Tetrahedron Letters No.9, pp. 837-839, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE ELECTROLYSIS OF SOME HYDROXYACETOPHENONES

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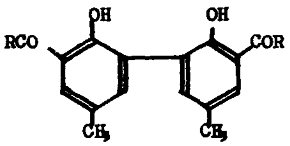
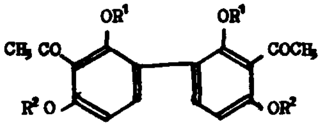
(Received 19 December 1966)

Attention has been drawn[1] to the scarcity of recent examples of successful electrolytic coupling reactions of phenols, and almost all previously reported studies[2,3] of such reactions, mainly by Fichter[2] and his colleagues, have been concerned with the electrolysis of phenols containing only alkyl and alkoxy substituents. It is now reported that an investigation of the electrolytic behaviour of phenols, including a re-examination of some of the earlier work, has been initiated, using conditions similar to those employed in the successful coupling of β-diketones[4], i.e. electrolysis in aqueous methanolic sodium hydroxide (0.1 M) at c. 50°, between smooth platinum electrodes with an anode current density of c. 1 amp. cm^{-2}., for 10 - 20% longer than the theoretical time.

The most interesting results so far obtained have been with hydroxyacetophenones. Although no dehydrogeno-dimer was formed in the electrolysis of p-hydroxyacetophenone, distillation in vacuo of the products from the electrolysis of o-hydroxyacetophenone gave a fraction which was found to contain 3,3'-diacetyl-4,4'-dihydroxybiphenyl, identified by undepressed m.p. on admixture with authentic material synthesised as previously described[5] by a double Fries rearrangement on the diacetate of 4,4'-dihydroxybiphenyl. Similar fractions from the electrolysis of 5-methyl-2-hydroxyacetophenone and from 5-methyl-2-hydroxybenzophenone afforded new dehydrogeno-dimers[*], to which structures Ia and Ib were assigned, since coupling must have occurred through the only unsubstituted reactive[**] position in both cases.



I a, R = CH_3
b, R = C_6H_5



II a, $R^1 = R^2 = H$
b, $R^1 = CH_3$, $R^2 = H$

Re-investigation of the electrolysis of resorcinol resulted in the recovery of the starting material in good yield and neither a biphenyl derivative nor the "unstable peroxide" reported to be formed under considerably different conditions[6], was obtained. Electrolysis of 2,6-dihydroxyacetophenone, however, gave a new dehydrogeno-dimer, which was formulated as IIa, since coupling must have occurred through either of the two equivalent reactive positions.[**]

TABLE I

Substrate	Dehydrogeno-dimer fraction		Dehydrogeno-dimer	
	b.p.	Yield(%)	Formula	m.p.
o-Hydroxyacetophenone	170-190°/1 mm.	7	-	215° †
5-Methyl-2-hydroxyacetophenone	230-240°/1 mm.	26	Ia	187°
5-Methyl-2-hydroxybenzophenone	250-260°/1 mm.	17	Ib	202°
2,6-Dihydroxyacetophenone	200°/1.5 mm.	52	IIa	230°

† (lit.[5] m.p. 219°)

These results, which are summarised in the Table, are of interest in view of current researches[7] into the role of oxidative coupling of phenols

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[*] Satisfactory elemental analysis and molecular weight determinations were obtained for all new compounds.

[**] *ortho*- or *para*- to the hydroxyl group.

in biosynthesis, particularly since 3,3'-diacetyl-4,4'-dihydroxy-2,2'-dimethoxybiphenyl (IIb) has been shown[8] to be a degradation product of ergoflavin and ergochrysin and it has been suggested[9] that oxidative coupling is involved in the biogenisis of ergoflavin.

REFERENCES

[1] A. I. Scott, Quart. Rev., XIX, 12 (1965)

[2] F. Fichter, Organische Electrochemie, Dresden (1942)

[3] M. J. Allen, Organic Electrode Processes, Chapman and Hall, London (1958)

[4] K. M. Johnston and J. D. Stride, Chem. Comm., 323 (1966)

[5] R. Pakkal, F. D. Thomas II, and W. C. Fernelius, J. Org. Chem., 25, 283, (1960)

[6] M. Abribat, Sci. Ind. photogr. (2), 1, 1, 41 (1930), in ref. 2 p. 113

[7] e.g. A. Penttila and H. M. Fales, Chem. Comm., 657 (1966) and H. Davies, H. Erdtmann, and M. Nilssen, Tetrahedron Letters, 2491, (1966)

[8] J. W. ApSimon, J. A. Corran, N. G. Creasey, K. Y. Sim, and W. B. Whalley, J. Chem. Soc., 4130 (1965)

[9] J. D. M. Asher, A. T. McPhail, J. Monteath Robertson, J. V. Silverton, and G. A. Sim, Proc. Chem. Soc., 210 (1963)