REACTION OF 4-ARYLAMINO-2-SULFOLENES WITH NUCLEOPHILIC REAGENTS

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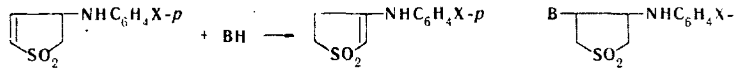
UDC 547.732.733.07

The nucleophilic reactions of 4-arylamino-2-sulfolenes with amines, alcohols, and mercaptans give 3-arylamino-2-sulfolenes and 3,4-substituted arylaminosulfolanes, the ratio between which depends on the nature of the reagents and the conditions.

Methods for the preparation of the previously undescribed arylaminosulfolanes [1] and arylaminosulfolenes [2] have been proposed, and the reactions of alkylaminosulfolanes with nucleophilic reagents have been investigated [3]. In the present paper we present data on the reaction of some nucleophilic reagents with 4-arylamino-2-sulfolenes (Ia-d).



I a-d II a-d III-VI

I, II a X=H; b X=CH$_3$; c X=OCH$_3$; d X=Cl; III B=C$_4$H$_9$NH; IV B=CH$_3$O; V B=C$_4$H$_9$O; VI B=C$_4$H$_9$S

It was found that competitive reactions — addition of BH to the double bond and isomerization* — occur in the reaction of 4-arylamino-2-sulfolenes with nucleophilic reagents. Mixtures of two compounds with R_f 0.25 and 0.5 (Table 1), which were separated by means of column chromatography, are formed as a result of the reaction. According to the results of elementary analysis, the substances with $R_f \sim 0.25$ are isomerization products, while those with $R_f \sim 0.5$ are addition products. Of the two possible structures, 3-arylamino-2-sulfolene (IIa-d) and 4-substituted 3-arylaminosulfolane (III-VI) structures, respectively, were assigned to the isomerization and addition products on the basis of their chemical behavior and IR spectra. It is known [4-6] that 3-alkoxy(or alkylthio)-3-sulfolenes in the presence of bases are practically irreversibly isomerized to 3-substituted 2-sulfolenes. The starting substances were regenerated in an attempt at alkaline isomerization of the compounds with $R_f \sim 0.25$; this indicates the stable position of the double bond in the ring. The IR spectrum of Ia contains the characteristic (for a cis double bond) δ_{C-H} frequency at 650 cm^{-1}, which is absent in the spectrum of IIa, and the band of N—H stretching vibrations is shifted appreciably to the long-wave region, while the frequency of the asymmetrical ν_{SO_2} absorption in the

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*When our research was complete and this paper was being prepared for publication, we became aware of a paper [8], the authors of which observed the similar isomerization of 4-arylamino-2-sulfolenes.

Institute of the Chemistry of Macromolecular Compounds, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1332-1334, October, 1974. Original article submitted March 15, 1973; revision submitted February 25, 1974.

TABLE 1. Products of the Transformation of 4-Arylamino-2-sulfolenes

Compound	mp, °C (from 30% methanol)	R_f	Empirical formula	Found, %		Calc., %		Yield, %
				S	N	S	N	
IIa	162—163	0,26	$C_{10}H_{11}NO_2S$	15,4	7,0	15,2	7,0	98
IIb	144—146	0,25	$C_{11}H_{13}NO_2S$	14,3	6,1	14,3	6,3	75
IIc	153—154	0,26	$C_{11}H_{13}NO_3S$	13,4	5,7	13,34	5,8	96
IId	169—170	0,25	$C_{10}H_{10}ClNO_2S$	13,0	5,65	13,1	5,7	97
IIIa	91—92	0,51	$C_{14}H_{22}N_2O_2S$	11,2	10,00	11,35	9,9	62
IVa	108—109	0,53	$C_{11}H_{15}NO_3S$	13,25	5,5	13,2	5,7	85
IVc	107—108	0,55	$C_{12}H_{17}NO_4S$	11,8	5,4	11,8	5,2	63
IVd	162—163	0,52	$C_{11}H_{14}ClNO_3S$	11,7	5,2	11,6	5,08	88
Va	56—58	0,32	$C_{14}H_{21}NO_3S$	11,4	4,6	11,3	4,9	47
VIa	—*	0,4†	$C_{14}H_{21}NO_2S_2$	21,3	4,2	21,4	4,6	98
VII	165—166		$C_{21}H_{27}NO_4S_3$	21,1	3,1	21,2	3,1	96

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*The product was isolated by column chromatography and had n_D^{20} 1.5770.

†Eluted with $CHCl_3$.

spectrum of IIa is shifted by ~40 cm^{-1}; this is possible in the case of reaction of the sulfonyl group through the double bond with the amino group [7]. The formation of II can be explained by migration of the double bond in the sulfolene ring from the 2 position to the 3 position and subsequent conversion of the 3-arylamino-3-sulfolenes to II, in which the position of the double bond is stabilized by donor-acceptor interaction of the p electrons of the nitrogen atom with the d orbitals of the sulfur atom of the sulfonyl group (see [4, 6]).

The absence of products of addition of BH to sulfolenes IIa-d indicates that the compounds with R_f ~ 0.5 have structures III-VI.

A mixture of 30% IIa and 62% 3-butylamino-4-phenylaminosulfolane (IIIa, Table 1) was obtained in the reaction of sulfolene Ia with n-butylamine. In the presence of alkali at 28°, sulfolene Ia reacts with primary alcohols (CH_3OH, C_4H_9OH) to give alkoxysulfolanes IVa and Va (Table 1) in 85 and 47% yields, respectively, and isomerization product IIa in 10 and 48% yields. In aqueous solutions in the presence of alkali and tertiary amines, sulfolenes Ia-d are isomerized practically completely to IIa-d. The chief product of the reaction with butyl mercaptan is 3-butylthio-4-anilinosulfolane (VIa), which was identified as the p-toluenesulfonamide (VII, Table 1).

The reagents are arranged in the following order with respect to decreasing yields of addition products: p-C_4H_9SH > p-$C_4H_9NH_2$ > CH_4H_9OH. The alcohols are arranged in the following order with respect to decreasing yields of addition products: primary C_1 > C_4> secondary.

An increase in the steric effect of a nucleophilic reagent, for example, in the case of tert- and sec-butyl alcohols, hinders the addition to sulfolene Ia, and the chief reaction product is isomerization product IIa. The yields of isomerization and addition products in the reaction of methanol with sulfolenes Ia-d at 60° are as follows: IIa-d 90, 81, 58, and 95%, IVa-d 6, 12, 33, and 4%.

Thus an increase in the temperature, an increase in the steric effect of the nucleophilic reagents, and electron-acceptor substituents (X = Cl) in arylsulfolenes I promote isomerization, while a decrease in temperature, an increase in the nucleophilicity of the reagents, and electron-donor substituents (X = CH_3, OCH_3) in arylsulfolenes I promote addition.

EXPERIMENTAL

4-Arylamino-2-sulfolenes (Ia-d). These compounds were obtained by the method in [2]. The products were chromatographed with a column and in a thin layer of activity II aluminum oxide with elution by $CHCl_3$—C_2H_5OH (97:3) for both column chromatography and thin-layer chromatography (TLC). The thin-layer chromatograms were developed with iodine vapors. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer.

3-Arylamino-2-sulfolenes (IIa-d, Table 1). A mixture of 0.01 mole of sulfolene I and 0.2 g of KOH in 20 ml of 10% dioxane–water solution was heated at 60° for 3 h. The mixture was then neutralized and evaporated, and the residue was crystallized from 30% aqueous methanol. The yield was 90-95%.

3-Butylamino-4-anilinosulfolane (IIIa, Table 1). A mixture of 0.01 mole of sulfolene Ia and 15 ml of butylamine was held at 28-30° for 10 h. The excess amine was removed, and the residue was separated by means of column chromatography. The yield of IIa was 33%, while the yield of IIIa was 62%.

3-Methoxy-4-arylaminosulfolanes (IVa-d, Table 1). A mixture of 0.01 mole of sulfolene I in 7 ml of dioxane and 0.2 g of KOH in 10 ml of methanol was held at 28 or 60° for 10 h. It was then neutralized and evaporated, and the residue was separated by means of column chromatography. Compounds Va and VIa (Table 1) were similarly obtained.

4-(N-Tosylanilino)-3-butylthiosulfolane (VI, Table 1). A mixture of 0.01 mole of VIa in 10 ml of pyridine and 1.9 g (0.01 mole) of toluenesulfonyl chloride in 20 ml of dioxane was held at 80° for 8 h. The dioxane and pyridine were removed by distillation, and the residue was washed with water and crystallized from 50% aqueous acetone.

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