

**981.** *Thiocyanogen Trichloride. Part II.<sup>1</sup> Derived Dichlorothiocyanato-compounds, particularly from Alcohols and Amines, and Their Decomposition Products.*

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Further reactions of thiocyanogen trichloride are described and are interpreted as involving initial production of dichlorothiocyanato-derivatives:  $\text{ClS}\cdot\text{CCl}_2\text{NCl} \longrightarrow \text{XS}\cdot\text{CCl}_2\text{NCl}$ .<sup>\*</sup> The latter are frequently unstable and the products isolated may arise from their decomposition. Alcohols initially form dichlorothiocyanogen S-alkoxides ( $\text{X} = \text{OR}$ ), which lose cyanogen chloride, and this is converted into a carbamate,  $\text{NH}_2\cdot\text{CO}_2\text{R}$ , by excess of alcohol. Secondary amines give amine-*N*-dichlorothiocyanates ( $\text{X} = \text{NR}_2$ ), which decompose to amine-*N*-sulphenyl chlorides,  $\text{R}_2\text{N}\cdot\text{SCl}$ , and these are converted into thiobisamines,  $\text{R}_2\text{N}\cdot\text{S}\cdot\text{NR}_2$ , by reaction with more amine. Addition of thiocyanogen trichloride to ethylene occurs less readily than to cyclohexene, while addition to acetylene requires photo-initiation. Irradiation is also necessary to effect homolytic substitution by thiocyanogen trichloride in the methyl group of toluene, but benzyl dichlorothiocyanate was not obtained pure, either by this method or from thiocyanogen trichloride and benzylmagnesium chloride. The dichlorothiocyanato-group may be regarded as pseudohalide in type. Some related compounds are prepared, including bis(bromochlorothiocyanogen), an analogue of the bis(dichlorothiocyanogen) previously described.

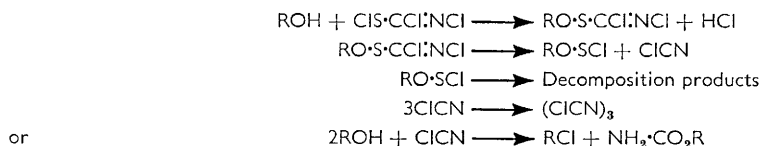
In an earlier paper<sup>1</sup> the structure  $\text{ClS}\cdot\text{CCl}_2\text{NCl}$  was assigned to thiocyanogen trichloride from chemical and infrared spectral evidence.<sup>\*</sup> Its resemblance to sulphenyl chlorides,  $\text{R}\cdot\text{SCl}$ , was exemplified by its addition to cyclohexene, giving 2-chlorocyclohexyl dichlorothiocyanate,  $\text{C}_6\text{H}_{10}\text{Cl}\cdot\text{S}\cdot\text{CCl}_2\text{NCl}$ , and by its reaction with iodide ion to give bis(dichlorothiocyanogen), which was assigned the disulphide structure,  $(\text{S}\cdot\text{CCl}_2\text{NCl})_2$ . Like thiocyanogen trichloride, these dichlorothiocyanato-compounds were reasonably stable when pure, but otherwise gradually lost cyanogen chloride, which polymerised to cyanuric chloride. Further reactions, all involving fission of the Cl-S bond of thiocyanogen trichloride, giving dichlorothiocyanato-compounds, at least as primary products, are discussed in the present paper. Particular attention has been paid to the reactions with alcohols and with secondary amines; their primary products,  $\text{RO}\cdot\text{S}\cdot\text{CCl}_2\text{NCl}$  and  $\text{NR}_2\cdot\text{S}\cdot\text{CCl}_2\text{NCl}$  respectively, lose cyanogen chloride very easily.

*Reaction with Alcohols.*—A very vigorous and extensive decomposition occurred when thiocyanogen trichloride was treated with ethanol, but a restricted reaction was effected by using equimolecular proportions in an inert solvent. Hydrogen chloride was then instantly evolved and the solution contained a distillable but unstable liquid which was presumably dichlorothiocyanogen S-ethoxide,  $\text{EtO}\cdot\text{S}\cdot\text{CCl}_2\text{NCl}$ . It began to deposit cyanuric chloride soon after distillation. Since acidic contaminants could have been a cause of its decomposition, a preparation was also carried out with a suspension of sodium ethoxide in place of ethanol, but the stability of the derivative was not thereby improved. When thiocyanogen trichloride was treated, in the absence of a solvent, with a large excess of a primary or secondary alcohol, the products consisted of hydrogen chloride, sulphur chlorides, sulphur dioxide, sweet-smelling liquids, gums, and carbamic esters of

<sup>\*</sup> It was pointed out in Part I that the preparation of thiocyanogen trichloride can be formulated in two ways; one suggests the structure  $\text{ClS}\cdot\text{CCl}_2\text{NCl}$ , and the other leads to the possibility of this or  $\text{ClS}\cdot\text{N}\cdot\text{CCl}_2$ . To avoid unnecessary complication in representing the course of reactions, the latter structure has been disregarded in this paper. If it is the true structure, the formulæ of initially formed derivatives would be  $\text{XS}\cdot\text{N}\cdot\text{CCl}_2$ , but the name "dichlorothiocyanate" could still conveniently be applied to the group  $\cdot\text{S}\cdot\text{N}\cdot\text{CCl}_2$  and, after loss of cyanogen chloride, the end products of reactions would be the same as those discussed in this paper.

<sup>1</sup> Part I, Bacon, Irwin, Pollock, and Pullin, *J.*, 1958, 774.

the alcohols. Carbamates were thus prepared from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, and benzyl alcohols. Yields, calculated on thiocyanogen trichloride, were in the range 20–40%, except for that of methyl carbamate, which was 66%. The following sequence of reactions appears to be involved:

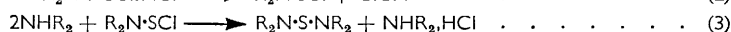
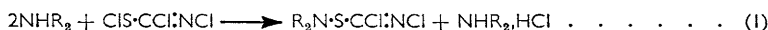


The dichlorothiocyanogen S-alkoxides, presumed to be the primary reaction products, are structurally related to sulphenic esters,  $\text{RO}\cdot\text{SR}'$ , many examples of which have been analogously prepared from sulphenyl chlorides.<sup>2,3</sup> The sulphenates have far greater stability than these dichlorothiocyanato-compounds; *e.g.*, decompositions of esters with the structure  $\text{RO}\cdot\text{SR}'$  [ $\text{R} = \text{Bu}^t$ ,  $\text{Bu}^s$ , cyclohexyl;  $\text{R}' = \text{CCl}_3$ , Ph, 2,4-( $\text{NO}_2$ ) $_2\text{C}_6\text{H}_3$ ] are reactions which occur at 120–200°.<sup>4</sup> The final step in the sequence shown above is a preparative method for carbamates which was reported long ago,<sup>5</sup> but has apparently not since been investigated. It seems to be difficult in the case of t-butyl alcohol, since no carbamate was isolated when excess of this alcohol was used under the usual conditions. Instead, cyanuric chloride was deposited and the solution yielded a distillable liquid, presumably dichlorothiocyanogen S-t-butoxide, which decomposed similarly to the ethoxy-derivative, though not quite as rapidly. No reaction was observed when a mixture of thiocyanogen trichloride and triphenylmethanol was briefly kept at 100°.

*Reaction with Secondary Amines.*—As a preliminary to studying reactions with amines, the effect of ammonia on thiocyanogen trichloride was examined. Admixture with a large excess of ammonia in ether led to a very fast reaction which principally involved only one of the three chlorine atoms, since ammonium chloride was obtained in an amount very little greater than is required by the reaction:



As expected, the product in solution was highly unstable and decomposed violently when the solvent was removed. To obtain *N*-dichlorothiocyanato-compounds of optimum stability, the use of secondary amines was necessary. Investigations with dimethylamine, diethylamine, di-isopropylamine, di-s-butylamine, dicyclohexylamine, piperidine, and morpholine showed that the reaction could be conducted in three clearly defined stages: formation of an amine-*N*-dichlorothiocyanate and amine hydrochloride; decomposition of the dichlorothiocyanato-compound to an amine-*N*-sulphenyl chloride and cyanogen chloride; conversion of the amine-*N*-sulphenyl chloride into the thiobisamine by treatment with more amine:



( $\text{NR}_2 = \text{NMe}_2$ ,  $\text{NEt}_2$ ,  $\text{NPr}_2$ ,  $\text{NBu}_2$ , dicyclohexylamino, piperidino, morpholino.)

Reaction (1) occurred spontaneously, exothermally, and quantitatively when the reagents were mixed in ethereal solution. The *N*-dichlorothiocyanates of dicyclohexylamine and piperidine were thus obtained as white crystals, and the others as liquids, when

<sup>2</sup> Kharasch, Potempa, and Wehrmeister, *Chem. Rev.*, 1946, **39**, 269.

<sup>3</sup> Kharasch, McQuarrie, and Buess, *J. Amer. Chem. Soc.*, 1953, **75**, 2658; Goodman and Kharasch, *ibid.*, 1955, **77**, 6541; Langford and Kharasch, *J. Org. Chem.*, 1957, **22**, 1673; 1958, **23**, 1694; Sosnovsky, *J.*, 1956, 3139.

<sup>4</sup> Irwin and Kharasch, *J. Amer. Chem. Soc.*, 1960, **82**, 2502.

<sup>5</sup> Echevarria, *Annalen*, 1851, **79**, 110; Wurtz, *ibid.*, p. 280; Nef, *ibid.*, 1895, **287**, 317.

solvent was removed. The infrared spectrum of *N*-dichlorothiocyantodicyclohexylamine showed strong bands in the 900 and 1600  $\text{cm}^{-1}$  regions, attributed to the group  $\text{SCNCl}_2$ .<sup>1</sup> Change occurred in these solids, even at  $-20^\circ$ , causing liquefaction and loss of weight, corresponding with decomposition according to equation (2). All the *N*-dichlorothiocyantes were completely converted into liquid *N*-sulphenyl chlorides in 1 hr. at  $40\text{--}50^\circ$ .

Reactions (1) and (2) provide a new preparative method for *N*-sulphenyl chlorides of secondary amines. Members of this class have been prepared in recent years by chemists of Farbenfabriken Bayer A.-G. using the reaction:  $\text{R}_2\text{N}\cdot\text{S}\cdot\text{S}\cdot\text{NR}_2 + \text{Cl}_2 \longrightarrow 2\text{R}_2\text{N}\cdot\text{SCl}$ . Dorlars has summarised this work in a review<sup>6</sup> which was not available at the time of our investigation. By vacuum-distillation we obtained analytically pure dimethylamine- and diethylamine-*N*-sulphenyl chloride, but the higher-boiling members of the group were subjected to reaction (3) without preliminary distillation. Dorlars<sup>6</sup> gives some examples of the reactivity of the S-Cl bond in these chlorides. We observed an unreported type of reaction between cyclohexene and dimethylamine-*N*-sulphenyl chloride, which presumably involved an addition to the olefinic bond, similar to that shown by *C*-sulphenyl chlorides,<sup>2,7</sup> giving a 2-chloro-1-sulphendialkylamide,  $-\text{CHCl}\cdot\text{CH}(\text{S}\cdot\text{NR}_2)-$ ; this product underwent much decomposition during attempted distillation. Another probable reaction of *N*-sulphenyl chlorides is substitution in activated aromatic nuclei, since the chlorides expected at stage (2) in reactions of thiocyanogen trichloride with diphenylamine or with *N*-methylaniline readily decomposed, with evolution of hydrogen chloride, to give intractable solid products, attributed to polycondensation. It is known<sup>8</sup> that *C*-sulphenyl chlorides cause substitution in phenols or aromatic amines without the aid of catalysts.

Reactions of the *N*-sulphenyl chlorides with more of the secondary amine occurred vigorously in ether, in accordance with equation (3), to give crystalline thiobisamines ( $\text{NR}_2 = \text{dicyclohexylamino-}, \text{piperidino-}, \text{morpholino-}$ ) or distillable liquids ( $\text{R} = \text{Me}, \text{Et}, \text{Pr}^i$ ), in yields varying from 87% ( $\text{R} = \text{cyclohexyl}$ ) to 7% ( $\text{R} = \text{Pr}^i$ ); the *s*-butyl derivative could not be distilled without decomposition. Some of these thiobisamines had previously been prepared<sup>9,10</sup> by the reaction:



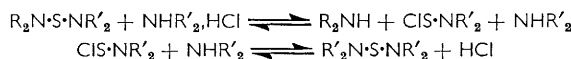
We attempted to prepare two examples of unsymmetrical thiobisamines by the use of a different amine at stage (3):



However, the only products isolated were the symmetrical compounds,  $\text{S}(\text{NR}'_2)_2$ . This suggests the occurrence of an exchange reaction:



Possibly this is a stepwise process, in which the hydrochloride of the secondary amine has a catalytic function:



<sup>6</sup> Dorlars, in "Methoden der Organischen Chemie" (Houben-Weyl), 4th edn., Vol. XI/2, G. Thieme Verlag, Stuttgart, pp. 745, 746, 748, and German patents there cited.

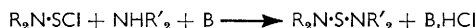
<sup>7</sup> Kharasch *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 1612; 1949, **71**, 2724; 1952, **74**, 3422; 1953, **75**, 3734.

<sup>8</sup> Buess and Kharasch, *J. Amer. Chem. Soc.*, 1950, **72**, 3529.

<sup>9</sup> Michaelis and Luxembourg, *Ber.*, 1895, **28**, 165; Michaelis, *ibid.*, p. 1012; Lengfeld and Stieglitz, *ibid.*, p. 575.

<sup>10</sup> Blake, *J. Amer. Chem. Soc.*, 1943, **65**, 1267; Burg and Woodrow, *ibid.*, 1954, **76**, 219.

It was later noted that some unsymmetrical thiobisamines had been prepared in the Bayer laboratories<sup>6</sup> by the inclusion of a tertiary amine (B) in the reaction mixture:



The vulnerability to acids of the N-S bond in thiobisamines is evident from observations by Michaelis.<sup>9</sup> We found (in the two cases examined) that they are cleaved by picric acid, which gives a picrate of the liberated secondary amine. However, a picrate thus prepared from the piperidino-compound by Michaelis<sup>9</sup> was claimed by him to be a salt of the thio-bisamine,  $(C_5H_{10}N)_2S \cdot 2C_6H_5(NO_2)_3 \cdot OH$ . Several examples of the ready fission of N-S bonds in a related group of compounds, dithiobisamines,  $R_2N \cdot S \cdot S \cdot NR_2$ , are given in a recent paper by Saville.<sup>11</sup>

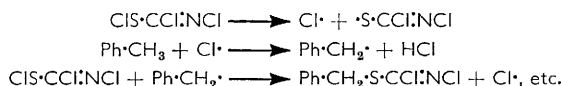
*Addition Reactions.*—Whereas the addition of thiocyanogen trichloride to cyclohexene is an easy reaction, giving a high yield of adduct,<sup>1</sup> reaction with ethylene, carried out in carbon tetrachloride in darkness, gave only a low yield of adduct:



An analytically pure sample of 1-chloro-2-dichlorothiocyanoethane was obtained.

Like 2,4-dinitrobenzenesulphenyl chloride,<sup>12</sup> thiocyanogen trichloride might be expected to add to acetylenic bonds. Ready reaction was observed with hex-3-yne and with phenyl-acetylene, but the products were too unstable for distillation. Reaction did not occur with acetylene unless ultraviolet irradiation was employed. Similarly, acetylene is known to be less reactive than hex-3-yne towards 2,4-dinitrobenzenesulphenyl chloride, and requires aluminium chloride as catalyst.<sup>12</sup> The product from acetylene and thiocyanogen trichloride, presumably 1-chloro-2-dichlorothiocyanoethylene, was distillable, but rapidly deposited cyanuric chloride; it could be kept long enough to discover that it showed peaks in the infrared absorption spectrum characteristic of dichlorothiocyano-compounds.<sup>1</sup>

*Homolytic Substitution in Toluene.*—The reactions of the S-Cl bond in thiocyanogen trichloride so far described are presumably ionic in their mechanism, except, probably, for the photo-initiated addition to acetylene. In the case of thiocyanogen monochloride,  $Cl \cdot SCN$ , we have accumulated much evidence for both heterolytic<sup>13</sup> and homolytic reactions<sup>14</sup> of the S-Cl bond. It was therefore of interest to observe the behaviour of thiocyanogen trichloride under conditions known to result in homolytic reaction in the case of the monochloride. Photo-initiated side-chain substitution in toluene was examined; a chain reaction to give benzyl dichlorothiocyanate was expected, by analogy with the known production<sup>14</sup> of benzyl thiocyanate with thiocyanogen monochloride under similar conditions:



Reaction occurred only if ultraviolet irradiation was employed, and gave a product which was converted into toluene- $\omega$ -thiol by lithium aluminium hydride and into toluene- $\omega$ -sulphonyl chloride by aqueous chlorine; such conversions had previously been carried out with both thiocyanato- and dichlorothiocyano-compounds.<sup>1</sup> Homolytic substitution in the methyl group of toluene, involving fission of the S-Cl bond of thiocyanogen trichloride, was thus demonstrated. The detailed course of the reaction is obscure, since pure fractions could not be isolated from the product, and analytical data were best

<sup>11</sup> Saville, *J.*, 1958, 2880.

<sup>12</sup> Kharasch and Assony, *J. Amer. Chem. Soc.*, 1953, **75**, 1081.

<sup>13</sup> Bacon and Guy, *J.*, 1960, 318.

<sup>14</sup> Bacon, Guy, Irwin, and Robinson, *Proc. Chem. Soc.*, 1959, 304; Bacon and Guy, unpublished data.

interpreted by the supposition that benzyl dichlorothiocyante, for which there was infrared spectral evidence, was accompanied by benzyl thiocyanate. Accordingly, an alternative preparation was attempted by the Grignard reaction:  $\text{CH}_2\text{Ph}\cdot\text{MgCl} + \text{ClS}\cdot\text{CCl}\cdot\text{NCl} \longrightarrow \text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{CCl}\cdot\text{NCl} + \text{MgCl}_2$ . The physical and chemical properties of the product suggested that it was a similarly impure sample of benzyl dichlorothiocyante; some benzyl disulphide was also observed. Hence, secondary effects are not confined to the photochemical method of preparing benzyl dichlorothiocyante. Photo-initiated reaction of triphenylmethane with thiocyanogen trichloride in carbon tetrachloride was unsuccessful.

*Preparation of Some Related Pseudohalogen Compounds.*—The reactions described here and in the earlier paper<sup>1</sup> demonstrate the existence of the somewhat unstable dichlorothiocyanto-group,  $\text{SCNCl}_2$ , of pseudohalide type, in several compounds derived from thiocyanogen trichloride. The latter may be regarded as a member of the halogen-pseudohalogen class,<sup>15</sup> in which the dichlorothiocyanto-group partners a chlorine atom. We have already described the production, by two methods, of a substance which, if the assigned structure  $(\text{S}\cdot\text{CCl}\cdot\text{NCl})_2$  is correct, would be the parent pseudohalogen, bis(dichlorothiocyano-gen).<sup>1</sup> It is intended to examine this compound further.

Meanwhile, a related pseudohalogen, bis(bromochlorothiocyano-gen), a liquid of moderate stability, has been prepared by the reaction:  $\text{S}_2\text{Cl}_2 + 2\text{BrCN} \longrightarrow (\text{S}\cdot\text{CBr}\cdot\text{NCl})_2$ . Similar treatment of cyanogen bromide with sulphur dichloride in place of sulphur monochloride gave a very small amount of a compound which may have had the structure  $\text{ClS}\cdot\text{CBr}\cdot\text{NCl}$ . Related to these compounds is the liquid assigned the structure  $\text{S}(\text{CCl}\cdot\text{NCl})_2$  and named sulphur bisdichlorocyanide, which appeared as a by-product in the preparation of thiocyanogen trichloride from thiocyanogen and chlorine.<sup>1</sup> It was suggested that this may have arisen from a side-reaction occurring during the preparation:  $\text{ClCN} + \text{ClS}\cdot\text{CCl}\cdot\text{NCl} \longrightarrow \text{S}(\text{CCl}\cdot\text{NCl})_2$ . This view now finds support in the preparation of sulphur bisdichlorocyanide, though in low yield, from a mixture of thiocyanogen trichloride and cyanogen chloride. Indications were also obtained of analogous addition of benzene-sulphenyl chloride to cyanogen chloride, but the product was too unstable to be isolated by distillation. All the reactions so far referred to in this section have been carried out in ethyl bromide solution at or below room temperature.

The preparation of further dichlorothiocyanto-compounds,  $\text{X}\cdot\text{SCNCl}_2$ , may be envisaged. Brief attention has been given to derivatives in which X is another pseudohalogen group. By treatment of thiocyanogen trichloride with silver cyanide or lead thiocyanate, higher-boiling and rather unstable liquids resulted, probably with the respective structures  $\text{NC}\cdot\text{S}\cdot\text{CCl}\cdot\text{NCl}$  and  $\text{NC}\cdot\text{S}\cdot\text{S}\cdot\text{CCl}\cdot\text{NCl}$ . They did not appear attractive as reagents.

## EXPERIMENTAL

*Thiocyanogen Trichloride.*—The reagent was prepared from solutions of thiocyanogen, in yields of up to 80%, as previously described.<sup>1</sup> Some alternative solvents to ethyl bromide were examined, but none was as satisfactory; *e.g.*, yields were only 20–25% in chloroform or carbon tetrachloride. Similar observations were made by Kaufmann and Liepe.<sup>16</sup> Thiocyanogen trichloride was also obtained (56%) in a single process by passing a stream of chlorine into a suspension of lead thiocyanate in ethyl bromide for 30 min. at room temperature, filtering, and distilling. The slow decomposition reported for pure thiocyanogen trichloride<sup>1</sup> is very greatly accelerated by hydrogen chloride; *e.g.*, passage of the gas into the trichloride for 30 min. at room temperature caused copious precipitation of cyanuric chloride. Abnormally low stability, noticed in certain preparations of thiocyanogen trichloride, may have been due to moisture inadvertently introduced with the lead thiocyanate. This salt should be dried in a vacuum over phosphorus pentoxide before use.

<sup>15</sup> Cf. Sharpe, *Quart. Rev.*, 1950, **4**, 115.

<sup>16</sup> Kaufmann and Liepe, *Ber.*, 1924, **57**, 923.



**Reaction with Alcohols.—Ethanol.** (a) An excess of absolute ethanol ( $\sim 0.25$  mole) was added dropwise, during about 15 min., to thiocyanogen trichloride (4.11 g., 0.025 mole) and the vigorous exothermic reaction was occasionally moderated by cooling. The colour of the reagent disappeared, some yellow gum was deposited, hydrogen chloride and sulphur dioxide were evolved, and the odour of sulphur chlorides was apparent. After another 15 min. at room temperature, excess of ethanol was removed under reduced pressure to leave a mixture of gum and crystalline ethyl carbamate. The latter was isolated (0.85 g., 38%) by distillation under reduced pressure and was recrystallised from benzene, followed by vacuum sublimation; m. p. and mixed m. p.  $46-47^\circ$  (lit.,<sup>17</sup>  $49^\circ$ ) (Found: C, 40.6; H, 8.0; N, 15.8. Calc. for  $C_3H_7NO_2$ : C, 40.4; H, 7.9; N, 15.75%).

(b) Ethanol (0.04 mole) in carbon tetrachloride (6 ml.) reacted immediately, with evolution of hydrogen chloride, when added dropwise to a stirred solution of thiocyanogen trichloride (0.04 mole) in carbon tetrachloride (25 ml.). After 30 min. the solvent was removed under reduced pressure, and the residue distilled to yield (probably) dichlorothiocyangen *S*-ethoxide (1.1 g., 16%), a red liquid, b. p.  $90-96^\circ/0.5$  mm., which soon began to deposit cyanuric chloride.

(c) Finely dispersed sodium (0.025 g.-atom) was stirred with an equivalent of absolute ethanol in ether (20 ml.) for 8 hr. and the resulting suspension of sodium ethoxide was stirred with a solution of thiocyanogen trichloride (0.025 mole) in ether (25 ml.) for 3 hr. Removal of the precipitated sodium chloride and distillation of the filtrate yielded a product which was probably dichlorothiocyangen *S*-ethoxide, b. p.  $110-120^\circ/2$  mm., a red liquid which decomposed as readily as that prepared by method (b).

**Other alcohols.** Carbamates were prepared and purified as described under method (a) for ethanol. In some cases it proved difficult to obtain analytically pure samples. The following were thus obtained: methyl carbamate (66%), as needles, m. p.  $53^\circ$  (lit.,<sup>18</sup>  $54^\circ$ ) (Found: C, 32.4; H, 6.4; N, 18.7. Calc. for  $C_2H_5NO_2$ : C, 32.0; H, 6.7; N, 18.7%); *n*-propyl carbamate (37%), as needles, m. p.  $60^\circ$  (lit.,<sup>17</sup>  $52.5^\circ$ , changing to  $60^\circ$  after 3 months' storage) (Found: C, 46.6; H, 8.7; N, 13.9. Calc. for  $C_4H_9NO_2$ : C, 46.6; H, 8.7; N, 13.6%); isopropyl carbamate (23%), as prisms, m. p.  $90-93^\circ$  (lit.,<sup>19</sup>  $92-93^\circ$ ) (Found: C, 46.0; H, 8.65; N, 13.8%); *n*-butyl carbamate (27%), as plates, m. p.  $51-53^\circ$  (lit.,<sup>17</sup>  $54^\circ$ ) (Found: C, 51.2; H, 9.5; N, 12.2. Calc. for  $C_5H_{11}NO_2$ : C, 51.3; H, 9.4; N, 12.0%); isobutyl carbamate (38%), as plates, m. p.  $64-65^\circ$  (lit.,<sup>20</sup>  $65-66^\circ$ ) (Found: C, 51.3; H, 8.9; N, 11.0%); *s*-butyl carbamate (17%), as needles, m. p.  $97^\circ$  (lit.,<sup>17</sup>  $94^\circ$ ) (Found: C, 51.0; H, 9.0; N, 12.2%); benzyl carbamate (36%), as impure plates, m. p.  $85-86^\circ$  (lit.,<sup>19</sup>  $86^\circ$ ) (Found: C, 62.9; H, 6.0; N, 10.3. Calc. for  $C_8H_9NO_2$ : C, 63.6; H, 6.0; N, 9.3%).

***t*-Butyl alcohol.** Treatment of the alcohol as described under method (a) for ethanol resulted in a vigorous reaction, during which hydrogen chloride was evolved and a considerable amount of cyanuric chloride was deposited. Filtration, distillation, and redistillation yielded a small amount of (probably) dichlorothiocyangen *S*-*t*-butoxide, b. p.  $76-78^\circ/2$  mm.,  $n_D^{25}$  1.5720, in which deposition of cyanuric chloride began after a few hours at room temperature.

**Reaction with Ammonia.**—Thiocyanogen trichloride (4.0 g.) in ether (30 ml.) was added to a large excess of a solution of ammonia (5 ml., measured as liquid) in ether (100 ml.). An immediate reaction occurred, with precipitation of ammonium chloride (1.4 g.; theory for reaction of one chlorine atom per mol. of trichloride, 1.3 g.). Evaporation of the filtrate at  $5^\circ$  left a reddish-purple liquid which decomposed very vigorously on slight warming, giving an insoluble brown resin.

**Reaction with Secondary Amines.**—(a) **Dimethylamine.** Thiocyanogen trichloride (12.3 g., 0.075 mole) in ether (50 ml.) was added during 30 min. to anhydrous dimethylamine (0.15 mole) in ether (150 ml.) kept at  $\sim 10^\circ$ . The precipitated dimethylamine hydrochloride (97%) was removed, solvent evaporated from the filtrate, and the residue distilled to yield *dimethylamine-N-sulphenyl chloride* (7.55 g., 90%), as a pale green liquid, b. p.  $34.5-35.5^\circ/15$  mm., with a penetrating odour (Found: C, 21.3; H, 5.5; Cl, 31.8; N, 12.4; S, 28.6.  $C_2H_4ClNS$  requires C, 21.5; H, 5.4; Cl, 31.8; N, 12.5; S, 28.7%). If left exposed to air it formed a white solid. Addition of the sulphenyl chloride to an excess of cyclohexene resulted in a vigorous reaction;

<sup>17</sup> Kraft and Herbst, *J. Org. Chem.*, 1945, **10**, 483.

<sup>18</sup> Schmidt, *Z. phys. Chem.*, 1907, **58**, 513.

<sup>19</sup> Thiele and Dent, *Annalen*, 1898, **302**, 245.

<sup>20</sup> Jacobson, *J. Amer. Chem. Soc.*, 1938, **60**, 1742.

distillation led to partial decomposition and yielded a product which was probably 2-chloro-cyclohexane-1-sulphendimethylamide (18%), a green-yellow liquid of unpleasant odour, b. p. 157°/1.8 mm.,  $n_D^{23}$  1.5449, not analytically pure.

Dropwise addition of dimethylamine-*N*-sulphenyl chloride (2.23 g., 0.02 mole) in ether (15 ml.) to anhydrous dimethylamine (0.04 mole) in ether (50 ml.) at room temperature resulted in a mildly exothermic reaction, with precipitation of dimethylamine hydrochloride (82%). Distillation of the filtrate yielded colourless lachrymatory *NN'*-thiobisdimethylamine (39%), m. p. 20°, b. p. 68°/87 mm. (lit.,<sup>10</sup> m. p. 20°, b. p. 33.5—36°/14 mm.) (Found: C, 40.0; H, 10.05; N, 23.15; S, 26.6. Calc. for  $C_4H_{12}N_2S$ : C, 40.0; H, 10.0; N, 23.3; S, 26.7%). Alternatively, a preparation<sup>10</sup> from sulphur dichloride (0.075 mole) and dimethylamine (0.33 mole) in ether gave the thiobisamine (30%), b. p. 74°/109 mm. (Found: C, 39.8; H, 9.95; N, 23.2; S, 26.3%). When the thiobisamine was briefly warmed on the water-bath with a slight excess of picric acid in ethanol, it yielded dimethylamine picrate, m. p. 161—162° (lit.,<sup>21</sup> 160—161°) (Found: C, 35.3; H, 3.9; N, 19.6. Calc. for  $C_8H_{10}N_4O_7$ : C, 35.0; H, 3.65; N, 20.4%).

(b) *Diethylamine*. Reaction with the anhydrous amine (0.15 mole), as described under (a), yielded on distillation *diethylamine-N-sulphenyl chloride* (50%), as an orange liquid of unpleasant odour, b. p. 56°/12 mm. (Dorlars<sup>6</sup> quotes 62—64°/13 mm.) (Found: C, 34.3; H, 7.4; Cl, 25.35; N, 9.95; S, 22.6.  $C_4H_{10}ClNS$  requires C, 34.4; H, 7.2; Cl, 25.4; N, 10.0; S, 22.95%). The sulphenyl chloride gave colourless *NN'*-thiobisdiethylamine (69%), of unpleasant odour, b. p. 74°/10 mm.,  $n_D^{23}$  1.4590 (lit.,<sup>9</sup> b. p. 87°/19 mm., 84—86°/15 mm.) (Found: C, 54.6; H, 11.3; N, 15.8; S, 18.0. Calc. for  $C_8H_{20}N_2S$ : C, 54.5; H, 11.4; N, 15.9; S, 18.2%).

(c) *Di-isopropylamine*. After similar reaction of the amine with thiocyanogen trichloride, filtration, and evaporation of the ether, there remained an unstable liquid residue of *N*-dichlorothiocyantoisopropylamine, which rapidly decomposed at 50°, evolving cyanogen chloride and leaving di-isopropylamine-*N*-sulphenyl chloride as a brown, pungent, viscous liquid, which formed a gum on heating above 50°. The crude sulphenyl chloride (0.05 mole) reacted with di-isopropylamine (0.10 mole) in ether, yielding pale green *NN'*-thiobisdi-isopropylamine (7%), of disagreeable odour, b. p. 40°/1 × 10<sup>-4</sup> mm.,  $n_D^{22}$  1.4699 (Found: C, 61.9; H, 11.8; N, 11.9; S, 13.6.  $C_{12}H_{28}N_2S$  requires C, 62.1; H, 12.1; N, 12.1; S, 13.8%). The thiobisamine, b. p. 45°/5 × 10<sup>-4</sup> mm.,  $n_D^{22}$  1.4689, was alternatively prepared (60%) by reaction of sulphur dichloride with di-isopropylamine in ether (Found: C, 61.85; H, 11.8; N, 11.8; S, 13.7%).

(d) *Di-*s*-butylamine*. The crude *N*-dichlorothiocyanto-derivative, the *N*-sulphenyl chloride, and *NN'*-thiobisdi-*s*-butylamine were obtained as described under (c). The thiobisamine could not be distilled at 10<sup>-4</sup> mm. without resinification. A sample prepared from sulphur dichloride behaved similarly.

(e) *Dicyclohexylamine*. Reaction of the amine (0.075 mole) with thiocyanogen trichloride in the usual way resulted in quantitative precipitation of the amine hydrochloride. Filtration and evaporation left *N*-dichlorothiocyantodicyclohexylamine (10.5 g., 91%) as colourless crystals which lost cyanogen chloride slowly even at -20°. Its infrared absorption spectrum contained strong bands at 882 and 1595 cm.<sup>-1</sup>, but was otherwise like that of dicyclohexylamine. In 1 hr. on the water-pump at 40° the compound lost cyanogen chloride (1.97 g.; theor. for the pure dichlorothiocyanto-amine, 2.09 g.), leaving dicyclohexylamine-*N*-sulphenyl chloride as a brown liquid which decomposed if heated. The crude sulphenyl chloride reacted readily with dicyclohexylamine in ether, yielding dicyclohexylamine hydrochloride (96%) and *NN'*-thiobisdicyclohexylamine (87%), which crystallised from light petroleum in colourless needles, m. p. 147—150° (Found: C, 73.6; H, 10.6; N, 7.2; S, 8.3.  $C_{24}H_{44}N_2S$  requires C, 73.5; H, 11.2; N, 7.15; S, 8.2%). The same compound resulted (92%) from reaction of the amine with sulphur dichloride.

(f) *Piperidine*. Reaction with thiocyanogen trichloride resulted in quantitative precipitation of piperidine hydrochloride and yielded *N*-dichlorothiocyantopiperidine as a colourless crystalline solid, which lost cyanogen chloride rapidly at 40°, leaving piperidine-*N*-sulphenyl chloride as a brown liquid. This reacted with piperidine in ether, giving piperidine hydrochloride (75%) and *NN'*-thiobispiperidine (58%), which crystallised from light petroleum in prisms, m. p. 75—76° (lit.,<sup>9</sup> 74°) (Found: C, 60.2; H, 9.8; N, 14.3; S, 15.8. Calc. for  $C_{10}H_{20}N_2S$ : C, 60.0; H, 10.0; N, 14.0; S, 16.0%).

<sup>21</sup> Walden, Ulich, and Birr, *Z. phys. Chem.*, 1927, **130**, 495.

(g) *Morpholine*. Reaction proceeded as described under (e) and (f) to give morpholine-*N*-sulphenyl chloride, which was unstable above 60°. On treatment with morpholine in ether it gave *NN'*-thiobismorpholine (25%), which crystallised from benzene in prisms, m. p. 128–129° (Blake<sup>10</sup> gives 125–126°); it was identical in m. p. and mixed m. p. with a sample prepared from sulphur dichloride<sup>10</sup> (Found: C, 47.0; H, 7.7; N, 13.7; S, 15.5. Calc. for C<sub>8</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S: C, 47.0; H, 7.85; N, 13.7; S, 15.7%). Treatment with excess of picric acid in ethanol gave morpholine picrate, m. p. 151–153° (lit.,<sup>22</sup> 151.6°) (Found: C, 38.1; H, 3.9; N, 17.7. Calc. for C<sub>10</sub>H<sub>12</sub>N<sub>4</sub>O<sub>8</sub>: C, 38.0; H, 3.8; N, 17.7%).

(h) *Diphenylamine*. Reaction in ether between the amine (0.10 mole) and thiocyanogen trichloride (0.05 mole) for 12 hr. at ~20° resulted in precipitation of diphenylamine hydrochloride (96%). Evaporation of the filtrate from this left a dark green liquid, apparently the *N*-sulphenyl chloride (11.4 g., 97%). When this was warmed to 30° sudden decomposition occurred, with evolution of hydrogen chloride and production of a resin, which was insoluble in common organic solvents and contained about one-third of the proportion of combined chlorine present in the sulphenyl chloride.

(i) *N-Methylaniline*. Reaction in ether with thiocyanogen trichloride yielded 92% of the theoretical amount of *N*-methylaniline hydrochloride in 1 hr. at ~20°. Colourless crystals appeared during evaporation of the filtrate but the residue was a yellow liquid, presumably the *N*-sulphenyl chloride, since it gave a precipitate of the amine hydrochloride when treated with more *N*-methylaniline in ether. The product of this reaction darkened and resinified.

*Attempted Preparation of Unsymmetrical NN'-Thiobisamines*.—(a) Diethylamine-*N*-sulphenyl chloride (0.02 mole) (see above) in ether (5 ml.) was added to anhydrous dimethylamine (0.04 mole) in ether (20 ml.); amine hydrochloride was filtered off, and the filtrate distilled. A fraction, b. p. 31°/10 mm., gave an analysis corresponding with *NN'*-thiobisdimethylamine (Found: C, 40.1; H, 9.5. Calc. for C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>S: C, 40.0; H, 10.0. Calc., for the desired unsymmetrical compound, C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>S: C, 48.7; H, 10.8%). Like authentic *NN'*-thiobisdimethylamine (see above), it was decomposed by picric acid to dimethylamine picrate, m. p. and mixed m. p. 161°.

(b) Di-*s*-butylamine-*N*-sulphenyl chloride (0.015 mole) (see above) reacted immediately in ether with dicyclohexylamine (0.03 mole), giving a precipitate of dicyclohexylamine hydrochloride (90%). On evaporation, the filtrate left a brown solid, which, when recrystallised from light petroleum, gave only *NN'*-thiobisdicyclohexylamine (see above) (0.7 g., i.e., 24%, calc. on conversion of the desired unsymmetrical thiobisamine), m. p. 147–150° (Found: C, 73.3; H, 10.8; N, 7.3; S, 8.2%).

*1-Chloro-2-dichlorothiocyanoethane*.—Ethylene was passed for 3 hr. into a 1.25M-solution of thiocyanogen trichloride in carbon tetrachloride in darkness at ~20°. After the solution had been kept in the dark for 12 hr. longer, distillation yielded pale green 1-*chloro-2-dichlorothiocyanoethane* (13%), with a disagreeable odour, b. p. 108°/20 mm., *n*<sub>D</sub><sup>25</sup> 1.5550 (Found: C, 18.7; H, 1.9; Cl, 55.3; N, 7.4; S, 16.5. C<sub>3</sub>H<sub>4</sub>Cl<sub>3</sub>NS requires C, 18.7; H, 2.1; Cl, 55.35; N, 7.3; S, 16.6%).

*Reaction with Acetylenic Hydrocarbons*.—Reaction of thiocyanogen trichloride with acetylene was unsuccessful under the conditions used for ethylene. When the procedure was repeated at ~40° with irradiation from a 250-w “Mazda” ME/D mercury-vapour lamp, distillation of the solution yielded some unchanged thiocyanogen trichloride, followed by a yellow liquid of unpleasant odour, probably 1-*chloro-2-dichlorothiocyanoethylene*, b. p. 90–100°/23 mm. It began to deposit cyanuric chloride almost immediately. An infrared absorption spectrum, quickly obtained, included very strong bands at 1594 and 907 cm.<sup>-1</sup>, found in other dichlorothiocyanates.<sup>1</sup> Reaction of hex-3-yne or phenylacetylene occurred rapidly and exothermally, without irradiation, with a M-solution of thiocyanogen trichloride in carbon tetrachloride. In both cases the product decomposed to cyanuric chloride and resin when distillation was attempted.

*Reaction with Toluene*.—When a toluene solution of thiocyanogen trichloride was maintained at 40° in darkness for several hours, no reaction products of toluene could be detected, but irradiation with the mercury-vapour lamp described above resulted in reaction. Typically, a 0.25M-solution of thiocyanogen trichloride in toluene (200 ml.) was irradiated in a quartz flask for 8 hr. at ~40°. Hydrogen chloride was slowly evolved and evaporation of the solvent under reduced pressure left a brown liquid, yielding a yellow distillate (35%), b. p. 70–80°/0.2

<sup>22</sup> Mitchell and Bryant, *J. Amer. Chem. Soc.*, 1943, **65**, 128.



mm. Colourless fractions were obtained on further distillation but none appeared to be a pure compound; similar results were obtained from other experiments. The N : S ratio in all samples was very close to 1, but values for C were usually higher, by up to 7%, than the theoretical figure for benzyl dichlorothiocyanate, and values for Cl were usually lower, by up to 7%; typical analyses corresponded reasonably well with a mixture of benzyl dichlorothiocyanate and benzyl thiocyanate in the ratio  $\sim 7 : 3$ . The infrared absorption spectra typically showed strong bands at 928 and 1596  $\text{cm}^{-1}$ , attributed to dichlorothiocyanate, and a weak band at 2167  $\text{cm}^{-1}$ , probably due to thiocyanate.

A sample of the redistilled product was reduced with lithium aluminium hydride by the procedure previously used.<sup>1</sup> This produced toluene- $\omega$ -thiol, b. p. 192–194°, characterised as benzyl 2,4-dinitrophenyl sulphide, m. p. 127–129° (lit.,<sup>23</sup> 130°) (Found: C, 53.7; H, 3.5; N, 9.5; S, 10.8. Calc. for  $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_4\text{S}$ : C, 53.8; H, 3.45; N, 9.7; S, 11.0%). A similar sample from the reaction was dissolved in cooled 10 : 1 acetic acid–water and treated for 15 min. with a stream of chlorine (cf. ref. 1). Dilution with water gave a precipitate of toluene- $\omega$ -sulphonyl chloride, m. p. 93–94°, undepressed on admixture with a sample obtained by grinding sodium toluene- $\omega$ -sulphonate with phosphorus pentachloride.

Preparation of benzyl dichlorothiocyanate was also attempted by reaction of benzyl-magnesium chloride (0.05 mole) and thiocyanogen trichloride (0.05 mole) in ether. Precipitated magnesium chloride was removed, and the solution distilled to yield a fraction (27%), b. p. 86–88°/0.4 mm., which was similar in analysis and infrared absorption spectrum to the product from the reaction of thiocyanogen trichloride and toluene. It was likewise reduced to toluene- $\omega$ -thiol and oxidised to toluene- $\omega$ -sulphonyl chloride. A by-product obtained from a similar Grignard reaction, but with benzylmagnesium chloride in 100% excess, was dibenzyl disulphide, m. p. and mixed m. p. 69–70°.

*Sulphur Bisdichlorocyanide*.—A solution of thiocyanogen trichloride (3.0 g.) and excess of cyanogen chloride (12 g.) in ethyl bromide (40 ml.) was kept in darkness at 0° for 10 days. Distillation yielded sulphur bisdichlorocyanide<sup>1</sup> (0.46 g., 11%), b. p. 67°/1 mm. (Found: Cl, 62.5; N, 12.65; S, 13.8. Calc. for  $\text{C}_2\text{Cl}_4\text{N}_2\text{S}$ : Cl, 62.8; N, 12.4; S, 14.1%).

*Bis(bromochlorothiocyanogen)*.—A solution of sulphur monochloride (0.05 mole) and cyanogen bromide (0.10 mole) in ethyl bromide (30 ml.) was kept for 6 days at  $\sim 17^\circ$ . A red colour developed and distillation yielded *bis(bromochlorothiocyanogen)* (7.0 g., 40%), as a deep red liquid, b. p. 36–37°/0.25 mm., with a relatively weak odour resembling that of sulphur monochloride (Found: N, 8.2; S, 18.0; Cl + Br, 66.0.  $\text{C}_2\text{Br}_2\text{Cl}_2\text{N}_2\text{S}_2$  requires N, 8.1; S, 18.4; Cl + Br, 66.6%). The infrared absorption spectrum (cf. ref. 1) showed strong bands at 1587, 1500, and 1076  $\text{cm}^{-1}$  and very strong bands at 917 and 532  $\text{cm}^{-1}$ . One sample (probably containing impurities) slowly deposited cyanuric bromide and the liquid portion then contained sulphur monochloride, b. p. 137°.

*Bromochlorothiocyanogen S-Chloride*.—The procedure used for *bis(bromochlorothiocyanogen)* was repeated with a mixture of sulphur dichloride (0.05 mole) and cyanogen bromide (0.05 mole). Removal of reagents and solvent gave only a 4% yield of (probably) bromochlorothiocyanogen S-chloride, a pungent orange-yellow liquid, b. p. 38–43°/12 mm.; the infrared absorption spectrum (cf. ref. 1) included very strong doublets at 1603 and 1587  $\text{cm}^{-1}$ , and at 921 and 902  $\text{cm}^{-1}$ .

*Dichlorothiocyanogen S-Cyanide and S-Thiocyanate*.—Excess of finely powdered silver cyanide (2 mol.) was stirred for 15 hr. at  $\sim 20^\circ$  with a 1.5M-solution of thiocyanogen trichloride in carbon tetrachloride. Filtration and distillation yielded (probably) *dichlorothiocyanogen S-cyanide* (54%), a yellow lachrymatory liquid, b. p. 75–77°/15 mm., which slowly deposited cyanuric chloride (Found: C, 15.6.  $\text{C}_2\text{Cl}_2\text{N}_2\text{S}$  requires C, 15.5%). A similar procedure with finely divided lead thiocyanate yielded (probably) *dichlorothiocyanogen S-thiocyanate*, a yellow liquid, b. p. 60°/0.7 mm., which had a faint odour and slowly deposited cyanuric chloride.

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<sup>23</sup> Bost, Turner, and Norton, *J. Amer. Chem. Soc.*, 1932, **54**, 1985.