Electrolytic Oxidation of Dicarboxylic Acids

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IN a continuing study of organic electrode reactions, we attempted the oxidation of disodium malonate in the hope of producing a carbene or carbene-like intermediate.

$$CH_2(CO_2^-Na^+)_2 \xrightarrow{-e^-} 2\,CO_2 + :CH_2$$

We report that the products of the electrolysis of disodium malonate in methanol and in the presence of cyclohexene gave no evidence for a carbene intermediate. A specific search for norcarane and the methylcyclohexene isomers proved negative.

The major product of the distillable material gave a mass spectrum which indicated cyclohexenyl methyl ether. The n.m.r. spectrum showed a multiplet at τ 7·8—8·5 (ring protons), a singlet τ 6·65 ($CH_3\cdot O$) and other multiplets at τ 6·25 ($CH\cdot O$) and τ 4·2 (CH:CH). The assigned values compare well with those reported for cyclohex-2-enol[1] and 3-methoxybutanol.[2] A comparison of the infrared spectra of the product with that of an authentic sample[3] of cyclohex-2-enyl methyl ether showed that they were identical with an additional small peak at 1745 cm.$^{-1}$ appearing in the former. This peak is attributed to a small ester impurity.

From this evidence we conclude that the diacid was probably oxidized in steps, and the resulting radicals abstracted an allylic hydrogen from cyclohexene forming a cyclohexenyl free-radical. Subsequent oxidation of the cyclohexenyl radical formed the corresponding carbonium ion which ultimately reacted with the methanol and thus resulted in the observed ether. The small ester impurity probably arose *via* a radical path.

Although we were unable to find evidence to support the presence of a carbene intermediate, it is interesting to note that in this reaction the formation of carbonium ions appears to be favoured over the free-radical pathway typical in a normal Kolbe electrolysis. We are presently studying the electrolysis of substituted malonates; preliminary evidence supports the above conclusions.

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[1] G. V. D. Tiers, Exploratory N.m.r. Studies, Project 737602, Minnesota Mining and Manufacturing Co., 1958.

[2] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, N.m.r. Spectra Catalog, Varian Associates, Palo Alto, Calif., Spectrum No. 120.

[3] Authentic cyclohex-2-enylmethyl ether was prepared from cyclohex-2-enol *via* a Williamson synthesis.