# The Facile Reduction of Acyl Halides into Aldehydes *via* Acylcarbonylferrates

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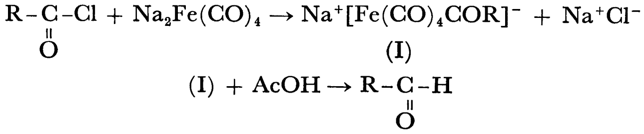
(Received June 11, 1971)

Previously, we reported that alkyl halides such as *n*-propyl iodide1) and ethyl α- or β-bromopropionate2) react with an ethanolic solution of tetracarbonylferrate, $Fe(CO)_4{}^{2-}$, with the absorption of carbon monoxide, to give a mixture of the corresponding carbonylated products, ethyl *n*-butyrate and *n*-butyraldehyde, and diethyl succinate and diethyl methylmalonate, respectively.

Recently, Cooke carried out an analogous reaction in tetrahydrofuran (THF) in the presence of triphenylphosphine; quenching it with acetic acid, he found that alkyl bromides are carbonylated to the corresponding aldehydes in high yields.3) In these reactions, it can reasonably be considered that acylcarbonylferrate complexes are formed as the reaction intermediates.1–3)

In this communication, we wish to report a facile reduction of acyl halides into aldehydes, which is considered to proceed *via* acyltetracarbonylferrates.

Acyl halides react with an equivalent mole of $Na_2Fe(CO)_4$ in THF at 0—60°C to give, after quenching with acetic acid, the corresponding aldehydes in high yields. This fact strongly suggests that sodium acyltetracarbonylferrates (I)4) are directly formed in high yields by the nucleophilic attack of $Fe(CO)_4^{2-}$ on the acyl carbon atom. Some results of typical reactions are shown in Table 1.



$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}Cl + Na_2Fe(CO)_4 \rightarrow \underset{(I)}{Na^+[Fe(CO)_4COR]^-} + Na^+Cl^-}$$

$$\mathrm{(I) + AcOH \rightarrow R{-}\underset{\underset{O}{\|}}{C}{-}H}$$

The reduction of benzoyl chloride to benzaldehyde illustrates a typical procedure. A THF solution of $Na_2Fe(CO)_4$3,5) (7.3 mmol) was prepared by adding, drop by drop, 1.0 m*l* of $Fe(CO)_5$ in 25 m*l* of THF to 4 m*l* of a 1% sodium amalgam in 25 m*l* of THF under argon at room temperature. After the amalgam had been removed through a side arm, to this solution was added 0.85 m*l* (7.3 mmol) of benzoyl chloride at 30°C; the mixture was stirred vigorously for 1 hr and then treated with 1.2 m*l* of glacial acetic acid. The mixture was stirred for an additional 5 min, then poured into 50 m*l* of water, and extracted with 20 m*l* of pentane and then 20 m*l* of ethyl ether, after which the organic extracts were submitted to glpc analysis.6)

Aromatic and aliphatic acyl halides are readily reduced to the corresponding aldehydes in high yields, indicating that the corresponding acyltetracarbonylferrates (I) are formed in high yields and that these complexes are thermally stable in the solution, even in the absence of a stabilizing ligand such as triphenylphosphine.3) The branched acyl complex, isobutyryltetracarbonylferrate, is also stable in the solution even at 60°C and does not isomerize to the normal acyl complex, in contrast with the branched acylcarbonylcobalt, which isomerizes to *n*-acylcarbonylcobalt.7)

The high yield of the aldehydes and the facility of the reaction procedures enable us to utilize this reaction instead of the Rosenmund reduction8) and reduction with $LiAlH(OR)_3$.9)

The acyltetracarbonylferrate (I) can possibly be utilized as a starting material for further organic syntheses. These reactions will be discussed in the near future.

Table 1. The reduction of acyl chlorides to aldehydes with $Na_2Fe(CO)_4$ in THF

| Exp. No. | Acyl chloride | Reaction condition temp. (°C) | time (hr) | Product | Yielda)% |
|---|---|---|---|---|---|
| 1 | Benzoyl chloride | 30 | 1 | Benzaldehyde | 95 |
| 2 | *p*-Chlorobenzoyl chloride | 0 | 1 | *p*-Chlorobenzaldehyde | 74 |
| 3 | *o*-Chlorobenzoyl chloride | 0 | 1 | *o*-Chlorobenzaldehyde | 65 |
| 4 | *n*-Butyryl chloride | 30 | 1 | *n*-Butyraldehyde | 75 |
| 5 | Isobutyryl chloride | 60 | 3 | Isobutyraldehyde | 71 |

a) Yield determined by glpc analysis using an appropriate internal standard previously calibrated against an authentic sample of pure aldehyde.

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6) The peak of aldehyde appears only after the reaction mixture is treated with acetic acid, not befor the quenching.

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