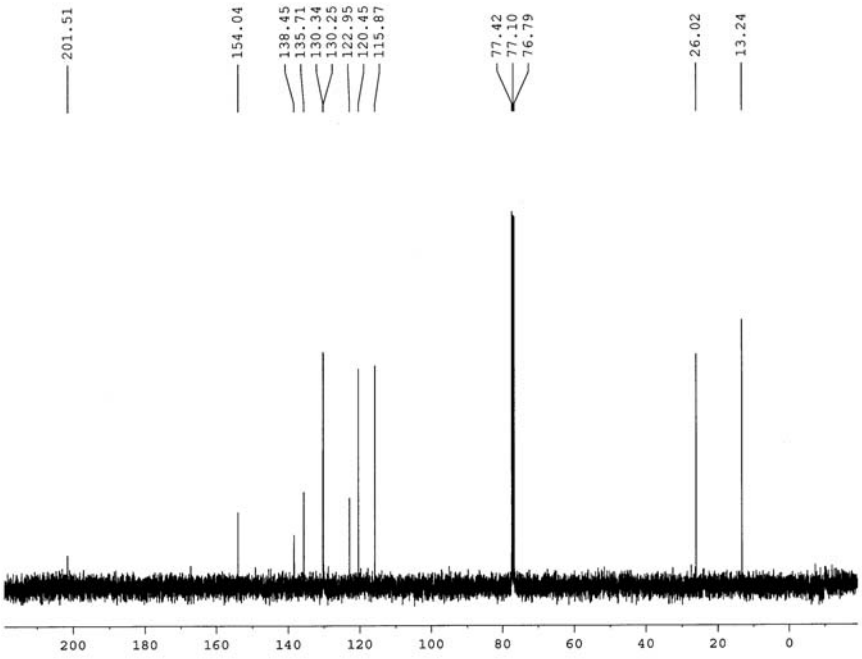
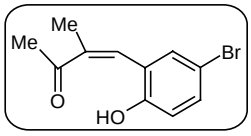


Fig. 32. ^{13}C NMR spectrum of compound **70a**

Compound 70b



Yield: 0.12 g (22 %).

Mp: 116–118 ^{o}C.

IR (KBr): 3341, 2924, 1651, 1628, 1595, 1491, 1410, 1271, 1177, 1115, 1007, 907 cm^{-1}.

^{1}H NMR: δ 1.96 (s, 3 H, =C(*C*H$_3$)), 2.47 (s, 3 H, OC(C*H*$_3$)), 5.31 (s, 1 H, C*H*=CMe), 6.78-7.36 (m, 3 H, Ar-*H*), 7.51 (s, 1 H, OH).

^{13}C NMR: δ 13.2 (s, =C(*C*H$_3$)), 26.0 (s, CO(*C*H$_3$)), 112.6 117.5, 124.9, 132.4, 132.7, 132.9, 140.1 (Ar-*C* + Ar-*C*=C(CH$_3$), 152.5 (s, C(O)*C*Me) 200.1 (s, *C*O).

LC-MS: *m/z* 253 $[M-2]^+$, 255 $[M]^+$.

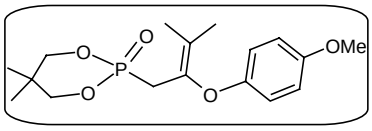
Anal. Calc. for $C_{10}H_{11}O_2Br$: C, 51.79; H, 4.35. Found: C, 51.74; H, 4.33.

3.11 Reactions of allenylphosphonates with phenols- synthesis of allylic/vinylic-phosphonyl ethers

(a) Reaction of allene 7c with phenol- Synthesis of allylic phosphono ether 71

To a solution of allene **7c** (1.04 g, 3.85 mmol) and phenol (4.62 mmol) in DMSO (4 mL) was added a 10% solution of DBU in DMSO (0.25 mL, corresponds to 0.025 g of DBU, 0.167 mmol), and the mixture heated at 80 ^oC for 6-8 h. Quenching with water (2 x 10 mL), and extraction with DCM (2 x 50 mL), removal of solvent and purification by silica gel column chromatography using hexane and ethyl acetate (1:4) afforded **71**.

$(OCH_2CMe_2CH_2O)P(O)CH_2$-C(O-4-MeO-$C_6H_4$)$CMe_2$ (71)



Yield: 1.12 g (85 %).

Mp: 66-69 ^oC.

IR (KBr): 2934, 2735, 2052, 1712, 1686, 1636, 1507, 1213, 828 cm^{-1}.

^1H NMR: δ 1.07 and 1.10 (2 s, 6 H, $C(CH_3)_2$), 1.73 (d, ^5J(P-H) = 6.0 Hz, 3 H, $C=C(CH_3)_2$(A)), 1.84 (d, ^5J(P-H) = 4.8 Hz, 3 H, $C=C(CH_3)_2$(B)), 2.87 (d, ^2J(P-H)= 21.2 Hz, 2 H, PCH_2), 3.79 (s, 3 H, OCH_3), 3.94 and 4.15 (2 dd → t, ^3J(P-H) = ^3J(H-H) = 11.6 Hz, 4 H, OCH_2), 6.84 (s, 4 H, Ar-*H*).

^{13}C NMR: δ 17.7 and 19.2 (2 d, ^4J(P-C) = 3.0 Hz, $C=C(CH_3)_2$), 21.4 and 21.7 (2 s, $C(CH_3)_2$), 26.3 (d, ^1J(P-C) = 137.0 Hz, PCH_2), 32.6 (d, ^3J(P-C) = 6.0 Hz, $C(CH_3)_2$), 55.8 (s, OCH_3) 75.7_8 and 75.8_4 (2 s, OCH_2), 123.3 (d, ^3J(P-C) = 12.0 Hz, $C=C(CH_3)_2$), 135.7 (d, ^2J(P-C) = 5.0 Hz, $C=C(CH_3)_2$), 114.9, 117.0, 149.8_9, 149.9_1, 154.9 [*cf.* Fig. 33].

^{31}P NMR: δ 20.2.

LC-MS: *m/z* 341 $[M+1]^+$.

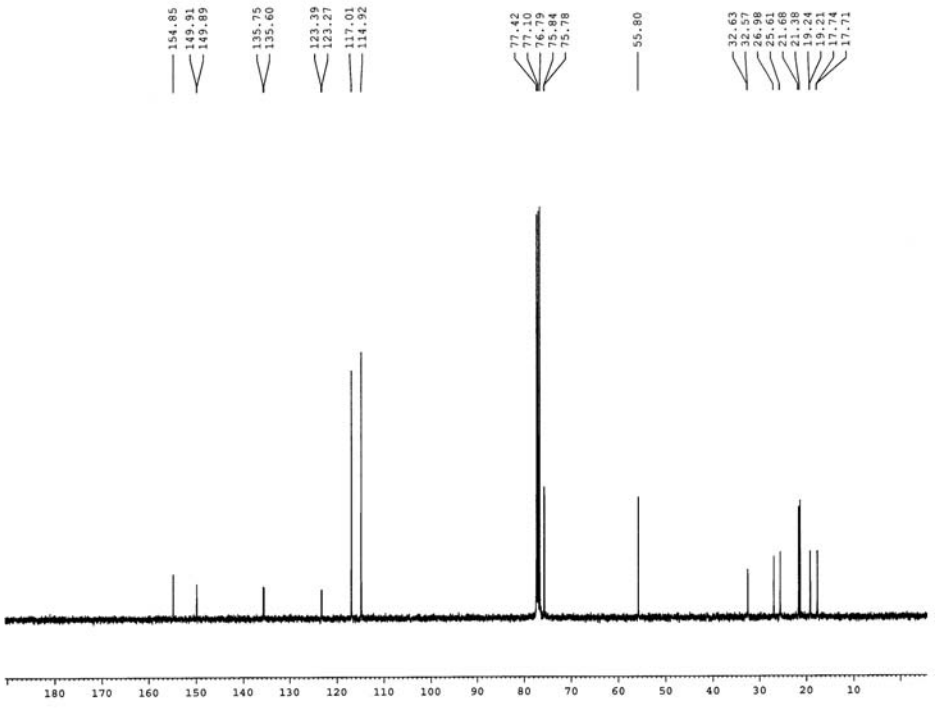
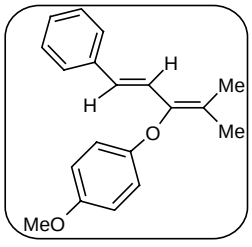


Fig. 33. ^{13}C NMR spectrum of compound **71**

(b) Utility of allylic phosphono ether 71- Synthesis of trans-1,3-[C_6H_5-CH=CH-C(O-C_6H_4-4-OMe)=CMe_2] (72) via HWE reaction

The phosphonate **71** (1.12 g, 2.83 mmol) in THF (15 mL) was slowly added to a suspension of NaH (0.27 g, 11.3 mmol) in THF (30 mL) at 0°C (5 min); the mixture was stirred at this temperature for 0.5 h. Then benzaldehyde (0.27 g, 2.55 mmol) in THF (10 mL) was added and the mixture stirred for 6 h at room temperature. Water (5 mL) was added and the aqueous layer extracted with ether (3x30 mL). The organic layer was collected, dried (Na_2SO_4), filtered and solvent removed from the filtrate to give a residue that was purified by column chromatography (ethyl acetate-hexane) to obtain **72.** Yield is based on the aldehyde.



Yield: 0.52 g (73%).

Mp: 68-70 °C.

IR (KBr): 3057, 2909, 1644, 1595, 1503, 1447, 1211, 1038, 957 cm^{-1}.

^{1}H NMR: δ 1.73 and 1.98 (2 s, 6 H, C=C(CH_3)$_2$), 3.75 (s, 3 H, -OCH_3), 6.54 (d, ^{3}J(H-H) = 15.6 Hz, 1 H, =C*H*), 6.79-6.87 (m, 4 H, Ar-*H*), 7.03 (d, ^{3}J(H-H) = 15.6 Hz, 1H, =C*H*), 7.17–7.36 (m, 5 H, Ar-*H*).

^{13}C NMR: δ 18.9 and 19.0 (2 s, 2 CH_3), 55.8 (s, OCH_3), 114.8, 115.4, 119.9, 125.3, 126.5, 127.4, 128.3, 128.6, 137.5, 144.0, 152.1 and 154.0 [*cf.* Fig. 34].

X-ray structure was determined for this compound.

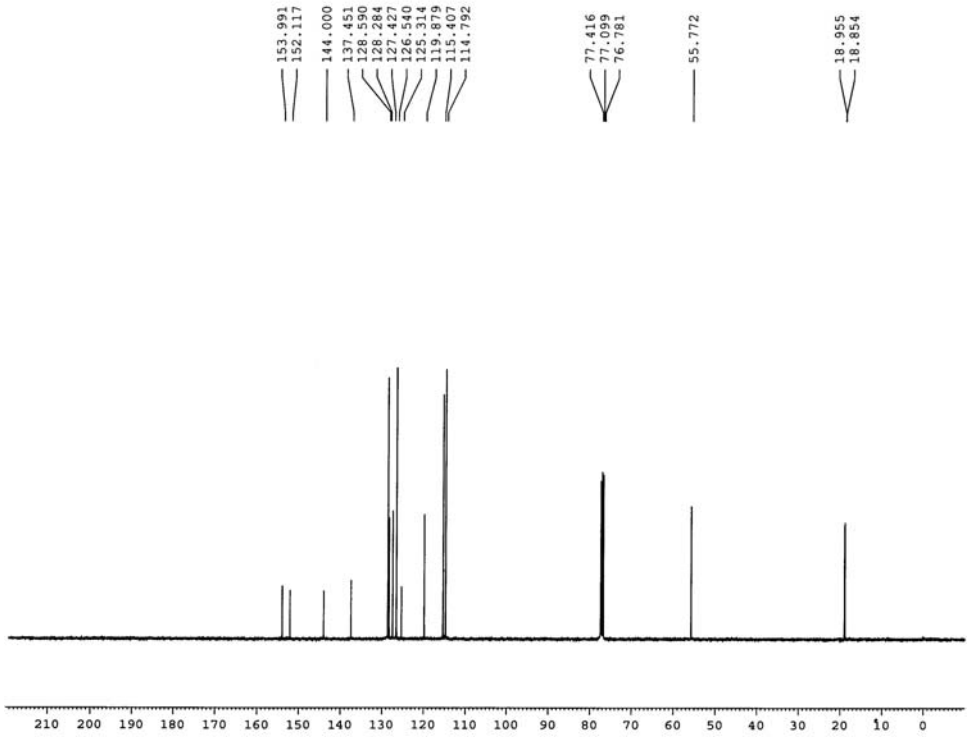


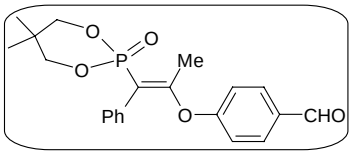
Fig. 34. ^{13}C NMR spectrum of compound **72**

(c) Reaction of allene 7e with phenols-synthesis of vinylphosphono ethers (73-74)

The procedure was similar to that described for **71**, using allene **7e** (0.422 g, 1.67 mmol) and phenol (2.51 mmol). The products were isolated by column chromatography using ethyl acetate and hexane (1:4). We separated the *E* and *Z* isomers. Yields using the *same* molar quantities were above 95% for all these compounds on the basis of ^{31}P NMR spectra of the reaction mixtures.

$(OCH_2CMe_2CH_2O)P(O)C(Ph)=C(O\text{-}4\text{-}CHO\text{-}C_6H_4)Me$ (73)

(i) *E*-isomer



Yield (*E*+*Z*): 0.59 g (92%).

Mp: 172–174 ^oC.

IR (KBr): 3044, 2971, 1696, 1632, 1595, 1503, 1254, 1227, 1059, 1009, 891 cm^{-1}.

^1H NMR: δ 0.70 and 1.04 (2 s, 6 H, $C(CH_3)_2$), 2.52 (s, 3 H, $C=C(CH_3)$), 3.58 (dd→t, ^3J(P-H) = ^2J(H-H) = 12.0 Hz, 2 H, OCH_2), 4.11-4.16 (m, 2 H, OCH_2), 6.99-7.83 (m, 9 H, Ar-*H*), 9.93 (s, 1 H, C*H*O).

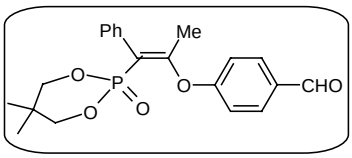
^{13}C NMR: δ 18.3 (s, $C=C(CH_3)$), 21.1 and 21.7 (2 s, $C(CH_3)_2$), 32.4 (d, ^3J(P-C) = 6.1 Hz, $C(CH_3)_2$), 75.5$_7$ and 75.6$_3$ (2 s, OCH_2), 116.9 (d, ^1J(P-C) = 187.1 Hz, P*C*), 118. 4, 127.5$_7$, 127.5$_9$, 128.1$_1$, 128.1$_2$, 129.9, 130.0, 131.7, 131.9, 132.0, 133.6, 133.7, 159.9, 163.6 (d, ^2J(P-C) = 31.9 Hz, PC(Ph)=*C*), 190.7 (s, *C*HO).

^{31}P NMR: δ 12.5.

LC-MS: *m/z* 387 $[M+1]^+$.

Anal. Calc. for $C_{21}H_{23}O_5P$: C, 65.28; H, 6.00. Found: C, 65.29; H, 5.98.

(ii) *Z*-isomer



Yield (*E*+*Z*): 0.59 g (92 %).

Mp: 174–176 ^oC.

IR (KBr): 3052, 2963, 1688, 1634, 1597, 1505, 1262, 1237,1154, 1061, 1007, 831 cm^{-1}.

^1H NMR: δ 0.83 and 1.05 (2 s, 6 H, $C(CH_3)_2$), 1.88 (s, 3 H, $C=C(CH_3)$), 3.65-3.70 (m, 2 H, OCH_2), 3.91 (dd→t, ^3J(P-H) = ^2J(H-H) = 12.0 Hz, 2 H, OCH_2), 7.20-791 (m, 9 H, Ar-*H*), 9.95 (s, 1 H, C*H*O).

^{13}C NMR: δ 17.7 (d, ^3J(P-C) = 10.8 Hz, $C=C(CH_3)$), 21.3 and 21.8 (2 s,

C(CH$_3$)$_2$), 32.4 (d, ^3J(P-C) = 6.1 Hz, C(CH$_3$)$_2$), 75.8 and 75.9 (2 s, OCH$_2$), 118.5, 118.9 (d, ^1J(P-C) = 176.1 Hz, PC), 128.1$_1$, 128.1$_3$,128.8, 129.9$_8$, 130.0$_2$, 132.0,132.2, 134.4$_7$, 134.5$_4$, 160.2, 162.1 (s, PC(Ph) = C), 190.8 (s, CHO).

^{31}P NMR: δ 11.3.

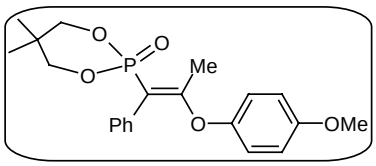
LC-MS: *m/z* 387 $[M+1]^+$.

Anal. Calc. for $C_{21}H_{23}O_5P$: C, 65.28; H, 6.00. Found: C, 65.36; H, 6.01.

X-ray structure was determined for this compound.

(OCH$_2$CMe$_2$CH$_2$O)P(O)C(Ph)=C(O-4-OMe-C$_6$H$_4$)Me (74)

(i) *E*- isomer



Yield (*E*+*Z*): 0.58 g (90%).

Mp: 174–177 ^{o}C.

IR (KBr): 3048, 2975, 2894, 1626, 1591, 1505, 1441, 1250, 1211, 1060, 1036, 1009 cm^{-1}.

^{1}H NMR: δ 0.65 and 0.95 (2 s, 6 H, C(CH_3)$_2$), 2.34 (s, 3 H, C=C(CH_3)), 3.56-3.62 (m, 2 H, OCH_2), 3.75 (s, 3 H, OCH_3) 4.81 (dd→t, ^3J(P-H) = ^2J(H-H) = 10.2 Hz, 2 H, OCH_2), 6.77-6.83 (m, 4 H, Ar-OCH$_3$-H), 7.22-7.35 (m, 5 H, Ar-H).

^{13}C NMR: δ 17.6 (s, C=C(CH$_3$)), 21.2 and 21.7 (2 s, C(CH$_3$)$_2$), 32.3 (d, ^3J(P-C) = 5.6 Hz, C(CH$_3$)$_2$), 55.7 (s, OCH$_3$), 75.2 and 75.3 (2 s, OCH$_2$), 110.3 (d, ^1J(P-C) = 194.4 Hz, PC), 114.6, 121.2, 127.1, 128.0, 130.5$_5$, 130.5$_9$, 134.7, 147.9, 156.4, 166.2 (d, ^2J(P-C) = 32.5 Hz, PC(Ph)=C) [*cf.* Fig. 35].

^{31}P NMR: δ 15.2.

LC-MS: *m/z* 389 $[M+1]^+$.

Anal. Calc. for $C_{21}H_{25}O_5P$: C, 64.94; H, 6.49. Found: C, 64.91; H, 6.46.

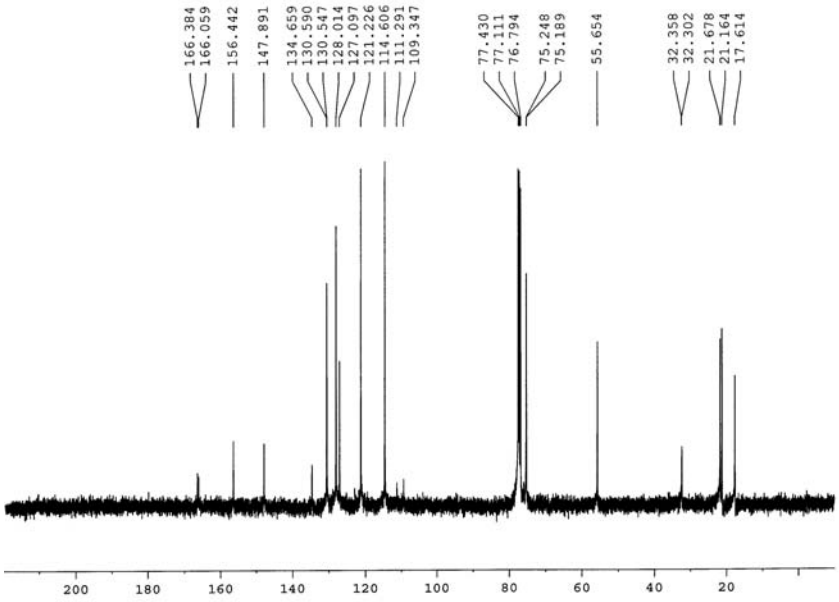
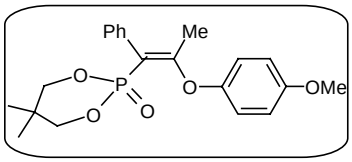


Fig. 35. ^{13}C NMR spectrum of compound (*E*)**-74**

(ii) *Z*-isomer



Yield(*E*+*Z*): 0.58 g (90%).

Mp: 159–162 ^{o}C.

IR (KBr): 3050, 3000, 2967, 1632, 1593, 1507, 1373, 1260, 1196, 1173, 1059, 1007 cm^{-1}.

^{1}H NMR: δ 0.87 and 1.08 (2 s, 6 H, C(CH_3)$_2$), 1.75 (s, 3 H, C=C(CH_3)), 3.75 (dd, ^{3}J(P-H) = 8.0 Hz, ^{2}J(H-H) = 12.0 Hz, 2 H, OCH_2), 3.79 (s, 3 H, OCH_3), 3.89-3.97 (m, 2 H, OCH_2), 6.85-7.07 (m, 4 H, Ar-*H*), 7.27-7.35 (m, 5 H, Ar-*H*).

^{13}C NMR: δ 17.4 (d, ^{3}J(P-C) = 11.0 Hz, C=C(*C*H$_3$)), 21.4 and 21.9 (2 s, C(*C*H$_3$)$_2$), 32.4 (d, ^{3}J(P-C) = 7.0 Hz, *C*(CH$_3$)$_2$), 55.7(s, O*C*H$_3$), 75.6$_8$ and 75.7$_4$ (2 s, O*C*H$_2$), 113.2 (d, ^{1}J(P-C) = 177.0 Hz, P*C*), 114.7, 121.0, 121.3, 127.5$_6$, 127.5$_8$, 128.6, 130.4, 130.5, 135.3$_6$, 135.4$_3$, 148.4, 156.5, 164.9 (s, PC(Ph)=*C*) [*cf.* Fig. 36].

^{31}P NMR: δ 11.1.

LC-MS: *m/z* 389 [M+1]$^{+}$.

Anal. Calc. for $C_{21}H_{25}O_5P$: C, 64.94; H, 6.49. Found: C, 65.05; H, 6.44.

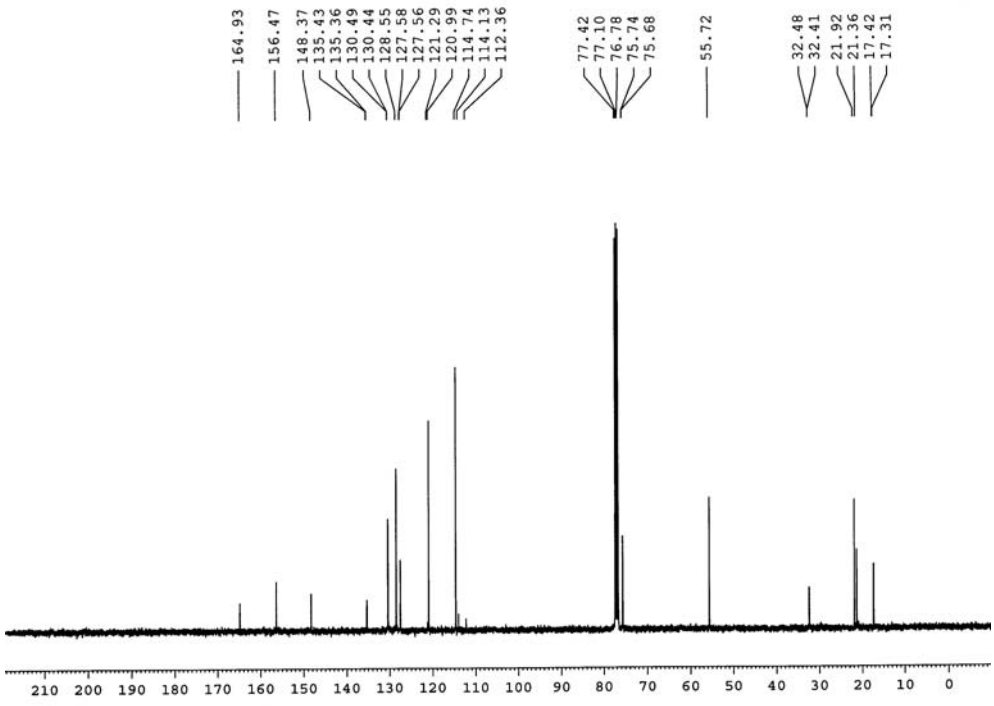
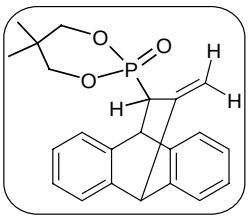


Fig. 36. ^{13}C NMR spectrum of compound (*Z*)**-74**

3.12 Reaction of allene 7a with anthracene: Synthesis of tetracyclic adducts 76 and 77 (*Note*: Compound 75, a possible product, was not formed)

A mixture of allenylphosphonate **7a** (0.43 g, 1.57 mmol) and anthracene (0.98 g, 5.50 mmol) in xylene (3 mL) was heated under reflux for 24 h. The solvent was distilled off. The combined yield of these compounds was 80% (76/77:1/4) on the basis of ^{31}P NMR spectrum of the reaction mixture. The residue was passed through silica gel column and compounds were purified by crystallization in hexane-dichloromethane because both were having the same R_f values.

Compound 76



Yield: 0.35 g (61%)

Mp: 176-178 ^{o}C

IR (KBr): 3010, 2885, 2298, 1467, 1270, 1056, 1003, 911 cm^{-1}.

^{1}H NMR: δ 0.89 and 1.03 (2 s, 6 H, C(C*H*$_3$)$_2$), 3.15 (d, ^{2}J(P-H) = 23.2 Hz, 1 H, PC*H*), 3.42-3.45 and 3.72-3.76 (2 m, 2 H, PCC*H* + PCCC*H*), 3.94

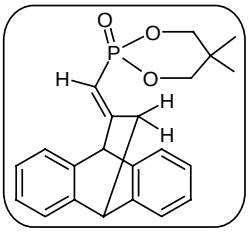
and 4.15 (2 dd, ^{3}J(H-H) = 10.8 Hz, ^{3}J(P-H) ~ 6.4 Hz, 2 H, OCH_2), 4.80–4.82 (m, 2 H, OCH_2), 5.18 and 5.36 (2 d, ^{2}J(H-H) = 4.8 Hz, CH_2) 7.11-7.42 (m, 8 H, Ar-*H*).

^{13}C NMR: δ 21.7 and 22.3 (2 s, C(CH$_3$)$_2$), 32.8 (d, ^{3}J(P-C) = 6.2 Hz, C(CH$_3$)$_2$), 43.0 (d, ^{1}J(P-C) = 138.3 Hz, PC), 45.2 (s, PCCH), 55.4 (d, ^{3}J(P-C) = 4.0 Hz, PCCCH) 74.5 and 75.3 (2 d, ^{2}J(P-C) = 6.3 Hz, OCH$_2$), 111.3 (d, ^{2}J(P-C) = 6.7 Hz, C=CH$_2$), 123.4, 123.5, 123.6, 123.7, 125.4, 126.2, 126.3,126.6, 140.1, 141.3, 142.0, 142.1, 143.0.

^{31}P NMR: δ 22.8.

LC-MS: *m/z* 367 [M+1]$^{+}$.

Compound 77



Yield: 0.04 g (7%)

Mp: 168-172 ^{o}C

IR (KBr): 2922, 2852, 2301, 1627, 1463, 1264, 1060, 1007, 909 cm^{-1}.

^{1}H NMR: δ 0.99 and 1.05 (2 s, 6 H, C(CH_3)$_2$), 2.83-2.85 (m, 2 H, PC=CCH_2), 3.67-4.12 (m, 4 H, OCH_2), 4.49 (br s, 1 H, C=C(CH$_2$)CH), 4.84 (s, 1 H, C=CCH), 5.78 (d, ^{2}J(P-H) = 19.6 Hz, 1 H, PCH) 7.11-7.32 (m, 8 H, Ar-*H*).

^{13}C NMR: δ 21.7 and 22.3 (2 s, C(CH$_3$)$_2$), 32.8 (d, ^{3}J(P-C) ~ 6.2 Hz, C(CH$_3$)$_2$), 36.0 (s, C=C(CH$_2$)CH), 44.6 (s, C=C(CH$_2$)), 58.1 (d, ^{3}J(P-C) = 23.3 Hz, PC=CCH) , 74.9 and 75.0 (2 s, OCH$_2$), 106.4 (d, ^{1}J(P-C) = 187.3 Hz, PC), 123.7, 124.0, 126.3,126.7, 139.8, 143.0.

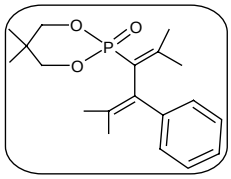
^{31}P NMR: δ 13.6.

LC-MS: *m/z* 367 [M+1]$^{+}$.

X-ray structure was determined for this compound.

3.13 Reaction of phenylboronic acid with phosphonate-allenol 8b: P*reparation of* [$(OCH_2CMe_2CH_2O)(O)P$-$C(=CMe_2)$-$(C(Ph)=(CMe_2)]$ (79)

A mixture of allenylphosphonate **8b** (0.43 g, 1.57 mmol), phenylboronic acid (0.23 g, 1.89 mmol) and $Pd(PPh_3)_4$ (5 mol%) in THF (30 mL) was stirred at room temperature for 24 h. The solvent was removed and compound **79** was purified by column chromatography (hexane-ethyl acetate).



Yield: 0.13 g (25%).

Mp: 216-218 ^{o}C.

IR (KBr): 3059, 2975, 2932, 1644, 1480, 1362, 1260, 1063, 984, 833 cm^{-1}.

^{1}H NMR: δ 0.75 and 1.01 (2 s, 6 H, $C(CH_3)_2$), 1.36 and 1.64 (2 s, 12 H, $C=C(CH_3)_2$), 3.48 (dd → t, ^{3}J(P-H) = ^{3}J(H-H) = 10.8 Hz, 2 H, OCH_2), 3.84 (dd → t, ^{3}J(P-H) = ^{3}J(H-H) = 11.7 Hz, 2 H, OCH_2), 7.28-7.37 (m, 5 H, Ar-*H*).

^{13}C NMR: δ 21.6, 21.9 (2 s, $C(CH_3)_2$), 28.4 and 30.0 (2 s, 2 $C=C(CH_3)_2$), 32.4 (d, ^{3}J(P-C) = 6.6 Hz, $C(CH_3)_2$), 75.3 and 75.4 (2 s, OCH_2), 88.7 (d, ^{2}J(P-C) = 22.3 Hz, $PC=C(CH_3)_2$), 89.2 (d, ^{3}J(P-C) = 19.7 Hz, $(Ph)C=C(CH_3)_2$), 127.9, 128.3, 128.4, 133.9 (Ar*C*), 129.9 (d, ^{1}J(P-C) = 183.7 Hz, P*C*), 160.7 (d, ^{2}J(P-C) = 9.9 Hz, PC=*C*(Ph)).

^{31}P NMR: δ 8.7.

LC-MS: *m/z* 335 $[M+1]^{+}$.

3.14 X-ray crystallography

A suitable crystal was mounted on a glass fiber (for **8a**, **10**, **16**, **17a-c**, **20**.H_2O, **33**, **34**, **36**, **38**, **52**, (*E*)-**56**, (*Z*)-**56**, (*Z*)-**66**, (*E*)-**67a**, (*E*)-**68a**, *trans*-**69b**, **70a**, (*E*)- **72,** (*Z*)-(**73**) and **77**) and X-ray data were collected at 293 K on an Enraf-Nonius MACH3 or on a Bruker AXS-SMART diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Structures were solved and refined using standard methods.[120] Absorption corrections were done using SADABS program, where applicable. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a Difference Fourier and refined isotropically. The terminal

carbon atoms of the *t*-butyl groups showed higher thermals than the N-C carbon for the compounds **16** and **17a-c**. Crystal data are summarized in Tables 5-10.

Table 5. Crystal data for compounds **8a, 10, 16 and 17a**[a]

Compd	**8a**	**10**	**16**	**17a**
Emp. formula	$C_9H_{15}O_4P$	$C_{11}H_{14}O_6P_2$	$C_{14}H_{24}N_2O_2P_2$	$C_{18}H_{32}N_2O_2P_2$
Formula weight	218.18	304.16	314.29	370.40
Crystal system	Monoclinic	Tetragonal	Orthorhombic	Monoclinic
Space group	*P2₁/n*	*I4(1)/a*	*Pnca*	*P2₁/c*
a /Å	8.7632(8)	12.9203(4)	11.556(2)	10.1983(13)
b /Å	9.3504(9)	12.9203(4)	17.406(4)	10.8569(14)
c /Å	13.8022(13)	16.8163(11)	18.298(4)	21.244(3)
α/deg	90	90	90	90
β/deg	105.62(10)	90)	90	100.984(2)
γ/deg	90	90	90	90
V /Å^3	1089.18(18)	2807.2(2)	3680.5(13)	2309.1(5)
Z	4	8	8	4
D_{calc} /g cm^{-3}]	1.331	1.439	1.134	1.065
μ /mm^{-1}	0.240	0.328	0.239	0.199
F(000)	464	1264	1344	800
Data/ restraints/ parameters	2634/ 0/ 138	1369/ 0/ 115	3240/ 0/ 203	4058/ 0 /227
S	1.024	1.095	1.075	1.019
R1 [I>2σ(I)]	0.0448	0.0334,	0.0493	0.0618
wR2 [all data]	0.1314	0.0943	0.1528	0.2020
Max./min. residual electron dens. [eÅ^{-3}]	0.381/ -0.251	0.239/ -0.240.	0.501/ -0.247	0.465/ -0.172

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 6. Crystal data for compounds **17b, 17c, 20**.H_2O and **33**[a]

Compd	**17b**	**17c**	**20**.H_2O	**33**
Emp. formula	$C_{18}H_{32}N_2O_2P_2$	$C_{17}H_{35}N_3O_2P_2$	$C_{30}H_{42}N_2O_7P_2$	$C_{18}H_{31}N_2O_6P$
Formula weight	370.40	375.42	604.60	402.42
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	*P2(1)/n*	$P\bar{1}$	$P2_1/n$
a /Å	7.5400(15)	9.4506(8)	8.786(2)	6.1082(6)
b /Å	8.9400(18)	13.7169(12)	12.570(3)	18.912(2)
c /Å	9.4900(19)	16.9175(14)	15.540(3)	19.611(2)
α/deg	62.84(3)	90	95.41(3)	90
β/deg	74.57(3)	96.5510(10)	97.33(3)	92.129(2)
γ/deg	89.33(3)	90	107.32(3)	90
V /Å^3	544.1(3)	2178.7(3)	1609.1(6)	2263.9(4)
Z	2	4	2	4
D_{calc} /g cm^{-3}]	1.130	1.145	1.248	1.181
μ /mm^{-1}	0.212	0.213	0.181	0.154
F(000)	200	816	644	864
Data/ restraints/ parameters	1922 /0 /114	3838 / 0/ 236	5667 /3 /403	3921/ 1/ 272
S	1.093	1.075	1.035	1.053
R1 [I>2σ(I)]	0.0652	0.0680	0.0591	0.0809
wR2 [all data]	0.1922	0.2096	0.1630	0.2496
Max./min. residual electron dens. [eÅ^{-3}]	0.639/-0.431	0.832/ -0.530	0.524/ -0.325	0.865/ -0.406

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 7. Crystal data for compounds **34, 36.H_2O, 38** and **52**[a]

Compd	**34**	**36.H_2O**	**38**	**52**
Emp. formula	$C_{14}H_{25}N_2O_4P$	$C_5H_{13}O_5P$	$C_{17}H_{22}N_2O_3$	$C_{22}H_{22}NO_2P$
Formula weight	316.33	184.12	302.37	363.38
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	*P2(1)/c*	*P2(1)2(1)2(1)*	$P\bar{1}$	*C2/c*
a /Å	6.9482(6)	6.1020(7)	10.8487(7)	17.8243(12)
b /Å	12.8961(11)	9.0781(10)	11.0447(7)	12.1139(8)
c /Å	19.833(16)	16.0975(17)	15.7402(10)	18.3548(13)
α/deg	90	90	95.532(10)	90
β/deg	99.45(10)	90	105.549(10)	104.222(10)
γ/deg	90	90	106.892(10)	90
V /Å^3	1753.0(3)	891.71(17)	1707.22(19)	3841.7(5)
Z	4	4	4	8
D_{calc} /g cm^{-3}]	1.199	1.371	1.176	1.257
μ /mm^{-1}	0.172	0.286	0.081	0.159
F(000)	680	392	648	1536
Data/ restraints/ parameters	3093/ 0/ 200	1566/ 0/ 114	5990/ 0/ 407	4664/ 0/ 237
S	1.059	1.053	1.027	1.037
R1 [I>2σ(I)]	0.0426	0.035	0.0484	0.0459
wR2 [all data]	0.1189	0.0942	0.1321	0.1249
Max./min. residual electron dens. [eÅ^{-3}]	0.264/ -0.258	0.272/ -0.220	0.313/ -0.209	0.378/ -0.233

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 8. Crystal data for compounds (*E*)-**56,** (*Z*)-**56,** (*Z*)-**66** and (*E*)-**67a**[a]

Compd	(*E*)-**56**	(*Z*)-**56**	(*Z*)-**66**	(*E*)-**67a**
Emp. formula	$C_{21}H_{20}BrO_4P$	$C_{21}H_{20}BrO_4P$	$C_{17}H_{23}O_5P$	$C_{16}H_{21}O_5P$
Formula weight	447.25	447.25	338.32	324.30
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P2(1)/c*	*P2(1)/c*	*P2(1)/c*	*C2/c*
a /Å	17.2552(15)	17.0547(18)	12.5236(11)	30.604(6)
b /Å	6.9174(6)	8.9540(9)	12.5105(11)	9.5310(19)
c /Å	17.6626(16)	12.7659(13)	11.2515(10)	11.840(2)
α/deg	90	90	90	90
β/deg	110.8840(10)	96.655(2)	96.7480(10)	109.73(3)
γ/deg	90	90	90	90
V /Å^3	1969.7(3)	1936.3(3)	1750.6(3)	3251.0(11)
Z	4	4	4	8
D_{calc} /g cm^{-3}]	1.508	1.534	1.284	1.325
μ /mm^{-1}	2.192	2.230	0.179	0.189
F(000)	912	912	720	1376
Data/ restraints/ parameters	3461/ 0/ 246	3406/ 0/ 246	3081/ 0/ 213	2858/ 0/ 203
S	1.086	1.133	1.036	1.036
R1 [I>2σ(I)]	0.0459	0.0348	0.0743	0.0490
wR2 [all data]	0.1357	0.1027	0.2282	0.1433
Max./min. residual electron dens. [eÅ^{-3}]	0.986/ -0.693	0.534/ -0.313	1.708/ -0.474	0.845/ -0.303

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 9. Crystal data for compounds (*E*)-**68a**, *trans*-**69a**, **70a** and (*E*)-**72**[a]

Compd	(*E*)-**68a**	**69a**	**70a**	(*E*)-**72**
Emp. formula	$C_{16}H_{19}O_4P$	$C_{16}H_{20}BrO_5P$	$C_{11}H_{12}O_2$	$C_{76}H_{80}O_8$
Formula weight	306.28	403.20	176.21	1121.40
Crystal system	Monoclinic	Tetragonal	Orthorhombic	Orthorhombic
Space group	*Pnma*	*I-4*	*Pna2(1)*	*P2(1)2(1)2(1)*
a /Å	20.990	21.347(2)	17.335(3)	20.479(4)
b /Å	7.0721(14)	21.347(2)	7.6229(12)	14.045(3)
c /Å	10.640(2)	16.098(2)	13.737(2)	5.577(1)
α/deg	90	90	90	90
β/deg	90	90	90	90
γ/deg	90	90	90	90
V /Å^3	1579.5(5)	3423.6(9)	1815.3(5)	1604.2(6)
Z	4	8	8	1
D_{calc} /g cm^{-3}]	1.288	1.565	1.289	1.161
μ /mm^{-1}	0.186	2.516	0.088	0.074
F(000)	648	1648	752	600
Data/ restraints/ parameters	1513/ 0/1.081	3000/ 0/ 212	1674/ 1/ 229	2798/ 0/ 193
S	1.081	1.053	1.242	1.429
R1 [I>2σ(I)]	0.0436	0.0463	0.0679	0.0745
wR2 [all data]	0.1205	0.1222	0.1592	0.1435
Max./min. residual electron dens. [eÅ^{-3}]	0.224/ -0.247	0.845/ -0.737	0.229/ -0.275	0.158/ -0.225

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

Table 10. Crystal data for compounds (*Z*)-**73** and **77**[a]

Compd	(*Z*)-**73**	**77**
Emp. formula	$C_{21}H_{23}O_5P$	$C_{22}H_{23}O_3P$
Formula weight	386.36	521.55
Crystal system	Monoclinic	Orthorhombic
Space group	*P2(1)/n*	*Pnma*
a /Å	13.137(3)	23.597(9)
b /Å	6.3248(16)	13.366(5)
c /Å	24.567(6)	6.132(3)
α/deg	90	90
β/deg	98.279(4)	90
γ/deg	90	90
V /Å^3	2809.4(4)	1934.0(14)
Z	4	4
D_{calc} /g cm^{-3}]	1.270	1.258
μ /mm^{-1}	0.164	0.160
F(000)	816	776
Data/ restraints/ parameters	3572/ 0/ 247	1782/ 0/ 135
S	1.145	1.257
R1 [I>2σ(I)]	0.0634	0.0679
wR2 [all data]	0.1429	0.1415
Max./min. residual electron dens. [eÅ^{-3}]	0.311/ -0.276	0.275/ -0.301

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

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PART B

REACTIVITY OF PHOSHORUS(III) COMPOUNDS WITH ACTIVATED ALKYNES, ALKENES AND ALLENES

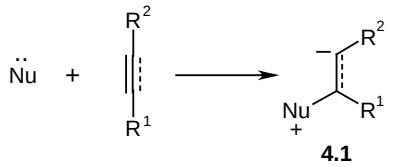
INTRODUCTION

This chapter deals with the literature on the formation of zwitterions from the reactions of phosphorus(III) compounds with unsaturated systems like alkenes, alkynes and allenes in the context of phosphine-catalyzed reactions and their application in the organic synthesis. A brief literature survey on spontaneous resolution is also presented.

4.1 Nucleophilic Catalysis: General Introduction

Addition of a nucleophile to electrophilic π systems, such as alkenes and alkynes generates zwitterionic species such as **4.1** (Scheme 4.1). These are reactive intermediates and can be captured by suitable substrates. After a series of transformations, the nucleophile (catalyst) gets eliminated from the system.

Scheme 4.1



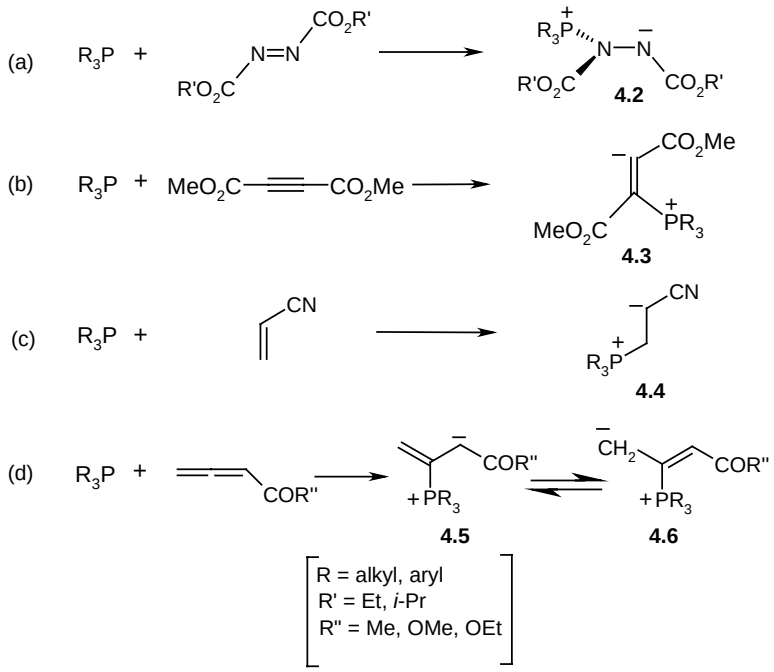
4.1

R^1 = H, Ph, Me, CO_2Me, etc.
R^2 = CO_2Me, CN, COMe, etc.

A number of nucleophiles such as tertiary phosphines, tertiary amines and carbenes have been used to generate zwitterionic intermediates. Among these, tertiary phosphines have been the most studied because (i) the nucleophilicity of the phosphines can be tuned by varying the substitutions on phosphorus, (ii) a phosphonium ion lends exceptional stability to a neighbouring anionic center and (iii) a variety of chiral acyclic and cyclic phosphines are readily available for screening in enantioselective synthesis. Thus phosphine activated/catalyzed reactions of unsaturated systems such as azodicarboxylates, alkynes, alkenes and allenes (Scheme 4.2) have found diverse and useful applications for a variety of

organic transformations. Several recent reviews have appeared on this topic recently.[1]

Scheme 4.2



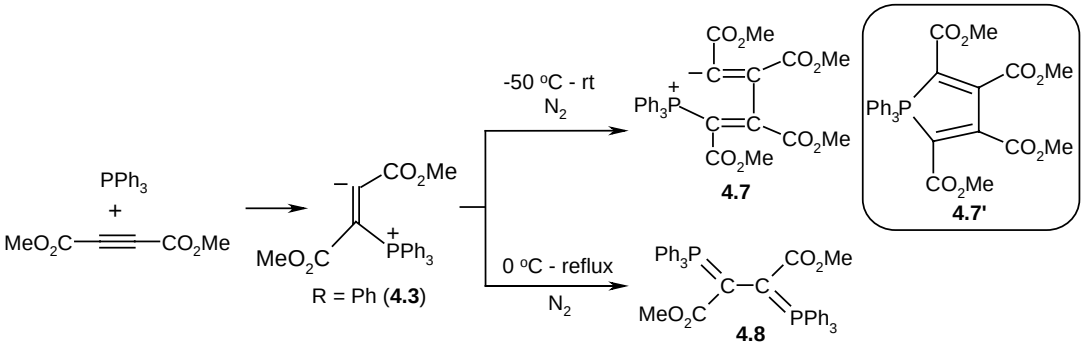
The reaction of triphenylphosphine with dialkyl azodicarboxylate leads to the zwitterion $Ph_3P^+N(CO_2R')$-N^-CO_2R' [**4.2** where R = Ph] which is the well known Morrison-Brunn-Huisgen intermediate (Scheme 4.2a). This combination is widely used in organic synthesis and is the critical component in the synthetically versatile Mitsunobu reaction.[2,3] Our group has worked earlier on the isolation of the Mitsunobu-type intermediates, and has been successful in the isolation and X-ray structural characterization of some of these intemediates.[4] In the phosphine activated reactions of dimethyl acetylenedicarboxylate (DMAD) with electrophiles, the species $R_3P^+C(CO_2Me)=C^-(CO_2Me)$ (**4.3**) is proposed as an intermediate (Scheme 4.2b). Similar intermediates utilizing other activated alkynes have also been proposed,[5] but to our knowledge, there is no structural proof for species of type **4.3**. The intermediate $R_3P^+CH_2CH^-CN$ (**4.4**) is proposed as the first step in phosphine-catalyzed Morita-Baylis-Hillman reaction, Rauhut–Currier reaction and also the polymerization of acrylonitrile (Scheme 4.2c).[6] This species (**4.4**) takes part in phosphine-catalyzed Michael reaction also.[6f] Morita-Baylis-Hillman (MBH) reaction is an atom economy reaction in which an activated alkene couples with an aldehyde or ketone in the presence of neucleophilic catalyst. In the MBH reaction first

reported by Morita and co-workers in 1968, tricyclohexylphosphine was used as a nucleophilic catalyst;[7a] Baylis and Hillman reported the use of a tertiary amine (DABCO) as the catalyst in 1972.[7b] The intramolecular Morita-Baylis-Hillman was first reported by Frater and further investigated by Murphy.[8] In Rauhut–Currier reaction, dimerization of activated alkenes is mediated by phosphines; intramolecular Rauhut–Currier reaction is quite useful for the synthesis of cyclopentene and cyclohexene derivatives.[9] Phosphines react with activated allenes also and give zwitterionic species **4.5** or **4.6** (Scheme 4.2d). These intermediates are involved in the nucleophile catalyzed reactions with electrophiles. Because of the selectivity and diversity of the products, several recent reports have emerged in this area.[10] However, until now, there is no structural proof for such zwitterions. Recently, Yu and co-workers as well as Kwon and co-workers have done theoretical calculations on the stability of such zwitterions; their studies also confirm that generation of a 1,3-dipolar species of type **4.5** or **4.6** is the first step in the phosphine-catalyzed reactions of activated allenes with electrophiles.[11,12]

4.2 Reactions of phosphines with dimethyl acetylenedicarboxylate (DMAD)

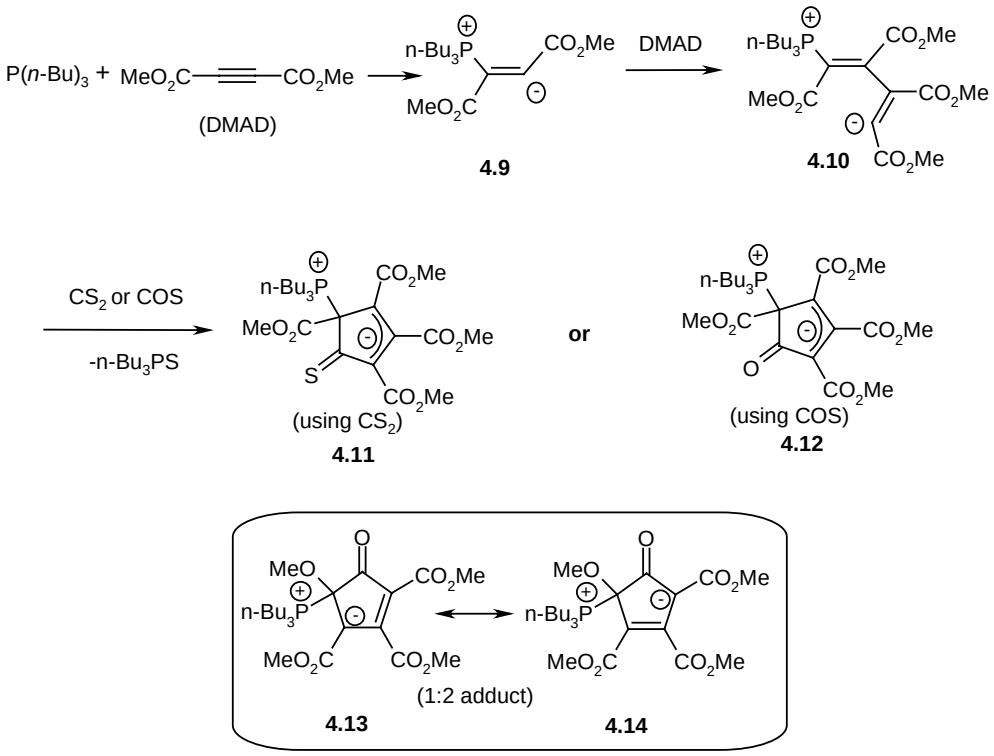
In earlier works of Tebby and co-workers, the reaction of triphenylphosphine (PPh_3) with DMAD at different temperatures/stoichiometries was reported to give different types of products *via* the zwitterion **4.3** (Scheme 4.3).[13a] One of these was the 1:2 adduct **4.7** obtained by performing the reaction at –50 ^oC. Structure **4.7'** (instead of **4.7**) is an alternative but possible structure for the 1:2 adduct. When a similar reaction was done at room temperature using an excess of PPh_3, the 2:1 adduct **4.8** was obtained as the major product.[13b] These results show that one needs to be cautious about the molar ratio of the phosphine to the alkyne while performing these reactions.

Scheme 4.3



In a later work, Aitken and co-workers used tri-*n*-butylphosphine [P(*n*-Bu)$_3$]-DMAD combination in the presence of COS/CS_2 and isolated the 1:2 compounds **4.11**/**4.12** *via* the intermediates **4.9/ 4.10** (Scheme 4.4).[14a] Compounds **4.11** and **4.12** are stabilized by extensive delocalization of the negative charge. They have also synthesized the adduct (*n*-Bu)$_3$P.2DMAD (**4.13**) in low yields from the reaction of P(*n*-Bu)$_3$ with two equivalents of DMAD.[14b] It is interesting to note that this compound is an isomer of the intermediate **4.10**. It is stabilized by extensive delocalization of the negative charge as shown by the two contributing structures **4.13** and **4.14**.

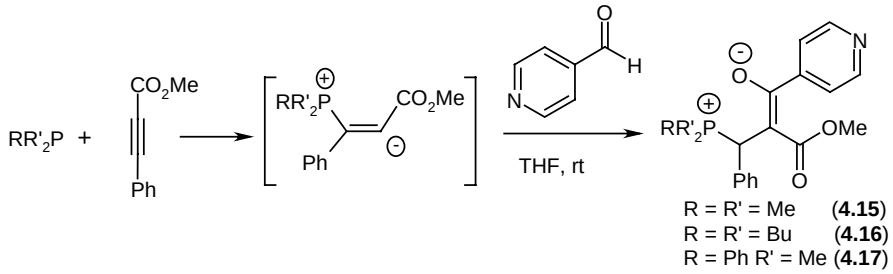
Scheme 4.4



Recently, Kwon and co-workers isolated stable phosphonium enolate zwitterions **4.15-4.17** from the conjugate addition of PMe_3/P(*n*-Bu)$_3$/PMe_2Ph to methyl phenylpropiolate and subsequent nucleophilic addition of the *in situ* generated zwitterions [similar to **4.3**] to 4-pyridinecarboxaldehyde (Scheme 4.5).[15] They have confirmed the structures of all the three by X-ray crystallography. In contrast, the reactions using $PMePh_2$ and PPh_3 did not provide any detectable zwitterions. These results show that electron-releasing alkyl substituents on the

phosphonium center play a critical role in stabilizing phosphonium enolate zwitterions.

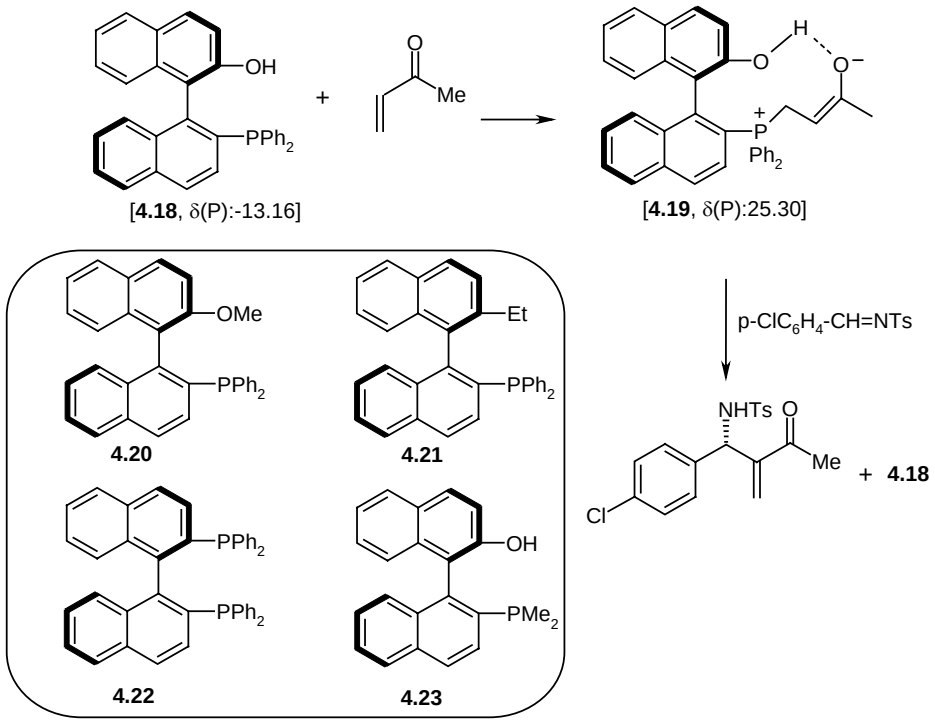
Scheme 4.5



4.3 Reactions of phosphines with activated alkenes

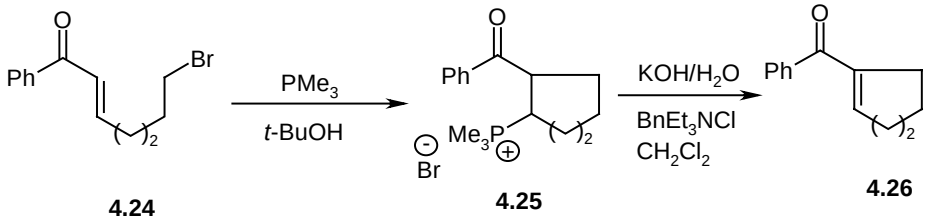
Shi et al. characterized the zwitterionic species **4.19** in the reaction of *N*-sulfonated imine with methyl vinyl ketone in the presence of the chiral phosphine **4.18** (Scheme 4.6) by ^{1}H and ^{31}P NMR spectra.[16a] Compound **4.18** shows a signal at δ –13.16 but after addition of methyl vinyl ketone, a new signal corresponding to the phosphonium enolate **4.19** appears at δ +25.30. The key factor is the intramolecular hydrogen bonding between the phenolic OH and the oxygen atom of carbonyl group that stabilizes the *in situ* formed enolate intermediate. This kind of hydrogen bonding is not possible in the remaining phosphines **4.20-4.22**, but is relevant in the case of **4.23**. Good yields (but low *ee*) of the Baylis-Hillman adducts in the reaction between 2-cyclopenten-1-one with *N*-sulfonated imine were obtained in the presence of **4.23**. Thus in these cases, hydrogen bonding has a role to play in the stabilization of intermediates that lead to the products.

Scheme 4.6



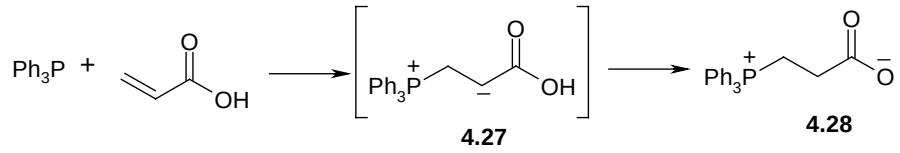
Recently, Krafft and co-workers reported the X-ray structure of ketophosphonium salt **4.25** obtained during the intramolecular Morita-Baylis-Hillman (MBH) reaction of **4.24** using trimethylphosphine as activator (Scheme 4.7). This result supports the proposed mechanistic pathway for the Baylis–Hillman reaction.[16b]

Scheme 4.7



In Phospha-Michael reaction, a zwitterion of type **4.4** (cf. Scheme 4.2c) acts as a base and the reaction proceeds like normal Michael reaction. Galkin and co-workers isolated betaine **4.28** in the reaction of PPh_3 and acrylic acid (Scheme 4.8).[17] This result also provides evidence for the intermediacy of **4.27**, which is similar to **4.4**.

Scheme 4.8

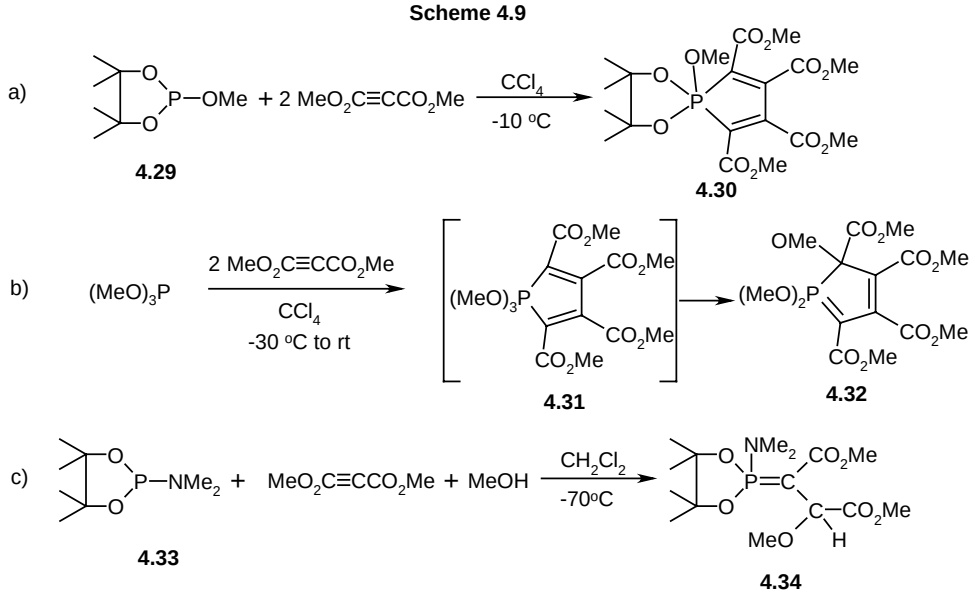


4.27 **4.28**

4.4 Reactions of P^{III} compounds other than phosphines with DMAD

Substituents on phosphorus influence the course of reaction with activated alkynes like DMAD. For example, cyclic phosphite **4.29** (scheme 4.29a) reacts with two equivalents of DMAD and gives pentacoordinate species **4.30,** which is analogous to compound **4.7'.** The corresponding reaction trimethylphosphite gave a pentacoordinate intermediate **4.31** (characterized by ^{31}P NMR) which was converted after 14 h to stable tetracoordinate phosphole **4.32** by the migration of the methoxy group (Scheme 4.9b).[18a] By contrast, the dimethylamino compound **4.33** reacts with DMAD and methanol to give **4.34** (Scheme 4.9c).[18b]

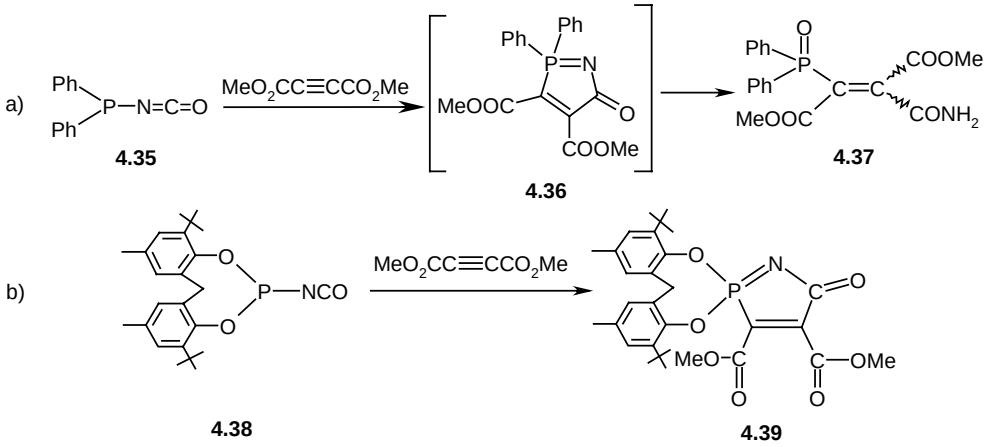
Scheme 4.9



4.29 **4.30** **4.31** **4.32** **4.33** **4.34**

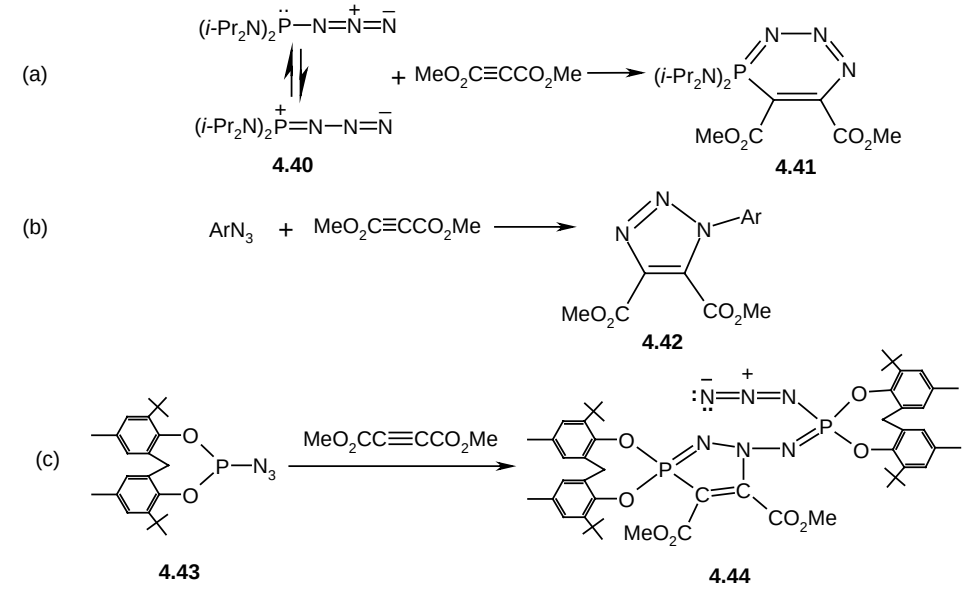
Diphenylisocyanatophosphine **4.35** reacts with DMAD to form the unstable azaphosphole **4.36**, which hydrolyzes to give the tetracoordinate (P=O) compound **4.37** (Scheme 4.10a).[19] More interesting is the reaction of phosphorus(III) isocyanate **4.38** with DMAD resulting in the novel phosphorus based heterocycle **4.39** (Scheme 4.10b) which has been reported from our laboratory.[20]

Scheme 4.10



Bis(diisopropylamino)phosphanyl azide $[(i\text{-}Pr)_2N]_2PN_3$ (**4.40**) undergoes 1,4-dipolar addition with DMAD at room temperature to form the six-membered ring heterocycle **4.41** (Scheme 4.11a).[21] This is in contrast to the formation of five-membered heterocycles **4.42** in the reaction of organic azides with DMAD (Scheme 4.11b).[22] A novel 1,3-(P,N) heterocyclic compound **4.44** was obtained from our laboratory by an unusual mode of cycloaddition reaction of phosphorus(III) azide **4.43** with DMAD (Scheme 4.11c).[20] Thus, although the azide and the isocyanate groups are isoelectronic, their behavior towards DMAD is significantly different (Schemes 4.10b and 4.11c).

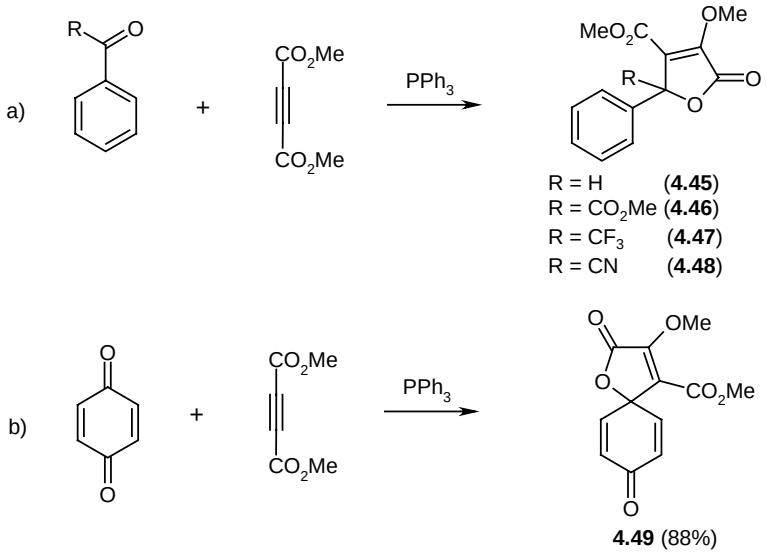
Scheme 4.11



4.5 Application of the zwitterions generated from the reactions of phosphines with activated alkynes in organic synthesis

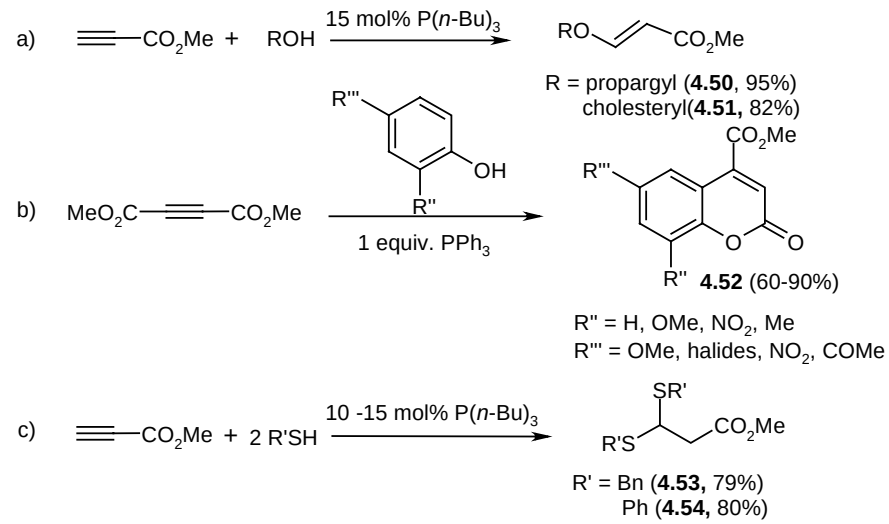
Winterfeldt and co-workers treated DMAD with benzaldehylde in the presence of PPh_3 to obtain γ-lactones **4.45**, albeit in low yields (< 20 %).[23a] Nozaki et al. reported better yields (up to 78 %) of the lactones **4.46**-**4.48** from a similar reaction using activated carbonyls (Scheme 4.12a).[23b] Nair and co-workers used benzoquinone and isolated spiro-fused heterocyclic compounds of type **4.49** in high yields (Scheme 4.12b).[23c]

Scheme 4.12



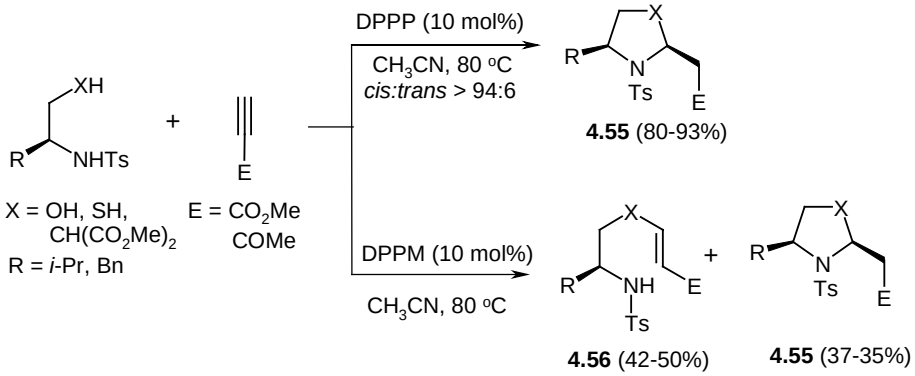
Alcohols react with methyl propiolate in the presence of P(*n*-Bu)$_3$ to give mono-addition products **4.50** and **4.51** *via* Michael addition (Scheme 4.13a).[24a] By contrast, Yavari and co-workers reported that phenols reacted with DMAD in the presence of PPh_3 to give coumarins of type **4.52** in good to excellent yields (Scheme 4.13b).[24b] When thiols like $PhCH_2SH$ or PhSH were treated with methyl propiolate in the presence of P(*n*-Bu)$_3$, the double addition products (dithioacetals) **4.53** and **4.54** were obtained (Scheme 4.13c).[24c]

Scheme 4.13



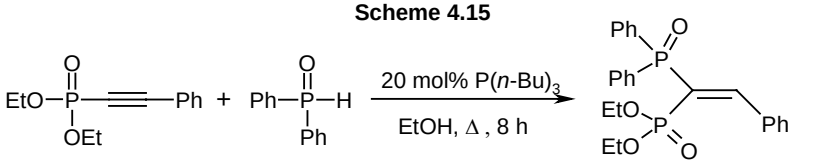
Recently, Sriramurthy et al. reported that bifunctional nucleophiles reacted with electron deficient alkynes in the presence of diphenylphosphinopropane (DPPP) to afford heterocycles of type **4.55** (Scheme 4.14).[25] It was found that the use of bisphosphine DPPM (diphenylphosphinomethane) afforded **4.56** as the major product. This method is convenient for the synthesis of oxazolidines, thiazolidines, pyrrolidines and octahydroindoles in good yields and high stereoselectivity.

Scheme 4.14



Taran and co-workers have prepared 2-aryl-1-vinyl-1,1-diphosphine dioxides very easily from P(*n*-Bu)$_3$ catalyzed reactions.[26] For example, the pronucleophile *H*-phosphine oxide $Ph_2P(O)H$ attacks the α-P position of alkynic phosphonate **4.57** in the presence of P(*n*-Bu)$_3$ to give vinyl-1,1-diphosphine dioxide **4.58** with high selectivity (Scheme 4.15).

Scheme 4.15

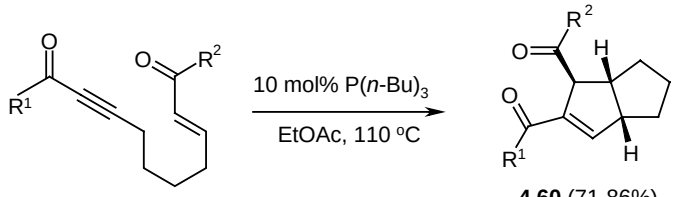


4.57 **4.58** [64%, *Z*/*E* :100/0]

Krische and co-workers have cyclized electron-deficient 1,7-enynes **4.59** in the presence of P(*n*-Bu)$_3$ to obtained diquinanes **4.60** in excellent yield and >95: 5 *diastereomeric excess* (Scheme 4.16a).[27a] The same strategy was used for the total synthesis of hirsutene **4.63** in which a single diastereomer **4.62** was generated in an intermediate step (Scheme 4.16b).[27b]

Scheme 4.16

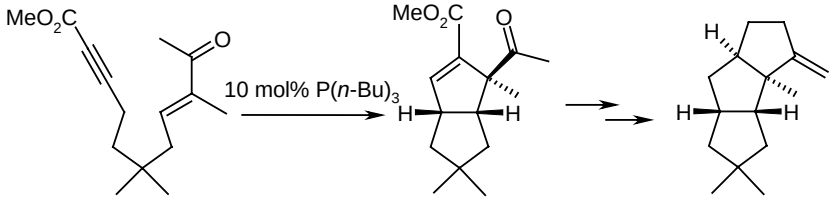
a)



4.59
R^1 = OMe, Me
R^2 = Phenyl, cyclopropyl, Me, SEt

4.60 (71-86%)

b)



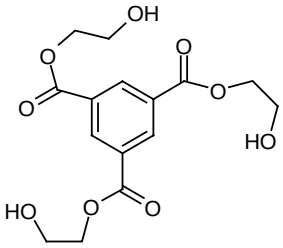
4.61 **4.62** **4.63**
hirsutene

4.6 Spontaneous resolution

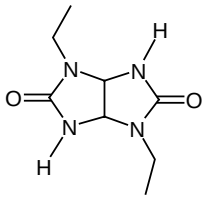
Spontaneous resolution is a phenomenon that involves segregation of enantiomers upon crystallization from an achiral system. The separation of enantiomers takes place because of stereogenic centers, planes of chirality, or atropoisomerism.[28] The occurrence of spontaneous resolution is of increasing interest in the pharmaceutical industry, materials science, and has even been linked to the terrestrial abundance of enantiomers in the natural world.[29] Spontaneous resolution in crystalline solids can be investigated by using several techniques like X-ray structure, CD, NMR and EPR spectroscopy. An X-ray structure on its own does not necessarily prove that spontaneous resolution has taken place because the

bulk of the crystal can be racemic. CD spectroscopy is a simple and better technique for checking the chirality of crystalline solids.

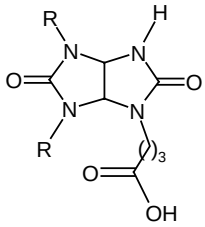
Spontaneous resolution occurs in organic compounds due to non-covalent bonds as well as molecular shape. These factors influence the packing of molecules in crystals.[30a,b] Chart 1 shows compounds **4.64**-**4.69** that undergo spontaneous resolution. Tris(2-hydroxyethyl)-1,3,5-benzenetricarboxylate **4.64** forms a chiral solid in which the helical chains are maintained by O–H…O–C hydrogen bonds and offset π–π stacking between the aromatic cores.[31] Spontaneous resolution occurs in dialkylglycolurils (**4.65**), in which each glycoluril monomer linked to two adjacent monomers by two amide N–H…O–C bonds.[32] Despite minor structural differences between compounds, all form homochiral layers but only some of them undergo spontaneous resolution. For instance, the carboxylic acid glycoluril derivative **4.66** spontaneously resolves while the corresponding ethyl analogue [R = Et with the same skeleton] does not. The achiral zwitterionic molecule 7-(N,N-dimethylpiperazinium)-7-oxo-8,8-dicyanoquinodimethane (DPODQ; **4.67**) is conformationally chiral.[33] Spontaneous resolution in 1*H*-pyrimidon-2-ones **4.68** is due to atropoisomerism.[34] *p*-Anisyl *α*-methylbenzyl ketone **4.69** undergoes spontaneous resolution in the presence of a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and gives optically active form of **4.69** with *ee* up to 72%.[35] It is important to know about systems such as these so that resolution of optically active compounds can be effected without the use of chiral resolving agents. This is one of the active areas in chemical research[36a,b] and has been briefly summarized here since such a phenomenon was observed in one of the systems investigated in the present work.



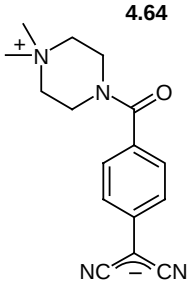
4.64



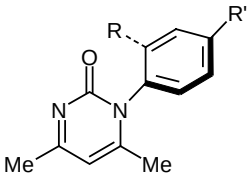
4.65



R = Me (**4.66**)

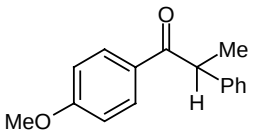


4.67



R = Me, Me, Cl
R' = H, Cl, Cl

4.68



4.69

Chart 1

OBJECTIVES OF THE PRESENT WORK-PART B

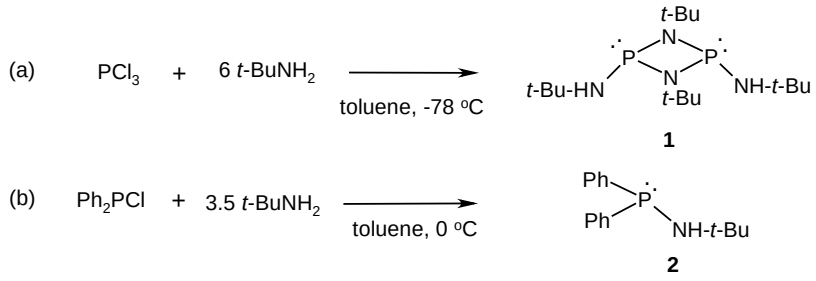
The main objective of this part of the work was to study the reaction of phosphorus(III) compounds with activated alkynes, alkenes and allenes in an effort to isolate and characterize compounds analogous to the proposed intermediates in the phosphine-catalyzed reactions involving such unsaturated systems. Since a chiral center was generated in the reaction with allenes, it was decided to investigate the spontaneous resolution of some of the products as well.

RESULTS AND DISCUSSION

5.1 Synthesis of P^{III} compounds [(*t*-BuNH)P(μ-N-*t*-Bu]$_2$ (1) and Ph_2P(NH-*t*-Bu) (2)

The cyclodiphosph(III)azane [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ [**1**, δ(P) 89.4] was prepared by using a literature procedure[36a] and purified by crystallization from toluene (Scheme 1a). The aminophosphine Ph_2P(NH-*t*-Bu) [**2**, δ(P) 22.7] was prepared by a slight modification of the literature procedure;[36b] because benzene is carcinogenic, we have used toluene as the solvent (Scheme 1b).

Scheme 1



5.2 Synthesis of allenylphosphonates 3a-c and the ester allene EtO_2C-C(H)=C=CH_2 (3d)

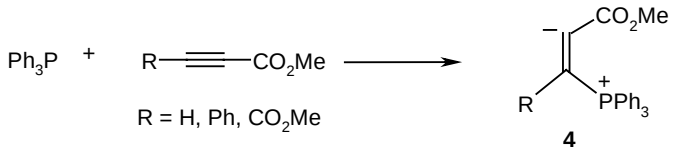
Synthesis of allenylphosphonates ($OCH_2CMe_2CH_2O$)PC(R)=C=CH_2 [R = H (**3a**), R = Me (**3b**), R = Ph (**3c**)] has been discussed in Part A (Chapter 3; labeled as compounds **7a**, **7i** and **7e**, respectively). The allene **3d** was prepared by the route shown in Scheme 2.[37]

Scheme 2

5.3 Reaction of P^{III} compounds with activated alkynes

As mentioned in Chapter 4, a significant number of useful applications for a variety of organic transformations utilizing the triphenylphosphine-dimethyl acetylenedicarboxylate (Ph_3P-DMAD) or the combination of a P^{III} compound and an electron-deficient alkyne has emerged in recent years.[5] We were interested in identifying intermediates of type **4** (cf. Scheme 3) in a more definitive way. When we added DMAD to triphenylphosphine (1:1 stoichiometry) in C_6D_6 solution in an NMR tube, we obtained a rather complicated ^{31}P NMR spectrum but there was a broad peak at δ 48.3 (30%) [other peaks: δ 26.1, 25.8, 24.7, 24.5, 24.2, 22.7, 17.8 and 9.7] close to that known for the Morrison-Brunn-Huisgen intermediate $Ph_3P^{+}N(CO_2Et)\text{-}N^{-}CO_2Et$ [δ(P) = 44.8].[3d] The broadness of the peak at δ 48.3 suggested an equilibrium between **4** and other species, as suggested by earlier workers.[13] Although we did not attempt to isolate any product from this reaction, the multitude of products formed reveals the complexity of this apparently simple reaction.

Scheme 3

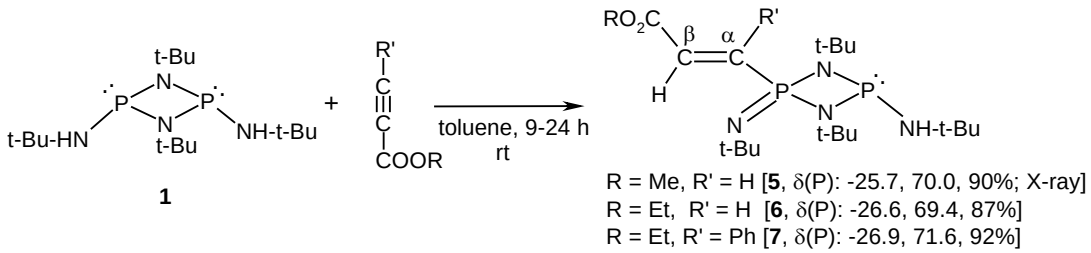


4

Our previous success with the traditional 'inorganic heterocycle', the cyclodiphosphazane $[(t\text{-BuNH})P(\mu\text{-N-}t\text{-Bu})]_2$ (**1**) in the isolation of the tautomeric forms of Morrison-Brunn-Huisgen type intermediates[4b] prompted us to utilize the same precursor for the reaction with electron-deficient alkynes. Thus the reaction of **1** with activated alkynes (methyl propiolate, ethyl propiolate and ethyl phenylpropiolate) led to compounds **5-7** (Scheme 4) in which the NH proton of the N*H*-*t*-Bu group had moved to the *β*–carbon of alkyne residue. In these reactions, only one of the phosphorus atoms of the cyclodiphosphazane ring participated and the other one remained as a spectator, as shown by ^{31}P NMR spectra of the reaction mixtures. For pure compounds **5-7**, the ^{31}P NMR spectra exhibit peaks at δ ~ -26 [P^{V} region] and ~ 70 [P^{III} region]. In the ^{1}H NMR spectra, the N*H* proton which is connected to P^{III} appears as a broad doublet at δ ~ 2.80 [^{2}J(P-H) ~ 6.0 Hz]. The ^{13}C NMR spectra are also useful for the identification of these compounds. The P*C* and

the carbonyl signals appear as doublet each at δ ~ 147 [^{1}J(P-C) =150-170 Hz] and ~ 166.6 [^{3}J(P-C) ~ 25.0 Hz], respectively. The structure of **5** was confirmed by X-ray crystallography (section 5.5).

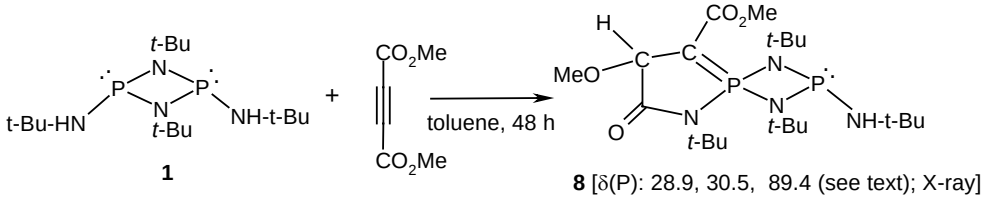
Scheme 4



R = Me, R' = H [**5**, δ(P): -25.7, 70.0, 90%; X-ray]
R = Et, R' = H [**6**, δ(P): -26.6, 69.4, 87%]
R = Et, R' = Ph [**7**, δ(P): -26.9, 71.6, 92%]

In contrast to the above, the reaction of **1** with DMAD in toluene leads to the novel heterocyclic product **8** (Scheme 5). The ^{31}P NMR spectrum shows two signals in the tetracoordinate region possibly due to the presence of isomeric forms (see below). The structure of **8** was proven by X-ray crystallography (later section 5.5).

Scheme 5

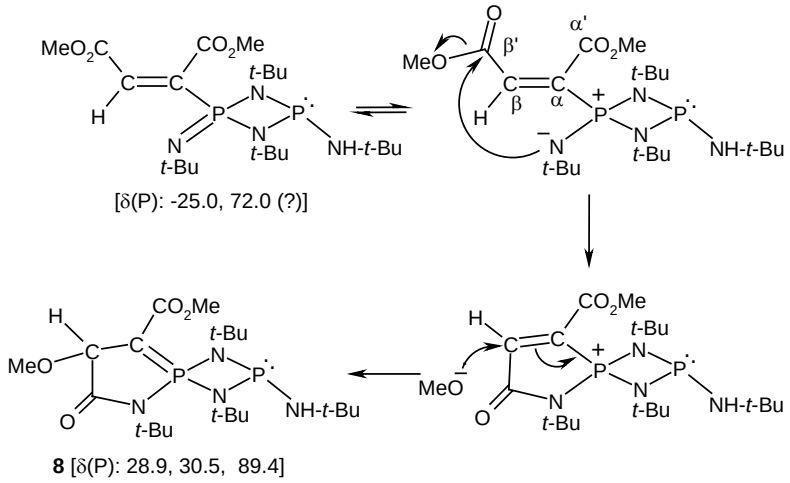


8 [δ(P): 28.9, 30.5, 89.4 (see text); X-ray]

A possible pathway for the formation of heterocycle **8** is given in Scheme 6. This involves a novel cyclization in which the tautomeric form of phosphazenic nitrogen attacks the carbonyl carbon of the DMAD [$MeO_2CC{\equiv}CCO_2Me$] residue. Although reactions involving a C=O or C=NTs group and acetylenes in the presence of PPh_3 also lead to ring formation with the methoxy migration,[23c,38,39] in our case cyclization involves a nitrogen which was a part of P^{III} component and attack of nitrogen occurs at the carbomethoxy group connected to carbon *β* to phosphorus. This feature adds another interesting facet to the reactions involving phosphine-alkyne combination. The initial reaction mixture, when **1** was treated with DMAD, showed major peaks (85%) at δ 72.2 (br), -25.0 (br), -35.3 (br), with the combined intensity of the peaks at δ -25.0 and -35.3 [P^{V} region] nearly the same as the one at δ 72.2 [P^{III} region]. These are clearly different from those for the final product **8**, but the peaks at δ 72.2 and -25.0 are close to that for **5** and clearly show that formation

of **8** occurs *via* a species similar to **5** or its Z-isomeric form. Theoretical calculations, as discussed below, also seem to indicate this.

Scheme 6



Possible pathway for the formation of the heterocycle **8**

It can be noted that at least four other isomeric forms (**5a-d**) are feasible for **5** (Fig. 1). To check the stability of these isomers, we have performed theoretical calculations (B3LYP/6-31G**) [with the help of my lab-mate] on the observed structure **5** and the isomeric forms **5a-d**. Destabilization (kcal/ mole) with respect to the crystallographically observed form **5** are as follows: **5** (0.00) < **5a** (+7.40) < **5b** (+30.68) and **5c** (+4.94) < **5d** (+36.38). Thus the theory agrees well with the experimental results. The difference in energy between *E* (i. e. **5**) and *Z* (i. e. **5a**) forms is not large. Hence, *E* and *Z* forms for the intermediate [(*t*-BuNH)P(N-*t*-Bu)$_2$P(=N-*t*-Bu)C(CO$_2$Me)=CH(CO$_2$Me) from the reaction of **1** with DMAD are also likely to be close in energy, facilitating the attack of nitrogen on carbonyl group at β-carbon in the cyclization leading to **8**.

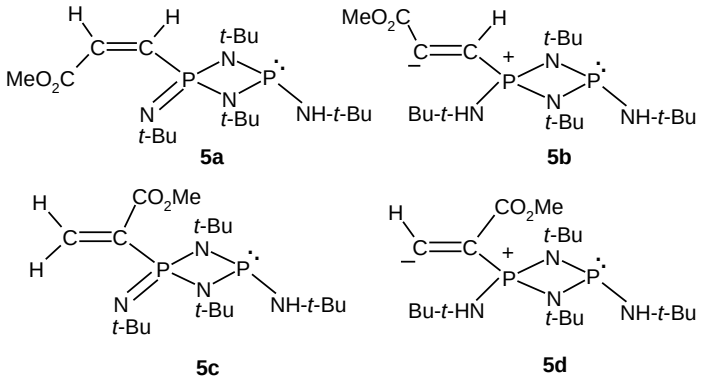
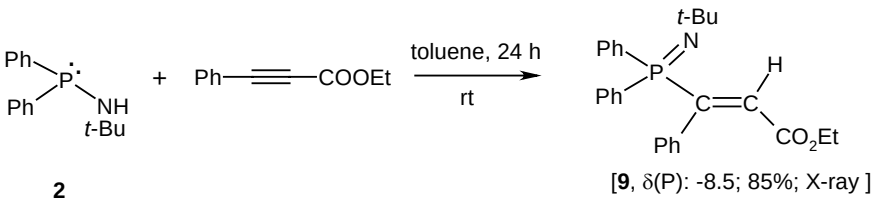


Fig. 1. Isomeric structures for **5** that were used for calculations.

Encouraged by the above results, we treated the acyclic aminophosphine $Ph_2P(NH\text{-}t\text{-}Bu)$ (**2**) with methyl propiolate. Although we could not isolate the pure compound, a clean peak at δ -14.5 (>85%), consistent with the formation of $Ph_2P(=N\text{-}t\text{-}Bu)(CH=CHCO_2Me)$, was observed in the ^{31}P NMR spectrum of the reaction mixture. Fortunately, in the reaction of **2** with ethylphenyl propiolate [$EtO_2CC{\equiv}CPh$], we have been successful in isolating the iminophosphonate $Ph_2P(N\text{-}t\text{-}Bu)\{C(Ph)=CH(CO_2Et)\}$ (**9**) (Scheme 7) in good yields. This observation clearly shows that the use of a P-NH-*t*-Bu group facilitates the isolation of P-C bonded compounds, but with the tautomeric imino structure. In the IR spectra, compound **9** showed a band at 1728 cm^{-1} due to ν(C=O) stretch. In the ^1H NMR spectrum, the observed integrated intensities of $C(CH_3)_3$, OCH_2, CH_2CH_3, =C*H* and C_6H_5 protons are consistent with the proposed structure. The structure of compound **9** was further confirmed by X-ray crystallography (section 5.5).

Scheme 7



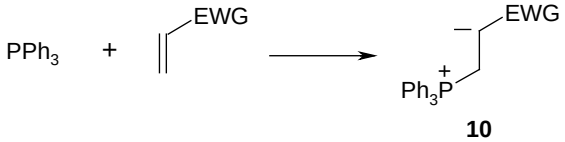
2

[**9**, δ(P): -8.5; 85%; X-ray]

5.4 Reactions of cyclodiphosphazane [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**1**) with activated alkenes

In phosphine-catalyzed reaction of activated alkenes (e.g., Morita-Baylis-Hillman reaction, Rauhut–Currier reaction, Michael reaction) zwitterionic species of type **10** was proposed as an intermediate in the first step. We have been interested in the isolation of intermediates of type **10** (Scheme 8).

Scheme 8

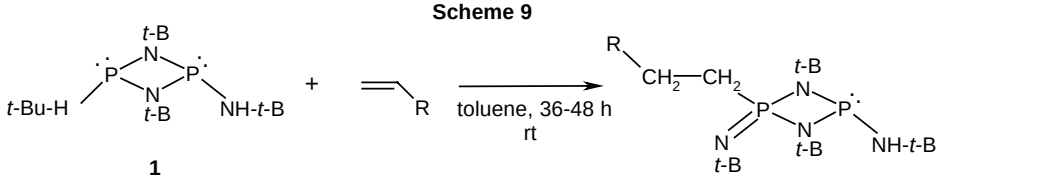


10

In the above context, we treated [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**1**) with unsymmetrical activated alkenes CH_2=CHR [R = CO_2R, CN, SO_2Et] and obtained compounds **11-15** (Scheme 9) that are tautomeric forms of the expected zwitterionic

species **10**. Thus these reactions are analogous to those with methyl propiolate discussed above. The P*C* signal for compounds **11-15** appears as a doublet at δ 25.8-29.0 [^{1}J(P-C) ~ 128.6-150.0 Hz] in the ^{13}C NMR spectra. The structure of compound **11** was further confirmed by X-ray crystallography (later section 5.5, Fig. **6**). We also treated **1** with methyl vinyl ketone. This reaction was faster than that with acrylates, but not clean. However a small amount of crystalline material obtained from the reaction mixture showed two peaks at δ(P) –5.9 and 71.6 which are in the same region as for the compounds **11-15**, suggesting that a similar compound was formed. The ^{1}H NMR spectrum was not clear, though.

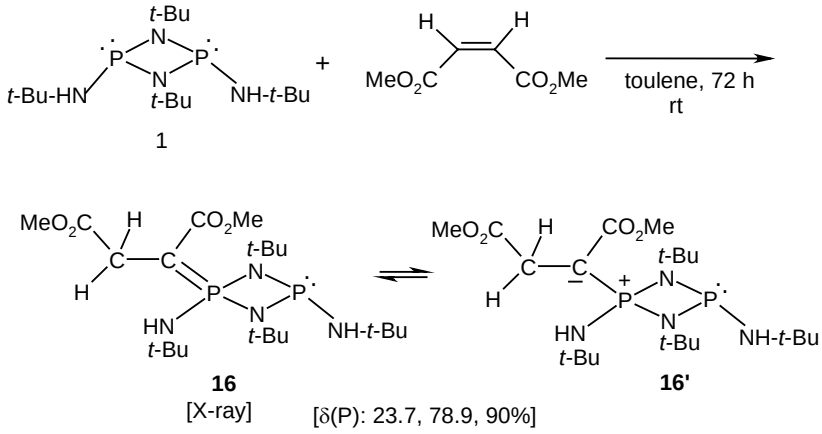
Scheme 9



R = CN [**11**, δ(P): -12.2, 73.0, 90%; X-ray]
R = CO_2Me [**12**, δ(P): -6.4, 72.3, 87%]
R = CO_2Et [**13**, δ(P): -6.2, 72.8, 90%]
R = CO_2-*t*-Bu [**14**, δ(P): -3.4, 72.1, 87%]
R = SO_2Et [**15**, δ(P): -10.4, 72.8, 82%]

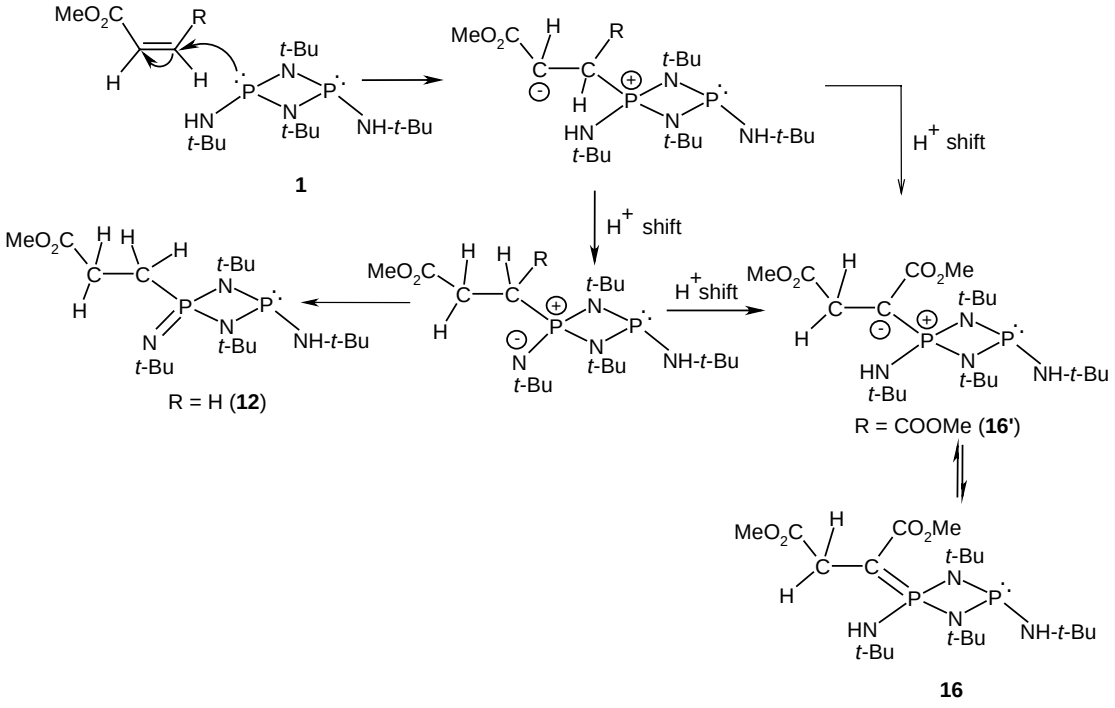
We also treated dimethyl maleate with **1** and obtained a stable ylide **16** (Scheme 10). Interestingly, the ^{31}P NMR spectrum of this compound exhibited peaks at δ 23.7 and 78.9, which are significantly different from those for **11-15** discussed above. In the ^{13}C NMR spectrum, the P-*C* carbon appears at δ 45.2 with a larger ^{1}J(P-C) [183.0 Hz] than those observed for **11-15** [^{1}J(P-C) = 128.6-150.0 Hz]. Notably, the ^{13}C NMR chemical shift value is not in the typical alkenic region perhaps because of interconversion between **16** and phosphonium form (**16'**) in $CDCl_3$ solution (Scheme 10). X-ray structure of **16** shows the presence of (*t*-BuNH)P-C(CO_2Me)-CH_2CO_2Me group (section 5.5).

Scheme 10



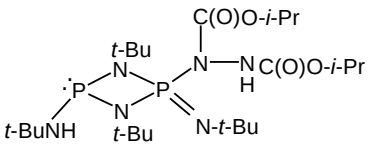
A possible mechanism for the formation of **12** and **16** is illustrated in Scheme 11. Formation of **11** and **13-15** takes place in a manner similar to that for **12**. The difference in the two types of products lies mainly in the location of a proton, on the nitrogen or on the α-carbon.

Scheme 11

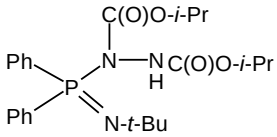


As mentioned earlier (Section 5.3), we had previously isolated tautomeric forms of Morrison-Brunn-Huisgen intermediates of type **17**.[4a] Thus, while the reaction of **1** with dialkyl azodicarboxylate $RO_2CN{=}NCO_2R$ leads to a phosphinimine of type **17** [R = *i*-Pr] with P=N(*t*-Bu) group, analogous reaction of **1**

with dimethyl maleate [$MeO_2CC{=}CCO_2Me$] leads to **16** which retains the P-NH(*t*-Bu) group at the reactive end. In this context, we reacted **2** with diisopropyl azodicarboxylate [DIAD; *i*-Pr-$O_2CN{=}NCO_2$-*i*-Pr] and obtained **18**. In this compound, the NH proton of the N*H*-*t*-Bu group has moved to the *β*–nitrogen of DIAD residue. By contrast, in **16** the hydrogen on *α*–carbon has moved to *β*–carbon. The ^{31}P NMR spectrum of **18** showed the expected peak at δ –12.5. The ^{1}H NMR spectrum is also consistent with the structure **18**. The structure of this compound was further confirmed by X-ray crystallography (section 5.5).

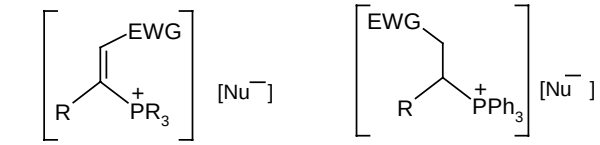


[**17**, δ(P): -28.7, 68.9]



[**18**, δ(P): -12.5; X-ray]

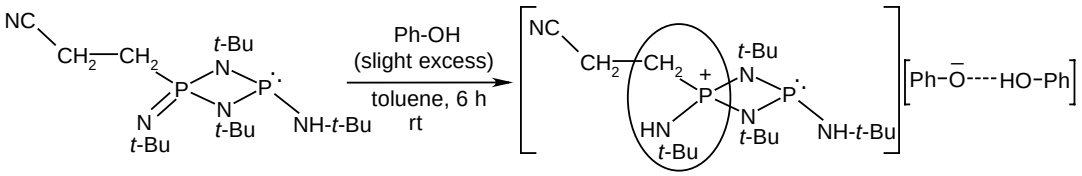
In the phosphine-catalyzed nucleophilic addition to alkynoates/ alkenoates, species such as **19/ 20** are also proposed as second stage intermediates, subsequent to the addition of ArOH/ROH to the Ph_3P-alkyne/-alkene mixture.[40] Hence we were interested in seeing whether ArOH/ROH undergo addition with our compounds (e.g. **5** or **11**) or not. If so, we will have some proof for the proposed mechanism. The ^{31}P NMR spectrum of the reaction mixture from [**5**+phenol] exhibited mainly two peaks (*ca* 85%) at δ 71.9 and –16.4; thus there is a downfield shift of ~9 ppm for the tetracoordinate region suggesting that a reaction occurs. In this case we could not isolate the product. Then we treated **11** with a slight excess (1:1.4) of phenol and obtained the addition product **21**.Ph-O-H…OPh (Scheme 12; for X-ray structure see section 5.5).[41] It is also interesting to note that a hydrogen-bonded complex of type $Ph_3P^{+}CH_2CH{=}CH(Me)\text{-}O^{-}\ldots HOAr$ is proposed in the phosphine-phenol co-catalyzed Morita-Baylis-Hillman (MBH) reaction using methyl vinyl ketone.[42] Thus it may be fruitful to study hydrogen-bonding effects in these co-catalyzed reactions in greater depth. It is also worth-mentioning that acrylonitrile is widely used in the MBH reaction. Finally, compound **21**.Ph-O-H…OPh provides the first structural proof for the involvement of phosphonium salts proposed in the system R_3P-activated alkene-ArOH.



EWG = CO_2R, C(O)R etc. R = Alkyl, CO_2Me etc. Nu = -OAr, -OR, thiobenzamidato etc. **(19)**

EWG = CN, CO_2R, C(O)Me Nu = oximato **(20)**

Scheme 12

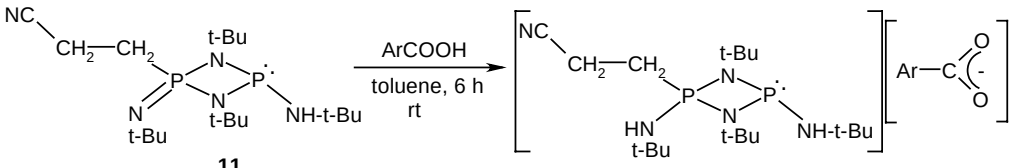


11

21 [δ(P) = 3.6, 75.7, 65%; X-ray]

The reaction of **11** with stoichiometric amounts of substituted benzoic acids gave the addition products **22-24** (Scheme 13). The ^{31}P NMR spectra of these compounds exhibited two peaks at δ 21.4-21.6 and 82.1-82.5, which are in the expected tetra- and tri-coordinate regions, respectively, but quite different from that for **11**. The ^{13}C NMR spectra for **22-24** show ^{1}J(P-C) of ~ 101 Hz [δ ~ 23.5] for the P-*C* carbon. This value is lower than that in **11** [^{1}J(P-C) = 135.0 Hz]. X-ray structural analysis was performed on the compound **23**.H_2O (section 5.5).

Scheme 13



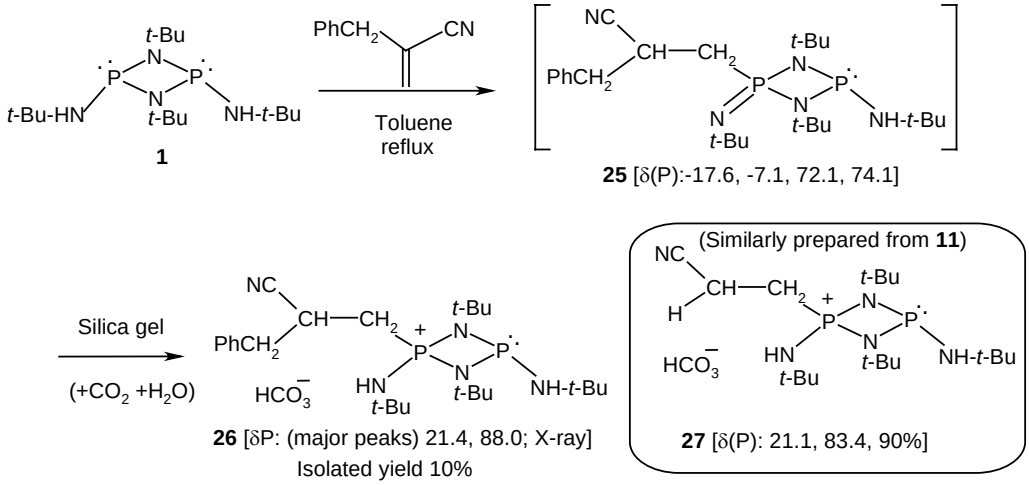
11

Ar = C_6H_5 [**22**, δ(P) = 21.4, 82.3, 90%]
Ar = 4-NO_2-C_6H_4 [**23**, δ(P) = 21.4, 82.5, 90%; X-ray]
Ar = 2-Br-C_6H_4 [**24**, δ(P) = 21.6, 82.1, 87%]

Compound **1** did not react with 2-benzyl-acrylonitrile[43] at room temperature. When the mixture was refluxed in toluene for 2 d, the signal for **1** disappeared in the ^{31}P NMR spectrum and the reaction mixture showed mainly four peaks [-17.6 and -7.1 (tetracoordinate) 72.1 and 74.1 (tricoordinate)] (Fig. 2). These peaks are most likely due to two isomeric species of **25** that differ about the P=N bond. Upon attempted purification through silica gel column, only the new ionic compound **26** [δ(P) 20.6 and 87.3 (85%); 30.1 and 90.0 (15%, possibly an isomer)] was isolated

(Scheme 14). The anion, analyzed as $[HCO_3]^-$ by X-ray crystallography (section 5.5, Fig.11), could have come from the absorption of adventitious carbon dioxide-moisture. In a similar way, compound **11** [δ(P) -12.9, 71.6], prepared as described above, on passing through silica gel column gave the ionic product **27** [δ(P) 21.1, 83.4]. Although these reactions were unique, we have not investigated this aspect further since the reaction with normal carboxylic acids also afforded analogous ionic compounds.

Scheme 14



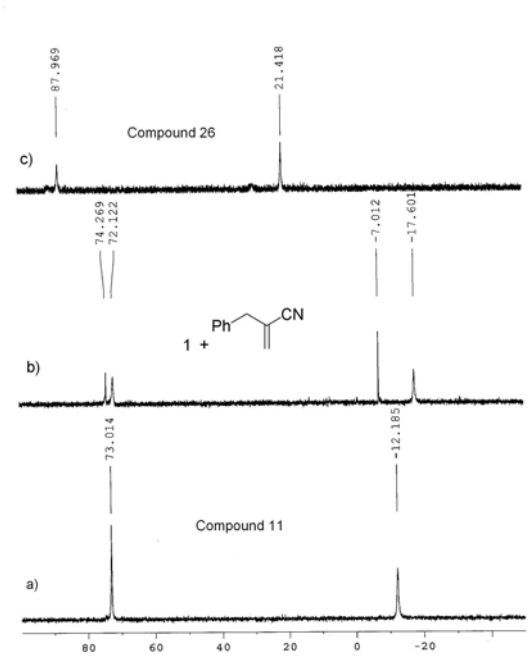


Fig. 2. The ^{31}P NMR spectra of a) pure compound **11**, b) reaction mixture of compound **1** + $(PhCH_2)(CN)C{=}CH_2$ containing **25** and c) pure compound **26.**

5.5 A brief description of the X-ray structures of 5, 8, 9, 11, 16, 18, 21.Ph-O-H…OPh, 23.H_2O and 26

The molecular structures of **5**, **8, 9** and **11** are shown in Figures 3-6. The P-N(imino) distances in **5, 9** and **11** (Table 1) are in the range 1.523±0.003 Å and are close to that found in (*t*-BuNH)P(μ-N-*t*-Bu)$_2$P[(N-*t*-Bu)(N-(CO_2Et)-N(H)(CO_2Et))] [1.533(1) Å].[4b] These are in the range expected for P=N bonds[44] and are shorter than the ring P-N distances in **5** and **8**. The P-N(ring) distances involving P^{III} are longer than those for P^{V} in **5**, **8** and **11**. In compound **8**, the P-N distance of 1.704(3) Å in the five-membered ring is fairly long and is in the range expected for a single bond.[45] The P-C distances are also in line with the structures as written, and the one for **8** is the shortest as expected. Thus the P(1)-C(17) distance in **8** is significantly shorter than the corresponding distance found in **5**, **9** or **11** showing that it has a double bond/ylidic character (in **8**, cf. Scheme 5).

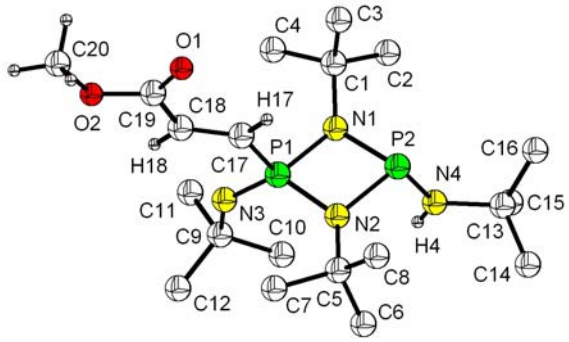


Fig. 3. Molecular structure of compound **5**.

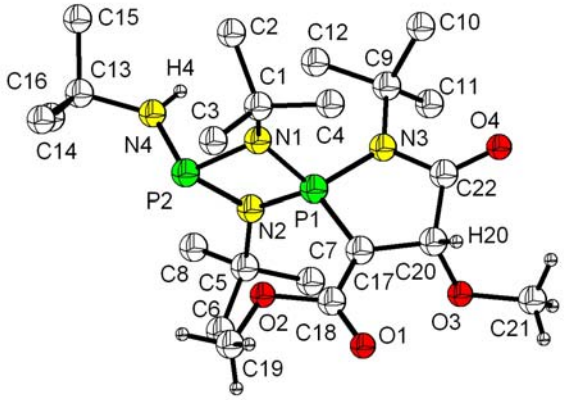


Fig. 4. Molecular structure of compound **8**.

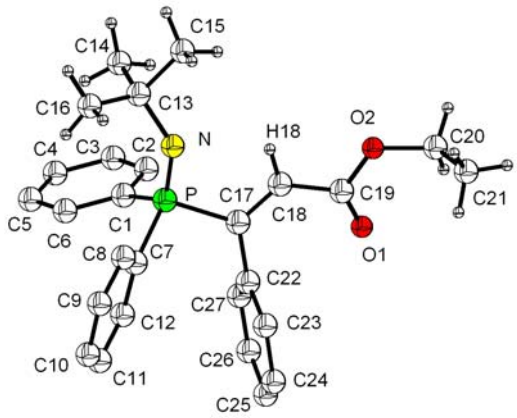


Fig. 5. Molecular structure of compound **9.**

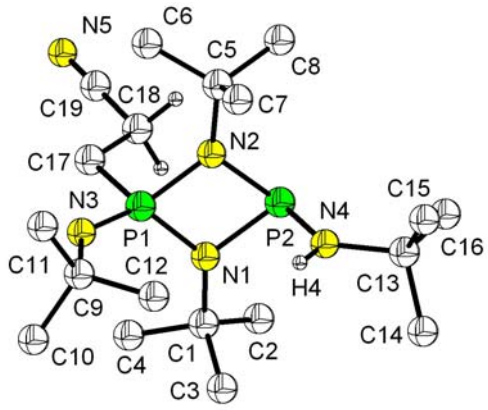
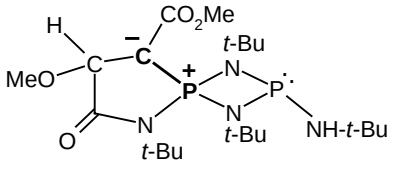


Fig. 6. Molecular structure of compound **11**.

Table 1. P-N and P-C bond distances (Å) with esd's for **5**, **8**, **9** and **11**

Compd	**5**	**8**	**9**[a]	**11**
P(1)-N(1)	1.680(3)	1.639(3)		1.678(2)
P(1)-N(2)	1.679(2)	1.657(3)		1.681(2)
P(1)-N(3)	1.521(2)	1.704(3)	1.525(4) (P-N)	1.526(2)
P(1)-C(17)	1.791(3)	1.697(4)	1.836(4) (P-C(17))	1.819(2)
P(2)-N(1)	1.744(3)	1.765(3)		1.735(2)
P(2)-N(2)	1.731(2)	1.756(3)		1.734(2)
P(2)-N(4)	1.651(3)	1.626(4)		1.657(2)

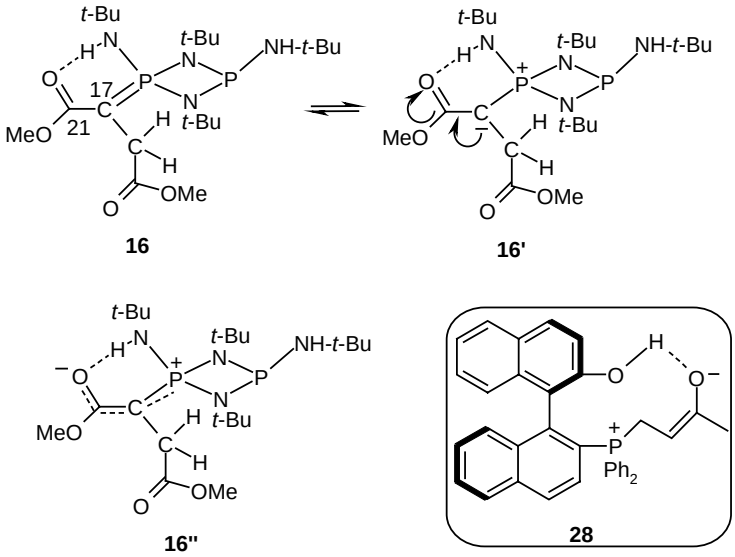
[a] Other bond distances P-C(1) 1.815(4), N-C(13) 1.465(6), C(17)-C(18) 1.328(5) Å.



(**8'**)

The X-ray structure of compound **16** (Scheme 15; Fig. 7) reveals some interesting features that are different from **11**. While in **11** there is clearly a P=N(*t*-Bu) group, in **16**, the original P-NH(*t*-Bu) is retained as shown by (a) longer P(1)-N(3) distance of 1.599(6) Å and (b) intramolecular hydrogen bonding between the carbonyl oxygen of the ester and the –N*H* proton. The P(1)-C(17) [1.715(5) Å] distance is shorter than those in **5**, **9** and **11**, but slightly longer than that in **8**. Thus this P-C bond is also ylidic and hence the structure of **16** can have significant contribution from the phosphonium form **16'** which is similar to **28** [characterized by ^{1}H and ^{31}P NMR]. The latter species was proposed as a MBH intermediate by Shi and coworkers.[16a] Based on the C(17)-C(21) distance of 1.405(8) Å in **16**, the compound may be better represented as **16"**. The bond distances in **16** are also consistent with X-ray structure of a previously reported phosphonium enolate.[46]

Scheme 15



16 **16'** **16"** **28**

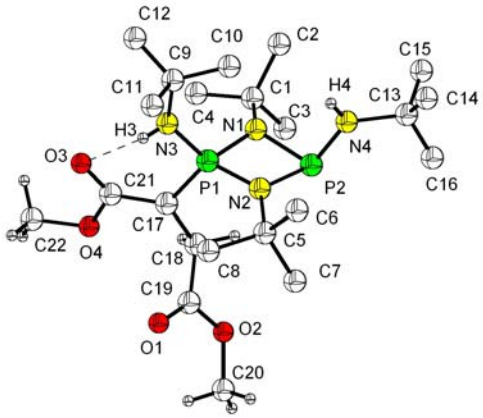


Fig. 7. Molecular structure of compound **16**; all the non-hydrogen atoms are labeled. Selected bond distances (Å): P(1)–N(1) 1.670(4), P(1)–N(2) 1.653(4), P(1)–N(3) 1.599(6), P(1)–C(17) 1.715(5), P(2)–N(1) 1.733(4), P(2)–N(2) 1.751(4), P(2)–N(4) 1.642(5), N(3)–C(9) 1.471(8), N(4)–C(13) 1.475(7), C(17)–C(18) 1.524(7), C(17)-C(21) 1.405(8), C(18)-C(19) 1.487(8). Hydrogen bond parameters (Å, Å, Å, °): N(3)-H(3)**…**O(3) 0.71(4), 2.20(5), 2.676(7), 126(5).

The molecular structure of compound **18** is shown in Figure 8. The P=N(*t*-Bu) distance of 1.528(2) Å is comparable to those in **5**, **9** or **11**. The presence of NH proton at the dialkyl azodicarboxylate residue is confirmed by weak intermolecular hydrogen bonding between the NH proton and the carbonyl oxygen of another molecule.

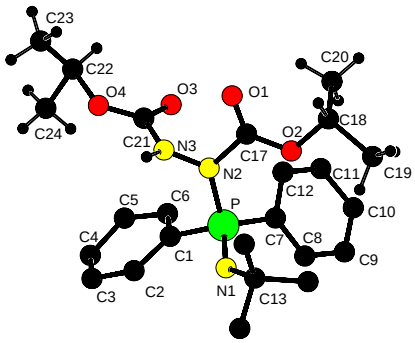


Fig. 8. Molecular structure of compound **18** (two molecules are present in the asymmetric unit). Selected bond distances (Å): P–N(1) 1.528(2), P–N(2) 1.7454(15), N(2)-N(3) 1.3942(19), N(2)-C(17) 1.385(2), O(1)-C(17) 1.198(2), O(2)-C(17) 1.332(2), P(1)-C(1) 1.8014(17), P(1)-C(7) 1.8139(18). Hydrogen bond parameters (Å, Å, Å, °): N(6)-H(6A)**…**O(3) 0.86, 2.47, 3.251(2), 151.4, Symmetry code: 0.5-x, 0.5+y, 1.5-z; N(3)-H(3A)**…**O(7) 0.86, 2.35, 3.157(2), 157.1, Symmetry code: 1.5-x, -0.5+y, 1.5-z.

Compounds **21**.Ph-O-H…OPh [Fig. 9] and **23**.H_2O [Fig. 10] are phosphonium salts with a P-N single bond as reflected by the comparatively longer bond distances [1.580(2) and 1.600(2) Å respectively] relative to the corresponding distances in **5**, **9** and **11**. However, these distances are significantly shorter than the P-N distance in the heterocycle **8** [1.704(3)], most likely due to favorable additional π-interactions.[46] No *cis-trans* isomerization of the NH-*t*-Bu substituents (with respect to the two phosphorus atoms of the cyclophosphazane ring) had taken place during these reactions. The X-ray structure of **21**.Ph-O-H…OPh shows that phenol moiety is involved in hydrogen bonding with phenoxide ion as well as N-*H* of the P^{v}-NH-*t*-Bu group. In **23**.H_2O a carboxylate oxygen is hydrogen bonded to the N-*H* of the P^{III}-NH-*t*-Bu group. Also, there is additional hydrogen bonding interaction involving a carboxylate oxygen and water as shown in Fig. 10. Although the presence of additional phenol in **21**.Ph-O-H…OPh looks rather awkward, analogous hydrogen bonding situations may be responsible for bringing the reactants together. This is an important point that needs to be borne in mind while giving mechanistic description of these reactions. Compound **26** [Fig. 11] is also a phosphonium salt. The anion in this compound was refined as bicarbonate, but the OH proton was not located (data also fitted well with nitrate anion crystallographically, but there was no source of this anion in our system). Here, bicarbonate oxygen is hydrogen bonded to both N-*H* of P^{v}-NH-*t*-Bu as well as P^{III}-NH-*t*-Bu. This feature is different from that in **23**.H_2O. The P(1)-C(17) distance is marginally shorter than those in **21**.Ph-O-H…OPh and **23**.H_2O. We believe that this anion is formed adventitiously through atmospheric carbon dioxide. This aspect was not studied further in this work.

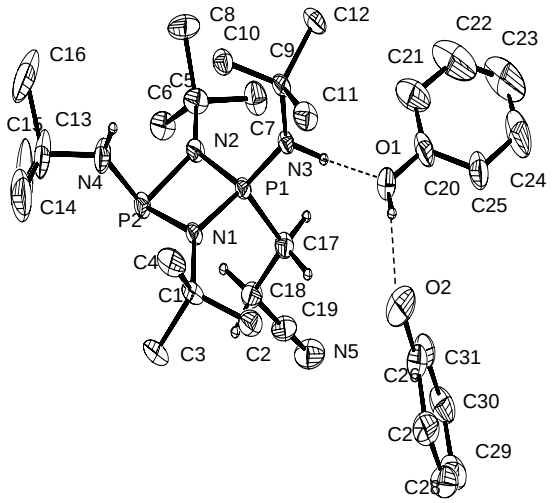


Fig. 9. An ORTEP drawing of compound **21**.Ph-O-H…OPh; all the hydrogen atoms are omitted except N(3) and O(1) hydrogen atoms. [Hydrogen bond parameters (Å, Å, Å, ^{o}): N(3)-H(3)**…**O(1') 1.02(3), 1.62(4), 2.626(3), 168(3); O(1')-H(1')**…**O(2') 0.93(6), 1.77(7), 2.525(5), 137(6), Symmetry code: 1+x, 1+y, z].

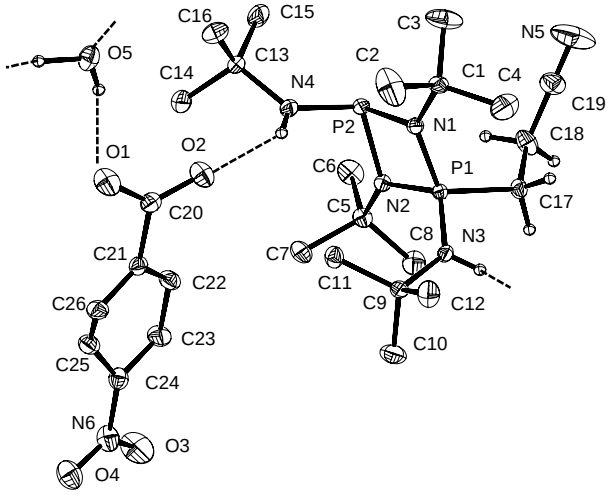


Fig. 10. An ORTEP diagram of **23**.H_2O. Hydrogen bond parameters (Å, Å, Å, ^{o}): N4-H4…O2' 0.75(3), 2.54(3), 3.188(4), 147(3); Symmetry code: 2-x, ½+y, 3/2-z, O5"-H5A"…O1' 0.78(3), 2.03(3), 2.782(3) 164(3); Symmetry code: x, ½-y, ½+z, O5"-H5B"…O1''' 1.12(7), 1.69(7), 2.789(3), 167(6); Symmetry code: x, ½-y, -½+z, N3-H3…O5'''' 0.80(3), 2.03(3), 2.824(3), 173(3); Symmetry code: 2-x, 1-y, 1-z.

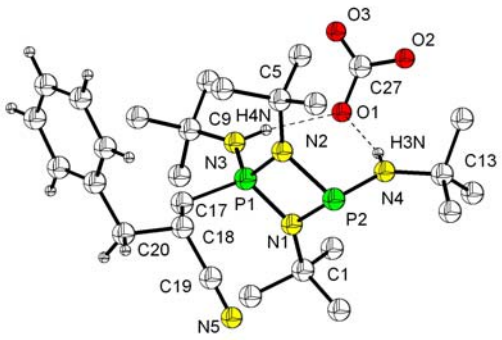


Fig. 11. Molecular structure of **26**. Hydrogen bond parameters: N(3)-H(4N)**…**O(1) 0.88(4), 2.00(4), 2.870(5) Å, 171(4)^{o}; N(4)-H(3N)**…**O(1) 0.87(4), 2.19(5), 3.042(5) Å, 166(4)^{o}.

Table 2. P-N and P-C bond distances (Å) with esd's for **21**.Ph-O-H…OPh and **23**.H_2O and **26**.

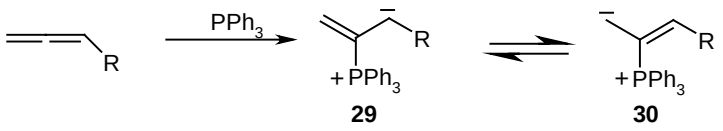
Compd	**21**.[Ph-O-H…OPh]	**23**.H_2O	**26**
P(1)-N(1)	1.647(2)	1.641(2)	1.633(3)
P(1)-N(2)	1.643(2)	1.641(2)	1.639(3)
P(1)-N(3)	1.580(2)	1.600(2)	1.607(3)
P(1)-C(17)	1.805(3)	1.812(2)	1.792(4)
P(2)-N(1)	1.747(2)	1.764(2)	1.756(3)
P(2)-N(2)	1.759(2)	1.773(2)	1.763(3)
P(2)-N(4)	1.629(3)	1.639(2)	1.641(4)

5.6 Reactions of P^{III} compounds with activated allenes

Allenes are versatile precursors in the synthesis of various natural products and heterocycles *via* nucleophile catalyzed reactions (Chapter 1). In these reactions, nucleophile attacks first at the *β*-carbon of the allene and gives zwitterions of type **29** and **30** (Scheme 16). Our interest has been in the isolation of the intermediates analogous to **29** and **30**. Thus in this work, we treated cyclophosphazane **1** with allenes **3a-c** and obtained compounds **31a-c** shown in the Scheme 17. It is clear from these reactions that the P^{III} end of the cyclophosphazane reacts with β-carbon of the allene. The difference between the proposed intermediate **29** and compounds **31a-c**

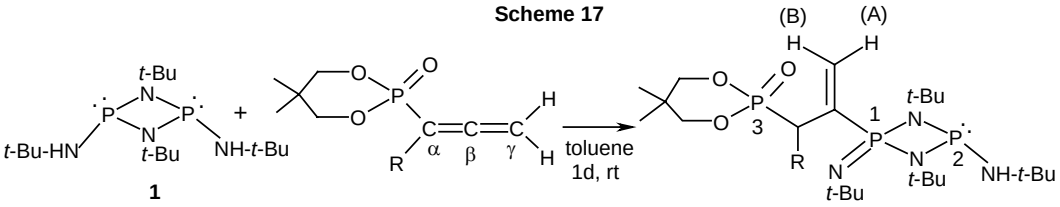
is that in the latter, the proton of the NH-*t*-Bu group from **1** has migrated to the *α*-carbon.

Scheme 16



R = CO_2Et, CO_2Me, COMe, $P(O)(OEt)_2$, etc.

Scheme 17



R = H (**3a**)
R = Me (**3b**)
R = Ph (**3c**)

R = H [**31a**, δ(P): -16.5, 23.5, 71.7, 85%]
R = Me [**31b**, δ(P): -17.9, 27.6, 71.0, 90%]
R = Ph [**31c**, δ(P): -19.4, 20.4, 70.5, 90%; X-ray]

In the ^{1}H NMR spectra for compounds **31a-c**, the two alkenic protons show doublets with different coupling constants at δ ~ 5.78 [=CH_AH$_B$ *cis* to P1 with ^3J(P-H) ~ 23 Hz] and δ ~ 6.5 [=CH$_A$$H_B$, *trans* to P1 with ^3J(P-H) ~ 51.0 Hz]. These ^3J(P-H) values between P and H located *cis* and *trans* to each other are nearly twice that of ^3J(H-H) values observed in normal alkenes (similar type of coupling is observed for the compound **9** in Chapter 2).[47] The ^{13}C NMR spectra of **31a-c** show the α-carbon [P(O)*C*] in the expected *aliphatic* region [δ 24.9-41.8] with a ^1J(P-C) value of 127 Hz. In compound **31c**, *ipso*-carbons of the four *C*Me$_3$ exhibit separate signals that could indicate that resolution of the enantiomers may be possible. In the ^{31}P NMR spectra, the tetracoordinate (at cyclodiphosphazane, P1 in Scheme 17) phosphorus nuclei appear as somewhat broad doublets at δ -16.5 [^3J(P-P) ~ 26.2 Hz] and -17.9 [^3J(P-P) ~ 30.5 Hz] for the compounds **31a** and **31b**, respectively. The ^2J(PNP) value is low in these cases. For **31c**, this ^2J(PNP) value is more and hence this tetracoordinate phosphorus (P1) appears as a doublet of doublet at δ -19.4 [^3J(P-P) ~ 35.4 Hz, ^2J(P-P) ~ 6.9 Hz] (Fig. 12). The structure of compound **31c** (both *S* and *R* forms; see below) was further confirmed by X-ray crystallography (Fig. 13).

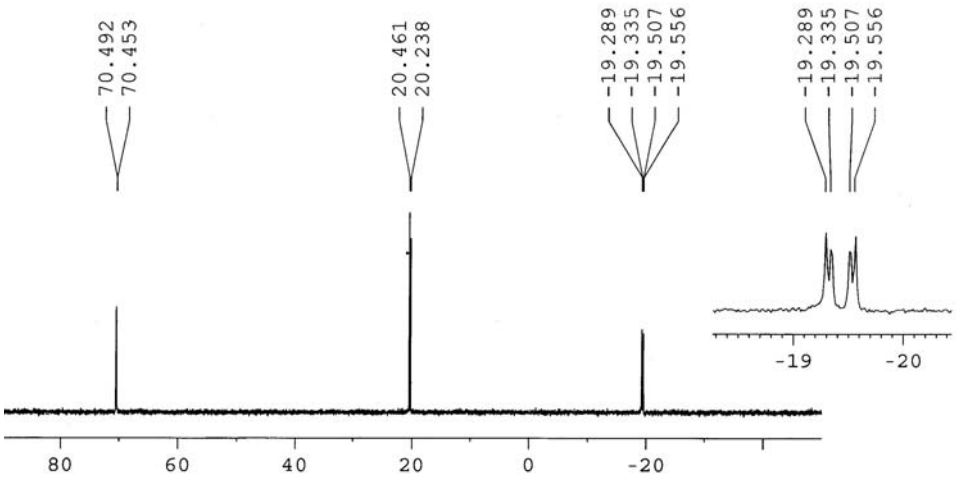
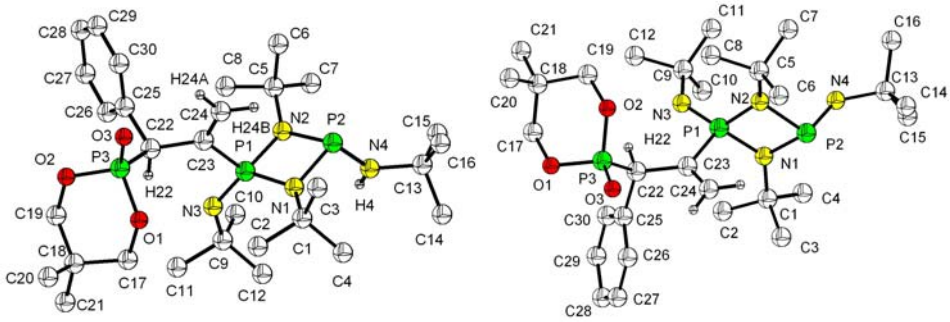


Fig. 12. The ^{31}P NMR spectrum of compound **31c**.



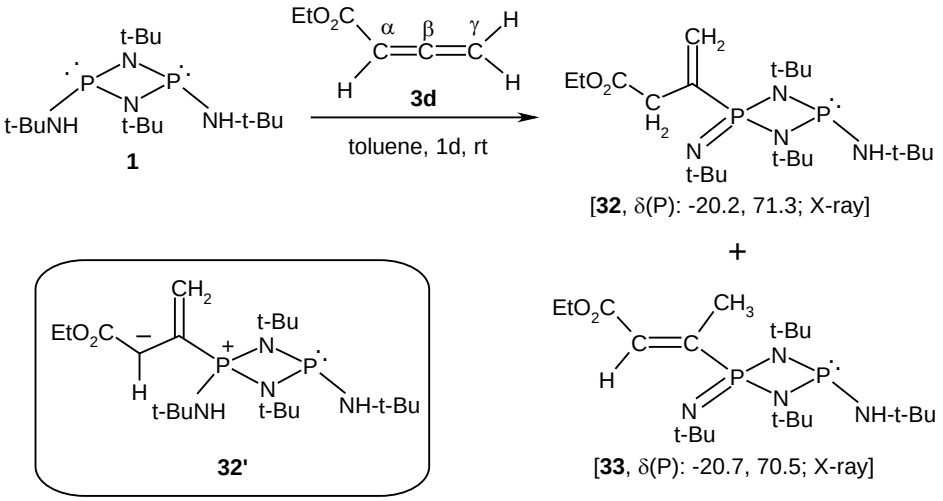
(**a**) (**b**)

Fig. 13. Molecular structures for the compounds (a) (*S*)-**31c** (b) (*R*)-**31c.** Selected bond lengths [Å] with esd's in parentheses follow. Compound (*S*)-**31c:** P(1)-C(23) 1.826(3), P(1)-N(1) 1.677(3), P(1)-N(2) 1.688(3), P(1)-N(3) 1.543(3), P(2)-N(1) 1.751(3), P(2)-N(2) 1.742(3) P(2)-N(4) 1.661(3) Å. [Hydrogen bond parameters: N(4)-H(4)**…**O(3) 0.91(5) 2.44(5) 3.286(5) Å, 155(4) ^{o}; symmetry code: -0.5+x, 1.5-y, z]. Compound (*R*)-**31c:** P(1)-C(23) 1.824(3), P(1)-N(1) 1.697(3), P(1)-N(2) 1.679(3), P(1)-N(3) 1.540(3), P(2)-N(1) 1.738(3), P(2)-N(2) 1.748(3) P(2)-N(4) 1.656(3) Å. [Hydrogen bond parameters: N(4)-H(4)**…**O(3) 0.78(5) 2.56(5) 3.284(5) Å, 154(4) ^{o}; symmetry code: 0.5+x, 0.5-y, z].

In contrast to the above, in the reaction using the ester allene **3d**, we obtained the rearranged product **33** by keeping the initially formed normal product **32** in solution over a period of 2 d (for complete conversion) (Scheme 18). Thus the allenylphosphonates and ester allene differ marginally as regards the nature of the

final product. Compounds **32** and **33** are both tautomeric forms of the expected zwitterionic species **32'**, which is also shown in Scheme 18. In the ^{1}H NMR spectrum, alkenic protons of compound **32** appear as a broad singlet at δ 5.55 [br, =CH$_A$*H*$_B$, *cis* to P] and a doublet at δ 5.70 [^{3}J(P-H) = 49.8 Hz, =CH$_A$*H*$_B$, *trans* to P] which are absent in **33**. For the latter compound, the P-C(C*H*$_3$) protons appear as a doublet at 2.00 [^{3}J(P-H) = 16.0 Hz] in the ^{1}H NMR spectrum. Also, in ^{13}C NMR spectra, compound **32** shows a doublet at δ 139.6 [^{1}J(P-C) = 137.5 Hz] while compound **33** shows the corresponding carbon at δ 154.2 [^{1}J(P-C) = 190.0 Hz]. The structures of compounds **32** and **33** were further confirmed by X-ray crystallography (Fig. 14 and Fig. 15). The bond parameters in these compounds are in the expected range.

Scheme 18



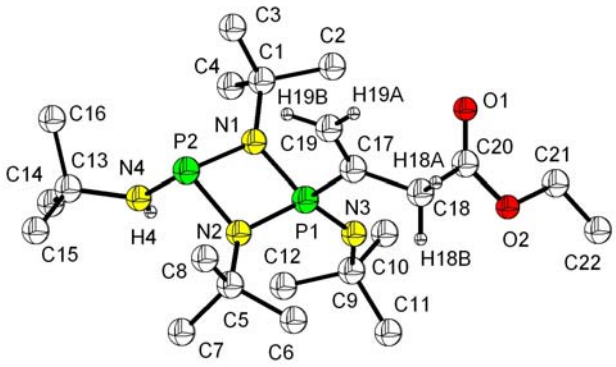


Fig. 14. Molecular structure of **32.** Selected bond lengths [Å] with esd's in parentheses**:** P(1)-C(17) 1.806(6), P(1)-N(1) 1.683(4), P(1)-N(2) 1.686(4), P(1)-N(3) 1.525(4), P(2)-N(1) 1.735(4), P(2)-N(2) 1.724(4), P(2)-N(4) 1.649(5).

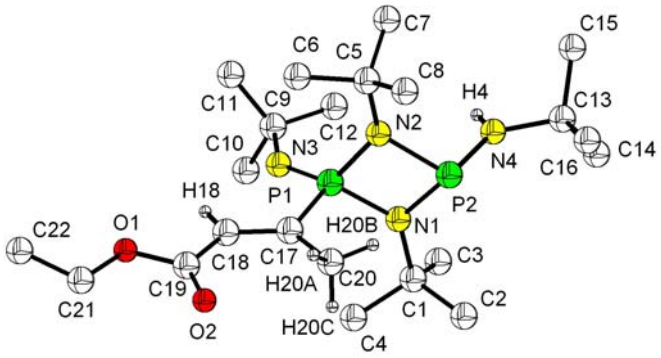
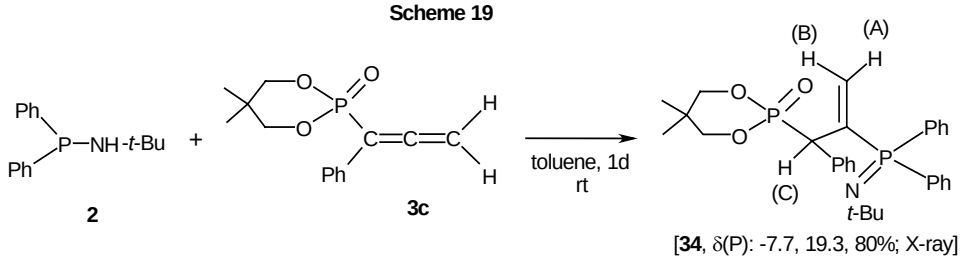


Fig. 15. Molecular structure of **33.** Selected bond lengths [Å] with esd's in parentheses**:** P(1)-C(17) 1.831(2), P(1)-N(1) 1.672(2), P(1)-N(2) 1.678(2), P(1)-N(3) 1.518(2), P(2)-N(1) 1.739(4), P(2)-N(2) 1.738(2), P(2)-N(4) 1.652(2) Å [Hydrogen bond parameters: N(4)-H(4)**…**O(2) 0.84(3) 2.49(3) 3.241(3) Å, 150(2) ^{o}; symmetry code: -0.5+x, 0.5-y, -0.5+z].

In an effort to see whether the above results are more general, we reacted the aminophosphine $Ph_2P(NH\text{-}t\text{-}Bu)$ (**2**) with the allene **3c**. This led to the phosphinimino product **34.** Thus the reaction is general for compounds with a P-NH-*t*-Bu group. In ^{1}H NMR spectrum, the two alkenic protons appear as doublet of doublet at δ 5.67 [^{3}J(P-H) = 22.2 Hz, ^{4}J(P-H) = 3.6 Hz, $=CH_AH_B$, *cis* to P] and δ 6.69 [^{2}J(P-H) = 46.8 Hz, ^{4}J(P-H) ~ 2.8 Hz, $=CH_AH_B$, *trans* to P]. The allylic proton [PC(Ph)*H*] appears as a doublet of doublet at δ 6.02 [^{3}J(P-H) and ^{2}J(P-H) = 14.4 and 19.2 Hz] (Fig. 16). In the ^{13}C NMR spectrum, the P(O)*C* carbon appears as a doublet of doublet at δ 37.5 [^{1}J(P-C) = 127.1 Hz, ^{2}J(P-C) ~ 7.0 Hz] and $P(Ph)_2C$

carbon appears as a doublet at δ 140.4 [^1J(P-C) = 120.3 Hz]. The structure of compound (*R*)-**34** was also proven by X-ray crystallography (Fig. 17).

Scheme 19



[**34**, δ(P): -7.7, 19.3, 80%; X-ray]

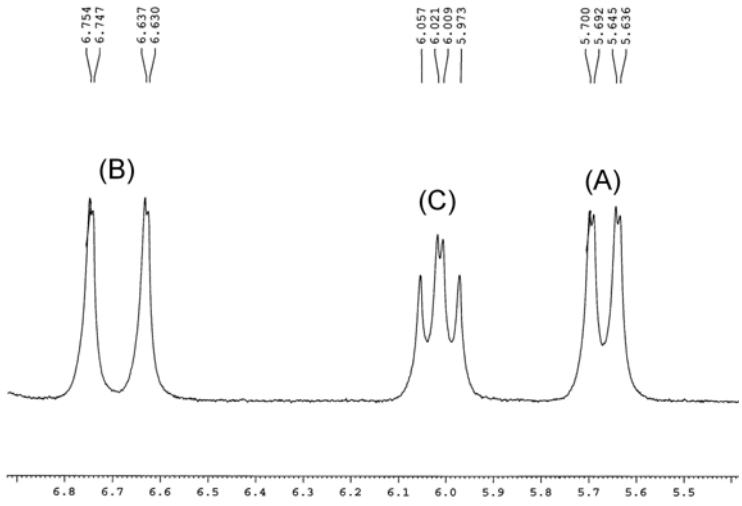


Fig. 16. A part of the ^{1}H NMR spectrum of **34** showing alkenic and allylic protons

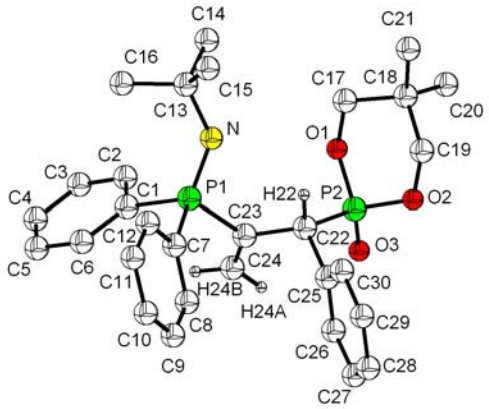


Fig. 17. Molecular structure of (*R*)-**34** [P(1)-C(23) 1.820(2), P(1)-N 1.542(2), P(2)-C(22) 1.822(2) Å].

It may be noted that in both the compounds **31c** and **34**, a chiral center is generated at C(22). Interestingly, both of these crystallized in the chiral space

groups, *Pna2$_1$* and *P2(1)2(1)2(1)*, respectively. The absolute configurations at the chiral center as suggested by *checkcif* are *S* and *R*, respectively. In the case of **31c**, we checked the structures of several crystals and were able to obtain the structures of both the *S* and the *R* enantiomers (Fig. 18).

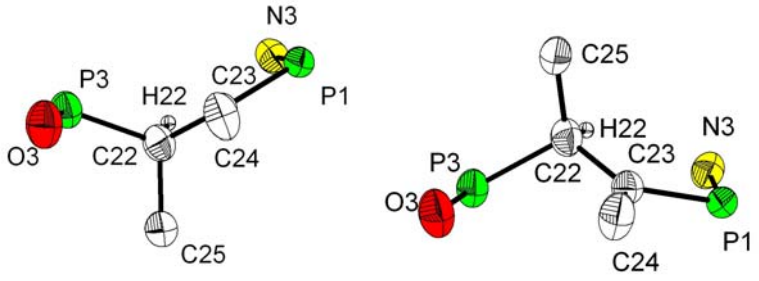


Fig. 18. A picture showing the *R* (left) and *S* (right) configurations at C(22) in the two different crystals of **31c**.

Although *a priori* identification of the crystals was not feasible because of similar morphology of the crystals, the above feature suggests that there is spontaneous resolution upon crystallization.[30] The CD spectra (Fig. 19) of the crystals showed expected features in the UV region, but in solution we were not able to get significant optical rotation. We are exploring this aspect further.

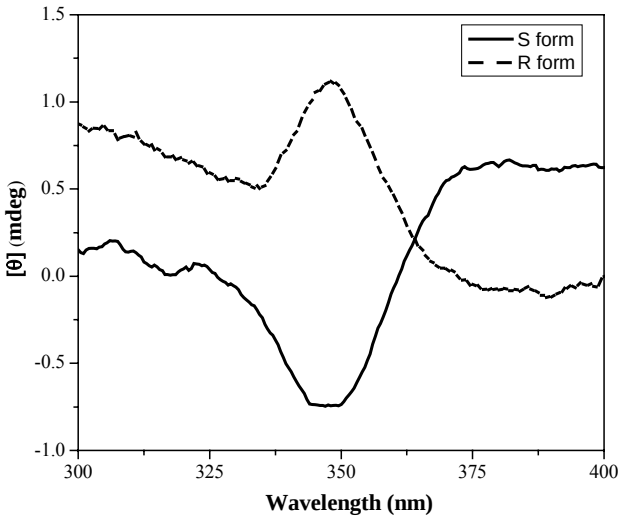


Fig. 19. CD spectra of *R* and *S* forms of crystals of **31c**.

SUMMARY - PART B

(1) We have provided a conclusive structural evidence for the initial phosphorus-carbon bond formation proposed in the phosphine-catalyzed reactions of activated alkynes/alkenes through the isolation of the tautomeric forms of the expected betaines. We have characterized a novel heterocycle **6** from the reaction of **1** with DMAD.

(2) Treatment of cyclophosphazane **1** with dimethyl maleate afforded stable ylide **16**, which is close to proposed intermediate in phosphine-catalyzed Morita-Baylis-Hillman reaction. Isolation of **21**.Ph-O-H…OPh is also significant since similar species are invoked in the phosphine-catalyzed reactions involving alcohols/ phenols.

(3) We have given the structural proof for the attack of P^{III} center at the β-carbon of allenylphosphonates **3a-c** and the ester allene **3d**. The NH proton of P-NH-*t*-Bu group migrates to α- or γ-carbon of the allene resulting in the formation of phosphinimines with different structures. Spontaneous resolution through crystallization has been observed in a couple of cases (**31c** and **34**) wherein a chiral center is generated during the reaction. In the case of **31c**, both the enantiomers have been characterized by X-ray crystallography.

EXPERIMENTAL SECTION

Details of the instruments, standards etc are already given in Chapter 3.

6.1 Synthesis of [(*t*-BuNH)P(μ-N-*t*-Bu]$_2$ (1) and Ph_2P(NH-*t*-Bu) (2)

Compound **1** [mp 142-144 ^oC; δ(P): 89.4] was synthesized by using a literature procedure.[36a]

Preparation of 2

To a stirred solution of Ph_2PCl (1.23 g, 5.57 mmol) in toluene (20 mL) was added *t*-butyl amine (1.43 g, 19.50 mmol) in toluene (10 mL) at 0 ^oC. After stirring for 12 h at room temperature, filtration followed by removal of solvent afforded **2**. In the literature, benzene was used as a solvent.[36b]

^{31}P NMR: δ 22.7 [known compound; lit. 22.5[36c]].

6.2 Synthesis of allenes

Synthesis of allenylphosphonates $(OCH_2CMe_2CH_2O)PC(R)=C=CH_2$ [R = H (**3a**), R = Me (**3b**), R = Ph (**3c**)] has already been described in Chapter 5 (compounds **7a**, **7e** and **7i**; section 5.2).

Synthesis of EtO_2C-CH=C=CH_2 (**3d**) {slightly modified from the literature}[37]

A solution of triethylamine (4.61 g, 45.5 mmol) in dichloromethane (50 mL) was added drop-wise to ethyl (triphenylphosphoranylidene)acetate in dichloromethane (150 mL) over a period of 5 min at 25 ^oC with continuous stirring. After stirring further for 10 min, the acetyl chloride (45.5 mmol) in dichloromethane (100 mL) was added drop-wise to the vigorously stirred solution over a period of 15 min, the reaction mixture stirred for 1 h, and the solvent removed. Hexane (200 mL) was added to the semisolid residue, and the slurry was allowed to stand for 2 h and shaken periodically to facilitate the extraction of the product. The mixture including the solid was filtered through a coarse frit (G-2), the solid was washed with hexane (50 mL), and the washings added to the filtrate. This solution was concentrated in *vacuo* to approximately one-fourth of the original volume at 25 °C. The mixture was

filtered again to remove traces of triphenylphosphine oxide, and the remaining solvent was then removed using a rotary evaporator. Distillation of the residue *in vacuo* [57–59°C/ 12–14 mm] afforded the allene **3d**.

Yield: 1.28 g (25 %).

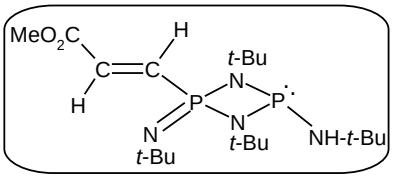
^{1}H NMR: δ 1.28 (t, ^3J(H-H) = 7.1 Hz, 3 H, OCH_2CH_3), 4.21 (q, ^3J(H-H) = 7.1 Hz, 2 H, OCH_2CH_3), 5.22 (d, ^4J(H-H) = 6.52 Hz, 2 H, $=CH_2$), 5.63 (d, ^4J(H-H) = 6.52 Hz, 1 H, C(*H*)=C).

This is a known compound.[37]

6.3 Reaction of P^{III} compounds with activated alkynes

(a) Synthesis of (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P(N-*t*-Bu){CH=CH(CO$_2$Me)} (5)

To a solution of **1** (0.572 g, 1.64 mmol) in toluene (10 mL), methyl propiolate (0.137 g, 1.64 mmol) was added *via* syringe at room temperature and the mixture was stirred for 4 h; the solution was concentrated *in vacuo* (to *ca* 1.5 mL) and cooled for 24 h at –4 °C to obtain crystals of **5**.



Yield: 0.638 g (90%).

Mp: 96-100 °C.

IR (KBr): 3347, 2971, 1717, 1632, 1368, 1327, 1232 cm^{-1}.

^{1}H NMR: δ 1.32 and 1.38 (2 s, 36 H, C(CH_3)$_3$), 2.81 (br d, ^2J(P-H) ~ 6.0 Hz, 1 H, N*H*), 3.76 (s, 3 H, CO_2CH_3), 6.59 (dd, ^3J(H-H) = 8.0 Hz, ^2J(P-H) = 16.0 Hz, 1 H, PC*H*), 6.79 (dd, ^3J(P-H) = 16.0 Hz, ^3J(H-H) = 8.0 Hz, 1 H, PCC*H*).

^{13}C NMR: δ 32.0 (t, ^3J(P-C) = 5.0 Hz, two of C(CH_3)$_3$), 33.4 (d, ^3J(P-C) = 10.0 Hz, C(CH_3)$_3$), 34.6 (d, ^3J(P-C) = 12.0 Hz, C(CH_3)$_3$), 51.4 (s, *C*(CH_3)$_3$), 51.7 (s, CO_2CH_3), 51.9 (d, ^2J(P-C) = 7.5 Hz, *C*(CH_3)$_3$), 52.5 (d, ^2J(P-C) = 10.0 Hz, *C*(CH_3)$_3$), 132.2 (s, *C*H ($COOCH_3$)), 147.5 (d, ^1J(P-C) = 168.9 Hz, P*C*), 166.3 (d, ^3J(P-C) = 25.0 Hz, *C*O_2CH_3) [*cf.* Fig. 20].

^{31}P NMR: δ -25.7, 70.0.

Anal. Calc. for $C_{20}H_{42}N_4O_2P_2$: C, 55.54; H, 9.78; N, 12.95. Found: C, 55.33; H, 9.67; N, 12.78.

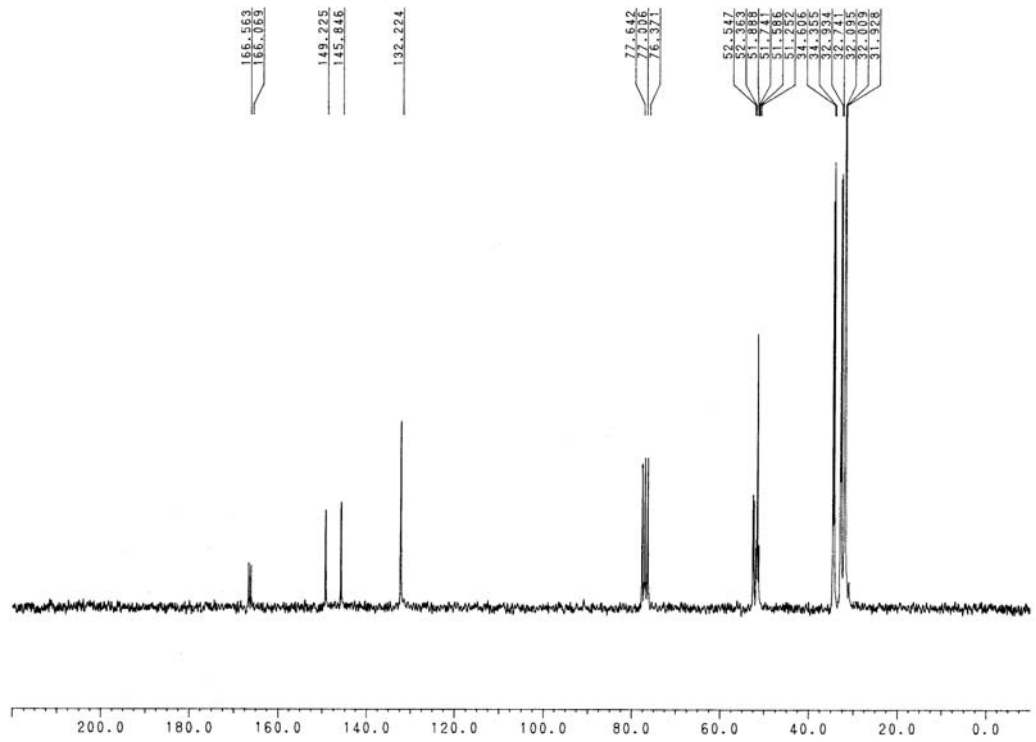
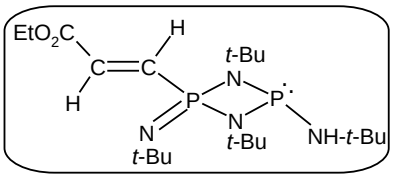


Fig. 20. ^{13}C NMR spectrum of compound **5**

***(b) Synthesis of* (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P[(N-*t*-Bu){CH=CH(CO$_2$Et)}] (6)**

The procedure was the same as that for **5** using **1** (0.73 g, 2.09 mmol) and ethyl propiolate (0.21 g, 2.09 mmol) [reaction time 9 h].



Yield: 0.81 g (87%).

Mp: 66-68 ^{o}C.

IR (KBr): 3343, 2971, 1715, 1624, 1368, 1327, 1231 cm^{-1}.

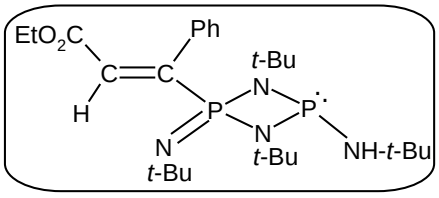
^{1}H NMR: δ 1.29-1.36 (2 s merged with those due to OCH_2CH_3, 39 H, OCH_2CH_3 + $C(CH_3)_3$), 2.80 (d, ^2J(P-H) = 7.8 Hz, 1 H, N*H*), 4.19 (q, ^3J(H-H) = 6.8 Hz, 2 H, OCH_2CH_3), 6.46-6.87 (m, AB part of ABX, X = phosphorus, 2 H, PC*H* + PCC*H*).

^{13}C NMR: δ 14.2 (s, OCH_2CH_3), 32.0 (s, $C(CH_3)_3$), 32.3 (d, ^3J(P-C) = 10.0 Hz, $C(CH_3)_3$), 34.4 (d, ^3J(P-C) = 13.0 Hz, $C(CH_3)_3$), 51.5 (d, ^2J(P-C) = 16.0 Hz, $C(CH_3)_3$), 51.9 (s, $C(CH_3)_3$), 52.5 (d, ^2J(P-C) = 10.0 Hz, $C(CH_3)_3$), 60.6 (s, $CO_2CH_2CH_3$), 132.8 (s, PC*C*), 147.0 (d, ^1J(P-C) = 167.5 Hz, P*C*), 168.5 (d, ^3J(P-C) = 25.0 Hz, *C*=O).

^{31}P NMR: δ -26.6, 69.4.

***(c) Synthesis of* (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P[(N-*t*-Bu){C(Ph)=CH(COOEt)}] (7)**

The procedure was the same as that for **5** using **1** (1.02 g, 2.94 mmol) and ethyl phenylpropiolate (0.51 g, 2.94 mmol) [reaction time 16 h].



Yield: 1.42 g (92%).

Mp: 73-77 ^{o}C.

IR (KBr): 3400, 3380 (vw), 2967, 1725, 1615, 1393, 1331, 1186 cm^{-1}.

^{1}H NMR: δ 1.01 (t, ^3J(H-H) = 7.0 Hz, 3 H, OCH_2CH_3), 1.30 and 1.32 (2 s, 36 H, $C(CH_3)_3$), 2.82 (br, 1 H, N*H*), 3.93 (q, ^3J(H-H) = 7.0 Hz, 2 H, OCH_2CH_3), 6.82 (br, 1 H, PCC*H*), 7.25 (~s, 5 H, Ar-*H*).

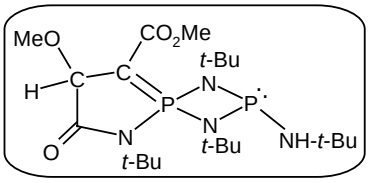
^{13}C NMR: δ 13.9 (s, OCH_2CH_3), 31.5 (s, $C(CH_3)_3$), 32.9 (d, ^3J(P-C) = 10.0 Hz, $C(CH_3)_3$), 34.2 (d, ^3J(P-C) = 11.0 Hz, $C(CH_3)_3$), 51.3, 51.6, 52.6 (3 s, $C(CH_3)_3$), 60.1 (s, $CO_2CH_2CH_3$), 126.9, 127.2, 129.2, 130.6 (d, ^1J(P-C) = 157.0 Hz, P*C* one of the peaks has merged with other peaks), 137.7 (s, PC*C*), 166.6 (d, ^3J(P-C) = 26.0 Hz, *C*=O).

^{31}P NMR: δ -26.9, 71.6.

***(d) Synthesis of* (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P[(N-*t*-Bu){C(CO$_2$Me)-CH(OMe)-(CO)}] (8)**

To a solution of **1** (0.554 g, 1.58 mmol) in toluene (15 mL), DMAD (0.225 g, 1.58 mmol) was added *via* syringe at 0^{o}C and the mixture was stirred for 20 min. The reaction mixture at this stage showed the following major peaks in the ^{31}P NMR: δ 90.2, 72.2 (br), 31.8, 30.1, -25.0 (br), -35.3 (br). The intensity of the broad

peaks corresponded to *ca* 85%. The solution was concentrated *in vacuo* (to *ca* 1 mL) and cooled at –4 °C for 48 h to obtain crystals of **8**.



Yield: 0.697 g (90%).

Mp: 174-178 °C.

IR (KBr): 3337, 2971, 1713, 1655, 1223, 1061 cm^{-1}.

^{1}H NMR: δ 1.34, 1.36, 1.40, 1.44, 1.46, 1.75 (many lines, together 36 H, $C(CH_3)_3$), 3.30 (br, 1 H, NH), 3.56 (minor) and 3.61 (major) [2 s, 6 H, OCH_3 + CO_2CH_3), 4.42 and 4.55 (2 d, the one at 4.55 is minor, ^3J(P-H) = 18.8 and 18.8 Hz respectively, 1 H, $CH(OCH_3)$).

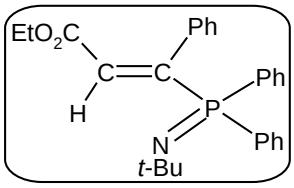
^{13}C NMR: δ 28 5 (s, $C(CH_3)_3$), 32.0 (d, ^3J(P-C) = 5.0 Hz, $C(CH_3)_3$), 32.5 (d, ^3J(P-C) = 10 Hz, $C(CH_3)_3$), 44.1, 44.3, 47.3, 48.8, 49.7, 52.1, 52.4, 54.5, 55.5, 54.8, 55.0, 57.2, 57.9 and 59.0 (many signals, $C(CH_3)_3$, OCH_3), 78.9, 79.2, 164.2, 174.8, 175.5 (as mentioned elsewhere,[3] the ^{13}C NMR spectrum was not very clear-cut for the assignment of signals).

^{31}P NMR: δ 28.9, 30.5, 89.4. The combined intensity of the tetracoordinate region (δ 28.9, 30.5) was nearly equal to the intensity of the signal at δ 89.4. This together with the ^{1}H NMR data suggests equilibrium in solution with an isomeric form for which P^{III} region is same but tetracoordinate phosphorus chemical shift is different.

Anal. Calc. for $C_{22}H_{44}N_4O_4P_2$: C, 53.86; H, 9.04; N, 11.42. Found: C, 53.86; H, 9.06; N, 11.67.

(e) Synthesis of $Ph_2P[(N\text{-}t\text{-}Bu)\{C(Ph)=CH(COOEt)\}]$ (9)

The procedure was the same as that for **5** using $Ph_2P(NH\text{-}t\text{-}Bu)$ (**2**) (0.82 g, 3.18 mmol) and ethyl phenylpropiolate (0.55 g, 3.18 mmol) [reaction time 24 h].



Yield: 1.16 g (85%).

Mp: 101-104 ^{o}C.

IR (KBr): 3055, 2963, 1728, 1620, 1437, 1265, 1194 cm^{-1}.

^{1}H NMR: δ 1.01 (t, ^{3}J(H-H) = 7.0 Hz, 3 H, OCH_2CH_3), 1.13 (s, 9 H, $C(CH_3)_3$), 4.00 (q, ^{3}J(H-H) = 7.0 Hz, 2 H, OCH_2CH_3), 6.58 (d, ^{3}J(P-H) ~ 7.0 Hz, 1 H, PCC*H*), 7.00-7.65 (m, 15 H, Ar-*H*).

^{13}C NMR: δ 13.7 (s, OCH_2CH_3), 31.5 (s, $C(CH_3)_3$), 32.9 (d, ^{3}J(P-C) = 10.0 Hz, $C(CH_3)_3$), 34.7 (br, $C(CH_3)_3$), 52.0 (br, $C(CH_3)_3$), 60.1 (s, $CO_2CH_2CH_3$), 127.3, 128.1, 128.7, 131.2, 131.6, 131.8, 140.0, 133.6 (Ar-C + PC +PCC), 165.0 (br, *C*=O).

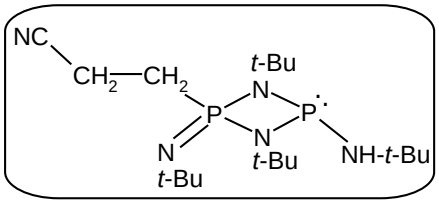
^{31}P NMR: δ –8.5.

Anal. Calc. for $C_{27}H_{30}NO_2P$: C, 75.14; H, 7.00; N, 3.26. Found: C, 75.42; H, 6.96; N, 3.17.

6.4 Reactions of cyclodiphosphazane 1 with activated alkenes

(a) Synthesis of (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P(N-*t*-Bu)(CH$_2$-CH$_2$-CN) (11)

The procedure was the same as that for **5** using **1** (0.571 g, 1.63 mmol) and acrylonitrile (0.086 g, 1.63 mmol) [reaction time 2 d].



Yield: 0.59 g (90%).

Mp: 88-91 ^{o}C.

IR (KBr): 3345, 2959, 2255, 2236, 1470, 1333, 1209 cm^{-1}.

^{1}H NMR: δ 1.29, 1.34 and 1.41 (3 s, 36 H, $C(CH_3)_3$), 2.29 (br, 4 H, PCH_2CH_2), 2.96 (br d, ^{2}J(P-H) = 16.0 Hz, 1 H, N*H*).

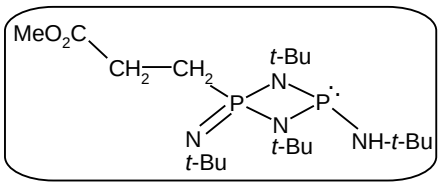
^{13}C NMR: δ 12.1 (s, $PCCH_2$), 29.0 (d, ^{1}J(P-C) = 135.0 Hz, P*C*), 31.9 (s, $C(CH_3)_3$), 32.8 (d, ^{3}J(P-C) = 10.0 Hz, $C(CH_3)_3$), 34.2 (d, ^{3}J(P-C) = 12.0 Hz, $C(CH_3)_3$), 51.9-52.4 (many lines, $C(CH_3)_3$), 119.5 (s, *C*N).

^{31}P NMR: δ -12.2, 73.0.

Anal. Calc. for $C_{19}H_{41}N_5P_2$: C, 56.84; H, 10.29; N, 17.44. Found: C, 56.63; H, 10.25; N, 17.19.

***(b) Synthesis of* (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P(N-*t*-Bu)(CH$_2$-CH$_2$CO$_2$Me) (12)**

The procedure was the same as that for **5** using **1** (0.74 g, 2.12 mmol) and methyl acrylate (0.18 g, 2.12 mmol) [reaction time 2 d].



Yield: 0.801 g (87%).

Mp: 60-62 ^{o}C.

IR (KBr): 3390, 2967, 1738, 1329, 1206 cm^{-1}.

^{1}H NMR: δ 1.31, 1.39 and 1.44 (3 s, 36 H, C(C*H*$_3$)$_3$), 2.20-2.32 (many lines, 4 H, PC*H*$_2$C*H*$_2$), 2.92 (br, 1 H, N*H*), 3.67 (s, 3 H, OC*H*$_3$).

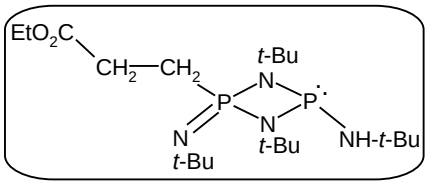
^{13}C NMR: δ 28.2 (d, ^{1}J(P-C) = 150.0 Hz, P*C*), 28.5 (s, PC*C*H$_2$), 31.5-34.2 (many lines, C(*C*H$_3$)$_3$), 51.3 (s, O*C*H$_3$), 51.0, 51.7, 52.0, 52.1 (4 lines, *C*(CH$_3$)$_3$), 173.2 (d, ^{3}J(P-C) = 23.0 Hz, *C*OMe).

^{31}P NMR: δ -6.4, 72.3.

LC-MS: m/z 435 [M+1]$^{+}$.

***(c) Synthesis of* (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P(N-*t*-Bu){CH$_2$-CH$_2$(CO$_2$Et)} (13)**

The procedure was the same as that for **5** using **1** (0.392 g, 1.12 mmol) and ethyl acrylate (0.13 g, 1.12 mmol) [reaction time 2 d].



Yield: 0.466 g (90%).

Mp: 68–70 ^{o}C.

IR (KBr): 3356, 2973, 1736, 1464, 1310, 1211 cm^{-1}.

^{1}H NMR: δ 1.24 (t, ^{3}J(H-H) = 6.8 Hz, 3 H, OCH$_2$C*H*$_3$), 1.31, 1.39, 1.44 (3 s, 36 H, C(C*H*$_3$)$_3$), 2.20-2.31 (many lines, 4 H, PC*H*$_2$C*H*$_2$), 3.05 (br, 1 H, N*H*), 4.12 (q, ^{3}J(H-H) = 6.8 Hz, 2 H, OC*H*$_2$CH$_3$).

^{13}C NMR: δ 14.2 (s, OCH$_2$*C*H$_3$), 27.9 (d, ^{1}J(P-C) = 134.0 Hz, P*C*), 28.6 (s, PC*C*H$_2$), 31.7 (s, C(*C*H$_3$)$_3$), 32.8 (d, ^{3}J(P-C) = 10.0 Hz, C(*C*H$_3$)$_3$), 34.2 (d, ^{3}J(P-C) = 12.0 Hz, C(*C*H$_3$)$_3$), 51.1 (d, ^{2}J(P-C) = 13.0 Hz,

$C(CH_3)_3$), 51.8 (d, ^2J(P-C) = 9.5 Hz, $C(CH_3)_3$), 52.2 (d, ^2J(P-C) = 7.5 Hz, $C(CH_3)_3$), 60.4 (s, OCH_2), 172.9 (d, ^3J(P-C) = 23.0 Hz, CO_2Et) [*cf.* Fig. 21].

^{31}P NMR: δ -6.2, 72.8.

LC-MS: m/z 449 $[M+1]^+$.

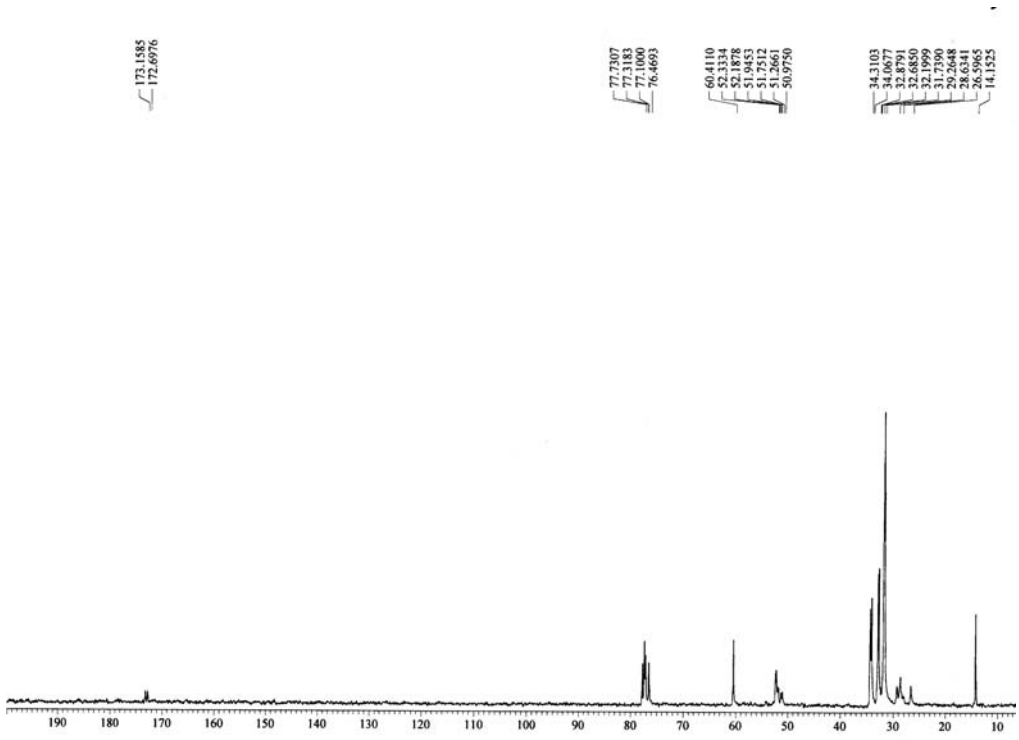
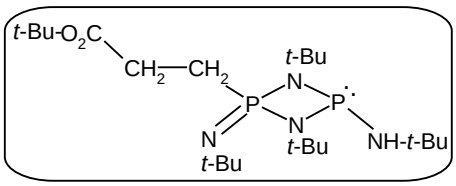


Fig. 21. ^{13}C NMR spectrum of compound **13**

***(d) Synthesis of* (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P(N-*t*-Bu){CH_2-CH_2(CO_2-*t*-Bu)} (14)**

The procedure was the same as that for **5** using **1** (1.34 g, 3.83 mol) and *t*-butyl acrylate (0.13 g, 1.12 mmol) [reaction time 36 h].



Yield: 1.586 g (87%).

Mp: 75-78 ^oC.

IR (KBr): 3356, 2971, 1732, 1364, 1321, 1219 cm^{-1}.

^{1}H NMR: δ 1.28 (s, 9 H, $CO_2C(CH_3)_3$), 1.37, 1.40 and 1.42 (3 s, 36 H, $NC(CH_3)_3$), 2.02-2.12 (m, 2 H, PCH_2), 2.21-2.32 (m, 2 H, $PCCH_2$), 2.95 (br, 1 H, N*H*).

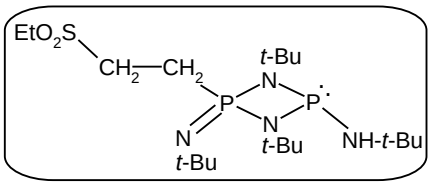
^{13}C NMR: δ 28.0 (s, $OC(CH_3)_3$), 28.2 (d, ^{1}J(P-C) = 134.0 Hz, P*C*), 29.9 (br s, $PCCH_2$), 31.7 (s, $C(CH_3)_3$), 32.8 (d, ^{3}J(P-C) = 10.0 Hz, $NC(CH_3)_3$), 34.3 (d, ^{3}J(P-C) = 12.0 Hz, $NC(CH_3)_3$), 51.1 (d, ^{2}J(P-C) = 15.0 Hz, $NC(CH_3)_3$), 51.8 (d, ^{2}J(P-C) = 10.0 Hz, $NC(CH_3)_3$), 52.3 (d, ^{2}J(P-C) = 13.0 Hz, $NC(CH_3)_3$), 80.3 (s, $OC(CH_3)_3$), 172.3 (d, ^{3}J(P-C) = 23.0 Hz, $CO_2C(CH_3)_3$).

^{31}P NMR: δ -3.4, 72.1.

LC-MS: m/z 477 $[M+1]^+$.

(e) Synthesis of (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P(N-*t*-Bu)(CH_2-CH_2SO_2Et) (15)

The procedure was the same as that for **5** using **1** (0.74 g, 2.12 mmol) and ethyl vinyl sulfone (0.28 g, 2.34 mmol) [reaction time 2 d].



Yield: 0.82 g (82%).

Mp: 92-97 ^{o}C.

IR (KBr): 3340, 2969, 1647, 1458, 1364, 1209, 1134 cm^{-1}.

^{1}H NMR: δ 1.28, 1.35 and 1.42 (3 s, 36 H, $C(CH_3)_3$), 1.36 (br, 3 H, CH_2CH_3), 2.42 (br, 2 H, PCH_2), 2.95 (br m, 5 H, $PCH_2CH_2 + SO_2CH_2 + NH$).

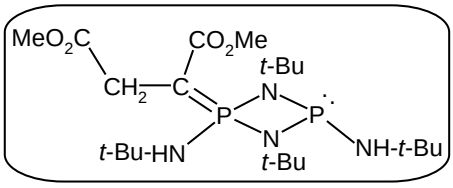
^{13}C NMR: δ 6.63 (s, CH_2CH_3), 25.8 (d, ^{1}J(P-C) = 128.6 Hz, P*C*), 31.8 (s, $C(CH_3)_3$), 32.8 and 34.2 (d each, ^{3}J(P-C) = 9.7, 12.1 Hz respectively, $C(CH_3)_3$), 46.8 and 47.3 (2 br s, $PCH_2CH_2 + SO_2CH_2$), 51.5 (d, ^{2}J(P-C) = 14.0 Hz, $C(CH_3)_3$), 52.1 (d, ^{2}J(P-C) = 8.5 Hz, $C(CH_3)_3$), 52.5 (d, ^{2}J(P-C) = 7.3 Hz, $C(CH_3)_3$).

^{31}P NMR: δ –10.4, 72.8.

Anal. Calc. for $C_{20}H_{46}N_4O_2P_2S$: C, 51.26; H, 9.89; N, 11.96. Found: C, 51.26; H, 9.90; N, 11.87.

***(f) Synthesis of* (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P(N-*t*-Bu){CH(CO$_2$Me)CH$_2$(CO$_2$Me)} (16)**

To a solution of **1** (0.531 g, 1.52 mol) in toluene (15 mL), dimethyl maleate (0.22 g, 1.52 mol) was added *via* syringe at room temperature, the mixture was stirred for 3 d and the solution concentrated *in vacuo* (*ca* 1.5 mL) and kept at -4 ^{o}C for 24 h to obtain the crystals of **16**.



Yield: 0.655 g (90%).

Mp: 138-141 ^{o}C.

IR (KBr): 3380, 2969, 1752, 1603, 1437, 1368, 1327, 1208 cm^{-1}.

^{1}H NMR: δ 1.32, 1.42 and 1.55 (3 s, 36 H, C(C*H*$_3$)$_3$), 2.65 (d, ^{3}J(H-H) = 14.4 Hz, 2 H, PC*C*H$_2$), 3.04 (d, ^{2}J(P-H) = 8.0 Hz, 1 H, N*H*), 3.54 and 3.65 (2 s, 6 H, OC*H*$_3$), 9.08 (d, ^{2}J(P-H) = 8.0 Hz, 1 H, N*H*).

^{13}C NMR: δ 30.9, 31.0, 32.2 and 32.8 (d each, ^{3}J(P-C) = 4.5, 4.5, 3.6 and 9.7 Hz respectively, C(*C*H$_3$)$_3$), 31.4 (s, PC*C*H$_2$), 45.2 (d, ^{1}J(P-C) = 183.0 Hz, P*C*), 49.8, 51.0 (2 s, O*C*H$_3$), 51.5, 51.8 (2 s, *C*(CH$_3$)$_3$) 52.6 (d, ^{2}J(P-C) = 6 Hz, *C*(CH$_3$)$_3$), 171.7 (d, ^{2}J(P-C) = 30.0 Hz, *C*O$_2$Me), 174.9 (d, ^{3}J(P-C) = 10.0 Hz, *C*O$_2$Me) [*cf.* Fig. 22].

^{31}P NMR: δ 23.7, 78.9.

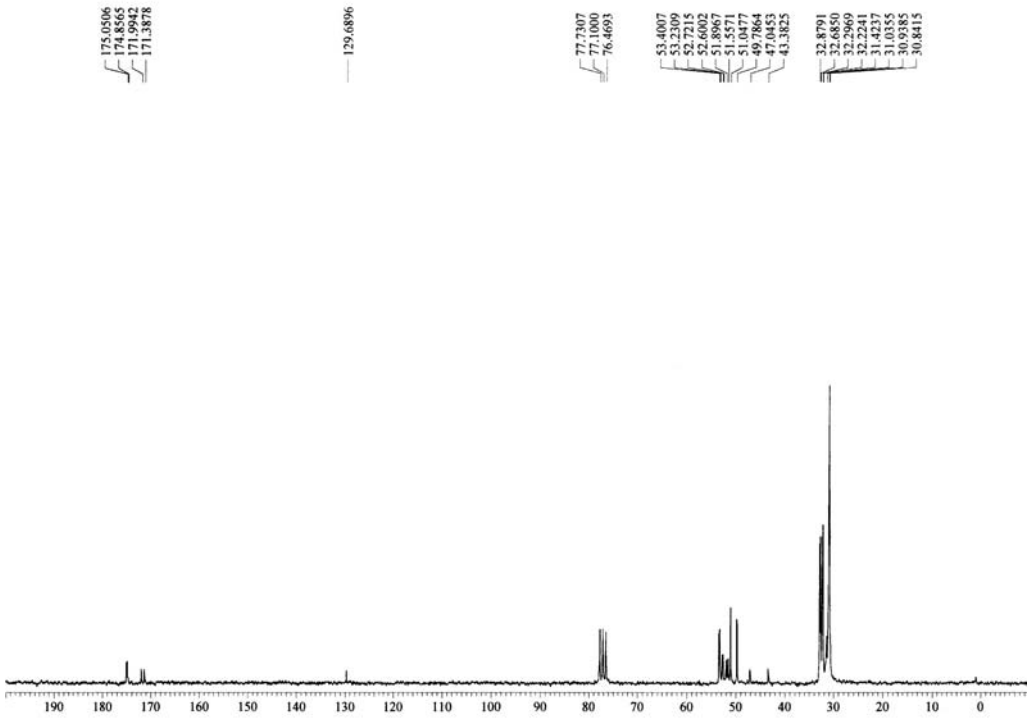


Fig. 22. ^{13}C NMR spectrum of compound **16**

6.5 Reaction of 2 with diisopropyl azodicarboxylate (DIAD): Isolation of $Ph_2P(=N\text{-}t\text{-}Bu)N(CO_2\text{-}i\text{-}Pr)\text{-}NH(CO_2\text{-}i\text{-}Pr)$ (18)

Compound **2** (1.10 g, 4.27 mmol) and DIAD (0.86 g, 4.27 mmol) were dissolved in toluene (4 mL), and the mixture stirred for 1 d. The solution was concentrated *in vacuo* to *ca* 1.5 mL and cooled for 1 d at –4 ^{o}C to obtain crystals of **18**. We were successful in purifying the compound to >95%. The structure of compound **18** was confirmed by X-ray crystallography.

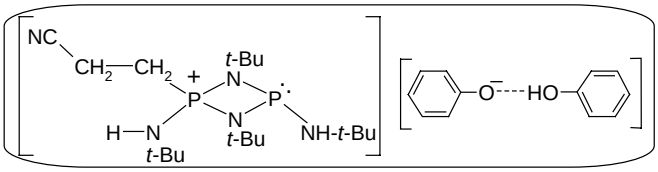
^{1}H NMR: δ 1.03-1.29 (m, 21 H, 2 CH(C*H*$_3$)$_2$ + C(C*H*$_3$)$_3$), 2.84 (br, 1 H, N*H*), 4.79-4.95 (m, 2 H, C*H*(CH$_3$)$_2$), 7.35-7.91 (m, 10 H, Ar-*H*).

^{31}P NMR: δ –12.5. A minor peak (ca 5%) at δ 18.5 was observed even for the crystalline material.

6.6 Reaction of $(t\text{-}Bu\text{-}HN)P(\mu\text{-}N\text{-}t\text{-}Bu)_2P(N\text{-}t\text{-}Bu)(CH_2\text{-}CH_2\text{-}CN)$ (11) with phenol: *Synthesis of* $(t\text{-}Bu\text{-}HN)P(\mu\text{-}N\text{-}t\text{-}Bu)_2P^{+}[(HN\text{-}t\text{-}Bu)\{CH_2\text{-}CH_2CN\}][Ph\text{-}O\text{-}H\ldots OPh]$ (21.Ph-O-H…OPh)

To a solution of **11** (0.599 g, 1.49 mmol) in toluene (10 mL), phenol (0.20 g, 2.13 mmol) was added all at once at room temperature and mixture was stirred for 6

h, later the solution was concentrated *in vacuo* (to *ca* 1.5 mL) and cooled to -4 ^{o}C for 24 h to obtain the crystals of **21**.Ph-O-H…OPh.



Yield: 0.58 g (65%).

Mp: 92-95 ^{o}C.

IR (KBr): 3380, 3100, 2971, 2180, 1589, 1472, 1370, 1071 cm^{-1}.

^{1}H NMR: δ 1.31, 1.45, 1.46 (3 s, 36 H, C(C*H*$_3$)$_3$), 2.15 (br, 2 H, PCC*H*$_2$), 2.48 (br, 3 H, PC*H*$_2$ + N*H*), 3.40 (br, 1 H, N*H*), 6.62 - 7.26 (m, 11 H, Ar-*H* + O*H*).

^{13}C NMR: δ 10.9 (s, PC*C*H$_2$), 26.6 (d, ^{1}J(P-C) = 121.3 Hz, P*C*), 31.8 (s, C(*C*H$_3$)$_3$), 32.3 (d, ^{3}J(P-C) = 9.0 Hz, C(*C*H$_3$)$_3$), 33.3 (d, ^{3}J(P-C) = 9.7 Hz, C(*C*H$_3$)$_3$), 52.0 (d, ^{2}J(P-C) = 14.5 Hz, *C*(CH$_3$)$_3$), 53.2 (s, *C*(CH$_3$)$_3$), 53.5 (d, ^{2}J(P-C) = 10.0 Hz, *C*(CH$_3$)$_3$), 116.3, 118.8, 119.0,129.1 and 129.5 (*C*N and Ar*C*), 158.2 (s, Ar*C*O).

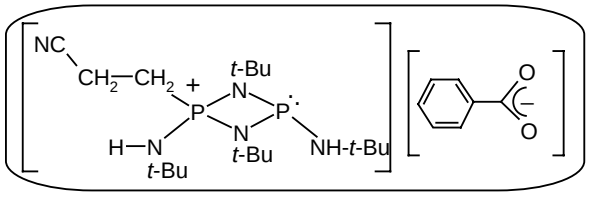
^{31}P NMR: δ 75.9 and 75.6 (probably a doublet, J ~ 24.0 Hz), 3.6 (br).

Anal. Calc. for $C_{31}H_{53}N_5O_2P_2$: C 63.13, H 9.06, N 11.86. Found: C 63.24, H 9.02, N 11.82.

6.7 Reaction of (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P(N-*t*-Bu)(CH$_2$-CH$_2$-CN) (11) with substituted benzoic acids

(a) Synthesis of (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P^{+}[(HN-*t*-Bu){CH$_2$-CH$_2$CN}](C$_6$H$_5$COO)$^{-}$] (22)

To a solution of **11** (0.432 g, 1.07 mmol) in toluene (10 mL), benzoic acid (0.13 g, 1.07 mmol) was added all at once, the mixture was stirred for 6 h, concentrated *in vacuo* (*ca* 2 mL) and cooled at -4 ^{o}C for 24 h to obtain crystals of **22**.



Yield: 0.504 g (90%).

Mp: 114-117 ^{o}C.

IR (KBr): 3298, 3057, 2971, 2245, 1597, 1552, 1368, 1196 cm^{-1}.

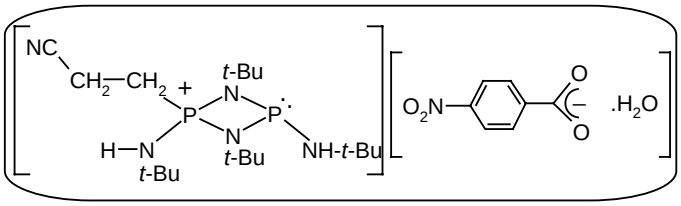
^{1}H NMR: δ 1.32, 1.52 and 1.55 (3 s, 36 H, C(CH_3)$_3$), 2.48 (br, 4 H, PCH_2+PCCH_2), 3 45 (br, 2 H, N*H*) 7.33 (br, 3 H, Ar-*H*), 8.07 (m, 2 H, Ar-*H*).

^{13}C NMR: δ 10.1 (s, PC*C*H$_2$), 23.7 (d, ^1J(P-C) = 101.0 Hz, P*C*), 31.4 and 31.7 (2 s, C(*C*H$_3$)$_3$), 32.5 (d, ^3J(P-C) = 10.0 Hz, C(*C*H$_3$)$_3$), 52.7 (d, ^2J(P-C) = 16.0 Hz, *C*(CH$_3$)$_3$), 54.5 (d, ^2J(P-C) = 6.0 Hz, *C*(CH$_3$)$_3$), 55.1 (d, ^2J(P-C) =7.0 Hz, *C*(CH$_3$)$_3$), 117.8 (d, ^3J(P-C) ~ 30.0 Hz, *C*N), 127.4, 129.4 and 139.0 (all Ar*C*) 172.4 (s, *C*O_2^-).

^{31}P NMR: δ 21.4, 82.3.

***(b) Synthesis of* (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P$^+$[(HN-*t*-Bu){CH$_2$-CH$_2$CN}](4-NO$_2$-C$_6$H$_4$COO$^-$) (H$_2$O) (23**.H$_2$O**)**

The procedure was similar to that for **22** using **11** (0.378 g, 0.94 mmol) and 4-nitrobenzoic acid (0.158 g, 0.94 mmol). The compound was crystallized in open air.



Yield: 0.48 g (90%).

Mp: 120-122 ^{o}C.

IR (KBr): 3368 (w), 3281, 2969, 2254, 1618, 1519, 1458, 1368, 1198 cm^{-1}.

^{1}H NMR: δ 1.34, 1.53 and 1.56 (3 s, br, 36 H, C(CH_3)$_3$), 2.34-2.44 (br, 4 H, PCH_2 + PCCH_2), 3.22-3.42 (br, 4 H, 2 N*H* + H_2O), 8.17 (s, 4 H, Ar-*H*).

^{13}C NMR: δ 10.0 (s, PC*C*H$_2$), 23.3 (d, ^1J(P-C) = 101.0 Hz, P*C*), 31.1 and 31.7 (2 s, C(*C*H$_3$)$_3$), 32.5 (d, ^3J(P-C) = 9.0 Hz, C(*C*H$_3$)$_3$), 52.8, 54.6, 55.3 (3 s, *C*(CH$_3$)$_3$), 117.6 (d, ^3J(P-C) = 20.0 Hz, *C*N), 122.8, 130.2, 145.5, 148.6 (Ar*C*), 170.2 (s, *C*O_2^-) [*cf.* Fig. 23].

^{31}P NMR: δ 21.4, 82.5.

Anal. Calc. for $C_{26}H_{48}N_6O_5P_2$: C, 53.23; H, 8.24; N, 14.32. Found: C, 53.32; H, 8.28; N, 14.32.

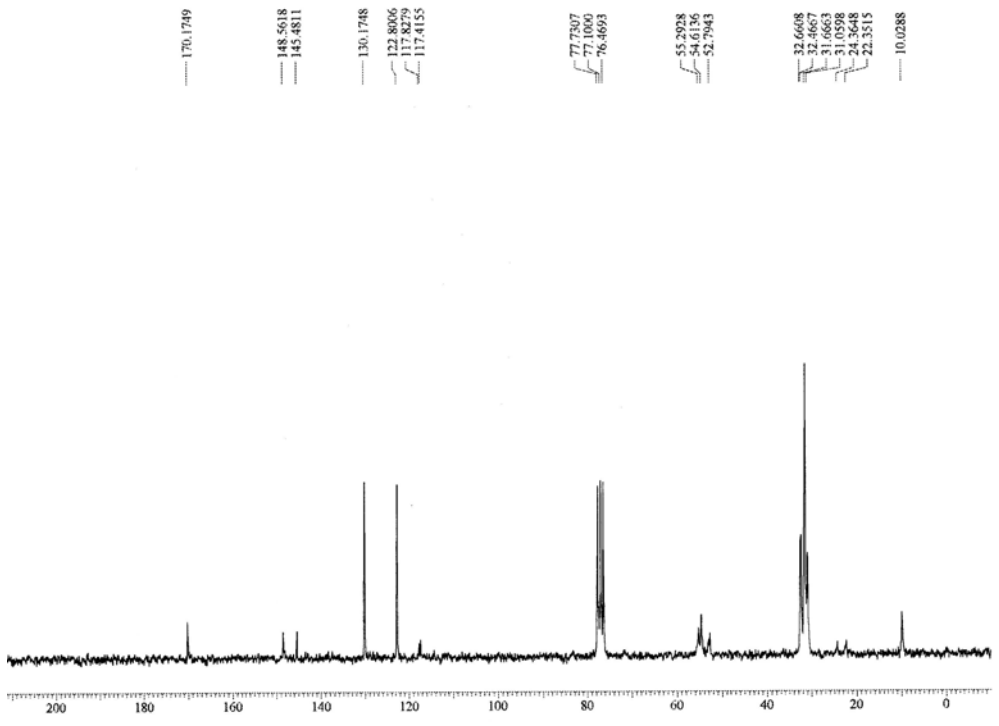
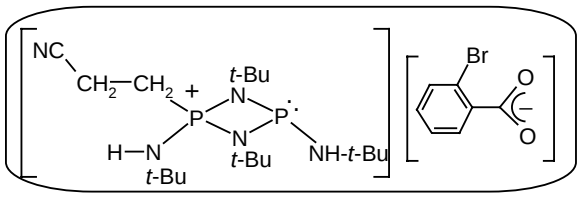


Fig. 23. ^{13}C NMR spectrum of compound **23.H_2O**

***(c) Synthesis of* (*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P$^+$[(HN-*t*-Bu){CH_2-CH_2(CN)}](2-Br-$C_6H_4COO)^-$ (24)**

The procedure was similar to that for **22** using **11** (0.49 g, 1.21 mmol) and 2-bromobenzoic acid (0.25 g, 1.21 mmol).



Yield: 0.635 g (87%).

Mp: 78-81 ^{o}C.

IR (KBr): 3408, 3129, 2971, 2240, 1599, 1370, 1198 cm^{-1}.

^{1}H NMR: δ 1.34, 1.52 and 1.60 (3 s, 36 H, C(CH_3)$_3$), 2.34 (br, 4 H, PCH_2+PCCH_2), 3.40-3 43 (br, 2 H, 2 N*H*), 7.01 - 7.53 (m, 4 H, Ar-*H*).

^{13}C NMR: δ 10.0 (s, PCCH_2), 23.3 (d, ^1J(P-C) = 101.0 Hz, P*C*), 31.2, 31.6 (2 s, C(*C*H_3)$_3$), 32.5 (d, ^3J(P-C) = 10.0 Hz, C(*C*H_3)$_3$), 52.8 (d, ^2J(P-C) = 12.0 Hz, *C*(CH$_3$)$_3$), 54.6, 55.5 (2 s, *C*(CH$_3$)$_3$), 117.6 (d, ^3J(P-

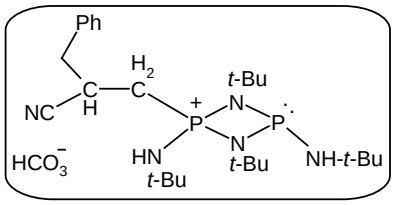
C) = 20.0 Hz, *C*N), 126.7, 128.1, 128.2, 129.1, 132.5 (Ar*C*), 173.1 (s, CO_2^-).

^{31}P NMR: δ 21.6, 82.1.

6.8 Reaction of cyclodiphosphazane 1 with 2-benzyl-acrylonitrile and acrylonitrile- Identification of 25 and isolation of bicarbonate salts 26 and 27

(a) *Synthesis of* [(*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P{(HN-*t*-Bu)CH$_2$-CH(CN)(CH$_2$Ph)}]$^+$[HCO$_3$]$^-$ (26)

To a solution of **1** (0.706 g, 2.02 mmol) in toluene (10 mL), 2-benzyl-acrylonitrile[43] (0.433 g, 3.03 mmol) was added *via* syringe at room temperature and mixture heated under reflux for 2 d. At this stage, the ^{31}P NMR spectrum showed mainly four peaks [-17.6 and -7.1 (tetracoordinate) 72.1 and 74.1 (tricoordinate)] corresponding to two species. These peaks are most likely due to two isomeric species of **25** that differ about the P=N bond. This solution was concentrated *in vacuo* and chromatographed (silica gel, 85% ethyl acetate- 15% hexane) to get **26** (0.11 g, 10%). The product eluted from column was different from that present before. Crystals were obtained at room temperature from dichloromethane-hexane mixture.



Yield: (isolated) 0.11 g (10%).

Mp: 206 (dec.).

IR (KBr): 3208, 3102, 2971, 2241, 1493, 1454, 1367, 1196 cm^{-1}.

^{1}H NMR: δ 1.35, 1.38, 1.52, 1.68 (4 s, 36 H, C(C*H*$_3$)$_3$), 2.82 (br m, 2 H, PC*H*$_2$), 3.02 (br m, 3 H, PCC*H* + PCCC*H*$_2$), 3.38 (br, 1 H, N*H*), 7.25-7.37 (m, 5H, Ar-*H*), 8.10 (br, 1 H, N*H*) (C-O*H* proton peak was too broad).

^{13}C NMR: δ 26.6 (s, PC*C*H), 30.9 (d, ^1J(P-C) ~ 121.0 Hz, P*C*, one of the peaks merged with peaks due to *t*-Bu carbons), 31.1, 31.4 (2 s, C(*C*H$_3$)$_3$), 32.5 (d, ^3J(P-C) ~ 10.0 Hz, C(*C*H$_3$)$_3$), 40.4 (d, ^3J(P-C) = 15.0 Hz,

C*H*$_2$Ph), 52.9-56.1 (many lines, *C*(CH$_3$)$_3$), 120.0 (s, *C*N), 128.1, 129.2, 129.6, 134.9 (the peak due to bicarbonate was too weak to be observed).

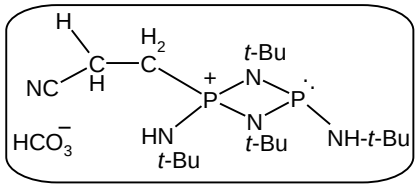
^{31}P NMR: δ 21.4, 88.0.

Anal. Calc. for $C_{27}H_{49}N_5O_3P_2$: C, 58.57; H, 8.92; N, 12.64. Found: C, 58.72; H, 8.81; N, 12.66.

X-ray structure was determined for this compound.

(b) *Synthesis of* [(*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P{(HN-*t*-Bu)CH$_2$-CH$_2$CN}]$^+$[HCO$_3$]$^-$ (27) [analogous to 26]

Compound **27** was obtained by passing compound **11** through a silica gel column using ethyl acetate-hexane (9:1) mixture as eluent.



Yield: 0.59 g (90%).

Mp: 182-183 ^{o}C (dec.).

IR (KBr): 3451, 3216, 2974, 2249, 1370, 1198 cm^{-1}.

^{1}H NMR: δ 1.34, 1.46, 1.52 (3s, 36 H, C(C*H*$_3$)$_3$), 2.38 (br, 2 H, PCH$_2$C*H*$_2$), 3.05 (br, 2 H, PC*H*$_2$), 3.35 (br, ~1 H, N*H*), the other N*H* and C-O*H* proton peaks were too broad.

^{13}C NMR: δ 9.9 (s, PC*C*H$_2$), 23.4 (d, ^1J(P-C) = 97.0 Hz, P*C*), 31.8, 32.3, 32.5 (3 s, C(*C*H$_3$)$_3$), 53.0 (d, ^2J(P-C) = 15.0 Hz, *C*(CH$_3$)$_3$), 54.7 and 56.1 (2 s, *C*(CH$_3$)$_3$), 117.5 (s, *C*N) (The peak due to bicarbonate was perhaps too weak to be observed).

^{31}P NMR: δ 21.1, 83.4.

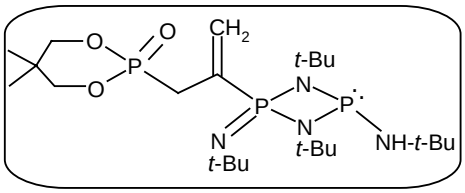
Anal. Calc. for $C_{20}H_{43}N_5O_3P_2$: C, 51.79; H, 9.34; N, 15.17. Found: C, 51.86; H, 9.32; N, 15.08.

6.9 Reactions of cyclodiphosphazane 1 and with activated allenes

6.91 *Reaction of 1 with allenylphosphonates 3a-c*

***(a) Synthesis of* [(*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P{(N-*t*-Bu)C(=CH$_2$)-CH$_2$-P(O)(OCH$_2$CMe$_2$CH$_2$O)] (31a)**

Cyclodiphosphazane **1** (0.316 g, 0.91 mmol) and allenylphosphonate **3a** (0.171 g, 0.91 mmol) were dissolved in toluene (4 mL), and the mixture was stirred for 1 d. The solution was concentrated *in vacuo* (to *ca* 1.5 mL) and cooled for 1 d at –4 ^{o}C to obtain crystals of **31a**.



Yield: 0.41 g (85%).

Mp: 150–153 ^{o}C.

IR (KBr): 3351, 2963, 2903, 1607, 1474, 1364, 1289, 1217, 1065, 887 cm^{-1}.

^{1}H NMR: δ 0.95 and 1.26 (2 s, 6 H, C(C*H*$_3$)$_2$), 1.33, 1.35 and 1.38 (3 s, 36 H, C(C*H*$_3$)$_3$), 2.79 (d, ^{2}J(P-H) = 7.6 Hz, 1 H, N*H*), 3.47 (dd, ^{3}J(P-H) ~ 9.7 Hz, ^{2}J(H-H) = 10.1 Hz, 2 H, OC*H*$_2$), 3.85 (dd, ^{3}J(P-H) = 7.6 Hz, ^{2}J(H-H) ~ 11.0 Hz, 2 H, OC*H*$_2$), 4.33 (d, ^{2}J(P-H) = 9.2 Hz, 2 H, P(O)C*H*$_2$), 5.79 (dd, ^{3}J(P-H) = 22.2 Hz, ^{4}J(P-H) ~ 3.7 Hz, 1 H, =C*H*$_A$H$_B$, *cis* to P)), 6.30 (d, ^{3}J(P-H) = 50.8 Hz, 1 H, =CH$_A$*H*$_B$, *trans* to P).

^{13}C NMR: δ 20.9 and 22.0 (2 s, C(*C*H$_3$)$_2$), 24.9 (d, ^{1}J(P-C) = 127.0 Hz, P(O)*C*H$_2$), 31.3 (dd→t, ^{3}J(P-C) ~ 4.5 Hz, two of C(*C*H$_3$)$_3$), 32.5 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 33.0 (d, ^{3}J(P-C) = 10.0 Hz, C(*C*H$_3$)$_3$), 34.5 (d, ^{3}J(P-C) = 12.0 Hz, C(*C*H$_3$)$_3$), 51.2, 51.4 and 52.1 (3 s, *C*(CH$_3$)$_3$), 52.4 (d, ^{2}J(P-C) = 8.0 Hz, *C*(CH$_3$)$_3$) 76.6 and 76.7 (2 s, O*C*H$_2$), 127.9 (s, PC=*C*H$_2$), 143.4 (d with low intensity, ^{1}J(P-C) ~ 162.9 Hz, P*C*=CH$_2$).

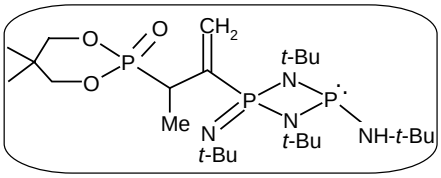
^{31}P NMR: δ -16.5 (d, ^{3}J(P-P) ~ 26.2 Hz), 23.5 (d, ^{3}J(P-P) ~ 26.2 Hz), 71.7.

LC-MS: *m/z* 537 [M+1]$^{+}$.

Anal. Calc. for C$_{24}$H$_{51}$N$_4$O$_3$P$_3$: C, 53.72; H, 9.58; N, 10.44. Found: C, 53.68; H, 9.55; N, 10.42.

***(b) Synthesis of* [(*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P{(N-*t*-Bu)C(=CH$_2$)-CH(Me)-P(O)(OCH$_2$CMe$_2$CH$_2$O)] (31b)**

In a procedure similar to that for **31a**, **1** (0.328 g, 0.94 mmol) and allenylphosphonate **3b** (0.190 g, 0.94 mmol) were used. The solution was concentrated *in vacuo* to *ca* 1.5 mL and cooled for 1 d at –4 ^{o}C to obtain crystals of **31b**.



Yield: 0.47 g (90%).

Mp: 186–189 ^{o}C.

IR (KBr): 3368, 2965, 1867, 1607, 1472, 1364, 1298, 1213, 1071, 1044 cm^{-1}.

^{1}H NMR: δ 1.00 and 1.17 (2 s, 6 H, C(C*H*$_3$)$_2$), 1.32, 1.35 and 1.37 (3 s, 36 H, C(C*H*$_3$)$_3$), 1.48 (dd, ^{3}J(P-H) = 10.9 Hz, ^{3}J(H-H) = 7.2 Hz, 3 H, P(O)CC*H*$_3$), 2.75 (d, ^{2}J(P-H) = 7.4 Hz, 1 H, N*H*), 3.80-4.51 (m, 5 H, P(O)C*H*+OC*H*$_2$), 5.78 (dd, ^{3}J(P-H) = 21.9 Hz, ^{4}J (P-H) ~ 4.6 Hz, 1 H, =C*H*$_A$H$_B$, *cis* to P), 6.31 (d, ^{3}J(P-H) = 51.8 Hz, 1 H, =CH$_A$*H*$_B$, *trans* to P).

^{13}C NMR: δ 17.8 (d, ^{2}J(P-C) = 3.7 Hz, P(O)C*C*H$_3$), 21.2 and 21.9 (2 s, C(*C*H$_3$)$_2$), 30.2 (d, ^{1}J(P-C) = 126.9 Hz, P(O)*C*(CH$_3$)), 31.4 (dd→t, ^{3}J(P-C) = 4.7 Hz, C(*C*H$_3$)$_3$), 31.6 (dd→t, ^{3}J(P-C) = 4.8 Hz, C(*C*H$_3$)$_3$), 32.5 (d, ^{3}J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 32.9 (d, ^{3}J(P-C) = 9.6 Hz, C(*C*H$_3$)$_3$), 34.4 (d, ^{3}J(P-C) = 12.2 Hz, C(*C*H$_3$)$_3$), 51.4 (d, ^{2}J(P-C) = 14.7 Hz, *C*(CH$_3$)$_3$), 52.0 (d, ^{2}J(P-C) = 8.7 Hz, *C*(CH$_3$)$_3$), 52.5 (d, ^{2}J(P-C) = 9.2 Hz, *C*(CH$_3$)$_3$), 52.6 (d, ^{2}J(P-C) = 8.0 Hz, *C*(CH$_3$)$_3$), 75.8 and 75.9 (2 br s, O*C*H$_2$), 128.6 (s, C=*C*H$_2$), 145.1 (d, ^{1}J(P-C) ~ 200 Hz, P*C*=CH$_2$).

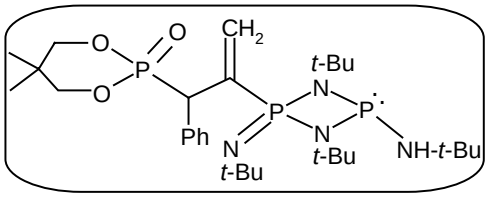
^{31}P NMR: δ -17.9 (d, ^{3}J(P-P) ~ 30.5 Hz), 27.6 (d, ^{3}J(P-P) ~ 30.5 Hz), 71.0.

LC-MS: 551 [M+1]$^{+}$.

Anal. Calc. for C$_{25}$H$_{53}$N$_4$O$_3$P$_3$: C, 54.53; H, 9.70; N, 10.17. Found: C, 68.65; H, 5.75.

***(c) Synthesis of* [(*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P{(N-*t*-Bu)C(=CH$_2$)-CH(Ph)-P(O)(OCH$_2$CMe$_2$CH$_2$O)] (31c)**

This compound was also prepared by a procedure similar to that for **31a**, using **1** (0.27 g, 0.78 mmol) and allenylphosphonate **3c** (0.20 g, 0.78 mmol).



Yield: 0.42 g (90%).

Mp: 152–154 ^{o}C.

IR (KBr): 3310, 2964, 2888, 1599, 1476, 1456, 1366, 1292, 1221, 1063 cm^{-1}.

^{1}H NMR: δ 0.96, 1.12, 1.25, and 1.37 (4 s, 42 H, C(C*H*$_3$)$_2$ + C(C*H*$_3$)$_3$), 2.67 (d, ^{2}J(P-H) = 7.6 Hz, 1 H, N*H*), 3.79-4.33 (m, 4 H, OC*H*$_2$), 5.78 (dd, ^{3}J(P-H) = 22.8 Hz, ^{4}J(P-H) = 4.0 Hz, 1 H, =C*H*$_A$H$_B$, *cis* to P), 6.04 (dd, ^{3}J(P-H), = 14.4 Hz, ^{2}J(P-H) = 18.0 Hz, 1 H, P(O)C*H*), 6.80 (d, ^{3}J(P-H) = 50.4 Hz, 1 H, =CH$_A$*H*$_B$, *trans* to P), 7.18-7.56 (m, 5 H, Ar-*H*).

^{13}C NMR: δ 21.0 and 22.0 (2 s, C(*C*H$_3$)$_2$), 31.0 (dd→t, ^{3}J(P-C) ~ 4.9 Hz, C(*C*H$_3$)$_3$), 31.3 (dd→t, ^{3}J(P-C) ~ 4.7 Hz, C(*C*H$_3$)$_3$), 32.4 (d, ^{3}J(P-C) = 6.5 Hz, *C*(CH$_3$)$_2$), 32.9 (d, ^{3}J(P-C) = 10.0 Hz, C(*C*H$_3$)$_3$), 34.6 (d, ^{3}J(P-C) = 12.0 Hz, C(*C*H$_3$)$_3$), 41.8 (dd, ^{1}J(P-C) = 125.5 Hz, ^{2}J(P-C) = 4.8 Hz, P(O)*C*(Ph)), 51.4 (d, ^{2}J(P-C) = 14.7 Hz, *C*(CH$_3$)$_3$), 52.2 (d, ^{2}J(P-C) = 8.4 Hz, *C*(CH$_3$)$_3$), 52.3 (d, ^{2}J(P-C) = 10.0 Hz, *C*(CH$_3$)$_3$), 52.6 (d, ^{2}J(P-C) = 8.2 Hz, *C*(CH$_3$)$_3$), 76.5 and 76.6 (2 s, OC*H*$_2$), 127.0, 127.1, 128.2, 128.3, 130.2,130.3, 136.2 (d, ^{2}J(P- C) = 5.5 Hz, PC=*C*H$_2$), 143.4 (d, ^{1}J(P-C) = 162.9 Hz, P*C*=CH$_2$) [*cf.* Fig. 24].

^{31}P NMR: δ -19.4 (dd, ^{3}J(P-P) ~ 35.4 Hz, ^{2}J(P-P) ~ 6.9 Hz), 20.3 (d, ^{3}J(P-P) ~ 35.4 Hz), 70.5 (d, ^{2}J(P-P) ~ 6.9 Hz).

LC-MS: *m/z* 613 [M+1]$^{+}$.

X-ray structure was determined for this compound.

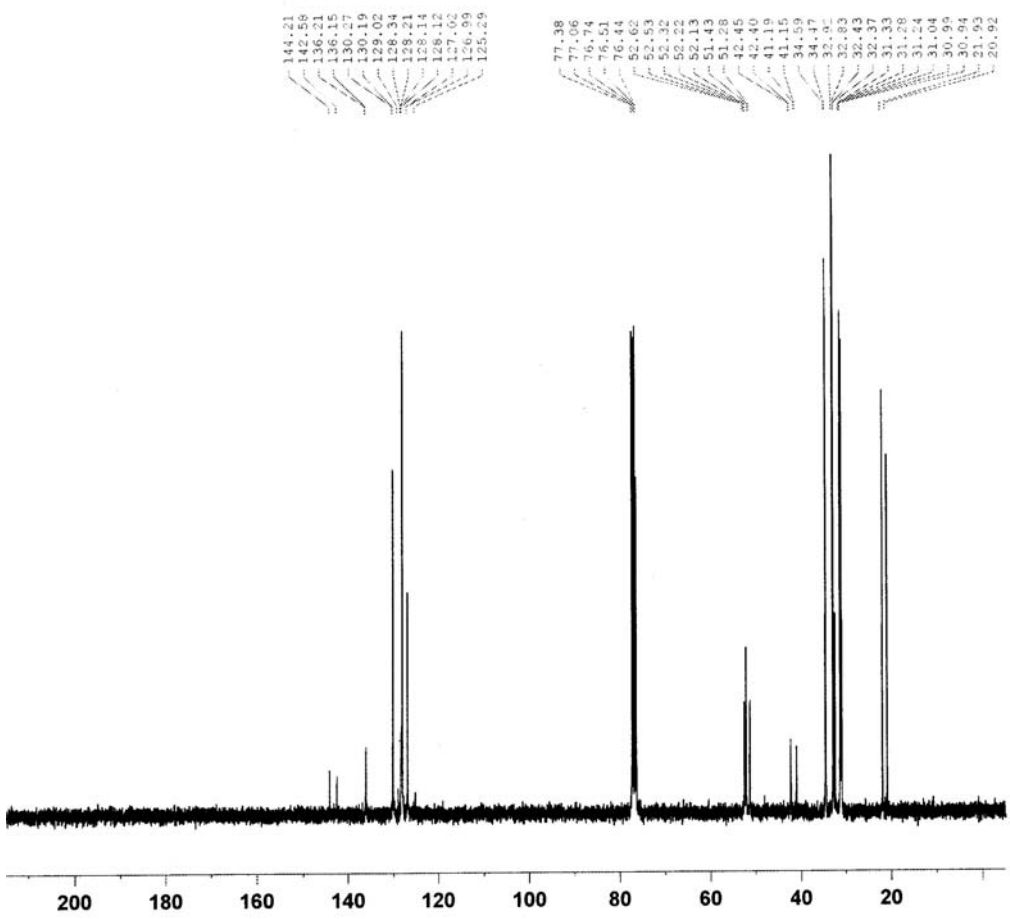
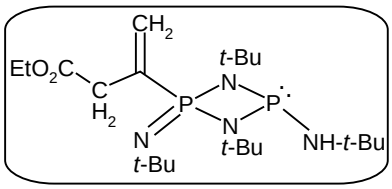


Fig. 24. ^{13}C NMR spectrum of compound **31c**

6.92 *Reaction of 1 with ester allene* EtO_2C-CH=C=CH_2: *Synthesis of* [(*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P{(N-*t*-Bu)C(=CH_2)-CH_2-COOEt)] (32) and [(*t*-Bu-HN)P(*μ*-N-*t*-Bu)$_2$P{(N-*t*-Bu)C(CH_3)=CH-COOEt)] (33)

Cyclodiphosphazane **1** (0.33 g, 0.95 mmol) and ester allene **3d** (0.13 g, 1.14 mmol) were dissolved in toluene (4 mL), and the mixture was stirred for 1 d. The solution was concentrated *in vacuo* (to *ca* 1.5 mL) and cooled for 1 d at –4 ^{o}C to obtain crystals of isomeric products **32-33**, in which the PN*H* proton moved to the *α* or *γ* carbon of the original allene. Although further purification proved to be difficult, the crystalline material obtained initially contained predominantly **32**. We were successful in isolating **32** in ca 95% purity and fortunately some crystals suitable for X-ray structure could be obtained. This solution, upon keeping for 2 d, gave **33** that could be purified by crystallization.

(a) Compound 32



Yield (see above): 0.35 g (80 %, purity ca 95%, rest was **33**).

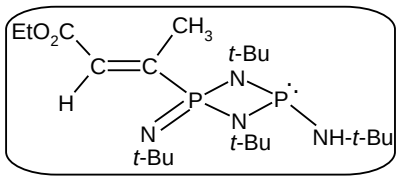
^{1}H NMR: δ 1.27 (t, ^3J(H-H) ~ 7.2 Hz, 3 H, CH_2CH_3), 1.33 and 1.38 (2 s, 36 H, $C(CH_3)_3$), 2.75 (br, 1 H, N*H*), 3.39 (br, 2 H, PCCH_2), 4.14 (q, ^3J(H-H) = 7.1 Hz, 2 H, CH_2CH_3), 5.55 (br, 1 H, $=CH_AH_B$, *cis* to P) 5.70 (d, 1 H, ^3J(P-H) = 49.8 Hz, $=CH_AH_B$, *trans* to P).

^{13}C NMR: δ 14.2 (s, CH_2CH_3), 31.4, 31.4_5, 31.4_7, 31.5_0, 31.5_4 and 31.6 (many lines, $C(CH_3)_3$), 32.9 (dd, ^3J(P-C) = 3.6 Hz and 9.6 Hz, $C(CH_3)_3$), 34.3 (d, ^3J(P-C) = 12.7 Hz, PCCH_2), 34.5 (d, ^3J(P-C) = 11.8 Hz, $C(CH_3)_2$), 51.6, 51.7, 52.3, and 52.4 (4 s, $C(CH_3)_3$), 59.8 (s, OCH_2CH_3), 126.4 (s, PC=CH_2), 139.6 (d, ^1J(P-C) = 137.5 Hz, P*C*), 163.8 (s, *C*OOEt). Detailed assignment was difficult because, during the time of recording, peaks due to **33** also appeared.

^{31}P NMR: δ -20.2, 71.3.

X-ray structure was determined for the crystals obtained.

(b) Compound 33



Yield: (~quantitative from **32**; see above).

Mp: 100–103 °C.

IR (KBr): 3329, 2965, 2874, 1703, 1615, 1460, 1372, 1316, 1190, 1047, 990 cm^{-1}.

^{1}H NMR: δ 1.25 (t, ^3J(H-H) ~ 7.2 Hz, 3 H, CH_2CH_3), 1.32, 1.33, 1.36 and 1.38 (4 s, 36 H, $C(CH_3)_3$), 2.00 (br d, ^3J(P-H) = 16.0 Hz, 3 H, PCCH_3), 2.87 (d, ^2J(P-H) = 7.2 Hz, 1 H, N*H*), 4.17 (q, ^3J(H-H) = 7.2 Hz, 2 H, CH_2CH_3), 7.16 (br, PC*H*).

^{13}C NMR: δ 14.3 (merged s, PC*C*H$_3$ + CH$_2$*C*H$_3$), 31.6 (dd→t, ^3J(P-C) ~ 5.0 Hz, two of C(*C*H$_3$)$_3$), 33.0 (d, ^3J(P-C) = 10.0 Hz, C(*C*H$_3$)$_2$), 34.5 (d, ^3J(P-C) = 12.0 Hz, C(*C*H$_3$)$_3$), 51.3 (d, ^2J(P-C) = 15.0 Hz, *C*(CH$_3$)$_3$), 51.7 (d, ^2J(P-C) = 7.0 Hz, *C*(CH$_3$)$_3$), 52.3 (d, ^2J(P-C) = 8.0 Hz, two of *C*(CH$_3$)$_3$), 59.9 (s, O*C*H$_2$CH$_3$), 130.1 (s, PC=*C*H), 154.2 (d, ^1J(P-C) = 190.0 Hz, P*C*), 166.7 (d, ^3J(P-C) = 26.0 Hz, *C*O$_2$Et).

^{31}P NMR: δ -20.7, 70.5.

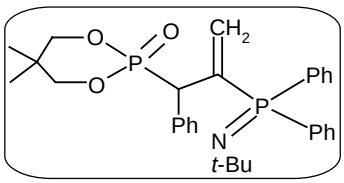
LC-MS: m/z 461 $[M+1]^+$.

Anal. Calc. for $C_{22}H_{46}N_4O_2P_2$: C, 57.37; H, 10.07; N, 12.16. Found: C, 57.46; H, 10.05; N, 12.08.

X-ray structure was determined for this compound.

6.10 Reaction of 2 with allenylphosphonate 3c*: Synthesis of* [(Ph)$_2$P{(N-*t*-Bu)C(=CH$_2$)-CH(Ph)-P(O)(OCH$_2$CMe$_2$CH$_2$O)] (34)

In a procedure similar to that for **31a**, **2** (0.24 g, 0.91 mmol) and allenylphosphonate **3c** (0.23 g, 0.91 mmol) were used.



Yield: 0.37 g (80%).

Mp: 147–149 ^{o}C.

IR (KBr): 2959, 2884, 1599, 1476, 1456, 1437, 1264, 1213, 1059, 1007 cm^{-1}.

^{1}H NMR: δ 0.82, 1.06 and 1.14 (3 s, 15 H, C(C*H*$_3$)$_2$ + C(C*H*$_3$)$_3$), 3.71-4.48 (m, 4 H, OC*H*$_2$), 5.67 (dd, ^3J(P-H) = 22.2 Hz,^4J(P-H) = 3.6 Hz, 1 H, =C*H*$_A$H$_B$, *cis* to P), 6.02 (dd, ^3J(P-H) and ^2J(P-H) = 14.4 and 19.2 Hz, 1 H, P(O)C*H*), 6.69 (dd, ^2J(P-H) = 46.8 Hz, ^4J(P-H) ~ 2.8 Hz, 1 H, =CH$_A$*H*$_B$, *trans* to P), 7.12-7.69 (m, 15 H, Ar-*H*).

^{13}C NMR: δ 20.9 and 22.2 (2 s, C(*C*H$_3$)$_2$), 32.6 (d, ^3J(P-C) = 6.6 Hz, *C*(CH$_3$)$_2$), 35.5 (d, ^3J(P-C) = 9.7 Hz, C(*C*H$_3$)$_3$), 37.5 (dd, ^1J(P-C) = 127.1 Hz, ^2J(P-C) ~ 7.0 Hz, P(O)*C*(Ph)), 51.9 (s, *C*(CH$_3$)$_3$), 76.6 and 76.9 (2 d, ^2J(P-C) ~ 6.4 Hz for both, O*C*H$_2$), 127.1, 127.8, 127.9, 128.0, 128.1, 128.5, 129.7, 129.8, 130.4, 130.8,131.3, 131.4, 131.5, 132.6, 132.7,

132.8, 132.9, 134.5, 135.0, 135.3, 135.7, 135.9 (Ar-*C* + PC=*C*H_2), 140.4 (d, ^1J(P-C) = 120.3 Hz, P*C*=CH_2).

^{31}P NMR: δ -7.6 (d, ^3J(P-P) = 30.6 Hz), 19.3 (d, ^3J(P-P) = 30.6 Hz).

LC-MS: *m/z* 520 $[M-1]^+$.

X-ray structure was determined for this compound.

6.11 X-ray crystallography

A suitable crystal was mounted on a glass fiber (for **5**, **8**, **9**, **11**, **16**, **18**, **21**.Ph-O-H…OPh, **23**.H_2O, **26**, (*S*)-**31c**, (*R*)-**31c**, **32**, **33** and **34**) and X-ray data were collected at 293 K on an Enraf-Nonius MACH3 or on a Bruker AXS-SMART diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Structures were solved and refined using standard methods.[48] Absorption corrections were done using SADABS program, where applicable. In some cases, the terminal carbon atoms of the *t*-butyl groups (especially **9**, (*R*)-**31c** and **32**) showed high thermals; a suitable disorder model for only compound **9** was adapted. The anion in **26** was refined as bicarbonate, but the OH proton was not located (data also fitted well with nitrate crystallographically, but there was no source of this anion in our system). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a Difference Fourier and refined isotropically. Crystal data are summarized in Tables 3-6.

Table 3. Crystal data for compounds **5, 8, 9** and **11**[a]

Compd	**5**	**8**[b]	**9**[c]	**11**
Emp. formula	$C_{20}H_{42}N_4O_2P_2$	$C_{22}H_{44}N_4O_4P_2$	$C_{27}H_{30}NO_2P$	$C_{19}H_{41}N_5P_2$
Formula weight	432.52	490.55	431.49	401.51
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	Cc	$Iba2$	$P2_1/n$
a /Å	18.098(1)	17.704(2)	19.157(4)	9.516(6)
b /Å	9.967(6)	9.596(1)	25.897(6)	16.595(1)
c /Å	16.170(9)	17.770(2)	9.905(15)	15.911(1)
α/deg	90	90	90	90
β/deg	112.870(1)	106.530(2)	90	91.692(1)
γ/deg	90	90	90	90
V /Å^3	2687.4(3)	2893.9(5)	4913.7(16)	2511.4(3)
Z	4	4	8	4
D_{calc} /g cm^{-3}]	1.069	1.126	1.167	1.062
μ /mm^{-1}	0.182	0.181	0.134	0.185
F(000)	944	1064	1840	880
Data/ restraints/ parameters	4730/ 0/ 270	5050/ 2/ 300	3486/ 1/ 284	4417/ 0/ 251
GOF (S)	1.064	1.053	0.926	1.038
R1 [I>2σ(I)]	0.0629	0.0647	0.0498	0.0536
wR2 [all data]	0.2011	0.1880	0.1325	0.1647
Max./min. residual electron dens. [eÅ^{-3}]	0.427/ -0.254	0.616/ -0.268	0.321/ -0.171	0.453/ -0.316

[a]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

[b]Flack parameter: 0.02(16)

[c]Flack parameter: 0.03(13)

Table 4. Crystal data for compounds **16, 18, 21**.Ph-O-H…OPh and **23**.H_2O[a]

Compd	**16**[b]	**18**	**21**.Ph-O-H…OPh	**23**.H_2O
Emp. formula	$C_{22}H_{46}N_4O_4P_2$	$C_{24}H_{34}N_3O_4P$	$C_{31}H_{53}N_5O_2P_2$	$C_{26}H_{48}N_6O_5P_2$
Formula weight	492.57	459.51	589.72	586.64
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	*P2(1)2(1)2(1)*	*P2(1)/n*	$P\bar{1}$	$P2_1/c$
a /Å	9.002(5)	10.634(7)	9.735(6)	9.599(4)
b /Å	17.787(9)	25.296(2)	11.248(6)	15.841(7)
c /Å	18.123(9)	19.330(1)	17.059(1)	21.048(9)
α/deg	90	90	92.455(1)	90
β/deg	90	91.9820(10)	105.381(1)	91.500(1)
γ/deg	90	90	93.314(1)	90
V /Å^3	2901.9(3)	5196.8(6)	1794.9(2)	3199.6(2)
Z	4	8	2	4
D_{calc} /g cm^{-3}]	1.127	1.175	1.091	1.218
μ /mm^{-1}	0.181	0.138	0.153	0.179
F(000)	1072	1968	640	1264
Data/ restraints/ parameters	5097/ 0/ 311	12451/ 0/ 593	6317/ 10/ 415	5637/ 0/ 380
GOF (S)	1.031	1.030	1.069	1.090
R1 [I>2σ(I)]	0.0746	0.0647	0.0602	0.0585
wR2 [all data]	0.2144	0.1622	0.1905	0.1458
Max./min. residual electron dens. [eÅ^{-3}]	0.467/ -0.213	0.372/ -0.193	0.375/ -0.257	0.477/ -0.233

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

[b] Flack parameter 0.14(18)

Table 5. Crystal data for compounds **26,** (*S*)-**31c,** (*R*)-**31c** and **32**

Compd	**26**	(*S*)-**31c**[b]	(*R*)-**31c**[c]	**32**
Emp. formula	$C_{27}H_{49}N_5O_3P_2$	$C_{30}H_{55}N_4O_3P_3$	$C_{30}H_{55}N_4O_3P_3$	$C_{22}H_{46}N_4O_2P_2$
Formula weight	553.67	612.69	612.69	460.57
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*P2(1)/n*	*Pna2(1)*	*Pna2(1)*	*P2(1)/c*
a /Å	10.478(1)	19.985(2)	19.966(4)	9.9107(1)
b /Å	17.990(2)	17.536(2)	17.548(4)	36.162(4)
c /Å	16.762(1)	10.139(1)	10.131(2)	8.592(1)
α/deg	90	90	90	90
β/deg	94.75(8)	90	90	114.562
γ/deg	90	90	90	90
V /Å^3	3149(5)	3553.3(6)	3549.4(12)	2800.7(6)
Z	4	4	4	4
D_{calc} /g cm^{-3}]	1.168	1.145	1.147	1.057
μ /mm^{-1}	0.172	0.201	0.201	0.178
F(000)	1200	1328	1328	972
Data/ restraints/ parameters	5534/ 0/ 342	5460/ 1/ 379	6231/ 1/ 379	4921/ 1/ 287
GOF (S)	1.077	1.022	1.271	1.006
R1 [I>2σ(I)]	0.0559	0.0491	0.0561	0.0817
wR2 [all data]	0.1708	0.1201	0.1332	0.2355
Max./min. residual electron dens. [eÅ^{-3}]	0.241/ -0.255	0.298/ -0.156	0.341/ -0.334	0.777/ -0.314

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

[b] Flack parameter: -0.05(10)

[c] Flack parameter: 0.02(11)

Table 6. Crystal data for compounds **33** and (*R*)-**34**[a]

Compd	**33**	(*R*)-**34**[b]
Emp. formula	$C_{22}H_{46}N_4O_2P_2$	$C_{30}H_{37}NO_3P_2$
Formula weight	460.57	521.55
Crystal system	Monoclinic	Orthorhombic
Space group	*P2(1)/n*	*P2(1)2(1)2(1)*
a /Å	9.589(8)	9.068(2)
b /Å	18.849(1)	11.551(3)
c /Å	15.706(1)	27.11(6)
α/deg	90	90
β/deg	98.2660(10)	90
γ/deg	90	90
V /Å^3	2809.4(4)	2839.9(11)
Z	4	4
D_{calc} /g cm^{-3}]	1.089	1.220
μ /mm^{-1}	0.177	0.184
F(000)	1008	1112
Data/ restraints/ parameters	4959/ 0/ 289	5598/ 0/ 330
GOF (S)	1.060	1.019
R1 [I>2σ(I)]	0.0573	0.0396
wR2 [all data]	0.1681	0.1015.
Max./min. residual electron dens. [eÅ^{-3}]	0.436/ -0.367	0.287/ -0.127

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{0.5}$

[b] Flack parameter: -0.03(8)

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APPENDIX

Publication numbers and atomic coordinates for X-ray structures reported in this thesis

I. Publication numbers for the published compounds

PART A: **Compounds 8a and 10: Publication no. 8 (Contents, p. xii)**

Compounds 16, 17a-b and 20.H_2O: Publication no. 4 (Contents, p. xii)

Compounds 33, 34, and 38: Publication no. 5 (Contents, p. xii)

PART B: **Compounds 5, 8, 9, 11, 21**.Ph-O-H…OPh **and 23**.H_2O**: Publication no. 2 (Contents, p. xii)**
Compounds (*S*)**-31c,** (*R*)**-31c, 32, 33 and 34: Publication no. 7 (Contents, p. xii)**

II. Selected atomic coordinates for compounds 17c, 36, 52, (*E*)-56, (*Z*)-56, (*Z*)-66, (*E*)-67a, (*E*)-68a, *trans*-69b, 70a, (*E*)-72, (*Z*)-73 and 77 from PART A and for compounds 16, 18 and 26 from PART B

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

PART A

Compound 17c

Atom	x	y	z	U(eq)
P(1)	5371(1)	8369(1)	794(1)	46(1)
P(2)	3942(1)	9281(1)	1706(1)	44(1)
O(1)	6002(3)	8681(2)	84(1)	63(1)
O(2)	3362(3)	8949(2)	2423(1)	65(1)
N(1)	3663(3)	8624(2)	868(2)	52(1)
N(2)	5679(3)	8991(2)	1637(2)	47(1)
N(3)	3589(3)	10410(2)	1491(2)	52(1)
C(1)	2376(4)	8451(3)	292(2)	58(1)
C(2)	2452(8)	9025(7)	-420(5)	206(5)
C(3)	2301(6)	7367(4)	94(3)	108(2)
C(4)	1063(5)	8659(6)	714(4)	144(3)
C(5)	6930(4)	9023(3)	2253(2)	61(1)
C(6)	8255(4)	8836(4)	1852(3)	85(1)
C(7)	6787(6)	8236(5)	2879(3)	113(2)
C(8)	7009(5)	10036(4)	2620(3)	104(2)
C(9)	2959(4)	11223(3)	1923(2)	62(1)
C(10)	1754(9)	11632(7)	1402(5)	203(5)

C(11)	2622(16)	10984(6)	2685(5)	259(8)
C(12)	3997(9)	12050(5)	1967(5)	165(4)
C(13)	5668(4)	7102(3)	972(2)	60(1)
C(14)	6304(4)	6562(2)	481(2)	63(1)
C(15)	6920(5)	6058(3)	-26(3)	75(1)
C(16)	6085(7)	5601(4)	-743(3)	108(2)
C(17)	8513(7)	5907(5)	66(5)	136(3)

Compound 36

Atom	x	y	z	U(eq)
P(1)	2857(1)	1713(1)	1665(1)	51(1)
O(1)	1925(3)	315(2)	2095(1)	61(1)
O(2)	2333(3)	2997(2)	2276(1)	60(1)
O(3)	1785(3)	1956(3)	862(1)	81(1)
O(4)	5352(3)	1593(3)	1646(1)	73(1)
O(5)	7663(3)	1163(3)	419(1)	72(1)
C(1)	2440(5)	106(2)	2969(2)	59(1)
C(2)	1721(4)	1419(3)	3487(1)	49(1)
C(3)	2801(5)	2784(3)	3152(2)	61(1)
C(4)	-763(4)	1564(3)	3474(2)	64(1)
C(5)	2506(6)	1165(4)	4381(2)	91(1)

Compound 52

Atom	x	y	z	U(eq)
P(1)	1700(1)	8873(1)	1620(1)	33(1)
N(1)	977(1)	8145(1)	1188(1)	41(1)
O(1)	1408(1)	6665(1)	1980(1)	53(1)
O(2)	277(1)	6608(1)	1100(1)	55(1)
C(1)	1584(1)	10195(1)	1159(1)	36(1)
C(2)	851(1)	10530(1)	754(1)	45(1)
C(3)	750(1)	11567(2)	427(1)	55(1)
C(4)	1375(1)	12264(1)	500(1)	59(1)
C(5)	2098(1)	11946(1)	904(1)	57(1)
C(6)	2205(1)	10914(1)	1237(1)	45(1)
C(7)	1719(1)	9153(1)	2591(1)	37(1)
C(8)	2304(1)	9782(1)	3044(1)	45(1)
C(9)	2282(1)	10017(1)	3776(1)	52(1)
C(10)	1678(1)	9642(2)	4055(1)	54(1)
C(11)	1090(1)	9035(2)	3607(1)	55(1)
C(12)	1108(1)	8792(1)	2877(1)	46(1)
C(13)	2635(1)	8333(1)	1578(1)	37(1)
C(14)	2821(1)	8304(1)	884(1)	47(1)
C(15)	3499(1)	7802(2)	816(1)	58(1)
C(16)	3991(1)	7337(2)	1430(1)	62(1)
C(17)	3812(1)	7358(2)	2114(1)	64(1)
C(18)	3133(1)	7848(2)	2194(1)	51(1)
C(19)	941(1)	7113(1)	1467(1)	41(1)
C(20)	94(1)	5581(1)	1431(1)	55(1)
C(21)	-769(1)	5565(2)	1308(2)	78(1)
C(22)	413(1)	4608(2)	1098(2)	78(1)

Compound (*E*)-56

Atom	x	y	z	U(eq)
P	8350(1)	1136(1)	5745(1)	39(1)
O(1)	9117(2)	838(3)	5464(2)	41(1)
O(2)	8114(2)	-988(4)	5906(2)	44(1)
O(3)	8527(2)	2433(4)	6442(2)	54(1)
O(4)	6330(2)	3375(4)	4087(1)	47(1)
Br	3662(1)	9380(1)	3483(1)	75(1)
C(1)	9782(2)	-405(5)	5975(2)	44(1)
C(2)	9457(2)	-2420(5)	6020(2)	42(1)
C(3)	8777(2)	-2273(6)	6380(2)	47(1)
C(4)	10158(3)	-3673(6)	6601(3)	63(1)
C(5)	9136(3)	-3364(7)	5186(2)	60(1)
C(6)	7530(2)	1796(5)	4840(2)	37(1)
C(7)	6965(2)	3144(5)	4823(2)	38(1)
C(8)	6954(2)	4372(5)	5482(2)	44(1)
C(9)	6373(2)	5728(5)	5377(2)	46(1)
C(10)	5729(2)	5975(5)	4600(2)	39(1)
C(11)	5104(3)	7377(5)	4439(2)	48(1)
C(12)	4503(2)	7479(5)	3688(2)	47(1)
C(13)	4480(2)	6211(6)	3076(2)	49(1)
C(14)	5097(2)	4828(6)	3232(2)	49(1)
C(15)	5717(2)	4749(5)	3977(2)	39(1)
C(16)	7484(2)	687(5)	4096(2)	37(1)
C(17)	7133(3)	-1121(6)	3937(2)	51(1)
C(18)	7138(3)	-2172(7)	3275(3)	62(1)
C(19)	7497(3)	-1417(7)	2767(2)	58(1)
C(20)	7837(3)	396(7)	2902(2)	58(1)
C(21)	7827(2)	1453(6)	3562(2)	49(1)

Compound (*Z*)-56

Atom	x	y	z	U(eq)
P	8223(1)	1888(1)	-518(1)	32(1)
O(1)	8947(1)	825(2)	-175(2)	36(1)
O(2)	8501(1)	3463(2)	-65(2)	40(1)
O(3)	8040(1)	1926(3)	-1661(2)	51(1)
O(4)	6677(1)	3234(2)	-492(2)	38(1)
Br	3568(1)	5770(1)	-2397(1)	52(1)
C(1)	9369(2)	943(3)	878(2)	37(1)
C(2)	9623(2)	2525(3)	1158(2)	38(1)
C(3)	8897(2)	3529(3)	1005(2)	42(1)
C(4)	10252(2)	3029(4)	479(3)	49(1)
C(5)	9948(2)	2549(5)	2326(3)	66(1)
C(6)	7438(2)	1224(3)	176(2)	32(1)
C(7)	6728(2)	1905(3)	60(2)	33(1)
C(8)	6018(2)	1353(3)	437(2)	38(1)
C(9)	5315(2)	1942(3)	106(2)	38(1)
C(10)	5251(2)	3180(3)	-625(2)	33(1)
C(11)	4536(2)	3789(3)	-1082(2)	38(1)
C(12)	4541(2)	4968(3)	-1767(2)	40(1)
C(13)	5236(2)	5592(3)	-1999(3)	47(1)
C(14)	5953(2)	5008(3)	-1556(2)	43(1)
C(15)	5951(2)	3799(3)	-888(2)	33(1)
C(16)	7547(2)	-201(3)	784(2)	35(1)
C(17)	7560(2)	-1553(3)	258(3)	50(1)
C(18)	7696(2)	-2873(4)	824(4)	66(1)
C(19)	7823(2)	-2851(4)	1905(4)	66(1)
C(20)	7804(2)	-1525(4)	2433(3)	58(1)
C(21)	7664(2)	-198(4)	1884(2)	43(1)

Compound (*Z*)-66

Atom	x	y	z	U(eq)
P	6920(1)	5034(1)	840(1)	48(1)
O(1)	6189(2)	5912(2)	144(2)	56(1)
O(2)	8067(2)	5231(2)	452(2)	55(1)
O(3)	6924(3)	5149(2)	2124(3)	82(1)
O(4)	7746(2)	2911(2)	1383(2)	63(1)
O(5)	7164(4)	88(3)	-493(3)	101(1)
C(1)	6325(3)	6128(3)	-1095(3)	57(1)
C(2)	7476(3)	6400(3)	-1250(3)	52(1)
C(3)	8166(3)	5458(3)	-797(3)	56(1)
C(4)	7834(4)	7422(3)	-587(4)	79(1)
C(5)	7545(4)	6558(4)	-2572(3)	78(1)
C(6)	6425(3)	3807(3)	221(3)	46(1)
C(7)	6869(2)	2873(3)	534(3)	44(1)
C(8)	6476(3)	1778(3)	134(3)	47(1)
C(9)	7449(3)	1126(3)	-213(3)	54(1)
C(10)	8357(3)	1179(3)	791(3)	52(1)
C(11)	9128(3)	386(4)	1021(4)	70(1)
C(12)	9963(3)	482(4)	1931(5)	83(2)
C(13)	10023(3)	1359(4)	2646(5)	80(1)
C(14)	9273(3)	2161(3)	2461(4)	68(1)
C(15)	8457(3)	2062(3)	1527(3)	53(1)
C(16)	5616(3)	1834(3)	-948(4)	69(1)
C(17)	6008(3)	1226(3)	1180(3)	56(1)

Compound (*E*)-67a

Atom	x	y	z	U(eq)
P	3101(1)	1775(1)	7767(1)	42(1)
O(1)	3331(1)	298(2)	7739(2)	52(1)
O(2)	3478(1)	2547(2)	8836(2)	49(1)
O(3)	2995(1)	2538(3)	6635(2)	69(1)
O(4)	1881(1)	1279(2)	8169(1)	48(1)
O(5)	1389(1)	1921(2)	4486(2)	65(1)
C(1)	3792(1)	335(3)	7644(2)	56(1)
C(2)	4130(1)	1155(3)	8673(2)	52(1)
C(3)	3937(1)	2607(3)	8718(2)	52(1)
C(4)	4211(1)	398(4)	9861(3)	85(1)
C(5)	4582(1)	1306(4)	8402(4)	85(1)
C(6)	2647(1)	1410(2)	8322(2)	42(1)
C(7)	2205(1)	1589(3)	7632(2)	45(1)
C(8)	2010(1)	2196(3)	6393(2)	59(1)
C(9)	1604(1)	1385(4)	5646(2)	59(1)
C(10)	1251(1)	1331(3)	6274(2)	48(1)
C(11)	777(1)	1314(3)	5686(2)	61(1)
C(12)	474(1)	1228(4)	6321(3)	69(1)
C(13)	646(1)	1195(4)	7553(3)	75(1)
C(14)	1117(1)	1233(3)	8155(2)	63(1)
C(15)	1414(1)	1290(2)	7505(2)	43(1)
C(16)	2778(1)	845(3)	9584(2)	57(1)

Compound (*E*)-68a

Atom	x	y	z	U(eq)
P(1)	3228(1)	2500	10270(1)	47(1)
O(2)	2768(1)	2500	9238(2)	56(1)
O(1)	3144(1)	749(2)	11184(1)	53(1)
O(3)	4913(1)	2500	8578(2)	61(1)
C(1)	2554(1)	751(3)	11911(2)	56(1)
C(2)	2492(1)	2500	12730(2)	53(1)
C(3)	3001(2)	2500	13748(3)	75(1)
C(4)	1833(2)	2500	13335(3)	70(1)
C(5)	4046(1)	2500	9908(2)	50(1)
C(6)	4261(1)	2500	8709(2)	50(1)
C(7)	3893(1)	2500	7563(2)	61(1)
C(8)	4168(1)	2500	6442(3)	75(1)
C(9)	4850(1)	2500	6323(3)	66(1)
C(10)	5181(2)	2500	5181(3)	94(1)
C(11)	5828(2)	2500	5160(4)	98(1)
C(12)	6166(2)	2500	6255(4)	87(1)
C(13)	5859(1)	2500	7405(3)	72(1)
C(14)	5201(1)	2500	7415(3)	57(1)
C(15)	4505(1)	2500	11007(3)	71(1)

Compound *trans*-69a

Atom	x	y	z	U(eq)
P	8429(1)	8514(1)	1614(2)	42(1)
O(1)	8041(2)	9098(2)	2251(5)	56(1)
O(2)	8134(1)	7933(1)	2563(5)	46(1)
O(3)	8418(2)	8469(2)	-315(5)	63(1)
O(4)	9316(2)	7781(2)	4712(4)	55(1)
O(5)	10312(1)	8460(2)	1962(5)	55(1)
Br	9982(1)	5909(1)	-936(1)	104(1)
C(1)	7698(2)	9113(2)	3921(7)	54(1)
C(2)	7334(2)	8521(2)	4242(7)	52(1)
C(3)	7786(2)	7975(2)	4251(7)	49(1)
C(4)	6822(2)	8415(3)	2884(10)	73(2)
C(5)	7058(3)	8582(3)	6142(9)	76(2)
C(6)	9235(2)	8634(2)	2458(6)	39(1)
C(7)	9708(2)	8259(2)	1359(6)	42(1)
C(8)	9637(2)	7570(2)	1694(6)	42(1)
C(9)	9782(2)	7122(2)	417(7)	51(1)
C(10)	9764(2)	6505(2)	810(9)	61(1)
C(11)	9596(3)	6306(2)	2519(10)	70(2)
C(12)	9435(2)	6741(2)	3789(8)	61(2)
C(13)	9464(2)	7375(2)	3353(7)	47(1)
C(14)	9276(2)	8431(2)	4390(6)	44(1)
C(15)	9252(2)	8787(3)	5777(8)	65(1)
C(16)	9375(2)	9339(2)	2211(8)	58(1)

Compound 70a

Atom	x	y	z	U(eq)
O(1)	7054(1)	1742(2)	7212(2)	52(1)
O(2)	10535(1)	2063(2)	7107(2)	59(1)

C(1)	7977(1)	-512(2)	7046(2)	34(1)
C(2)	7206(1)	8(2)	7145(2)	37(1)
C(3)	6631(1)	-1244(2)	7188(3)	44(1)
C(4)	6800(2)	-2983(7)	7116(5)	51(1)
C(5)	7554(2)	-3526(6)	6971(4)	45(1)
C(6)	8128(2)	-2291(6)	6930(4)	39(1)
C(7)	8579(2)	841(5)	7022(4)	37(1)
C(8)	9329(2)	709(6)	7259(3)	33(1)
C(9)	9834(2)	2266(6)	7112(4)	40(1)
C(10)	9510(3)	4051(7)	7034(5)	50(1)
O(3)	4453(2)	1663(4)	4394(3)	57(1)
O(4)	7930(2)	2061(5)	4613(3)	56(1)
C(11)	9730(2)	-905(6)	7626(4)	43(1)
C(12)	5374(2)	-546(6)	4724(3)	33(1)
C(13)	4605(2)	-54(6)	4538(4)	37(1)
C(14)	4032(3)	-1343(7)	4516(4)	49(1)
C(15)	4196(3)	-3061(7)	4707(4)	52(1)
C(16)	4941(3)	-3538(6)	4926(4)	48(1)
C(17)	5516(3)	-2317(6)	4940(4)	39(1)
C(18)	5969(2)	815(5)	4737(3)	34(1)
C(19)	6731(2)	660(5)	4562(4)	33(1)
C(20)	7237(2)	2246(6)	4668(4)	37(1)
C(21)	6894(3)	4022(6)	4828(5)	53(1)
C(22)	7135(2)	-982(6)	4254(4)	44(1)

Compound (*E*)-72

Atom	x	y	z	U(eq)
O(1)	**4099(1)**	**2509(2)**	**6206(4)**	**59(1)**
O(2)	**3198(1)**	**-1188(2)**	**6813(5)**	**67(1)**
C(1)	**3857(2)**	**3666(3)**	**10159(8)**	**75(1)**
C(2)	**4536(2)**	**3396(2)**	**9391(6)**	**51(1)**
C(3)	**4642(2)**	**2802(2)**	**7562(6)**	**52(1)**
C(4)	**5266(2)**	**2471(2)**	**6677(6)**	**52(1)**
C(5)	**5348(2)**	**1935(2)**	**4724(7)**	**56(1)**
C(6)	**5963(2)**	**1568(2)**	**3753(6)**	**51(1)**
C(7)	**5957(2)**	**1036(3)**	**1664(7)**	**64(1)**
C(8)	**6523(2)**	**662(3)**	**720(7)**	**74(1)**
C(9)	**7107(2)**	**811(3)**	**1820(8)**	**71(1)**
C(10)	**7128(2)**	**1344(3)**	**3867(8)**	**70(1)**
C(11)	**6565(2)**	**1723(2)**	**4818(7)**	**62(1)**
C(12)	**5072(2)**	**3869(3)**	**10798(7)**	**65(1)**
C(13)	**3882(1)**	**1578(2)**	**6459(6)**	**46(1)**
C(14)	**4044(2)**	**988(2)**	**8328(6)**	**52(1)**
C(15)	**3806(2)**	**74(2)**	**8391(6)**	**54(1)**
C(16)	**3397(1)**	**-261(2)**	**6610(6)**	**48(1)**
C(17)	**3224(2)**	**344(2)**	**4771(6)**	**56(1)**
C(18)	**3464(2)**	**1262(3)**	**4718(6)**	**58(1)**
C(19)	**2842(2)**	**-1580(3)**	**4862(8)**	**77(1)**

Compound (*Z*)-73

Atom	x	y	z	U(eq)
P	7393(1)	11208(1)	803(1)	39(1)
O(1)	6321(1)	10256(3)	560(1)	50(1)
O(2)	8044(2)	11057(3)	320(1)	50(1)
O(3)	7316(2)	13373(3)	984(1)	60(1)
O(4)	6492(1)	9415(3)	1713(1)	45(1)
O(5)	3078(2)	2483(4)	1992(1)	80(1)
C(1)	6322(3)	8279(5)	262(1)	61(1)
C(2)	6917(3)	8453(5)	-219(1)	57(1)

C(3)	8007(3)	9130(6)	-3(1)	63(1)
C(4)	6400(3)	9987(6)	-647(1)	69(1)
C(5)	6972(4)	6231(6)	-468(2)	102(2)
C(6)	7989(2)	9410(4)	1318(1)	37(1)
C(7)	7473(2)	8645(4)	1702(1)	41(1)
C(8)	7897(2)	7230(5)	2162(1)	58(1)
C(9)	9097(2)	8880(5)	1323(1)	43(1)
C(10)	9402(2)	6857(5)	1222(2)	65(1)
C(11)	10427(3)	6378(6)	1228(2)	88(1)
C(12)	11153(3)	7915(7)	1333(2)	83(1)
C(13)	10863(3)	9920(7)	1430(2)	73(1)
C(14)	9839(2)	10416(5)	1424(1)	56(1)
C(15)	5728(2)	8043(4)	1816(1)	39(1)
C(16)	4997(2)	8865(5)	2106(1)	48(1)
C(17)	4197(2)	7608(5)	2203(1)	53(1)
C(18)	4111(2)	5558(5)	2016(1)	46(1)
C(19)	4855(2)	4760(5)	1723(1)	46(1)
C(20)	5663(2)	5997(4)	1623(1)	44(1)
C(21)	3247(3)	4264(6)	2132(2)	63(1)

Compound 77

Atom	x	y	z	U(eq)
P(1)	886(1)	2500	5979(2)	40(1)
O(1)	507(1)	1575(2)	5377(4)	61(1)
O(2)	1043(1)	2500	8275(5)	63(1)
C(1)	207(2)	1587(4)	3299(6)	80(1)
C(2)	-156(2)	2500	3013(8)	77(2)
C(3)	-371(3)	2500	638(9)	142(4)
C(4)	-652(2)	2500	4586(9)	114(3)
C(5)	1453(2)	2500	4075(6)	39(1)
C(6)	2006(2)	2500	4551(6)	31(1)
C(7)	2272(2)	2500	6804(6)	35(1)
C(8)	2455(2)	2500	2760(6)	35(1)
C(9)	2819(1)	1587(2)	3149(4)	35(1)
C(10)	2916(1)	816(2)	1700(5)	45(1)
C(11)	3283(1)	57(2)	2276(6)	57(1)
C(12)	3533(1)	44(3)	4310(6)	61(1)
C(13)	3431(1)	803(2)	5786(5)	50(1)
C(14)	3077(1)	1591(2)	5207(4)	37(1)
C(15)	2926(2)	2500	6560(6)	34(1)

PART B

Compound 16

Atom	x	y	z	U(eq)
P(1)	9045(1)	-234(1)	693(1)	46(1)
P(2)	8725(1)	1032(1)	35(1)	49(1)
N(1)	9670(4)	189(2)	-69(2)	52(1)
N(2)	7923(4)	500(2)	744(2)	48(1)
N(3)	8315(6)	-1046(3)	593(4)	76(2)
N(4)	7493(5)	1067(3)	-632(3)	61(1)
O(1)	10326(7)	393(3)	2846(2)	96(2)
O(2)	11610(6)	1349(2)	2391(2)	90(2)
O(3)	10308(5)	-1654(2)	1512(3)	74(1)
O(4)	12086(5)	-974(3)	2054(2)	75(1)
C(1)	10978(6)	36(4)	-527(3)	68(2)
C(2)	10547(10)	-45(6)	-1317(4)	131(4)

C(3)	12048(9)	735(8)	-483(6)	170(5)
C(4)	11817(12)	-612(7)	-254(5)	180(6)
C(5)	6878(6)	775(4)	1309(3)	64(2)
C(6)	5345(7)	887(5)	943(4)	94(2)
C(7)	7393(8)	1519(5)	1624(5)	104(3)
C(8)	6752(10)	199(6)	1927(5)	124(3)
C(9)	7135(8)	-1379(4)	136(6)	104(3)
C(10)	6472(12)	-844(5)	-372(6)	160(5)
C(11)	5795(14)	-1568(8)	689(10)	230(7)
C(12)	7708(16)	-2082(6)	-140(8)	251(10)
C(13)	7139(7)	1715(4)	-1109(3)	63(2)
C(14)	5644(13)	1715(10)	-1324(12)	309(14)
C(15)	7780(30)	1647(13)	-1789(10)	400(20)
C(16)	7570(20)	2365(6)	-817(11)	313(15)
C(17)	10335(6)	-331(3)	1383(3)	49(1)
C(18)	11207(7)	375(3)	1582(3)	59(1)
C(19)	10953(7)	677(3)	2337(3)	59(2)
C(20)	11457(16)	1737(4)	3087(4)	143(5)
C(21)	10817(6)	-1039(3)	1631(3)	55(1)
C(22)	12674(8)	-1670(5)	2323(4)	104(3)

Compound 18

Atom	x	y	z	U(eq)
P(1)	5497(1)	2109(1)	6518(1)	42(1)
P(2)	4359(1)	4934(1)	6944(1)	49(1)
N(1)	6619(1)	2423(1)	6264(1)	51(1)
N(2)	5659(1)	1428(1)	6635(1)	49(1)
N(3)	6092(2)	1257(1)	7286(1)	54(1)
N(4)	3245(2)	4581(1)	6757(1)	61(1)
N(5)	4220(2)	5402(1)	7607(1)	53(1)
N(6)	3922(2)	5920(1)	7427(1)	57(1)
O(1)	5926(2)	588(1)	6234(1)	88(1)
O(2)	5268(1)	1246(1)	5523(1)	60(1)
O(3)	4130(1)	993(1)	7573(1)	70(1)
O(4)	5860(2)	840(1)	8264(1)	72(1)
O(5)	4110(2)	5630(1)	8749(1)	90(1)
O(6)	4452(1)	4789(1)	8423(1)	64(1)
O(7)	5943(1)	6197(1)	7596(1)	61(1)
O(8)	4348(1)	6765(1)	7341(1)	66(1)
C(1)	5197(2)	2327(1)	7384(1)	48(1)
C(2)	6113(2)	2595(1)	7754(1)	72(1)
C(3)	5894(3)	2774(1)	8414(1)	97(1)
C(4)	4745(3)	2682(1)	8697(1)	94(1)
C(5)	3838(2)	2417(1)	8341(1)	82(1)
C(6)	4042(2)	2240(1)	7682(1)	64(1)
C(7)	3982(2)	2165(1)	6064(1)	47(1)
C(8)	3755(2)	2619(1)	5681(1)	64(1)
C(9)	2603(3)	2696(1)	5348(1)	86(1)
C(10)	1666(2)	2324(1)	5401(1)	86(1)
C(11)	1869(2)	1875(1)	5786(1)	73(1)
C(12)	3021(2)	1793(1)	6116(1)	58(1)
C(13)	7426(2)	2402(1)	5666(1)	57(1)
C(14)	8313(3)	2872(1)	5728(2)	92(1)
C(15)	8182(2)	1893(1)	5673(1)	72(1)
C(16)	6656(3)	2448(1)	4987(1)	94(1)
C(17)	5640(2)	1040(1)	6131(1)	57(1)
C(18)	5000(3)	874(1)	4956(1)	84(1)
C(19)	4939(5)	1208(2)	4319(2)	155(2)
C(20)	3811(3)	581(2)	5095(2)	126(1)
C(21)	5238(2)	1021(1)	7699(1)	56(1)
C(22)	5092(3)	604(1)	8801(1)	83(1)
C(23)	4743(4)	1027(2)	9294(2)	125(1)
C(24)	5886(3)	172(1)	9119(2)	108(1)
C(25)	4634(2)	5346(1)	6203(1)	55(1)
C(26)	5750(2)	5614(1)	6121(1)	69(1)

C(27)	5939(3)	5904(1)	5526(1)	89(1)
C(28)	5031(3)	5925(1)	5014(1)	96(1)
C(29)	3922(3)	5655(1)	5081(1)	98(1)
C(30)	3726(3)	5365(1)	5673(1)	76(1)
C(31)	5866(2)	4630(1)	7167(1)	51(1)
C(36)	6834(2)	4877(1)	7542(1)	59(1)
C(32)	6057(2)	4118(1)	6930(1)	64(1)
C(33)	7192(2)	3862(1)	7075(1)	80(1)
C(34)	8129(2)	4112(1)	7451(1)	79(1)
C(35)	7961(2)	4618(1)	7680(1)	71(1)
C(37)	2390(2)	4211(1)	7073(1)	72(1)
C(38)	1588(2)	4502(1)	7592(2)	95(1)
C(39)	1536(3)	3998(1)	6479(2)	104(1)
C(40)	3087(3)	3756(1)	7431(2)	105(1)
C(41)	4249(2)	5302(1)	8311(1)	61(1)
C(42)	4687(3)	4619(1)	9142(1)	84(1)
C(43)	3495(4)	4429(2)	9436(2)	143(2)
C(44)	5619(4)	4176(2)	9115(2)	162(2)
C(45)	4844(2)	6287(1)	7472(1)	52(1)
C(46)	5234(2)	7198(1)	7279(1)	71(1)
C(47)	4520(3)	7687(1)	7472(2)	122(1)
C(48)	5707(3)	7203(1)	6561(2)	112(1)

Compound 26

Atom	x	y	z	U(eq)
P(1)	6634(1)	1203(1)	8180(1)	38(1)
P(2)	6470(1)	1893(1)	9495(1)	42(1)
N(1)	7581(3)	1393(2)	8977(2)	40(1)
N(2)	5536(3)	1675(2)	8603(2)	39(1)
N(3)	6987(3)	1520(2)	7330(2)	49(1)
N(4)	6852(3)	2772(2)	9410(2)	50(1)
N(5)	6992(4)	-280(2)	10098(2)	85(1)
C(1)	8991(4)	1297(2)	9202(3)	56(1)
C(2)	9206(4)	1305(3)	10117(3)	80(2)
C(3)	9424(4)	558(3)	8883(3)	78(2)
C(4)	9702(4)	1939(3)	8849(3)	85(2)
C(5)	4234(3)	1941(2)	8324(2)	43(1)
C(6)	4333(4)	2618(2)	7785(3)	68(1)
C(7)	3560(4)	2157(3)	9054(3)	68(1)
C(8)	3493(4)	1328(2)	7880(3)	72(1)
C(9)	7280(5)	1239(3)	6524(2)	64(1)
C(10)	7220(7)	1909(3)	5978(3)	124(3)
C(11)	8608(6)	895(4)	6575(4)	113(2)
C(12)	6356(6)	654(3)	6197(3)	96(2)
C(13)	6881(4)	3346(3)	10040(3)	66(1)
C(14)	8206(5)	3705(3)	10074(4)	121(3)
C(15)	5879(5)	3938(2)	9805(3)	71(1)
C(16)	6617(6)	3005(3)	10837(3)	97(2)
C(17)	6266(4)	234(2)	8066(2)	46(1)
C(18)	5599(4)	-126(2)	8751(2)	48(1)
C(19)	6421(5)	-198(2)	9493(3)	60(1)
C(20)	5030(4)	-904(2)	8501(3)	60(1)
C(21)	4055(4)	-855(2)	7799(3)	55(1)
C(22)	2827(5)	-611(3)	7896(4)	80(2)
C(23)	1957(6)	-520(3)	7236(6)	103(2)
C(24)	2342(8)	-682(4)	6491(5)	115(3)
C(25)	3520(8)	-924(4)	6392(4)	114(2)
C(26)	4384(6)	-1022(3)	7046(3)	81(2)
C(27)	7007(4)	3604(2)	7423(3)	49(1)
O(1)	7558(3)	3047(2)	7711(2)	77(1)
O(2)	6763(4)	4110(2)	7859(3)	112(1)
O(3)	6777(4)	3675(2)	6722(3)	113(1)