

# Physical Sciences Section

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## FORMATION OF SULPHUR-SULPHUR BONDS BY THE NUCLEOPHILIC ATTACK ON SULPHENYL HALIDES AND THIOCYANATES

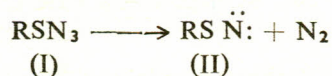
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**Abstract.** Aromatic sulphenyl chlorides were treated with sodium azide to prepare the corresponding sulphenyl azides in the presence of nitrene trapping agents, i.e. dimethyl sulphoxide, cyclohexene and norbornylene. No expected adduct was obtained but instead the corresponding disulphides were found in quantitative yields. Similar results were obtained when sulphenyl thiocyanate was treated with sodium azide. Disulphides did not either react with sodium azide or iodine azide. Sulphenylsodium salt also gave the corresponding disulphide in very high yield.

Sulphenyl azide (I) is to the author's knowledge, yet to be prepared. Benzenesulphenyl azide,<sup>1</sup> the first of its class, has been reported to give the corresponding nitrene. It seems of interest to study the reactions which could proceed through the intermediate formation of sulphenyl azide. If sulphenyl azide was actually produced and then lost its N to generate a sulphenyl nitrene (II), an aziridine formation would be expected in the presence of olefinic compounds, while in the presence of dimethyl sulphoxide sulphenyldimethylsulphoximine would be expected.



Sodium azide was treated with *p*-toluenesulphenyl chloride in acetonitrile, in the presence of dimethyl sulphoxide at  $-30^\circ\text{C}$ , nitrogen was evolved and dark red colouration was observed which gradually disappeared and nearly quantitative yield of *p*-toluenedisulphide was obtained. The substituted aromatic sulphenyl chlorides gave the corresponding disulphides (Table 1).

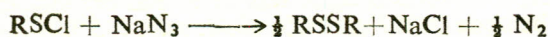
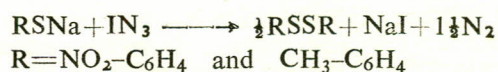


TABLE 1.

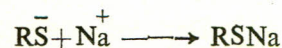
R	RSSR (% yield)	M.p.
$\text{C}_6\text{H}_5$	98	57-58°
<i>p</i> - $\text{CH}_3$ - $\text{C}_6\text{H}_4$	90	45-46°
<i>p</i> - $\text{NO}_2$ - $\text{C}_6\text{H}_4$	96	184-86°
<i>m</i> - $\text{NO}_2$ - $\text{C}_6\text{H}_4$	95	195°
2,4-di- $\text{NO}_2$ - $\text{C}_6\text{H}_3$	98	198-9°

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The reaction between the iodine azide and *p*-nitrobenzenesulphenylsodium in a mixture of acetonitrile and dimethyl sulphoxide was carried out, the red colouration of sodium salt (III) slowly discharged with the evolution of nitrogen gas. The product isolated from the reaction mixture was the corresponding disulphide in about 85% yield. Similar results were obtained when acetonitrile was used as solvent and norbornylene was used as sulphenyl azide trapping agent.

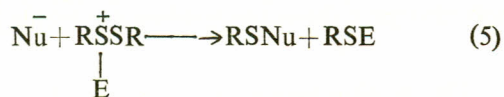
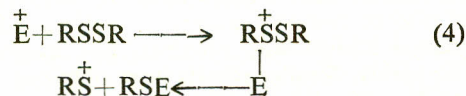


The sulphenyl thiocyanates have been reported to resemble the sulphenyl halides,<sup>2</sup> as thiocyanogen is believed to be pseudohalogen. Reaction between *o*-nitrobenzenesulphenyl thiocyanate, and sodium azide was carried out under similar conditions, using the same solvents. Brisk evolution of nitrogen was observed alongwith formation of dark red colouration, which slowly discharged. The reaction mechanism could be postulated on the basis of these results. The initial attack of the azide ion on the sulphenyl chloride or thiocyanate gives the sulphenyl anion. The sulphenyl anion in turn reacts with  $\text{Na}^+$  to give sodium salt (III) which gives the dark colouration in the reaction. The sodium salt could then react with the sulphenyl chloride or sulphenyl thiocyanate to give the corresponding disulphide, sodium chloride and sodium thiocyanate respectively.



$\text{X} = \text{Cl}$  or  $\text{SCN}$ ;  $\text{R} = \text{C}_6\text{H}_5$ —,  $\text{CH}_3$ — $\text{C}_6\text{H}_4$ —,  $\text{NO}_2\text{C}_6\text{H}_4$ —, and di- $\text{NO}_2$ . $\text{C}_6\text{H}_4$ —

The sulphur-sulphur bonds are subject to both homolytic and heterolytic cleavage.<sup>3</sup> Homolytic cleavage occurs by direct dissociation (eq 1) or as a result of attack of a free radical on one of the sulphur atoms (eq 2). Heterolytic cleavage can involve attack by a nucleophile<sup>6</sup> (eq 3) or assistance by electrophile (eq 4) or both<sup>8</sup> (eq 5).



These results encouraged us to look at the reactions of disulphides with sodium azide and iodine azide; but all the efforts to prepare sulphenyl azide proved to be unsuccessful as the disulphide was recovered in quantitative yield from the reaction mixture, although the reaction time was prolonged up to one week, with stirring at room temperature in acetonitrile and dimethyl sulphoxide mixture. The temperature was also raised to refluxing (82°) but no change in results was observed.

The benzenesulphenyl azide has been reported to be stable at low temperature, therefore, attempts were made at 0–35°. Iodine azide was also used, keeping in view the work of Kice<sup>3,8</sup> as both the nucleophile and electrophile (eqs 4, 5) could be involved in the reaction; but results similar to those of the sodium azide were obtained.

It could be concluded in the light of these results that in the reactions between sodium azide or iodine azide with sulphenyl chloride or sulphenyl thiocyanate the nucleophilic attack converts the sulphenyl group into a better leaving group than the chloride or thiocyanate groups.

### Experimental

#### Reaction of *p*-Toluenesulphenyl Chloride with Sodium Azide

A solution of *p*-toluenesulphenyl chloride (2.0 g) in acetonitrile (20 ml) was added dropwise with stirring, in 20 min to a suspension of sodium azide (20 g) in a mixture of acetonitrile (60 ml) and dimethyl sulphoxide (15 ml) at –35° (external bath temperature was –40°). Dark red colouration appeared soon after the addition of sulphenyl chloride. The mixture was stirred at –30° for ½ hr, during this time the colour disappeared with evolution of gas, leaving a yellow solution. The solvent was removed and residue crystallised from benzene and light petroleum (1:1) mixture. *p*-Toluenedisulphide (1.366 g, 90% yield, m.p. 45–46°) was obtained, spectral data resembled to the one reported in literature.

#### Reaction with Other Sulphenyl Chlorides

**Benzenesulphenyl Chloride.** Under the conditions stated above, benzenedisulphide, m.p. 57–58° was obtained in 98% yield.

***m*-Nitrobenzenesulphenyl Chloride.** Under the conditions mentioned above *m*-nitrobenzenedisulphide (m.p. 195°) was obtained in 95% yield.

***p*-Nitrobenzenesulphenyl Chloride.** Under the above mentioned conditions *p*-nitrobenzenedisulphide (m.p. 181°) was obtained in 96% yield.

**2,4-Dinitrobenzenesulphenyl Chloride.** Reaction carried under the the conditions mentioned above gave 2,4-dinitrobenzenedisulphide (m.p. 198–99°C) in 98% yield.

#### Reaction of *p*-Toluenesulphenyl Chloride with Azide Ion

*p*-Toluenesulphenyl chloride (4.0 g) in acetonitrile (20 ml) was added dropwise in 15 min, to a suspension of sodium azide (4.5 g) in acetonitrile (90 ml) at –35° (temperature of the bath was kept near –40°C) and allowed to stir for 10 min. To the dark red solution cyclohexene (20 ml) was added. The colour discharged in about 20 min after which the temperature was allowed to rise to that of room temperature. Chloroform (100 ml) was added, the reaction mixture was filtered, washed twice with water, dried and the solvent evaporated. The residue chromatographed on silica column and two fractions obtained. (1) *p*-Toluenedisulphide (2.327 g, 75% yield, m.p. 45–6°) IR fits the structure. (2) *p*-Toluenochlorocyclohexenesulphide. (1.214 g, 20% yield, m.p. 36–38°, lit m.p. 37–38°) IR spectrum fits the structure.

#### Reaction of *o*-Nitrobenzenesulphenyl Thiocyanate with Azide Ion

To a solution of *o*-nitrobenzenesulphenyl thiocyanate (0.424 g) in dry dimethyl sulphoxide (30 ml), sodium azide (0.65) was added at room temperature. Brisk evolution of nitrogen started as soon as sodium azide was added and the colour of reaction mixture became dark red. The reaction mixture was stirred for 1 hr, poured into cold water and precipitate filtered. *o*-Nitrobenzenedisulphide. was dried and crystallised from benzene (0.307 g, 100% yield, m.p. 195°).

#### Attempted Reaction of *p*-Nitrobenzenedisulphide with Iodine Azide

*p*-Nitrobenzenedisulphide (1.5 g) was dissolved in chloroform (100 ml) and dimethyl sulphoxide (20 ml) and to this solution iodine azide (25 ml of 0.11 mole) was added dropwise at –35° with stirring. The temperature was allowed to rise to room temperature in about 3 hr and stirring was continued overnight. The reaction mixture was treated with water, organic layer separated, dried (MgSO<sub>4</sub>) and *p*-nitrobenzenedisulphide was recovered in quantitative yield.

#### Reaction of *p*-Nitrobenzenesulphenylsodium with Iodine Azide

*p*-Nitrobenzenesulphenylsodium (1.7 g) was taken in acetonitrile (150 ml) and dimethylsulphoxide (10

ml). To the stirred solution iodine azide (15 ml, 11 mole) was added dropwise at  $-35^{\circ}$ . The red colour of the sodium salt slowly discharged (about 1 hr). The reaction mixture was warmed up to room temperature and the solvent was evaporated under reduced pressure. The residue gave *p*-nitrobenzenedisulphide (1.271 g, 85% yield, m.p. 181).\*

#### References

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\*When this reaction was carried out in the presence of norbornylene, no adduct of sulphenyl azide was obtained. *p*-Nitrobenzenedisulphide was obtained in 80% yield.
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