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NUCLEOPHILIC ADDITION TO THE PHENOXAZONIUM CATION

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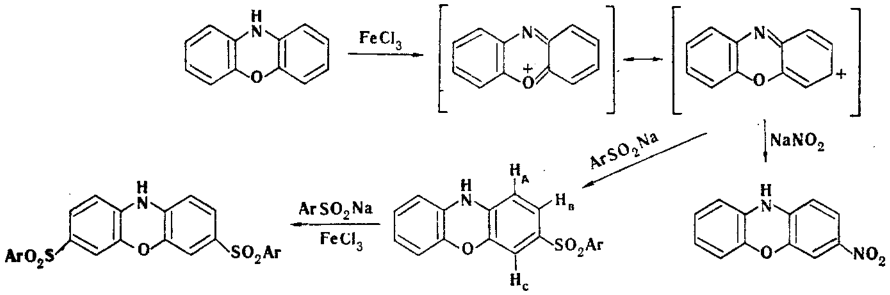
At the instant of its formation of oxidation of phenoxazine with ferric chloride, the phenoxazonium cation adds arenesulfinate and nitrite ions to give 3-arylsulfonyl- and 3-nitrophenoxazines, respectively. It is shown that the introduction of a second sulfonyl group proceeds more slowly and gives 3,7-di(arylsulfonyl)-phenoxazines in low yields. The PMR spectra of the synthesized compounds are examined in comparison with 3-substituted phenothiazines.

Continuing our search for stabilizers and antioxidants of polymeric materials, we undertook the oxidation of phenoxazine with ferric chloride in the presence of arenesulfinate and nitrite ions.

It is known [1, 2] that 1,4-oxazine and 1,4-thiazine systems readily form saltlike structures. The presence of an unstable o-quinoid cation is responsible for their high activity with respect to nucleophilic substitution in the 3 position.



III a, b II a,b I

II, III a Ar = C$_6$H$_5$; b Ar = C$_6$H$_4$CH$_3$

At the instant of its formation in the oxidation of phenoxazine with ferric chloride, the phenoxazonium ion readily adds nitrite and arenesulfinate ions to give I and IIa,b, respectively.

Nitrophenoxazine I was identical to the 3-nitrophenoxazine described in [4], and this confirms incorporation of the substituent in the 3 position. The product (II) of the addition of the arenesulfinate ion is completely similar to the corresponding rearrangement product [3] and can be identified as 3-arylsulfonylphenoxazine. The introduction of a second sulfonyl group proceeds more slowly and gives 3,7-di(arylsulfonyl)phenoxazines (IIIa,b) in low yields.

Characteristic absorption bands of NH (3350–3400 cm^{-1}), NO$_2$ (1530, 1330 cm^{-1}), and SO$_2$ (1140-1160 cm^{-1}) groups are present in the IR spectra of the synthesized I, IIa,b, and IIIa,b.

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TABLE 1. Data from the PMR Spectra of Some Phenoxazines and Phenothiazines

Compound	Chemical shifts of the protons, δ, ppm				SSCC, J, Hz		
	A	B	C	NH	AB	AC	BC
Phenoxazine*[7,8]	6,48	6,70	6,60	7,15	7,86	0,30	1,41
Phenoxazine*[7]	6,70	6,96	6,92	7,77	7,86	0,35	1,31
3,7-Dibromophenothiazine†	6,65	7,03	6,98	—	8,50	0,57	2,09
V	5,63	6,30	5,70	8.02	9,30	0	2,00
IIa	5,39	6,16	5,85	7,75	8,30	0	2,00
IIb	5,45	6,19	6,06	7,89	8,30	0	2,00
IV	5,38	6,15	5,84	7,81	8,00	0	2,00

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*In acetone.

†In $CDCl_3$ with respect to tetramethylsilane.

An analysis of the PMR spectra of phenoxazines IIa,b and the previously synthesized [5] 2,3-dichloro-7-phenylsulfonylphenoxazine (IV) and 3-phenylsulfonylphenothiazine (V) [6] and a comparison of the data obtained in this study with the literature data [7, 8] make it possible to conclude that the arylsulfonyl group in all of the above compounds is in the para position relative to the nitrogen atom. The multiplets at 6.35-6.85 ppm (IIa, IV, and V) are signals of the protons of the aromatic ring of the arylsulfonyl group; the introduction of a p-tolylsulfonyl group (IIb) eliminates this multiplicity and leads to a characteristic AB system (δ_{AB} 6.28 ppm, $\Delta\nu$ 40 Hz, J_{AB} = 8 Hz). The complex multiplet at 5.40-5.80 ppm (IIa,b and V) was assigned to the signals of the unsubstituted benzenoid ring of the phenoxazine (phenothiazine) system. This was confirmed by the PMR spectra of 2,3-dichloro-7-phenylsulfonyl phenoxazine (IV), for which only singlets of protons in the 1 and 4 positions (δ 5.42 and 5.54 ppm, respectively) are observed.

The assignment of the signals of the protons of the arylsulfonyl-substituted benzenoid ring of IIa,b and IV was made on the basis of the spin-spin coupling constants (SSCC) and the chemical shifts of the unsubstituted phenoxazine and phenothiazine (Table 1). The SSCC and the chemical shifts of the ABC protons of the synthesized phenoxazines are close to the corresponding values for 3-phenylsulfonyl- and 3,7-dibromophenothiazines [7], and this unambiguously indicates orientation of the arylsulfonyl groups in the para position relative to the nitrogen atom.

A characteristic feature of the PMR spectra of IIa,b, IV, and V is an intense signal of the proton of an NH group.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of deuterodimethul sulfoxide solutions of the compounds were recorded with a Varian HA-100 spectrometer with tert-C_4H_9OH as the external standard. The purity of the compounds was monitored by thin-layer chromatography (TLC) on Silufol UV-254.

3-Phenylsulfonylphenoxazine (IIa). A solution of 15 mmole of ferric chloride in 30 ml of acetic acid was added dropwise to a solution of 5 mmole of phenoxazine and 5 mmole of sodium benzenesulfinate in acetic acid, and the mixture was allowed to stand for 2 h. It was then filtered, and the filtrate was poured into water. The resulting precipitate was removed by filtration, dried, and chromatographed on Al_2O_3 in chloroform. Workup gave IIa, with mp 209-211°, in 40% yield. Found, %: N 4.1; S 9.8. $C_{18}H_{13}NO_3S$. Calculated, %: N 4.3; S 9.9.

A similar procedure was used to obtain 3-tolylsulfonylphenoxazine IIb (42% yield, mp 178-180°. Found, %: N 4.0; S 9.5. $C_{19}H_{15}NO_3S$. Calculated, %: N 4.2; S 9.6 % and 3-nitrophenoxazine I (50% yield, mp 196-199°. Found, %: N 12.3. $C_{12}H_8N_2O_3$. Calculated: N 12.2%.

3,7-Di(phenylsulfonyl)phenoxazine (IIIa). A solution of 1.5 mmole of IIa, 3 mmole of sodium benzenesulfinate, and 15 mmole of ferric chloride in 50 ml of acetic acid was refluxed for 20 h, after which it was poured into water, and the resulting precipitate was removed by filtration, dried, and chromatographed on Al_2O_3 in chloroform. Workup gave IIIa, with mp 184-186°, in 21% yield. Found, %: N 2.6; S 14.3. $C_{24}H_{17}NO_5S_2$. Calculated, %: N 3.0; S 14.2.

A similar procedure was used to obtain 3,7-di(tolylsulfonyl)phenoxazine (IIIb), with mp 212-214°, in 25% yield. Found, %: N 2.9; S 13.5. $C_{26}H_{21}NO_5S_2$. Calculated, %: N 2.98; S 13.7.

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BASICITIES AND STRUCTURES OF 2-(N-ARYLAMINOMETHYLENE)-3(2H)-BENZO[b]-THIOPHENONES, -BENZO[b]FURANONES, AND -BENZO[b]SELENOPHENONES*

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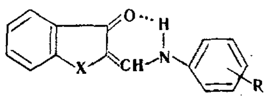
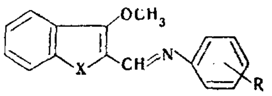
The ionization constants of the conjugate acids of the reaction series 2-(N-arylaminomethylene)-3(2H)-benzo[b]thiophenones, -benzo[b]furanones, and -benzo[b]selenophenones were determined by potentiometric titration in anhydrous acetonitrile. The electronic and vibrational spectroscopic data showed that the protonation center in the molecules of these compounds is the carbonyl oxygen atom. It was established by correlation analysis that N-aryl substituents affect the protonation center primarily via an induction mechanism.

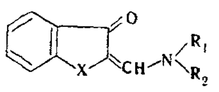
We have previously shown that 2-(N-arylaminomethylene)-3(2H)-benzo[b]thiophenones, -benzo[b]furanones, and -benzo[b]selenophenones exist in the form of enamino ketone structures I in the solid state and in solution [2-4]. The strong polarization of the amino enone system of π bonds leads to induction of a considerable negative charge on the carbonyl oxygen atom [5, 6]. This provides a basis to expect that precisely the carbonyl oxygen atom in I will be the protonation center.



I



II



III

I-III a X=O; b X=S; c X=Se

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*Communication XVIII from the series "Basicities and structures of azomethines and their structural analogs." See [1] for communication XVII.

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