New organic synthetic methods using iron carbonyl reagents

M. Periasamy*, C. Rameshkumar, U. Radhakrishnan and A. Devasagayaraj
School of Chemistry, University of Hyderabad, Central University P.O., Hyderabad 500 046, India

Investigations carried out on the preparation and synthetic applications of iron carbonyl reagents are reviewed. Reaction of $Na_2Fe(CO)_4$, prepared by the reduction of $FeCl_3$ in THF with sodium naphthalenide under CO atmosphere at 25°C, with alkyl bromides gives the corresponding aldehydes, ketones and carboxylic acids under appropriate conditions. Reaction of $NaR(CO)Fe(CO)_4$ with CuCl at 25°C in THF, leads to the formation of 1,2-diketones. However, in the presence of methylacrylate in addition to the 1,2-diketones the corresponding acyllactones are also formed. Mechanistic pathways and intermediates involved are discussed. Reactions of $NaHFe(CO)_4$/RX or $[HFe_3(CO)_{11}]$ reagents with alkynes lead to the formation of the corresponding α,β-unsaturated carboxylic acids and/or the cyclobutenediones after $CuCl_2{\cdot}2H_2O$ oxidation. Possible intermediates and mechanistic pathways are discussed.

Introduction

In recent years, the metal carbonyls are increasingly used in organic synthesis. Many transition elements form stable neutral metal carbonyls, anionic metal carbonyls, hydrido metal carbonyls, and their derivatives[1–4]. These derivatives display unique reactivities in oxidation, reduction, isomerization, oligomerization, carbonylation and polymerization processes[5,6]. They have been also used extensively in C–C bond formation reactions[7,8].

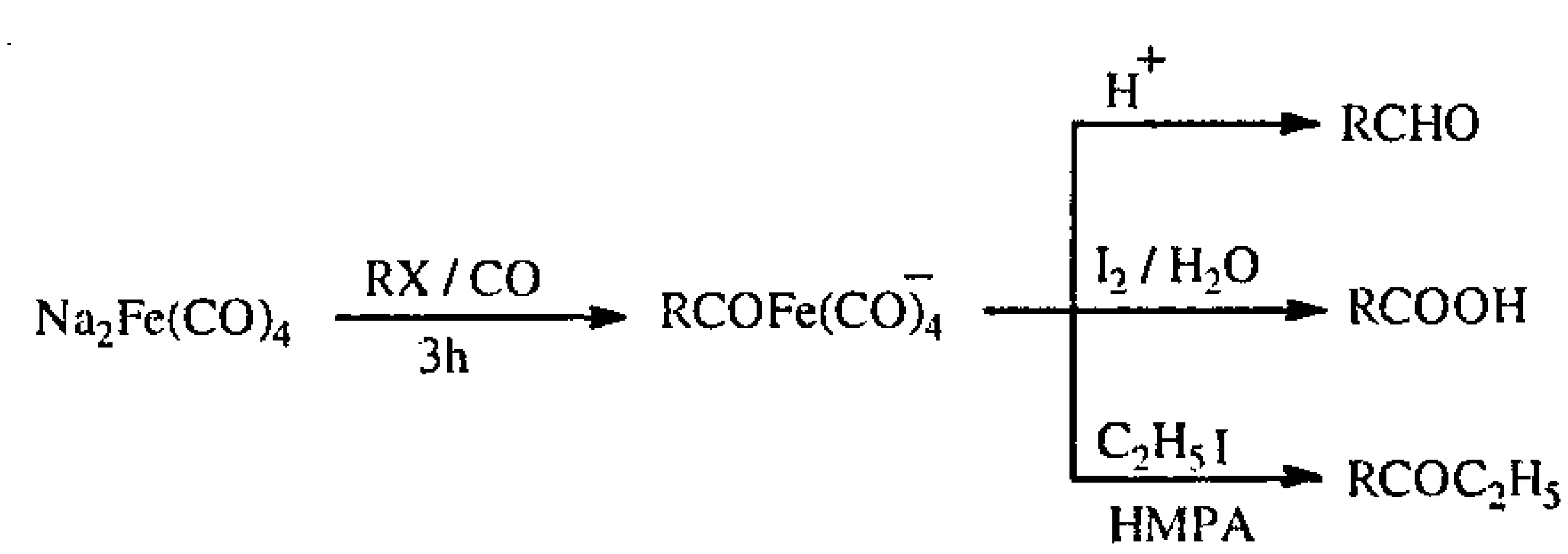
Among various transition metal carbonyls, the organoiron complexes have potential in all these aspects[9]. We have undertaken efforts to prepare readily accessible reactive iron carbonyl reagents for applications in organic synthesis. We describe the results of these investigations in this article.

Methods of preparation of $Na_2Fe(CO)_4$

The super nucleophile $Na_2Fe(CO)_4$ (Collman reagent) has been demonstrated to be a versatile reagent in several organic transformations[10]. Numerous methods have been reported for the preparation of this reagent from readily available starting materials[10–13]. The $Na_2Fe(CO)_4$ reagent is useful as a nucleophile in the conversion of alkyl bromides, iodides, and tosylates into aldehydes, ketones, carboxylic acid derivatives, esters and amides[10]. It is generally prepared using $Fe(CO)_5$, sodium and benzophenone. However, use of polar benzophenone might pose problems during the isolation of products. Hence, we have developed a method for *in situ* generation of $Na_2Fe(CO)_4$ from $Fe(CO)_5$ using Na/naphthalene[14]. Naphthalene can be readily separated from polar products. It was also observed that the $Na_2Fe(CO)_4$ can be prepared directly from $FeCl_3$ using Na/naphthalene and CO in THF (eq. 1)[14].

$$\text{Na} + \text{Naphthalene} \xrightarrow[\text{CO}]{\text{FeCl}_3} \text{Na}_2\text{Fe(CO)}_4. \quad (1)$$

The formation of $Na_2Fe(CO)_4$ has been confirmed by performing the anticipated reactions with aliphatic halides to obtain the corresponding aldehydes, carboxylic acids and ketones (Scheme 1)[10]. It has been proposed that $NaRCO[Fe(CO)_4]$ is the intermediate involved in all these transformations. We have decided to investigate further applicatons of this intermediate species.

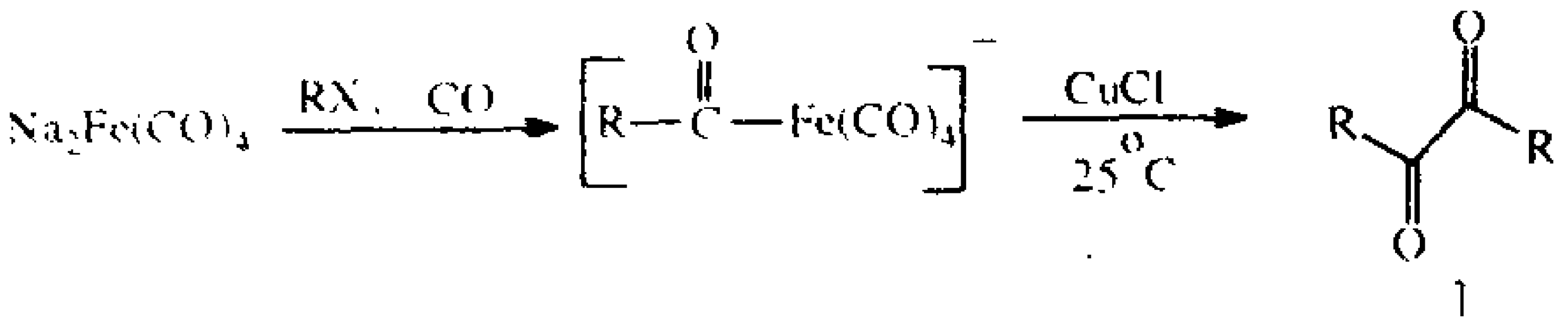


Scheme 1.

Reaction of $NaRCO[Fe(CO)_4]$ with CuCl

The acylmetals such as 'RCOCu' are one of the most sought after intermediates in organometallic chemistry. It was anticipated that the use of CuCl in the place of H^+ (Scheme 1) could lead to the formation of 'RCOCu'. However, it was observed that the reaction of NaRCO $[Fe(CO)_4]$ with CuCl gives the corresponding 1,2-diketones (70–90%)[15]. This transformation is a general one and several alkyl bromides are converted into the corresponding 1,2-diketones (eq. 2).

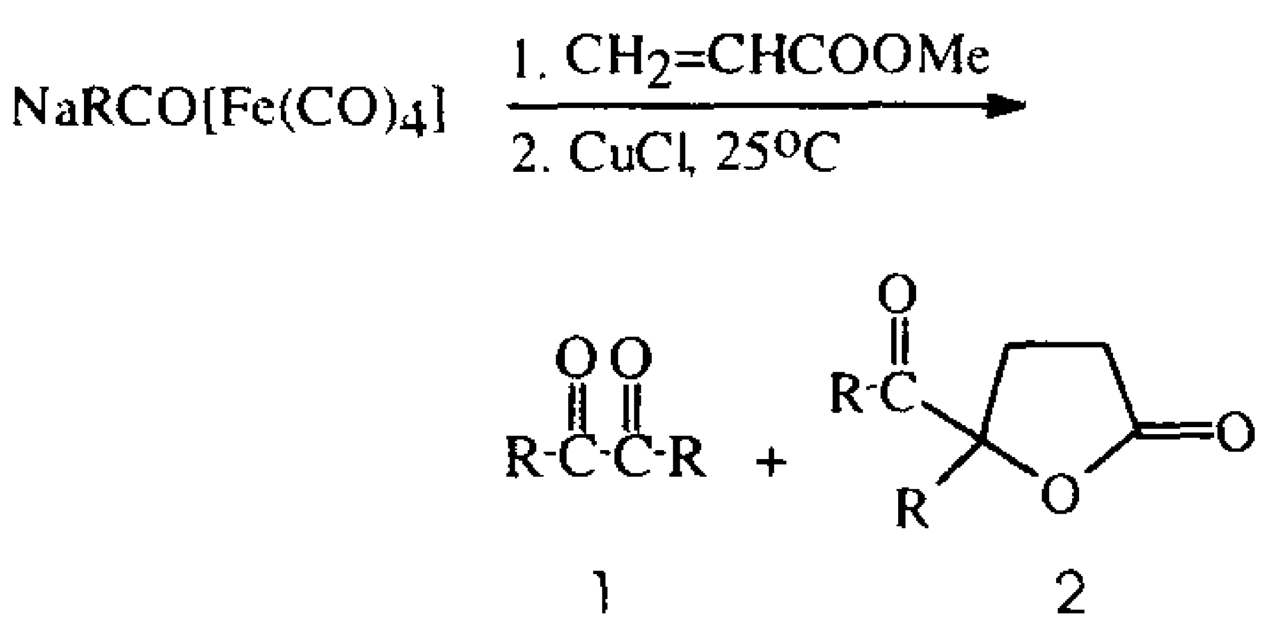
*For correspondence. (e-mail: mpsc@uohyd.ernet.in)



(2)

RX	1
a) CH_3-$(CH_2)_5$-Br	78%
b) CH_3-$(CH_2)_9$-Br	80%
c) CH_3-$(CH_2)_7$-Br	85%
d) CH_3-$(CH_2)_4$-Br	79%
e) CH_3-$(CH_2)_3$-Br	90%
f) $(CH_2$=CH)-$(CH_2)_4$-Br	74%
g) CH_3OCO-$(CH_2)_3$-Br	73%

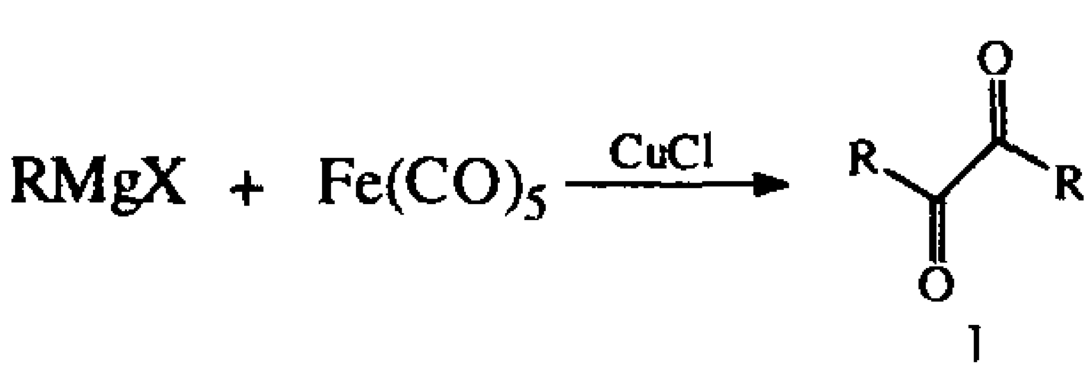
It was thought that the intermediate should be characteristic of 'RCOCu' species and hence, would be expected to undergo 1,4-addition with α,β-unsaturated compounds. However, it was found that addition of methylacrylate to the NaRCO[$Fe(CO)_4$]/CuCl system leads to the formation of 1,2-diketones (20–28%) and the acyllactones (35–52%) (eq. 3)[16].



(3)

RX	1	2
a) CH_3-$(CH_2)_7$-Br	20%	50%
b) CH_3-$(CH_2)_4$-Br	28%	45%
c) CH_3-$(CH_2)_{15}$-Br	25%	35%
d) CH_3-$(CH_2)_2$-Br	23%	44%
e) CH_3-$(CH_2)_3$-Br	22%	49%
f) CH_3-$(CH_2)_5$-Br	20%	52%
g) $(CH_2$=CH)-$(CH_2)_4$-Br	21%	40%

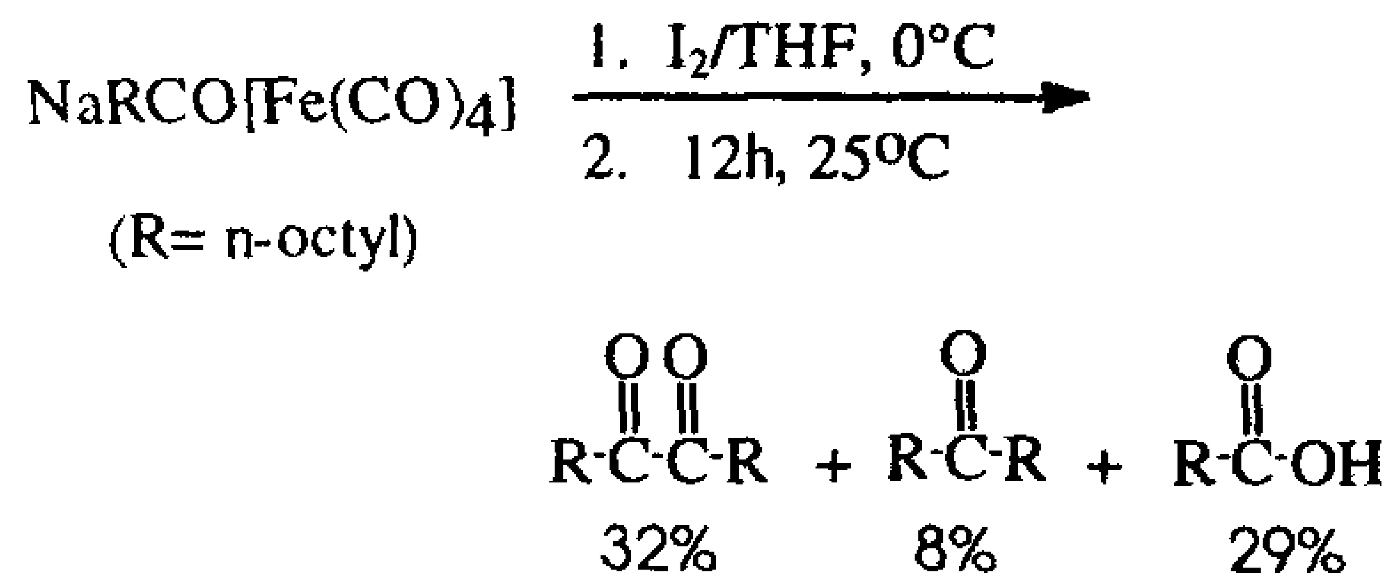
It was also observed that RCO[$Fe(CO)_4$]$^-$ generated *in situ* using RMgX (R = *n*-butyl) with $Fe(CO)_5$ in THF after treatment with CuCl gives the corresponding 1,2-diketone (45–50%) (eq. 4)[16].



(4)

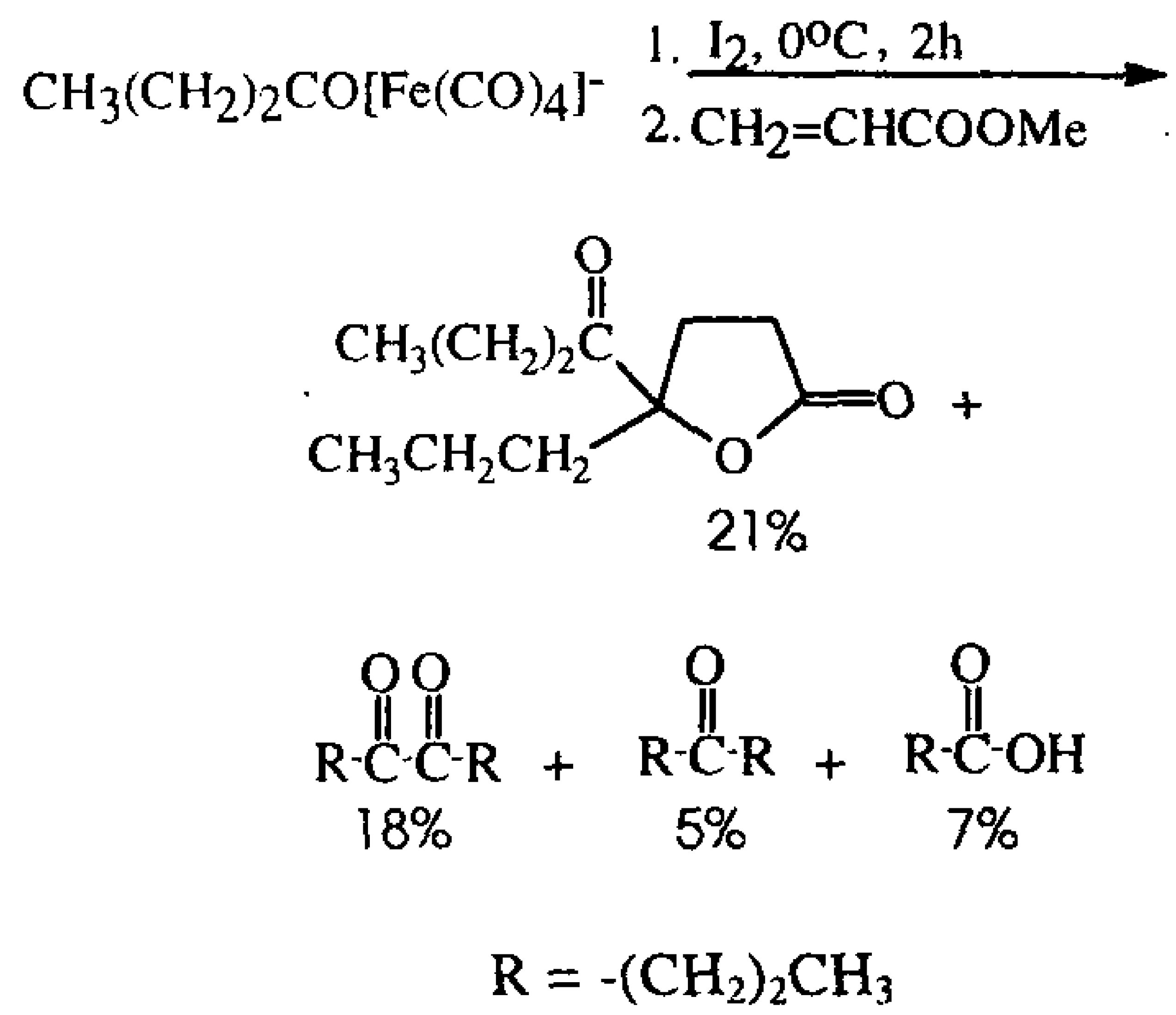
RX	1
a) $CH_3(CH_2)_3$-Br	45%
b) $CH_3(CH_2)_7$-Br	48%
c) Ph-Br	50%

The 1,2-diketone is also formed (32% yield) in the reaction of NaRCO[$Fe(CO)_4$] (R = *n*-octyl) with I_2 in THF besides the corresponding 1,2-diketone (32%), dialkyl ketone (8%) and 1-nonoic acid (29%) (eq. 5)[16].



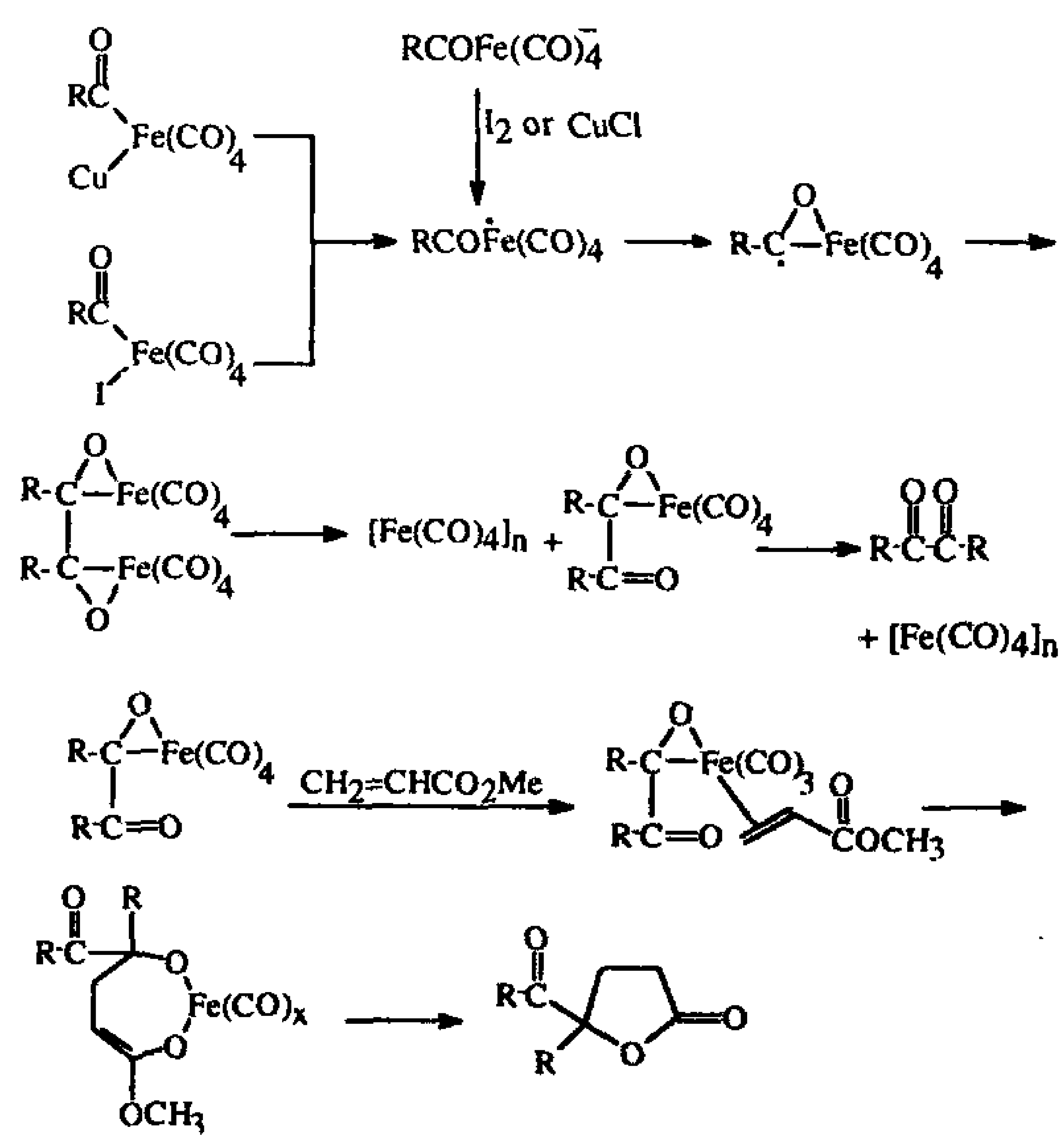
(5)

Also, the reaction of NaRCO[$Fe(CO)_4$] with I_2 in the presence of methylacrylate produces acyllactone along with other products (eq. 6)[16].



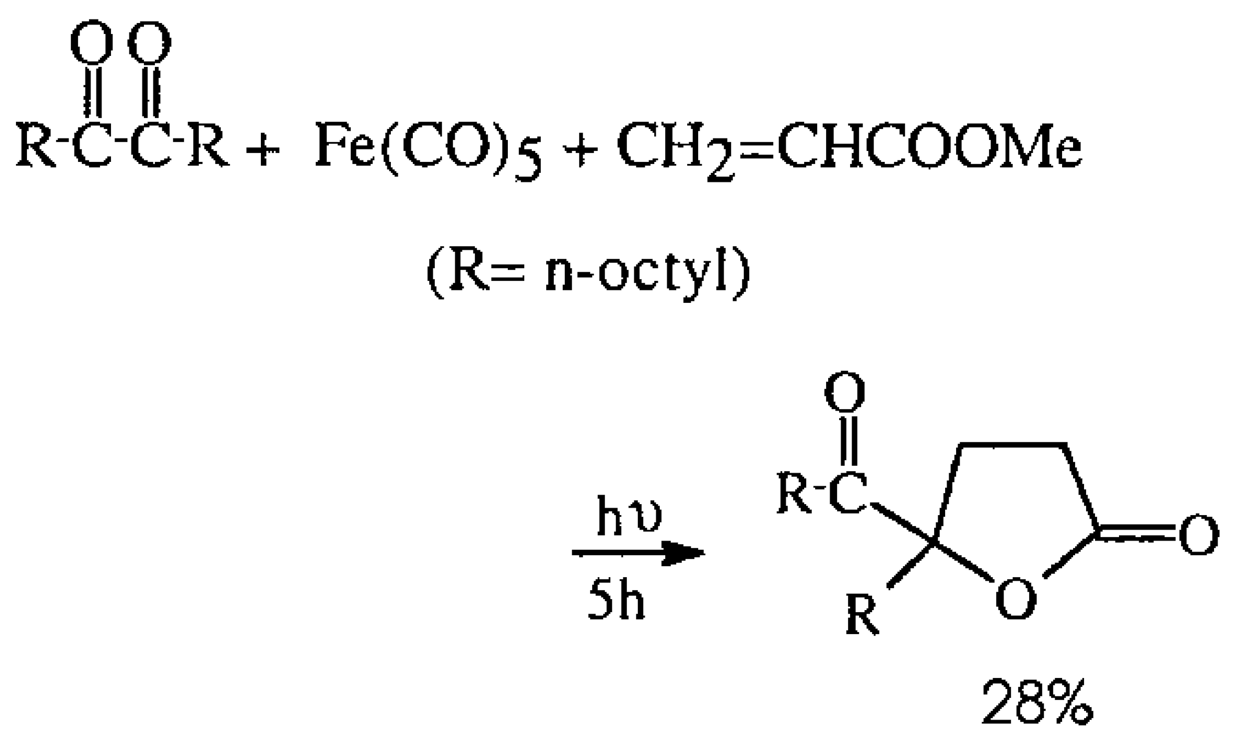
(6)

It seems likely that, the $RCO\dot{F}e(CO)_4$ species is responsible for the formation of 1,2-diketones (20–28%) and acyllactones (35–52%). It may be formed through either the homolysis of I(RCO)$Fe(CO)_4$ and Cu(RCO)$Fe(CO)_4$ or more likely through one-electron oxidation by CuCl or I_2 (Scheme 2).



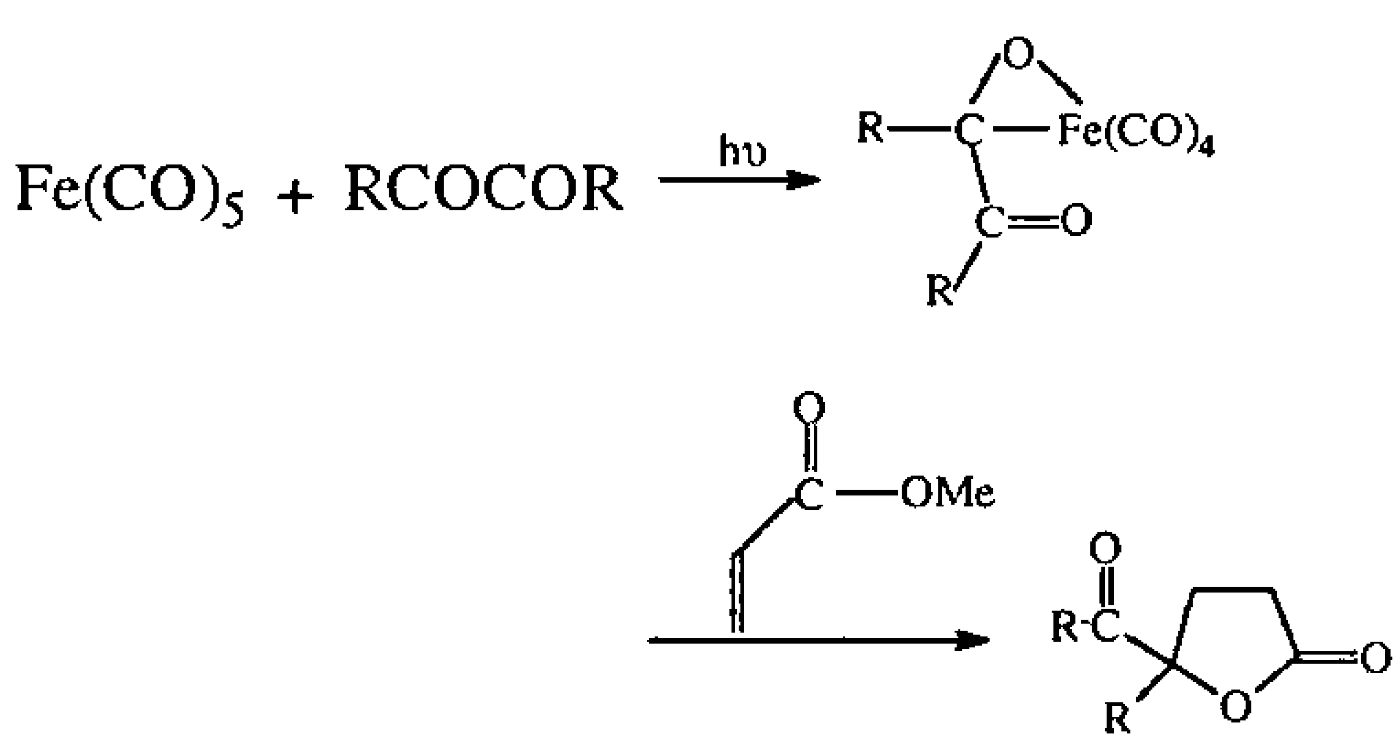
Scheme 2.

We have also examined the photochemical reaction of a mixture of $Fe(CO)_5$, RCOCOR (R = *n*-octyl) and methylacrylate using a 450ω medium pressure mercury lamp for 5 h to examine whether the anticipated co-ordinatively unsaturated '$Fe(CO)_4$' species could react with the 1,2-diketone and methylacrylate to give acyllactone. Indeed, the corresponding acyllactone was obtained in 28% yield (eq. 7)[16].



(7)

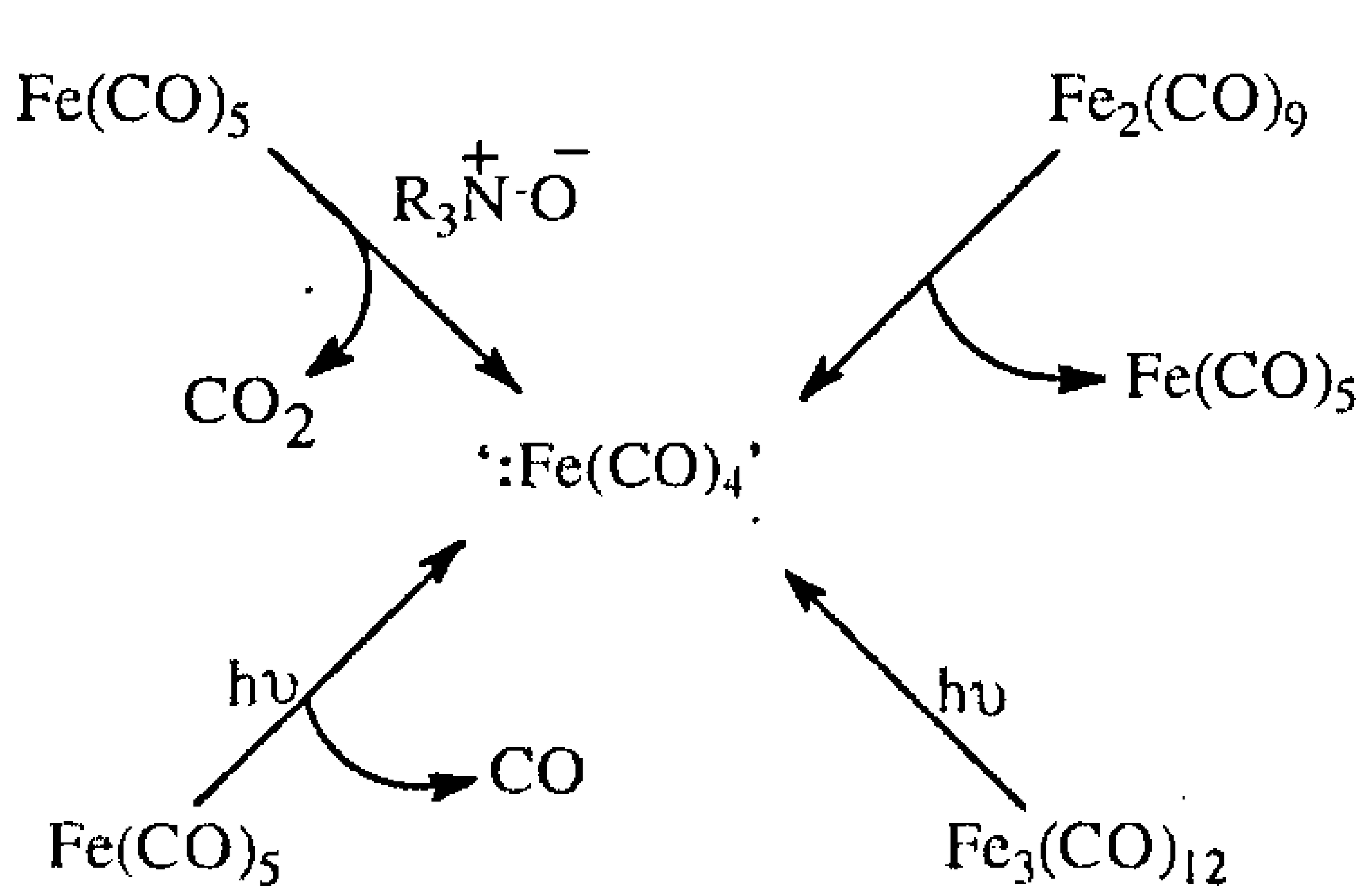
This result illustrates the ability of the co-ordinatively unsaturatd iron carbonyl species to react with 1,2-diketone and methylacrylate to give acyllactone (Scheme 3).



Scheme 3.

Preparation of '$Fe(CO)_4$'

The co-ordinatively unsaturated species '$:Fe(CO)_4$' is isolobal with carbene and hence it is expected to have interesting reactivities. It has been previously prepared by the methods outlined in Scheme 4 (refs 17–21).



Scheme 4.

The '$Fe(CO)_4$' forms addition complexes with CH_3CN, acetone, amines and phosphines. During our efforts on the synthetic applications of $Na_2Fe(CO)_4$, we became interested in the preparation and applications of these species.

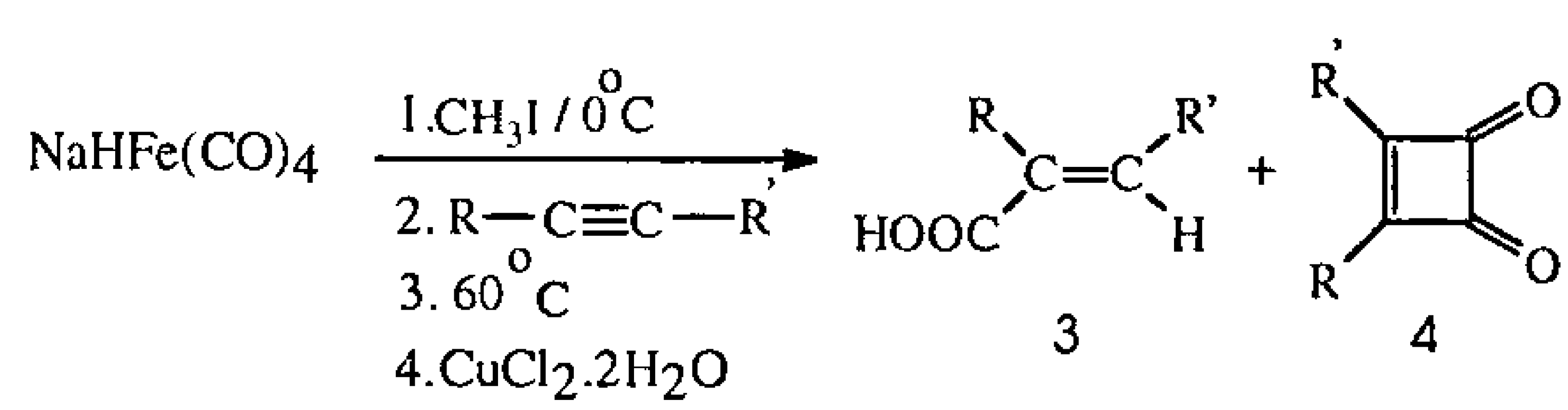
Whitmire *et al.*[22] previously reported the formation of $Fe(CO)_4(CH_3CN)$ and CH_4 in the reaction of $[Et_4N]HFe(CO)_4$ with CH_3I in CH_3CN (eq. 8).

$$[Et_4N]HFe(CO)_4 + CH_3I \xrightarrow{CH_3CN} Fe(CO)_4(CH_3CN) + CH_4\uparrow. \quad (8)$$

Since $HFe(CO)_4^-$ can be readily prepared through the reaction of $Na_2Fe(CO)_4$ with CH_3COOH, we have examined this method of generation of '$Fe(CO)_4$' as it would serve as a simple alternative procedure.

Double carbonylation of alkynes

It was observed that the $NaHFe(CO)_4/CH_3I$ reagent combination reacts with alkynes at 60°C followed by $CuCl_2.2H_2O$ oxidation giving the corresponding cyclobutenediones (27–42%) and the α,β-unsaturated carboxylic acids (10–22%) (eq. 9)[23].



(9)

R	R′	3	4
a) -Ph	-Ph	22 %	42%
b) $-C_5H_{11}$	$-SiMe_3$	12 %	37%
c) $-C_8H_{17}$	$-SiMe_3$	12 %	31%
d) C_5H_{11}	$-CH_2CH=CH_2$	10 %	32%
e) C_5H_{11}	$-C_5H_{11}$-CH(OH)		27%
f) C_5H_{11}	$-CPh(OH)(CH_3)$		31%

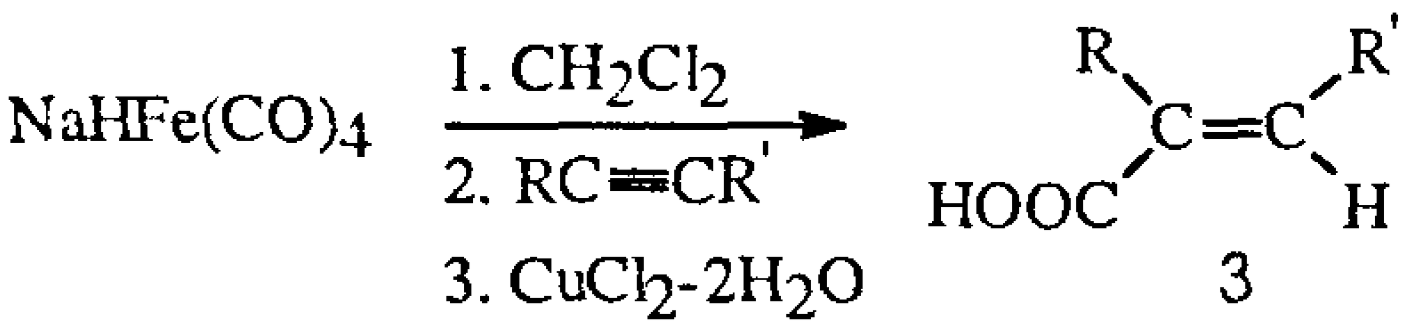
The transformation has been found to be general. Several substituted alkynes, propargyl alcohol derivatives and enynes were converted to the corresponding cyclobutenediones and α,β-unsaturated carboxylic acids. We have investigated these transformations further to standardize conditions to obtain cyclobutenediones or α,β-unsaturated carboxylic acids from alkynes in acceptable yields. The results are described here.

Reaction of $NaHFe(CO)_4/CH_2Cl_2$ system with alkynes

It has been reported by Whitmire and Lee[24] that the $HFe(CO)_4^-$ slowly decomposes to $[HFe_3(CO)_{11}]^-$ in CH_2Cl_2 through the '$Fe(CO)_4$' intermediate (eq. 10)[24].

$$2\,HFe(CO)_4^- \xrightarrow{CH_2Cl_2} 2\,\text{`}Fe(CO)_4\text{'} \xrightarrow{HFe_3(CO)_4^-} HFe_3(CO)_{11}^- \quad (10)$$

We have carried out experiments using CH_2Cl_2 in the place of CH_3I to examine any difference in reactivity. It was observed that the species generated *in situ* by treating $NaHFe(CO)_4$ (1 equiv.) with CH_2Cl_2 (13 equiv.) in THF on reaction with terminal and internal alkynes give the hydrocarboxylated products in a regio and stereocontrolled fashion (42–60%) after $CuCl_2.2H_2O$ oxidation (eq. 11)[25]. The reaction proceeds satisfactorily under mild conditions at 25°C.

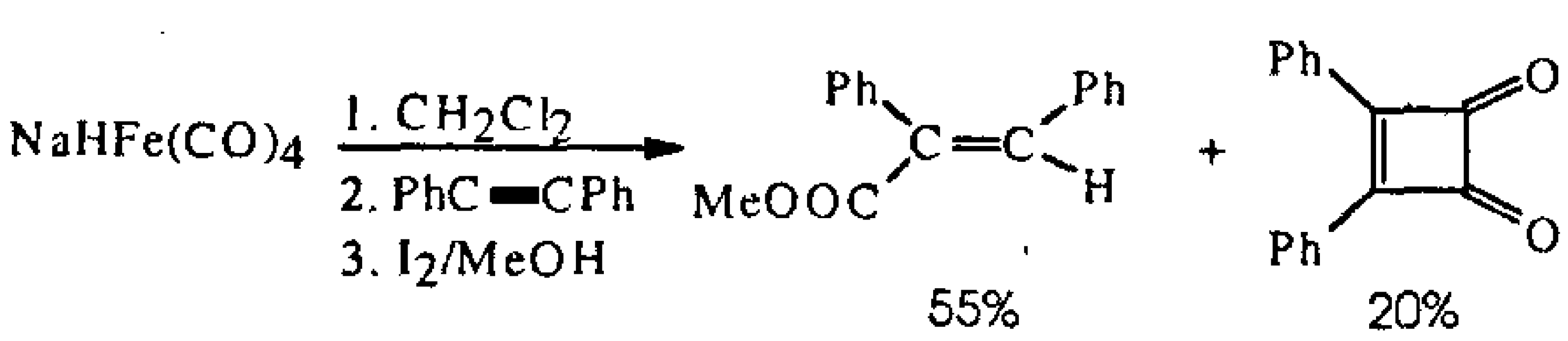


(11)

R	R′	3
a) -Ph	-Ph	60%
b) $-C_5H_{11}$	$-SiMe_3$	41%
c) $-C_8H_{17}$	$-SiMe_3$	37%
d) C_5H_{11}	-H	50%
e) C_8H_{17}	-H	42%

The presence of CH_2Cl_2 as a co-reactant is required for this transformation. It was observed that the reaction leads to low yield of carboxylic acid (< 10%) without CH_2Cl_2. As mentioned earlier, the reaction of $[Et_4N]HFe(CO)_4$ with CH_2Cl_2 affords $[HFe_3(CO)_{11}]^-$. Presumably, the reactive species responsible for the formation of both cyclobutenediones and carboxylic acids may be derived from these species.

It is well-known that acylferrate anion $[RCOFe(CO)_4]^-$ reacts with I_2 in the presence of nucleophiles such as CH_3OH and R_2NH to give the corresponding carboxylic acid derivatives[10]. A similar type of reactivity may be anticipated for the intermediate formed here. Regio- and stereoselective synthesis of α,β-unsaturated carboxylic acid derivatives could be achieved if such generalizations could be made. Indeed, this has been observed (eq. 12)[26].

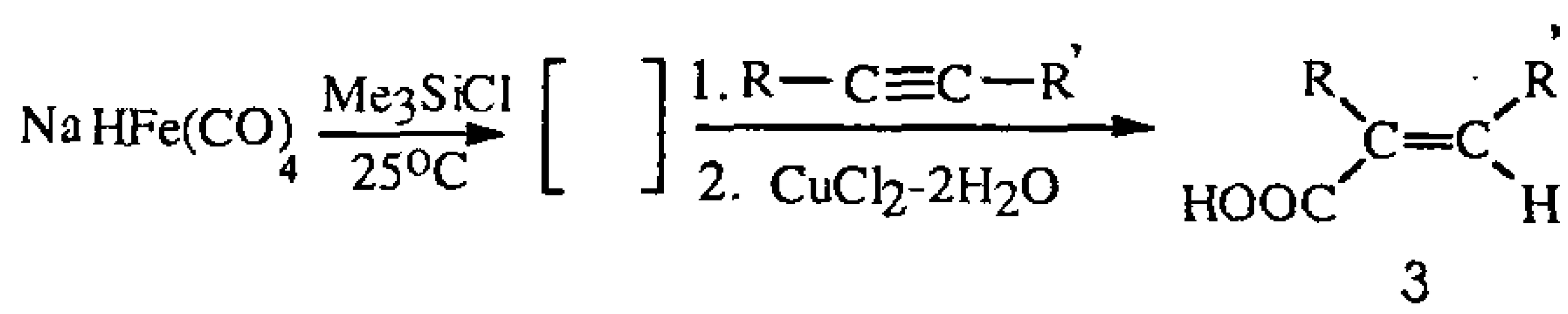


(12)

The intermediate generated *in situ* in the reaction (eq. 11) upon I_2 treatment in the presence of methanol, gives the methyl ester besides the corresponding cyclobutenedione. The corresponding amide (50%) was obtained when diethylamine was used instead of CH_3OH. Similar transformations were also observed with 1-heptyne.

Reaction of $NaHFe(CO)_4/Me_3SiCl$ system with alkynes

We have also examined the reactivity of the species generated using $NaHFe(CO)_4/Me_3SiCl$ combination to compare the results obtained using alkyl halides. It was observed that the intermediate complex, generated *in situ* by treating $NaHFe(CO)_4$ (3 equiv.) with Me_3SiCl (3 equiv.) reacts with terminal and internal alkynes (1 equiv.) at 25°C to yield α,β-unsaturated carboxylic acids (45–54%) with excellent regio- and stereoselectivities (eq. 13)[26].

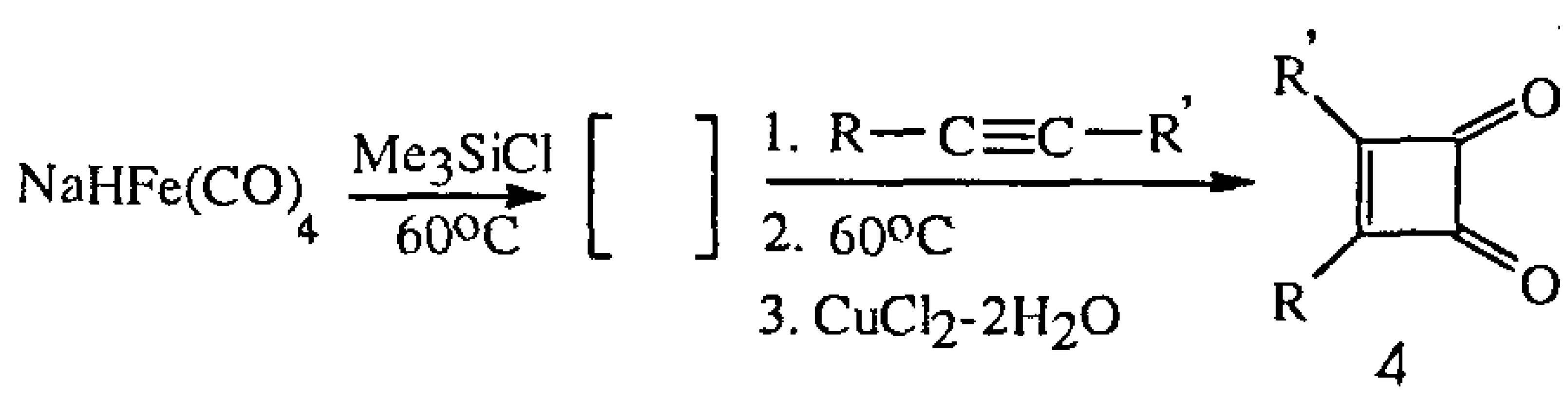


(13)

R	R′	3
a) -Ph	-Ph	54%
b) $-C_5H_{11}$	$-SiMe_3$	50%
c) $-C_5H_{11}$	-H	49%
d) C_8H_{11}	-H	45%

The reaction was found to be general and various alkynes were converted to (E)-alkenoic acids. This reactivity pattern is similar to that realized using the $NaHFe(CO)_4/CH_2Cl_2$ reagent system. In all these cases, the corresponding cyclobutenediones were obtained in very low yields (< 5%).

An interesting temperature effect was noted for this reaction. It was found that the reagent, prepared using $NaHFe(CO)_4/Me_3SiCl$ at 60°C, on reaction with diphenylacetylene followed by $CuCl_2.2H_2O$ oxidation produced cyclobutenedione (51–63%) as the only product (eq. 14)[26].



(14)

R	R′	4
a) -Ph	-Ph	63%
b) $-C_5H_{11}$	$-SiMe_3$	51%
c) $-C_8H_{17}$	$-SiMe_3$	53%
d) $-C_5H_{11}$	$-CH_2\text{-}CH{=}CH_2$	60%
e) $-C_5H_{11}$	-H	56%
f) $-C_8H_{17}$	-H	57%

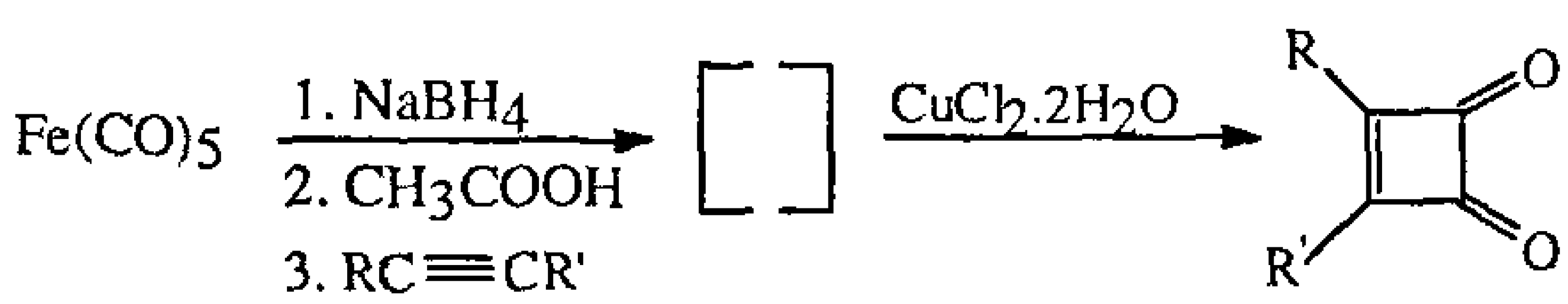
The reaction was found to be general. The corresponding cyclobutenediones were obtained in relatively good yields using representative terminal, internal and substituted alkynes. It has been reported that the $R_3Si(H)Fe(CO)_4$ on heating gives '$Fe(CO)_4$' species which readily undergoes trimerization to $Fe_3(CO)_{12}$ (refs 27–29).

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

Since the reaction of CH_2Cl_2 with $NaHFe(CO)_4$ was reported to give $HFe_3(CO)_{11}^-$, we decided to investigate the reactivity of these species with alkynes. The $[HFe_3(CO)_{11}]^-$ species has been previously prepared using $Fe(CO)_5$-$NaBH_4/CH_3OH/CH_3COOH$ in THF and isolated as PPN salt in 73% yield (eq. 15)[30].

$$NaBH_4 + Fe(CO)_5 \xrightarrow[2.\ CH_3COOH]{1.\ CH_3OH} HFe_3(CO)_{11}^- \quad (15)$$

It was observed that the $[HFe_3(CO)_{11}]^-$ species, prepared *in situ* using $Fe(CO)_5/NaBH_4/CH_3COOH$ reacts with alkynes to give the corresponding cyclobutenediones in good yield (60–73%) after $CuCl_2.2H_2O$ oxidation (eq. 16)[31]. Several alkynes were converted to the corresponding cyclobutenediones.



4

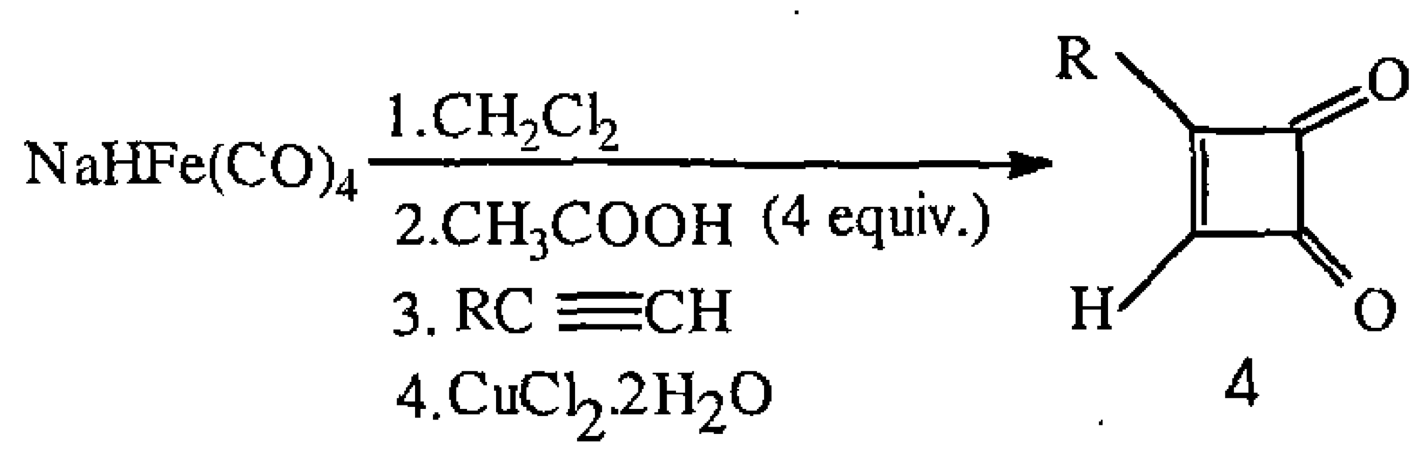
(16)

R	R′	4
a) $-C_5H_{11}$	-H	72%
b) $-C_6H_{13}$	-H	69%
c) $-C_8H_{17}$	-H	70%
d) $-C_{10}H_{21}$	-H	68%
e) -Ph	-H	65%
f) $-C_5H_{11}$	$-CH_2-CH=CH_2$	60%
g) $-C_5H_{11}$	$-CH(C_5H_{11})(OH)$	61%
h) C_5H_{11}	$-CPh(CH_3)(OH)$	63%

The UV-spectra recorded for the reaction mixture in all these reagent combinations described above exhibit characteristic absorptions reported for $[HFe_3(CO)_{11}]^-$ in solution[32]. If the reactive species is derived from this reagent, then the reactivity difference between the species generated using $Fe(CO)_5$–$NaBH_4$–CH_3COOH in THF and the reagent prepared using $NaHFe(CO)_4/CH_2Cl_2$ in THF is difficult to rationalize. The reaction of the former combination with alkynes leads to cyclobutenediones (eq. 16) and the latter results in the formation of α,β-unsaturated carboxylic acid (eq. 11). Presumably, the CH_3COOH used to destroy the excess $NaBH_4$ may play a role in the formation of the reactive species from $[HFe_3(CO)_{11}]^-$ (eq. 17).

$$HFe_3(CO)_{11}^- + CH_3COOH \longrightarrow H_2Fe_3(CO)_{11} \longrightarrow \text{'}Fe_3(CO)_{11}\text{'} + H_2 \quad (17)$$

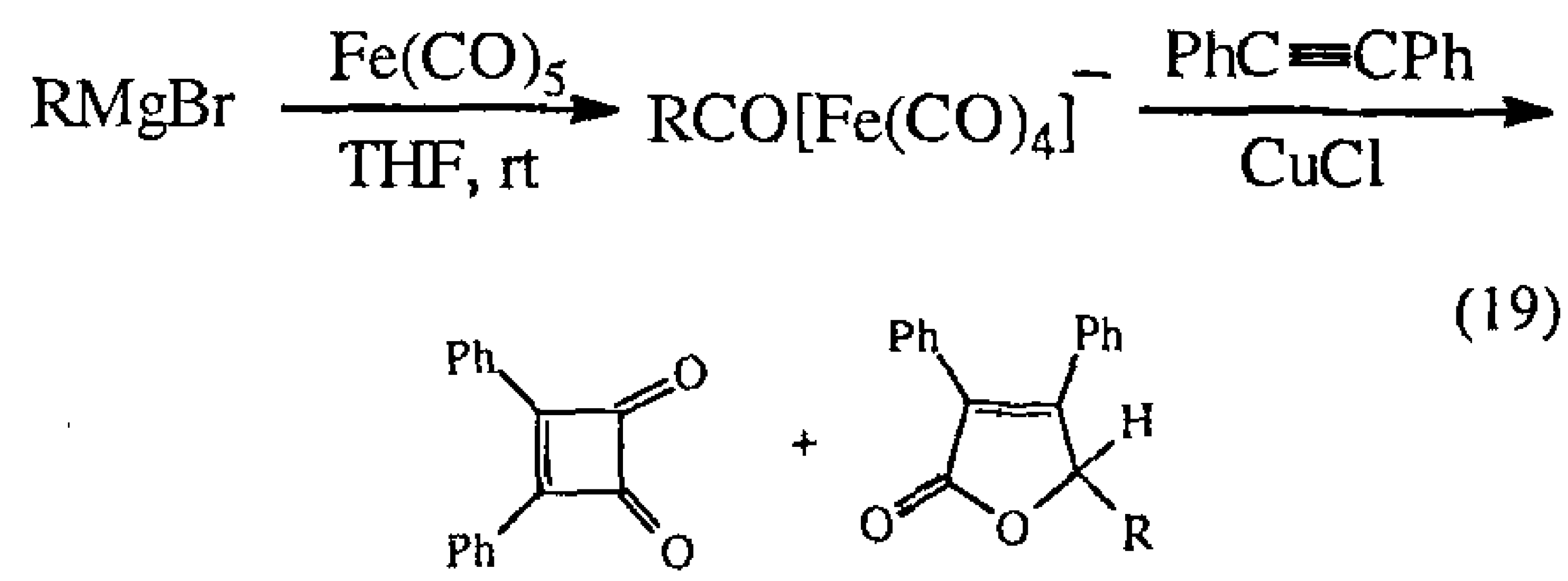
If this is the case, use of an additional amounts of CH_3COOH in the reaction using $NaHFe(CO)_4/CH_2Cl_2$ should also give similar results. Indeed, this was observed. The corresponding cyclobutenedione was obtained in 33% yield and the α,β-unsaturated carboxylic acid was not formed under these conditions (eq. 18)[26].



4

(18)

An interesting acylation-cyclization was observed when $RCO[Fe(CO)_4]^-$ was treated with CuCl in the presence of alkynes and CH_3CN in THF at room temperature. The corresponding butenolides (26–32%) besides cyclobutenediones (10–13%) were formed. Control reactions indicated that the CuCl is necessary for this transformation (eq. 19)[33].

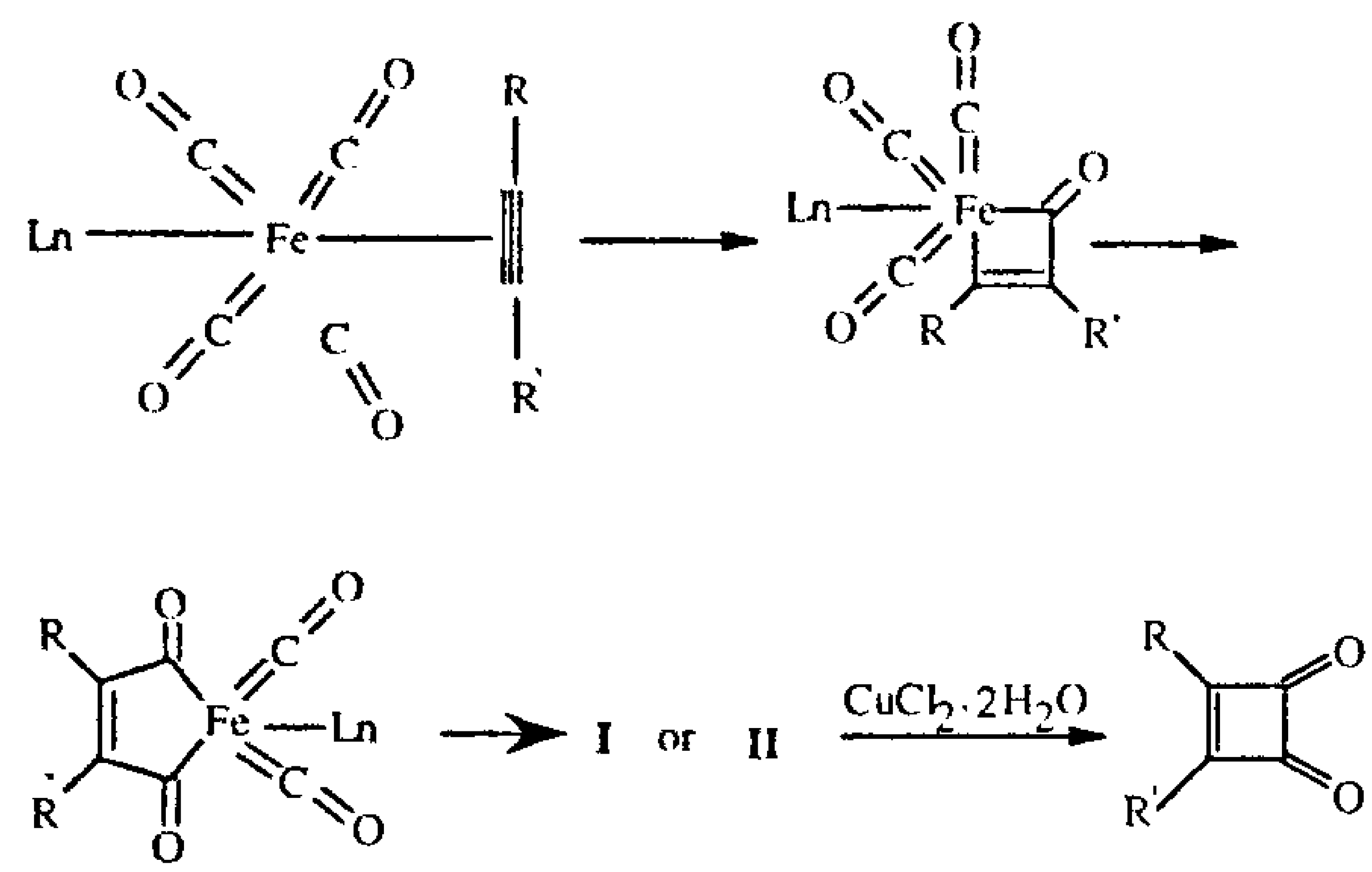


(19)

R	4	5
a) CH_3CH_2Br	13%	26%
b) $CH_3(CH_2)_3Br$	10%	32%
c) $CH_3(CH_2)_5Br$	10%	35%

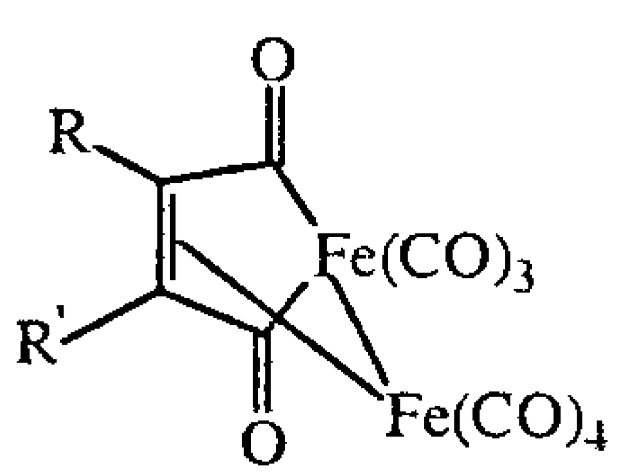
Mechanism and intermediates

The reactive species formed in all these seems to be co-ordinatively unsaturated, fluxional, polymeric iron carbonyl species. A tentative mechanistic pathway for the formation of cyclobutenediones can be visualized as shown in Scheme 5.

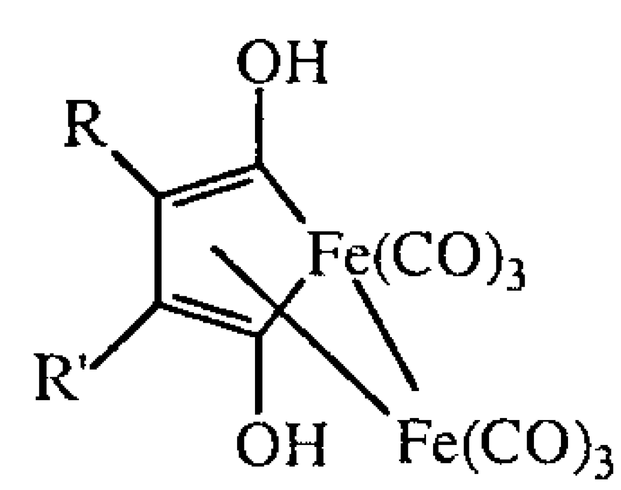


Scheme 5.

The intermediates involved may be of the type **I** or **II**. The species **II** has been reported to give cyclobutenediones on oxidation using $FeCl_3$ (ref. 34).

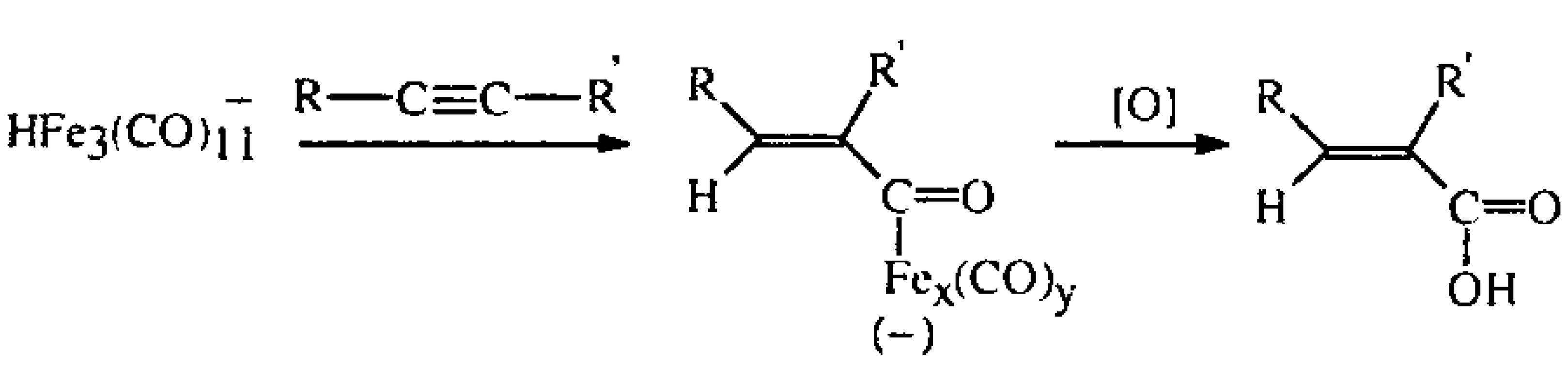


I



II

The formation of α,β-unsaturated carboxylic acids may take place through hydrometallation of the alkynes by $[HFe_3(CO)_{11}]^-$ produced under the reaction conditions (Scheme 6).



Scheme 6.

Conclusion

The $Na_2Fe(CO)_4$ reagent prepared using $Fe(CO)_5$/Na/naphthalene and $FeCl_3$ /Na/naphthalene and CO was used for the synthesis of $NaRCOFe(CO)_4$. The reaction of $NaRCOFe(CO)_4$ with CuCl or I_2 leads to the formation of 1,2-diketones RCOCOR, RCOR and RCOOH. It was found that the reaction of $NaRCOFe(CO)_4$ with CuCl or I_2 in the presence of methyl acrylate leads to the formation of acyllactone besides RCOCOR, RCOR and RCOOH. It appears that the $RCO\dot{F}e(CO)_4$ species formed, either from $Cu(RCO)Fe(CO)_4$ and $I(RCO)Fe(CO)_4$ through homolysis of Fe–Cu and Fe–I bonds or through one-electron oxidation of $Na[RCOFe(CO)_4]$ by CuCl or I_2, may be responsible for the formation of 1,2-diketones and acyllactones via the intermediacy of η2-type complexes. It was also observed that the reagent generated using RMgBr and $Fe(CO)_5$ on treatment with CuCl gives the corresponding 1,2-diketones.

A new double carbonylation of alkynes has been observed using the $NaHFe(CO)_4$–CH_3I reagent system to obtain the corresponding cyclobutenediones besides α,β-unsaturated carboxylic acids. The reaction of the reagent generated using $NaHFe(CO)_4$ and CH_2Cl_2 with alkynes gave α,β-unsaturated carboxylic acids [(E)-isomer] (37–60% yields) in a regio- and stereoselective manner after $CuCl_2.2H_2O$ oxidation. This reagent system was also demonstrated to be useful in the synthesis of certain α,β-unsaturated carboxylic esters and amides albeit in moderate yields. The reaction of $NaHFe(CO)_4/Me_3SiCl$ and alkynes at 25°C, followed by $CuCl_2.2H_2O$ oxidation gave the corresponding α,β-unsaturated carboxylic acids (45–54% yields) with good regio- and stereoselectivity. The yields are slightly better than that obtained using the $NaHFe(CO)_4$/ CH_2Cl_2 system in some cases. However, the latter method requires the use of the inexpensive CH_2Cl_2 and hence is advantageous for synthetic applications. It was also observed that addition of alkynes to the species generated in the reaction of $NaHFe(CO)_4/Me_3SiCl$ at 60°C followed by $CuCl_2.2H_2O$ oxidation leads to the corresponding cyclobutenediones which have been obtained in 60–73% yields in the reaction of alkynes with $Fe(CO)_5$–$NaBH_4$–CH_3COOH system. This method using $NaBH_4$ is more convenient for application than using $NaHFe(CO)_4$–Me_3SiCl system and the yields are also better in some cases.

1. Wender, I. and Pino, P., *Organic Syntheses via Metal Carbonyls*, Wiley Interscience, New York, 1977, vol. 1, 2.
2. Haidue, I and Zukerman, J. J., *Basic Principles in Organometallic Chemistry* (ed. Watter De Gruyter), New York, 1985.
3. Beck, I., *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 168.
4. Ellis, J. E., Chi, K. M., DiMaio, A. J., Frerichs, S. R., Stemzel, J. R., Rheingol, L. and Haggerty B. S., *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 194.
5. Davis, S. G., *Organotransition Metal Chemistry: Applications to Organic Synthesis*, Pergmon, Oxford, 1986.
6. Collman, J. P. and Hegedus, L. S., *Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, California, 1987.
7. Pauson, P. L., *Tetrahedron*, 1985, **41**, 5855.
8. Nayori, R., *Acc. Chem. Res.*, 1979, **12**, 61.
9. Hayakawa, Y., Bab, Y., Makino, S. and Nayori, R., *J. Am. Chem. Soc.*, 1978, **100**, 1786.
10. Collman, P., *Acc. Chem. Res.*, 1975, **8**, 342.
11. Gladysz, J. A. and Tans, W., *J. Org. Chem.*, 1978, **43**, 2279.
12. Collman, J. P., Finke, R. G., Cawse, J. N. and Brauman, J. I., *J. Am. Chem. Soc.*, 1977, **99**, 2515.
13. Krumholz, P. and Stettiner, H. M. A., *J. Am. Chem. Soc.*, 1949, **71**, 3035
14. Devasagayaraj, A. and Periasamy, M., *Transition Metal Chem.*, 1991, **16**, 503.

15. Devasagayarai, A. and Periasamy, M., *Tetrahedron Lett.*, 1992, **33**, 1227.
16. Periasamy, M., Devasagayaraj, A. and Radhakrishnan, U., *Organometallics*, 1993, **12**, 1424.
17. Poliakoff, M. and Tumer, J. J., *J. Chem. Soc. Dalton Trans.*, 1974, 2276.
18. Black, J. D. and Brataerman, P. S., *J. Organomet. Chem.*, 1975, **85**, c7.
19. Kane, V. V., Light, J. R. C. and Whiting, M. C., *Polyhedron*, 1985, **13**, 1656.
20. Pearson, A. J. and Dubbert, R. A., *Organometallics*, 1994, **13**, 1656.
21. Pearson, A. J. and Perosa, A., *Organometallics*, 1995, **14**, 5178.
22. Whitmire, K. H., Lee, T. R. and Lewis, E. S., *Organometallics*, 1986, **5**, 987.
23. Periasamy, M., Radhakrishnan, U., Brunet, J. J., Chauvin, R. and El-zaizi, A. W., *J. Chem. Soc. Chem. Commun.*, 1996, 1499.
24. Whitmire, K. H. and Lee, T. R., *J. Organomet. Chem.*, 1985, **282**, 95.
25. Periasamy, M., Radhakrishnan, U., Rameshkumar, C. and Brunet, J. J., *Tetrahedron Lett.*, 1997, **8**, 1623.
26. Periasamy, M., Rameshkumar, C., Radhakrishnan, U. and Brunet, J. J., *J. Org. Chem.*, 1998, **63**, 4930.
27. Nasta, M. N. and MacDiarmid, A.G., *J. Am. Chem. Soc.*, 1971, **93**, 2813.
28. Jetz, W. and Graham, W. A. G., *J. Am. Chem. Soc.*, 1969, **91**, 3375.
29. Jetz, W. and Graham, W. A. G., *Inorg. Chem.*, 1971, **10**, 4.
30. Hodali, H. A., Arcus, C. and Shriver, D. F., *Inorg. Synth.*, 1980, **20**, 218.
31. Periasamy, M., Rameshkumar, C. and Radhakrishnan, U., *Tetrahedron Lett.*, 1997, **38**, 7229.
32. Case, J. R. and Whiting, M. C., *J. Chem. Soc.*, 1960, 4632.
33. Radhakrishnan, U. and Periasamy, M., *Organometallics*, 1997, **16**, 1800.
34. Sternberg, H. W., Friedel, R. A., Markby, R. and Wender, I., *J. Am. Chem. Soc.*, 1956, **78**, 3621.

ACKNOWLEDGEMENTS. We thank the UGC, CSIR and DST (New Delhi) for financial support. This work is also supported by the Special Assistance Programme of the UGC (New Delhi).