THE SYNTHESIS OF OXIDES OF SULFOLENE AND SOME OF ITS METHYL DERIVATIVES

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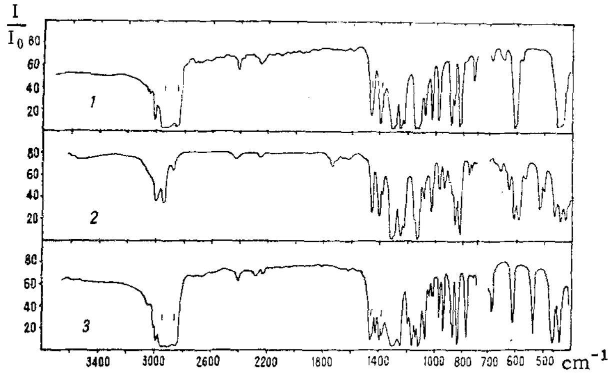
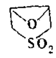
The synthesis of the oxides of 3-sulfolene, 2-methyl-3-sulfolene, and 3-methyl-3-sulfolene by the reaction of the corresponding 3-sulfolenes with peracetic acid has been described.

One of the most widely used methods for obtaining α-oxides of unsaturated compounds is that using peracetic acid as oxidizing agent. However, when sulfolene was treated with peracetic acid it was impossible to obtain sulfolene oxide, and in all cases a mixture of the mono- and diacetates or a diol of sulfolene was obtained [1, 2]. The use of redistilled peracetic acid in benzene solution, ether, and other inert solvent usually leads to the formation of α-oxides [3]. Sulfolene oxide is obtained either from sulfolane bromohydrin by splitting off hydrogen bromide [4] or from sulfolene by the action of 98% formic acid and 30% hydrogen peroxide [2].

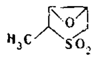


IR spectra (UR-10 instrument, slit program 4, the strokes denote the bands of the paraffin oil); 1) 3-sulfolene oxide; 2) 2-methyl-3-sulfolene oxide; 3) 3-methyl-3-sulfolene oxide.

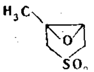
In the present paper we give details of the preparation of oxides of 3-sulfolene (I), 2-methyl-3-sulfolene (II), and 3-methyl-3-sulfolene (III) by the action of peracetic acid on the corresponding sulfolenes. The oxidation was carried out with the distilled concentrated acid prepared by Arbuzov's method [3] and containing no mineral impurities. The oxidation was carried out both in solutions in benzene and acetic acid and in the absence of the solvent.



I



II



III

As the investigations have shown, the oxide rings in sulfolene oxides are exceptionally stable in comparison with olefin oxides, and are not opened even when the sulfolenes are oxidized with concentrated peracetic acid in the absence of a solvent. The table gives the characteristics of the sulfolene oxides obtained.

In the IR spectrograms, the epoxide ring is shown by strong absorption bands in the range from 770 to 1000 cm^{-1} (asymmetric vibrations of the ring) and also in the 3000 cm^{-1} region (ν_{C-H}) [6]. In agreement with literature data [7], the spectrum of the compound with the trisubstituted epoxide ring III had a band at 780 cm^{-1} of lower frequency than in the spectra of I and II. Compounds I and II also had bands at 830 cm^{-1}, i.e., at just that frequency which is ascribed in the literature to a cis-substituted epoxy ring.

EXPERIMENTAL

Oxides of sulfolenes I, II, and III. The calculated amount of peracetic acid (concentration 75–90 vol. %) and 30% excess was added to a flask containing the appropriate sulfolene (synthesized by published methods [8, 9]) with obligatory ice-water cooling. The reaction mixture was left at room temperature for 7–10 days. In the case of I and III, the crystals that formed were filtered off on a porous filter, washed with 5% ammonia solution, and dried in vacuum. After evaporation in vacuum, the filtrate yielded a further small amount of oxide. The yield was 56–57%. On reaction with HBr, the oxide of I gave the bromohydrin with mp 193°–193.5° C, which corresponds to literature data [4]. In the case of II, after the end of the reaction the

Characteristics of the Sulfolene Oxides Synthesized

Compound	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	S	C	H	S	
I	159—160*	$C_4H_6O_3S$	35.85	4.17	23.6	35.81	4.51	23.9	57
II	59— 61**	$C_5H_8O_3S$	40.90	5.38	—	40.53	5.44	21.64	12
III	91— 91.5	$C_5H_8O_3S$	40.69	5.40	21.40	40.53	5.44	21.64	56

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*Mp 159°–160° C [2], 130° C [4], 124°–126° C [5].

**The oxide II was distilled and had bp 112° C (0.1 mm); d_4^{20} 1.3732; n_D^{20} 1.4992. Found: MR_D 31.68. Calculated for $C_5H_8O_3S$: MR_D 31.40. It crystallized on standing.

volatile products were removed in vacuum, the residue was diluted with a ten-fold volume of ether, and the solution was neutralized with 5% ammonia. After the ether had been evaporated off, the residue was distilled in vacuum. In the reaction of III with peracetic acid in benzene solution, the reaction was carried out, as mentioned above, with a 30% concentration of III in benzene. When the reaction was carried out in acetic acid solution, 10 vol. % peracetic acid was used. The oxides were soluble in ethanol, benzene, and acetone. The constants of the oxides are given in the table.

Diacetate of III. A solution of 5 g of the oxide in 75 ml of acetic anhydride and 1.5 ml of concentrated H_2SO_4 was heated at 100° C for 2 hr. After neutralization with solid $CaCO_3$, a precipitate deposited, and after crystallization from benzene and acetone this had mp 145° C. Found, %: C 43.06; H 5.61; S 13.39. Calculated for $C_9H_{14}O_6S$, %: C 43.18; H 5.64; S 12.82. According to the literature [1], mp 140°–142.5° C.

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