SOME STUDIES IN THE PHENOXAZINE SERIES

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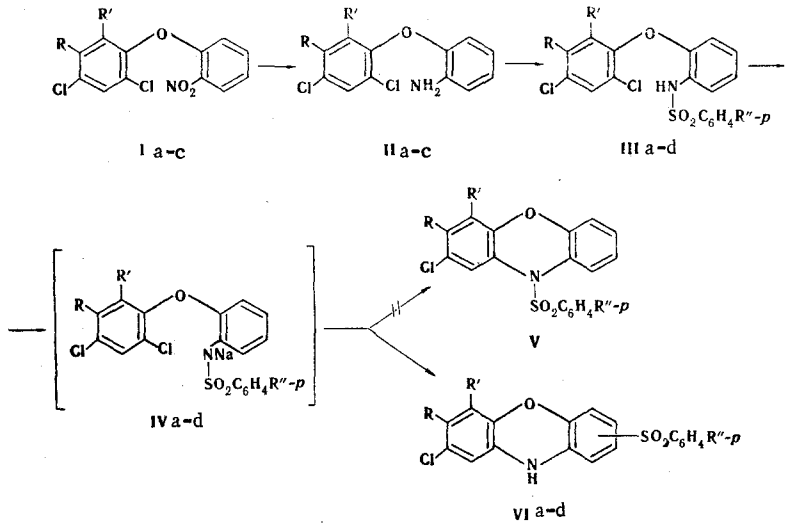
In the cyclization of 2-chloroaryl 2'-arenesulfamidoaryl ethers to N-arylsulfonylphenoxazines rearrangement of the latter to C-arylsulfonyl-substituted phenoxazines is observed.

In order to search for stabilizers for polymeric materials we made an attempt to synthesize the previously undescribed 10-arylsulfonyl-substituted phenoxazines by cyclization of arenesulfamidophenyl phenyl ethers (IIIa-d) [1-3], from which sodium salts IV were initially obtained; the salts were subsequently heated in dimethylformamide (DMF) for cyclization to 10-arylsulfonylphenoxazines (V).



I a-c II a-c III a-d

IV a-d V VI a-d

I a R=R′=H; b R=Cl, R′=H; c R=H, R′=Cl; III a R=R′=R″=H; b R=Cl, R′=R″=H; c R=H, R′=Cl, R″=H; d R=Cl, R′=H, R″=CH_3

The quantitative compositions of the products were in satisfactory agreement with the proposed formulas. However, the IR spectra indicate migration of the arylsulfonyl group from the nitrogen atom in the condensed ring of the phenoxazine molecule to give VI. As in the spectrum of unsubstituted phenoxazine, the IR spectra of VI contain characteristic absorption bands at 700-1700 cm^{-1}; in addition, the stretching vibrations of the SO_2 group are found at 1140-1160 cm^{-1}. The spectra of VI contain the intense absorption of the stretching vibrations of the NH group at 3330-3350 cm^{-1}, whereas this absorption should vanish in the spectra of V.

Cyclization does not take place in less polar solvents, particularly in pyridine. An attempt to cyclize 2-chloro-4-methylphenyl and 2-bromo-4-methylphenyl 2'-benzenesulfamidophenyl ethers did not give the desired results, and this indicates the necessity for activation of the halogen by electron-acceptor substituents.

We independently observed the rearrangement of 10-arylsulfonylphenoxazines VII, obtained by acylation of phenoxazine with arenesulfonyl chlorides.

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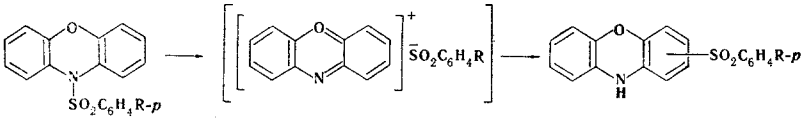
TABLE 1. Yields and Physical Constants of the Synthesized Compounds

Compound	mp, °C	Empirical formula	Found, %			Calc., %			IR spectrum, cm^{-1}				Yield, %
			Cl	N	S	Cl	N	S	NH_2	NH	SO_2	—O—	
I a	57—58	$C_{12}H_7Cl_2NO_3$	24,9	4,9	—	25,0	4,9	—	—	—	—	1345	42
I b	72—73	$C_{12}H_6Cl_2NO_3$	33,3	4,3	—	33,3	4,4	—	—	—	—	1345	48
I c	142—143	$C_{12}H_6Cl_3NO_3$	33,3	4,4	—	33,3	4,4	—	—	—	—	1350	40
II b	50—51	$C_{12}H_8Cl_3NO$	36,9	4,6	—	36,9	4,8	—	3440	—	—	—	86
									3360	—	—	—	
II c	121—122	$C_{12}H_8Cl_3NO$	36,6	5,0	—	36,9	4,8	—	3460	—	—	—	79
									3375	—	—	—	
III a	148—150	$C_{18}H_{13}Cl_2NO_3S$	18,0	3,5	8,1	18,0	3,5	8,1	—	3240	1170	—	97
III b	107—109	$C_{18}H_{12}Cl_3NO_3S$	24,8	3,2	7,3	24,8	3,3	7,5	—	3255	1170	—	98
III c	177—178	$C_{18}H_{12}Cl_3NO_3S$	24,4	3,3	7,3	24,8	3,3	7,5	—	3245	1160	—	94
III d	141—142	$C_{19}H_{14}Cl_3NO_3S$	23,7	3,0	7,2	24,0	3,1	7,2	—	3325	1165	—	96
VI a	242—244 (dec.)	$C_{18}H_{12}ClNO_3S$	10,9	3,9	9,2	11,0	4,0	9,2	—	3350	1150	—	38
VI b	272—273 (dec.)	$C_{18}H_{11}Cl_2NO_3S$	18,0	3,4	8,1	18,1	3,6	8,2	—	3300	1125	—	47
VI c	251—253 (dec.)	$C_{18}H_{11}Cl_2NO_3S$	17,7	3,6	8,0	18,1	3,6	8,2	—	3320	1150	—	38
VI d	253—254 (dec.)	$C_{19}H_{13}Cl_2NO_3S$	17,4	3,4	7,8	17,5	3,4	7,9	—	3330	1135	—	30
VII a	160—161	$C_{18}H_{13}NO_3S$	—	4,0	9,6	—	4,3	9,9	—	—	1170	—	76
VII b	174—176	$C_{19}H_{15}NO_3S$	—	4,3	9,8	—	4,2	9,6	—	—	1170	—	82
VII c	179—181	$C_{18}H_{12}ClNO_3S$	10,2	4,2	9,6	9,9	3,9	9,0	—	—	1170	—	50
X a	209—211	$C_{18}H_{13}NO_3S$	—	4,1	10,2	—	4,3	9,9	—	3330	1150	—	75
X b	178—180	$C_{19}H_{15}NO_3S$	—	4,3	10,0	—	4,2	9,6	—	3400	1150	—	60
X c	205—207	$C_{18}H_{12}ClNO_3S$	9,6	3,8	8,9	9,9	3,9	9,0	—	3330	1150		70



VII a-c VIII IX a-c

VII a R=H; b R=CH_3; c R=Cl

The formation of IX was confirmed by the presence in its IR spectrum of an intense absorption band at 3330-3350 cm^{-1} (NH) and also by its complete analogy with the spectrum of phenoxazine, except for the band at 1160-1180 cm^{-1} (SO_2).

The rearrangement proceeds considerably more slowly in solvents less polar than DMF. Migration of the arylsulfonyl residue apparently proceeds through intramolecular ionization of VII to give VIII, which is subsequently converted to IX.

The rearrangement of VII discovered in this research makes it possible to assert that in the case of the cyclization of diphenyl ethers III, N-substituted phenoxazines V are formed initially and then undergo rearrangement to give VI under the same conditions as in the case of VII.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The purity of the products was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates in chloroform.

2-Chlorophenyl 2'-Nitrophenyl Ethers (Ia-d, Table 1). A mixture of 0.05 mole of chlorophenol, 0.05 mole of o-nitrochlorobenzene, 0.05 mole of potassium carbonate, and 0.2 g of freshly prepared copper powder was stirred at 150-160° for 5 h, after which it was poured into 5% NaOH. The resulting mixture was filtered, and the filtrate was extracted with benzene. The benzene extract was dried, the benzene was evaporated, and the resulting precipitate was crystallized from cyclohexane. Compound Ia was isolated by vacuum distillation.

2-Chlorophenyl 2'-Aminophenyl Ethers (IIa-c, Table 1). A solution of 5 g of I in alcohol was refluxed with stirring for 6 h with 10 g of zinc and 3 ml of concentrated HCl, after which the mixture was filtered, and the cooled filtrate was poured into water. The resulting precipitate was removed by filtration, dried, and crystallized from heptane. In the case of Ia, the initial product was an oil, which was separated from the water and acylated without purification.

2-Chlorophenyl 2'-Arenesulfamidophenyl Ethers (IIIa-d). A solution of 0.01 mole of II and 0.015 mole of arenesulfonyl chloride in pyridine was allowed to stand for 10 h, after which it was poured into water with vigorous stirring. The resulting precipitate was removed by filtration, dried, and crystallized from cyclohexane.

X-Arylsulfonylchlorophenoxazines (VIa-d, Table 1). A 5-mmole sample of sodium methoxide and 5 mmole of III were dissolved in 30 ml of methanol, after which the solvent was removed by vacuum distillation, 50 ml of DMF was added to the residue, and the mixture was refluxed for 7 h. It was then cooled and poured into water. The resulting precipitate (where necessary, NaCl was added for coagulation) was removed by filtration, dried, washed with benzene, and crystallized from nitromethane.

10-Arylsulfonylphenoxazines (VIIa-c, Table 1). A solution of 0.01 mole of phenoxazine and 0.015 mole of arenesulfonyl chloride in 2 ml of pyridine was allowed to stand for 4 h, after which the resulting precipitate was washed with isopropyl alcohol, removed by filtration, dried, and crystallized from isopropyl alcohol.

X-Arylsulfonylphenoxazines (IXa-c, Table 1). A solution of 0.01 mole of VII in DMF was refluxed for 20 h, after which it was cooled and poured into 2% NaCl. The resulting precipitate was removed by filtration, dried, washed with benzene, and crystallized from nitromethane. An additional amount of the reaction product was isolated by evaporation of the benzene washes.

LITERATURE CITED

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POLYMETHINE DYES – FURO[3,2-e]INDOLENINE DERIVATIVES

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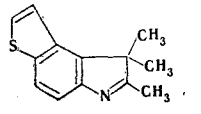
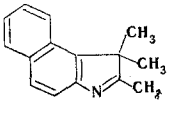
7,8,8'-Trimethylfuro[3,2-e]indolenine and polymethine dyes of various types that are derivatives of this base were synthesized. It is shown that incorporation of a furo[3,2] group in the 4 and 5 positions of the indolenine residue in the cyanines leads to a smaller bathochromic shift of the absorption maxima than does the introduction of thieno and benzo groups in the same position.

On passing from dyes with a 3,3-dimethylindolenine residue to the corresponding 4,5-thieno[3,2]derivatives (I) one observes a smaller bathochromic shift of the absorption maximum than on passing to 4,5-benzoindolenine derivatives (II). The basicity of the thieno[3,2-e]indolenine residue is appreciably higher than that of the 3,3-dimethylindolenine residue [1].

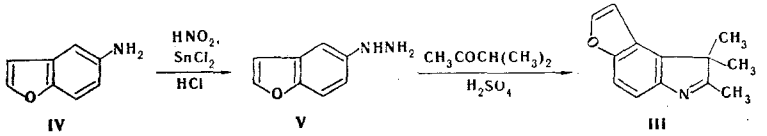


I



II

We have synthesized a new analogous heterocyclic base – 7,8,8'-trimethylfuro[3,2-e]indolenine (III) – from 5-aminobenzofuran (IV) (see [2]):



IV V III

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