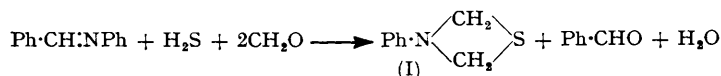


830. The Action of Hydrogen Sulphide on Certain Aromatic Amines in the Presence of Formaldehyde.

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Aniline and *p*-toluidine are shown to condense with hydrogen sulphide and formaldehyde to give tetrahydrothiadiazines, thia-azetidines, and dihydrodithiazines. *m*-Toluidine failed to give a tetrahydrothiadiazine.

PREVIOUS papers (*J.*, 1950, 208; 1953, 143) have recorded the action of hydrogen sulphide on methyleneimines obtained from cyclohexylamine, benzylamine, and substituted benzylamines. Recently we found that the action of hydrogen sulphide on benzylideneaniline in the presence of formaldehyde leads, contrary to expectation, to 3-phenyl-1-thia-3-azetidine and benzaldehyde:



Accordingly we re-investigated the action of hydrogen sulphide and formaldehyde on aniline. Wohl (*Ber.*, 1886, **19**, 2345) failed to obtain a crystalline product from this reaction, and Le Fèvre and Le Fèvre (*J.*, 1935, 865) reported an oily product which gave trithioformaldehyde on hydrolysis with hot hydrochloric acid.

Levi (*Atti R. Accad. Lincei*, 1929, **9**, 790) described the preparation of thiadiazines (II) from aniline, *p*-toluidine, and benzylamine, but gave no details about the proportions of hydrogen sulphide and formaldehyde used.

In our hands, aniline and *p*-toluidine yielded, not only the tetrahydrothiadiazines (II), but also the thia-azetidines (as I) and the dihydrodithiazines (III). The thiadiazines were



obtained when 1 mol. of hydrogen sulphide in aqueous-ethanolic formaldehyde was condensed with 2 mols. of the amine: aniline gave a 75% yield of (II; R = Ph), and *p*-toluidine a 65% yield of (II; R = *p*-C₆H₄Me) with a small amount of 3-*p*-tolyl-1-thia-3-azetidine (as I), but *m*-toluidine gave only (20%) 3-*m*-tolyl-1-thia-3-azetidine, and *o*-toluidine gave an oil. Use of smaller proportions of hydrogen sulphide gave no thiadiazine.

Condensation of 2 mols. of hydrogen sulphide with 1 mol. of amine in aqueous ethanolic formaldehyde gave mixtures of the thia-azetidine (as I) and the dithiazine (III), save that *o*-toluidine again gave an oil.

All eight cyclic products rapidly decomposed, when heated with hydrochloric acid, to trithioformaldehyde and the amine hydrochloride.

EXPERIMENTAL

Tetrahydro-1-thia-3:5-diazines.—Hydrogen sulphide was passed through a mixture of ethanol (25 c.c.) and formaldehyde (25 c.c. of 40%) until 0.5 mol. had been absorbed. This solution was then added to a solution of the amine (10 g.) in ethanol (25 c.c.) at 0°. An oil separated, which crystallised overnight at 0°. Recrystallisation from ethanol gave 3:5-diphenyltetrahydro-1-thia-3:5-diazine, m. p. 103° (Levi, *loc. cit.*, gives m. p. 103°) (10.3 g.) (Found: C, 70.1; H, 6.1; N, 11.3; S, 13.0. Calc. for C₁₅H₁₆N₂S: C, 70.3; H, 6.3; N, 10.9; S, 12.5%), and 3:5-di-*p*-tolyltetrahydro-1-thia-3:5-diazine, m. p. 105° (Levi, *loc. cit.*, gives m. p. 105°) (8.6 g.) (Found: C, 71.5; H, 7.2; N, 10.2; S, 11.1. Calc. for C₁₇H₂₀N₂S: C, 71.8; H, 7.0; N, 9.9; S, 11.3%); the latter was separated from the thia-azetidine (1.5 g.) during the crystallisation.

1-Thia-3-azetidines and 5:6-Dihydro-1:3-dithia-5-azines.—Reaction was effected as above except that 2 mols. of hydrogen sulphide in ethanol (50 c.c.) and formaldehyde solution (50 c.c.; 40%) were used. The liquid became opalescent and an oil separated from which, on refrigeration overnight at 0°, a sticky solid was obtained. This was fractionally crystallised from

ethanol or acetone, the thia-azetidines being in the least soluble fraction; the dithiazines crystallised with difficulty.

In this way aniline gave 3-phenyl-1-thia-3-azetidine (2.8 g.), plates, m. p. 172° (from ethanol) (Found: C, 63.8; H, 6.4; S, 20.9; N, 9.0. C_8H_9NS requires C, 63.5; H, 6.0; S, 21.2; N, 9.3%) and 5:6-dihydro-5-phenyl-1:3-dithia-5-azine (13.9 g.), m. p. 109° (from aqueous ethanol at 0°) (Found: C, 55.0; H, 5.8; S, 32.1; N, 6.8. $C_9H_{11}NS_2$ requires C, 54.8; H, 5.6; S, 32.5; N, 7.1%). *p*-Toluidine gave 3-*p*-tolyl-1-thia-3-azetidine (2.6 g.), needles, m. p. 174° (from ethanol) (Found: C, 65.2; H, 6.5; S, 19.1; N, 8.4. $C_9H_{11}NS$ requires C, 65.4; H, 6.7; S, 19.4; N, 8.5%), and 5:6-dihydro-5-*p*-tolyl-1:3-dithia-5-azine, m. p. 142° (from aqueous ethanol at 0°) (Found: C, 56.7; H, 6.3; S, 29.9; N, 6.8. $C_{10}H_{13}NS_2$ requires C, 56.9; H, 6.2; S, 30.4; N, 6.6%). *m*-Toluidine gave 3-*m*-tolyl-1-thia-3-azetidine, needles, m. p. 183° (from acetone), sparingly soluble in ethanol (Found: C, 65.2; H, 6.8; S, 19.5; N, 8.7%), and 5:6-dihydro-5-*m*-tolyl-1:3-dithia-5-azine, m. p. 120° (from acetone or ethanol) (Found: C, 56.7; H, 6.3; S, 29.9; N, 6.6%).

3-Phenyl-1-thia-3-azetidine from Benzylideneaniline.—Benzylideneaniline (2 g.) (recrystallised from ethanol) was dissolved in ethanol (20 c.c.), and treated with a solution of hydrogen sulphide (1 mol.) in aqueous formaldehyde (20 c.c.; 40%) gradually at 0°. A crystalline precipitate (1.26 g.) separated on storage overnight at 0°. This crystallised from ethanol and was shown by analysis to be the phenylthia-azetidine. After acidification of the mother-liquor with dilute hydrochloric acid, the benzaldehyde was removed in ether and on oxidation gave 1.03 g. of benzoic acid.

In general the above compounds were soluble in ethanol, methanol, and acetone, readily soluble in benzene, very soluble in chloroform and pyridine, and sparingly soluble in light petroleum.