TRIQUINANES : SYNTHESES AND TRANSFORMATIONS

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
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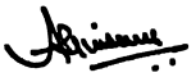
C O N T E N T S

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 Professor G. Mehta.

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



A. SRIKRISHNA

CERTIFICATE

Certified that the work contained in this thesis entitled: 'Triquinanes: Syntheses and Transformations' has been carried out by Mr. A. Srikrishna, under my supervision and the same has not been submitted elsewhere for a Degree.

G. Mehta

GOVERDHAN MEHTA
(THESIS SUPERVISOR)

G. Mehta

D E A N
SCHOOL OF CHEMISTRY

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SRIKRISHNA

PREFACE

Although cyclopentanes (quinanes) have been known in chemical literature for over a century and in Nature from time immemorial, interest in their syntheses and reactions has remained on a low key until recently. Strange as it may seem, this could be traced to the fact that till 1960, relatively few cyclopentanoids of reasonable complexity were known that could constitute challenging targets and the practicing organic chemists in this era were largely preoccupied and fascinated by the steroidal systems and annulated six membered rings. However, discoveries and developments of the past decade in the chemistry of natural and unnatural products have rekindled interest in the synthetic design of polycyclopentanoids (polyquinanes) and a flurry of activity is currently underway in this area. The main focus of this high intensity effort, around the world, has been the design of synthetic strategies for the rapid and efficient acquisition of polycyclopentanoid frameworks, adorned with different functionalities and stereochemical patterns. The present thesis entitled 'TRIQUINANES: SYNTHESES AND TRANSFORMATIONS' is a topical investigation in an area of high contemporary interest and describes a novel and speedy synthesis and transformations of linearly fused tricyclopentanoid ring system. The thesis is divided into two chapters:

1. A Novel Synthetic Approach to Linearly Fused Tricyclopentanoids *via* Photo-thermal Olefin Metathesis; 2. Synthesis of Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undecanes: A Novel Tris-homocubane System, and an appendix. The subject matter of each chapter has been organised under the headings: Abstract, Introduction, Results and discussion and Experimental.

The first chapter delineates a simple and expeditious synthetic approach to the functionalised triquinane system. The key concept in this synthetic sequence is the *photo-thermal olefin metathesis* of cheap, abundantly available Diels-Alder adducts of 1,3-cyclopentadiene and p-benzoquinones. Thus, the Diels-Alder adduct of 1,3-cyclopentadiene and p-benzoquinone on photolysis and thermolysis was smoothly transformed to *cis*, *syn*, *cis*-triquinane bis-enone in just two steps and in excellent yield. Several examples that demonstrate the generality of this theme have been worked out and are described. Some interesting transformations of the triquinane bis-enone, involving olefin isomerisation, functional group transposition and intramolecular cyclisations are also incorporated in this chapter. An up-to-date account of the currently available synthetic methodologies for the triquinane systems provides the backdrop to the present investigation and forms the introductory part of the first chapter.

The second chapter of the thesis describes a novel photochemical (intramolecular $\pi^2_s + \pi^2_s$ cycloaddition) entry to the pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undecane, a difficultly accessible trishomocubane derivative. An interesting observation made during this study was the facile acid catalysed reversal of the photochemical cyclisation. This observation suggested the possible role of the considerably strained pentacyclic trishomocubane system in the reversible storage of solar energy.

During the course of the main investigation, time was available during late nights and weekends to make exploratory forays into another arena. These meanderings provided delightful diversions and proved rewarding. For example, a simple, preparatively useful method for the synthesis of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decan-9-one (basketanone) and its congeners from COT was devised. Some interesting photochemical reactions and chemical transformations were also encountered enroute to the basketanone ring system. These results are briefly reported in the appendix to this thesis.

CHAPTER I

A NOVEL SYNTHETIC APPROACH TO LINEARLY FUSED TRICYCLOPENTANOIDS *via* PHOTO-THERMAL OLEFIN METATHESIS

I.1 ABSTRACT

A new, speedy and efficient approach to linearly fused tricyclopentanoids bearing the tricyclo[6.3.0.$0^{2,6}$]undecane (triquinane) frame of high contemporary interest is delineated. The key concept in this synthetic sequence to triquinane system is the novel photo-thermal metathesis of cheap, abundantly available, Diels-Alder adduct of 1,3-cyclopentadiene and p-benzoquinone. Thus, photolysis of *endo*-tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-diene-3,6-dione (71) furnished the known pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undeca-8,11-dione (72), which on regiospecific thermal fragmentation of the cyclobutane ring gave *cis*, *syn*, *cis*-tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione (73) as the sole product in quantitative yield. The *cis*, *syn*, *cis*-triquinane based bis-enone 73, with stereo-

chemical integrity and adequate functionality is rendered available in just three steps and in exceptionally high yield. Some examples that demonstrate the generality of the photothermal metathetic sequence enumerated above are also documented.

Several interesting transformations of readily available bis-enone 73, which establish its structure unambiguously and indicate its wider uses in synthesis, are described. Foremost among these is the smooth thermal isomerisation of the cis, syn, cis-bis-enone 73 to the cis, anti, cis-isomer 104 and the tetrasubstituted bis-enone 96. This adds to the versatility of our triquinane synthesis as both the cis, syn, cis- and cis, anti, cis-isomers can be obtained from the same precursor. Another useful theme emanating from 73 involved alkylative enone transposition and formation of cis, syn, cis-bis-enone 111. Finally, inter- and intramolecular Michael additions, in tandem, to triquinane based bis-enone 73 provide a facile entry to the difficultly accessible tetracyclo[5.4.0.$0^{3,10}$.$0^{4,8}$]undecane system 120.

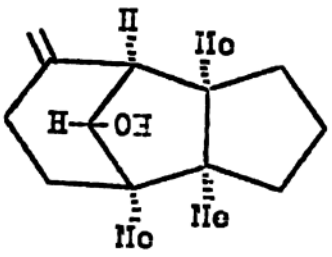
In order to put the main theme of this chapter in its proper perspective, an up-to-date account of the existing methodologies for assembling linearly fused tricyclopentanoids has been provided and forms the introduction to this chapter.

I.2 INTRODUCTION

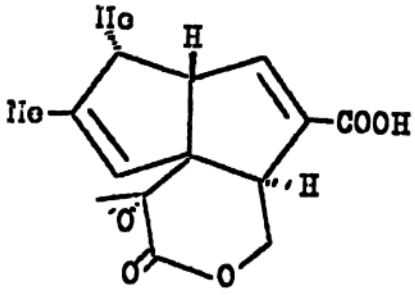
The past decade has witnessed an upsurge of interest in the development of synthetic methodologies for the rapid and efficient acquisition of a wide variety of polycyclopentanoids (Polyquinanes[+]).[1] This high level of interest and activity has been stimulated and sustained by the unravelling of many new and interesting cyclopentanoid carbon skeleta from plant, marine and fungal sources on one hand and by the organic chemist's quest for exotic, symmetric, all carbon polyhedra, e.g., Woodward's triquinacene,[2] Eaton's peristylane[3] and Paquette's dodecahedrane,[4] on the other. A partial list of naturally occuring polyquinanes,[5-14] highlighting Nature's ingenuity in creating five membered rings with generous sprinkling of functionalities and stereochemical delicacies is displayed in Chart I.1. The Chart I.2 depicts some enchanting cyclopentanoid frames,[1-4,15-21] which are manifestations of organic chemist's sense of imagination and creativity, lure of symmetry, and fascination for molecular architecture of common geometrical objects. Together, the representative polyquinane formulations in Charts I.1 and I.2

[+]Poly+quin+anes (quin, abbreviation of quintet or quintuplet, meaning five, f L. quintus). We find the colloquial name, polyquinane, both pleasant and convenient in conversational chemistry for the rapidly growing family of polyfused cyclopentanoids.[1]

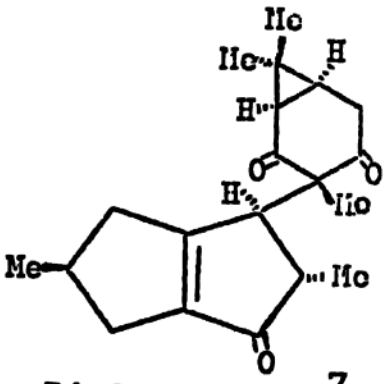
CHART I.1



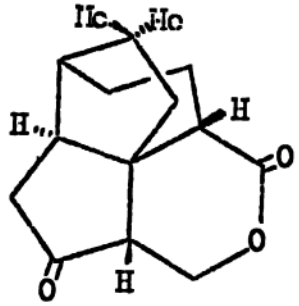
Gymnomitrol[5]



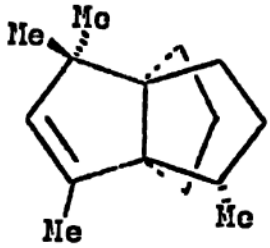
Pentalenolactone[6]



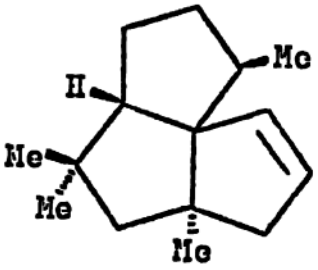
Riolozatrione[7]



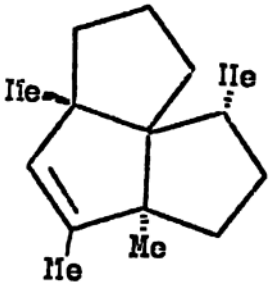
Quadrone[8]



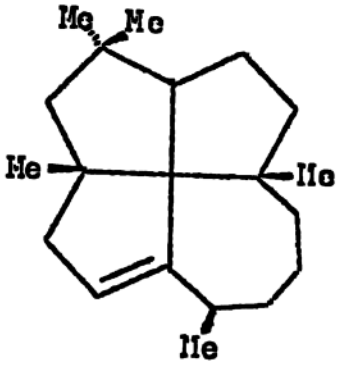
Modhephene[9]



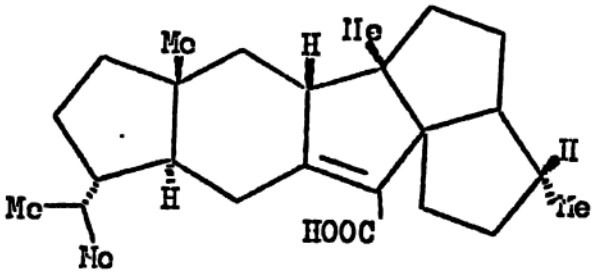
Silphenene[10]



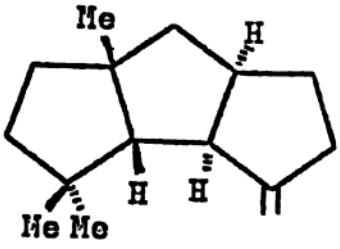
Isocomene[11]



Laurenene[12]

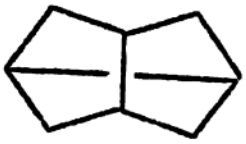


Retigeranic acid[13]

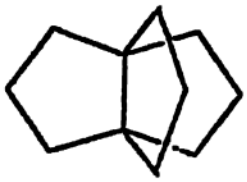


Capnellene[14]

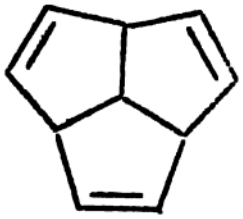
CHART I.2



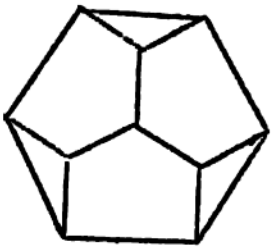
Bisnoradamentane[15]



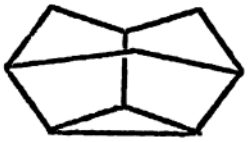
[3.3.3]propellane[16]



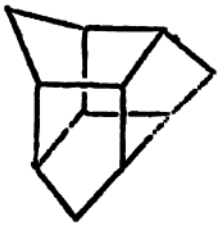
Triquinacene[2]



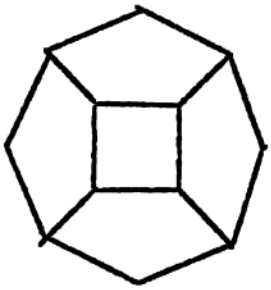
Diademane[17]



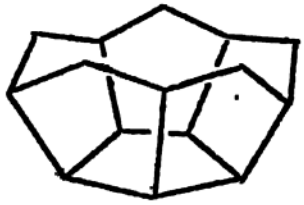
[3]peristylane[18]



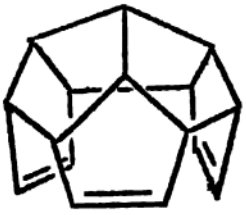
Trishomocubane[19]



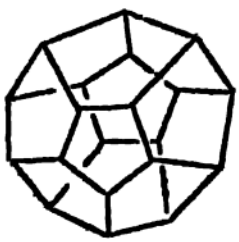
[4]peristylane[20]



[5]peristylane[3]



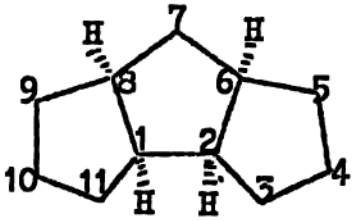
Hexaquinacene[21,1b]



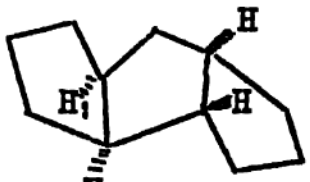
Dodecahedrane[4]

provide not only a veritable feast of tantalising and challenging synthetic targets but also reflects on the highly evolved state and degree of sophistication that synthetic organic chemistry has reached. Indeed, most of the targets in Charts I.1 and I.2 have either already succumbed to some brilliant synthetic assaults or are on the threshold of being tamed.

Among the various polyquinanes, the two stereoisomeric C_{11}-triquinanes[+] (*cis*, *syn*, *cis*-1 and *cis*, *anti*, *cis*-2), representing three linearly fused cyclopentane rings, have



1



2

received relatively greater attention due to the fact that the *cis*, *anti*, *cis*-isomer 2 embraces the basic carbocyclic framework of biologically important sesquiterpenoids of the hirsutane family (e.g., hirsutene 3, coriolin 4, hirsutic

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[+]We have frequently used this colloquial term for the linearly fused tricyclopentanoids. In the von Baeyer system of nomenclature: tricyclo[6.3.0.$0^{2,6}$]undecane; IUPAC nomenclature: decahydro-1H-cyclopenta(a)pentalene. See, footnote 2 in reference 3.

acid 5)[22-24] and marine natural products,[25] capnellane 6 The folded form, the cis, syn, cis-isomer 1 can, in another arena (see Chart I.2) function as the basic building block for elaboration and evolution towards dodecahedrane[1] and its immediate, logical precursors[+]. The two parent tricyclopentanoid hydrocarbons 1 and 2, to our information, have not been synthesised and characterised. However, their ΔH_f^o values have been calculated[26] employing both Engler (E) and Allinger (A) force fields and 2, ΔH_f^o -24.96 (E), -20.45 (A), has been shown to be marginally more stable than the hindered, folded form 1, ΔH_f^o -23.24 (E), -19.23 (A).

In the recent past, quite a few, new and orderly synthetic strategies have been worked out for assembling the linearly fused tricyclopentanoid frames. However, many of these approaches have been target oriented endeavours and the

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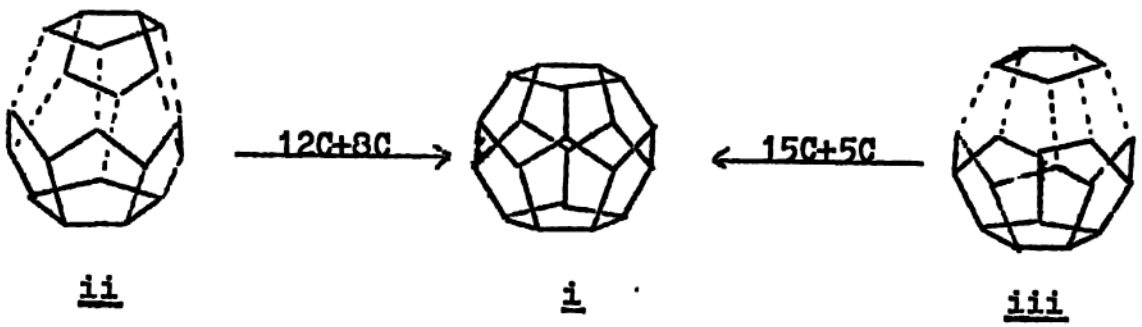
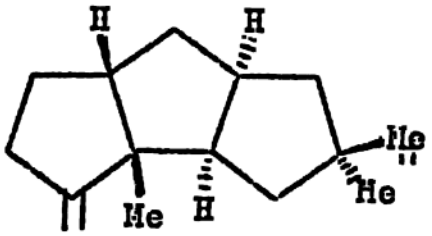
[+]Among the early and efficient pathways conceived to conquer dodecahedrane i were the bipartite approaches involving union of two complementary polyquinanes. The polyquinane fragments in ii and iii should be quite readily accessible from the cis, syn, cis-triquinane of the type 1.



ii i iii



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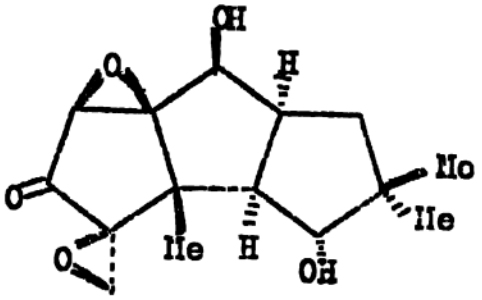

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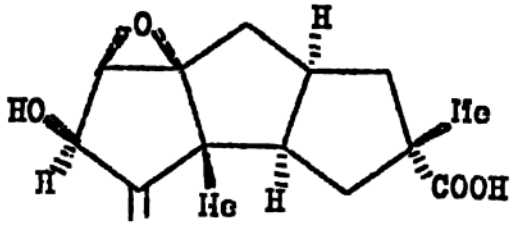

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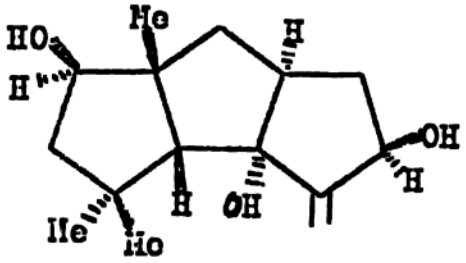
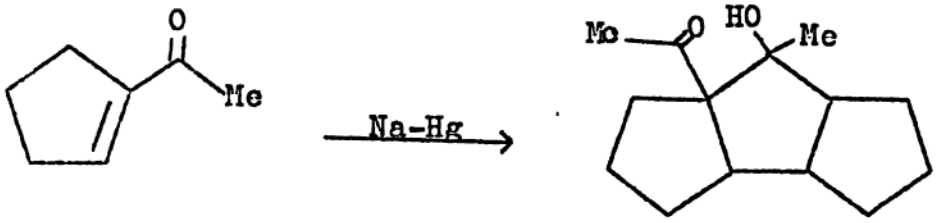


6

generality of most of them remains to be firmly established. Before delineating the general theme developed in the present study for the rapid acquisition of tricyclopentanoids, it will be useful and instructive to make a quick, schematic, survey of the existing methodologies for the synthesis of this ring system. For the convenience of presentation, we will discuss the known synthetic routes to linearly fused tricyclopentanoids in the following sequence. To start with, we look at the different approaches that directly lead to the tricyclopentanoid ring system. Some of these were clearly accidental or unanticipated encounters while others were

planned, thoughtful endeavours. We, then move to the tailor made strategies that have been specifically evolved to achieve a particular objective. Finally, we consider the 5,5 ⟶ 5,5,5 ring routes in which a cyclopentane ring is annulated to the preformed and suitably functionalised bicyclo [3.3.0]octane moiety. It is this particular approach, that has been widely employed for the synthesis of biologically important sesquiterpenes of the hirsutene family.

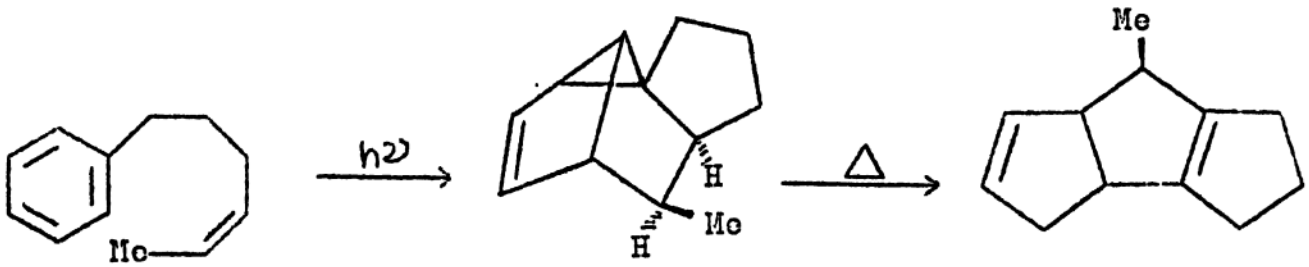
One of the earliest approaches to tricyclopentanoid framework 7 was by Casals[27] involving reductive coupling and cyclisation of 1-acetyl cyclopentene with sodium amalgam. This serendipitious discovery has been somehow relegated to



7

obscurity inspite of the fact 7 is obtained in 40% yield in a single step operation from a readily available starting material.

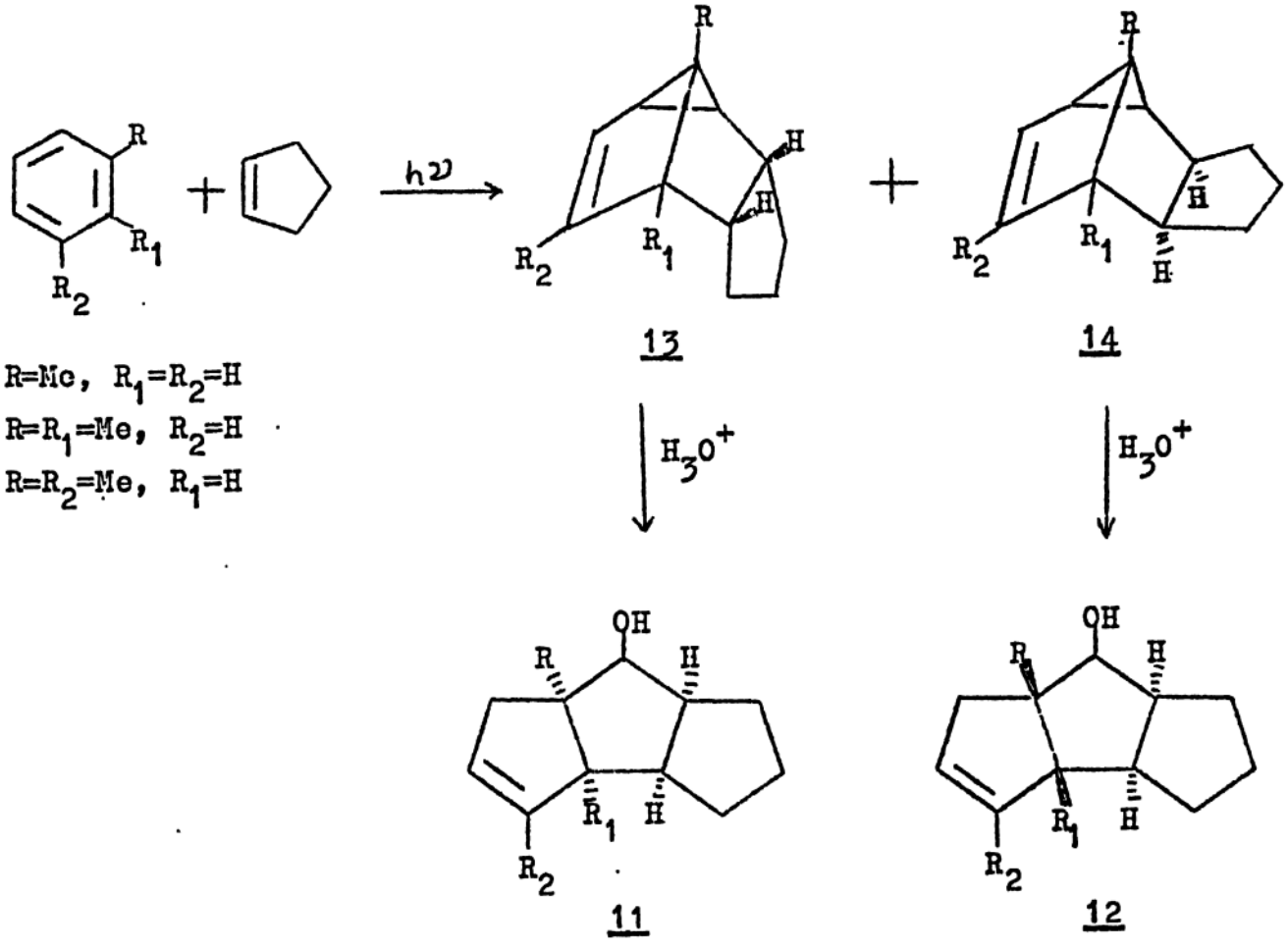
Several entries into the triquinanes have emanated from the exploitation of the 1,3-photocycloaddition products of aromatics to olefins. Morrison[28] employed the intramolecular variant of the arene - olefin photocycloaddition reaction



8 9 10

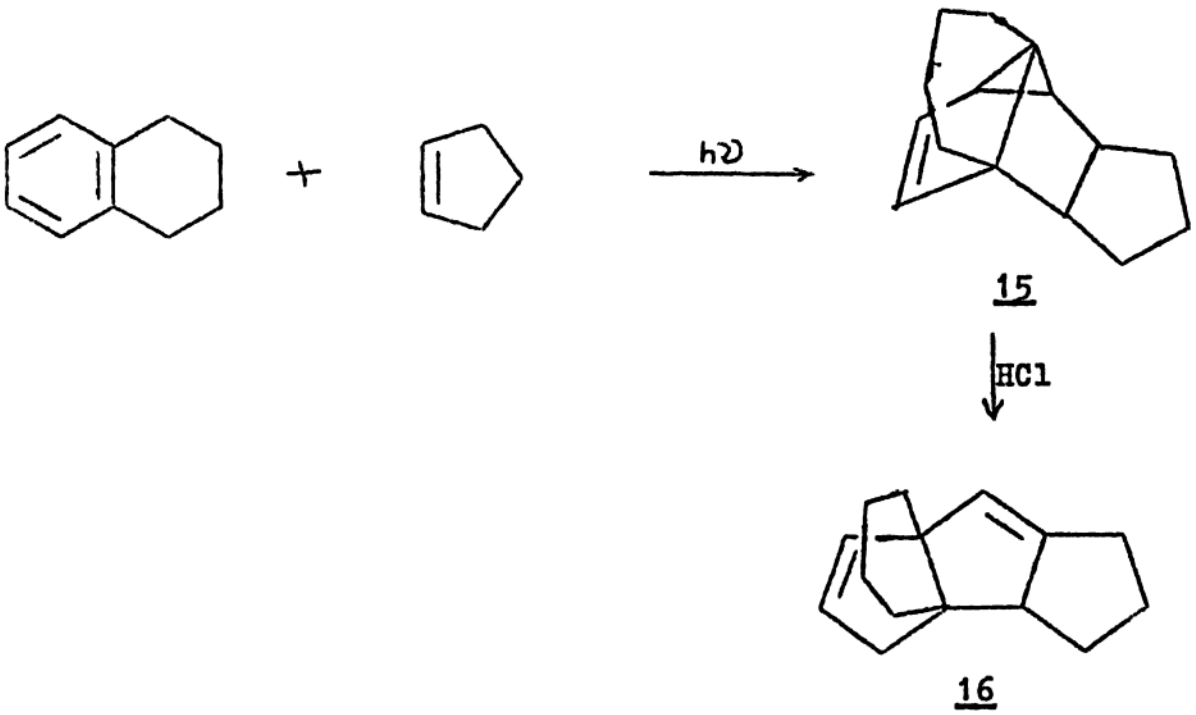
followed by stereoselective thermal reorganisation to gain access to the tricyclopentanoid system. Thus, photolysis of cis-6-phenyl-2-hexene 8 yielded tetracyclic olefin 9, which on thermolysis furnished 10. Srinivasan[29] utilising the more

SCHEME I.1



conventional intermolecular arene - olefin photoaddition described a fairly general approach to both the cis, syn, cis- and cis, anti, cis-triquinanes 11 and 12 (Scheme I.1). The endo- and exo-tetracyclic compounds 13 and 14, obtained from arene-cyclopentene photocycloaddition, underwent smooth acid catalysed cyclopropane cleavage to furnish 11 and 12, respectively. However, the exacting reaction conditions, instability of tetracyclic products and capricious yields (1-11%) are limiting factors to its wider synthetic utility. A further example[30] of this approach is the synthesis of tetracyclic propellane 16 incorporating three linearly fused five membered rings via the photocycloadduct 15 of tetralin and cyclopentene (Scheme I.2).

SCHEME I.2

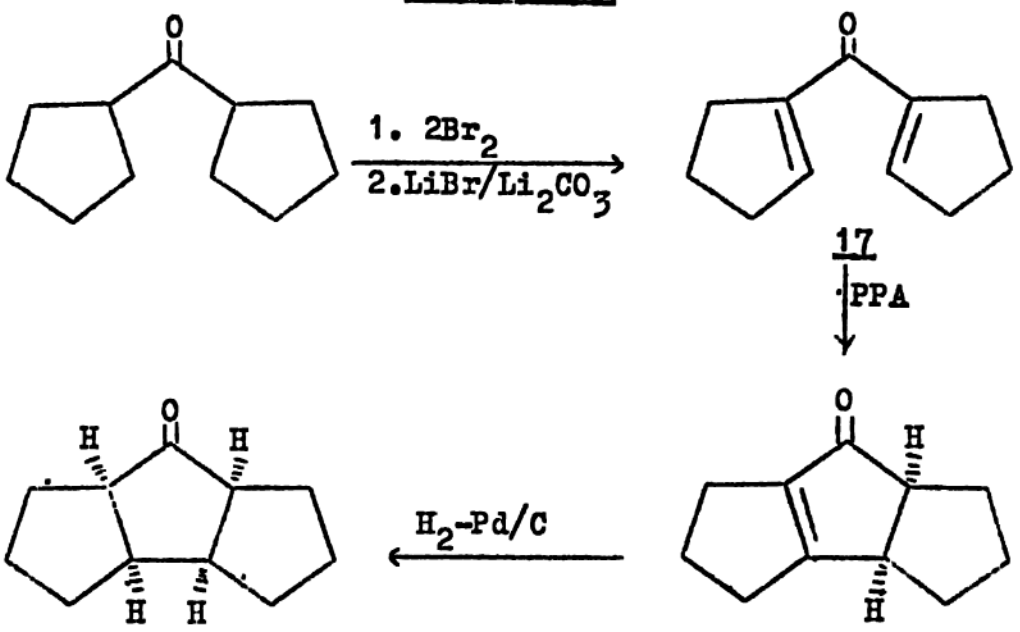


15

16

The first set of systematic approaches to the cis, syn, cis-triquinane system came from Eaton's laboratory.[31] Although classical in conception, the first Eaton methodology appears to be preparatively efficient and of general applicability. The key to this approach is the Nazarov-type cyclisation of the cross conjugated ketone 17 to the tricyclic system 18. Catalytic hydrogenation of 18 furnished

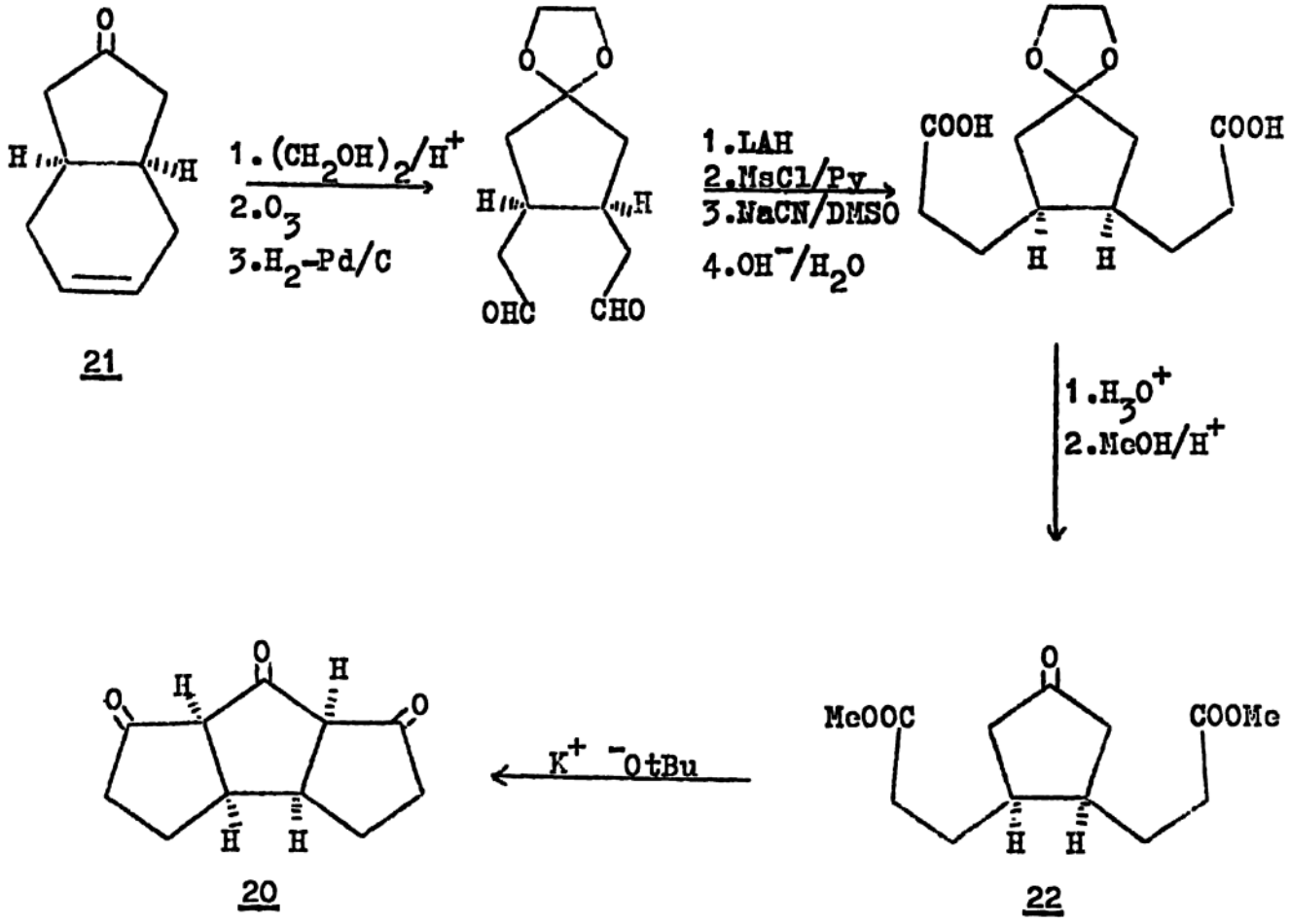
SCHEME I.3



19 18

the folded cis, syn, cis-ketone 19 (Scheme I.3), whose structure and C_s symmetry followed from the incisive analysis of ^{13}C NMR resonances. Another approach by Eaton,[31] directed towards the all cis-tricyclic triketone 20 starts with readily available bicyclo[4.2.0]oct-3-en-8-one 21 as the starting material and the steps are outlined in Scheme I.4. Oxidative

SCHEME I.4



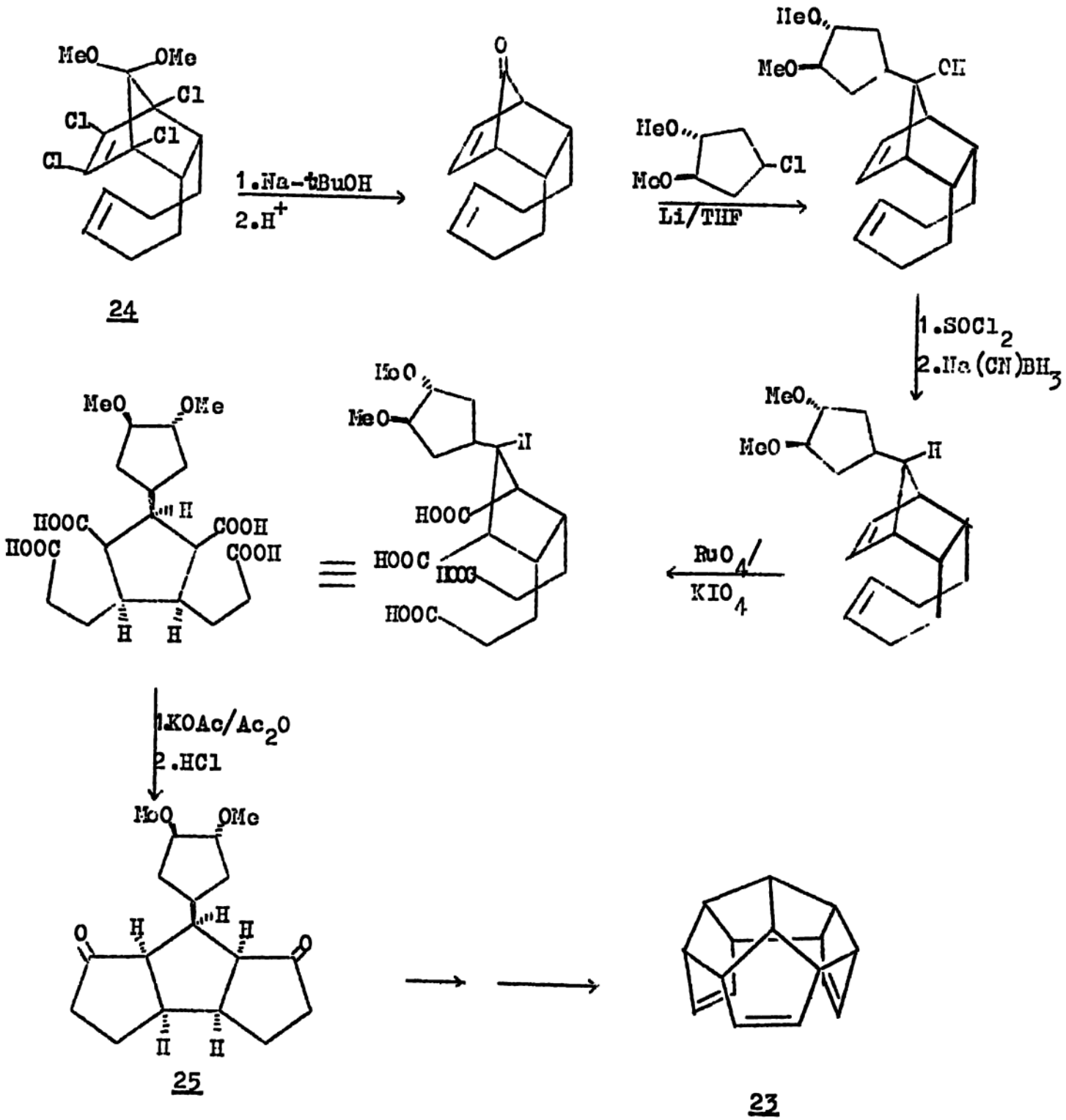
21 20 22

degradation of 21 and homologation led to the diester 22, whose cis-disposed functionality ensured the generation of requisite all cis-stereochemistry after the base catalysed cyclisation.

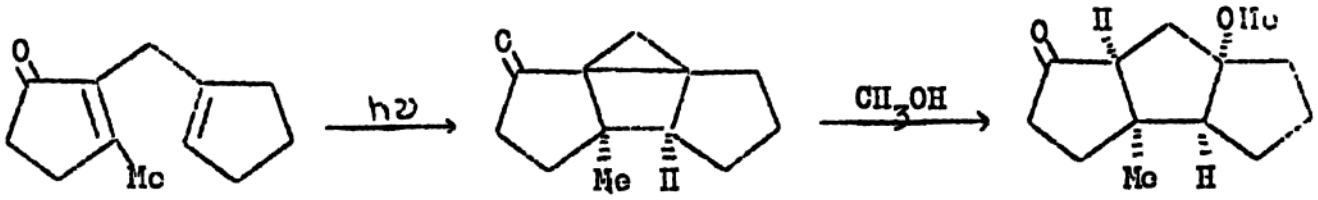
The third approach of Eaton,[1b] elegant in conception and immaculate in execution, was primarily designed to synthesise the hexaquinacene 23 enroute to dodecahedrane. The salient features of this theme starting from 5,5-dimethoxy-tetrachlorocyclopentadiene-1,5-cyclooctadiene Diels-Alder

adduct 24 are depicted in Scheme I.5. The most pleasing part is the creation of requisite stereochemical array in the triquinane derivative 25.

SCHEME I.5



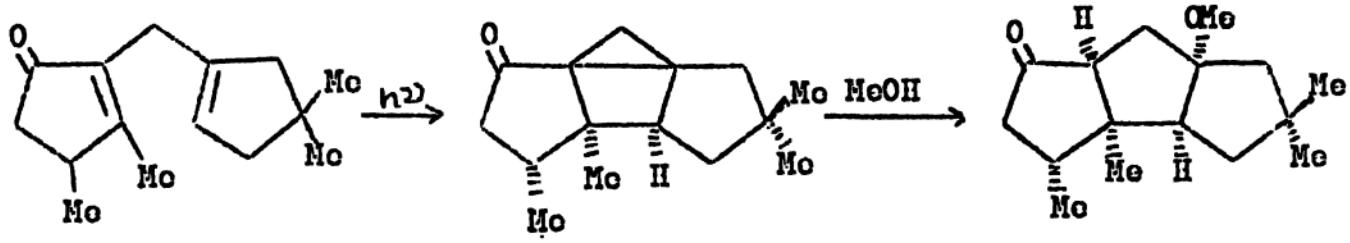
A potentially useful route to cis, syn, cis-triquinanes involving intramolecular $\pi^2_s + \pi^2_s$ photocycloaddition of dicyclopentenylmethane 26 to 27 and in situ nucleophilic ring opening of the strained central bond of the bicyclo[2.1.0]pentane moiety present in 27 to 28, has been delineated by



26 27 28

Pattenden and coworkers.[32] In an apparent bid to build the hirsutane skeleton the same strategy was applied to the C_{15} precursor 29, but the resulting product 30 possessing the unwanted cis, syn, cis-stereochemistry thwarted further efforts towards sesquiterpene hydrocarbon hirsutene 3 (Scheme I.6).

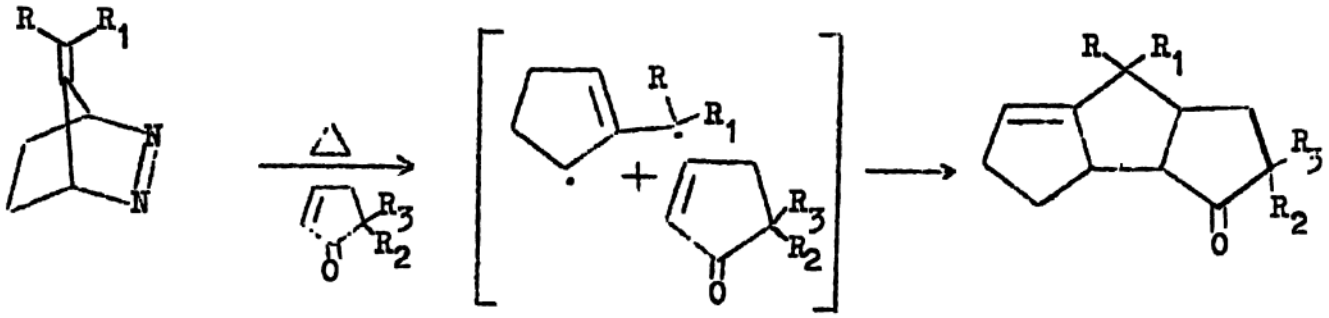
SCHEME I.6



29 30

Little[33-35] has described a novel and general approach to triquinanes involving inter- and intramolecular capture of 1,3-diyl's related to trimethylenemethane. In the intermolecular version,[33] the bicyclic azo compound 31 (derived from fulvene-azoester Diels-Alder adduct) is thermally decomposed in the presence of a 1,3-diyl trapping agent, like cyclopentene to furnish the tricyclopentanoid skeleton 32

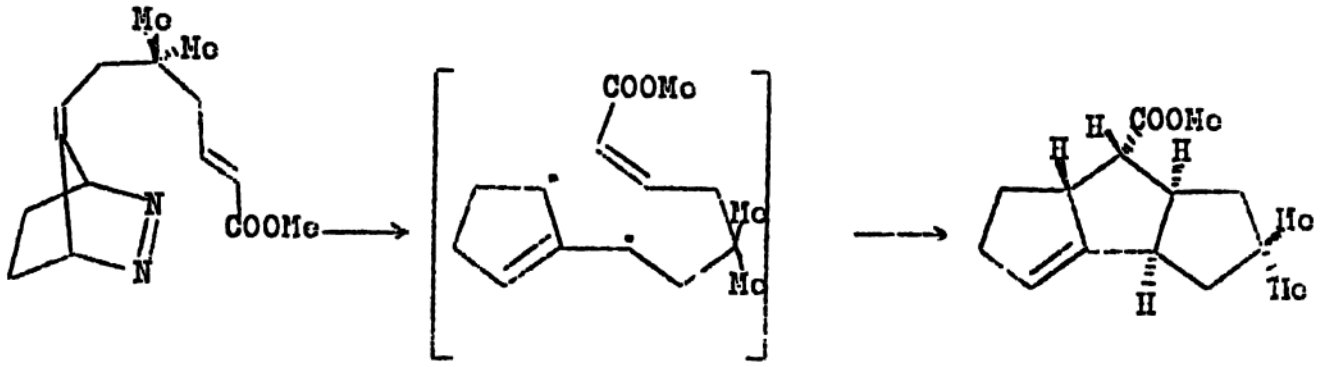
SCHEME I.7



31 32

(Scheme I.7). In the intramolecular version,[34] the 1,3-diyl precursor moiety and the diylophile are custom built into the same substrate. Thus, thermal decomposition of bicyclic

SCHEME I.8

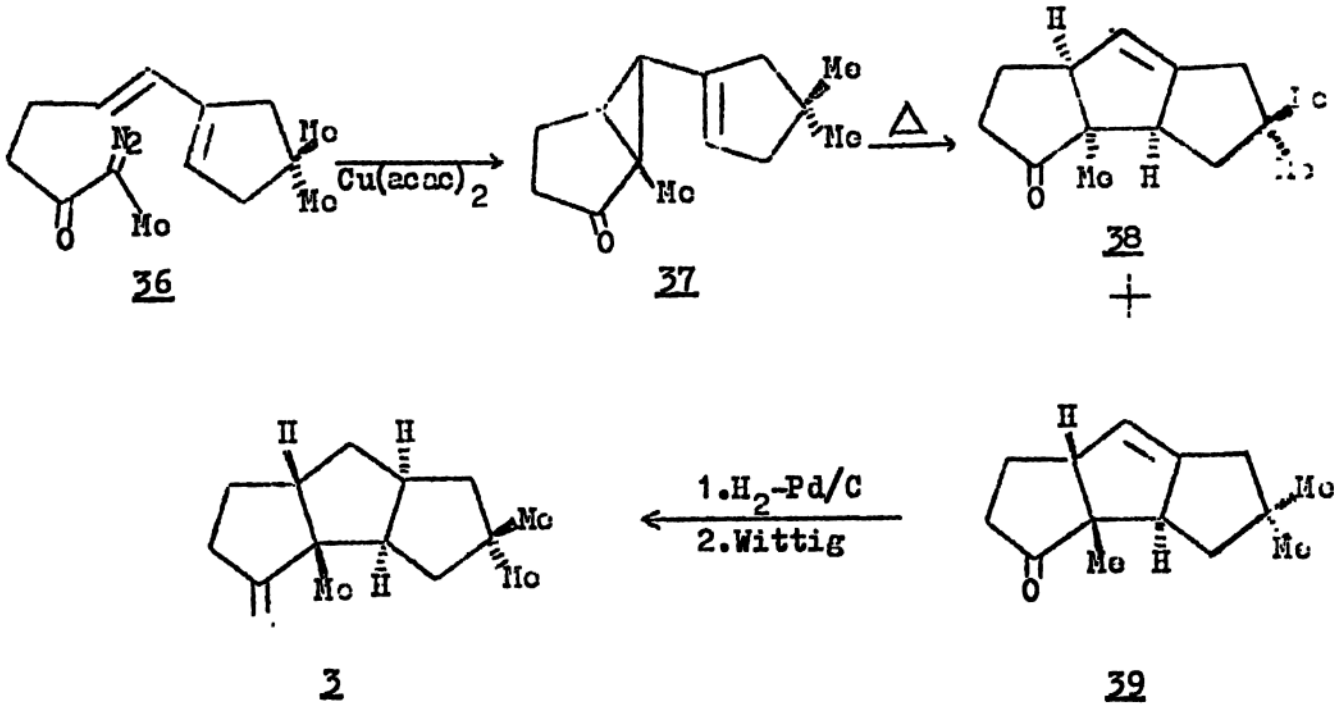


33 34 35

azo compound 33 resulted in the direct formation of 35 via the 1,3-diyl intermediate 34 (Scheme I.8). The intramolecular reaction is notable for its high degree of stereoselectivity compared to the intermolecular reaction. As would be expected, the intramolecular diyl trapping theme has been further applied to a total synthesis of sesquiterpene hydrocarbon (±)-hirsutene 3 employing appropriately functionalised substrate.[35]

Recently, a cyclopentene annulation methodology involving intramolecular carbenoid insertion to 1,3-dienes followed by thermal vinylcyclopropane-cyclopentene rearrange-

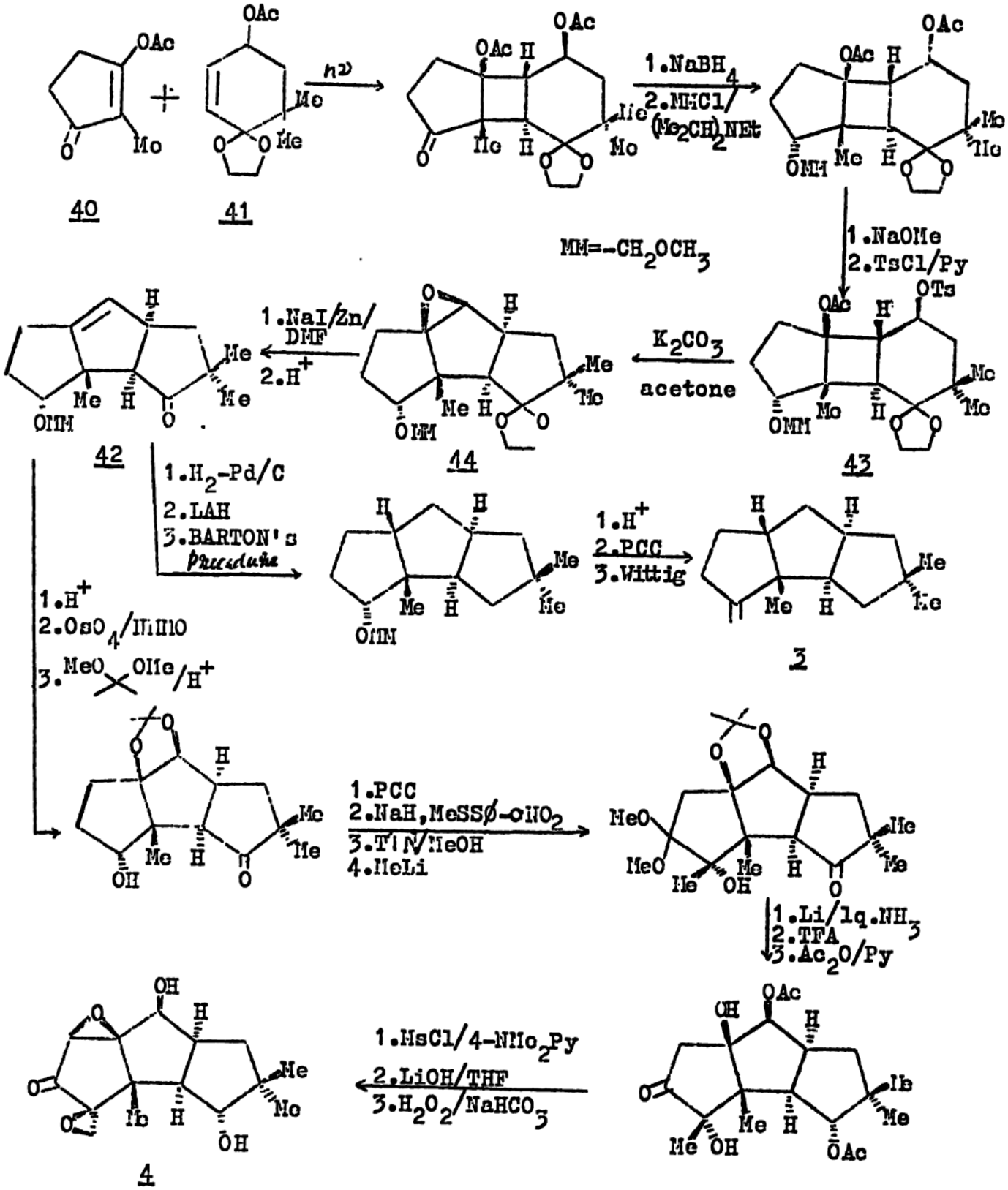
SCHEME I.9



ment has been evolved by Hudlicky[36] for the synthesis of tricyclopentanoid framework. For example, decomposition of diazoketone 36 (prepared in five steps from cyclopentene aldehyde) in presence of $Cu(acac)_2$ furnished the vinylcyclopropane 37 which on thermal activation or transition metal catalysis was transformed into epimeric tricyclopentanoids 38 and 39. The tricyclic ketone 39 has been further transformed into (±)-hirsutene 3 through routine functional group manipulations (Scheme I.9).[36]

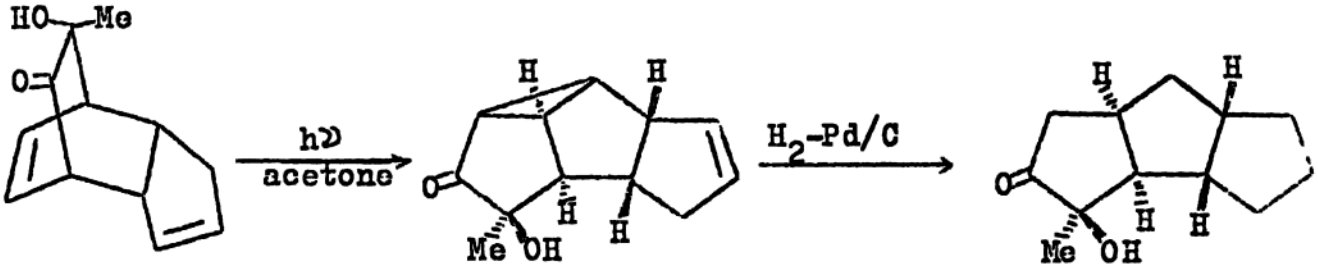
Tatsuta et.al., have developed a new stereocontrolled approach to the cis, anti, cis-triquinane system that has culminated in the total synthesis of (±)-coriolin 4. Indeed, both the hydrocarbon 3 and the highly functionalised antibiotic 4 have been synthesised[37,38] from the same tricyclic precursor 42. The key step of the Tatsuta synthesis is the unique solvolytic rearrangement of the 6,4,5-fused ring system 43 to the desired 5,5,5-ring system 44 in the requisite cis, anti, cis-stereochemical pattern. The initial 6,4,5-ring system 43 was readily obtained via the photochemical $\pi^2_s + \pi^2_s$ cycloaddition of pre-assembled precursors 40 and 41. The entire synthetic sequence leading to (±)-hirsutene 3 and the first total synthesis of (±)-coriolin 4 is summarised in Scheme I.10.

SCHEME I.10


40
41
hν
1.NaBH4
2.MHCl/(Me2CH)2NEt
MM=-CH2OCH3
1.NaOMe
2.TsCl/Py
K2CO3
acetone
1.NaI/Zn/DMF
2.H+
42
14
43
1.H2-Pd/C
2.LAH
3.BARTON's procedure
1.H+
2.PCC
3.Wittig
3
1.H+
2.OsO4/NMMO
3.MeO OMe/H+
1.PCC
2.NaH,MeSSØ-oNO2
3.TiN/MeOH
4.MeLi
1.Li/liq.NH3
2.TFA
3.Ac2O/Py
1.MsCl/4-NMe2Py
2.LiOH/THF
3.H2O2/NaHCO3
4

Yonemitsu's group[39] has reported a two step entry into cis, anti, cis-triquinane derivative 47 employing the photochemical oxa-di-π-methane rearrangement of the tricyclic β,γ-unsaturated ketone 45 followed by hydrogenolytic cleavage of the cyclopropane ring in 46 (Scheme I.11).

SCHEME I.11



45 46 47

The most commonly employed and conceptually straightforward approach to the triquinanes is through the cyclopentane annulation of the preformed cis-bicyclo[3.3.0]octane framework.+ Lansbury[40] was the first to exploit this theme for the synthesis of triquinanes related to hirsutane family, utilising his chloro-olefin annulation[41] sequence for appending a cyclopentane ring on the cis-bicyclo[3.3.0]octane system. Thus, bicyclic ketone 48 was transformed to tricyclics 49,

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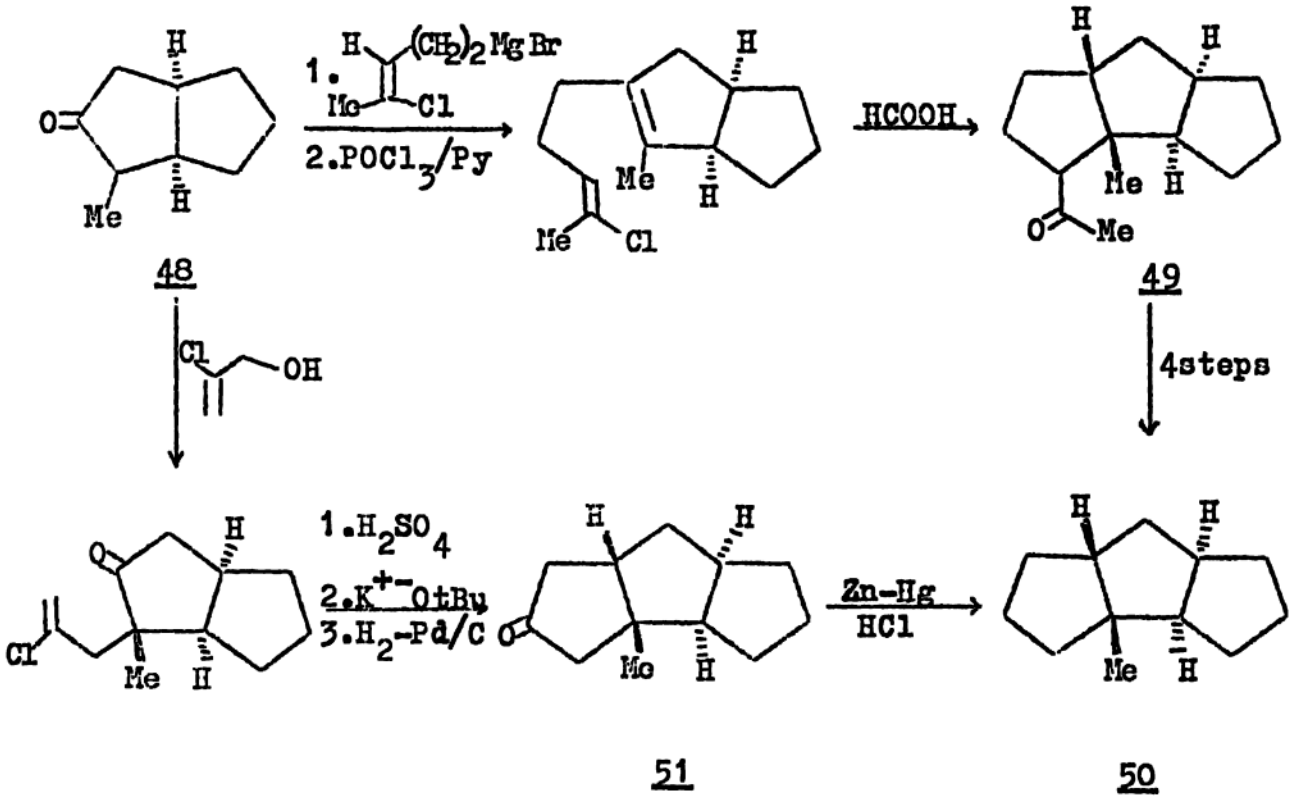
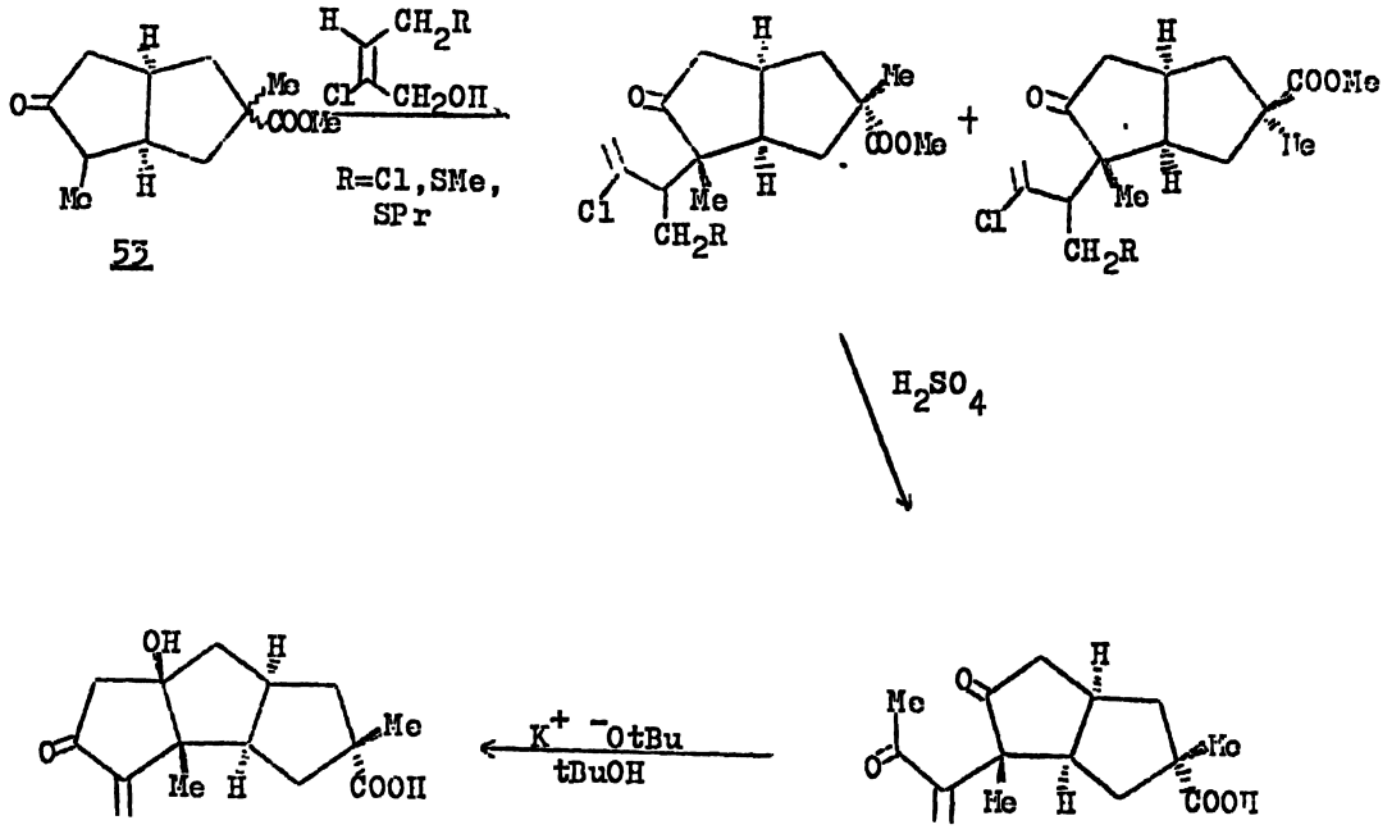
+This approach is particularly suited for cis, anti, cis-fused triquinanes as the incoming cyclopentane ring will be formed preferentially on the exo-face of the folded cis-bicyclo[3.3.0]octane moiety.

SCHEME I.12



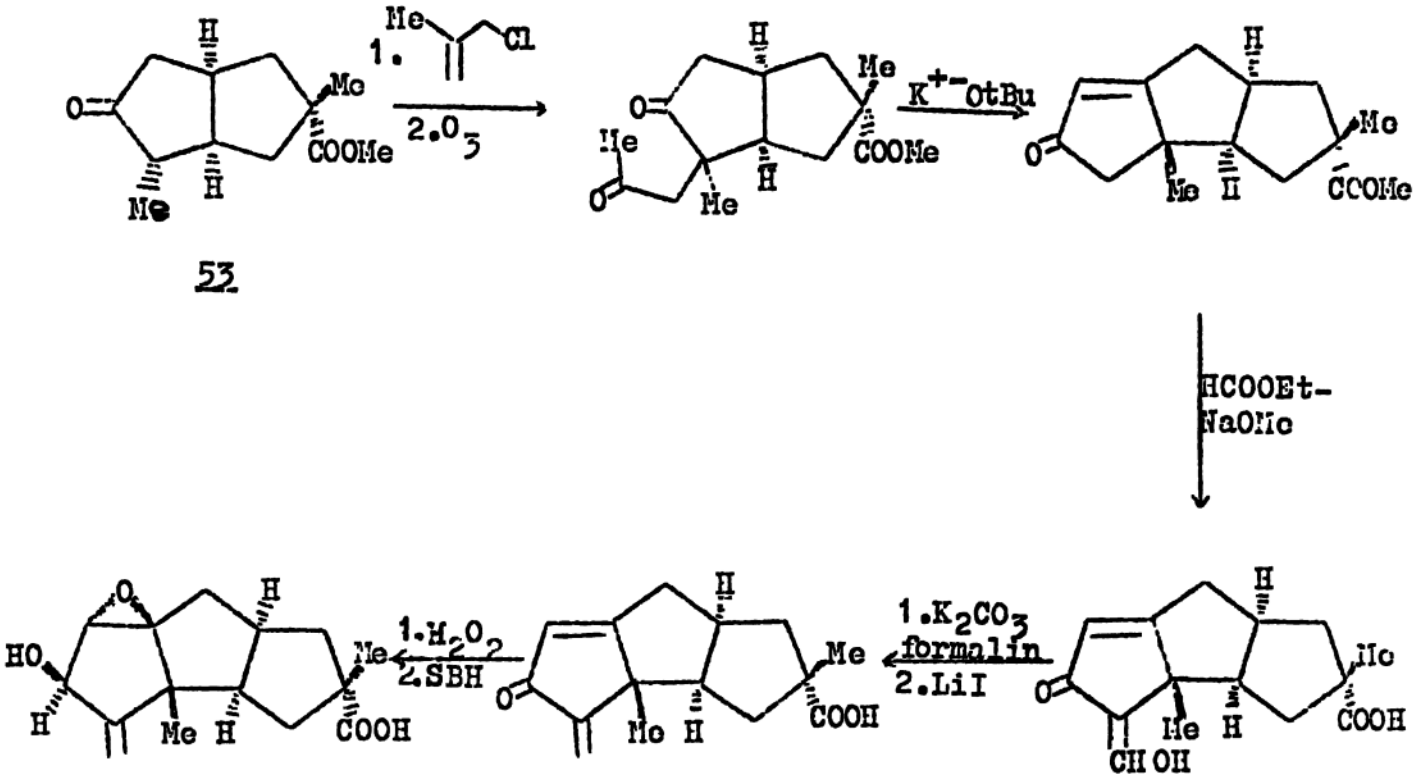
50 and 51 as indicated in Scheme I.12. Further refinement of the same theme has led to the synthesis of biologically active isohirsutic acid 52 (hirsutic acid N)[42] starting from bicyclic ketone 53 as depicted in Scheme I.13. The notable feature is the stereo- and regioselective Claisen alkylation of 53 with substituted trans-β-chloro-crotyl alcohol.

SCHEME I.13



Concurrently with the efforts of Lansbury in USA, Matsumoto and his group[43] in Japan achieved the first total synthesis of (±)-hirsutic acid 5 employing the cis-bicyclo [3.3.0]octane route and the steps involved in their successful endeavour are revealed in Scheme I.14. The starting material in the Matsumoto approach was, quite predictably, same as the Lansbury ketone 53, but in this case the stereochemically homogeneous 53 was employed.

SCHEME I.14

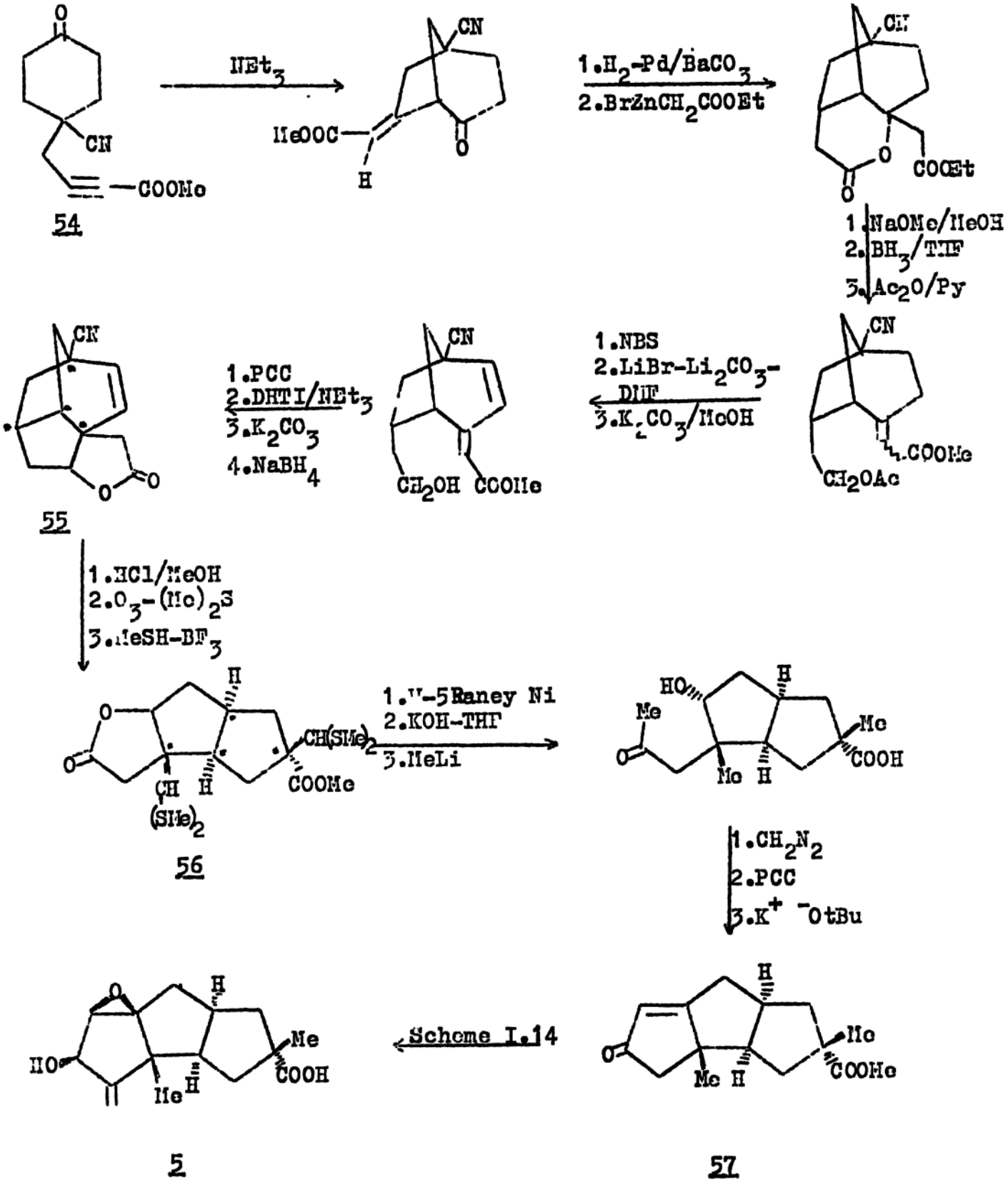


53

5

Trost and coworkers[44] have also recently reported a stereocontrolled synthesis of (±)-hirsutic acid 5. The highlight of the Trost theme is the imposition of steric control on four chiral centres by building them into a rigid bridged template 55 and then unravelling them at an appropriate time (step 55 ⟶ 56 involving oxidative cleavage of double bond, Scheme I.15). Readjustment of functional groups in 56 leads to the tricyclic enone 57. The earlier approaches of Matsumoto[43] and Lansbury[42] as well as of Trost converge

SCHEME I.15

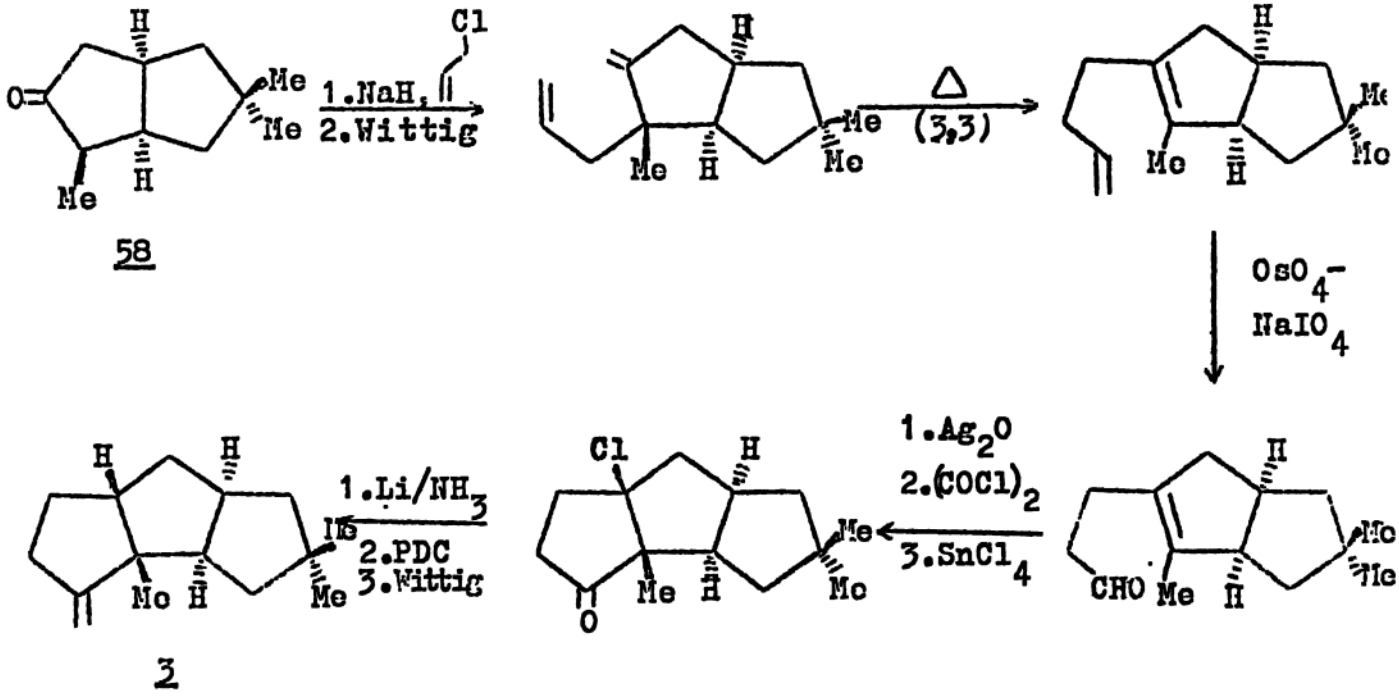


54 55 56 57 5

on this tricyclic enone 57. The task of building the key bridged tricyclic system 55 in the Trost synthesis was accomplished from cyclohexanone derivative 54 in a series of synthetic operations involving two intramolecular Michael additions (Scheme I.15).

Research groups led by Nozoe and Shibata[22] were the first to report the synthesis of tricyclic hydrocarbon (±)-hirsutene isolated by them from the hydrocarbon fraction of the fermentation broth of Coriolus consors. The underlying theme of their synthetic effort was the regioselective introduction of the side chain on to the bicyclic ketone 58 and

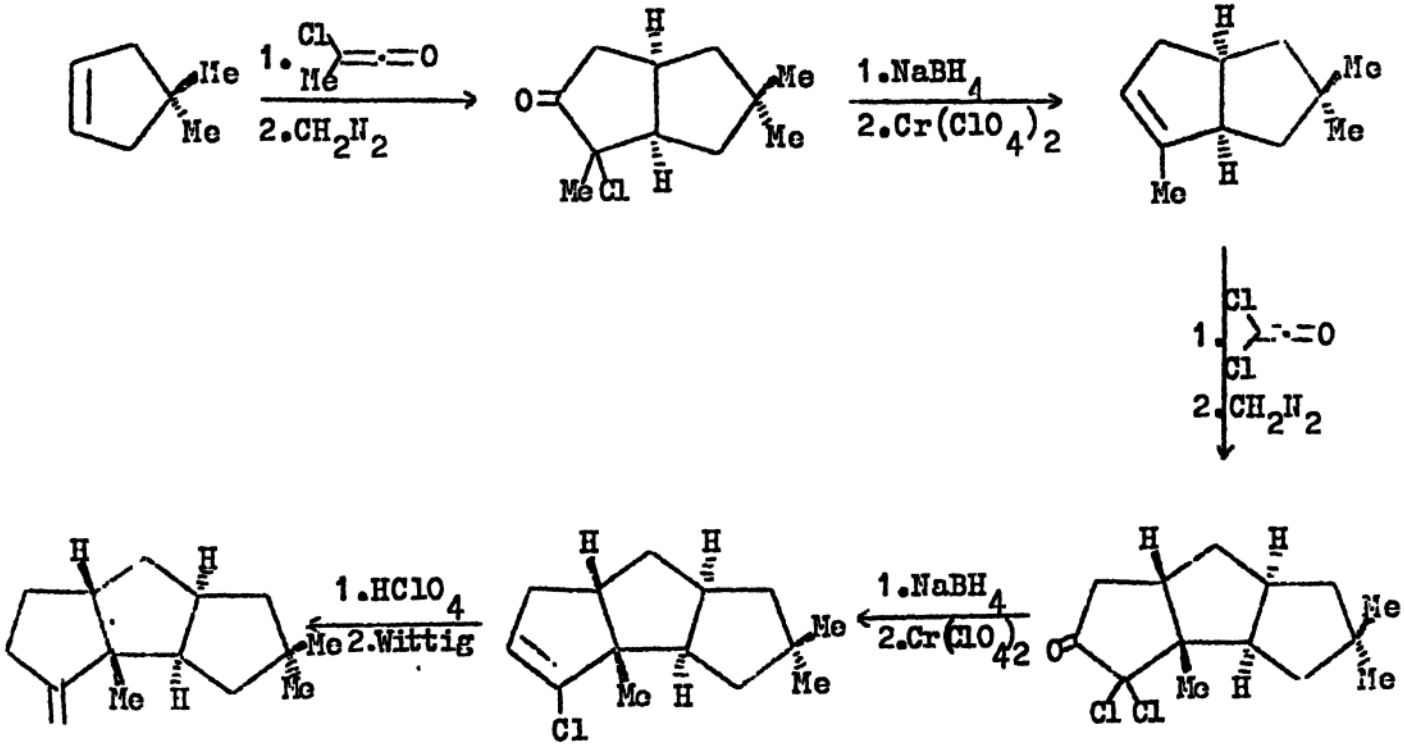
SCHEME I.16



formation of the third five membered ring through an intramolecular acylation reaction. The steps leading to 3 from 58 are schematically presented in Scheme I.16.

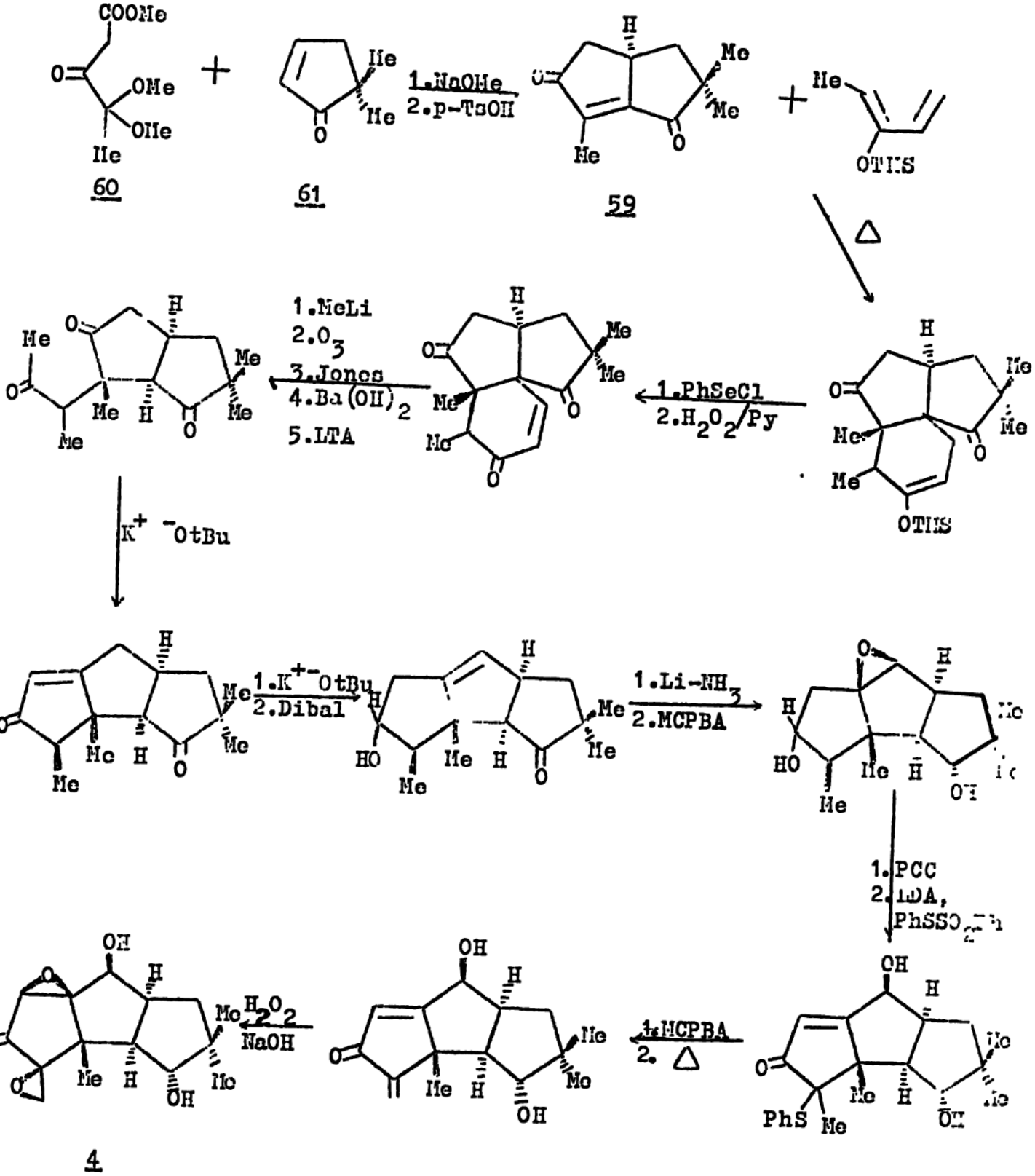
The most pleasing illustration of the bicyclo[3.3.0] octane route to the tricyclopentanoids is the Greene's[45] synthesis of (±)-hirsutene 3, employing reiterative haloketene cycloaddition-diazomethane ring expansion sequence. Starting from 4,4-dimethyl cyclopentene (±)-hirsutene 3 was obtained in a short, economical sequence (Scheme I.17).

SCHEME I.17



3

SCHEME I.18


COOMe
OMe
OMe
Me
60
Me
Me
O
61
1.NaOMe
2.p-TsOH
H
Me
Me
O
Me
59
Me
OTMS
△
H
O
Me
Me
H
Me
Me
Me
1.MeLi
2.O3
3.Jones
4.Ba(OH)2
5.LTA
H
O
Me
Me
Me
O
1.PhSeCl
2.H2O2/Py
H
O
Me
Me
Me
O
OTMS
K+ -OtBu
H
Me
Me
H
O
Me
1.K+-OtBu
2.Dibal
H
HO
Me
Me
H
O
Me
1.Li-NH3
2.MCPBA
O
H
H
HO
Me
Me
H
OH
1.PCC
2.LDA,
PhSSO2Ph
OH
O
Me
H
OH
Me
4
H2O2
NaOH
OH
H
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Me
H
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1.MCPBA
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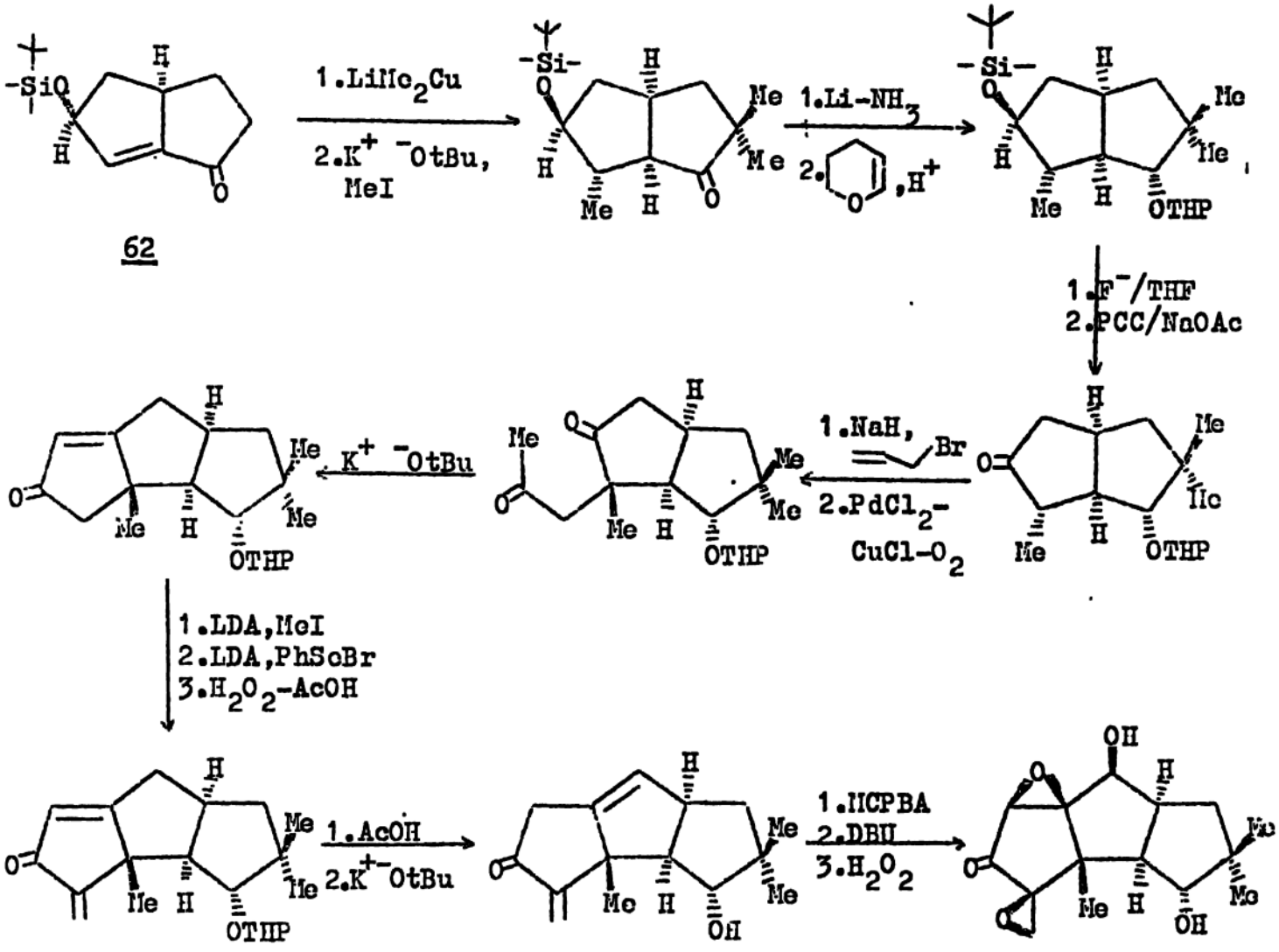
OH
H
O
Me
PhS
Me
H
OH
Me

Two fine syntheses of coriolin 4, the biologically important metabolite from Coriolus consors, reported recently by Danishefsky[46] and Ikegami,[47] follow the bicyclo[3.3.0] octane approach and the third five membered ring is appended via aldol condensation-dehydration steps. While the key

SCHEME I.19

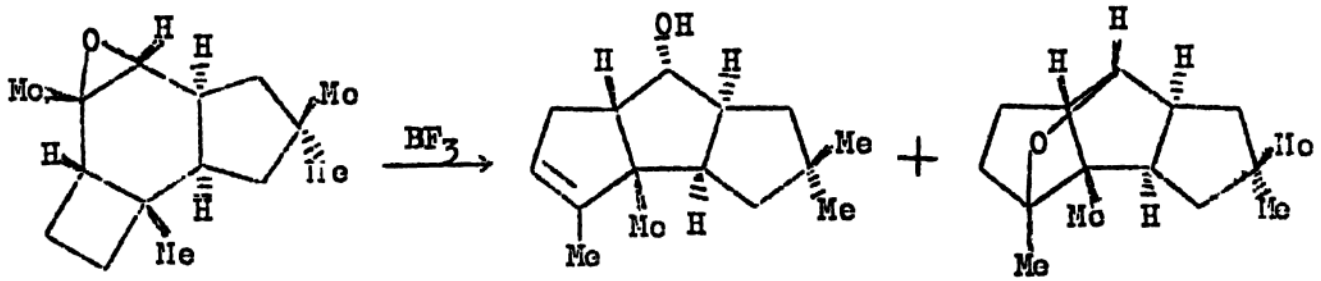


62

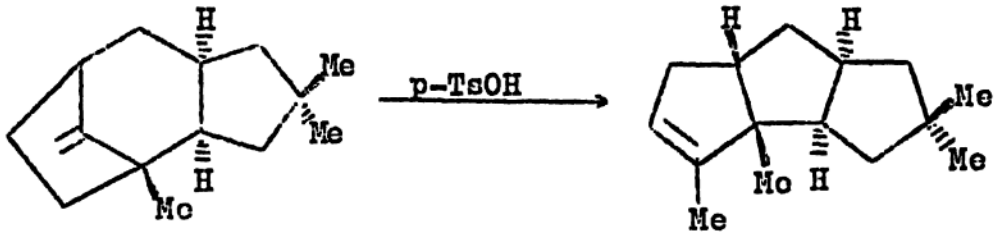
starting bicyclic ene-dione 59 in the Danishefsky route (Scheme I.18) is prepared from β-keto ester 60 and cyclopentenone 61 via Michael addition, the bicyclic enone 62 of Ikegami approach (Scheme I.19) is obtained from 1,3-cyclooctadiene. The outstanding feature of these approaches is the methodology adopted for the creation of high degree of functionality on the tricyclic frame in a stereoselective manner. Particularly fascinating aspect of these strategies is the introduction of the secondary hydroxyl group at C_7 on the central five membered ring.

Finally, a few interesting and biogenetically patterned transformations to hirsutane ring system have been reported, that provide new entry into the cis, anti, cis-triquinane framework. For example, Lewis acid catalysed rearrangement[48] of protoilludene epoxide 63 furnishes, among other products, tricyclopentanoids 64 and 65. Similarly, acid catalysed rearrangement of tricyclic olefin 66 yields the double bond isomer 67 of hirsutene.[49] These transformations not only provide further avenues for synthetic exploitation but shed light on the close biogenetic relationship of these humulene derived sesquiterpenoid carbon skeletons.[+]

[+]Total syntheses of (±)-hirsutene 3 and coriolin 4 has also been achieved in our laboratory.[69,70] The details of this synthesis will be reported in the forthcoming Ph.D. dissertation of Mr. A. Veera Reddy.



63 64 65



66 67

In the foregoing pages and schemes, an attempt has been made to provide an up-to-date account of the known methods for the construction of the triquinane framework. Most of these synthetic studies appeared in literature during the past four or five years as a result of burgeoning interest in the synthesis of polycyclopentanoids. When the present studies were initiated (1977-78) on a general synthetic approach to triquinanes, in pursuance of objectives enumerated above, the only preparatively exploitable routes available to this ring system were those by Eaton[31] and these too were multistep ventures. It was also the time when the biological potential of coriolins e.g., 4 was attracting attention and dodecahedrane had already

emerged as one of the prized synthetic targets in organic chemistry. Consequently, there was a timely need and ample scope for the development of convenient, reliable and versatile route to both cis, syn, cis-1 and cis, anti, cis-2 linearly fused triquinane ring systems.

In our quest for simple, general method for the synthesis of tricyclo[6.3.0.$0^{2,6}$]undecane (triquinane) system, we conceived of a novel two step photo-thermal metathetic sequence+ (Scheme I.20)[50] that involves a symmetry allowed and

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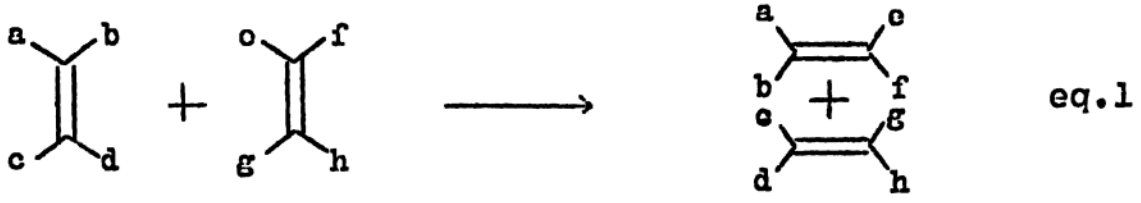
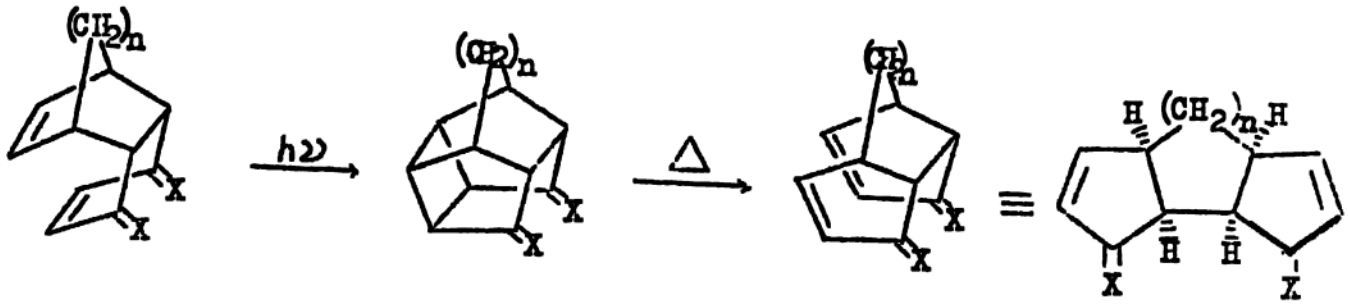
+The classical olefin metathesis reaction (eq.1) involves interchange of two alkylidene moieties between two olefins and is usually brought about by special catalytic recipes derived from W, Mo, Ta & Al. The mechanism of this reaction is a subject of much current effort and is quite complex.[51]



eq.1

The overall transformation 68 ⟶ 70 in Scheme I.20 is essentially an intramolecular olefin metathesis sequence brought about in a stepwise manner. Since the two discrete steps involved in the overall metathetic change 68 ⟶ 70 are a photochemical cycloaddition and a thermal cycloreversion, we coin the name PHOTO-THERMAL metathesis for such transformations. The stepwise photo-thermal metathetic sequence is full of interesting possibilities and it is hoped that many new synthetic applications will emerge from this idea. Some notable successes have already been achieved.[52,69,70]

SCHEME I.20



68 69 70

facile photochemical $\pi^2_s + \pi^2_s$ cycloaddition (68 ⟶ 69) and a regiospecific thermal fragmentation of the saturated four membered ring (69 ⟶ 70). The short, straightforward strategy depicted in this scheme has many attractive and advantageous features: (i) the tricyclic system 68, with requisite endo-geometry, can be obtained from cheap, readily available starting materials, e.g. 1,3-cyclopentadiene (n=1) and p-benzoquinone (X=O) via the standard Diels-Alder reaction;[53] (ii) the yields in the Diels-Alder reaction leading to 68 and its photochemical cage cyclisation[54] to 69 are generally good to excellent and thereby enhance the overall preparative value of this strategy; (iii) the thermal cyclobutane fragmentation in rigid, bridged pentacyclic template 69 ensures stereoselective formation of cis, syn, cis-triquinane system, adequately and appropriately functionalised; (iv) the overall three step conversion of diene and dienophile to the triquinane 70 employs, quite remarkably, only heat and light as the

reagents and (v) the scheme has the flexibility for the structural manipulations that can provide convenient entry into other tricyclic systems of current interest. Furthermore, as the cis, syn, cis-triquinane system has folded shape and is sterically crowded, it should be amenable to isomerisation to the less hindered and thermodynamically more stable cis, anti, cis-form and thus the strategy outlined in Scheme I.20 is capable of providing entry to both the stereoisomeric forms of triquinane frame-work.

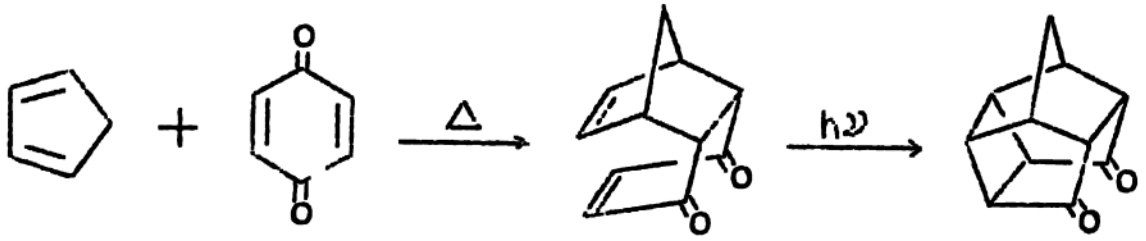
In this chapter of the thesis, we delineate a general preparative route to several functionalised cis, syn, cis-triquinanes and describe some useful synthetic transformations of these systems. Some of these transformations have provided novel and purposeful routes to new polycyclic systems. Furthermore, adding to the versatility of our approach is the description of a thermal isomerisation of cis, syn, cis-triquinanes to cis, anti, cis-form, endowed with the requisite stereochemical pattern of hirsutene 3, coriolin 4, hirsutic acid 5 and capnellane 6 group of natural products.

I.3 RESULTS AND DISCUSSION

Implementation of the strategy outlined in Scheme I.20 for the syntheses of triquinanes required the selection of a suitable endo-tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-diene

derivative for the contemplated photo-thermal metathesis sequence. The first choice was automatically the readily obtainable and well characterised Diels-Alder endo-adduct 71 of 1,3-cyclopentadiene and p-benzoquinone.[55] Photolysis of 71 is known to proceed smoothly in Sunlight or on UV irradiation to the pentacyclic dione 72 (Scheme I.21).[54] The crucial

SCHEME I.21

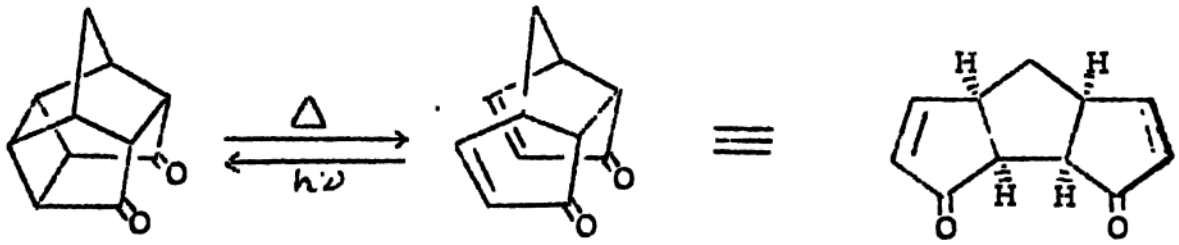


71 72

step then was the thermal fragmentation of the pentacyclic dione 72. However, it is recorded in literature[54a] that 72 is recalcitrant towards thermal activation. Cookson et.al.[54a] during their pioneering studies on intramolecular $\pi^2_s + \pi^2_s$ type of photocycloadditions had attempted thermolysis of 72 and cryptically observed that ''.....under mild heating it sublimed unchanged while at higher temperature a black tar was formed. However, on one occasion, traces of yellow needles, smelling of p-benzoquinone were formed accompanied by cyclopentadiene''. Heating 72, either neat or in solution upto $\sim 400^{o}C$, essentially corroborated Cookson's observations

and no trace of the expected cycloreversion product was to be found. But, undeterred by the thermal refractoriness of 72, we decided to subject it to flash thermolysis conditions at elevated temperatures.

Sublimation of 72 through a quartz tube at 560°C (1 torr) led to its quantitative conversion to the triquinane system 73, mp.107-8°C (silky flakes from carbon tetrachloride).



72 73

The bis-enone 73 could be conveniently prepared in 5-10 g lots, required no separation manoeuvre and was obtained pure from the pyrolysate simply by direct crystallisation! Its infrared spectrum (Fig.I.1) showed conjugated enone absorption at 1725 sh, 1715, 1695 sh and 1590 cm^{-1} diagnostic of 2-cyclopentenone substructure. The ultraviolet spectrum had λ_{max} at 219 nm (ε = 10,500) and supported the presence of 2-cyclopentenone chromophore (λ_{max} = 215±5 nm). The ^{1}H and ^{13}C NMR spectra of 73 further confirmed the presence of 2-cyclopentenone moiety (characteristic β-proton resonance[56] at δ7.44, Fig.I.2 and strongly deshielded β-carbon resonance[57]

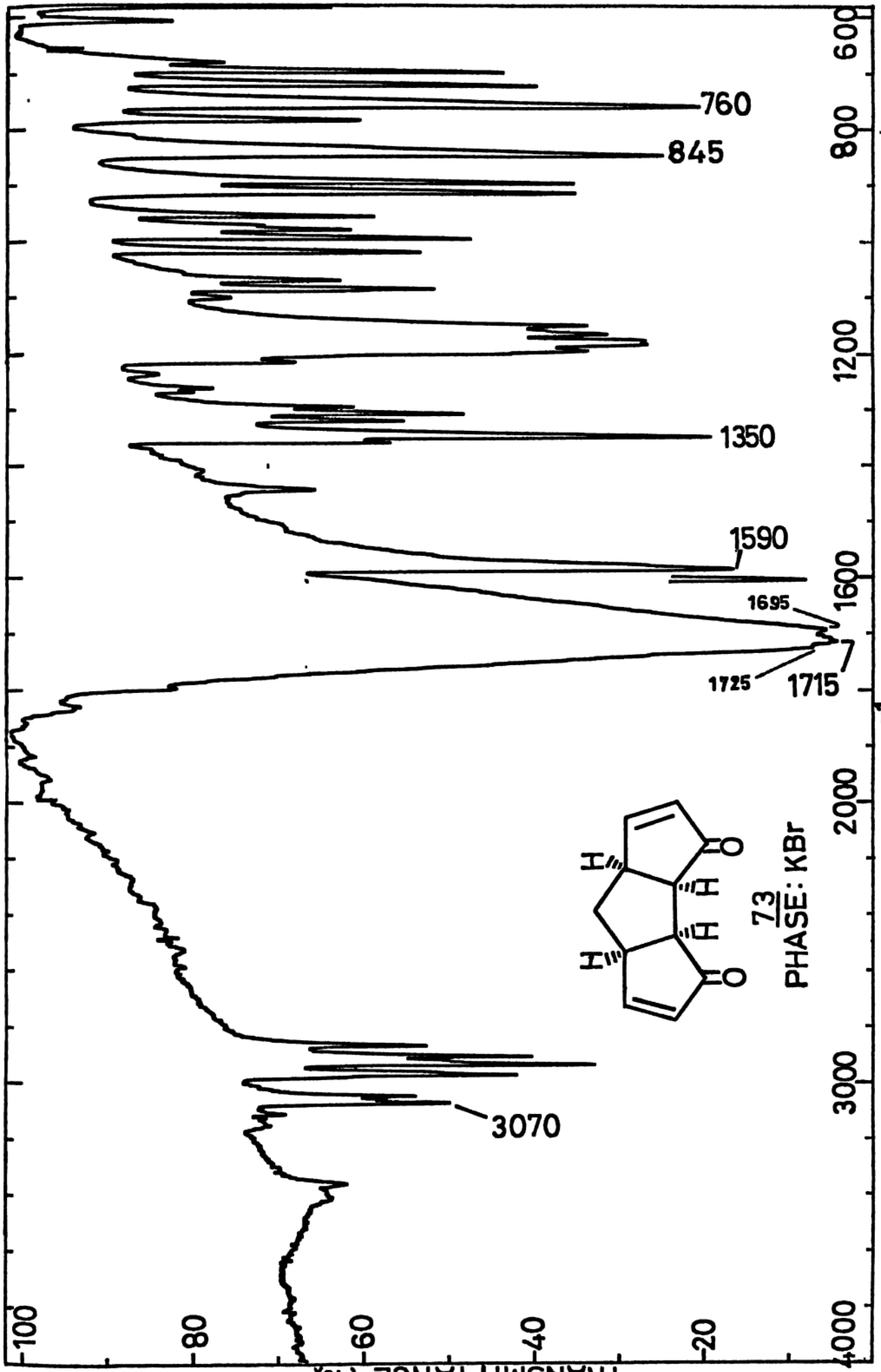


FIG I.1 IR spectrum of bis-enone 73

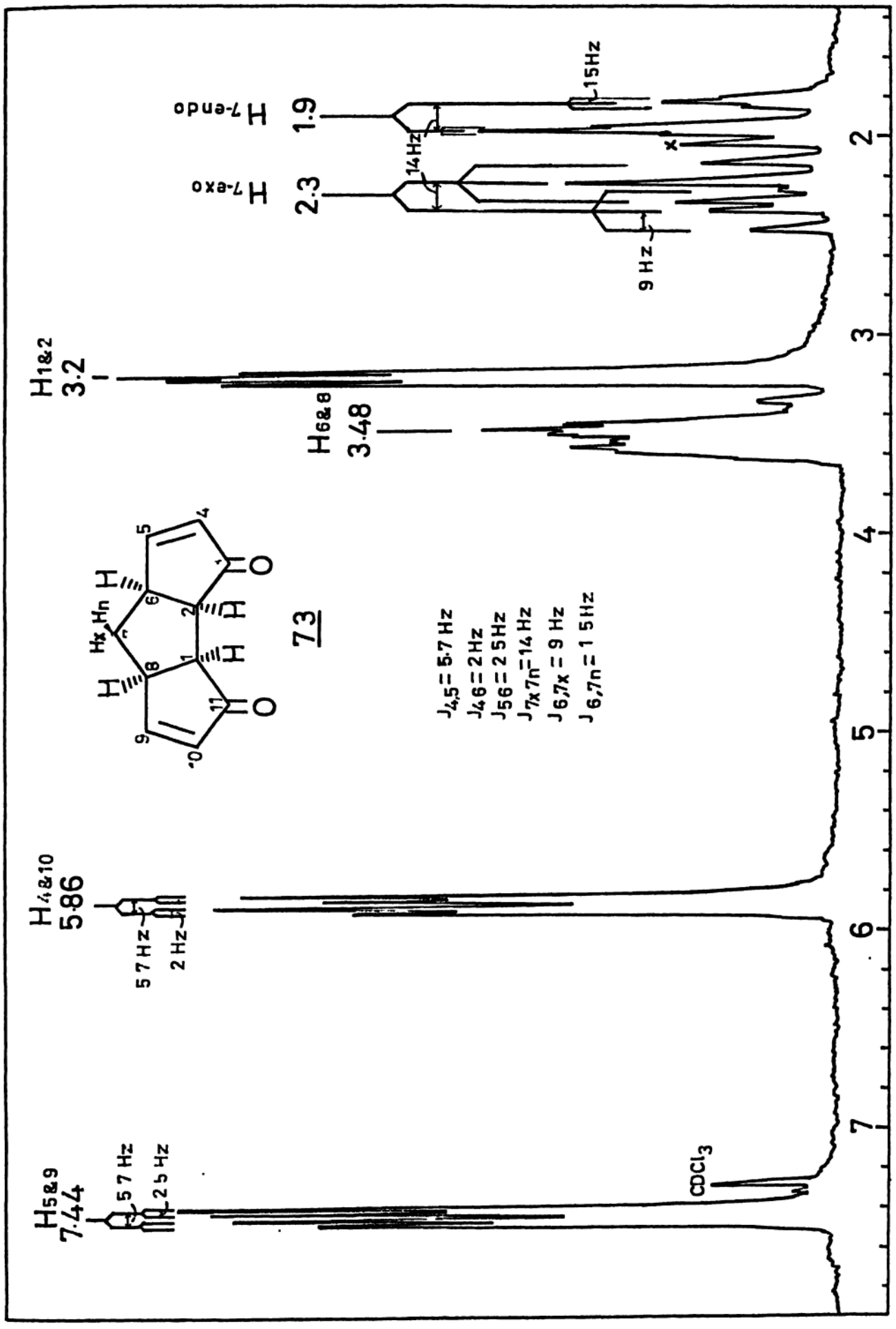


FIG I·2 · ^{1}H NMR (100 M Hz) spectrum of 73

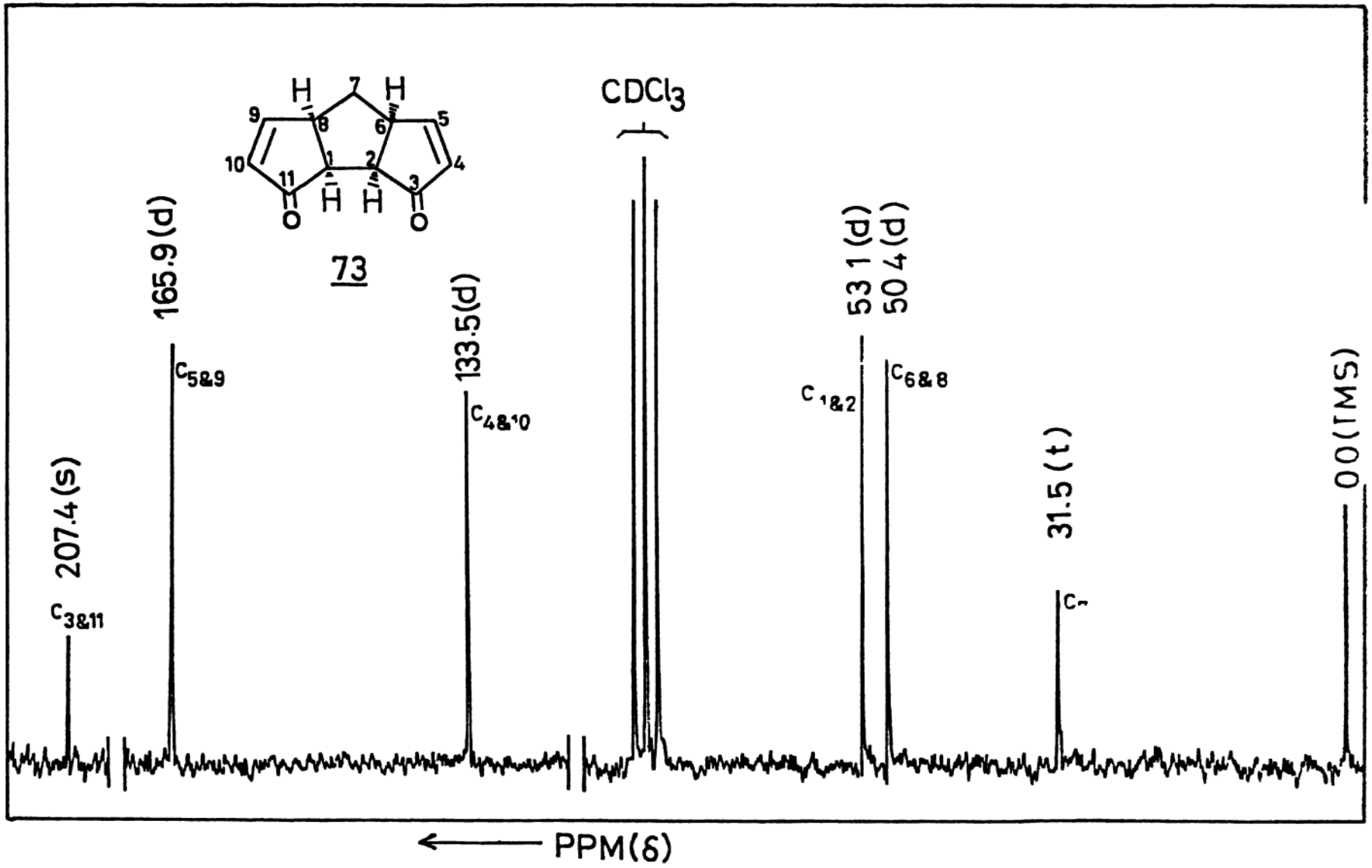
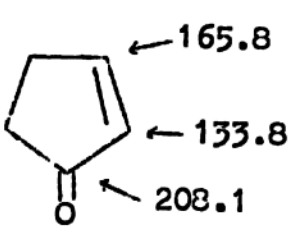


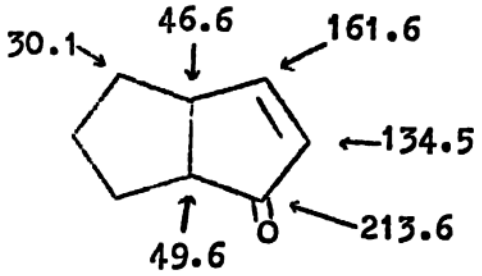
FIG I·3 · ^{13}C NMR (25.0 MHz) spectrum of 73

at δ165.9, Fig.I.3) and established the elements of mirror plane symmetry (C_s) in the molecule with five discrete proton resonances centered at δ7.44, 5.86, 3.48, 3.2, 2.1 (1:1:1:1:1) and six carbon resonances at δ207.4(s), 165.9(d), 133.5(d), 53.1(d), 50.4(d), 31.5(t) (2:2:2:2:2:1). Complete ^{1}H and ^{13}C NMR assignments for 73 are displayed in Fig.I.2 and I.3 and also summarised in experimental section. The ^{13}C NMR resonances of 73 showed[3,57,58] expected similarity with the other structurally related quinanes 74, 75 and 76 as indicated in Scheme I.22. The triquinane based bis-enone structure 73 for the sole thermolysis product of pentacyclic dione 72 was thus rigorously established.

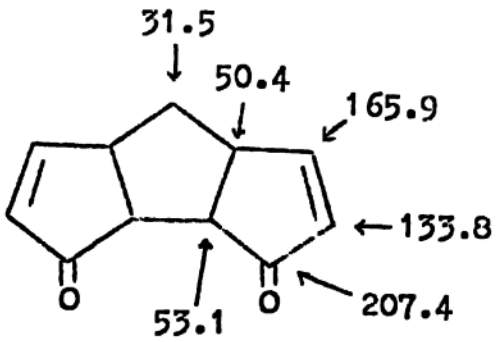
SCHEME I.22



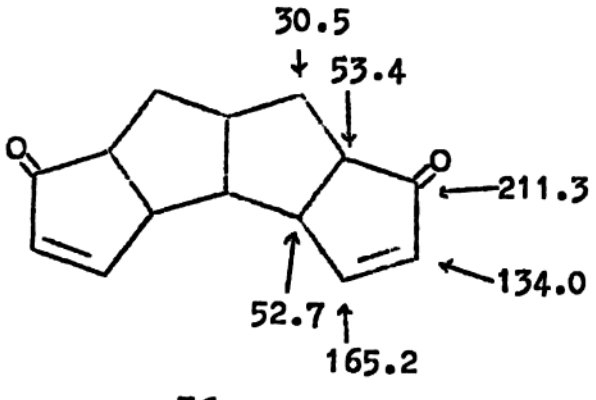
74



75



73



76

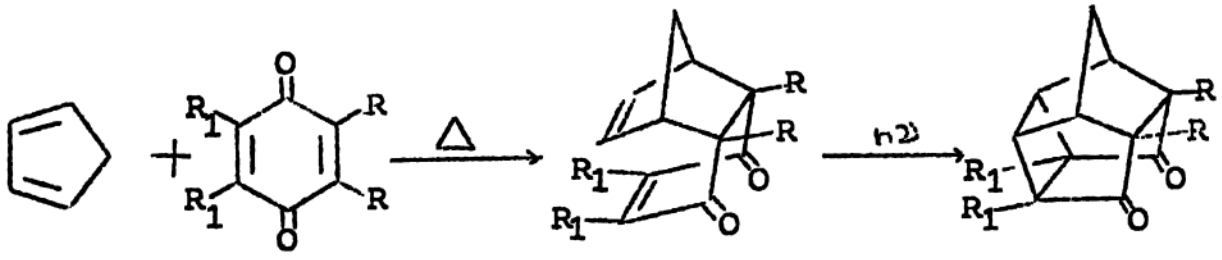
The assignment of cis, syn, cis-stereochemistry (C_s symmetry) to 73 was strongly suggested on the basis of its genesis from pentacyclic dione 72 and received further support from the incisive analysis of the foregoing spectral data. For example, the infrared carbonyl absorptions of 73 at 1725, 1715 and 1695 in KBr dispersion were reduced to a single absorption at 1722 in chloroform solution and led to the inference that some solid state interactions exist between the two carbonyl groups which are apparently relaxed in solution. Similar indication of through space interaction between carbonyls is revealed by small blue shift in the UV spectrum of 73 (λ_{max} = 219 nm) compared to bicyclo[3.3.0] oct-3-en-2-one 75 (λ_{max} = 221nm)[59] and tetracyclic bis-enone 76 (λ_{max} = 228 nm)[3] and the carbonyl shielding in the ^{13}C NMR spectrum of 73 at δ207.4 (cf. 75 and 76, Scheme I.22). However, a firm, unambiguous decision in favour of all cis-stereostructure 73 was arrived at on the basis of its facile and quantitative intramolecular $\pi^2_s + \pi^2_s$ cycloaddition back to pentacyclic dione 72 on exposure to either UV light or more economically and conveniently to the abundant sub-tropical Sunlight. Subsequent chemical transformations of 73 (vide infra) were fully consonant with its all cis-folded geometry.

Having demonstrated the efficacy of the photo-thermal

metathesis sequence for creating the cis, syn, cis-bis-enone 73 from 72, attention was turned towards establishing the generality of the key thermolysis step leading to the uncaging of the pentacyclic frame to the triquinane derivatives.+ Three more examples are described here to fortify confidence in the Scheme I.20 and its preparative utility. Two examples are of halo-substituted derivatives of 72, while the third is of a homologous system.

Diels-Alder adducts 79 and 80 were readily prepared[60,61] from cyclopentadiene and 2,3,5,6-tetrachlorobenzoquinone (chloranil 77) and 2,3-dichlorobenzoquinone 78. Irradiation of the tricyclic endo-adducts 79 and 80 using 450 W Hanovia UV lamp in ethyl acetate yielded the pentacyclic

SCHEME I.23



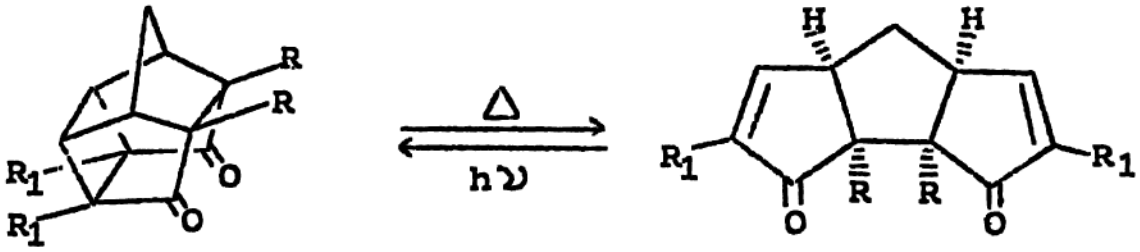
77. $R=R_1=Cl$ 79. $R=R_1=Cl$ 81. $R=R_1=Cl$

78. $R=H$, $R_1=Cl$ 80. $R=H$, $R_1=Cl$ 82. $R=H$, $R_1=Cl$

+More than 20 examples of the theme depicted in Scheme I.20 and leading to various triquinanes have been successfully worked out in our laboratory.

diones 81 and 82 (Scheme I.23).[54a]

Thermal activation of tetrachloro pentacyclic dione 81 in diphenyl ether (DPE) at 240°C for 30 min led to near quantitative formation of the bis-enone 83, mp.149-50°C (off-white needles from benzene-hexane). Stereostructure



81. $R=R_1=Cl$

82. $R=H$, $R_1=Cl$

83. $R=R_1=Cl$

84. $R=H$, $R_1=Cl$

of 83 and its inherent symmetry was clearly revealed by its spectral characteristics. The UV spectrum showing λ_{max} at 244 nm and IR bands at 1750, 1603 and 1585 cm^{-1} indicated the presence of 2-cyclopentenone substructure bearing halogen substituents on the olefinic bond and in the vicinity of the carbonyl group. The ^1H NMR spectrum (Fig.I.4) showed only four sets of signals at δ7.3, 3.73, 2.84, 2.04 in a ratio of 2:2:1:1. The ^{13}C NMR spectrum (Fig.I.5) had signals at δ190.2(s), 154.2(d), 133.7(s), 76.7(s), 56.6(d) and 30.4(t) in a ratio of 2:2:2:2:2:1. More compelling evidence in support of formulation 83 flows from its extremely facile

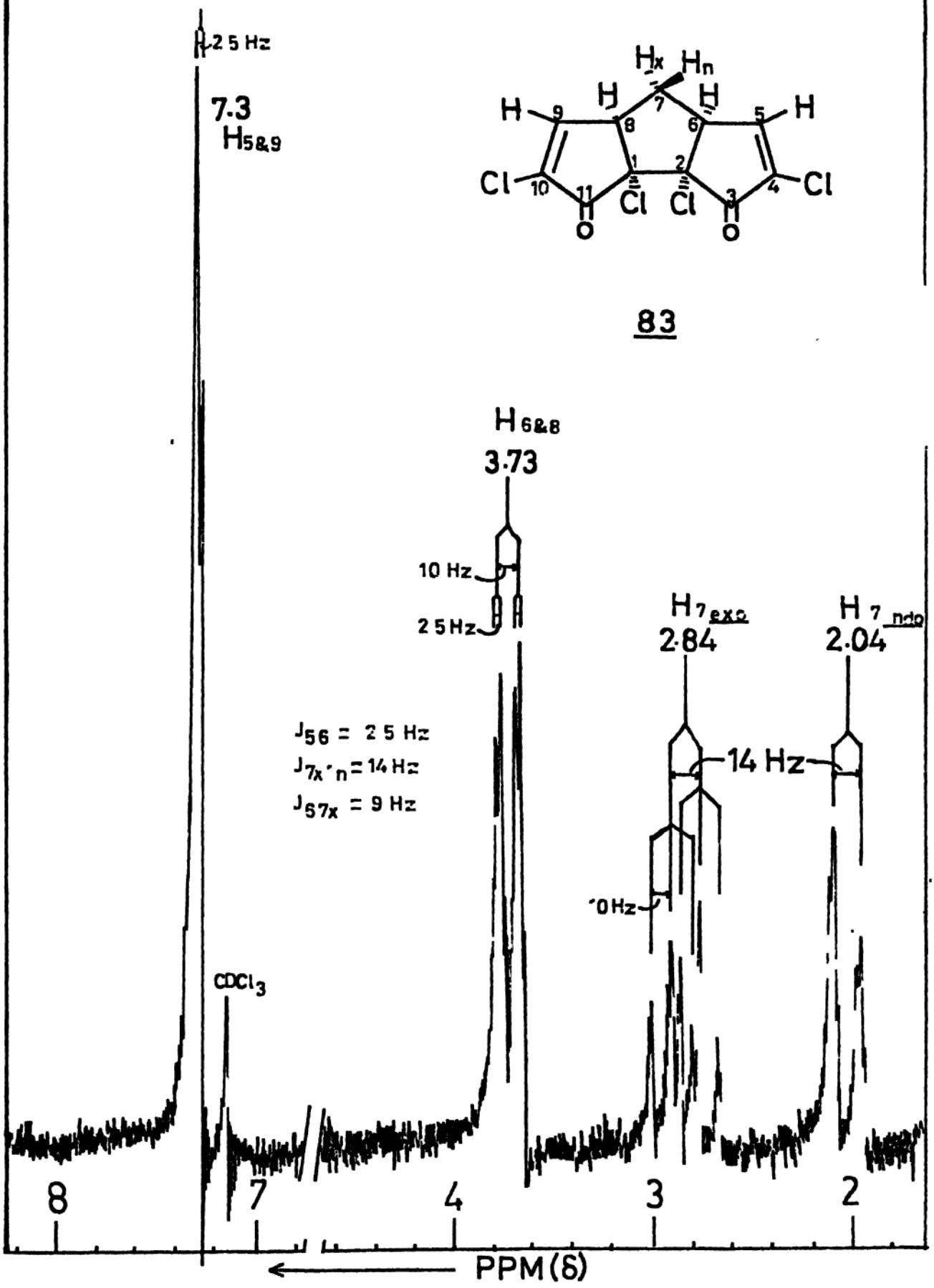


FIG I·4: ^{1}H NMR (100 MHz) spectrum of 83

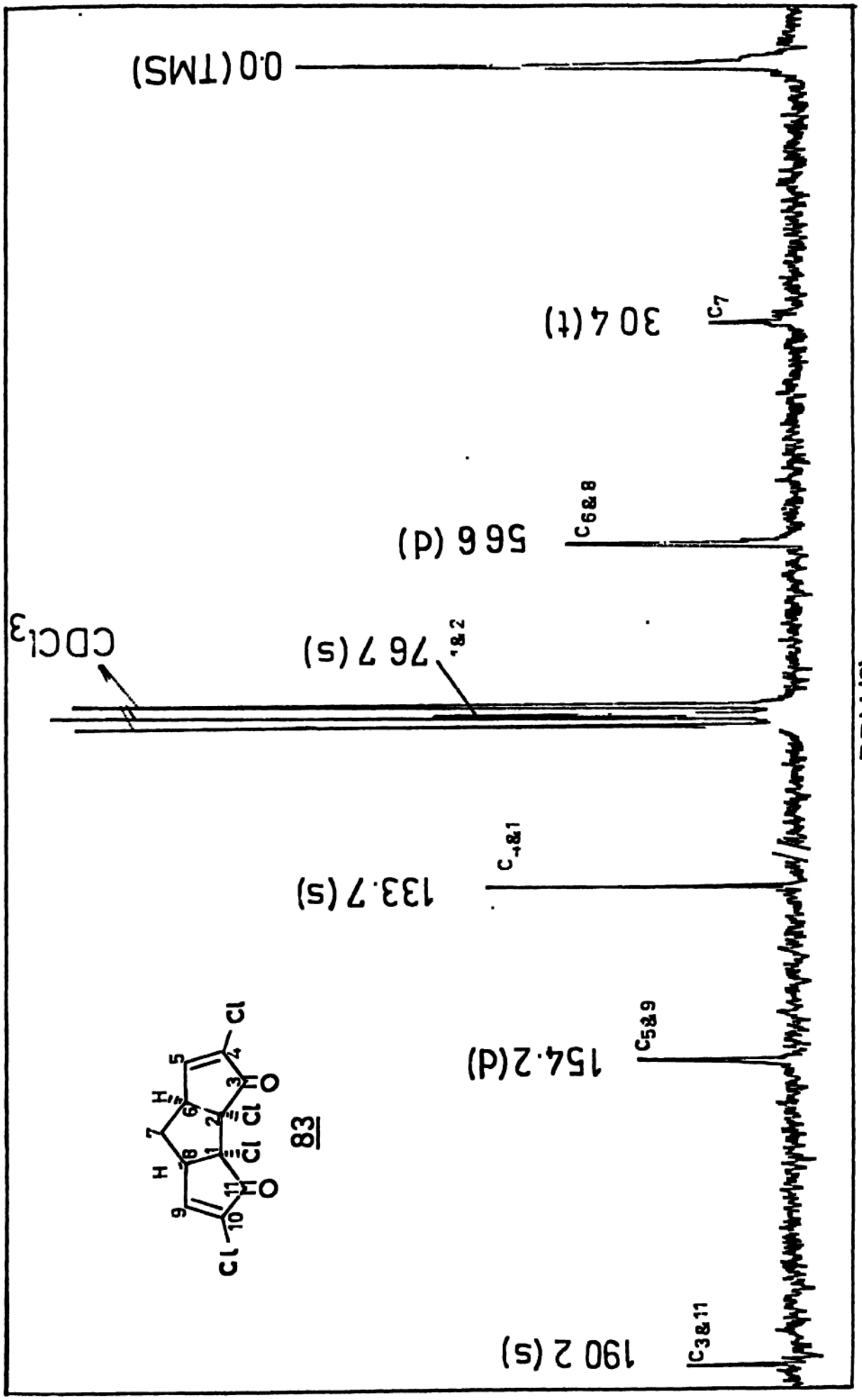
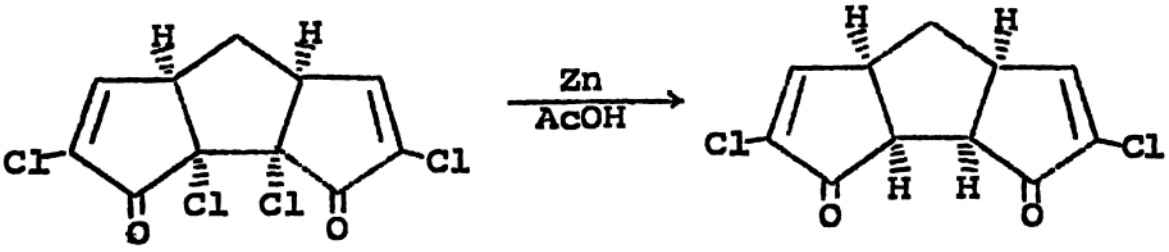


FIG I.5 . ^{13}C NMR (25.0 MHz) spectrum of 83

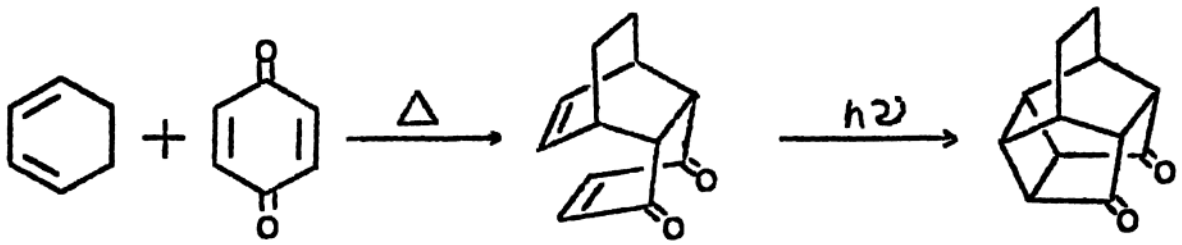
and quantitative photocyclisation to 81 in ethyl acetate (pyrex) on exposure to Sunlight for a few minutes. In more or less identical manner, the related pentacyclic dione 82 on heating in DPE (220°C, 1 hr) furnished the bis-enone 84, mp.186-7°C in over 80% yield. Assignment of stereostructure to 84 was readily accomplished on the basis of its spectral characteristics (vide experimental). The dichloro bis-enone 84 also reverted back to the pentacyclic dione 82 on exposure to Sunlight. Finally, the bis-enones 83 and 84 could be correlated directly as dechlorination of 83 with zinc in boiling acetic acid furnished 84 in 80% yield.



83 84

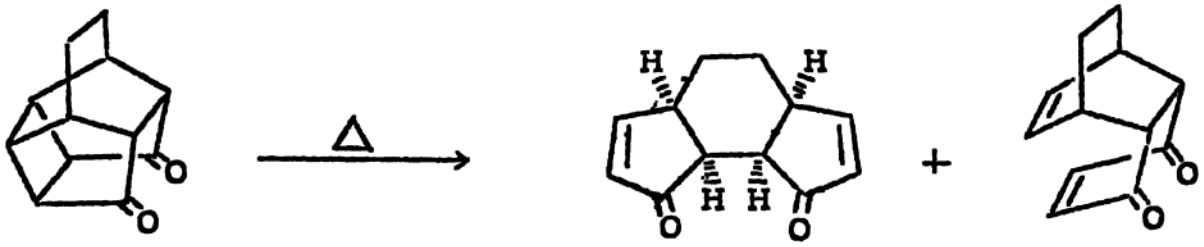
The last example of the photo-thermal metathesis reported here is of the Diels-Alder adduct 85 of 1,3-cyclohexadiene and p-benzoquinone.[62] Photolysis of 85 readily furnished the known pentacyclic dione 86 (Scheme I.24).[54a] Sublimation of the dione 86 through a quartz column at 600°C (1 torr) furnished the tricyclic bis-enone 87, mp.104-5°C in 8% yield along with substantial amounts of p-benzoquinone.

SCHEME I.24



85 86

The structure of 87 follows from its spectral parameters. The UV spectrum showing λ_{max} at 218 nm (ε = 15,200) and infrared bands at 1700 and 1585 cm^{-1} indicated the presence of 2-cyclopentenone moiety. The ^{1}H NMR spectrum (Fig.I.6)



86 87 85

displayed four sets of resonances at δ7.42, 6.22, 2.6-3.3 and 1.0-2.0 in a ratio of 1:1:2:2 with characteristic chemical shift and multiplicity of the α and β protons of the 2-cyclopentenone part structure. The ^{13}C NMR spectrum (Fig.I.7) showed the elements of mirror plane symmetry and the six resonances at δ209.3(s), 163.9(d), 133.7(d), 45.3(d), 40.9 (d) and 22.4(t) fitted eminently with the assigned structure.

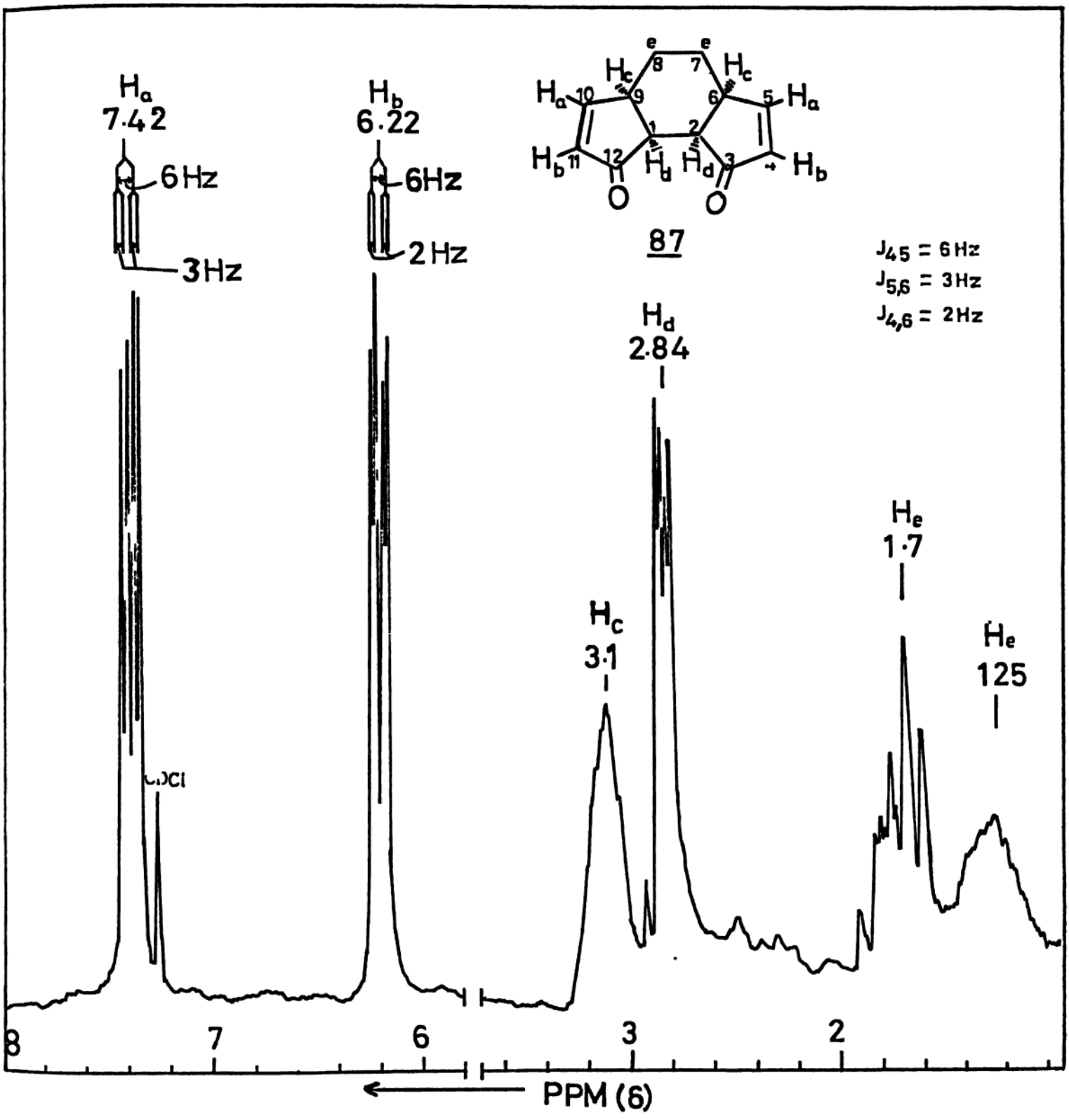


FIG I 6 : ^{1}H NMR (100 MHz) spectrum of 87

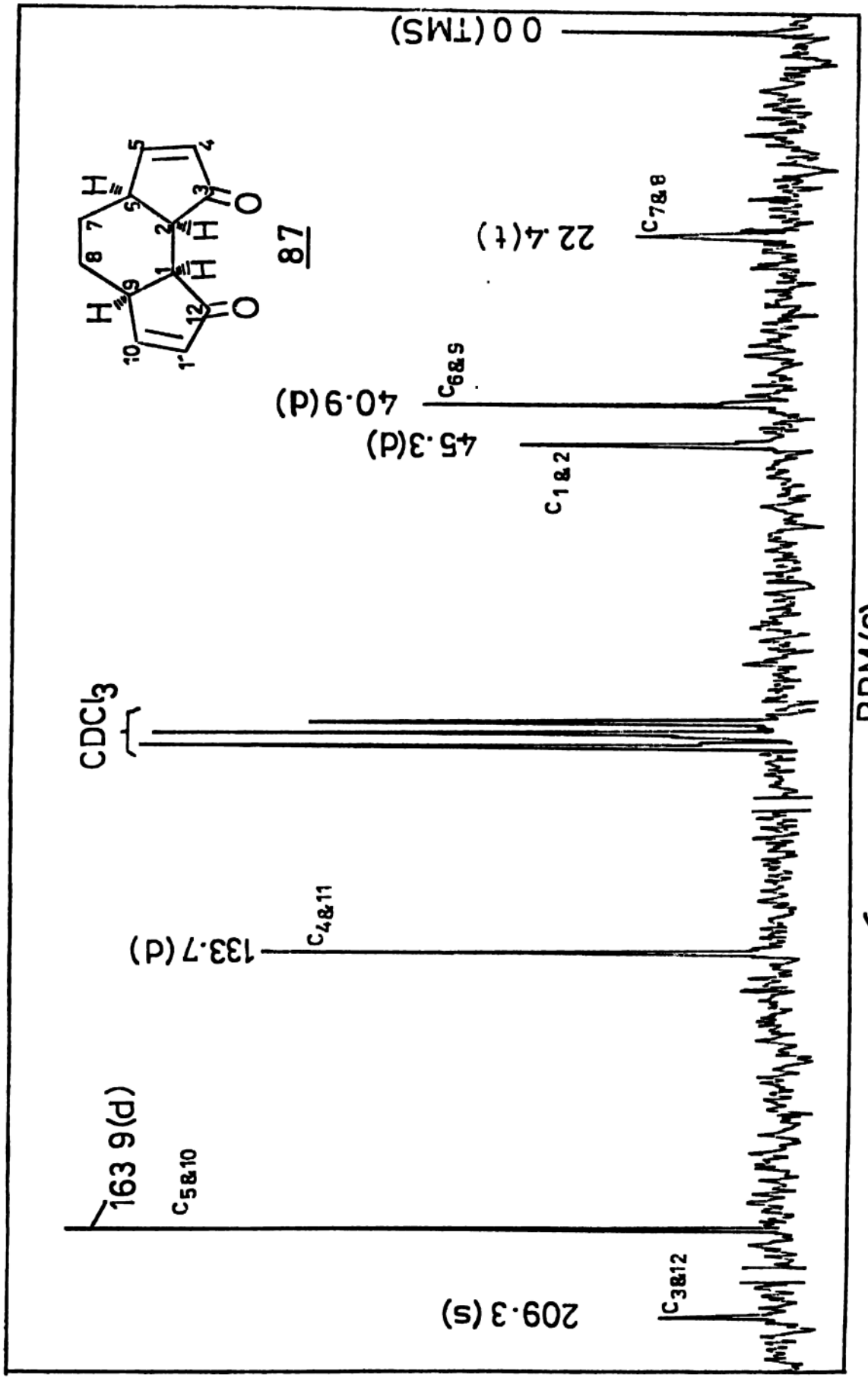
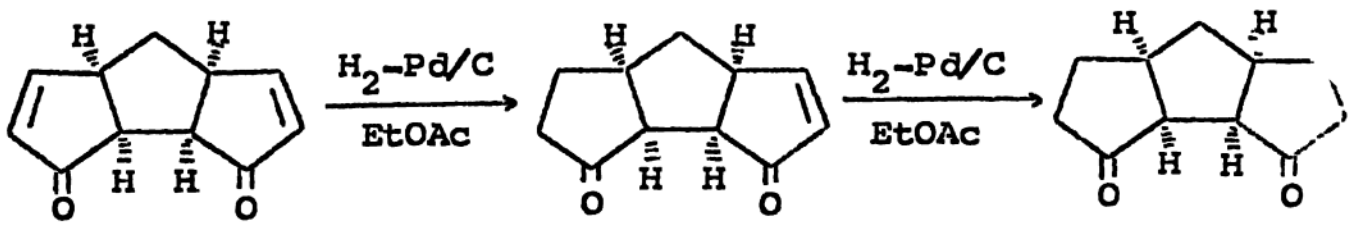


FIG I 7 ^{13}C NMR (25.0 MHz) spectrum of 87

Although the 1,3-cyclohexadiene-p-benzoquinone adduct 85 was not isolated, its formation could be inferred from the high yields (70-80%) of benzoquinone obtained from the pyrolysate. While the yield of 87 in this reaction was not very heartening, still the photo-thermal strategy provided a convenient and useful entry to a functionalised cis, syn, cis-tricyclo[7.3.0.$0^{2,6}$]dodecane derivative.

Attention was now turned to the exploration of chemistry of the readily and quite abundantly available all cis-bis-enone 73. While the symmetrical disposition of functionality in the bis-enone 73 proved advantageous for its exploitation in one arena, efforts in another direction necessitated chemodifferentiation and relocation of two enone moieties. Towards the latter objectives, several reactions of 73 were studied.

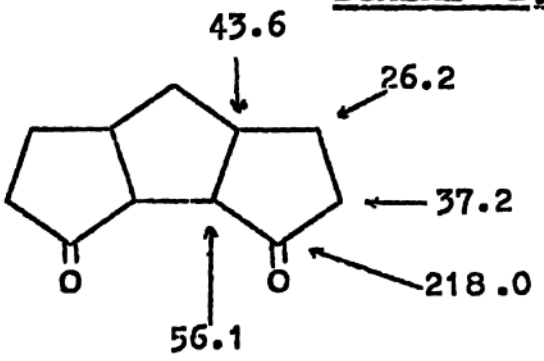
The bis-enone 73 could be catalytically hydrogenated either partially to dihydroderivative 88, mp.59-60°C or



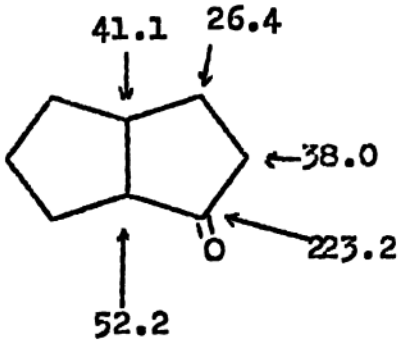
73 88 89

fully to the tetrahydrodione 89, mp.93-4°C. The ^{1}H NMR spectrum of 89 was quite featureless but its ^{13}C NMR spectrum (Fig.I.8) showed its symmetry and its close spectral resemblance[58] to cis-bicyclo[3.3.0]octan-2-one 90 (Scheme I.25). The carbonyl resonance at δ218.0 was once again indicative of some through space interaction between the two carbonyls

SCHEME I.25



89



90

in an all cis-tricyclic frame.

Sodium borohydride reduction of dione 89 in methanol furnished a 6:5:3 mixture of hemiacetals 91 and 92 and trans-diol 93. The three were easily separated by column chromatography and their structures deduced from their spectral characteristics. In case of the lactol 91, the presence of 11 carbon signals in the ^{13}C NMR spectrum (Fig.I.9) and in particular the resonance at δ118.4 (singlet in off resonance spectrum) due to -O-C-OH functionality was particularly revealing. Formation of 91 from 89 further showed the proximity of two carbonyl groups in the all cis-triquinane frame.

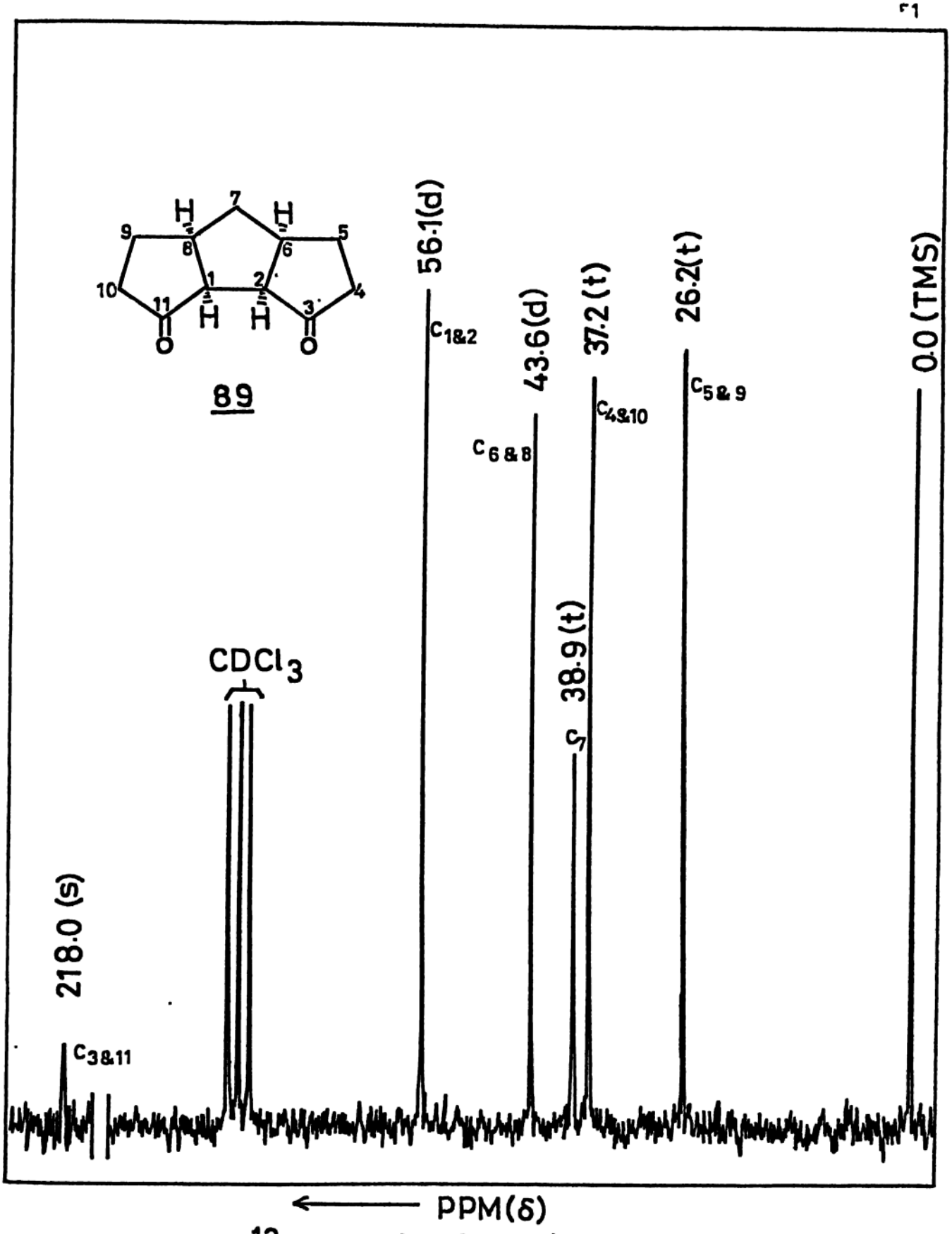


FIG I·8 : ^{13}C NMR (25·0 MHz) spectrum of 89

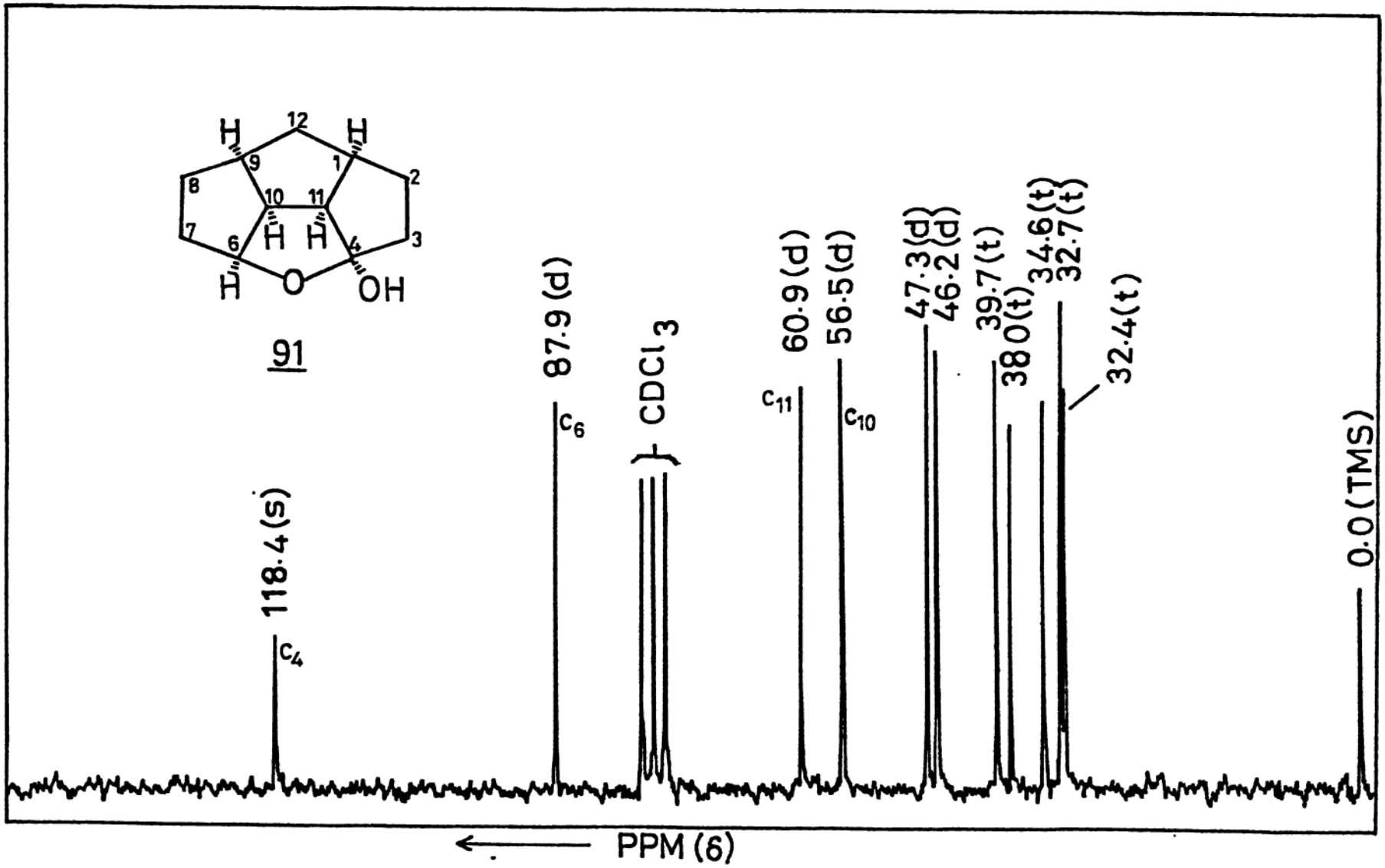
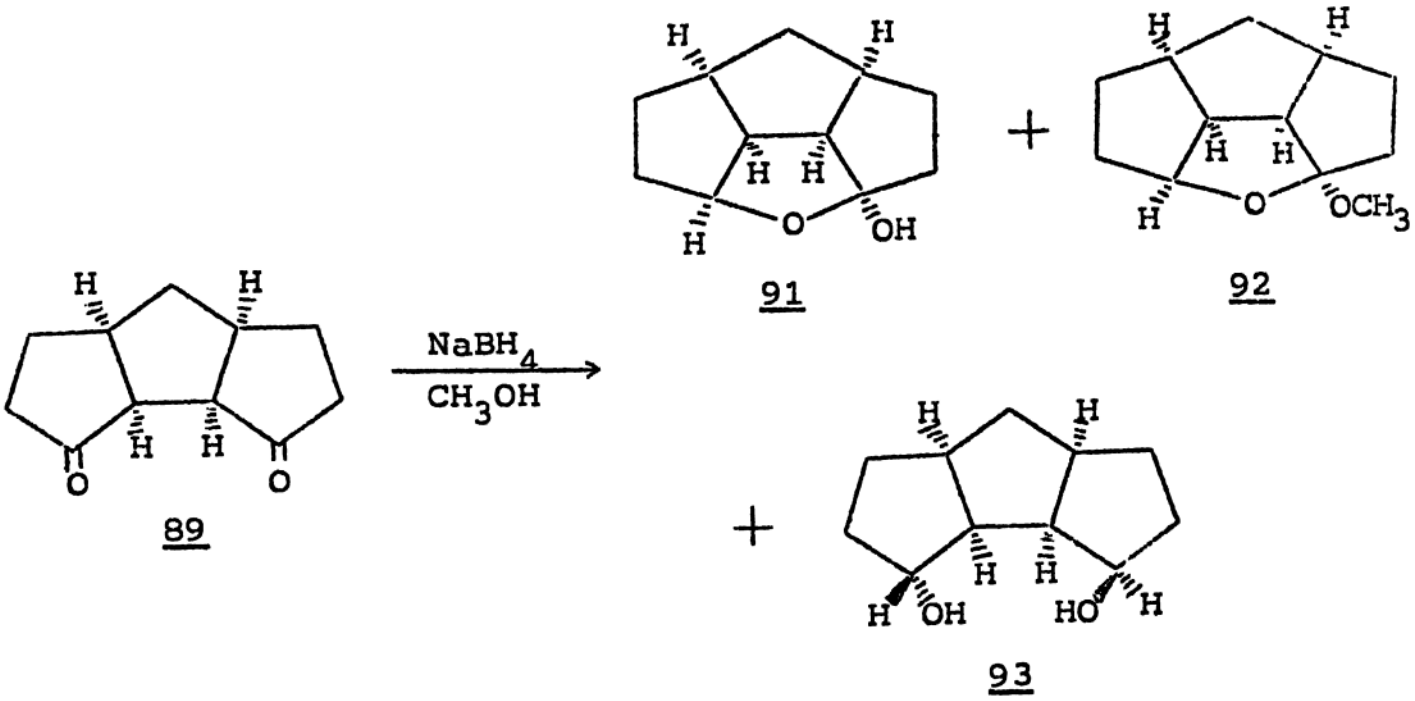


FIG I·9 · ^{13}C NMR (25.0 MHz) spectrum of 91



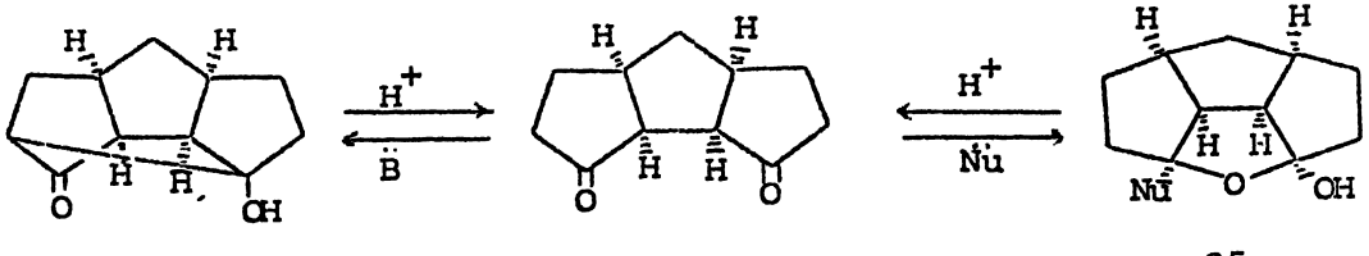
91 92

89

93

Unfortunately, this proximity proved to be an impediment in the many functionalisation reactions of 89 with nucleophiles and base due to intervention of intramolecular reactions e.g. 94 and 95. Protonation of these species led to

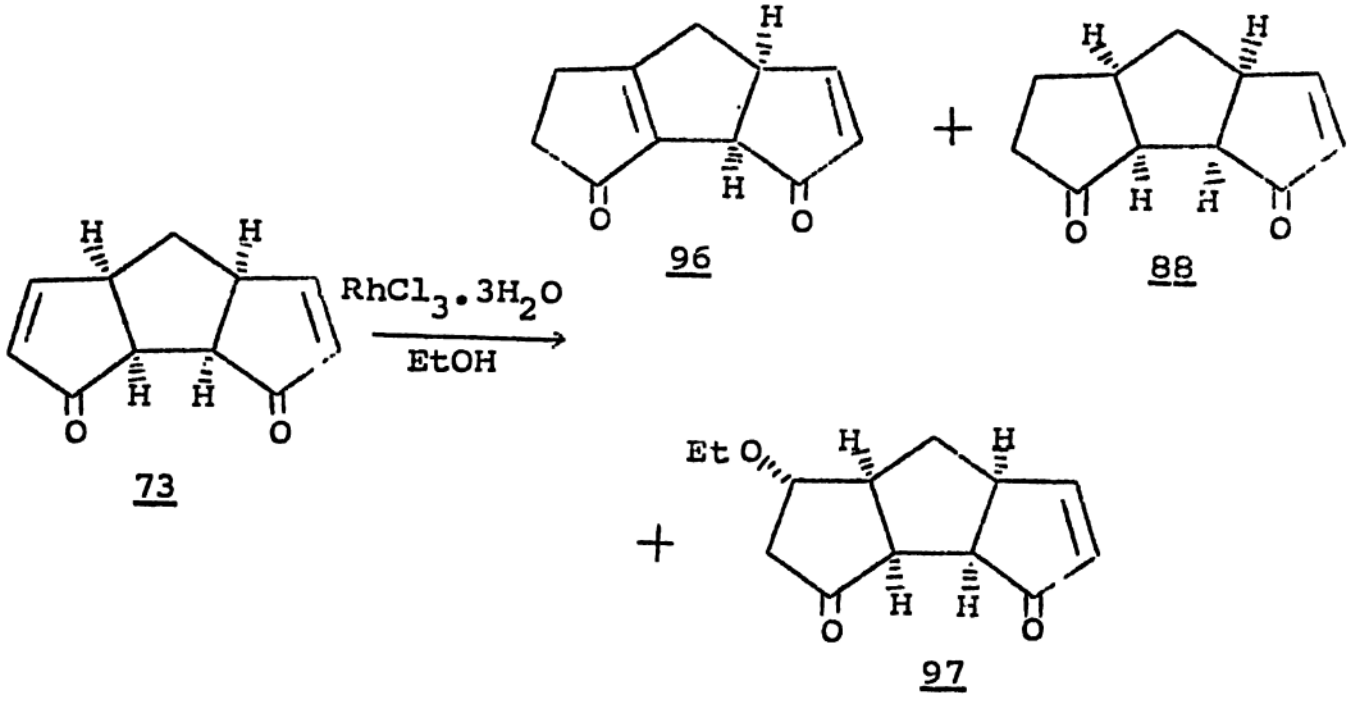
SCHEME I.26



94 89 95

the recovery of starting material 89 (Scheme I.26).

In order to relocate the olefinic bonds in the bis-enone 73, rhodium (III) catalysed isomerisation[63] was attempted. When an ethanolic solution of 73 in presence of catalytic amounts of $RhCl_3.3H_2O$ was heated in a sealed tube, isomerisation of one of the disubstituted double bonds in 73 to the fully substituted position was observed and a 6:2:1 mixture of 96, 88 and 97 was obtained in 70% yield.



73 96 88 97

The structure of the new bis-enone 96, mp.102-3°C, emerged mainly from the ^{13}C NMR data (Fig.I.10) which at once indicated the presence of tetrasubstituted olefinic C's of an enone moiety at δ185.1(s) and 143.8(s) and were very reminiscent of the corresponding C's in structurally related

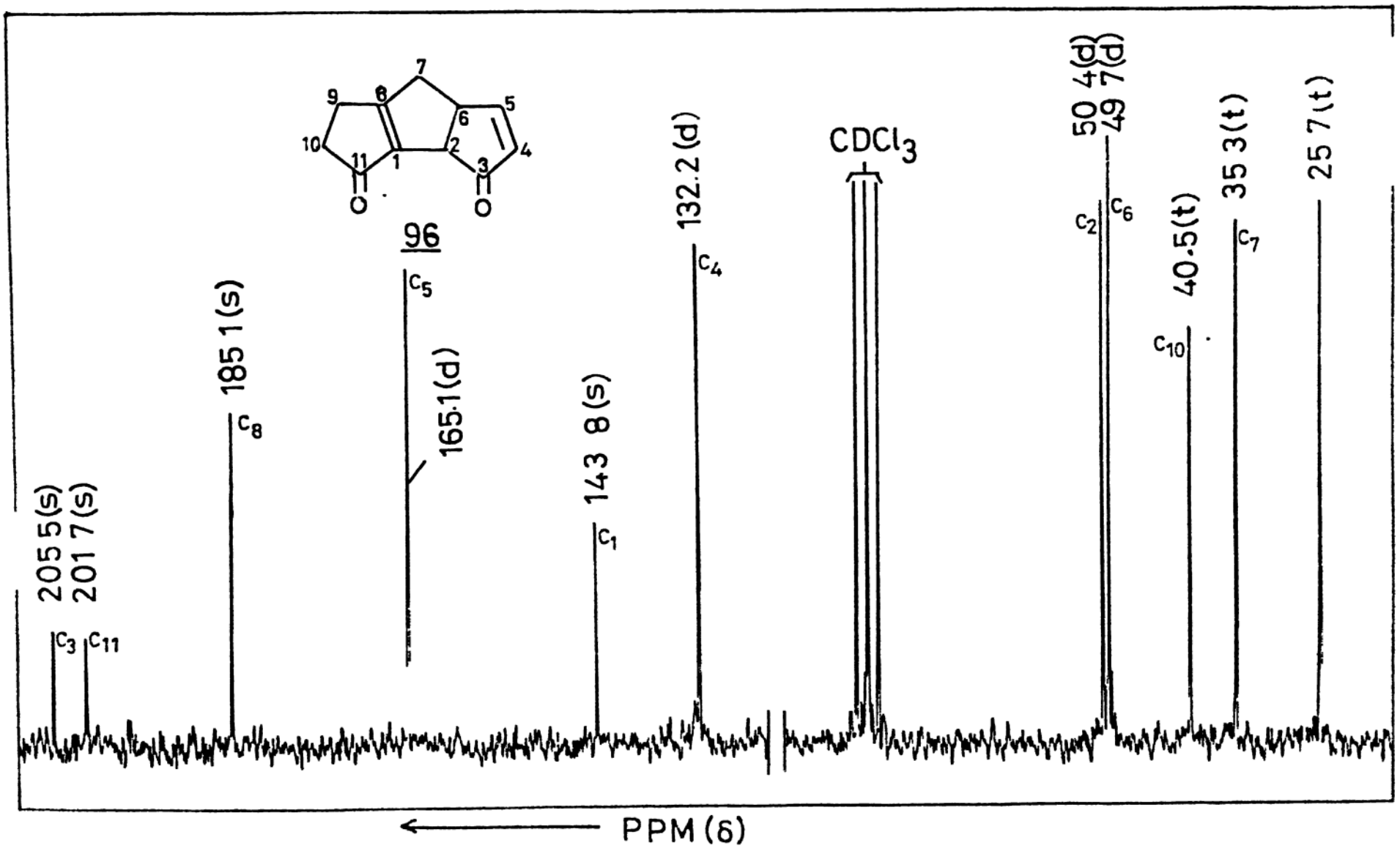
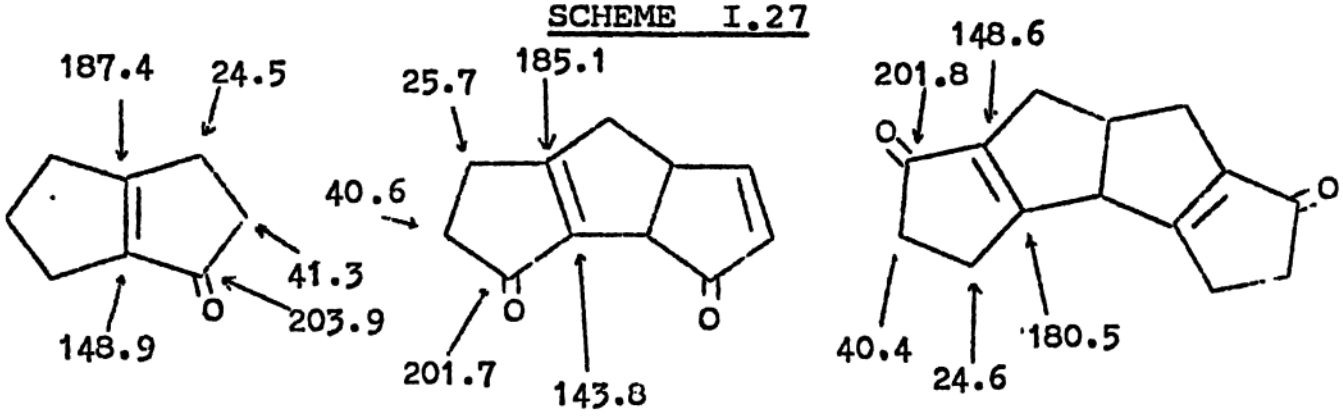


FIG I 10 ^{13}C NMR 25 0 MHz) spectrum of 96

SCHEME I.27

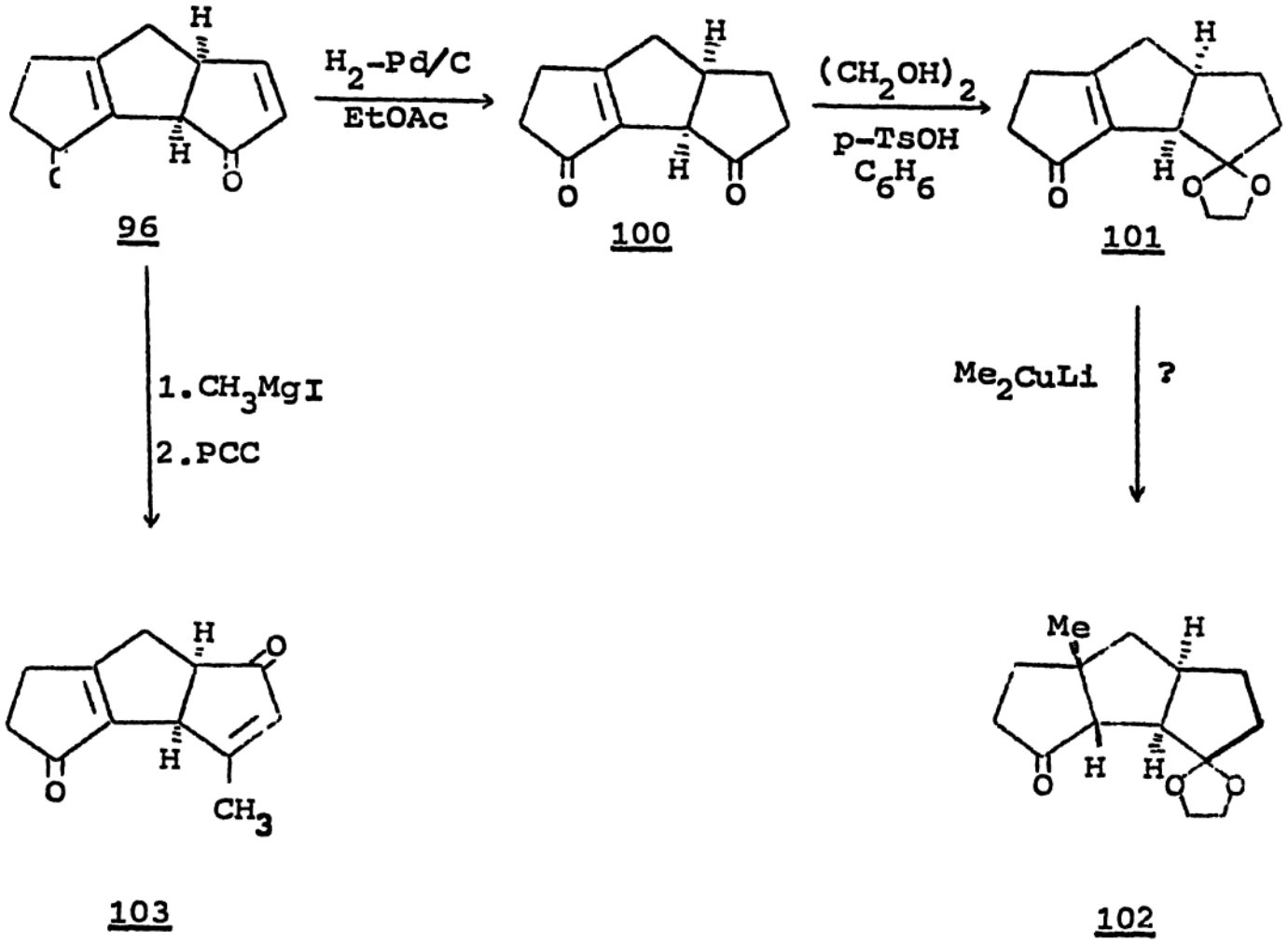


98 96 99

polyquinanes 98 and 99 (Scheme I.27).[3,58] The minor products 88 and 97 were formed through partial reduction and Michael addition of ethanol to 73, respectively. There is precedence[63] for these side reactions during rhodium catalysed isomerisations.

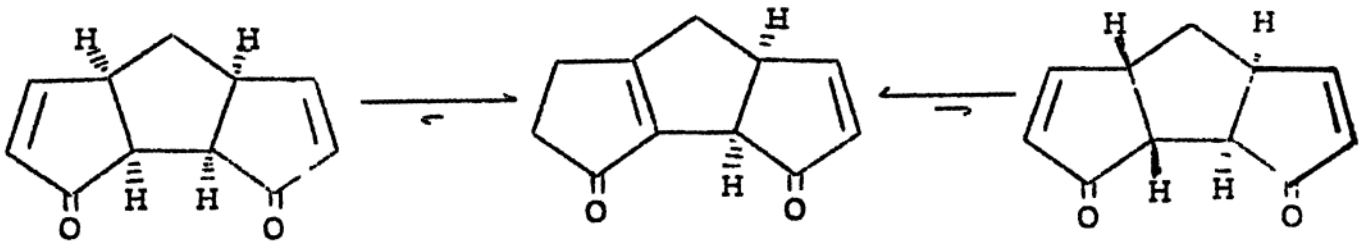
A few useful functional group transformations of 96 are summarised in Scheme I.28. These were probing experiments undertaken with a view to generate functional group pattern suitable for natural product synthesis. For example, partial hydrogenation of 96 to 100 and selective protection of the saturated carbonyl group furnished the enone 101, that could be transformed *via* cuprate addition to 102 having an angular methyl group. Similarly, 96 was transformed to 103, mp.109-10°C in a two step sequence (*vide infra*)[64] involving Grignard addition and pyridinium chlorochromate (PCC) oxidation.[65]

SCHEME I.28



Since the isomerised bis-enone 96 had a strategic double bond that would enable introduction of an angular methyl group (see, capnellane framework, 6)[25] via conjugate addition or could be oxidatively cleaved to a bicyclo[6.3.0] undecane system (e.g. precapnellane,[66] fusicoccin[67] etc.) the need for a better and more efficient preparation of 96 from 73 was felt. Towards this end, it was observed that 73 underwent smooth thermal isomerisation (260°C, diphenyl

ether, 20 min) and 96 could be isolated in about 80% yield as the only new product of the reaction along with starting all cis-bis-enone 73. Attempts to drive the reaction to completion indicated that the two bis-enones 73 and 96 were in thermal equilibrium. This observation encouraged us to carefully scout the reaction mixture for the missing cis, anti, cis-isomer 104. When either the all cis-bis-enone 73 or the tetrasubstituted bis-enone 96 were thermally activated under more stringent conditions (305°C, benzylbenzoate, 5 min) and the resulting reaction mixture carefully analysed by GLC,



73 96 104

it showed the presence of three components in an approximate ratio of 1:3:27. The mixture was resolved on a silica gel column and all the three products were obtained pure. The minor and the major products were readily identified as 73 and 96, respectively. The third compound, mp.99-100°C, to our great delight, turned out to be the cis, anti, cis-triquinane based bis-enone 104. The structure of 104 followed from its UV spectrum: λ_{max} 222 nm (ε = 12,500) and IR spectrum: 1715 sh, 1695 cm^{-1}, both of which showed the

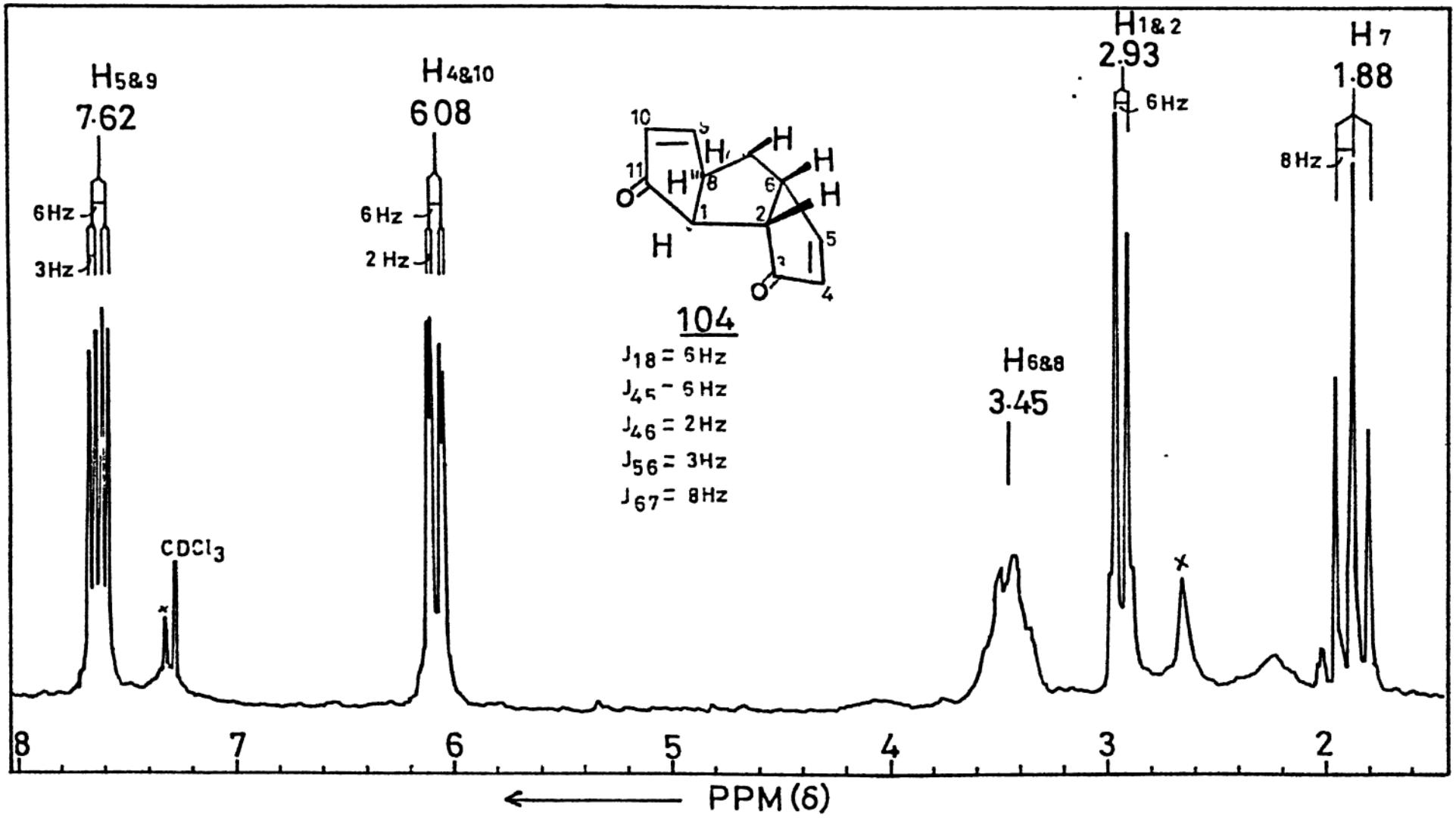


FIG 1.11: ^{1}H NMR (100 MHz) spectrum of 104

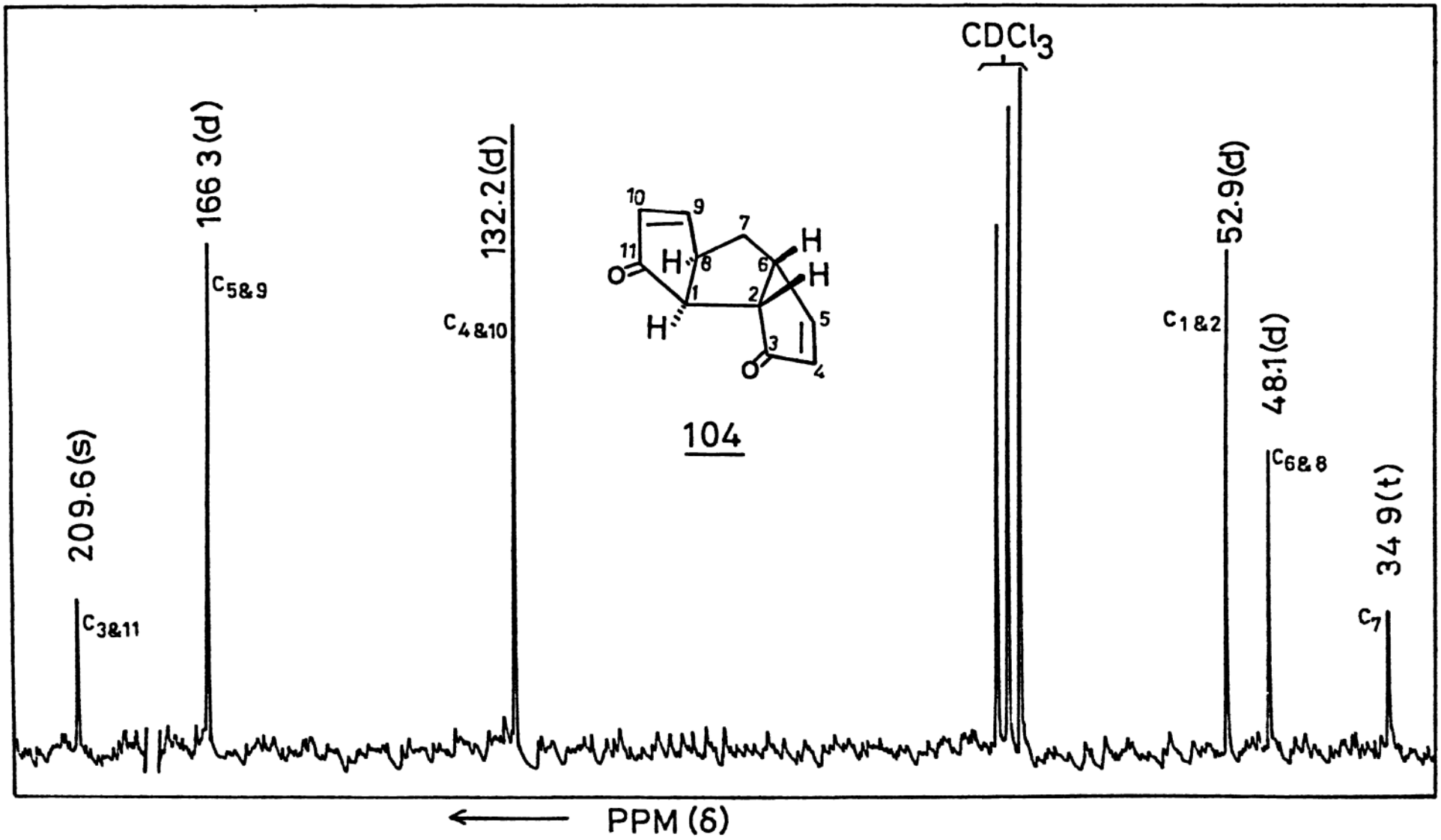


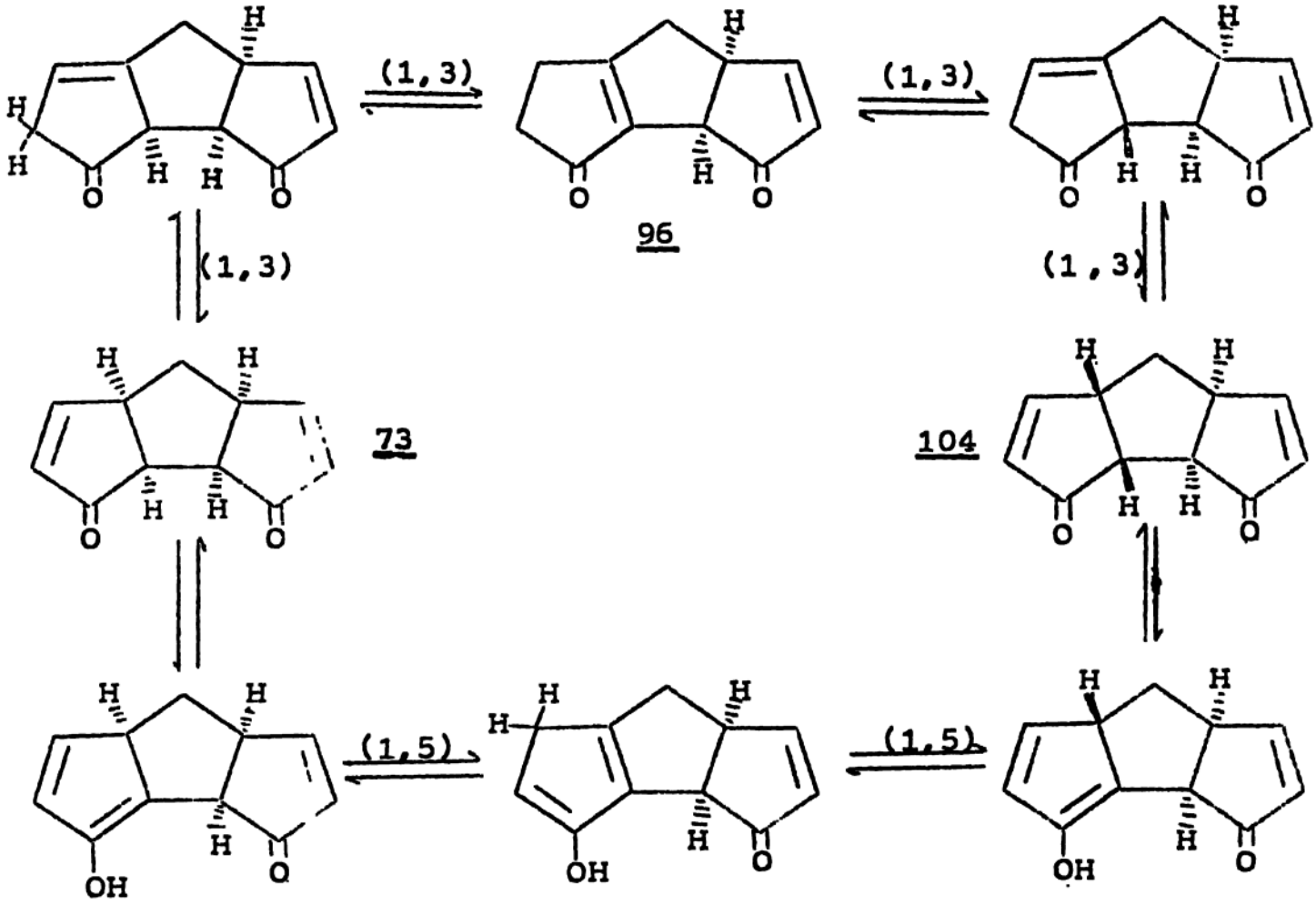
FIG I.12 : ^{13}C NMR (25.0 MHz) spectrum of 104

presence of a 2-cyclopentenone moiety. The ^{1}H NMR (Fig.I.11) and ^{13}C NMR (Fig.I.12) spectra of the cis, anti, cis-isomer 104 were not only similar to the all cis-73 but had very distinctive, diagnostic features that clinched its structure unambiguously. For example, the ^{1}H NMR spectrum showed the expected presence of five resonances at δ7.62, 6.08, 3.45, 2.93, 1.88 in a ratio of 1:1:1:1:1. However, the presence of a clean triplet at δ1.88 (J=8Hz) due to the C_7 methylene was decisive in showing the equivalence of C_7 exo- and C_7 endo- protons (due to C_2 symmetry)[31] and thus establishing the cis, anti, cis-stereochemistry of 104. The ^{13}C NMR resonances, δ209.6(s), 166.3(d), 132.2(d), 52.9(d), 48.1(d), 34.9(t), of 104 when compared with 73 further reinforced its formulation

The thermal equilibration of bis-enones 73 and 96 can be considered either proceeding through thermal [1,5] sigmatropic shifts in 1,3-cyclopentadiene intermediates (Scheme I.29) or through a series of symmetry disallowed thermal [1,3] shifts.[68] The concerted [1,5] shifts, a priori, should be favoured and occur even at lower temperature if sufficient concentration of the enol form can be generated. However, we find that the presence of base (vide infra) e.g. sodium methoxide, did not generate detectable amounts of cis, anti, cis-isomer 104. It is, therefore, reasonable to favour a series of [1,3] shifts to account

for the observed equilibrium (Scheme I.29).

SCHEME I.29

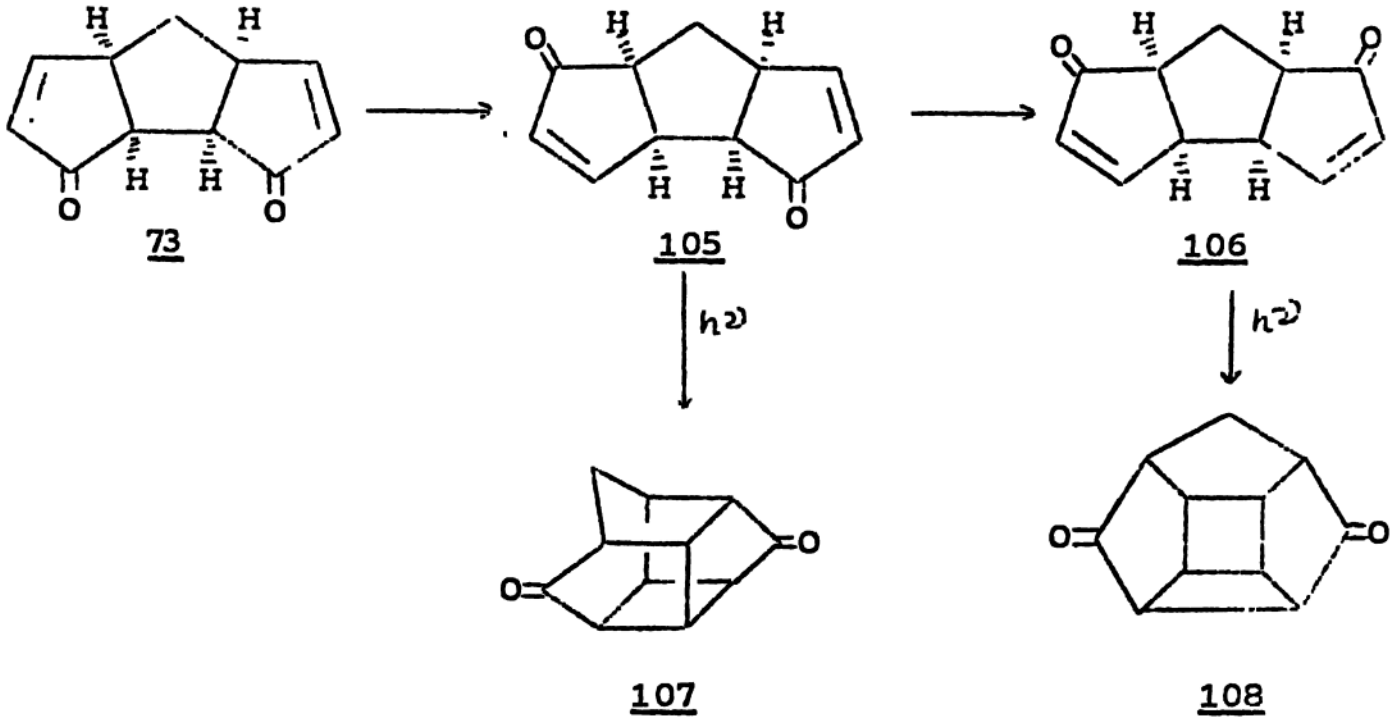


The formation of the cis, anti, cis-isomer 104 via the thermal isomerisation of 73 was a very useful and satisfying observation as it provided to us a simple method for generating the stereochemistry present in naturally occurring triquinanes. Indeed, parallel studies in our laboratory have culminated in the total syntheses of (±)-hirsutene 3

and (±)-coriolin 4 employing this thermal isomerisation as the control step.[69,70]

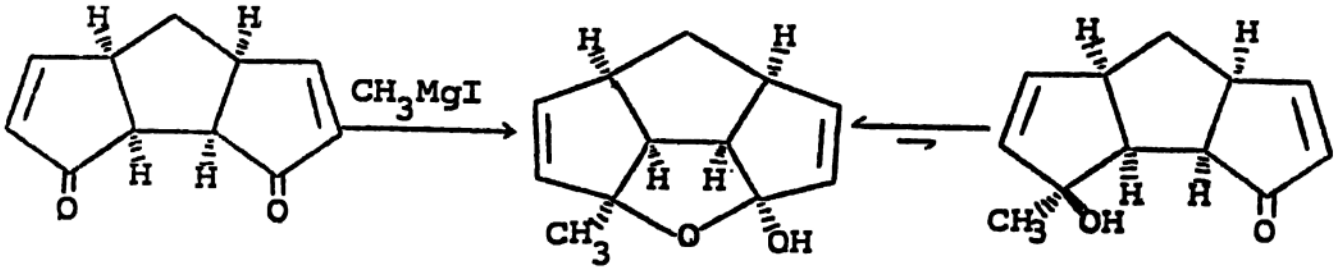
Another set of manipulations with 73 that appeared promising were to transpose the enone moieties, in a sequential manner, first to the single transposed system 105 and then to the fully transposed system 106. Transposed bisenones 105 and 106 can serve as potential precursors of novel systems 107 and 108 via intramolecular photochemical $_{\pi}2_{s}$ + $_{\pi}2_{s}$ cyclisation (Scheme I.30). Our successful preparation of 107 is described in the next chapter of this thesis but 106 and 108 have alluded us so far. To us, 108 appears to

SCHEME I.30



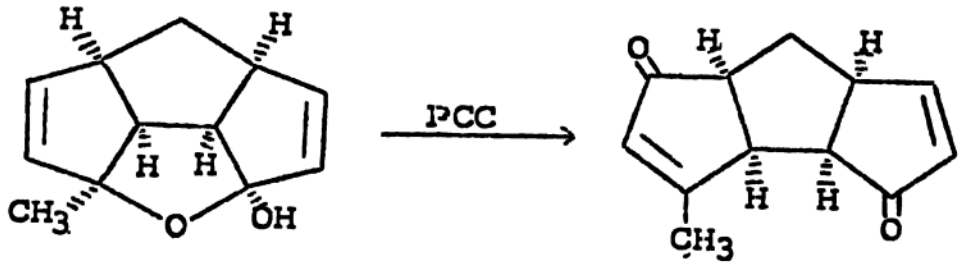
be the most promising and logical precursor for [4]-peristylane (Chart I.2).

Several efforts at this enone transposition employing the variants of Wharton[71] reaction proved abortive. However, partial success could be achieved utilising the alkylative enone transposition sequence.[64] Thus reaction of 73 with methylmagnesium iodide (1.3 molar equivalent) in THF and chromatography led to the isolation of crystalline hemiketal 109, mp.100-3°C, which from its spectral data (vide experimental) appeared to be in equilibrium with its open



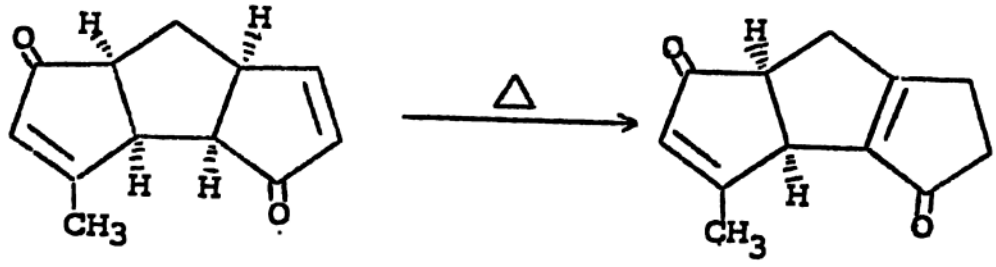
73 109 110

ketol form 110. PCC oxidation[65] of 109 resulted in the formation of the single transposed bis-enone 111, mp.105-6°C. The alkylated bis-enone 111 could be prepared from 73 in about 30% yield without isolation of the intermediate 109. The reaction was not very clean and several minor products were formed in this sequence but were neither isolated nor characterised. The structure of 111 rests secured on its

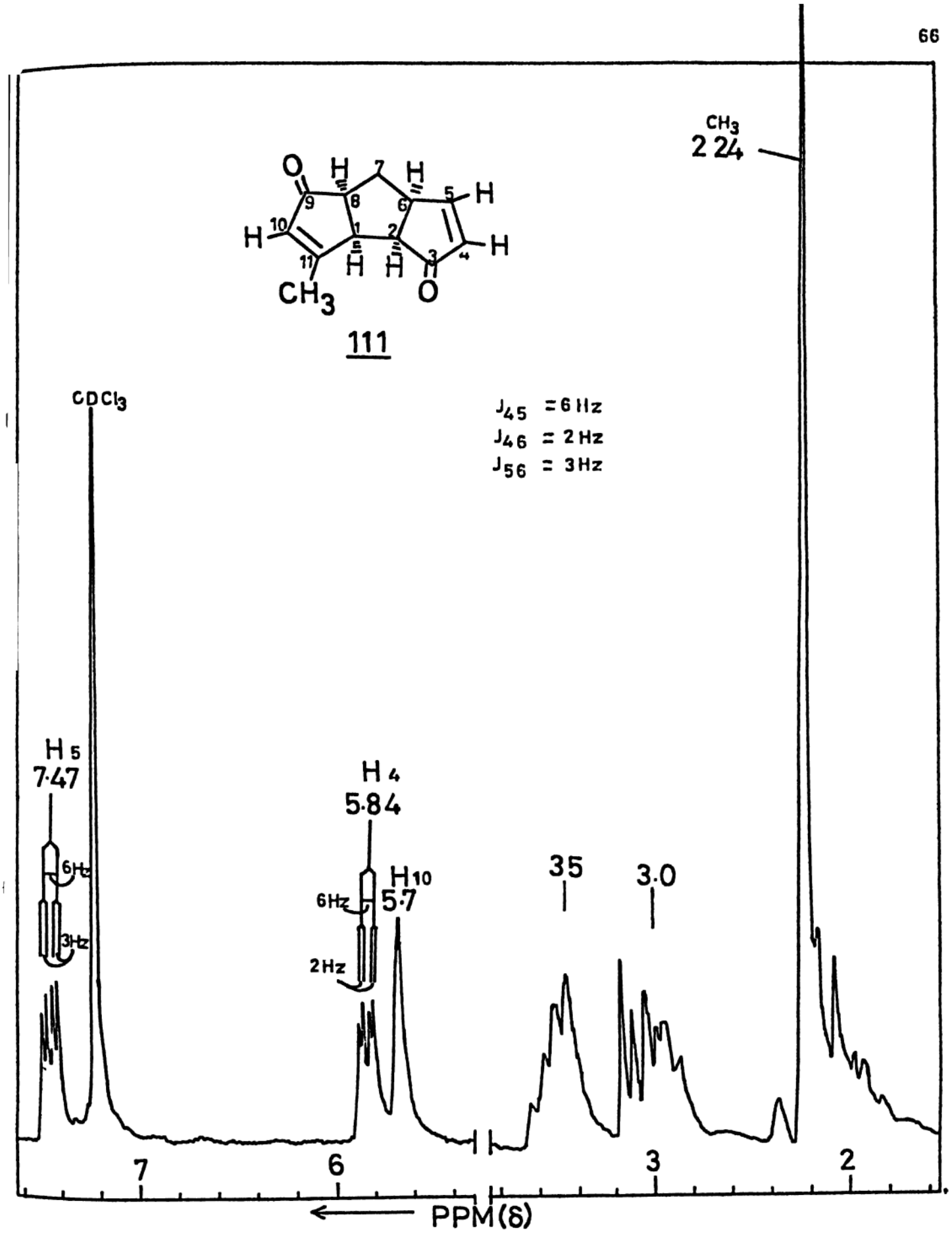


109 111

^{1}H NMR spectrum (Fig.I.13) which exhibited three diagnostic olefinic proton resonances at δ7.47, 5.84 and 5.7, only one of which (δ7.47) was due to the β-proton of the 2-cyclopentenone moiety. In addition, the olefinic methyl resonated down field at δ2.24 being placed on a β-carbon of an α,β-unsaturated ketone. The ^{13}C NMR spectrum (Fig.I.14) confirmed these assignments through four olefinic carbon resonances at δ178.4(s), 168.1(d), 133.6(d), 129.6(d) with appropriate multiplicities. Like the bis-enone 73, the transposed bis-enone 111 also underwent thermal isomerisation (benzyl benzo-



111 103



111

FIG I 13 : ^{1}H NMR (100 MHz) spectrum of 111

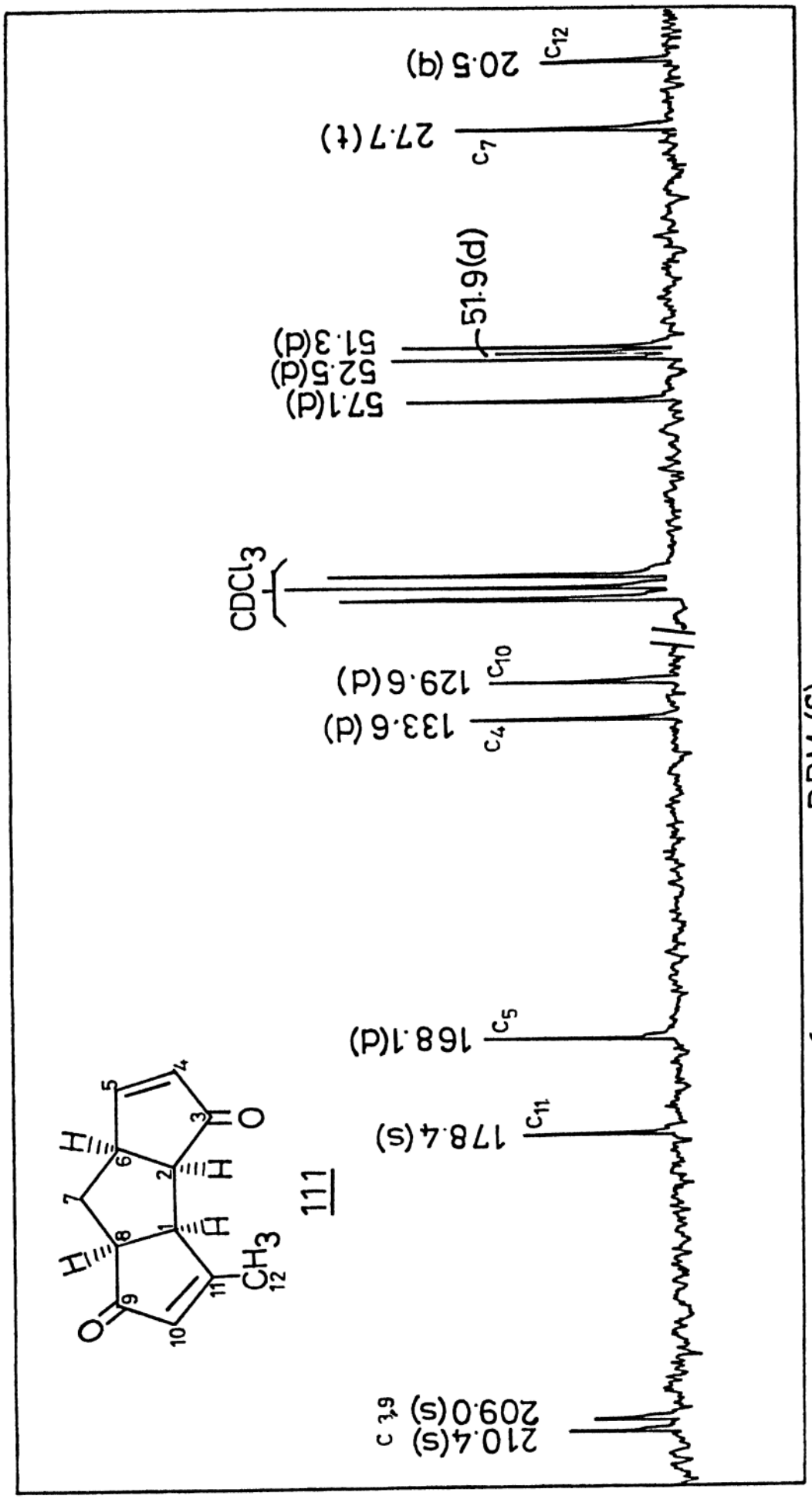
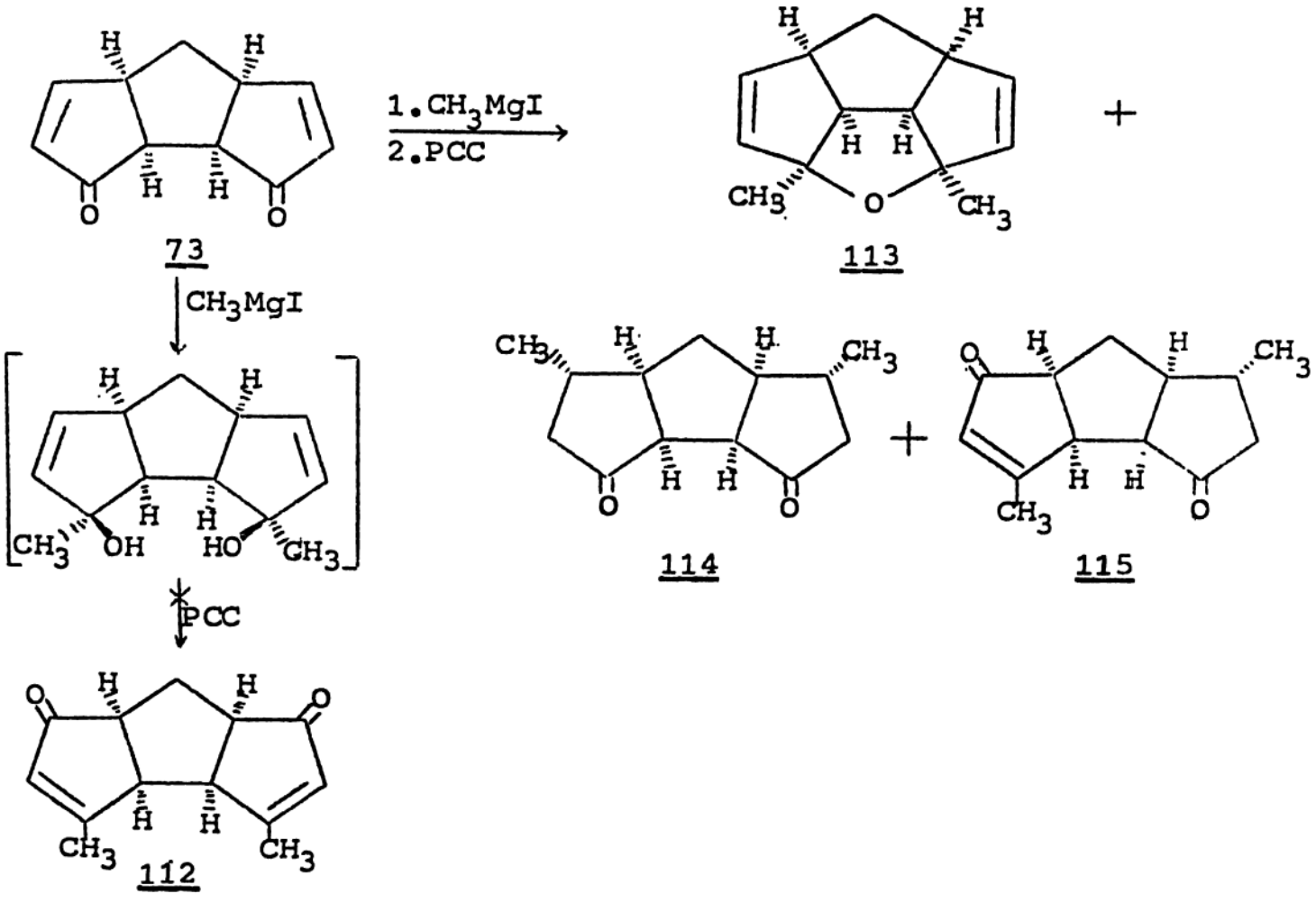


FIG I14: ^{13}C NMR (25.0 MHz) spectrum of 111

ate, 300°C, 30 min) to the tetrasubstituted compound 103 (vide supra).

Attempts at complete alkylative transposition of 73 to 112 via reaction with large excess of Grignard reagents under a variety of time, temperature, solvent and concentration regimes followed by PCC oxidation led only to a complex mixture of undesired products. In a typical run with 6-8 fold excess of Grignard reagent followed by PCC oxidation, compounds 113, 114 and 115 could be fished out from the reac-

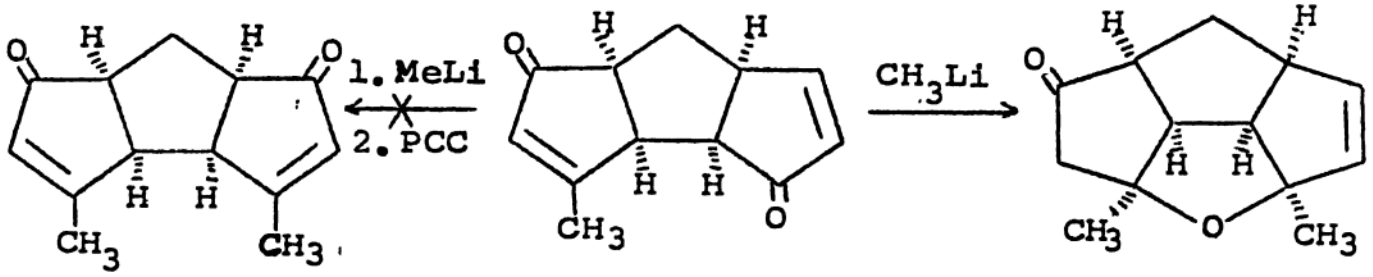
SCHEME I.31



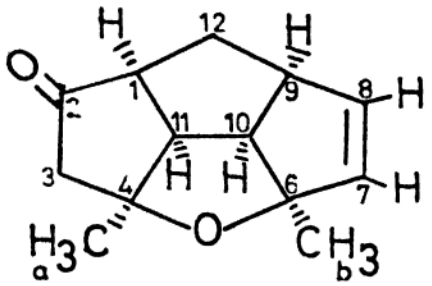
73 113 114 115 112

tion mixture in 8, 7 and 60% yields, respectively (Scheme I.31). The structures of products 113-115 were arrived at on the basis of complementary spectral (^{1}H and ^{13}C NMR) data summarised in the experimental section. Formation of the tetracyclic ether 113 in the excess Grignard reaction did indicate the formation of the desired bis-tertiary diol, the likely precursor of 112 but apparently it is too labile and forms the stable ether 113. Attempts to oxidise 113 directly to the doubly transposed bis-enone 112 with Jones reagent,[72] Kiliani's reagent[73] and in chromic acid-ether reagent[64b] were of no avail.

Consequently, transposition of the second enone moiety in the half transposed bis-enone 111 was attempted through the addition of alkyllithium reagents, known for their preference for 1,2-additions.[64b,74] Reaction of 111 with ethereal methyllithium resulted in initial 1,2-addition and concomitant intramolecular Michael addition to furnish the



112 111 116



116

$J_{7,8} = 5$ Hz

FIG I.15 : ^{1}H NMR spectrum (100 MHz) of 116

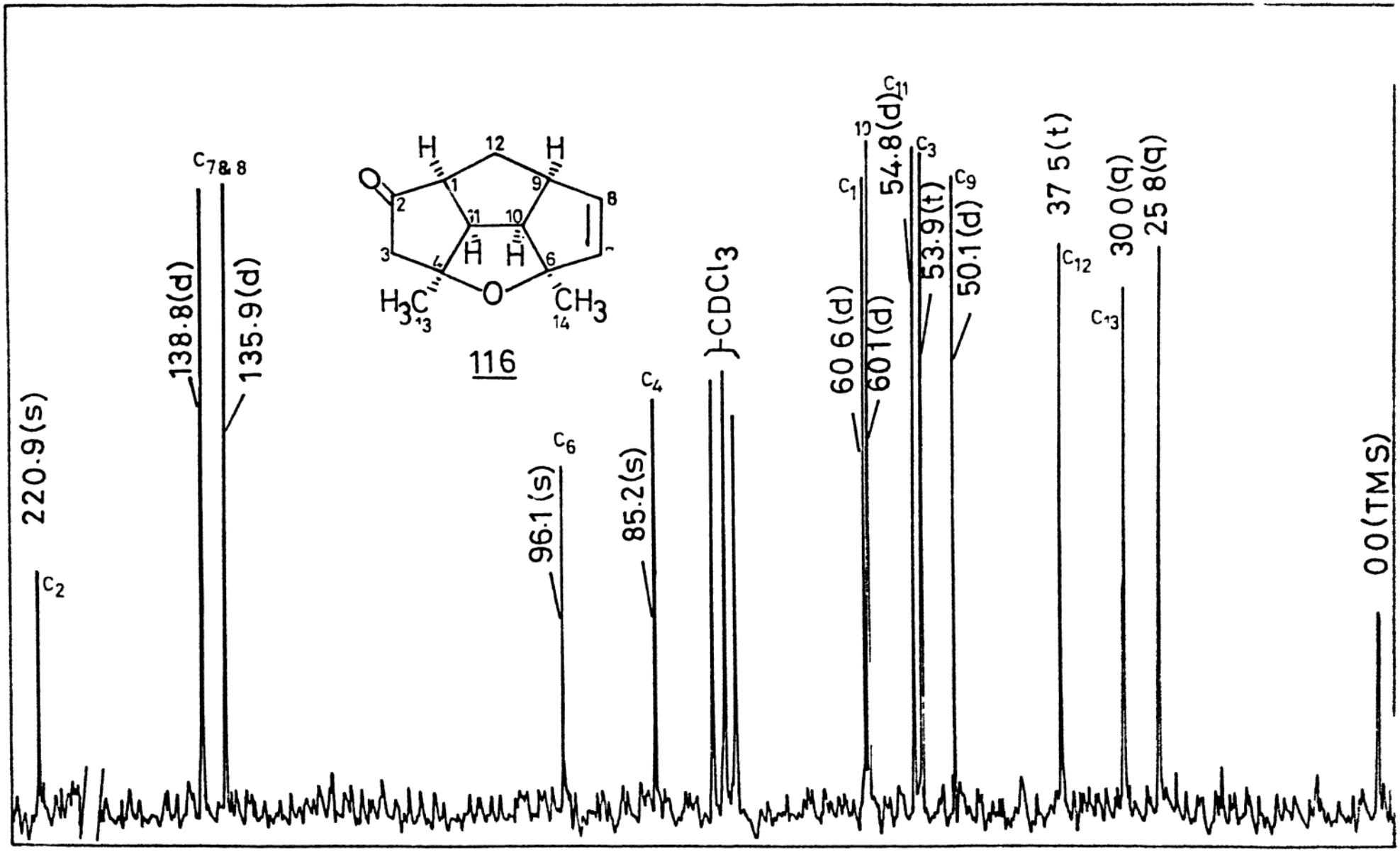
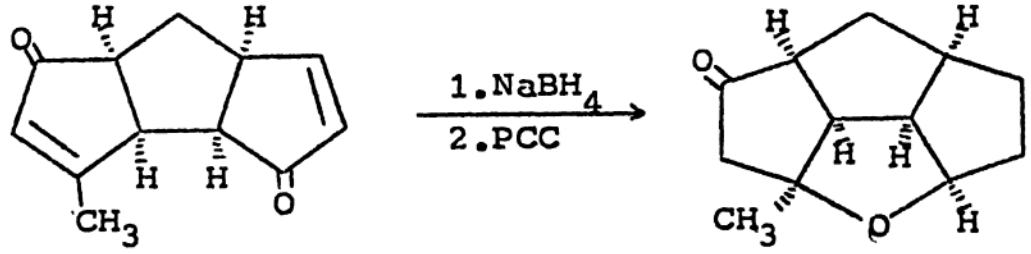


FIG I 16 ^{13}C NMR (25.0 MHz) spectrum of 116

5-oxatetraquinane 116 in 45% yield. Structure of 116 was revealed through the presence of cyclopentanone absorption in the IR spectrum (1740 cm^{-1}) and the presence of two quaternary methyl singlets in the ^1H NMR spectrum (Fig.I.15) at δ1.54 and 1.4. In confirmity with this assignment, the ^{13}C NMR spectrum (Fig.I.16) showed two quaternary carbon singlets at δ96.1 and 85.2 for the carbon atoms bearing the ether bridge. In a manner similar to the formation of 116, the sodium borohydride reduction and PCC oxidation[65] of 111 furnished the 5-oxatetraquinane 117. In this case, 1,4-addition

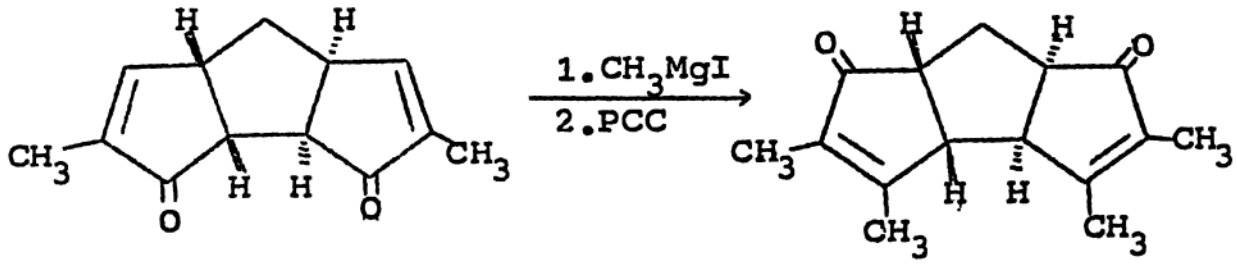


111 117

of hydride to the enone had obviously preceded the reduction of the carbonyl group and intramolecular Michael addition. There is ample precedence for the 1,4-hydride additions to 2-cyclopentenones.[75]

Two explanations can be offered for our inability to effect complete alkylative transposition of 73 to 112. Firstly, the addition of Grignard reagent or alkyllithium reagent to 111 generates an intermediate that is sterically

well disposed for the facile intramolecular Michael addition (5 exo trig ring closure)[76] to form the 5-oxatetraquinane system (e.g. 116). Secondly, the dialkylated transposed bis-enone 112 is considerably hindered due to the steric interference between the two methyl groups in the folded all cis-geometry. That the two explanations offered above are indeed valid is borne out by the fact that when dimethyl cis, anti, cis-bis-enone 118[+] was subjected to the two step alkylative transposition, fully transposed tetramethyl cis, anti, cis-bis-enone 119 was obtained in 50% yield. The structure of



118 119

119 followed from its ^{1}H NMR spectrum (Fig.I.17) which was free from olefinic proton resonances and from the simple eight line ^{13}C NMR spectrum (Fig.I.18) with resonances at δ209.8(s), 168.7(s), 135.0(s), 52.1(d), 51.7(d), 29.9(t), 15.7(q) and 8.2(q).

[+]Prepared by Mr. A. Veera Reddy of our laboratory in connection with some other project. We thank Mr. Veera Reddy for the generous gift of 118.

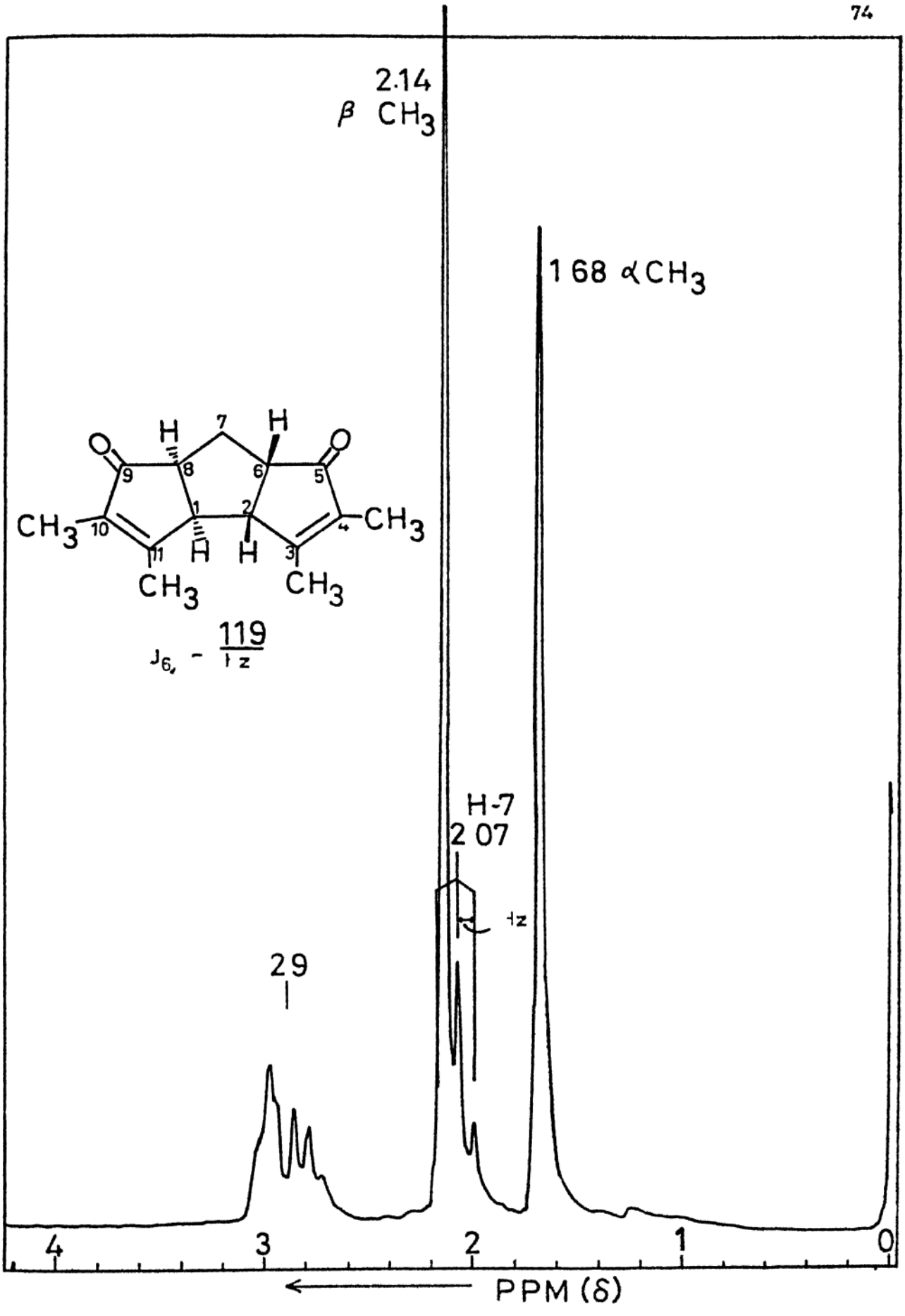


FIG I·17 ^{1}H NMR (100 MHz) spectrum of 119

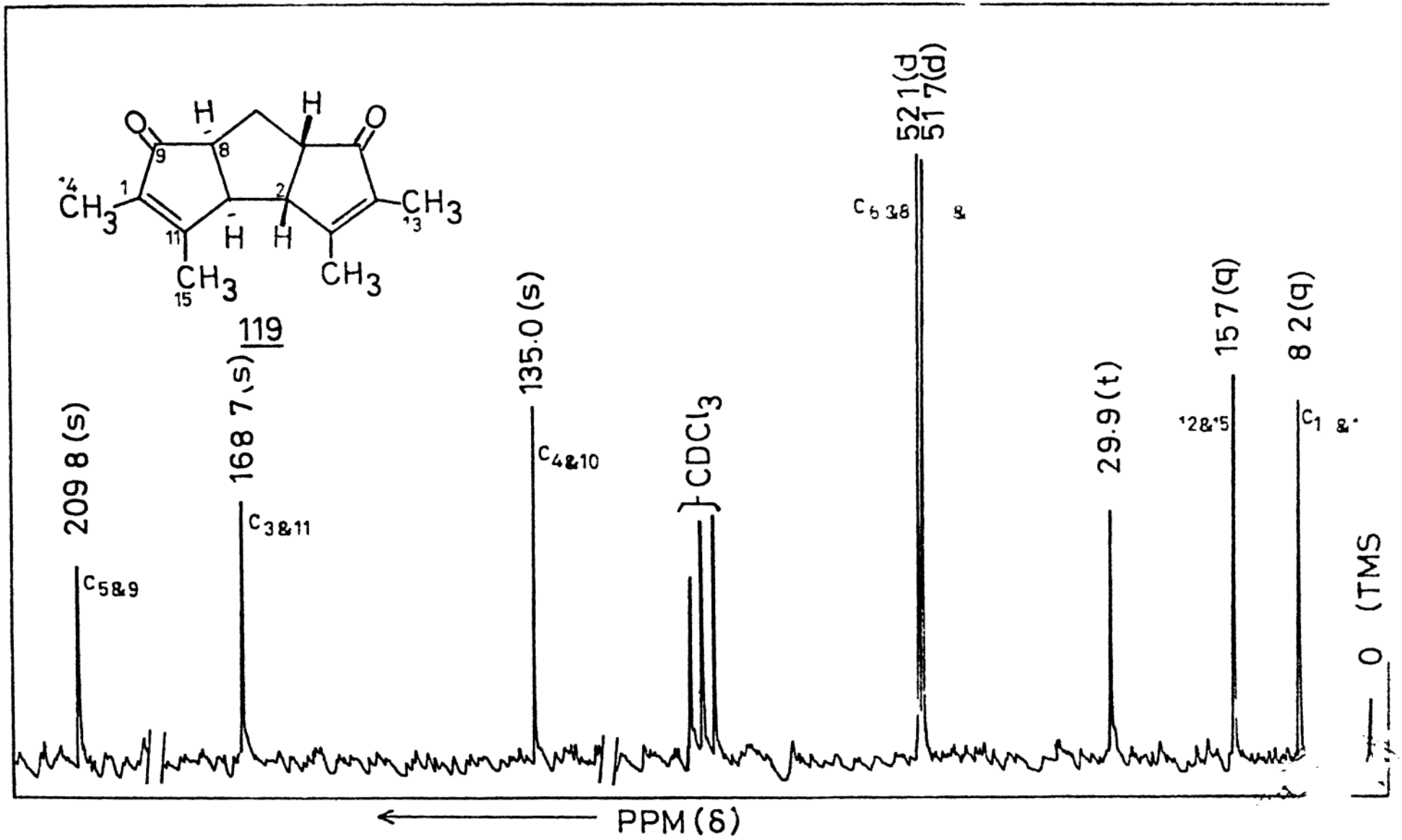


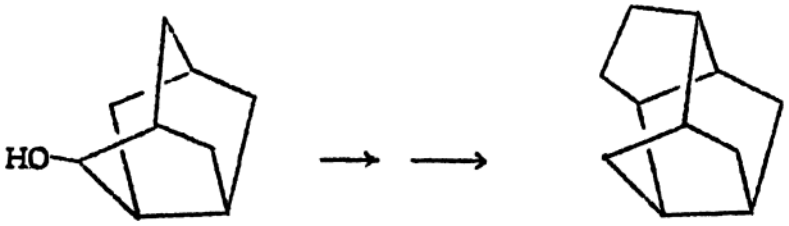
FIG 118 ^{13}C NMR (25 0 MHz) spectrum of 119

While considering various options for the relocation of double bonds in the bis-enone 73, it was considered reasonable to study its base catalysed isomerisations. For example, such base catalysed isomerisations have proved their worth in the prostanoid area for effecting useful PGA $\longrightarrow$PGE $\longrightarrow$PGB type conversions.[77] Consequently, reaction of 73 with sodium methoxide was explored and this provided a novel, unanticipated entry into difficultly accessible tetracyclo [5.4.0.$0^{3,10}$.$0^{4,8}$]undecane system.+ On hind sight, such a reaction course did not appear unexpected in view of the all cis-folded shape of 73.

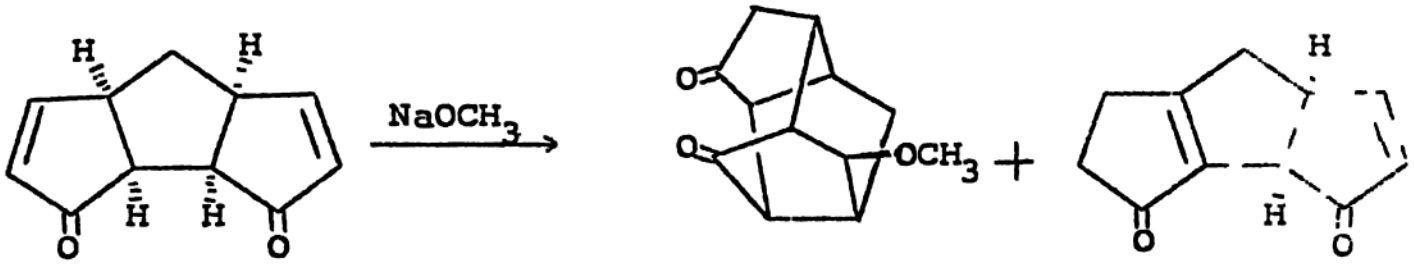
Exposure of 73 to excess of sodium methoxide in methanol furnished a 4:3 mixture of two products. The minor product was readily recognised as the isomerised bis-enone 96. The major product, mp.148-9°C, analysed for $C_{12}H_{14}O_3$,

---

+To our knowledge, only one multistep approach to the tetracyclo[5.4.0.$0^{3,10}$.$0^{4,8}$]undecane (2,9-ethanonoradamentane) system ii has been reported in literature from exo-2-nor adamentanol i by Schleyer and coworkers.[78]

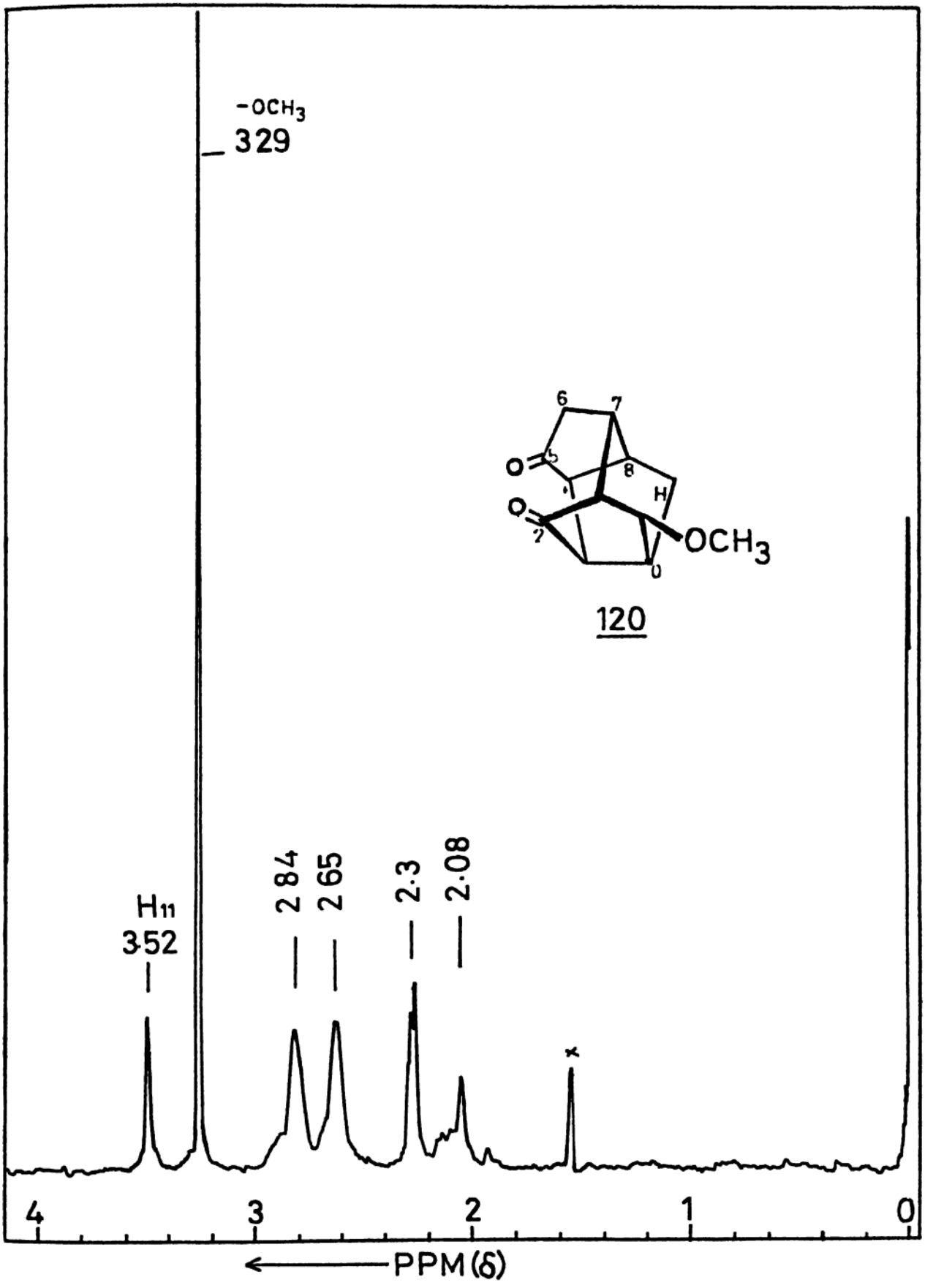


i ii



73 120 96

and indicated incorporation of methanol into the molecule. The ^{1}H NMR spectrum (δ3.29, 3H, s, Fig.I.19) confirmed the surmise and showed the absence of any olefinic protons. Only other clearly discernible resonance in the ^{1}H NMR spectrum was the presence of a singlet at δ3.52 due to the proton attached to the carbon bearing methoxy group. This was corroborated by the ^{13}C NMR spectrum (Fig.I.20) which show a resonance at δ83.1(d) due to the methoxy bearing carbon and at δ55.5(q) due to the methoxy carbon. The ^{13}C NMR also demonstrated the absence of olefinic C's and thus established the tetracyclic nature of the molecule. Lastly, the IR spectrum: 1750 cm^{-1} (broad) and ^{13}C NMR resonances at δ214.5(s) and 211.4(s) showed the remaining two oxygen atoms in the molecule to be present as part of cyclopentanone substructure. All the foregoing spectral data in conjunction with mechanistic consideration firmly established the tetracyclic structure 120. The plausible mechanism



120

FIG I 19 : ^{1}H NMR (100MHz) spectrum of 120

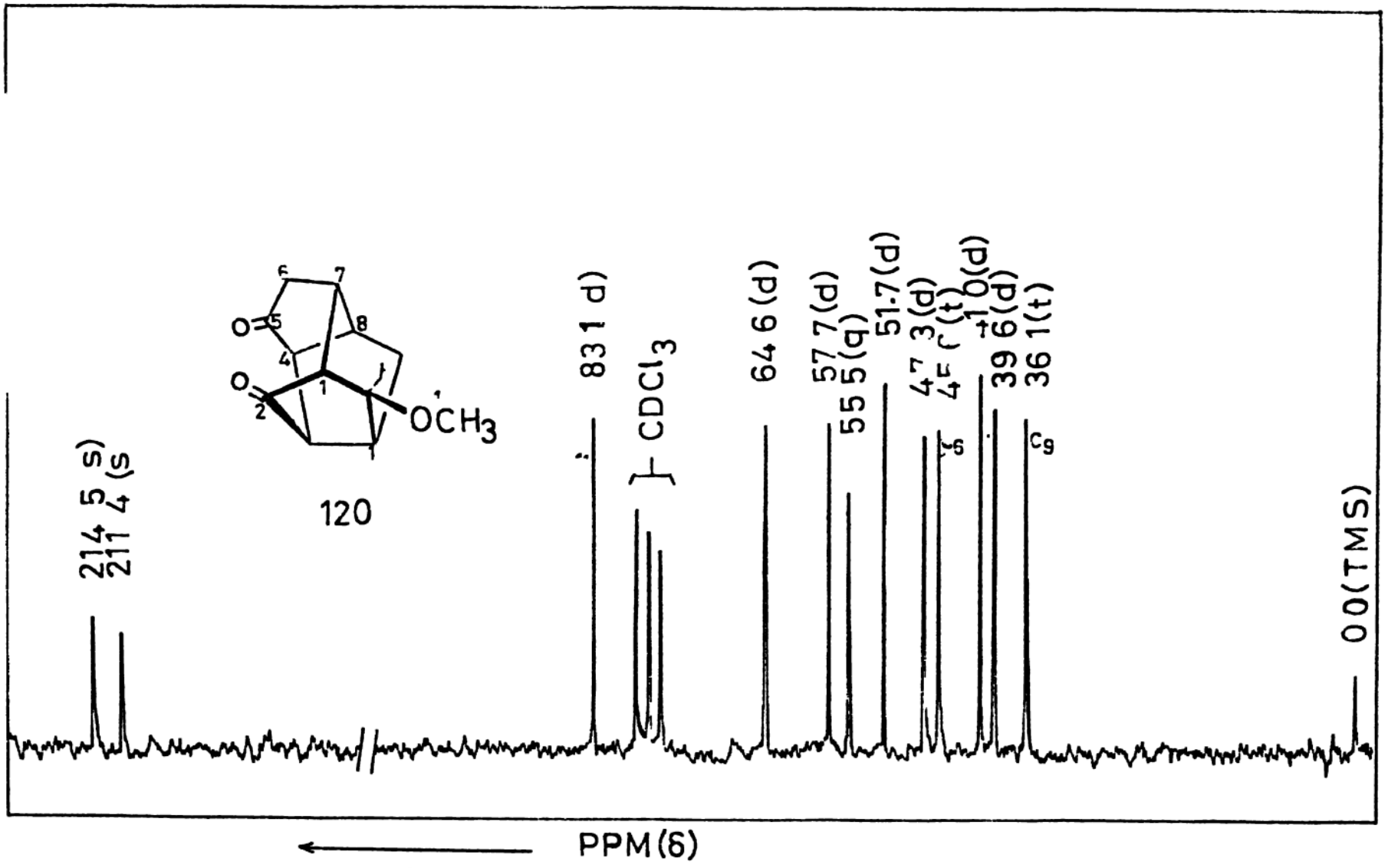
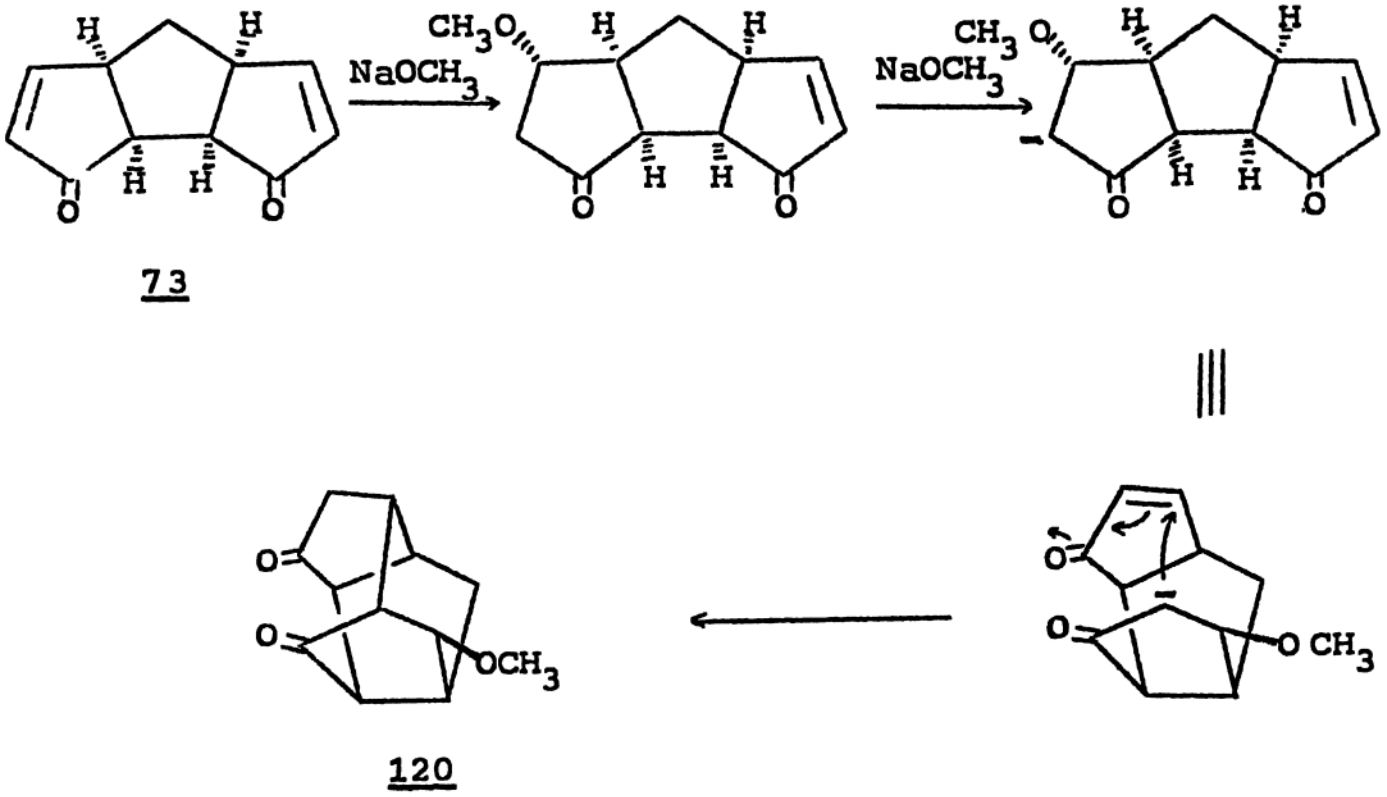


FIG I20 ^{13}C NMR (25.0 MHz) spectrum of 120

SCHEME I.32

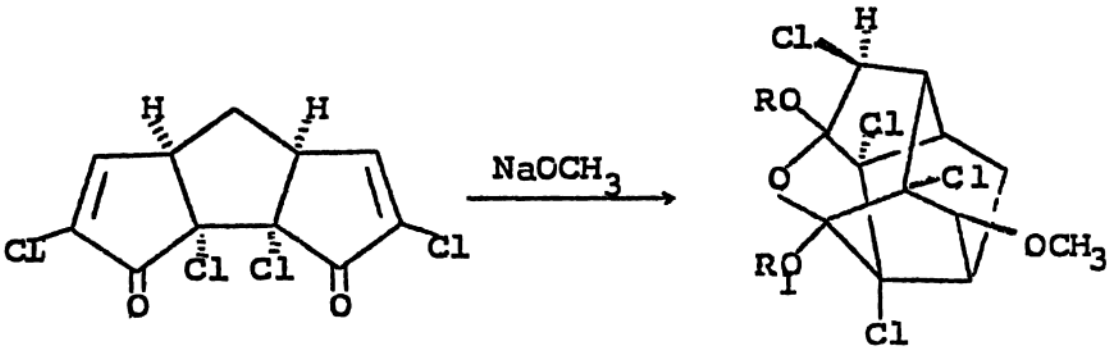


73

120

involving sequential inter and intramolecular Michael additions is depicted in Scheme I.32.

The tandem Michael additions (Scheme I.32) to bis-enone 73 seems to be a general reaction of this type of cis,syn, cis-tricyclopentanoid ring system. For example, tetrachloro bis-enone 83 on treatment with methanolic sodium methoxide yielded a single crystalline compound, mp.207°C in 65% yield. The elemental analysis $C_{13}H_{14}Cl_4O_4$ indicated addition of two molecules of methanol. The IR spectrum was devoid of any carbonyl absorption but had a broad discrete absorption at 3390 cm^{-1} due to hydroxyl group. The addition



83

121

R=H, R_1=CH_3 or

R=CH_3, R_1=H

of two moles of methanol was clearly shown in the ^{1}H NMR spectrum (Fig.I.21) which had methoxyl singlets at δ3.63 and 3.55. The ^{1}H NMR spectrum further exhibited a singlet at δ5.06 (1H, exchangeable with D_2O), a doublet at δ4.09(1H) and a singlet at δ3.25(1H). The three resonances were assigned due to the proton at the hydroxyl, proton attached to the carbon bearing chlorine and the proton attached to the carbon bearing methoxyl group, respectively. The ^{13}C NMR spectrum (Fig.I.22) confirmed the presence of all these functionalities and in addition showed quaternary carbon singlets at δ109.6 and 105.2. The signals were characteristic of carbon atoms bearing hydroxy-ether (-O-$\dot{C}$-OH) and methoxy-ether (-O-$\dot{C}$-OCH_3) functionality. The ^{13}C NMR spectrum was devoid of any carbonyl carbon resonances. The spectral data summarised above in conjunction with the absence of carbonyl groups and the fact that two molecules of methanol have added, led to structural formulation 121.

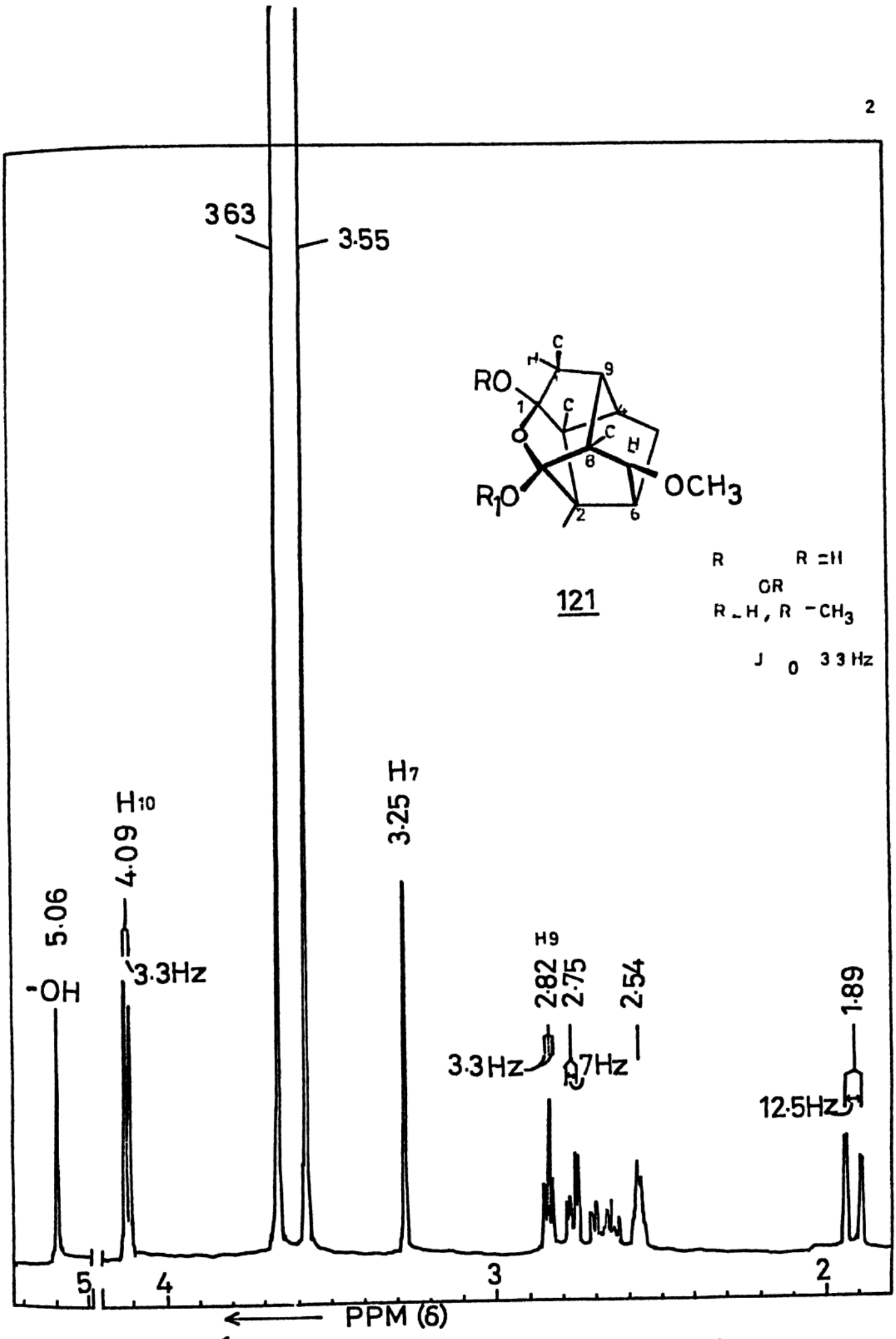


FIG I·21: ^{1}H NMR (270MHz) spectrum of 121

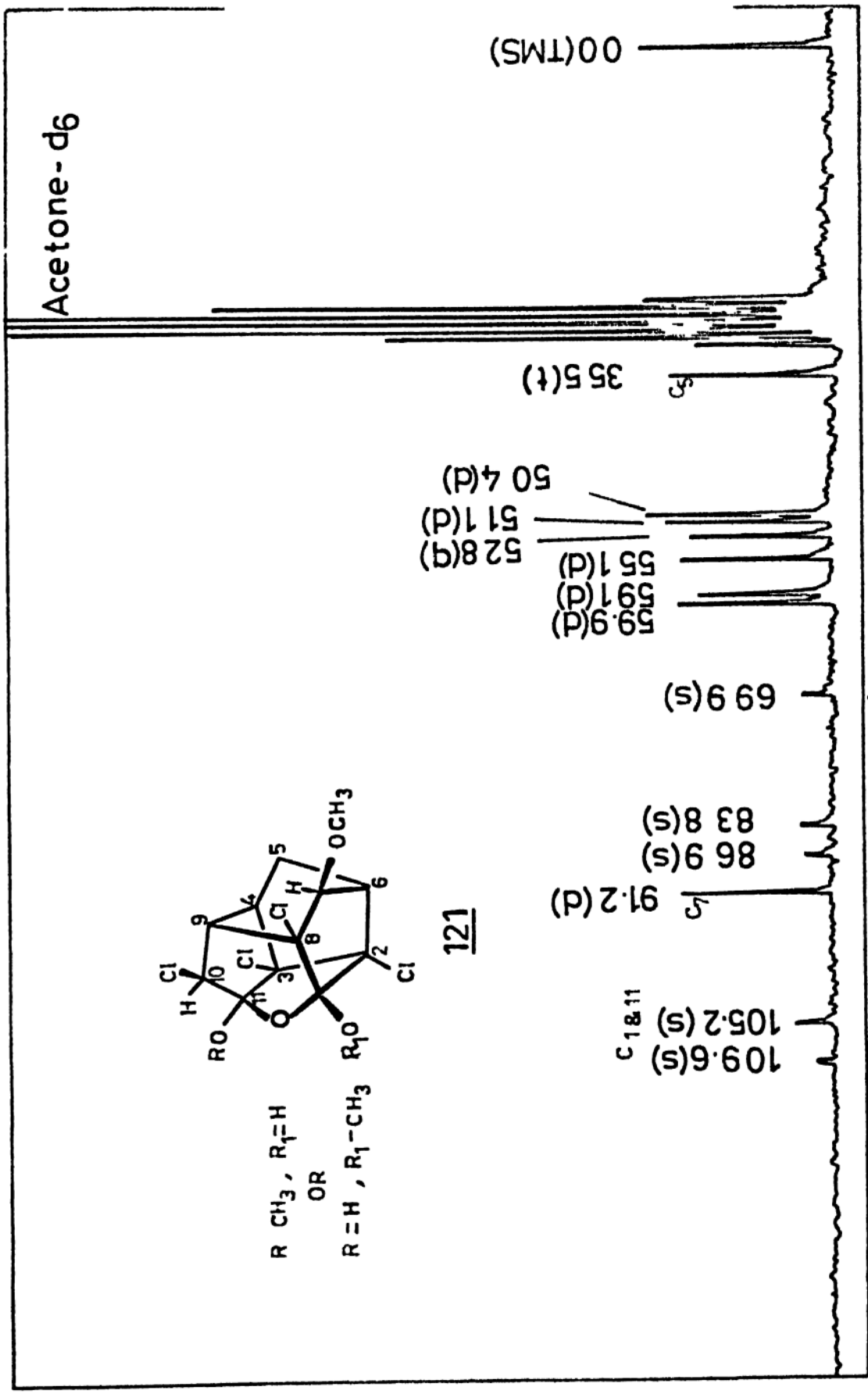
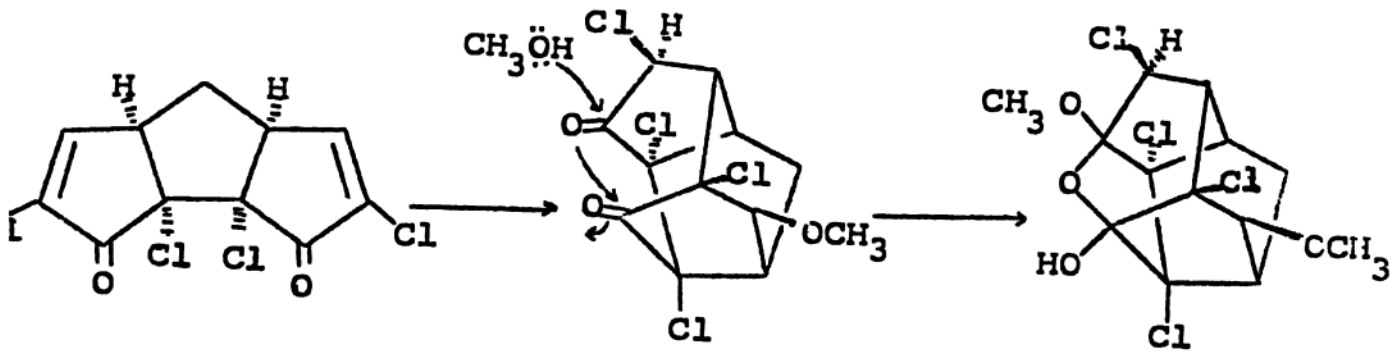


FIG 122 ^{13}C NMR(25.0MHz) spectrum of 121

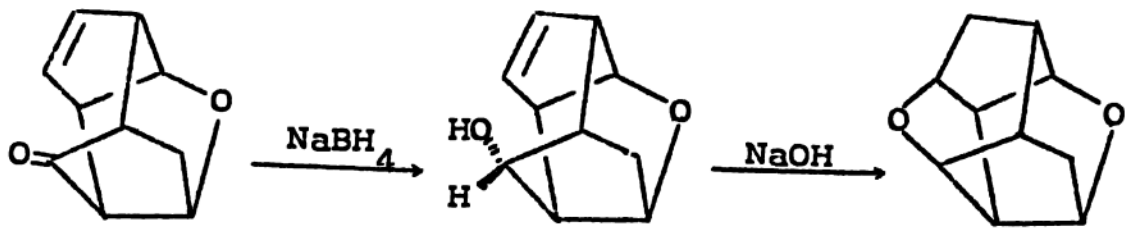
SCHEME I.33



83 121

It seems that initially formed product 122 of inter-and intra-molecular Michael addition of methanol to 83 further adds methanol transannularly to the proximate carbonyl groups (Scheme I.33). Inspection of molecular models reveals close proximity between the two carbonyl groups at C_2 and C_5 for a facile transannular ketalisation. Indeed, a dioxa-analog 124 of 121 has been reported recently[79] which involves trans-

SCHEME I.34



123 124

annular nucleophilic cyclisation of 123 as shown in Scheme I.34.

In view of the relative ease with which tetracyclo [5.4.0.$0^{3,10}$.$0^{4,8}$]undecane system is obtained from bis-enones 73 and 83, the method reported here should be of preparative value in gaining entry to this interesting and scarcely accessible ring system. There is much current interest in the chemistry of compounds related to 121.

In conclusion, the protocols of a three step photothermal metathetic sequence leading to linearly fused tricyclopentanoid (triquinane) framework, efficiently and expeditiously, employing cheap, abundantly available starting materials have been established. A fair sampling of interesting chemical transformations of the triquinane based bis-enone 73 have been reported. These transformations open new avenues for the design and construction of more enchanting synthetic targets of current interest.

I.4 EXPERIMENTAL

All melting points were recorded on a Buchi SMP-20 apparatus and are uncorrected. Boiling points refer to bath temperatures. UV, IR, ^{1}H NMR (100 MHz), ^{1}H NMR (270 MHz) and ^{13}C NMR (25.0 MHz) spectra were recorded on Shimadzu 200S

spectrophotometer, Perkin-Elmer 297 spectrophotometer, Jeol MH-100 spectrometer, Brucker 270 MHz spectrometer (Bangalor NMR facility) and Jeol FX-100 spectrometer, respectively. ^{1}H NMR and ^{13}C NMR chemical shifts are given in δ scale using Me_4Si as internal standard. In the ^{13}C NMR spectra, off resonance multiplicities, when recorded, are given in parentheses. The standard abbreviations s, d, t, q and m refer to singlet, doublet, triplet, quartet and multiplet, respectively. Elemental analyses were carried out on a Hewlett-Packard 185-B CHN analyser. GLC analyses were performed on a Hewlett-Packard 5830 A analytical instrument using Apiezon-L(6' x 1/8'' stainless steel) column at oven temperature in the range of 200-250°C. High resolution mass measurements were carried out on AEI MS-5076 mass-spectrometer. Hydrogenations were carried out on Parr hydrogenation apparatus in 250 ml pressure bottles.

Analytical thin layer chromatographies (TLC) were performed on (10x5 cm) glass plates coated (250 mμ) with Acme's silica gel G (containing 13% calcium sulfate as binder). Visualisation of the spots was achieved by exposure to iodine vapor. Acme's silica gel (100-200 mesh) was used in the column chromatography. Moisture sensitive reactions were carried out using standard syringe-septum techniques. Dry diethyl ether and tetrahydrofuran(THF) were prepared by distillation over sodium and stored over pressed sodium

wire. Dichloromethane was distilled over P_2O_5. Diphenyl ether (DPE) was purified and dried through filtration from a neutral alumina column. The pet ether refers to fraction boiling between 60 and 80°C. All solvent extracts were washed with brine, dried over Na_2SO_4 and concentrated on a Buchi-EL rotary evaporator.

Tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-dien-3,6-dione(71):[55]

To an ice cold solution of freshly prepared p-benzoquinone (20 g, 0.18 mol) in dry benzene (50 ml) was added freshly cracked cyclopentadiene (12.3 g, 0.18 mol) with gentle swirling of the flask. After the addition was complete, the reaction flask was left aside at room temperature for 2 hr for crystallisation. Filtration gave 28 g (88%) of the adduct 71, pale yellow crystals, mp.76°C (Lit[55] 75-6°C).

IR spectrum (KBr), ν_{max}: 1670 cm^{-1} (carbonyl).

Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undeca-8,11-dione(72):[54a]

A solution of the adduct 71 (35 g, 0.2 moles) in ethyl acetate (850 ml) was purged with a slow stream of dry nitrogen for 20 min. The solution was then irradiated with a Hanovia 450 W medium pressure mercury vapor lamp in a quartz immersion well using a pyrex filter for 2 hr. Evaporation of the solvent and direct crystallisation from benzene-pet ether furnished 31.5 g (90%), stout, white

crystals of the pentacyclic dione 72, mp.243-44°C (Lit[54a] 245°C).

IR spectrum (KBr), ν_{max}: 1750 cm^{-1} (carbonyl).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ2.2-3.0(8H,m,ring CH), 1.7(2H,AB quartet, $-CH_2-$).

^{13}C NMR spectrum (22.64 MHz, $CDCl_3$): δ211.9(s,C=O), 54.8(d), 44.7(d), 43.9(d), 40.5(t,CH_2), 38.9(d).

Tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione(73):

Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undeca-8,11-dione (72, 2 g, 11.5 mmoles) was slowly sublimed (150°C/1 mm) through a quartz tube [1.5x30 cms, packed with quartz chips, connected to a vacuum line and provided with a collection flask and liquid nitrogen trap. The quartz tube was heated with a nichrome wire wound around it and was insulated with asbestos padding. The temperature was controlled by a variac and was measured by a Chromel-Alumel thermocouple on a Keithley digital multimeter. The quartz tube was preheated and equilibrated at 560°C]. The solid condensate in the receiver was collected and directly crystallised from carbon tetrachloride to furnish 1.92 g (96%) of the bis-enone 73 as white silky flakes, mp.107-8°C.

UV spectrum, λ_{max}^{MeOH}: 219 nm (ε = 10,500).

IR spectrum (KBr, Fig.I.1), ν_{max}: 1725 sh, 1715, 1695 sh and 1590 cm^{-1} (cyclopentenone).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.I.2): δ7.44 (2H,dd,J_1=5.7Hz,J_2=2.5Hz,-C<u>H</u>=CH-Ċ=O), 5.86(2H,dd,J_1=5.7Hz, J_2=2Hz,-CH=C<u>H</u>-Ċ=O), 3.48(2H,m,H_1 and H_2), 3.2(2H,m,H_6 and H_8), 2.3(1H,td,J_1=14Hz,J_2=9Hz,H_7<u>exo</u>), 1.90(1H,td,J_1=14Hz, J_2=1Hz,H_7<u>endo</u>).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.I.3): δ207.4 (s,C=O), 165.9(d,-<u>C</u>H=CH-Ċ=O), 133.5(d,-CH=<u>C</u>H-Ċ=O), 53.1(d, C_1 and C_2), 50.4(d,C_6 and C_8), 31.5(t,C_7).

Analysis for $C_{11}H_{10}O_2$ Calcd: C,75.84; H,5.79.
Found: C,75.74; H,5.90.

<u>Sunlight photolysis of tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione(73)</u>:

A solution of bis-enone <u>73</u> (35 mg, 0.2 mmole) in 10 ml of acetone was prepared in a pyrex RB flask and carefully purged with a slow stream of drynitrogen for 10 min. The flask was then exposed to Sunlight for 12 hr. The solvent was removed and the residual solid was identified as the pentacyclic dione <u>72</u> by comparison (TLC, IR spectrum) with the authentic sample.

2,4,5,7-Tetrachloro tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-dien-3,6-dione(79):

A benzene (200 ml) solution of chloranil (77, 24.6 g, 0.1 mole) and freshly cracked cyclopentadiene (10 g, 0.15 mole) was refluxed for 30 min. Evaporation of the solvent and crystallisation from dichloromethane-methanol furnished 30 g (96%) of the adduct 79 as light brown needles, mp.146°C (Lit[60] 146°C).

IR spectrum (KBr), ν_{max}: 1700 (carbonyl), 1565 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ6.13(2H,m,olefinic), 3.62(2H,m,bridgehead CH), 2.47(1H,d,J=10Hz,H-C-H), 2.06(1H, d,J=10Hz,H-C-H).

1,7,9,10-Tetrachloro pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undeca-8,11-dione(81):

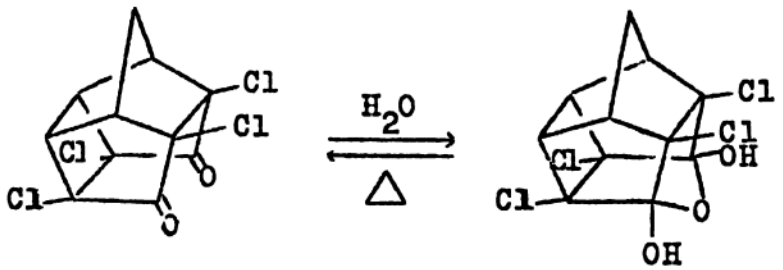
A solution of the adduct 79 (20 g, 0.06 mole) in ethyl acetate (850 ml) was purged with a slow stream of dry nitrogen for 20 min. The solution was then irradiated with a Hanovia 450 W medium pressure mercury vapour lamp in a quartz immersion well using a pyrex filter for 20 min. Evaporation of the solvent and crystallisation from chloroform-pet ether furnished 19 g (95%) of a mixture of the pentacyclic diketone 81 and its symmetrical hydrate 124, mp.211-4°C dec. (Lit[54a] 215°C dec.). On repeated sublimation, the hydrate free

dione 81, could be obtained from this mixture. However, for the present investigation the symmetrical hydrate 124 was employed as such and was duly characterised.

IR spectrum (KBr), ν_{max}: 3520, 3480 cm^{-1} (hydroxyl).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ3.88(2H,s,exchanged with D_2O,-OH), 3.12(2H,m,ring CH), 2.98(2H,m,ring CH), 2.34 (1H,d,J=12Hz,H-C-H), 1.82(1H,d,J=12Hz,H-C-H).

^{13}C NMR (25.0 MHz, DMSO-d_6): δ107.5(>C<$^{OH}_{O-}$), 87.0 (C-Cl), 74.9(C-Cl), 51.8, 46.5, 40.8(CH_2).



81 124

4,5-Dichloro tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-dien-3,6-dione (80):[61]

A solution of 2,3-dichlorobenzoquinone (78, 5 g, 28.2 mmoles) and freshly cracked cyclopentadiene (3 g, 45.5 mmoles) in 20 ml of benzene was magnetically stirred at room temperature for 30 min. Concentration and crystallisation from benzene-hexane furnished 6.2 g (91%) of the adduct 80, mp.106-8.5°C (Lit[61] 109-10°C).

IR spectrum (KBr), ν_{max}: 1685 (carbonyl), 1560 cm^{-1} (olefinic).

^{1}H NMR spectrum (100 MHz, $CDCl_3$): δ6.16(2H,s,olefini 3.62(2H,brs), 3.4(2H,m), 1.6(2H,m,CH_2).

1,7-Dichloro pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undeca-8,11-dione(82):

A solution of the adduct 80 (5 g, 20.6 mmoles) in 300 ml of ethyl acetate was carefully purged with a slow stream of dry nitrogen for 10 min. The solution was then irradiated with a Hanovia 450 W medium pressure mercury vapour lamp in a pyrex immersion well for 30 min. Evaporation of the solvent and crystallisation from benzene-hexane furnished 4.5 g (90%) of the pentacyclic diketone 82, which was sublimed at 130°C/ 1 mm., mp.203-5°C.

IR spectrum (KBr), ν_{max}: 1782, 1760 cm^{-1} (carbonyl).

^{1}H NMR spectrum (100 MHz, Acetone-d_6): δ2.5-3.1(6H,m, ring CH), 1.52-2.1(2H,AB quartet,J=11Hz,CH_2).

^{13}C NMR spectrum (25.0 MHz, DMSO-d_6, mixture of dione and its symmetrical hydrate): δ202.7(s,C=O), 109.0(s,>C<$^{OH}_{O-}$), 77.3(s,C-Cl), 70.6(s,C-Cl), 55.5(d), 51.5(d), 50.0(d), 48.7 (d), 43.3(d), 42.0(d), 2 methylene signals were merged in DMSO-d_6 resonances.

Analysis for $C_{11}H_8Cl_2O_2$ Calcd: C,54.35; H,3.2.
Found: C,54.72; H,3.52.

1,2,4,10-Tetrachloro tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione(83):

A solution of 1,7,9,10-tetrachloro pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undeca-8,11-dione (81, 5 g, 16 mmoles) in 25 ml of diphenyl ether was refluxed (260°C) for 15 min. The reaction mixture was charged on a silica gel (100 g) column and was thoroughly eluted with pet ether to remove diphenyl ether. Further elution of the column with benzene furnished 4.8 g (96%) of tetrachloro bis-enone 83, which was recrystallised from benzene-pet ether as white needles, mp.150°C.

UV spectrum, λ_{max}^{MeOH}: 244 nm (Extinction coefficient could not be calculated as the absorption dropped too fast on exposure to the UV lamp, perhaps due to facile intramolecular cage cyclisation. This could be readily confirmed by time scan).

IR spectrum (KBr), ν_{max}: 1750, 1603 and 1585 cm^{-1} (cyclopentenone).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.I.4): δ7.3(2H,d, J=2.5Hz,-CH=C(Cl)-C=O), 3.73(2H,dd,J_1=10Hz,J_2=2.5Hz,H_6 and H_8), 2.85(1H,td,J_1=14Hz,J_2=10Hz,H_{7exo}), 2.05(1H,d,J=14Hz, H_{7endo}).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.I.5): δ190.2 (s,C=O), 154.2(d,-CH=C(Cl)-C=O), 133.7(s,-CH=C(Cl)-C=O), 76.7(s,C-Cl), 56.6(d,C_6 and C_8), 30.4(t,CH_2).

Analysis for $C_{11}H_6Cl_4O_2$ Calcd: C,42.3; H,1.92.
Found: C,42.45; H,2.03.

Sunlight photolysis of 1,2,4,10-tetrachloro tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione(83):

A solution of tetrachloro bis-enone 83 (100 mg, 0.32 mmole) in 20 ml of ethyl acetate was carefully purged with a slow stream of dry nitrogen in a pyrex RB flask. The solution was then exposed to Sunlight for 30 min. The solvent was removed and the product was identified as pentacyclic dione 81 by comparison (TLC, IR spectrum) with an authentic sample.

4,10-Dichloro tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione(84):

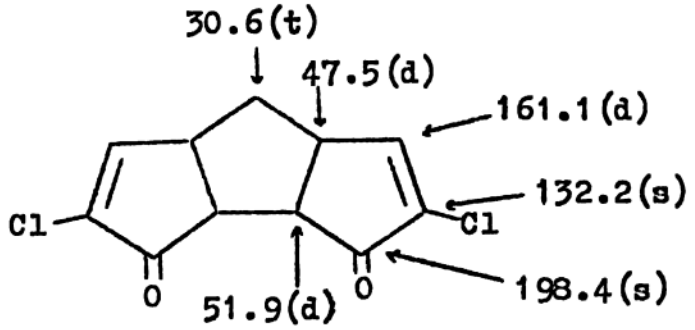
A solution of 1,7-dichloro pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undeca-8,11-dione (82, 0.5 g, 2 mmoles) in 5 ml of diphenyl ether was magnetically stirred at 220°C for 50 min. The solution was diluted with benzene (10 ml) and charged on a silica gel (15 g) column and chromatographed. The diphenyl ether was first eluted with benzene. Elution with 15% ethyl acetate-benzene furnished 150 mg of the starting dione 82. Further elution of the column with 20% ethyl acetate-benzene furnished 340 mg (68%) of the dichloro bis-enone 84, which crystallised as white, sugary crystals from dichloromethane-pet ether, mp.186-7°C.

UV spectrum, λ_{max}^{MeOH}: 235.5 nm (ε = 5,700).

IR spectrum (KBr), ν_{max}: 1730 and 1595 cm^{-1} (cyclopentenone).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ7.35(2H,d,J=2.5Hz, -CH=C(Cl)-C=O), 3.16-3.7(4H,m,bridgehead CH), 2.34(1H,td, J_1=14Hz,J_2=8Hz,H_7exo), 1.9(1H,td,J_1=14Hz,J_2=2Hz,H_7endo).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ198.4, 161.1, 132.2, 51.9, 47.5, 30.6. The assignments and multiplicities are displayed on the structure shown below.



84

Analysis for $C_{11}H_8Cl_2O_2$ Calcd: C,54.35; H,3.32.
Found: C,54.85; H,3.58.

Sunlight photolysis of 4,10-dichloro tricyclo[6.3.0.$0^{2,6}$] undeca-4,9-dien-3,11-dione(84):

A solution of dichloro bis-enone 84 (100 mg,0.4 mmole) in 20 ml of ethyl acetate was carefully purged with a slow stream of dry nitrogen in a pyrex RB flask. The solution was then exposed to Sunlight for 5 hr. The solvent was removed and the product was identified as penta-

cyclic dione 82 by comparison (TLC, IR spectrum) with an authentic sample.

Dechlorination of 1,2,4,10-tetrachloro tricyclo[6.3.0.$0^{2,6}$] undeca-4,9-dien-3,11-dione(83):

To a refluxing solution of tetrachloro bis-enone 83 (0.5 g, 1.6 mmoles) in 15 ml of glacial acetic acid was added, in small portions, zinc dust (228 mg, 3.5 mmoles) over a period of 5 min. The reaction mixture was refluxed for 1 hr, cooled and neutralised by carefully pouring in aqueous $NaHCO_3$ solution. The reaction mixture was extracted with dichloromethane (30 ml x 3), the extract was washed and dried. Evaporation of the solvent furnished 315 mg (81%) of the crystalline dichloro bis-enone 84, mp.186-7°C. This was found to be identical (TLC, IR spectrum) with the sample obtained earlier from the thermal fragmentation of pentacyclic dione 82.

Tricyclo[6.2.2.$0^{2,7}$]dodeca-4,9-dien-3,6-dione(85):[62]

A solution of freshly sublimed p-benzoquinone (2 g, 18.5 mmoles) and 1,3-cyclohexadiene (3.5 g, 43.7 mmoles) in 20 ml of benzene was refluxed for 5 hr. Benzene was removed under reduced pressure and the adduct 85 was crystallised from pet ether (2 g, 58%), mp.85-6°C (Lit[62] 86°C).

IR spectrum (KBr), ν_{max}: 1665 cm^{-1} (carbonyl).

Pentacyclo[6.4.0.$0^{2,7}$.$0^{3,11}$.$0^{6,10}$]dodeca-9,12-dione(86):[54a]

A solution of the adduct 85 (2 g, 10.6 mmoles) in ethyl acetate (120 ml) was purged with a slow stream of purified nitrogen for 20 min. The solution was then irradiated with a 450 W Hanovia medium pressure mercury vapour lamp in a quartz immersion well using a Vycor filter for 7 hr. Removal of solvent gave a white amorphous solid. Crystallisation from pet ether furnished 1.5 g (75%) of white crystalline 86, which was twice sublimed at 160°C/1 mm, mp.255°C (Lit[54a] 256°C).

IR spectrum (KBr), ν_{max}: 1745 cm^{-1} (Carbonyl).

^1H NMR spectrum (60 MHz, $CDCl_3$): δ2.0-3.0(8H,m), 1.8(4H,m).

^{13}C NMR spectrum (22.64 MHz, $CDCl_3$): δ211.4(s), 48.2 (d), 47.5(d), 35.6(d), 31.5(d), 16.7(t).

Tricyclo[7.3.0.$0^{2,6}$]dodeca-4,10-dien-3,12-dione(87):

Pentacyclo[6.4.0.$0^{2,7}$.$0^{3,11}$.$0^{6,10}$]dodeca-9,12-dione (86, 1 g, 5.32 mmoles) was slowly sublimed (140°C/1 mm) through a quartz tube at 600°C (±15°), as described earlier. The yellow condensate in the liquid nitrogen trap was dissolved in dichloromethane. Removal of solvent gave 400 mg (70%) of a yellow solid and was identified as benzoquinone by comparison (mp, IR spectrum) with an authentic

sample. The condensate in the delivery tube was charged on a small silica gel (5 g) column and chromatographed. Elution with 40% ethyl acetate furnished 80 mg (8%) of the bis-enone 87, which was crystallised from dichloromethane-pet ether as colorless plates, mp.104-5°C.

UV spectrum, λ_{max}^{MeOH}: 218 nm (ε = 15,200).

IR spectrum (KBr), ν_{max}: 1700 and 1585 cm^{-1} (cyclopentenone).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.I.6): δ7.42(2H, dd,J_1=6Hz,J_2=3Hz,-C<u>H</u>=CH-Ċ=O), 6.22(2H,dd,J_1=6Hz,J_2=2Hz,-CH=C<u>H</u>-Ċ=O), 2.9-3.3(2H,m,H_6 and H_9), 2.84(2H,dd,J_1=5Hz,J_2=2Hz, H_1 and H_2), 1.0-2.0(4H,m,CH_2).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.I.7): δ209.3 (s,C=O), 163.9(d,-<u>C</u>H=CH-Ċ=O), 133.7(d,-CH=<u>C</u>H-Ċ=O), 45.3(d, C_1 and C_2), 40.9(d,C_6 and C_9), 22.4(t,C_7 and C_8).

Analysis for $C_{12}H_{12}O_2$ Calcd: C,76.57; H,6.43.
Found: C,75.80; H,6.55.

<u>Tricyclo[6.3.0.$0^{2,6}$]undeca-3,11-dione(89)</u>:

A solution of bis-enone <u>73</u> (4 g, 23 mmoles) in 20 ml of ethyl acetate was hydrogenated over 10% Pd-C (250 mg) catalyst at 2 atmospheres in a 250 ml pressure bottle using a Parr-hydrogenation apparatus for 30 min. The catalyst

was filtered and the filtrate was concentrated. Crystallisation of the oily residue from dichloromethane-pet ether furnished 4 g (98%) of the tetrahydro dione 89 as stout, colourless prims, mp.92-3°C.

IR spectrum (KBr), ν_{max}: 1735 cm^{-1} (cyclopentanone).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ2.8(4H,brs,bridgehead CH), 1.0-2.6(10H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.I.8): δ218.0 (s,C=O), 56.1(d,C_1 and C_2), 43.6(d,C_6 and C_8), 38.9(t,C_7), 37.1(t,C_4 and C_{10}), 26.2(t,C_5 and C_9).

Analysis for $C_{11}H_{14}O_2$ Calcd: m/e 178.0994.
Found: m/e 178.0961.

Controlled hydrogenation of tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione(73):

A solution of bis-enone 73 (1 g, 5.75 mmoles) in 15 ml of ethyl acetate was hydrogenated over 10% Pd-C (45 mg), catalyst at 1 atmosphere for 15 min. The catalyst was filtered and the filtrate was concentrated. Column chromatography of the product on a silica gel (25 g) column and elution with 20% ethyl acetate-benzene furnished 550 mg (54%) of the tetrahydro compound 89, which was identified by comparison (TLC, IR spectrum) with the sample obtained earlier.

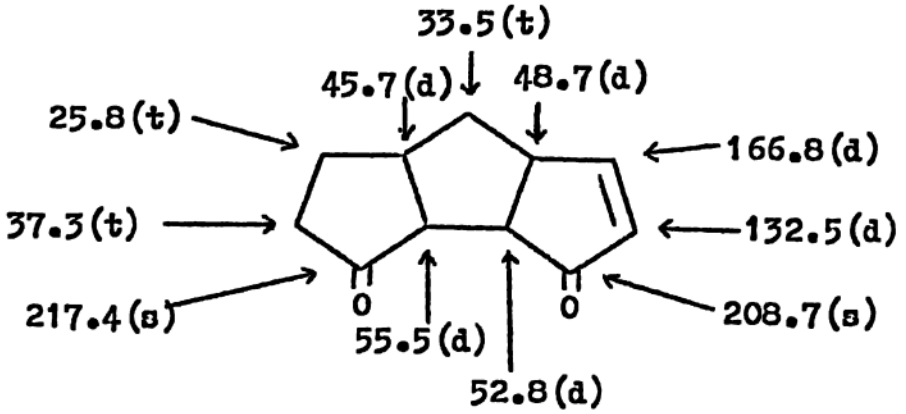
Further elution of the column with 30% ethyl acetate-benzene furnished 360 mg (35%) of the partially hydrogenated compound 88, which was bulb to bulb distilled (150°C/0.6 and then crystallised from carbon tetrachloride-pet ether, mp.59-60°C.

UV spectrum, λ_{max}^{MeOH}: 225 nm (ε = 7,480).

IR spectrum (KBr), ν_{max}: 1740 (cyclopentanone), 1705 and 1585 cm^{-1} (cyclopentenone).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ 7.58(1H,dd,J_1=6Hz, J_2=3Hz,-CH=CH-C=O), 5.86(1H,dd,J_1=6Hz,J_2=2Hz,-CH=CH-C=O), 3.48(1H,m), 1.2-3.2(9H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ 217.4, 208.7, 166.8, 132.5, 55.5, 52.8, 48.7, 45.7, 37.3, 33.5, 25.8. The assignments and multiplicities are displayed on the structure shown below.



88

Analysis for $C_{11}H_{12}O_2$ Calcd: C,74.98; H,6.86.

Found: C,74.63; H,6.95.

Finally, elution of the column with 50% ethyl acetate-benzene furnished 80 mg of the starting bis-enone 73.

Sodium borohydride reduction of tricyclo[6.3.0.$0^{2,6}$]undeca-3,11-dione(89):

To a magnetically stirred solution of the dione 89 (500 mg, 2.81 mmoles) in 10 ml of methanol was added sodium borohydride (190 mg, 5.1 mmoles) over a period of 5 min. The reaction mixture was stirred for 30 min at room temperature and then quenched by addition of few drops of dilute HCl. Most of the methanol was removed under reduced pressure and the mixture was diluted with water (20 ml) and extracted with dichloromethane (20 ml x 3). The dichloromethane extract was washed and dried. Evaporation of the solvent furnished 500 mg of crude viscous material and was charged on a silica gel (15 g) column. Elution with 5% ethyl acetate-benzene furnished 150 mg (27%) of the methoxy compound, 4-methoxy 5-oxatetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodecane (92) as an oil, and was bulb to bulb distilled (120°C/1 mm).

IR spectrum (neat), ν_{max}: 1090 cm^{-1}.

^{1}H NMR spectrum (100 MHz, $CDCl_3$): δ4.62(1H,t,J=4Hz, HC-O-), 3.26(3H,s,$-OCH_3$), 2.3-3.2(4H,m, bridgehead CH), 1.3-2.3(10H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ121.3(s,>C<$^{OCH_3}_{O-}$),

87.8(d,CH-O-), 60.8(d), 56.4(d), 47.2(d) and 45.2(d), bridgehead C's, 50.7(q,-OCH_3), 37.9(t), 35.1(t), 34.5(t), 32.6(t), 32.1(t).

Further elution of the column with 20% ethyl acetate-benzene furnished 180 mg (35%) of the lactol, 5-oxatetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodecan-4-ol (91), which was crystallised from pet ether as colourless, stout prisms, mp.96-7°C.

IR spectrum (KBr), ν_{max}: 3380 cm^{-1} (hydroxyl).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ4.79(1H,dd,J_1=5Hz, J_2=3Hz,HC-O-), 3.31(1H,s,exchanged with D_2O,-OH), 2.3-3.3 (4H,m,bridgehead CH), 1.3-2.2(10H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.I.9): δ118.4 (s,>C<$^{OH}_{O-}$), 87.9(d,CH-O-), 60.9(d), 56.5(d), 47.3(d) and 46.2 (d), bridgehead C's,. 39.7(t), 38.1(t), 34.6(t), 32.7(t), 32.3(t).

Final elution of the column with 30% ethyl acetate-benzene furnished 80 mg (16%) of the endo, exo-tricyclo [6.3.0.$0^{2,6}$]undeca-3,11-diol (93), which crystallised from dichloromethane-pet ether as white needles, mp.88°C.

IR spectrum (KBr), ν_{max}: 3250 cm^{-1} (hydroxyl).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ4.84(2H,brs,-OH), 4.24(2H,dd,J_1=16Hz,J_2=8Hz,CH-OH), 1.0-2.9(13H,m,ring CH),

0.96(1H,dd,J_1=20Hz,J_2=11Hz).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ76.8(d,CH-OH), 73.9(d,CH-OH), 56.4(d), 49.0(d), 45.9(d) and 43.4(d), bridge-head C's, 43.8(t), 35.5(t), 35.0(t), 28.3(t), 26.8(t).

Analysis for $C_{11}H_{18}O_2$ Calcd: m/e 182.1307.
Found: m/e 182.1306.

Isomerisation of tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione(73) with Rhodium chloride trihydrate:

A solution of bis-enone 73 (530 mg, 3.05 mmoles) and rhodium chloride trihydrate (37 mg, 0.15 mmole) in 10 ml of absolute ethanol was heated in a sealed corning glass tube (capacity 20 ml) to 105°C (±3°) for 20 hr. The sealed tube was cooled, carefully opened and filtered through a short celite column. The GLC analysis of the crude mixture indicated 70% conversion to a mixture of three products in the ratio of 12:2:1. The total mixture was charged on a silica gel (15 g) column and chromatographed. Careful elution with 10% ethyl acetate-benzene and pooling of appropriate fractions (monitored by TLC) furnished the two minor products.

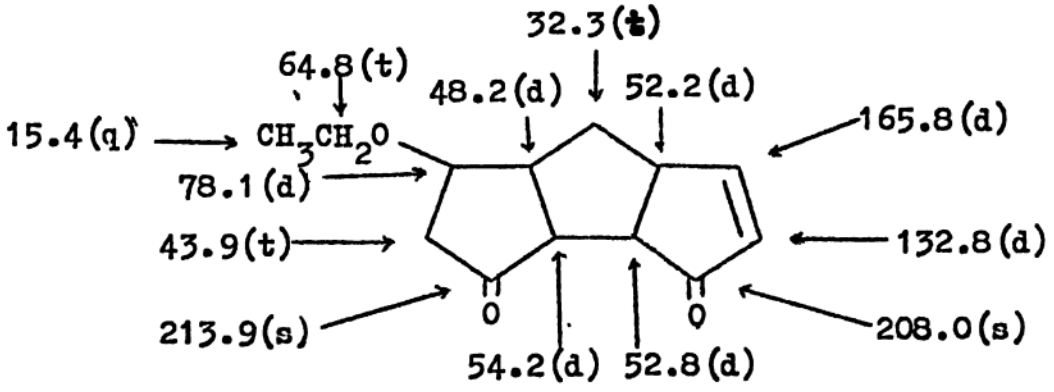
The first product (35 mg, 10%) was bulb to bulb distilled (120°C/1 mm) and characterised as tricyclo[6.3.0.$0^{2,6}$] undec-4-en-3,11-dione (88) by comparison (TLC and IR spectrum) with the partially hydrogenated product of bis-enone 73.

The second minor product (20 mg, 4%) was bulb to bulb distilled (150°C/1 mm) and characterised as 9-ethoxy tricyclo [6.3.0.$0^{2,6}$]undec-4-en-3,11-dione (97).

IR spectrum (neat), ν_{max}: 1745 (cyclopentanone), 1705 and 1585 cm^{-1} (cyclopentenone).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ7.57(1H,dd,J_1=6Hz, J_2=3Hz,-C<u>H</u>=CH-C=O), 6.03(1H,dd,J_1=6Hz,J_2=2Hz,-CH=C<u>H</u>-C=O), 3.78(1H,td,J_1=6Hz,J_2=5Hz,<u>H</u>C-OEt), 3.43(2H,q,J=7Hz,-OC<u>H_2</u>CH_3), 1.3-3.6(8H,m,ring CH), 1.18(3H,t,J=7Hz,-OCH_2C<u>H_3</u>).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ213.9, 208.0, 165.8, 132.8, 78.1, 64.8, 54.2, 52.8, 52.2, 48.2, 43.9, 32.3, 15.4. The assignments and multiplicities are displayed on the structure shown below.



97

Analysis for $C_{13}H_{16}O_3$ Calcd: C,70.89; H,7.32.
Found: C,70.63; H,7.34.

Elution of the column with 40% ethyl acetate-benzene furnished 150 mg of the starting bis-enone 73, which was

identified by comparison (TLC, GLC and IR spectrum) with authentic sample. Final elution of the column with ethyl acetate furnished 240 mg (70%) of the isomerised bis-enone, tricyclo[6.3.0.$0^{2,6}$]undeca-1(8),4-dien-3,11-dione (96), which was crystallised from carbon tetrachloride, mp.102-3°C.

UV spectrum, λ_{max}^{MeOH}: 218 (ε = 13,100), 242(sh) nm (ε = 5,640).

IR spectrum (KBr), ν_{max}: 1708, 1595 (-CH=CH-C=O), 1695 and 1625 cm^{-1} (-C=C-C=O).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ7.58(1H,dd,J_1=6Hz, J_2=3Hz,-CH=CH-C=O), 6.1(1H,dd,J_1=6Hz,J_2=2Hz,-CH=CH-C=O), 4.04(1H,m,H_2), 3.56(1H,m,H_6), 1.9-3.15(6H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.I.10): δ205.5 (s,-CH=CH-C=O), 201.7(s,-C=C-C=O), 185.1(s,-C=C-C=O), 165.1 (d,-CH=CH-C=O), 143.8(s,-C=C-C=O), 132.2(d,-CH=CH-C=O), 50.4(d,C_2), 49.7(d,C_6), 40.6(t,C_{10}), 35.3(t,C_7), 25.7(t,C_9).

Analysis for $C_{11}H_{10}O_2$ Calcd: C,75.84; H,5.79.
Found: C,75.49; H,5.45.

Tricyclo[6.3.0.$0^{2,6}$]undec-1(8)-en-3,11-dione(100):

A solution of isomerised bis-enone 96 (350 mg, 2 mmoles) was hydrogenated over 10% Pd-C (15 mg) catalyst at 1 atmosphere for 20 min. Catalyst was removed by fil-

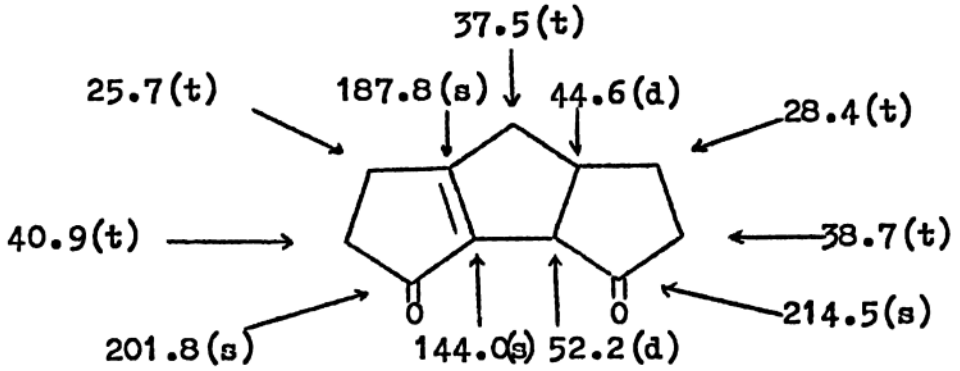
tration and the filtrate concentrated. Crystallisation from carbon tetrachloride furnished the partially hydrogenated compound 100 (350 mg) in quantitative yield, mp.74-6°:

UV spectrum, λ_{max}^{MeOH}: 242 nm (ε = 7,000).

IR spectrum (KBr), ν_{max}: 1735 (cyclopentanone), 1695 and 1625 cm^{-1} (cyclopentenone).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ3.4(2H,brs,bridgehead CH), 1.6-3.5(10H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ214.5, 201.8, 187.8, 144.0, 52.2, 44.6, 40.9, 38.7, 37.5, 28.4, 25.7. The assignments and multiplicities are displayed on the structure shown below.



100

Analysis for $C_{11}H_{12}O_2$ Calcd: C,74.98; H,6.86.
Found: C,74.69; H,6.85.

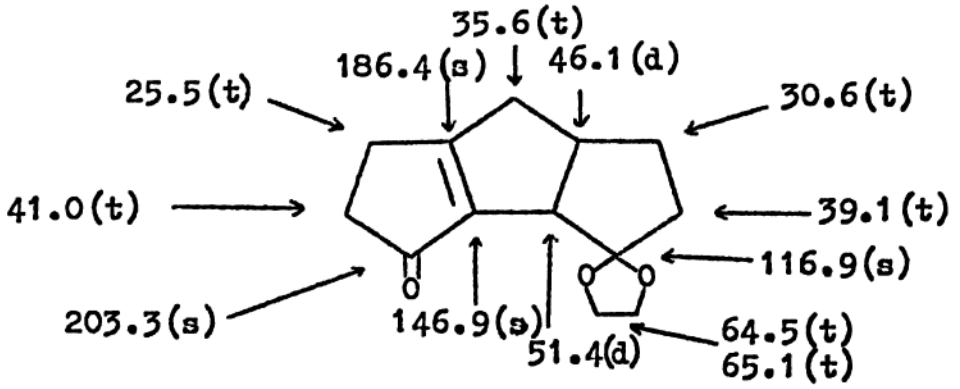
Tricyclo[6.3.0.$0^{2,6}$]undec-1(8)-en-3,11-dione-3-ethylene ketal(101):

A solution of partially hydrogenated compound 100 (350 mg, 2 mmoles), ethanediol (0.5 ml) and p-toluenesulphonic acid (5 mg) in 30 ml of benzene was refluxed with a Dean-Stark water separator for 15 min. The reaction mixture was diluted with benzene (30 ml), washed with aqueous $NaHCO_3$ and dried. Evaporation of the solvent furnished 375 mg (85%) of the monoketal 101, and was crystallised from pet ether, mp.68-9°C.

IR spectrum (KBr), ν_{max}: 1690 and 1640 cm^{-1} (cyclopentenone).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ3.6-4.2(4H,m, $-OCH_2CH_2O-$), 2.8-3.5(3H,m), 2.2-2.8(5H,m), 1.0-2.2(4H,m).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ203.3, 186.4, 146.9, 116.9, 65.1, 64.5, 51.4, 46.1, 41.0, 39.1, 35.6, 30.6, 25.5. The assignments and multiplicities are displayed on the structure shown below.



101

Analysis for $C_{13}H_{16}O_3$ Calcd: C,70.89; H,7.32.
Found: C,70.67; H,7.37.

11-Methyl tricyclo[6.3.0.$0^{2,6}$]undeca-2(6),10-dien-3,9-dione (103):

To a magnetically stirred suspension of magnesium (61 mg, 0.0025 g atom) in 7 ml of dry ether was added dropwise a solution of methyl iodide (500 mg, 3.5 mmole) in 3 ml of dry ether. The mixture was stirred until all the magnesium had dissolved. The methylmagnesium iodide was syringed out and injected into a magnetically stirred solution of tricyclo [6.3.0.$0^{2,6}$]undeca-1(8),4-dien-3,11-dione (96, 350 mg, 2 mmoles) in 5 ml of dry THF and 15 ml of dry ether. The reaction mixture was stirred vigorously for 30 min at room temperature and then quenched by careful addition of saturated NH_4Cl solution. The organic layer was separated and the aqueous phase was extracted with dichloromethane (20 ml x 2). The combined organic extracts were washed and dried. Evaporation of the solvent furnished 500 mg of crude material, which was taken in 5 ml of dichloromethane and added to a magnetically stirred suspension of pyridinium chlorochromate (430 mg, 2 mmoles)[65] in 5 ml of dichloromethane. The heterogeneous reaction mixture was stirred vigorously for 4 hr at room temperature and then charged on a silica gel (20 g) column and chromatographed. Elution with 20% ethyl acetate-benzene furnished 82 mg (30%) of transposed bis-enone 103

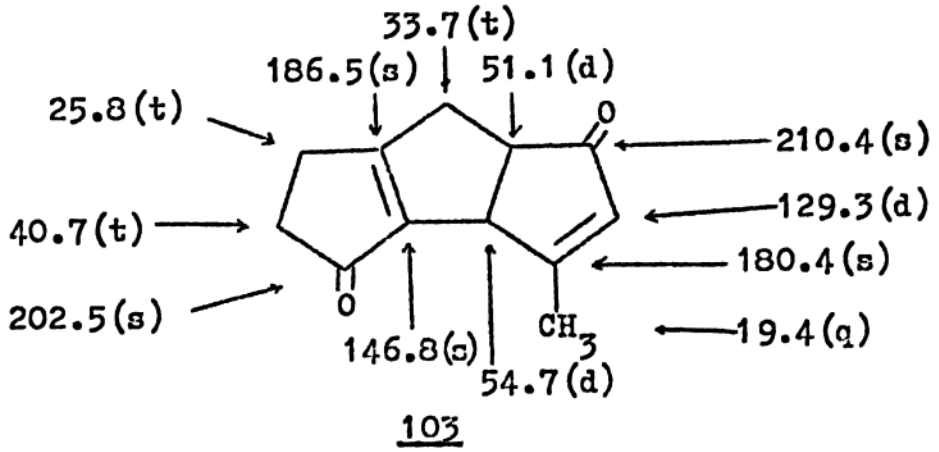
and was crystallised from dichloromethane-pet ether as white needles, mp.108-10°C.

UV spectrum, λ_{max}^{MeOH}: 223 (ε = 23,400), 240 nm (merged, ε = 8,700).

IR spectrum (KBr), ν_{max}: 1685 (carbonyl), 1638 and 1615 cm^{-1} (olefinic).

^{1}H NMR spectrum (100 MHz, $CDCl_3$): δ5.8(1H,s,olefinic), 3.88(1H,brs) and 3.52(1H,m), bridgehead CH, 2.08-3.1(6H,m, ring CH), 2.3(3H,s,$\underline{CH}_3$-$\dot{C}$=CH-$\dot{C}$=O).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ210.4, 202.5, 186.5, 180.4, 146.8, 129.3, 54.7, 51.1, 40.7, 33.7, 25.8, 19.4. The assignments and multiplicities are displayed on structure shown below.



103

Analysis for $C_{12}H_{12}O_2$ Calcd: C,76.57; H,6.43.
Found: C,76.18; H,6.23.

Tricyclo[6.3.0.$0^{2,6}$]undeca-1(8),4-dien-3,11-dione(96):

A solution of bis-enone 73 (1 g, 5.75 mmoles) in DPE (10 ml) was refluxed (260°C) for 30 min. The solution was diluted with benzene (10 ml), charged on a silica gel (20 g) column and chromatographed. Diphenyl ether was removed first by eluting with benzene. Elution of the column with 40% ethyl acetate-benzene furnished 100 mg (10%) of starting bis-enone 73.

Final elution of the column with ethyl acetate furnished 720 mg (72%) of the isomerised bis-enone 96, which was identified by comparison (TLC, GLC and IR spectrum) with the sample obtained in the $RhCl_3.3H_2O$ isomerisation of bis-enone 73.

Thermal equilibration of tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione(73); Isolation of cis, anti, cis-tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione(104):

A solution of bis-enone 73 (1 g, 5.75 mmoles) in 5 ml of benzyl benzoate was maintained at 305°C in a salt bath for 3 min. GLC analysis of the mixture indicated the presence of three components in the ratio of 1:2:12. The reaction mixture was diluted with dichloromethane (10 ml) and charged on a silica gel (20 g) column and chromatographed. Benzyl benzoate was eliminated by elution with dichloromethane. Further elution of the column with 20% ethyl acetate-benzene furnished 20 mg (2%) of the cis, anti, cis-bis-enone 104,

which was crystallised from dichloromethane-hexane, mp.99-100°C.

UV spectrum, λ_{max}^{MeOH}: 222 nm (ε = 12,500).

IR spectrum (KBr), ν_{max}: 1715 sh, 1695, 1580 cm^{-1} (cyclopentenone).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.I.11): δ7.62(2H, dd,J_1=6Hz,J_2=3Hz,-CH=CH-C=O), 6.08(2H,dd,J_1=6Hz,J_2=2Hz, -CH=CH-C=O), 3.45(2H,m,H_6 and H_8), 2.93(2H,d,J=6Hz,H_1 and H_2), 1.88(2H,t,J=8Hz).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.I.12): δ209.6 (s,C=O), 166.3(d,-CH=CH-C=O), 132.2(d,-CH=CH-C=O), 52.9(d, C_1 and C_2), 48.1(d,C_6 and C_8), 34.9(t,C_7).

Further elution of the column with 40% ethyl acetate-benzene furnished 10 mg of the starting bis-enone 73 and final elution of the column with ethyl acetate furnished 720 mg (72%) of the isomerised bis-enone 96, which was identified by comparison (TLC, IR spectrum, GLC) with the sample obtained earlier.

11-Methyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-dione(111):

To a magnetically stirred suspension of magnesium (365 mg, 0.015 g atom) in 15 ml of dry ether was added dropwise a solution of methyl iodide (4.54 g, 32 mmoles) in 5 ml of dry

ether. The mixture was stirred at room temperature until all the magnesium had dissolved. The methylmagnesium iodide was syringed out and injected slowly into a magnetically stirred solution of the bis-enone 73 (2 g, 11.5 mmoles) in 20 ml of dry THF. The reaction mixture was stirred for 20 min at room temperature and quenched by careful addition of saturated NH_4Cl solution. The organic layer was separated and the aqueous phase was extracted with dichloromethane (50 ml x 2). The combined organic extract was washed and dried. Evaporation of the solvent furnished 3 g of crude material containing approximately 30% of the lactol 109. An analytical sample of the lactol 109 (in equilibrium with its open ketol form 110) was prepared by chromatographing the crude lactol on a silica gel column and elution with 15% ethyl acetate-benzene. The product was crystallised from dichloromethane-pet ether, mp.100-3°C.

IR spectrum (KBr), ν_{max}: 3400 (hydroxyl), 1710(weak), 1690(weak) (cyclopentenone), 1620 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$, mixture of 110 and 109 in the ratio of 1:7): δ7.6(dd,J_1=6Hz,J_2=3Hz,-CH=CH-C=O), 6.18(brs,-OH), 5.96(dd,J_1=6Hz,J_2=2Hz,-CH=CH-C=O), 5.68(1H, ½AB,J=6Hz), 5.5(1H,½AB,J=6Hz), 5.3(1H,½AB,J=6Hz) and 5.14 (1H,½AB,J=6Hz), olefinic, 3.88(1H,brs,-OH), 2.7-3.3(4H,m, bridgehead CH), 1.76(2H,brs,CH_2), 1.46(3H,s,CH_3), 1.33(s, -CH=CH-C(OH)-CH_3).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ139.1(d), 136.3 (d), 134.7(d) and 133.0(d), olefinic C's,, 119.9(s,$>C<^{OH}_{O-}$), 97.0(s,$CH_3-\underline{C}-O$), 60.2(d), 57.9(d), 51.4(d) and 50.3(d), bridgehead C's, 34.3(t,CH_2), 26.8(q,CH_3).

The crude lactol 109 (3 g) obtained above was taken in 15 ml of dichloromethane and added to a magnetically stirred suspension of pyridinium chlorochromate (3 g, 14 mmoles)[65] in 10 ml of dichloromethane. The heterogeneous reaction mixture was stirred vigorously for 4 hr at room temperature and filtered through a silica gel (20 g) column with large volume of dichloromethane. Evaporation of the solvent furnished 650 mg (30%) of the single transposed bis-enone 111, and was recrystallised from dichloromethane-pet ether as white flakes, mp.105-6°C.

UV spectrum, λ^{MeOH}_{max}: 223 (ε = 14,900), 315 nm (ε = 140).

IR spectrum (CH_2Cl_2), ν_{max}: 1710 (carbonyl), 1618 (trisubstituted olefin), 1590 cm^{-1} (disubstituted olefin).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.I.13): δ7.46(1H, dd,J_1=6Hz,J_2=3Hz,-$\underline{H}$C=CH-$\dot{C}$=O), 5.84(1H,dd,J_1=6Hz,J_2=2Hz,-HC=C$\underline{H}$-$\dot{C}$=O), 5.7(1H,brs,$CH_3-\dot{C}=C\underline{H}-\dot{C}=O$), 3.2-3.65(2H,m,bridgehead CH), 2.7-3.2(2H,m,bridgehead CH), 1.8-2.4(2H,m,CH_2), 2.24 (3H,s,$C\underline{H}_3-\dot{C}=CH-\dot{C}=O$).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.I.14): δ210.4

(s) and 209.0(s), >C=O , 178.4(s,CH_3-$\underline{C}$=CH-$\underline{C}$=O), 168.1(d,-$\underline{CH}$=CH-$\underline{C}$=O), 133.6(d,-CH=$\underline{CH}$-$\underline{C}$=O), 129.6(d,CH_3-$\underline{C}$=$\underline{CH}$-$\underline{C}$=O), 57.1(d) 52.5(d), 51.9(d) and 51.3(d), bridgehead C's, 27.7(t,CH_2), 20.5(q,CH_3).

Mass spectrum: m/e 188; Mol. Wt. ($C_{12}H_{12}O_2$): 188.

Analysis for $C_{12}H_{12}O_2$ Calcd: C,76.57; H,6.43.
Found: C,76.54; H,6.6.

Thermolysis of 11-methyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-dione(111):

A solution of single transposed bis-enone 111 (15 mg, 0.08 mmole) in 1 ml of benzyl benzoate was maintained at a temperature of 290°C in a salt bath for 30 min. The reaction mixture was diluted with benzene (5 ml) and charged on a silica gel (5 g) column. Benzyl benzoate was removed by elution with benzene. Further elution of the column with 20% ethyl acetate-benzene furnished 12 mg (80%) of the isomerised bis-enone 103, which was identified by comparison (TLC, IR spectrum) with the sample obtained by the alkylative transposition of the isomerised bis-enone 96.

Alkylative transposition reaction of tricyclo[6.3.0.$0^{2,6}$] undeca-4,9-dien-3,11-dione(73) with excess methylmagnesium iodide and PCC oxidation:

To a magnetically stirred suspension of magnesium (850 mg, 0.035 g atom) in 10 ml of dry ether was added dropwise a solution of methyl iodide (7.1 g, 50 mmoles) in 10 ml

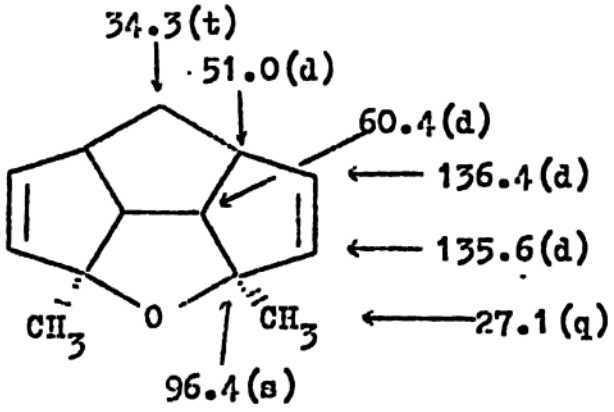
of dry ether. The mixture was stirred until all the magnesium had dissolved. To this solution of methylmagnesium iodide was added dropwise a solution of bis-enone 73 (1 g, 5.75 mmoles) in 10 ml of dry THF over a period of 10 min. The reaction mixture was stirred vigorously at room temperature for 20 min and then quenched by careful addition of saturated NH_4Cl solution. Extraction with ether (25 ml x 3), washing, drying and evaporation of the solvent furnished 1.2 g of crude material which was directly used for the next oxidation step.

The crude mixture obtained above (1.2 g) was dissolved in 10 ml of dichloromethane and added to a magnetically stirred suspension of pyridinium chlorochromate (1.5 g, 7 mmoles)[65] in 10 ml of dichloromethane. The heterogeneous reaction mixture was stirred vigorously at room temperature for 4 hr and filtered through a silica gel (10 g) column. Evaporation of the solvent furnished 1 g of crude material which showed the presence of several components (TLC). This material was charged on a silica gel (25 g) column and chromatographed. Elution with benzene furnished 80 mg (8%) of 4,6-dimethyl 5-oxatetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodecane 113, and was bulb to bulb distilled (95°C/0.5 mm).

IR spectrum (neat), ν_{max}: 3050, 1620 and 750 cm^{-1} (olefinic).

^{1}H NMR spectrum (100 MHz, $CDCl_3$): δ5.42(2H,½AB,J=6Hz, HC=CH), 5.19(2H,½AB,J=6Hz,HC=CH), 3.04(4H,brs,bridgehead CH), 1.75(2H,m,CH_2), 1.37(6H,s,CH_3).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ136.4, 135.6, 96.4, 60.4, 51.0, 34.3, 27.1. Assignments and multiplicities are displayed on structure shown below.



113

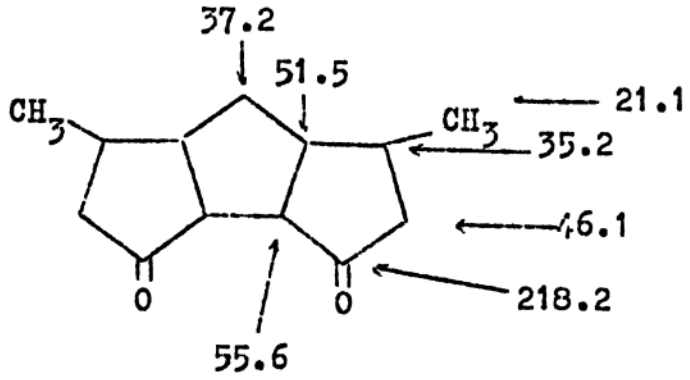
Analysis for $C_{13}H_{16}O$ Calcd: C,82.94; H,8.57.
Found: C,82.78; H,8.73.

Elution of the column with 10% ethyl acetate-benzene and careful pooling of appropriate fractions (monitored by TLC) furnished two more purified products. The less polar product 80 mg (7%) was bulb to bulb distilled (140°C/1 mm) and characterised as 5,9-dimethyl tricyclo[6.3.0.$0^{2,6}$] undeca-3,11-dione (114) (GLC indicated only 80% purity).

IR spectrum (neat), ν_{max}: 1745 cm^{-1} (cyclopentanone)

^{1}H NMR spectrum (100 MHz, $CDCl_3$): δ1.0-3.2(12H,m, ring CH), 1.08(6H,d,J=6Hz,CH_3).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ218.2, 55.6, 51.5, 46.1, 37.2, 35.2, 21.1. Assignments are displayed on the structure shown below



114

The more polar, major product 760 mg (65%) was also bulb to bulb distilled (160°C/1 mm), and solidified on refrigeration. This compound was characterised as 5,11-dimethyl tricyclo[6.3.0.$0^{2,6}$]undec-10-en-3,9-dione (115) on the basis of spectral data.

UV spectrum, λ_{max}^{MeOH}: 234 nm (ε = 8,300).

IR spectrum (neat), ν_{max}: 1738 (cyclopentanone), 1700 and 1615 cm^{-1} (cyclopentenone).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ5.84(1H,brs,olefinic), 3.56(1H,dd,J_1=11Hz,J_2=7Hz,H_1), 3.04(2H,m,bridgehead CH), 1.6-2.8(6H,m,ring CH), 2.2(3H,s,$C\underline{H}_3$-$\dot{C}$=CH-$\dot{C}$=O), 1.04 (3H,d,J=6Hz,CH_3).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ218.7(s,cyclopentanone), 211.4(s,cyclopentenone), 179.5(s,CH_3-$\underline{\dot{C}}$=CH-$\dot{C}$=O),

130.9(d,CH_3-$\dot{C}$=$\underline{C}$H-$\dot{C}$=O), 55.0(d), 54.6(d), 54.0(d) and 53.5 (d), bridgehead C's , 46.7(t,C_4), 34.5(d,C_7), 30.6(t,C_5), 20.1(q,CH_3), 19.8(q,CH_3).

Analysis for $C_{13}H_{16}O_2$ Calcd: C,76.44; H,7.90.
Found: C,76.46; H,7.42.

4,6-Dimethyl 5-oxatetracyclo[7.2.1.$O^{4,11}$.$O^{6,10}$]dodec-7-en-2-one(116):

To a magnetically stirred suspension of lithium dust (8.4 mg, 0.0012 g atom) in 3 ml of dry ether was added a solution of methyl iodide (200 mg, 1.6 mmoles) in 3 ml of dry ether. The reaction mixture was stirred until all the lithium had dissolved. The methyllithium solution was syringed out and injected into an ice cold solution of single transposed bis-enone 111 (95 mg, 0.5 mmole) in dry THF (2 ml)-dry ether (2 ml) mixture with magnetic stirring. The cooling bath was removed and the reaction mixture was stirred for 30 min at room temperature. The reaction was quenched by addition of 1 ml of 20% HCl, diluted with water (10 ml) and extracted with ether (20 ml x 2). The ether extract was washed and dried. Evaporation of the solvent furnished 80 mg of a crude material, which on filtration through a short silica gel (5 g) column in 5% ethyl acetate-benzene followed by bulb to bulb distillation (120°C/1 mm) furnished 46 mg (45%) of the oxatetraquinane 116.

IR spectrum (neat), ν_{max}: 1740 (carbonyl), 3050 and 1620 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.I.15): δ5.46(2H, ABquartet,J=6Hz,olefinic), 3.1(3H,m,bridgehead CH), 1.8-2.9 (5H,m,ring CH), 1.55(3H,s,CH_3), 1.4(3H,s,CH_3).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.I.16): δ220.9 (s,C=O), 138.8(d,HC=CH), 135.9(d,CH=CH), 96.1(s,C_6), 85.2(s, C_4), 60.6(d), 60.1(d), 54.8(d) and 50.1(d), bridgehead C's, 53.9(t,C_3), 37.5(t,C_{12}), 30.0(q,CH_3), 25.8(q,CH_3).

Analysis for $C_{13}H_{16}O_2$ Calcd: C,76.44; H,7.90.
Found: C,76.12; H,8.23.

4-Methyl 5-oxatetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodecan-2-one(117):

To a magnetically stirred solution of single transposed bis-enone 111 (47 mg, 0.25 mmole) in 5 ml of methanol was added, in small portions, sodium borohydride (27 mg, 0.73 mmole) over a period of 3 min. The reaction mixture was stirred overnight. Most of the methanol was removed under reduced pressure and the contents of the flask were diluted with water (10 ml) and extracted with dichloromethane (15 ml 2). The organic extract was washed and dried. Evaporation of the solvent furnished 48 mg of a crude hydroxy compound.

IR spectrum (neat), ν_{max}: 3420 cm^{-1}.

The above alcohol was taken in 3 ml of dichloromethane

and added to a magnetically stirred suspension of pyridinium chlorochromate (100 mg, 0.48 mmole)[65] in 4 ml of dichloromethane. The suspension was stirred vigorously at room temperature for 2 hr and filtered through a small silica gel (5 g) column. Evaporation of the solvent and bulb to bulb distillation (100°C/1 mm) furnished 40 mg (80%) of the oxatetraquinane 117.

IR spectrum (neat), ν_{max}: 1740 cm^{-1} (carbonyl).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ4.4(1H,brs,HC-O-), 1.2-3.4(12H,m,ring CH), 1.35(3H,s,CH_3).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ218.5(s,C=O), 87.3(s,CH_3-C-O-), 84.4(d,CH-O-), 58.0(d), 57.5(d), 55.8(d) and 46.5(d), bridgehead C's, 52.6(t,C_3), 34.7(t), 34.2(t), 30.9(t), 23.8(q,CH_3).

Analysis for $C_{12}H_{16}O_2$ Calcd: C,74.97; H,8.39.
Found: C,75.03; H,8.37.

3,4,10,11-Tetramethyl cis, anti, cis-tricyclo[6.3.0.$0^{2,6}$]undeca-3,10-dien-5,9-dione(119):

To a magnetically stirred suspension of magnesium (100 mg, 0.0041 g atom) in 5 ml of dry ether was added a solution of methyl iodide (850 mg, 6 mmoles) in 5 ml of dry ether. The reaction mixture was stirred at room temperature until all the magnesium had dissolved. To this solution of methylmagnesium iodide was added, dropwise, a solution of

4,10-dimethyl cis, anti, cis-tricyclo[6.3.0.$0^{2,6}$]undeca-4,[illegible]-dien-3,11-dione (118, 100 mg, 0.5 mmole) in 3 ml of dry T[illegible]. The reaction mixture was stirred at room temperature for [illegible] min and quenched by careful addition of saturated NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with dichloromethane (15 ml x 2). The combined organic extract was washed and dried. Evaporation of the solvent furnished 120 mg of a crude alcohol.

IR spectrum (neat), ν_{max}: 3400 cm^{-1}.

The crude alcohol was taken in 5 ml of dichloromethane and added to a magnetically stirred suspension of pyridinium chlorochromate (215 mg, 1 mmole) in 5 ml of dichloromethane. The heterogeneous reaction mixture was stirred vigorously at room temperature for 2 hr and filtered through a short silica gel (10 g) column. Evaporation of the solvent furnished 57 mg (50%) of the double transposed bis-enone 119, which was crystallised from dichloromethane-pet ether, mp.112-13°C.

UV spectrum, λ_{max}^{MeOH}: 238 nm (ε = 21,000).

IR spectrum (KBr), ν_{max}: 1695 and 1640 cm^{-1} (cyclopentenone).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.I.17): δ2.6-3.1 (4H,en,bridgehead CH), 2.14(3H,s,$C\underline{H}_3$-$\dot{C}$=$\dot{C}$(CH_3)-$\dot{C}$=O), 2.07(2H, t,J=8Hz,CH_2), 1.68(3H,s,CH_3-$\dot{C}$=$\dot{C}$($C\underline{H}_3$)-$\dot{C}$=O).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.I.18): δ209.8 (s,C=O), 168.7(s,CH_3-$\underline{C}$=$\dot{C}$(CH_3)-$\dot{C}$=O), 135.0(s,CH_3-$\dot{C}$=$\underline{\dot{C}}$(CH_3)-$\dot{C}$=O), 52.1(d,C_6 and C_8), 51.7(d,C_1 and C_2), 29.9(t,C_7), 15.7(q, $\underline{C}H_3$-$\dot{C}$=$\dot{C}$(CH_3)-$\dot{C}$=O), 8.2(q,CH_3-$\dot{C}$=$\dot{C}$($\underline{C}H_3$)-$\dot{C}$=O).

Analysis for $C_{15}H_{18}O_2$ Calcd: C,78.23; H,7.88.
Found: C,77.92; H,8.01.

Reaction of tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione(73) with sodium methoxide:

To an ice cold magnetically stirred solution of bis-enone 73 (175 mg, 1 mmole) in 5 ml of absolute methanol was added sodium methoxide (200 mg, 3.6 mmoles) in small portions over a period of 5 min. The cooling bath was removed and the reaction mixture was stirred at room temperature for 10 min. Most of the methanol was removed under reduced pressure and the reaction mixture was diluted with water (15 ml). Acidification with dilute HCl, extraction with dichloromethane (15 ml x 3) and usual work-up furnished 170 mg of crude material. This material was charged on a silica gel (10 g) column and chromatographed. Careful elution with 20% ethyl acetate-benzene furnished 65 mg (32%) of 11-methoxy tetracyclo[5.4.0.$0^{3,10}$.$0^{4,8}$]undeca-2,5-dione (120), and was crystallised from dichloromethane-pet ether, mp.148-9°C.

IR spectrum (KBr), ν_{max}: 1745 cm^{-1} (carbonyl).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.I.19): δ3.52(1H,

s,$\underline{H}C$-OCH_3), 3.29(3H,s,-$OC\underline{H}_3$), 2.84(3H,brs,bridgehead CH), 2.65(3H,brs,bridgehead CH), 2.3(2H,m,$C\underline{H}_2$-$\dot{C}$=O), 1.9-2.2(2H, m,CH_2).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.I.20): δ214.5(s) and 211.4(s),>C=O , 83.1(d,$\underline{C}H$-OCH_3), 64.6(d), 57.7(d), 55.5 (q,-OCH_3), 51.7(d), 47.3(d), 45.6(t,-$\underline{C}H_2$-$\dot{C}$=O), 41.0(d), 39.6 (d), 36.1(t,C_9).

Analysis for $C_{12}H_{14}O_3$ Calcd: C,69.89; H,6.84.
Found: C,69.95; H,6.74.

Further elution of the column with 40% ethyl acetate-benzene furnished 35 mg of the unreacted starting material. Final elution of the column with ethyl acetate furnished 42 mg (30%) of tricyclo[6.3.0.$0^{2,6}$]undeca-1(8),4-dien-3,11-dione (96) which was identified by comparison (TLC, GLC and IR spectrum) with the sample obtained in the $RhCl_3.3H_2O$ isomerisation of starting bis-enone 73.

2,3,8,10-Tetrachloro, 1(or 11),7-dimethoxy 12-oxapentacyclo [6.4.0.$0^{2,6}$.$0^{3,11}$.$0^{4,9}$]dodecan-11(or-1)-ol(121):

To an ice cold magnetically stirred solution of tetrachloro bis-enone 83 (500 mg, 1.6 mmoles) in 15 ml of absolute methanol was added in small portions sodium methoxide (200 mg, 3.6 mmoles) over a period of 5 min. Most of the methanol was removed under reduced pressure, diluted with water, acidified with dilute HCl and extracted with dichloromethane (30 ml x 2).

The organic extract was washed and dried. Evaporation of the solvent and filtration through a small silica gel (5 g) column using 5% ethyl acetate-benzene furnished 400 mg (65%) of 2,3,8,10-tetrachloro, 1(or 11),7-dimethoxy 12-oxapentacyclo[6.4.0.$0^{2,6}$.$0^{3,11}$.$0^{4,9}$]dodecan-11(or-1)-ol (121), and was crystallised from dichloromethane-pet ether, mp.207°C.

IR spectrum (KBr), ν_{max}: 3390 cm^{-1} (hydroxyl).

^{1}H NMR spectrum (270 MHz, $CDCl_3$, Fig.I.21): δ5.06(1H, s,exchanged with D_2O,-OH), 4.0((1H,d,J=3.3Hz,HC-Cl), 3.63(3H, s,-OCH_3), 3.55(3H,s,-OCH_3), 3.25(1H,s,HC-OCH_3), 2.82(1H,t, J=3.3Hz,H_9), 2.75(1H,dd,J_1=7Hz,J_2=2.5Hz), 2.5-2.7(1H,m), 2.54 (1H,m), 1.89(1H,dd,J_1=12.5Hz,J_2=1.1Hz).

^{13}C NMR spectrum (25.0 MHz, Acetone-d_6, Fig.I.22): δ109.6(s,>C<(O-)(O-CH_3)), 105.2(s,>C<(O-)(OH)), 91.2(d,CH-OCH_3), 86.9(s), 83.8 (s) and 69.9(s),C-Cl , 59.9(d), 59.1(d), 55.1(q?), 52.8(q, -OCH_3), 51.1(d), 50.4(d), 35.5(t,CH_2).

Analysis for $C_{13}H_{14}Cl_4O_4$ Calcd: C,41.49; H,3.72.
Found: C,41.46; H,3.69.

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CHAPTER II

SYNTHESIS OF PENTACYCLO [5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]UNDECANES: A NOVEL TRISHOMOCUBANE SYSTEM

II.1 ABSTRACT

A novel synthetic approach to the pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undecane system is delineated. The key step in the synthesis is the efficient intramolecular $_{\pi}2_{s}$ + $_{\pi}2_{s}$ photocycloaddition of triquinane based bis-enones 24, 29, 36 and 42 to 2-substituted pentacyclic diones 43-46. The precursor alkylated bis-enones 24, 29, 36 and 42 were obtained in a two step sequence, involving alkylative enone transposition, from the symmetrical bis-enone 7.

The 2-substituted pentacyclic diones 43, 45 and 46 undergo facile acid catalysed reversal to the bis-enones 24, 36 and 42 in high yield and under gentle, ambient conditions.

The efficient photocycloaddition of the triquinane system 22 to the considerably strained pentacyclic framework 47 and its mild reversal back to 22, points to the potential of this system for the storage of solar energy.

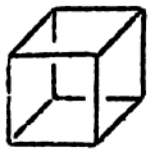
II.2 INTRODUCTION

Molecular design and rearrangements of strained polycyclic compounds have been areas of intense activity and sustained fascination in recent years.[1] This high level of interest in the bridged carbocyclic systems emanated from a variety of considerations. For example, many carbocyclic systems possess interesting shapes and symmetries, reminiscent of familiar objects in daily life (e.g., cube,[2] prism,[3] window,[4] etc.) and constitute an enticing arena for the creativity of synthetic organic chemists. Some of these bridged cyclic systems are also strained, and highly prone to a variety of carbonium ion, thermal, photochemical and transition metal catalysed rearrangements.[5] These rearrangements have often provided mechanistic insight into many intriguing reactions, served as probes for investigating 'structure-activity' relationships[6] and helped to complement, contradict or confirm the existing theoretical predictions. More recently, strained polycyclic frames have attracted attention as the 'storehouse' for storage of solar energy in the form of energy rich chemical bonds.[7]

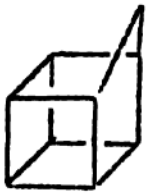
Among the various types of small strained carbocycles, those belonging to the cubane 'cage' family are of special interest on several counts. Besides cubane (1), other members of this family having 8 to 11 carbon atoms are simply derived through insertion of one or more carbon atoms into any of the bonds of the parent cubane (1). Some representative examples[8,9] of homologous cubanes (1-6) derived in this manner are displayed in Chart II.1. Many of these homocubanes have been synthesised in recent years, duly characterised and several facets of their chemical reactivity explored.[5,8,9] However, for many years until the dawn of sixties, investigation of these interesting systems was hampered due to the formidable synthetic challenge associated with the construction of these molecules. Indeed, construction of multiple cyclobutane bonds in a polycyclic frame was an odious task and a major impediment to the conquest of these molecules. But, with the advent and discovery of facile intramolecular $_{\pi}2_s + _{\pi}2_s$ photocycloadditions,[10] a way was cleared for the rational and expeditious acquisition of these caged, space-enclosing polycyclic systems. The preparative ease and efficacy, as well as apparent generality of these intramolecular photocycloadditions did much to rekindle interest in this exciting arena.

In the previous chapter of this thesis, a facile intramolecular $_{\pi}2_s + _{\pi}2_s$ photocycloaddition of C_{11}-bis-enone 7 to the pentacyclic dione 8, formally a trishomocubane system,

CHART II.1



1



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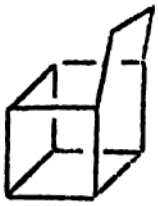
3



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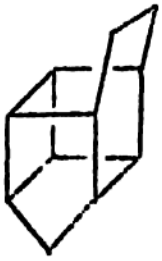

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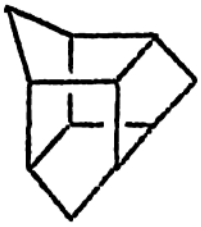


6

Nomenclature:

1. Cubane: Pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane.[8]

2. Homocubane: Pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane.[8]

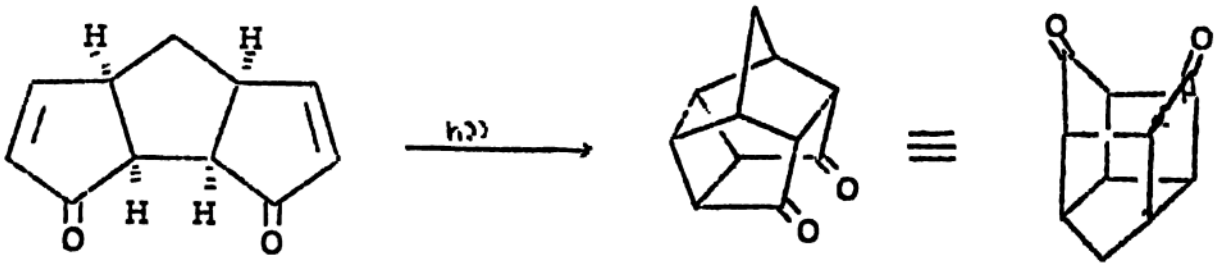
3. 1,3-Bishomocubane: Pentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane.[8]

4. 1,1'-Bishomocubane: Pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$] decane.[8]

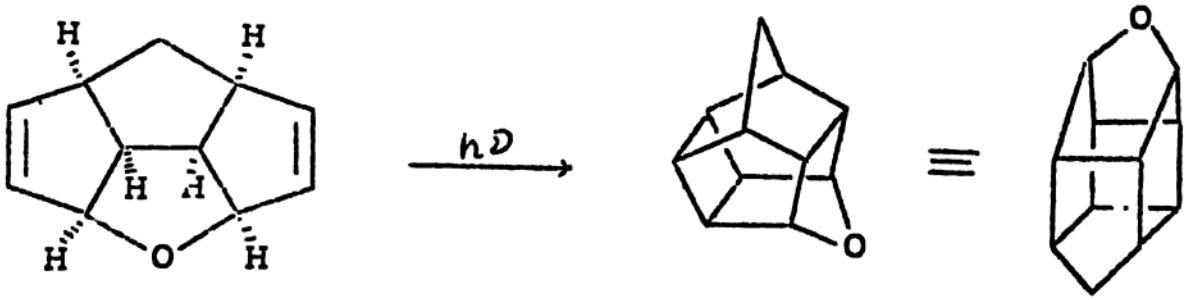
5. 1,1,3-Trishomocubane: Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$] undecane.

6. D_3-Trishomocubane: Pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$] undecane.[9]

has been described. Several other examples of intramolecular photocycloaddition of cis, syn, cis-triquinanes with identical disposition of olefinic bonds, e.g. 9 → 10, have been encountered in this laboratory.[11] A natural extension of



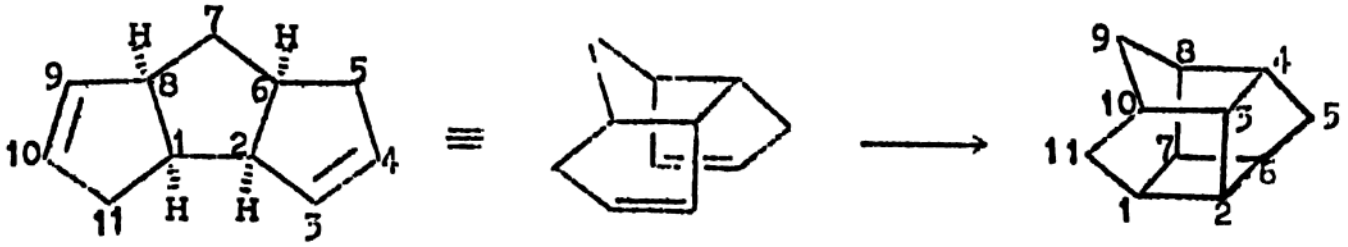
7 8



9 10

these observations was the possibility of generating new pentacyclic C_{11}-trishomocubanes through intramolecular photocycloaddition of triquinane based olefinic precursors having different disposition of double bonds in the cis, syn, cis-tricyclic frame. For example, relocation of double bonds (Δ^3 and Δ^9) in all cis-triquinane frame as in 11 (Scheme II.1), on photolysis would lead to pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$] undecane (12). Similarly, further relocation (Δ^3 and Δ^{10}) of olefinic bonds to 13 and intramolecular photocycloaddition

SCHEME II.1



11 12

13 14

provides possible access to pentacyclo[5.4.0.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$] undecane framework 14 (Scheme II.1).

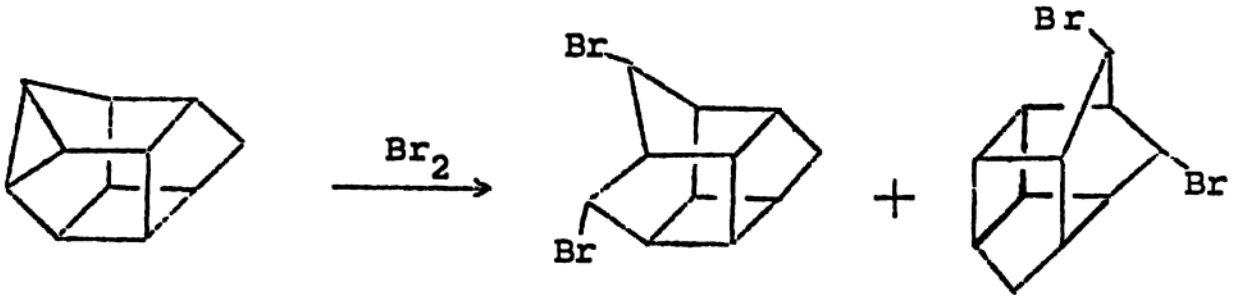
The pentacyclic trishomocubane systems+ 12 and 14 have

+The C_{11} derived pentacyclic systems constitute an interesting family. The number of possible pentacyclic structures, elucidated by the structure generating programme JAL-30XA is a mind bogling 15,358. However, by applying Schleyer approximations[12] and eliminating structures with tetrabridged carbon atoms, the number of structures can be reduced to 482. Further rejection of structures containing interwined bridges, cyclopropane rings and more than one cyclobutane ring reduced the possible pentacyclic frames to a manageable 6. Among these,

contd.

been largely elusive and only few, chance encounters are recorded in literature. In 1976, Marchand and coworkers[13] considered a possible trishomocubane formulation 15 for the product of bromination of their novel hexacyclic hydrocarbon 16 (Scheme II.2). However, unambiguous structural proof for a pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undecane frame was not furnished.

SCHEME II.2



16 15

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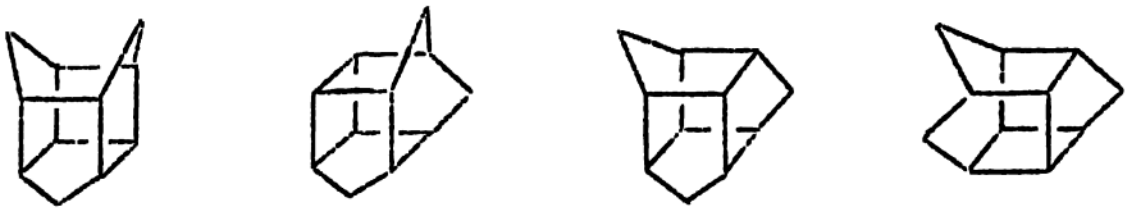
only 4 (i-iv) are trishomocubanes.



i ii iii iv

Nomenclature:

i Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane.

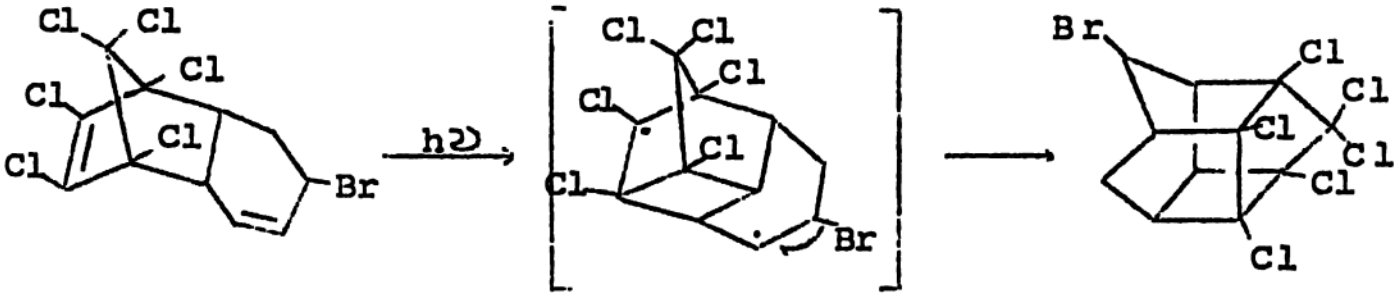
ii Pentacyclo[5.4.0.$0^{2,5}$.$0^{3,10}$.$0^{4,8}$]undecane.

iii Pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane 6.

iv Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undecane 12.

More recently, tricyclic bromide 17 obtained from th hexachlorocyclopentadiene-1,3-cyclohexadiene Diels-Alder adduct has been shown[14] to give pentacyclic bromide 18. Th.s novel transformation has been interpreted as proceeding throu'gh an intermediate 19 and involves a 1,2-bromine migration (Schem. II.3). The preliminary account of this work does not provide any definitive proof for the structural assignment to 18 as a pentacyclic trishomocubane derivative.

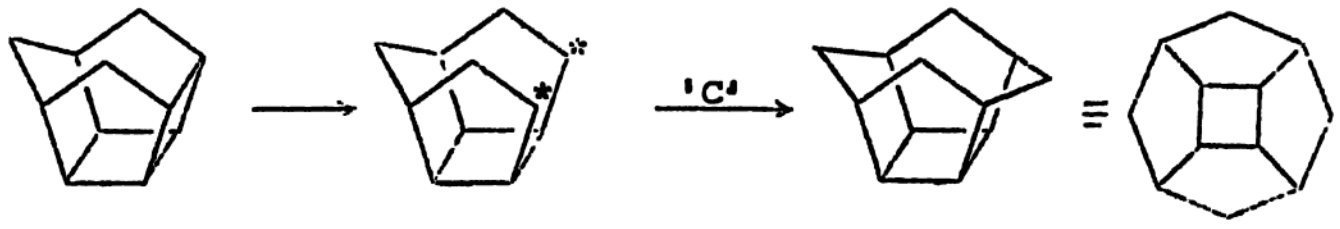
SCHEME II.3



17 19 18

The pentacyclic system 14 to our knowledge remains unknown. It has many alluring structural features. The foremost being its potential to serve as the precursor of [4]-

SCHEME II.4

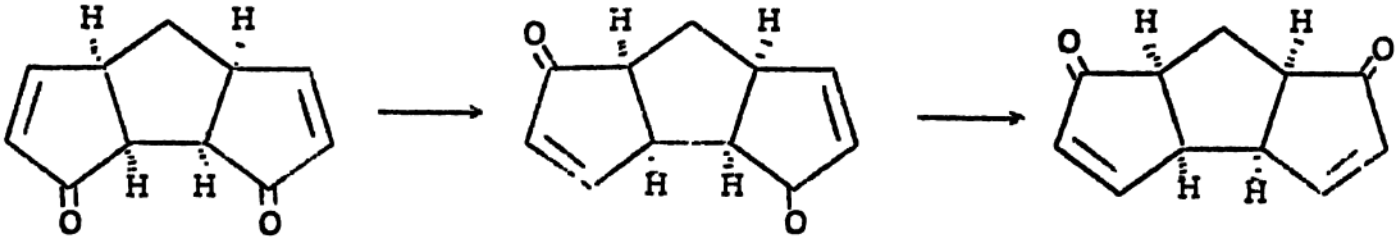


14 4-Peristylane

peristylane as shown in Scheme II.4.

In view of the lack of availability of reliable and authentic methods to gain access to the trishomocubane systems 12 and 14, it was considered interesting to attempt synthesis of these novel ring systems employing the intramolecular $\pi^2_s + \pi^2_s$ photochemical cycloaddition as the key step as depicted earlier in Scheme II.1. The immediate task was then to acquire all cis-triquinane dienes with Δ^3, Δ^9 and Δ^3, Δ^{10} transannularly disposed double bonds. For the preparation of these triquinane derivatives, the symmetrical cis, syn, cis-bis-enone 7, available readily and in quantity, appeared to be the starting material of choice. Transposition of either or both of the enone moieties in 7 was then expected to furnish the requisite trishomocubane precursors 20 and 21 for the contemplated photochemical cycloaddition (Scheme II.5).

SCHEME II.5



7 20 21

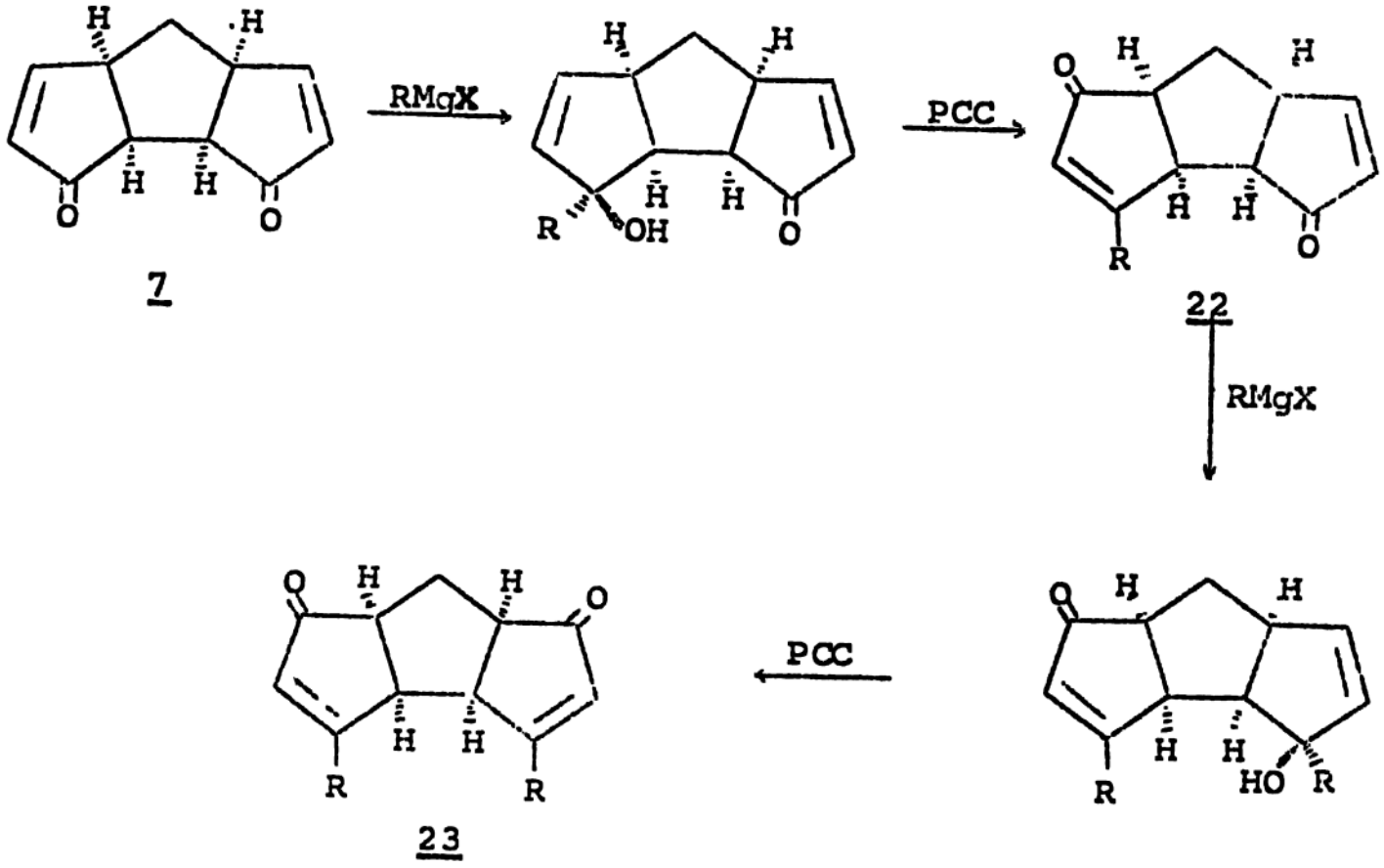
In this chapter of the thesis, we describe the synthesis of several derivatives of the singly transposed bis-enone system 20 and their ready and efficient photochemical cycli-

sation to the novel pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undecane system 12. In addition, we also unravel an interesting acid catalysed rearrangement of the pentacyclic trishomocubane system 12, back to its precursor triquinane derivative. This facile acid catalysed reversal of the photochemical cycloaddition, in a strained molecular framework, points to the possibility of utilizing this system for the storage of solar energy.

II.3 RESULTS AND DISCUSSION

As already mentioned above, the first objective in the contemplated synthesis of trishomocubane systems 12 and 14 was the transposition of the enone moieties in the cis, syn, cis-bis-enone 7. Towards this end, several methodologies were explored. However, all of them, including the usually reliable Wharton reaction,[15] proved unsuccessful. Recourse was then taken to alkylative enone transposition strategy[16] as outlined in Scheme II.6. In this manner, it was sought to carry out the transposition of bis-enone 7 in a sequential manner, first to the single transposed bis-enone 22 and then to the fully transposed bis-enone 23. At the outset, four different alkyl groups (methyl, allyl, phenyl and p-methoxyphenyl) were chosen for the alkylative transposition reactions on 7. The results of the alkylative transposition of bis-enone 7 are reported first.

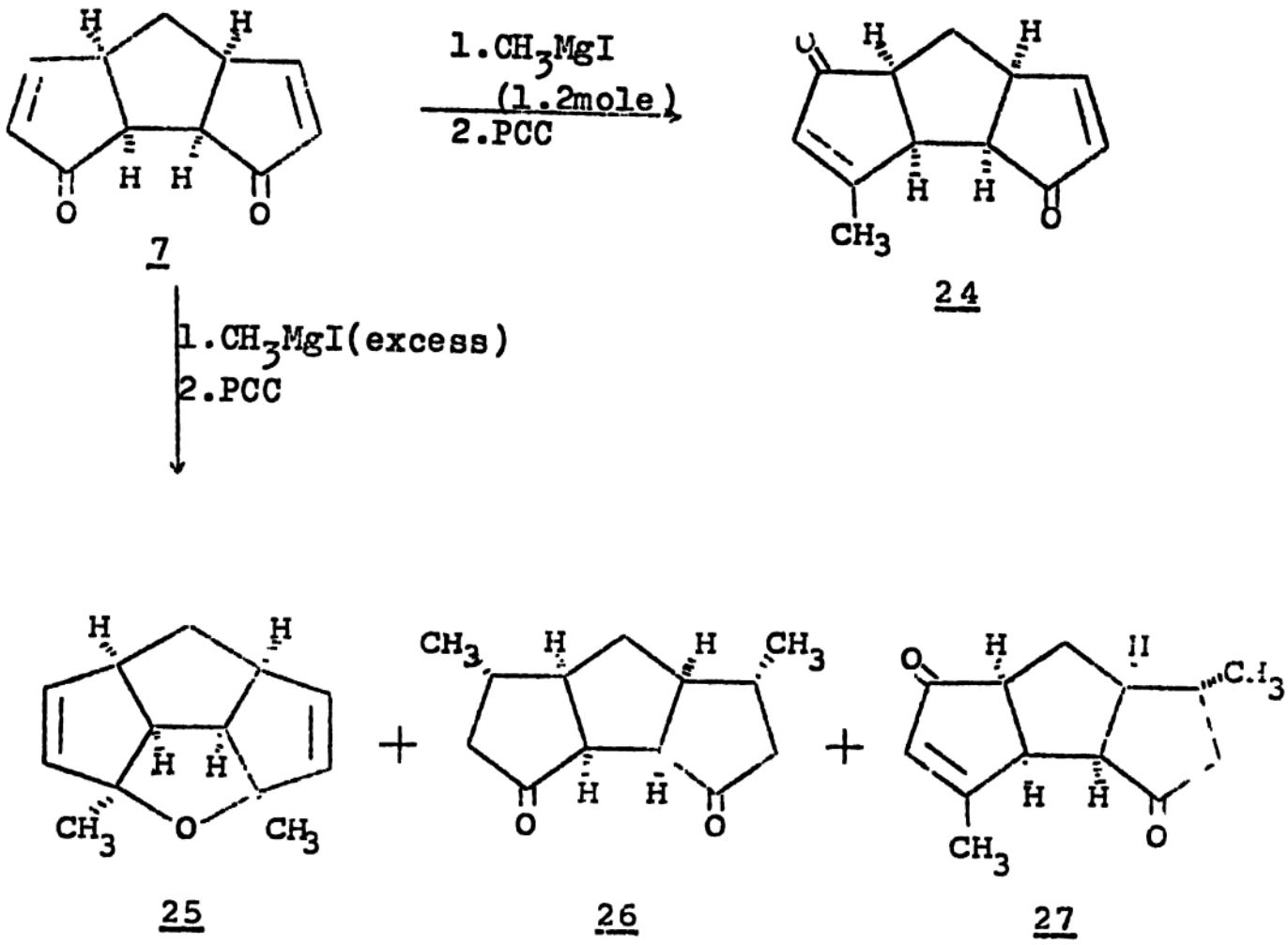
SCHEME II.6



Reaction of 7 with 1.2 molar excess of methylmagnesium iodide and pyridinium chlorochromate (PCC) oxidation[17] furnished the requisite methyl substituted, single transposed bis-enone 24 in 30% yield. On the other hand, reaction of 7 with excess methylmagnesium iodide followed by PCC oxidation took a more complicated course. These reactions have been described in the first chapter and are summarised here in Scheme II.7 for the sake of continuity.

Reaction of bis-enone 7 with 1.2 molar excess of allylmagnesium chloride furnished a mixture containing several products (TLC). Careful chromatography on silica gel resulted

SCHEME II.7



7 24 25 26 27

in the isolation of a crystalline compound, mp.114-5°C, in 25% yield. The compound was devoid of any carbonyl absorption in the IR spectrum but had a hydroxyl absorption at 3370 cm^{-1} and could be readily assigned structure 28 on the basis of its ^{1}H and ^{13}C NMR spectral data (vide experimental).[18,19] The ^{13}C NMR spectrum of 28, besides the usual expected signals, exhibited two diagnostic quaternary carbon singlets at δ 119.9 and 99.3 due to -O-C(-)-OH and -C(-)-O- type

of functionalities, respectively. PCC oxidation[17] of 28 led to the allyl substituted single transposed bis-enone 29.

7 28 29

The ^{1}H NMR spectrum (Fig.II.1) of 29 had in all six olefinic protons, but more significantly, only one deshielded proton on the β carbon of an α,β-unsaturated ketone at δ 7.48. In conformity with this observation the ^{13}C NMR spectrum (Fig. II.2) had a singlet at δ180.1 due to the alkyl substituted β carbon of an α,β-unsaturated cyclopentenone. While allyl substituted bis-enone 29 could be obtained in two steps after isolation of the intermediate hemi-ketal 28 followed by PCC oxidation, for practical purposes the crude product of Grignard reaction was directly oxidised with PCC and chromatographed on a silica gel column. In this way, 29 could be consistently obtained in yields of >25% from bis-enone 7.

In an effort to prepare the fully transposed diallyl bis-enone 30, reaction of 7 with excess Grignard reagent was studied. Exposure of 7 to 6-8 fold excess of allylmagnesium chloride in THF resulted in the formation of a very complex

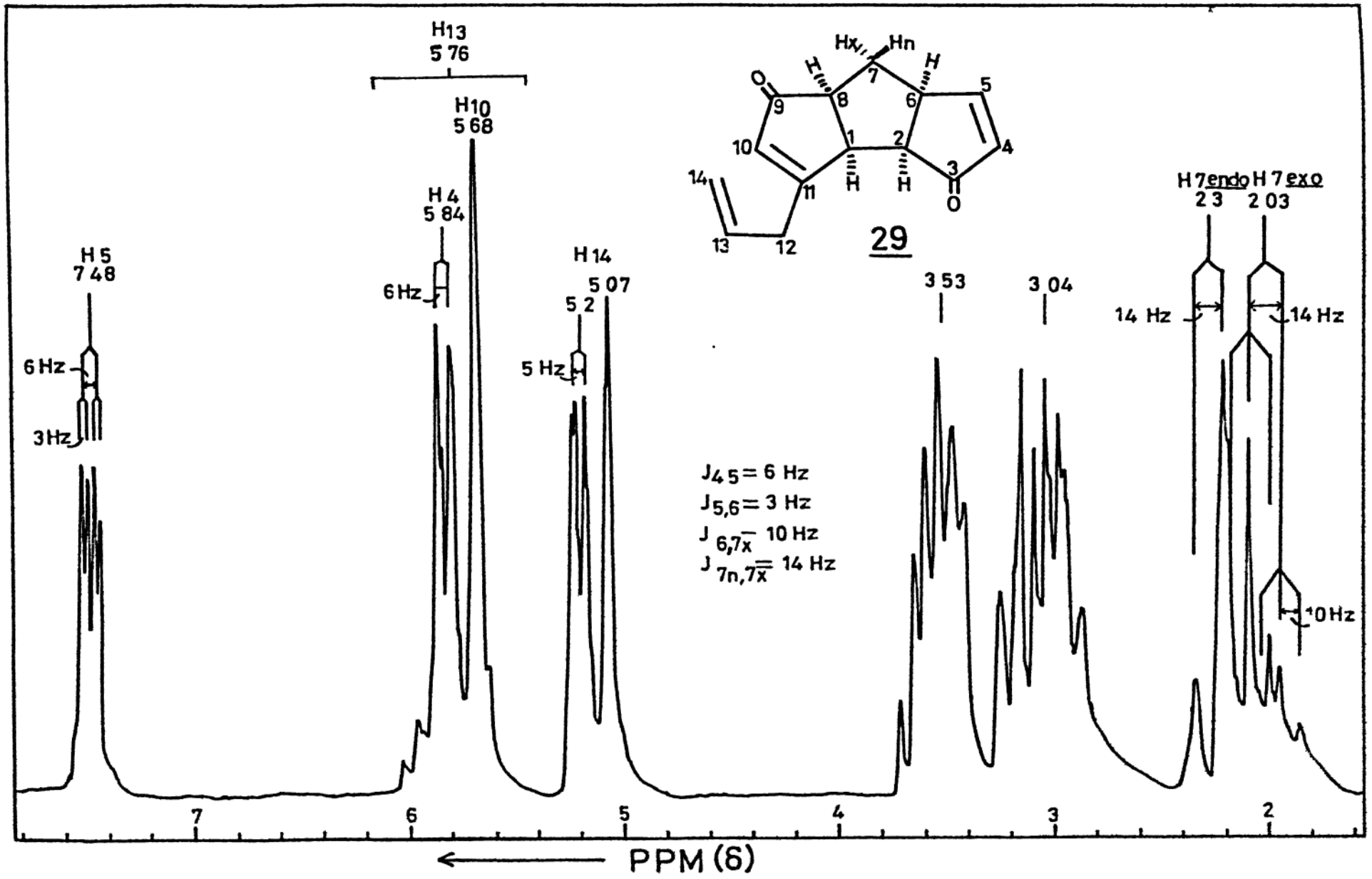


FIG II 1 : ^{1}H NMR (100 MHz) spectrum of 29

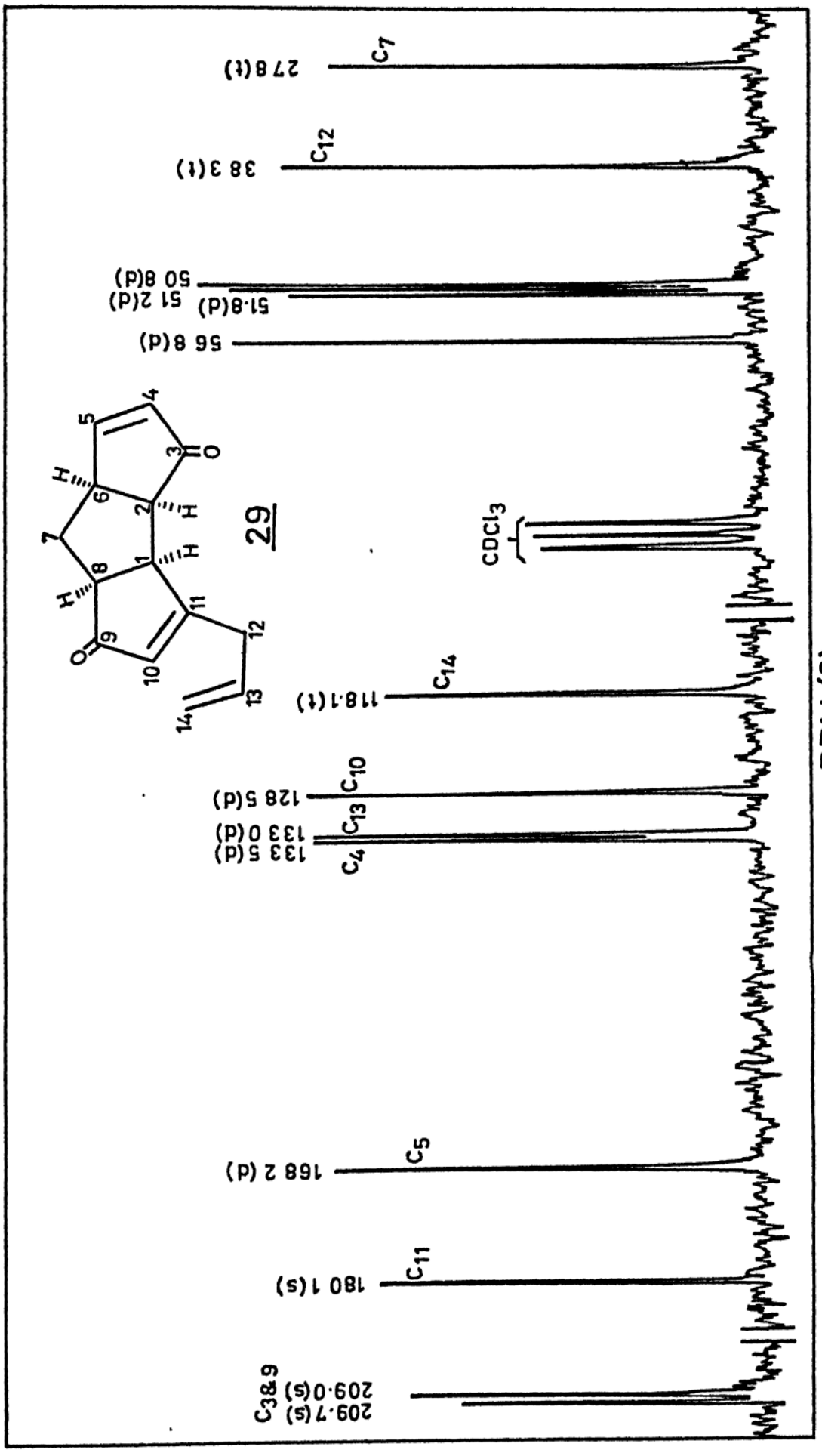
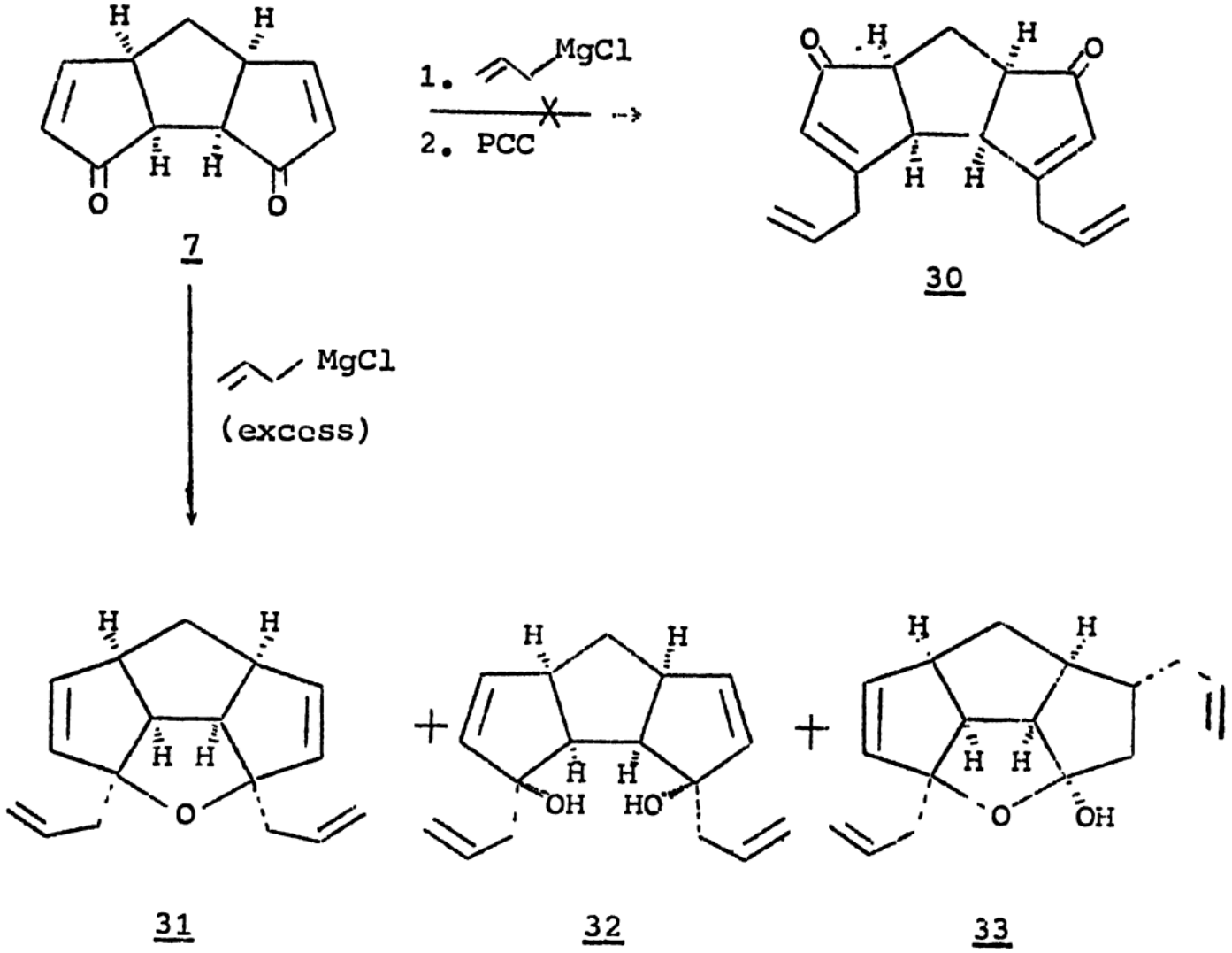


FIG II.2: ^{13}C NMR (25.0 MHz) spectrum of 29

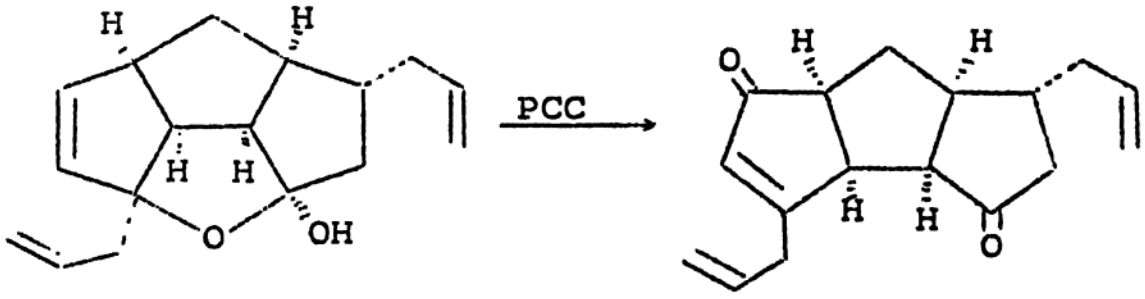
SCHEME II.8



7 30 31 32 33

mixture of products (TLC). However, careful column chromatography effected neat separation of three compounds 31, 32 and 33 in 8, 33 and 25% isolated yields, respectively (Scheme II.8). Structures to all the three products 31, 32 and 33 rest secured on the basis of compelling ^{1}H and ^{13}C NMR data summarised in the experimental section. The spectral parameters for all three compounds indicated incorporation of two allyl residues in each case and 31, 32 were conspicuous by the symmetry elements (9 line ^{13}C NMR spectra) present in them. Structure of

33 was further fortified by its oxidation with PCC[17] to the ene-dione 34. The transposed enone 34 exhibited both saturated (IR: 1730 cm^{-1}, ^{13}C NMR: δ218.1) and α,β-unsaturated (IR: 1700 cm^{-1}, ^{13}C NMR: δ210.7) carbonyl absorptions besides the characteristic β-carbon singlet of the enone moiety at δ181.3 in the ^{13}C NMR spectrum.

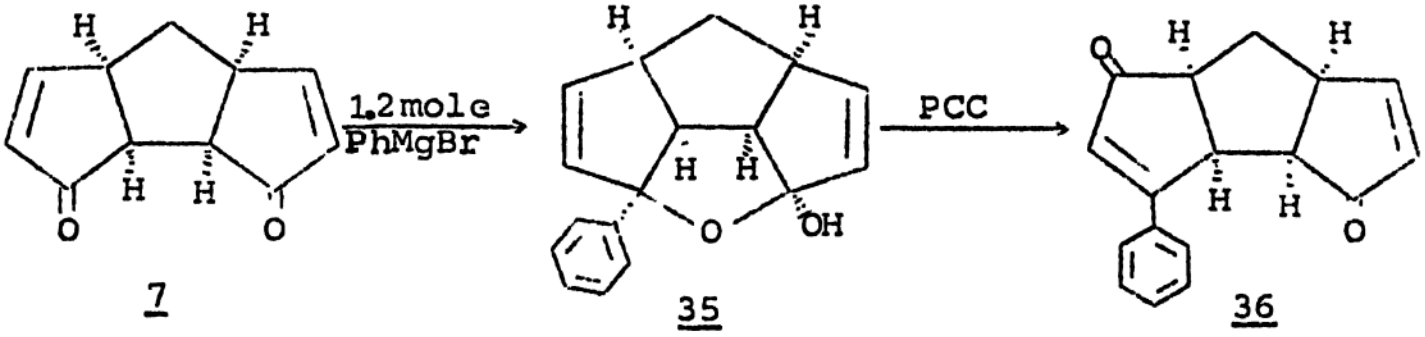


33 34

It was particularly gratifying to have encountered the symmetrical bis-tertiary diol 32 in the excess Grignard reaction, for this was the anticipated precursor of the doubly transposed bis-enone 30. However, the elation at being in possession of 32 turned out to be short lived, as it simply dehydrated to the stable tetracyclic ether 31, on being contacted with any oxidising agent (e.g., PCC,[17] Jones reagent,[20] PDC,[21] etc.). The 5-oxatetraquinane 31 itself proved to be a stubborn customer, not amenable to either oxidation or cleavage with a wide variety of reagents.

Reaction of the bis-enone 7 with phenylmagnesium bromide (1.2 molar excess) and chromatography of the resulting

mixture led to isolation of hemi-ketal 35, mp.134-35°C. Structure of 35 follows from the lack of carbonyl absorption in the IR spectrum, presence of hydroxyl absorption at 3410 cm^{-1} and the characteristic carbon resonances at δ120.5(s) and 100.3(s) in the ^{13}C NMR spectrum ascribable to -O-C(-OH)- and -C(-O-)- type of functionalities. PCC oxidation[17] of 35 yielded the desired single transposed bis-enone 36, mp.111-2°C.



7 35 36

The ^{1}H NMR spectrum (Fig.II.3) and ^{13}C NMR spectrum (Fig.II.4) fully accounted for the structural features present in 36. For practical purposes, the transposed bis-enone 36 was directly prepared from 7, in two steps, without isolation of the intermediate hemi-ketal 35. The yield of 36 was not very heartening from the preparative angle but it could be consistently obtained, quite conveniently, in 20-25% yield from 7.

Once again, in a vain bid for the elusive, fully transposed bis-enone 37, reaction of 7 with large excess of phenylmagnesium bromide was studied. The outcome of the reaction is shown in Scheme II.9 and is very much reminiscent of the

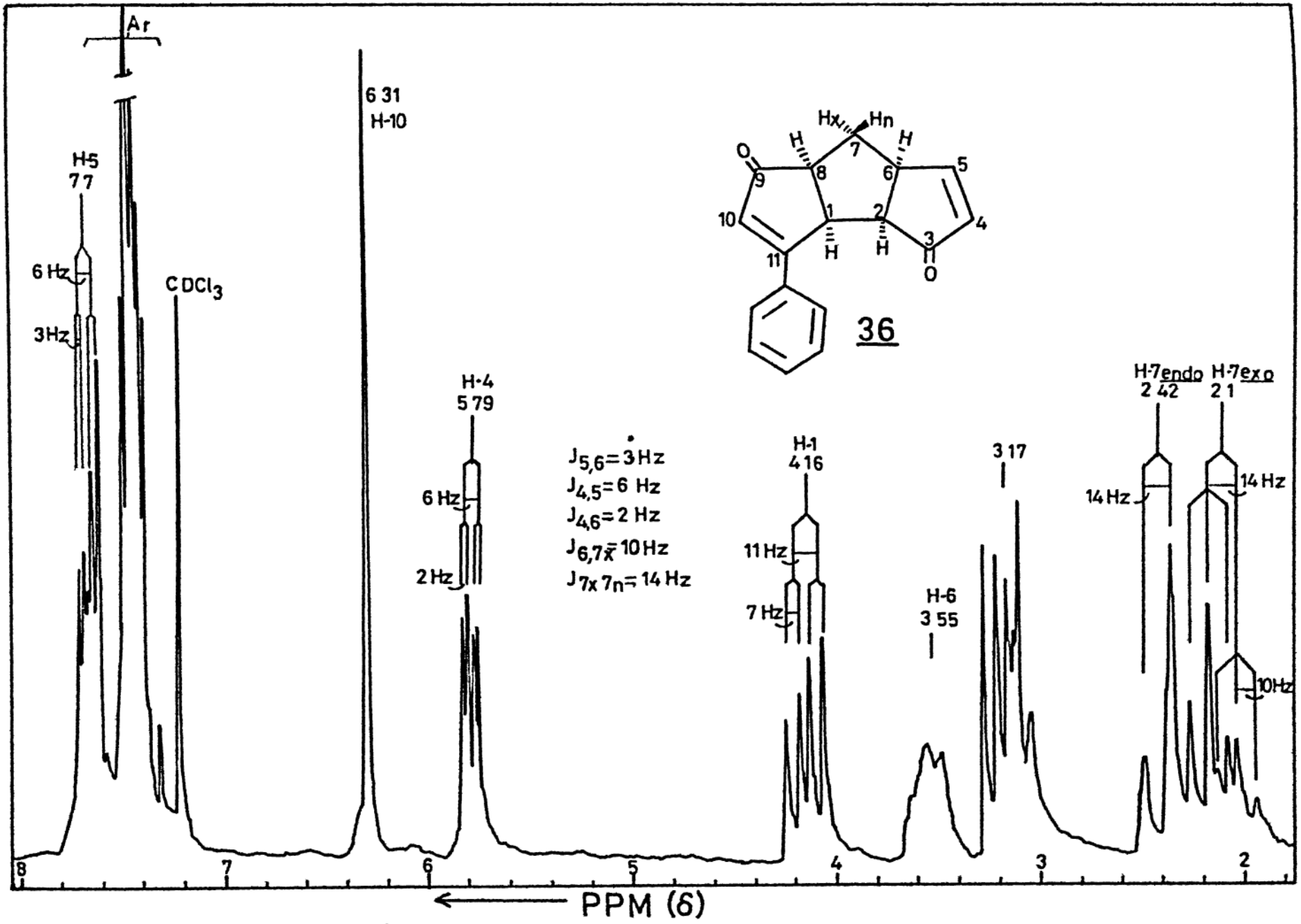


FIG II 3 ^{1}H NMR (100 MHz) spectrum of 36

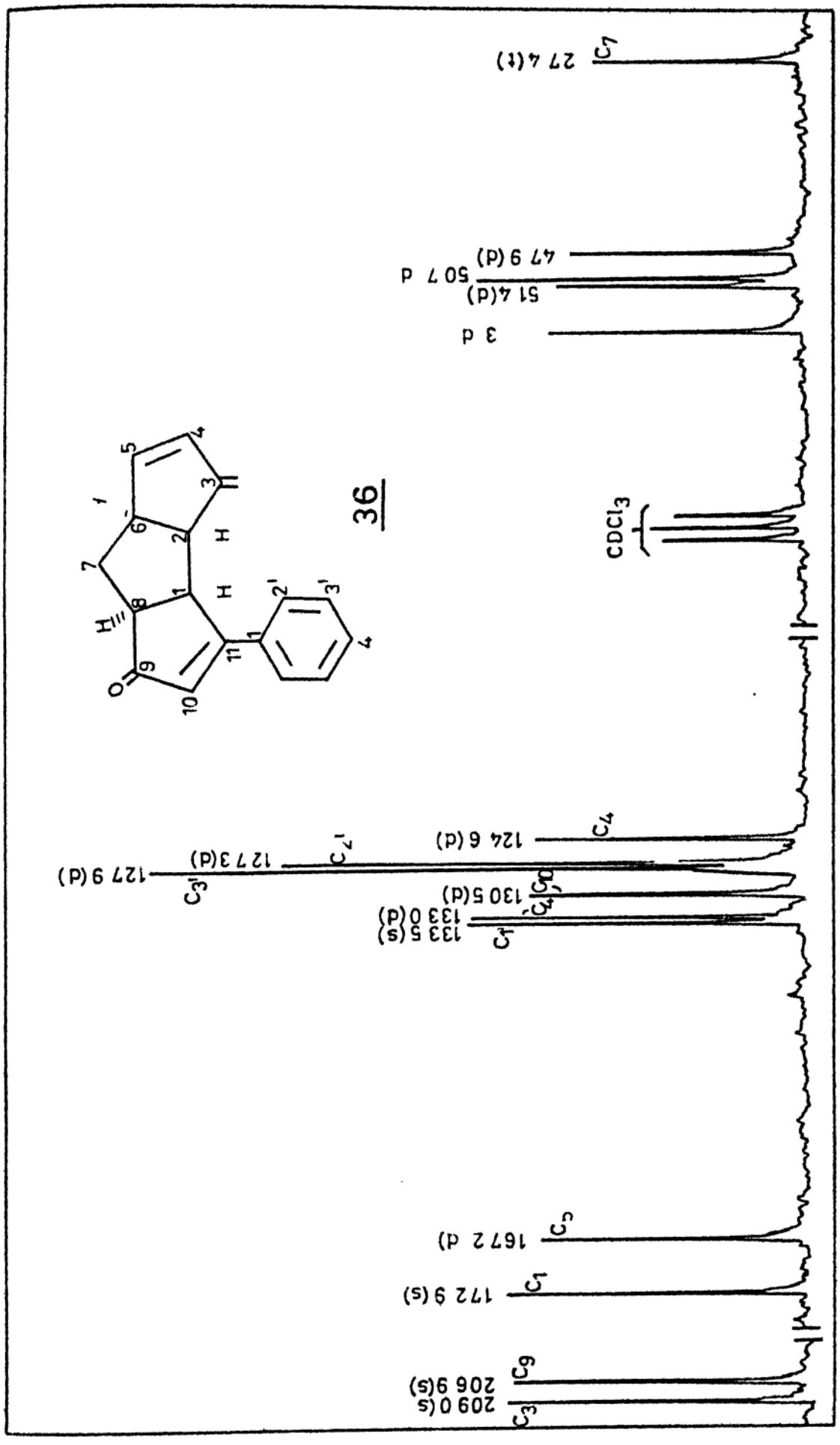
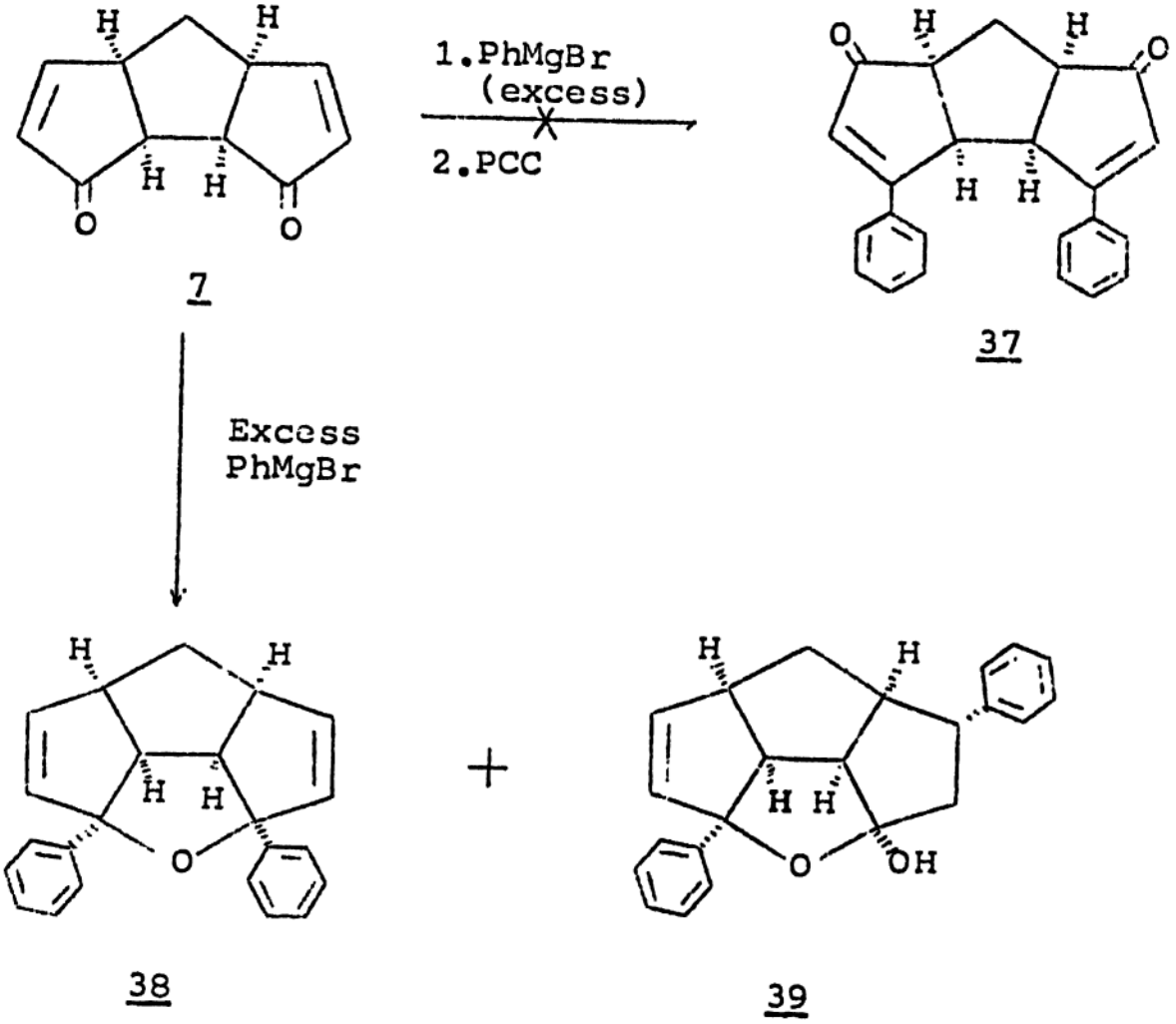


FIG II 4 ^{13}C NMR (25.0 MHz) spectrum of 36

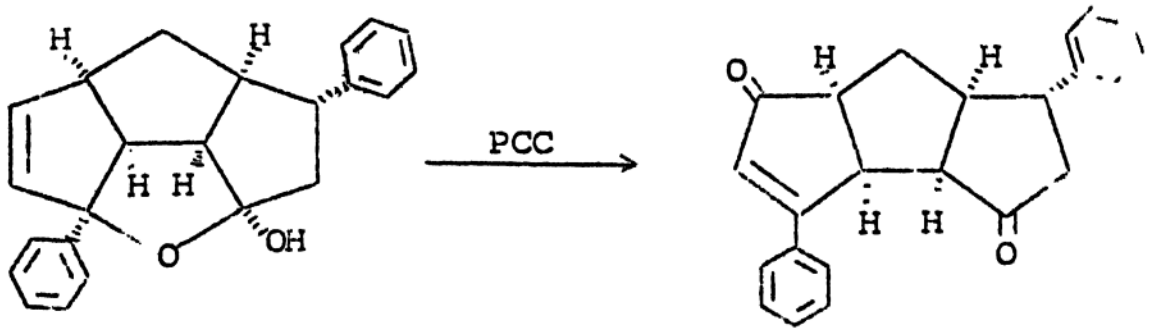
SCHEME II.9



7 37 38 39

response of 7 to excess methylmagnesium iodide and allylmagnesium chloride (vide supra). A 1:5 mixture of diphenylated products 38 and 39 was realised. Structure of 38 followed from its symmetry, ^{1}H and ^{13}C NMR data and was found to be identical with an authentic sample available in our laboratory.[+] The hemi-ketal 39, mp.137-8°C, produced from 1,2 and 1,4-Grignard additions to the two enone moieties, was recognised from its spectral data and further through its

[+]See, footnote on next page.



39 40

transformation to diphenylated enone 40, mp.128-9°C, via PCC oxidation.[17]

Finally, reaction of bis-enone 7 with p-methoxyphenylmagnesium bromide was investigated. Reaction of 7, even with controlled quantities of Grignard reagent, gave a highly polar, intractable product mixture. Careful chromatography yielded the hemi-ketal 41 in poor yield. PCC oxidation[17] of 41 furnished the required single transposed bis-enone 42,

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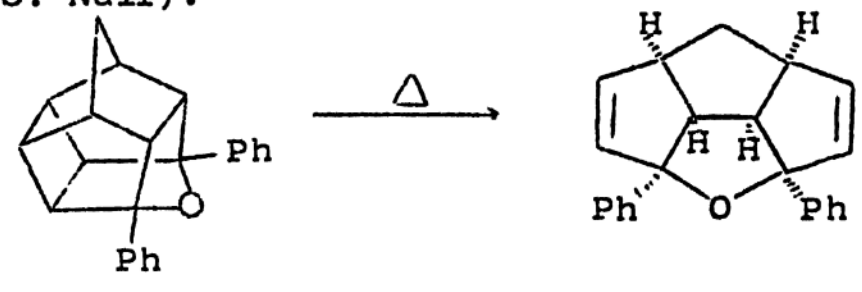
5-Oxatetraquinane 38 was readily available from the thermolysis of the diphenyl oxa-birdcage compound i (prepared by Mangalam S. Nair).[11]



i 38

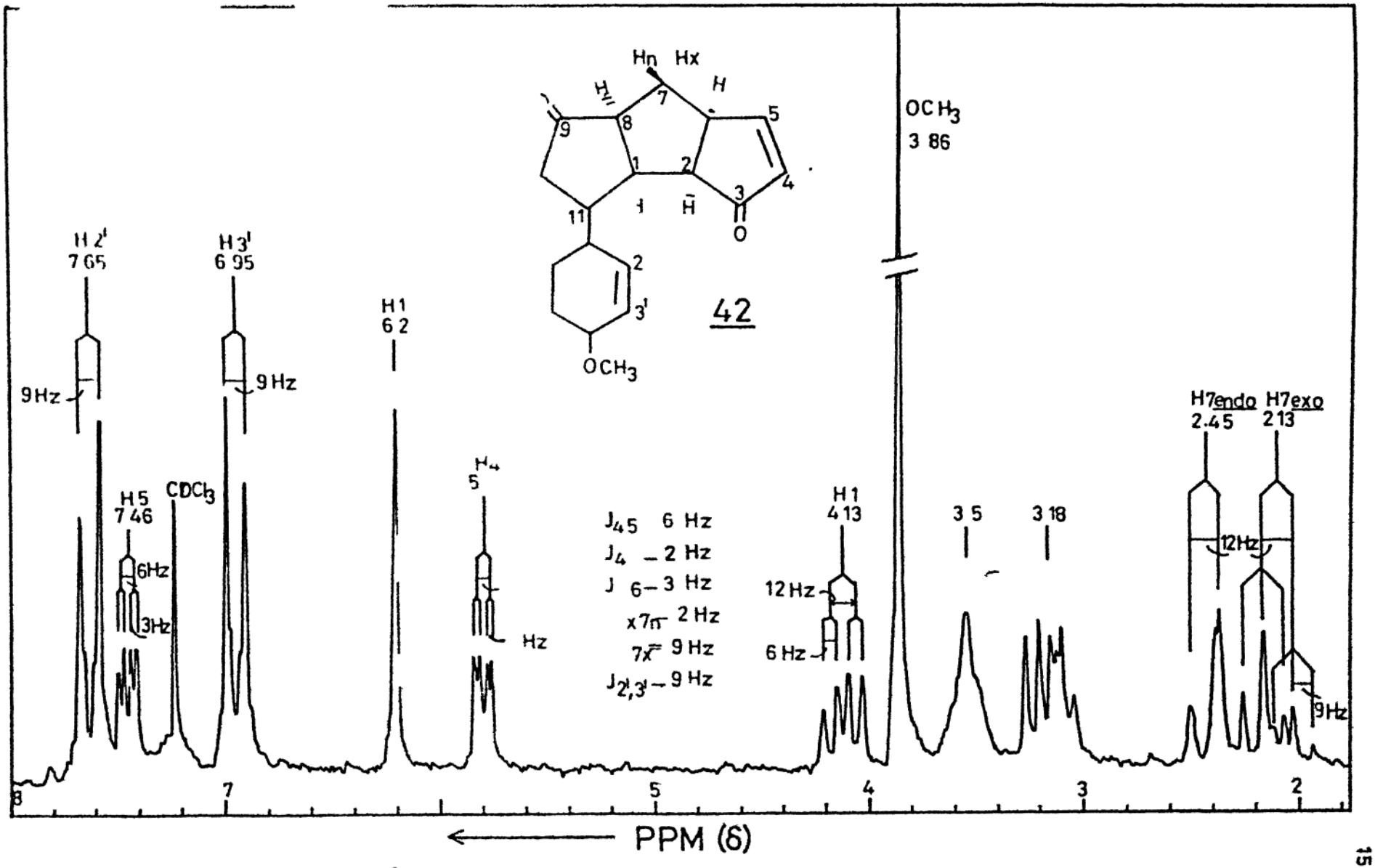


FIG II 5 ^{1}H NMR (100 MHz) spectrum of 42

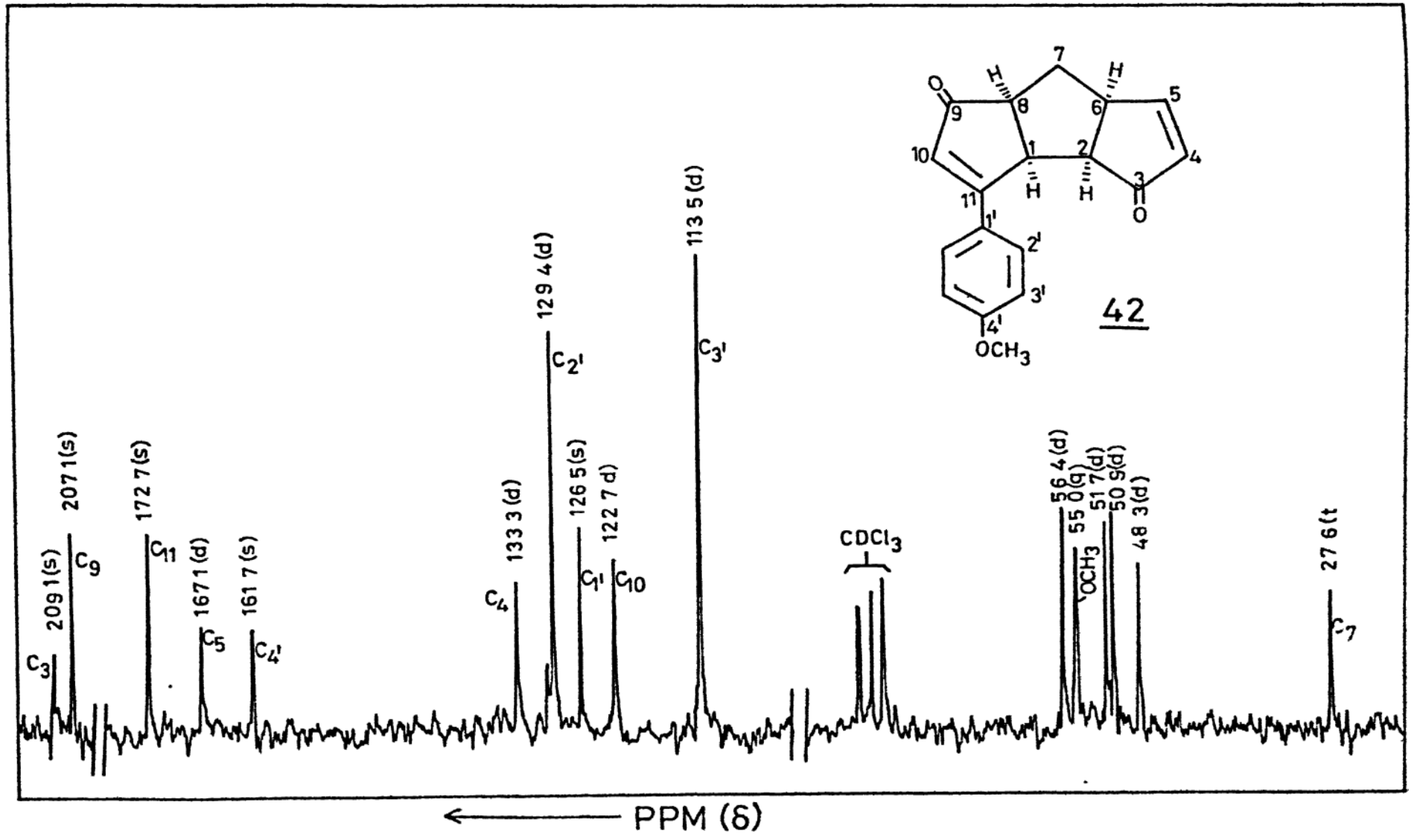
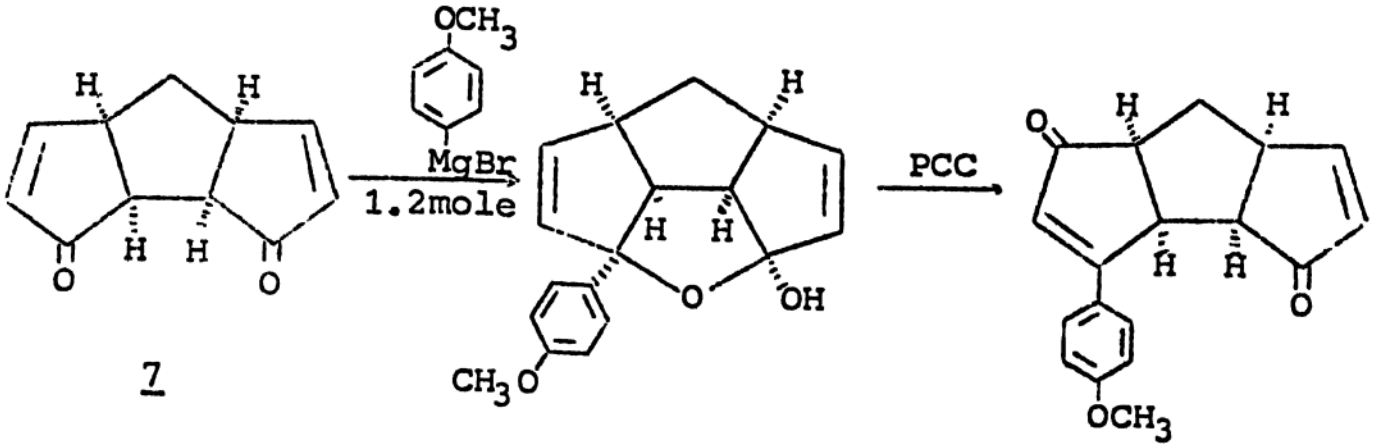


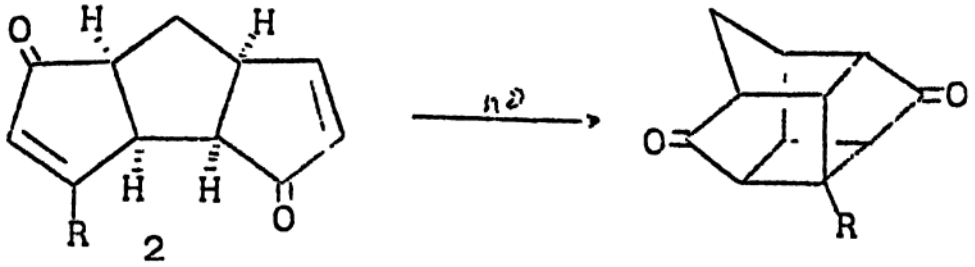
FIG II 6 ^{13}C NMR (25 0 MHz) spectrum of 42



7 41 42

mp.134-5°C and its structure followed from the analysis of its ^{1}H NMR (Fig.II.5) and ^{13}C NMR (Fig.II.6) spectral data. In spite of several experimental manipulations, employing different temperature and concentration regimes, the requisite p-methoxyphenylated bis-enone 42 could only be obtained in lamentably poor yield of ~10%.

Having obtained all the four desired single transposed bis-enones 24, 29, 36 and 42, the stage was set for the study of their intramolecular photocycloaddition to the projected trishomocubane system. As expected, photolysis of all the four bis-enones proved to be facile and efficient. Exposure of an ethyl acetate solution of 24, 29, 36 and 42 to irradiation from either a 450 W Hanovia UV lamp or Sunglight, through pyrex filter, resulted in their rapid depletion and emergence of a new spot on the TLC plate. The photolysis, in each case, was complete within 1 hr (see Table II.1) and high, nearly



22 → 47

24. R = methyl
29. R = allyl
36. R = phenyl
42. R = p-methoxyphenyl

43. R = methyl
44. R = allyl
45. R = phenyl
46. R = p-methoxyphenyl

quantitative yields of the photolysed products 43-46 could be realised. Photolysis in Sunlight, quite expectedly, required longer reaction times.

The preparatively efficient photolysis of bis-enones 24, 29, 36 and 42 to pentacyclic compounds 43-46 also exhibited high quantum efficiency. The quantum yields in the four cases, measured employing potassium ferrioxalate actinometry [22] were 0.80, 0.82, 0.92 and 0.48, respectively (Table II.1). The quantum yields were measured at 360 nm employing corning 7-60 filter (see, experimental section).

The structures of the pentacyclic diones 43-46 follow from complementary, unambiguous and overwhelming spectral evidence. To start with, the broad enone absorption around 1700 cm^{-1} in the starting bis-enones was now replaced by two

TABLE II.1

Quantum yields and other data related to the photolysis of bis-enones 24, 29, 36 and 42.

Substrate	UV spectrum λ_{max}^{MeOH} nm(ε)	Irradiation using UV lamp[a]		Irradiation in Sunlight[b]		Quantum Yield[c]
		Time	Yield%	Time	Yield%	
24	223(14,900) 315(140)	20 min	97	2 hr	95	0.80
29	222(15,350) 328(100)	20 min	100	2 hr	97	0.82
36	220(15,500) 296(17,500)	15 min	100	2 hr	94	0.92
42	222(15,500) 325(22,200)	45 min	90	3 hr	85	0.48

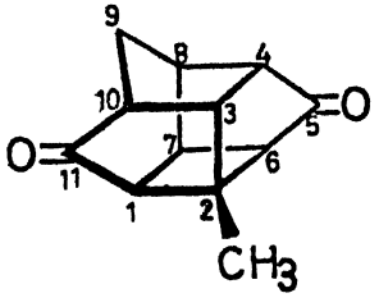
a. Irradiation was carried out in ethyl acetate (4-5 mmole) using a 450 W Hanovia medium pressure mercury vapor lamp in a quartz immersion vessel using a pyrex filter.

b. Irradiation was carried out in ethyl acetate (6-8 mmole) in a pyrex flask.

c. Quantum yield was determined using standard potassium ferrioxalate actinometry method.[22]

discrete absorptions in the carbonyl region at 1735 and 1760 cm^{-1} in the photolysed products. The two carbonyl groups in 43-46 are parts of bicyclo[2.2.1]heptan-7-one and bicyclo[3.2.1]octan-8-one substructure present in them[23,24] and therefore the two carbonyl vibrations in the IR spectra are in the appropriate and expected range. The ^1H NMR spectra of 43-46 were transparent in the olefinic proton region (except the olefinic and aromatic protons of substituents) and only exhibited overlapping multiplets in the region of δ2.0-3.5. The ^1H NMR spectrum (Fig.II.7) of the methyl substituted compound 43, however, reaffirmed the predicted course of the photolysis, as the methyl group now resonated as a sharp singlet at δ1.1. The ^{13}C NMR spectra of 43-46 are displayed in Figs.II.8-II.11. Each compound exhibited two distinct ^{13}C resonances due to the two saturated carbonyl groups (C_5 and C_{11}) and was devoid of olefinic carbon signals except those of substituents (allyl and aromatic). Furthermore, the signal due to the quaternary carbon (C_2) bearing the substituent was distinctive and readily identifiable.

An interesting reaction, which not only placed the structures of pentacyclic trishomocubanes 43-46 beyond the realm of ambiguity but also opened new and exciting prospects for their meaningful utilisation in another arena, was now encountered. Exposure of the p-methoxyphenyl substituted pentacyclic dione 46 to catalytic amounts of p-toluenesul-



43

FIG II 7. ^{1}H NMR(100MHz) spectrum of 43

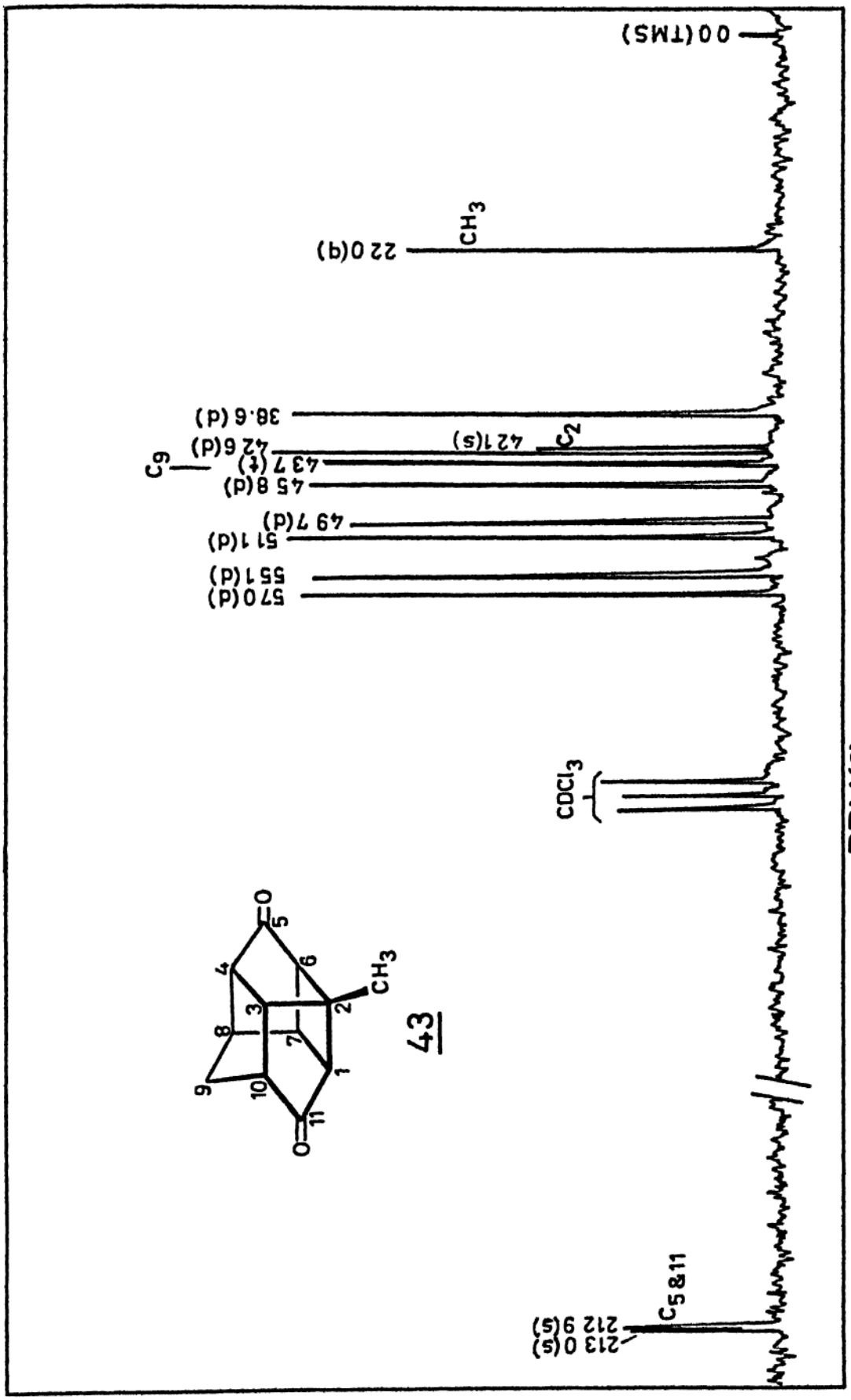


FIG II.8 . ^{13}C NMR (25.0 MHz) spectrum of 43

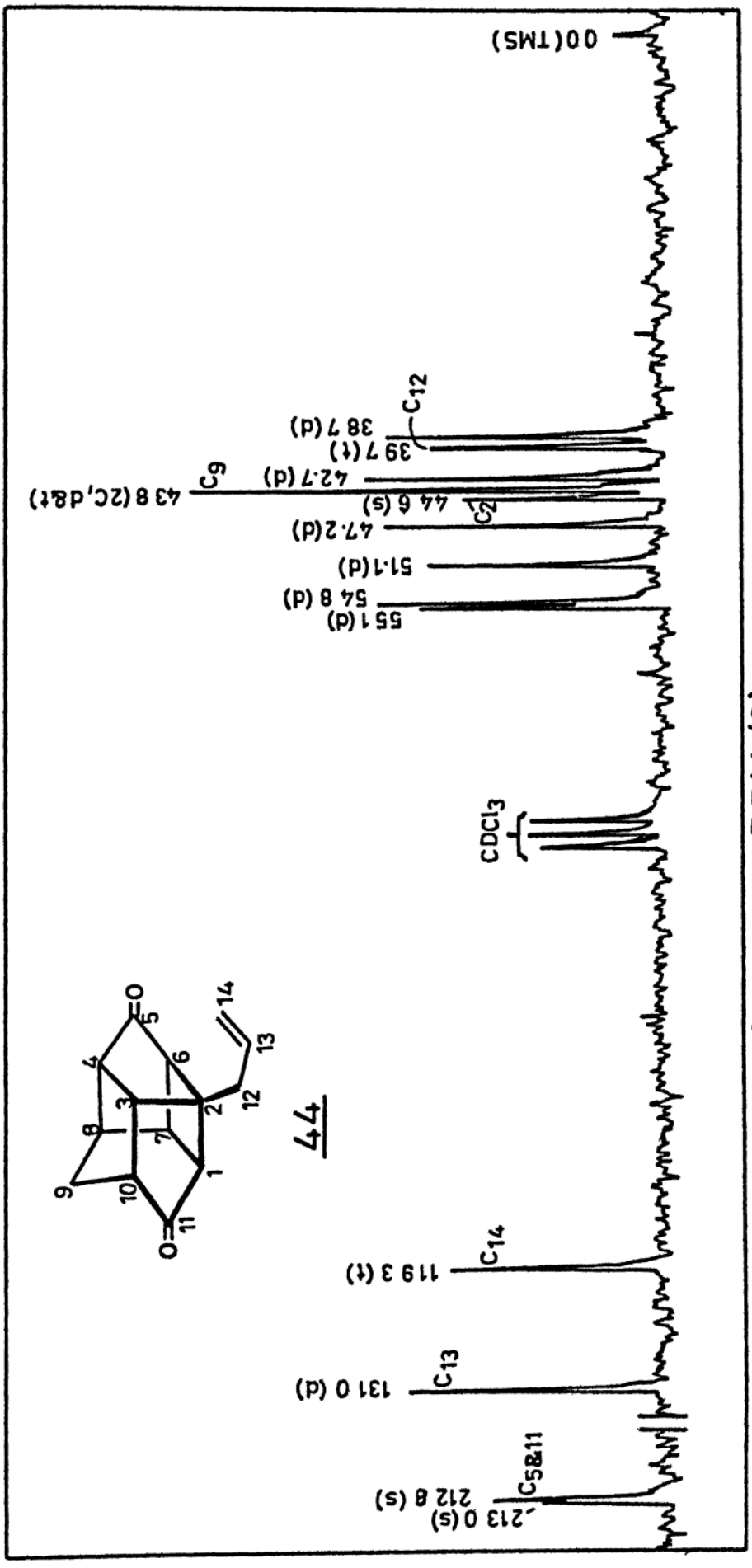


FIG II.9 · ^{13}C NMR (25.0 MHz) spectrum of 44

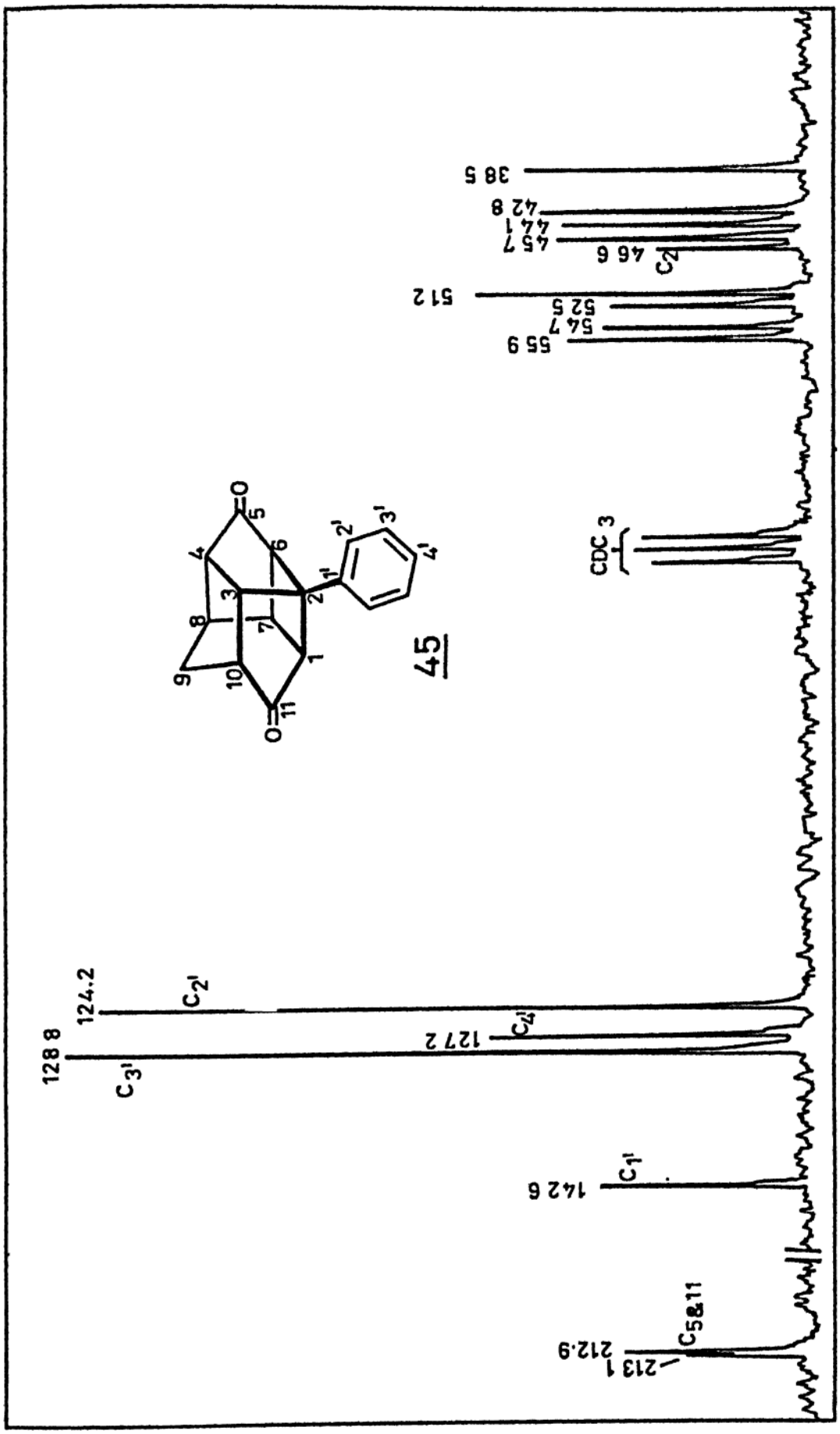


FIG II.10: ^{13}C NMR (25.0 MHz) spectrum of 45

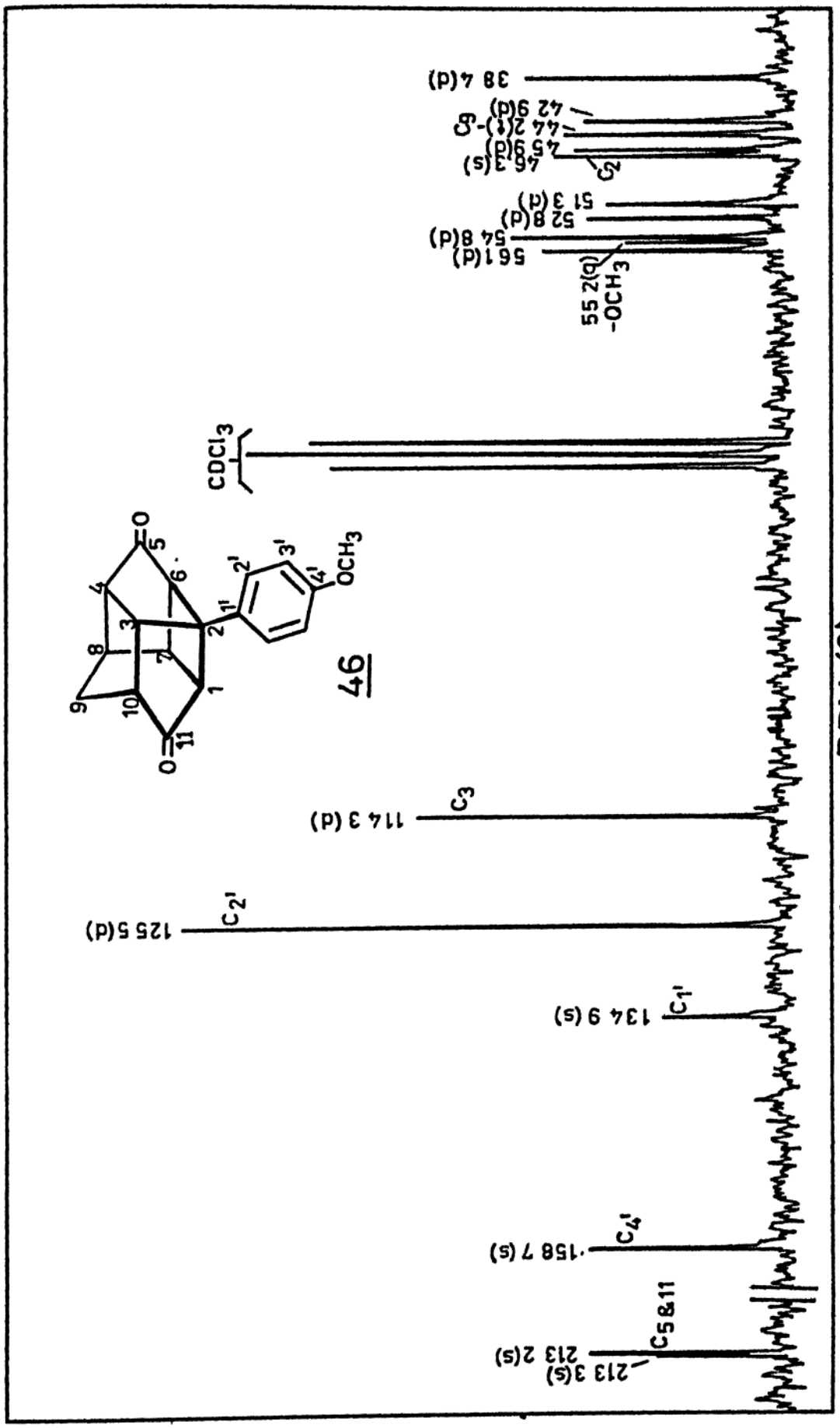
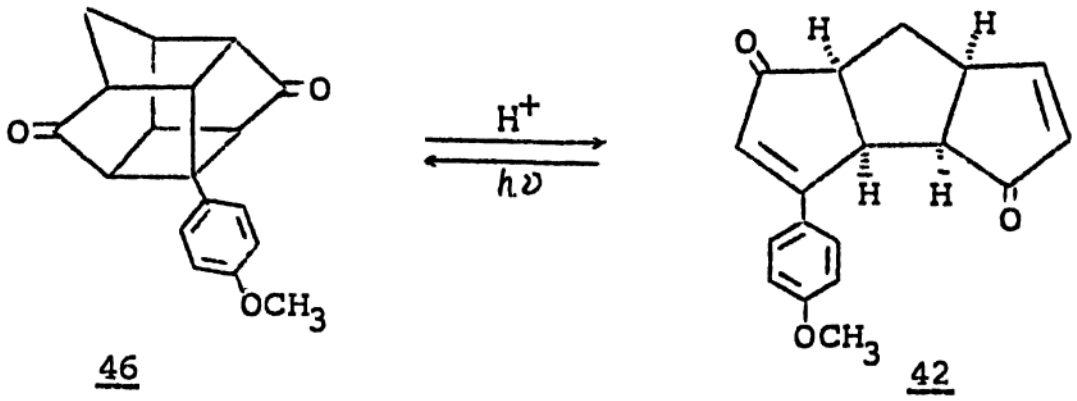
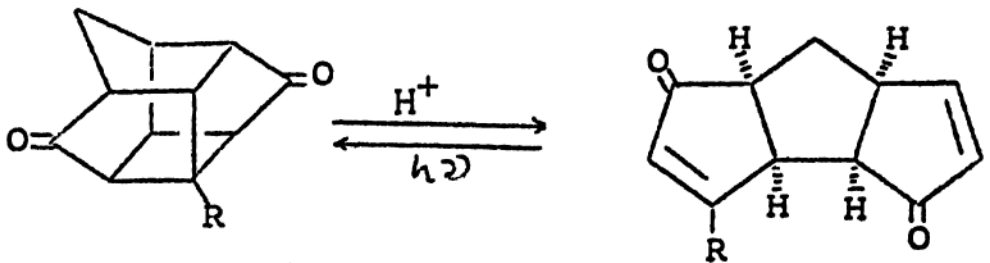


FIG II-11. ^{13}C NMR (25·0 MHz) spectrum of 46



46 42

phonic acid in benzene solution at room temperature (30°C) resulted in its rearrangement to the bis-enone 42 within 2 hr and in near quantitative yield. The use of BF_3-etherate as the catalyst was much better and 46 reverted to 42, almost instantly, at room temperature and in quantitative yield. Other protic acids could also be employed but they were less efficient and required longer reaction times. For example, 46⟶42 rearrangement required nearly 30 min in trifluoro-acetic acid.



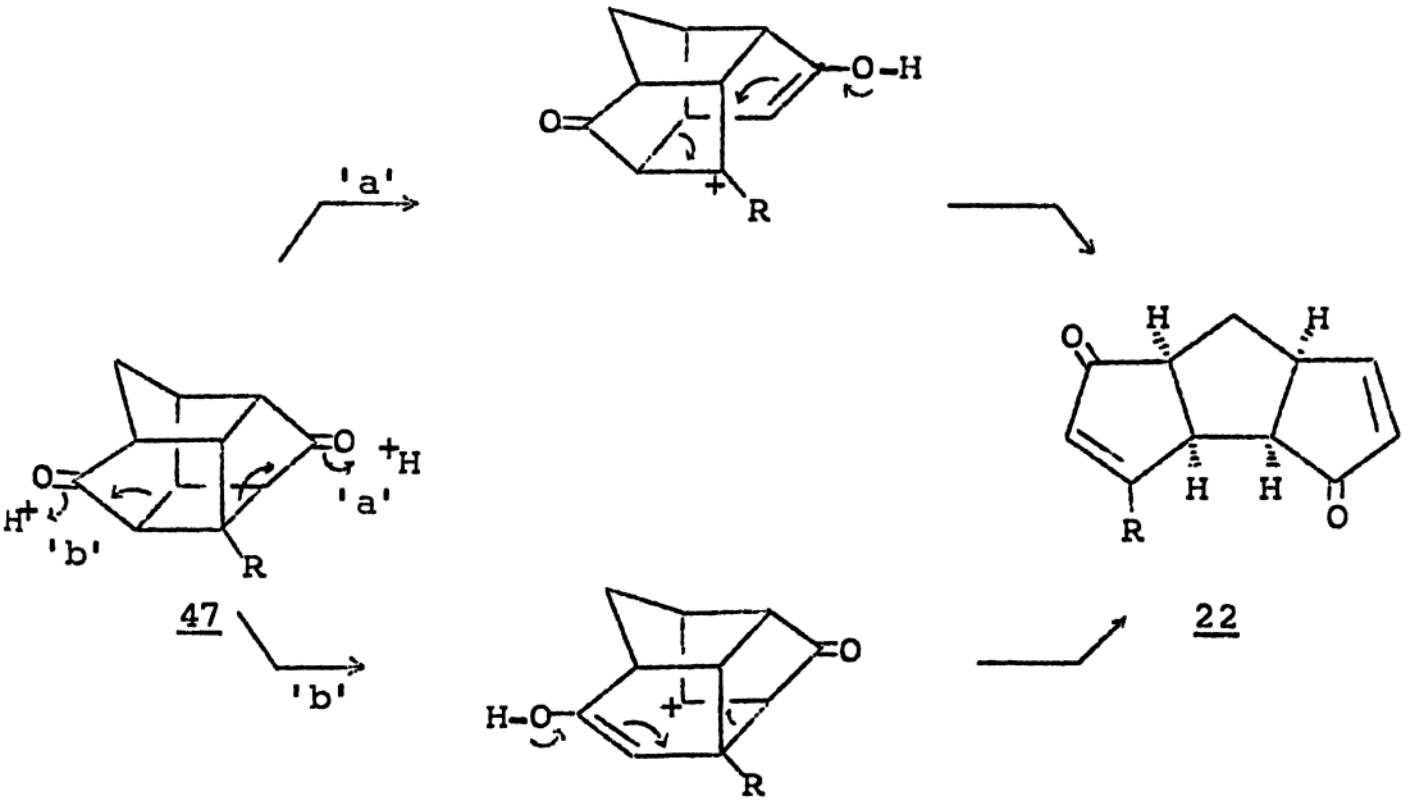
43. R = methyl
45. R = phenyl

24. R = methyl
36. R = phenyl

In a similar manner, the phenyl and methyl substituted diones 43 and 45 also reverted to the precursor bis-enones 24 and 36, respectively, but the reaction in case of methyl substituted pentacyclic dione 43, was less efficient and a regression in reactivity in going from p-methoxyphenyl, phenyl to methyl was conspicuously discernible (Table II.2).

Two mechanistic proposals for this facile acid catalysed rearrangement of 2-substituted pentacyclic diones to triquinane based bis-enones merit attention and are shown in

SCHEME II.10



R = methyl or phenyl or p-methoxyphenyl

TABLE II.2

Acid catalysed rearrangement of 2-substituted pentacyclo [5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undeca-5,11-diones (47) to 11-substituted tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-diones (22).

Substrate	p-Toluenesulphonic acid[a]		Boron trifluoride etherate[b]		Product
	Time/Temp	Yield%	Time/Temp	Yield%	
43	6 hr/110°C	20	2 hr/80°C	65	24
45	2 hr/80°C	100	40 min/30°C	100	36
46	2 hr/30°C	100	5 min/30°C	100	42

a. 0.2 M equivalent of acid in either benzene or toluene was used.

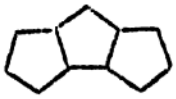
b. 0.5 M solution of BF_3-Et_2O in benzene was used (4-5 mole equivalent).

Scheme II.10. The two mechanisms differ in the site of initial protonation of the carbonyl group (C_5 *vs* C_{11}) and in the temporal sequence for the cleavage of C_1-C_7 and C_2-C_6 bonds. Among the two mechanisms, the path 'a' is favoured at the moment, on following grounds. It would be reasonable to expect preferential protonation of the more strained C_5-carbonyl group (7-ketonorbornane type) as compared to the C_{11}-carbonyl group. Rate determining cleavage of C_2-C_6 bond in protonated 47 would furnish the stabilised tertiary carbonium ion 48; which on charge neutralisation with concomitant C_1-C_7 cleavage provides the triquinane derivative 22. The profound effect of the carbonium ion stabilising substituents on the rate of 47 ⟶ 22 rearrangement is fully consonant with this mechanistic deduction.

The extremely mild and efficient acid catalysed isomerisation of 47 to 22 indicated that the system 47 ⇌ 22 may be a potential candidate for the reversible storage of solar energy.[7] At the first sight, the various responses and attributes of 47 ⇌ 22 system acquiesces well with the stringent norms for the reversible storage of light energy. For example, there is large, positive ground state enthalpy difference between 47 and 22 (Table II.3 gives data for parent systems 49 and 12 obtained from molecular mechanics calculation).[12,25] The quantum efficiency for the 47 ⇌ 22 is good, approaching unity in some cases (Table II.1) and the photoreaction can be

Table II.3

Calculated heats of formation of tricyclo[6.3.0.$0^{2,6}$]undecane 49 and pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undecane 12.

				Δ	
ΔH_f^o of 12 (KCal/mole)[12]		ΔH_f^o of 49 (KCal/mole)[25]		ΔH_f^o of 12-49 (KCal/mole)	
Engler	Allinger	Engler	Allinger	Engler	Allinger
23.88	26.58	-23.24	-19.28	47.12	45.86

carried out over a broad wavelength region. Lastly, the energy rich photoproduct 47 has good Kinetic stability and can be catalytically reversed at room temperature and in high yield. However, these are only preliminary indications and at best provide incentive for further detailed exploration in this arena of much contemporary interest.

In conclusion, we have delineated the first authentic entry into the pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undecane system via a photochemical $\pi^2_s + \pi^2_s$ cycloaddition and described the syntheses of several 2-substituted derivatives of this ring system. The presence of carbonyl functionality at C_5 and C_{11} provide opportunities for the preparation of several derivatives of this ring system through routine

functional group manipulations. The pentacyclic diones 43, 45 and 46 readily undergo acid catalysed reversal to their tricyclic precursors. The mild reversal points to the possible role and potential of this ring system in storage of solar energy.

II.4 EXPERIMENTAL

For a general write-up on the experimental section, see Chapter I.4.

11-Allyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-dione(29):

To a magnetically stirred suspension of magnesium (365 mg, 0.015 g atom) in 5 ml of dry ether was added dropwise a solution of allyl chloride (2.8 g, 36 mmoles) in 5 ml of dry ether. The mixture was stirred at room temperature until all the magnesium had dissolved. The allylmagnesium chloride was syringed out and injected slowly into a magnetically stirred solution of the bis-enone 7 (2 g, 11.5 mmoles) in 20 ml of dry THF. The reaction mixture was stirred for 20 min at room temperature, quenched by careful addition of saturated NH_4Cl solution and extracted with ether (50 ml x 2). The ether extract was washed and dried. Evaporation of the solvent furnished 1.4 g of the crude material containing approximately 60% of the hemi-ketal 28. An analytical sample of the hemi-ketal was prepared by filtering the crude hemi-ketal through a silica

gel column with 10% ethyl acetate-benzene. Crystallisation from pet ether furnished the colourless needles of the hemi-ketal 28, mp.114-5°C.

IR spectrum (KBr), ν_{max}: 3370 (hydroxyl), 1640 and 1625 cm^{-1} (olefinic)

^1H NMR spectrum (100 MHz, $CDCl_3$): δ4.8-6.04(7H,complex m,olefinic), 3.74(1H,s,-OH), 2.6-3.4(4H,m,bridgehead CH), 2.5 (2H,dd,J_1=7Hz,J_2=1.5Hz,allylic CH_2), 1.76(2H,m,CH_2).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ138.8(d), 137.5 (d), 133.9(d) and 133.3(d,2c), olefinic C's, 119.9(s,>C<$^{OH}_{O-}$), 117.7(t,C=$\underline{C}H_2$), 99.3(s,-CH_2-$\underline{C}$-O-), 59.8(d), 55.4(d), 51.6(d) and 50.3(d), bridgehead C's, 43.9(t,allylic CH_2), 34.3(t,CH_2).

The above crude hemi-ketal 28 (1.4 g) was taken in 5 ml of dichloromethane and added to a magnetically stirred suspension of pyridinium chlorochromate (2 g, 9.2 mmoles)[17] in 8 ml of dichloromethane. The heterogeneous reaction mixture was stirred vigorously for 7 hr at room temperature. The reaction mixture was filtered through a silica gel (10 g) column with large volume of dichloromethane. Evaporation of the solvent furnished 615 mg (25% overall in two steps) of the single transposed bis-enone 29, and was crystallised from pet ether, mp.68°C.

UV spectrum, λ_{max}^{MeOH}: 222 (ε = 15,350), 328 nm (ε = 100).

IR spectrum (KBr), ν_{max}: 1705 and 1685 (carbonyl), 1645, 1615 and 1590 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.II.1): δ7.48(1H, dd,J_1=6Hz,J_2=3Hz,-C<u>H</u>=CH-C(=O)-), 5.84(1H,d,J=6Hz,-CH=C<u>H</u>-C(=O)-), 5.68(1H,s,-CH_2-C(=O)-C<u>H</u>=C(-O)-), 5.4-6.06(1H,m,-C<u>H</u>=CH_2), 5.2(1H,d, J=5Hz), and 5.07(1H,s), -CH=C<u>H_2</u>, 2.8-3.8(6H,m,bridgehead CH and allylic CH_2), 2.3(1H,d with st,J=14Hz,H_7<u>endo</u>), 2.03(1H,td, J_1=14Hz,J_2=10Hz,H_7<u>exo</u>).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.II.2): δ209.7 (s) and 209.0(s), >C=O, 180.1(s,-CH_2-C(=O)-C<u>H</u>=C(-O)-), 168.2(d, -C<u>H</u>=CH-C(=O)-), 133.5(d,-CH=C<u>H</u>-C(=O)-), 133.0(d,-C<u>H</u>=CH_2), 128.5(d, -CH_2-C(=O)-C<u>H</u>=C(-O)-), 118.1(t,C=C<u>H_2</u>), 56.8(d), 51.8(d), 51.2(d) and 50.8(d), bridgehead C's, 38.3(t,allylic CH_2), 27.8(t,CH_2).

Analysis for $C_{14}H_{14}O_2$ Calcd: C,78.48; H,6.59.
Found: C,78.27; H,6.8.

<u>Reaction of tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-diene-3,11-dione(7) with excess allylmagnesium chloride</u>:

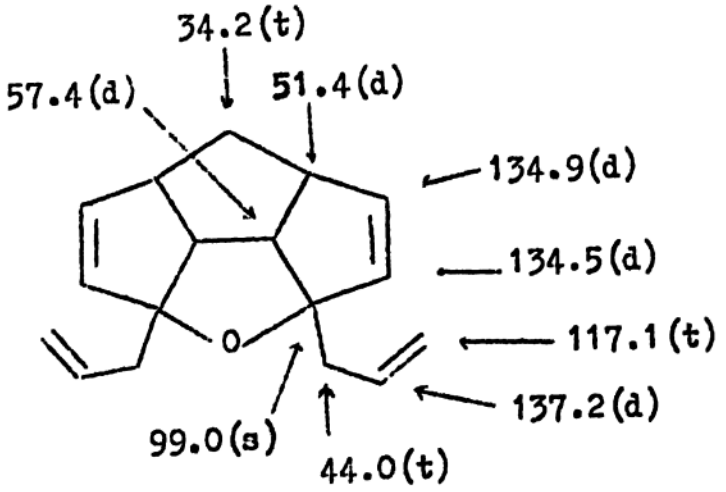
To a magnetically stirred suspension of magnesium (730 mg, 0.03 g atom) in 10 ml of dry ether was added dropwise a solution of allyl chloride (3 g, 39.2 mmoles) in 5 ml of dry ether. The mixture was stirred at room temperature until all the magnesium had dissolved. To this solution of allyl-magnesium chloride was added a solution of bis-enone <u>7</u> (1 g, 5.75 mmoles) in 6 ml of THF over a period of 15 min. The

reaction mixture was stirred vigorously at room temperature for 30 min, quenched by careful addition of saturated NH_4Cl solution and extracted with ether (25 ml x 3). The ether extract was washed and dried. Evaporation of the solvent furnished 1.1 g of crude material which was charged on a silica gel (25 g) column and chromatographed. Elution with benzene furnished 100 mg (8%) of 4,6-diallyl 5-oxatetracyclo[7.2.1.$0^{4,11}.0^{6,10}$]dodeca-2,7-diene (31) and was bulb to bulb distilled (150°C/0.6 mm).

IR spectrum (neat), ν_{max}: 1642, 910 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ4.7-6.1(10H,m,olefinic), 3.06(4H,brs,bridgehead CH), 2.24(4H,d with st,J=6Hz, allylic CH_2), 1.8(2H,brs,H_{12}).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ137.2, 134.9, 134.5, 117.1, 99.0, 57.4, 51.4, 44.0, 34.2. Assignments and multiplicities are displayed on the structure shown below



31

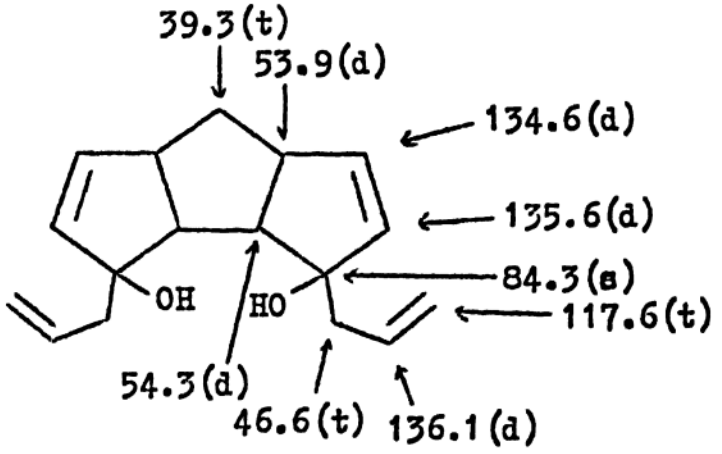
Analysis for $C_{17}H_{20}O$ Calcd: C,84.96; H,8.39.
Found: C,84.80; H,8.15.

Careful elution of the column with 5% ethyl acetate-benzene furnished 500 mg (33%) of 3,11-diallyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-diol (32) which was crystallised from pet ether, mp.70-1°C.

IR spectrum (KBr), ν_{max}: 3200, 1640, 905 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ5.6-6.1(2H,m,-C<u>H</u>=CH_2), 5.84(2H,dd,J_1=6Hz,J_2=2.5Hz,-C<u>H</u>=CH-), 5.58(2H,dd,J_1=6Hz,J_2=2Hz,-CH=C<u>H</u>-), 5.15(2H,d,J=4Hz) and 5.02(2H,s), C=C<u>H_2</u>, 3.96(2H,s,-O<u>H</u>), 2.0-3.4(9H,m,ring CH), 1.24(1H,td,J_1=12Hz, J_2=9Hz,H_7<u>exo</u>).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ136.1, 135.6, 134.6, 117.6, 84.3, 54.3, 53.9, 46.6, 39.3. Assignments and multiplicities are displayed on the structure shown below.



<u>32</u>

Analysis for $C_{17}H_{22}O_2$ Calcd: C,79.03; H,8.58.
Found: C,79.56; H,8.65.

Further elution of the column with the same solvent furnished 370 mg (25%) of the hemi-ketal, 4,8-diallyl 5-oxa-tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodec-2-en-6-ol (33) and was bulb to bulb distilled (160°C/0.6 mm).

IR spectrum (neat), ν_{max}: 3400, 1640 and 915 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ5.2-6.0(2H,m,-C<u>H</u>=CH_2), 5.64(1H,d,J=5Hz,-C<u>H</u>=CH-), 5.42(1H,d,J=5Hz,-CH=C<u>H</u>-), 4.6-5.2(4H,m,C=C<u>H_2</u>),4.4(1H,s,-OH), 3.1(3H,brs,bridgehead CH), 2.5(1H,d,J=7Hz), 1.0-2.2(8H,m), 0.84(1H,m).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ137.9(d,-<u>C</u>H=CH-), 136.9(d,-<u>C</u>H=CH_2), 134.4(d,-CH=<u>C</u>H-), 133.2(d,-<u>C</u>H=CH_2), 117.0 (s,>C<$^{OH}_{O-}$), 116.7(t,C=<u>C</u>H_2), 114.8(t,C=<u>C</u>H_2), 102.0(s,CH_2-<u>C</u>-O-), 61.6(d), 55.6(d), 53.3(d) and 51.9(d), bridgehead C's, 45.9 (C_7), 44.1(t,allylic CH_2), 42.8(d,C_9), 38.3(t,allylic CH_2), 34.6(t,C_{12}).

Analysis for $C_{17}H_{22}O_2$ Calcd: C,79.03; H,8.58.
Found: C,79.16; H,8.07.

<u>5,11-Diallyl tricyclo[6.3.0.$0^{2,6}$]undec-10-en-3,9-dione(34)</u>:

To a magnetically stirred suspension of pyridinium chlorochromate (400 mg, 1.86 mmoles)[17] in 10 ml of dichloro-

methane was added the hemi-ketal 33 (200 mg, 0.75 mmole) in 5 ml of dichloromethane. The heterogeneous reaction mixture was stirred vigorously for 4 hr at room temperature and filtered through a short silica gel (10 g) column. Evaporation of the solvent furnished 160 mg (80%) of the en-dione 34 as an oil, which was bulb to bulb distilled (160°C/1 mm). The distilled material solidified on refrigeration.

IR spectrum (neat), ν_{max}: 1730 (cyclopentanone), 1700 and 1610 (cyclopentenone), 1640 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ5.5-6.2(3H,m,olefinic), 4.85-5.45(4H,m,C=C$\underline{H}_2$), 1.6-3.8(13H,m).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ218.1(s,cyclopentanone), 210.7(s,cyclopentenone), 181.3(s,CH_2-$\underline{C}$=CH-$\underline{C}$=O), 135.8(d,-$\underline{C}$H=CH_2), 133.3(d,-$\underline{C}$H=CH_2), 129.6(d,CH_2-$\underline{C}$=$\underline{C}$H-$\underline{C}$=O), 118.2(t,C=$\underline{C}H_2$), 116.9(t,C=$\underline{C}H_2$), 54.3(d), 53.9(d), 52.0(d) and 51.5(d), bridgehead C's, 43.6(t,C_4), 39.5(t,allylic CH_2), 38.2(d,C_5), 37.8(t,allylic CH_2), 31.1(t,C_7).

Analysis for $C_{17}H_{20}O_2$ Calcd: C,79.65; H,7.86.
Found: C,79.66; H,8.16.

Reaction of 3,11-diallyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-diol(32) with PCC:

To a magnetically stirred suspension of pyridinium chlorochromate (430 mg, 2 mmole)[17] in 10 ml of dichloromethane

was added a solution of the diol 32 (260 mg, 1 mmole) in 5 ml of dichloromethane. The heterogeneous reaction mixture was stirred vigorously for 2 hr and filtered through a short silica gel (5 g) column. Evaporation of the solvent furnished 200 mg (84%) of 4,6-diallyl 5-oxatetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$] dodeca-2,7-diene (31), which was identified by comparison (TLC, IR spectrum) with the sample obtained earlier.

11-Phenyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-dione(36):

To a magnetically stirred suspension of magnesium (365 mg, 0.015 g atom) in 15 ml of dry ether was added dropwise a solution of bromobenzene (2.35 g, 15 mmoles) in 7 ml of dry ether. The mixture was stirred at room temperature until all the magnesium had dissolved. The phenylmagnesium bromide was syringed out and injected slowly into a magnetically stirred solution of the bis-enone 7 (2 g, 11.5 mmoles) in 20 ml of dry THF. The reaction mixture was stirred vigorously at room temperature for 20 min and quenched by careful addition of saturated NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with dichloromethane (50 ml x 2). The combined organic extract was washed and dried. Evaporation of the solvent furnished 3.2 g of crude material containing approximately 25% of the hemi-ketal 35. An analytical sample of the hemi-ketal was prepared by filtering the crude hemi-ketal through a silica gel column with 10% ethyl acetate-benzene, followed by crystallisation from

dichloromethane-hexane, mp.134-5°C.

IR spectrum (KBr), ν_{max}: 3410 (hydroxyl), 1625 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ6.75-7.5(5H,m,aromatic), 5.6(2H,m), 5.34(1H,d,J=6Hz) and 5.2(1H,d,J=6Hz) (olefinic), 4.02(1H,s,-CH), 2.75-3.5(4H,m,bridgehead CH), 1.74(2H,brs,CH_2).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ145.3(aromatic), 138.8, 137.6, 134.0 and 133.3 (olefinic), 128.0(2C), 126.6 and 124.7(2C), aromatic, 120.5($>C<^{OH}_{O-}$), 100.3(Ph-C-O-), 60.7, 59.8, 51.8 and 50.3, bridgehead C's, 34.1(CH_2).

Analysis for $C_{17}H_{16}O_2$ Calcd: C,80.93; H,6.39.
Found: C,81.64; H,6.54.

The crude hemi-ketal 35 (3.2 g) was taken in 15 ml of dichloromethane and added to a magnetically stirred suspension of pyridinium chlorochromate (3 g, 14 mmoles)[17] in 10 ml of dichloromethane. The heterogeneous reaction mixture was stirred vigorously for 7 hr at room temperature and filtered through a silica gel (10 g) column. The crude product (1.2 g) obtained was recharged on a silica gel (20 g) column and chromatographed. Elution with 20% ethyl acetate-benzene furnished 650 mg (22.5%) of the single transposed bis-enone 36, which was crystallised from carbon tetrachloride, mp. 111-2°C.

UV spectrum, λ_{max}^{MeOH}: 296 (ε =17,500), 220 nm (ε = 15,500).

IR spectrum (CH_2Cl_2), ν_{max}: 1705 (carbonyl), 1602, 1595 and 1575 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.II.3): δ7.7(1H, dd,J_1=6Hz,J_2=3Hz,-HC=CH-C=O), 7.3-7.8(5H,m,aromatic), 6.31 (1H,s,Ph-C=CH-C=O), 5.79(1H,dd,J_1=6Hz,J_2=2.5Hz,-CH=CH-C=O), 4.16(1H,dd,J_1=11Hz,J_2=7Hz,H_1), 3.52(1H,m) and 2.9-3.3(2H,m), bridgehead CH, 2.42(1H,½AB,J=14Hz,H_7endo), 2.1(1H,td,J_1= 14Hz,J_2=10Hz,H_7exo).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.II.4): δ209.0 (s,C_3), 206.9(s,C_9), 172.9(s,Ph-C=CH-C=O), 167.2(d,-CH=CH-C=O), 133.5(s,aromatic), 133.0(d,-CH=CH-C=O), 130.5(d,Ph-C= CH-C=O), 127.9(d,2C), 127.3(d,2C) and 124.6(d), aromatic, 56.3(d), 51.4(d), 50.7(d) and 47.9(d), bridgehead C's, 27.4 (t,CH_2).

Analysis for $C_{17}H_{14}O_2$ Calcd: C,81.58; H,5.64.
Found: C,81.14; H,5.72.

Reaction of tricyclo[6.3.0.$0^{2,6}$]undeca-4,9-dien-3,11-dione(7) with excess phenylmagnesium bromide:

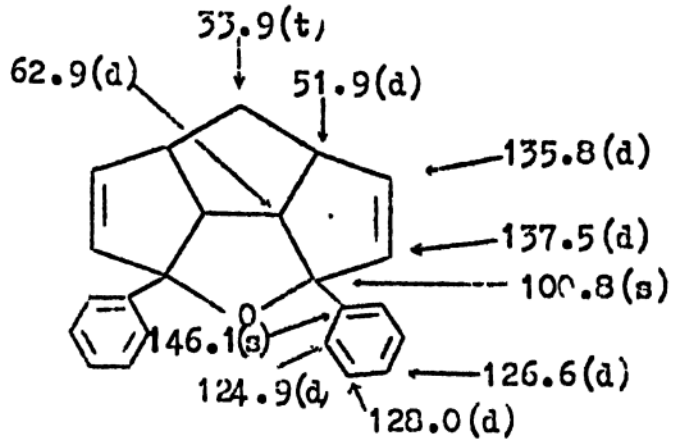
To a magnetically stirred suspension of magnesium (375 mg, 0.015 g atom) in 15 ml of dry ether was added dropwise a solution of bromobenzene (2.4 g, 15.5 mmoles) in 5 ml of dry

ether. The reaction mixture was stirred until all the magnesium had dissolved. To this phenylmagnesium bromide solution was added a solution of bis-enone 7 (522 mg, 3 mmoles) in 10 ml of dry THF over a period of 15 min. The reaction mixture was stirred vigorously for 20 min at room temperature and quenched by careful addition of saturated NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with dichloromethane (25 ml x 3). The combined organic extract was washed and dried. Evaporation of the solvent furnished 1.5 g of crude material which was charged on a silica gel (25 g) column and chromatographed. Elution with benzene afforded 100 mg (11%) of 4,6-diphenyl-5-oxa-tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodeca-2,7-diene (38), which was crystallised from pet ether, mp.145-6°C.

IR spectrum (CCl_4), ν_{max}: 1600 cm^{-1} (aromatic).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ7.0-7.6(10H,m, aromatic), 5.7, 5.42(4H,AB quartet,J=5Hz,-HC=CH-), 3.0-3.48 (4H,m,bridgehead CH), 1.86(2H,brs,CH_2).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ146.1, 137.5, 135.8, 128.0, 126.6, 124.9, 100.8, 62.9, 51.9, 33.9. Assignments and multiplicities are displayed on the structure shown below.



38

Analysis for $C_{23}H_{20}O$ Calcd: C,88.43; H,6.45.

Found: C,88.22; H,6.39.

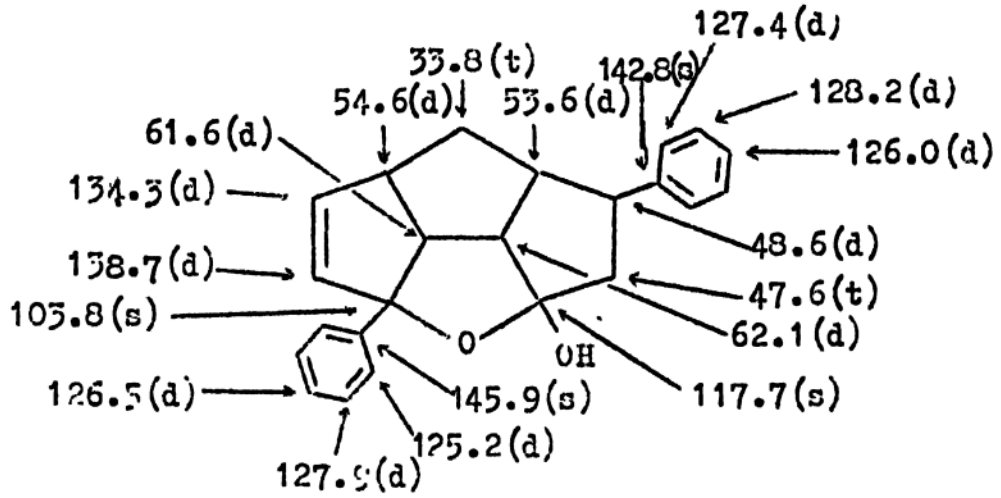
Further elution of the column with 20% ethyl acetate-benzene furnished 450 mg (50.5%) of the hemi-ketal, 4,8-diphenyl-5-oxatetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodec-2-en-6-ol (39), which was crystallised from dichloromethane-pet ether, mp. 137-8°C.

IR spectrum (KBr), ν_{max}: 3400 cm^{-1} (hydroxyl).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ7.0-7.6(10H,m,aromatic), 5.93, 5.69(2H,ABquartet,J=6Hz,-CH=CH-), 4.73(1H,s, -OH), 3.30(4H,m,bridgehead CH), 1.9-2.7(3H,m), 1.66(2H,brs, H_{12}).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ145.9, 142.8, 138.7, 134.3, 128.2(2C), 127.9(2C), 127.4(2C), 126.5, 126.0, 125.2(2C), 117.7, 103.8, 62.1, 61.6, 54.6, 53.6, 48.6, 47.6, 33.8. Assignments and multiplicities are displayed on

structure shown below.



39

Analysis for $C_{23}H_{22}O_2$ Calcd: C,83.60; H,6.71.

Found: C,83.61; H,6.64.

5,11-Diphenyl tricyclo[6.3.0.$0^{2,6}$]undec-10-en-3,9-dione(40):

To a magnetically stirred suspension of pyridinium chlorochromate (215 mg, 1 mmole)[17] in 5 ml of dichloromethane was added a solution of the hemi-ketal 39 (220 mg, 0.66 mmole) in 2 ml of dichloromethane. The heterogeneous reaction mixture was stirred vigorously at room temperature for 4 hr and filtered through a short silica gel (5 g) column. Evaporation of the solvent furnished 190 mg (85%) of the transposed enone 40, which was crystallised from dichloromethane-pet ether, mp.128-9°C.

UV spectrum, λ_{max}^{MeOH}: 292 nm (ε = 15,250).

IR spectrum (KBr), ν_{max}: 1740 (cyclopentanone), 1680 (cyclopentenone), 1570 and 1590 cm^{-1} (olefinic).

^{1}H NMR spectrum (100 MHz, $CDCl_3$): δ7.0-7.8(10H,m,aromatic), 6.48(1H,d,J=1Hz,olefinic), 4.26(1H,dd,J_1=11Hz,J_2=6Hz, H_1), 2.7-3.35(4H,m,bridgehead CH and benzylic CH), 2.0-2.5 (4H,m,CH_2).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ215.3(s,cyclopentanone), 210.6(s,cyclopentenone), 175.0(s,Ph-$\underline{\dot{C}}$=CH-$\dot{C}$=O), 131.2(d,Ph-$\dot{C}$=$\underline{C}$H-$\dot{C}$=O), 142.6(s), 133.5(s), 128.5(d,2C), 128.3 (d,2C), 127.4(d,2C), 127.2(d), 126.8(d,2C) and 126.6(d),aromatic C's, 55.2(d), 54.8(d), 54.1(d) and 48.9(d), bridgehead C's, 45.3(t,C_4), 45.1(d,benzylic), 30.5(t,C_7).

Analysis for $C_{23}H_{20}O_2$ Calcd: C,84.12; H,6.14.
Found: C,83.78; H,6.65.

<u>11-p-Methoxyphenyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-dione(42)</u>:

To a magnetically stirred suspension of magnesium (365 mg, 0.015 g atom) in 30 ml of dry ether was added dropwise a solution of p-bromoanisole (2.8 g, 15 mmoles) in 15 ml of dry ether. The mixture was stirred at room temperature until all the magnesium had dissolved. The p-methoxyphenylmagnesium bromide solution was syringed out and injected slowly into a magnetically stirred solution of the bis-enone 7 (2 g, 11.5 mmoles) in 20 ml of dry THF at room temperature. The reaction mixture was stirred vigorously for 20 min and quenched by careful addition of saturated NH_4Cl solution.

The organic layer was separated and the aqueous layer was extracted with dichloromethane (50 ml x 2). The combined organic extract was washed and dried. Evaporation of the solvent furnished 3.5 g of crude viscous material containing approximately 12% of the hemi-ketal 41. An analytical sample (quite unstable) of the hemi-ketal was prepared by chromatography on a silica gel column. Elution with 20% ethyl acetate-benzene furnished the hemi-ketal as viscous material.

IR spectrum (neat), ν_{max}: 3400 cm^{-1} (hydroxyl).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ7.26(2H,d,J=9Hz) and 6.8(2H,d,J=9Hz), aromatic, 5.7(2H,m), 5.43(1H,d,J=5Hz) and 5.26(1H,d,J=5Hz), olefinic, 3.75(3H,s,$-OCH_3$), 3.22(4H,m, bridgehead CH), 1.82(2H,m,CH_2).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ158.5(C-OCH_3), 139.3, 137.6, 134.0 and 133.1 (olefinic), 128.4, 125.9(2C) and 113.5(2C), aromatic, 120.5(>C<OH/O), 100.2(Ar-C-O-), 60.8, 60.1, 51.8 and 50.5, bridgehead C's, 55.2($-OCH_3$), 34.2(CH_2).

The crude hemi-ketal 41 (3.5 g) obtained above was taken in 8 ml of dichloromethane and added to a magnetically stirred suspension of pyridinium chlorochromate (3 g, 14 mmoles)[17] in 10 ml of dichloromethane. The heterogeneous reaction mixture was stirred vigorously for 5 hr at room temperature and then filtered through a silica gel (20 g) column. The product obtained was recharged on a silica gel (20 g) column and chromatographed. Elution with 30% ethyl acetate-

benzene furnished 320 mg (10%) of the single transposed bis-enone 42, which was crystallised from dichloromethane-pet ether, mp.134-5°C.

UV spectrum, λ_{max}^{MeOH}: 222 (ε = 15,500) and 325 nm (ε = 22,200).

IR spectrum (CH_2Cl_2), ν_{max}: 1710 (carbonyl), 1600, 1590 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.II.5): δ7.65(2H, d,J=9Hz,$H_{2'}$), 7.46(1H,dd,J_1=6Hz,J_2=3Hz,-C<u>H</u>=CH-C=O), 6.95(2H, d,J=9Hz,$H_{3'}$), 6.2(1H,s,Ar-C=C<u>H</u>-C=O), 5.78(1H,dd,J_1=6Hz,J_2= 2Hz,-CH=C<u>H</u>-C=O), 4.13(1H,dd,J_1=12Hz,J_2=6Hz,H_1), 3.86(3H,s, $-OCH_3$), 3.5(1H,m) and 2.9-3.3(2H,m), bridgehead CH, 2.45(1H, ½AB,J=12Hz,H_7<u>endo</u>), 2.13(1H,td,J_1=12Hz,J_2=9Hz,H_7<u>exo</u>).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.II.6): δ209.1 (s,C_3), 207.1(s,C_9), 172.7(s,Ar-<u>C</u>=CH-C=O), 167.1(d,-<u>C</u>H=CH-C=O), 161.7(s,<u>C</u>-OCH_3), 133.3(d,-CH=<u>C</u>H-C=O), 129.4(d,2C,$C_{3'}$), 126.5(s,$C_{1'}$), 122.7(d,Ar-C=<u>C</u>H-C=O), 113.5(d,2C,$C_{2'}$), 55.0(q, $-O\underline{C}H_3$), 56.4(d), 51.7(d), 50.9(d) and 48.3(d), bridgehead C's, 27.6(t,CH_2).

<u>2-Methyl pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undeca-5,11-dione(43)</u>:

A solution of 11-methyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-dione (24, 500 mg, 2.66 mmoles) in 120 ml of ethyl acetate was carefully purged with a slow stream of dry nitrogen

for 15 min. The solution was then irradiated with a Hanovia 450 W medium pressure mercury vapour lamp in a quartz immersion well using a pyrex filter for 40 min. Alternatively, the photolysis can be carried out in a pyrex flask in Sunlight for 2 hr. After the completion of the photolysis, solvent was evaporated and the crude photolysate was crystallised from dichloromethane-hexane. The pentacyclic dione 43 (485 mg, 97%) crystallised as heavy prisms, mp.200-1°C.

IR spectrum (KBr), ν_{max}: 1760, 1730 cm^{-1} (carbonyl).

^1H NMR spectrum (100 MHz, $CDCl_3$, Fig.II.7): δ2.6-3.1 (4H,m), 2.0-2.55(5H,m), 1.1(3H,s,$-CH_3$).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.II.8): δ213.0 (s) and 212.9(s),>C=O , 57.0(d), 55.0(d), 51.1(d), 49.7(d), 45.8(d), 43.7(t,CH_2), 42.6(d), 42.1(s,C-CH_3), 38.6(d), 22.0 (q,CH_3).

Analysis for $C_{12}H_{12}O_2$ Calcd:C,76.57; H,6.43.
Found:C,76.21; H,6.09.

2-Allyl pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undeca-5,11-dione(44):

A solution of 11-allyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-dione (29, 320 mg, 1.5 mmoles) in 120 ml of ethyl acetate was carefully purged with a slow stream of dry nitrogen for 15 min. The solution was then irradiated with a Hanovia 450 W medium pressure mercury vapour lamp in a quartz

immersion well using a pyrex filter for 25 min. Alternatively the irradiation can be carried out in a pyrex flask in Sunlight for 3 hr. After the completion of the photolysis, evaporation of the solvent and bulb to bulb distillation (120°C/0.6 mm) furnished 320 mg (100%) of the diketone 44. Crystallisation from dichloromethane-pet ether furnished the crystalline compound, mp.69-70°C.

IR spectrum (KBr), ν_{max}: 1760 and 1735 (carbonyl), 1640 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ5.2-5.8(1H,m,-CH=CH_2), 4.8-5.2(2H,m,-CH=CH_2), 2.6-3.18(5H,m,ring CH), 1.9-2.6 (6H,m).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.II.9): δ213.0 (s) and 212.8(s),>C=O , 131.0(d,-CH=CH_2), 119.3(t,-CH=CH_2), 55.1(d), 54.8(d), 51.1(d), 47.2(d), 44.6(s,C_2), 43.8(2C,t and d), 42.7(d), 39.7(t), 38.7(d).

Analysis for $C_{14}H_{14}O_2$ Calcd: C,78.48; H,6.59.
Found: C,78.24; H,6.65.

2-Phenyl pentacyclo[5.4.0.$0^{2,6}$.$0^{3.10}$.$0^{4,8}$]undeca-5,11-dione(45):

A solution of 11-phenyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-dione (36, 250 mg, 1 mmole) in 120 ml of ethyl acetate was carefully purged with a slow stream of dry nitrogen for 15 min. The solution was then irradiated with a Hanovia 450 W medium

pressure mercury vapor lamp in a quartz immersion well using a pyrex filter for 15 min. Alternatively the photolysis can be carried out in a pyrex flask in Sunlight for 2.5 hr. After the completion of the photolysis, solvent was evaporated and the crude photolysate was crystallised from carbon tetrachloride to furnish 250 mg (100%, colourless needles) of the cage dione 45, mp.146-7°C.

IR spectrum (KBr), ν_{max}: 1765, 1740 cm^{-1} (carbonyl).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ7.3(3H,m) and 6.95 (2H,m) (aromatic), 2.2-3.5(9H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.II.10): δ213.1 and 212.9, >C=O , 142.6, 128.8(2C), 127.2 and 124.2(2C), aromatic, 55.9, 54.7, 52.5, 51.2, 46.6, 45.7, 44.1, 42.8, 38.5.

Analysis for $C_{17}H_{14}O_2$ Calcd: C,81.58; H,5.64.
Found: C,81.06; H,5.34.

2-p-Methoxyphenyl pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undeca-5,11-dione(46):

A solution of 11-p-methoxyphenyl tricyclo[6.3.0.$0^{2,6}$] undeca-4,10-dien-3,9-dione(42, 280 mg, 1 mmole) in 120 ml of ethyl acetate was carefully purged with a slow stream of dry nitrogen for 10 min. The solution was then irradiated with a Hanovia 450 W medium pressure mercury vapor lamp in a quartz immersion well using a pyrex filter for 50 min. Alternatively,

the photolysis can be carried out in a pyrex flask in Sunlight for 4 hr. After the completion of the photolysis, solvent was evaporated and the crude photolysate was filtered through a short silica gel (10 g) column using 5% ethyl acetate-benzene. Evaporation of the solvent furnished 255 mg (91%) of the pentacyclic dione 46, and was crystallised from dichloromethane-pet ether, mp.168-9°C.

IR spectrum (KBr), ν_{max}: 1760, 1735 (carbonyl), 1615 cm^{-1} (aromatic).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ6.5-7.0(4H,m,aromatic), 3.76(3H,s,$-OCH_3$), 2.1-3.5(9H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig.II.11): δ213.3 (s) and 213.2(s), >C=O , 158.7(s), 134.9(s), 125.5(d,2C) and 114.3(d,2C), aromatic, 56.1(d), 55.2(q,$-OCH_3$), 54.8(d), 52.8(d), 51.3(d), 46.3(s,C_2), 45.9(d), 44.2(t,CH_2), 42.9(d), 38.4(d).

Analysis for $C_{18}H_{16}O_3$ Calcd: C,77.12; H,5.75.
Found: C,77.33; H,5.52.

Photoreversion of 2-p-methoxyphenyl pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undeca-5,11-dione(46) with PTSA:

A solution of the dione 46 (5 mg, 0.018 mmole) and catalytic amount of p-toluenesulphonic acid in 3 ml of benzene was stirred at room temperature for 2 hr. The reaction

mixture was diluted with benzene, washed with aqueous $NaHCO_3$ and dried. Evaporation of the solvent furnished 5 mg (100%) of the bis-enone 42, which was characterised by comparison (TLC, IR spectrum) with the authentic sample.

Photoreversion of 2-p-methoxyphenyl pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undeca-5,11-dione(46) with boron trifluoride etherate:

A solution of the pentacyclic dione 46 (100 mg, 0.36 mmole) and boron trifluoride etherate (0.2 ml) in 5 ml of dry benzene was magnetically stirred at room temperature for 5 min. The reaction mixture was diluted with more benzene (15 ml), washed with aqueous $NaHCO_3$ and dried. Evaporation of the solvent furnished the bis-enone 42 in quantitative yield and was identified by comparison (TLC and IR spectrum) with the authentic sample.

Photoreversion of 2-p-methoxyphenyl pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$]undeca-5,11-dione(46) with trifluoroacetic acid:

A solution of pentacyclic dione 46 (5 mg, 0.018 mmole) and trifluoroacetic acid (5 drops) in 3 ml of dichloromethane was stirred at room temperature for 30 min. The reaction mixture was diluted with dichloromethane (5 ml), washed with aqueous $NaHCO_3$ and dried. Evaporation of the solvent furnished 5 mg (100%) of the bis-enone 42, which was identified by comparison (TLC, IR spectrum) with the authentic sample.

Photoreversion of 2-methyl pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}] undeca-5,11-dione(43) with PTSA:

A solution of pentacyclic dione 43 (100 mg, 0.53 mmole) and p-toluenesulphonic acid (120 mg, 0.7 mmole) in 5 ml of toluene was refluxed for 6 hr. The reaction mixture was diluted with benzene (15 ml), washed with aqueous sodium bicarbonate and dried. Evaporation of the solvent and filtration through a small silica gel (5 g) column furnished 20 mg (20%) of the bis-enone 24, which was identified by comparison (TLC and IR spectrum) with the authentic sample.

Photoreversion of 2-methyl pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}] undeca-5,11-dione(43) with boron trifluoride etherate:

A solution of pentacyclic dione 43 (100 mg, 0.53 mmole) and boron trifluoride etherate (0.4 ml) in 5 ml of dry benzene was refluxed for 2 hr. The reaction mixture was diluted with benzene (15 ml), washed with aqueous $NaHCO_3$ and dried. Evaporation of the solvent furnished 65 mg (65%) of the bis-enone 24, which was identified by comparison (TLC, IR spectrum) with authentic sample.

Photoreversion of 2-phenyl pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}] undeca-5,11-dione(45) with PTSA:

A solution of pentacyclic dione 45 (5 mg, 0.02 mmole) and catalytic amount of p-toluenesulphonic acid in 3 ml of benzene was refluxed for 2 hr. The reaction mixture was diluted with more benzene (5 ml), washed with aqueous $NaHCO_3$

and dried. Evaporation of the solvent furnished 5 mg (100%) of the bis-enone 36 which was identified by comparison (TLC, IR spectrum) with the authentic sample.

Photoreversion of 2-phenyl pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$] undeca-5,11-dione(45) with boron trifluoride etherate:

A solution of the pentacyclic dione 45 (100 mg, 0.4 mmole) and boron trifluoride etherate (0.2 ml) in 5 ml of dry benzene was magnetically stirred at room temperature for 40 min. The yellow reaction mixture was diluted with more benzene (15 ml), washed with aqueous $NaHCO_3$ and dried. Evaporation of the solvent furnished the bis-enone 36 quantitatively and was identified by comparison (TLC, IR spectrum) with the authentic sample.

Determination of quantum yields:

For the measurement of quantum yields, potassium ferrioxalate actinometry[22] was employed. All irradiations were carried out, under identical conditions (static), using a Hanovia 450 W medium pressure mercury vapour lamp in a quartz immersion well and the light was filtered using a corning 7-60 filter (300 nm to 390 nm with a maximum flux at 360 nm).

Determination of the intensity of light:

A 3 ml solution of potassium ferrioxalate ($\sim$0.006 M, made by dissolving 73.6 mg of potassium ferrioxalate in

22.5 ml of water and 2.5 ml of 1N H_2SO_4 in dark) in a test tube was irradiated for 5 min. After the irradiation, the sample was transferred into a 10 ml standard flask (protected from light) and 0.8 ml of 0.1% 1,10-phenanthroline (w/v) solution, 1.5 ml buffer (prepared by mixing 15 ml of 1N NaOAc and 9 ml of 1N H_2SO_4) were successively added. The volume was made-up to 10 ml with water. The flask was stored in dark for 1 hr along with a blank solution prepared in an identical manner using a 3 ml solution of unirradiated potassium ferrioxalate. Finally, the optical density of the irradiated solution was determined (1.255) with reference to unirradiated solution at 510 nm.

Intensity of the light, $I = \frac{A.V}{\varepsilon.\phi.t}$ (A = absorbance, V = volume of the final solution, ε = molar extinction coefficient of Fe^{2+}-1,10-phenanthroline complex at 510 nm, ϕ = quantum efficiency of potassium ferrioxalate for the wavelength used, t = time of irradiation).

Hence, $I = \frac{1.255 \times 10}{1.11 \times 10^4 \times 1.23 \times 5} = 1.8384$ Einsteins/min.

Quantum efficiency of 11-methyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-dione(24):

A 3 ml solution of the bis-enone 24 (1.14×10^{-2}M in ethyl acetate) was irradiated for 20 min. After the completion of irradiation, the optical densities of irradiated (0.648) and unirradiated solutions (0.375) were measured at

325 nm.

Hence, number of moles of 24 reacted = 0.296×10^{-2}

$$\phi = \frac{0.296\times10^{-2}}{1.8384\times10^{-4}\times20} = 0.805$$

Quantum efficiency of 11-allyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-dione(29):

A 3 ml solution of the bis-enone 29 (0.194×10^{-2}M in ethyl acetate) was irradiated for 20 min. After the completion, the optical densities of irradiated (0.548) and unirradiated solutions (0.816) were measured at 325 nm.

Hence, number of moles of 29 reacted = 0.301×10^{-2}

$$\phi = \frac{0.301\times10^{-2}}{1.8384\times10^{-4}\times20} = 0.82$$

Quantum efficiency of 11-phenyl tricyclo[6.3.0.$0^{2,6}$]undeca-4,10-dien-3,9-dione(36):

A 3 ml solution of the bis-enone 36 (0.412×10^{-2}M in ethyl acetate) was irradiated for 10 min. After the completion of the irradiation the optical densities of irradiated (0.506) and unirradiated solutions (0.862) were measured after a dilution of 100 times at 289 nm.

Hence, number of moles of 36 reacted = 0.170×10^{-2}

$$\phi = \frac{0.170\times10^{-2}}{1.8384\times10^{-4}\times10} = 0.92$$

Quantum efficiency of 11-p-methoxyphenyl tricyclo[6.3.0.$0^{2,6}$] undeca-4,10-dien-3,9-dione(42):

A 3 ml solution of the bis-enone 42 (0.346×10^{-2}M in ethyl acetate) was irradiated for 10 min. After the completion of the irradiation the optical densities of the irradiated (0.610) and unirradiated solutions (0.812) were measured after a dilution of 100 times at 316 nm.

Hence, number of moles of 42 reacted = 0.086×10^{-2}

$$\phi = \frac{0.086\times10^{-2}}{1.8384\times10^{-4}\times10} = 0.48$$

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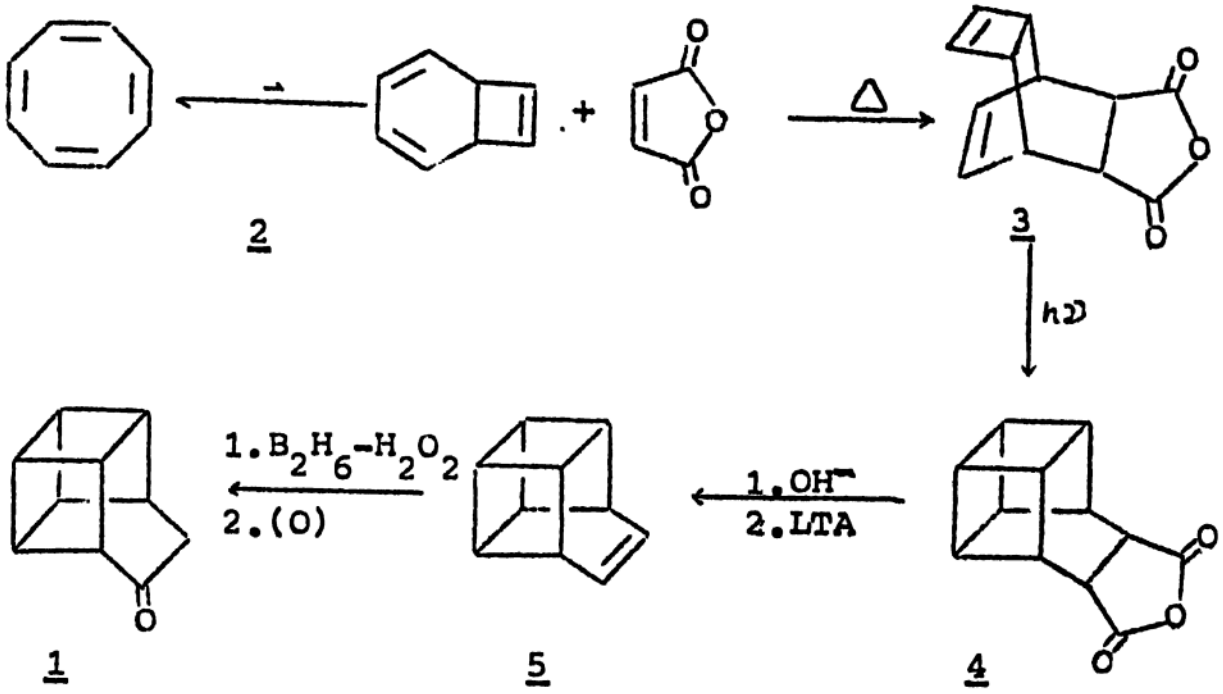
APPENDIX

CONVENIENT SYNTHESIS OF 1,8-BISHOMOCUBANONE (BASKETANONE) AND ITS CONGENERS

Among the various polycyclic molecules of current interest, the space-enclosing members of the cubyl cage family occupy position of special vintage as they are interesting substrates for a variety of thecretical, mechanistic and synthetic studies.[1] In connection with a project, concurrently underway in this laboratory, on the novel carbonium ion rearrangements of cubyl systems, triggered *via* Schmidt fragmentation of cubyl-ketones,[2] the pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$] decan-9-one (1,8-bishomocubanone, basketanone 1) was required in some quantity. Basketanone 1 has been prepared previously *via* hydroboration and oxidation of basketene 5 (Scheme 1).[3] The pentacyclic alkene 5 in turn was prepared[3,4] from cyclooctatetraene (COT, 2) *via* Diels-Alder cycloaddition with maleic anhydride (2⟶3),[5] photochemical $_{\pi}2_{s}$ + $_{\pi}2_{s}$ ring closure (3⟶4) and oxidative bis-decarboxylation (4⟶5). This methodology to 1 *via* basketene 5 is both circuitous and inefficient (25% yield in each of the crucial steps, 3⟶4 and 4⟶5). Furthermore, COT is no longer available, for the asking, from BASF and its commercial price has escalated sharply

SCHEME 1



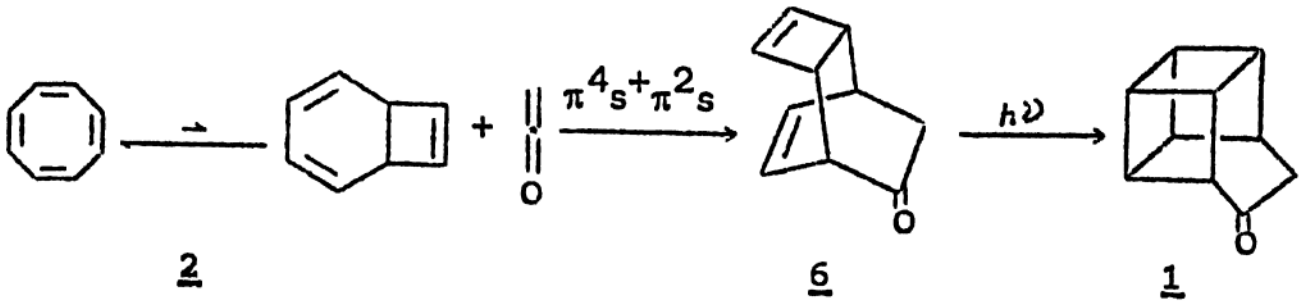
2 3 1 5 4

and quite disproportionately. Therefore, a need arose to develop a short, direct and preparatively useful route to 1. In the appendix to this thesis, convenient preparations of basketanone 1 and its congeners, snoutanone 16, basketane 14 and tricyclo[4.2.2.$0^{2,5}$]deca-3,7-dien-9-ones 6 and 11, are reported. Results of photochemistry of 6, studied in connection with its transformation to 1, proved to be quite interesting and are also described.

Ideally, the shortest route to 1 would be *via* addition of ketene or more precisely ketene-equivalent,[6] to COT to give tricyclic dienone 6 and further intramolecular photochemical ring closure to the pentacyclic ketone 1 (Scheme 2). However, this scheme is beset with practical difficulties. Firstly, COT either responds poorly[7] to the commonly deployed

ketene equivalents (e.g., α-chloroacrylonitrile, α-acetoxy acrylonitrile, etc.) or reacts in an unwanted fashion (e.g.,

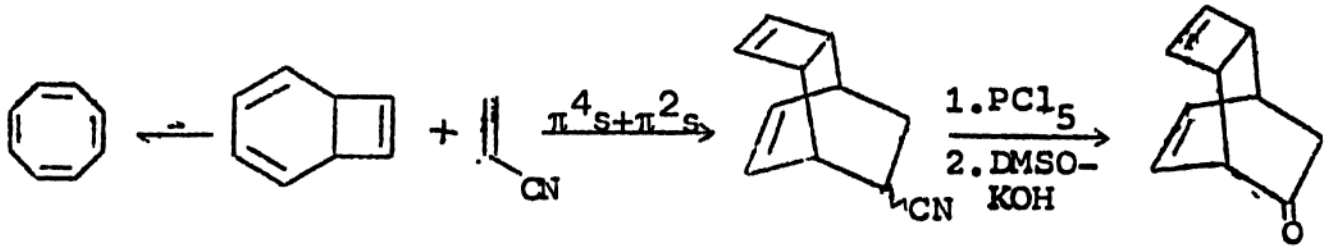
SCHEME 2



2 6 1

nitroethylene[8]). Secondly, even if one were to obtain the dienone 6 (using an inconvenient procedure developed by Freeman, Scheme 3),[7] its photochemical cycloaddition to 1 was expected to present some problems. Indeed, being a β,γ-unsaturated enone, 6 might undergo 1,3-acyl shift and oxa-di-π-methane rearrangement in competition with the intramolecular $\pi^2_s + \pi^2_s$ cycloaddition.[9] In order to circumvent the aforementioned difficulties and evolve a straightforward route to

SCHEME 3

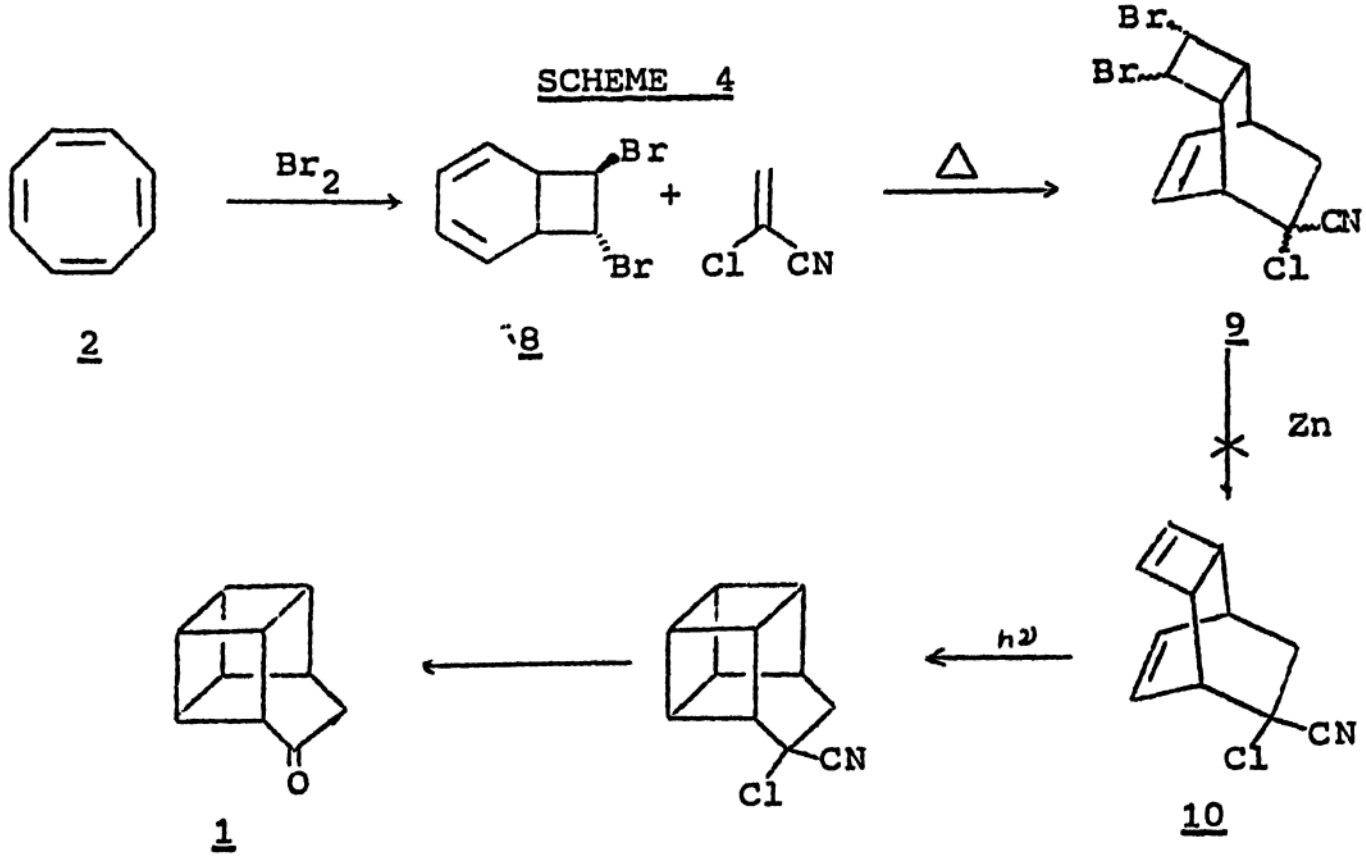


2 7 1

1, several different strategies were considered and pursued. The results of these studies are briefly described alongside the successfully evolved route to basketanone 1 and its congeners.

Since COT is unresponsive to common ketene equivalents (*vide supra*),[6] it was considered desirable to deploy a more reactive derivative of COT in the Diels-Alder reaction with the ketene equivalents. It is known that halogenated derivatives of COT, e.g., dibromoCOT 8, are much more reactive in cycloadditions than COT.[5,10] Also, as a double bond can be readily regenerated from vicinal dibromo compound, dibromo-COT can in effect serve as a 'reactive COT equivalent'. A route depicted in Scheme 4 was therefore envisaged. This effort began on a promising note. Indeed, dibromoCOT, reacted with α-chloroacrylonitrile in a sealed tube (105°C, 8 hr) to furnish the adduct 9 in >60% yield. However, attempts to debrominate 9 to 10 with zinc in dimethylformamide, under a

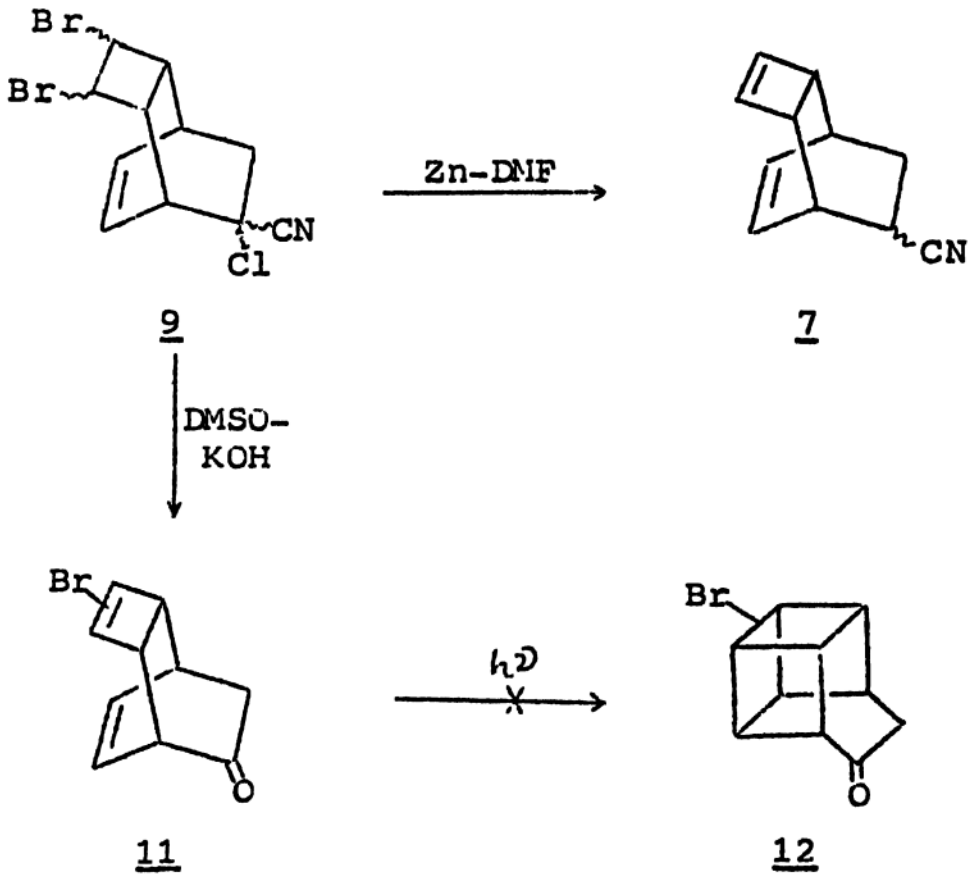
SCHEME 4



2 8 9 10 1

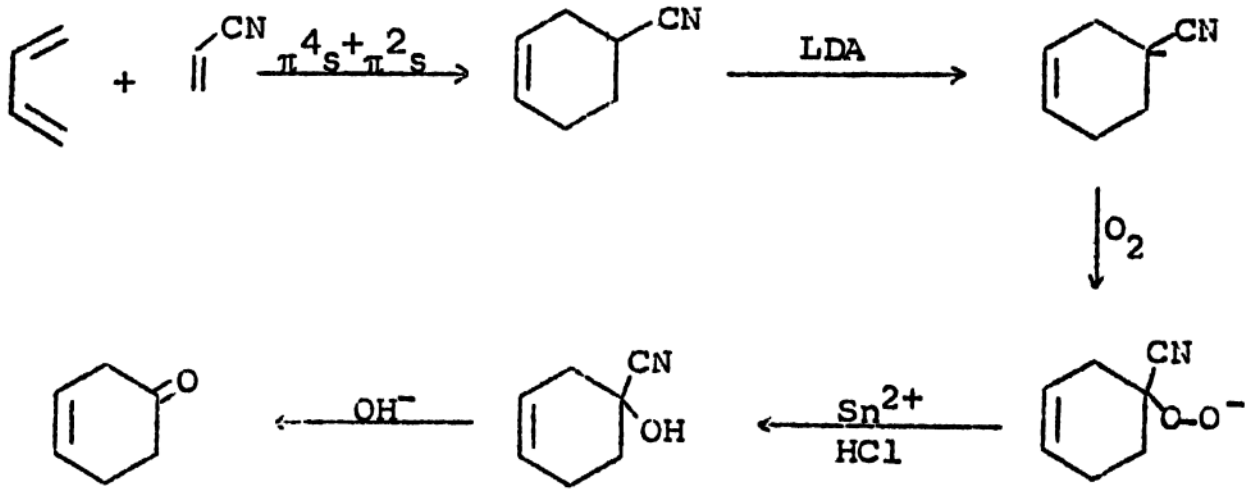
variety of conditions, led to simultaneous dechlorination and only 7 could be isolated as the reaction product (Scheme 5). Exposure of 9 to other dehalogenating agents (e.g., sodium phenanthrenide)[11] led to similar results with little evidence of the presence of required compound 10. Reaction of 9 with potassium hydroxide in DMSO at ambient temperature resulted in facile unravelling of the carbonyl group[7,12] together with concomitant dehydrobromination and tricyclic dienone 11 was obtained in good yield. Attempts to effect intramolecular photocycloaddition in 11 to bromobasketanone 12 proved unsuccessful, but led to some interesting results and these are described later in this section.

SCHEME 5



In the light of the experience gained in above experiments, it was decided to pursue a slightly different approach. Attention was now turned towards the selection of ketene equivalent,[6] which not only reacts readily with COT but in which the carbonyl unravelling step could be carried out either before or after photocycloaddition step. It is implicit in this strategy that the ketene equivalent must be photo-stable. A perusal of various ketene equivalents indicated that the Watt's oxidative decyanation strategy (Scheme 6),[13] involving

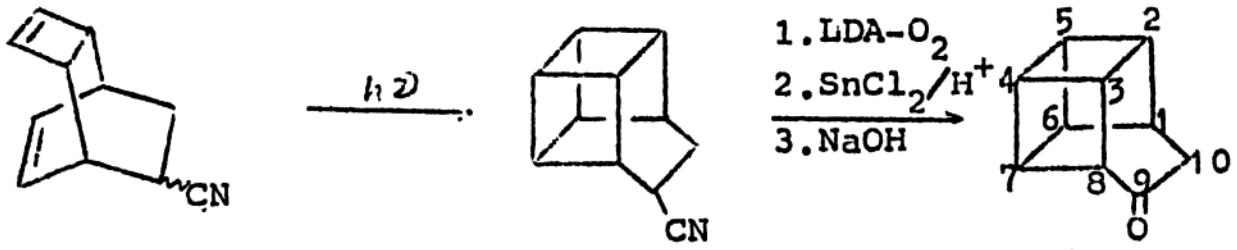
SCHEME 6



the intermediacy of α-hydroperoxynitriles, could be conveniently exploited in the present case. In relation to the problem at hand, it meant that acrylonitrile could serve as a ketene equivalent and a straightforward route to basketanone 1 emerged (Scheme 7).

The readily available[7] COT-acrylonitrile adduct 7, on

SCHEME 7



7 13 1

photolysis, under high dilution conditions (vide experimental), furnished the intramolecular $\pi^2_s + \pi^2_s$ photocycloaddition product 13 in 70% yield.[14] When subjected to Watt's oxidative decyanation sequence (a single pot operation), the caged cyano compound 13 furnished basketanone 1, mp.82-3°C in about 50% yield. The ketone 1 was fully characterised on the basis of its IR, ^1H and ^{13}C NMR spectral data. Its ^{13}C NMR spectrum (Fig. 1) was particularly revealing and showed eight resonances at δ 211.4(s), 47.8(d), 44.5(d), 43.1(d), 41.7(2C,d), 39.0(2C, d), 36.8(d) and 36.3(t) for the ten carbon atoms (C_2,C_6 and C_3,C_7 are equivalent). Thus, a simple, practical, three step sequence from COT to basketanone 1 is established.

The pentacyclic cyano compound 13, quite readily available from COT, proved to be a versatile precursor for the preparation of some useful compounds of this series. For example, reductive decyanation[15] of 13 with potassium in HMPA-CH_3OH furnished basketane 14 in 65% yield (Scheme 8) in only three steps from COT. This constitutes a most direct and

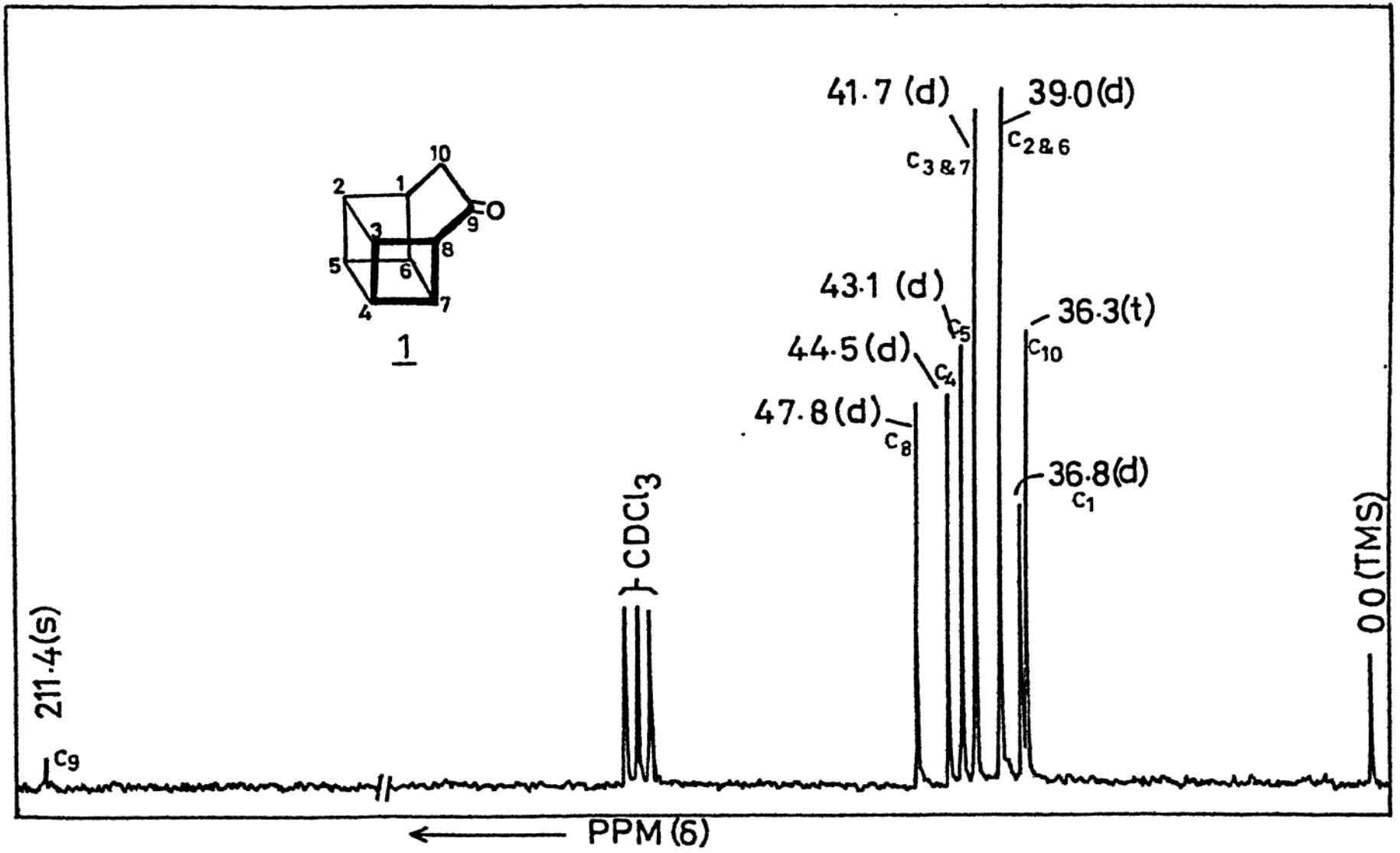
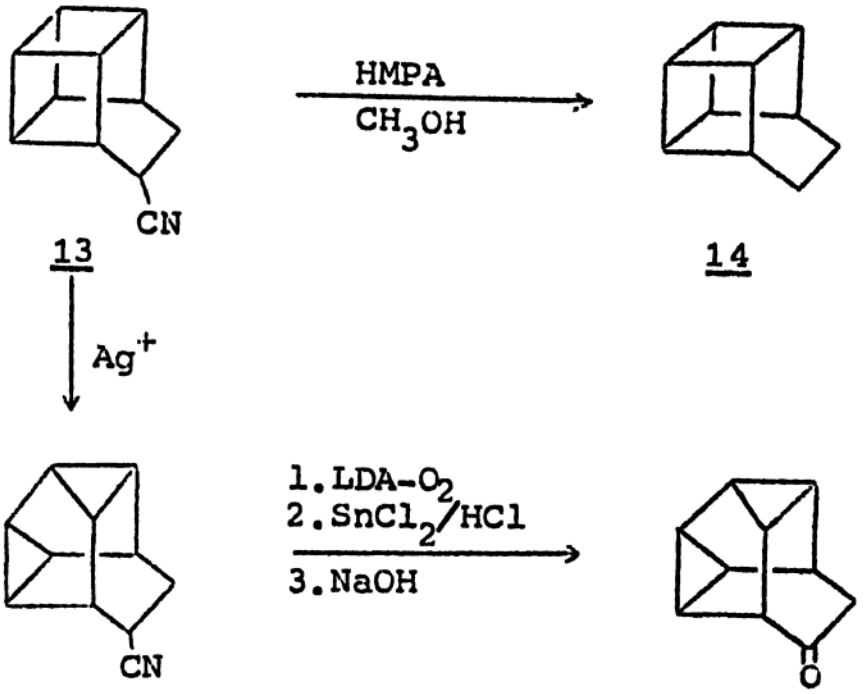


FIG 1 ^{13}C NMR (25·0 MHz) spectrum of 1

SCHEME 8



convenient method to this caged hydrocarbon. In another series of transformations, snoutanone 16 was synthesised from the pentacyclic cyano compound 13. The key transition metal catalysed isomerisation of the basketane ring system to the snoutane system[16] was simply effected by a passage of 13 through a silver nitrate impregnated silica gel column.[17] The nitrile 13 was thereby quantitatively transformed to 15. Oxidative decyanation of 15, as described above, furnished snoutanone 16 in 50% yield (Scheme 8). The identity of 16 was established through its IR and ^1H NMR spectral data and more convincingly through its ^{13}C NMR resonances (Fig. 2). As expected, 16 exhibited seven resonances at δ214.4(s), 48.2 (d), 38.1(t), 35.1(d), 31.6(2C,d), 31.4(2C,d) and 30.4(2C,d)

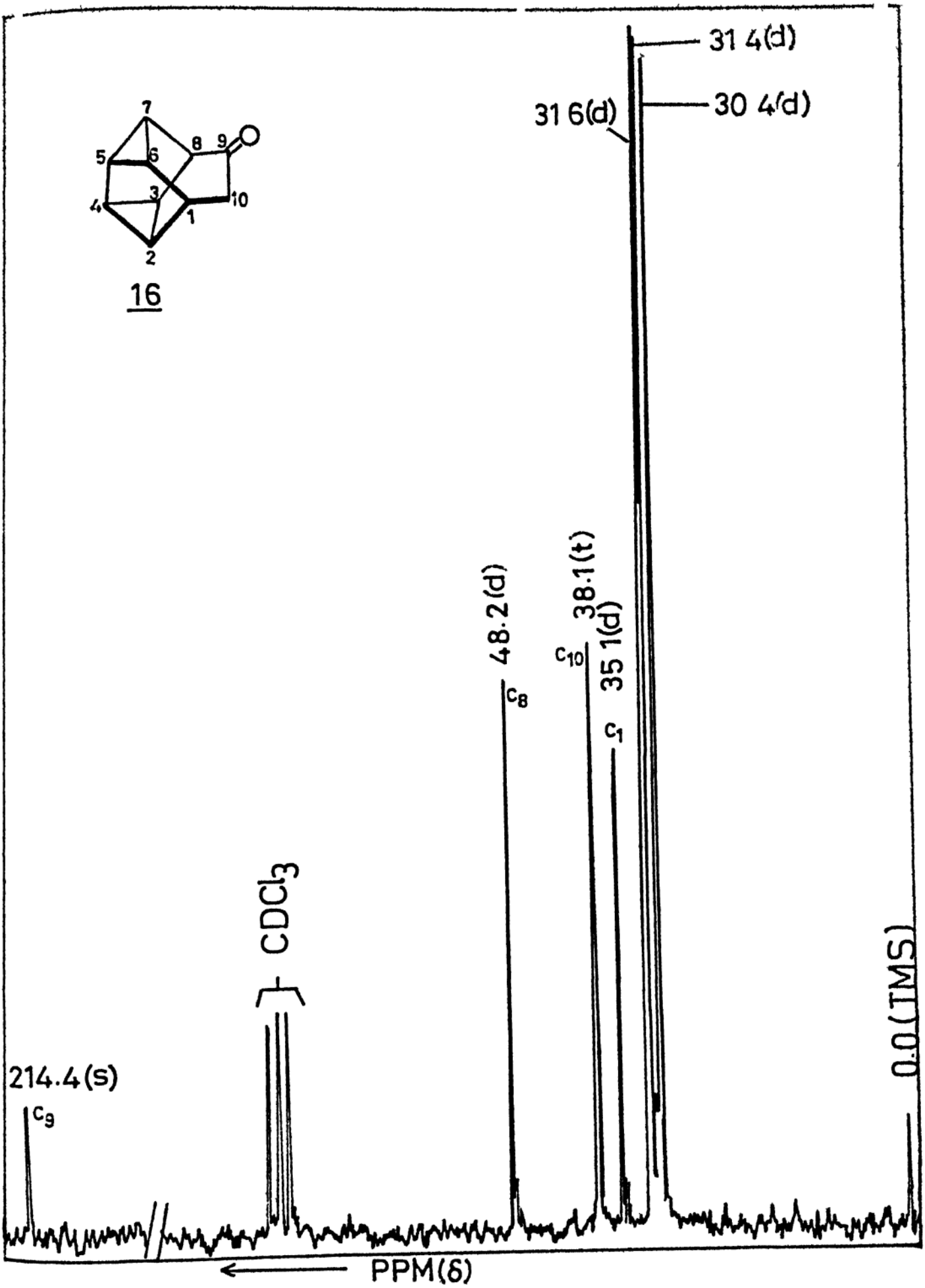
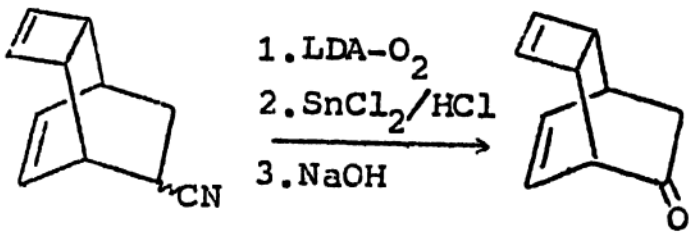


FIG 2 : ^{13}C NMR(25.0 MHz) spectrum of 16

with six cyclopropane C's appearing as three equivalent pairs of resonances.

The successful preparation of pentacyclic ketones 1 and 16 from the corresponding nitriles *via* the Watt's procedure[13] suggested the possibility of preparing the tricyclic dienone 6 from the COT-acrylonitrile adduct 7 in one step operation. Consequently, 7 was subjected to the protocols of



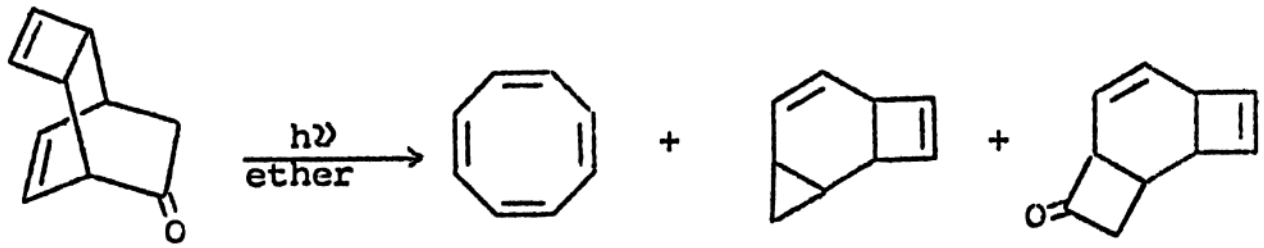
7 6

oxidative decyanation and dienone 6 was obtained in 75-80% yield. The efficient transformation of 7 to 6 makes available the tricyclo[4.2.2.$0^{2,5}$]deca-3,7-dien-9-one in two steps from COT and in good yield. The procedure is easier to execute and gives better yields of 6 in comparison to the earlier route of Freeman.[7]

The ready availability of β,γ-unsaturated dienone 6 and its bromo derivative 11 (*vide supra*) provided the impetus to study their photochemical transformations. It was also anticipated that conditions could be delineated for their direct cage cyclisation to the basketane ring system. The

tricyclo[4.2.2.$0^{2,5}$]deca-3,7-dien-9-ones, 6 and 11, being interesting β,γ-unsaturated ketones, bearing an additional double bond and cyclobutane ring, were also expected to show interesting photochemical transformations via 1,3-acyl shift and oxa-di-π-methane rearrangement.[9]

Irradiation of ether solution of 6 in a quartz vessel with 450 W medium pressure mercury vapour lamp for 10 min led to the formation of three products in a ratio of 1:2:4 as indicated by GLC analysis. The product composition and yields showed marked susceptibility to the reaction time and concentration. In a typical run, photolysis of 6 as indicated above and careful chromatography on silica gel led to the isolation of COT 2 (40%), tricyclic cyclopropane derivative 17 (10%) and tricyclic cyclobutanone 18 (20%). COT was readily identified.

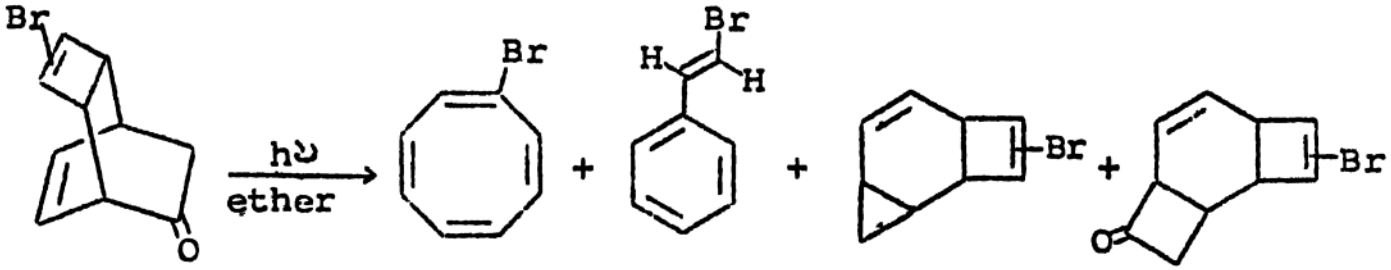


6 2 17 18

Compound 17 was not obtained pure and was contaminated with COT but its spectral parameters (vide experimental) and their close resemblance with bromo derivative 21 (vide infra) established its presence. Structure of 18 was deduced from its IR absorption at 1785 cm^{-1} (cyclobutanone), ^1H NMR signals

due to four olefinic protons at δ6.2(2H), 6.0(1H) and 5.56 (1H) and ^{13}C NMR resonances at δ206.2, 140.0, 139.2, 129.3 and 119.0 due to five sp^2 carbon atoms.

Irradiation of 11 under conditions identical to that of 6 for 15 min furnished a mixture of products along with some starting material. The crude reaction mixture, which also contained some polymeric impurities, was resolved by silica gel and alumina chromatography into four products, 19, 20, 21 and 22. Structures for 19-22 were deduced on the

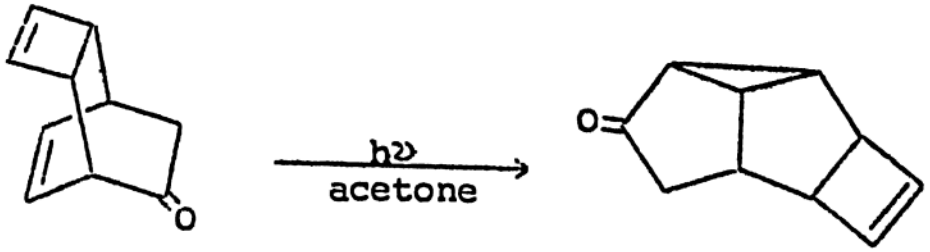


11 19 20 21 22

basis of complementary spectral data (IR, ^1H and ^{13}C NMR) summarised in the experimental section, trans-β-Bromostyrene 20 encountered in this reaction is probably an artefact formed from the facile rearrangement of bromoCOT.[10] In a separate experiment, it was also shown that 22 was the precursor of 19 and 21.

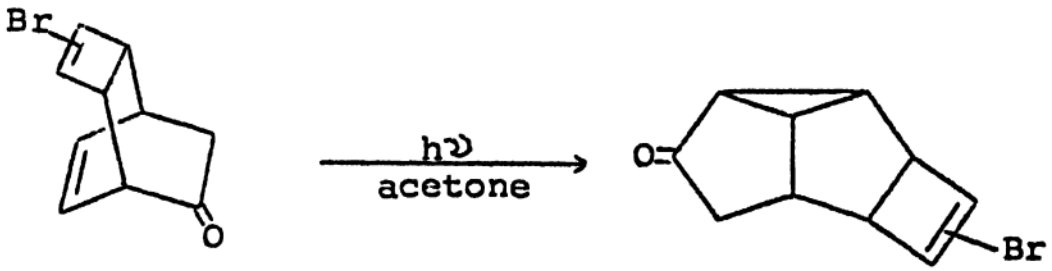
Attention was now turned towards the sensitised photolysis of 6 Photolysis of 6 in a quartz vessel with 450 W lamp for 10 min resulted in the formation of a major volatile

product (66% by GLC analysis) along with some starting material and polymeric impurities. The structure of 23 follows



6 23

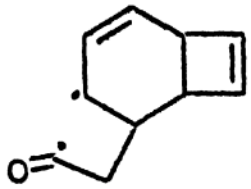
from its IR spectrum, 1730 cm^{-1}, ^{1}H NMR signals at δ6.2(1H), 6.1(1H) and ^{13}C NMR resonances at δ214.5, 140.1, 138.6, 58.7, 50.9, 49.7, 37.4, 36.6, 35.9 and 32.7. In an identical fashion, photolysis of 11 furnished the tetracyclic bromo ketone 24 in 44% yield after column chromatography. Spectral parameters of 24, summarised in experimental section, fully supported its formulation.



11 24

Formation of 1,2-shift (oxa-di-π-methane rearrangement) products (23 and 24) and 1,3-shift products (18 and 22) from β,γ-unsaturated ketones 6 and 11 on sensitised and direct photolysis, respectively, was mechanistically unexceptional.[9] There is ample precedence for this mode of reactivity. The

hydrocarbon products could be accounted for *via* a diradical intermediate 25 which can either loose ketene or CO. The tri-



25

cyclic compounds 17, 18, 21 and 22 obtained in this study are endowed with requisite functionality to serve as direct precursors of either annulated benzocyclopropenes[18] and benzocyclobutenes[19] or σ-homo benzene derivatives of current interest.[20]

In summary, simple, direct synthetic routes to basketanone 1, basketane 14, snoutanone 16 and tricyclo[4.2.2.$0^{2,5}$] deca-3,7-dien-9-ones 6 and 11, have been delineated. In an effort to transform 6 directly to basketanone 1, its photochemistry was investigated and it provided a facile entry to several useful small ring polycyclics.

EXPERIMENTAL

For a general write-up on the experimental section, see Chapter I.4. Some of the ^{1}H NMR (60 MHz) and ^{13}C NMR (22.64 MHz) spectra reported here were recorded on a Varian A-60 spectrometer and Brucker WH-90 spectrometer, respectively.

The GLC analyses were performed on a Hewlett-Packard 5830A analytical instrument using Carbowax-20M (6'x1/8'' stainless steel) column at oven temperature in the range of 150-200°C.

7,8-trans-Dibromo bicyclo[4.2.0]octa-2,4-diene(8):[5]

To a solution of COT (2, 5.4 g, 0.05 mole) in 12 ml of dichloromethane, cooled in ice bath, was added a solution of bromine (8 g, 0.05 mole) in 16 ml of dichloromethane over a period of 2 hr. Ice bath was removed and the reaction mixture was stirred at room temperature for 2 hr. The solvent was removed under reduced pressure at room temperature and the dibromoCOT (8) was distilled, bp.72-6°C/0.7 mm. Yield 10 g (75%). This material was solidified on refrigeration.

3,4-Dibromo 9-chloro 9-cyano tricyclo[4.2.2.$0^{2,5}$]dec-7-ene(9):

A solution of dibromoCOT (8, 9.25 g, 0.035 mole), α-chloroacrylonitrile (9.25 g, 0.105 mole) and 2,6-ditert. butyl phenol (0.1 g) was heated in a sealed corning glass tube (3.5 cms x 12 cms, N_2 atmosphere) to 105°C (±5) for 8 hr. The sealed tube was cooled, carefully opened and the contents filtered through a silica gel (100 g) column using 20% benzene-pet ether as eluent. Crystallisation of appropriate fractions (monitored by TLC) from carbon tetrachloride furnished 7.5 g (61%) of the adduct 9, mp.181-2°C.

IR spectrum (KBr), ν_{max}: 3090 (olefinic), 2250 cm^{-1} (cyano).

^{1}H NMR spectrum (100 MHz, $CDCl_3$): δ6.3-6.9(2H,m,olefinic), 4.77(1H,dd,J_1=10Hz,J_2=7Hz,HC-Br), 4.23(1H,dd,J_1=7Hz, J_2=6Hz,HC-Br), 2.8-3.7(4H,m,bridgehead CH), 2.35(1H,dd,J_1= 15Hz,J_2=2Hz,H-C-H), 2.14(1H,dd,J_1=15Hz,J_2=4Hz,H-C-H).

Analysis for $C_{11}H_{10}Br_2ClN$ Calcd: C,37.55; H,2.84; N,3.98. Found: C,37.58; H,3.04; N,4.04.

3-(or 4-)Bromo tricyclo[4.2.2.$0^{2,5}$]deca-3,7-dien-9-one(11):

To a magnetically stirred solution of the Diels-Alder adduct 9 (3.52 g, 10 mmoles) in 12 ml of dimethyl sufloxide was added a hot solution of KOH (1.5 g, 85% assay) in 1 ml of water. After stirring at room temperature for 13 hr, the reaction mixture was poured in ice-water (40 ml) and extracted with hexane (25 ml x 3). The organic extract was washed well with water and dried. Evaporation of the solvent furnished 2.1 g of crude ketone which on direct sublimation (70°C/0.6 mm) furnished 1.95 g (86%) of bromo ketone 11. The product appeared to be a regioisomeric mixture of two bromides from which the major bromide was crystallised from hexane, mp. 83-4°C.

IR spectrum (KBr), ν_{max}: 1730 (carbonyl), 1615, 1565 cm^{-1} (olefinic).

^{1}H NMR spectrum (60 MHz, $CDCl_3$): δ5.9-6.5(3H,m,olefinic), 2.7-3.4(4H,m,bridgehead CH), 2.2(1H,dd,J_1=19Hz,J_2=3Hz)

and 1.73(1H,dd,J_1=19Hz,J_2=2Hz), $C\underline{H}_2$-$\dot{C}$=O.

^{13}C NMR spectrum (22.64 MHz, $CFCl_3$): δ139.1, 134.1, 127.0 and 119.0 (olefinic), 53.5, 50.0, 46.6, 37.4, 35.7 (carbonyl carbon not seen).

Analysis for $C_{10}H_9BrO$ Calcd: C,53.33; H,4.0.
Found: C,53.58; H,3.79.

9-Cyano tricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene (7):[7]

A solution of COT (2, 2 g, 19.2 mmoles), acrylonitrile (2.1 g, 40 mmoles) and p-tert-butyl catechol (0.05 g) were sealed in a corning glass tube (10 cms x 1.5 cms, N_2 atmosphere) and heated to 180°C for 18 hr. The tube was cooled in ice, carefully opened and filtered through a silica gel (20 g) column using 20% benzene-pet ether. Distillation (90°C/0.1 mm) furnished 900 mg (30%) of the adduct 7 as an epimeric mixture.

IR spectrum (neat), ν_{max}: 2245 (cyano), 3130, 3055 and 1562 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ5.8-6.2(4H,m,olefinic), 3.2(1H,t,J=4Hz,$\underline{H}$C-CN), 2.3-3.05(4H,m,ring CH), 1.45-2.1(2H,m,CH_2).

9-Cyano pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane(13):[14]

A solution of the Diels-Alder adduct 7 (1.5 g, 9.56 mmoles) in 850 ml of 2% acetone-benzene was carefully purged

with a slow stream of dry nitrogen for 20 min. The solution was then irradiated with a Hanovia 450 W medium pressure mercury vapour lamp in a quartz immersion well using a Vycor filter for 35 hr. Solvent was removed and the crude photolysate (1.8 g) was filtered through a silica gel (20 g) column using 50% benzene-pet ether as eluent. The product on bulb to bulb distillation (120°C/1.2 mm) furnished 1.05 g (70%) of cyano basketane 13.

IR spectrum (neat), ν_{max}: 2240 cm^{-1} (cyano).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ2.5-3.5(9H,m), 1.8(2H,m).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ123.1(s,cyano), 43.7(d), 43.2(d), 38.9(d), 38.5(d), 38.4(d), 36.9(d), 33.3 (d), 30.5(d), 22.0(t,$\underline{C}H_2$), 19.3(d,$\underline{C}H$-CN).

Pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decan-9-one(1):

To a magnetically stirred cold (alcohol-liquid nitrogen bath, -70 to -80°C) solution of lithium diisopropylamide (6 mmoles) in 10 ml of dry THF [prepared by the addition of 5 ml of 1.6 M n-butyllithium in hexane to a stirring solution of diisopropylamine (605 mg, 6 mmoles) in 5 ml of dry THF at -78°C] was added cyano basketane (13, 630 mg, 4 mmoles) in 3 ml of dry THF. Dry oxygen gas was bubbled at a moderate flow rate into the lithionitrile solution at the same

temperature for 40 min. The reaction was quenched by the addition of 20 ml of 1 M stannous chloride in 2 M hydrochloric acid and the mixture was stirred at ice temperature for 2 hr. The reaction mixture was diluted with water (50 ml) and extracted with ether (25 ml x 3). The ether extract was washed with 1 M aqueous sodium hydroxide (20 ml x 2) and dried. Evaporation of the solvent and direct sublimation (80°C/5 mm) furnished 290 mg (50%) of the basketanone 1 leaving behind a small uncharacterised residue. Recrystallisation of the sublimed solid from pet ether furnished the crystalline compound, mp.82-3°C (Lit[3] 85-7°C).

IR spectrum (CCl_4), ν_{max}: 1728, 1710 cm^{-1} (carbonyl).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ3.1-3.7(8H,m,ring CH), 2.13(2H,s,$-CH_2-\overset{\prime}{C}=O$).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig. 1): δ211.4 (s,C=O), 47.8(d), 44.5(d), 43.1(d), 41.7(2C,d), 39.0(2C,d), 36.8(d), 36.3(t,CH_2).

Pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane(14):

To an ice cold magnetically stirred suspension of finely cut potassium (156 mg, 4 mg atom) in 5 ml of dry ether, cyano basketane (13, 314 mg, 2 mmoles) in 2 ml of dry ether, dry methanol (70 mg, 2.2 mmole) and hexamethyl-phosphoramide (0.75 ml) were successively added. Stirring was continued

and the reaction mixture was allowed to warm upto room temperature over a period of 30 min. After stirring for another 30 min the reaction mixture was cooled in an ice bath and quenched by careful addition of ice water (1 ml). The reaction mixture was diluted with ether (25 ml) and washed with water (10 ml x 3) and dried. Evaporation of the solvent and direct sublimation (50°C/20 mm) furnished 170 mg (65%) of basketane 14. Recrystallisation from methanol furnished sugary crystals of the hydrocarbon 14, mp.105°C (Lit[4] 102.5-104.5°C).

^{1}H NMR spectrum (100 MHz, $CDCl_3$): δ2.8-3.25(6H,m), 2.6(2H,brs), 1.35(4H,t,J=1.5Hz).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ43.6(2C,d), 39.8 (4C?,d), 32.6(2C,d), 16.8(2C,t,CH_2).

9-Cyano pentacyclo[4.4.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]decane(15):

A solution of cyano basketane (13, 1.57 g, 10 mmoles) in 5 ml of benzene was charged on a silver nitrate (15%) impregnated silica gel (25 g) column and left overnight. Elution with benzene followed by bulb to bulb distillation (110°C/1.0 mm) furnished 1.57 g (100%) of cyano snoutane (15), which was solidified on refrigeration.

IR spectrum (neat), ν_{max}: 2240 (cyano), 3040, 795 and 755 cm^{-1} (cyclopropyl).

^{1}H NMR spectrum (100 MHz, $CDCl_3$): δ2.6(2H,m,CH_2), 2.43(1H,brs,HC-CN), 1.2-2.1(8H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ124.2 (cyano), 34.5, 29.9, 29.7, 29.3, 29.2, 27.0, 26.2, 25.9, 25.7, 22.7.

Analysis for $C_{11}H_{11}N$ Calcd: C,84.04; H,7.05; N,8.91.
Found: C,84.22; H,7.10; N,8.51.

Pentacyclo[4.4.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]decan-9-one(16):

To a magnetically stirred cold (alcohol-liquid nitrogen bath, -70 to -80°C) solution of lithium diisopropylamide [3 mmoles, prepared by the addition of 2.5 ml of 1.6 M n-butyllithium (hexane) to a stirred solution of diisopropylamine (303 mg, 3 mmoles) in 2 ml of dry THF at -78°C] was added cyano snoutane (15, 314 mg, 2 mmoles) in 3 ml of THF. Dry oxygen gas was bubbled at a moderate flow rate into the lithionitrile solution at the same temperature for 1 hr. The reaction was quenched by the addition of 10 ml of 1 M stannous chloride in 2 M hydrochloric acid and the mixture was stirred at ice temperature for 2 hr. The reaction mixture was diluted with water (20 ml) and extracted with ether (35 ml x 2). The ether extract was washed with 1N aqueous sodium hydroxide (20 ml x 2) and dried. Evaporation of the solvent and bulb to bulb distillation (upto 100°C/1.5 mm) furnished 148 mg (51%) of snoutanone (16) as an oil leaving behind a small quantity of uncharacterised residue. The ketone solidified

on refrigeration and could be crystallised from pet ether as a low melting solid.

IR spectrum (neat), ν_{max}: 1725 (carbonyl), 3045, 795 and 750 cm^{-1} (cyclopropyl).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ2.5-2.9(2H,m,CH_2), 1.9-2.3(4H,m,ring CH), 1.4-1.9(4H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$, Fig. 2): δ214.4(s, C=O), 48.2(d,C_8), 38.1(t,-$\underline{C}H_2$-$\underline{C}$=O), 35.1(d,C_1), 31.6(2C,d), 31.4(2C,d) and 30.4(2C,d), cyclopropyl C's.

Tricyclo[4.2.2.$0^{2,5}$]deca-3,7-dien-9-one(6):

To a magnetically stirred cold (alcohol-liquid nitrogen bath, -70 to -80°C) solution of lithium diisopropylamide [6 mmoles, prepared by adding 5 ml of 1.6 molar n-butyllithium in hexane to a stirred solution of diisopropylamine (605 mg, 6 mmoles) in 5 ml of dry THF at -78°C] was added 9-cyano tricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene (7, 630 mg, 4 mmoles) in 5 ml of dry THF. Dry oxygen gas bubbled at a moderate flow rate into the lithionitrile solution for 30 min at the same temperature. The reaction was quenched by the addition of 12 ml of 1 M stannous chloride in 2 M hydrochloric acid and stirred for 1 hr at ice temperature. The reaction mixture was diluted with water (50 ml) and extracted with ether (25 ml x 3). The ether extract was washed with 1 M sodium

hydroxide solution (25 ml x 3) and dried. Evaporation of the solvent furnished 600 mg of crude product which was filtered through a silica gel (20 g) column using benzene as eluent. The product on bulb to bulb distillation (90°C/8 mm) furnished 450 mg (77%) of the dienone 6 which was solidified on refrigeration.

IR spectrum (neat), ν_{max}: 3140, 3060, 1620 and 1560 (olefinic), 1720 cm^{-1} (carbonyl).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ5.7-6.3(4H,m,olefinic), 2.6-3.15(4H,m,ring CH), 2.1(1H,dd,J_1=16Hz,J_2=3Hz) and 1.75(1H,dd,J_1=16Hz,J_2=2Hz), $-C\underline{H}_2-\overset{\|}{C}=O$.

Photolysis of tricyclo[4.2.2.$0^{2,5}$]deca-3,7-dien-9-one(6) in ether:

A solution of dienone 6 (100 mg, 0.654 mmole) in 120 ml of dry ether was carefully purged with a slow stream of dry nitrogen for 10 min. The solution was then irradiated with a Hanovia 450 W medium pressure mercury vapour lamp in a quartz immersion well for 10 min. Solvent was evaporated and the crude photolysate was charged on a silica gel (15 g) column and chromatographed. Elution with pet ether furnished 45 mg (55%) of hydrocarbon mixture, which was analysed by GLC. GLC indicated the presence of 80% COT and another slightly higher retention time peak (15%) might correspond to tricyclo[5.2.0.$0^{2,4}$]non-5,8-diene (17).

^{1}H NMR spectrum (100 MHz, CCl_4):δ5.4-6.4(m,olefinic), 5.8(COT), 3.4(m), 3.1(m), 2.4(m), 0.3(m,cyclopropyl).

Elution of the column with 30% benzene-pet ether furnished 30 mg (30%) of the cyclobutanone 18, which was bulb to bulb distilled (100°C/1 mm).

IR spectrum (neat), ν_{max}: 1785 cm^{-1} (cyclobutanone).

^{1}H NMR spectrum (100 MHz, $CDCl_3$): δ6.2(2H,d with st, J=2Hz, cyclobutene), 6.02(1H,m,HC=CH), 5.56(1H,dd,J_1=10Hz, J_2=4Hz,HC=CH), 2.7-3.7(6H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ206.2(C=O), 140.0, 139.2, 129.4 and 119.0(olefinic), 58.2, 50.2, 42.9, 39.8, 24.6.

Analysis for $C_{10}H_{10}O$ Calcd: C,82.19; H,6.85.
Found: C,82.48; H,7.01.

Photolysis of 3-(or 4-)bromo tricyclo[4.2.2.$0^{2,5}$]deca-3,7-dien-9-one(11) in ether:

A solution of bromo ketone 11 (500 mg, 2.22 mmoles) in 120 ml of dry ether was carefully purged with a slow stream of dry nitrogen for 10 min. The solution was then irradiated with a Hanovia 450 W medium pressure mercury vapour lamp in a quartz immersion well for 13 min. The solvent was evaporated and the crude photolysate was charged on a silica gel (15 g) column and chromatographed. Elution

with pet ether furnished 140 mg (30%) of hydrocarbon mixture. Further elution of the column with 50% benzene-pet ether and careful pooling up of fractions (monitored by TLC) furnished 200 mg (40%) of 9-(or 10-)bromo tricyclo[6.2.0.$0^{2,5}$]deca-6,9-dien-4-one (22), which on bulb to bulb distillation (120°C/ 0.6 mm) followed by refrigeration furnished the solid compound, mp.40-6°C.

IR spectrum (neat), ν_{max}: 1790 (carbonyl), 1650, 1590 cm^{-1} (olefinic).

^1H NMR spectrum (60 MHz, $CDCl_3$): δ6.3(1H,d,J=1.5Hz, cyclobutene), 6.05(1H,qd,J_1=10Hz,J_2=2Hz,HC=CH), 5.72(1H,dd, J_1=10Hz,J_2=3Hz,HC=CH), 3.6(2H,m), 2.7-3.5(4H,m).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ205.0 (C=O), 137.9, 126.0, 122.2 and 121.0 (olefinic), 58.4, 50.2, 45.4, 42.2, 24.2.

Analysis for $C_{10}H_9BrO$ Calcd: C,53.33; H,4.00.
Found: C,53.36; H,4.08.

Further elution of the column furnished 80 mg (16%) of starting bromo ketone 11.

The hydrocarbon mixture was heated to 100°C for 10 min to convert all the bromoCOT to trans-β-bromostyrene and the mixture was charged on an alumina (15 g) column and carefully eluted with pet ether. The first two fractions furnished

45 mg (10%) of 8-(or 9-)bromo tricyclo[5.2.0.$0^{2,4}$]nona-5,8-diene (21).

UV spectrum, λ_{max}^{MeOH}: 210 nm (ε = 7,500).

IR spectrum (neat), ν_{max}: 1650 and 1590 cm^{-1} (olefinic).

^1H NMR spectrum (100 MHz, $CDCl_3$): δ6.4(1H,s,cyclobutene), 6.15(1H,brd,J=9Hz,HC=CH), 5.46(1H,dd,J_1=9Hz,J_2=4Hz,HC=CH), 3.40(1H,d,J=5Hz,H_7), 3.22(1H,t,J=4Hz,H_1), 0.8-1.36(3H,m, cyclopropyl CH), 0.2(1H,m,cyclopropyl CH).

Further fractions of the column furnished 40 mg (10%) of trans-β-bromostyrene.

^1H NMR spectrum (100 MHz, $CDCl_3$): δ7.26(5H,s,aromatic), 6.95 and 6.8(2H,ABquartet,J=14Hz,olefinic).

Tetracyclo[5.3.0.$0^{2,10}$.$0^{3,6}$]dec-4-en-9-one(23):

An acetone solution (120 ml) of tricyclo[4.2.2.$0^{2,5}$] deca-3,7-dien-9-one (6, 80 mg, 0.55 mmole) was carefully purged with a slow stream of dry nitrogen for 10 min. The solution was then irradiated with a 450 W Hanovia medium pressure mercury vapour lamp for 7 min in a quartz immersion well. The GLC analysis indicated 85% conversion to the product. Solvent was evaporated and the crude photolysate was charged on a silica gel (10 g) column and chromatographed. Elution with 50% benzene-pet ether furnished 10 mg of starting

dienone 6. Further elution of the column with 60% benzene-pet ether furnished 40 mg (5%) of the tetracyclic ketone 23, which was bulb to bulb distilled (90°C/0.5 mm).

IR spectrum (neat), ν_{max}: 1730 cm^{-1} (carbonyl)

^1H NMR spectrum (100 MHz, $CDCl_3$): δ6.2(1H,d,J=3Hz, CH=CH), 6.1(1H,d with st,J=2Hz,HC=CH), 3.45(1H,brs,H_3),2. 2.4-3.0(3H,m,ring CH), 1.7-2.4(4H,m,ring CH).

^{13}C NMR spectrum (25.0 MHz, $CDCl_3$): δ214.5(C=O), 140.1 and 138.6 (olefinic), 58.7, 50.9, 49.7, 37.4, 36.6, 35.9, 32.7.

Analysis for $C_{10}H_{10}O$ Calcd: C,82.19; H,6.85.
Found: C,82.55; H,6.42.

4-(or 5-)Bromo tetracyclo[5.3.0.$0^{2,10}$.$0^{3,6}$]dec-4-en-9-one(24):

A solution of bromo ketone 11 (500 mg, 2.22 mmoles) in 120 ml of acetone was carefully purged with a slow stream of dry nitrogen for 10 min. The solution was then irradiated with a Hanovia 450 W medium pressure mercury vapour lamp in a quartz immersion well for 40 min. GLC analysis indicated 85% conversion. The solvent was evaporated and the crude photolysate was charged on a silica gel (15 g) column and chromatographed. Elution with 50% benzene-pet ether furnished 40 mg of starting bromo ketone 11. Further elution of the column with 60% benzene-pet ether furnished 220 mg (44%) of the tetracyclic ketone 24, which on bulb to bulb distillation

(120°C/0.6 mm) followed by refrigeration furnished solid compound, mp.42-9°C.

IR spectrum (neat), ν_{max}: 1735 (carbonyl) and 1585 cm^{-1} (olefinic).

^{1}H NMR spectrum (60 MHz, $CDCl_3$): δ6.2(1H,d,J=1.5Hz, olefinic), 3.6(1H,brs,allylic), 2.35-3.2(4H,m,ring CH), 1.75-2.35(3H,m,ring CH).

^{13}C NMR spectrum (22.64 MHz, $CFCl_3$+$CDCl_3$): δ213.6(s), 138.6(d), 123.5(s), 59.0(d), 57.6(d), 51.3(t), 37.5(d), 36.4 (2C,d), 32.9(d).

Analysis for $C_{10}H_9BrO$ Calcd: C,53.33; H,4.00.
Found: C,53.78; H,3.95.

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