(concentrations identical with kinetic run) was refluxed at 64.0° for 17 days (*ca.* 400 hr). On cooling to room temperature 1.10 g (19.5%) of a white solid separated, mp 173–176°, mp 185–186° after one recrystallization from acetone, undepressed on admixture with authentic I. Removal of acetone from the filtrate at reduced pressure gave an aqueous suspension of 2.50 g of a white solid, mp 125–135°; recrystallization of this material from acetone–water gave 1.80 g (32%) of colorless crystals, mp 144–146°, undepressed with authentic II.

A solution of 5.66 g of II in 166 ml of acetone–100 ml of water was treated in a manner identical with that described for I above. Filtration of the cooled solution gave 1.30 g (23%) of colorless crystals, mp 179–182°, mp 188–190° after one recrystallization from acetone, undepressed with authentic I. Removal of all volatile material from the filtrate at reduced pressure in a rotary film evaporator left 4.0 g of a clear gum residue. Addition of water to the cloud point of a hot acetone solution of this gum gave, on cooling, 1.50 g (27%) of a white solid, mp 137–141°, mp 145–146° on recrystallization from acetone–water, undepressed on admixture with authentic II.

Resolution of Adducts I and II.—To a stirred solution at 25° of 2.0 g (5.9 mmoles) of I in 10 ml of dry dimethyl sulfoxide was added, dropwise, over a 35-min period, 1.19 g of *l*-brucine (2.95 mmoles) dissolved in 10 ml of dimethyl sulfoxide. The dropping funnel was washed with an additional 5 ml of solvent and stirring of the homogeneous solution continued for another 24 hr at 25°.

The reaction mixture was poured into 200 ml of ice–water and the precipitated solid was recovered by filtration. Reprecipitation from 5 ml of DMSO, followed by crystallization from acetonitrile, gave 0.75 g of a white solid, mp 174–176°, $[\alpha]^{24}\text{D}$ −13.7° (*c* 7.0, DMSO). A further precipitation from DMSO, followed successively by trituration with two 100-ml portions of 2% HCl, and by two recrystallizations from acetonitrile, gave 0.21 g of I*, mp 184.5–185°, $[\alpha]^{24}\text{D}$ −8.6° (*c* 7.0, DMSO).

Anal. Calcd for $C_8H_{12}Cl_2O_4S_3$: C, 28.40; H, 3.58; Cl, 20.90; S, 28.40. Found: C, 28.74; H, 3.43; Cl, 20.73; S, 28.47.

To a solution of 1.53 g (4.5 mmoles) of II in 10 ml of dry DMSO was added 0.91 g of brucine (2.25 mmoles) under conditions identical with those described for I. Dilution of the DMSO solution with 200 ml of ice–water gave 0.67 g of a gummy solid, mp 103–119°. Reprecipitation of this material from 3 ml of DMSO followed by two successive triturations with 100-ml portions of 2% HCl gave 0.30 g of a white solid. Recrystallization from acetonitrile yielded 0.14 g of colorless crystals, mp 150–151°, $[\alpha]^{24}\text{D}$ 0° (*c* 7.0, DMSO).

Polarimetric Rate of Rearrangement of I.—Compound I* (510 mg), partially resolved in the manner indicated above, mp 184–185°, $[\alpha]^{24}\text{D}$ −6.13° (*c* 7.0, DMSO), was dissolved in 10 ml of warm acetone and diluted with 6 ml of water. A jacketed deciliter cell which had been preheated to 64.0° by circulation of a thermostated water bath was rapidly charged with this solution to capacity and closed. The clear, optically transparent system was then placed in a Rudolph Model 70 polarimeter readable to 0.01°. One hour was allowed for temperature equilibration and the optical rotation of the solution was then measured at the specified time intervals. The reported values were an average of six readings, three left and three right, with a deviation not greater than 0.01 from the average. (See Table III.) The polarimetric rate constant (k_α), 4 × 10^{-6} sec^{-1}, was determined from the slope of the plot of the first-order kinetic expression $\ln \alpha_0/\alpha = k_\alpha t$, where $\alpha_0 = 0.28$.

TABLE III

Time, hr	α, deg
..	0.28
2	0.28[a]
20	0.21
44	0.16

[a] Calculated as 0.27, assuming $k_\alpha = 4 \times 10^{-6}$ sec^{-1}.

Michael Addition of Dimethylamine to VI.—The crystalline, unsaturated trisulfone VIA (2.98 g, 0.01 mole) was added in small portions to 25 ml of a stirred 40% aqueous solution of dimethylamine over a 5-min period at ambient temperature. The bright yellow suspension became homogeneous after stirring for an additional 55 min at ambient temperature; suction filtration left negligible residue. Removal of the volatile material from this deep yellow filtrate at 1 mm in a rotary film evaporator, followed by repeated trituration with toluene and subsequent evaporation left 4.05 g of a red-brown oil, neut equiv ($HClO_4$–HOAc), 163 and 165. (Calcd for stoichiometric addition of 2 equiv of amine, 3.88 g; neut equiv, 194.) This residue was then leached three times with ether followed by removal of the volatile material at 1.0 mm; 2.25 g of a methanol-soluble red-brown oil remained, neut equiv ($HClO_4$–HOAc), 189 and 188.

Subjection of 2.66 g (0.01 mole) of the unsaturated sulfide III to identical reaction conditions gave on filtration of the colorless suspension 2.45 g (92%) of recovered III, mp 159–160°.

Acknowledgment.—We are indebted to John D. Famularo, Thomas A. McLaughlin, and Dr. T. L. Popper for technical assistance.

Chemistry of Sulfolene.[1] I. Addition of Benzenesulfenyl Chlorides[2]

DOUGLAS I. RELYEA

Research Center, UniRoyal United States Rubber Company, Wayne, New Jersey 07470

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Benzenesulfenyl chlorides add readily to sulfolene in acetic acid at 25° to form 3-chloro-4-phenylthiotetrahydrothiophene 1,1-dioxides. The orientation of addition was established by demonstration of the distinction between the adducts of *p*-bromobenzenesulfenyl chloride with sulfolene and with the 2,3-dihydro isomer of sulfolene. The *trans* configuration of the sulfolene–benzenesulfenyl chloride adduct **3** was shown by the identity of **3** with the material derived from 3,4-epoxytetrahydrothiophene 1,1-dioxide by reaction first with sodium thiophenoxide and then with thionyl chloride. Rate constants are given for the slow solvolysis of the sulfolene adducts in 80% ethanol at 96.18° together with approximate rates of the rapid base-promoted elimination at 25°.

It was recently reported that products of addition of sulfur dichloride to sulfolene (**1**) have the *cis* configuration.[3] This assignment, based upon the slow rates of solvolysis of the adducts but now revised to the *trans* configuration in the light of other evidence,[4] was a surprising one in view of the well-established *trans* addition of arenesulfenyl chlorides to cyclopentene[5a] and to cyclohexene[5b] as well as to other less closely related cyclic olefins.[6,7] The initial report of Lewis and Emmons[3] suggested that **1** might be unique in its reaction with sulfur halides and raised the possibility

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[1] 2,5-Dihydrothiophene 1,1-dioxide or butadiene sulfone.

[2] Contribution No. 259 from these laboratories.

[3] S. N. Lewis and W. D. Emmons, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, Abstract P89.

[4] S. N. Lewis and W. D. Emmons, *J. Org. Chem.*, **31**, 3572 (1966).

[5] (a) H. L. Goering and K. L. Howe, *J. Am. Chem. Soc.*, **79**, 6542 (1957); (b) H. L. Goering, D. I. Relyea, and D. W. Larsen, *ibid.*, **78**, 348 (1956).

[6] H. Kwart, R. K. Miller, and J. L. Nyce, *ibid.*, **80**, 887 (1958).

[7] S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *ibid.*, **87**, 5679 (1965).

TABLE I

trans-3-CHLORO-4-PHENYLTHIOTETRAHYDROTHIOPHENE 1,1-DIOXIDES

Compd	Phenyl substituent	Mp, °C	Formula	Calcd, % C	H	Cl	S	Found, % C	H	Cl	S
2	p-t-C_4H_9	85–86	$C_{14}H_{19}ClO_2S_2$	52.73	6.01	11.12	20.11	52.58	5.70	11.20	19.59
3	None	74–75	$C_{10}H_{11}ClO_2S_2$	45.67	4.22	13.49	24.40	45.31	4.30	13.85	24.04
4	m-CH_3 + p-Cl	108–109	$C_{11}H_{12}Cl_2O_2S_2$	42.45	3.89	20.60	22.78	42.32	3.71		
5	p-Cl	88–89	$C_{10}H_{10}Cl_2O_2S_2$	40.41	3.39	21.58	23.86	40.20	3.44	21.56	23.52
6	p-Br	77–78	$C_{10}H_{14}BrClO_2S_2$	35.15	2.95	33.76[a]	18.77	35.68	3.01	33.69[a]	19.43

[a] Total halogen.

TABLE II

SOLVOLYSIS OF 3-CHLORO-4-PHENYLTHIOTETRAHYDROTHIOPHENE 1,1-DIOXIDES AND RELATED COMPOUNDS IN 80% ETHANOL AT 96.18°

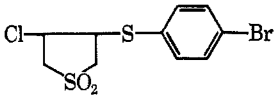
Compd	Rate, 10^5 sec^{-1}
2	2.34
3	1.76
4	1.60
5	1.43
6	1.33
8	4.92
9	0.1[a]
10	1800[a]
1-SCl_2 adducts	0.3[b]
3-Chlorosulfolane	0.01[b]

[a] Extrapolated from data of Goering and Howe.[5] [b] Estimated from data of Lewis and Emmons.[3]

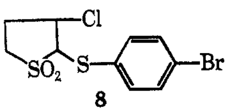
that similar *cis* addition might result in the reaction of benzenesulfenyl halides with **1**. Since the preparation of a series of 1-benzenesulfenyl chloride adducts had been started in this laboratory prior to the initial Lewis and Emmons report,[3] it was of interest to determine the correctness of our assumption of the *trans* configuration of the adducts.

Benzenesulfenyl chlorides add rapidly to **1** in acetic acid solvent at 25°. The five new adducts prepared in this way are listed in Table I. These adducts were characterized by elemental analysis and infrared spectrophotometry and by oxidation to the corresponding phenylsulfonyl derivatives which will be described elsewhere.

It has been shown by other workers that **1** and its 2,3-dihydro isomer (**7**) both form the same adducts with many reagents, including water,[8] methanol,[8] hydrazine,[9] and diethyl sodiomalonate.[10] It is possible that the basic character of these addends leads to common products from **1** and **7** by a prior conversion of **1** into more reactive isomer **7**, but in any event it was desirable to establish whether a sulfenyl chloride reacts with **1** and **7** to form identical or different products. *p*-Bromobenzenesulfenyl chloride adds to **1** and **7** at qualitatively similar rates to form different isomeric products **6** and **8**, respectively. The structure of **8** is assigned on the basis of the rapid hydroxide-promoted elimination of hydrogen chloride at 25° in ethanol which indicates the 2-H-3-Cl orientation of the lost elements of hydrogen chloride. Adduct **3**, in which the proton lost as hydrogen chloride must be located in the 2 position, undergoes base-promoted elimination in ethanol at 25° at nearly the same rate as does **8**.

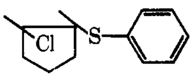


6



8

It has been shown by Goering and Howe[5a] that the *cis* (**9**) and *trans* (**10**) isomers of 2-phenylthiocyclopentyl chloride undergo solvolysis in 80% ethanol at 118° at rates which are in the ratio of 1:18,000. The rate enhancement for solvolysis of **10** is due to neighboring-group assistance by the *trans* phenylthio substituent. Therefore it appeared that measurement of solvolysis rates for 2–6 would provide direct evidence for assignment of *cis* or *trans* configuration. These rates are given in Table II. Comparison of solvolysis rates of 2–6 with model compounds **9** and **10** suggests that the adducts of **1** have the *cis* configuration. However, when **3** was synthesized by the route **11** → **12** → **3** (which has been shown to give the *trans* product in the cyclohexane series[5]), a liquid was obtained whose infrared spectrum was the same as that of the sulfenyl halide adduct and which could be crystallized upon seeding with the adduct. Therefore all the adducts 2–6 and **8** are assigned the *trans* configuration.[11]



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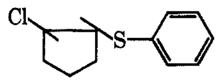
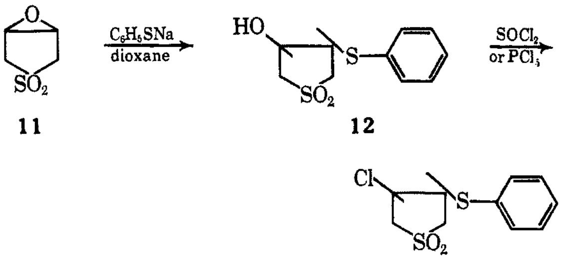


10



11 **12**

3

The unexpectedly low rates of solvolysis of 2–6 may be due to interaction between the $S^{\delta+}$–$O^{\delta-}$ dipoles of the sulfone group and the developing $C^{\delta+}$–$Cl^{\delta-}$ dipole of the transition state. These dipoles would have large parallel components oriented perpendicular to the ring in such a way as to be mutaully repelling. It is known that electronic effects of this type are transmitted effectively within the volume of a saturated molecule.[12] Further it has been observed that the sulfone group of **1** has a deactivating influence on the C–C double bond opposite the sulfone group.[13] However, all of the

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(8) H. J. Backer and J. Strating, *Rec. Trav. Chim.*, **62**, 815 (1943).

(9) C. S. Argyle and R. A. Reed, U. S. Patent 3,196,163 (1965).

(10) H. E. Faith, M. P. Kautsky, and B. E. Abreu, *J. Org. Chem.*, **27**, 2889 (1962).

(11) The same assignment of structure to **3** has been made by Lewis[4] who graciously furnished copies of his manuscript prior to publication.

(12) H. Kwart and L. J. Miller, *J. Am. Chem. Soc.*, **83**, 4552 (1961), and references cited therein.

(13) H. Bluestone, R. Bimber, R. Berkey, and Z. Mandel, *J. Org. Chem.*, **26**, 346 (1961).

adducts **2–6** show an enhanced rate of solvolysis by a factor of approximately 10^2 over the value estimated for 3-chlorosulfolane from the data of Lewis and Emmons,[3] suggesting a limited amount of neighboring group assistance by the phenylthio group. Finally, it may be noted that the Hammett ρ value calculated from the rate constants for **2–6** (Table II) is −0.553. This moderate negative value is more reminiscent of the −1.388 value reported for the *trans*-2-chlorocyclopentyl aryl sulfides[5a] than of the very small −0.070 value found for the corresponding *cis* series.

Experimental Section

Benzenesulfenyl Chlorides.—With one exception these were prepared by chlorinolysis of the corresponding thiophenols in carbon tetrachloride at 0–5° according to the procedure of Almasi and Gants.[14] 4-Chloro-3-toluenesulfenyl chloride was prepared by the chlorination of *m*-toluenethiol under the same conditions. The following physical properties [substituent, boiling point, pressure (mm), $n^{20}\text{D}$, lit.[14] $n^{20}\text{D}$] were observed for the benzenesulfenyl chlorides: none, 57–59° (2), 1.6115, 1.6120; *p*-Br, 92–95° (0.2), 1.6550, 1.6547; *p*-Cl, 77–79° (0.2), 1.6277, 1.6290; *p*-*t*-C_4H_9, 79–85° (0.2), 1.5810, none; *m*-CH_3 + *p*-Cl, 64–80° (0.1), 1.6124, 1.6165.

2,3-Dihydrothiophene 1,1-Dioxide.—This material was prepared by isomerization of sulfolene under the combined action of aqueous sodium hydroxide and ultraviolet light described by Krug, Tichelaar, and Didot.[15] It was confirmed that very low yields (1–3%) result when either agent is used alone. A maximum yield of 22.4% of 2,3-dihydrothiophene 1,1-dioxide, mp 51–53°, bp 120° (0.3 mm), $n^{20}\text{D}$ (supercooled) 1,5045, was obtained. The reported values[15] are mp 49–50, bp 114–116° (0.1 mm).

Addition of Benzenesulfenyl Chlorides to Dihydrothiophene 1,1-Dioxides.—In a typical experiment, a solution of 7.1 g (0.060 mole) of 2,3-dihydrothiophenene 1,1-dioxide in 25 ml of glacial acetic acid was treated with 13.4 g (0.060 mole) of *p*-bromobenzenesulfenyl chloride at 28°. Over the course of 8 hr there was an exotherm to 35° accompanied by disappearance of the red color of the sulfenyl halide. After another 16 hr the mixture was filtered to separate 10.25 g (50%) of colorless needles. Recrystallization from a mixture of 20 ml of benzene and 50 ml of carbon tetrachloride gave 5.5 g of pure 2-(4-bromophenylthio)-3-chlorotetrahydrothiophene 1,1-dioxide, mp 115–116°, mixture melting point with the adduct of *p*-bromobenzenesulfenyl chloride and **1**, 66–78°.

Anal. Calcd for $C_{10}H_{10}BrClO_2S_2$: C, 35.15; H, 2.95; Br + Cl, 33.76. Found: C, 35.61; H, 2.91; Br + Cl, 34.17.

***trans*-3-Hydroxy-4-phenylthiotetrahydrothiophene 1,1-Dioxide.**—Sodium thiophenoxide was prepared by treating a solution of 27.5 g (25.7 ml, 0.25 mole) of Eastman White Label thiophenol in 250 ml of dioxane with 5.75 g (0.25 g-atom) of sodium and 15 ml of absolute ethanol. The addition of 34.6 g (0.25 mole) of Gallard–Schlesinger 3,4-epoxysulfolane caused a vigorous exotherm which continued for 15 min. After heating for another 15 min, the light orange-brown mixture was cooled to 25° and quenched in 2500 ml of distilled water and 30 ml of concentrated hydrochloric acid. The suspension was extracted with four 200-ml portions of chloroform. The combined chloroform extracts were washed with two 200-ml portions of 10% aqueous sodium hydroxide, then with 200 mll of distilled water, and finally dried over magnesium sulfate. Evaporation of solvent gave 22 g (36%) of crude product which crystallized upon cooling. Recrystallization from ethyl acetate gave pure material, mp 141–142°, whose infrared spectrum showed principal peaks at 3400 (CH), 3040 (aromatic CH), 2925 and 2850 (aliphatic CH), 1100 and 1270 (secondary OH), 1120 and 1300 (SO_2), and 687 and 744 cm^{-1} (aromatic ring).

Anal. Calcd for $C_{10}H_{12}O_3S_2$: C, 49.16; H, 4.95; S, 26.24. Found: C, 48.97; H, 4.84; S, 25.98.

Reaction of *trans*-3-Hydroxy-4-phenylthiotetrahydrothiophene 1,1-Dioxide with Thionyl Chloride.—A solution of 1.0 g (4.09 mmoles) of *trans*-3-hydroxy-4-phenylthiotetrahydrothiophene 1,1-dioxide in 3 ml (4.9 g, 41.2 mmoles) of thionyl chloride was heated at reflux for 60 hr. The solution was run into 50 ml of water. The organic product was separated by extraction with three 15-ml portions of chloroform. The combined extracts were dried and evaporated to give 0.8 g of light brown oil whose infrared spectrum closely resembled that of **3**. Chromatography through activated alumina (Brockman grade 1) with chloroform elutant gave a light yellow liquid whose infrared spectrum was the same as that of **3** and which could be made to crystallize by addition of **3**.

Kinetic Measurements.—The sealed-ampoule technique of Goering and Espy[16] was used for the solvolysis of 0.02 *M* solutions of the benzenesulfenyl chloride–**1** adducts in 80% (v/v, measured at 25°) ethanol at 96.18°. Ampoules were withdrawn from the thermostated bath at uniform intervals so that rate constants could be calculated by the Guggenheim method.[17]

The reversible reaction of hydrogen chloride with ethanol solvent

$$HCl + C_2H_5OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_2H_5Cl + H_2O$$

was also studied at 96.18° by the sealed-ampoule technique. The rate constants were found to be $k_1 = 5.50 \times 10^{-6}\ \text{sec}^{-1}$ and $k_2 = 28.9 \times 10^{-6}\ \text{sec}^{-1}$. These values were used to carry out the correction for downward drift of rate constants owing to hydrogen chloride solvolysis reported by Goering and Howe.[5a] It was found that this correction amounted to only a few per cent under the most extreme conditions (slowest solvolyzing compound, last 25% of reaction) because of the low value of k_1 and the HCl-favoring equilibrium at this temperature.

The rapid base-promoted eliminations from **3** and **8** were followed qualitatively at 25° in an ultraviolet spectrophotometer cell. At concentrations of **3** or **8** equal to $0.02 \times 10^{-3}\ M$ and sodium hydroxide concentration of 0.1 *M* both adducts had half-lives of about 0.5 hr.

Acknowledgment.—Helpful conversations with Dr. Walter Nudenberg and Professor Harold Kwart and the technical assistance of Miss Blanche Szewczyk are gratefully acknowledged.

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(14) L. Almasi and A. Gants, *Chem. Ber.*, **94**, 725 (1961).

(15) R. C. Krug, G. R. Tichelaar, and F. E. Didot, *J. Org. Chem.*, **23**, (1958).

(16) H. L. Goering and H. H. Espy, *J. Am. Chem. Soc.*, **78**, 1454 (1956).

(17) See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p 48.