be detected in the heated product. When the flesh had become somewhat stale, the same heat treatment yielded the gas in relatively large amounts. Added cystine increased the amount of residual hydrogen sulfide only in the case of the stale flesh. The cause of this difference in results with fresh and stale flesh was traced to the ability of the fresh flesh, and, conversely, the inability of the stale flesh, to destroy hydrogen sulfide formed by the heating. The gas is destroyed apparently by oxidation. Cystine added to fresh flesh, as well as that present in combined form in the flesh, is partially destroyed by this heating.

On the plausible assumption that the effect of processing a can of fish is the same as the effect of the above-mentioned heat treatment in a sealed tube, it may be concluded that the presence of considerable hydrogen sulfide in a canned product of this nature indicates that the raw material at the time of canning was in poor condition.

It is recognized that sulfur compounds other than cystine may exist in the protein or other constituents of the flesh examined, but the possibility of their existence therein need not be considered in connection with this study. While these results were obtained with fish flesh, which procedure had the advantage that the raw material could be obtained in fresh condition at any time desired with little inconvenience, it is probable that similar results would be obtained with other flesh products. Therefore, the conclusion seems justified that when flesh products in general are heated at temperatures above 100° some of the cystine is destroyed and hydrogen sulfide derived therefrom may be detected in the product, providing the gas is not oxidized by the material during the heating process.

WASHINGTON, D. C.

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

THE BECKMANN REARRANGEMENT OF SALICYLHYDROXAMIC ACID DERIVATIVES[1]

BY ALFRED W. SCOTT AND J. H. MOTE

RECEIVED JUNE 20, 1927 PUBLISHED OCTOBER 5, 1927

Several benzene derivatives containing an hydroxyl group and a nitrogenous group in the ortho position to each other can be converted into oxycarbanil by suitable treatment.[2] Especially in the cases of urea and urethan derivatives is there the possibility of the intermediate formation

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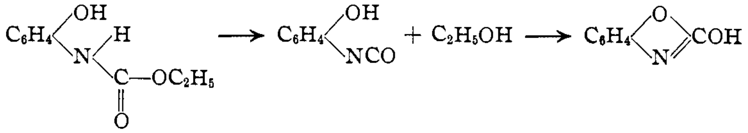
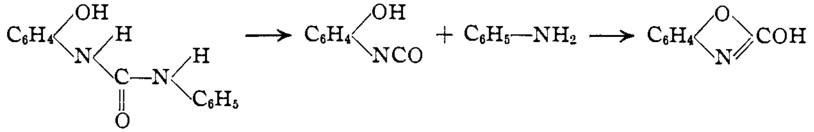
[1] This paper is based upon a thesis presented by Mr. J. H. Mote to the Graduate School of the University of Georgia, in partial fulfilment of the requirements for the degree of Master of Science.

[2] (a) Groenvik, *Bull. soc. chim.*, **25**, 177 (1876); (b) Kalckhoff, *Ber.*, **16**, 1828 (1883); (c) Leuckart, *J. prakt. Chem.*, [2] **41**, 327 (1890); (d) Bender, *Ber.*, **19**, 2269, 2951 (1886); (e) Sandmeyer, *Ber.*, **19**, 2656 (1886); (f) Chetmicki, *Ber.*, **20**, 177 (1887); (g) Jacoby, *J. prakt. Chem.*, [2] **37**, 29 (1888); (h) Lellmann and Bonhöffer, *Ber.*, **20**, 2126 (1888).

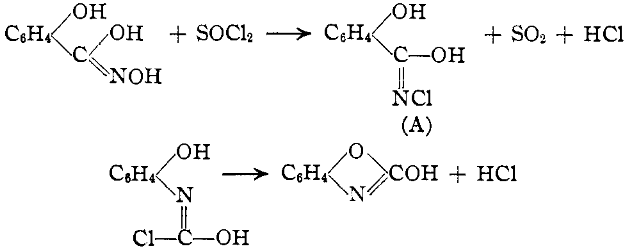
of an isocyanate, for instance, in the pyrogenic treatment of *o*-oxyphenylurethan by Groenvik[2a] or in the decomposition of *o*-oxydiphenylurea in



an alkaline aqueous solution by Leuckart.[2c]

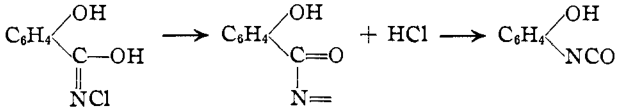


Marquis[3] studied the rearrangement of salicylhydroxamic acid when it was treated with thionyl chloride. He assumed a true Beckmann rearrangement to take place and explained the formation of oxycarbanil without the intermediate formation of an isocyanate, as follows.



(A)

According to the theory advanced by Stieglitz[4] the change of the radical from C to N would be caused by the loss of HCl from (A) and the formation of univalent nitrogen. After the interchange the compound would assume the structure of an isocyanate, as follows.



and consequently the formation of the oxycarbanil would take place from the isocyanate.

However Struve and Radenhausen[5] in a study of the rearrangement of *o*-oxybenzazide in boiling water obtained *sym.*-di-*o*-oxyphenylurea, carbon dioxide and nitrogen. This is the Beckmann rearrangement of the Curtius type[6] and according to the theory of the mechanism advanced by Stieglitz is assumed to proceed as follows.

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[3] Marquis, *Compt. rend.*, **143**, 1164 (1907).

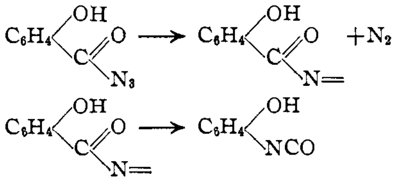
[4] References given by Stieglitz and Leech, THIS JOURNAL, **36**, 272 (1914).

[5] Struve and Radenhausen, *J. prakt. Chem.*, [2] **52**, 241 (1895).

[6] Curtius and Leimbach, *ibid.*, [2] **65**, 20 (1902).

I

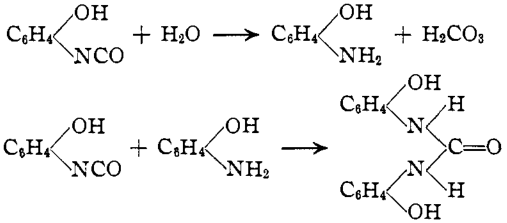
II



In the presence of water the isocyanate would hydrolyze to give an amine and carbonic acid. The amine would then react with some unchanged isocyanate to give a *sym.*-di-substituted urea.

III

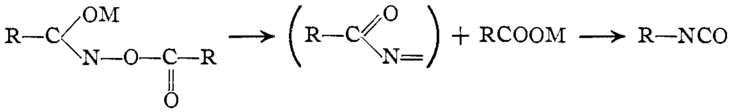
IV



In the reactions of both Marquis and of Struve and Radenhausen the same isocyanate would seem to be formed as an intermediate product in the rearrangement. However, in one instance a *sym.*-di-substituted urea resulted and in the other oxycarbanil was formed. Of course, since the experiments of Marquis were carried out in non-aqueous solution, this would account for the absence of the urea in their case and would indicate that the oxycarbanil was formed directly from the isocyanate in the absence of water. However, in the work of Leuckart[2c] in an alkaline aqueous solution oxycarbanil was the product formed.

In view of these results, we decided to study another type of Beckmann rearrangement that should give us the same isocyanate, both in aqueous solution and in the dry state.

According to the theory of Stieglitz the alkali salts of the esters of hydroxamic acids undergo rearrangement as follows.



This isocyanate in aqueous solution would be expected to behave in accordance with Reactions III and IV given above. We studied a rearrangement of this type using the alkali salts of the acetyl and benzoyl esters of salicylhydroxamic acid. The isocyanate formed from these salts should be the same as that occurring in the cases previously discussed.

In aqueous solution oxycarbanil and an acetate or a benzoate were isolated from the mixture after rearrangement. We were unable to detect the presence of *o*-aminophenol, which would indicate the formation of *sym.*-dioxyphenylurea and its subsequent decomposition. Furthermore, when the salts were exploded by heating, there was no trace of the characteristic odor of an isocyanate which is usually obtained when the salts of hydroxamic acid esters are decomposed by heat.

It would seem, therefore, that when the derivatives of salicylhydroxamic acid undergo the Beckmann rearrangement either in aqueous solution or in the dry state no isocyanate is formed or at least only momentarily. Oxycarbanil is formed, seemingly, either during the course of Reaction II or at least immediately upon its completion.

Experimental Part

Salicylhydroxamic Acid was prepared by the method of Jeanrenaud.[7]

The Acetyl Ester ($C_6H_4(OH)CONHOCOCH_3$) was prepared by mixing 1 g. of salicylhydroxamic acid with an excess of acetic anhydride and warming the mixture on a water-bath. The mixture became soft, then hardened. Acetic acid came off in the form of a vapor. The ester was recrystallized from alcohol and water and found to melt at 142°; yield, 0.60 g.

Anal. Subs., 0.7200: 48.0 cc. of N (21°, 745.04 mm.). Calcd. for $C_9H_9O_4N$: N, 7.18. Found: 7.31.

The Potassium Salt of the Acetyl Ester was made by dissolving the ester in the least amount of absolute alcohol and treating the ester with alcoholic potash. The salt was precipitated on the addition of absolute ether. It was filtered off and washed with absolute alcohol and then with anhydrous ether. The salt was dried for one hour in a desiccator over concentrated sulfuric acid and was found to explode after fifteen seconds when immersed in a bath at 85°.

When the salt was exploded, we were unable to detect any odor of isocyanate, which might have been formed as an intermediate product and which is usually noticeable when hydroxamic acids are rearranged.

Rearrangement took place when the salt was dissolved in water and heated to boiling. On cooling down, oxycarbanil separated out as white needles which were recrystallized from hot water and found to melt at 139°. On acidifying the filtrate, acetic acid was set free. It was recognized by its odor. The aqueous solution from the rearrangement was diazotized and heated. We were unable to detect the presence of any pyrocatechol by the iron chloride reaction. This seems to show that there was no *o*-aminophenol present, which would indicate the formation of an urea which might subsequently change over into oxycarbanil.

The properties of the rearrangement product agreed in all respects with the oxycarbanil described in the literature.

Anal. Subs., 0.2063: 20.8 cc. of N (27°, 748.6 mm.). Calcd. for $C_6H_5O_2N$: N, 11.38. Found: 10.99.

The Benzoyl Ester ($C_6H_4(OH)CONHOCOC_6H_5$) was prepared by two methods.

(a) By the Schotten-Baumann reaction: To 1 g. of salicylhydroxamic acid was added an aqueous solution of sodium hydroxide containing 0.26 g. of sodium hydroxide (1 equiv.) and the mixture shaken until all dissolved. Then 0.92 g. of benzoyl chloride was added and the mixture thoroughly stirred to ensure thorough mixing. The flask was kept cool during the reaction.

The product was recrystallized from alcohol and water and found to melt at 153°; yield, 0.80 g.

(b) By fusion with benzoic anhydride: Salicylhydroxamic acid (1 g.) was mixed

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[7] Jeanrenaud, *Ber.*, **22,** 1270 (1889).

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.

ATHENS, GEORGIA

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

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

BY CHARLES BARKENBUS, ELI B. FRIEDMAN AND RAYMOND K. FLEGE

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).