[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE ACTION OF HYDROXYLAMINE UPON SULFINIC ACIDS AND THEIR DERIVATIVES[1]

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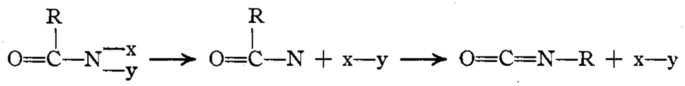
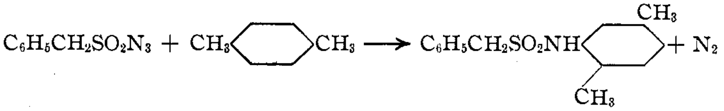
Introduction

Many organic derivatives of nitrogen, such as hydroxamic acids, halogen amides, azides and other similar compounds, are particularly sensitive to changes which involve molecular rearrangements. In all such cases, some radical attached to a carbon atom "wanders" to a nitrogen atom; the first tangible product of rearrangement observed is an isocyanate. Stieglitz[2] was the first to propose a satisfactory theory which correlates all rearrangements of this type; he assumed the formation of an intermediate product, a derivative of univalent nitrogen, to be the prime essential to such rearrangements.



$$O{=}\overset{R}{C}{-}N\begin{smallmatrix}-x\\-y\end{smallmatrix} \longrightarrow O{=}\overset{R}{C}{-}N + x{-}y \longrightarrow O{=}C{=}N{-}R + x{-}y \qquad (1)$$

But there are certain organic acids which yield derivatives of the favorable type mentioned above, and yet these derivatives show no inclination to undergo rearrangement. Thus, several investigators[3] have failed to find evidence of rearrangement in the case of halogen derivatives of benzenesulfonamide, $C_6H_5SO_2NHX$, although such compounds might be expected to resemble halogen amides of carboxylic acids in this particular. Furthermore, Curtius and Hass[4] observed a similar indifference on the part of the azide of benzenesulfonic acid, $C_6H_5SO_2N_3$. In this instance, the failure to rearrange cannot be attributed to the inability of the group N_3 to lose nitrogen (N_2), because even hydrocarbons such as toluene react with this azide. Similarly, the azide of benzylsulfonic acid, $C_6H_5CH_2SO_2N_3$, reacts with *p*-xylene and with naphthalene by addition.



(2)

The observations made by Piloty[5] in the study of benzenesulfonhydroxamic acid show that this acid departs radically from the usual reaction ex-

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[1] This article is based upon a thesis presented by Herbert F. Whalen, in 1924, to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903).

[3] Hoogewerff and van Dorp, *Rec. trav. chim.*, **6**, 373 (1888); *Ber.* (Ref.) **21**, 291 (1888). Chattaway, *J. Chem. Soc.*, **87**, 145 (1905).

[4] Curtius and Hass, *J. prakt. Chem.*, **102**, 87 (1921).

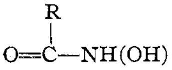
[5] Piloty, *Ber.*, **29**, 1560, 2324 (1896).

pected of a monohydroxamic acid; no rearrangement has been observed. Concentrated solutions of alkalies cause a decomposition of it in the following way.

$$2C_6H_5SO_2NHOH + 4KOH \longrightarrow 2C_6H_5SO_2K + K_2N_2O_2 + 4H_2O \qquad (3)$$

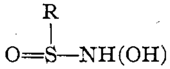
A sulfinate and a hyponitrite are formed.

The departure from the norm displayed by these derivatives of sulfonic acids suggested the problem of preparing derivatives of benzenesulfinic acid. From a theoretical point of view this would be quite alluring, for the hydroxamic acids (azides, or halogen amides) of benzenesulfinic acid and of carboxylic acids are similarly constituted, and might be expected to show a similarity in chemical behavior.



$$O{=}\overset{\overset{R}{|}}{C}{-}NH(OH)$$

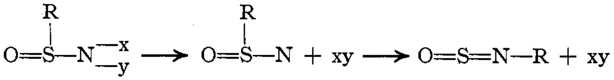
A



$$O{=}\overset{\overset{R}{|}}{S}{-}NH(OH)$$

B

Furthermore, the thionylamines which would be expected as the rearrangement products of a sulfinhydroxamic acid or its derivatives, are known compounds and could be identified easily.



$$O{=}\overset{\overset{R}{|}}{S}{-}N\genfrac{}{}{0pt}{}{-x}{-y} \longrightarrow O{=}\overset{\overset{R}{|}}{S}{-}N + xy \longrightarrow O{=}S{=}N{-}R + xy \qquad (4)$$

We have tried to prepare the hydroxamic acids of benzenesulfinic acid and of *p*-toluenesulfinic acid. Most of the methods commonly employed in making hydroxamic acids of carboxylic acids were applied; the action of free hydroxylamine upon the acid chlorides, the amides or esters, and the thermal decomposition of the hydroxylammonium salt. Ethyl benzenesulfinate showed no tendency to react with free hydroxylamine; in the other cases, even when the reaction was carried out in absolute ether at the temperature of solid carbon dioxide and ether, the chief product observed was *benzenesulfonamide,* $C_6H_5SO_2NH_2$, *not benzenesulfinhydroxamic acid.*

There are at least two ways of explaining these results. In the first place, benzenesulfinhydroxamic acid may be formed, and then converted into the amide by indirect oxidation.

$$C_6H_5SO{-}NH(OH) \longrightarrow C_6H_5SO_2NH_2 \qquad (5)$$

In the second place, hydroxylamine might act upon the derivative of benzenesulfinic acid directly as an oxidizing agent. With benzenesulfinyl chloride the reaction would be formulated as follows:

$$\begin{gathered} NH_2OH + C_6H_5SOCl \longrightarrow NH_3 + C_6H_5SO_2Cl \\ C_6H_5SO_2Cl + 2NH_3 \longrightarrow C_6H_5SO_2NH_2 + NH_4Cl \end{gathered} \qquad (6)$$

If the second interpretation were correct, it would be expected that benzenesulfonyl chloride would convert some of the hydroxylamine into benzenesulfonhydroxamic acid (Piloty's acid), $C_6H_5SO_2NHOH$, which is a solid, melting at about 126°; but no trace of this acid could be found among the products. Therefore, the first interpretation appears more plausible.

Furthermore, benzenesulfinic acid, itself, reacts smoothly with free hydroxylamine to give a salt:

$$C_6H_5SO.OH + NH_2OH \longrightarrow C_6H_5SO.ONH_3(OH) \qquad (7)$$

No oxidation of the sulfinic acid was observed in the preparation of this salt since the product contained no ammonium benzenesulfonate. When it was heated it lost water. By this change we hoped to secure benzenesulfinhydroxamic acid, just as certain hydroxylammonium salts of carboxylic acids yield hydroxamic acids.[6]

$$\begin{matrix} RCO.ONH_3(OH) \longrightarrow RCO.NH(OH) + H_2O \\ RSO.ONH_3(OH) \longrightarrow RSO.NHOH + H_2O \end{matrix} \qquad (8)$$

But in this case, also, only benzenesulfonamide was isolated.

Some of these experiments were repeated with *p*-toluenesulfinic acid. In these reactions no evidence of the hydroxamic acid was secured. The amide of *p*-toluenesulfonic acid was the chief reaction product.

Experimental Part

I. Action of Hydroxylamine upon Benzenesulfinic Acid and Its Derivatives

Benzenesulfinic acid was prepared according to the Friedel-Crafts method[7] by passing dry hydrogen chloride and sulfur dioxide into benzene in the presence of aluminum chloride.

Hilditch and Smiles[8] state that benzenesulfinyl chloride may be prepared as a solid (m. p., 38°) by the action of thionyl chloride upon benzenesulfinic acid in petroleum ether. Their work was repeated, but no acid chloride could be obtained. The oil that remained after evaporation of the petroleum ether gave a small amount of a brownish solid when ether was added to it. These crystals melted at 42–44°, were insoluble in water or in a solution of potassium hydroxide, and consisted of the phenyl benzenethiosulfonate, $C_6H_5SO_2.S.C_6H_5$. When the ether filtrate was evaporated, crystals of benzenesulfinic acid remained.

According to Braun and Kaiser,[9] benzenesulfinyl chloride can be prepared as a liquid by distillation of the product obtained by the action of benzenesulfinic acid and thionyl chloride.

Twenty-five g. of benzenesulfinic acid was treated, at 0°, with 25 g. of thionyl chloride and, after the reaction had ceased, the flask was warmed slightly on the water-bath. The excess of thionyl chloride[10] was removed in a vacuum, first at room tem-

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[6] Jones and Oesper, *Am. Chem. J.*, **42,** 518 (1909).

[7] Knoevenagel and Kenner, *Ber.*, **41,** 3315 (1908).

[8] Hilditch and Smiles, *Ber.*, **41,** 4113 (1908).

[9] Braun and Kaiser, *Ber.*, **56B,** 549 (1923).

[10] The thionyl chloride was purified and the yellow color entirely removed by distillation, first over quinoline, then over linseed oil and finally over pure beeswax. The chloride purified in this manner apparently contains no impurities which may act cata-

perature, and finally at 50°. The oil that remained was distilled at a pressure of 3–4 mm.; it boiled at 85–90°. It was a light yellow liquid that fumed in the air, and was very readily hydrolyzed to yield benzenesulfinic acid.

A. Action of Hydroxylamine upon Benzenesulfinyl Chloride

1.—A solution of 5.6 g. of benzenesulfinyl chloride in 15 cc. of absolute ether was treated, at 0°, or at the temperature obtained by solid carbon dioxide and ether, with 2.3 g. (two equivalents) of free hydroxylamine. The hydroxylamine was added very slowly while the solution was shaken. A white crystalline product was removed to a filter, washed quickly with ether, and dried in a desiccator. The dry substance was extracted with benzene; the portion of the solid (1.8 g.) which was insoluble in the benzene melted at 84–85°. It showed the characteristic behavior of an hydroxylamine salt, and consisted of basic hydroxylammonium chloride, $(NH_2OH)_2.HCl$, which melts at 85°. The benzene solution was evaporated, and a small crystalline residue obtained which melted between 136° and 145°. When it was recrystallized from warm water, colorless plates, m. p. 150–151°, separated. The ether filtrate and washings were evaporated to dryness on the water-bath. The residue melted at 145–150° and weighed 4.2 g. Recrystallized from warm water, it melted at 150°. Its properties corresponded with those of benzenesulfonamide.

No test for an hydroxamic acid could be obtained.

Anal. Subs., 0.2250: $BaSO_4$, 0.2758. Calcd. for $C_6H_7SO_2N$: S, 20.37. Found: 19.84.

2.—A solution of 2.1 g. of sodium hydroxide in a small amount of water was added to a concentrated solution of 1.8 g. of hydroxyl-ammonium chloride in water. Then 4.2 g. of benzenesulfinyl chloride was added slowly. The solid which formed was separated, dried and extracted with ethyl acetate. The insoluble residue, crystallized from water, gave white crystals that melted at 150–151° (3.5 g.).

Anal. Subs., 0.1732: $BaSO_4$, 0.2565. Calcd. for $C_6H_5SO_2.NH_2$. S, 20.37. Found: 20.33.

It did not reduce ammoniacal silver nitrate. This excluded the possibility of the presence of any hydroxamic acid. In fact, the white silver salt of benzenesulfonamide was obtained by adding silver nitrate to a slightly ammoniacal solution of it.

B. Hydroxylammonium Salt of Benzenesulfinic Acid.—Free hydroxylamine was added to a cold alcohol solution of the acid, and the salt was precipitated by ether. Recrystallized from methyl alcohol and ether it gave colorless crystals that melted at 83–85°.

Anal. Subs., 0.1975: N_2, 13.1 cc. Calcd. for $C_6H_5SO.ONH_3OH$: N, 8.00. Found: 7.81.

A sample of the salt weighing 1.98 g. was heated for ten hours at 100–110° in an oil-bath. The tube containing the salt was attached to a weighed calcium chloride tube. When the weight of the sample had become constant, the increase in weight of the calcium chloride tube amounted to 0.1550 g. (calculated, 0.23 g.). The residue in the tube was extracted with ether and, after evaporation of the solvent and recrystallization of the brownish residue from warm water, white crystals were obtained, which melted at 150° and had the characteristic properties of benzenesulfonamide.

C. Action of Hydroxylamine upon Benzenesulfinamide.—Equivalent amounts of this amide and of hydroxylammonium chloride were dissolved in water and alcohol and the solution was allowed to stand for 15 hours at room temperature.

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lytically. [Hans Meyer and Schlegl, *Monatsh.*, **34,** 569 (1913).] Hans Meyer, "Analyse und Konstitutionsermittlung Organischer Verbindunge," [J. Springer, Berlin, **1916,** third ed., p. 556].

In a second experiment, benzenesulfinamide in absolute alcohol was treated with one equivalent of free hydroxylamine. The temperature of the mixture was maintained at the boiling point for 24 hours. Solids were obtained from these reaction mixtures which, after recrystallization from water, yielded crystals of benzenesulfonamide; m. p., 150–151°.

II. Action of Hydroxylamine upon *p*-Toluenesulfinyl Chloride

p-Toluenesulfinic acid was made by the method suggested by Knoevenagel and Kenner[7] and from it *p*-toluenesulfinyl chloride was prepared by the method of Braun and Kaiser.[9]

1.—A solution of 8.4 g. of hydroxylammonium chloride in 32 cc. of water containing 9.6 g. of sodium hydroxide was treated with 3.5 g. of toluenesulfinyl chloride. The reaction product, a white crystalline material weighing 3.1 g., was extracted with ether, and after evaporation of the solvent, the residue was recrystallized from water, forming white crystals; m. p., 136°. No test for a hydroxamic acid could be obtained. The crystals consisted of *p*-toluenesulfonamide.

Toluenesulfinyl chloride was dissolved in dry benzene and the solution treated with free hydroxylamine. The observations were similar to those recorded for benzenesulfinyl chloride. Crystals of *p*-toluenesulfonamide, m. p. 135–136°, were obtained but no hydroxamic acid.

Summary

The hydroxamic acids of sulfinic acids possess a constitution similar to that of the hydroxamic acids of carboxylic acid. Consequently, they would be expected to show a similar chemical behavior, undergoing rearrangement to form thionylamines, which are well known and easily identified.

However, all attempts to prepare the hydroxamic acids of benzenesulfinic and *p*-toluenesulfinic acids, even when the reactions were carried out in absolute ether at low temperature, resulted in the formation of the corresponding sulfonamides.

The most plausible explanation of these results assumes the formation of the hydroxamic acid, followed by immediate intramolecular oxidation to give benzenesulfonamide.

The hydroxylammonium salt of benzenesulfinic acid, $C_6H_5SO_2NH_3(OH)$, was prepared. When it was heated, water was eliminated, but benzenesulfonamide and not benzenesulfinhydroxamic acid was formed.

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