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

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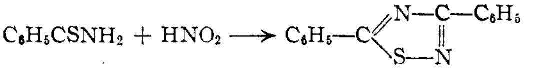
The Reaction of Nitrous Acid with Thiobenzamides

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

RECEIVED FEBRUARY 25, 1952

Since nitrous acid has been used to facilitate the conversion of amides to acids[1] 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]



I

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°.[2] 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 Sudborough[1] 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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The Reaction of Disubstituted Nitrosamines with Lithium Aluminum Hydride[1]

BY CALVIN HANNA AND F. W. SCHUELER

RECEIVED MARCH 3, 1952

Previously[2] 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 Roll[3] 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 Benington[4] 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.

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

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