

The Anodic Oxidation of Carbanions in Ethanol

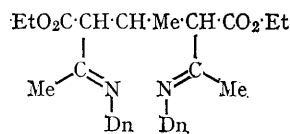
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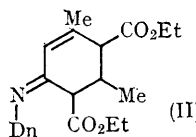
WE have shown that all the products obtained when an ethanolic solution of ethyl sodioacetoacetate is electrolysed at a platinum anode, with a mercury cathode, arise by the base-catalysed condensation of ethyl acetoacetate and acetaldehyde. Presumably the resonance-stabilised radicals formed by the anodic oxidation of the carbanions abstract hydrogen from the solvent to give radicals which by disproportionation lead to acetaldehyde and ethanol. The products were treated with 2,4-dinitrophenylhydrazine, and the derivatives were separated by a combination of column and thin-layer chromatography. The characterisation of several closely related derivatives, with structures which include (I) and (II) leaves no doubt about the nature of the products. Diethyl $\alpha\alpha'$ -diacetylsuccinate is the only previously reported^{1,2} product of the electrolysis of ethyl sodioacetoacetate, but we have been unable to detect any of compound (III) which is formed³ from this diketo-ester and 2,4-dinitrophenylhydrazine.

The two major products from the electrolysis of

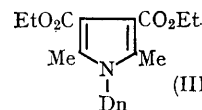
diethyl sodiomalonate in ethanol are tetraethyl ethane-1,1,2,2-tetracarboxylate (as previously reported¹) and tetraethyl 2-methylpropane-1,1,3,3-tetracarboxylate, which arise by the coupling of diethyl malonate radicals, and the condensation of diethyl malonate with acetaldehyde respectively.



(I)



(II)



(III)

(Dn = 2,4-dinitroanilino)

(Received, August 6th, 1965; Com. 494.)

¹ S. P. Mulliken, *Amer. Chem. J.*, 1893, **15**, 523; T. Okubo and S. Tsutsumi, *Technol. Reports Osaka Univ.*, 1963, **13**, (589), 495.

² J. B. Weems, *Amer. Chem. J.*, 1894, **16**, 569.

³ T. D. Binns, Thesis, Sheffield, 1965.