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, **1**, 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.

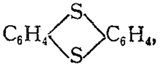
monochloride, sulphur dichloride, thionyl chloride, etc., but failed to obtain ethyl tetrasulphide from ethyl mercaptan and sulphur monochloride. Thomas and Riding (*loc. cit.*) also failed to obtain ethyl tetrasulphide, but Chakravarti (*J.C.S.*, 1923, **123**, 954) has shown that this can be obtained 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 :—

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

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

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

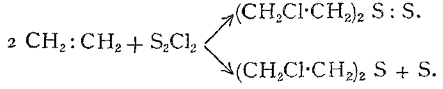
$$(RS{\cdot}S)_2 + 2S = (RS.S)_2\ S_2 \qquad (IV)$$

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 ββ-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:

$$(RS)_2\,Cu + S = 2\,(RS\text{—}) + CuS\,;\ 2\,(RS\text{—}) + S = RS{\cdot}S{\cdot}SR.$$

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; $C_{12}H_8Br_2S_3$ 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. $C_{12}H_8I_2S_3$ 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.

Departments of Organic Chemistry,
University College of Science & Technology,
Calcutta,
and
Indian Institute of Science,
Bangalore.

[Accepted, 11-3-30]