[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

CARBITHIOIC ACID STUDIES. II. CYCLOHEXYLCARBITHIOIC ACID AND VARIOUS DERIVATIVES

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A number of carbithioic acids have been reported; however, the chemistry of these compounds seems to have been neglected. Recently Bost and Mattox[1] studied tolyl-4-carbithioic acid and found that the –CSSH group showed a striking resemblance to the –COOH group in some cases, while in others a great dissimilarity was noted.

In view of the fragmentary knowledge of the reactions of the –CSSH group, and of carbithioic acids in general, work has been extended to a new acid, cyclohexylcarbithioic acid. Its synthesis, its chemical and physical properties, and certain derivatives are described.

Cyclohexylcarbithioic acid resembles its oxygen analog in the formation of salts, esters and toluides. It yields neither an acid chloride nor a thioamide. Oxidizing agents convert it into hexahydrobenzoic acid. The thioacyl peroxide was not obtainable.

Experimental Part

Cyclohexylcarbithioic Acid.—The Grignard reagent was made in the usual way from 0.5 mole of cyclohexyl bromide and 12.2 g. of magnesium. To this was added 38.1 g. of carbon disulfide and the method adopted by Bost and Mattox[1] in the preparation of tolyl-4-carbithioic acid followed, both in the preparation of the acid and in its purification.

Cyclohexylcarbithioic acid is a reddish-brown liquid with a putrid odor, and slowly decomposes on exposure to air. It distils with decomposition. It is soluble in most of the organic solvents. The acid is rather stable in ether solution. All its salts are stable. The sodium salt was used in the preparation of most of the derivatives.

Silver Salt of Cyclohexylcarbithioic Acid.—A saturated solution of silver acetate was added slowly, with stirring, to an ether solution of the acid until precipitation was complete. The precipitate was filtered, washed with water, alcohol and toluene, and dried. It is slightly soluble in hot alcohol and toluene.

Preparation of Esters.—The methyl and ethyl esters were made from the sodium salt of the acid and the corresponding alkyl sulfates. The propyl and butyl esters were made by refluxing equivalent quantities of the sodium salt and the corresponding alkyl bromides. The esters were purified by the usual method.

***p*-Toluide of Cyclohexylcarbithioic Acid.**—Ten grams of *p*-toluidine, 6 g. of the dry sodium salt and 6 ml. of concentrated hydrochloric acid were heated to gentle boiling in a beaker for thirty minutes. The mass was extracted with 50 ml. of hot toluene, boiled with charcoal, filtered and allowed to crystallize. The toluide separated in large colorless needles. It is soluble in hot alcohol, toluene and benzene.

Attempt to Prepare the Thioamide.—The method adopted by Bost and Mattox[1]

[1] Bost and Mattox, THIS JOURNAL, **52**, 332 (1930).

in the preparation of the amide of tolyl-4-carbithioic acid was used. After a few days a solid separated. It consisted of white glistening leaflets melting at 185–187°. The product contained nitrogen but no sulfur. Further investigation showed the substance to be the amide of hexahydrobenzoic acid.

Action of Oxidizing Agents.—To an ether solution of the acid at room temperature was added concentrated nitric acid with stirring until the color was discharged. After several hours the product was extracted with ether and purified through its sodium salt. It melted at 28° and gave negative tests for sulfur. Other tests showed the substance to be hexahydrobenzoic acid.

TABLE I

DATA ON DERIVATIVES

Compound	Color	Solvent	M. p. or b. p., °C.
1 Silver salt	Brick-red	Insoluble	163
2 *p*-Toluide	Colorless	Alcohol	160
3 Methyl ester	Orange-red	....	90 (3 mm.)
4 Ethyl ester	Orange-red	....	106 (5 mm.)
5 *n*-Propyl ester	Orange-red	....	106 (3 mm.)
6 *n*-Butyl ester	Orange-red	....	145 (5 mm.)

TABLE II

ANALYSES

		Sulfur, %		Silver, %	
	Formula	Calcd.	Found	Calcd.	Found
1	$C_7H_{11}S_2Ag$	24.01	23.99	40.39	40.31
2	$C_{14}H_{19}NS$	13.75	13.87		
3	$C_8H_{14}S_2$	36.80	36.69		
4	$C_9H_{16}S_2$	34.06	34.12		
5	$C_{10}H_{18}S_2$	31.70	31.80		
6	$C_{11}H_{20}S_2$	29.65	29.75		

Summary

1. A new carbithioic acid has been prepared and its properties described.

2. The acid readily forms salts, esters and toluides.

3. Attempts to prepare the acid chloride and thioamide met with failure.

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