273. *Reactions between Hexamethylenetetramine and Phenolic Compounds. Part I. A New Method for the Preparation of* 3- *and* 5-*Aldehydosalicylic Acids.*

By J. C. Duff and E. J. Bills.

Hexamethylenetetramine and salicylic acid, heated in aqueous solution, gave, not the expected 3- and 5-hydroxymethylsalicylic acids, but 3- and 5-aldehydosalicylic acids, which were readily separated by means of benzene. *m*- and *p*-Hydroxybenzoic acids under the same conditions gave complex amorphous products.

Preparation of 3- *and* 5-*Aldehydosalicylic Acids.*—Salicylic acid (40 g.) hexamethylenetetramine (27 g.), and H_2O (300 c.c.) were boiled under reflux for 16 hrs., the cooled solution acidified with 4*N*-HCl (300 c.c.), and the yellow ppt. dried and extracted with four lots of C_6H_6 (100 c.c.) at 70°. The insol. portion, cryst. from boiling H_2O (charcoal), yielded 7·5 g. of 5-aldehydosalicylic acid. The C_6H_6 solution was evaporated, the residue dissolved in 3*N*-NH_3 (200 c.c.), and 10% $BaCl_2$ (100 c.c.) and 2*N*-NaOH (50 c.c.) added at 50°. After 2 hrs., the ppt. of barium 3-aldehydosalicylate was collected and decomposed with dilute HCl, and 3·3 g. of 3-aldehydosalicylic acid obtained by crystallisation of the resulting ppt. from boiling H_2O. Salicylic acid (20 g.) was recovered from the alkaline filtrate.

The identity of the acids was confirmed by their aldehyde reactions, m. p.'s (also of their oximes), equiv. (titration), and by conversion into the corresponding hydroxy*iso*phthalic acids and hydroxymethylsalicylic acids by oxidation and reduction respectively.

The two aldehydosalicylic acids, unlike salicylic acid, when titrated in EtOH with $Ba(OH)_2$ aq., had equiv. 83, exactly half of that found in H_2O.

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274. *The Action of Sulphur on Amines. Part III. The Recognition of Trithio*-o-*toluidine as* 2 : 2'-*Diamino*-5 : 5'-*ditolyl Trisulphide.*

By H. H. Hodgson and H. V. France.

Dithio-*o*-toluidine (Hodgson, J., 1912, **101**, 1693) has now been identified as 2 : 2'-*diamino*-5 : 5'-*ditolyl disulphide* by its preparation from 5-bromo-2-nitrotoluene. Since in aqueous sodium trisulphide solution it is readily converted by atmospheric oxidation into trithio-*o*-toluidine (*loc. cit.*), this must be 2 : 2'-*diamino*-5 : 5'-*ditolyl trisulphide*. The ready coupling of the diazotised compounds with alkaline β-naphthol is in harmony with these constitutions, for if the sulphur atoms were in the *o*-position to the amino-groups, an insoluble non-coupling diazotoluene sulphide should be produced by the action of nitrous acid (compare Hodgson, J., 1924, **125**, 1856).

Preparation of 2 : 2′-*Diamino*-5 : 5′-*ditolyl Disulphide.*—5-Bromo-2-nitrotoluene (2·5 g.) was boiled under reflux with Na_2S_2 (17 g.) and H_2O (75 c.c.) for 40 hrs., unchanged material and 5-bromo-*o*-toluidine were removed by steam-distillation, and the cooled filtered solution was oxidised with air. The ppt. produced was extracted with dil. HCl, and the bases recovered by means of NH_3 aq. As they appeared to be a mixture of di- and tri-sulphides, they were reduced with Zn and HCl aq., the 2-amino-5-tolylthiol produced was treated with 10% NaOH aq., and the filtered solution oxidised with air. 2 : 2′-*Diamino*-5 : 5′-*ditolyl disulphide*, which was rapidly ppted., crystallised from 50% EtOH aq. in long colourless rhombs, m. p. 112° (alone or mixed with dithio-*o*-toluidine) (Found : S, 23·4. $C_{14}H_{16}N_2S_2$ requires S, 23·2%). The hydrochlorides of the two specimens had m. p. and mixed m. p. 256—257°, and the acetyl derivatives, 224—225°.

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