DEVELOPMENT OF NEW ORGANIC SYNTHETIC METHODS BASED ON TRANSITION METAL REAGENTS AND AROMATIC RADICAL ANIONS

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

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MARCH 1995

To

My Father and Madhu

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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.

M. RAMA REDDY

CERTIFICATE

Certified **that** the work contained in this thesis entitled **"Development** of **New Organic Synthetic Methods Based on Transition Metal Reagents and Aromatic Radical Anions"** has been carried out by **M. Rama Reddy,** under my supervision and the same has not been submitted elsewhere for a degree.

M. Periasamy
14/3/95

PROFESSOR M. PERIASAMY
(THESIS SUPERVISOR)

DEAN
SCHOOL OF CHEMISTRY

ACKNOWLEDGEMENTS

It is with high regards and profound respect, I wish to express my deep sense of gratitude to Prof. M. Periasamy for his stimulating guidence and persistent inspiration throughout my research tenure.

I am grateful to Prof. G. Mehta, Prof. R. Jagannathan, Prof. K.D. Sen and Prof. P.S. Zacharias, Deans, School of Chemistry for providing all facilities to carry out my work. I wish to thank Dr. D. Basavaiah for extending his co-operation and valuable discussions. All the faculty members have been helpful, I thank them all.

Thanks are also due to Dr. A.V. Rama Rao, Dr. A.K. Vairamani and Dr. B.M. Chowdhary, IICT, Hyderabad for providing the mass spectra for some of the compnounds.

I would like to extend my heartfelt thanks to Drs. A.D. Sagayaraj, Y. Suseela, Ch. Kishan Reddy, J.V. Bhaskar Kanth and my other colleagues Messrs. A.S.B. Prasad, M.L.N. Rao, U.R. Krishnan, L.V. Raman, P. Bharathi and C.R. Ramanathan.

It is pleasure to thank my friends R.R. Kallu, P. Chebium, H.K.R. Santapuram, V.R. Kalla, N.R. Gavva, A.C.S. Reddy, D.S. Reddy, R.K. Peddinti, S.G. Bodige, T.A. Rao, J.S. Rao, P.Y. Reddy, P.R.S. Sharma, G.V.B. Reddy, P.D. Rao, Jagadeesh, V.R.P. Reddy, V.R. Palle, M.P. Kumar, P.B. Rao, S.P. Raju, Praveen, V.K. Kallu, S. Banda, G. Shubraveti and all my other friends, who made my stay here an enjoyable and memorable one.

All the non teaching staff of the school have been extremely helpful, I thank them all. Messrs. S. Satyanarayana, V. Bhaskar Rao, K.R.B.V. Prasad, Satya Bhaskar, Ramana, Shetty and Mrs. Vijaya Lakshmi are a few to mention.

I wish to express my profound gratitude to my mother, brothers, sisters and other relatives for their constant encouragement and support throughout my academic career.

I wish to extend my sincere thanks to the University authorities for providing all the neccessary facilities for this work.

Financial assistance from the CSIR and DST is gratefully acknowledged.

M. RAMA REDDY

ABBREVIATIONS

Am	amyl
atm	atmosphere
CAN	ceric ammonium nitrate
Cp	π-cyclopentadienyl, η^5-C_5H_5
CRA	complex reducing agent
Cat	catalytic
DBE	1,2-dibromoethane
DBU	1,8-diazabicylco[5.4.0]undec-7-ene
DCM	dichloromethane
DCE	1,2-dichloroethane
DME	dimethoxy ethane
DMF	N,N-dimethylformamide
DEPT	distortionless enhancement by polarization transfer
Et	ethyl
HOAc	acetic acid
HMPA	hexamethylphophoric triamide
i-Pr	iso propyl
LAH	lithium aluminium hydride
M	metal
Me	methyl
n	primary
NMP	N-methylpyrrolidine
t	tertiary
OTf	triflate, OSO_2CF_3
OTs	p-toluenesulphonyl
r.t	room temperature
THF	tetrahydrofuran
TMS	tetramethylsilane
X	halide

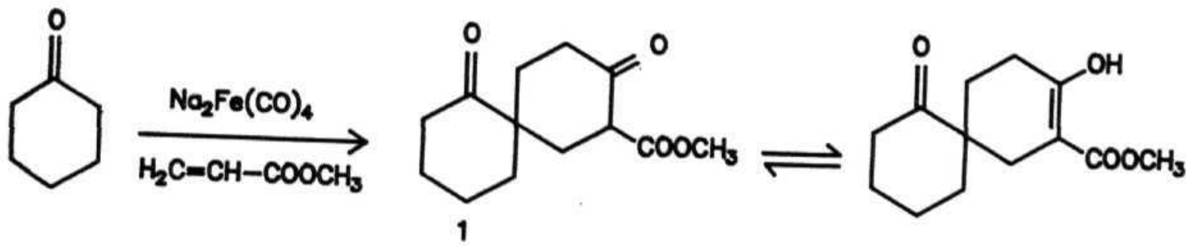
Synopsis

This thesis deals with investigations on the "Development of New Organic Synthetic Methods based on Transition Metal Reagents and Aromatic Radical Anions." It comprises of three chapters. Each chapter is subdivided into three parts, Background and Objectives, Results and Discussion and Experimental section along with References. The work described in this thesis is exploratory in nature.

The first chapter describes the studies on the reactivities of $Fe(CO)_4^{2-}$, $Fe(CO)_4^{2-}$/CuX and $Co(CO)_4^{-}$/CuX reagent combination, undertaken to investigate (i) the reactivity of Cu-M containing compounds, (ii) possibility of preparation of coordinatively unsaturated :$FeCO_4$ species. In order to facilitate the discussion, synthesis and utilization of the $Na_2Fe(CO)_4$ and $NaCo(CO)_4$ complexes are briefly discussed in this chapter.

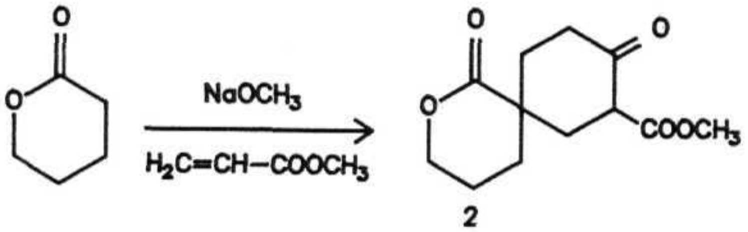
In the course of studies directed towards the use of the $Na_2Fe(CO)_4$ /CuCl combination for the synthesis of η^2-complexes of ketones, it was observed that the $Na_2Fe(CO)_4$ reagent readily reacts with cyclohexanone and methyl acrylate under ambient conditions to give the product 1 (53%) in which a cyclohexyl ring constructed on the active methylene moiety (Scheme.1)

Scheme. 1



It was found that the transformation is general one and several other ketones, esters, lactones and nitriles have been converted to the corresponding cyclic β-keto esters in moderate to good yields (48-62%). The transformation can be rationalized by the sequence of reactions involving double Michael additions followed by Dieckmann cyclization.

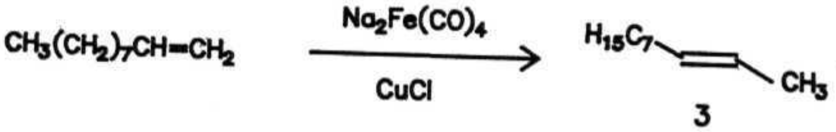
If in this transformation the $Na_2Fe(CO)_4$ acts as a base, then there is a possibility to achieve this using other more readily accessible bases such as alkoxides. Indeed, this was observed. It was found that sodium methoxide readily reacts with ketones, esters, nitriles and lactones in the presence of methyl acrylate to give the product with a cyclohexyl ring constructed on the active methylene moiety 2 (Eq. 1) in moderate (40-56%) yield.



2

—— (1)

We have also examined the reactivity of the $^{2-}Fe(CO)_4/CuCl$ combinations with α,β-unsaturated esters and olefins which could react with coordinatively unsaturated species. It was found that the species produced in this way isomerizes 1-decene to trans 2-decene 3 (Eq.2) in 83% yield.



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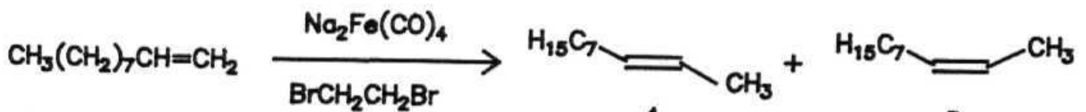
—— (2)

The utility of the $Fe(CO)_4^{2-}$/CuCl reagent system is further illustrated by the isomerization of several other alkenes in good yields (76-87%).

It was also found that the reaction using $BrCH_2CH_2Br$ in the place of CuCl also results in isomerization of alkenes selectively under mild conditions. Whereas the reactions with 1-decene and 1-dodecene lead to mixture of cis and trans-2-decenes, 4 and 5 (Eq. 3), the reactions with allyl benzenes and β-pinenes gave results similar to that observed using the $Na_2Fe(CO)_4$/CuCl reagent system.

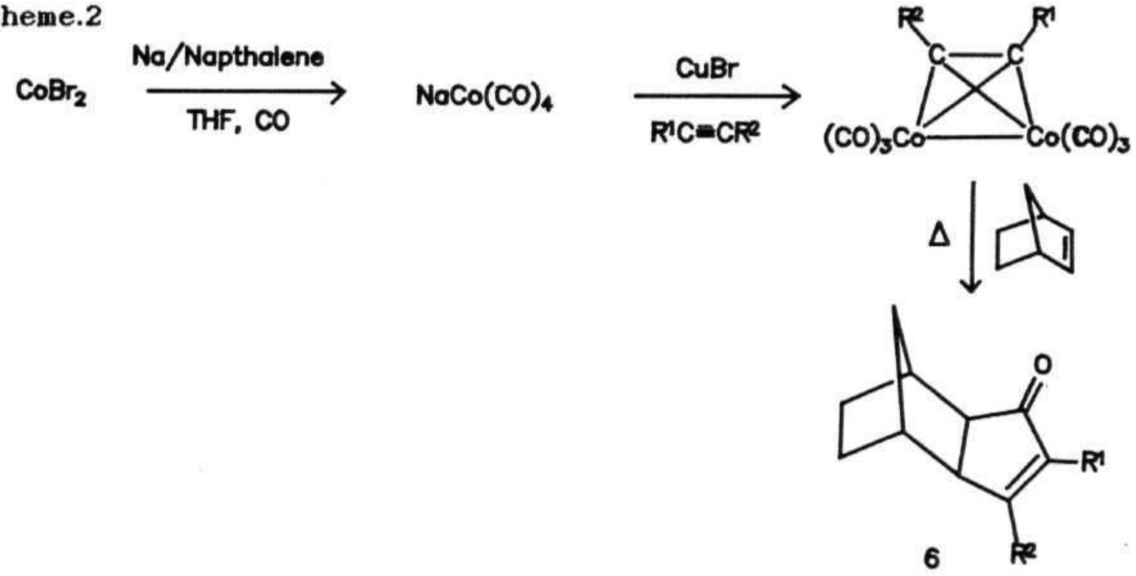


4 5 — (3)

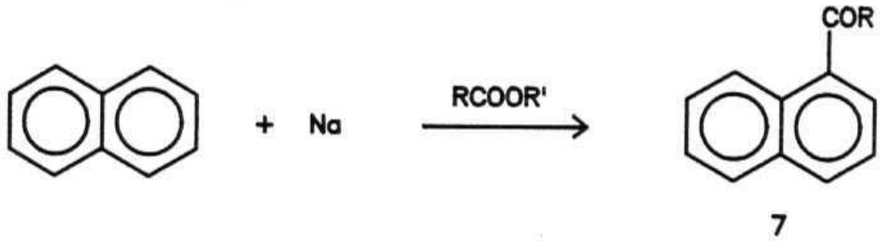
In order to examine whether $:Fe(CO)_4$ species is involved in these transformations, we have carried out the reactions in the presence of α,β-unsaturated carbonyl compounds. The results are discussed.

The reactivities of the $NaCo(CO)_4$/CuX combination towards alkenes and alkynes were also examined. It was found that the alkyne–$Co_2(CO)_6$ complexes can be synthesized using $NaCo(CO)_4^-$, prepared by the reduction $COBr_2$ with sodium naphthalenide under CO atmosphere, followed by CuBr treatment in the presence of alkynes. It was observed that heating of a mixture of the alkyne - $Co_2(CO)_6$ complexes obtained in situ in this way with norbornene leads to the formation of the corresponding cyclopentenone derivatives 6 in moderate to good yields (53-84%) (Scheme 2).

Scheme.2



The second chapter describes investigations on the reaction of anion radicals derived from poly cyclic aromatic hydrocarbons with carbon monoxide and carboxylic acid esters. It was found that radical anions, prepared by the reaction of polycyclic aromatic hydrocarbons with sodium, react with carboxylic acid esters to give the corresponding acylated aromatics 7 in moderate to good yields (43-74%) (Eq. 4).



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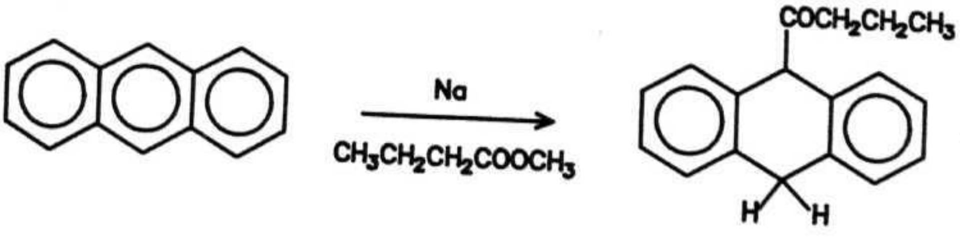
In the case of sodium anthracenide and phenanthrenide, the resulting products are the corresponding dihydro aromatic compounds (Eq. 5).

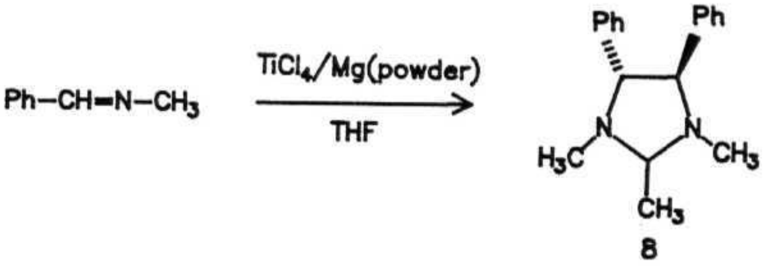


—— (5)

However, in the case of ethyl formate, all hydrocarbons anion radicals gave the corresponding aromatic aldehydes.

A brief investigation on the synthesis and utilization of acetylene diolate $C_2O_2^{2-}$ led us to investigate the reaction of CO with sodium naphthalenide in THF. These results are discussed.

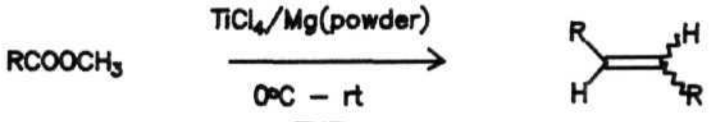
The third chapter deals with investigations on the reactivities of the low valent titanium reagents generated using the $TiCl_4/Mg/BrCH_2CH_2Br$ or $TiCl_4/Mg$ (powder) combinations. We have found that the low valent titanium species generated in this way reacts with N-methyl imine to give an unusual product which was identified as the corresponding cyclic imidazolidine derivative 8 in 54% yield (Eq. 6).



(6)

Several other N-alkyl imines have been converted to the corresponding cyclic imidazolidine derivatives in (58-74%) moderate to good yields. We have also examined the reactions of this interesting low valent 'Ti' species with various functional groups such as olefins, ketones and olefinic ketones. The results are discussed.

Very recently, we have observed **that** this interesting titanium reagent reacts with certain carboxylic acid esters to give the corresponding disubstituted olefins 9 in 60–75% yields (Eq. 7).



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—— (7)

These results are discussed considering the reports of the reaction of esters with the McMurry type low valent Ti reagents.

CHAPTER 1

STUDIES ON THE REACTIVITIES OF $^{-2}Fe(CO)_4$, $^{-2}Fe(CO)_4/CuX$ AND $^{-}Co(CO)_4/CuX$ REAGENT COMBINATION

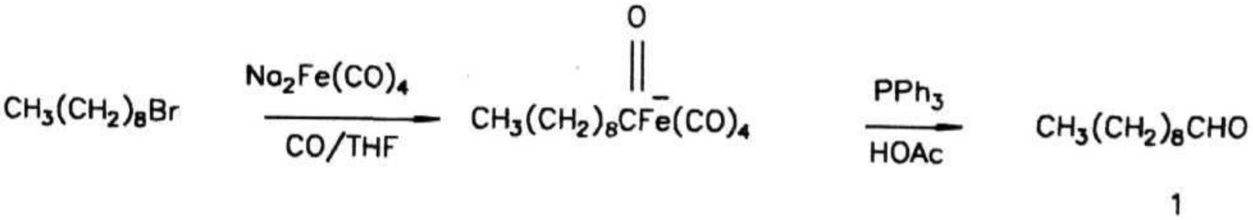
1.1. Background and objectives:

In recent years there is immense interest in the development of new organic synthetic methods based on organotransition metal chemistry. However, only few organotransition metal reagents have been widely utilized. Some of the most versatile and useful transition metal reagents developed thus far are the organoiron[1] and organocobalt[2] compounds.

These transition elements form stable neutral metal carbonyls,[3,4] anionic metal carbonyls,[3-10] hydridometal carbonyls[3,4] and their derivatives. The metal carbonyl derivatives display unusual catalytic activity in oxidation, reduction, isomerization, oligomerization, carbonylation and polymerization processes.[11,12] They have been used extensively in carbon-carbon bond formation reactions.[illegible]

The super nucleophile, $^{-}\mathrm{Fe(CO)}_4$ reagent (Collman reagent), has been shown to be useful in many interesting transformations.[1] For example, it is useful in the conversion of aliphatic halides and tosylates into aldehydes 1 (Scheme 1),[17] ketones 2 and 3, carboxylic acids, esters and amides (Eq. 1 and 2).[18-20]

Scheme 1.



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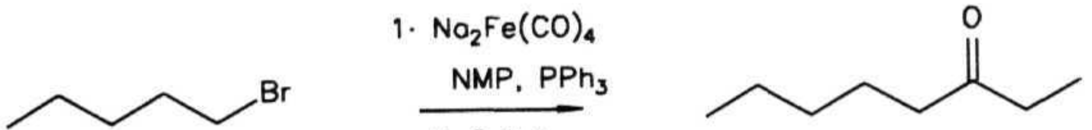

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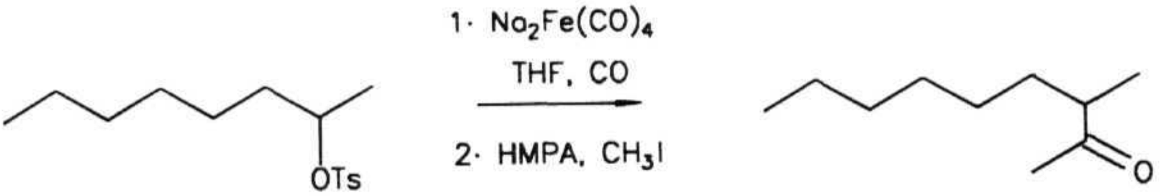

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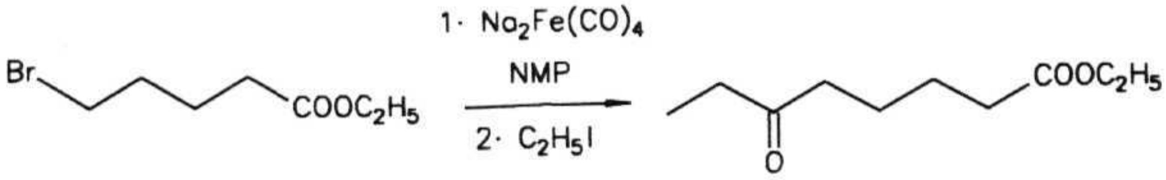
— (2)

The most remarkable and potentially useful features of the $^{-2}\mathrm{Fe(CO)_4}$ reagent are its toleration of organic functional groups. Collman et *al* illustrated this in the conversion of a 5-bromo ester into the 6-keto ester 4 (Eq. 3).[19]

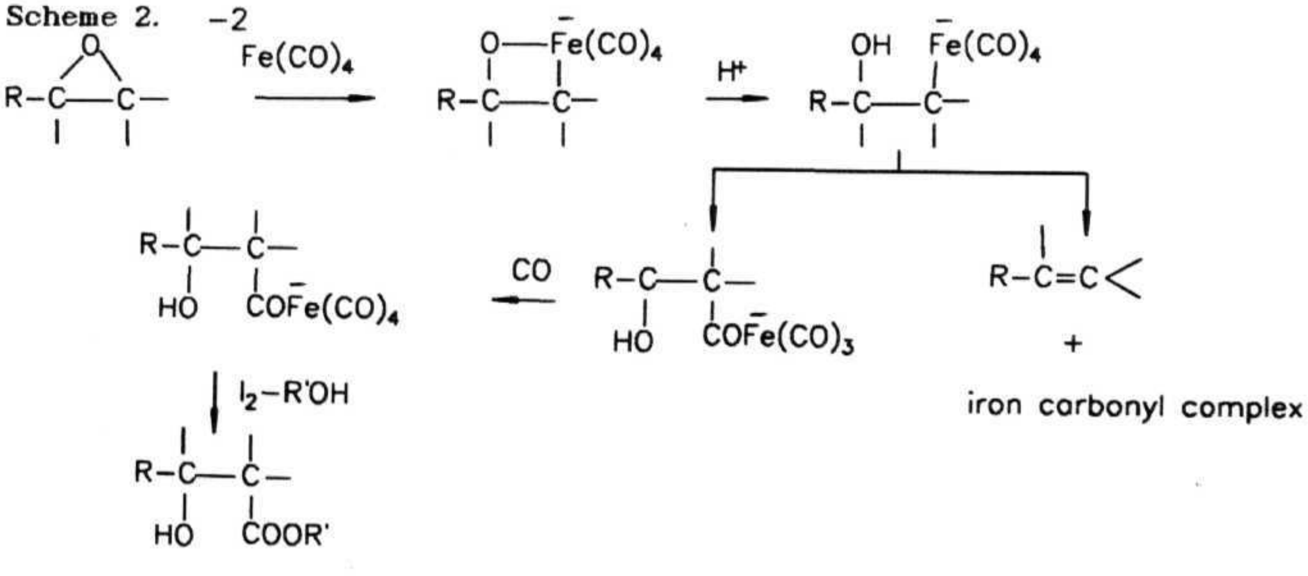


4

— (3)

Ethanolic solutions of $^{-2}\mathrm{Fe(CO)_4}$ react with epoxides to give β-hydroxy esters 5 (Scheme 2).[20–22]

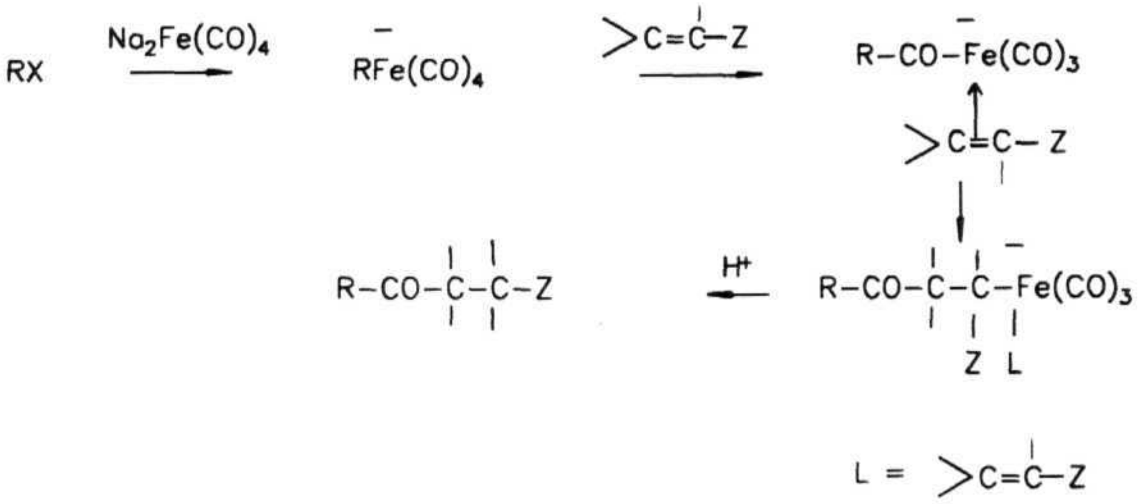
Scheme 2.



5

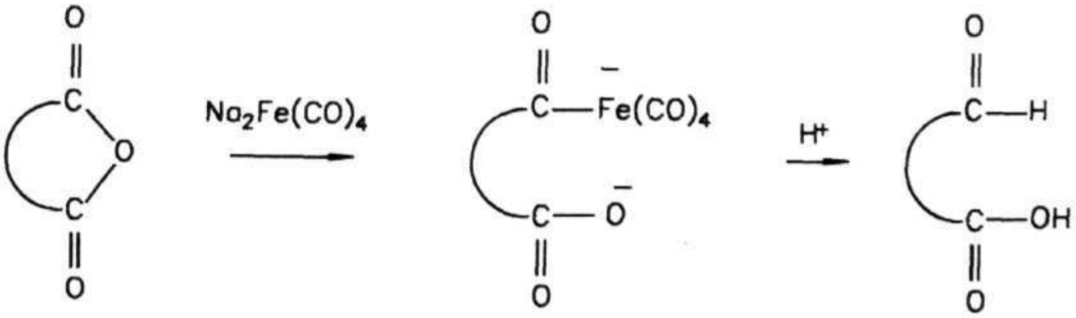
A method for the direct **hydroacylation** of Michael acceptors through sequential insertion reactions of organotetracarbonyl ferrates to obtain **β-ketoesters**, ketones and nitriles from common alkylating agents has been reported **(Scheme** 3).[23]

Scheme 3.



Watanabe *et al* reported the facile synthesis of aldehydes and aldehydic acids 6 from aliphatic and aromatic carboxylic acid anhydrides using $Na_2Fe(CO)_4$ (Scheme 4).[24]

Scheme 4.



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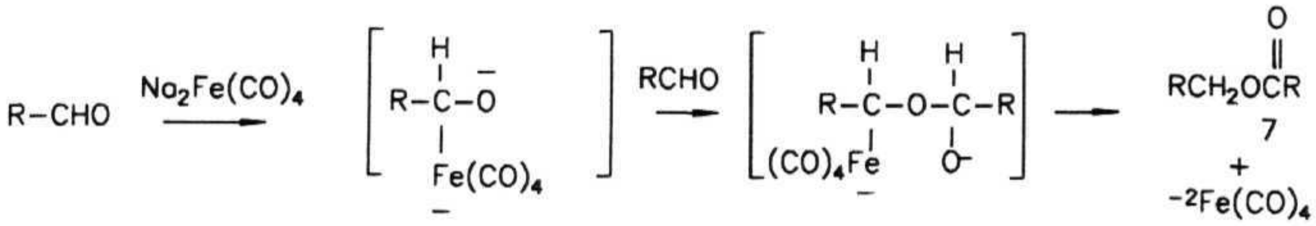
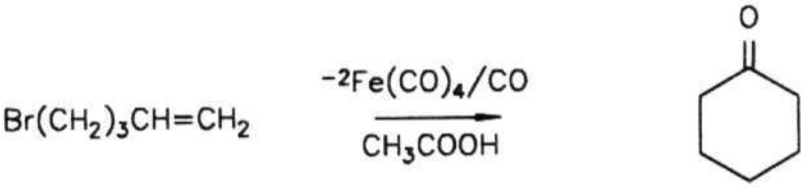
The $Na_2Fe(CO)_4$ is also efficient catalyst for the dismutation of aromatic aldehydes to esters. Aliphatic aldehydes undergoes such dismutation to give 7 upon treatment with ${}^{-2}Fe(CO)_4$[25] (Scheme 5).

Scheme 5.



This reagent also converts ν-ethylenic bromides and tosylates into cyclohexanones 8, 9 and fl-allenic bromides 10 into cyclopentenones 11 (Eq. 4-6).[26]



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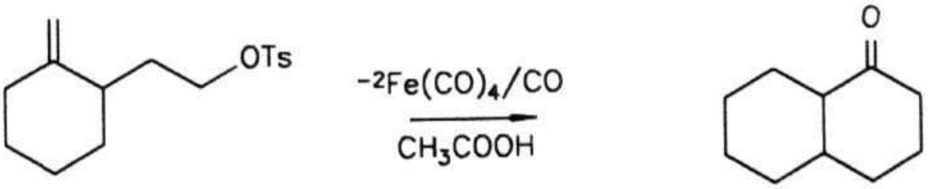

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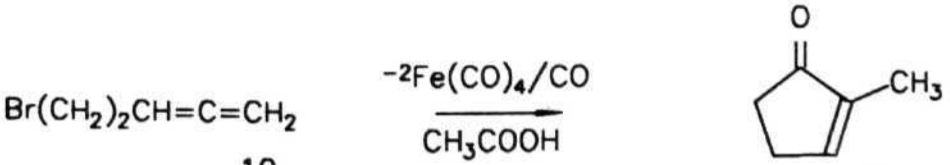

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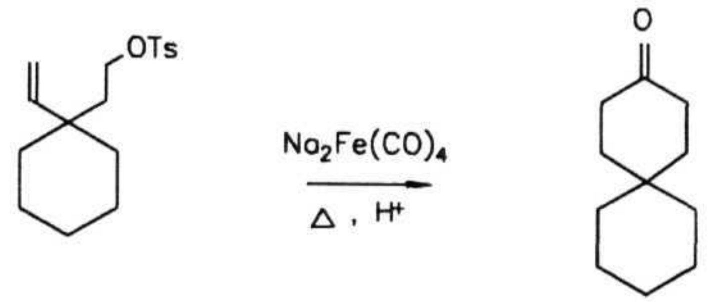
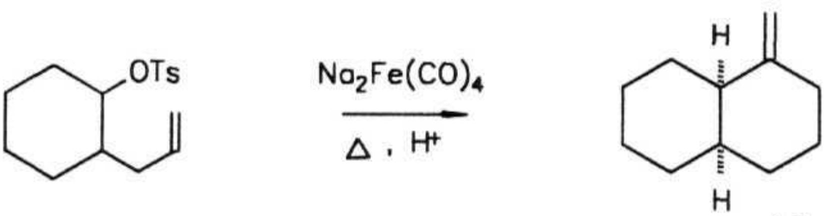
11

— (6)

McMurry reported several interesting carbonylative cyclizations using disodium ${}^{-2}Fe(CO)_4$ (Eq. 7,8).[27]

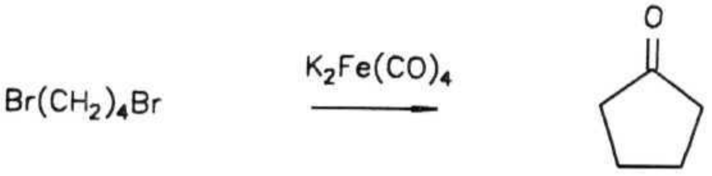


12 — (7)

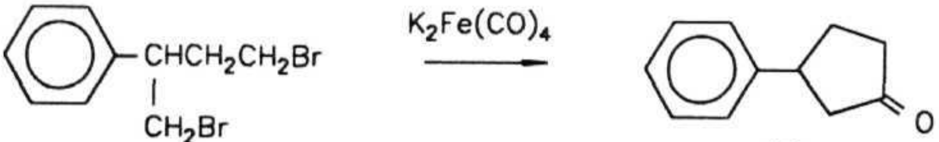


13 — (8)

Five membered cyclic ketones 14 and 15 were prepared from 1,4-dihalobutanes using $K_2Fe(CO)_4$ (Eq. 9,10).[28]

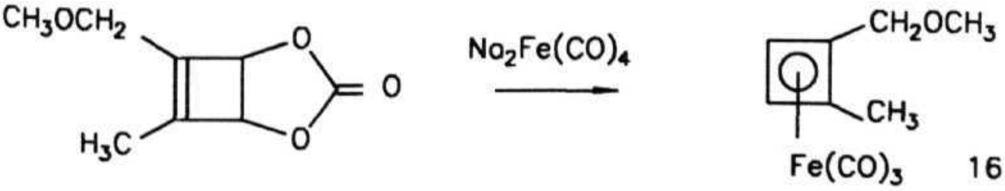


14 — (9)

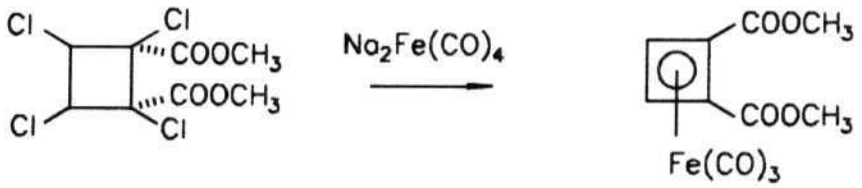


15 — (10)

This reagent has been found to be one of the most convenient reagent for the synthesis of cyclobutadiene complexes 16 and 17 for mechanistic and synthetic studies (Eq. 11,12).[29,30]



16 — (11)



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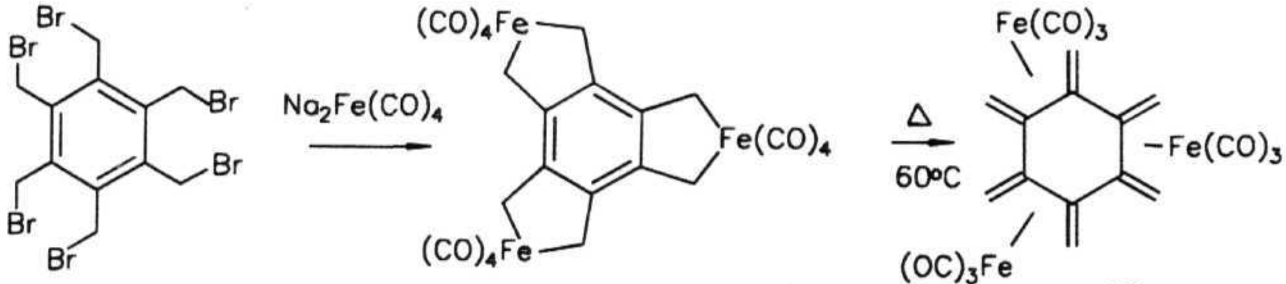
— (12)

It is also useful in the synthesis of a series of theoretically interesting complexes of iron such as 18 (Scheme. 6).[31,32]

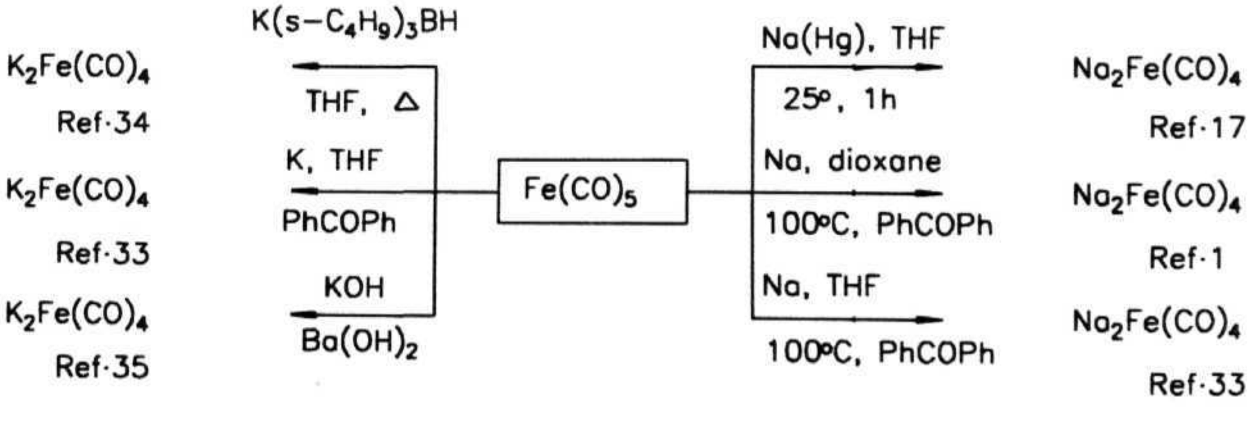
Scheme 6.



18

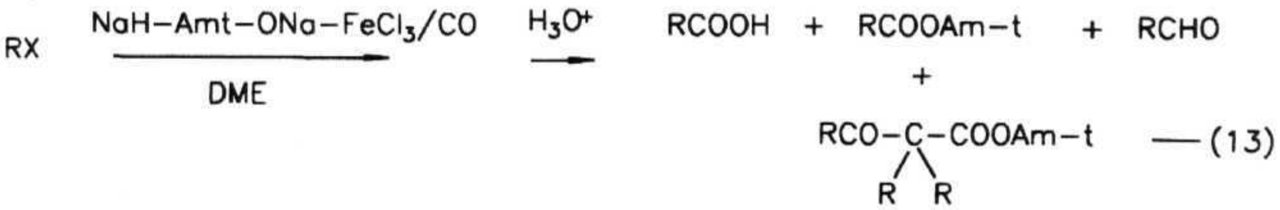
This useful reagent can be prepared in several ways (Chart 1).

Chart 1.



However, it appeared that this reagent is not widely applied by main stream organic chemists. Presumably, the difficulty in the preparation and handling of this reagent, made it not very much attractive for synthetic applications. Unlike $Na_2Fe(CO)_4$, $K_2Fe(CO)_4$ is not spontaneously flammable in air, though $K_2Fe(CO)_4$ has not been used as extensively as $Na_2Fe(CO)_4$.

Sometime back a project was undertaken in this laboratory to prepare such metal carbonyl reagents from non-metal carbonyl starting materials in the line of Caubere *et al* who have first obtained interesting reactive species (termed as FeCRACO) by the reduction of $FeCl_3$ by NaH-sodium tert-amyloxide combination under carbon monoxide atmosphere.[36] The FeCRACO, prepared in this way, has been used for carbonylation of primary, secondary and tertiary alkyl halides at atmospheric pressure of CO (Eq. 13>.[37]



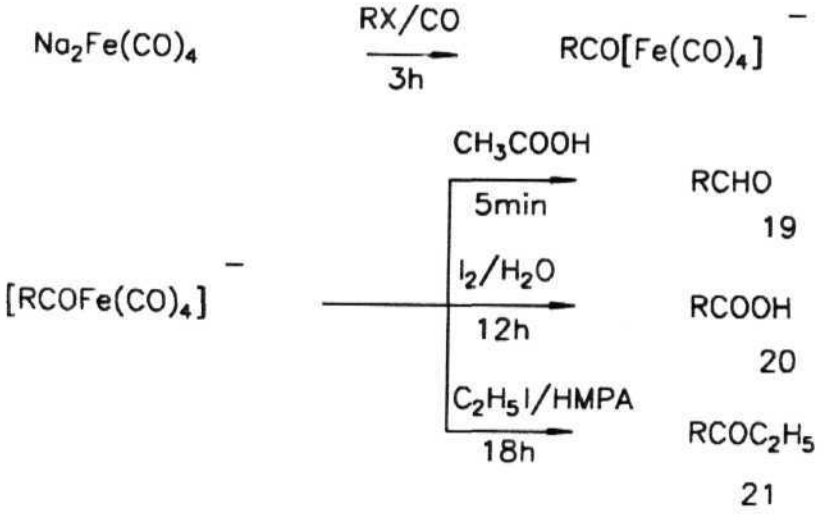
$$RX \xrightarrow[DME]{NaH-Amt-ONa-FeCl_3/CO} \xrightarrow{H_3O^+} RCOOH + RCOOAm\text{-}t + RCHO + RCO\text{-}C(R)(R)\text{-}COOAm\text{-}t \quad (13)$$

It was observed in this laboratory that $NaBH_4$ and MgH_2 reduce $FeCl_3$ into neutral iron carbonyl species.[38] It was also found that $Fe(CO)_4^{-2}$ reagent can be readily prepared by the reduction of $FeCl_3$ with sodium naphthalenide at atmospheric pressure of carbon monoxide (Eq. 14).[39]

$$FeCl_3 + Na(C_{10}H_8) \xrightarrow[25^\circ C,\ 3h]{CO} \xrightarrow[25^\circ C,\ 4h]{Na} Na_2Fe(CO)_4 \quad (14)$$

The formation of the $^{2-}Fe(CO)_4$ reagent in situ is further illustrated by the reaction with alkyl halides to give aldehydes 19, acids 20, and ketones 21 (Scheme 7).[39]

Scheme 7.

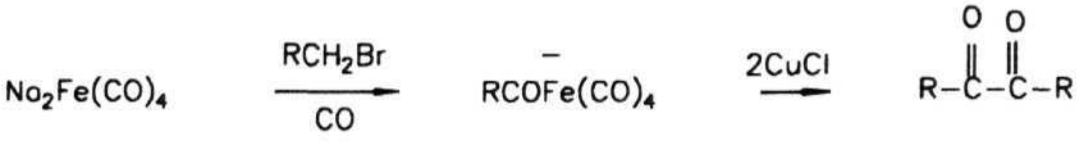


It is well known that reactive low valent metal **carbonyls** can be prepared by reducing transition metal salts with alkali metal naphthalenide in THF.[40] For example, sodium naphthalenide reduces $Cr(CO)_6$ to $Na_2Cr(CO)_5$ in THF.[41] It was thought that the $Na_2Fe(CO)_4$ reagent could be prepared by analogous reduction of $Fe(CO)_5$.[39] Eventually, a practical method employing $Fe(CO)_5$, the least expensive iron carbonyl and metallic sodium using an electron carrier, such as naphthalene in THF solvent has been developed (Eq. 15).[39]

$$Fe(CO)_5 \ + \ Na \xrightarrow[\text{THF, 1h, rt}]{\text{naphthalene}} Na_2Fe(CO)_4 \qquad —(15)$$

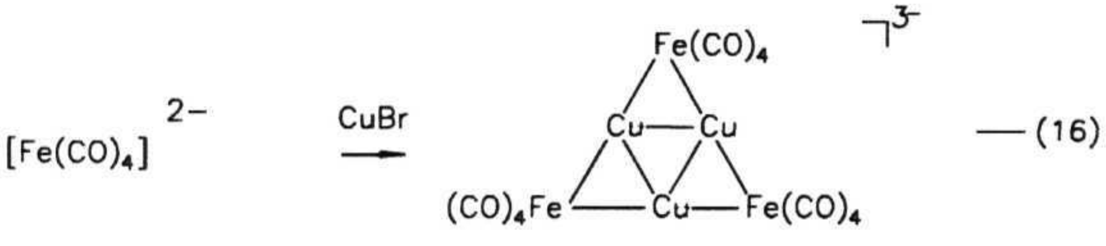
Recently, it was observed in this laboratory that the $Na_2Fe(CO)_4$ is useful for converting alkyl bromides into **1,2-diketone** 22 on treatment with CuCl under carbon monoxide atmosphere (Scheme 8).

Scheme 8.



22

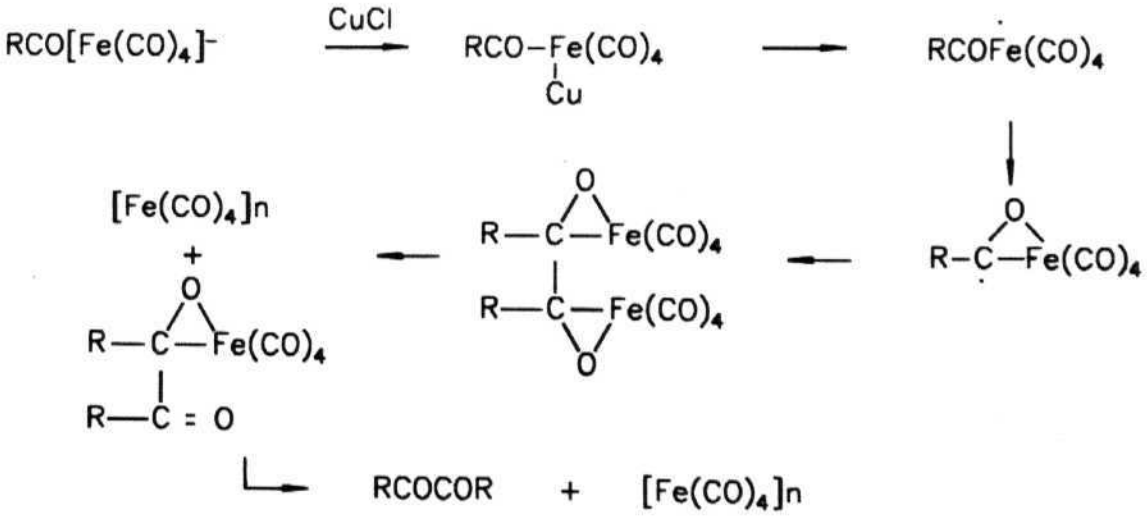
It has been reported that $[Fe(CO)_4]^{2-}$ reacts with CuCl or CuBr to give the metal cluster 23, $Na_3[Cu_3Fe_3(CO)_{12}]$ which contain Fe–Cu bonds (Eq. 16).[43]



23

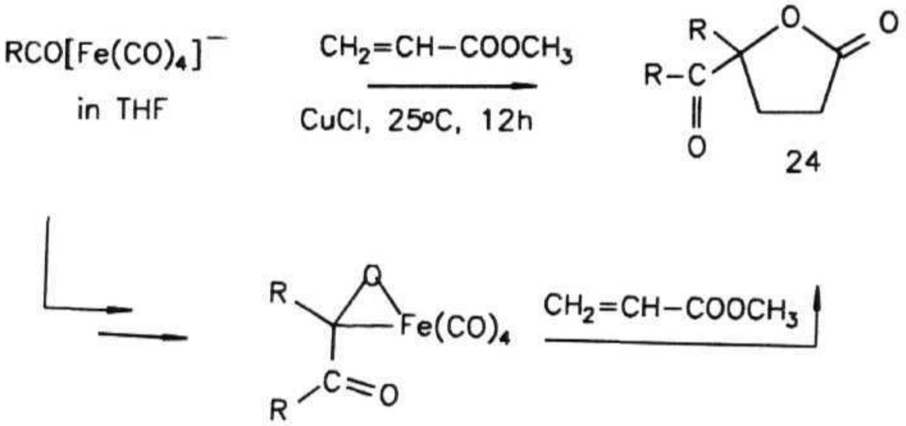
It was thought that a similar reaction would take place in the reaction of $RCO[Fe(CO)_4]^-$ with CuCl. Hence, a tentative mechanism of the 1,2-diketone formation has been visualized considering the intermediacy of species containing Fe-Cu bonds in the oxidation of the $RCO\overset{-}{F}e(CO)_4$ species by the CuCl to give the corresponding $RCO\dot{F}e(CO)_4$ species (Scheme 9).[44]

Scheme 9.



It was also found that the $RCO[Fe(CO)_4]^-$ reagent prepared in this way on reaction with methyl acrylate followed by CuCl treatment gives acyl lactones 24 (Scheme 10).[44] It was thought that the acyl lactone could have formed through the reaction of the acrylate with the corresponding η^2-$Fe(CO)_4$ complex.

Scheme 10.



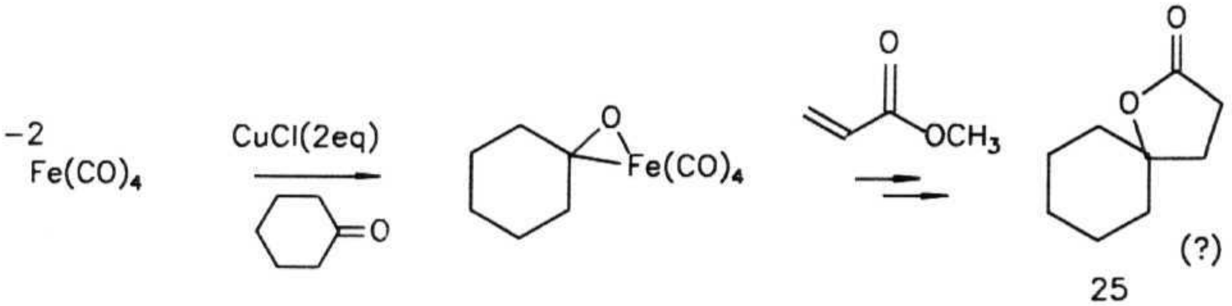
We have undertaken this research work to investigate the reactivity of the species that would be formed in the reaction of $^{-2}Fe(CO)_4$ with CuCl with organic substrates.

1.2. Results and Discussion:

1.2.1: Construction of cyclohexyl ring at the α-methylene moieties of ketones, esters, lactones and nitriles using $Na_2Fe(CO)_4$:

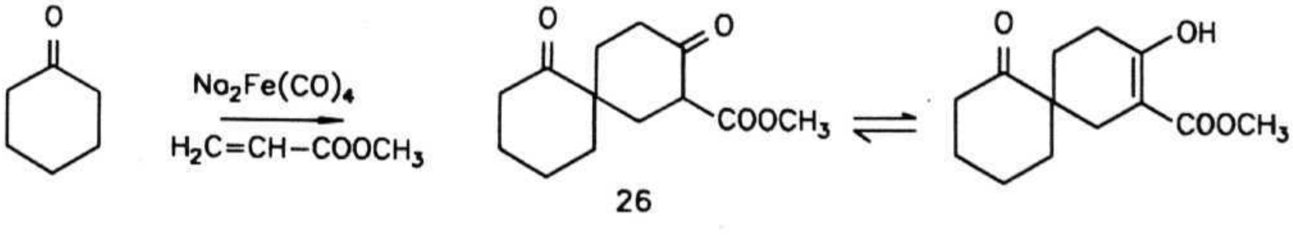
It was thought that the oxidation of $^{-2}Fe(CO)_4$ **with** CuCl in the presence of ketones would result in the formation of the corresponding q^2 complexes which could then react with methyl acrylate to *give* the corresponding acyl lactone 25 after work up in the same way as described previously (Scheme 11).

Scheme 11.



However, when the reaction was carried by the addition of CuCl to a mixture containing $^{-2}Fe(CO)_4$ and cyclohexanone followed by methyl acrylate treatment, the product obtained was the β-ketoester 26 (Scheme 12).[45] The reaction also takes place in the absence of CuCl.

Scheme **12.**



It was found that the transformation is a general one and several other ketones, esters, lactones and nitriles can be converted to the corresponding cyclic products (Table 1). Reactions of $Na_2Fe(CO)_4$ (2 eq) with one equivalent of ketones, esters, lactones and nitriles followed by with methyl acrylate (2 eq) treatment gives the corresponding cyclic β-keto esters (Table 1).

The transformation can be rationalized by the sequence of reactions involving double Michael additions[46] followed by Dieckmann cyclization[47] (Scheme 13).

Scheme 13.

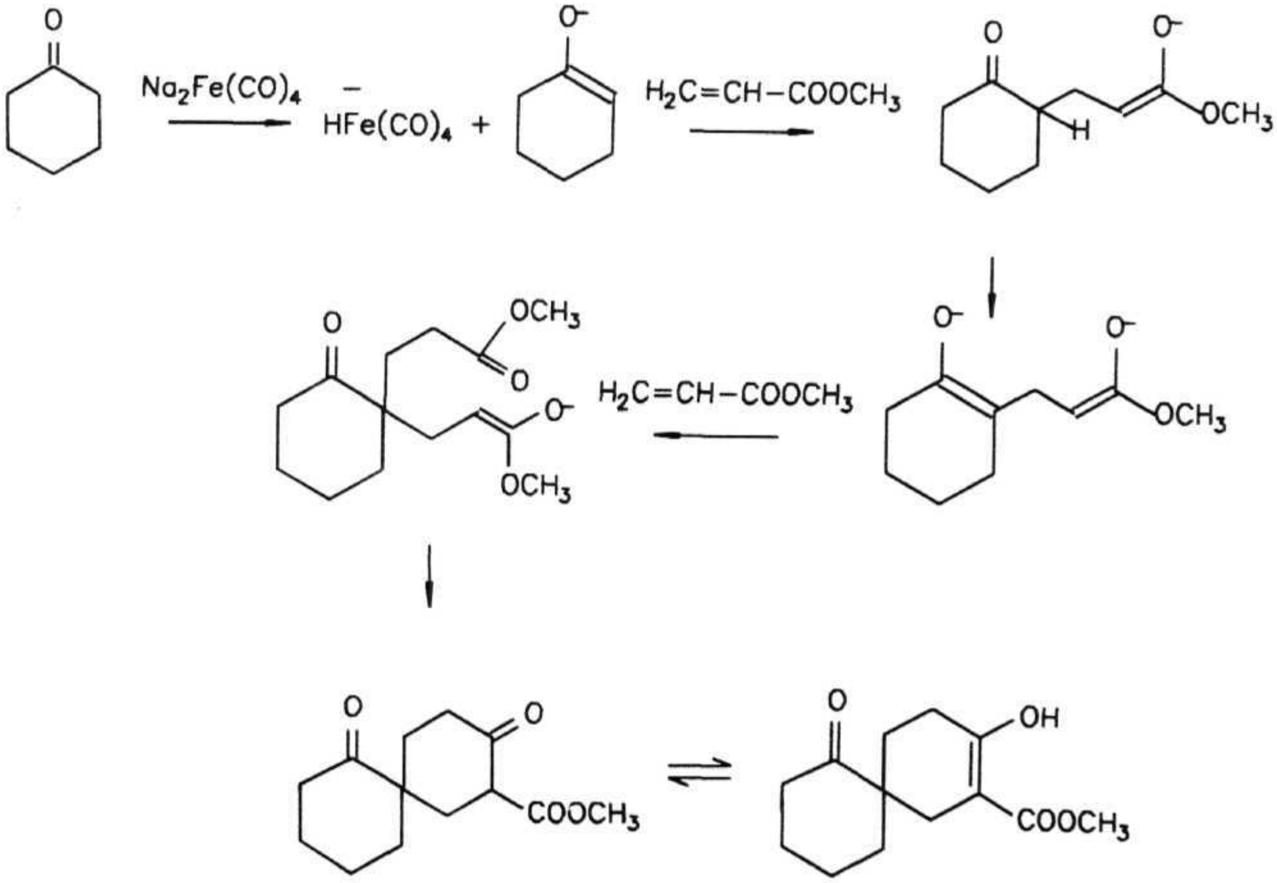
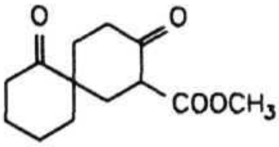
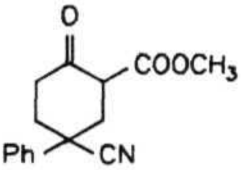
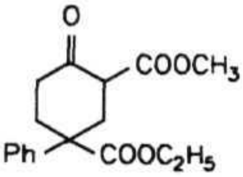
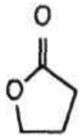
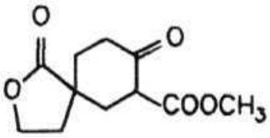
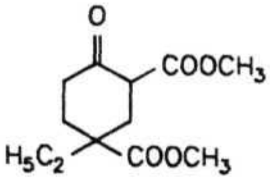
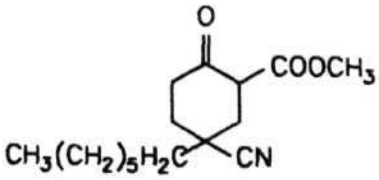


Table 1: Synthesis of cyclic β-keto **esters from active methylene compounds and methyl acrylate using** $Na_2Fe(CO)_4$.

S·No	Substrate	Product [a]	Yield(%) [b]
1·			53
2·	$PhCH_2CN$		62
3·	$PhCH_2COOC_2H_5$		59
4·			55
5·	$CH_3(CH_2)_2COOCH_3$		48
6·	$CH_3(CH_2)_7CN$		49

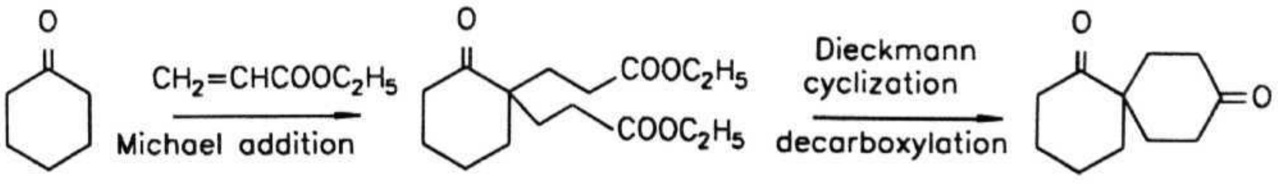
a) The products were identified by the spectral data (IR, ^1H and ^{13}C NMR), Mass spectral data (ED were obtained for products in entries (1, 2, 3 and 4). For entries (2, 3 and 4) elemental analyses were also obtained (see experimental section).

b) Yields of the products were calculated based on the amount of substrate (ketones, esters. nitriles and lactones) used.

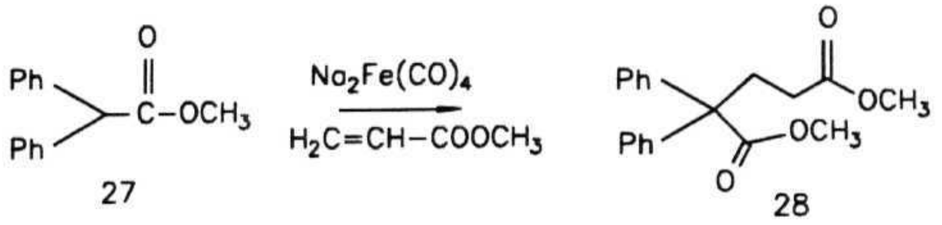
The reactions were carried out using 10 mmol of the organic substrate, 20 mmol of $Na_2Fe(CO)_4$ and 20 mmol of methyl acrylate in THF (50 ml), to obtain the cyclic β-keto esters in moderate to good yields (48-62%). When the reaction was carried out using 40 mmol of $Na_2Fe(CO)_4$, higher yields (~15% more) were obtained.

The cyclic product obtained in the above reaction of cyclohexanone and acrylate has been previously prepared through a two step sequence for utilization in the synthesis of some biologically active compounds (Scheme 14>.[48]

Scheme 14.



We have also observed that the reaction in the case of an α-methine derivative 27 gives the corresponding alkylated product 28 as expected (Eq. 17).

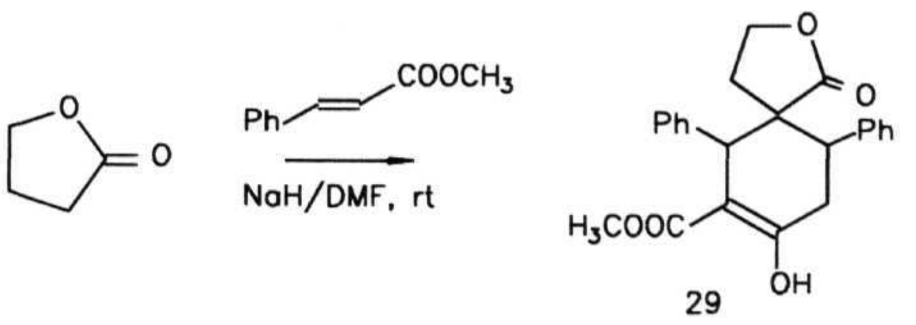


— (17)

Also, it was found that the addition of methyl acrylate followed by the organic substrates resulted in the formation of some unidentified polymeric compounds. In the control experiment without using "$Fe(CO)_4$", the starting materials were recovered along with small amount of the (<5%) of β-keto ester.

1.2.2. Construction of cyclohexyl ring at the α-methylene moieties of ketones, esters, lactones and nitriles using $NaOCH_3$:

If the transformation outlined in the Scheme 12 goes through the enolate intermediate (Scheme 13), then there is a possibility to achieve this using other more readily accessible bases such as alkoxides. Surprisingly, to our knowledge, no such general transformation has been reported. However, it has been briefly mentioned that the lactone enolate derived from butyrolactone on treatment with methyl cinnamate yields the corresponding cyclic β-keto ester 29 in 35–55% yields (Eq. 18).[49]



— (18)

We have observed that sodium methoxide readily reacts with ketones, esters, lactones, nitriles in the presence of methyl acrylate to give the same product with a cyclohexyl ring constructed on the active methylene moiety. Reaction of $NaOCH_3$ (2 eq) with 1 eq of ketones, esters, lactones and nitriles followed by treatment with methyl acrylate (2 eq) leads to the formation of cyclic β-keto esters in 40-56% yield. Again, the transformation is a general one and the cyclic products were obtained in 40-56% yields, when sodium methoxide is utilized in the place of $Na_2Fe(CO)_4$ (Table 2).

There was no improvement in yields when the reaction was carried out using excess sodium methoxide. Also, the reaction of sodium methoxide with benzyl cyanide and methyl crotonate gave only the mono alkylated Michael addition product 30 and no cyclic product was formed (Eq. 19).

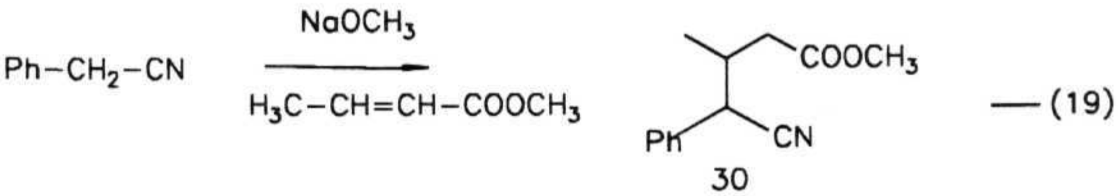
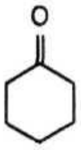
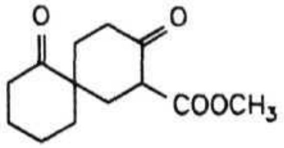
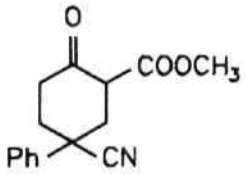
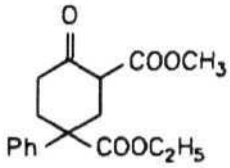
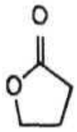
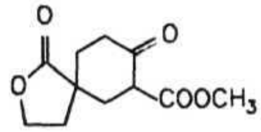
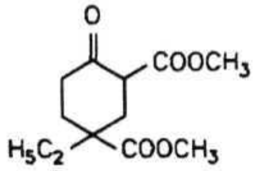
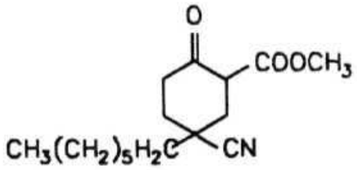
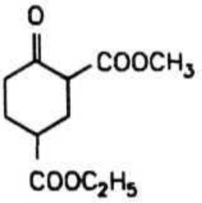
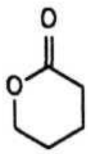
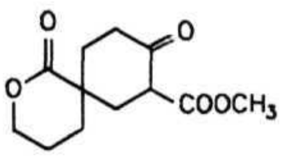
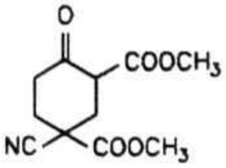


Table 2: Synthesis of cyclic β-keto esters from active inethylene compounds and methyl acrylate using sodium methoxide.

S·No	Substrate	Product[a]	Yield(%)[b]
1·			42
2·	$PhCH_2CN$		56
3·	$PhCH_2COOC_2H_5$		52
4·			50
5·	$CH_3(CH_2)_2COOCH_3$		41
6·	$CH_3(CH_2)_7CN$		45
7·	$CH_3COOC_2H_5$		40
8·			48

...contd.

...Table 2 contd.

9.	$NCCH_2COOCH_3$		**54**

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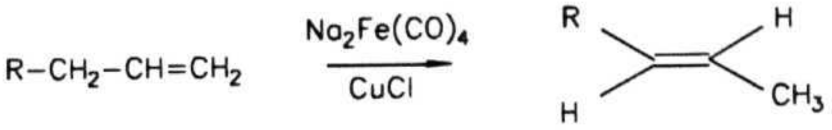
a) The products were identified by the spectral data (IR, ^{1}H and ^{13}C NMR). Mass spectral data (ED were obtained for products in entries (1, 2, 3, 4). For entires (2, 3 and 4) elemental analyses were also obtained.

b) Yields of the products were calculated based on the amount of substrate (ketones, esters, nitriles and lactones) used.

1.2.3: Isomerization of 1-alkenes using the $Na_2Fe(CO)_4/CuCl$ reagent system:

The $:Fe(CO)_4$ species is isolobal with carbene. Such species have been previously prepared by the photolysis/thermolysis of $Fe(CO)_5$ or $Fe_2(CO)_9$ in the presence of substrates which can react with these species.[12] Also, oxidation of $Fe(CO)_5$ with $R_3N^+\text{-}O^-$ results in the formation of $:Fe(CO)_4$ reagent.[12] It was thought that these $:Fe(CO)_4$ species should be formed in the oxidation of $^{-2}Fe(CO)_4$ with CuCl (2 eq) similar to the formation of $\overset{\bullet}{R}COFe(CO)_4$ in the reaction of $RCO\overset{-}{F}e(CO)_4$ with CuCl. We have decided to examine this by performing the reaction in the presence of olefins which can also complex with such species.

It was found that the species produced in this way isomerizes certain alkenes (Eq. 20).

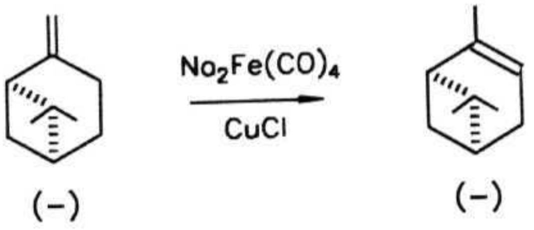


— (20)

The reagent prepared using $Na_2Fe(CO)_4$ (10 mmol) and CuCl (20 mmol) in THF (60 ml) isomerizes 1-decene (10 mmol) to trans 2-decene in 12h at room temperature. The ^{13}C NMR spectrum of the product revealed the absence of 1-decene and other isomers of decene. It is interesting to note that the isomerization of 1-alkene using the $Fe(CO)_5$ at high temperature and $NaHFe(CO)_4$ leads to mixture of 2-alkenes and 3-alkenes.[13,50,51]

Clearly, the present reagent is more selective. The selectivities of the $[Fe(CO)_4]^{2-}$/CuCl reagent system is further illustrated by the isomerization of certain other alkenes (Table 3) in good yields (76-87%).

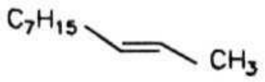
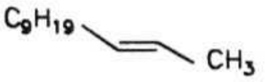
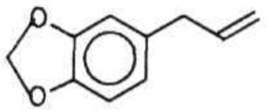
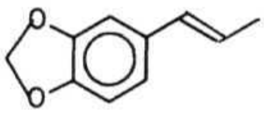
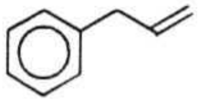
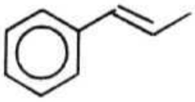
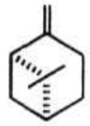
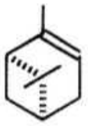
In the course of efforts to optimize the conditions for this transformation, we have observed that when more than 10 mmol of an olefinic substrate (eg., safrole) was used, equivalent amount of starting material remained unreacted under these conditions. Hence, the isomerization is stoichiometric. Isomerization of (-)-β-pinene to (-) α-pinene 31 reveals that there is no skeletal rearrangement in this case (Eq. 21).



31

—(21)

Table 3: Isomerization of olefins using $Na_2Fe(CO)_4/CuCl$ reagent system:

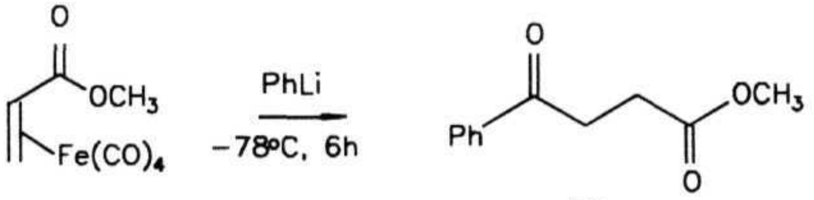
Entry No	1–Alkene [a]	2–Alkene	Yield [b]
1.	$C_8H_{17}-CH=CH_2$		83
2.	$C_{10}H_{21}-CH=CH_2$		80
3.			87
4.			76
5.	 (±)	 (±)	79
6.	 (−)	 (−)	78

a. All reactions were carried out for 12h at 25 °C under N_2 atmosphere with $Na_2Fe(CO)_4$ (10 mmol) 1-alkene (10 mmol) and CuCl (20 mmol) in THF (60 ml) and oxidized with CAN (10 mmol).

b. Yields are of products isolated by column chromatography on silica gel. The products were identified by spectral data (IR, ^1H and ^{13}C NMR) and comparison with data of authentic samples.

1,5-Cyclooctadiene and 4-vinylcyclohexene failed to undergo isomerization under these reaction conditions. Furthermore, there was no isomerization of 1-decene when the reaction was carried out in the absence of CuCl. It was also found that the isomerization does not take place when the reaction was carried out by the addition of CuCl followed by 1-decene. This indicates that the reactive species is not stable and the olefin must be present when the reactive iron carbonyl species is generated.

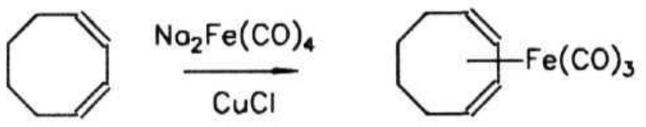
It has been reported that $Na_2Fe(CO)_4$ reacts with CuBr to give clusters containing Fe-Cu bonds.[43] Infrared spectrum of the mixture prepared using $Na_2Fe(CO)_4$ (10 mmol) and CuCl (20 mmol) in THF under the present reaction conditions exhibits two strong broad bonds at 1970 cm^{-1} and 1870 cm^{-1}, similar to those reported for the cluster anions.[43] However, we have carried out further experiments to examine whether the reaction of $Na_2Fe(CO)_4$ with two equivalents of CuCl would give :$Fe(CO)_4$ unit which can be used for complexation with α,β-unsaturated carbonyl compounds. For example, it has been reported that the $Fe(CO)_4$ complex of methyl acrylate on reaction with phenyl lithium at -78 °C gives the product 32 in 67% yield (Eq. 22).[52]



32

— (22)

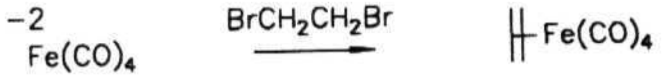
The $Na_2Fe(CO)_4/2CuCl$ combination failed to give a similar transformation on treatment with methyl acrylate followed by the addition of PhLi or PhMgBr at -78°C. However, addition of CuCl (2 eq) to $Na_2Fe(CO)_4$ (1 eq) in the presence of 1,3-cyclooctadiene and followed by stirring the reaction mixture for 12h at room temperature resulted in the formation of a small amount (<10%) of the corresponding diene-$Fe(CO)_3$ 33 complex (Eq. 23).



— (23)

1.2.4: Isomerization of 1-alkenes using the $Na_2Fe(CO)_4/BrCH_2CH_2Br$ system:

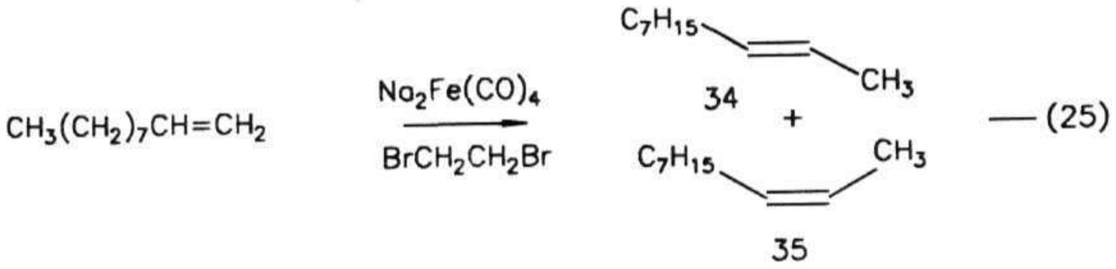
It was of interest to utilize the reagent such as 1,2-dibromoethane for reaction with $^{-2}Fe(CO)_4$ and compare the reactivity of the resulting complexes with alkenes (Eq. 24).



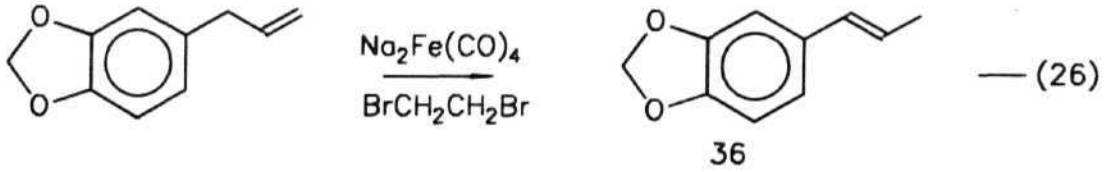
— (24)

Although, formation of this complex has been reported in the reaction of $TfO-CH_2CH_2-OTf$ with $^{-2}Fe(CO)_4$, the synthetic utility has not been examined.[53]

We have found that the reaction of the reagent prepared using $Na_2Fe(CO)_4/BrCH_2CH_2Br$ also isomerizes alkenes under mild conditions (Table 4). The reagent prepared using $Na_2Fe(CO)_4$ (10 mmol) and $BrCH_2CH_2Br$ (10 mmol) in THF (60 ml) isomerizes 1-decene (10 mmol) to a mixture of trans-and cis 2-decenes (34 and 35) in 12h at room temperature. The NMR data of the mixture indicate that the trans-2-decene is the major product (>80%) (Eq. 25).

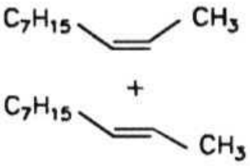
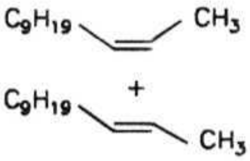
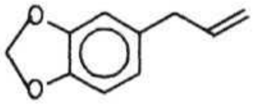
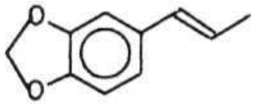
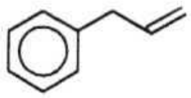
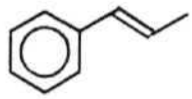
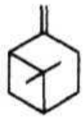


Whereas the reaction with 1-decene and 1-dodecene leads to a mixture of cis- and trans-2-alkenes, the results in the reaction with safrole, allyl benzene and β-pinene are the same (i.e., trans olefins) as those observed with the $Na_2Fe(CO)_4$/CuCl reagent system (Eq. 26).



Although both $Na_2Fe(CO)_4$/CuCl and $Na_2Fe(CO)_4/BrCH_2CH_2Br$ reagent systems give species that could isomerize certain alkenes, the reactivities are somewhat different. We have observed that $Na_2Fe(CO)_4/BrCH_2CH_2Br$ reagent combination also isomerizes only one equivalent of the alkenes and the alkenes should be present in the medium when the $BrCH_2CH_2Br$ is added to the ${}^{-2}Fe(CO)_4$ reagent. Also, retention of stereochemistry is illustrated

Table 4: Isomerization of alkenes using $Na_2Fe(CO)_4$ /$BrCH_2CH_2Br$system:

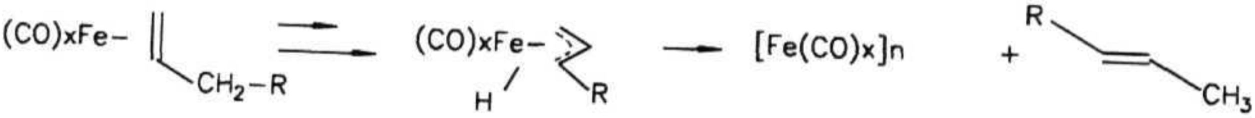
Entry No	1-Alkene [a]	2-Alkene	Yield(%) [b]
1.	$C_8H_{17}-CH=CH_2$		80
2.	$C_{10}H_{21}-CH=CH_2$		76
3.			81
4.			75
5.	 (±)	 (±)	78
6.	 (–)	 (–)	79

a. Reactions were carried out for 12h at 25 °C under N_2 atmosphere with $Na_2Fe(CO)_4$ (10 mmol), 1-alkene (10 mmol) and $BrCH_2CH_2Br$ (10 mmol) in THF (60 ml) and oxidized with CAN (10 mmol).

b. Yields are of products isolated by column chromatography on silica gel. The products were identified from spectral data (IR, ^1H and ^{13}C NMR) by comparison with data of authentic samples.

in the conversion of (−)-β-pinene to (−)-α-pinene. Again, 1,5-cyclooctadiene and 4-vinylcyclohexene were unaffected under these conditions. Presumably, these reagent combinations give reactive olefin complexes, which undergo isomerization (Scheme 15).

Scheme 15.

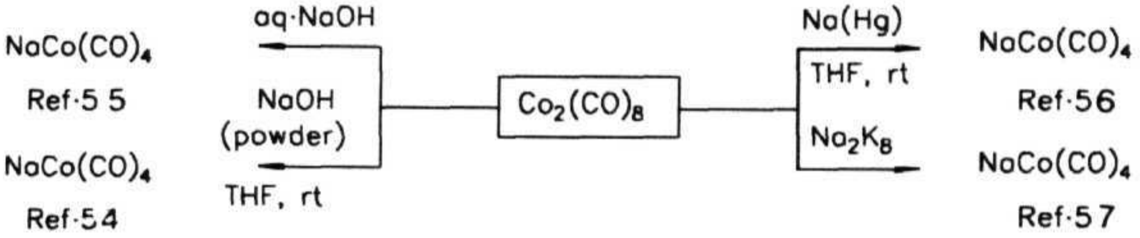


However, we do not have data at hand in support of the mechanism and intermediates involved.

1.2.5: Synthetic utility of the $^{-}Co(CO)_4/CuX$ reagent system.

The $NaCo(CO)_4$ can be prepared in several ways as outlined in Scheme 16.

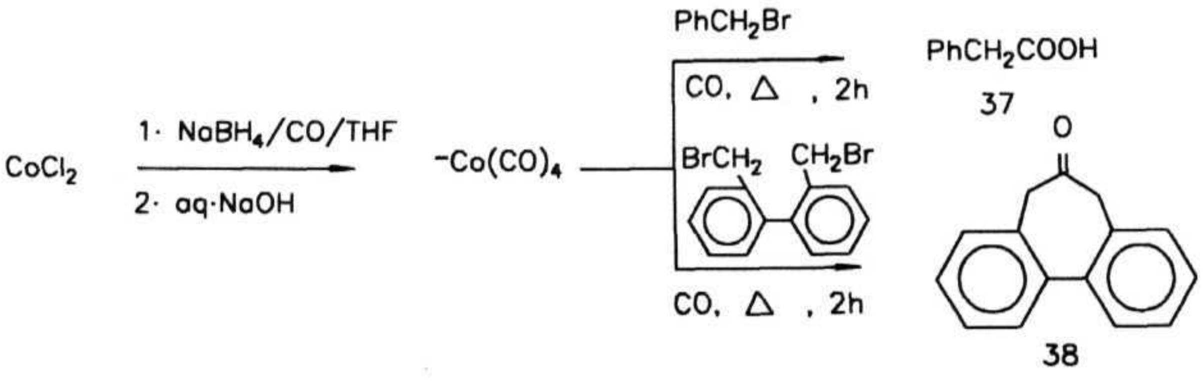
Scheme 16.



Again, the first serious efforts in the synthesis of the cobaltcarbonyl species in situ for utilization have been made by Caubere and co-workers.[58-72] In a series of reports, these authors described that the complex reducing agents (CRA), NaH-Amt-ONa-Co(OAC)$_2$ in the presence of carbon monoxide, can generate CoCRACO species containing NaCo(CO)$_4$ species at room temperature and atmospheric pressure.[60-70] The CoCRACO combinations have been utilized for several synthetic applications.[71,72]

It was observed in this laboratory that the reagent prepared in situ in THF under carbon monoxide atmosphere using CoCl$_2$ and NaBH$_4$ system on treatment with aq. NaOH gives $[Co(CO)_4]^-$.[73] The reagent prepared in this way has been utilized for the conversion of benzyl halides into the corresponding acids 37 and cyclic ketones 38 (Scheme. 17).[74,75]

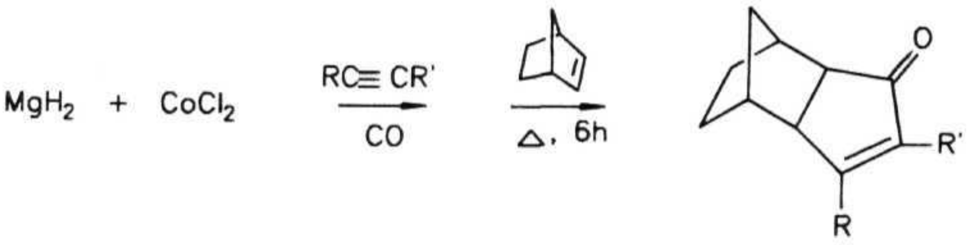
Scheme 17.



However, the mixture prepared in this way, before the addition of aq. NaOH, also contains >B–H species which hydroborates alkenes. Moreover, it was thought that the aqueous medium may not be suitable, since many organometallic reactions need dry conditions.

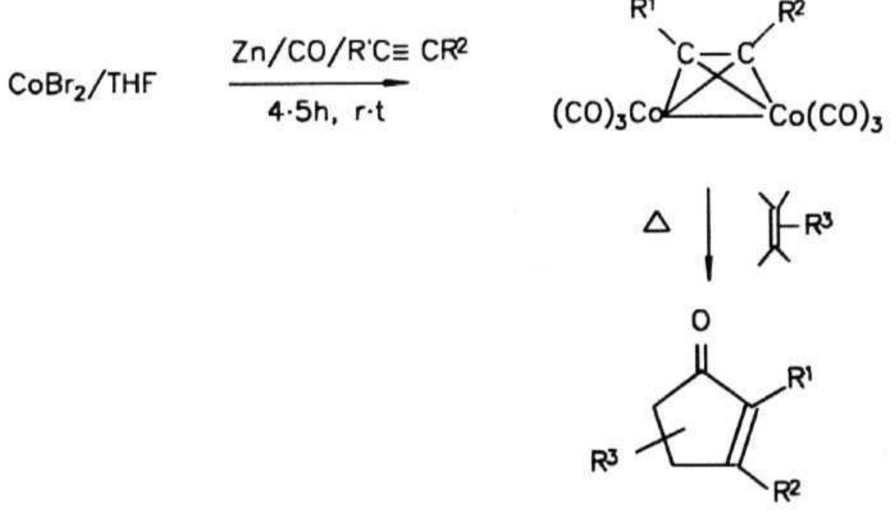
It was also found in this laboratory that the reaction of MgH_2 with $CoCl_2$ at 0°C under carbon monoxide gives $Co_2(CO)_8$ which undergoes the Pauson-Khand reaction with alkynes and norbornene (Scheme 18).[76]

Scheme 18.



It was also observed that anhydrous $CoBr_2$ can be reduced by Zn to give the corresponding alkyne complexes in THF in the presence of alkynes and carbon monoxide. The alkyne complexes prepared in situ in this way undergo the Pauson-Khand cyclization with representative alkenes (Scheme 19).[77]

Scheme 19.



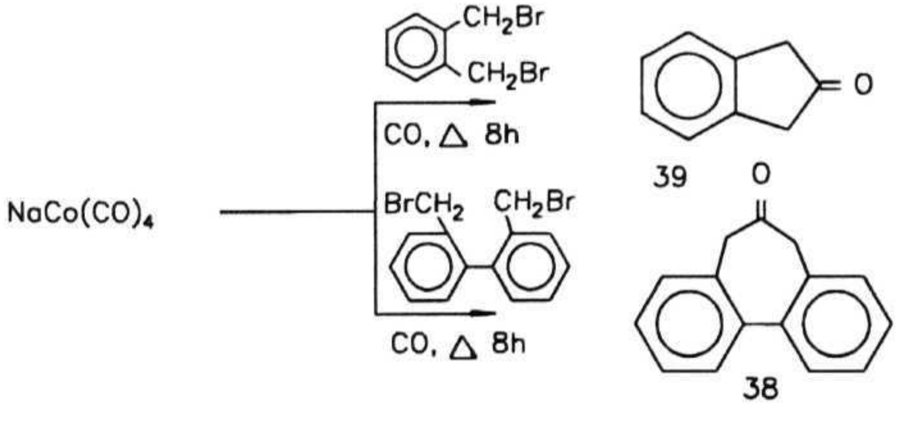
The formation of the alkyne complexes here is not entirely unexpected since it has been reported that CoI_2 on reduction with Zn in t-Bu OH/toluene under CO for 2 hrs gives the corresponding $Co_2(CO)_8$ in 38% yield.[78]

It was envisaged that the reduction of $CoCl_2$ or $CoBr_2$ by sodium naphthalenide in THF under carbon monoxide atmosphere would give $NaCo(CO)_4$ as it was observed with $FeCl_2$. Indeed, this was observed (Eq. 27).[76]

$$CoBr_2/CoCl_2 \xrightarrow[\text{THF, CO, 3h, rt}]{\text{Na/naphthalene}} NaCo(CO)_4 \quad \text{— (27)}$$

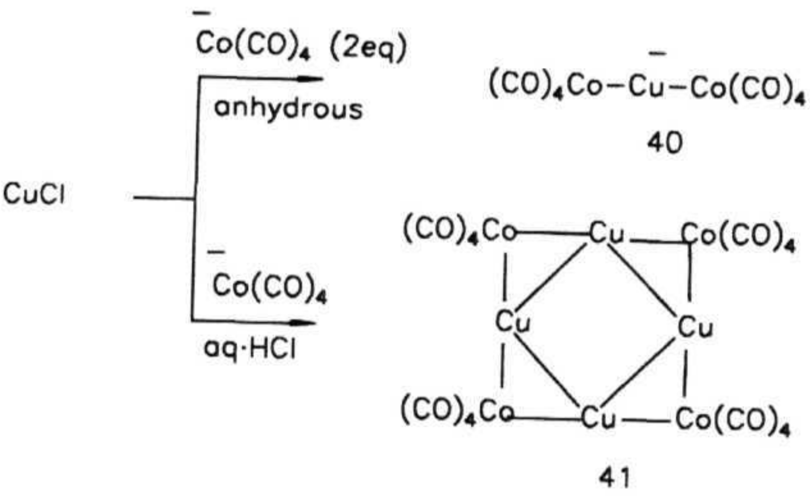
The formation of $NaCo(CO)_4$ was further confirmed by performing the carbonylative cyclization of certain benzyl halides (Scheme 20).[76]

Scheme 20.



It has been reported that the $NaCo(CO)_4$ reagent gives $(CuCo(CO)_4]_n$ complex 40 and 41 on treatment with CuCl under certain conditions (Scheme 21).[79]

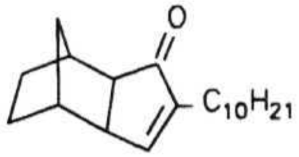
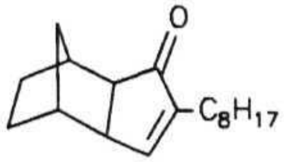
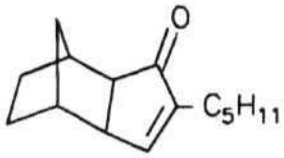
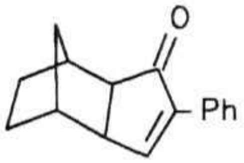
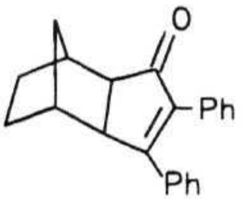
Scheme 21.



It was of interest to examine the reaction of such species containing Cu-Co bonds with alkenes and alkynes. We have observed that the alkenes such as 1-decene do not react with the species produced by the reaction of $NaCo(CO)_4$ with CuCl. However, it was observed that heating of a mixture of $NaCo(CO)_4$, CuBr and an alkyne with norbornene gives the corresponding cyclopentenone derivatives in moderate to good yields (Table 5).[80] Most probably, this transformation would go through the formation of the alkyne-$Co_2(CO)_6$ complex followed by Pauson-Khand reaction with norbornene.

The reactions were carried out using a mixture of anhydrous $CoBr_2$ (10 mmol), sodium (30 mmol), naphthalene (10 mmol), alkyne (5 mmol) and CuBr (10 mmol) in THF (60 ml) for 6h while bubbling CO at room temperature. Norbornene (10 mmol) was added and the contents were stirred further at 65°C for 4h (note the change in time in the case of diphenylacetylene, Table 5). After work up, the Pauson-Khand cyclopentenone derivatives 42 (Scheme 22) were isolated in 53-84% yield.

Table. 5: Reaction of (alkyne)$Co_2(CO)_6$ complexes prepared in THF using $CoBr_2$/ Na/naphthalene/Cu Br with norbornene.[a]

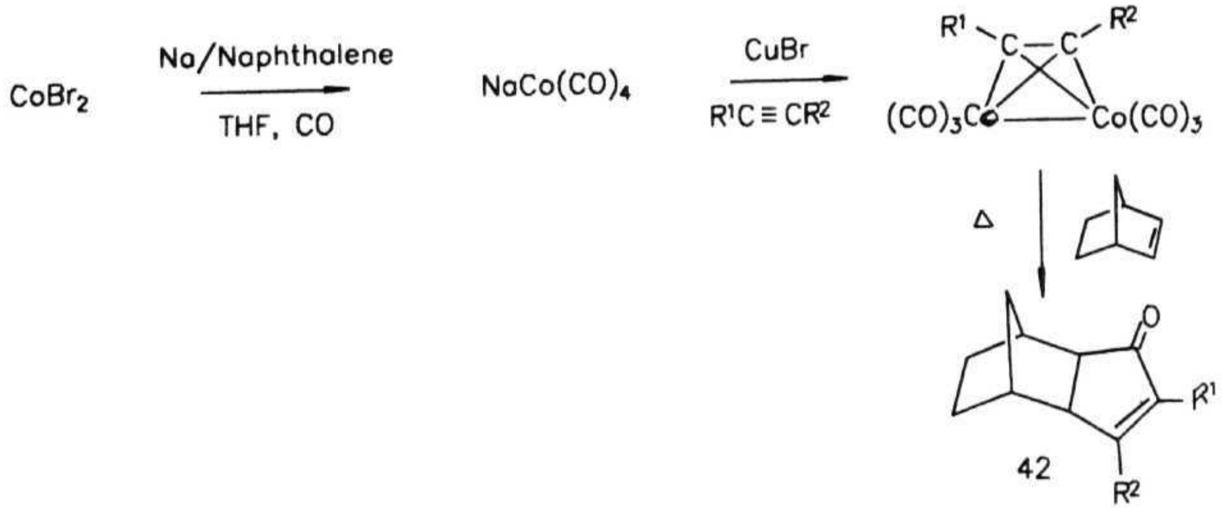
S·No	Alkyne	Time	Product [b]	Yield(%) [c]
1·	n-$C_{10}H_{21}C\equiv CH$	4h		76
2·	n-$C_8H_{17}C\equiv CH$	4h		65
3·	n-$C_5H_{11}C\equiv CH$	4h		62
4·	$PhC\equiv CH$	4h		84
5·	$PhC\equiv CPh$	12h		53

a. All reactions were carried out using $CoBr_2$ (10 mmol), Na (30 mmol), naphthalene (10 mmol), alkyne (5 mmol), norbornene (10 mmol) and CuBr (10 mmol).

b. All products were identified by spectral data (IR, ^{1}H and ^{13}C NMR) and comparison with the data reported in literature.

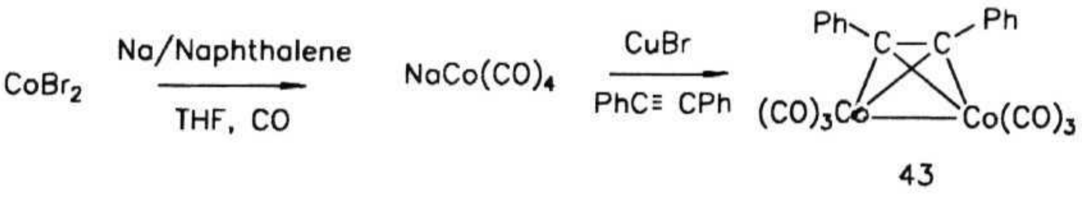
c. Yields are of isolated products, calculated based on the **amounts** of alkynes utilized.

Scheme 22.



Also, it was found that the alkyne complexes can be prepared at 25 ℃. For **example,** when we carried out the reaction in the presence of diphenylacetylene (5 **mmol**) for 6h at 25°C, after work up, PhCsCPh $Co_2(CO)_6$ complex 43 (Scheme 23) was isolated in 40% yield.

Scheme 23.

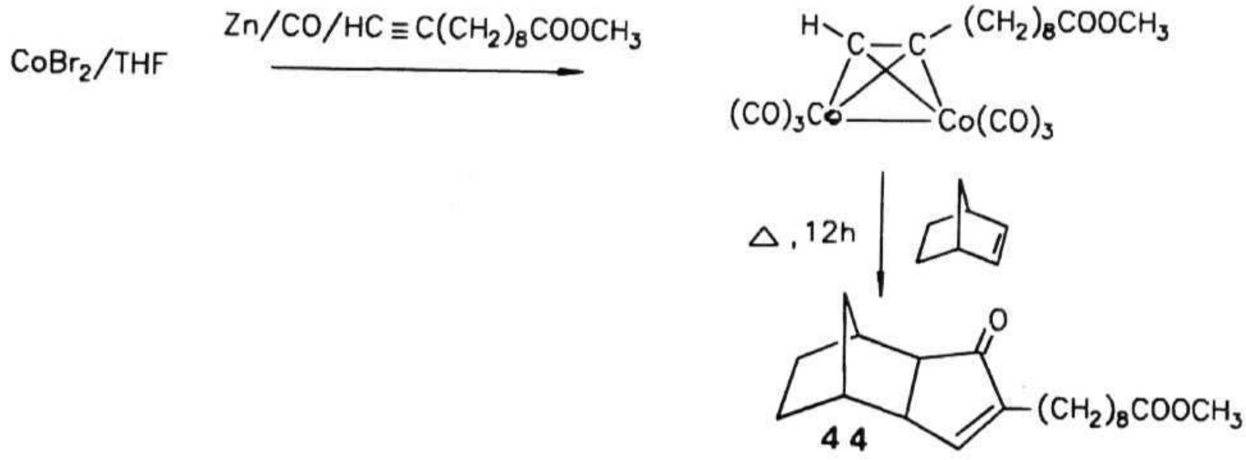


The yields are somewhat less compared to those obtained in the previous method utilizing metallic **zinc** for reduction in some cases. It was also found that this reagent system is more complicated. For example the reaction with methyl **1-undecynoate** and norbornene gave a complex mixture of products. Similar reaction using 1-decyne and norbornene in the presence of ester (1 eq) also gave a complex mixture of products. Presumably, the $NaCo(CO)_4/CuCl$ system still has species which react with ester moiety to give condensation reaction similar to that observed previously with the $Na_2Fe(CO)_4/CuCl$ combination.

In order to compare the results obtained using the $NaCo(CO)_4/CuCl/Alkyne$ combination with the $CoBr_2/Zn/CO/alkyne$ system, we have carried out the Pauson-Khand reaction of the methyl 1-undecynoate with norbornene.

The reaction was carried out using 10 mmol of $CoBr_2$ Zn dust (11 mmol) and 5mmol of methyl undecynoate in 60 ml THF at room temperature for 3h. Norbornene (10 mmol) was added and the mixture was stirred at 65 °C for 12h to obtain the corresponding cyclopentenone derivative 44 in 91% yield (Scheme 24).

Scheme 24.



Clearly, the $CoBr_2/Zn/CO/alkyne$ combination is more suitable for use in Pauson-Khand reaction and hence we did not pursue the studies of the reagent prepared using $CuCl/\overline{\ }Co(CO)_4$ combination further.

1.2.6. Conclusion:

The $Na_2Fe(CO)_4$ reagent prepared in situ using $Fe(CO)_5$/sodium naphthalenide system was utilized for the construction of cyclohexyl ring at the α-methylene moieties of carbonyl and nitrile substrates in moderate to good yields. The simple, general one pot method for the construction of cyclohexyl ring at the α-methylene moeities of ketones, lactones, esters and nitriles has been also acheived using $NaOCH_3$ in the place of $Na_2Fe(CO)_4$.

The $Na_2Fe(CO)_4$/CuCl combination was found to be useful for the isomerization of 1-alkenes to obtain trans-2-alkenes in good yields. The procedure developed utilizing the $Na_2Fe(CO)_4/BrCH_2CH_2Br$ combination for the isomerization under mild conditions should be also useful. The results also indicate that the reaction of $Na_2Fe(CO)_4$ with CuCl or 1,2-dibromoethane provides easy access to organometallic reagents with interesting reactivities.

Simple, convenient procedures have been developed for the synthesis of alkyne-$Co_2(CO)_6$ complexes for application in Pauson-Khand cyclopentenone synthesis. The procedure utilizing metallic zinc for the reduction of $CoBr_2$ has been found to give cleaner reaction. The reagent prepared in this way tolerate the presence of an ester group in the alkyne where as the method utilizing the sodium/naphthalene/CuBr combination leads to complications. In addition to use in Pauson-Khand cyclopentenone synthesis, the alkyne complexes are also useful in masking the reactivity of alkynes and also in other useful transformations (e.g., Nicholas reaction).[81] Accordingly, the synthesis of these complexes, utilizing readily accessible reagents, should make these metal carbonyls more attractive for synthetic applications.

1.3. Experimental Section

1.3.1. 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 FT5300 with polystyrene as reference. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL-FX-100 and Bruker-AC-200 spectrometers with chloroform-d as a solvent and TMS as reference (6 =0 ppm). Elemental analyses were performed on a Perkin-Elmer elemental analyzer model-240 C. Gas chromatographic analyses were carried out on a Chemito-2 instrument equipped with a flame ionisation detector on an SE-30 or carbowax column using nitrogen as carrier gas. Analytical thin layer chromatographic tests were carried out on glass plates (3 x 10 cm) coated with 250 mesh Acme's silica gel G or G_{254} containing 13% calcium Sulfate as binder. The spots were visualized by short exposure to iodine vapor or UV light. Column chromatography was carried out using Acme's silica gel (100-200 mesh).

All glassware was predried at 140°C in an air oven for 4h, assembled hot and cooled under a stream of dry nitrogen. Unless, otherwise mentioned, all the operations and transformations of reagents were carried out using standard syringe, septum techniques recommended for handling air sensitive organometallic compounds.[82] Reagents prepared *in situ* in solvents were transformed using 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 a Buchi-EL-rotary evaporator. All yields reported are isolated yields of materials judged homogeneous by TLC, IR and NMR spectroscopy.

Ironpentacarbonyl supplied by Fluka, Switzerland was used. Commercially available ketones, esters, nitriles and lactones were used in the experiments. Methyl acry late and methyl crotonate (Fluka) were distilled before use. Naphthalene supplied by LOBA-chemie, India was sublimed before use. The olefins utilized were commercial samples supplied by Fluka, Switzerland and 1,2-dibromoethane BDH, England were distilled before use. CuCl, CuBr (Fluka) were 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 3 hours.

1-Decyne, phenylacetylene and diphenylacetylene were prepared following a reported procedure.[83] 1-Heptyne utilized was supplied by Fluka, Switzerland. Activated zinc dust was prepared by treating commercial zinc dust with 1% H_2SO_4 followed by washing succesively with H_2O and acetone and then drying at 150°C for 4h under vacuum.[84] Anhydrous $CoBr_2$ was prepared from the hydrated complex. It was kept in the air oven at 150°C for 5-6h, further dried at 150°C for 4h under vacuum and was kept under nitrogen in a desiccator.

Carbon monoxide was generated by drop wise addition of formic acid 98% to con.H_2SO_4 96% at 90^{o} C using an apparatus recommended for utilization in the carbonylation of organoboranes.[82]

1.3.2. 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 (50ml)], cyclohexanone (0.98 g, 10 mmol) was added and stirred for 1h under nitrogen atmosphere. To this mixture methyl acrylate (7.72 g, 20 mmol) was added and the mixture was further stirred for 12h at 25 ^{o}C. The resulting mixture was poured into acetone (40 ml) containing $CuCl_2$ (5.38 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) brine (30 ml), dried over $MgSO_4$ and concentrated. The residue was subjected to column chromatography, hexane eluted naphthalene, and 4% ethyl acetate in hexane eluted cyclic β-keto ester 26 (53%, 1.26 g).

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

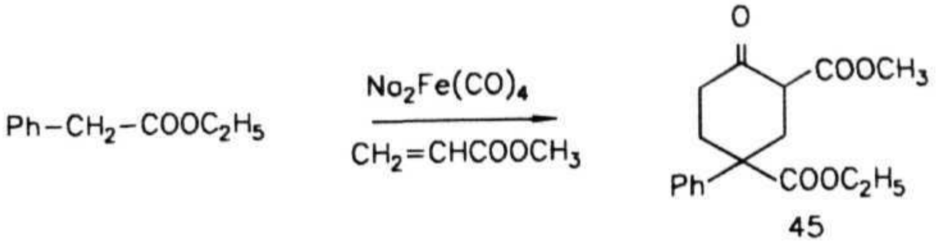
^{1}H NMR : 8 ppm 1.62-2.58 (m, 14H), 2.84 (m, 1H), 3.72 (s, 3H)

^{13}C NMR : 6 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%)

The above procedure was followed for other substrates (entries 1.3.3 to 1.3.7). The physical constant and spectral data obtained are summarized below.

1.3.3.



45

Yield : 59% (1.8 g)

IR (neat) : 1710, 1640, 1600 cm^{-1}

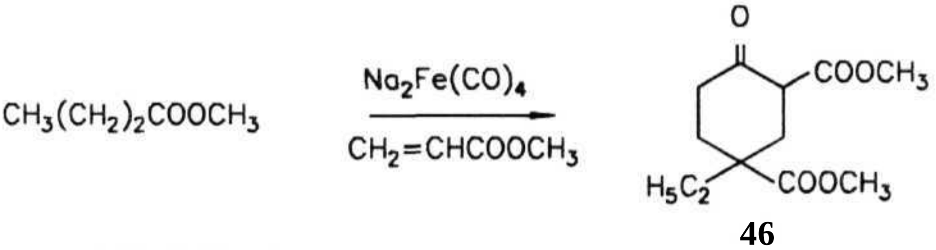
^{1}H NMR : 6 ppm 1.21 (t, 3H), 2.10–3.11 (m, 8H), 3.70 (s, 3H), 7.21-7.30 (m, 5H) (Spectrum no. 1)

^{13}C NMR : 6 ppm 13.8, 26.5, 29.3, 30.6, 48.9, 51.3, 52.1, 60.8, 95.9, 125.8, 127.2, 128.6, 141.4, 171.3, 172.5, 174.8.(Spectrum no.2)

Ms(EI) : m/z 304 (M$^+$ 10%)

Analysis :	C%	H%
calcd for		
$C_{17}H_{20}O_5$:	67.1	6.62
Found :	67.5	6.66.

1.3.4.



46

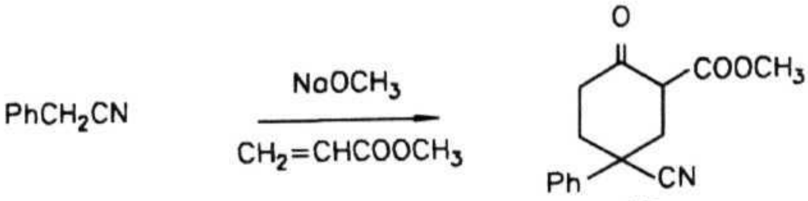
Yield : 48% (1.16 *g)*

IR (neat) : 1730, 1650, 1600 cm"^{1}

^{1}H NMR : 6 ppm 0.90 (t, 3H), 1.51 (q, 2H), 1.90–2.51 (m, 6H), 3.4 (s, 3H), 3.6 (s, 3H)

^{13}C NMR : δ ppm 13.2, 17.9, 27.1, 32.6, 35.6, 51.3, 51.6, 125.8, 138.0, 167.0, 173.1, 179.5.

1.3.5.



47

Yield : 62% (1.60 g)

M.P. : 95°C

IR (KBr) : 2230, 1650, 1600 cm"^{1}

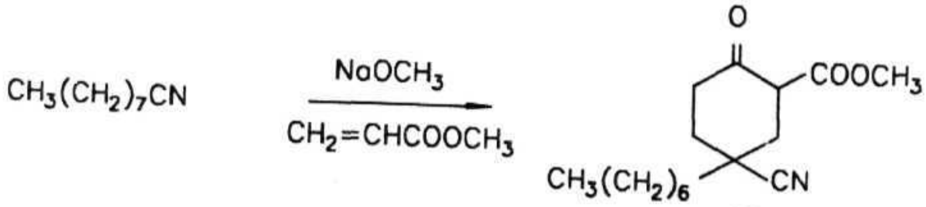
^{1}H NMR : 6 ppm 2.10–3.11 (m, 6H), 3.76 (s, 3H), 7.22-7.60 (m, 5H), 12.20 (s, 1H) (Spectrum no. 3)

^{13}C NMR : 6 ppm 27.1, 31.4, 34.8, 41.1, 51.7, 95.1, 122.2, 125.7, 128.6, 129.3, 139.4, 170.8, 172.2. (Spectrum no. 4)

Ms (ED : m/z 257 (M^{+}, 40%) (Spectrum no. 5)

Analysis :	C%	H%	NX
calcd for			
$C_{15}H_{15}O_3N$:	70.02	5.88	5.44
Found :	70.09	5.97.	5.26

1.3.6.



48

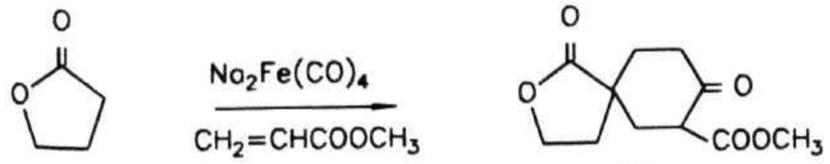
Yield : 49% (1.36 g)

IR (neat) : 2200, 1730, 1640 cm"^{1}

^{1}H NMR : 6 ppm 0.96 (t, 3H), 1.40 (m, 10H), 1.71 (m, 2H), 2.3-2.8 (m, 4H), 3.76 (s, 3H)

^{13}C NMR : 6 ppm 13.5, 16.5, 22.2, 25.0, 26.9, 28.2, 28.6, 31.3, 32.5, 51.0, 119.5, 125.4, 128.2, 166.2, 172.7

1.3.7.



49

Yield : 55% (1.26 g)

M.P. : 92°C

IR (KBr) : 1720, 1620 cm"^{1}

^{1}H NMR : 6 ppm 1.56-2.68 (m, 9H), 3.8 (s, 3H), 4.36 (t, 2H)

^{13}C NMR : 6 ppm 25.5, 27.6, 29.4, 32.8, 41.0, 51.4, 65.1, 94.7, 170.7, 172.7, 180.5

Ms (ED : m/z 226 (M^+, 25%)

Analysis		CX	H%
calcd for			
$C_{11}H_{14}O_5$	:	58.39	6.24
Found	:	58.89	6.23.

1.3.8. Reaction of methyl 1,1-diphenylacetate 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, 16 mmol) in THF (50 ml)], methyl 1,1-diphenylacetate (2.26 *g*, 10 mmol) was added and stirred for 1h under nitrogen atmosphere. To this mixture methyl acrylate (1.72 g, 20 mmol) was added and the mixture was further stirred for 12h at 25°C. The resulting mixture was poured into acetone (40 ml) containing $CuCl_2$ (5.38 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 organic extract was washed with water (20 ml), brine (30 ml) dried over $MgSo_4$ and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene and 5% ethyl acetate in hexane eluted the ester 28.

Yield : 80%. (1.25 g)

IR (neat) : 1730, 1710 cm^{-1}

^{13}C NMR : 6 ppm 30.4, 33.1, 51.4, 52.3, 59.6, 127.1, 128.1, 128.8, 142.2, 173.7, 174.3.

Analysis		C%	H%
calcd for			
$C_{19}H_{20}O_4$	:	73.05	6.45
Found	:	73.00	6.49.

1.3.9. Examination of the reverse addition of ethyl phenylacetate and methyl acrylate using $Na_2Fe(CO)_4$:

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)] methyl acrylate (1.72 g. 20 mmol) was added and stirred for 1h under nitrogen atmosphere. To this mixture, ethyl phenylacetate (1.64 g, 10 mmol) was added and the mixture was further stirred for 12h at 25 °C. The resulting mixture was poured into acetone (40 ml) containing $CuCl_2$ (5.38 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 water (20 ml), brine (30 ml), dried over $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene, and 3% ethyl acetate in hexane eluted ethyl phenylacetate quantitatively. Ethyl acetate (5%) in hexane eluted an unidentified polymeric compound.

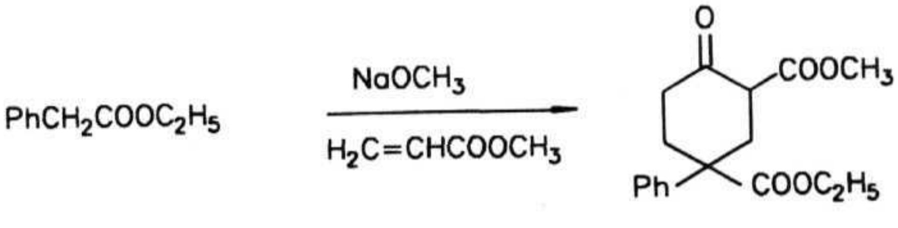
1.3.10: Reaction of cyclohexanone with methyl acrylate in the presence of NaOMe.

To a suspension of NaOMe (1.08 g, 20 mmol) in THF (40 ml) cyclohexanone (0.98 g, 10 mmol) was added and dried for 1h at 25 °C under nitrogen atmosphere. To this solution methyl acry late (1.72 g, 20 mmol) was added and further stirred for 10h at 25 °C. The resulting 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), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. The cyclic β-keto ester 26 (42%, 1.01 g) was eluted using 4% ethyl acetate in hexane.

The physical constant and the spectral data of the β-keto ester were found to be similar to that obtained previously (1.3.2).

Similar procedure was followed for other substrates (entries 1.3.11 to 1.3.18). The physical constant and the spectral data for the cyclic β-keto esters (entries 1.3.11 to 1.3.18) obtained in reactions using $NaOCH_3$ are summarized below.

1.3.11.



45

Yield : 52% (1.6 g)

IR (neat) : 1710, 1640, 1600 cm^{-1}

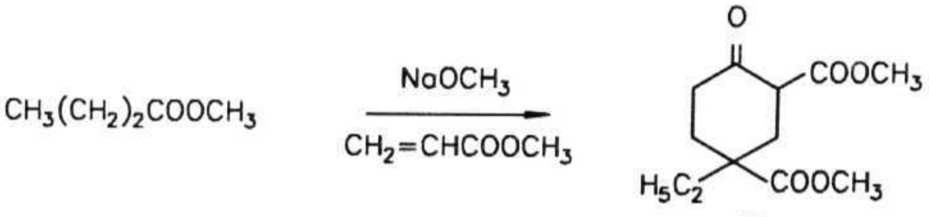
^{1}H NMR : 6 ppm 1.21 (t, 3H), 2.10–3.11 (m, 8H), 3.70 (s, 3H), 7.21-7.30 (m, 5H) (Spectrum no. 1)

^{13}C NMR : 6 ppm 13.8, 26.5, 29.3, 30.6, 48.9, 51.3, 52.1, 60.8, 95.9, 125.8, 127.2, 128.6, 141.4, 171.3, 172.5, 174.8.(Spectrum no.2)

Ms(EI) : m/z 304 (M^+ 10%)

Analysis		C%	H%
calcd for			
$C_{17}H_{20}O_5$	:	67.1	6.62
Found	:	67.5	6.66.

1.3.12.

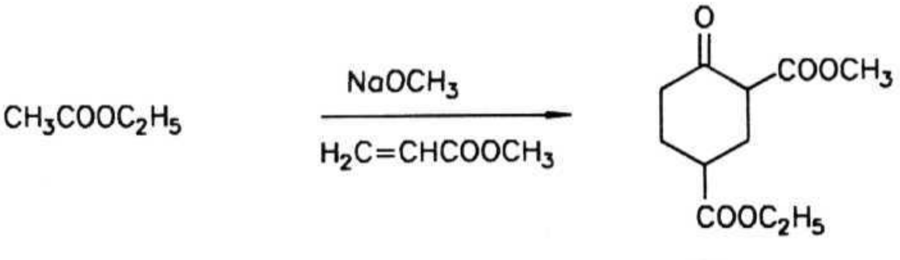


46

Yield : 41% (1.0 g)

The physical constant and the spectral data of the β-keto ester were found to be same as that obtained previously (1.3.4).

1.3.13.



50

Yield : 40% (0.90 g)

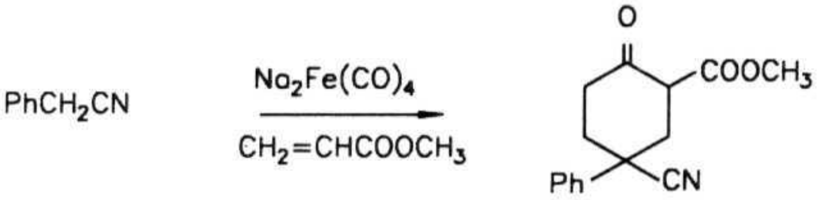
IR (neat) : 1730, 1640, 1600 cm^{-1}

^{1}H NMR : 6 ppm 1.20 (t, 3H), 2.40–2.71 (m, 6H), 3.65 (s, 3H), 4.10 (q, 2H)

^{13}C NMR (45°C): 6 ppm 13.9, 25.7, 27.4, 29.4, 46.1, 51.2, 51.8, 59.1, 77.4, 95.2, 170.8, 172.5, 175.0.

^{13}C NMR (25°C): 6 ppm 13.9, 25.6, 27.1, 32.6, 32.9, 38.8, 51.2, 51.6, 60.1, 60.5, 98.0, 117.3, 125.4, 125.7, 136.5, 138.8, 163.4, 172.1, 174.2.

1.3.14.

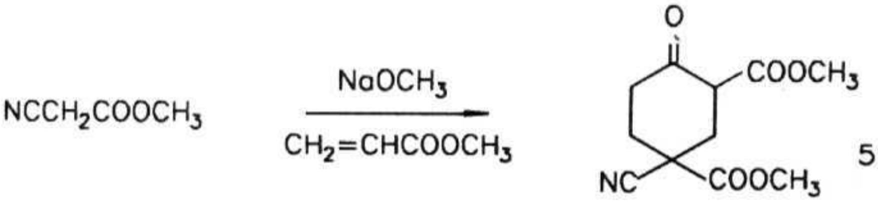


47

Yield : 56% (1.45 g)

The physical constant and the spectral data of the product were found to be same as that obtained previously (1.3.5).

1.3.15.



51

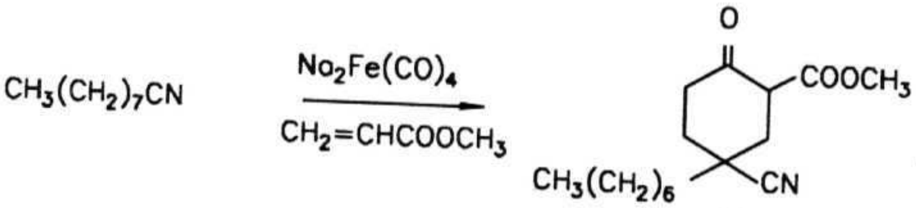
Yield : 54% (1.36 g)

IR (neat) : 2220, 1730, 1650, 1610 cm"^{1}

^{1}H NMR : 6 ppm 2.10–2.91 (m, 6H), 3.75 (s, 3H), 3.82 (s, 3H)

^{13}C NMR : 6 ppm 25.7, 28.0, 30.1, 42.2, 51.8, 53.8, 93.7, 118.3, 168.6, 170.1, 171.7.

1.3.16:

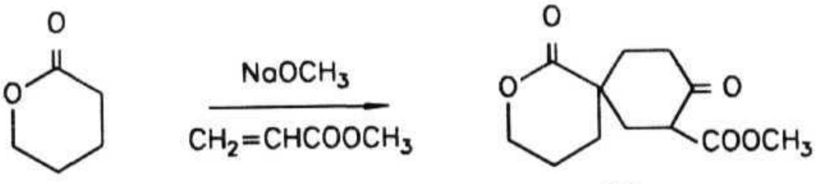


48

Yield : 45% (1.24 g)

The physical constant and the spectral data of the product were found to be same as that obtained previously (1.3.6)

1.3.17.



52

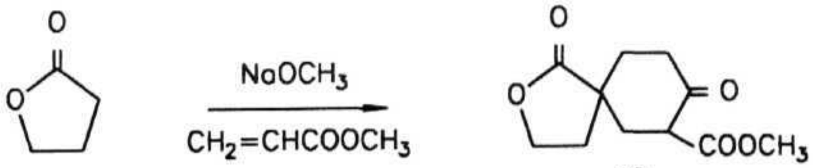
Yield : 48% (1.16 g)

IR (neat) : 1720, 1620 cm^{-1}

^{1}H NMR : 6 ppm 1.50–2.81 (m, 10H), 3.70 (s, 3H), 4.31 (r, 2H)
(Spectrum no. 6)

^{13}C NMR : 6 ppm 20.2, 25.1, 28.9, 30.1, 31.6, 40.6, 51.6, 70.0, 94.6, 170.5, 172.7, 175.8. (Spectrum no. 7)

1.3.18:



49

Yield : 50% (1.14 g)

The physical constant and the spectral data of the product were found to be same as that obtained previously (1.3.7).

1.3.19. Reaction of benzyl cyanide with methyl crotonate in the presence of $NaOCH_3$:

To a suspension of $NaOCH_3$ (1.08 g, 20 mmol) in THF (40 ml), benzyl cyanide (1.17 g, 10 mmol) was added and stirred for 1h at 25 °C under nitrogen atmosphere. To this solution methyl crotonate (2.00 g, 20 mmol) was added and further stirred for 10h at 25 °C. The resulting 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), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. The ester 30 moles (2.00 g, 78%) was eluted using 5% ethyl acetate in hexane.

IR (neat) : 2200, 1740 cm"^{1}

^{13}C NMR : 6 ppm 15.41, 22.88, 34.88, 41.95, 51.24, 118.77, 127.48, 127.83, 128.65, 129.95, 134.13, 171.83.

1.3.20: Isomerization of 1-decene into trans-2-decene using the $Na_2Fe(CO)_4$/ Cu Cl system:

To a suspension of $Na_2Fe(CO)_4$ [prepared using $Fe(CO)_5$ (2.16 g, 11mmol), Na (0.51 g, 22 mmol) and naphthalene (1.28g, 10 mmol)] in THF (60 ml)] 1-decene (1.4 g, 10 mmol) was added and stirred for 2h under nitrogen atmosphere. To this mixture CuCl (2.00 g, 20 mmol) was added during 30 minutes using a solid addition flask and the reaction mixture **was** further stirred for lOh at room temperature. The resulting mixture was poured into water (30 ml) containing ceric ammonium nitrate (5.48 g, 10 mmol) to decompose the metal carbonyl. The organic phase was separated and the aqueous phase was saturated with NaCl and extracted with ether (2 x 30 ml). The combined organic extract was washed with water (20 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography to obtain trans-2-decene (83%, 1.16 g) using hexane as an eluent.

B.P. : 57°C/10 mm {Lit.[85] B.P. 58°C/10 mm}

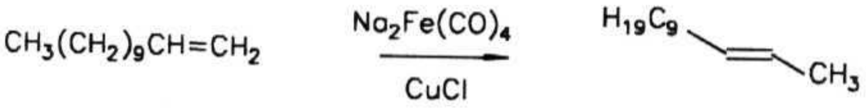
IR (neat) : 2960, 2850, 950 cm^{-1}

^1H NMR : 6 ppm 0.9 (t, $-CH_3$), 1.3 (s, $-CH_2$), 1.9 (d, trans $-CH_3$), 2.3 (q, $-CH_2$), 6.4 (m, -CH)

^{13}C NMR : 6 ppm 13.9, 17.7, 22.6, 29.2, 29.6, 31.8, 32.5, 124.5, 131.7.

The above procedure utilizing the $Na_2Fe(CO)_4$/CuCl system was followed for the isomerization of other olefins (entries 2.3.21 to 2.3.25) and the physical constant and spectral data are presented below.

1.3.21:



Yield : 80% (1.35 g)

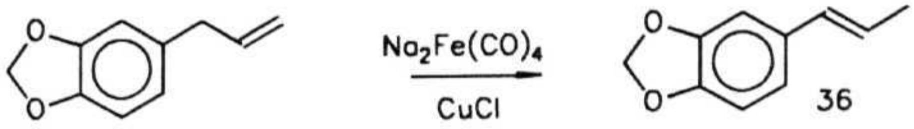
B.P. : 59°C/10 mm

IR (neat) : 2900, 2850, 950 cm^{-1}

^1H NMR : 6 ppm 0.9 (t, CH_3), 1.3 (s, $-CH_2$), 1.9 (d- trans $-CH_3$), 2.6 (q, $-CH_2$), 6.4 (m, -CH)

^{13}C NMR : δ ppm 13.8, 17.7, 22.6, 28.8, 29.2, 29.5, 31.8, 32.2, 124.4, 130.8.

1.3.22:



Yield : 87% (1.38 g)

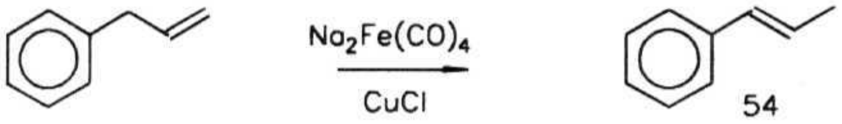
B.P. : 120°C/10 mm {Lit.[86] B.P. 111°/6 mm}

IR (neat) : 3010, 1600, 1240, 950 cm"^{1}

^{1}H NMR : 6 ppm 1.9 (d, $-CH_3$), 5.94 (s, $-CH_2$), 6.2 (m, -CH), 6.7 and 6.8 (s, phenyl CH)

^{13}C NMR : 6 ppm 18.06, 100.83, 105.3, 108.1, 120.0, 123.7, 130.7, 132.53, 146.5, 148.0.

1.3.23:



Yield : 76% (0.9 g)

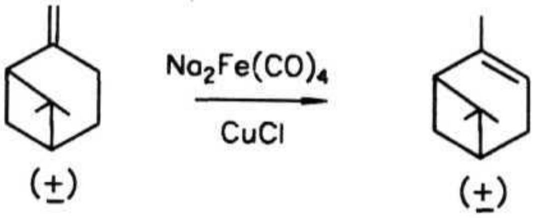
B.P. : 70°C/12 mm {Lit.[87] B.P. 176°/760 mm}

IR (neat) : 3026, 1599, 962, 734 cm"^{1}

^{1}H NMR : δ ppm 1.9 (d, $-CH_3$), 6.4 (m, -CH), 7.3 (m, $-C_6H_5$)

^{13}C NMR : 6 ppm 18.4, 125.7, 125.9, 126.9, 128.3, 131.2, 138.0.

1.3.24:



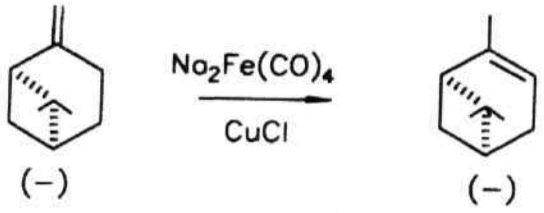
Yield : 79% (1.08 g)

IR (neat) : 2950, 1460, 800 cm"^{1}

^1H NMR : δ ppm 1.82 (s, CH_3), 1.2 (m, 2H), 1.7 (m, 2H), 2.2 (m, 2H), 5.2 (t, CH)

^{13}C NMR : δ ppm 21.0, 23.2, 26.6, 31.5, 31.7, 38.2, 41.0, 48.3, 116.1, 144.4.

1.3.25:



$[\alpha]_D^{25}$ = −19.4 (neat)

$[\alpha]_D^{25}$ = −19.0 (neat)

Yield : 78% (1.06 g)

Spectral data of the product was found to be similar to that obtained in the previous experiment (1.3.24).

1.3.26: Examination of the question whether the isomerization reaction using $Na_2Fe(CO)_4$/CuCl system is catalytic or not:

To a suspension of $Na_2Fe(CO)_4$ [prepared using $Fe(CO)_5$ (2.16 g, 11mmol), Na (0.51 g, 22 mmol) and naphthalene (1.28 g, 10 mmol)] in THF (60 ml) safrole (3.24 g, 20 mmol) was added and stirred for 2h under nitrogen atmosphere. To this mixture CuCl (2.00 g, 20 mmol) was added during 30 minutes using a solid addition flask and the reaction mixture was further stirred for 10h at room temperature. The resulting mixture was poured into water (30 ml) containing ceric ammonium nitrate (5.48 g, 10 mmol) to decompose the metal carbonyl. After work up, The residue was subjected to column chromatography using hexane as an eluent to obtain a mixture of safrole and the isomerized product. The ^1H NMR spectral data indicated that the ratio is 1:1.

1.3.27: Attempted complexation of methyl acrylate with $Fe(CO)_4$ unit utilizing $Na_2Fe(CO)_4$/CuCl reagent system and decomplexation with PhLi:

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 (1.28 g, 10 mmol)] in THF (60 ml), methyl acrylate (0.86 g, 10 mmol) was added and stirred for 2h under nitrogen atmosphere. To this mixture, CuCl (2.00 g, 20 mmol) was added during 30 minutes using a solid addition flask. The reaction mixture was further stirred for 10h at room temperature, followed by the addition of phenyllithium (prepared from 10 mmol of bromobenzene) at -78°C and stirring at -78°C for 6h. The mixture was poured into water (30 ml), the organic phase was separated and the aqueous phase was saturated with NaCl and extracted with ether (2 x 30 ml). The combined organic extract was washed with water (20 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene and 5% ethyl acetate in hexane eluted unidentified polymeric compound.

1.3.28: Reaction of 1,3-cyclooctadiene with the $Na_2Fe(CO)_4$/CuCl system :

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 (1.28 g, 10 mmol)] in THF (60 ml), 1,3-cyclooctadiene (1.08 g, 10 mmol) was added and stirred for 2h under nitrogen atmosphere. To this mixture CuCl (2.00 g, 20 mmol) was added during 30 minutes using a solid addition flask and the reaction mixture was further stirred for 10h at room temperature. The resulting mixture was poured into hexane (30 ml) and filtered. The filtrate was concentrated, the residue was subjected to column chromatography using hexane as eluent and isolated starting 1,3-cyclooctadiene (>90%) and the corresponding metal carbonyl complex of cyclooctadiene (0.19 g, 8%).

IR (neat) : 2940, 1980, 1440, 920 cm"^{1}

^{13}C NMR : 6 ppm 23.06, 28.0, 29.64, 126.0, 127.89, 131.0, 184.0.

1.3.29: Isomerization of 1-decene into 2-decene using $Na_2Fe(CO)_4$/$BrCH_2CH_2Br$ system:

To a suspension of $Na_2Fe(CO)_4$ [prepared using $Fe(CO)_5$ (2.16 g, \i mmol), Na (0.51 g, 22 mmol) and naphthalene (1.28 g, 10 mmol)] in THF (60 ml). 1-Decene (1.4 g, 10 mmol) was added and stirred for 2h under nitrogen atmosphere. To this mixture 1,2-dibromoethane (1.87 g, 10 mmol) was added slowly and the reaction mixture was further stirred for 10h at room temperature. The resulting mixture was poured into water (30 ml), containing ceric ammonium nitrate (5.48 g, 10 mmol) to decompose metal carbonyl. The organic phase was separated and the aqueous phase was saturated with NaCl and extracted with ether (2 x 30 ml). The combined organic extract was washed with water (20 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography to obtain a mixture of cis- and trans-2-decene (80%, 1.13 g) using hexane as eluent. The ^{1}H NMR data of the mixture indicates that the trans-2-decene is the major product (<80%).

B.P. : 56-57°C/10 mm {Lit.[85] B.P. 58°/10 mm}

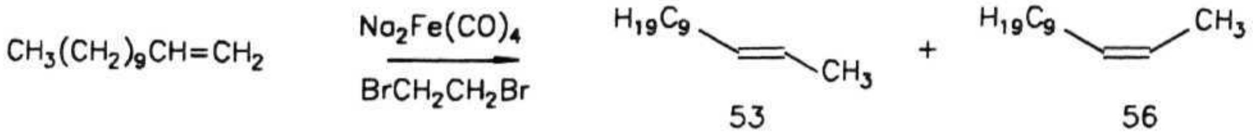
IR (neat) : 2960, 2850, 980, 900 cm"^{1}

^{1}H NMR : 6 ppm 0.9 (t, $-CH_3$), 1.3 (s, $-CH_2$), 1.8 (d, cis- CH_3), 1.9 (d, trans - CH_3), 2.3 (q, $-CH_2$), 6.4 (m, -CH)

^{13}C NMR : 6 ppm 13.9, 14.2, 17.7, 22.2, 22.6, 29.2, 29.6, 31.6, 32.1, 32.5, 32.9, 124.5, 129.6, 130.4, 131.7

Similar product mixture was obtained following the above procedure for the isomerization of 1-dodecene. The physical constant and spectral data are presented below.

1.3.30:



Yield : 76% (1.28 g)

B.P. : 59 °C/10 mm

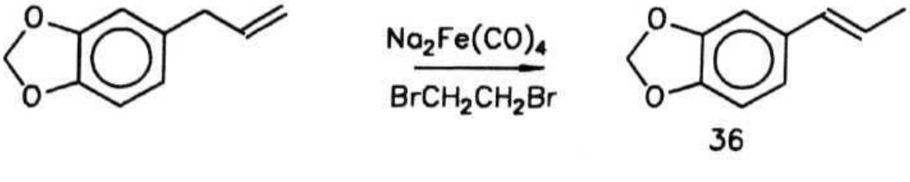
IR (neat) : 2900, 2850, 960, 900 cm^{-1}

^1H NMR : 6 ppm 0.9 (t, $-CH_3$), 1.3 (s, $-CH_2$), 1.8 (d, cis $-CH_3$), 1.9 (d, trans-CH_3), 2.7 (q, $-CH_2$), 6.4 (m, -CH)

^{13}C NMR : 6 ppm 13.4, 13.8, 17.5, 22.1, 22.6, 25.5, 29.3, 29.6, 32.2, 32.5, 34.7, 124.4, 129.4, 130.7, 131.8.

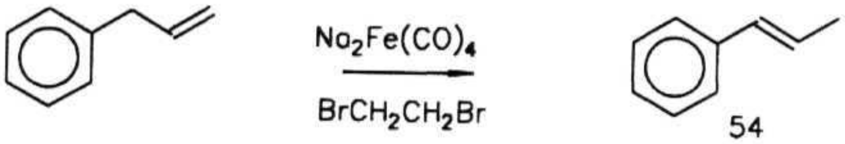
The above procedure utilizing the $Na_2Fe(CO)_4/BrCH_2CH_2Br$ system was followed for the isomerization of other 1-alkenes (entries 1.3.31 to 1.3.34) and the physical constant and spectral data of the trans-2-alkenes obtained in these experiments (entries 1.3.31 to 1.3.34) were identical to the data of the samples previously (1.3.22 to 1.3.25) obtained using the $Na_2Fe(CO)_4/CuCl$ system.

1.3.31:



Yield : 81% (1.3 g)

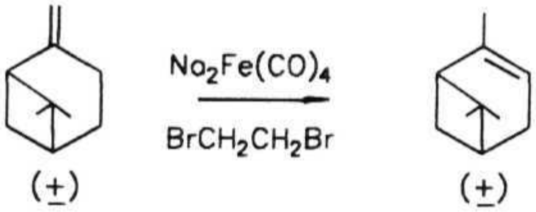
1.3.32:



54

Yield : 75% (0.89 g)

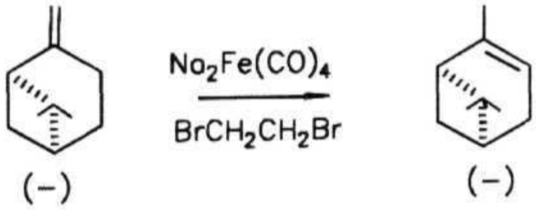
1.3.33:



55

Yield : 78% (1.06 g)

1.3.34:



31

Yield : 79% (1.08 g)

1.3.35: Preparation of methyl 10-undecynoate:

10-Undecynoic acid was prepared from 10-undecenoic acid bromination and dehydrobromination following a reported procedure.[88] It was esterified following a closely related procedure.[89] DBU (3.0 g, 20 mmol) was added to a magnetically stirred mixture of 10-undecynoic acid (3.6 g, 20 mmol) and

CH_3I (3.5 g, 25 mmol) in benzene (20 ml). The reaction mixture was further stirred for 3h at 60°C. Ether (20 ml) was added to the reaction mixture and the solution was washed with 3N HCl (10 ml), water (30 ml), brine (20 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was distilled to isolate methyl 10-undecynoate (85%, 3.4 g).

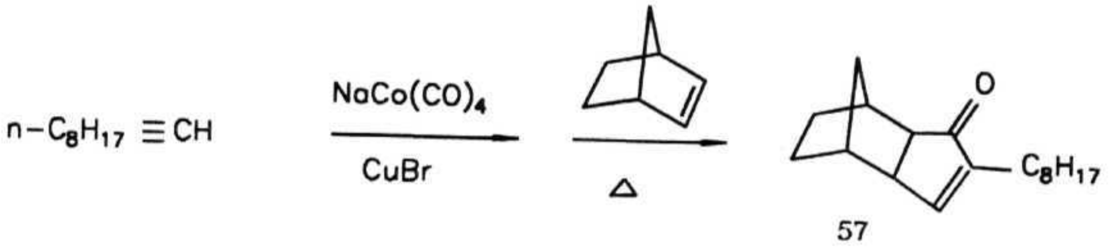
B.P. : 120°C/15mm, {Lit.[90] B.P. 121°C/15 mm}

IR (neat) : 3298, 2932, 2856, 1739, 1437, 1172 cm^{-1}

^{13}C NMR : δ ppm 18.4, 24.9, 28.5, 28.7, 29.1, 34.1, 51.4, 68.1, 85.0, 174.3.

1.3.36: Preparation of (1-decyne)hexacarbonyl dicobalt complex using $NaCo(CO)_4$/CuBr and its reaction with norbornene:

CuBr (1.43 g, 10 mmol), 1-decyne (0.69, 5 mmol) was added to $NaCo(CO)_4$ [prepared using $CoBr_2$ (2.18 g, 10 mmol), Na (0.69 g, 30 mmol) and naphthalene (1.28 g, 10 mmol)] in THF (60 ml) under CO atmosphere. The contents were stirred for 6h at 25°C. Norbornene (0.94 g, 10 mmol) was added and further stirred at 65°C for 4h. The resulting mixture was added to H_2O (60 ml). Hexane (40 ml) was added and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2 x 30 ml). The combined organic extract was washed with brine (20 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column and the cyclopentenone derivative 57 was isolated using hexane/ethyl acetate (95:5) as eluent.



Yield : 65% (0.85 g)

IR (neat) : 3025, 2950, 1700, 1630, 1440, 1180, 1040 cm

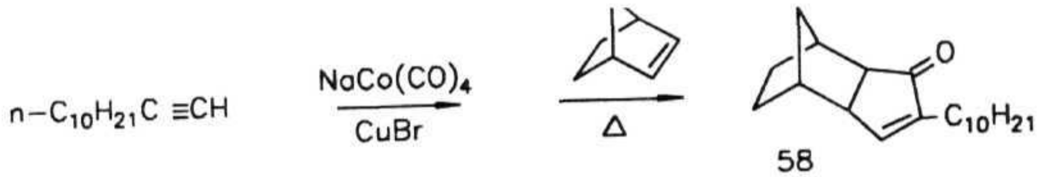
^{1}H NMR : 6 ppm 0.8 (t, 3H), 1.0-1.6 (m, 20H), 2.1 (m, 2H), 2.3 (br s, 1H), 2.5 (br s, 1H), 7.0 (br s, 1H)

^{13}C NMR : 6 ppm 13.6, 22.2, 24.3, 27.4, 28.0, 28.6, 28.8, 30.5, 31.4, 37.7, 38.5, 47.7, 53.4, 149.2, 158.1, 210.3

Ms (m/z) : 260 (M^+, 50%), 232 (10%), 163 (100%)

The above procedure utilizing the $NaCo(CO)_4/CuBr$ system was followed for the Pauson-Khand cyclization reactions of other substrates (entries 1.3.37 to 1.3.39). The physical constant and spectral data obtained are summarized below.

1.3.37:



58

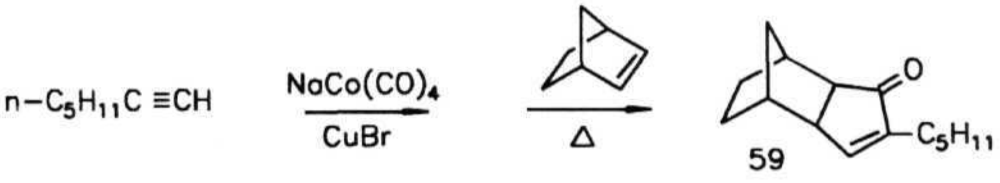
Yield : 76% (1.1 g)

IR (neat) : 2950, 1700, 1620, 1440, 1180, 1040 cm"^{1}

^{1}H NMR : 6 ppm 0.8 (t, 3H), 1.2-1.7 (m, 24H), 2.1 (m, 2H), 2.4 (br s, 1H), 2.6 (br s, 1H), 7.1 (br s, 1H)

^{13}C NMR : 6 ppm 13.9, 22.5, 24.6, 27.8, 28.3, 29.0, 29.5, 30.9, 31.8, 38.0, 38.9, 48.0, 53.7, 149.4, 158.2, 210.6.

1.3.38:



59

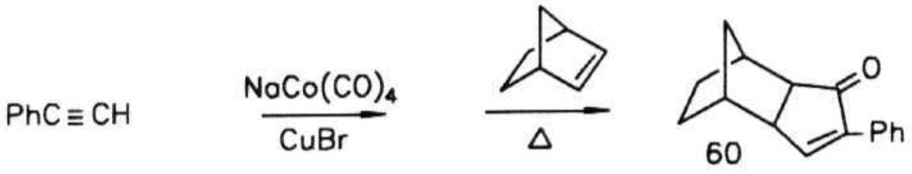
Yield : 62% (0.68 g)

IR (neat) : 2957, 2872, 1699, 1456, 1186, 1053 cm^{-1}

^{1}H NMR : δ ppm 0.9 (t, CH_3), 1.1-1.7 (m, 14H), 2.1 (m, 2H), 2.3 (br s, 1H), 2.5 (br s, 1H), 7.1 (br s, 1H) (Spectrum no. 8)

^{13}C NMR : δ ppm 13.2, 21.7, 24.0, 26.8, 27.8, 28.4, 30.2, 31.0, 37.4, 38.2, 47.4, 53.1, 148.9, 157.7, 209.8. (Spectrum no. 9)

1.3.39:



Yield : 84% (0.95 *g)*

M.P. : 92^{o}C {Lit.^{91} m.p. 93-95°C}

IR (KBr) : 3040, 3025, 2950, 1695, 1610, 1600, 1320, 1300, 765, 700 cm"^{1}

^{1}H NMR : *6* ppm 0.9-1.1 (m, 2H), 1.1-1.8 (m, 4H), 2.3-2.5 (m, 3H), 2.6 (m, 1H), 7.2-7.5 (m, 5H), 7.6-7.8 (m, 1H)

^{13}C NMR : *6* ppm 28.4, 29.1, 31.2, 38.3, 39.4, 47.7, 54.9, 127.1, 128.4, 131.6, 146.1, 160.3, 209.1.

Ms (m/z) : 224 (M^{+}, 100%), 196 (10%), 158 (75%), 156 (60%)

Analysis :	C%	H%
Calcd for		
$C_{16}H_{16}O$	85.60	7.14
Found	85.43	7.17

1.3.40: Preparation of (Ph-C≡C-Ph)hexacarbonyl dicobalt complex:

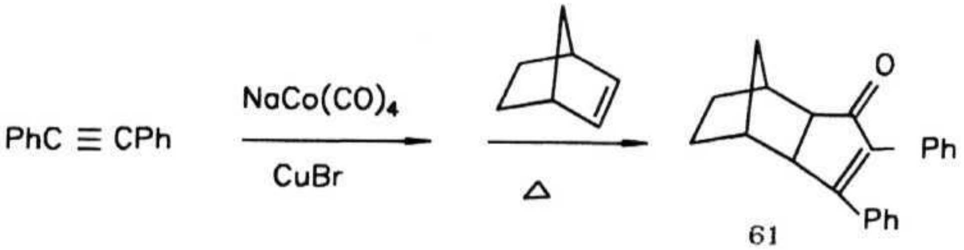
CuBr (1.43 *g,* 10 mmol) and diphenylacetylene (0.89 *g, 5* mmol) were added to $NaCo(CO)_4$ [prepared using $CoBr_2$ (2.18 g, 10 mmol), Na (0.69 g, 30 mmol) and naphthalene (1.28 g, 10 mmol) J in THF (60 ml) under *CO* atmosphere. The contents were stirred for 6h at 25 °C. During this time the reaction mixture was turned to reddish brown. The resulting mixture was taken in hexane (50 ml), washed with H_2O (40 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column and the complex $(Ph-C{\equiv}C-Ph)Co_2(CO)_6$ was isolated in 40% (0.92 g) yield using hexane as eluent.

M.P. : 106°C {Lit.[92] m.p. 109 °C}

IR (KBr) : 3025, 2100, 2025, 800, 760 cm^{-1}

1.3.41: Preparation of $(Ph-C{\equiv}C-Ph)$hexacarbonyl dicobalt complex using $NaCo(CO)_4/CuBr$ and its reaction with norbornene:

CuBr (1.43 g, 10 mmol) and diphenylacetyiene (0.89 g, 5 mmol) were added to $NaCo(CO)_4$ [prepared using $CoBr_2$ (2.18 g, 10 mmol), Na (0.69 g, 30 mmol) and naphthalene (1.28 g, 10 mmol)] in THF (60 ml) under CO atmosphere. The contents were stirred for 6h at 25 °C. Norbornene (0.94 g, 10 mmol) was added and further stirred at 65 °C for 12h. The resulting mixture was added to H_2O (60 ml). Hexane (40 ml) was added and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2 x 30 ml). The combined organic extract was washed with brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column and the cyclopentenone derivative 61 was isolated using 5% ethyl acetate in hexane as eluent.



61

Yield : 53% (0.79 g)

M.P. : 92°C {Lit.[91] m.p. 93-95°C}

IR (KBr) : 3040, 3025, 2950, 1695, 1610, 1600, 1320, 1300, 765, 700 cm"^{1}

^{1}H NMR : 6 ppm 0.9-1.7 (m, 6H), 2.3-2.6 (m, 3H), 3.2 (d, 1H), 7.1-7.3 (m, 10H)

^{13}C NMR : δ ppm 28.8, 29.0, 31.6, 38.4, 39.5, 50.8, 54.1, 127.9, 128.5, 128.7, 129.5 129.6, 132.4, 135.3, 170.1, 208.8.

1.3.42: Attempted Pauson-Khand cyclization reaction of methyl 10-undecynoate using Na $Co(CO)_4$./CuBrsystem in the presence of **norbornene:**

CuBr (1.43 g, 10 mmol) and methyl-10-undecynoate (0.98 g, 5 mmol) were added to $NaCo(Co)_4$ [prepared using $CoBr_2$ (2.18 g, 10 mmol), Na (0.69 g, 30 mmol) and naphthalene (1.28 g, 10 mmol)] in THF (60 ml) under CO atmosphere. The contents were stirred for 6h at 25°C. Norbornene (0.94 g, 10 mmol) was added and further stirred at 65°C for 12h. The resulting mixture was added to H_2O (60 ml). Hexane (40 ml) was added and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2 x 30 ml). The combined organic extract was washed with brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography on a silica gel column using 5% ethyl acetate in hexane as eluent to obtain complex mixture of product along with some starting material.

The starting material was recovered quantitatively, when the reaction mixture was stirred for 24h at room temperature after the addition of norbornene.

1.3.43: Preparation of (methyl undecynoate) hexacarbonyl dioobalt complex through reduction of $CoBr_2$ with Zn and its reaction with norbornene:

A mixture of anhydrous $CoBr_2$ (2.18 g, 10 mmol), Zn dust (0.72 g, 11 mmol) and methyl undecynoate (0.98 g, 5 mmol) in THF (60 ml) was stirred for 3h while bubbling CO at 25°C. During this time the reaction mixture was turned to reddish-brown. The CO atmosphere was replaced by N_2, norbornene (0.94 g, 10 mmol) was added and the contents were stirred for 4h at 65°C. The reaction mixture was added to H_2O (60 ml). Hexane (40 ml) was added and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2 x 30 ml). The combined organic extract was washed with brine (20 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column. The cyclopentenone derivative 44 was isolated using hexane/ethyl acetate (95:5) as eluent.

Yield : 91% (1.45 g)

IR (neat) : 3050, 3025, 2950, 1700, 1640, 800 cm^{-1}

^1H NMR : δ ppm 0.8-1.1, 1.1-1.6 (m, 22H), 2.0-2.3 (m, 3H), 2.5 (br s, 1H), 3.6 (s, 3H), 7.0 (br s, 1H) (Spectrum no. 10)

^{13}C NMR : 6 ppm 24.2, 24.4, 27.3, 27.9, 28.6, 28.8, 30.5, 33.4, 37.6, 38.5, 47.6, 50.7, 53.3, 148.9, 157.9, 173.4, 210.1. (Spectrum no. 11)

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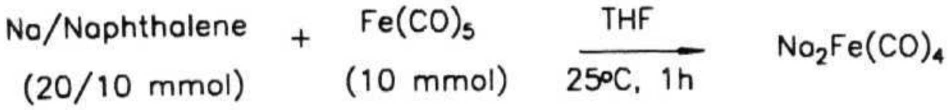
CHAPTER 2

REACTION OF AROMATIC ANION RADICALS WITH CARBOXYLIC ACID ESTERS

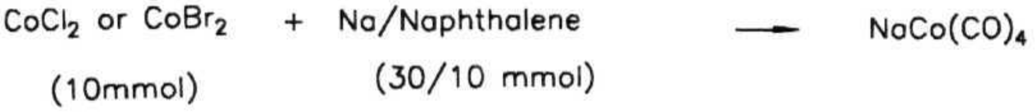
A NEW METHOD OF ACYLATION OF AROMATIC RINGS

2.1.1 Background and objectives:

As described in Chapter 1, convenient methods have been developed for the preparation of $Na_2Fe(CO)_4$[1] and $NaCo(CO)_4$[2] through reduction of $FeCl_3$ or $Fe(CO)_5$ and CoX_2 respectively in THF with naphthalene anion radical under carbon monoxide atmosphere (Eq. 1,2).



$$\underset{(20/10\ mmol)}{Na/Naphthalene} + \underset{(10\ mmol)}{Fe(CO)_5} \xrightarrow[25^{\circ}C,\ 1h]{THF} Na_2Fe(CO)_4 \quad —\ (1)$$



$$\underset{(10mmol)}{CoCl_2\ or\ CoBr_2} + \underset{(30/10\ mmol)}{Na/Naphthalene} \longrightarrow NaCo(CO)_4 \quad —(2)$$

Although the resulting solutions exhibit reactivities anticipated for the $Fe(CO)_4^{-2}$ and $Co(CO)_4^{-}$ species, it is not certain whether these species are formed quantitatively as it is known that naphthalene anion radical itself reacts with carbon monoxide.[3] So, we have decided to examine the reactivity of the naphthalene anion radical with carbon monoxide.

A report briefly indicates that the reaction of carbon monoxide with alkali metal and aromatic hydrocarbons like naphthalene, anthracene, $O\text{-}Ph_2C_6H_4$ and biphenyl in THF leads to a complex mixture of products.[3] It was reported that after work up, the organic layer contains products containing CO_2H and OH groups and a dihydro aromatic ring. Although the products have not been characterized completely it was concluded that data are in accordance with a compound formed by intramolecular Cannizzarro reaction after benzoin condensation. The aqueous layer has been reported to contain rhodizinic acid and α- and β- diketone moieties which might have been derived by the reaction of alkali metal and carbon monoxide. There has been no other report, to our knowledge on the reaction of aromatic hydrocarbons and alkali metal combination with carbon monoxide. However, it has been known for a long time that the alkali metals react with carbon monoxide to give $C_2O_2^{2-}$. The problem is as old as organic chemistry itself.

For example, Justus Liebig reported[4] that the reaction of carbon monoxide with molten potassium gave potassium carbonyl '$K_2C_2O_2$'. Later, Buchner confirmed that this compound is the potassium salt of acetylene diolate.[5,6] (Eq. 3).

$$2CO \xrightarrow{K(molten)} 2K^{+}\ \overset{-}{O}-C\equiv C-\overset{-}{O} \qquad \text{—(3)}$$

Pearson observed that the same compound could be prepared by the reductive coupling of carbon monoxide with alkali metals in liquid ammonia (Eq. 4). The structure of the acetylene diolate has been also confirmed by X-ray crystallography.[7]

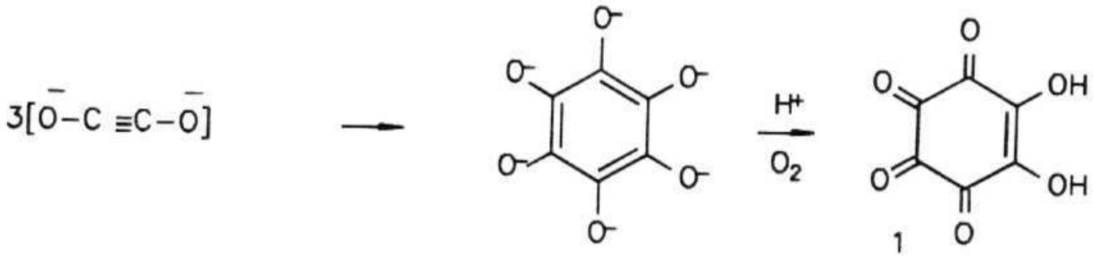
$$2CO \xrightarrow[(M\ =\ Li,\ K)]{M/NH_3} 2M^{+}\ \overset{-}{O}-C\equiv C-\overset{-}{O} \qquad \text{—(4)}$$

A more convenient method has been developed using sodium-potassium alloy for the reductive coupling of carbon monoxide in THF, in the presence of crown ethers (Eq.5).[8]

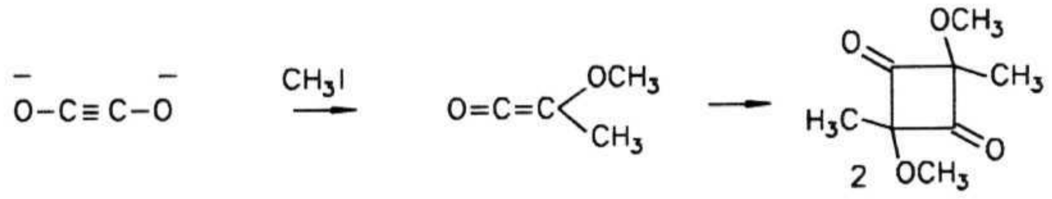
$$2CO \xrightarrow[\text{Crown ether}]{\text{Na}-\text{K alloy}} \bar{O}-C\equiv C-\bar{O} \qquad —(5)$$

There have been some reports describing the stability and reactivity of this reagent with certain electrophiles. The acetylene diolate is thermally unstable and it trimerizes readily at 100 °C to give $C_{b\,b}^{6-}$. This species gives rhodizinic acid 1 on acid treatment in air (Scheme. 1).[9]

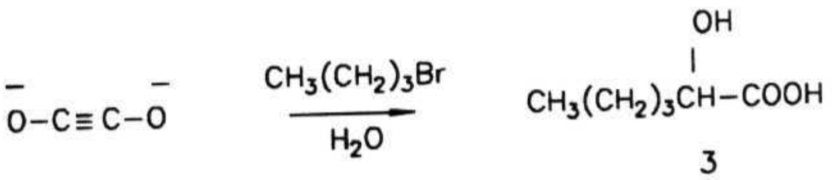
Scheme 1.



It also reacts with alkyl halides to give the products 2, 3 derived from the corresponding ketene intermediate as outlined below (Eq. 6,7).[g]



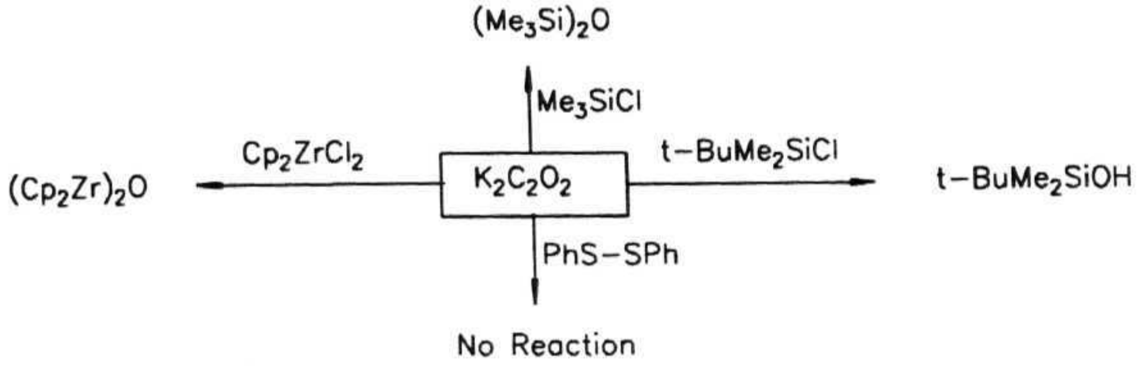
—(6)



$$\bar{O}-C\equiv C-\bar{O} \xrightarrow[H_2O]{CH_3(CH_2)_3Br} CH_3(CH_2)_3\underset{\textstyle 3}{\overset{\textstyle OH}{\overset{|}{C}}}H-COOH \qquad —(7)$$

Recently, Barber and **Whitesides** have studied the reaction of the species $K_2C_2O_2$ with several electrophiles and obtained the results outlined in Scheme. 2.[10,11]

Scheme 2.

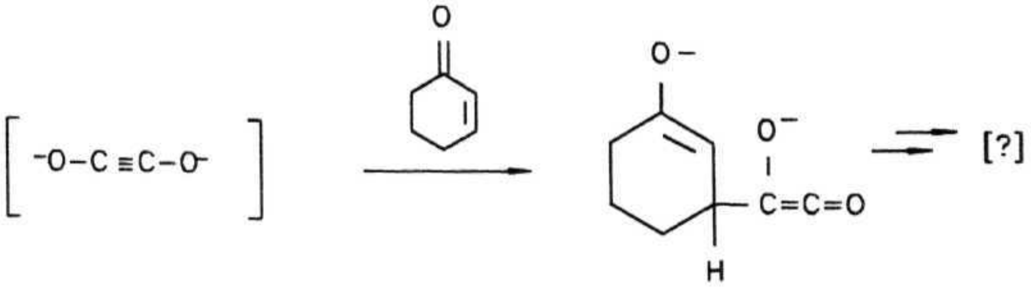


More recently, Lippard mentioned that these reactions with electrophiles lead to oxygen obstraction leaving behind intractable carbon containing products.)[1,12] However, it is not clear that the oxygen atoms in these products are derived from the diolate.

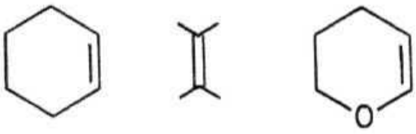
Although some interesting reactivities have been reported synthetic applications of these species which should serve as a good synthon for incorporation of two carbon units into organic compounds has not been studied in detail. The lack of interest in the synthetic utilization of the acetylene diolate may be due to the absence of detailed procedure for its preparation. So, it appeared desirable to examine the preparation and reactivities of the $C_2O_2^{2-}$ species.

Initially, we have examined the Michael reaction of the anticipated acetylene diolate $C_2O_2^{2-}$ with Michael accepters such as methyl acrylate, methyl crotonate and cyclohexenone (Scheme 3).

Scheme 3.



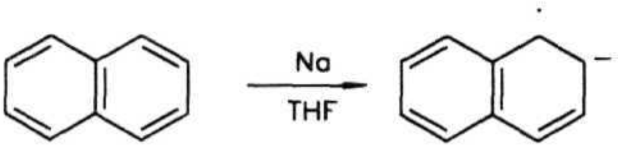
These reactions were not clean and only a complex mixture of unidentified products were obtained. It was thought that 'ketene' intermediates would be involved. In order to examine this, the reactions were carried out in the presence of the following olefins as ketene traps.



However, it was found that only the products containing the ester and naphthalene moieties were obtained. So, it was decided to examine the reactivity of the aromatic anion radicals with carboxylic acid esters and carbon monoxide in individual reactions.

It may be relevant here to briefly review the reports on the reactivity pattern of the aromatic anion radicals.

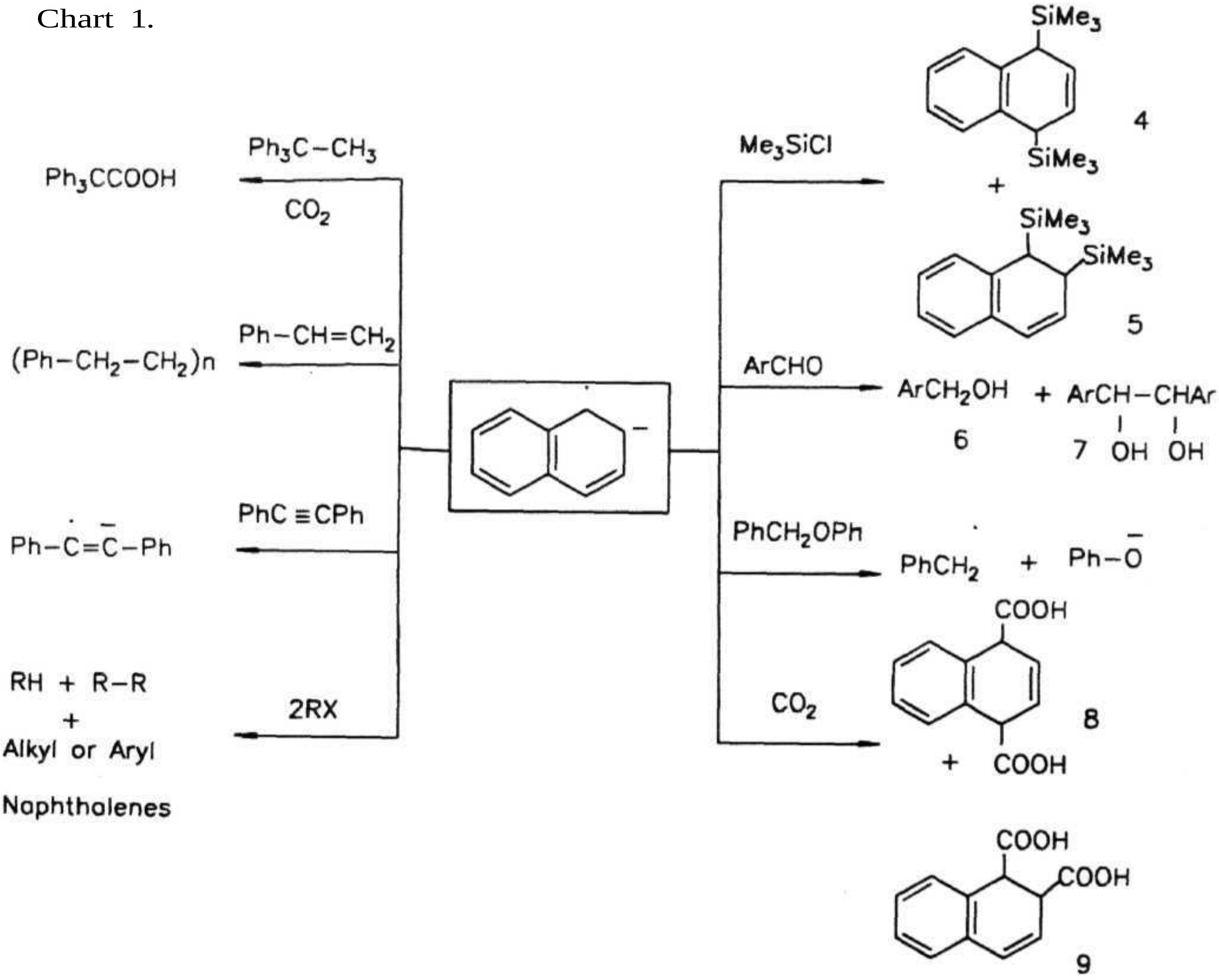
The aromatic radical anions can be prepared in THF by the addition of an alkali metal to aromatic hydrocarbons. For example, the naphthalene anion radical can be readily prepared by the reduction of naphthalene with sodium in THF (Eq. 8). The chemistry of naphthalene anion radical has been well studied compared to other radical anions. The results have been reviewed.



— (8)

These aromatic radical anions are very much useful and have a very rich chemistry. They react with a variety of compounds such as alkanes, alkenes, alkynes, aliphatic and aromatic halides, aldehydes, ketones and carbon dioxide (Chart. 1).[13-24]

Chart 1.



The anion radicals react with alkanes undergo cleavage, on the addition of CO_2 to give corresponding acids.[13—15] The most common reaction of alkenes is polymerization.[16,17] Terminal alkynes lose a proton to radical anions. Diphenylacetyiene, having no acidic hydrogens accepts either one or two electrons in THF to form the radical anion or dianion respectively.[18] Alkyl or aryl halides react with radical anions to yield a variety of products,[19] which are shown in Chart 1. Upon treatment with sodium naphthalenide, trimethyl silyl chloride forms 1,4-bis(trimethyl silyl)-naphthalene 4 as the major product (38%) and l,2-bis(trimethyl silyl)- naphthalene 5 as the minor product (19%).[20] Reactions of aromatic aldehydes and ketones with sodium naphthalenide lead to reduction and reductively coupled products 6 and 7 respectively (Chart. 1), which reflect either a one or two electron reduction.[21]

Ethers are the solvents of choice in the preparation and reactions of alkali metal aromatic radical anions and dianions. The formation of anion radicals are highly dependent on solvation.[22] Ethers react with radical anions and dianions more slowly than other functional groups. The overall reaction of the ethers is the cleavage (Chart 1).[23] Naphthalene, anthracene and phenanthrene have been treated with carbondioxide to give dicarboxylic acids 8 and 9 as major products.[24]

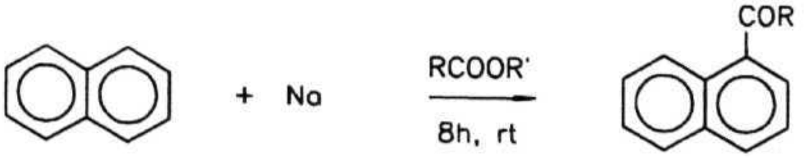
2.2. Results and Discussion

2.2.1 Reaction of aromatic anion radicals with carboxylic acid esters:

It has been briefly reported that the reaction of sodium naphthalenide and ethyl laurate leads to the formation of mono lauryl naphthalene in 60% yield.[25] The author of this excellent review article indicated that the alkylation products are dihydronaphthalene derivatives.[21] Unfortunately, the author did not describe the experimental conditions. To our knowledge, no other report appeared on this reaction. It was also mentioned in the review article that the reaction of ethyl benzoate with sodium naphthalenide resulted in reductive coupling to give benzoin and benzil as products originating via routes in which the naphathalenide functions as an electron donor.[21] Again, unfortunately, the experimental detail was not described and the findings were the unpublished results of the authors research group.[21]

We have found that the reaction of the sodium naphthalenide with carboxylic acid esters leads to the formation of the corresponding formyl and acyl aromatic compounds in moderate to good yields (Scheme 4).

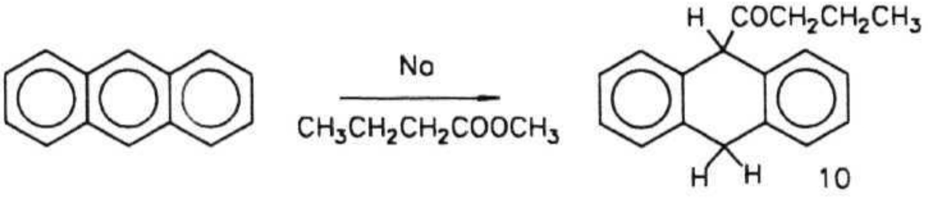
Scheme **4.**



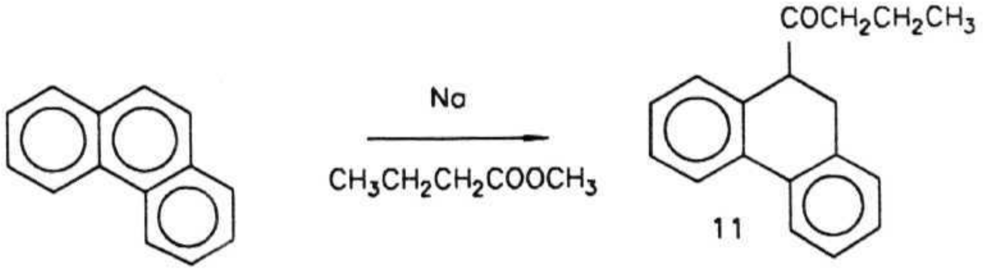
R	Yield (%)
$CH_2CH_2CH_3$	74
CH_3	60
H	55

The reactions were carried out utilizing the aromatic hydrocarbon (10 mmol), sodium (10 mmol) in THF (60 ml) and the aliphatic ester (5 mmol) to obtain the corresponding aromatic ketones in moderate to good yields (43-74%) (Table 1).

The reaction with methyl butyrate in the case of anthracenide and phenanthrenide resulted in dihydro aromatic compounds 10 and 11 respectively (Eq. 9,10).

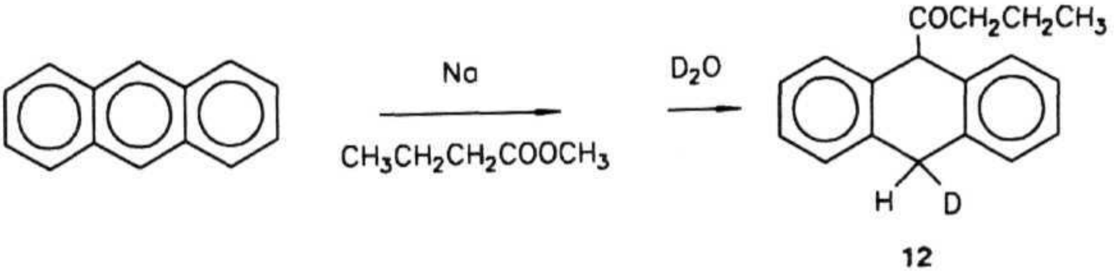


—(9)



—(10)

However, in the case of ethyl formate all hydrocarbons gave the aromatic aldehydes (entries 5-7, Table 1). In order to further examine the difference in the case of the anthracenide, we have carried out an experiment in which the quenching of the reaction was carried out with D_2O. It was found that one of the benzylic hydrogen was replaced by deuterium in this case (Eq. 11)



12

—(11)

This observation may also throw light on the course of this reaction. The mechanisms of the reactions of electrophiles with aromatic anion radicals have not been studied in detail. Weissman proposed a nucleophilic path for carboxylation of aromatic radical anion with carbon dioxide.[-u] A tentative mechanism may be visualized for the transformations observed here (Scheme 5).

Scheme 5.

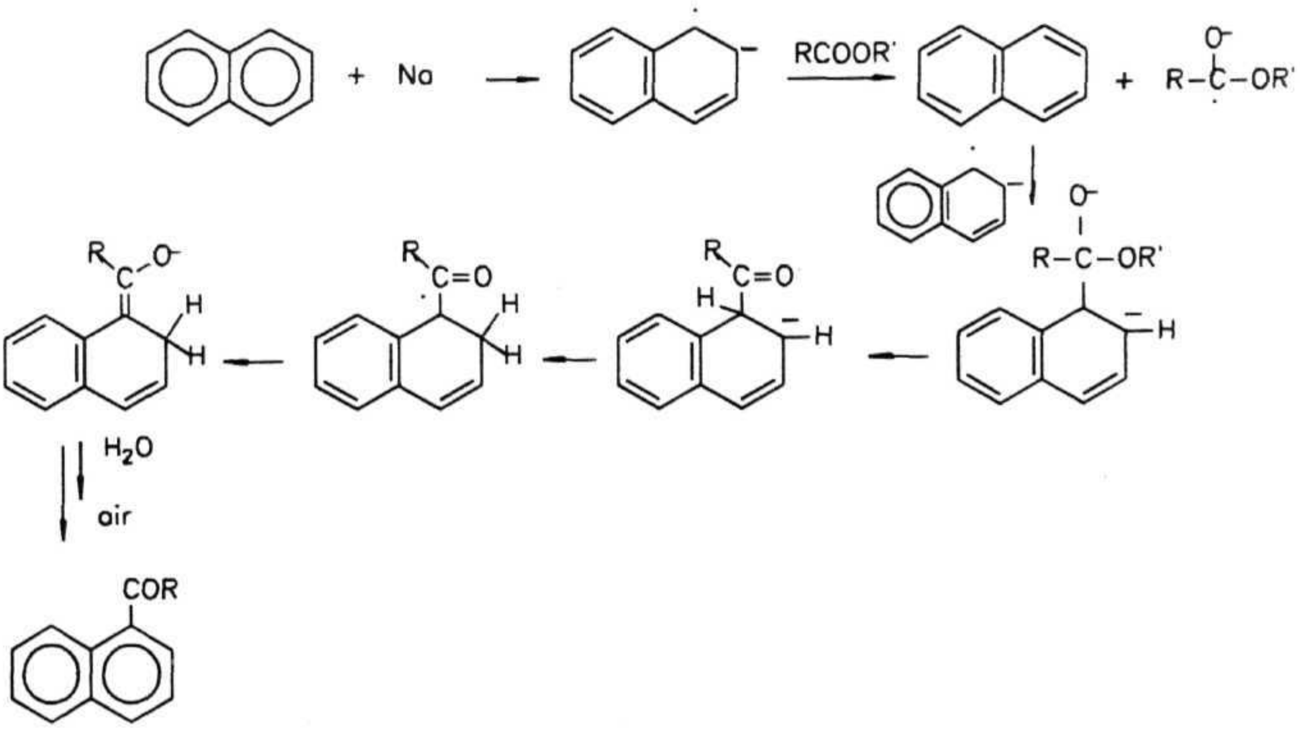
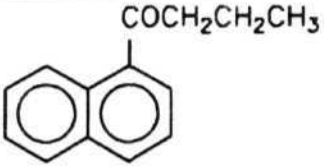
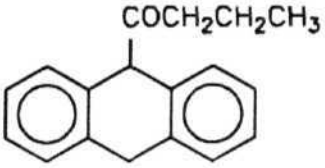
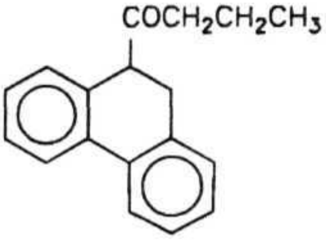
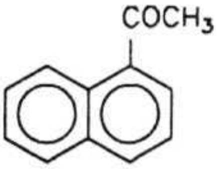
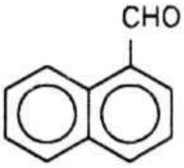
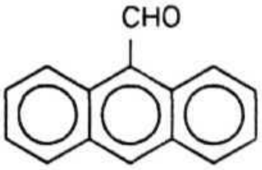
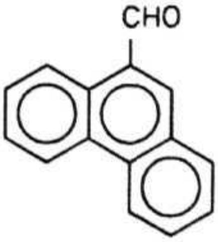


Table 1: Reaction of aromatic radical anions with carboxylic acid esters.

Entry[a]	Aromatic Hydrocarbon	Ester	Product[b]	Yield %[c]
1.	Naphthalene	$CH_3CH_2CH_2COOCH_3$		74
2.	Anthracene	$CH_3CH_2CH_2COOCH_3$		68
3.	Phenanthrene	$CH_3CH_2CH_2COOCH_3$		63
4.	Naphthalene	$CH_3COOC_2H_5$		60
5.	Naphthalene	$HCOOC_2H_5$		55
6.	Anthracene	$HCOOC_2H_5$		49
7.	Phenanthrene	$HCOOC_2H_5$		43

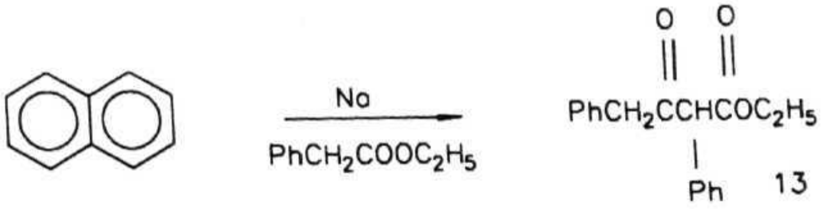
a. In all cases, the reactions were carried out using aromatic hydrocarbon (10 mmol), sodium (10 mmol) and ester (5 mmol) in THF (60 ml) for 8h at room temperature.

b. All products were identified by spectral data (IR, ^{1}H and ^{13}C NMR)

c. Yields are of isolated products, based on the ester utilized.

Presumably, the dihydro derivative undergoes air oxidation in the case of naphthalene. Whereas, in the case of anthracene and phenanthrene the corresponding dihydroaromatic derivatives are obtained.

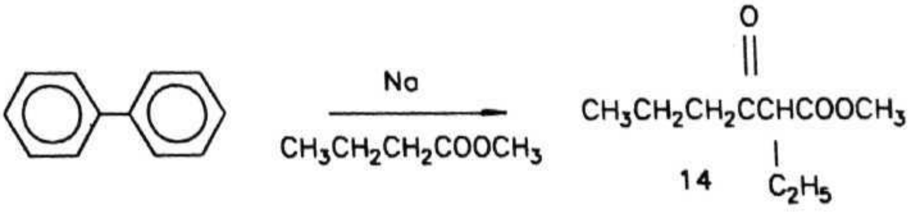
In the case of the readily enolizable ethyl phenylacetate, only the corresponding condensation product 13 was obtained (Eq. 12)



$$PhCH_2\overset{O}{\overset{\|}{C}}\underset{\underset{Ph}{|}}{C}H\overset{O}{\overset{\|}{C}}OC_2H_5$$

13 —(12)

Also, sodium biphenylide on reaction with esters resulted only in the formation of Claisen condensation product 14 (Eq. 13).

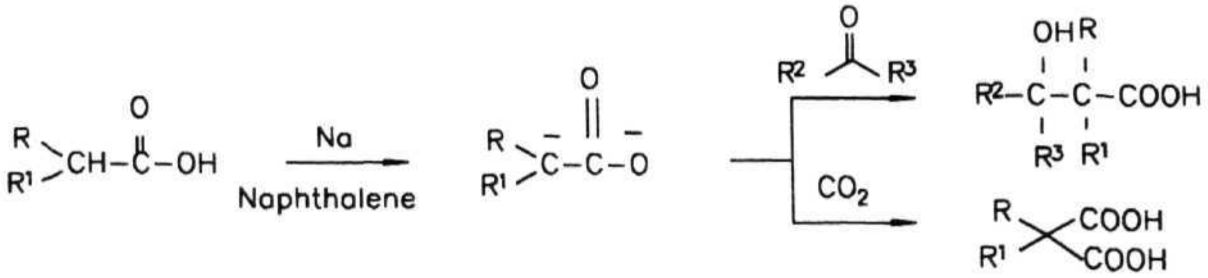


$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}\underset{\underset{C_2H_5}{|}}{C}HCOOCH_3$$

14 –(13)

Formation of such condensation reactions is not entirely unexpected as it is known that the alkali metal aromatic radical anions have been used in such applications (Scheme. 6).[21,27]

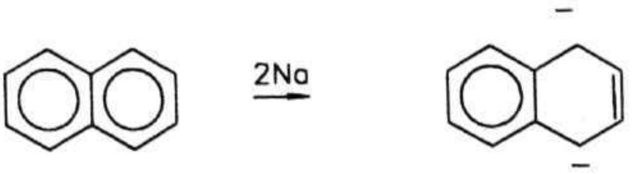
Scheme 6.



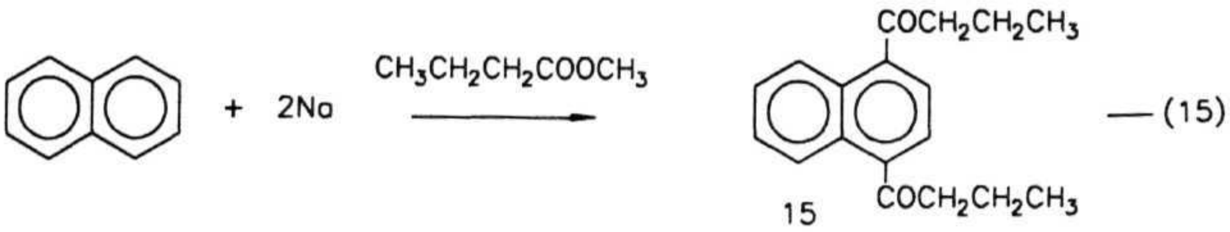
In the experiments carried out during the present studies, in all cases small amounts of unidentified polar compounds have been also obtained as side products. Presumably, these products result from the competing condensation reactions described above.

2.2.2. Reactivity of the dianions:

Formation of the dianion of naphthalene was first reported by Shatenshtein *et. al.*, and later by Smid.[28-30] It can be readily prepared by the addition of 2 eq of sodium to 1 eq of naphthalene in THF (Eq. 14).

 —(14)

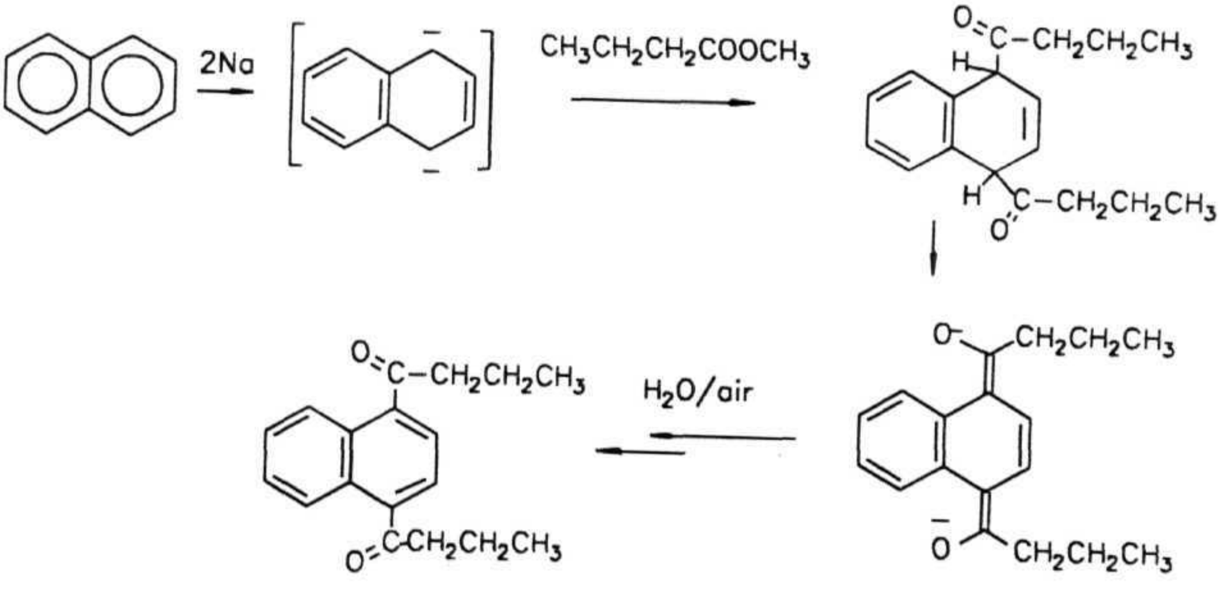
We have observed that the dianion prepared in this way reacts with methyl butanoate to give 1,4-diacylnaphthalene 15 (Eq. 15).



15 — (15)

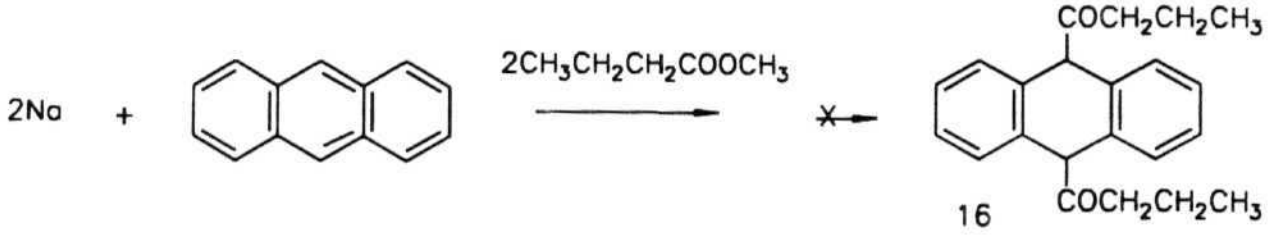
The reaction was carried out using naphthalene (10 mmol), sodium (20mmol) and methyl butanoate (10 mmol) for 8h at room temperature to obtain the corresponding 1,4-diacylnaphthalene in 43% yield. It was found that the 1-acylnaphthalene on reaction with sodium did not yield this product. This indicates that this reaction does not go through the initial formation of the monoacylated products. Perhaps, in this case the reaction goes through the mechanism outlined in Scheme 7.

Scheme 7.



Surprisingly, in the reaction with anthracene, the expected dihydro derivative 16 was not obtained (Scheme 8). Only, unidentified products were isolated.

Scheme 8.



16

2.2.3. Reaction of naphthalene anion radicals with CO.

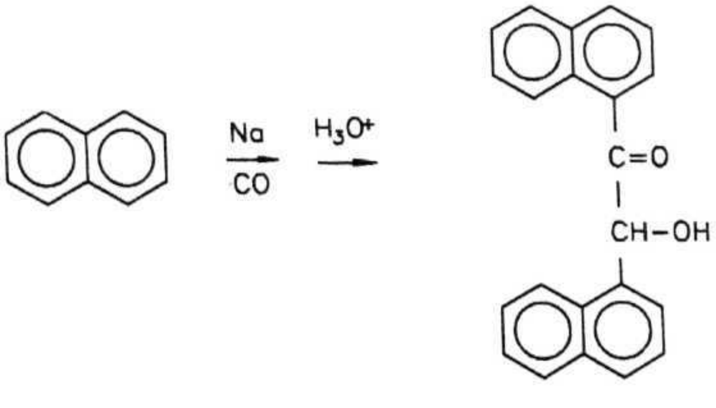
As outlined in introductory section, the $C_2O_2^{2-}$ has been prepared by the reduction of CO with molten potassium[5] or alkali metals in ammonia.[7] Although the latter method could be attractive for synthetic applications, the presence of trace amounts of NH_3 may not be suitable for the studies of the reactions with electrophiles. A more recent procedure utilizing Na/K alloy for the reduction requires the use of expensive crown ether as a solvent.[8] So, we decided to examine the use of readily accessible alkali metal naphthalenides for the reductive coupling of CO to obtain $C_2O_2^{2-}$ under ambient conditions (Eq. 16).

$$2CO \xrightarrow[\text{THF, 0°C}-\text{r.t}]{\text{Na/Naphthalene}} \overset{+}{Na}\overset{-}{O}-C\equiv C-\overset{-}{O}\overset{+}{Na} \qquad \text{— (16)}$$

Preliminary results revealed that the naphthalene is participating in the product formation as indicated by the formation of several naphthalene containing carbonyl products. This observation is not unexpected since it has been briefly reported that naphthalene anion radical gives intramolecular Cannizzarro reaction of the product derived from the initial carbonylation. However, the products were not identified.[3]

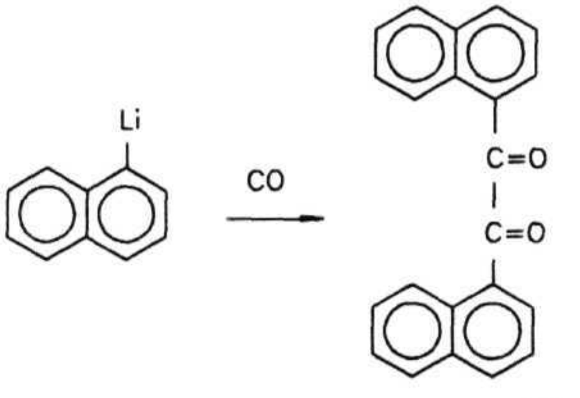
We have found that the reaction of a 1:1 mixture of naphthalene and sodium with CO gives several unidentified products. However, the reaction using sodium (20 mmol), naphthalene (10 mmol) in THF (60 ml), while passing carbon monoxide for 10 hours at room temperature followed by usual work up, resulted in the isolation of a major product which has been identifed *frs* 17 (Scheme 9), besides small amount of unidentified more polar side products.

Scheme 9.



17

Clearly, the reaction takes a different course compared to the literature report which describes intramolecular Cannizzarro reaction.[3] However, the reactivity observed here is reminescent of the reaction of carbon monoxide with 1-naphthyllithum which has been reported to give the corresponding 1,2-diketone 18 under certain conditions (Eq. 17).[31]

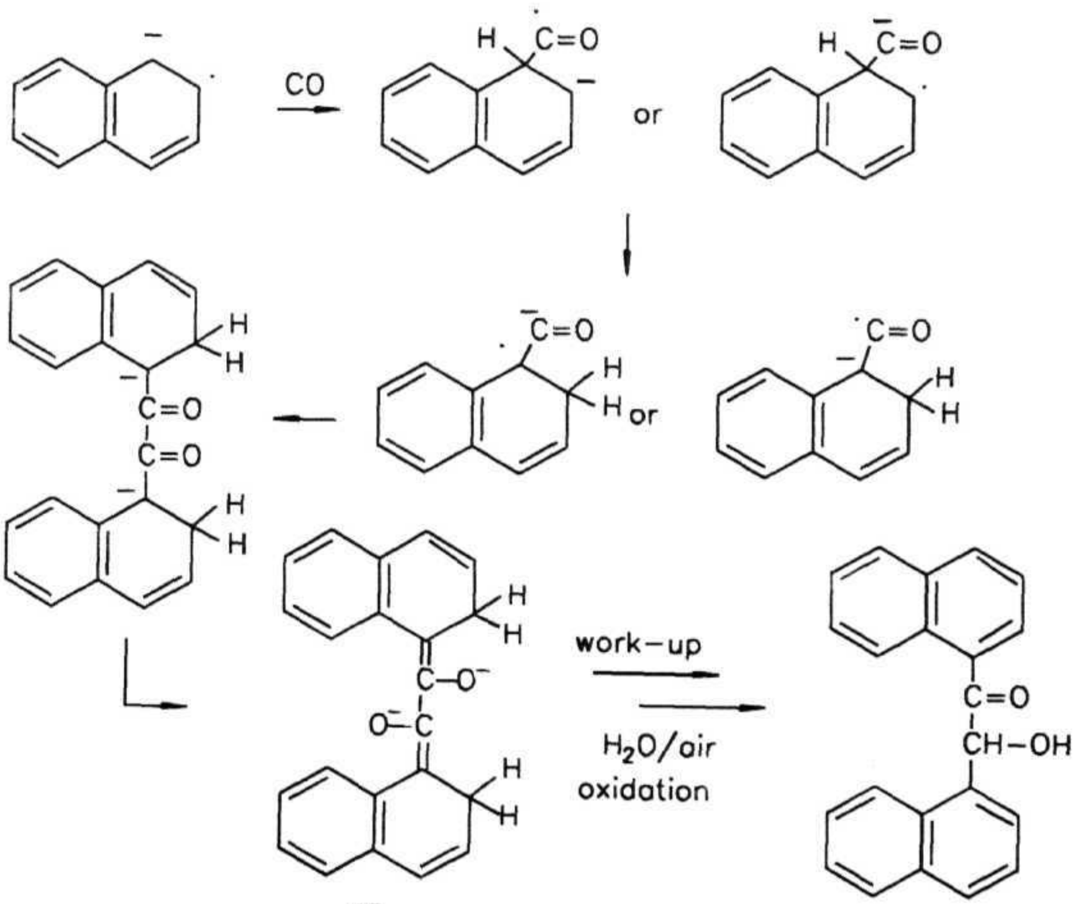


— (17)

18

The carbonylation reaction in the present case also may go through similar dimerization reaction of the anions or radicals (Scheme 10).

Scheme 10.



19

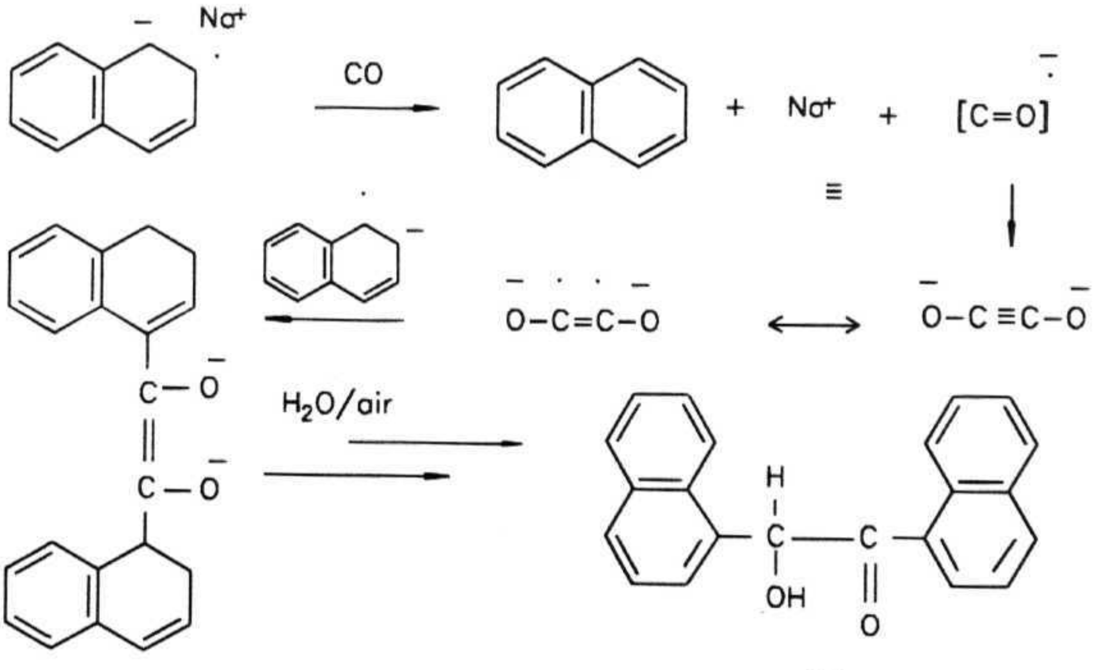
17

Very recently, **Nudelman** *et. al,* presented evidence for electron transfer mechanism in the reaction of RLi with CO to give the corresponding cation radical- anion radical pair (Eq. 18).[32]

$$\mathrm{Ar{-}Li} + \mathrm{CO} \longrightarrow [\mathrm{ArLi}]^{\dot{+}}\ [\mathrm{CO}]^{\dot{-}} \qquad (18)$$

A similar reaction of naphthlene anion radical would lead to the anion radical of CO which could then **dimerize** to give $C_2O_2^-$ (Scheme 11). If this $C_2O_2^{2-}$ could behave like a dianion radical then it could react with naphthalene anion radical (2 equivalents) to give the intermediate 20 which on workup/air oxidation could yield the observed product.

Scheme 11.



20

17

However, we do not have any evidence/data in support of these mechanisms and the intermediates involved.

2.2.4. Conclusion

New methods of nucleophilic formylation and acylation of alkali metal aromatic radical anions, utilizing readily available aromatic hydrocarbon such as naphthalene, anthracene and phenanthrene have been developed. The radical anions prepared in this way react with aliphatic esters such as methyl butanoate, ethyl formate, ethyl acetate to give the corresponding acylated and formylated aromatic and dihydro aromatics in moderate to good yields. The brief investigation undertaken on the synthesis and reactivity of the dianions is also promising for further development.

Although the preliminary efforts on the reductive coupling of carbon monoxide to obtain the $C_2O_2^{2-}$ and the reactivity of the species with various Michael acceptors and ketene traps were not fruitful, the results obtained on the double carbonylation of naphthalene anion radical will be useful in the synthesis of such compounds.

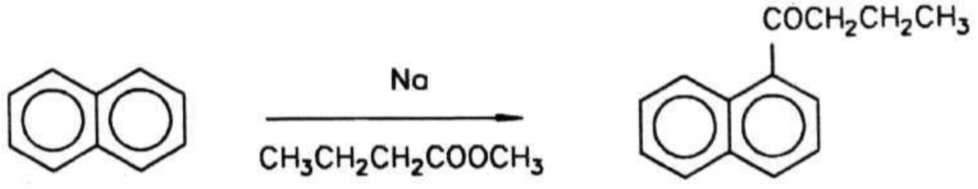
2.3 : Experimental Section:

2.3.1: General Information:

Several informations given in the experimental section of Chapter 1 are also applicable for the experiments outlined here. **All** aromatic hydrocarbon samples were sublimed before use. The esters utilized **were** commercial samples or prepared following standard procedures.[33]

2.3.2: Nucleophilic acylation of naphthalene with methyl butanoate:

Sodium (0.23 g, 10 mmol) was added to naphthalene (1.28 g, 10 mmol) in THF (60 ml) and stirred for 30 minutes at room temperature under nitrogen atmosphere. Methyl butanoate (0.5 g, 5 mmol) was added to the stirred reaction mixture of the naphthalene anion radical and further stirred for 8h at room temperature. The resulting mixture was quenched with dil.HCl (10 ml) and the organic phase was separated. The aqueous phase was extracted with ether (2 x 30 ml). The combined organic extract was washed with water (40 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column and n-propyl-1-naphthyl ketone 21 was isolated in 79% using 3% ethyl acetate in hexane as eluent.



21

Yield : 74% (0.73 g)

B.P. : 180°C/12mm {lit.[34] B.P. 178-179°C/12mm}

IR (neat) : 3025, 2950, 1680, 1460, 760 cm^{-1}

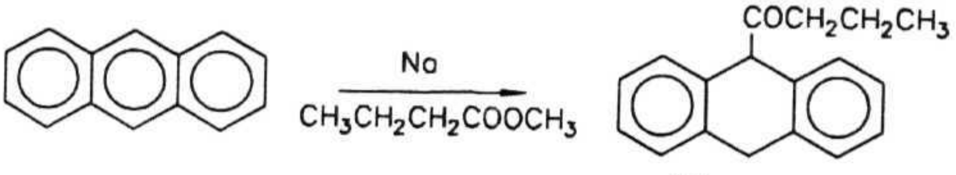
^{1}H NMR : δ ppm 0.8 (t, 3H), 1.6 (m, 2H), 2.7 (t, 2H), 7.0–7.6 (m, 7H) (Spectrum no. 12)

^{13}C NMR : δ ppm 13.3, 17.9, 43.8, 124.2, 125.7, 126.2, 127.1, 127.5, 128.3, 132.1, 133.8, 136.2, 204.5. (Spectrum no. 13)

Ms (m/z) : 198 (M^{+}, 40%), 127 (100%). (Spectrum no. 14)

The above procedure was followed for the acylation of anthracene and phenanthrene (entries 2.3.3 and 2.3.4). The physical constant and spectral data obtained are summarized below.

2.3.3



10

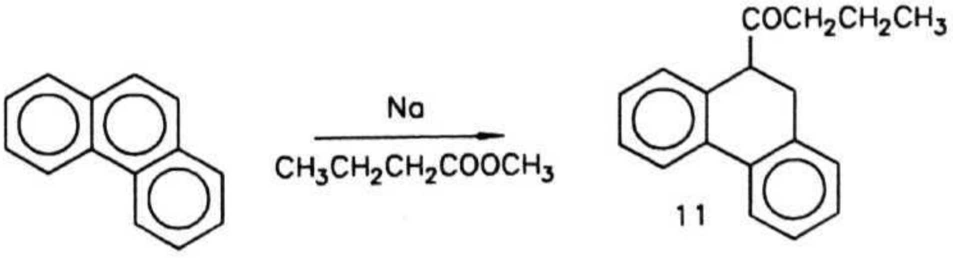
Yield : 68% (0.85 g)

IR (neat) : 3022, 2962, 2874, 1711, 1452, 1122, 740 cm^{-1}

^{1}H NMR : δ ppm 0.76 (t, 3H), 1.49 (m, 2H), 2.39 (t, 2H), 4.0–4.2 (dd, 2H), 5.0 (s, 1H), 7.3 (m, 8H) (Spectrum no. 15)

^{13}C NMR : δ ppm 13.2, 16.9, 35.2, 41.3, 60.8, 126.3, 126.8, 127.1, 128.1, 128.6, 133.5, 135.7, 207.1. (Spectrum no. 16)

2.3.4



11

Yield : 63% (0.78 g)

IR (neat) : 3028, 2961, 2874, 1709, 1454, 1130, 742 cm^{-1}

^{1}H NMR : δ ppm 0.8 (t, 3H), 1.5 (m, 2H), 2.3 (t, 2H), 3.2-3.4 (dd, 2H), 3.8 (s, 1H), 7.2-7.9 (m, 8H)

^{13}C NMR : δ ppm 13.6, 16.9, 31.4, 42.8, 52.2, 123.7, 124.3, 127.3, 127.8, 128.2, 128.7, 129.4, 133.7, 134.8, 135.1, 210.3.

2.3.5: Reduction of **the** ketone **21 to 1-naphthylbutanol using $NaBH_4$**

Sodium borohydride (0.19 g, 5 mmol) was added to the ketone 21 (0.5 g, 2.5 mmol) in THF 15 ml. Water (2-3 drops) was added and the mixture was stirred for 2h at room temperature. The reaction was quenched with water (5 ml). Ether (20 ml) was added and the organic phase was seperated. The aqueous phase was extracted with ether (2 x 20 ml). The combined organic extract was successively washed with water (30 ml), brine (20 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column using 5% ethyl acetate in hexane to obtain the α-naphthyl-1-butanol quantitatively.

IR (neat) : 3368, 3051, 2957, 2872, 1458, 1028, 798, 777 cm"^{1}

^{13}C NMR : 6 ppm 13.8, 19.2, 40.4, 70.7, 122.8, 122.9, **125.4,** 125.8, 127.7, 128.8, 130.4, 133.8, 140.7.

This experiment was carried out to ascertain the nature of the carbonyl group in the starting material.

2.3.6: Examination of D_2O incorporation in the acylation reaction of anthracene with methyl butanoate:

Sodium (0.23 g, 10 mmol) was added **to** anthracene (1.78 g, 10 mmol) in THF (60 ml) and the mixture stirred for 30 minutes at room temperature under nitrogen atmosphere. Methyl butanoate (0.5 g, 5 mmol) was added to this reaction mixture of anthracene anion radical and further stirred for 8h at room temperature. The resulting mixture was quenched with D_2O (0.1 g, 5 mmol) and stirred for 1h at room temperature. Dil. HC1 (10 ml) was added and the organic phase was separated. The aqueous phase was extracted with ether (2 x 30 ml). The combined organic extract was washed with water (40 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column and deuterium incorporated n-propyl-9-anthryl ketone 12 was isolated in 70% yield using 5% ethyl acetate *in* hexane as eluent.

Yield : 70% (0.88 g)

IR (neat) : 3020, 2962, 2874, 1707, 1452, 744 cm''^{1}

^{1}H NMR : 6 ppm 0.8 (t, 3H), 1.6 (m, 2H), 2.4 (m, 1H), 4.0-4.4 (dd, 2H), 5.1 (s, 1H), 7.4 Cm, 8H)

^{13}C NMR : δ ppm 13.6, 17.2, 35.5, 41.7(t-CHD), 61.3, 126.7, 127.5, 128.4, 128.5, 133.8, 136.0, 207.7.(Spectrum no. **18)**

2.3.7: Nucleophilic acylation of naphthalene with ethyl acetate:

Sodium (0.23 g, 10 mmol) was added to naphthalene (1.28 g, 10 mmol) in THF (60 ml) and stirred for 30 minutes at room temperature under nitrogen atmosphere. Ethyl acetate (0.44 g, 5 mmol) was added to the stirred reaction mixture of naphthalene anion radical and further stirred for 8h at room temperature. The resulting mixture was quenched with dil.HCl (10 ml) and the organic phase was separated. The aqueous phase was extracted with ether (2 x 30 ml). The combined organic extract was washed with water (40 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column using 2% ethyl acetate in hexane as eluent to obtain **1-acetylnaphthalene** in 65% yield.

Yield : 60% (0.50 g)

B.P. : 155-156^{o}C/15mm {lit.[34] B.P. 148-150°C/8mm}

IR (neat) : 3051, 2928, 1678, 1240, 802, 775 cm"^{1}

^{1}H NMR : 6 ppm 2.7 (s, 3H), 7.4-8.0 (m, 7H)

^{13}C NMR : 6 ppm 29.9, 124.4, 126.1, 126.5, 128.1, 128.5, 128.7, 130.2, 133.0, 134.1, 135.6, 201.8.

2.3.6: Nucleophilic formylation of naphthalene with ethyl formate:

Sodium (0.23 g, 10 mmol) was added to naphthalene (1.28 g, 10 mmol) in THF (60 ml) and stirred for 30 minutes at room temperature under nitrogen atmosphere. Ethyl formate (0.37 g, 5 mmol) was added to the stirred reaction mixture of naphthalene anion radical and further stirred for 8h at room temperature. The resulting mixture was quenched with dil.HCl (10 ml) and the organic phase was separated. The aqueous phase was extracted with ether (2 x 30 ml). The combined organic extract was washed with water (40 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column using 2% ethyl acetate in hexane as eluent to isolate **1-naphthaldehyde** in 55% yield.

Yield : 55% (0.43 g)

B.P. : $152^{\circ}C/15mm$ {lit.^{35} B.P. $150^{\circ}C/13mm$}

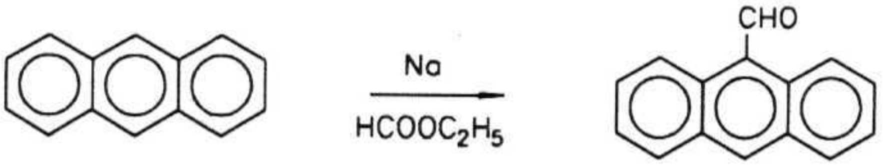
IR (neat) : 3057, 2934, 2725, 1689, 1168, 802, 773 cm^{-1}

^{1}H NMR : δ ppm 7.4-8.2 (m, 7H), 9.3 (s, 1H)

^{13}C NMR : δ ppm 124.9, 127.0, 128.5, 129.1, 133.4, 135.3, 136.6, 193.5.

The above procedure was followed for the formylation of anthracene and phenanthrene (entries 2.3.9 and 2.3.10). The physical constant and spectral data obtained are summarized below.

2.3.9:



22

Yield : 49% (0.50 g)

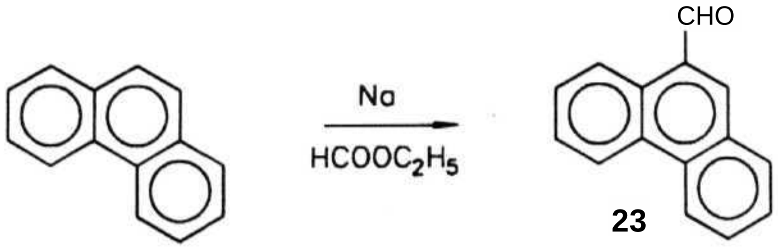
M.P. : $103^{\circ}C$ {lit.^{36} M.P. $104-105^{\circ}C$}

IR (KBr) : 3024, 2924, 2728, 1668, 1282, 1047, 731 cm^{-1}

^{1}H NMR : δ ppm 7.5-9.0 (m, 9H), 11.5 (s, 1H)

^{13}C NMR : δ ppm 123.5, 125.6, 127.1, 128.2, 129.1, 130.9, 133.9, 135.1, 193.7.

2.3.10:



23

Yield : 43% (0.44 g)

M.P. : 101°C {lit.^{37} M.P. $99-100^{\circ}C$}

IR (KBr) : 3059, 2926, 2729, 1689, 1454, 1066, 746 cm^{-1}

^{1}H NMR : δ ppm 7.8-9.0 (m, 9H), 10.64 (s, 1H)

^{13}C NMR : δ ppm 122.8, 123.0, 126.0, 127.3, 127.7, 128.3, 130.2, 130.4, 141.3, 193.6.

2.3.11: Attempted nucleophilic acylation of naphthalene using ethyl phenylacetate:

Sodium (0.23 g, 10 mmol) was added to naphthalene (1.28 g, 10 mmol) in THF (60 ml) and stirred for 30 minutes at room temperature under nitrogen atmosphere. Ethyl phenylacetate (0.82 g, 5 mmol) was added to the stirred reaction mixture of naphthalene anion radical and further stirred for 8h at room temperature. The resulting mixture was quenched with dil.HCl (10 ml) and the organic phase was separated. The aqueous phase was extracted with ether (2 x 30 ml). The combined organic extract was washed with water (40 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica *gel* column using 5% ethyl acetate in hexane eluted the Claisen condensation product 13 which was identified by spectral data.

IR (neat) : 3032, 2982, 1736, 1693, 1454, 1030, 754 cm^{-1}

^{13}C NMR : δ ppm 14.1, 41.4, 49.1, 60.7, 124.3, 124.8, 126.4, 126.7, 127.5, 127.9, 128.5, 128.6, 129.0, 129.2, 134.3, 135.1, 171.4, 192.0.

In the attempted nucleophilic acylation reaction of naphthalene with methyl benzoate following the above procedure, the starting material was isolated quantitatively.

2.3.12: Attempted nucleophilic acylation of biphenyl with methyl butanoate:

Sodium (0.23 g, 10 mmol) was added to biphenyl (1.54 g, 10 mmol) in THF (60 ml) and stirred for 4h at room temperature under nitrogen atmosphere. Methyl butanoate (0.5 g, 5 ml) was added to the reaction mixture and further stirred for 8h at room temperature. The resulting mixture was quenched with dil.HCl (10 ml) and the organic phase was separated. The aqueous phase was extracted with ether (2 x 30 ml). The combined organic extract was washed with water (40 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column using 4% ethyl acetate in hexane to elute the Claisen condensation product 14 quantitatively.

IR (neat) : 2900, 2850, 1735, 1700, 1440, 1190, 1020 cm"^{1}

^{13}C NMR : δ ppm 11.6, 13.2, 16.6, 21.3, 43.5, 51.8, 60.1, 170.0, 204.7.

2.3.13: Nucleophilic diacylation of naphthalene with methyl butanoate:

Sodium (0.46 g, 20 mmol) was added to naphthalene (1.28 g, 10 mmol) in THF (60 ml) and stirred for 1h at room temperature under nitrogen atmosphere. Methyl butanoate (1.0 g, 10 mmol) was added to the reaction mixture and further stirred for 8h at room temperature. The resulting mixture was quenched with dil.HCl (10 ml) and the organic phase was separated. The aqueous phase was extracted with ether (2 x 30 ml). The combined organic extract was washed with water (40 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column to obtain 1,4-diacylnaphthalene 15 in 43% using 5% ethyl acetate in hexane as eluent.

Yield : 43% (1.15 g)

IR (neat) : 3032, 2961, 2874, 1709, 1456, 750 cm^{-1}

^{1}H NMR : 6 ppm 1.0 (t, *GE),* 1.9 (m, 4H), 3.0 (t, 4H), 7.5-8.4 (m, 6H) (Spectrum no. 19)

^{13}C NMR : δ ppm 13.17, 17.82, 44.6, 124.59, 125.83, 127.89, 130.41, 140.48, 204.3. (Spectrum no. 20)

Ms (m/z) : 268 (M^{+}, 30%), 225 (100%), 197 (30%), 126 (38%) (Spectrum no. 21)

2.3.14: Carbonylation reaction of naphthalene in the presence of sodium:

Sodium (0.46 g, 20 mmol) was added to naphthalene (1.28 g, 10 mmol) in THF (60 ml) and stirred for 30 minutes at room temperature under nitrogen atmosphere. Carbon monoxide was passed into the stirred dark green reaction mixture of naphthalene anion radical for 10h. The carbon monoxide atmosphere was replaced by N_2 and the resulting mixture was quenched with dil.HCl (10 ml). The organic phase was separated. The aqueous phase was extracted with ether (2 x 30 ml). The combined organic extract was washed with water (40 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column using 6% ethyl acetate in hexane as eluent to isolate the 1,1'-naphthoin in 70% yield.

Yield : 70% (1.1 g)

M.P. : 140°C {lit.[38] M.P. 138-139°C}

IR (KBr) : 3395, 3053, 1682, 1267, 1105, 738 cm^{-1}

^{1}H NMR : δ ppm 3.6 (br s, 1H), 4.97 (s, 1H), 7.5-8.3 (m, 14H)

^{13}C NMR : 6 ppm 65.5, 123.0, 127.1, 127.9, 128.9, 129.0, 129.5, 129.6, 130.7, 132.4, 136.1, 198.3.

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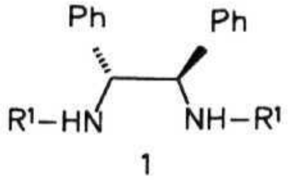
CHAPTER 3

INVESTIGATIONS ON THE REACTIVITIES OF THE $TiCl_4/Mg$ (POWDER) REAGENT COMBINATION

3.1. Background and Objectives:

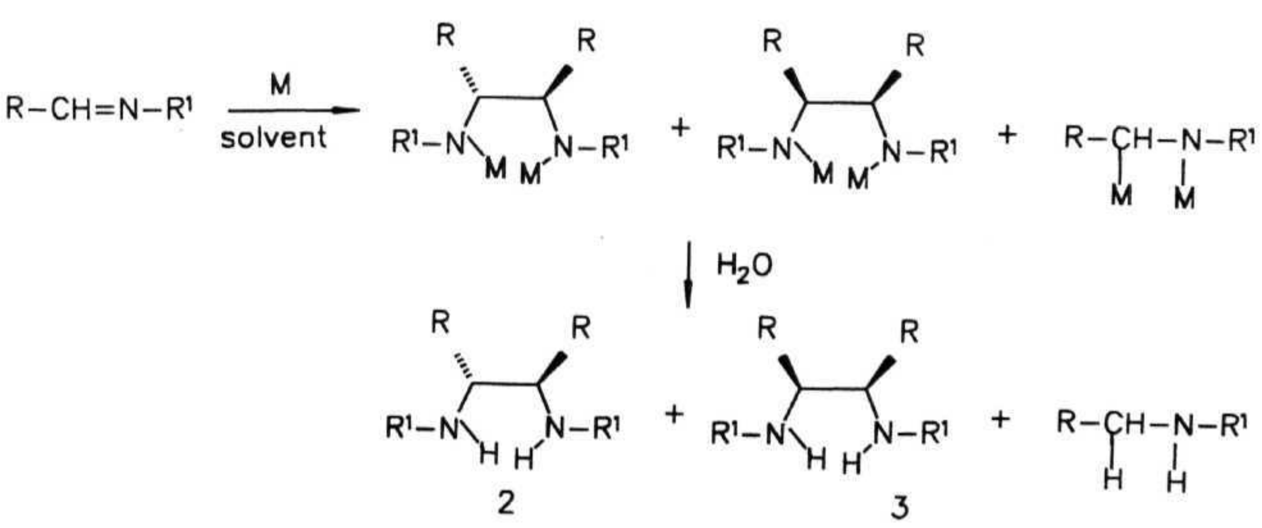
In connection with a research programme on the hydroborations and reductions using amine boranes,[1,2] we were looking for a method of synthesis of the chiral diamine system 1.



1

Several methods have been reported for the synthesis of such diamines (Scheme 1).[3] Under certain conditions, the reduction of imines (RCH = NR') proceeds with dimerization to give a diastereomeric mixture of N,N-disubstituted 1,2-disubstituted ethylenediamines 2 and 3. This reaction takes place when reducing agents such as sodium, magnesium and magnesium-magnesium iodide, aluminium and aluminum amalgam reagents are utilized.[4,5]

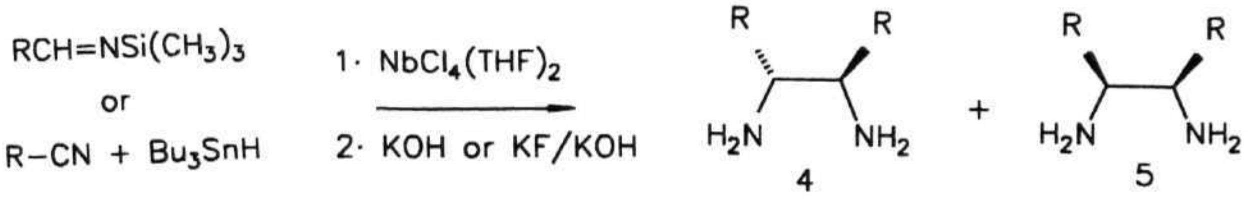
Scheme 1.



The reductive **dimerization** products are generally obtained as a 50:50 mixture of the diastereomeric diamines.[u]

Recently, a synthesis of unsubstituted vicinal **diamines** 4 and 5, potential precursors for the substituted amines has been reported. In this method, the starting material is either N-(trimethylsilyl)imines or nitriles and the reducing reagent is the niobium reagent, $NbCl_4(THF)_2$ (Scheme 2).[7]

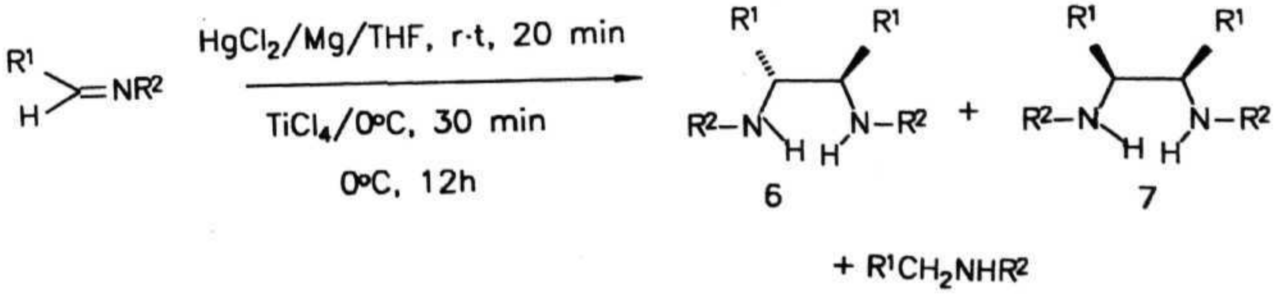
Scheme 2.



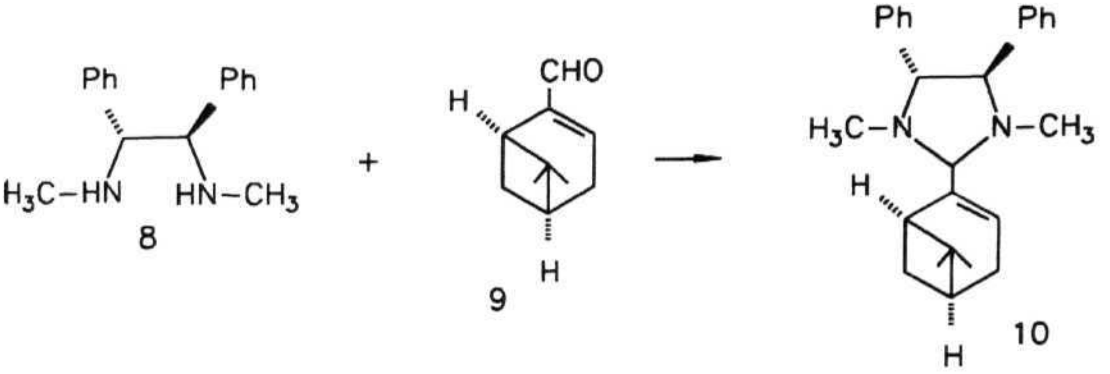
The dl and meso ratio is dependent on the nature of substituent R (19:1 for R is aryl and 2:1 for R is alkyl).

More recently, Alexakis and co-workers reported the synthesis of the symmetrical vicinal (R ,R)-dl-diamines 6 from the corresponding imines using low valent titanium species generated utilizing titanium tetrachloride and magnesium amalgam reagent system (Scheme 3).[u]

Scheme 3.

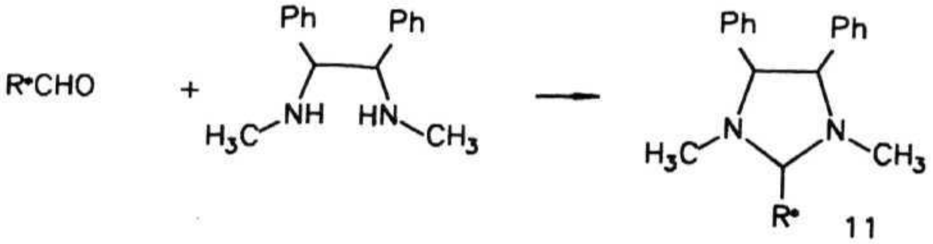


The ratio of the C_2 symmetric vicinal **(R ,R) -dl-diamines** and its **meso** (R , S) isomers obtained in this reaction is 80:20. These authors have also developed an efficient method for the resolution of the racemic **N,N'-dimethyl 1,2-diphenylethylenediamine** (DMPEDA) through fractional crystallization of the salts obtained using optically active tartaric acid. The resolved DMPEDA 8 was treated with an optically active (-)myrtenal 9 to obtain the corresponding imidazolidine 10 (Eq. 1).[9] Its diastereomeric purity was determined by NMR analysis to assess the optical purity of the starting diamine.



(1)

Recently, this chiral diamine system has been utilized in certain interesting applications (Eq. 2),[10]

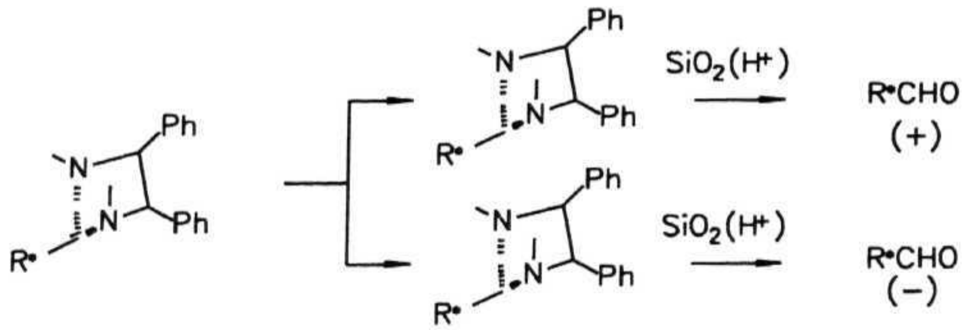


(2)

Enatiomeric purities of chiral aldehydes have been readily determined by ^1H NMR analysis of the **imidazolidines.** The diasteromeric **imidazolidines** were easily separated by silica gel column chromatography which can be

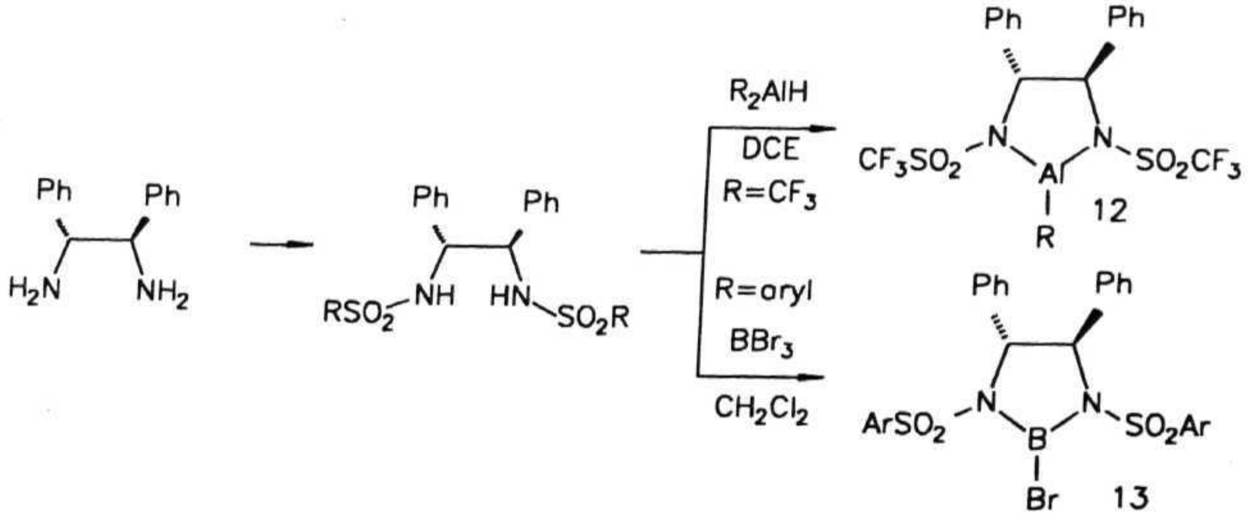
converted into enantiomerically pure aldehydes by acid hydrolysis (Scheme. 4).[10]

Scheme 4.



Corey *et. al.*, developed new useful chiral auxiliaries 12 and 13 using the corresponding unsubstituted vicinal diamine (Scheme 5).[11,12]

Scheme 5.



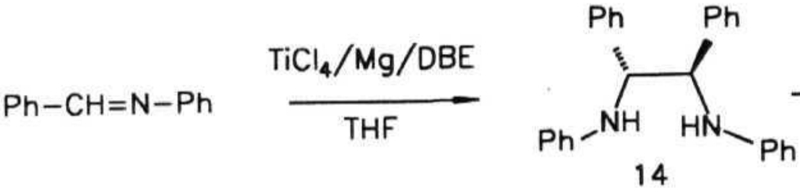
These reagents function effectively as chiral Lewis acids in a number of useful enantioselective Diels-Alder and aldol reactions.

In the course of the synthesis of these diamines from the corresponding imines through reductive coupling using the $TiCl_4/Mg$ (powder) combination, we have obtained certain interesting results and hence decided to investigate the reactivities of this reagent system further.

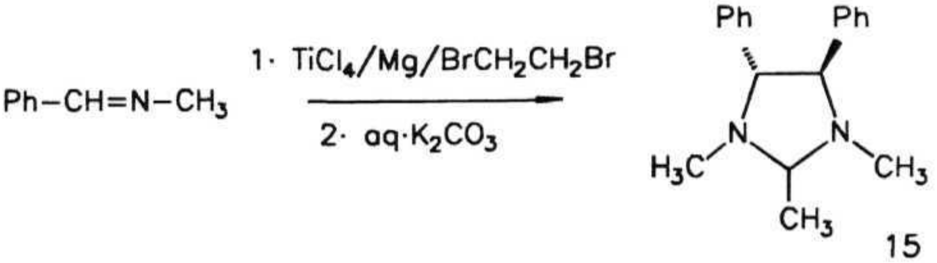
3.2. Results **and** Discussion

3.2.1. Reductive coupling of imines:

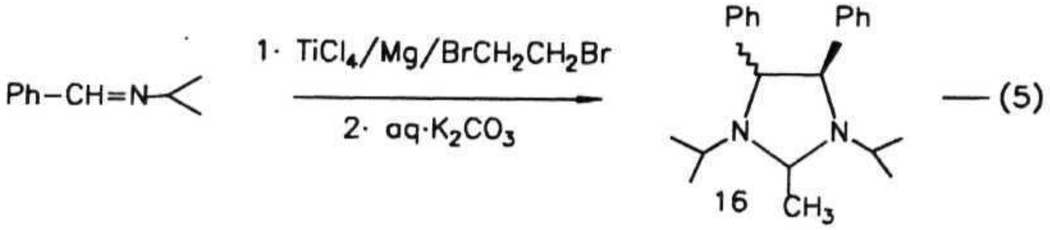
We have found that the the reaction of low valent titanium species generated by the **$TiCl_4$**/Mg(powder)/BrCH$_2$**CH**$_2$Br combination in THF with **N-phenylbenzalimine** gives **dl-N,N-diphenyl-1,2-diphenylethylenediamine** 14 (Eq. 3).


—(3)

However, when the reaction was carried out using the **N-methyl** derivative an unusual product was obtained which was identified as the corresponding cyclic derivative 15 (Eq. **4).**


—(4)

It was observed that the reagent prepared using **$TiCl_4$** (15 **mmol**), Mg powder (25 mmol) and **1,2-dibromoethane** (10 mmol) in THF (60 ml) at 0°C **on** reaction with **N-methylbenzalimine** (10 mmol) gives the **d,l-imidazolidine** derivative (54%) in 10 h at room temperature. The reaction has been found to be a general one as illustrated using certain other **N-alkyl** imines. The imidazolindine derivatives have been obtained in good yields (Table 1). Under these conditions, N-propyl and N-benzyl derivatives also give the corresponding d,l-imidazolidine derivatives. However, dl and meso in imidazolidine derivatives 16 were obtained in the case of N-cyclohexyl and N-isopropyl derivatives (Eq. 5). In the case of N-α-methylbenzyl derivative also mixture of diastereomers were obtained.



Initially, our interest was not on the studies of the mechanism of the formation of imidazolidine derivatives. However, later we became interested on studying the reactivity of the titanium species involved in this interesting transformation. We have utilized 1,2-diboromoethane in order to activate the magnesium.[13] So, it was first thought that the CH_3CH- grouping in the product could have come from the dibromoethane. Later, it was found that this transformation works equally well without using 1,2-dibromoethane (Eq. 6). However, the yields are somewhat less (20%) in these experiments.

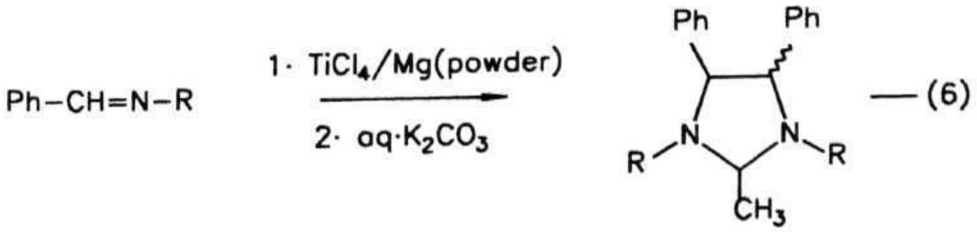
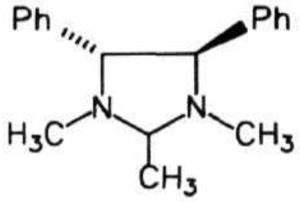
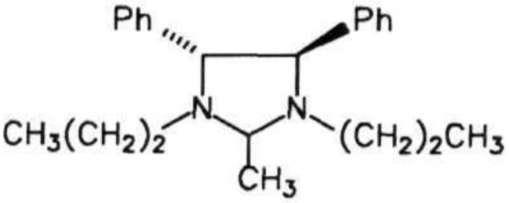
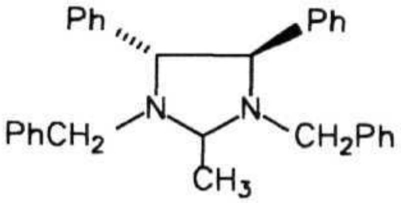
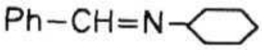
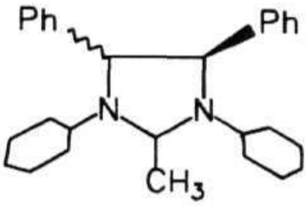
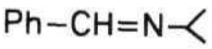
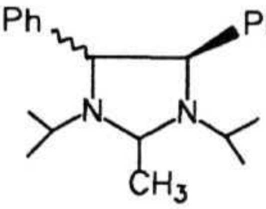
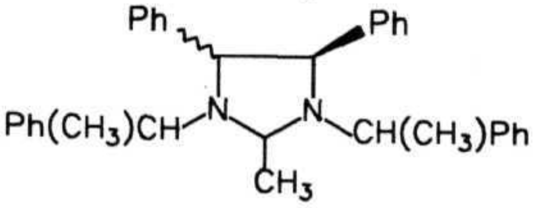


Table 1: Conversion of **imines** to **imidazolidine** derivatives using **$TiCl_4/Mg/BrCH_2CH_2Br$** system.

Entry[a]	Substrate	Product[b]	Yield %[c]
1.	Ph−CH=N−CH_3		54
2.	Ph−CH=N−$(CH_2)_2CH_3$		63
3.	Ph−CH=N−CH_2−Ph		70
4.			74
5.			66
6.	Ph−CH=N−CH(CH_3)Ph		58

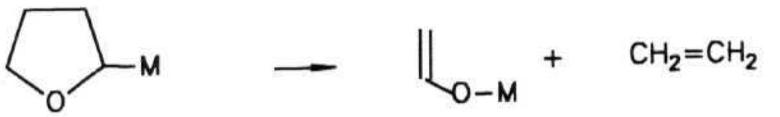
a. In al) entries the reactions were carried out using TiCl$_4$ (15 mmol), Mg (25 mmol) and 1,2-dibromoethane (10 mmol) at 0^{o}C in THF (60 ml) and the imines (10 mmol) at room temperature for 10h.

b) All products were identified by spectral data (IR, ^{1}H and ^{13}C NMR). Mass spectral data (ED was obtained for product 1. For products 3,4 and 6 satisfactory elemental analyses were also obtained (see experimental section).

o) Yields are of purified products based on the starting imine utilized.

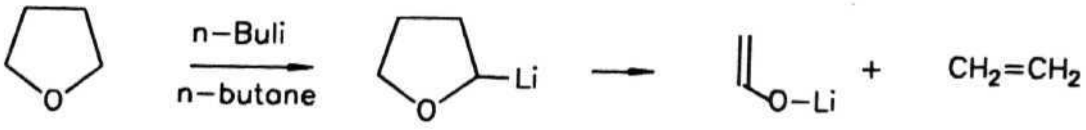
d) Isolated as a mixture of d,l- and meso-imidazolidine derivatives.

A possibility is that the TiCl$_4$/Mg system may generate certain reactive species of titanium and/or Mg-X species which might metal late THF, leading to cleavage of THF (Eq. 7).



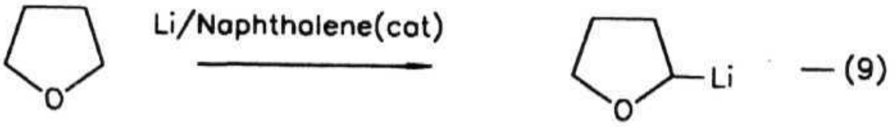
—(7)

This type of cleavage of tetrahydrofuran in the reaction with organometallic reagents is not uncommon. For example, n-BuLi abstracts proton from THF to give n-butane and metallated THF which undergoes further clevage into ethylene and enolate moieties (Eq. 8).[14]



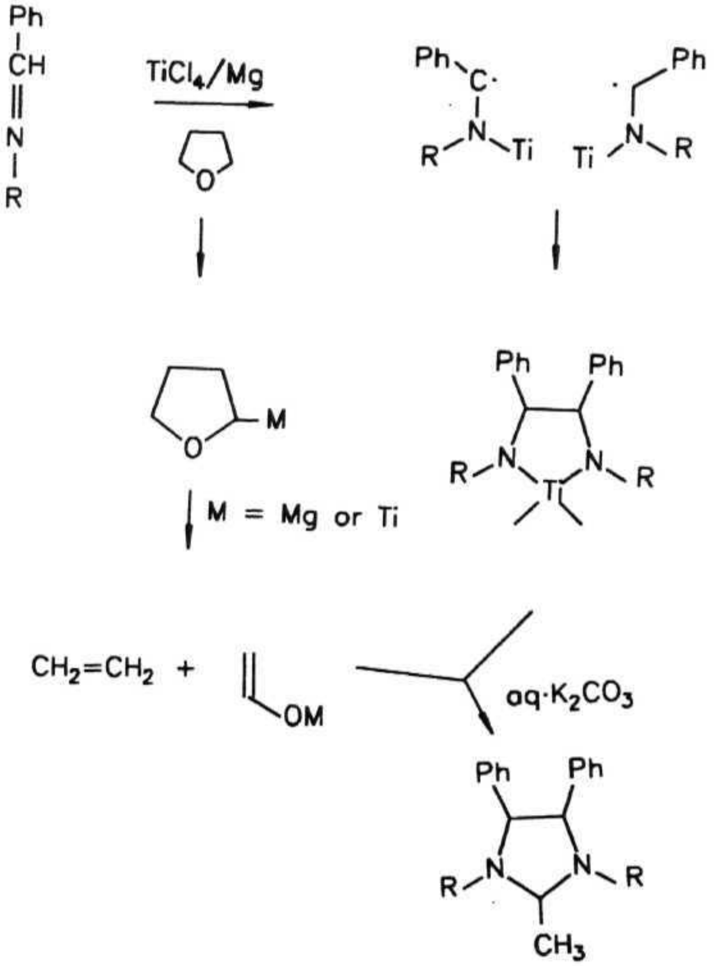
—(8)

More recently, it was reported that Li/naphthalene reagent combination **metallates** THF (Eq. 9).[15]



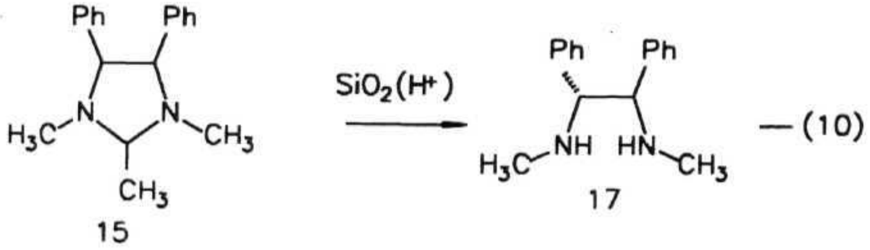
Keeping these observations in mind a tentative mechanism for this transformation may be visualised as shown in Scheme 6.

Scheme 6.



Presumably, the product diamine reacts with the acetaldehyde formed in the reaction of the metal enolate under the reaction conditions. As mentioned earlier in the introductory section, such cyclic compounds can be readily prepared through the reaction of aldehydes with the diamines following the procedure of Alexakis and co-workers (Eq. 1).[10]

The formation of imidazolidine derivatives in the reactions of imines with low valent titanium species generated by $TiCl_4$/Mg/DBE or $TiCl_4$/Mg (powder) combinations was further confirmed by hydrolysis of the cyclic derivative 15 with wet silica gel to obtain the C-symmetrical diamine 17 (Eq. 10).

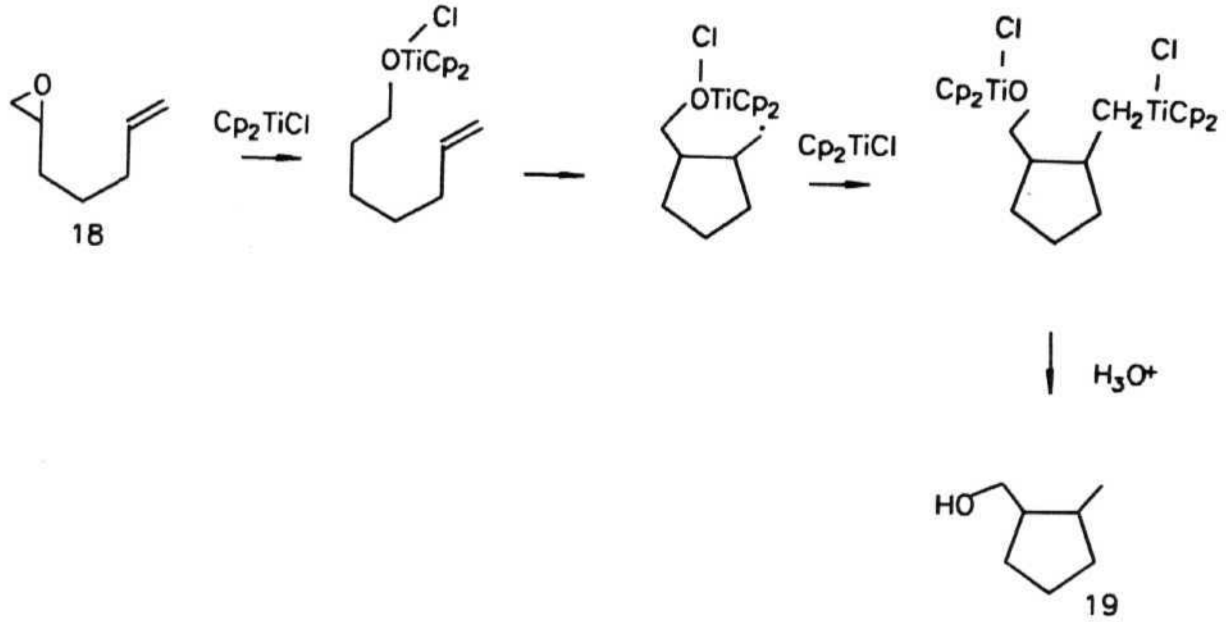


The McMurry type low valent Ti species are generally prepared in refluxing THF.[16] The Ti reagent is prepared under relatively mild conditions in the present studies. So, we have decided to examine the reactivity of the $TiCl_4$/Mg(powder) combination with different organic substrates.

3.2.2. Reductive coupling of olefins:

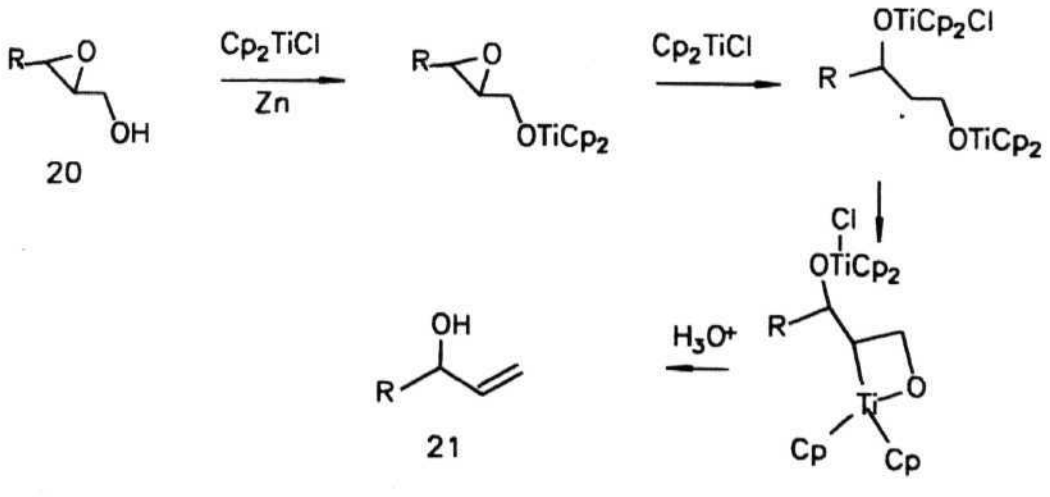
In recent years there is increased interest in the development of radical induced cyclization reactions. It has been reported that the Cp_2TiCl reagent or the Cp_2TiCl_2/Zn combination is useful in cyclizations involving radical intermediates. For example, Nugent and Rajanbabu have recently shown that epoxy olefins of the type 18 undergo Cp_2TiCl promoted cyclizations to obtain cyclopentane methanol 19 (Scheme 7).[17,18]

Scheme 7.



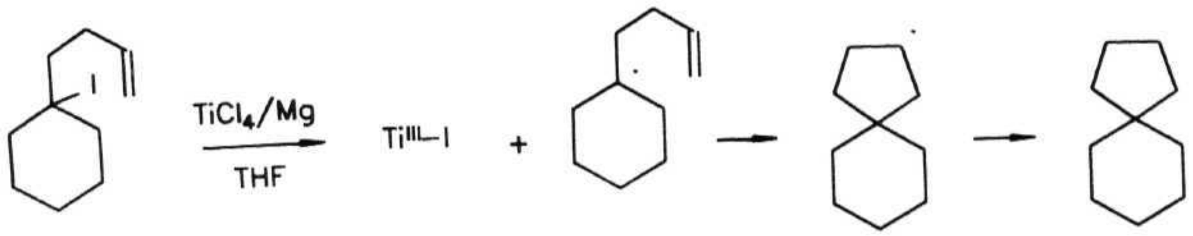
More recently, Yadav *et al* reported the titanocene induced regio selective deoxygenation of 2,3-epoxyalcohols 20 to obtain allylic alcohols 21 (Scheme 8).[19]

Scheme 8.



McMurry and others have shown that the Ti halides and reducing agent combinations lead to Ti(0) and other low valent titanium species.[20,21] We decided to examine such cyclization reactions starting from the alkenyl iodides of the type 22. It was thought that it may be possible to achieve radical cyclization product 23 outlined below (Scheme 9) using low valent titanium species generated by the $TiCl_4$/Mg (powder) combination.

Scheme 9.



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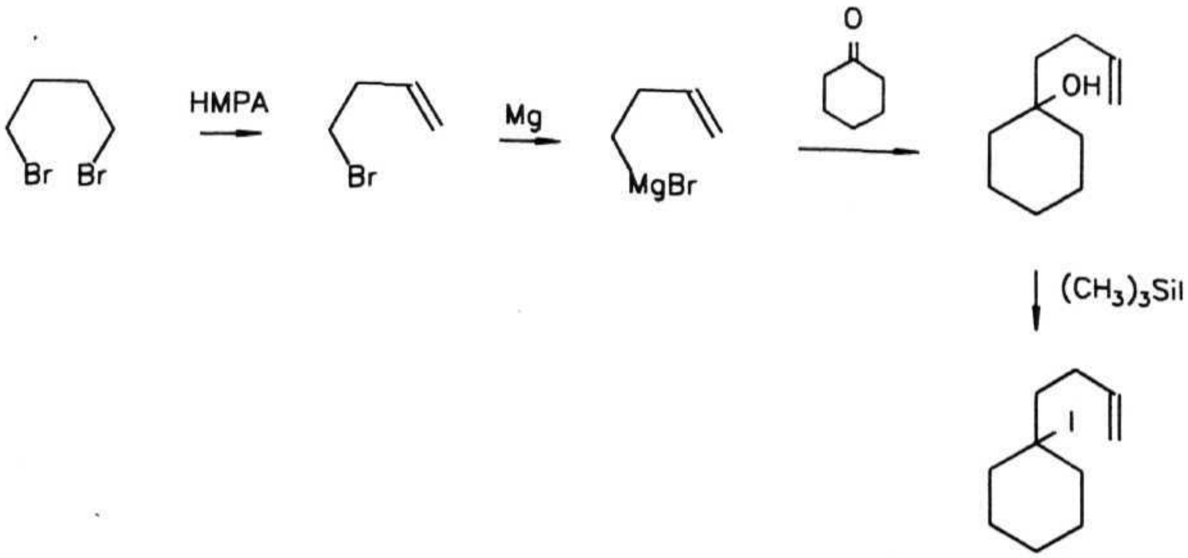
23

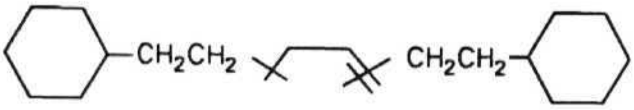
This alkenyl iodide 22 has been prepared using 1,4-dibromobutane and cyclohexanone following a closely related reported procedure (Scheme 10).[22–24]

Scheme 10.



22

It was found that the reaction of this alkenyl iodide (10 mmol) with the low valent titanium species generated using $TiCl_4$ (15 mmol) and Mg powder (25 mmol) in THF (60 ml) at room temperature followed by hydrolysis with aq.K_2CO_3 solution gave a mixture of hydrocarbons. The ^{13}C NMR data of this product was somewhat complex but the mass spectrum showed m/z at 276. This m/z is in accordance with the dimer 24 of the hydrocarbon that would be formed by the reduction of the iodide moiety. The complexity of the ^{13}C NMR spectrum indicate the presence of several isomeric olefins.



24

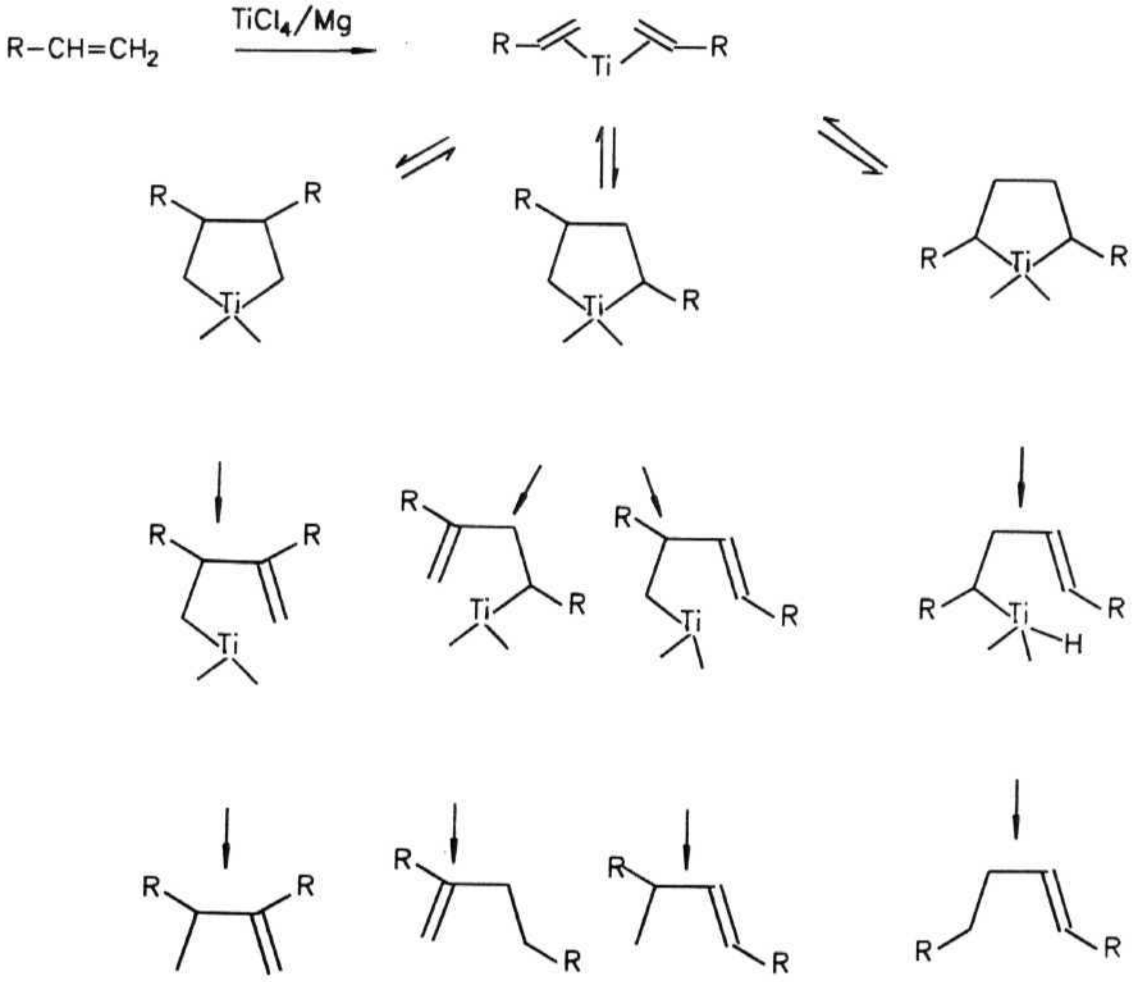
Encouraged by the prospect of dimerizing the olefins under relatively mild conditions, we have carried out the reactions with 1-decene and 1-octene, in order to examine of this type of reactivity of the low valent titanium reagent and obtained similar results.

It has been reported that the titanium alkoxide/trialkylaluminium combinations catalyzes dimerization of ethylene to 1-butene.[25] Several authors have proposed different types of mechanisms for this transformation.-- In another report, the reagent prepared using $CpTiCl_2$/alkali metal amalgam combination dimerizes ethylene to 1-butene.[27] Also, Wreford and co-workers have reported that the $(C_4H_6)_2Ti(dmpe)$ catalyzes the dimerization of ethylene.[28] A mechanism involving formation of a metallocyclopentane complex has been proposed (Scheme 11).[28]

Scheme 11.

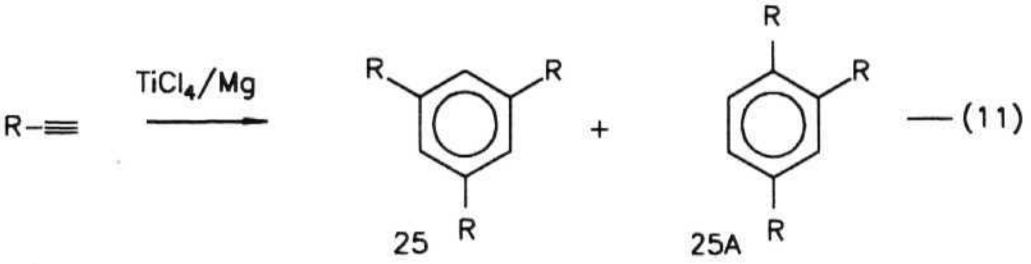
It was thought that the present results could be explained if the titanium species dimerize the olefins to various olefinic products via the formation of metallocyclopentanes (Scheme 12).

Scheme 12.



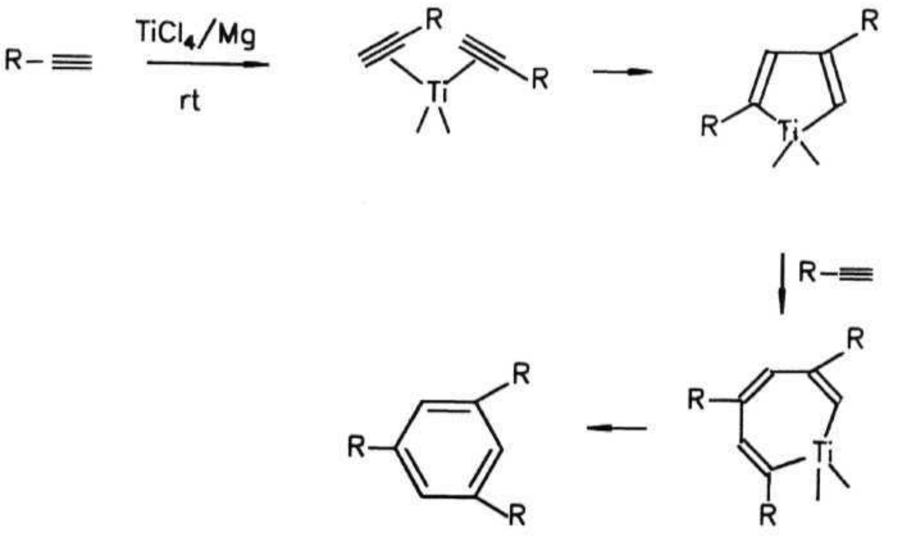
The reactions were carried out using 1-alkenes (10 mmol) with $TiCl_4$

(15 mmol) and magnesium powder (25 mmol) in THF (60 ml) at room temperature followed by hydrolysis with aq.K_2CO_3 solution to obtain in a mixture of hydrocarbon products. 1-Decene and 1-octene were dimerized to obtain the corresponding hydrocarbon mixtures in 68% and 65% in yields respectively. It was observed that only terminal olefin is reactive under these conditions. 1-Alkynes on reaction with this system gave the trimerized product 25 (Eq. 11).



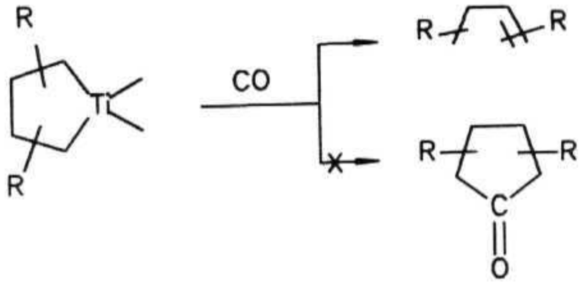
For example, 1-heptyne (10 mmol) on reaction with the low valent titanium generated using $TiCl_4$ (15 mmol) and magnesium powder (25 mmol) gave the 1,3,5 and 1,2,4 isomers 25 and 25A in 78% yield. The transformation may be rationalized by the tentative mechanism outlined in Scheme 13.

Scheme 13.



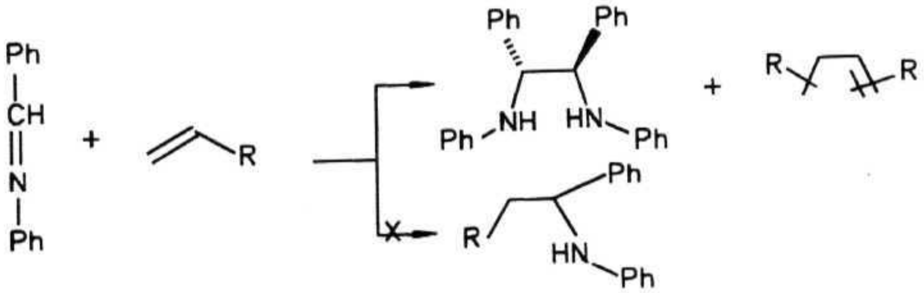
These dimerization and trimerization reactions of 1-alkenes and 1-alkynes with low valent titanium are ineffective at 0 °C. In the attempted carbonylation reaction of 1-decene with low valent titanium reagent prepared in this way in the presence of carbon monoxide also resulted in dimerization and no carbonylated product could be obtained (Scheme 14).

Scheme 14.



It was found that the reaction of N-phenylimines and 1-decene with the $TiCl_4$/Mg combination gave only the imidazolidine derivative and the mixture of hydrocarbon products. The product derived from the coupling of the olefin and imine was absent (Scheme 15).

Scheme 15.



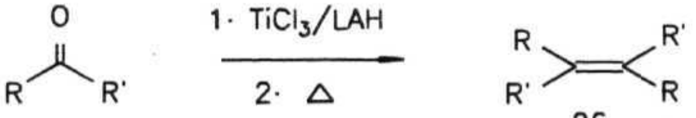
Although these transformations involving olefins are interesting and perhaps may have significance elsewhere (industrial applications), they are not useful for laboratory synthesis.

1.2.3. Reductive coupling of ketones:

The use of low valent transition metals in carbon-carbon bond forming reactions is well recognized. An intensively studied class of *C-C* bond forming reactions is the reductive carbonyl coupling reactions.[10,23-32] In most cases, such applications employ the oxophilic low valent early transition metal, titanium. In order to provide electron-rich metal centers, a large variety of reductive methods for generating low valent titanium species have been employed. These, reductions commonly use titanium halides as convenient, reducible metal sources.

A large number of reducing agents have been employed to generate the low valent titanium reagent system. Among the most common reagent systems are $TiCl_3/LiAlH_4$,[33] $TiCl_4/Zn$,[34] $TiCl_3/Zn-Cu$,[35] $TiCl_3/Mg$,[36] $TiCl_4/Mg-Hg$[37] and $CpTiCl_2/LiAlH_4$.[37]

Low valent titanium reagents obtained in these ways, react with aldehydes and ketones to give the corresponding olefins or pinacols 26-30 (Eq. 12-16).



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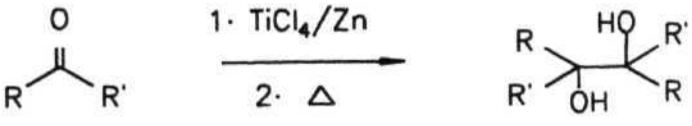
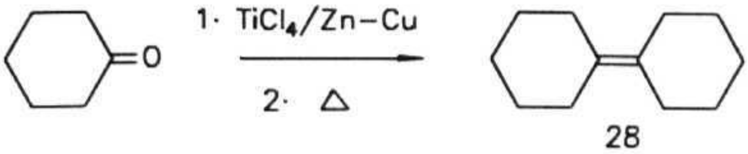


27

—(13)



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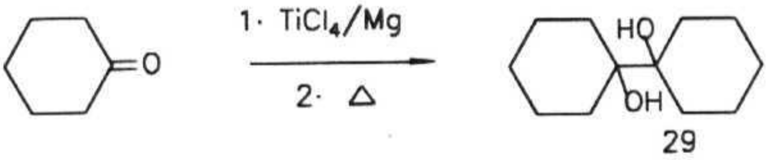

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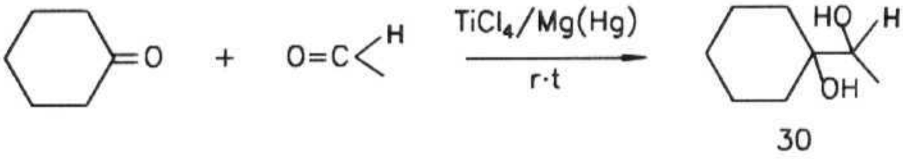
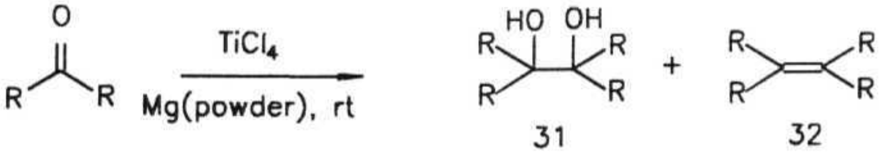


- (16)

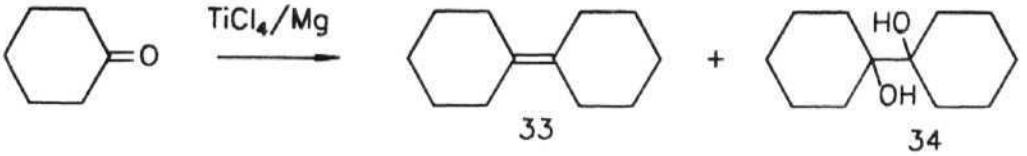
We have observed that the reaction of the $TiCl_4$/Mg (powder) reagent combination with ketones (cyclohexanone and acetophenone) gives corresponding pinacols 31 and olefins 32 (Eq. 17).



— (17)

The reaction of cyclohexanone (10 mmol) with low valent titanium species generated using $TiCl_4$ (15 mmol) and magnesium powder (25 mmol) gives cyclohexylidine 33 (40%) and bicyclohexyl-l,2-diol 34 (45%) (Eq. 18).

Similarly, the reaction of acetophenone under these conditions produced 2,3-diphenylbutene (38%) and 2,3-diphenyl-2,3-butanediol (43%).



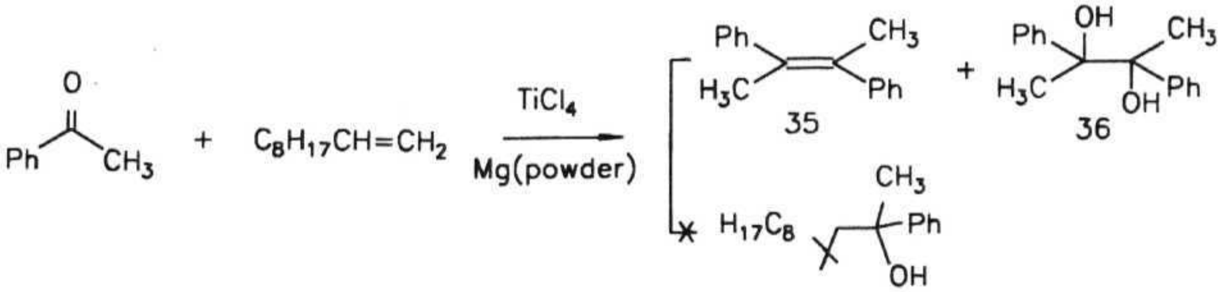
— (18)

The results are not entirely unexpected since a variety of carbonyl compounds undergo reductive coupling in inter- or intramolecular fashion to give the corresponding pinacols or olefins. Various aspects of the titanium induced coupling have been reviewed by McMurry.[16] The mechanism of such transformation has been discussed in several articles.[29-32]

3.2.4. Reductive coupling of olefinic ketones.

Next, we have examined whether a ketone and a olefin can be coupled to give the expected alcoholic products. We have carried out the reactions using acetophenone and 1-decene. However, only a mixture of diol and hydrocarbon products were obtained and the expected cross coupled product were not obtained (Scheme 16).

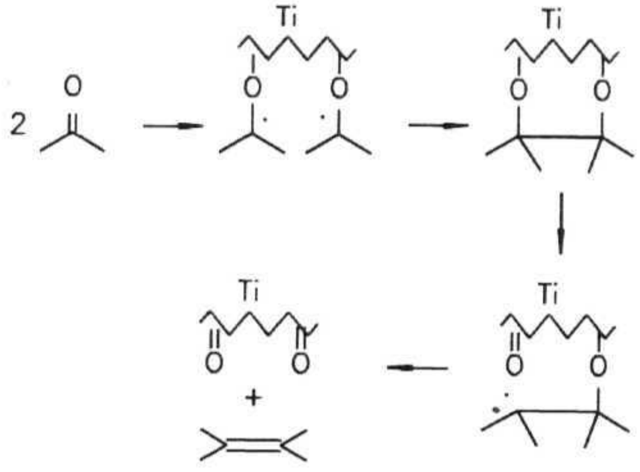
Scheme 16.



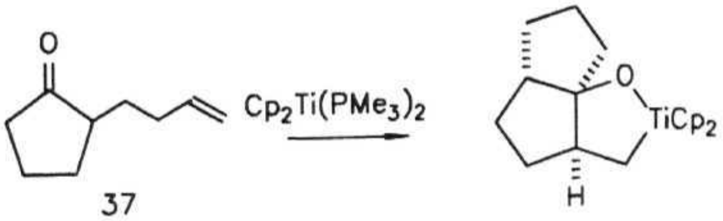
For example, the reaction of acetophenone (5 mmol) and 1-decene (5 mmol) with $TiCl_4$ (15 mmol) and mesh magnesium (25 mmol) gives the mixture of hydrocarbon derived from 1-decene dimerization (35%) and 2,3-dipheny-2-butene 35 (20%), 2,3-diphenyl 2,3-butanediol 36 (25%) derived from reductive coupling of acetophenone.

It is generally accepted that in the McMurry type coupling of carbonyl compounds using low valent titanium species, the reaction takes place in several steps.[16] Reductive dimerization of the starting ketone to give the initial formation of the corresponding radicals, formation of pinacols and finally deoxygenation of the pinacolate in the surface of the titanium (Scheme 17).[16]

Scheme 17.

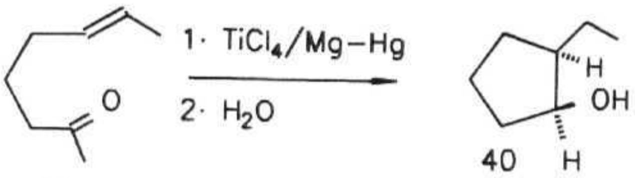


Obviously, there have been efforts to harness the reactivity of such radical intermediates for synthetic utilization. For example, the reaction of δ-enones 37 with $Cp_2Ti(PMe_3)_2$, formed by the reduction of Cp_2TiCl_2 with magnesium amalgam induces an intramolecular cyclization to afford the corresponding cyclic titanium derivative 38 (Eq. 19).[38]



37 38 — (19)

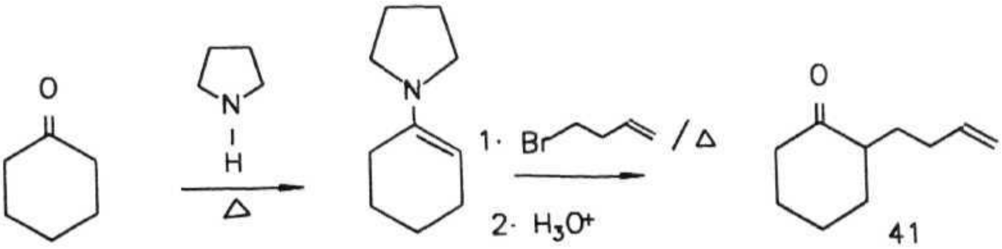
The reactivity of the $TiCl_4/Mg/Hg$ combination has been briefly investigated for the cyclization of a δ-enone 39 to obtain the trans isomer of the corresponding cyclopentanol 40 (Eq. 20).[39]



39 40 — (20)

Although, as discussed previously, we have not observed intermolecular coupling of a olefin and a ketone, we have decided to examine the utility of the $TiCl_4/Mg$ (powder) reagent combination using some readily accessible olefinic ketones. The olefinic ketones 2-butenylcyclohexanone 41, 2-butenylcyclopentanone 42 have been prepared following closely related reported procedures (Scheme 18).[40]

Scheme 18.



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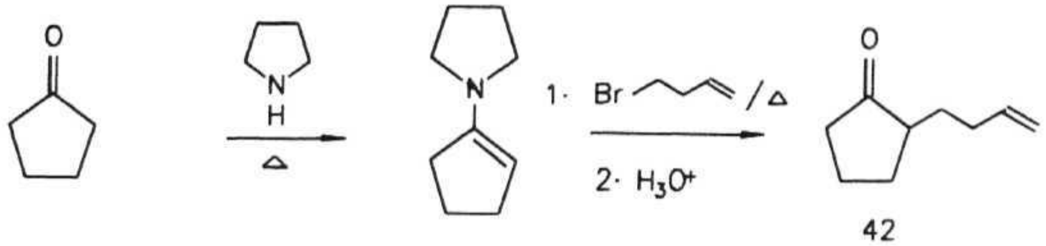
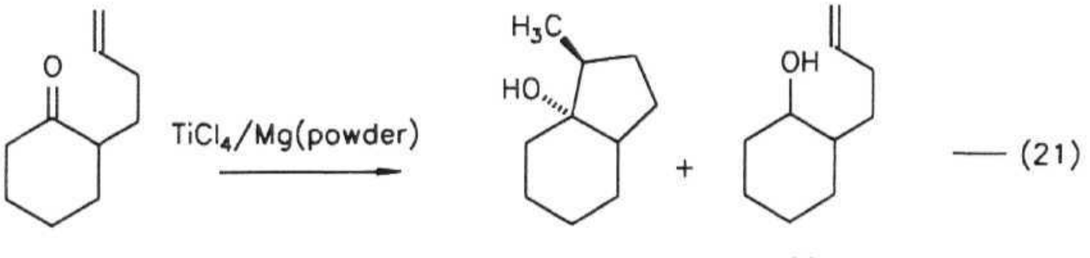


42

The reaction of the δ-enone 41 with low valent titanium species generated using $TiCl_4$/Mg (powder) reagent system, gave a mixture of bicyclic tertiary alcohol 43 and the carbonyl reduction product 44 (Eq. 21).



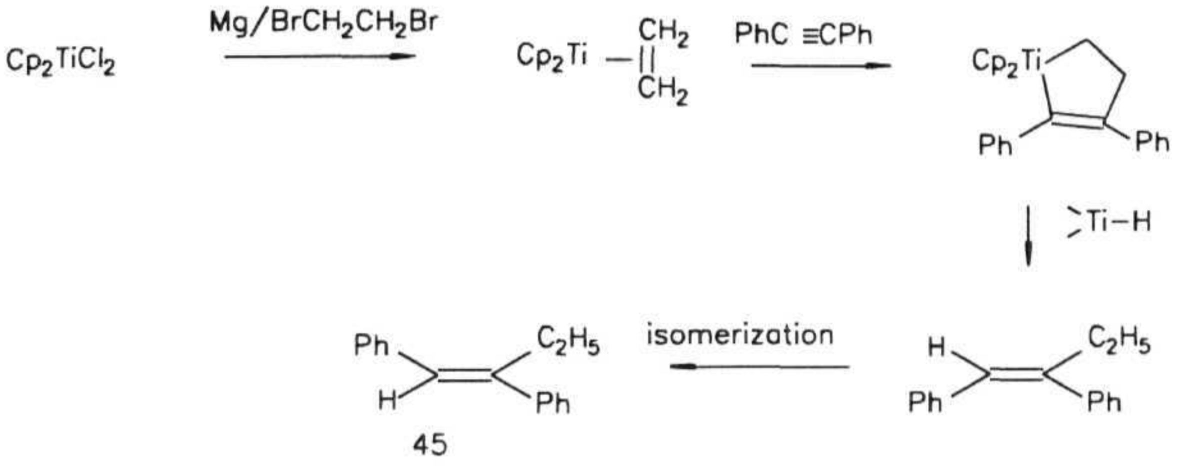
41 43 44

A similar product mixture was also obtained in the reductive cyclization of 2-butenylcyclopentanone.

3.2.5: Reductive coupling of carboxylic acid esters:

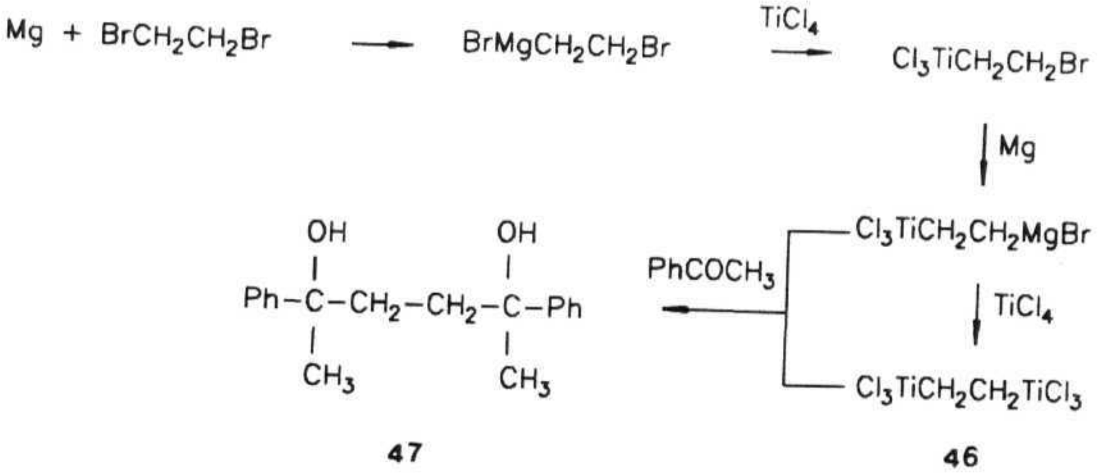
In the course of efforts to synthesize the elusive titanocene 'Cp_2Ti' for synthetic utilization, it was observed in this laboratory that the reaction of Cp_2TiCl_2 with Grignard grade magnesium and 1,2-dibromoethane in the presence of diphenylacetylene leads to the formation of 1,2-diphenyl~(E)-l-butene 45 (Scheme 19).[41]

Scheme 19.

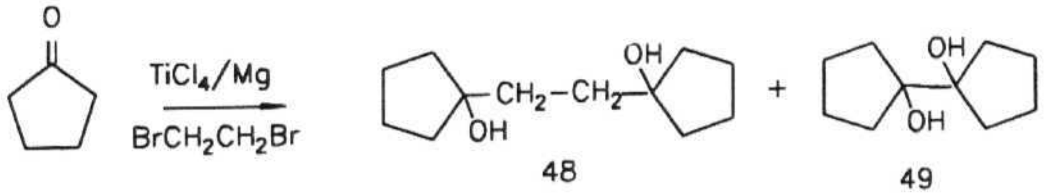


Further work **in** this laboratory led to the invention of a new 1,2-diorganometallic reagent system 46 derived from $TiCl_4$/Mg/$BrCH_2CH_2Br$ combination in THF. This 1,2-diorganometallic reagent generated *in situ* reacts with certain ketones to give the corresponding 1,4-diols 47 (Scheme. 20)[42]

Scheme 20.



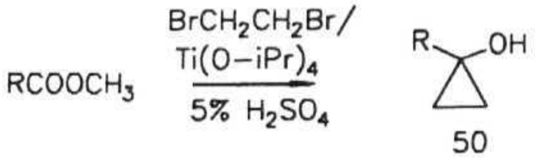
In some cases, the reaction is not clean and the 1,2-diols 49 are also formed along with 1,4-diols 48 through reductive coupling of the ketone by the low valent titanium species (Eq. 22).



— (22)

Unfortunately, this transformation did not proceed with higher 1,2-dibromoalkanes. Also, similar transformation was not observed with other types of carbonyl compounds such as aldehydes and esters.

Later, Kulinkovich *et al* have reported that the EtMgBr/Ti(O–ipr)$_4$ reagent combination reacts with carboxylic acid esters to give the corresponding 1-alkylcyclopropanols 50 (Eq. 23).[43]

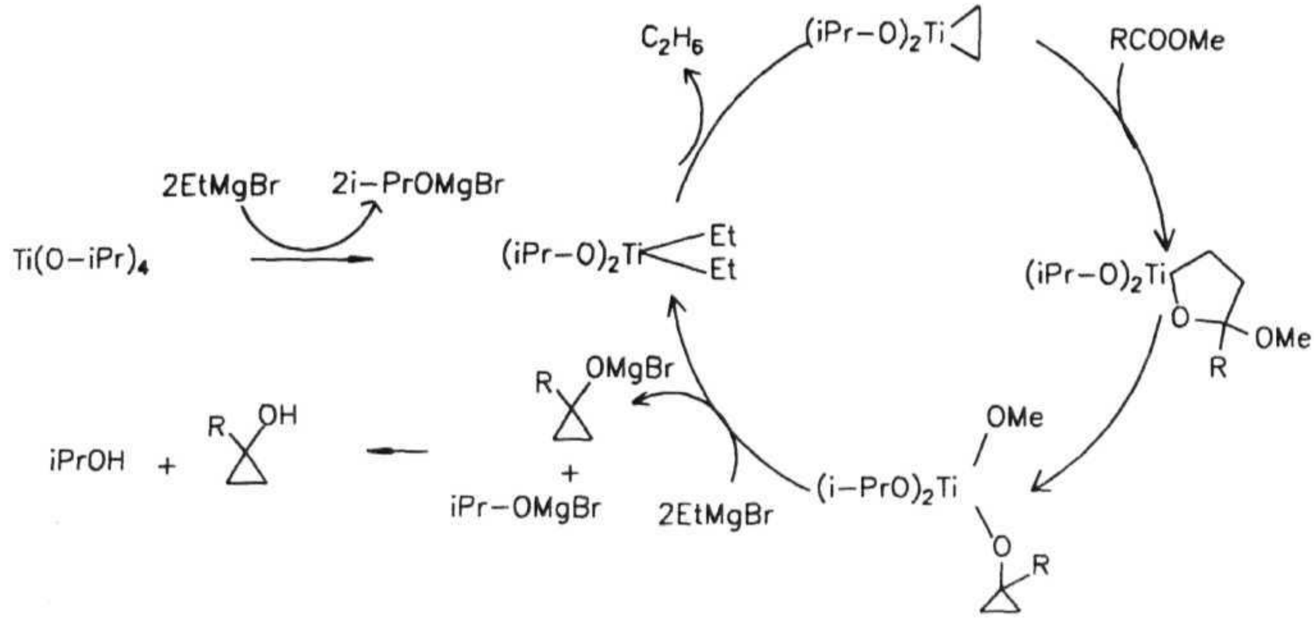


50

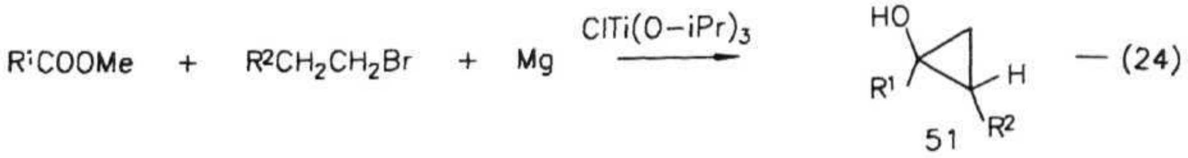
— (23)

This transformation was rationalized by postulating the initial formation of an organotitanium intermediate, which is then transformed into the titanocyclopropane derivative. This metallocyclopropane then reacts in the double alkylation of the methyl ester to afford the corresponding cyclopropanol derivatives (Scheme 21).

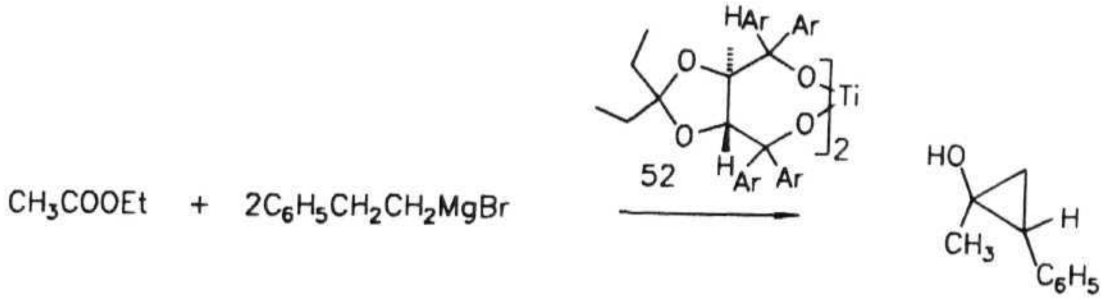
Scheme 21.



In 1994, during the preparation of this dissertation Corey, Rao and Noe reported that the $RCH_2CH_2Br/Mg/ClTi(O\text{-}ipr)_3$ system reacts with carboxylic acid esters to give the corresponding 1,2-dialkylcyclopropanol, 51 with complete diastereoselectivity (Eq. 24).[44]



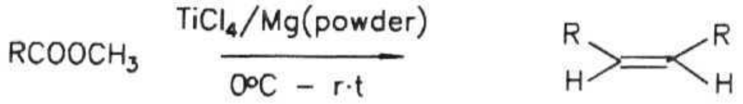
An asymmetric version of the reaction has been reported using the chiral Ti-catalyst 52 (Eq. 25).



— (25)

These interesting transformations, especially, the most recent reports on the subject, prompted us to investigate the reactivity of the interesting $TiCl_4$/Mg (powder) combination with carboxylic acid esters. We have observed that the reagent prepared in this way reacts with representative carboxylic acid esters to give the corresponding Z-olefins (Scheme 22).

Scheme 22.

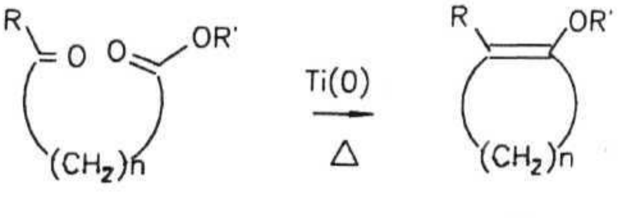


R	Yield(%)	
C_7H_{15}	75	53
C_9H_{19}	80	54
Ph	60	55

The transformation has been found to be a general one and this is illustrated by the reaction with certain other carboxylic acid esters (Scheme 22). Obtention of Z-olefins in these cases is interesting. It is of interest to note that McMurry reported that benzaldehyde gives E-stilbene (i.e., trans-stilbene) under his reaction conditions (refluxing

THF).[35] The present case, (R = Ph) the ^1H-NMR spectral data of the product show 1:1 correspondence with those reported for Z-stilbene (i. e., cis-stilbene).[45] The olefins obtained in other cases (i. e,. R = C_7H_{15} and R = $C\ H_9$), are known compounds but the spectral data were not published.[46,47] However, comparision of the spectral data with those reported for anologous derivatives (eg. E- and Z-4-octenes) indicates that the olefinic products at hand are the symmetrical Z-alkenes, contaminated by ≅ 5-10% of the corresponding E-alkenes (small hump in the olefinic carbon signal in the ^{13}C NMR spectra down field to the ^{13}C signal of the Z-alkenes).[48-50]

These results are surprising since McMurry noted that the esters are not very much reactive towards low valent titanium reagents. Even in the report describing an intramolecular coupling of a ketone with an ester 56, the resulting product is an enol-ether 57 (Eq. 26).[51]

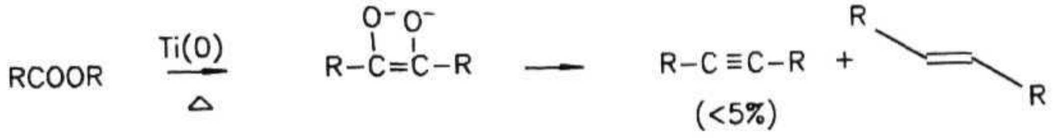


56 57

— (26)

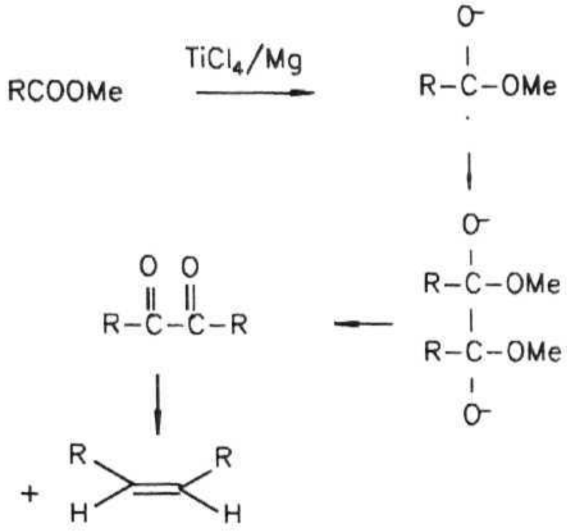
However, it is interesting to note that in 1978 McMurry *et al* reported that the reaction of esters with 'zero' valent titanium formed by the reduction of titanium halide with potassium as reducing agent gave a small amount of (<5%) the corresponding disubstituted alkyne and alkenes (Scheme 23>.[35]

Scheme 23.



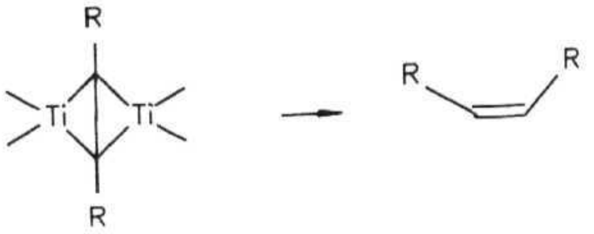
However, in the new reaction of esters with the $TiCl_4$/Mg the products are disubstituted Z-olefins. The results may be rationalized by considering the McMurry type reductive coupling of carbonyl compounds (Scheme 24).[40] However, formation of alkenes instead of alkynes is not clearly understood.

Scheme 24.



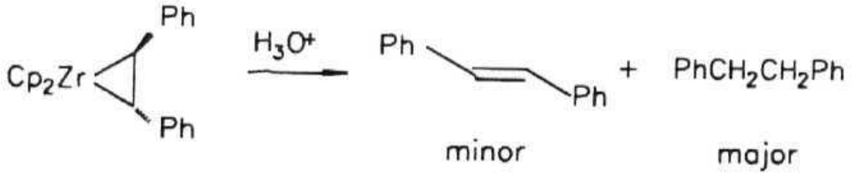
Recently, it has been observed in this laboratory that several other carboxylic acid derivatives such as acids, amides and nitrilies also yield the corresponding dialkyl Z-olefins in varying yields on reaction with $TiCl_4$/Mg(powder) in THF under these condition.[52] These conditions are somewhat mild compared to the conditions (THF reflux) employed by McMurry et. al., in their efforts to obtain alkynes from esters.[35] As discussed earlier. McMurry et. al., obtained about 5% alkyne-alkene mixture and concluded that their results are not fruitful.[35]

The obtention of better yields in the conversion of carboxylic acid derivatives to obtain under the present reaction conditions should make this transformation useful for synthetic applications. However, the reason for the formation of alkenes instead of the expected alkynes is not clearly understood. A possibility is that the transformation may go through a metallocyclopropane intermediate which then decomposes to olefin (Eq. 27).



— (27)

Such a reactivity is somewhat reminescent of the reactions of certain zirconium derivatives (Eq. 28,29).[53]



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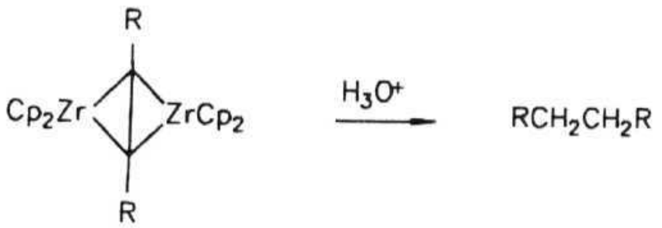


— (29)

However, further work is necessary to examine these possibilities under the present reaction conditions.

1.2.5. Conclusion:

A simple, convenient one pot synthesis of imidazolidine derivatives from imines has been developed using the low valent titanium reagent prepared *in situ* using $TiCl_4$/Mg (powder).

Efforts were made to harness the reactivities of the $TiCl_4$/Mg (powder) in the initial phase of this work but we were not fully successful in developing 'clean' synthetic methods. Neverthless, the experimental results uncovered should be useful for further developments.

Very recently, interesting results were obtained in the reactivities of reagent system towards carboxylic derivatives which should be also useful for synthetic applications.

3.3. Experimental Section

3.3.1. General Information:

Several informations described in Chapter 1 and 2 are also applicable here. Tetrahydrofuran was distilled over benzophenone-sodium. Magnesium (50 mesh) supplied by Fluka, Switzerland was utilized. The alkenes utilized were commercial samples supplied by Fluka, Switzerland. The alkynes were prepared following a reported procedure.[54] Titanium(IV) tetrachloride supplied by Riedel was used. Aldehydes, ketones and amines supplied by Ranbaxy, India, were distilled before use. The imines and enamines utilized were prepared following standard procedures.[55]

3.3.2: Reaction of N-methyl benzalimine with low valent titanium generated by $TiCl_4/Mg/BrCH_2CH_2Br$ reagent system:

Magnesium mesh (0.60 g, 25 mmol) was added to $TiCl_4$ (2.83 g, 15 mmol) in THF (60 ml) and 1,2-dibromoethane (1.85 g, 10 mmol) was added dropwise for 5 minutes at 0°C under nitrogen atmosphere. The contents were stirred for 30 minutes at 0°C and N-methyl benzalimine (1.39 g, 10 mmol) was added. The reaction mixture was warmed to room temperature and stirred further for 10h. The black reaction mixture was quenched with saturated K_2CO_3 solution (5 ml). The resulting mixture was poured into water (50 ml) 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 successively washed with brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column. The liuidazolidine derivative 15 was isolated in 59% yield using 3% ethyl acetate in hexane as eluent.

Yield : 54% (0.718 g)

IR (neat) : 3075, 2950, 1460, 1180, 770, 710 cm"1

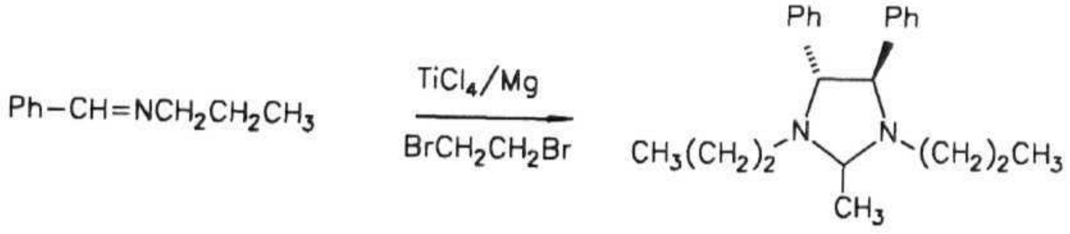
^{1}H NMR : 6 ppm 1.1-1.2 (d, 3H), 2.0-2.1 (s, 6H), 3.1-3.5 (m, 2H), 3.5-3.8 (q, 1H), 6.7-7.4 (m, 10H) (Spectrum no. 22)

^{13}C NMR : δ ppm 15.3, 33.6, 36.6, 74.4, 125.8, 126.6, 138.5, 139.0 (Spectrum no. 23)

Ms (m/z) : 266 (M^+ 25%), 251 (100%) (Spectrum no. 24)

The above procedure was followed for other substrates (entries 3.3.3 to 3.3.7). The physical constant and spectral data obtained are presented below.

3.3.3.



58

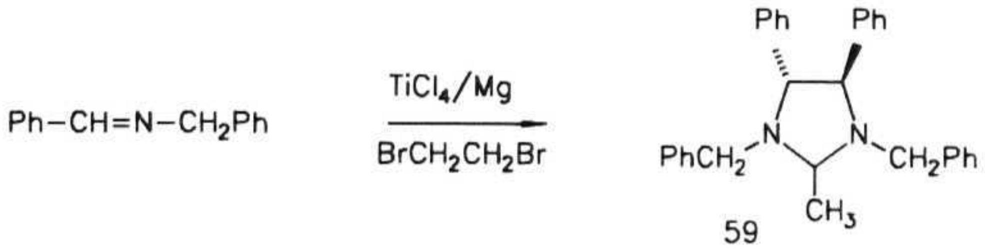
Yield : 63% (1.0 g)

IR (neat) : 3061, 2962, 1601, 1452, 760, 700 cm^{-1}

^{1}H NMR : δ ppm 0.7-0.8 (m, 3H), 0.9-1.4 (m, 10H), 1.8-2.0 (m, 4H), 3.3-3.6 (m, 2H), 4.2 (q, 1H), 6.8-7.4 (m, 10H)

^{13}C NMR : 6 ppm 11.85, 11.94, 17.71, 21.34, 22.56, 48.06, 57.56, 74.28, 76.85, 78.03, 126.87, 127.28, 127.78, 128.08, 128.53, 140.48, 142.00.

3.3.4:



59

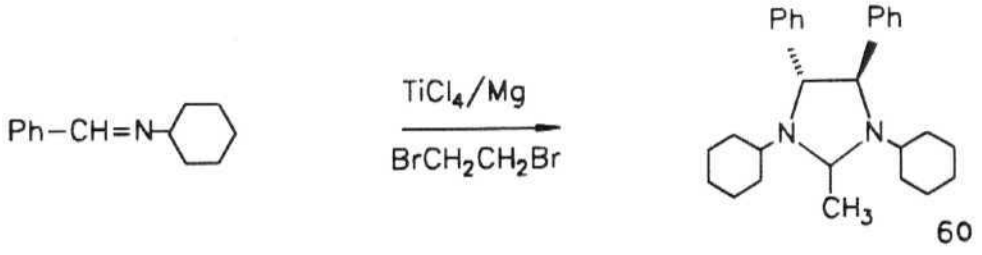
Yield : 70% (1.46 g)

IR (neat) : 3059, 2968, 1601, 1265, 740, 700 cm^{-1}

^{1}H NMR : 6 ppm 1.0 (d, 3H), 2.1 (s, 4H), 3.4-3.9 (m, 2H), 4.2 (q, 1H), 7.1-7.6 (m, 20H) (Spectrum no. 25)

^{13}C NMR : 6 ppm 17.6, 50.2, 58.5, 73.9, 75.9, 77.3, 126.6, 126.8, 127.3, 127.7, 128.0, 128.3, 128.4, 128.5, 128.8, 129.2, 129.6,137.4. 139.6, 139.9, 141.0. (Spectrum no. 26)

3.3.5:



60

Yield : 74% (1.48 g)

M.P. : 127°C

IR (KBr) : 3026, 2934, 2849, 1458, 1126, 758, 700 cm^{-1}

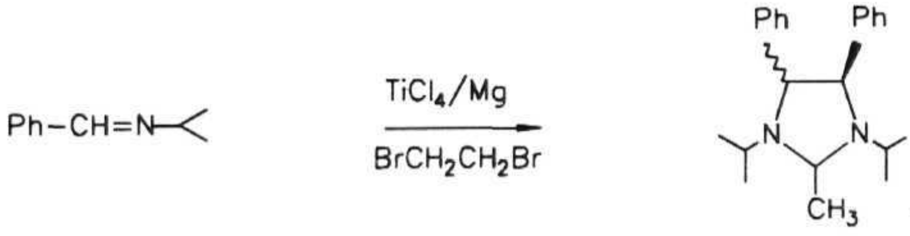
^{1}H NMR : 6 ppm 0.9-1.1 (m, 3H), 1.4-1.9 (m, 20H), 2.1-2.2 (m, 2H), 3.7 (q, 1H), 6.9-7.3 (m, 10H)

^{13}C NMR : δ ppm 24.53, 24.95, 26.10. 32.3, 34.6, 53.03, 65.11, 126.48, 127.11, 127.85, 128.03, 128.34, 141.98.

Additional minor peak, corresponding to the meso diastereomer were also present.

Analysis :	C	H	N
Calcd for $C_{28}H_{38}N_2$	83.52	9.51	6.97
Found	83.45	9.49	7.00

3.3.6:



16

Yield : 66% (1.05 g)

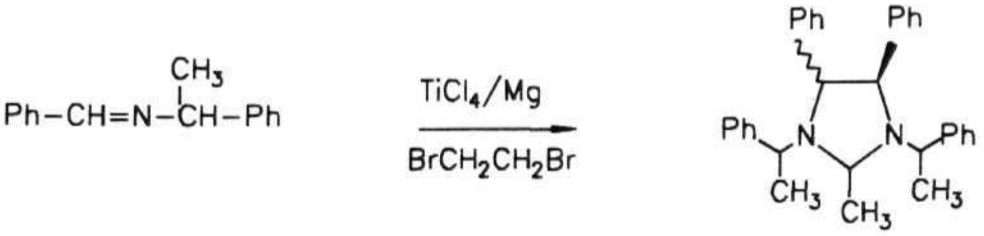
IR (neat) : 3026, 2962, 2926, 1493, 1452, 761, 700 cm^{-1}

^1H NMR : δ ppm 1.0-1.6 (m, 15H), 2.1-2.3 (m, 2H), 3.4-4.3 (m, 3H), 6.9-7.5 (m, 10H)

^{13}C NMR : δ ppm 12.0, 12.1, 22.3, 22.5, 25.2, 25.3, 31.9. 54.7, 54.9, 65.8, 66.2, 126.7. 127.3, 127.9, 128.3, 141.7, 145.6.

Additional minor peak corresponding to the meso compound were also present.

3.3.7:



61

Yield : 58% (1.28 g)

IR (neat) : 3061, 2964, 1601, 1452, 760, 700 cm^{-1}

^{1}H NMR : δ ppm 1.1-1.5 (m, 9H), 2.1-2.2 (m, 2H), 3.3-3.7 (m, 2H), 3.8-4.0 (q, 1H), 6.9-7.4 (m, 20H)

^{13}C NMR ; δ ppm 22.54, 24.65, 54.76, 64.15, 65.00, 66.71, 66.46, 126.56, 126.66, 127.05, 127.21, 127.77, 127.96, 128.57, 128.54, 128.82, 141.06, 141.68, 146.36.

Additional minor peak, corresponding to the cis-3,4-diphenyl diastereonaer were also present.

3.3.8: Hydrolysis of **imidazolidine** derivative 15 (product obtained in 3.3.2) with wet silica gel:

Silica gel 1.5 g (230–450 mesh) was taken in DCM (2 ml) and 15% H_2SO_4 (11 drops, ~ 1 ml) was added with stirring. The imidazolidine (0.67 g, 2.5 mmol) was added to the wet silica gel and the reaction mixture was stirred for 12h at room temperature. The resulting mixture was neutralized with $NaHCO_3$ (0.1 g) and filtered on sintered glass funnel. Water (20 ml) and DCM (20 ml) were added to the filtrate and separated the organic layer. The aqueous layer was extracted with DCM (20 ml). The combined organic extract was dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography on a silica gel. Ethyl acetate (4%) in hexane eluted N,N-dimethyl-1,2-diphenylethylenediamine.

Yield : 80% (0.48 g)

IR (neat) : 3410, 3050, 2850. 1600, 1480, 750. 700 cm^{-1}

^{1}H NMR : δ ppm 1.9 (s, 2H), 2.1 (s, 6H), 3.3 (s, 2H), 6.8-7.4 (m, 10H)

^{13}C NMR : δ ppm 34.12, 71.06, 127.0, 127.53, 128.0, 128.1, 128.65, 138.65, 141.0.

The spectral data showed 1:1 correspondence with the data reported.[10]

3.3.9: Reaction of N-phenylbenzal imine with low valent titanium generated by $TiCl_4/Mg/BrCH_2CH_2Br$ reagent system:

Magnesium mesh (0.60 g, 25 mmol) **was** added to $TiCl_4$ (2.83 g, 15 mmol) in THF (60 ml) and followed by 1,2-dibromoethane (1.85 g, 10 mmol) for 5 minutes at 0°C under nitrogen atmosphere. The contents were stirred for 30 minutes at 0°C and N-phenylbenza] imine (1.81 g, 10 mmol) was added. The reaction mixture was warmed to room temperature and stirred further for 10h. The black reaction mixture was quenched with saturated K_2CO_3 solution (5 ml). It was poured into water (50 ml) and the organic phase was separated. The aqueous layer was saturated with NaCl and extracted with ether (2 x 40 ml). The combined organic extract was washed with brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column to obtain N,N-diphenyl-1,2-diphenylethylene diamine in 40% yield.

Yield	:	40% (0.73 g)
M.P.	:	155°C {lit.[8] M.P. 153°C}
IR (KBr)	:	3375, 3050, 2850, 1600. 1480, 750, 700 cm^{-1}
^1H NMR	:	δ ppm 4.5 (s, 4H, NH and N CH), 6.4-7.1 (m, 20H)
^{13}C NMR	:	δ ppm 64.0, 114.2. 118.2, 127.5, 127.7, 128.5. 129.2, 140.0. 147.2.

The spectral data showed 1:1 correspondence with the **data** reported for this compound.[8]

3.3.10: Reaction of N-methylbenzal imine with low valent titanium generated by $TiCl_4$/Mg(powder) reagent system:

Magnesium mesh (0.60 g, 25 mmol) was added to $TiCl_4$ (2.83 g, 15 mmol) in THF (60 ml) under nitrogen atmosphere at 0°C. The contents were stirred for 30 minutes and N-methylbenzal imine (1.39 g, 10 mmol) was added. The reaction mixture was warmed to room temperature and stirred further for 10h. The black reaction mixture was quenched with saturated K_2CO_3 solution (5 ml). The resulting mixture was poured into water (50 ml) and the organic phase was separated. The aqueous layer was saturated with NaCl and extracted with ether (2 x 40 ml). The combined organic extract was washed with brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column to obtain imidazolidine derivative (20%) using 3% ethyl acetate in hexane as eluent along with imine reduced product. The physical constant and spectral data of the imidazolidine derivative were found to be identical to the data of the product obtained previously (3.3.2).

3.3.11: Reaction of the olefinic iodide 22 with low valent titanium generated by $TiCl_4$/Mg system:

Magnesium mesh (0.60 g, 25 mmol) was added to $TiCl_4$ (2.83 g, 15 mmol) in THF (60 ml) under nitrogen atmosphere at 0°C. The contents were stirred for 30 minutes and olefinic iodide 22 (2.64 g, 10 mmol) was added. The reaction mixture was brought to room temperature and stirred further for 12h. The black mixture was quenched with saturated K_2CO_3 solution (5 ml). It was poured into water (50 ml) and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2 x 30 ml). The combined organic extract was washed with brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column to obtain a mixture of hydrocarbon products 24 using hexane as eluent.

Yield : 70% (0.96 g)

IR (neat) : 2950, 2900, 1440, 960 cm^{-1}

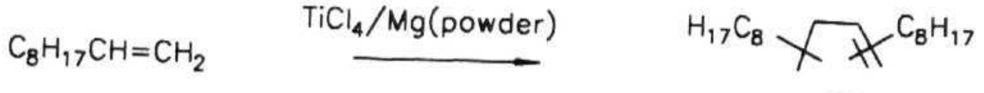
^{1}H NMR : δ ppm 0.9-1.9 (m, 32H), 3.46-3.66 (m, 2H), 5.22-5.44 (m, 2H)

^{13}C NMR : δ ppm 14.2, 22.5, 22.7, 23.1, 26.3, 26.5, 26.8, 28.1, 28.4, 29.7, 30.0, 30.4, 33.1, 33.4, 37.1, 37.3, 37.7, 129.5.

Ms (m/z) : 276 (M^{+} 12%), 138 (50%), 83 (100%).

Reaction with some other 1-alkenes resulted in similar mixture of products with low valent titanium reagent generated by $TiCl_4$/Mg system following the above procedure. The physical constant and spectral data obtained are summarized below.

3.3.12:



62

Yield : 68% (0.88 g)

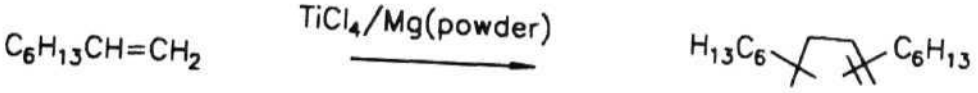
IR (neat) : 2950, 2900, 1440, 920 cm^{-1}

^{1}H NMR : δ ppm 1.0 (t-6H), 1.2-1.5 (m, 26H), 2.2-2.4 (m, 4H), 5.4 (m, 2H)

^{13}C NMR : δ ppm 14.0, 17.7, 21.7, 29.2, 29.6, 29.7, 32.0, 32.6, 33.8, 123.9, 124.5, 131.7, 139.9

Ms (m/z) : 280 (M^{+} 10%), 140 (40%), 57 (100%)

3.3.13:



63

Yield : 65% (0.73 g)

IR (neat) : 2950, 2900, 1460, 920 cm^{-1}

^1H NMR : δ ppm 1.0 (t, 6H), 1.2-1.5 (m, 10H), 2.0-2.2 (m, 4H), 5.0-5.2 (m, 2H)

^{13}C NMR : 6 ppm 14.2, 17.9, 22.0, 22.9, 29.5, 29.9, 30.2, 30.4, 32.1, 35.1, 36.7, 124.7, 126.2, 132.8, 142.7

Ms (m/z) : 224 (M^+ 8%), 112 (20%), 57 (100%).

3.3.14: **Reaction of 1-heptyne with low valent titanium** generated by the $TiCl_4$/Mg system:

Magnesium mesh (0.60 g, 25 mmol) was added to $TiCl_4$ (2.83 g, 15 mmol) in THF (60 ml) under nitrogen atmosphere at 0°C. The contents were stirred for 30 minutes and 1-heptyne (0.43 g. 5 mmol) was added. The reaction mixture was brought to room temperature and stirred further for 12h. The reaction mixture was quenched with saturated K_2CO_3 solution (5 ml). The resulting mixture was poured into water (50 ml) and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2 x 30 ml). The combined organic extract was washed with brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column to isolate the product which was identified as a mixture 1,3,5 and 1,2,4-tripentylbenzenes (25, 25A).

Yield : 78% (0.3 g)

IR (neat) : 3025, 2975, 2950, 2870, 1600, 1460, 720 cm^{-1}

^1H NMR : δ ppm 0.8 (t, 9h), 2.1-2.4 (m, 18H), 1.9-2.5 (m, 6H), 6.6-7.3 (m, 3H)

^{13}C NMR : δ ppm 14.0, 22.6, 29.5, 32.0, 32.1, 32.4, 32.8, 35.7, 36.0, 125.6, 126.0, 128.4, 129.1, 129.4, 137.8, 140.1, 140.4, 142.8.

Ms (m/z) : 288 (M^+ 40%), 217 (20%), 175 (100%).

3.3.15: Reductive coupling of ketones with low valent titanium generated by $TiCl_4$/Mg system:

Magnesium mesh (0.60 g, 25 mmol) was added to $TiCl_4$ (2.83 g, 15 mmol) in THF (60 ml) under nitrogen atmosphere at 0°C and the contents were stirred for 30 minutes. Cyclohexanone (0.88, 10 mmol) was added to the reaction mixture and warmed to room temperature. The black reaction mixture was stirred for further 12h and quenched with saturated K_2CO_3 solution (5 ml). The resulting mixture was poured into water (50 ml) and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2 x 30 ml). The combined organic extract was washed with brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography to obtain cyclohexylidene cyclohexane 33 (40%) using hexane as eluent. Ethyl acetate (15%) in hexane eluted bicyclohexyl-1,2-diol 34 (45%).

Spectral data for cyclohexylidene cyclohexane 33:

M.P. : 54°C {lit.[35] 52-53°C}

IR (KBr) : 3025, 2950, 2875, 1460, 1280 cm^{-1}

^{13}C NMR : δ ppm 27.5, 28.8, 30.3, 129.0

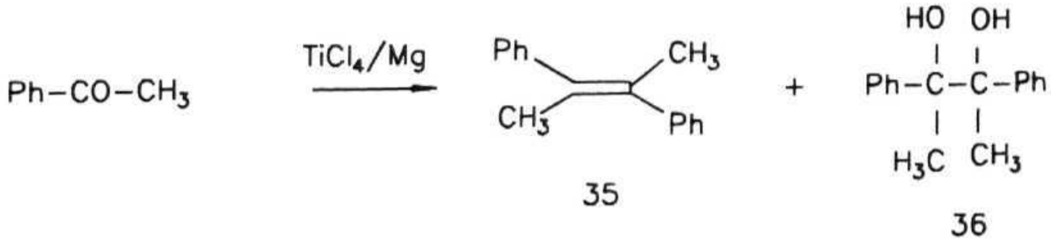
Spectral data for bicyclohexyl-1,2-diol 34:

M.P. : 123°C {Lit.[56] 124.5-125.5°C}

IR (KBr) : 3400, 2950, **1460, 1160 cm^{-1}**

^{13}C **NMR : 6 ppm 21.7, 25.8, 30.6, 75.6.**

3.3.16:



The above procedure was followed for the reaction of acetophenone using low valent titanium species. The physical constant and spectral data obtained for 2,3-diphenyl 2-butene 35 (38%) and 2,3-diphenyl 2,3-butanediol 36 (43%) are prsented below.

Spectral data for 35:

M.P. : 107°C {lit.[46] 103-106^{o}C}

IR (KBr) : 3050. 2900, 1600, 760, 700 cm"^{1}

^{1}H NMR : 6 ppm 1.9 (s, 3H). 2.1 (s, 3H). 6.9-7.3 (m, 10H)

^{13}C NMR : δ ppm 21.4, 22.4, 125.6. 126.3, 127.6. 128.2, 12.9.3. 133.1, 144.6.

Spectral data for 36.

M.P. : 119°C {lit.[57] M.P. 120^{o}C}

IR (KBr) : 3450, 3050, 2950, 1280 cm"^{1}

^{13}C **NMR** : δ ppm 24.7, 78.8, 127.0, 127.1, 143.5.

3.3.17: Reductive cyclization of olefinic ketone 41 with low valent titanium generated by TiCl$_4$/Mg system:

Magnesium mesh (0.60 g, 25 mmol) was added to TiCl$_4$ (2.83 g, 15 mmol) in THF (60 ml) under nitrogen atmosphere at 0°C and the contents were stirred for 30 minutes. 2-Butenylcyclohexanone (1.42 g, 10 mmol) was added to the black reaction mixture and it was brought to room temperature and stirred further for 12h. The reaction mixture was quenched with saturated K_2CO_3 solution (5 ml). The resulting mixture was poured into water (50 ml) and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2 x 30 ml). The combined organic extract was washed with brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column to obtain a mixture of products containing 43 and 44 using 6% ethyl acetate in hexane as eluent.

IR (neat) : 3400, 2950, 2875, 1460, 1270, 1120, 800 cm"^{1}

^{13}C NMR : 6 ppm 13.0, 14.1, 20.4, 22.5, 23.0, 24.8, 26.4, 27.6, 29.4, 31.0, 31.8, 32.9, 33.5, 36.1, 40.5, 46.8, 69.0, 80.8, 114.2, 139.1.

A similar product mixture was obtained in the attempted reductive cyclization of 2-butenyl cyclopentanone 42.

3.3.18: Reductive coupling of methyl caproate with $TiCl_4$/Mg reagent system:

Methyl caproate (0.79 g, 5 mmol) was added to $TiCl_4$ (0.94 g, 5 mmol) in THF (60 ml). Magnesium mesh (0.46 g, 20 mmol) was added to this mixture under nitrogen atmosphere and stirred for 1h at 0°C. The reaction mixture was brought to room temperature and stirred further for 3h at room temperature. The resulting black colored solution was poured into ice-cold 10% H_2SO_4 (75 ml) and the organic phase was separated. The aqueous phase was saturated with NaCl and extracted with ether (2 x 30 mmol). The combined organic extract was washed with brine (30 ml), dried over anhydrous $MgSo_4$ and concentrated. The residue was chromatographed on a silica gel column to obtain Z-7-hexadecene using hexane as eluent.

Yield : 75% (0.42 g)

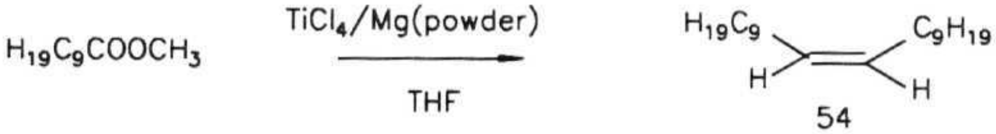
IR (neat) : 2924, 2854, 1464, 1377 cm"^{1}

^{1}H NMR : 6 ppm 0.7(t-6H), 1.1 (m, 20H), 1.4 (m, 2H), 1.8 (m, 2H), 5.1 (q-2H)

^{13}C NMR : 6 ppm 14.0, 22.6, 27.2, 29.3, 29.5, 29.7, 31.9. 129.8

The above procedure was followed for other substrates (entries 3.3.19 to 3.3.20). The physical constant and spectral data obtained are presented below.

3.3.19:



54

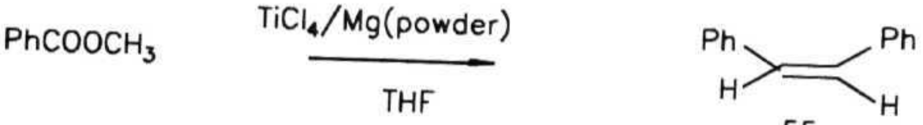
Yield : 80% (0.48 g)

IR (neat) : 2957, 2924, 2854, 1464. 1377, 721 cm"^{1}

^{1}H NMR : 6 ppm 0.7 (t-6H), 1.0–1.2 (m, 28H), 1.5-1.9 (m, 4H), 5.1 (q-2H)

^{13}C NMR : 6 ppm 14.0, 22.6, 27.2, 29.3, 29.6, 29.7, 31.9, 129.8 (Spectrum no. 28)

3.3.20:



55

Yield : 60% (0.27 g), obtained as a liquid.

IR (neat) : 3055, 3024, 2361, 1601, 1446, 779 cm^{-1}

^{1}H NMR : 6 ppm 6.5 (s, 2H), 7.1 (m, 10 H)

^{13}C NMR : δ ppm 127.0, 128.1, 128.8, 129.2, 130.1, 137.1

^{1}H NMR spectral data show 1:1 correspondence with that reported for Z-stilbene (i. e., cis-stilbene).[45]

3.4. References

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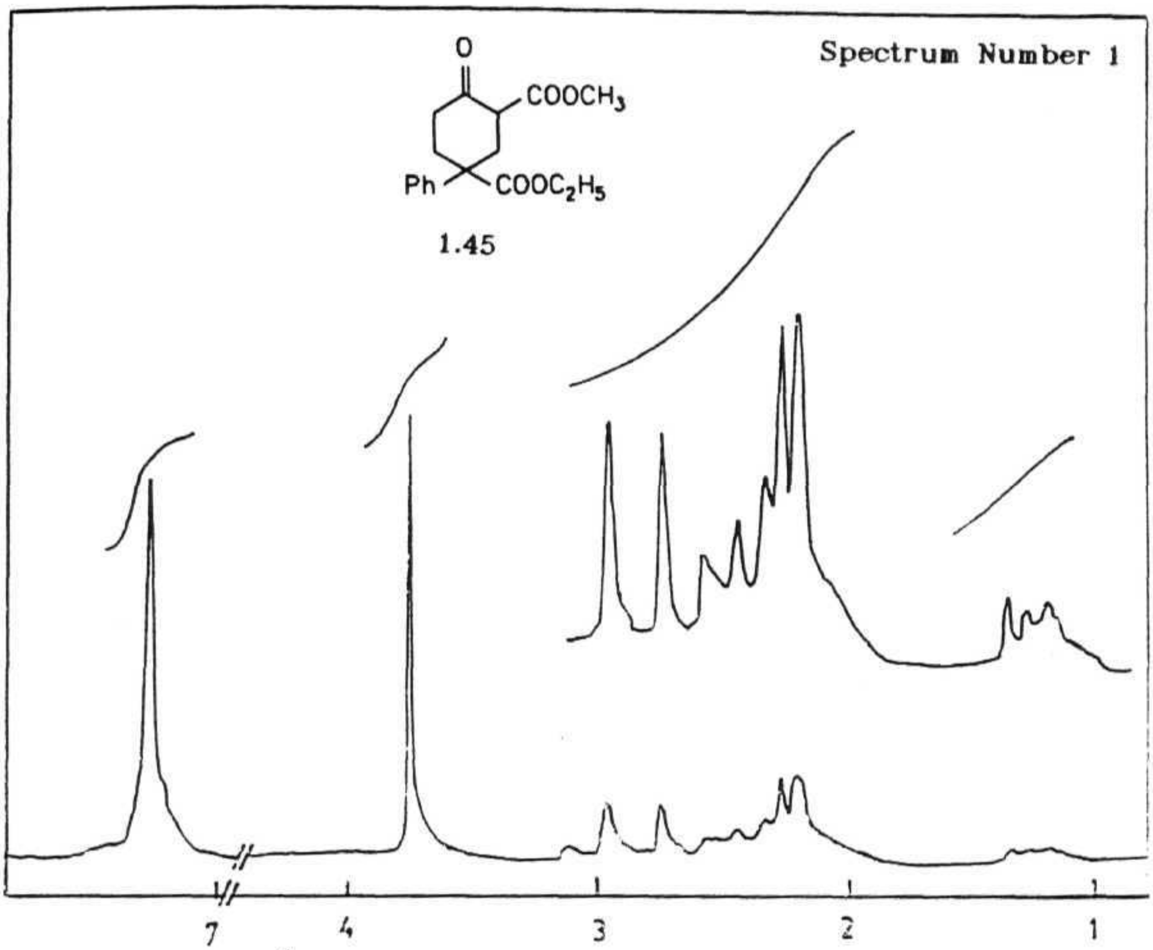

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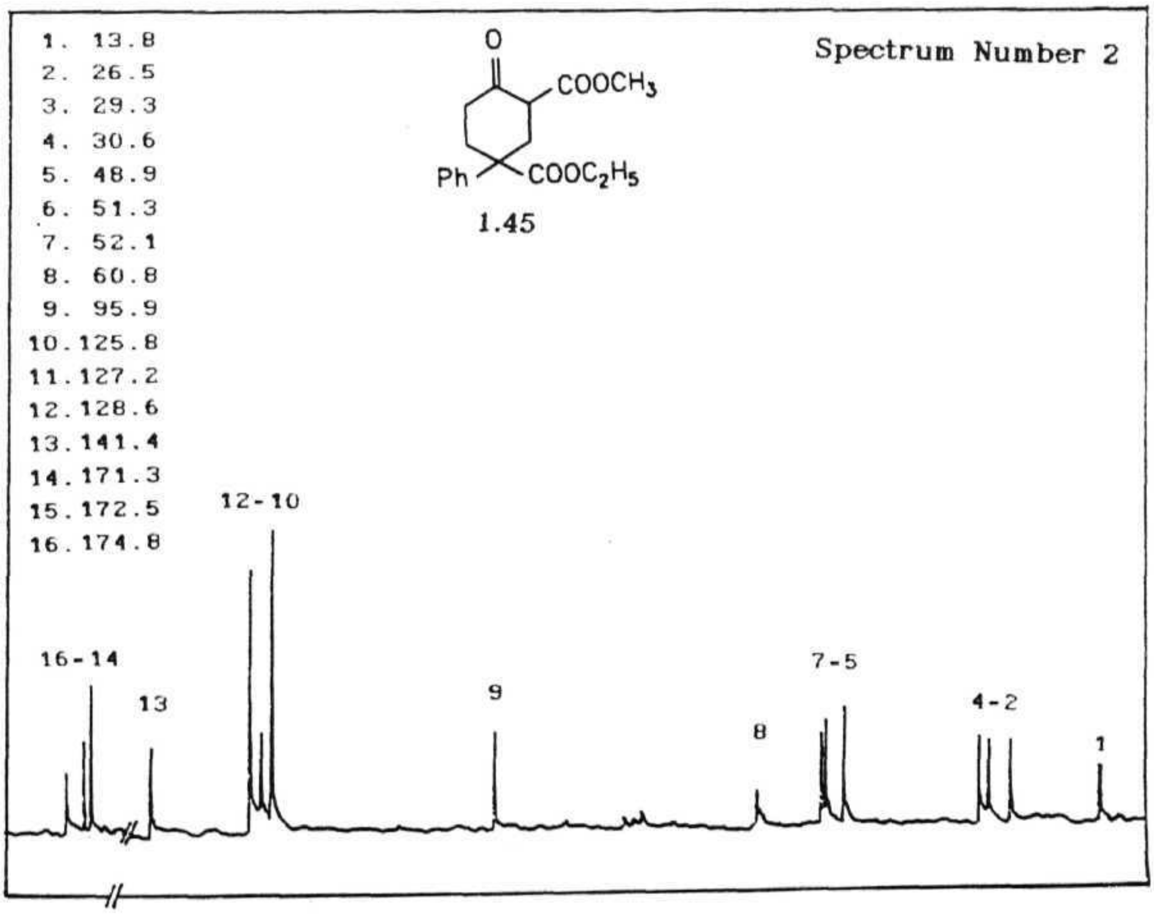

1.45

1. 13.8
2. 26.5
3. 29.3
4. 30.6
5. 48.9
6. 51.3
7. 52.1
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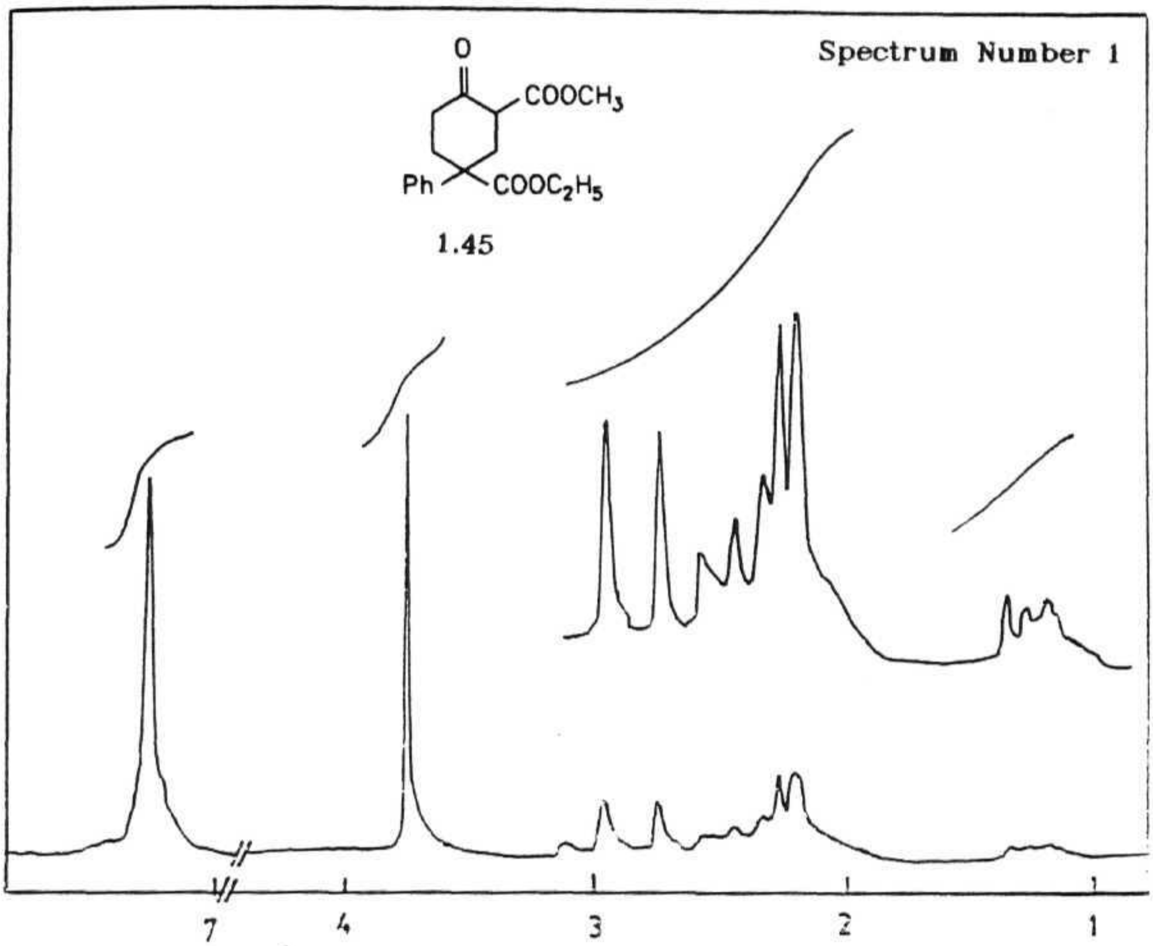
16. 174.8



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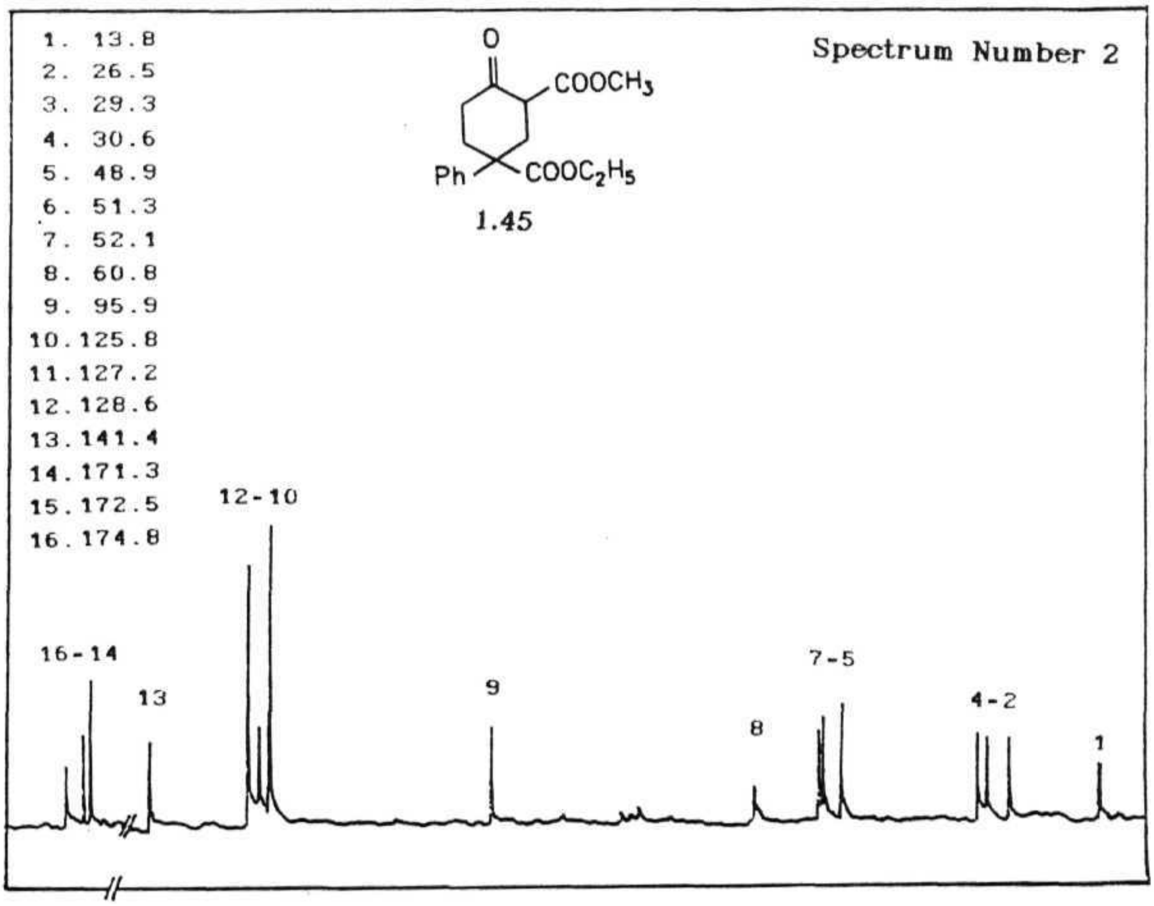

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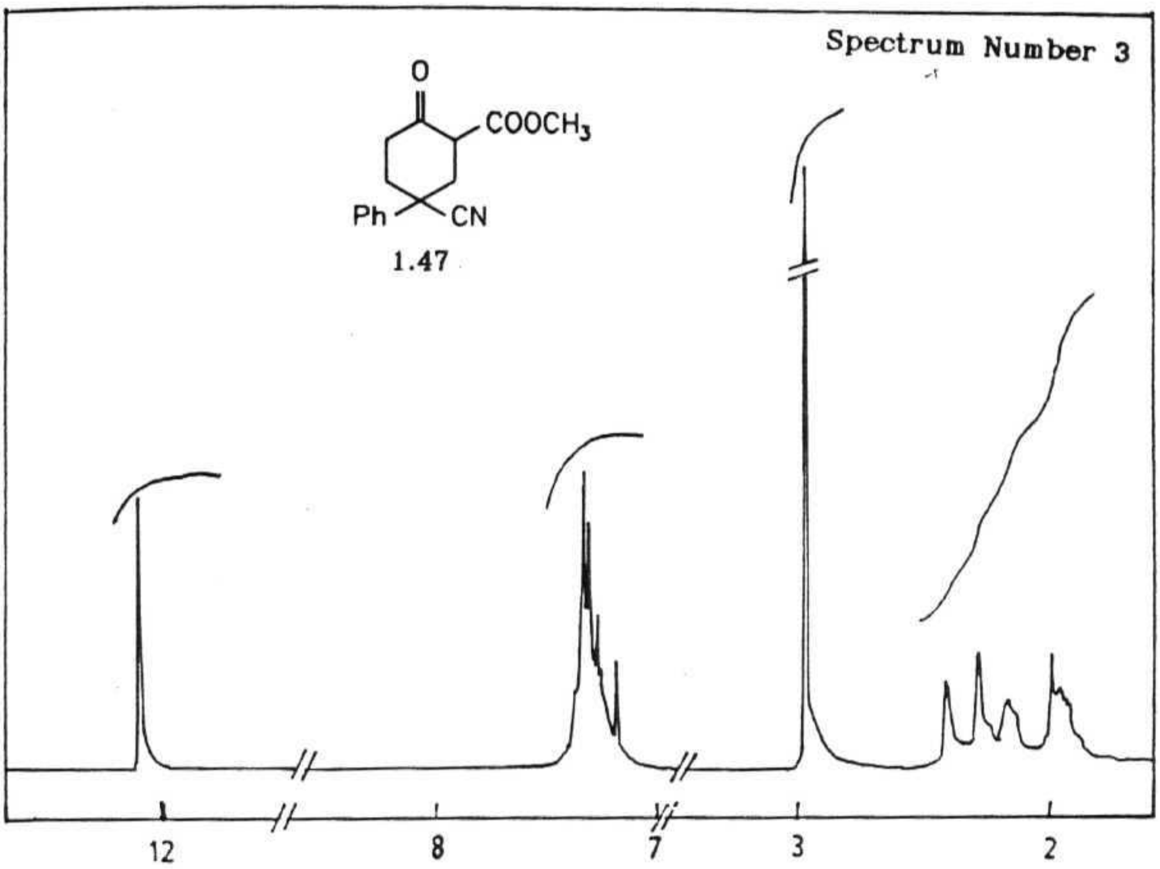

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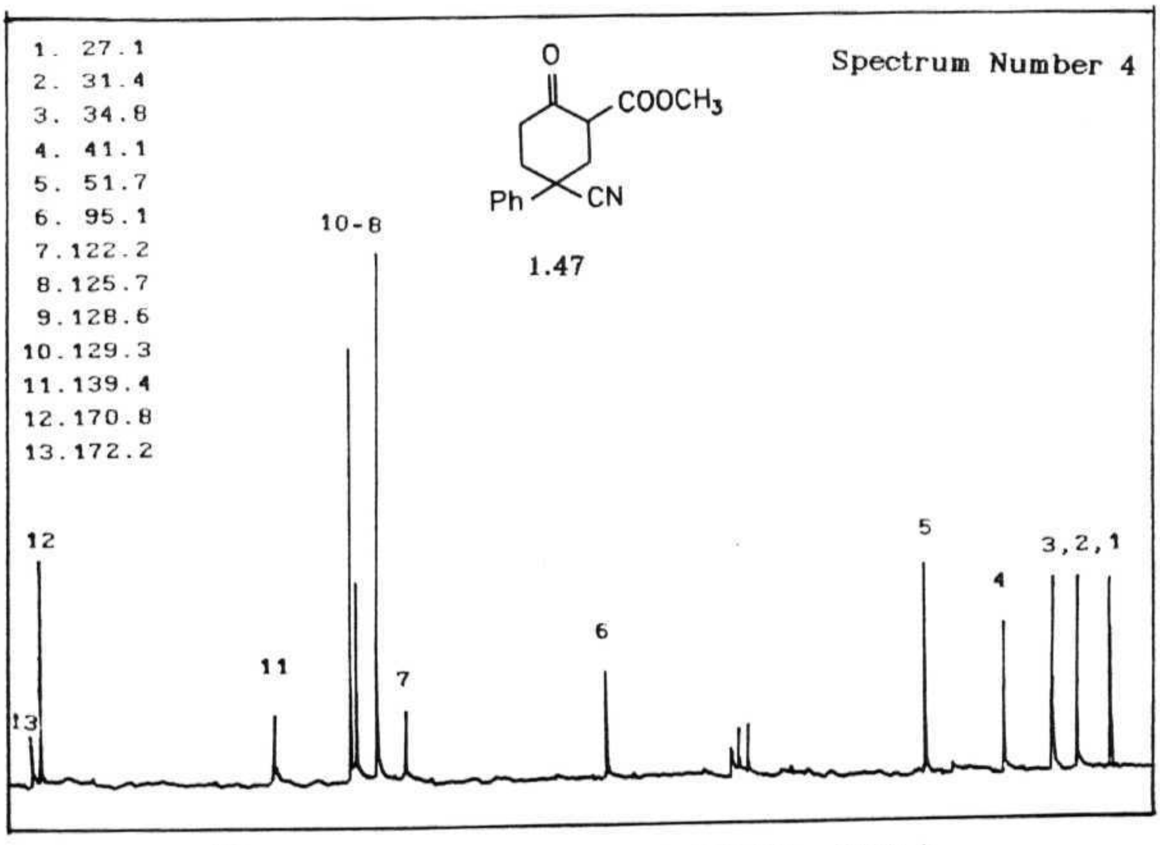

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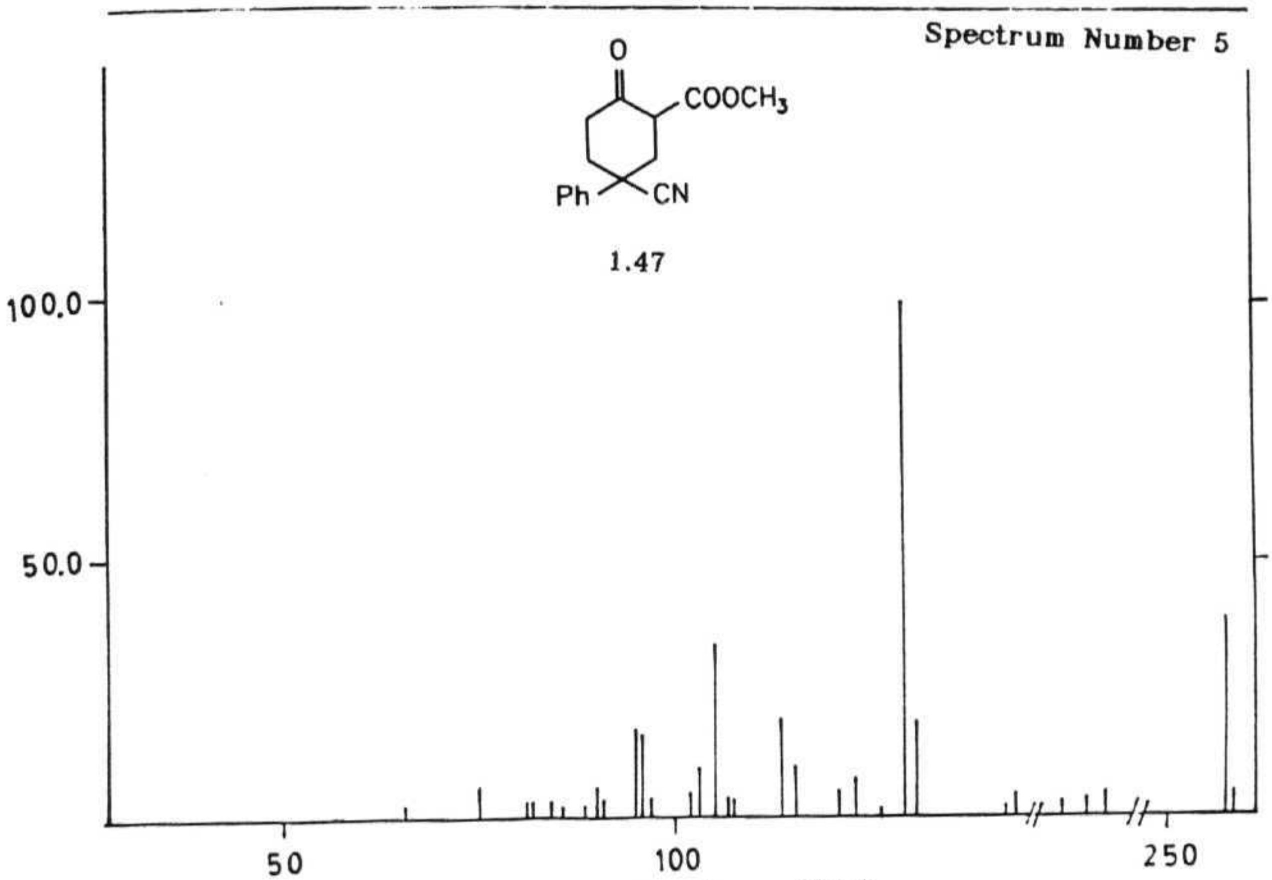

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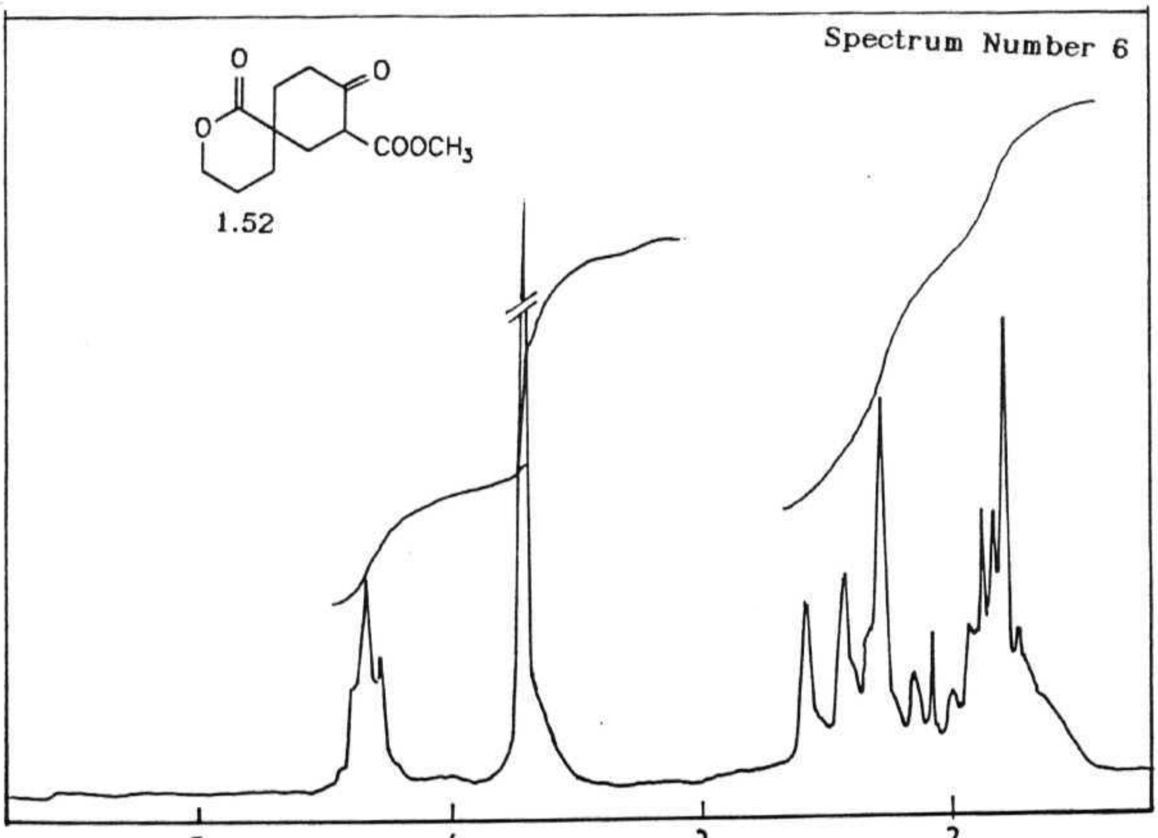

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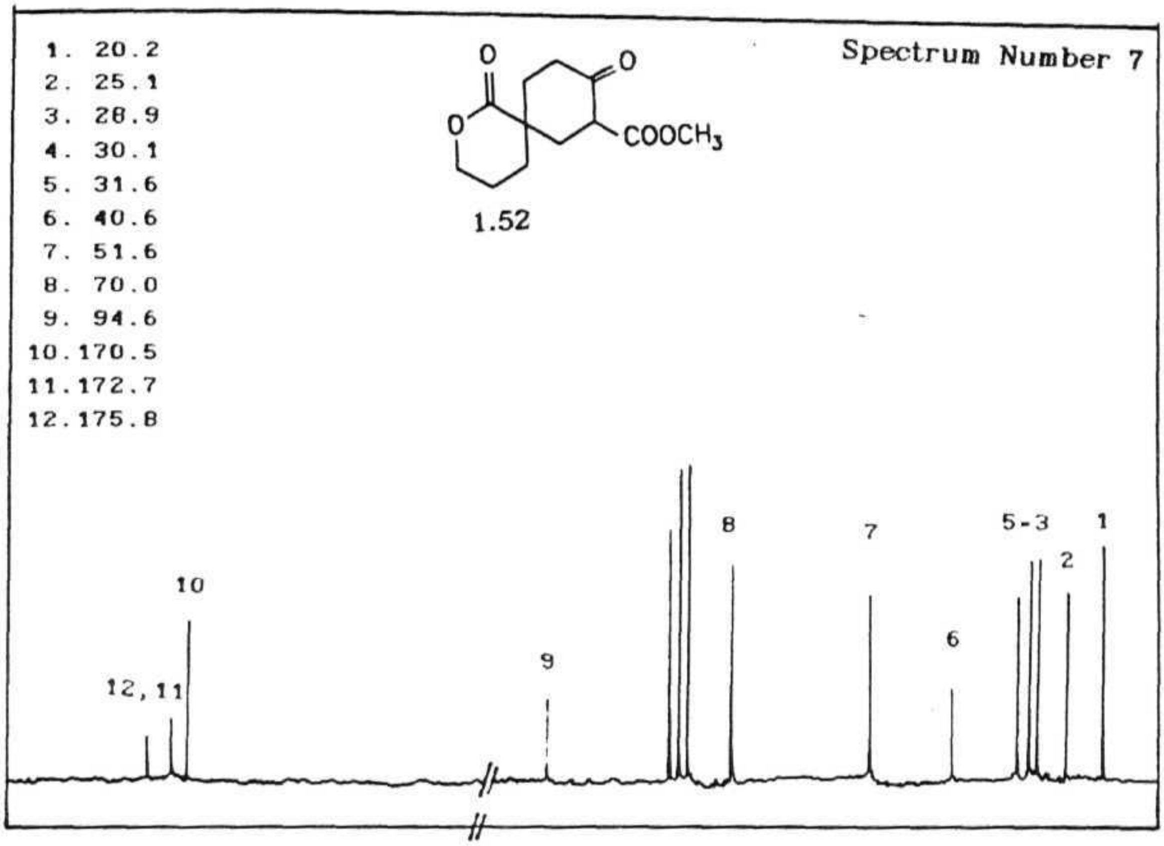

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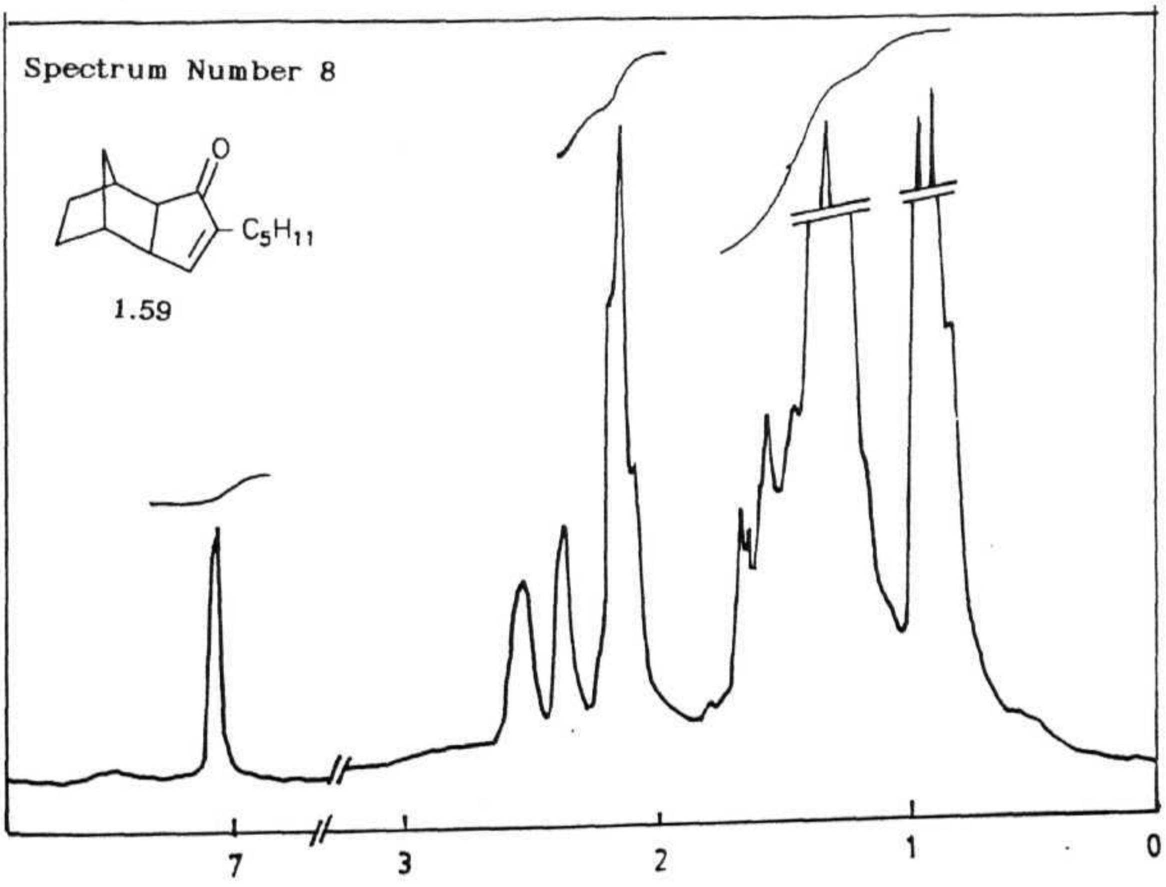

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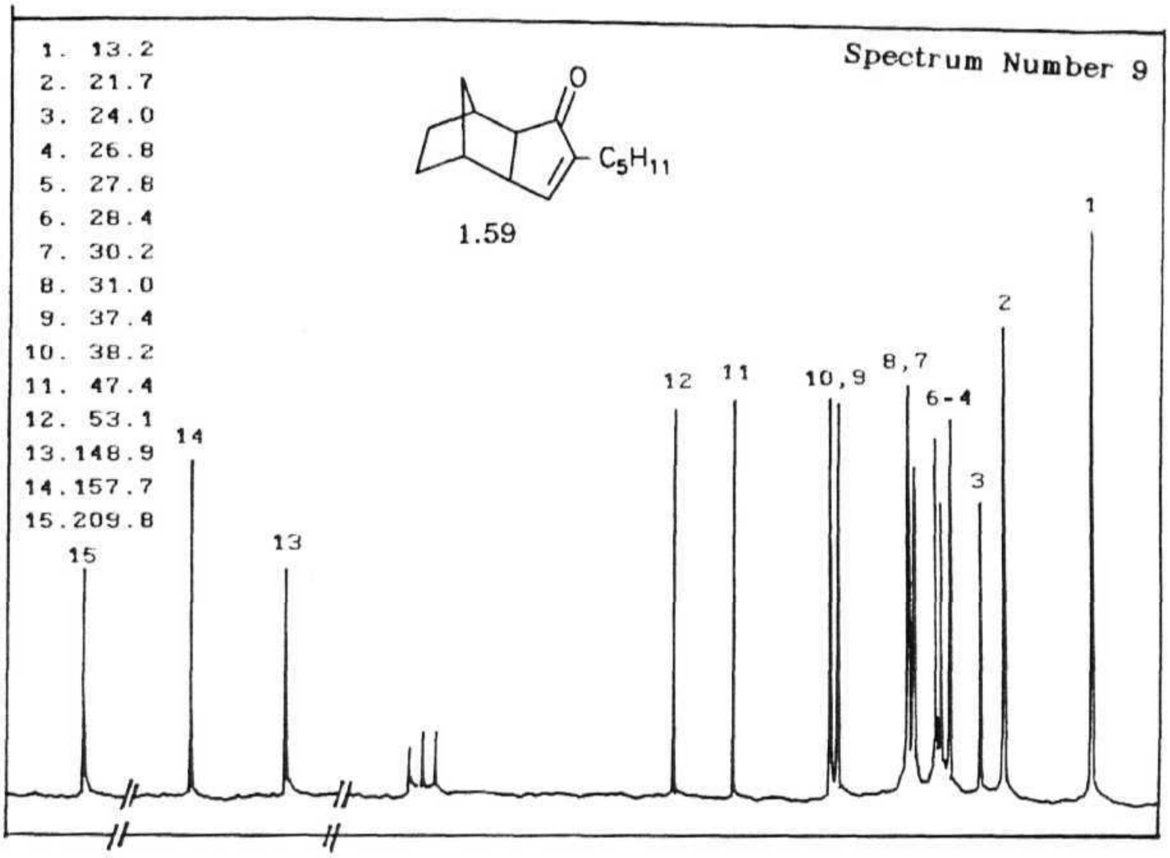

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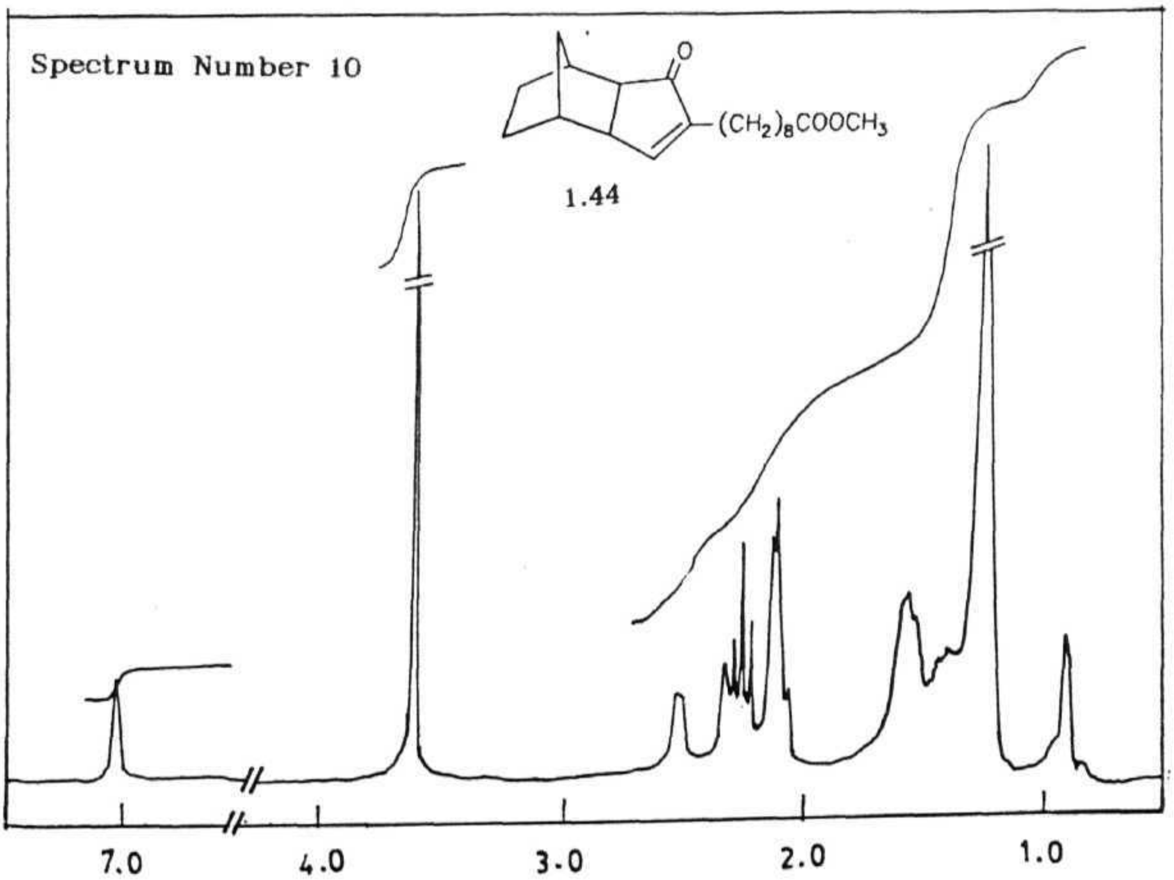

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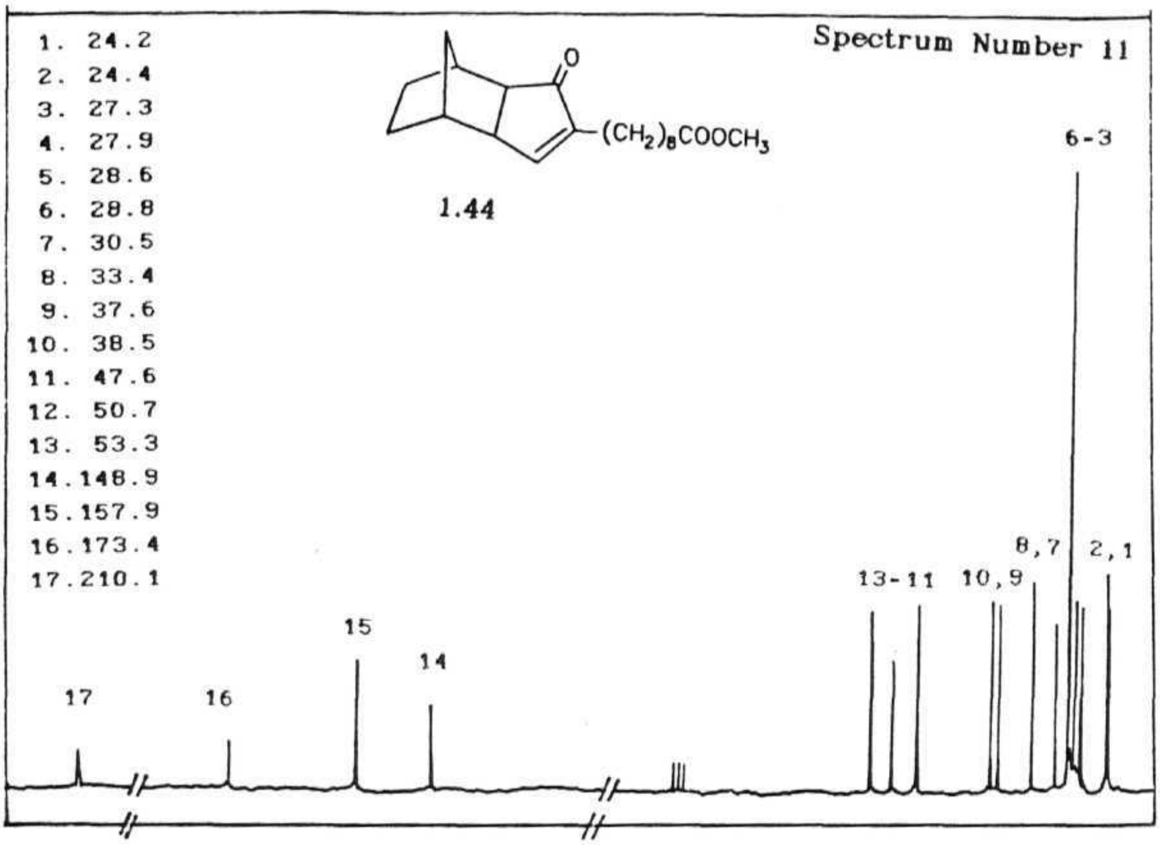

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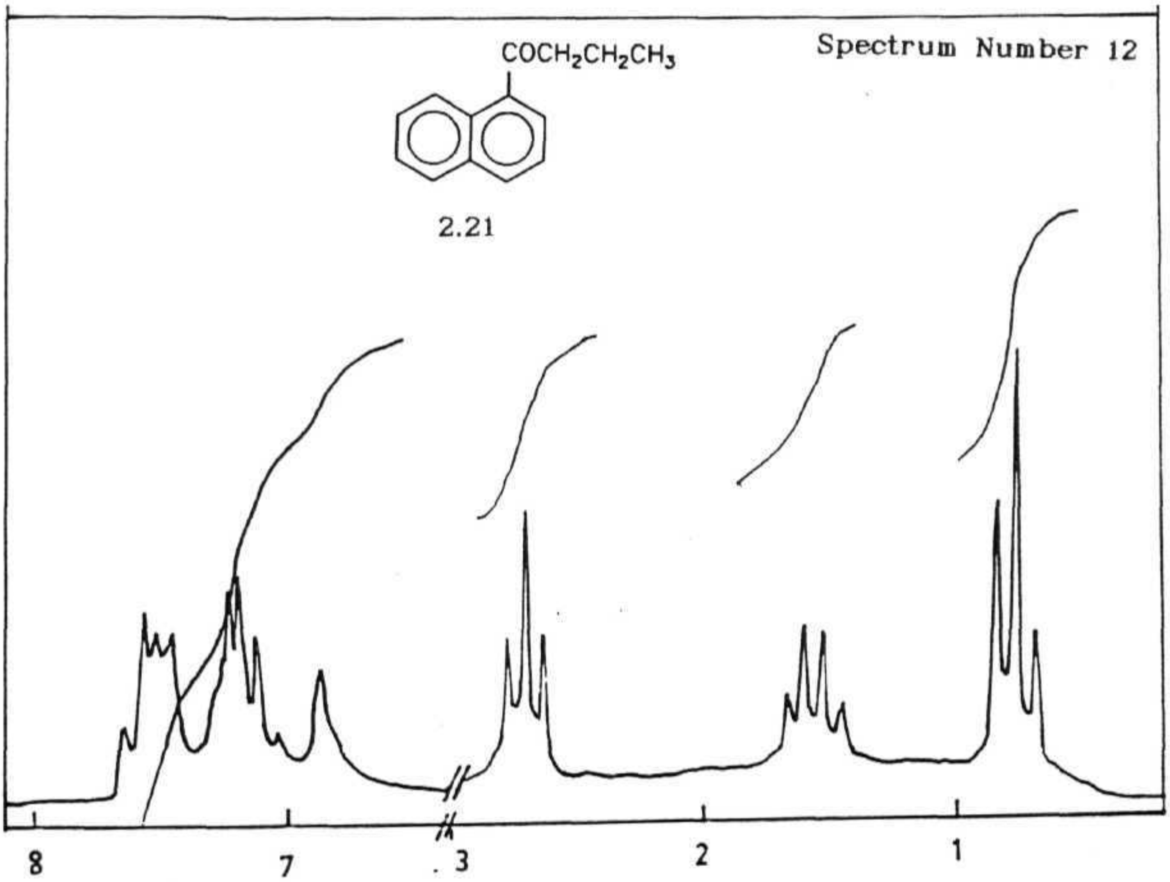

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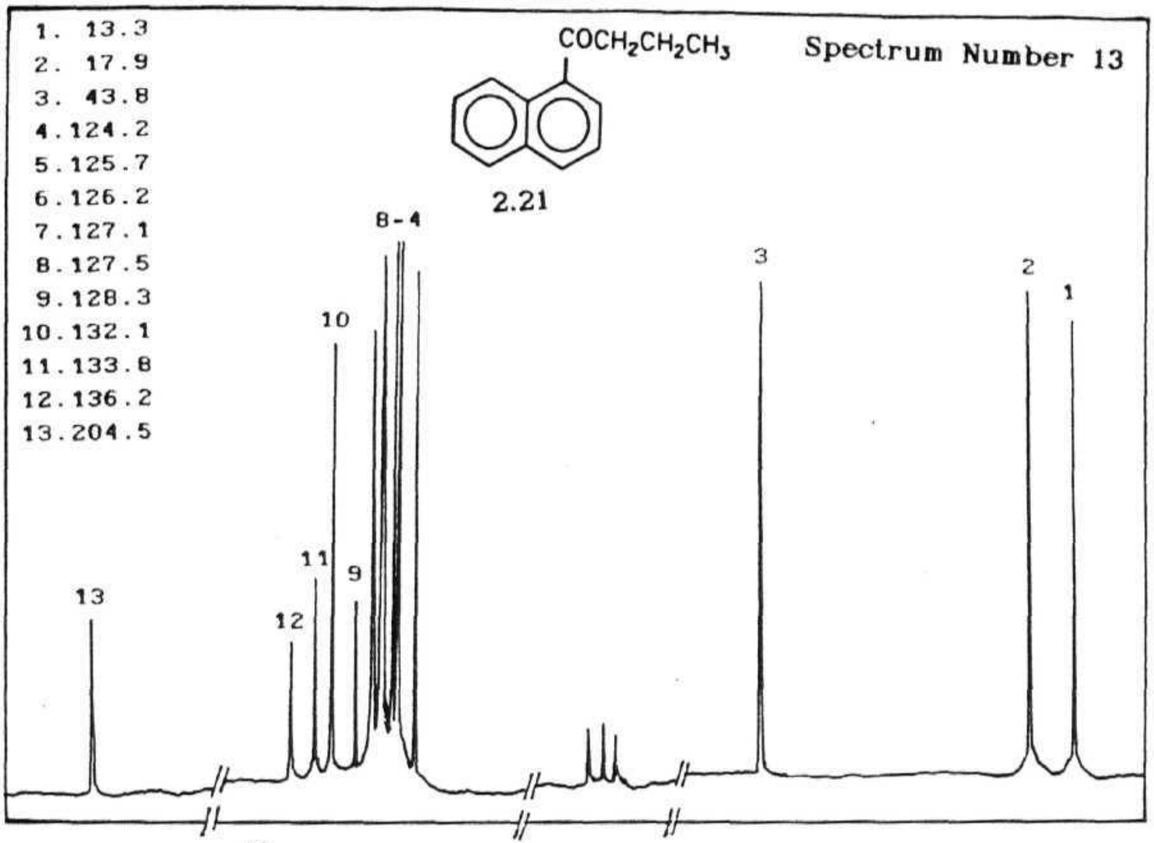

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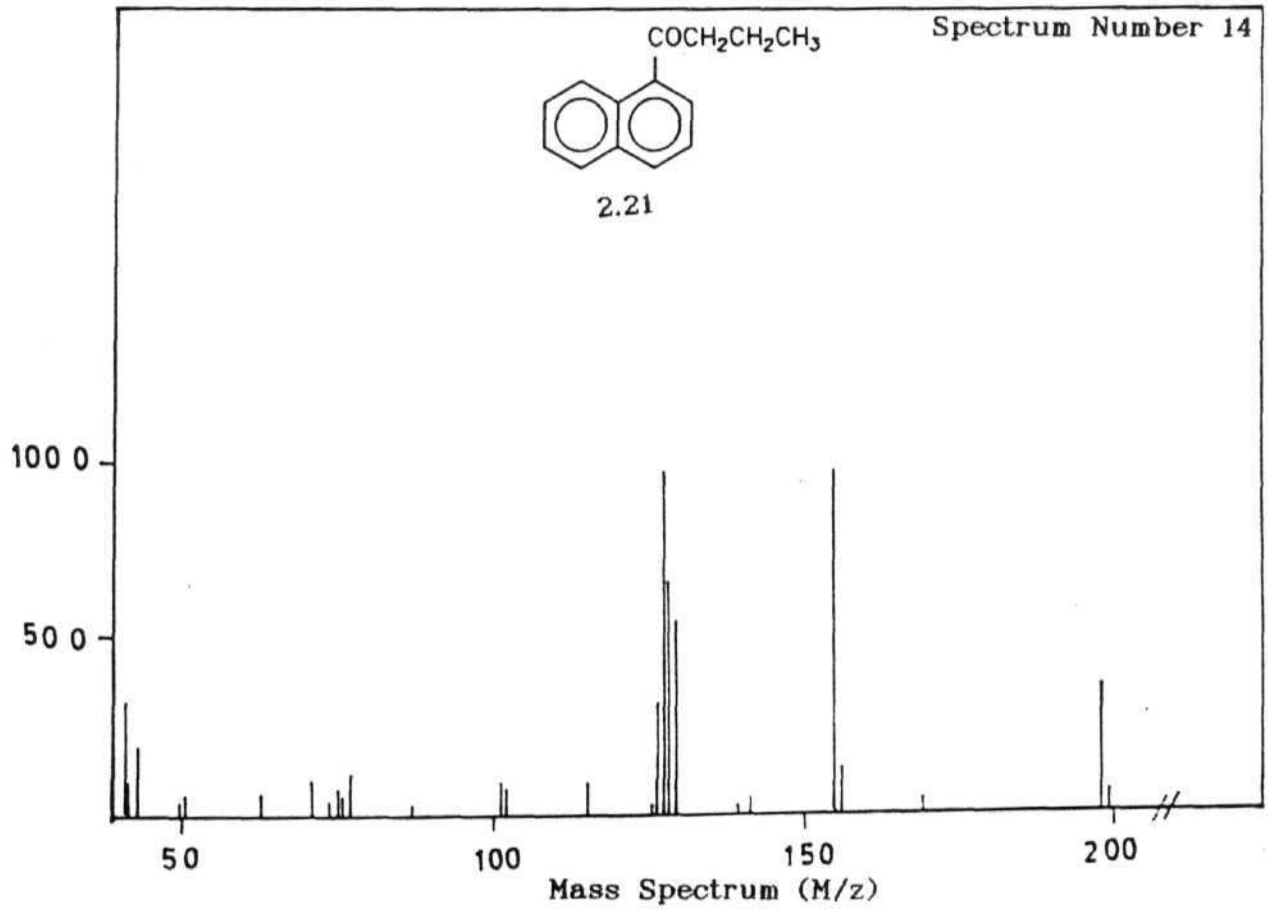

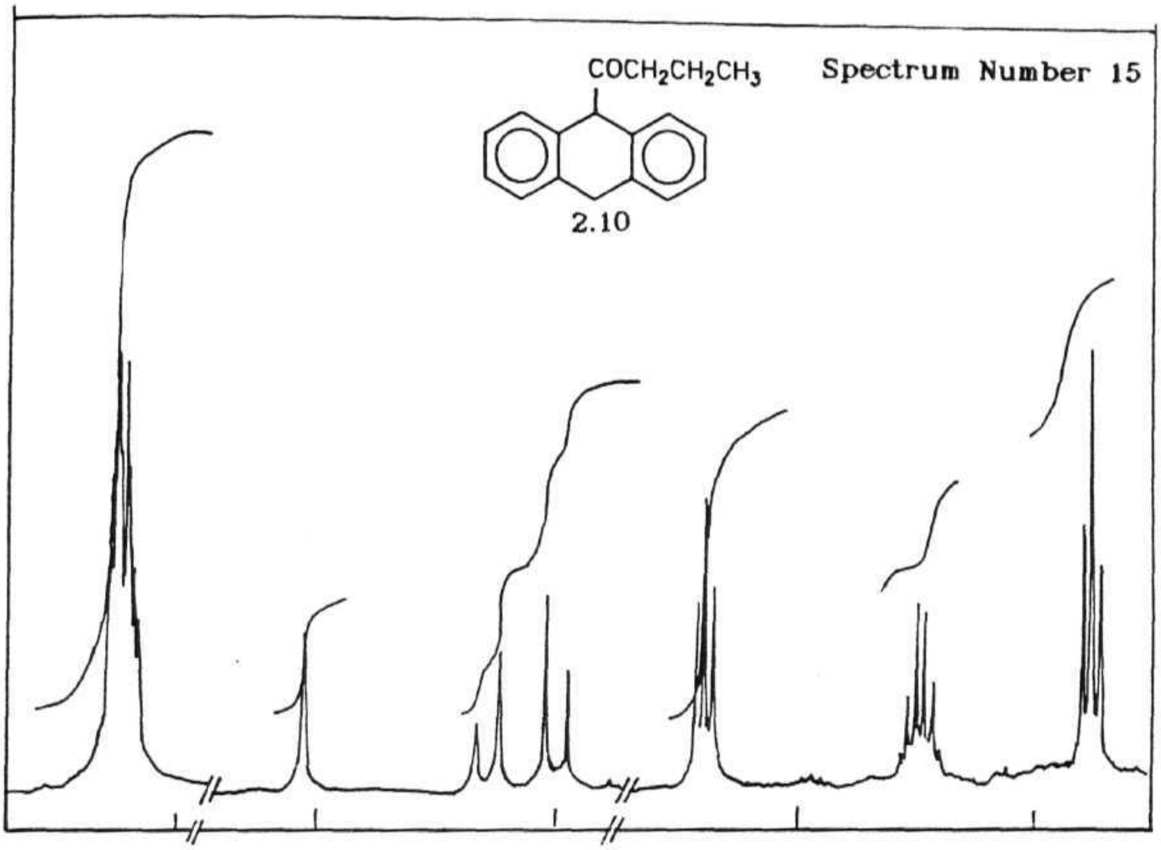

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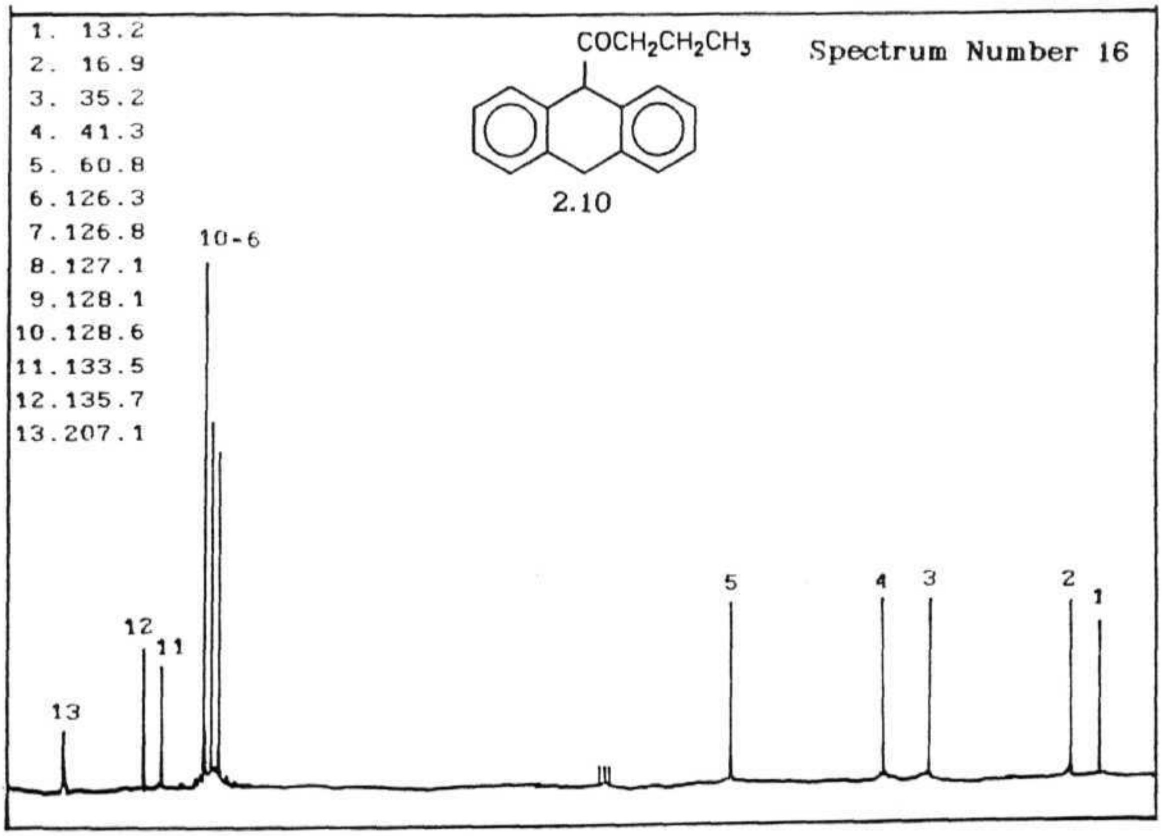

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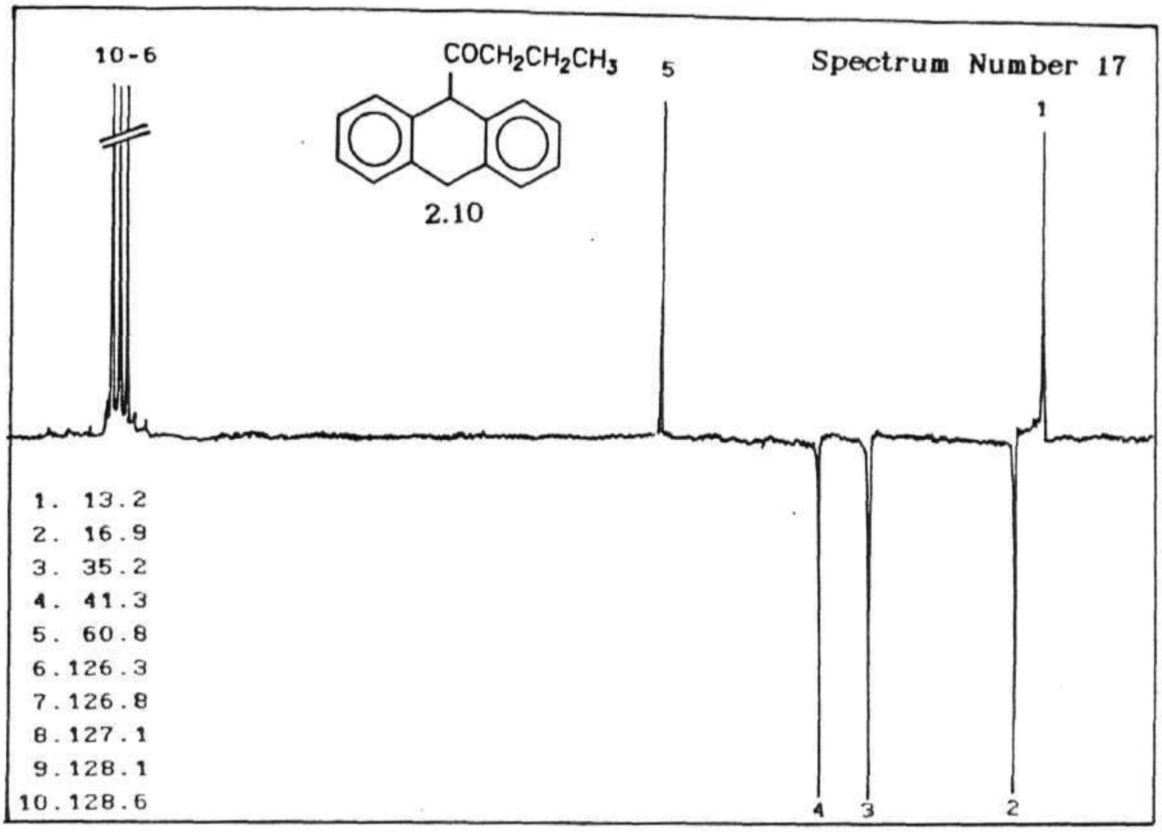
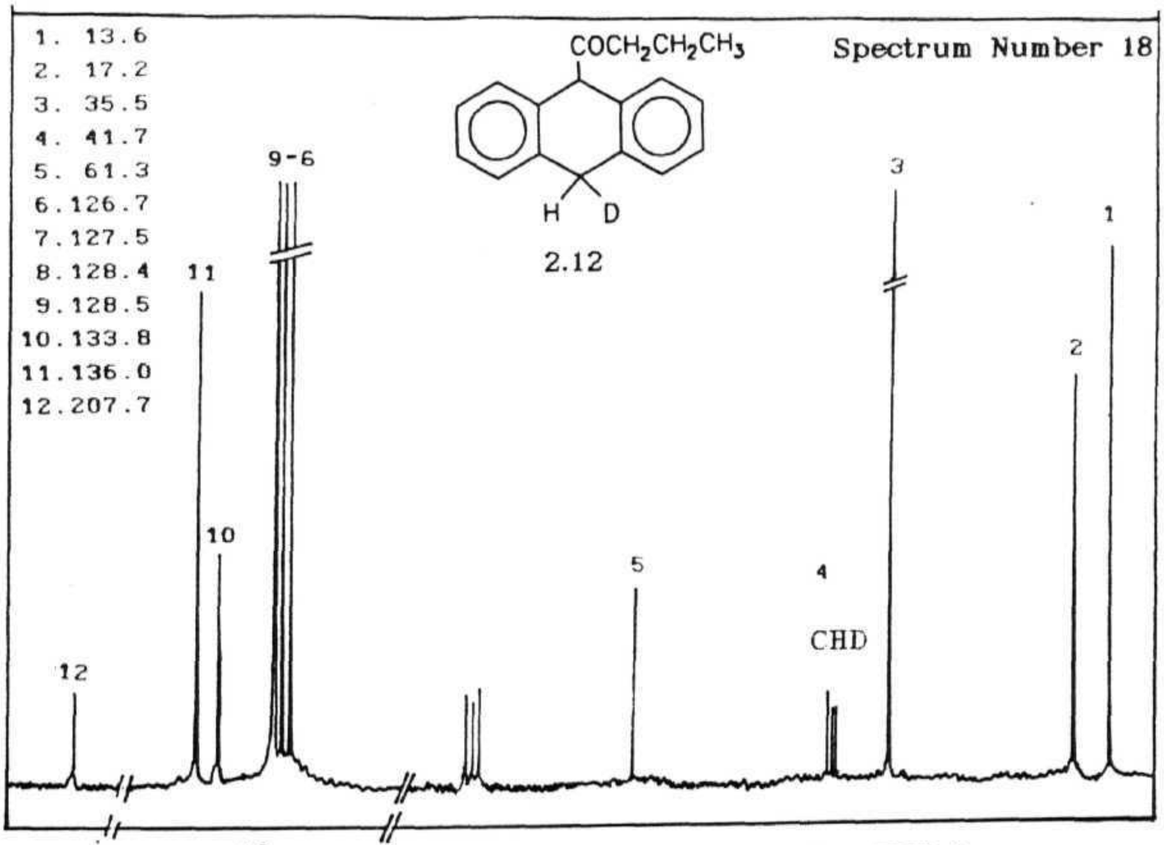


DEPT Spectrum, CH3, CH up and CH2 down (50 MHz, CDCl3)



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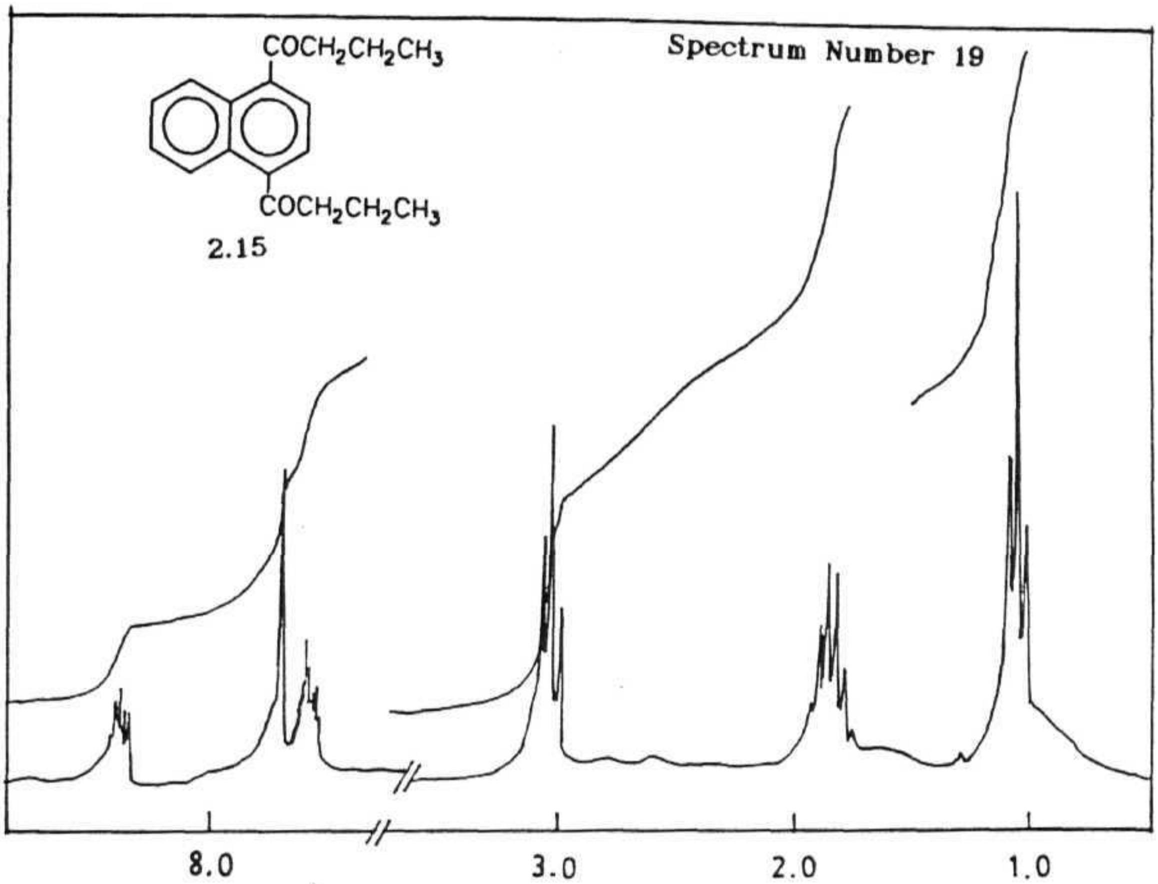

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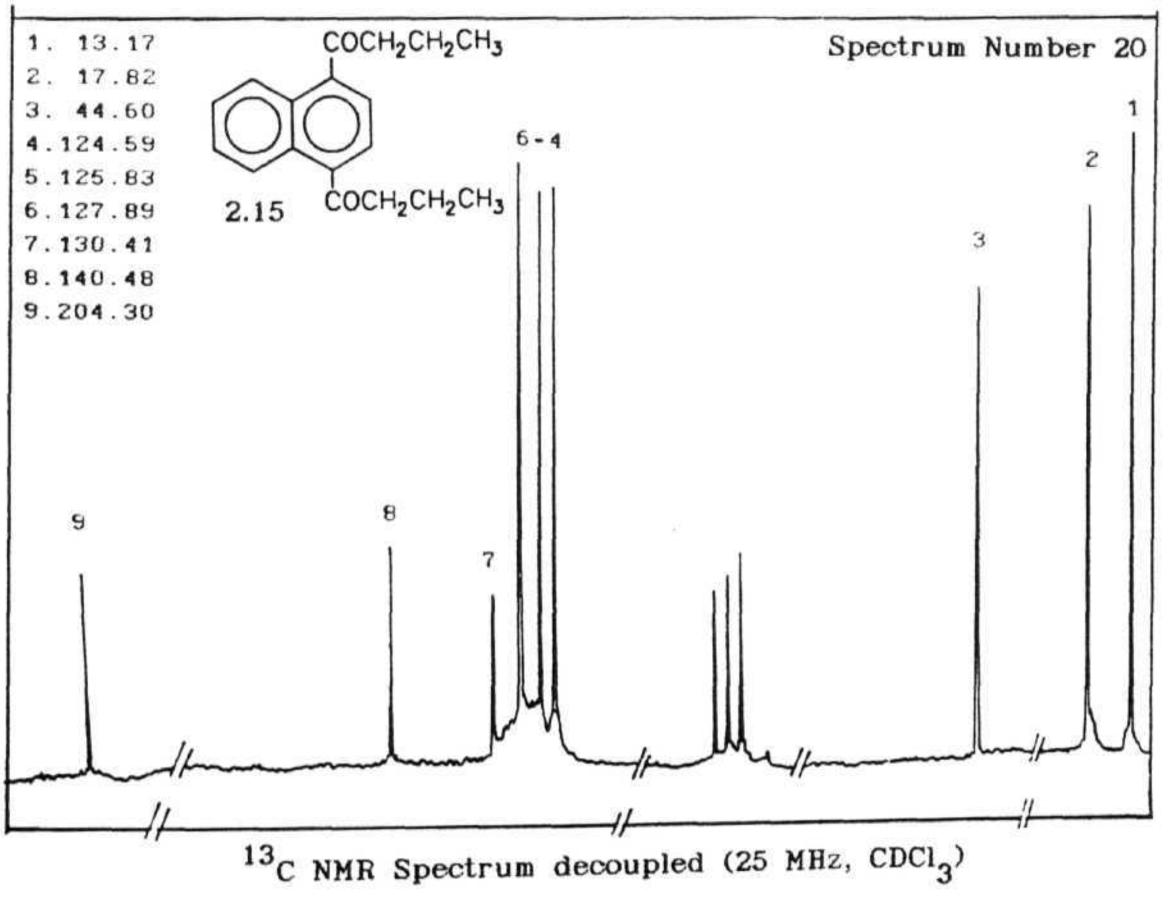

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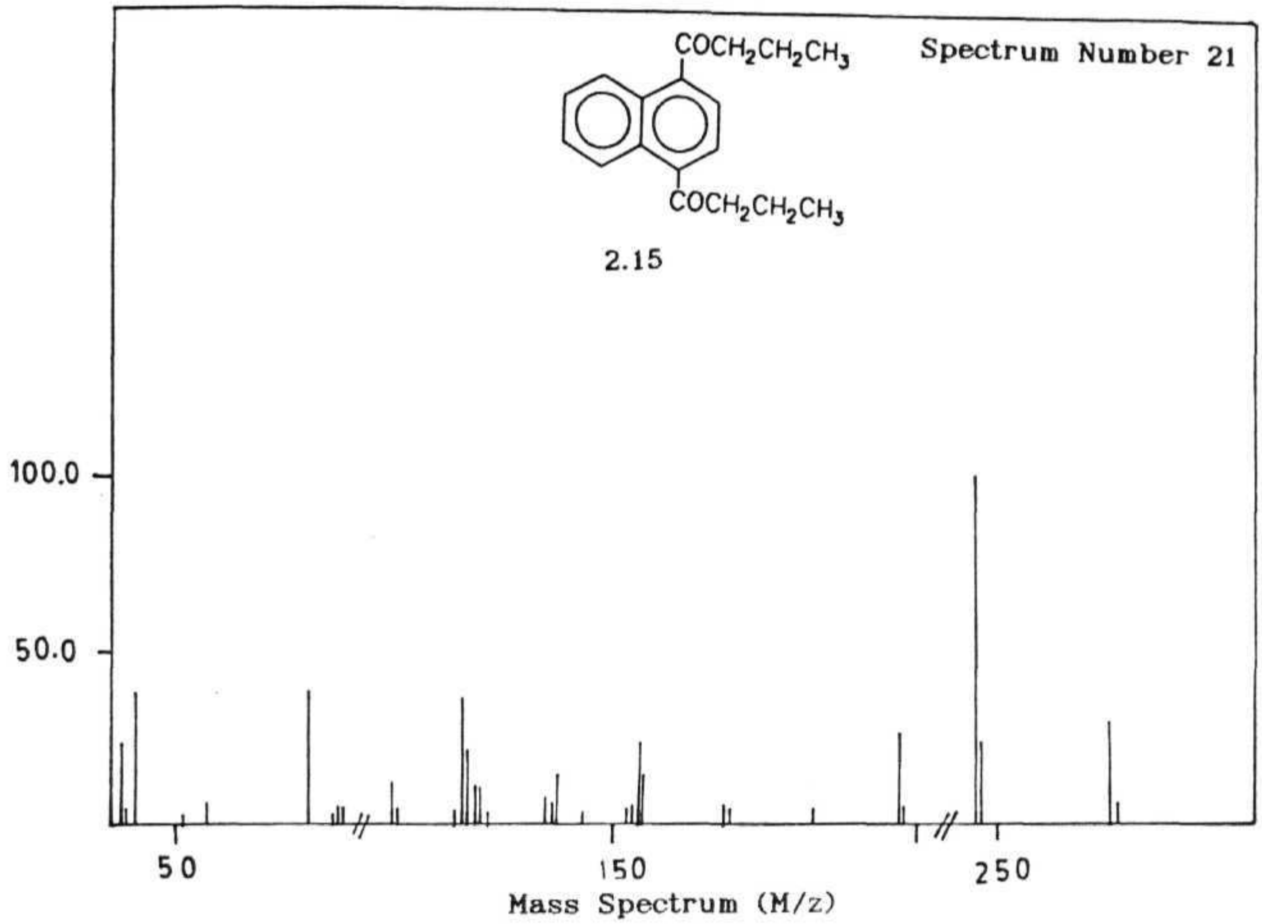
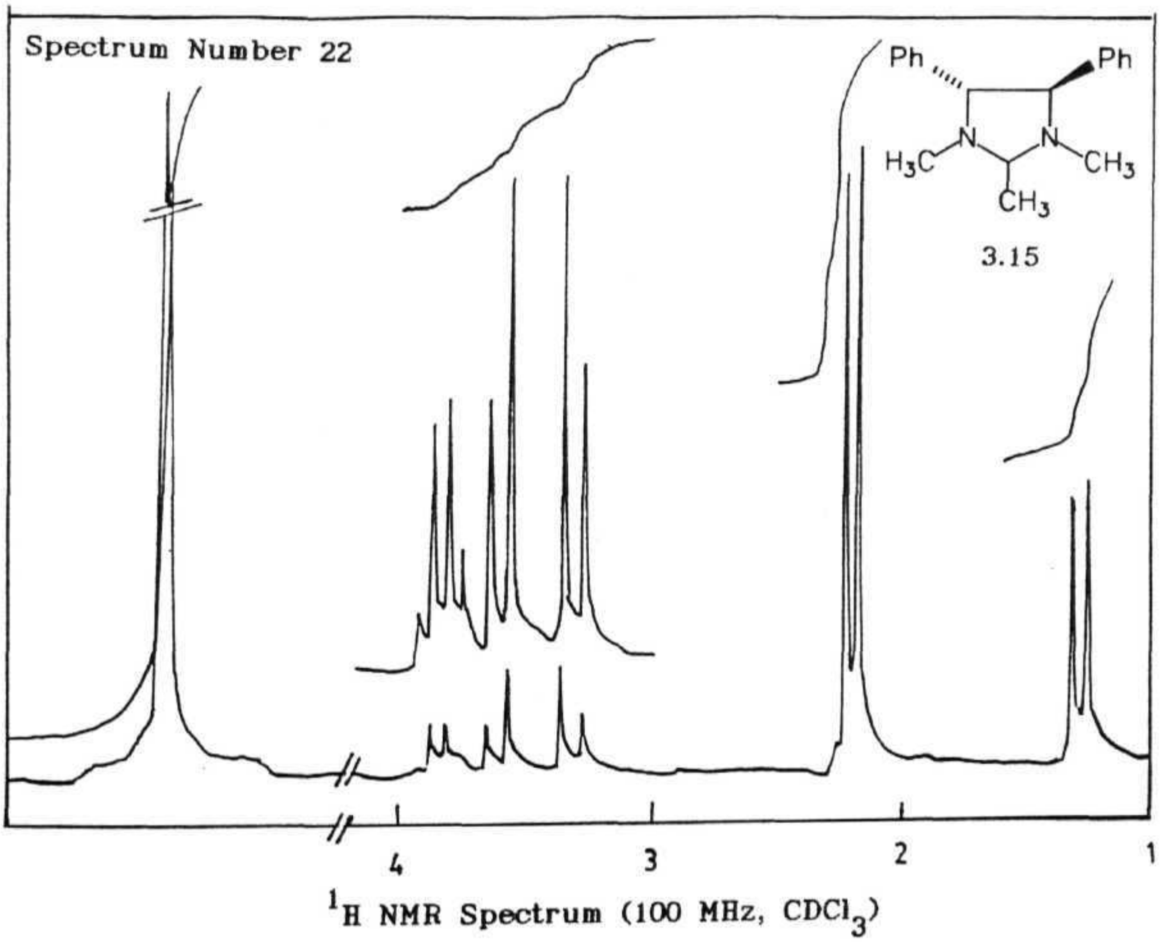
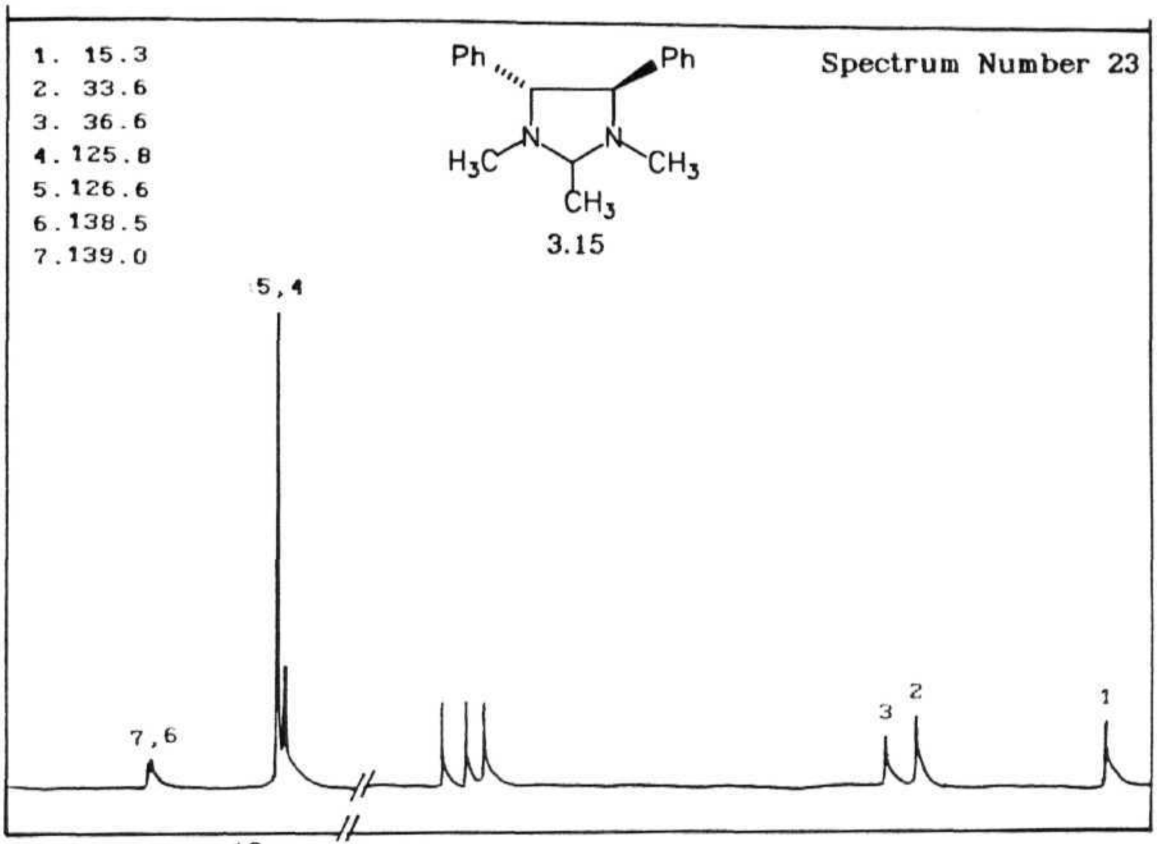

COCH$_2$CH$_2$CH$_3$
COCH$_2$CH$_2$CH$_3$
Spectrum Number 21
2.15
100.0
50.0
50
150
250
Mass Spectrum (M/z)


Spectrum Number 22
Ph
Ph
N
N
H$_3$C
CH$_3$
CH$_3$
3.15
4
3
2
1
^{1}H NMR Spectrum (100 MHz, CDCl$_3$)

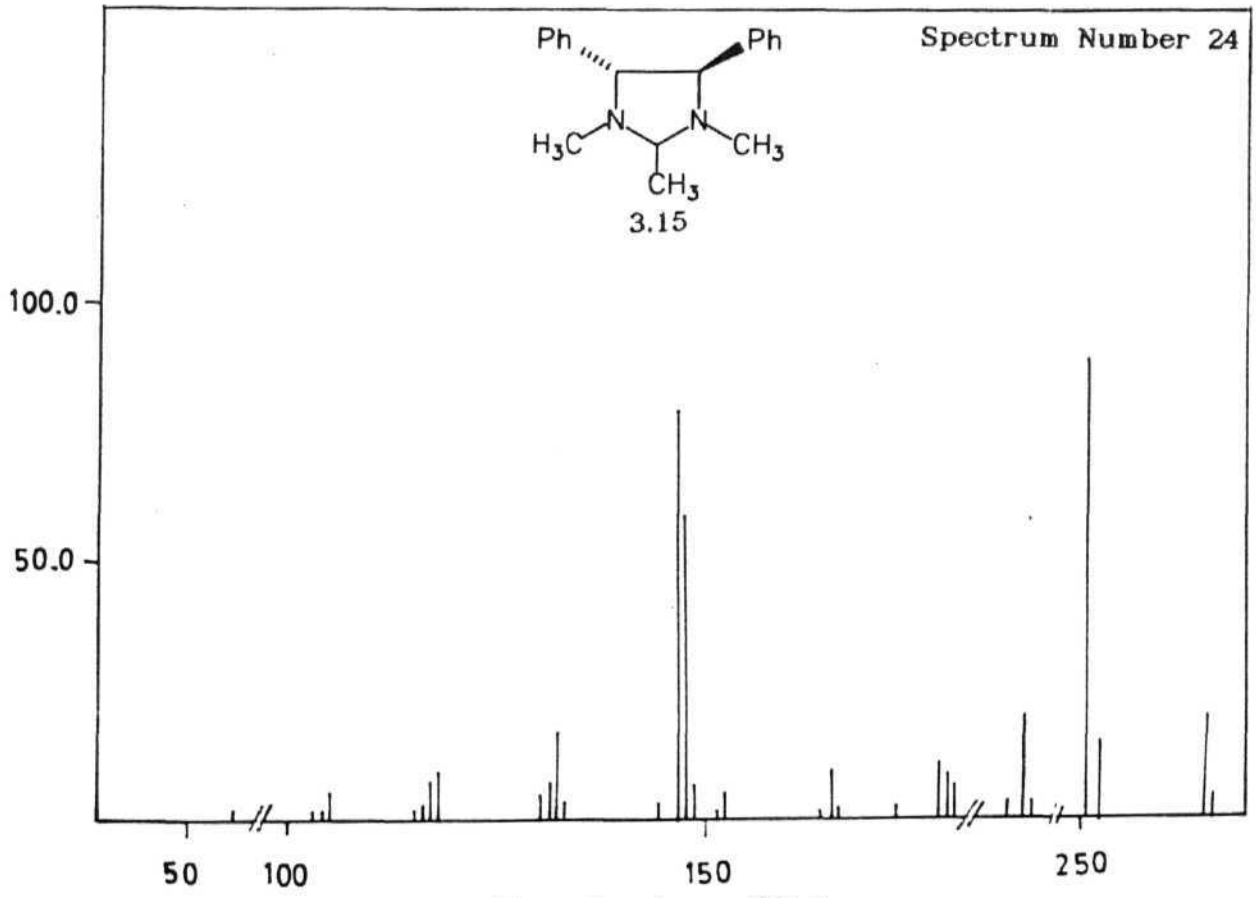


1. 15.3
2. 33.6
3. 36.6
4. 125.8
5. 126.6
6. 138.5
7. 139.0

3.15

Spectrum Number 23

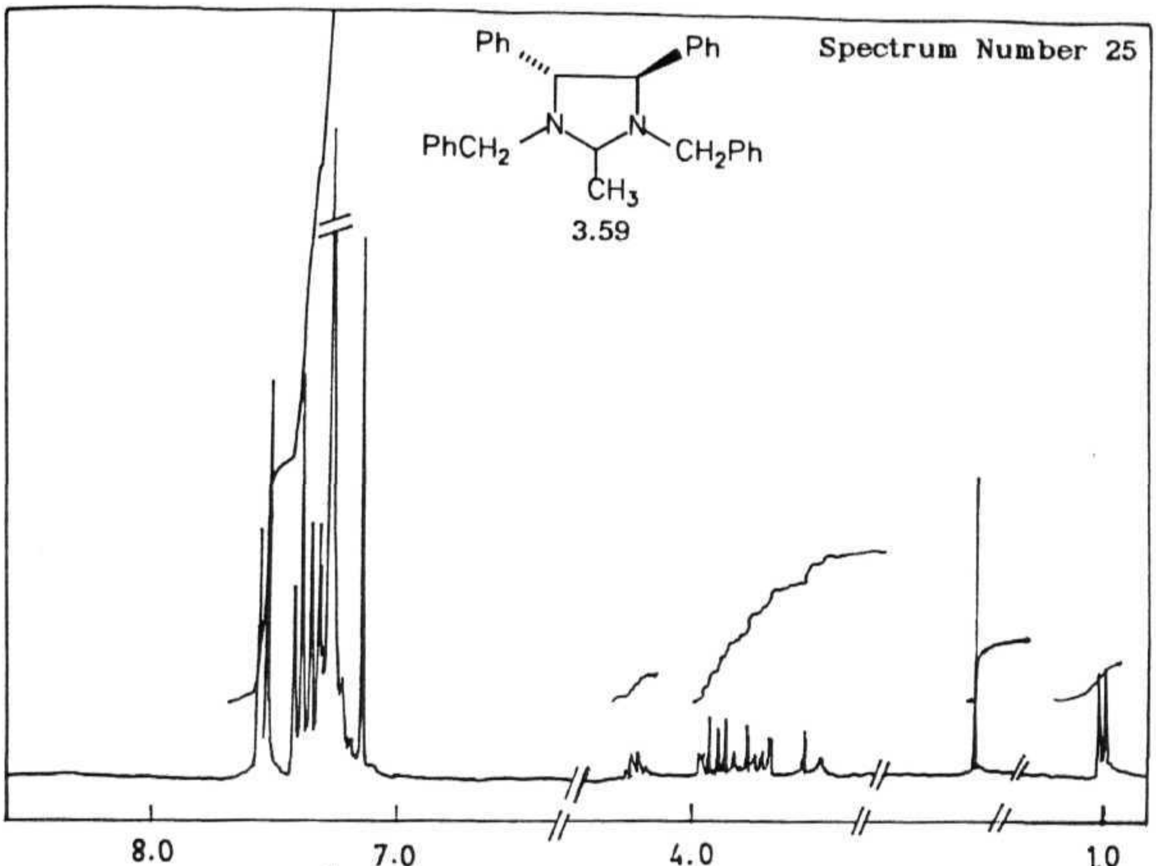
^{13}C NMR Spectrum decoupled (25 MHz, $CDCl_3$)



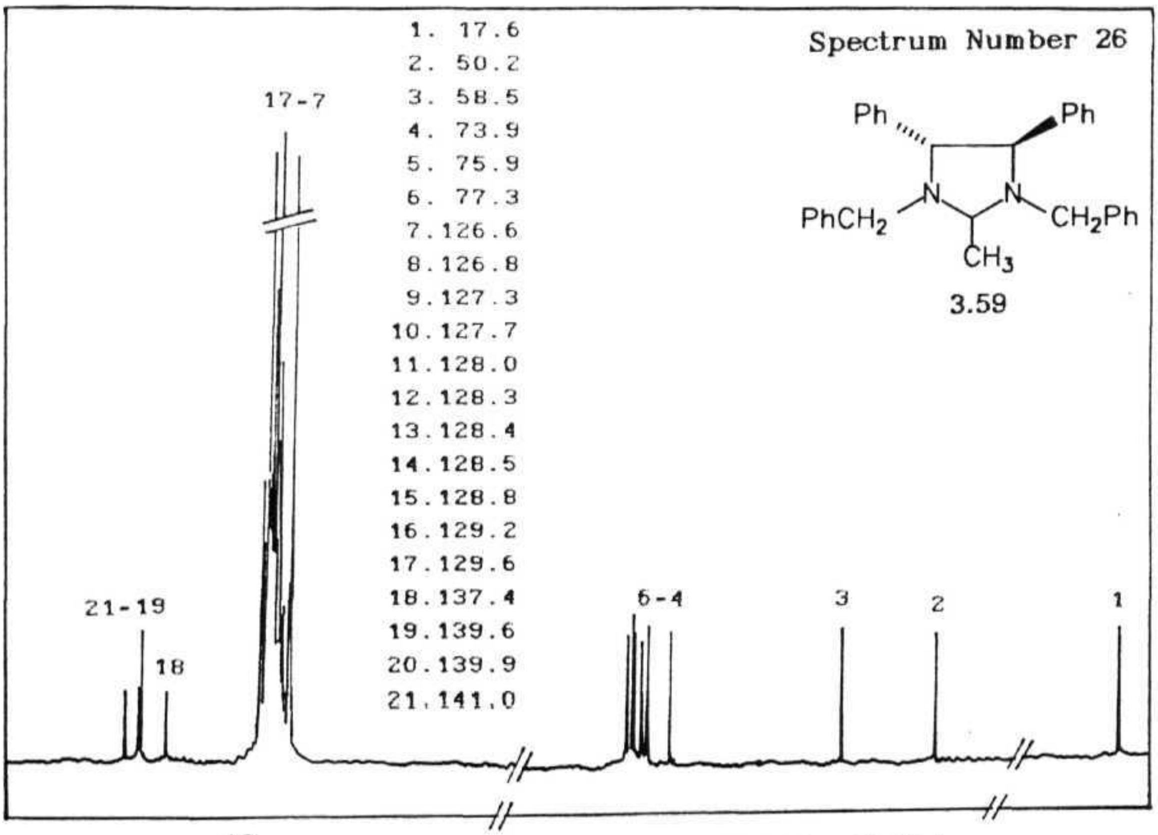
3.15

Spectrum Number 24

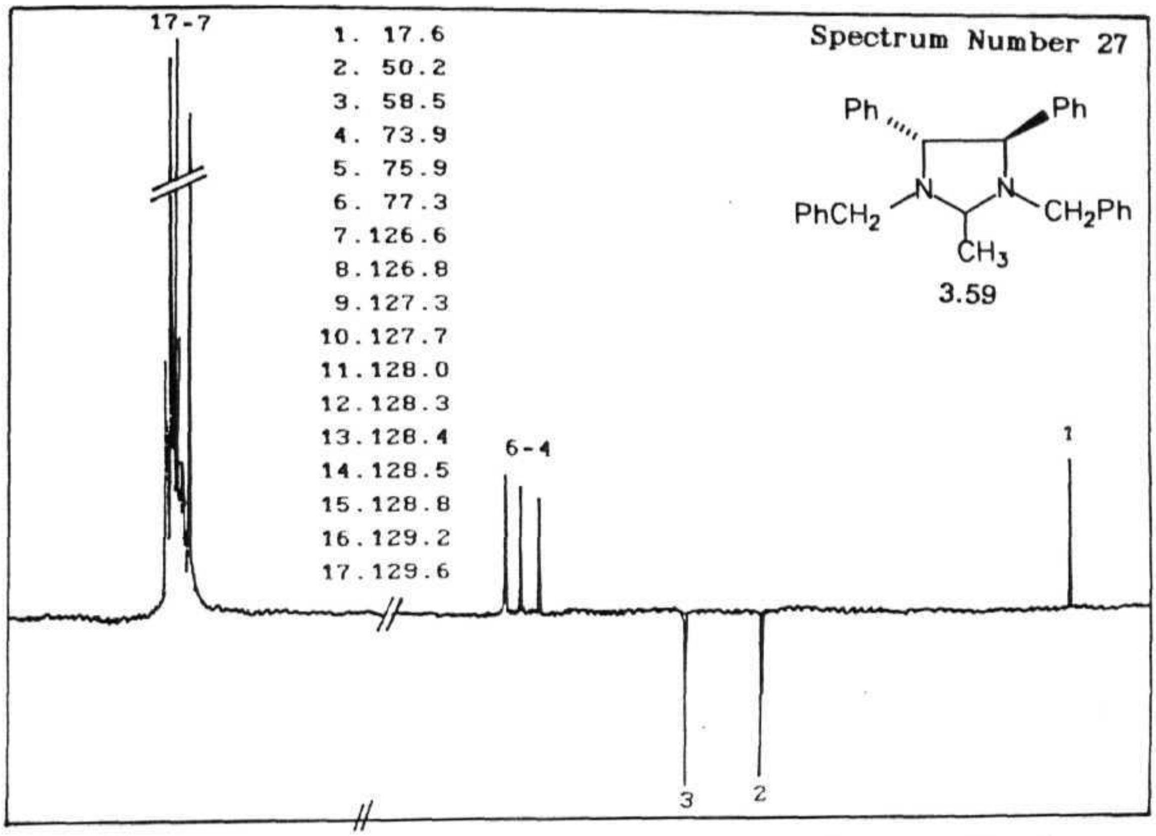
Mass Spectrum (M/z)



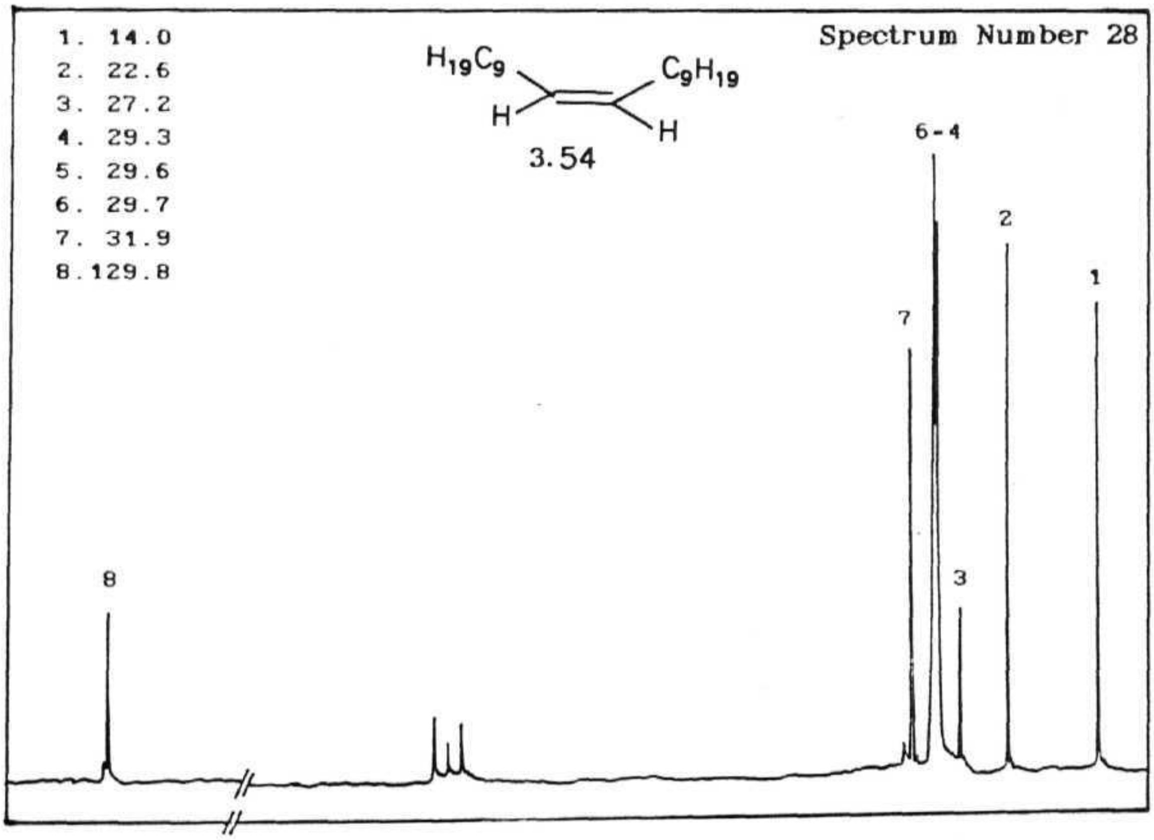
^{1}H NMR Spectrum (200 MHz, CDCl$_3$)



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



DEPT Spectrum, CH3, CH up and CH2 down (50 MHz, CDCl3)



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

LIST OF PUBLICATIONS

(i) Convenient one pot methods for the construction of cyclohexyl ring at the α - methylene moieties of ketones, esters, lactones and nitriles through a Michael addition-Dieckmann cyclization sequence.
M. Periasamy, M. Rama Reddy, U. Radhakrishnan and A. Devasagayaraj
J. Org. Chem., 1993, **58**, 4997.

(ii) Simple convenient methods for the preparation of alkyne-$Co_2(CO)_6$ complexes from $CoBr_2$ for application in Pauson-Khand cyclopentenone synthesis
M. Periasamy, M. Rama Reddy and A. Devasagayaraj
Tetrahedron.1994, 50, 6955.

(iii) Isomerization of 1-alkenes using the $Na_2Fe(CO)_4/CuCl$ and $Na_2Fe(CO)_4/BrCH_2CH_2Br$ reagent systems
M. Rama Reddy and M. Periasamy
J. Organomet. Chem., 1995, 0000.

(iv) Nucleophilic formylation and acylation of polyaromatic hydrocarbon radical anions
M. Rama Reddy and M. Periasamy
To be submitted for publication

(v) Low valent titanium induced one pot synthesis of substituted imidazolidines
M. Rama Reddy and M. Periasamy
To be submitted for publication

(vi) Low valent titanium mediated reductive coupling of esters
M. Rama Reddy and M. Periasamy
To be submitted for publication

Poster Presentations

(i) Low valent titanium mediated reductive coupling of imines.
M. Rama Reddy, M. Periasamy and J.V. Bhaskar Kanth
Pre - IUPAC international conference on metal mediated organic synthesis held at Pune, India (December 8-9, 1994)

(ii) Reactions of organometallic reagents derived from $NaCo(CO)_4$ and $Na_2Fe(CO)_4$ systems with alkenes and alkynes
M. Rama Reddy and M. Periasamy
IUPAC 10th International conference on organic synthesis held at Bangalore, India (December 11-16, 1994)