The Chemistry of Fungi. Part XXIV. The Formation of Diquinones.*

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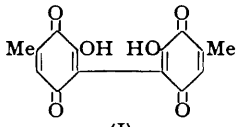
With hydrogen chloride 2-methoxy-6-*n*-propylquinone † forms the diquinone (XIV) and the dibenzofuran (XV; R = H) in addition to the expected 2-chloro-5-methoxy-3-*n*-propylquinol. The relation between this reaction and the self-condensation of methoxyquinone (Erdtman, *Proc. Roy. Soc.*, 1934, *A*, **143**, 191) is discussed. From results obtained by varying the reaction conditions and by condensing representative quinones with appropriate phenols, a mechanism for the self-condensation has been deduced. The naturally occurring diquinones phoenicin and oosporein are probably not formed by an analogous process.

FROM the symmetrical nature of the diquinones phoenicin (I), produced by *Penicillium phoenicum* van Beyma and by *P. rubrum* Grasberger and Stroll (Posternak, Ruelius, and Tcherniak, *Helv. Chim. Acta*, 1943, **26**, 2031), and oosporein (II), a metabolite of *Oospora colorans* van Beyma (Kögl and Wessem, *Rec. Trav. chim.*, 1944, **63**, 5), together with the formation of the structurally related benzoquinones fumigatin (III) by *Aspergillus fumigatus* Fresenius (Anslow and Raistrick, *Biochem. J.*, 1938, **32**, 803) and spinulosin (IV) by *A. fumigatus* and by *A. spinulosum* Thom (Raistrick, *Chem. and Ind.*, 1938, **57**, 293) it would appear that the diquinones arise from appropriate mononuclear quinones by some form of coupling reaction.

Methoxyquinone † (VI), which has been isolated recently from fermented wheat germ in which it occurs with 2 : 6-dimethoxyquinone (V) (Cosgrove, Daniels, Whitehead, and Goulden, *J.*, 1952, 4821), has long been known to undergo acid-catalysed coupling to a blue substance which can be oxidised to the diquinone (VII) or reduced to the diquinol (VIII). That the blue substance might either be the quinhydrone of (VII) and (VIII) or have the "indigoid" structure (IX) (Erdtman, *Proc. Roy. Soc.*, 1943, *A*, **143**, 191) does not affect the following discussion. Clearly, linkage to form (VII) occurs in the position alternative to that in phoenicin (I) but, because this difference could be a result of the steric influence of the methyl group, we have examined the corresponding coupling with the relatively accessible compound, 2-methoxy-6-*n*-propylquinone (X; R = H).



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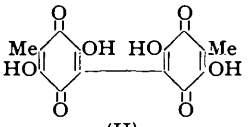

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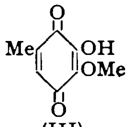

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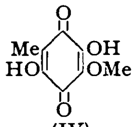

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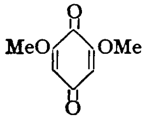

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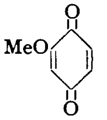

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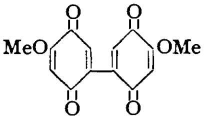

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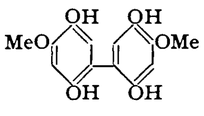

(VIII)

Rearrangement of *O*-allyl-4-nitroguaiacol to 6-allyl-4-nitroguaiacol (XI), followed by catalytic hydrogenation, provided a crude amine, which on oxidation furnished the quinone (X; R = H), but, as the last stage involved strongly acidic media, much of the quinone was destroyed by coupling and the yields were poor. This undesirable feature was avoided by starting with 6-*n*-propylguaiacol, which on persulphate oxidation furnished

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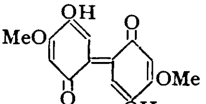
* Part XXIII, *J.*, 1954, 3713.

† Throughout the discussion, the term "quinone" is used for brevity, in place of the systematic 1 : 4-benzoquinone.

2-methoxy-6-*n*-propylquinol (XII; R = H). Controlled oxidation of this quinol then gave excellent yields of the corresponding quinone. Being required for comparison with the hydrogen chloride adduct from the quinone (X; R = H), authentic 2-chloro-5-methoxy-3-*n*-propylquinol (XII; R = Cl) was synthesised from 5-chloroguaiacol. By the Claisen rearrangement of the allyl ether of this phenol and subsequent hydrogenation of the product, 5-chloro-6-*n*-propylguaiacol (XIII) was obtained, which on oxidation furnished 2-chloro-5-methoxy-3-*n*-propylquinone (X; R = Cl) and this was reduced to the quinol (XII; R = Cl).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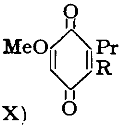
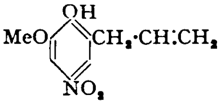

(X)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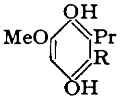
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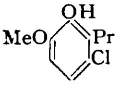
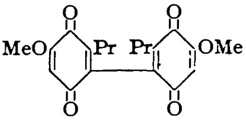
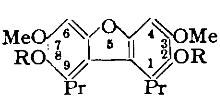

(XIII)

But little of the chloroquinol (XII; R = Cl) was formed by the action of hydrogen chloride on 2-methoxy-6-*n*-propylquinone (X; R = H) in chloroform, and the main part of the product was a chlorine-free mixture of the 4 : 4′-dimethoxy-2 : 2′-di-*n*-propyldiquinone (XIV) and, in place of the expected diquinol (XVI), 2 : 8-dihydroxy-3 : 7-dimethoxy-1 : 9-di-*n*-propyldibenzofuran (XV; R = H) (Ring Index no. 1719). This dibenzofuran, which gave a colour reaction with sulphuric acid typical of coumarones, had phenolic properties and formed a diacetate (XV; R = Ac) used for a molecular-weight determination. The oxidation of the dibenzofuran (XV; R = H) to the diquinone (XIV) indicated the relation of the two compounds and this was defined by reduction of the diquinone to the corresponding diquinol (XVI) which regenerated the dibenzofuran (XV; R = H) on dehydration. Cyclisation of the diquinol (XVI) is easily effected with hydrogen chloride, thus accounting for the production of the dibenzofuran instead of the diquinol in the coupling reaction. In contrast, the 4 : 4′-dimethoxydiquinol (VIII) is stable under the same conditions.


(XIV)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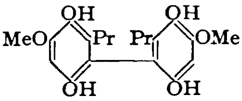
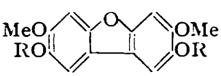

(XVI)

Because the quinone (X; R = H) has two positions at which coupling might occur, the structure (XV; R = Ac) for the diacetate of the dibenzofuran was established by an unambiguous synthesis from the 4 : 4′-dimethoxydiquinol (VIII) which has been oriented by Erdtman (*loc. cit.*). With phosphoric acid the diquinol (VIII) was cyclised to 2 : 8-dihydroxy-3 : 7-dimethoxydibenzofuran (XVII; R = H) and, on being heated in diethylaniline containing a little acetic anhydride, the diallyl ether (XVII; R = CH_2·CH:CH_2) of this supplied 2 : 8-diacetoxy-1 : 9-diallyl-3 : 7-dimethoxydibenzofuran (XVIII) together with an unidentified substance. Hydrogenation of (XVIII) then gave (XV; R = Ac).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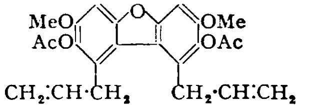
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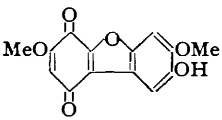
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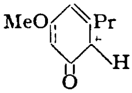
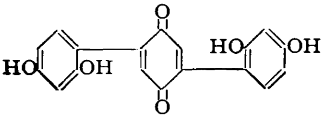

(XX)

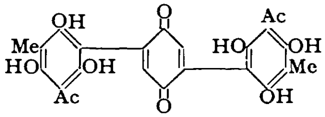
Although it was now clear that the propyl groups did not direct orientation in the coupling process, they had other marked effects, of which the relative ease of dehydration of the diquinols has been mentioned. On being heated in 1-bromonaphthalene, the diquinone (VII) is converted into a product to which Erdtman (*Proc. Roy. Soc.*, 1934, *A*, **143**, 223) has allocated structure (XIX), and the stability of the dipropyl analogue (XIV) under similar conditions affords support for this conclusion. It is less easy to see why the diquinone (XIV) does not form a hydrogen chloride adduct of the type studied by Lindbergh and his co-workers (*Acta Chem. Scand.*, 1950, **4**, 1192; 1951, **5**, 885). Further, a substance similar to the blue coupled product from methoxyquinone is not formed by the action of acids on the *n*-propylquinone (X; R = H) or by the interaction of solutions of the di-*n*-propyldiquinone (XIV) and the di-*n*-propyldiquinol (XVI) even at —70°. If the blue product is a quinhydrone, the absence of the homologue is only to be expected because a quinhydrone could not be obtained from the parent 2-methoxy-6-*n*-propylquinone (X; R = H). The similar resistance to quinhydrone formation shown by duroquinone disappears at low temperatures (Bothner-By, *J. Amer. Chem. Soc.*, 1951, **73**, 4228) and has been attributed by Michaelis and Granick (*ibid.*, 1944, **66**, 1023) to interaction between the methyl groups in the complex. If, however, the blue product has the alternative structure (IX), the introduction of two *n*-propyl groups *ortho* to the central double bond might well prevent the system from retaining the necessary planar configuration, thus permitting dismutation to the corresponding diquinone and diquinol.

It is usual to consider that the addition of hydrogen chloride to quinones involves a cationic species, here conveniently represented by (XX), which adds chloride ion and then aromatises to the chloroquinol, and it follows that an increased chloride-ion concentration would favour such an addition. When chloroform was replaced by ether, which forms an oxonium chloride with the reagent, the reaction between hydrogen chloride and the *n*-propylquinone (X; R = H) gave a much improved yield of the chloroquinol (X; R = Cl) at the expense of the coupled products.

Because it is acid-catalysed and fails with quinones, *e.g.*, with the chloroquinone (X; R = Cl) or 2-methoxy-5-methylquinone, in which the electron-deficient centres corresponding to that in (XX) are blocked, the coupling process appears to involve the same cationic residue (XX). It is unlikely, however, that the coupled products are formed by the interaction of this cationoid entity (XX) and a second molecule of quinone, which is itself electron-deficient at the point where combination would take place. In view of the formation of the chloroquinol (XII; R = Cl) in the coupling reaction with the *n*-propylquinone the action of hydrogen chloride on methoxyquinone was re-investigated and there was isolated a small quantity of 5-chloro-2-methoxyquinol which appears to have escaped notice hitherto. In the reaction with the quinone (X; R = H) it is reasonable to assume, therefore, that initially the mixture contains, in addition to the chloroquinol (XII; R = Cl), the quinol (XII; R = H) resulting from the action of (XII; R = Cl) on the quinone (X; R = H). This quinol (XII; R = H) would be strongly anionoid at the position appropriate for interaction with (XX), thus leading to the diquinol (XVI) which can then be cyclised to the dibenzofuran (XV; R = H) or be oxidised to the diquinone (XIV). This oxidation could be effected by 2-methoxy-6-*n*-propylquinone or the chloroquinone (X; R = Cl), thereby regenerating 2-methoxy-6-*n*-propylquinol (XII; R = H) required for a fresh cycle. Thus the reaction, once initiated, would continue in the absence of large amounts of the chloroquinol (XII; R = Cl) or of the corresponding quinone. In support of this hypothesis it has been found that the *n*-propylquinol (XII; R = H) and the analogous quinone (X; R = H) interact to give the dibenzofuran (XV; R = H) in yield superior to that obtained in the coupling reaction and without the formation of the corresponding diquinone or quinol. Other conditions, *e.g.*, with sulphuric acid in acetic acid, in which coupling has been observed, can be accommodated by variations of the same scheme.

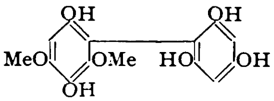


(XXI)



(XXII)

From this argument it appears that non-methoxylated quinones do not couple easily largely because the corresponding quinols are insufficiently anionoid. Nevertheless, quinones of this type would be expected to undergo acid-catalysed condensation with more reactive phenols. Thus Pummerer and Huppman (*Ber.*, 1927, **60**, 1442) obtained the quinhydrone of (XXI) from *p*-benzoquinone and resorcinol in 10% sulphuric acid, and, in the present work, even acetic acid induced a condensation between *p*-benzoquinone and *C*-methylphloracetophenone leading to (XXII) or the related quinol. The inverse state of affairs obtains with 2 : 6-dimethoxyquinone (V), where the reactivity of the cationoid entity is enfeebled by the electromeric effect of the additional methoxyl group. Thus the quinone (V) does not add hydrogen chloride or undergo self-condensation but it does react with the intensely anionoid compound phloroglucinol, giving (XXIII).



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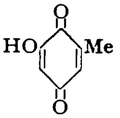

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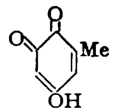

(XXV)

As similar considerations apply to the coupling of the hydroxyquinone (XXIV) even if this existed in the *o*-quinonoid form (XXV), it seems improbable that the natural diquinones (I) and (II) are formed according to this mechanism or by any simple variation of it.

EXPERIMENTAL

*2-Methoxy-*6-n-*propyl-*1 : *4-benzoquinone* (X; R = H).—(*a*) A mixture of 4-nitroguaiacol (9·5 g.), potassium carbonate (10 g.), and allyl bromide (6 g.) was heated in boiling acetone (100 ml.) until the orange colour faded. A solution of the product in ether was washed with dilute aqueous sodium hydroxide, dried, and evaporated, leaving an oil which crystallised from light petroleum (b. p. 40—60°), giving O-*allyl-4-nitroguaiacol* in pale yellow rectangular prisms (8 g.), m. p. 53° (Found : 57·7; H, 5·2; N, 6·5. $C_{10}H_{11}O_4N$ requires C, 57·4; H, 5·3; N, 6·7%). This ether (5 g.) was rearranged in boiling quinoline during 30 min. and, after the reaction mixture had been diluted with ether and freed from quinoline by 10% sulphuric acid, the phenolic product was isolated with the aid of 10% aqueous sodium hydroxide. Liberated from the alkaline extracts by dilute hydrochloric acid, *6-allyl-4-nitroguaiacol* (XI) formed yellowish prisms (2 g.), m. p. 72°, from light petroleum (b. p. 40—60°) (Found : C, 57·6; H, 5·2; N, 6·7; OMe, 14·9. $C_9H_8O_3N{\cdot}OMe$ requires C, 57·4; H, 5·3; N, 6·7; OMe, 14·8%). This allylnitroguaiacol (4 g.), dissolved in methanol (100 ml.), was simultaneously hydrogenated and reduced with hydrogen and a 2% palladium–charcoal catalyst in ½ hr. On isolation the crude 4-amino-6-*n*-propylguaiacol was mixed with a solution of ferric sulphate (50 g.) in water (500 ml.), and the oxidation product immediately separated with steam. Extracted with ether from the yellow distillate, *2-methoxy-*6-n-*propyl-*1 : *4-benzoquinone* crystallised from light petroleum (b. p. 40—60°) in yellow rectangular prisms (0·3 g.), m. p. 78—79°, $\lambda_{max.}$ 266 mμ (log ε 4·25), which sublimed easily, were readily soluble in the common organic solvents, and gave a red colour with aqueous sodium hydroxide or concentrated sulphuric acid (Found : C, 66·5; H, 6·63; OMe, 17·0. $C_9H_9O_2{\cdot}OMe$ requires C, 66·7; H, 6·7; OMe, 17·2%).

(*b*) When shaken in methanol (100 ml.) containing 2% palladium–charcoal (1 g.), 6-allylguaiacol (6 g.) (Claisen and Tietze, *Annalen*, 1926, **449**, 81) rapidly absorbed hydrogen (910 ml., *ca.* 1 mol.) and on distillation the product gave 6-n-*propylguaiacol* as an oil (5 g.), b. p. 142°/20 mm. (Found : C, 72·2; H, 8·2. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5%).

Sodium nitrite (2·2 g.), dissolved in water (6 ml.), was added to a solution of sulphanilic acid (6·3 g.) and anhydrous sodium carbonate (1·6 g.) in water (30 ml.), and the mixture was poured on ice (3·5 g.) and concentrated hydrochloric acid (6·5 ml.). 15 Minutes later 6-*n*-propylguaiacol (5 g.) in 20% sodium hydroxide (30 ml.) was added to this mixture and next day the resulting dye was reduced *in situ* at 80° with concentrated hydrochloric acid (22 ml.) and stannous chloride (10 g.). The crude aminoguaiacol present in this reaction mixture was oxidised with ferric sulphate (80 g.) in water (500 ml.) to 2-methoxy-6-*n*-propyl-1 : 4-benzoquinone which was isolated by steam-distillation, forming yellow plates, m. p. and mixed m. p. 78—79°. The yield of quinone was very poor.

(*c*) Potassium persulphate (7 g.), in water (250 ml.), was added during 2 hr. to a stirred solution of 6-*n*-propylguaiacol (5 g.) in 10% aqueous sodium hydroxide kept at 10°. 12 Hours later the red solution was acidified (Congo-red), filtered through cotton wool to remove tar, acidified to litmus, and kept at 100° for 1 hr. From the brown resinous product, which was isolated with ether, boiling light petroleum (b. p. 80—100°) extracted 2-*methoxy*-6-n-*propylquinol* (XII; R = H), forming needles (1·5 g.), m. p. 106°, easily soluble in organic solvents except light petroleum and readily soluble in aqueous sodium hydroxide (Found: C, 66·0; H, 7·5; OMe, 17·1. $C_9H_{11}O_2{\cdot}OMe$ requires C, 65·9; H, 7·7; OMe, 17·0%). Oxidation of this quinol (6 g.) in 10% acetic acid (30 ml.) with 2% aqueous chromic acid (100 ml.) at 0° during ½ hr. gave an almost quantitative yield of 2-methoxy-6-*n*-propyl-1 : 4-benzoquinone, m. p. and mixed m. p. 78—79°.

5-*Chloro*-6-n-*propylguaiacol* (XIII).—The product from the interaction of 5-chloroguaiacol (6·0 g.) (Jona and Pozzi, *Gazzetta*, 1911, **41**, I, 722), potassium carbonate (6 g.), and allyl bromide (5·5 g.) in acetone (100 ml.) on the steam-bath for 4 hr. was isolated in the usual way and on distillation gave O-*allyl*-5-*chloroguaiacol* (5 g.), b. p. 142°/20 mm. (Found: OMe, 15·4. $C_9H_8OCl{\cdot}OMe$ requires OMe, 15·6%). On being boiled with dimethylaniline (4 g.) for 1 hr., this ether (4·5 g.) was completely isomerised. The cooled reaction mixture was diluted with ether, freed from the base with dilute sulphuric acid, dried (Na_2SO_4), and evaporated, leaving 6-*allyl*-5-*chloroguaiacol* as an oil (3·7 g.), b. p. 150°/20 mm. (Found: C, 60·2; H, 5·4; OMe, 15·3. $C_9H_8OCl{\cdot}OMe$ requires C, 60·5; H, 5·5; OMe, 15·6%). The *benzoate* separated from methanol in plates, m. p. 78° (Found: C, 67·3; H, 5·1; OMe, 10·3. $C_{16}H_{12}O_2Cl{\cdot}OMe$ requires C, 67·2; H, 4·9; OMe, 10·2%). The allylguaiacol (8 g.) in methanol (30 ml.) containing 0·5% palladium-charcoal (2 g.) was allowed to absorb one mol. (895 ml.) of hydrogen (*ca.* 10 min.). Evaporation of the filtered solution and distillation of the residue furnished 5-*chloro*-6-n-*propylguaiacol* as an oil (7·5 g.), b. p. 156°/20 mm. (Found: C, 59·7; H, 6·3. $C_{10}H_{13}O_2Cl$ requires C, 59·9; H, 6·5%), giving a *benzoate* which separated from dilute alcohol in needles, m. p. 100° (Found: OMe, 10·3. $C_{16}H_{14}O_2Cl{\cdot}OMe$ requires OMe, 10·2%).

2-*Chloro*-5-*methoxy*-3-n-*propylquinol* (XII; R = Cl).—This quinol was prepared by the method (*b*) employed for 2-methoxy-6-*n*-propylquinone. 5-Chloro-6-*n*-propylguaiacol (4 g.) in 10% aqueous sodium hydroxide (50 ml.) at 0° was mixed with diazotised sulphanilic acid (6 g.). Next day the solution was treated with concentrated hydrochloric acid (22 ml.) and stannous chloride (10 g.), and then heated at 90° until the colour changed to brown before oxidation with ferric sulphate (80 g.). After isolation by steam-distillation followed by extraction with ether the greenish resinous product was crystallised from light petroleum (b. p. 40—60°), giving 2-*chloro*-5-*methoxy*-3-n-*propyl*-1 : 4-*benzoquinone* (X; R = Cl) in greenish-yellow rectangular prisms (2·0 g.), m. p. 92°, which readily sublimed and formed a pink solution in alkali and a red one in concentrated sulphuric acid (Found: C, 56·2; H, 5·3; Cl, 16·3; OMe, 14·3. $C_9H_8O_2Cl{\cdot}OMe$ requires C, 55·9; H, 5·1; Cl, 16·6; OMe, 14·5%). This quinone (1 g.), suspended in water (50 ml.), was treated with sulphur dioxide until no further change was apparent and the white precipitate then collected, dried, and purified from light petroleum (b. p. 60—80°), giving 2-*chloro*-5-*methoxy*-3-n-*propylquinol* in colourless prisms (0·8 g.), m. p. 103—104°, which, on oxidation with chromic acid in acetic acid, regenerated the parent quinone (Found: C, 55·8; H, 6·2; Cl, 16·1; OMe, 14·2. $C_9H_{10}O_2Cl{\cdot}OMe$ requires C, 55·4; H, 6·0; Cl, 16·4; OMe, 14·3%).

2 : 8-*Diallyloxy*-3 : 7-*dimethoxydibenzofuran* (XVII; R = $CH_2{\cdot}CH{:}CH_2$).—The blue coupled product (10 g.) from methoxyquinone was heated under reflux with zinc dust (2 g.) in 55% acetic acid (200 ml.) until the blue colour disappeared (*ca.* 20 min.), and after the addition of 2N-hydrochloric acid (5 ml.) the hot solution was filtered immediately. On cooling, the filtrate deposited fawn prisms (7·2 g.), m. p. 210° (decomp.), of 2 : 5 : 2′ : 5′-tetrahydroxy-4 : 4′-dimethoxydiphenyl, the properties of which agreed exactly with those reported by Erdtman (*Proc. Roy. Soc.*, 1934, *A*, **143**, 191). When sifted into syrupy phosphoric acid (25 ml.) at 180°, this quinol (4 g.) at once gave a blue solution which on cooling deposited lilac crystals. After being diluted with an equal volume of water, the mixture was filtered and the solid was washed with much water and crystallised from alcohol or benzene-light petroleum (b. p. 60—80°) giving 2 : 8-*dihydroxy*-3 : 7-*dimethoxydibenzofuran* (XVII; R = H) in colourless plates, m. p. 188°, $\lambda_{max.}$ 316 mμ (log ε 4·4), which gave an intense blue concentrated sulphuric acid reaction [Found: C, 64·8; H, 4·5; OMe, 23·8. $C_{12}H_6O_3(OMe)_2$ requires C, 64·6; H, 4·7; OMe, 24·0%]. The *diacetate* separated from dilute alcohol in needles, m. p. 200° [Found: C, 63·0; H, 4·7; OMe, 18·2. $C_{16}H_{10}O_5(OMe)_2$ requires C, 6·28; H, 4·7; OMe, 18·2%]. Prepared from this dihydroxydibenzofuran (2 g.), potassium carbonate (2 g.), and allyl bromide (1·6 ml.) in refluxing acetone (200 ml.) during 6 hr. and recrystallised from dilute alcohol, 2 : 8-*diallyloxy*-3 : 7-*dimethoxydibenzofuran* formed flat needles (1·5 g.), m. p. 112—113°.

insoluble in alkalis and giving a deep blue sulphuric acid reaction (Found : C, 70·6; H, 6·2. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%).

2 : 8-*Diacetoxy*-3 : 7-*dimethoxy*-1 : 9-*di*-n-*propyldibenzofuran* (XV; R = Ac).—A mixture of 2 : 8-diallyloxy-3 : 7-dimethoxydibenzofuran (5 g.), diethylaniline (40 ml.), and acetic anhydride (5 ml.) in nitrogen was heated (oil-bath at 180—190°) for 5 hr., cooled, diluted with ether (200 ml.), and filtered. Freed from diethylaniline by hydrochloric acid, the filtrate was evaporated, leaving a yellow gum which solidified on trituration with methanol. The solid (5 g.) appeared to be a complex mixture from which two compounds were isolated by fractional crystallisation from alcohol and ethyl acetate alternately. The less soluble *substance* formed prisms (0·5 g.), m. p. 220°, from alcohol having a blue sulphuric acid reaction and resisting hydrogenation under mild conditions (Found : C, 66·9; H, 6·3; OMe, 14·8%). Purified from alcohol, the more soluble fraction gave 2 : 8-*diacetoxy*-1 : 9-*diallyl*-3 : 7-*dimethoxydibenzofuran* in prisms (1·8 g.), m. p. 166°, with a blue sulphuric acid reaction [Found : C, 67·8; H, 6·0; OMe, 15·1. $C_{22}H_{16}O_5(OMe)_2$ requires C, 67·9; H, 5·7; OMe, 14·6%]. Hydrogenated with a 2% palladium–charcoal catalyst (0·5 g.) in alcohol (200 ml.), this diallyldibenzofuran (0·5 g.) absorbed 2 mols. of hydrogen in 5 min. and on isolation the resulting 2 : 8-*diacetoxy*-3 : 7-*dimethoxy*-1 : 9-*di*-n-*propyldibenzofuran* separated from alcohol in squat prisms (0·5 g.), m. p. 169°, having a blue sulphuric acid reaction [Found : C, 67·1; H, 6·7%; *M* (Rast), 405. $C_{24}H_{28}O_7$ requires C, 67·3; H, 6·5%; *M*, 428].

Action of Hydrogen Chloride on 2-*Methoxy*-6-n-*propyl*-1 : 4-*benzoquinone*.—Hydrogen chloride was led into a solution of the quinone (2 g.) in chloroform (50 ml.) for 1 hr. and the solvent removed in a vacuum, leaving a brown residue which solidified. This was triturated with a little methanol to remove resin, together with a very small quantity of 2-chloro-5-methoxy-3-*n*-propylquinol (XII; R = Cl) which separated from boiling light petroleum (b. p. 40—60°) in prisms, m. p. and mixed m. p. 103°. Fractional crystallisation of the main residual product from methanol gave a less soluble fraction of 4 : 4′-*dimethoxy*-6 : 6′-*di*-n-*propyldiphenyl*-2 : 5-2′ : 5′-*diquinone* (XIV) which on repeated purification from the same solvent formed yellow hexagonal prisms (0·6 g.), m. p. 172°, $\lambda_{max.}$ 272 mμ (log ε 4·3), subliming unchanged at 180° (bath)/0·001 mm., and giving an orange colour with sulphuric acid and a pink with aqueous sodium hydroxide [Found : C, 67·2; H, 6·2; OMe, 17·1. $C_{18}H_{16}O_4(OMe)_2$ requires C, 67·0; H, 6·1; OMe, 17·3%]. Recrystallised from dilute methanol, the more soluble fraction gave 2 : 8-*dihydroxy*-3 : 7-*dimethoxy*-1 : 9-*di*-n-*propyldibenzofuran* (XV; R = H) in rectangular plates (0·7 g.), m. p. 152°, $\lambda_{max.}$ 227, 312 mμ (log ε 4·6, 4·45), subliming unchanged at 170° (bath)/0·001 mm., soluble in aqueous sodium hydroxide but not in aqueous sodium carbonate, and giving a deep blue sulphuric acid reaction [Found : C, 69·8; H, 7·0; OMe, 17·8. $C_{18}H_{18}O_3(OMe)_2$ requires C, 69·8; H, 6·9; OMe, 18·0%]. The diacetate (XV; R = Ac) was identical with an authentic specimen, m. p. and mixed m. p. 169°.

When the chloroform was replaced by ether in the foregoing experiment there was formed a crude solid which on fractional crystallisation from methanol gave three products. The least soluble fraction was the diquinone (0·4 g.), m. p. and mixed m. p. 172°, the middle fractions consisted chiefly of the dibenzofuran (0·5 g.), m. p. and mixed m. p. 152° on purification, and the most soluble material, isolated by dilution with water, was 2-chloro-5-methoxy-3-*n*-propylquinol (0·6 g.), m. p. and mixed m. p. 103—104°.

Interconversion of the Diquinone (XIV) *and the Corresponding Dibenzofuran* (XV; R = H).—The dibenzofuran (XV; R = H) (0·5 g.) in boiling alcohol (15 ml.) was treated with ferric chloride (1 g.) for 30 min. and the solution diluted with ether, thoroughly washed with water, dried, and evaporated, leaving 4 : 4′-dimethoxy-6 : 6′-di-*n*-propyldiphenyl-2 : 5-2′ : 5′-diquinone (0·25 g.), m. p. and mixed m. p. 172°.

The diquinone (0·5 g.) suspended in water (20 ml.) containing methanol (5 ml.), was reduced by sulphur dioxide in 20 min. The white precipitate was collected, washed with water, and crystallised from dilute methanol, giving 3 : 6 : 3′ : 6′-*tetrahydroxy*-4 : 4′-*dimethoxy*-2 : 2′-*di*-n-*propyldiphenyl* (XVI) in prisms (0·45 g.), m. p. 190°, which were easily oxidised in air and gave a red solution in aqueous sodium hydroxide and an emerald-green sulphuric acid reaction (Found : C, 66·2; H, 7·2. $C_{20}H_{26}O_6$ requires C, 66·3; H, 7·2%). The *tetra-acetate* separated from dilute alcohol in plates or prisms, m. p. 160°, $\lambda_{max.}$ 280 mμ (log ε 3·6) (Found : C, 63·3; H, 6·6. $C_{28}H_{34}O_{10}$ requires C, 63·4; H, 6·5%). The dibenzofuran (XV; R = H) (0·15 g.), which sublimed from an intimate mixture of the diquinol (0·2 g.) and phosphoric oxide (0·5 g.) kept at 190°/0·05 mm., was produced in the same yield when the diquinol in chloroform was treated with hydrogen chloride at 0° for 1 hr., and was identified by comparison with an authentic specimen.

*Action of Hydrogen Chloride on Methoxy-*1 : 4-*benzoquinone.*—Methoxy-1 : 4-benzoquinone was stable in dilute acetic acid or even in dilute (<1%) mineral acids. 2N-Mineral acids caused immediate coupling (cf. Erdtman, *loc. cit.*).

The methoxyquinone (1 g.) in ice-cold chloroform (25 ml.) was treated with a stream of hydrogen chloride for 5 min. and the blue precipitate (0·95 g.) collected and identified with the product prepared according to the directions of Erdtman (*loc cit.*). The residue left on evaporation of the chloroform liquor was extracted with boiling light petroleum (b. p. 40—60°). The extracts were cooled, and, after removal of a little insoluble blue compound, concentrated, and chilled. The resulting crystalline precipitate was purified from the same solvent, giving a small amount of 2-chloro-5-methoxyquinol, m. p. 128°, undepressed on admixture with an authentic specimen (Asp and Lindbergh, *Acta Chem. Scand.*, 1950, **4**, 60).

Condensation of 2-*Methoxy*-6-n-*propylquinol with* 2-*Methoxy*-6-n-*propyl*-1 : 4-*benzoquinone.*—A slow stream of hydrogen chloride was led into a solution of the quinone (50 mg.) and the quinol (50 mg.) in chloroform (5 ml.). An hour later the solution was evaporated and the residue was thoroughly extracted with boiling light petroleum (b. p. 60—80°). On cooling, the concentrated extracts deposited a reddish mass (70 mg.) of 2 : 8-dihydroxy-3 : 7-dimethoxy-1 : 9-di-*n*-propyldibenzofuran (XV; R = H), forming colourless plates, m. p. and mixed m. p. 152°, from methanol.

2 : 5-*Di*-(3-*acetyl*-2 : 4 : 6-*trihydroxy*-5-*methylphenyl*)-1 : 4-*benzoquinone* (3 : 3′′-*Diacetyl*-2 : 4 : 6 : 2′′ : 4′′ : 6′′-*hexahydroxy*-5 : 5′′-*dimethyl*-p-*terphenyl*-2′ : 5′-*quinone*) (XXII).—A solution of *p*-benzoquinone (1·1 g.) in acetic acid (30 ml.), containing powdered *C*-methylphloracetophenone (0·9 g.), was vigorously stirred for 24 hr. and the solid product isolated, dried in air, and washed with cold methanol, leaving the *quinone* (XXII) as bright yellow prisms (0·8 g.), m. p. 245° (decomp.) after blackening at 190°, insoluble in alcohol, dioxan, chloroform, or ethyl acetate and decomposing in warm acetic acid (Found: C, 61·5; H, 4·6. $C_{24}H_{20}O_{10}$ requires C, 61·5; H, 4·3%). In aqueous sodium carbonate this quinone gave a green, and in 2N-aqueous sodium hydroxide a red, solution; the sulphuric acid reaction was deep greenish-red, changing to purple and finally inky-blue on warming. The methanolic washings of the quinone were concentrated, giving quinhydrone in glistening green-black crystals (0·2 g.), m. p. 171° (decomp.).

2 : 5-*Di*-(3-*acetyl*-2 : 4 : 6-*trihydroxy*-5-*methylphenyl*)*quinol* (3 : 3′′-*Diacetyl*-2 : 4 : 6 : 3′ : 5′ : 2′′ : 4′′ : 6′′-*octahydroxy*-5 : 5′′-*dimethyl*-p-*terphenyl*).—(*a*) A stirred solution of *p*-benzoquinone (0·55 g.) in acetic acid (10 ml.), containing *C*-methylphloracetophenone (0·9 g.), was kept at 60° for 1 hr. The mixture became red and the nature of the solid changed. Next day the pink solid was collected, washed with acetic acid and then ether, and dried, giving 2 : 5-*di*-(3-*acetyl*-2 : 4 : 6-*trihydroxy*-5-*methylphenyl*)*quinol* in prisms (0·85 g.), m. p. 270° (decomp.) (Found: C, 61·7; H, 5·0. $C_{24}H_{22}O_{10}$ requires C, 6·16; H, 4·7%). This quinol, which is soluble in alcohol, gave a transient green-brown ferric reaction, a brilliant red solution in 2N-aqueous sodium hydroxide, and a rose-red warm sulphuric acid reaction. With the corresponding quinone it appeared to form a dark red quinhydrone which could not be satisfactorily characterised.

(*b*) Sodium hydrogen sulphite (0·3 g.) was added to the quinone (XXIII) (0·3 g.) suspended in acetic acid (4 ml.) and water (1 ml.). The mixture was warmed gently and further small amounts of sulphite were added until the yellow colour of the mixture faded. The precipitate of the quinol was collected, washed thoroughly with hot distilled water, and crystallised from acetic acid, forming cream prisms (0·24 g.), m. p. 267° (decomp.), having the same colour reactions as the compound obtained by method (*a*) (Found: C, 61·5; H, 5·0%).

3 : 6 : 2′ : 4′ : 6′-*Pentahydroxy*-2 : 4-*dimethoxydiphenyl* (XXIII).—An intimate mixture of anhydrous phloroglucinol (1·3 g.) and 2 : 6-dimethoxy-1 : 4-benzoquinone (1·7 g.) was moistened with acetic acid and warmed, giving a dark solution from which, 15 minutes later, a solid separated on cooling. A pure product was not obtained from this but the mother liquor slowly deposited a white solid which on crystallisation from water furnished 3 : 6 : 2′ : 4′ : 6′-*pentahydroxy*-2 : 4-*dimethoxydiphenyl* in prisms, m. p. 250° (decomp.), with a negative ferric reaction in water [Found: C, 53·3; H, 5·6; OMe, 19·3, 19·5. $C_{12}H_8O_5(OMe)_2,H_2O$ requires C, 53·8; H, 5·2; OMe, 19·9%]. Attempted recrystallisation of this phenol from acetic acid caused partial decomposition. On being warmed, the lilac solution of the compound in concentrated sulphuric acid became green and then purple.

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