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CONVERSION OF ORGANIC HALIDES BY CO INTO ALDEHYDES USING ELECTROREDUCED $Fe(CO)_5$

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Summary : Reduction of $Fe(CO)_5$ and RX (RX = EtI ; $PhCH_2Br$) by controlled potential electrolysis leads to the production of $Fe(CO)_5^{\dot{-}}$ and R$^{\cdot}$ radicals which, in CO, undergo stoechiometric carbonylation of the organic halide into aldehyde, after hydrolysis.

The use of the highly nucleophilic tetracarbonyl ferrate dianion, $Fe(CO)_4^{=}$ in organic and inorganic syntheses[1,2] has markedly grown in recent years. However, its sensivity[3] accounts for its limited use in carbonylation. Recently, an improved preparation of $Fe(CO)_4^{=}$ was described, involving hydroxide ions in phase transfer catalysis conditions[4].

Production of the radical anion $Fe(CO)_5^{\dot{-}}$ by electrochemical reduction of $Fe(CO)_5$ has been described by DESSY et al[5]. NARAYANAN and KOCHI[6] have established the interception of the electrogenerated radical anion $Fe(CO)_5^{\dot{-}}$ by tri-n-butyltin hydride to afford the well known formyliron carbonyl anion $Fe(CO)_4CHO^-$.

We now report the synthesis and the use of the reduced $Fe(CO)_5^{\dot{-}}$ species in the carbonylation of organic halides (EtI, EtBr and $PhCH_2Br$).

Controlled-potential electrolyses of a solution of the organic halide (0.89 mmol) in 30 mL of THF with small amounts of NBu_4PF_6 (ca 5 to 10 mg) are carried out in a one-compartment cell on a platinum basket cathode with a sacrificial iron anode. The electrolysis is performed after addition of 0.89 mmol of $Fe(CO)_5$ by fractions of ca 0.125 mmol under nitrogen and stopped after two electrons are consumed per iron atom. Nitrogen is displaced by CO and the solution is treated with 1 millimole of acetic acid for 15 min and analyzed by GLC.

Cyclic voltammetry of $Fe(CO)_5$ in THF + 0.1 M NBu_4PF_6 on a platinum electrode shows, as expected from a previous report[5], the formation of the radical anion $Fe(CO)_5^{\dot{-}}$ at E = -1.85V (vs Ag/AgCl). Cyclic voltammetry data for $PhCH_2Br$, EtI and EtBr, obtained in THF on a platinum electrode, indicate that their electrochemical reduction occurs respectively at -1.95, -2.3 and -2.7 volts (vs Ag/AgCl)(see table). Coulommetric experiments are carried out on $Fe(CO)_5$-RX mixtures at -2 and -2.5 volts. The results are compared in the table.

Table - Electroreduction of $\mathrm{Fe(CO)_5}$ in the presence of RX in THF^{a}

Run	RX	Reduction^{b} potential of RX(<u>vs</u>/Ag/AgCl)	Electrolysis^{c} potential (<u>vs</u>/Ag/AgCl)	Conv of RX %	Sel^{d} %	other products
1	EtI	- 2.3	- 2	10	5^{e}	-
2	$\mathrm{PhCH_2Br}$	- 1.95	- 2	75	29^{f}	$\mathrm{PhCH_3}$:35%;$\mathrm{(PhCH_2\text{-})_2}$:36%
3	EtI	- 2.3	- 2.5	87	70^{e}	$\mathrm{C_2H_4;C_2H_6;C_4H_{10}}$
4	EtBr	≤- 2.7^{g}	- 2.5	5	5^{e}	-
5	$\mathrm{PhCH_2Br}$	- 1.95	- 2.5	82	16^{f}	$\mathrm{PhCH_3}$:42%;$\mathrm{(PhCH_2\text{-})_2}$:42%

[a] In the conditions summarized in the text. [b] From cyclic voltammetry data. [c] $\mathrm{Fe(CO)_5 + e^- \longrightarrow Fe(CO)_5^{\cdot-}}$ reduction occurs at -1.85V. [d] Mole of aldehyde/mole of RX consumed x100. [e] Propanal. [f] phenylethanal. [g] The reduction peak of EtBr is hidden by the solvent reduction.

From these results, it appears that both $\mathrm{Fe(CO)_5}$ and RX must be reduced to $\mathrm{Fe(CO)_5^{\cdot-}}$ and $\mathrm{R^\cdot}$ to obtain good yields in aldehydes. The lack of selectivity and the production of bibenzyle and toluene as major products from $\mathrm{PhCH_2Br}$ are consistent with the direct reduction of $\mathrm{PhCH_2Br}$ into $\mathrm{PhCH_2^-}$ and also with the dimerization in solution of $\mathrm{PhCH_2^\cdot}$ produced by reduction of $\mathrm{PhCH_2Br}$ by $\mathrm{PhCH_2^-}$ [7]. Thus, the following reaction mechanism for selective aldehyde production can be proposed :

$$\left.\begin{array}{l} \mathrm{RX + e^- \longrightarrow RX^{\cdot-} \longrightarrow X^- + R^\cdot} \\ \mathrm{Fe(CO)_5 + e^- \longrightarrow Fe(CO)_5^{\cdot-}} \end{array}\right] \longrightarrow \mathrm{RFe(CO)_4^-}$$

$$\mathrm{RFe(CO)_4^- + CO \longrightarrow RCOFe(CO)_4^- \xrightarrow{H^+} RCHO + Fe(CO)_4}$$

REFERENCES AND NOTES

1. M.P. COOKE, J. Amer. Chem. Soc., **92**, 6080 (1970); J.P. COLLMAN, R.G.FINKE, J.N. CAWSE and J.I. BRAUMAN, J. Amer. Chem. Soc., **99**, 2515 (1977), and references therein.
2. J.P. COLLMAN, R.G. FINKE, P.L. MATLOCK, R. WAHREN, R.G. KOMOTO and J.I. BRAUMAN, J. Amer. Chem. Soc., **100**, 1119 (1978).
3. J.P. COLLMAN and R.G. KOMOTO, US patent (appl. filed 11 june 1973); J.A. GLADYSZ and W. TAM, J. Org. Chem., **43**, 2279 (1978); J.J. BRUNET, C. SIDOT and P. CAUBERE, J.Org. Chem., **46**, 3147 (1981).
4. H. Des ABBAYES, Isr. J. Chem. **26**, 249 (1985).
5. R.E. DESSY, F.E.STARY, R.B.KING and H. WALDROP, J. Amer. Chem. Soc., **88**, 471 (1966)
6. B.A. NARAYANAN and J.K. KOCHI, J. Organomet. Chem., **272**, C49 (1984).
7. D.A. KOCH, B.J. HENNE and D.E. BARTAK, J. Electrochem. Soc., **134**, 3062 (1987).

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