

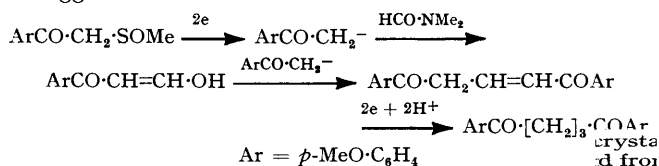
Formation of a δ -Diketone in the Cathodic Cleavage of a β -Keto-sulphoxide

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Electrolytic reductive cleavage on mercury of the β -keto-sulphoxide, *p*-methoxy-2-(methylsulphinyl)acetophenone at pH 12 in aqueous dimethylformamide gives as main product a δ -diketone, 1,3-di-*p*-anisoylpropane. *i.e.* a compound containing an odd number of carbon atoms. It is suggested that this compound is formed *via* a carbanionic mechanism, dimethylformamide acting as a formylating agent.

THE cathodic cleavage of β -keto-sulphoxides, yielding ketones as the main product, has recently been described.¹ Mercury is used as the cathode in a divided cell, and the pH value of the catholyte is maintained at 11 by automatic titration with mineral acid. The solvent is 50% aqueous dimethylformamide, and potassium nitrate is used as the supporting electrolyte.

During the electrolysis of *p*-methoxy-2-(methylsulphinyl)acetophenone, the pH value on one occasion was allowed inadvertently to rise to over 12.5. In this run, a ^{ate is used electrolytically} by-product, 1,3-di-*p*-anisoylpropane, separate ^{phenone, inadvertently} in the catholyte. To explain the formation of this δ -diketone the mechanism indicated in Scheme 1 is suggested.

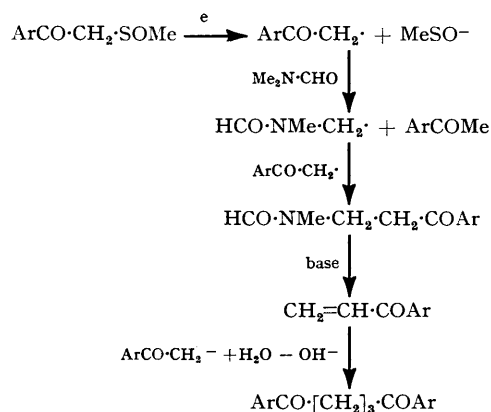


SCHEME 1 Carbanion mechanism for formation of 1,3-di-*p*-anisoylpropane

It is interesting to compare the present result with those obtained by Brettle and his co-workers²⁻⁴ on anodic oxidation of dialkyl sodiomalonates and similar enol salts in various non-aqueous solvents. In addition to the expected dimers, homologues containing one or two more carbon atoms (depending upon the particular solvent used) were obtained. Brettle and his co-workers have suggested a radical mechanism for the formation of these unexpected compounds.

With this work in mind, it was easy to suggest an alternative explanation in the present case, too. Al-

though, contrary to the conditions in Brettle's work, ours is a cathodic process, radicals may be formed upon electron transfer through cleavage of a C-S bond. Scheme 2 illustrates the formation of the δ -diketone according to this hypothetical route.



SCHEME 2 Radical mechanism for formation of 1,3-di-*p*-anisoylpropane

The origin of the odd, central carbon atom in the final product is different in the two cases represented by Schemes 1 and 2, being respectively, the carbonyl carbon atom and a methyl carbon atom of the dimethylformamide. By modifying the solvent, Brettle and co-workers could trace the origin to the methyl group in their case. When, for example, *NN*-dimethylacetamide was used, the same product was obtained. On the contrary, different products were obtained in methanol and in ethanol, respectively.

² T. D. Binns and R. Brettle, *J. Chem. Soc. (C)*, 1966, 336.

³ R. Brettle and J. G. Parkin, *J. Chem. Soc. (C)*, 1967, 1352.

⁴ R. Brettle and D. Seddon, *J. Chem. Soc. (C)*, 1970, 1153.

¹ B. Lamm and B. Samuelsson, *Acta Chem. Scand.*, 1969, **23**, 691.

The same technique was applied in our case. Two other solvents, aqueous *NN*-dimethylacetamide and aqueous *NN*-diethylformamide, were tried, but in neither case was any δ -diketone obtained. These results can only be reconciled with the mechanism illustrated in Scheme 1, particularly since Brettle and his co-workers obtained even higher yields of 'methylene-incorporation' products in *NN*-dimethylacetamide than in dimethylformamide. A precedent for the last step in Scheme 1, reduction of the unsaturated ketone $\text{ArCO}\cdot\text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{COAr}$, is described in the literature; reduction of benzylideneacetophenone and benzylideneacetone in basic solution gives the corresponding ketones.⁵

A modification of the carbanionic mechanism (Scheme 1) could involve formation of some formaldehyde through hydrolysis of the dimethylformamide and reduction. One molecule of formaldehyde might then be attacked stepwise by two carbanions $\text{ArCO}\cdot\text{CH}_2^-$ (with intervening elimination) to yield the final product. This is, however, made less likely by the fact that under still more basic conditions (0.5 pH unit) than those giving optimal yield of the δ -diketone, hardly any of the latter compound is formed. If the pH value is too high the concentration of $\text{ArCO}\cdot\text{CH}=\text{CH}\cdot\text{OH}$ (see Scheme 1) may be insufficient to allow the reaction with $\text{ArCO}\cdot\text{CH}_2^-$ to proceed at a sufficient rate, the β -keto-aldehyde being in equilibrium with its conjugate base. Hydrolysis of dimethylformamide to yield formic acid should increase with pH in this range and its subsequent reactions should not be retarded.

⁵ R. Pasternak, *Helv. Chim. Acta*, 1948, **31**, 753.

⁶ R. N. Gourley and J. Grimshaw, *J. Chem. Soc. (C)*, 1968, 2388.

In order to obtain optimum yields of the δ -diketone the latter had to be removed continuously by passing the catholyte through a filter. Otherwise the δ -diketone became further reduced. The reduction of 1,3-dianisoylpropane has been studied by Gourley and Grimshaw.⁶

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus.

The electrolyses were performed in the apparatus previously described,⁷ with the difference that the anolyte and catholyte were separated by a sintered glass diaphragm of porosity 3. A filter was connected in series with the pump.

In a typical run, *p*-methoxy-2-(methylsulphonyl)acetophenone¹ (10.6 g, 0.05 mol) was dissolved in 50% aqueous dimethylformamide (200 ml) containing potassium nitrate (10 g) as supporting electrolyte. The pH of the catholyte as measured by a glass electrode was adjusted to 12 with 2*M*-sodium hydroxide. The catholyte was then titrated automatically with 2*M*-hydrochloric acid. The potentiostat (Amel model 555) was adjusted to -1.3 V *vs.* a standard calomel electrode. The electrolysis was interrupted when the residual current was attained. The 1,3-di-*p*-anisoylpropane collected on the filter was recrystallized from ethanol; yield 3.5 g (50%), m.p. 101° (lit.,⁶ 99–100°).

Dilution of the catholyte with water (300 ml), saturation with sodium chloride, and extraction with pentane (3 \times 250 ml) afforded crude *p*-methoxyacetophenone (2.4 g 34%) as the product of normal cleavage.

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⁷ B. Lamm and B. Samuelsson, *Acta Chem. Scand.*, 1970, **24**, 561.