

chloride and metal are heated together at 350–400° for one week in a sealed, evacuated tube.

The results of the present investigation are summarized in Table I.

TABLE I

THE REACTION OF NIOBIUM PENTACHLORIDE WITH NIOBIUM

Approximately 0.6 g. of niobium metal powder was used in each experiment

Expt.	NbCl ₅ / Nb	Temp., °C.	Products	Cl/Nb in products after removal of any excess NbCl ₅
1	5/1	350	Lg. needles of NbCl ₄ with NbCl ₅	4.0/1
2	5/1	400	Lg. needles of NbCl ₄ with NbCl ₅	4.0/1
3	4/1	400	NbCl ₄ needles with NbCl ₅ , some NbCl ₃	3.6/1
4	2/1	450–500	Inert NbCl ₃ and Nb	2.70/1
5	3/2	400–450	Inert NbCl ₃ and Nb	2.71/1
6	1/1	475–500	Inert NbCl ₃ and Nb	2.68/1

The tetrachloride is somewhat soluble in ethanol, methanol, camphor, diisobutyl ketone and acetone and sparingly soluble in ethyl ether. It is believed that the tetrachloride reacts with these solvents, because hydrogen chloride vapor could be detected coming from the solutions, even when the solvents were carefully dried. Niobium tetrachloride is also moderately soluble in the monomethyl ether of ethylene glycol: no hydrogen chloride could be detected above these violet solutions.

It is surprising that the products from the last three experiments cited in Table I had an almost constant composition (approximately Nb₃Cl₈) in view of the varying conditions employed and the different ratios of pentachloride to metal. However, X-ray analyses showed that the material was a mixture of trichloride and metal. Moreover, although the trichloride can be sublimed (*in vacuo*) at about 500°,² the trichloride could not be removed from these mixtures by vacuum sublimation. Rather, at about 600°, a black sublimate of niobium tetrachloride appeared on a cold-finger condenser in a sublimation apparatus. If no condenser is employed, the tetrachloride disproportionates immediately and gives the tri- and pentachlorides.

Therefore, one must assume that niobium trichloride and niobium react at elevated temperatures and form some lower chloride (perhaps Nb₃Cl₈), which disproportionates and forms the metal and tetrachloride near 600°.

Analyses of samples from experiments 1, 2 and 3 were carried out by hydrolysis of the product in dilute ammonia. These solutions were acidified with nitric acid in order to oxidize the niobium. The niobium pentoxide, thus formed, was precipitated with ammonia, filtered, ignited and weighed and the chlorine was determined as silver chloride in the acidified filtrate. Samples from experiments 4, 5 and 6 were fused with sodium carbonate

(2) C. H. Brubaker and R. C. Young. *THIS JOURNAL*, **78**, 4179 (1951).

and the cooled melts were dissolved in water. These solutions were acidified with nitric acid, the pentoxide was precipitated with ammonia and chlorine was determined as silver chloride from the acidified filtrate.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

Dimethylcarbonyldimethylthiocarbonyl Disulfide

BY EARL C. GREGG, JR.

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The novel method by which the subject compound may be prepared prompted this note.

The action of bromine on bis-(dimethylthiocarbonyl) sulfide is to precipitate the sulfide completely as a rust colored solid of unknown structure which is comprised of one mole of the sulfide and five gram-atoms of bromine as determined by the weight of the product. This rust colored solid reacts with cold water to form a relatively unstable, colorless solid (I), m.p. 108–110° (uncor.). Elemental analysis and molecular weight determination of I require an empirical formula C₈H₁₂N₂OS₃. A polarogram of I exhibits a well-defined reduction wave, Fig. 1, characteristic of bis-(diethylthiocarbonyl) disulfide.¹ The reduction potential and

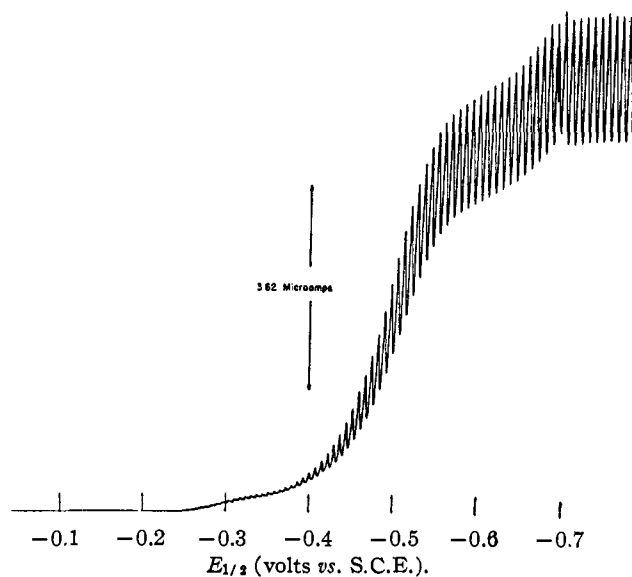


Fig. 1.

adsorption wave character suggest the presence of the >N-C-S-S-C-N< group.¹ However, an in-

fared spectrum of I, Fig. 2 center, exhibits both a carbonyl band at 5.94 μ and a thiocarbonyl band at 6.62 μ .² To fit this evidence the above structural group may be modified to >N-C-S-S-C-N<.

The infrared spectrum of I has bands common to

(1) E. C. Gregg and W. P. Tyler. *THIS JOURNAL*, **78**, 4561 (1950).
(2) Private communication. This assignment is in agreement with the extensive work not yet published on the thiocarbonyl absorption band by Mr. J. J. Shipman.

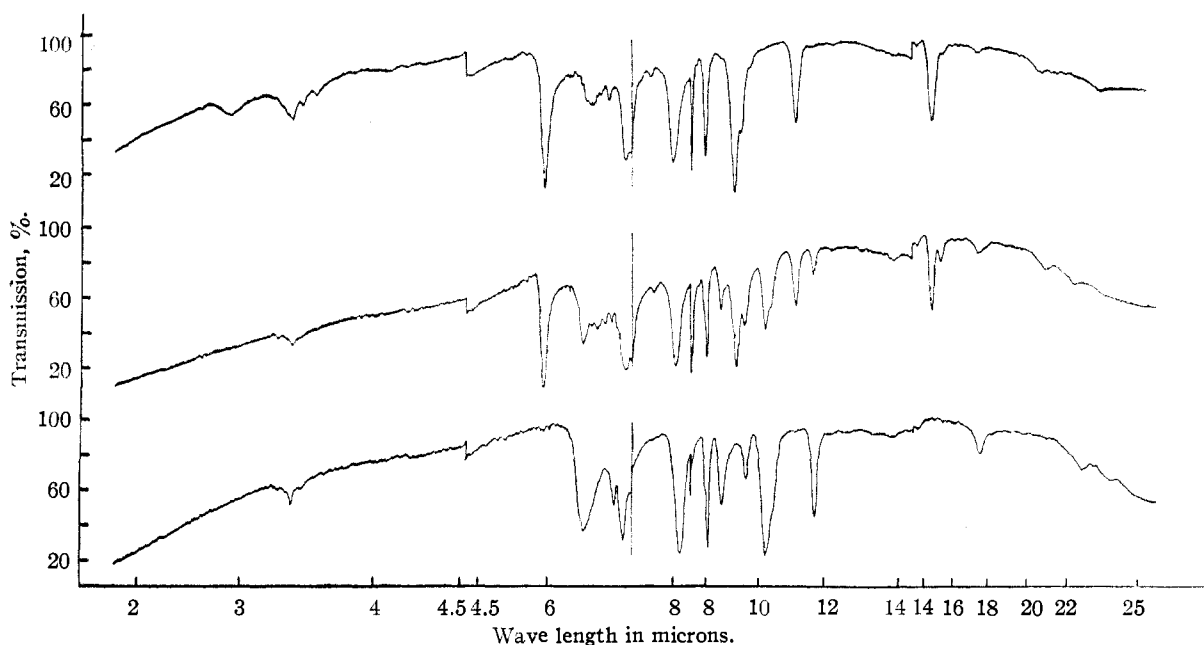
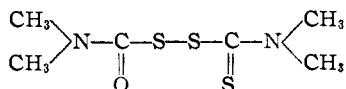


Fig. 2.—Top, dimethylcarbamylyl disulfide (mull); center, dimethylcarbamylyldimethylthiocarbamylyl disulfide (mull); bottom, dimethylthiocarbamylyl disulfide (mull); mull oils were Fluorolube from 2–7.4 μ and mineral oil from 7.4–25 μ .

the spectra of the related symmetrical disulfides, bis-(dimethylcarbamylyl) disulfide (II), Fig. 2 top, and bis-(dimethylthiocarbamylyl) disulfide (III), Fig. 2 bottom. A structure in agreement with all the above evidence is a mixed disulfide of a type which has not been reported, namely



That compound I is not an equimolar mixture of II and III may be demonstrated by the solubility of the compounds in various solvents. Compound II is soluble in water, methanol and benzene. Compound I is insoluble in water, but soluble in methanol and benzene. Compound III is insoluble in water and methanol, but soluble in benzene. If compound I were a mixture of II and III, complete solution in methanol could not be effected.

The sharp melting point of I suggests at once that I is not a double compound.

Compound I is an accelerator of rubber vulcanization and has an activity comparable to compound III, an ultra-accelerator. Compound II has no accelerator activity. Kawaoka³ found that the zinc derivative of I, zinc dimethylthiocarbamate, had strong accelerator activity. Compound I is too unstable to be used as a practical rubber accelerator.

Experimental

Dimethylcarbamylyldimethylthiocarbamylyl Disulfide.—A sample of 20 g. (0.096 mole) of bis-(dimethylthiocarbamylyl) sulfide⁴ was dissolved in 200 ml. of benzene. To this solution at room temperature was added with stirring over a five-minute period a solution of 38.4 g. (0.48 gram-atom) of bromine in 100 ml. of carbon tetrachloride. A deep orange solid precipitated immediately. The stirring was continued until a uniform suspension was obtained. The insoluble orange colored precipitate was filtered off and washed with

benzene, carbon tetrachloride and diethyl ether, respectively. The precipitate was added to 250 ml. of an ice-water mixture and the suspension stirred until all the orange solid had reacted. The temperature of the reaction mixture was not allowed to rise above 5°. A lemon-yellow solution formed and subsequently a colorless solid precipitated, m.p. 108–110° (uncor.) after one crystallization from methanol. Continued recrystallization to further purify the compound I resulted in decomposition. The weight of the colorless precipitate was 15.0 g. (0.059 mole) which is equivalent to 61% yield based on the assumption that one mole of compound I is theoretically available from one mole of bis-(dimethylthiocarbamylyl) sulfide.

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{N}_2\text{OS}_2$: C, 32.12; H, 5.39; N, 12.49; O, 7.13; S, 42.87; mol. wt., 224.36. Found: C, 31.90, 32.03; H, 5.27, 5.36; N, 12.46, 12.48; S, 42.39, 42.28; O (difference), 7.92; mol. wt., 223, 224.

Bis-(dimethylcarbamylyl) Disulfide.—A stream of carbonyl sulfide⁵ was passed into 20 ml. of anhydrous dimethylamine in a flask immersed in melting ice until five grams had been absorbed. Colorless hygroscopic crystals of dimethylammonium dimethylthiocarbamate formed. The entire mixture was added to 50 ml. of petroleum ether and the solvent removed by decantation. The salt was dissolved in 20 ml. of water and an aqueous solution of iodine was added until the iodine color just persisted. The aqueous solution was extracted with benzene and the benzene layer evaporated. The residue consisted of colorless crystals of bis-(dimethylcarbamylyl) disulfide. This compound is a powerful sternutator so that care should be taken not to allow fine particles of it to get suspended in the air. This disulfide may be crystallized from carbon tetrachloride with which it forms an addition compound of unknown composition. The addition compound decomposes when the crystals are allowed to air dry at room temperature to leave the pure disulfide, m.p. is 90–91° (uncor.). The disulfide will decompose after standing for two days at room temperature or three to four days under refrigeration. It may be kept pure indefinitely, however, if it is suspended in carbon tetrachloride where it exists as the stable addition compound. Whenever some of the compound is desired, the addition compound may be filtered off.

The polarogram was recorded on a Sargent model XX polarograph by the techniques described in reference 1. The infrared spectra were taken on the B. F. Goodrich infrared spectrometer described elsewhere.⁶

(3) Y. Kawaoka, *J. Soc. Rubber Ind. Japan*, **16**, 397 (1943).

(4) The compound was obtained from the Naugatuck Chemical Division of the U. S. Rubber Company.

(5) R. Fisher, *Biochem. Z.*, **125**, 12 (1921).

(6) Presented at the Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, June, 1951.

Acknowledgment.—The author wishes to express his gratitude to Mr. J. J. Shipman for obtaining the infrared spectra contained in this note.

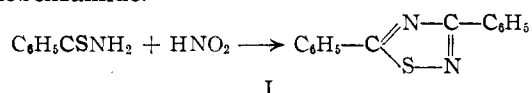
RESEARCH CENTER
THE B. F. GOODRICH CO.
BRECKSVILLE, OHIO

The Reaction of Nitrous Acid with Thiobenzamides

BY M. W. CRONYN AND T. W. NAKAGAWA

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Since nitrous acid has been used to facilitate the conversion of amides to acids¹ the reaction of this reagent with thioamides has been investigated as a possible method for the preparation of thioacids. Thiobenzamide was treated with nitrous acid in concentrated sulfuric acid, acetic acid-water, dioxane-water and absolute ethanol. In each case the principal product isolated was 3,5-diphenyl-1,2,4-thiadiazole (I). The identity of the product was established by comparison with the thiadiazole resulting from the action of iodine in alcohol on thiobenzamide.²



Experimental

The thiobenzamide, m.p. 115–116°, was prepared according to the method of Cahours.³

a. Acetic Acid-Water.—A cold solution of 5.0 g. of sodium nitrite in 50 ml. of water was added dropwise with stirring to a solution of 8.0 g. of thiobenzamide in 130 ml. of glacial acetic acid and 100 ml. of water cooled in an ice-bath. The mixture was diluted with water and 4 g. of a crude solid, m.p. 76–79°, was obtained. Solution of the crude material in 150 ml. of absolute ethanol gave 1.6 g. of a red insoluble solid; and, after treatment with Nuchar, there was obtained from the alcohol solution 2.4 g. (30%) of a product, m.p. 85–88° after crystallization from alcohol-water. Repeated recrystallization of a sample gave material with a m.p. of 89–90°. Analysis indicated a diphenylthiadiazole. By the action of iodine in ethanol on thiobenzamide 3,5-diphenyl-1,2,4-thiadiazole was prepared in 77% yield with a melting point of 87–88°. A mixed melting point with the nitrous acid product was undepressed.

b. Dioxane-Water.—Using the same procedure in a mixture of dioxane and 2 *N* hydrochloric acid there was obtained 3 g. of a crude product; m.p. 78–82°, which gave 2.2 g. of purified material, m.p. 87–88°.

c. Butyl Nitrite in Ethanol.—To a cold solution of 2.0 g. of thiobenzamide and 0.43 g. of hydrogen chloride in 30 ml. of absolute ethanol there was added, dropwise with stirring, 1.5 g. of freshly distilled butyl nitrite. The reaction mixture was allowed to come to room temperature and was poured into water. After crystallization from ethanol there was obtained 1.5 g. (75%) of 3,5-diphenyl-1,2,4-thiadiazole; m.p. 86.5–87.5°.

d. Concentrated Sulfuric Acid.—The procedure of Sudborough¹ for the conversion of benzamide to the acid was applied. A crude yield of 2.7 g. was obtained from 5 g. of the thiobenzamide. The product was more impure than in the other cases but the principal constituent had a m.p. of 81–85° and its mixed melting point with 3,5-diphenyl-1,2,4-thiadiazole gave no depression.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA

(1) L. Bouveault, *Bull. soc. chim.*, [3] 9, 368 (1892); J. J. Sudborough, *J. Chem. Soc.*, 67, 601 (1895).

(2) A. W. Hofmann and S. Gabriel, *Ber.*, 25, 1578 (1892).

(3) Cahours, *Compt. rend.*, 27, 239 (1848); S. Gabriel and P. Heymann, *Ber.*, 23, 158 (1890).

The Reaction of Disubstituted Nitrosamines with Lithium Aluminum Hydride¹

BY CALVIN HANNA AND F. W. SCHUELER

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Previously² we reported the preparation of unsymmetrical dimethylhydrazine by adding 1 mole of *N*-nitrosodimethylamine to 2 moles of lithium aluminum hydride in ether. Using similar conditions, 1 mole of *N*-nitrosodiphenylamine added to 4 moles of LiAlH₄ gave only diphenylamine. The compounds used in this study were the mixed alkylaryl nitrosamine, *N*-nitrosomethylaniline, the dicyclic substituted nitrosamine, *N*-nitrosodicyclohexylamine which was chosen as a dialkyl nitrosamine of dimensions comparable to nitrosodiphenylamine. Finally, *N*-nitrosopiperidine, as a heterocyclic alkyl type, completed the group studied. The nitroso compounds were prepared by method of Hartman and Roll³ previously reported in the literature.

The above nitrosamines were reduced using lithium aluminum hydride to give 1-methyl-1-phenylhydrazine (77%), 1,1-dicyclohexylhydrazine (48%), and *N,N*-pentamethylenehydrazine (75%). The above results would indicate that dialkyl, alkylaryl, dicyclohexyl and cyclic nitrosamines may be satisfactorily reduced to the corresponding unsymmetrical hydrazine using lithium aluminum hydride. *N*-Nitrosodiphenylamine is reduced by a large excess of lithium aluminum hydride to diphenylamine.² Poirier and Benington⁴ have demonstrated that under controlled conditions, by adding *N*-nitrosodiphenylamine to an equal molar quantity of lithium aluminum hydride or better yet through an "inverse" order of addition, unsymmetrical diphenylhydrazine may be obtained in yields up to 90%. Whether the reduction of nitrosamines, particularly diarylnitrosamines, stops at the hydrazine or proceeds to the amine depends greatly upon the quantity of lithium aluminum hydride. The N–O bond is much more polar than the N–N bond, consequently, it must be attacked first by lithium aluminum hydride. The polar character of the N–N bond is presumably enhanced by aromatic rings so that excess lithium aluminum hydride readily converts diarylnitrosamines directly to diarylamines.

Experimental

Reduction of Nitrosamines.—To 3.6 g. (0.1 mole) of lithium aluminum hydride in 150 ml. of tetrahydrofuran was slowly added a solution of 0.1 mole of the nitrosamine in 200 ml. of tetrahydrofuran. A colored complex forms. This is especially true with *N*-nitrosomethylaniline which yields a pink complex during the addition. This color should be discharged by vigorous stirring before more nitrosamine is added otherwise the reaction, once started, will react violently with much foaming. After the completion of the addition of the nitrosamine, the reaction mixture was stirred for an additional hour. Acetone (5 ml.) was used to decompose the excess reagent and to the resulting mixture 100 ml. of 30% sodium hydroxide was added with stirring.

(1) This work was aided by a grant from the U. S. Public Health Service.

(2) F. W. Schueler and Calvin Hanna, *THIS JOURNAL*, 73, 4996 (1951).

(3) W. W. Hartman and L. V. Roll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 460.

(4) R. H. Peirier and F. Benington, *THIS JOURNAL*, 74, 8192 (1952).