NEW REACTIVE IRON CARBONYL REAGENTS FOR APPLICATIONS IN ORGANIC SYNTHESIS

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

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To My Father and Mother

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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, under the supervision of Professor M. Periasamy.

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.

(C. Rameshkumar)

Certificate

Certified that the work embodied in this thesis entitled **'New Reactive Iron Carbonyl Reagents for Applications in Organic Synthesis** ' has been carried out by Mr. C. Rameshkumar, under my supervision and the same has not been submitted elsewhere for a Degree.

M. Periasamy
24/4/2000

PROFESSOR M. PERIASAMY
(THESIS SUPERVISOR)

Kd Sen
25.4

DEAN
SCHOOL OF CHEMISTRY

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Financial assistance from the UGC is gratefully acknowledged.

C. Rameshkumar

Abbreviations

THF : tetrahydrofuran
r.t : room temperature
eq. : equation
equiv. : equivalent
n : primary
t : tertiary
M : metal
L or Ln : ligand
TMEDA : N,N,N',N'-tetramethylethylenediamine
DMF : N,N-dimethylformamide
DME : 1,2-dimethoxyethane
DMSO : dimethylsulphoxide
TFA : trifluoro acetic acid
PPNC1 : μ-nitrido-bis-(triphenyl-phosphorous)(1+) chloride
Me : methyl
Ph : phenyl
liq. : liquid
M.P : melting point
NMP : N-methylpyrrolidine
EI : electron impact

Abstract

This thesis describes studies on the **"New Reactive Iron Carbonyl Reagents for Applications in Organic Synthesis".** It comprises of three chapters. Each chapter is subdivided into four parts, namely Introduction, Results and Discussion, Conclusions and Experimental Section along with References. The work described in this thesis is exploratory in nature and the chapters are arranged in the order the investigations were executed.

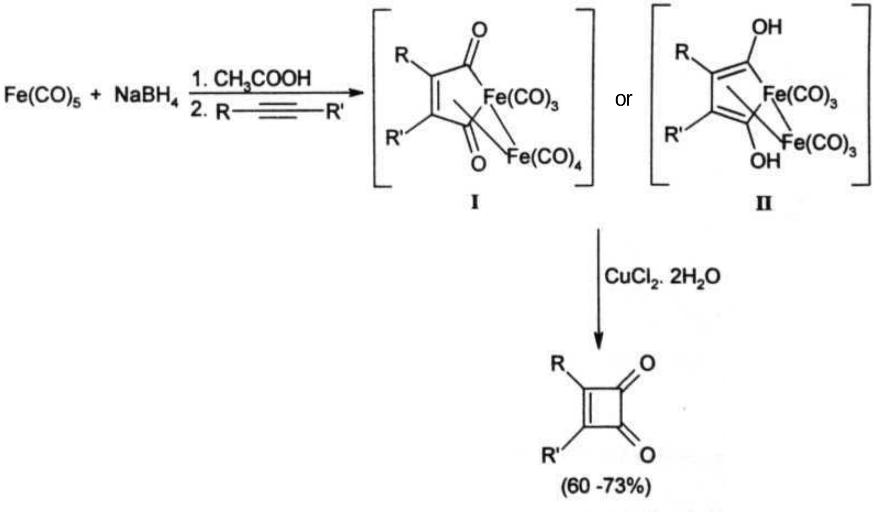
The first chapter describes the investigations on the reactions of alkynes with iron carbonyl species, prepared *in situ* using $Fe(CO)_5/NaBH_4/CH_3COOH$ and $Fe_3(CO)_{12}$/amine systems. In the introductory section, a brief review on the methods of preparation and synthetic applications of the readily accessible $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Na_2Fe(CO)_4$, $HFe(CO)_4^-$, $HFe_2(CO)_8^-$, $[HFe_3(CO)_{11}]^-$, $H_2Fe(CO)_4$, $H_2Fe_3(CO)_{11}$ and the coordinatively unsaturated iron carbonyl species such as "$Fe(CO)_4$", and "$Fe_2(CO)_8$" are presented.

Previously, it was observed in this laboratory that the reactive iron carbonyl species, prepared using the $HFe(CO)_4^-/RX$ (RX - CH_3I or Me_3SiCl) combination, on reaction with alkynes followed by $CuCl_2.2H_2O$ oxidation gives cyclobutenediones in

moderate to good yields. The U.V spectra recorded for the iron carbonyl species, prepared using the $Fe(CO)_5/NaBH_4/CH_3COOH$ and the $NaHFe(CO)_4/RX$ (RX - CH_3I, CH_2Cl_2 and Me_3SiCl) reagent combinations, exhibit characteristic λ_{max} in solution in the region reported for $[HFe_3(CO)_{11}]^-/H_2Fe_3(CO)_{11}$ species.

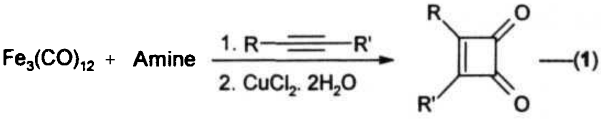
The reaction of alkynes with the iron carbonyl species $[HFe_3(CO)_{11}]^-$, prepared *in situ* by the reduction of $Fe(CO)_5$ using $NaBH_4$ in the presence of excess CH_3COOH in THF, gives the corresponding cyclobutenediones in good yields (60-73%) after $CuCl_2.2H_2O$ oxidation (Scheme 1).

Scheme 1



Presumably, the transformation may go through the intermediacy of coordinatively unsaturated iron carbonyl species that could lead to the formation of maleoyl iron complexes of the type I or hydroxy ferrole iron complexes of the type II (Scheme 1).

We have also investigated the use of amines to prepare coordinatively unsaturated species from $Fe_3(CO)_{12}$. It was observed that amines such as *n*-butylamine, *n*-octylamine, benzylamine, piperidine, pyrrolidine, triethylamine and DMF facilitate the reaction of alkynes with the $Fe_3(CO)_{12}$ in THF to give the corresponding cyclobutenediones at 25 °C in moderate to good yields (28-61%) after $CuCl_2.2H_2O$ oxidation (eq. 1). This transformation may be rationalized by considering the reaction of alkynes with coordinatively unsaturated species of the type "$Fe_3(CO)_{11}$" or "$Fe_2(CO)_8$".



(28-61%)

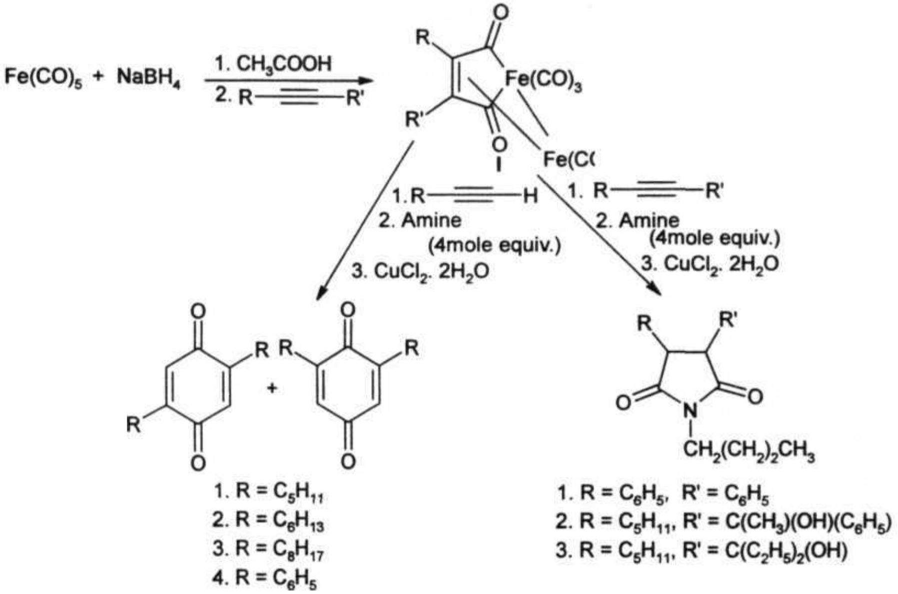
Several alkynes were converted to the corresponding cyclobutenediones using $Fe_3(CO)_{12}$ in THF in the presence of *n*-butylamine at 25 °C, in moderate to good yields (25-61%), after $CuCl_2.2H_2O$ oxidation.

We have also examined the possibility of generating the coordinatively unsaturated species by photolysis of the $Fe_3(CO)_{12}$ and studied its reactivity with 1-heptyne in benzene at 25 °C. The results are discussed.

The second chapter describes the results of investigations carried out to exploit the alkyne-iron intermediate complexes I (Scheme 1) for further synthetic applications. Various methods of preparations and synthetic applications of these iron carbonyl complex derivatives are reviewed in the introductory section.

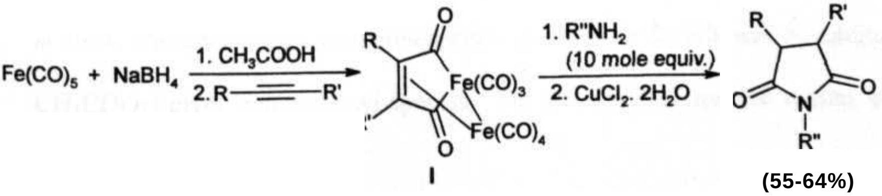
It was observed that the intermediate iron carbonyl complexes, prepared in THF using $Fe(CO)_5$, $NaBH_4$ and CH_3COOH in the presence of amines (4 mole equiv.), react with one more equivalent of 1-alkyne at 25 °C to give the corresponding disubstituted benzoquinones (55-65%) after $CuCl_2.2H_2O$ oxidation (Scheme 2). It was found that amines such as *n*-butylamine, benzylamine, pyrrolidine and piperidine also give the same result. Attempts were also made to prepare mixed benzoquinones in this way through sequential addition of two different 1-alkynes.

Scheme 2



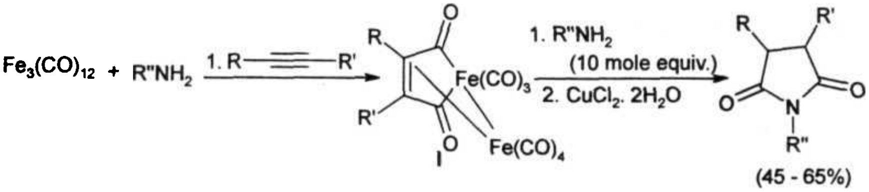
The disubstituted alkynes give the corresponding cyclic imides under these conditions (Scheme 2). Further, it was observed that the cyclic imide derivatives are obtained in 55-64% yields from both 1-alkynes and disubstituted alkynes using excess of primary amine (10 mole equiv.) (Scheme 3).

Scheme 3



Moreover, in the presence of excess of **amine** (10 mole equiv.), the alkyne-iron carbonyls, prepared using the $Fe_3(CO)_{12}$, ***n*-butylamine** and alkynes in THF also give the corresponding cyclic **imides** (45-65%) along with traces of cyclobutenediones (5-10%) after $CuCl_2\,2H_2O$ oxidation (Scheme 4).

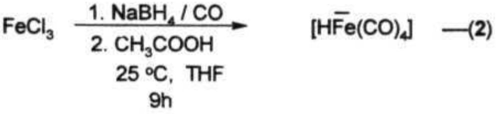
Scheme 4



Probable reaction pathways and the intermediates that may be involved in the conversion of alkynes to benzoquinones and cyclic imides are discussed.

In chapter 3, investigations of the reactivity of iron carbonyl species, prepared *in situ* using $FeCl_3/NaBH_4/CO/CH_3COOH$ reagent system, are described. In the introductory section, the methods of preparation of transition metal carbonyl species using different reducing agents under CO atmosphere and their synthetic applications are briefly reviewed.

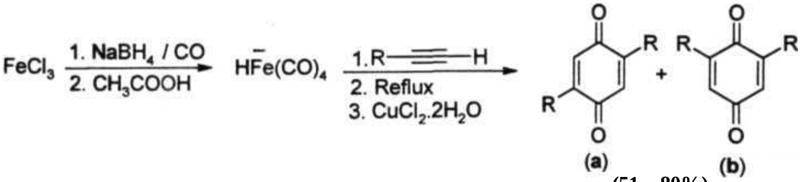
It was observed that the reduction of anhydrous $FeCl_3$ using $NaBH_4$ in THF at 25 °C while bubbling CO at atmospheric pressure for 9h followed by addition of CH_3COOH gives iron carbonyl species. The **I.R** and U.V spectral studies of this reaction mixture indicate the presence of the iron carbonyl species, $[HFe(CO)_4]^-$ (eq. 2).



$$FeCl_3 \xrightarrow[\substack{2.\ CH_3COOH \\ 25\ ^\circ C,\ THF \\ 9h}]{1.\ NaBH_4\ /\ CO} [H\overset{-}{F}e(CO)_4] \quad —(2)$$

The iron carbonyl species, prepared in this way, react with 1-alkynes in THF at refluxing temperature to give disubstituted benzoquinones in moderate to good yields (51-80%) after $CuCl_2.2H_2O$ oxidation (Scheme 5).

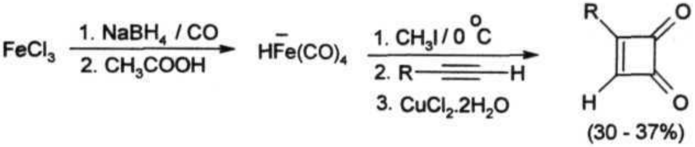
Scheme 5



(51 - 80%)

Interestingly, addition of CH_3I at 0 °C to the species, prepared in this way, followed by reaction with 1-alkynes at 25 °C, for 12h in THF gives the corresponding cyclobutenediones after $CuCl_2.2H_2O$ oxidation, albeit only in moderate yields (30-37%) (Scheme 6). The corresponding benzoquinones are not formed under these conditions.

Scheme 6



The results are discussed in comparison with that obtained in the reaction of alkynes with iron carbonyl intermediates prepared from $Fe(CO)_5$ and $Fe_3(CO)_{12}$.

Chapter 1

Studies on the Conversion of Alkynes to Cyclobutenediones using Iron Carbonyl Species

1.1 Introduction

Although the transition metal carbonyls were discovered more than 100 years ago, their applications in organic synthesis are relatively new. In recent years, a large number of transition metal carbonyls have been used as stoichiometric reagents and catalysts in a wide range of organic transformations. Transition metal reagents offer practical synthetic alternatives to the nucleophilic, electrophilic and cyclization processes involving C-C bond forming reactions.[2-4] Also, the metal carbonyls display unique reactivities in oxidation, reduction, isomerization and polymerization processes.[5,6]

Among various transition metal carbonyls, the iron carbonyls are by far the most versatile reagents. The mono and polynuclear iron carbonyls form a variety of stable organoiron complexes with different organic substrates.[7] A brief review on the applications of some readily accessible iron carbonyl reagents will be helpful for the discussion.

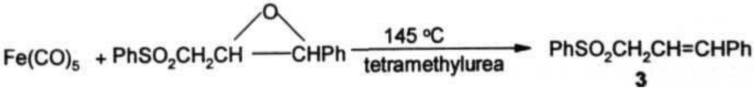
1.1.1 Synthetic applications of $Fe(CO)_5$

The $Fe(CO)_5$ can be prepared by the direct reaction of CO with finely divided iron, at high temperature and pressure.[8] It is also a commercially available, inexpensive reagent. Normally, $Fe(CO)_5$ is inert to ligand substitution, except under thermal, photochemical or under the influence of reagents which promote CO dissociation. It catalyzes the oxidation of gaseous CO to CO_2 at very high temperatures.[9]

The $Fe(CO)_5$ is sensitive to oxidising agents. The amine oxides react with $Fe(CO)_5$ to give the corresponding amine 1 and $Fe(CO)_4$ (eq. 1).[10] Also, N-alkyl and N-arylbenzamide oximes undergo reduction with $Fe(CO)_5$ to give the corresponding amidines 2 (eq. 2).[11] Reaction with epoxides gives the corresponding olefins 3 (eq. 3).[12]

$$Fe(CO)_5 + Me_3\overset{+}{N}\overset{-}{O} \longrightarrow \underset{\mathbf{1}}{Me_3N} + Fe(CO)_4 + CO \quad \text{---(1)}$$

$$RC(NHPh)\text{=}NOH \xrightarrow[\text{THF, reflux}]{Fe(CO)_5} \underset{\mathbf{2}}{RC(NHPh)\text{=}NH} \quad \text{---(2)}$$

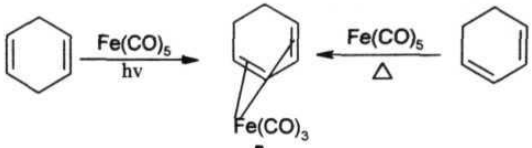


---(3)

Reaction of aryl gem-dihalides with $Fe(CO)_5$ gives the coupled olefins 4 in good yields (eq. 4).[13]

$$2\,Ar_2CX_2 + 2\,Fe(CO)_5 \longrightarrow \underset{\mathbf{4}}{Ar_2C\text{=}CAr_2} + 2\,FeX_2 + 10\,CO \quad \text{---(4)}$$

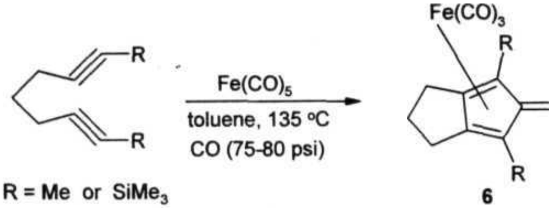
It is well-known that the conjugated and non-conjugated dienes react readily with $Fe(CO)_5$ to give the corresponding **diene-$Fe(CO)_3$** complexes 5 (eq. **5**).[14]



5

---(5)

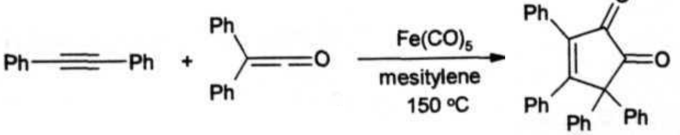
Also, the $Fe(CO)_5$ reacts with alkynes at high temperatures to give the corresponding **cyclopentadienone-$Fe(CO)_3$** complexes 6 (eq. 6).[15]



6

–(6)

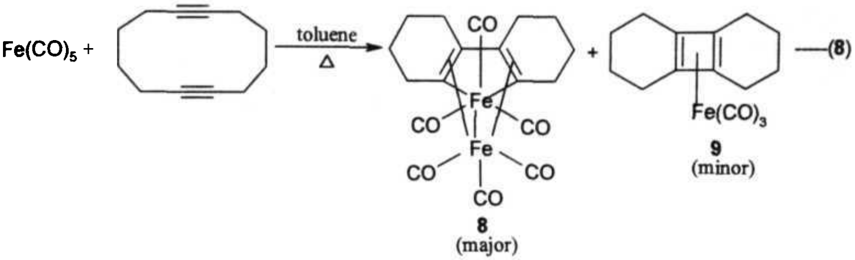
Further, direct cycloaddition reaction of alkynes with diphenylketene has been achieved in the presence of $Fe(CO)_5$ at high temperature to obtain the corresponding cyclopentenedione 7 (eq. 7).



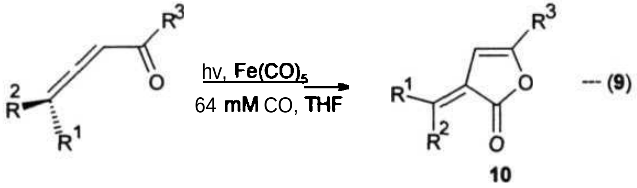
7

---(7)

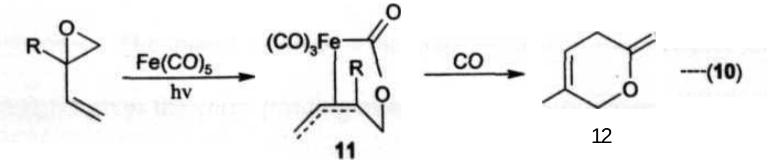
It has been reported that **1,7-cyclododecadiyne** reacts with **$Fe(CO)_5$** to give the iron carbonyl complexes, 8 (major product) and 9 (minor product) (eq. 8).[17]



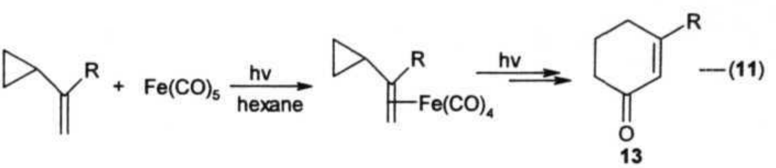
Recently, an **$Fe(CO)_5$** mediated cycloaddition reaction of allenyl ketones with CO has been reported under photochemical conditions, to obtain the corresponding butenolide derivatives 10 (eq. 9).[18]



Ley *et al* discovered that **$Fe(CO)_5$** reacts with an **olefinic** epoxide under photochemical conditions to give the 6-membered lactone 12 (eq. 10), via a **π**-lactonyl iron complex intermediate **11.**[19]



Also, the photochemical reaction of $Fe(CO)_5$ with vinyl cyclopropane derivatives leads to the vinylic π-complex intermediate, that on ring opening gives the corresponding cyclohexenone **13** (eq. **11**).[120]



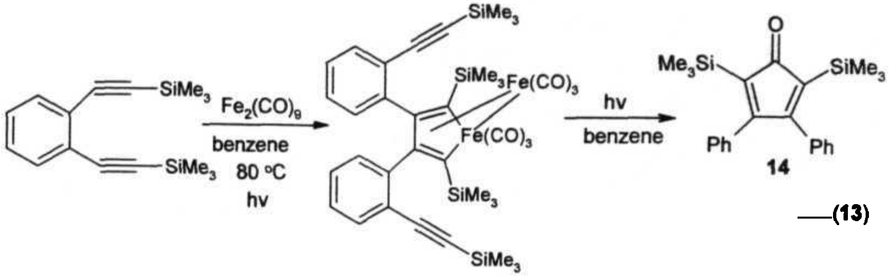
1.1.2 Synthetic applications of $Fe_2(CO)_9$

The standard method of preparation of $Fe_2(CO)_9$ involves photolysis of $Fe(CO)_5$ in acetic acid with a medium pressure mercury lamp or under sunlight (eq. 12).[21] The $Fe_2(CO)_9$ is also commercially available.

$$Fe(CO)_5 \xrightarrow[CH_3COOH]{h\nu} Fe_2(CO)_9 \qquad \text{----(12)}$$

The $Fe_2(CO)_9$ exhibits greater reactivity than that of $Fe(CO)_5$ in several applications. It is of interest to briefly review some of the important applications of $Fe_2(CO)_9$ here.

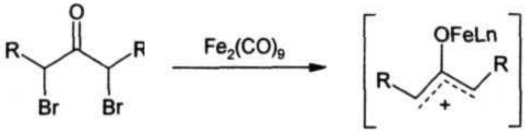
It has been reported that the $Fe_2(CO)_9$ on reaction with 1,2-bis((trimethylsilyl)ethynyl)benzene gives four products under photochemical conditions. The major product is an iron-complexed metallacycle that upon photolysis gives the corresponding metal free cyclopentadienone 14 (eq. 13).



14

—(13)

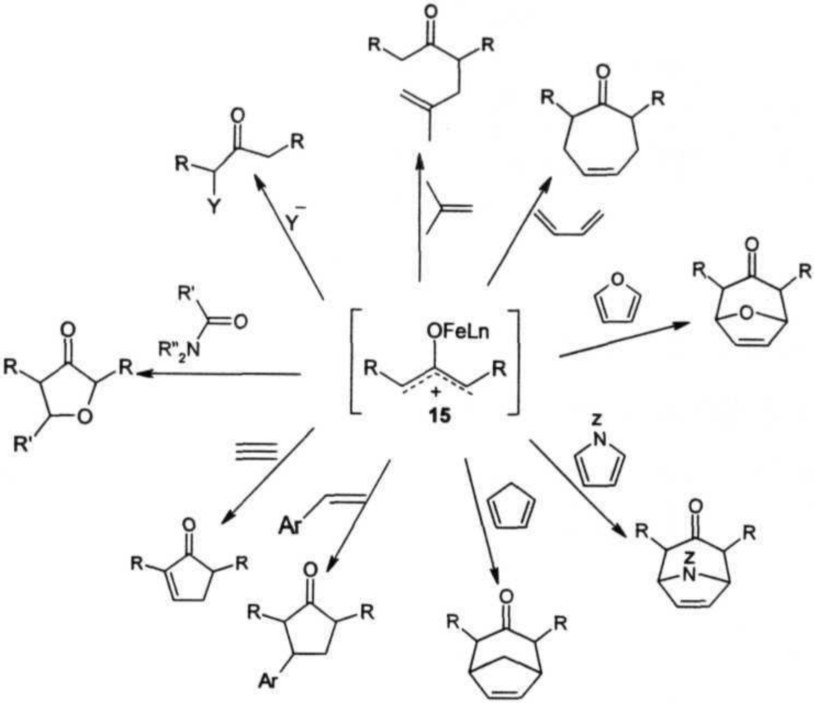
One of the most interesting and important applications of $Fe_2(CO)_9$ is for the preparation of **oxyallyl-iron** complex 15 (eq. 14) from the respective **α,α'-dibromoketone**. This complex 15 readily undergoes cycloaddition reactions with a variety of unsaturated substrates (Scheme **1**).[23,24]



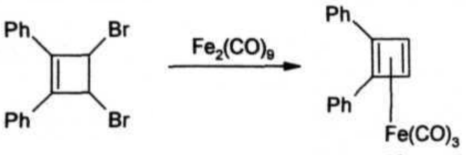
15

—(14)

Scheme 1



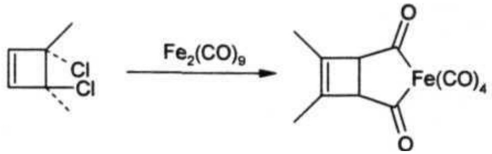
Substituted cyclobutadiene iron complexes 16 can be readily prepared through reaction of $Fe_2(CO)_9$ with the respective dibromocyclobutene derivatives (eq. 15).[25]



16

—(15)

However, the reaction of $Fe_2(CO)_9$ with trans-3,4-dichloro-3,4-dimethyl cyclobutene gives the corresponding acyl tetracarbonyliron complex 17 (eq. 16).[26]



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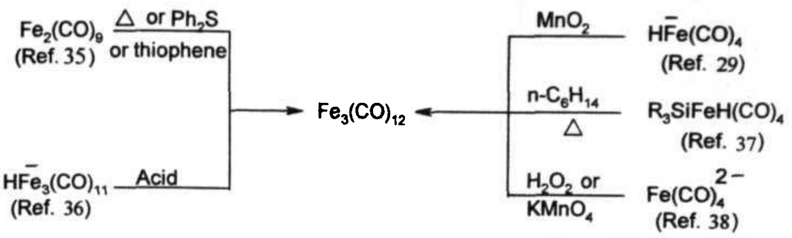
17

Recent reports on the low-temperature photochemical reactions of $Fe_2(CO)_9$ in argon or nitrogen matrix reveal the loss of one CO from the $Fe_2(CO)_9$ to yield the coordinatively unsaturated species "$Fe_2(CO)_8$".[27] These species react with ligands (L) to give $Fe(CO)_4L$ and "$Fe(CO)_4$".[28]

1. 1. 3 Synthetic applications of $Fe_3(CO)_{12}$

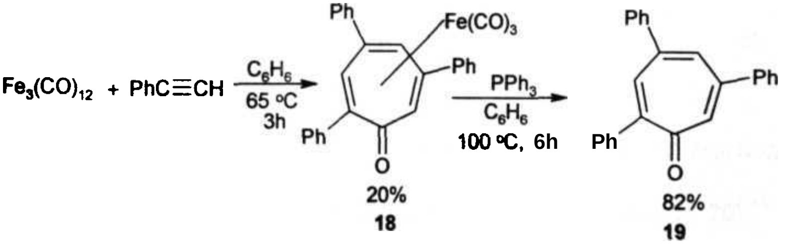
Several methods are available for the preparation of $Fe_3(CO)_{12}$ (Scheme 2). However, oxidation of $HFe(CO)_4^-$ by MnO_2 is the preferred one.[29] The $Fe_3(CO)_{12}$ is dark green in colour. It exhibits greater reactivity than $Fe(CO)_5$ in several reactions.[30] It is somewhat less reactive compared to $Fe_2(CO)_9$. Under photolysis and thermolysis, the $Fe_3(CO)_{12}$ dissociates into "$Fe(CO)_4$" and its derivatives.[31*34]

Scheme 2



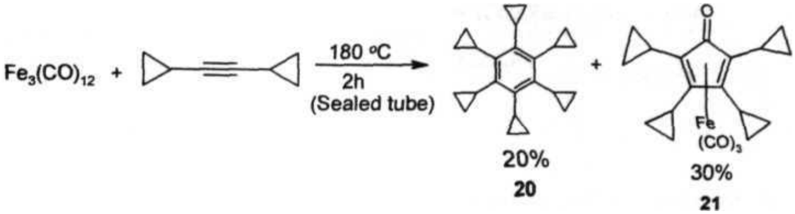
Some of the important synthetic applications of $Fe_3(CO)_{12}$ are briefly reviewed here.

Acetylene and monoaryl substituted acetylene derivatives react with the $Fe_3(CO)_{12}$, to give the tropone complexes 18. Decomplexation of 18 using PPh_3 affords the corresponding tropone 19 (eq. 17).[39]



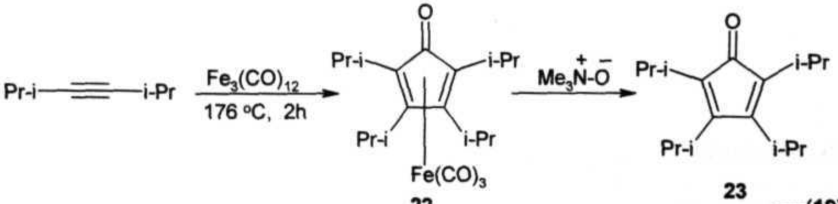
—(17)

At elevated temperature in sealed tube, the $Fe_3(CO)_{12}$ reacts with dicyclopropylacetylene to give the corresponding hexacyclopropylbenzene 20 as well as the iron carbonyl derivative of the cyclopentadienone 21 (eq. 18).



-(18)

Also, the $Fe_3(CO)_{12}$ reacts with diisopropylacetylene to give the corresponding cyclopentadienone derivative 22 at elevated temperatures. The metal-free dienone 23 was obtained in 71% yield upon oxidation of 22 using trimethylamine oxide (eq. 19).[41]



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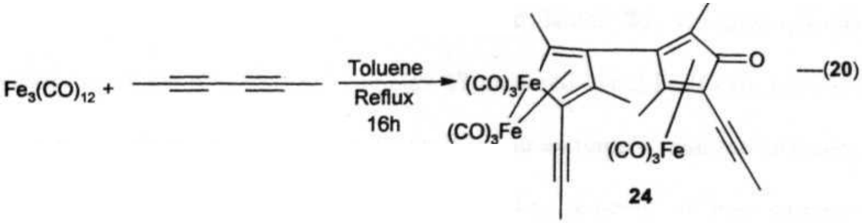
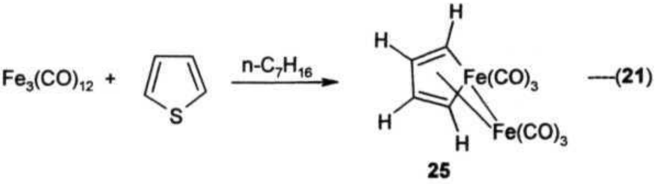
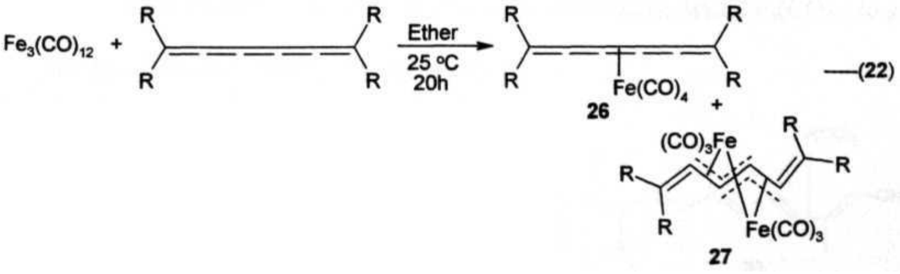
A novel trimetallic product 24 was obtained in the reaction of 2,4-hexadiyne with $Fe_3(CO)_{12}$ in toluene at refluxing temperature (eq. 20).[42]



At elevated temperatures, thiophene and **$Fe_3(CO)_{12}$** undergo a novel reaction resulting in the removal of the sulphur atom from the thiophene ring to give the iron tricarbonyl complex 25 (eq. 21).[43]

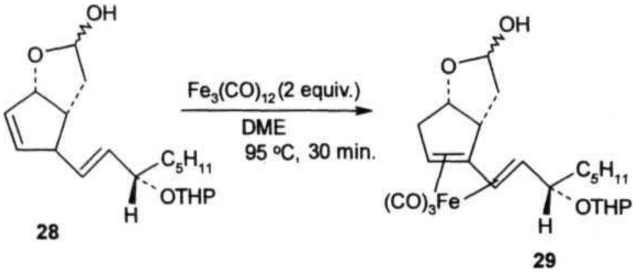


Tetra-t-butylhexapentaene reacts with the **$Fe_3(CO)_{12}$** to give a mixture of the yellow monoolefin complex 26 and the red diiron complex 27 (eq. 22).[46]



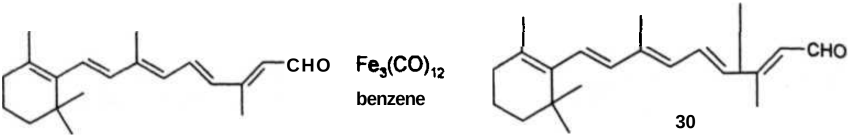
Corey *et al* successfully converted the lactol 28, to prostoglandin derivatives via the iron carbonyl complex 29 prepared using $Fe_3(CO)_{12}$ (Scheme 3). Since, the prostoglandins are very sensitive, an extremely mild method using Collin's reagent was developed for the oxidative removal of iron carbonyl group.[45]

Scheme 3



15-tetrhydropyranyl derivative
of **Prostaglandin** B

It has been reported that vitamin A aldehyde reacts with $Fe_3(CO)_{12}$ to give the mono-adduct 30 in 45% yield (eq. **23**).[44]

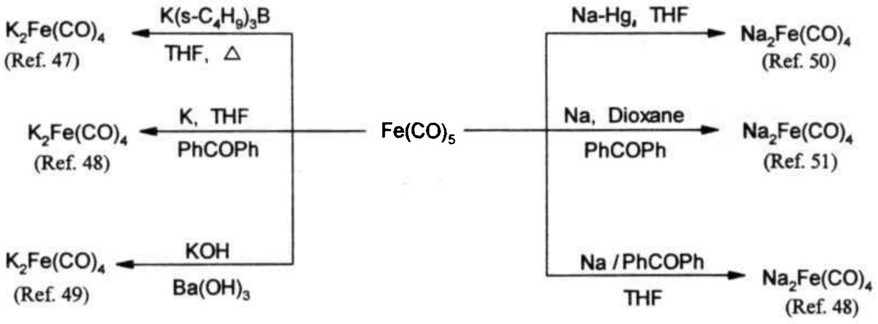


—(23)

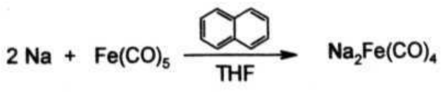
1. 1. 4 Preparation and applications of $Na_2Fe(CO)_4$

The super nucleophile $Na_2Fe(CO)_4$ (Collman's reagent) has been demonstrated to be a versatile reagent in many organic transformations.[51] Numerous methods are available for the preparation of this **useful** reagent from readily available starting materials (Scheme 4).

Scheme 4



Practically useful procedures have been developed in this laboratory for the preparation of $Na_2Fe(CO)_4$ through the reduction of either readily available $FeCl_3$ (eq. 25) or the inexpensive $Fe(CO)_5$ with **sodium-naphthalenide** (eq. 24).[52] In the case of $FeCl_3$, the reaction has been carried out at atmospheric pressure of CO (eq. **25**).[52]



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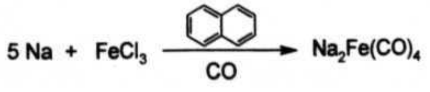
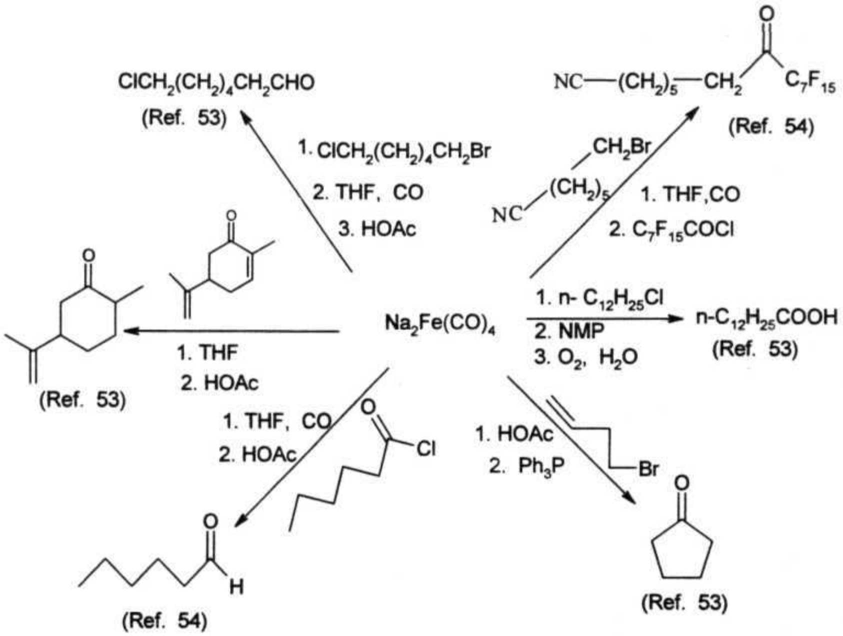


------(25)

An excellent review appeared describing synthetic applications of the $Na_2Fe(CO)_4$ (Scheme **5**).[51]

Scheme **5**

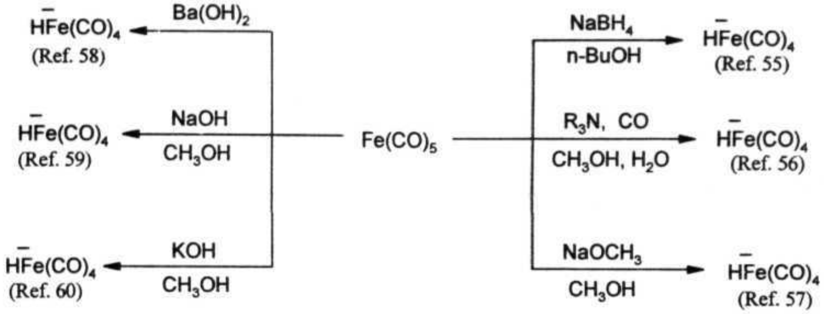


1. 1. 5 Preparation and applications of hydrido iron carbonyls

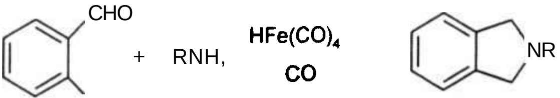
a) Synthetic applications of $HFe(CO)_4$

Several methods are available for the preparation of $HFe(CO)_4^-$ (Scheme 6).

Scheme 6

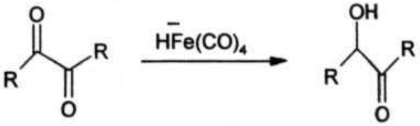


An excellent review on the applications of $HFe(CO)_4^-$ reagent has been published.[7c] Reductive amination of phthalaldehyde using primary amines and $KHFe(CO)_4$ gives the corresponding isoindoline derivatives 31 (eq. 26).[61]



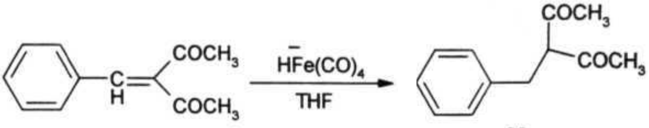
31 —(26)

Recently, it has been reported that certain 1,2-diketones are reduced to hydroxy ketones 32 in good yields by $KHFe(CO)_4$ (eq. 27).[62]



32 -----(27)

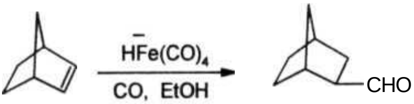
The $HFe(CO)_4^-$ reagent is useful in the selective reduction of the double bond in the Knoevenagal condensates to obtain the corresponding reduced products **33** (eq. **28).**[63]



33

—(28)

The $KHFe(CO)_4$ effects hydroformylation of strained olefins to give the corresponding aldehydes 34 with high stereo-selectivity. The reaction is facilitated by higher CO pressure (eq. **29).**[64] However, carbonylation of simple olefins is not successful under these conditions.



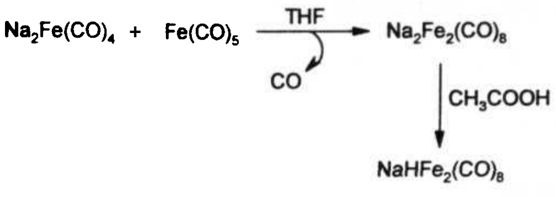
34

—(29)

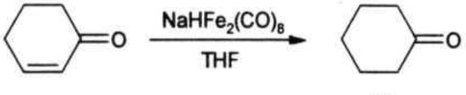
b) Synthetic applications of $HFe_2(CO)_8^-$

A simple method for the preparation of $NaHFe_2(CO)_8$ has been reported (Scheme 7).[65]

Scheme 7



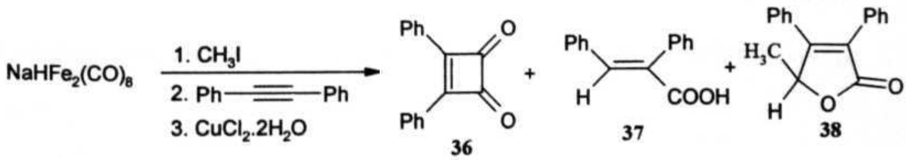
yields (eq. 30).[65]



-----(30)

35

In this laboratory, it was observed that the $NaHFe_2(CO)_8$ prepared in this way on reaction with CH_3I and diphenylacetylene gives a mixture of cyclobutenedione 36, a,p-unsaturated carboxylic acid 37 and butenolide 38 (eq. 31).[66]

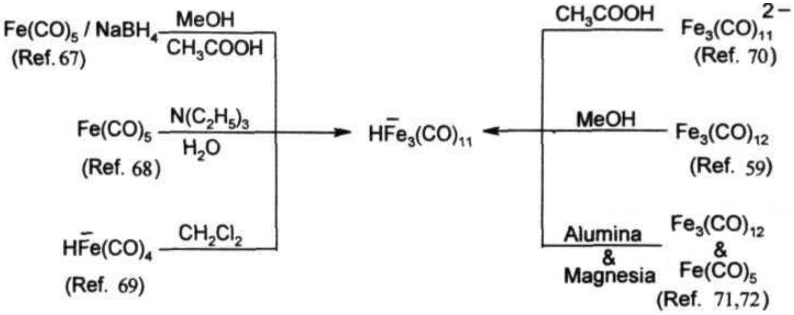


—(31)

c) Synthetic applications of $HFe_3(CO)_{11}^-$

Numerous methods are available for the preparation of this species from readily available starting materials (Scheme 8).

Scheme 8

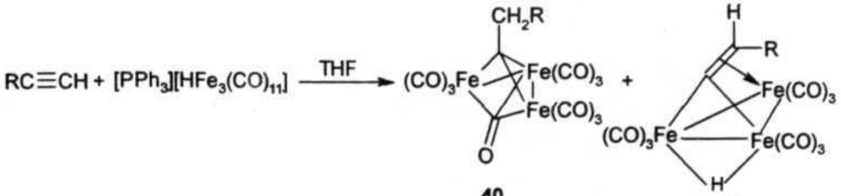


It has been reported that the reaction of $HFe_3(CO)_{11}^-$ with fluorosulphuric acid gives the $H_2Fe_3(CO)_{11}$ 39 species in solution (eq. 32).[73]

$$H\bar{F}e_3(CO)_{11} \xrightarrow[\text{ether}]{HSO_3F} \text{"}H_2Fe_3(CO)_{11}\text{"} \qquad \text{----(32)}$$

39

The $HFe_3(CO)_{11}^-$ reacts with 1-alkynes in THF to give iron carbonyl complexes of type 40 and 41 that were separated by fractional crystallization (eq. 33).[74]

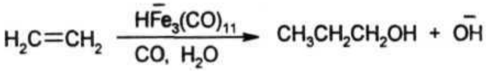


40

41

——(33)

Also, the $HFe_3(CO)_{11}^-$ reagent reacts with ethylene to give *n*-propanol 42 (eq. 34).[75] Presumably, the initially formed aldehyde is hydrogenated by the hydrido iron carbonyl species.

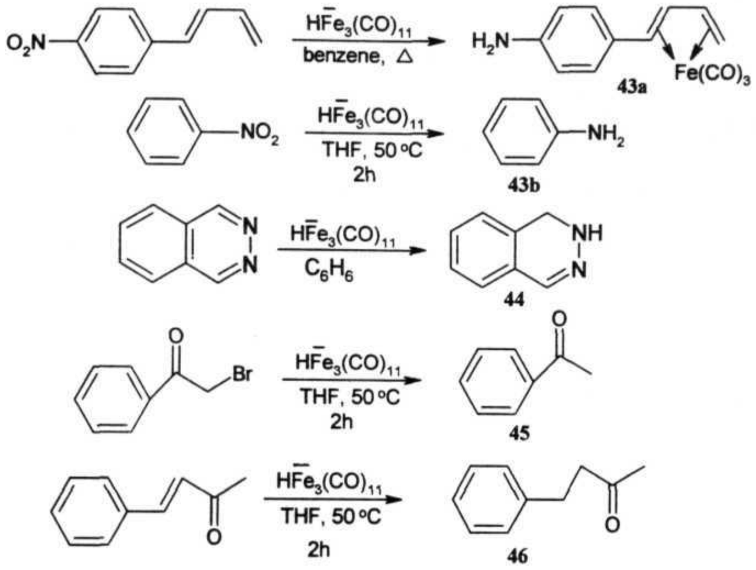


$$H_2C{=}CH_2 \xrightarrow[CO,\ H_2O]{H\bar{F}e_3(CO)_{11}} CH_3CH_2CH_2OH + \bar{O}H \qquad \text{—(34)}$$

42

Moreover, the $HFe_3(CO)_{11}^-$ reduces nitroarenes to amines 43a, 43b, carbon-nitrogen double bonds to 44, carbon-halogen bonds to 45 and a,P-unsaturated carbonyl compounds to 46 in good yields (Scheme 9).[59,68,]

Scheme 9



d) Synthetic applications of $H_2Fe(CO)_4$

The $H_2Fe(CO)_4$ can be readily prepared from iron carbonyl anions by acidification (eq. 35).[77]

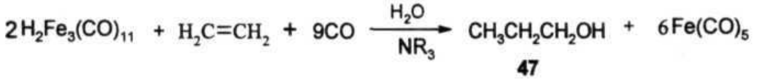
$$Fe(CO)_5 \xrightarrow{\text{aq. NaOH}} H\bar{F}e(CO)_4 \xrightarrow[-78\ ^\circ C]{H_2SO_4} H_2Fe(CO)_4 \quad \text{----(35)}$$

It is unstable above -10 °C, but it can be stored for long periods of time at **liq.N_2** temperature.[77]

The "$H_2Fe(CO)_4$" was considered as intermediate in the Reppe's hydroformylation reactions.[78]

e) Synthetic applications of $H_2Fe_3(CO)_{11}$

The dihydrido derivative $H_2Fe_3(CO)_{11}$ is also highly unstable. It decomposes above −40 °C. It was suggested that these species may be responsible for the conversion of ethylene to *n*-propanol 47 in hydroformylation reactions (eq. **36**).[79]



$$2H_2Fe_3(CO)_{11} + H_2C{=}CH_2 + 9CO \xrightarrow[NR_3]{H_2O} \underset{\mathbf{47}}{CH_3CH_2CH_2OH} + 6Fe(CO)_5 \quad \text{—(36)}$$

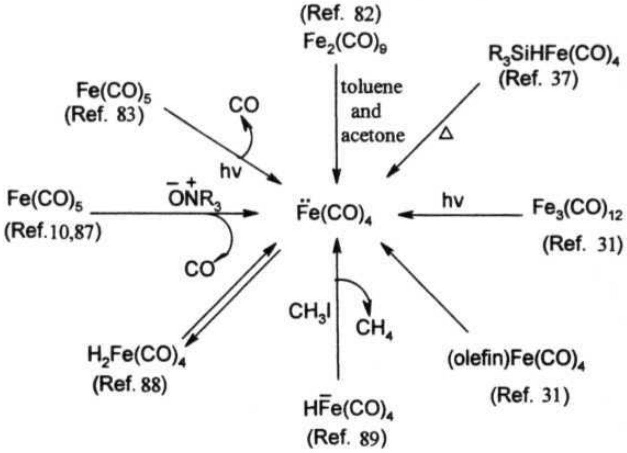
1.1.6 Preparation and applications of "$Fe(CO)_4$"

In many organic transformations using $Fe(CO)_5$, the reactive species involved may be the electronically and coordinatively unsaturated species such as "$Fe(CO)_4$". This species is "*isolobal*" with carbene "CH_2".[80] The *isolobal* analogy explains the similarities between organic and inorganic molecules of similar electronic structure.

As our objective is to develop new organic synthetic methods using coordinatively unsaturated iron carbonyl species such as "$Fe(CO)_4$", prepared *in situ* using readily accessible iron carbonyl reagents, it may be helpful for discussion to briefly review the preparation and applications of the "$Fe(CO)_4$" species.

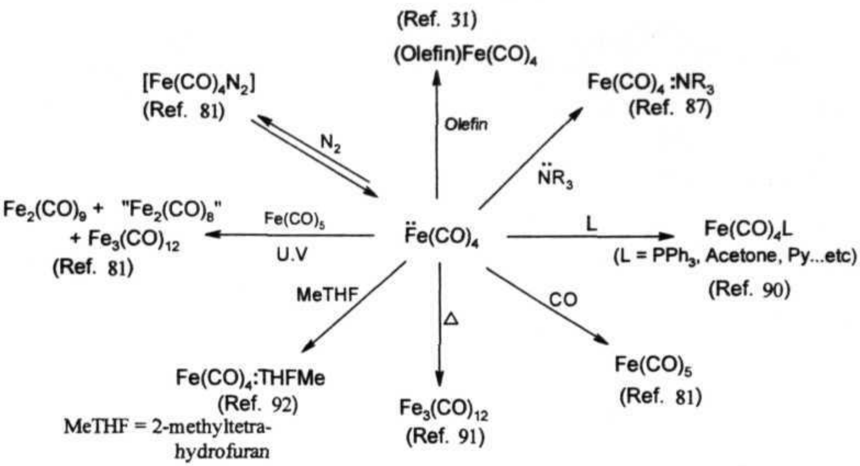
Several methods are available for the preparation of this species *in situ* (Scheme 10). Its physical properties have been studied in matrices .[81]

Scheme 10



The "$Fe(CO)_4$" is highly unstable. It forms addition complexes with variety of organic molecules. Some of the simple addition reactions are summarized below (Scheme 11).

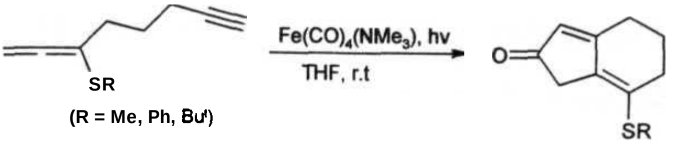
Scheme 11



The intermediate complex $Me_3N{:}Fe(CO)_4$ 48 obtained in the reduction of Me_3NO by $Fe(CO)_5$, acts as a catalyst for the addition of CCl_4 to unsaturated substrates, to give the corresponding chlorinated product 49 (eq. 37).[84]

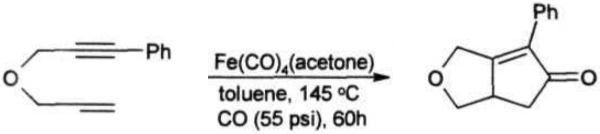
$$H_2C{=}CH(CH_2)_4Me \xrightarrow[\substack{CCl_4 \\ 15h}]{Me_3N{:}Fe(CO)_4\ \mathbf{48}} \underset{\mathbf{49}}{Cl_3CCH_2CHCl(CH_2)_4Me} \qquad \text{-(37)}$$

The $Me_3N{:}Fe(CO)_4$ complex 48 reacts with **1-(ω-alkynyl)-1,2-propadienyl** sulphides to give bicyclic dienones 50 through the corresponding η^3**-allyl** iron complexes under photochemical conditions (eq. 38).



50 —08)

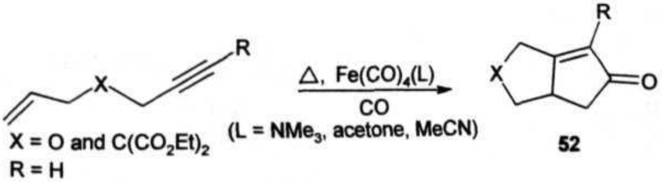
An interesting Pauson-Khand type alkyne-alkene coupling reaction promoted by the iron carbonyl species $Fe(CO)_4(acetone)$, (prepared by stirring $Fe_2(CO)_9$ with acetone and toluene) was reported (eq. 39).[80]



—(39)

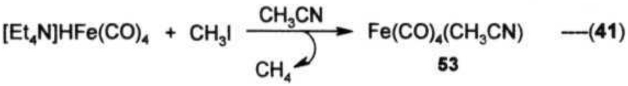
51

The "Fe(CO)4" species prepared under different conditions were used in various alkyne-alkene coupling reactions to obtain a variety of cyclopentenones 52 (eq. 40).[93]



52 ----(40)

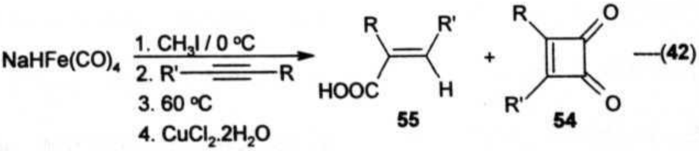
Whitemire *et a!* reported that the reaction of $[Et_4N]HFe(CO)_4$ with CH_3I in CH_3CN leads to the formation of $Fe(CO)_4(CH_3CN)$ 53 and CH4.[89] Acetone has been also obtained in this reaction (eq. 41).[89] It was suggested that the acetone arises from the reaction of CH_3I with "$Fe(CO)_4$".[89]



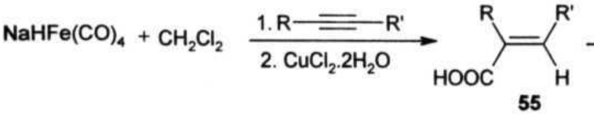
$$[Et_4N]HFe(CO)_4 + CH_3I \xrightarrow[CH_4]{CH_3CN} \underset{53}{Fe(CO)_4(CH_3CN)} \quad \text{---(41)}$$

Since our objective is to generate coordinatively unsaturated iron carbonyl species *in situ* and study its reactivity, we became interested in examining the reactivity pattern of "$Fe(CO)_4$" species generated using the $NaHFe(CO)_4/RX$ system with alkynes.

Preliminary experiments using the $NaHFe(CO)_4/CH_3I$ reagent combination revealed that the iron carbonyl species, generated in this way, reacts with alkynes to give the corresponding cyclobutenediones 54 (27-42%) and the **α,β-unsaturated carboxylic** acids 55 (10-22%) after $CuCl_2.2H_2O$ oxidation (eq. *42)!**

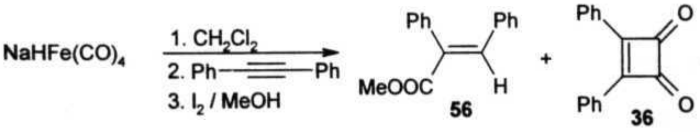


The use of CH_2Cl_2 in the place of CH_3I gave the corresponding hydrocarboxylated products 55 in a regio- and stereoselective fashion after $CuCl_2.2H_2O$ oxidation (eq. **43**).[95a]



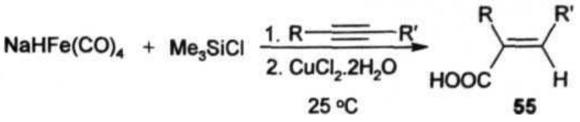
—(43)

Also, the corresponding methyl ester 56 was obtained, upon I_2 treatment in the presence of methanol followed by $CuCl_2.2H_2O$ oxidation, besides traces of the corresponding cyclobutenedione 36 (eq. **44**).[95a] Further, the corresponding amide was obtained when diethylamine was used instead of CH3OH.



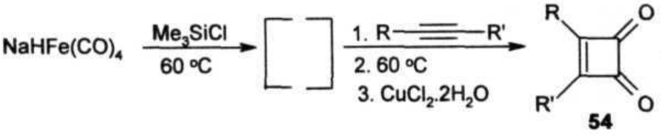
—(44)

The reactivity of the species prepared using $NaHFe(CO)_4/Me_3SiCl$ combination was also examined to compare the results obtained using CH_3I and CH_2Cl_2. It was observed that the intermediate iron carbonyl species, prepared using the $NaHFe(CO)_4$ and Me_3SiCl, reacts with alkynes to give the corresponding a,P-unsaturated carboxylic acids 55 with excellent regio- and stereoselectivities (eq. **45**).[95b]



—(45)

An interesting temperature effect was observed in the reaction with the $NaHFe(CO)_4/Me_3SiCl$ system. It was found that the reaction with alkyne at 60 °C followed by $CuCl_2·2H_2O$ oxidation gave the corresponding cyclobutenedione 54. The α,β-unsaturated carboxylic acid was not formed under these conditions (eq. 46).[95b]



—(46)

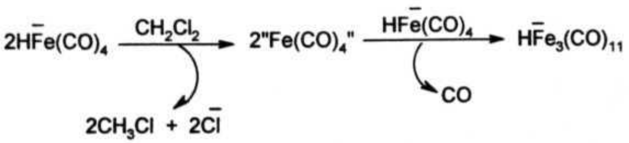
We have undertaken further investigations to understand the reactive species, mechanistic pathway and scope of this transformation. The results are described in this chapter.

1. 2 Results and Discussion

1. 2. 1 U.V. spectral studies of the reactive iron carbonyl species obtained in the reaction of $HFe(CO)_4^-/RX$ system in THF

As outlined in the introductory section, the iron carbonyl species obtained in the reaction of $HFe(CO)_4^-$ with various RX reagents reacts with alkynes to give the corresponding cyclobutenediones 54 and a,P-unsaturated carboxylic acids **55** (eq. **42-46).** It was of interest to understand the nature of the iron carbonyl species formed under these conditions.

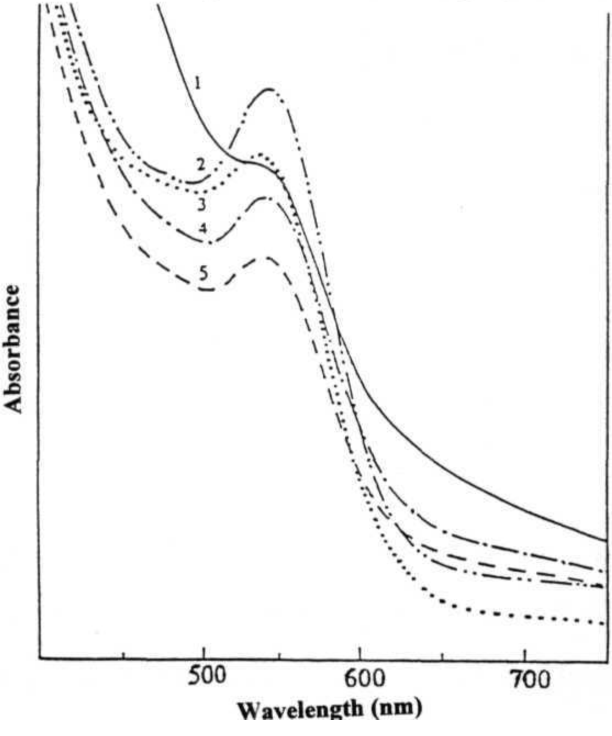
Whitmire *et. al.* reported that the $HFe(CO)_4^-$ slowly decomposes in CH_2Cl_2 to $[HFe_3(CO)_{11}]^-$ through the "$Fe(CO)_4$" intermediate (eq. 47).[69]



—(47)

The U.V. spectra of the $HFe_3(CO)_{11}^-$ in THF solution have been reported. We have examined the U.V. spectra of the solutions obtained in the reaction of $HFe(CO)_4^-$ with RX (RX = CH_3I or CH_2Cl_2 or Me_3SiCl). **Indeed,** the U.V spectra recorded for the iron carbonyl species (Figure 1) prepared under these conditions exhibit characteristic (λ_{max} = 525 nm) absorption data reported for the $[HFe_3(CO)_{11}]^-/H_2Fe_3(CO)_{11}$ species in solution.[96]

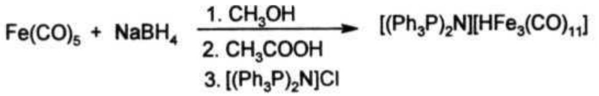
Figure 1. U.V. spectra for iron carbonyl species



1. $NaHFe(CO)_4/CH_3I$ in THF at 25 °C
2. $NaHFe(CO)_4/CH_2Cl_2$ in THF at 25 °C
3. $Fe(CO)_5/NaBH_4/CH_3COOH$ in THF at 25 °C
4. $NaHFe(CO)_4/Me_3SiCl$ in THF at 25 °C
5. $NaHFe(CO)_4/Me_3SiCl$ in THF at 60 °C

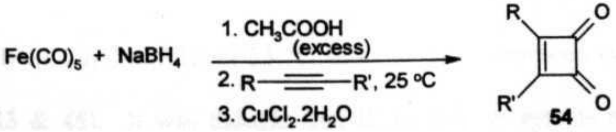
1. 2. 2 Reaction of alkynes with iron carbonyl species prepared using $Fe(CO)_5$, $NaBH_4$ and CH_3COOH

To further examine the possibility, whether the $[HFe_3(CO)_{11}]^-$ or related species is responsible for the formation of cyclobutenedione 54, we have decided to prepare the $[HFe_3(CO)_{11}$]" species following a reported procedure to study its reactivity with alkyne. The $[HFe_3(CO)_{11}]^-$ species has been previously prepared using $Fe(CO)_5$, $NaBH_4$, CH_3OH and CH_3COOH in THF and isolated as PPN salt in 73% yield (eq. 48).[67]



$$Fe(CO)_5 + NaBH_4 \xrightarrow[\substack{2.\ CH_3COOH \\ 3.\ [(Ph_3P)_2N]Cl}]{1.\ CH_3OH} [(Ph_3P)_2N][HFe_3(CO)_{11}] \quad \text{—(48)}$$

We have observed that the $[HFe_3(CO)_{11}]^-$ species, prepared *in situ* in THF using $Fe(CO)_5$, $NaBH_4$ and CH_3COOH, reacts with alkynes at 25 °C to give the corresponding cyclobutenediones 54 in good yields (60-73%) after $CuCl_2.2H_2O$ oxidation (eq. 49).[97] Several alkynes were converted to the corresponding cyclobutenediones 54. The results are summarized in Table 1.



54

—(49)

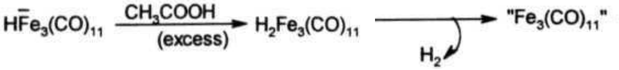
Evidently, the reagent system can tolerate unmasked hydroxyl functional group (entries 7 and 8, Table 1). The formation of cyclobutenedione from an enyne (entry 6, Table 1) indicates that the iron carbonyl reagent reacts with alkynes without affecting the olefin moiety.

The yields of the cyclobutenediones obtained following this method are somewhat better (63-71%) than that realized using the $NaHFe(CO)_4/RX$ system (eq. 42 & 46). Moreover, the preparation of $NaHFe(CO)_4$ requires $Na_2Fe(CO)_4$ which in turn is prepared from $Fe(CO)_5$/Na/Naphthalene. However, the preparation of the reactive iron carbonyl species through the reaction of $Fe(CO)_5$ with $NaBH_4$ and CH_3COOH reagent is relatively less complicated. Further, in this method, the reaction is carried out under ambient conditions and hence it should be more convenient for synthetic applications.

We have also made attempts to isolate the iron carbonyl species as PPh_3 derivative for NMR spectral analysis. Unfortunately, only a complex mixture of products was isolated in the reaction with Ph_3P. However, the U.V spectrum recorded for this reagent system is similar to the spectra recorded for the $HFe(CO)_4^-/RX$ reagent system in THF (Figure 1).[96]

As outlined in the introductory section, the reaction of $HFe(CO)_4^-/CH_2Cl_2$ and $HFe(CO)_4^-/Me_3SiCl$ at 25 °C leads to a,p-unsaturated carboxylic acids 55 (eq. 43 & 45). It was thought that if the reactive species responsible for the conversion of alkynes to the corresponding cyclobutenediones 54 is derived from the $HFe_3(CO)_{11}^-$ species, then the difference in reactivity between the species generated using $Fe(CO)_5/NaBH_4/CH_3COOH$ and $NaHFe(CO)_4/RX$ reagent systems is difficult to rationalize. Whereas, the reaction of the former combination with alkynes leads to the corresponding cyclobutenediones 54 (eq. 49), the latter results in the formation of a,P-unsaturated carboxylic acids 55 (eq. 42).

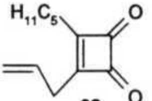
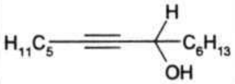
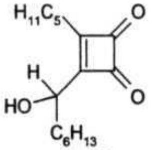
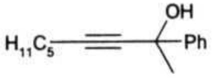
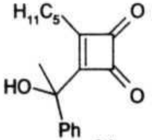
Probably, the CH_3COOH used to destroy the excess $NaBH_4$ in the former case may play a role in the formation of the reactive species from the $[HFe_3(CO)_{11}]^-$.[93] Presumably, in the presence of excess CH3COOH, the $HFe_3(CO)_{11}^-$ may give the $H_2Fe_3(CO)_{11}$, which may dissociate into "$Fe_3(CO)_{11}$" and H_2 (eq. 50).[73] The "$Fe_3(CO)_{11}$" species upon further reaction with alkynes would give the corresponding cyclobutenediones 54.



—(50)

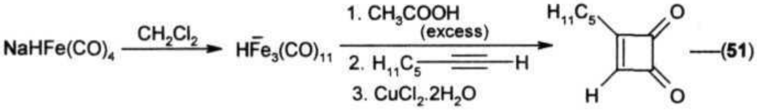
If this is the case, use of an additional amount of CH_3COOH to the iron carbonyl species prepared using $NaHFe(CO)_4/CH_2Cl_2$ reagent system (eq. 42) should also give the corresponding cyclobutenedione 54. Indeed, this was observed. It was found that the reaction of the iron carbonyl species prepared

Table 1: Reaction of $Fe(CO)_5/NaBH_4/CH_3COOH$ system with alkynes

S.No	Alkyne	Product[a]	Yield (%)[b]
1.	R = C_5H_{11}, R' = H	**57**	73[c]
2.	R = C_6H_{13}, R' = H	**58**	69[c]
3.	R = C_8H_{17}, R' = H	**59**	70[c]
4.	R = $C_{10}H_{21}$, R' = H	**60**	68[c]
5.	R = C_6H_5, R' = H	**61**	65[d]
6.		 **62**	60
7.		 **63**	61
8.		 **64**	63[e]

a) Products were identified from the spectral data IR, ^{13}C NMR, ^1H NMR and Mass. b) Yields are of products isolated by column chromatography and based on the amount of alkynes used. c) The spectral data of products 58, 59, and 60 are comparable to the spectral date reported for the product 57." d) For the cyclobutenedione 61, the M.P data is comparable with the reported data.[99] e) For the cyclobutenedione 64, HRMS data were also obtained.

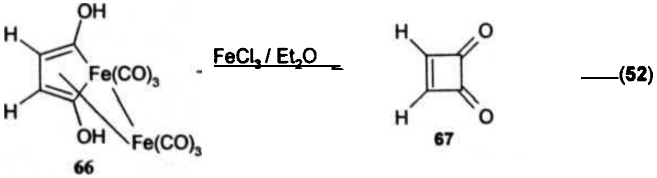
after the addition of excess CH_3COOH to the $NaHFe(CO)_4/CH_2Cl_2$ reagent system in THF, reacts with **1-heptyne** at 25 °C to give the corresponding cyclobutenedione 57 in 33% yield after $CuCl_2.2H_2O$ oxidation. The corresponding a,P-unsaturated carboxylic acid 55 was not formed under these conditions (eq. **51**).[93]



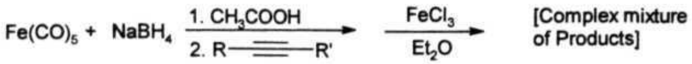
57

1. 2. 3 Mechanism and intermediates

It was reported that the reaction of acetylene with an alkaline solution of $Fe(CO)_5$ leads to the dienol complex 66 at room temperature.[1 no] However, the yields of such complexes are poor for higher alkynes even after a long reaction time (3 days).[100] Also, it was reported that the $FeCl_3$ oxidation of complex **66** in ether yields cyclobutenedione 67 (eq. 52).[101]

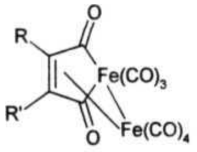


The use of $FeCl_3$ in the place of $CuCl_2.2H_2O$ (eq. 53) for oxidation under the present conditions gave only a complex mixture of products.[97,93]

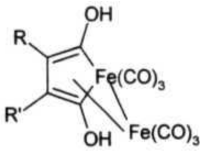


$$Fe(CO)_5 + NaBH_4 \xrightarrow[\text{2. R}-\equiv-\text{R'}]{\text{1. }CH_3COOH} \xrightarrow[Et_2O]{FeCl_3} \text{[Complex mixture of Products]} \tag{53}$$

However, the present transformation may still go through the formation of the **alkyne-iron** complex 65 or dienol complex 66. Oxidation of these complexes using $CuCl_2.2H_2O$ may lead to the formation of **cyclobutenedione**.[97,93]

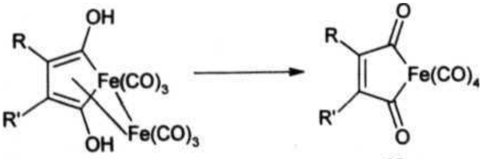


65



66

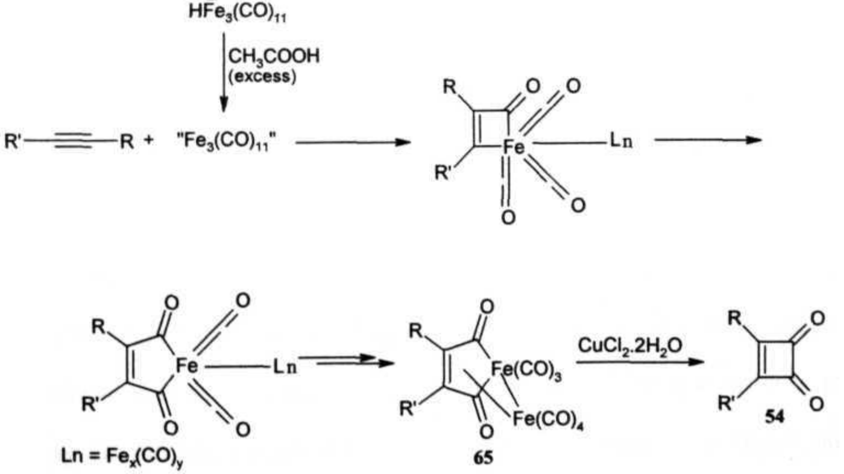
Also, it has been reported that the hydroxy ferrole iron complexes 66 and the maleoyl iron complexes 68 are structurally and chemically **related.**[100] The maleoyl iron complexes 68 can be obtained upon oxidation of **66.**[100]



66 **68**

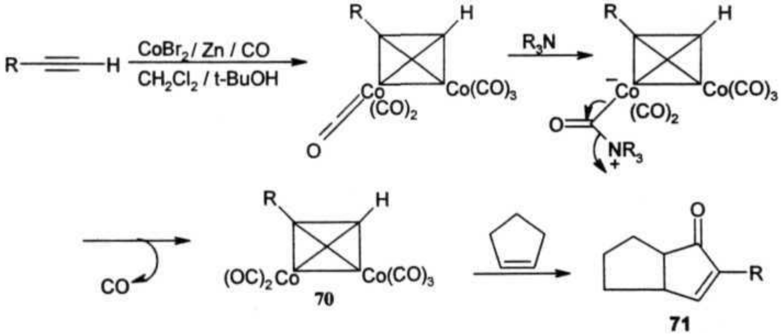
Accordingly, the possibility of existence of the iron carbonyl complex of the type 65, cannot be ruled out under the reaction conditions described here. Hence, a tentative mechanistic pathway for the formation of cyclobutenediones can be visualized as shown in Scheme 12.[93] The iron carbonyl complex of the type 65 could result from the coordination of the alkyne moiety to the **coordinatively** unsaturated iron carbonyl species of the type **"$Fe_3(CO)_{11}$"** followed by carbon monoxide insertion.[102] Oxidation of 65 with **$CuCl_2.2H_2O$** would give the corresponding cyclobutenedione 54.

Scheme 12



We have also investigated this double carbonylation process further to understand the nature of the iron carbonyl species responsible for this transformation. It was thought that the use of the readily accessible $Fe_3(CO)_{12}$ could serve as a source for the preparation of the coordinatively unsaturated species. Recently, it has been reported by **Yamaguchi** *et al*[103a] as well as in this laboratory[103b] that amines can induce the **Pauson-Khand** reaction of alkyne-cobalt complexes under ambient conditions through formation of coordinatively unsaturated cobalt carbonyl species 70 (Scheme 13).[103b]

Scheme 13



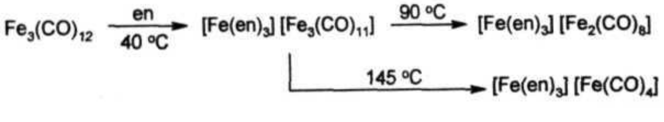
We have examined the possibility whether the coordinatively unsaturated species of type "$Fe_3(CO)_{11}$" can be generated using the $Fe_3(CO)_{12}$/amine reagent combination so as to compare its reactivity with that of the species obtained using the $Fe(CO)_5$, $NaBH_4$ and CH_3COOH reagent system. The results are discussed in the next section.

1. 2. 4 Reaction of alkynes with coordinatively unsaturated iron carbonyl species formed in the reaction of $Fe_3(CO)_{12}$ with amines

The $Fe_3(CO)_{12}$ is more reactive towards Lewis bases than $Fe(CO)_5$. It reacts with liq.NH_3 to give the complexes $Fe_2(CO)_8^{2-}$ and $Fe(CO)_4^{2-}$ (eq. 54).[104]

$$4Fe_3(CO)_{12} + 30\,NH_3 \xrightarrow[20\,°C]{14\text{ days}} 3\,[Fe(NH_3)_6]\,[Fe_2(CO)_8] + 3\,(NH_4)_2\,Fe(CO)_4 + 3\,CO(NH_2)_2 + 9\,CO \quad \text{-(54)}$$

The reaction of the $Fe_3(CO)_{12}$ with ethylenediamine (en) has been extensively studied.[105] Whereas the reaction at 90 °C gives $Fe_2(CO)_8^{2-}$ and $Fe_3(CO)_{11}^{2-}$, the $Fe(CO)_4^{2-}$ complex is formed at 145 °C (eq. 55).[105]

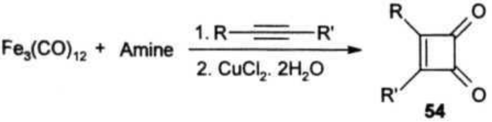


—(55)

In refluxing acetone or benzene, in the presence of phenanthroline (phen.), the $Fe_3(CO)_{12}$ dissociates into the $Fe_2(CO)_8^{2-}$ derivative (eq. 56).[106]

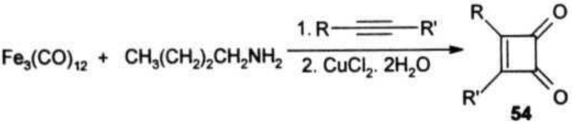
$$Fe_3(CO)_{12} + 3\,\text{Phen} \longrightarrow [Fe(\text{Phen})_3]\,[Fe_2(CO)_8] + 4\,CO \quad \text{----(56)}$$

We have observed that amines facilitate the reaction of $Fe_3(CO)_{12}$ with alkynes in THF to give the corresponding cyclobutenediones 54 after $CuCl_2.2H_2O$ oxidation. Amines such as *n*-butylamine, *n*-octylamine, benzylamine, pyrrolidine, piperidine, triethylamine and DMF were employed for this purpose (eq. 57).[107] The results are summarized in Table 2.



—(57)

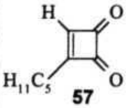
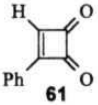
The use of *n*-butylamine gives better results (entry 1, Table 2) (eq. 58).[107]



-(58)

Accordingly, we have carried out the reaction of several other alkynes under these conditions. Evidently, this reagent system can tolerate unmasked functional groups such as hydroxyl and trimethylsilyl (entries 5-8, Table 3).

Table 2: Reaction of the **$Fe_3(CO)_{12}$/amine** system with alkynes

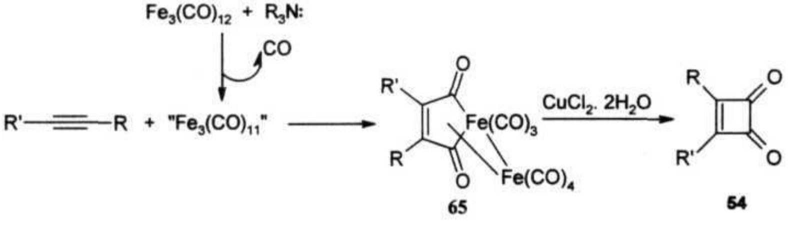
S.No	Amine	Alkyne	Product[a]	Yield(%)[b]
1.	$CH_3(CH_2)_3NH_2$	R = C_5H_{11}	 **57**	61
2.	$CH_3(CH_2)_7NH_2$	R = C_5H_{11}	**57**	45
3.	Piperidine	R = C_5H_{11}	**57**	33
4.	Pyrrolidine	R = C_5H_{11}	**57**	30
5.	$PhCH_2NH_2$	R = C_5H_{11}	**57**	37
6.	$(C_2H_5)_3N$	R = C_5H_{11}	**57**	28
7.	DMF	R = C_5H_{11}	**57**	31
8.	$CH_3(CH_2)_3NH_2$	R = C_6H_5	 **61**	41
9.	$CH_3(CH_2)_7NH_2$	R = C_6H_5	**61**	28
10.	$(C_2H_5)_3N$	R = C_6H_5	**61**	18

a) Products were identified from the spectral data IR, ^{13}C NMR, ^{1}H NMR and Mass and compared with the reported data.[98, 99]

b) Yields are of products isolated by column chromatography.

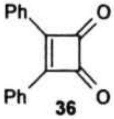
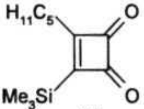
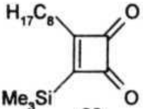
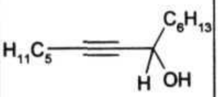
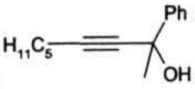
A tentative mechanistic pathway for the formation of cyclobutenediones can be visualized through steps outlined in Scheme 14. Presumably, the amine may help in the removal of one of the CO ligands from the $Fe_3(CO)_{12}$ to give the coordinatively unsaturated reactive species $Fe_3(CO)_{11}$" that on further reaction with alkynes, followed by CO insertion would give the alkyne-iron complex intermediate 65.[102] Oxidation of 65 with $CuCl_2.2H_2O$ would produce the corresponding cyclobutenediones 54 (Scheme 14).

Scheme 14



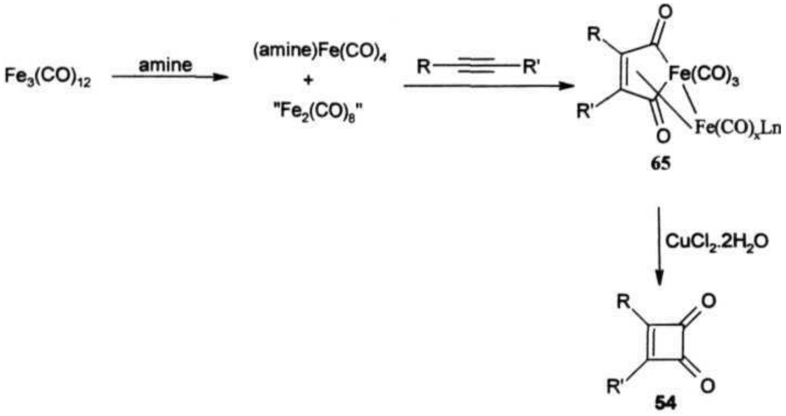
However, the possibility that the amine may split the $Fe_3(CO)_{12}$ into the species such as $Fe(CO)_4$(amine) and "$Fe_2(CO)_8$" cannot be ruled out. The "$Fe_2(CO)_8$" produced in this way can pick up an alkyne followed by CO insertion to give the alkyne-iron complex intermediate 65. Oxidation of 65 with $CuCl_2.2H_2O$ would then produce the corresponding cyclobutenedione 54 (Scheme 15).[107]

Table 3: Reaction of $Fe_3(CO)_{12}$/*n*-butylamine system with alkynes

S.No	Alkyne	Product[a]	Yield(%)[b]
1.	$R = C_5H_{11}$, $R' = H$	**57**	61
2.	$R = C_6H_{13}$, $R' = H$	**58**	54
3.	$R = C_6H_5$, $R' = H$	**61**	41
4.	$R, R' = C_6H_5$	 **36**	45
5.	$R = C_5H_{11}$, $R' = SiMe_3$	 **65**	28
6.	$R = C_8H_{17}$, $R' = SiMe_3$	 **66**	25
7.		**63**	33
8.		**64**	37

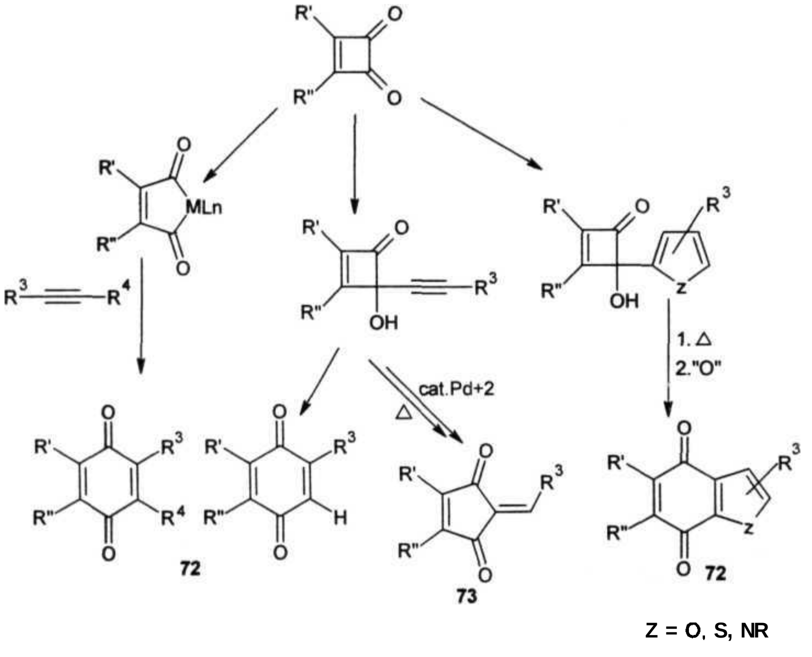
a) Products were identified from the spectral data IR, ^1H NMR, ^{13}C NMR and Mass. The spectral data of product 57, 58 and 61 were identical to the reported data.[98,99] For the products 64 and 65 HRMS data were also obtained. b) Yields are of products isolated by column chromatography using hexane/ethyl aceute (98:2) as eluent and based on the amount of alkynes used.

Scheme 15



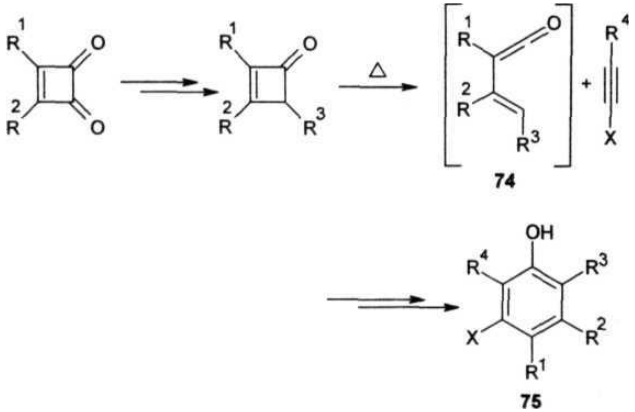
The cyclobutenediones have been used as starting materials for the synthesis of highly functionalized, biologically active molecules. A number of methods are available for the conversion of cyclobutenediones to benzoquinones 72 and cyclopentenone derivatives 73 (Scheme 16).[108]

Scheme 16



It has been also reported that under thermolysis, the cyclobutenones form vinyl ketenes 74 that on further reaction with an alkyne produce the corresponding substituted polycyclic aromatics 75 (Scheme 17).[109]

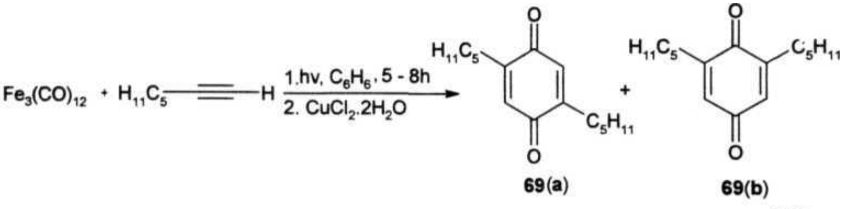
Scheme 17



Accordingly, the one-pot methods described here for the conversion of alkynes to cyclobutenediones have considerable synthetic potential.

1. 2. 5 Photochemical reaction of $Fe_3(CO)_{12}$ with 1-heptyne

We have also examined the possibility of preparing the coordinatively unsaturated iron carbonyl species from $Fe_3(CO)_{12}$ under photochemical conditions. It was observed that the reaction of $Fe_3(CO)_{12}$ and 1-heptyne in benzene under irradiation at 253.7 nm for 5-8h, gives the corresponding benzoquinones **69(a)** and **69(b)** in 55% yield after $CuCl_2.2H_2O$ oxidation (eq. **59**). Since the conversion of alkynes to benzoquinones has been already reported using $Fe(CO)_5$ and alkynes under photolysis,[110] we did not pursue further studies on this method of conversion of alkynes to the corresponding benzoquinones.



—(59)

1.2.6 Reaction of $Fe(CO)_5$/amine reagent system with alkynes

We have also examined the possibility whether coordinatively unsaturated species such as $Fe(CO)_4$ or related species can be prepared using the $Fe(CO)_5$/*n*-butylamine reagent combination for reaction with alkynes. It was observed that the reaction of $Fe(CO)_5$ (6 mmol) and *n*-butylamine (2.75 mmol) with phenylacetylene (1.25 mmol), did not proceed and the alkyne remained unaffected. Here, it is of interest to note that *n*-butylamine, pyrrolidine and piperidine form only some unidentified addition complexes with the $Fe(CO)_5$.[111]

1. 3 Conclusions

The iron carbonyl species $HFe_3(CO)_{11}^-$, prepared using the $Fe(CO)_5/NaBH_4$ and CH_3COOH reagent system at 25 °C, reacts with alkynes in THF, to give the corresponding cyclobutenediones in good yield (60-73%) after $CuCl_2.2H_2O$ oxidation.

Also, certain amines facilitate the double carbonylation reaction of alkynes using $Fe_3(CO)_{12}$. The reaction of iron carbonyl species, prepared in THF using $Fe_3(CO)_{12}$ and *n*-butylamine at 25 °C, with various alkynes gives the corresponding cyclobutenediones in moderate to good yields (25-61%).

It appears that the cyclobutenediones would have formed through the reaction of alkynes with coordinatively unsaturated iron carbonyl species such as "$Fe_3(CO)_{11}$"or "$Fe_2(CO)_8$" through a maleoyl iron complexes of the type 65.

1. 4 Experimental Section

1. 4. 1 General information:

Melting points reported in this thesis are uncorrected and were determined using a **Buchi-510** capillary point apparatus. Infrared spectra were recorded on **Perkin-Elmer IR** spectrometer Model JASCO FT 5300 with polystyrene as reference. ^{1}H NMR (200 MHz) and ^{13}CNMR (50 MHz) spectra were taken in $CDCl_3$ unless otherwise stated and TMS as reference (8 = 0 ppm). The chemical shifts are reported in ppm on the δ scale relative to $CDCl_3$ (77.0 ppm) and coupling constants are reported in Hz. Elemental analyses were performed on a Perkin-Elmer elemental analyzer model-240C. The UV spectra were recorded with a JASCO model 7800 spectrophotometer. The photochemical reactions were carried out in a photochemical reactor (Srinivasan-Griffin-Rayonet type) comprising of eight UV-tubes (wave length 253.7 nm) fitted in a heavy metal enclosure. The reaction mixture was kept in quartz tube for irradiation. Analytical thin layer chromatographic tests were carried out on glass plates (3 x 10 am) coated with 250 mu acme's silica gel-G or GF_{254} containing 13% calcium sulphate as binder. The spots were visualized by short exposure to iodine vapour or UV light. Chromatographic purification was conducted by column chromatography using 100-200 mesh silica gel obtained from Acme Synthetic Chemicals, India.

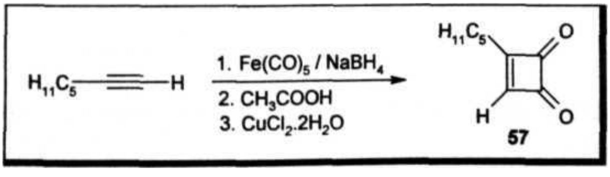
All glassware were pre-dried at 140 °C in an air oven for 4h, assembled hot and cooled under a stream of dry nitrogen. Unless, otherwise mentioned, all the operations and transformations of reagents were carried out using standard syringe, septum technique recommended for handling air sensitive organometallic compounds. Reagents prepared *in situ* in solvents were transformed using a double ended stainless steel (Aldrich) needle under a stream of nitrogen whenever required.

In all experiments, a round bottom flask of appropriate size with a side arm, a side septum, a magnetic stirring bar, a condenser and a connecting tube attached to a mercury bubbler were used. The outlet of the mercury bubbler was connected to a long tube to the atmosphere. All dry solvents and reagents (liquids) used were distilled from appropriate drying agents just before use. As a routine practice, all organic extracts were concentrated on Buchi-EL-rotary evaporator. All yields reported are isolated yields of material judged homogenous by TLC, IR and NMR spectroscopy.

Iron pentacarbonyl supplied by Fluka, Switzerland and Aldrich, USA was used. $NaBH_4$ supplied by Aldrich, USA was used. Naphthalene supplied by LOBA-Chemie, India was sublimed before use. The $Fe_3(CO)_{12}$ was prepared using a reported procedure.[29] The commercially available 1-heptyne, CH_2Cl_2, and CH3COOH were distilled and used in the experiments. The alkynes used in the reactions were prepared following a reported procedure. Tetrahydrofuran supplied by E-Merck, India was distilled over sodium-benzophenone before use.

1.4.2 Reaction of $[HFe_3(CO)_{11}]^-$ with alkynes

The $Fe(CO)_5$ (2.9 g, 15 mmol) in THF (15 mL) was added drop wise for 1h to $NaBH_4$ (0.567 g, 15 mmol) in THF (50 mL), and stirred for 8h at 25 °C under nitrogen atmosphere. Acetic acid (2.7 g, 45 mmol) was added and stirred for 30 min. Subsequently, 1-heptyne (0.24 g, 2.5 mmol) was added and the contents were further stirred for 12h. The metal carbonyl complex was decomposed using $CuCl_2 2H_2O$ (6.8 g, 40 mmol) in acetone (25 mL). Saturated aq.NaCl was added and the contents were extracted with ether (100 mL). The combined organic extract was washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Ethyl acetate (2%) in hexane eluted the cyclobutenedione 57 (73%, 0.275 g).[98]



Yield : 56% (0.21 g)

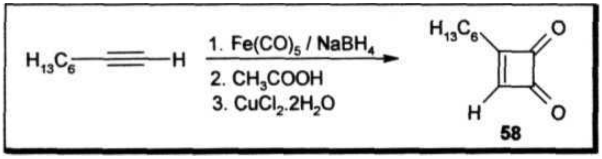
IR(neat) :1778 cm^{-1}

^{1}H NMR (CDCl$_3$) : δ ppm 0.82 (t, J=7.3,3H), 1.27-1.40 (m,4H), 1.70-1.83 (m, 2H), 2.81 (t, J=7.3 Hz, 2H), 9.20 (s, 1H)

^{13}C NMR (CDCl$_3$) : 8 ppm 13.7, 22.1, 25.6, 27.1, 31.2, 184.8, 196.6, 199.9, 208.3

MS (EI) : m/z 152 (M$^+$, 13%), 81 [(M$^+$-C$_5$H$_{11}$), 20%]

The above procedure was followed for the conversion of other alkynes to the corresponding cyclobutenediones.



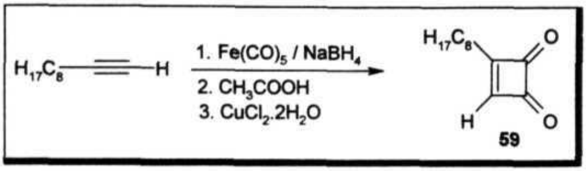
58

Yield : 69% (0.285 g)

IR (neat) : 1786 cm^{-1}

^{1}H NMR (CDCl$_3$) : 8 ppm 0.89 (t, J=7.3 Hz, 3H), 1.2-2.7 (m, 8H) 2.81 (t, J=7.2 Hz, 2H), 9.1 (s, 1H)

^{13}C **NMR** **(CDCl$_3$)** : 8 **ppm** 13.9, 25.9, 26.8, 28.9, 29.6, 31.8, 184.9, 196.7, 199.9,208.3



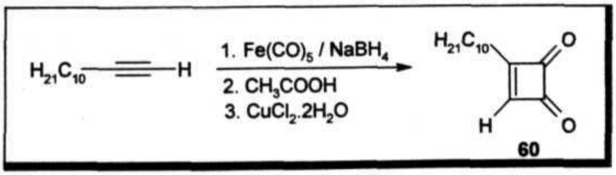
59

Yield : 70% (0.320 g)

IR (neat) :1788 cm^{-1}

^{1}H **NMR** (CDCl$_3$) : δ ppm 0.88 (t, J=7.3 Hz, 3H), 1.2-2.5 **(m,** 12H) 2.85 (t, J=7.3 **Hz,** 2H), 9.2 (s, 1H)

^{13}C NMR **(CDCl$_3$)** : δ ppm 14.0, 22.6, 26.0, 27.5, 29.3, 29.7, **31.7,** 31.9, 184.8, **196.6, 199.7,** 208.4.



60

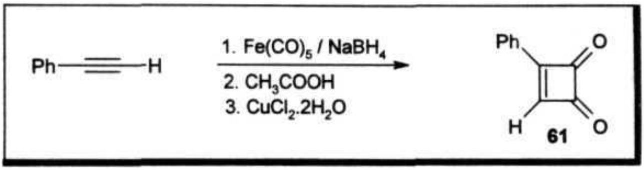
Yield : 68% (0.375 g)

IR(neat) :1774 **cm^{-1}**

^{1}H NMR (CDCl$_3$) : 8 ppm 0.81 (t, **J=7.2 Hz,** 3H), 1.23-2.42 **(m,** 16H), 2.75 (t, J=7.4 Hz, 2H), 9.21 (s, **1H) (Spectrum No. 1)**

^{13}C NMR (CDCl$_3$) : 8 ppm **13.9,** 22.6, 25.9, 26.3, **29.1,** 29.2, 29.5, 29.6, **31.8, 31.9, 198.7,** 199.1, **199.4, 203.4 (Spectrum** No. **2)**

MS **(EI)** : **m/z** 222 (M$^+$, 25%), 81 [(M$^+$-C$_{10}$H$_{21}$),60%]



61

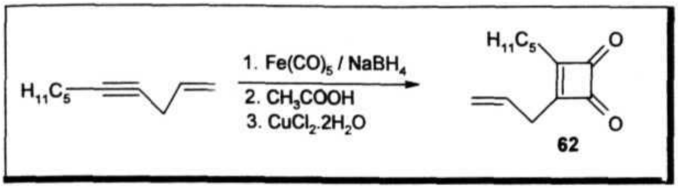
Yield : 65% (0.240 g)

M.P : 152-153 °C **(Lit.[99]** 152-153 ^{o}**C)**

IR(KBr) : 1768 cm"^{1}

H NMR **(CDCl$_3$)** : δ ppm 7.3-8.0 **(m,** 5H), 9.5 (s, 1H)

^{13}C NMR **(CDCl$_3$)** : 8 ppm 128.6, **129.4, 129.5, 134.6,** 178.3, **195.5, 196.0, 197.7**



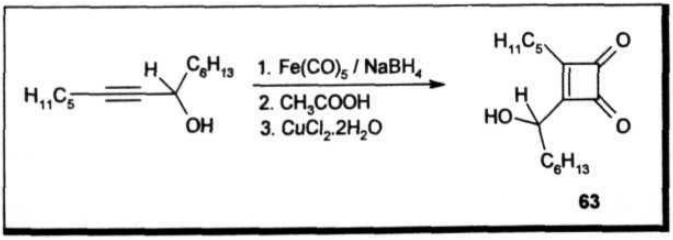
Yield : 60% (0.290 g)

IR(neat) : 1768, 1631 cm^{-1}

^{1}H NMR (CDCl$_3$) : δ ppm 0.91 (t, J= 7.1 Hz, 3H); 1.25-1.80 (m, 6H); 2.05 (d, J= 6.9 Hz, 2H); 2.75 (t, J= 7.7 Hz, 2H); 6.49 (dd, J= 7.7, 1.8 Hz, 2H), 7.36 (m, 1H)

^{13}C NMR (CDCl$_3$) : 5 ppm 13.7, 19.9, 22.1, 25.8, 26.4, 31.7, 119.4, 146.6, 190.5, 195.7,197.8, 198.3

MS (EI) : m/z 192 (M$^+$, 12%), 121 [(M$^+$-CH$_2$(CH$_2$)$_3$, 20%].



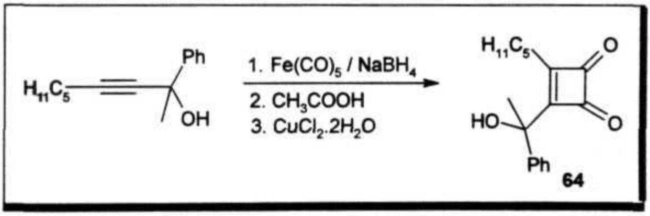
Yield : 61% (0.405 g)

IR (neat) : 3450, 1788 cm^{-1}

H NMR (CDCl$_3$) : 5 ppm 0.88 (t, J= 6.8 Hz, 3H); 0.90 (t, J= 6.9 Hz, 3H); 1.28-1.37 (m, 14H); 2.89 (t, J= 7.2 Hz, 2H); 4.98 (t, J= 6.0 Hz, 3H) **(Specrtum No. 3)**

^{13}C NMR (CDClj) : 8 ppm **13.8, 13.9,** 22.2, 22.4, 24.9, 26.0, 26.9, 28.9, 31.5, 31.8, 35.0, 68.6, 197.3, 198.4, 201.8, 202.7 **(Spectrum No. 4)**

MS (EI) : m/z 266 (M^++1, 5%), 195 [(M^++1)-C_5H_{11}, 16%]



64

Yield : 63% (0.428 g)

IR(neat) :3476,1786 cm^{-1}

^{1}H NMR (CDC1,) : 8 ppm 0.86 (t, J= 6.9 Hz, 3H), 1.25-1.78 (m, 6H), 1.99 (s, 3H), 2.3 (s, 1H), 2.8 (t, J= 7.3 Hz, 2H), 7.26-7.65 (m, 5H)

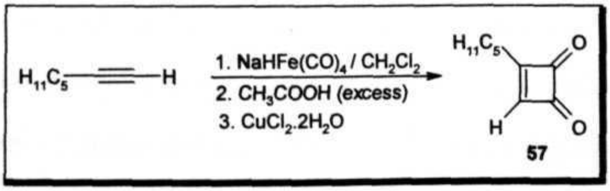
^{13}C NMR (CDCl$_3$) : 8 ppm 13.7, 22.1, 26.9, 28.4, 29.3, 31.8, 74.9, 124.9, 125.3, 128.3, 128.8, 196.4, 198.5, 201.2, 202.9

MS (EI) : m/z 272 (M^+, 4%), 121 (M^+-(Ph-C(OH)CH$_3$)$^+$, 60%]

HRMS : m/z (M+), calcd. 272.141245, found 272.141843.

1.4.3 Reaction of $NaHFe(CO)_4/CH_2Cl_2/CH_3COOH$ (excess) reagent system with 1-heptyne

The $NaHFe(CO)_4$ (6 mmol) in THF (30 mL) [prepared by acidification of $Na_2Fe(CO)_4$ (6 mmol) with CH_3COOH (6 mmol, 0.39 g)] was treated with 5 mL of CH_2Cl_2 under nitrogen atmosphere. After 1h, CH_3COOH (4 equiv.) (24 mmol, 1.6g) was added and stirring continued for 30min. Subsequently, 1-heptyne (2.5 mmol, 0.24 g) was added and the contents were stirred further for 12h. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (20 mmol, 3.4 g) in acetone (15 mL). Saturated aq.NaCl was added and the resulting solution was extracted with ether (100 mL), washed with brine (15 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography on silica gel. Ethyl acetate (2%) in hexane **eluted the** cyclobutenedione 57 (33%).[98]



Yield 33%

The spectral data were identical to the data of sample obtained in previous experiments.

1. 4. 4 Preparation of $Fe_3(CO)_{12}$

A reported procedure involving MnO_2 oxidation of $NaHFe(CO)_4$ was followed.[29] The $Fe(CO)_5$ (30g, 0.015 mol) and methanol (85 mL) are placed in a three necked 1 lit. flask fitted with a stirrer, nitrogen inlet and a refluxing condenser. The reaction mixture was treated with a solution of 22.5g of NaOH in 45 mL of H_2O. The mixture was stirred for about 30 min. and then treated with 70 mL of saturated NH_4Cl solution.

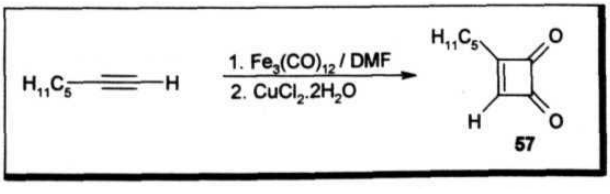
Meanwhile the MnO_2 was prepared by cautiously adding 32.3g of $KMnO_4$ in water (150 mL) with of 95% ethanol (50 mL) under stirring in a large beaker covered with a watch glass. Stirring was continued further to get a brown precipitate of MnO_2.

The suspension of MnO_2 thus obtained was added to the $HFe(CO)_4^-/NH_4Cl$ solution. The reaction mixture was stirred for 2-3h. The excess MnO_2 was then decomposed by gradual addition of a solution of 20g of iron(II) sulphate 7-hydrate dissolved in dil.H_2SO_4 (about 2N, 125 mL). The mixture was then treated with 1:1 H_2SO_4 (150 mL). The black precipitate of $Fe_3(CO)_{12}$ is then filtered and washed successively with hot dil.H_2SO_4 (~2N, 200 mL), 100 mL of

95% ethanol (100 mL) and pentane (75 mL) and dried under vacuum. Yield 18g (70%).

1.4.5 Reaction of $Fe_3(CO)_{12}$/amine or amide reagent system with alkynes

The $Fe_3(CO)_{12}$ (3.02 g, 6 mmol) and DMF (0.130g, 2.75 mmol) in THF (50 mL) were stirred under N_2 for 30 min. at 25 °C. 1-Heptyne (0.120 g, 1.25 mmol) was added and the stirring was continued further for 12h. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (1.7g. 10 mmol) in acetone (10 mL). Saturated aq.NaCl (25 mL) was added, and the resulting solution was extracted with ether (100 mL), washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Ethyl acetate (2%) in hexane eluted the cyclobutenedione 57 (0.058g, 31%).[98,107]

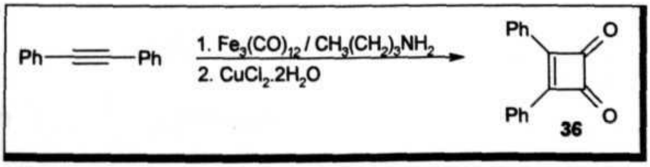


Yield :31%

The above experimental procedure was followed for the reaction of $Fe_3(CO)_{12}$ with other amines and alkynes. The results are summarized in the Table 2. The spectral data of the products were identical to the data obtained in previous experiments.

1.4.6 Reaction of $Fe_3(CO)_{12}/CH_3(CH_2)_3NH_2$ reagent system with alkynes

The $Fe_3(CO)_{12}$ (3.02 g, 6 mmol) and *n*-butylamine (0.201 g, 2.75 mmol) in THF (50 mL) were stirred under N_2 for 30 min. at 25 °C. Diphenylacetylene (0.225 g, 1.25 mmol) was added and the stirring was continued for further 12h. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (1.7g. 10 mmol) in acetone (10 mL). Saturated aq.NaCl (25 mL) was added, and the resulting solution was extracted with ether (100 mL), washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Ethyl acetate (2%) in hexane eluted the cyclobutenedione 36 (45%).[98]



Yield : 45%

M.P. : 95-96 °C (Lit.[98] M.P. 97 °C)

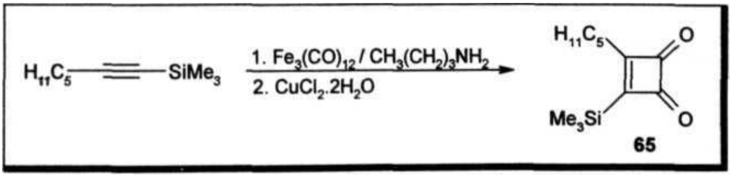
IR(KBr) : 1780 cm^{-1}

H NMR (CDCl$_3$) : 6 ppm 7.45-7.68 (m, 6H), 8.14 (m, 4H) (**Spectrum** No. **5)**

^{13}C NMR (CDCl$_3$) : 5 ppm 128.7, 129.7, 131.2, 134.6, 187.4, 196.1 **(Spectrum No. 6)**

MS (EI) : m/z 235 (M+1, 12%), 179 [(M$^+$+1)-(Ph$_2$C$_2$ +1), 100%] (**Spectrum** No. 7)

The above procedure was followed for the conversion of other alkynes to the corresponding cyclobutenediones. The results are summarized below and also in Table 3.



65

Yield : 28%

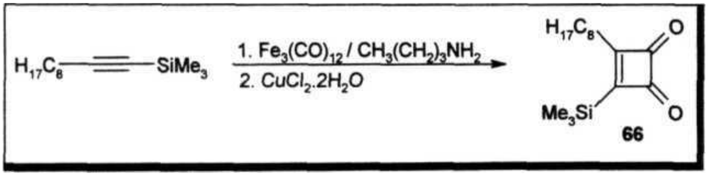
IR (neat) :1774 cm^{-1}

^{1}H NMR ($CDCl_3$) : 8 **ppm** 0.35 (s, 9H); 0.92 (t, J= 6.9 Hz, 3H); 1.17-1.67 **(m,** 6H); 2.87(t, **J=** 7.3 **Hz,** 2H) **(Spectrum No. 8)**

^{13}C NMR ($CDCl_3$) : 8 ppm -2.1, 13.7, 22.2, 26.5, 29.0, 31.8, 200.1, 201.4, 207.7, **211.3 (Spectrum** No. 9)

MS (EI) : **m/z:** 224 (M^+, 10%), 154 [(M^+-$CH_2(CH_2)_3CH_3$), 100%], 73 [$(SiMe_3)^+$,60%]

HRMS : **m/z** (M^+) calcd. 224.123258, found: 224.123138.



Yield : 25%

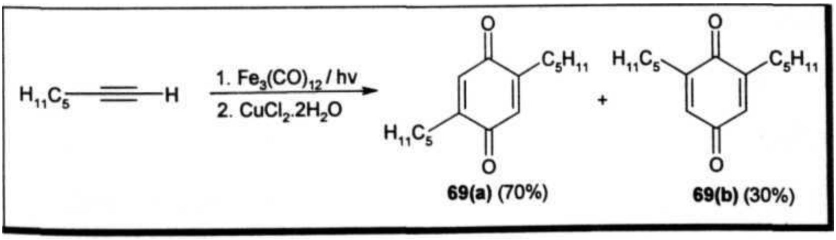
IR(neat) :1774 **cm^{-1}**

^{1}H NMR ($CDCl_3$) : 8 ppm 0.35 (s, 9H); 0.87 **(t, J=** 6.9 **Hz,** 3H); **1.20-1.67 (m, 12H); 2.79 (t, J= 7.1 Hz, 2H)**

^{13}**C NMR** ($CDCl_3$) **: δ ppm -2.1,** 14.0,22.5,26.8,29.0,29.6,31.5,31.7,200.0, 207.6,211.2

1.4. 7 Photochemical reaction of $Fe_3(CO)_{12}$ with 1-heptyne

A solution of $Fe_3(CO)_{12}$ (6 mmol, 3.02 g) and 1-heptyne (0.240 g, 2.5 mmol) in benzene (50 mL) was irradiated at 253.7 nm for 6h under nitrogen atmosphere. The reaction mixture was poured into $CuCl_2.2H_2O$ (10 mmol, 1.7g) in acetone (20 mL). Saturated aq.NaCl (30 mL) was added and the resulting solution was extracted with ether (2 x 20 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography on silica gel. Hexane eluted the benzoquinones **69(a)** (70 %) and 69(b) (30%).[110] The percentage composition of isomer (a) and (b) were calculated from the ^1H NMR signal intensities.[110]



69(a) (70%) 69(b) (30%)

Yield : 55%

IR (neat) : 1657 cm^{-1}

^{1}H NMR (CDCl$_3$) : 6 ppm 0.89 (t, J = 6.8 Hz, 12 H for **69a** and **69b),** 1.16-2.46 (m, 32 H for **69a** and **69b),** 6.50 (s, 2H for **69a),** 6.52 (s, 2H for **69b).**

^{13}C NMR (CDCl$_3$) : δ ppm 13.6,22.2,27.4,28.5,29.0,31.3, 131.9, 132.4, 149.2,149.6,187.4,187.7.

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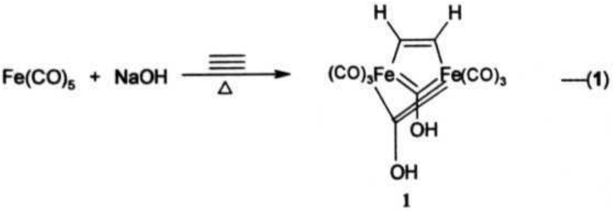
Chapter 2

Studies on Synthetic Applications of Iron Carbonyl Complexes Prepared Using Alkynes

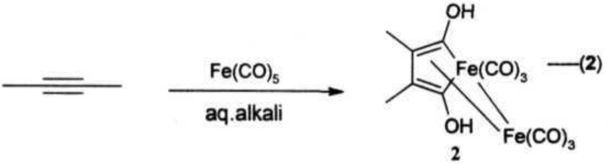
2.1 Introduction

As discussed in Chapter 1, the double carbonylation reactions of alkynes would most probably go through the intermediacy of maleoyl iron complexes (Scheme 12, Chapter 1). Such maleoyl iron complexes undergo a variety of interesting reactions under different conditions.[1] The results of investigations carried out to exploit such intermediates for further synthetic applications are discussed here. It may be of interest to briefly review the reports on the preparation of such iron carbonyl complexes and their synthetic applications.

In 1953, Reppe first reported the iron carbonyl acetylene complexes of the formula $(RC{\equiv}CR)H_2Fe_2(CO)_8$.[2] Later, Sternberg *et al* proposed the structure 1 for this complex (eq. 1).[3] The complex 1 contains two acidic hydrogens, which can be benzoylated and methylated. An improved method for the preparation of the complex was also reported.[3]



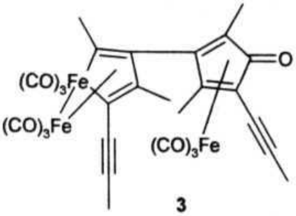
In 1961, Hock *et al* studied the organoiron complexes first reported by Reppe. The structure of the complex 2 isolated in the reaction of but-2-yne with aq.alkaline solution of $Fe(CO)_5$ has been determined by X-ray crystallographic data (eq. 2).[4]



Several such ferrole iron carbonyl complexes of the type 2 have been prepared using alkynes and iron carbonyls.[5] Also, it has been demonstrated that both the hydroxy ferrole and maleoyl iron complexes are structurally and chemically related.[6] A brief review of the reports on the methods of preparations and synthetic applications of the ferrole iron carbonyl complexes will be helpful for the discussion.

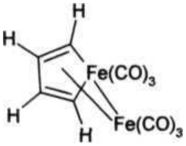
2.1.1 Methods of preparation of ferrole iron carbonyl derivatives

The ferrole iron carbonyl derivatives can be prepared using $Fe_3(CO)_{12}$. As outlined in the introductory section in chapter 1, the $Fe_3(CO)_{12}$ on reaction with 2,4-hexadiyne in toluene at refluxing temperature gives a trimetallic product 3 (eq. 20, Chapter 1).[7]

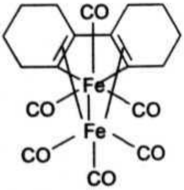


3

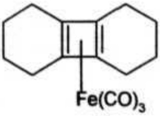
Also, at elevated temperatures, thiophene and **$Fe_3(CO)_{12}$** undergo a novel reaction resulting in the removal of the sulphur atom to give the iron tricarbonyl complex 4 (eq. 21, Chapter **1**).[8]



Several other such complexes have been also reported. For example, 1,7-cyclododecadiyne reacts with **$Fe(CO)_5$** to give the iron carbonyl complexes, 5 (major product) and 6 (minor product) (also see eq. 8, Chapter **1**).[9]

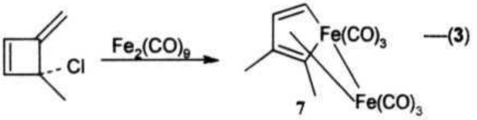


5
(major)

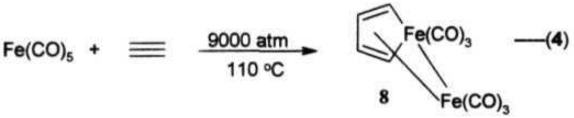


6
(minor)

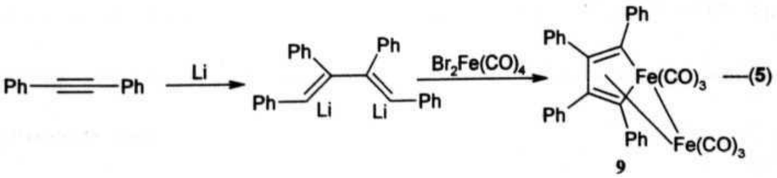
Reaction between **3-methyl-3-chloro-4-methylenecyclobut-1-ene** and $Fe_2(CO)_9$ gives the **2,3-dimethylferrole** complex 7 as a major product, in addition to small amounts of side products (eq. 3).[10]



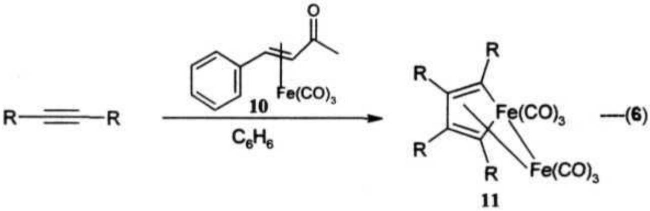
Also, the reaction of $Fe(CO)_5$ with acetylene, conducted at 110 °C and 9000 atm, gave the ferrole iron complex 8 (eq. 4).[11]



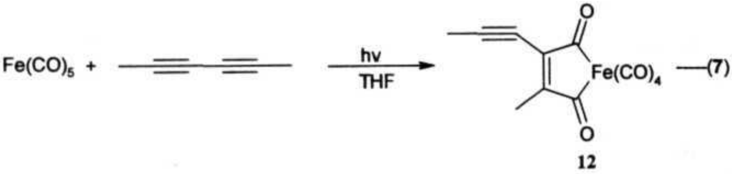
A direct reaction between **1,4-dilithio-1,2,3,4-tetraphenylbutadiene** and $Br_2Fe(CO)_4$ gave the tetraphenylferrole iron complex 9 (eq. 5).[12]



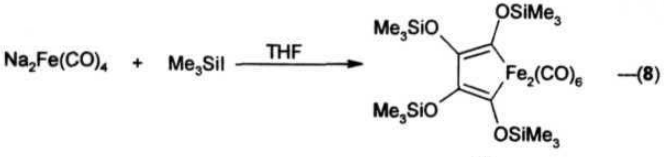
Reactions of alkynes with the benzalacetone iron complex $[C_6H_5CH=CHC(O)CH_3]Fe(CO)_3$ **10** in boiling benzene gives the corresponding tricarbonylferrole-iron tricarbonyl derivatives **11** (eq. 6).[13]



Also, U.V irradiation of $Fe(CO)_5$ and dimethyl-1,3-diyne in THF gave the maleoyl iron complex 12 derivative (eq. 7). Its structure has been determined by X-ray crystallographic data.[14]



An unusual product of the formula $[(Me_3SiO)_2Fe(CO)_3]_2$ 13 has been obtained in the reaction of Me_3SiI with $Na_2Fe(CO)_4$ in THF (eq. 8).[1516] The molecular structure of the complex 13 has been assigned on the basis of spectroscopic data.

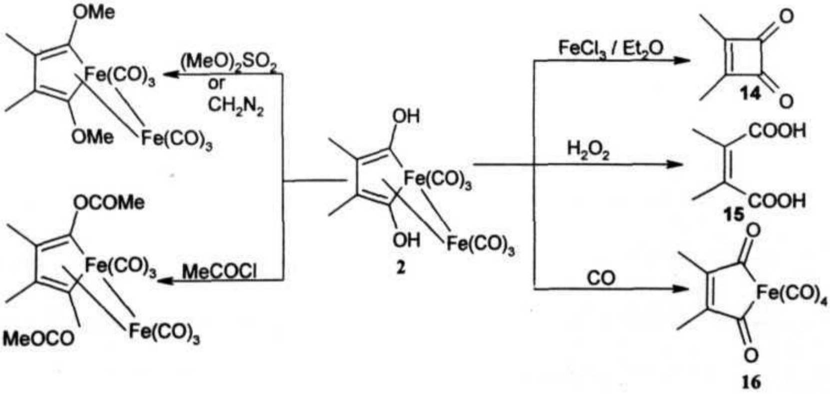


13 —(8)

2.1.2 Synthetic applications of ferrole iron complexes

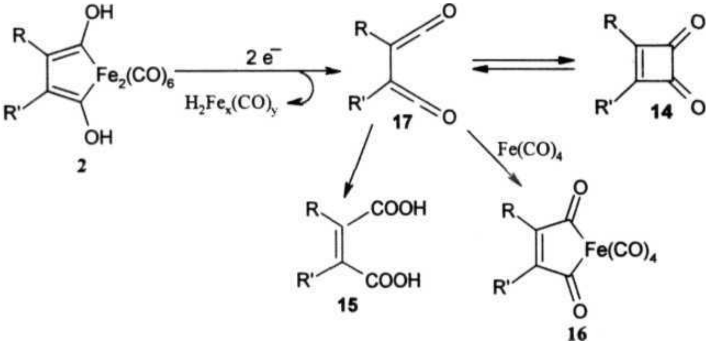
The hydroxy ferrole iron complex 2 undergoes interesting organic transformations under different conditions. A variety of synthetically useful organic compounds such as cyclobutenediones 14, maleic acids 15 and maleoyl iron complexes 16 were obtained from the complex 2 (Scheme 1).[17]

Scheme 1

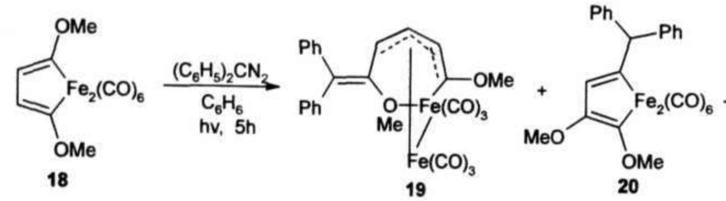


The formation of these products has been rationalized as outlined in Scheme 2. The cyclobutenedione 14 may have formed via a bisketene 17. The maleic acid 15 could have also formed via the bisketene 17 in alkaline solution. The **maleoyl** iron complexes 16 would result from **complexation** of 17 with $Fe(CO)_4$ (Scheme 2).[18]

Scheme 2

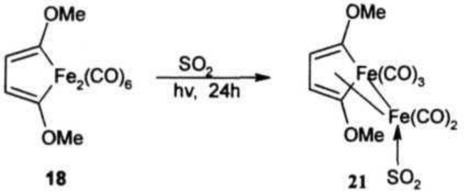


Photochemical reaction of the hydroxy ferrole iron derivative 18 with diphenyl diazomethane involves insertion of diphenylcarbene into a carbon-iron bond without destruction of complex 18. The structures of the products 19 and 20 were assigned after X-ray crystallographic data analysis (eq. 9) [19,20]



—(9)

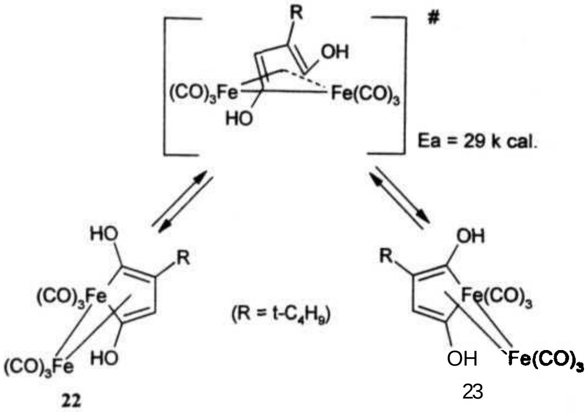
After U.V irradiation of 18 in boiling SO_2 for one day, an orange-red complex 21 was formed in 55% yield (eq. 10). Interestingly, in complex 21, one of the CO moieties of the starting complex is replaced by SO_2.[21]



—(10)

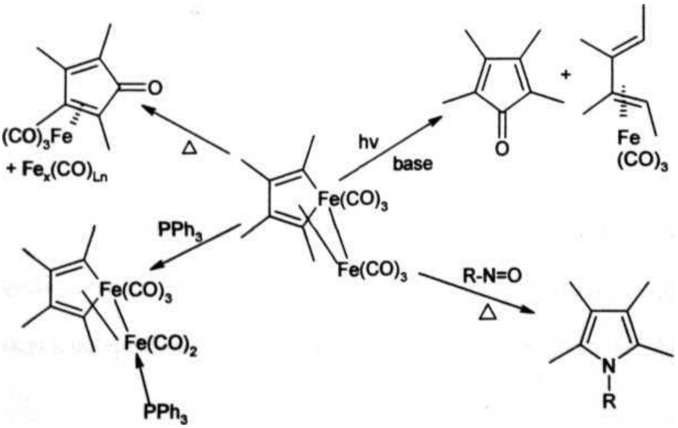
The enantiomeric hydroxy ferrole iron pairs 22 and 23 were separated using chiral camphorsulphonyl chloride (Scheme 3).[22] Alkaline hydrolysis of the camphorsulphonate gave the enantiomers 22 and 23. The enantiomers 22 and 23 racemize at elevated temperatures by an intramolecular interchange of the two $Fe(CO)_3$ groups[22] through an activation energy barrier of 29 k.cal.[22]

Scheme 3



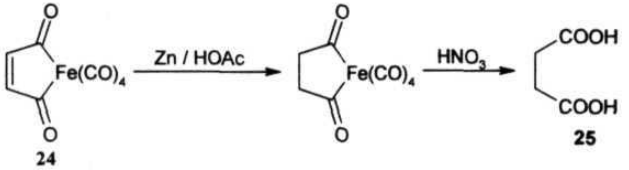
A few more applications of the ferrole iron carbonyl derivatives are summarized in Scheme 4.[17]

Scheme 4



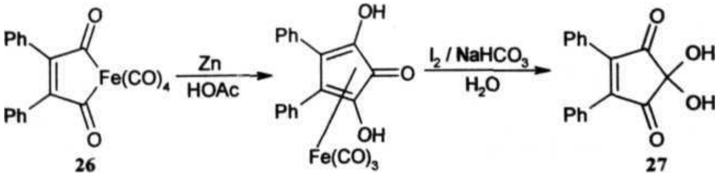
2.1.3 Synthetic applications of maleoyl iron complexes

The reduction of maleoyl iron complexes 24, prepared directly from alkyne and $Fe_3(CO)_{12}$ in hydrocarbon solvents,[23b] with Zn/HOAc followed by HNO_3 treatment gives the corresponding succinic acid derivatives 25 (eq. 11).[23a]



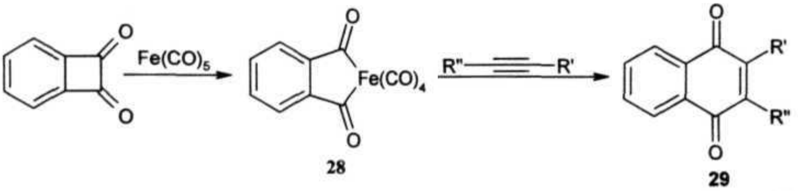
—(11)

However, the phenylsubstituted maleoyl iron complex 26 upon Zn/HOAc reduction and $I_2/NaHCO_3$ treatment affords the corresponding hydrated trione 27 (eq. 12).[24]



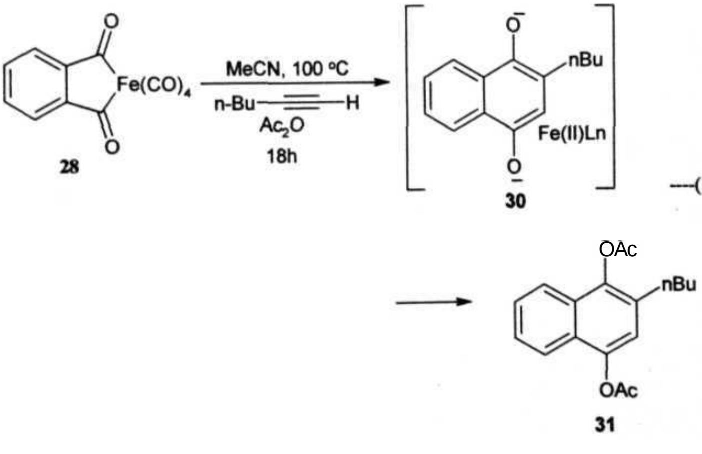
-(12)

Cyclobutenediones are useful starting materials for the preparation of polycyclic aromatic compounds through ring expansion reactions.[1] For example, benzocyclobutenediones on reaction with Fe(C0)5 readily gives the phthalyl iron derivative 28 that on further reaction with alkynes affords the corresponding naphthoquinones 29 (eq. 13).[25]



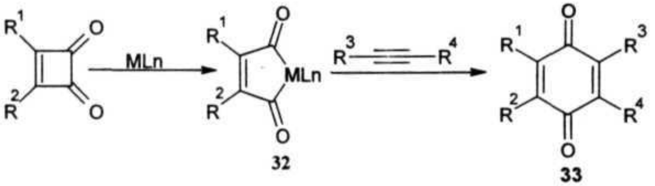
------(13)

In the above reaction, the black, insoluble complex 30 is the precursor to the naphthoquinone product 29. This presumption was confirmed by obtaining the corresponding hydroquinone diacetate 31, when acetic anhydride was added to the above reaction mixture (eq. 14).[26]



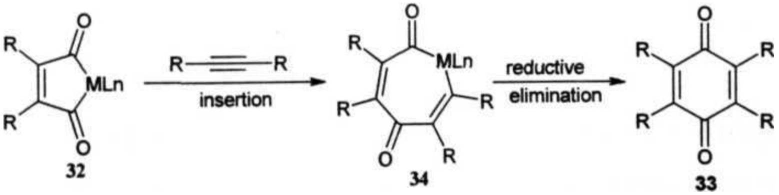
----(14)

Also, simple maleoyl iron complexes 32, prepared from their respective cyclobutenediones and metal carbonyls, followed by subsequent reaction with an **alkyne** gives the corresponding benzoquinones 33 (eq. 15).[27]



—(15)

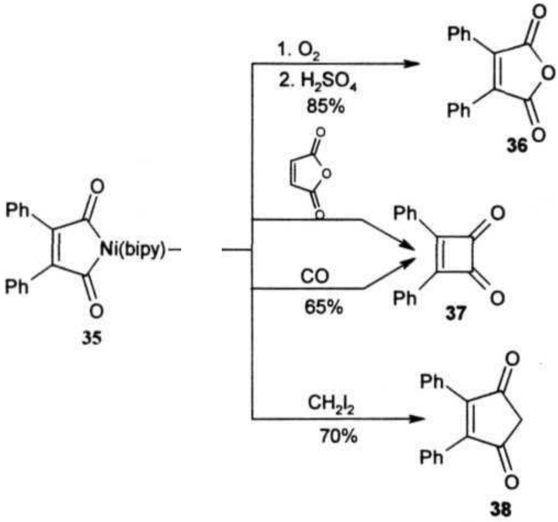
Here, the intermediate of the type 34 has been postulated to account for the quinone formation. The reaction occurs by insertion of an alkyne to the maleoyl iron complex 32, giving metallacycle 34 which then undergoes reductive elimination to give the corresponding benzoquinone 33 (eq. 16).[27]



—(16)

It may be of interest to note here that the maleoyl nickel complex 35 also undergoes interesting transformations under different conditions to give useful organic compounds (Scheme **5**).[28,29]

Scheme 5



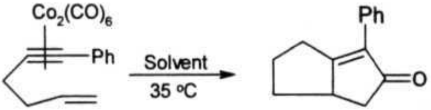
As we have a simple method of preparation of maleoyl iron complexes *in situ* using alkynes and iron **carbonyls** as described in Chapter 1, we have examined the synthetic applications of these complexes. The results are described in this chapter.

2. 2 Results and Discussion

2. 2. 1 Reaction of alkyne-iron carbonyl complexes prepared using 1-alkynes, $Fe(CO)_5$, $NaBH_4$ and CH_3COOH with 1-alkynes in the presence of amines

Recently, Yamaguchi *et al* observed that certain primary amines facilitate the Pauson-Khand reaction of alkyne-$Co_2(CO)_6$ complexes under ambient conditions (Scheme 6).[30]

Scheme 6

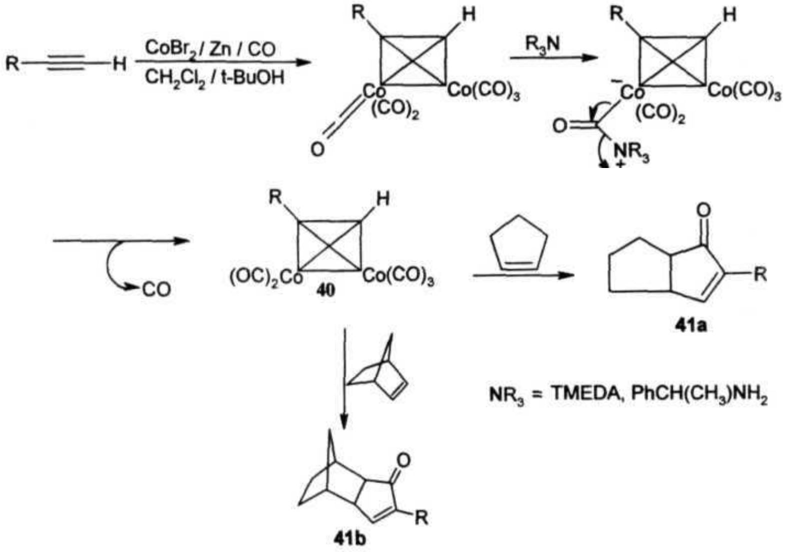


39

Solvent	Yield
Et_3N	1%
$n\text{-}BuNH_2$	54%

Also, it was found in this laboratory that certain amines facilitate the reaction of $Co_2(CO)_6$-alkyne complexes, prepared *in situ* using the cobalt carbonyl species generated by the reagent system $CoBr_2/Zn/CO$, with olefins to give the corresponding cyclopentenones 41 under ambient conditions.[41] The transformation may be visualized by the mechanistic pathway shown in Scheme 7. The amine may induce the removal of one of the CO from the alkyne-cobalt complex to give the coordinatively unsaturated complex 40, which on further reaction with **olefin** gives the corresponding cyclopentenone 41a and 41b (Scheme 7).[31]

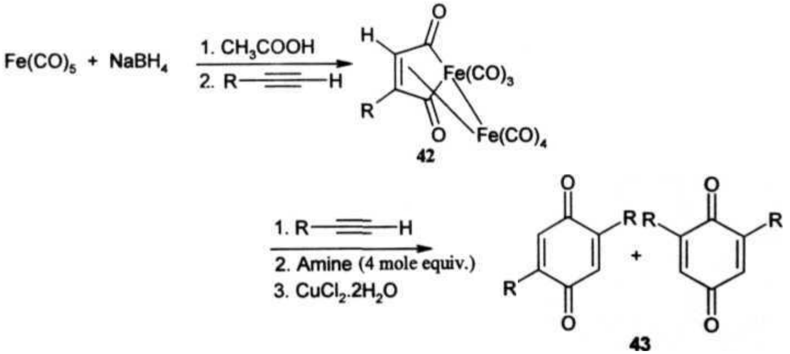
Scheme 7



This interesting effect of amines on alkyne-cobalt complexes prompted us to examine the effect of various amines on the **alkyne-iron** complex 42, that has been proposed as the intermediate in the conversion of alkynes to cyclobutenediones described in Chapter 1.

We have examined the effect of amines on the reaction of the alkyne-iron complexes 42 formed *in situ* in the reaction of **1-alkynes, $Fe(CO)_5$, $NaBH_4$** and **CH_3COOH** with an **alkyne** or olefin. Whereas the olefins such as norbornene and cyclopentene are not reactive towards the alkyne-iron complex 42, prepared *in situ* in THF, the 1 -alkynes react in the presence of amines (4 mole equiv.), to give the corresponding disubstituted benzoquinones 43 in moderate to good yields (45-61%) after **$CuCl_2.2H_2O$** oxidation (Scheme 8). Traces of the corresponding cyclobutene-diones (2-5%) and cyclic imides (5-10%, see later in Section 2. 2. 3) were also obtained.

Scheme 8



The results are summarized in Table 1. It was also observed that the amine is necessary for this transformation. Only the corresponding cyclobutenediones were isolated without using amine.[32] Amines such as ***n*-butyl-**

amine, pyrrolidine, piperidine and benzylamine are used for this transformation. Also, it was found that in the presence of *n*-butylamine the conversion is better (Table 1).

The above transformation can be rationalized by the mechanism shown in Scheme 9. The amine may remove one of the iron carbonyl moiety from the alkyne-iron complex 42 to give iron complex intermediate of type 44. Further reaction of 44 with another equiv. of 1-alkyne could give the intermediate 45. Oxidation of 45 may then produce the benzoquinones 43. It is interesting here to note that the intermediate complexes of the type 45 have been reported in the reaction between alkynes and iron carbonyl reagents under certain conditions.[33]

Scheme 9

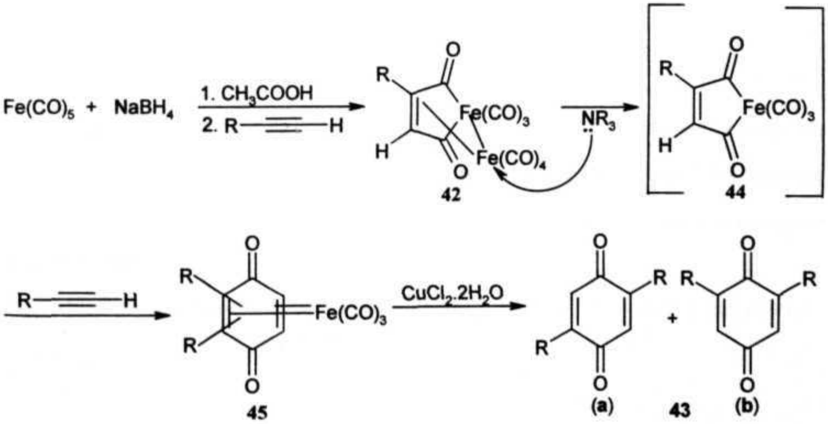
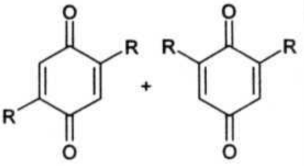


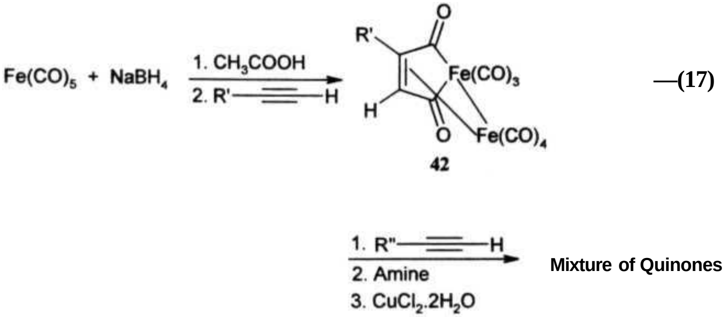
Table 1: Reaction of alkyne-iron complexes prepared using **1-alkynes, $Fe(CO)_5$, $NaBH_4$** and **CH_3COOH** with **1-alkynes** in the presence of amines

S.No	Alkyne	Product[a]		Yield[b] (%)
	R—≡—H	(a)	(b)	
1.	$R = C_5H_{11}$	**46a** (60%)	**46b** (40%)	60
2.	$R = C_6H_5$	**47a** (52%)	**47b** (48%)	45
3.	$R = C_6H_{13}$	**48a** (65%)	**48b** (35%)	61
4.	$R = C_8H_{17}$	**49a** (71%)	**49b** (39%)	51

a) Products were identified from the spectral data IR, ^{13}C NMR, and ^{1}H NMR. For the compounds 47a, 47b and 48a, 48b the spectral data show 1:1 correspondence with the reported data.[34] The percentage compositions of isomers (a) and (b) were calculated from the ^{1}H NMR signal intensities and compared with the reported data.[34]

b) Yields are of products isolated by column chromatography and based on the amount of alkynes used.

Attempts were also made to prepare mixed benzoquinones through sequential addition of two different 1-alkynes. Unfortunately, only a complex mixture of the corresponding benzoquinones were isolated in these experiments (eq. **17).**



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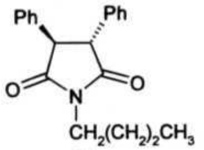
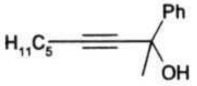
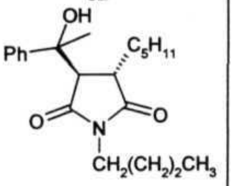
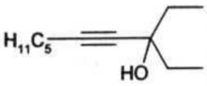
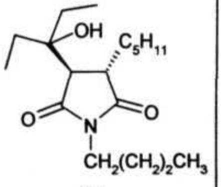
2.2.2 Reaction of alkyne-iron carbonyl complexes prepared using disubstituted alkynes, $Fe(CO)_5$, $NaBH_4$ and CH_3COOH with disubstituted alkynes in the presence of amines

The alkyne-iron complexes, prepared using diphenylacetylene and propargyl alcohol derivatives, react with *n*-butylamine and one more equiv. of alkynes to give the corresponding cyclic imide derivatives 50 besides traces of cyclobutenediones (2-5%) after $CuCl_2.2H_2O$ oxidation (Scheme 10). The results are summarized in Table 2. The corresponding benzoquinones were not formed

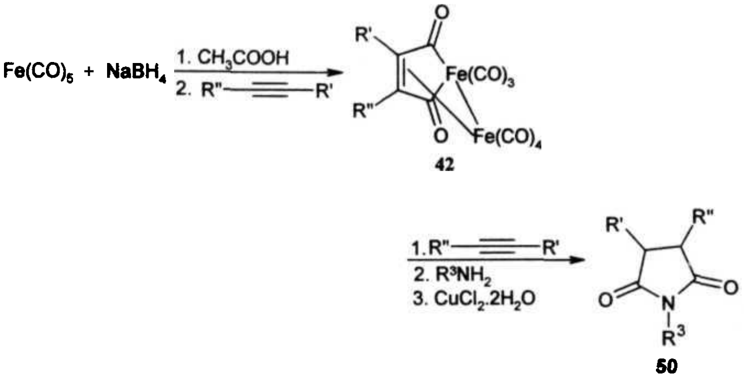
Table 2. Reaction of alkyne-iron complexes prepared using disubstituted alkynes, $Fe(CO)_5$, $NaBH_4$ and CH_3COOH with disubstituted alkynes in the presence of amines

S.No	Alkyne	Product[a]	Yield[b]
1.	Ph—≡—Ph	 **52**	[c] 25%
2.		 **53**	[c] 36%
3.		 **54**	[c] 28%
4.	Ph—≡—$SiMe_3$	Ph—≡—≡—Ph **55**	[d] 46%

a) Products were identified from the spectral data IR, ^{13}C NMR, ^{1}H NMR, Mass and elemental analysis. The spectral data are comparable with the reported data for similar derivatives.[3*] b) Yields are of products isolated by column chromatography and based on the amount of alkynes used. c) Stereochemistry of products 52-54 assigned on the basis of ^{1}H NMR data. These data are comparable with the data reported for similar derivatives." d) M.P. 87 °C, (lit.[38] M.P. 87-88 °C).

in these cases. Presumably, the disubstituted alkynes may pose steric difficulties for further reaction with another alkyne.

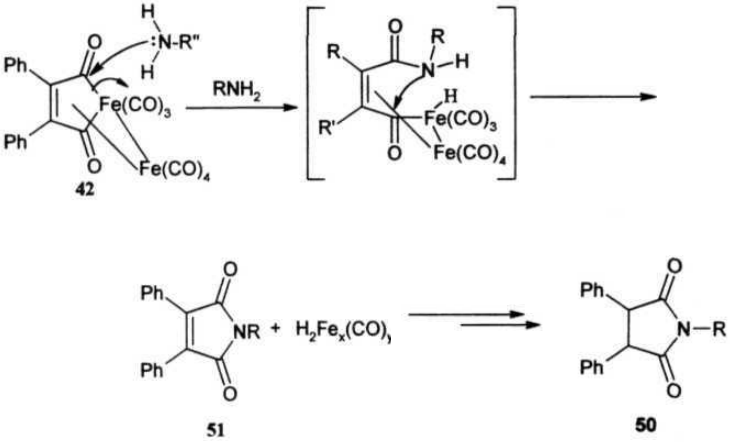
Scheme 10



The formation of cyclic imides 50 can be explained by the mechanism shown in Scheme 11. The reaction of alkyne-iron complexes of diphenylacetylene and propargyl alcohol derivatives, with *n*-butylamine may take a different course to give the intermediate complex of the type 51, along with hydrido iron carbonyl species. These hydrido species may reduce the double bond of 51 to give the cyclic imide 50.[35]

The results are summarized in Table 2. We have also observed that the use of other amines such as pyrrolidine and triethylamine gave only the corresponding cyclobutenediones after $CuCl_2.2H_2O$ oxidation. It appears that the primary amines and the hydrido iron carbonyl species are necessary for the formation of cyclic **imides** (Scheme **11)**.

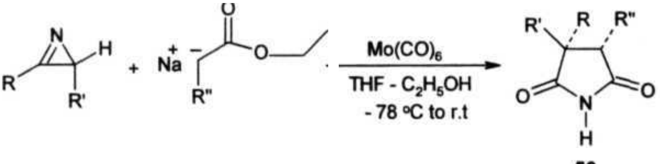
Scheme 11



Here, it is of interest to note that the hydrido iron carbonyl species "$H_2Fe(CO)_4$" is unstable and highly reactive. It was proposed in Reppe's hydroformylation reactions that the $H_2Fe(CO)_4$ species hydrometallate double **bonds.**[35a] Also, it is well-known that the hydrido iron carbonyls are useful in conjugate reduction of a,p-unsaturated carbonyl **compounds.**[35t]

The cyclic imides obtained in this transformation (Scheme 11) were identified from the spectral data **(IR,** ^{13}C NMR, ^{1}H NMR, and Mass) and elemental analysis. These data are comparable with the data reported for similar compounds.[36] Stereochemistry of products 52-54 were assigned on the basis of ^{1}H NMR data. The methine protons of 52 give doublet signals in the ^{1}H NMR spectrum at 6 4.0 (J = 10 Hz). Also, the methine protons of 53 and 54 give quartet signals at 6 2.44 (J = 5.8 Hz) and 2.43 (J - 5.7 Hz) and doublet signals at 6 2.7 (J - 3.8 Hz) and 2.78 (J = 3.8 Hz) respectively in the ^{1}H NMR spectrum. These data are comparable with the data reported for similar derivatives.[37]

Recently, **Alper** *et al* reported that the reaction of sodium diethyl malonate with molybdenum hexacarbonyl at 25 °C followed by opening of the 2-phenylazirine in THF at -78 °C, gives the corresponding cyclic **imide** 56 (eq. **18**).[37c]



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56

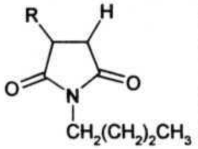
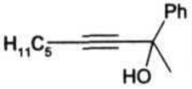
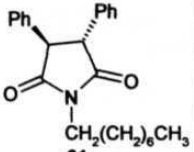
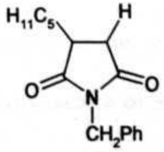
Accordingly, the present method is useful as an alternative method for such applications.

2. 2. 3 Reaction of alkyne-iron carbonyl complexes obtained using mono- and disubstituted alkynes in the presence of excess amine

To our knowledge, direct conversion of alkynes to the corresponding cyclic imides has not been reported using iron carbonyl reagents. Hence, conversion of different alkynes to the corresponding cyclic imides under mild conditions would be synthetically useful. Accordingly, we have further investigated the above transformation to prepare cyclic imides from various mono- and disubstituted alkynes using different primary amines.

It was observed that the addition of excess amines (10 mole equiv.) at 25 °C in THF, to the alkyne-iron complexes 42, prepared using alkynes, $Fe(CO)_5$, $NaBH_4$ and CH_3COOH, leads to the corresponding cyclic imide derivatives 50 in moderate to good yields (55-64%) along with traces of cyclobutenediones (2-5%) (Scheme **12**).[40a] This transformation was found to be general and various mono- and disubstituted alkynes were converted to the corresponding cyclic imide derivatives 50 using different amines. The results are summarized in Table 3. The formation of cyclic imides 50 can be also tentatively explained by the mechanism shown in Scheme **11**.[40a]

Table 3: Reaction of iron carbonyl complexes obtained using mono- and disubstituted alkynes, $Fe(CO)_5$, $NaBH_4$ and CH_3COOH in the presence of excess amine

S.No	Alkyne	Amine	Product[a]	Yield[b]
	$R-\equiv-H$	$CH_3(CH_2)_3NH_2$		
1.	$R = C_6H_5$	$CH_3(CH_2)_3NH_2$	**57**	55%
2.	$R = C_6H_{13}$	$CH_3(CH_2)_3NH_2$	**58**	62%
3.	$R = C_5H_{11}$	$CH_3(CH_2)_3NH_2$	**59**	57%
4.	$R = C_8H_{17}$	$CH_3(CH_2)_3NH_2$	**60**	59%
5.	$Ph-\equiv-Ph$	$CH_3(CH_2)_3NH_2$	**52**	55%[c]
6.		$CH_3(CH_2)_3NH_2$	**53**	64%[c]
7.		$CH_3(CH_2)_3NH_2$	**54**	61%[c]
8.	$Ph-\equiv-Ph$	$CH_3(CH_2)_7NH_2$	 **61**	53%[c]
9.	$H_{11}C_5-\equiv-H$	$PhCH_2NH_2$	 **62**	51%

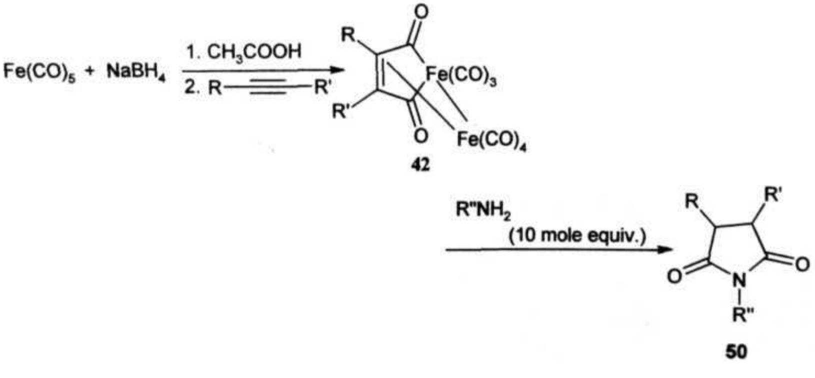
Footnote to Table 3

a) Products were identified from the spectral data **IR, ^{13}C NMR,** 'H **NMR,** Mass and elemental anlaysis. The spectral data are comparable to the data reported for similar derivatives.[36]

b) Yields are of products isolated by column chromatography and based on the alkynes used.

c) Stereochemistry assigned on the basis of 'H NMR data. These data are comparable with the data reported for similar derivatives.[37] The spectral data of 61 are comparable with the data for the compound 53. Also, the data of 62 are comparable with the data of 59.

Scheme 12

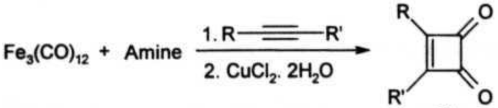


Also, addition of another equivalent of alkyne in the above reaction (Scheme 12) did not make any change in the reactivity pattern of the alkyne-iron complexes. Further, it was observed that the use of amines such as pyrrolidine, piperidine and triethylamine gave only a mixture of the corresponding benzoquinones and cyclobutenediones.

The cyclic imides are useful for the synthesis of pyrrolidine derivatives[41] that are important in medicinal chemistry.[42] For example, derivatives of such imides have proven applications in the treatment of arthritis,[43] tuberculosis,[44] convulsion and epilepsy.[4] Accordingly, the simple one-pot method of conversion of alkynes to cyclic imides described here would serve as a simple alternative method for the synthesis of these derivatives.

2. 2. 4 Reaction of iron carbonyl complexes prepared using $Fe_3(CO)_{12}$, alkyne with excess amine

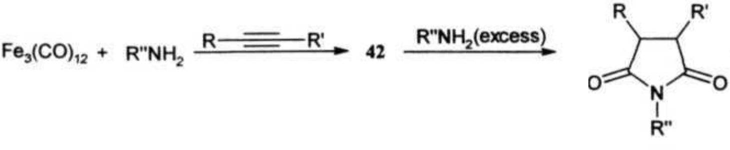
In the Chapter 1, we described that the iron carbonyl species prepared using the $Fe_3(CO)_{12}$ and amines, react with alkyne in THF at 25 °C, to give the corresponding cyclobutenedione **63**.[40b] We have explained the results through the formation of alkyne-iron complex intermediate 42 (eq. 19).



63

—(19)

Hence, we have also examined the effect of excess amines on the iron carbonyl complexes 42 prepared using the **$Fe_3(CO)_{12}$**, alkynes and **amines.**[40b] It was observed that addition of excess amines (10 mole equiv.) to the intermediate **alkyne-iron** complex 42 prepared using the **$Fe_3(CO)_{12}$** (6 mmol), **amine** (2.75 mmol) and alkynes (1.25 mmol) in THF, gives the corresponding cyclic **imides** 50 (45-65%) along with traces of cyclobutenediones (5-10%) after **$CuCl_2.2H_2O$** oxidation (eq. 20). Also, it was found that this conversion is general and several alkynes are converted to the corresponding cyclic imides 50. The results are summarized in Table 4.



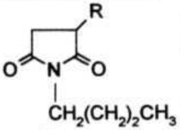
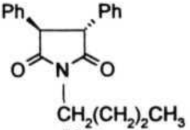
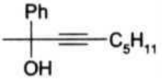
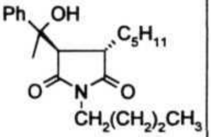
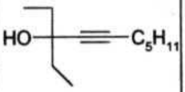
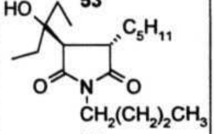
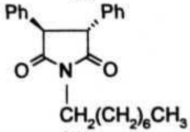
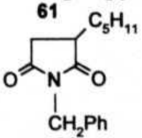
50

··—(20)

Under these conditions, use of tertiary amines and pyridine leads to the corresponding benzoquinones and cyclobutenediones. Also, in the case of trimethylsilyl substituted alkynes only the corresponding **cyclobutenediones,**[40b] and **1,3-diynes** are obtained and the corresponding cyclic imides were not formed.

The formation of cyclic imides 50 can be rationalized through the steps outlined in Scheme 13 (see also Scheme 11).

Table 4: Reaction of iron carbonyl complexes prepared using $Fe_3(CO)_{12}$, **alkyne** with excess amine

S.No	Alkyne	Amine	Product^a	Yield (%)^b
	$R-\equiv-H$	$CH_3(CH_2)_3NH_2$		
1.	R = Ph	$CH_3(CH_2)_3NH_2$	**57**	45
2.	R = C_6H_{13}	$CH_3(CH_2)_3NH_2$	**58**	61
3.	R = C_5H_{11}	$CH_3(CH_2)_3NH_2$	**59**	65
4.	$Ph-\equiv-Ph$	$CH_3(CH_2)_3NH_2$	 **52**	51^c
5.		$CH_3(CH_2)_3NH_2$	 **53**	58^c
6.		$CH_3(CH_2)_3NH_2$	 **54**	49^c
7.	$Ph-\equiv-Ph$	$CH_3(CH_2)_7NH_2$	 **61**	46^c
8.	$H_{11}C_5-\equiv-H$	$PhCH_2NH_2$	 **62**	55

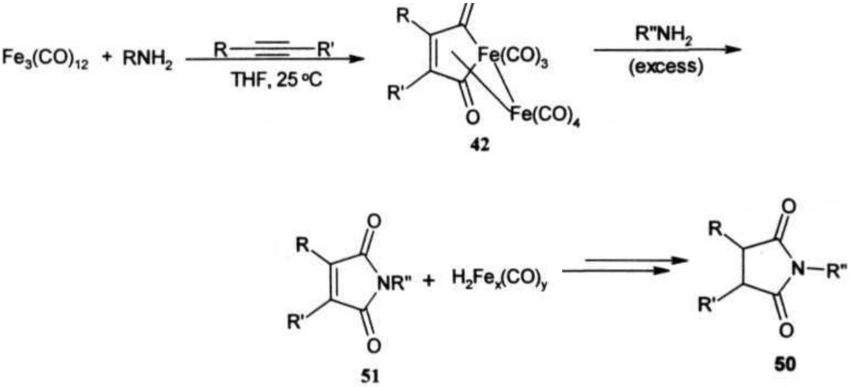
Footnote to table 4

a) Products were identified from the spectral data (IR, ^{13}C NMR, ^{1}H NMR and Mass) and elemental analysis. The spectral data are comparable with the reported data of similar derivatives.[36]

b) Yields are of products isolated by column chromatography and based on the amount of alkynes used.

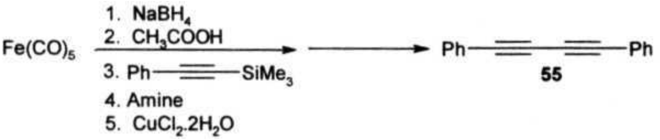
c) Stereochemistry assigned on the basis of ^{1}H NMR data. These data are comparable with the data reported for similar derivatives.[37]

Scheme 13



2. 2. 5 Reaction of iron carbonyl complexes with $PhC{\equiv}CSiMe_3$ and primary amines

It was observed that the alkyne-iron complex, prepared using 1-phenylyne-(trimethyl)-silane, on reaction with *n*-butylamine in THF at 25 °C, gives the corresponding 1,3-diyne 55 in 46% yield (Table 2) after $CuCl_2.2H_2O$ oxidation (eq. 21).[38]



—(21)

Presumably, the $PhC{\equiv}CH$ could have first formed in the reaction of $PhC{\equiv}CSiMe_3$ under these conditions that may have reacted with $CuCl_2$ to give the 55. It is of interest to note that the 1-alkynes give the corresponding symmetrical 1,3-diynes in the presence of certain Cu(II) complexes.[39]

2. 3 Conclusions

The **alkyne-iron** complexes prepared using the **$Fe(CO)_5$, $NaBH_4$, CH_3COOH** and **1-alkyne** reagent system in THF give the corresponding benzoquinones after reaction with another equiv. of 1-alkyne in the presence of amines.

These complexes are also **successfully** converted to the corresponding cyclic **imides** in moderate to good yields. Such cyclic **imides** are very useful starting materials for the synthesis of the corresponding pyrrolidine derivatives. Accordingly, it is anticipated that the one-pot methods of conversion of alkynes to the corresponding cyclic imides described here would stimulate further work in this area.

2. 4 Experimental Section

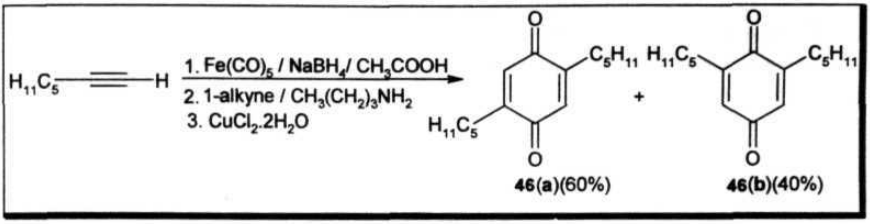
2. 4. 1 General information:

Most of the informations given in the experimental section of Chapter 1 are also applicable for the experiments outlined here. The commercially available amines were distilled before use. Alkynes (except 1-heptyne) were prepared following reported procedures.[46]

2. 4. 2 Reaction of iron carbonyl complexes prepared using 1-alkynes, $Fe(CO)_5$, $NaBH_4$ and CH_3COOH with 1-alkynes and *n*-butylamine (4 mole equiv.)

The $Fe(CO)_5$ (2.9 g, 15 mmol) in THF (15 mL) was added drop wise for 1h to $NaBH_4$ (0.567 g, 15 mmol) in THF (50 mL), and stirred for 8 h at 25 °C under nitrogen atmosphere. Acetic acid (2.7 g, 45 mmol) was added and stirred for 30 min. Subsequently, 1-heptyne (0.24 g, 2.5 mmol) was added and the contents were further stirred for 4 h. Then, additional amount of 1-heptyne (0.24 g, 2.5 mmol) and *n*-butylamine (0.73g, 10 mmol) were added and the contents were further stirred for 12h at 25 °C. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (6.8 g, 40 mmol) in acetone (25 mL). Saturated aq.NaCl (20 mL) was added and the contents were extracted with ether (100 mL). The combined organic extract was washed with brine (15 mL), dried over anhydrous

$MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane). Hexane eluted the mixture of benzoquinones **46a** and **46b.**[34]



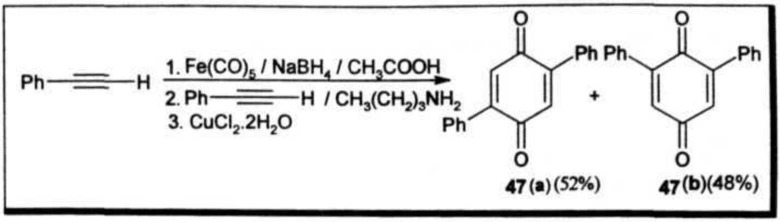
Yield : 60% **(0.188** g)

IR(neat) :1657 **cm^{-1}**

^{1}H NMR **(CDCl$_3$)** : δ **ppm** 0.89 (t, **J** = 6.8 Hz, **12** H), **1.16-2.46 (m,** 32 H for 46a and 46b), **6.50** (s, 2H for **46a), 6.52** (s, 2H for **46b)** (Spectrum No. 10)

^{13}C NMR (CDCl$_3$) : δ ppm 13.6, 22.2, 27.4, 28.5, 29.0, 31.3, 131.9, 132.4, 149.2, 149.6, 187.4, 187.7 **(Spectrum** No. 11).

The above procedure was followed for the conversion of other 1-alkynes to the corresponding benzoquinones. The spectral data are comparable with the data reported for similar derivatives.[34] The percentage **compositions** of the benzoquinone **isomers** (a) and (b) were calculated from the H NMR signal intensities.[34]

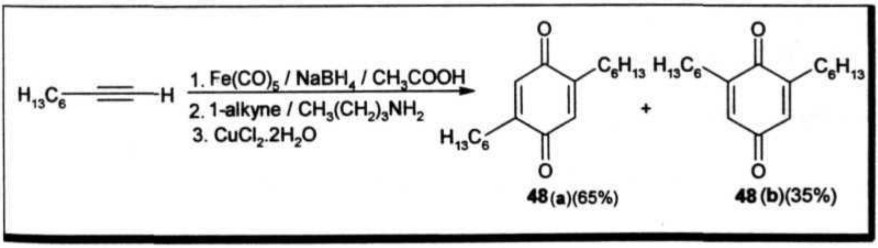


Yield : 45% **(0.123** g)

IR(KBr) : 1649 **cm^{-1}**

^{1}H NMR **(CDCl$_3$)** : 8 ppm 6.84 (s, 2H for **47a),** 6.88 (s, 2H for **47b),** 7.45 **(m,** 20 H for **47a** and **47b)**

^{13}C NMR **(CDCl$_3$)** : δ ppm 128.4, 129.4, 130.0, 132.6, 133.2, 146.5,187.5 **(Spectrum** NO. 12)

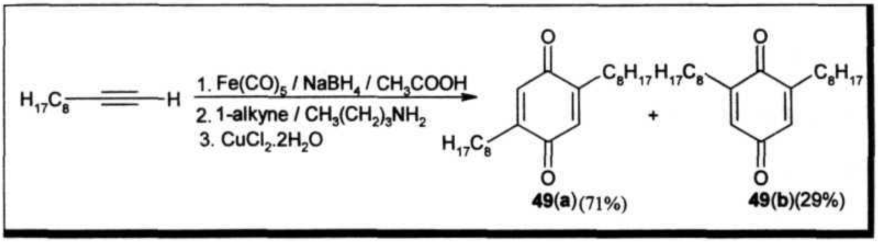


Yield : 61% **(0.210** g)

IR (neat) : 1657 **cm^{-1}**

^{1}H NMR **($CDCl_3$)** : 8 **ppm** 0.89 (t, J = 6.8 Hz, **12** H for **48a** and **48b), 1.16-2.46 (m,** 40 H for **48a** and **48b),** 6.50 (s, 2H for **48a),** 6.52 (s, 2H for **48b)**

^{13}C **NMR ($CDCl_3$)** : § ppm 13.6, 22.1, 27.3, 28.6, 29.0, 31.1, 131.9, 132.4, **149.1, 149.5, 187.3, 187.6.**



Yield : 51% **(0.213** g)

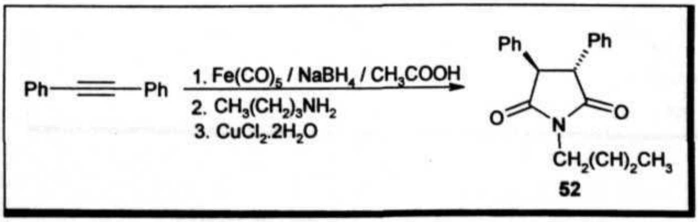
IR(neat) : **1655 cm-1**

^{1}H NMR **($CDCl_3$)** : 8 ppm 0.90 **(t, J** = 6.7 **Hz,** 12 H for **49a** and **49b),** 1.18-1.70 **(m,** 48H for **49a** and **49b),** 2.44 **(m,** 8H for **49a** and **49b),** 6.48 (s, 2H for **49a), 6.51** (s, 2H for **49b).**

^{13}C NMR **($CDCl_3$)** : 8 ppm 13.9, 22.5, 27.8, 28.6, 29.0, 29.2, 29.7, 31.7, 131.6, 132.4, **149.1, 149.5, 187.3,** 187.8 **(Spectrum No. 13)**

2. 4. 3 Reaction of iron carbonyl complexes prepared using disubstituted alkynes, $Fe(CO)_5$, $NaBH_4$, and CH_3COOH with disubstituted alkynes and *n*-butylamine (4 mole equiv.)

The $Fe(CO)_5$ (2.9 g, 15 mmol) in THF (15 mL) was added drop wise for 1h to $NaBH_4$ (0.567 g, 15 mmol) in THF (50 mL), and stirred for 8 h at 25 °C under nitrogen atmosphere. Acetic acid (2.7 g, 45 mmol) was added and stirred for 30 min. Subsequently, diphenylacetylene (0.455 g, 2.5 mmol) was added and the contents were further stirred for 4 h. Additional amount of diphenylacetylene (0.455g, 2.5 mmol) and *n*-butylamine (0.73g, 10 mmol) were added and the contents were further stirred for 12 h at 25 °C. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (6.8 g, 40 mmol) in acetone (25 mL). Saturated aq.NaCl (20 mL) was added and the contents were extracted with ether (100 mL). The combined organic extract was washed with brine (15 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Ethyl acetate/hexane (2:98) eluted the cyclic imide 52.



Yield : 25% (0.190 g)

IR(neat) : 1778, 1705 cm$^{''1}$

^{1}H NMR ($CDCl_3$) : 8 ppm 1.1-1.8 (m, *TH)*, 3.6 (t, J = 7.3 Hz, 2H), 4.1 (d, J =10 Hz, 2H), 7.15-7.6 (m, 1 OH)

^{13}C NMR ($CDCl_3$) : δ (ppm): 13.7, 20.2, 29.9, 39.1, 55.3, 127.8, 128.2, 128.5, 129.1, 136.9, 176.5

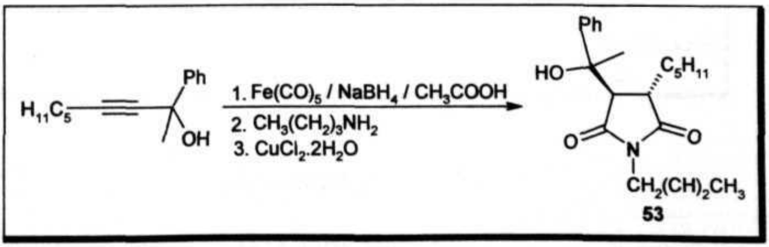
MS (EI) : m/z 307 (M^+, 26%), 265 [(M^+-C_3H_7+1), 10%]

Elemental analysis for $C_{20}H_{21}O_2N$

Calcd. : C, 78.12; H, 6.84; N, 4.56

Found : C, 78.25; H, 6.90; N, 4.52.

The spectral data are comparable to the spectral data reported for similar derivatives.[36] The above method was also followed for the conversion of other disubstituted alkyne derivatives to the corresponding cyclic imides.



Yield : 36% (0.302 g)

IR(neat) : 1766, 1689 cm-1

^{1}H NMR ($CDCl_3$) : 6 ppm 0.75-1.53 (m, 18H), 1.62 (s, 3H), 2.44 (q, J = 5.8 Hz, 1H), 2.7 (d, J = 3.8 Hz, 1H), 3.4 (t, J = 7.2 Hz, 2H), 7.2-7.4 (m, 5H) (Spectrum No. 14)

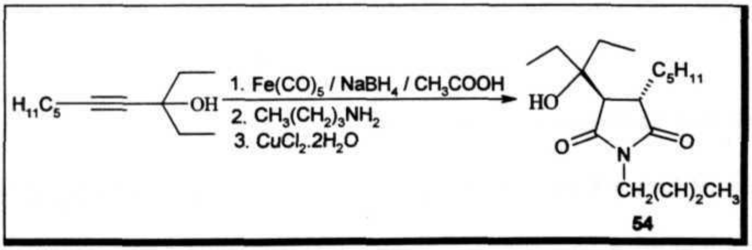
^{13}C NMR ($CDCl_3$) : 5 ppm 13.4, 13.7, 19.9, 22.1, 24.6, 25.1, 29.5, 31.2, 31.3, 38.3, 42.7, 57.0, 74.8, 125.6, 127.7, 128.2, 143.6, 178.5, 179.1 (Spectrum No. 15)

MS(EI) : m/z 347 (M^+, 2%), 329 [(M^+-H_2O), 10%] (Spectrum No. 16)

Elemental analysis for $C_{21}H_{31}O_2N$

Calcd. : C, 73.04; H, 8.98; N, 4.05

Found : C, 73.10; H, 9.15; N, 4.11.



54

Yield : 28% (0.215 g)

IR (neat) : 3487, 1766, 1693 cm^{-1}

^{1}H NMR (CDCl$_3$) : 8 ppm 0.8-1.0 (m, 14H), 1.2-1.8 (m, 14H), 2.43 (q, J = 5.7 Hz, 1H), 2.78 (d, J = 3.8Hz, 1H), 3.45 (t, J = 7.1 Hz, 2H) (Spectrum No. 17)

^{13}C NMR (CDCl$_3$) : δ ppm 7.2, 7.6, 13.3, 13.6, 19.8, 22.1, 25.1, 28.2, 28.8, 29.2, 29.4, 31.5, 38.2, 42.1, 51.6, 75.6, 178.9, 179.5 (Spectrum No. 18)

MS (EI) : m/z 293 [(M$^+$-H$_2$O), 2%], 282 [40%] (Spectrum No. 19)

Elemental analysis for $C_{18}H_{33}O_3N$

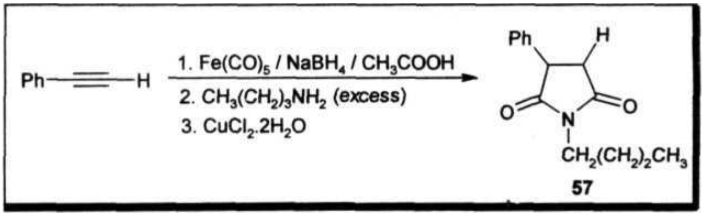
Calcd. : C, 69.45; H, 10.61; N, 4.50

Found : C, 69.51; H, 10.60; N, 5.00.

2. 4. 4 Reaction of iron carbonyl complexes prepared using alkynes, $Fe(CO)_5$, $NaBH_4$ and CH_3COOH with *n*-butylamine (10 mole equiv.)

The $Fe(CO)_5$ (2.9 g, 15 mmol) in THF (15 mL) was added drop wise for 1h to $NaBH_4$ (0.567 g, 15 mmol) in THF (50 mL), and stirred for 8 h at 25 °C under nitrogen atmosphere. Acetic acid (2.7 g, 45 mmol) was added and stirred for 30 min. Subsequently, phenylacetylene (0.255 g, 2.5 mmol) was added and stirred for 4h. *n*-Butylamine (1.8 g, 25 mmol) was added and the contents were further stirred for 12 h at 25 °C. The metal carbonyl complex was decomposed using

$CuCl_2.2H_2O$ (6.8 g, 40 **mmol)** in acetone (25 mL). Saturated **aq.NaCl** (20 mL) was added and the contents were extracted with ether **(100** mL). The combined organic extract was washed with brine **(15** mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, **hexane/ethyl** acetate). Ethyl acetate (2:98) in hexane eluted the cyclic **imide** derivative 57 **(0.310** g, 55%).[36]



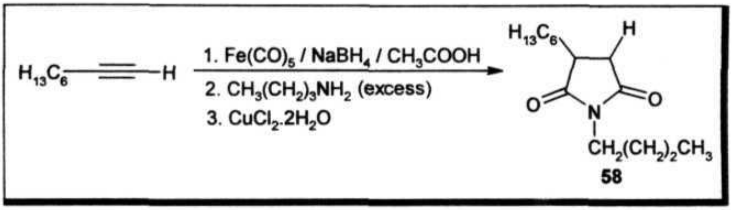
Yield : 55% **(0.310** g)

IR (neat) : 1766, **1707 cm^{-1}**

^{13}C NMR (CDCl$_3$) : 8**ppm 10.1, 18.6,21.5, 27.7,** 36.2, 38.5,128.0, 128.8, **132.4, 172.5, 175.9**

^{1}H NMR (CDCl$_3$) : 8 ppm 0.6-1.8 **(m,** 5H), 2.81 **(d,** J = 13.3 **Hz,** 1H), 2.85 **(d,** J = 13.5 Hz, 1H), 3.1 (q, 2H), 3.8 **(t,** 2H), 4.01 **(t,** 1H), 7-7.5 **(m,** 5H).

The above procedure was also followed for the conversion of other alkynes to the corresponding cyclic imide derivatives. The spectral data are comparable with the data reported for similar derivatives.[36,37]



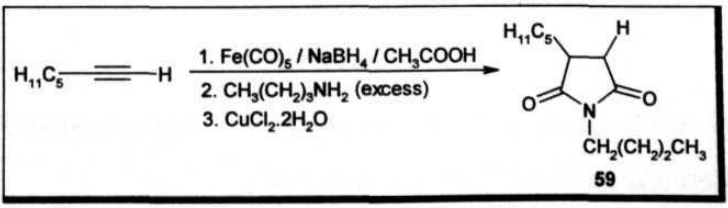
58

Yield : 62% (0.360 g)

IR(neat) : 1786, 1703 cm^{-1}

^{1}H NMR (CDCl$_3$) : 8 ppm 0.8-1.9 (m, 20H), 2.09 (m, 1H), 2.3 (d, J = 13.3 Hz, 1H), 2.7 (d, J = 13.2 Hz, 1H), 3.4 (t, J = 7.2 Hz, 2H)

^{13}C NMR (CDCl$_3$) : 8 ppm 13.3, 13.7, 19.8, 22.3, 26.4, 28.8, 29.5, 31.2, 31.3, 34.1,38.2,39.6,176.4,179.7.



59

Yield : 57% (0.310 g)

IR(neat) : 1772, 1703 cm^{-1}

^{1}H NMR ($CDCl_3$) : 6 ppm 0.6-1.87 (m, 18H), 1.92 (m, 1H), 2.1 (d, J = 13.6 Hz, 1H), 2.6 (d, J= 13.2 Hz, 1H), 3.3 (t, J = 7.3 Hz, 2H)

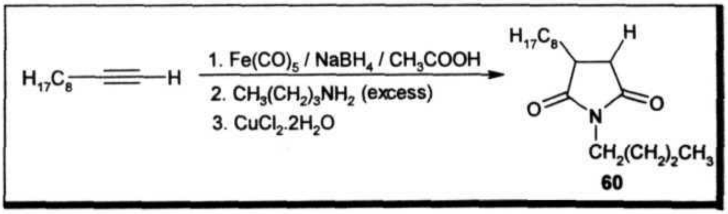
^{13}C NMR ($CDCl_3$) : 6 ppm 13.2, 13.5, 19.7, 22.1, 26.1, 29.4, 31.0, 31.2, 34.0, 38.0,39.5,176.4,179.6

MS(EI) : m/z 225 (M^+,4%), 168 [(M^+-C_4H_9), 15%]

Elemental analysis for $C_{13}H_{23}O_2N$

Calcd. : C, 69.33, H, 10.22; N, 6.22

Found : C, 69.32; H, 10.27; N, 6.21.



60

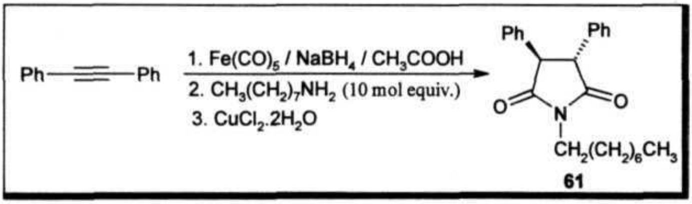
Yield : 59% (0.385 g)

IR (neat) : 1770, 1703 cm"^{1}

^{13}C NMR ($CDCl_3$) : 8 ppm 13.3, 13.8, 19.8, 22.4, 26.5, 27.8, 29.1, 29.6, 31.2, 31.6, 32.1, 34.2, 38.2, 39.7, 176.7, 179.9.

^{1}H NMR (CDCl$_3$) : 6 ppm 0.7-1.95 (m, 24H), 2.1 (m, 1H), 2.2 (d, J = 13.4 Hz, 1H), 2.7 (d, J - 13.3 Hz, 1H), 3.2 (t, J = 7.3, 2H).

The cyclic imides 52, 53 and 54 were also prepared from the corresponding alkynes following this proedure.[36,37] The results are summarized in the Table 3. The procedure was also followed for other amines. The data are given here.



61

Yield : 53% (0.473 g)

IR(neat) : 1776, 1707 cm^{-1}

^{1}H NMR (CDCl$_3$) : 8 ppm 0.9-1.8 (m, 15H), 3.7 (t, J = 7.4 Hz, 2H), 4.1 (d, J = 10 Hz, 2H), 7.1-7.4 (m, 10H)

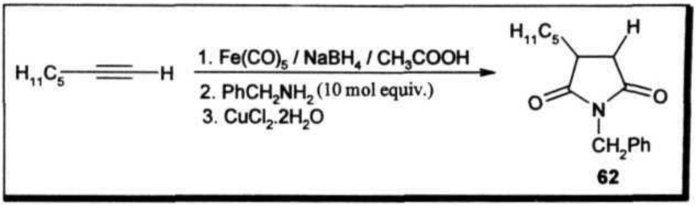
^{13}C NMR (CDClj) : δ ppm 14.1, 22.6, 26.8, 27.7, 29.1, 31.7, 39.3, 55.3, 127.7, 129.1, 136.9, 176.3

MS(EI) : m/z 363 (M$^+$, 12%), 265 [(M$^+$-CH$_2$(CH$_2$)$_5$CH$_3$+1), 10%]

Elemental analysts for $C_{24}H_{29}O_2N$

Calcd. : C, 79.34; H, 7.98; N, 3.86

Found : C, 79.52; H, 8.10; N, 3.88.



Yield : 51% (0.321 g)

IR (neat) : 1766, 1707 cm^{-1}

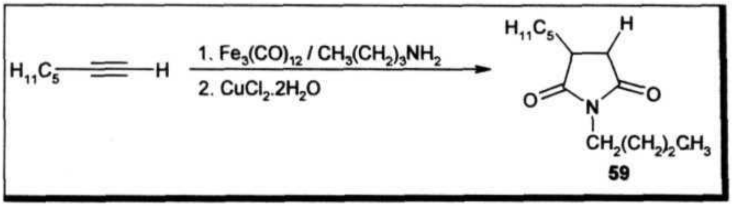
^{13}C NMR ($CDCl_3$) : 6 ppm 10.1, 18.6, 21.5, 27.5, 27.7, 30.6, 36.2, 38.5, 128.0, 128.8, 132.4, 172.5, 175.9

'H **NMR ($CDCl_3$)** : 8 ppm 0.91.92 (m, 12H), 2.4 (d, J = 13.4 Hz, 1H), 2.77 (d, J = 13.6 Hz, 1H), 4.2 (s, 2H), 7.2-7.4 (m, 5H).

2. 4. 5 Reaction of iron carbonyl complexes prepared using $Fe_3(CO)_{12}$, *n*-butylamine and alkynes with excess of *n*-butylamine

A mixture of $Fe_3(CO)_{12}$ (3.02 g, 6 mmol) and *n*-butylamine (0.201 g, 2.75 mmol) in THF (50 mL) under N_2 atmosphere was stirred for 30 min. at 25 °C. 1-Heptyne (0.120 g, 1.25 mmol) was added and the stirring was continued for 3h. *n*-

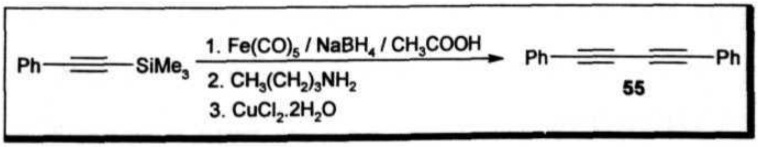
Butylamine (12.5 mmol, 0.9 g) was added and the contents were further stirred for 12h at 25 °C. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (1.7g. 10 mmol) in acetone (10 mL). Saturated aq.NaCl (25 mL) was added, and the resulting solution was extracted with ether (100 mL), washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Ethyl acetate (2:98) in hexane eluted the cyclic imide 59 (0.183 g, 65%).[36]



The spectral data are comparable with the data of the 59 obtained in experiments using $Fe(CO)_5/NaBH_4/CH_3COOH$ and alkynes.[36,37] The above procedure was followed for the conversion of other alkynes to the corresponding cyclic imides. The results are summarized in Table 4. Also, the procedure was followed using other amines. These results are also given in Table 4.

2. 4. 6 Reaction of iron carbonyl complex prepared using $PhC{\equiv}CSiMe_3$, $Fe(CO)_5$, $NaBH_4$, and CH_3COOH with $PhC{\equiv}CSiMe_3$ and *n*-butylamine (4 mole equiv.)

The $Fe(CO)_5$ (2.9 g, 15 mmol) in THF (15 mL) was added drop wise for 1h to $NaBH_4$ (0.567 g, 15 mmol) in THF (50 mL), and stirred for 8 h at 25 °C under nitrogen atmosphere. Acetic acid (2.7 g, 45 mmol) was added and stirred for 30 min. Subsequently, l-phenylyne-(trimethyl)-silane (0.435 g, 2.5 mmol) was added and the contents were further stirred for 4h. l-Phenylyne-(trimethyl)-silane (0. 435 g, 2.5 mmol) and *n*-butylamine (1.23g, 10 mmol) were added and the contents were further stirred for 12h at 25 °C. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (6.8 g, 40 mmol) in acetone (25 mL). Saturated aq.NaCl (20 mL) was added and the contents were extracted with ether (100 mL). The combined organic extract was washed with brine (15 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane). Hexane eluted the 1,3-diyne 55 (Yield: 46%, 0.220 g).[38]



Yield : 46% (0.220 g)

M.P. : 87 °C (lit.[38] 87-88 °C)

IR (KBr) : 3058 cm^{1}

^{1}H NMR **($CDCl_3$)** : **δ ppm 7.1** -7.4 9 **(m, 1** OH)

^{13}C NMR **($CDCl_3$)** **: δ** ppm 74.0, 81.0, 121.9, 128.4, **129.1, 132**.5

The spectral data show 1:1 correspondence with the data reported in the literature.[38]

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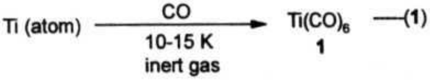
Chapter 3

Studies on the Preparation of Reactive Iron Carbonyl Species via Reduction of $FeCI_3$ Using $NaBH_4$ and CO for Synthetic Applications

3.1 Introduction

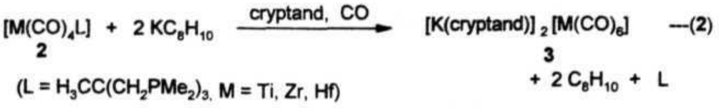
Studies undertaken towards the preparation of iron carbonyl species *in situ* via reduction of $FeCl_3$ using $NaBH_4$ in the presence of CO for synthetic applications are described in this chapter. It may be of interest to briefly review the methods reported for the preparation of metal carbonyls through reductions in the presence of carbon monoxide.

In recent years, there has been sustained interest in the preparation of unusual early transition metal carbonyls. For example, it has been reported that the matrix cocondensation reaction of Ti atoms with CO, either pure or diluted with the inert gases, at 10-15 K gives the unusual 16-electron $Ti(CO)_6$ complex 1 (eq. **1**).[1]



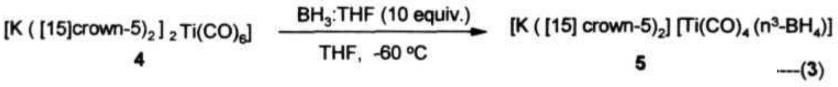
$$\text{Ti (atom)} \xrightarrow[\text{10-15 K, inert gas}]{\text{CO}} \underset{\mathbf{1}}{Ti(CO)_6} \quad \text{---(1)}$$

The synthesis of hexacarbonyltitanate, zirconate, and **hafnate,** was achieved by reductive carbonylation of $[M(CO)_4L]$ 2 with potassium naphthalenide as reducing agent in the presence of cryptands and CO (eq. 2).[1]

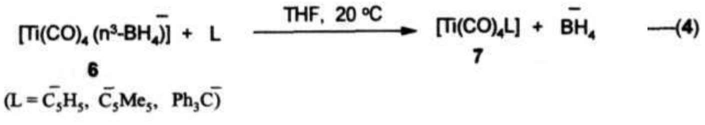


The 'exhaustively' reduced carbonylmetalates $M(CO)_4^{6-}$ (M = Ti, Zr, Hf) have not yet been prepared. However, Ellis *et al* isolated the corresponding triphenylstannyl derivatives.[1]

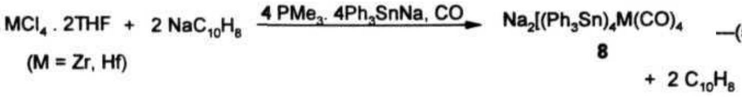
Recently, it has been reported that the reaction of the $K([15]crown\text{-}5)_2]_2Ti(CO)_6$ complex 4 with $BH_3{:}THF$ in THF at -60 °C gives the air sensitive compound 5 (eq. 3).[2]



Also, the $[Ti(CO)_4(\eta^3\text{-}BH_4)]^-$ undergoes nucleophilic reactions with L (L = $C_5H_5^-$, $C_5Me_5^-$, Ph_3C^-) to give the titanium carbonyl complex 7 (eq. 4).

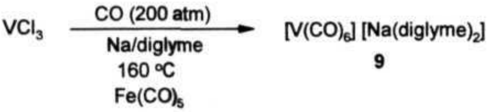


First examples of eight-coordinate metal carbonyls of Zr and Hf have been synthesized recently (eq. 5).[2]



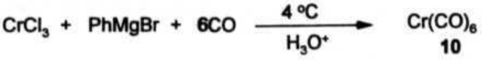
$$\underset{(M = Zr,\ Hf)}{MCl_4 \cdot 2THF} + 2\,NaC_{10}H_8 \xrightarrow{4\,PMe_3,\ 4Ph_3SnNa,\ CO} \underset{\mathbf{8}}{Na_2[(Ph_3Sn)_4M(CO)_4]} + 2\,C_{10}H_8 \quad \text{—(5)}$$

The carbonyls of vanadium, niobium and tantalum were first prepared by reductive carbonylation of the corresponding metal halides under CO. For example, the preparation of $[V(CO)_6]^-$ involves the reaction of VCl_3 with CO (200 atm) and Na in diglyme at 160 °C. The $Fe(CO)_5$ has been used as a catalyst in this reaction. After filtration and precipitation, $[Na(diglyme)_2][V(CO)_6]$ complex 9 was obtained (eq. 6).[3]



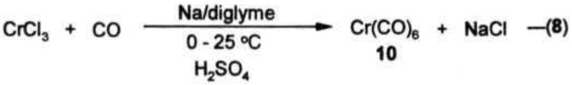
$$VCl_3 \xrightarrow[\substack{Na/diglyme \\ 160\ ^\circ C \\ Fe(CO)_5}]{CO\ (200\ atm)} \underset{\mathbf{9}}{[V(CO)_6]\,[Na(diglyme)_2]} \quad \text{—(6)}$$

The $Cr(CO)_6$ can be synthesized by the reaction of anhydrous $CrCl_3$ at atmospheric pressure of CO and a large excess of phenylmagnesium bromide at 4 °C, followed by acid hydrolysis (eq. 7).[4] It is a commercially available reagent.



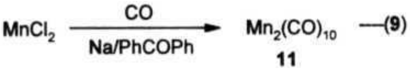
$$CrCl_3 + PhMgBr + 6CO \xrightarrow[H_3O^+]{4\ ^\circ C} \underset{\mathbf{10}}{Cr(CO)_6} \quad \text{--(7)}$$

A preferred method for the synthesis of $Cr(CO)_6$ involves the reaction of a chromium(III) salt with a suitable reducing agent in the presence of CO. These reductive carbonylation reactions give higher yields and reproducible results (eq. 8).[4]



$$CrCl_3 + CO \xrightarrow[\substack{0-25\ ^\circ C \\ H_2SO_4}]{Na/diglyme} \underset{\mathbf{10}}{Cr(CO)_6} + NaCl \quad \text{—(8)}$$

In 1958, Closson *et al* described the synthesis of $Mn_2(CO)_{10}$ 11 using sodium ketyl of benzophenone as a reducing agent with $MnCl_2$ at 200 to 700 atm of CO pressure (eq. 9).[5]



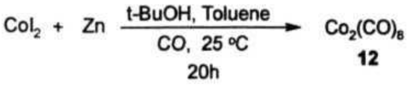
$$MnCl_2 \xrightarrow[Na/PhCOPh]{CO} \underset{\mathbf{11}}{Mn_2(CO)_{10}} \quad \text{—(9)}$$

The best method of preparation of $Mn_2(CO)_{10}$ requires the use of aluminium alkyl as reducing agent.[6a] The $Mn_2(CO)_{10}$ is also commercially available.

The $Ni(CO)_4$ is one of the earliest metal carbonyls prepared. It is a volatile compound (b.p[6b] 43 °C) and highly toxic. The objective in this laboratory is to prepare useful cobalt and iron carbonyls via reduction of the readily accessible cobalt and iron complexes. Hence, a brief review on the preparation and synthetic applications of these carbonyls will be helpful for the discussion.

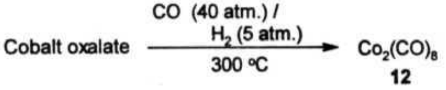
3. 1. 1 Preparation and synthetic applications of cobalt carbonyls

There are several reports on the preparation of the useful $Co_2(CO)_8$ reagent (12). A low pressure preparation of $Co_2(CO)_8$ was reported using cobalt(II) iodide and Zn powder under CO (eq. 10).[7]



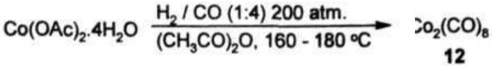
$$CoI_2 + Zn \xrightarrow[CO,\ 25\ ^{\circ}C,\ 20h]{t\text{-}BuOH,\ Toluene} \underset{\mathbf{12}}{Co_2(CO)_8} \quad \text{---(10)}$$

Reduction of cobalt oxalate with H_2 (5 atm) and CO (40 atm) at high temperature and pressure gives the $Co_2(CO)_8$ (eq. 11).[8]



$$\text{Cobalt oxalate} \xrightarrow[300\ ^{\circ}C]{CO\ (40\ atm.)\ /\ H_2\ (5\ atm.)} \underset{\mathbf{12}}{Co_2(CO)_8} \quad \text{---(11)}$$

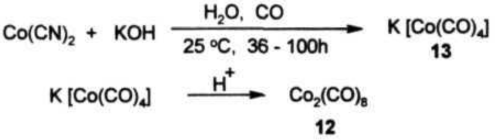
Also, it has been reported that the cobalt acetate, suspended in acetic anhydride, on reaction with 1:4 mixture of H_2 and CO at 160-180 °C under 200 atm pressure gives the $Co_2(CO)_8$ (eq. 12).



—(12)

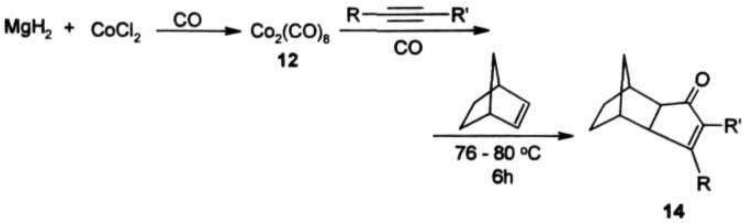
A convenient laboratory synthesis of $Co_2(CO)_8$ requires the initial preparation of $KCo(CO)_4$ (13) by passing CO through an alkaline suspension of cobalt cyanide. On acidification, the initially formed $HCo(CO)_4$ decomposes thermally to give $Co_2(CO)_8$ (Scheme **1**).[9,10]

Scheme 1

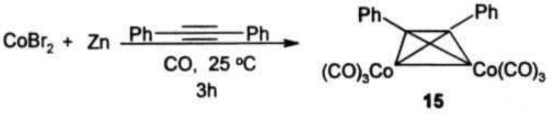


Several simple, practical methods have been developed in this laboratory for the preparation of cobalt carbonyls *in situ* from its halides using different reducing agents under CO. These cobalt carbonyl species have been used for several interesting organic transformations. For example, it was found that the reduction of $CoCl_2$ with MgH_2 at 0 °C under CO gives cobalt carbonyl 12, which undergoes the Pauson-Khand reaction with alkyne and norbornene to give the corresponding cyclopentenones 14 upon heating at 70 °C (Scheme 2).

Scheme 2

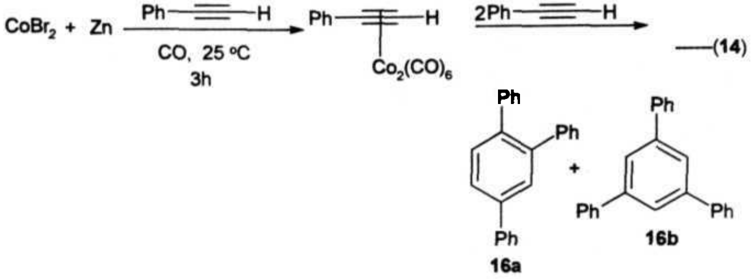


The reductive carbonylation of **$CoBr_2$** using Zn at CO atmosphere in THF gives cobalt carbonyl, which reacts with diphenylacetylene to give alkyne-**$Co_2(CO)_6$** complex 15. Formation of this complex in the reaction mixture was spectroscopically confirmed (eq. **13)**.[11]



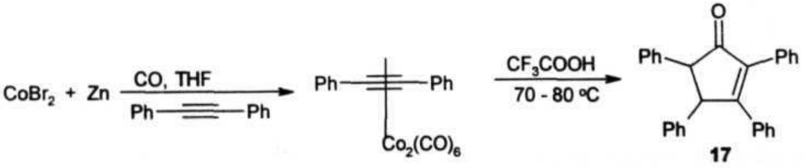
–(13)

Interestingly, the alkyne-cobalt complex prepared following the above procedure using phenylacetylene on further heating with two more equivalents of phenylacetylene gives the corresponding tri-substituted benzene 16a and 16b (eq. 14).[12]



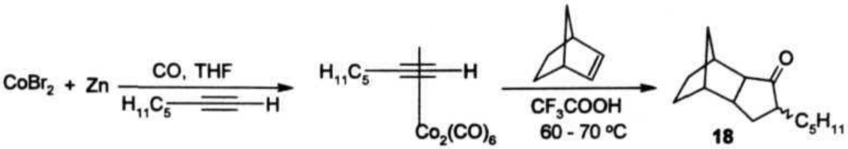
The alkyne-cobalt complex, prepared using diphenylacetylene, $CoBr_2$/Zn under CO atmosphere at 70-80 °C in THF, gives tetraphenylcyclopentenone 17 after decomplexation with CF_3COOH (Scheme 3).[13]

Scheme 3



Also, the cobalt carbonyl complex of 1-heptyne reacts with norbornene in the presence of TFA, to give the reduced Pauson-Khand product 18 (Scheme 4).[14]

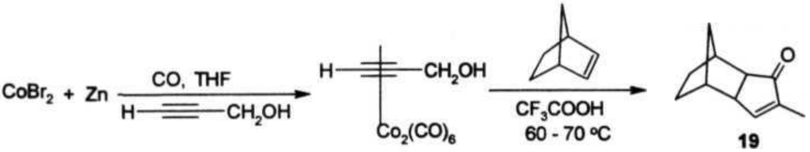
Scheme 4



18

However, the Pauson-Khand reaction, carried out using the cobalt complex derived from propargyl alcohol with **norbornene** at 65-70 °C for 12h, in the presence of TFA, gives the corresponding methyl substituted cyclopentenone 19 (Scheme 5).[15]

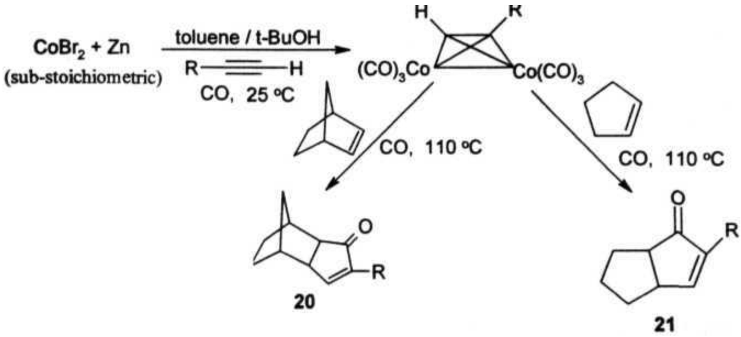
Scheme 5



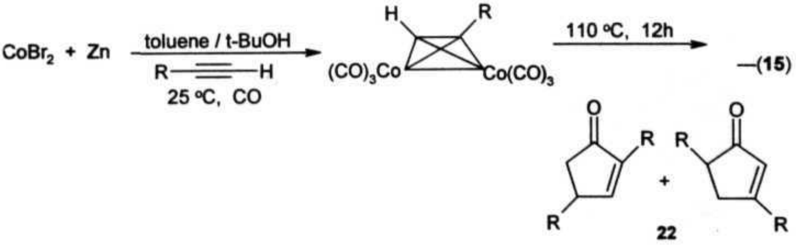
19

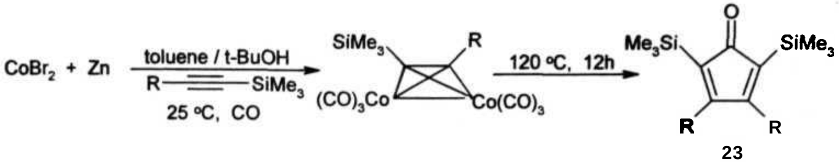
Recently, a new protocol for the Pauson-Khand reaction of alkyne-$Co_2(CO)_6$ complexes, prepared using **sub-stoichiometric** amounts of $CoBr_2$, and Zn at atmospheric pressure of CO, has been **reported.**[15] These complexes on heating with olefins give the corresponding Pauson-Khand products 20 and 21 (Scheme **6).**[15]

Scheme 6



Also, the **alkyne-$Co_2(CO)_6$** complexes prepared *in situ* in the absence of added olefins, give the corresponding cyclopentenones 22 & 23 on heating in toluene (eq. **15, 16**).[17]

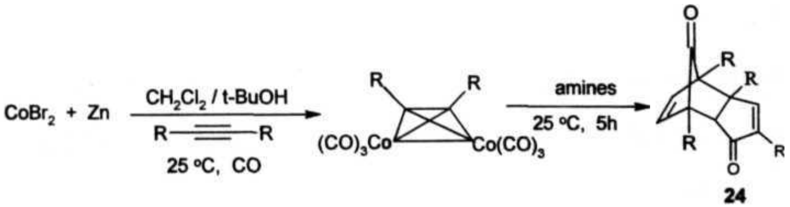




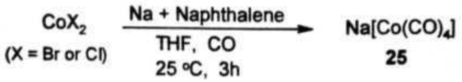
------(16)

Further, the Pauson-Khand reaction can be carried out under ambient conditions in the presence of DMSO or amines.[16] Moreover, the **alkyne-$Co_2(CO)_6$** complexes, prepared as above, give substituted dicyclopentadienones 24 under ambient conditions in the presence of amines or DMSO (Scheme **7).**[17]

Scheme 7

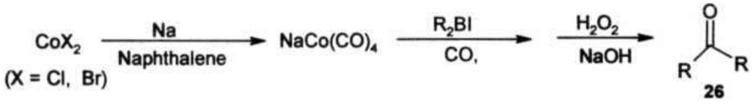


A practically simple method for the generation of Na[Co(CO)4] 25 has been developed by reducing cobalt halides **($CoCl_2$ or $CoBr_2$)** using sodium naphthalenide. The cobalt carbonyl 25 prepared in this way was used for the carbonylative cyclization of certain benzyl halides (eq. 17).

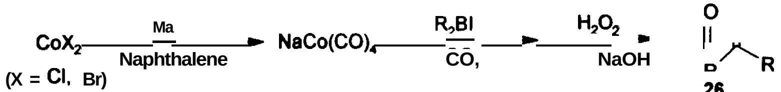


—(17)

Also, it was found that the iodoalkylboranes prepared by the hydroboration of alkenes with **BH_2I-complex** can be carbonylated in the presence of NaCo(CO)4 to obtain the corresponding dialkyl ketones 26 after **H_2O_2/NaOH** oxidation (eq. **18**).[18]

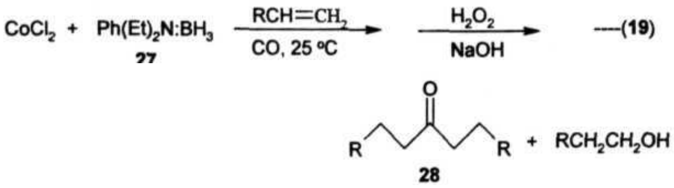


-----(18)



(18)

The cobalt carbonyl reagent, prepared in the reaction of **$Ph(Et)_2N{:}BH_3$** 27 complex (1 equiv.) in benzene and anhydrous **$CoCl_2$** (1 equiv.) in THF under CO, is useful for the carbonylation of alkene (2 equiv.) to obtain the corresponding dialkyl ketone 28 after oxidation with **H_2O_2/NaOH**. The alcohol resulting from hydroboration-oxidation was also obtained as a side product (eq. **19**).[19]



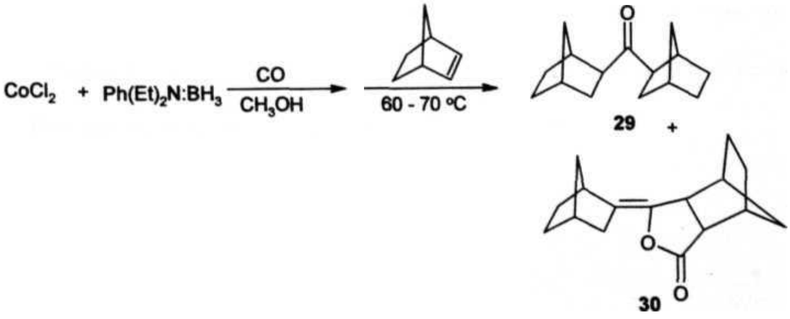
----(19)

Presumably, the $Ph(Et)_2N{:}BH_3$ 27 on reaction with $CoCl_2$ would give the H_2BHCl and cobalt hydride species. The latter could yield the cobalt carbonyl $Co_2(CO)_8$, in the presence of CO (eq. 20).[20]

$$\underset{27}{Ph(Et)_2N{:}BH_3} + CoCl_2 \xrightarrow{CO} H_2BHCl + HCoCl \xrightarrow{CO} \underset{12}{Co_2(CO)_8} \quad \text{—(20)}$$

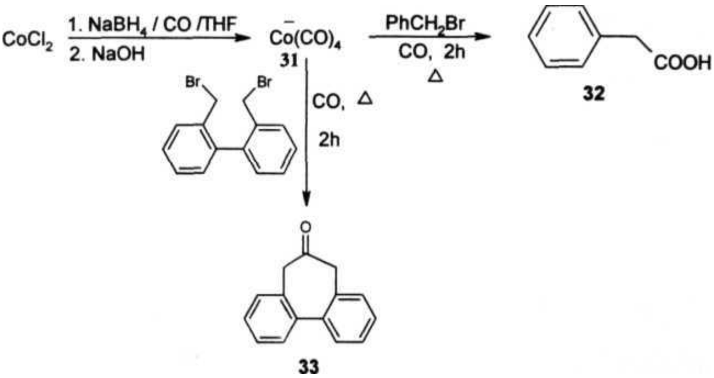
Also, the cobalt carbonyl species, prepared using the $Ph(Et)_2N{:}BH_3$ 27 complex (1 equiv.) in methanol and anhydrous $CoCl_2$ (1 equiv.) in THF under CO, is useful for the carbonylation of **norbornene** to give the ketone 29 and the lactone 30 (Scheme **8).**[21]

Scheme 8



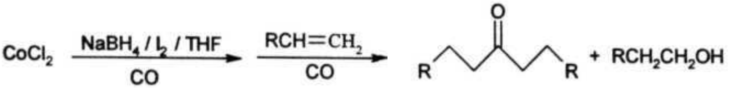
The reduction of $CoCl_2$ with $NaBH_4$ under CO also produces cobalt carbonyl species. For example, the cobalt carbonyl species prepared *in situ* in THF under CO atmosphere using $CoCl_2$ and $NaBH_4$ reagent system on treatment with aq.NaOH gives $Co(CO)_4^-$ 31. The species prepared in this way was utilized for the carbonylation of benzyl halide to phenyl acetic acid (32) and 2,2'-bis(bromomethyl)biphenyl to the corresponding cyclic ketone 33 (Scheme 9).[22]

Scheme 9

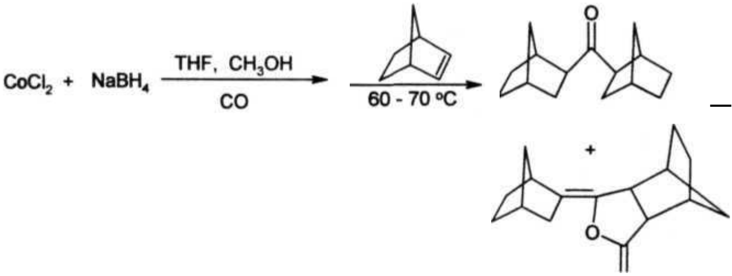


Several other synthetic applications have been carried out using the cobalt carbonyl species prepared *in situ* by the reduction of $CoCl_2$ with $NaBH_4$ and CO. They are summarized in equations **21-23**.[21,22]

$$RCH{=}CH_2 \xrightarrow[\text{THF, CO}]{CoCl_2 / NaBH_4 / PPh_3} \xrightarrow[CH_3OH]{I_2} RCH_2CH_2COOCH_3 \quad \text{---(21)}$$



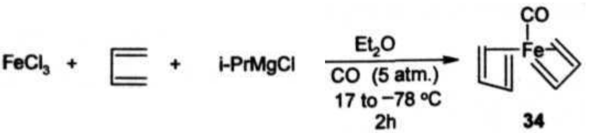
—(22)



—(23)

3. 1. 2 Preparation and applications of iron carbonyls

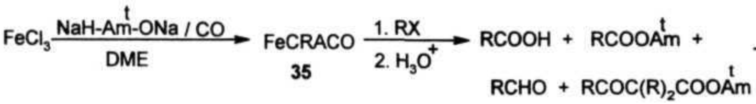
The butadiene iron carbonyl complex 34 has been prepared via carbonylation of an ether solution of $FeCl_3$, butadiene and isopropylmagnesium chloride while bubbling CO (5 aim) (eq. 24). The butadiene complex prepared following this procedure has been used as a catalyst for the oligomerization of 1,3-butadiene in toluene to a mixture of cyclic and linear dimers.[23-26]



34

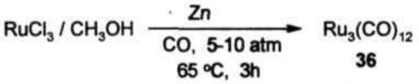
—(24)

Interesting reactive species (termed FeCRACO) (35) were prepared *in situ* by the reduction of $FeCl_3$ by NaH-sodium tert-amyloxide combination under CO (eq. 25). The reagent prepared in this way has been used for the carbonylation of primary, secondary and tertiary alkyl halides.[27,28]



---(25)

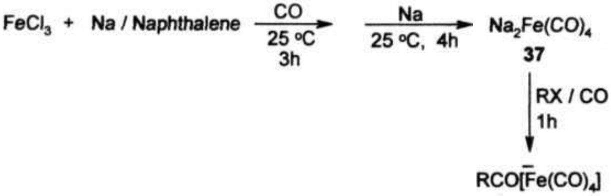
It has been reported that the $RuCl_3$ in CH_3OH in the presence of Zn under CO (5-10 atm) at 65 °C, gives the $Ru_3(CO)_{12}$ (36) in good yield (eq. 26).[29]



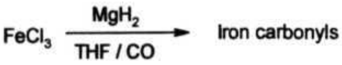
---(26)

Early studies in this laboratory indicated that the reduction of $FeCl_3$ with Zn at 1 atm. of CO does not produce iron carbonyls.[11] However, the super nucleophile $Na_2Fe(CO)_4$ (Collman's reagent) (37)[30] was prepared in THF, by reducing the anhydrous $FeCl_3$ using sodium naphthalenide under CO (1 atm) at 25 °C. The $Na_2Fe(CO)_4$ prepared by this method was used in several reactions characteristic of $Na_2Fe(CO)_4$ (Scheme 10).[31] This reagent has also been used for the preparation of $NaHFe(CO)_4$ for applications in the reaction with alkyl halides and alkynes to obtain cyclobutenediones after $CuCl_2.2H_2O$ oxidation (introductory section, Chapter 1).

Scheme 10



Also, a brief earlier investigation indicated that the $NaBH_4$ and MgH_2 reagents reduce $FeCl_3$ under CO atmosphere to unidentified iron carbonyl species (eq. 27). The presence of iron carbonyl species in the reaction mixture was confirmed by analyzing the **IR spectrum.**[11]



—(27)

As discussed in the chapter 1, reduction of $Fe(CO)_5$ with $NaBH_4$ followed by CH_3COOH treatment leads to reactive iron carbonyl species. It would be advantageous to prepare such reactive iron carbonyl derivatives using readily accessible reagents such as $FeCl_3$ and $NaBH_4$ under CO. Hence, we have undertaken the investigations described in this chapter.

3. 2 Results and Discussion

3. 2. 1 Preparation of iron carbonyl species via reduction of $FeCl_3$ using $NaBH_4$ in the presence of CO

It has been reported that the reduction of $FeCl_3$ with excess $LiBH_4$ in diethyl ether gives iron(II) borohydride that decomposes slowly at -10 °C and rapidly at 0 °C to produce the diborane, hydrogen and pyrophoric residue containing boron and iron (eq. 28).[32]

$$3\,LiBH_4 + FeCl_3 \xrightarrow{Et_2O} 3\,LiCl + \tfrac{1}{2}H_2 + \tfrac{1}{2}B_2H_6 + Fe(BH_4)_2 \quad \text{—(28)}$$

Preliminary studies in this laboratory indicated that the reaction of $NaBH_4$ (3 equiv.) with $FeCl_3$ in THF results in the formation of species that hydroborates olefins (eq. 29).[33]

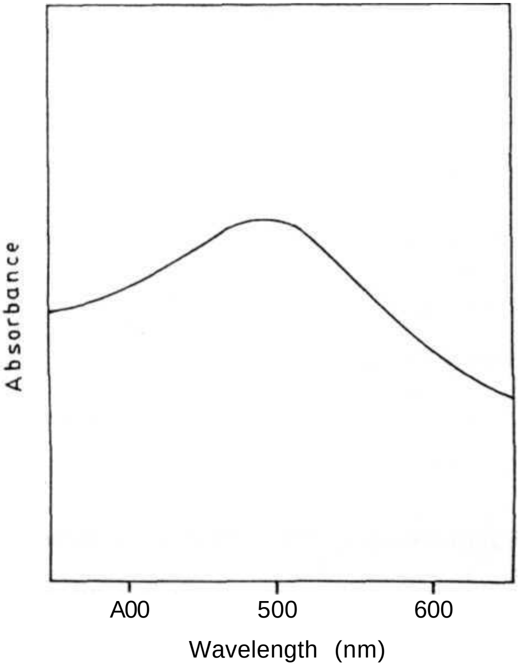
$$RCH{=}CH_2 \xrightarrow[2.\ H_2O_2\,/\,\bar{O}H]{1. FeCl_3\,/\,NaBH_4\,/\,THF} RCH_2CH_2OH \quad \text{---(29)}$$

We have observed that the reduction of anhydrous $FeCl_3$ (10 mmol) with $NaBH_4$ (40 mmol) in THF at 25 °C followed by addition of CH_3COOH (68 mmol) while bubbling CO at atmospheric pressure for 9h gives iron carbonyl species (eq. 30).[34] The presence of iron carbonyl species in the reaction mixture was confirmed by the I.R spectral data of the solution (strong bands at 2044 cm^{-1} and 1986 cm^{-1}).[35a] The U.V spectrum of the solution (λ_{max}: 490 nm) (Figure 1) indicated the presence of metal carbonyl species of the type $[HFe(CO)_4]^-$ (eq. **30**).[35b]

$$FeCl_3 \xrightarrow[\text{2. CH}_3\text{COOH, 9h, 25 °C}]{\text{1. NaBH}_4\text{ / CO / THF}} [HFe(CO)_4]^- \text{——— (30)}$$

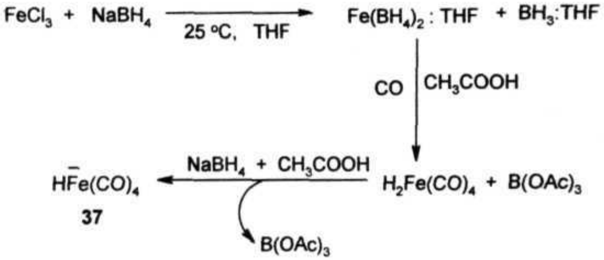
37

Figure 1. U.V spectrum for iron carbonyl prepared



The formation of $HFe(CO)_4^-$ *in situ* using the $FeCl_3$, $NaBH_4$, CO and CH3COOH reagent system can be tentatively visualized as shown in Scheme **11**. However, presence of other iron carbonyl species along with the $HFe(CO)_4^-$ species cannot be ruled out.

Scheme **11**



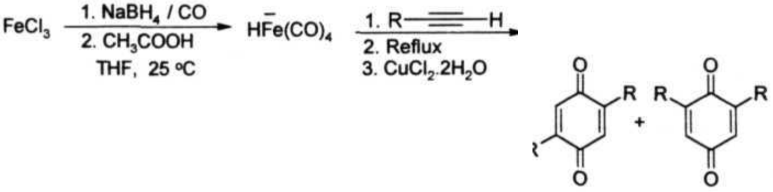
We have also undertaken efforts towards isolation of the iron carbonyl species as PPh_3, pyrazine or pyridine derivatives. However, these efforts were not successful.[36] Accordingly, we proceeded with the synthetic applications of the $HFe(CO)_4^-$ species prepared in this way.

3.2.2. Reaction of iron carbonyl species prepared using $FeCl_3$, $NaBH_4$, CH_3COOH and CO with 1-alkynes

It was observed that the reagent prepared as above, reacts with **1-alkynes** in THF, at refluxing temperature for 12h to give disubstituted benzoquinones 38

(a) and 38(b) in moderate to good yields (51-80%) after $CuCl_2.2H_2O$ oxidation (Scheme 12).[34] Several 1-alkynes were converted to the corresponding benzoquinones. The results are summarized in Table 1. Percentage composition of isomer (a) and (b) were calculated from the ^1H NMR signal intensities.[37]

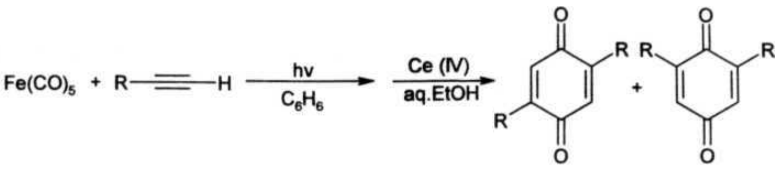
Scheme 12



38 (a) 38 (b)

Also, it was found that the reaction at 25 °C gave the corresponding benzoquinones in poor yields (10-20%). Further, internal alkynes such as diphenylacetylene, l-heptynyl-(trimethyl)-silane and propargyl alcohol derivatives did not react even under refluxing conditions.[34]

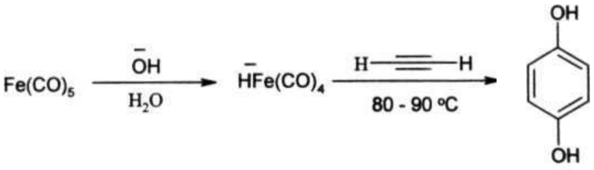
Here, it may be of interest to note that the $Fe(CO)_5$ on reaction with 1-alkynes under photolysis gives a mixture of benzoquinones **39(a)** and 39(b) in moderate yields (27-50%) after oxidation (eq. 31).[37] The internal alkynes failed to give the expected benzoquinones under these conditions.



39 (a) 39(b)

----- (31)

Also, it was reported that the iron carbonyl reagent prepared using $Fe(CO)_5$ in alkaline solution, on reaction with acetylene at high temperature gives the hydroquinone 40 (eq. 32).[38a]

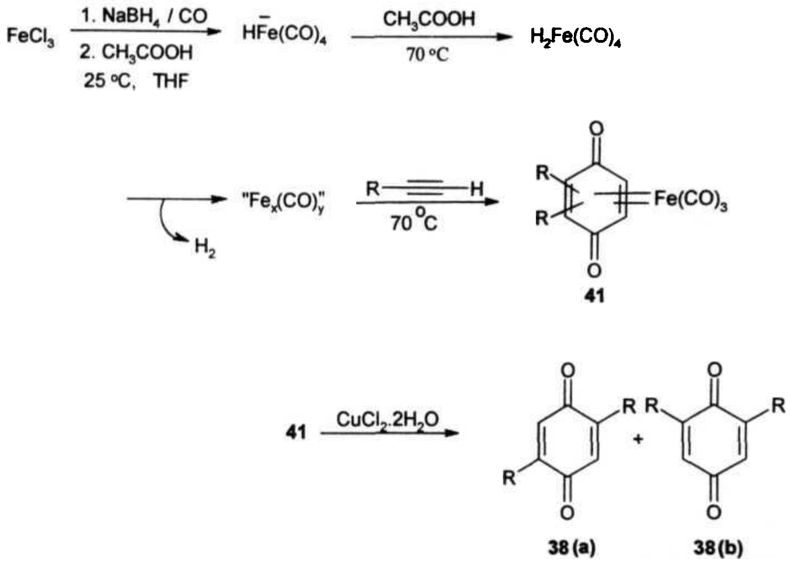


40

—(32)

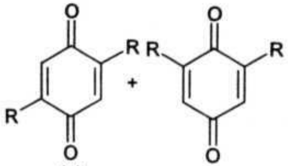
It is well-known that $Fe(CO)_5$ reacts with NaOH to give $HFe(CO)_4^-$.[38c] Accordingly, the formation of hydroquinone may be rationalized by considering the intermediacy of similar reactive species (Scheme 12). Presumably, at high temperature the hydrido iron carbonyl $[HFe(CO)_4]^-$ species reacts with acetic acid (or H_2O, eq. 32) to give coordinatively unsaturated species that on further reaction with 1-alkynes gives the intermediate complex of the type 41 or the corresponding hydroquinone.[38a,39,40] Oxidation of 41 or the corresponding hydroquinone using $CuCl_2.2H_2O$ would give the benzoquinones 38(a) and 38(b) (Scheme 13).

Scheme 13



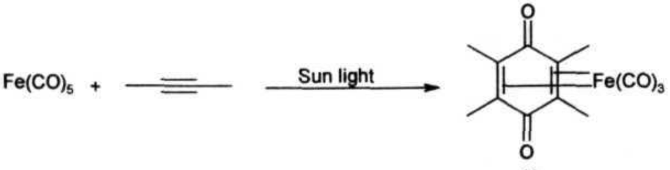
Similarly, the photochemical reaction of alkyne with Fe(CO)5 in THF, would also give the intermediate complex **41** through coordinatively unsaturated iron carbonyl species (eq. 33, see also eq. **31**).[40]

Table 1: Reaction of iron carbonyl species prepared using **$FeCl_3$**, **$NaBH_4$**, and **CH_3COOH** under CO with ROCH at 70 °C

S.No	1-Alkyne	Product ^{a}	Yield ^{b}
	R—≡—H	 (a) (b)	
1.	R = C_6H_{13}	**42a** (65%) **42b** (35%)	72 %
2.	R = Ph	**43a** (52%) **43b** (48%)	51 %
3.	R = C_5H_{11}	**44a** (60%) **44b** (40%)	80 %
4.	R = C_8H_{17}	**45a** (71%) **45b** (29%)	51 %

a) Products were identified from the spectral data IR, ^{1}H NMR and ^{13}C NMR and comparison with the reported data.[37] The spectral data for the compounds **42a, 42b** and **43a, 43b** show 1:1 correspondence with the reported data.[37] The spectral data for the compounds **44a, 44b** and **45a, 45b** are comparable with the data for the compounds **42a, 42b.** The percentage compositions of isomers (a) and (b) were calculated from the ^{1}H NMR signal intensities and compared with the reported data.[37]

b) Yields are of products isolated by column chromatography using hexane as eluent and based on the 1-alkynes used.

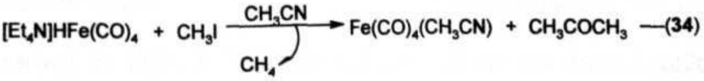


41 —(33)

Previously, we have prepared reactive iron carbonyl species from $HFe(CO)_4^-$ through reaction with CH_3I (see introductory Section, Chapter 1). Accordingly, we have examined the reaction of the $HFe(CO)_4^-$ species prepared using $FeCl_3$, $NaBH_4$ and CO (Scheme 11) with CH_3I. The results obtained are presented in the next section.

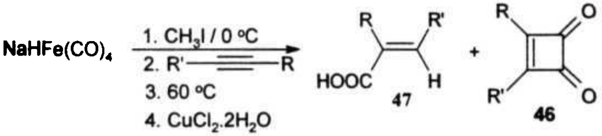
3. 2. 3 Reaction of iron carbonyl species prepared using $FeCl_3$, $NaBH_4$, CH_3COOH and CO with CH_3I and 1-alkynes

The method of generating coordinatively unsaturated iron carbonyl species "$Fe(CO)_4$" using the $HFe(CO)_4^-/CH_3I$ reagent system (eq. 34) is practically simple and convenient for further synthetic applications.[41]



$$[Et_4N]HFe(CO)_4 + CH_3I \xrightarrow[CH_4]{CH_3CN} Fe(CO)_4(CH_3CN) + CH_3COCH_3 \quad \text{—(34)}$$

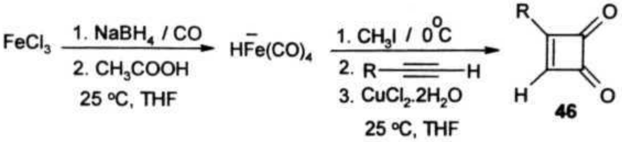
As discussed in the Chapter 1, the coordinatively unsaturated species prepared using the $NaHFe(CO)_4$ (prepared *in situ* from $Na_2Fe(CO)_4$ and CH3COOH) and CH3I has been used for the double carbonylation of alkynes to the corresponding cyclobutenediones 46 and α,β-unsaturated carboxylic acids 47 after $CuCl_2.2H_2O$ oxidation (eq. 35).[42]



· —(35)

We examined the preparation of such coordinatively unsaturated species by adding CH_3I to the $NaHFe(CO)_4$, prepared using $FeCl_3$, $NaBH_4$, acetic acid and CO to study its reactivity with alkynes. Interestingly, addition of CH_3I at 0 °C to the iron carbonyl species, prepared *in situ* using the $FeCl_3/NaBH_4$-CO/CH_3COOH reagent system, followed by reaction with 1-alkynes at 25 °C for 12h in THF, gives the corresponding cyclobutenediones 46 after $CuCl_2.2H_2O$ oxidation. However, the yields are only moderate (30-37%) (eq. 36). Several 1-alkynes were converted to the corresponding cyclobutene-diones. The results are summarized in Table 2. The benzoquinones 38 are not formed under these conditions.

We have also examined the effect of temperature on this reaction. It was observed that the addition of CH_3I at 0 °C followed by reaction with 1-alkynes at 70 °C gives a mixture of benzoquinones 38 and cyclobutenediones 46.[34]

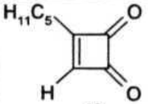
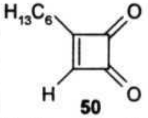
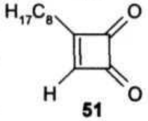
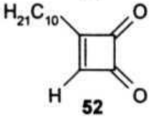
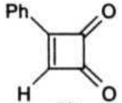


—(36)

Internal alkynes such as diphenylacetylene, trimethylsilyl substituted alkynes and propargyl alcohol derivatives did not give the expected cyclobutenediones under these conditions.

A tentative mechanistic pathway for the formation of cyclobutenediones can be visualized as shown in Scheme 14. Presumably, the coordinatively unsaturated iron carbonyl species generated after the addition of CH3I,[41] reacts with the 1-alkyne moiety followed by CO insertion to give the intermediate alkyne-iron complex 47. Oxidation of 47 with $CuCl_2.2H_2O$ would lead to the formation of the corresponding cyclobutenediones 46 (Scheme 14).[47] However, due to the presence of reducing agents in the reaction mixture, the possibility of formation of the hydroxy ferrole iron complex 48 cannot be ruled out (see Scheme 12, Chapter 1).

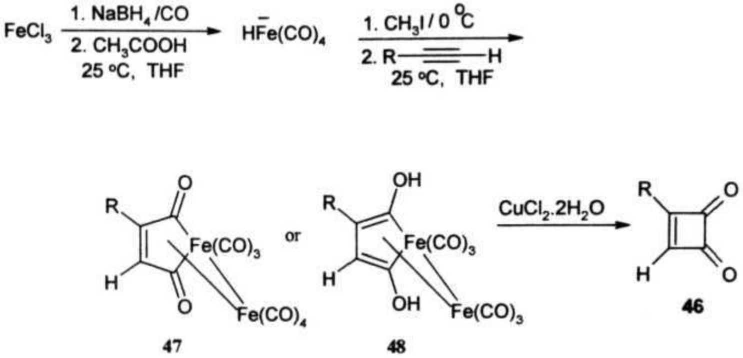
Table 2: Reaction of iron carbonyl species prepared using $FeCl_3$, $NaBH_4$, CH_3COOH and CO with CH_3I and $RC\equiv CH$

S.No	1-Alkyne	Product[a]	Yield[b]
1.	$H_{11}C_5-\!\equiv\!-H$	 **49**	37 %
2.	$H_{13}C_6-\!\equiv\!-H$	 **50**	35 %
3.	$H_{17}C_8-\!\equiv\!-H$	 **51**	32 %
4.	$H_{21}C_{10}-\!\equiv\!-H$	 **52**	31 %
5.	$Ph-\!\equiv\!-H$	 **53**	30 %

a) Products were identified from the spectral data **IR**, ^1H **NMR**, ^{13}C **NMR** and Mass. These data are 1:1 correspondence with the data reported in Chapter 1, also comparable with the reported **data.**[44,45]

b) Yields are of products isolated by column chromatography using hexane/ethyl acetate (98:2) as eluent and based on the **1-alkynes** used.

Scheme 14



Though, the yields of cyclobutenediones obtained are only moderate, the one-pot synthetic operation described here, through preparation of the reactive iron carbonyl species starting from simple bench-top chemicals, should be useful for further synthetic exploitation.

3.3 Conclusions

A new method for the preparation of iron carbonyl species *in situ* in THF using simple bench-top chemicals $FeCl_3$, $NaBH_4$ and CH_3COOH in the presence of CO under mild conditions has been developed. The spectral data recorded show that species prepared in this way may be $HFe(CO)_4^-$.

The iron carbonyl species prepared in this way is useful for the conversion of 1- alkynes to the corresponding benzoquinones and cyclobutenediones under different conditions. The cyclobutenediones and benzoquinones are versatile starting materials for the synthesis of biologically active compounds. Accordingly, this one-pot method of conversion of 1-alkynes to the corresponding benzoquinones and cyclobutenediones using the simple bench-top chemicals should be useful for further synthetic applications.

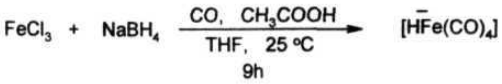
3. 4 Experimental Section

3. 4. 1 General information:

Several informations given in the experimental section of Chapter 1 are also applicable for the experiments outlined here. The commercially available anhydrous $FeCl_3$, CH_3COOH and CH_3I were used in the experiments. The alkynes used in the reactions (except 1-heptyne) were prepared by following reported procedure.[46] All reactions and manipulation were conducted under a dry nitrogen atmosphere. Carbon monoxide was generated by dropwise addition of formic acid (98%) to conc.H_2SO_4 (96%) at 90 °C using an apparatus recommended for use in the carbonylation of organoboranes.[47] The CO was pre-dried by passing through a jar filled with anhydrous KOH pellets before passing into the reaction mixture.

3. 4. 2 Preparation of $HFe(CO)_4$ *in situ* in THF using $FeCl_3$, $NaBH_4$ and CH_3COOH under CO atmosphere

Anhydrous $FeCl_3$ (1.26 g, 10 mmol) in THF (50 mL) was added slowly for 1h to $NaBH_4$ (1.54 g, 40 mmol) in THF (100 mL) while bubbling CO at 25 °C. The reaction mixture was further stirred for 9h at 25 °C under CO . Acetic acid (4 g, 68 mmol) was added slowly and the mixture was stirred further for 30 min. The CO bubbling was replaced by N_2 atmosphere. The IR and UV spectra were recorded.[35]

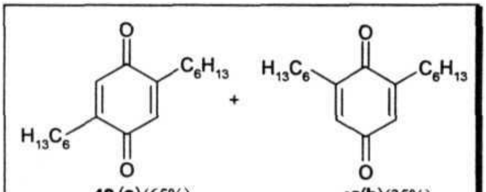


IR (neat) :2044,1986 cm^{-1}

UV (λ_{max}) : 490 nm (see Figure 1)

3. 4. 3 Reaction of iron carbonyl species prepared using $FeCl_3$, $NaBH_4$, CH_3COOH and CO with RC≡CH

Anhydrous $FeCl_3$ (1.26 g, 10 mmol) in THF (50 mL) was added slowly for 1h to $NaBH_4$ (1.54 g, 40 mmol) in THF (100 mL) while bubbling CO at 25 °C. The reaction mixture was further stirred for 9h at 25 °C under CO. Acetic acid (4 g, 68 mmol) was added slowly and the mixture was stirred further for 30 min. The CO bubbling was replaced by N_2 atmosphere and 1-octyne (0.090 g, 1.25 mmol) was added and the contents were refluxed at 70 °C for 12h. The metal carbonyls in the reaction mixture were decomposed by adding $CuCl_2.2H_2O$ (6.8 g, 40 mmol) in acetone (20 mL) at 25 °C. Saturated aq. NaCl (40 mL) was added and the contents were extracted with ether (100 mL). The combined organic extract was washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane). Hexane eluted the benzoquinones 42a(65%) and 42b(35%) (72%, 0.113 g).[37]



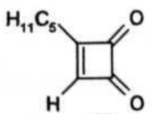
42 (a)(65%) **42(b)**(35%)

The spectral data for the compounds 42-45 were identical to the data reported for the same compounds obtained in the experiments described earlier (Experimental Section 2. 4. 2, Chapter 2).

The above procedure was followed for the conversion of other 1-alkynes to the corresponding benzoquinones. The data are summarized in Table 1. The spectral data are comparable with the reported data.[37] Also, these data show 1:1 correspondence with the data reported for the same compounds (see Experimental Section 2. 4. 2, Chapter 2). The percentage compositions of isomers (a) and (b) were calculated from the ^1H NMR signal intensities. Similar ^1H NMR analysis of benzoquinone mixtures has been previously reported.[37]

3. 4. 4 Reaction of iron carbonyl species prepared using $FeCl_3$, $NaBH_4$, CH_3COOH and CH_3I under CO with RC≡CH

Anhydrous $FeCl_3$ (1.26 g, 10 mmol) in THF (50 mL) was added slowly for 1h to $NaBH_4$ (1.54 g, 40 mmol) in THF (100 mL) while bubbling CO at 25 °C. The reaction mixture was further stirred for 9h at 25 °C under CO. Acetic acid (4 g, 68 mmol) was added slowly and stirred further for 30 min. The CO bubbling was replaced by N_2 atmosphere and CH_3I (2.84 g, 20 mmol) was added at 0 °C. Stirring was continued for 30 min. Subsequently, 1-heptyne (0.12 g, 1.25 mmol) was added and the contents were stirred for 12h at 25 °C. The metal carbonyls in the reaction mixture were decomposed by adding $CuCl_2.2H_2O$ (6.8 g, 40 mmol) in acetone (20 mL) at 25 °C. Saturated aq. NaCl solution (40 mL) was added and the contents were extracted with ether (100 mL). The organic extract was washed with brine (20 mL).saturated aq.$Na_2S_2O_3$ solution, dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Ethyl acetate (2:98) in hexane eluted the cyclobutenedione 49 (37%, 0.070g).[44a]



49

The above procedure was followed for the conversion of other 1-alkynes to the corresponding cyclobutenediones. The data are given in Table 2. The spectral data for the compounds **49-53** were identical to the data reported for the same compounds obtained in the experiments described earlier (see Experimental Section **1. 4.** 2 Chapter **1**).[44,45]

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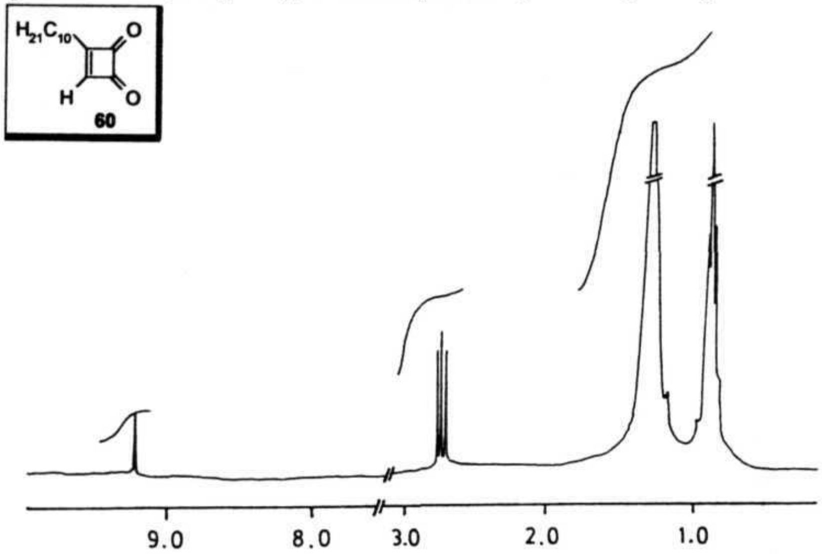
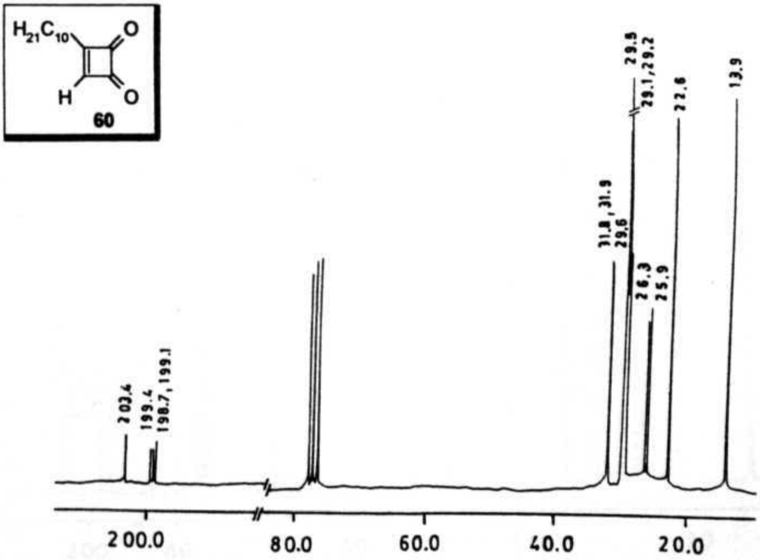
REPRESENTATIVE SPECTRA

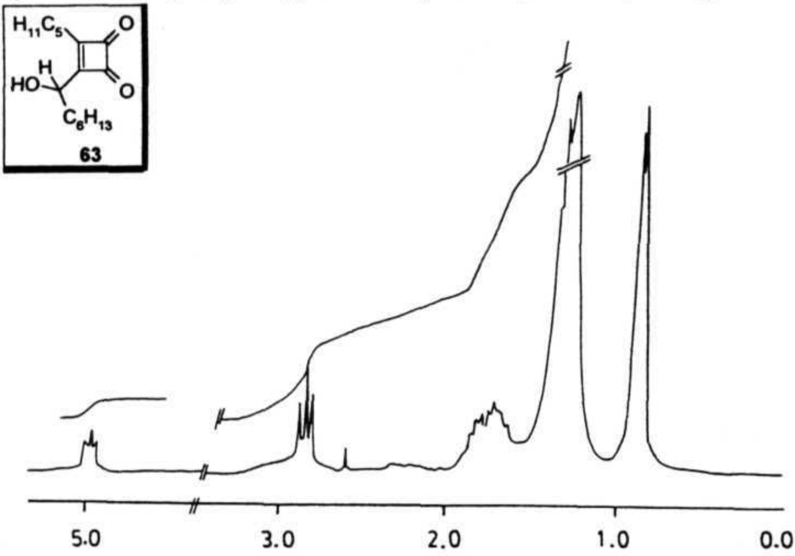
Spectrum No 1 (Chapter 1), ^{1}H NMR Spectrum (200 MHz, CDCl$_3$)



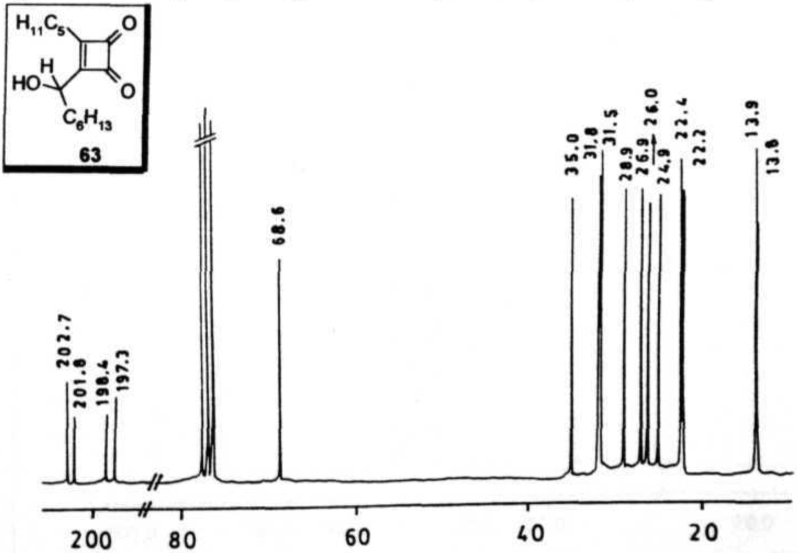
Spectrum No 2 (Chapter 1), ^{13}C NMR Spectrum (50 MHz, CDCl$_3$)



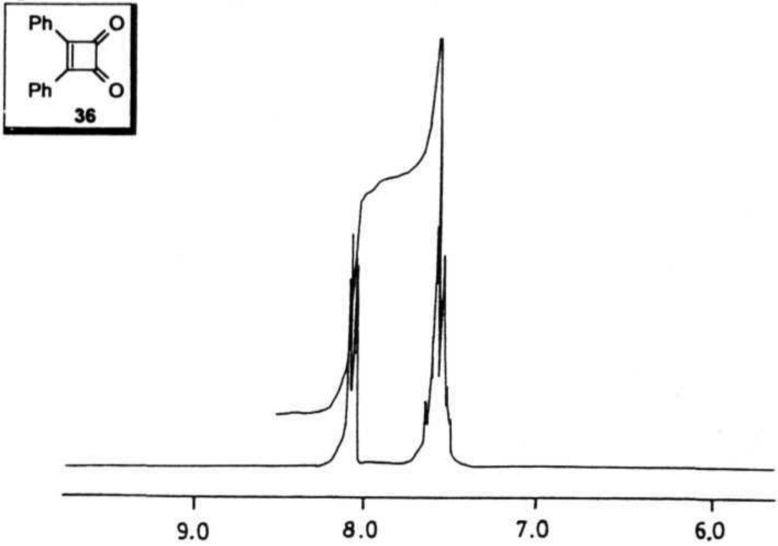
Spectrum No 3 (Chapter 1), ^{1}H NMR Spectrum (200 MHz, CDCl$_3$)



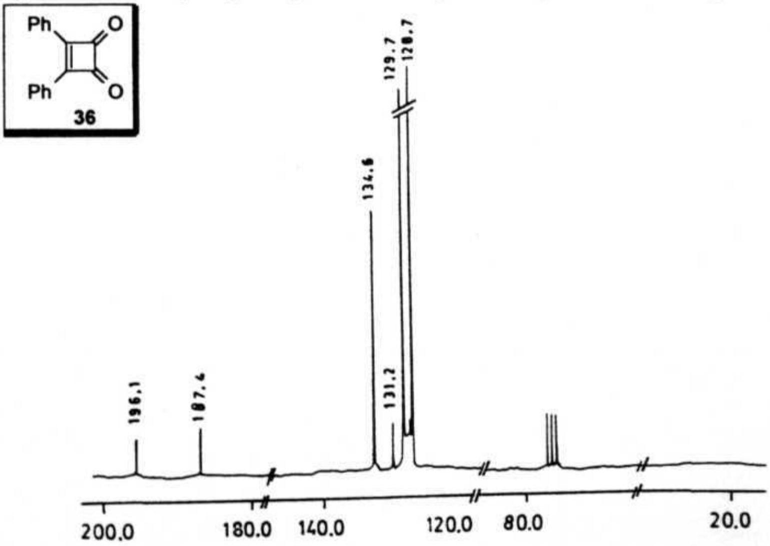
Spectrum No 4 (Chapter 1), ^{13}C NMR Spectrum (50 MHz, CDCl$_3$)



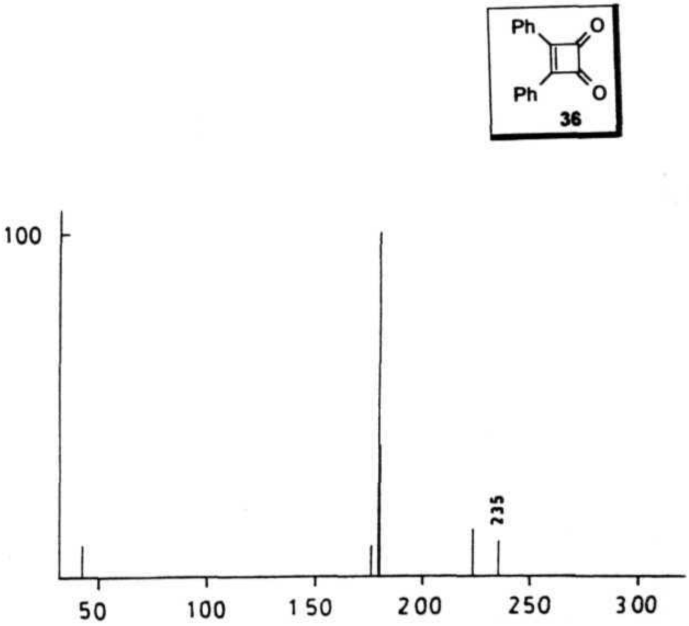
Spectrum No 5 (Chapter 1), ^{1}H NMR Spectrum (200 MHz, $CDCl_3$)



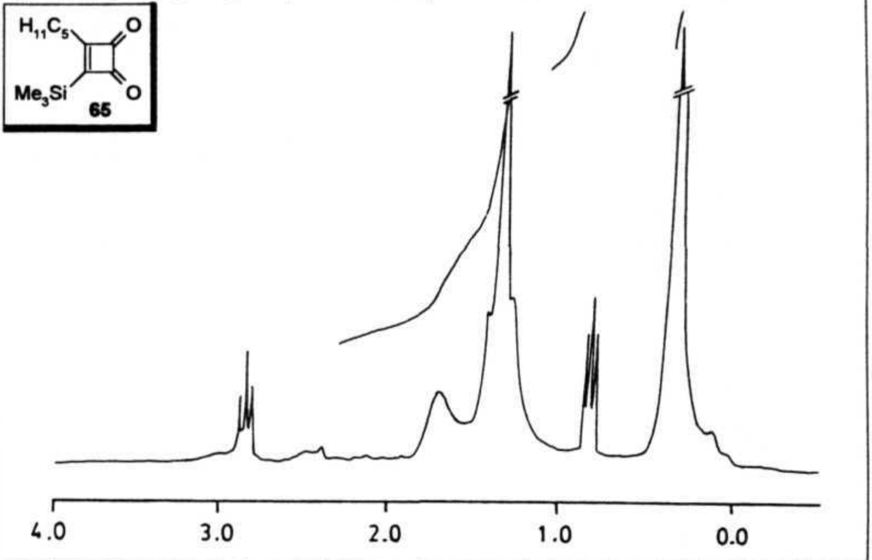
Spectrum No 6 (Chapter 1), ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



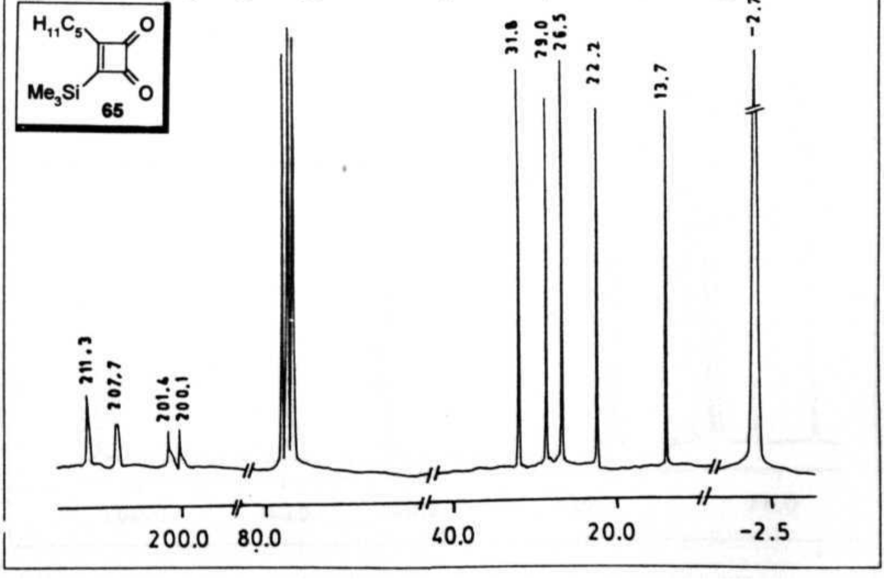
Spectrum No 7 (Chapter1), Mass Spectrum (m/z)



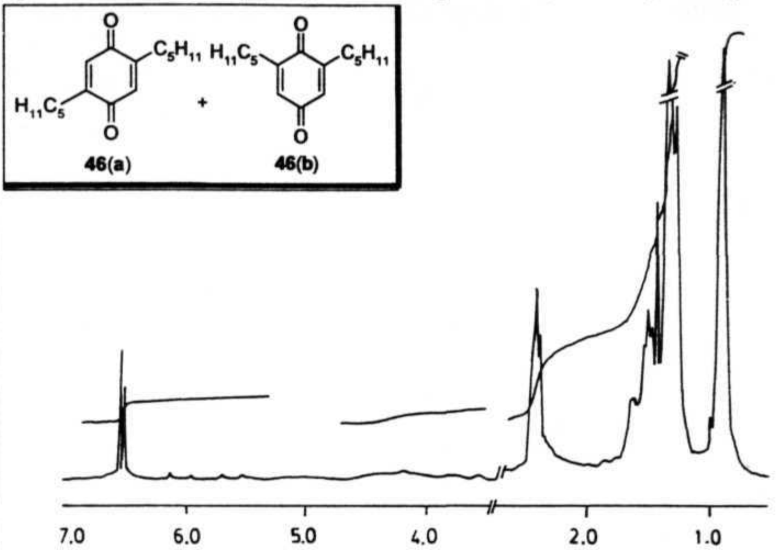
Spectrum No 8 (Chapter 1), ^{1}H NMR Spectrum (200 MHz, CDCl$_3$)



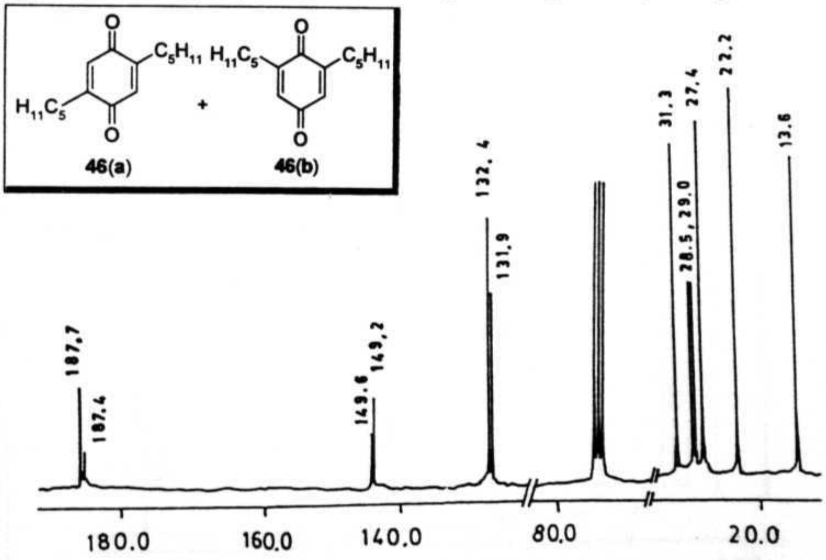
Spectrum No 9 (Chapter 1), ^{13}C NMR Spectrum (50 MHz, CDCl$_3$)



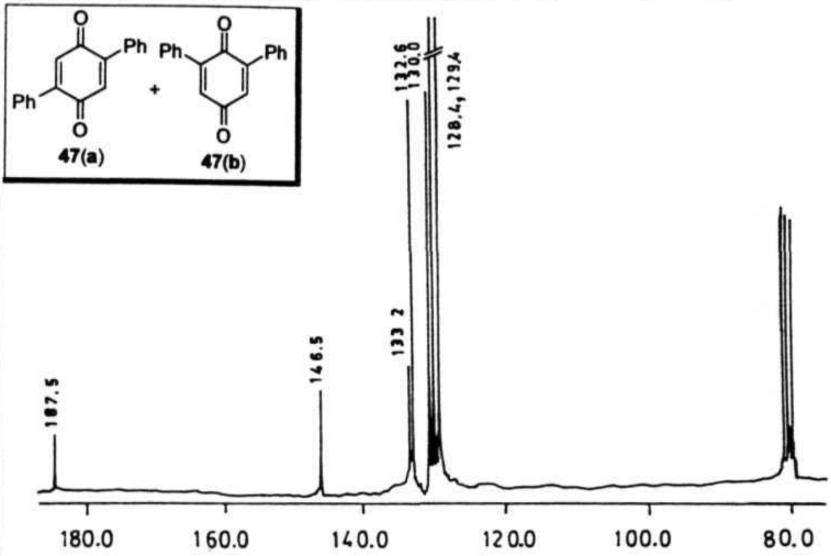
Spectrum No 10 (Chapter 2), ^{1}H NMR Spectrum (200 MHz, CDCl$_3$)



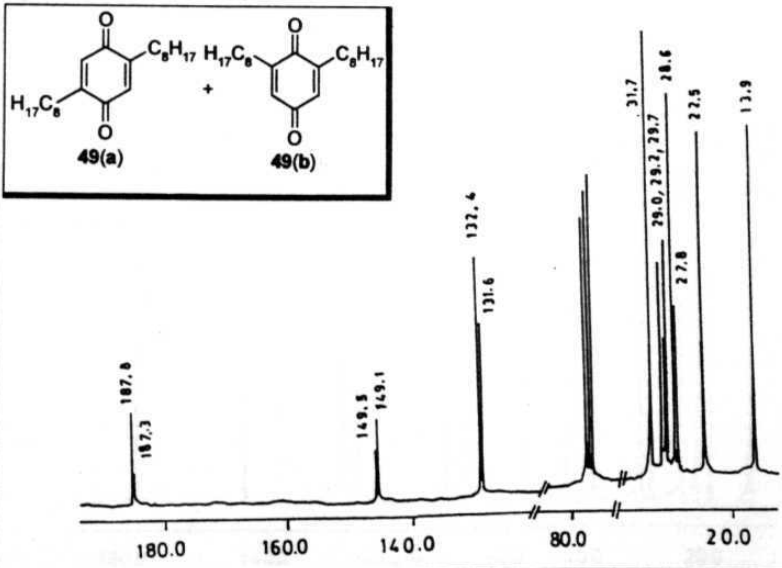
Spectrum No 11 (Chapter 2), ^{13}C NMR Spectrum (50 MHz, CDCl$_3$)



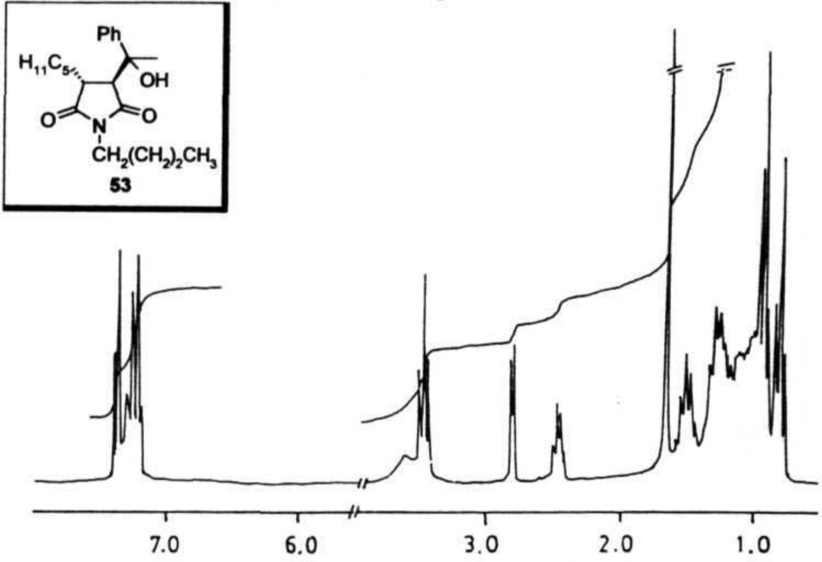
Spectrum No 12 (Chapter 2), ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



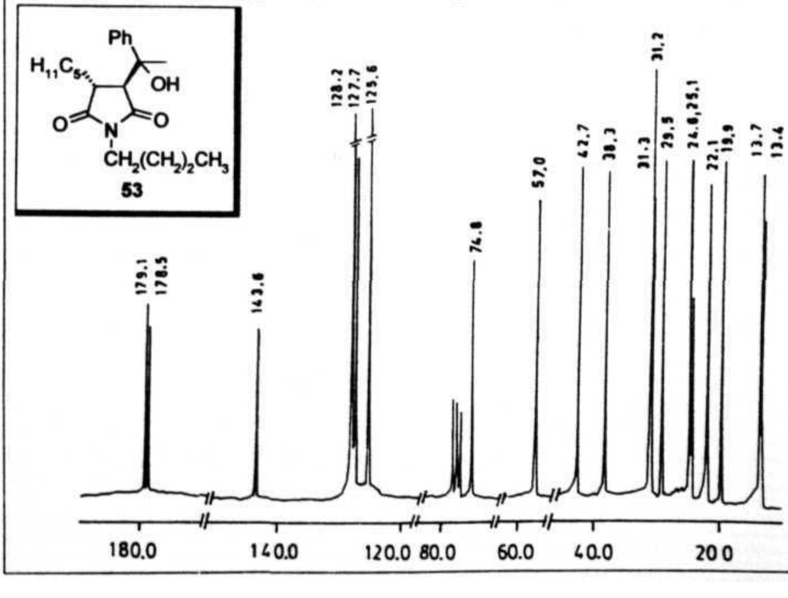
Spectrum No 13 (Chapter 2), ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



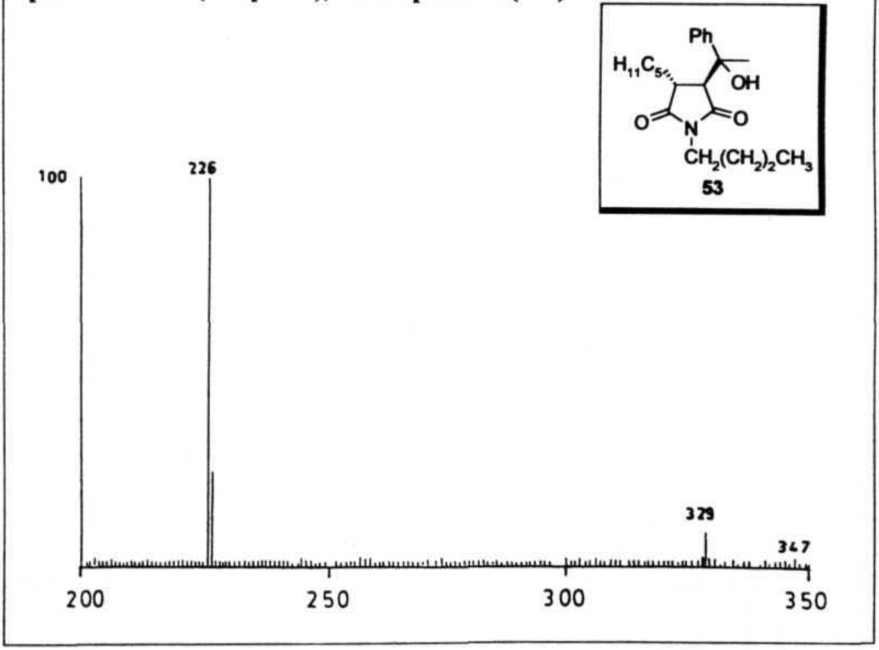
Spectrum No 14 (Chapter 2), ^{1}H NMR Spectrum (200 MHz, CDCl$_3$)



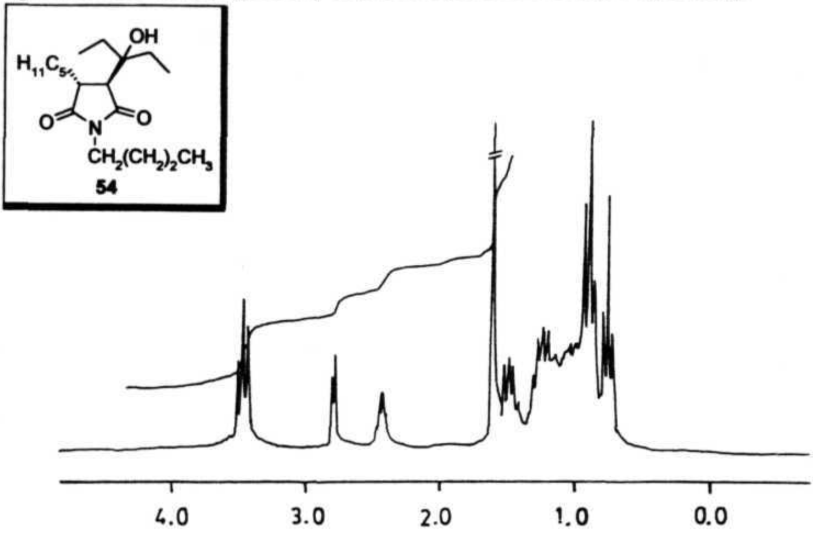
Spectrum No 15 (Chapter 2), ^{13}C NMR Spectrum (50 MHz, CDCl$_3$)



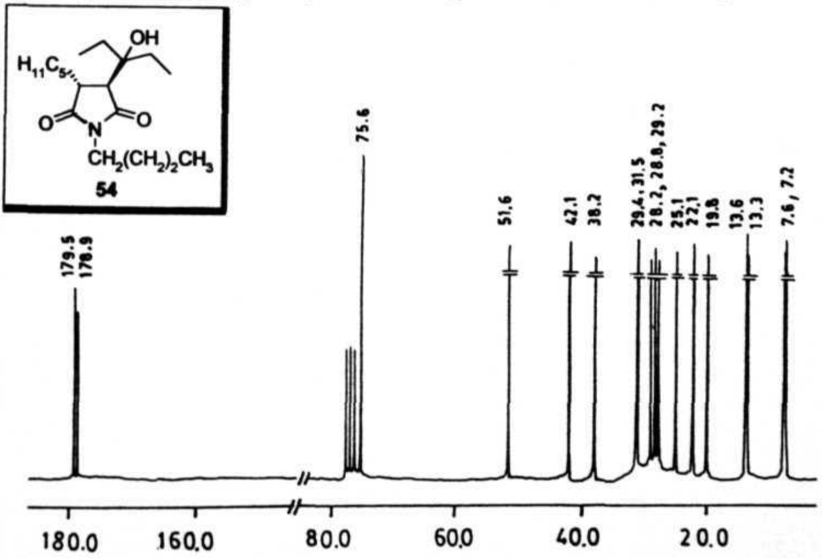
Spectrum No 16 (Chapter 2), Mass Spectrum (m/z)



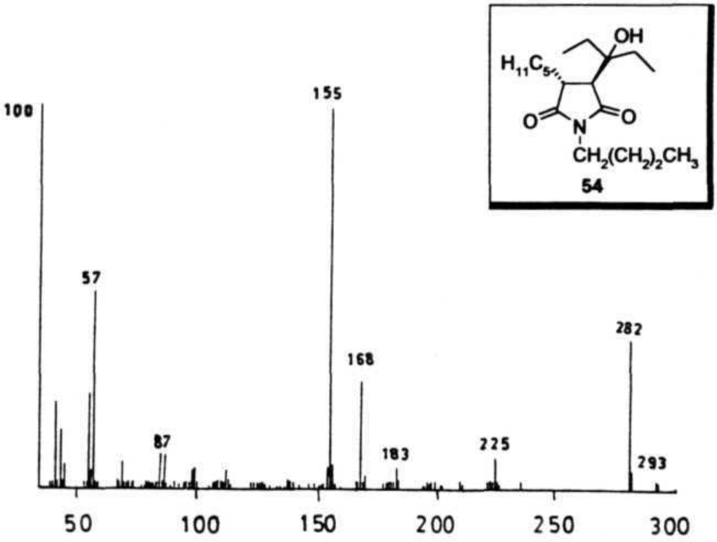
Spectrum No 17 (Chapter 2), ^{1}H NMR Spectrum (200 MHz, $CDCl_3$)



Spectrum No 18 (Chapter 2), ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



Spectrum No 19 (Chapter 2) Mass Spectrum (m/z-H_2O)



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LIST OF PUBLICATIONS

1. A new method for the regio and stereoselective hydrocarboxylation of alkynes using $NaHFe(CO)_4/CH_2Cl_2$ system

   M. **Periasamy**, U. Radhakrishnan, C. **Rameshkumar** and J.J. Brunet, *Tetrahedron Lett. 1991,38,* 1623.

2. Novel reaction of the $[HFe_3(CO)_{11}]^-$ reagent with alkynes: A new synthesis of cyclobutenediones

   M. Periasamy, C. Rameshkumar and U. Radhakrishnan, *Tetrahedron Lett.* **1997,** *38,* 7229.

3. New convenient one-pot methods of conversion of alkynes to cyclobutenediones or a,P-unsaturated carboxylic acids using novel reactive iron carbonyl reagents

   M. Periasamy, C. Rameshkumar, U. Radhakrishnan and J.J. **Brunet,** *J. Org. Chem.* **1998,** ***63*****, 4930.**

4. Amine induced carbonylation of alkynes to cyclobutenediones using $Fe_3(CO)_{12}$

   C. Rameshkumar and M. Periasamy, *Tetrahedron Lett.* (in press).

5. Reactive iron carbonyl reagent via reduction of $FeCl_3$ using $NaBH_4$ in the presence of CO: Conversion of 1-alkynes to benzoquinones and cyclobutene-diones

   C. Rameshkumar and M. Periasamy *Organometallics* (in press).

6. Novel Method of Conversion of Alkynes to Cyclic Imides Using Iron Carbonyl Complexes

   C. Rameshkumar and M. Periasamy (Communicated)

7. New One-Pot Methods of Conversion of Alkynes to Cyclobutenediones or Benzoquinones or Cyclic Imides Using Iron Carbonyl Reagents

   M. Periasamy and C. Rameshkumar (Under Preparation)

Review Article

1. New organic synthetic methods using iron carbonyl reagents

   M. Periasamy, C. Rameshkumar, U. Radhakrishnan and A. Devasagayaraj, *Current Science* (in press).