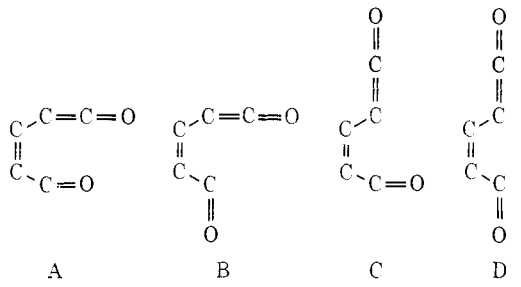
bands with band centers near 1245, 1370, and 1650 cm^{-1} are not as yet identified; they are apparently polymeric species.

The intensities of the absorptions assigned to the ketene II showed no leveling off after 15 hr of photolysis, indicating that at 20°K the back reaction to α-pyrone is not occurring. The intensity of the band assigned to photo-α-pyrone III was never more than 15% of the intensity of the C=O stretching mode (1690 cm^{-1}) of the ketene II.

High-resolution spectra of the region near 2140 cm^{-1} showed four distinct absorptions. These we assign to the four accessible isomers of the ketene.



A B C D

Presumably ketene A is formed first and rearranges thermally or photochemically to the more stable isomers. Photolysis with 3650-Å light effected interconversion of the isomers without photolysis. The different isomers could also be detected on the carbonyl absorption at 1690 cm^{-1}.

We have shown by direct identification that the ketene II is the principle photoproduct of the photolysis of α-pyrone with 3130-Å light. The lactone III is a minor product. At cryogenic temperatures the thermal back reaction of the ketene to α-pyrone is prevented.

Apparently at more usual temperatures, the thermal back reaction occurs and the ketene is present at a low steady-state concentration. Reaction will occur *via* the ketene if the appropriate reactants are present (*e.g.*, methanol). If the ketene cannot react, the photoproduct will be the less reactive lactone III.

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Richard G. S Pong, James S. Shirk*
Department of Chemistry, Illinois Institute of Technology
Chicago, Illinois 60616
Received July 31, 1972

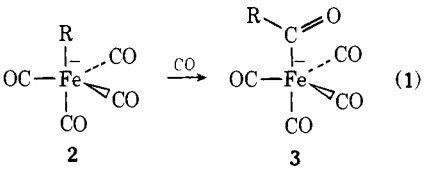
Selective Syntheses of Aliphatic Carboxylic Acids, Esters, and Amides Using Sodium Tetracarbonylferrate(−II)

Sir:

Recently we have shown $Na_2Fe(CO)_4$ (**1**) to be a practical reagent for the preparation of aliphatic aldehydes[1] and unsymmetrical ketones.[2] The significance of these new methods derives from their stereospecificity and their toleration of functional groups. Applications of **1** for the synthesis of carboxylic acids, esters,[3] and amides are described herein.

Aliphatic halides and tosylates react with **1** to give anionic alkyltetracarbonyliron(0) complexes **2**,[4] a process which can be viewed either as an SN2 displacement at carbon[5] or as an oxidative addition to the d^{10} iron (−II).[6] In the presence of CO, cation-assisted alkyl migration[7] affords anionic acyl complexes **3**.[4]

$$Na_2Fe(CO)_4 + RX \longrightarrow$$
1



2 **3** (1)

Halogenation of the acyl complexes **3** yields carboxylic acids, esters, and amides (eq 3–5)—apparently through the intermediacy of an acid halide. Oxidation of the acyl complexes **3** with O_2 or NaClO affords carboxylic acids directly (eq 2).

$$\mathbf{2}\text{ or }\mathbf{3} \xrightarrow{O_2\text{ or NaOCl}} \xrightarrow{H_2O\text{–}H^+} RCOOH \quad (2)$$

$$\mathbf{2}\text{ or }\mathbf{3} \xrightarrow{X_2\text{–}H_2O} RCOOH \quad (3)$$

$$\mathbf{2}\text{ or }\mathbf{3} \xrightarrow{X_2\text{–}R'OH} RCO_2R' \quad (4)$$

$$\mathbf{2}\text{ or }\mathbf{3} \xrightarrow{X_2\text{–}R'R''NH} RCO_2NR'R'' \quad (5)$$

Surprisingly, halogenation or oxidation (O_2 or NaClO) of the iron alkyls **2** also gives carboxylic acids and acid derivatives (eq 2–5). Either these reagents induce migratory insertion or they trap the unsaturated tetracoordinate acyl intermediate proposed in the migratory insertion mechanism.[7,8]

The scope of these procedures is illustrated in Tables I and II.[9] Using primary aliphatic halides and tosylates all of the routes to esters, amides, and acids (eq 2–5) give nearly quantitative yields by gc; however, isolated yields are about 80%. Secondary substrates are less satisfactory due to competing olefin-forming elimination reactions. These eliminations are minimized in THF, a solvent most compatible with the acyl

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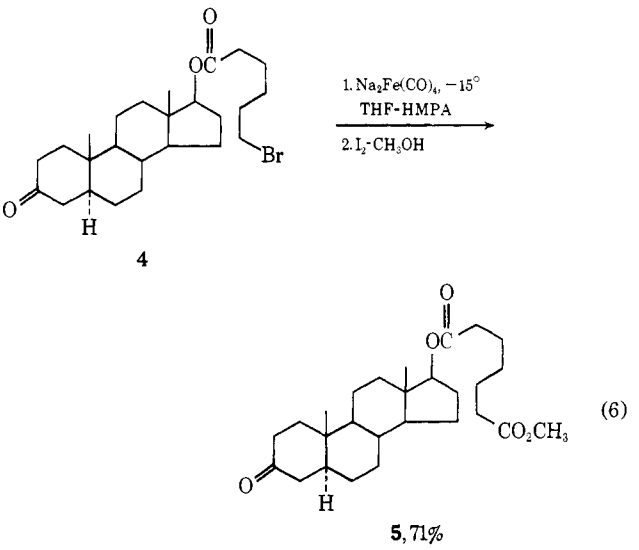
(2) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972).
(3) Esters have been prepared by related methods: Y. Takegami, Y. Watanabe, H. Masada, and I. Kanaya, *Bull. Chem. Soc. Jap.*, **40**, 1456 (1967); H. Masada, M. Mizuno, S. Suza, Y. Watanabe, and Y. Takegami, *ibid.*, **43**, 3824 (1970).
(4) Examples of both the alkyl, **2**, and the acyl, **3**, complexes have been isolated and thoroughly characterized: W. O. Siegl and J. P. Collman, *J. Amer. Chem. Soc.*, **94**, 2516 (1972).
(5) Kinetic studies have shown the rate law for the alkylation in THF to be $-d[RX]/dt = k_2[RX][Na_2Fe(CO)_4]$: J. N. Cawse and J. P. Collman, unpublished results.
(6) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).
(7) J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Amer. Chem. Soc.*, **94**, 5905 (1972).
(8) This intermediate, $Na(RCO)Fe(CO)_3^-$, was suggested as the active species in our ketone synthesis by J. Halpern, 14th International Congress on Coordination Chemistry, Toronto, Can., June 22, 1972.
(9) Procedures for preparing the alkyl, **2**, and acyl, **3**, complexes are given in ref 2. In method 2, O_2 was bubbled into a solution of 10 mmol of the alkyl or acyl for 1 hr, 70 ml of H_2O was added, and the reaction was stirred for 5 hr. The reaction was then filtered and the aqueous filtrate was extracted (ether). The extractions were dried, the solvent was removed, and the product distilled or recrystallized. In methods 3, 4, and 5 the alkyl or acyl solution was cooled (0° in NMP, −15° in THF or THF–HMPA) and for each millimole of complex, 0.5–1 ml of water, alcohol, or amine was added followed by 10 mmol of I_2 in 5 ml of THF. After stirring 0.5 hr at −15° and 0.5–12 hr at 25°, the mixture was diluted with ether, washed with $NaHSO_3$ solution and water, and dried, the solvent removed, and the residue distilled or purified by chromatography.

Table I. RX ⟶ RCOOH

RX[a]	Intermediate	Solvent[b]	Cleaving agent	% yield[c,d]
n-$C_5H_{11}Br$	Acyl **3**	THF	O_2	(97)
n-$C_6H_{13}Br$	Acyl **3**	THF	O_2	82
n-$C_{12}H_{25}Br$	Acyl **3**	THF	NaClO	65
n-$C_{12}H_{25}Br$	Alkyl **2**	THF	O_2	84
n-$C_{12}H_{25}Cl$	Alkyl **2**	MP	O_2	84
n-$C_{12}H_{25}Br$	Alkyl **2**	MP	I_2–H_2O	78
$ClCH_2(CH_2)_4CH_2Br$	Acyl **3**	THF	O_2	84[e]
$C_6H_{13}CHBrCH_3$	Acyl **3**	MP–THF	O_2	44 (68)[f]

[a] Used 1–10 mmol of RX, slight excess of $Na_2Fe(CO)_4$, 10 psi of CO for acyl. [b] MP, *N*-methyl-2-pyrrolidone. [c] Products characterized by ir, pmr, melting points, and for new compounds by elemental analysis. [d] Yields in parentheses by glpc using a calibrated internal standard. Other yields for isolated products after recrystallization or distillation. [e] Product 7-chloroheptanoic acid. [f] Yield of the acyl as determined by glpc by quenching with acetic acid to form the aldehyde.



4

5, 71%

(6)

routes.[10] Secondary tosylates give yields comparable to those obtained with primary substrates *via* the acyl routes in THF. With secondary bromides gc yields drop to around 50%; secondary iodides and cyclohexyl or cyclopentyl halides and tosylates give even lower yields.

Polar solvents such as HMPA and *N*-methyl-2-pyrrolidone (MP) allow less reactive substrates such as alkyl chlorides to be used, but in these solvents alkyl migration is inhibited. Hence alkyl routes are preferred in such cases. Benzylic halides alkylate readily, but migration to form the acyl is slow even in THF; nevertheless high yields may be obtained using the alkyl routes in THF.

These reactions exhibit remarkable selectivity. In THF primary bromides react with **1** at a rate $>10^4$ faster than the corresponding chlorides[5] allowing 1-bromo-6-chlorohexane to be converted into 7-chloroheptanoic acid (84%, Table I). Ester and ketone groups are not affected under the reaction conditions.[11] Hence ethyl 5-bromovalerate gave ethyl methyl adipate (95% by gc, Table II) and the steroidal bromo keto ester **4** gave the corresponding methyl ester **5** (71% isolated, eq 6).

While we have not yet explored the stereochemistry of these reactions, the common intermediates involved make it likely that the stereospecificity observed in one of our earlier ketone syntheses[2] will also be found here.

Table II. RX ⟶ ester or amide

RX[a]	Intermediate	Solvent[b]	Product[c]	% yield[d]
n-$C_8H_{17}Cl$	Alkyl **2**	MP	n-$C_8H_{17}CO_2C_2H_5$	89 (96)
n-$C_8H_{17}Br$	Alkyl **2**	THF–HMPA	n-$C_8H_{17}CO_2C_2H_5$	88 (99)
n-$C_8H_{17}Br$	Acyl **3**	THF	n-$C_8H_{17}CO_2C_2H_5$	84 (99)
$CH_3(CH_2)_5CH(CH_3)OTs$	Acyl **3**	THF	$CH_3(CH_2)_5CH(CH_3)CO_2C_2H_5$	(85)
$BrCH_2(CH_2)_2CH_2CO_2C_2H_5$	Alkyl **2**	THF–HMPA	$H_3CO_2CCH_2(CH_2)_2CH_2CO_2C_2H_5$	(95)
n-$C_5H_{11}Br$	Acyl **3**	THF	n-$C_5H_{11}CON(C_2H_5)_2$	(80)

[a–d] Same as Table I; 15% HMPA.

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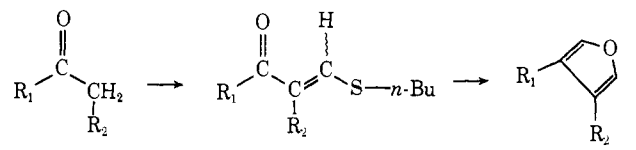
James P. Collman,* Stanley R. Winter, Robert G. Komoto
Department of Chemistry, Stanford University
Stanford, California 94305
Received July 31, 1972

A General Method for the Synthesis of 3- and 3,4-Substituted Furans. Simple Syntheses of Perillene and Dendrolasin

Sir:

The reaction of *n*-butylthiomethylene derivatives[1] of ketones with dimethylsulfonium methylide[2] affords good yields of 3- or 3,4-substituted furans. The sequence shown in Scheme I which incorporates this reaction constitutes a widely applicable method for the

Scheme I



(10) The alkyl intermediates **3** are unstable in THF (with no HMPA or MP present) at 25° in the concentrations normally used (about 0.25 *M*). Although decomposition is slower at lower temperatures and concentrations, formation of the alkyl intermediates is also slower. Thus the acyl intermediate can normally be prepared from a given halide in higher yield than can the corresponding alkyl intermediate *in THF* (no HMPA or MP added).

(11) With 5-chloro-2-pentanone neither the acyl or alkyl complex could be formed, apparently due to enolate formation followed by cyclization to methyl cyclopropyl ketone.

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