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WATSON, F.I.C., CHAIRMAN OF EDITORIAL BOARD.

I.—ACTION OF SULPHUR MONOCHLORIDE ON MERCAPTANS. PART II.[1]

Formation of Organic Trisulphides and Hexasulphides.

By P. P. Patel, I. Sengupta and G. C. Chakravarti.

The formation and structure of organic straight chain polysulphides as high as the pentasulphide have received considerable attention from several investigators and in most cases general methods have been elaborated for the preparation of such compounds. Spring and Demarteau (*Bull. Soc. Chim.*, 1889, iii, **I**, 314) obtained diethyl disulphide by the interaction of ethyl bromide or iodide and aqueous sodium polysulphides. This reaction was shown by Blanksma (*Rec. trav. chim.*, 1901, **20**, 121; *Proc. K. Akad. Wetensch., Amsterdam*, 1901, **3**, 81) to be a general one and he prepared several aliphatic and aromatic disulphides from the respective halides and sodium sulphide. He claims that tri- and tetrasulphides also can be obtained by treating the halides with sodium tri- and tetrasulphides; but the work of Thomas and Rule (*J.C.S.*, 1917, **111**, 1063) throws much doubt on the existence of alkali trisulphides themselves and in that case the organic trisulphides obtained by Blanksma have to be regarded as produced by degradation of higher polysulphides. Recently the preparation of pure anhydrous alkali tetra- and pentasulphides by Rule and Thomas (*J.C.S.*, 1914, **105**, 177, 2819) has enabled Thomas and Riding (*J.C.S.*, 1923, **123**, 3271; *ibid.*, 1924, **125**, 2214, 2460) to standardise methods for the synthesis and study of the organic pentasulphides; these authors are the first to prove by molecular weight determination in the case of the ethyl compound and by examining the tetra-iodo-derivative of the allyl compound, that these pentasulphides are definite entities and not solutions, or mixtures of the lower sulphides with sulphur.

Many workers have obtained organic polysulphides by different methods. Otto (*J. pr. Chem.*, 1888, ii, **37**, 211) claimed to have obtained phenyl tetrasulphide by the action of hydrogen sulphide on phenylsulphinic acid. Troeger and Hornung (*ibid*, 1899, ii, **60**, 133) prepared a few organic tri- and tetrasulphides by the action of sulphur dichloride and monochloride respectively on mercaptans in carbon disulphide solutions. Holmberg (*Annalen*, 1908, **359**, 81) obtained various polysulphides by the interaction of mercaptans and sulphur

[1] Part I appeared in the *Journal of the Chemical Society*, 1923, 123, 954.

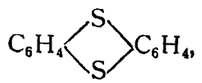
monochloride, sulphur dichloride, thionyl chloride, etc., but failed to obtain ethyl tetrasulphide from ethyl mercaptan and sulphur monochloride. Thomas and Riding (*loc. cit.*) also failed to obtain ethyl tetrasulphide, but Chakravarti (*J.C.S.*, 1923, **123**, 954) has shown that this can be obtained very easily by modifying Holmberg's method and he thus prepared several other organic tetrasulphides. Smythe and Aquila Forster (*J.C.S.*, 1910, **97**, 1195) have obtained benzyl di- and trisulphides by the slow action of sulphur dioxide on benzyl mercaptan, and benzyl tetrasulphide by the action of sulphur monochloride on the mercaptan in carbon tetrachloride solution.

Some polysulphides have been prepared by the action of sulphur on alkyl monosulphides (Muller, *J. pr. Chem.*, 1871, ii, **4**, 40; Klason, *ibid*, 1877, ii, **15**, 216) while Hinsberg (*Ber.*, 1910, **43**, 1874–79) states that disulphides when heated in a sealed tube to a high temperature give a mixture of mono- and trisulphides in the proportion required by the equation

$$2R_2S_2 = R_2S + R_2S_3.$$

Thomas and Riding (*loc. cit.*), however, in an extended investigation of these compounds, have found no evidence of such reactions.

Organic hexasulphides have not yet been recognised and no method is known by which they can be obtained. The only mention in the literature of a hexasulphide is by Onufrowicz (*Ber.*, 1890, **23**, 3370) who obtained an uncrystallisable solid by the action of sulphur monochloride on benzene containing a small quantity of iodine, and which on analysis corresponded to diphenyl hexasulphide; as it could not be purified, it may be a mixture of many substances and the sulphur might have attacked two or more points in the benzene nucleus. The behaviour of sulphur monochloride towards aromatic hydrocarbons in presence of the aluminium-mercury couple has already been investigated by Cohen and Skirrow (*J.C.S.*, 1899, **75**, 887) who obtained diphenylene-disulphide,



from benzene.

The present work aimed at investigating the action of sulphur monochloride on mercaptans in a suitable solvent, thus in the first instance repeating Holmberg's work in a modified way. While in progress, it was observed that, although tetrasulphides in general could be obtained by Troeger and Hornung's method in carbon disulphide, and also by Smythe and Forster's modification replacing carbon disulphide by carbon tetrachloride, the action takes an altogether different

course if conducted in boiling anhydrous benzene. In experiments to be presently described, sulphur monochloride, while reacting with different mercaptans in anhydrous benzene, has given the trisulphides associated with small quantities of thick oils which in several cases were separated pure by following the method of Thomas and Riding (*loc. cit.*) applied to pentasulphides. From analysis, they appear to be the hexasulphides, and the only possibility of their being liquid pentasulphides containing sulphur in solution or pseudo-solution is precluded by the fact that most of the aromatic compounds solidify in a freezing mixture whereas dibenzyl pentasulphide prepared by Thomas and Riding (*loc. cit.*) is a liquid even at —80°. Moreover, the individuality of these purified hexasulphides was tested by separating them into two or more different fractions by suitable solvents and estimating sulphur in each. There can be therefore no doubt that these hexasulphides are definite entities.

Reactions involved in the process may be represented by the following equations:—

$$2\ R{\cdot}SH + S_2Cl_2 = (RS)_2S : S + 2\ HCl \qquad (I)$$

$$(RS)_2S : S = R\,S{\cdot}S{\cdot}SR + S \qquad (II)$$

$$2\ R{\cdot}SH + S_2Cl_2 = (RS.S)_2 + 2\ HCl \qquad (III)$$

$$(RS{\cdot}S)_2 + 2S = (RS.S)_2\,S_2 \qquad (IV)$$

R being C_2H_5, $CH_3{\cdot}C_6H_4$, $C_6H_5{\cdot}CH_2$, BrC_6H_4, C_6H_5, etc.

These reactions are explained on the assumption that sulphur monochloride acts simultaneously in the forms,

$$ClS{\cdot}SCl\ (a)$$
$$Cl_2S{:}S\ \ (b).$$

in equilibrium under experimental conditions, an assumption which is not arbitrary. In studying the action of sulphur monochloride on unsaturated hydrocarbons, Guthrie (*Quart. Jour. Chem. Soc.*, 1860, **12**, 116; 1861, **13**, 134; *Annalen*, 1861, **119**, 91; 1862, **121**, 110), Pope (*J. Soc. Chem. Ind.*, 1919, **38**, 469 R), Green (*ibid*, 469 R) Conant, Hartshorn and Richardson (*J. Amer. Chem. Soc.*, 1920, **42**, 585), Gibson and Pope (*J. C. S.*, 1920, **117**, 271) and Mann, Pope and Vernon (*ibid*, 1921, **119**, 634) found that sulphur monochloride reacts with ethylene in the form (*b*):—

$$2\ CH_2{:}CH_2 + S_2Cl_2 \begin{cases} \nearrow (CH_2Cl{\cdot}CH_2)_2\ S : S. \\ \searrow (CH_2Cl{\cdot}CH_2)_2\ S + S. \end{cases}$$

However, the recent study by Naik and his co-workers (Naik, *J. C. S.*, 1921, **119**, 379, 1231; 1922, **121**, 2592: Naik and Bhatt,

J. Indian Chem. Soc., 1927, **4**, 525) of sulphur monochloride acting on methylene groups, indicates attack in the form (*a*) for dithioketones; the dithio-ethers produced are so stable that they can be nitrated to tetranitro-derivatives by fuming nitric acid. Benzyl tetrasulphide obtained by Smythe and Forster (*loc. cit.*) and many tetrasulphides obtained by Chakravarti (*loc. cit.*) and other workers are remarkably stable and should more properly be represented as $(RS{\cdot}S)_2$. Thus it seems that whether sulphur monochloride reacts in one form or the other, or in both simultaneously, depends on the class of compounds with which it combines and on the experimental conditions.

In the present case sulphur monochloride in its dual capacity produces tetrasulphides as represented in equations I and III. The tetrasulphide formed in I is decomposed at the temperature of boiling benzene into the trisulphide and sulphur as represented in II. This sulphur in its nascent state combines according to IV with the stable tetrasulphide formed in III to yield the hexasulphide. Such a conversion of lower sulphides into polysulphides by the absorption of sulphur is not unusual (Cf. Muller, *loc. cit.*; Klason, *loc cit.*). The formation of $\beta\beta$-dichloro-diethyl tri- and pentasulphides from sulphur monochloride and ethylene observed by Conant, Hartshorn and Richardson (*loc. cit.*), also must be due to action of this type.

Moreover, the above explanation is established by the larger quantities of trisulphides obtained, as required by the equations, and also by the detection of di-β-naphthyl tetrasulphide formed in the case of β-naphthyl mercaptan, when the absorption of sulphur according to equation IV is very slow. It is interesting to note in this connection that Thomas and Riding (*loc. cit.*) could not find any appreciable change in a mixture of β-naphthyl halide and anhydrous potassium pentasulphide, even after more than three months. Probably such highly retarded action is characteristic of the naphthalene ring.

The only general and suitable method known for preparing open chain organic trisulphides is the one by Troeger and Hornung (*loc. cit.*), in which sulphur dichloride acts on the mercaptan thus

$$2R{\cdot}SH + SCl_2 = RS{\cdot}S{\cdot}SR + 2HCl;$$

but general opinion does not altogether favour the individuality of sulphur dichloride, as the following passage from Fritz Ephraim (*Inorganic Chemistry*, 1926, page 499) indicates.

"A chlorination product of the formula SCl_2 intermediate between SCl_4 and S_2Cl_2 was formerly supposed to exist, because liquids of that composition had a much browner colour than S_2Cl_2 and SCl_4. If, however, S_2Cl_2 is gradually saturated with chlorine, the solutions

formed have properties which change continuously with variation in their chlorine content; when represented graphically, they show no break or transition point at the composition SCl_2. Thus the m.p. curve only shows maxima at the compositions SCl_4 and S_2Cl_2 and the chlorine content of the vapour rises quite regularly with increase in the chlorine content of the liquid."

Holmberg (*loc. cit.*), however, states that the compounds described as trisulphides by Troeger and Hornung are possibly equivalent mixtures of di- and tetrasulphides, for an undistilled portion of the oil, on analysis, gave the results for the trisulphide; but this is untenable, because these authors give for the trisulphides sharp melting points closely approximating to those of the trisulphides obtained in the present case. A second convenient method for preparing trisulphides is already mentioned, and appears to be the first observation in which sulphur monochloride reacting with mercaptans can form trisulphides in general. A third and perhaps the most convenient method for preparing organic trisulphides was discovered while acting with excess of sulphur on various copper mercaptides; preparation of organic trisulphides by this method also forms a part of the present work.

The method is again a modification of Holmberg's method in which he heated sodium and potassium mercaptides with sulphur, obtaining disulphides. If, however, a dry copper mercaptide is heated for 9 to 10 hours in boiling benzene, with flowers of sulphur slightly in excess, black precipitates of copper sulphide settle, while the filtered solution gives the trisulphide in good yield. The process appears to be quite simple; the mercaptide loses copper which combines with sulphur to form copper sulphide, while the radicles which otherwise would have combined to yield the disulphide, take up an atom of sulphur from its excess and form the trisulphide thus:

$$(RS)_2Cu + 2S = RS{\cdot}S{\cdot}SR + CuS.$$

This observation is important and interesting as offering strong evidence for the existence of radicles containing monovalent sulphur atoms. The work of Lecher (*Ber.*, 1915, **48**, 524; 1920, **53**, 577) may be recalled in this connection. Lecher's assumption is based on the indirect evidence that certain sulphides when heated show colorations differing from those of the ordinary solutions of the sulphides, whereas in the present instance the formation of the trisulphides cannot be explained on any other basis than that the free monovalent sulphur radicles take up molecular sulphur thus:

$$(RS)_2Cu + S = 2(RS—) + CuS;\ 2(RS—) + S = RS{\cdot}S{\cdot}SR.$$

That the trisulphide is not the product of sulphur absorption by the disulphide, if formed, was shown by an experiment with sulphur

and a disulphide, all other conditions remaining the same; after the notified period the disulphide was recovered unchanged. The only alternative explanation of trisulphide formation through decomposition of the disulphide into an equivalent mixture of mono- and trisulphides, as observed by Hinsberg (*loc. cit.*), does not hold because in no case was the monosulphide obtained.

EXPERIMENTAL.

Sulphur monochloride was purified by distillation in absence of moisture from a mixture of sulphur flowers and highly absorbent charcoal.

Interaction of p-*Tolyl Mercaptan and Sulphur Monochloride: Formation of Ditolyl Trisulphide.*

Sulphur monochloride (3 g.) in anhydrous benzene (50 c.c.) was added to *p*-tolyl mercaptan (5·5 g.) also dissolved in about 50 c.c. of benzene and left under a condenser with a guard tube. A vigorous reaction ensued with evolution of hydrogen chloride, and when it had subsided, the mixture was heated under reflux for about half an hour by which time the evolution of hydrogen chloride stopped. The benzene was distilled and the oily residue subjected to steam distillation which removed excess of mercaptan and also the disulphide. The semi-solid mass obtained on cooling was separated from water and extracted repeatedly with hot glacial acetic acid which on cooling deposited an oil followed gradually by crystals. The decanted liquid gave crystals and the first precipitate of oil on standing overnight set to a pasty semi-solid mass, which also gave crystals on a porous tile. Both products were recrystallised twice from acetic acid, absolute alcohol also being applicable. Ditolyl trisulphide formed minute colourless plates melting at 82–83°; Troeger and Hornung (*loc. cit.*) gave 76–77°, while Holmberg, who prepared it by the action of thionyl aniline on *p*-tolyl mercaptan, found 81–82° (Found: C, 60·01; H, 5·75; S, 34·96. $C_{14}H_{14}S_3$ requires C, 60·43; H, 5·04; S, 34·53 per cent.).

Ditolyl trisulphide is extremely soluble in benzene, ether, chloroform and ligroin; it is also soluble in hot alcohol. Attempts to obtain double compounds with various metallic halides were fruitless.

Ditolyl Hexasulphide.—After repeated extraction with acetic acid the semi-solid mass was further extracted five times with boiling absolute alcohol to remove lower polysulphides, when a homogenous yellowish oil was obtained. This oil (about 1 g.) was mixed with light petroleum (150 c.c., b.p. 40–60°) and kept in a closed vessel for

a week, to precipitate free sulphur as described by Thomas and Riding with pentasulphides. The solution was then filtered from a small quantity of precipitated sulphur and the solvent removed, the residual oil being kept in an evacuated vessel over phosphoric oxide for 4–5 days and then analysed.

When estimating sulphur by Carius' method in compounds containing a very high percentage, low results are generally obtained due to the formation of sulphonic acids, the nitric acid alone being incapable of oxidising all sulphur to sulphuric acid; hence the fusion method is usually adopted. If, however, a few drops of bromine are added to the nitric acid, equally satisfactory results are obtained and much time is saved; all sulphur estimations of higher polysulphides in the present work were made by this method (Found: S, 50·4. $C_{14}H_{14}S_6$ requires S, 51·0 per cent.). The oil was then separated into two fractions by extractions with hot alcohol, and the higher fraction purified as above (Found: S, 50·8 per cent.).

Di-*p*-tolyl hexasulphide is a thick, yellowish brown, mobile oil having the faint but persistent disagreeable odour characteristic of polysulphides. It is soluble in cold petrol, but very sparingly in boiling absolute alcohol. When shaken in petrol solution with electrolytic copper or mercury, it readily begins to form black precipitates of metallic sulphides. With piperidine it gives a reddish-brown coloration which disappears on acidification, indicating an additive compound of this base. A sample of the ditolyl hexasulphide after six months seemed to contain a solid lower sulphide as a result of decomposition.

Interaction of Copper p-*Tolyl Mercaptide with Sulphur: Formation of Ditolyl Trisulphide.*

The powdered mercaptide (3 g.) was suspended in dry benzene (50 c.c.) and boiled under reflux for 9 to 10 hours with excess of pure powdered sulphur (0·7 g.). The black copper sulphide which slowly separated was filtered and the benzene removed by distillation; the thick yellow oil remaining was extracted with hot alcohol which on cooling deposited colourless plates of ditolyl trisulphide melting at 82–83° after recrystallisation from alcohol. It is identical with the trisulphide obtained from *p*-tolyl mercaptan and sulphur monochloride, and was not accompanied by the monosulphide.

Interaction of p-*Bromophenyl Mercaptan and Sulphur Monochloride: Formation of* pp'-*Dibromodiphenyl Trisulphide.*

p-Bromophenyl mercaptan (7·5 g.) dissolved in 50 c.c. of dry benzene was treated with 20 c.c. of dry benzene containing sulphur

monochloride (2·5 g.). The reaction proceeded as in the case of *p*-tolyl mercaptan with evolution of hydrogen chloride the mixture being then heated under reflux and well protected from moisture for about an hour to complete the reaction. Benzene was distilled and the crude oily product extracted six or seven times with warm alcohol. The concentrated extracts on cooling gave yellow crystals which on recrystallisation from alcohol formed pale yellow prismatic plates, m.p. 69°. (Found: S, 24·75; Br, 38·32; C_{12} H_8 Br_2 S_3 requires S, 23·53; Br, 39·21 per cent.).

pp'-*Dibromo-diphenyl Trisulphide* does not seem to have been described; it is soluble in all ordinary solvents and can be best crystallised from petrol (b. p. 40–60°).

pp'-*Dibromo-diphenyl Hexasulphide.*—The residual oil after extraction in the previous experiment was extracted again two or three times, dried and kept dissolved in petrol in a closed vessel for a week when the pure hexasulphide separated as in the previous case. (Found: S, 39·13. $C_{12}H_8Br_2S_6$ requires S, 38·1 per cent.). It is slightly deeper in colour than the *p*-tolyl compound and solidifies on cooling in ice, being a deep brown heavy oil at the ordinary temperature.

Interaction of p-*Iodophenyl Mercaptan and Sulphur Monochloride: Formation of* pp'-*Diiododiphenyl Trisulphide.*

Iodophenyl mercaptan (4·7 g.) in 50 c.c. of dry benzene was added to 14 c.c. of a 10 per cent solution of sulphur monochloride in benzene and the reaction carried out exactly as before, the solution becoming much coloured, probably on account of the liberation of iodine. The pasty mass left on evaporation of benzene was extracted with alcohol from which the *pp'*-diiododiphenyl trisulphide was obtained by fractional crystallisation; it is very unstable and becomes brown owing to separation of iodine. The freshly prepared substance, after repeated crystallisation from alcohol, forms yellow leaflets, m.p. 91° (Found: S, 19·12; I, 49·81. C_{12} H_8 I_2 S_3 requires S, 19·12; I, 50·65 per cent.). pp'-*Diiododiphenyl trisulphide* also has not been described. The hexasulphide is naturally expected to be very unstable and could not be obtained pure.

Interaction of Benzyl Mercaptan and Sulphur Monochloride: Formation of Dibenzyl Trisulphide.

Benzyl mercaptan (6 g.) diluted with dry benzene (30 c.c) was treated under reflux with sulphur monochloride (2·8 g.) diluted with 20 c.c. of dry benzene. When evolution of hydrogen chloride had ceased,

benzene was distilled and the residual oil extracted with small quantities of alcohol which on concentration and cooling in ice deposited oily drops. These, when rubbed with alcohol, gave a solid forming minute white plates, m.p. 47–48°, on crystallisation from alcohol (Found: S, 34·42. $C_{14}H_{14}S_3$ requires S, 34·53 per cent.).

Dibenzyl trisulphide has been obtained by Smythe and Forster (*loc. cit.*) by the action of sulphur dioxide on benzyl mercaptan; they give 49° as the m.p.

Dibenzyl Hexasulphide.—The oil, after removing the trisulphide, was further extracted with hot alcohol, dried and dissolved in a large volume of petrol as before. After about a week the solvent was distilled and the oil thoroughly dried in vacuum over phosphoric oxide (Found: S, 51·77. $C_{14}H_{14}S_6$ requires S, 51·00 per cent.)

Dibenzyl hexasulphide is a faint yellow, highly refractive oil and is more stable than *p*-tolyl compound; it solidifies in a freezing mixture although dibenzyl pentasulphide obtained by Thomas and Riding (*loc. cit.*) does not solidify at —80°. Dibenzyl hexasulphide also gives with piperidine a coloration which is destroyed by acid.

Interaction of Copper Benzyl Mercaptide and Sulphur: Formation of Dibenzyl Trisulphide.

By heating together sulphur (0·5 g.) and copper benzyl mercaptide (2·3 g.) in 60 c.c. of anhydrous benzene under reflux for ten to eleven hours, an oily mass was obtained, which on cooling solidified and formed white plates, m. p. 48°, when recrystallised from alcohol. It is identical with the specimen from sulphur monochloride and benzyl mercaptan, and is not accompanied by monosulphide.

Reaction between Phenyl Mercaptan and Sulphur Monochloride.

Phenyl mercaptan (10 g.) diluted with 30 c.c. of dry benzene was treated with sulphur monochloride (3 g.) dissolved in 20 c.c. of dry benzene; when evolution of hydrogen chloride had ceased, benzene was removed and the product steam distilled. Half of the residual oil, freed from sulphur, was separated into two fractions (1) soluble in alcohol, (2) insoluble in alcohol, by repeated fractional precipitation (1. Found: S, 43·3. $C_{12}H_{10}S_3$ requires S, 38·4: per cent. 2. Found, S, 52·0. $C_{12}H_{10}S_6$ requires S, 55·5 per cent.).

Thus the ordinary method of fractional precipitation did not succeed in this case, each sulphide appearing to be contaminated with

some of the other. The second half of the residual oil was therefore distilled under 30 mm. pressure, most of the distillate being collected at 240–260° and leaving a mass resembling pasty sulphur. The fluid distillate contained a solid which was filtered at the pump and crystallised from alcohol, when it melted at 60° and was found to be *p*-diphenyl disulphide. The liquid distillate appeared to be the trisulphide. It can be said that a higher sulphide was formed during the reaction, but on distillation decomposed to the lower sulphides including the disulphide (cf. Thomas and Riding, *loc. cit.*). This reaction is the only one in the aromatic series giving rise to the tri- and hexasulphides, both of which are liquids; hence the failure in complete separation and purification of the two.

Reaction between β-Naphthyl Mercaptan and Sulphur Monochloride: Formation of ββ′-Dinaphthyl Trisulphide.

The reaction of β-naphthyl mercaptan, (7 g.) and sulphur monochloride (3 g.) was conducted in benzene under the conditions previously described. Benzene was removed, and after steam distillation the oily product extracted several times with alcohol. On concentrating and cooling the collected extracts, the white flocculent solid was recrystallised from absolute alcohol and separated into two fractions, the less soluble being again crystallised and melting at 99°. This is the ββ′-dinaphthyl tetrasulphide of Troeger and Hornung (*loc. cit.*). The second fraction on recrystallisation from alcohol gave m.p. 107–108° (Found: S, 27·68. $C_{20}H_{14}S_3$ requires S, 27·43 per cent.). In this case the sulphides being solids, separation was extremely difficult, and a sample of the hexasulphide suitable for analysis could not be obtained.

Copper β-Naphthyl Mercaptide and Sulphur.—The reaction took place as in the case of *p*-tolyl mercaptide and the product was ββ′-dinaphthyl trisulphide melting at 107–108°.

Di-ββ′-naphthyl Disulphide and Sulphur.—This experiment was designed to show whether the trisulphide is formed on absorption of sulphur by the disulphide (see introduction). Di-ββ′-naphthyl disulphide (2·5 g.), m.p. 139°, and 50 c.c. of dry benzene containing 1 gram (4 atoms) of sulphur were heated under reflux for 10 to 12 hours, almost all the disulphide being recovered unchanged.

Interaction of Ethyl Mercaptan and Sulphur Monochloride. Formation of Diethyl Trisulphide.

Ethyl mercaptan (12·4 g.) was mixed with anhydrous benzene (50 c.c.), cooled with ice water and a well cooled solution of sulphur monochloride (13·5 g.) in dry benzene gradually added with shaking. When the evolution of hydrogen chloride ceased after heating the mixture finally on water bath, the solvent was distilled and the oily liquid, with a strong odour of garlic, steam distilled. Unchanged mercaptan and the disulphide came over rapidly; the first portion of the distillate containing these substances was rejected and the oil which volatilized extremely slowly with steam was collected with ether; after drying and removing the solvent a clear reddish brown oil remained. This was freed from the last traces of ether over phosphoric oxide in an evacuated desiccator (Found: S, 62·5. $C_4H_{10}S_3$ requires S, 62·34 per cent.).

Diethyl Hexasulphide.—The brown residue from steam distillation was again subjected to a rapid current of steam for one full day, yielding a few oily drops, the residue being treated with ether which left pasty sulphur. The solution having been dried and evaporated, the hexasulphide was dissolved in a large volume of petrol and kept for a week in a closed vessel; the petrol was filtered and distilled, leaving a reddish brown oil of penetrating odour. (Found: S, 76·7. $C_4H_{10}S_6$ requires S, 76·8 per cent.). Diethyl hexasulphide slowly decomposes on prolonged steam distillation or long standing (6 months).

Propyl Mercaptan and Sulphur Monochloride: Formation of Dipropyl Trisulphide.

The reaction was conducted as in preparing the ethyl compound; after distillation in steam and fractionation, a clear yellowish mobile liquid was obtained (Found: S, 52·92. $C_6H_{14}S_3$ requires S, 52·74 per cent.) The residue was found chiefly to consist of sulphur showing that the hexasulphide was decomposed.

n-*Butyl Mercaptan and Sulphur Monochloride: Formation of Di-n-butyl Trisulphide.*

The reaction was conducted as before, yielding a clear yellow oil (Found: S, 45·23. $C_8H_{18}S_3$ requires S, 45·71 per cent.). The residue in the flask was further steam-distilled for some time and extracted with ether, the dry oil from which was dissolved in petrol; after several days, the filtered solution was evaporated and the pure oil analysed (Found: S, 55·83. $C_8H_{18}S_4$ and $C_8H_{18}S_6$ require S, 52·5 and 62·3 per cent., respectively). It is therefore probably a mixture of the tetra- and hexasulphides; on standing for three days solid sulphur appeared.

SUMMARY.

The organic open chain hexasulphides are a distinct class of compounds which can be obtained conveniently by the action of sulphur monochloride on mercaptans, trisulphides in considerable quantity being simultaneously produced.

Sulphur dichloride of doubtful composition thus need not be used for preparing the trisulphides.

Another most convenient method for the synthesis of these trisulphides is the action of sulphur on copper mercaptides.

The last observation is strong evidence in favour of the existence free radicles containing monovalent sulphur.

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[Accepted, 11-3-30]

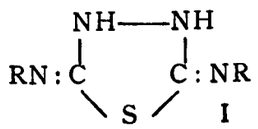
II.—ACTION OF SULPHUR MONOCHLORIDE ON MERCAPTANS. PART III.

OXIDATION OF UNSYMMETRICALLY SUBSTITUTED HYDRAZODITHIODICARBONAMIDES TO THIODIAZOLES.

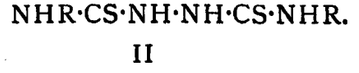
By P. P. Patel and G. C. Chakravarti.

Having discussed in the previous communication, the action of sulphur monochloride on mercaptans, it seemed interesting to ascertain its effect on 'potential' mercaptans. Chakravarti (*J. C. S.*, 1923, **123**, 964) stated that sulphur monochloride is capable of distinguishing real mercaptans from potential mercaptans, thus attributing to it a property resembling that ascribed to chloropicrin by Rây and Das (*J. C. S.*, 1922, **121**, 323). Chakravarti's view was based on the partial or complete separation of sulphur when potential mercaptans react with sulphur monochloride, no separation occurring in the case of real mercaptans; he acted upon potential mercaptans, e.g., thiobenzoic acid and thiocarbanilide with sulphur monochloride and in some cases identified the products.

A typical class of potential mercaptans was chosen, for besides the confirmation of the rule observed by Chakravarti, an interesting condensation giving rise to more definite products was anticipated. It is well known that 4-substituted thiosemicarbazides of the general formula, $NHR{\cdot}CS{\cdot}NH{\cdot}NH_2$, like thiocarbamides, in their aqueous or alcoholic alkaline solutions react in the tautomeric form, $NHR{\cdot}C(SH):N{\cdot}NH_2$, or $NR:C(SH){\cdot}NH{\cdot}NH_2$, and for this the work of Guha and Sen (*J. Indian Chem. Soc.* 1927, **4**, 43) bears ample evidence. When, therefore, sulphur monochloride is allowed to react, at low temperatures, with such tautomeric forms of 4-substituted thiosemicarbazides condensation takes place and generally thiodiazoles (I) are formed along with small quantities of the corresponding hydrazodithiodicarbonamide derivatives (II):

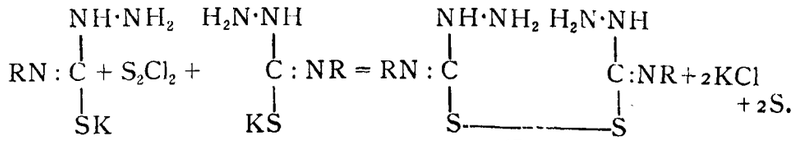


I



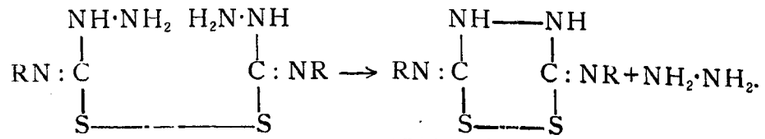
II

potassium salt of the thiosemicarbazide at the mercaptanic groups, with liberation of potassium chloride and formation of an intermediate disulphide (not isolated) thus :—



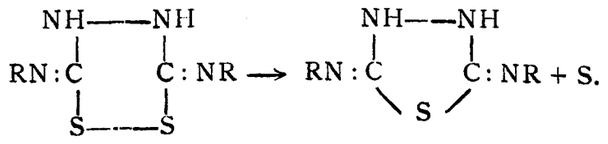
(Intermediate disulphide.)

The disulphide then, under the conditions suitable for ring closure, is converted into another intermediate compound (a dithio-ring structure) with elimination of hydrazine as follows :—



(Dithio-ring compound.)

The dithio-ring compound, like disulphides with adjacent double bonds, decomposes with separation of sulphur (Cf. From, Layer and Ners, *Annalen*, 1923, **433**, 1) to yield the thiodiazole (I) thus :—



The formation of the hydrazodithiodicarbonamide derivative (II) follows the partial decomposition of the thiosemicarbazide into hydrazine and mustard oil. While preparing the potassium derivative of the thiosemicarbazide by adding the latter to the calculated quantity of absolute alcoholic potash, a certain amount of water is formed as under :—

$$NR:C(SH)\cdot NH\cdot NH_2 + KOH = NR:C(SK)\cdot NH\cdot NH_2 + H_2O.$$

The water thus formed reacts partially with sulphur monochloride used in the reaction and produces hydrogen chloride, which even at ordinary temperature can decompose such thiosemicarbazides into hydrazine and the corresponding mustard oil, the latter uniting with unchanged thiosemicarbazide to produce (II) :—

$$NR:C:S + NH_2\cdot NH\cdot CS\cdot NHR = NHR\cdot CS\cdot NH\cdot NH\cdot CS\cdot NHR.$$

We have substantial evidences in support of the above mechanism. Firstly, the formation of mustard oil has been observed, and secondly, the yield of II varies directly with the temperature of the reaction, within certain limitations. In a freezing mixture of ice and salt, the formation of II was altogether checked, the only product being I, while at room-temperature, II was the only product. Moreover, in every experiment at low temperatures, the mustard oil was found to have been formed. These observations show that when the temperature is sufficiently low, though slight decomposition into the mustard oil and hydrazine takes place, reaction of the mustard oil with the thiosemicarbazide does not occur, but that at comparatively higher temperatures decomposition proceeds to the formation of II.

That hydrochloric acid is responsible for changing the thiosemicarbazide to the hydrazodithiodicarbonamide derivative was confirmed by an independent experiment. When a small quantity of 4-phenylthiosemicarbazide was heated for a short time with dilute alcoholic hydrochloric acid solution, sparingly soluble *Sym*-diphenylhydrazodithiodicarbonamide was precipitated. In this connection it should be pointed out that the conclusion of Pulvermacher (*Ber.*, 1893, **26**, 2812 ; *ibid*, 1894, **27**, 613) that phenylthiocarbamide is formed by the action of hydrogen chloride on 4-phenylthiosemicarbazide, seems doubtful.

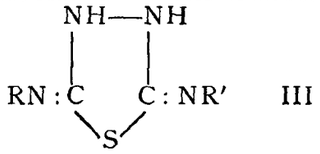
The action of sulphur monochloride on 4-phenyl, 4-*p*-tolyl- and 4-*o*-tolylthiosemicarbazides has been studied and the products described. With 4-phenylthiosemicarbazide under different conditions interesting results were not obtained. On slowly adding the agent in chloroform to a solution of 4-phenylthiosemicarbazide in the same solvent probably an unstable double compound was formed, giving sulphur and phenyl thiosemicarbazide hydrochloride on treatment with alcohol or water. A very small quantity of *Sym*-diphenylhydrazodithiodicarbonamide also separated.

The reaction with disubstituted thiosemicarbazides was also tried, but with little success. When sulphur monochloride in benzene was added to the tautomeric form of 1:4-phenyl-*p*-tolylthiosemicarbazide (stable, m.p. 176°), obtained by dissolving the thiosemicarbazide in a calculated quantity of potash, much decomposition occurred with formation of tar. If the reaction was conducted in chloroform without alcoholic potash, copious fumes of hydrogen chloride were evolved and the only product was a snuff coloured amorphous substance (of a high indefinite m.p.) precipitated by xylene from the pyridine solution of the crude product.

From 1:4-diphenylthiosemicarbazide an amorphous product free from sulphur, m.p. above 200° and having nitrogen 17·6 per cent, was

obtained by carrying out the reaction under similar conditions. Thus with 1 : 4-disubstituted thiosemicarbazides, unlike 4-monosubstituted, the reaction is complicated and the amorphous products may not even be ring compounds, but open chain compounds of very high molecular weight, as shown by their high melting points. The diminished basicity of 1 : 4-disubstituted thiosemicarbazides having a negative group like phenyl in the 1-position may be responsible for preventing ring closure (cf. Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502).

Unsymmetrical thiodiazoles of structure,



however, are not known : it appeared likely that these might also be obtained by the action of mild oxidising agents on dissimilarly substitued hydrazodithiodicarbonamides of the general formula, NHR·CS·NH·NH·CS·NHR′. Only one such carbonamide has been prepared by From, Soffner and Frey (*Annalen*, 1923, **434**, 285). In the course of this investigation several similar derivatives have been prepared and converted into thiodiazoles of the general formula III, by the action of iodine ; these, like I and II, also form diacetyl derivatives. During study of this reaction it was observed that boiling pyridine converts all 1, 6-disubstituted hydrazodithiodicarbonamides into the corresponding thiodiazoles.

EXPERIMENTAL

Interaction of the Potassium Derivative of 4-Phenylthiosemicarbazide and Sulphur Monochloride. Formation of 2 : 5-Diphenyldiimino-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole and Sym-Diphenylhydrazodithiodicarbonamide.

4-Phenylthiosemicarbazide (6 g.) was dissolved in 25 c.c. of absolute alcoholic potash containing 8·036 g. per 100 c.c. and while stirred a solution of sulphur monochloride (3 g.) in 25 c.c. of dry benzene was gradually added ; an orange colour changing to yellowish white developed. Stirring was continued for 15 minutes more and the liquid filtered through a fluted paper was pink. The residue was washed on the paper three times with hot absolute alcohol and the collected filtrates concentrated to one-third yielded on cooling a small amount of solid ; on crystallisation from boiling alcohol or pyridine diluted with water it melted at 184° with effervescence (Found: C, 55·58 ; H, 4·45 ; N, 19·27 ; S, 21·16. $C_{14}H_{14}N_4S_2$ requires C, 56·00 ;

H, 4·00 ; N, 18·66 ; S, 21·33 per cent.). The compound is easily soluble in dilute alkalis and readily loses sulphur when treated with iodine in a suitable solvent ; it is identical with *Sym*-diphenylhydrazodithiodicarbonamide.

The mother liquor was further concentrated and cooled, yielding a solid which crystallised from alcohol or dilute acetone in lustrous plates, m.p. 247° (Found : C, 62·75 ; H, 4·21 ; N, 19·8 ; S, 12·2. $C_{14}H_{12}N_4S$ requires C, 62·70 ; H, 4·47 ; N, 20·8 ; S, 11·9 per cent.). The compound was identified with 2,5-diphenylimino-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4 : thiodiazole (Guha, *J. Amer. Chem. Soc.*, 1923, **45**, 1036) ; From, Layer and Nerz (*loc. cit.*), however, give 243° while Busch and Schmidt (*Ber.*, 1913, **46**, 2240) give 240° as the m.p. of the thiodiazole. The substance is soluble in hot alcohol, acetone, pyridine, but sparingly in ether and chloroform. The *diacetyl* derivative from acetic anhydride was crystallised from alcohol and melted at 225° (Found : N, 16·68. $C_{18}H_{16}O_2N_4S$ requires N, 16·00 per cent.).

4-p-Tolylthiosemicarbazide and Sulphur Monochloride.

4-*p*-Tolylthiosemicarbazide from *p*-tolyl mustard oil and hydrazine hydrate melts at 139–140° after several crystallisations from alcohol ; Guha and Ray (*J. Amer. Chem. Soc.*, 1925, **47**, 385) give 172°, while Busch and Ulmer (*Ber.*, 1902, **35**, 1744) obtaining it by an indirect method give 134–135°.

4-*p*-Tolylthiosemicarbazide (6·5 g.) was dissolved in 25 c.c. of the specified alcoholic potash and treated with sulphur monochloride (3 g.) in 25 c.c. of dry benzene ; *sym*-di-*p*-tolylhydrazodithiodicarbonamide was one of the products and melts at 198° with gas evolution (Found : N, 16·4 ; S, 19·0. $C_{16}H_{18}N_4S_2$ requires N, 17·0 ; S, 19·9 per cent.).

2 : 5-Di-*p*-tolyldi-imino-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole was separated from the above hydrazo-compound by the procedure adopted previously, and after crystallisation from alcohol melts at 248° (Found : N, 18·56 ; S, 10·98. $C_{16}H_{16}N_4S$ requires N, 18·91 ; S, 10·81 per cent.). The *diacetyl* derivative melts at 172° (Found : N, 15·25. $C_{20}H_{20}O_2N_4S$ requires N, 15·13 per cent.), but Guha (*loc. cit.*) gives 235°.

4-o-Tolylthiosemicarbazide and Sulphur Monochloride.

With 4-*o*-tolylthiosemicarbazide (m.p. 145°) the reaction gave two products which were separated as already described ; *sym*-Di-*o*-tolylhydrazodithiodicarbonamide melts at 175°, From, Soffner and Frey (*Annalen*, 1923, **434**, 285) giving 179° (Found : N, 17·3 ; S, 19·72. $C_{16}H_{18}N_4S_2$ requires N, 17·0 ; S, 19·9 per cent.). The second product,

2 : 5-di-*o*-tolyldi-imino-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, crystallises from alcohol and melts at 222°, and appears to be new (Found : N, 18·86 ; S, 10·25. $C_{16}H_{16}N_4S$ requires N, 18·91 ; S, 10·81 per cent.).

The *diacetyl* derivative crystallises from alcohol and melts at 257° (Found : N, 1505. $C_{20}H_{20}O_2N_4S$ requires N, 15·13 per cent.).

4-Phenylthiosemicarbazide and Sulphur Monochloride at varying Temperatures.

(*a*) *In a freezing mixture.*—A solution of 4-phenylthiosemicarbazide (6 g.) in 25 c.c. of the specified alcoholic potash was cooled in the freezing mixture while stirred, and a solution of sulphur monochloride (3 g.) in anhydrous benzene admitted drop by drop. When the reaction seemed completed, the pink solution was filtered from sulphur and potassium chloride. After washing the solid several times with alcohol the collected filtrates were concentrated and cooled in a freezing mixture, when a white solid separated and crystallised from alcohol in plates melting at 247° ; a second crop had the same m.p.

(*b*) At 27°.—An almost quantitative yield of *sym*-diphenylhydrazodithiodicarbonamide, m.p. 184°, was obtained without a trace of the thiodiazole.

Action of boiling Pyridine on sym-*Diphenylhydrazodithiodicarbonamide.*

The hydrazo-compound dissolved in boiling pyridine gave a clear solution which on cooling deposited much less solid than was originally taken, and was found to be unchanged substance. On cooling the mother liquor with ice nothing separated, but dilution with water gave a precipitate which, when recrystallised from alcohol, melted at 246° and was found to be 2 : 5-diphenyldiimino-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole.

4-Phenylthiosemicarbazide and Sulphur Monochloride in Chloroform.

4-Phenylthiosemicarbazide (16·7 g.) heated under reflux with 600 c.c. of dried chloroform gave an almost clear solution ; to this was added a solution of sulphur monochloride (6·75 g.) in 25 c.c. of dry chloroform, with shaking, and allowed to remain for some time with a calcium chloride guard-tube. The faint yellow solution was then filtered from about 9–10 grams of 4-phenylthiosemicarbazide hydrochloride, and after most of the solvent was distilled, there remained a thick oil smelling of phenyl mustard oil; treatment with ether gave *sym*-diphenylhydrazodithiodicarbonamide melting at 184°.

2 : 5-*Phenyl*-o-*tolyldiimino*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole.*

4-Phenylthiosemicarbazide and *o*-tolyl mustard oil (molecular proportion) in boiling alcohol gave 1 : 6-phenyl-*o*-tolylhydrazodithiodicarbonamide which, crystallised from dilute pyridine, melts at 179°. The oxidation was conducted according to the method of From, Layer and Nerz (*loc. cit.*), an alcoholic solution of iodine being added in small portions to 1 : 6-phenyl-*o*-tolylhydrazodithiodicarbonamide (7 g.) in 80 c.c. of 95 per cent. boiling alcohol under reflux. Addition of iodine was stopped when a permanently brown and almost clear solution was obtained. The filtrate from sulphur gave a copious white precipitate of the thiodiazole with caustic potash and this when crystallised from 95 per cent. alcohol melts at 200° (Found : N, 20·5. $C_{15}H_{14}N_4S$ requires N, 19·9 per cent.). The *diacetyl* derivative was crystallised from alcohol, m. p. 223° (Found : N, 15·92. $C_{19}H_{18}O_2N_4S$ requires N, 15·3 per cent.).

2 : 5-*Phenyl*-m-*tolyldiimino*-2 : 3 : 4 : 5-*tetra-hydro*-1 : 3 : 4-*thiodiazole.*

1 : 6-Phenyl-*m*-tolylhydrazodithiodicarbonamide prepared from 4-phenylthiosemicarbazide and *m*-tolyl mustard oil melts at 180°. The thiodiazole obtained from this by oxidation as described in the last case melts at 216°, when crystallised from alcohol (Found : N, 20·3. $C_{15}H_{14}N_4S$ requires N, 19·9 per cent.). The *diacetyl* derivative crystallised from alcohol melts at 177° (Found : N, 15·69. $C_{19}H_{18}O_2N_4S$ requires N, 15·3 per cent).

2 : 5-o-*Tolyl*-m-*tolyldiimino*-2 : 3 : 4 : 5-*tetrahydro* 1 : 3 : 4-*thiodiazole.*

1 : 6-*o*-Tolyl-*m*-tolylhydrazodithiodicarbonamide prepared from 4-*o*-tolylthiosemicarbazide and *m*-tolyl mustard oil melts at 166°. The thiodiazole obtained by oxidation melts at 190° when crystallised from alcohol ; the *diacetyl* derivative melts at 231° (Found : N, 14·75. $C_{20}H_{20}O_2N_4S$ requires N, 14·73 per cent.).

2 : 5-m-*Xylyl*-m-*tolyldiimino*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole.*

1 : 6-*m*-Xylyl-*m*-tolylhydrazodithiodicarbonamide prepared from 4-*m*-xylylthiosemicarbazide (m.p. 142°) and *m*-tolyl mustard oil melts at 161°. The thiodiazole obtained by oxidation melts at 190° ; the *diacetyl* derivative melts at 263° (Found : N, 13·93. $C_{21}H_{22}O_2N_4S$ requires N, 14·21 per cent.).

2 : 5-o-*Tolyl*-m-*xylyldiimino* 2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole.*

1 : 6-*o*-Tolyl-*m*-xylylhydrazodithiodicarbonamide obtained from 4-*o*-tolylthiosemicarbazide and *m*-xylyl mustard oil (b.p. 258°), melts at

164°. The thiodiazole crystallises from alcohol and melts at 205°; the *diacetyl derivative* melts at 224° (Found: N, 14.33. $C_{21}H_{22}O_2N_4S$ requires N, 14·21 per cent.).

2 : 5-*Phenyl*-m-*xylyldiimino*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole.*

1:6-Phenyl-*m*-xylylhydrazodithiodicarbonamide from 4-phenylthiosemicarbazide and *m*-xylyl mustard oil melts at 171°. The thiodiazole crystallised from alcohol melts at 189°; the *diacetyl derivative* crystallised from alcohol melts at 120° (Found: N, 14·73. $C_{20}H_{20}O_2N_4S$ requires N, 14·73 per cent.).

SUMMARY.

Interaction of sulphur monochloride and 4-substituted thiosemicarbazides gives thiodiazoles along with small quantities of hydrazodithiodicarbonamides.

Several new mixed hydrazodithiodicarbonamides have been prepared and oxidised to the corresponding thiodiazoles.

Pyridine has been found to act as a ring closing agent on hydrazodithiodicarbonamide and its derivatives.

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