

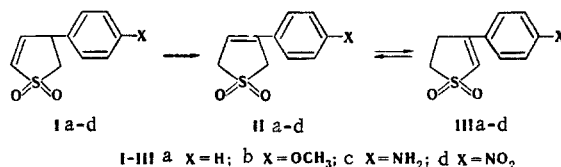
ISOMERIZATION OF 3-ARYL-4-SULFOLENES
AND THEIR REACTION WITH SOME NUCLEOPHILIC
REAGENTS

T. É. Bezmenova, S. M. Lukashov,
V. P. Tantsyura, T. S. Lutsii,
A. F. Rekasheva, and T. D. Zaika

UDC 547.733:541

Bases convert 3-(4-substituted phenyl)-4-sulfolenes to 3-aryl-3-sulfolenes, which are subsequently isomerized to 3-aryl-2-sulfolenes. The ratios of the products depend on the character of the substituent in the phenyl ring, and electron-acceptor substituents accelerate the isomerization.

We have found that 3-aryl-4-sulfolenes (Ia-d), synthesized via the Friedel-Crafts reaction [1], are converted in aqueous and alcohol solutions of bases (alkali, alkoxides, and amines) to the isomeric 3-aryl-3-sulfolenes (IIa-d) and 3-aryl-2-sulfolenes (IIIa-d).



Compounds Ia-c are converted to IIa-c in 0.01 M KOH at 20-40°C, and further isomerization to IIIa-c occurs in 0.4-1.0 M KOH. The reaction Id → IId was carried out in 0.001-0.005 M KOH, and the reaction IId → IIId was carried out in 0.01-0.05 M KOH.

It was shown by means of thin-layer chromatography (TLC) and PMR and UV spectroscopy that the isomerization of Ia-d to IIa-d under the selected conditions is practically irreversible. In the isomerization of 3-aryl-3-sulfolenes to the corresponding 3-aryl-2-sulfolenes an equilibrium mixture of products is formed if X = H, NO₂, whereas when X = OCH₃, NH₂, the equilibrium is shifted completely to favor 3-substituted isomers IIId and IIId. The results are in agreement with the results of isomerization of 3-methoxy-3-sulfolene [2].

The IR spectra of the compounds obtained in this research do not contain the C-H frequency characteristic for a cis double bond [3] at 640-670 cm⁻¹ that is present in the IR spectra of starting Ia-d, and the intensity of the frequency of the C = C bond is increased due to conjugation with an aromatic ring.

The PMR spectrum of the starting compound has the typical group of lines of a three-spin ABX system at 2.8-4.6 ppm, a narrow doublet centered at 6.85 ppm, and a signal of protons of a phenyl ring. The two protons of the methylene group in the 2 position and the proton attached to the carbon atom in the 3 position correspond to the ABX system. The vinyl protons attached to the carbons in the 4 and 5 positions of the sulfolene ring unexpectedly have identical chemical shifts. This is probably associated with the effect of the magnetic anisotropy of the phenyl ring and also with the strong electron-acceptor effect of the adjacent SO₂ group, which leads to the anomalous chemical shifts of the protons of the vinyl system [4]. The intensities of the signals of the protons of the sulfolene ring (2 : 1 : 2) are in agreement with their assign-

Institute of the Chemistry of Macromolecular-Weight Compounds, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 8, pp. 1072-1077, August, 1975. Original article submitted August 29, 1974.

©1976 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

TABLE 1. Arylsulfolenes

Compound	x	y	mp, °C	R _f	Empirical formula	Found, %			
						C	H	N	S
Ia	H		84—85 ¹						
Ib	OCH ₃	3-Sulfolen-4-yl	118—119 ¹						
Ic	NH ₂		157—158	0,16	C ₁₀ H ₁₁ NO ₂ S	57,3	5,2	6,7	15,1
Id	NO ₂		145—146	0,25	C ₁₀ H ₉ NO ₂ S	50,4	3,9	6,2	13,4
IIa	H		132—133	0,47	C ₁₀ H ₁₀ O ₂ S	61,5	5,2		16,6
IIb	OCH ₃	3-Sulfolen-3-yl	130—131	0,37	C ₁₁ H ₁₃ O ₃ S	58,8	5,6		14,2
IIc	NH ₂		175—176	0,13	C ₁₀ H ₁₁ NO ₂ S	57,8	5,4	6,3	15,3
IId	NO ₂		195—196	0,28	C ₁₀ H ₉ NO ₂ S	50,4	3,9	6,1	13,5
IIIa	H		171—172	0,3	C ₁₀ H ₁₀ O ₂ S	61,7	5,3		16,4
IIIb	OCH ₃	3-Sulfolen-2-yl	148—149	0,16	C ₁₁ H ₁₃ O ₃ S	58,7	5,7		14,3
IIIc	NH ₂		224—225	0,10	C ₁₀ H ₁₁ NO ₂ S	57,1	5,3		15,3
IV	H	4-(3-Butylthio)-sulfolanyl	95—96	0,60	C ₁₄ H ₂₀ O ₂ S ₂	59,3	7,4	6,2	22,5
V	H	4-(3-Sulfolanyl-sulfatosodium)	380 dec.	—	C ₁₀ H ₁₁ O ₅ S ₂ Na	40,2	3,6		21,5

ment. The signals of the protons of the sulfolene ring in the spectra of isomers IIa and IIIa in one case are in the form of a quintet, quartet, and multiplet centered at 3.97, 4.17, and 6.50 ppm, respectively, with a relative intensity of 2:2:1, and in the other case are in the form of two narrow peaks at 3.34 and 7.13 ppm with a relative intensity of 4:1.

An appreciable shift of one of the absorption bands of the phenyl ring to the longwave region when it is conjugated with a double bond [5] is observed in the UV spectra of the isomeric sulfolenes (Table 1). The differences in the UV spectra of the isomeric arylsulfolenes were used for a study of the kinetics of migration of the double bond in the sulfolene ring. The kinetics of the base-catalyzed isomerization of 3-sulfolenes and 3-methyl-3-sulfolenes to 2-sulfolene and 3-methyl-2-sulfolene have been described [6, 7]. No kinetic data on the isomerization of 3-substituted-4-sulfolenes are available.

The isomerization was accomplished in a 10% solution of dioxane in water under pseudomonomolecular conditions (100:1 excess of KOH). The rate of isomerization is described by the equation

$$\frac{dx}{dt} = k_2[AC][KOH]$$

The k_2 , E , and ΔS^\ddagger values found from the temperature dependence of k_2 are presented in Table 2. The fact that a linear relationship exists between $\Delta H = E_{\text{exp}} - RT$ and $T\Delta S^\ddagger$ in the isomerization of 3-aryl-3-sulfolenes to the corresponding 3-aryl-2-sulfolenes with a slope of almost unity indicates the mutual compensation of the changes in the heats and entropies of activation. Under these conditions, the activation parameters found cannot serve for the evaluation of the mechanism of the reaction under investigation.

A comparison of the k_2 values in the isomerization of 3-phenyl-4-sulfolene and 3-phenyl-2-sulfolene to 3-phenyl-3-sulfolene (Ia \rightarrow IIa and IIIa \rightarrow IIa) shows that the rate of the first reaction is higher by a factor of 300 than that of the second and higher by a factor of almost two orders of magnitude than the rate of migration of the double bond from the 3 position to the 2 position (IIa \rightleftharpoons IIIa). The Ia \rightarrow IIa conversion has a lower activation energy. The high value of the equilibrium constant of the reaction IIa \rightleftharpoons IIIa as com-

TABLE 2. Results of Isomerization of 3-Aryl-4-sulfolenes

Reaction	$k_2 \cdot 10^3$, liter \cdot mole ⁻¹ sec ⁻¹			E, kcal \cdot mole ⁻¹	ΔS^\ddagger , eu
	20°	30°	40°		
Ia \rightarrow IIa	26,2	62,1	156	16,29	-12,29
Ib \rightarrow IIb	—	31,39	—		
Ic \rightarrow IIc	—	9,6	—		
Id \rightarrow IID	896	2590	7940	19,80	+6,70
IIa \rightarrow IIIa	0,25	0,846	2,08	19,24	-11,12
IIIa \rightarrow IIa	0,075	0,276	0,636	19,39	-12,88
IIb \rightarrow IIIb	0,52	1,22	2,65	14,85	-14,84
IIc \rightarrow IIIc	0,347	1,001	2,70	18,59	-12,90

Calc. %				UV spectrum, $\lambda_w, \text{nm} (\epsilon)$	PMR spectrum, chemical shifts, δ , ppm, in $(\text{CD}_3)_2\text{CO}$					Yield, %
C	H	N	S		C_6H_5	2-H ₂	3-H	4-H	5-H	
				— —	C_6H_5 7.30	2-H ₂ 3.00 3.70	3-H 4.45	4-H 6.85	5-H 6.85	90
57.4	5.3	6.6	15.3	— —						70
50.2	3.8	5.9	13.4	260 (4300 ± 100)						
61.8	5.2		16.5	251 (18300 ± 500)	C_6H_5 7.30	2-H ₂ 3.97	4-H 6.50	5-H ₂ 4.17	4.17	96
				257 (2600 ± 300)		3.97				98
58.6	5.7		14.2	260 (14500 ± 300)						
57.4	5.3	6.6	15.3	305 (8300 ± 100)						99
50.2	3.8	5.9	13.4	260 (11000 ± 300)						99
61.8	5.2		16.5	257 (5900 ± 100)	C_6H_5 7.30	2-H 7.13	2-H 3.34	5-H ₂ 3.34		50
58.6	5.7		14.2	267 (18200 ± 500)						99
57.4	5.3	6.6	15.3	280 (18400 ± 500)						99
59.1	7.8		22.8	340 (7000 ± 200)						89
40.3	3.7		21.5							95

pared with the isomerization of 3-sulfolene to 2-sulfolene [7] is probably responsible for the increased stability of IIIa as compared with 2-sulfolene. In the series of arylsulfolenes Ia-d the change in the k_2 value satisfies the Hammett equation with σ^P substituent constants [8]:

$$\lg k = 0.0621 + 2.457 \sigma^P$$

with correlation coefficient $r = 0.995$ and computational error $S = 0.092$. The positive ρ value constitutes evidence for acceleration of the reaction by electron-acceptor substituents in the para position of the phenyl ring and retardation by electron-donor substituents.

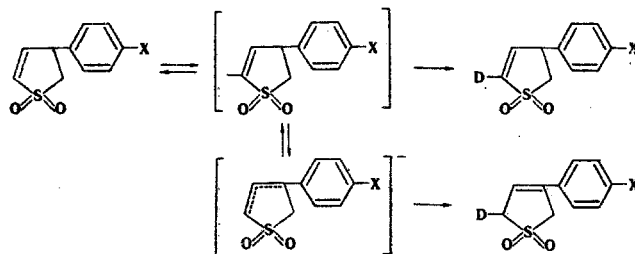
During the investigation of the reactions $\text{Ia} \rightarrow \text{IIa}$ and $\text{IIa} \rightleftharpoons \text{IIIa}$ in D_2O with NaOD we found that exchange of the vinyl protons in the 2 and 5 positions by deuterium, as in [9], precedes migration of the double bond in Ia and IIIa. This can be judged from the decrease in the intensity and the conversion of the signal of the vinyl protons at 6.85 ppm in the spectrum of Ia to a singlet with retention of the original form and intensity of the signals of the remaining protons. The signal of the vinyl proton at 7.13 ppm in the spectrum of IIIa vanishes, and the form of this signal at 3.34 ppm changes because of exchange of the proton by deuterium in the 2 and 5 positions prior to the appearance of the signal of the vinyl proton of isomer IIa. The addition of NaOD to a solution of IIa in D_2O leads to exchange of only the allyl protons in the 2 and 5 positions of the sulfolene ring, as may be judged from the disappearance in the PMR spectrum of the sig-

TABLE 3. Results of the Isomerization of 3-Phenyl-3-sulfolene

KOH	$k_{\text{obs}} = \frac{k_2}{k_1 + k_{-1}}$	K	k_1, sec^{-1}	k_{-1}, sec^{-1}	$k_2, \text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$	$k_{-2}, \text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$
20°						
0.799	$2.50 \cdot 10^{-4}$	3.27	$1.91 \cdot 10^{-4}$	$5.85 \cdot 10^{-5}$	$2.39 \cdot 10^{-4}$	$7.32 \cdot 10^{-5}$
0.872	$2.41 \cdot 10^{-4}$	3.38	$1.86 \cdot 10^{-4}$	$5.50 \cdot 10^{-5}$	$2.41 \cdot 10^{-4}$	$7.12 \cdot 10^{-5}$
0.998	$3.58 \cdot 10^{-4}$	3.40	$2.76 \cdot 10^{-4}$	$8.13 \cdot 10^{-5}$	$2.70 \cdot 10^{-4}$	$8.14 \cdot 10^{-5}$
		3.35			$2.50 \cdot 10^{-4}$	$7.52 \cdot 10^{-5}$
30°						
0.152	$1.79 \cdot 10^{-4}$	2.92	$1.33 \cdot 10^{-4}$	$4.57 \cdot 10^{-5}$	$8.76 \cdot 10^{-4}$	$3.01 \cdot 10^{-4}$
0.568	$5.16 \cdot 10^{-4}$	3.44	$3.99 \cdot 10^{-4}$	$1.16 \cdot 10^{-4}$	$7.03 \cdot 10^{-4}$	$2.04 \cdot 10^{-4}$
0.779	$1 \cdot 10^{-3}$	2.974	$7.48 \cdot 10^{-4}$	$2.58 \cdot 10^{-4}$	$9.60 \cdot 10^{-4}$	$3.23 \cdot 10^{-4}$
		3.11			$8.46 \cdot 10^{-4}$	$2.76 \cdot 10^{-4}$
40°						
0.520	$1.41 \cdot 10^{-3}$	3.48	$1.018 \cdot 10^{-3}$	$3.14 \cdot 10^{-4}$	$2.01 \cdot 10^{-3}$	$6.04 \cdot 10^{-4}$
0.635	$1.37 \cdot 10^{-3}$	3.34	$1.051 \cdot 10^{-3}$	$3.24 \cdot 10^{-4}$	$1.65 \cdot 10^{-3}$	$5.10 \cdot 10^{-4}$
0.779	$2.67 \cdot 10^{-3}$	3.33	$2.05 \cdot 10^{-3}$	$6.2 \cdot 10^{-4}$	$2.57 \cdot 10^{-3}$	$7.96 \cdot 10^{-4}$
		3.35			$2.08 \cdot 10^{-3}$	$6.36 \cdot 10^{-4}$

nals at 3.97 and 4.17 ppm and conversion of the signal of the vinyl proton in the 4 position (6.5 ppm) to a singlet because of the absence of splitting in the protons of the methylene group in the 5 position.

The results can be explained by isomerization via the scheme



The migration of the double bond from the 3 position to the 2 position has been previously described [2, 6]. Products of addition to the double bond of the sulfolene ring were isolated from the reaction of Ia with NaHSO_3 and $\text{C}_4\text{H}_9\text{SH}$ in the presence of $\text{C}_4\text{H}_9\text{SNa}$.

EXPERIMENTAL METHOD

Column chromatography and thin-layer chromatography (TLC) on a loose layer of activity II Al_2O_3 (elution with ether and chloroform) were used for the separation and evaluation of the individuality of the compounds. The chromatograms were developed in iodine vapor.

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with an SF-16 spectrophotometer. The PMR spectra of solutions of the compounds in $(\text{CD}_3)_2\text{CO}$ with and without NaOD were recorded with a Varian-60A spectrometer with hexamethyl disiloxane as the internal standard.

3-Aryl-4-sulfolenes Ia, Ib, and Id were previously obtained in [1].

3-(4-Aminophenyl)-4-sulfolene (Ic, Table 1). A mixture of 4.8 g (0.02 mole) of Id, 2.4 g of tin metal, and 30 ml of HCl was heated to 60° and stirred until Id dissolved. The solution was then neutralized with alkali solution to pH 7.5-8 and extracted with boiling benzene. The benzene was evaporated, and the residue was crystallized from methanol to give 3.8 g of Ic.

3-Phenyl-3-sulfolene (IIa, Table 1). A 1.96-g (0.01 mole) sample of Ia was dissolved in a mixture of 5 ml of butylamine and 1 ml of water, and the mixture was stirred at room temperature for 2 h. The resulting precipitate was removed by filtration and recrystallized from methanol to give 1.9 g of IIa.

3-Aryl-3-sulfolene (IIb-d, Table 1). These compounds were obtained by the method used to prepare IIa.

3-Phenyl-2-sulfolene (IIIa, Table 1). A solution of 1.96 g (0.01 mole) of Ia in 10 ml of dioxane was stirred with 10 ml of 1 M KOH at 50° for 2 h, after which it was cooled to room temperature, and the resulting precipitate was removed by filtration and separated with a column (20 mm in diameter and 400 mm high) filled with Al_2O_3 to give 0.9 g of IIa and 0.95 g of IIIa.

3-Aryl-2-sulfolenes (IIIb, c Table 1). These compounds were obtained by the methods used to prepare IIIa.

Sodium 3-Phenylsulfolane-4-sulfonate (V, Table 1). A 2-g sample of Ia was refluxed in 10 ml of a 40% solution of sodium bisulfite for 1 h, after which the precipitate was removed by filtration and crystallized from water to give 2.9 g of V.

3-Butylthiophenylsulfolane (IV, Table 1). A 0.4-g sample of sodium and 0.9 g of n-butanethiol were dissolved in 5 ml of methanol, and 2 g of Ia was added to the resulting solution of sodium butylthiolate. The mixture was stirred at 0° for 2 h, after which it was neutralized with HCl and vacuum evaporated. The residue was crystallized from methanol to give 2.5 g of IV.

Isomerization: Kinetic Measurements. The kinetic experiments were carried out in the thermostated cuvette of an SF-16 spectrophotometer (with an accuracy of $\pm 0.2\%$). The solutions of the starting compounds in dioxane ($\approx 4 \cdot 10^{-4}$ M) and of KOH in water (0.01-0.1 M) were thermostated prior to mixing. The time at which the solutions were mixed was taken as the start of the reaction, and the change in the optical density of the solution at a selected wavelength was measured at definite time intervals up to D_∞ , at which point the optical density of the solution remained practically constant with time. The D_∞ values observed for Ia-d and IIb, c in the experiments coincided with the values calculated from the molar extinction coefficients (ϵ) of the corresponding isomers and the starting concentration of the compounds, and this indicated practically 100% conversion and was in agreement with the results of monitoring of the reaction by TLC. The ϵ values at the working wavelengths (λ_w) are presented in Table 1.

In the case of the isomerization of IIa to IIIa the optical densities at two wavelengths were determined, inasmuch as the absorption curves of the two isomers are superimposed on one another over the entire spectrum; their concentrations were calculated from the following formulas [5]:

$$C_{IIa} = \frac{\epsilon_{IIIa\lambda_2} \frac{D_{\lambda_1}}{l} - \epsilon_{IIIa\lambda_1} \frac{D_{\lambda_2}}{l}}{\epsilon_{IIa\lambda_1} \cdot \epsilon_{IIIa\lambda_2} - \epsilon_{IIIa\lambda_1} \cdot \epsilon_{IIa\lambda_2}}$$

$$C_{IIIa} = \frac{\epsilon_{IIa\lambda_1} \frac{D_{\lambda_2}}{l} - \epsilon_{IIa\lambda_2} \frac{D_{\lambda_1}}{l}}{\epsilon_{IIa\lambda_1} \cdot \epsilon_{IIIa\lambda_2} - \epsilon_{IIIa\lambda_1} \cdot \epsilon_{IIa\lambda_2}}$$

The rate constant for the isomerizations Ia-d \rightarrow IIa-d and IIb, c \rightarrow IIIb, c were found from the equation for a unidirectional first-order reaction:

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

where D_t is the optical density of the solution at time t .

The equilibrium constant and the sum of the rate constants of the forward and reverse reactions were calculated for the reversible reaction IIa \rightleftharpoons IIIa [10].

$$K = \frac{C_{\text{eq}}}{C_0 - C_{\text{eq}}}; \quad k_1 + k_{-1} = \frac{1}{t} \ln \frac{C_{\text{eq}}}{C_{\text{eq}} - C_t}$$

and the following values were found:

$$k_1 = \frac{K}{1+K} (k_1 + k_{-1}); \quad k_{-1} = \frac{k_1 + k_{-1}}{K}$$

where C_0 , C_t , and C_{eq} are the concentrations of the substance at the start of the reaction, at time t , and in the equilibrium state.

The experiments were repeated no less than three times, and the data were averaged. The results of the kinetic measurements are presented in Tables 2 and 3.

LITERATURE CITED

1. T. É. Bezmenova, S. M. Lukashov, and Yu. N. Usenko, *Khim. Geterotsikl. Soedin.*, 764 (1973).
2. M. Prochazka and M. Palacek, *Coll. Czech. Chem. Commun.*, **31**, 3744 (1966).
3. V. West, *Applications of Spectroscopy in Chemistry* [Russian translation] Moscow (1959), p. 323.
4. J. Emsley, J. Feeney, and L. Sutcliffe, *High-Resolution NMR spectroscopy*, Pergamon, Oxford (1965, 1966).
5. O. V. Sverdlova, *Electronic Spectra in Organic Chemistry* [in Russian], Khimiya, Leningrad (1973), p. 139.
6. H. Zimmermannova and M. Prochazka, *Coll. Czech. Chem. Commun.*, **30**, 286 (1965).
7. L. K. Brice, W. M. Chang, J. E. Smith, and S. M. Sullivan, *J. Phys. Chem.*, **71**, 2814 (1967).

8. K. D. Riche and U. F. Sedger in: Modern Problems of Physical Organic Chemistry [Russian translation], Mir, Moscow (1967), p. 498.
9. C. D. Broadus, J. Amer. Chem. Soc., 88, 3863 (1966).
10. N. N. Émanuél' and D. G. Knorre, Course in Chemical Kinetics, [in Russian], Moscow (1969), p. 162.