NOTES.

A New Addition Compound of Phenol and Hexamethylenetetramine. By L. H. SMITH and K. N. WELCH.

IN the reaction between formaldehyde, ammonia, and phenol it has been found that besides the well-known addition product, $C_6H_{12}N_4,3C_6H_6O$, of Moschatos and Tollens (*Annalen*, 1892, **272**, 271) there is produced a *compound*, $C_{12}H_{18}ON_4$ (Found : C, 61·6; H, 7·5; N, 23·9. $C_{12}H_{18}ON_4$ requires C, 61·8; H, 7·7; N, 23·9%), which crystallises from alcohol in elongated prisms, m. p. 176—176·5° (decomp.). The latter appears to be a 1 : 1 addition compound of hexamethylenetetramine and phenol, since (1) it may be also prepared by crystallisation of an equimolecular mixture of phenol and hexamethylenetetramine from alcohol; (2) crystallisation of the compound from water in the presence of excess of phenol gives the well-known 1 : 3 addition compound; (3) shaking of its aqueous solution with ether extracts phenol (identified by m. p. and as *s*-tribromophenol), while hexamethylenetetramine remains in the aqueous solution (identified by m. p. and as the " nitroso " compound) (Griess and Harrow, *Ber.*, 1888, **21**, 2737).

The 1 : 1 addition compound is the more stable in the presence of alcohol, since on repeated recrystallisation from that solvent the 1 : 3 addition compound progressively loses phenol and is converted into the 1 : 1 compound.

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The Preparation of p-*Dimethylaminobenzyl Alcohol.* By L. H. SMITH and K. N. WELCH.

BY the action of potassium hydroxide on *p*-dimethylaminobenzaldehyde Rousset (*Bull. Soc. chim.*, 1894, **1**, 318) obtained a solid, m. p. 62°, which he described as *p*-dimethylaminobenzyl alcohol. Braun and Kruber (*Ber.*, 1912, **45**, 2978) and Clemo and Smith (J., 1928, 2423) could not repeat his result. Geigy & Co. (D.R.-P. 105,105) obtained the "alcohol" by the action of formaldehyde on dimethylaniline, but Cohn (*Chem.-Ztg.*, 1900, **24**, 564) was unable to do so. Braun and Kruber upheld the claim of Geigy & Co. and stated that they had obtained a 2% yield of the alcohol. Clemo and Smith, however, showed that the true alcohol, obtained (in 20% yield) by reduction of *p*-dimethylaminobenzaldehyde, did not correspond either in its physical properties or in those of its derivatives with the material obtained by Rousset or with that obtained by Braun and Kruber. By modification of the method of Geigy & Co. the alcohol corresponding in properties with that described by Clemo and Smith has now been obtained in yields of 55—65% of the theoretical, allowing for recovered dimethylaniline. *p*-Dimethylaminobenzyl alcohol is extremely sensitive to traces of acids, especially at a high temperature; moreover, the reaction of formaldehyde with dimethylaniline is probably reversible. The following modifications were therefore adopted.

A mixture of dimethylaniline (60 c.c.), concentrated hydrochloric acid (100 c.c.), and 40% formalin (400 c.c.) was kept at 37° for 48 hours. The product was then cooled in a freezing-mixture and, after the addition of ice (160 g.), an excess of concentrated sodium hydroxide solution was gradually added, the temperature not being allowed to rise above 0°. The separated bases were extracted and partially dried (calcium chloride) in ether, the ether was evaporated on a water-bath, water and gaseous formaldehyde were removed at about 80°/20 mm. (this treatment was necessary in order to obtain a high vacuum during the final distillation), and the product was finally distilled under 1 mm. from a Claisen flask fitted with a short Vigreux fractionating column in the side limb. Dimethylaniline (20 g.) was recovered below 122°/*ca.* 1 mm. and 29·5 g. of the alcohol, b. p. 122—128°/*ca.* 1 mm., were isolated, leaving a residue (8 g.) consisting largely of 4 : 4′-tetramethyldiaminodiphenylmethane. It is advisable to carry out all stages of the preparation from the neutralisation to the final distillation rapidly, consistent with the maintenance of as low a temperature as possible.

On redistillation *p*-dimethylaminobenzyl alcohol was obtained as a very pale yellow oil with a faint pleasant smell, b. p. 125°/1 mm. (Found : N, 9·2. Calc. : N, 9·3%), $n_D^{14°}$ 1·5727, $d_{4°}^{14}$ 1·059, hence $[R_L]_D$ 47·00 [calc. from R_L (benzyl alcohol) + R_L (dimethylaniline) — R_L (benzene), 47·02]. It is oxidised rather readily on exposure to air and after some time *p*-dimethylaminobenzaldehyde can be detected by its characteristic reaction with indole.

The methiodide of the alcohol, obtained after the method of Clemo and Smith, had m. p. 232°, and the benzoate had m. p. 88—89° [Clemo and Smith give 232° (decomp.) and 91° respectively], but the *m*-nitrobenzoate could not be prepared.—UNIVERSITY OF MELBOURNE

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