The Red Colour given by Coal-tar Phenols and Aqueous Alkalis. Isolation of a Quinone derived from a Tetrahydroxytetramethyldiphenyl.

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The phenolic constituents of coal tar, particularly from low-temperature carbonisation processes, give red solutions in aqueous alkalis owing to simultaneous aerial oxidation of *C*-alkylated catechols and resorcinols. A study has been made of the red colouring matter derived from 3 : 5-dimethylcatechol and 2 : 4-dimethylresorcinol. Oxidative coupling of these phenols is limited by nuclear substitution, and gives in almost quantitative yield the crystalline monosodium salt of a quinone derived from 2 : 4 : 3′ : 4′-tetrahydroxy-3 : 5 : 2′ : 6′-tetramethyldiphenyl (III). The structure of (III) was established by Ullmann condensation of 4-iodo-3 : 5-dimethylveratrole and 2 : 4-dimethoxy-3 : 5-dimethyliodobenzene to 2 : 4 : 3′ : 4′-tetramethoxy-3 : 5 : 2′ : 6′-tetramethyldiphenyl (IX), subsequent demethylation and oxidation giving a quinone identical with that previously obtained.

The dihydroxyquinone derived from (III) might possess any of three different structures, and it is shown to be a tautomeric substance capable of reacting in the *o*-benzoquinonoid form (XII) and one or both of the diphenoquinone forms (X) and (XI). The effects of steric factors on the central carbon–carbon bond in these quinones are discussed.

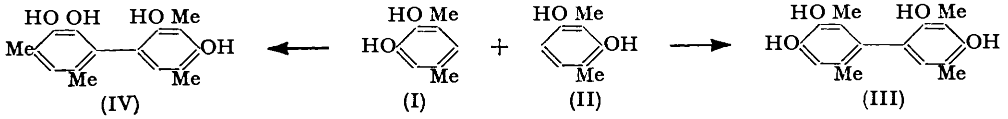
It has long been known that coal tars, particularly those prepared by the low-temperature carbonisation of coal, impart red-brown or red colours to aqueous solutions of alkalis. These red colours have been recognised as arising from aerial oxidation of phenolic material, and have proved an embarrassment in the manufacture of colourless and non-staining disinfectants and sheep dips, and even in the disposal of waste water from low-temperature plants. Gluud (*Ges. Abhandl. Kenntnis Kohle*, 1918, **3**, 66) thought that the colour was due to catechol, and Currey (*J. Soc. Chem. Ind.*, 1923, **42**, 379T) separated a phenolic fraction, distilling at about 250°, which was responsible for the colour; this fraction consisted principally of catechol, but other polyhydric phenols were present. Edwards (*ibid.*, 1924, **43**, 145T) suggested that an oxidation-condensation reaction of a phenol occurred, with production of a derivative of rosolic acid or of coumaranone. The oxidative nature of the process was clearly demonstrated by MacLeod, Chapman, and Wilson (*ibid.*, 1926, **45**, 401T), who concluded that the coloured compound resulted from " a benzenoid–quinonoid transformation with subsequent oxidation to a deeper coloured compound."

Burke and Caplan (*Ind. Eng. Chem.*, 1927, **19**, 34) showed that catechol itself was not responsible for the production of the red colour, but found that the active substance or substances could be separated from the phenolic fraction of low-temperature coal tar by extraction into aqueous borax (with which catechols form strongly acidic complexes), and regeneration therefrom and final distillation. They thus obtained a colourless oil of constant refractive index, b. p. 256°, which did not crystallise even at —20°; analyses and molecular weight agreed with a molecular formula $C_8H_{10}O_2$. It was concluded that this material was a homogeneous dimethylcatechol; the fluorescein test which it gave was thought to be due, not to a resorcinol, but to the dimethylcatechol itself. Burke and Caplan further concluded that as the compound was not the known solid 3 : 5- or 4 : 5-dimethylcatechol, it must be either 3 : 4- or 3 : 6-dimethylcatechol. The inadequacy of this suggestion became apparent when these two dimethylcathechols were synthesised. 3 : 6-Dimethylcatechol has m. p. 101° (Loudon and Scott, *J.*, 1953, 268; Baker, Bondy, Gumb, and Miles, *J.*, 1953, 1615), and 3 : 4-dimethylcatechol has m. p. 84—85° (Baker *et al.*, *loc. cit.*); both crystallise extremely easily and a 1 : 1 mixture of the two has m. p. about 65°. Moreover, 3 : 6-dimethylcatechol gives a purple colour when oxidised in aqueous alkaline solution, and 3 : 4-dimethylcatechol gives a deep, reddish-brown, rather than the typical red colour, under the same conditions.

A major advance was reported by Bristow in 1947 (*J. Inst. Fuel*, 1947, **20**, 109), namely, that the red colour was produced only by the simultaneous oxidation in alkaline solution of a homocatechol and derivatives of resorcinol (see also Low Temperature Carbonisation Limited, Bolsover, Chesterfield, B.P. 621,639/1949). It was later found (Baker *et al.*, *loc. cit.*) that for the production of the typical red colour the catechol must have a methyl group in a position *para* to one or other of the hydroxyl groups, but that the nature of the resorcinol was not critical. The introduction of further nuclear methyl groups into either the catechol or the resorcinol was found to change the colour from orange to bright red, and the most brilliant red colour was given by a mixture of 3 : 5-dimethylcatechol and 2 : 4-dimethylresorcinol. In the light of these facts it seems probable that the material separated by Burke and Caplan contained 3 : 5- and 3 : 6-dimethylcatechol and small quantities of 2-methyl-, 4-methyl-, and 2 : 4-dimethyl-resorcinol which would be in part extracted with the catechols; all these compounds are known to occur in low-temperature coal tar.

At the outset of the present investigation, it was clear that the red colouring matters were the alkali salts of hydroxylated quinonoid compounds. The red solutions become yellow or orange on the addition of acid, and colourless on reduction in presence of either alkali or acid. It was also evident that oxidative coupling occurred between the catechol and the resorcinol, followed by further oxidation to a quinone.

It was decided to investigate in detail the oxidative coupling of 3 : 5-dimethylcatechol (I) with 2 : 4-dimethylresorcinol (II), because the chances of obtaining a single product from what otherwise would certainly be a complex reaction mixture, were expected to be greatly improved by restricting the number of reactive nuclear positions at which coupling or oxidation might occur, and in conformity with this it was found that reaction between the two components (I) and (II) was unique in that it readily yielded a well-crystalline product. 2 : 4-Dimethylresorcinol (II) is reactive only at position 6, and reaction in 3 : 5-dimethylcatechol (I) is restricted to positions 4 and 6, and analogy suggests that position 4 is likely to be the more reactive. No trialkylcatechol was available.

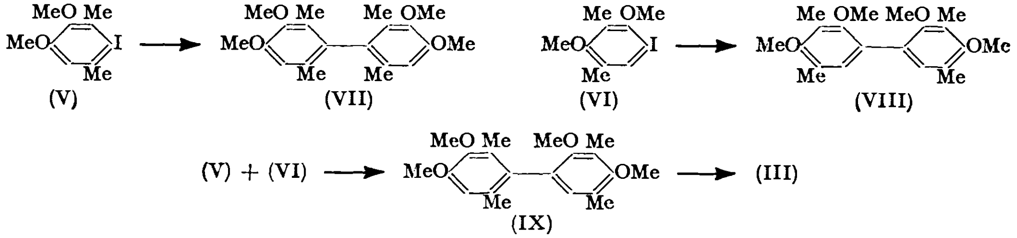


When air was drawn through a solution of equal quantities of 3 : 5-dimethylcatechol (I) and 2 : 4-dimethylresorcinol (II) in 1% aqueous sodium hydroxide containing sodium carbonate, a dark magenta, crystalline solid slowly separated from the intensely red solution. This solid, which was produced in extremely high yield, is the monosodium salt, probably hydrated, of the bright orange parent substance, $C_{16}H_{16}O_4$, which yielded a yellow, crystalline diacetyl derivative, $C_{16}H_{14}O_2(OAc)_2$. The substance $C_{16}H_{16}O_4$ was reduced by sodium dithionite in alkaline solution, and by zinc dust in acetic acid; catalytic reduction resulted in the uptake of one mol. of hydrogen. These reduced solutions when alkaline were rapidly reoxidised by air to give the original colouring matter, and attempts to effect methylation or acetylation of this presumed tetrahydroxy-compound gave uncrystallisable products. The evidence suggested that the red colouring matter was the monosodium salt of a quinone derived from a dihydroxy-tetramethyl-diphenyl; the possibility that the compound might be a quinone of the type $O{:}C_6H_4{:}CH{\cdot}CH{:}C_6H_4{:}O$ (see Yohe, Hill, Dunbar, and Scheidt, *J. Amer. Chem. Soc.*, 1953, **75**, 2688) was excluded by the elementary analysis, by the absorption of only one mol. of hydrogen on catalytic reduction, and by synthetical evidence described below.

The sodium salt of the quinone is intensely coloured: one part in 10^5, 10^6, and 10^7 parts of water gives bright red, pink, and just discernibly pink solutions respectively. The substance is an indicator, changing from red to yellow over the pH range 7·3—5·2, and it dyes silk and wool (see Experimental section).

The reaction in the production of the colouring matter must be, first, oxidative coupling to give a tetrahydroxydiphenyl derivative (III), or rather less probably (IV), and, secondly, removal of two atoms of hydrogen to form a quinone. Confirmation of the structure (III) of the parent tetrahydroxy-compound was obtained by synthesis in the following way.

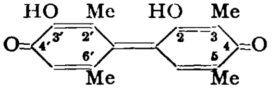
3 : 5-Dimethylcatechol (I) and 2 : 4-dimethylresorcinol (II) were each dimethylated, and the dimethyl ethers treated with iodine and mercuric oxide in boiling ethanol, yielding 4-iodo-3 : 5-dimethylveratrole (V) and 1-iodo-2 : 4-dimethoxy-3 : 5-dimethylbenzene (VI) respectively. Proof of the position of the iodine atom in (V) is given later. Ullmann coupling reactions were then carried out on each of these iodo-compounds separately, and on a mixture of the two. Compound (V) gave 3 : 4 : 3′ : 4′-tetramethoxy-2 : 6 : 2′ : 6′-tetramethyldiphenyl (VII), m. p. 173°, and compound (VI) gave 2 : 4 : 2′ : 4′-tetramethoxy-3 : 5 : 3′ : 5′-tetramethyldiphenyl (VIII), m. p. 107°. The mixed Ullmann reaction with both (V) and (VI) gave a mixture of the two solid, symmetrical diphenyls (VII) and (VIII) which are both very sparingly soluble in ether, and the liquid, asymmetrical 2 : 4 : 3′ : 4′-tetramethoxy-3 : 5 : 2′ : 6′-tetramethyldiphenyl (IX) which is totally miscible with ether.

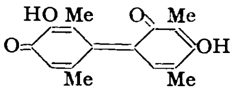


The asymmetrical diphenyl (IX) was demethylated with hydrobromic acid in acetic acid, and the resulting 2 : 4 : 3′ : 4′-tetrahydroxy-3 : 5 : 2′ : 6′-tetramethyldiphenyl (III) was oxidised under the same alkaline conditions as were used in the oxidative coupling of 3 : 5-dimethylcatechol (I) with 2 : 4-dimethylresorcinol (II). The behaviour of this tetrahydroxytetramethyl-diphenyl (III) was exactly the same as that of the mixture of (I) and (II), and the resulting crystalline sodium salt gave the orange quinonoid compound in 93·5% yield from (IX); this was identical in all respects, including the melting-point of the diacetyl derivative, with the compound prepared previously. The very high yield of the quinone from (IX) shows that (IX), although not crystalline, could not have contained more than traces of the two solid symmetrical diphenyls (VII) and (VIII), and proves the orientation of the oxygen atoms and methyl groups in the final quinone. It may be added that similar demethylation and alkaline oxidation of the two diphenyls (VII) and (VIII) gave dark brownish solutions which when acidified deposited only traces of flocculent materials.

The structure of the orange quinone derived from (III) by removal of two atoms of hydrogen is not easy to determine, and the evidence cited below proves that in solution it exhibits prototropic tautomerism. Three quinonoid structures may be derived from the tetrahydroxy-compound (III): the *pp*′-diphenoquinone (X), the *op*′-diphenoquinone (XI),

(X)

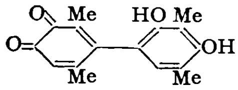


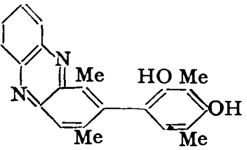


(XI)

and the *o*-benzoquinone (XII). In all these structures the oxygen atom in position 4′ of the catechol nucleus is in the carbonyl form. Considered as individual substances, (X) would appear to be the most probable, as many stable *pp*′-diphenoquinones have been prepared. *op*′-Diphenoquinones corresponding to (XI) are not known, and the *o*-benzoquinone (XII) appears unlikely in view of the known instability of these compounds, and the fact that *o*-quinones cannot usually be prepared by aerial oxidation of catechols in alkaline solution. Nevertheless, the quinone can react as (XII) because it gives a quinoxaline derivative (XIII) in high yield when treated with *o*-phenylenediamine in glacial acetic acid; this quinoxaline gives a diacetyl derivative. When, however, the diacetyl derivative of the original quinone was condensed with *o*-phenylenediamine under the same conditions it gave a quinoxaline in small yield, which proved to be a *mono*acetyl derivative of (XIII), acetylation of which gave the diacetyl derivative of (XIII) previously prepared. Moreover, when the diacetyl derivative of the quinone was treated with *o*-phenylenediamine under completely anhydrous conditions, no reaction occurred, so that it cannot be derived from the *o*-benzoquinone structure (XII). Therefore the formation of a monoacetylated quinoxaline as described above is due to partial deacetylation of the acetoxyl group in position 3 of the catechol nucleus, thus permitting the formation of an *o*-quinonoid grouping.

(XII)





(XIII)

Hence the diacetyl derivative of the original quinone must be derived either from structure (X) or from structure (XI), and it follows that the quinone is capable in solution of exhibiting tautomerism between at least forms (X) or (XI) and (XIII), and there can be little doubt that both forms (X) and (XI) can participate in the mobile system. The three structures are related to a common bivalent anion in which there is mesomerism involving the oxygen atoms in positions 2, 4, and 3′. In the solid state, the quinone most probably exists in the *pp*′-diphenoquinone form (X).

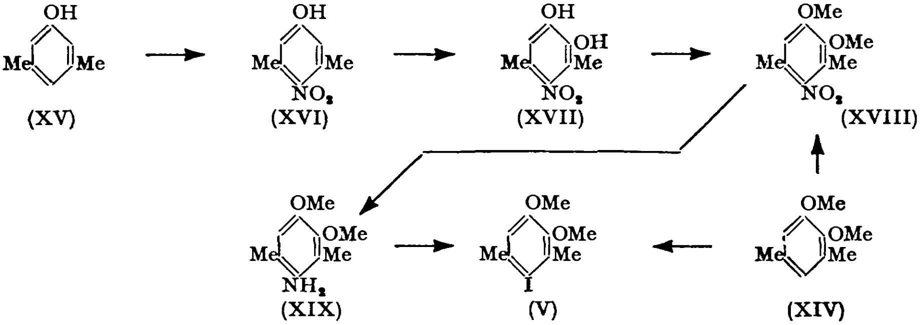
A diphenoquinone may normally be expected to be planar, and *cis*- and *trans*-isomers have been reported in the case of 3 : 3′-dimethyl-*pp*′-diphenoquinone (Moir, *S. African J. Sci.*, 1911, **8**, 253). Planar *cis*- and *trans*-forms are most unlikely in the case of the quinonoid structures (X) and (XI) owing to steric interference between the hydroxyl or carbonyl group in position 2 and the methyl groups in positions 2′ and 6′. This interference can be avoided by twisting, through a considerable angle (probably not less than 45°), and perhaps bending the molecule about the central bond, but this can only be done with loss of resonance energy and the assumption of enantiomorphous conformations. Nevertheless, that some degree of conjugation occurs between the two rings is proved by the occurrence of forms (X) or (XI) (or both) and by the very marked change of colour and in intensity of colour when the free quinone is converted into its sodium salt. The fact that the quinone reacts readily and even unexpectedly in the *o*-benzoquinonoid form (XII) may perhaps be attributed to the fact that in this form there is minimum steric interference.

Whatever may be the precise structure and conformation of the quinone, the hydroxyl group in position 2 will be sterically hindered, and this may in part account for the failure to obtain a homogeneous dimethyl ether of the quinone. Steric hindrance will also affect the reactivity of the hydroxyl group in position 2 of the related 2 : 4 : 3′ : 4′-tetrahydroxy-3 : 5 : 2′ : 6′-tetramethyldiphenyl (III) from which homogeneous tetramethyl and tetra-acetyl derivatives could not be obtained.

The quinone has a very well-defined absorption maximum at 434 mμ, and two lower maxima at shorter wavelengths. The same type of curve is shown by *pp*′-diphenoquinone which has its main maximum at 398 mμ (Brown and Todd, *J.*, 1954, 1282), and by 3 : 5 : 3′ : 5′-tetramethyl-, -tetra-*tert*.-butyl-, and -tetrachloro-*pp*′-diphenoquinone which exhibit strong maxima at 414, 420, and 435 mμ respectively.

The structure, that of 4-iodo-3 : 5-dimethylveratrole (V), assigned to the product obtained by the direct iodination of 3 : 5-dimethylveratrole (XIV) was established by independent synthesis. 3 : 5-Dimethylphenol (XV) was nitrated, and the steam-involatile *p*-nitrophenol derivative (XVI) separated from the mixture of isomerides. Application of the Elbs persulphate oxidation to (XVI) gave 3 : 5-dimethyl-4-nitrocatechol (XVII), which when methylated gave 3 : 5-dimethyl-4-nitroveratrole (XVIII), a product which was identical with that prepared by the direct nitration of 3 : 5-dimethylveratrole (XIV). Reduction of the nitro-compound (XVIII) gave 4-amino-3 : 5-dimethylveratrole (XIX), which was converted into 4-iodo-3 : 5-dimethylveratrole (V) *via* the diazonium salt. This iodo-compound was identical with the direct iodination product of 3 : 5-dimethylveratrole (XIV). The orientation disclosed is that expected in a derivative of veratrole.

The salt of the quinone described in this paper is certainly not the only colouring matter formed by the alkaline oxidation of phenols from low-temperature carbonisation and other coal tars. Catechols in general give brownish solutions in alkalis, and virtually any mixture of a catechol with a resorcinol gives some kind of red-brown or red colour. From the present work it seems likely that the compounds which contribute to the more purely red colours are quinones derived from 2 : 4 : 3′ : 4′-tetrahydroxydiphenyls, and of these substances the intensely coloured and very stable salt described in this paper may well be of major importance.



EXPERIMENTAL

Reaction between 3 : 5-*Dimethylcatechol and* 2 : 4-*Dimethylresorcinol.*—3 : 5-Dimethylcatechol (I) (5·0 g.) and 2 : 4-dimethylresorcinol (II) (5·0 g.) were dissolved in 1% aqueous sodium hydroxide (200 c.c.) containing anhydrous sodium carbonate (19·5 g.), and air was aspirated through the solution for 14 hr. The red colour became progressively darker, and the magenta, crystalline *salt* which slowly separated was collected, washed with a little ice-cold water, and dried (yield 12·1 g.) (Found in material dried at 100°/0·1 mm.: Na, 7·4. $C_{16}H_{15}O_4Na$ requires Na, 7·8%). This salt was suspended in water (100 c.c.) and acidified with hydrochloric acid, and the orange precipitate collected, washed, and crystallised several times from hot methanol, giving the *quinone* as orange needles (*ca.* 9·0 g.), m. p. 227—228° (decomp.) (Found : C, 70·6; H, 5·9. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%). If the sodium carbonate is omitted in the preparation, the sodium salt of the quinone is not precipitated and the free quinone may be obtained by acidification; after one crystallisation from methanol, the yield is 92% (9·10 g.).

The quinone dyes silk and wool, the colours being red in alkali and yellow in acid. On wool mordanted with iron, aluminium, and chromium the colours are red-brown, orange, and brown respectively, and on similarly mordanted silk, the colours are orange, yellow-orange, and bronze-orange respectively; the colours are not greatly changed by alteration of pH. It does not dye cotton or mordanted cotton.

The *diacetyl* derivative was prepared from the quinone (0·5 g.) by suspension in acetic anhydride (10 c.c.) and treatment with pyridine (3 drops), and after ½ hr. the solution was heated on the water-bath for 2 hr. and poured into water. The precipitated oil, which solidified, was dissolved in ether, the ethereal solution washed with water and aqueous sodium hydrogen carbonate, and, after removal of the ether, the solid was crystallised several times from methanol, giving lemon-yellow needles (0·62 g.), m. p. 143—144·5° (Found : C, 67·3; H, 5·5. $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·6%). An acetyl determination gave the unexpectedly high figure of 34·6% [$C_{16}H_{14}O_2(OAc)_2$ requires Ac, 24·2%], but it was found that the parent dihydroxyquinone itself gave an apparent acetyl value of 12·1% which must be due to breakdown of the molecule with formation of a volatile acid, possibly acetic acid. Hence the diacetyl derivative will give an acetyl value which is fictitiously 9·2% too high, thus bringing the value of the genuine acetyl groups to 25·4%.

3 : 5-*Dimethylveratrole.*—3 : 5-Dimethylcatechol (10 g.) in anhydrous acetone (120 c.c.) and benzene (80 c.c.) was boiled under reflux for 3 hr. with anhydrous potassium carbonate (40 g.) and methyl sulphate (10 c.c.). Further similar quantities of potassium carbonate and methyl sulphate were then added, boiling continued for 16 hr., and the filtered solution distilled, giving 3 : 5-*dimethylveratrole* as a colourless oil (11·2 g.), b. p. 118°/16 mm. [Found : C, 72·4; H, 8·6; OMe, 37·6. $C_8H_8(OMe)_2$ requires C, 72·3; H, 8·4; OMe, 37·3%].

Dimethyl Ether of 2 : 4-*Dimethylresorcinol*.—This was prepared from 2 : 4-dimethylresorcinol (10 g.) as in the case of the preceding compound. The *dimethyl ether* was obtained as a very pale yellow oil (11·0 g.), b. p. 114—115°/20 mm. (Found : C, 71·7; H, 7·9; OMe, 35·8%).

4-*Iodo*-3 : 5-*dimethylveratrole* (V).—3 : 5-Dimethylveratrole (4·07 g., 1 mol.) in ethanol (15 c.c.) was stirred under reflux on a boiling-water bath, and iodine (12·5 g., 2 mols.) and mercuric oxide (10·5 g., 2 mols.) were added in small portions during 3 hr., fresh additions being made only when the colour due to free iodine had disappeared. After removal of the ethanol under diminished pressure, the residue was extracted several times with boiling light petroleum (b. p. 60—80°) (total, 200 c.c.), giving an oil which solidified. This was dissolved in ether (100 c.c.), shaken with 20% aqueous sodium iodide (3 × 25 c.c.), then with water, dried ($MgSO_4$), and distilled, giving 4-*iodo*-3 : 5-*dimethylveratrole* (V), which was crystallised several times from ethanol and obtained as colourless needles (5·34 g.), m. p. 62·5—63·0° [Found : C, 41·6; H, 4·8; I, 43·6; OMe, 21·5. $C_8H_7I(OMe)_2$ requires C, 41·1; H, 4·5; I, 43·5; OMe, 21·2%].

1-*Iodo*-2 : 4-*dimethoxy*-3 : 5-*dimethylbenzene* (VI).—The dimethyl ether of 2 : 4-dimethylresorcinol (6·1 g.) was iodinated and the product isolated essentially as in the foregoing case. The 1-*iodo*-2 : 4-*dimethoxy*-3 : 5-*dimethylbenzene* was finally obtained as a pale yellow liquid (7·5 g.), b. p. 159—161°/16 mm. (Found : C, 41·9; H, 4·6; I, 42·7; OMe, 22·1%).

3 : 4 : 3′ : 4′-*Tetramethoxy*-2 : 6 : 2′ : 6′-*tetramethyldiphenyl* (VII).—4-Iodo-3 : 5-dimethylveratrole (V) (3·0 g.) and freshly activated copper bronze (Kleiderer and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 4219) (3·0 g.) were heated in a metal-bath at 220° for 2 hr. with occasional stirring. The product was extracted with hot methanol (3 × 30 c.c.), filtered, boiled with charcoal, cooled, collected, and crystallised several times from this solvent. 3 : 4 : 3′ : 4′-*Tetramethoxy*-2 : 6 : 2′ : 6′-*tetramethyldiphenyl* was obtained as flat rhombs (1·07 g.), m. p. 172·5—173° [Found : C, 72·7; H, 7·6; OMe, 38·2. $C_{16}H_{14}(OMe)_4$ requires C, 72·7; H, 7·9; OMe, 37·6%].

2 : 4 : 2′ : 4′-*Tetramethoxy*-3 : 5 : 3′ : 5′-*tetramethyldiphenyl* (VIII).—The Ullmann reaction was carried out as in the preceding case, but with 1-iodo-2 : 4-dimethoxy-3 : 5-dimethylbenzene (VI) (5 g.). The extraction was effected with ethyl acetate, and the product crystallised several times from methanol, giving 2 : 4 : 2′ : 4′-*tetramethoxy*-3 : 5 : 3′ : 5′-*tetramethyldiphenyl* (VIII) (2·44 g.), as colourless plates, m. p. 107—108° (Found : C, 72·8; H, 7·8; OMe, 38·7%).

Ullmann Reaction on a Mixture of 4-*Iodo*-3 : 5-*dimethylveratrole* (V) *and* 1-*Iodo*-2 : 4-*dimethoxy*-3 : 5-*dimethylbenzene* (VI). *Formation of* 2 : 4 : 3′ : 4′-*Tetramethoxy*-3 : 5 : 2′ : 6′-*tetramethyldiphenyl* (IX).—The two iodo-compounds (V) and (VI) (4·705 g. each) were mixed by melting, freshly activated copper bronze (9·41 g.) was added, and the mixture heated in a metal-bath at 190—200° for 6 hr. with occasional stirring. The product was then extracted with hot ethyl acetate (4 × 50 c.c.), giving a brown oil (5·93 g.) which was subjected to steam-distillation to remove unchanged iodo-compounds. The steam-distillate (total, 2200 c.c.) yielded first unchanged (VI) (1·55 g.), then unchanged (V) (1·2 g.), then an oil (0·51 g.), and finally a very sparingly volatile, halogen-free oil (0·04 g.), presumably a mixture of the three diphenyls (VII), (VIII), and (IX). To the residual, viscous oil (2·56 g.), which was also halogen-free, was added a little ether. A crystalline solid separated and this was collected; the ethereal solution was evaporated and treated with ether as before, again giving a little solid material. This process was repeated 8 times, whereafter no more crystals were obtained; fractional crystallisation of these united products gave the symmetrical diphenyls (VII) (0·59 g.) and (VIII) (0·78 g.). The final non-crystalline product (1·145 g.) was steam-distilled, and the distillate (8 l.) extracted with ether, giving a colourless oil (0·81 g.) which was distilled in a micro-still at 85°/0·1 mm. This 2 : 4 : 3′ : 4′-*tetramethoxy*-3 : 5 : 2′ : 6′-*tetramethyldiphenyl* (IX) could not be obtained crystalline (Found : C, 72·7; H, 7·7; OMe, 37·8%).

Demethylation and Subsequent Alkaline Oxidation of 2 : 4 : 3′ : 4′-*Tetramethoxy*-3 : 5 : 2′ : 6′-*tetramethyldiphenyl* (IX).—The diphenyl (IX) (0·47 g.) was boiled under reflux with acetic acid (7 c.c.) and 50% aqueous hydrobromic acid (7 c.c.) for 6 hr., water (200 c.c.) added, the product extracted with ether (3 × 75 c.c.), dried, distilled, and the residue boiled in methanol with charcoal and recovered, giving a light-brown resin (0·334 g.) which did not crystallise. This product is undoubtedly essentially 2 : 4 : 3′ : 4′-tetrahydroxy-3 : 5 : 2′ : 6′-tetramethyldiphenyl (III).

The resinous material (0·334 g.) was dissolved in 1% aqueous sodium hydroxide half saturated with sodium carbonate (5·5 c.c.), and air was drawn through the solution for 1½ hr. The precipitated magenta solid was separated by centrifugation, washed once with a little ice-cold water, suspended in water (15 c.c.), and acidified with hydrochloric acid. The precipitate crystallised from methanol (charcoal) as orange needles (0·31 g.), m. p. 227—228° (decomp.) undepressed on admixture with the specimen of the quinone previously described (Found : C, 70·2; H, 6·0. Calc. for $C_{16}H_{16}O_4$: C, 70·6; H, 5·9%). The identity of the two specimens was further confirmed by converting the new material into the diacetyl derivative as previously described; it formed lemon-yellow needles, m. p. and mixed m. p. 143—144·5°.

Reaction of the Quinone with o-*Phenylenediamine. Formation of the Quinoxaline* (XIII).—The quinone (2·29 g., 1 mol.) and *o*-phenylenediamine (1·1 g., 1·2 mols.) were heated to boiling in glacial acetic acid (50 c.c.), then cooled, and the yellow solid was collected, washed, and crystallised from methanol, giving yellow needles (2·56 g., 88·5%), m. p. 194—195° (Found: C, 76·3; H, 5·7; N, 8·2. $C_{22}H_{20}O_2N_2$ requires C, 76·7; H, 5·8; N, 8·1%). Reaction with acetic anhydride and a few drops of pyridine gave the *diacetyl derivative* which separated from methanol in yellow, hexagonal plates, m. p. 206—207° (Found: C, 72·6; H, 5·6; N, 6·6. $C_{26}H_{24}O_4N_2$ requires C, 72·7; H, 5·6; N, 6·5%).

Reaction of the Diacetyl Derivative of the Quinone with o-*Phenylenediamine. Monoacetyl Derivative of the Quinoxaline* (XIII).—The condensation was carried out as in the preceding case, the cooled acetic acid solution diluted with water, and the solid fractionally crystallised from methanol, giving the unchanged diacetyl derivative (84%) and the *monoacetyl derivative* (11%) of the quinoxaline (XIII) as yellow, rectangular plates, m. p. 207—208° (Found: C, 74·4; H, 5·8; N, 6·9. $C_{24}H_{22}O_3N_2$ requires C, 74·6; H, 5·7; N, 7·2%). On admixture with the diacetyl derivative of the quinoxaline the m. p. was 190—195° Acetylation of the monoacetyl derivative of the quinoxaline with acetic anhydride and pyridine gave the diacetyl derivative previously described.

The diacetyl derivative of the quinone was recovered unchanged after being boiled with *o*-phenylenediamine in benzene for 3 hr., anhydrous ethanol for 4 hr., or acetic acid and a trace of acetic anhydride for 4 hr.

1 : 3-*Dimethoxy*-2 : 4-*dimethyl*-6-*nitrobenzene*.—The dimethyl ether of 2 : 4-dimethylresorcinol (8·25 g.) was dissolved in acetic acid (80 c.c.) and concentrated nitric acid (4·5 c.c.) added. Next day the solution was poured into water (500 c.c.) and extracted with ether, the extracts were steam-distilled, and the product was again taken up in ether and finally distilled, giving 1 : 3-*dimethoxy*-2 : 4-*dimethyl*-6-*nitrobenzene* as a light yellow oil (5·0 g.), b. p. 110—112°/0·3 mm. (Found: C, 56·9; H, 6·1; N, 6·9. $C_{10}H_{13}O_4N$ requires C, 56·9; H, 6·2; N, 6·6%).

3 : 5-*Dimethyl*-4-*nitrophenol* (XVI).—The mononitration of 3 : 5-dimethylphenol was carried out as described by Adams and Stewart (*J. Amer. Chem. Soc.*, 1941, **63**, 2861), but the tedious removal of the *o*-nitrophenol derivative, 3 : 5-dimethyl-2-nitrophenol, by steam-distillation was in part avoided by several preliminary extractions with cold light petroleum in which the required *p*-nitrophenol derivative, 3 : 5-dimethyl-4-nitrophenol (XVI), is very sparingly soluble. Crystallisation of (XVI), m. p. 107—108°, is conveniently effected from hot, very dilute hydrochloric acid.

3 : 5-*Dimethyl*-4-*nitrocatechol* (XVII).—To a stirred solution of 3 : 5-dimethyl-4-nitrophenol XVI) (25 g., 1 mol.) in water (900 c.c.) containing sodium hydroxide (30 g.) was added finely powdered potassium persulphate (40·5 g., 1 mol.) during 3 hr. After being kept for 48 hr., the red solution was acidified with dilute dihydrochloric acid (Congo-red), precipitating unchanged 3 : 5-dimethyl-4-nitrophenol (11·2 g.) of which a further quantity (3·7 g.) was obtained by extracting the filtrate with ether. To the aqueous solution was now added an excess of concentrated hydrochloric acid, the mixture boiled for ½ hr. to hydrolyse the phenyl sulphate group, cooled, and extracted with ether (5 × 100 c.c.), and the recovered product crystallised from methanol (charcoal) and then from water. 3 : 5-*Dimethyl*-4-*nitrocatechol* (8·7 g.) was obtained as thick, yellow plates, m. p. 124—125° (Found: C, 52·3; H, 4·9; N, 7·3. $C_8H_9O_4N$ requires C, 52·5; H, 4·9; N, 7·7%). When kept under anhydrous conditions it becomes dark brown. Its alcoholic solution becomes emerald-green on addition of a trace of ferric chloride. The *dibenzoyl* derivative forms colourless needles, m. p. 87—88°, from ethanol (Found: C, 67·7; H, 4·3; N, 3·8. $C_{22}H_{17}O_6N$ requires C, 67·5; H, 4·3; N, 3·6%).

3 : 5-*Dimethyl*-4-*nitroveratrole* (XVIII).—(a) *Nitration of* 3 : 5-*dimethylveratrole*. 3 : 5-Dimethylveratrole (11·3 g.) was dissolved in glacial acetic acid (55 c.c.) and concentrated nitric acid (12·5 c.c.) added. Next day the solution was poured into water, and after cooling to 0° the yellow solid was collected, washed, and crystallised several times from light petroleum (b. p. 60—80°) (yield 3·1 g.). 3 : 5-*Dimethyl*-4-*nitroveratrole* forms pale yellow needles, m. p. 86—86·5° [Found: C, 57·0; H, 6·2; N, 6·6; OMe, 29·8. $C_8H_7O_2N(OMe)_2$ requires C, 56·9; H, 6·2; N, 6·6; OMe, 29·4%].

(b) *Methylation of* 3 : 5-*dimethyl*-4-*nitrocatechol*. To 3 : 5-dimethyl-4-nitrocatechol (XVII) (3·65 g.) in ethanol (50 c.c.) were added alternately (½ hr.) in portions, with shaking in an atmosphere of nitrogen, methyl sulphate (38·4 c.c.) and a concentrated solution of potassium hydroxide in water (50% w/w) (51 g.). The temperature was kept at about 50°. The ethanol was then removed under diminished pressure, the mixture heated on the water-bath for ½ hr., water added, and the solid collected and crystallised from light petroleum (charcoal), giving 3 : 5-dimethyl-4-nitroveratrole (3·0 g.), m. p. and mixed m. p. 86—87°.

4-Amino-3 : 5-dimethylveratrole (XIX).—3 : 5-Dimethyl-4-nitroveratrole (0·43 g.) was catalytically reduced in ethyl acetate (100 c.c.) in presence of Raney nickel (*ca.* 0·5 g.) at 3 atm. Filtration and removal of the solvent gave the crude amino-compound as a readily oxidisable, light brown oil which solidified at 0°. The N-*benzoyl* derivative, prepared by reaction with benzoyl chloride in pyridine, separated from 50% ethanol in minute plates, m. p. 169·5—170·5° [Found: C, 71·7; H, 6·5; N, 5·2; OMe 21·2. $C_{15}H_{13}ON(OMe)_2$ requires C, 71·6; H, 6·7; N, 4·9; OMe, 21·8%].

4-Iodo-3 : 5-dimethylveratrole (V) *from 4-Amino-3 : 5-dimethylveratrole* (XIX).—Crude 4-amino-3 : 5-dimethylveratrole (above) (0·5 g.) was dissolved in concentrated sulphuric acid (0·4 c.c.), diluted with water (3·3 c.c.), and diazotised at 0° by the addition of sodium nitrite (0·2 g.) in water (2·0 c.c.). The excess of nitrous acid was destroyed by urea, sodium iodide (0·63 g.) in water (2 c.c.) added, and the solution stirred for 1 hr., kept for 4 hr., heated on the steam-bath for 2 hr., and steam-distilled. The distillate yielded to ether a solid which after crystallisation from ethanol (charcoal) formed needles (0·62 g.), m. p. 62·5—63°, undepressed when mixed with the specimen of 4-iodo-3 : 5-dimethylveratrole previously prepared.

Ultraviolet absorption characteristics of the quinone, $C_{16}H_{16}O_4$, *in ethanol.*

$\lambda_{\text{max.}}$ (mμ)	$\log_{10} \varepsilon$	$\lambda_{\text{min.}}$ (mμ)	$\log_{10} \varepsilon$
434·0	4·19	322·0	3·68
303·5	3·71	275·0	3·50
258·6	3·80	248·0	3·74

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