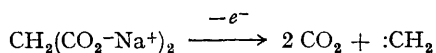


Electrolytic Oxidation of Dicarboxylic Acids

By E. K. SPICER and H.-G. GILDE

(Department of Chemistry, Marietta College, Marietta, Ohio 45750)

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.



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 norcaradiene 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 ($\text{CH}_3\text{-O}$) and other multiplets at τ 6.25 (CH-O) and τ 4.2 (CH:CH). The assigned values compare well with those reported for cyclohex-2-enol¹ and 3-methoxybutanol.² A comparison of the infrared spectra of the product with that of an authentic sample³ 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.

We acknowledge financial support from the Research Corporation, and we thank Dr. W. W. Paudler for the n.m.r. and mass spectra.

(Received, February 27th, 1967; Com. 194.)

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.