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CHEMISTRY OF ALKALI METAL TETRACARBONYLFERRATES. REDUCTION OF ACID CHLORIDES TO ALDEHYDES BY A POLYMER-SUPPORTED IRON CARBONYL COMPLEX

GIANFRANCO CAINELLI, FRANCESCO MANESCALCHI and ACHILLE UMANI-RONCHI
Istituto Chimico "G. Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna (Italy)

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Summary

The polymer-supported $HFe(CO)_4^-$ anion can be easily prepared from potassium tetracarbonylhydridoferrate by an ion-exchange process with the chloride form of the anion-exchange resin Amberlyst A-26. This polymeric reagent, which can be readily dehydrated by washing with anhydrous solvents, reduces acid chlorides to the corresponding aldehydes under mild conditions.

Introduction

Several remarkable results have been obtained during the past decade by the application to organic synthesis of the alkali metal tetracarbonylferrates, $M_2Fe(CO)_4$, and of the corresponding tetracarbonylhydridoferrates, $MHFe(CO)_4$ [1]. These inexpensive, versatile and selective reagents have been used in the reductive alkylation of carbonyl compounds with aldehydes [2,3], the reductive alkylation of amines with aldehydes [4,5], dehalogenation [6], desulfurization [7], and in the hydrogenation of the carbon–carbon double bond of α,β-unsaturated carbonyl compounds [8].

In recent years, we have found that the use of tetracarbonylhydridoferrates in organic syntheses can be noticeably improved by attaching these reagents to a polymeric matrix via an anion-exchange process. In this way the work-up is substantially simplified because the reaction products are easily isolated, the iron-containing byproducts being left on the polymeric support.

The tetracarbonylhydridoferrate anion (I), prepared in alcoholic solution from iron pentacarbonyl and potassium hydroxide, as described elsewhere [9], rapidly and quantitatively exchanges, under an inert atmosphere, with the chloride ions of the anion exchange resin Amberlyst A 26 (Rohm and Haas) simply on stirring the resin (II) for a few min with a solution of the hydride I.

The resin III, washed to neutrality with water and then with dry solvents (methanol and ether), has been used [10] in the conversion of alkyl halides to the

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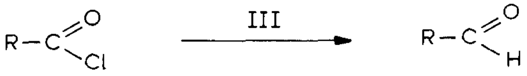
$$\mathrm{Fe(CO)_5} + 3\,\mathrm{KOH} \longrightarrow \underset{(\mathrm{I})}{\mathrm{KHFe(CO)_4}} + \mathrm{K_2CO_3} + \mathrm{H_2O}$$

$$\underset{(\mathrm{II})}{\textcircled{P}\text{-}\mathrm{Ph{-}CH_2{-}\overset{+}{N}(CH_3)_3}}\ \mathrm{Cl^-} + \mathrm{KHFe(CO)_4} \longrightarrow \mathrm{KCl} + \underset{(\mathrm{III})}{\textcircled{P}\text{-}\mathrm{Ph{-}CH_2{-}\overset{+}{N}(CH_3)_3}}\ \mathrm{HFe(CO)_4^-}$$

corresponding aldehydes, in the dehalogenation of *vic*-dibromoalkanes, α-bromoketones, α-bromoesters and aromatic bromides, as well as in the reduction of aromatic nitro compounds.

Results and discussion

We now report that the same dehydrated reagent, III, can be employed for the reduction of acid chlorides to aldehydes under mild conditions:



The most important step in our procedure is to carry out, to the maximum possible extent, the dehydration of the reagent. This condition is accomplished by the exhaustive washing of the functionalized polymer with dry solvents such as THF or acetone. To this end the preparation of the tetracarbonylferrate anion is performed in a round bottomed flask equipped with a side arm, which is connected to the exterior through a glass frit. The washing of the resin-supported hydride can then be carried out in the same vessel under an inert atmosphere.

The acid chloride (mol ratio 1 : 3 with respect to the capacity of the resin) is then added in a few ml of solvent and the mixture stirred at reflux; the reaction being monitored by TLC, GLC or IR spectroscopy of the solution. The reaction proceeds whatever the nature of the solvent employed: THF, acetone, hydrocarbons and chlorinated hydrocarbons have been used with comparable results.

As soon as the conversion is complete, the solution is filtered from the resin, and the latter is rinsed with two portions of the solvent. The combined filtrate and washings are evaporated and the isolated reaction product characterized by IR. ^{1}H NMR and mass spectroscopy and by comparison with authentic samples. The results are summarized in Table 1.

Satisfactory yields were generally obtained with aliphatic substrates although, as expected, a certain amount of side-products (mainly the anhydride) was sometimes found, probably due to the residual unremovable water in the resin. It is also worth noting that the exhausted polymer can be regenerated, with no significant loss of activity, by washing soon after the reaction with an aqueous nitric acid solution (1 : 1), then with aqueous potassium hydroxide (2 *M*) and finally with dilute hydrochloric acid.

The reagent appears to be unsuitable for the conversion to the corresponding aldehydes of aromatic acid chlorides containing a nitro group, and of α,β-unsaturated acid chlorides.

The reduction of acid chlorides by iron carbonyl derivatives has also been described by Watanabe et al. [11] and by Cole and Pettit [12]: the former employed

TABLE 1

REDUCTION OF ACID CHLORIDES TO ALDEHYDES BY THE POLYMER-SUPPORTED $FeH(CO)_4^-$ ANION [a]

Product	Reaction conditions		Yield [b] (%)
	Solvent (at reflux)	Time (min)	
$CH_3(CH_2)_8CHO$	THF [c]	75	80
$C_6H_{11}CHO$	THF	45	85
$CH_3OCO(CH_2)_7CHO$	THF	60	90
$CH_3(CH_2)_{10}CHO$	THF [d]	120	94
$OHC(CH_2)_8CHO$	THF	60	85
C_6H_5CHO	CH_2Cl_2	60	93
p-ClC_6H_4CHO	THF	60	55
$2,4,6(CH_3)_3C_6H_2CHO$	CH_2Cl_2	60	53
$(C_6H_5)_2CHCHO$	THF	60	90

[a] Reduction of acid chlorides to aldehydes using the polymeric reagent polystyryl diphenylphosphine tetrahydroborate copper has also been described [13]. [b] Yields are for the pure isolated compounds. [c] Also performed in acetone (GLC yield 90%) and in CH_2Cl_2 (GLC yield 92%). [d] Also performed in cyclohexane (GLC yield 96%).

the iron tetracarbonyl dianion and the latter tetramethylammonium tetracarbonylhydridoferrate.

The easier preparation of the reagent and the simple work up of the reaction product represent the major advantages of the method we have described here.

Experimental

The reactions were carried out under dry, oxygen-free argon. Tetrahydrofuran (THF) was distilled over sodium diphenylketyl and acetone was dried over phosphorus pentoxide and distilled.

Preparation of the polymer-supported $HFe(CO)_4^-$ reagent, III

To a solution of KOH (1.4 g, 25 mmol) in 1 : 1 water-ethanol (25 ml), pentacarbonyliron (1.2 ml, 8 mmol) was added under argon and the mixture was stirred for 2 h at room temperature. To this red-brown solution, 6 g of Amberlyst A 26 (chloride form, ion exchange resin as purchased) was added. After being stirred for 15 min the liquid phase appeared colorless, the tetracarbonylhydridoferrate anion being bound to the polymer to give a resin with a capacity of about 1.5 mmol/g. After being rinsed to neutrality with deaerated water the resin was washed with anhydrous THF or acetone (200 ml, in portions) and finally with a few ml of the solvent to be used in the reaction.

Decanal from decanoyl chloride (general procedure)

To the polymer-supported tetracarbonylhydridoferrate anion, III (8 mmol), prepared as previously described, decanoyl chloride (0.57 g, 3 mmol) in THF (5 ml) was added and the mixture was stirred at reflux for one hour while the conversion of the starting material was followed using the IR spectrum of the reaction solution. As soon as the reaction was over, the liquid phase was filtered off, the resin was rinsed with two 10 ml portions of THF and the combined filtrate and washings evaporated under reduced pressure. Bulb to bulb distillation of the residue gave 0.37 g (80%) of decanal. IR (neat) 1720 cm^{-1} ν(C=O); ^1H NMR ($CDCl_3$) δ 0.9 (m, CH_3), 1.2–1.9 (m, $(CH_2)_7$), 2.1–2.5 (m, CH_2–CHO), 9.8 ppm (CHO).

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