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A simple and convenient method for the synthesis of cyclobutenediones from alkynes using new $Fe(CO)_5$/NaH/MeI reagent system

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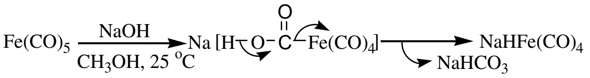
ABSTRACT

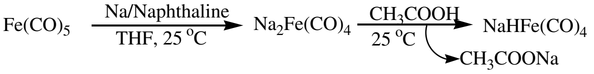
Iron carbonyl complexes prepared *in situ* using the $Fe(CO)_5$/NaH/MeI reagent combination and alkynes at 25 °C give the corresponding cyclobutenediones in 50–65% yields after $CuCl_2 \cdot 2H_2O$ oxidation.

1. Introduction

The chemistry of metal carbonyls, especially the iron carbonyl reagents, has been the subject of considerable interest [1]. Synthesis of multifunctional molecules with reactive moieties have spurred research activity in organometallics, particularly in the development and use of metal carbonyl reagents [2–4]. Previously, several organic transformations using iron carbonyls have been developed in this laboratory [5]. The reactivity of the easily accessible inexpensive but relatively less reactive $Fe(CO)_5$ reagent can be enhanced using several chemical promoters such as R_3NO, KOMe, R_3PO, KH and $NaBH_4$ to facilitate the CO dissociation [6,7,12]. It has been reported that the reaction of $[Et_4N]HFe(CO)_4$ with MeI in CH_3CN leads to the formation of $Fe(CO)_4(CH_3CN)$ and CH_4 [8]. This method of generation of "$Fe(CO)_4$" *in situ* would serve as a simple alternate method for synthetic applications of this species [9]. Such reactive iron carbonyl reagent systems have been previously prepared using $NaHFe(CO)_4$ species which in turn needs to be prepared using $Fe(CO)_5$/NaOH in methanol [3c] or $Fe(CO)_5$/Na/naphthaline followed by reaction with carboxylic acids in THF [5a] (Eqs. 1 and 2).



$$Fe(CO)_5 \xrightarrow[CH_3OH,\ 25\ ^{\circ}C]{NaOH} Na[H{-}O{-}\overset{\overset{O}{\|}}{C}{-}Fe(CO)_4] \longrightarrow NaHFe(CO)_4 + NaHCO_3 \qquad (1)$$



$$Fe(CO)_5 \xrightarrow[THF,\ 25\ ^{\circ}C]{Na/Naphthaline} Na_2Fe(CO)_4 \xrightarrow[25\ ^{\circ}C]{CH_3COOH} NaHFe(CO)_4 + CH_3COONa \qquad (2)$$

In continuation of these efforts on the synthesis and applications of reactive iron carbonyls, we have developed a novel method for the generation of "$Fe(CO)_4$" species using the NaH, $Fe(CO)_5$ and MeI reagent system through a formyl ferrate intermediate [10]. We wish to report that the reactive iron carbonyl species prepared *in situ* directly in this way further reacts with alkynes and gives an intermediate that can be converted to the corresponding cyclobutenediones after oxidation with $CuCl_2 \cdot 2H_2O$.

2. Results and discussions

We have examined the preparation of the reactive species *in situ* using the readily accessible $Fe(CO)_5$ and NaH combination with an objective of developing a relatively less complicated procedure. The $Fe(CO)_5$ reagent reacts with NaH to give the $Na[HFe(CO)_4]$ species [10] and the subsequent reaction with MeI is expected to produce the coordinatively unsaturated "$Fe(CO)_4$" species which undergoes reaction with alkynes to give the corresponding cyclobutenediones after oxidation with $CuCl_2 \cdot 2H_2O$ (Scheme 1). Several alkynes were converted to the corresponding cyclobutenediones [11] following this procedure. The yields of this reaction are moderate to good (50–65%). The results are summarized in Table 1.

In these reactions, the NaH (6 equiv.), $Fe(CO)_5$ (6 equiv.) and MeI (6 equiv.) were used in larger quantities as the initially formed

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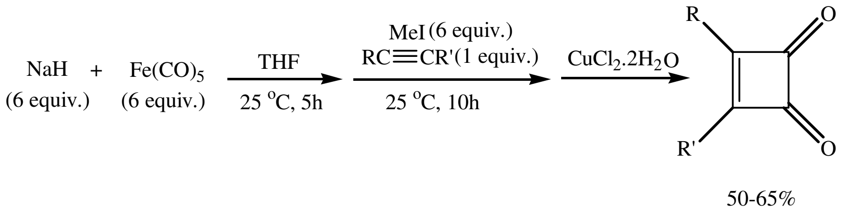
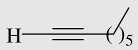
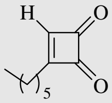
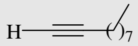
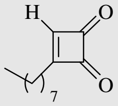
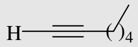
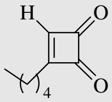
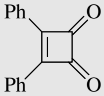
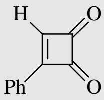
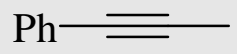
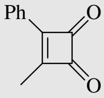
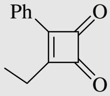


Scheme 1.

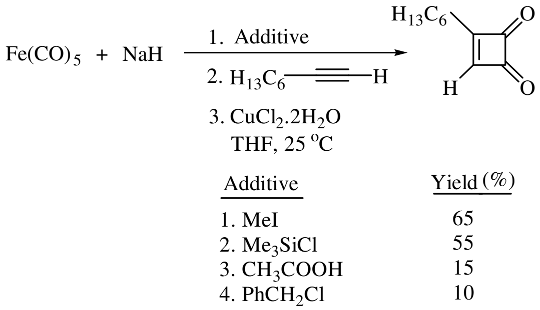
Table 1
Synthesis of cyclobutenediones with $Fe(CO)_5$/NaH/MeI reagent system[a]

Entry	Alkyne	Product[b]	Yield[c] (%)
1		 **2a**	65
2		 **2b**	55
3		 **2c**	50
4	Ph—≡—Ph	 **2d**	52
5	Ph—≡—H	 **2e**	55
6		 **2f**	56
7		 **2g**	51

[a] All the reactions were carried out using $Fe(CO)_5$ (7.5 mmol), NaH-55% (15 mmol), MeI (7.5 mmol) and alkyne (1.25 mmol) in THF (35 mL).

[b] The product was identified by spectral data (IR, ^1H NMR, ^{13}C NMR and mass) and comparison with reported data [5].

[c] Yields reported are for the isolated products and based on the amount of alkynes used.



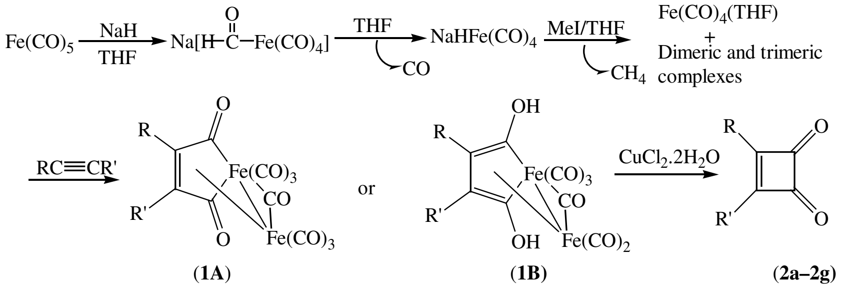
Additive	Yield (%)
1. MeI	65
2. Me_3SiCl	55
3. CH_3COOH	15
4. $PhCH_2Cl$	10

Scheme 2.

"$Fe(CO)_4$" would also form dimeric and trimeric iron carbonyl species. We have examined the use of other reagents like $PhCH_2Cl$, CH_3COOH and Me_3SiCl in the place of MeI. In these cases also the cyclobutenediones were obtained after $CuCl_2 \cdot 2H_2O$ oxidation but in lesser yields (10–55%) (Scheme 2).

Though, THF was found to be a suitable solvent, CH_3CN also gave comparable results. However, the use of solvents like $CHCl_3$ and CH_2Cl_2 gave unidentified mixture of iron carbonyl products. Presumably, the coordinating solvents may form weak complexes with the coordinative unsaturated species like monomeric $Fe(CO)_4$ or dimeric $Fe_2(CO)_9$ or $Fe_2(CO)_8$ or trimeric $Fe_3(CO)_{11}$ that help in realizing cleaner reaction [5,11,12].

The formation of cyclobutenediones from the $NaHFe(CO)_4$ and alkynes can be explained by considering a tentative mechanism depicted in Scheme 3. Addition of the $Fe(CO)_5$ to the NaH in THF would give the $NaHFe(CO)_4$, which on reaction with MeI could generate the "$Fe(CO)_4$ THF" along with dimeric and trimeric iron carbonyl spices that can further react with alkynes followed by CO insertion to give the maleoyl complex of the type **1A** or the ferrole complex of the type **1B** [5]. Such complexes could give the cyclobutenediones after $CuCl_2 \cdot 2H_2O$ oxidation.



Scheme 3.

3. Conclusion

We have developed a simple and convenient method for the synthesis of cyclobutenediones using easily accessible and inexpensive starting resource such as NaH. The present *in situ* method of preparation of coordinatively unsaturated iron carbonyl species for synthetic applications has advantages over the erstwhile known methods since this method avoids the use of $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ which are in turn to be prepared from $Fe(CO)_5$ [12]. Cyclobutenedione and their derivatives have been used as NLO materials [13a], growth regulators, potassium channel openers, drug molecules [13b,13c,13d], anion recognition systems [14], chiral ligands [15] and versatile starting materials for the synthesis of multifunctional molecules [16]. Hence, easy accessibility of these derivatives should facilitate further research in these areas.

4. Experimental

General: ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ and TMS was used as reference ($\delta = 0$ ppm). Melting points are uncorrected. IR spectra were recorded on a JASCO FT-5300 instrument with polystyrene as reference. Mass spectral analysis was carried out on VG 7070H mass spectrometer using EI technique at 70 eV. $Fe(CO)_5$ and NaH (55–60%) supplied by Fluka and Finar, respectively. The alkynes used in the reactions (except heptyne) were prepared by following reported procedure [17]. THF was distilled over sodium benzophenone ketyl system. Chromatographic purification was conducted by column chromatography using 100–200 mesh silica gel obtained from Acme Synthetic Chemicals, India. All reactions and manipulations were carried out under nitrogen atmosphere. All the yields reported are isolated yields of materials, judged homogeneous by TLC analysis.

4.1. Preparation of cyclobutenedione using the $Fe(CO)_5$/NaH/MeI reagent system

The $Fe(CO)_5$(1.45 g, 7.5 mmol) was added dropwise to the NaH (0.33 g, 7.5 mmol) in THF (35 mL) at 25 °C under dry nitrogen. And stirred for another 5 h at same temperature. The above reaction mixture was treated with CH_3I (1.06 g, 7.5 mmol) at 0 °C under dry N_2 atmosphere. After 10 min diphenylacetylene (0.22 g, 1.25 mmol) was added and further stirred for 10 h at room temperature. The metal carbonyl complexes were oxidised using $CuCl_2 \cdot 2H_2O$ (2.5 g, 15 mmol) in acetone (10 mL). Saturated NaCl solution was added and the contents were extracted with ether (2×40 mL). The combined extracts were washed successfully with saturated $Na_2S_2O_3$ solution and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane–EtOAc). Ethyl acetate (2%) in hexane eluted the 3,4-diphenyl-3-cyclobutene-1,2-dione **2d**.

Compound **2a**: yield: 65%, 0.135 g; IR (neat) = 1784 cm^{-1}; ^1H NMR: $\delta = 9.24$ (s, 1H), 2.72 (t, $J = 6.0$ Hz, 2H), 1.32–1.67 (m, 2H), 1.22–1.30 (m, 6H), 0.79 (t, $J = 8$ Hz, 3H); ^{13}C NMR: $\delta = 208.4$, 200.1, 196.7, 185.0, 31.2, 28.8, 27.4, 25.8, 22.3, 13.7; MS (EI): m/z 167 (M+1).

Compound **2b**: yield: 55%, 0.133 g; IR (neat) = 1786 cm^{-1}; ^1H NMR: $\delta = 9.22$ (s, 1H), 2.71 (t, $J = 8.0$ Hz, 2H), 1.63–1.67 (m, 2H), 1.20–1.25 (m, 10H), 0.79 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR: $\delta = 208.4$, 200.1, 196.7, 184.9, 31.9, 29.2, 29.0, 28.9, 27.5, 25.9, 22.6, 13.9; MS (EI): m/z 195 (M+1).

Compound **2c**: yield: 50%, 0.095 g; IR (neat) = 1786 cm^{-1}; ^1H NMR: $\delta = 9.20$ (s, 1H), 2.81 (t, $J = 7.3$ Hz, 2H), 1.70–1.83 (m, 2H), 1.27–1.40 (m, 4H), 0.82 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR: $\delta = 208.3$, 199.9, 196.6, 184.8, 31.2, 27.1, 25.6, 22.1, 13.7; MS (EI): m/z 151 (M−1).

Compound **2d**: yield: 52%, 0.152 g; mp 95–96 °C (lit.[5,18c,18d] mp 97 °C); IR (KBr) = 1780 cm^{-1}; ^1H NMR: $\delta = 8.14$ (m, 4H), 7.45–7.68 (m, 6H); ^{13}C NMR: $\delta = 196.2$, 187.6, 133.5, 131.2, 129.4, 128.3; MS (EI): m/z 235 (M+1).

Compound **2e**: yield: 55%, 0.108 g; mp 152–153 °C (lit.[5,18c,18d] mp 152–153 °C); IR (KBr) = 1768 cm^{-1}; ^1H NMR: $\delta = 9.5$ (s, 1H), 7.3–8.0 (m, 5H); ^{13}C NMR: $\delta = 197.7$, 196.0, 195.5, 178.3, 134.6, 129.5, 129.4, 127.3; MS (EI): m/z 159 (M+1).

Compound **2f**: yield: 56%, 0.120 g; mp 98–100 °C (lit. [18a] mp 98–100 °C); IR (KBr) = 1782, 1765 cm^{-1}; ^1H NMR: $\delta = 7.99$ (m, 2H), 7.25-7.57 (m, 3H), 2.64 (s, 3H); ^{13}C NMR: $\delta = 198.4$, 197.0, 193.7, 191.3, 133.5, 129.4, 128.6,12.4; MS (EI): m/z 173 (M+1). Anal. Calc. for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.66; H, 4.70%.

Compound **2g**: yield: 51%, 0.118 g; mp 64–66 °C (lit. [18b] mp 62 °C); IR (KBr) = 1778, 1755 cm^{-1}; ^1H NMR: $\delta = 7.93$ (m, 2H), 7.47–7.56 (m, 3H), 2.99 (q, $J = 6.0$ Hz, 2H), 2.1 (t, $J = 6.0$ Hz, 3H); ^{13}C NMR: $\delta = 198.7$, 198.3, 197.5, 190.3, 133.5, 129.5, 128.5, 21.1, 10.3; MS (EI): m/z 187 (M+1). Anal. Calc. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.51; H, 5.42%.

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