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Amine induced carbonylation of alkynes to cyclobutenediones using $\text{Fe}_3(\text{CO})_{12}$

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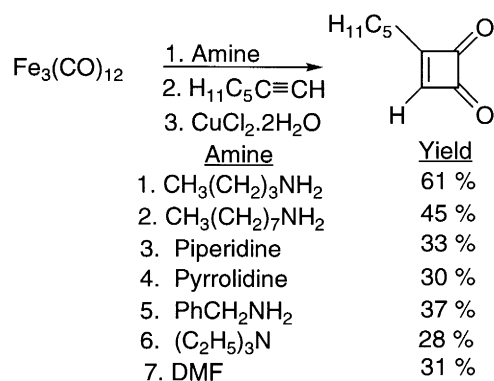
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Abstract

Iron carbonyl species, prepared in situ in THF using $\text{Fe}_3(\text{CO})_{12}$, react with alkynes at 25°C, in the presence of certain amines, to give the corresponding cyclobutenediones in moderate to good yields (25–61%) after $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ oxidation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: alkynes; amines; carbonylation; cyclobutenediones.

Iron carbonyls have been increasingly used in organic synthesis in recent years.^{1–5} The readily accessible, inexpensive $\text{Fe}(\text{CO})_5$ is not reactive towards organic substrates under ambient conditions. The $\text{Fe}(\text{CO})_5$ reacts with amine oxides to give reactive coordinatively unsaturated ' $\text{Fe}(\text{CO})_4$ ' species.^{6–8} Also, it was reported that amines such as *n*-butylamine, pyrrolidine and piperidine form addition complexes with $\text{Fe}(\text{CO})_5$.^{9,10} In continuation of studies on the synthetic applications of iron carbonyl species,^{11–13} we became interested in the application of the $\text{Fe}_3(\text{CO})_{12}$ for the preparation of reactive iron carbonyl



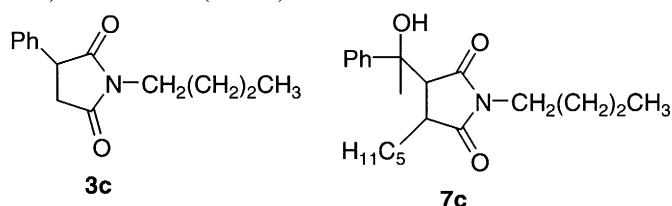
Scheme 1.

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species. The $\text{Fe}_3(\text{CO})_{12}$ species is a precursor to a variety of organoiron compounds.^{14–17} Under photolysis, it dissociates into ‘ $\text{Fe}(\text{CO})_4$ ’.^{18,19} Recently, it was reported that the Pauson–Khand reaction of alkyne– $\text{Co}_2(\text{CO})_6$ species is facilitated by certain amines.^{20,21} Accordingly, we have examined the effect of amines on the reactivity of alkynes with $\text{Fe}_3(\text{CO})_{12}$. We report here that amines facilitate the reaction of alkynes with $\text{Fe}_3(\text{CO})_{12}$ to give the corresponding cyclobutenediones after $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ oxidation (Scheme 1).

The $\text{Fe}_3(\text{CO})_{12}$ reacts with alkynes in the presence of *n*-butylamine at 25°C to give the corresponding cyclobutenediones in moderate to good yields (25–61%) after $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ oxidation (Table 1). Several alkynes were converted to the corresponding cyclobutenediones. It was observed that other amines such as *n*-octylamine, benzylamine, pyrrolidine, piperidine, triethylamine and DMF also give the same cyclobutenediones (28–45%). However, it was observed that the use of *n*-butylamine gives better yields (25–61%) (Scheme 1).

Evidently, this reagent system can tolerate unmasked functional groups such as hydroxyl and trimethylsilyl (entries 5, 6, 7 and 8 Table 1). Also, in the case of *n*-butylamine (entries 3 and 7 Table 1) traces of cyclic imides (**3c** and **7c**) are formed (2–5%) under these conditions.²²

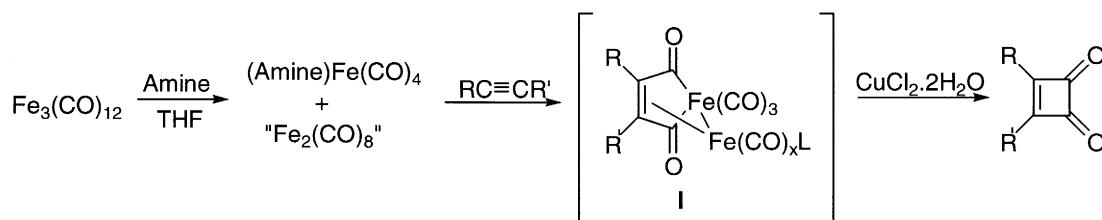


The following is the typical procedure: The $\text{Fe}_3(\text{CO})_{12}$ was prepared following a reported procedure.²³ The $\text{Fe}_3(\text{CO})_{12}$ (3.02 g, 6 mmol) and *n*-butylamine (0.201 g, 2.75 mmol) in THF (50 mL) under N_2 atmosphere was stirred for 30 min at 25°C. 1-Heptyne (0.120 g, 1.25 mmol) was added and the stirring was continued for a further 12 h. The metal carbonyl complex was decomposed using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.7 g mmol) in acetone (10 mL). Saturated aq. NaCl (25 mL) was added, and the resulting solution was extracted with ether (100 mL), washed with brine (20 mL), dried over anhydrous MgSO_4 and concentrated. The residue was subjected to column chromatography (silica gel, hexane/ethyl acetate). Ethyl acetate (2%) in hexane eluted cyclobutenedione **1a** (0.116 g, 61%).²⁴

A tentative mechanistic pathway for the formation of cyclobutenediones can be visualised as shown in Scheme 2. Presumably, the amine may help in the splitting of the $\text{Fe}_3(\text{CO})_{12}$ to give (amine) $\text{Fe}(\text{CO})_4$ and ‘ $\text{Fe}_2(\text{CO})_8$ ’ species, which on further reaction with alkynes could give the intermediate complex of the type **I**. Oxidation of **I** with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ would produce the corresponding cyclobutenediones.¹³

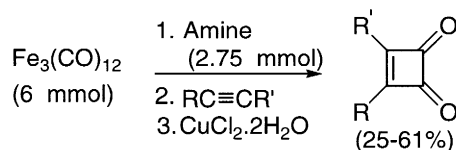
Yields are of products isolated by column chromatography using hexane:ethyl acetate (98:2) as eluent and based on the amount of alkynes used.

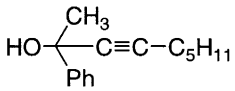
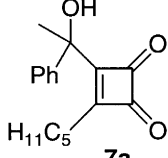
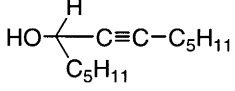
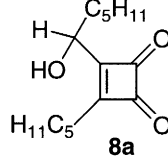
To examine the possibility whether coordinatively unsaturated ‘ $\text{Fe}(\text{CO})_4$ ’ species can be prepared



Scheme 2.

Table 1
Reaction of $\text{Fe}_3(\text{CO})_{12}$ with alkyne in the presence of *n*-butylamine in THF



S.No.	Alkyne	Product ^a	Yield (%) ^b
1.	R= C ₅ H ₁₁ , R'= H	1a	61
2.	R= C ₆ H ₁₃ , R'= H	2a	54
3.	R= C ₆ H ₅ , R'= H	3a	41
4.	R, R'= Ph	4a	45
5.	R= C ₅ H ₁₁ , R'= SiMe ₃	5a	28
6.	R= C ₈ H ₁₇ , R'= SiMe ₃	6a	25
7.			37
8.			33

a) Products were identified from spectral data (IR, ¹H NMR, ¹³C NMR and Mass).²² The spectral data of product **1a** and **4a** were identical to the reported data.²⁴ The spectral data of products **2a** and **3a** are comparable to the spectral data reported for compound **1a**. For the cyclobutenediones, **5a** and **7a** HRMS data were also obtained.

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

using $\text{Fe}(\text{CO})_5$, we carried out the reaction with $\text{Fe}(\text{CO})_5$ (6 mmol), *n*-butylamine (2.75 mmol) and phenylacetylene (1.25 mmol).^{9,10} However, only the starting alkyne was recovered.

In conclusion, the simple, convenient procedure for the double carbonylation of alkynes to obtain the corresponding cyclobutenediones using a readily available iron carbonyl reagent system described here should be attractive for synthetic applications.

Acknowledgements

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- Spectral data: ¹³C NMR (CDCl₃) data: (δ ppm): (**1a**) 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⁺-C₅H₁₁), 20%]. (**2a**) 13.9, 25.9, 26.8, 28.9, 29.6, 31.8, 184.9, 196.7, 199.9, 208.3. (**3a**) 14.0, 22.6, 26.0, 27.5, 29.3, 29.7, 31.7, 31.9, 184.8, 196.6, 199.7, 208.4. (**4a**) 128.7, 129.7, 131.2, 134.6, 187.4, 196.1. (**3c**) 10.1, 18.6, 21.5, 27.7, 30.6, 36.2, 38.5, 124.0, 132.4, 172.5, 175.9. (**5a**) -2.1, 13.7, 22.2, 26.5, 29.0, 31.8, 200.1, 201.4, 207.7, 211.3. MS (EI): *m/z*: 224 (M), 154 (B); HRMS; *m/z* calcd: 224.123258, found: 224.123138. (**6a**) -2.1, 14.0, 22.5, 26.8, 29.0, 29.6, 31.5, 31.7, 200.0, 207.6, 211.2. (**7a**) 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%). HRMS; *m/z* calcd: 272.141243 found: 272.141843. (**7c**) 13.4, 13.7, 19.9, 22.1, 24.6, 25.1, 29.5, 31.2, 31.3, 38.3, 42.7, 57.0, 74.8, 125.6, 127.7, 128.2, 143.6, 178.5, 179.1. MS (EI); *m/z*: 347. Anal. calcd for C₂₁H₃₁O₃N: C, 73.04; H, 8.98; N, 4.05. Found: C, 73.10; H, 9.15; N, 4.11. (**8a**) 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⁺-C₅H₁₁, 16%).
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