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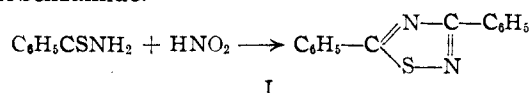
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The Reaction of Nitrous Acid with Thiobenzamides

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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.

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(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.*, 22, 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 LiAlH_4 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. Poirier and F. Benington, *THIS JOURNAL*, 74, 8192 (1952).

The tetrahydrofuran layer was separated and evaporated *in vacuo* to an oil. This oil was fractionally distilled, dissolved in abs. ether and dried over sodium hydroxide pellets. The pure hydrazine was obtained by fractionally distilling this ether solution.

N-Nitrosomethylaniline was reduced to 1-methyl-1-phenylhydrazine⁵ in 77% yield which is an oil boiling at 106–109° (13 mm.).

N-Nitrosopiperidine was reduced to N,N-pentamethylenehydrazine⁶ in 75% yield. It is an oil boiling at 146–148° (730 mm.).

N-Nitrosodicyclohexylamine was reduced to 1,1-dicyclohexylhydrazine in 48% yield. It is a white crystalline solid boiling at 95–98° (4 mm.) which sublimes above 162°. The hydrochloride forms white flaky crystals from ether, m.p. 238–240° (cor.). The methiodide forms small white plates from abs. ether, m.p. 250–252° (cor.). *Anal.* Calcd. for hydrochloride C₁₂H₂₄N₂Cl: Cl, 15.23. Found: Cl, 14.94. *Anal.* Calcd. for methiodide C₁₂H₂₇N₂I: I, 37.51. Found: I, 37.06.

Skita and Rolfe⁷ attempted to prepare 1,1-dicyclohexylhydrazine by reducing N-nitrosodicyclohexylamine with zinc and hydrochloric acid and obtained dicyclohexylamine. When they used zinc in absolute alcohol with acetic acid no hydrazine could be isolated.

The 1,1-dicyclohexylhydrazine has a nauseating and irritating odor beyond that produced by high molecular weight amines. This compound in lethal doses in white mice produces convulsions characteristic of central nervous system stimulation. The LD₅₀ dose in mice by the intraperitoneal route is 77 mg./kg.

(5) W. W. Hartman and L. V. Roll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 418.

(6) Knorr, *Ann.*, **221**, 299 (1883).

(7) Skita and Rolfe, *Ber.*, **53**, 1251 (1920).

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Preparation of Telluric Acid

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Several methods for the preparation of telluric acid have been reported in the literature and are listed by Gilbertson.¹ These methods either give an impure product or require large excesses of oxidizing agent and special preparation of the tellurium. The preparation as developed by Mathers and co-workers² is the most widely used. However, purification of the crude telluric acid thus obtained required repeated recrystallizations from concentrated nitric acid solutions.

Hydrogen peroxide is the ideal oxidizing agent, but when it is used alone or in the presence of an acid, a very large excess of peroxide is needed. In basic solutions the oxidation of tellurium dioxide by a slight excess of hydrogen peroxide proceeds nicely to completion. By using ammonia solutions, the by-products are readily separated from the telluric acid.

Experimental

The commercial grade tellurium dioxide³ (approximately 76% pure) was found to contain impurities which vigorously catalyzed the decomposition of hydrogen peroxide. The tellurium dioxide was purified by dissolving it in 5 N sodium hydroxide. After filtering, the tellurium dioxide was reprecipitated by adding 10 N nitric acid to the filtrate until the solution was acid to phenolphthalein. The supernatant

(1) L. I. Gilbertson, *This Journal*, **55**, 1460 (1933).

(2) F. C. Mathers, C. M. Rice, H. Broderick and R. Torney, *Inorganic Syntheses*, **3**, 145 (1950).

liquid was then decanted and the precipitate washed five times with distilled water. The purified material was dried for 24 hours at 110°. This method produced a compound of about 98% purity. Subsequent repetition of the above procedure made no appreciable change in the purity, because of coprecipitation of sodium salts.

Preliminary determinations revealed no apparent reaction between pure tellurium dioxide and 30% hydrogen peroxide. However, in the presence of dilute ammonia solution some oxidation occurred with the formation of a gum which prevented further reaction. Nevertheless the reactions occurring in concentrated ammonium hydroxide produced a white crystalline precipitate of an ammonium tellurate which did not interfere with the oxidation of the tellurium dioxide.

Procedure.—A ten-gram sample of tellurium dioxide, purified and oven-dried, was placed in a 250-ml. erlenmeyer flask fitted with a rubber stopper. To the flask was added a mixed solution of 10 ml. of 30% hydrogen peroxide and 75 ml. of concentrated ammonium hydroxide. After the pressure generated by the initial reaction had subsided the flask was stoppered and set aside. During this period, the flask was frequently shaken. After 24 hours, the mixture was heated on a steam-bath until the vapors were free of ammonia, and the volume of solution had been reduced to 45 ml. Next, 10 ml. of concentrated nitric acid was added to the above solution. During the addition of the nitric acid, the ammonium tellurate dissolved. After 24 hours the supernatant liquid was removed from the crystals of telluric acid which had formed, and the liquid was further concentrated to 20 ml. Another 10 ml. of concentrated nitric acid was added and after an additional 24 hours the crops of crystals were combined. Further purification was accomplished by one recrystallization from distilled water. This method produces telluric acid of 99.99% purity and in yields of 75–80%. The telluric acid was analyzed by the method of Gooch and Howland.³ The flame test and Nessler reagent showed that the telluric acid was not contaminated with either sodium or ammonium ions.

(3) F. A. Gooch and J. Howland, *Am. J. Sci.*, [3] **48**, 375 (1894).

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The Effect of Fluorine on Praseodymium Trifluoride

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Since it has been shown that cerium tetrafluoride could be prepared quantitatively from cerous fluoride with fluorine at 500°,¹ it was thought to be of interest to determine what effect elemental fluorine would have on praseodymium trifluoride at this and other temperatures. Klemm² fluorinated praseodymium trichloride and obtained a mixture of the chloride and fluoride.

Experimental

Fluorine was prepared by the apparatus described by Von H. von Wartenberg.¹ A graphite anode was used. The rate of production of fluorine was about 35 ml. per minute.

A combustion boat was made from a fluorite cupel since most other substances which might be used for a boat are reacted upon by fluorine at temperatures above 500°.

A nickel tube $1/8$ " in thickness, $7/8$ " inside diameter and 14" in length was used to house the combustion boat. The reaction tube was heated to the desired temperatures in an electric combustion furnace. The joints between the apparatus and the reaction tube were sealed with plaster of Paris. Before each run the system was dried by air.

Praseodymium trifluoride was prepared by the addition of hydrofluoric acid to a solution of the trichloride which had been warmed to 80°. The precipitate was filtered and

(1) Von H. von Wartenberg, *Z. anorg. allgem. Chem.*, **244**, 337 (1940).

(2) Klemm and Henkel, *ibid.*, **220**, 180 (1934).