

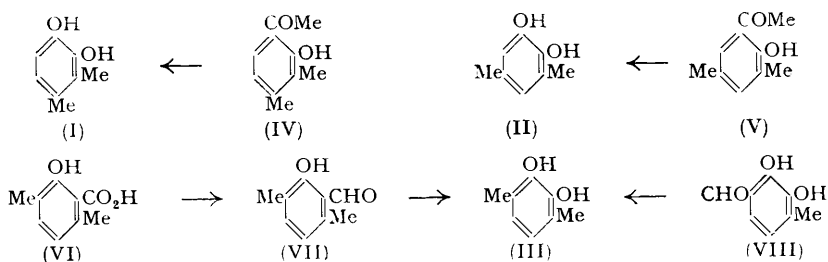
324. 3 : 4-, 3 : 5-, and 3 : 6-Dimethylcatechol.

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3 : 4-, 3 : 5-, and 3 : 6-Dimethylcatechol have been synthesised by the oxidation of 2-hydroxy-3 : 4-dimethylacetophenone, 2-hydroxy-3 : 5-dimethylacetophenone, and 2-hydroxy-3 : 6-dimethylbenzaldehyde respectively by hydrogen peroxide in aqueous tetramethylammonium hydroxide. 3 : 5- and 3 : 6-Dimethylcatechol have been isolated from coal tar produced by low-temperature carbonisation. Certain alkyl-catechols and -resorcinols are jointly responsible for the red colour produced when phenolic fractions of low-temperature carbonisation coal tar are dissolved in alkalis.

OF the four dimethyl catechols only the 3 : 5- (II) and 4 : 5-dimethyl derivatives were definitely known when this work was started. Since then Loudon and Scott (*J.*, 1953, 268) have synthesised 3 : 6-dimethylcatechol (III). Further investigation of the properties of (II) and (III), and the preparation of 3 : 4-dimethylcatechol (I), are of interest, since it was probable that (I) and (III) might occur in low-temperature carbonisation coal tar.

Burke and Caplan (*J. Ind. Eng. Chem.*, 1927, **19**, 34) observed that certain phenolic fractions of low-temperature carbonisation coal tar gave red solutions in aqueous alkalis. The substance, or substances, responsible for the red colour were isolated by extraction into aqueous borax (a characteristic property of catechols), and from this solution they were liberated by acidification and obtained finally as a colourless oil, b. p. 256°/760 mm., 116—117°/2 mm., which yielded an intensely red solution in aqueous sodium hydroxide. Analysis of the oil established the formula $C_8H_{10}O_2$, and, by excluding the known ethyl- and 3 : 5- and 4 : 5-dimethyl-catechol, they concluded that it must be the unknown 3 : 4- or 3 : 6-dimethylcatechol.



We have now synthesised 3 : 4-dimethylcatechol (I), m. p. 84—85°, and find that it dissolves in 1% aqueous sodium hydroxide to a deep, brownish-red solution. The colour slowly becomes browner, and is due to oxidation since only a faint yellow is produced in the absence of oxygen, but when such a solution is shaken with air the brownish-red colour develops rapidly. We have also prepared 3 : 6-dimethylcatechol (III), m. p. 101°, by two methods differing from that used by Loudon and Scott, and find that it gives a purple solution in alkalis in presence of air. We conclude that the material isolated by Burke and Caplan may have contained 3 : 4-dimethylcatechol, but the presence of other, probably isomeric compounds is suggested by the fact that their product did not solidify even at low temperatures, and by other considerations discussed in the sub-section below.

The synthesis of 3 : 4-dimethylcatechol (I) was achieved as follows. 2-Hydroxy-3 : 4-

dimethylacetophenone (IV) was prepared from 2 : 3-dimethylphenyl acetate by reaction with aluminium chloride. This ketone (IV) was then oxidised by hydrogen peroxide in aqueous tetramethylammonium hydroxide (3 equivalents), giving 3 : 4-dimethylcatechol (I) in 25% yield. When the oxidation was carried out in aqueous potassium hydroxide the yield was only 2.5%, and mixtures of potassium hydroxide and tetramethylammonium hydroxide gave intermediate yields of (I). This is a further instance of the advantage of using tetramethylammonium hydroxide as alkali in certain Dakin oxidations, in order to obtain ionised, rather than covalent, salts (Baker, McOmie, and Ulbricht, *J.*, 1952, 1825). When benzyltrimethylammonium hydroxide (Triton B) was used the yield of (I) was 18%.

3 : 5-Dimethylcatechol (II) was prepared in a similar manner from 2 : 4-dimethylphenyl acetate. The Fries rearrangement with aluminium chloride gave 2-hydroxy-3 : 5-dimethylacetophenone (V), and oxidation of this *o*-hydroxy-ketone with hydrogen peroxide in aqueous tetramethyl ammonium hydroxide gave 3 : 5-dimethylcatechol (II). The oxidation was unsuccessful when sodium hydroxide was used as the alkali. The substance gave a solid diacetyl derivative.

3 : 6-Dimethylcatechol (III) cannot be prepared from 2 : 5-dimethylphenyl acetate by a similar series of reactions, because the Fries rearrangement is accompanied by extensive migration of a methyl group with formation of 2-hydroxy-3 : 5-dimethylacetophenone (Auwers, Bundesmann, and Wieners, *Annalen*, 1926, 447, 162). Hence attention was turned to 2-hydroxy-3 : 6-dimethylbenzaldehyde (VII) which has been prepared in 4% yield by the Gattermann reaction (Anselmino, *Ber.*, 1902, 35, 4099; Clemo, Haworth, and Walton, *J.*, 1929, 2376). Formylation of *p*-xylenol with hexamine in acetic acid (Duff and Bills, *J.*, 1934, 1305) gave a 21% yield of 4-hydroxy-2 : 5-dimethylisophthalaldehyde, and formylation with hexamine in glycerol-glyceroboric acid (Duff, *J.*, 1941, 547) gave 7% of the dialdehyde. Small yields of the dialdehyde were also obtained by the Gattermann reaction using zinc cyanide, and, accompanied by 1% of the monoaldehyde (VII), by the Tiemann-Reimer reaction. As these methods were unsatisfactory, *p*-xylenol was submitted to the Kolbe reaction, giving 2-hydroxy-3 : 6-dimethylbenzoic acid (VI); this was then reduced with sodium amalgam in presence of boric acid and *p*-toluidine, and the resulting Schiff's base hydrolysed (method of Weil, *Ber.*, 1908, 41, 4147) giving the aldehyde (VII) in 40% yield from the acid (VI). Finally (VII) was submitted to the Dakin oxidation in presence of tetramethylammonium hydroxide, giving 3 : 6-dimethylcatechol (III) in 74% yield.

The 2-hydroxy-3 : 6-dimethylbenzoic acid (VI), m. p. 195°, was identical with that prepared in a different manner by Stollé and Knebel (*Ber.*, 1921, 54, 1220), but differed from the acid, m. p. 137°, prepared by Oliveri by heating *p*-xylenol and sodium in carbon dioxide (*Gazzetta*, 1882, 12, 166). The nature of this latter product is unknown (see Beilstein, "Handbuch der organischen Chemie," 4th Edn., 2nd. Suppl., 1949, Vol. IV, p. 163).

3 : 6-Dimethylcatechol (III) was also prepared from 3-methylcatechol, which when formylated by the hexamine-glyceroboric acid method (Duff, *loc. cit.*) gave a small yield of 2 : 3-dihydroxy-4-methylbenzaldehyde (VIII). Clemmensen reduction then gave 3 : 6-dimethylcatechol (III).

Observations on the Red Colour of Alkaline Solutions of Phenols from Low-temperature Carbonisation Processes.—The higher fractions of such phenols, when dissolved in dilute aqueous sodium hydroxide, rapidly develop red colours when shaken in air. This holds for the whole range of phenols boiling above 260°, and indicates that more than one compound is responsible. Burke and Caplan (*loc. cit.*) concluded that the colour reaction was due to catechols, since if these substances are removed by alkali borates the reaction is not given. This work has been confirmed, and a patent (B.P. 621,639) describes a process for removing the substances responsible for the red colour, based on extraction with alkali borates.

Catechols alone do not give the red colour reaction; 3 : 4-dimethylcatechol (I), however, gives a red-brown colour, but this substance has not yet been found in coal tar. Five pure catechols, all isolated from coal tar, produced by low-temperature carbonisation, were tested with dilute alkali, but none gave the red colour observed with the phenolic

fraction of coal tar; these were catechol, 3- and 4-methylcatechol, and 3 : 5- and 3 : 6-dimethylcatechol. Eventually, it was found that the typical colour reaction is produced by the simultaneous oxidation of certain catechols and a resorcinol in alkaline solution. From the limited information available it appears that, in order to give the colour reaction, the catechol must have a methyl group in a position *para* to one or other of the hydroxyl groups. The structure of the resorcinol is not critical, though it was deduced, from six resorcinols tested with 4-methylcatechol, that additional methyl groups tend to modify the colour from orange to red. Again, the colours produced with resorcinols and 3 : 5-dimethylcatechol are redder than those obtained with 4-methylcatechol. Thus simultaneous oxidation of 2 : 4-dimethylresorcinol and 3 : 5-dimethylcatechol in alkaline solution gave a crimson colour. 3-Methylcatechol and 3 : 6-dimethylcatechol gave no red or orange colour with any of the alkylresorcinols yet tested.

The test is carried out by dissolving a small quantity of the resorcinol in 1% aqueous sodium hydroxide, adding the catechol, and shaking the mixture with access to air. If first the catechol is added to the alkali, blue or brown colours result, and the red colour is masked or not produced. Addition of stronger alkali tends to give orange colours; dilution with water accentuates the red colour.

EXPERIMENTAL

2-Hydroxy-3 : 4-dimethylacetophenone (IV).—This ketone (b. p. 145—148°/26 mm.) was prepared in 90% yield by heating 2 : 3-dimethylphenyl acetate (4 mols.) at 155—165° for 1½ hr. with aluminium chloride (5 mols.), and distilling the product in steam after addition of dilute hydrochloric acid. The procedures of Auwers and Mauss (*Annalen*, 1928, **460**, 240) and of Smith and Opie (*J. Org. Chem.*, 1941, **6**, 427) gave 60 and 69% yields respectively.

3 : 4-Dimethylcatechol (I).—2-Hydroxy-3 : 4-dimethylacetophenone (IV) (3 g., 1 mol.) was dissolved in 10% aqueous tetramethylammonium hydroxide (44 c.c.; 3 mols.) at room temperature, and 6% aqueous hydrogen peroxide (14.5 c.c., 1.25 mol.) added in an atmosphere of nitrogen. After 2 min. a slow rise of temperature to 48° occurred (10 min.), and after ½ hr. the solution was warmed to 50° and allowed to cool. Acidification with dilute sulphuric acid gave crude unchanged ketone which was removed by shaking with light petroleum (b. p. 60—80°), and the aqueous layer then extracted with warm ethyl acetate (5 × 20 c.c.). The ethyl acetate extracts yielded a dark oil which partly solidified; this was extracted with light petroleum (b. p. 60—80°; 2 × 50 c.c.), and the extracts were concentrated, giving 3 : 4-dimethylcatechol (I), which, after several recrystallisations from light petroleum (b. p. 40—60°), had m. p. 84—85° (yield 25%) (Found : C, 69.7; H, 7.0. C₈H₁₀O₂ requires C, 69.5; H, 7.2%). An alcoholic solution of this catechol derivative is coloured intensely blue-green on addition of a little aqueous ferric chloride, and the colour changes to yellow-brown on dilution with water. When this compound (I) was first isolated and crystallised from light petroleum (b. p. 40—60°) it was obtained in needles which melted sharply at 61° and liquefied in contact with a little water. It was later always obtained with the higher m. p., and this more stable, probably dimorphic form does not liquefy in contact with water.

The *diacetyl* derivative separates from light petroleum (b. p. 60—80°) in compact prisms, m. p. 89—90° (Found : C, 64.9; H, 6.1. C₁₂H₁₄O₄ requires C, 64.9; H, 6.3%). The *di-benzoyl* derivative, prepared by reaction with benzoyl chloride (3 mols.) in pyridine, separates from ethyl acetate in flat prisms, m. p. 127—128° (Found : C, 76.5; H, 5.3. C₂₂H₁₈O₄ requires C, 76.3; H, 5.2%).

1 : 2-Dimethoxy-3 : 4-dimethylbenzene.—The catechol (I) was boiled in acetone with excess of methyl sulphate and potassium carbonate for 10 hr. The acetone-soluble product was distilled 3 times, giving a very pale yellow liquid, b. p. 70—72°/0.3 mm. [Found : C, 72.6; H, 8.3; OMe, 38.2. C₈H₈(OMe)₂ requires C, 72.3; H, 8.4; OMe, 37.4%].

3 : 5-Dimethylcatechol (II).—2-Hydroxy-3 : 5-dimethylacetophenone (V) (m. p. 53—54°) was prepared in 38% yield from 2 : 4-dimethylphenylacetate by the Fries rearrangement (Auwers, Lechner, and Bundesmann, *Ber.*, 1925, **58**, 45). To this ketone (V) (6 g., 1 mol.) in 10% aqueous tetramethylammonium hydroxide (88 c.c., 3 mols.) was added at room temperature 6% aqueous hydrogen peroxide (29.2 c.c., 1.25 mols.) in an atmosphere of nitrogen. The temperature rose to 54° (5 min.) and after ½ hr. the solution was warmed to 55° and allowed to cool. Acidification precipitated unchanged ketone, and the filtered solution was extracted with warm ethyl acetate (4 × 50 c.c.), yielding a dark oil. This was extracted with hot light petroleum (b. p. 60—80°;

2 × 50 c.c.), yielding, after several crystallisations from the same solvent, 3 : 5-dimethylcatechol (II) (25%), needles, m. p. 70—71° (Found : C, 69.3; H, 7.1. Calc. for C₈H₁₀O₂ : C, 69.5; H, 7.2%). An alcoholic solution of (II) became olive-green on addition of a trace of aqueous ferric chloride, and the colour became yellow on addition of more water. 3 : 5-Dimethylcatechol was previously prepared by Hodgkinson and Limpach (*J.*, 1893, 63, 108) and by Caldwell and Thompson (*J. Amer. Chem. Soc.*, 1939, 61, 2354) who employed other processes.

The *diacetyl* derivative, prepared by heating (II) with acetic anhydride and a trace of pyridine, separates from light petroleum (b. p. 40—60°) as cubes, m. p. 59—60° (Found : C, 64.8; H, 6.2. C₁₂H₁₄O₄ requires C, 64.9; H, 6.3%).

2-Hydroxy-3 : 6-dimethylbenzoic Acid (VI) [with Mr. A. J. PRICE].—To *p*-xylenol (50 g.) in boiling xylene (400 c.c.) was added at intervals sodium (21 g.) in small portions (6 hr.) whilst a vigorous stream of carbon dioxide was delivered near the bottom of the flask. Passage of carbon dioxide at the b. p. was continued for a further 15 hr., unchanged sodium destroyed with 90% ethanol, the mixture poured into water (400 c.c.), and the aqueous layer acidified. The precipitated 2-hydroxy-3 : 6-dimethoxybenzoic acid separated from a mixture of ethanol (180 c.c.) and water (250 c.c.) in needles (20 g., 27%), m. p. 195° (Stollé and Knebel, *loc. cit.*, gave m. p. 195°). It gives a dark violet-blue ferric chloride reaction in alcoholic solution, which acquires a violet tinge on dilution with water.

2-Hydroxy-3 : 6-dimethylbenzaldehyde (VII).—The preceding acid (VI) (2.5 g., 1 mol.) was neutralised with warm, 5% aqueous sodium carbonate and then diluted (to 150 c.c.), *p*-toluidine (2.5 g., 1.5 mols.) added, and the mixture warmed to obtain a clear solution which was vigorously shaken and cooled. Sodium chloride (40 g.) and boric acid (2.5 g.) were next added, the mixture was stirred, and 2% sodium amalgam (*ca.* 150 g.) was added gradually (3 hr.), with addition of more boric acid at intervals to keep the solution faintly acid. When all the amalgam had reacted the mixture was decanted from the mercury and filtered, and to the solid was added 2N-hydrochloric acid (100 c.c.) to hydrolyse the arylidene-*p*-toluidine, and the whole was steam-distilled. The distillate yielded to ether a solid which was crystallised from light petroleum (b. p. 40—60°), giving 2-hydroxy-3 : 6-dimethylbenzaldehyde as yellow needles, m. p. 61—62° (*loc. cit.*, m. p. 62—63°).

2 : 3-Dihydroxy-4-methylbenzaldehyde (VIII).—Anhydrous glycerol (30 g.) and boric acid (7 g.) were heated for ½ hr. at 170°, hexamine (5 g.) and 3-methylcatechol (5 g.) were then added, and the mixture was kept at 150° for ¼ hr. After addition of concentrated sulphuric acid (6 c.c.) in water (20 c.c.), steam-distillation and extraction of the distillate (2 l.) with ether gave a solid which was crystallised from light petroleum (b. p. 80—100°), giving 2 : 3-dihydroxy-4-methylbenzaldehyde (0.37 g.) as yellow needles or cubes (dimorphic), m. p. 85° (Found : C, 63.4; H, 5.2. C₈H₈O₃ requires C, 63.3; H, 5.3%). Its alcoholic solution gives an intense blue-green colour with ferric chloride. The colour and steam-volatility of this catechol derivative are characteristic of 2 : 3-dihydroxy-carbonyl compounds in general (see Baker and Smith, *J.*, 1936, 346).

3 : 6-Dimethylcatechol (III).—(a) *By oxidation of 2-hydroxy-3 : 6-dimethylbenzaldehyde* (VII). The aldehyde (VII) (1 g., 1 mol.) was dissolved in warm 10% aqueous tetramethylammonium hydroxide (18.5 c.c., 3 mols.), and 6% aqueous hydrogen peroxide (4.8 c.c., 1.25 mols.) added in an atmosphere of nitrogen. An exothermic reaction set in (temp. rise to 40°); the solution was later heated to 50°, and when cold was acidified with dilute sulphuric acid, filtered, and extracted with hot ethyl acetate (3 × 30 c.c.). The extracts yielded a dark brown solid which was extracted with light petroleum (b. p. 60—80°; 2 × 20 c.c.), and the extracts were concentrated, giving 3 : 6-dimethylcatechol as fine needles (74%), which after several recrystallisations from light petroleum had m. p. 101° (Found : C, 69.1; H, 7.0. Calc. for C₈H₁₀O₂ : C, 69.5; H, 7.2%). Its alcoholic solution gave an olive-green colour with a trace of aqueous ferric chloride, and the colour becomes brown on the addition of water. The *dibenzoyl* derivative crystallised from alcohol as rhombs, m. p. 101° (Found : C, 76.0; H, 5.0. C₂₂H₁₈O₄ requires C, 76.3; H, 5.2%). 3 : 6-Dimethylcatechol prepared by Loudon's method (*loc. cit.*) has m. p. 104°, and a mixed m. p. was 101—102°.

(b) *By reduction of 2 : 3-dihydroxy-4-methylbenzaldehyde* (VIII). The aldehyde (VIII) (0.35 g.) was boiled for 2 hr. with concentrated hydrochloric acid (7 c.c.), water (3 c.c.), and spongy amalgamated zinc (2 g.). Extraction with ether and crystallisation of the product first from toluene and then from light petroleum gave 3 : 6-dimethylcatechol (0.10 g.), m. p. and mixed m. p. 100°.

Isolation of 3 : 5-Dimethylcatechol (II) from Coal Tar derived from Low-temperature Carbonisation.—A phenolic fraction (915 g.), b. p. *ca.* 261°, of the tar, consisting mainly of

monohydric phenols, was shaken at 45° with butyl acetate (900 c.c.) and an aqueous solution (400 c.c.) containing boric acid (40 g.) and sodium hydroxide (24 g.), which removed all the catechols from the organic layer. The aqueous layer was acidified, cooled, and filtered, and the residual boric acid, contaminated with a brown oil, was washed with a little ether (washings A). The aqueous filtrate was shaken with light petroleum (b. p. 100—120°) (80 c.c.), giving 3 layers. The dark, intermediate layer was mixed with the washings (A) and distilled in *vacuo*, giving a viscous, pale yellow liquid (16 g.). The lowest, aqueous layer was extracted with ether and the product distilled in *vacuo*, giving an oil (5 g.) which solidified. Crystallisation of the distilled oil from the intermediate layer was induced by seeding with this solid. The united solids were washed with a little toluene and crystallised from this solvent, giving 3 : 5-dimethylcatechol (6.6 g.) as colourless cubes, m. p. and mixed m. p. 71° (Found : C, 69.4; H, 7.4. Calc. for C₈H₁₀O₂ : C, 69.5; H, 7.3%). It separates from water in needles. The diacetyl derivative had m. p. and mixed m. p. 59—60° (Found : C, 64.6; H, 6.1%).

Isolation of 3 : 6-Dimethylcatechol (III) from Coal Tar derived from Low-temperature Carbonisation.—The phenolic fraction, b. p. 244—249°, of the tar consists chiefly of monohydric phenols, but the presence of catechol derivatives was shown by the formation of a white precipitate on addition of aqueous lead acetate to an alcoholic solution of the mixed phenols. This fraction (1535 g.) and benzene (700 c.c.) was shaken with 3 portions (200, 100, and 100 c.c.) of an aqueous solution containing boric acid (16% wt./vol.), and sodium hydroxide (10% wt./vol.), which completely removed the catechols from the benzene layer (lead acetate test). The combined borate extracts were acidified, extracted with ether, and distilled in *vacuo*, giving a colourless oil (110 g.) miscible with water; it solidified when seeded with 3-methylcatechol. Crystallisation from toluene gave several crops of 3-methylcatechol (cubes) (70 g.), and the final mother-liquor when kept for several days deposited both 3-methylcatechol and needle-shaped crystals which were separated by hand and recrystallised from toluene. This substance (0.2 g.), m. p. 100°, alone or when mixed with 3 : 6-dimethylcatechol (III), showed all the properties of (III) described above. A further amount (1 g.) of 3 : 6-dimethylcatechol (III) was obtained from the toluene mother-liquors by repeated shaking with water, the other catechols being preferentially extracted; concentration of the toluene solution gave crystalline (III).

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