with an excess of benzoic anhydride and the whole warmed on a water-bath. The mixture became soft, then hardened again. Benzoic acid sublimed during the reaction. The mixture was repeatedly extracted with ligroin in order to remove all of the benzoic acid and unchanged benzoic anhydride. The ester was recrystallized from alcohol and water and found to melt at 153°; yield, 1.02 g.

Anal. Subs., 0.5639: 28.9 cc. of N (25°, 748.3 mm.). Calcd. for $C_{14}H_{11}O_4N$: N, 5.45. Found: 5.50.

The Potassium Salt of the Benzoyl Ester was prepared by the addition of the calculated quantity of alcoholic potash to the ester in absolute alcohol solution. The salt was precipitated by the addition of absolute ether.

The salt after drying for one hour over concentrated sulfuric acid was treated like the potassium salt of the acetyl ester and was found to explode after fifteen seconds when immersed in a bath at 81°. No odor of isocyanate was noticed when the substance exploded.

The salt on being dissolved in water and heated rearranged giving potassium benzoate and oxycarbanil. The potassium benzoate was recognized by causing benzoic acid to precipitate by the addition of acid to the solution. The benzoic acid after recrystallization melted at 121.5° and resembled in all respects the benzoic acid described in the literature.

Sodium Salt of Benzoyl Ester was prepared by treating the ester in absolute alcohol solution with the calculated quantity of sodium alcoholate. On the addition of absolute ether the sodium salt separated out. It decomposed on heating but gave no odor of isocyanate. In water solution it underwent rearrangement very much as the potassium salt.

Summary

The acetyl and benzoyl esters of salicylhydroxamic acid and their salts were made. Upon undergoing the Beckmann rearrangement these salts gave oxycarbanil instead of a *sym.*-di-substituted urea usually obtained under similar conditions from the alkali salts of the esters of other hydroxamic acids.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

THE REACTION OF PARA-SUBSTITUTED BENZYL CHLORIDES WITH SODIUM HYDROGEN SULFIDE

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RECEIVED JULY 14, 1927 PUBLISHED OCTOBER 5, 1927

Several years ago in connection with some work in progress at that time, there was needed some *p*-cyanobenzyl mercaptan. In attempting to prepare this compound by the action of sodium hydrogn sulfide on *p*-cyanobenzyl chloride a mixture of *p*-cyanobenzyl sulfide and *p*-cyanobenzyl disulfide was obtained instead of the mercaptan.[1] Shortly after our observation Horn[2] obtained the same results using *p*-nitrobenzyl chloride and found that the *p*-nitrobenzyl mercaptan was incorrectly described in the literature. Chloro-acetophenone also gives a mixture

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[1] Friedman, *Thesis*, University of Kentucky, **1922.**

[2] Horn, THIS JOURNAL, **43,** 2610 (1921).

of the corresponding sulfide and disulfide when treated with sodium hydrogen sulfide.[3]

Since *p*-cyanobenzyl mercaptan and its derivatives are not described in the literature it was thought advisable to study the reaction of sodium hydrogen sulfide with *p*-cyanobenzyl chloride.

In order to study this reaction it was first necessary to prepare *p*-cyanobenzyl mercaptan and the corresponding sulfide and disulfide. The mercaptan was made by hydrolyzing 2-*p*-cyanobenzylmercapto-4-methyl-6-oxypyrimidine with dilute hydrochloric acid. The sulfide and disulfide were made by the usual methods.

The following reactions will account for the formation of *p*-cyanobenzyl sulfide and disulfide.

I $p\text{-CNC}_6\text{H}_4\text{CH}_2\text{Cl} + \text{NaHS} \longrightarrow p\text{-CNC}_6\text{H}_4\text{CH}_2\text{SH} + \text{NaCl}$

II $2\ p\text{-CNC}_6\text{H}_4\text{CH}_2\text{SH} + \text{O} \longrightarrow (p\text{-CNC}_6\text{H}_4\text{CH}_2)_2\text{S}_2 + \text{H}_2\text{O}$

III $p\text{-CNC}_6\text{H}_4\text{CH}_2\text{SH} + \text{NaHS} \longrightarrow p\text{-CNC}_6\text{H}_4\text{CH}_2\text{SNa} + \text{H}_2\text{S}$

IV $p\text{-CNC}_6\text{H}_4\text{CH}_2\text{SNa} + p\text{-CNC}_6\text{H}_4\text{CH}_2\text{Cl} \longrightarrow (p\text{-CNC}_6\text{H}_4\text{CH}_2)_2\text{S} + \text{NaCl}$

The formation of the disulfide is due to oxidation of the mercaptan and can be eliminated by carrying out the reaction in a non-oxidizing medium such as hydrogen or hydrogen sulfide. The formation of the sulfide first necessitates the formation of the sodium salt, which in turn reacts with *p*-cyanobenzyl chloride. With a slight excess of sodium hydrogen sulfide, as is generally used, the sulfide will be formed provided Reactions III and IV proceed as fast or faster than Reaction I. By adding sodium hydrogen sulfide to the reaction mixture as fast as it is used up, the mercaptan should be formed in greater amount provided the speed of Reaction I is the greatest. Only traces of the mercaptan could be obtained using this condition, which indicated that Reactions III and IV proceed as fast as Reaction I or faster. The only condition that gave enough mercaptan to isolate was when hydrogen sulfide was used as the non-oxidizing medium and sodium hydrogen sulfide was added as fast as it reacted. Other non-oxidizing media such as hydrogen gave only traces of the mercaptan. This can be explained by the retarding action of hydrogen sulfide on Reaction III. The best experimental conditions for the formation of the mercaptan are given in the experimental part, though many other runs were made using various solvents and temperatures.

In order to see what influence other groups might have, two small runs were made using *p*-carbethoxybenzyl chloride. In this case the resulting crude mercaptan and sulfide were obtained in about equal amounts. These results would indicate that the different groups in the para position affect the speeds of Reactions I, III and IV, but in varying amounts. The

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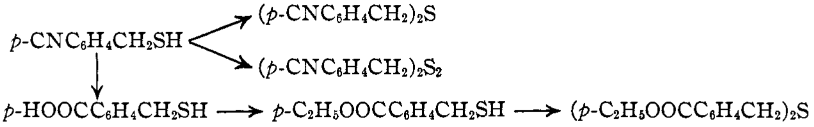
[3] (a) Tafel and Mauritz, *Ber.*, **23**, 3474 (1890). (b) Bertil Groth, *Arkiv. Kemi Mineral Geol.*, **9**, No. I, 63 (1924).

negative groups such as the nitro, cyano and carbethoxy seem to increase the speeds of Reactions III and IV, though not to the same extent. The positive chlorine in the para position, on the other hand, does not seem to increase the speeds of Reactions III and IV, since *p*-chlorobenzyl mercaptan has been made by treating *p*-chlorobenzyl chloride with potassium hydrogen sulfide and no mention was made of sulfide formation.[4]

During the course of these experiments the following compounds were made, as shown by the diagram.



$$\begin{tikzcd}
 & (p\text{-}CNC_6H_4CH_2)_2S & \\
p\text{-}CNC_6H_4CH_2SH \arrow[ur] \arrow[dr] \arrow[dd] & & \\
 & (p\text{-}CNC_6H_4CH_2)_2S_2 & \\
p\text{-}HOOCC_6H_4CH_2SH \arrow[r] & p\text{-}C_2H_5OOCC_6H_4CH_2SH \arrow[r] & (p\text{-}C_2H_5OOCC_6H_4CH_2)_2S
\end{tikzcd}$$

p-Carboxybenzyl mercaptan could not be made from *p*-carboxybenzyl chloride by treating with sodium hydrogen sulfide since the sodium salt of this acid reacts with itself to give a complex ester.[5] Attempts to prepare the sulfide or disulfide of *p*-carboxybenzyl mercaptan directly from it or by hydrolysis of the corresponding cyano or carbethoxy compounds always resulted in amorphous, white compounds having no definite melting point and insoluble in all solvents. The *p*-cyanobenzyl disulfide is light yellow, which may be due to partial dissociation into the free radicals.[6]

Experimental Part

2-*p*-Cyanobenzylmercapto-4-methyl-6-oxypyrimidine.—To 750 cc. of absolute alcohol were added 12.14 g. of sodium and 75 g. of 2-thio-4-methyl-6-oxypyrimidine. The mixture was stirred vigorously while being heated for two hours in a boiling water-bath. To the resulting sodium salt was added 80.4 g. of *p*-cyanobenzyl chloride and the heating and stirring were continued until the reaction mixture was neutral. On cooling, the white amorphous solid was filtered off, washed well with water and dried at 110° for 12 hours; weight, 133 g. The crude product was crystallized from glacial acetic acid in white, microscopic plates, m. p. 240–241°; yield 110 g. or 86.5%.

Anal. Calcd. for $C_{13}H_{11}ON_3S$: N, 16.34. Found: 16.27, 16.28.

***p*-Cyanobenzyl Mercaptan.**—One hundred and fifty g. of 2-*p*-cyanobenzylmercapto-4-methyl-6-oxypyrimidine and 1500 cc. of 6 *N* hydrochloric acid were heated to boiling with stirring for one hour. The solid pyrimidine gradually became oily and finally a thick oil remained. The mixture on cooling was extracted with ether, the ether layer washed with dilute sodium carbonate solution and water and then dried over anhydrous sodium sulfate. On distilling off the ether 82 g. of crude oil were obtained, which distilled at 135–138° at 7 mm. The oil solidified on cooling to a white crystalline mass having the characteristic garlic odor, m. p. 37°; yield 75 g. or 86.2%. It gave a white precipitate with alcoholic mercuric nitrate.

Anal. Calcd. for C_8H_7NS: S, 21.47. Found: 20.63, 20.79.

***p*-Cyanobenzyl Sulfide.**—The calculated amount of sodium was added to 100 cc.

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[4] Jackson and White, *Am. Chem. Jour.*, **2**, 167 (1880).

[5] Barkenbus and Holtzclaw, This Journal, **47**, 2189 (1925).

[6] Lecher, *Ber.*, **48**, 524, 1425 (1915).

of absolute alcohol and to this solution were added 5 g. of *p*-cyanobenzyl mercaptan and 5 g. of *p*-cyanobenzyl chloride. The mixture was refluxed for four hours until neutral. The alcohol was evaporated off and the crude solid shaken up with water, filtered and crystallized from 95% alcohol, giving fine, white, odorless needles; m. p. 115°; yield 6 g. or 67.7%.

Anal. Calcd. for $C_{16}H_{12}N_2S$: N, 10.61. Found: 10.47, 10.48.

***p*-Cyanobenzyl Disulfide.**—Five g. of *p*-cyanobenzyl mercaptan was dissolved in 100 cc. of 95% alcohol and 25 cc. of concentrated ammonium hydroxide added. After standing exposed to the air for four days a light yellow, crystalline solid came out and was crystallized from 95% alcohol giving light yellow, odorless, flat needles; m. p. 148°; yield 3.5 g. or 70.4%.

Anal. Calcd. for $C_{16}H_{12}N_2S_2$: N, 9.46. Found: 9.32.

Reaction of Sodium Hydrogen Sulfide with *p*-Cyanobenzyl Chloride.—Fifty g. of *p*-cyanobenzyl chloride was dissolved in 400 cc. of absolute alcohol and to this solution was added an absolute alcohol solution of sodium hydrogen sulfide made by saturating a sodium ethylate solution with hydrogen sulfide. A fast stream of hydrogen sulfide was passed into the boiling alcohol solution during the experiment. The sodium hydrogen sulfide solution was added very slowly while the mixture was stirred vigorously and the reaction mixture was tested every minute for alkalinity with methyl red. At no time was it alkaline until the calculated amount of sodium hydrogen sulfide had been added, indicating that the reaction took place as fast as it was added. As soon as the reaction mixture became alkaline, it was made slightly acid with hydrochloric acid and allowed to stand overnight in an atmosphere of hydrogen sulfide. A large amount of light yellow needles separated out. These were filtered off with suction, washed well with alcohol and then suspended in water to dissolve the sodium chloride. They were again filtered, washed well with water and dried at 100° for twelve hours. On crystallizing from 95% alcohol, long white needles were obtained, m. p. 115°, which indicated the sulfide.

The alcoholic filtrate was evaporated in a stream of hydrogen and a reddish oil mixed with some salt was left. The oil was taken up in ether, dried over anhydrous sodium sulfate and distilled. Eleven g. of crude oil was obtained, which on redistillation gave 5 g. of *p*-cyanobenzyl mercaptan; m. p. 32°; yield 10.2%; yield of *p*-cyanobenzyl sulfide, 34 g. or 78.2%. This was the best yield obtained of the mercaptan out of many different runs.

Reaction of Sodium Hydrogen Sulfide with *p*-Carbethoxybenzyl Chloride.—The calculated amount of alcoholic sodium hydrogen sulfide solution was added very slowly to a boiling solution of 35 g. of *p*-carbethoxybenzyl chloride in 175 cc. of absolute alcohol. Sodium chloride precipitated out immediately, and the reaction mixture did not become alkaline until all of the sodium hydrogen sulfide solution had been added. It was then made slightly acid and poured into five volumes of water. An oil separated out which was taken up in ether and dried over anhydrous sodium sulfate. On evaporating the ether, 33 g. of crude oil remained, which on distilling yielded 19.7 g. of a clear oil with a garlic odor; b. p. 135–160° at 8 mm. The oil, even on redistilling, was impure, as shown by analysis, but it was identified as *p*-carbethoxybenzyl mercaptan by converting some of it into the sulfide. The residue from the original distillation was taken up in 95% alcohol, decolorized with carbon, and allowed to crystallize, giving long white asbestos-like needles; m. p. 78°; yield 9 g. Analysis showed this to be *p*-carbethoxybenzyl sulfide.

Anal. Calcd. for $C_{20}H_{22}O_4S$: S, 8.93. Found: 9.22, 9.16.

***p*-Carboxybenzyl Mercaptan.**—Five g. of *p*-cyanobenzyl mercaptan and 150 cc. of concentrated hydrochloric acid were heated to boiling with vigorous stirring for three hours. A white solid separated out which was filtered off, dissolved in dilute sodium carbonate solution and then filtered from a small amount of insoluble material. On acidification a white, amorphous solid was obtained which was crystallized from 95% alcohol, giving white microscopic needles with only a faint odor; m. p. 176°; yield 5 g. or 89.3%.

Anal. Calcd. for $C_8H_8O_2S$: S, 18.89. Found: 18.41, 18.50.

p-Carbethoxybenzyl Mercaptan.—Twenty-two g. of p-carboxybenzyl mercaptan was dissolved in 200 cc. of absolute alcohol which had been previously saturated with dry hydrogen chloride gas and the mixture heated under a reflux condenser for twelve hours. The resulting solution was filtered from a small amount of insoluble material, evaporated to 100 cc. and then poured into 500 cc. of water. The oil which separated was dissolved in ether, the ether solution washed free from acid and then dried over anhydrous sodium sulfate. After evaporating off the ether the remaining oil was distilled to a colorless and nearly odorless oil; b. p. 140–141° at 6 mm.; yield 19.1 g. or 74.2%.

Anal. Calcd. for $C_{10}H_{12}O_2S$: S, 16.32. Found: 16.15, 16.29.

p-Carbethoxybenzyl Sulfide.—The calculated amount of freshly prepared alcoholic sodium sulfide solution was slowly added with rapid stirring to a boiling solution of 5 g. of p-carbethoxybenzyl chloride in 100 cc. of alcohol. When all the sodium sulfide solution had been added, the mixture was cooled and diluted with water. The white precipitate was filtered off and crystallized from alcohol producing white, asbestos-like needles; m. p. 78°; yield 3.5 g. or 77.7%. A mixture of this compound with the product obtained by the reaction of p-carbethoxybenzyl chloride with sodium hydrogen sulfide had the same melting point.

Summary

The reaction of p-cyanobenzyl chloride with sodium hydrogen sulfide has been studied, and a mixture of p-cyanobenzyl sulfide and disulfide was obtained instead of the mercaptan. If a non-oxidizing atmosphere is used, only a very small amount of p-cyanobenzyl mercaptan is formed, the main product being the sulfide. Negative groups such as the nitro, cyano and carbethoxy in the para position of substituted benzyl chlorides favor the formation of the sulfide, while the positive chlorine favors the formation of the mercaptan.

p-Cyanobenzyl mercaptan, p-carboxybenzyl mercaptan, p-carbethoxybenzyl mercaptan, p-cyanobenzyl sulfide, p-cyanobenzyl disulfide and p-carbethoxybenzyl sulfide have been prepared and described.

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