

596. 2 : 4-Dimethylresorcinol.

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2 : 4-Dimethylresorcinol has been isolated from the ammoniacal liquors from the distillation of coal, and has been synthesised from 4-formyl-2-methylresorcinol.

A PHENOLIC product, $C_8H_{10}O_2$, m. p. 110° , was isolated as described in the Experimental section from the ammoniacal liquors obtained during the low-temperature carbonisation of bituminous coal by the "Coalite" process.

The compound gave a weak but definite fluorescein reaction, and, under closely defined conditions, a transient bluish colour with ferric chloride. Titration with bromine in acetic acid was instantaneous and ceased when one molecule of the phenol had reacted with one molecule of bromine with liberation of hydrogen bromide. The only dihydric phenols, $C_8H_{10}O_2$, which could show this behaviour are 2 : 4- and 4 : 6-dimethylresorcinol; the latter is known and has m. p. 125° . The phenol now isolated is, therefore, 2 : 4-dimethylresorcinol, which according to Asahina and Nonomura (*J. Pharm. Soc. Japan*, 1934, 54, 488) has m. p. 112° , contrary to earlier erroneous claims. This conclusion was confirmed by a direct comparison of the material isolated from the ammoniacal liquor with the synthetical phenol prepared (a) by the catalytic reduction of resorcinol-2 : 4-dialdehyde (Asahina and Nonomura, *loc. cit.*; Hassall and Todd, *J.*, 1947, 611), and (b) by the Clemmensen reduction of 4-formyl-2-methylresorcinol.

Hassall and Todd (*loc. cit.*) have reported a 94% yield of 2 : 4-dimethylresorcinol by reduction of resorcinol-2 : 4-dialdehyde with hydrogen in presence of palladium oxide. In our hands this catalyst yielded a product crystallising in yellow needles, m. p. $130-135^\circ$, which was not further examined, and the success of the operation appears to be very sensitive to the method of preparation of the catalyst. In a small-scale experiment palladium-black was found to be moderately satisfactory, but owing to the inaccessibility of resorcinol-2 : 4-dialdehyde the method is not suitable for the preparation of 2 : 4-dimethylresorcinol in quantity. 2-Methylresorcinol is now available from the "Coalite" process (see below), and its formylation to 4-formyl-2-methylresorcinol, followed by Clemmensen or catalytic reduction, affords the most practical method for the synthesis of 2 : 4-dimethylresorcinol.

Reference books wrongly give the melting-point of 2 : 4-dimethylresorcinol as *ca.* 148° . Wischin (*Ber.*, 1890, 23, 3113; cf. Pfannenstill, *J. pr. Chem.*, 1892, 46, 153) disulphonated *m*-xylene and by alkali fusion of the acid chloride obtained a phenol, m. p. 146° ($149-150^\circ$) (not

analysed), which was assumed to be 2 : 4-dimethylresorcinol. The same compound (also not analysed) appears to have been prepared by the alkaline fusion of 5-iodo-2 : 4-dimethylbenzenesulphonic acid (Bauch, *Ber.*, 1890, **23**, 3119), but it was finally shown by Asahina and Nonomura to be 2-hydroxy-5-methylbenzoic acid. They prepared genuine 2 : 4-dimethylresorcinol from resorcinol-2 : 4-dialdehyde which had been orientated by Baker, Kirby, and Montgomery (*J.*, 1932, 2876).

EXPERIMENTAL.

Isolation of 2 : 4-Dimethylresorcinol.—The ammoniacal liquor from the low-temperature carbonisation process was exhaustively extracted with butyl acetate and, after removal of the solvent by distillation, the residue was fractionated under diminished pressure to remove monohydric phenols boiling below 240°/760 mm. The residual dihydric phenols were further fractionated to give a fraction, b. p. 125—130°/4 mm., from which 2-methylresorcinol was separated by crystallisation from toluene. Careful fractionation of the resulting mother-liquors gave a cut with a boiling range of 117—118°/2 mm. (270—271°/760 mm.), which slowly solidified. Finally, after 3 crystallisations from toluene containing 10% of butyl acetate, the product was obtained as colourless needles, m. p. 110° (Found : C, 69.5; H, 7.3. Calc. for $C_8H_{10}O_2$: C, 69.6; H, 7.3%).

4-Formyl-2-methylresorcinol.—This aldehyde was previously prepared on a small scale in unstated yield by Jones and Robertson (*J.*, 1932, 1691), who record m. p. 150° after sintering at 147°.

A mixture of 2-methylresorcinol (20 g.), anhydrous zinc cyanide (40 g.), and anhydrous ether (180 c.c.) was vigorously agitated (mercury-sealed stirrer) and a rapid stream of hydrogen chloride passed in for 1½ hours. The ether was then decanted from the aldimine hydrochloride which, after being washed twice with ether, was dissolved in water (250 c.c.), and the solution was heated for 1 hour on a water-bath. More water (600 c.c.), alcohol (100 c.c.), and charcoal were then added, the solution was filtered hot, and the crystals were collected, after being kept overnight, and dried (19.5 g., 79%). These melted at 152—153° after softening at 150°. By saturation of the mother-liquor with salt and extraction with ether (3 × 200 c.c.) a further amount of the aldehyde (0.5 g.; m. p. 144—148°) was obtained.

2 : 4-Dimethylresorcinol.—Granulated zinc (20 g.) was washed 3 times with warm dilute hydrochloric acid (see Robinson and Shah, *J.*, 1934, 1497) and then amalgamated. A mixture of the zinc amalgam, ethanol (12 c.c.), and 10% hydrochloric acid (40 c.c.) was heated on a water-bath, and the above aldehyde (2.0 g.) added in portions during ¾ hour. After a further 2 hours' heating, concentrated hydrochloric acid (8 c.c.) was added and heating continued for 2 hours. The separated solution was then saturated with salt and extracted with ether (4 × 100 c.c.). The extracts yielded a brown oil, which partly crystallised on seeding, and this was extracted with boiling light petroleum (b. p. 60—80°) (4 × 50 c.c.). The combined extracts yielded white needles (0.83 g.), m. p. 108—109°. Repetition of this extraction gave 2 further crops of the phenol (0.32 g., m. p. 104—105°; and 0.14 g., m. p. 102—105°).

Part of the first crop was recrystallised 3 times from light petroleum, giving white needles, m. p. 110—110.5°, alone or mixed with a sample of the material from coal tar (Found : C, 69.5; H, 7.1%). The identity of the two samples was confirmed by the similarity of their X-ray powder photographs kindly taken by Dr. T. Malkin, and by the identity of their characteristic reaction with ferric chloride which is best exhibited as follows. The phenol (10 mg.) is dissolved in water (1 c.c.) and a drop of dilute aqueous ferric chloride added. A deep slate-blue colour is produced which fades through green to yellow in a few seconds, and a yellow flocculent precipitate then more slowly separates. The formation of this yellow solid is doubtless caused initially by oxidative coupling of the phenolic nuclei.

Titration of 2 : 4-dimethylresorcinol in acetic acid with a solution of bromine in acetic acid was complete when 1 mol. of bromine had reacted, and evaporation of the solution at room temperature left a solid residue which crystallised with difficulty from warm light petroleum (b. p. 60—80°) in slightly coloured, flat prisms, m. p. *ca.* 104°. This compound, probably 6-bromo-2 : 4-dimethylresorcinol, is rather unstable and consequently difficult to purify; it becomes brown when kept.

7-Hydroxy-4 : 6 : 8-trimethylcoumarin.—Ethyl acetoacetate (0.3 c.c.) was added to an ice-cooled solution of 2 : 4-dimethylresorcinol (0.23 g.) in concentrated sulphuric acid (2 c.c.), and the mixture kept at 0° for 24 hours. After dilution with water and cooling to 0° the yellow precipitate was collected, washed, dried (0.30 g., 88%), and crystallised twice from dilute ethanol, giving *7-hydroxy-4 : 6 : 8-trimethylcoumarin* as colourless needles, m. p. 220—221° (Found : C, 70.2; H, 6.1. $C_{15}H_{12}O_3$ requires C, 70.6; H, 5.9%). Solutions of the coumarin in dilute alkali, alcohol, or concentrated sulphuric acid show an intense blue fluorescence.

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[Received, July 29th, 1949.]