REACTION OF 3-CHLORO-3-SULFOLENE AND 3-CHLORO-2-SULFOLENE WITH ALKYL(ARYL)AMINES

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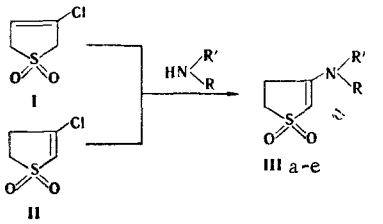
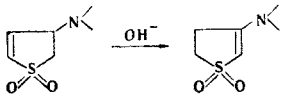
The corresponding 3-alkylamino-2-sulfolenes are formed in the reaction of 3-chloro-3-sulfolene and 3-chloro-2-sulfolene with aliphatic amines. It was established that under the influence of the amines 3-chloro-3-sulfolene initially undergoes isomerization to 3-chloro-2-sulfolene with subsequent replacement of the chlorine atom by the amine component. 3-Chloro-3-sulfolene and 3-chloro-2-sulfolene are inert in the reaction with aromatic amines that have low basicities.

The synthesis of 4-aryl- and 3-aryl(alkyl)amino-2-sulfolenes has been previously described [1-4]. In the present communication we present the results of a study of the reaction of 3-chloro-3-sulfolene (I) and 3-chloro-2-sulfolene (II) with alkyl(aryl)amines.

We established by thin-layer chromatography that only 3-alkylamino-2-sulfolenes (IIIa-e) (Table 1) are formed in the reaction of aliphatic amines with I and II:



To obtain proof for the 3-alkylamino-2-sulfolene structure we accomplished the independent synthesis of IIIc,e by isomerization of 4-piperidyl-2-sulfolene and 4-dimethylamino-2-sulfolene in the presence of sodium hydroxide by the method described in [6, 7]. The identical character of the compounds obtained



by the two methods was confirmed by their IR spectra and the absence of melting-point depressions in the case of mixtures of the compounds.

Aromatic amines that have low basicities do not replace the chlorine atom in II and do not induce isomerization of I to II under the conditions selected. Taking into account these data and the data in [5], as well as our results from the isomerization of 4-aryl(alkyl)amino-2-sulfolenes [6, 7], we may assume two probable schemes for the formation of the 3-alkylamino-2-sulfolenes (IIIa-e):

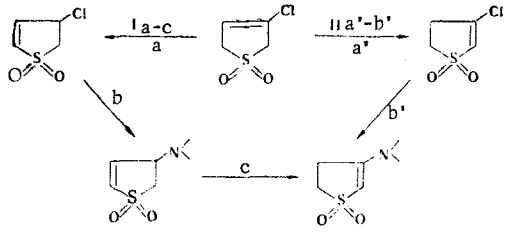


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TABLE 1. Characteristics of the Compounds Obtained

Compound	R	R′	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %	
				N	S		N	S	I	III from II
IIIa	H	C_4H_9	123—124	7,5	17,0	$C_8H_{15}NO_2S$	7,4	16,9	91	92
IIIb	H	$-CH_2-CH=CH_2$	115—116	8,1	18,3	$C_7H_{11}NO_2S$	8,1	18,5	90	91
IIIc		$-(CH_2)_5-$	122—123	6,7	15,3	$C_9H_{15}NO_2S$	6,9	15,6	90	92
IIId		$-(CH_2)_2O(CH_2)_2-$	179—180	6,7	15,4	$C_8H_{13}NO_3S$	6,9	15,7	93	92
IIIe	CH_3	CH_3	162—164	8,8	19,9	$C_6H_{11}NO_2S$	8,7	19,9	95	96

Steps Ia-b were proposed by Prochazka [5]. To verify step Ic we accomplished the reacting of 4-morpholinyl- and 4-piperidyl-2-sulfolenes with morpholine and piperidine under the conditions of the reaction of I with aliphatic amines, as a result of which we obtained the addition products 3,4-dipiperidylsulfolane (IV), 3,4-dimorpholinylsulfolane (V), and 3-morpholinyl-4-piperidylsulfolane (VI). Isomerization products, viz., 3-morpholinyl-2-sulfolene and 3-piperidyl-2-sulfolene, were not detected by thin-layer chromatography (TLC). This makes it possible to assume that the reaction of aliphatic amines with 3-chloro-3-sulfolene is realized via scheme IIa′-b′. 3-Chloro-2-sulfolene, which was obtained by the reaction of 3-chloro-3-sulfolene with ammonium hydroxide, also confirms scheme IIa′-b′.

EXPERIMENTAL

Chromatography on a loose layer of activity II aluminum oxide was used to evaluate the course of the reaction and the purity of the substances; the chromatograms were developed with iodine vapors.

3-Piperidyl-2-sulfolene (IIIc) (Table 1). A) A 3.4-g (0.04 mole) sample of piperidine was added to a solution of 1.5 g (0.01 mole) of I in 35 ml of methanol, and the mixture was heated at 55-60°C for 8 h. The methanol and excess piperidine were removed by distillation, and the residue was washed with 4 ml of cold water and crystallized from 50% aqueous methanol.

B) The reaction of 0.75 g (0.005 mole) of II and 1.7 g (0.02 mole) of piperidine under the conditions of experiment A gave 0.9 g (90%) of sulfolene IIIc.

C) A total of 10 ml of a 1.5 N NaOH solution was added to a solution of 2.0 g (0.01 mole) of 4-piperidyl-2-sulfolene in 10 ml of dioxane, and the mixture was heated with stirring at 60°C for 5 h. The resulting solution was then neutralized with 1 N HCl and evaporated. The residue was washed with 4 ml of cold water and crystallized from 50% ethanol to give 1.5 g (75%) of IIIc. No melting-point depressions were observed for mixtures of this product with the IIIc obtained in experiments A and B.

3-Dimethylamino-2-sulfolene (IIIe). The reaction of 1.6 g (0.01 mole) of 4-dimethylamino-2-sulfolene under conditions similar to those in the synthesis of IIIc by method C gave 1.5 g (94%) of sulfolene IIIe. Compounds IIIa-c,e (Table 1) were obtained by reaction of I and II with butyl-, allyl-, morpholinyl-, and dimethylamines under the conditions of experiment A.

3-Chloro-2-sulfolene (II). A total of 10 ml of 25% ammonium hydroxide was added to a solution of 1.5 g (0.01 mole) of 3-chloro-3-sulfolene in 35 ml of methanol, and the mixture was stirred at room temperature for 6 h and at 50°C for 5 h. The resulting solution was evaporated, and the oily residue was extracted with chloroform. Workup of the extract gave 0.6 g (40%) of II with mp 87-88°C (from 5% ethanol). No melting-point depression was observed for a mixture of this product with 3-chloro-2-sulfolene synthesized by the method in [5].

3,4-Dipiperidylsulfolane (IV). A 2.0-g (0.01 mole) sample of 4-piperidyl-2-sulfolene and 4.3 g (0.05 mole) of piperidine were dissolved in 130 ml of methanol, and the solution was heated at 60°C for 20 h, after which it was evaporated, and the residue was washed with 5 ml of cold water and crystallized from methanol to give 2.74 g (96%) of a product with mp 150-151°C. Found: N 9.7; S 11.3%. $C_{14}H_{26}N_2O_2S$. Calculated: N 9.7; S 11.2%. The identical character of the IV that we obtained by the method in [8] and by the addition of piperidine to 4-piperidyl-2-sulfolene was proved by the absence of a melting-point depression for a mixture of the two samples and their IR spectra.

3-Morpholinyl-4-piperidylsulfolane (VI). A) A solution of 2.0 g (0.01 mole) of 4-morpholinyl-2-sulfolene and 2.6 g (0.03 mole) of piperidine in 25 ml of methanol was heated at 60°C for 25 h, after which the methanol and excess piperidine were removed by distillation, and the residue was crystallized from 50% aqueous acetone to give 2.6 g (92%) of a product with mp 141-142°C. Found: N 9.7; S 11.1%. $C_{13}H_{24}N_2O_3S$. Calculated: N 9.7; S 11.1%.

B) A 7.8-g (0.09 mole) sample of morpholine was added to a solution of 2.0 g (0.01 mole) of 4-piperidyl-2-sulfolene in 20 ml of methanol, and the mixture was heated at 60°C for 10 h. The resulting solution was evaporated, and the residue was crystallized from 50% aqueous acetone to give 2.7 g (98%) of VI. No melting-point depression was observed for mixtures of the products obtained in experiments A and B.

3,4-Dimorpholinylsulfolane (V). A 2.0-g (0.01 mole) sample of 4-morpholinyl-2-sulfolene and 8.7 g (0.1 mole) of morpholine were dissolved in 70 ml of methanol, and the solution was heated at 60°C for 20 h. It was then evaporated, and the residue was crystallized from 10% ethanol to give 2.6 g (90%) of a product with mp 167-168°C. Found: N 9.5; S 11.1%. $C_{12}H_{22}N_2O_4S$. Calculated: N 9.6; S 11.0%.

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SYNTHESIS OF ω,ω'-DIARYL-SUBSTITUTED 2,5-DIVINYLTHIOPHENES

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The phosphonate modification of the Wittig reaction was used to synthesize ω,ω'-diaryl-substituted 2,5-divinylthiophenes that contain phenyl, 4-biphenylyl, 2-naphthyl, 9-anthryl, and 2-thienyl groups, as well as functional substituted 2,5-distyrylthiophenes.

Vinyl derivatives of thiophene have found application as optical bleaches [1] and biologically active substances [2, 3]. These compounds, which include various chromophore groupings, may, like the analogous benzene derivatives [4], be of interest as effective luminophores.

We have synthesized ω,ω'-diaryl-substituted 2,5-divinylthiophenes (DDVT) that contain phenyl, 2-naphthyl, 4-biphenylyl, 9-anthryl, and 2-thienyl groups, as well as functional substituted 2,5-distyrylthiophenes (Table 1).

The arylthienylethylenes described in the literature were obtained by various methods [5, 6]. In particular, arylthienylethylenes were synthesized via the Wittig reaction both from formylthiophene [7] and from chloromethylthiophene [8]. However, a mixture of the cis and trans isomers is obtained in both cases.

For the synthesis of the DDVT we used the phosphonate modification of the Wittig reaction [9], which does not have this disadvantage; the reaction products are, as a rule, the trans isomers.

To obtain the DDVT we first used diethyl thiophenebis(methylenephosphonate) (I), since the use of 2,5-diformylthiophene as the starting compound would lead to complication of the synthesis and make it a multistep process.

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