The Electrolysis of β-Diketones

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THE only previous account of the electrolysis of β-diketones appears to be that by Mulliken,[1] who reported that the prolonged electrolysis of acetylacetone in 50% aqueous methanol afforded a small quantity (2%) of tetra-acetylethane (I).

TABLE

β-Diketone	Solvent	Dehydrogen-dimer Formula	 m.p.	Yield (%)
Acetylacetone	Water	(I)	191°*	11
Cyclohexane-1,3-dione (IIa)	Water	(IIIa)	131°	20
5-Phenylcyclohexane-1,3-dione (IIb)	50% Aqueous methanol	(IIIb)	224°	20
5,5-Dimethylcyclohexane-1,3-dione (IIc)	20% Aqueous methanol	(IIIc)	195°	30
5-Methylcyclohexane-1,3-dione (IId)	25% Aqueous methanol	(IIId)	151°	50

* m.p. 191° (ref. 3).

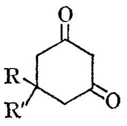
We now report that when this reaction was repeated in aqueous sodium hydroxide (0·1M) using smooth platinum electrodes and an anode current density of 1 amp cm.$^{-2}$, a considerably better yield (11%) of (I) was obtained. Attempts to increase the yield of (I) further, by variation of the duration or temperature of the electrolysis, or the composition of the solvent, have so far failed.

The electrolysis of several cyclic β-diketones (II) in aqueous or aqueous methanolic sodium hydroxide solution gave even higher yields of new dehydrogeno-dimers (III) and the results of these experiments are summarised in the Table.

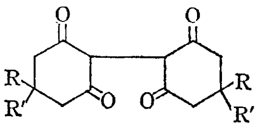
The n.m.r. spectrum of the dehydrogeno-dimer of (IId) provides support for the proposed structure (IIId), and also indicates that when the compound is dissolved in carbon tetrachloride, approximately 25% of the labile hydrogen is attached to oxygen, although the relative proportion of mono- and bis-enols is not known. The infrared spectra of the dehydrogeno-dimers corresponding to (III) show that they exist exclusively in bis-enol forms in the solid state.

These coupling reactions are analogous to those which take place during the electrolysis of phenols yielding hydroxybiphenyls,[2] and probably proceed *via* production at the anode and subsequent dimerisation in the carbon-centred form of the mesomeric radicals of type (IV). Kharasch, McBay, and Urry[3] proposed that tetra-acetylethane arises by the coupling of radicals of type (IV) when acetyl peroxide is allowed to decompose in acetylacetone.

$(MeCO)_2\cdot CH\cdot CH(CO\cdot Me)_2$ (I)

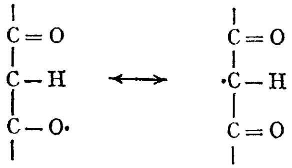


(II)



(III)

a; R = R′ = H; b; R = H, R′ = Ph; c; R = R′ = Me; d; R = H, R′ = Me



(IV)

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[1] S. P. Mulliken, *Amer. Chem. J.*, 1893, **15**, 523.

[2] F. Fichter, "Organische Electrochemie", Dresden, 1942, p. 110.

[3] M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Amer. Chem. Soc.*, 1948, **70**, 1270.