REACTION OF SULFOLENE WITH BENZENESULFONYL CHLORIDE

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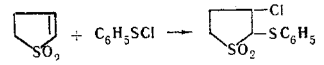
2-Phenylthio-3-chlorosulfolane instead of the expected phenylsulfonylchlorosulfolane was isolated by the reaction of 2-sulfolene with benzenesulfonyl chloride at 180 deg C, catalyzed by a mixture of cuprous chloride and triethylamine hydrochloride. Oxidation of this product with hydrogen peroxide in acetic acid gave 2-phenylsulfonyl-2-sulfolene, the structure of which was proved by the IR and PMR spectra.

The addition of sulfonyl halides to unsaturated compounds, catalyzed by radical initiators (peroxide compounds, cuprous chloride, UV light), is well known [1]. As applied to sulfolenes, this reaction was of interest to us as a method for the one-step synthesis of sulfolanyl sulfones.

However, experiments indicated that benzenesulfonyl chloride does not give adducts with 2- and 3-sulfolenes at 80 deg under irradiation with a PRK-2 lamp in benzene and in the absence of solvent.

The reaction could be accomplished with 2-sulfolene* at 180 deg with catalysis by a mixture of cuprous chloride and triethylamine hydrochloride in excess benzenesulfonyl chloride and in acetonitrile, benzonitrile, acetic acid, and methylene chloride. However, instead of the expected phenylsulfonylchlorosulfolane, the reaction product was phenylthiochlorosulfolane, which, from the melting point and IR spectrum, was identical to the compound obtained by alternative synthesis from benzenesulfenyl chloride and 2-sulfolene via the method in [2]:



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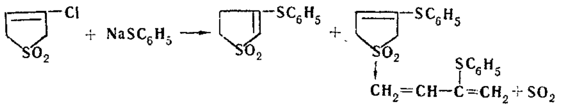
Oxidation of the chlorosulfide with hydrogen peroxide in acetic acid gave an unsaturated sulfone (preparation A), the IR spectrum of which contained a band at 1617 cm^{-1}, characteristic for a double bond, which was absent in the spectrum of the starting compound. The absence of chlorine was confirmed by elementary analysis.

In order to elucidate the structure of the compound obtained (A), its PMR spectrum was compared with the spectrum of unsubstituted sulfolene described in [3,4], and with the spectra of 3-phenylthio-2-sulfolene and 3-phenylsulfonyl-2-sulfolene. The latter was obtained via the method in [5] by reaction of sodium thiophenoxide with 3-chloro-3-sulfolene in alcohol with subsequent decomposition of the 3-phenylthio-3-sulfolene:



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*The reaction was not carried out with 3-sulfolene under these conditions because of its low thermal stability.

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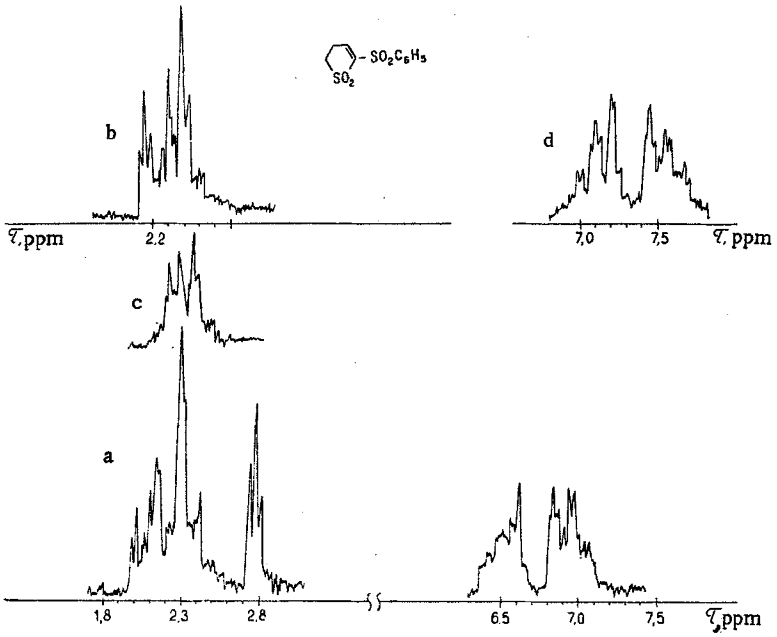

Fig. 1. PMR spectra of 3-phenylsulfonyl-2-sulfolene in: a) $CHCl_3$; b) DMSO; c) DMSO-D_2O; d) nitrobenzene.

The 3-phenylthio-2-sulfolene obtained was oxidized with hydrogen peroxide to the corresponding sulfone (preparation B). A depression of 40 deg was observed in the melting point of a mixture of samples A and B.

The PMR spectra were obtained with a Varian A-60-A high-resolution spectrometer with an operating frequency of 60 MHz with tetramethylsilane (TMS) as the internal standard in $CHCl_3$, $CDCl_3$, nitrobenzene, dimethyl sulfoxide, and dimethyl sulfoxide with added water or D_2O at 20 and 40 deg. This set of solvents had to be used because of the low solubility of sample A in chloroform. Sample B, on the other hand, is quite soluble in chloroform. Its spectrum (Fig. 1a) in $CDCl_3$ consists of four groups of signals: two multiplets of equal intensity centered at $\tau = 6.95$ and 6.52 with respect to TMS, due to the four-spin AA'-BB' system of H atoms in the 4 and 5 positions; a triplet at $\tau = 2.8$ ppm with a width of 4 Hz, which, from its relative intensity and in analogy with the spectrum of 3-phenylthio-2-sulfolene, should be ascribed to the vinyl H atom in the 2-positions*; the multiplet of a substituted benzene ring centered at $\tau = 2.2$ ppm. In DMSO (Fig. 1b) the benzene ring signal is shifted to the strong field, while the vinyl H signal, without changing its form, is shifted to a weak field and appears on the opposite side of the benzene ring signal as compared with the spectrum in $CDCl_3$. A portion of the spectrum in the stronger field region is masked by strong solvent signals.

The pronounced shift in the vinyl hydrogen signal in polar solvents is apparently caused by the formation of a hydrogen bond between this proton and the solvent as a result of the relatively high acidity of the vinyl hydrogen in the $-SO_2CH{=}CSO_2-$ fragment between the two sulfonyl groups.

The addition of a ten-molar excess of D_2O to a solution of B in DMSO leads to the disappearance of the vinyl H triplet and to a decrease in the relative† intensity of the group of signals with $\tau = 2.2$ and 2.36 ppm, which attests to deuterium exchange with the vinyl hydrogen.

The diamagnetic portion of the spectrum in nitrobenzene remained practically unchanged as compared with the spectrum in $CDCl_3$.

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*The triplet splitting does not exceed 1.5 Hz. The low spin-spin coupling constant is characteristic for a long-range interaction and is due to splitting by H_4 or H_5.

†The intensity was determined relative to the methyl group signal from $(CH_3)_3COH$.

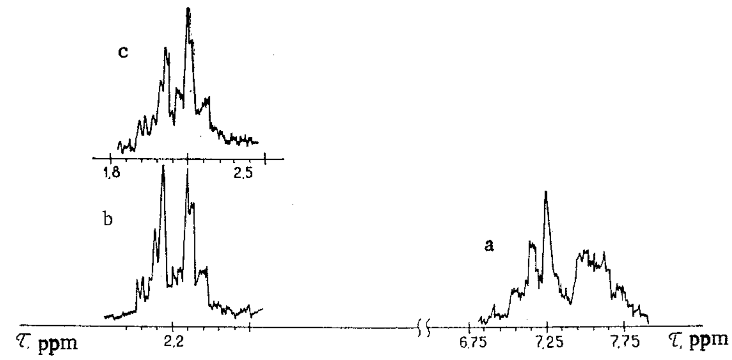

Fig. 2. PMR spectra of 2-phenylsulfonyl-2-sulfolene in: a) nitrobenzene; b) DMSO; c) DMSO-D_2O.

The spectrum of A in nitrobenzene (Fig. 2a) also contained two groups of lines that coincide in position with the H_4 and H_5 signals in B under the same conditions. However, the first signal is a broad peak in which the individual lines cannot be distinguished, while in the spectrum of B this signal is well resolved. The shape of the second signal ($\tau = 7.2$) coincides with the shape of the same signal in B.

In DMSO (Fig. 2b) there is one complex multiplet centered at $\tau = 2.25$ ppm that coincides in position and relative intensity (0.80 and 0.77) with the analogous signal in the spectrum of B (Fig. 1b).

The equal intensities of the signals of A and B is evidence that the H_3 vinyl signal in A is overlapped by the phenyl group signal. This might have been expected for a small shift to strong field the H_3 signal is compared with the H_2 signal in the spectrum of B. The addition of D_2O has no effect whatsoever on the shape of the multiplet, which agrees with weakening of the acidity of H_3 in comparison with H_2 with a decrease in the effect of the electron-accepting sulfonyl groups.

Thus, the PMR spectra of samples A and B confirm the similar structures but not the identical character of these compounds in accordance with the data of thin-layer chromatography and the melting-point depression of mixtures of them. The character of the H_4 signal and the shift in the vinyl H signal to strong field make it possible to assign the 2-phenylsulfonyl-2-sulfolene structure to compound A.

The ability of sulfolenes to readily add arenesulfenyl chlorides and the structure of the product we obtained make it possible to assume that, under the conditions described, benzenesulfonyl chloride is probably reduced to benzenesulfenyl chloride [6], which then adds to 2-sulfolene according to scheme I.

EXPERIMENTAL

2-Phenylthio-3-chlorosulfolane. A. A mixture of 2.4 g (0.02 mole) of 2-sulfolene, 7.4 g (0.04 mole) of benzenesulfonyl chloride, 0.056 g of cuprous chloride, and 0.11 g of triethylamine hydrochloride in 2.5 ml of acetonitrile was heated in an ampule at 180 deg for 8 h. At the end of the reaction the acetonitrile and unchanged benzenesulfonyl chloride were removed in vacuo. The residue was treated with water to extract unchanged 2-sulfolene and then recrystallized from methanol to give 1.2 g (20%) of 2-phenylthio-3-chlorosulfolane with mp 89 deg: after repeated recrystallization it melted at 92.5-93.5 deg. The purity of the product was verified by thin-layer chromatography* on activity III aluminum oxide; R_f 0.41. Found %: C 46.08; H 4.20; S 24.03; Cl 13.90. $C_{10}H_{11}O_2S_2Cl$. Calc. %: C 45.71; H 4.22; S 24.40; Cl 13.49.

B. A mixture of 2.4 g (0.02 mole) of 2-sulfolene and 2.9 g (0.02 mole) of benzenesulfenyl chloride was heated at 100 deg in 8.5 ml of acetic acid for 5 h. The reaction mass was diluted with water and cooled with with ice to give 4.3 g (82%) of 2-phenylthio-3-chlorosulfolane (after two recrystallizations from methanol) with mp 92.5-93.5 deg and R_f 0.41.

2-Phenylsulfonyl-2-sulfolene. Hydrogen peroxide [3 ml (30%)] was added to a solution of 3.1 g (0.012 mole) of 2-phenylthio-3-chlorosulfolane in 60 ml of acetic acid, and the mixture was heated on a boiling-

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*Diethyl ether was used as the eluent for thin-layer chromatography of the compounds, and the chromatograms were developed with iodine vapors.

water bath for 5 h. The residue after vacuum removal of the acetic acid was recrystallized from methanol to give 2.2 g (70%) of 2-phenylsulfonyl-2-sulfolene with mp 190-191 deg and R_f 0.155 (after repeated recrystallization). Found %: C 46.39; H 3.92; S 24.70. $C_{10}H_{10}O_4S_2$. Calc. %: C 46.49; H 3.90; S 24.32. The IR spectra contained double bond frequencies at 1617 cm^{-1} and SO_2 group frequencies at 1100, 1150, and 1330 cm^{-1}.

3-Phenylthio-2-sulfolene. A solution obtained from 5.5 g (0.05 mole) of thiophenol and 1.1 g (0.05 mole) of sodium in 40 ml of absolute ethanol was added dropwise with stirring to 7.6 g (0.05 mole) of 3-chloro-3-sulfolene in 110 ml of absolute ethanol. The NaCl was removed by filtration, and 9 g of a voluminous brown precipitate was isolated from the filtrate. Thin-layer chromatography indicated the presence of three products in the precipitate: unchanged 3-chloro-3-sulfolene (R_f 0.74), 3-phenylthio-2-sulfolene (R_f 0.55), and 3-phenylthio-3-sulfolene (R_f 0.41). The 3-sulfolene derivatives (R_f 0.41 and 0.74) were removed from the precipitate by decomposition at 150-160 deg for 1.5 h under water aspirator pressure. The residue was recrystallized from methanol to give 3-phenylthio-2-sulfolene (R_f 0.55) with mp 144 deg. Found %: C 53.20; H 4.60; S 28.40; $C_{10}H_{10}O_2S_2$. Calc. %: C 53.07, H 4.45; S 28.33.

3-Phenylsulfonyl-2-sulfolene. Oxidation of 5.1 g of 3-phenylthio-2-sulfolene with excess [5 ml (24%)] hydrogen peroxide in 60 ml of acetic acid gave 4.8 g (83%) of sulfone with mp 153-154 deg and R_f 0.43. Found %: C 46.40; H 3.62; S 24.54. $C_{10}H_{10}O_4S_2$. Calc. %: C 46.49; H 3.90 S 24.82.

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