4',4"(5")-Diethoxymethyl-DB18C6 (XVII). A solution of 0.23 g IX in 5 ml absolute alcohol was boiled for 7 h, neutralized with a $NaHCO_3$ solution, and extracted with chloroform. The solvent was removed and the residue was chromatographed on a column using chloroform—alcohol (50:1). Yield 0.07 g (30%).

Analogously prepared: 4',4"(5")-dimethoxymethyl-DB18C6 (XVIII), yield 25%; 4',4"(5")-dipropoxymethyl-DB18C6 (XIX), yield 32%; and 4',4"(5")-dibutoxymethyl-DB18C6 (XX), yield 28%.

4',4"(5")-Dioxyethoxymethyl-DB18C6 (XXI). To 0.08 g potassium dispersed in 10 ml absolute benzene were added dropwise 5.5 ml absolute ethyleneglycol and a solution of 0.45 g IX in 10 ml benzene. The mixture was boiled for 1 h. The glycol layer was separated, diluted with water, and extracted with chloroform. After removal of solvent the residue was dissolved in acetone and precipitated with hexane. The wet product (0.25 g, 55%) was purified on a column with chloroform—alcohol (50:1). Yield 0.15 g (30%).

Analogously prepared: 4',4"(5")-dioxypropoxymethyl-DB18C6 (XXII), yield 35%; and 4',4"-(5")-dioxybutoxymethyl-DB18C6 (XXIII), yield 32%.

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# REACTION OF CHLOROSULFONYLTHIOLENE- AND -THIOLANE-1,1-DIOXIDES WITH AMINES AND HYDROXYCOMPOUNDS

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Sulfonylamides and sulfonylesters of thiolene- and thiolane-1,1-dioxides are prepared by reaction of chlorosulfonylthiolene- and -thiolane-1,1-dioxides with amines and hydroxycompounds. The structure of the compounds is proved based on IR spectra and $^{13}$C NMR spectroscopy.

Derivatives of thiolene-1,1-dioxides are known to be used successfully for synthesis of difficultly available functionally-substituted dienes [1-3]. Further use of such dienes in the Diels-Alder reaction leads to substituted cyclohexenes [4, 5]. The presence of a sulfur-containing substituent in the diene enables the regioselective course of the reaction. This allows the preparation of products which are unattainable or difficultly available by other routes [6, 7]. Earlier, the synthesis of chlorosulfonylthiolene- and -thiolane-1,1-dioxides I-IV was reported [8, 9]. Compound IV was synthesized from trans-3-hydroxy-4-isothioureido-

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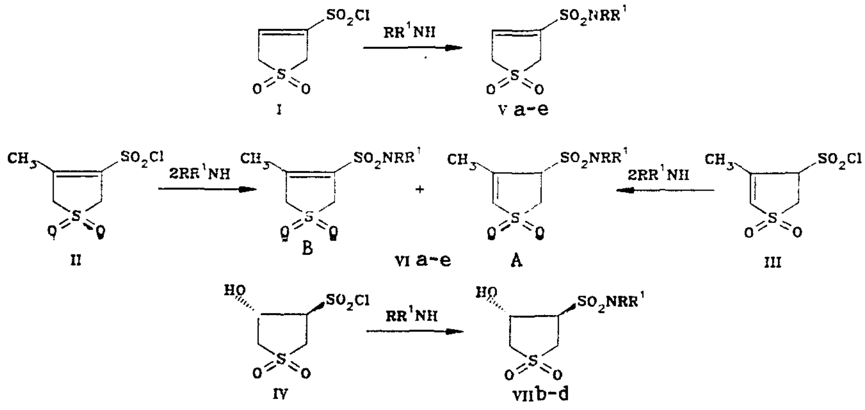
0009-3122/89/2504-0393 $12.50

thiolane-1,1-dioxide sulfate which was prepared from oxirano-3,4-thiolane-1,1-dioxide under conditions leading to products with exclusively trans-structures [10, 11].

In the present work, the reaction of sulfonylchlorides I-IV with amines and hydroxycompounds is described. This allows the number of sulfones which are capable of generating functionally-substituted dienes to be expanded substantially. Sulfonylchlorides I-IV readily react with amines with formation of the corresponding sulfonylamides.

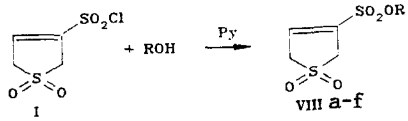
It is interesting to note that in contrast to compound I, which forms derivatives of 3-thiolene-1,1-dioxide Va-e, sulfonylchlorides II and III react with amines with formation of inseparable mixtures of isomers VIa-e (A + B), which differ in the position of the double bond in the thiolene-1,1-dioxide ring. (Formula, top, following page.)

Equilibrium mixtures of isomers are known to be formed in the presence of the bases of 3-substituted 3-thiolene-1,1-dioxides [12]. The nature of the substituent determines the position of the equilibrium between these isomers. Electron-donor substituents practically completely drive the equilibrium toward the formation of 3-substitued 2-thiolene-1,1-dioxides in which the substituent can react through the double bond with the $SO_2$ group [13].



V, VI, VII a $R=R^1=H$; b $R=R^1=C_2H_5$; c $R=H$, $R^1=t\text{-}C_4H_9$; d $R=H$, $R^1=C_6H_5$; e R, $R^1=C_4H_8O$

In the case of compounds VIa-e, the positive inductive effect of the methyl group stabilizes both isomer A and B since the $CH_3$ group can interact both with the $SO_2$ group of the ring (isomer A) and with the $SO_2$ group of the substituent (isomer B). The presence of isomers in the mixtures of compounds VIa-e was established based on $^{13}C$ NMR spectral data (Table 1). Earlier we showed that the difference of chemical shifts of the $CH_2$ groups signals of the thiolene-1,1-dioxide ring in the $^{13}C$ NMR spectra of five-membered cyclic sulfones can be used for determination of the double bond position in them [8]. The presence in the spectra, taken without proton decoupling, of products VIa-e of two triplets with a small difference of chemical shifts between their centers (4.7-5.6 ppm) and two singlets of the $sp^2$-hybridized carbon atoms of the thiolene-1,1-dioxide ring indicates the presence in the mixtures of 3,4-disubstituted 3-thiolene-1,1-dioxides (isomer B). At the same time, a triplet and doublet of $sp^3$-hybridized carbon atoms of the thiolene-1,1-dioxide ring are present in the spectra. The substantial shift of the CH group doublet to weak field (by comparison with the analogous signal of the β-carbon atom of the 2-thiolene-1,1-dioxide) indicates the presence of a strong electron-acceptor group bonded to this carbon atom. Besides this, a singlet and doublet of the $sp^2$-hybridized carbon atoms are present in the spectra. This, in combination with the foregoing data confirms the presence in the mixtures of VIa-e of 4-aminosulfonyl-3-methyl-2-thiolene-1,1-dioxides (isomer A).



VIII a $R=C_2H_5$; b $R=C_6H_5$; c $R=o\text{-}BrC_6H_4$; d $R=m\text{-}ClC_6H_4$; e $R=p\text{-}BrC_6H_4$; f $R=p\text{-}NO_2C_6H_4$

Reaction of sulfonylchloride I with hydroxycompounds leads to esters of 3-sulfo-3-thiolene-1,1-dioxide (VIIIa-f).

TABLE 1. $^{13}C$ NMR Spectra (δ, ppm) of Mixtures of Sulfonylamides VIa-e

| Compound | Isomers | $C_2$ | $C_3$, s | $C_4$ | $C_5$,t | Other carbon atoms |
|---|---|---|---|---|---|---|
| VIa | A | 131,6 d | 140,0 | 65,7 d | 51,6 | $CH_3$ 18,7 q |
|  | B | 62,1 t | 146,2 | 131,8 s | 56,7 | $CH_3$ 16,1 q |
| VIb | A | 132,0 d | 142,7 | 65,3 d | 51,9 | $CH_3$ 17,5 q; $C_2H_5$ 14,1 q; 41,9 t |
|  | B | 61,9 t | 145,8 | 129,5 s | 56,4 | $CH_3$ 15,7 q; $C_2H_5$ 14,2 q; 42,5 t |
| VIc | A | 131,4 d | 140,4 | 66,4 d | 51,6 | $CH_3$ 17,4 q; *t*-$C_4H_9$ 55,1 s; 29,7 q |
|  | B | 62,0 t | 146,0 | 131,8 s | 56,4 | $CH_3$ 15,3 q; *t*-$C_4H_9$ 55,1 s; 29,7 q |
| VId | A | 131,8 d | 144,6 | 63,6 d | 50,9 | $CH_3$ 17,2 q; $C_6H_5$ 121,5 d; 125,4 d; 129,3 d; 136,5 s |
|  | B | 61,7 t | 145,3 | 128,1 s | 56,3 | $CH_3$ 15,4 q; $C_6H_5$ 122,7 d; 125,8 d; 129,4 d; 136,9 s |
| VIe | A | 132,8 d | 143,2 | 64,0 d | 51,4 | $CH_3$ 17,7 q; $C_4H_8NO$ 46,0 t; 66,4 t |
|  | B | 61,9 t | 146,0 | 127,5 s | 57,2 | $CH_3$ 16,3 q; $C_4H_8NO$ 45,9 t; 66,3 t |

TABLE 2. Spectra of Compounds Va-e, VIIb-d, and VIIIa-f

| Compound | IR spectrum, $cm^{-1}$ |  |  | $^{13}C$ NMR spectrum, ppm |  |  |  |
|---|---|---|---|---|---|---|---|
|  | $\nu SO_2$ | $\nu SO_2N(SO_2O)$ | $\nu NH(OH)$ | $C_{(2)}$, t | $C_{(3)}$ | $C_{(4)}$, d | $C_{(5)}$, t |
| Va | 1120, 1300 | 1140, 1340 | 3350, 3250 | 53,8 | 139,6 s | 128,7 | 57,4 |
| Vb | 1120, 1310 | 1150, 1350 | — | 54,1 | 137,2 s | 131,6 | 57,5 |
| Vc | 1090, 1250 | 1110, 1275 | 3300 | — | — | — | — |
| Vd | 1130, 1370 | 1170, 1330 | 3280 | 54,8 | 136,5 s | 134,9 | 58,2 |
| Ve | 1130, 1310 | 1160, 1340 | — | 58,4 | 139,0 s | 138,3 | 61,6 |
| VIIb | 1100, 1310 | 1160, 1350 | (3570) | 62,5 | 69,7 d | 62,1 | 50,3 |
| VIIc | 1130, 1305 | 1140, 1315 | 3290, (3480) | 58,1 | 68,1 d | 67,0 | 51,9 |
| VIId | 1120, 1300 | 1150, 1345 | 3140, (3480) | 61,5 | 68,6 d | 60,8 | 49,5 |
| VIIIa | 1140, 1320 | (1170, 1350) | — | 53,7 | 133,4 s | 134,6 | 57,5 |
| VIIIb | 1140, 1310 | (1190, 1370) | — | — | — | — | — |
| VIIIc | 1100, 1280 | (1120, 1330) | — | — | — | — | — |
| VIIId | 1130, 1315 | (1190, 1370) | — | — | — | — | — |
| VIIIe | 1140, 1330 | (1160, 1370) | — | 54,1 | 148,9 s | 139,1 | 57,8 |
| VIIIf | 1130, 1310 | (1150, 1370) | — | — | — | — | — |

Isomerization of the double bond in this case, as for preparation of compounds Va-e, is not observed.

Absorption bands of the N–H stretching appear in the IR spectra of compounds Va-e and VIIb-d (Table 2) besides absorption bands of the $SO_2$ group for sulfones Va, c, d and VIIc, d. In the spectra of sulfones VIIb-d, a broad strong band of the OH group stretch is seen. The position of the double bond in compounds Va-e and VIIIa, e is established on the basis of $^{13}C$ NMR spectral data (Table 2). The presence in the spectra of these sulfones of two triplets of the $sp^3$-hybridized carbon atoms with a small difference of chemical shifts between their centers (3.2-3.8 ppm) and also a singlet and doublet of the $sp^2$-hybridized carbon atoms of the thiolene-1,1-dioxide ring is characteristic of 3-substituted 3-thiolene-1,1-dioxides. Two triplets and two doublets of the $sp^3$-hybridized carbon atoms of the thiolane-1,1-dioxide ring are present in the $^{13}C$ NMR spectra of sulfones VIIb-d. This confirms the structure of these 3,4-disubstituted thiolane-1,1-dioxides.

## EXPERIMENTAL

IR spectra were taken on a UR-20 instrument as KBr pellets. $^{13}C$ NMR spectra in acetone-$D_6$ were obtained on a Bruker CXP-200 (50 MHz) spectrometer in a pulsed mode with subsequent Fourier deconvolution. Resonance settings were stabilized using D nuclei of the solvent. All chemical shifts are given relative to TMS, the acetone-$D_6$ signal was set at 29.2 ppm [14]. Characteristics of the synthesized compounds are given in Tables 1-3. Elemental analyses for C, H, S, and Hal correspond with those calculated.

3-Amidosulfonyl-3-thiolene-1,1-dioxide (Va). Through a solution of 2.17 g (0.01 mole) sulfonylchloride I in 40 ml ethylacetate at 5-10°C were passed with vigorous mixing 0.448 liter (0.02 mole) of dry ammonia. After 1.5-2 h the precipitate which formed was filtered and washed with 20 ml water. The insoluble part was combined with the precipitate obtained upon evaporation of the filtrate and was recrystallized.

TABLE 3. Characteristics of Synthesized Compounds

| Compound | Empirical formula | mp, °C | Yield, % |
|---|---|---|---|
| Va | $C_4H_7NO_4S_2$ | 176...178[*1] | 75,0 |
| Vb | $C_8H_{15}NO_4S_2$ | 72...73[*2] | 67,5 |
| Vc | $C_4H_{15}NO_4S_2$ | 144...145[*1] | 77,5 |
| Vd | $C_{10}H_{11}NO_4S_2$ | 152...153[*1] | 53,5 |
| Ve | $C_8H_{13}NO_5S_2$ | 167...168[*1] | 94,0 |
| VIa | $C_4H_8NO_4S_2$ | 164...166[*1] | 42,5 |
| VIb | $C_9H_{17}NO_4S_2$ | 89...90[*1] | 43,5 |
| VIc | $C_9H_{17}NO_4S_2$ | 129...131[*1] | 46,0 |
| VId | $C_{11}H_{13}NO_4S_2$ | 133...134[*2] | 70,0 |
| VIe | $C_9H_{15}NO_5S_2$ | 158...159[*1] | 39,0 |
| VIIb | $C_8H_{17}NO_5S_2$ | 145...147[*1] | 38,5 |
| VIIc | $C_8H_{17}NO_5S_2$ | 155...156[*2] | 43,0 |
| VIId | $C_{10}H_{13}NO_5S_2$ | 155...156[*1] | 41,0 |
| VIIIa | $C_6H_{10}O_5S_2$ | 100...101[*3] | 91,1 |
| VIIIb | $C_{10}H_{10}O_5S_2$ | 141...142[*2] | 41,0 |
| VIIIc | $C_{10}H_9BrO_5S_2$ | 131...132[*2] | 11,0 |
| VIIId | $C_{10}H_9ClO_5S_2$ | 116...117[*4] | 20,5 |
| VIIIe | $C_{10}H_9BrO_5S_2$ | 146...148[*2] | 12,0 |
| VIIIf | $C_{10}H_9NO_7S_2$ | 147...149[*5] | 9,0 |

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[*1] From water.
[*2] From ethanol.
[*3] From $CH_2Cl_2$.
[*4] From $CHCl_3$.
[*5] From methanol.

3-Amidosulfonyl-3-thiolene-1,1-dioxides (Vb-d) (Table 3) were prepared analogously from sulfonylchloride I by addition of the corresponding amines.

Mixtures of 4-amidosulfonyl-3-methyl-2-thiolene-1,1-dioxides with 4-amidosulfonyl-3-methyl-3-thiolene-1,1-dioxides (VIa-e) (Table 3) were prepared analogously from sulfonylchlorides II or III and the corresponding amines.

trans-3-Hydroxy-4-diethylamidosulfonylthiolane-1,1-dioxide (VIIb). A solution of 2.35 g (0.01 mole) sulfonylchloride IV in 60 ml ethylacetate was added at 0-5°C with vigorous mixing to a solution of 2.06 ml (0.02 mole) diethylamine in 50 ml ethylacetate. After 1 h the mixture was filtered. The filtrate was evaporated with an aspirator to dryness. The residue was recrystallized.

trans-3-Hydroxy-4-amidosulfonylthiolane-1,1-dioxides (VIIc, d) (Table 3) were prepared analogously from sulfonylchloride IV and the corresponding amines.

Ethyl Ester of 3-Sulfo-3-thiolene-1,1-dioxide (VIIIa). A mixture of 2.17 g (0.01 mole) sulfonylchloride I and 25 ml ethanol was boiled for 2 h and the solution was evaporated to dryness. The oil obtained was treated with 10 ml water and the precipitate which formed was recrystallized.

Phenyl Ester of 3-Sulfo-3-thiolene-1,1-dioxide (VIIIb). To a solution of 2.17 g (0.01 mole) sulfonylchloride I and 0.95 g (0.01 mole) phenol in 50 ml ethylacetate at 20-30°C were added with vigorous mixing 0.79 ml (0.01 mole) pyridine. The mixture was stirred for 1-1.5 h. The precipitate was filtered and the filtrate was evaporated with an aspirator. The oil which separated was treated with 10 ml of a mixture of ethanol:water (2:1). The precipitate obtained was recrystallized.

Aryl esters of 3-sulfo-3-thiolene-1,1-dioxide (VIIIc-f) (Table 3) were prepared analogously from sulfonylchloride I and the corresponding substituted phenols.

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