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THE REACTION OF AMMONIUM POLYSULPHIDE WITH BENZYLIDENE CHLORIDE AND SOME DERIVATIVES THEREOF

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Abstract—The reaction of ammonium polysulphide with benzylidene chloride and certain of its chloro, methoxy and methyl derivatives has been investigated. Benzylidene chloride, *p*-chlorobenzylidene chloride *p*-methoxybenzylidene chloride and *p*-methylbenzylidene chloride gave the corresponding thiobenzamides. *o*-Chlorobenzylidene chloride afforded bis-*o*-chlorobenzyl disulphide and under different conditions a polymer. 2,6-Dichlorobenzylidene chloride gave bis-2,6-dichlorobenzyl trisulphide.

FROMM and Schmoldt[1] obtained β-trithiobenzaldehyde along with a higher polymer[2] of thiobenzaldehyde by the action of sodium sulphide on benzylidene chloride. When sodium hydrogen sulphide was used, dibenzyl sulphide was obtained. It has now been found that when benzylidene chloride is heated with ammonium polysulphide in aqueous isopropanolic solution containing ammonia thiobenzamide is one of the products; the yield was variable and in the best experiment was 49%. A deep red oil insoluble in alcohol was another product and this may be similar to the polymeric material obtained by Wood and Bost[3] by the action of hydrogen sulphide on benzylidene chloride. Though thiobenzamide has been obtained from benzaldehyde, ammonia and sulphur by heating at 170–180° in a sealed tube,[4] this is the first observation of the preparation of thiobenzamide directly from benzylidene chloride. Thioamides are formed also from *p*-chloro, *p*-methoxy and *p*-methyl benzylidene chlorides though in poorer yields: 22%, 17% and 14% respectively. No thioamide was formed from *o*-chlorobenzylidene chloride. The products were a small amount of a crystalline solid along with a red oil. The crystalline product is found to have the empirical formula $C_{14}H_{11}Cl_2NS$, but in the mass spectrometer, it showed mass peaks up to mass 627 and so is a polymer which was not further investigated.

When the experiment with *o*-chlorobenzylidene chloride was performed using an excess of hydrogen sulphide (but not of ammonia), bis-*o*-chlorobenzyl disulphide was the only product and it was obtained in almost quantitative yield. When 2, 6-dichlorobenzylidene chloride was treated with ammonium polysulphide under similar conditions, a crystalline product was obtained also in quantitative yield. Analysis indicated the formula $C_{14}H_{10}Cl_4S_3$ and accordingly it is considered to be di-2,6-dichlorobenzyl trisulphide (I). This structure is also confirmed by the NMR spectrum taken in $CDCl_3$ which showed the presence of 6 aromatic protons (multiplets near τ 2·75) and 4

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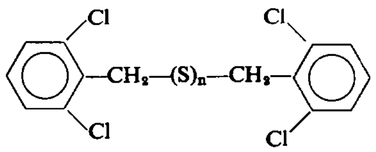
[1] E. Fromm and P. Schmoldt, *Ber. Dtsch. Chem. Ges.* **40**, 2869 (1901).

[2] E. Fromm and P. Schmoldt, *Ber. Dtsch. Chem. Ges.* **40**, 2861 (1907).

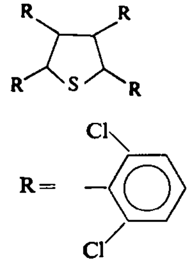
[3] J. H. Wood and R. W. Bost, *J. Amer. Chem. Soc.* **59**, 1011 (1937).

[4] D.R.P. 405675, *Chem. Z.* **1**, 1529 (1925).

aliphatic protons (singlet at τ 5·55). When this trisulphide was heated with copper powder with a view to convert it into a thiophene derivative, only the corresponding tetrahydro thiophene derivative (II) was obtained. The formation of an aromatic thiophene ring was probably prevented by steric hindrance. Also the attempted desulfurization of the trisulphide with hydrazine hydrate in alcohol yielded only the corresponding disulphide (III).



I n=3
III n=2



II

EXPERIMENTAL

Ammonium polysulphide solution was prepared freshly before use according to the directions given in the Organic Reactions.[5] All m.ps are uncorrected. Light petroleum refers to the fraction b.p. 60–80°.

Action of ammonium polysulphide on benzylidene chloride. A mixture of benzylidene chloride (10 g). ammonium polysulphide (25 ml), aqueous ammonia (25 ml, *d*, 0·88) and 2-propanol (50 ml) was left overnight at room temp and then refluxed with stirring for 4 hr. Most of the liquid was evaporated under red. press. and the residue was taken up in benzene and the solution washed with brine, dried over $MgSO_4$ and the benzene evaporated. The residue was crystallized from benzene–light petroleum to give *thiobenzamide*, m.p. 116–117° (4 g) agreeing with authentic thiobenzamide in its IR absorption spectrum.

p-*Chlorothiobenzamide.* A mixture of *p*-chlorobenzylidene chloride[6] (10 g), ammonium polysulphide (20 ml), aqueous ammonia (20 ml) and EtOH (100 ml) was left overnight at room temp and then refluxed with stirring for 4 hr. The alcohol was evaporated *in vacuo* and the residue recrystallized from water to give *p*-chlorothiobenzamide (2 g, 22%) as pale yellow plates, m.p. 130–131° (lit.[7] m.p. 131°).

p-*Methoxythiobenzamide.* A solution of *p*-methoxybenzylidene chloride[8] (10 g), ammonium polysulphide (30 ml), EtOH (50 ml) and ammonia (30 ml) was left at room temp for 60 hr and then heated under reflux for 7 hr. The solvent was evaporated *in vacuo* and the residue lixiviated with hot 25% aqueous alcohol (200 ml). The alcoholic extract on cooling gave a yellow solid which, on crystallization from benzene, gave the *thioamide* (1·6 g, 17%) as yellow needles, m.p. 149–151° (lit[7] m.p. 148–149°).

p-*Methylthiobenzamide.* A mixture of *p*-methylbenzylidene chloride[9] (15 g), ammonium polysulphide (45 ml), ammonia (45 ml) and EtOH (180 ml) treated as in the previous experiment, gave the *thioamide* (1·7 g, 14%) as lemon yellow plates from benzene, m.p. 166–168° (lit.[10] m.p. 168°).

Action of ammonium polysulphide on o-*chlorobenzylidene chloride.*

Isolation of the polymer. A solution of *o*-chlorobenzylidene chloride[11] (20 g) ammonium polysulphide (100 ml), 2-propanol (100 ml) and aqueous ammonia (75 ml) was left at room temp for 3

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[5] *Organic Reactions* Vol. III, p. 92.

[6] J. B. Shoesmith and R. H. Slater, *J. Chem. Soc.* 218 (1926).

[7] A. E. S. Fairfull, J. L. Lowe and D. A. Peak, *J. Chem. Soc.* 742 (1952).

[8] H. Schmidt, *Ber. Dtsch. Chem. Ges.* **41**, 2331 (1908).

[9] F. Azinger and G. Lock, *Monatsh.* **62**, 341 (1933).

[10] R. W. Bost and W. J. Mattox, *J. Amer. Chem. Soc.* **52**, 332 (1930).

[11] A. Erdman, *Liebig's Ann.* **272**, 151 (1893).

days and then heated under reflux for 4 hr. The solvent was evaporated *in vacuo* and the residue lixiviated with toluene. Evaporation of the toluene gave a sticky solid which after several recrystallizations from toluene yielded the polymer as thick prisms, m.p. 192–194°. (Found: 57·2; H, 3·7; Cl, 23·2; N, 5·0; S, 10·8; $C_{14}H_{11}Cl_2NS$ requires: C, 56·8; H, 3·7; Cl, 23·9; N, 4·7; S, 10·8%.) The mol wt could not be determined by Rast method, but in the mass spectrometer mass peaks up to 627 were found.

Isolation of bis-o-*chlorobenzyl disulphide*. A mixture of *o*-chlorobenzylidene chloride (10 g), ammonium polysulphide solution (60 ml) and 2-propanol (60 ml) was saturated at 0° with H_2S and the resulting solution was left at room temp overnight. The crystalline solid that separated was collected, washed with cold MeOH and recrystallized from MeOH to yield the *disulphide* as lustrous plates (7·8 g), m.p. 92–93°; lit[11] m.p. 87·5°. (Found: C, 53·4; H, 3·8; Cl, 22·3; S, 20·4. Calc. for $C_{14}H_{12}Cl_2S_2$: C, 53·3; H, 3·8; Cl, 22·4; S, 20·3%.)

Di-2,6-dichlorobenzyl trisulphide (I). A mixture of 2,6-dichlorobenzylidene chloride (5 g), ammonium polysulphide solution (15 ml), aqueous ammonia (15 ml) and EtOH (80 ml) was kept overnight at room temp and then refluxed for 16 hr. The liquid was evaporated *in vacuo*, and the residue crystallized from benzene to yield the *trisulphide* (3·4 g) as colourless fine needles, m.p. 175–176°. (Found: C, 40·8; H, 2·8; Cl, 33·4; S, 23·2. $C_{14}H_{10}Cl_4S_3$ requires: C, 40·4; H, 2·4; Cl, 34·1; S 23·1%.) When the mol wt was determined by the Rast method and by ebullioscopic method in benzene, it gave a mol wt of only 326, whereas the above formula requires a mol wt of 416. The compound gave in the mass spectrometer 3 peaks in the mol ion at m/e 414, 416 and 418 which correspond respectively to the presence of 0, 1 and 2 atoms of chlorine isotope ^{37}Cl which is a normal distribution in tetrachloro compounds. No explanation could be offered now for this apparent discrepancy.

Tetra-2,6-dichlorophenyltetrahydrothiophene (II). A mixture of the above trisulphide (10 g) and Cu-powder (20 g) was heated with stirring under N^2 at 180–200° for 3 hr.[12] The mixture was extracted with acetone and the solvent evaporated. The residue was crystallized from benzene–MeOH to yield the *tetrahydrothiophene* (2 g) as colourless needles, m.p. 115–117°. (Found: C, 50·3; H, 3·1; Cl, 41·9; S, 5·5. $C_{28}H_{16}Cl_8S$ requires: C, 50·3; H, 2·4; Cl, 42·4; S, 4·8%.)

Di-(2,6-dichloro) benzyl disulphide (III). A mixture of (6 g), hydrazine hydrate (18 ml) and EtOH (30 ml) was refluxed for 6 hr and the insoluble unchanged material was filtered off (1·7 g). From the filtrate on cooling, the *disulphide* was obtained as colourless needles (3 g) which was recrystallized from alcohol, m.p. 110–112°. (Found: C, 44·1; H, 2·8; Cl, 36·3; S, 16·0. $C_{14}H_{10}Cl_4S_2$ requires: C, 43·8; H, 2·6; Cl, 36·9; S, 16·7%.)

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[11] G. Speroni and G. Mannelli, *Gazz.* **70**, 472 (1940).

[12] L. B. Reynolds and J. A. Stanfield, *J. Amer. Chem. Soc.* **74**, 2878 (1952).