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REDUCTION OF ACID CHLORIDES TO ALDEHYDES BY MEANS OF THE HYDRIDOIRONTETRACARBONYL ANION

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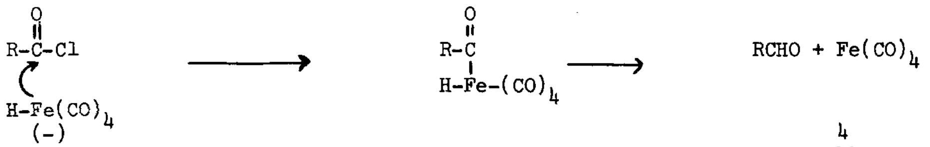
The hydridotetracarbonylferrate anion has recently shown to be of use in reductive alkylation,[1,2] reductive alkylation of amines with formaldehyde,[3-5] hydroacylation,[6] dehalogenation,[7] desulfurization[8] and hydrogenation of the carbon-carbon double bond of an α,β-unsaturated carbonyl.[9] Herein we describe a mild and facile method of reduction of acid chlorides to aldehydes in excellent yields by means of this reagent.

Acid chlorides react smoothly with the hydridoironcarbonyl anion (1) in aprotric solvents in a 2:3 molar ratio to generate the corresponding aldehyde and the salt of the known hydridotriironundecarbonyl anion (2) as indicated in equation 1.

$$2RCOCl \;+\; \underset{\mathbf{1}}{3NMe_4.HFe(CO)_4} \;\longrightarrow\; 2RCHO \;+\; 2NMe_4Cl \;+\; \underset{\mathbf{2}}{NMe_4.HFe_3(CO)_{11}} \qquad (1)$$

We consider that the mechanism of the reaction involves nucleophilic attack of the mononuclear iron anion (1) to generate the acylhydride complex (3) which then undergoes reductive



1 **3** **4**

elimination with formation of the aldehyde and iron tetracarbonyl (4). The iron tetracarbonyl reacts with the mononuclear anion **1** to generate the trinuclear anion **2**[10] which is relatively inert under these reaction conditions[11] and therefore a greater than unity molar ratio of

$(CO)_4HFe^-$ anion to acid chloride is required for complete conversion to the aldehyde.

The results of the application of this method as applied to several acid chlorides are summarized in Table I. The yields of aldehyde are very good, the ease and simplicity of this reagent should provide an improvement over existing methods. However, the reagent does not appear to be compatible with aromatic acid chlorides containing a nitro group nor does it appear to be very attractive for the conversion of α,β unsaturated acid chlorides to α,β unsaturated aldehydes.

Table I

Acid Chloride	Reaction Time	Percentage Aldehyde Yield
Benzoyl Chloride	1.25 hrs	91[a]
2-Furoyl chloride	4.0 hrs	90[a]
Hexanoyl chloride	1.25 hrs	99[a]
Cyclohexanecarboxylic acid chloride	2.75 hrs	95[a]
ρ-Bromobenzoyl chloride	1.0 hr	80[a], 75[b]
Cinnamoyl chloride	1.75 hrs	22[a]
Isobutyryl chloride	1.75 hrs	99[a], 82[c]
Pivaloyl chloride	1.5 hrs	80[c]
Acetyl chloride	3.0 hrs	100[a]
ρ-Nitrobenzoyl chloride	0-1 hr	0[d]

(a) Determined by g.l.c. analysis.

(b) Isolated yield of aldehyde.

(c) Isolated yield of 2,4-dinitrophenyl hydrazone of the aldehyde.

(d) The reducing reagent apparently attacks the nitro group. Vigorous reaction between $HFe^-(CO)_4$ and nitrobenzene, methyl-ρ-nitrobenzoate and ρ-nitrobenzaldehyde giving the corresponding amino derivatives was observed in each case.

The above reduction is closely related to the reduction of acid chlorides with $Na_2Fe(CO)_4$ as reported by Watanabe and coworkers.[12] In this latter process the acid chloride is presumably attacked by the $Fe(CO)_4$ dianion to give, after protonation with glacial acetic acid, the same hydrido acyl species **3**. The method reported here offers certain advantages in that the reducing agent is less expensive and much easier prepared.

Experimental

(a) Preparation of Tetramethylammonium Hydridoirontetracarbonyl. Iron pentacarbonyl (5.0 ml, 7.0 g) is added to a solution of potassium hydroxide (7.0 g) and tetramethyl ammonium bromide (7.5 g) in distilled water (40 ml). The mixture is stirred under inert gas (argon) for 24 hours at which time the tetramethyl ammonium hydridoiron carbonyl salt appears as a light brown precipitate.[13] The mixture is filtered under an inert gas and the residual solid washed with deaerated water (300 ml) then dried under vacuum. The salt (5.7 g, 66.0%) is light pink in color; it is mildly air sensitive and is best handled under an inert atmosphere.

(b) Reduction of Acyl Chlorides. The acid chloride (2-4 mmoles) in dry methylene chloride (8.0 ml) is added via a syringe to the hydridoiron carbonyl salt contained under argon in a flask fitted with a rubber septum (the acid chloride to iron carbonyl salt is in a 1:2 molar ratio.) The mixture is stirred magnetically at room temperature until the formation of aldehyde is complete (1-4 hours, see Table I.) In order to isolate the aldehyde the methylene chloride is evaporated at reduced pressure and at low temperature (-10°) and the aldehyde extracted from the residue with ether.

The data in Table I pertaining to g.l.c. analysis were obtained by dilution of the total reaction mixture to a known volume followed by comparison of the chromatogram with standard solutions.

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11. In separate experiments we have shown that acid chlorides do not react rapidly with salts of the $HFe_3(CO)_{11}$ anion under comparable reaction conditions.
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13. If desired, the time may be shortened by conducting the reaction homogeneously in aqueous alcohol (30 minutes) followed by addition of water to precipitate the desired product.