ELECTROCHEMICAL CHLOROMETHYLATION OF CH-ACIDS BY THE ACTION of $\mathrm{CH}_2\mathrm{Cl}_2$

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We are the first to report that the cathodic electrolysis of β -dicarbonyl compounds (I), containing an activated C-H bond, in CH₂Cl₂ leads to the formation of their chloromethyl derivatives (II) in 40-60% yield. This reaction may be described by a scheme involving the cathodic generation of a carbanion from (I) and its reaction with CH₂Cl₂ by a nucleophilic substitution mechanism to give (II).

$$\begin{array}{c} R^{1} & R^{1} & R^{1} \\ EtOOC-CH \xrightarrow{+ e} EtOOC-C^{-} \xrightarrow{CH_{2}Cl_{2}} EtOOC-C-CH_{2}Cl \\ R^{2}CO & R^{2}CO & R^{2}CO & (IIa-c) \\ (Ia-c) & \end{array}$$

 $R^1 = Me, R^2 = OEt(a); R^1 = R^2 = Me, R^1 = CH_2CH_2CN, R^2 = OEt(c).$

During the electrolysis, (II) may undergo dehalogenation but the methylation products, $EtO_2CC(R^1)(Me)COR^2$, are formed in only 7-10% yield under the conditions described. On the other hand, the methylation reaction is predominant [1] upon the electrolysis of NH-acids in CH_2Cl_2 .

The electrolyses of 0.1 mole/liter (Ia)-(Ic) were carried out in a diaphragm cell at 20°C in 0.25 N Bu₄NBr in absolute CH_2Cl_2 on a platinum cathode (1.5-1.6 F/mole, 2-3 mA/cm²) in an argon atmosphere. CH_2Cl_2 was distilled off the reaction mixture and the residue was extracted with hexane. Hexane was distilled off and distillation of the residue in vacuum gave (II) and a trace of (III) (the product ratio was determined by gas-liquid chromatography). The structures of the compounds obtained were supported by chromato-mass spectrometry and PMR spectroscopy.

LITERATURE CITED

1. M. E. Niyazymbetov, T. K. Baryshnikova, V. A. Petrosyan, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2874 (1987).

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