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

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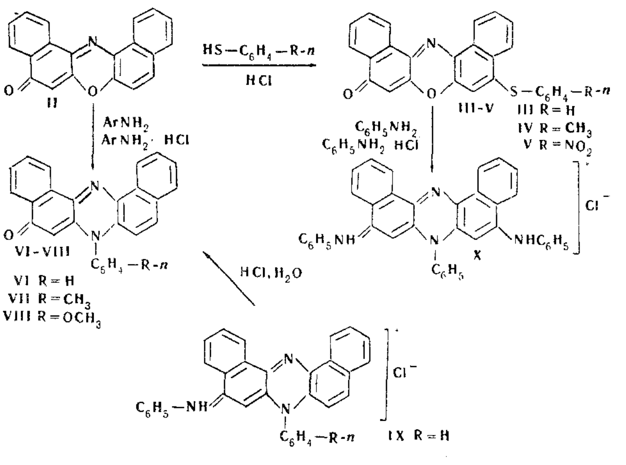
*Found, %: C 77.00; H 3.78. Calculated, %: C 77.02; H 3.73.

presence of aniline hydrochloride (without the use of ethanol as solvent), a more complex reaction takes place with the conversion of the oxazine ring into a diazine ring (VI) [similar conversions are known for the dibenzophenoxazines] [4]. The structure of VI was confirmed by the identity of its spectrum in the visible region with the spectrum of 7-phenyldibenzo[a, j]-phenazin-9-one obtained by the hydrolysis of 9-aryl-amino-7-phenyldibenzo[a, j]phenazinium chloride (IX) synthesized by Fischer and Hepp's method [5]. The elementary analysis and the IR spectrum are also in agreement with the structure VI. In the 1635 cm^{-1} region there is a strong band which may be ascribed to the stretching vibrations of the carbonyl group (the same band is found in I and II). The NH band, which appears clearly at 3250 cm^{-1} in 5-anilinobenzo[a]-phenoxazin-9-one [2] is, of course, absent here.

The reaction of III with aniline (on boiling in the presence of aniline hydrochloride) takes place in an interesting manner. Judging from the elementary analysis, the reaction product may be ascribed the structure **X**, i.e., obviously, not only the conversion of the oxazine ring into a diazine ring but also the replacement of the the arylthio residue by an arylamine residue has taken place. The IR spectrum is in agreement with the structure **X**: ν_{CO} stretching vibrations are absent, and the presence of a broad "trough" in the 3270–2913 cm^{-1} region with several low-intensity bands shows the ammonium nature of the bond of the nitrogen atom with the delocalized positive charge.



The differences in the reactivity of II as compared with I that have been mentioned can be explained by the electron-accepting influence of the second, [j], benzene nucleus. This influence is shown in the lower degree of polarization of the carbonyl group, as follows from the results of polarographic reduction. For II have been found $E_{1/2} = -0.28$ and -0.97 V and for I $E_{1/2} = -0.17$ and -0.99 V [in dimethylformamide solution with a support of tetraethylammonium iodide relative to the mercury pool], i.e., II is reduced with somewhat greater difficulty than I. The decrease in the polarity of the carbonyl group creates a smaller possibility for the induction of a δ^+ charge in position 5 and lowers the capacity for nucleophilic addition reactions. At the same time, the basicity of the oxazine oxygen atom rises and under the conditions of boiling with aniline hydrochloride protonation takes place at the ring oxygen atom and not that of the carbonyl group. As a result, the ring opens and the aniline residue subsequently enters the ring.

EXPERIMENTAL

5-Phenylthiodibenzo[a, j]phenoxazin-9-one (III). A mixture of 0.3 g of **II** [6] (with mp 278–280° C; literature [6] 277–278° C), 2 ml of thiophenol, and 5 drops of concentrated HCl was boiled in 10 ml of ethanol for 4 hr and was then left at room temperature for another 2–3 hr. The precipitate was filtered off and washed with a small amount of ethanol; to complete oxidation of the oxo compound, the product was heated at 70–80° C with 10 ml of 10% aqueous $FeCl_3$. The **III** was filtered off, washed with ethanol, and crystallized from dimethylformamide or pyridine.

5-p-Tolylthio- and 5-p-nitrophenylthiodibenzo[a, j]phenoxazin-9-ones (**IV** and **V**; see table) were obtained similarly.

7-Phenyldibenzo[a, j]phenazin-9-one (VI). a) A mixture of 0.2 g of **II**, 0.4 g of aniline hydrochloride, and 2 ml of aniline was boiled until the solid matter dissolved and the color of the solution changed to crimson-red. Then 5 ml of water was added and the excess of aniline distilled off with steam. The precipitate was filtered off and washed with water to give 0.2 g (~90%) of brown prisms with a metallic luster having mp 295–297° C (decomp.) (aqueous dimethylformamide or ethanol), literature [7] 295° C. Found, %: C 83.70; H 4.36; N 7.33. Calculated for $C_{26}H_{16}N_2O$, %: C 83.85; H 4.33; N 7.52.

b) A mixture of 0.5 g of **IX** [5], 3 ml of glacial acetic acid, and 8 ml of conc. HCl was heated in a sealed tube at 250–255° C for 14 hr. The reaction mixture was then heated as described by Fischer and Hepp [7]. Mp 295–297° C (decomp.). The product was identical with that obtained by method (a) in respect of its visible and IR spectra.

Similarly, the reaction of **VI** with p-toluidine and p-anisidine (in the presence of their hydrochlorides) gave, respectively, VII and **VIII**. For **VII**, mp 297–299° C (decomp.) (aqueous dimethylformamide). Found, %: C 83.95; H 4.81; N 7.30. Calculated for $C_{27}H_{18}N_2O$, %: C 83.92; H 4.69; N 7.25. For **VIII**, mp 333–335° C (decomp.) (aqueous dimethylformamide). Found, %: C 80.69; H 4.59; N 6.68. Calculated for $C_{27}H_{18}N_2O_2$, %: C 80.58; H 4.51; N 6.96.

5, 9-Dianilino-7-phenyldibenzo[a, j]phenazinium chloride (X). A mixture of 0.1 g of **III**, 0.2 g of aniline hydrochloride, and 3 ml of aniline was boiled until the smell of thiophenol had disappeared (~8 hr). Then 10 ml of water was added and the excess of aniline distilled off with steam. The precipitate was filtered off to give 0.1 g of dark blue needles with a green tinge, mp 305–307° C (decomp.) (aqueous pyridine). Found, %: C 79.00; H 4.92; N 10.14; Cl 6.08. Calculated for $C_{38}H_{27}N_4Cl$, %: C 79.36; H 4.73; N 9.74; Cl 6.17.

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