Oxidation of Veratrole by Quinones

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9,10-PHENANTHRENEQUINONE and acenaphthenequinone react with veratrole in 70% v/v aqueous sulphuric acid to give the condensation products 2,3,6,7-tetramethoxyphenanthro[9,10-*l*]phenanthrene and 2,2-bis-(3,4-dimethoxyphenyl)acenaphthenone respectively.[1] A completely different reaction occurs when quinones having higher oxidation potentials are used. Thus a mixture of chloranil (2·5 moles), veratrole (1·0 mole) and 70% v/v aqueous sulphuric acid kept at room temperature for 10 days deposited a blue precipitate from which a colourless solid $C_{18}H_6(OMe)_6$ (73%), m.p. 317—318·5° (evacuated capillary), was obtained. The ultraviolet absorption of this substance resembles that of triphenylene while the proton magnetic resonance spectrum shows singlets at τ 2·20 and 5·85 corresponding respectively to 18 methoxyl protons and to 3 pairs of *para*-orientated aromatic protons, and the compound is accordingly 2,3,6,7,10,11-hexamethoxytriphenylene (I).[2] Tetrachloro-1,2-benzoquinone was almost as effective as chloranil in this oxidation but bromanil, 2,3-dichloro-5,6-dicyano-, and 2,6-dichloro-1,4-benzoquinone gave somewhat lower yields. The same product was formed when a mixture of 3,4,3′,4′-tetramethoxybiphenyl (1·0

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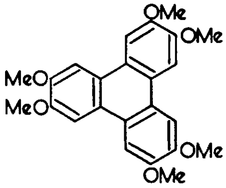
[1] I. M. Davidson, O. C. Musgrave, and (in part) D. L. Manson, *J. Chem. Soc.*, 1965, in the press.
[2] I. M. Davidson, M.Sc. Thesis, Aberdeen, 1963.

mole) and veratrole (1·0 mole) was treated with chloranil (5·7 mole) in 70% v/v aqueous sulphuric acid. The yield (154% based on the veratrole alone) indicates that the tetramethoxybiphenyl is incorporated very efficiently into the product and is therefore an intermediate in the oxidation of veratrole by chloranil. As chloranil is a powerful abstractor of hydride-ion in acid solution,[3] we suggest that the oxidation of veratrole proceeds by a series of hydride-ion abstractions each accompanied by a substitution reaction of the resulting cation giving consecutively 3,4,3′,4′-tetramethoxybiphenyl, 3,4,4′,5′,3″,4″-hexamethoxy-*o*-terphenyl, and the hexamethoxytriphenylene (I). A by-product,[4] m.p. 314·5—316°, recently obtained in very low (0·08%) yield from the acylation of veratrole by acetyl chloride and aluminium chloride in toluene has also been formulated as the hexamethoxytriphenylene (I) and appears to be identical with our product; in this case the oxidising agent is presumably atmospheric oxygen. We have found that veratrole is not appreciably oxidised under typical Scholl conditions[5] using nitrobenzene and aluminium chloride.

The formation of the hexamethoxytriphenylene (I) in high yield by the reaction of veratrole with chloranil is the simplest synthesis of a substituted triphenylene from readily available starting materials yet reported.



(I)

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[3] E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 1954, 3548.

[4] F.-H. Marquardt, *J. Chem. Soc.*, 1965, 1517.

[5] A. T. Balaban and C. D. Nenitzescu, "Friedel-Crafts and Related Reactions," ed. G. A. Olah, Interscience Publishers, New York, 1964, Vol. II, part 2, p. 979.