was stirred, thionyl chloride was added slowly in small portions until gas was no longer evolved from the mixture upon addition of a fresh increment of the reagent. The mixture was then filtered, and the hexane was removed from the filtrate under reduced pressure at room temperature. After the hexane had been removed, the residue of *p*-methoxybenzenesulfinyl chloride was subjected to a vacuum of 0.1 mm at 50° for 0.5 hr to remove any excess thionyl chloride. It was then used immediately in the subsequent step.

The sulfinyl chloride prepared above was dissolved in 30 ml of anhydrous ether and 15 g of dry sodium *p*-methoxybenzenesulfinate was added in portions to this solution. The mixture was stirred for 30 min at 0°. The crude sulfinyl sulfone was then removed by filtration. It was freed of sodium chloride by an extensive series of triturations with small amounts of ice–water. Any organic impurities were removed by several triturations with small amounts of ice-cold ether. The purified sulfinyl sulfone was then dried under high vacuum and stored in a desiccator at −20° until used, mp 100–101°.

Anal. Calcd for $C_{14}H_{14}O_5S_2$: C, 51.19; H, 4.32. Found: C, 51.10; H, 4.24.

***p*-Chlorobenzenesulfinyl *p*-Tolyl Sulfone (III).**—*p*-Chlorobenzenesulfinyl chloride, prepared in the same manner as for the preparation of IIc,[18] was treated with sodium *p*-toluenesulfinate using the same general procedure described for the preparation of IId. Work-up of the reaction and purification of the sulfinyl sulfone were also analogous. *p*-Chlorobenzenesulfinyl *p*-tolyl sulfone, mp 88°, exhibits infrared and ultraviolet spectral properties consistent with those expected from the spectra of the other sulfinyl sulfones.

Anal. Calcd for $C_{13}H_{11}ClO_3S_2$: C, 49.60; H, 3.52. Found: C, 50.30; H, 3.70.

Solvents.—The purification of acetic acid and the preparation of the various acetic acid–water and acetic acid–water–sulfuric acid solutions were carried out as described in the preceding paper.[2]

Acetic Acid-*d*.—Deuterium oxide (2.25 moles) was slowly added with stirring to freshly fractionally distilled (20 plate column) acetic anhydride (2.31 moles). The two-phase mixture was stirred and *gradually* heated to reflux. (Miscibility of the two phases appeared complete at 80–90°.) The solution was heated at reflux for 1 hr and was then fractionally distilled through a 25-cm silvered, vacuum-jacketed Vigreux column using a reflux ratio of 10:1. After discarding a small forerun (16 g, bp 114–117°) there was obtained 254 g of acetic acid-*d*, bp 117–117.5°.

Sulfuric acid-d_2 was purchased from Calbiochem. Its sulfuric acid content was determined by titration with standard base. The remainder of the material was assumed to be deuterium oxide.

Procedure for Rate and Equilibrium Studies.—The same apparatus and procedures described in the preceding paper[2] were used. Most of the rate data were obtained by starting with the sulfinic acid and following the build-up of the sulfinyl sulfone to its equilibrium concentration. However, a number of runs were also made starting with the sulfinyl sulfone and following its disappearance. In all cases investigated agreement between k_r values obtained by the two methods was excellent.

Extinction coefficients and absorption maxima for IIb–d were determined by the same method used for IIa in the earlier paper.[2] They are IIb, 300 mμ (ϵ 7000); IIc, 306 mμ (ϵ 8000); IId, 306 mμ (ϵ 13,000). In the *p*-anisyl system, unlike the other I–II equilibria studied, the sulfinic acid itself has a large enough extinction coefficient at 306 mμ so that it contributes something to the absorbance of the solution at this wavelength. As a result, to obtain the absorbance of a Id–IId solution owing to IId alone one must correct the measured absorbance using the following equation: $A_{\mathrm{IId}} = A_{\mathrm{soln}} - 11C_{\mathrm{ArSO_2H}}$.

Sulfolene[1]–Sulfur Dichloride Adducts. Stereochemical Considerations[2]

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Contribution from the Rohm and Haas Company, Philadelphia, Pennsylvania

Received May 12, 1966

The reaction of sulfolene with sulfur dichloride in methylene chloride gave two isomeric adducts, characterized as *dl*- and *meso*-*trans*-4,4′-dichloro-3,3′-disulfolanyl sulfides. Oxidation was accomplished with retention of geometrical integrity. Dehydrochlorination of each isomeric pair gave, in turn, a common product related by oxidation. Partial resolution of the *dl* adduct was effected simply by stereoselective dehydrochlorination with *l*-brucine. Despite their structural similarity to "mustard gas," the adducts solvolyzed very slowly in aqueous acetone. Considerable ion-pair return during solvolysis was suggested by scrambling of recovered adduct and confirmed by the polarimetric rate of rearrangement of optically active material.

The addition of sulfenyl halides to olefinic unsaturation has been extensively investigated in recent years and considerable evidence has accumulated supporting its *trans* nature.[3–7] Although the stereochemistry of sulfur dichloride addition to double bonds has received less attention, by analogy, *trans* addition might also have been anticipated. The reaction of sulfur dichloride with excess sulfolene therefore was expected to yield novel *trans*-2-chloroalkyl sulfides, of possible interest in a variety of applications because of their "mustard gas"[8,9] character.

Results

The reaction of sulfur dichloride with 2 equiv of sulfolene proceeded at a moderate rate in methylene chloride at ambient temperatures, unaccelerated appreciably by either Lewis acid or ultraviolet radiation. Approximately equal quantities of two isomeric solids, I and II, analyzing correctly for 2:1 sulfolene–sulfur dichloride adducts, were isolated as the major reaction products in 60–90% yield; no other characterizable products were obtained, but their presence was not excluded.

In the presence of weak base, both I and II readily dehydrochlorinated in high yield to a common diunsaturated sulfide III. When this dehydrochlorination was performed in dimethyl sulfoxide with less than a stoichiometric equivalent of *l*-brucine, partially resolved I* (shown as $[\alpha]^{24}\mathrm{D}$ $-8.6°$) was recovered under conditions identical with those from which recovered II had no rotation.

Rapid oxidation of the isomeric adducts I and II with hydrogen peroxide in hot acetic acid gave cleanly,

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(1) Butadiene sulfone or 2,5-dihydrothiophene 1,1-dioxide.

(2) Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(3) N. Kharasch and co-workers, *J. Am. Chem. Soc.*, **69**, 1612 (1947); **75**, 3734 (1953); **75**, 6030 (1953); **75**, 6035 (1953); **78**, 1207 (1956).

(4) D. J. Cram, *ibid.*, **71**, 3883 (1949).

(5) H. L. Goering, D. I. Relyea, and K. L. Howe, *ibid.*, **79**, 2502 (1957).

(6) H. Kwart and R. K. Miller, *ibid.*, **78**, 5678 (1956); **80**, 887 (1958).

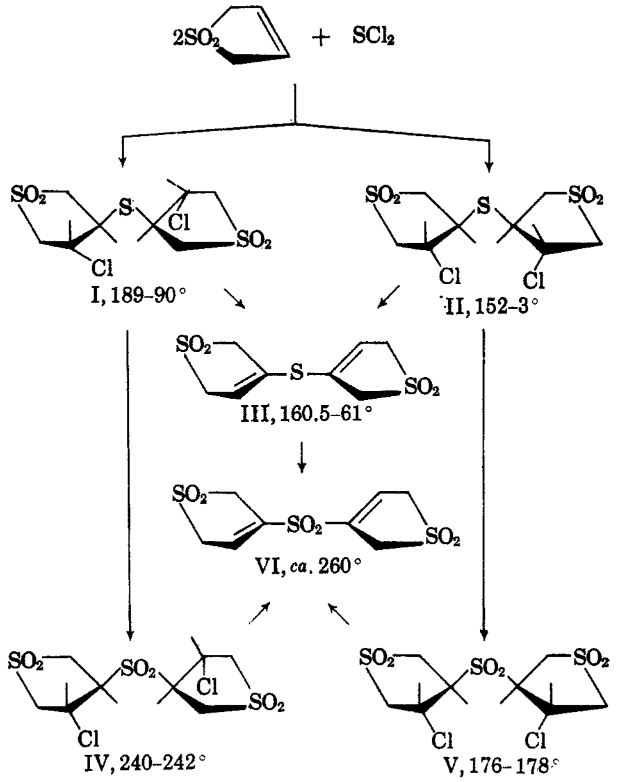
(7) For a recent review of sulfenyl halide addition to olefins and the nature of the products, see K. D. Gunderman, *Angew Chem. Intern. Ed. Engl.*, **2**, 674 (1963).

(8) R. C. Fuson and co-workers, *J. Org. Chem.*, **11**, 469 (1946), and following papers.

(9) P. D. Barlett and C. G. Swain, *J. Am. Chem. Soc.*, **71**, 1406 (1949).

in high yield, the isomeric dichloro trisulfones IV and V, respectively. When the oxidation of II was allowed to proceed slowly at lower temperatures, a considerable quantity of the high-melting trisulfone IV was obtained. Dehydrochlorination of IV and V produced the same diunsaturated sulfone VI which was in turn identical with that obtained from hydrogen peroxide oxidation of the unsaturated sulfide III. The suggested reaction scheme with appropriate structural assignments is illustrated in Chart I.

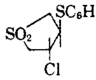
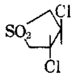
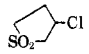
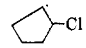
Chart I



Solvolyses of the adducts I and II in 37.5% aqueous acetone at 64° obeyed first-order kinetics. The rate constants (k) are summarized in Table I with that of *trans*-3-chloro-4-thiophenoxysulfolane (IX) prepared by each of the independent reaction sequences illustrated in Chart II. When the solvolysis solutions of initially pure I and pure II were worked up after 25% organic chlorine loss had occurred (400 hr), in each case unsolvolyzed adduct was recovered (50%) as a 1:1 mixture of the two isomers. The rate of this rearrangement (I → II) was determined by measuring the decrease with time in the optical rotation of a 37.5% aqueous acetone solution of partially resolved I* maintained at 64° in a thermostated polarimeter tube. The first-order polarimetric rate constant (k_α) is recorded in Table I.

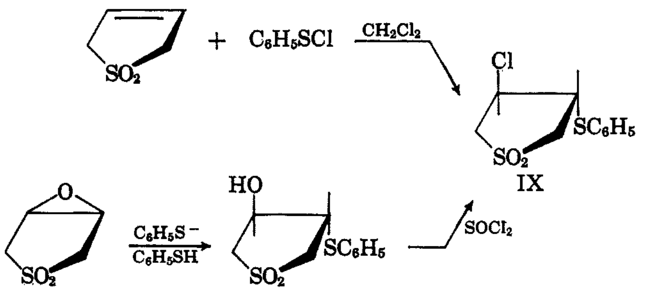
Table I

Rates of Solvolysis in 37.5% Aqueous Acetone[a] at 64.0°

Compd	10^7k, sec^{-1}
I	2.4
II	2.6
I*	40[b]
V	>32[c]
	15.4[d]
	>0.4[e]
	<0.1[f]
	8.3[g]

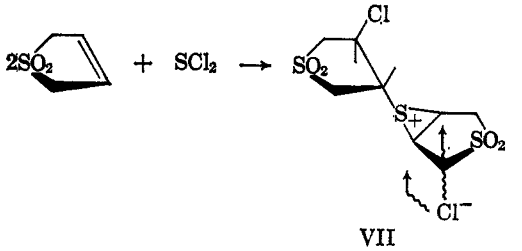
[a] 62.5 vol % acetone–37.5 vol % water. [b] Rate of rotation loss (k_α) of optically active I under similar conditions. [c] Minimum value; reaction essentially complete at first point; diunsaturated product VI isolated in good yield. [d] Followed to 55% organic chlorine loss. [e] Followed to 5% organic chlorine loss. [f] <1% organic chlorine loss. [g] Estimated from data reported elsewhere.

Chart II



Discussion

The stereospecific *trans* addition of sulfenyl halides to olefins has been attributed to the intermediate formation of an episulfonium ion,[10] which subsequently collapses by halide ion attack from its unhindered side. Similar addition of sulfur dichloride to sulfolene and the resultant sulfenyl chloride intermediate to another molecule of sulfolene should give two isomeric adducts (I and II) *via* the collapse of the episulfonium intermediate VII. Inspection of molecular models readily verified the dissimilarity of these two structures. Regardless of the stereochemistry of the initial sulfenyl chloride intermediate (*cis* or *trans*), two isomeric adducts of essentially equal probability will be produced on collapse of VII. Therefore, since only two major products were observed experimentally, stereospecificity in both steps is implied. Assignment of *trans* structure to the adducts is supported by their solvolytic behavior.



VII

Clearly, the high solvolytic reactivity of β-chloroethyl sulfides is due to the participation of the sulfide group[11] in the rate-determining ionization step. Such assistance is dramatically evident in the rate enhancement (10^5) displayed by the product of benzenesulfenyl chloride addition to cyclopentene, *trans*-2-chlorocyclo-

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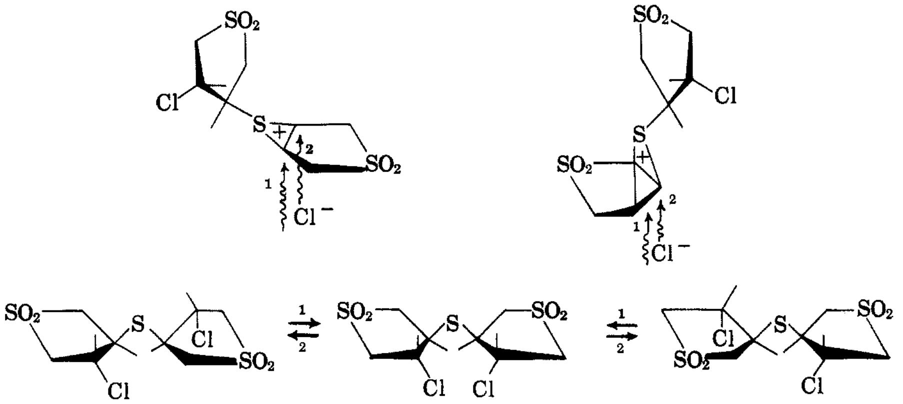
[10] For recent work confirming the existence of similar episulfonium salts, see D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **29**, 2702 (1964).

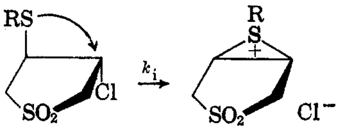
[11] S. Winstein and co-workers, *J. Am. Chem. Soc.*, **70**, 828 (1948); **72**, 5795 (1950).

CHART III



d- or *l*-I *meso*-II *l*- or *d*-I

pentyl phenyl sulfide, with respect to its *cis* isomer and cyclopentyl chloride.[12] Products resulting from the *trans* addition of sulfenyl halides to sulfolene should also possess the *trans* orientation of sulfur and chlorine atoms[13] required for the solvolytic participation of neighboring sulfur (VIII). Although the extremely low rate constants of I, II, and the model compound IX (compare cyclopentyl chloride) do not easily lend themselves to interpretation in terms of assisted solvolyses, a degree of participation is evident when they are compared, more appropriately, to the negligible rate of solvolysis of 3-chlorosulfolane under the same conditions (<1% organic chlorine loss after 250 hr at 64°). Furthermore, the actual first-order rate enhancement must be larger than that suggested by inspection of Table I since even the minimal chloride ion liberated from 3-chlorosulfolane under the solvolytic conditions is more likely a result of bimolecular elimination than unimolecular ionization.[16] The relatively small observed rates, therefore, must be attributed to unfavorable ion–dipole interaction during ionization (VIII), and not to an unfavorable geometry for anchimeric assistance.



VIII

The rate constants k_{I} and k_{II} are themselves sufficiently small that it is important to recognize the danger of misinterpreting, as a false indication of rate-determining ionization, a possible pseudo-first-order rate of E2 elimination in the aqueous media. The susceptibility of the adducts to this manner of chloride ion liberation is emphasized by the rapid dehydrochlorination of the oxidized, undoubtedly nonassisted, adduct V under solvolytic conditions (Table I). Participation of sulfur in a common ionic intermediate, however, is clearly indicated by the facile interconversion of I and II under the solvolytic conditions, as well as the isolation of a considerable quantity of the rearranged dichlorotrisulfone IV when the oxidation of II with hydrogen peroxide in acetic acid was allowed to proceed slowly. Although these interconversions are decidedly cases of ion-pair return, they are nonetheless surprising in such a highly solvating media as 40% aqueous acetone.[17] Return, rather than loss, of chloride ion supports a short lifetime for the episulfonium ionization intermediate VIII and emphasizes the considerable role ion–dipole interaction must play in the behavior of the tetramethylene sulfone nucleus.

Assignment of the *dl* and *meso* structures to the high- and low-melting isomers, respectively, is required by the optical data. It is interesting that racemization of *d*- or *l*-I requires two successive chlorine shifts (one in each ring) and must pass by way of the *meso* structure II (see Chart III). Loss in rotation of partially resolved I* is thus a reflection of the rearrangement of active I to inactive II and not the racemization of I. A quantitative estimate of the extent of ion-pair return is provided by the polarimetric rate of this rearrangement (k_α). Since collapse of the episulfonium ionization intermediate (Chart III) occurs with essentially equal probability at either position 1 or 2 to give inactive II or return active I, respectively, loss in rotation occurs only 50% of the time. Therefore the first-order rate of ionization (k_i) is twice k_α or *ca.* 8×10^{-6} sec^{-1}. Ionization occurs about 30 times faster than solvolysis in aqueous acetone. Thus k_i is a more appropriate measure of the degree of participation in the adducts than their titrimetric rate constants. In light of this k_i/k ratio, it is not surprising that the solvolysis rates of I and II were nearly identical, since they were represented by identical mixtures of unreacted dichloride after only 50 hr or 5% total reaction.

Consistent with the reported facile elimination of β-chlorosulfolanes under alkaline conditions to give the corresponding α,β-unsaturated sulfolane,[18] similar dehydrochlorination of adducts I and II might have been expected to occur adjacent to the sulfone moiety to give

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(12) H. L. Goering and K. L. Howe, *J. Am. Chem. Soc.* **79**, 6542 (1957).

(13) Coplanarity of the participating atoms has also been established as a requirement for assisted ionization.[14] It is likely that the tetramethylene sulfone nucleus is conformationally well approximated by cyclopentane, and little strain is required for cyclopentane to assume a conformation in which adjacent *trans* bonds are coplanar.[15]

(14) S. J. Cristol and R. P. Arganbright, *J. Am. Chem. Soc.*, **79**, 3441 (1957).

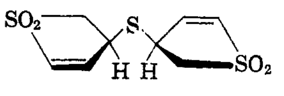
(15) J. Weinstock, S. N. Lewis, and F. G. Bordwell, *ibid.*, **78**, 6072 (1956).

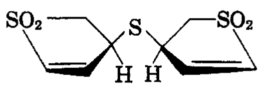
(16) The apparent first-order solvolytic rate constants of 3-chlorosulfolane and *trans*-3,4-dichlorosulfolane (see Table I) are not properly related in terms of a first-order ionization. The additive inductive effect of the second chlorine atom in the latter compound would have been expected to depress its rate of first-order solvolysis with respect to chlorosulfolane[11] if ionization were indeed rate determining in these nonassisted examples.

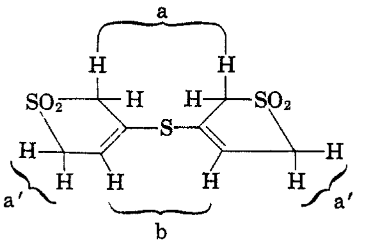
(17) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **79**, 1602 (1957).

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

the isomeric bisunsaturated compounds X and XI, respectively. Instead, however, the same diunsaturated compound was obtained from both adducts under relatively mild conditions.


X


XI



III

It is obvious that a single product can result only after asymmetry loss at the α-sulfide carbon atom. The assigned structure is well supported by ultraviolet and nmr spectra. Inspection of the comparative ultraviolet data in Table II offers compelling proof that III is in fact a divinyl sulfide. Furthermore, only two groups of protons, a and b, in the required area ratio of 4:1 are evident in the nmr spectra (d_6-DMSO) at τ 6.03 and 3.73, respectively; perhaps the slight dissimilarity in shielding of the protons a and a′ is responsible for a slight irregularity in the symmetry of this former peak. Symmetrical signals in the proper area ratio for the corresponding a and b protons of sulfolene were observed at τ 6.31 and 4.07, respectively.

The dehydrochlorination rate enhancement supplied by a *trans* orientation of the hydrogen and chlorine substituents in β-chloro sulfones has been well documented.[5] No similar quantitative information is available concerning the basic dehydrochlorination of β-chloro sulfides. Although they are known to be much more reactive than alkyl halides, they require more strenuous conditions for dehydrochlorination than the β-chloro sulfones.[19] Adducts I and II might possibly undergo a kinetically controlled *cis* elimination of hydrogen chloride to give III directly, however, it is doubtful that this would occur at a rate faster than that for β-halo sulfone elimination. It is more likely that III is a result of thermodynamic control and arises from the kinetically favored products X and XI *via* a prototropic shift. Allyl sulfides are known to be very susceptible to prototropic shift giving the corresponding propenyl sulfide in alkaline solution.[20,21] The protons indicated in X and XI would be particularly labile, being adjacent both to a vinyligous sulfone and a sulfide. Certainly III would be the more stable product by virtue of the increased resonance energy and the reduction of nonbonded atom repulsions concomitant with its formation. In any case, if III results from an isomerization of the kinetically controlled products X and XI, the rate of their isomerization is faster than that of Michael addition of dimethylamine, since the reaction of I and II with excess dimethylamine gave only the divinyl sulfide III and not XII. As expected, conversion of the divinyl sulfide III to its corresponding sulfone VI allowed a smooth Michael addition of dimethylamine to give a mixture of the isomeric adducts XIII.

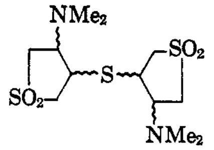
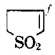

XII
XIII, S=SO$_2$

TABLE II

COMPARATIVE ULTRAVIOLET ABSORPTION OF SELECTED VINYL SULFIDES AND SULFONES IN ETHANOL

Compd	λ_{max}, mμ	ϵ_{max}
$(CH_2{=}CH)_2S$[a]	240, 255	41,800, 38,000
$(CH_3CH{=}CH)_2S$[b]	238–239	8700
$CH_2{=}CH{-}S{-}i\text{-}Pr$[a]	230	6000
$(CH_2{=}CH)_2SO_2$[c]	<190[d]	800[e]
[f]	<220[d]	26[e]
[f]	<220[d]	0[e]
III	238, 258	5720, 3820

[a] C. C. Price and C. E. Scott, *J. Am. Chem. Soc.*, **81**, 2672 (1959). [b] D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956). [c] E. S. Waight, *J. Chem. Soc.*, 2440 (1952). [d] W. J. Bailey and E. W. Cummins, *J. Am. Chem. Soc.*, **76**, 1932 (1954). [e] Reported at 220 mμ. [f] No maxima observed at higher wavelengths.

Experimental Section[22]

Addition of Sulfur Dichloride to Sulfolene.—A bright red solution of 10.3 g (0.10 mole) of sulfur dichloride and 26.6 g (0.20 mole) of sulfolene in 100 ml of methylene chloride was allowed to stand at ambient temperature for 48 hr. Filtration of the resultant light yellow suspension gave 9.4 g (28%) of a white, crystalline solid, mp 175–180° dec. Recrystallization from acetonitrile gave I, mp 189–190°.

Anal. Calcd for $C_8H_{12}Cl_2O_4S_3$: C, 28.40; H, 3.58; Cl, 20.90; S, 28.40. Found: C, 28.51; H, 3.63; Cl, 20.39, 20.52; S, 28.32.

On dilution of the light yellow filtrate from I with ether, 11.4 g (34%) of a granular white solid, mp 142–150° (dec at 180°) separated. Recrystallization from acetonitrile gave II, mp 152–153°. Melting point on admixture with I was at 147–175°.

Anal. Calcd for $C_8H_{12}Cl_2O_4S_3$: C, 28.40; H, 3.58; Cl, 20.90; S, 28.40. Found: C, 28.31; H, 3.48; Cl, 20.54, 20.54; S, 28.59.

Dehydrochlorination of Adducts I and II.—To a stirred suspension of 17.0 g (0.05 mole) of I in 50 ml of acetone at ambient temperature was added 7.5 ml (0.11 mole) of 30% aqueous ammonia solution; after 2 hr the ammoniacal odor had disappeared. Dilution of the yellow suspension with twice its volume of water gave 10.0 g of a white powder, mp 142–144°, upon filtration; an additional 3.3 g of white needles, mp 149–151°, crystallized from the filtrate on standing (quantitative yield of crude material). Crystallization of the combined solid material from acetonitrile gave a 55% recovery of IIIA, mp 160.0–161.0° dec.

To a stirred suspension of 17.0 g (0.05 mole) of II in 50 ml of acetone was added 7.5 ml (0.11 mole) of 30% aqueous ammonia solution under conditions identical with those described for I. Dilution of the yellow suspension with twice its volume of water gave 7.5 g of a white, crystalline solid, mp 152–153°; an additional 5.3 g of solid, mp 152–154°, separated from the filtrate on standing (97% yield of crude material). Crystallization of the combined solids from acetonitrile gave a 70% recovery of IIIB, mp 160.5–161.0° dec. Melting point of B on admixture with A showed no depression, 160.5–161.0°.

Anal. Calcd for $C_8H_{10}O_4S_3$: C, 36.10; H, 3.79; S, 36.10. Found: C, 36.57, 36.37; H, 3.79, 3.93; S, 36.64, 36.47.

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(19) E. Rothstein, *J. Chem. Soc.*, 1550, 1553 (1940).

(20) See Table II, footnote *f*.

(21) D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952).

(22) All melting points are uncorrected.

The infrared spectra of A and B were superimposable; the nmr spectra in dimethyl sulfoxide *vs.* tetramethylsilane were also identical, exhibiting only two peaks attributable to the unsaturated sulfide at τ 6.03 (slightly unsymmetrical singlet) and 3.73 (multiplet) in the area ratio of 4:1 (planimeter), respectively. The ultraviolet spectra in absolute ethanol displayed two maxima at 238 and 258 mμ, with extinction coefficients of 5720 and 3820, respectively.

Reaction of Adducts I and II with Excess Dimethylamine.—To 25 ml of a stirred 40% aqueous solution of dimethylamine (large excess) at ambient temperature was added 1.70 g (0.005 mole) of crystalline I in small portions over a 5-min period. After stirring the resultant, colorless suspension for an additional 55 min, filtration, followed by a water and 95% ethanol wash, gave 1.15 g (87%) of III mp 157–158°.

The treatment of 1.70 g (0.005 mole) of II in an exactly analogous manner also gave 1.15 g (87%) of III, mp 155–156°.

Oxidation of Dehydrochlorination Product III.—A stirred suspension of 10.0 g (0.038 mole) of the sulfide III in a solution of 10.0 g (0.08 mole) 30% aqueous hydrogen peroxide and 100 ml of glacial acetic acid was heated; at 70° clarity was observed, followed by an exotherm to 115° where a white solid began to separate. Filtration of the cooled reaction mixture gave 10.5 g (95%) of the sulfone which exhibited no melting point when heated rapidly in an oil bath; the material appeared to lose crystallinity and turned brown with the release of a white smoke at 260°. Recrystallization from acetonitrile gave compound VIA, mp *ca.* 260° (brown melt which rapidly decomposed with concomitant release of a white smoke), if the sample was directly immersed in a bath at 260°; no characteristic odor was noted on decomposition. Samples IIIA and B were indistinguishable in their behavior under the reaction conditions, giving products identical in yield, infrared spectra, and thermal characteristics.

Anal. Calcd for $C_8H_{10}O_6S_3$: C, 32.30; H, 3.36; S, 32.30. Found: C, 32.04; H, 3.43; S, 31.90.

Oxidation of Adducts I and II.—A stirred suspension of 10.0 g (0.03 mole) of I in a solution of 3.4 g (0.03 mole) of 30% aqueous hydrogen peroxide and 100 ml of glacial acetic acid was heated; at 65°, homogeneity was achieved followed by a rapid exotherm to 115° where a white solid began to separate. Filtration of the cooled reaction mixture gave 6.5 g of the sulfone (quantitative yield based on peroxide), mp 240–242°. Recrystallization from acetonitrile gave IV, mp 240–242°.

Anal. Calcd for $C_8H_{12}Cl_2O_6S_3$: C, 25.90; H, 3.24; Cl, 19.15; S, 25.90. Found: C, 25.81; H, 3.18; Cl, 19.09; S, 26.13.

The treatment of 10.0 g (0.03 mole) of II in analogous manner gave 6.0 g of the sulfone, mp 170–172°. Recrystallization from acetonitrile gave V, mp 176–178°.

Anal. Calcd for $C_8H_{12}Cl_2O_6S_3$: C, 25.90; H, 3.24; Cl, 19.15; S, 25.90. Found: C, 26.03; H, 3.32; Cl, 19.40, 19.52; S, 25.77.

Dehydrochlorination of Oxidized Adducts IV and V.—To a stirred suspension of 1.78 g (0.0048 mole) of IV in 50 ml of methanol in an ice bath was added dropwise 100 ml of a 0.0958 *M* solution of sodium methoxide in methanol (0.0096 mole) over a 1.5-hr period; the resultant pale yellow suspension was stirred for an additional 2 hr in the ice bath. Filtration followed by successive washing with methanol, water, and ether gave 1.40 g (98%) of an unsaturated trisulfone. Recrystallization from acetonitrile gave VIB, mp *ca.* 260° (when immersed in bath at 260°).

The treatment of 1.78 g (0.0048 mole) of V with 100 ml of 0.0958 *M* methanolic sodium methoxide solution in a manner analogous to that described for B gave 1.30 g (91%) of an unsaturated trisulfone. Recrystallization from acetonitrile gave VIC, mp *ca.* 260° (when immersed in bath at 260°).

Anal. Calcd for $C_8H_{10}O_6S_3$: C, 32.30; H, 3.36; S, 32.30. Found: C, 32.51; H, 3.42; S, 32.25.

The unsaturated trisulfones VIB and C displayed exactly the same melting point behavior as that outlined previously for VIA, the sulfone resulting from the oxidation of the unsaturated sulfide III. The infrared spectra of VIA–C were superimposable; their nmr spectra in dimethyl sulfoxide, although not easily interpreted, were essentially the same.

***trans*-3-Hydroxy-4-thiophenoxytetrahydrothiophene 1,1-Dioxide.**—A solution of 4.1 g (37 mmoles) of thiophenol and 5.0 g (37 mmoles) of 3-epoxysulfolane,[23] in anhydrous methanol was refluxed for 2 hr in the presence of 5 mole% of sodium methoxide and allowed to stir at room temperature overnight. Removal of the solvent under reduced pressure and crystallization of the residue from methanol ether gave 6.78 g (85%) of product, mp 120–123°.

Anal. Calcd for $C_{10}H_{12}O_3S_2$: C, 49.18; H, 4.95; S, 26.22. Found: C, 48.77; H, 4.92; S, 26.24.

***trans*-3-Chloro-4-thiophenoxytetrahydrothiophene 1,1-Dioxide.**—A solution of 5.0 g (20 mmoles) of *trans*-3-hydroxy-4-thiophenoxytetrahydrothiophene 1,1-dioxide and 7.0 g (59 mmoles) of freshly distilled thionyl chloride in chloroform was refluxed for 48 hr in the presence of 3 drops of pyridine. After evaporation of the volatile material under reduced pressure, the residue was crystallized from ether yielding 4.43 g (82%) of product, mp 76–78°. Recrystallization from ether–chloroform gave IX, mp 79–80°.

Anal. Calcd for $C_{10}H_{11}ClO_2S_2$: C, 45.70; H, 4.22; Cl, 13.52; S, 24.33. Found: C, 45.77; H, 4.12; Cl, 13.37; S, 24.24.

Benzenesulfenyl Chloride.—According to the method of Emde,[24] a solution of 33.0 g (0.30 mole) of thiophenol in 100 ml of dry benzene was added to a suspension of 40.0 g (0.30 mole) of N-chlorosuccinimide in 400 ml of dry benzene under a nitrogen atmosphere. After stirring at room temperature for 2 hr the supernatant liquid was decanted, concentrated, and distilled under reduced pressure, giving 28.5 g of red oil, bp 50–52° (1.7 mm).

Reaction of Sulfolene with Benzenesulfenyl Chloride.—A solution of 6.12 g (42 mmoles) of benzenesulfenyl chloride in 40 ml of methylene chloride was added dropwise to a solution of 5.0 g (42 mmoles) of sulfolene in 75 ml of methylene chloride under an atmosphere of nitrogen and stirred at room temperature overnight. After removal of the solvent under reduced pressure, 11.7 g of an oil remained which crystallized completely on standing. Recrystallization from ether–chloroform gave 9.2 g (83%) of colorless crystals (mp 79–80°), undepressed on admixture with authentic 3-chloro-4-thiophenoxytetrathiophene 1,1-dioxide. The infrared spectra of these two materials were identical in all respects.

Anal. Calcd for $C_{10}H_{11}ClO_2S_2$: C, 45.70; H, 4.22; Cl, 13.52; S, 24.33. Found: C, 45.57; H, 4.12; Cl, 13.81; S, 24.61.

3-Chlorotetrahydrothiophene 1,1-Dioxide.—A solution of 8.5 g of 3-hydroxytetrahydrothiophene 1,1-dioxide,[23] 20 g of freshly distilled thionyl chloride, and 3 drops of pyridine in 75 ml of chloroform was refluxed for 50 hr and stripped, and the residue, after two low-recovery crystallizations from ether, gave 3.5 g of a colorless, crystalline solid, mp 55–56° (lit.[25] mp 60–61°).

***trans*-3,4-Dichlorotetrahydrothiophene 1,1-Dioxide.**—Colorless plates, mp 129–131°, were obtained according to the method of Bluestone, *et al.*;[18] the *trans* structure was confirmed by infrared absorption at 8.33 μ in acetonitrile.

Kinetic Procedure.—A solution of 10–20 mmoles of the appropriate chloride in 125 ml of acetone–75 ml of water was brought to reflux in a 500-ml flask equipped with a reflux condenser, a thermometer, magnetic stirring bar, and a serum cap closing the third neck. The stirred solutions were maintained at an equilibrium reflux temperature at 64.0° and, at specified time intervals, 20.0-ml samples of the refluxing solution were withdrawn from the reaction flasks with a syringe and immediately subjected to Volhard analysis for ionic chloride in the usual manner. A good linear dependence of the data to a graphical representation of the first-order kinetic expression, ln $a/a - x = kt$,[26] was obtained, where a = initial mmoles of organic chloride and x = mmoles of chloride ion liberated at time t. The rate constants were determined from the slope of these lines and are summarized in Table I.

Recovery of Unsolvolyzed Adducts.—A solution of 5.66 g (0.0167 mole) of I in 166 ml of acetone and 100 ml of water

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[23] Obtained from Gallard-Schlessinger Corp.

[24] H. Emde, German Patent 804,572 (1951).

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

[26] In the bifunctional molecules I and II, ln $2a/2a - x = kt$ was used as the kinetic expression, assuming that both chlorines solvolyze at the same rate. Thus the calculated infinity ($2a$) is twice the initial concentration of adduct. The work of Bartlett and Swain[9] suggests that the error in the observed rate constants introduced by this assumption is not large. In the unlikely event that the remaining chlorine of the hydrolysis intermediate is substantially less reactive and is not lost under the solvolytic conditions, the appropriate kinetic expression would be ln $a/a - x = kt$, and the actual rate constants would have been about twice those reported for k_{I}, k_{II}. Conversely, if the second chlorine were lost substantially faster than the first, the actual constants for the rate-determining step would have derived from ln $4a/4a - x$ and would have been about half those reported.

(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°, $[\alpha]^{24}\mathrm{D}$ −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°, $[\alpha]^{24}\mathrm{D}$ −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°, $[\alpha]^{24}\mathrm{D}$ 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°, $[\alpha]^{24}\mathrm{D}$ −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°.

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

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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).