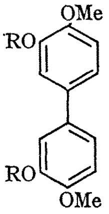
Formation of Polycyclic Quinones in Oxidations of 3,3',4,4'-Tetramethoxybiphenyl and Veratrole

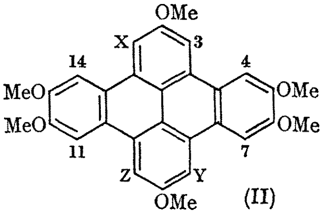
By O. C. MUSGRAVE* and C. J. WEBSTER
(*Chemistry Department, The University, Old Aberdeen* AB9 2UE)

Summary The oxidation of 3,3',4,4'-tetramethoxybiphenyl by chloranil in 70% v/v aqueous sulphuric acid gives 2,5,6,9,12,13-hexamethoxydibenzo[*fg,op*]naphthacene-1,8-quinone (III) in 75% yield while the isomeric 1,10-quinone (IV) is formed in 7% yield during the oxidation of veratrole under similar conditions.

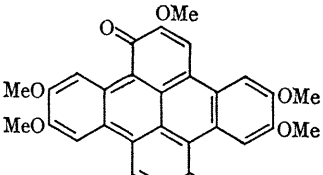
3,3'4,4'-TETRAMETHOXYBIPHENYL (Ia) is oxidised by chloranil in 70% v/v aqueous sulphuric acid and gives as the sole isolable product (75%) an almost insoluble, involatile, intense purple quinone (Q_t). Consistent analytical values could not be obtained for this, but it forms a leucoacetate $C_{24}H_6(OMe)_6(OAc)_2$ m.p. 316—317·5° and a leucomethyl ether $C_{24}H_6(OMe)_8$ m.p. 222·5—223·5° indicating the molecular formula $C_{24}H_6O_2(OMe)_6$. By successive reduction, demethylation, and acetylation the quinone gave an octa-acetate $C_{24}H_6(OAc)_8$ which shows u.v. absorption resembling very closely that[1] of dibenzo[*fg,op*]naphthacene $C_{24}H_{14}$ so establishing that it has the same conjugated system [as in (II)]. The C_{24} skeleton indicates that the quinone is formed from two molecules of the tetramethoxybiphenyl by repeated Scholl reactions followed by oxidative demethylation of the resulting octamethoxy compound $C_{24}H_6(OMe)_8$. Of the three possible arrangements of the methoxy-groups in the latter compound the most favoured sterically is (II; X = Y = MeO, Z = H) and this structure is in full accord with the observed n.m.r. spectrum which shows the presence of four kinds of methoxy-proton (s, 6H τ 6·04, 5·85, 5·83, and 5·75) and of only three types of aromatic proton [s, 2H, τ 2·03 and 1·85 (3-H and 10-H; 4-H and 11-H) and τ 0·63 (7-H and 14-H)]. There are ten different ways in which the oxidative demethylation of (II; X = Y = MeO, Z = H) might occur to give a quinone but eight of the possible structures can be excluded by the following observations. Firstly the n.m.r. spectrum of the leucoacetate shows the presence of only three types of aromatic proton (s, 2H) τ 1·76, 1·55, and 1·32 implying that a centrosymmetric arrangement is present in the parent quinone. Secondly, the isolation of 4,5-dimethoxyphthalic acid from the chromic acid oxidation of the quinone indicates that the terminal rings of the naphthacene system are benzenoid, not quinonoid. The two structures for the quinone Q_t remaining to be considered are the 2,5,6,9,12,13-hexamethoxy-1,8-quinone (III) and the closely related 1,5,6,8,12,13-hexamethoxy-2,9-quinone. A decision between these became possible when the preparation of the quinone was repeated using the partly deuteriated tetramethoxybiphenyl (Ib). The product was found by mass spectrometry to have been formed without loss of deuterium which indicates that the quinone Q_t has the structure (III) since formation of the 2,9-quinone would have resulted in the loss of two trideuteriomethyl groups during the oxidative demethylation step.



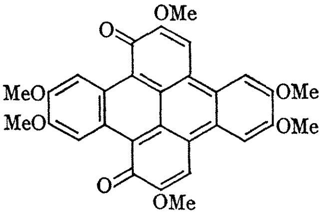
(I)
(a); R=CH_3
(b); R=CD_3



(II)



(III)



(IV)

We have previously reported[2] that veratrole is efficiently oxidised by chloranil in 70% v/v aqueous sulphuric acid to give 2,3,6,7,10,11-hexamethoxytriphenylene and have now isolated the minor product (7%) which is responsible for the intense purple colour of the reaction mixture. This proves to be a quinone (Q_v) with properties which resemble those of the quinone Q_t (III). Q_v leucoacetate, m.p. 275—277·5°, is closely related to Q_t leucoacetate, and Q_v leucomethyl ether, m.p. 283—284°, to Q_t leucomethyl ether. In each case the two compounds have the same molecular formula and show similar u.v. absorption. It follows that the Q_v derivatives also contain the conjugated system shown in (II) and that Q_v itself, like Q_t, is a hexamethoxydibenzo[*fg,op*]naphthacenequinone with the molecular formula $C_{24}H_6O_2(OMe)_6$. The orientation of the substituents in the Q_v series was established in the following manner. The n.m.r. spectrum of Q_v leucomethyl ether is very similar to that of the corresponding Q_t derivative (II; X = Y = OMe, Z = H) showing the presence of four types of methoxy-proton (s, 6H τ 6·02, 5·82, 5·77, and 5·71) and three kinds of aromatic proton (s, 2H τ 1·95, 1·75, and 0·53). A symmetrical structure is again indicated and the only one which is in accordance with the n.m.r. data and which can be derived from veratrole by an acceptable sequence of reactions is (II; X = Z = MeO, Y = H). The aromatic protons of Q_v leucoacetate show n.m.r. signals (s, 2H τ 1·73, 1·57, and 1·30) which are almost the same as those of the Q_t leucoacetate (II; X = Y = OAc, Z = H) implying that the aromatic protons in the two compounds are in identical environments. The only structure for Q_v leucoacetate which permits this is (II; X = Z = OAc, Y = H) and it follows that the quinone Q_v is the 2,5,6,9,12,13-hexamethoxy-1,10-quinone (IV). This would appear to be formed by Scholl reactions between veratrole and 2,3,6,7,10,11-hexamethoxytriphenylene which would give the octamethoxy compound (II; X = Z = OMe, Y = H). The latter would then undergo oxidative demethylation of the hindered methoxy-groups at C-1 and C-10. We were unable to confirm this experimentally however because the very low solubility of the hexamethoxytriphenylene in 70% v/v aqueous sulphuric acid effectively prevented its reaction with veratrole.

The above oxidation of 3,3′,4,4′-tetramethoxybiphenyl provides the simplest and most efficient method yet discovered[1,3] for the preparation of compounds containing the dibenzo[*fg,op*]naphthacene nucleus.

(*Received, April* 28*th*, 1969; *Com.* 575.)

---

[1] E. Clar, 'Polycyclic Hydrocarbons', Academic Press, London, 1964, vol. 2, p. 148.
[2] I. M. Matheson, O. C. Musgrave, and C. J. Webster, *Chem. Comm.*, 1965, 278.
[3] N. P. Buu-Hoï and D. Lavit-Lamy, *Bull. Soc. chim. France*, 1966, 2500.