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ELECTROCHEMICAL CARBOXYLATION OF BENZAL CHLORIDE

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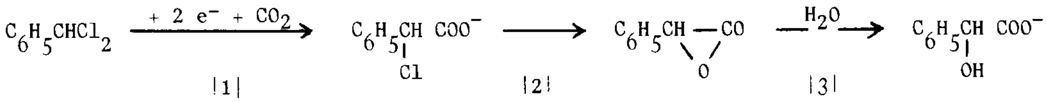
The electrocarboxylation of benzal chloride to -chlorophenylacetic and phenylmalonic acids is realized in diaphragmless cells with aluminium sacrificial anodes. Yields respectively up to 50 % and 30 % can be obtained. Phenylacetic acid is always present among the products.

The electrochemical carboxylation of organic monohalides is a promising procedure for the synthesis of carboxylic acids. On the contrary, the selective monocarboxylation and the dicarboxylation of gem-dihalides seemed to be impossible, following the experimental procedure proposed for monohalides. In fact, Wawzonek and Shradel (1) by electrocarboxylation of benzal chloride obtained, in very poor yields, only phenylacetic and mandelic acids, and did not detect any trace of phenylmalonic and α-chlorophenylacetic acids. The Authors propose a reaction mechanism in which the first step, the monocarboxylation to chlorophenylacetic acid, is followed by an intramolecular cyclization to the corresponding α-lactone, which would react rapidly with residual water to form mandelic acid :



$$C_6H_5CHCl_2 \xrightarrow[|1|]{+\ 2\ e^-\ +\ CO_2} C_6H_5\underset{\textstyle Cl}{CH}\ COO^- \xrightarrow[|2|]{} \underset{\textstyle \setminus\ O\ /}{C_6H_5CH - CO} \xrightarrow[|3|]{H_2O} C_6H_5\underset{\textstyle OH}{CH}\ COO^-$$

Our research group has been recently involved in the electrocarboxylation of organic monohalides (2) . In the course of this research we discovered that it is possible to improve substantially the yields of the carboxylation of these substrates introducing, in the electrolytic solution, inorganic species released by suitable sacrificial anodes. In this communication we report the first results we have obtained extending our investigation to the electrocarboxylation of gem-dihalides. Using aluminium anodes, in diaphragmless cells, we have realized the mono and the dicarboxylation of benzal chloride with appreciable yields. Al(III) species, continuously released by the sacrificial anode, totally hinder the formation of mandelic acid. Most probably

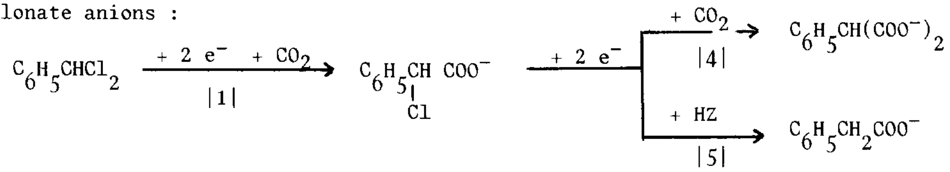
TABLE. ELECTROCHEMICAL CARBOXYLATION OF BENZAL CHLORIDE

expt.	substrate	pCO_2	F/M	product yields(% vs. converted substrate)		
n°	moles.10^{-2}	Atm		phenylacetic	Cl-phenylacetic	phenylmalonic
1	1.62	1	1.87	29	52	--
2	0.81	1	4.99	28	32	17
3	1.95	7	4.7	29	28	30
4	1.95	24	4.16	10	55	20

Solvent-supporting electrolyte = DMF(50cm^3)-Bu_4NBr 0.1M; anode = Al 99.9% ; cathode = Zn 99% ; cathodic current density 100 A m^{-2} ; F/M = charge passed vs. moles of substrate; Al salts (see text) were hydrolized and the acids were determined chromatographically; conversions = 80 - 100%.

there is a coordination of the intermediate carboxylate anions onto the metal cations, with the consequent inhibition of the reaction |2| . In fact, in the effluents from the electrolyses the acids are present as Al(III) salts. It can be deduced from the results summarized in the table that it is possible to address the synthesis towards the monocarboxylation to α-chlorophenylacetic acid controlling the quantity of charge passed through the cell (expt. 1) or the concentration of carbon dioxide in the electrolytic solution (expt. 4). Phenylacetic acid yield can be minimized only at very high concentrations of carbon dioxide (expt. 4) .

It is rather obvious to assume that the process goes through the intermediate α-chlorophenylacetate anion which, by further reduction gives rise to both phenylacetate and phenylmalonate anions :



$$C_6H_5CHCl_2 \xrightarrow[|1|]{+\,2\,e^- \;\; +\,CO_2} C_6H_5\underset{Cl}{CH}\,COO^- \xrightarrow{+\,2\,e^-} \left[\begin{array}{l} \xrightarrow[|4|]{+\,CO_2} C_6H_5CH(COO^-)_2 \\ \xrightarrow[|5|]{+\,HZ} C_6H_5CH_2COO^- \end{array}\right.$$

The protic agent HZ , active in addressing the synthesis towards the undesired phenylacetic acid (react.|5|) could be the solvent (N,N-dimethylformamide) or, most probably, benzal chloride itself, which could be involved in a self protonation mechanism.

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2) G. Silvestri, S. Gambino, G. Filardo, Italian Pat. Appl. N° 21789 A/82 (1982)/

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