ISOMERIZATION OF 4-AMINO-2-SULFOLENES

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The base-catalyzed isomerization of 4-arylamino- and 4-morpholino-2-sulfolenes to 3-substituted 2-sulfolenes was investigated by UV spectroscopy. A shift in the ν_{as} frequencies of the SO_2 group was noted in the IR spectra of the latter.

The base-catalyzed isomerization of 3-sulfolene to 2-sulfolene is accomplished under mild conditions to give an equilibrium mixture of both isomers [1]. In the case of 3-substituted 3-sulfolenes it has been shown that the percentage of 3-substituted 2-sulfolenes increases successively in the order of substituents $H \sim Cl < CH_3 \ll OCH_3$, tert-$C_4H_9S$ [2].

It seemed of interest to investigate the conversion of 4-substituted 2-sulfolenes, by means of which one can detect migration of the multiple bond from one α,β position to another. In the present paper we present data on the isomerization of 4-arylamino- (I-IV) and 4-morpholino-2-sulfolenes (V), which were previously synthesized in [3, 4]. In the preparative syntheses we established that I-V are practically completely isomerized to 3-arylamino- (VI-IX) and 3-morpholino-2-sulfolenes (X).

The structures of the reaction products were proved by comparison of their IR and UV spectra with the spectra of the starting reagents. In I-IV (Table 1) the amino group in the 4 position of the 2-sulfolene has almost no effect on the absorption of the SO_2 group. The frequencies of the asymmetrical stretching absorption of the SO_2 group in 2-sulfolene [5] and amines I-IV are close to one another. On the other hand, an appreciable shift of ν_{as} (SO_2) is observed for 3-amino-2-sulfolenes (VI-IX, Table 1); this shift can be explained by the donor–acceptor interaction of the nitrogen and sulfur atoms of the amino and sulfo groups. The IR spectra of 3-amino-2-sulfolenes, for example, X (Fig. 1a), also contain the intense frequency of a double bond shifted by 30-40 cm^{-1} to the low-frequency region as compared with the absorption in starting amine V (Fig. 1b).

An appreciable difference in the structures of the starting materials and final products of isomerization shows up when their UV spectra are compared. Whereas 4-amino-2-sulfolenes absorb at < 220 nm, the UV spectra of 3-amino-2-sulfolenes contain a sharp maximum of rather high intensity at 240-275 nm (Table 2). Unsubstituted 2-sulfolene absorbs at 215 nm ($\varepsilon = 193$) [1]. Thus the introduction of an amino group into the 3 position of 2-sulfolene is accompanied by an appreciable bathochromic shift of the absorption maximum. The auxochromic effect of an amino group in 3-amino-2-sulfolenes, as described [6] for cyclic α,β-unsaturated β-amino ketones, also changes slightly in the VI-IX series as a function of the nature of the substituent in the aromatic ring.

We used the shift in the absorption maximum in the UV spectra of the products of isomerization in comparison with the spectra of the starting compounds in order to quantitatively monitor the reaction with time.

The isomerization of the investigated 4-amino-2-sulfolenes in excess alkali and amines is described by a first-order kinetic equation. The first-order reaction in substrate is confirmed by the constancy of the

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TABLE 1. Frequencies of the Stretching Vibrations of the SO_2 Group of Arylamino-2-sulfolenes*

Compound	ν_s, cm^{-1}	ν_{as}, cm^{-1}
I	1090	1240
II	1100	1268
III	1090	1245
IV	1100	1242
VI	1105, 1140	1286
VII	1095, 1140	1282
VIII	1099, 1140	1286
IX	1097, 1140	1285

* The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer.

TABLE 2. UV Spectra of 3-Amino-2-sulfolenes*

Compound	λ_{max}, nm	ε
VI	270	14800
VII	272	11200
VIII	272	16400
IX	273	12000
X	245	13800

* The UV spectra of 10% aqueous dioxane solutions of the compound were recorded with an SF-16 spectrophotometer.

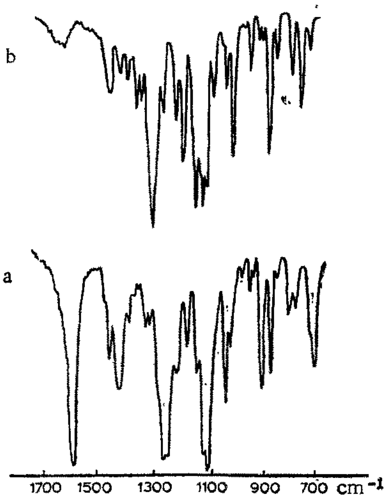


Fig. 1

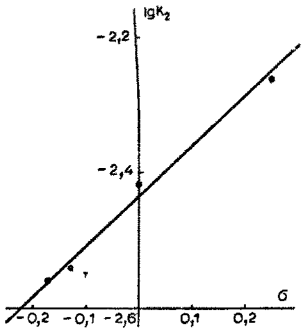


Fig. 2

Fig. 1. IR spectra: a) 3-morpholino-2-sulfolene (X); b) 4-morpholino-2-sulfolene (V).

Fig. 2. Dependence of k_2 on the nature of the substituent in arylaminosulfolenes I-IV at 30°C.

observed rate constants as the starting concentration of the compound is changed. The pseudo first-order rate constants (k_{obs}) of all of the compounds are linearly related to the KOH concentration (Table 3), so that the kinetic equation has the form

$$\frac{d[AS]}{dt}=k_2[AS][KOH],$$

where AS is 4-amino-2-sulfolene.

It was shown by additional experiments carried out in solutions in 1 M KCl that a salt effect is practically absent in the isomerization of I-V within the limits of the investigated concentrations and temperatures. Practically no reaction occurs in aqueous dioxane solution.

Secondary (I-IV) and tertiary (V) amines are isomerized in the presence of catalysts. The rate of isomerization of V is lower than the rates of isomerization of I-IV, and electron-acceptor substituents facilitate their isomerization in I-IV, whereas electron-donor substituents hinder it (Fig. 2). The changes

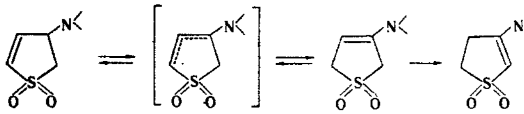
TABLE 3. Results of Isomerization of 4-Amino-2-Sulfolenes

Compound	k_2, liter·mole^{-1}·sec^{-1}			E, kcal/mole	$\Delta S^{\neq}$, eu
	30°	40°	50°		
I	0,0039±0,0005	0,0067±0,0006	0,0182±0,0018	15,1	−22,3
II	0,0021±0,0004		0,0141±0,0014		
III	0,0026±0,0003	0,0067±0,0008	0,0151±0,0006	16,9	−16,5
IV	0,005±0,001	0,0118±0,0015	0,025±0,004	15,7	−19,4
V	0,00095±0,0001	0,0023±0,0003	0,0045±0,0006	15,1	−24,3

in k_2 under the influence of substituents satisfy the Hammett equation with σ^n substituent constant [7] ("approximate" correlation):

$$\lg k = -2.41 + 0.77\sigma^n.$$

The data obtained correspond to a reaction scheme involving the formation of a mesomeric carbanion, which is then protonated with migration of the double bond:



The resulting 3-amino-3-sulfolene is unstable under the reaction conditions and is isomerized practically completely via a previously described scheme [1, 2] to 3-amino-2-sulfolene, in which the double bond is stabilized by donor–acceptor interaction of the nitrogen and sulfur atoms.

The acceleration of the reaction in the case of I–IV as compared with V can be explained by additional stabilization of the intermediately formed carbanion through conjugation with the aromatic system. The energy parameters of the reaction (Table 2), determined from the change in k_2 at 30, 40, and 50°, correspond to a carbanion mechanism for isomerization with intermolecular proton transfer. The activation energies (E) and entropies ($\Delta S^{\neq}$) are close to the values found in the reaction involving migration of the double bond from the 3 position to the 2 position, the carbanion mechanism of which has been established by kinetic [1] and isotopic [8] methods.

EXPERIMENTAL METHOD

The course of the isomerization was monitored quantitatively from the buildup of isomerization products VI–X at the UV absorption maximum, at which the intensity of absorption of the starting compounds is low. An SF-16 spectrophotometer, the thermostatted cuvette of which served as the reaction vessel, was used. The isomerization was studied in the presence of potassium hydroxide and buffer solutions of diethylethanolamine and triethanolamine in 10% aqueous dioxane solution under pseudo-monomolecular conditions. The experiments were duplicated at least four to five times, and the results were averaged.

We used the following first-order equation to calculate the observed rate constant (Table 2):

$$\ln \frac{D_\infty}{D_\infty - D_t} = k_{\text{obs}} \cdot t,$$

where D_∞ and D_t are the optical densities of the solution at the end of the reaction and at time t, respectively. The D_∞ values observed in the experiments coincided with the values calculated from the molar extinction coefficient of the appropriate 3-amino-2-sulfolene and the starting concentration of 4-amino-2-sulfolene; this indicates practically 100% isomerization and is in agreement with the results of an investigation of the reaction by thin-layer chromatography [3, 4].

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