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Chemistry of Alkali Metal Tetracarbonylferrates. Synthesis of Aldehydes and Reductive Dehalogenation by a Polymer-Supported Iron Carbonyl Complex

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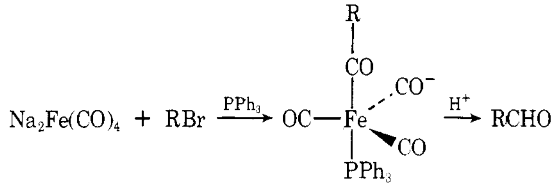
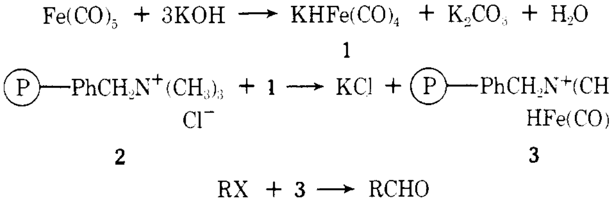
Received August 1, 1977.



Recently several works have demonstrated that alkali metal tetracarbonylferrates ($M_2Fe(CO)_4$) and the corresponding alkali metal tetracarbonylhydridoferrates ($MHFe(CO)_4$) are useful reagents in organic synthesis.[1] The treatment of an aldehyde or a ketone containing the partial structure CH_3COR or $R'CH_2COR$ with an aldehyde in the presence of $MHFe(CO)_4$ in ethanol or water results in reductive alkylation of the carbonyl compound in high yield.[2] Moreover, $M_2Fe(CO)_4$ is able to convert alkyl halides, acid chlorides, and carboxylic anhydrides into ketones and carboxylic acid derivatives.[3] Aldehydes are also obtained in high yield from alkyl halides in the presence of added triphenylphosphine or CO.[4] We now find that similar results can be obtained supporting the reagent on a polymeric matrix by an exchange process with an ion-exchange resin (Amberlyst A-26) in the chloride form. The tetracarbonylhydridoferrate anion, prepared in alcoholic solution from iron pentacarbonyl and potassium hydroxide as described elsewhere,[5] rapidly and quantitatively exchanges, under an inert atmosphere, with the chloride ion simply on stirring the resin **2** a few minutes with the solution of hydride **1**. The resin **3** prepared by this method, filtered off and washed as indicated in the Experimental Section, was directly utilized to convert alkyl halides to homologous aldehydes in THF solution under reflux. The choice of the solvent is critical to avoid side reactions. In fact, in benzene, isooctane, and petroleum ether the autocondensation of aldehyde was prevailing. Hexane seems to be useful, although the yield is, in this case, lower. The results of the application of this system to several alkyl halides are summarized in Table I. The yields of the aldehydes are very high and the ease and simplicity of the method seem to provide an improvement over other existing procedures. We have to note, however, that alkyl chlorides fail to react while secondary alkyl halides are subjected to E2 elimination in the presence of the basic iron complex **3**.



$$Fe(CO)_5 + 3KOH \longrightarrow \underset{\mathbf{1}}{KHFe(CO)_4} + K_2CO_3 + H_2O$$

$$\underset{\mathbf{2}}{\textcircled{P}\!-\!PhCH_2N^+(CH_3)_3\ Cl^-} + \mathbf{1} \longrightarrow KCl + \underset{\mathbf{3}}{\textcircled{P}\!-\!PhCH_2N^+(CH_3)_3\ HFe(CO)_4^-}$$

$$RX + \mathbf{3} \longrightarrow RCHO$$

The most remarkable advantages of our technique are the possibility of a facile drying of the reagent and the ease of separation of the reaction products, which are simply recovered by filtering off the resin while the iron complex remains bound to the polymer. As a matter of fact the separation of iron-containing byproducts from the organic compounds constitutes a hard to solve problem which limits the usefulness of the usual procedure in solution.[4] Moreover, with our resin **3** there is no need for added ligand to perform the reaction as is necessary with Cooke's procedure.[4]

A possible explanation of this remarkable difference is that on the resin the migratory insertion required is induced by the halogen anion formed. It has been indeed demonstrated that the nucleophilicity of halogen ions is strongly enhanced if they are bonded on the resin.[6]

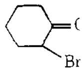
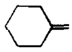
Table I. Reaction of the Polymer-Supported $FeH(CO)_4^-$ Anion with Alkyl Halides

Alkyl halide	Registry no.	Product[a]	Registry no.	Solvent[b,c]	Yield, %[d]
n-$C_7H_{15}Br$	629-04-9	n-$C_7H_{15}CHO$	124-13-0	THF	90
n-$C_8H_{17}Br$	111-83-1	n-$C_8H_{17}CHO$	124-19-6	THF	90
n-$C_8H_{17}Br$		n-$C_8H_{17}CHO$		Hexane[e]	60
n-$C_8H_{17}I$	629-27-6	n-$C_8H_{17}CHO$		THF	95
$C_6H_5CH_2CH_2Br$	103-63-9	$C_6H_5CH_2CH_2CHO$[f]	104-53-0	THF	80
$EtOCO(CH_2)_3Br$	2969-81-5	$EtOCO(CH_2)_3CHO$[g]	22668-36-6	THF	85

[a] All products were identified by comparison with authentic samples and by spectroscopic data. [b] At reflux for 4 h. [c] The use of other solvents as benzene, isoctane, and petroleum ether (75–120) caused the formation of autocondensation products. [d] Yields were determined by GLC using an internal standard. [e] At reflux for 10 h. [f] Product isolated and identified as 2,4-dinitrophenylhydrazone.

0022-3263/78/1943-1598$01.00/0

Table II. Reductive Dehalogenation by Polymer-Supported $FeH(CO)_4^-$ Anion

Alkyl halide	Registry no.	Product[b]	Registry no.	Yield,[c] %
$C_6H_5COCH_2Br$	70-11-1	$C_6H_5COCH_3$	98-86-2	90
	822-85-5		108-94-1	92
$CH_3(CH_2)_3CH(Br)COOCH_3$		$CH_3(CH_2)_4COOCH_3$	106-70-7	81
$C_6H_5CH(Br)C_6H_5$	776-74-9	$C_6H_5CH_2C_6H_5$	101-81-5	85
$C_6H_5CH(Br)CH(Br)C_6H_5$	5789-30-0	*trans*-$C_6H_5CH{=}CHC_6H_5$	103-30-0	85

[a] The reaction were performed in THF at room temperature for 5 h. [b] Products were identified by comparison with authentic samples. [c] Yields were determined by GLC internal standard method. [d] At reflux.

We have also found that the reaction of polymer-supported $HFe(CO)_4^-$ anion **3** with certain types of halides gives the dehalogenated product in good to excellent yields (Table II): α-bromo ketones, esters, and aromatic bromide functionalities are employed as substrates.[7]

The reaction is performed in THF at room temperature for 5 h and once more the product is easily recovered from the mixture by simple filtration.

We can conclude that ease of workup and greater effectiveness are the general features of the reactions described above, which were developed as part of a program carried out in our laboratory with the trend to demonstrate the usefulness of polymer-supported anions in organic synthesis.

Experimental Section

General. ^1H NMR spectra were measured in $CDCl_3$ solution by a Perkin-Elmer R1 2B instrument with tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 7108 infrared spectrophotometer and the mass spectra (MS) were taken on a Varian Mat III (70 eV). Vapor-phase chromatography was performed on a Hewlett-Packard 5750 instrument equipped with 5% SE 30 stainless steel column (10 ft × 0.25 in.). Anhydrous diethyl ether and tetrahydrofuran (THF) were obtained by distillation from sodium wires and then from $LiAlH_4$.

Preparation of the Polymer-Supported $HFe(CO)_4^-$ Reagent. To a stirred solution of KOH (5.6 g, 100 mmol) in water–ethanol 50:50 (100 mL) pentacarbonyliron (4.5 mL, 33 mmol) was added under argon. The mixture was stirred for 2 h under reflux. To this red-brown solution 24 g of Amberlyst A-26 (chloride form ion-exchange resin, Rohm and Haas, as purchased) was added.

After stirring for 15 min the exchange was complete and the tetracarbonylhydridoferrate anion was bound on the polymer support and the liquid phase appeared colorless: we can hence assume for our resin a capacity of about 1.5 mmol/g. After rinsing with deaerated water to neutrality and then with dry methanol and dry ether, the resin was dried by blowing with argon and then was directly used for the reaction in order to avoid traces of iron complexes in the solution.

Efforts to regenerate the resin, at the moment, failed to give useful, reproducible results.

Pelargonaldehyde from *n*-Octyl Bromide (General Procedure). The polymer-supported tetracarbonylhydridoferrate anion (**3**; 33 mmol), obtained as previously described, was transferred into a reaction flask equipped with a mechanical stirrer, reflux condenser, and argon inlet. *n*-Octyl bromide (11 mmol) was added along with THF (50 mL) and the mixture was refluxed for 4 h, following the starting material conversion by GLC. As soon as the reaction was complete, the resin was filtered off and the filtrate slowly distilled under reduced pressure to remove the solvent. Bulb-to-bulb distillation of the residue affords 1.40 g of pelargonaldehyde (90%): IR (neat) 1720 (C═O); NMR ($CDCl_3$) δ 0.9 (m, CH_3), 1.2–1.9 (m, $(CH_2)_6$), 2.1–2.5 (m, CH_2CHO), 9.8 (CHO); MS *m/e* 142 (M^+).

Acetophenone from ω-Bromoacetophenone (General Procedure). The polymer-supported tetracarbonylhydridoferrate anion (**3**; 33 mmol) was added to ω-bromoacetophenone (11 mmol) in THF (50 mL). After stirring for a 4 h at room temperature, the resin was filtered off and the solvent carefully removed by distillation under reduced pressure. Bulb-to-bulb distillation of the residue affords 1.2 g of acetophenone (90%) identified by comparison with an authentic sample.

Registry No.—Iron carbonyl complex, 18716-80-8.

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m-Chloroperbenzoic Acid Oxidation of 2-Trimethylsilyloxy-1,3-dienes. Synthesis of α-Hydroxy and α-Acetoxy Enones

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Received August 16, 1977

Synthetic methods for the introduction of oxygen functionality to the α-carbon of enone systems have relied almost exclusively upon treatment of the appropriate enone with lead(IV) acetate (LTA).[1] However, erratic yields as well as high reaction temperatures mitigate against the general use of this procedure. Since α-oxygenated enones continue to serve as important synthetic intermediates, as evidenced by recent syntheses of acorenone-B,[2] pyroangolensolide,[3] and prostaglandin anologues,[4] improved methods for the production of these useful compounds should be welcomed.

We report an efficient and extremely mild method for the preparation of both α-hydroxy enones (**1**) and α-acetoxy enones (**2**). Treatment of 2-trimethylsilyloxy-1,3-dienes (**3**) with *m*-chloroperbenzoic acid (MCPBA), followed by hydrolysis or acetylation, affords **1** or **2**, respectively. In the former instance, the crude reaction mixture resulting from the treatment of **3** with MCPBA is separated from the *m*-chlorobenzoic acid and the solvent (hexane) removed in vacuo. Treatment of the crude residue with a a methylene chloride solution of triethylammonium fluoride,[5] followed by aqueous workup,