# 1,2-Bis-(5-methyl-1,4-benzoquinon-2-yl)ethylene

By **S. E. Hunt** and **A. S. Lindsey**, Division of Molecular Science, National Physical Laboratory, Teddington

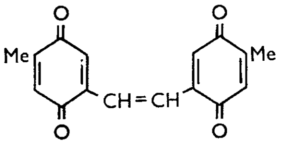
The synthesis of 1,2-bis-(5-methyl-1,4-benzoquinon-2-yl)ethylene is described.

CONJUGATED quinones exhibit unusual properties such as photodynamism,[1] photochromism,[2] and semi-conduction.[3-5] Linearly linked benzoquinones have been described by Erdtman *et al.*,[6] but a dibenzoquinone linked through a simple conjugative bridge, such as –CH=CH–, has not yet been described. Such a compound was required for a comparative study of the properties of bridged quinones;[7,8] we have therefore prepared 1,2-bis-(5-methyl-1,4-benzoquinon-2-yl)ethylene (I). The immediate precursor (II) for this was prepared by three different routes.

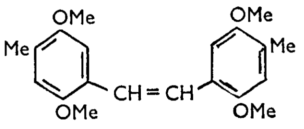
In the first route[9] acid-catalysed condensation of chloral hydrate with 2,5-dimethoxytoluene afforded 1,1,1-trichloro-2,2-bis-(2,5-dimethoxy-*p*-tolyl)ethane (III), the structure of which was confirmed by hydrogenation to the unsymmetrical ethane (IV) and by dehydrochlorination to (V). Treatment of the trichloroethane (III) with zinc dust and ammonia provided the stilbene (II), hydrogenation of which gave the symmetrical ethane (VI).

The second route was based on desulphurisation[10] of the trimer of 2,5-dimethoxythiotolualdehyde to give the stilbene (II) directly; this was then chromatographically purified.

A third route utilised dehydrogenation of 1,2-bis-(2,5-dimethyl-*p*-tolyl)ethane (VI) prepared by the method described earlier.[11] Dehydrogenation with selenium dioxide gave only low yields of the stilbene, which was difficult to obtain pure from other products. However good yields of the stilbene were conveniently obtained with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[12] as dehydrogenation agent. In this case the product was readily purified by chromatography on alumina.



(I)



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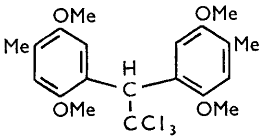

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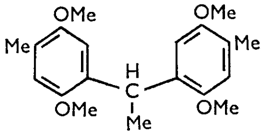

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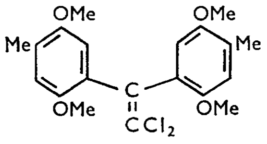

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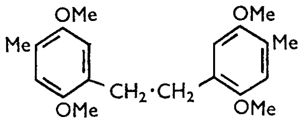
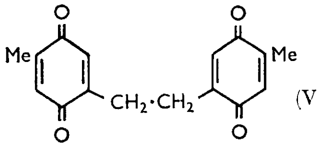


(VI)



(VII)

Al-Attar and Wizinger[13] have reported good conversion of 2-bromo-1,1-bis-(2,5-dimethoxy-*p*-tolyl)ethane into the stilbene (II) by heating under reflux with pentanol. Formation of the stilbene in this case most probably occurs through rearrangement of an intermediately generated carbonium ion, and a similar mechanism is applicable to the reaction involving alkaline reduction of the trichloroethane (III) described above.

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[1] H. Brockmann, *Proc. Chem. Soc.*, 1957, 304; *Fortschr. Chem. org. Naturstoffe*, 1957, **14**, 141.

[2] W. Luck and H. Sand, *Angew. Chem. Internat. Edn.*, 1964, **3**, 570.

[3] H. A. Pohl and E. H. Engelhardt, *J. Phys. Chem.*, 1962, **66**, 2085; H. A. Pohl and D. A. Opp, *ibid.*, p. 2121.

[4] L. A. Blumenfel'd, A. A. Berlin, N. G. Matveera, and A. E. Kalmanson, *Vysokomol. Soedineniya*, 1959, **1**, 1647.

[5] V. P. Parini, Z. S. Kazokova, M. N. Okorokova, and A. A. Berlin, *Vysokomol. Soedineniya*, 1961, **3**, 402.

[6] H. Erdtman, M. Granath, and G. Schultz, *Acta Chem. Scand.*, 1954, **8**, 1442.

[7] S. E. Hunt, A. S. Lindsey, and N. G. Savill, *J. Chem. Soc.* (*B*), 1967, 791, and references cited therein.

[8] M. E. Peover and A. S. Lindsey, to be published.

[9] W. Feuerstein, *Ber.*, 1901, **34**, 415.

[10] W. H. Laarhoven, R. J. F. Nivard, and E. Havinga, *Rec. Trav. chim.*, 1961, **80**, 775.

[11] S. E. Hunt and A. S. Lindsey, *J. Chem. Soc.*, 1962, 4550.

[12] D. Burn, D. N. Kirk, and V. Petrow, *Proc. Chem. Soc.*, 1960, 14.

[13] Y. Al-Attar and R. Wizinger, *Helv. Chim. Acta*, 1963, **46**, 1286.

The tetramethoxystilbene (II) was demethylated with pyridinium chloride to give the tetrahydroxy-derivative, which proved sensitive to aerial oxidation and was characterised as the tetra-acetate. Oxidation of the diquinol with silver oxide afforded the deep yellow diquinonylethylene (I), which was unstable in light or air.

The i.r. spectrum of the diquinonylethylene shows some marked differences from that of the corresponding ethane. New absorption bands at 3045, 1598, 1319, 1289, and 923 cm.$^{-1}$ are considered indicative of a central *trans*-olefinic bond. The band at *ca.* 685 cm.$^{-1}$ may, however, indicate the presence of some *cis*-isomer. The carbonyl absorption of the diquinonylethylene lies at 1656 cm.$^{-1}$, with a second, weaker absorption at about 1635 cm.$^{-1}$. The shift of both bands with respect to the 1669 cm.$^{-1}$ band of 2,5-dimethylbenzoquinone is indicative of ring conjugation. This is further supported by the polarographic data,[8] which show a large positive $E_2 - E_1$ value, and first and second $E_0$ values of 641 and 572 mv respectively.

## EXPERIMENTAL

Microanalyses were carried out by the microanalytical section of this laboratory. U.v. absorption spectra were measured with an Optica CF4 grating spectrophotometer. I.r. absorption spectra of solids dispersed in potassium chloride discs were measured with a Grubb-Parsons G.S.3 double-beam grating instrument. Molecular weights of compounds in toluene solution were determined with a Mechrolab vapour pressure osmometer.

*1,1,1-Trichloro-2,2-bis-(2,5-dimethoxy-*p*-tolyl)ethane* (III).—Concentrated sulphuric acid (30 ml.) was added during 15 min. to an ice-cooled solution of 2,5-dimethoxytoluene (7·5 g.) and chloral hydrate (4·25 g.) in glacial acetic acid (10 ml.). After 5 min. the solution was added to ice–water and the precipitated solid was filtered off and washed with water; it gave the *trichloroethane* (10 g.), m.p. 129—130° (from ethanol) (Found: C, 55·6; H, 5·4; Cl, 24·5%; *M*, 428. $C_{20}H_{23}Cl_3O_4$ requires C, 55·4; H, 5·4; Cl, 24·5%; *M*, 434), $\nu_{max.}$ 3050, 2920, 2820, 1503, 1450, 1392, 1323, 1203, 1184, 1109, 1037, *ca.* 1005, 980, 876, 854, 787, 714, and 672 cm.$^{-1}$.

When the trichloroethane (1·5 g.) was heated under reflux with ethanolic potassium hydroxide for several hr. it gave 1,1-*dichloro*-2,2-*bis*-(2,5-*dimethoxy*-p-*tolyl*)*ethylene* (0·65 g.), m.p. 143—144° [from light petroleum (b.p. 60—80°)] (Found: C, 60·1; H, 5·5; Cl, 17·9. $C_{20}H_{22}Cl_2O_4$ requires C, 60·45; H, 5·6; Cl, 17·9%), $\nu_{max.}$ 3000, 2985, 2955, 2930, 2840, 1604, 1503, 1461, 1438, 1392, 1374, 1280, 1273, 1230, 1203, 1177, 1140, 1040, 1004, 938, 864, 850, 769, 717, 694, and 678 cm.$^{-1}$.

Reduction of the trichloroethane (0·5 g.) under hydrogen in the presence of palladium (10%) on charcoal and anhydrous sodium hydrogen carbonate was slow (48 hr.). The product (0·25 g.) had m.p. 94—95° [from light petroleum (b.p. 60—80°)] and was confirmed to be the unsymmetrical ethane by mixed m.p., i.r. spectrum, and elemental analysis. An authentic sample was prepared as described below.

1,1-*Bis*-(2,5-*dimethoxy*-p-*tolyl*)*ethane* (IV).—To a stirred mixture of paraldehyde (10 ml.) and conc. hydrochloric acid (50 ml.) in dioxan (100 ml.) was added a solution of 2,5-dimethoxytoluene (20 g.) in dioxan (40 ml.). Hydrogen chloride was passed through the mixture for 60 min. The mixture was then added to ice-water and the precipitated solid gave [from light petroleum (b.p. 60—80°)] the disubstituted ethane (18 g.), m.p. 94—95° (Found: C, 72·7; H, 7·9. Calc. for $C_{20}H_{26}O_4$: C, 72·7; H, 7·9%).

1,2-*Bis*-(2,5-*dimethoxy*-p-*tolyl*)*ethylene* (II).—To a stirred solution of the trichloroethane (III) (17·5 g.) in ethanol (200 ml.) and aqueous ammonia (*d* 0·880; 100 ml.) at the boiling point was added zinc dust (80 g.) in portions, and the mixture was heated under reflux for 41 hr. It was filtered hot, and the solid was extracted with ether in a Soxhlet apparatus. Evaporation of the ether left the stilbene (II) (1·4 g.) which gave pale yellow prisms, m.p. 163—164° [from light petroleum (b.p. 60—80)] (Found: C, 73·4; H, 7·5%; *M*, 326. Calc. for $C_{20}H_{24}O_4$: C, 73·2; H, 7·4%; *M*, 328), $\nu_{max.}$ 3027, 2942, 2920, 2830, 1512, 1466, 1447, 1400, 1370, 1337, 1300, 1268, 1248, 1207, 1188, 1120, 1044, 998, 963, 851, and 668 cm.$^{-1}$, $\lambda_{max.}$ (n-hexane) 214, 289, and 354 mμ (log ε 4·48, 4·08, and 4·27). Solutions of the stilbene exhibited an intense blue fluorescence under u.v. light, characteristic for *trans*-stilbenes.[10]

Further work-up of the crystallisation mother liquors yielded the disubstituted ethane (IV) (4·5 g.), m.p. 94—95°.

1,2-*Bis*-(2,5-*dimethoxy*-p-*tolyl*)*ethylene* (II) *from* 2,5-*Dimethoxythiotolualdehyde*.—A solution of hydrogen sulphide was passed into 2,5-dimethoxytolualdehyde,[14] m.p. 85° (11 g.), in anhydrous ethyl acetate (100 ml.), previously saturated with hydrogen chloride, until no further precipitation of the trimeric thiobenzaldehyde occurred. The dry product (11·5 g.) had m.p. 266°.

The thiobenzaldehyde (11·5 g.), intimately mixed with freshly prepared copper powder, was heated under nitrogen at 275° for 1·25 hr. When cool, the solid was extracted with benzene; addition of light petroleum (b.p. 80—100°) precipitated the crude stilbene (2·75 g.), which was then chromatographed on alumina, and gave [from light petroleum (b.p. 60—80°)] the stilbene (II), m.p. 164°, identical with that obtained previously.

Relatively uncontaminated samples of the stilbene were obtained by carrying out the desulphurisation of the thioaldehyde trimer in diglyme under reflux for 1 hr. (yield 31%).

Copper powder was freshly prepared by adding zinc dust to 0·1M-copper sulphate, filtering after 30 min. and washing with water and ethanol. The copper was dried at 120° for 10 min.

*Dehydrogenation of* 1,2-*Bis*-(2,5-*dimethoxy*-p-*tolyl*)*ethane* (VI).—(i) *With selenium dioxide*. The symmetrical ethane (VI) (2·0 g.), freshly resublimed selenium dioxide (1·35 g.), and diethylene glycol dimethyl ether (40 ml.) were heated under nitrogen in a metal bath at 165 ± 3° for 60 min. When the mixture was cool, the selenium and unchanged selenium dioxide were filtered off and the bulk of the product (1·72 g.) was precipitated by pouring the mixture into water. The product (500 mg.) was chromatographed to give starting material (415 mg.) and the stilbene (II) (5 mg.), identified by its i.r. spectrum.

(ii) *With* 2,3-*dichloro*-5,6-*dicyano*-1,4-*benzoquinone*. The symmetrical ethane (VI) (5·9 g.) in anhydrous benzene (50 ml.) was added dropwise to a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (4·06 g.) in the same solvent (50 ml.) under reflux during 3 hr. The mixture was then diluted with light petroleum (b.p. 60—80°) (250 ml.) and the 2,3-dichloro-5,6-dicyano-1,4-quinol (4·0 g.) was recovered.

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[14] A. A. Sayigh, H. Ulrich, and M. Green, *J. Chem. Soc.*, 1964, 3482.

The filtrate was passed through a short column of neutral alumina (activity 1) and from the first fraction [50% benzene–light petroleum (b.p. 60—80°) (3 l.)] a solid (3·65 g.) was obtained which gave stilbene (II) m.p. 164° [from light petroleum (b.p. 60—80°)] (Found: C, 73·2; H, 7·4. Calc. for $C_{20}H_{24}O_4$: C, 73·1; H, 7·4%), identical (i.r. spectrum) with the other samples.

*Hydrogenation of the stilbene* (II).—The stilbene (850 mg.) in ethanol (50 ml.) was shaken under hydrogen in the presence of 10% palladium on charcoal (800 mg.) until hydrogen (*ca.* 1 mol.) had been adsorbed. The product (VI) (810 mg.) closely corresponded [m.p. and mixed m.p. (124—125°), elemental analysis, and i.r. spectrum] to an authentic specimen.[7]

1,2-*Bis*-(2,5-*dihydroxy*-p-*tolyl*)*ethylene*.—The stilbene (II) (2 g.) was heated with pyridinium chloride (10 g.) under nitrogen for 1 hr. at 200°. The mixture was then cooled and deoxygenated water (10 ml.) was added to dissolve the pyridinium chloride. The insoluble diquinol was filtered off under a blanket of nitrogen and washed with ice-cold deoxygenated water to give [from aqueous ethanol (under nitrogen)] the *diquinol*, m.p. 320° (decomp.) (Found: C, 70·5; H, 5·7. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%), $\nu_{max.}$ 3250, 3055, 2972, 2940, 2855, 1795, 1640, 1615, 1596, 1534, 1435, 1295, 1232, 1180, 1160, 1098, 1040, 1000, 960, 866, 852, 746, and 708 cm.$^{-1}$. Acetylation with acetic anhydride–pyridine gave the *tetra-acetate*, m.p. 237—238° (from ethyl acetate) (Found: C, 65·4; H, 5·6. $C_{24}H_{24}O_8$ requires C, 65·5; H, 5·5%).

1,2-*Bis*-(5-*Methyl*-1,4-*benzoquinon*-2-*yl*)*ethylene* (I).—The stilbene (II) (1·0 g.) in dry dimethoxyethane (150 ml.) was shaken with silver oxide (3 g.) and anhydrous sodium sulphate (5 g.) for several hr. with exclusion of light and air. Light petroleum (b.p. 60—80°) (300 ml.) was then added and the precipitate was extracted with boiling light petroleum (b.p. 60—80°). The *diquinonylethylene* gave deep orange needles (250 mg.), plunge m.p. 160° (from light petroleum) (Found: C, 71·9; H, 4·3. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%), $\nu_{max.}$ 3045, 2965, 2920, 1656, 1635, 1612, 1598, 1567, 1426, 1373, 1348, 1319, 1289, 1270, 1238, 1186, 1141, 1126, 1070, 1000, 923, 854, 716, *ca.* 685, and 570 cm.$^{-1}$. The compound deteriorated, particularly in the presence of light or air.

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