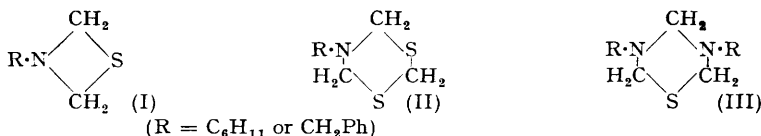


28. The Action of Hydrogen Sulphide on Certain Methyleneimines. Part II.*

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The reaction of hydrogen sulphide with *N*-methylene-*cyclohexylamine* and -benzylamine in the presence of formaldehyde has been re-examined. The experiments have been extended to *p*-methoxy- and 2 : 4 : 6-trimethyl-*N*-methylenebenzylamine.

It has been shown (Part I *) that reaction of hydrogen sulphide and formaldehyde with *N*-methylene-*cyclohexylamine* or -benzylamine leads to dissimilar products formulated as (I) and (II) or (III) respectively. This was thought to be due to the methyleneimines having monomeric and dimeric structures respectively, but their infra-red absorption spectra show that in fact neither is monomeric. This discrepancy has now been shown to be largely apparent, for under somewhat different conditions *N*-methylenecyclohexylamine affords a product of type (III), and *N*-methylenebenzylamine yields a compound of the type (I) though a benzyl analogue of (II) has so far proved unobtainable. Moreover, in the cases of *p*-methoxy- and 2 : 4 : 6-trimethyl-*N*-methylenebenzylamine compounds of all three types (I), (II), and (III) have been obtained.



Preliminary experiments revealed, first, that variation in the volume of formaldehyde used had no effect on the type of compound formed, provided that the weight of hydrogen sulphide was constant. Secondly, the passage of hydrogen sulphide at temperatures above normal quickly gave rise to the formation of intractable complexes of low nitrogen content. Except in the case of *N*-methylenebenzylamine, it was convenient to carry out the experiments on aqueous-ethanolic formaldehyde solutions of the methyleneimines as the latter were not readily precipitated from this medium by water.

The previous failure to obtain 3 : 5-dicyclohexyltetrahydro-1-thia-3 : 5-diazine (III ; R = C₆H₁₁) was thought to have one of two causes : either the thiadiazine was readily converted into 3-cyclohexyl-1-thia-3-azetidine or 5-cyclohexyl-5 : 6-dihydro-1 : 3-dithia-5-azine ; or excess of hydrogen sulphide favoured the formation of the monomeric form of methylenecyclohexylamine, which then condensed with formaldehyde and hydrogen sulphide to give (I) and/or (II) (R = C₆H₁₁). With the latter possibility in mind, attempts were made to produce 3 : 5-dicyclohexyltetrahydro-1-thia-3 : 5-diazine by using the calculated quantity of hydrogen sulphide, but the product was mainly 3-cyclohexyl-1-thia-3-azetidine, with a small quantity of 5-cyclohexyl-5 : 6-dihydro-1 : 3-dithia-5-azine. Experiments in which various weights of hydrogen sulphide were used have finally shown that, by adding it to a mixture of *N*-methylenecyclohexylamine and formaldehyde, approx. 60% of the theoretical amount of hydrogen sulphide dissolved in formaldehyde solution, a solution can be obtained which remains clear after 24 hours ; from this 3 : 5-dicyclohexyltetrahydro-1-thia-3 : 5-diazine was readily obtained on the addition of water.

A similar result was obtained with *N*-methylenebenzylamine. In contrast, *p*-methoxy- and 2 : 4 : 6-trimethyl-*N*-methylenebenzylamine afforded chiefly a product of type (III) but each gave also a little (I). *N*-Methylene-*cyclohexylamine* and -benzylamine gave high yields of the corresponding thiazetidine (I) when treated in the presence of formaldehyde with 1—2 mols. of hydrogen sulphide. The other methyleneimines gave mixtures of types (I) and (III) from which type (I) was obtained in good yield.

It is noteworthy that, save with *N*-methylenecyclohexylamine from which a small amount of 5-cyclohexyl-5 : 6-dihydro-1 : 3-dithia-5-azine was isolated, compounds of type (II) have not been detected, despite the fact that both *p*-methoxy- and 2 : 4 : 6-tri-

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methyl-*N*-methylenebenzylamine yield compounds of type (II) under slightly different conditions. A crystalline thiosulphate was obtained from *p*-methoxybenzylamine. It is hoped to examine the reaction of other aldehydes towards the methyleneimines in the presence of hydrogen sulphide.

EXPERIMENTAL

p-Methoxy-*N*-methylenebenzylamine.—*p*-Methoxybenzylamine (5.5 c.c.) was dissolved in ethanol, and 40% formaldehyde solution (3.5 c.c.) added. The mixture, which became hot, was cooled. After several hours, the precipitated solid was removed and on crystallizing from ethanol gave *p*-methoxy-*N*-methylenebenzylamine as steel-grey needles, m. p. 115–116° [Found: N, 9.4%; *M* (Rast), 151. $C_9H_{11}ON$ requires N, 9.4%; *M*, 149]. *N*-Methylene-cyclohexylamine and -benzylamine were prepared by the same method. 2:4:6-Trimethyl-*N*-methylenebenzylamine was prepared by Fuson and Denton's method (*J. Amer. Chem. Soc.*, 1941, **63**, 654).

Tetrahydro-1-thia-3:5-diazines.—The preparation of 3:5-dicyclohexyltetrahydro-1-thia-3:5-diazine illustrates the general procedure used for the preparation of compounds of type (III). To a solution of *N*-methylenecyclohexylamine (1 g.) in ethanol (25 c.c.) was added 40% formaldehyde solution (10 c.c.). The mixture was cooled to <20°. Any solid separating was removed. Meanwhile, hydrogen sulphide was passed with cooling through 40% formaldehyde solution (10 c.c.) until the increase in weight was 0.09 g. (0.60 mol.). The solutions were mixed and kept overnight at 0°, remaining clear. Gradual addition of water then precipitated the thiadiazine as needles. In later experiments, it was found advisable to seed the liquor after addition of a little water, to avoid precipitation as an oil. Recrystallization from ethanol–water gave the pure compound in needles, m. p. 51° (Found: C, 67.2; H, 10.4; S, 11.7. $C_{15}H_{28}N_2S$ requires C, 67.2; H, 10.4; S, 11.9%).

3:5-Dibenzyltetrahydro-1-thia-3:5-diazine. Condensation was effected by the general method but without the preliminary addition of formaldehyde, as this tended to precipitate the methyleneimine. 0.7 Mol. of hydrogen sulphide was used and the thiadiazine separated overnight. A further quantity was obtained on addition of a small quantity of water to the filtrate. Recrystallized from ethanol it was obtained as needles, m. p. 92–93° (Found: C, 71.6; H, 7.3; N, 10.1; S, 10.6. Calc. for $C_{17}H_{20}N_2S$: C, 71.8; H, 7.0; N, 9.8; S, 11.3%).

3:5-Di-*p*-methoxybenzyltetrahydro-1-thia-3:5-diazine. On use of the general method, crystals separated after 3 hours. Collection after 24 hours and repeated recrystallization from ethanol gave needles, m. p. 162° (Found: C, 66.3; H, 7.0; N, 8.0, 8.1; S, 9.3, 9.5. $C_{19}H_{24}O_2N_2S$ requires C, 66.3; H, 7.0; N, 8.1; S, 9.3%). The thiadiazine was also obtained by passing hydrogen sulphide through an ethanolic solution of the methyleneimine admixed with formaldehyde. As soon as separation commenced, passage of hydrogen sulphide was stopped and the flocculent precipitate removed. Recrystallized from ethanol, it gave the thiadiazine in needles, m. p. 162°.

3:5-Di-(2:4:6-trimethylbenzyl)tetrahydro-1-thia-3:5-diazine. 2:4:6-Trimethyl-*N*-methylenebenzylamine was dissolved in boiling ethanol (60 c.c.) and the general procedure followed. After 24 hours the precipitated thiadiazine was recrystallized from ethanol (needles: m. p. 158–159°) (Found: C, 74.6; H, 8.7; N, 7.4; S, 8.5. $C_{23}H_{32}N_2S$ requires C, 75.0; H, 8.7; N, 7.6; S, 8.7%). It dissolves in chloroform, acetone, or boiling ethanol or methanol.

Preparation of 1-Thia-3-azetidines (I).—*General method*. The methyleneimine (1 g.) was dissolved in boiling ethanol (25 c.c.), 40% formaldehyde solution (10 c.c.) was added, and the mixture cooled. Any solid remaining was removed. Hydrogen sulphide was passed into a further quantity of 40% formaldehyde solution (10 c.c.) until the increase in weight was 0.3 g. This solution was then added to the methyleneimine mixture. Separation of crystals began almost immediately but the mixture was left overnight at 0° to complete the separation. Recrystallization was usually from alcohol or from acetone.

3-cyclohexyl-1-thia-3-azetidine crystallized from acetone in needles, m. p. and mixed m. p. 118–119° (yield, 0.7 g.).

3-Benzyl-1-thia-3-azetidine (yield 0.6 g.), crystallized from ethanol, had m. p. 116° (0.5 g.) (Found: C, 65.1; H, 7.0; N, 8.2; S, 18.9. $C_9H_{11}NS$ requires C, 65.6; H, 6.7; N, 8.5; S, 19.3%).

3-*p*-Methoxybenzyl-1-thia-3-azetidine was obtained in needles, m. p. 144–145° (Found: N, 7.45; S, 16.2. $C_{10}H_{13}ONS$ requires N, 7.2; S, 16.4%), after fractional crystallization from ethanol to remove the thiadiazine.

3-(2:4:6-Trimethylbenzyl)-1-thia-3-azetidine. 2:4:6-Trimethyl-*N*-methylenebenzylamine

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(1 g.) needed 60 c.c. of boiling ethanol for dissolution. The azetidine, m. p. 145—161°, was removed and a further quantity obtained on addition of water to the filtrate. Recrystallized from hot methanol-acetone, this *thia-azetidine* was obtained as needles, m. p. 182° (Found : N, 6·9; S, 15·4. $C_{12}H_{17}NS$ requires N, 6·7; S, 15·4%). A small quantity of the corresponding thiadiazine was obtained from the mother-liquor.

5 : 6-*Dihydro-5-(2 : 4 : 6-trimethylbenzyl)-1 : 3-dithia-5-azine*.—2 : 4 : 6-Trimethyl-*N*-methylenebenzylamine (5 g.) was dissolved in the min. of cold dioxan and formaldehyde (40% solution) was added until a faint opalescence was evident. The solution was saturated with hydrogen sulphide with cooling and then kept overnight. Addition of water precipitated a sticky oil from which 5 : 6-*dihydro-5-(2 : 4 : 6-trimethylbenzyl)-1 : 3-dithia-5-azine* was obtained on extraction with ethanol; it had m. p. 102° (Found : C, 61·5; H, 7·7; S, 25·2, 25·5; N, 5·4, 5·3. $C_{13}H_{19}NS_2$ requires C, 61·5; H, 7·5; S, 25·3; N, 5·5%). This compound was similarly obtained when hot ethanol replaced dioxan.

5 : 6-*Dihydro-5-p-methoxybenzyl-1 : 3-dithia-5-azine*.—40% Formaldehyde solution (10 c.c.) was saturated with hydrogen sulphide at room temperature and added to *p*-methoxy-*N*-methylenebenzylamine (1 g.) in ethanol (25 c.c.) containing 40% formaldehyde solution (10 c.c.). Hydrogen sulphide was then passed in for 20 minutes and the solution set aside overnight. Water was then added, precipitating a sticky solid. On extraction with ethanol, the solid remaining after evaporation recrystallized from aqueous alcohol as needles of the 5 : 6-*dihydrodithiazine*, m. p. 53° (Found : N, 6·0; S, 26·5. $C_{11}H_{15}ONS_2$ requires N, 5·8; S, 26·5%).

p-Methoxybenzylamine Thiosulphate.—*p*-Methoxybenzylamine (1 g.) was dissolved in ethanol (10 c.c.) and the solution saturated with hydrogen sulphide. Air was passed through the mixture. *p*-Methoxybenzylamine thiosulphate separated. Recrystallized from ethanol it had m. p. 181° (decomp.). It was soluble in water and gave the usual reactions for thiosulphates [Found : S, 16·4. $(C_8H_{11}ON)_2H_2S_2O_3$ requires S, 16·4%].

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