NOTES.

m-*Toluidine*-6-*sulphonic Acid*. By MADHAVLAL S. SHAH, CHINUBHAI T. BHATT, and DARAB D. KANGA.

ON sulphonating *m*-toluidine, Limpricht (*Ber.*, 1874, **7**, 448) and Lorenz (*Annalen*, 1874, **172**, 185) obtained a monosulpho-derivative which on replacement of its amino-group by hydrogen produced *o*-toluenesulphonic acid. Lorenz concluded that the acid is *m*-toluidine-2-sulphonic acid, but Ostwald (*Z. physikal. Chem.*, 1889, **3**, 412) inferred from conductivity measurements that it is *m*-toluidine-6-sulphonic acid.

We prepared Limpricht's *m*-toluidinesulphonic acid in quantity and obtained from it, by diazotisation and subsequent decomposition with water, *m*-cresol-6-sulphonic acid (Claus and Krauss, *Ber.*, 1887, **20**, 3089). Methylation of this gave 3-methoxytoluene-6-sulphonic acid (Haworth and Lapworth, J., 1923, **123**, 2988). For further confirmation, the methoxytoluenesulphonic acid was converted into 6-thiol-3-methoxytoluene, b. p. 253—254°, 6-methylthiol-3-methoxytoluene, b. p. 272°, and 6-methylsulphonyl-3-methoxybenzoic acid, m. p. 180°, identical with those described by us (J., 1933, 1375).

m-*Toluidine*-6-*sulphonic Acid*.—Limpricht (*loc. cit.*) and Lorenz (*loc. cit.*) obtained a mixture of mono- and di-sulphonic acids on sulphonating *m*-toluidine. By the following modification, only *m*-toluidine-6-sulphonic acid is produced. A mixture of redistilled *m*-toluidine (b. p. 199—200°; 15 g.) and fuming sulphuric acid (SO_3 20%; 60 g.) was heated at 125° for 8 hours, cooled, and treated with ice: *m*-toluidine-6-sulphonic acid, which separated, was washed, pressed, and crystallised from water (yield, 24 g.). The barium salt, large prisms, contained 9 molecules of water [Found: Ba, 23·9; H_2O, 31·6. Calc. for $(C_7H_8O_3NS)_2Ba,9H_2O$: Ba, 24·0; H_2O, 31·7%], and the tribromo-derivative, obtained on bromination, crystallised from alcohol in needles, m. p. 101°, in agreement with the observations of Limpricht (*loc. cit.*) and Lorenz (*loc. cit.*).

m-*Cresol*-6-*sulphonic Acid*.—The above toluidinesulphonic acid (10 g.) was diazotised with nitrous fumes, and the diazo-compound isolated in colourless crystals (8 g.), decomp. 107—108°, by treatment with absolute alcohol and cooling of the solution in a freezing mixture (Found: N, 13·2. Calc. for $C_7H_8O_4N_2S$: N, 13·0%). The diazo-compound was decomposed with boiling water, and the resulting cresolsulphonic acid converted into the barium salt, tufts of needles [Found : Ba, 26·0; H_2O, 3·2. Calc. for $(C_7H_7O_4S)_2Ba,H_2O$: Ba, 25·9; H_2O, 3·4%], and the potassium salt, long needles (Found : K, 14·2; H_2O, 16·4. Calc. for $C_7H_7O_4SK,2\frac{1}{2}H_2O$: K, 14·4; H_2O, 16·6%), identical with the barium and the potassium *m*-cresol-6-sulphonate described by Claus and Krauss (*loc. cit.*). Haworth and Lapworth's figures (J., 1924, **125**, 1304), both found and calculated, for the barium salt are low; their calculated value for the potassium salt is incorrect for a dihydrate, but their found value agrees with that obtained by us.

3-*Methoxytoluene*-6-*sulphonic Acid*.—The methoxytoluenesulphonic acid obtained from the above cresolsulphonic acid on methylation, yielded, *via* a syrupy sulphonyl chloride, a sulphonamide, needles, m. p. 128—129°, and a sulphonanilide, clusters of needles or leaflets, m. p. 104°, and the former gave on oxidation 5-methoxy-*o*-benzoicsulphinimide, m. p. 242°, all identical with the compounds derived from 3-methoxytoluene-6-sulphonic acid by Haworth and Lapworth's method (*loc. cit.*).—THE MADHAVLAL RANCHHODLAL SCIENCE INSTITUTE, GUJARAT COLLEGE, AHMEDABAD, INDIA. [*Received, July* 16*th*, 1934.]

Preparation of Arylcarbimides. By DOUGLAS V. N. HARDY.

IN preparing *p*-xenylcarbimide by the method of Morgan and Pettet (J., 1931, 1125) it was observed that, as carbonyl chloride is passed into the boiling toluene solution of *p*-xenylamine, a bulky white precipitate accumulates until a pasty consistency is reached. The solid matter then gradually dissolves until eventually there remains a residue of *s*-di-*p*-xenylcarbamide, which does not decrease in amount on prolonged treatment with carbonyl chloride. It was concluded that the transitory precipitate consists of *p*-xenylamine hydrochloride, which passes into *p*-xenylcarbimide, and that *s*-di-*p*-xenylcarbamide is produced by interaction of the carbimide with free *p*-xenylamine :

$$R{\cdot}NH_2 + COCl_2 = R{\cdot}NCO + 2HCl;\ R{\cdot}NH_2 + R{\cdot}NCO = R{\cdot}NH{\cdot}CO{\cdot}NHR;$$
$$R{\cdot}NH_2 + HCl = R{\cdot}NH_2,HCl;\ R{\cdot}NH_2,HCl + COCl_2 = R{\cdot}NCO + 3HCl$$

To avoid the wasteful conversion of xenylamine into the carbamide a toluene solution of the amine was saturated with hydrogen chloride prior to passing carbonyl chloride, with the anticipated result that not only was an enhanced yield of carbimide obtained but no carbamide was formed.

There is little doubt that many other arylcarbimides may be obtained with advantage by this procedure, which has successfully been applied to the preparation of phenylcarbimide. This method of preparing the latter offers advantages over that described by Hentschel (*Ber.*, 1884, **17**, 1284; Houben, " Die Methoden der Organischen Chemie," 3rd Edition, **3**, 11).

Phenylcarbimide.—A hot (preferably not boiling) solution of aniline (93 g.) in toluene (1000 c.c.) was saturated with hydrogen chloride, and carbonyl chloride then passed in at the boiling point until a clear solution was obtained. By careful fractional distillation through a 2′ 6″ all-glass Dufton column toluene was removed and phenylcarbimide was collected between 158° and 168° (yield, 99 g.; *i.e.*, 83%).

p-*Xenylcarbimide*.—A solution of *p*-xenylamine (55 g.) in toluene (500 c.c.) was similarly treated. Toluene was removed by distillation from an oil-bath, and crude *p*-xenylcarbimide precipitated by addition of light petroleum (b. p. 40—60°). After recrystallisation from the same solvent the yield was 58 g. (91%).

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