acid was soluble in water, slightly soluble in alcohol, and insoluble in other organic solvents. Crystallized from a dilute methyl alcoholic solution, it melted at 140° with decomposition. The yield was almost quantitative.

0.1668 g. subst. gave 44.8 cc. of N_2 at 14° and 745 mm. (over 30% KOH solution).
Calc. for $C_2H_6O_2N_2$: N, 31.09. Found: N, 31.16.

Summary.

The foregoing pages are a record of the method of preparation of dichloroacethydroxamic acid; of the benzoyl ester of dichloroacethydroxamic acid; of the hydroxylammonium salt of trichloroacethydroxamic acid; of glycocoll hydroxamic acid; and an investigation of the products obtained by the rearrangement of dichloroacethydroxamic acid, and of its benzoyl ester when they were subjected to the action of heat.

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI.]

A STUDY OF β-BENZYLFORMHYDROXAMIC ACID.

BY LAUDER WILLIAM JONES AND M. CANNON SNEED.[1]

Received January 5, 1917.

Of the type of substituted hydroxylamines to which β-benzylformhydroxamic acid belongs, β-phenylformhydroxamic acid, β-benzylacethydroxamic acid, and β-benzoylbenzhydroxamic acid, are the only representatives known. The first of these compounds was described by Bamberger and Destraz[2] who obtained it by treating β-phenylhydroxylamine with formic acid. They found that β-phenylformhydroxamic acid, upon distillation with phosphorus pentoxide, gave phenylisocyanate. Both β-benzoylbenzylhydroxamic acid and β-acetylbenzylhydroxamic acid were prepared by Beckman.[3]

It has been shown that many β-substituted hydroxylamines and β-disubstituted hydroxylamines, on treatment with mild dehydrating agents, undergo intramolecular oxidation yielding aldehydes and amines (or ammonia). Thus, Walder showed that the chief products obtained by treating β-dibenzylhydroxylamine either with acetyl chloride, or with a solution of hydrogen chloride in acetic acid (Beckmann's mixture), were benzylamine and benzaldehyde.

It would be expected that β-acyl-β-alkyl(aryl)hydroxylamines containing an oxidizable acyl group, such as formyl, might behave towards mild dehydrating agents in a manner similar to β-dibenzylhydroxylamine, and that they would offer still another possibility for intramolecular

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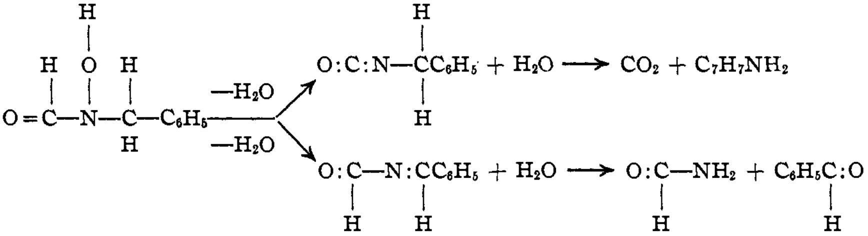
[1] The material presented here is used by Sneed in his dissertation in part fulfilment of the requirements for the Ph.D. degree of the University of Cincinnati.

[2] *Ber.*, **35**, 1884 (1902).

[3] *Ibid.*, **26**, 2631 (1893).

oxidation on treatment with strong dehydrating agents, such as phosphorus pentoxide, and might yield isocyanates. Will oxidation take place in both directions simultaneously; or will it proceed exclusively in one direction if suitable dehydrating agents are employed? It was for the purpose of answering these questions that the present problem was undertaken.

Of the substituted acylhydroxylamines, β-benzylformhydroxamic acid was selected to study the problem. This led to the preparation of this substance, which was accomplished by the action of formic ethyl ester on β-benzylhydroxylamine. As stated above, it will be observed that this compound, $O : CH — N(OH) — CH_2C_6H_5$, by the loss of water, offers two possibilities for intramolecular oxidation when treated with dehydrating agents.



Now, β-benzylformhydroxamic acid is a derivative of formic acid, hydroxylamine, and benzyl alcohol, since these are the substances which are employed in its preparation, and also the ones which it would yield when completely hydrolyzed. If, however, a molecule of water is eliminated by means of dehydrating agents, a process which in itself cannot be construed as either oxidation or reduction, the intermediate products, benzylisocyanate and the aldimide, $OHC — N = CHC_6H_5$, no longer combine with water to give β-benzylformhydroxamic acid, or its decomposition products named above, but to give carbonic acid and benzylamine in the one case, and formic acid, ammonia and benzaldehyde in the other case.

It is pertinent, therefore, to ask at what stage in the reaction the oxidation-reduction takes place, and by what mechanism it may be explained. No obvious answer to these two questions is to be found in the usual equations expressing the reaction as given above.

A consideration of these transformations from an electronic point of view will serve to make clear the intramolecular oxidations suggested. There are many reasons for believing that the hydroxyl group in hydroxylamine, and in its derivatives, functions as a positive hydroxyl group, $+O — +H$.[1] Before there can be a loss of a molecule of water, $H+ — OH$, a negative hydroxyl group must be available. This condition could arise by an exchange of two negative electrons between nitrogen and oxy-

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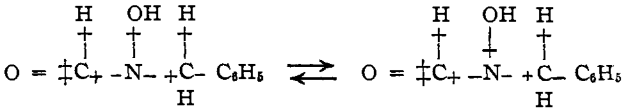
[1] Stieglitz, THIS JOURNAL, 36, 289 (1914); Jones, *Ibid.*, 36, 1272 (1914).

gen, which may be considered as the first stage in the process of oxidation-reduction.



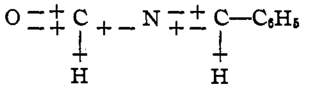
$$O = \ddagger\overset{\overset{H}{\overset{+}{|}}}{C}{+}\,{-}\overset{\overset{OH}{\overset{+}{|}}}{N}{-}\,{+}\underset{H}{\overset{\overset{H}{\overset{+}{|}}}{C}}{-}\,C_6H_5 \rightleftarrows O = \ddagger\overset{\overset{H}{\overset{+}{|}}}{C}{+}\,{-}\overset{\overset{OH}{\underset{+}{|}}}{N}{-}\,{+}\underset{H}{\overset{\overset{H}{\overset{+}{|}}}{C}}{-}\,C_6H_5$$

(I). (II).

By the loss of water from β-benzylformhydroxamic acid (Formula II), two isomers of the following electromeric formulas would be expected to result, depending upon the direction in which the molecule of water is removed:

(1) $O \substack{-\,+\\-\,+} C \substack{-\,+\\+\,-} N \substack{\\-\,+} C_7H_7$

(2)

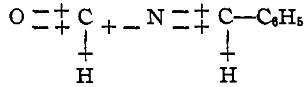


$$O \substack{-\,+\\-\,+} \underset{\underset{H}{\overset{|}{+}}}{C} \substack{\\+\,-} N \substack{-\,+\\+\,-} \underset{\underset{H}{\overset{|}{+}}}{C}\text{—}C_6H_5$$

By hydrolysis alone, the first electromer could not give carbon dioxide and benzylamine, nor could the second yield formamide and benzaldehyde, but, in each case, the original compound would be regenerated, or both electromers would be hydrolyzed to give β-benzylhydroxylamine and formic acid. In order that the substances previously mentioned may result from hydrolysis there must be a transfer of negative electrons from carbon to nitrogen to give electromers of the following formulas:

(1a) $O \substack{-\,+\\-\,+} C \substack{+\,-\\+\,-} N \substack{\\-\,+} C_7H_7$

(2a)



$$O \substack{-\,+\\-\,+} \underset{\underset{H}{\overset{|}{+}}}{C} \substack{\\+\,-} N \substack{-\,+\\-\,+} \underset{\underset{H}{\overset{|}{+}}}{C}\text{—}C_6H_5$$

These are the only electromers which would yield respectively carbon dioxide and benzylamine on hydrolysis in the one case (1*a*), and formamide and benzaldehyde in the other case (2*a*).

It has been pointed out that Walder obtained benzylamine and benzaldehyde by treating β-dibenzylhydroxylamine with Beckmann's mixture, and that Bamberger and Destraz got phenylisocyanate as a product by distilling β-phenylformhydroxamic acid with phosphorus pentoxide. With the hope of obtaining similar results, the actions of Beckmann's mixture and of phosphorus pentoxide upon β-benzylformhydroxamic acid were studied.

Experimental Part.

1. In the preparation of β-benzylformhydroxamic acid, β-benzylhydroxylamine was used. Methods of preparation of β-benzylhydroxylamine are described in the literature by Behrend and Leuchs[1] and by Beckmann,[2] but these investigators have failed to give explicit directions and to state their yields. We have obtained the best results by modifying

[1] This Journal, **257**, 213, 216 (1890).

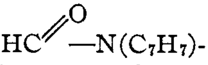
[2] *Ber.*, **22**, 438 (1889).

one of the methods employed by Behrend and Leuchs,[1] and for this reason we shall give a rather detailed account of our modifications.

1. The Preparation of β-Benzylhydroxylamine.—To a solution of 14 g. of hydroxylammonium chloride and 50 g. of benzyl chloride in 200 cc. of 70% alcohol, 60 g. of crystallized sodium carbonate were added. The mixture was then boiled for two hours in a flask provided with a reflux condenser. The product was filtered, and to the filtrate sufficient ice water was added to precipitate the β-dibenzylhydroxylamine. The flask was then placed in a freezing mixture where it was allowed to remain until complete precipitation had taken place. Upon filtration, 26 g. of pure white, needle-like crystals of β-dibenzylhydroxylamine melting at 123° were obtained.

Eighteen grams of β-dibenzylhydroxylamine were placed in separatory funnel with 30 cc. of ether, and concentrated solutions of 13.5 g. of potassium hydroxide and 72 g. of potassium hydroxide were added. The mixture was shaken vigorously until the oxidation of the β-benzylhydroxylamine was complete. The process of oxidation required only ten minutes. The isoaldoxime was separated by three extractions with ether. Upon evaporation of the ether, a residue of 17 g. of β-benzylisobenzaldoxime resulted. The pure substance was obtained by precipitating it from an ether solution with ligroin. It melted at 81°.

Seventeen grams of the isoaldoxime were treated with 34 cc. of concentrated hydrochloric acid, and steam was passed through the mixture until all the benzaldehyde had distilled. The resulting product, free from the aldehyde, was then heated over a low flame until the greater portion of hydrochloric acid had been driven off. To the cool residue, a cold saturated solution of sodium carbonate was added until the solution reacted neutral to litmus. A small amount of solid remained which was separated by filtration. To the filtrate, after it had been cooled to 0°, enough sodium carbonate was added to make the solution distinctly alkaline. After an hour, pure β-benzylhydroxylamine had precipitated from the filtrate. The solid residue obtained from the first filtration was extracted with ligroin from which a small amount of the same substance was recovered. In this way, 6 grams of the pure compound, which melted at 57°, were obtained.



2. The Preparation of β-Benzylformhydroxamic Acid, $\mathrm{HC}\overset{\mathrm{O}}{/\!\!/}-\mathrm{N(C_7H_7)}$-(OH).—A solution of 4 g. of β-benzylhydroxylamine in 8 g. of formic ethyl ester was kept at room temperature, for 14 days. At the end of this time, a test portion of the mixture showed no reduction of copper acetate, but gave a copper salt. The contents of the flask were transferred to an evaporating dish, and the solution was evaporated *in vacuo* until a thick

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[1] *Loc. cit.*, p. 216.

paste remained. This paste was placed over solid potassium hydroxide in a desiccator and kept in a cool place to facilitate crystallization. At the end of three days most of it had crystallized. The substance was separated from impurities by dissolving it in ether and precipitating it with ligroin. Only enough ligroin was added to give a slight turbidity. Upon evaporation of the ether, crystals of β-benzylformhydroxamic acid separated as long white needles. The yield was three grams, or 67% of the theory.

0.2211 g. subst. gave 19.2 cc. N_2 at 25.5° and 738.4 mm. (over 30% KOH solution).
0.2028 g. subst. gave 0.4720 g. CO_2 and 0.1126 g. H_2O.
Calc. for $C_8H_9O_2N$: C, 63.54; H, 6.00; N, 9.27. Found: C, 63.48; H, 6.16; N, 9.45.

β-Benzylformhydroxamic acid was readily soluble in ether and in alcohol, and slightly soluble in water. Its melting point was 49° to 50°. It showed little, if any, decomposition at its boiling point. With a hot alcoholic solution of the acid, a concentrated solution of copper acetate precipitated a copper salt as grayish blue crystals. The salt was purified by recrystallization from hot 60 to 70% alcohol. It decomposed without melting.

0.3394 g. subst. gave 0.0593 g. copper.
Calc. for $C_{16}H_{16}O_4N_2Cu$: Cu, 17.48. Found: Cu, 17.47.

3. Action of Beckmann's Mixture on β-Benzylformhydroxamic Acid.—Two grams of β-benzylformhydroxamic acid were digested for two hours, on a water bath, with an excess of a solution of dry hydrogen chloride in glacial acetic acid (Beckmann's mixture). The benzaldehyde which was produced during the operation was extracted with ether. The aldehyde was identified by converting it, through the action of phenylhydrazine, into benzalphenylhydrazone; 0.3 g. of the hydrazone, melting at 152.5°, was obtained. Upon treatment with chloroform and alcoholic potash, a portion of the solution which remained after the extraction of benzaldehyde gave an isocyanide reaction for a primary amine, probably benzylamine. Another portion reduced an ammoniacal solution of silver nitrate. The remainder of the solution upon evaporation, gave a residue consisting chiefly of ammonium chloride. It is likely that both formic acid and ammonium chloride resulted from the hydrolysis of formamide. From these results it is evident that β-benzylformhydroxamic suffered intramolecular oxidation, as we have previously indicated, in one direction giving benzaldehyde and formamide, and in another direction yielding benzylamine and carbon dioxide. (See p. 676.)

4. Action of Phosphorus Pentoxide upon β-Benzylformhydroxamic Acid.—Five grams of β-benzylformhydroxamic acid thoroughly mixed with an excess of phosphorus pentoxide were subjected to distillation. On heating the mixture gently by means of a water bath, the components reacted violently. Practically the entire contents of the flask became a black tarry mass. When the water bath was replaced by a metal bath, a few drops of liquid which smelled strongly of an isocyanate were obtained. By treating the distillate with aniline, a crystalline product, phenylbenzylurea, melting at 167° to 168°, resulted.

Summary.

1. β-Benzylformhydroxamic acid was obtained by the action of β-benzylhydroxylamine on formic ethyl ester.
2. β-Benzylformhydroxamic acid gave a characteristic copper salt.
3. β-Benzylformhydroxamic acid upon treatment with Beckmann's mixture suffered intramolecular oxidation in two directions giving carbon dioxide and benzyl amine in the one case, and formamide and benzaldehyde in the other.
4. β-Benzylformhydroxamic acid, upon treatment with phosphorus pentoxide, suffered intramolecular oxidation giving benzylisocyanate.

CINCINNATI, OHIO.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

A NEW CLASS OF PHTHALEINS—MIXED PHTHALEINS—FORMED BY HEATING *p*-HYDROXYBENZOYL-*o*-BENZOIC ACID WITH PHENOLS.

BY W. R. ORNDORFF AND MISS R. R. MURRAY.

Received January 15, 1917.

Phenolphthaleinoxime and the Preparation of *p*-Hydroxybenzoyl-*o*-benzoic Acid.—Phenolphthaleinoxime was prepared by Friedländer's[1] method. The following proportions of the materials employed were found to be advantageous: 50 g. phenolphthalein, 50 g. potassium hydroxide, 500 cc. water and 12.5 g. hydroxylamine hydrochloride (calculated 10.9 g.). It was found best to follow the course of the reaction with frequent tests made by withdrawing a small portion of the alkaline liquid from the flask while heating in the water bath to 80°, neutralizing with acetic acid and filtering off the precipitated oxime. When the filtrate, on addition of alkali, gives no color or only a faint pink the flask should be removed from the water bath, 100 cc. alcohol added, and the whole treated with acetic acid until slightly acid. The oxime is thus obtained pure as a sulfur-yellow precipitate, easily filtered. It should be washed with at least 500 cc. hot distilled water and allowed to dry in the air. The yield is quantitative.

The oxime prepared in this manner dissolves readily and *completely* in boiling dilute sulfuric acid (1 to 8), giving a bright yellow solution. When this solution has boiled from five to ten minutes, the color fades and white flakes appear on the surface. After this is observed, the boil-

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[1] *Ber.*, 26, 172 (1893).