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ELECTROSYNTHESIS OF ALCOHOLS FROM ORGANIC HALIDES AND KETONES OR ALDEHYDES

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Abstract :

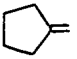
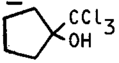
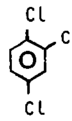
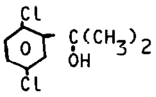
The electrosynthesis of a wide range of alcohols from organic halides and ketones or aldehydes is achieved under simple and mild conditions in an undivided electrolytic cell using different sacrificial anodes.

Earlier attempts to obtain alcohols by electroreduction of organic halides in the presence of carbonyl compounds have not been very successful. Benzylic and allylic halides gave satisfactory results, but these reactions are limited either by the use of hexamethylphosphorotriamide (1), a suspect of carcinogenicity, or by the exclusive use of allyl bromide in a very elegant process using electrochemically recycled tin (2). The cathodic reduction of CCl_4 or CCl_4-$CHCl_3$ mixtures, described by Schäfer (3) and Shono (4), gave trichloromethylcarbinols with good yields. This could also be applied to the synthesis of alcohols such as $RCHOHCCl_2CO_2CH_3$ from methyl trichloroacetate and various aldehydes.

We have recently reported a new and efficient method for the electrocarboxylation of organic halides using an undivided electrolytic cell and a sacrificial magnesium anode (5). The same process is now extended to the electrosynthesis of alcohols from organic halides and ketones or aldehydes (6).

The cell is a glass vessel (35 ml) fitted with two electrodes. The anode is a magnesium, aluminium, zinc or iron rod and the cathode is a cylindrical grid of stainless steel. Aprotic solvents such as dimethylformamide (DMF), tetramethylurea (TMU) or acetonitrile (AN) are used, and contain a small amount of supporting electrolyte (Bu_4NBF_4, Bu_4NBr, Bu_4NI or Et_4NBr, 2.10^{-2} M). The organic halide concentration is 1 M. Current densities as high as 4 A/dm^2 are applied. The cell is immersed in a cold bath to keep the temperature of

Table I

RX (mmoles)	>C=O (mmoles)	Solvent (30 ml)	Anode	Products (isolated yield based on RX)
$PhCH_2Cl$ (26)	CH_3COCH_3 (130)	DMF or DMF (5ml)- CH_3COCH_3 (25 ml)	Mg or Al	$PhCH_2\underset{OH}{C}(CH_3)_2$ <u>1</u> (70-75 %)
$PhCH_2Cl$ (26)	CH_3COCH_3 (130)	CH_3CN	Al	<u>1</u> (35 %)
$PhCH_2Cl$ (26)	CH_3COCH_3 (130)	TMU	Mg	<u>1</u> (75 %)
$PhCH_2Cl$ (26)	CH_3COCH_3 (130)	TMU	Zn	<u>1</u> (40 %)
$PhCH_2Cl$ (26)	$CH_3COC_2H_5$	DMF (5 ml)- $CH_3COC_2H_5$ (25 ml)	Mg	$PhCH_2-\overset{CH_3}{\underset{OH}{C}}-C_2H_5$ (50 %)
$PhCH_2Cl$ (30)	$CH_3(CH_2)_6-CHO$ (30)	DMF	Mg	$Ph-CH_2-\underset{OH}{C}H-(CH_2)_6-CH_3$ (60 %)
$CH_2=C\genfrac{}{}{0pt}{}{CH_3}{CH_2Cl}$ (23)	CH_3COCH_3	DMF (5 ml)- CH_3COCH_3 (25 ml)	Al	$CH_2=\overset{CH_3}{C}-CH_2\underset{OH}{C}(CH_3)_2$ (95 %)
$CH_3-CH=CH-CH_2Cl$ (30)	CH_3COCH_3	DMF (5 ml)- CH_3COCH_3 (25 ml)	Al	$CH_3-CH=CH-CH_2-\underset{OH}{C}(CH_3)_2$ <u>2</u> (30%) $CH_2=CH-\underset{CH_3}{C}H-\underset{OH}{C}(CH_3)_2$ <u>3</u> (65 %)
$CH_2=CH-\overset{Cl}{C}H-CH_3$ (30)	CH_3COCH_3	DMF (5 ml)- CH_3COCH_3 (25 ml)	Al	<u>2</u> (44 %) <u>3</u> (51 %)
$CH_2=C\genfrac{}{}{0pt}{}{CH_3}{CH_2Cl}$ (30)	PhCHO (150)	DMF	Al	$PhCHOH-CH_2-\underset{CH_3}{C}=CH_2$ (60 %)
$CH_3CHClCO_2C_2H_5$ (30)	CH_3COCH_3 (150)	DMF	Mg	$(CH_3)_2\underset{OH}{C}-\underset{CH_3}{C}H-CO_2C_2H_5$ (45 %)
$Cl_2CHCO_2CH_3$ (25)	CH_3COCH_3	DMF (5 ml)- CH_3COCH_3 (25 ml)	Zn	$(CH_3)_2\underset{OH}{C}-\underset{Cl}{C}H-CO_2CH_3$ (40 %)
CCl_4 (30)	CH_3COCH_3	DMF (5 ml)- CH_3COCH_3 (25 ml)	Zn	$(CH_3)_2\underset{OH}{C}-CCl_3$ (45 %)
CCl_4 (30)	PhCHO	DMF	Zn	$PhCHOHCCl_3$ <u>4</u> (80 %)
CCl_4 (30)	PhCHO	DMF	Fe	<u>4</u> (60 %)
CCl_4 (50)	 (100)	DMF	Zn	 (45 %)
CF_3Br a)	PhCHO (35)	DMF	Zn	$PhCHOHCF_3$ (98 %) b
CF_3Br a)	$CH_3(CH_2)_6CHO$ (35)	DMF	Zn	$CH_3-(CH_2)_6CHOHCF_3$ (90 %) b
CF_3Br a)	$PhCH_2COCH_3$ (35)	DMF	Zn	$PhCH_2\underset{OH}{C}\genfrac{}{}{0pt}{}{CF_3}{CH_3}$ (20 %) b
 (26)	CH_3COCH_3	DMF (5 ml)- CH_3COCH_3 (25 ml)	Mg	 (60 %)

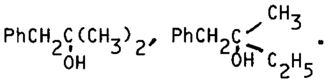
a) Electrolysis is performed under atmospheric pressure of gazeous CF_3Br

b) Yield based on initial >C=O.

the electrolyte between 0° C and 30° C. A constant current intensity is maintained until the quantity of electricity reaches 2-2.5 moles of electrons per mole of initial RX. Unreacted RX and side products such as R-H or R-R are analyzed by GPC. The alcohol is recovered by aqueous hydrolysis, purified by column chromatography and identified by NMR and mass spectroscopy.

Table I presents some results that clearly demonstrate the wide scope of the process and describe the influence of some experimental parameters.

It appears that the reaction can be successfully applied to various classes of organic halides, and ketones as well as aldehydes.

The process is particularly convenient to prepare products of industrial interest such as  $PhCH_2C(OH)(CH_3)_2$, $PhCH_2C(OH)(CH_3)C_2H_5$. These products have been prepared on a larger scale by forcing the electrolyte (1 to 2 l) to flow through a stainless steel tube acting as the cathode surrounding a magnesium or aluminium rod.

The electrochemical reactions can be written as follows :

$$\text{M-ne} \longrightarrow M^{n+} \text{ for the anodic process}$$

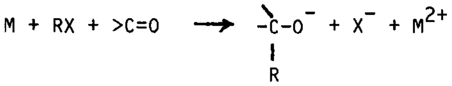
(proof was given by weighing the anode before and after the electrolysis)

$$RX + 2e \longrightarrow R^- + X^- \text{ for the cathodic process}$$

$$R^- + {>}C{=}O \longrightarrow R{-}C{-}O^-$$

The main side-reactions are the formation of RH and aldol-type condensation products of the carbonyl compound.

It can be considered that the present electrosynthesis, according to the total balance :



$$M + RX + {>}C{=}O \longrightarrow R{-}C{-}O^- + X^- + M^{2+}$$

consists of an electroassisted Barbier reaction. However, we have verified that the chemical reaction does not occur spontaneously under the conditions of solvent and temperature choosen for the electrosynthesis.

In some experiments the nature of the sacrificial anode appeared to be a crucial factor. The M/M^{n+} redox potential must be low enough to allow RX to be reduced and not M^{n+}.

The M^{n+} cation can activate the carbonyl or C-X linkage, stabilize the intermediary carbanion R^- or even associate with the product to limit further reaction.

We now attempt to elucidate the mechanism of the reaction and examine its scope and limitation.

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