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Novel Reaction of the $[HFe_3(CO)_{11}]^-$ Reagent with Alkynes: A New Synthesis of Cyclobutenediones

Mariappan Periasamy,* Chellappan Rameshkumar and Ukkiramapandian Radhakrishnan

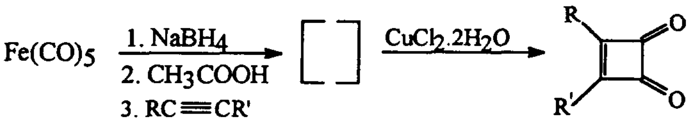
School of Chemistry, University of Hyderabad, Hyderabad-500 046, India.

Abstract: Reaction of the $[HFe_3(CO)_{11}]^-$ species generated *in situ* using $Fe(CO)_5$ and $NaBH_4/CH_3COOH$ in THF with alkynes, followed by $CuCl_2.2H_2O$ oxidation leads to the corresponding cyclobutenediones in 60-73% yields. © 1997 Elsevier Science Ltd.

The metal carbonyl reagents have been increasingly used in organic synthesis in recent years.[1] In continuation of our efforts on the synthesis and utilisation of reactive iron carbonyls,[2] we report here a novel, interesting double carbonylation of alkynes using the $[HFe_3(CO)_{11}]^-$ reagent to obtain the corresponding cyclobutenediones after $CuCl_2.2H_2O$ oxidation.

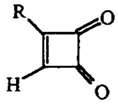
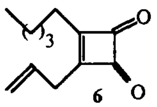
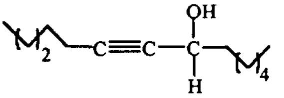
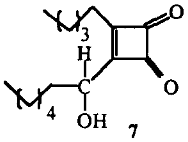
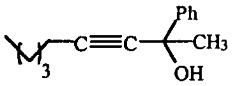
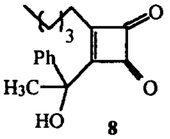
The $[HFe_3(CO)_{11}]^-$ species has been previously prepared using $Fe(CO)_5$ and $NaBH_4/CH_3OH$-CH_3COOH in THF and isolated in 70% yield as PPN salt.[3] We have observed that the $[HFe_3(CO)_{11}]^-$ species,[4,5] prepared *in situ* following a similar procedure reacts with alkynes to give the corresponding cyclobutenediones in good yields (60-73%) after $CuCl_2.2H_2O$ oxidation[6] (Scheme 1). Several alkynes were converted to the corresponding cyclobutenediones. The results are summarised in the Table 1.

Scheme 1.



Evidently, this reagent system can tolerate unmasked functional groups such as hydroxy group (entries 7 and 8, Table 1). The formation of cyclobutenedione from an enyne shows that the reagent reacts with alkyne without affecting the olefin moiety (entry 6, Table 1).

Table 1 : Reaction of $Fe(CO)_5/NaBH_4$ with alkynes[a].

S.No	Substrate	Product[b]	Yield[c]
	$R\text{-}C\equiv C\text{-}H$		
1	$R = C_5H_{11}$	1	73[d]
2	$R = C_6H_{13}$	2	69[d]
3	$R = C_8H_{17}$	3	70[d]
4	$R = C_{10}H_{21}$	4	68[d]
5	$R = C_6H_5$	5	65[d]
6		 6	60
7		 7	61
8		 8	63[e]

a) All reactions were carried out using $Fe(CO)_5$ (15 mmol), $NaBH_4$ (15 mmol), CH_3COOH (45 mmol) and alkynes (2.5 mmol) in THF (50 mL).

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

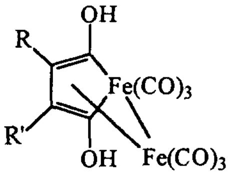
c) Yields are of products isolated by column chromatography using hexane/ethyl acetate (98:2) as eluent and based on the amount of alkynes used.

d) The spectral data of product **1** (IR, ^1H NMR, ^{13}C NMR) were identical to the data reported for this compound (Ref.15). The spectral data of product **2**, **3**, and **4** are comparable to the spectral data reported for compound **1**.

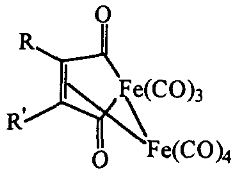
e) For the cyclobutenedione **8**, HRMS data were also obtained.

The following is the typical procedure: The $Fe(CO)_5$ (2.9 g, 15 mmol) in THF (15 mL) was added drop wise for 1h to $NaBH_4$ (0.567 g, 15 mmol) in THF (50 mL), and stirred for 8 h at 25°C under nitrogen atmosphere. Acetic acid (2.7 g, 45 mmol) was added and stirred for 30 min. 1-Heptyne (0.24 g, 2.5 mmol) was added and the contents were further stirred for 12 h. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (6.8 g, 40 mmol) in acetone (25 mL). Saturated aq.NaCl (30 mL) was added and the contents were extracted with (100 mL) ether. The combined organic extract was washed with brine, dried and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Ethyl acetate (1%) in hexane eluted cyclobutenedione **1** (73%, 0.275 g).[6]

Although the mechanism of this transformation is not clear, previous reports on the reaction of iron carbonyls with alkynes may provide information about the intermediate species involved. It has been reported that $Fe(CO)_5$ reacts with alkynes to give the corresponding cyclobutadiene-$Fe(CO)_3$ complexes or cyclopentadienone-$Fe(CO)_3$ complexes under different conditions.[7] Whereas di-tert-butylacetylene on reaction with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ gives the $(t\text{-}Bu_2C_2)Fe_2(CO)_6$ or $(t\text{-}Bu_2C_2)_2Fe_2(CO)_4$ complexes,[8] acetylene and monosubstituted acetylenes have been reported to give the corresponding tropone derivatives.[9] A mixture of 2,5- and 2,6- disubstituted quinones is obtained in the photochemical reaction of $Fe(CO)_5$ with some monosubstituted alkynes.[9] The quinones have been also obtained in 30% yield in the reaction of alkynes with $Fe(CO)_5$ in aqueous alkali at 80-90° C.[10] However, acetylene gives the dienol complex **I** at room temperature which after $FeCl_3$ oxidation in ether yields cyclobutenedione.[11] It has been reported that the yields of the dienol complexes **I** were poor for higher alkynes even after a long reaction time (3 days). More recent studies reveal that the complex **I** is formed as one among more than 10 products.[12] We have observed that the use of $FeCl_3$ in the place of $CuCl_2.2H_2O$ (Scheme 1) leads to a complex mixture of products. However, the intermediacy of species of the type **I** or **II** cannot be ruled out for the transformation reported here.



I



II

Cyclobutenediones and their adducts are highly versatile starting materials for the synthesis of variety of carbocyclic and heterocyclic products.[13] It has been suggested that some of them might exhibit antitumor activity.[14] Hence, availability of a single pot procedure for the synthesis of cyclobutenediones using the readily accessible $[HFe_3(CO)_{11}]^-$ reagent described here should be helpful for further developments in this area.

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6. **Spectral Data 1) :** **^{13}C NMR :** δ ppm 13.7, 22.1, 25.6, 27.1, 31.2, 184.8, 196.6, 199.9, 208.3.; **MS (EI) :** m/z 152 (M^+, 13%), 81 [(M^+-C_5H_{11}), 20%] **2) :** **^{13}C NMR :** δ ppm 13.9, 25.9, 26.8, 28.9, 29.6, 31.8, 184.9, 196.7, 199.9, 208.3. **3) :** **^{13}C NMR :** δ ppm 14.0, 22.6, 26.0, 27.5, 29.3, 29.7, 31.7, 31.9, 184.8, 196.6, 199.7, 208.4. **4) :** **^{13}C NMR :** δ ppm 13.9, 22.6, 25.9, 26.3, 29.1, 29.2, 29.5, 29.6, 31.8, 31.9, 198.7, 199.1, 199.4, 203.4; **MS (EI) :** m/z 222 (M^+, 25%), 81 [M^+-$C_{10}H_{21}$, 60%] **5) :** **^{13}C NMR :** δ ppm 127.7, 128.6, 129.5, 134.6, 178.3, 195.5, 196.0, 197.7. **6) :** **^{13}C NMR :** δ ppm 13.7, 19.9, 22.1, 25.8, 26.4, 31.7, 119.4, , 146.6, 190.5, 195.7, 197.8, 198.3. **MS (EI)** : m/z 192 (M^+, 12%), 121 [(M^+-CH_2-$(CH_2)_3$-CH_3), 20%]. 7) : **^{13}C NMR :** δ ppm 13.8, 13.9, 22.2, 22.4, 24.9, 26.0, 26.9, 28.9, 31.5, 31.8, 35.0, 68.6, 197.3, 198.4, 201.8, 202.7: **MS (EI) :** m/z 266 (M^++1, 5%), 195 [(M^+-C_5H_{11}), 16%]. **8) :** **^{13}C NMR :** δ ppm 13.7, 22.1, 26.9, 28.4, 29.3, 31.8, 74.9, 124.9, 125.3, 128.3, 128.8, 196.4, 198.5, 201.2, 202.9; **MS (EI) :** m/z 272 (M^+, 4%), 121 [$\{PhC(OH)CH_3\}^+$, 60%]; **HRMS :** m/z (M^+) calcd. 272.141245, found 272.141843.
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