Electroformylation of Organic Halides in *N*,*N*-Dimethylformamide: an Efficient Electrosynthesis of Aldehydes

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In a cell fitted with a sacrificial magnesium anode and a modified cathode, the electroreduction of organic halides in *N*,*N*-dimethylformamide (DMF) gives aldehydes in good yields.

Since the first report by Bouveault,[1] it has been well established that organometallic species, including Grignard reagents, may be formylated by *N*,*N*-dimethylformamide (DMF)[2] to give, upon acidic workup, the corresponding aldehydes (equation 1).

$$\mathrm{RMgX + HCONMe_2 \rightarrow R{-}CH(OMgX){-}NMe_2 \xrightarrow{H_2O,\,H^+} RCHO + Me_2NH} \quad (1)$$

As an alternative the generation of carbanionic species by electroreduction of organic halides (RX) in DMF has been attempted but, until now, the yields were very low.[3] It has been shown that the use of sacrificial anodes of Mg, Al, or Zn improves the electroreductive coupling of RX with electrophilic reagents such as CO_2,[4,5] or carbonyl compounds.[6] We then attempted the synthesis of aldehydes RCHO by exhaustive electrolyses of RX in DMF.

The undivided cell, described elsewhere,[5] is fitted with a magnesium rod as the anode and a stainless steel (or nickel) grid as the cathode. The DMF solution contains RX (0.5 M) and Bu_4NBr (4×10^{-2} M) as supporting electrolyte. The electrolyses are carried out at room temperature and at constant current (1 A dm^{-2}). Complete consumption of RX requires 2.2 F. Aldehydes are obtained upon acidic workup and recovered by suitable extraction. Results reported in

Table 1. Electroformylation of organic halides.

Entry	Reagent	Electrolytic coating (method)[a]	Aldehyde	Yield[b] (%)
1	PhBr	no	PhCHO	36(30)
2	$4\text{-}FC_6H_4Br$	no	$4\text{-}FC_6H_4CHO$	25
3	$PhCH_2Cl$	no	$PhCH_2CHO$	30
4	$Me(CH_2)_7Br$	no	$Me(CH_2)_7CHO$	30
5	PhBr	Zn(A)	PhCHO	66
6	$4\text{-}CF_3C_6H_4Cl$	Zn(A)	$4\text{-}CF_3C_6H_4CHO$	70(55)
7	$PhCH_2Cl$	Zn(A)	$PhCH_2CHO$	67
8	PhBr	Cd(B)	PhCHO	75
9	$4\text{-}CF_3C_6H_4Cl$	Cd(A)	$4\text{-}CF_3C_6H_4CHO$	70(60)
10	$4\text{-}CF_3C_6H_4Cl$	Cd(B)	$4\text{-}CF_3C_6H_4CHO$	71
11	$4\text{-}CF_3C_6H_4Cl$	Cd(C)	$4\text{-}CF_3C_6H_4CHO$	80
12	$3\text{-}MeOC_6H_4Br$	Cd(B)	$3\text{-}MeOC_6H_4CHO$	69(56)
13	$4\text{-}FC_6H_4Br$	Cd(B)	$4\text{-}FC_6H_4CHO$	47
14	$1,2,4\text{-}Cl_3C_6H_3$	Cd(B)	$2,5\text{-}Cl_2C_6H_3CHO$[c]	50
15	$Me(CH_2)_7Br$	Cd(B)	$Me(CH_2)_7CHO$	30
16	2-Bromothiophene	Cd(B)	2-Thiophene carboxaldehyde	65
17	$4\text{-}CF_3C_6H_4Cl$	Sn(B)	$4\text{-}CF_3C_6H_4CHO$	85

[a] For methods A,B,C see the text. [b] G.c. yield; yield of isolated product in parentheses. [c] Main isomer: 2,5-dichlorobenzaldehyde.

Table 1 (entries 1—4) show that aldehydes are formed in only moderate yields, RH and RR being the main products.

We found that the yield of aldehyde is appreciably increased when the cathode is coated with a deposit of a metal M (M = Zn, Cd, or Sn) obtained by electroreduction of a salt MX_2 ($X^- = Br^-, Cl^-, AcO^-$). Similar results are obtained when this electrodeposition of M is carried out either prior to the electrolysis of RX (method A) or directly from the mixture of MX_2 and RX (method B). The same modified cathode can be used several times (method C). All the other experimental conditions are the same as those mentioned above and results are in Table 1 (entries 5—17).

Further investigations are necessary to understand the role of the electrodeposited metal and to define the scope and the limitations of the process. For the time being, it has been observed that the working potential of the modified cathode is much less cathodic than that measured for the unmodified one. Voltamperometric studies indicate similar behaviour since the RX electroreduction signal is anodically shifted (0.3 to 0.6 V) when a microelectrode is coated with electrolytic zinc, cadmium, or tin. No such effect is observed with other metallic deposits (Cu, Co, Ni) either in analytical or electrosynthetic experiments.

In addition, the Mg^{II} ions arising from the anode oxidation are certainly involved in the cathodic reaction since the aldehyde yield is very low in a divided cell,[3] even, as we have found, if a modified cathode is used.

In conclusion, the association of both techniques of sacrificial magnesium anode and modified cathode provides an efficient synthesis of some valuable aldehydes from organic halides.[7] This easily carried out one-pot reaction avoids the preparation and handling of organometallic intermediates in ethereal solvent, DMF being used both as the solvent and the formylating agent.

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