DEVELOPMENT OF ORGANIC SYNTHETIC METHODS USING IRON CARBONYL REAGENTS

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

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Dedicated To
My Parents, Brothers
and Teachers

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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, 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.

U. Radhakrishnan

U. RADHAKRISHNAN

CERTIFICATE

Certified that the work embodied in this thesis entitled **'Development of Organic Synthetic Methods Using Iron Carbonyl Reagents'** has been carried out by Mr. U. Radhakrishnan, under my supervision and the same has not been submitted elsewhere for a Degree.

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ABBREVIATIONS

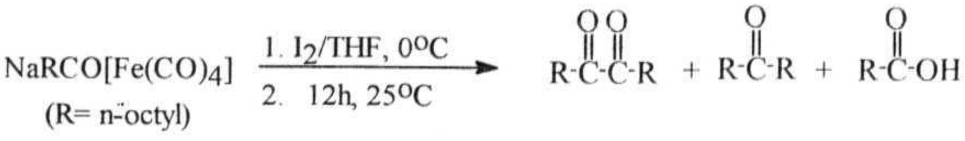
Bu-	butyl
CAN	ceric ammonium nitrate
CI	chemical ionisation
CTAB	cetyltriethylammonium bromide
E	electrophile
Et	ethyl
EI	electron impact
eq	equivalent
eqn	equation
HMPA	hexamethylphosphoric triamide
L or Ln	ligand
Me	methyl
M	metal
m-CPBA	*meta*-chloroperbenzoic acid
NBS	N-bromosuccinimide
NMP	N-methylpyrrolidine
OAc	acetyl
OTs	tosylate
n-	primary
Ph	phenyl
PTC	phase transfer catalyst
THF	tetrahydrofuran
TMSCl	trimethylsilyl chloride

ABSTRACT

This thesis describes studies on the **"Development of Organic Synthetic Methods using Iron Carbonyl Reagents".** It comprises of three chapters. Each chapter is subdivided into three parts, namely **Introduction, Results and Discussion** 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 reactivity of $RCOFe(CO)_4^-$ with I_2 and CuCl which led to a novel double carbonylation process. In the introductory section, a brief review on methods of preparation of $Na_2Fe(CO)_4$ and **its** synthetic applications are presented.

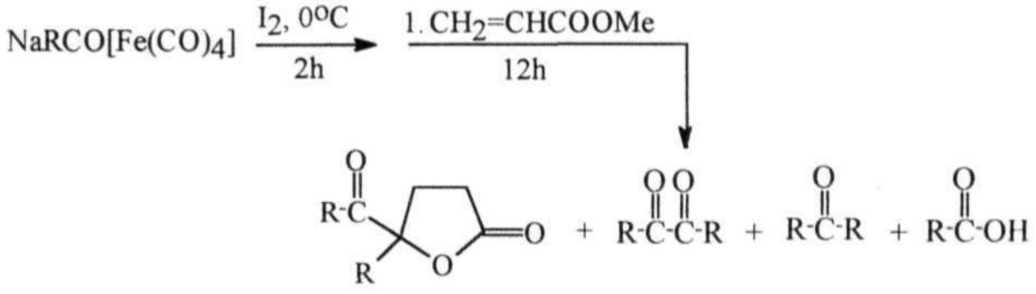
We have investigated the reaction of I_2 with $RCOFe(CO)_4^-$ in order to compare these results previously obtained in this laboratory with the $RCOFe(CO)_4^-/CuCl$ system. It has been observed that the reaction of $RCOFe(CO)_4^-$ with I_2 gives the corresponding 1,2-diketone (RCOCOR) (32%), dialkyl ketone (RCOR) (8%) and RCOOH (29%) (eqn 1).



$$\underset{(R=\text{ n-octyl})}{NaRCO[Fe(CO)_4]} \xrightarrow[\text{2. 12h, 25}^{o}\text{C}]{\text{1. }I_2\text{/THF, 0}^{o}\text{C}} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}R + R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \quad ..(1)$$

In experiments using methyl acrylate and $RCOFe(CO)_4^-/I_2$ system the corresponding acyllactones, 1,2-diketones, dialkyl ketones and carboxylic acids were obtained (Scheme 1).

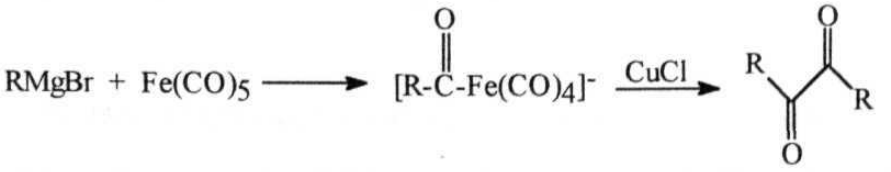
Scheme 1



R= n-hexyl	21%	18%	5%	7%
R=n-propyl	19%	16%	4%	6%

The results may be rationalized by envisaging the formation of $RCO\dot{F}e(CO)_4$ either through homolysis of both $I(RCO)Fe(CO)_4$ and $Cu(RCO)Fe(CO)_4$ or through one electron oxidation of $RCOFe(CO)_4^-$ by CuCl or I_2. Mechanism involving Fe(CO)4-a-diketone complex is considered to explain the results.

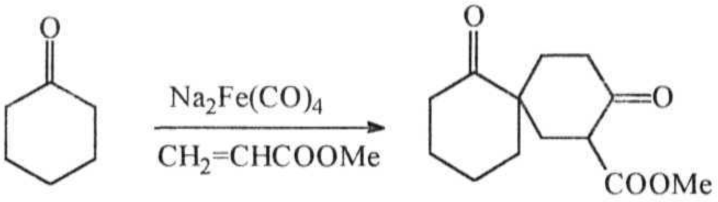
The R-M species on reaction with $Fe(CO)_5$ give $RCOFe(CO)_4^-$ which undergoes various useful transformations. However, the reactivity of $RCOFe(CO)_4^-$ generated in this way with CuCl has not been studied. We have observed that the reaction of $RCOFe(CO)_4^-$ with CuCl leads to the formation of the corresponding 1,2-diketones in moderate yields (eqn 2).



..(2)

Attempts were made to prepare cyclic 1,2-diketones through the reaction of $BrMg(CH_2)_nMgBr$ with $Fe(CO)_5$ and CuCl. However, the anticipated cyclic 1,2-diketones were not obtained.

In the second chapter, efforts undertaken towards further synthetic utilization of $Na_2Fe(CO)_4$ are described. In the course of an investigation on the synthesis of η^2-complexes of ketones, it was observed that the $Na_2Fe(CO)_4$ reagent readily reacts with cyclohexanone and methyl acrylate under ambient conditions to give the corresponding p-keto ester. In this transformation, a new cyclohexyl ring is constructed at the active methylene moiety (eqn 3).

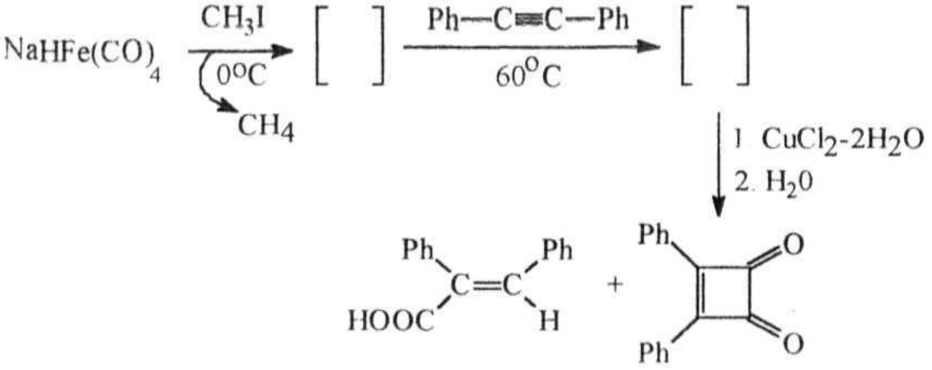


..(3)

It was found that the transfonnation is general and several other ketones were converted to the corresponding P-keto esters in moderate yields. The transformation can be rationalised by a sequence of reactions involving double Michael additions followed by Dieckmann cyclization through enolate intermediates. We have also observed that the cyclic products are obtained when $NaOCH_3$ was utilized in the place of $Na_2Fe(CO)_4$. Surprisingly, such a simple transformation has not been reported earlier.

The third chapter deals with the investigations of the reactivities of iron carbonyl species generated using the $NaHFe(CO)_4$/RX and $NaHFe(CO)_4/Me_3SiCl$ reagent combinations towards various alkynes. In the introductory section, various methods of preparation and synthetic applications of $NaHFe(CO)_4$ and "$Fe(CO)_4$", are briefly discussed.

Originally, Whitmire *et al* observed the formation of the weak complex $Fe(CO)_4(CH_3CN)$, in the reaction of $[Et_4N]HFe(CO)_4$ with CH3I in CH3CN. It was of our interest to utilize the $Fe(CO)_4(CH_3CN)$ prepared in this way for synthetic applications. We have found that the reagent generated *in situ* by the reaction of $NaHFe(CO)_4$ with CH_3I reacts with diphenylacetylene to give the corresponding cyclobutenedione and α,β-unsaturated carboxylic acid in moderate yields (eqn 4).



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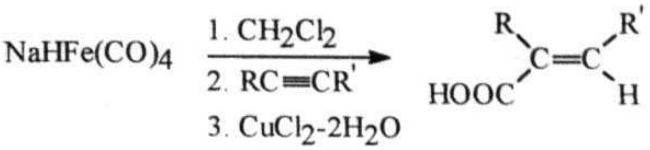
Several other alkynes have been converted to the corresponding cyclobutenediones and α,β-unsaturated carboxylic acids.

It has been also observed that the reaction using CH_2Cl_2 in the place of CH_3I results in the formation of α,β-unsaturated carboxylic acids as a major product in a regio- and stereoselective manner besides traces of cyclobutenediones (eqn 5). The generality of this process was examined by performing the experiment with several other alkynes.



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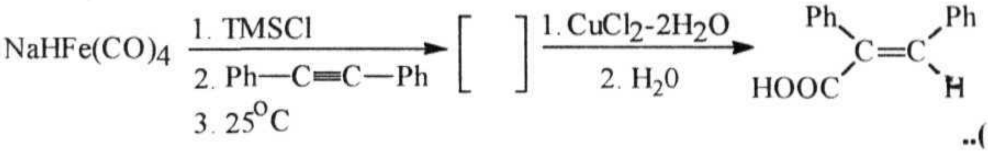
We have also utilized the readily available Me_3SiCl (TMSC1) in combination with $NaHFe(CO)_4$ for the carbonylation of alkynes. In this case, the carbonylation studies gave fruitful results. It was observed that the reaction of $NaHFe(CO)_4$/TMSCl with alkynes at room temperature (25°C) results in corresponding hydrocarboxylated products in a regio- and stereoselective fashion (eqn 6).



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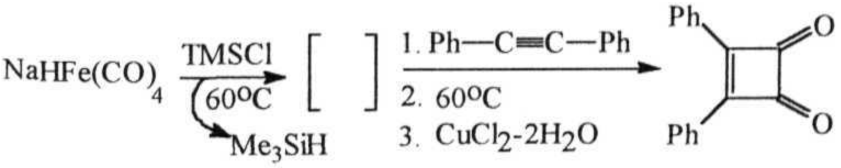
Surprisingly, it was found that the reaction at 60°C produced the corresponding cyclobutenedione as the only product in good yields (eqn 7).



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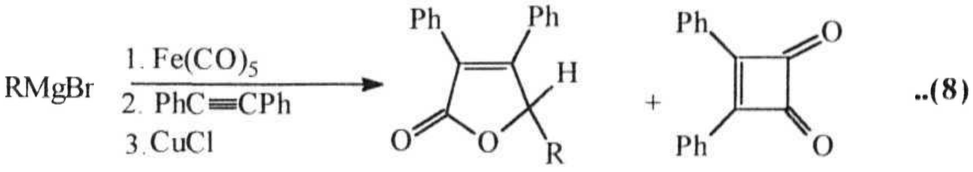
Tentative mechanisms are discussed to explain the formation of cyclobutenediones and α,β-unsaturated carboxylic acids in the experiments summarized above.

We have also examined the reaction of alkynes with the $NaHFe_2(CO)_8/CH_3I$ and the $(CO)_4Fe(CH_3CN)$ complex, prepared through photolysis of $Fe(CO)_5$ inCH_3CN. The results are discussed.

In a previous study on the reaction of $RCOFe(CO)_4^-/CuCl$, the intermediacy of $RCO\dot{F}e(CO)_4$ and $Fe(CO)_4$-α-diketone complexes were considered. In order to compare the reactivities expected for these species with other reagent combinations described in this chapter, we have investigated the reactions in the presence of alkynes. It was observed that the $RCOFe(CO)_4^-$ reagent generated using RMgBr and $Fe(CO)_5$ reacts with alkynes and CuCl to give the corresponding butenolides and cyclobutenediones in moderate yields (eqn 8).



..(8)

The probable reaction pathways and the intermediates responsible for the formation of the cyclobutenediones and butenolides are discussed.

CHAPTER 1

Studies on the Reactivities of $R(CO)Fe(CO)_4^-$ with I_2 or CuCl: Synthetic and Mechanistic Studies of the Formation of 1,2-Diketones

1.1 Introduction

In recent years, transition **metal** reagents find several interesting and unique applications in synthetic organic chemistry. In several occasions, these reagents have been used by synthetic organic chemists to avoid usual complications in chemical reactions .[1] Through organometallic reagents, it becomes possible to achieve bond forming reactions between atoms in almost any sort of functional environment, regardless of the presence or absence of any particular polarity.[2] Molecules which are too unstable can be stabilised by complexing it with metals. The transition metals can be also used to alter the stereochemical and stereoelectronic course of organic transformations.[3]

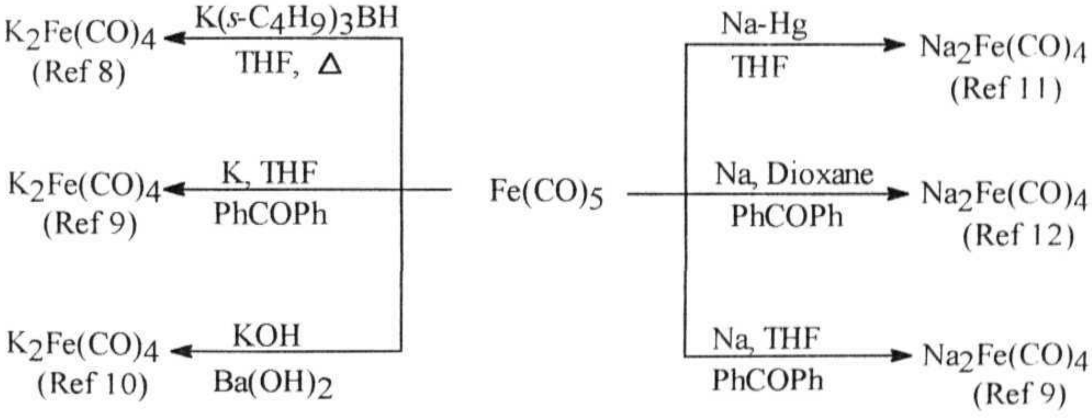
The major class of organometallic compounds, namely the metal complexes of carbon monoxide, has become a subject of extensive research which will obviously continue to grow. Carbonyl complexes of the transition metals are of immense interest because of their unusual reactivity and potential as homogeneous catalysts in oxidation, reduction, isomerization, oligomerization, carbonylation and polymerization reactions.[4,5] Indeed, the work with the metal carbonyls provided the concepts such as 7r-complex formation between the unsaturated compounds and transition metals, the ligand and substrate insertions, the associative and dissociative mechanisms, and the oxidative and reductive eliminations.[5] .

Among various transition metal carbonyl complexes, the organoiron complexes have potential in all these aspects.[6] The iron carbonyls are known to form stable neutral, anionic and hydrido carbonyl complexes.[7] In recent years, the $Na_2Fe(CO)_4$ has been shown to be a useful synthetic reagent. Since, our objective is to develop new synthetic methods using $Na_2Fe(CO)_4$, **a** brief review on the synthesis and utilization of this reagent will be helpful.

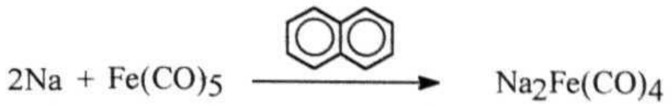
1.1.1 Synthesis and Applications of $Na_2Fe(CO)_4$

The super nucleophile $Na_2Fe(CO)_4$ ((Tollman reagent) has been demonstrated to be a versatile reagent in many organic transformations.[12] Numerous methods are available for the preparation oi' this useful reagent from readily available starting materials (Scheme 1).[8-12]

Scheme 1



Practically useful procedures have been developed in this laboratory for the preparation of $Na_2Fe(CO)_4$ through the reduction of either readily accessible $FeCl_3$ or the inexpensive $Fe(CO)_5$ with sodium-naphthalenide (eqn 1).[13] In the case of $FeCl_3$, the reaction has been carried out at atmospheric pressure of CO (eqn 2).[13]



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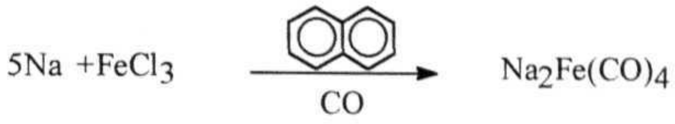
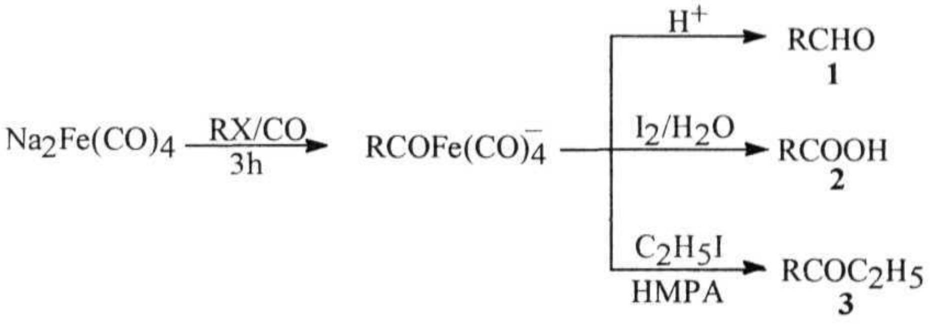


(2)

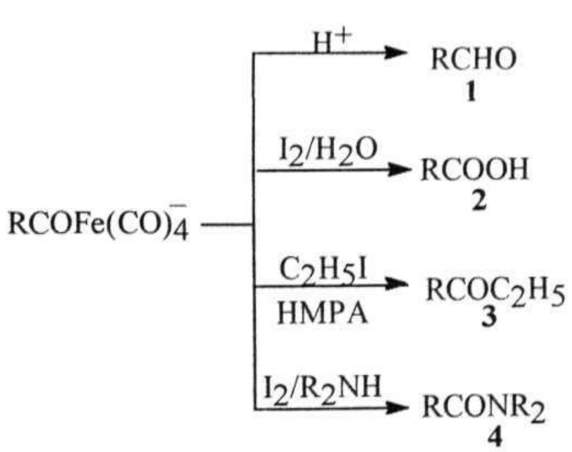
The formation of $Na_2Fe(CO)_4$ has been confirmed by performing the anticipated reactions with aliphatic halides to obtain the corresponding aldehydes, carboxylic acids and ketones (Scheme 2).[13]

Scheme 2



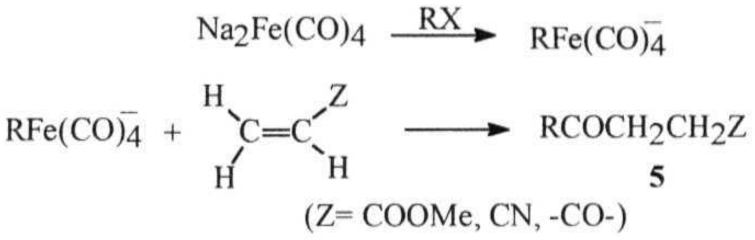
Previously, Collman *et al* demonstrated the synthetic applications of $Na_2Fe(CO)_4$, in the conversion of aliphatic halides and sulphonates to aldehydes, unsymmetrical ketones, carboxylic acids, esters and amides (Scheme 3).[12]

Scheme 3



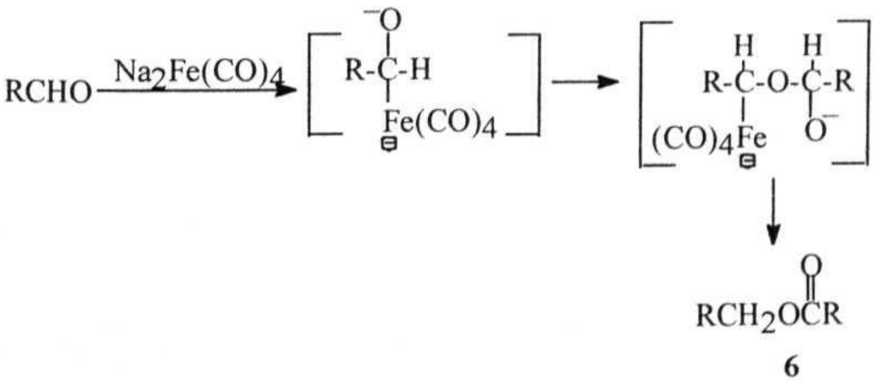
Principal advantages of these methods are high yields, stereospecificily and toleration of unmasked functional groups.[12]

Cooke *et.al* reported that the $NaRFe(CO)_4$ intermediate undergoes multiple insertion reactions with a variety of Michael acceptors giving p-keto derivatives of esters, ketones and nitriles respectively (eqn 3).[14]



..(3)

It has been reported that aromatic aldehydes undergo Tishchenko type reaction to give esters upon treatment with $Na_2Fe(CO)_4$. In this reaction, the ferrate complex acts both as a base and hydride transfer agent (eqn 4).[15]



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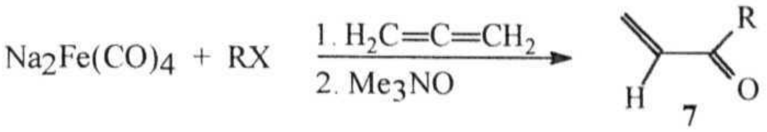
(4)

Guinot *et al* used the acyliron anion and allene for the synthesis of a, β-unsaturated ketones in good yield. The organic product was liberated from the intermediate complex by amine oxide oxidation (eqn 5).[16]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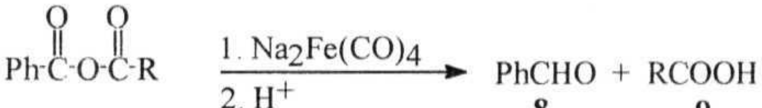
(5)

It is well known **that** the carboxylic acid anhydrides react with $Na_2Fe(CO)_4$ to give the reduced products *i.e.* aldehydes or aldehydic acids. Acyclic acid anhydrides give aldehydes and carboxylic acids (eqn 6), while, cyclic derivatives give aldehydic acids (eqn 7).[17]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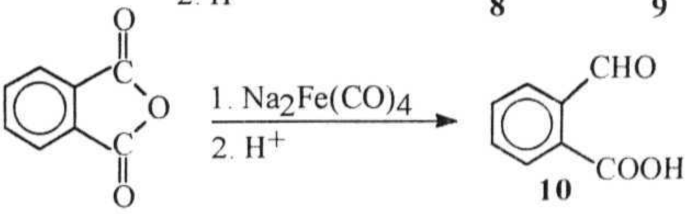
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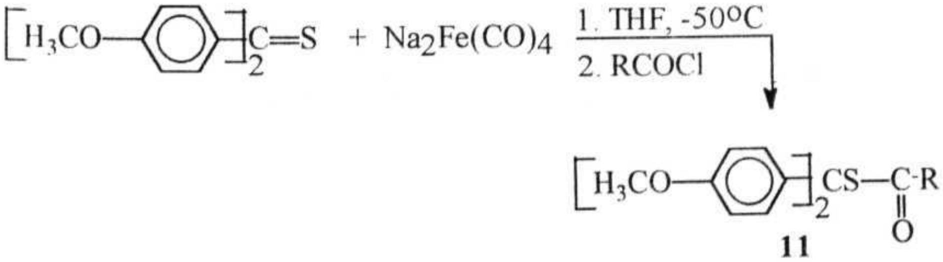
(7)

Alper and his co-workers reported that the $Na_2Fe(CO)_4$ on reaction with a non enolizable thione and subsequent addition of an acid chloride affords thio esters in modest yields (eqn 8).[18]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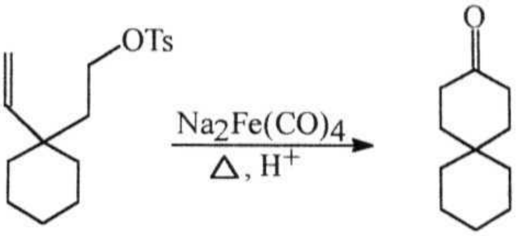
(8)

An interesting, potentially useful reaction has been reported in the synthesis of cycloalkanones through carbonylative cyclization of olefinic tosylates with $Na_2Fe(CO)_4$ (eqn 9).[19]



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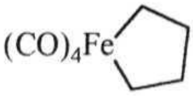
(9)

Metallocyclopentanes, have been prepared by the nucleophilic elimination-cycloaddition of tetramethylene bis(trifluoromethanesulfonate) with $Na_2Fe(CO)_4$ (eqn 10).[20]

$[Fe(CO)_4]^{2-} + (CF_3O_3SCH_2CH_2)_2 \longrightarrow (CO)_4Fe$



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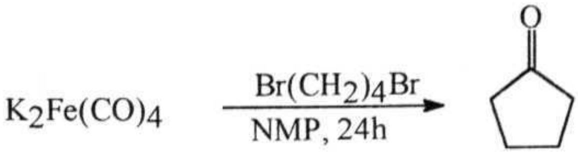
(10)

Yamashita and his co-workers developed a facile synthetic method for the five membered cyclic ketones from 1,4-dihalo compounds using $K_2Fe(CO)_4$ as a carbonylating agent (Scheme 4).[21]

Scheme 4



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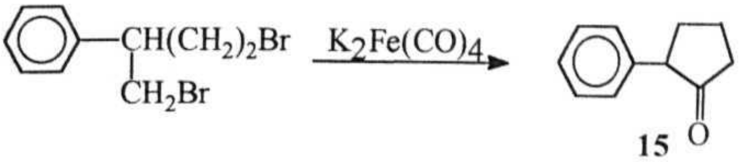

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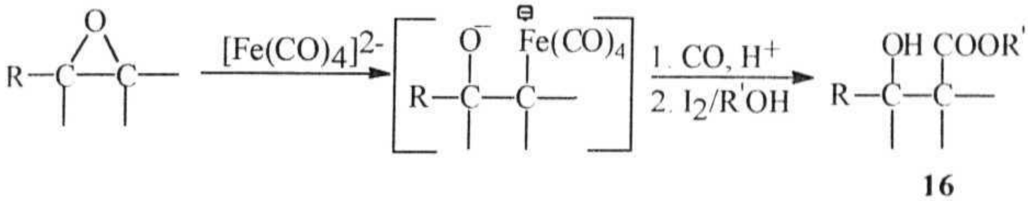
Reaction of ethanolic solutions of $Na_2Fe(CO)_4$ with epoxides followed by oxidative decomposition using I_2 gives p-hydroxy esters (eqn 11).[22,23]



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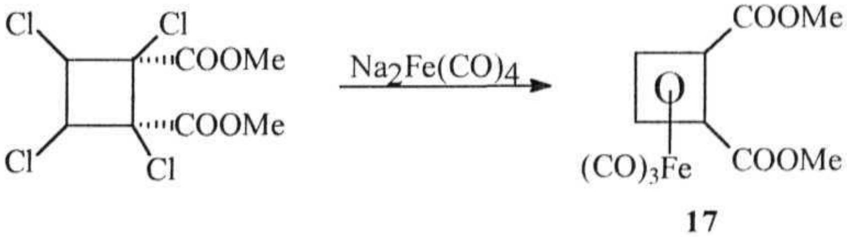
..(11)

Cyclobutadiene, which has only fleeting existence, has been generated *in situ* and isolated as stable cyclobutadieneiron tricarbonyl complexes using $Na_2Fe(CO)_4$. The complexed cyclobutadiene undergoes a variety of electrophilic substitution reactions (eqn 12).[24]



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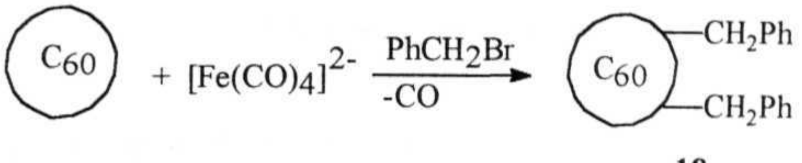
..(12)

New synthesis of fullerene derivatives, which have potentiality in a wide range of material science applications, have been prepared using $Na_2Fe(CO)_4$ (eqn 13)25



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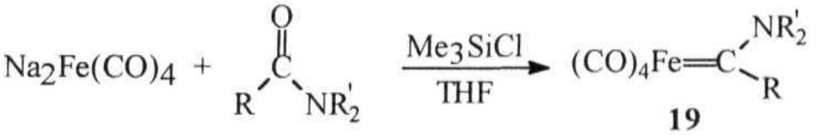
Recently, it has been reported that the (aminocarbene)tetracarbonyliron (0) complexes without hydrogen atoms at the a-position of carbene atom can be easily prepared by the reaction of amides with $Na_2Fe(CO)_4$ and chlorotrimethyl silane in THF solution (eqn 14).[26]



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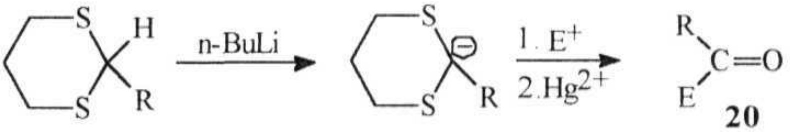
As outlined earlier, we have easy access to $Na_2Fe(CO)_4$ using $FeCl_3$ or $Fe(CO)_5$. We have decided to further examine the synthetic utility of the $Na_2Fe(CO)_4$ reagent and also to investigate the reactivity of the $R(CO)Fe(CO)_4^-$/CuCl or I_2 systems.

1.2 Results and Discussion

1.2.1 Reaction of $(RCO)Fe(CO)_4^-$ with I_2:

There has been immense interest towards the development of a method for the synthesis of nucleophilic acylanion $RC(O)^-M^+$, where the CO polarization will be δ^- on the carbon atom of carbonyl group.[27] However, these attempts did not succeed in a substantial way. Subsequently, organic chemists developed an alternative methodology involving "masked acylanion synthons or equivalents" (eqn 15).[28,29]



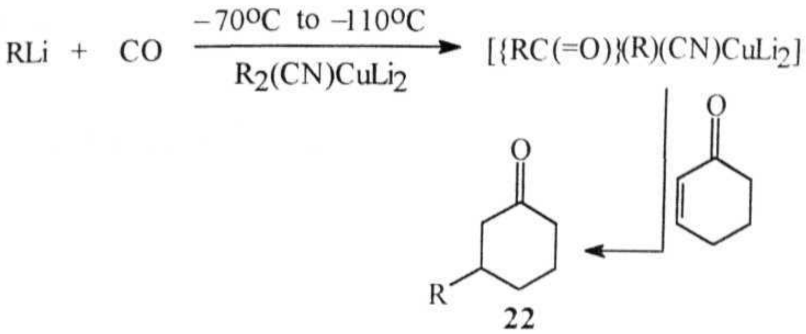
20 (15)

In recent years, Seyferth *et al* have developed a low temperature *in situ* synthesis of "RCOLi". Addition of these species to electrophiles gives useful organic products (eqn 16).[30]

$$RLi + CO \xrightarrow{-110^oC} \text{"RCOLi"} \xrightarrow{R^1CO_2R^2} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^1 \qquad (16)$$

21

More recently, an acyl cuprate reagent, $[(RCO)(R)(CN)CuLi_2]$ prepared at -70°C to -110°C has been used in the acylation of α,β-unsaturated compounds (eqn 17).[31-35]



22

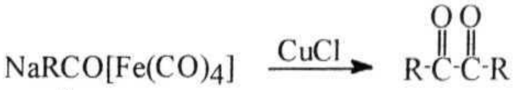
(17)

As it has been discussed earlier, a simple method was developed in this laboratory for the preparation of the Collman reagent *in situ* by the reduction of $FeCl_3$ or $Fe(CO)_5$ using sodium-naphthalenide radical anion (eqn 1 and eqn 2).[13]

It was thought that the acyl species of the type "RCOCu" would result in the reaction between $Na(RCO)Fe(CO)_4$ and CuCl (eqn 18).

$$NaRCO[Fe(CO)_4] \xrightarrow{CuCl} \text{"RCOCu"} + NaCl \quad (18)$$

During this investigation, it was observed in this laboratory that the reaction of $Na(RCO)Fe(CO)_4$ with CuCl al room temperature affords 1,2-diketones (eqn 19).[36]

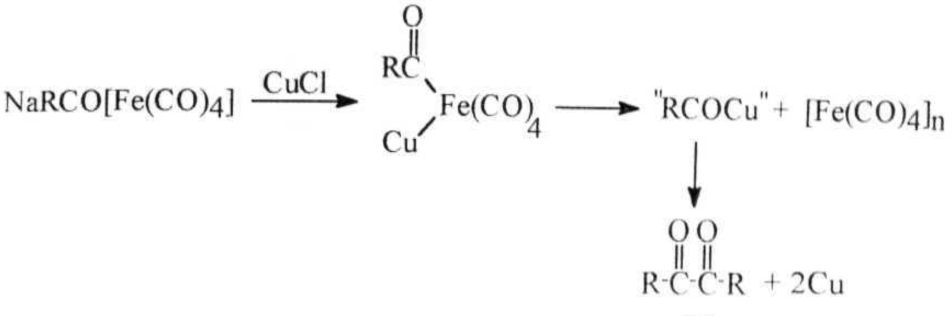


$$NaRCO[Fe(CO)_4] \xrightarrow{CuCl} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \quad (19)$$

23

Initially, it was envisaged that this transformation may go through the sequence which might involve "RCOCu" intermediate (Scheme 5).

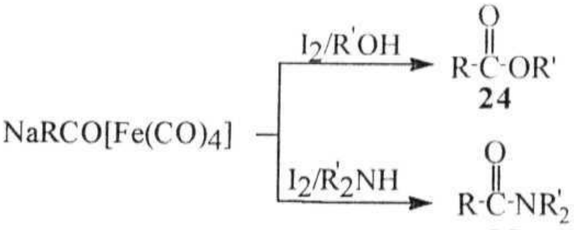
Scheme 5



23

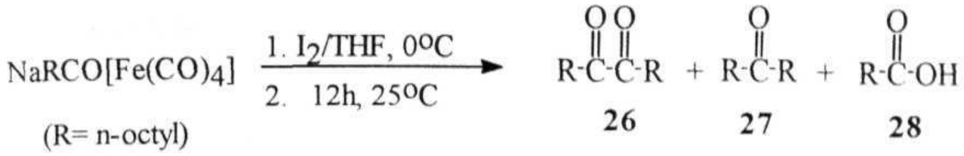
It is well known that the $Na(RCO)Fe(CO)_4$ on treatment with I_2 in the presence of nucleophiles undergoes various useful transformations (Scheme 6).[12]

Scheme 6



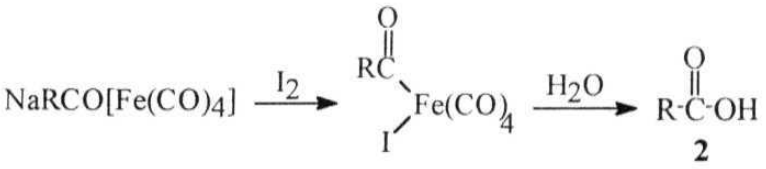
In these transformations, "RCOI" has been proposed as an intermediate.[12] However, the reactivity of $Na(RC0)Fe(C0)4$ with I_2 has not been studied in the absence of nucleophiles. Reaction of Br_2 with $ArCO[Ni(CO)_3]^-$ 'nas been reported to give the corresponding 1,2-diketones and diaryl ketones.[37] Similar products could be expected in the reaction of $Na(RC0)Fe(C0)4$ with I_2. Hence, it was thought that the reaction using I_2 will throw some light on the mechanism of the formation of 1,2-diketone observed in the reaction using CuCl. Therefore, it was decided to examine the reaction of $Na(RCO)Fe(CO)_4$ with I_2.

It was observed that the reaction of $Na(RCO)Fe(CO)_4$ (R= n-octyl) with I_2(1 eq) in THF at 0°C for 2h and for 12h at 25°C leads to 1-nonoic acid (29%), the corresponding 1,2-diketone (32%) and the dialkyl ketone (8%) (eqn 20).[38]



(20)

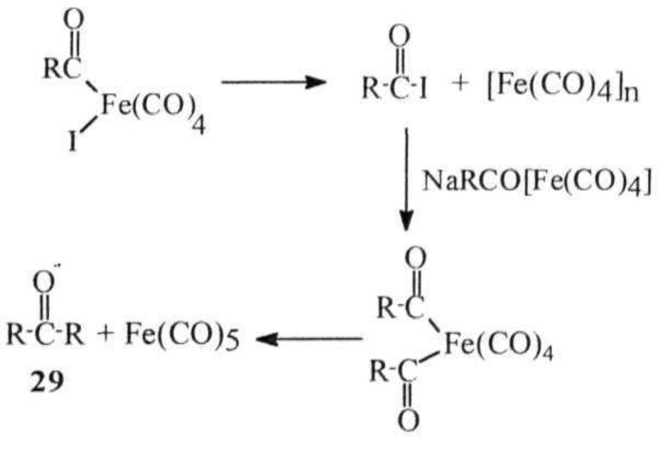
The reaction of I_2 with $Na(RCO)Fe(CO)_4$ is not clean compared to that realised with the $Na(RCO)Fe(CO)_4$ /CuCl system, but the interesting point is that the 1,2-diketone is also formed in this case. Presumably, the carboxylic acid could have formed by the attack of H_2O on the $I(RCO)Fe(CO)_4$ species (eqn 21).



(21)

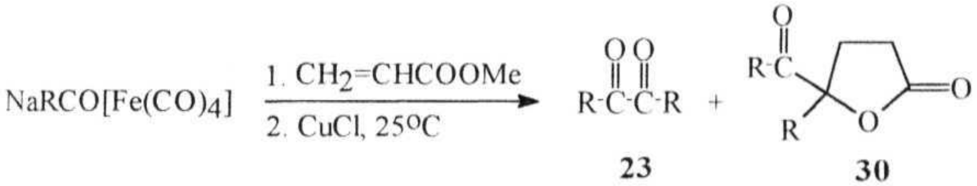
If the I(RC0)Fe(C0)4 could exhibit reactivities similar to "RCOI", the formation of dialkyl ketone is not unexpected since it is known that the reaction of R'COCl with Na(RC0)Fe(C0)4 gives dialkyl ketones (Scheme 7).[12]

Scheme 7



1.2.2 Reaction of Na(RCO)Fe(CO)4 with I_2 in the presence of methyl acrylate

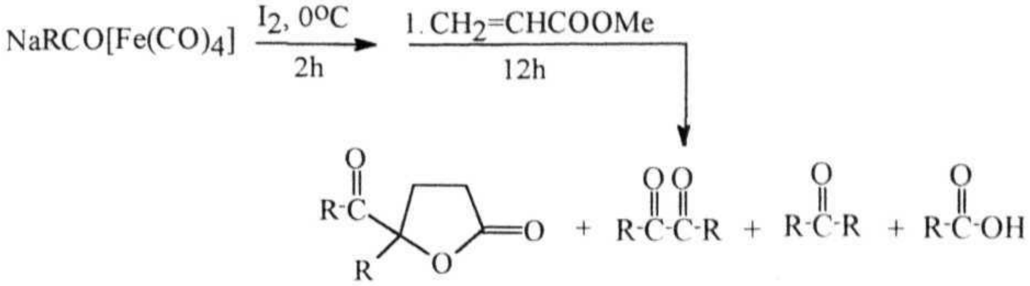
It has also been observed earlier that the reaction of Na(RCO)Fe(CO)4 with CuCl in the presence of methyl acrylate produces acyllactones (35-52%) and 1,2-diketones (20-28%) (eqn 22).[38]



(22)

Since, both the reagent systems, $Na(RCO)Fe(CO)_4/CuCl$ and $Na(RCO)Fe(CO)_4/I_2$, lead to the formation of 1,2-diketones, it was decided to examine the reactivity of the $Na(RCO)Fe(CO)_4/I_2$ combination in the presence of methyl acrylate. The reaction was carried out using Na(RCO)Fe(CO)4 (R= n-hexyl) (1 eq), I_2 (1 eq) and methyl acrylate (3 eq). After the workup and column chromatography, the corresponding acyllactone (21%), 1,2-diketone (18%), dialkyl ketone (6%), and heptanoic acid (7%) were isolated (Scheme 8). The product distribution and the reactivity pattern was found to be same when 1-bromopropane was used (Scheme 8).[38]

Scheme 8

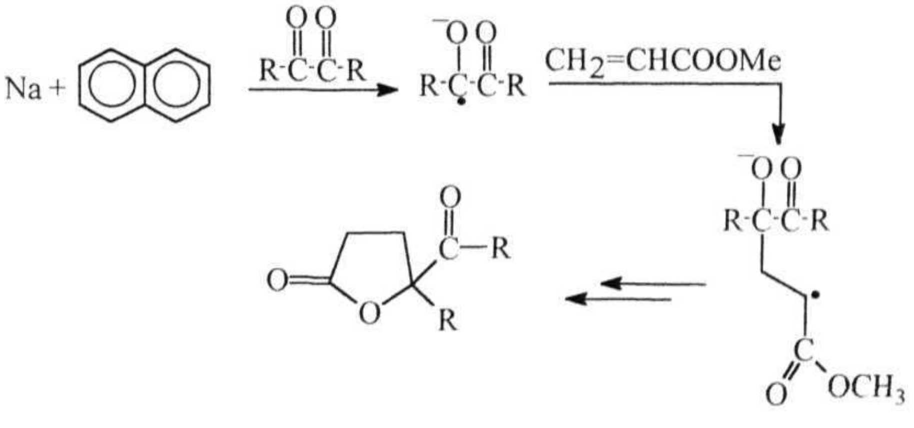


R= n-hexyl **31** (a)21% (b)18% (c)5% (d)7%

R=n-propyl **32** (a)19% (b)16% (c)4% (d)6%

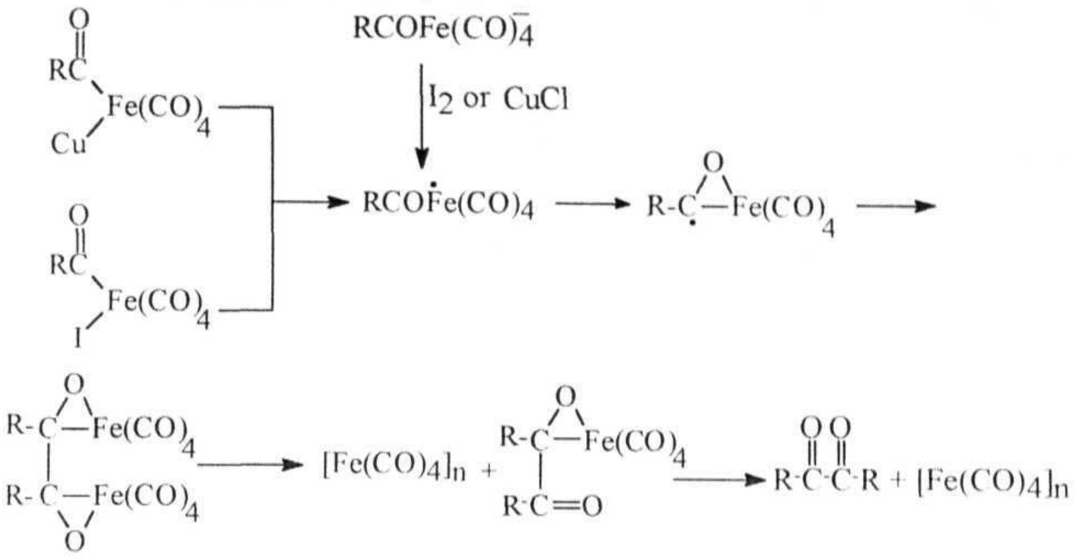
The formation of acyllactone in the reaction of $Na(RCO)Fe(CO)_4/I_2$ with methyl acrylate rules out the possibility of this product being produced through one electron reduction of the 1,2-diketone by some unused sodium-naphthalenide, since, it is unlikely to survive in the presence of I_2 (Scheme 9).

Scheme 9



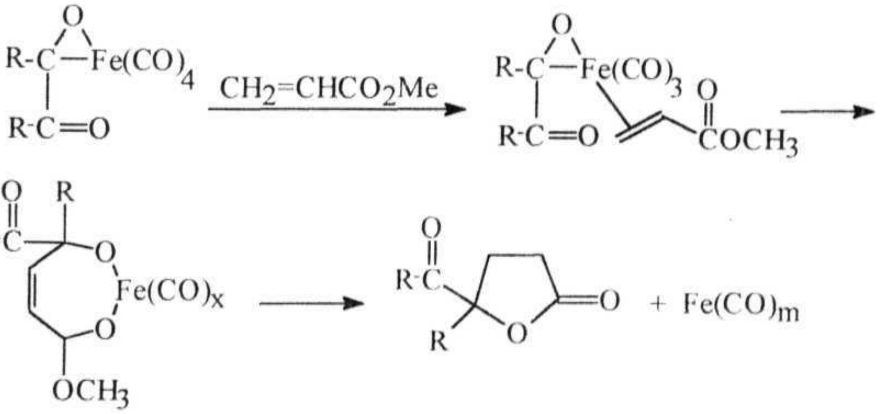
It seems likely that, the $RCO\overset{\bullet}{F}e(CO)_4$ species is responsible for the formation of 1,2-diketones and acyllactones. It may be formed through either the homolysis of I(RC0)Fe(C0)4 and Cu(RC0)Fe(C0)4 or more likely through one electron oxidation by CuCl or I_2 (Scheme 10).

Scheme 10

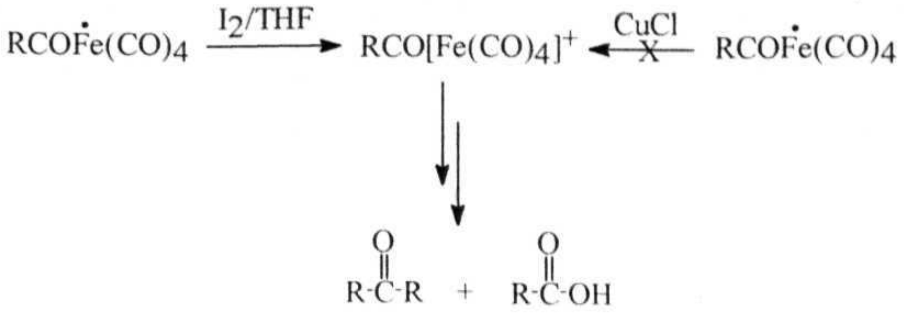


The lactone formation may be rationalized as outlined in Scheme 11.

Scheme 11



In the case of $Na(RCO)Fe(CO)_4/I_2$, the reaction is somewhat unclean. Probably, the I_2 might further oxidize the $RCOFe(CO)_4$ to $RCO[Fe(CO)_4]^+$ which may not be formed in the reaction using CuCl (eqn 23).



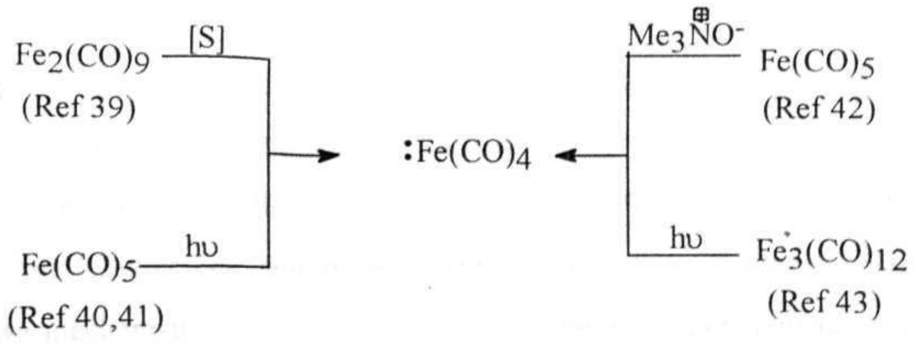
..(23)

1.2.3 **Photochemical** reaction of $\mathbf{Fe(CO)_5}$ with 1,2-diketone and **methyl** acrylate .

In the mechanism proposed for the formation of 1,2-diketones (Scheme 10) and the acyllactones (Scheme 11), it is visualized that the olefin gets inserted into an η^2–bound ketone. This implies that a 1,2-diketone should react with "$Fe(CO)_4$" and methyl acrylate to give the acyllactone.

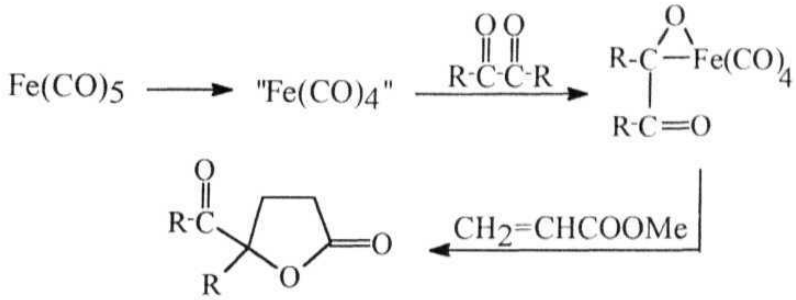
The "$Fe(CO)_4$" is a coordinatively unsaturated, 16 electron species. It can be generated using $Fe_2(CO)_9$ or from $Fe(CO)_5$ on irradiation or using Fe(CO)5 through oxidative removal of one CO with amine oxide or by irradiation of $Fe_3(CO)_{12}$ (Scheme 12)[39-43]

Scheme 12

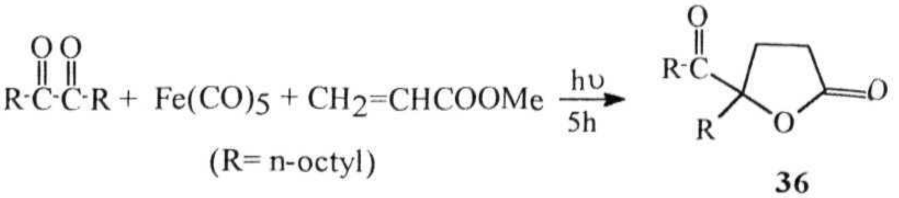


It was expected that the "Fe(C0)4" generated *in situ,* by one of the methods mentioned in the Scheme 12, on reaction with 1,2-diketone would give the corresponding η^2-complex which in turn upon reaction with methyl acrylate could lead to the formation of the acyllactone (Scheme 13).

Scheme 13



In order to examine the reactivity anticipated for the "$Fe(CO)_4$" species, we carried out the photolysis of a mixture of $Fe(CO)_5$, RCOCOR (R= n-octyl), and methyl acrylate using a 450 W medium pressure mercury lamp for 5h. After workup, the corresponding acyllactone was isolated in 28% yield along with an unidentified metal carbonyl and unreacted 1,2-diketone (eqn 24).[38]



36

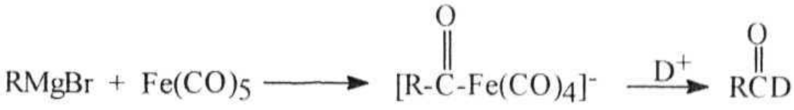
..(24)

The acyllactone was not formed, when the reaction was carried out in the absence of $Fe(CO)_5$. Although the yield of the acyllactone is poor, the result illustrates the ability of the coordinatively unsaturated iron carbonyl species to react with 1,2-diketone and methyl acrylate to give acyllactone. Hence, the tentative mechanistic proposals outlined in Scheme 10 and Scheme 11, are not unreasonable.

1.2.4 Reaction of RMgBr and $Fe(CO)_5$ with CuCl

Transition metal carbonyl complexes are known to form mechanistically and theoretically interesting compounds on reaction with nucleophiles.[2] The organomagnesium compounds are reactive towards metal carbonyls and add reductively to form rather stable anionic metal complexes.[5] The neutral carbonyls of iron are also reactive towards organomagnesium compounds to form the corresponding acyl ferrate complexes.[44]

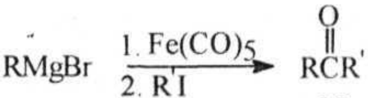
Only few reports appeared in the literature, that describes the synthetic applications of $RCOFe(CO)_4^-$ generated in the reaction of RMgBr with $Fe(CO)_5$. A practically useful method has been developed for the synthesis of deuterated aldehydes (aldehyde-d) from Grignard reagents using $Fe(CO)_5$ as the carbonylating agent (eqn 25).[44]



$$RMgBr + Fe(CO)_5 \longrightarrow [R\overset{O}{\overset{\|}{C}}\text{-}Fe(CO)_4]^- \xrightarrow{D^+} R\overset{O}{\overset{\|}{C}}D \qquad (25)$$

37

Yamashita *el al* reported the formation of dialkyl ketone through alkylation of $R(CO)Fe(CO)_4^-$ (eqn 26)[45]



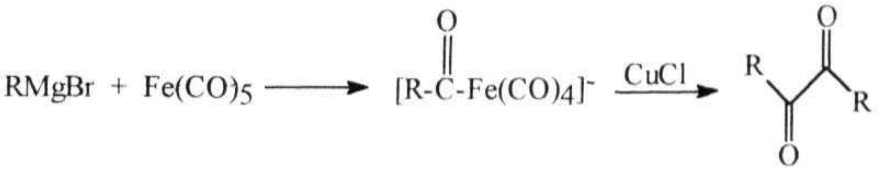
$$RMgBr \xrightarrow[2.\ R'I]{1.\ Fe(CO)_5} R\overset{O}{\overset{\|}{C}}R' \qquad \textbf{(26)}$$

38

As mentioned earlier, a novel double carbonylation reaction was observed in the reaction of $Na(RCO)Fe(CO)_4$ with CuCl. In continuation of this study, we have decided to synthesise the $RCOFe(CO)_4^-$ species using RMgX and $Fe(CO)_5$ for studying its reaction with CuCl.

The reaction was carried out as follows: $RCOFe(CO)_4^-$, was generated *in situ* by the reaction of RMgBr (R= n-butyl) with $Fe(CO)_5$ in THF. The mixture was treated with CuCl and stirred further for 4h. After workup and column chromatography, the 1,2-diketone was isolated (Scheme 14).

Scheme 14

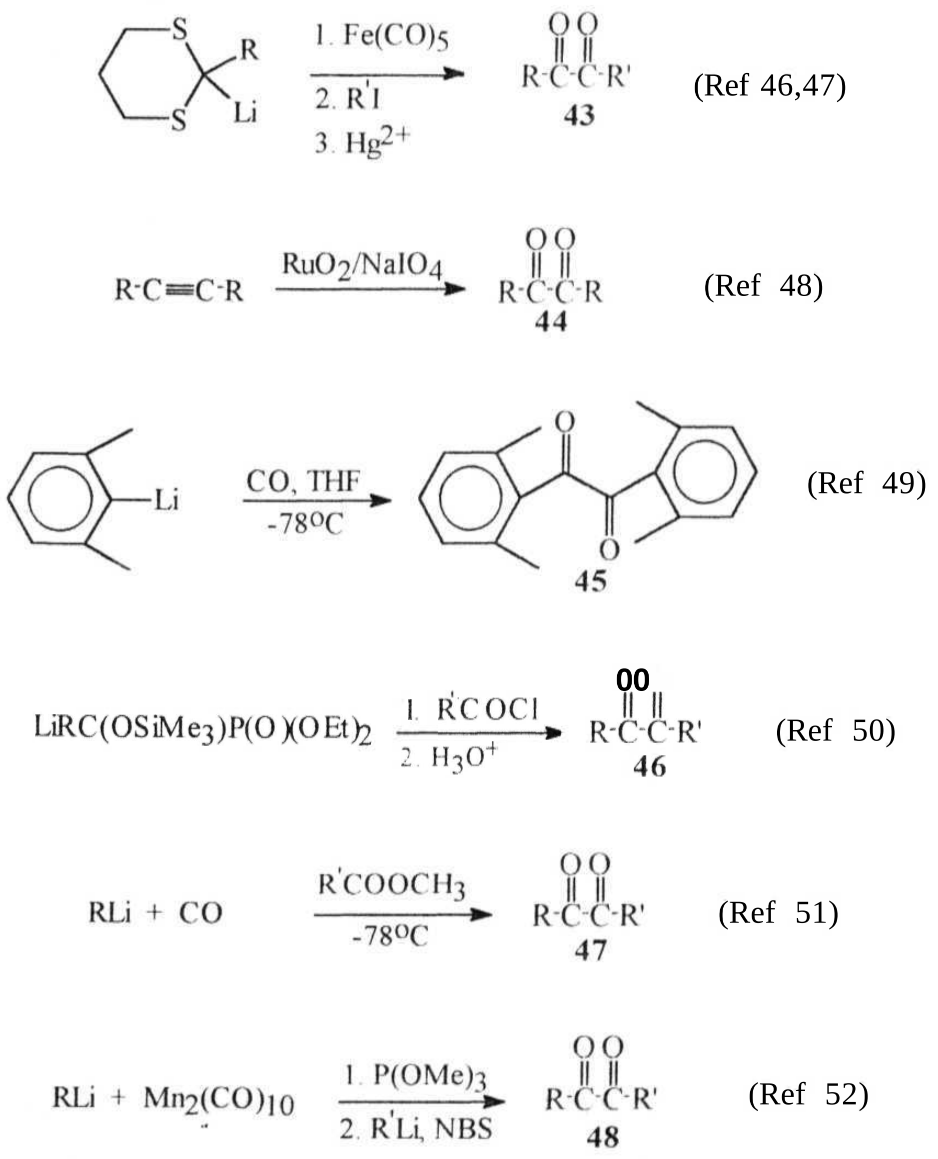


R= n-Butyl	39	45%
R= n-Octyl	40	48%
R= n-hexyl	**41**	48%
R= Ph	42	50%

It was found that the transformation is general and several other alkyl bromides were converted to the corresponding 1,2-diketone. It may be of interest to note that aryl bromides can also be used as substrates for the synthesis of 1,2-diketones (42) in this way which is not possible using $Na_2Fe(CO)_4$. Even though, the yields are somewhat low and toleration of functional groups sensitive to Grignard reagent are not possible under these reaction conditions, this method can be considered as an alternate method for the 1,2-diketone synthesis discussed earlier.

Number of methods have been reported for the synthesis of a-diketones (Scheme 15).[46-52]

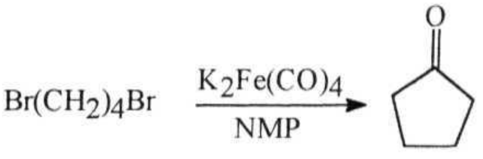
Scheme 15



The present method may serve as a good alternate procedure for the synthesis of a-diketones since it requires readily available starting materials.

1.2.5 Attempts towards synthesis of cyclic a-diketones

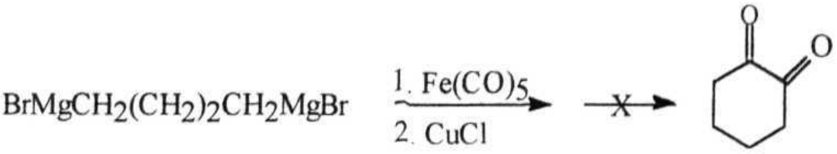
As shown in the earlier section, the reaction of $Na(RCO)Fe(CO)_4$ or $RMgBr/Fe(CO)_5$ (Scheme 14) with CuCl gives a-diketone in good yields. It has been reported that 1,4-dibromides on reaction with $K_2Fe(CO)_4$ gives cyclopentanones in moderate yields (eqn 27).[21]



12

(27)

In continuation of the investigation on the a-diketone synthesis, we envisaged the synthesis of cyclic a-diketones in the reaction of 1,4-dibromide/Mg with $Fe(CO)_5$ and CuCl. When the reactions were carried out, the expected cyclic a-diketones were not obtained. Only some unidentified products were isolated in small amounts (eqn 28).



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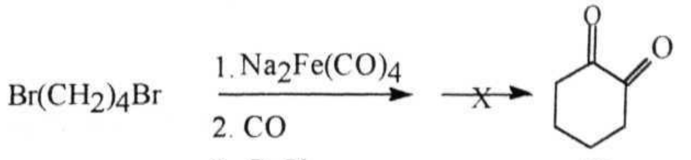
(28)

It was thought that the Grignard reagent may be formed in low yields which may be responsible for the complications. It was expected that the $Na_2Fe(CO)_4$ may give better results. To examine this, the reactions were carried out using $Na_2Fe(CO)_4$ and the 1,4-dibromide. Unfortunately, the expected cyclic diketone was not obtained. Instead, only unidentified compounds were isolated (eqn 29).



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..(29)

Attempts towards the synthesis of cyclic a-diketones using dibromides such as 1,5-dibromopentane, 1,6-dibromohexane and 1,10-dibromodecane, were also not successful.

1.3 Conclusions

The $Na_2Fe(CO)_4$ reagent, prepared using $Fe(CO)_5$/Na/naphthalene was utilized for the synthesis of $NaRCOFe(CO)_4$. The reaction of $NaRCOFe(CO)_4$ with I_2 leads to the formation of 1,2-diketones (RCOCOR), RCOR and RCOOH. It was found that the reaction of $Na(RCO)Fe(CO)_4$ with I_2 in the presence of methyl acrylate leads to the formation of acyllactone besides RCOCOR, RCOR and RCOOH. It appears that the $(RCO)Fe(CO)_4$ species formed, either from $I(RCO)Fe(CO)_4$ and $Cu(RCO)Fe(CO)_4$ through homolysis of Fe-I and Fe-Cu bonds or through one electron oxidation of $(RCO)Fe(CO)_4^-$ by I_2 or CuCl, may be responsible for the formation of 1,2-diketone and acyllactone via the intermediacy of η^2-type of complexes. It was also observed that the reagent generated using RMgBr and $Fe(CO)_5$ on treatment with CuCl gives the corresponding 1,2-diketones. Attempted synthesis of cyclic 1,2-diketones was not successful.

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 1310 and JASCO FT 5300 with polystyrene as reference. ^{1}H and ^{13}C NMR spectra were recorded on JEOL-FX-100 and Bruker-AC-200 spectrometer with chloroform-d as a solvent and TMS as reference (8 = 0 ppm). Elemental analyses were performed on a Perkin-Elmer elemental analyzer model-240 C. Analytical thin layer chromatographic tests were carried out on glass plates (3 x 10 cm) coated with 250 mμ acme's silica gel-G or G_{254} containing 13% calcium Sulfate as binder. The spots were visualized by short exposure to iodine vapour or UV light. Column chromatography was carried out using acme's silica gel (100-200 mesh).

All glassware was pre-dried at 140^{o}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.[53] Reagents prepared *in situ* in solvents were transformed using a double ended stainless steel (Aldrich) needle under a stream of nitrogen whenever required.

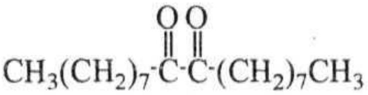
In all experiments, a round bottom flask of appropriate size with a side arm, a side septum, a magnetic stirring bar, a condenser and a connecting tube attached to a mercury bubbler were used. The outlet of the mercury bubbler was connected by a long tube to the atmosphere. All dry solvents and reagents (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 materials judged homogenous by TLC, IR and NMR spectroscopy.

Iron pentacarbonyl supplied by Fluka, Switzerland and Aldrich, USA were used. Commercially available ketones were used in the experiments. Methyl acrylate and methyl crotonate (Fluka) were distilled before use. Naphthalene supplied by LOBA-Chemie, India was sublimed before use. Alkyl bromides were supplied by Fluka, Switzerland and magnesium mesh supplied by Aldrich, USA were used. CuCl (Fluka) was further purified on treatment with distilled water containing SO_2. After decanting the water, it was washed with dry ether, ethanol and dried under vacuum at 100°C for 3h.

Tetrahydrofuran supplied by E-Merck, India was kept over sodium-benzophenone ketyl and freshly distilled before the use. Carbon monoxide was generated by dropwise addition of formic acid 98% to con. H_2SO_4 96% at 90°C using an apparatus recommended for utilization in the carbonylation of organoboranes.[53]

1.4.2 Reaction of $Na(RCO)Fe(CO)_4$ with I_2:

To a suspension of $Na_2Fe(CO)_4$ [prepared using Fe(CO)5 (2.16 g, 11 mmol), Na (0.51 g, 22 mmol) and naphthalene (1.02 g, 8 mmol)] in THF (40 mL) 1-bromooctane (1.93 g, 10 mmol) was added and CO was bubbled for 30 min at 25°C. The CO atmosphere was replaced by dry N_2 atmosphere and the mixture was cooled to $0^{o}C$. I_2 (2.53 g, 10 mmol) dissolved in THF (30 mL) was added dropwise to the reaction mixture using a pressure equalizer. The mixture was stirred for 3h at 0°C and 12h at 250C and then poured into acetone (40 mL) containing $CuCl_2.2H_2O$ (6.8 g, 40 mmol) to decompose the iron carbonyl. Saturated aqueous NaCl (30 mL) was added , the organic layer was separated and the aqueous layer was extracted with ether (2 x 30 mL). The combined organic extract was washed successively with saturated $Na_2S_2O_3$ (20 mL) and H_2O (20 mL) and then dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. The fraction containing the dialkyl ketone, 1,2 diketone and 1-nonoic acid was isolated. The 1,2 diketone 26 (0.47 g, 32%), dialkyl ketone 27 (0.11 g, 8%) and 1-nonoic acid 28 (0.45 g, 29%) were further separated by preparative TLC.



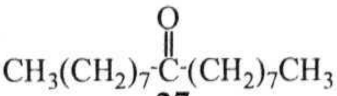
$CH_3(CH_2)_7\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7CH_3$

26

IR (neat) : 1710 cm^{-1}

^1H NMR : δ ppm 0.82 (t, J=7.0 Hz, 6H), 1.08-1.68 (m, 24H), 2.66 (t, J= 7.2 Hz, 4H)

^{13}C NMR : δ ppm 13.9, 22.6, 23.1, 29.1, 29.3, 31.8, 36.0, 200.3



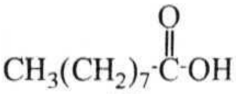
$CH_3(CH_2)_7\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7CH_3$

27

IR (neat) : 1710 cm^{-1}

^1H NMR : δ ppm 0. 8 (m, 6H), 1.2 (m, 20H), 1.5 (m, 4H), 2.3 (t, J= 7.1 Hz, 4H)

^{13}C NMR : δ ppm 13.9, 22.5, 23.7, 29.1, 29.2, 29.3, 31.7, 42.5, 210.7



$CH_3(CH_2)_7-C(=O)-OH$

28

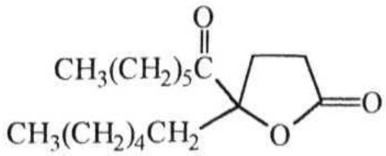
IR (neat) : 1710 cm^{-1}

^{1}H NMR : δ ppm 0.9 (t, J= 6.9 Hz, 3H), 1.3 (m, 10H), 1.7 (m, 2H), 2.3 (t, J= 7.1 Hz, 2H), 10.2 (s, 1H)

^{13}C NMR : δ ppm 13.8, 22.5, 24.5, 29.1, 31.7, 34.0, 180.7

1.4.3 Reaction of methyl acrylate with the reagent generated using $Na(RCO)Fe(CO)_4$ and I_2

To a suspension of $Na_2Fe(CO)_4$ [prepared using $Fe(CO)_5$ (2.16 g, 11 mmol), Na (0.51 g, 22 mmol) and naphthalene (1.02 g, 8 mmol)] in THF (40 mL), 1-bromohexane (1.65 g, 10 mmol) was added and CO was bubbled for 30 min at 25°C. The CO atmosphere was replaced by dry N_2 atmosphere and the mixture was cooled to 0°C. I_2 (2.53 g, 10 mmol) dissolved in THF (30 mL) was added dropwise to the reaction mixture using a pressure equalizer. The mixture was stirred further for 3h at 0°C. Methyl acrylate (2.58 g, 30 mmol) was added and the mixture was stirred for 2h at 0^0C and 12h at 25^0C. CH3COOH was added and the mixture was poured into acetone (40 mL) containing $CuCl_2.2H_2O$ (6.8 g, 40 mmol) to decompose the iron carbonyl. Saturated aqueous NaCl (30 mL) was added , the organic layer was separated and the aqueous layer was extracted with ether (2 x 30 mL). The combined organic extract was washed successively with saturated $Na_2S_2O_3$ (20 mL) and H_2O (20 mL) and then dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. The acyllactone **31a** and a mixture of 1,2-diketone **31b**, dialkyl ketone **31c,** and 1-heptanoic acid **31d** were isolated along with small amounts of several unidentified products. The dialkyl ketone, 1,2-diketone and 1-heptanoic acid were further separated by preparative TLC.



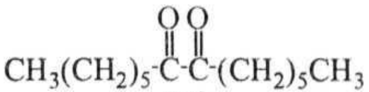
31a

Yield : 21% (0.39 g)

IR (neat) : 1720, 1790 cm^{-1}

^1H NMR : δ ppm 0.80 (t, J= 6.9 Hz, 6H), 1.14-1.92 (m, 16H), 2.04 (t, J= 7.2 Hz, 2H), 2.32 (t, J= 7.1 Hz, 2H), 2.42-2.62 (m, 4H)

^{13}C NMR : δ ppm 13.5, 22.0, 22.4, 22.8, 27.6, 28.2, 28.8, 29.4, 31.0, 31.1, 37.2, 37.9, 91.6, 175.5, 210.4



$CH_3(CH_2)_5\text{-}C(=O)\text{-}C(=O)\text{-}(CH_2)_5CH_3$

31b

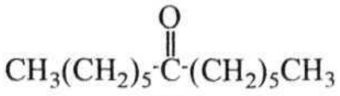
Yield : 18% (0.21 g)

IR (neat) : 1705 cm^{-1}

^1H NMR : δ ppm 0.80 (t, J= 7.0 Hz, 6H), 1.06-1.60 (m, 16H), 2.60 (t, J=7.2 Hz, 4H)

^{13}C NMR : δ ppm 13.8, 22.4, 28.8, 31.5, 35.9, 199.7

MS (EI) :m/z 226 (M^+, 2%), 113 (RCO^+, 100%)



$CH_3(CH_2)_5\text{-}C(=O)\text{-}(CH_2)_5CH_3$

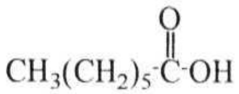
31c

Yield : 5% (0.045 g)

IR (neat) : 1710 cm^{-1}

^{1}H NMR : δ ppm 0.80 (m, 6H), 1.2 (m, 12H), 1.4 (m, 4H), 2.3 (t, J= 7.2 Hz, 4H)

^{13}C NMR : δ ppm 13.5, 22.1, 23.4, 28.5, 31.2, 42.3, 210.8



$CH_3(CH_2)_5\overset{\overset{O}{\|}}{C}\text{-}OH$

31d

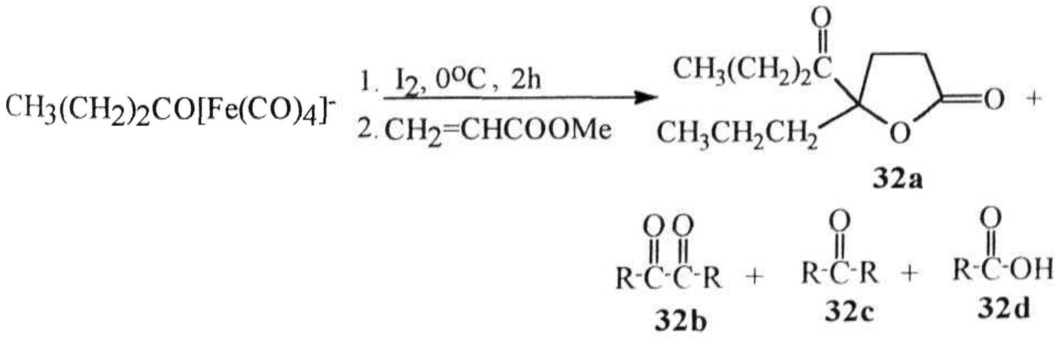
Yield : 7% (0.091 g)

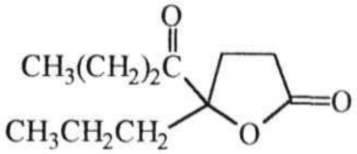
IR (neat) : 1710 cm^{-1}

^{1}H NMR : δ ppm 0.80 (t, J= 6.9 Hz, 3H), 1.3 (m, 6H), 1.6 (m, 2H), 2.3 (t, J= 7.1 Hz, 2H), 10.4 (s, 1H)

^{13}C NMR : δ ppm 13.8, 22.4, 24.5, 28.6, 31.4, 34.0, 180.6

The spectral data of 31a and **31b** were identical to that for the samples previously obtained using NaRCOFe(CO)$_4$/CuCl in this laboratory.[38] The above procedure was followed for n-propyl bromide. The data are summarized below.





32a

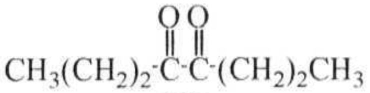
Yield : 19% (0.19 g)

IR (neat) : 1720, 1790 cm^{-1}

^{1}H NMR : δ ppm 0.88 (t, J= 7.0 Hz, 6H), 1.10-1.96 (m, 4H), 2.08 (t, J= 7.2 Hz, 2H), 2.20-2.68 (m, 6H) **(Spectrum No 2)**

^{13}C NMR : δ ppm 13.5, 14.0, 16.4, 16.8, 28.2, 29.8, 39.8, 40.4, 92.2, 176.2, 211.0 **(Spectrum No 1)**

MS (Cl) : m/z 198 (M$^+$, 2%), 127 [(M$^+$-RCO), 100%],



$CH_3(CH_2)_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_2CH_3$

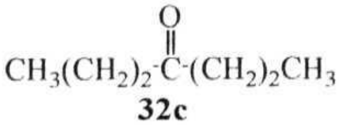
32b

Yield : 16% (0.11 g)

IR (neat) : 1705 cm^{-1}

^{1}H NMR : δ ppm 0.92 (t, J= 7.0 Hz, 6H), 1.36-1.76 (m, 4H), 2.72 (t, J= 7.2 Hz, 4H)

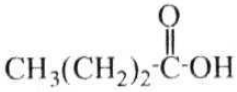
^{13}C NMR : δ ppm 13.4, 16.4, 37.7, 199.9



$CH_3(CH_2)_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_2CH_3$

32c

Yield : 4% (0.02 g)



$CH_3(CH_2)_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$

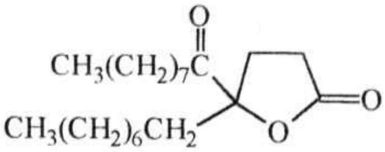
32d

Yield : 6% (0.05 g)

The spectral data of **32a** and **32b** were identical to that for the sample previously obtained using $NaRCOFe(CO)_4/CuCl$ in this laboratory.[38] The spectral data of RCOR 32c and RCOOH **32d** were identical to that of authentic samples.

1.4.4 Photochemical reaction of Fe(CO)5 with methyl acrylate and 1,2-diketone

A mixture containing RCOCOR (R= n-octyl), (0.141 g, 0.5 mmol), $Fe(CO)_5$ (0.39 g, 2 mmol) and methyl acrylate (0.13 g, 1.5 mmol) in benzene (10 mL) was irradiated for 4.5h using a 450W medium pressure mercury lamp and pyrex filter. It was poured into H_2O (3 mL) containing ceric ammonium nitrate (1.64 g, 3 mmol) to decompose the iron carbonyl. The organic phase was separated and the aqueous phase was saturated with NaCl and extracted with ether (2 x 10 mL). The combined organic extracts were washed with brine (10 mL), dried and concentrated. The residue was subjected to column chromatography. Ethyl acetate (4%) in hexane eluted an unidentified iron carbonyl complex (0.098 g) and ethyl acetate (10%) in hexane eluted acyllactone 36 (28%, 0.045 g). The unreacted 1,2-diketone 40 (0.07 g) was also recovered.



36

IR (neat) : 1720, 1790 cm^{-1}

^1H NMR : δ ppm 0.80 (t, J= 7.0 Hz, 6H), 1.02-1.90 (m, 24H),
2.02 (t, J= 7.2 Hz, 2H), 2.30 (t, J= 7.1 Hz, 2H), 2.42-2.60 (m, 4H)

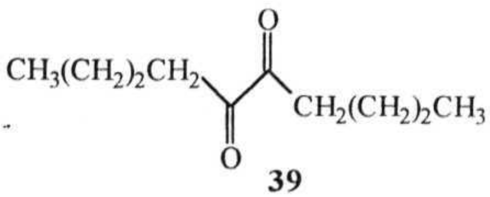
^{13}C NMR : δ ppm 13.6, 22.4, 22.8, 23.0, 27.9,28.9, 29.0, 29.1, 29.4, 29.5, 31.5,37.4,38.0,91.9, 175.5,210.6

MS (CI) : m/z 336 (M^+, 65%), 197 [(M^+-RCO), 100%]

The spectral data of 36 were identical to that for the sample previously obtained using $NaRCOFe(CO)_4/CuCl$ in this laboratory.[38]

1.4.5 Reaction of RMgBr with $Fe(CO)_5$ in the presence of CuCl

Magnesium mesh (0.23 g, 10 mmol) was taken in THF (50 mL) under N_2 atmosphere and n-butyl bromide (1.37 g, 10 mmol) was added at 25°C. The contents were stirred for lh at 25°C and $Fe(CO)_5$ (2.16 g, 10 mmol) was added. The reaction mixture was stirred for lh at 25°C and CuCl (2.0 g, 20 mmol) was added and stirred further for 10h at 25°C. The resultant mixture was poured into acetone (40 mL) containing $CuCl_2.2H_2O$ (6.8 g, 40 mmol) to decompose iron carbonyl. Saturated aq. NaCl was added and the organic phase was separated. The aqueous layer was extracted with ether (2 x 40 mL). The combined organic extracts were washed with H_2O (20 mL) and brine (30 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Ethyl acetate (1%) in hexane eluted the a-diketone (39) (45%, 0.385 g).



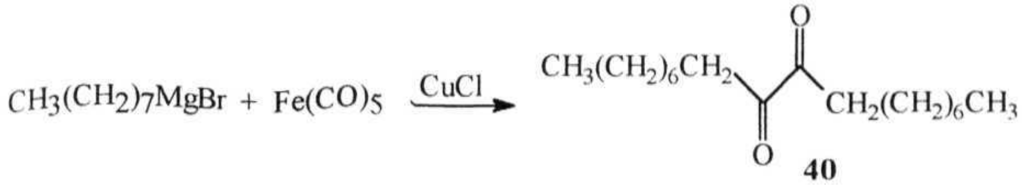
39

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

^{1}H NMR : δ ppm 0.80 (t, J= 6.9 Hz, 6H), 1.08-1.60 (m, 8H), 2.62 (t, J= 7.0 Hz, 4H)

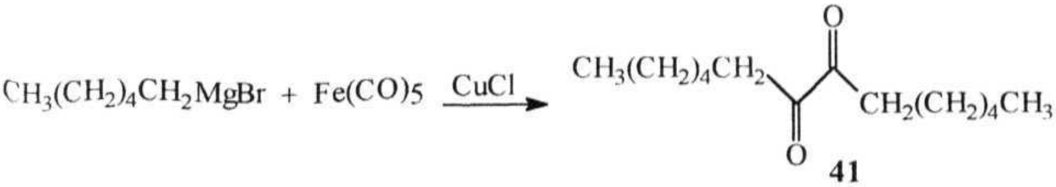
^{13}C NMR : δ ppm 13.4, 22.0, 24.9, 35.4, 199.8

The above procedure was followed for the conversion of other bromides to the corresponding a-diketones. The spectral data of the α-diketones obtained in experiments using n-hexyl bromide and n-octyl bromide show 1:1 correspondence with the data of the samples obtained previously using $NaRCOFe(CO)_4/I_2$.



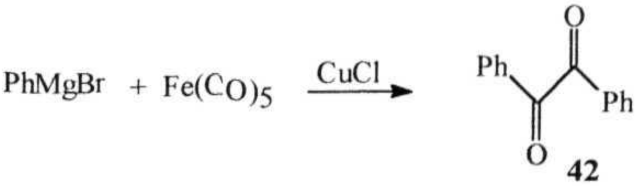
40

Yield : 48% (0.88 g)



41

Yield : 48% (0.575 g)



42

Yield : 50% (0.525 g)

M.P : 93°C (Lit[54] m.p. 93-95°C)

IR (neat) : 1661 cm^{-1}

^{13}C NMR : δ ppm 129.0, 129.9, 133.0, 134.9, 194.4

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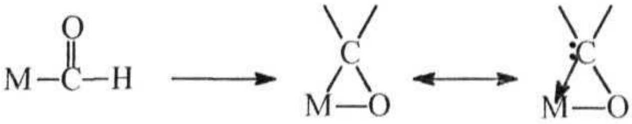
CHAPTER 2

Studies on New Synthetic Applications of $Na_2Fe(CO)_4$

2 1 Introduction

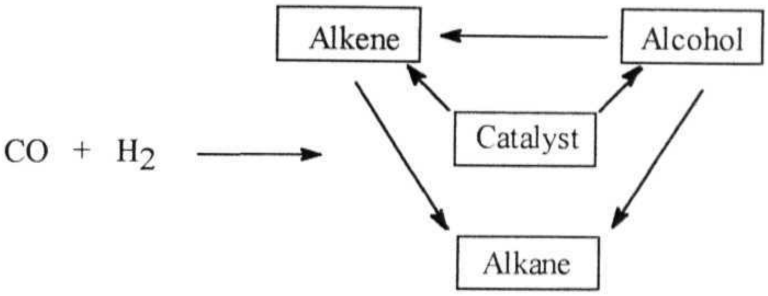
Transition metal complexes are known to form stable η^2-complexes with unsaturated compounds such as olefins, alkynes and carbonyl compounds.[1] Among these species, olefin complexes are very well studied. The hetero analogues such as, η^2-ketone complexes are far less in number but are attracting a rapidly increasing interest.[2] The oxophilicity and unsaturation in the coordination of metal centre are the important parameters to promote the η^2-bonding mode, in which both carbon and oxygen of the carbonyl compound coordinate to the metal centre. In such complexes, the carbon is expected to show carbenoid character (the reversal of polarity).[3]



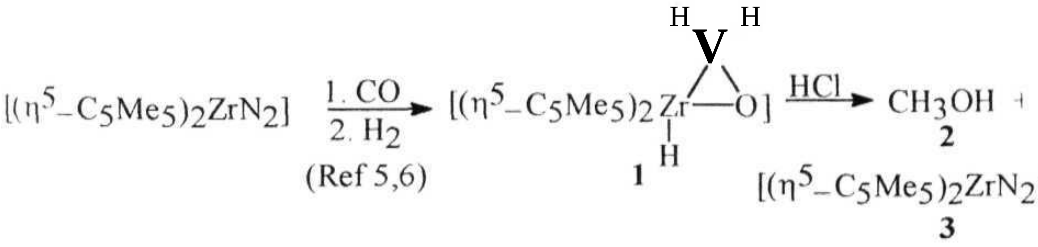
In this section, the synthesis and reactions of some η^2-acyl complexes are briefly reviewed, as our original objective was to synthesise iron carbonyl-η^2-ketone complexes through the experiments outlined in this Chapter.

The Fisher-Tropsche synthesis is one of the useful and fascinating reaction mediated by transition metal catalysts.[4,5] It has been proposed that η^2-acyl complexes are intermediates in this reaction.[5,6] The intermediacy of η^2-complexes are significant as it represents the reduction of a coordinated carbonyl by molecular hydrogen (Scheme 1).

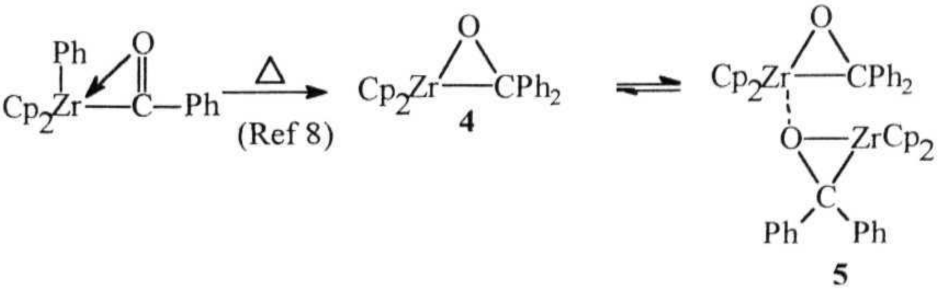
Scheme 1



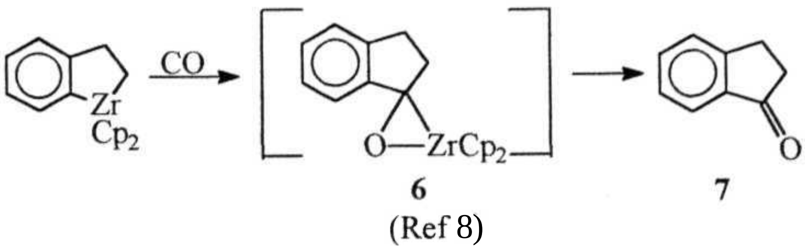
The early transition metals have high oxophilicity and hence, the kelones and aldehydes form η2-complexes with these metals.[7] Several reactions involving η2-complexes of early transition metals are summarized in eqns 1-7.



(1)

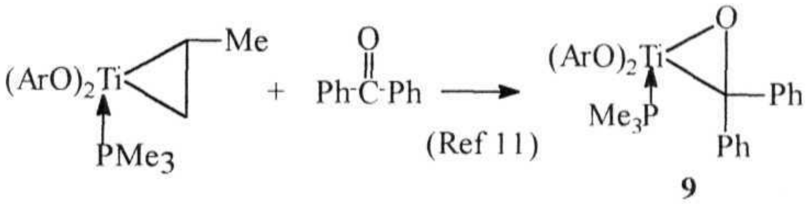


-(2)

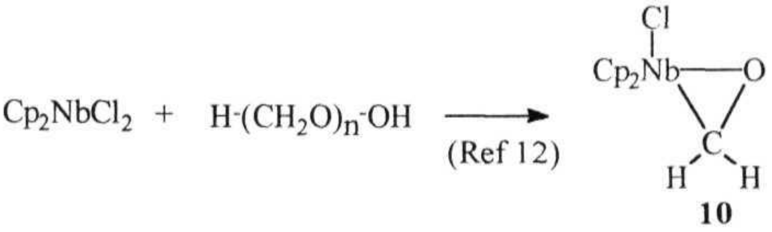


(3)

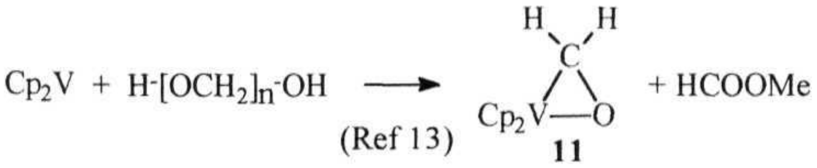
$$Cp_2Zr[Si(SiMe_3)_3]Cl \xrightarrow[\text{(Ref 10)}]{CO} Cp_2Zr[\eta^2\text{-}COSi(SiMe_3)_3]Cl \xrightarrow{HCl} \underset{\mathbf{8}}{(Me_3Si)_3SiCHO} \qquad (4)$$



(5)



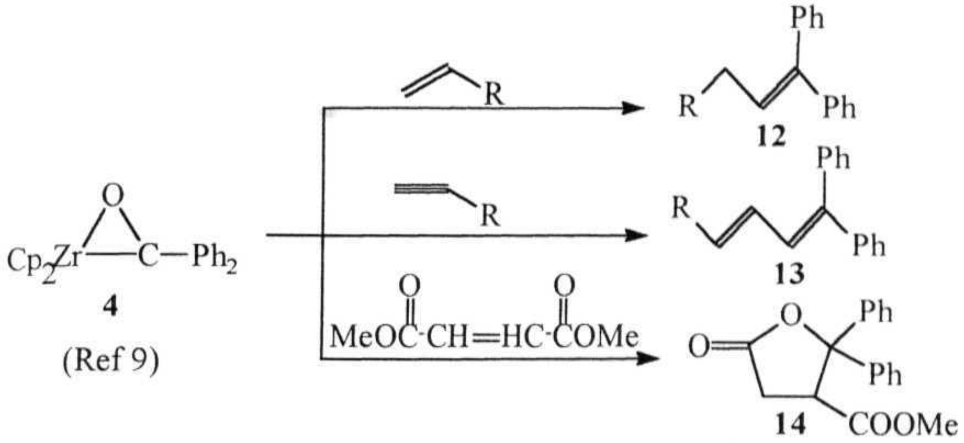
(6)



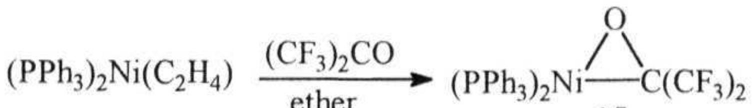
(7)

The η^2-zirconium complex (4) undergoes some useful transformations (Scheme 2).[9]

Scheme 2



However, very little is known about the η^2-acyl complexes of late transition metals. Penfold *et al* found that replacement of ethylenc in $(PPh_3)_2Ni(C_2H_4)$ with hexaflouroacetone produced the corresponding η^2-acyl complex 15 (eqn 8).[14]



$$(PPh_3)_2Ni(C_2H_4) \xrightarrow[\text{ether}]{(CF_3)_2CO} (PPh_3)_2Ni(O)C(CF_3)_2 \quad .(8)$$

15

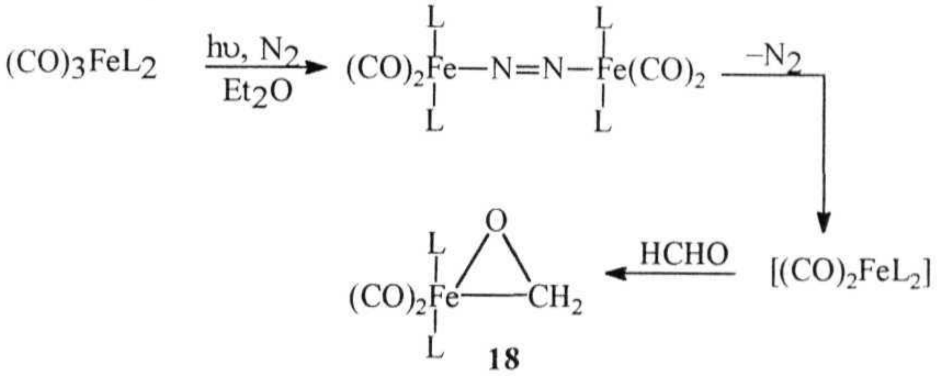
Kochi and his co-workers reported that $Ni(PEt_3)_4$ on reaction with benzophenone affords air sensitive η^2-acyl derivative of nickel. The reaction is facilitated by electron withdrawing substituents and retarded by electron rich substituents (eqn 9).[15]

$$Ni(PEt_3)_4 + Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ph \longrightarrow (PEt_3)_2Ni(O)CPh_2 \quad (9)$$

16

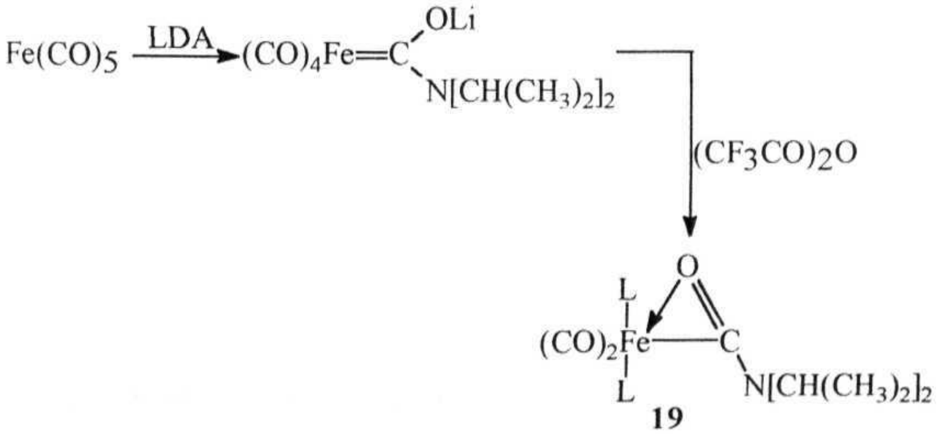
The less oxophilic iron carbonyl is also known to form η^2-acyl complexes by the reaction of formaldehyde with a μ-dinitrogen complex generated *in situ* upon the photolysis of $Fe(CO)_3[P(OMe_3)_2]$ under nitrogen atmosphere (Scheme 3).[16]

Scheme 3



18

Recently, Anderson *et al* reported the formation of η^2-acyl complexes of iron through sequential treatment of $Fe(CO)_5$ with LDA, $(CF_3CO)_2O$ and PPh_3 in diethyl ether (eqn 10).[17]



19

(KM

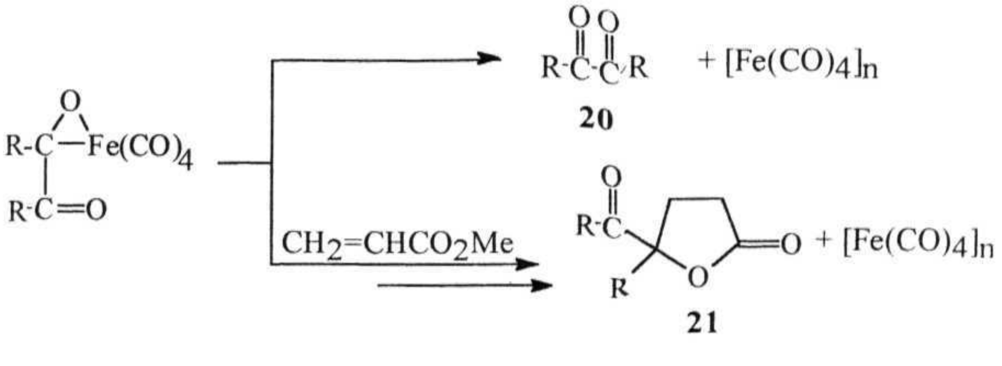
It was of our interest to examine the synthesis of η^2-complexes of ketones with iron carbonyls for synthetic applications.

2.2 Results and Discussion

2.2.1 Studies on the reaction of the Ketones and methyl acrylate with $Na_2Fe(CO)_4$ and CuCl

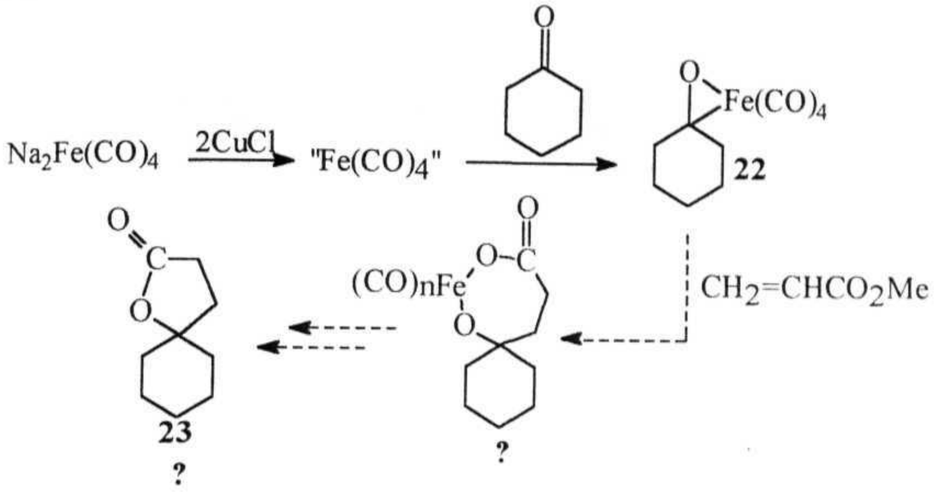
As outlined in the introductory section, certain aldehydes and ketones form η^2-complexes with early transition metal complexes.[7] However, very little is known about the η^2-complexes of iron carbonyl, although η^2-complexes of the type $L(CO)Fe(OCH_2)$ have been prepared with formaldehyde.[16] As discussed in Chapter I, the η^2-complex has been proposed as an intermediate in the formation of 1,2-diketones and acyllactones in the reaction of $Na(RCO)Fe(CO)_4$ with CuCl in the presence of methyl acrylate (Scheme 4).[18]

Scheme 4

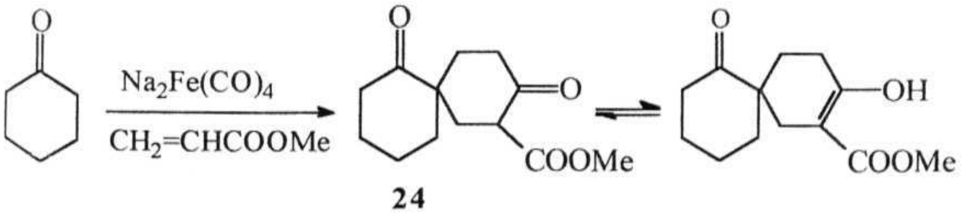


It was of our interest to examine the formation of η^2-complexes with "$Fe(CO)_4$" through oxidation of $Na_2Fe(CO)_4$ with CuCl in the presence of a ketone and methyl acrylate (Scheme 5).

Scheme 5



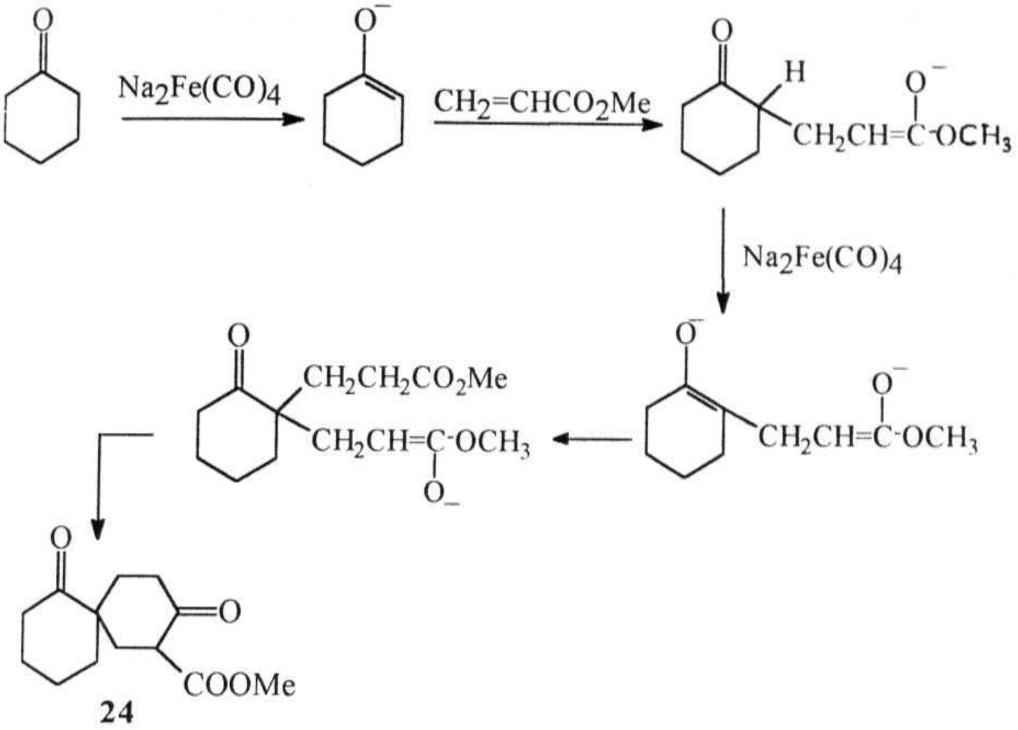
However, when the reaction of $Na_2Fe(CO)_4$ (20 mmol) was carried out with CuCl (20 mmol) in the presence of cyclohexanone (10 mmol) and methyl acrylate (20 mmol), only the cyclic p-keto ester 24 was obtained (53%) (eqn 11).[19]



(11)

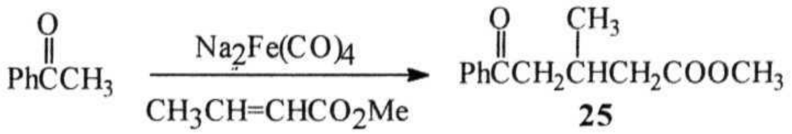
It was also found that this p-keto ester was obtained even in the absence of CuCl. Most probably, the $Na_2Fe(CO)_4$ acts as a base and initiates the double Michael addition-Dieckmann condensation as outlined in the Scheme 6.[20,21]

Scheme 6



Several other ketones were also converted to the corresponding β-keto esters [Table 1].

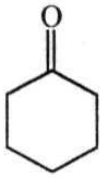
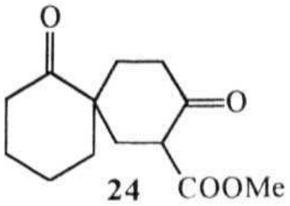
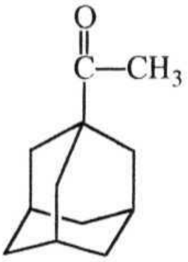
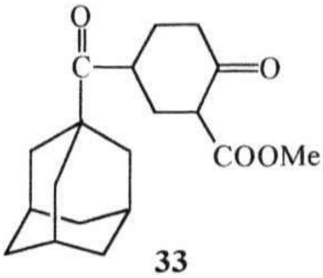
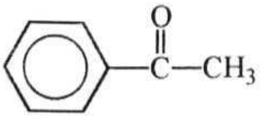
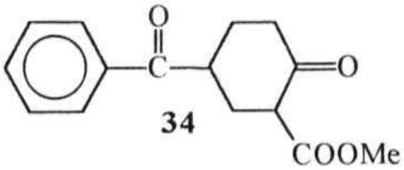
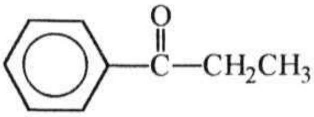
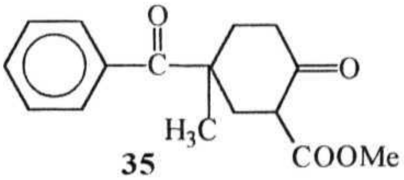
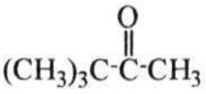
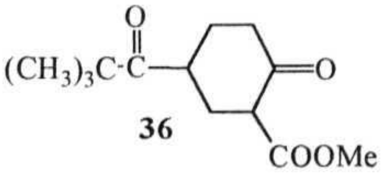
When the reaction was carried out with methyl crotonate in the place of methyl acrylate, the corresponding mono alkylated product was obtained instead of the cyclic β-keto ester (eqn 12).



$$\mathrm{Ph\overset{\overset{O}{\|}}{C}CH_3} \xrightarrow[\mathrm{CH_3CH{=}CHCO_2Me}]{\mathrm{Na_2Fe(CO)_4}} \mathrm{Ph\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{CH_3}{|}}{C}HCH_2COOCH_3} \quad (12)$$

25

Table 1: Reaction of $Na_2Fe(CO)_4$ with Ketones and Methyl acrylate[a]

S No	Substrate	Product[b]	Yield (%)[c]
1		 **24**	53
2		 **33**	49[d]
3		 **34**	58
4		 **35**	43
5		 **36**	48

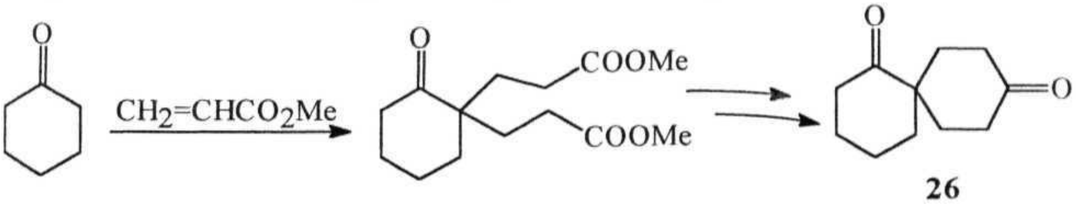
a) All reactions were carried out using ketones (10 mmol), $Na_2Fe(CO)_4$ [prepared using $Fe(CO)_5$ (22 mmol), Na (44 mmol) and naphthalene (16 mmol)] and methyl acry late (20 mmol).

b) The cyclic β-keto esters were identified by the analysis of spectral data (IR, ^1H NMR, ^{13}C NMR and Mass). The data are given in Experimental section.

c) Yields are of products isolated by column chromatography with 4% ethyl acetate in hexane as an eluent and based on the ketones used.

d) Satisfactory elemental analyses were obtained for this product.

We have observed that the yield of the cyclic β-keto ester increased by 15% when excess of (4 eq) of $Na_2Fe(CO)_4$ was utilized. The cyclic [3-keto ester obtained in the above reaction of cyclohexanone and acrylate has been previously prepared through a two step sequence for utilization in the synthesis of compound 26 for examining its biological activity (eqn 13).[22]

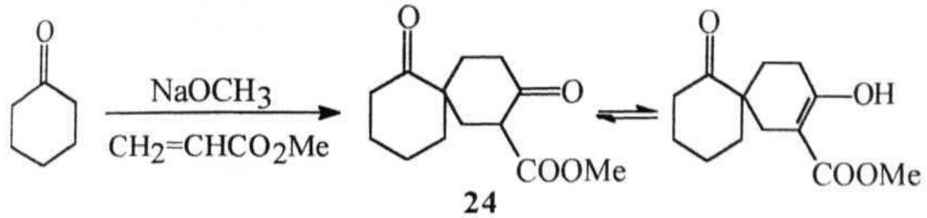


26

..(13)

2.2.2 Construction of cyclohexyl ring at the α-methylene moiety of ketones using $NaOCH_3$

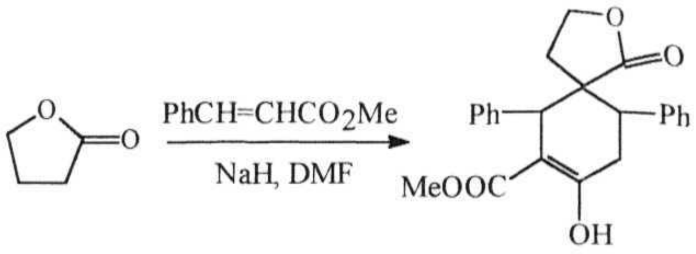
In the above mentioned transformation, the $Na_2Fe(CO)_4$ acts as a base to generate the enolate intermediate. It was anticipated that such a reactivity would also be realized using the alkoxide bases such as $NaOCH_3$. Indeed, it was observed that the cyclic p-keto ester 24 was formed in the reaction of cyclohexanone with methyl acrylate in the presence of $NaOCH_3$ (eqn 14). Again, the transformation is found to be general and the corresponding cyclic products were obtained in moderate yields (40-56%) (Table 2).[19]



24

(14)

Surprisingly, this relatively simple transformation has not been reported earlier. However, it has been briefly mentioned that the lactone enolate, derived from butyrolactone, on treatment with methyl cinnamate, yields the corresponding enol form of cyclic p-keto ester (eqn 15).[23]

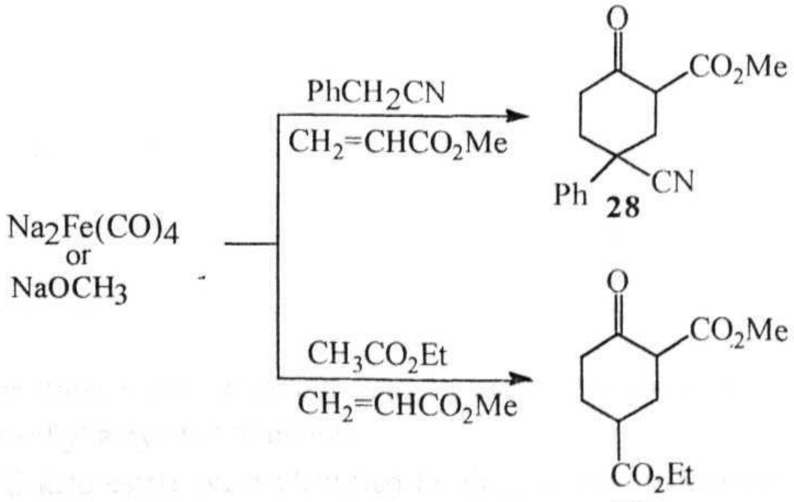


27

..(15)

In this laboratory, similar results were also obtained in reactions using several other compounds containing active methylene groups (Scheme 7). 19

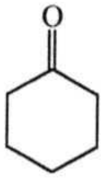
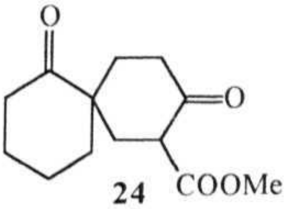
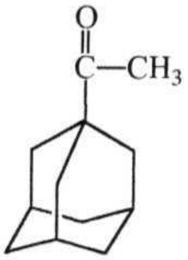
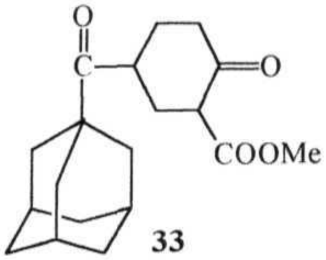
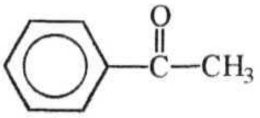
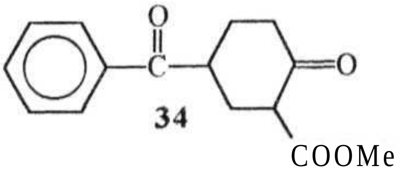
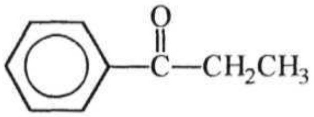
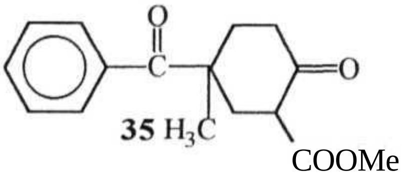
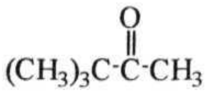
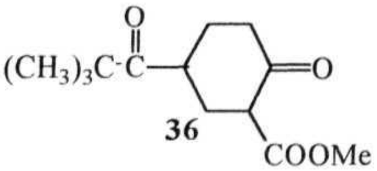
Scheme 7



28

29

Table 2 : Reaction of $NaOCH_3$ with Ketones and Methyl acrylate[a]

S.No	Substrate	Product[b]	Yield(%)[c]
1		 24	42
2		 33	45[d]
3		 34	55
4		 35	42
5	 $(CH_3)_3C-\overset{O}{\overset{\|}{C}}-CH_3$	 36	40

a) All reactions were carried out using $NaOCH_3$ (20 mmol), ketones (10 mmol) and methyl acrylate (20 **mmol**).

b) The β-keto esters were identified by the analysis of spectral data (IR, ^1H NMR, ^{13}C NMR and Mass). The data are given in experimental section.

c) Yields are of products isolated by column chromatography with 4% ethyl acetate in hexane as eluent and based on the ketones used.
d) Satisfactory elemental analyses were obtained for this compound.

2.2.3 Reaction of Na/Naphthalene/CO system with carbonyl compounds

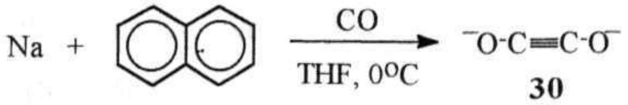
It is well known that the carbon monoxide accepts one electron to form radical anion which on dimerization gives acetylene diolate ($C_2O_2^{2-}$) (eqn 16).[24]

$$\begin{aligned} &\mathrm{CO} + e \longrightarrow \mathrm{CO}^{\bar{\cdot}} \\ &2\,\mathrm{CO}^{\bar{\cdot}} \longrightarrow {}^{-}\mathrm{O{-}C{\equiv}C{-}O}^{-} \end{aligned} \qquad (16)$$

30

Although, there are several reports on the synthesis of $C_2O_2^{2-}$ by the reductive coupling of CO using molten potassium/sodium,[25] sodium or potassium in liquid ammonia[26] and Na-K alloy/crown ether,[24] the synthetic utilities of this species have not been explored in detail.

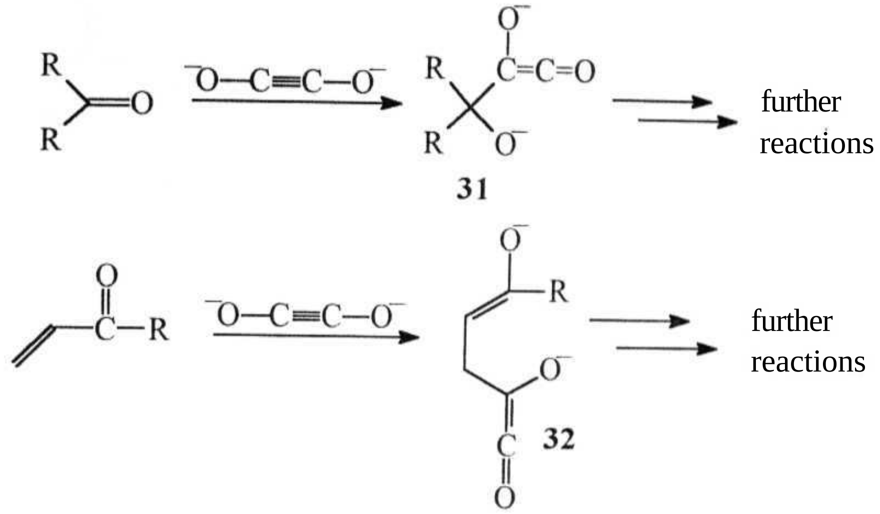
We have attempted to use sodium-naphthalene as a one electron carrier for the reductive coupling of CO to $C_2O_2^{2-}$ for utilization in developing synthetic methods (eqn 17).



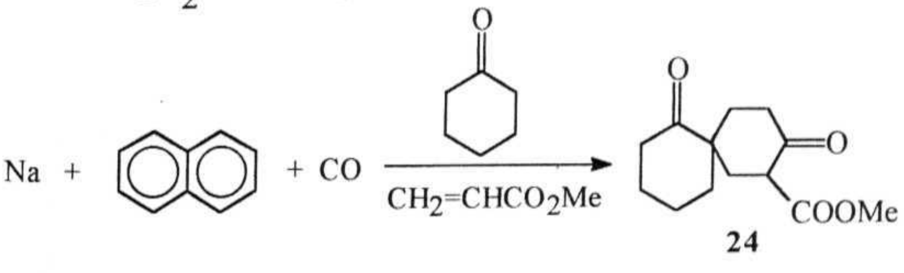
(17)

It was anticipated that the acetylene diolate $C_2O_2^{2-}$ would have the properties similar to that of enolates. Therefore, we have decided to examine the reactivity of $C_2O_2^{2-}$ with carbonyl compounds (Scheme 8).

Scheme 8



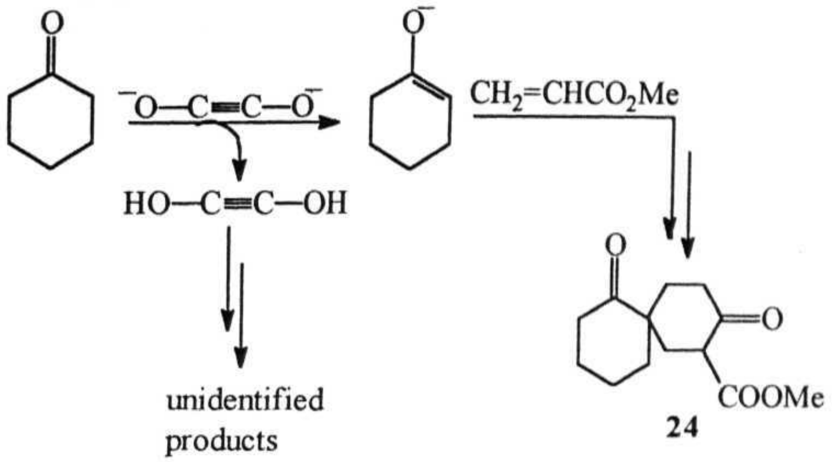
We have examined the reactions with cyclohexanone and methyl acrylate. It was observed that the sequential treatment of Na/naphthalene/CO with ketones and methyl acrylate gave the cyclic β-keto ester in moderate yield (eqn 18, Table 3) and the $C_2O_2^{2-}$ derived products were not obtained.



(18)

Presumably, in this transformation the $C_2O_2^{2-}$ behaves like a base to produce ketone enolates which on reaction with methyl acrylate give cyclic β-keto esters (Scheme 9).

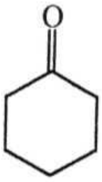
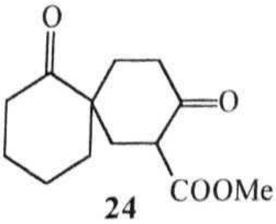
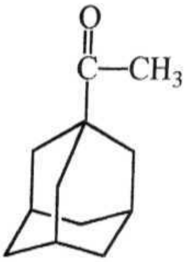
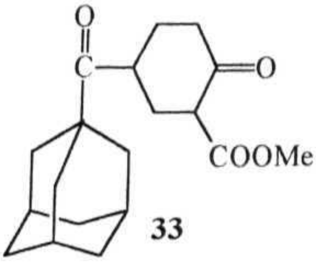
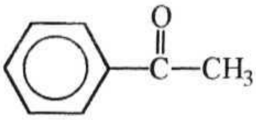
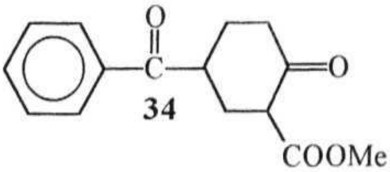
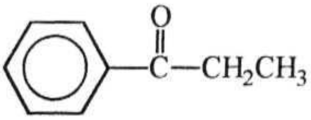
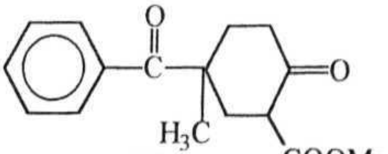
Scheme 9



The intermediacy of other species, such as dimerized or trimerized product of $C_2O_2^{2-}$, cannot be ruled out in this reaction. Although the mechanistic picture is not clear, it is interesting to point out that the inexpensive sodium-naphthalenide can be utilized here for this transformation.

Unfortunately, our objective of preparation of η^2-complexes through oxidation of $Na_2Fe(CO)_4$ using CuCl in the presence of ketones failed. However, we have continued with our efforts and discovered certain iron carbonyl species with interesting reactivities. These results are described in Chapter 3.

Table 3 : Reaction of Na/Naphthalene/CO with ketones and Methyl acrylate

S.No	Substrate	Product^b	Yield(%)^c
1		 **24**	46
2		 **33**	48^d
3		 **34**	51
4		 **35**	50

a) All reactions were carried out using sodium (22 mmol), naphthalene (10 mmol), ketones (5 mmol) and methyl acrylate (20 mmol).

b) The p-keto esters were identified by the analysis of spectral data (IR, ^1H NMR, ^{13}CNMR and Mass). The data are given in experimental section.

c) Yields are of products isolated by column chromatography with 4% ethyl acetate in hexane as eluent and based on the ketones used.

d) Satisfactory elemental analyses were obtained for this compound.

2.3. Conclusions

The $Na_2Fe(CO)_4$ reagent prepared *in situ* using Na/naphthalene with $Fe(CO)_5$ was utilized for the construction of cyclohexyl ring at the α-methylene moieties of ketones in moderate yields. The transformation was rationalized by the sequence of reactions involving double Michael addition and Dicckmann cyclization. The use of $NaOCH_3$ in the place of $Na_2Fe(CO)_4$ also lead to the construction of cyclohexyl ring at a-methylene moieties of ketones.

Attempts have been made to synthesise acetylene diolate ($C_2O_2^{2-}$) for utilization in reactions with carbonyl compounds. However, only the β-keto esters were obtained and carbon monoxide insertion products were not observed.

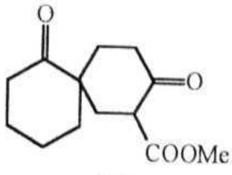
2.4 Experimental section

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 alkyl halides, ketones and methyl aciylate were distilled and used in the reactions. Naphthalene was sublimed before use. The sodium methoxide utilized was freshly prepared using sodium and methanol under N_2 atmosphere.

2.4.2 Reaction of cyclohexanone and methyl acrylate in the presence of $Na_2Fe(CO)_4$

To a suspension of $Na_2Fe(CO)_4$ [prepared using $Fe(CO)_5$ (4.32 g, 22 mmol), Na (1.02 g, 44 mmol) and naphthalene (2.04 g, 16 mmol)] in THF (50 mL) cyclohexanone (0.98 g, 10 mmol) was added and the mixture stirred for 1h under N_2 atmosphere. To this mixture, methyl acrylate (1.72 g, 20 mmol) was added and stirred for 10h at 25°C. The mixture was poured into acetone (40 mL) containing $CuCl_2.2H_2O$ (6.8 g, 40 mmol) to decompose the iron carbonyl. Water (40 mL) was added and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2 x 40 mL). The combined organic extract was washed with H_2O (20 mL) and brine (30 mL), dried and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene, and ethyl acetate (4%) in hexane eluted cyclic β-keto ester **24.**



24

Yield : 53% (1.26 g)

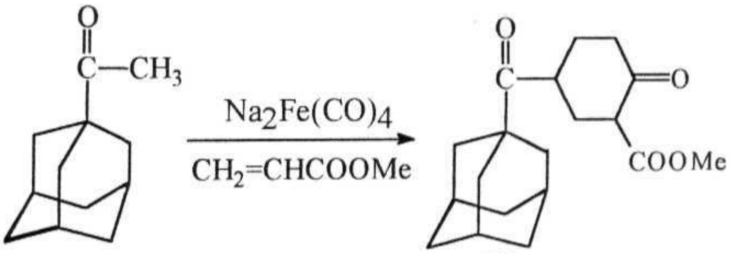
IR (neat) : 1610, 1650, 1700 cm^{-1}

^{1}H NMR : δ ppm 1.62-2.58 (m, 14H), 2.84 (m, 1H), 3.72 (s, 3H)

^{13}C NMR : δ ppm 20.2, 25.1, 27.2, 27.8, 29.1, 36.6, 37.7, 46.5, 50.7, 94.5, 170.3, 172.1, 213.7

MS (EI) : m/z 238 (M$^+$, 80%), 206 [(M$^+$-OCH$_3$), 92%]

The above procedure was followed for other substrates (Table 1). The physical constant and spectral data obtained are summarized below:



33

Yield : 49% (1.56 g)

M.P : 85°C

IR (neat) : 1615, 1650, 1700 cm^{-1}

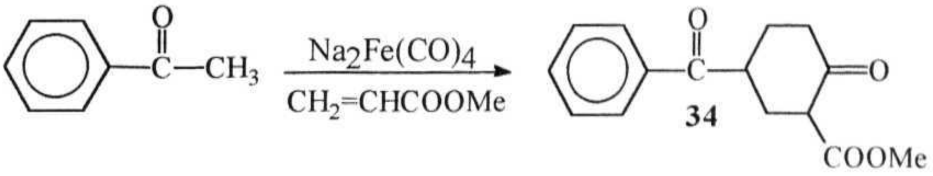
^{1}H NMR : δ ppm 1.64-2.48 (m, 22H), 3.08 (m, 1H), 3.71 (s, 3H) **(Spectrum No 7)**

^{13}C NMR : δ ppm 25.3, 26.2, 28.0, 28.6, 36.7, 37.8, 38.1, 39.5, 47.2, 51.5, 96.7, 171.3, 172.3, 217.1**(Spectrum No 6)**

MS (EI) : m/z 318 [(M$^+$+1), 20%)], 135 [(Adamantyl)$^+$, 100%]

Analysis **Calcd. for** $C_{19}H_{25}O_4$

Calcd	C% 71.69	H%8.17
Found	C% 71.32	H%8.37



34

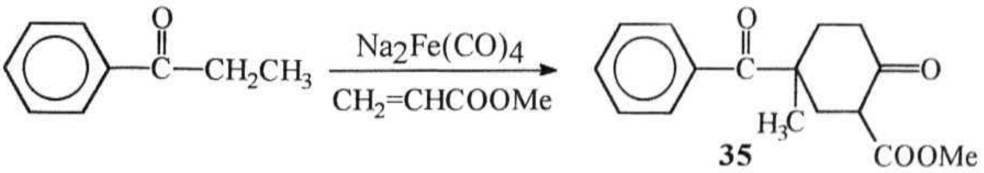
Yield : 58% (1.51 g)

IR (neat) : 1610, 1650, 1705 cm^{-1}

^{1}H NMR : δ ppm 1.65-2.64 (m, 7H), 3.32 (m, 1H), 3.62 (s, 3H), 7.22-7.50 (m, 3H), 7.74-7.94 (m, 2H) (**Spectrum No 5**)

^{13}C NMR : δ ppm 24.1, 25.0, 28.0, 40.8, 51.0, 96.0, 128.0, 128.4, 132.8, 135.6, 171.0, 172.3, 201.8 (**Spectrum No 4**)

MS (EI) : m/z 260 (M^+, 60%) 238[(M^+-OCH_3), 50%] (**Spectrum No 3**)



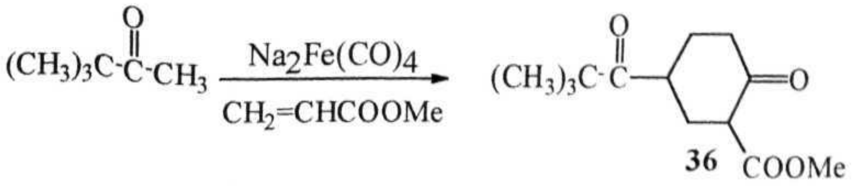
35

Yield : 43% (1.44 g)

IR (neat) : 1610, 1650, 1700 cm^{-1}

^{1}H NMR : δ ppm 1.40 (s, 3H), 1.64-1.98, 2.04-2.40 (m, 6H), 3.02 (m, 1H), 3.60 (s, 3H), 7.28-7.48 (m, 3H), 7.52-7.64 (m, 2H)

^{13}C NMR : δ ppm 24.1, 26.1, 30.7, 32.1, 46.2, 51.0, 95.6, 127.2, 127.9, 130.8, 138.1, 171.0, 172.3, 207.3



Yield : : 48% (1.22 g)

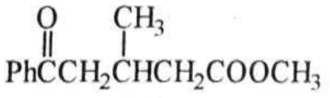
IR (neat) : 1610, 1650, 1700 cm^{-1}

^{1}H NMR : δ ppm 1.04-1.20 (m, 9H), 1.64-2.60 (m, 7H), 2.84 (m, 1H), 3.64 (s, 3H)

^{13}C NMR : δ ppm 25.0, 25.4, 25.8, 28.0, 39.8, 44.3, 50.8, 96.1, 170.7, 172.2, 216.9

2.4.3 Reaction of acetophenone with methyl crotonate in the presence of $Na_2Fe(CO)_4$

To a suspension of $Na_2Fe(CO)_4$ [prepared using $Fe(CO)_5$ (4.32 g, 22 mmol), Na (1.02 g, 44 mmol) and naphthalene (2.04 g, 16 mmol)] in THF (40 mL), acetophenone (1.21 g, 10 mmol) was added and the mixture stirred for 1h under N_2 atmosphere. To this mixture methyl crotonate (2.0 g, 20 mmol) was added and stirred for 10h at 25°C. The mixture was poured into acetone (40 mL) containing $CuCl_2.2H_2O$ (6.8 g, 40 mmol) to decompose the iron carbonyl. Water (40 mL) was added and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2 x 40 mL). The combined organic extract was washed with H_2O (20 mL) and brine (30 mL), dried and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene and ethyl acetate (4%) in hexane eluted monoalkylated ester 25.



$$\mathrm{Ph\overset{O}{\overset{\|}{C}}CH_2\overset{CH_3}{\overset{|}{C}}HCH_2COOCH_3}$$

25

Yield : 50% (1.10 g)

IR (neat) : 1680, 1740 cm^{-1}

^{1}H NMR : δ ppm 0.96-1.08 (d, J= 6.8 Hz, 3H), 2.24-3.04 (m, 5H), 3.64 (s, 3H), 7.32-7.56 (m, 3H), 7.84-7.98 (m, 2H)

^{13}C NMR : δ ppm 19.8, 26.5, 40.5, 44.5, 51.1, 127.9, 128.4, 132.7, 136.8, 172.6, 198.8

2.4.4 Reaction of cyclohexanone with methyl acrylate in the presence of sodium methoxide

To a suspension of NaOMe (1.08 g, 20 mmol) in THF (40 mL) cyclohexanone (0.98 g, 10 mmol) was added and the mixture stirred for 1h under N_2 atmosphere. To this mixture methyl acrylate (1.72 g, 20 mmol) was added and further stirred for 10h at 25^{o}C. The mixture was poured into dil.HCl (15 mL), the organic phase was separated, and the aqueous phase was extracted with ether. The combined organic phase was washed successively with H_2O (20 mL) and brine (30 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. The cyclic (3-keto ester (24) (1.01 g, 42%) was eluted using ethyl acetate (4%) in hexane.

This procedure was followed for other ketones (Table 2). The samples of cyclic (3-keto esters obtained in this way were found to be identical to that obtained using $Na_2Fe(CO)_4$.

2.4.5 Reaction of sodium-naphthalene-CO with cyclohexanone and methyl acrylate

The sodium-naphthalenide anion radical was prepared using Na (0.51 g, 22 mmol) and naphthalene (1.28 g, 10 mmol) in THF (60 mL) by stirring for 1h. The CO gas was bubbled into this solution for 2h at 25°C. To this reaction mixture cyclohexanone (0.49 g, 5 mmol) was added and stirred for 30 min at 25°C, methyl acrylate (0.86 g, 10 mmol) was added and stirred for 6h at 25°C. The resulting mixture was extracted with ether (2 x 30 mL), washed with dil. HCl and brine, dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene. The cyclic β-keto ester (24) (46%, 0.55 g) was isolated using ethyl acetate (4%) in hexane.

The above procedure was followed for other ketones (Table 3). The cyclic β-keto esters were found to be identical to that of the samples obtained using $Na_2Fe(CO)_4$.

2.5 References

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CHAPTER 3

Studies Towards the Development of Reactive Iron Carbonyl Species from $Fe(CO)_5$

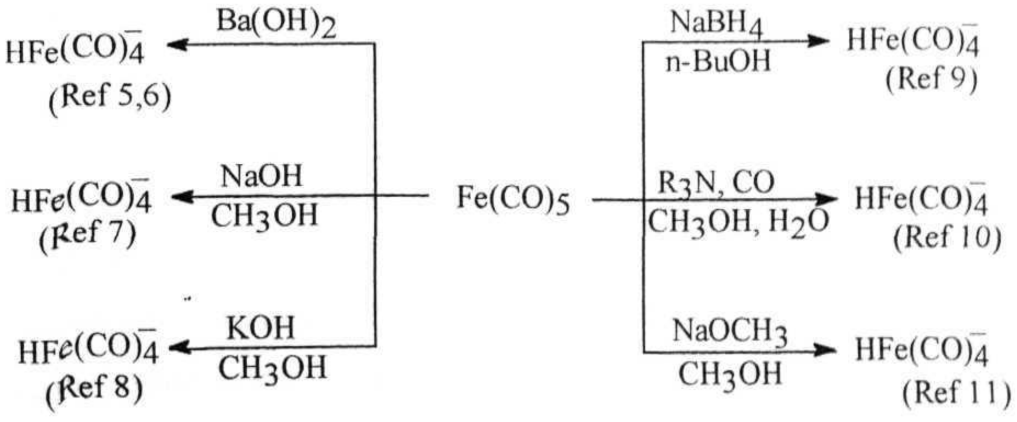
3.1 Introduction

As discussed in Chapter 2, efforts towards the preparation of η^2-ketone-$Fe(CO)_4$ complexes through oxidation of $Na_2Fe(CO)_4$ with CuCl in the presence of ketones were complicated by the highly basic nature of $Na_2Fe(CO)_4$ (Chapter 2). So, we were looking for another source of iron carbonyl species which could serve this purpose. It was thought that the relatively less basic species, $NaHFe(CO)_4$ would be more appropriate for use in the generation of "$Fe(CO)_4$".[1-3] The $HFe(CO)_4^-$ has proven synthetic utility.[4] A brief review of the synthesis and application of this reagent will facilitate the discussion.

Synthesis of $HFe(CO)_4^-$

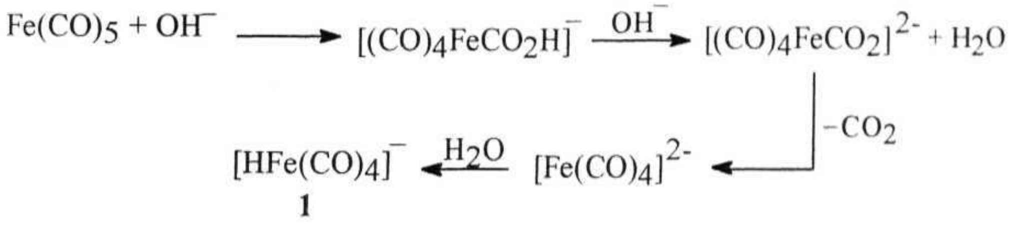
Several methods are available for the preparation of $HFe(CO)_4^-$ (Scheme 1)[5-11]

Scheme 1



The reaction of $Fe(CO)_5$ with alkali in alcohol or aqueous medium is widely used for the preparation of $HFe(CO)_4^-$. The mechanism of formation of this species involves the attack of the hydroxide ion on a carbonyl ligand to give a metallocarboxylic acid. The decarboxylation of this intermediate leads to $Fe(CO)_4^{2-}$ which is protonated to give $HFe(CO)_4^-$ (Scheme 2).[12]

Scheme 2



A practically useful and simple method for the preparation of $HFe(CO)_4^-$ has been developed by Collman *et al* by careful acidification of the $Na_2Fe(CO)_4$ followed by filtration of the sodium carboxylate (eqn 1).[13]

$$Na_2Fe(CO)_4 + CH_3COOH \xrightarrow{THF} \underset{\mathbf{1}}{NaHFe(CO)_4} + CH_3COONa \qquad (1)$$

Synthetic applications of $HFe(CO)_4^-$

The $HFe(CO)_4^-$ is a versatile reagent used in many organic transformations. It is brownish, highly hygroscopic, oxygen sensitive substance, and is isoelectronic with $HCo(CO)_4$.[4] Synthetic applications include carbonylation, reduction and hydrogen transfer reactions. The following section describes synthetic applications of $HFe(CO)_4^-$.

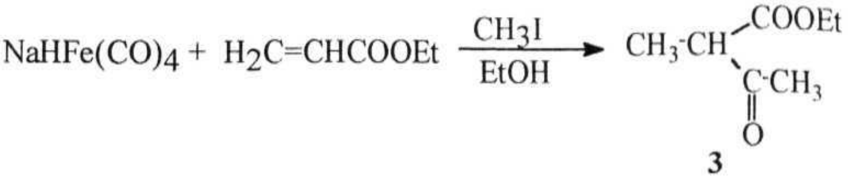
Carbonylation reactions

Brunet *et al* reported that $KHFe(CO)_4$ effects hydroformylation of strained alkenes, with high stereoselectivity.[14] The reaction is facilitated by higher CO pressure. Under these conditions, carbonylation of simple alkenes was not successful (eqn 2).[14]

2

(2)

The reaction of $HFe(CO)_4^-$ with ethyl acrylate in ethanol leads to carbonylation in the presence of a reactive alkyl halide or I_2 (eqn 3).[16]



$$NaHFe(CO)_4 + H_2C{=}CHCOOEt \xrightarrow[EtOH]{CH_3I} CH_3\text{-}CH(COOEt)(C(=O)CH_3)$$

3

-(3)

However, it has been reported that in alkaline medium, $HFe(CO)_4^-$ catalyzes the hydrocarboxylation of acrylic acid under mild conditions (eqn 4).[22]

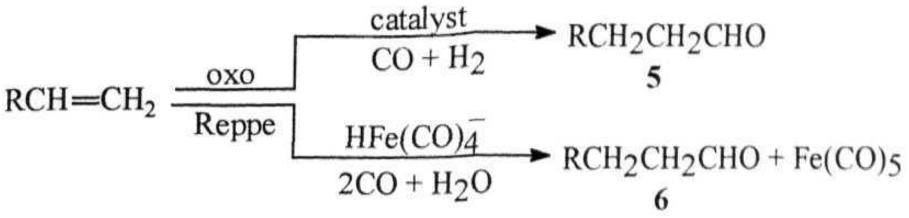
$$H_2C{=}CH\text{-}COOH \xrightarrow[CO]{Ca(OH)_2,\ Fe(CO)_5} CH_3\text{-}CH(COOH)(COOH)$$

4

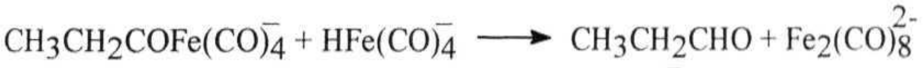
(4)

The hydroformylation is an important industrial process. Reppe modified the oxo process using H_2O as a proton source instead of H_2 gas and iron carbonyl as a catalyst (Scheme 3).[17]

Scheme 3

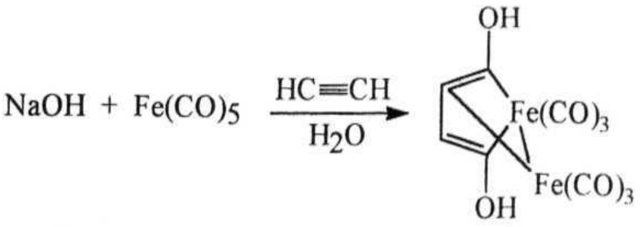


In later studies of the Reppe reaction, Petit *et al* noted that pH plays an important role.[18] King *et al* proposed a detailed mechanism for hydroformylation.[18] They observed that the aldehyde liberation is the rate determining step (eqn 5).



$$CH_3CH_2COFe(CO)_4^- + HFe(CO)_4^- \longrightarrow \underset{7}{CH_3CH_2CHO} + \underset{8}{Fe_2(CO)_8^{2-}} \qquad (5)$$

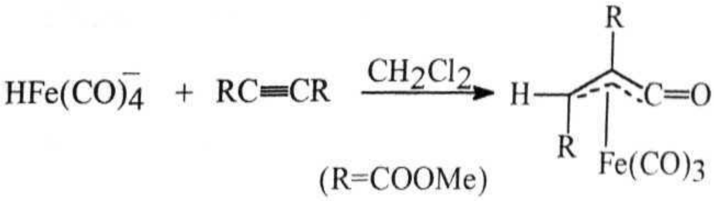
The reaction of $Fe(CO)_5$ in aq. alkaline solution with acetylene was first disclosed by Reppe.[19] A compound with the formula $Fe_2C_{10}H_4O_8$ was isolated. Later, Wender *et al* obtained the same complex in the reaction of $NaHFe(CO)_4$ and acetylene in H_2O in good yields (eqn 6).[20]



9

..(6)

Substituted alkynes were found to give poor yields under these conditions. However, certain activated alkynes react with $HFe(CO)_4^-$ to give the corresponding addition product (eqn 7).[21]



10

-(7)

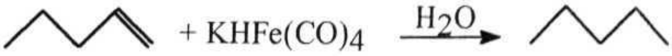
The mechanisms of these reactions are not clearly understood.

The $HFe(CO)_4^-$, generated *in situ* using catalytic amount of $Fe(CO)_5$ and trimethylamine, was found to convert methanol into ethanol under high CO pressure (eqn 8).[23]

$$CH_3OH + H_2 + CO \xrightarrow[Me_3N]{Fe(CO)_5} \underset{\mathbf{11}}{CH_3CH_2OH} + CO_2 \qquad (8)$$

Reduction and reductive alkylation

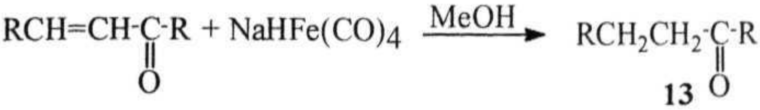
Wender and his co-workers shown that $KHFe(CO)_4$ reacts with 1-pentene at high temperature to yield the corresponding alkane (eqn 9).[15]



12

(9)

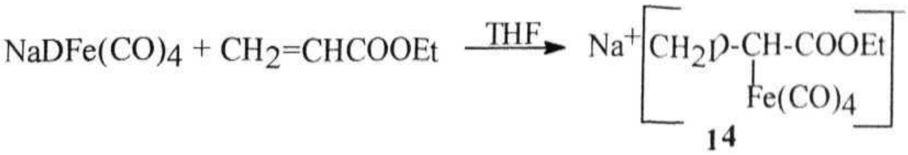
A simple, useful method was reported for the reduction of α,β-unsaturated ketones using the reagent generated *in situ* from $Fe(CO)_5$ in alkaline solution (eqn 10).[24]



$$RCH{=}CH\text{-}\underset{\underset{O}{\|}}{C}\text{-}R + NaHFe(CO)_4 \xrightarrow{MeOH} RCH_2CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}R \qquad (10)$$

13

Collman *et al* disclosed the selective reduction of α,β−unsaturated ketones, esters and lactones in high yields under mild conditions. [25] Furthermore, they have shown that the addition of $NaDFe(CO)_4$ to ethyl acrylatc in THF is fully regioselective and irreversible (eqn 11).[25]

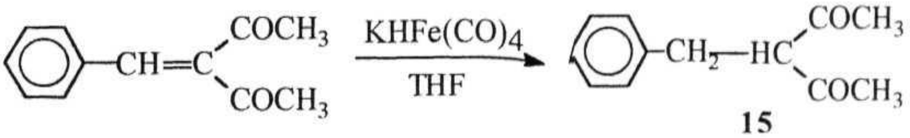


$$NaDFe(CO)_4 + CH_2{=}CHCOOEt \xrightarrow{THF} Na^+\left[CH_2D\text{-}\underset{Fe(CO)_4}{\underset{|}{CH}}\text{-}COOEt\right]^- \quad (11)$$

14

A similar complex has been isolated as PPN^+ salt and its structure was determined by X-ray diffraction studies.[25]

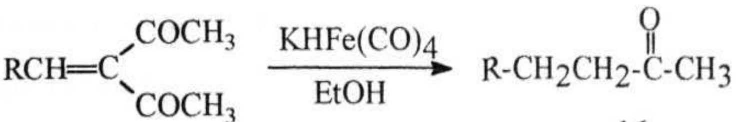
The $HFe(CO)_4^-$ reagent in THF has been found to be useful in the selective reduction of the double bond in Knoevenagel condensates to obtain the corresponding reduced products (eqn 12).[26]



15

(12)

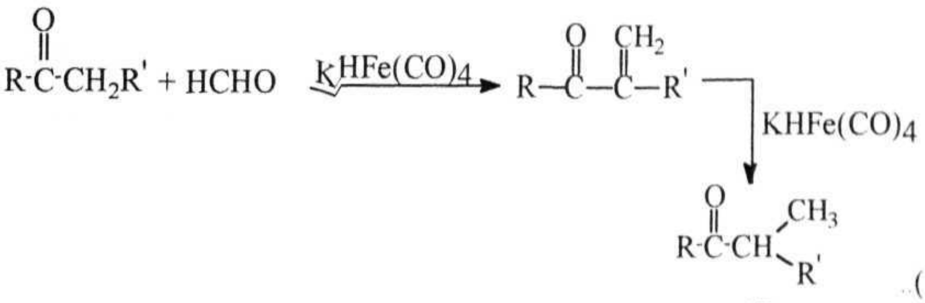
However, reductive deacylation was observed in the reaction of $HFe(CO)_4^-$ with Knoevenagel condensates in ethanol (eqn 13).[27]



16

(13)

The a,p-unsaturated derivatives, generated *in situ* in the reaction of $HFe(CO)_4^-$ with ketones and formaldehyde, are further reduced to obtain saturated products (eqn 14).[11]



17 ..(14)

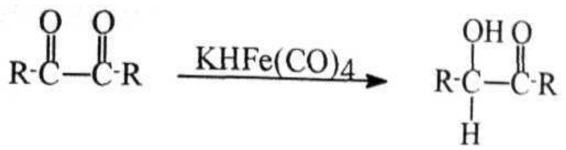
The reduction of aldehydes to alcohols using $NaHFe(CO)_4$ is very slow. However, it has been observed that the $HFe(CO)_4^-$ associated with the tetraethylammonium cation reduces aldehydes significantly (eqn 15).[28]

$$RCHO + [Et_4N]HFe(CO)_4 \xrightarrow{EtOH} \underset{\mathbf{18}}{RCH_2OH} \quad ..(15)$$

Petit *et al* used $KHFe(CO)_4$ for the reduction of acid chlorides to aldehyde (eqn 16)[29]

$$2RCOCl + 3HFe(CO)_4^- \xrightarrow{CH_2Cl_2} \underset{\mathbf{19}}{2RCHO} + \underset{\mathbf{20}}{[Fe(CO)_4]_n} \quad ..(16)$$

Recently, it has been reported by Brunet *et al* that certain 1,2-diketones are selectively reduced to hydroxy ketones in good yields by $KHFe(CO)_4$ (eqn 17).[30]



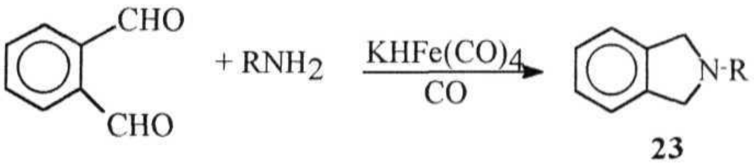
21 ..(17)

A thorough study on the use of $KHFe(CO)_4$ for the reductive alkylation of primary amines has been reported (eqn 18).[31]

$$RCHO + R'NH_2 \xrightarrow[EtOH,\ H_2O]{KHFe(CO)_4} RCH_2NHR' \qquad ..(18)$$

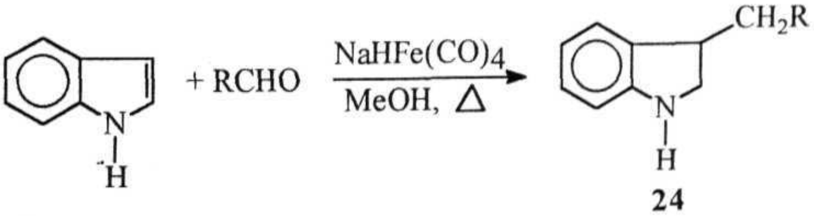
22

The procedure followed for the N-alkylation was also extended for the synthesis of 2-substituted isoindolines (eqn 19).[32]



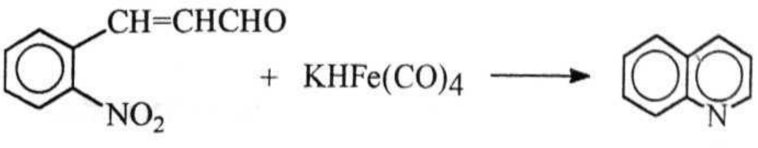
23 (19)

Reductive alkylation of indoles utilizing $HFe(CO)_4^-$ has been reported. The 3-alkylidene(indolenidine) has been proposed as an intermediate (eqn 20).[33]



24 ..(20)

The $KHFe(CO)_4$ was found to be useful in the synthesis of quinoline in quantitative yields (eqn 21).[34]



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(21)

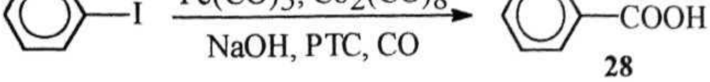
Reaction of $HFe(CO)_4^-$ with alkyl halides

The reactivity of $HFe(CO)_4^-$ with alkyl halides varies with the solvent polarity and the nature of the counter cation. Recently, it has been reported that $[PPN]^+[HFe(CO)_4]^-$ is unreactive toward n-BuBr and *t*-BuBr in THF at 26°C.[35]

Watanabe *et al* reported the carbonylation of an alkyl halide using $KHFe(CO)_4$ in ethanol to obtain aldehyde and ester after oxidative decomposition (eqn 22).[8]

$$CH_3CH_2CH_2I + KHFe(CO)_4 \xrightarrow[\text{2. } I_2/EtOH]{\text{1. EtOH, CO}} \underset{\mathbf{26}}{CH_3CH_2CH_2CHO} + \underset{\mathbf{27}}{CH_3CH_2CH_2COOEt} \quad ..(22)$$

The $HFe(CO)_4^-$ in combination with $Co(CO)_4^-$ catalyzes the carbonylation of iodobenzene to benzoic acid under phase transfer conditions. The reaction involves electron transfer from $HFe(CO)_4^-$ to the aryl halide to give an aryl radical which on reaction with $Co(CO)_4^-$ gives the carbonylated product (eqn 23).[36]



28

(23)

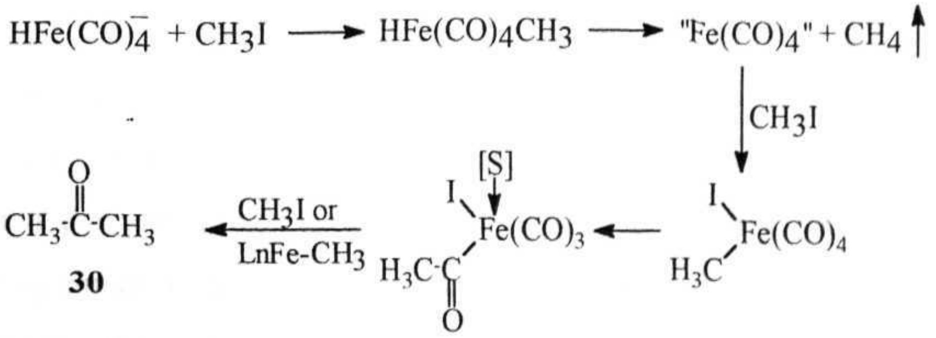
Whitmire *et al* examined the possibility of preparing unstable hydrido-alkyl complexes $HFe(CO)_4R$. In the course of these investigations, these authors observed the formation of $Fe(CO)_4(CH_3CN)$ and CH_4 in the reaction of $[Et_4N]HFe(CO)_4$ with CH_3I in CH_3CN (eqn 24)[37]

$$[Et_4N]HFe(CO)_4 + CH_3I \xrightarrow{CH_3CN} \underset{\textbf{29}}{Fe(CO)_4(CH_3CN)} + CH_4\uparrow \qquad (24)$$

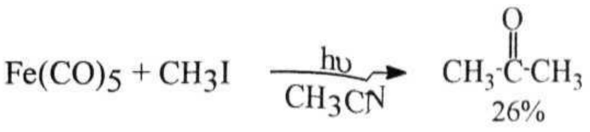
The reaction proceeds well with CH_3I, while the reactions with C_2H_5I, $(CH_3)_2CHI$ were less satisfactory. Further, it has been reported that the $Fe(CO)_4(CH_3CN)$ complex is highly air sensitive and unstable in solution. The authors were unable to isolate and characterize it further.[37]

Surprisingly, acetone was also observed as a product in the reaction of CH_3I with $HFe(CO)_4^-$ (24-44% yield). The acetone formation is quite slow compared to the consumption of $HFe(CO)_4^-$ and CH_4 production.[37] The authors proposed a mechanism, in which it was suggested that the acetone arises from the reaction of CH_3I with unsaturated "$Fe(CO)_4$" (Scheme 4).

Scheme 4



In order to further support this hypothesis, the authors generated $Fe(CO)_4(CH_3CN)$ by photochemical irradiation of $Fe(CO)_5$ in CH3CN. Interestingly, irradiation of $Fe(CO)_5$ in CH_3CN in the presence of CH3I yielded acetone in moderate yields (eqn 25).[37]



$$Fe(CO)_5 + CH_3I \xrightarrow[CH_3CN]{h\upsilon} CH_3\overset{O}{\overset{\|}{C}}CH_3 \qquad (25)$$

26%

30

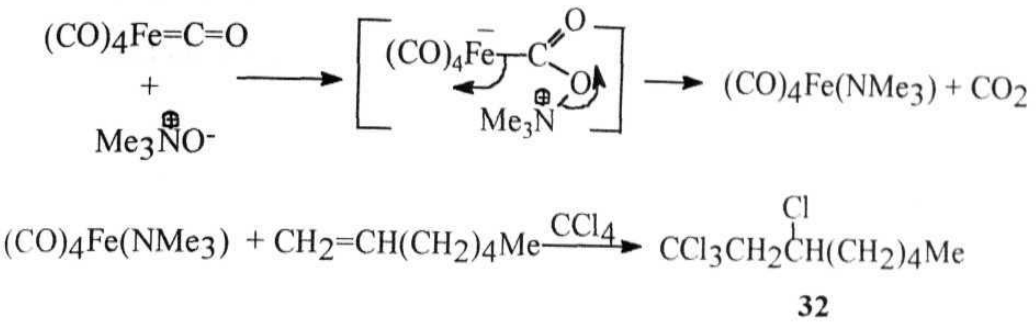
We have decided to explore this method of generation of "$Fe(CO)_4$" as it would serve as a simple alternate to other reported procedures [(*e.g.* UV irradiation of $Fe(CO)_5$[38] or $Fe_3(CO)_{12}$[39] or thermal reaction of $Fe_2(CO)_9$[40] or oxidative displacement of one CO of $Fe(CO)_5$ using an amine oxide[41,42] (Chapter 1, Scheme 12)].

In the absence of coordinating solvents, such as THF, CH3CN, amine or acetone or suitable reactants, the "$Fe(CO)_4$" species has been reported to undergo trimerization or polymerization.[42]

Synthetic Applications of "$Fe(CO)_4$"

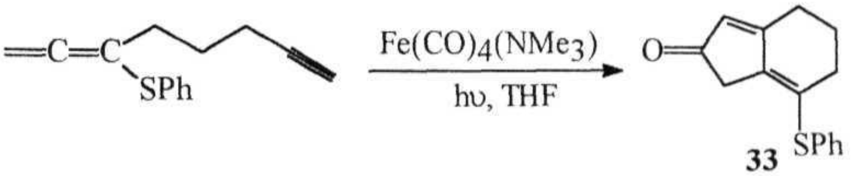
It may be of interest to briefly review the synthetic utilization of the "$Fe(CO)_4$" species which will facilitate the discussion of the results. It has been reported that, the trimethylamine-tetracarbonyl iron complex, prepared using $Fe(CO)_5$ and amine oxide acts as a catalyst in the addition of CCl_4 to unsaturated substrates (Scheme 5).[41]

Scheme 5



32

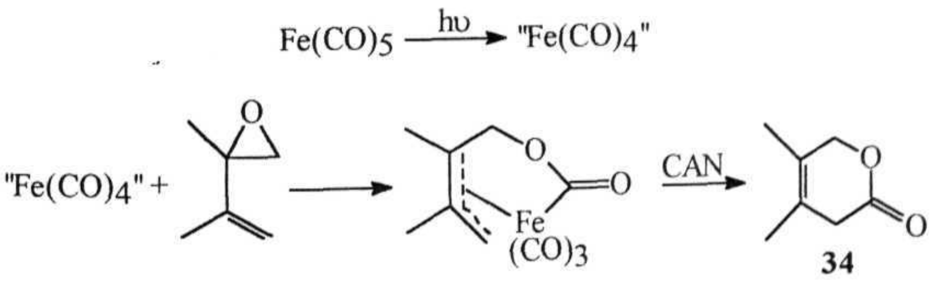
Under the photochemical conditions, 1-(ω-alkynyl)-1,2-propadienyl sulfide reacts with $Fe(CO)_4(NMe_3)$ to give bicyclic dienone 33 through the corresponding η^3-allyl iron complex (eqn 26).[42]



33 ..(26)

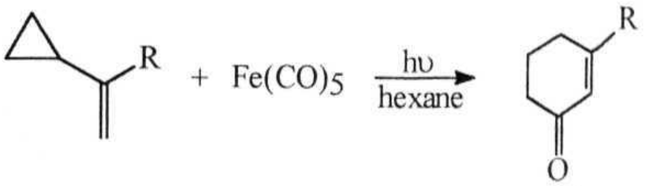
Ley *et al* demonstrated that "$Fe(CO)_4$" species reacts with an allyl epoxidc to form (π-lactonyl) iron complex which undergoes several useful transformations (Scheme 6).[43]

Scheme 6



34

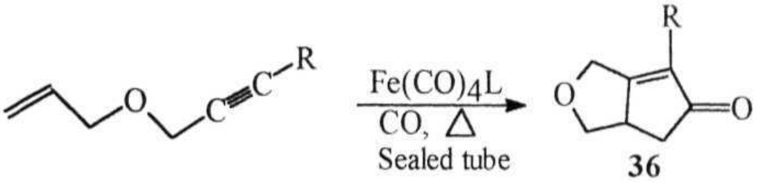
The reaction of "$Fe(CO)_4$", generated by the irradiation of $Fe(CO)_5$ with vinyl cyclopropane systems leads to the vinylic 7r-complex intermediate which on ring opening gives the corresponding cyclohexenone (eqn 27).[44]



35

.(27)

Pearson and his co-workers used $Fe(CO)_4L$, prepared by stirring $Fe_2(CO)_9$ in solvents such as acetone or CH3CN or THF, for the cyclization of enynes to the corresponding cyclopentenone derivatives (eqn 28).[40]

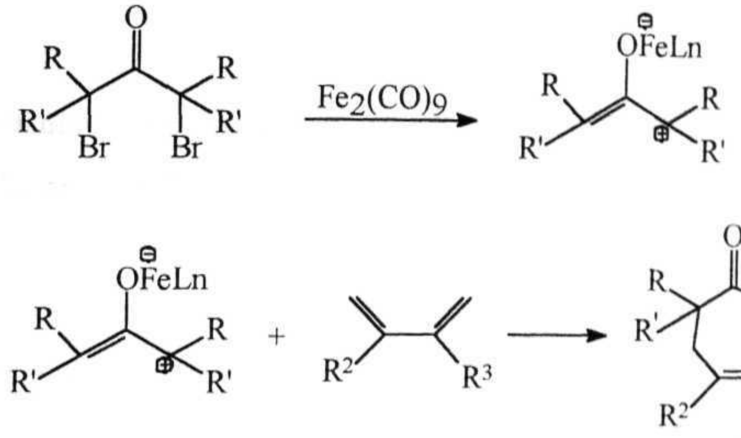


36

..(28)

Noyori *et al* developed a facile synthetic method for the preparation of iron stabilised oxallyl cation using $Fe_2(CO)_9$. Trapping of the oxallyliron (II) species with 1,3-dienes produces seven membered ring ketones directly (Scheme 7).[45]

Scheme 7



37

The $Fe_2(CO)_9$ can be considered as a convenient source of "$Fe(CO)_4$" without the requirement of heat or light to produce it. The mechanistic study revealed that the nucleophilic attack of electron rich Fe(0) in "$Fe(CO)_4$" on the highly reactive a,a'-dibromoketones. Loss of the bromides gives the iron stabilised oxallylcation.[45]

Preliminary experiments using $KHFe(CO)_4/CH_3I$ in THF/CH3CN solvent mixture indicated that the expected $Fe(CO)_4[CH_3CN]$ did not react with ketones or 1,2-diketones/methyl acrylate combination as envisaged in Scheme 5, Chapter 2. However, the product mixture, obtained in the reaction of $KHFe(CO)_4/CH_3I$ with diphenylacetylene followed by $CuCl_2$ oxidation, was found to contain the corresponding cyclobutenedione (IR, NMR, GC-MS analysis).[46]

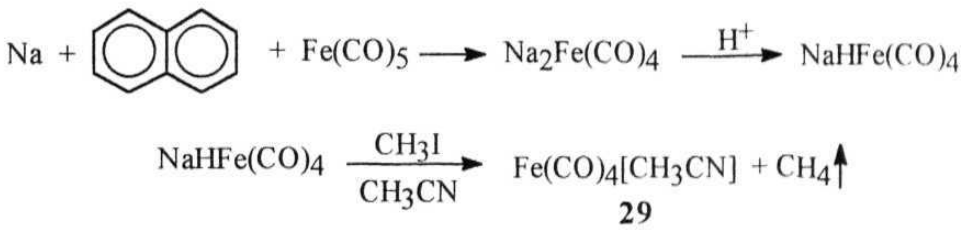
We describe detailed studies on some interesting transformations realized with the iron carbonyl reagent generated using $HFe(CO)_4^-$ and certain alkyl halides in this Chapter.

3.2 Results and Discussion

3.2.1a Double Carbonylation of Alkynes using $NaHFe(CO)_4/CH_3I$: A New Method of Preparation of Cyclobutenediones

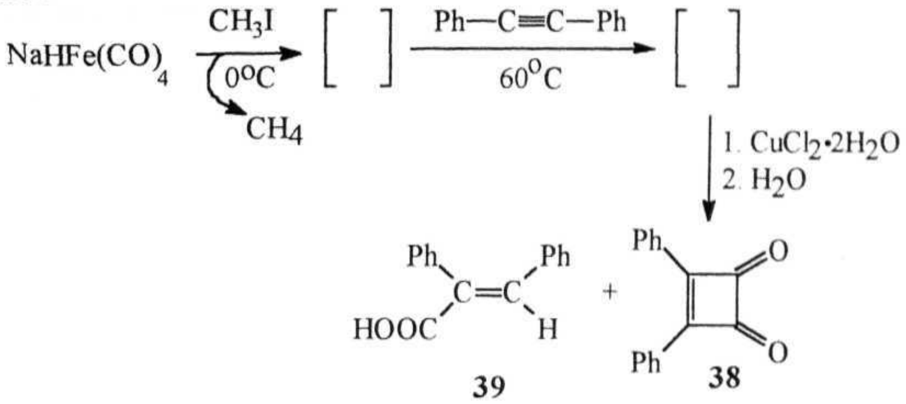
In our pursuit of studying carbonylation reactions, we became interested in examining the reactivity pattern of "$Fe(CO)_4$" complexes. As mentioned in the Chapter I, the $Na_2Fe(CO)_4$ can be prepared in THF by the reduction of $Fe(CO)_5$ with sodium-naphthalenide.[47] The $NaHFe(CO)_4$ in turn can be readily prepared upon acetic acid treatment following the Collman protocol.[13] The $NaHFe(CO)_4$ species prepared in this way was treated with CH3CN and CH3I to examine the reactivities of the resulting iron carbonyl species 29 (Scheme 8).

Scheme 8



There was gentle gas evolution upon addition of CH3I, which indicated that the reaction proceeded as anticipated. After extensive experimentation, it was observed that the reagent generated by the reaction of $NaHFe(CO)_4$ (2 eq), With CH_3I (2 eq) and CH3CN (5 mL) in THF reacts with diphenylacetylene (1 eq) to give the corresponding cyclobutenedione 38 and the α,β-unsaturated carboxylic acid 39 after $CuCl_2.2H_2O$ oxidation (Scheme 9). It was also found that the reaction took place even without using CH_3CN.[48]

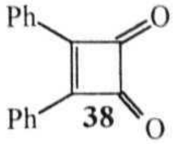
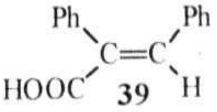
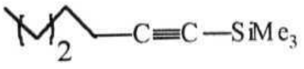
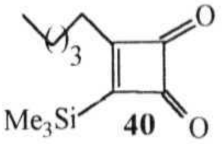
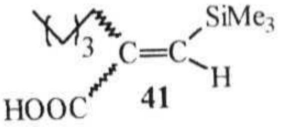
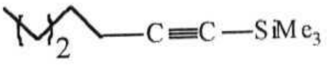
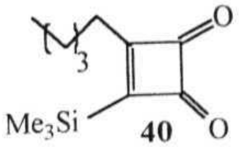
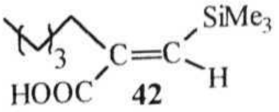
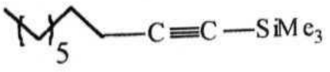
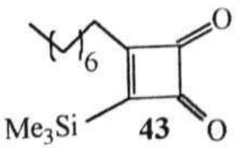
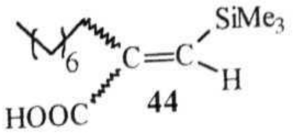
Scheme 9

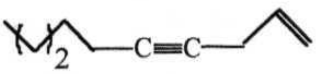
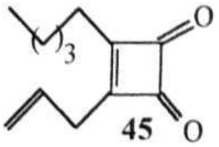
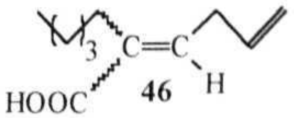
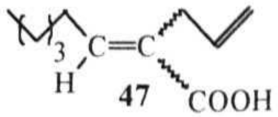
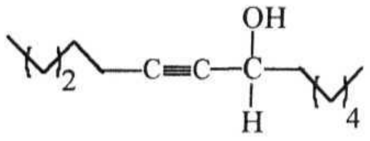
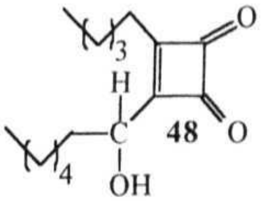
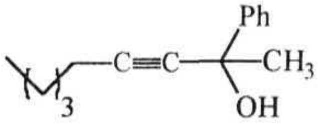
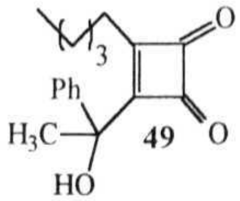


The transformation has been found to be general and various substituted alkynes were converted to the corresponding cyclobutenediones and α,β-unsaturated carboxylic acids (Table 1). The formation of cyclobutenedione is interesting, since, it is formed through a formal double carbonylation process. It was observed that when the reaction was carried out without using CH_3I, only a small amount of α,β-unsaturated carboxylic acid was formed (<10%) and the conversion is poor. Also, the cyclobutenedione was not formed here.

The propargylalcohol derivatives also give the corresponding cyclobutenediones (entries 6 and 7, Table 1) under these conditions. These results illustrate the compatibility of hydroxyl group in this transformation. In all these cases, some unidentified side products were isolated besides cyclobutenediones. The formation of cyclobutenedione from an enyne (entry 5, Table 1) shows that the reagent generated *in situ* reacted with alkyne without affecting the olefin moiety.

Table 1: Reaction of $NaHFe(CO)_4/CH_3I$ with alkynes[a]

S.No	Substrate	Temp	Product[b]	Yield(%)[c]
1	Ph—C≡C—Ph	60°C	 **38**	42[d]
			 **39**	22[e]
2		60°C	 **40**	37[f]
			 **41**	12
3		25°C	 **40**	23[f]
			 **42**	20[g]
4		60°C	 **43**	31
			 **44**	12

5		60°C	 **45**	32
			 **46**	10
			 **47**	
6		60°C	 **48**	27
7		60°C	 **49**	31

a) All reactions were carried out using $NaHFe(CO)_4$ [generated by acidification of $Na_2Fe(CO)_4$ (6 mmol) with CH_3COOH (6 mmol)], CH3I (5 mmol) and alkynes (2.5 mmol).

b) Cyclobutenediones were identified by analysis of spectral data (IR, ^1H NMR, ^{13}C NMR and Mass). The α,β-unsaturated carboxylic acids were obtained as a mixture of isomers except compound 39 and 42 which were obtained as single stereoisomer (entries 1 and 3).

c) Yields are of products isolated by column chromatography and calculated based on the amount of alkynes utilized.

d) The cyclobutenedione 38 was identified by analysis of spectral data (IR, ^1H NMR, ^{13}C NMR and Mass) and comparison with the reported data.[72,90]

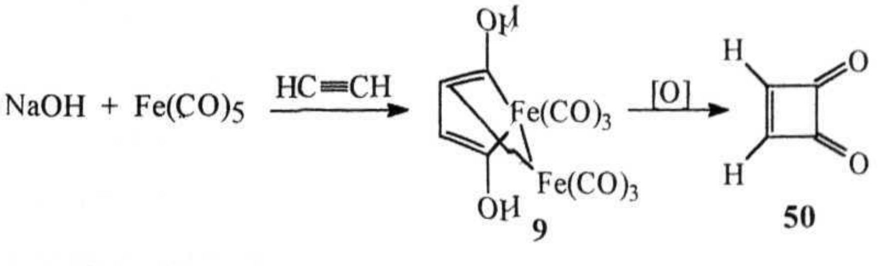
e) Satisfactory elemental analysis data were also obtained for product 39 (see experimental section).

0 For the cyclobutenedione 40 HRMS data were also obtained (SIT experimental section).

g) The regio- and stereoselectivity of product 42 was confirmed by comparing the spectral data obtained for the methyl ester with the reported data.[49]

The carboxylic acids formed (entries 2,4 and 5, Table 1) at 60°C were found to be mixture of stereoisomers. However, when the reaction was carried out at 25°C (entry 3, Table 1), the corresponding (E)-p-silyl-a,P-unsaturakd carboxylic acid 42 (20%) was isolated and the Z-isomer was not formed. The stereochemistry of this product was confirmed by comparing the ^{13}C NMR and ^{1}H NMR spectral data obtained for the methyl ester with the data reported in the literature.[49]

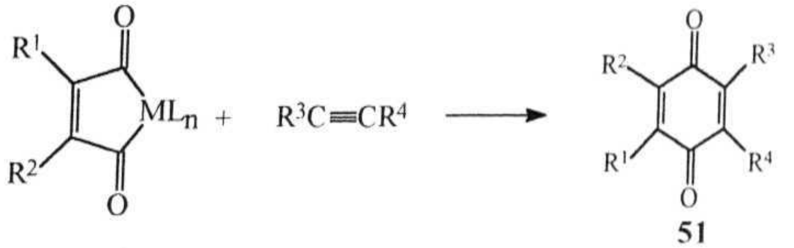
The obtention of cyclobutenediones here is reminiscent of that realized in the reaction of aq $NaOH/Fe(CO)_5$ with acetylene to get the reduced binuclear complex 9, which has been reported to yield the cyclobutenedione 50 on $FeCl_3$ oxidation (eqn 29).[51] However, it has been mentioned that the reduced complex of the type 9 has been obtained with dimethylacetylene in very low yield even after a long reaction time (3 weeks).[51]



(29)

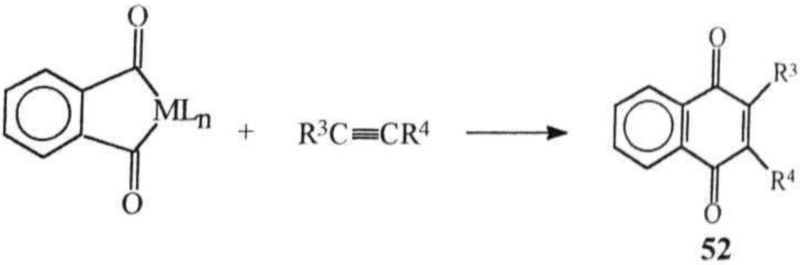
More recently, Sappa *et al* reported that the $NaOH/Fe(CO)_5$ system in refluxing methanol on treatment with substituted alkynes produced the reduced complex of the type 9 in 5% yield besides 7 to 10 other iron carbonyl complexes.[52] In the present case, the cyclobutenediones may result from the complex of the type 9.

It may be of interest to note here that the maleoyi iron complexes and similar cobalt complexes have been used by Liebeskind and his co-workers extensively in the synthesis of benzoquinone and napthoquinone derivatives (eqns 30 and 31).[53]



51

(30)

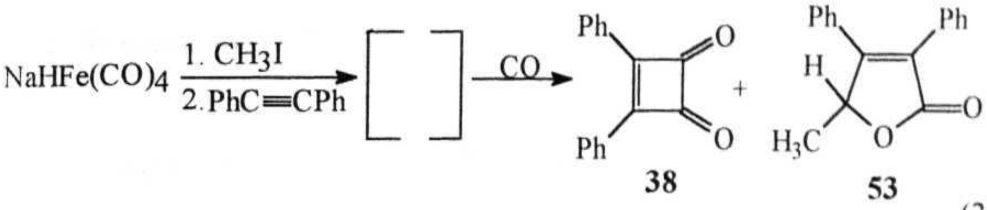


52

(3D

3.2.1b Reaction under CO atmosphere

Unfortunately, in the above mentioned transformations, a mixture of cyclobutenediones and α,β-unsaturated carboxylic acids are formed. It is well known that conversions in metal carbonyl mediated reactions are generally improved under CO atmosphere.[1,2] To examine such a possibility here, the experiment was performed under CO atmosphere. It was found that in this case, cyclobutenedione 38 (30%) and the corresponding butenolide 53 (21%) were formed (eqn 32).

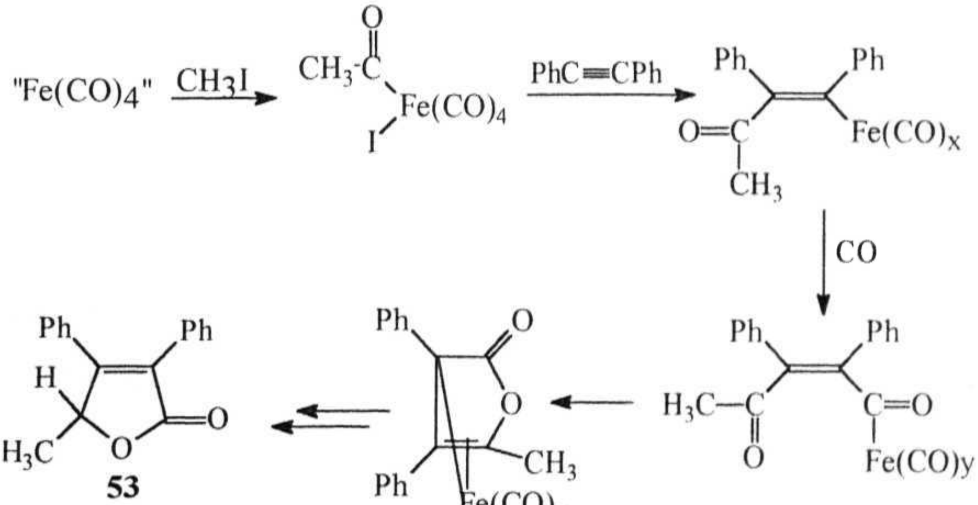


..(32)

Although, the yields of the cyclobutenedione 38 was not improved, it is interesting to note that the butenolide 53 is obtained here instead of the carboxylic acid 39.

As outlined in the introductory section, the CH3I gives acetone on reaction with "Fe(CO)4" through the intermediacy of $(CH_3CO)Fe(CO)_xI$ species. Presumably, the CO facilitates the formation of such species leading to acylatioii of the acetylene followed by cyclization (Scheme 10).

Scheme 10



As it will be discussed later, such butenolides are also formed in certain other conditions.

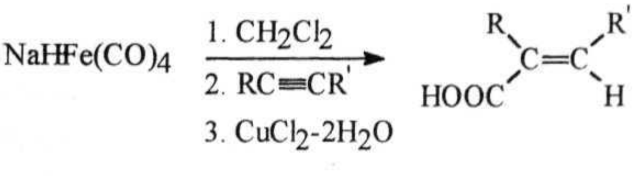
3.2.2a Reaction of $NaHFe(CO)_4/CH_2Cl_2$ with Alkynes

In the reaction of $NaHFe(CO)_4/CH_3I$ with alkynes, the nature of the species that leads to the formation of cyclobutenediones and α,β-unsaturated carboxylic acids is not clearly understood (Scheme 9). In order to understand the reaction mechanism, more informations are needed about the intermediates involved in this reaction. So, we have decided to investigate the reactions using other alkyl halides.

It has been reported by Whitmire *et al* that the $HFe(CO)_4^-$ slowly decomposes to $HFe_3(CO)_{11}^-$ in CH_2Cl_2 through the intermediacy of "$Fe(CO)_4$" (eqn 33).[54]

$$2HFe(CO)_4^- \longrightarrow 2\text{"}Fe(CO)_4\text{"} \xrightarrow{HFe(CO)_4^-} \underset{\mathbf{54}}{HFe_3(CO)_{11}^-} \qquad ..(33)$$

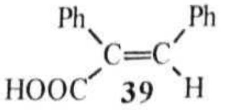
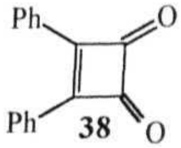
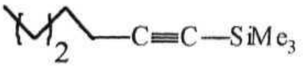
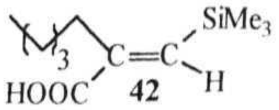
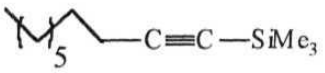
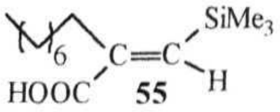
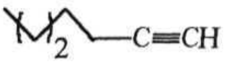
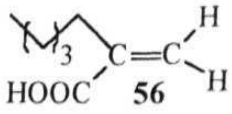
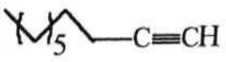
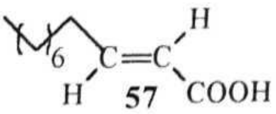
It is possible that such species may be the intermediates in this reaction. So, we have carried out experiments using CH_2Cl_2 in the place of CH_3I. It was observed that in this case, the hydrocarboxylated products, (E)-alkenoic acids with good regio and stereoselectivities were isolated. The reaction proceeds at 25°C. The results are summarized in the Table 2 (eqn 34).



..(34)

Hydrocarboxylation is considered as an industrially important reaction for the large scale production of acrylic acid derivatives from acetylene gas.[55] Due to the symmetric nature of acetylene, there is no possibility of regio- or stereo-

Table 2: Reaction of $NaHFe(CO)_4/CH_2Cl_2$ with $RC\equiv CR'$ in THF[a]

S.No	Substrate	Temp	Product[b]	Yield[c]
1	$Ph-C\equiv C-Ph$	50°C	 39	60[d]
			 38	21
2		25°C	 42	41[e]
3		25°C	 55	37[e]
4		25°C	 56	50[f]
5		25°C	 57	42[f]

a) All reactions were carried out using $NaHFe(C0)_4$ (6 mmol)[generated by acidification of $Na_2Fe(CO)_4$ with CH_3COOH (6 mmol)] CH_2Cl_2 (5 mL) and alkyne (2.5 mmol).

b) The α,β-unsaturated carboxylic acids were identified by analysis of spectral data (IR, ^1H NMR, ^{13}CNMR and Mass).

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

d) The compound 39 was identified by comparing the spectral data with that reported in literature.[89] Satisfactory elemental analysis data also were obtained for this compound (see also Table 1).

e) The regio- and stereoselectivity of the products in entries 2 and 3 were confirmed by comparing the ^{13}C and ^{1}H NMR spectral data obtained for the corresponding methyl ester with the data reported in literature.[49]

f) The regio- and stereochemistry of products in the entries 4 and 5 were confirmed by the analysis of spectral data and comparison with the reported data.[56]

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isomers formation. In the case of unsymmetrical alkynes, the hydrocarboxylation can lead to four isomeric products (two regio- and two stereoisomers). However, in the present transformation all alkynes are converted to a single regio- and stereoisomer of (E)-alkenoic acids. The regio- and stereoselectivity of the reactions are confirmed by NMR analysis and by the comparison of the ^{13}C-NMR and ^{1}H-NMR data with the data of compounds reported in the literature.[49,56,89]

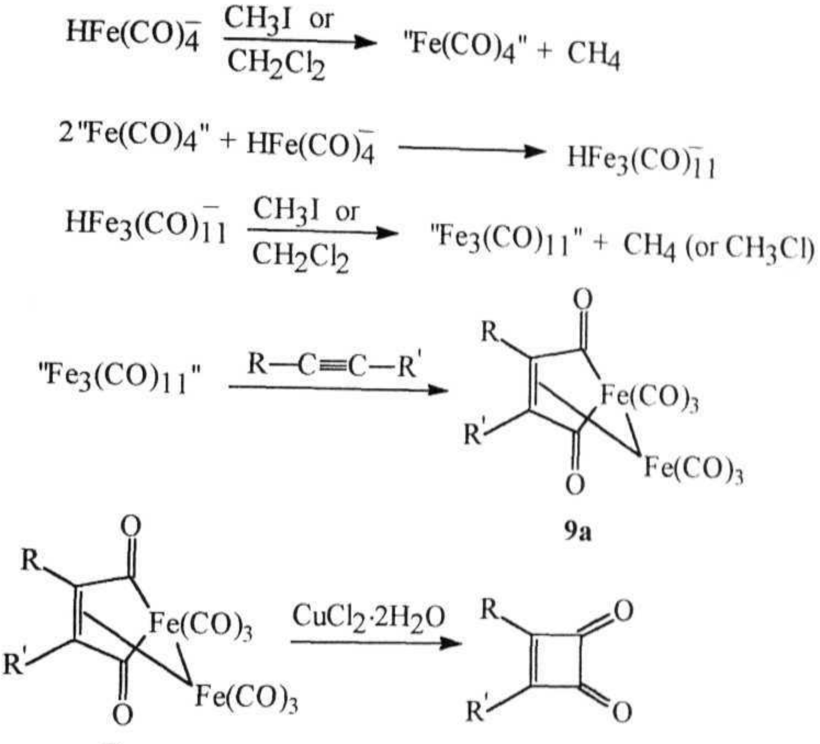
It was observed that diphenylacetylene is readily carbonylated to obtain the (E) isomer of 2,3-diphenylpropenoic acid at 25°C. The conversions and yields were better when the experiments were carried out at 50°C. However, at this temperature, the corresponding cyclobutenedione was also isolated as a side product (21%). In the case of other alkynes (Table 2, entries 2-5), the reaction proceeds well at room temperature to give the P-(E)-alkenoic acids and only traces of the corresponding cyclobutenediones (2-5%) were isolated.

Surprisingly, in the case of 1-decyne (entry 5, Table 2), α-carbonylation (i.e. at terminal position) occurs while β-carbonylation was observed with 1-heptyne (entry 4). Alper *et al* reported that the steric bulk of the alkyne substituent affects the stereo- and regioselectivity.[36] It seems likely that the increase in the chain length may be responsible for this unusual result with 1-decyne. However, the corresponding silyl derivative of 1-decyne (entry 3, Table 2) undergoes α-carbonylation rather than β-carbonylation. Presumably, here the bulkiness of trimethylsilyl group overcomes the effect of chain length.

The β-trimethylsilyl-(E)-α,β-unsaturated carboxylic acids (entry 2 and 3, Table 2) are potential intermediates for synthetic applications as they have silyl group and carbonyl group in adjacent carbon atoms. Much efforts have been directed previously towards the synthesis of such compounds.[49]

We have also observed that the CH_2Cl_2 is required for this transformation and the reaction gives <10% of carboxylic acid in the absence of CH_2Cl_2. As mentioned earlier, it has been observed by Whitmire *et al* that the reaction of $[Et_4N]HFe(CO)_4$ with CH_2Cl_2 affords $HFe_3(CO)_{11}^-$.[37] This could be the intermediate responsible for the formation of both cyclobutenedione and carboxylic acid. The ratio of the products *(i.e.* cyclobutenedione and α,β-unsaturated carboxylic acid) may depend on the relative rates of the removal of hydride species from $NaHFe_3(CO)_{11}$ to give electronically and coordinatively unsaturated polymeric iron carbonyl species of the type "$Fe_3(CO)_{11}$". This species on reaction with alkyne could give the complex 9a which in turn could be converted into cyclobutenediones upon oxidation (Scheme 11).

Scheme **11**

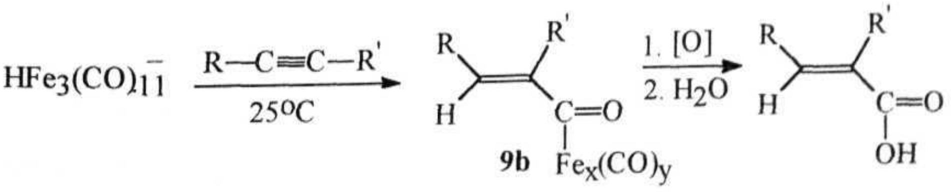


9a

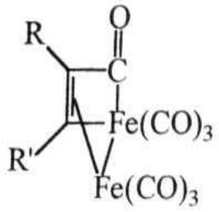
9a

The $HFe_3(CO)_{11}^-$ species may be responsible for the formation of α,β-unsaturated carboxylic acids. The $HFe_3(CO)_{11}^-$ mediated hydrometallation of the alkynes could lead to the complex 9b which on oxidative decomplexation could give α,β-unsaturated carboxylic acids (Scheme 12).

Scheme 12



9b

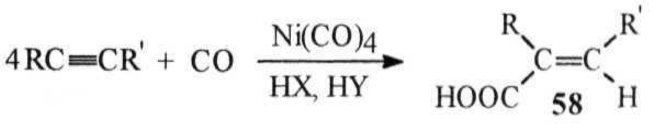


9c

Initially, it was thought that the vinylic hydrogen might have come from the reaction of the complex 9c with water in the $CuCl_2.2H_2O$. In order to examine this possibility, we carried out oxidative decomplexation using $CuCl_2.2D_2O$ (prepared by adding D_2O to anhydrous $CuCl_2$). However, it was observed that the α,β-unsaturated carboxylic acid isolated was devoid of deuterium. Most probably, the vinylic hydrogen might have come from the $HFe_3(CO)_{11}^-$ or an equivalent species through hydrometallation.

The reaction of $HFe_3(CO)_{11}^-$ with CH3I to produce methane and "$Fe_3(CO)_{11}$" could be expected to be faster than the reaction with CH_2Cl_2. This may be the reason for the formation of α,β-unsaturated carboxylic acids as a major product in the case of CH_2Cl_2 and cyclobutenedione as a major product in the reaction using CH_3I. However, this mechanistic proposal can be only tentative. The mechanism of the formation of cyclobutenediones and a,p-unsaturated carboxylic acids will be further discussed in the section **3.2.3b.**

The interest in this transformation arises from its relevance to the synthesis of oxygenated products from hydrocarbons mediated by metal complexes. Various transition metal reagents have been used for the hydrocarboxylation of alkynes. Among these metals Ni, Co and Pd reagents have been most widely used for the hydrocarboxylation of alkynes. The hydrocarboxylation of the alkynes was originally fonnulated by Reppe using nickel carbonyl in the presence of acid and alcohol as outlined in the eqn 35.[57]

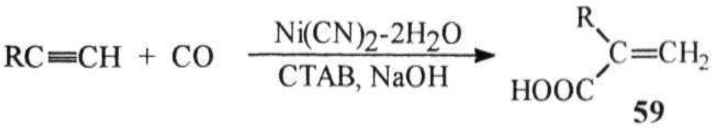


58

HY= alcohol HX= acid

.(35)

Alper *et al* reported the regiospecific hydrocarboxylation of the alkynes catalyzed by nickel cyanide under phase transfer conditions (eqn 36).[56]



59

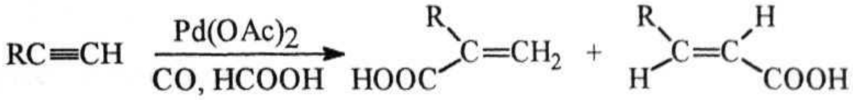
(36)

Hydroesterification of acetylenic substrates can be also carried out in the presence of cobalt carbonyl reagents (eqn 37).[55]

$$RC\equiv CH + CO + MeOH \xrightarrow[HCo(CO)_4]{Co_2(CO)_8,\ or} RCH{=}CHCOOMe \quad (37)$$

60

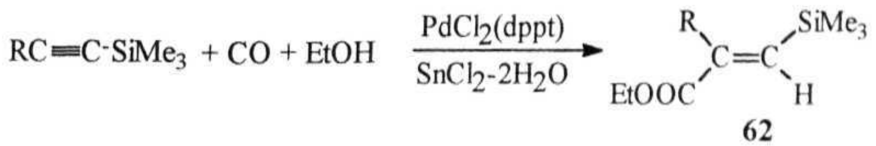
Recently, $Pd(OAc)_2$ mediated hydrocarboxylation of alkynes to a mixture of regioisomers in the presence of fonnic acid under high CO pressure has been reported (eqn 38).[56b]



61a 61b

(38)

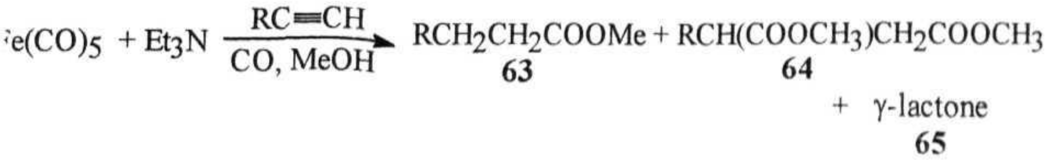
Takeuchi *et al* observed the palladium mediated hydroesterification of trimethylsilyl alkynes to obtain the (E)-β-ethoxycarbonylvinylsilane 62 (eqn 39).[49]



62

(39)

It has been reported that direct hydrocarboxylation of substituted alkynes mediated by iron carbonyl yielded a mixture of saturated mono ester 63, diester 4 and lactone 65 (eqn 40).[58]



$$\text{e(CO)}_5 + Et_3N \xrightarrow[\text{CO, MeOH}]{RC\equiv CH} \underset{\mathbf{63}}{RCH_2CH_2COOMe} + \underset{\mathbf{64}}{RCH(COOCH_3)CH_2COOCH_3} + \underset{\mathbf{65}}{\gamma\text{-lactone}}$$

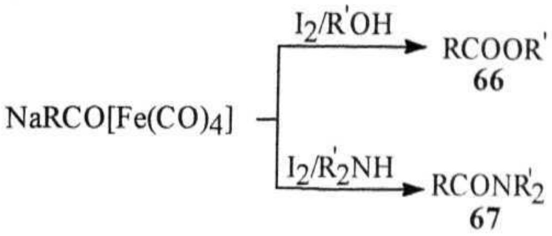
(40)

The present transformation using $NaHFe(CO)_4/CH_2Cl_2$ is carried out under ambient conditions to obtain (E)-alkenoic acids with 100% regio- and stereoselectivity. Hence, it is a good alternate method for the hydrocarboxylation of alkynes.

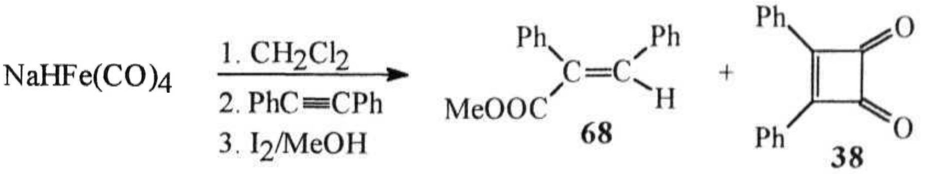
3.2.2b Synthesis of a,P-unsaturated carboxylic esters and amides

It is **well** known that the reaction of acylferrate anion with I_2 in the presence of nucleophiles, gives carboxylic acids, esters and amides (Scheme 13).[13]

Scheme 13



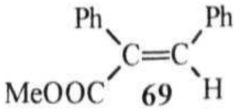
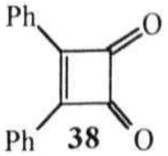
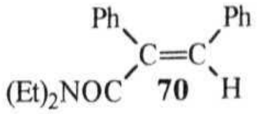
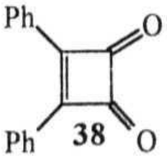
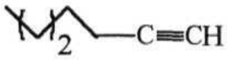
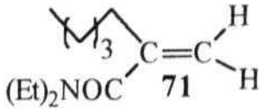
A similar type of reactivity was anticipated for the intermediate (Scheme 12) formed in the reaction of $NaHFe(CO)_4/CH_2Cl_2$, with I_2 in the presence of nucleophiles. Regio- and stereoselective synthesis of a,P-unsaturated carboxylic acid derivatives could be achieved if such generalizations could be made. Indeed, it has been observed. The intermediate generated *in situ* in the reaction of $NaHFe(CO)_4/CH_2Cl_2$/alkyne upon I_2 treatment in the presence of methanol, gives the (E)-isomer of methyl 2,3-diphenylpropionate 68 besides the corresponding cyclobutenedione 38 (eqn 41).



(41)

The corresponding amide 70 was obtained, when diethylamine was used in the place of MeOH (entry 2, Table 3). The corresponding amide was also obtained in the case of 1-heptyne (entry 3, Table 3). The transformation may go through the following reaction pathway similar to that suggested for hydrocarboxylation (Scheme 14).

Table 3 ; Reaction of $NaHFe(CO)_4/CH_2Cl_2/RC{\equiv}CR'$ with I_2/ROH or R_2NH[a]

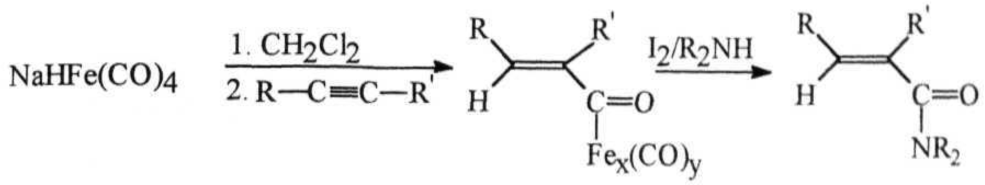
S.No	Substrate	Temp	Product[b]	Yield(%)[c]
1	Ph—C≡C—Ph	50°C		55
				20
2	Ph—C≡C—Ph	50°C		50
				20
3		25°C		35

a) All reactions were carried out using $NaHFe(CO)_4$ [generated by acidification of $Na_2Fe(CO)_4$ using CH_3COOH (6 mmol)], CH_2Cl_2 (5 mL), alkyne (2.5 mmol) and MeOH (5 mL) or diethylamine (5 mL).

b) Products were identified by analysis of spectral data (IR, ^1H NMR, ^{13}C NMR and mass). The amide 71 was identified by comparing the spectral data with that of the reported data.[89]

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

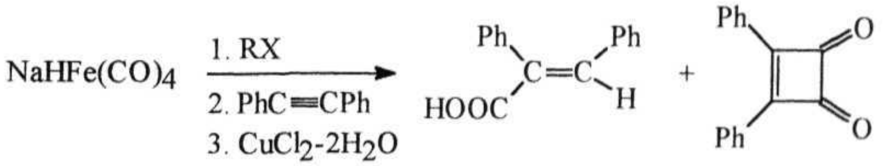
Scheme 14



3.2.2c Reaction of $NaHFe(CO)_4$ with CHCI3 or $BrCH_2CH_2Br$ and Alkyne

As discussed earlier, the reaction of $NaHFe(CO)_4/CH_3I$ with alkynes leads to the corresponding cyclobutenediones as the major products after $CuCl_2.2H_2O$ oxidation. Further, the reagent, generated using $NaHFe(CO)_4$ and CH_2Cl_2, gives a,p-unsaturated carboxylic acids as the major products. In order to further examine the effect of halides, we have investigated the reaction using $CHCl_3$ and $BrCH_2CH_2Br$. The results are summarized in Scheme 15.

Scheme 15



RX = $CHCl_3$ **39** 18% **38** 3%

RX = $BrCH_2CH_2Br$ **39** 25% **38** 2%

However, the yield of cyclobutenedione is not improved and the reactivity is similar to that observed previously. In summary, a simple procedure has been developed for the regio- and stereoselective hydrocarboxylation of various alkynes to α,β-unsaturated carboxylic acids and its derivatives under ambient conditions using $NaHFe(CO)_4$.

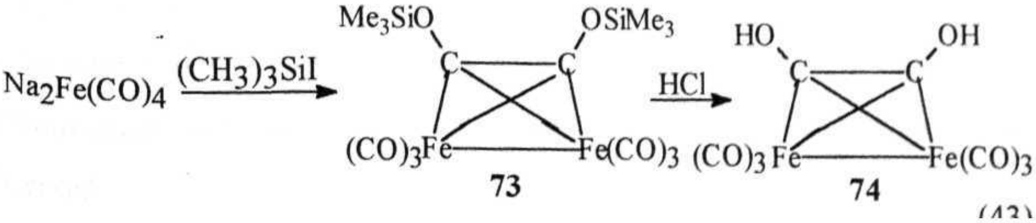
3.2.3a Reaction of $NaHFe(CO)_4$/TMSCl with Alkynes

Iron carbonyl is known to form complexes of the type $M_2Fe(CO)_4$ (M= Sn, Si and Ge) with main group elements.[60] Among these, the compounds containing Fe-Si bond has been found to be highly reactive. This section outlines our efforts on the synthesis and reactivity of reagents prepared in the reaction of $NaHFe(CO)_4$ with TMSCl.

Graham *et al* investigated the synthesis of compounds containing Fe-Si bond and demonstrated the formation of $R_3Si(H)Fe(CO)_4$ under thermal as well as photochemical conditions (eqn 42).[61,62]

$$Fe(CO)_5 + R_3SiH \xrightarrow[\Delta]{h\nu \text{ or}} \underset{\textbf{72}}{R_3SiFeH(CO)_4} \qquad \textbf{.(42)}$$

MacDiarmod *et al* synthesized compounds of the empirical formulae $[(CH_3)_3Si]_2Fe(CO)_4$ and $(CH_3)_3Si(H)Fe(CO)_4$.[60] These are believed to be dimeric compounds. Whereas the complex 73 is obtained by the reaction of $(CH_3)_3SiI$ with $Na_2Fe(CO)_4$, reaction of the complex 73 with anhydrous HCl affords compound 74 (eqn 43).

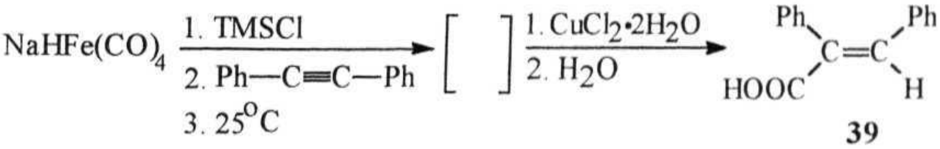


73

74

(43)

We have decided to examine the reactivity of the species generated using $NaHFe(CO)_4$/TMSCl combination in order to compare the results obtained using the alkyl halides. It was observed that the intermediate complex, generated *in situ* by treating $NaHFe(CO)_4$ (3 eq) with TMSC1 (3 eq) reacts with terminal and internal alkynes (1 eq) to yield α,β-unsaturated carboxylic acids with excellent regio- and stereoselectivities (eqn 44).



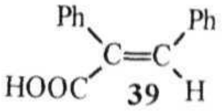
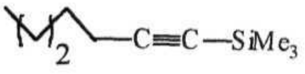
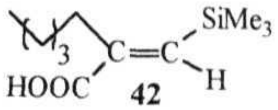
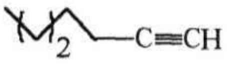
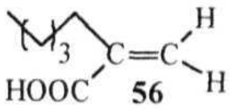
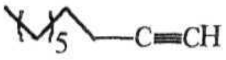
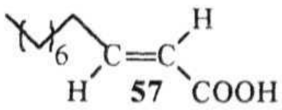
39

(44)

The reaction was found to be general and various alkynes were converted to (E)-alkenoic acids (Table 4). This reactivity pattern is similar to that realized using $NaHFe(CO)_4/CH_2Cl_2$. In all these cases, the corresponding cyclobutenediones were obtained in very low yields (<5%). Even in the case of diphenylacetylene, which gave 20% cyclobutenedione with $NaHFe(CO)_4$-CH_2Cl_2, the α,β-unsaturated carboxylic acid was isolated as the major product (53%) besides only traces (<5%) of the corresponding cyclobutenedione.

The stereochemistry of the (E)-alkenoic acids was confirmed by comparison of ^{13}C and ^{1}H NMR spectral data with that of the reported compounds.[49,56,89] Again, in the case of 1-decyne (entry 4, Table 4), a-carbonylation (i.e. at terminal position) rather than β-carbonylation was observed.

Table 4 : Reaction of $NaHFe(CO)_4$/TMSCl with $RC\equiv CR'$ at 25°C[a]

S.No	Substrate	Temp	Product[b]	Yield(%)[c]
1	$Ph-C\equiv C-Ph$	25°C	 39	54[d]
2		25°C	 42	50[e]
3		25°C	 56	49[f]
4		25°C	 57	45[f]

a) All reactions were carried out using $NaHFe(CO)_4$ (7.5 mmol) [generated using acidification of $Na_2Fe(CO)_4$(7.5 mmol) with CH_3COOH (6 mmol)J, TMSC1 (7.5 mmol) and alkynes (2.5 mmol).

b) Products were identified by analysis of the spectral data (IR, ^1H NMR, ^{13}C NMR and Mass).

c) Yields are of products isolated by column chromatography using hexane/ethyl acetate (97:3) as eluent and based on the amount of alkynes used.

d) The compound 39 was identified by comparing the spectral data with that reported in the literature.[89]

e) The regio- and stereoselectivity of the product 42 was confirmed by comparing the ^{13}C and ^1HNMR spectral data obtained for the methyl ester with the data reported in literature.[49]

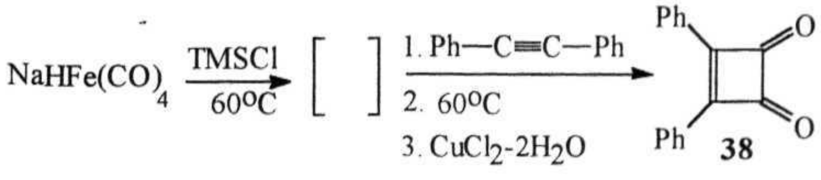
f) The regio- and stereospecificity of the products 56 and 57 were confirmed by analysis of spectral data and comparison with the reported data.[56] The spectral data are given in the experimental section.

3.2.3b Effect of Temperature on the Reaction of $NaHFe(CO)_4/TMSCl$ with Alkynes

Graham *et al* reported the formation of electronically and coordinatively unsaturated "$Fe(CO)_4$" species, by slightly heating the $R_3Si(H)Fe(CO)_4$. This "$Fe(CO)_4$" species readily trimerizes to give $Fe_3(CO)_{12}$ (eqn 45)62

$$R_3SiHFe(CO)_4 \xrightarrow[\Delta]{} R_3SiH + \text{"}Fe(CO)_4\text{"} \longrightarrow \underset{\mathbf{75}}{Fe_3(CO)_{12}} \qquad \textbf{(45)}$$

As discussed previously, we were looking for methods to generate "$Fe(CO)_4$" under mild conditions using inexpensive reagents. To examine the possibility of utilizing the above reaction (eqn 45) in our study, series of experiments were carried out. It was found that the reagent, prepared using $NaHFe(CO)_4/TMSCl$ at 60°C, on reaction with diphenylacetylene followed by $CuCl_2 \cdot 2H_2O$ oxidation produced cyclobutenedione 38 (63%) as the only product (eqn 46).

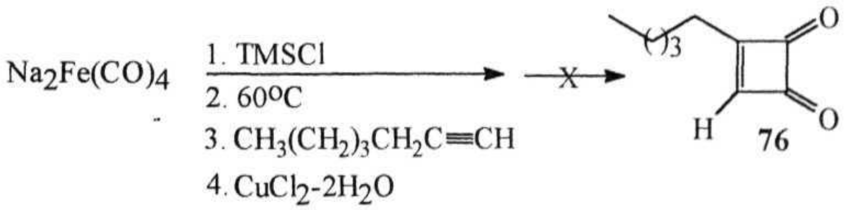


(46)

The reaction was found to be general. The corresponding cyclobutenediones were obtained in relatively good yields (51-63%) using various terminal, internal and substituted alkynes (Table 5).

As discussed previously, the reagent generated using the $NaHFe(C())_4$-CH_3I and $NaHFe(CO)_4/CH_2Cl_2$ combinations gave mixture of cyclobutenediones and α,β-unsaturated carboxylic acids. In the present case, clearly, the reagent system is more selective. Furthermore, interestingly, the terminal alkynes which gave unclean reaction using the $NaHFe(CO)_4/CH_3I$ combination, gave good yields of cyclobutenediones with $NaHFe(CO)_4/TMSCl$ at 60°C.

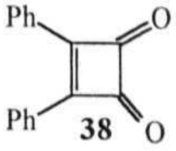
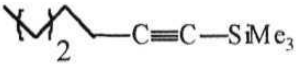
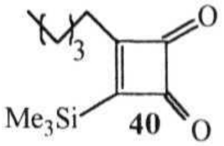
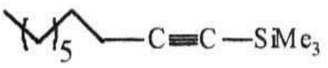
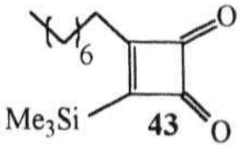
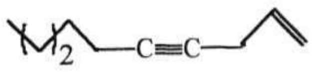
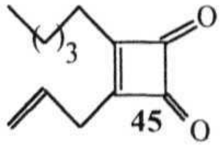
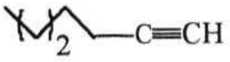
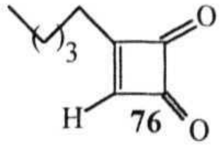
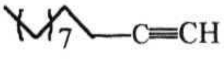
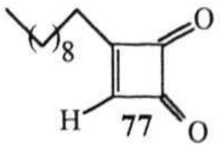
As mentioned earlier, it has been reported that the reaction of $Na_2Fe(CO)_4$ with TMSI gives the complex 73.[60] We have observed that the reaction of the reagent prepared using $Na_2Fe(CO)_4/TMSCl$ with alkyne yielded only some unidentified iron carbonyl complex, which indicates that the complex of the type 73 may not be an intermediate in the formation of cyclobutenediones or α,β-unsaturated carboxylic acids under the present reaction conditions (eqn 47).



-(47)

In the reaction of $NaHFe(CO)_4/CH_3I$ and $NaHFe(CO)_4/CH_2Cl_2$ with alkynes, the "$Fe_3(CO)_{11}$" and $HFe_3(CO)_{11}$ have been proposed as intermediate species (Scheme 12). In the case of $NaHFe(CO)_4/TMSCl$ also the reactive

Table 5 : Reaction of $NaHFe(CO)_4$/TMSCl with alkynes at 60°C[a]

S.No	Substrate	Product[b]	Yield[c]
1	Ph—C≡C—Ph	 **38**	63[d]
2		 **40**	51[e]
3		 **43**	53
4		 **45**	60
5		 **76**	56[f]
6		 **77**	57[f]

a) All reactions were carried out using $NaHFe(C0)_4$ (7.5 mmol) [generated using acidification of $Na_2Fe(CO)_4$ (7.5 mmol) with CH_3COOH (6 mmol)] TMSC1 (7.5 mmol) and alkynes (2.5 mmol).

b) Products were identified by analysing the spectral data (IR, ^1H NMR, ^{13}C NMR and Mass). The spectral data were found to be identical to that of the samples obtained using $NaHFe(CO)_4/CH_3I$.

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

d) The cyclobutenedione 38 was identified by analysis of spectral data (IR, ^1H NMR, ^{13}C NMR and Mass) and comparison with the reported data.[72]

e) For the cyclobutenedione 40 HRMS were also obtained (see also Table 1).

f) The spectral data of product 76 (IR, NMR) were identical to the data reported for this compound.[90] The spectral data of product 77 are comparable to the spectral data reported for the cyclobutenedione (R= C_5H_{11}).[90] The spectral data for the products 76 and 77 are given in the experimental section.

---

species could be "$Fe_3(CO)_{11}$" and $HFe_3(CO)_{11}^-$. The hydride abstraction to form silane is expected to be slow at 25°C compared to reaction at 60°C. This could lead to the formation of α,β-unsaturated carboxylic acids in the former case and cyclobutenediones in the latter case (scheme 16).

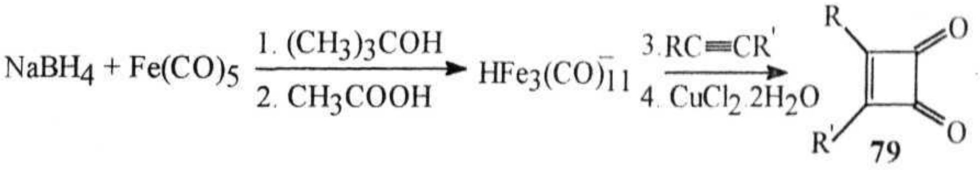
Scheme 16

$$HFe(CO)_4^- \xrightarrow{TMSCl} \text{"}Fe(CO)_4\text{"} + Me_3SiH$$

$$2\,\text{"}Fe(CO)_4\text{"} + HFe(CO)_4^- \longrightarrow HFe_3(CO)_{11}^-$$

$$HFe_3(CO)_{11}^- \xrightarrow[60^oC]{TMSCl} \underset{\mathbf{78}}{\text{"}Fe_3(CO)_{11}\text{"}}$$

Recently, it was observed in this laboratory that the $HFe_3(CO)_{11}^-$, prepared using $NaBH_4/Fe(CO)_5$ under the conditions described in the literature,[64] reacts with alkynes to give the corresponding cyclobutenediones as the only products (65-75%) (eqn 48).[63] This observation strongly suggests that the species involved in the formation of cyclobutenedione is produced from the reaction of $HFe_3(CO)_{11}^-$ with CH_3COOH which could be most probably the unsaturated "$Fe_3(CO)_{11}$" species (eqn 49).

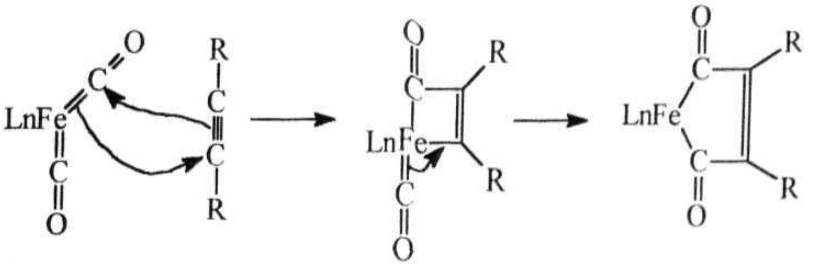


(48)

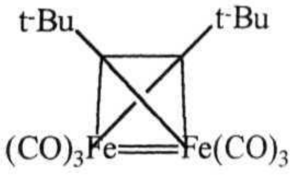
$$HFe_3(CO)_{11}^- + CH_3COOH \longrightarrow H_2Fe_3(CO)_{11} \longrightarrow \underset{\textbf{78}}{"Fe_3(CO)_{11}"} + H_2 \qquad (49)$$

However, the mechanistic proposals outlined here can be only tentative. Presumably, the double carbonylation would take place in two steps under the present reaction conditions (Scheme 17),

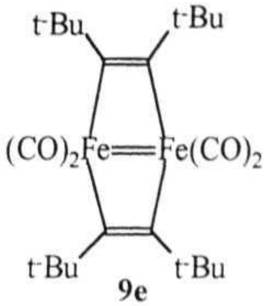
Scheme 17



Most probably, the two step mechanism would go through prior coordination of the alkynes to the metal. Sterically hindered alkynes (*e.g.* R-C≡C-R, R= t-butyl) are known to form dinuclear iron complexes under thermal conditions using $Fe_2(CO)_9$[65] and $Fe_3(CO)_{12}$.[66]



9d



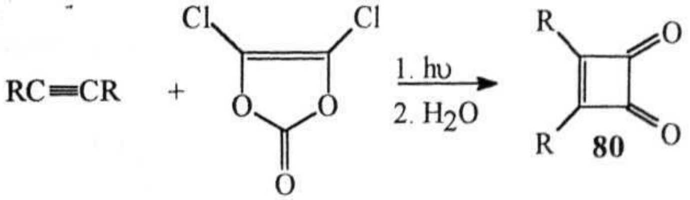
9e

However, carbonylations of such complexed alkynes have not been reported. Obviously, we have a long way to go in order to gel a clear mechanistic picture.

Iron carbonyls have been reported to undergo a variety of reactions with alkynes to give cyclopentenones, quinones, butadiene-$Fe(CO)_3$ complexes as products.[2,55] However, these reports do not describe the formation of cyclobutenediones.

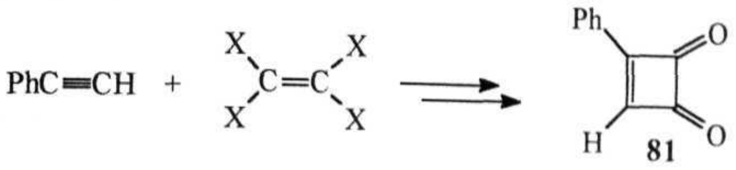
Several methods are available in the literature for the synthesis of cyclobutenediones. The preparative chemistry of cyclobutenediones has been reviewed in three comprehensive articles by Schmidt and Ried which describes the following methods (eqn 50-55).[67]

Addition of alkyne to olefinic carbonates



..(50)

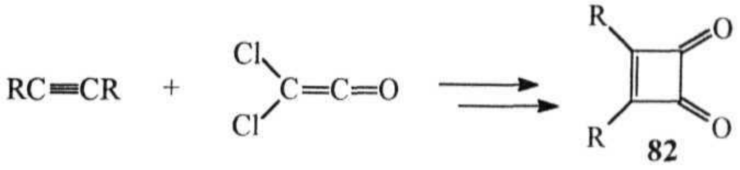
Addition of alkyne to tetrahaloethene



81

(51)

Addition of alkyne to ketene



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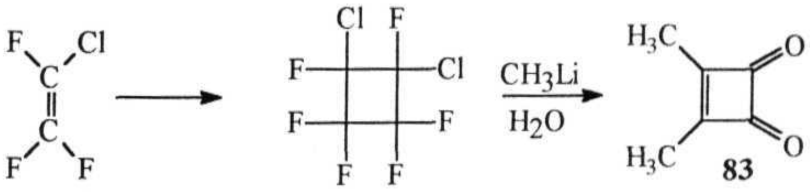
(52)

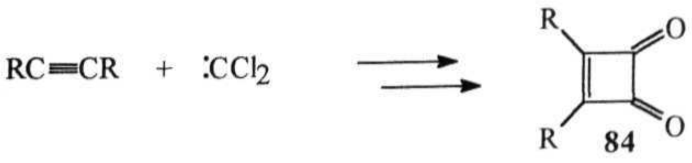
Dimerization of tetrahaloethene



83

(53)

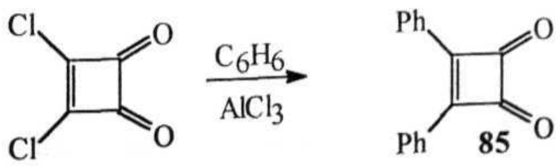
Addition of alkyne to carbene



84

(54)

From squaric acid derivative

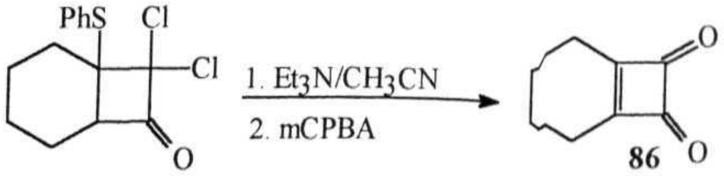


85

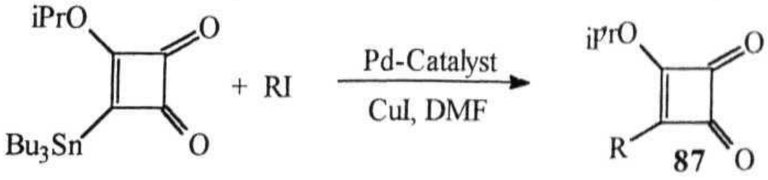
(55)

The yields in the above mentioned reactions are generally not high.

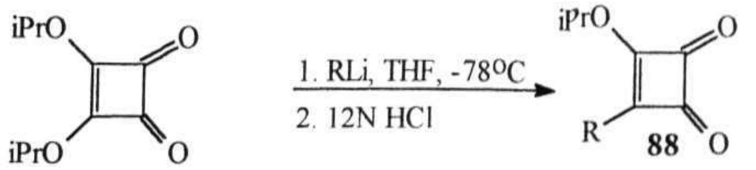
Liebeskind *et al* reported new methods for the synthesis of cyclobutenediones in high yields (eqn 56-58).[68-70]



(56)



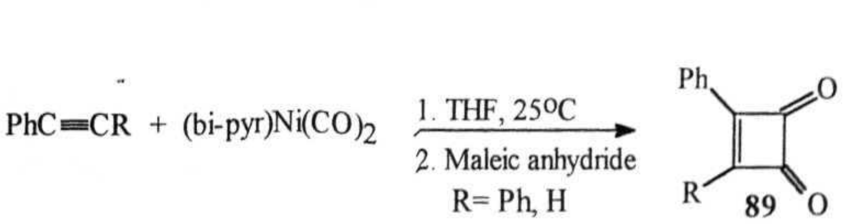
(57)



(58)

Moore and his co-workers have developed some useful methods for the synthesis of cyclobutenediones through a similar approach[71]

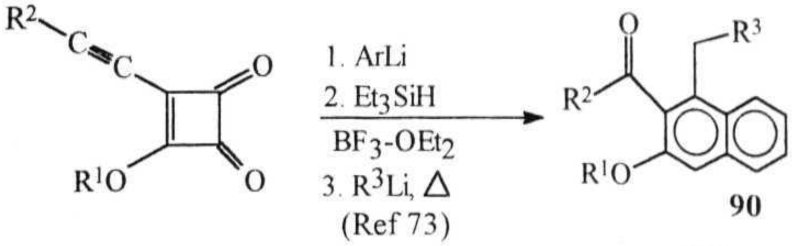
A nickel bipyridyl complex has been found to be useful in the synthesis of cyclobutenediones (89) (eqn 59).[72]



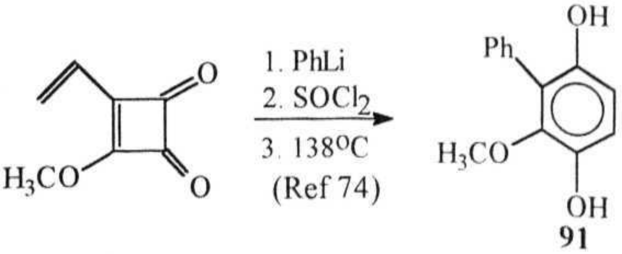
(59)

Among the methods described above for the synthesis of cyclobutenediones, no procedure stands out as sufficiently general to allow the preparation of diversely substituted compounds. Most of the procedures require multistep synthesis, involving different reagents and reaction conditions for the introduction of functional groups into the cyclobutenedione. So, the single pot procedure developed during this studies, using simple reagents and easily available inexpensive starting materials, should be useful for the synthesis of diversely substituted derivatives of cyclobutenediones.

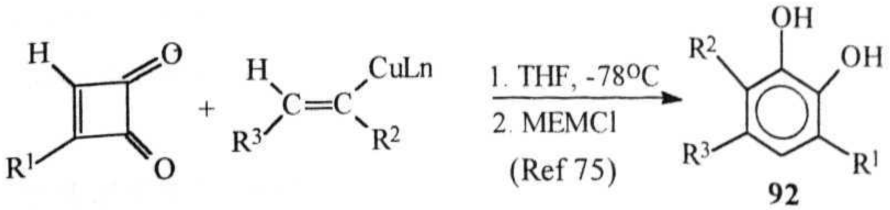
Cyclobutenediones and their adducts are highly versatile starting materials for the synthesis of variety of carbocyclic and heterocyclic products such as highly substituted naphthalenes,[73] phenols,[74] catechols,[75] heterocycles[76] and highly oxygenated angularly fused polycyclic aromatics[77] (eqn 60-64).



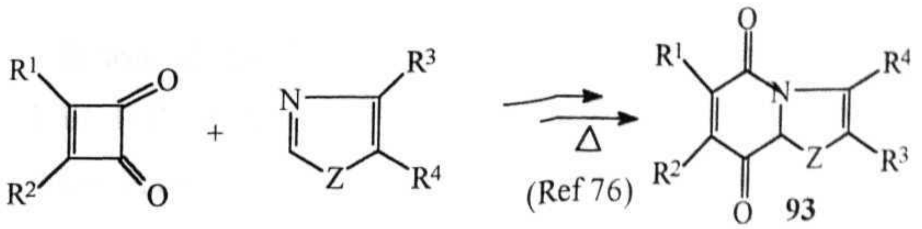
•(60)



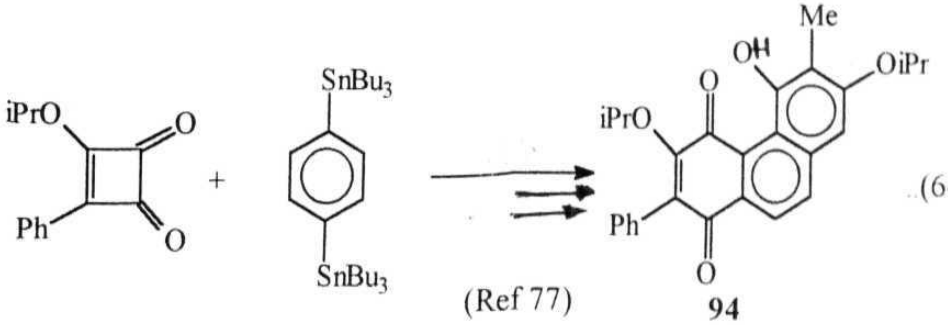
.(61)



..(62)



..(63)



..(64)

Certain cyclobutenediones exhibit biological activity and it has been suggested that some of them might show antitumor activity.[78,79] Hence, the availability of a single pot procedure for the synthesis of cyclobutenediones using the iron carbonyl reagents described here should be helpful for further development in this area.

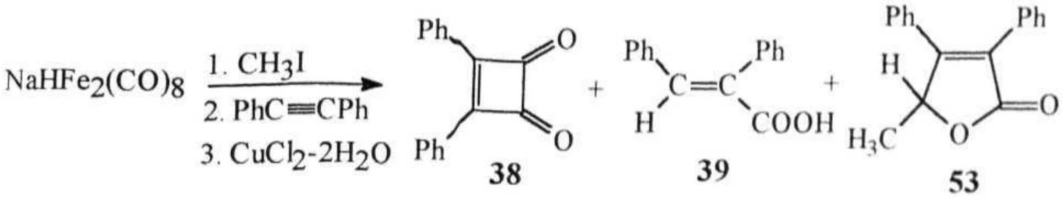
3.2.4 Reaction of $NaHFe_2(CO)_8/CH_3I$ with diphenylacetylene

As discussed earlier, the $HFe_3(CO)_{11}^-$ may be responsible for the reactivity observed with alkynes. The other iron carbonyl species which we have not studied so far is $NaHFe_2(CO)_8$ This can be readily prepared by following Collman's procedure as outlined in eqn 65.[13]

$$Na_2Fe(CO)_4 + Fe(CO)_5 \xrightarrow[25^oC]{THF} Na_2Fe_2(CO)_8 \xrightarrow{H^+} NaHFe_2(CO)_8$$

..(65)

It was observed that addition of diphenylacetylene to $NaHFe_2(CO)_8$-CH3I in THF at 25°C for 12h followed by $CuCl_2.2H_2O$ oxidation gives cyclobutenedione 38 (26%), α,β-unsaturated carboxylic acid 39 (8%) and butenolide 53 (33%) (eqn 66).



(66)

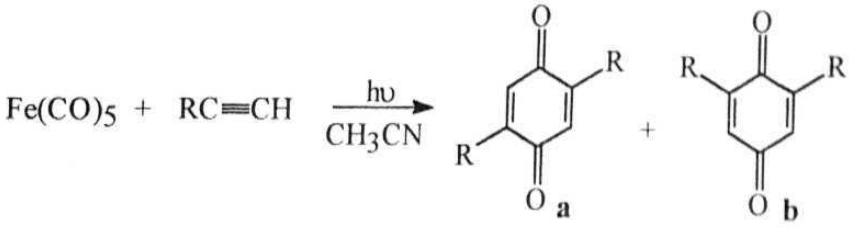
Although the reactivity observed is similar to that observed with the $NaHFe(CO)_4/RX$ systems, the reaction is not clean here and hence we did not pursue studies on this reagent further.

3.2.5 Photochemical reaction of $Fe(CO)_5$ with alkynes in CH_3CN:

As mentioned in the introductory section, Whitmire *et al* suggested the formation of $Fe(CO)_4[CH_3CN]$ complex in the reaction of $[R_4N]HFe(CO)_4$ with CH3I in CH_3CN and also in the photochemical reaction.[37] It is not clear that similar "Fe(CO)4" species is formed under the present reaction conditions. However, we decided to investigate the species formed under photolytic conditions from $Fe(CO)_5$ in CH3CN.

An experiment was carried out by irradiating the mixture of $Fe(CO)_5$ and 1-heptyne in CH3CN for 8 hrs under N_2 atmosphere [Srinivasan-Griffin-Rayonet type reactor, which comprises of eight UV-tubes of wave length 253.7 nm]. After oxidative decomposition, a mixture of 2, 5- **and** 2, 6 -disubstituted benzoquinones were isolated (64%). The reaction is found to be general. Some other terminal alkynes also reacted in a similar fashion (Scheme 18).

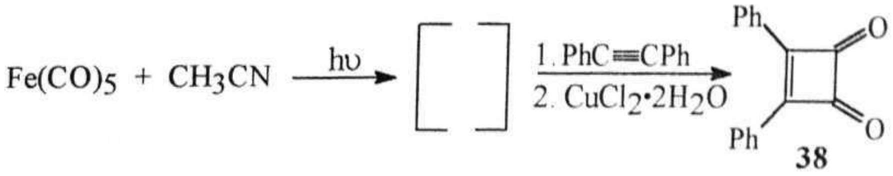
Scheme 18



R= $CH_3(CH_2)_4$	**95**	64%
R= $CH_3(CH_2)_7$	**96**	50%
R= Ph	**97**	40%

A similar reactivity has been reported for terminal alkynes with $Fe(CO)_5$ under photolytic conditions.[80]

Interestingly, the expected cyclobutenediones were not isolated. It was thought that the difference in the reactivity may be due to the reaction of "$Fe(CO)_4$" with two alkynes to give quinones under the photolytic conditions. In order to avoid the formation of quinones, we have first irradiated $Fe(CO)_5$ in CH3CN to obtain $Fe(CO)_4[CH_3CN]$ and carried out the further reaction with diphenylacetylene in the absence of light. Unfortunately, only 10% of cyclobutenedione 38 was isolated besides unreacted diphenylacetylene. The conversion was poor under several reaction conditions. Increase in the irradiation time and increase of the reaction temperature after the addition of alkyne were not helpful (eqn 67).



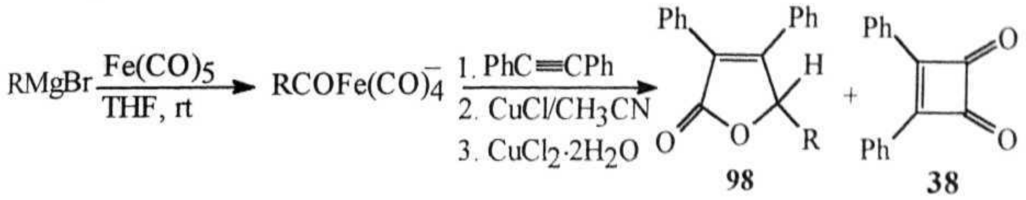
(67)

Even this low conversion was not observed with 1-heptyne and the corresponding cyclobutenedione was not formed. Unfortunately, it is not clear whether the "$Fe(CO)_4$" is formed in adequate amount here. Further, it is possible that the species involved here may be different from that obtained using the $NaHFe(CO)_4/RX$ reagent combinations. Further studies under photolytic conditions using lamps of other wavelengths should be fruitful.

3.2.6 Reaction of RMgBr and $Fe(CO)_5$ with CuCI in the presence of alkynes

As discussed in Chapter 1, it has been observed in this laboratory that the reaction of $NaRCOFe(CO)_4$ with $CuCl$ gives the corresponding 1,2-diketones. It was envisaged that this transformation may produce $[Fe(CO)_4]_n$ as one of the products (Chapter 1, Scheme 5). In our efforts towards utilization of the "$Fe(CO)_4$", we became interested in examining this reagent system in studies with alkynes.

An interesting carbonylative acylation-cyclization was observed when the $RCOFe(CO)_4^-$ (10 mmol) [generated *in situ* using RMgBr (10 mmol) (R= ethyl bromide) and $Fe(CO)_5$ (10 mmol)] was reacted with $CuCl$ (20 mmol) in the presence of diphenylacetylene (5 mmol) and CH_3CN (5 mL) in THF (35 mL) at room temperature (eqn 68). Some other alkyl halides were also converted into butenolides under these conditions (Table 6).

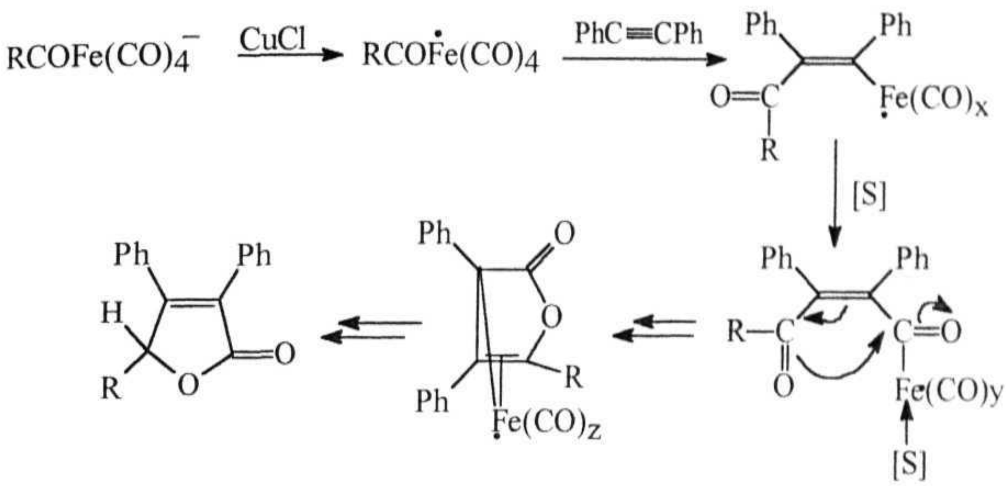


(68)

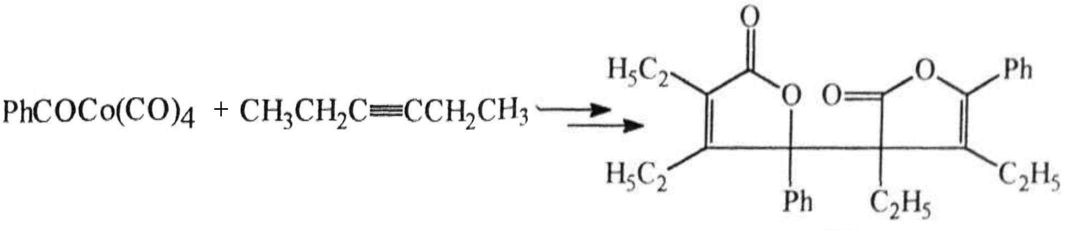
Control experiments indicated that the CuCl is necessary for this transformation. Interestingly, the reaction of phenylacelylene leads to stereoselective formation of only one isomer albeit in low yields (entry 4, Table 6). In the case of 1-hexyl bromide, the corresponding acyclic 1,2-diketone is also formed as a side product.

It appears that the reactivity of $RCOFe(CO)_4^-$/CuCl with alkynes is similar to the reactivity of $NaHFe(CO)_4/CH_3I/CO$ system as the cyclobutenedione 38 is also formed in both cases. A probable path way for the butenolide may involve the acylation of alkyne which could lead to the formation of π-vinyl iron complex similar to the reactivity reported for certain cobalt carbonyl species (Scheme 19, see also eqn 70). [81] The obtention of the butenolides implies that the reaction of $RCOFe(CO)_4^-$ with CuCl may help in the formation of a reactive acylating species such as $RCO\dot{Fe}(CO)_4$. This may be responsible for the acylation of alkynes. However, the mechanism (Scheme 19) can be only tentative as we do not have evidence for the intermediates suggested.

Scheme 19



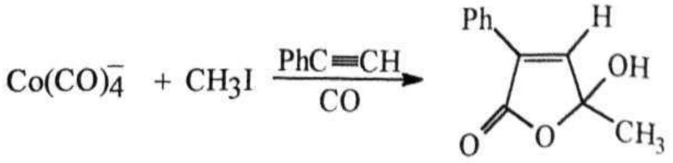
Insertion of metal carbon bond into C-C or C-0 multiple bonds visualized in Scheme 19 in key steps has been encountered in several transition metal mediated processes.[1] In recent years, migratory insertion of "RCO" species in $RCOM(CO)_n$ complex into alkyne mediated by several transition metals has been extensively studied.[82] For instance, Heck reported the formation of rc-allyl **lactonyl complex from disubstituted alkynes with an acylcobalt carbonyl** complex (eqn 69).[83]



103

..(69)

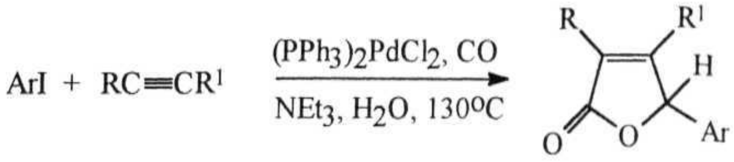
Alper et.al reported the formation of hydroxy butenolides through $Co_2(CO)_8$-catalyzed carbonylation of alkynes in the presence of CH_3I (eqn 70).[81]



104

(70)

It has been reported that $Pd(PPh_3)_2Cl_2$ catalyzes the carbonylation of alkynes to give the corresponding 2-butenolides 105 (eqn 71).[84]

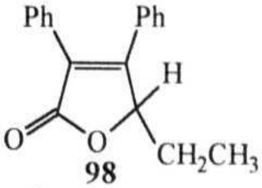
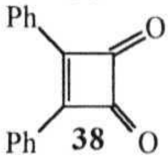
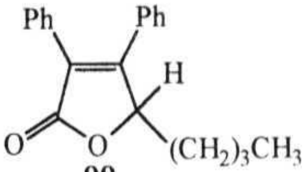
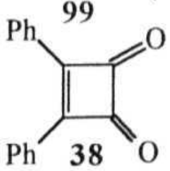
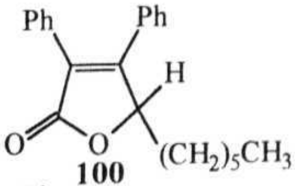
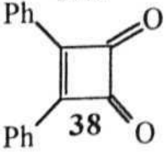
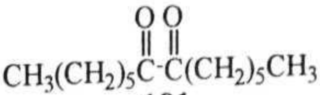
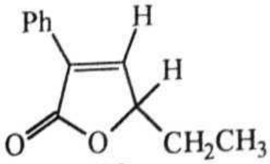


105

(71)

The manganese carbonyls are also known to mediate this type of reaction.[85] However, the iron carbonyls are not known to facilitate acylation of alkynes. Even though, the yields of the products in the present iron carbonyl mediated process are only moderate (Table 6), the double carbonylation reaction leading to the formation of butenolides is interesting, since, five fragments are put together in a single pot procedure. Further work using alkyl substituted alkynes and unsymmetrical alkynes should be fruitful.

Table 6 : Reaction of RCOFe(CO)$_4^-$/alkynes with CuCl[a]

S.No	RBr	Alkyne	Product[b]	Yield (%)[c]
1.	CH_3CH_2Br	$PhC\equiv CPh$	 **98**	26[d]
				13
2	$CH_3(CH_2)_3Br$	$PhC\equiv CPh$	 **99**	32
				10
3	$CH_3(CH_2)_5Br$	$PhC\equiv CPh$	 **100**	35
				10
			 $CH_3(CH_2)_5\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}(CH_2)_5CH_3$ **101**	18
4	CH_3CH_2Br	$PhC\equiv CH$	 **102**	32[e]

a) All reactions were carried out using RBr (10 mmol), Mg (10 mmol), $Fe(CO)_5$ (10 mmol), alkyne (5 mmol) and CuCl (20 mmol).

b) Products were identified by analysis of spectral data (IR, ^1H NMR, ^{13}C NMR and Mass). The spectral data of cyclobutenedione 38 show 1 : 1 correspondence with the samples previously obtained using $NaHFe(CO)_4$-CH_3I system.

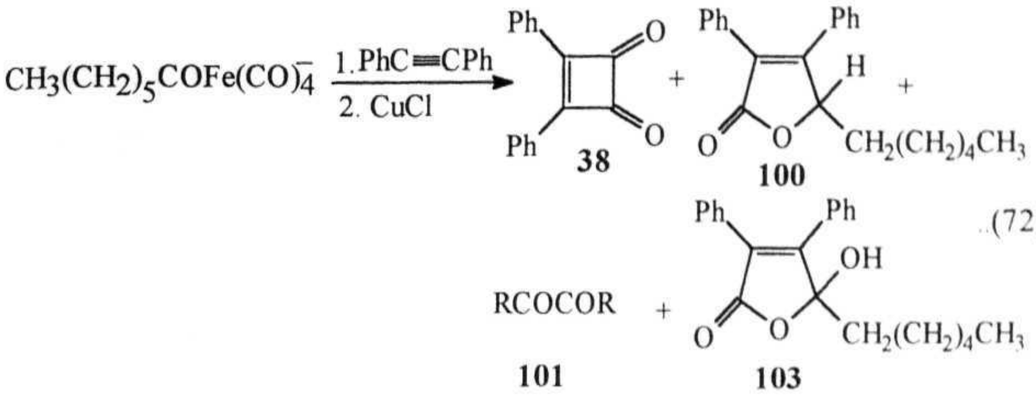
c) Yields are of products isolated by column chromatography and based on the amount of alkynes used.

d) The butenolide 98 was identified by analysis of spectral data and also comparison with the reported data.[82b]

e) The butenolide **102** was identified by comparison of the spectral data with the data reported for the corresponding methyl derivative.[85]

3.2.6a Reaction of $NaRCOFe(CO)_4$ with diphenylacetylene and CuCl

It was of our interest to investigate the reaction of $NaRCOFe(CO)_4$ [generated using $Na_2Fe(CO)_4$, alkyl halides and CO] with alkynes and CuCl. Further, it will be useful to examine the reactivity of $NaRCOFe(CO)_4$-alkyne/CuCl in order to compare with the $RMgBr/Fe(CO)_5/CuCl$ system, as both are known to give the corresponding 1,2-diketones. The experiment was carried out using CuCl (10 mmol), $NaRCOFe(CO)_4$ (R= n-hexyl), diphenylacetylene (5 mmol) in THF (30 mL). After workup and column chromatography the cyclobutenedione 38 (10%), butenolide **100** (31%), 1,2-diketone **101** (37%) and hydroxy butenolide **103** (35%) were isolated (eqn 72).

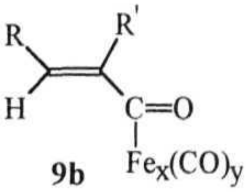


..(72)

Although, the reaction is less clean here compared to that realized using $RMgBr/Fe(CO)_5$ system (eqn 67), the percentage conversion is better. When an excess amount of CuCl (2 eq) was used, the 1,2-diketone 101 was isolated in 50% yield and other products were isolated only in very small amounts.

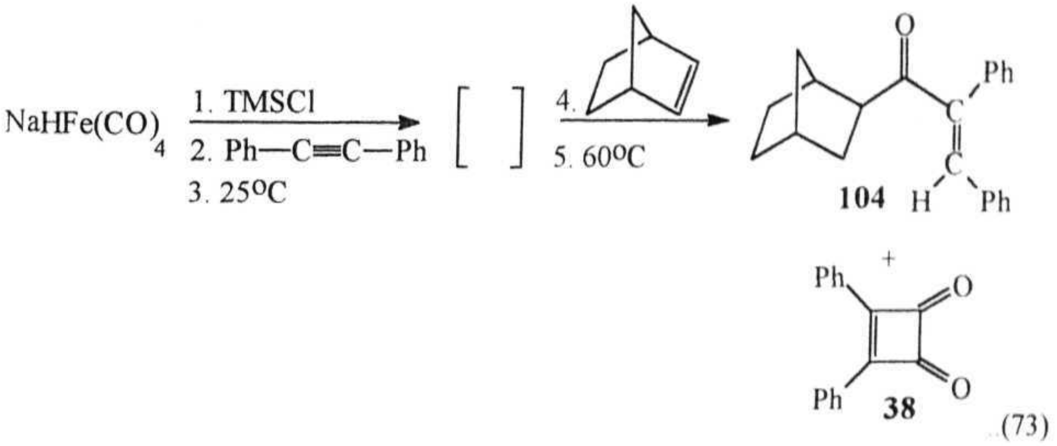
3.2.7 Reaction of NaHFe(CO)4/TMSCl with diphenylacetylene and norbornene

It has been proposed earlier (Section 3.2.3a) that the hydrocarboxylation of the alkynes using $NaHFe(CO)_4/TMSCl$ would go through the inteimediacy of the acyliron species 9b (Scheme 12).



9b

In order to examine whether these species could insert into olefins, we have carried out the reaction with norbornene. It has been found that the reagent generated using $NaHFe(CO)_4/TMSCl$ on reaction with diphenylacetylene and norbornene affords norbornyl vinyl ketone **104** (52%) and cyclobutenedione 38 (30%) (eqn 73).



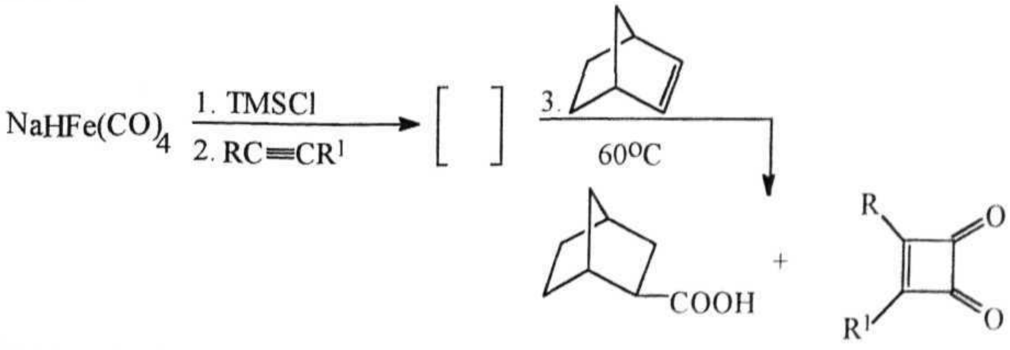
104

38

(73)

Unfortunately, in the reaction with other alkynes, only the corresponding cyclobutenediones and the *exo*-norbornane carboxylic acid **105** were obtained (Scheme 21).

Scheme 21



R= $CH_3(CH_2)_3CH_2$, R'= H	**105**	48%	**76**	30%
R= $CH_3(CH_2)_3CH_2$, R'=$SiMe_3$	**105**	57%	**40**	20%

The expected vinyl ketones were not formed in these reactions. Hence, we did not pursue these studies further.

3.3 Conclusions

A new transformation has been uncovered in the carbonylation of alkynes using $NaHFe(CO)_4/CH_3I$ system to obtain the corresponding cyclobutenediones and α,β-unsaturated carboxylic acids. The reaction of $NaHFe(CO)_4$ with CH_2Cl_2 and alkynes proceeded to yield α,β-unsaturated carboxylic acids [(E)-isomer] in moderate yields in a regio- and stereoselective manner. This reaction was also demonstrated to be useful in the synthesis of certain α,β-unsaturated carboxylic esters and amides.

The reaction of $NaHFe(CO)_4$ with TMSCl and alkynes at room temperature (25°C) followed by $CuCl_2.2H_2O$ oxidation gave the α,β-unsaturated carboxylic acids in moderate yields, again in a regio- and stereoselective fashion. It was also observed that addition of alkynes to the species generated in the reaction of $NaHFe(CO)_4/TMSCl$ at 60°C followed by $CuCl_2.2H_2O$ oxidation lead to the corresponding cyclobutenediones. The reactivity of the reagent prepared using $RCOFe(CO)_4^-/CuCl$ was also investigated. In this case, the corresponding butenolides and cyclobutenediones were isolated.

It appears that the cyclobutenediones could have formed through the reaction of alkynes with coordinatively unsaturated iron carbonyl species such as "$Fe_3(CO)_{11}$" and the α,β-unsaturated carboxylic acids might have formed via the hydrometalation of alkynes by $HFe_3(CO)_{11}^-$ Although the mechanistic picture is only tentative, it should be helpful for further development of these reagent systems. Also, the one pot methods developed for the synthesis of α,β-unsaturated carboxylic acids, butenolides and cyclobutenediones should be useful for synthetic applications.

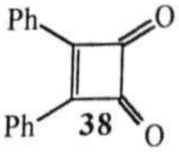
3.4 Experimental Section

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 \-heptyne, CH_3I, CH_2Cl_2, TMSC1 and $CHCl_3$ were used in the experiments. The alkynes used in the reactions were prepared by following a reported procedure.[86] 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.

3.4.2 Reaction of $NaHFe(CO)_4$ with CII3I and diphenylacetylene:

The suspension of $NaHFe(CO)_4$ in THF (30 mL) [generated by careful acidification of $Na_2Fe(CO)_4$ (6 mmol) using CH_3COOH (6 mmol, 0.39 g)J was reacted with CH3I (5 mmol, 0.71g) at 0°C under dry N_2 atmosphere. After 10 min, diphenylacetylene (2.5 mmol, 0.45 g) was added and the contents were further stirred for 8h at 60°C. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (3.4 g, 20 mmol) in acetone (15 mL). Saturated aq.NaCl (30 mL) was added and the resulting solution was extracted with ether. The combined extracts were washed with saturated $Na_2S_2O_3$ solution and brine, dried and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Hexane eluted naphthalene, ethyl acetate (1%) in hexane eluted cyclobutenedione 38 (42%, 0.24 g) and ethyl acetate (3%) in hexane eluted carboxylic acid 39 (22%, 0.125g).



38

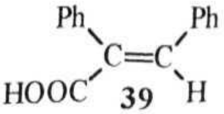
M.P. : 95-96^{o}C (Lit[72] M.P. 97^{o}C)

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

^{1}H NMR : δ ppm 7.45-7.68 (m, 6H), 8.14 (m, 4H) (**Spectrum No 10**)

^{13}C NMR : δ ppm 128.7, 129.7, 131.2, 134.6, 187.4, 196.1 (**Spectrum No 9**)

MS (EI) : m/z 235 [(M^{+}+1), 12%), 179 [($Ph_2C_2^{+}$+1), 100%] (**Spectrum No 8**)



39

M.P : 171.5^{o}C (Lit[87] M.P: 172-173)

IR (neat) : 1678 cm^{-1}

^{1}H NMR : δ ppm 7.1-7.4 (m, 10H), 7.9 (s, 1H) (**Spectrum No 18**)

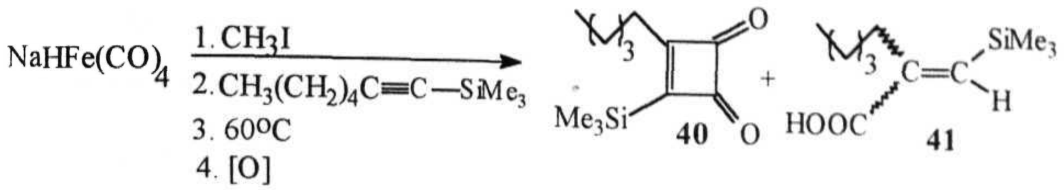
^{13}C NMR : δ ppm 128.1, 128.3, 128.7, 129.5, 129.8, 130.9, 131.7, 134.4, 135.4, 142.6, 173.5 (**Spectrum No 17**)

MS(EI) : m/z: 224 (M^{+}, 20%), 179 [(Ph_2C_2+1)$^{+}$, 100%]

Analysis calcd for $C_{15}H_{12}O_2$

Calcd	C% 80.30,	H% 5.35
Found	C% 80.04;	H% 5.80

The above procedure was followed for the conversion of other alkynes to the corresponding cyclobutenediones and a,P-unsaturated carboxylic acids. The spectral data are summarised below.



Cyclobutenedione 40

Yield : 37% (0.207 g)

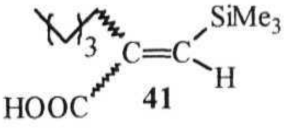
IR(neat) : 1774 cm^{-1}

^1H NMR : δ 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 12)**

^{13}C NMR :δ ppm -2.1, 13.7, 22.2, 26.5, 29.0, 31.8, 200.1, 201.4, 207.7, 211.3 **(Spectrum No 11)**

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

HRMS Calcd 224.1231; Found 224.1232

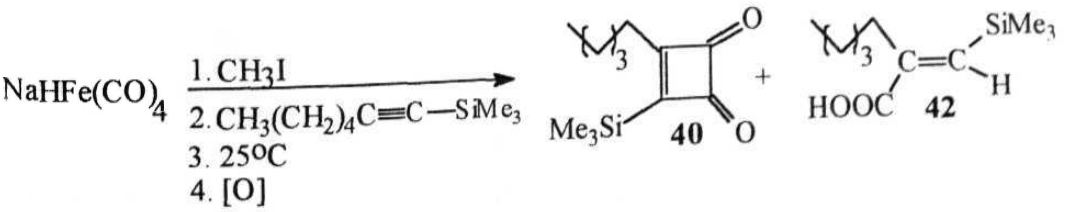


Yield : 12% (0.064 g)

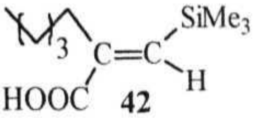
IR(neat) : 1697 cm^{-1}

^1H NMR :δ ppm 0.32 (s, 9H), 0.96 (t, J= 6.8 Hz, 3H), 1.25-2.46 (m, 8H), 6.96 (s, 1H), 7.38 (s, 1H)

^{13}C NMR : δ ppm -0.46, 13.9, 22.5, 29.9, 31.8, 32.1, 128.3, 143.6, 147.3, 152.4, 172.7



The spectral data of the cyclobutenedione 40 were found to be same as that reported in the earlier experiment. The data of the α,β-unsaturated carboxylic acid 42 are reported here.



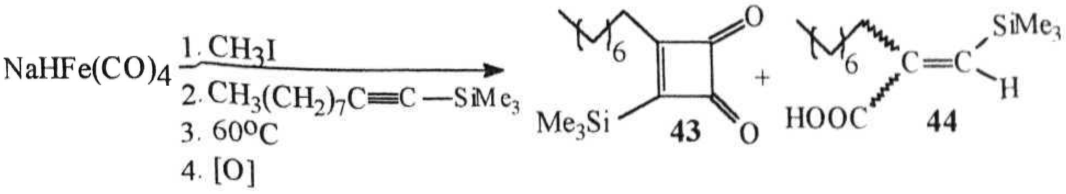
42

Yield : 20% (0.108 g)

IR (neat) : 1687 cm^{-1}

^{1}H NMR : δ ppm 0.19 (s, 9H), 0.89 (t, J= 6.7 Hz, 3H), 1.27-1.6 (m, 6H), 2.3 (t, J= 6.9 Hz, 2H), 7.0 (s, H) (**Spectrum No 20**)

^{13}C NMR : δ ppm -0.49, 13.9, 22.4, 29.8, 31.8, 32.1, 143.6, 147.3, 172.8 (**Spectrum No 19**)



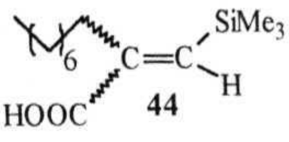
Cyclobutenedione 43

Yield : 31% (0.206 g)

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

^{1}H NMR :δ 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 : δ ppm -2.1, 14.0, 22.5, 26.8, 29.0, 29.6, 31.5, 31.7, 200.0, 207.6, 211.2



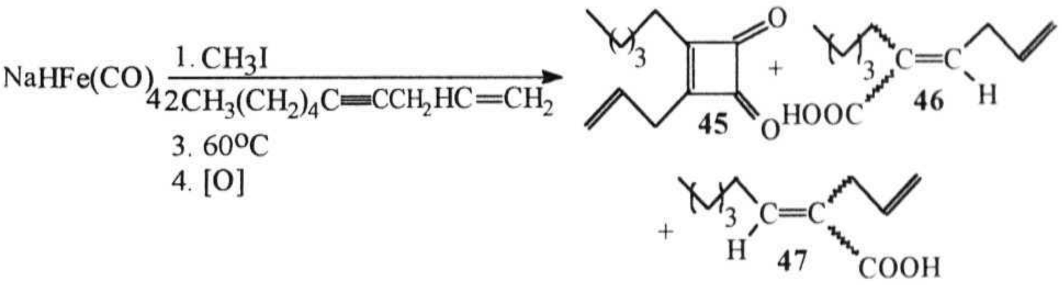
44

Yield : 12% (0.076 g)

IR (neat) : 1689 cm^{-1}

^1H NMR : δ ppm 0.19 (s, 9H), 0.88 (t, J= 6.7 Hz, 3H), 1.21-2.62 (m, 14H), 6.97 (s, 1H), 7.36 (s, 1H)

^{13}C NMR : δ ppm -0.42, 14.1, 22.7, 29.2, 29.4, 29.9, 30.2, 31.9, 33.6, 128.3, 131.6, 143.7, 147.3, 172.6



Cyclobutenedione 45

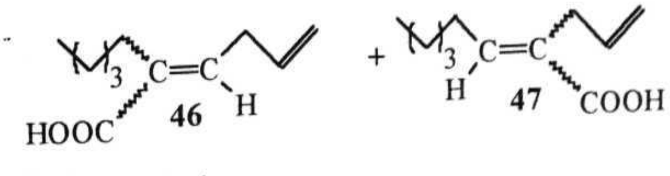
Yield : 32%, (0.154 g)

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

^1H NMR : 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, 1H), 7.36 (m, 1H)

^{13}C NMR : δ 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-$(CH_2)_3CH_3$), 20%]

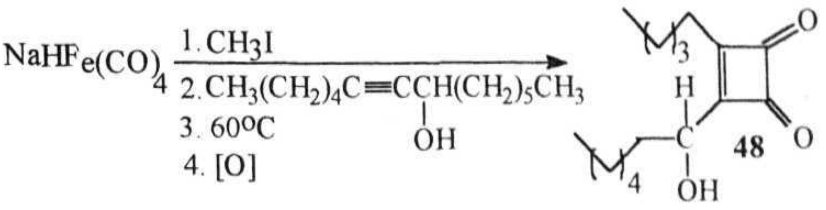


Yield : 10% (0.048 g)

IR (neat) : 1687, 1639 cm^{-1}

^1H NMR : δ ppm 0.8 (t, J= 7.0 Hz, 3H), 1.1-2.6 (m, 16H), 3.08 (m, 4H), 4.96-5.21 (m, 2H), 5.76-5.92 (m, 1H), 6.82-7.53 (m, 3H)

^{13}C NMR : δ ppm 13.9, 22.4, 28.2, 28.7, 30.4, 31.6, 31.7, 115.1, 116.3, 128.2, 129.0, 131.9, 135.2, 141.7, 146.9, 172.8



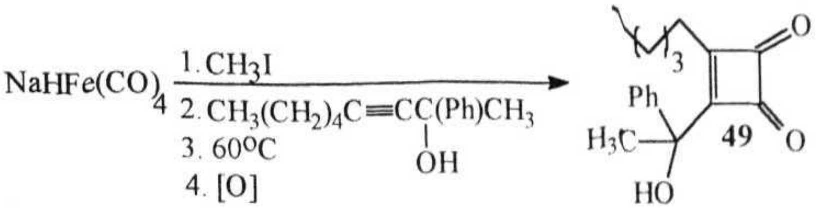
Yield : 27% (0.179 g)

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

^{1}H NMR : δ 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) **(Spectrum No 14)**

^{13}C NMR :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 13)**

MS(EI) : m/z: 266 (M^{+}+1, 5%), 195 [(M^{+}-C$_5$H$_{11}$, 16%]



Yield : 31% (0.211 g)

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

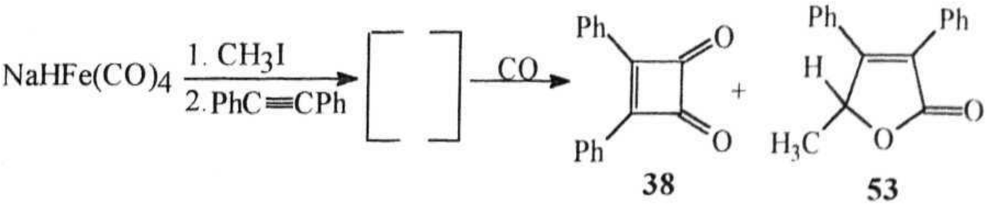
^{1}H NMR : δ ppm 0.86 (t, J= 6.9 Hz, 3H), 1.25-1.78 (m, 6H), 1.99 (s, 3H), 2.3 (s, 1H), 2.8 (t, J= 7.3 Hz, 2H), 7.26-7.65 (m, 5H)

^{13}C NMR : δ 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 [{PhC(OH)CH$_3$}$^{+}$, 60%]

3.4.3 Reaction of $NaHFe(CO)_4$ with CH3I and diphenylacetylene under CO atmosphere:

The suspension of $NaHFe(CO)_4$ in THF (30 mL) [generated by careful acidification of $Na_2Fe(CO)_4$ (6 mmol) using CH_3COOH (6 mmol, 0.39 g)J was treated with CH3I (5 mmol, 0.71g) at 0^oC under dry N_2 atmosphere. After 10 min, diphenylacetylene (2.5 mmol, 0.45 g) was added and the contents were further stirred for 8h. The CO gas was bubbled through the reaction mixture for 8 h at 25°C. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (3.4 g, 20 mmol) in acetone (15 mL). Saturated aq.NaCl (30 mL) was added and the resulting solution was extracted with ether. The combined extracts were washed successfully with saturated $Na_2S_2O_3$ solution and brine, dried and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Ethyl acetate (1%) in hexane eluted the cyclobutenedione 38 (30%, 0.18 g) and ethyl acetate (3%) in hexane eluted butenolide 53 (21%, 0.13 g).



The spectral data of cyclobutenedione 38 were identical to that obtained for **the** sample using the $NaHFe(CO)_4/CH_3I$ system. The data of the butenolide 53 are reported below.

IR (neat) : 1753 cm^{-1}

IR (neat) : 1753 cm^{-1}

^{1}H NMR : δ ppm 1.45 (d, J= 6.9 Hz, 3H), 5.61 (q, J= 6.9 Hz, 1H), 7.20-7.53 (m, 10H) **(Spectrum No 25)**

^{13}C NMR : δ ppm 19.1, 78.2, 126.0, 128.1, 128.5, 128.6, 129.0, 129.3, 130.0, 130.7, 131.2, 161.8, 172.3 **(Spectrum No 24)**

MS (EI) : m/z 250 (M^+, 98%), 207 [{(M^+-COO)+1}, 90%] **(Spectrum No 23)**

Elemental analysis calcd for $C_{17}H_{14}O_2$

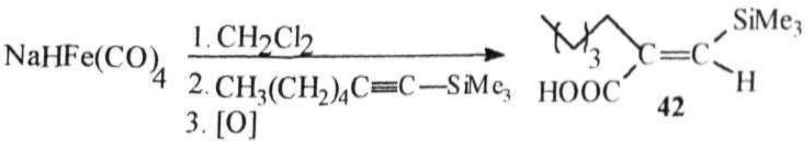
Calcd	C% 81.60	H%5.60
Found	C% 81.25	H%5.65

3.4.4 Reaction of $NaHFe(CO)_4$ with diphenylacetylene in the presence of CH_2Cl_2

The $NaHFe(CO)_4$ (6 mmol) in THF (30 mL) [generated 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, diphenylacetylene (2.5 mmol, 0.45 g) was added and the contents were heated to 50°C and stirred for 8hrs. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (20 mmol, 3.4 g) in acetone (15 mL). Saturated aq.NaCl (30 mL) was added and the resulting solution was extracted with ether, washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Ethyl acetate (1%) in hexane eluted the cyclobutenedione 38 (21%, 0.25 g) and α,β unsaturated carboxylic acid 39 (60%, 0.387) was isolated using ethyl acetate (2%) in hexane.

The cyclobutenedione 38 and α,β-unsaturated carboxylic acid 39 were identified by comparison with the samples obtained using the $NaHFe(CO)_4/CH_3I$ system.

The above procedure was followed for the conversion of other alkynes to the corresponding α,β-unsaturated carboxylic acids and the results are summarized below and also in Table 2.



Yield : 41% (0.219 g)

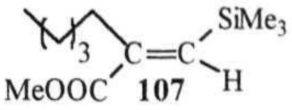
IR (neat) : 1687 cm^{-1}

^1H NMR : δ ppm 0.19 (s, 9H), 0.89 (t, J= 6.7 Hz, 3H), 1.27-1.6 (m, 6H), 2.3 (t, J= 6.85 Hz, 2H), 7.0 (s, H) **(Spectrum No 20)**

^{13}C NMR : δ ppm -0.49, 13.9, 22.4, 29.8, 31.8, 32.1, 143.6, 147.3, 172.8 **(Spectrum No 19)**

The regio- and stereochemistry of the product was confirmed by comparing the spectral data obtained for the methyl ester with the reported data.[49] The methyl ester was prepared following a reported procedure [88]

A solution of methyl iodide (1.5 mmol, 0.212 g) in 10 mL of benzene was added to a solution of (E)-β-silylcarboxylic acid (42) (1 mmol, 0.214 g) and DBU (1 mmol, 0.152 g) in benzene (20 mL). This mixture was stirred at room temperature for 6h. The reaction mixture was then washed with water, dried over anhydrous $MgSO_4$ and concentrated. The residue was passed through a column of silica gel to obtain the ester **107** (80%, 0.183 g).

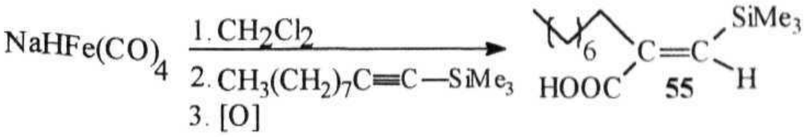


107

IR (neat) : 1718 cm^{-1}

^{1}H NMR : δ ppm 0.19 (s, 9H), 0.89 (t, J= 6.6 Hz, 3H), 1.22-1.6 (m, 6H), 2.4 (t, J= 6.9 Hz, 2H), 3.75 (s, 3H), 6.8 (s, 1H) (**Spectrum No 22**)

^{13}C NMR : δ ppm -0.389, 13.9, 22.4, 29.8, 32.0, 32.1, 51.7, 140.6, 147.9, 167.8 (**Spectrum No 21**)



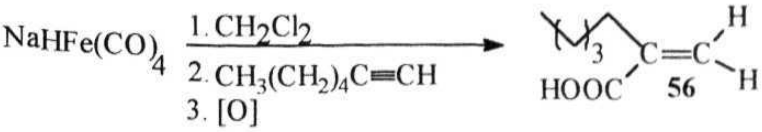
55

Yield : 37% (0.237 g)

IR (neat) : 1687 cm^{-1}

^{1}H NMR : δ ppm 0.17 (s, 9H), 0.87 (t, J= 6.8 Hz, 3H), 1.27 (m, 12H), 2.29 (t, J= 6.85 Hz, 3H), 6.97 (s, 1H)

^{13}C NMR : δ ppm -0.45, 14.1, 22.6, 29.2, 29.4, 29.9, 30.1, 31.8, 143.6, 147.2, 172.7



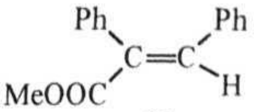
56

Yield : 50% (0.165 g)

IR (neat) : 1697 cm^{-1}

^{1}H NMR : δ ppm 0.89 (t, J= 7.0 Hz, 3H), 1.37 (m, 6H), 2.26 (t, J= 7.4 Hz, 2H), 5.64 (d, J= 1.3 Hz, 1H), 6.28 (d, J= 1.3 Hz, 1H)

^{13}C NMR : δ ppm 13.9, 22.4, 28.1, 31.4, 126.7, 140.4, 172.9.



68

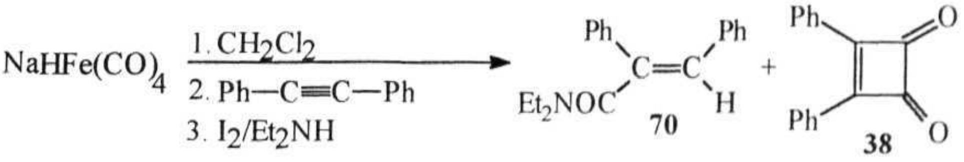
IR (neat) : 1714 cm^{-1}

^1H NMR : δ ppm 3.84 (s, 3H -OCH_3), 6.93-7.98 (m, 11H)

^{13}C NMR : δ ppm 52.4, 127.9, 128.2, 128.7, 129.1. 129.8, 130.6, 131.5, 142.5, 168.3

MS (El) : m/z 238 (M^+, 70%), 178 [(M^+-$COOCH_3$), 95%]

The above procedure was followed for the conversion of diphenyl acetylene into the amide 70 using diethylamine in the place of methanol. The results are summarized below.



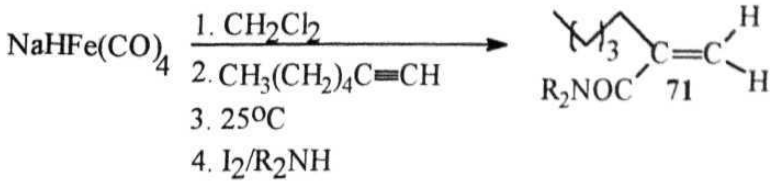
The cyclobutenedione 38 isolated in these experiments was identical to the sample obtained previously using the $NaHFe(CO)_4/CH_3I$ system. The spectral data of the amide derivative 70 are reported here.

Yield : 50% (0.35 g)

IR (neat) : 1633 cm^{-1}

^1H NMR : δ ppm 1.09 (t, J= 7.2 Hz, 3H), 3.14 (q, J= 7.0 Hz, 2H), 6.6 (s, 1H), 7.1-7.6 (m, 10H)

^{13}C NMR : δ ppm 13.2, 42.3, 127.5, 127.9, 128.3, 129.2, 129.7, 130.4, 134.8, 135.5, 138.3, 164.9, 171.09.



Yield : 35% (0.176 g)

IR (neat) : 1620 cm^{-1}

^1H NMR : δ ppm 0.91 (t, J= 6.9 Hz, 3H), 1.15 (t, J= 7.1 Hz, 6H), 1.20-1.55 (m, 6H), 2.29 (t, J= 7.3 Hz, 2H), 3.41 (m, 4H), 5.02 (d, J= 1.3 Hz, 1H), 5.10 (d, J= 1.3 Hz, 1H)

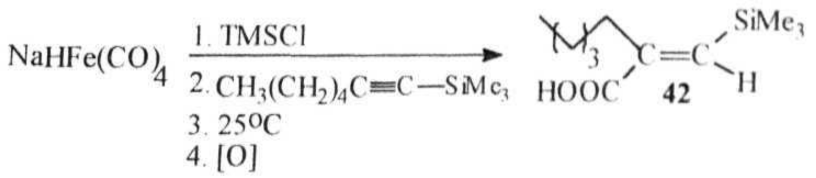
^{13}C NMR : δ ppm 13.8, 22.3, 26.9, 31.4, 34.3, 112.4, 145.9, 172.0

The spectral data of 71 showed 1:1 correspondence with the reported data.[88]

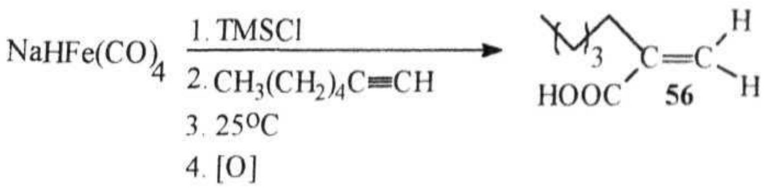
3.4.6 Reaction of $NaHFe(CO)_4/TMSCl$ with diphenylacetylene at 25°C

The $NaHFe(CO)_4$ (7.5 mmol) [generated by acidification of $Na_2Fe(CO)_4$ (7.5 mmol) with CH_3COOH (6 mmol, 0.39 g) in THF (30 mL)] was treated with TMSCl (7.5 mmol, 0.81 g) under nitrogen atmosphere. After 1h, diphenylacetylene (2.5 mmol, 0.45 g) was added and the contents were stirred for 8hrs at 25°C. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (20 mmol, 3.4 g) in acetone (15 mL). Saturated aq.NaCl (30 mL) was added and the resulting solution was extracted with ether, washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Traces (<5%) of the corresponding cyclobutenedione 38 was isolated using ethyl acetate (1%) in hexane and the α,β−unsaturated carboxylic acid 39 (54%, 0.3 g) was isolated using ethyl acetate (2%) in hexane.

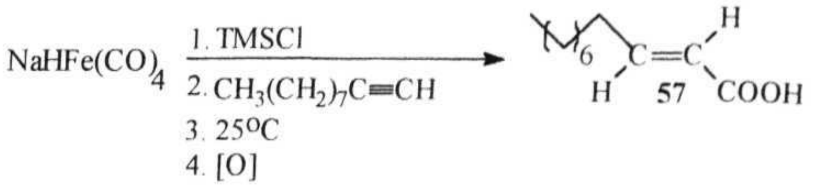
The above procedure was followed for the conversion of other alkynes to the corresponding α,β-unsaturated carboxylic acids and the results are reported below. The spectral data were found to be same as those obtained for the samples previously isolated using the $NaHFe(CO)_4/CH_2Cl_2$ reagent system.



Yield : 50% (0.268 g)



yield : 45% (0.161 g)



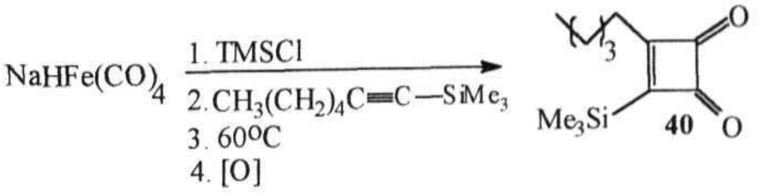
Yield : 51% (0.234 g)

3.4.7 Reaction of $NaHFe(CO)_4$/TMSCl with diphenylacetylene at $60^{o}C$

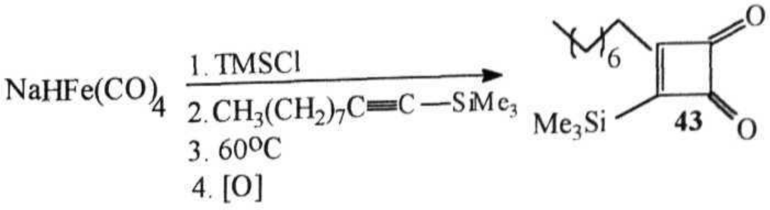
The $NaHFe(CO)_4$ (7.5 mmol) in THF (30 mL) [generated by acidification of $Na_2Fe(CO)_4$ (7.5 mmol) with CH_3COOH (6 mmol, 0.39 g)J **was treated with** TMSC1 (7.5 mmol, 0.81 g) under nitrogen atmosphere. The reaction mixture was stirred for 1h at 50°C, after cooling the reaction mixture, diphenylacetylene (2.5

mmol, 0.45 g) was added and the contents were stirred for 8hrs at 60°C. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (20 mmol, 3.4 g) in acetone (15 mL). Saturated aq.NaCl (30 mL) was added, the resulting solution was extracted with ether, washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. The cyclobutenedione 38 (63%, 0.383 g) was isolated using ethyl acetate (1%) in hexane.

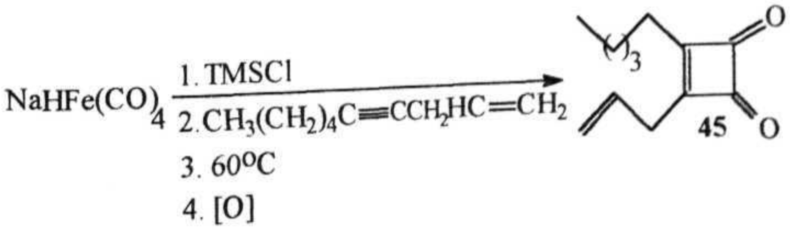
The above procedure was followed for the conversion of other alkynes to the corresponding cyclobutenediones and the results are reported below. The cyclobutenediones 40, 43 and 45 were identified by comparison with the samples obtained in previous experiments.



Yield : 51% (0.29 g)

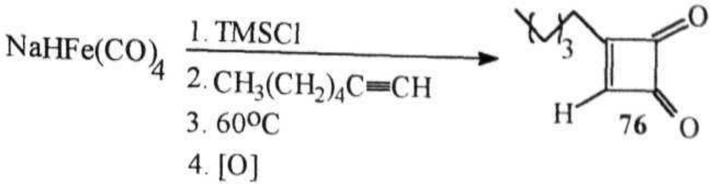


Yield : 53% (0.355 g)



Yield : 60% (0.29 g)

Yield : 60% (0.29 g)



Yield : 56% (0.21 g)

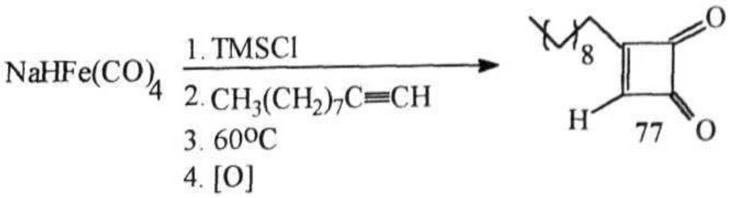
IR (neat) : 1788 cm^{-1}

^{1}H NMR : δ ppm 0.82 (t, J= 7.3 Hz, 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 : δ 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 spectral data of 76 showed 1:1 correspondence with the reported data.[90]



Yield : 51% (0.32 g)

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

^{1}H NMR : δ 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 16)**

^{13}C NMR : δ 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 15)**

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

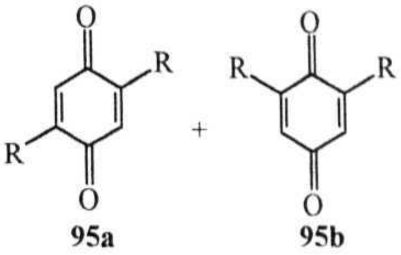
3.4.8 Reaction of $NaHFe_2(CO)_8$ with CH3I and diphenylacetylene

The $Na_2Fe_2(CO)_8$ (6 mmol) was generated treating $Na_2Fe(CO)_4$ (6 mmol) in dry THF (30 mL) with Fe(C0)5 (5 mmol, 0.98 g). Acetic acid (6 mmol, 0.39 g) was carefully added to this suspension to prepare $NaHFe_2(CO)_8$. The CH3I (5 mmol, 0.71g) was added at 0^oC under dry N_2 atmosphere. After 10 min, diphenylacetylene (2.5 mmol, 0.45 g) was added and the contents were further stirred for 8h. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (3.4 g, 20 mmol) in acetone (15 mL). Saturated aq.NaCl (30 mL) was added and the contents were extracted with ether. The combined extracts were washed successively with saturated $Na_2S_2O_3$ solution and brine, dried and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Ethyl acetate (1%) in hexane eluted cyclobutenedione 38 (26%, 0.15 g), ethyl acetate (3%) in hexane eluted butenolide 53 (33%, 0.208 g) and ethyl acetate (4%) in hexane eluted carboxylic acid 39 (8%, 0.47 g).

The cyclobutenedione 38, butenolide 53 and a,p-unsaturated carboxylic acid 39 were identified by comparison with the samples obtained in previous experiments.

3.4.9 Photochemical reaction of $Fe(CO)_5$ with 1-heptyne in CH_3CN

A solution containing $Fe(CO)_5$ (5 mmol, 0.098 g) and 1-heptyne (5 mmol, 0.48 g) in CH3CN (30 mL) was irradiated [UV-lamp 253.7 nm] for 6 h under N_2 atmosphere. The resulting mixture was poured into $CuCl_2.2H_2O$ (20 mmol, 3.4 g) 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 (2 x 20 mL) , dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Ethyl acetate (1%) in hexane eluted a mixture of 2,6- and 2,5- disubstituted quinones 95 (64%, 0.4 g).

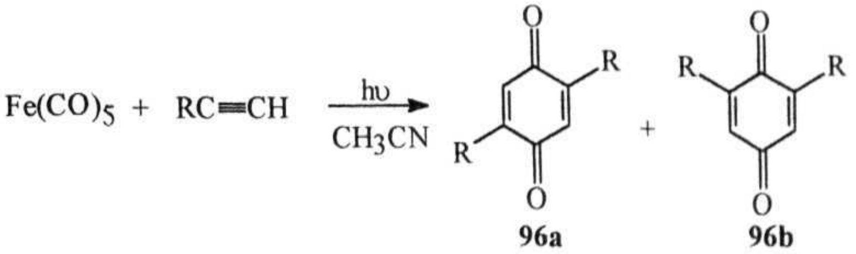


(R= $CH_3(CH_2)_3CH_2$)

IR (neat) : 1657, 1612 cm^{-1}

^1H NMR : 0.89 (t, J= 6.8 Hz, 12H), 1.16-1.68 (m, 32H), 2.46 (m, 8H), 6.48(s, 1H), 6.51 (s, 1H)

^{13}C NMR : δ ppm 13.8, 22.3, 28.2, 28.8, 31.4, 131.9, 132.4, 149.1, 149.5, 187.7



(R= $CH_3(CH_2)_6CH_2$)

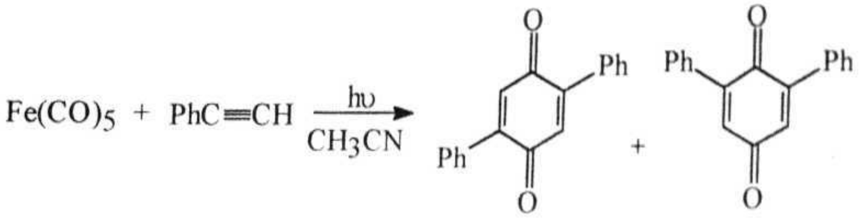
Yield : 50% (0.41 g)

I.R (KBr) : 1655, 1612 cm^{-1}

^1H NMR : 0.90 (t, J= 6.7 Hz, 12H), 1.18-1.70 (m, 48H), 2.44 (m, 8H), 6.49(s, 1H), 6.52 (s, 1H)

^{13}C **NMR** : δ ppm 14.0, 22.5, 27.8, 29.1, 29.2, 31.7, 132.0, 132.5, 149.3, 149.9, 188.0

The data of the mixtures of 95a and **95b, 96a** and **96b** are comparable to the spectral data of dialkyl substituted (R= n-octyl) quinones.[80]



97a **97b**

Yield : 40% (0.26 g)
IR (KBr) : 1649, 1610 cm^{-1}
^1H NMR : 6.84 (s, 1H), 6.88 (s, 1H), 7.45 (m, 20H)
^{13}C NMR : δ ppm 128.5, 129.0, 129.3, 132.6, 133.2, 145.9, 146.5, 186.9, 187.5

The product mixture 97a and 97b was identified by comparison of the spectral data with the reported data.[80]

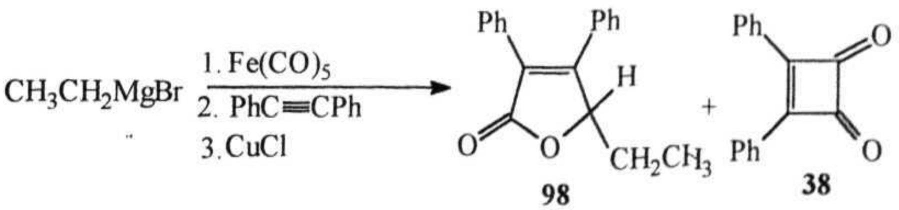
3.4.10 Photochemical reaction of $Fe(CO)_5$ with CH_3CN and diphenyl-acetylene

A solution containing $Fe(CO)_5$ (5 mmol, 0.098 g) in CH_3CN (30 mL) was irradiated [UV-lamp, 253.7 nm] for 6 h under N_2 atmosphere. To this, diphenylacetylene (0.36 g, 2 mmol) was added and the mixture was stirred at 25°C for 8 h (without light) under nitrogen atmosphere. It was poured into $CuCl_2.2H_2O$ (20 mmol, 3.4 g) 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, dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography.

Hexane eluted unreacted diphenylacetylene (0.3 g), ethyl acetate **(1%)** in hexane eluted cyclobutenedione 38 (10%, 0.047 **g).**

3.4.11 Reaction of (RCO)Fe(CO)$_4^-$ with diphenylacetylene in the presence of CuCl

Magnesium mesh (0.23 g, 10 mmol) was taken in THF (50 mL) with ethyl bromide (1.08 g, 10 mmol) at 25°C under nitrogen atmosphere. The contents were stirred for 1h, and $Fe(CO)_5$ (2.16 g, 10 mmol) was added. The reaction mixture was stirred for lh at 25°C. Diphenylacetylene (0.89 g, 5 mmol), CuCl (2.0 g, 20 mmol) and CH3CN (5 mL) were added and stirred further for 10h at 25°C. The resultant mixture was poured into acetone (40 mL) containing $CuCl_2.2H_2O$ (6.8 g, 40 mmol) to decompose the iron carbonyl. Saturated aq NaCl was added and the organic phase was separated. The aqueous layer was extracted with ether (2 x 40 mL). The combined organic extracts were washed with H_2O (20 mL) and brine (30 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Ethyl acetate (1%) in hexane eluted cyclobutenedione 38 (13%, 0.23 g) and ethyl acetate (3%) in hexane eluted butenolide 98 (26%, 0.35 g).



The cyclobutenedione 38 was identified by comparison with the sample obtained earlier using the $NaHFe(CO)_4/CH_3I$ system. The physical constant and spectral data for the butenolide 98 are reported here.

M.P. : 132.5 (Lit [82b] M.P. 133-4)

IR (neat) : 1753 cm^{-1}

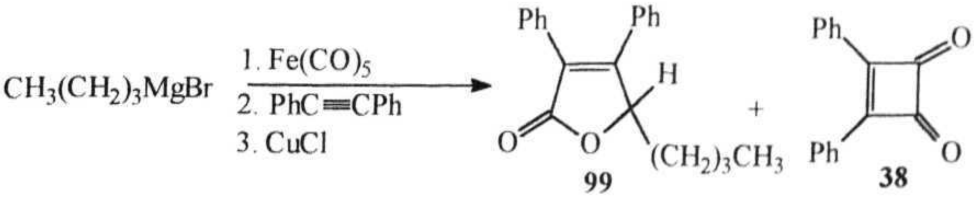
^1H NMR : δ ppm 0.89 (t, J= 7.4 Hz, 3H), 1.61 (m, 1H), 1.94 (m, 1H), 5.45 (dd, J= 6.8, 6.8 Hz, 1H), 7.21-7.45 (m, 10H) **(Spectrum No 27)**

^{13}C NMR : δ ppm 8.2, 25.7, 82.4, 128.1, 128.6, 129.0, 129.3, 130.0, 131.3, 160.2, 172.6, **(Spectrum No 26)**

MS (EI) : m/z 264 (M^+, 13%), 235 [(M^+-C_2H_5), 100%], 179 [($Ph_2C_2^+$+1), 80%]

The physical constant and spectial data show 1:1 correspondence with the reported data.[82b]

The above procedure was followed for the conversion of several other alkyl bromides to the corresponding butenolides. The results are summarized below.



Butenolide 99

Yield : 32% (0.46 g)

IR (neat) : 1753 cm^{-1}

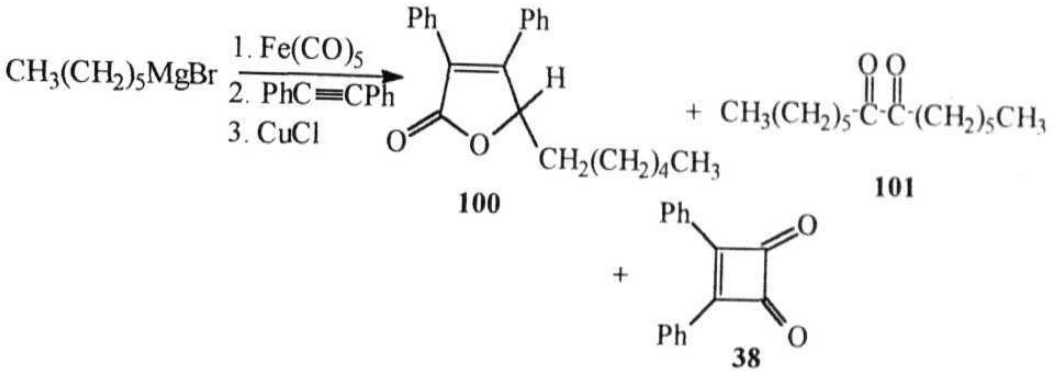
^1H NMR : δ ppm 0.88 (t, J= 7.3 Hz, 3H), 1.29-1.53 (m, 6H), 5.46 (m, 1H), 7.24-7.40 (m, 10H)

^{13}C NMR : δ ppm 13.7, 22.3, 26.5, 32.6, 81.7, 128.1, 128.4, 128.9, 129.3, 130.0, 131.4, 160.6, 172.5

MS (EI) : m/z 292 (M^+, 12%), 178 [$(Ph_2C_2)^+$, 85%]

Cyclobutenedione **38**

Yield : **10%** (0.23 g)



Butenolide 100

Yield : 35% (0.28 g)

IR (neat) : 1753 cm^{-1}

^1H NMR : δ ppm 0.85 (t, J= 7.3 Hz, 3H), 1.23-1.97 (m, 10H), 5.48 (m, 1H), 7.22-7.38 (m, 10H)

^{13}C NMR : δ ppm 13.9, 22.4, 24.3, 28.8, 31.5, 32.9, 81.7, 126.7, 128.0, 128.5, 128.9, 129.9, 131.5, 160.5, 172.4

MS (EI) : m/z 320 [$(M^{+}+1)$, 20%)], 235 [$(M^{+}-C_6H_{13})$, 28%], 179 [$(Ph_2C_2+1)^{+}$, 100%]

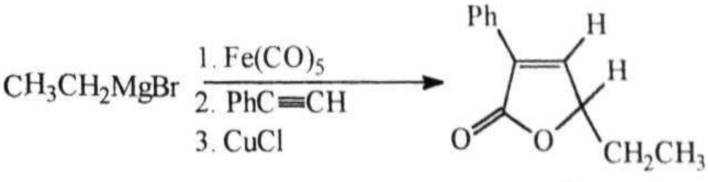
Cyclobutenedione 38

Yield : 10% (0.23 g)

$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R$ **101**

Yield :18% (0.395 g)

The spectral data of cyclobutenedione 38 were identical to the data of the sample previously obtained using the $NaHFe(CO)_4/CH_3I$ system. The spectral data of 1,2-diketone 101 showed 1:1 correspondence with that of the samples obtained in Chapter 1.



102

Butenolide **103**

Yield : 32% (0.15 g)

IR (neat) : 1755 cm^{-1}

^1H NMR : δ ppm 1.06 (t, J= 6.8 Hz, 3H), 1.78-2.11 (m, 2H), 5.0 (dt, J= 1.5, 6.8, 1H), 7.40 (m, 3H), 7.54 (d, J= 1.5 Hz, 1H), 7.87 (m, 2H)

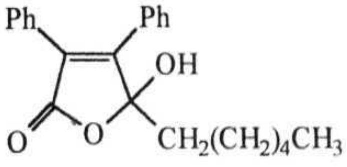
^{13}C NMR : δ ppm 9.1, 26.7, 81.5, 127.1, 128.6, 129.6, 131.6, 132.6, 147.9, 171.8

MS (EI) : m/z 188 (M^+, 45%), 159 [(M^+-C_2H_5), 20%], 103 [(PhC_2H^++1), 100%]

The spectral data of **102** are comparable to the reported data of the corresponding methyl derivative.[85]

3.4.12 Reaction of Na(RCO)Fe(CO)4 with diphenylacetylene in the presence of CuCl

To a suspension of $Na_2Fe(CO)_4$ (10 mmol) in THF (30 mL) [prepared using $Fe(CO)_5$ (2.16 g, 11 mmol), Na (0.51 g, 22 mmol) and naphthalene (1.02 g, 8 mmol)] 1-bromohexane (1.65 g, 10 mmol) was added and CO was bubbled for 30 min at 25°C. The CO atmosphere was replaced by dry N_2 atmosphere. Diphenylacetylene (0.89 g, 5 mmol) and CuCl (2.0 g, 20 mmol) was added to the reaction mixture. The mixture was stirred for 12h at 25^0C. The mixture was poured into acetone (40 mL) containing $CuCl_2.2H_2O$ (6.8 g, 40 mmol) to decompose the iron carbonyl. Saturated aqueous NaCl (30 mL) was added , the organic layer was separated , the aqueous layer was extracted with ether (2 x 30 mL). The combined organic extracts were washed with brine (25 mL) and then dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene. Ethyl acetate (0.5%) in hexane eluted 1,2-diketone **101** (37%, 0.2 g) and ethyl acetate (1%) in hexane eluted cyclobutenedione 38 (10%, 0.059 g). The butenolide **100** (31%, 0.25 g) was eluted by ethyl acetate (3%) in hexane and hydroxybutenolide **103** (35%, 0.3 g) was isolated using ethyl acetate (5%) in hexane.



103

IR (neat) : 3354, 1738 cm^{-1}

^1H NMR : δ ppm 0.83 (t, J= 7.0, 3H), 1.18-2.1 (m, 10H), 2.35 (t, J= 7.45 Hz, 1H), 7.25-7.62 (m, 10H)

^{13}C NMR : δ ppm 13.8, 22.6, 22.7, 28.8, 31.3, 36.7, 107.4, 128.3, 128.6, 128.7, 128.9, 129.5, 129.8, 130.9, 157.9, 171.0

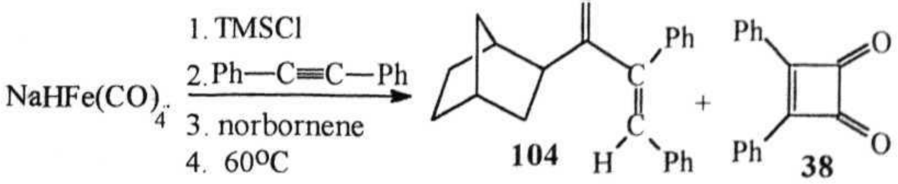
(Spectrum No 28)

MS (EI) : m/z 336 (M^+, 20%), 251 [{M^+-$(CH_2)_5CH_3$}, 90%], 178 [$(Ph_2C_2)^+$, 100%]

The 1,2-diketone (101), cyclobutenedione (38) and butenolide **(100)** were identified by comparison with the samples obtained earlier.

3.4.13 Reaction of $NaHFe(CO)_4$/TMSCl with diphenylacetylene and norbornene at 60°C

The $NaHFe(CO)_4$ (6 mmol) in THF (30 mL) [generated by acidification of $Na_2Fe(CO)_4$ (6 mmol) with CH_3COOH (6 mmol, 0.39 g)] was treated **with** TMSCl (5 mmol, 0.54 g) under nitrogen atmosphere. The reaction mixture was stirred for 1h at 25°C, diphenylacetylene (2.5 mmol, 0.45 g) was added and the contents were stirred for 12hrs at 25°C. To this, norbornene (5 mmol, 0.452 g) was **added** and the contents were further stirred at 60°C for 8h. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (20 mmol, 3.4 g) in acetone (15 mL). Saturated aq.NaCl (30 mL) was added. **The** contents were extracted with ether, washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene, ethyl acetate (0.5%) in hexane eluted vinyl ketone **104** (51%, 0.41 g) and cyclobutenedione 38 (30%, 0.183 g) was isolated using ethyl acetate (1%) in hexane.



The cyclobutenedione 38 was identified by comparison with the sample obtained earlier. The spectral data for the norbornyl vinyl ketone **104** are reported here.

IR (neat) : 1684 cm^{-1}

^{1}H NMR : δ ppm 1.06-2.15 (m, 9H), 2.46 (m, 1H), 7.02-7.42 (m, 10H), 7.62 (s, 1H)

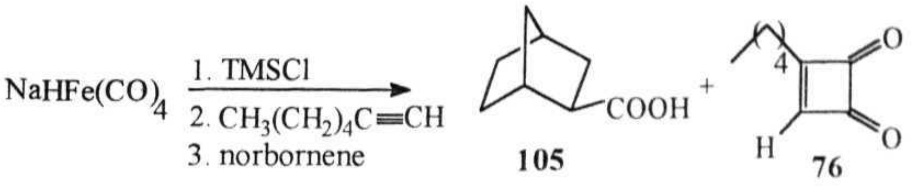
^{13}C NMR : δ ppm 28.8, 29.6, 34.1, 36.1, 36.3, 40.9, 49.9, 127.7, 128.2, 128.9, 129.8, 130.7, 135.0, 137.8, 202.9.

MS (EI) : m/z 302 (M^+, 10%), 207 [$(Ph_2C_2HCO)^+$, 58%), 179 [$(Ph_2C_2H)^+$, 100%]

3.4.14 Reaction of $NaHFe(CO)_4$/TMSCl with 1-heptyne and norbornene at 60°C

The $NaHFe(CO)_4$ (6 mmol) in THF (30 mL) [generated by acidification of $Na_2Fe(CO)_4$ (6 mmol) with CH3COOH (6 mmol, 0.39 g)J was treated will) TMSC1 (5 mmol, 0.81 g) under nitrogen atmosphere. The reaction mixture was stirred for 1h at 25°C, 1-heptyne (2.5 mmol, 0.243 g) was added and the contents were stirred for 12hrs at 25°C. To this, norbornene (5 mmol, 0.452 g) was added and the contents were further stirred at 60°C for 8h. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (20 mmol, 3.4 g) in acetone (15 mL). Saturated aq.NaCl (30 mL) was added. The contents were extracted with ether, washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene, ethyl acetate (1%) in hexane eluted cyclobutenedione 76

(30%, 0.183 g) and norbornane carboxylic acid **105** (48%, 0.338 g) was eluted using ethyl acetate (2%) in hexane.

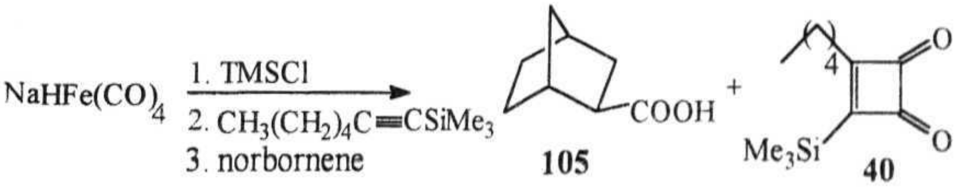


Norbornane carboxylic acid 105

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

^1H NMR : 0.8-2.8 (m, 11H), 11.35 (br s, 1H)

^{13}C NMR : δ ppm 28.5, 29.4, 34.0, 36.0, 36.5, 40.9, 46.4, 182.4



Norbomane carboxylic acid **105**

Yield : 57% (0.375 g)

Cyclobutenedione 40

Yield : 20% (0.112 g)

The spectral data of the norbomane carboxylic acid show 1:1 correspondence with the reported data J[4] The cyclobutenediones 76 and 40 were identified by comparison with the samples obtained in previous experiments.

3.5 References

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REPRESENTATIVE SPECTRA

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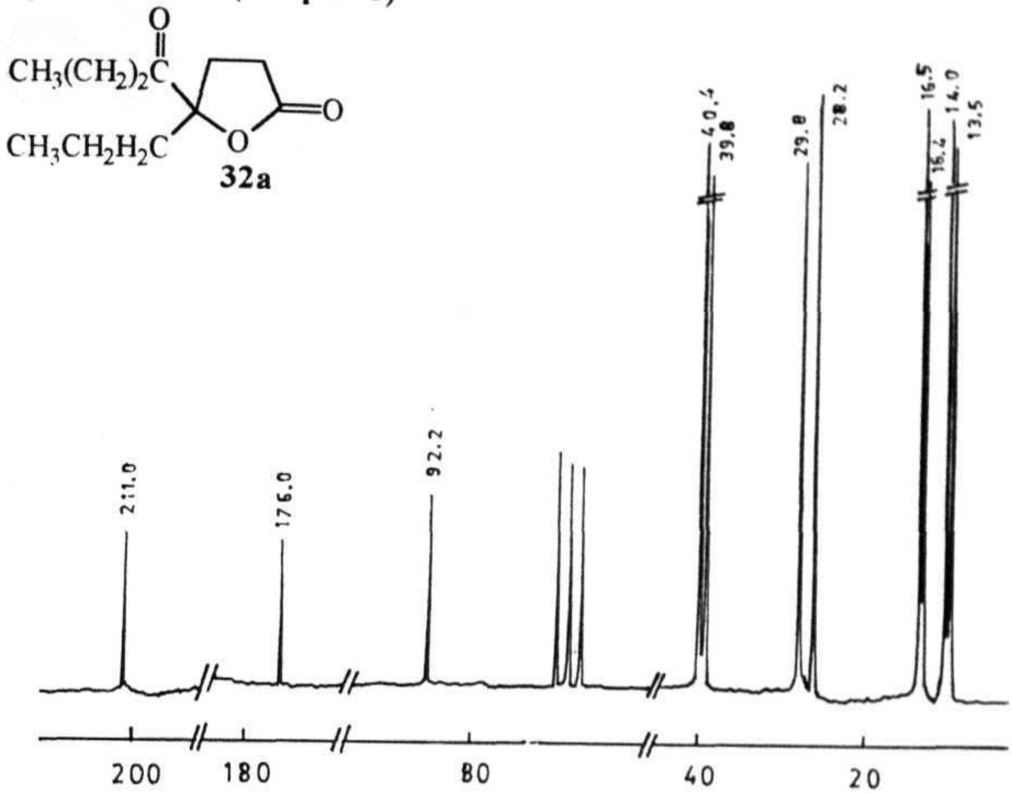

^{13}C NMR Spectrum (25 MHz, CDCl$_3$)

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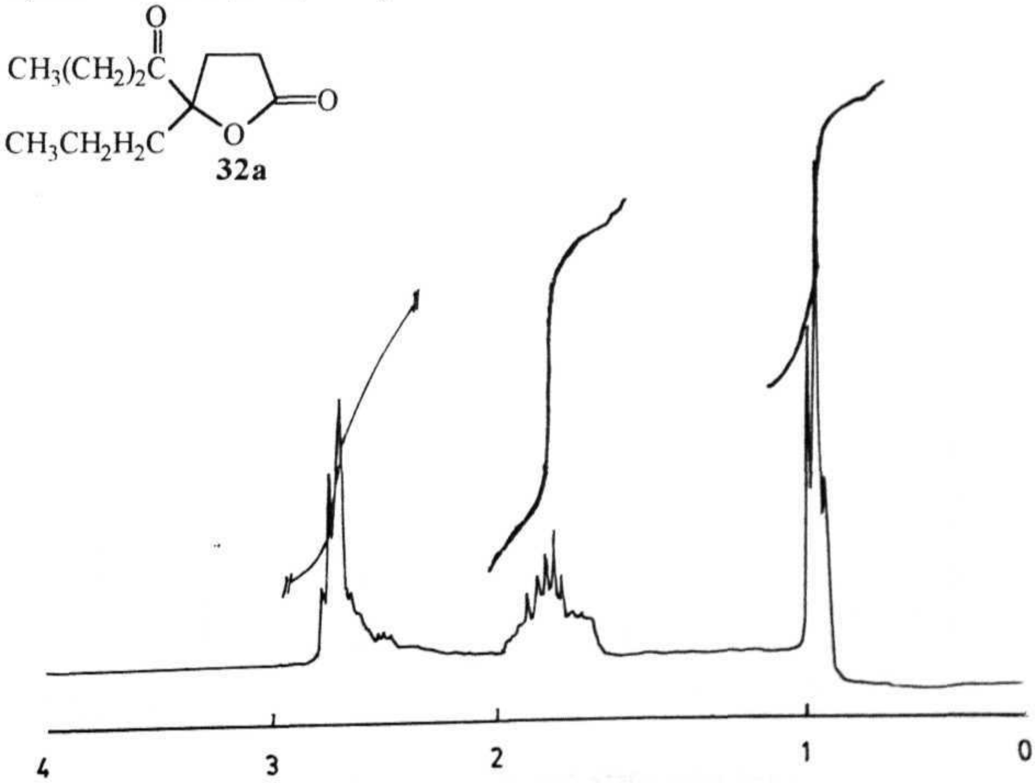

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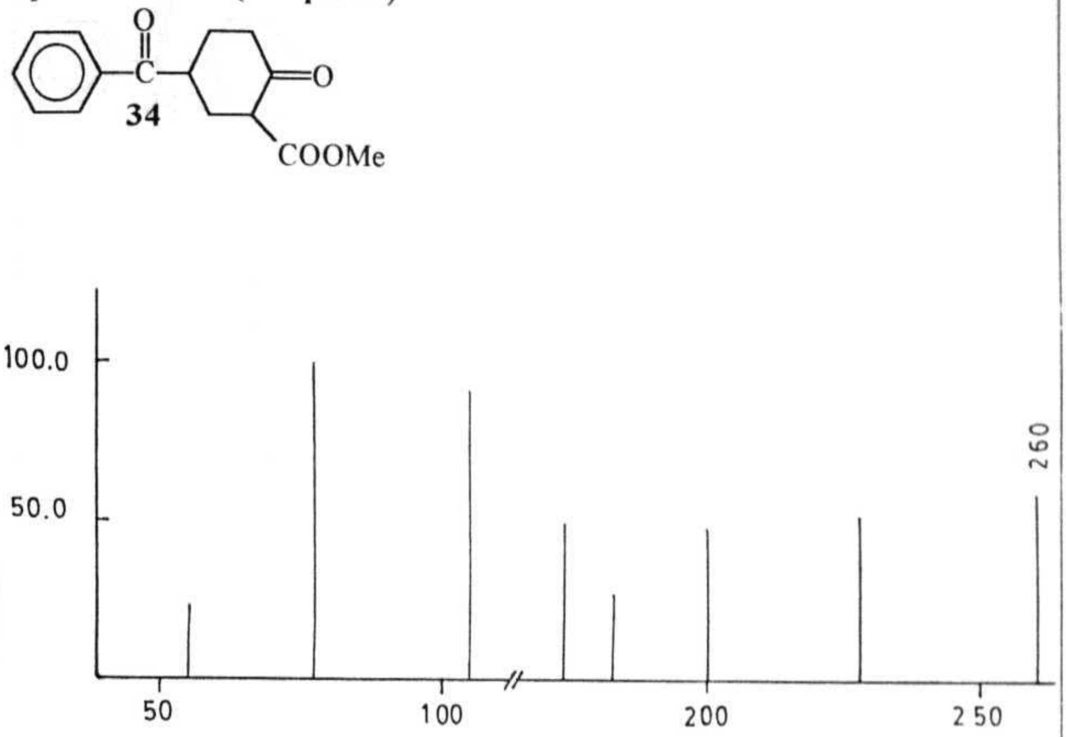

Mass Spectrum (m/z)

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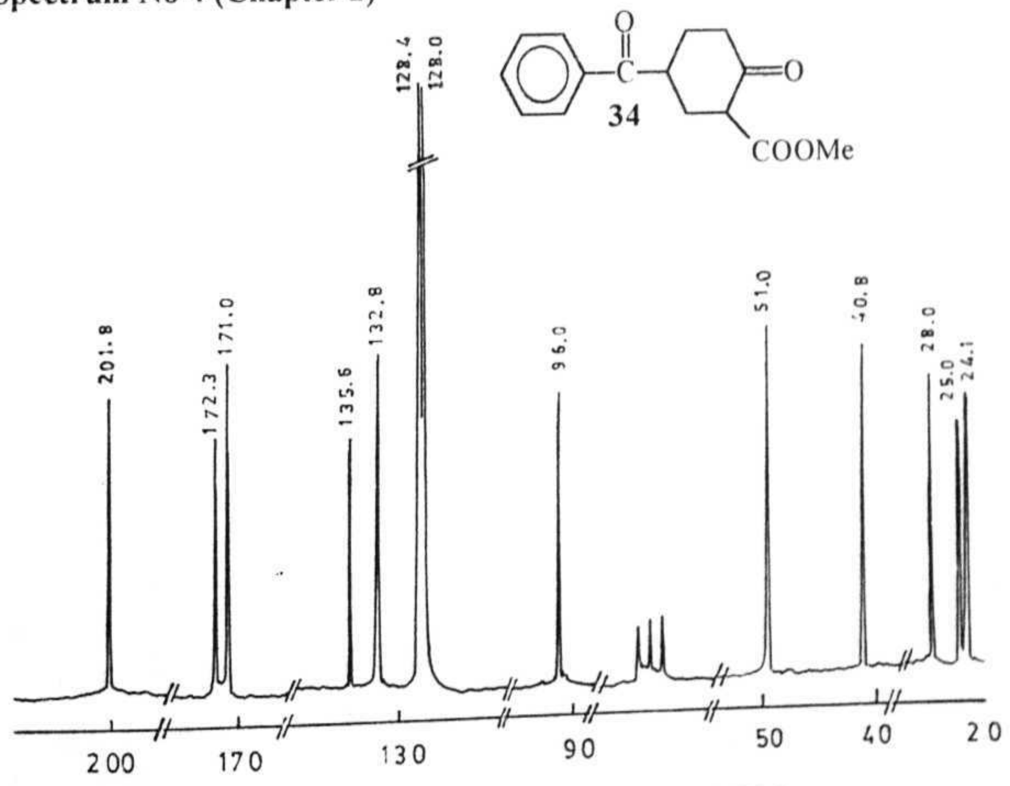

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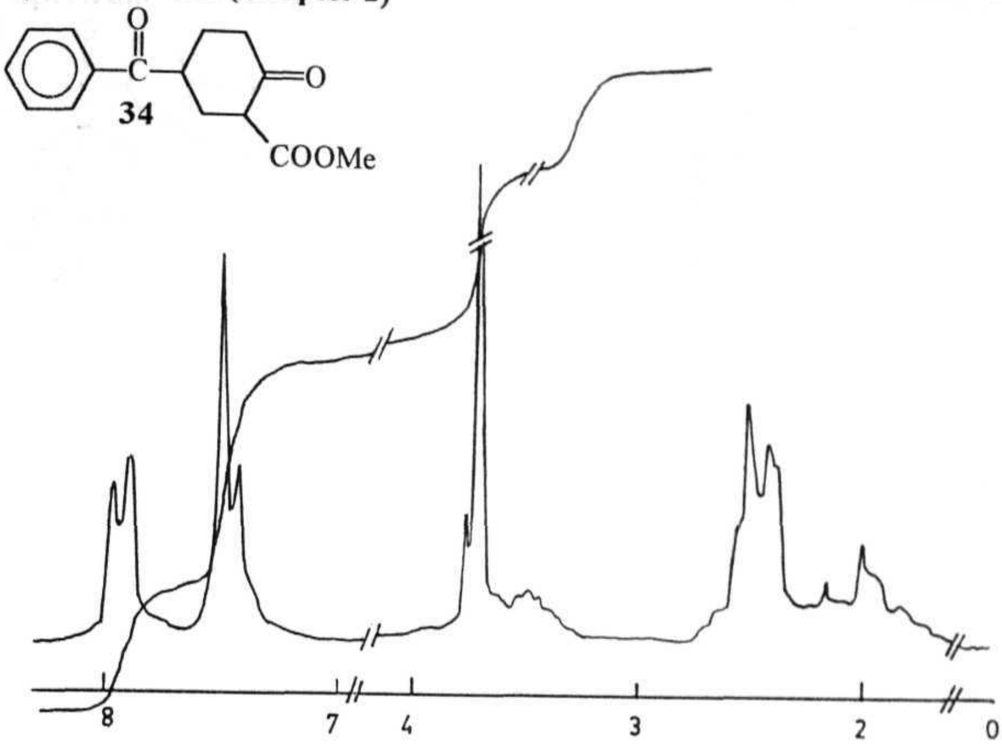

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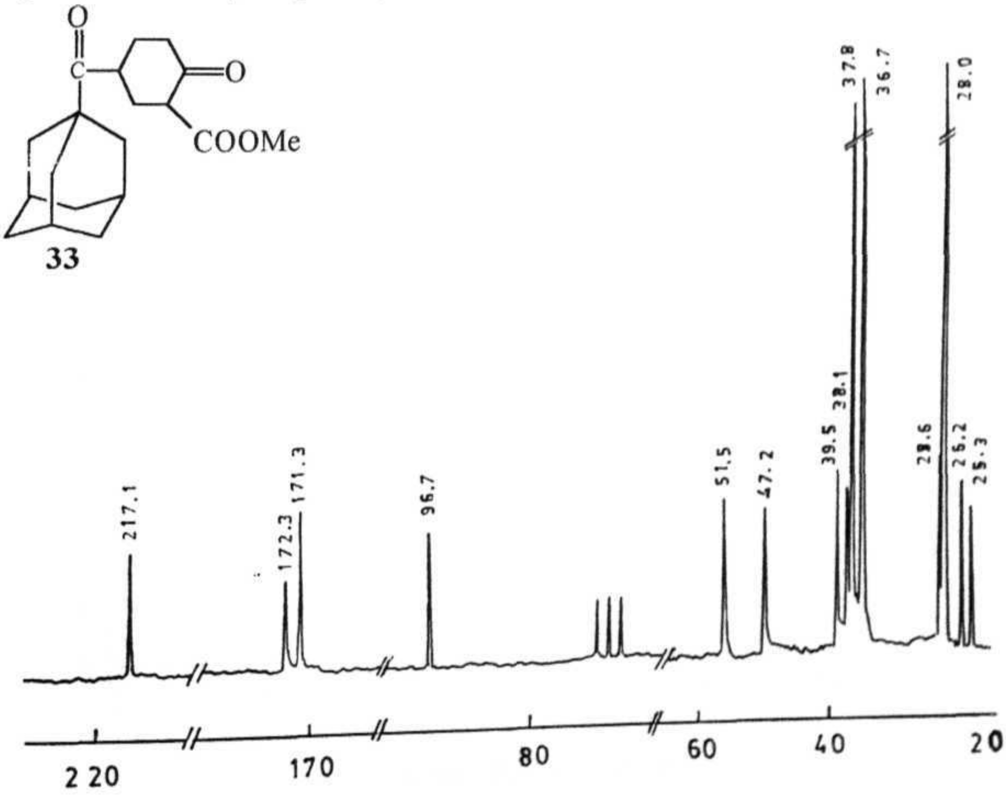

^{13}C NMR Spectrum (25 MHz, CDCl$_3$)

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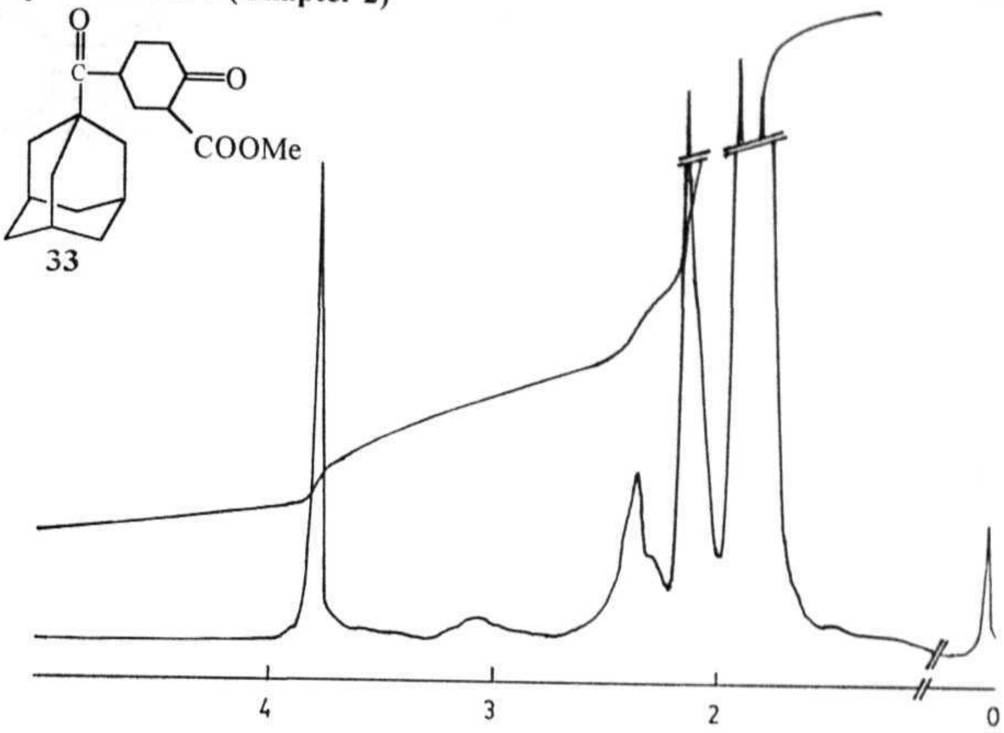

^{1}H NMR Spectrum (100 MHz, CDCl$_3$)

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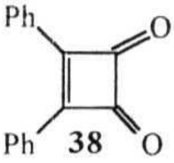

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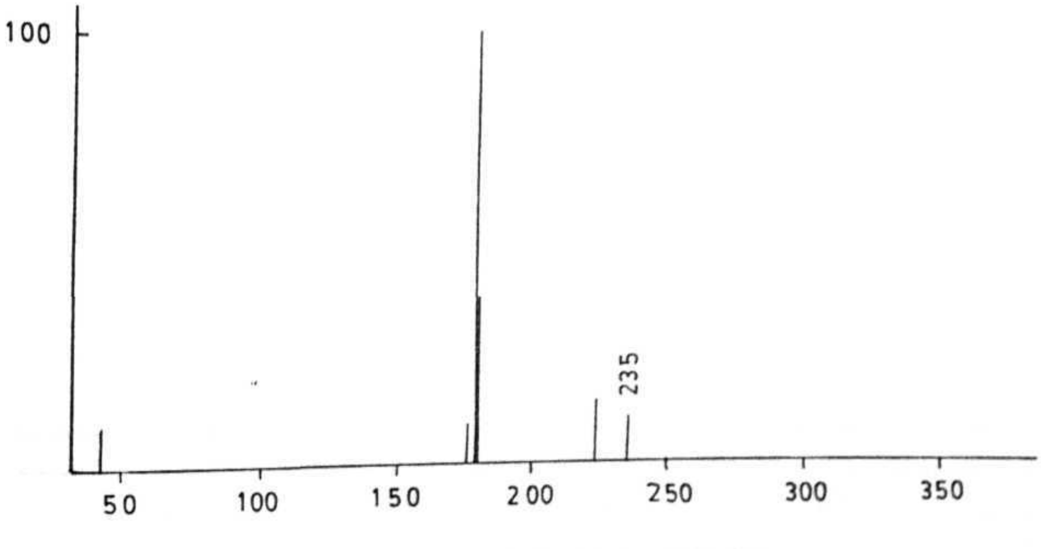

Mass Spectrum (m/z)

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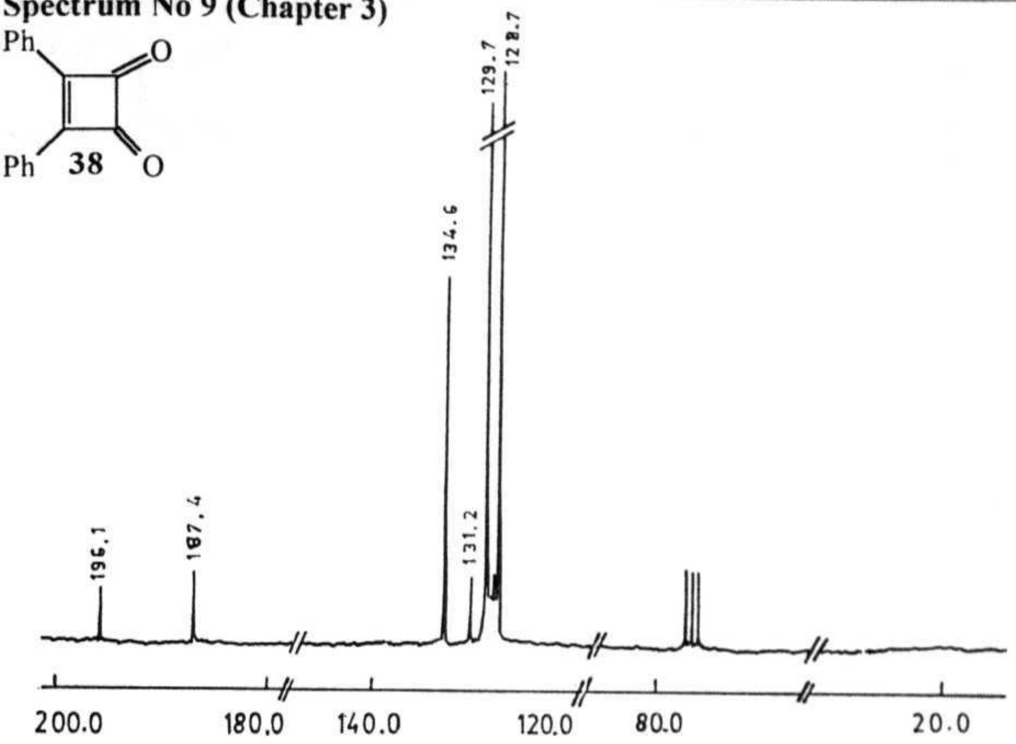

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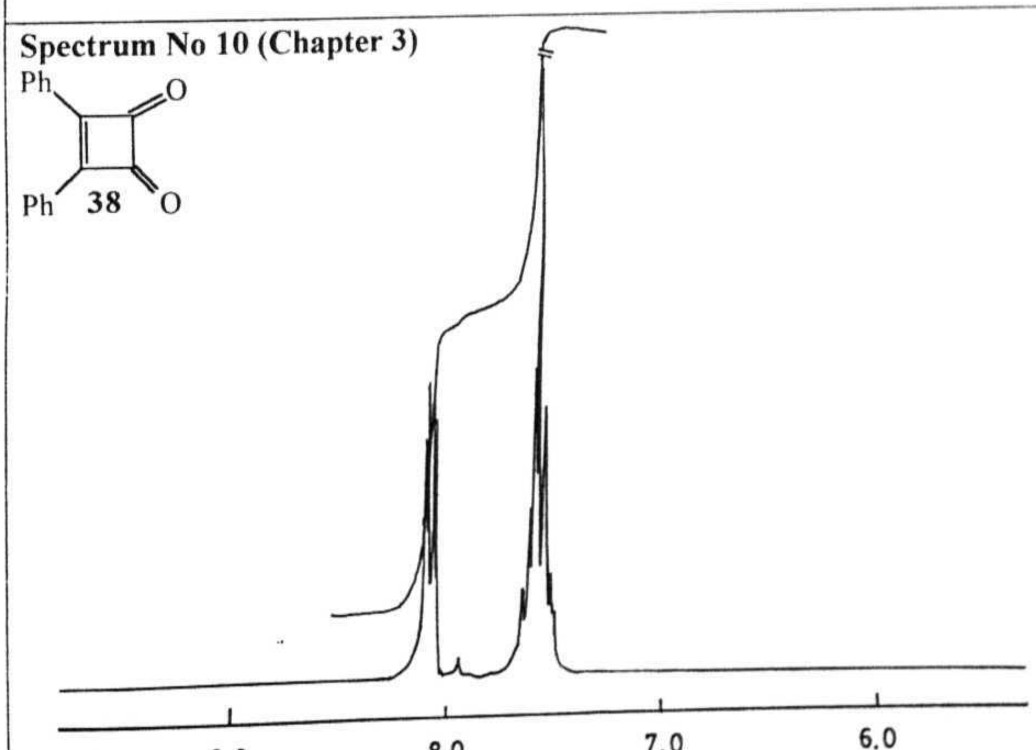
^{13}C NMR Spectrum (50 MHz, $CDCl_3$)

Spectrum No 10 (Chapter 3)



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^1H NMR Spectrum (200 MHz, $CDCl_3$)

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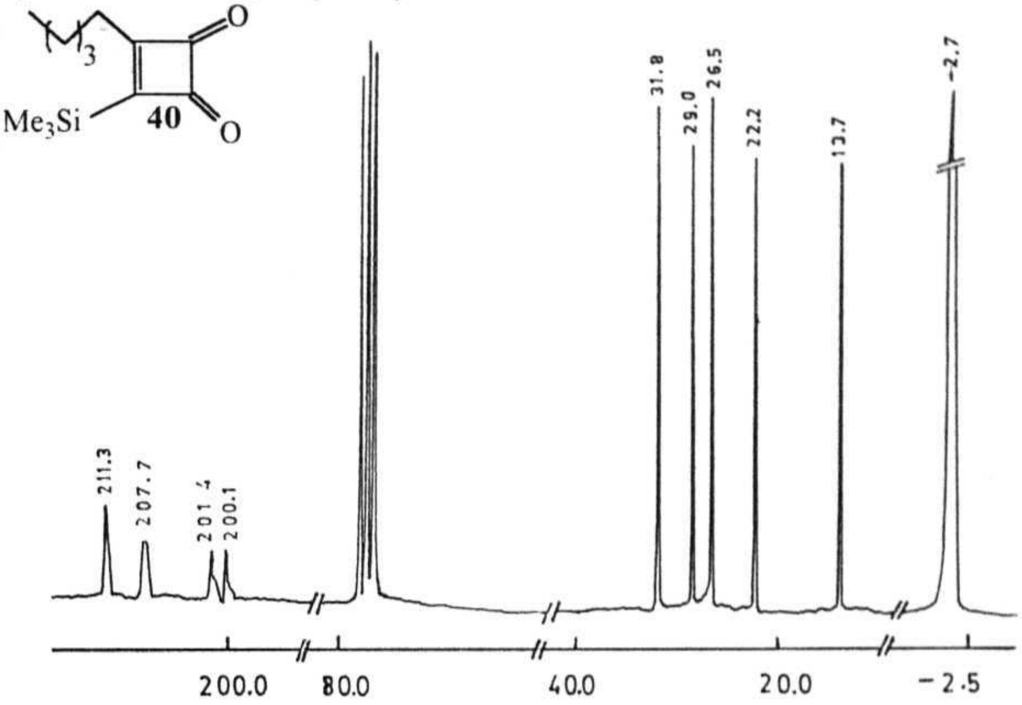

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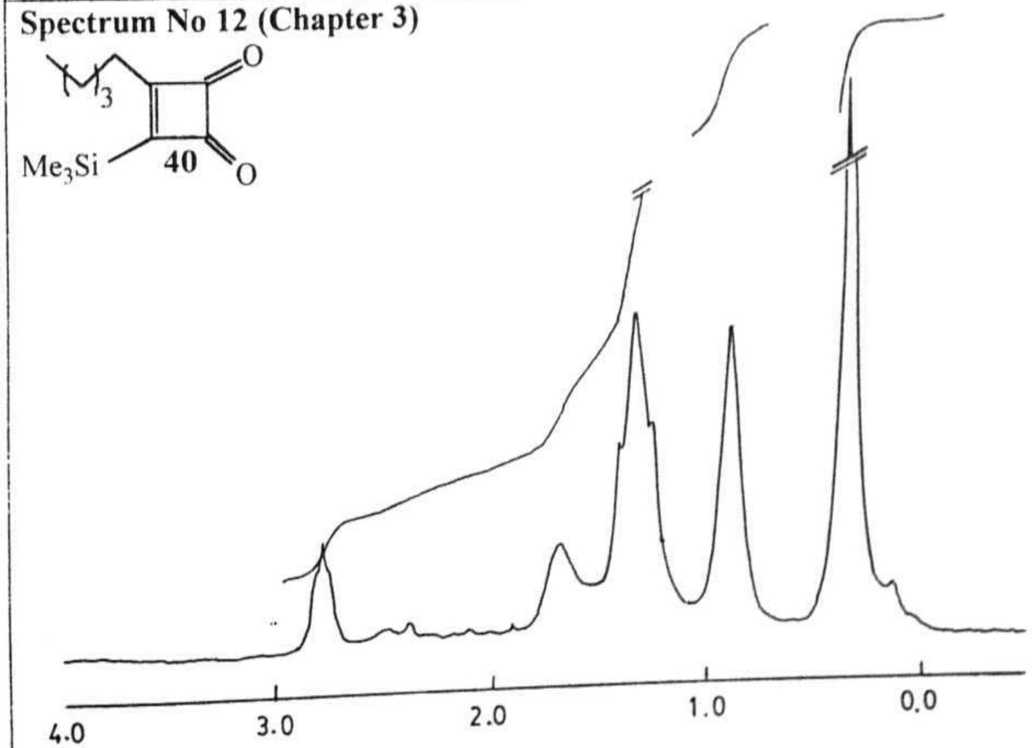

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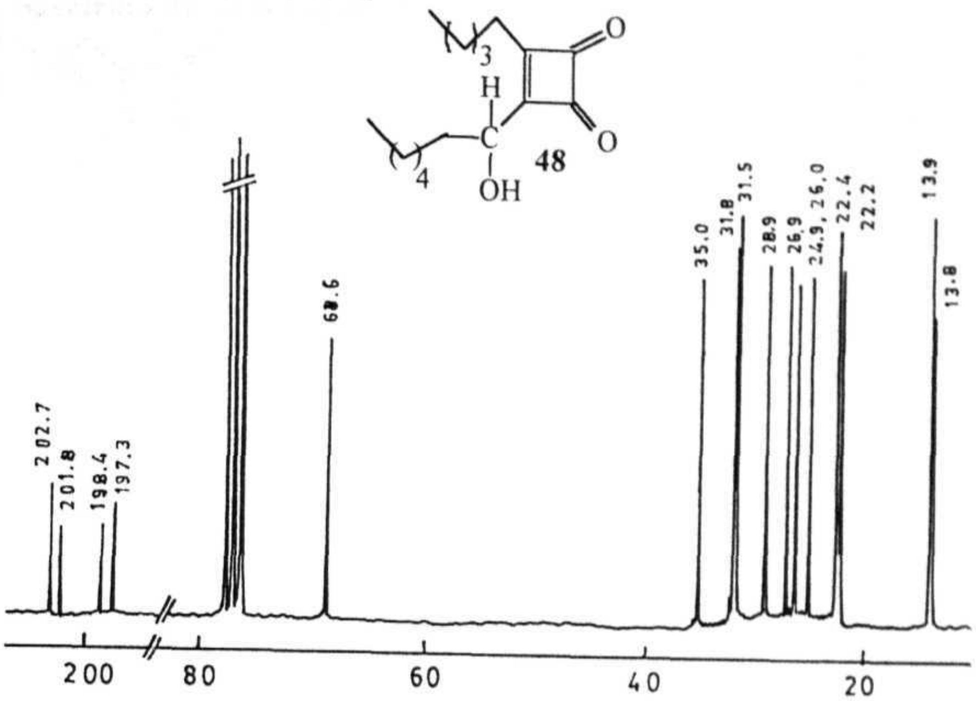

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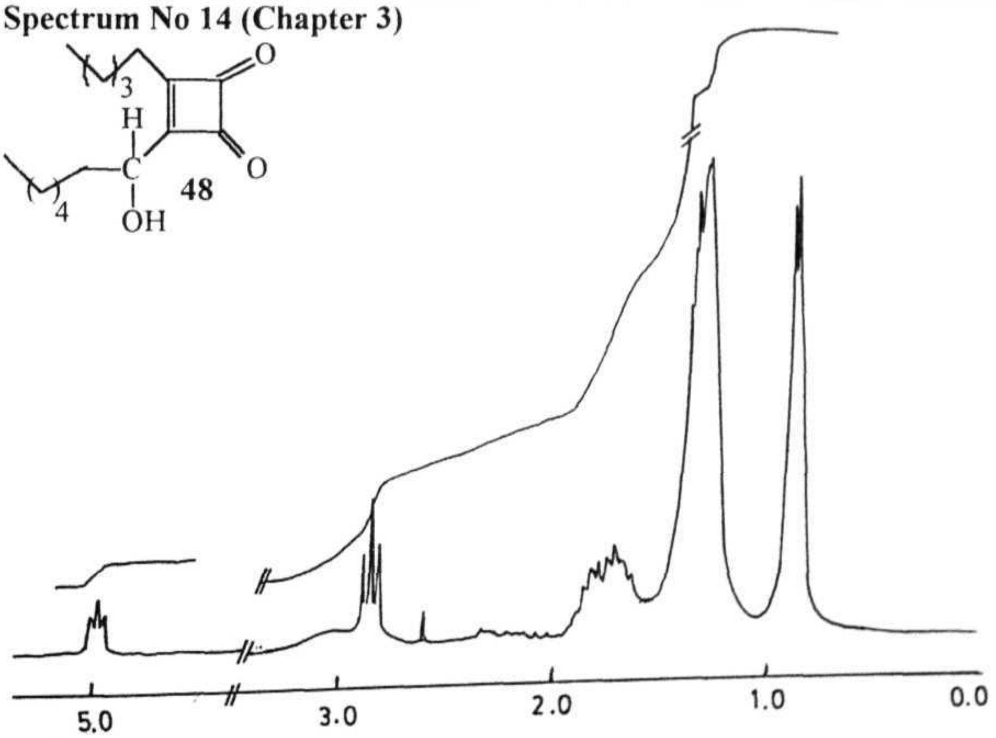

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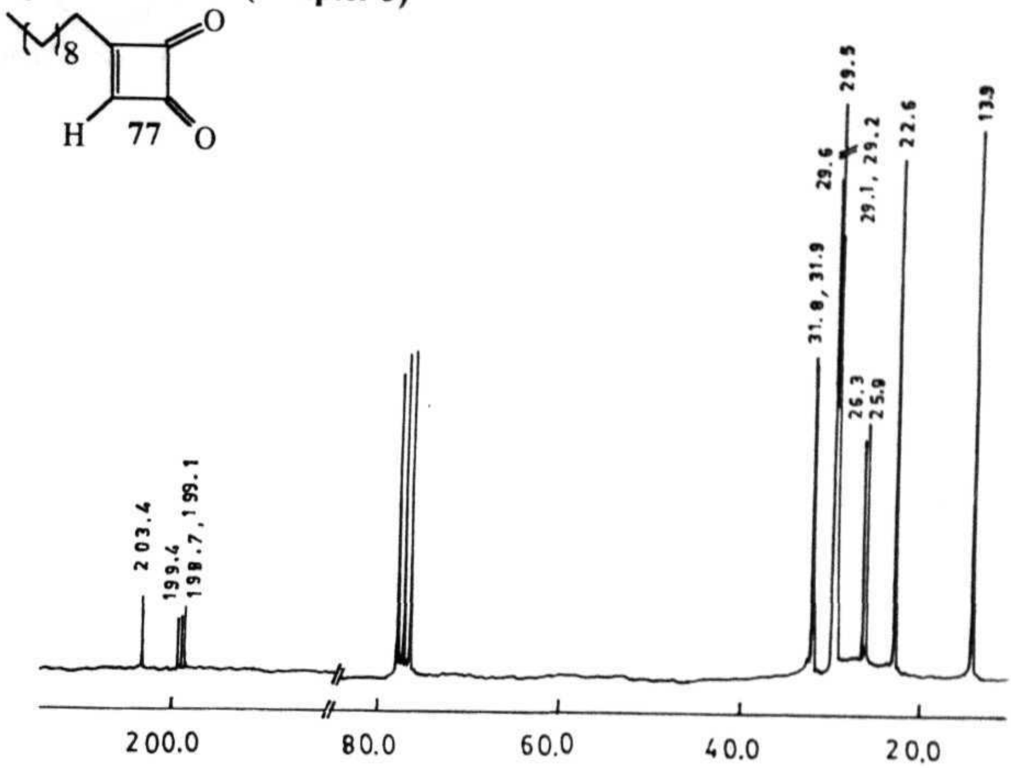

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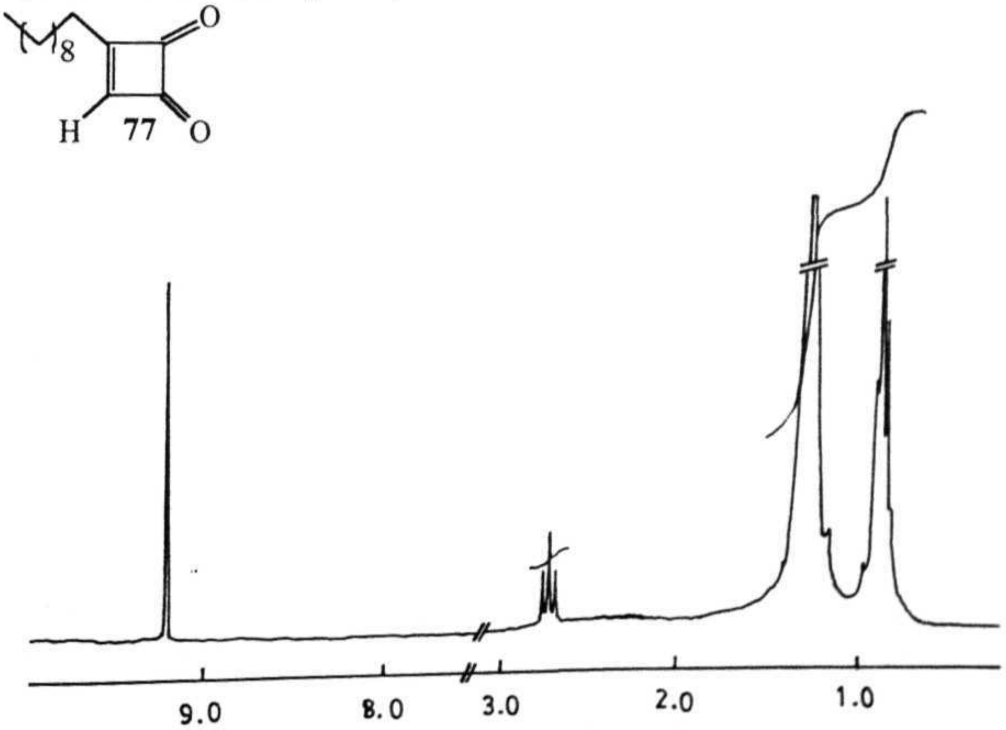
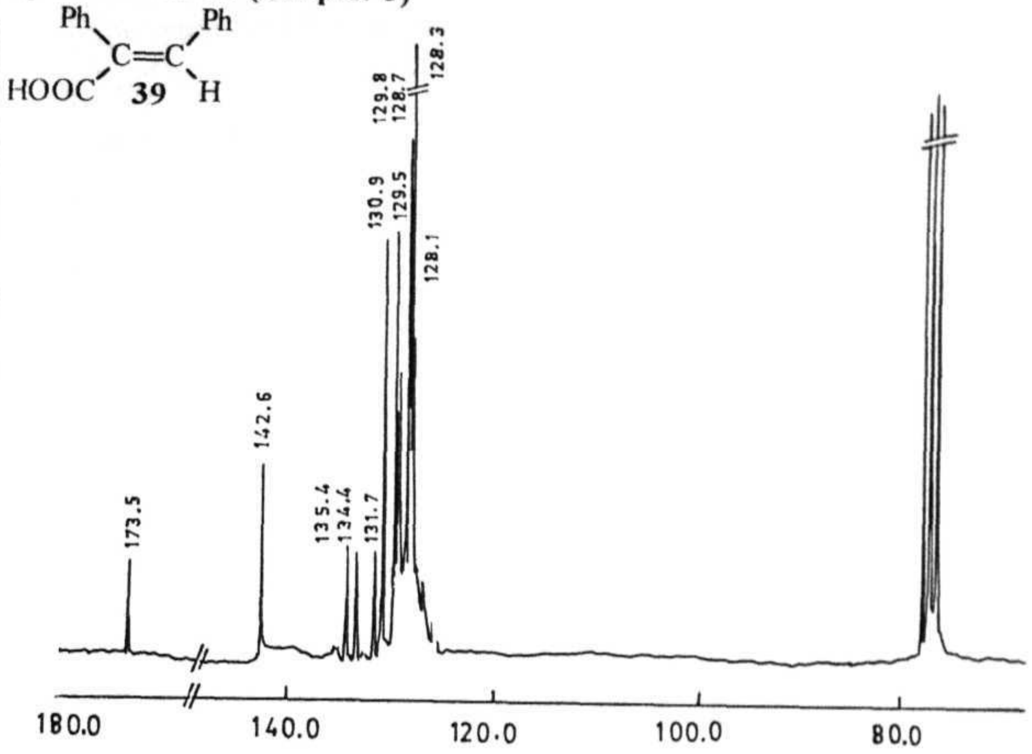


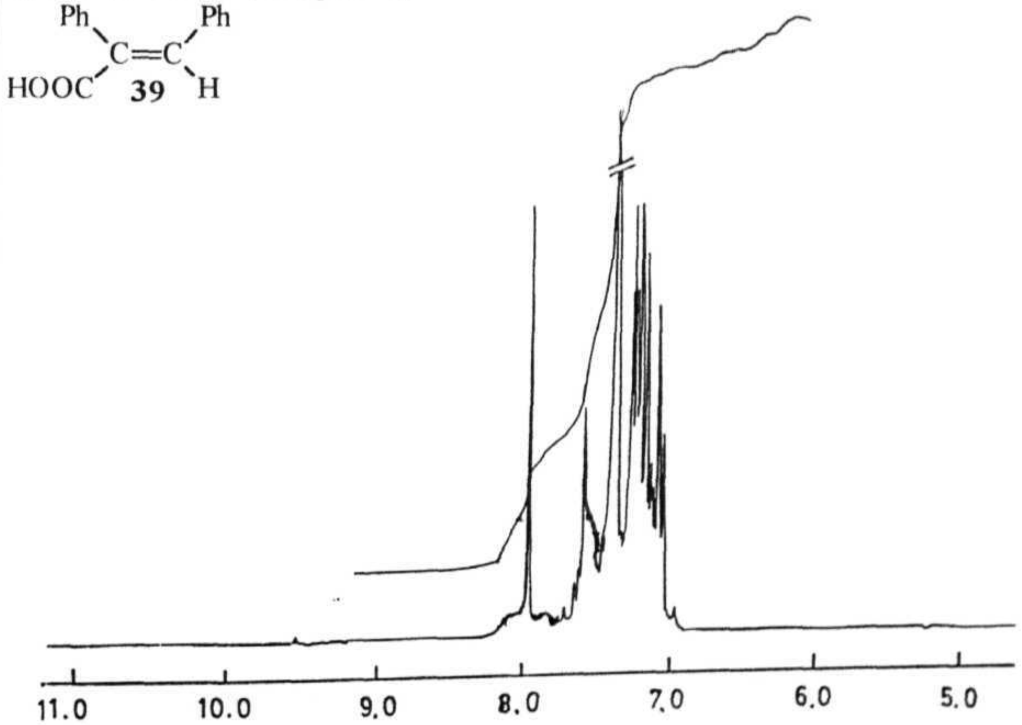
^1H NMR Spectrum (200 MHz, $CDCl_3$)

Spectrum No 17 (Chapter 3)



^{13}C NMR Spectrum (50 MHz, CDCl$_3$)

Spectrum No 18 (Chapter 3)



^{1}H NMR Spectrum (200 MHz, CDCl$_3$)

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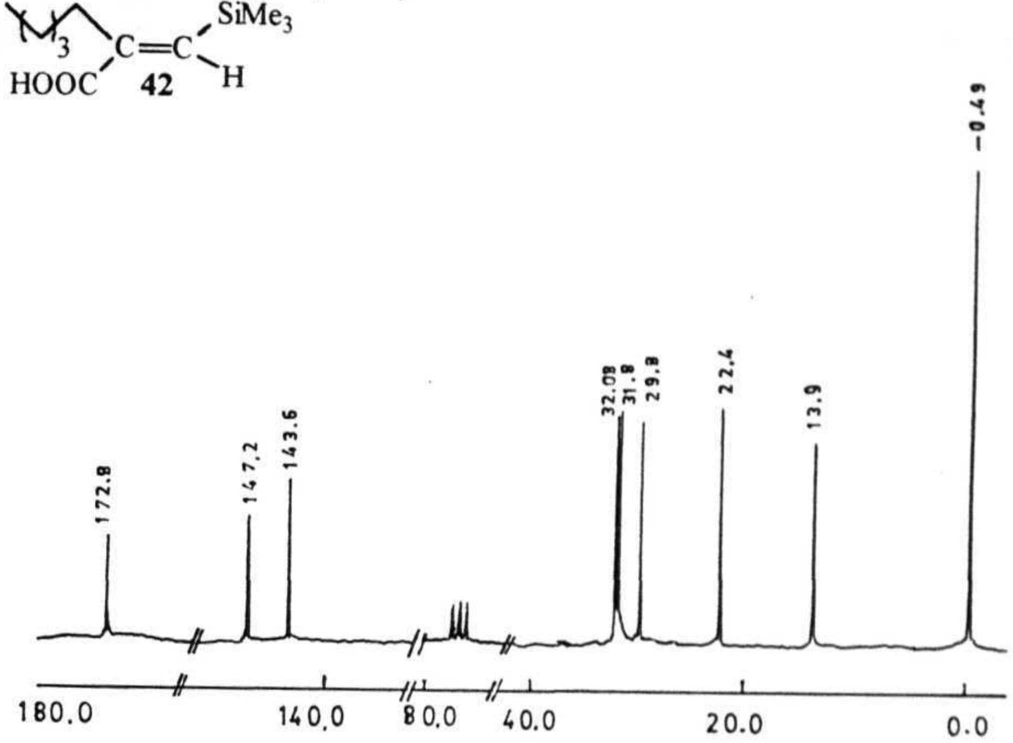

^{13}C NMR Spectrum (50 MHz, CDCl$_3$)

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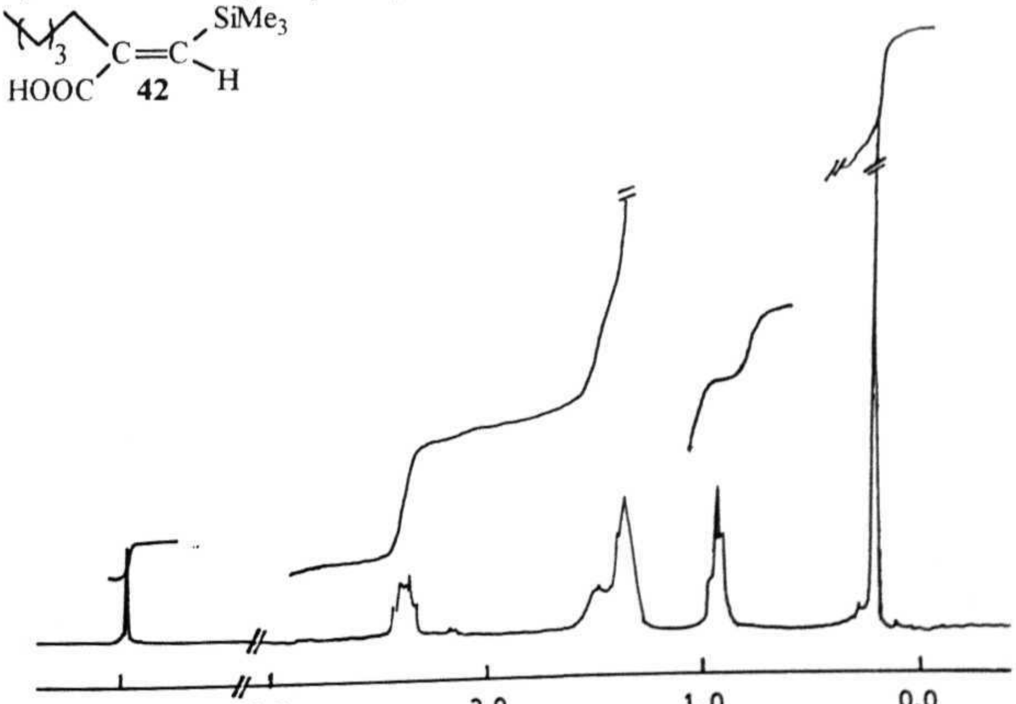

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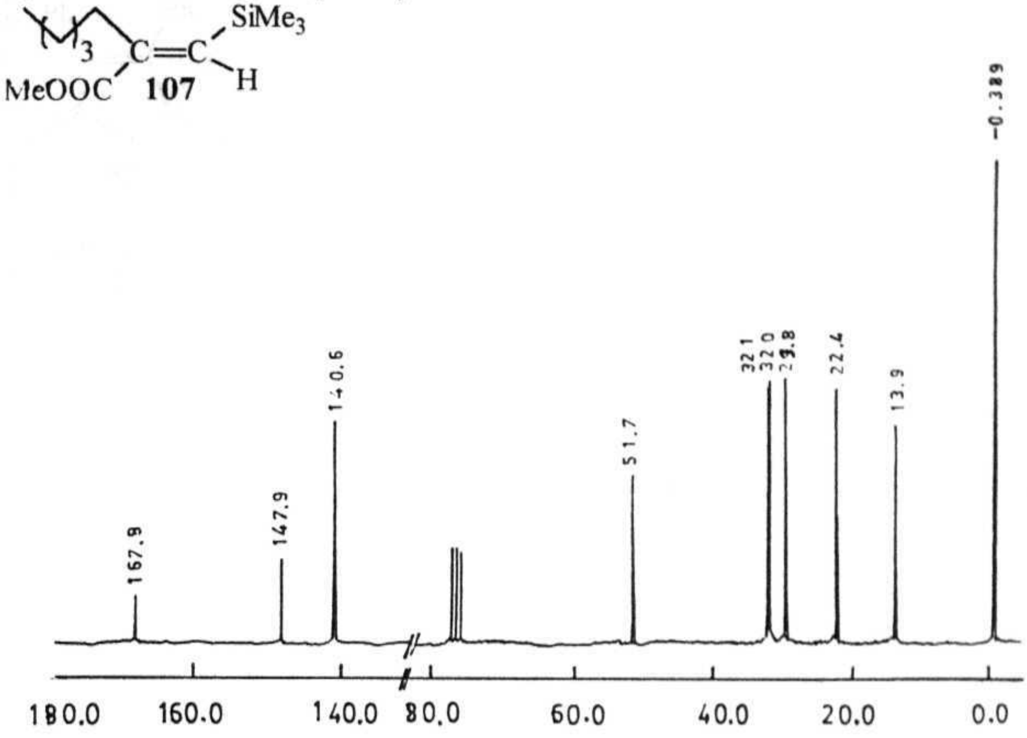

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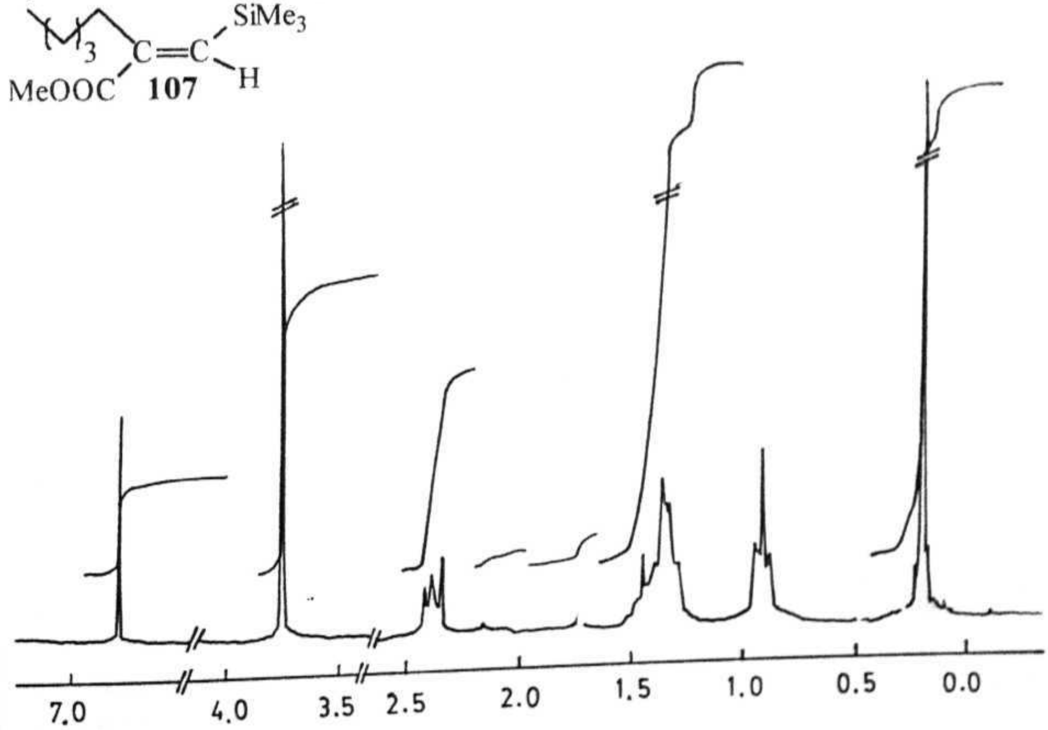
^{13}C NMR Spectrum (50 MHz, $CDCl_3$)

Spectrum No 22 (Chapter 3)



107

^{1}H NMR Spectrum (200 MHz, $CDCl_3$)

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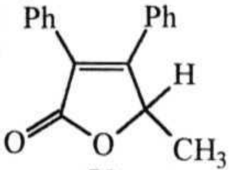

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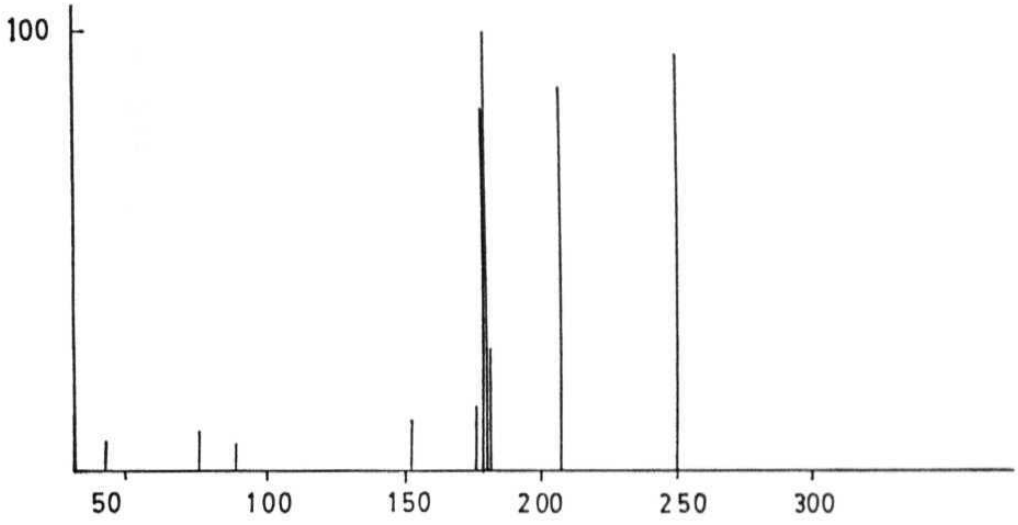
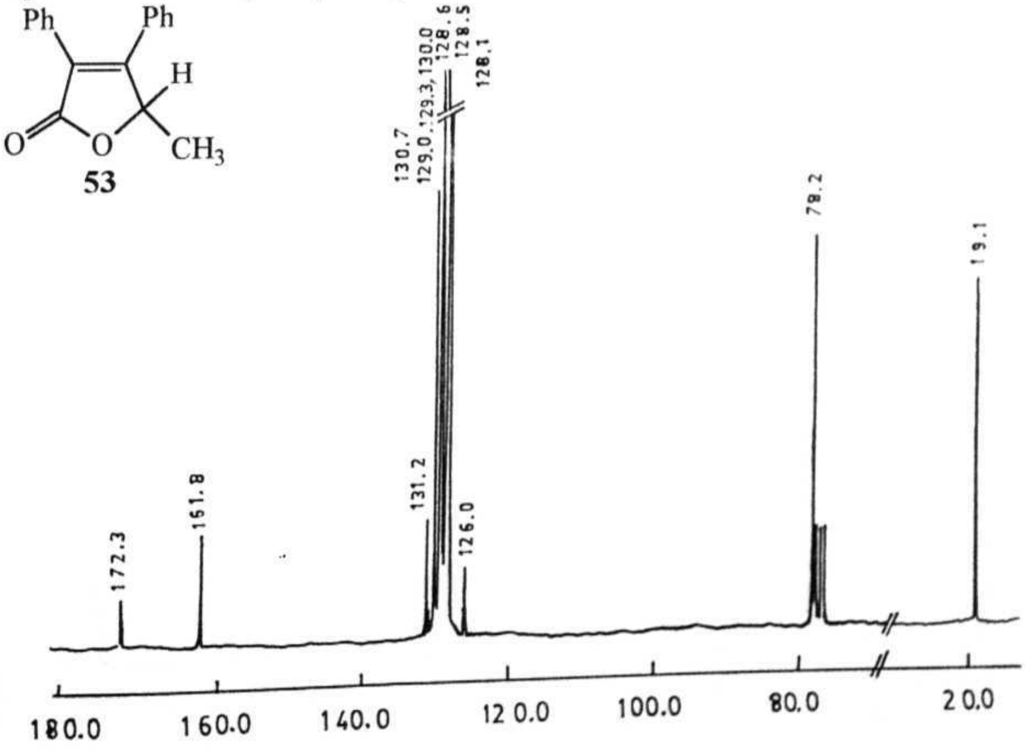


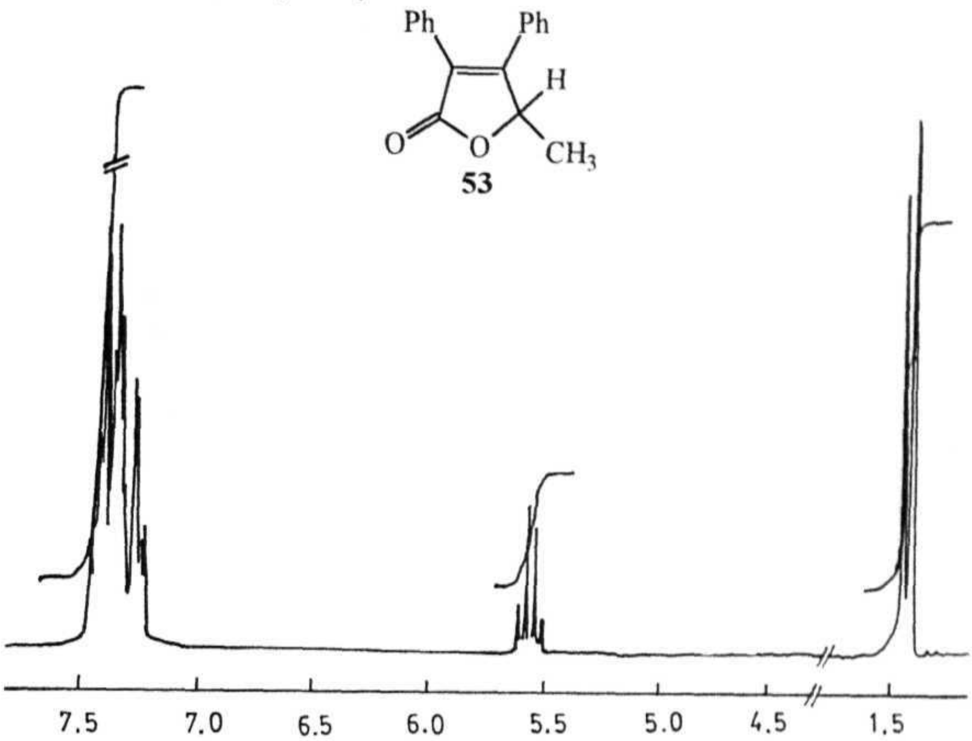
Mass Spectrum (m/z)

Spectrum No 24 (Chapter 3)



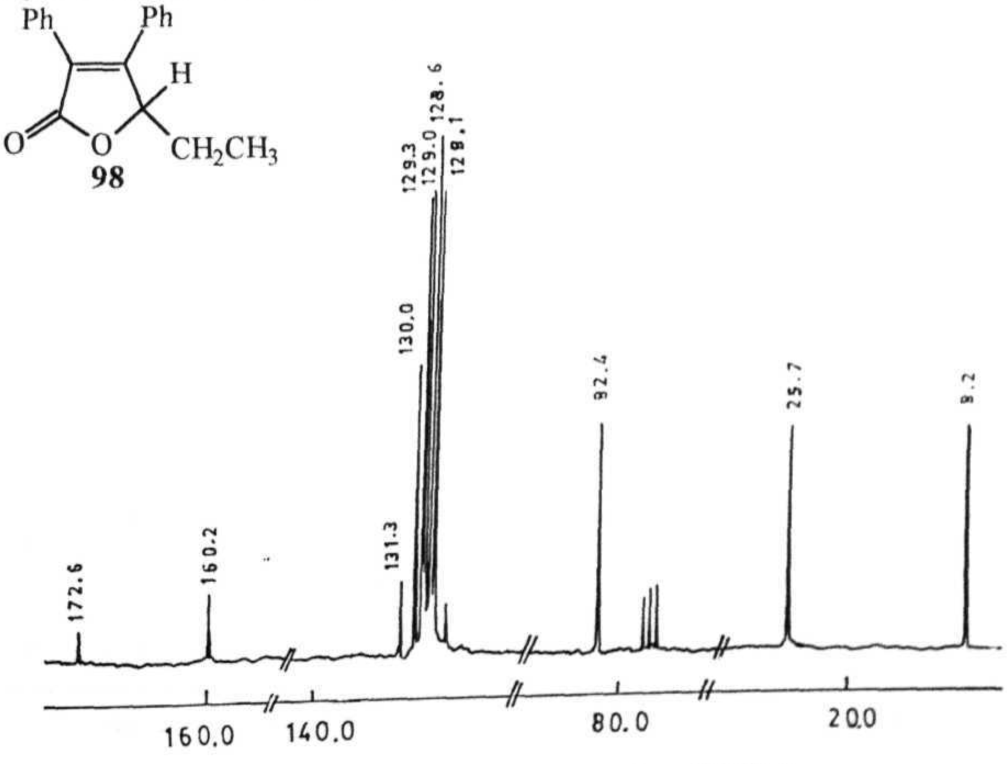
^{13}C NMR Spectrum (50 MHz, $CDCl_3$)

Spectrum No 25 (Chapter 3)



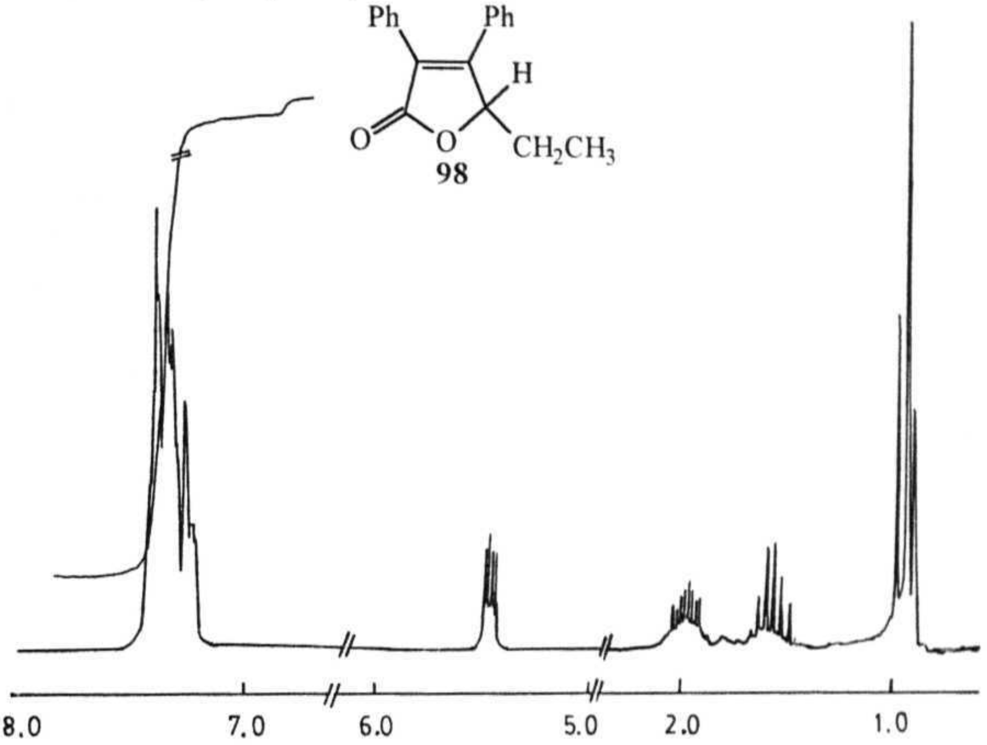
^{1}H NMR Spectrum (200 MHz, CDCl$_3$)

Spectrum No 26 (Chapter 3)



^{13}C NMR Spectrum (50 MHz, CDCl$_3$)

Spectrum No 27 (Chapter 3)



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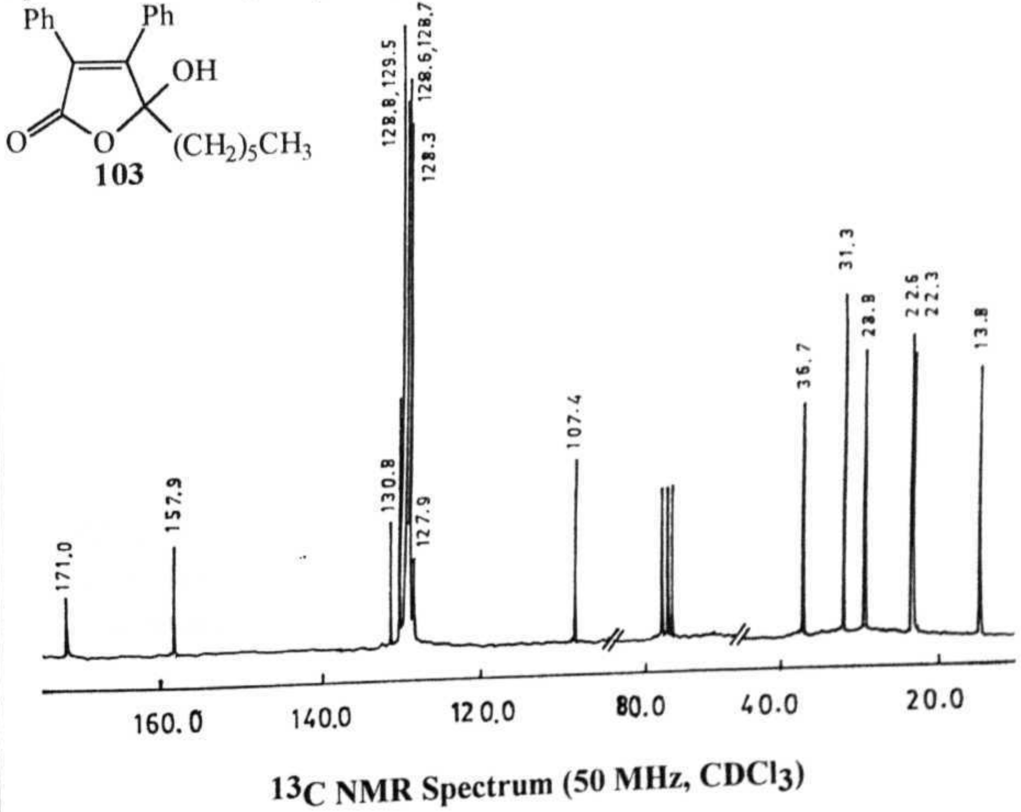
^{1}H NMR Spectrum (200 MHz, $CDCl_3$)

Spectrum No 28 (Chapter 3)



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^{13}C NMR Spectrum (50 MHz, $CDCl_3$)

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1. Reaction of $Na(RCO)Fe(CO)_4$ with CuCl or *ty* Synthetic and Mechanistic Studies of the Formation of 1,2-Diketones in a Novel Double-Carbonylation Process.
M. Periasamy, A. Devasagayaraj, U. **Radhakrishnan**
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2. Convenient One-Pot Methods for the Construction of Cyclohexyl rings at α-methylene moities of Ketones, Esters, Lactones and Nitriles through a Michael Addition-Dieckmann Cyclization sequence.
M. Periasamy, M.Ramareddy, U.Radhakrishnan, A. Devasagayaraj
J.Org.Chem, 1993, *58*, 4997.

3. Double Carbonylation of Alkynes using $NaHFe(CO)_4$.
M. Periasamy, U. Radhakrishnan, J.J. Brunet, R. Chuavin, A.W. Elzaizi
J.Chem.Soc,Chem.Commun., 1996, 1499.

4. A new method for regio and stereoselective hydrocarboxylation of Alkynes using $NaHFe(CO)_4$
M. Periasamy, U. Radhakrishnan, C. Rameshkumar, J.J. Brunet
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5. The $NaHFe(CO)_4/Me_3SiCl$ reagent system: Synthesis of Cyclobutenediones or a,p-unsaturated carboxylic acids from alkynes.
M. Periasamy, U. Radhakrishnan
(Communicated).

6. Novel double Carbonylation Reactions of alkynes using $RMgX/Fe(CO)_5/CuCl$
M. Periasamy, U. Radhakrishnan
(Communicated).

7. Synthesis of cyclobutenediones using iron carbonyl reagents: Intermediates and Reaction Mechanism
M. **Periasamy**, U. Radhakrishnan
(Manuscript under Preparation)

REVIEW ARTICLES

1. Cobalt(III) acetate as Reagent for Organic Synthesis
M. Periasamy, **U.** Radhakrishnan
Encyclopaedia of Reagents for Organic **Synthesis,** John & Wiley 1995, *2,* 1029.

2. Ceric Ammonium Sulfate as Reagent for Organic Synthesis
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