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Reaction of the RMgX/Fe(CO)$_5$/CuCl System with Alkynes: Novel Double Carbonylation Leading to Butenolides and Cyclobutenedione

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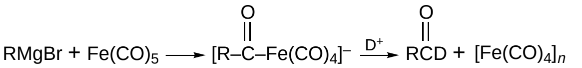
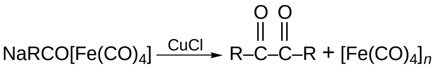
Summary: Reaction of RMgX with Fe(CO)$_5$ and CuCl leads to the formation of 1,2-diketones in moderate yields. The reagent system gives the corresponding butenolides and cyclobutenedione in the presence of alkynes.

The organomagnesium compounds readily add to metal carbonyls to give rather stable anionic metal complexes.[1,2] For example, the reaction of RMgX with Fe(CO)$_5$ leads to the corresponding acylferrate species.[3] Earlier investigations of this chemistry focused on the preparation of aldehydes and ketones (eq 1).[3,4]



$$\mathrm{RMgBr + Fe(CO)_5 \longrightarrow [R{-}\overset{O}{\overset{\|}{C}}{-}Fe(CO)_4]^- \xrightarrow{D^+} R\overset{O}{\overset{\|}{C}}D + [Fe(CO)_4]_{\mathit{n}}} \tag{1}$$

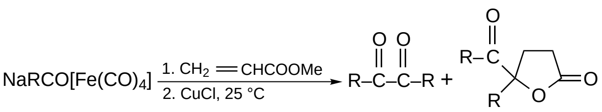
Previously, we have observed a novel double-carbonylation reaction in the reaction of Na(RCO)Fe(CO)$_4$ with CuCl (eq 2).[5]



$$\mathrm{NaRCO[Fe(CO)_4] \xrightarrow{CuCl} R{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R + [Fe(CO)_4]_{\mathit{n}}} \tag{2}$$

We describe here further results on the utilization of the reactive species generated using RMgX/Fe(CO)$_5$/CuCl in THF. This reagent system leads to the formation of the corresponding 1,2-diketones as expected (Scheme 1). The yields are somewhat lower than those realized using the NaRCOFe(CO)$_4$ and CuCl reagent system.[5] However, the aryl bromides can be also used as substrates here (Scheme 1).

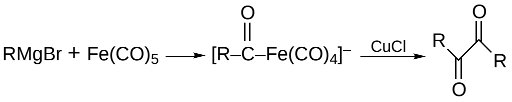
Previously, we have observed that the reaction of the NaRCO[Fe(CO)$_4$]−CuCl system with methyl acrylate results in the formation of novel acyl lactones besides 1,2-diketones (eq 3).[6]



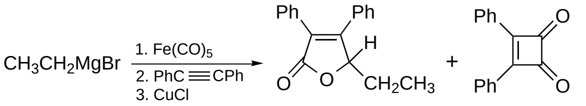
(3)

We have undertaken efforts to examine the use of other substrates to trap the "RCO" moiety obtained using the RMgX/Fe(CO)$_5$/CuCl reagent system (Scheme 1). Indeed, we have observed an interesting transformation involving carbonylative acylation−cyclization in the reaction of RCOFe(CO)$_4^-$ (generated *in situ* using RMgBr (10 mmol; R = ethyl bromide) and Fe(CO)$_5$ (10 mmol)) with CuCl (20 mmol) in the presence of diphenylacetylene (5 mmol) and CH$_3$CN (5 mL). The corresponding butenolide **2a** (26%) and cyclobutenedione **2b** (13%) formed after CuCl$_2$·2H$_2$O oxidation (eq 4). Some other alkyl halides also give butenolides under these conditions (Table 1).

Scheme 1



1a: R = *n*-Butyl (45%)
1b: R = *n*-Octyl (48%)
1c: R = *n*-Hexyl (48%)
1d: R = Ph (50%)



2a **2b** (4)

Interestingly, the reaction of phenylacetylene leads to the formation of only one regioisomer, **5a**, albeit in low yield (entry 4, Table 1). Further, we have observed that the reaction of RLi (R = *n*-butyl), Fe(CO)$_5$, and diphenylacetylene in the presence of CuCl gave butenolide **3a** (15%) and cyclobutenedione **2b** (5%).

The cyclobutenedione formation is reminiscent of the transformation previously observed in the reaction of the [HFe(CO)$_4$]$^-$/CH$_3$I reagent combination with alkynes,[7] which has been reported to give CH$_4$ and a "Fe(CO)$_4$" complex under certain conditions.[8] The results indicate that similar coordinatively unsaturated iron carbonyl complexes formed in the present case.

A probable pathway for the butenolide formation may involve the acylation of alkyne through the intermediacy of a (π-vinyl)iron complex (Scheme 2). It has been reported that certain cobalt carbonyl species give similar reactions with alkynes.[9] Control experiments indicated that CuCl is necessary for this transformation. This implies that the intermediate formed in the reaction of RCOFe(CO)$_4^-$ with CuCl may help in the acylation of

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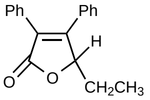
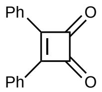
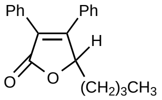
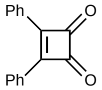
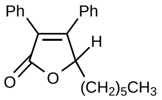
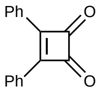
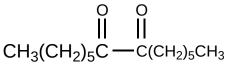
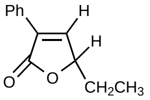
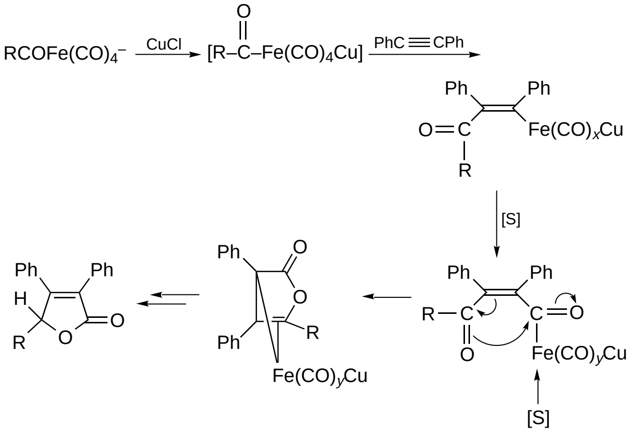
Table 1. Reaction of $RCOFe(CO)_4^-$/Alkynes with CuCl[a]

entry no.	RBr	alkyne	product[b]	yield (%)[c]
1	CH_3CH_2Br	$PhC\equiv CPh$	 **2a**	26
			 **2b**	13
2	$CH_3(CH_2)_3Br$	$PhC\equiv CPh$	 **3a**	32
			 **2b**	10
3	$CH_3(CH_2)_5Br$	$PhC\equiv CPh$	 **4a**	35
			 **2b**	10
			 $CH_3(CH_2)_5C(=O)-C(=O)(CH_2)_5CH_3$ **1c**	18
4	CH_3CH_2Br	$PhC\equiv CH$	 **5a**	32

[a] All reactions were carried out using RBr (10 mmol), Mg (10 mmol), $Fe(CO)_5$ (10 mmol), alkyne (5 mmol), and CuCl (20 mmol). [b] Products were identified by analysis of spectral data (IR, ^1H NMR, ^{13}C NMR, and mass). The butenolides were identified by the analysis of spectral data. The butenolide **2a** was identified by the analysis of spectral data and comparison with the reported data.[12b] The cyclobutenedione **2b** was identified by the analysis of spectral data and comparison with the reported data.[18] The regioselectivity of the butenolide **5a** was confirmed by comparison of the spectral data with the data reported for the corresponding methyl derivative.[13] [c] Yields are of products isolated by column chromatography and are based on the amounts of alkynes used.

alkynes (Scheme 2).[10] A previous report describes that $Na_2Fe(CO)_4$ reacts with CuCl to give the metal cluster $Na_3[Cu_3Fe_3(CO)_{12}]$ containing Fe−Cu bonds.[11] Presumably, CuCl may react with $RCOFe(CO)_4^-$ to give similar types of intermediates. However, this type of acyl insertion into alkynes assisted by CuCl does not have precedent and we do not have evidence for the intermediates suggested. Hence, the mechanism proposed in Scheme 2 can be only tentative.

Scheme 2



In recent years, there have been several reports describing the migratory insertion of the "RCO" moiety present in $RCOM(CO)_n$ complexes into alkynes.[12] Among various transition metals, complexes of Mn,[13] Co,[9] and Pd[14] have been found to be useful. An earlier report describes that acyl migration from $RCOFe(CO)_4^-$ to ethylene gives $RCOC_2H_5$, but the reaction failed with higher alkenes.[15] Hence, the present transformation involving acyl moiety insertion into alkynes illustrates the further utility of the readily accessible $RCOFe(CO)_4^-$ species. The transformation leading to butenolide (Scheme 2) is interesting, since four fragments are put together in a single-pot operation.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry nitrogen. Tetrahydrofuran was freshly distilled over sodium−benzophenone. $Fe(CO)_5$ supplied by Fluka Switzerland was utilized. CuCl (Fluka) was further purified by washing successively with distilled H_2O containing SO_2, dry ether, and ethanol and dried under vacuum at 100 °C for 2−3 h. Alkyl bromides supplied by Fluka Switzerland were used. The alkynes used in the reactions were prepared by following a reported procedure.[16]

All melting points reported here are uncorrected and were determined using a Buchi 510 capillary point apparatus. Infrared spectra were recorded on a Perkin-Elmer IR Model spectrometer 1310 and a JASCO-FT Model 5300 instrument with polystyrene as reference. ^1H NMR and ^{13}C NMR spectra of samples in $CDCl_3$ were recorded on JEOL FX-100 and Bruker AC-200 spectrometers. Column chromatography was carried out using Acme silica gel (100−200 mesh).

Reaction of RMgBr with $Fe(CO)_5$ in the Presence of CuCl: 1,2-Diketone Synthesis. Magnesium mesh (0.23 g, 10 mmol) was taken up in THF (50 mL) under an N_2 atmosphere, and *n*-butyl bromide (1.37 g, 10 mmol) was added at 25 °C. The contents were stirred for 1 h at 25 °C, and $Fe(CO)_5$ (2.16 g, 10 mmol) was added. The reaction mixture was stirred for 1 h, CuCl (2.0 g, 20 mmol) was added, and the mixture was stirred further for 10 h at 25 °C. The resultant mixture was poured into acetone (40 mL) containing $CuCl_2\cdot 2H_2O$ (6.8 g, 40 mmol) to decompose the iron carbonyl species. Saturated aqueous NaCl was added, and the organic phase was separated. The aqueous layer was extracted with ether (2 × 40 mL). The combined organic extracts were

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(10) A reviewer suggested that CuCl may act as a CO scrubber and hence may facilitate the reaction. This is another possibility. However, the formation of 1,2-diketones in the absence of alkynes indicates that of CuCl may play more of a role than this.[6]

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washed with H_2O (20 mL) and brine (30 mL), dried over anhydrous $MgSO_4$, and concentrated. The residue was subjected to column chromatography. Ethyl acetate (1%) in hexane eluted the α-diketone **1a** (45%, 0.385 g). IR (neat): 1707 cm^{-1}. ^{1}H NMR: δ (ppm) 0.80 (t, $J = 6.9$ Hz, 6H), 1.08−1.60 (m, 8H), 2.62 (t, $J = 7.0$ Hz, 4H); ^{13}C NMR: δ (ppm) 13.4, 22.0, 24.9, 35.4, 199.8.

The above procedure was followed for the conversion of other bromides to the corresponding α-diketones. The spectral data are reported below.

1b: yield 48% (0.88 g). IR (neat): 1710 cm^{-1}. ^{1}H NMR: δ (ppm) 0.82 (t, $J = 7.0$ Hz, 6H), 1.08−1.68 (m, 24H), 2.66 (t, $J = 7.2$ Hz, 4H). ^{13}C NMR: δ (ppm) 13.9, 22.6, 23.1, 29.1, 29.3, 31.8, 36.0, 200.3.

1c: yield 48% (0.575 g). IR (neat): 1705 cm^{-1}. ^{1}H NMR: δ (ppm) 0.80 (t, $J = 7.0$ Hz, 6H), 1.06−1.60 (m, 16H), 2.60 (t, $J = 7.2$ Hz, 4H). ^{13}C NMR: δ (ppm) 13.8, 22.4, 28.8, 31.5, 35.9, 199.7. MS (EI): m/z 226 (M$^+$, 2%), 113 (RCO$^+$, 100%).

1d: yield 50% (0.525 g). Mp: 93 °C (lit[16] mp 93−95 °C). IR (neat): 1661 cm^{-1}. ^{13}C NMR: δ (ppm) 129.0, 129.9, 133.0, 134.9, 194.4.

The spectral data for 1,2-diketones **1a**−**c** were identical with those for the samples previously obtained using $NaRCOFe(CO)_4/CuCl$ in this laboratory.[5] The spectral data for 1,2-diketone **1d** showed a 1:1 correspondence with the reported data.[16]

Reaction of $(RCO)Fe(CO)_4^-$ with Diphenylacetylene in the Presence of CuCl: Formation of Butenolides and Cyclobutenedione 2b. Magnesium mesh (0.23 g, 10 mmol) was placed in THF (50 mL) with ethyl bromide (1.08 g, 10 mmol) at 25 °C under a nitrogen atmosphere. The contents were stirred for 1 h, and $Fe(CO)_5$ (2.16 g, 10 mmol) was added. The reaction mixture was stirred for 1 h at 25 °C. Subsequently, diphenylacetylene (0.89 g, 5 mmol), CuCl (2.0 g, 20 mmol), and CH_3CN (5 mL) were added, and the mixture was stirred for a further 10 h at 25 °C. The contents were poured into acetone (40 mL) containing $CuCl_2 \cdot 2H_2O$ (6.8 g, 40 mmol) to decompose the iron carbonyl species. Saturated aqueous NaCl was added, and the organic phase was separated. The aqueous layer was extracted with ether (2 × 40 mL). The combined organic extracts were washed successively with H_2O (20 mL) and brine (30 mL), dried over anhydrous $MgSO_4$, and concentrated. The residue was subjected to column chromatography. Ethyl acetate (1%) in hexane eluted cyclobutenedione **2b** (0.23 g, 13%), and ethyl acetate (3%) in hexane eluted butenolide **2a** (0.35 g, 26%).

2a: mp 132.5 °C (lit.[17] mp 133−134 °C), IR (neat): 1753 cm^{-1}. ^{1}H NMR: δ (ppm) 0.89 (t, $J = 7.4$ Hz, 3H), 1.41−2.21 (m, 2H), 5.45 (dd, $J = 6.8, 6.8$ Hz, 1H), 7.21−7.45 (m, 10H). ^{13}C NMR: δ (ppm) 8.2, 25.7, 82.4, 128.1, 128.6, 129.0, 129.3, 130.0, 131.3, 160.2, 172.6. MS (EI): m/z 264 (M$^+$, 13%), 179 [$(Ph_2C_2 + 1)^+$, 100%].

2b: yield 13% (0.23 g). Mp: 95−96 °C (lit.[18] mp 97 °C). IR (neat): 1780 cm^{-1} . ^{1}H NMR: δ (ppm) 7.45−7.68 (m, 6H), 8.14 (m, 4H). ^{13}C NMR: δ (ppm) 128.7, 129.7, 131.2, 134.6, 187.4, 196.1. MS (EI): m/z 235 [(M$^+$ + 1), 12%], 179 [$(Ph_2C_2^+ + 1)$, 100%].

The physical constant and spectral data of **2a** showed a 1:1 correspondence with the reported data.[12b] The cyclobutenedione **2b** was identified by comparison of the spectral data with the reported data.[17] The above procedure was followed for the conversion of several other alkyl bromides into the corresponding butenolides. The results are summarized below.

3a: yield 32% (0.46 g). IR (neat): 1753 cm^{-1}. ^{1}H NMR: δ (ppm) 0.88 (t, $J = 7.3$ Hz, 3H), 1.29−1.53 (m, 6H), 5.46 (m, 1H), 7.24−7.40 (m, 10H). ^{13}C NMR: δ (ppm) 13.7, 22.3, 26.5, 32.6, 81.7, 128.1, 128.4, 128.9, 129.3, 130.0, 131.4, 160.6, 172.5. MS (EI): m/z 292 (M$^+$, 12%), 178 [$(Ph_2C_2)^+$, 100%].

2b: yield 10% (0.23 g).

4a: yield 35% (0.28 g). IR (neat): 1753 cm^{-1}. ^{1}H NMR: δ (ppm) 0.85 (t, $J = 7.3$ Hz, 3H), 1.23−1.97 (m, 10H), 5.48 (m, 1H), 7.22−7.38 (m, 10H). ^{13}C NMR: δ (ppm) 13.9, 22.4, 24.3, 28.8, 31.5, 32.9, 81.7, 126.7, 128.0, 128.5, 128.9, 129.9, 131.5, 160.5, 172.4. MS (EI): m/z 320 [$(M + 1)^+$, 20%], 235 [$(M - R)^+$, 28%], 179 [$(Ph_2C_2 + 1)^+$, 100%].

1c: yield 18% (0.395 g).

The spectral data for cyclobutenedione **2b** and 1,2-diketone **1c** were identical with the data for the samples obtained in earlier experiments.

5a: yield 32% (0.15 g). IR (neat): 1755 cm^{-1}. ^{1}H NMR: δ (ppm) 1.06 (t, $J = 6.8$ Hz, 3H), 1.78−2.11 (m, 2H), 5.0 (dt, $J = 1.5, 6.8$ Hz, 1H), 7.40 (m, 3H), 7.54 (d, $J = 1.5$ Hz, 1H), 7.87 (m, 2H). ^{13}C NMR: δ (ppm) 9.1, 26.7, 81.5, 127.1, 128.6, 129.6, 131.6, 132.6, 147.9, 171.8. MS (EI): m/z 188 (M$^+$, 45%), 159 [$(M^+ - C_2H_5)$, 20%], 103 [$(PhC_2H^+ + 1)$, 100%].

The spectral data for **5a** are comparable to the data reported for the corresponding methyl derivative.[13]

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