CONDENSATION OF UNSATURATED CYCLIC SULFONES WITH ALDEHYDES

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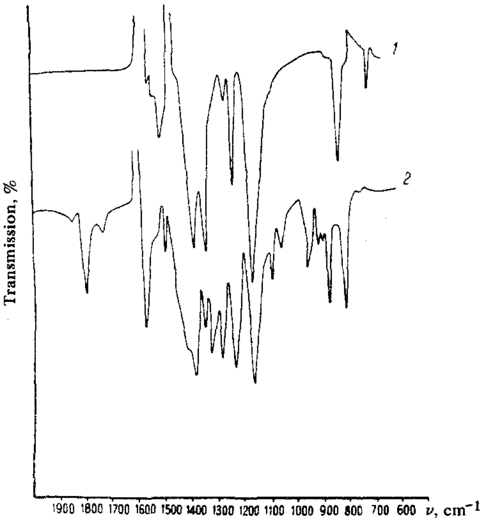
The reactivity of the 2(5) positions of dihydrothiophene dioxide has been studied. Their condensation with aldehydes leads to the formation of 2(5)-substituted derivatives containing a conjugated system of double bonds.

Unsaturated cyclic sulfones, or sulfolenes, which are obtained by the condensation of butadiene hydrocarbons with sulfur dioxide, have been studied in a number of investigations. These investigations have related mainly to the addition reactions of hydrogen, halogens, alcohols, amines, mercaptans, etc. to the double bond (positions 3 and 4) [1, 2]. There is no information in the literature on the reactivity of the 2 and 5 positions of the sulfolenes.



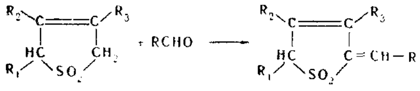
IR spectra: 1) 2,5-dihydrothiophene 1,1-dioxide; 2) 2-(1-heptenyl)-2,5-dihydrothiophene 1,1-dioxide.

In the present work we studied the reactivity of methylene groups in positions 2 and 5, and this in terms of their capacity for reacting with aldehydes.

The sulfone group, having marked electron-accepting properties, causes a lowering of the electron density on the neighboring carbon atoms in the sulfolene molecule which leads to the protonation of the hydrogens attached to them. Consequently, a reaction of the sulfolenes and aldehydes in an alkaline medium in the manner of the aldol condensation was expected with high probability. As the subjects of study, we took 2,5-dihydrothiophene 1,1-dioxide (3-sulfolene) and its methyl homologs 3,4- and 2,4-dimethylsulfolenes. For condensation with these substances we used butyraldehyde and enanthaldehyde.

The reactions with the aldehydes were carried out under the conditions of the crotonic condensation in the presence of alkali and a polymerization inhibitor, pyrogallol. The experiments showed that the optimum conditions for condensation are a temperature of 50° C, a time of 3 hr. in ethanol, with the necessary additions of alkali and pyrogallol, and at a molar ratio of sulfolene to aldehyde of 1 : 2. The products of the condensation of the sulfolenes with the aldehydes consisted of white crystalline substances with low melting points, soluble in benzene, ethanol, and water, and insoluble in ether. In each individual case butyric and enanthic acids were formed as by-products, these being identified from their refractive indices, boiling points, densities, and molecular refractions. The formation of these acids probably takes place through the autoxidation of the aldehydes.

In the reaction of the sulfolenes with aldehydes, three types of products are theoretically possible, namely alcohols, the products of their dehydration (compounds II), and sulfolanyl ketones (the products of the addition of the aldehydes at the double bond). In addition, with a twofold excess of aldehyde the formation of the products of double addition at positions 2 and 5 is possible. The molecular weights determined cryoscopically in benzene for some addition products and the results of elementary analysis indicate the addition of only one molecule of aldehyde with the elimination of water in all cases. This is also shown by the results of a determination of the bromine number for the product of the addition of butyraldehyde to 3-sulfolene (found 185.5; calculated 186.0). Thus, there are reasons for stating that formula II must be assigned to the products of the addition of aldehydes to sulfolenes.



I II

Additional proofs were obtained in a study of the infrared spectra of the initial sulfolenes and the products of the addition of enanthaldehyde to them. The spectra both of the starting materials and of the reaction products contained strong absorption bands at 840–820 cm^{-1} corresponding to =CH deformation vibrations; similarly, bands close to 790–730 cm^{-1} (C—S stretching vibrations) and two bands in the 1300–1100 cm^{-1} range (S=O stretching vibrations in sulfones) were found in all the spectra. The spectral curves of the condensation products were characterized, in addition, by the presence of a strong absorption band in the 1695–1625 cm^{-1} range (figure), which must be assigned to the stretching vibrations of a C=C bond conjugated with a double bond in the ring [3].

The combination of all these data permits the definitive conclusion that in the condensation of sulfolenes

Characteristics of the Alkenylsulfolenes (II) Obtained

R_1	R_2	R_3	R	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
						C	H	S	C	H	S	
H	H	H	C_3H_7	40.5	$C_8H_{12}O_2S$*	55.3 55.3	6.6 6.7	—	55.8	7.0	—	63
H	H	H	C_6H_{13}	34	$C_{11}H_{18}O_2S$**	61.9	8.4 8.4	15.4	61.6	8.5	15.0	60
CH_3	H	CH_3	C_6H_{13}	36	$C_{13}H_{22}O_2S$	64.1	9.1	12.8	64.4	9.2	13.2	69
H	CH_3	CH_3	C_3H_7	48	$C_{10}H_{16}O_2S$	59.5	8.0	16.3	59.9	8.0	16.0	64
H	CH_3	CH_3	C_6H_{13}	38	$C_{13}H_{22}O_2S$	64.6	9.1	12.9	64.4	9.2	13.2	62

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*Found: mol. wt. 186. Calculated: mol. wt. 172.

**Found: mol. wt. 206. Calculated: mol. wt. 214.

with aldehydes the aldehydes add at the methylene group in position 2(5) with the elimination of water and the formation of a compound containing a system of conjugated double bonds.

EXPERIMENTAL

2,5-Dihydrothiophene 1,1-dioxide was obtained from 1,3-butadiene and liquid sulfur dioxide by their reaction in sealed tubes at 80° C [4].

2,4-Dimethyl-2,5-dihydrothiophene 1,1-dioxide was obtained from diacetonealcohol by its reduction with lithium aluminum hydride, dehydration of the resulting 2-methylpentane-2,4-dione in the presence of aniline hydrobromide, and condensation of the 2-methylpentadiene so obtained with sulfur dioxide as described above.

3,4-Dimethyl-2,5-dihydrothiophene 1,1-dioxide was obtained by the reaction of 2,3-dimethylbutadiene with sulfur dioxide. The starting material for the synthesis of the 2,3-dimethyl-1,3-butadiene was pinacol, which was dehydrated in the presence of aniline hydrobromide.

2-(1-Heptenyl)-2,5-dihydrothiophene 1,1-dioxide. A mixture of 100 ml of 10% NaOH and 80 ml of ethanol was heated to 45–50° C. With stirring, half of a previously prepared mixture of 22.8 g of enanthaldehyde and 11.8 g of 3-sulfolene in 50 ml of ethanol were added, followed by 0.2 g of pyrogallol. After 15 min, the second half of the mixture was added, and stirring was continued at the same temperature for 3 hr. After cooling, the reaction mixture was extracted with benzene, and the benzene was then distilled off. The oily product was frozen at −25° C and was then transferred to a Schott filter, well pressed out, and washed with ether. This yielded 9.9 g of a slightly yellowish substance forming, after recrystallization from ethanol, colorless needles with mp 34° C.

The other substances given in the table were obtained analogously.

The IR spectra of all the substances were taken in paraffin oil on a UR-10 instrument with KBr, LiF, and NaCl prisms. We express our thanks to K. V. Aglitskaya for recording the spectra.

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