70. *Condensation Products of Phenols and Ketones. Part II. Catechol and Acetone.**

By Wilson Baker and John C. McGowan.

A condensation product of catechol and acetone, $C_{21}H_{24}O_4$, has been proved to be 5 : 6 : 5′ : 6′-tetrahydroxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene as was suggested by one of the authors in 1934. The structure as a bis-1 : 1′-*spiro*hydrindene was established by oxidation with potassium permanganate, phoronic anhydride, $C_{11}H_{16}O_4$, being isolated. Aerial oxidation in alkaline solution led to the opening of both catechol nuclei and formation of a tetracarboxylic acid without loss of carbon atoms; this acid on reduction and decarboxylation yielded a bis-*spirocyclo*pentene, $C_{17}H_{28}$, whose properties are consistent only with the given positions of the hydroxyl groups in the original compound.

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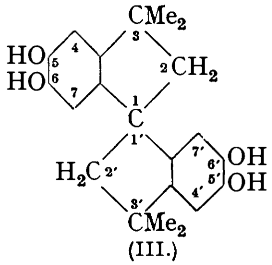
* The paper by Baker entitled " The Condensation of Catechol with Acetone " (J., 1934, 1678) is to be regarded as Part I of the series.

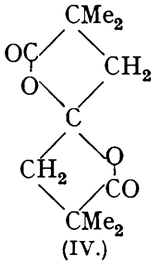
CATECHOL condenses with acetone in presence of acetic and hydrochloric acids to form a compound $C_{21}H_{24}O_4$ (I), which is equivalent to $2C_6H_4(OH)_2 + 3C_3H_6O - 3H_2O$. This substance was first prepared by Fabinyi and Széky (*Ber.*, 1905, **38**, 2307), who suggested the improbable structure $(HO)_2C_6H(CMe_2)_3C_6H(OH)_2$ (II), which, as pointed out by Ghiglieno (*Atti R. Accad. Sci. Torino*, 1912, **47**, 16), does not account for the ready formation of a tetrabromo-derivative on treatment with bromine in acetic acid. Ghiglieno showed that the compound could be produced equally easily when catechol was condensed, not with acetone, but with the equivalent amount of phorone (compare Baker, *loc. cit.*), and he suggested the structure $[(HO)_2C_6H_3]_2C(CH{:}CMe_2)_2$. This, however, cannot be correct, because, as pointed out by Fisher, Furlong, and Grant (*J. Amer. Chem. Soc.*, 1936, **58**, 820), such a compound would yield a polybromo-derivative containing more than four atoms of bromine, and would show the unsaturation characteristic of ethylenic compounds. We have been unable to reduce (I) or its tetramethyl ether by catalytic methods, and similar negative results under more drastic conditions have been recorded by Remesat (Dissert., Berlin, 1930, " Versuchung über die Kondensation von Brenzkatechin und Guajacol mit Aldehyden und Ketonen "). Remesat also carried out a number of high-temperature but uninformative degradations of (I) which threw no new light on its structure, and he retained the original formula (II).

Sükösd (*Acta Lit. Sci. Univ. Hung. Francisco-Josephinae*, 1932, **2**, 230; *Amer. Chem. Abs.*, 1933, **27**, 1873) obtained a condensation product of guaiacol and acetone and suggested for it a structure analogous to (II). Fisher, Furlong, and Grant (*loc. cit.*), however, have shown that the dimethyl ether of Sükösd's compound is identical with the tetramethyl ether of (I), so that the objections to (II) apply equally to the guaiacol–acetone compound.

The condensation product, $C_{21}H_{24}O_4$ (I), of catechol and acetone was reinvestigated in 1934 (Baker, *loc. cit.*), and the suggestion was made that it was probably 5 : 6 : 5′ : 6′-tetrahydroxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene (III), on the following grounds. (1) It contains four phenolic groups, yielding a tetra-acetate, tetrabenzoate, and tetramethyl ether, and a double ortho-quinone reducible to the original compound; (2) four hydrogen atoms and four only are instantaneously replaced by bromine on treatment with bromine in acetic acid; most probably this involves two hydrogen atoms in each of the catechol nuclei; (3) it contains no ethylenic bonds; (4) phorone is an intermediate in its formation. With regard to (2) it has now been found that under the same conditions 5 : 6-dihydroxyhydrindene readily yields 4 : 7-*dibromo*-5 : 6-*dihydroxyhydrindene.*



(III.)



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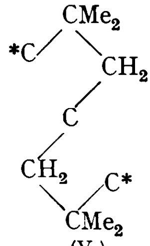
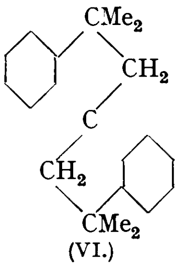


(V.)



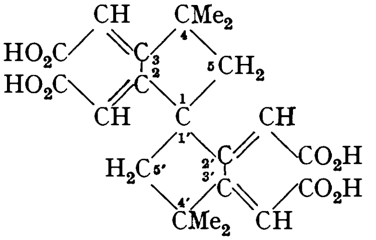
(VI.)

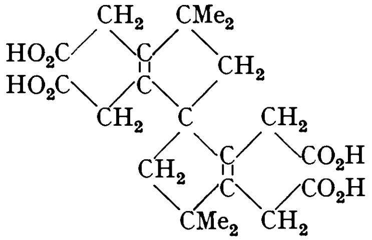
Although the structure (III) appeared to be the only one consistent with the then known facts and has been accepted by recent workers (Fisher, Furlong, and Grant), there was little direct proof of its accuracy, but the experiments now recorded prove that the substance is a tetrahydroxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene of the type (III), the only point not established with *absolute* rigidity being the positions of the hydroxyl groups, although no reasonable doubt can be entertained that they occupy positions 5, 6, 5′, and 6′ as in (III).

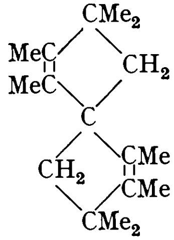
Oxidation of (I) with potassium permanganate and treatment of the product with acetic anhydride led to the isolation in small yield of phoronic anhydride (IV). Phoronic anhydride was also obtained similarly from the carefully purified tetra-acetate of (I). This established the presence in the compound of the grouping (V). It is clear that, of the nine carbon atoms in the grouping $\cdot CMe_2\cdot CH_2\cdot C\cdot CH_2\cdot CMe_2\cdot$, none could have formed part of an aromatic nucleus, and these nine carbon atoms therefore represent the three molecules of acetone involved in the condensation, and it is to be noted that they are combined as in phorone. The two remaining carbon atoms marked with asterisks in (V) must, therefore, have formed part of the two catechol nuclei,* so that the structure may be expanded to (VI). Of the remaining eight hydrogen atoms not shown in (VI), four are present in hydroxyl groups, and four as nuclear hydrogen atoms (because the compound yields a tetrabromo-derivative), so that the central carbon atom, which becomes a carbonyl group during oxidation, must be quaternary, and this can only be achieved by its being united to the two aromatic nuclei in two positions ortho to the CMe_2 groups, as in (III). For stereochemical reasons it is clearly impossible that the central carbon atom in (VI) could be united to the aromatic nuclei in the positions meta or para to the CMe_2 groups.

With regard to the hydroxyl groups it is almost certain from a consideration of the general activity of catechol and of guaiacol, which gives a product with the same orientation, that these occupy positions 5, 6, 5′, and 6′ as in (III). Evidence from the great stability of the corresponding *o*-quinone (Baker, *loc. cit.*; Fisher, Furlong, and Grant, *loc. cit.*) is of no value, because we have now found that 5 : 6-*hydrindenequinone* is not more stable or more readily formed than *o*-benzoquinone itself. Again, arguments based on coupling experiments in the case of the guaiacol condensation product (Fisher, Furlong, and Grant) are inconclusive, and, in view of the note of Fieser and Lothrop (*J. Amer. Chem. Soc.*, 1937, **59**, 945), are of very doubtful value. Evidence very strongly supporting the structure (III) has now been obtained from a study of the properties of another oxidation product of the compound $C_{21}H_{24}O_4$ (I).

Aerial oxidation of (I) in aqueous alkaline solution results in the absorption of four atoms of oxygen and formation of a tetracarboxylic acid, $C_{17}H_{20}(CO_2H)_4$, which, if the hydroxyl groups occupy the positions shown in (III), must be 2 : 3 : 2′ : 3′-*tetra*(*carboxymethylene*)-4 : 4 : 4′ : 4′-*tetramethylbis*-1 : 1′-spirocyclo*pentane* (VII). This acid (VII) yields phoronic acid, isolated as its anhydride, when oxidised with potassium permanganate, and, when reduced with sodium amalgam, takes up two molecules of hydrogen, giving 4 : 4 : 4′ : 4′-*tetramethylbis*-1 : 1′-spirocyclo*pentene*-2 : 3 : 2′ : 3′-*tetra-acetic acid* (VIII), this partial reduction with sodium amalgam being characteristic of muconic acid and derivatives. *Methyl* and *ethyl* esters of (VIII) were prepared. The calcium and barium salts


(VII.)


(VIII.)


(IX.)

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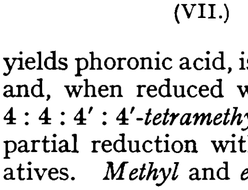
* It should be pointed out for the sake of completeness that these two carbon atoms could not have been ortho- or para-carbon atoms of one catechol nucleus, since the former would require a 7- and a 3-membered ring fused one to each of the two aromatic nuclei, and the latter a chain of five carbon atoms connecting the para-positions of one nucleus and a 3-membered ring fused to the other. If, however, they were two meta-carbon atoms of one nucleus, this would lead to the structure annexed. Apart from its intrinsic improbability a compound of such structure could not be expected to yield a double ortho-quinone on oxidation with fuming nitric acid in alcohol, nor could it give any satisfactory explanation for the formation of the acids $C_{21}H_{24}O_8$ and $C_{21}H_{28}O_8$ or the hydrocarbon $C_{17}H_{28}$, here represented by the formulæ (VII), (VIII), and (IX), which clearly involves two symmetrically placed catechol nuclei.



of (VII) and (VIII) are much more soluble in cold than in hot water. When heated, the acid (VIII) readily loses four molecules of carbon dioxide, yielding a hydrocarbon $C_{17}H_{28}$, 2 : 3 : 4 : 4 : 2′ : 3′ : 4′ : *4′-octamethylbis*-1 : 1′-spirocyclo*pentene* (IX). This hydrocarbon readily combines with four atoms of bromine in acetic acid solution, but does not undergo catalytic reduction with hydrogen in presence of either palladium chloride, palladium deposited on strontium carbonate, or Adams's platinum oxide catalyst under three atmospheres pressure. This failure to reduce gives very strong support to the structure (IX), and hence to the structure (III) for the original condensation product, since owing to the methyl groups attached to the double bonds in (IX), and the quaternary nature of the adjacent carbon atoms 1, 4, and 4′, resistance to reduction might well be expected. If, however, the hydroxyls in the condensation product occupied either positions 4, 5, 4′, and 5′ or positions 6, 7, 6′, and 7′, then the hydrocarbon $C_{17}H_{28}$ would contain two ethylidene groups, $CH_3{\cdot}CH\colon$, and no resistance to reduction could be expected. The simultaneous loss of four molecules of carbon dioxide from (VIII) also indicates that the carboxyl groups are all very similarly placed in the molecule, which would not be the case if (VIII) were derived from catechol–acetone condensation products possessing either of the two alternative arrangements of the hydroxyl groups. Further, if the hydroxyls occupied positions 6, 7, 6′, and 7′, then the acid corresponding to (VIII) would have carboxyl groups united to carbon atoms 2 and 2′ and would be a glutaric acid derivative; as such it would be expected that these two carboxyl groups would yield an anhydride on heating instead of losing carbon dioxide.

Many unsuccessful attempts have been made to degrade the very stable tetramethyl ether of (III) to *m*-hemipinic acid, and thus to establish the positions of the methoxyl groups. Among the recorded conditions are treatment with potassium permanganate in acetone and pyridine solution (Remesat, Baker), and with chromic anhydride in acetic acid (Fisher, Furlong, and Grant). Fusion with caustic alkalis under a variety of conditions, both with and without the addition of oxidising agents, has also given negative results. Attempts to resolve the guaiacol–acetone condensation product by means of its di-*l*-menthoxyacetate were unsuccessful, the ester being obtained only as a non-crystalline resin.

A crystallographical examination of the dimorphic forms of the tetramethyl ether of (III) (see Part I) was kindly undertaken by Mr. H. M. Powell of the Department of Mineralogy, University Museum, Oxford, who reports as follows :—

" Crystals of the β modification belong to the anorthic system and develop the forms {100} {010} {001} {110} {$\bar{1}$10} {201} {$\bar{2}$01}. From measurements of interfacial angles on the goniometer the crystallographic constants are calculated to be $a : b : c = 1{\cdot}408 : 1 : 0{\cdot}5578$; $\alpha = 108°\ 46'$, $\beta = 103°\ 51'$, $\gamma = 82°\ 12'$. Etch figures and the absence of pyroelectric effect show that the crystals have a centre of symmetry. *X*-Ray photographs obtained with copper radiation give the unit cell dimensions as $a_0 = 21{\cdot}64$, $b_0 = 14{\cdot}35$, $c_0 = 7{\cdot}99$ A. The density was found to be 1·15 g./c.c. and hence the number of molecules per unit cell is $4{\cdot}02 \approx 4$.

" The α-form is tetragonal. The crystals are badly formed bipyramids and are optically uniaxial. Oscillation photographs obtained with copper radiation show that there is a pseudo-cell of dimensions $a_0 = 8{\cdot}40$, $c_0 = 33{\cdot}0$ A. The density was found to be 1·11 g./c.c. and the calculated number of molecules per unit cell is $3{\cdot}96 \approx 4$. Very faint intermediate layer lines obtained on oscillation about the *a* axis show, however, that the true *a* dimension is four times that of the pseudo-cell and hence indicate a cell sixteen times this size.

" For both modifications the cell size and density therefore give a molecular weight in agreement with the proposed formula for this substance, and models constructed for the purpose show that the molecules may be packed into the space available."

The elucidation of the structure of other condensation products of acetone and phenols along the lines described in this paper is in progress. It has already been established that both hydroxyquinol and *m*-cresol yield derivatives of 4 : 4 : 4′ : 4′-tetramethylbis-2 : 2′-*spiro*chroman, but that pyrogallol gives a 3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene.

EXPERIMENTAL.

Oxidation of the Compound $C_{21}H_{24}O_4$ *and Isolation of Phoronic Anhydride* (IV).—5 : 6 : 5′ : 6′-Tetrahydroxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene (III) (10 g.) was finely powdered, and a warm saturated aqueous solution of potassium permanganate slowly added with constant agitation, until the colour of the solution indicated that it was present in considerable excess; the mixture was then kept overnight. After passage of excess of sulphur dioxide the liquid was extracted with ether, and the extract dried over sodium sulphate and distilled, leaving a somewhat rancid-smelling liquid (4·5 g.); this contained acetic acid, and, judging by the odour, possibly also *iso*butyric and *iso*valeric acids.* This was refluxed with acetic anhydride (10 c.c.) for 1 hour, and, after shaking with water, was submitted to steam distillation. The distillate yielded to ether an oil which solidified in contact with water; the solid (about 0·5 g.) was collected, washed with cold dilute sodium hydroxide solution and water, dried, and crystallised first from light petroleum (b. p. 60—80°), and then twice from light petroleum (b. p. 80—100°). The phoronic anhydride separated in long flat prisms, m. p. 128—129° (Found : C, 62·4; H, 7·6; *M*, 220. Calc. for $C_{11}H_{16}O_4$: C, 62·3; H, 7·5%; *M*, 212).

Phoronic anhydride was also obtained by the oxidation of pure 5 : 6 : 5′ : 6′-tetra-acetoxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene, m. p. 174—175°, which had been twice crystallised from alcohol, and submitted to a preliminary hydrolysis with a little alcoholic potassium hydroxide, the alcohol being removed before the addition of the permanganate.

A specimen of phoronic anhydride was synthesised by the action of acetic anhydride on phoronic acid (Pinner, *Ber.*, 1881, **14**, 1070). After crystallising twice from light petroleum, (b. p. 80—100°) it had m. p. 128·5—129·5°, undepressed on admixture with the anhydride previously prepared. All specimens were identical in their crystalline habit.

Oxidation of the Compound $C_{21}H_{24}O_4$ *and Isolation of* 2 : 3 : 2′ : 3′-*Tetra*(*carboxymethylene*)-4 : 4 : 4′ : 4′-*tetramethylbis*-1 : 1′-spirocyclo*pentane* (VII).—5 : 6 : 5′ : 6′-Tetrahydroxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene (III) (10 g.), dissolved in a solution of sodium hydroxide (40 g.) in water (300 c.c.), was oxidised by bubbling air through the solution for 50 hours, a layer of light petroleum (b. p. 100—120°) being floated on the solution to prevent frothing. Ether (100 c.c.) was now added to the solution, which was cooled and stirred during the addition of excess of hydrochloric acid. A pale yellow, crystalline powder separated and a small amount of resinous material was taken up by the ether. After an hour the product was collected and washed thoroughly with water and ether (yield, 8·9 g.; 75% of the theoretical). For analysis it was crystallised three times from 50% aqueous acetic acid, and dried in a vacuum over potassium hydroxide at 100°, being obtained as a very pale yellow, microcrystalline powder, m. p. about 260° with evolution of carbon dioxide [Found : C, 62·1; H, 5·9; equiv., by titration with cold sodium hydroxide solution and phenolphthalein, 100·7. $C_{17}H_{20}(CO_2H)_4$ requires C, 62·4; H, 5·9%; equiv., 101].

2 : 3 : 2′ : 3′-*Tetra*(*carboxymethylene*)-4 : 4 : 4′ : 4′-*tetramethylbis*-1 : 1′-spirocyclo*pentane* is very sparingly soluble in hot water, ether, acetone, and ethyl acetate, but soluble in alcohol and acetic acid. It does not react with bromine in acetic acid, and is apparently unaltered by boiling with excess of acetic anhydride for 10 hours. The barium salt was prepared by heating a solution of the acid in the minimum quantity of dilute aqueous ammonia with excess of barium acetate, collecting the precipitate at the boiling point, and washing it with boiling water. This salt is easily soluble in cold water, but very sparingly soluble in hot water. When oxidised with potassium permanganate solution as described under the similar oxidation of the condensation product (III), the acid ultimately yielded phoronic anhydride, m. p. 126—127° (the mixed m. p. with the synthetical anhydride, m. p. 128·5—129·5°, was 128—129°). The product obtained by heating the acid above its m. p. was mainly resinous, but a small quantity of a yellow volatile hydrocarbon possessing a powerful terpene-like odour was isolated by steam distillation.

4 : 4 : 4′ : 4′-*Tetramethylbis*-1 : 1′-spirocyclo*pentene*-2 : 3 : 2′ : 3′-*tetra-acetic Acid* (VIII).—2 : 3 : 2′ : 3′-Tetra(carboxymethylene)-4 : 4 : 4′ : 4′-tetramethylbis-1 : 1′-*spirocyclo*pentane (VII) (20 g.), suspended in water (400 c.c.), was heated on a steam-bath, and 4% sodium amalgam added at intervals with occasional stirring until reduction was complete (about 8 hours). The solution was cooled, filtered, and acidified with hydrochloric acid, and the solid precipitate

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* On several occasions this liquid became pasty with crystals of phoronic anhydride after a few hours. The spontaneous deposition of the anhydride, however, could not be relied upon, and it was found convenient to treat the product with acetic anhydride.

collected after an hour and washed thoroughly with water. It was recrystallised twice from aqueous alcohol, being obtained in minute hexagonal plates, m. p. about 260° (decomp.) (yield, almost quantitative) [Found: C, 61·4; H, 6·7; equiv. by titration with cold sodium hydroxide solution and phenolphthalein, 104·1. $C_{17}H_{24}(CO_2H)_4$ requires C, 61·8; H, 6·8%; equiv., 102]. This acid is oxidised by a warm solution of potassium permanganate but does not decolourise a solution of bromine in acetic acid. The calcium salt was prepared by boiling a solution of the sodium salt with a solution of calcium acetate; it was collected while hot and washed with boiling water. This salt is much more soluble in cold water than hot; 100 g. of water dissolve 14·2 g. at 15°, but only 0·57 g. at 100° (compare calcium citrate); the cold aqueous solution is rather viscous and froths easily. No smooth decomposition takes place on distillation of the calcium salt and no ketone appears to be produced.

The *tetramethyl* ester of this acid was prepared by refluxing a solution of the acid in ten times its weight of absolute methyl alcohol containing anhydrous hydrogen chloride for 8 hours. After the addition of excess of sodium bicarbonate solution the ester was extracted with ether, and the ethereal solution dried and distilled. The residual ester was distilled twice under diminished pressure, and the middle fraction collected in each case. It formed an odourless, pale yellow oil, b. p. 195°/0·36 mm., 202°/0·53 mm. (Found: C, 64·6; H, 7·9; *M*, 437. $C_{25}H_{36}O_8$ requires C, 64·6; H, 7·8%; *M*, 464). The *tetra-ethyl* ester, obtained in the same way, formed an odourless, pale yellow oil, b. p. 243°/2 mm. (Found: C, 66·5; H, 8·6; *M*, 528. $C_{29}H_{44}O_8$ requires C, 66·9; H, 8·5%; *M*, 520).

2 : 3 : 4 : 4 : 2′ : 3′ : 4′ : 4′-*Octamethylbis*-1 : 1′-spirocyclo*pentene* (IX).—4 : 4 : 4′ : 4′-Tetramethylbis-1 : 1′-*spirocyclo*pentene-2 : 3 : 2′ : 3′-tetra-acetic acid (VIII) (20 g.) was heated in a small flask in portions of 5 g. until nothing further distilled. The product was submitted to steam-distillation, and the volatile oil (5·1 g.) extracted from the distillate with ether. It formed a colourless liquid, b. p. 130—131°/18 mm., 250°/760 mm. (Found: C, 88·0; H, 11·9. $C_{17}H_{28}$ requires C, 87·9; H, 12·1%), with a weak, rather fatty odour. It is soluble in most organic solvents, but does not mix completely with acetic acid. It yields no picrate or picrolonate.

As usually prepared, this hydrocarbon reacts with potassium permanganate in the cold, but when treated with hydrogen and a catalyst under any of the conditions described in the theoretical part of the paper it rapidly takes up about 1/6 mol. of hydrogen, and is not further reduced (complete reduction of $C_{17}H_{28}$ requires 2 mols. of hydrogen), but the product is then completely unattacked by potassium permanganate. This result is probably to be ascribed to a trace of the unreduced acid (VII) in the acid (VIII) from which the hydrocarbon is prepared. In spite of its reluctance to combine with hydrogen the hydrocarbon (IX) readily decolourises bromine water and a solution of bromine in acetic acid in the cold, and the amount of bromine taken up in the latter case proves the presence of two double bonds in the molecule. A solution of (IX) (treated with hydrogen and platinum oxide under 3 atms. for 4 hours) was titrated with a 10% solution of bromine in acetic acid, the final end-point being determined by an external starch–potassium iodide indicator; bromine corresponding to 1·96 mols. was absorbed for each molecule of hydrocarbon.

4 : 7 : 4′ : 7′-*Tetrabromo*-5 : 6 : 5′ : 6′-*tetramethoxy*-3 : 3 : 3′ : 3′-*tetramethylbis*-1 : 1′-spiro*hydrindene*.—4 : 7 : 4′ : 7′-Tetrabromo-5 : 6 : 5′ : 6′-tetrahydroxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene (4 g.) (Baker, *loc. cit.*) in methyl alcohol (7 c.c.) was treated alternately with excess of methyl sulphate and 20% aqueous potassium hydroxide, the mixture being allowed to boil. The solid *product* was collected, washed with dilute alkali solution and water, and crystallised twice from alcohol, forming microscopic needles, m. p. 205° (Found: Br, 45·0. $C_{25}H_{28}O_4Br_4$ requires Br, 44·9%).

5 : 6-*Dihydroxyhydrindene*.—5 : 6-Dimethoxyhydrindene (12 g.), glacial acetic acid (100 c.c.), and hydrobromic acid (100 c.c.; *d* 1·5) were refluxed for 6 hours. After dilution with a large volume of water, the dihydroxy-compound was extracted with ether, and the extracts shaken with excess of sodium bicarbonate solution and distilled, leaving a crystalline mass of a hydrate (10·5 g.), m. p., after drying at 100° in a vacuum over calcium chloride, 114—115° (cf. Mills and Nixon, J., 1930, 2510).

4 : 7-*Dibromo*-5 : 6-*dihydroxyhydrindene*.—A solution of 5 : 6-dihydroxyhydrindene (1 g.) in acetic acid (8 c.c.) was treated with a solution of bromine (2·13 g.; 2 mols.) in acetic acid (2 c.c.). Instant bromination occurred, and after 24 hours the rhombic plates which had separated were collected, boiled with charcoal in dilute alcoholic solution, precipitated by water, dried, and crystallised from light petroleum. The *product* formed fine prisms, m. p. 95° with previous softening (Found: Br, 51·5. $C_9H_8O_2Br_2$ requires Br, 51·9%).

5 : 6-*Hydrindenequinone.*—To 5 : 6-dihydroxyhydrindene (1 g.) in dry ether (20 c.c.) were added anhydrous sodium sulphate (3 g.) and silver oxide (3 g.). The mixture became warm and was boiled for 1 minute; the liquid was filtered rapidly, and the residue washed with a little ether. Evaporation of the filtrate to about 1/3 of its volume led to the separation of the *quinone* in bright red needles, which were collected and placed in an evacuated desiccator. The quinone melted at about 87°, and the crystals turned dark in a few hours; it reacted immediately with water (Found : C, 71·9; H, 4·2. $C_9H_8O_2$ requires C, 72·9; H, 5·4%). The substance may be recrystallised from ether or dioxan, but the solutions are not very stable.

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THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, January* 28*th*, 1938.]