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Reaction of $Na(RCO)Fe(CO)_4$ with CuCl or I_2: Synthetic and Mechanistic Studies of the Formation of 1,2-Diketones in a Novel Double-Carbonylation Process

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Reaction of $Na(RCO)Fe(CO)_4$ with CuCl at 25 °C in THF leads to the formation of 1,2-diketones, RCOCOR (70–90% yield). The reaction was carried out in the presence of methyl acrylate in order to get information about possible intermediates. In these runs, the 1,2-diketones (20–28%) and acyllactones (35–52%), derived from two alkyl and two CO groups and one acrylate moiety, are formed. The reaction of I_2 with $Na(RCO)Fe(CO)_4$ was investigated in order to compare the reactivities with the $Na(RCO)Fe(CO)_4$/CuCl system. In this case, the reaction is not clear and the 1,2-diketone (32%), dialkyl ketone (8%), and RCOOH (29%) (R = *n*-octyl) are obtained. When the reaction of $Na(RCO)Fe(CO)_4$ was carried out with I_2 in the presence of methyl acrylate, the acyllactones (19–21%), 1,2-diketones (16–18%), dialkyl ketones (4–5%), and RCOOH (6–7%) are isolated. It is proposed that the formation of 1,2-diketone takes place through the decomposition of $Cu(RCO)Fe(CO)_4$ or $I(RCO)Fe(CO)_4$ to $RCOFe(CO)_4$ followed by the formation of η^2 complexes of 1,2-diketones as fleeting intermediates.

Introduction

Nucleophilic metal acyl derivatives $(RCO)^-M^+$ have been sought for a long time by synthetic organic chemists. Though acyl and aryl derivatives of silicon[1] and transition metals[2] are known, these are not potent nucleophiles. Attempts to prepare acyl derivatives of Li, Mg, Zn, and Al, metals whose alkyl and aryl complexes are potent nucleophilic reagents, have met with little success. Organic chemists developed an alternate synthetic methodology involving masked acyl anion synthons or equivalents.[3] In recent years, Seyferth and co-workers developed acyllithium reagents through carbonylation of RLi species (-110 to -135 °C) for nucleophilic acylations.[4] More recently, an acylcuprate reagent, $[(RC{=}O)(R)(CN)CuLi_2]$, prepared at -78 to -110 °C, has been used in the acylation of α,β-unsaturated compounds.[5]

The development of methods for the preparation of active metal acyls or equivalents under mild conditions would be synthetically useful, and we wish to report here our studies directed toward the preparation of "R(C=O)M" reagents using the Collman reagent $Na(RCO)Fe(CO)_4$.

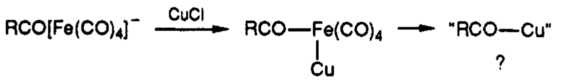
Results and Discussion

We have recently developed convenient methods for the generation of $Na_2Fe(CO)_4$ by the reduction of $FeCl_3$ or $Fe(CO)_5$ using the Na/naphthalene system.[6] It is known that $Na(RCO)Fe(CO)_4$ readily reacts with electrophiles.[7]

$$RCO[Fe(CO)_4]^- \xrightarrow{H^+} RCHO \qquad (1)$$

$$RCO[Fe(CO)_4]^- \xrightarrow{C_2H_5I} RCOC_2H_5 \qquad (2)$$

It has been reported that $[Fe(CO)_4]^{2-}$ reacts with CuCl or CuBr to give the metal clusters $Na_3[Cu_3Fe_3(CO)_{12}]$, which contain Fe–Cu bonds.[8] It was thought that a similar formation would take place in the reaction of $RCO[Fe(CO)_4]^-$ with CuCl. It was of interest to examine the possible in situ generation of "RCOCu" species from such species (eq 3).



$$RCO[Fe(CO)_4]^- \xrightarrow{CuCl} RCO{-}\underset{\displaystyle Cu}{\underset{|}{Fe(CO)_4}} \longrightarrow \underset{?}{\text{"}RCO{-}Cu\text{"}} \qquad (3)$$

We have observed that, when 2 equiv of CuCl was added to $RCO[Fe(CO)_4]^-$ (R = *n*-hexyl) in THF and this mixture was stirred for 1.5 h, $CH_3(CH_2)_5COCO(CH_2)_5CH_3$ was isolated in 78% yield (eq 4).

$$Na_2Fe(CO)_4 \xrightarrow[\text{CO, 30 min}]{CH_3(CH_2)_5Br} RCO[Fe(CO)_4]^- \xrightarrow[\text{1.5 h}]{2CuCl} CH_3(CH_2)_5COCO(CH_2)_5CH_3 \qquad (4)$$

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It was found that the transformation is a general one and several other alkyl bromides are converted into the corresponding 1,2-diketones.[9] The results are summarized in Scheme I.

Scheme I

$$[Fe(CO)_4]^{2-} \xrightarrow[(2)\,CO]{(1)\,RBr} RCO[Fe(CO)_4]^- \xrightarrow[25\,°C,\,1\,h]{CuCl} \underset{\mathbf{1a\text{–}h}}{RCOCOR}$$

(1) $R = CH_2(CH_2)_4CH_3$; **1a**, 78%

(2) $R = CH_2(CH_2)_8CH_3$; **1b**, 80%

(3) $R = CH_2(CH_2)_6CH_3$; **1c**, 85%

(4) $R = CH_2(CH_2)_3CH_3$; **1d**, 79%

(5) $R = CH_2(CH_2)_2CH_3$; **1e**, 90%

(6) $R = CH_2(CH_2)_3CH{=}CH_2$; **1f**, 74%

(7) $R = CH_2(CH_2)_2COOCH_3$; **1g**, 70%

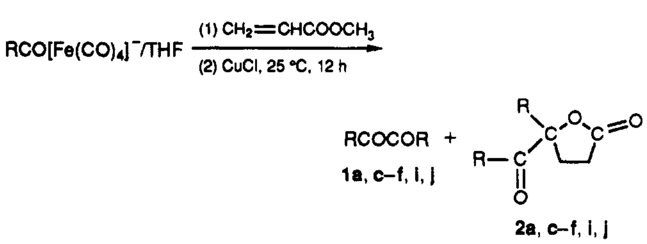
(8) $R = CH_2(CH_2)_3COOCH_3$; **1h**, 73%

The $RCO[Fe(CO)_4]^-$ species containing certain olefinic moieties is known to undergo cyclization to give cyclic ketones.[10] When 5-bromopentene was utilized in the above experiment, cyclohexanone was isolated in 30% yield and the corresponding 1,2-diketone was not formed. However, when 6-bromohexene was utilized, the corresponding 1,2-diketone (**1f**) was isolated in 74% yield (entry 6, Scheme I). The sensitive ester group is tolerated under the present reaction conditions as indicated by entries 7 and 8 (Scheme I).

It is not clear whether this transformation (Scheme I) goes through an "RCOCu" intermediate. However, if such intermediates are formed, then the formation of RCOCOR from the thermal decomposition of such intermediates is not entirely unexpected. It is unlikely that the formation of RCOCOR would take place through $R\dot{C}O$ free radicals, since such derivatives readily undergo decarbonylation.[11]

It was thought that the intermediate would be characteristic of "RCOM" species and hence expected to undergo 1,4-addition with α,β-unsaturated compounds. In order to examine this possibility, we carried out a series of experiments using α,β-unsaturated derivatives in the reaction of $RCO[Fe(CO)_4]^-$ with CuCl. Adding methyl vinyl ketone before adding CuCl to $RCO[Fe(CO)_4]^-$ in THF followed by stirring the reaction mixture for 12 h at 25 °C gave a complex mixture of products. Use of acrylonitrile in place of the methyl vinyl ketone gave a cleaner reaction, but the product was found to be oligomeric. Methyl crotonate did not react under these conditions. The reaction was relatively clean when CuCl (20 mmol) was added to a mixture of $RCO[Fe(CO)_4]^-$ (10 mmol) and methyl acrylate (35 mmol) at 25 °C, and the mixture was further stirred for 12 h at 25 °C. After workup and column chromatography yellow 1,2-diketones and colorless acyllactones were isolated (Scheme II).

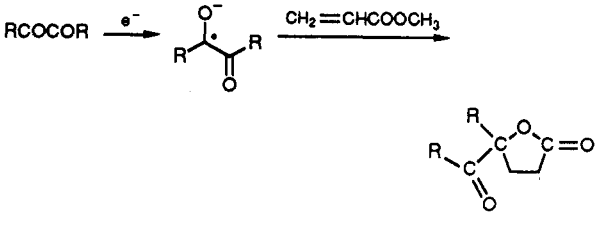
Scheme II



(1) $R = CH_2(CH_2)_4CH_3$; **1a**, 20%; **2a**, 52%
(2) $R = CH_2(CH_2)_6CH_3$; **1c**, 20%; **2c**, 50%
(3) $R = CH_2(CH_2)_3CH_3$; **1d**, 28%; **2d**, 45%
(4) $R = CH_2(CH_2)_2CH_3$; **1e**, 22%; **2e**, 49%
(5) $R = CH_2(CH_2)_3CH{=}CH_2$; **1f**, 21%; **2f**, 50%
(6) $R = CH_2(CH_2)_{14}CH_3$; **1i**, 25%; **2i**, 35%
(7) $R = CH_2CH_2CH_3$; **1j**, 23%; **2j**, 44%

The formation of acyllactone from alkyl bromide (Scheme II) is interesting, since five fragments are put together in a single-pot transformation. However, it does not answer the question about the formation of 1,2-diketone from alkyl bromide. Since a product of the type $RCOCH_2CH_2COOCH_3$ is not formed, it is unlikely that the formation of 1,2-diketone goes through an "RCOCu" intermediate.

We have performed several experiments in order to examine whether the acyllactone is formed after the 1,2-diketone. When methyl acrylate was included 1.5 h after the addition of CuCl to $RCO[Fe(CO)_4]^-$ [R = *n*-hexyl] and the mixture stirred for 15 h, the only product isolated was the 1,2-diketone in 75% yield. Also, the acyllactone was not formed when CuCl, 1,2-diketone, and methyl acrylate were stirred under these reaction conditions. It is clear that methyl acrylate does not react with the 1,2-diketone after it is formed. It has been reported that the reduction of ketone using SmI_2 in the presence of methyl acrylate gives the corresponding lactone.[12] Accordingly, it is possible that single-electron reduction of the 1,2-diketone followed by the reaction of anion radical with methyl acrylate could result in the formation of acyllactone (eq 5).



(5)

In order to examine whether the acyllactone could have been derived from the reaction of some unused sodium naphthalenide, we carried out an experiment using 1,2-diketone, sodium naphthalenide, and methyl acrylate. However, in this case only a complex mixture of polymeric products were obtained and the acyllactone was not present in the mixture.

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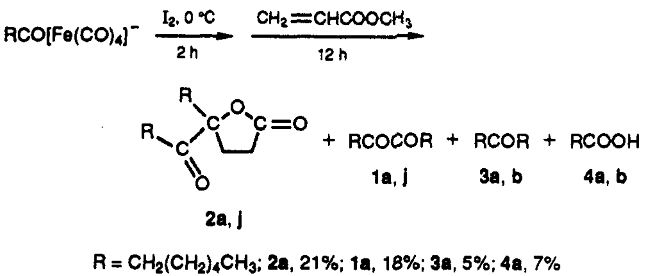
Scheme III



R = $CH_2(CH_2)_4CH_3$; **2a**, 21%; **1a**, 18%; **3a**, 5%; **4a**, 7%
R = $CH_2CH_2CH_3$; **2j**, 19%; **1j**, 16%; **3b**, 4%; **4b**, 6%

Reaction of Br_2 with $ArCO(Ni(CO)_3)^-$ has been reported to give 1,2-diketone and diaryl ketone.[13] Similar products could be expected for the reaction of $RCO[Fe(CO)_4]^-$ with I_2, and hence, this reaction would throw some light on the formation of 1,2-diketones.

It is known that $RCO[Fe(CO)_4]^-$ on treatment with I_2 in the presence of nucleophiles undergoes various useful transformations.[7] The "RCOI" species has been proposed as an intermediate in these cases. However, the reactivity of $RCO[Fe(CO)_4]^-$ with I_2 has not been studied in the absence of nucleophiles. We thought that it would be useful to examine the reactivities of the $RCO[Fe(CO)_4]^-/I_2$ system, in order to compare with the results obtained in the $RCO[Fe(CO)_4]^-/CuCl$ system. It was observed that the reaction of I_2 with $RCO[Fe(CO)_4]^-$ (R = *n*-octyl) in THF at 0 °C for 2 h and further stirring for 12 h at 25 °C gives nonanoic acid (29%), the corresponding 1,2-diketone (32%), and dialkyl ketone (8%), along with small amounts of other unidentified products.

The reaction of I_2 with $RCO[Fe(CO)_4]^-$ is not clean compared to the reaction of CuCl with $RCO[Fe(CO)_4]^-$. However, the 1,2-diketones are also formed in the reaction of $RCO[Fe(CO)_4]^-$ with I_2. Although the formation of 1,2-diketone in the $RCO[Fe(CO)_4]^-/I_2$ and $RCO[Fe(CO)_4]^-/CuCl$ systems need not go through a common intermediate, we carried out an experiment by adding methyl acrylate after the addition of I_2 in THF. After workup and column chromatography acyllactone **2j** (19%), butanoic acid (6%), 1,2-diketone (16%), and the dialkyl ketone (4%) were isolated. When 1-bromohexane was used in the above experiment, the corresponding acyllactone (21%), heptanoic acid (7%), 1,2-diketone (18%), and dialkyl ketone (5%) were isolated (Scheme III).

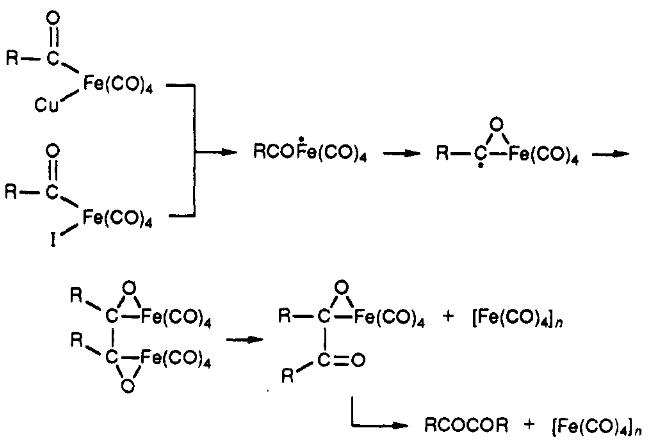
The formation of acyllactone in the reaction of $RCO[Fe(CO)_4]^-/I_2$ with methyl acrylate rules out the possibility of this product being produced through single-electron reduction of 1,2-diketone by some unused sodium naphthalenide, since it is unlikely to survive in the presence of I_2.

It seems likely that both $I(RCO)Fe(CO)_4$ and $Cu(RCO)Fe(CO)_4$ could give $RCO\dot{F}e(CO)_4$ through homolysis, which may be responsible for the formation of 1,2-diketone and acyllactone (Scheme IV).

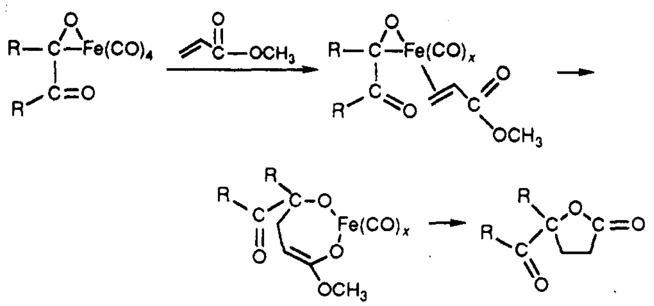
Another possibility is that $RCO\dot{F}e(CO)_4$ may be formed through one-electron oxidation of $RCO[Fe(CO)_4]^-$. Whereas this intermediate is unlikely to be affected any more by CuCl, it may undergo further oxidation with I_2, leading to other products.

Aldehydes and ketones are known to form η^1 and η^2 complexes[14,15] with metal carbonyl species, and the complex $L(CO)Fe(OCH_2)$[16] is known. Hence, formation of these species as fleeting intermediates as suggested in Scheme IV is not entirely unlikely. Reactions of such intermediates with methyl acrylate (free or precoordinated) could explain the formation of acyllactone (Scheme V).

Scheme IV



Scheme V



The olefin insertion, as outlined in Scheme V, into an η^2-bound ketone is not known with late-transition-metal complexes, although such C–C bond formation reactions have been reported for η^2-ketone complexes of zirconium.[17] The reaction sequences shown in Scheme V imply that a 1,2-diketone should react with $Fe(CO)_4$ and methyl acrylate to give acyllactone.[18] In order to examine this, we carried out photolysis of a mixture of $Fe(CO)_5$, RCOCOR (R = octyl), and methyl acrylate using a 450-W medium-pressure mercury lamp for 4.5 h at 25 °C. After workup the corresponding acyllactone was isolated in 28% yield, along with the 1,2-diketone and an unidentified metal carbonyl complex containing the octyl moiety. The acyllactone was not formed when the photolysis was carried out in the absence of $Fe(CO)_5$. Although the yield of acyllactone is poor, the result illustrates the ability of the coordinatively unsaturated iron carbonyl species to react with 1,2-diketone and methyl acrylate to give acyllactone.

However, the formation of polymeric products in the reaction of $RCO[Fe(CO)_4]^-/CuCl$ in the presence of methyl vinyl ketone and acrylonitrile is still not understood. The intermediacy of radicals other than those given in Scheme

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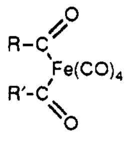
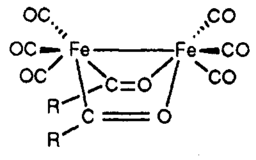
[18] We thank the reviewers, as their comments led us to think along these lines.

V cannot be ruled out. Also, the intermediacy of bis(acyl) complexes of types I and II cannot be ruled out. The



I



II

intermediate II on thermal decomposition at 55 °C gives 63% dialkyl ketones (RCOR), 11% RCOCOR, and 15% RR (R = n-C_9H_{19}).[19] The reaction of CuCl with RCO[$Fe(CO)_4]^-$ was relatively clean, and the dialkyl ketone was not formed. Although the mechanistic picture is not very clear, the double-carbonylation reactions leading to the formation of 1,2-diketones and the corresponding acyllactones should be synthetically useful.

Experimental Section

All reactions were carried out under an atmosphere of predried nitrogen. All transfers and manipulations of compounds were carried out under a nitrogen atmosphere. Tetrahydrofuran was freshly distilled over benzophenone–sodium. $Fe(CO)_5$ supplied by Fluka Switzerland was utilized. CuCl (Fluka) was further purified on treatment with distilled H_2O containing SO_2, washed with dry ether and ethanol, and dried under vacuum at 100 °C for 2–3 h. Alkyl bromides supplied by Fluka Switzerland were used. $CH_3O_2C(CH_2)_3Br$ and $CH_3O_2C(CH_2)_4Br$ were prepared respectively from butyro- and valerolactones on treatment with HBr and further esterification of the 1-bromo acids.

All melting points reported are uncorrected and were determined using a Buchi-510 capillary point apparatus. Infrared spectra were recorded on a Perkin-Elmer IR spectrometer, Model 257, with polystyrene as reference. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer with chloroform-d as a solvent and TMS as reference (δ 0 ppm). Elemental analyses were performed on a Perkin-Elmer elemental analyzer, Model 240 C. Column chromatography was carried out using ACME silica gel (100–200 mesh).

Reaction of Na(RCO)Fe(CO)$_4$ with CuCl. To a suspension of $Na_2Fe(CO)_4$ prepared using $Fe(CO)_5$ (2.16 g, 11 mmol), Na (0.51 g, 22 mmol), and naphthalene (1.02 g, 8 mmol) in THF (40 mL) was added 1-bromohexane (1.65 g, 10 mmol), and CO was bubbled for 30 min at 25 °C. The CO atmosphere was replaced by dry N_2, CuCl (2 g, 20 mmol) was added, and the mixture was stirred for 1.5 h at 25 °C. The mixture was poured into H_2O (40 mL) containing ceric ammonium nitrate (CAN; 8.22 g, 15 mmol) to decompose the iron carbonyl. The organic phase was separated and the aqueous phase was saturated with NaCl and extracted with ether (2 × 30 mL). The combined organic extracts were washed with brine (30 mL), dried over anhydrous $MgSO_4$, and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene. 1,2-Diketone **1a** was isolated in 78% yield (0.88 g) using 2% ethyl acetate in hexane as an eluent. **1a**: mp 37–38 °C (lit.[20] mp 38–39 °C); IR (melt) ν_{max} 1705 cm^{-1}; ^1H NMR δ 0.80 (t, $-CH_3$, 6H), 1.06–1.60 (m, $-CH_2-$, 16H), 2.60 (t, $-H_2CCOCOCH_2-$, 4H); ^{13}C NMR δ 13.8 ($-CH_3$), 22.4, 23.0, 28.8, 31.5, 35.9, 199.7 ($-COCO-$): MS (EI) m/e 226 (M^+, 2%), 113 (RCO^+, 100%).

The above procedure was followed for the conversion of several other alkyl bromides into the corresponding 1,2-diketone, and the results are summarized below and also in Scheme I.

1b: yield 80% (1.35 g); mp 67 °C (lit.[21b] mp 67–68 °C); IR (KBr) ν_{max} 1710 cm^{-1}; ^1H NMR δ 0.80 (t, $-CH_3$, 6H), 1.04–1.60 (m, $-CH_2-$, 32H), 2.60 (t, $-CH_2COCOCH_2-$, 4H); ^{13}C NMR δ 13.8 ($-CH_3$), 22.6, 23.0, 29.1, 29.3, 29.4, 29.5, 31.8, 35.9, 199.9 ($-COCO-$); MS (CI) m/e, 338 (22%, M^+), 169 (RCO^+, 100%); MS (EI) m/e 169 (RCO^+, 100%).

1c: yield 85% (1.20 g); mp 49–51 °C (lit.[21b] mp 50–52 °C); IR (KBr) ν_{max} 1710 cm^{-1}; ^1H NMR δ 0.82 (t, $-CH_3$, 6H), 1.08–1.68 (m, $-CH_2-$, 24H), 2.66 (t, $-CH_2COCOCH_2-$, 4H); ^{13}C NMR δ 13.9 ($-CH_3$), 22.6, 23.1, 29.1, 29.3, 31.8, 36.0, 200.3 ($-COCO-$).

1d: yield 79% (0.78 g); bp 90 °C/3 mm (lit.[22] bp 90–92 °C/3 mm); IR (neat) ν_{max} 1705 cm^{-1}; ^1H NMR δ 0.82 (t, $-CH_3$, 6H), 1.04–1.64 (m, $-CH_2-$, 12H), 2.66 (t, $-CH_2COCOCH_2-$, 4H); ^{13}C NMR δ 13.7 ($-CH_3$), 22.3, 22.6, 31.2, 37.8, 199.5 ($-COCO-$).

1e: yield 90% (0.77 g); bp 60–61 °C/6 mm (lit.[21a] bp 90–91 °C/12 mm); IR (neat) ν_{max} 1705 cm^{-1}; ^1H NMR δ 0.80 (t, $-CH_3$, 6H), 1.08–1.60 (m, $-CH_2-$, 8H), 2.62 (t, $-CH_2COCOCH_2-$, 4H); ^{13}C NMR δ 13.4 ($-CH_3$), 22.0, 24.9, 35.4, 199.8 ($-COCO-$).

1f: yield 74% (0.82 g); IR (neat) ν_{max} 900, 980, 1640, 1705, 3050 cm^{-1}; ^1H NMR δ 1.24–1.64 (m, $-CH_2-$, 8H), 1.82–2.3 (m, $-CH_2-$, 4H), 2.60 (t, $-CH_2COCOCH_2-$, 4H), 4.72–5.04 (m, $=CH_2$, 4H), 5.60 (m, $-CH=$, 2H); ^{13}C NMR δ 22.1, 28.0, 33.1, 35.4, 114.5 ($-CH=CH_2$), 138.0 ($-CH=CH_2$), 199.5 ($-COCO-$); MS (EI) m/e 111 (2 RCO^+, 50%).

1g: yield 70% (0.90 g); mp 60 °C; IR (KBr) ν_{max} 1200, 1240, 1730 (broad) cm^{-1}; ^1H NMR δ 1.84 (m, $-CH_2-$, 4H), 2.28 (t, $-OCOCH_2-$, 4H), 2.68 (t, $-CH_2COCOCH_2-$, 4H), 3.60 (s, $-OCH_3$, 6H); ^{13}C NMR δ 18.0, 32.6, 34.8, 51.4 ($-OCH_3$), 173.5 ($-COOCH_3$), 198.6 ($-COCO-$); MS (EI) m/e 129 [$\{CH_3CO_2(CH_2)_3CO\}^+$, 100%]. Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.81; H, 6.98. Found: C, 55.44; H, 7.00.

1h: yield 73% (1.04 g); mp 68 °C; IR (KBr) ν_{max} 1200, 1240, 1730 (broad) cm^{-1}; ^1H NMR δ 1.52 (m, $-CH_2-$, 8H), 2.24 (t, $-OCOCH_2-$, 4H), 2.64 (t, $-CH_2COCOCH_2-$, 4H), 3.56 (s, $-OCH_3$, 6H); ^{13}C NMR δ 22.1, 23.9, 33.3, 35.1, 51.1 ($-OCH_3$), 173.4 ($-COOCH_3$), 199.0 ($-COCO-$); MS (CI) m/e 287 (M + 1, 62%); 143 (RCO^+, 100%); MS (EI) m/e 143 (RCO^+, 55%). Anal. Calcd for $C_{14}H_{22}O_6$: C, 58.74; H, 7.60. Found: C, 58.91; H, 7.61.

Reaction of Na(RCO)Fe(CO)$_4$ with Methyl Acrylate in the Presence of CuCl. To a suspension of $Na_2Fe(CO)_4$ prepared using $Fe(CO)_5$ (2.16 g, 11 mmol), Na (0.51 g, 22 mmol), and naphthalene (1.02 g, 8 mmol) in THF (40 mL) was added 1-bromohexane (1.65 g, 10 mmol), and CO was bubbled for 30 min at 25 °C. The CO atmosphere was replaced by a dry N_2 atmosphere, methyl acrylate (2.5 g, 30 mmol) was added, and the mixture was stirred for 5 min. CuCl (2 g, 20 mmol) was added over 30 min using a solid addition flask, and the mixture was further stirred for 13 h at 25 °C. The resulting mixture was poured into acetone (40 mL) containing $CuCl_2$ (5.38 g, 40 mmol) to decompose the iron carbonyl. Saturated aqueous NaCl (30 mL) was added, and the organic phase was separated. The aqueous layer was extracted with ether (2 × 40 mL). The combined organic extracts were washed with H_2O (20 mL) and brine (30 mL) and then dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Hexane eluted naphthalene. Ethyl acetate (2%) in hexane eluted 1,2-diketone **1a** (0.23 g, 20% yield), and ethyl acetate (10%) in hexane eluted acyllactone **2a** (0.73 g, 52% yield). **2a**: IR (neat) ν_{max} 920, 1140, 1720, 1790, 2950 cm^{-1}; ^1H NMR δ 0.80 (t, $-CH_3$, 6H), 1.14–1.92 (m, alkyl methylene protons, 16H), 2.04 (t, 2H), 2.32 (t, 2H), 2.42–2.62 (m, 4H); ^{13}C NMR δ 13.5, 22.0, 22.4, 22.8, 27.6, 28.2, 28.8, 29.4, 31.0, 31.1, 37.2, 37.9, 91.6, 175.5 ($-COO-$), 210.4 ($-CO-$).

The spectral data of the 1,2-diketones obtained were identical with the data of the samples previously obtained.

The above procedure was followed for the conversion of several other alkyl bromides into the corresponding acyllactone and 1,2-diketones. The results are summarized below and also in Scheme II.

2c: yield 50% (0.85 g); IR (neat) ν_{max} 920, 1140, 1720, 1790, 2950 cm^{-1}; ^1H NMR δ 0.80 (t, $-CH_3$, 6H), 1.02–1.90 (m, alkyl methylene protons, 24H), 2.02 (t, 2H), 2.30 (t, 2H), 2.42–2.60 (m,

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4H); ^{13}C NMR δ 13.6, 22.4, 22.8, 23.0, 27.9, 28.9, 29.0, 29.1, 29.4, 29.5, 31.5, 37.4, 38.0, 91.9, 175.5 (–*C*OO–), 210.6 (–*C*O–); MS (CI) *m/e* 336 [M$^+$, 65%], 197 [(M – RCO)$^+$, 100%]; MS (EI) *m/e* 197 [(M – RCO)$^+$, 100%].

2d: yield 45% (0.57 g); IR (neat) ν_{max} 920, 1140, 1720, 1790, 2950 cm^{-1}; ^{1}H NMR δ 0.80 (t, –CH$_3$, 6H), 1.04–1.92 (m, alkyl methylene protons, 12H), 2.04 (t, 2H), 2.32 (t, 2H), 2.44–2.62 (m, 4H); ^{13}C NMR δ 13.6, 22.0, 22.1, 22.4, 22.7, 27.8, 29.5, 30.9, 31.5, 37.3, 38.0, 91.8, 175.5 (–*C*OO–), 210.4 (–*C*O–); MS (CI) *m/e* 255 (M + 1, 100%), 155 [(M – RCO)$^+$, 90%]; MS (EI) *m/e* 254 (M$^+$, 2%), 155 [(M – RCO)$^+$, 55%].

2e: yield 49% (0.55 g); IR (neat) ν_{max} 920, 1140, 1720, 1790, 2950 cm^{-1}; ^{1}H NMR δ 0.80 (t, –CH$_3$, 6H), 1.12–1.92 (m, alkyl methylene protons, 8H), 2.04 (t, 2H), 2.28 (t, 2H), 2.44 (t, 2H), 2.60 (t, 2H); ^{13}C NMR δ 12.7, 21.2, 21.7, 24.1, 24.4, 27.2, 28.8, 36.4, 37.1, 91.2, 175.1 (–*C*OO–), 210.1 (–*C*O–).

2f: yield 40% (0.56 g); IR (neat) ν_{max} 920, 1140, 1640, 1720, 1790, 2950, 3060 cm^{-1}; ^{1}H NMR δ 0.90–2.12 (m, alkyl methylene protons, 12H), 2.12–2.40 (m, 4H), 2.40–2.68 (m, 4H), 4.76–5.04 (m, =CH$_2$, 4H), 5.48–5.88 (m, =CH–, 2H); ^{13}C NMR δ 19.5, 21.0, 22.0, 26.6, 27.6, 29.7, 32.9, 35.2, 36.8, 89.8, 114.2, 137.8, 175.2 (–*C*OO–), 210.5 (–*C*O–).

2i: yield 35% (0.98 g); mp 57 °C; IR (KBr) ν_{max} 920, 1140, 1720, 1790, 2950 cm^{-1}; ^{1}H NMR δ 0.88 (t, –CH$_3$, 6H), 1.10–2.08 (m, alkyl methylene protons, 56H), 2.24 (t, 2H), 2.30–2.72 (m, 6H); ^{13}C NMR δ 13.6, 22.2, 22.5, 22.9, 27.8, 28.6, 28.9, 29.2, 31.4, 37.2, 38.0, 91.8, 175.5 (–*C*OO–), 210.7 (–*C*O–). Anal. Calcd for $C_{37}H_{70}O_3$: C, 79.00; H, 12.46. Found: C, 78.62; H, 12.45.

1i: yield 25% (0.63 g); mp 88 °C; IR (KBr) ν_{max} 1705 cm^{-1}; ^{1}H NMR δ 0.8 (t, –CH$_3$, 6H), 1.12–1.60 (m, –CH$_2$–, 56H), 2.71 (t, –CH$_2$COCOCH$_2$–, 4H).

2j: yield 44% (0.44 g); IR (neat) ν_{max} 920, 1140, 1720, 1790, 2950 cm^{-1}; ^{1}H NMR δ 0.88 (t, –CH$_3$, 6H), 1.10–1.96 (m, alkyl methylene protons, 4H), 2.08 (t, 2H), 2.20–2.68 (m, 6H); ^{13}C NMR δ 13.5, 14.0, 16.4, 16.8, 28.2, 29.8, 39.8, 40.4, 92.2, 176.2 (–*C*OO–), 211.0 (–*C*O–); MS (CI) *m/e* 198 (M$^+$, 2%), 127 [(M – RCO)$^+$, 100%].

1j: yield 23% (0.16 g); bp 166 °C/760 mm (lit.[23] bp 168 °C/760 mm); IR (neat) ν_{max} 1705 cm^{-1}; ^{1}H NMR δ 0.92 (t, –CH$_3$, 6H), 1.36–1.76 (m, –CH$_2$–, 4H), 2.72 (t, –H$_2$CCOCOCH$_2$–, 4H); ^{13}C NMR δ 13.4, 16.4, 37.7, 199.9 (–*C*O*C*O–).

Reaction of Na(RCO)Fe(CO)$_4$ with I$_2$. To a suspension of $Na_2Fe(CO)_4$ prepared using $Fe(CO)_5$ (2.16 g, 11 mmol), Na (0.51 g, 22 mmol), and naphthalene (1.02 g, 8 mmol) in THF (40 mL) was added 1-bromooctane (1.93 g, 10 mmol), and CO was bubbled for 30 min at 25 °C. The CO atmosphere was replaced by dry N$_2$, and the mixture was cooled to 0 °C. I$_2$ (2.53 g, 10 mmol) dissolved in THF (30 mL) was added dropwise to the reaction mixture using a pressure equalizer. The mixture was stirred for 3 h at 0 °C and 12 h at 25 °C and then poured into acetone (40 mL) containing $CuCl_2$ (5.38 g, 40 mmol) to decompose the iron carbonyl. Saturated aqueous NaCl (30 mL) was added, the organic layer was separated, and the aqueous layer was extracted with ether (2 × 30 mL). The combined organic layers were washed successively with saturated $Na_2S_2O_3$ (20 mL) and brine (30 mL) and then dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Mixtures of ketone and diketone and nonan-1-oic acid (0.45 g, 29%) were isolated along with several other unidentified products. RCOCOR (R = *n*-octyl) (0.47 g, 32%) and dialkyl ketone (0.11 g, 8%) were separated by preparative TLC and identified by ^{13}C NMR, ^{1}H NMR, and comparison with the spectral data of authentic samples obtained previously using CuCl.

Reaction of Methyl Acrylate with the Reagent Generated Using Na(RCO)Fe(CO)$_4$ and I$_2$. To a suspension of $Na_2Fe(CO)_4$ prepared using $Fe(CO)_5$ (2.16 g, 11 mmol), Na (0.51 g, 22 mmol), and naphthalene (1.02 g, 8 mmol) in THF (40 mL) was added 1-bromopropane (1.23 g, 10 mmol), and CO was bubbled for 30 min at 25 °C. The CO atmosphere was replaced by dry N$_2$, and the mixture was cooled to 0 °C. I$_2$ (2.53 g, 10 mmol) dissolved in THF (30 mL) was added dropwise to the reaction mixture using a pressure equalizer. The mixture was stirred for 3 h at 0 °C, methyl acrylate (30 mmol) was added, and the mixture was stirred for 2 h at 0 °C and for 12 h at 25 °C. CH_3COOH (2 mL) was added. The mixture was then poured into acetone (40 mL) containing $CuCl_2$ (5.38 g, 40 mmol) to decompose the iron carbonyl. Saturated aqueous NaCl (30 mL) was added, the resulting solution was extracted with ether (2 × 30 mL), and the extracts were washed with saturated $Na_2S_2O_3$ (20 mL) and brine (30 mL) and then dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography. Acyllactone **2j** (0.19 g, 19%) and a mixture of dialkyl ketone, 1,2-diketone, and butanoic acid **4b** (0.05 g, 6%) were isolated along with several other unidentified products. The RCOCOR species **1j** (0.11 g, 16%) and RCOR **3b** compound (*n*-propyl; 0.02 g, 4%) were separated using preparative TLC.

When the experiment was carried out with 1-bromohexane, RCOCOR **1a** (0.21 g, 18%), RCOR **3a** (0.05 g, 5%), acyllactone **2a** (0.30 g, 21%), and RCOOH **4a** (0.09 g, 7%) were isolated.

The spectral data of the acyllactone and 1,2-diketone obtained in the above experiment were identical with the data of the sample obtained previously in the reaction of Na(RCO)Fe(CO)$_4$ (R = *n*-propyl, *n*-hexyl) with CuCl in the presence of methyl acrylate. The spectral data of the dialkyl ketones **3a,b** and acids **4a,b** were found to be identical with those of authentic samples.

Photochemical Reaction of Fe(CO)$_5$ with Methyl Acrylate and 1,2-Diketone. A mixture containing RCOCOR (R = octyl; 0.141 g, 0.5 mmol), $Fe(CO)_5$ (0.39 g, 2 mmol), and methyl acrylate (0.13 g, 1.5 mmol) in benzene (10 mL) was irradiated for 4.5 h using a 450-W medium-pressure mercury lamp and Pyrex filter. It was poured into H$_2$O (3 mL) containing ceric ammonium nitrate (1.64 g, 3 mmol) to decompose the iron carbonyl. The organic phase was separated, and the aqueous phase was saturated with NaCl and extracted with ether (2 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried, and concentrated. The residue was subjected to column chromatography. Ethyl acetate (2%) in hexane eluted unreacted 1,2-diketone (0.020 g, 14%), ethyl acetate (4%) in hexane eluted an iron carbonyl complex (0.098 g) (not identified), and ethyl acetate (10%) in hexane eluted acyllactone (28%, 0.045 g).

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