

## Studies on Humic Acids

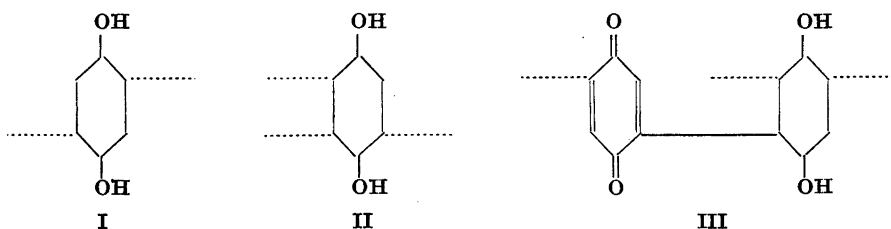
## VI. Triquinone and Tetraquinone \*

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In order to gain information about the properties of phenolic polyphenyls believed to be structurally related to "phenol" or "quinone humic acids" tri- and tetrahydroquinone, their methylethers (X and XIII) and acetates as well as the corresponding tri- and tetraquinones (V and VI) have been prepared. The hydroquinones are extremely sensitive to oxidation, turning blue when exposed to air. Deep blue "quinhydrones" are obtained on partial oxidation with chromic acid. The polymerisation of the quinones in alkali has been studied and compared with that of benzoquinone. The U.V. absorption of the methylethers and acetates indicates a low degree of inter-nuclear conjugation and especially that of the acetates exhibits similarities with the U.V. absorption of the "leucoacetates" obtained by reductive acetylation of "quinone humic acid".

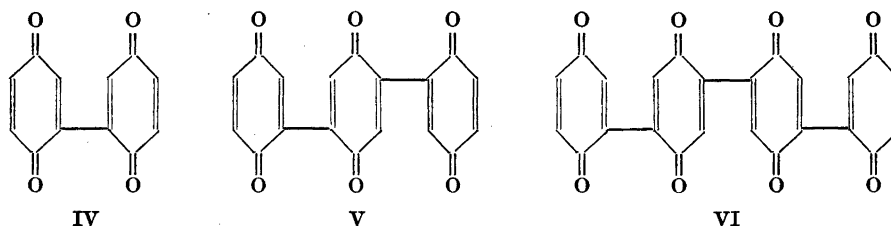
Our studies on the action of weak alkali *e.g.* sodium acetate, on *p*-benzoquinone has led us to believe that the amorphous "quinone humic acids" so formed, essentially are partly oxidised polyhydroquinones containing such elements as I, II and III<sup>1</sup>.



The degree of oxidation is highly dependent upon the alkalinity as shown by the amount of hydroquinone simultaneously formed in the reaction. Structure III serves only as an illustration of the theory and nothing can be said about the most probable distribution of the dissociable hydrogen atoms.

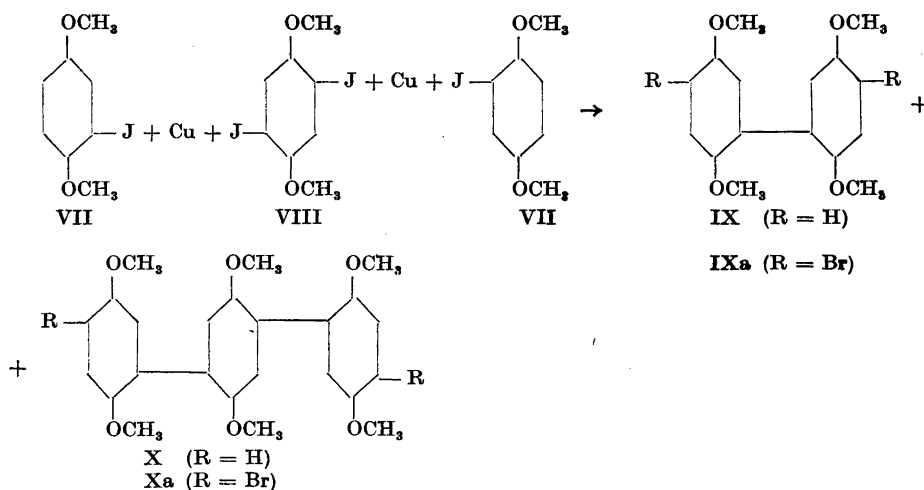
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It is clear that an increased knowledge about the properties of polyhydroquinones and their corresponding quinones would be of interest in relation to the chemistry of humic acids. Diquinone (IV) and the corresponding hydroquinone are known but higher members of the series have not been described. We now record the synthesis of triquinone (V) and tetraquinone (VI) and acetates and methylethers of the corresponding hydroquinones.



Diquinone (IV) is obtained by oxidation of the corresponding hydroquinone, 2,5,2',5'-tetrahydroxydiphenyl, which is easily available through demethylation of 2,5,2',5'-tetramethoxydiphenyl (IX), a product of the Ullmann coupling of iodohydroquinone dimethylether <sup>2</sup>. It is interesting in relation to the present research, that Barth and Schreder <sup>3</sup> have obtained dihydroquinone by alkali-fusion of hydroquinone. Other reaction products included a hexahydroxydiphenyl which was probably 2,4,5,2',4',5'-hexahydroxydiphenyl and an extremely oxidisable compound which may have been a trihydroquinone. In our previous paper we recorded the formation of dihydroquinone, albeit in a very small yield, from quinone by the action of strong sodium acetate solution.

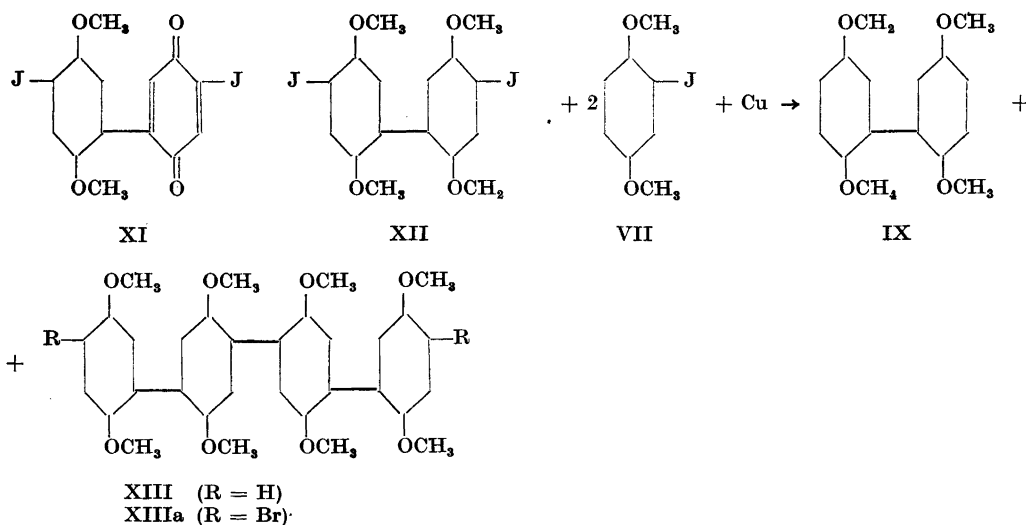
The mixed Ullmann coupling of an excess iodohydroquinone-dimethylether (VII) and 2,5-diiodohydroquinonedimethylether (VIII) yielded a mixture containing 2,5,2',5'-tetramethoxydiphenyl (IX) and 2,5-dimethoxy-1,4-bis-[2,5-dimethoxyphenyl]-benzene (X) from which these components could be separated by fractional distillation and crystallisation:



Demethylation of IX and X with pyridinium hydrochloride proceeded without complications. Trihydroquinone (X; OH instead of OCH<sub>3</sub>) is very unstable and is easily oxidised to blue products, especially when moist. Acetylation gave the hexaacetate and oxidation with chromic acid afforded triquinone (V). With insufficient amounts of chromic acid, blueblack crystalline "quinhydrones" were obtained. By varying the amount of chromic acid, products could be obtained which may have contained 1 or 2 quinonoid nuclei. They were very similar, yielding triquinone on further oxidation and like triquinone gave trihydroquinone hexaacetate on reductive acetylation, but were not further characterised. Triquinone is a yellow substance which is very sparingly soluble in organic solvents. Only 10 mg substance were dissolved after 48 hours' continuous extraction with chloroform in a Soxhlet apparatus. Triquinone may be recrystallised from ethyl benzoate but this operation must be carried out quite rapidly to avoid extensive decomposition. Recoveries larger than 50 % were not obtained. Diquinone may be recrystallised from ethanol, but this is not advisable because the substance suffers some decomposition in ethanol solution. Triquinone is more stable to alcohol, but this is probably due to its low solubility.

During earlier studies on the action of sulphuric acid in acetic acid on quinone we were able to isolate — apart from large amounts of polymeric products and hydroquinone — a small amount of a compound C<sub>18</sub>H<sub>10</sub>O<sub>4</sub> which was probably an *o*-(or *p*-) diphenylbenzene derivative<sup>4</sup>. As it gives a diacetate and a dimethylether, it is probably a dihydroxy-*triphenylene* dioxide. This compound could not be obtained by a similar treatment of trihydroquinone (X; OH instead of OCH<sub>3</sub>) which was recovered unchanged. Hence trihydroquinone is probably not an intermediate product in the formation of the compound C<sub>18</sub>H<sub>10</sub>O<sub>4</sub>.

According to Posternak *et al.*<sup>5</sup> oxidation of iodohydroquinone dimethylether with chromic acid gives 2,5-dimethoxy-4,4'-diiodo-diphenylquinone-2',5'



(XI). This quinone was reduced to the corresponding phenol followed by methylation to 4,4'-diiodo-2,5,2',5'-tetramethoxydiphenyl (XII). Mixed Ullmann coupling with excess iodohydroquinone dimethylether (VII) afforded a mixture of 2,5,2',5'-tetramethoxydiphenyl (IX) and 2,5,2',5'-tetramethoxy-4,4'-bis-[2,5-dimethoxyphenyl]-diphenyl (XIII) separated by distillation and crystallisation.

The demethylation of the quaterphenyl derivative XIII presented no difficulties but the phenol was easily oxidised in air turning blue and it was therefore acetylated to the stable octaacetate or oxidised with chromic acid to tetraquinone VI. Due to its insolubility this quinone could not be recrystallised from any organic solvent and was therefore not obtained quite pure. On reductive acetylation, however, it afforded the above octaacetate in almost quantitative yield.

In the mixed Ullmann couplings high molecular byproducts were always obtained, obviously due to coupling of the bifunctional iodides, but as the monofunctional iodide was always used in large excess the amount of such products was small.

Bromination of the di-, tri- and tetrahydroquinone methylethers IX, X and XIII in chloroform invariably yielded dibromoderivatives as the sole crystalline products and their structures are therefore certainly IXa, X a and XIII a.

The melting points of the mono—tetranuclear methylethers, acetates and quinones, and for comparative purposes, those of the parent hydrocarbons are recorded in Table 1. The melting points of the hydrocarbons and methylethers increase regularly with increasing molecular weight but the four-nuclear acetate possesses a lower melting point than the three-nuclear acetate. The former is probably dimorphous. However, no indication of dimorphism was found with the other acetates. It has not been possible to explain this abnormality but we believe that the observed low melting point is correct and that there may be some connexion with the spectrochemical peculiarities of the acetates discussed below. A similar abnormality was found for the dibrominated octamethoxyquaterphenyl (XIII a).

Table 1. Melting points of benzene-, diphenyl-, terphenyl- and quaterphenyl derivatives.

Number of nuclei	M. p. of hydrocarbon	M. p. of methyl-ethers	M.p. of di-bromo-methyl-ethers	M. p. of acetates	M. p. of quinones
1	5.5°	56°	145° *	123°	116°
2	70°	105°	155°	169°	194°
3	210°	189°	280°	244°	darkens at about 230°
4	320°	246°	261°	218° (234°)	darkens at 230—270° black at 350°

\* 2,5-dibromohydroquinone dimethylether.

The U.V. absorption curves of the methylethers and the acetates have been determined since they possess a considerable theoretical interest and because the latter allow certain comparisons to be made with the U.V. absorption curves of "leucoquinonehumic acid" acetates<sup>1</sup>.

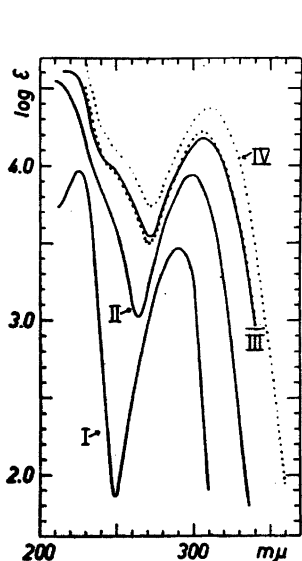


Fig. 1. Methylethers

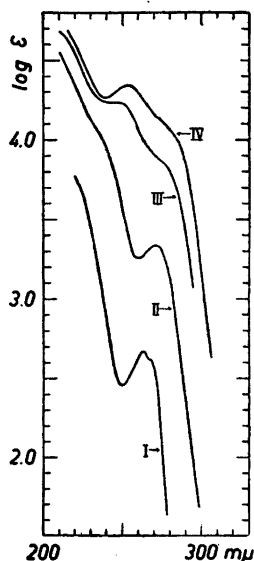


Fig. 2. Acetates

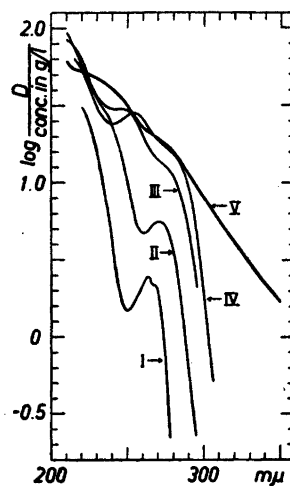


Fig. 3. Acetates on a weight by weight basis

U. V.-absorption in 95 % ethanol (—) and in dioxan (.....) for I: hydroquinone derivatives, II: dihydroquinone derivatives, III: trihydroquinone derivatives, IV: tetrahydroquinone derivatives, V: "leucoquinonehumic acid acetate."

The U.V. absorption of the methylethers (Fig. 1) exhibits regular shifts of the long-wave maximum towards red, indicating the presence of successively larger chromophores, or in other words, increasing conjugation. However, the  $\epsilon$ -value of this maximum is, for each substance, lower than for the corresponding *p*-polyphenyl<sup>6</sup>, indicating decreased conjugation due to the methoxyl substituents. The diphenyl K-band of the dimer, which appears as a widening of the short-wave band at about 250  $m\mu$ , also has a low intensity for the same reason. The absorption of the tri- and tetramer in the same region indicates the presence of diphenyl chromophores also in these compounds, in other words, there seems to be a certain amount of conjugation not extending over more than two nuclei. (No bands are reported for the corresponding hydrocarbons in this region<sup>6,7</sup>.)

Fig. 2 shows the absorption curves of the acetoxy compounds. The long-wave absorption of these substances is so low and occurs at such low wavelengths (*cf.* terphenyl and quaterphenyl<sup>6</sup>) that there can be very little conjugation beyond the diphenyl stage. Some diphenyl conjugation seems to occur (250—260  $m\mu$  band).

In Fig. 3 the absorption of the acetoxy compounds is compared with that of the product obtained through reductive acetylation of "sodium acetate humic acid", all curves being referred to a weight by weight basis. With increasing molecular size, the model compounds gradually approach a limit absorption curve which, if our views on the structure of the polymeric products is correct, should be similar to that of the latter at least below 300  $m\mu$ . This is indeed the case and although this product is undoubtedly more complex, it thus seems to contain a large proportion of polyphenyl elements similar to those of the model acetates.

Hydroquinone, dihydroquinone and trihydroquinone may be separated by paper partition chromatography. Employing a water saturated mixture of 9 parts of benzene and 1 part of methanol the  $R_F$ -values 0.3, 0.18 and 0.08 were obtained, bisdiazotised benzidine being used to locate the spots.

When oxidised with the theoretical amount of chromic acid, dihydroquinone affords the corresponding "quinhydrone"<sup>3</sup>. Similarly trihydroquinone may be oxidised to products containing one or two quinonoid nuclei. All these products possess very strong indigo blue colours and such quinhydrone-like compounds are obviously responsible for the coloration of di-, tri- and tetrahydroquinone on autoxidation in air.

In Table 2 some results of the action of alkali on various quinones are recorded. The experiments were carried out as described in part VI<sup>1</sup> except that the amount of hydroquinone formed was estimated by oxidation of the filtrate from the humic acid and isolation of the quinone.

Table 2. Formation of humic acids and hydroquinones from various quinones by the action of alkali.

Quinone	g Quinone used	Amount of NaOH used	Time hours	Colour	ml conc. HCl used for acidification	% Humic acid	% Hydroquinone
Diquinone	0.6	15 ml 20 %	0.5	brown	12	45	1
4,4'-Dimethoxydiquinone	1.2	15 ml 20 %	1.0	green changing to brown	12	20 *	14
—, —	1.0	25 ml 8 %	1.0	green	8	20	3
Toluquinone	1.1	15 ml 20 %	0.5	green changing to brown	12	40	35

\* The aqueous solution was distilled and found to contain methanol (about 45 % of theory).

The result obtained with diquinone is particularly interesting and fits in well with our theory on the polymerisation of quinone in alkali. According to this theory diquinone would be expected to yield a brown polymerisation product in which every second nucleus should be quinonoid (as in III) and no dihydroquinone should be found. The deep green solution obtained from qui-

none and toluquinone indicates a low degree of oxidation of the polymers. When shaken with air these solutions turn brown due to further oxidation. On acidification both the green and the brown solutions give amorphous humic acids which may be collected by filtration or centrifugation and washed with dilute hydrochloric acid. When they are dissolved in alkali the original colours reappear. The "leucoacetates" obtained on reductive acetylation of such quinone humic acids which are soluble in alkali with a brown colour, may be hydrolysed with alkali in the absence of air to products which on aeration are initially coloured deep green. Like diquinone tri- and tetraquinone immediately give brown solutions with alkali. In the presence of hydroquinone, however, di-, tri- and tetraquinone give green solutions with alkali, just as "diquinhydrone" and the above mentioned "quinhydrone" of triquinone. 4,4'-dimethoxydiquinone, however, like quinone gives a green colour with alkali, but as seen from Table 2 4,4'-dimethoxyquinone gives considerable amounts of the corresponding hydroquinone. A further complication consists in extensive demethylation.

#### EXPERIMENTAL

*2,5,2',5'-Tetrahydroxydiphenyl and 2,5,2',5'-tetraacetoxydiphenyl.* 2,5,2',5'-Tetra-methoxydiphenyl (15 g) was heated one hour to 200–210° with freshly distilled pyridine hydrochloride (40 g). The slightly discoloured melt (a) was cooled, dissolved in water and extracted continuously with ether. The crude phenol was recrystallised from water containing a little sulphur dioxide. M. p. 240° (decomp.). — The tetraacetate was obtained from the isolated phenol or preferentially from the melt (a) by heating with acetic anhydride containing a little pyridine. The solution was poured into water and the precipitate crystallised from dilute acetic acid. Overall yield 75 %. M. p. 168–169°. (Found:  $\text{CH}_3\text{COO}$  58.1. Calc. for  $\text{C}_{12}\text{H}_8(\text{OCOCH}_3)_4$ :  $\text{CH}_3\text{COO}$  58.0.)

*Diquinone (IV).* The demethylation melt (a) was dissolved in water (200 ml) and the solution was poured, in portions, into a solution of sodium dichromate (40 g) in 2 N sulphuric acid (750 ml) with cooling and stirring. The precipitated diquinone was immediately collected and washed successively with water, alcohol and ether, dried and dissolved in hot chloroform. To the filtered solution ether was added until crystallisation occurred. On cooling pure diquinone (8.2 g or 70 % overall yield) was obtained. M. p. 192–194°. When heated with alcohol or water brown, amorphous substances were slowly formed.

*2,5-Dimethoxy-2',5'-dihydroxy-4,4'-diiododiphenyl.* 2,5-Dimethoxy-4,4'-diiodo-di-phenyl quinone-2',5' (XI) was dissolved in warm acetic acid and zinc dust added in portions until the solution was colourless. The reaction mixture was filtered into cold water yielding a precipitate of almost pure hydroquinone m. p. 186–190° raised to 192–193° by recrystallisation from acetic acid. (Found:  $\text{OCH}_3$  12.9. Calc. for  $\text{C}_{12}\text{H}_4\text{J}_2(\text{OH})_2(\text{OCH}_3)_2$ :  $\text{OCH}_3$  13.1.)

*2,5,2',5'-Tetramethoxy-4,4'-diiododiphenyl (XII).* The above phenol was dissolved in lukewarm ethanol, an excess of dimethyl sulphate was added, followed, in portions, by the same volume of sodium hydroxide (40 g  $\text{NaOH}/100$  ml). The tetramethylether separated almost immediately in a theoretical yield m. p. 173–177° raised to 181.5–182° by crystallisation from ethanol. (Found:  $\text{OCH}_3$  23.6. Calc. for  $\text{C}_{12}\text{H}_4\text{J}_2(\text{OCH}_3)_4$ :  $\text{OCH}_3$  23.6.)

*2,5-Diiodohydroquinone dimethylether (VIII).* This compound was obtained either according to the method of Robinson<sup>8</sup> employing an excess of iodine chloride or by the following method. Hydroquinone dimethylether (50 g) was dissolved in ethanol (200 ml) and the solution heated under reflux. In portions and alternately iodine (200 g) and precipitated mercuric oxide (75–100 g) was added. The hot solution was filtered and crude diiodohydroquinone dimethylether crystallised from the filtrate. The mother liquor was evaporated and dissolved in benzene which had previously been employed to extract the mercuric iodide precipitate. The solution was shaken with alkaline sodium iodide

solution to remove dissolved mercuric iodide and then concentrated. The diiododerivative was purified by recrystallisation from ethanol. Yield 70–80 %.

*2,5-Dimethoxy-1,4-bis-[2,5-dimethoxyphenyl]-benzene (X).* A mixture of monoiodo-hydroquinone dimethylether (19.5 g), 2,5-diiodohydroquinone dimethylether (3.5 g) and copper bronze (23 g) was heated to 180° and the temperature slowly raised. The reaction took place at 220–230° and the mixture thickened. The temperature was increased to 260–265° to complete the reaction, the whole operation requiring about 20–30 minutes. The crushed reaction mixture was mixed with cotton wool and extracted with chloroform in a Soxhlet apparatus for two hours. The brownish, chloroform-soluble product from four runs (43 g) was fractionately distilled at a pressure of 0.5 mm and the following fractions collected: 1. B. p. <185° (27 g); 2. B. p. 185–275° (13 g); 3. Residue (3 g). Fraction 1 was redistilled and an oily portion, b. p. <105° discarded. The next fraction, b. p. 105–185° (24 g) yielded 2,5,2',5'-tetramethoxydiphenyl (18 g) on treatment with ethanol. Fraction 2 was also redistilled when a mixture (a) of the diphenyl- and terphenyl derivatives (4 g) was recovered at a temperature below 200°. The fraction 200–290° (b. 9 g) was recrystallised twice from acetic anhydride (10–20 ml) m. p. 166–183 raised to 169–186°, and once from methylethylketone yielding the pure terphenyl derivative, m. p. 188–189°. The mother liquors were evaporated and the residues mixed with fraction a and refractionated as described above. Total yield of the terphenyl derivative 4.5 g. Small crystals, sparingly soluble in ethanol and ether but soluble in chloroform. (Found: C 69.8; H 6.4; OCH<sub>3</sub> 45.4; Mol. wt. (camphor) 410. Calc. for C<sub>18</sub>H<sub>8</sub>(OCH<sub>3</sub>)<sub>6</sub>: C 70.2; H 6.4; OCH<sub>3</sub> 45.6; Mol. wt. 410.)

*2,5-Dihydroxy-1,4-bis-[2,5-dihydroxyphenyl]-benzene and its hexaacetate.* 2,5-Dimethoxy-1,4-bis-(2,5-dimethoxyphenyl)-benzene (0.5 g) was added to freshly distilled pyridine hydrochloride (4 g) and the mixture heated one hour to 200–210° in an atmosphere of carbon dioxide. The cooled melt (a) was treated with water containing sulphur dioxide (50 ml) when the phenol was obtained as a fine suspension. It is very sparingly soluble in ether and is best collected by centrifugation. The compound is relatively soluble in ethanol and is so labile towards oxygen that no attempts were made to obtain it in a pure state. When moist it is immediately coloured deep blue. In the dry state it is somewhat more stable, but is soon coloured blue superficially. The m. p. appears to be between 280–290°. — The hexaacetate is obtained by dissolving the pyridine-hydrochloride melt (a) in hot acetic anhydride (20 ml containing a little pyridine) and pouring the solution into water. Yield 91 % calculated on the methoxy compound. It is crystallised from strong acetic acid or ethyl-glycol. The compound is soluble in chloroform and sparingly soluble in ethanol and ether. M. p. 243–244°. (Found: C 61.8; H 4.6; CH<sub>3</sub>COO 60.1; OCH<sub>3</sub> 0. Calc. for C<sub>18</sub>H<sub>8</sub>(OCOCH<sub>3</sub>)<sub>6</sub>: C 62.3; H 4.5; CH<sub>3</sub>COO 61.3.)

*Triquinone (V).* The pyridine hydrochloride melt (a) was dissolved in water (25 ml) and the suspension poured, in portions, into a solution (40 ml) of chromic acid solution made from 5 g sodium dichromate and a mixture of 1 part of concentrated and 3 parts of 2 N sulphuric acid. The temperature must not be allowed to rise. At each addition a transient dark coloration was observed changing into yellow. The precipitated deep yellow triquinone was immediately filtered, (double filter papers), and washed with water, alcohol and ether. Yield 90 % calculated on the methoxy compound. Triquinone may be recrystallised from ethyl benzoate by pouring the substance into the hot solvent, immediate filtration and cooling. The mother liquor is always coloured strongly brown. Reductive acetylation with zinc, acetic acid, acetic anhydride and a trace of pyridine gave the hexaacetate of the corresponding hydroquinone in quantitative yield (mix. m. p.). Triquinone has no melting point but turns dark at about 230°. (Found: C 65.8; H 2.6. Calc. for C<sub>18</sub>H<sub>8</sub>O<sub>6</sub>: C 67.6; H 2.5.) The sample contained some ash which partly accounts for the low carbon content. Due to the extremely low solubility of triquinone a complete purification is difficult to achieve.

*2,5,2',5'-Tetramethoxy-4,4'-bis-[2,5-dimethoxyphenyl]-diphenyl. (XIII).* A mixture of iodohydroquinonedimethylether (19 g), 4,4'-diiodo-2,5,2',5'-tetramethoxydiphenyl (3.9 g) and copper bronze (23 g) was heated in the usual way and then continuously extracted 24 hours with chloroform. The product (18.1 g) was distilled at low pressure (0.4 mm) and a fraction collected boiling below 190° (12.5 g) which on crystallisation from alcohol yielded 2,5,2',5'-tetramethoxydiphenyl (11 g) followed by another boiling between 190 and 300° (3.8 g). The latter was powdered and extracted with boiling acetone (75 ml). The undissolved residue (2.8 g m. p. 241–244°) was recrystallised from nitrobenzene



(25 ml), m. p. 245–246°. It may also be recrystallised from dibutylphthalate. It is very sparingly soluble in most organic solvents but somewhat soluble in chloroform. (Found: C 70.7; H 6.3; OCH<sub>3</sub> 45.2. Calc. for C<sub>24</sub>H<sub>10</sub>(OCH<sub>3</sub>)<sub>8</sub>: C 70.3; H 6.3; OCH<sub>3</sub> 45.5.)

*2,5,2',5'-Tetrahydroxy-4,4'-bis-[2,5-dihydroxyphenyl]diphenyl and its octaacetate.* Very finely divided 2,5,2',5'-tetramethoxy-4,4'-bis-[2,5-dimethoxyphenyl]-diphenyl (0.35 g) was introduced into a flask and pyridinium hydrochloride (5 g) distilled directly into it. Carbon dioxide was passed into the flask which was heated for one–two hours to 205–215°. After cooling, the slightly discoloured melt was either dissolved in water containing sulphur dioxide, when a colourless very fine suspension of the hydroquinone was obtained, or was directly acetylated by heating with acetic anhydride (20 ml) containing a drop of pyridine. The hydroquinone could be collected by centrifugation but because of its instability no attempts were made to characterise it. It is rapidly coloured blue even in the dry state. The octaacetate was obtained in an almost quantitative yield and was recrystallised from hot acetic acid or ethyl glycol. The melting point was found to be 215–218.5°.

In a few cases, especially, when the octaacetate had been distilled in a high vacuum and the melt induced to crystallise by moistening with methanol, a m. p. of 212–213° was observed followed by solidification and renewed melting at 233–234°. (Found: C 62.1; H 4.6; CH<sub>3</sub>COO 60.8; OCH<sub>3</sub> 0. Calc. for C<sub>24</sub>H<sub>10</sub>(OCOCH<sub>3</sub>)<sub>8</sub>: C 62.3; H 4.6; CH<sub>3</sub>COO 61.2.)

*Tetraquinone (VI).* This compound was prepared from demethylated 2,5,2',5'-tetramethoxy-4,4'-bis-[2,5-dimethoxyphenyl]-diphenyl by oxidation with chromic acid in exactly the same way as triquinone. Yellowish crystal powder which turns brown from about 230° and is black at 350°. It is extraordinarily insoluble in all solvents and could not be recrystallised. (Found: C 64.6; H 2.3. Calc. for C<sub>24</sub>H<sub>10</sub>O<sub>8</sub>: C 67.6; H 2.4.)

The preparation on ignition yielded some ash containing chromium. On reductive acetylation an almost quantitative yield of the corresponding octaacetate was obtained.

*Bromination of (a) 2,5,2',5'-tetramethoxydiphenyl, (b) 2,5-dimethoxy-1,4-bis-[2,5-dimethoxyphenyl]-benzene and (c) 2,5,2',5'-tetramethoxy-4,4'-bis-[2,5-dimethoxyphenyl]-diphenyl.* The phenol ethers were dissolved in chloroform and an excess (in case c only a slight excess) of bromine in chloroform added. After 30 minutes the solutions were shaken with a dilute sodium carbonate solution, dried and evaporated. The bromoderivatives were recrystallised (a) from ethanol, (b) from acetic anhydride and (c) from nitrobenzene.

From (a) slender needles (probably IX a) were obtained, m. p. 154–155°. (Found: OCH<sub>3</sub> 28.2. Calc. for C<sub>12</sub>H<sub>8</sub>(OCH<sub>3</sub>)<sub>4</sub>Br<sub>2</sub>: OCH<sub>3</sub> 28.6.) From (b) small compact crystals (probably X a), m. p. 278–280° were obtained. (Found: OCH<sub>3</sub> 32.2. Calc. for C<sub>18</sub>H<sub>8</sub>(OCH<sub>3</sub>)<sub>6</sub>Br<sub>2</sub>: OCH<sub>3</sub> 32.7.) From (c) a fine crystal powder (probably XIII a) was obtained, m. p. 259–261°. (Found: OCH<sub>3</sub> 35.2. Calc. for C<sub>24</sub>H<sub>8</sub>(OCH<sub>3</sub>)<sub>8</sub>Br<sub>2</sub>: OCH<sub>3</sub> 35.2.)

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