temperature range 51° to 298°K., are reported for $CaCl_2$, $FeCl_2$, $MgCl_2$, and $MnCl_2$ in the anhydrous crystalline state.

The entropy values at 298.16°K. are 27.2 ± 0.4 for $CaCl_2$, 28.7 ± 0.8 for $FeCl_2$, 21.4 ± 0.2 for $MgCl_2$, and 28.0 ± 0.8 for $MnCl_2$.

Free energy of formation values at 298.16°K., computed from entropies and heats of formation, are −179,800 for $CaCl_2$, −72,600 for $FeCl_2$, −141,500 for $MgCl_2$, and −102,900 for $MnCl_2$ (calories per gram formula mass).

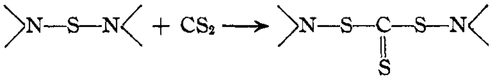
BERKELEY, CALIF. RECEIVED JULY 9, 1942

[CONTRIBUTION FROM THE MONSANTO CHEMICAL COMPANY, NITRO, WEST VIRGINIA]

The Reaction of Carbon Disulfide with Amine Sulfides

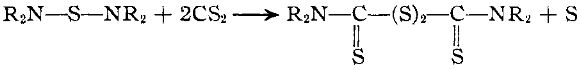
BY EDWARD S. BLAKE

A secondary amine sulfide and carbon disulfide were combined with the expectation of producing trithiocarbonate compounds in accordance with the equation



However, the reaction did not proceed in this manner but rather resulted in the formation of tetra substituted thiuram polysulfides. Furthermore, the course of the reaction is determined by the substituent groups present in the respective amine sulfides.

Aliphatic amine monosulfides, namely, dimethyl and diethyl amine monosulfides, gave the corresponding tetra alkyl thiuram disulfide with the liberation of sulfur; the general reaction is as follows

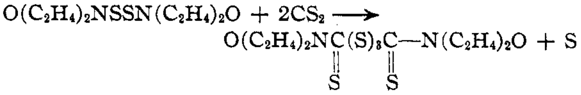


$$R_2N{-}S{-}NR_2 + 2CS_2 \longrightarrow R_2N{-}\underset{\underset{S}{\|}}{C}{-}(S)_2{-}\underset{\underset{S}{\|}}{C}{-}NR_2 + S$$

The yields were 99.1 and 64.8%, respectively, and the purity of the tetra methyl compound was excellent.

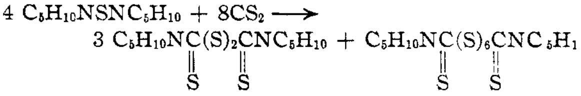
No aliphatic amine disulfides were used because of the difficulty in obtaining these compounds in a high degree of purity since upon purification they are prone to break down into mixtures of amine monosulfide and polysulfides.

The heterocyclic amine sulfides behave differently toward carbon disulfide than do the aliphatic amine monosulfides. Both morpholine mono- and disulfides yield (94 to 96%) the thiuram trisulfide. The monosulfide retains all of its sulfur and the disulfide liberates one atom of sulfur, thus

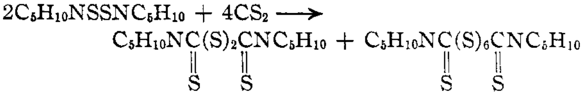


$$O(C_2H_4)_2NSSN(C_2H_4)_2O + 2CS_2 \longrightarrow O(C_2H_4)_2N\underset{\underset{S}{\|}}{C}(S)_3\underset{\underset{S}{\|}}{C}{-}N(C_2H_4)_2O + S$$

Piperidine mono and disulfides reacted strikingly to yield not wholly one product as in the case of the morpholine sulfides but rather to yield a mixture of the thiuram disulfide and the thiuram hexasulfide. The thiuram hexasulfide in both instances is formed in direct ratio to the sulfur present in the amine sulfide reacted.

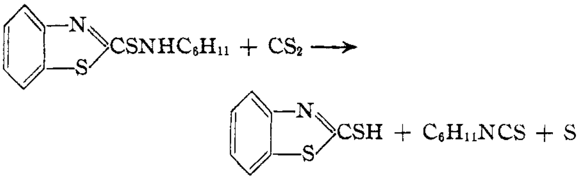


$$4\,C_5H_{10}NSNC_5H_{10} + 8CS_2 \longrightarrow 3\,C_5H_{10}N\underset{\underset{S}{\|}}{C}(S)_2\underset{\underset{S}{\|}}{C}NC_5H_{10} + C_5H_{10}N\underset{\underset{S}{\|}}{C}(S)_6\underset{\underset{S}{\|}}{C}NC_5H_1$$

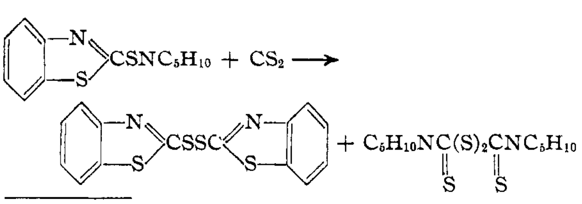


$$2C_5H_{10}NSSNC_5H_{10} + 4CS_2 \longrightarrow C_5H_{10}N\underset{\underset{S}{\|}}{C}(S)_2\underset{\underset{S}{\|}}{C}NC_5H_{10} + C_5H_{10}N\underset{\underset{S}{\|}}{C}(S)_6\underset{\underset{S}{\|}}{C}NC_5H_{10}$$

The action of carbon disulfide on N-substituted 2-benzo-thiazole-sulfenamides, a special type of amine sulfide, proceeds in a manner which again is determined by the substituents present in the amide group. N-Cyclohexyl-2-benzothiazole-sulfenamide, a sulfenamide of a primary amine, reacts[1] to produce 2-mercaptobenzothiazole and cyclohexylisothiocyanate in excellent yields as shown by the equation



2-Benzothiazole-sulfen-piperidide, a sulfenamide of a secondary amine, reacts to yield 2,2′-dithiobisbenzothiazole and cyclopentamethylenethiuram disulfide



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[1] This reaction was first observed by M. W. Harman, this Laboratory.

TABLE I

AMINE SULFIDES

Compd.	( )-Sulfide	Yield, %	B. p., °C.	mm.	M. p., °C. (uncor.)	Formula	Analyses, % Nitrogen		Sulfur	
							Calcd.	Found	Calcd.	Found
1	Dimethylamine-mono-[a]	54.1	33.5–36 128–130	14 750	20[b]	$C_4H_{12}N_2S$	23.33	23.30	26.66	26.41
2	Morpholine-mono-	42.2			125–126	$C_8H_{16}O_2N_2S$	13.72	13.76	15.68	15.70
3	Morpholine-di-	85.4			124–125	$C_8H_{16}O_2N_2S_2$	11.86	11.86	27.11	27.00

Compound 1 was prepared in ethyl ether; Compounds 2 and 3 were prepared in petroleum ether (b. p. 87–98°). Low yields on the monosulfides are probably due in part to the formation of some disulfide which is lost by purification. [a] Schenck [*Ann.*, **290**, 171 (1896)] reported the speculative preparation of this compound from nitrogen sulfide and dimethylamine. [b] Crystallizing point.

It is of interest here to note that this reaction proceeds at room temperature in either acetone or ether. In acetone the reaction is completed in less than thirty-one hours while in ether more than twenty-eight days are required. The reaction product from acetone was less pure.

Amine sulfoxides such as piperidine sulfoxide did not react with carbon disulfide.

Experimental

All but three of the amine sulfides used in this paper are recorded in the literature references and were prepared accordingly. A general method for the preparation of the three new amine sulfides is described below and the properties and analyses[2] are recorded in Table I.

Amine Sulfides.—To a solution of 4.4 moles of the amine in 2000 cc. of dry inert solvent kept below 5° was added dropwise with vigorous stirring a solution of 1 mole of the respective sulfur chloride[3] dissolved in 200 cc. of the solvent. Stirring was continued until the reaction mixture had warmed up to room temperature. The precipitate was filtered off and washed with solvent.

Compound 1 was readily soluble and was obtained as a residue by distillation of the solvent through a fractionating column. The residue was purified by distillation through a six-inch Vigreux column. The clear colorless liquid is a lachrymator and possesses a repulsive odor.

Compounds 2 and 3 were filtered off with the amine hydrochloride from which they were freed by thoroughly washing of the dry precipitate with water. Evaporation under vacuum of the reaction solvent from Compound 2 yielded a small second crop of crystals. Both of the white crystalline compounds were recrystallized from ethyl alcohol.

Tetramethyl-thiuram Disulfide.—Dimethylamine monosulfide (0.25 mole) was added dropwise with cooling and stirring to 125 cc. of carbon disulfide. After stirring for three hours, the pure snow white tetramethyl-thiuram disulfide[4] was filtered off; yield 59.5 g. (99.1%); m. p. 150–152°[5] without recrystallization. Evaporation of the carbon disulfide yielded 7.25 g. of sulfur after washing with 100 cc. of benzene.

Tetraethyl-thiuram Disulfide.—Diethylamine monosulfide[6] [b. p. 79–80° (14 mm.); yield 52.2%] was treated in essentially the same manner as described above. During the reaction an unidentified gas was evolved. At completion of the reaction the carbon disulfide was removed under a vacuum, leaving a semi-crystalline residue which on washing with ether (100 cc.) became more crystalline. Recrystallization from alcohol yielded (64.8%) tetraethyl-thiuram disulfide,[7] m. p. 69–70°.

Di-(morpholyl-N-thiocarbamyl) Trisulfide.—Morpholine disulfide (0.2 mole) was dissolved in 600 cc. of carbon disulfide to which two drops of morpholine had been added and the solution was refluxed with stirring for twenty-four hours. The morpholine catalyst is unnecessary except when very pure disulfide is employed. The yellow crystalline di-(morpholyl-N-thiocarbamyl) trisulfide which separated melted at 146–147°; yield 68.5 g. (96.2%). After recrystallization from benzene the product melted at 152–153°. Evaporation of the carbon disulfide and subsequent washing of the residue with chloroform (50 cc.) yielded 5.8 g. of sulfur; calcd., 6.4 g.

Anal. Calcd. for $C_{10}H_{16}O_2N_2S_5$: N, 7.86; S, 44.94. Found: N, 7.78; S, 44.88.

Morpholine monosulfide when treated as above required a somewhat longer reflux period but yielded the same product (94.3%) as shown by a mixed melting point. Evaporation of the solvent and treatment of the residue as described above yielded only a trace of free sulfur.

Cyclopentamethylene-thiuram Disulfide and Hexasulfide.—A benzene (100 cc.) solution of piperidine monosulfide[8] (0.1 mole) (m. p. 73–75°) and 20 g. of carbon disulfide was stirred at room temperature for forty-eight hours. The white crystalline product which separated from the benzene solution was filtered off and washed with benzene; yield 8 g. (Crop 1) (calcd. 11.2 g.); m. p. 135–136°. Recrystallization from chloroform gave a product melting at 137–138° which was identified by analysis as cyclopentamethylene-thiuram hexasulfide. This melting point is higher than the melting point (129°)[9] reported in the literature.

Anal. Calcd. for $C_{12}H_{20}N_2S_8$: N, 6.25; S, 57.14. Found: N, 6.29; S, 57.10.

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(2) All of the analyses were carried out by M. C. Throdahl and R. F. Cassidy, this Laboratory.

(3) Sulfur dichloride was freshly prepared according to Pope and Heycock, English Patent 142,879.

(4) Braum and Kaiser, *Ber.*, **56**, 551 (1923).

(5) All crystalline products resulting from a reaction described in this paper, and not supported by analyses, were identified by mixed melting points.

(6) Lengfeld and Stieglitz, *Ber.*, **28**, 575 (1895); no yield given.

(7) Grodzki, *ibid.*, **14**, 2757 (1881).

(8) Michaelis, *ibid.*, **28**, 1013 (1895).

(9) Levi, *Gazz. chim. ital.*, **61**, 377 (1931).

Removal of the benzene filtrate under vacuum below 50° yielded 28 g. of a white crystalline residue. Recrystallization from alcohol yielded 22 g. (calcd. 24 g.) of cyclopentamethylene-thiuram disulfide[10]; m. p. 129–130°. An insoluble residue of 2 g. (Crop 2) remained which on recrystallization from chloroform melted at 137°.

The theoretical yields recorded above are calculated on the assumption that all of the sulfur from the piperidine monosulfide reacted to produce the hexasulfide. This assumption is further substantiated by the yields which are obtained on treating piperidine disulfide[11] (0.1 mole; m. p. 64–65°) in a like manner. The corresponding yields of the hexasulfide were: Crop 1, 17.5 g., m. p. 138–140°; Crop 2, 3.5 g. (calcd. 22.4 g.). On removal of the benzene filtrate as before, a crystalline residue of 21.5 g. was obtained. Recrystallization from alcohol gave 15 g. (calcd. 16 g.) of the disulfide; m. p. 128–129°.

Cyclohexyl Isothiocyanate.—N-Cyclohexyl-2-benzothiazole-sulfenamide[12] (167 g., m. p. 100–102°) was dissolved in 2500 cc. of ether, treated with 96 g. of carbon disulfide and the solution stirred for seventy-two hours. After removal of the solvent under vacuum, the crystalline residue was filtered off and washed with petroleum ether.

The precipitated 2-mercaptobenzothiazole was separated from the sulfur by solution in dilute sodium hydroxide (3%). Precipitation by acidification yielded 96.2 g. (90.9%) of 2-mercaptobenzothiazole; m. p. 178–179°.

Distillation of the residue after evaporation of the petroleum ether yielded 77 g. (86%) of cyclohexyl isothiocyanate,[13] b. p. 97–98° (11–12 mm.) or 222° (749 mm.).

Action of Carbon Disulfide on 2-Benzothiazole-sulfen-piperidide.—2-Benzothiazole-sulfen-piperidide[14] (0.2 mole; m. p. 79–80°) was dissolved in 700 cc. of ether containing 45 g. of carbon disulfide and the solution was allowed to stand for thirty days. The crystalline precipitate which formed was filtered off; yield 59.5 g. Evaporation of the ether yielded 7 g. of additional material.

The combined precipitate was treated with 1500 cc. of acetone and filtered, leaving a residue of 2,2′-dithiobisbenzothiazole; yield 22.8 g. (68.6%); m. p. 178–179°. Evaporation of the acetone and repeated recrystallization of the residue from alcohol after treatment with decolorizing charcoal yielded 15.8 g. (49.3%) of cyclopentamethylenethiuram disulfide; m. p. 130–131°.

Summary

1. A new reaction, that of carbon disulfide on amine sulfides and on sulfenamides, has been demonstrated; the course of the reaction is determined by the substituents present in the amine and in the amide group.

2. Four new compounds: dimethylamine monosulfide, morpholine monosulfide, morpholine disulfide, and di-(morpholyl-N-thiocarbamyl) trisulfide, have been synthesized.

3. A new method has been reported for the preparation of cyclohexyl isothiocyanate, and for tetra substituted thiuram disulfides and hexasulfides.

NITRO, WEST VA. RECEIVED MARCH 13, 1942

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[10] Ehrenberg, *J. prakt. Chem.*, [2] **36**, 129 (1887).

[11] Michaelis and Luxembourg, *Ber.*, **28**, 166 (1895).

[12] Harman, U. S. Patent 2,191,656.

[13] Skita and Rolfes, *Ber.*, **53**, 1247 (1920).

[14] Tschunkur and Kohler, U. S. Patent 2,045,888.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Hydrogen Fluoride as a Condensing Agent. XVII. The Addition of an Alkyl Chloride to the Double Bond[1]

BY J. H. SIMONS AND A. C. MEUNIER

As a continuation of the investigation of the catalytic activity of hydrogen fluoride, we have studied the reactions of an alkyl chloride with olefins. Hydrocarbons, phenols, alcohols, and acids have previously been added to olefins by the catalytic influence of hydrogen fluoride; but we have found in this investigation that an alkyl halide can be added to an unsubstituted olefin.

Tertiary butyl chloride reacted with cyclohexene to produce a number of products. Cyclohexyl chloride and cyclohexyl fluoride were produced in large amounts. The chloride was probably formed by direct addition to cyclohexene of hydrogen chloride, which was split out from the *t*-butyl chloride. A large intermediate fraction, consisting of an inseparable mixture of aliphatic chlorides and olefins, was very similar to the product obtained in this Laboratory[2] by the reaction of *t*-butyl chloride itself with hydrogen fluoride. A higher boiling chloride, obtained in an 11% yield, subsequently was identified as 1-chloro-3-*t*-butylcyclohexane.

With trimethylethylene, *t*-butyl chloride reacted to produce no isolatable addition product, because of the similarity of such an addition product to the components of the inseparable aliphatic mixture obtained from *t*-butyl chloride itself.

The secondary chloride, isopropyl chloride,

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[1] For the previous paper of this series, see THIS JOURNAL, **64**, 1356 (1942).

[2] Simons, Fleming, Whitmore and Bissinger, *ibid.*, **60**, 2267 (1938).