and recrystallized from ethanol-dioxane (10:1).

<u>3,5-Diaminoanthra[1,9-c,d]isoxazol-6-ones (IIIe-h,k-o)</u>. A 0.01-mole sample of the isoxazolone (Ib-d) was stirred in DMF with 0.05 mole of the amine, after which the mixture was maintained at $0-5^{\circ}$ C for 10-15 h. The final products were removed by filtration and recrystallized from ethanol-dioxane (10:1).

<u>Reductive Arylamination of 5-Chloroanthra[1,9-c,d]isoxazol-6-one (Ia).</u> A 0.01-mole sample of Ia was refluxed with 0.015 mole of arylamine in 30-50 ml of DMF for 1.5-2 h, after which the mixture was cooled to 100-110°C and treated with 20-30 ml of water heated to 50-60°C. The resulting suspension was cooled to 5-10°C and filtered, and the reaction products were recrystallized from ethanol or acetic acid. This procedure gave 1-amino-4- (R-phenylamino) anthraquinones IVa-h in the following yields: IVa, R = H, 80%; IVb, R = p-CH₃, 95%; IVc, R = o-CH₃, 89%; IVd, R = 2,4-di-CH₃, 71%; IVe, R = p-Br, 97%; IVg, R = m,o-CH₃, 80%; IVh, R = p,o-C₂H₅, 83%.

<u>Arylamination of 1-Azido-4-chloroanthraquinone</u>. This process was carried out in complete analogy with the preceding procedure using an equimolar amount of 1-azido-4-chloroanthraquinone in place of isoxazolone IA. 1-Amino-4-arylaminoanthraquinones IVa-h were obtained in 70-80% yields. Compounds IV had spectral characteristics that were similar to the literature values [5].

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REACTION OF SULFOLENE OXIDES WITH ACYL

CHLORIDES AND CHLORO ETHERS

L. A. Mukhamedova, L. I. Kursheva, and F. S. Khasyanzyanova

The reaction of sulfolene and 3-methylsulfolene oxides with acetyl chloride, benzoyl chloride, and chlorodimethyl and chloromethyl ethyl ethers was studied. It is shown that sulfolene oxides are rather stable in acidic media and undergo ring opening only when they are heated above 100°C under pressure. In the case of the unsymmetrical 3-methylsulfolene oxide the oxide ring undergoes opening to a greater extent on the side of the carbon atom that bears the alkyl substituent.

The oxide rings of sulfolene oxides are exceptionally stable in acidic media, as one can judge from the method used to prepare them [1]. The aim of the present research was to study the reactions of sulfolene oxide (I) and 3-methylsulfolene oxide (II) with carboxylic acid chlorides and chloro ethers in the presence of acid catalysts and to establish the order of addition of the reagents to unsymmetrical oxide II.

Whereas the reactions of olefin and cyclo-olefin oxides with chlorine-containing reagents proceed rather readily [2], the reactions of sulfolene oxides I and II with acetyl chloride, benzoyl chloride, and chlorodimethyl and chloromethyl ethyl ethers could be realized only under pressure by heating above 100°C in absolute benzene. The characteristics of III-X and XVII are presented in Table 1.

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TABLE 1. Characteristics of Sulfolanyl Chloro Esters and Ethers RC

Com- pound	R	R'	mp, °C	Found, %				Empirical formula	Calc., %				Yield,
				с	н	СІ	s	Lanpineer formate	с	н	Cl	s	%
111 1V VI VII VII1 VII1 IX XVII	H CH ₃ H CH ₃ H CH ₃ H CH ₃ CH ₃	$\begin{array}{c} CH_{3}CO\\ CH_{3}CO\\ C_{6}H_{5}CO\\ C_{6}H_{5}CO\\ C_{6}H_{5}CO\\ CH_{3}OCH_{2}\\ CH_{3}OCH_{2}a\\ C_{7}H_{5}OCH_{2}\\ C_{7}H_{5}OCH_{2}b\\ H\end{array}$	$\begin{array}{c} 110,5-112\\ 133-134\\ 135-137\\ 102-104\\ 67-69\\ 44-46\\ 107-109\\ \end{array}$	33,83 37,01 48,00 49,40 33,62 36,73 36,57 39,08 32,53	4.40 4,91 4,04 4,55 5,27 5,71 5,54 6,18 5,10	17,22 15,88 13,41 12,01 16,99 15,00 15,45 14,69 19,13	15,02 14,21 12,03	$\begin{array}{c} C_{6}H_{9}O_{4}SCI\\ C_{7}H_{11}O_{4}SCI\\ C_{12}H_{13}O_{4}SCI\\ C_{12}H_{13}O_{4}SCI\\ C_{6}H_{11}O_{4}SCI\\ C_{7}H_{13}O_{4}SCI\\ C_{7}H_{13}O_{4}SCI\\ C_{7}H_{16}O_{4}SCI\\ C_{8}H_{16}O_{5}SCI\\ C_{5}H_{9}O_{3}SCI\\ \end{array}$	33,88 37,17 48,08 49,90 33,56 36,75 36,75 39,58 32,52	4,26 4,88 4,04 4,54 5,16 5,72 5,72 6,23 4,91	$16,69 \\ 15,64 \\ 12,92 \\ 12,29 \\ 16,53 \\ 15,52 \\ 15,52 \\ 14,62 \\ 19,22$	15,07 14,12 11,67 11,10 14,93 14,02 14,02 13,21 17,36	$ \begin{array}{c} 63\\ 43\\ 80\\ 50\\ 66\\ 64\\ 64\\ 59\\ 38\end{array} $

^a This compound had bp 145-146 °C (0.05 mm), n_D^{20} 1.5099, and d_4^{20} 1.3872. ^b This compound had bp 137-138 °C (0.07 mm), n_D^{20} 1.5010, and d_4^{20} 1.3546.

The formation of two isomers is possible in the case of oxide II in the reaction with acid chlorides. Analysis by thin-layer chromatography (TLC) showed the presence of one reaction product. Its structure was established on the basis of data from the PMR spectrum. The spectrum of IV contains two singlets at δ 1.8 and 2.17 ppm, which are related to the protons of two methyl groups, signals at 3.17-4.03 ppm, which correspond to the protons of two methylene groups, and a multiplet resonance signal, which corresponds to a lone ring proton. Its chemical shift (δ 5.48 ppm) coincides with the chemical shift of the methylidyne proton attached to the C₄ atom in the spectrum of 3-chloro-4-acetoxysulfolane (III). At the same time, the spectrum III contains a resonance signal at δ 4.60 ppm, which on the basis of spectral tables [3], we assigned to the C₃ atom (this signal is absent in the spectrum of IV). A similar picture is also observed in the case of benzoxy derivatives V and VI. These data enabled us to assign structures IVa and VIa to the products of the reaction of oxide II with acyl chlorides.

The reactions of oxides I and II with chloro ethers to give addition products VII-X were carried out in the presence of boron trifluoride etherate. In the case of oxide II both possible structural isomers in a ratio of $\sim 80:20$ (according to the data from gas-liquid chromatography) are formed in the reaction with chloro ethers.

The PMR spectra of products VIII and X contain a lone signal at δ 4.75 ppm (O-CH₂), a quartet at 4.44 ppm, which we assigned to a methylidyne proton attached to the C₄ atom $[{}^{3}J_{H_4}(H_5^{i}) = 5.0 \text{ Hz}, {}^{3}J_{H_4}(H_5^{i})_2 = 2.0 \text{ Hz}]$, signals at 3.78 and 3.40 ppm[C₅-H₅ⁱ, C₅-H₅^{i'}, J_{H'}(H_5^{i'}) = 13.8 \text{ Hz}], and signals at 3.52 ppm, which correspond to the protons of two methylene groups attached to the C₅ and C₂ atoms. Signals at 1.83 and 1.61 ppm with an integral intensity ratio of ~4.5:1 are observed in the region of the spectrum related to the resonance of the protons of a methyl group.

To establish the structures of the reaction products we realized the dehydrochlorination of VIII and X with alcoholic potassium hydroxide in order to obtain unsaturated compounds of the XI and XII type; a mixture consisting of an unsaturated compound, with the composition $C_5H_8O_3S$, and a crystalline product, with mp 75-76.5°C and the composition $C_7H_{14}O_4S$, was isolated. A split signal of methyl protons at δ 2.05 ppm, as well as a signal at δ 6.62 ppm, the intensity of which corresponds to one olefin proton, is observed in the PMR spectrum of the unsaturated compound. A band of a double bond (ν 1645 cm⁻¹) and a broad band of hydroxy absorption at 3200-3700 cm⁻¹ are observed in the IR spectrum. A comparison of the spectra of VIII and X and the unsaturated compound shows a shift of the higher-intensity signal of the methyl protons (1.83 ppm) in the spectra of products VIII and X to the low-field region (2.05 ppm) in the spectrum of the unsaturated compound; this is characteristic for the position of a methyl group attached to a double bond. On the basis of the spectral data and the results of elementary analysis, we assigned the 3-methyl-4-hydroxy-2-sulfolene structure (XIII), which could have been formed from VIII and X as a result of splitting out of HCl and subsequent saponification of the ester group in XIa and XIIA, to the unsaturated compound.

Thus, in the mixture of isomers a and b of VIII and X, higher percentages ($\sim 80\%$) of the a isomers are observed.

The crystalline product with mp 75-76.5°C does not give a melting point depression when it is mixed with genuine 3-methyl-3-hydroxy-4-ethoxysulfolane (XV) [4]. The latter could have been formed under the reaction conditions as a result of the addition of the ethanol present in the reaction medium to the cis-substituted double bond of unsaturated alcohol XIV, which is formed in the same way as alcohol XIII. The IR and

PMR spectra of product XV and the previously obtained sample [4] are also identical.

It follows from the material set forth above that the reaction of sulfolene oxides I and II with acyl chlorides and chloro ethers is realized via a scheme involving the initial formation of an onium salt or a complex with a Lewis acid with subsequent rapid attack of the nucleophilic particle (CI) on the carbon atom of the oxide ring to give addition products. In the case of unsymmetrical oxide II the cleavage of the oxide ring occurs to a greater extent on the side of the carbon atom that bears the alkyl substituent; this is in agree-ment with the concepts of Parker and Isaaks on the direction of opening of the oxide rings of unsymmetrical oxide in an acidic medium [5].



It should be noted that sulfolene oxides I and II sometimes gave chlorohydrins instead of the expected products in the reaction with chloro ethers in the presence of ZnCl_2 or concentrated H_2SO_4 . This was more often observed in the case of oxide I, for which the known 3-chloro-4-hydroxysulfolane (XVI) [6] was obtained in high yield. A compound with the composition $C_5\text{H}_9\text{ClO}_3$ S was isolated in very small amounts in the reaction of oxide II with chloromethyl ethyl ether in the presence of H_2SO_4 . The same compound was obtained by alternative synthesis by the action of HCl in benzene on oxide II. A signal of methyl protons at δ 1.86 ppm is observed in its PMR spectrum, while a band of hydroxy absorption at 3300-3600 cm⁻¹ is present in its IR spectrum. The IR spectrum of the compound in CHCl₃ contains the band of a free OH group at 3615 cm⁻¹. On the basis of a comparison with the known ν_{OH} frequency of 3580 cm⁻¹, which corresponds to the tertiary hydroxy group in XV, the 3-methyl-3-chloro-4-hydroxysulfolane structure (XVII) can be assigned to the chloro-hydrin.

EXPERIMENTAL

The IR spectra of the compounds between KBr plates and in solution in $CHCl_3$ (d 5 mm, c 0.01 mole) were obtained with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in chloroform were recorded with Varian T-60 and Tesla BS-497 spectrometers with tetramethylsilane as the internal standard. Analysis by GLC was performed with a Khrom-4 chromatograph with a 250 by a 0.3-cm column filled with 15% PFMS on Chromaton N-AW-DMCS (0.200-0.250 mm) at 200°C with a flame-ionization detector.

Starting oxides I and II were obtained by the method in [1]. The chloro ethers were obtained by the method in [8].

Chloroacetoxysulfolanes (III and IV). A 15-ml sample of absolute benzene and 0.02 mole of acetyl chloride were added to 0.015 mole of oxides I and II, and the mixture was heated in a sealed glass tube at 120-130°C for 13 h (for oxide I) or at 80°C for 7 h (for oxide II). The tube was then opened, the excess benzene and acetyl chloride were removed by distillation, and the precipitate was removed by filtration and recrystallized from ethanol to give the corresponding III and IV (Table 1).

<u>3-Chloro-4-benzoxysulfolane (V).</u> A 15-ml sample of absolute benzene and 0.02 mole of benzoyl chloride were added to 0.015 mole of oxide I, and the mixture was heated in a sealed tube at 130-160°C for 20 h. The tube was opened, and the reaction mixture was worked up as indicated above to give V (Table 1).

<u>3-Methyl-3-chloro-4-benzoxysulfolane (VI)</u>. Absolute benzene (30 ml), 0.07 mole of benzoyl chloride, and six drops of $BF_3 \cdot O(C_2H_5)_2$ were added to 0.054 mole of oxide II, and the mixture was heated in a sealed tube at 100-120°C for 24 h. Workup of the reaction mixture by the method described above and recrystallization of the precipitate from chloroform gave VI (Table 1).

<u>3-Chloro-4-methoxymethoxy-, 3-methyl-3(4)-chloro-4(3)-methoxy-methoxy-, 3-chloro-4-ethoxy-</u> <u>methoxy-, and 3-methyl-3(4)-chloro-4(3)-ethoxymethoxysulfolanes (VII-X).</u> Absolute benzene (25 ml), 0.094 mole of the corresponding chloro ether, and six drops of $BF_3 \cdot O(C_2H_5)_2$ were added to 0.059 mole of oxide I or II, and the mixture was heated in a sealed tube at 110-130°C for 17-20 h. The excess solvent and reagent were removed by vacuum distillation to give the corresponding addition products VII-X (Table 1).

<u>3-Chloro-4-hydroxysulfolane (XVI)</u>. Absolute benzene (20 ml), 0.032 mole of chlorodimethyl ether, and 0.04 g of $ZnCl_2$ were added to 0.02 mole of oxide I, and the mixture was heated in a tube at 140-160°C for 16 h. Workup yielded 3.28 g (86%) of XVI with mp 163-165°C (mp 160°C [6]). Found: C 28.26; H 4.10; Cl 21.32; S 18.66%. C₄H₇ClO₃S. Calculated: C 28.15; H 4.14; Cl 20.80; S 18.79%.

<u>Dehydrochlorination</u>. This reaction was carried out by the method in [7]. A solution of 1 g (0.017 mole) of KOH in 10 ml of absolute ethanol was added with stirring in the course of 1 h to 2.56 g (0.01 mole) of VIII or X in 20 ml of absolute ethanol, and the mixture was stirred at 40-70 °C for 4 h. It was then cooled, and the precipitated KCl was removed by filtration. The filtrate was neutralized and evaporated, and the residue was vacuum distilled. Fraction 1 [0.54 g (35%) of XIII] had bp 115-116 °C (0.06 mm) and n_D^{20} 1.4925. Found: C 40.34; H 5.7%. C₅H₈O₃S. Calculated C 40.54; H 5.44%; Fraction 2 [0.18 g (9%) of XV] had bp 142-145 °C (0.07 mm); the liquid product crystallized on standing to give a solid with mp 75-76.5 °C (from ethanol). Found: C 43.72; H 7.26%. C₇H₁₄O₄S. Calculated: C 43.32; H 7.27%.

<u>3-Methyl-3-chloro-4-hydroxysulfolane (XVII).</u> A) A mixture of 0.02 mole of oxide II, 0.032 mole of chlorodimethyl ether, two drops of concentrated H_2SO_4 , and 20 ml of benzene was heated in a tube at 100-110°C for 8 h, after which the benzene was removed by distillation, and the residue was washed to remove the acid and extracted with chloroform. Removal of the chloroform gave 0.5 g (13%) or XVII (Table 1).

B) A mixture of 15 g (0.1 mole) of oxide II, 12 ml of concentrated HCl (30% excess), and 45 ml of absolute benzene was heated in a sealed tube at 100-120°C for 20 h, after which the tube was opened, and the precipitate was removed by filtration, washed with cold water, and recrystallized from chloroform to give XVII.

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