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Organic Sulfur Compounds. XIII. The Reactions of *p*-Toluenesulfinyl Chloride with Azides

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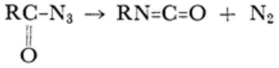
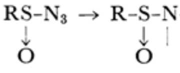
Attempts to prepare a sulfinyl azide resulted in the formation of the sulfonyl azide, disulfide, and thiolsulfonate; of these products, the first two were considered to be disproportionation products of the intermediate, sulfinyl azide. The reaction of a sulfinic acid with hydrazoic acid gave a sulfonamide. No rearrangement similar to the Curtius or the Schmidt reaction was observed.

Recently a photochemical rearrangement of a sulfonyl azide has been reported,[1] although this class of compounds has been established as giving no intramolecularly rearranged products on thermal decomposition.[2-5] No sulfinyl azide (I) has, to the authors' knowledge, yet been prepared. Since the analogous carboxylic azides are known to decompose thermally to give nitrogen and the rearranged product, isocyanate (reaction 1), it seemed of interest to study the reactions which could proceed through the intermediate formation of a sulfinyl azide. If a sulfinyl azide was actually produced and then lost its nitrogen to generate a sulfinyl nitrene (II), an intramolecular rearrangement to a *N*-sulfinylamine (III) would be expected.



$$\mathrm{R\underset{\underset{O}{\|}}{C}{-}N_3 \rightarrow RN{=}C{=}O + N_2} \qquad (1)$$



$$\mathrm{R\underset{\underset{O}{\downarrow}}{S}{-}N_3 \rightarrow R{-}\underset{\underset{O}{\downarrow}}{S}{-}\underset{|}{N}{-} + N_2} \qquad (2)$$

(I) (II)

$$\mathrm{II \rightarrow \underset{(III)}{R{-}N{=}S{=}O}} \qquad (3)$$

In this paper, the results of attempts to synthesize sulfinyl azides by several alternative routes will be described.

When sodium azide was treated with *p*-toluenesulfinyl chloride in benzene, only a small amount of nitrogen was evolved. After the reaction was quenched by water a considerable amount of *p*-toluenesulfinic acid was recovered, whereas there was no indication of the presence of *p*-toluidine, which should be formed by the hydrolysis of the expected product of the rearrangement, *N*-sulfinyl-*p*-toluidine. When methylene chloride was used as the solvent, the reaction was again sluggish, and the volume of the nitrogen evolved was only one-tenth of the calculated amount. Among the reaction products, 15 mol.% of *p*-toluenesulfonyl azide was detected by infrared spectroscopy.

On the other hand, the reaction in acetonitrile was rather rapid. After the reaction mixture had been let stand for 4 days at room temperature, the mixture was diluted with water and extracted with methylene chloride; the formation of a substantial amount of *p*-toluenesulfonyl azide was again observed, while there was no trace of sulfinyl-*p*-toluidine or *p*-toluidine in the products.

The reaction between silver azide and *p*-toluenesulfinyl chloride in benzene was also very slow and stopped halfway.

Sodium azide and silver azide are almost insoluble in the above solvents. This was considered to be the main reason for the slow rate of reaction.

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[1] W. Lwowski and E. Scheiffele, *J. Am. Chem. Soc.*, **87**, 4359 (1965).

[2] O. C. Dermer and M. T. Edmison, ibid., **77**, 70 (1955).

[3] J. F. Heacock and M. T. Edmison, ibid., **82**, 3460 (1960).

[4] G. Smolinsky and B. I. Feuer, ibid., **86**, 3085 (1964).

[5] J. E. Franz, C. Osuch and M. W. Dietrich, *J. Org. Chem.*, **29**, 2922 (1964).

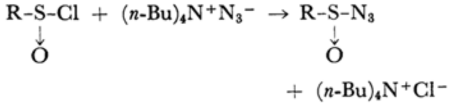
Indeed, when a solution of *p*-toluenesulfinyl chloride in *N*, *N*-dimethylformamide was slowly added to a solution of sodium azide in the same solvent, which could dissolve some sodium azide upon being warmed, the evolution of nitrogen started immediately and reached a total of 78 mol.%. From the reaction mixture, 40 mol.% of *p*-toluenesulfonyl azide and small amounts of *p*, *p*-ditolyl disulfide, *p*-toluenesulfonamide, and sodium *p*-toluenesulfonate were isolated. Again in this case, *p*-toluidine or *N*-sulfinyl-*p*-toluidine was not detected among the products.

Reactive *N*-sulfinylamines, such as sulfinyl sulfonamide, have been reported to react with dimethylformamide to give azomethine derivatives⁶⁾; the reaction of *N*, *N*-diphenylformamide with sulfinyl sulfonamide has been also described.⁷⁾ Therefore, it is possible that the reaction of sodium azide with *p*-toluenesulfinyl chloride in dimethylformamide gave a sulfinylamine, which reacted further with the solvent to form a condensed product instead of *p*-toluidine. However, no reaction was observed between *N*-sulfinylaniline and dimethylformamide when these reactants were heated on a water bath for several hours. This suggests that if a *N*-sulfinylamine (III) was formed by the intramolecular rearrangement of a sulfinyl nitrene (II), the former would be stable under the reaction conditions and could, therefore, be isolated.

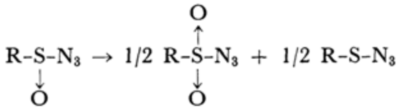
The material balance in the reaction of sodium azide with *p*-toluenesulfinyl chloride in dimethylformamide was far from satisfactory. Most probably, some reaction product other than the sulfinylamine reacted with the solvent to give volatile compounds, which could escape notice during the treatment of the reaction mixture.

Finally, the reaction of *p*-toluenesulfinyl chloride with a solution of tetra-*n*-butylammonium azide in benzene was examined. The reaction proceeded very rapidly at room temperature, accompanied by the evolution of about 75 mol.% of nitrogen. Among the products, *p*-toluenesulfonyl azide (38%), *p*-tolyl *p*-toluenethiolsulfonate (13%), and *p*, *p*-ditolyl disulfide were detected. A close examination of every fraction of the reaction mixture confirmed the absence of *N*-sulfinyl-*p*-toluidine and its hydrolyzed product.

Consequently, the reaction of *p*-toluenesulfinyl chloride with azide ions may be concluded to result not in the formation of the expected rearrangement product of the sulfinyl nitrene II, but in the formation of several other possible products; their formation can best be explained by assuming the disproportionation of the possible intermediate, a sulfinyl azide I, as is shown below:



$$\mathrm{R{-}\underset{\underset{O}{\downarrow}}{S}{-}Cl + (\mathit{n}\text{-}Bu)_4N^+N_3^- \rightarrow R{-}\underset{\underset{O}{\downarrow}}{S}{-}N_3 + (\mathit{n}\text{-}Bu)_4N^+Cl^-} \quad (4)$$



$$\mathrm{R{-}\underset{\underset{O}{\downarrow}}{S}{-}N_3 \rightarrow 1/2\ R{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}N_3 + 1/2\ R{-}S{-}N_3} \quad (5)$$

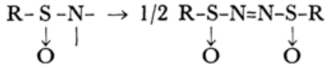
(IV)

$$\mathrm{1/2\ R{-}S{-}N_3 \rightarrow 1/4\ R{-}S{-}N{=}N{-}S{-}R + 1/2\ N_2} \quad (6)$$

$$\mathrm{1/4\ R{-}S{-}N{=}N{-}S{-}R \rightarrow 1/4\ RS{-}SR + 1/4\ N_2} \quad (7)$$

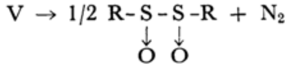
Although the existence of sulfenyl azides has not been established, Kharasch⁸⁾ has described how the reaction of sulfenyl chlorides with sodium azide gives the disulfide as the only isolatable product, probably via the reactions 6 and 7.

Although the mechanism of the formation of the thiolsulfonate is uncertain at present, the following reaction sequence may be tentatively presumed to be applicable:



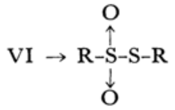
$$\mathrm{R{-}\underset{\underset{O}{\downarrow}}{S}{-}\underset{|}{N}{-} \rightarrow 1/2\ R{-}\underset{\underset{O}{\downarrow}}{S}{-}N{=}N{-}\underset{\underset{O}{\downarrow}}{S}{-}R} \quad (8)$$

(III) (V)



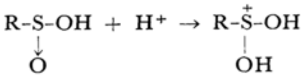
$$\mathrm{V \rightarrow 1/2\ R{-}\underset{\underset{O}{\downarrow}}{S}{-}\underset{\underset{O}{\downarrow}}{S}{-}R + N_2} \quad (9)$$

(VI)

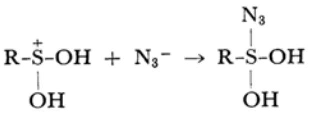


$$\mathrm{VI \rightarrow R{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}S{-}R} \quad (10)$$

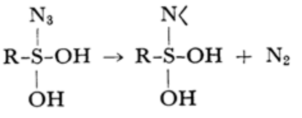
The reaction of *p*-toluenesulfinic acid with hydrogen azide in a benzene-water mixture was also attempted in order to find out whether any reaction similar to the Schmidt reaction of carboxylic acids occurs. The only product identified was *p*-toluenesulfonamide, and no toluidine salt was detected, showing the absence of the molecular rearrangement in this reaction also. The formation of sulfonamide could be attributed to the following reaction mechanism:



$$\mathrm{R{-}\underset{\underset{O}{\downarrow}}{S}{-}OH + H^+ \rightarrow R{-}\overset{+}{\underset{\underset{OH}{|}}{S}}{-}OH} \quad (11)$$



$$\mathrm{R{-}\overset{+}{\underset{\underset{OH}{|}}{S}}{-}OH + N_3^- \rightarrow R{-}\overset{\overset{N_3}{|}}{\underset{\underset{OH}{|}}{S}}{-}OH} \quad (12)$$



$$\mathrm{R{-}\overset{\overset{N_3}{|}}{\underset{\underset{OH}{|}}{S}}{-}OH \rightarrow R{-}\overset{\overset{N\langle}{|}}{\underset{\underset{OH}{|}}{S}}{-}OH + N_2} \quad (13)$$

(VII)

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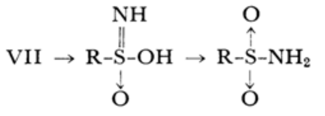
6) G. Kresze and R. Albrecht, *Angew. Chem.*, **74**, 781 (1962); R. Albrecht, G. Kresze and B. Mlakar, *Chem. Ber.*, **97**, 483 (1964).

7) G. Tosolini, *Chem. Ber.*, **94**, 2731 (1961).

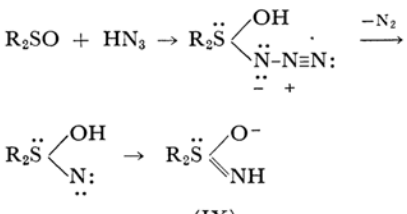
8) N. Kharasch, "Organic Sulfur Compounds," Vol. 1, Pergamon Press, New York (1961), p. 377.



$$\mathrm{VII} \rightarrow \mathrm{R{-}}\overset{\substack{\mathrm{NH}\\ \|}}{\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}}\mathrm{{-}OH} \rightarrow \mathrm{R{-}}\overset{\substack{\mathrm{O}\\ \uparrow}}{\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}}\mathrm{{-}NH_2}$$

(VIII)

Although the proposed intermediate, the hydroxysulfoximine VIII, is not known, the related sulfoximine IX has been shown to be formed by the reaction of a sulfoxide with hydrazoic acid,⁹⁾ probably according to the following reaction mechanism:



(IX)

Experimental

Materials.—Tetra-*n*-butylammonium azide was prepared by distilling an aqueous hydrogen azide solution, collecting the distillate directly in a solution of tetra-*n*-butylammonium hydroxide in water, and evaporating the resulting salt solution to complete dryness under reduced pressure.¹⁰⁾

The Reaction of *p*-Toluenesulfinic Acid with Hydrazoic Acid.—To a cooled mixture of 1 g. of sodium azide, 1 ml. of water, and 6 ml. of benzene, 0.7 g. of concentrated sulfuric acid was added. A solution of 1.5 g. of *p*-toluenesulfinic acid in benzene was added to the above solution under cooling. After one night, the benzene layer was separated and evaporated to leave 0.5 g. of *p*-toluenesulfonamide. The aqueous layer was made alkaline and extracted with ether in order to check for the presence of *p*-toluidine, but no residue remained after the evaporation of the solvent.

The Reaction of Sodium Azide with *p*-Toluenesulfinyl Chloride in Dimethylformamide.—When 1.5 g. of sodium azide was warmed with 200 ml. of dimethylformamide which had been dehydrated by calcium hydride and rectified, most of the salt dissolved. When a solution of 4.0 g. of sulfinyl chloride (23 mmol.) in 15 ml. of the same solvent was then added to the above azide solution at room temperature, the reaction started immediately, accompanied by a rapid evolution of gas; the total volume of gas was 450 ml. (18 mmol.) The solvent was removed from the reaction mixture under reduced pressure, and the residue was treated with methylene chloride. From the insoluble part, 0.59 g. (15 mol.%) of *p*-toluenesulfonamide and some sodium *p*-toluenesulfonate were isolated. The part soluble in methylene chloride was fractionated by column chromatography over alumina to obtain 0.16 g. of *p, p*-ditolyl disulfide (2.8 mol.%) and 1.8 g. of *p*-toluenesulfonyl azide (39 mol.%).

The Reaction of Tetra-*n*-butylammonium Azide with *p*-Toluenesulfinyl Chloride.—To a warm solution of 4.1 g. of the azide (14.4 mmol.) in 100 ml. of dry benzene, there was added, drop by drop, 2.5 g. of sulfinyl chloride (13.9 mmol.) in 30 ml. of benzene; a vigorous evolution of gas was observed, the volume totalling 245 ml. (75 mol.%). After one night, the reaction mixture was shaken with water, the benzene layer was dried, and subjected directly to infrared measurement; it was estimated that 1.04 g. of *p*-toluenesulfonyl azide (76% of the theoretical yield based on the reactions 4 and 5) and 0.52 g. of *p*-tolyl *p*-toluenethiolsulfonate (13 mol.%) were formed. The elution chromatography of the solute of the above solution with petroleum ether gave 0.43 g. of pure *p, p*-ditolyl disulfide (identified by its m. p. and infrared spectrum) (48% of the theoretical yield based on the reactions 5—7); its presence in the original benzene solution could not be detected by infrared spectroscopy because of the coincidence of the key bands of the disulfide with those of the other major products. The aqueous extract of the reaction mixture was evaporated to dryness under reduced pressure to give 4.0 g. of tetra-*n*-butylammonium chloride (14 mmol.); no *p*-toluenesulfonic acid nor amine compound was detected in this residue by means either of infrared spectroscopy or of such other characteristic reactions as the formation of *S*-benzylthiuronium sulfonate.

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9) F. Misani, T. W. Fair and L. Reiner, *J. Am. Chem. Soc.*, **73**, 459 (1951); H. R. Bentley and J. K. Whitehead, *J. Chem. Soc.*, **1950**, 2081; **1952**, 1572.

10) E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai and Y. Pocker, *J. Chem. Soc.*, **1957**, 1228.