$Cl_3N_2O_2S$: C, 25.59; H, 3.94; N, 9.95; S, 11.39. Found: C, 25.64; H, 3.91; N, 10.65; S, 11.39.

General Procedure for the Reduction of the N,N-Dichlorosulfonamide–Unsaturate Adducts.—A solution of 0.1 mol of adduct in 100 ml of methylene chloride was vigorously stirred at ambient temperature with a solution of 0.3 mol of sodium sulfite in 150 ml of water for about 0.5 hr, or until the organic layer failed to give a positive test with potassium iodide–starch paper. The layers were then separated; the aqueous layer was extracted with methylene chloride. The organic extracts were combined and dried over sodium sulfate. The solvent was evaporated at aspirator pressure and ambient temperature to give the reduced sulfonamide. These materials were recrystallized from one or more of the following solvents or solvent pairs: benzene, carbon tetrachloride, cyclohexane, ether, and benzene–pentane. The following sulfonamides were prepared: $C_6H_5SO_2NHCH_2CH(Cl)CH_3$, 89%, mp 79–80°. *Anal.* Calcd for $C_9H_{12}ClNO_2S$: C, 46.25; H, 5.55; N, 6.00; S, 13.72. Found: C, 46.50; H, 5.55; N, 6.43; S, 13.55. *p*-$ClC_6H_4SO_2NHCH_2CH(Cl)CH_3$, 87%, mp 105–108°. *Anal.* Calcd for $C_9H_{11}Cl_2NO_2S$: C, 40.32; H, 4.13; N, 5.22; S, 11.96. Found: C, 40.09; H, 4.40; N, 5.26; S, 12.24. $(CH_3)_2NSO_2NHCH_2CH(Cl)CH_3$, 84%, mp 25–26°. *Anal.* Calcd for $C_5H_{13}ClN_2O_2S$: C, 29.92; H, 6.53; N, 13.95; S, 15.98. Found: C, 30.09; H, 6.69; N, 14.06; S, 15.97. $C_6H_5SO_2NHCH_2CH(Cl)C_6H_5$, 95%, mp 45–47°. *Anal.* Calcd for $C_{14}H_{14}ClNO_2S$: C, 56.85; H, 4.77; N, 4.73; S, 10.84. Found: C, 56.31; H, 4.97; N, 4.61; S, 10.54. $(CH_3)_2NSO_2NHCH_2CH(Cl)C_6H_5$, 92%, mp 69–70°. *Anal.* Calcd for $C_{10}H_{15}ClN_2O_2S$: C, 45.71; H, 5.75; N, 10.66; S, 12.20. Found: C, 45.71; H, 5.83; N, 10.53; S, 12.21. $C_6H_5SO_2NHCH_2CH{=}CHCH_2Cl$, 85%, oil. *Anal.* Calcd for $C_{10}H_{12}ClNO_2S$: C, 48.88; H, 4.92; N, 5.70; S, 13.05. Found: C, 49.10; H, 4.96; N, 5.71; S, 13.38. *p*-$ClC_6H_4SO_2NHCH_2CH{=}CHCH_2Cl$, 78%, mp 78–79°. *Anal.* Calcd for $C_{10}H_{11}Cl_2NO_2S$: C, 42.87; H, 3.96; N, 5.00; S, 11.44. Found: C, 42.71; H, 3.88; N, 4.98; S, 11.23. $CH_3SO_2NHCH_2CH{=}CHCH_2Cl$, 87%, mp 26–27°. *Anal.* Calcd for $C_5H_{10}ClNO_2S$: C, 32.69; H, 5.49; N, 7.63; S, 17.46. Found: C, 32.51; H, 5.60; N, 7.47; S, 17.96. $C_6H_5SO_2NHCH_2C(Cl){=}CHCH_2Cl$, 81%, mp 83–84°. *Anal.* Calcd for $C_{10}H_{11}Cl_2NO_2S$: C, 42.87; H, 3.96; N, 5.00; S, 11.44. Found: C, 42.96; H, 3.93; N, 5.02; S, 11.50. *p*-$ClC_6H_4SO_2NHCH_2C(Cl){=}CHCH_2Cl$, 78%, mp 78–80°. *Anal.* Calcd for $C_{10}H_{10}Cl_3NO_2S$: C, 38.17; H, 3.20; N, 4.45; S, 10.19. Found: C, 37.99; H, 3.05; N, 4.47; S, 10.20. $CH_3SO_2NHCH_2C(Cl){=}CHCH_2Cl$, 84%, mp 157–158°. *Anal.* Calcd for $C_5H_9Cl_2NO_2S$: C, 27.53; H, 4.16; N, 6.42; S, 14.70. Found: C, 27.49; H, 4.33; N, 6.47; S, 14.65. $(CH_3)_2NSO_2NHCH_2C(Cl){=}CHCH_2Cl$, 84%, mp 25–26°. *Anal.* Calcd for $C_6H_{12}Cl_2N_2O_2S$: C, 29.16; H, 4.99; N, 11.34; S, 12.97. Found: C, 29.65; H, 4.90; N, 11.24; S, 13.03.

Registry No.—Tropylene, 115-07-1; styrene, 100-42-5; butadiene, 106-99-0; chloroprene, 126-99-8; isobutylene, 115-11-7; 3-chloro-2-methyl-1-propene, 563-47-3; VII, 2948-79-0; N,N-dichlorobenzenesulfonamide, 473-29-0; N,N-dichloromethylsulfonamide, 17396-47-3; N,N-dichloro-*p*-chlorobenzenesulfonamide, 17260-65-0; N,N-dichloro-N,N-dimethylsulfamide, 13882-13-8.

Acknowledgment.—The authors wish to thank Miss M. Miciak and Mr. J. J. Clemens for their competent technical assistance.

Sulfilimines and Sulfoximines Derived from 4-*t*-Butylthiane[1,2a]

CARL R. JOHNSON[2b] AND JUAN J. RIGAU[2c]

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received May 13, 1968

The stereochemical course of the reactions of Chloramine-T with 4-*t*-butylthiane and of N-sulfinyl-*p*-toluenesulfonamide, *p*-toluenesulfonyl isocyanate, and *p*-toluenesulfonyl azide with 4-*t*-butylthiane 1-oxides was examined. The stereochemistry of the N-tosylsulfilimine grouping was correlated with the known configurations of the sulfoxide group in the 4-*t*-butylthiane system by N alkylation of the sulfilimine, followed by hydrolysis of the adduct salt to sulfoxide. New compounds prepared in this series include the isomeric N-tosylsulfilimines, the "free" sulfoximines, and the N-tosylsulfoximines.

The potential asymmetry at the sulfur atom in sulfilimines and sulfoximines has been established by the resolution of appropriately substituted examples.[3] A number of methods are now available for the preparation of sulfilimines and sulfoximines. Those of interest to the present work are briefly described. The well-known reaction of sulfides with chloramines, especially Chloramine-T, has been used in a typical preparation of sulfilimines by Leandri and Spinelli.[4] Recently the reactions of sulfoxides with *p*-toluenesulfonyl isocyanate[5] and N-sulfinyl-*p*-toluenesulfonamide to produce[6] sulfilimines have been described. The latter reaction is reported to proceed with inversion of configuration at the sulfur atom.[7] The most direct method for the synthesis of sulfoximines would appear to be the oxidation of sulfilimines. It is noteworthy that, at the present time, only potassium permanganate and the salts of per acids are known to effect this oxidation and, then, in the large majority of cases, only in low yield.[7b,8] A general method for the production of sulfoximines is given by the reaction of sulfoxides with hydrazoic acid (sodium azide in a mixture of sulfuric acid and chloroform).[9] Horner and Christmann[10] have obtained N-benzoyldimethylsulfoximine from the reaction of dimethyl sulfoxide and benzoyl azide under the influence of light. Very recently Kwart and Khan[11] have prepared N-benzenesulfonyldimethylsulfoximine by the use of di-

(1) (a) Part XII in the Series Chemistry of Sulfoxides and Related Compounds. (b) Part XI: C. R. Johnson, J. J. Rigau, M. Haake, D. McCants, Jr., J. E. Keiser, and A. Geertsema, *Tetrahedron Lett.*, 3719 (1968). (c) Portions of this work were presented at the Second International Symposium on Organic Sulfur Chemistry, Groningen, The Netherlands, May 1966.

(2) (a) We gratefully acknowledge support of this work by The National Science Foundation (GP 5944). (b) Alfred P. Sloan Research Fellow, 1965–1968. (c) Supported by the Economic Development Administration, Commonwealth of Puerto Rico.

(3) (a) S. G. Clark, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 188 (1927); (b) G. Kresze and B. Wustrow, *Chem. Ber.*, **95**, 2692 (1962).

(4) G. Leandri and D. Spinelli, *Ann. Chim.* (Rome), **50**, 1616 (1960).

(5) C. King, *J. Org. Chem.*, **25**, 352 (1960).

(6) G. Schulz and G. Kresze, *Angew. Chem. Intern. Ed. Engl.*, **2**, 736 (1963).

(7) (a) J. Day and D. J. Cram, *J. Amer. Chem. Soc.*, **87**, 4398 (1965). (b) Shortly after this article was submitted a communication appeared describing stereospecific interconversions of optically active sulfoxides, sulfilimines, and sulfoximines [D. R. Rayner, D. M. von Schriltz, and D. J. Cram, *ibid.*, **90**, 2721 (1968)].

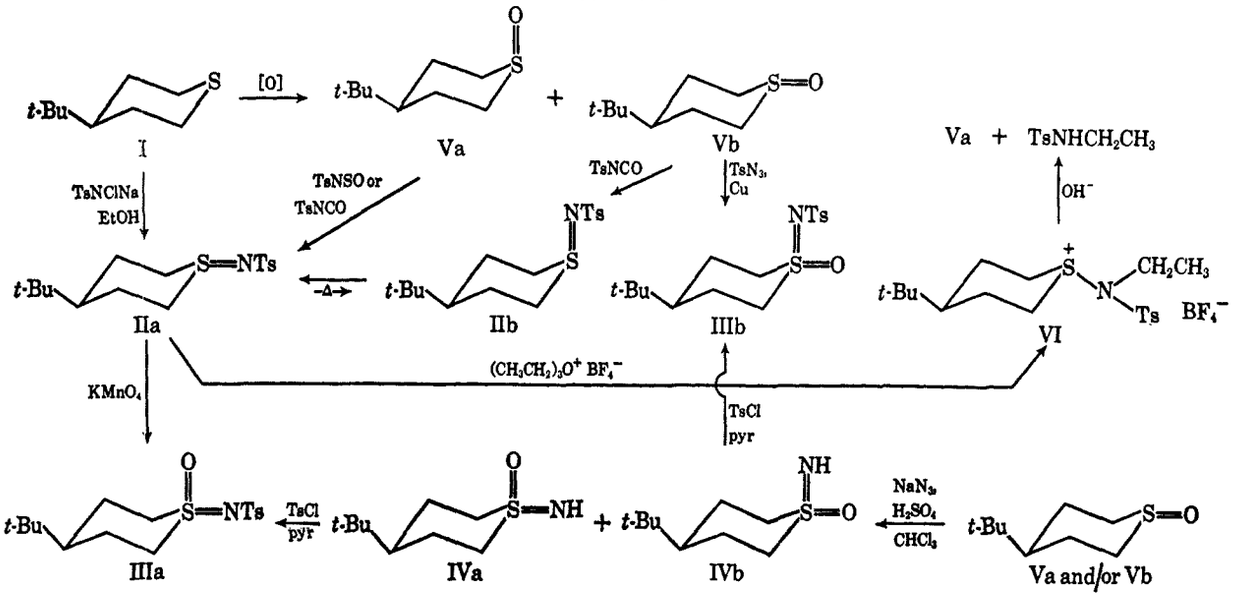
(8) H. R. Bentley and J. K. Whitehead, *J. Chem. Soc.*, 2081 (1950).

(9) J. K. Whitehead and H. R. Bentley, *ibid.*, 1572 (1952).

(10) L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963).

(11) H. Kwart and A. A. Khan, *J. Amer. Chem. Soc.*, **89**, 1950 (1967).

SCHEME I



methyl sulfoxide as a trap for the nitrene produced by the copper-catalyzed decomposition of benzenesulfonyl azide. In this paper we report our findings concerning the stereochemical course of certain of these reactions[12] in the 4-*t*-butylthiane system. Our results are summarized in Scheme I.

Reaction of 4-*t*-butylthiane (I) with Chloramine-T in ethanol afforded, in 95% yield, an N-*p*-toluenesulfonyl- (or N-tosyl-) sulfilimine. The *trans* structure IIa was assigned to this material based on the three lines of evidence detailed below.

(1) Alkylation[1b] of the sulfilimine with triethyloxonium fluoroborate gave, in excellent yield, the N-ethyl salt (VI). Hydrolysis of the salt with aqueous base gave the sulfoxide Va[13] and N-ethyl-*p*-toluenesulfonamide. Based on analogy with the hydrolysis of alkoxysulfonium salts[13] it can be safely suggested that this hydrolysis occurred with inversion of configuration at the sulfur atom.

(2) Oxidation of the sulfilimine with potassium permanganate gave a single sulfoximine (IIIa) which was isomeric with that (IIIb) obtained upon treatment of *cis*-4-*t*-butylthiane 1-oxide (Vb) with *p*-toluenesulfonyl azide in the presence of Raney copper. This reaction proceeded in poor yield (10%), the major material obtained being starting sulfoxide of *unaltered* configuration (Vb).

(3) The identical sulfilimine was obtained by reaction of sulfoxide Va with *p*-toluenesulfonyl isocyanate or N-sulfinyl-*p*-toluenesulfonamide. The latter reaction, which we examined in both benzene and pyridine as solvents, has been shown by Day and Cram,[14] in the case of an optically active sulfoxide, to proceed with inversion of configuration. Since the present system is relatively strain free and uncluttered, it is reasonable to assume inversion to occur here also.

Treatment of the *trans*-4-*t*-butylthiane 1-oxide (Vb) with N-sulfinyl-*p*-toluenesulfonamide in benzene afforded a single sulfilimine (IIb),[15] mp 150–151.5°, which was isomeric with that (IIa) previously obtained (mp 187–188°). After standing for 2 days at room temperature the melting point of IIb had changed to 173–175°. After recrystallization, this material had a melting point and a mixture melting point identical with those of IIa. It thus appears that the axial sulfilimine is unstable with respect to isomerization to the equatorial sulfilimine. It should be noted that insufficient difference was found in the infrared (ir) spectra of the isomers IIa and IIb to render the spectra useful for identification of the individual isomers. Qualitative ultraviolet (uv) spectroscopy revealed a relatively strong band at 228 mμ in 95% ethanol or cyclohexane for compound IIa and a corresponding absorption at 229 (95% ethanol) and 230 mμ (cyclohexane) for compound IIb.

A mixture of the isomeric "free" sulfoximines was obtained by reaction of sulfoxides Va and Vb with sodium azide and sulfuric acid in chloroform. From a 50:50 mixture of the isomeric sulfoxides Va and Vb a 53% yield of a mixture of sulfoximines consisting of 63% IVa and 37% IVb was obtained. The unreacted sulfoxide was recovered and found to consist of an equilibrium mixture of isomers Va (95%) and Vb (5%). Apparently, equilibration of the sulfoxides

(12) The stereochemical relationships of some sulfoxides, sulfilimines, and sulfoximines derived from optically active methyl-*p*-tolyl sulfoxide and the *p*-chlorophenylthiane 1-oxides have been examined by M. A. Sabol, R. W. Davenport, K. K. Andersen, *Tetrahedron Lett.*, 2159 (1968). We thank these authors for informing us of their results prior to publication.

(13) C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 1109, 5404 (1965).

(14) Day and Cram (ref 7a) have suggested "a mechanism involving a trigonal–bipyramidal intermediate or transition state in which the entering and leaving groups occupy radial positions . . ." In the formulation of the intermediate of transition state two molecules of N-sulfinylsulfonamide were implicated. Their preliminary results, indeed, suggested that the reaction is second order in N-sulfinyl-*p*-toluenesulfonamide. However, their reaction was conducted in pyridine which catalyzes the dimerization of N-sulfinylsulfonamides: W. Wucherpfenning and G. Kresge, *Tetrahedron Lett.*, 1671 (1966).

$$RSO_2N{=}SO \xrightarrow{\text{pyridine}} RSO_2N{=}S{=}NSOR + SO_2$$

(15) A referee has suggested the possibility that the compound reported as IIb is, in actual fact, a crystalline modification of IIa. This possibility can not be entirely ruled out because of the strong similarity in the ir and uv spectra, as well as the mobility on tlc of the two materials. The two substances, however, were obtained under identical chromatographic conditions, and it would not appear likely that two different crystalline modifications would form.

TABLE I
NMR RESULTS OF SULFOXIMINE ISOMERS IVa AND IVb AT 60 MHz

Compound	Solvent	Concentration, mg/ml	N-H resonance, δ
IVa	$CDCl_3$	300	2.83
	$CDCl_3$	150	2.71
	DMSO-d_6	100	3.43
IVb	$CDCl_3$	300	2.42
	$CDCl_3$	150	2.33
	DMSO-d_6	100	3.27

under the reaction conditions occurs faster than sulfoximine production; the ratio of isomeric sulfoximines is almost independent of the isomeric composition of the starting sulfoxides. As expected, it was found that the sulfoximines, once formed, show no isomerization or decomposition when resubjected to the reaction conditions. The free sulfoximines were separated on silica gel thin layer plates developed with isopropyl alcohol, isomer IVb showing the lower R_f value. The isomers IVa and IVb were converted into the previously prepared N-tolylsulfoximines (IIIa and IIIb) on reaction with *p*-toluenesulfonyl chloride in pyridine.

An ir study of the "free" sulfoximines IVa and IVb in methylene chloride revealed an N–H band at 3328 cm^{-1}. In the nmr spectra the N–H resonance was found to be sensitive to structure and concentration (Table I).

The reaction of sulfonyl azides with 4-*t*-butylthiane and its 1-oxides under photolytic conditions gave complex reaction mixtures. The instability of the products of interest under these conditions make this approach unsuccessful. No sulfoximines or sulfilimines were isolated from these reactions.

Experimental Section

Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. Separation and purification of all substances were accomplished or monitored by thin layer or gas phase chromatography. Melting points were determind by the open capillary method and are uncorrected. Spectra were obtained on a Perkin-Elmer Model 621 ir spectrophotometer, a Cary-14 uv spectrophotometer, and a Varian A-60A nmr spectrometer.

The preparation of 4-*t*-butylthiane has been previously reported. The *cis*- and *trans*-4-*t*-butylthiane 1-oxides were prepared by the *t*-butyl hypochlorite oxidation method and by hydrolysis of the corresponding alkoxysulfonium salts. Synthesis of *p*-toluenesulfonyl azide was accomplished by a variation of the literature procedure.[16] N-Sulfinyl-*p*-toluenesulfonamide was prepared according to Kresze and Maschke.[17] Raney copper (Raney Catalyst Co., Inc.) and *p*-toluenesulfonyl isocyanate (The Upjohn Co., Carwin Organic Chemicals) are commercially available.

Reaction of 4-*t*-Butylthiane with Chloramine-T.—The reaction was carried out according to the general procedure of Leandri and Spinelli.[4] The product was isolated by elution from a silica gel column with chloroform, followed by ethyl acetate. The latter fraction contained the pure ***trans*-N-*p*-toluenesulfilimine (IIa)**: 95%; mp 187–188°; $\nu_{CH_2Cl_2}$ 963 and 980 cm^{-1} (S=N).

Anal. Calcd for $C_{16}H_{25}NO_2S_2$: C, 58.71; H, 7.64. Found: C, 58.58; H, 7.58.

Reactions of 4-*t*-Butylthiane 1-Oxides with N-Sulfinyl-*p*-toluenesulfonamide and *p*-Toluenesulfonyl Isocyanate. A.—To 0.174 g of pure *trans*-4-*t*-butylthiane 1-oxide (Vb) dissolved in 2 ml of dry benzene was slowly added 0.235 g of the *p*-toluene-N-sulfinylsulfonamide in 2 ml of benzene. The solution was stirred at 0° for 15 min and then at room temperature overnight. The products were separated by column chromatography (silica gel–ethyl acetate). An intermediate fraction was isolated containing 27 mg (8%) of the corresponding **sulfilimine (IIb)**, mp 150–151.5°, uncrystallized, which gave a single spot on tlc. Remaining fractions consisted of *p*-toluenesulfonamide and unreacted sulfoxide.

Anal. Calcd for $C_{16}H_{25}NO_2S_2$: C, 58.71; H, 7.64. Found: C, 58.44; H, 7.60.

B.—A parallel reaction with the *cis*-sulfoxide (Va) gave 6% of the corresponding sulfilimine IIa, mp 178–180°, uncrystallized. When the reaction mixture was refluxed for 10 hr, the yield increased to 8%.

C.—A reaction employing 1.00 g of *p*-toluenesulfonyl isocyanate and 0.68 g of Va in 15 ml of dry pyridine was stirred for 12 hr at room temperature. The elimination of the pyridine was partially effected by azeotropic distillation with toluene before resolving the mixture by column chromatography. Sulfilimine IIa was obtained in 13% yield.

Alkylation of Sulfilimine IIa with Triethyloxonium Fluoroborate and Hydrolysis of the Resulting Salt.—Pure *trans*-sulfilimine IIa (0.326 g, 1 mmol) was added to a solution of triethyloxonium fluoroborate (0.190 g, 1 mmol) in 10 ml of methylene chloride. The reaction was maintained at room temperature for 3 hr. The solution was filtered and anhydrous ethyl ether was added until precipitation was complete. The oily precipitate was washed with ether. Recrystallization from methylene chloride–ether afforded the pure **salt VI**: 75%; mp 175–176°; $\nu_{CH_2Cl_2}$ 811, 862, and 873 cm^{-1} (S—N).

Anal. Calcd for $C_{18}H_{30}BF_4NO_2S_2$: C, 46.50; H, 6.79. Found: C, 46.28; H, 6.43.

Hydrolysis of the pure adduct VI was effected by dissolution in water and adding 0.1 *N* sodium hydroxide to a phenolphthalein end point. The reaction mixture was extracted with methylene chloride, and the solvent was evaporated. Analysis of the reaction mixture by gas chromatography and preparative tlc (alumina–ethyl ether) revealed an almost quantitative yield of *cis*-4-*t*-butylthiane 1-oxide (Va), N-ethyl-*p*-toluenesulfonamide, and trace amounts of the parent sulfilimine IIa.

Reaction of 4-*t*-Butylthiane 1-Oxides with Hydrazoic Acid.—To 2.0 g of a 50:50 mixture of *cis*- and *trans*-sulfoxides Va and Vb in 8 ml of chloroform was added 2.73 g of sodium azide and then 3 ml of concentrated sulfuric acid. The reaction was heated at 48–55° for 60 hr. The reaction mixture was poured into a separatory funnel; water was added; and the chloroform layer was separated. The aqueous layer was again extracted with chloroform. Both the aqueous and organic layers were retained. The combined chloroform extracts were dried over sodium sulfate. Evaporation yielded 1.005 g of unreacted sulfoxides (95:5 ratio, *cis*–*trans*). Sodium hydroxide solution was added to the aqueous phase until slightly basic. The solution was extracted several times with chloroform. The combined chloroform extracts were dried over sodium sulfate. Evaporation of the chloroform provided 1.174 g of a mixture of the isomeric free sulfoximines IVa and IVb. Column chromatogaphy on silica gel with ethyl acetate followed by isopropyl alcohol gave a 1.6:1 ratio of **sulfoximine IVa**, mp 179.5–180.5°, to **sulfoximine IVb**, mp 157–157.5°. Neither isomer appears to be hygroscopic; both can be sublimed (65° at 0.1 mm) or recrystallized from ethyl acetate–hexane.

Anal. Calcd for $C_9H_{19}NOS$: C, 57.10; H, 10.12. Found (IVa): C, 56.84; H, 10.07. Found (IVb): C, 57.09; H, 10.07.

No equilibration or decomposition of the sulfoximines was found after refluxing with sodium azide–sulfuric acid–chloroform mixture at 60° for 36 hr.

Oxidation of *trans*-Sulfilimine IIa with Basic Permanganate.—To 500 ml of distilled water was added 0.46 g of potassium permanganate, 10 ml of sodium hydroxide (3%), and 0.76 g of sulfilimine IIa. The heterogeneous reaction was stirred under reflux for 2 hr. Sodium sulfite was added to destroy any remaining permanganate, and the mixture was filtered. The residue was washed with methylene chloride, and the combined filtrates were extracted with methylene chloride. The combined methylene chloride extracts were dried over sodium sulfate and evaporated. The product mixture was fractionated by chromatographic elution on silica gel with ethyl acetate. The **N-tosylsulfoximine IIIa** was recrystallized from ethyl acetate–cyclohexane: 13%; mp 167–167.5°. Unreacted sulfilimine (67%) and some *p*-toluenesulfonamide were also recovered.

(16) O. C. Dermer and M. T. Edmison, *J. Amer. Chem. Soc.*, **77**, 70 (1955); W. Lwowski and E. Scheiffele, *ibid.*, **87**, 4359 (1965).

(17) G. Kresze and A. Maschke, German Patent 1,117,566 (1961); *Chem. Abstr.*, **57**, 11110e (1962).

Anal. Calcd for $C_{16}H_{25}NO_3S_2$: C, 55.99; H, 7.34; S, 18.97. Found: C, 56.39; H, 7.47; S, 18.70.

Conversion of Sulfoximines IVa and IVb into N-*p*-Toluenesulfonyl Derivatives IIIa and IIIb.—To 3 ml of dry pyridine, 0.1 g of *p*-toluenesulfonyl chloride and 50 mg of free sulfoximine IVa were added; the mixture was stirred at room temperature for 12 hr. The mixture was poured into water and extracted with chloroform; the solvent was evaporated; and the pyridine was removed by azeotropic distillation with toluene. Column chromatography (silica gel–chloroform, then ethyl acetate) provided 92 mg (96%) of the **N-tosylsulfilimine IIIa**, identical in all respects with that obtained above by oxidation.

An analogous reaction with the free sulfoximine IVb gave the **N-tosylsulfilimine IIIb**: 95%; mp 172.5–173.5° (benzene–cyclohexane).

Anal. Calcd for $C_{16}H_{25}NO_3S_2$: C, 55.99; H, 7.34; S, 18.97. Found: C, 56.24; H, 7.37; S, 18.76.

Reaction of *trans*-4-*t*-Butylthiane 1-Oxide with *p*-Toluenesulfonyl Azide.—Following the method of Kwart and Khan, *trans*-sulfoxide Vb (80 mg), *p*-toluenesulfonyl azide (90 mg), and Raney copper (10 mg) in 5 ml of methanol were refluxed for 15 hr. Chromatography of the reaction product revealed unreacted starting sulfoxide and an N-tosylsulfoximine identical in all respects with IIIb obtained above.

Registry No.—I, 768-30-9; IIa, 17604-09-0; IIb, 17659-00-6; IIIa, 17604-10-3; IIIb, 17659-01-7; IVa, 17604-11-4; IVb, 17604-12-5; VI, 17604-13-6.

A Study of Aliphatic Sulfonyl Compounds. IX. Polar Effects in Ethylene- and 2-Propene-1-sulfonyl Chlorides[1a]

J. PRESTON[1b] AND ROBERT B. SCOTT, JR.[2]

Departments of Chemistry, University of Alabama, University, Alabama 35486, and The University of Mississippi, University, Mississippi 38677

Received May 21, 1968

Rates of ethanolysis of ethylenesulfonyl and 2-propene-1-sulfonyl chloride were found to be significantly faster and only slightly faster, respectively, than that of a saturated sulfonyl chloride. Although infrared and mass spectra suggest that in the case of the former there may be some allylic participation by the α double bond to give the resonance stabilized sulfonylium ion intermediate, enhancement of ethanolysis is not that great and probably is largely polar in origin. There is no evidence in the latter case for homoallylic enhancement to form the conjugated unsaturated sulfonylium ion, and the small increase in rate of ethanolysis probably is entirely due to a polar effect. From the activated state parameters of $\Delta H^* = 15.4$ and 17.7 kcal and $\Delta S^* = -7.5$ and -5.9 eu for ethanolysis of ethylenesulfonyl chloride and 2-propene-1-sulfonyl chloride, respectively, it is clear that the lower enthalpy of activation is responsible for the faster rate of ethanolysis. Alkylation of ethanolic hydrogen chloride with ethyl ethylenesulfonate is somewhat faster than with ethyl 2-propene-1-sulfonate, the former reacting at substantially the same rate as the ethyl ester of a saturated sulfonic acid. There was no spectral evidence for participation of either double bond in the case of these esters. From activated state parameters of $\Delta H^* = 21.0$ and 23.1 kcal and $\Delta S^* = +4.0$ and $+9.3$ eu, respectively, for ethyl ethylenesulfonate and 2-propene-1-sulfonate, it appears that the considerably greater increase in activation entropy in the case of the latter is more than offset by the increased enthalpy of activation. It was shown that a "polymeric vinylsulfonyl chloride" (obtained from ammonium ethylenesulfonate and phosphorus pentachloride) reported in the literature probably was only 2-chloroethanesulfonyl chloride with an impurity of ethyl ethylenesulfonate.

Previously[3-7] the steric requirements of several branched-chain sulfonyl compounds were compared by a study of the ethanolysis of saturated aliphatic sulfonyl chlorides and alkylation by the corresponding ethyl esters. However, all of the aliphatic compounds studied were saturated and were compared only with analogously branched primary alkyl halides as to steric effects; no important polar contributions could be correlated with those of alkyl halides. In other work, the polar effects of a carbonyl group in *dl*-10-camphorsulfonyl chloride[8] and of a chloro group in 3-chloro-1-propanesulfonyl chloride[9] upon ethanolysis (Table I) have been studied but these are rather special cases. Thus, in the case of the former, the halogen may be displaced by anchimeric assistance from the keto group or its hemiacetal, while in the latter the chain chlorine probably is too far removed to have a significant polar effect on sulfonyl reactivity.

TABLE I

RATES OF ETHANOLYSIS OF SELECTED SULFONYL CHLORIDES AT 84°

Sulfonyl chloride	10^4k, min^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
Ethylene-[a]	880[a]	15.4	−7.5
dl-10-Camphor-[b]	171		
Benzene-[c]	145	16.1	−10.9
2-Propene-1-	102	17.7	−5.9
1-Octane-[d]	89		
3-Chloro-1-propane-[e]	70	8.2	−35.2
α-Toluene-[b]	63		
2,3-Dimethyl-1-butane-[f]	48		
2-Octane-[d]	14		

[a] Calculated for 84° (see Table III for experimentally determined values of k). [b] See ref 8. [c] See ref 7. [d] See ref 3. [e] See ref 9. [f] See ref 4.

In the present report the effect of unsaturation was studied in the ethanolysis of ethylene- and 2-propene-1-sulfonyl chlorides. The relative activity of the corresponding ethyl esters as alkylating agents also was investigated.

Results and Discussion

The previous studies[3-9] of the ethanolysis of aliphatic sulfonyl chlorides have led to the conclusion that substituents sterically affect alcoholysis in the same

(1) (a) From the Ph.D. Dissertation of J. Preston, University of Alabama, 1957. (b) Chemstrand Research Center, Inc., Durham, N. C.

(2) To whom inquiries should be addressed at the Department of Chemistry, The University of Mississippi, University, Miss. 38677.

(3) R. B. Scott, Jr., and R. E. Lutz, *J. Org. Chem.*, **19**, 830 (1954).

(4) R. B. Scott, Jr., and M. S. Heller, *ibid.*, **20**, 1159 (1955).

(5) R. B. Scott, Jr., and M. J. Gordon, *ibid.*, **21**, 385 (1956).

(6) R. B. Scott, Jr., and H. L. McLeod, *ibid.*, **21**, 388 (1956).

(7) R. B. Scott, Jr., and J. B. Gayle, *ibid.*, **21**, 391 (1956).

(8) J. B. Gayle, Dissertation, University of Alabama, 1953.

(9) M. J. Gordon, Dissertation, University of Alabama, 1960.