Reactive Iron Carbonyl Species via Reduction of $FeCl_3$ with $NaBH_4$ in the Presence of CO: Conversion of 1-Alkynes to Benzoquinones and Cyclobutenediones

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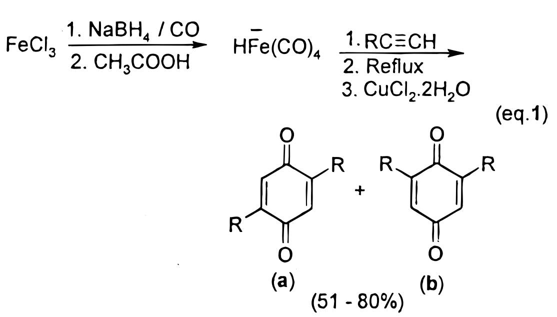
Summary: Iron carbonyl species, prepared in situ at 25 °C through reduction of anhydrous $FeCl_3$ with $NaBH_4$ in the presence of carbon monoxide and acetic acid in THF, reacts with 1-alkynes at reflux temperature to give the corresponding benzoquinones after $CuCl_2$•$2H_2O$ oxidation in moderate to good yields (51−80%). Also, these species upon CH_3I treatment followed by reaction with 1-alkynes lead to the formation of the corresponding cyclobutenediones in moderate yields (30−37%) after $CuCl_2$•$2H_2O$ oxidation.

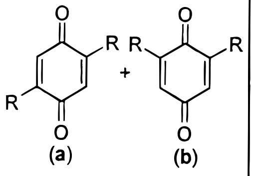
There has been continued interest in the preparation of new, unusual metal carbonyls by the reduction of transition-metal complexes in the presence of CO.[1] Iron carbonyl complexes were also prepared using $FeCl_3$ and reducing agents under CO.[2] Recently, a simple method for the preparation of the supernucleophile $Na_2Fe(CO)_4$ in situ through reduction of anhydrous $FeCl_3$ using sodium naphthalenide has been reported from this laboratory.[3] In continuation of these efforts, we report here that 1-alkynes are converted to benzoquinones or cyclobutenediones in moderate to good yields by iron carbonyl species prepared using anhydrous $FeCl_3$, $NaBH_4$, and CH_3COOH under CO at atmospheric pressure.

It was reported that the reduction of $FeCl_3$ with excess $LiBH_4$ in diethyl ether gives iron(II) borohydride, which decomposes slowly at −10 °C and rapidly at 0 °C.[4] We have observed that the reduction of anhydrous $FeCl_3$ (10 mmol) with $NaBH_4$ (40 mmol) in THF at 25 °C followed by addition of CH_3COOH (68 mmol) while bubbling CO at atmospheric pressure for 9 h gives iron carbonyl species (eq 1). The presence of iron carbonyl species in the reaction mixture was confirmed by the IR spectral data of the solution (strong bands at 2044 and 1986 cm^{-1}).[5a] The UV spectrum of the solution (λ_{max} 490 nm) indicated the presence of metal carbonyl species of the type $[HFe(CO)_4]^-$.[5b] However, the presence of a mixture of iron carbonyl species cannot be ruled out.



(eq.1)

Table 1. Reaction of $FeCl_3$/$NaBH_4$/CO/CH_3COOH Reagent System with 1-Alkynes at 70 °C

S.No	1-Alkyne	Product[a]	Yield[b]
	RC≡CH		
1.	R = C_6H_{13}	**1a** (65%) **1b** (35%)	72 %
2.	R = Ph	**2a** (52%) **2b** (48%)	51 %
3.	R = C_5H_{11}	**3a** (60%) **3b** (40%)	80 %
4.	R = C_8H_{17}	**4a** (71%) **4b** (29%)	51 %

[a] Products were identified by the spectral data (IR, ^1H NMR, and ^{13}C NMR) and comparison with the reported data.[6] The percentage compositions of isomers **a** and **b** were calculated from the ^1H NMR signal intensities and compared with the reported data. [b] Yields are of products isolated by column chromatography using hexane as eluent and based on the 1-alkynes used.

We have observed that the reagent, prepared as above, reacts with 1-alkynes in THF at refluxing temperature for 12 h to give disubstituted benzoquinones in moderate to good yields (51−80%) after $CuCl_2$•$2H_2O$ oxidation (eq 1).[6] The results are summarized in Table 1. Also, the reaction at 25 °C gave the benzoquinones in poor yields (10−20%) and the internal alkynes such as diphenylacetylene, 1-heptynyltrimethylsilane, and propargyl alcohol derivatives did not react even under refluxing conditions. The percentage compositions of isomers **a** and **b** were calculated from ^1H NMR signal intensities and compared with the data reported for

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(1) Ellis, J. E.; Beck, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2489 and references cited therein.

(2) (a) Carbonaro, A.; Greco, A. *J. Organomet. Chem.* **1970**, *25*, 477. (b) Carbonaro, A.; Cambisi, F. *J. Organomet. Chem.* **1972**, *44*, 171.

(3) Devasagayaraj, A.; Periasamy, M. *Transition Met. Chem.* **1991**, *16, 503.*

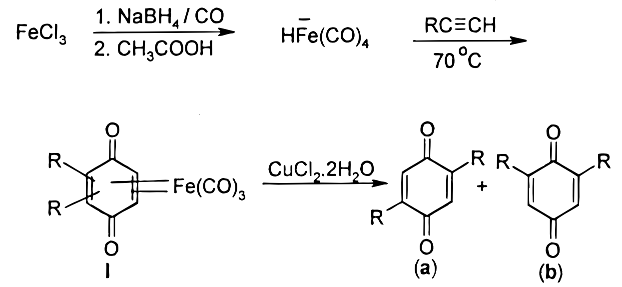
(4) Schaeffer, G. W.; Roscoe, J. S.; Stewart, A. C. *J. Am. Chem. Soc.* **1956**, *78*, 729.

(5) (a) Farmery, K.; Kilner, M.; Greetrex, R.; Greenwood, N. N. *J. Chem. Soc. A* **1969**, 2339. (b) Case, J. R.; Whiting, M. C. *J. Chem. Soc.* **1960**, 4632.

(6) Maruyama, K.; Shio, T.; Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1877.

10.1021/om991017x CCC: $19.00

Scheme 1

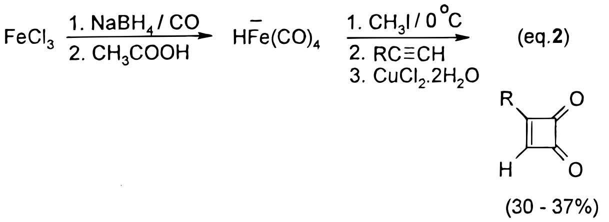


similar compounds obtained in the reaction of $Fe(CO)_5$ with alkynes under photolysis.[6]

The formation of benzoquinones may be rationalized by considering the formation of the hydridoiron carbonyl of the type $[HFe(CO)_4]^-$ species in the reaction of $FeCl_3$, $NaBH_4$, CO, and CH_3COOH.[5] Reaction of 1-alkynes with these species would lead to the intermediate complex of the type **I**.[7] Oxidation of **I** using $CuCl_2{\cdot}2H_2O$ may lead to the corresponding benzoquinones (Scheme 1).

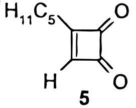
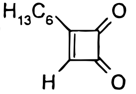
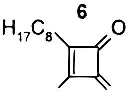
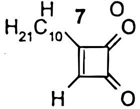
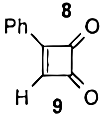
It is of interest to note that the $HFe(CO)_4^-$ on reaction with alkynes gives the corresponding quinones.[7c] Previously, we have reported that $NaHFe(CO)_4$, prepared using $Na_2Fe(CO)_4$ and CH_3COOH, on CH_3I treatment gives coordinatively unsaturated iron carbonyl species that on further reaction with alkynes yields the corresponding cyclobutenediones after $CuCl_2{\cdot}2H_2O$ oxidation.[8] Presumably, the $HFe(CO)_4^-$ reacts with CH_3I to give the $H(CH_3)Fe(CO)_4$ complex, which reductively eliminates methane to give a coordinatively unsaturated species[9] that reacts with the starting $HFe(CO)_4^-$ to form reactive polynuclear iron carbonyl species.

We have also examined the effect of CH_3I on the $HFe(CO)_4^-$ reagent prepared in situ as above. Interestingly, addition of CH_3I at 0 °C gives gas evolution and the resulting iron carbonyl species reacts with 1-alkynes at 25 °C for 12 h in THF to give the corresponding cyclobutenediones after $CuCl_2{\cdot}2H_2O$ oxidation. Though the cyclobutenediones are obtained only in moderate yields (30−37%), the products can be easily separated free of trace amounts of highly polar unidentified products by column chromatography (eq 2). The results



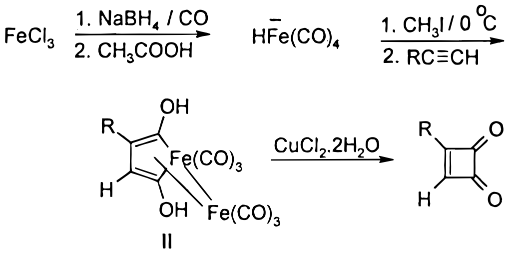
are summarized in Table 2. The corresponding benzoquinones are not formed under these conditions. We have also examined the effect of temperature on this reaction. It was observed that addition of CH_3I at 0 °C followed by reaction with 1-alkynes at 70 °C gives a mixture of benzoquinones and cyclobutenediones. Internal alkynes did not give the corresponding cyclobutenediones under these conditions.

Table 2. Reaction of $FeCl_3/NaBH_4/CO/CH_3COOH/CH_3I$ Reagent System with 1-Alkynes at 25 °C

S.No	1-Alkyne	Product[a]	Yield[e]
1.	$H_{11}C_5C{\equiv}CH$	 **5**	37 %[b]
2.	$H_{13}C_6C{\equiv}CH$	 **6**	35 %[c]
3.	$H_{17}C_8C{\equiv}CH$	 **7**	32 %[c]
4.	$H_{21}C_{10}C{\equiv}CH$	 **8**	31 %[c]
5.	PhC≡CH	 **9**	30 %[d]

[a] Products were identified by the spectral data (IR, ^1H NMR, ^{13}C NMR, and mass) and compared with the reported data.[12] [b] The spectral data of product **5** are in a 1:1 correspondence with the reported data. [c] The spectral data of compounds **6**−**8** are comparable to the spectral data reported for compound **5**. [d] The cyclobutenedione **9** has been reported (mp 151−152 °C; lit.[12c] mp 152−153 °C). [e] Yields are of products isolated by column chromatography using hexane/ethyl acetate (98:2) as eluent and are based on the 1-alkynes used.

Scheme 2



A tentative mechanistic pathway for the formation of cyclobutenediones can be visualized as shown in Scheme 2. The intermediate iron complex of the type **II**[10] would result from the coordination of the 1-alkyne moiety to the coordinatively unsaturated iron carbonyl species formed after the addition of CH_3I.[10] Oxidation of **II** using $CuCl_2{\cdot}2H_2O$ may lead to the formation of corresponding cyclobutenediones.[11]

In conclusion, we have developed a simple, convenient procedure for the in situ generation of new reactive iron carbonyl species using anhydrous $FeCl_3$ and $NaBH_4$ under a CO atmosphere. It is well-known that benzo-

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quinones, cyclobutenediones, and their derivatives are versatile starting materials used in the synthesis of a variety of biologically active compounds.[13] Accordingly, the procedure described here for the one-pot method of conversion of 1-alkynes to the corresponding benzoquinones and cyclobutenediones should be useful for synthetic applications.

Experimental Section

General Methods. ^1H (200 MHz) and ^{13}C NMR (50 MHz) spectra were taken in $CDCl_3$ unless otherwise stated, with TMS as reference (δ 0 ppm). The chemical shifts are reported in ppm on the δ scale relative to $CDCl_3$ (77.0 ppm), and coupling constants are reported in Hz. All IR spectra were recorded on a JASCO FT-5300 instrument with polystyrene as reference. The UV spectra were recorded with a JASCO Model 7800 spectrophotometer. Chromatographic purification was conducted by column chromatography using 100−200 mesh silica gel obtained from Acme Synthetic Chemicals (India). The alkynes used in the reactions (except 1-heptyne) were prepared by following a reported procedure.[14] THF supplied by E. Merck (India) was distilled over sodium−benzophenone ketyl before use. All reactions and manipulations were conducted under a dry nitrogen atmosphere. All yields reported are isolated yields of materials judged homogeneous by TLC and IR and NMR spectroscopy. Carbon monoxide was generated by dropwise addition of formic acid (98%) to concentrated H_2SO_4 (96%) at 90 °C using an apparatus recommended for use in the carbonylation of organoboranes.[15] The CO was predried by passing through a jar filled with anhydrous KOH pellets before bubbling into the reaction mixture.

1. Reaction of $FeCl_3/NaBH_4/CO/CH_3COOH$ Reagent System with 1-Alkynes at 70 °C. The anhydrous $FeCl_3$ (1.26 g, 10 mmol) in THF (50 mL) was added slowly for 1 h to $NaBH_4$ (1.54 g, 40 mmol) in THF (100 mL) while bubbling CO at 25 °C. The reaction mixture was further stirred for 9 h at 25 °C, while CO was bubbled through it. Acetic acid (4 g, 68 mmol) was added slowly, and this mixture was stirred further for 30 min. The CO bubbling was replaced by a nitrogen atmosphere, 1-octyne (0.090 g, 1.25 mmol) was added, and the contents were refluxed at 70 °C for 12 h. The metal carbonyls in the reaction mixture were decomposed by adding $CuCl_2{\cdot}2H_2O$ (6.8 g, 40 mmol) in acetone (20 mL) at 25 °C. Saturated aqueous NaCl (40 mL) was added, and the contents were extracted with ether (100 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous $MgSO_4$, and concentrated. The residue was subjected to column chromatography (silica gel, hexane). Hexane eluted the benzoquinones **1a**,**b** (72%, 0.113 g).[6]

The above procedure was followed for the conversion of other 1-alkynes to the corresponding benzoquinones, and the spectral data are reported below. The spectral data for benzoquinones **1a**,**b** and **2a**,**b** showed 1:1 correspondence with the reported data.[6]

3a,**b**: yield 80% (0.112 g); IR (neat) 1657 cm^{-1}; ^1H NMR: δ (ppm) 6.50 (s, 2H), 6.52 (s, 2H); ^{13}C NMR δ (ppm) 13.6, 22.2, 27.4, 28.5, 29.0, 31.3, 131.9, 132.4, 149.2, 149.6, 187.4, 187.7.

4a,**b**: yield 51% (0.098 g); IR (neat) 1655 cm^{-1}; ^1H NMR δ (ppm) 6.48 (s, 2H), 6.51 (s, 2H); ^{13}C NMR δ (ppm) 13.9, 22.5, 27.8, 28.6, 29.0, 29.2, 29.7, 31.7, 131.6, 132.4, 149.1, 149.5, 187.3, 187.8. The spectral data of compounds **3a,b** and **4a,b** are comparable to the reported data for the compounds **1a**,**b** and **2a**,**b**.[6]

2. Reaction of $FeCl_3/NaBH_4/CO/CH_3COOH/CH_3I$ Reagent System with 1-Alkynes at 25 °C. Anhydrous $FeCl_3$ (1.26 g, 10 mmol) in THF (50 mL) was added slowly for 1 h to $NaBH_4$ (1.54 g, 40 mmol) in THF (100 mL) while bubbling CO at 25 °C. The reaction mixture was further stirred for 9 h at 25 °C while CO was bubbled through it. Acetic acid (4 g, 68 mmol) was added slowly, and this mixture was stirred further for 30 min. The CO bubbling was replaced by a nitrogen atmosphere, CH_3I (2.84 g, 20 mmol) was added at 0 °C, and stirring was continued for 30 min. 1-Heptyne (0.12 g, 1.25 mmol) was added, and the contents were stirred for 12 h at 25 °C. The metal carbonyls in the reaction mixture were decomposed by adding $CuCl_2{\cdot}2H_2O$ (6.8 g, 40 mmol) in acetone (20 mL) at 25 °C. Saturated aqueous NaCl solution (40 mL) was added, and the contents were extracted with ether (100 mL). The organic extract was washed with brine (20 mL) and saturated aqueous $Na_2S_2O_3$ solution, 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 **5** (37%, 0.070 g).[12a]

The above procedure was followed for the conversion of other 1-alkynes to the corresponding cyclobutenediones, and the spectral data are reported below. The spectral data showed 1:1 correspondence with the reported data.

5: yield 37% (0.070 g); IR (neat) 1778 cm^{-1}; ^1H NMR δ (ppm) 0.82 (t, $J = 7.3$ Hz, 3H), 1.27−1.40 (m, 4H), 1.70−1.83 (m, 2H), 2.81 (t, $J = 7.3$ Hz, 2H), 9.20 (s, 1H); ^{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), 81 (B).

6: yield 35% (0.077 g); IR (neat) 1786 cm^{-1}; ^1H NMR δ (ppm) 0.89 (t, $J = 7.3$ Hz, 3H), 1.2−2.7 (m, 8H), 2.81 (t, $J = 7.2$ Hz, 2H), 9.1 (s, 1H); ^{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.

7: yield 32% (0.085 g); IR (neat): 1788 cm^{-1}; ^1H NMR δ (ppm) 0.88 (t, $J = 7.3$ Hz, 3H), 1.2−2.5 (m, 12H), 2.85 (t, $J = 7.3$ Hz, 2H), 9.2 (s, 1H); ^{13}C NMR δ (ppm) 14.0, 22.6, 26.0, 27.5, 29.3, 29.7, 31.9, 184.8, 196.6, 199.7, 208.4.

8: yield 31% (0.086 g); IR (neat) 1774 cm^{-1}; ^1H NMR δ (ppm) 0.81 (t, $J = 7.2$ Hz, 3H), 1.23−1.42 (m, 16H), 2.75 (t, $J = 7.4$ Hz, 2H), 9.21 (s, 1H); ^{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), 81 (B).

9: yield 30% (0.060 g); mp 151−152 °C (lit.[12c] mp 152−153 °C); IR (KBr) 1768 cm^{-1}; ^1H NMR δ (ppm) 7.3−8.0 (m, 5H), 9.5 (s, 1H); ^{13}C NMR δ (ppm) 128.6, 129.4, 129.5, 134.6, 178.3, 195.5, 196.0, 197.7.

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Supporting Information Available: Figures giving ^{13}C NMR spectra of the compounds **2**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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