CLIII.—*Some Derivatives of* m-*Xylene.*

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m-*Xylorcinolcarboxylic Acid.*—The procedure adopted by one of us (A. R.) and Robinson (J., 1927, 2196) for the preparation of *p*-orsellinic acid has proved suitable for the preparation of *m*-xylorcinolcarboxylic acid (compare Kostanecki, *Ber.*, 1886, **19**, 2323). A mixture of *m*-xylorcinol (Robertson and Robinson, *loc. cit.*) (5 g.), potassium carbonate (10 g.), and glycerol (10 g.) was heated (oil-bath at 130°) for 5 hours in an atmosphere of carbon dioxide. Addition of 15% hydrochloric acid to the cooled reaction mixture precipitated *m*-xylorcinolcarboxylic acid (4 g.), which crystallised from dilute alcohol in colourless prismatic needles, m. p. 199—200° (decomp.) (Kostanecki, *loc. cit.*, gives m. p. 196°) (Found : C, 59·5; H, 5·7. Calc. for $C_9H_{10}O_4$: C, 59·4; H, 5·5%). The acid quickly decomposes in boiling water into *m*-xylorcinol and carbon dioxide. The ferric chloride reaction is green in alcohol and pure blue in water. This acid, unlike β-orcinolcarboxylic acid (Robertson and Stephenson, this vol., p. 313), is not esterified in boiling methyl or ethyl alcohol. If sodium bicarbonate is used in the preparation, the yield is halved.

6-*Methoxy*-m-4-*xylidine.*—4-Nitro-*m*-6-xylenol (1 mol.) was methylated with methyl sulphate (2 mols.) and 20% aqueous sodium hydroxide (2·5 mols.) (compare Pfaff, *Ber.*, 1883, **16**, 1136). The alkali-insoluble ether crystallised from alcohol in pale yellow needles, m. p. 56—57°. Iron powder (80 g.) was added in portions of 10 g. at intervals of 3 minutes to a boiling solution of the nitro-ether (60 g.) in alcohol (300 c.c.) and concentrated hydrochloric acid (20 c.c.), and the mixture was refluxed for 5 hours, a test then showing that reduction was complete. The filtered solution was concentrated to 100 c.c., cooled, saturated with hydrogen chloride, and kept in an ice-chest. After some hours, the hydrochloride was collected, and a further quantity was isolated from the mother-liquor by concentration to 50 c.c. and renewed saturation with hydrogen chloride. The salt crystallised in glistening prisms; total yield, 50 g. Agitation of a suspension of the salt in excess of bicarbonate solution gave the amine, m. p. 83° after crystallisation from benzene–ligroin and then from dilute alcohol (colourless needles). The *acetyl* derivative crystallised from water in needles, m. p. 160° (Found : C, 68·6; H, 7·5. $C_{11}H_{15}O_2N$ requires C, 68·7; H, 7·4%).

6-*Methoxy*-m-4-*xylenol.*—The foregoing hydrochloride (17 g.) was dissolved in 10% sulphuric acid (200 c.c.) and crushed ice (200 g.) was added after sudden cooling and shaking to ensure the separation of small crystals. Sodium nitrite (6 g.), dissolved in water (50 c.c.), was then introduced, and the mixture stirred for 15 minutes. The filtered diazo-solution was gradually added to boiling 10% sulphuric acid (600 c.c.). On cooling, 6-*methoxy*-m-4-*xylenol* separated in pale yellow crystals. Recrystallisation from ligroin gave the substance in colourless needles, m. p. 80° (Found: C, 70·9; H, 7·8. $C_9H_{12}O_2$ requires C, 71·0; H, 8·0%). It is readily soluble in alcohol, ether, and benzene. The phenol does not give a ferric chloride reaction.

2-*Hydroxy*-6-*methoxy*-3 : 5-*dimethylbenzaldehyde*.—Condensation of the monomethyl ether of xylorcinol and hydrogen cyanide in the presence of hydrogen chloride and zinc chloride after the method of Gattermann gave a compound which on solution in water reverted to the original ether. The aldehyde was subsequently obtained by partial methylation of *m*-xylorcylaldehyde (1 mol.) (Robertson and Robinson, *loc. cit.*) with methyl iodide (1·5 mols.) and excess of potassium carbonate in acetone under reflux on the steam-bath for 2 hours. After removal of the potassium salts the acetone was distilled under diminished pressure, and the alkali-soluble residue crystallised from dilute methyl alcohol. The *aldehyde* formed slender colourless needles, m. p. 52° (Found: C, 66·4; H, 6·3. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·3%). The substance gives a dark green ferric chloride reaction almost identical with that given by *m*-xylorcylaldehyde. It is insoluble in water and readily soluble in alcohol, acetone, or ethyl acetate. Condensation of the aldehyde with ω-methoxyacetoveratrone (Pratt and Robinson, J., 1923, **123**, 745) with hydrogen chloride in dry ethyl acetate by the method of Robinson gave 3 : 5 : 3′ : 4′-tetramethoxy-6 : 8-dimethylflavylium chloride in red-brown prisms; the *ferrichloride* crystallised from acetic acid in elongated red-brown prisms, m. p. 177—178° (Found: C, 45·6; H, 4·3. $C_{21}H_{23}O_5,FeCl_4$ requires C, 45·6; H, 4·2%).

m-Xylorcinol does not condense with acetonitrile by the method of Hoesch.

We are indebted to the Chemical Society for a grant which has in part defrayed the cost of this investigation.

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[*Received, March 25th,* 1930.]