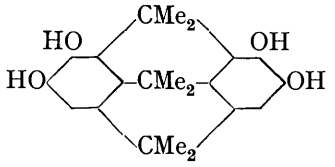
367. *The Condensation of Catechol with Acetone.*

By Wilson Baker.

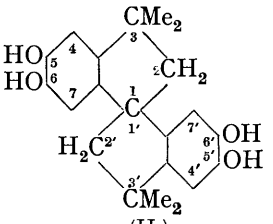
The claim of Causse (*Compt. rend.*, 1892, **115**, 49; *Bull. Soc. chim.*, 1892, **7**, 563) that catechol (and also resorcinol and quinol) condenses with acetone in presence of hydrochloric acid at room temperature to give an acetal, $(CH_3)_2C(O{\cdot}C_6H_4{\cdot}OH)_2$, has never been substantiated, and Schmidlin and Lang (*Ber.*, 1910, **43**, 2816) were unable to obtain this type of condensation product with resorcinol, but by the interaction of catechol, acetone, and concentrated hydrochloric acid for 14 days at room temperature they obtained in very poor yield an impure, dark green substance, m. p. 255—270° (decomp.), which was not further investigated. It is probable that this crude compound was really identical with a condensation product of catechol and acetone previously obtained and investigated in some detail by Fabinyi and Széky (*Ber.*, 1905, **38**, 2307).

Fabinyi and Széky heated catechol with acetone, acetic acid, and concentrated hydrochloric acid under pressure at 145° for 1½ hours, the solution subsequently depositing a crystalline product, which separated from alcohol in almost colourless needles, m. p. 314—316° (decomp.), of the molecular formula $C_{21}H_{24}O_4$. The compound was phenolic, gave a green solution in alkalis and a green ferric chloride reaction, a tetra-acetyl derivative, $C_{29}H_{32}O_8$, m. p. 174°, a tetrabenzoyl derivative, $C_{49}H_{40}O_8$, m. p. 234°, and a tetrabromo-derivative, $C_{21}H_{20}O_4Br_4$, m. p. 130°. Oxidation in alcohol with fuming nitric acid gave a bright red substance, $C_{21}H_{20}O_4$, which appeared to be a double *o*-quinone; a similar quinone was obtained by oxidation of the tetrabromo-derivative. Fabinyi and Széky tentatively

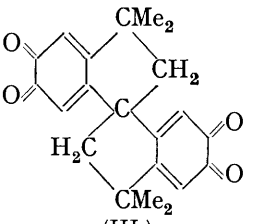
proposed the structure (I) for the condensation product, from which they derived the tetra-acetyl and the tetrabenzoyl derivative and the quinone.*



(I.)



(II.)



(III.)

It appeared very unlikely that the condensation product could be correctly represented by (I), because this structure could not account in any simple way for the production of a tetrabromo-derivative, and also because of the improbability of producing the system of four fused rings indicated by (I). Complete reinvestigation of the product has, therefore, been made, and it is now shown to possess an entirely different structure.

The compound is best prepared, both as regards yield and purity of product, by heating the mixture of catechol, acetone, acetic acid, and concentrated hydrochloric acid on the steam-bath at atmospheric pressure, a 50—60% yield being obtained, calculated on the catechol employed. The compound was shown to be identical with that described by Fabinyi and Széky, both by its properties and analysis and by the formation of the tetra-acetyl derivative, the quinone, and a tetrabromo-derivative. The last has m. p. 231° (instead of 130°) and, contrary to the previous statement, is completely stable towards water, even at 100°. Methylation of the condensation product readily gave a very characteristic, dimorphic tetramethyl ether, $C_{25}H_{32}O_4$, and this could also be obtained by the simultaneous hydrolysis and methylation of the tetra-acetyl derivative. Further, it was found that the quinone could be reduced by sulphur dioxide to the original tetrahydroxyphenol, identified by its tetra-acetyl derivative and its tetramethyl ether.

These experiments definitely established the molecular formula ascribed to the compound by Fabinyi and Széky, and showed that it was produced by the condensation of two molecules of catechol and three molecules of acetone with loss of three molecules of water. It was evident that the four hydroxyl groups of the two catechol nuclei were free, and that, in order to account for the formation of the tetrabromo-derivative, there must be four free positions in the aromatic nuclei.

The three acetone molecules taking part in the reaction suggested that the condensation was between two molecules of catechol and a molecule of phorone, and this was borne out by the production of the compound from catechol, phorone, acetic acid, and hydrochloric acid as readily as from acetone. The replacement of the phorone by mesityl oxide gave a much poorer yield, and the production of the substance must be accounted for by the fact that mesityl oxide is partly decomposed by dilute acids (Claisen, *Ber.*, 1874, **7**, 1169; *Annalen*, 1876, **180**, 20), thus allowing the production of a small quantity of phorone.

With the recognition that the condensation proceeds *via* phorone, there is only one reasonable possibility for the structure of the compound, namely (II), and it is therefore to be regarded as 5 : 6 : 5′ : 6′-*tetrahydroxy*-3 : 3 : 3′ : 3′-*tetramethylbis*-1 : 1′-spiro*hydrindene*. It is probably produced by the condensation of two molecules of catechol with the known phorone dihydrochloride, $[(CH_3)_2CCl{\cdot}CH_2{\cdot}]_2CO$, although the possibility of direct interaction of catechol with phorone is not excluded. The tetra-acetyl, tetramethyl, and tetrabenzoyl derivatives are derived normally from (II); the quinone is to be represented by (III), and the tetrabromo-derivative is 4 : 7 : 4′ : 7′-*tetrabromo*-5 : 6 : 5′ : 6′-*tetrahydroxy*-3 : 3 : 3′ : 3′-*tetramethylbis*-1 : 1′-spiro*hydrindene*. It may be observed that (II) and its derivatives possess molecular asymmetry and should be capable of optical resolution.

* (Note added in proof.) This condensation product of catechol and acetone has recently been reinvestigated by K. Remesat (Dissert., Berlin, 1931, "Versuchung über die Kondensation von Brenzkatechin und Guajacol mit Aldehyden und Ketonen"). The work, however, throws no new light on the constitution of the compound, and the original structure (I) is retained.

Again, the rather remarkable ease of formation and stability of the *o*-quinone (III) is possibly to be attributed to the disposition of the double and the single bonds in the aromatic nuclei, the single bonds between the aromatic and the saturated five-membered rings being the arrangement favoured in a hydrindene derivative (Mills and Nixon, J., 1930, 2510).

Fabinyi and Széky describe compounds prepared by the condensation of catechol with methyl ethyl ketone and with diethyl ketone, and from their molecular formulæ, method of preparation and properties it is clear that they are exactly analogous to the compound (II).

Experimental.

Condensation of Catechol with Acetone.—Catechol (264 g.; 2 mols.), acetone (285 c.c.; 3·3 mols.), acetic acid (600 c.c.), and concentrated hydrochloric acid (480 c.c.) were heated under reflux on the steam-bath for 48 hours. Crystals began to separate after 6 hours and the amount slowly increased, though the substance is almost wholly deposited during the first 24 hours. The crystalline material was collected, crushed, washed thoroughly with cold acetic acid, then water, and dried (yield, 240 g.). When the acetic acid was omitted, the yield fell to 12% and the product was rather dark and sticky.

The properties of the compound agree with those described by Fabinyi and Széky, but it is best crystallised from alcohol–acetic acid. The substance (5 g.) was dissolved in alcohol (40 c.c.) at the b. p. (charcoal), and to the filtered solution boiling acetic acid (50 c.c.) was added. The solution slowly deposited a colourless microcrystalline powder, m. p. about 315°, which was dried in a vacuum at 100° (Found: C, 74·0; H, 7·3. Calc. for $C_{21}H_{24}O_4$: C, 74·1; H, 7·1%).

Condensation of Catechol with Phorone.—Catechol (22 g.; 2 mols.), phorone (13·8 g.; 1 mol.), acetic acid (50 c.c.), and concentrated hydrochloric acid (40 c.c.) were heated on the steam-bath for 24 hours. Crystals appeared after 7 hours (yield, 16 g.; 47%). The compound was identified by its tetra-acetyl derivative, m. p. 175°, and its characteristic dimorphic tetramethyl ether (below), m. p. 158°.

Condensation of Catechol with Mesityl Oxide.—Catechol (22 g.; 2 mols.), mesityl oxide (9·8 g.; 1 mol.), acetic acid (50 c.c.), and concentrated hydrochloric acid (40 c.c.) were heated on the water-bath for 24 hours (yield, 5·9 g.; 17%). The compound was identified as above.

The Tetra-acetyl Derivative.—The condensation product (10 g.) was boiled with acetic anhydride (50 c.c.) and anhydrous sodium acetate (10 g.) for 4 hours (compare Fabinyi and Széky). On shaking with water, the acetyl derivative slowly crystallised, but solidification was rapid when the substance was rubbed with alcohol. It separated from alcohol in colourless, thick, dagger-like prisms, m. p. 175° (Found: C, 68·6, 68·5; H, 6·3, 6·6; Ac, 35·8, 36·4, 36·3. Calc. for $C_{29}H_{32}O_8$: C, 68·5; H, 6·3; Ac, 33·9%). This acetyl derivative was also obtained by the acetylation of the reduced quinone (below).

Tetramethyl Ether.—The condensation product (20 g.), methyl alcohol (20 c.c.), and methyl sulphate (30 c.c.) were shaken with excess of 20% potassium hydroxide solution, added in portions; further quantities of methyl sulphate (30 c.c.) and alkali were then added, the mixture being allowed to boil. A crystalline solid separated and was collected, washed with water, and dried (yield, 23·7 g.). It was crystallised several times from alcohol and obtained in thick rhombic plates (Found: C, 75·8, 75·9; H, 8·2, 8·1; OMe, 31·3, 31·3. $C_{25}H_{32}O_4$ requires C, 75·8; H, 8·2; OMe, 31·3%). This *tetramethyl* ether is dimorphic, and frequently separates from hot solutions in pointed bi-pyramids (α-form), m. p. 158°, the solution then depositing more slowly the rhombic form (β-form), which has no well-defined melting point owing to conversion into the α-form. When the melting point of the β-form is taken in the usual way, the clear crystals become opaque at 125°, show signs of melting in contact with the glass at somewhat higher temperatures, and finally melt at 158°. When plunged into the melting-point bath at 130°, the substance partly melts; but when placed in the bath at 140° it melts completely, and during about a minute resolidifies and then melts at 158°; on cooling, it resolidifies completely above 140°. A hot solution of the β-form in alcohol, when seeded with the α-form, deposits the substance in the α-form. The tetramethyl ether dissolves in concentrated sulphuric acid to a pale yellowish-orange solution which develops a green fluorescence. It is stable to potassium permanganate in hot pyridine or acetone. The same tetramethyl ether was obtained also by methylating the reduced quinone (below) and by the simultaneous hydrolysis and methylation of the tetra-acetyl derivative.

Oxidation to the Quinone.—(a) (compare Fabinyi and Széky). The condensation product

(15 g.) was dissolved in hot alcohol (150 c.c.) and cooled to 10°, and fuming nitric acid (12 c.c.; *d* 1·5) added slowly with stirring, the temperature being kept below 30°. The quinone rapidly separated after the addition of the nitric acid, and was collected after a few hours, washed with alcohol and with water, and dried (yield, 12 g.). It formed small, dark brownish-red crystals which persistently retained a small amount of nitric acid and gave varying analyses for carbon and hydrogen (Found : C, 72·8—73·9; H, 5·7—6·0. Calc. for $C_{21}H_{20}O_4$: C, 75·0; H, 6·0%).

(b) The condensation product (15 g.) was dissolved in hot alcohol (150 c.c.), and to the filtered solution a mixture of concentrated nitric acid (10 c.c.; *d* 1·42) and acetic acid (10 c.c.) was added slowly whilst the temperature was kept at 0—5°. The mixture was kept at 0° for several hours and at room temperature for 20 hours; the quinone was then collected, washed with alcohol and with water, boiled with water for 15 minutes, and recrystallised four times from glacial acetic acid. The product was ultimately boiled with water and dried at 100° in a vacuum over sodium hydroxide (Found : C, 74·7; H, 6·0%). This product has a deep bright red colour.

Reduction of the Quinone.—The finely powdered quinone (6 g.) was suspended in 50% acetic acid (60 c.c.) and reduced by the passage of sulphur dioxide at 60° until the colour became pale orange. Fine sandy crystals now separated; these, after cooling and addition of water, were collected, washed, and dried at 100° (yield, 5 g.). The substance had all the properties of the original condensation product and was identified by the tetra-acetyl derivative, m. p. 175°, and the tetramethyl ether, m. p. 158°.

Tetrabromo-derivative.—The powdered condensation product (25 g.) was suspended in acetic acid (200 c.c.) at 40°, and a solution of bromine (20 c.c.) in acetic acid (40 c.c.) added during 5 minutes with shaking. When solution had occurred, the liquid was filtered; on cooling, it deposited crystals. They were collected and washed with cold acetic acid and with water (yield, 27 g.). The pure compound is best obtained by recrystallisation from dilute acetic acid, and then from carbon tetrachloride, in which it is moderately readily soluble. It separates in bunches of prismatic needles, m. p. 231° (decomp., with slight previous softening) (Found : Br, 48·4. Calc. for $C_{21}H_{20}O_4Br_4$: Br, 48·7%). Fabinyi and Széky describe the substance as being unstable towards water, being converted into a pink substance. The crude compound does turn red on treatment with water, but the substance responsible for this colour is removed by the initial thorough washing with acetic acid, the substance being thereafter unaltered by water.

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THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, August 9th,* 1934.]