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ELECTROCHEMICAL PREPARATION AND REACTIONS OF UNMASKED ACYL-ANION SYNTHONS[1]

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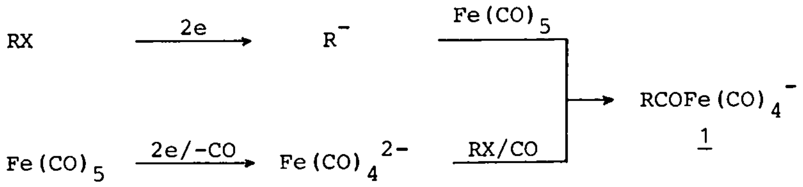
Summary: Organic halides can be converted into carbonyl compounds by electroreducing a mixture of them and $Fe(CO)_5$ in acetonitrile first and adding an electrophile to this mixture.

A synthetic operation may often require transfer of an acyl group as it were a nucleophilic acyl anion. While acyl anions are not commonly synthetically accessible, there are a variety of reagents which are synthetically equivalent to acyl anions, permitting the umpolung of carbonyl reactivity.[2] Means of acquisition of organometallic acyl-anion-transfer reagents, by addition of carbanion donors such as organolithium compounds[3] and Grignard reagents[4] to metal carbonyls, or from reaction of metal carbonyl anions with alkyl halides[5,6] invites us to the straightforward electroreduction of a pair of an organic halide and a metal carbonyl. It has been known that, while electroreduction of alkyl halides leads to carbanions by way of anion radicals and/or radicals,[7] metal carbonyls are electrochemically reduced to relevant anions.[8]



(1)

The reaction between 1-bromopentane and $Fe(CO)_5$ was examined in detail. First of all, suitable solvent—electrolyte systems were sought by using divided cells, and the best results were achived with the acetonitrile (AN)—Et_4NOTs system as shown in Table.[9] When nonhalide electrolyte anions were used, sparingly soluble compounds formed coatings on the anode surface and led to a progressive increase in the cell voltage. Bu_4NI as an anodic addi-

$$RX + Fe(CO)_5 \xrightarrow{2e} \underline{1} \xrightarrow{H^+} RCHO \qquad (2)$$

Table. Conversion of 1-Bromopentane to Hexanal[a]

Solvent	Electrolyte	Cell[b]	Additive	Cathode[c]	Electricity[d] F/mol	Conversion %	Yield[e] %
AN	Et_4NBr	D	None	SS	2.0	88	71
AN	Et_4NOTs	D	f	SS	2.0	83	68
AN	Et_4NOTs	D	f	Pt	2.0	82	67
AN	Et_4NOTs	D	f	Cu	2.0	82	66
AN	Et_4NOTs	D	f	Ni	2.0	79	65
AN	Et_4NOTs	D	f	Pb	2.0	88	63
AN	Et_4NOTs	D	f	Hg	2.0	74	58
AN	Et_4NOTs	D	f	C	2.0	76	52
AN	Bu_4NClO_4	D	f	SS	2.0	83	57
AN	Bu_4NBF_4	D	f	SS	2.0	86	54
DMF	Et_4NOTs	D	f	SS	2.0	92	33
NMP	Et_4NOTs	D	f	SS	2.0	69	14
AN	Et_4NOTs	U	None	Pt	2.0	37	20
AN	Et_4NOTs	U	None	Pt	1.0	15	9
AN	Et_4NBr	U	None	Pt	2.0	42	23

[a] n-$C_5H_{11}Br$, 0.005 mol; $Fe(CO)_5$, 0.005 mol; Pt anode; current, 0.05 A. Proton donor, 2N HCl. [b] D, divided; U, undivided. [c] SS, steinless steel; C, vitreous carbon. [d] At present a character of denominator can not be specified between n-$C_5H_{11}Br$ and $Fe(CO)_5$. [e] Based on n-$C_5H_{11}Br$ used. [f] Bu_4NI.

tive was effective to avoid such a situation. Cathode materials had little effect on the yield of product. The use of an undivided cell remarkably depressed conversion.

In conversion of 1-halogenated pentanes into hexanal, the order of product yield became RBr > RI > RCl.

The cathodically generated iron acylate anions 1 react with another alkyl halide to afford ketones. For example, the iron caproylate anion gave, after quenching with methyl iodide, 2-heptanone in 37% yield. When equimolar amounts of benzyl bromide and $Fe(CO)_5$ were electroreduced and then treated with aqueous 2N HCl, dibenzyl ketone, toluene, and dibenzyl were formed in 53, 27, and 1% yield, respectively.[10] In this case, the second alkylation occurs during the electroreaction to afford the symmetrical ketone.

The preparation of hexanal from 1-bromopentane illustrates a typical procedure. The reaction was carried out in a divided cell with a stainless steel plate cathode having an area of 18 cm^2 and a Pt plate anode having the same area. The catholyte was made up of 50 mL of AN that contains 1-bromopentane (5 mmol), $Fe(CO)_5$ (5 mmol), and Et_4NOTs (3.5 g, 11.6 mmol). The anolyte was an AN solution that contains the same supporting electrolyte and the additive. During the electroreaction, the cathode and anode compartments were magnetically stirred under N_2 and a current of 50 mA was passed for about 5 h at a room temperature. The reduction was terminated after passage of 2 F/mol of added substrate.[11] After hydrolytic workup with aqueous 2N HCl, GLC analysis showed the presence of hexanal (68% yield based on 1-bromopentane used; 83% yield based on the substrate unrecovered) as the only product, together with a small amount of the bromide unreacted.

Recently, Petit and coworkers have made a brief report of electrochemical conversion of organic halides into aldehydes using $Fe(CO)_5$.[12] They used an undivided cell, THF solvent, and acetic acid as s source of formyl hydrogen. Under the conditions, the alkyl iodide was more suitable to the organic substrate.

The mechanism and scope of this reaction will be reported elsewhere.

References and Notes

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9. When organic bromides are used as substrates, the use of the AN—Et_4NBr system can also be recommended. The crude product obtained after evaporation of the solvent indicated the IR absorption band characteristic of the acyl C—O stretch[3b] at 1600 cm^{-1}. In a series of experiments, with a protolytic isolation procedure, the formation of the aldehyde is taken as a measure of acylation at iron.

10. (a) Identical products have also been produced by phase-transfer carbonylation.[6b] (b) Treatment of $Na_2Fe(CO)_4$ with benzyl bromide at -78°, followed by quenching with acetic acid at 25°, gives toluene as the major product along with a small amount of phenylacetaldehyde: M. P. Cooke, Jr., J. Am. Chem. Soc., 92, 6080 (1970).

11. Complete consumption of the bromide requires 2.2 F/mol.

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