REACTION OF 5-PHENYL- AND 4,5-DIPHENYLOXAZOLINE-2-THIONES

WITH ARENEDIAZONIUM SALTS

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The corresponding 2-arylthio-5-phenyloxazoles, 2-arylthio-4-arylazo-5-phenyloxazoles, and 2-arylthio-4,5-diphenyloxazoles are formed by the action of arenediazonium salts on 5-phenyl- and 4,5-diphenyloxazoline-2-thiones.

Continuing our study of the 0,S-arylation of azolethiones [1], we investigated the reaction of arenediazonium salts with 5-phenyl- and 4,5-diphenyloxazoline-2-thiones (Ia, b). It has been shown by IR spectroscopy [2, 3] that they exist in the thione form (I) in the crystalline state. However, if there are substituents in the 4 and 5 positions of the oxazole ring, the presence of two tautomeric forms ( $I \neq II$ ) is possible [4]. Compounds I may therefore by arylated at the sulfur atom by the action of arenediazonium salts. It was found that S-arylation does not occur in aqueous alkali or aqueous acetone. 2-Aryl-thio-5-phenyloxazoles (IVa-d) and 2-arylthio-4,5-diphenyloxazoles (IVe-m) were obtained under 0,S-arylation conditions [1], and in individual cases 2-arylthio-4-arylazo-5-phenyloxazoles (V) are also formed in small amounts from Ia, and di(4,5-diphenyl-2-oxazolyl) disulfide (VI) is also formed from Ib.



The structures of IV-V were proved by alkaline and acid hydrolysis reactions, aminolysis, and hydrazinolysis. The corresponding thiophenols and their oxidation products — diaryl disulfides — were isolated in all cases. In addition, 4,5-diphenyl-2-oxazolinone (VII) was detected among the products of reaction of IVf with phenylhydrazine, whereas 2-(p-chlorophenyl)amino-4,5-diphenyloxazole (VIII) was detected among the products of reaction of IVk with p-chloroaniline.

 $\begin{array}{ccc} C_{6}H_{5} \sim C & & NH \\ C_{6}H_{5} \sim C_{O} \sim C = 0 \end{array} \qquad \begin{array}{cccc} C_{6}H_{5} - C & & NH \\ C_{6}H_{5} - C_{O} \sim C - NH \\ C_{6}H_{5} - C - NH \\ C_$ 

The UV spectra of IVc,d,f,j contain only one absorption maximum (~300 nm), whereas the UV spectra of starting I contain two maxima (~280 and 300 nm). This makes it possible to

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Com- pound	mp (bp), °C	Empirical formula	Found, %			Calc., %			Yield,
			С	н	s	С	H	s	%
IVa IVb IVc IVd IVf IVf IVf IVf IVj* IVk IV1 IVm	$\begin{array}{c} 41-42\\ 37\\ 35-36\\ 60-62\\ (144)\\ 31-32 (dec.)\\ (140)\\ 40-41 (dec.)\\ (152)\\ (168)\\ (170)\\ Viscous mass\\ Viscous mass\\ \end{array}$	$\begin{array}{c} C_{15}H_{11}NOS\\ C_{15}H_{10}CINOS\\ C_{16}H_{19}NO_2S\\ C_{16}H_{19}NO_2S\\ C_{21}H_{15}NOS\\ C_{22}H_{17}NOS\\ C_{22}H_{17}NO_2S\\ C_{21}H_{14}CINOS\\ C_{21}H_{14}B_{17}NOS\\ C_{21}H_{14}B_{17}NOS\\ C_{21}H_{14}H_{20}S\\ C_{21}H_{14}NOS\\ C_{21}H_{14}N_{20}S\\ C_{21}H_{19}NO_{2}S\\ C_{24}H_{19}NO_{2}S\\ C_{24}H_{19}NO_{3}S\\ \end{array}$	71,4 62,4 	4,5 3,8 	12,4 11,0 11,3 10,5 9,5 9,2 8,7 9,1 7,6 8,8 8,8 8,8 8,8 8,8	71,2 62,6  76,6  73,5   74,0 	4,4 3,5 	12,2 11,1 11,3 10,7 9,7 9,3 8,9 7,8 8,6 8,6 8,6 8,6 8,0	35 45 20 30 40 60 50 30 50 45 30 40 43

TABLE 1. 2-Arylthio-5-phenyloxazoles (IVa-d) and 2-Arylthio-4,5-diphenyloxazoles (IVe-m)

\*Found: N 7.7%. Calculated: N 7.5%.

assume that the maximum at 280 nm is due to the thioamide form (I), whereas the maximum at 300 nm is due to the imidothio form (II).

Compounds I exist primarily in the thioamide form in the crystalline state, inasmuch as their spectra contain intense frequencies of the stretching vibrations of the thioamide group (at 1530 cm<sup>-1</sup>) and a low-intensity band of the C-SH bond (at 825-830 cm<sup>-1</sup>). However, the intensity of the latter increases sharply in the spectra of the S-arylation products, and this corresponds to the absorption of C-S-C fragment, whereas the frequency of the stretching vibrations of a thioamide group (at 1530 cm<sup>-1</sup>) vanishes. These results are in agreement with the data in [2-4].

## EXPERIMENTAL METHOD

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of dioxane solutions  $(5 \cdot 10^{-5} \text{ M})$  were recorded with a Specord spectrophoto-meter.

<u>2-Arylthio-5-phenyloxazoles (IVa-d) and 2-Arylthio-4,5-diphenyloxazoles (IVe-m).</u> A 3-mmole sample of I was dissolved in 200 ml of acetone, and a solution of 0.12 g of NaOH in 5 ml of water was added. After 1 h, the solution was cooled to 0°, a solution of 0.8 g of sodium acetate in 5 ml of water and 10 g ice were added, after which a solution of arenediazonium salts (3 mmole of arylamine, 0.9 ml of concentrated HCl, 10-20 ml of water, 0.21 g of NaNO<sub>2</sub> in 3 ml of water and 10-15 g of ice;\* diazotization time 1 h) was added at 0-5°. After 18 h, the acetone was vacuum evaporated, and 100 ml of water was added to the residue. After 1 h, the mass was extracted with 100 ml of ether. The ether layer was separated and evaporated to dryness, and the residue was dissolved in 50 ml of benzene. The benzene solution was chromatographed on aluminum oxide (layer height 5 cm, diameter 1 cm). The second zone (from yellow to light-red) was selected, and the solvent was vacuum evaporated to constant weight. Low-melting or oily products ranging in color from orange to red were obtained; the products were soluble in acetone, alcohol, dioxane, benzene, and diethyl ether, less soluble in petroleum ether, and insoluble in water.

In the preparation of IVb, 2-(p-chlorophenyl)-4-(p-chlorophenylazo)-5-phenyloxazole (V) (2% yield, mp 172°. Found: C 59.5; H 3.2; N 9.9; S 7.6%.  $C_{21}H_{13}Cl_2N_3OS$ . Calculated: C 59.3; H 3.1; N 9.9; S 7.7%) was precipitated from the benzene solution after chromatography with a threefold quantity of petroleum ether, after which IVb was isolated from the filtrate after evaporation of the solvent.

<u>Alkaline Hydrolysis of IVi.</u> A solution of 0.15 g of IVi and 0.15 g of NaOH in 5 ml of ethanol was refluxed on a water bath for 4 h. After 12 h, the red solution was acidified with HCl, and the resulting precipitate was removed by filtration. The filtrate was evaporated to one-third of its original volume, 25 ml of  $H_2O$  was added, and the resulting oil was extracted with ether. The ether was evaporated, and the oily residue of di(p-bromo-

\*In the synthesis of IVd, j, k, the amounts of HCl and sodium acetate were tripled.

phenyl) disulfide began to crystallize after 1 week to give a product with mp 90-92° (from ethanol) (mp 93-94° [5]).

4,5-Diphenyl-2-oxazolinone (VI). A 0.15-g (0.44 mmole) sample of 2-(p-tolylthio)-4,5diphenyloxazole (IVf) was heated with 0.05 g (0.44 mole) of phenylhydrazine at 130° for 2 h in a flask equipped with an air condenser. White crystals of di-(p-tolyl) disulfide, with mp 44-45° (mp 44.5-45.5° [5]), were deposited in the air condenser. At the end of the reaction, 10 ml of benzene was added, and the white crystalline precipitate of VI was removed by filtration, washed with benzene, and dried to give a product with mp 226-227° (mp 211° [6]) in 30% yield. Found: N 5.7%. C15H11NO2. Calculated: N 5.9%. A similar product was obtained by fusing IVk with p-chloroaniline (1:1) and by alkaline hydrolysis of IVk.

2-(p-Chlorophenylamino)-4,5-diphenyloxazole (VII). A 0.1-g (0.3 mmole) sample of 2-(p-nitrophenylthio)4,5-diphenyloxazole (IVk) was fused with 0.07 g (0.6 mmole) of p-chloroaniline at 130° for 2 h in a flask equipped with a reflux condenser, after which the mixture was cooled, and 5 ml of benzene was added. The resulting precipitate was removed by filtration, and the filtrate was chromatographed on aluminum oxide (layer height 5 cm, diameter 1 cm). The light-yellow zone was selected, and the benzene was evaporated until the residue had a constant weight. A viscous orange mass was obtained in 76% yield. Found: C 75.2; H 4.5; N 8.2%. C<sub>21</sub>H<sub>15</sub>ClN<sub>2</sub>O. Calculated: C 75.0; H 4.3; N 8.1%.

The solid that deposited on the condenser gave a positive qualitative reaction for thiophenol [7].

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