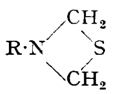
48. *The Action of Hydrogen Sulphide on Certain Methyleneimines. Part I.*

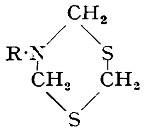
By Eric R. Braithwaite and John Graymore.

Hydrogen sulphide reacts with *N*-methylene*cyclo*hexylamine in the presence of formaldehyde to give N-cyclo*hexylthioformaldine*, but in the absence of formaldehyde the main product is 5-cyclo*hexyl*-5 : 6-*dihydro*-1 : 3-*dithia*-5-*azine*. With methylenebenzylamine, hydrogen sulphide and formaldehyde give a single product, 3 : 5-dibenzyltetrahydro-1-thia-3 : 5-diazine. This difference can be ascribed to the dimeric structure of methylenebenzylamine.

Wohl (*Ber.*, 1886, **19**, 2345) obtained a product from formaldehyde saturated with hydrogen sulphide by adding methylamine. He described it as methylthioformaldin (II; R = CH_3). Le Fèvre (*J.*, 1935, 865) obtained a four-membered ring compound formulated as (I; R = CH_3) by first saturating an aqueous solution of methylamine with hydrogen sulphide and then adding formaldehyde solution; the author observed that on dissolving his product in warm acetone, conversion into Wohl's methylthioformaldin took place. No other six-membered ring compound of the type described by Wohl was obtained.



(I.)



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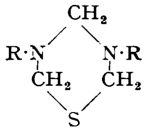
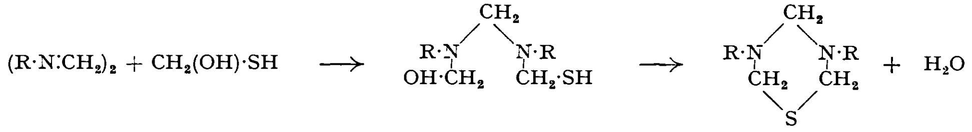


(III.)

We considered that it should be possible to obtain compounds of types (I), (II), and (III) from suitable amines, formaldehyde, and hydrogen sulphide. Formaldehyde is known to condense with *cyclo*hexylamine (*J.*, **1947**, 1118) and with benzylamine to give readily crystallisable methyleneimines. As the formation of a thialdine in the Wohl–Le Fèvre reaction is probably preceded by the formation of a methyleneimine, it seemed reasonable to use the methyleneimines as starting points. Consequently, a study of the reaction was made with formaldehyde and hydrogen sulphide on the one hand, and *N*-methylene*cyclo*hexylamine or *N*-methylenebenzylamine on the other.

Aqueous-alcoholic solutions of the methyleneimines were accordingly treated with formaldehyde. The mixtures were cooled to keep the temperature below 25°, and a stream of hydrogen sulphide passed in. In each case a single crystalline product separated in excellent yield, but whereas *N*-methylene*cyclo*hexylamine gave a *thioformaldine* of type (I; $R = C_6H_{11}$), *N*-methylenebenzylamine gave 3 : 5-*dibenzyltetrahydro*-1-*thia*-3 : 5-*diazine* (III; $R = CH_2Ph$).

It had been noted that, although both methyleneimines can be precipitated from alcoholic solution by the addition of water, yet *N*-methylene*cyclo*hexylamine was not precipitated from alcoholic solution even by the addition of excess of formaldehyde (40% formalin). *N*-Methylenebenzylamine on the other hand was precipitated. These observations seemed to indicate that the former, a monomer, adds formaldehyde to give in all probability $C_6H_{11}N(CH_2{\cdot}OH)_2$, which condenses with hydrogen sulphide to give (I; $R = C_6H_{11}$). *N*-Methylenebenzylamine, a dimer, could not combine with formaldehyde and it is therefore probable that the dibenzyl compound (III; $R = CH_2Ph$) is produced as follows:



An aqueous-alcoholic solution of *N*-methylene*cyclo*hexylamine in the absence of formaldehyde reacted exothermally with hydrogen sulphide. With the temperature kept below 25°, two crystalline compounds were eventually obtained, namely, 5-cyclo*hexyl*-5 : 6-*dihydro*-1 : 3-*dithia*-5-*azine* similar to the thioformaldine described by Wohl (II; $R = C_6H_{11}$) and a smaller quantity of type (I).

Repeated attempts to make 5-*cyclo*hexyl-5 : 6-dihydro-1 : 3-dithia-5-azine from (I) by the action of hydrogen sulphide in the presence of formaldehyde were unavailing, so it might well be that (I) and (II) ($R = C_6H_{11}$) are formed independently from the methyleneimine by condensation with $CH_2(OH){\cdot}SH$ and $CH_2(OH){\cdot}S{\cdot}CH_2{\cdot}SH$, respectively. The first stage in the reaction of hydrogen sulphide with the methyleneimine is undoubtedly the partial breakdown of the latter to give *cyclo*hexylamine,

$$C_6H_{11}{\cdot}N{:}CH_2 + H_2O + H_2S \longrightarrow C_6H_{11}{\cdot}NH_2 + CH_2(OH){\cdot}SH$$

since cyclo*hexylamine thiosulphate* slowly separates from the residual liquor.

When hydrogen sulphide was passed into the aqueous-alcoholic solution of *N*-methylene*cyclo*hexylamine without temperature control, the temperature rose rapidly with the separation of a voluminous non-nitrogenous solid. Its melting point and general properties indicated that it was the compound which Wohl obtained by the action of hydrogen sulphide upon an aqueous or alcoholic solution of hexamine. Wohl assigned to it the formula $(CH_2S)_n$. Analyses of the compound now obtained did not agree with his findings. It is hoped to deal with this problem later.

After removal of the bulky insoluble precipitate, the filtrate was allowed to evaporate spontaneously, leaving a residue of *cyclo*hexylamine thiosulphate. Marrin, Achterhof, Conway, and Boord (*J. Amer. Chem. Soc.*, 1931, **53**, 2682) showed that the hydrosulphides of certain amines oxidised in air to the corresponding thiosulphates. The thiosulphates of *cyclo*hexylamine and *benzylamine* separated in considerable yields when air was blown through an alcoholic solution of the amine saturated with hydrogen sulphide.

All three thioformaldines decompose when heated with hydrochloric acid—(I) rapidly, (II) and (III) slowly—to give trithioformaldehyde (cf. Le Fèvre, *J.*, **1935**, 865). Similarly, they all decompose when heated under reflux in alcoholic solution in a stream of hydrogen sulphide to give the non-nitrogenous compound described above.

EXPERIMENTAL.

cyclo*Hexylthioformaldine* (3-cyclo*Hexyl*-1-*thia*-3-*azetidine*).—*N*-Methylene*cyclo*hexylamine (5·0 g.), freshly prepared and recrystallised from ethanol, was dissolved in alcohol (50 c.c.), and formaldehyde (25 c.c. of a 40% solution) added. After a few minutes, hydrogen sulphide was passed in for 10 minutes, the temperature being kept below 25°. The resulting solid was removed. The process was repeated until no further yield (total, 4·3 g.) was obtained. The *thioformaldine* crystallised from acetone in needles, m. p. 118—120° (Found: C, 60·6; H, 9·4; N, 8·9. $C_8H_{15}NS$ requires C, 61·1; H, 9·5; N, 8·9%). It was soluble in acetone, methanol, benzene, chloroform, or light petroleum. A solution in ethanol gave with an alcoholic solution of hydrogen chloride a crystalline *hydrochloride*, m. p. >120° (decomp.) (Found: N, 7·17; Cl, 18·0. $C_8H_{16}NClS$ requires N, 7·2; Cl, 18·3%).

The mother compound (0·4 g.) was dissolved in aqueous alcohol and heated under reflux (10 minutes). The solution was cooled, and water added, whereupon glistening needles were obtained which on recrystallisation gave 5-*cyclo*hexyl-5 : 6-dihydro-1 : 3-dithia-5-azine, m. p. and mixed m. p. 58°.

*cyclo*Hexylthioformaldine (1 g.), dissolved in dilute hydrochloric acid (50 c.c.) and heated under reflux, rapidly decomposed with evolution of formaldehyde and separation of trithioformaldehyde in needles (m. p. and mixed m. p. 216°). The mother-liquor after cooling and removal of the solid gave, with benzoyl chloride and sodium hydroxide, benzo*cyclo*hexylamide (m p. and mixed m. p. with an authentic specimen 160°).

5-cyclo*Hexyl*-5 : 6-*dihydro*-1 : 3-*dithia*-5-*azine*.—Methylene*cyclo*hexylamine (26 g.) was dissolved in ethanol (50 c.c.), and water was added until the mixture remained faintly opaque. Hydrogen sulphide was passed in at 0° for 1—2 hours. The precipitate (5·8 g.) which separated was recrystallised first from aqueous alcohol and finally from ethanol, forming long needles, m. p. 58°, of the *dithia-azine* (Found: C, 53·35; H, 8·5; N, 7·1; S, 31·0. $C_9H_{17}NS_2$ requires C, 53·2; H, 8·4; N, 6·9; S, 31·5%). It was insoluble in water, moderately soluble in acetone, and soluble in benzene or chloroform.

The filtrate from the first precipitate slowly deposited needles, m. p. 105—106° (1 g.); these recrystallised from acetone in needles and were identified as *cyclo*hexylthioformaldine (m. p. and mixed m. p. 118°). The filtrate from the above was distilled into 2N-hydrochloric acid and gave *cyclo*hexylamine hydrochloride (m. p. and mixed m. p. 204—205°).

5-cyclo*Hexyl*-5 : 6-*dihydro*-1 : 3-*dithia*-5-*azine hydrochloride* was obtained by passing hydrogen chloride through a solution of the parent compound in light petroleum, with cooling. It separated from ethanol in white needles, m. p. 185° (Found: Cl, 14·9. $C_9H_{18}NClS_2$ requires Cl, 14·6%).

The hydrochloride (0·75 g.) was dissolved in concentrated hydrochloric acid (10 c.c.), and the solution heated under reflux for 3 hours. A white solid (0·28 g.) separated and after recrystallisation from acetone was identified as trithioformaldehyde, needles, m. p. and mixed m. p. 216°.

cyclo*Hexylamine Thiosulphate*.—Methylene*cyclo*hexylamine (18 g.) was dissolved in ethanol, and the solution saturated with hydrogen sulphide for 5 hours, the temperature rising to 45°. The solid deposited was repeatedly washed with hot ethanol until no further solution appeared to take place. The solution was filtered hot, and, on cooling, silvery white plates of cyclo*hexylamine thiosulphate* separated, m. p. 198° (decomp.). It gave the usual reactions of thiosulphates (Found: C, 45·9; H, 8·8; N, 8·9. $C_{12}H_{28}O_3N_2S_2$ requires C, 46·15; H, 8·9; N, 8·9%). The insoluble residue, m. p. 175°, was nitrogen-free but its structure has not yet been determined. The thiosulphate was obtained directly by saturating an ethanolic solution of *cyclo*hexylamine with hydrogen sulphide and passing air through the mixture until no further precipitate was obtained. Recrystallised from ethanol it gave white leaflets, m. p. 198° (decomp.) [Found: 0·9995 g. = 31·9 c.c. of 0·01N-iodine solution. $(C_6H_{11}{\cdot}NH_3)_2S_2O_3$ requires 31·8 c.c.].

3 : 5-*Dibenzyltetrahydro*-1-*thia*-3 : 5-*diazine*.—Methylenebenzylamine (5·0 g.) was dissolved in ethanol (50 c.c.), and formaldehyde (15 c.c. of a 40% solution) which had previously been saturated with hydrogen sulphide was added. A stream of hydrogen sulphide was passed in until the temperature rose to 25°. The solution became opaque after 15 minutes; it was set aside for 24 hours, and the crystals which separated were removed by filtration, and then recrystallised from ethanol in long needles, m. p. 92° (Found: C, 71·8; H, 7·05; N, 9·4, 9·5; S, 10·8. $C_{17}H_{20}N_2S$ requires C, 71·8; H, 7·0; N, 9·8; S, 11·0%). This 3 : 5-*dibenzyltetrahydro*-1-*thia*-3 : 5-*diazine* was dissolved in light petroleum, and the solution saturated with hydrogen chloride. The white *dihydrochloride* which separated was removed and crystallised from ethanol; it had m. p. 130—140° (decomp.) (Found: Cl, 20·1. $C_{17}H_{22}N_2Cl_2S$ requires Cl, 19·9%). When heated under reflux for 3 hours with concentrated hydrochloric acid, the parent substance (0·75 g.) gave trithioformaldehyde (0·1 g.).

Benzylamine Thiosulphate.—Benzylamine (10 g.) was dissolved in ethanol (40 c.c.), and the solution saturated with hydrogen sulphide. Air was passed through the mixture and *benzylamine thiosulphate* slowly separated in silvery leaflets (10 g.). These crystallised from ethanol in leaflets, m. p. 182° (decomp.) [Found: 0·9995 g. = 30·2 c.c. of 0·01N-iodine. $(C_6H_5{\cdot}CH_2{\cdot}NH_3)_2S_2O_3$ requires 30·3 c.c.].

Analyses were by Drs. Weiler and Strauss.

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