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SYNTHESIS OF CARBOXYLIC ESTERS FROM ALKYL HALIDES AND ALKOXIDES USING PENTACARBONYLIRON AS A CARBONYLATING REAGENT

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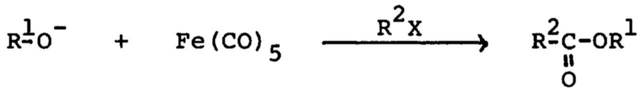
Carboxylic esters were prepared under mild conditions in high yields from alkyl halides and alkoxides using pentacarbonyliron as a carbonylating reagent.

In recent years, pentacarbonyliron has been shown to be a useful carbonylating reagent for the preparation of aldehydes,[1)] ketones,[2)] carboxylic acid derivatives,[3,4)] and *N*,*N'*-disubstituted ureas.[5)]

In this letter, we wish to report a novel synthetic route to carboxylic esters from alkyl halides and alkoxides using pentacarbonyliron as a carbonylating reagent. In this route, pentacarbonyliron can be used without reducing to disodium tetracarbonylferrate, $Na_2Fe(CO)_4$,[3,6)] and the products are obtained in high yields under mild reaction conditions.



$$R^1\text{-}O^- \quad + \quad Fe(CO)_5 \xrightarrow{R^2X} R^2\text{-}\underset{\underset{O}{\|}}{C}\text{-}OR^1 \qquad [1]$$

Table 1. Synthesis of carboxylic esters

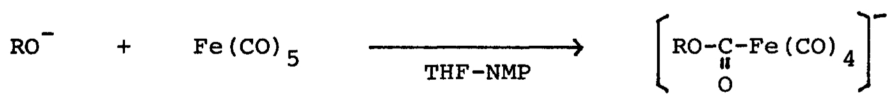
Run	Alkoxide	Halide	Solvent	Product	Yield(%)[a)]
1	$iso\text{-}C_3H_7ONa$	C_2H_5I	THF-NMP	$C_2H_5COOC_3H_7\text{-}iso$	80
2	$n\text{-}C_4H_9ONa$	$n\text{-}C_3H_7I$	THF-NMP	$n\text{-}C_3H_7COOC_4H_9\text{-}n$	62
3	$n\text{-}C_4H_9ONa$	C_2H_5I	THF-NMP	$C_2H_5COOC_4H_9\text{-}n$	68
4	$n\text{-}C_4H_9ONa$	C_2H_5I	THF	$C_2H_5COOC_4H_9\text{-}n$	30
5	$C_6H_5CH_2ONa$	C_2H_5I	THF-NMP	$C_2H_5COOCH_2C_6H_5$	61
6	$C_6H_5CH_2ONa$	C_2H_5I	THF	$C_2H_5COOCH_2C_6H_5$	20
7	C_2H_5ONa	$BrCH_2COOC_2H_5$	THF-NMP	$CH_2(COOC_2H_5)_2$	48

a) Based on an amount of pentacarbonyliron.

General procedure was as follows. A solution of alkoxide (11 mmol) and an equimolar amount of pentacarbonyliron in tetrahydrofuran-*N*-methylpyrrolidone (1:1 V/V, 20 ml) was stirred for 1 hr at room temperature under argon, and alkyl halide (22 mmol) was then injected. After 24 hr, the solvent was removed under reduced pressure and the residual liquid was extracted with diethyl ether. The extract was washed with water and dried (Na_2SO_4) overnight, and the products were separated by distillation or column chromatography. The products were identified by means of ir, nmr, elemental analyses and glpc. The typical results are shown in Table 1. In these reactions, carboxylic esters were obtained in high yields from the corresponding alkyl halides and alkoxides. As an alkyl halides, ethyl bromoacetate was also employed (Run 7), showing the toleration of this reaction condition to an ester linkage. Alkyl chlorides, however, are unreactive in accord with the expected reactivity sequence RI $>$ RBr $>$ RCl.

Addition of *N*-methylpyrrolidone as co-solvent to the suspension of alkoxides in tetrahydrofuran remarkably improved the yields of the carboxylic esters (Run 3 and 4, 5 and 6). This solvent effect may be partly due to an increase of the solubility of the alkoxides and to the removal of the cation from a tight ion pairing situation. In fact, the suspension of alkoxides in tetrahydrofuran became homogeneous by adding *N*-methylpyrrolidone.

In these reactions, we assume that alkoxycarbonyltetracarbonylferrates (I)[7]



$$RO^- + Fe(CO)_5 \xrightarrow[\text{THF-NMP}]{} \left[RO\text{-}\underset{\underset{O}{\parallel}}{C}\text{-}Fe(CO)_4\right]^- \qquad [2]$$

(I)

are formed as intermediates from the alkoxides and pentacarbonyliron (Eq. [2]), which react with the alkyl halides in a similar manner to acyl carbonylferrates.[2]

The facility of the reaction procedure, mildness of the reaction conditions and the good yields of the products may make it possible to utilize this reaction for introducing alkoxycarbonyl groups into alkyl halides.[8] Other applications of this reaction are currently explored in our laboratories.

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