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CHEMISTRY OF ALKALI METAL TETRACARBONYLFERRATES. SYNTHESIS OF AMINES AND DEHALOGENATION REACTIONS BY A POLYMER SUPPORTED IRON CARBONYL COMPLEX

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Summary

The polymer-supported $HFe(CO)_4^-$ can be easily prepared from potassium tetracarbonylhydridoferrate by an ion-exchange process with an ion-exchange resin (Amberlyst A 26) in its chloride form. It selectively reduces nitroarenes to amines, and reacts with 1,2-dibromoalkanes to give alkenes in good to excellent yields.

The alkali metal tetracarbonylferrates ($M_2Fe(CO)_4$) and the corresponding alkali metal tetracarbonylhydridoferrates ($MHFe(CO)_4$) have been the subject of intensive investigation during the past decade [1]. In recent years these species have been used in various important types of reaction [2]. Among these are the conversion of alkyl halides, acid chlorides and carboxylic anhydrides into aldehydes [3], ketones and carboxylic acid derivatives [4], and the reductive alkylation of a carbonyl compound or of an amine with an aldehyde [5]. Furthermore, aldehydes can be obtained from alkyl halides supporting the potassium tetracarbonylhydridoferrate (I) on a polymeric matrix by an exchange process with an ion exchange resin (Amberlyst A 26) in the chloride form [6].

The tetracarbonylhydridoferrate anion, prepared in alcoholic solution from iron pentacarbonyl and potassium hydroxide, as described elsewhere [7], rapidly and quantitatively exchanges with the chloride ion simply on stirring the resin (II) a few minutes under an inert atmosphere with the solution of hydride (I). The resin (III) prepared was filtered off and washed with water to neutrality and then with dry methanol and dry ether, and then directly utilized to convert alkyl halides to the corresponding aldehydes in refluxing tetrahydrofuran in very good yields [6] (Scheme 1).

A notable difference between this and an procedure [3a] is that no addition of ligand is required.

The promising results prompted us to extend the study of this new reagent (III), and we examined its reactions with other substrates, such as aromatic nitro-compounds, vic-dibromoalkanes and α-bromoketones in order to provide convenient

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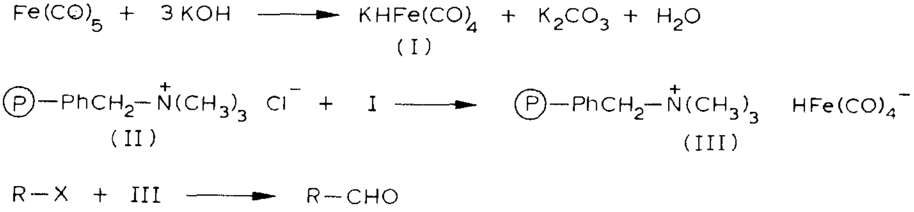
SCHEME 1



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

$$\underset{(II)}{\text{Ⓟ}{-}PhCH_2{-}\overset{+}{N}(CH_3)_3\ Cl^-} + I \longrightarrow \underset{(III)}{\text{Ⓟ}{-}PhCH_2{-}\overset{+}{N}(CH_3)_3}\ \ HFe(CO)_4^-$$

$$R{-}X + III \longrightarrow R{-}CHO$$

methods for the preparation of amines, alkenes and ketones.

It was found that treatment of aromatic nitro-compounds with III in tetrahydrofuran gives the corresponding primary amines in very good yields.

$$R{-}C_6H_4NO_2 \xrightarrow{III} R{-}C_6H_4NH_2$$

$(R = CH_3, CHO, OCH_3, OC_6H_5, Cl)$

The reagent III was conveniently prepared by percolating the red-brown solution of potassium tetracarbonylhydridoferrate in ethanol/water under argon through a chromatographic column containing the resin (Amberlyst A-26 in the chloride form).

A solution of the aromatic nitro-compound in anhydrous tetrahydrofuran was then passed through the column during 30 min. The product was recovered simply by removing the solvent. Specific examples are listed in Table 1. To ensure maximum yield a 2/1 molar ratio of reagent and nitroarene was necessary. The products were identified either by comparison with authentic samples or from their spectra (including mass spectra) and, in some cases, elemental analysis.

Such reduction of the nitro group appears to be a valuable synthetic method, especially since it can be carried out in the presence of some other reducible groups. The selectivities of III is shown by the conversion of *m*-nitro and *p*-nitrobenzaldehyde into *m*-amino and *p*-aminobenzaldehyde, respectively. The ease and simplicity of our reaction, that is involving the solution of the nitro-compound through a column of III, is an advantage over other procedures.

Under similar conditions α-bromoacetophenone is converted into acetophenone. Alkenes can be obtained in good to excellent yields by treating the polymer-sup-

TABLE 1

REDUCTION OF NITROARENES BY III

Substrate	Product[a]	Yield (%)[b]
p-$ClC_6H_4NO_2$	p-$ClC_6H_4NH_2$	92
p-$C_6H_5C_6H_4NO_2$	p-$C_6H_5C_6H_4NH_2$	85
p-$CH_3OC_6H_4NO_2$	p-$CH_3OC_6H_4NH_2$	75
p-$OHCC_6H_4NO_2$	p-$OHCC_6H_4NH_2$	80
p-$H_2NC_6H_4NO_2$	p-$H_2NC_6H_4NH_2$	75
m-$OHCC_6H_4NO_2$	m-$OHCC_6H_4NH_2$	90

[a] Products were identified by comparison with authentic samples. [b] Yields refer to pure isolated compounds.

TABLE 2

DEBROMINATION OF VIC-DIBROMOALKANES BY III

Substrate	Product[a]	Yield (%)[b]
1,2-dibromooctane	1-octene	80
1,2-dibromoundecane	1-undecene	75
1,2-dibromooctadecane	1-octadecene	77

[a] Products were identified by comparison with authentic samples. [b] Yields were determined by GLC with use of an internal standard method.

ported $HFe(CO)_4^-$ anion with 1,2-dibromoalkanes. The reaction is carried out in refluxing tetrahydrofuran for 6 h with a 6/1 ratio of reagent to substrate. The product is easily recovered from the mixture by filtration (Table 2).

$$C_6H_5\text{-}CO\text{-}CH_2Br \xrightarrow{III} C_6H_5COCH_3$$

$$R\text{-}CHBrCH_2Br \xrightarrow{III} R\text{-}CH{=}CH_2$$

This new reduction technique under heterogeneous conditions appears to be general and provides an attractive alternative to previously synthetic methods.

Experimental

All reactions were carried out under dry, oxygen-free argon. Tetrahydrofuran (THF) was obtained in anhydrous and oxygen-free form by distillation over sodium benzophenone ketyl under argon. $Fe(CO)_5$ was purchased from Merck.

Preparation of the polymer-supported $HFe(CO)_4^-$ reagent in chromatographic column

To a stirred solution of KOH (5.6 g, 100 mmol) in water/ethanol (100 ml), $Fe(CO)_5$ (4.5 ml, 33 mmol) was added under argon. The mixture was stirred for 2 h under reflux. After cooling, the red-brown solution was percolated for 20 min under argon through a chromatographic column containing 24 g of Amberlyst A-26 (chloride form ion exchange resin, Carlo Erba, as purchased).

After rinsing with deaerated water to neutrality, the tetracarbonylhydrido ferrate-resin (III) was eluted with anhydrous methanol then dry ether, and then dried in a stream of argon.

p-Chloroaniline from p-chloronitrobenzene, (general procedure)

A solution of *p*-chloronitrobenzene (2.52 g, 16 mmol) in anhydrous THF (50 ml) was passed during 30 min through the column containing the polymer-supported tetracarbonylhydridoferrate anion (III) (33 mmol), obtained as described above. The solvent was then distilled off under reduced pressure and the residue extracted with ether. The extract was acidified with aqueous HCl and the aqueous phase was neutralized with Na_2CO_3 and extracted again with ether. The *p*-chloroaniline (1.9 g; 92%) was obtained by evaporation of the solvent.

1-Undecene from 1,2-dibromoundecane (general procedure)

The polymer-supported tetracarbonylhydrido ferrate anion (III) (33 mmol), obtained as described above, was transferred into a reaction flask equipped with a mechanical stirrer, reflux condenser and argon inlet. 1,2-Dibromoundecane (1.9 g, 6 mmol) was added along with THF (50 ml) and the mixture was refluxed for 6 h, the disappearance of the starting material being monitored by GLC. The yield of 1-undecene was determined by GLC with use of an internal standard method.

Acetophenone from α-bromoacetophenone

A solution of α-bromoacetophenone (2.19 g, 11 mmol) in anhydrous THF (50 ml) was percolated during 30 min through a column containing III (33 mmol). After removal of the solvent under reduced pressure the residue was chromatographed on silica gel with hexane/ether (9/1) as eluent, to give acetophenone in 84% yield.

References

1 T. Mitsudo, Y. Watanabe, M. Yamashita and Y. Takegami, Chem. Lett., (1974) 1385; H. Alper, Tetrahedron Lett., (1975) 2257; Y. Watanabe, M. Yamashita, M. Igami, T. Mitsudo and Y. Takegami, Bull. Chem. Soc. Jpn., 49 (1976) 2824; H. Alper and Hang-Nam Palk, J. Org. Chem., 42 (1977) 3522.
2 J.P. Collman, Acc. Chem. Res., 8 (1975) 342 and references therein.
3 (a) M.P. Cooke, J. Amer. Chem. Soc., 92 (1970) 6080; (b) J.P. Collman, S.R. Winter and R.G. Komoto, J. Amer. Chem. Soc., 95 (1973) 249.
4 J.P. Collman, S.R. Winter and D.R. Clark, J. Amer. Chem. Soc., 94 (1972) 1788.
5 G. Cainelli, M. Panunzio and A. Umani-Ronchi, Tetrahedron Lett., (1973) 2491; G.P. Boldrini, M. Panunzio and A. Umani-Ronchi, Synthesis, (1974) 733; G.P. Boldrini, M. Panunzio and A. Umani-Ronchi, Chem. Comm., (1974) 359; G. Cainelli, M. Panunzio and A. Umani-Ronchi, J. Chem. Soc. Perkin Trans., 1 (1975) 1273.
6 G. Cainelli, F. Manescalchi, M. Panunzio and A. Umani-Ronchi, J. Org. Chem., 43 (1978) 1598.
7 P. Krumholz and H.M.A. Stettiner, J. Am. Chem. Soc., 71 (1949) 3035.