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Synthesis of Cyclobutenediones and Anhydrides from Alkynes Using the $Fe(CO)_5/Me_3NO$ Reagent System

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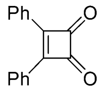
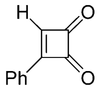
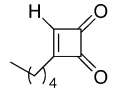
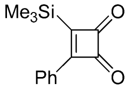
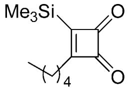
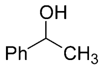
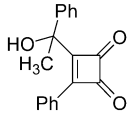
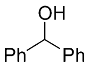
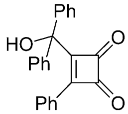
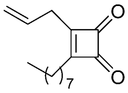
Summary: Coordinatively unsaturated "$Fe(CO)_4$" species prepared using inexpensive Me_3NO and $Fe(CO)_5$ reacts with alkynes under ambient conditions to give cyclobutenediones in moderate to good yields (50–75%) after $CuCl_2$·$2H_2O$ oxidation. The corresponding cyclic anhydrides are obtained in 60–80% yields when an excess of the amine oxide was used.

Introduction

The requirement of efficient reagents for the preparation of multifunctional molecules continues to spur research activity in the development of new synthetic methods employing organometallic reagents, particularly using metal carbonyls.[1–3] Generally, commercially available metal carbonyls are coordinatively saturated, 18-electron species, and hence one of their CO ligands should be removed for them to participate in chemical reactions. Several chemical promoters such as R_3NO, R_3PO, KOMe, KH, and $NaBH_4$ were reported to facilitate the CO dissociation.[4–7] Trimethylamine *N*-oxide (Me_3NO) is a well-known mild, efficient oxidizing agent, which removes one of the carbonyl ligands of $Fe(CO)_5$ as CO_2 to form the reactive, coordinatively unsaturated "$Fe(CO)_4$" species.[5,7] During the course of our efforts on the preparation of reactive iron carbonyl species for applications in organic synthesis,[6] we have observed that the unsaturated "$Fe(CO)_4$" species, prepared using the inexpensive $Fe(CO)_5/Me_3NO$ reagent system, reacts with alkynes to give the corresponding cyclobutenediones or the anhydrides after $CuCl_2$ oxidation. The results are described here.

Table 1. Reaction of Alkynes (2.5 mmol) with $Fe(CO)_5$ (15 mmol) and Me_3NO (12 mmol) Followed by $CuCl_2$·$2H_2O$ Oxidation

Entry	Alkyne R	R'	Product[a]	Product Number	Yield[b] %
1	C_6H_5	C_6H_5		**3a**	73
2	H	C_6H_5		**3b**	62
3	H	C_5H_{11}		**3c**	50
4	Me_3Si	C_6H_5		**3d**	75
5	Me_3Si	C_5H_{11}		**3e**	68
6		C_6H_5		**3f**	70
7		C_6H_5		**3g**	65
8	C_3H_5	C_8H_{17}		**3h**	57

[a] Products were identified by the spectral data (IR, ^1H, ^{13}C NMR, and MS) and comparison with reported data.[8] [b] Yields reported are for the isolated products and based on the amount of alkynes used.

Results and Discussion

We have observed that $Fe(CO)_4$, prepared in THF using Me_3NO and $Fe(CO)_5$, reacts with alkynes at room temperature to give corresponding diones in moderate to good yields (50–75%) after $CuCl_2$·$2H_2O$ oxidation (eq 1). Several alkynes were converted to cyclobutenediones, and the results are summarized in Table 1. Evidently, this reagent system tolerates unmasked functional groups such as hydroxyl and silyl groups (entries 4–7). The formation of cyclobutenedione from enyne shows

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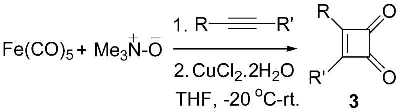
that this reagent system reacts with alkynes without affecting the olefin moiety (entry 8). In the case of 1-heptyne, the corresponding cyclobutenedione is obtained in lower yield besides a mixture of the corresponding 2,5- and 2,6-dialkylbenzoquinones (30%, 60:40) (entry 3, Table 1).

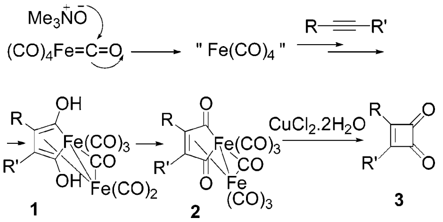


(1)

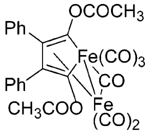
Although THF was found to be a suitable solvent, other solvents such as CH_3CN and acetone also gave comparable results. However, the use of solvents such as $CHCl_3$ and CH_2Cl_2 gave unidentified mixtures of carbonyl products. Presumably, the coordinating solvents may form weak complexes with the $Fe(CO)_4$ species that help in this transformation.[7a,b]

The formation of cyclobutenediones from alkynes can be explained by considering a tentative mechanism depicted in Scheme 1. Addition of $Fe(CO)_5$ to a solution of Me_3NO in THF at −20 °C gives a red-colored solution with immediate evolution of CO_2 through the nucleophilic attack of amine oxide to coordinated CO.[7] These species would further react with alkynes followed by CO insertion to give maleoyl complexes of type **1** or ferrole complexes of type **2**. Such complexes could give cyclobutenediones after $CuCl_2{\cdot}2H_2O$ oxidation.[8c,d]

Scheme 1



We have also made efforts to identify the intermediate species involved in the above transformation. It was observed that the addition of Et_3N and CH_3COCl to the iron carbonyl formed in situ in the reaction of $Fe(CO)_4$ and alkyne in THF gives the iron complex **5** in 48% yield (Figure 1).[6,10]

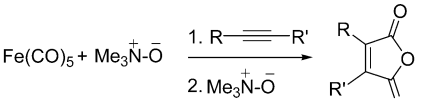


5

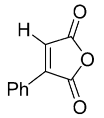
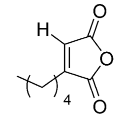
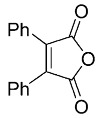
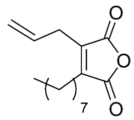
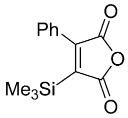
Figure 1. Diacetylferrole complex.

We have also observed that use of excess amine oxide gives the corresponding cyclic anhydrides (60−80%) after $CuCl_2{\cdot}2H_2O$ oxidation along with traces of cyclobutenediones (3−5%), Table 2.

Table 2. Reaction of Alkynes (2.5 mmol) with $Fe(CO)_5$ (10 mmol) and Me_3NO (15 mmol)



4

Entry	R	R'	Product[a]	Compound Number	Yield[b] %
1	H	C_6H_5		**4a**	72
2	H	C_5H_{11}		**4b**	68
3	C_6H_5	C_6H_5		**4c**	80
4	C_3H_5	C_8H_{17}		**4d**	60
5	C_6H_5	C_6H_5		**4e**	75

[a] Products were identified by the spectral data (IR, ^1H, ^{13}C NMR, and MS) and comparison with reported data (entries 1 and 3).[9] [b] Yields reported are for the isolated products and based on the amount of alkynes used.

In conclusion, the present 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 prepared from $Fe(CO)_5$.[5] Me_3NO is a mild, efficient oxidizing agent.[5a,b] Since it is transformed into the volatile trimethylamine, it does not interfere with the isolation of products. Cyclobutenediones and their derivatives have proven applications. They have been used as NLO materials,[11a,b] growth regulators, potassium channel openers, drug molecules,[11c−j] anion recognition systems,[12] chiral

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ligands,[13] and versatile starting materials for the synthesis of multifunctional molecules.[14] Hence, easy accessibility of this useful class of compounds via the procedure reported here should facilitate research in these areas.

Experimental Section

General Procedures. ^{1}H NMR (400 and 200 MHz) and ^{13}C NMR (100 and 50 MHz) spectra were recorded on a Bruker spectrometer in $CDCl_3$, and TMS was used as reference (δ = 0 ppm). Melting points are uncorrected. IR spectra were recorded on a JASCO FT-5300 instrument with polystyrene as reference. Mass spectral analyses were carried out on a VG 7070H mass spectrometer using the EI technique at 70 eV. Elemental analyses were carried out using a Thermo Finnigan/Flash EA1112 CHN analyzer. $Fe(CO)_5$ and Me_3NO were supplied by Fluka and Aldrich, respectively. The alkynes used in the reactions (except heptyne) were prepared by following the reported procedure.[15] THF was distilled over sodium benzophenone ketyl. 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 analyses.

Preparation of Cyclobutenediones 3a–3h. To a solution of anhydrous Me_3NO (0.9 g, 12 mmol) in THF (30 mL) was dropwise added $Fe(CO)_5$ (1.9 mL, 15 mmol) in THF (40 mL) over a period of 30 min at −20 °C under dry nitrogen. The reaction starts with immediate evolution of CO_2, and the color changes from yellow to dark brown. The reaction mixture was stirred for another 1 h and slowly brought to room temperature. Diphenylacetylene (0.44 g, 2.5 mmol) was added, and the contents were further stirred for 10 h at room temperature. The metal carbonyl complexes were oxidized using $CuCl_2 \cdot 2H_2O$ (4.2 g, 25 mmol) in acetone (15 mL). A saturated NaCl solution was added, and the contents were extracted with ether (2 × 75 mL). The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane−EtOAc). Ethyl acetate (1%) in hexane eluted the 3,4-diphenyl-3-cyclobutene-1,2-dione **3a**.

3a. Yield: 0.43 g (73%). The sample was crystallized from hexane−ethyl acetate (97:3). Mp: 95−96 °C (lit.[8a−d] mp 97 °C). IR (KBr): 1780 cm^{-1}. ^{1}H NMR (200 MHz): δ 8.14 (m, 4H); 7.45−7.68 (m, 6H). ^{13}C NMR (50 MHz): δ 196.1, 187.4, 134.6, 131.2, 129.7, 128.7. MS (EI): *m/z* 235 [M$^+$, 12%].

3b. Yield: 0.24 g (62%). The sample was crystallized from hexane−ethyl acetate (97:3). Mp: 152−153 °C (lit.[8a−d] mp 152−153 °C). IR (KBr): 1768 cm^{-1}. ^{1}H NMR (200 MHz): δ 9.5 (s, 1H); 7.3−8.0 (m, 5H). ^{13}C NMR (50 MHz): δ 197.7, 196.0, 195.5, 178.3, 134.6, 129.5, 129.4, 128.6.

3c. Yield: 0.19 g (50%). IR (neat): 1778 cm^{-1}. ^{1}H NMR (200 MHz): δ 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 (50 MHz): δ 208.3, 199.9, 196.6, 184.8, 31.2, 27.1, 25.6, 22.1, 13.7. MS (EI): *m/z* 152 [M$^+$, 13%].

3d. Yield: 0.43 g (75%). The sample was crystallized from hexane−ethyl acetate (97:3). Mp: 101−102 °C (lit.[8e] mp 102.8−103.2 °C). IR (neat): 1774, 1766 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.8−7.2 (m, 5H); 0.45 (s, 9H). ^{13}C NMR (100 MHz): δ 202.6, 200.3, 199.3, 197.8, 133.5,129.4,129.3 129.2,−1.8. MS (EI): *m/z* 230 [M$^+$, 8%].

3e. Yield: 0.38 g (68%). IR (neat): 1778, 1766 cm^{-1}. ^{1}H NMR (200 MHz): δ 2.87 (t, J = 7.3, 2H); 1.17−1.67 (m, 6H); 0.92 (t, J = 6.9 Hz, 3H); 0.35 (s, 9H). ^{13}C NMR (50 MHz): δ 211.3, 207.7, 201.5, 200.1, 31.7, 29.1, 26.9, 22.2, 13.7; −2.1. MS (EI): *m/z* 224 [M$^+$, 10%].

3f. Yield: 0.49 g (70%). IR (neat): 3479, 1789, 1770 cm^{-1}. ^{1}H NMR (400 MHz): δ 8.2−7.2 (m, 10H); 2.9 (s, 1H); 2.1 (s, 3H). ^{13}C NMR (50 MHz): δ 197.8, 196.5, 195.8, 189.2, 142.6, 133.6, 131.2, 128.9, 128.8, 128.4, 127.6, 124.9, 74.9, 28.2. MS (EI): *m/z* 278 [M$^+$, 15%].

3g. Yield: 0.55 g (65%). IR (neat): 3483, 1784, 1768 cm^{-1}. ^{1}H NMR (400 MHz): δ 8.4−7.3 (m, 15H); 3.2 (s, 1H). ^{13}C NMR (50 MHz): δ 198.4, 197.5, 195.2, 189.8, 141.4, 133.5, 131, 128.9, 128.8, 128.7, 128.4, 80.5. MS (EI): *m/z* 340 [M$^+$, 8%]. Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74. Found: C, 81.22; H, 4.73.

3h. Yield: 0.33 g (57%). IR (neat): 3033, 1776, 1768 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.3−7.1 (m, 1H); 6.4 (dd, J = 10.7, 1.5 Hz, 2H); 2.6 (t, J = 7.5 Hz, 2H); 1.9 (dd, J = 5.5, 1.5 Hz, 2H); 1.6 (m, 2H); 1.2 (m, 10H); 0.8 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz): δ 198.2, 197.8, 195.6, 190.4, 146.5, 119.4, 31.7, 29.6, 29.1, 29, 26.5, 26.2, 22.5, 20, 14. MS (EI): *m/z* 234 [M$^+$, 12%]. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46; Found: C, 77.06; H, 9.47.

Preparation of Cyclic Anhydrides 4a–d. To a solution of anhydrous Me_3NO (1.1 g, 15 mmol) in THF (30 mL) was dropwise added $Fe(CO)_5$ (1.3 mL, 10 mmol) in THF (40 mL) over a period of 30 min at −20 °C under dry nitrogen. Diphenylacetylene (0.44 g, 2.5 mmol) was added and slowly allowed to reach room temperature. Stirring was furthur continued for 10 h at room temperature. The metal carbonyl complexes were oxidized using $CuCl_2 \cdot 2H_2O$ (4.2 g, 25 mmol) in acetone (15 mL). After usual wokup the residue was subjected to column chromatography (silica gel, hexane−EtOAc). Ethyl acetate (1%) in hexane eluted the cyclic anhydride **4a**.

4a. Yield: 0.31 g (72%). The sample was crystallized from hexane−ethyl acetate (95:5). Mp: 119−120 °C (lit.[9a] mp 120−121 °C). IR (neat): 3117, 1839, 1765 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.3−7.9 (m, 5H); 7.0 (s, 1H). ^{13}C NMR (50 MHz): δ 164.5, 163.6, 146.6, 146.5, 133.7, 129.3, 129, 126.4. MS (EI): *m/z* 174 [M$^+$, 10%].

4b. Yield: 0.29 g (68%). IR (neat): 3111, 1842, 1772 cm^{-1}. ^{1}H NMR (200 MHz): δ 6.5 (s, 1H); 2.5 (t, J = 7.1 Hz, 2H); 0.8−1.9 (m, 9H). ^{13}C NMR (50 MHz): δ 165.8, 164.0, 153.8, 128.4, 31.1, 26.5, 25.8, 22.1, 13.7. MS (EI): *m/z* 168 [M$^+$, 12%]. Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.25; H, 7.20.

4c. Yield: 0.5 g (80%). The sample was crystallized from hexane−ethyl acetate (95:5). Mp: 156−158 °C (lit.[9b] mp 156 °C). IR (neat): 1822, 1757, 1637 cm^{-1}. ^{1}H NMR (200 MHz): δ 8.1−7.2 (m, 10H). ^{13}C NMR (50 MHz): δ 164.8, 138.2, 131.1, 129.7, 128.9, 127.2.

4d. Yield: 0.37 g (60%). IR (neat): 1840, 1769 cm^{-1}. ^{1}H NMR (200 MHz): δ 5.8 (m, 1H); 5.2 (dd, J = 7.5, 1.5 Hz, 2H); 3.1 (d, J = 6.3 Hz, 2H); 2.4 (t, J = 7.0 Hz, 2H); 1.4 (m, 2H); 1.1 (m, 10H); 0.7 (t, J = 6.2 Hz, 3H). ^{13}C NMR (50 MHz): δ 165.6, 165.4, 145.2, 141.3, 131.1, 118.2, 31.6, 29.4, 29.1, 28.9, 28.2, 27.6, 24.2, 22.5, 13.8. MS (EI): *m/z* 250 [M$^+$, 8%].

4e. Yield: 0.46 g (75%). The sample was crystallized from hexane−ethyl acetate (95:5). Mp: 99−101 °C IR (neat): 1832, 1770 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.59−7.45 (m, 5H); 0.25 (s, 9H). ^{13}C NMR (100 MHz): δ 168.3, 166.6, 156.8, 145.4, 132,

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130.5, 129.8, 129.3, −0.1. MS (EI): *m/z* 246 [M$^+$, 10%]. Anal. Calcd for $C_{13}H_{14}O_3Si$: C, 63.39; H, 5.73; Si 11.4. Found: C, 63.43; H 5.79.

Preparation of Acyloxyferrole Complex 5. To a solution of anhydrous Me_3NO (0.9 g, 12 mmol) in THF (30 mL) was dropwise added $Fe(CO)_5$ (1.9 mL, 15 mmol) in THF (40 mL) over a period of 30 min at −20 °C under dry nitrogen. Diphenylacetylene (0.44 g, 2.5 mmol) was added and stirred for 2 h at room temperature. Then Et_3N (1.4 mL, 10 mmol) and CH_3COCl (1 mL, 15 mmol) were added, and the contents were further stirred for 12 h. Ether (100 mL) was added, and the reaction mixture was washed successively with H_2O (40 mL) and brine (2 × 50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane−EtOAc). Ethyl acetate (1%) in hexane eluted the ferroyl complex **5** (yield 0.72 g, 48%). This complex is relatively stable, but standing for long periods or exposure to air leads to decomposition. It was crystallized from methanol. Mp: 152−155 °C (dec) (lit.[10] mp 152−155 °C (dec)). IR (KBr): 2083, 2042, 2005, 1956, 1749 cm^{-1}. ^{1}H NMR (200 MHz): δ 1.9 (s, 6H); 7.18−7.25 (m, 10H). ^{13}C NMR (50 MHz): δ 211.8, 207.7, 205.3, 185.5, 168.4, 130.7, 130.5, 128.5, 127.9, 125.6, 20.6.

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Supporting Information Available: ^{13}C NMR spectra of compounds **3a**−**3h**, **4a**−**4e**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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