

**CONVERSION OF ORGANIC HALIDES BY CO INTO ALDEHYDES
USING ELECTROREDUCED $\text{Fe}(\text{CO})_5$**

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

The use of the highly nucleophilic tetracarbonyl ferrate dianion, $\text{Fe}(\text{CO})_4^{2-}$ in organic and inorganic syntheses^{1,2} has markedly grown in recent years. However, its sensitivity³ accounts for its limited use in carbonylation. Recently, an improved preparation of $\text{Fe}(\text{CO})_4^{2-}$ was described, involving hydroxide ions in phase transfer catalysis conditions⁴.

Production of the radical anion $\text{Fe}(\text{CO})_5^{\cdot -}$ by electrochemical reduction of $\text{Fe}(\text{CO})_5$ has been described by DESSY et al⁵. NARAYANAN and KOCHI⁶ have established the interception of the electrogenerated radical anion $\text{Fe}(\text{CO})_5^{\cdot -}$ by tri-n-butyltin hydride to afford the well known formyliron carbonyl anion $\text{Fe}(\text{CO})_4\text{CHO}^-$.

We now report the synthesis and the use of the reduced $\text{Fe}(\text{CO})_5^{\cdot -}$ 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 $\text{Fe}(\text{CO})_5$ 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.

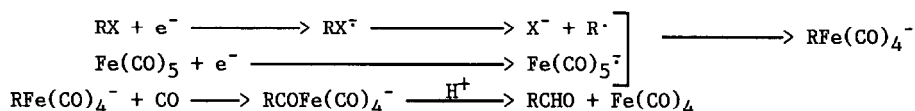
Cyclic voltammetry of $\text{Fe}(\text{CO})_5$ in THF + 0.1 M NBu_4PF_6 on a platinum electrode shows, as expected from a previous report⁵, the formation of the radical anion $\text{Fe}(\text{CO})_5^{\cdot -}$ at E = -1.85V (vs Ag/AgCl). Cyclic voltammetry data for PhCH_2Br , EtI and EtBr, obtained in 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). Coulometric experiments are carried out on $\text{Fe}(\text{CO})_5$ -RX mixtures at -2 and -2.5 volts. The results are compared in the table.

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

Run	RX	Reduction ^b potential of $\text{RX}(\underline{\text{vs}}/\text{Ag}/\text{AgCl})$	Electrolysis ^c potential $(\underline{\text{vs}}/\text{Ag}/\text{AgCl})$	Conv of RX %	Sel ^d %	other products
1	EtI	- 2.3	- 2	10	5 ^e	-
2	PhCH ₂ Br	- 1.95	- 2	75	29 ^f	PhCH ₃ :35%; (PhCH ₂ -) ₂ :36%
3	EtI	- 2.3	- 2.5	87	70 ^e	C ₂ H ₄ ; C ₂ H ₆ ; C ₄ H ₁₀
4	EtBr	≤ - 2.7 ^g	- 2.5	5	5 ^e	-
5	PhCH ₂ Br	- 1.95	- 2.5	82	16 ^f	PhCH ₃ :42%; (PhCH ₂ -) ₂ :42%

^aIn the conditions summarized in the text. ^bFrom cyclic voltammetry data. ^c $\text{Fe}(\text{CO})_5 + e^- \longrightarrow \text{Fe}(\text{CO})_5^-$ reduction occurs at -1.85V. ^dMole of aldehyde/mole of RX consumed x100. ^ePropanal. ^fphenylethanal. ^gThe reduction peak of EtBr is hidden by the solvent reduction.

From these results, it appears that both $\text{Fe}(\text{CO})_5$ and RX must be reduced to $\text{Fe}(\text{CO})_5^-$ and R^\cdot to obtain good yields in aldehydes. The lack of selectivity and the production of bibenzyle and toluene as major products from PhCH₂Br are consistent with the direct reduction of PhCH₂Br into PhCH₂⁻ and also with the dimerization in solution of PhCH₂[·] produced by reduction of PhCH₂Br by PhCH₂⁻ ⁷. Thus, the following reaction mechanism for selective aldehyde production can be proposed :



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