

THE REACTION OF BENZENSULFINYL CHLORIDE
WITH SODIUM AZIDE

by

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Bachelor of Science

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Stillwater, Oklahoma

1949

Submitted to the Department of Chemistry
Oklahoma Agricultural and Mechanical College

In Partial Fulfillment of the Requirements

for the Degree of

MASTER OF SCIENCE

1950

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ACKNOWLEDGMENT

The author wishes to express his sincere gratitude to Dr. Samuel H. Lee who initially suggested this work. In his capacity as thesis adviser Dr. Lee has given patient direction and assistance throughout the course of the work.

The author also gratefully acknowledges the financial aid given him by the Oklahoma Agricultural and Mechanical College in the form of a Graduate Fellowship.

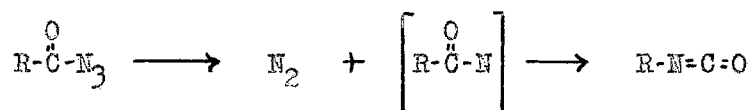
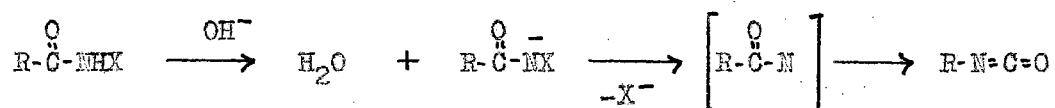
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INTRODUCTION

The thermal decomposition of acid azides to isocyanates and nitrogen is known as the Curtius rearrangement. The reaction is a preparative method for isocyanates and for compounds derivable from isocyanates (44).

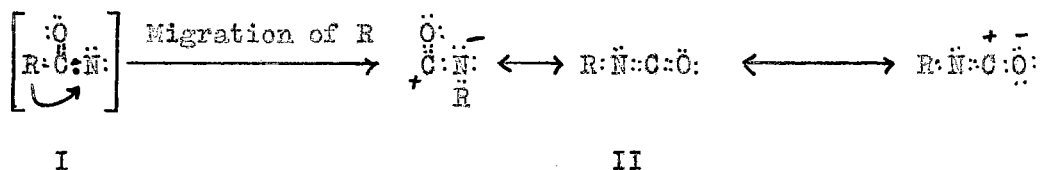
The Curtius rearrangement is quite similar to the Hoffman (44) and Lossen rearrangements (45) in that all three involve an intramolecular shift of an R group to the nitrogen atom, and the formation of isocyanates:

Curtius rearrangementHoffman or Lossen rearrangement

When X is a halogen atom the reaction is called the Hoffman rearrangement and when X is an organic acid group it is known as the Lossen rearrangement.

Both the Curtius and Hoffman rearrangements offer convenient methods of replacing a carboxyl group by an amino group, but the Lossen rearrangement has little preparative value and has been primarily of theoretical interest.

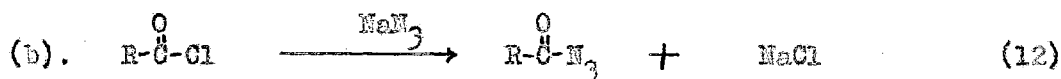
The fragment inclosed in brackets is commonly postulated as the intermediate in the Curtius, Hoffman and Lossen rearrangements. Its rearrangement may be electronically represented as follows:



and the driving force may be presumed to arise from the tendency of the electronically deficient nitrogen atom in I to acquire electrons from the

neighboring carbon atom. When this occurs the R group with its two electrons migrates to the nitrogen atom resulting in the formation of the isocyanate (II).

In general two methods for the preparation of organic acid azides are available:



The method described in Curtius' numerous papers involves treatment of hydrazides in cold aqueous solution with nitrous acid, although he was early aware of the acid chloride-sodium azide method (26) which was used by others (18) (28) (38). In the first method the required hydrazides are commonly prepared from esters by reaction with hydrazine. The acid chloride-sodium azide method can be carried out under anhydrous conditions (39) (19) (31) or with aqueous sodium azide (27). Use of anhydrous conditions is the only practical one for highly reactive chlorides or for the preparation and rearrangement of very unstable azides.

Carboxylic azides in general undergo the Curtius rearrangement with the formation of the corresponding isocyanates. This rearrangement proceeds almost quantitatively at comparatively low temperatures (41). The sulfonazides, however, do not undergo this rearrangement although they do undergo thermal decomposition at relatively high temperatures, losing nitrogen and forming sulfonamides or substituted sulfonamides (2) (13).

It may be assumed that the sulfonazide loses nitrogen in a manner similar to that of the carboxylic azides forming a fragment containing an

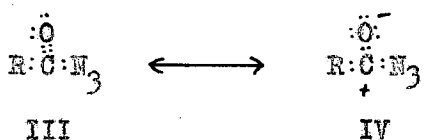
electronically deficient nitrogen atom. This fragment, however, does not stabilize itself by a rearrangement. Instead, it has been known to react with such inert solvents as benzene and toluene forming N-substituted sulfonamides. In the case of toluene the ortho and para substitution products were obtained, the ortho derivative predominantly, but none of the meta derivative could be isolated (10). Since the ortho derivative is predominant, one is led to the conclusion that the steric interaction of the methyl group in the toluene and the two oxygen atoms on the sulfur atom in the sulfonazide residue plays only a minor role in directing the course of the reaction. Furthermore, the appearance of the ortho and para derivatives to the exclusion of the meta derivative indicates that a free radical type mechanism is involved, although this has not been investigated. The azide residue of sulfonazides also may act as a dehydrogenating agent on the reaction medium and generate from it, by dehydrogenation, characteristic products which are formed by a union of the molecular residues formed. Frequently they are difficult to isolate and are such complex compounds that their method of formation is obscure (2) (9) (11).

It is noteworthy that such differences should exist between the carboxylic azides and the sulfonazides: the carboxylic azides lose nitrogen at comparatively low temperatures, whereas the evolution of nitrogen from sulfonazides occurs at relatively high temperatures; the carboxylic azides rearrange forming the isocyanate, whereas the sulfonazides do not undergo rearrangement at all. The comparatively great thermal stability of the sulfonazide and its apparent failure to undergo rearrangement may be explained by one or more of the following reasons: (a) the two oxygen atoms connected to the sulfur atom in the sulfonazide residue sterically hinder the shift of the R group from the sulfur atom to the electronically deficient nitrogen atom;

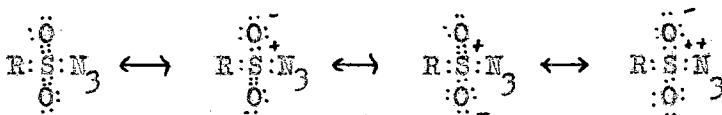
(b) the sulfur atom, being much larger than the carbon atom, places the R group at so great a distance from the electronically deficient nitrogen atom that the rearrangement is prevented; (c) the electronegativity of the sulfur atom is of such a nature as to resist any release of electrons either by the adjacent nitrogen atom or by the sulfur atom itself, and this causes greater thermal stability of the sulfonazide and prevents the rearrangement of the azide residue. Electronegativity, as used here, refers to the power of an atom in a molecule to attract electrons to itself (35).

Considering these two extremes in behavior, it would be interesting to know what course is followed by the sulfinazides, which are similar in structure to the carboxylic azides and yet retain the central sulfur atom. One would expect the sulfinazides to have a behavior intermediate between that of the carboxylic azides and that of the sulfonazides. The following electronic representations of the resonance forms of carboxylic azides, sulfonazides, and sulfinazides will serve to demonstrate the similarities and differences in structure that exist among the three:

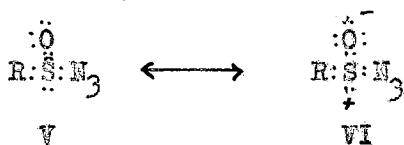
Carboxylic azide



Sulfonazide



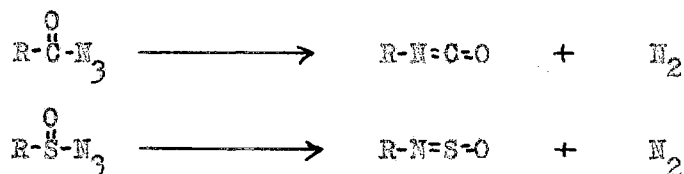
Sulfinazide



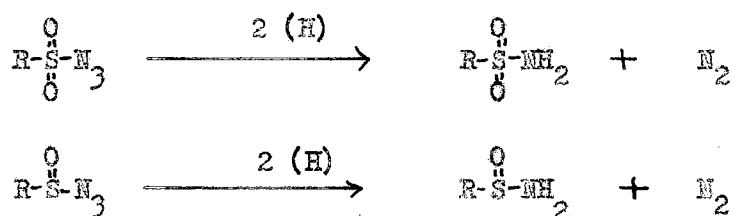
The similarity in electronic structure existing between III and V and between IV and VI is immediately evident, the only difference being an unshared pair of electrons present on the sulfur atom and not present on the carbon atom. One would predict the sulfonazide to be quite stable because of the numerous resonance forms that contribute to its structure and also because of its similarity to the sulfones, which are quite inert (1). This is indeed the case. However, the sulfinazides are similar to the sulfoxides in structure, and therefore can be expected to be very reactive. The unshared pair of electrons (V, VI) would render the sulfinazide highly susceptible to oxidation, whereas the true double bond character (V) would lead to ease of reduction, both reactions being characteristic of sulfoxides. This would indicate that auto oxidation-reduction would be likely to occur.

The sulfinic acids themselves are very unstable compounds. Relatively few references are made to aliphatic sulfinic acids and some of the fairly simple members of the series are unknown, doubtless because of their instability. Since the aliphatic sulfinic acids decompose rapidly they usually must be isolated as the zinc, barium, or other salts. The aromatic sulfinic acids, although apparently more stable than the aliphatic, likewise undergo decomposition on standing. The products of the decomposition of sulfinic acids are sulfonic acids and thiolsulfonic esters. This decomposition is actually an auto oxidation-reduction. Sulfinic acids are readily oxidized to sulfonic acids by air, hydrogen peroxide, nitric acid, and other oxidizing agents. In the preparation of sulfinic acids by reduction of sulfonyl chlorides with zinc dust mercaptans are always obtained in varying amounts. In fact, if the solution is made slightly acid, the mercaptan is the principal product of the reduction (20).

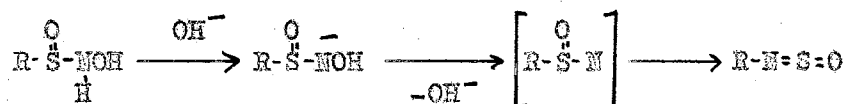
If the sulfinazide does resemble the carboxylic azides in ability to rearrange, the product of rearrangement would be a thionyl amine, $R-N=S=O$:



The thionyl amine could be hydrolyzed readily to a primary amine and sulfur dioxide (29). If, however, the sulfinazide behaves as the sulfonazide, the product of decomposition would be the sulfinamide:



Whalen and Jones (43) in a study somewhat analogous to this work attempted to prepare the hydroxamic acid derivative of benzenesulfinic acid. Benzenesulfinyl chloride was treated with hydroxylamine, but the product of the reaction was benzenesulfonamide rather than the hydroxamic acid derivative. The authors assumed that the hydroxamic acid derivative had formed and had undergone intramolecular oxidation-reduction. This tends to support the conclusion, previously drawn from consideration of the electronic structures, that the residue from the azide would be highly susceptible to oxidation. They had hoped that the hydroxamic acid derivative would lose water and rearrange to the thionyl amine:



Curtius and Lorenzen (14) reported an unsuccessful attempt to prepare benzenesulfinhydrazide, presumably to be used to prepare benzenesulfinazide.

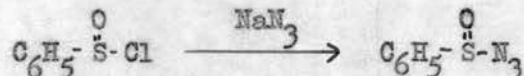
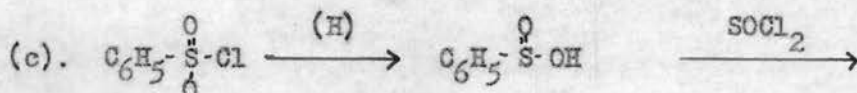
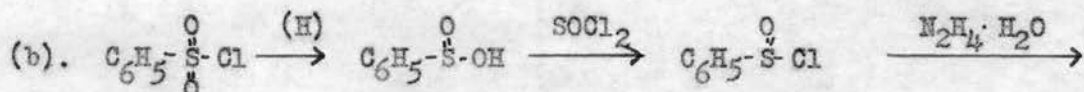
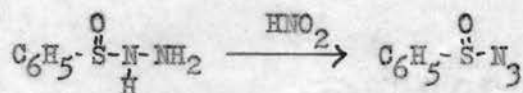
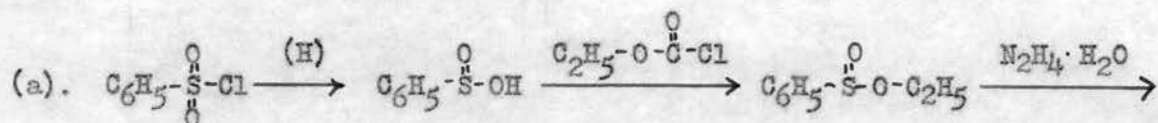
Treatment of the ethyl ester of benzenesulfinic acid with hydrazine hydrate, however, did not result in formation of the expected benzenesulfinhydrazide. The only products of the reaction isolated and identified were diphenyl disulfide, nitrogen, ethanol and water. The yield of diphenyl disulfide was only about 10% of the theoretical yield and no explanation was attempted as to the course of the reaction. The ethyl ester used in this reaction was prepared from sodium benzenesulfinate and ethyl chlorocarbonate (34).

FORMULATION OF THE PROBLEM

Since the sulfonazides are more stable to thermal decomposition than the carboxylic azides and do not undergo an analogous rearrangement, it would be interesting to study the sulfinazides to see which they resemble more closely, the sulfonazides or the carboxylic azides, both with respect to thermal stability and the ability to rearrange. No sulfinazide has been prepared as yet, and comparatively few sulfinic acid derivatives have been identified and reported. The feasibility of establishing a sulfur-nitrogen bond in a sulfinic acid derivative was confirmed by Braun and Kaisers' (6) preparation and characterization of benzenesulfinazide. Benzenesulfinazide was selected as the first sulfinazide to be prepared and studied, primarily because the starting products were easily accessible, because definitive information was available on benzazide and benzenesulfonazide for comparative purposes, and because the benzene nucleus afforded an excellent opportunity to attempt alteration of the course of the reaction by placing different substituent groups on the nucleus.

In the initial vision of this problem it was hoped that the following might be accomplished: (a) preparation and characterization of benzenesulfinazide; (b) determination of the temperature at which the azide first evolves nitrogen; (c) determination of the course of the reaction by isolation and identification of the products of the reaction; and (d) determination of whether the course of the reaction might be altered by the presence of substituent groups on the benzene nucleus.

In general there are three methods that might be used in the synthesis of benzenesulfinazide:



Method (a) has been attempted by Curtius without success, since treatment of ethyl benzenesulfinate with hydrazine hydrate did not result in formation of the hydrazide (14). Method (b) has not yet been attempted but requires the preparation of benzenesulfinhydrazide, which has not been reported, as an intermediate in the synthesis. Method (c) offers a shorter, more direct route to the azide than does either (a) or (b) and both intermediates in this synthesis have been prepared and characterized. It was therefore decided to use Method (c) in the attempted synthesis.

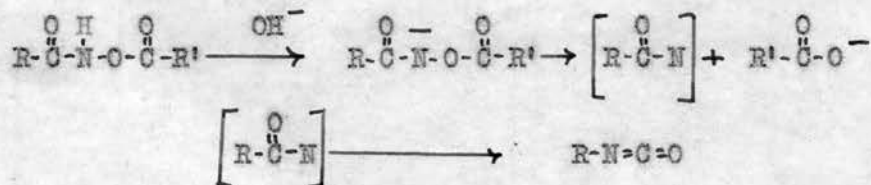
A study of the following physical constants of benzoic acid, benzenesulfonic acid, benzenesulfinic acid, and their derivatives enables a rough estimate to be made regarding the physical state of benzenesulfinazide:

Melting Points of Derivatives of

	<u>Benzoic acid</u>	<u>Benzenesulfonic acid</u>	<u>Benzenesulfinic acid</u>
Acid	121.7° (25)	44° (25)	83-84° (33)
Chloride	-0.5° (25)	14.5° (25)	38° (23)
Azide	27° (32)	liquid (15)	?

Unfortunately, data are not available on the melting point of benzenesulfonazide. The sulfinic acid and the sulfinyl chloride both have higher melting points than do the corresponding sulfonic acid and the sulfonyl chloride, and this would indicate that the melting point of the sulfinazide would be higher than the sulfonazide. Since benzazide has a melting point 27.5° higher than benzoyl chloride, one would expect the sulfinazide to have a melting point higher than the sulfinyl chloride. Although this analogy is by no means complete because of the limited data available, one is led to speculate that the benzenesulfinazide would be a solid at room temperature.

Although no effort has been made to determine the effect of substituents on the Curtius rearrangement, an investigation of this type has been conducted on the Lossen rearrangement. Since the two rearrangements are quite similar, it may be assumed that conclusions drawn from a study of the Lossen rearrangement will also be valid for the Curtius rearrangement. Renfrow and Hauser (37) in a study of the potassium salts of a series of meta and para substituted dibenzhydroxamic acids have demonstrated that the rate-determining step in the Lossen rearrangement is dependent on the electron-releasing or electron-attracting power of the R and R' groups.



When R' is electron-releasing the rearrangement proceeds much more slowly than when R' is electron-attracting. Conversely, they were able to establish

the fact that when R is electron-attracting the rearrangement proceeds much more slowly than when R is electron-releasing. This means essentially that the reaction proceeds more slowly when the electrons forming the bond between the nitrogen atom and the oxygen atom are held more closely to the nitrogen atom and that the reaction is more rapid when the electrons are held not so firmly to the nitrogen atom. It seems probable that the thermal decomposition of acid azides would be affected in a similar manner. On applying these considerations to the azides, the benzenesulfonyl group seems to exert a much greater attraction for electrons than does the benzoyl group. This inductive effect apparently draws the electrons away from the two nitrogen atoms that split off as nitrogen gas and therefore renders the sulfonazide more stable than the carboxylic azide.

In a purely qualitative sense we may compare the electron-attracting power of the benzoyl, sulfonyl, and sulfinyl groups by examining the ionization constants of benzoic acid, benzenesulfonic acid, and benzenesulfinic acid. If the electrons are held quite firmly to the fragment of an acid that becomes the anion, the hydrogen is held less firmly and is therefore in a more favorable position to become a proton. The relative size of the ionization constant of an acid is thus indicative of the relative electron-attracting power of the anion fragment. A large ionization constant for an acid indicates that the anion fragment is strongly electron-attracting; a small ionization constant indicates that the anion fragment is either weakly electron-attracting or perhaps electron-repelling. Following are the values of the ionization constants for the acids listed:

<u>Acid</u>	<u>Ionization Constant</u>
Benzoic acid (24)	6.27×10^{-5}
Benzenesulfinic acid (8)	3.0×10^{-2}
Benzenesulfonic acid (21)	stronger than hydrochloric acid

This indicates that the electron-attracting power of the benzenesulfinyl group lies in a position intermediate between the benzoyl group and the benzenesulfonyl group. It can therefore be expected that the benzenesulfinazide will show thermal instability at some temperature intermediate between the decomposition temperatures of the benzazide and the benzenesulfonazide.

If this is indeed the case, it seems possible that the course of the decomposition of benzenesulfinazide might be altered to resemble either the decomposition of the benzazide (readily measurable at 45° with rearrangement) or that of the benzenesulfonazide (very slow at 105° without rearrangement). If the benzene nucleus of the benzenesulfinazide is substituted by sufficiently powerful electron-repelling groups the decomposition of the sulfinazide might conceivably follow the course of the benzenesulfonazide decomposition. If the benzene nucleus is substituted by sufficiently powerful electron-attracting groups, the sulfinazide might possibly follow the course of the benzazide decomposition.

EXPERIMENTAL

All chemicals used in this experiment were reagent grade unless otherwise indicated. The petroleum ether (30-60°) employed throughout the experiment had been dried and stored over sodium. The melting points of all compounds and derivatives were determined in a copper block heated by a small flame and are uncorrected.

Preparation of benzenesulfinic acid1. By zinc dust reduction of benzenesulfonyl chloride

The benzenesulfinic acid was first prepared by reduction of benzenesulfonyl chloride with zinc dust (44). In a 2-l., three-neck, round-bottom flask equipped with an electrically driven stirrer was placed 300 ml. of water which was heated to 70° by passing in dry steam. The steam was shut off and 40 g. of zinc dust (90 percent pure) was added with thorough stirring. Then 44 g. (0.25 mole) benzenesulfonyl chloride (technical grade, Eastman Kodak Company) was added dropwise over a period of 10 minutes. The reaction mixture was stirred for an additional 10 minutes, then dry steam was passed into the solution until the temperature had reached 90°. The steam was discontinued and the reaction mixture was stirred for another 10 minutes. Then 12 g. (0.3 mole) of sodium hydroxide in 25 ml. of water was added. Finely powdered sodium carbonate was added in 5-g. portions until the solution was strongly basic to litmus. The reaction mixture was filtered and the filtrate was concentrated to one-fourth its original volume on a steam bath. When the solution was cooled in an ice bath, crystals of sodium benzenesulfinate separated and were collected by filtration. The filtrate was further concentrated and cooled producing more sodium benzenesulfinate. The crystals were air dried overnight (no efflorescence was noted as reported (44) with

sodium p-toluenesulfinate). The yield of sodium benzenesulfinate was 32.9 g., which corresponds to 65.8 percent of the theoretical yield if the salt is considered to be the dihydrate as was the p-toluenesulfinate.

The sodium salt (32.9 g.) was then dissolved in the minimum amount of water (approximately 100 ml.) and 6 N hydrochloric acid was added to precipitate the acid. The acid was collected by filtration, washed with cold water, and dried in a vacuum desiccator over concentrated sulfuric acid. The yield was 17 g. of benzenesulfonic acid, which was 48 percent of the theoretical amount based on the benzenesulfonyl chloride.

2. By sodium sulfite reduction of benzenesulfonyl chloride

A better method of preparing benzenesulfonic acid is that of Smiles and Bere (40), which uses sodium sulfite to reduce the sulfonyl chloride. Even better yields than those reported by Smiles and Bere were obtained when a higher temperature was employed and the reaction mixture was kept basic throughout.

One mole, 126 g., of anhydrous sodium sulfite was added to 600 ml. of water in an open beaker and the solution was heated on the steam bath to 85°. Benzenesulfonyl chloride (0.5 mole, 88g.) was then added over a period of 10 minutes with constant stirring of the solution. It was essential that the reaction mixture be kept slightly basic at all times, since failure to do so invariably resulted in a poorer yield (30-40 percent). A 40 percent solution of sodium hydroxide was added at intervals as required, to accomplish this end. The reaction was complete in about 15 minutes and the mixture was allowed to cool before filtering. Concentrated hydrochloric acid was added until the sulfonic acid precipitate formed. The solution was then chilled, and the acid was collected by filtration, washed with ice water and

dried in a vacuum desiccator over concentrated sulfuric acid. The yield of benzenesulfonic acid was 58 g. (m.p., 81-83°; Otto (31) reported m.p., 83-84°). This represented a yield of 67 percent of the theoretical amount based on benzenesulfonyl chloride.

Purification of the thionyl chloride

The thionyl chloride used in this experiment was the technical grade manufactured by Eastman Kodak Company. It was purified by distillation from quinoline and redistillation from boiled linseed oil (17).

Preparation of activated sodium azide

Technical grade sodium azide, manufactured by Eastman Kodak Company, was prepared in the activated form by trituration with hydrazine hydrate and precipitation by acetone (41) (30). In all cases the sodium azide was activated not more than two hours before it was used in the reaction mixture.

Preparation of benzenesulfinyl chloride

The benzenesulfinyl chloride was prepared in general by the procedure described by Hilditch and Smiles (23), but certain modifications proved advantageous. Since the reaction between benzenesulfinyl chloride and sodium azide was also to be performed in petroleum ether, the acid chloride was not isolated before the reaction with sodium azide.

Benzenesulfonic acid was placed in a 500-ml., three-neck, round-bottom flask and enough petroleum ether (dried over sodium) was added to cover the acid, which is practically insoluble in this solvent. However, when the acid was treated directly with thionyl chloride, as described by Hilditch and Smiles (23), the yields were very poor (less than ten percent) in the three preparations attempted. The flask was protected from moisture by a calcium chloride drying tube. Thionyl chloride was then added over a period of three

hours by a dropping funnel. The reaction proceeded vigorously, was endothermic, and was considered complete when the acid residue disappeared and no more odor of sulfur dioxide or hydrogen chloride was detected. The time required was usually 12 to 18 hours. Excess thionyl chloride was removed by the aspirator at room temperature. The yield of benzenesulfinyl chloride was practically quantitative. The reaction mixture was not, as Hilditch and Smiles directed (23), heated on the water bath. Invariably this caused the formation of an insoluble gummy residue which answered the description of the disulfoxide found by Hilditch (22).

The benzenesulfinic acid used in the preparation of the benzenesulfinyl chloride must be thoroughly dried before treatment with thionyl chloride. When the acid is dry, the reaction mixture becomes pale yellow in color; but when the acid is not dry the reaction mixture develops an amber shade and even may be dark brown in color.

Reactions of benzenesulfinyl chloride with sodium azide

In Experiment No. 1 the benzenesulfinyl chloride was treated with sodium azide in petroleum ether at room temperature in the presence of air. In Experiment No. 2 the reaction between benzenesulfinyl chloride and sodium azide was performed in petroleum ether at dry ice-acetone temperature in an inert atmosphere, and before warming up to room temperature the solvent was changed to acetone. The concentrations of the reactants in Experiments No. 1 and No. 2 were the same. Experiment No. 3 was performed essentially as Experiment No. 2 with only two exceptions: the concentrations of reactants were only one-third of the concentrations in Experiment No. 2; the solvent was petroleum ether throughout.

Experiment No. 1

The reaction was conducted at room temperature in a 250-ml., three-neck, round-bottom flask protected from moisture by a calcium chloride drying tube. The solvent was 100 ml. of petroleum ether dried over sodium. To the acid chloride, prepared from 27 g. (0.19 mole) of benzenesulfinic acid, was added 14 g. (0.21 mole) of activated sodium azide. The reaction mixture was stirred constantly by an electrical stirrer.

No reaction was evident for about five minutes. At this time evolution of gas was noted and the reaction flask became quite warm. The solution turned from very pale yellow to a deeper yellow color and some crystallization of a yellow substance was noted. The reaction was allowed to continue for 2 $\frac{1}{2}$ hours. About a milliliter of the petroleum ether solution was withdrawn by a pipette to make a carbylamine test for aniline as described later (page 22), but the results were negative. The reaction mixture was filtered and the filtrate was evaporated by an aspirator leaving about 3-4 ml. of a pale yellow oil. The precipitate was extracted with acetone and the acetone was evaporated by an aspirator leaving 6 g. of a crude, pale yellow product (m.p., 135-139°). Recrystallization of this solid from ethanol gave a white solid with m.p., 146-148°. This product was subsequently identified as benzenesulfonamide, as described on page 22. The pale yellow oil was not identified at this time, but sulfur was found to be present after sodium fusion.

The inorganic salt residue (13 g.) left from the acetone extraction of the solid was presumed to be a mixture of sodium azide and sodium chloride. Addition of five percent aqueous silver nitrate produced a white precipitate which was partially soluble in dilute nitric acid. Silver azide is soluble

in dilute nitric acid, whereas silver chloride is not (42). No attempt was made to isolate the silver salts at this time because of the highly explosive nature of silver azide (16).

Experiment No. 2

Benzenesulfonic acid (58 g., 0.41 mole) was placed in 200 ml. of petroleum ether in a 500-ml., three-neck, round-bottom flask. The acid chloride was then prepared as previously described.

The reaction flask was placed in a dry ice-acetone bath and an electrical stirrer was introduced. Natural gas was passed over the solution at this time to protect the reaction mixture from air oxidation. This gas was dried by passage through a calcium chloride drying tube and oxygen was removed from it by bubbling through a basic pyrogallol solution. At this point activated sodium azide (27.7 g., 0.41 mole) was added to the reaction flask. After 24 hours the petroleum ether was withdrawn by suction filtration using a sintered-glass filter stick, and 100 ml. of pre-cooled, reagent acetone was placed in the flask and stirred. The flask was removed from the dry ice-acetone bath and stirring was discontinued. The temperature of the flask was allowed to rise to room temperature, and a thermometer was introduced into the solution when evolution of gas was noted. The temperature at this time was approximately -25° . The reaction mixture was cooled quickly and evolution of gas ceased.

A 500-ml. gas burette was mounted and the evolved gas was passed through the following absorption train:

1. Basic pyrogallol solution to remove oxygen,
2. A calcium chloride drying tube,
3. A dry ice-acetone trap to catch condensable vapors,

4. Mineral oil to absorb any noncondensable hydrocarbons.
5. A 40 percent solution of sodium hydroxide to remove any acidic gases such as carbon dioxide or sulfur dioxide.

The volume of the gas, which was odorless and noncombustible, was 7.37 l. at 30°. On the assumption that the gas is nitrogen and that it came from the decomposition of benzenesulfinazide, 7.37 l. represents a yield of 73 percent of the theoretical amount based on the benzenesulfinic acid.

Toward the end of the evolution of nitrogen the contents of the flask became warm (46°) and acquired a dark red-brown color. At this time a faint odor of sulfur dioxide was detected. The solution was filtered and the precipitate was washed three times with acetone. (Extreme caution must be exercised in performing this reaction: on one occasion when the reaction mixture was allowed to approach room temperature rapidly a rather violent explosion occurred at around -5°.) The acetone solution was allowed to evaporate spontaneously and left a dark brown residue. The residue was dissolved in hot ethanol from which white crystals appeared on cooling in a salt-ice bath. This crystals melted at 143-146° and were identified as benzenesulfonamide (page 22). About 12 g. of the crude product was obtained.

The petroleum ether solution was then concentrated by the aspirator leaving about 15 ml. of a pale yellow, oily product. The oil distilled under 100-mm. pressure with extensive decomposition. No constant boiling point was obtained but it was evident that the boiling point was in the neighborhood of 170-185°.

The inorganic salt residue (31 g.) left from the acetone extraction was assumed to contain only sodium chloride and sodium azide. A dried, weighed sample was dissolved in water and five percent silver nitrate solution was

added until precipitation was complete. The solution was made slightly acid with dilute nitric acid and the precipitate remaining was collected in a Gooch crucible and weighed as silver chloride. The mixture was found to be 78 percent sodium chloride by weight, which means 80 percent of the original sodium azide was converted to sodium chloride in the course of the reaction.

Experiment No. 3

In order to study the concentration effect, 20 g. (0.14 mole) of benzenesulfinic acid was converted to the acid chloride in 200 ml. of petroleum ether. The flask was placed in a dry ice-acetone bath and 9.2 g. (0.14 mole) activated sodium azide was added. The reaction was conducted in a 500-ml., three-neck, round-bottom flask from which air was excluded in the manner described in Experiment No. 2. The solution was stirred continuously for 24 hours.

The petroleum ether was not withdrawn as in Experiment No. 2, but the reaction flask was merely removed from the dry ice-acetone bath and occasionally recooled to prevent too rapid heating with constant stirring all the while. The intense coloration noted in Experiment No. 2, when acetone was the solvent, did not develop in the petroleum ether solution. The pale yellow color of the original sulfinyl chloride solution persisted throughout the reaction and deepened somewhat when the temperature was raised to that of the room in the last stages of the reaction. The volume of nitrogen, purified and collected as in Experiment No. 2, amounted to 0.8 liter at 32°, which represents a yield of 22.8 percent of the theoretical amount based on benzenesulfinic acid.

About one-fourth of the vigorously stirred reaction mixture was removed and filtered. The crystalline mass thus obtained was extracted with 10 ml.

of acetone and the extract was placed on a watch glass in a vacuum desiccator over concentrated sulfuric acid. The acetone evaporated quickly leaving very pale yellow crystals (m.p., 112-117°). On recrystallization from ethanol the melting point was 117-119°. The following morning the melting point was 92-112° and the pale yellow color had disappeared. Recrystallization from ethanol left white crystals (m.p., 146-148°) which were identified as benzenesulfonamide (page 22). The very faintly yellow compound (m.p., 117-119°) was presumed to be benzenesulfinamide (m.p., 121°) (20) which apparently underwent air oxidation to the sulfonamide overnight.

The carbylamine test (page 22) was performed on 3-4 drops of the petroleum ether solution from the reaction but the results were negative indicating that aniline was not present.

A small portion of the ether solution from the reaction mixture was allowed to evaporate on a watch glass in air. The solution fumed in moist air. When the fuming ceased, crystals had formed around the edge and a small pool (about 1 ml.) of pale yellow liquid was left. The mixture was extracted with 4 ml. of petroleum ether. The crystals did not dissolve and were separated by filtration. Evaporation of this petroleum ether extract left a pale yellow liquid identified as thiophenol (page 22). The crystals were recrystallized from water and identified as benzenesulfonic acid by melting point, solubility behavior, and other physical properties.

In isolating in a similar manner the products of the remaining three-quarters of the reaction mixture, the acetone extraction of the crystals was evaporated by the aspirator leaving benzenesulfonamide (m.p., 145-147). None of the compound (m.p., 117-119°) presumed to be benzenesulfinamide was obtained.

The major products isolated from the entire reaction mixture were 6 g. (0.042 mole) of benzenesulfonic acid, 4 g. (0.036 mole) of thiophenol, 7 g. (0.044 mole) of benzenesulfonamide, and 9 g. of inorganic salt residue.

Some of the inorganic salt was placed in water and the solution was made basic with sodium hydroxide. This solution on heating produced the faint odor of ammonia (or low molecular weight amine). Determination of the volatile base by refluxing the salt in basic solution, absorbing the basic vapor in standardized hydrochloric acid, and titrating with standardized sodium hydroxide solution showed 0.008 equivalent of base obtained from the total inorganic salt residue.

A sample of petroleum ether from the reaction mixture was collected by distillation and a determination of unsaturation by titration with bromine in carbon tetrachloride showed 0.00066 mole of unsaturation present. A blank was run but no unsaturation was detected in the original petroleum ether.

Identification of compounds:

The benzenesulfonamide was identified by melting point, mixed melting point, and preparation of N-xanthylbenzenesulfonamide (m.p., 200-200.5°) by the method described by Phillips and Frank (36) (mixed melting point was also taken of N-xanthyl derivative). Qualitative tests (7) following sodium fusion also indicated the presence of sulfur and nitrogen.

Thiophenol was identified by preparation of the 2,4-dinitrodiphenyl sulfide (m.p., 121°) and subsequent oxidation of this compound to the sulfone (m.p., 161°) (7). The presence of sulfur was established by a qualitative test (7) following sodium fusion.

The carbylamine reaction for primary amines was performed in the tests conducted for aniline, since this test is very sensitive for aromatic amines.

A few drops of the mixture suspected of containing aniline were placed in a test tube containing 4 drops of chloroform and 2 ml. of 2 N potassium hydroxide in methanol. The mixture was warmed slightly and the odor noted. Aniline, if present, would react with the chloroform and potassium hydroxide to form phenyl isocyanide, which has a nauseating odor easily detectable in extremely minute quantities (?).

DISCUSSION

Preparation of benzenesulfinic acid

The reduction of benzenesulfonyl chloride by zinc dust (44) did not prove to be very satisfactory for obtaining the acid. Extensive decomposition of the acid had occurred after two days in a vacuum desiccator over concentrated sulfuric acid. In addition the overall yield from benzenesulfonyl chloride to benzenesulfinic acid was at best only about 50 percent. Better yields may be obtained by the sodium sulfite method of Smiles and Bere (40), and it was found in this work that warming the reaction mixture and keeping it basic improved these yields even more. The acid prepared in this manner begins to show signs of decomposition only after five days in a vacuum desiccator over concentrated sulfuric acid. The yield of benzenesulfinic acid based on the benzenesulfonyl chloride is 65-75 percent of the theoretical amount. The sodium sulfite reduction requires less time and fewer operations, results in a larger yield, gives a more stable product, and is less expensive than reduction by zinc dust.

Preparation of benzenesulfinyl chloride

Three attempts to prepare benzenesulfinyl chloride by treatment of benzenesulfinic acid directly with excess thionyl chloride, as described by Hilditch and Smiles (23), resulted in very poor yields. However, when the reaction between the acid and thionyl chloride was conducted in petroleum ether over an extended period (12-18 hours), practically quantitative yields of the acid chloride were obtained. To prevent undesirable side reactions thoroughly dried benzenesulfinic acid must be used and the reaction mixture must not be heated on the water bath, since heating causes the formation of

an insoluble, gummy residue answering the description of the disulfoxide found by Hilditch (22).

Reaction of benzenesulfinyl chloride and sodium azide

Benzenesulfinazide was not isolated and characterized as such in this study. However, considerable experimental evidence supports the assumption that benzenesulfinazide is the compound which resulted from the reaction of benzenesulfinyl chloride and sodium azide: (a) a highly reactive compound, thermally unstable at temperatures above -25° , was formed at dry ice-acetone temperature in petroleum ether; (b) in its thermal decomposition the compound evolved nitrogen gas; (c) benzenesulfonamide was identified as an ultimate product of the decomposition; and (d) sodium azide was converted to sodium chloride in the course of the reaction.

Since thermal instability is a characteristic property of acid azides, the assumption that the compound formed is benzenesulfinazide is in line with the known character of other acid azides. From purely theoretical considerations (page 10), however, it was not anticipated that benzenesulfinazide would show thermal instability at a temperature as low as -25° . Although the electronegativity of the group to which the azide radical is attached in a molecule doubtless exerts an influence on the stability of an acid azide, this does not seem to be the only contributing factor.

The evolution of nitrogen gas, a characteristic property of acid azides, that accompanied the warming up of the reaction mixture also supports the assumption that an acid azide was present. In Experiment No. 2 the nitrogen evolved is 73 percent of the theoretical amount based on benzenesulfinic acid, if the nitrogen is assumed to arise from the decomposition of benzenesulfinazide. It does not seem possible to account for this nitrogen as coming from

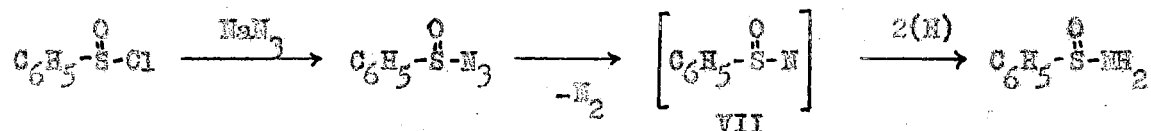
any source other than the acid azide.

If benzenesulfinazide did exist as a product of the reaction of benzenesulfinyl chloride and sodium azide, the sulfinazide could follow one, or both, of two courses in its thermal decomposition (page 6). If its decomposition follows the course of the carboxylic azides, thionyl aniline would be produced. However, if it behaves as the sulfonazides, benzenesulfinamide or a substituted benzenesulfinamide (or the oxidation product, the sulfonamide) would result from its decomposition. Therefore the presence of either thionyl aniline or a benzenesulfinamide (or benzenesulfonamide) would lend further support to the assumption that benzenesulfinazide had been present. Only negative evidence was obtained for the presence of thionyl aniline, but it was possible on one occasion (page 21) to identify a compound by melting point as benzenesulfinamide, which presumably underwent air oxidation overnight to benzenesulfonamide. The identification of this compound definitely established that a sulfur-nitrogen bond had been formed in the course of the reaction, and indicated that the sulfur-nitrogen bond had once been of an acid azide nature.

If the reaction between benzenesulfinyl chloride and sodium azide proceeds with the formation of benzenesulfinazide, the inorganic salt product of the reaction would contain sodium chloride (page 9). The analysis of the inorganic salt residue showed that 80 percent of the original sodium azide (page 20) had been converted to sodium chloride, which is a slightly greater percentage than would be predicted from the volume of nitrogen evolved (73 percent), if both analyses are substantially correct. That part of the sodium chloride in excess of that expected from the nitrogen evolved could result from traces of impurities remaining from the preparation of the benzene-

sulfinyl chloride, i. e., hydrogen chloride or thionyl chloride. Another possible explanation of the excess sodium chloride is advanced later (page 28) in this report.

In view of the evidence presented above, it was felt with some certainty that benzenesulfinazide was the product of the reaction between benzenesulfinyl chloride and sodium azide. The formation of benzenesulfinazide and the probable course of its major decomposition may be represented by:



The azide residue (VII) must have acted as a dehydrogenating agent on the petroleum ether--unsaturation was detected in the petroleum ether (page 22)--in a manner similar to the sulfonazide residue (2) and the product of this reaction was benzenesulfinamide, which subsequently underwent oxidation to benzenesulfonamide. The oxidation could have occurred at the expense of air, unreacted benzenesulfinyl chloride, benzenesulfinazide, or a combination of these. The following table of quantitative data determined in Experiment No. 3 will aid in the discussion of this oxidative process. Presumably the reclaimed benzenesulfinic acid resulted from the hydrolysis of unreacted acid chloride, although it is possible that some of the acid could have come from the hydrolysis of undecomposed benzenesulfinazide. However, this latter possibility seems remote in view of the thermal instability of the azide, since the azide would probably not be present at the time of hydrolysis.

If the amide or azide acts as the oxidizing agent with thiophenol as the reduced product, a nitrogen fragment would exist in the reaction mixture,

TABLE OF DATA - EXPERIMENT NO. 3

<u>Starting product</u>	<u>Number of Moles</u>
Benzenesulfinic acid	0.140
<u>Recovered products</u>	
Benzenesulfonamide	0.044
Thiophenol	0.036
Benzenesulfinic acid (reclaimed by hydrolysis)	0.042
Total of recovered products:	<u>0.122</u>
<u>Miscellaneous</u>	
Unsaturation in petroleum ether	0.0007
Ammonia (or amine)	0.008

and indeed traces of ammonia (or low molecular weight amine) were found in the inorganic salt as shown in the above table. If the sulfinyl chloride is the oxidizing agent, the chlorine fragment would be lost, conceivably as hydrogen chloride, which could react with sodium azide producing sodium chloride and hydrazoic acid. Such a process would lead to a higher chloride content in the inorganic salt residue than would be predicted by measurement of the nitrogen evolved. This seems to be supported by the results of Experiment No. 2, in which the nitrogen evolved was 73 percent of the theoretical amount, while analysis of the inorganic salt showed 80 percent of the original sodium azide had been converted to sodium chloride.

The method of formation of the thiophenol is obscure, although it is probably the reduction product resulting from the oxidation of benzenesulfinamide to the sulfonamide, since benzenesulfonamide and thiophenol exist in substantially equimolar quantities. Air oxidation of some benzenesulfinamide could explain the difference in quantities of these products.

The small amount of unsaturation found in the petroleum ether is not considered a major obstacle to the definition of the petroleum ether as the source of hydrogen in the reaction, because the molecular residues formed by dehydrogenation could condense without the formation of an unsaturated product (page 3). In addition low molecular weight unsaturated products could have been lost because of their high volatility. Considering all this, it is remarkable that any unsaturation was detected at all.

RECOMMENDATIONS

After reviewing the results of this experimental work, the author feels that additional study of this problem would prove fruitful. The following suggestions are presented: (a) that the reaction between the acid chloride and sodium azide be performed in normal heptane or normal hexane solution rather than petroleum ether in order that the unsaturated and condensed products of the reaction may be more easily detected and identified; (b) that nitrogen be employed as the inert atmosphere rather than natural gas; (c) that the reaction be performed using various concentrations in order to cast more light on the effect of concentration on the course of the reaction; (d) that the sulfinazide be isolated and characterized at low temperatures where it is apparently stable; (e) that an attempt be made to prepare the sulfinazide by the acid hydrazide method; (f) and that the reaction be extended to include other sulfinic acid derivatives, such as p-toluenesulfinyl chloride, etc.

SUMMARY

1. The sodium sulfite reduction of benzenesulfonyl chloride to benzenesulfinic acid has been compared with the zinc dust method and has been shown to be more satisfactory from the standpoint of time, yield, and cost.

Certain important modifications of the sodium sulfite method have been devised which gave even better yields of a more stable product.

2. By varying the procedure described by Hilditch and Smiles (23) it was possible to increase substantially the yield of benzenesulfinyl chloride from the action of thionyl chloride on benzenesulfinic acid.

3. Dry activated sodium azide and benzenesulfinyl chloride in petroleum ether were found to react at dry ice-acetone temperature forming a compound that is thermally unstable at temperatures above -25° .

4. Although the compound formed by the reaction of benzenesulfinyl chloride and sodium azide was not isolated and characterized as such, it was shown indirectly to be benzenesulfinazide.

5. A scheme was suggested to account for the major products of the decomposition, thiophenol and benzenesulfinamide (the sulfinamide is readily oxidized to sulfonamide).

6. The compound presumed to be benzenesulfinazide was even more unstable thermally than benzazide although the course of its decomposition followed that of benzenesulfonazide.

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In February, 1948 he married Marguerite Hobbs of Honolulu, Hawaii, and in January, 1949 a daughter, Susan Jalland, was born.

THESIS TITLE: The Reaction of Benzenesulfinyl Chloride and
Sodium Azide

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