## BRIEF COMMUNICATIONS

# REACTION OF N, N-DICHLOROSULFONAMIDES WITH ARYL ISOTHIOCYANATES

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The reaction of aryl isothiocyanates with the N, N-dichloroamides of arenesulfonic acids and with the morpholide of sulfamic acid has been studied. Instead of the expected products of the oxidative imination of the aryl isothiocyanates, 2-(arylsulfonylamino)benzothiazoles and 2-(morpholinosulfonylamino)benzothiazoles, respectively, were obtained.

According to the literature [1–3], the action of the sodium salts of chloroamides of sulfonic acids on certain compounds of bi- and tetravalent sulfur leads to oxidative imination. Oxidative imination has not been studied for aryl isothiocyanates.

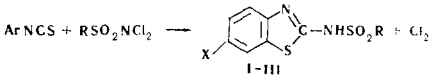
All attempts to perform the oxidative imination of phenyl isothiocyanate by the action of the sodium salts of the chloroamides of benzene- and toluenesulfonic acids were unsuccessful. The reaction of aryl isothiocyanates with N, N-dichlorides of arenesulfonic acids and the morpholide of sulfamic acid [4] gave colorless crystalline high-melting substances stable on boiling in water and in solutions of sulfuric acid and caustic soda (see table).

The reactions were carried out in chloroform or benzene solutions with careful heating to avoid the vigorous decomposition of the N, N-dichlorosulfonamides. The reactions of N, N-dichlorosulfonamides with phenyl and p-methoxyphenyl isothiocyanates gave reaction products containing small amounts of chlorine (2–4%) probably as a result of partial chlorination. When a current of ethylene was passed through the reaction mixture to trap the chlorine the reaction products contained no chlorine.

It was found that the compounds obtained are not products of the oxidative imination of the aryl isothiocyanates in accordance with the scheme:

$$ArNCS + RSO_2NCl_2 \xrightarrow{-Cl_2} ArN{=}C{-}S{-}N{-}SO_2R$$

When aryl isothiocyanates react with dichlorosulfonamides, the formation of a benzothiazole ring takes place with the production of 2-(arylsulfonylamino)-benzothiazoles (I, II) and 2-(morpholinosulfonylamino)-benzothiazoles (III):

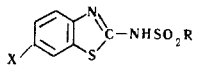


I-III

The structure of the 2-sulfonylaminobenzothiazoles I, II, and III was shown by the independent synthesis of compounds **Ia** and **IIa**, which were obtained by the reaction of 2-aminobenzothiazole in pyridine with benzenesulfonyl and p-toluenesulfonyl chlorides, respectively, and also by their IR spectra.

All the compounds exhibited bands of the deformation vibrations of products o-disubstituted in a benzene nucleus at 770–735 $cm^{-1}$, bands of the C=N stretching vibrations for the benzothiazole ring at 1640–1590 $cm^{-1}$, and absorption bands for the $SO_2$ group at 1160–1120 and 1350–1310 $cm^{-1}$.

The N, N-dichlorosulfonamides react with p-methoxyphenyl isothiocyanate considerably more readily than with p-nitrophenyl isothiocyanate, which is explained by the influence of the electron-donating or



| Compound | R | X | Mp, °C | Empirical formula | Amount | Found, % | Calculated, % | Yield, % |
|---|---|---|---|---|---|---|---|---|
| Ia | $C_6H_5$ | H | 261—262 | $C_{13}H_{10}N_2O_2S_2$ | C<br>H<br>S | 53.60<br>3.40<br>21.64 | 53.79<br>3.44<br>22.06 | 56 |
| Ib | $C_6H_5$ | *p*-$CH_3O$ | 244—245 | $C_{14}H_{12}N_2O_3S_2$ | N<br>S | 8.65<br>19.68 | 8.75<br>19.92 | 65 |
| Ic | $C_6H_5$ | *p*-$NO_2$ | 270—272 | $C_{13}H_9N_3O_4S_2$ | S | 19.41 | 19.51 | 25 |
| IIa | *p*-$CH_3C_6H_4$ | H | 235—236 | $C_{14}H_{12}N_2O_2S_2$ | C<br>H<br>S | 55.87<br>4.09<br>19.27 | 55.30<br>3.96<br>20.10 | 47 |
| IIb | *p*-$CH_3C_6H_4$ | *p*-$CH_3O$ | 224—227 | $C_{15}H_{14}N_2O_3S_2$ | N<br>S | 8.59<br>18.83 | 8.45<br>19.15 | 68 |
| IIc | *p*-$CH_3C_6H_4$ | *p*-$NO_2$ | 249—250 | $C_{14}H_{11}N_3O_4S_2$ | S | 19.40 | 19.55 | 19 |
| IIIa | N-Morpholino | H | 202—203 | $C_{11}H_{13}N_3O_3S_2$ | C<br>H<br>S | 49.25<br>4.17<br>22.04 | 49.31<br>4.52<br>22.22 | 65 |
| IIIb | N-Morpholino | *p*-$CH_3O$ | 185—186 | $C_{12}H_{15}N_3O_4S_2$ | N<br>S | 12.51<br>18.83 | 12.71<br>19.39 | 76 |
| IIIc | N-Morpholino | *p*-$NO_2$ | 176—177 | $C_{11}H_{12}N_4O_5S_2$ | S | 20.63 | 20.70 | 24 |

electron-accepting substituent in the aryl isothiocyanates on the reactivity of the sulfur atom, to which the chlorine cation adds initially, with the formation of radicals with respect to the nitrogen of the sulfonamides and the carbon of the isothiocyanate group. This affects the yields of the reaction products, which amounted to 76% for compounds **IIb** and 19–24% for compounds **IIc** and **IIIc**.

## EXPERIMENTAL

**2-(Arylsulfonylamino)benzothiazoles and 2-(morpholinosulfonylamino)benzothiazoles.** An aryl isothiocyanate (0.02 mole) was added to a solution of 0.02 mole of freshly-prepared N,N-dichlorosulfonamide in 30 ml of anhydrous chloroform or benzene (the solution must previously be well dried with sodium sulfate), a current of ethylene was passed through, and the reaction mixture was brought to a temperature of 50–60° C and stirred for 1 hr–1 hr 30 min. The reaction product that separated after the cooling of the mixture (in some cases after the solvent had been driven off) was washed with ether. It was crystallized from ethanol, forming colorless needles. All the substances were very sparingly soluble in the cold in the usual organic solvents. In the case of the reaction with p-nitrophenyl isothiocyanate, the reaction mixture was boiled for 2–3 hr.

**2-(Phenylsulfonyl)benzothiazole (Ia).** A solution of 0.01 mole of 2-aminobenzothiazole and 0.01 mole of benzenesulfonyl chloride was heated in 30 ml of pyridine at 100° C for 1 hr. After cooling, the reaction mixture was poured into water. The product was filtered off and crystallized from ethanol, mp 261–262° C.

**2-(p-Tolylsulfonylamino)benzothiazole (IIa)** was obtained similarly, bp 234–236° C. Mixtures of the two substances with compounds **Ia** and IIa given in the table exhibited no depression of the melting point.

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# ADDITION OF THIOPHENOLS AND ARYLAMINES TO DIBENZO[a,j]-PHENOXAZIN-9-ONE

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Thiophenols undergo nucleophilic addition to dibenzo[a,j]phenoxazin-9-one (**II**) in position 5, forming 5-arylthiodibenzo[a,j]phenoxazin-9-ones (**III–V**). With arylamines in the presence of their hydrochlorides, **II** is converted on heating into N-aryldibenzo[a,j]phenazine derivatives.

It has been shown previously that the reaction of thiophenols [1] and arylamines [2] with benzo[a]phenoxazin-9-one (**I**) leads to the addition of these compounds to **I** at position 5.

In this work it has been established that the nucleophilic addition of thiophenols and arylamines can also be carried out in the case of compound **II**, but the second, [j], benzene nucleus is found to have a considerable influence on the reactivity of the substance.

Thus, the addition of thiophenols to **I** takes place even in the cold [1] while **II** does not react under these conditions. Only under more severe conditions—on boiling in ethanol in the presence of concentrated hydrochloric acid—are the red compounds **III–V** formed (see scheme).

The reaction of arylamines with **II** also takes place differently from that with **I**: on being boiled in ethanol with aniline in the presence of aniline hydrochloride as described by Fischer and Hepp [2], **I** smoothly forms 5-anilinobenzo[a]phenoxazin-9-one, while **II** does not react with aniline under these conditions. Under more severe conditions, when **II** is boiled with aniline in the

5-Arylthiodibenzo[a,j]phenoxazin-9-ones

| Compound | R | External form | Mp, °C (decomp.) | Empirical formula | Found, % | | Calculated, % | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | N | S | N | S | |
| III | H | Red needles | 292—294 | $C_{26}H_{15}NO_2S$* | 3.29 | 8.12 | 3.46 | 7.90 | 89 |
| IV | $CH_3$ | Brown-red needles | 289—291 | $C_{27}H_{17}NO_2S$ | 3.13 | 7.76 | 3.34 | 7.64 | 90 |
| V | $NO_2$ | Red needles | 305—307 | $C_{26}H_{14}N_2O_4S$ | 6.30 | 6.95 | 6.22 | 7.12 | 85 |

*Found, %: C 77.00; H 3.78. Calculated, %: C 77.02; H 3.73.