Double carbonylation of alkynes using $NaHFe(CO)_4$

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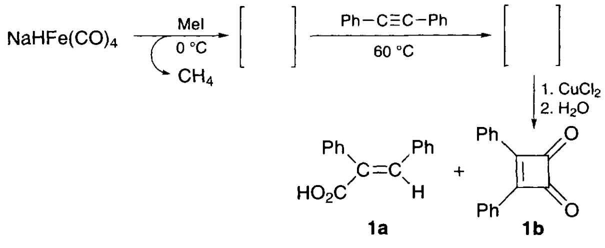
The reagent generated *in situ* using $NaHFe(CO)_4$ and MeI in THF, on reaction with alkynes followed by $CuCl_2$ oxidation, gives the corresponding cyclobutenediones in moderate yields (27–42%) in addition to the corresponding α,β-unsaturated carboxylic acids (10–22%).

Carbonylation reactions mediated by transition metals havebeen the subject of immense interest.[1] Among various metals used for carbonylations, $Fe(CO)_5$ finds important place in the stoichiometric and catalytic carbonylation reactions.[2] Here we report a novel double carbonylation of alkynes to cyclobutenediones utilising the reagent generated *in situ* from $NaHFe(CO)_4$ and MeI.

Whitmire *et al.* observed the formation of $Fe(CO)_4[MeCN]$ complex **I** in the reaction of $R_4N[HFe(CO)_4]$ with methyl iodide in acetonitrile.[3] In our studies of carbonylation reactions using iron carbonyl species,[4] we became interested in examining the reactivity of the complexes **I**. We observed that the reagent generated after treating $NaHFe(CO)_4$ with MeI in THF reacts with diphenylacetylene to give cyclobutenedione **1a** and the corresponding α,β-unsaturated carboxylic acid **1b**, Scheme 1.

The reaction is found to be general and various substituted alkynes are converted into the corresponding cyclobutenediones and α,β-unsaturated carboxylic acids, Table 1. The prop-2-ynyl alcohol derivatives also give cyclobutenedione (entries **6a** and **7a**). These results illustrate the compatibility of the hydroxy group in this transformation. In these cases, only some unidentified side products were isolated besides cyclobutenediones. The carboxylic acids formed [entries **2b**, and **4b**] at 60 °C are mixtures of stereoisomers. However, when the reaction was carried out at 25 °C with alkyne **2** (entry **3**) the corresponding (*E*)-β-silyl-α,β-unsaturated carboxylic acid was isolated in 20% yield and the *Z*-isomer was not formed.[5]

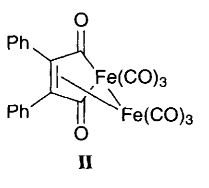
Although Whitmire *et al.* reported the formation of '$Fe(CO)_4$' complex **I** in the reaction of $R_4NH[Fe(CO)_4]$ with MeI in MeCN, it is not clear that this species is formed



Scheme 1

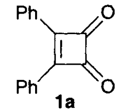
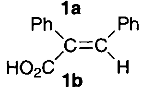
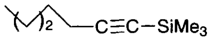
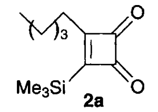
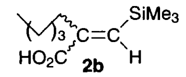
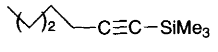
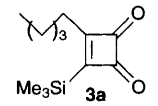
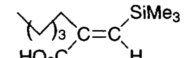
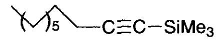
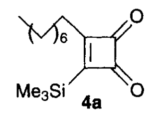
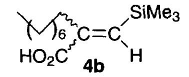
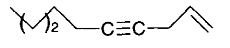
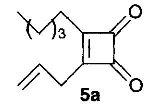
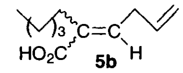
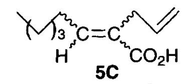
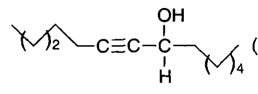
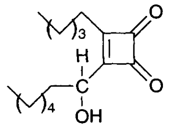
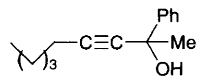
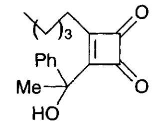
'$Fe(CO)_4$'

I



II

Table 1 Reaction of $NaHFe(CO)_4$ with MeI/RC≡CR′ in THF

Substrate (number)		*T*/°C	Product[a]	Yield[b] (%)
Ph—C≡C—Ph	(1)	60	 **1a**	42
			 **1b**	22
	(2)	60	 **2a**	37
			 **2b**	12
	(3)	25	 **3a**	23
			 **3b**	20
	(4)	60	 **4a**	31
			 **4b**	12
	(5)	60	 **5a**	32
			 **5b**  **5C**	10
	(6)	60	 **6a**	27
	(7)	60	 **7a**	31

[a] Products were identified by spectral data. [b] Yields are for isolated products, calculated on the basis of alkyne used.

exclusively under the present conditions.[3] The possibility of the presence of polymeric iron carbonyl species cannot be ruled out. The cyclobutenedione may result from the complex of the type **II**.

The α,β-unsaturated carboxylic acids may result from the reaction of alkynes with hydridoiron carbonyl species present in the reaction medium. However, we observed that when the reaction was carried out without using MeI only a small amount of α,β-unsaturated carboxylic acid was formed ($< 10\%$) and the conversion was poor. This indicates that a more reactive species is formed in the presence of MeI.

The production of cyclobutenedione is similar to the result obtained using the aq. NaOH–$Fe(CO)_5$ system with acetylene, where the reduced binuclear complex of the type **II** which was obtained was reported to yield cyclobutenedione on $FeCl_3$ oxidation.[6] However, it has been mentioned that the reduced complex **II** was obtained in very low yield with dimethylacetylene even after a long reaction time (3 weeks).[7] More recently, Sappa *et al.* reported that the NaOH–$Fe(CO)_5$ system in refluxing methanol, on treatment with substituted alkynes, gave the reduced complex **II** in 5% yield besides 7–10 other iron carbonyl complexes.[8] In the present case, the cyclobutenediones may result from complex **II**. Such maleoyl iron complexes have been shown to be useful in organic synthesis.[2b]

Although the mechanistic picture is not clear, the formation of cyclobutenediones in this one pot procedure is interesting since the dione is formed through a formal double carbonylation process. Cyclobutenediones of this type and their adducts are highly versatile starting materials for the synthesis of variety of carbocyclic and heterocyclic products.[9]

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Footnotes

† *Typical experimental procedure*: the $NaHFe(CO)_4$ [generated by careful acidification of $Na_2Fe(CO)_4$ (6 mmol)] in dry THF (30 ml) was treated with MeI (5 mmol, 0.71 g) at 0 °C under dry N_2. After 10 min diphenylacetylene (2.5 mmol, 0.45 g) was added and the contents were further stirred for 8 h at 60 °C. The metal carbonyl complex was decomposed using $CuCl_2.2H_2O$ (2.7 g, 20 mmol) in acetone (15 ml). Saturated aq. NaCl (30 ml) was added, and the resulting solution was extracted with diethyl ether. The combined extracts were washed with saturated $Na_2S_2O_3$ solution and brine, dried and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene. Ethyl acetate (1%) in hexane eluted the cyclobutenedione **1a** (42%, 0.24 g) and ethyl acetate (3%) in hexane eluted carboxylic acid **1b** (22%, 0.125 g).

‡ ^{13}C NMR data for **1a**: δ_C For: 196.1, 187.4, 134.6, 131.2, 129.7, 128.7; For **2a**: δ_C 211.3, 207.7, 201.4, 200.1, 31.8, 29.0, 26.5, 22.2, 13.7 and −2.1. For **4a**: δ_C 211.2, 207.6, 200.0, 31.7, 31.5, 29.6, 29.0, 26.8, 22.5, 140.0, and −2.1. For **5a**: δ_C 198.3, 197.8, 195.7, 190.5, 146.6, 119.4, 31.7, 26.4, 25.8, 22.1, 19.9 and 13.7. For **6a**: δ_C 202.7, 201.8, 198.4, 197.3, 68.6, 35.0, 31.8, 31.5, 28.9, 26.9, 26.2, 24.9, 22.5, 22.2, 13.9 and 13.8. For **7a**: δ_C 202.9, 201.2, 198.5, 196.4, 128.8, 128.3, 125.3, 124.9, 74.9, 31.8, 29.3, 28.4, 26.9, 22.1 and 13.7.

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