1976

Some reactions of 2-chloroethanesulfonyl chloride

Paul Zielinski

SOME REACTIONS OF 2-CHLOROETHANESULFONYL CHLORIDE

PART 1: THE FORMATION OF 2-METHYLAMINO-N-OCTADECYLETHANESULFONAMIDE FROM 2-CHLOROETHANESULFONYL CHLORIDE

PART 2: THE FORMATION OF ETHYL ETHENESULFONATE FROM 2-CHLOROETHANESULFONYL CHLORIDE OR ETHENESULFONYL CHLORIDE; A MECHANISTIC STUDY.

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2-Chloroethanesulfonyl chloride (2) was reacted with octadecylamine (3) in the presence of triethylamine to give N-octadecylethenesulfonamide (4), which was reacted with methylamine to give 2-methylamino-N-octadecyl-ethanesulfonamide (1). The first reaction involves formation of the sulfonamide and dehydrohalogenation. The second reaction is a Michael addition. The formation of 1 is favored in a polar, protic medium. An aprotic, less polar medium produces an unwanted di-Michael adduct $CH_3N(CH_2CH_2SO_2NHC_{18}H_{37})_2$ (8), and polymer. The intramolecular hydrogen bonded structure of 1 is discussed.

ABSTRACT

PART 2: THE FORMATION OF ETHYL ETHENESULFONATE FROM 2-CHLOROETHANESULFONYL CHLORIDE OR ETHENESULFONYL CHLORIDE; A MECHANISTIC STUDY.

2-Chloroethanesulfonyl chloride (2) or ethenesulfonyl chloride (11) when added to benzene containing ethanol-d and triethylamine produces undeuterated (14) and some α-monodeuterated ethyl ethenesulfonate (14'). The sulfene $[CH_2=C=SO_2]$ (c) from 11, and possibly $[ClCH_2CH=SO_2]$ (b) from 2, account for the α-monodeuterated ester. Deuterium was not incorporated by simple exchange. There is circumstantial evidence for the 1,3-sigmatropic rearrangement of b to give 11. The reaction of 2-bromoethanesulfonyl chloride (15) with base shows that olefin formation to give 11 is greatly favored over sulfene formation, $[BrCH_2CH=SO_2]$ (g). The sulfene c, and the suspected sulfene b may collapse with triethylamine·HCl to give an undeuterated ester or be trapped by ethanol-d to give an α-monodeuterated ester. The fact that a mixture of esters are produced means that no one process is operating exclusively in Scheme II.

PART 1: THE FORMATION OF 2-METHYLAMINO-N-OCTADECYLETHANESULFONAMIDE FROM 2-CHLOROETHANESULFONYL CHLORIDE.

INTRODUCTION

The synthesis of 2-methylamino-N-octadecylethanesulfonamide (1) from

$$CH_3NHCH_2CH_2SO_2NHC_{18}H_{37}$$

1

2-chloroethanesulfonyl chloride (2) was studied to evaluate its economics

$$ClCH_2CH_2SO_2Cl$$

2

and feasibility. Compound 2 was reacted with octadecylamine (3) in the presence of triethylamine to give N-octadecylethenesulfonamide (4).

$$ClCH_2CH_2SO_2Cl + C_{18}H_{37}NH_2 \xrightarrow{2\ Et_3N} CH_2{=}CHSO_2NHC_{18}H_{37} \qquad \text{I}$$

2 3 4

Compound 4 was reacted with methylamine to give 1.

$$CH_2{=}CHSO_2NHC_{18}H_{37} + CH_3NH_2 \longrightarrow CH_3NHCH_2CH_2SO_2NHC_{18}H_{37} \qquad \text{II}$$

4 1

Reaction I involves formation of the sulfonamide and dehydrohalogenation. Reaction II may be considered a Michael addition, i.e. the addition of a nucleophile to an activated double bond.

HISTORICAL

In 1885 Leymann[1] reported that 2 (1 mole) reacted with aniline (3 moles) to yield 2-phenylaminoethanesulfonanilide ($\phi NHCH_2CH_2SO_2NH\phi$) (5) and a small amount of "phenylanhydrotaurine". Sixteen years later, Autenrieth and Rudolph[2] identified Leymann's "phenylanhydrotaurine" as ethenesulfonanilide ($CH_2{=}CHSO_2NH\phi$) (6).

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[1] H. Leymann, Chem. Ber. 18, 869 (1885).

[2] W. Autenreith and P. Rudolph, ibid. 34, 3467 (1901).

$$ClCH_2CH_2SO_2Cl + \phi NH_2 \longrightarrow \phi NHCH_2CH_2SO_2NH\phi + CH_2{=}CHSO_2NH\phi \qquad III$$

$$\underline{2} \qquad\qquad \underline{5} \qquad\qquad \underline{6}$$

In 1945 Goldberg[3] repeated Leymann's work and reacted 2 with other aliphatic and aromatic amines. An attempt to isolate 2-chloroethanesulfonanilide ($ClCH_2CH_2SO_2NH\phi$) failed. Compound 2 (1 mole) was reacted with aniline (2 moles) in acetone at 8-10°C. Compound 6 and a small amount of 5 were found. Similar results were obtained with p-toluidine (H_2N-C$_6$H$_4$-CH_3), p-anisidine (H_2N-C$_6$H$_4$-OCH_3), and p-phenetidine (H_2N-C$_6$H$_4$-OCH_2CH_3). With aliphatic amines (i.e. cyclohexylamine, piperidine) only N,N'-disubstituted taurinamides (C$_6$H$_{11}$-$NHCH_2CH_2SO_2NH$-C$_6$H$_{11}$, C$_5$H$_{10}$N-$CH_2CH_2SO_2$-NC$_5$H$_{10}$) were obtained.

Goldberg reasoned that three reactions are involved when 2-chloroethanesulfonyl chloride (2) is treated with amines:

(a) the formation of the sulfonamide

(b) dehydrohalogenation

(c) addition of the amine to the double bond.

The rates of both a and b are fast. The rate of c depends on the structure and nucleophilicity of the amine. Reaction c is favored by an unhindered, very nucleophilic amine. A hindered, less nucleophilic amine will disfavor c.

In 1954, Kostsova[4] and coworkers reported substituted ethenesulfonanilides formed from 2 and p-nitroaniline, 2-aminopyridine, and those aromatic amines employed by Goldberg.

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[3]A. A. Goldberg, J. Chem. Soc., 464 (1945).

[4]A. G. Kostsova, L. S. Shvetsova, and I. I. Kalganova, Zh. Obshch. Khim. 24, 1397 (1954).

Petrov and Nelmysheva[5] reacted 2 (1 mole) with dimethylamine (3 moles) or diethylamine (3 moles) at -10° to yield the corresponding ethenesulfonamides ($CH_2=CHSO_2NR_2$, R=CH_3, CH_2CH_3). When an excess of the amine was used, disubstituted taurinamides were formed ($R_2NCH_2CH_2SO_2NR_2$, R=CH_3, CH_2CH_3).

In 1972 Kostosova[6] added to his earlier work. Compound 2 (1 mole) and aniline (3 moles) in warm Et_2O gave a 50% yield of 6. In refluxing benzene the yield of 6 was 70%. When aniline was in eight fold excess the only product formed was 5 in 70% yield.

Although 2-chloroethanesulfonamides have not been isolated in the presence of amines, a few have been reported.[7] The compounds reported in this reference are azo dyes and their structures are too complex to be given here. Hydrogen chloride may be added across the double bond of some ethenesulfonamides to yield the corresponding 2-chloroethanesulfonamides. However in this study, 4 in benzene would not add HCl at 25°. The same was true of the ethenesulfonamides prepared by Goldberg.

RESULTS AND DISCUSSION

On the basis of Goldberg's work, it was anticipated that 4 could further react with 3 to give the undesired 2-octadecylamino-N-octadecylethanesulfonamide (7).

$$ClCH_2CH_2SO_2Cl + C_{18}H_{37}NH_2 \xrightarrow{2\ Et_3N} CH_2=CHSO_2NHC_{18}H_{37} \qquad \text{I}$$

2 3 4

$$3 + 4 \longrightarrow C_{18}H_{37}NHCH_2CH_2SO_2NHC_{18}H_{37} \qquad \text{IV}$$

7

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[5]K. A. Petrov and A. A. Nelmysheva, ibid. 29, 1494 (1959).

[6]A. G. Kostsova and I. V. Ol'gert, Khim. Seraorg. Soedin., Soderzh. Neftyakh Neftprod. 9, 270 (1972).

[7]I. Yamase, T. Kitao, N. Kuroki, and K. Konishe, Kogyo Kagaku Zasshi 65, 217 (1962).

It was necessary to design conditions for reaction I to maximize the yield of 4. Assuming that 4 is initially formed followed by 7, unit stoichiometry, low temperature, and short reaction time would favor formation of 4. The poor solubility of 3 in organic solvents was a hinderance. Reaction I was carried out in benzene (25°) to give pure 4 in 50% yield. Compound 7 was detected in the liquors of this reaction by nmr (nuclear magnetic resonance) and ms (mass spectrometry). Furthermore, reaction IV was independently carried out to give a quantitative yield of 7.

Reaction II presented similar problems. The product 1 can further react to give the di-Michael adduct 8. Di-Michael adducts are well known in Michael additions.

$$CH_2{=}CHSO_2NHC_{18}H_{37} + CH_3NH_2 \longrightarrow \underset{\underline{1}}{CH_3NHCH_2CH_2SO_2NHC_{18}H_{37}} \qquad \text{II}$$

$$\underline{1} + \underline{4} \longrightarrow \underset{\underline{8}}{CH_3N(CH_2CH_2SO_2NHC_{18}H_{37})_2} \qquad \text{V}$$

Reaction V was also carried out independently to give 8 in quantitative yield.

VARIATION OF REACTION CONDITIONS FOR REACTION II

Reaction II was carried out a number of ways and the results are summarized in Table 1.

Table 1

Run	Reagent	(molar ratio reagent/4)	Solvent	T, °C	Products (% yield)
1	CH_3NH_2	10	THF	25,60	8(50), Polymer (50)
2	CH_3NH_2	14.3	THF	-20,20	8(~50)[a], 1(~50)[a]
3[b]	40% CH_3NH_2	28	H_2O	90	1(80), 8(low)[c]
4	$CH_3NH_3^+Cl^-$	2	CH_3OH	60	1(~80)[d], 8(low)[d]

[a]Compounds 1 and 8 were detected by ir (infrared spectrometry), ms and the product ratio estimated by nmr.

[b]Carried out in a pressure vessel.

[c]Evidenced by nmr, ir.

[d]Believed on the basis of ir since the spectrum of this material resembled the crude from Run 3.

In Run 1, 8 was identified by ir, ms, nmr in the extract (chloroform). The material which was not extractable had physical properties which were so different from the other octadecyl compounds synthesized (high melting (127-132°), insoluble in common organic solvents) that it was believed to be polymeric. A nmr spectrum could not be obtained due to its insolubility. The mass spectrum was of no help in assigning a structure. The largest fragment detected was m/e 311.3 ($C_{20}H_{41}NO$), the largest sulfur containing m/e 135.0 ($C_4H_9NO_2S$), and the base peak was m/e 120.0 ($C_3H_6NO_2S$).

The product ratio in Run 2 was estimated by nmr. Although the molecular ion of 8 (m/e 749.6) was not found, the ion $C_{18}H_{37}NHSO_2CH_2CH_2NCH_3CH_2CH_2^+$. (m/e 417.3) was detected. Compound 1 was detected by ir. No attempt was made to separate 1 and 8.

The material isolated from Run 3 was mainly 1 as determined by ir, with an impurity believed to be 8. Compound 1 was purified by formation of its hydrochloride followed by neutralization. The hydrochloride of 1 is insoluble in THF. It was independently observed that the hydrochloride of 8 is soluble in THF (40°). The solubility of 8·HCl is due to its greater aliphatic character.

The ir spectrum of the crude material from Run 4 was similar to the crude from Run 3. On this basis, it was believed that the product ratios were similar to Run 3. No attempt was made to purify Run 4.

These four runs show that formation of 1 is favored in a protic, polar medium (water, methanol). An aprotic, less polar medium (THF) favors undesired products. It may be that if 1 is initially formed, hydrogen

bonding between the solvent and the methylamino or sulfonyl function would not allow 1 to further react to give the di-Michael adduct 8.

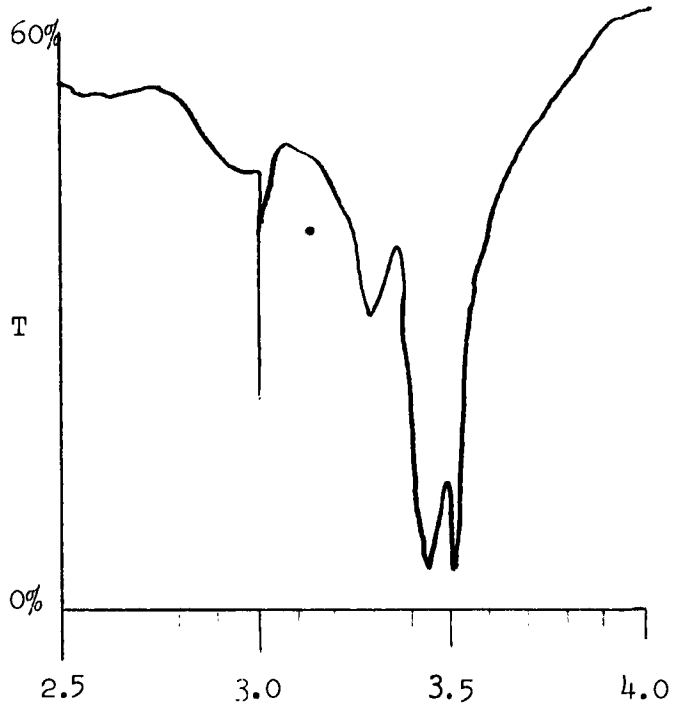
HYDROGEN BONDING AS DETECTED BY IR

The ir (KBr) spectra of 1, 4; 7, 8; and 9, 10 in the 2.50-4.00 micron region are shown in Figures 1a, 1b, and 1c, respectively.

Compound

$CH_3NHCH_2CH_2SO_2NHC_{18}H_{37}$

1



$CH_2{=}CHSO_2NHC_{18}H_{37}$

4

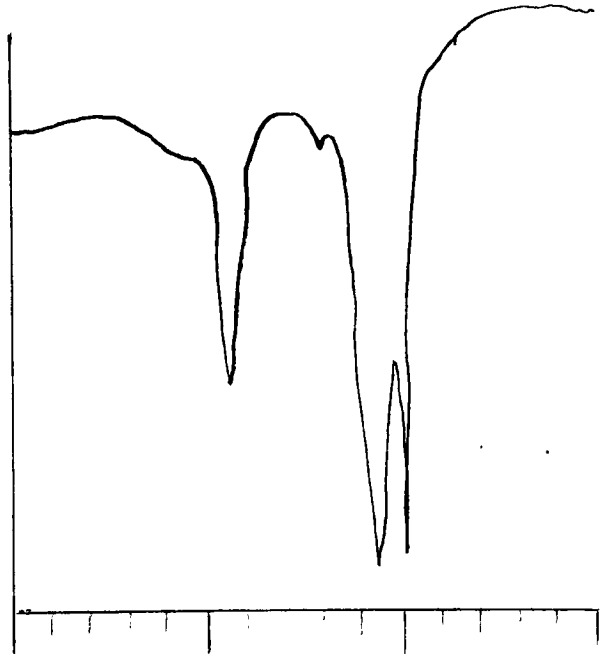
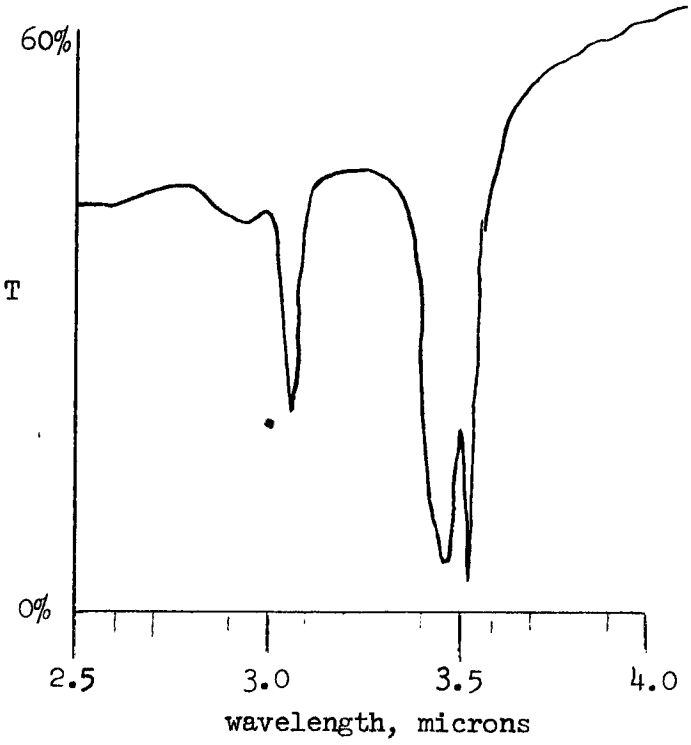


Figure 1a

Compound

$C_{18}H_{37}NHCH_2CH_2SO_2NHC_{18}H_{37}$

7



$CH_3N(CH_2CH_2SO_2NHC_{18}H_{37})_2$

8

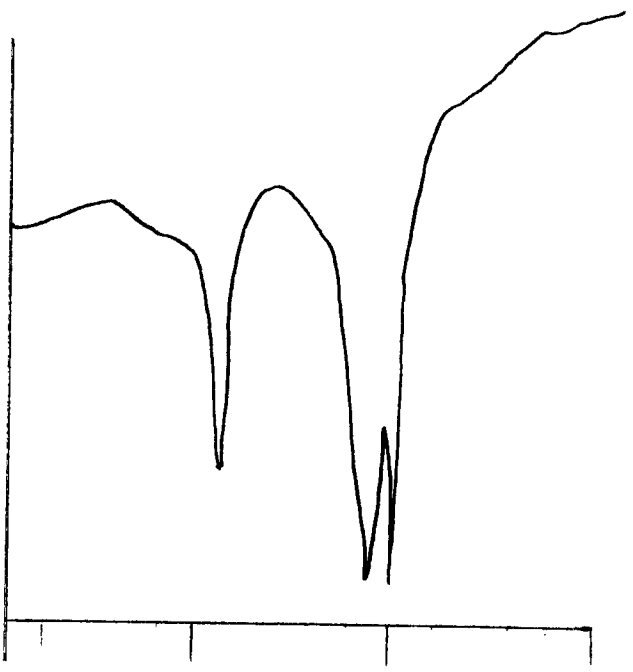
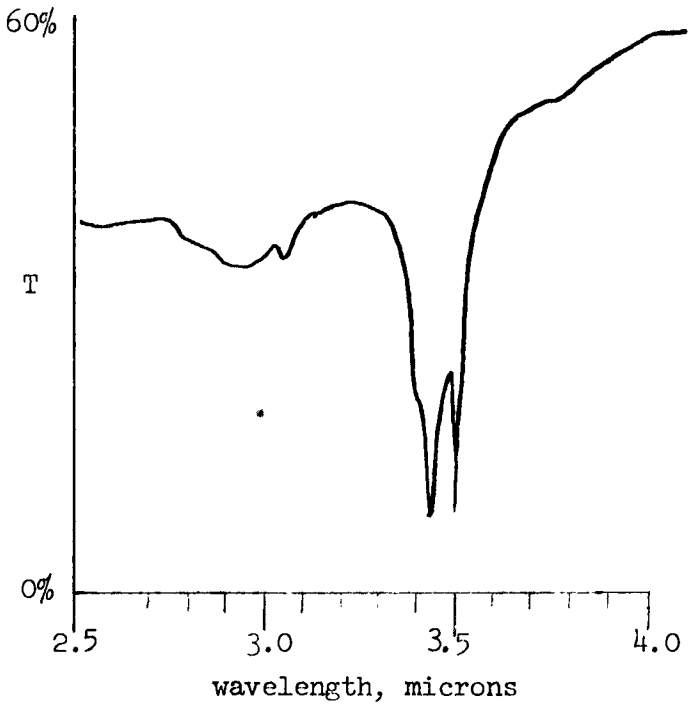


Figure 1b

Compound

$CH_3NHCH_2CH_2SO_2NCH_3C_{18}H_{37}$

9



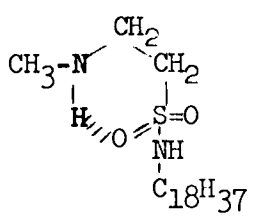
$(CH_3)_2NCH_2CH_2SO_2NHC_{18}H_{37}$

10

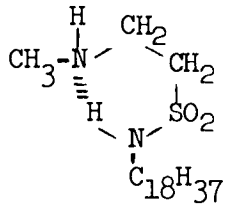
Figure 1c

Compounds 4 and 8 (whose only amino protons are sulfonamido protons) have a narrow, medium intensity band at 3.05 microns ascribed to the sulfonamido N-H stretch. Ir (CCl_4) solution experiments indicate that the proton is intermolecularly hydrogen bonded to an oxygen of a sulfonyl group. Compound 7 has a band similar to 4 and 8 at 3.05 microns. It appears that the additional secondary N-H stretch occurs at the same frequency as the bonded sulfonamido N-H stretch.

Compound 1 has a very sharp, medium intensity band at 3.00 microns and a broad, weak intensity band centered at 3.30 microns. The two bands are due to intramolecular hydrogen bonding, which was verified by ir (CCl_4) solution spectra. Two possible conformations are proposed in Fugure 2. Both are six membered rings formed by intramolecular hydrogen bonding.



A

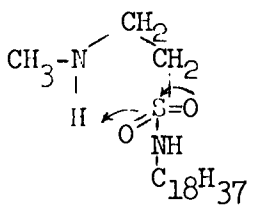


B

Figure 2.

ARGUMENT FOR A

The broad band centered at 3.30 microns is due to hydrogen bonding between the N-methylamino proton and an electron rich oxygen. The oxygen must supply electron density for this hydrogen bond. The other oxygen donates electron density to sulfur to compensate for the electron density lost by the hydrogen bonded oxygen (Figure 3).



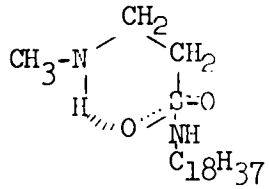


Figure 3.

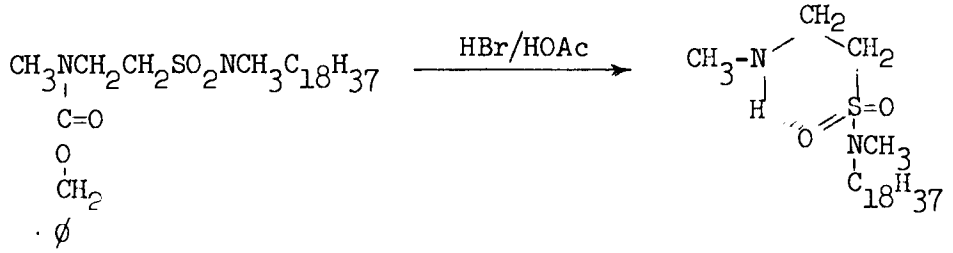
This leaves only one oxygen, instead of two, to form a hydrogen bond with a sulfonamido proton. Furthermore, this oxygen has already donated electron density and is not capable of forming a hydrogen bond. Thus, the free sulfonamido N-H stretch is a very sharp band at shorter wavelength. The bulky octadecyl group in 7 does not allow this type of intramolecular hydrogen bonding. o-Benzenesulfonylphenol and o-benzenesulfinylphenol participate in intramolecular hydrogen bonding similar to A (Figure 4).[8]

Figure 4.

ARGUMENT FOR B

The sulfonamido proton is the most acidic proton in the molecule and the N-methylamino nitrogen the most basic site in the molecule. Again, 7 is too bulky for this type of intramolecular hydrogen bonding.

To resolve this problem it was necessary to synthesize two model compounds, 2-methylamino-N-methyl-N-octadecylethanesulfonamide (9), a compound allowing only an "A" type H-bonding conformation,

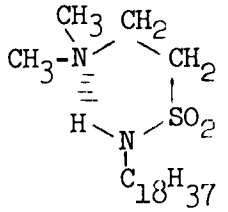


VI

9

[8] C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Company, New York, N.Y., 1962, pp 73-76; E. D. Amstutz, I. M. Hunsberger, and J. J. Chessik, J. Amer. Chem. Soc. 73, 1220 (1951).

and 2-dimethylamino-N-octadecylethanesulfonamide (10), allowing only a "B" type H-bonding conformation.

$CH_2=CHSO_2NHC_{18}H_{37}$ + $(CH_3)_2NH$ ⟶  VII

4

10

It was believed that a methyl group in place of a hydrogen was not bulky enough to hinder hydrogen bonding. Compounds 9 and 10 were identified by nmr and ms.

No N-H stretch was observed for 9. Apparently, the bonded N-H stretch of 9 is so broad that it is not seen, or it occurs in the normal aliphatic C-H stretching region. This implies that the A conformation is correct as written. Compound 10 has a strong, narrow band at 3.05 microns, similar to 4, 7, and 8. This implies that the sulfonamido proton of 10 is intermolecularly hydrogen bonded to a sulfonyl oxygen. These results indicate that 1 is intramolecularly hydrogen bonded as shown by A and not by B.

CONCLUSIONS

Reaction I produces 4, a Michael acceptor. Unit stochiometry, low temperature, and short reaction time hinders the formation of 7, an unwanted Michael adduct. Reaction II produces 1. A polar, protic medium favors the formation of 1. An aprotic, less polar medium produces the unwanted di-Michael adduct 8 and polymer. It is believed that 1 is hydrogen bonded with the solvent in the first case and therefore is not allowed to further react to give unwanted products. Compound 1 exists as a six membered intramolecular hydrogen bonded ring. The N-methylamino proton is hydrogen bonded to an oxygen of the sulfonyl group.

EXPERIMENTAL

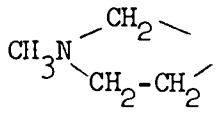
Melting points are uncorrected. Infrared spectra were recorded on a Beckmann IR10 spectrometer, proton nmr spectra on a Varian Associates T60 spectrometer, and mass spectra on an AEI MS902 spectrometer.

N-Octadecylethenesulfonamide (4). Octadecylamine (3) (106.0 g, 0.4 mol), triethylamine (88.0 g, 0.88 mol) and benzene (800 ml) were warmed to obtain solution, then cooled to 25° in an ice bath. 2-Chloroethanesulfonyl chloride (2) (65.2 g, 0.4 mol) in benzene (500 ml) was added as quickly as possible (15 min) to maintain this temperature. The ice bath was removed and the mixture stirred at 25° for 30 minutes. The triethylamine·HCl was filtered and washed with benzene. The filtrate was concentrated under vacuum and the residue dissolved in THF (800 ml) and filtered to remove additional salt. The filtrate was concentrated under vacuum and the residue crystallized from hexane (1400 ml) to give 4 (71.0 g, 50% yield), m.p. 63-64°. Selected spectral data: ir (KBr) 3.05 microns (m, NH), 3.28 (w, CH_2=CH), 7.65 and 8.85 (s, SO_2), 10.4 (m, C=C). nmr ($CDCl_3$) δ6.8-5.9 (m, 3H, CH_2=CH), 4.9 (broad t, 1H, NH), 3.0 (broad m, 2H, $NHCH_2C_{17}H_{35}$), 1.8-1.0 (broad s, 32H, $CH_2(CH_2)_{16}CH_3$), 0.9 (broad t, 3H, $(CH_2)_{16}CH_3$), ms (relative intensity) 359.6 (1) P, 268.3 (20) $NHC_{18}H_{37}$, 120.0 (100) CH_2=$CHSO_2NHCH_2$, 91.0 (11) CH_2=$CHSO_2$.

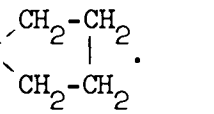
2-Octadecylamino-N-octadecylethanesulfonamide (7). Octadecylamine (3) (5.3 g, 0.02 mol) and N-octadecylethenesulfonamide (4) (7.2 g, 0.02 mol) were refluxed in THF (100 ml) for 3 hours. The solvent was removed under vacuum to give 7 (12.0 g, 95%), m.p. 94-97°. The CH_2=CH group was absent in both the ir and nmr. ir (KBr) 3.05 microns, (m, NH), 7.75 and 8.88 (s, SO_2). nmr ($CDCl_3$) δ3.2-2.4 (broad m, 10H, $CH_2NHCH_2CH_2SO_2NHCH_2$) 1.3 (broad s, 64 H, $CH_3(CH_2)_{16}CH_2$), 0.9 (broad t, 6H, $(CH_2)_{17}CH_3$). ms (relative intensity) 628.6 (0.4) P, 403.3 (2) $CH_2CH_2NHCH_2CH_2SO_2NHC_{18}H_{37}$ 389.3 (15)

$CH_2NHCH_2CH_2SO_2NHC_{18}H_{37}$, 268.3 (17) $C_{18}H_{37}NH$, 120.0 (39) $CH_2{=}CHSO_2NHCH_2$, 30.0 (100) CH_2NH_2. The last two ions result from rearrangement.

Di-Michael adduct (8). N-Octadecylethenesulfonamide (4) (7.2 g, 0.02 mol), and 2-methylamino-N-octadecylethanesulfonamide (1) (7.8 g, 0.02 mol) were refluxed in THF (60 ml) for 1 hour. The solvent was removed under vacuum to give 8 (15.0 g, 100%) m.p. 123-125° (softens 115°). The $CH_2{=}CH$ group was absent in both the ir and nmr. ir (KBr) 3.05 microns (s, NH), 7.7 and 8.85 (s, SO_2). nmr ($CDCl_3$) δ5.5 (broad s, 2H, NH), 3.3-2.2 (broad m, 15H, $\underline{CH_3}N(\underline{CH_2CH_2}SO_2NH\underline{CH_2}C_{17}H_{35})_2$), 0.9 (broad d, 6H, $(CH_2)_{17}\underline{CH_3}$). ms (relative intensity) (A molecular ion was not found.) 417.3 (1) $C_{18}H_{37}NHSO_2CH_2CH_2NCH_3CH_2CH_2$, 135.0 (2)



, 120.0 (100) $CH_2{=}CHSO_2NHCH_2$, 85.1 (3)



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2-Methylamino-N-octadecylethanesulfonamide (1). Run 1. Methylamine (10.0 g, 0.32 mol) in THF (100 ml, -10°) was added to N-octadecylethene-sulfonamide (4) (11.0 g, 0.03 mol) in THF (100 ml). The mixture was stirred at 25° for 1 hour, then at 60° for 30 minutes. The mixture was cooled and filtered. The white solid was slurried in hexane (200 ml) and collected (12.1 g). The chloroform soluble portion of this solid was determined by ir, nmr, ms to be the di-Michael adduct (8) (6.0 g, 50%). The insoluble portion was believed to be polymeric (6.0 g, 50%), m.p. 127-132°.

Run 2. N-Octadecylethenesulfonamide (4) (16.0 g, 0.045 mol) in THF (150 ml) was added to a solution of methylamine (20.0 g, 0.645 mol) in THF (150 ml, -20°) over 30 minutes. The solution was stirred for 2 hours as the temperature rose to 20°. The solvent was removed under vacuum and the resulting white solid slurried in hexane (200 ml) to give a 50:50 mixture (16.0 g) of the di-Michael adduct (8) (50%) and 2-methylamino-N-

octadecylethanesulfonamide (1) (50%). The compounds were detected by ir, nmr, ms and the product ratio estimated by nmr.

Run 3. N-Octadecylethenesulfonamide (4) (18.0 g, 0.05 mol) and 40% aqueous methylamine (100 ml, 28 mol) were heated at 90° in a closed vessel for 30 minutes. The solvent was removed under vacuum to give a white solid, believed to be a complex of the sulfonamide and methylamine. Further heating under vacuum at 90° changed the solid to an oil. The oil was crystallized from hexane (200 ml) to give crude 2-methylamino-N-octadecylethanesulfonamide (1) (17.0 g, 87%). An impurity, the di-Michael adduct (8) was detected by ir. The crude 1 was dissolved in THF (200 ml) and HCl was bubbled in to obtain 1·HCl. The salt was filtered at 40° and washed with THF (200 ml, 40°). The salt was dissolved in aqueous ethanol and made basic with Na_2CO_3. The solvent was removed under vacuum and the residue extracted with hexane to give 1 (15.7 g, 80%), m.p. 79-81°. ir (KBr) 3.0 microns (m, NH), 3.3 (broad w, NH), 7.75, 7.85, 8.80, 8.90 (s, SO_2). nmr ($CDCl_3$) δ3.9 (broad s, 2H, $CH_3\underline{NH}CH_2CH_2SO_2\underline{NH}C_{18}H_{37}$), 3.2-3.0 (broad m, 6H, $CH_3NHCH_2CH_2SO_2NHCH_2C_{17}H_{35}$), 2.4 (s, 3H, CH_3N), 1.3 (broad s, 32H, $CH_2(CH_2)_{16}CH_3$), 0.9 (broad t, 3H, $(CH_2)_{17}CH_3$). ms (relative intensity) 390.3 (1.38) P, 268.3 (8) $NHC_{18}H_{37}$, 151.1 (7) $CH_3NHCH_2CH_2SO_2NHCH_2$, 57.1 (100) $CH_3NHCH{=}CH_2$, 44.0 (40) $H_3NCH{=}CH_2$.

Run 4. N-Octadecylethenesulfonamide (4) (3.6 g, 0.01 mol) and methylamine hydrochloride (1.34 g, 0.02 mol) were refluxed in methanol (100 ml) for 1 hour. The mixture was stirred with solid Na_2CO_3, the solvent removed under vacuum, and the residue crystallized from hexane. The ir spectrum of this material (3.3 g, 85%) was similar to the crude from Run 3.

2-Methylamino-N-methyl-N-octadecylethanesulfonamide (9).

2-(N-Benzyloxycarbonyl-N-methyl)amino-N-methyl-N-octadecylethanesulfonamide (11.0 g, 0.02 mol) and HBr (30% in acetic acid, 100 ml) were stirred in acetic acid (200 ml) at 40° for 1 hour. The solvent was removed under

vacuum at 30°. The residue was slurried in ethanol, filtered, and washed to give 9·HBr. The salt was dissolved in aqueous ethanol, made basic with Na_2CO_3, and the solvent removed under vacuum. The residue was crystallized from hexane to give 9 (5.0 g, 50%) m.p. 48-50°. ir (KBr) 7.60 and 8.90 microns (s, SO_2). nmr ($CDCl_3$) δ3.2-3.0 (broad m, 6H, $NCH_2CH_2SO_2NCH_2C_{17}H_{35}$), 2.8 (s, 3H, $NCH_3C_{18}H_{37}$), 2.4 (s, 3H, $CH_3NCH_2CH_2SO_2$), 1.2 (broad s, 32H, $CH_2(CH_2)_{16}CH_3$), 0.9 (broad d, 3H, $(CH_2)_{17}CH_3$). ms (relative intensity) 404.3 (1) P, 303.3 (5) $SONCH_3C_{18}H_{37}$, 284.3 (35) $H_2NCH_3C_{18}H_{37}$, 282.3 (31) $CH_2{=}NHC_{18}H_{37}$, 122 (5) $CH_3NHCH_2CH_2SO_2$, 59.1 (35) $CH_3NHCH_2CH_3$, 58.1 (21) $CH_3NH_2CH{=}CH_2$, 57.1 (100) $CH_3NHCH{=}CH_2$, 44.0 (96) $H_3NCH{=}CH_2$.

2-Dimethylamino-N-octadecylethanesulfonamide (10). N-Octadecylethenesulfonamide (4) (3.6 g, 0.01 mol) and dimethylamine (1.35 g, 0.03 mol) were stirred in ethanol (100 ml) at 25° for 3 hours. The solvent was removed under vacuum and the residue crystallized from hexane (30 ml) to give 10 (3.0 g, 75%), m.p. 78-80°. ir (KBr) 3.05 microns (s, NH), 7.70 and 8.80 (s, SO_2). nmr ($CDCl_3$) δ4.9 (broad s, 1H, NH), 3.3-2.6 (broad m, 6H, $NCH_2CH_2SO_2NCH_2$), 2.3 (s, 6H, $(CH_3)_2N$), 1.3 (broad s, 32H, $CH_2(CH_2)_{16}CH_3$), 0.9 (broad d, 3H, $(CH_2)_{17}CH_3$). ms (relative intensity) 404.3 (1) P, 136.0 (8) $(CH_3)_2NCH_2CH_2SO_2$, 72.1 (8) $(CH_3)_2NHCH{=}CH_2$, 71.1 (58) $(CH_3)_2NCH{=}CH_2$, 58.1 (100) $(CH_3)_2N{=}CH_2$.

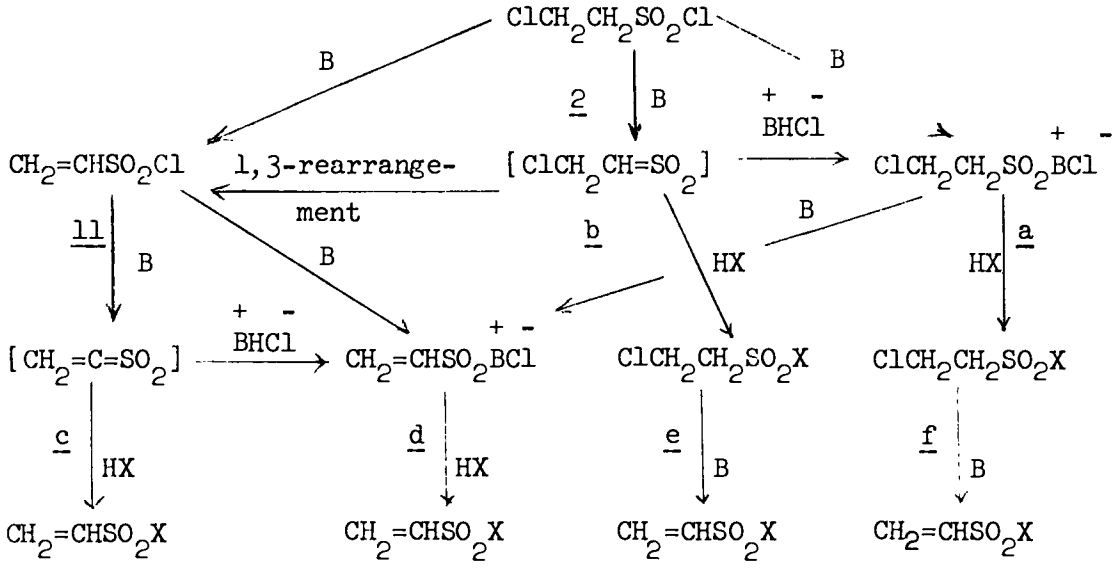
PART 2: THE FORMATION OF ETHYL ETHENESULFONATE FROM 2-CHLOROETHANESULFONYL CHLORIDE OR ETHENESULFONYL CHLORIDE; A MECHANISTIC STUDY.

INTRODUCTION

Part I of this paper described the reaction of 2-chloroethanesulfonyl chloride (2) with octadecylamine (3) in the presence of triethylamine to give N-octadecylethenesulfonamide (4).

$$\underset{1}{ClCH_2CH_2SO_2Cl} + \underset{3}{C_{18}H_{37}NH_2} \xrightarrow{Et_3N} \underset{4}{CH_2{=}CHSO_2NHC_{18}H_{37}} \qquad \text{I}$$

Scheme I shows four proposed mechanistic pathways for this reaction.* The base triethylamine has been replaced by the symbol B, and the nucleophile octadecylamine by HX.

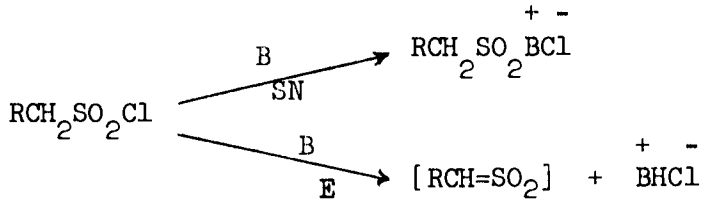


Scheme I

This scheme includes sulfene intermediates $[ClCH_2CH{=}SO_2]$ (b) and $[CH_2{=}C{=}SO_2]$ (c). It is well known that when a sulfonyl chloride (or bromide, or anhydride) with at least one α-hydrogen is treated with base, nucleophilic substitution competes with elimination to form a sulfonium salt or

*Although these reactions may be reversible, reverse arrows have been omitted in Schemes I and II for the sake of clarity.

sulfene respectively.



These intermediates then react with a nucleophile to give the same products.

$$RCH_2SO_2\overset{+}{B}Cl^- + HX \longrightarrow RCH_2SO_2X + \overset{+}{B}HCl^-$$

$$[RCH{=}SO_2] + HX \longrightarrow RCH_2SO_2X$$

The present case is complicated because 2-chloroethanesulfonyl chloride (2) can conceivably undergo elimination to yield ethenesulfonyl chloride (11), the sulfene [$ClCH_2CH{=}SO_2$] (b), or the sulfonium salt a.

HISTORICAL

Sulfenes are reactive intermediates; none have been isolated. The proof for their existence lies in their ketene-like reactions. Three reviews have been published in the last decade.[9-11]

Wedekind and Schenk[12] proposed the name "sulfene" and attempted to synthesize phenylsulfene [$\phi CH{=}SO_2$] in 1911. Phenylmethanesulfonyl chloride (ϕCH_2SO_2Cl) was reacted with triethylamine to yield trans-stilbene ($\phi CH{=}CH\phi$). They proposed the following reaction sequence.

$$\phi CH_2SO_2Cl + Et_3N \longrightarrow [\phi CH{=}SO_2] + \overset{+}{Et_3}NHCl^-$$

$$[\phi CH{=}SO_2] \longrightarrow \phi\dot{C}H + SO_2$$

$$2\ \phi\dot{C}H \longrightarrow \phi CH{=}CH\phi$$

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[9] G. Opitz, Angew. Chem., Int. Ed. Engl. 6, 107 (1967).

[10] W. E. Truce and L. K. Liu, Mech. React. Sulfur Compounds 4, 145 (1969).

[11] J. F. King, Accounts Chem. Res. 8, 10 (1975).

[12] E. Wedekind and D. Schenk, Chem. Ber. 44, 198 (1911).

A standard test for sulfene intermediacy is to use a deuterated nucleophile as a sulfene trap.[13-15] Thus one deuterium is incorporated α to the sulfonyl group.

$$[RCH{=}SO_2] \quad + \quad DX \longrightarrow RCHDSO_2X$$

The absence of dideuteration proves that deuterium is not incorporated by simple exchange.

King and Lee[16] applied a kinetic test for sulfene intermediacy. Since attempts to isolate a sulfene or observe one as a transitory intermediate had failed, they reasoned that the sulfene is consumed rapidly, and the measured rate of reaction should be independent of the concentration of the sulfene trap. They found this to be true of the reaction

$$CH_3SO_2Cl \quad + \quad Et_3N \quad + \quad ROH \longrightarrow CH_3SO_3R \quad + \quad Et_3\overset{+}{N}H\overset{-}{Cl}$$

$$R{=}CH_2CH_2CH_3,\ CH(CH_3)_2$$

which was first order in CH_3SO_2Cl and Et_3N, but zero order in ROH.

Sulfenes may also be characterized by reaction with nucleophilic olefins such as enamines, ynamines, ketene acetals and aminals, and vinyl ethers.[17,18] An example is the reaction of N-(1-propenyl)piperidine (12)

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[13] W. E. Truce, R. W. Campbell, and J. R. Norell, J. Amer. Chem. Soc. 86, 288 (1964).

[14] W. E. Truce and R. W. Campbell, ibid. 88, 3599 (1966).

[15] J. F. King and T. Durst, ibid. 86, 287 (1964); 87, 5684 (1965).

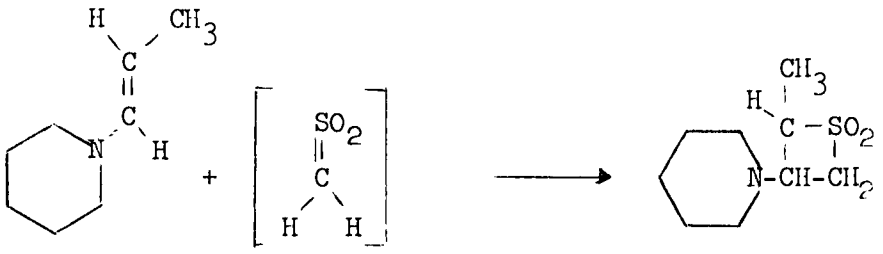
[16] J. F. King and T. W. S. Lee, ibid. 91, 6524 (1969).

[17] H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N.Y., 1967.

[18] L. L. Muller and J. Hamer, "Synthesis of Heterocyclic Four-Membered Rings," Interscience, New York, N.Y., 1967, pp 212-240.

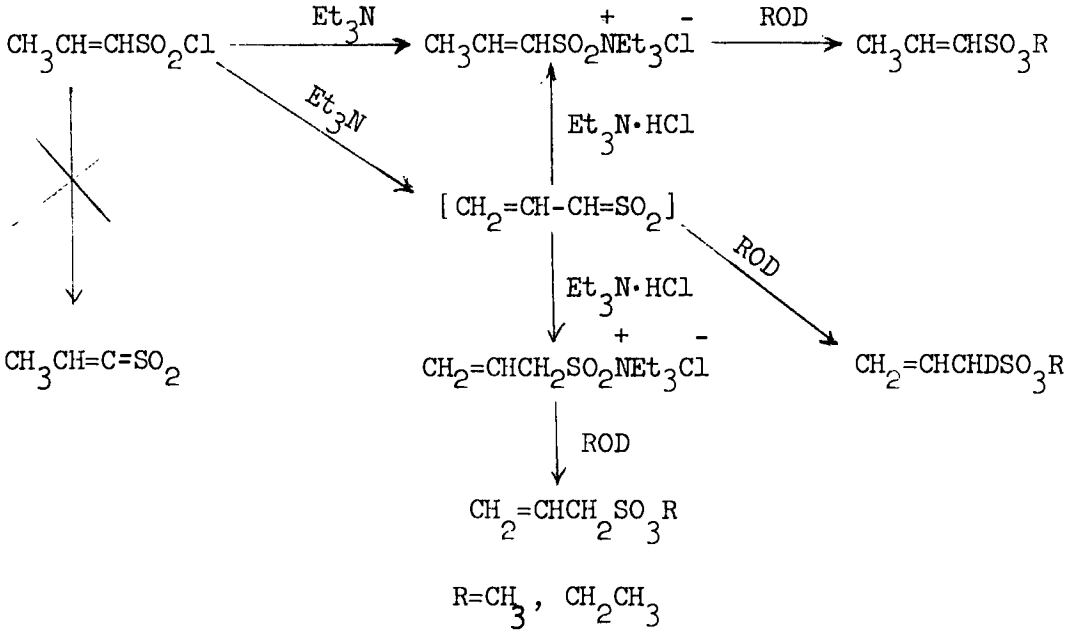
with CH_3SO_2Cl to give the 4-membered sulfone, 2-methyl-3-piperidinothietane-1,1-dioxide (13).[19]

$$CH_3SO_2Cl + Et_3N \longrightarrow [CH_2{=}SO_2] + Et_3\overset{+}{N}H\overset{-}{Cl}$$



12 13

Truce and Campbell[14] reacted propene-1-sulfonyl chloride ($CH_3CH{=}CHSO_2Cl$) with triethylamine and methanol-d or ethanol-d. Direct displacement, isomerization of the double bond, and 1,4-elimination to give vinylsulfene [$CH_2{=}CH{-}CH{=}SO_2$] were observed, but no 1,2-elimination to give the cumulated sulfene [$CH_3CH{=}C{=}SO_2$] was observed.



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[19] G. Opitz and H. Adolph, Angew. Chem., Int. Ed. Engl. 1, 113 (1962).

It is interesting to note that the cumulated sulfene [$CH_3CH{=}C{=}SO_2$] which was not observed by Truce and Campbell is a derivative of the cumulated sulfene [$CH_2{=}C{=}SO_2$] (c) observed in the present work.

Le Berre and coworkers[20], in their work on synthesis of sulfobetaines ($\geqslant\overset{+}{N}CH_2CH_2SO_3^-$) from tertiary amines and ethenesulfonyl chloride (11), reported circumstantial evidence for the intermediate sulfene complex [$\geqslant\overset{+}{N}CH_2CH{=}SO_2$, Cl^-].

King and Harding[21] subjected 11 to flash thermolysis (1100°) and produced α-chloroacetaldehyde. They proposed the following reaction sequence.

$$\underset{\underline{11}}{CH_2{=}CHSO_2Cl} \xrightarrow[1100°]{\triangle} \underset{\underline{b}}{[ClCH_2CH{=}SO_2]} \longrightarrow ClCH_2\overset{O}{\overset{\|}{C}}H + SO$$

The sulfene intermediate b is also considered in the present study of the formation of ethyl ethenesulfonate (14).

The base catalyzed hydrolysis of alkanesulfonyl chlorides and arylmethanesulfonate esters (ϕCH_2SO_2OR) where OR is a good leaving group (e.g., 2,4-dinitrophenyl, 2,6-dinitrophenyl, 4-chloro-2-nitrophenyl, 2-chloro-4-nitrophenyl) proceed via a concerted E2 mechanism.[14,16,22,23]

The hydrolysis rates of 2 under various conditions have been determined.[24,25] Preston and Scott[26] have studied the ethanolysis of 11. They observed a

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[20] A. Le Berre, A. Etienne, and B. Dumaitre, Bull. Soc. Chim. Fr. 3, 954 (1970).

[21] J. F. King and D. R. K. Harding, Chem. Commun., 959 (1971).

[22] J. F. King and T. W. S. Lee, Can. J. Chem. 49, 3724 (1971).

[23] K. T. Douglas, A. Steltner, and A. Williams, Chem. Commun., 353 (1975).

[24] I. Hedlund, Ark. Kemi, Mineral. Geol. 14A, 6, 1 (1940).

[25] R. Foon and A. N. Hambly, Aust. J. Chem. 15, 684 (1962).

[26] J. Preston and R. B. Scott, J. Org. Chem. 33, 4343 (1968).

large peak at m/e 91 in the mass spectrum of 11 corresponding to $CH_2=CHSO_2^+$. and the fact that 14 readily alkylates ethanol.

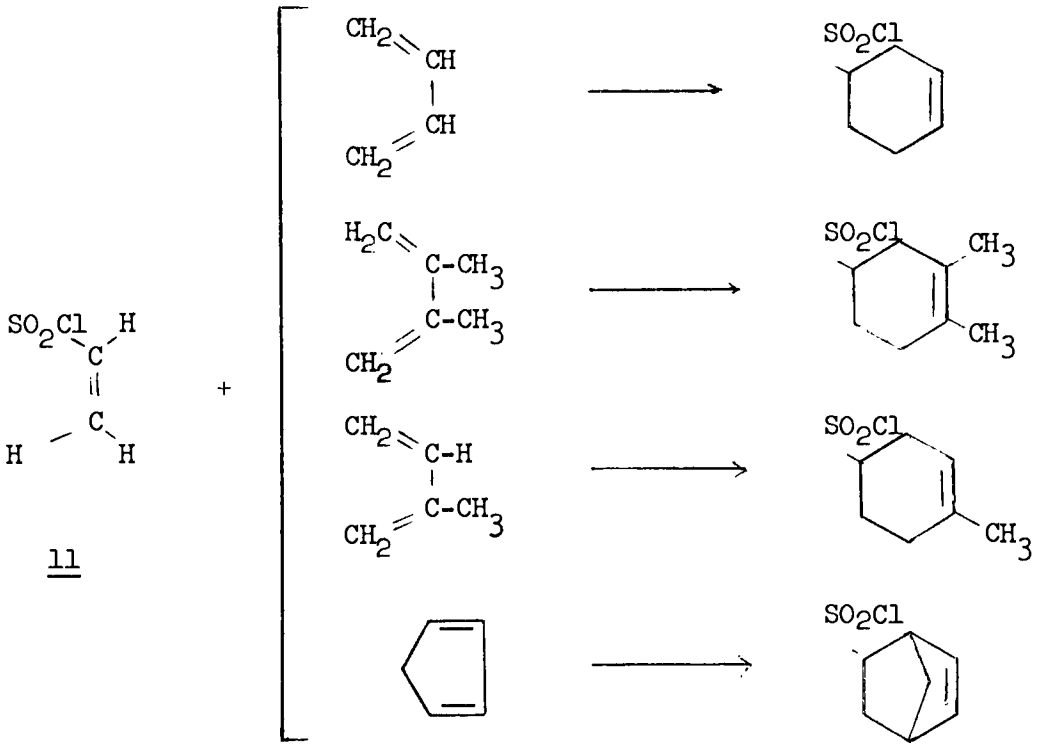
$$CH_2=CHSO_3Et + EtOH \longrightarrow CH_2=CHSO_3H + Et_2O \qquad \text{VIII}$$

14

Both of these observations were made in the present study.

Berdnikov and Aminova[27] found that the Hückel molecular orbital method correctly predicted the polarographic behavior of 11. Ethenesulfonyl chloride (11) was reduced with a break of the S-Cl bond. Molecular orbital calculations for sulfenes have been made by a number of workers.[28,29] It was concluded that electron-donating substituents should stabilize sulfenes.

Ethenesulfonyl chloride (11) may also react through its olefinic bond with dienes to give Diels-Alder adducts.[30]



11

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[27] E. A. Berdnikov and R. M. Aminova, Dokl. Akad. Nauk SSSR 209, 607 (1973).

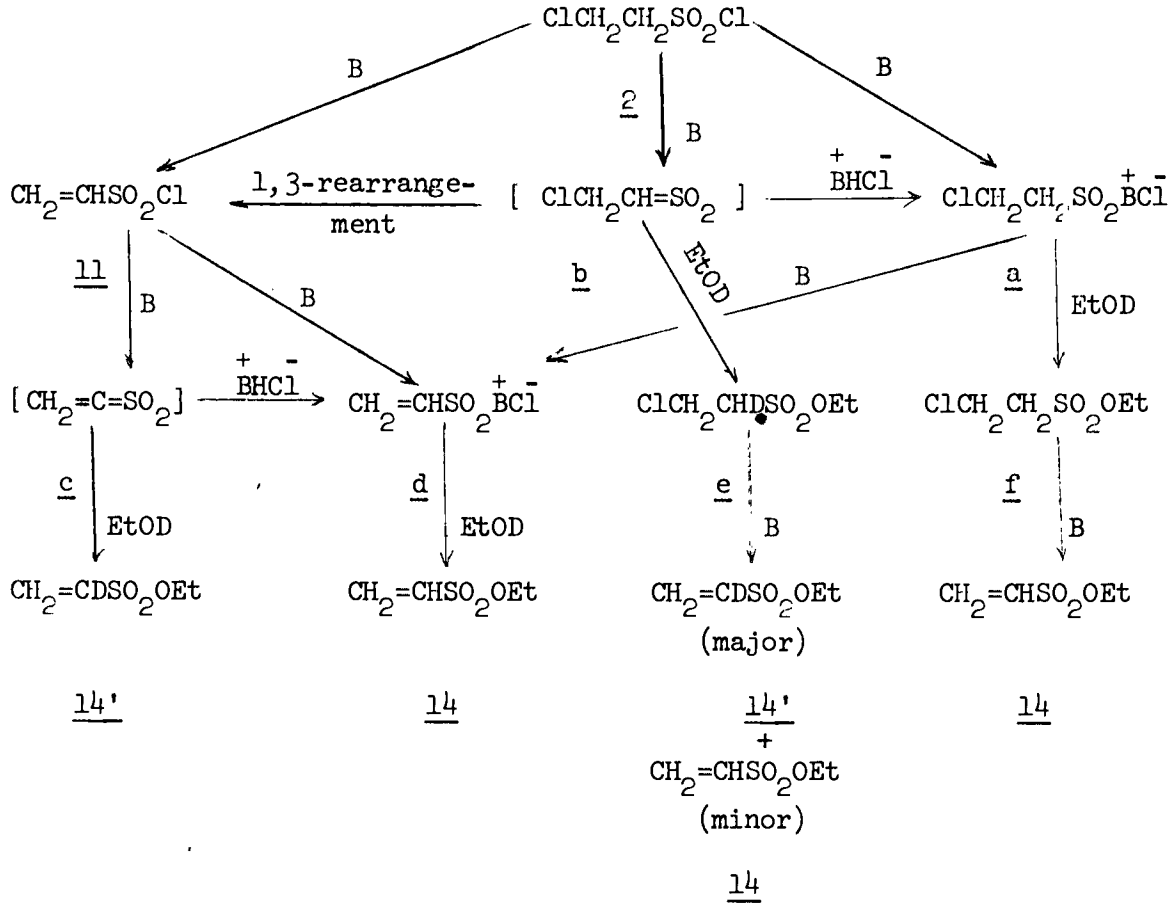
[28] J. P. Snyder, J. Org. Chem. 38, 3965 (1973).

[29] K. N. Houk, R. W. Strozier and J. A. Hall, Tetrahedron Lett. 11, 897 (1974).

[30] H. R. Snyder, H. V. Anderson, and D. P. Hallada, J. Amer. Chem. Soc. 73, 3258 (1951).

RESULTS AND DISCUSSION

Scheme II shows the results of substituting EtOD for HX.

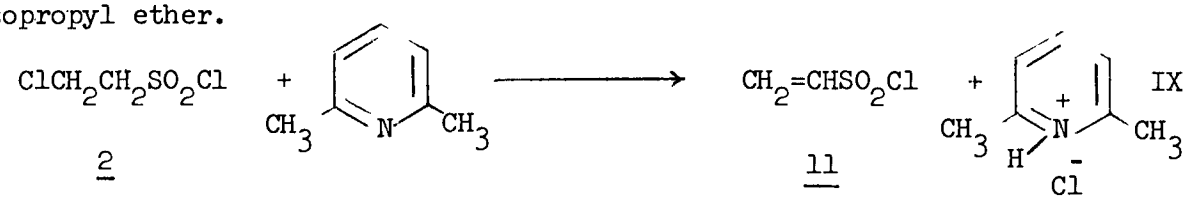


Scheme II

Two of these pathways incorporate deuterium, two do not.

In a series of experiments, 2-chloroethanesulfonyl chloride (2) or ethenesulfonyl chloride (11) was added to benzene at 20° containing triethylamine and ethanol-d. Ethyl ethenesulfonate (14,14') was produced in 44-92% yield containing 5.3 to 17.8% of the α-monodeuterated species.

Ethenesulfonyl chloride (11) was produced in 52% yield by adding 2,6-lutidine in isopropyl ether to 2-chloroethanesulfonyl chloride (2) in isopropyl ether.



Rondestvedt[31] reported that reaction IX was carried out in ethyl ether to produce ethenesulfonyl chloride (11) in 72% yield. This yield could not be duplicated in this study. When reaction IX was carried out in ethyl ether and the ether removed, the residue was determined by nmr to be ethenesulfonyl chloride (11) (47%), 2-chloroethanesulfonyl chloride (2) (25%) and ethyl ethenesulfonate (14) (25%), the result of 11 reacting with solvent.

$$CH_2{=}CHSO_2Cl + Et_2O \longrightarrow [CH_2{=}CHSO_2Cl \cdot O(Et)Et] \longrightarrow CH_2{=}CHSO_2OEt + EtCl \qquad X$$

11   14

When the sterically hindered isopropyl ether was used as the solvent, the residue was ethenesulfonyl chloride (11) (85%) and 2-chloroethanesulfonyl chloride (2) (15%). No isopropyl ethenesulfonate was found.

2-Chloroethanesulfonyl chloride (2) dissolved in benzene was added to benzene containing triethylamine (2.2 equivalents) and ethanol-d (1 or 2 equivalents) to produce undeuterated (14) and α-monodeuterated ethyl ethenesulfonate (14').

$$ClCH_2CH_2SO_2Cl + X\ EtOD \xrightarrow{2Et_3N} CH_2{=}CHSO_2OEt + CH_2{=}CDSO_2OEt \qquad XI$$

2   (X = 1,2)   14 major   14' minor

Ethenesulfonyl chloride (11) was treated with triethylamine (1.1 equivalents) and ethanol-d (1 or 2 equivalents) to produce the same esters.

$$CH_2{=}CHSO_2Cl + X\ EtOD \xrightarrow{Et_3N} CH_2{=}CHSO_2OEt + CH_2{=}CDSO_2OEt \qquad XII$$

11   (X = 1,2)   14 major   14' minor

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[31] C. S. Rondestvedt, Jr., J. Amer. Chem. Soc. 76, 1926, (1954).

The results of reactions XI and XII are given in Table 2.

Table 2

Results of formation of ethyl ethenesulfonate (14), (14') from ethanol-d.

Sulfonyl chloride	Et_3N (eq.)	EtOD (eq.)	ester (% yield)	Composition (14')/(14)
$ClCH_2CH_2SO_2Cl$ (2)	2.2	1	44	7.7/92.3
$ClCH_2CH_2SO_2Cl$ (2)	2.2	2	92	16.0/84.0
$CH_2=CHSO_2Cl$ (11)	1.1	1	48	5.3/94.7
$CH_2=CHSO_2Cl$ (11)	1.1	2	70	17.8/82.2

Deuterium incorporation was determined by mass spectrometry. Ethyl ethenesulfonate (14) produces the base peak $CH_2=CHSO_2^+$. (m/e 91) and the intense ion (50% of base peak) $CH_2=CHSO_2OCH_2^+$. (m/e 121). Associated with with these are ions of m/e 92 and m/e 122 due to $^{12}C^{13}CH_3O_2S$, $^{12}C_2H_2DO_2S$, $^{12}C_2H_4O_2S$ and $^{12}C_2{}^{13}CH_5O_3S$, $^{12}C_3H_4DO_3S$ respectively. The intensity of the 92 and 122 ions in an ester produced from ethanol-d were compared to the 92 and 122 ions found in an undeuterated standard. Ions of m/e 93 and 123 corresponding to dideuteration were not observed.

Deuterium was not incorporated by simple exchange as evidenced by the absence of dideuterated ions in the mass spectrum. Furthermore, 2-chloroethanesulfonyl chloride (2), ethenesulfonyl chloride (11), and undeuterated ethyl ethenesulfonate (14) were separately stirred in benzene containing triethylamine, triethylamine·HCl, and ethanol-d. Compounds 2, 11, and 14 that were recovered did not contain deuterium in excess of natural abundance. In addition, triethylamine·HCl in benzene containing triethylamine did not exchange with EtOD.

Thus, the deuterated ester $CH_2=CDSO_2OEt$ (14') could only be produced from the sulfene [$ClCH_2CH=SO_2$] (b) or the cumulated sulfene [$CH_2=C=SO_2$] (c). Although the production of an α-monodeuterated ester from 2 need not come from b, the α-monodeuterated ester produced from 11 must come from c. These results constitute the first evidence for the existence of this sulfene.

Reactions XI and XII with 1 equivalent of ethanol-d produced ester of nearly the same composition in similar yields. Reactions XI and XII with 2 equivalents of ethanol-d produced ester of similar composition (two to three times more deuterium than the first case) but in different yield. The difference in yield can be explained by a "salt effect". The stoichiometric equations for reactions XI and XII with 2 equivalents of ethanol are:

$$ClCH_2CH_2SO_2Cl + 2\ Et_3N + 2\ EtOH \longrightarrow$$

2

$$CH_2=CHSO_2OEt + 2\ Et_3N\cdot HCl + EtOH \qquad \text{XI}$$

14

$$CH_2=CHSO_2Cl + Et_3N + 2\ EtOH \longrightarrow$$

11

$$CH_2=CHSO_2OEt + Et_3N\cdot HCl + EtOH \qquad \text{XII}$$

14

Ethyl ethenesulfonate (14) is known to be a good alkylating agent.[20,26] In the case of reaction XII above, the Et_3NHCl salt was filtered from the reaction mixture and the solvent removed from the filtrate to yield the crude ester and salt. The ir spectrum of this salt showed the presence of sulfonate anion. In the case of reaction XI above, as with XI and XII with 1 equivalent of ethanol-d, the $Et_3N\cdot HCl$ salt was filtered from the reaction mixture and the solvent removed from the filtrate to yield the crude ester only. When reaction XI is carried out with 2 equivalents of ethanol, the remaining

equivalent of ethanol solvates the 2 equivalents of salt. In reaction XII, the remaining equivalent of EtOH is not entirely solvated to 1 equivalent of $Et_3N \cdot HCl$. Some of the ester is lost by alkylation of the ethanol.

$$CH_2{=}CHSO_2OEt + EtOH \longrightarrow [CH_2{=}CHSO_2OEt] \longrightarrow CH_2{=}CHSO_2OH + EtOEt \qquad \text{VIII}$$

14

This explains the additional salt in the residue and the reduced yield of ester.

When reaction XI and XII were carried out with 2 equivalents of ethanol-d, the ratio of α-monodeuterated ester to undeuterated ester increased two to three times. These results indicate that at least some sulfene $[CH_2{=}C{=}SO_2]$ (c), and possibly $[ClCH_2CH{=}SO_2]$ (b), is initially formed. Sulfene c, and the unconfirmed sulfene b can either collapse with Et_3NHCl and yield normal substitution products, or be trapped by ethanol-d to yield α-monodeuterated ester.

$$[ClCH_2CH{=}SO_2] \quad \text{b}$$

$$\xrightarrow{Et_3N \cdot HCl} ClCH_2CH_2SO_2\overset{+}{N}Et_3\overset{-}{Cl} \quad \text{a} \xrightarrow[Et_3N]{EtOD} CH_2{=}CHSO_3Et \quad 14 \qquad \text{XI'}$$

$$\xrightarrow{EtOD} ClCH_2CHDSO_3Et \quad \text{e} \xrightarrow{Et_3N} CH_2{=}CDSO_3Et \quad 14' \text{ major} + CH_2{=}CHSO_3Et \quad 14 \text{ minor}$$

$$[CH_2{=}C{=}SO_2] \quad \text{c}$$

$$\xrightarrow{Et_3N \cdot HCl} CH_2{=}CHSO_2\overset{+}{N}Et_3\overset{-}{Cl} \quad \text{d} \xrightarrow{EtOD} CH_2{=}CHSO_3Et \quad 14 \qquad \text{XII'}$$

$$\xrightarrow{EtOD} CH_2{=}CDSO_3Et \quad 14'$$

An increase in ethanol-d causes more sulfene to be trapped and produces more α-monodeuterated ester. This effect has been observed by Truce and Campbell.[14]

Schemes I and II include a possible 1,3-sigmatropic rearrangement.

$$[ClCH_2CH{=}SO_2] \longrightarrow CH_2{=}CHSO_2Cl \qquad \text{XIII}$$

b 11

These rearrangements (where an all carbon framework is concerned) are rare in the thermal mode. However, Woodward and Hoffmann[32] state that when the migrating group has an available low-lying π orbital the process may be altered. In the present case, chlorine is migrating to sulfur. Both atoms have low-lying d orbitals.

To help resolve this problem, 2-bromoethanesulfonyl chloride (15) was treated with triethylamine in benzene. A 1,3-sigmatropic rearrangement of the bromo analog of b, i.e. $[BrCH_2CH{=}SO_2]$ (g), would yield the previously unreported ethenesulfonyl bromide (16). Scheme III shows the formation of 16.

$$BrCH_2CH_2SO_2Cl \xrightarrow{B} CH_2{=}CHSO_2Cl \qquad \text{XIV}$$

15 11

$$BrCH_2CH_2SO_2Cl \xrightarrow{B} [BrCH_2CH{=}SO_2] \longrightarrow CH_2{=}CHSO_2Br \qquad \text{XIII'}$$

15 g 16

Scheme III

The salt formed in this reaction was filtered, the solvent removed from the filtrate, and the residue distilled to yield a mixture of 11, 15, 16, (61%, 31%, 7%). It is interesting to note that 11 was formed in nine-fold excess over the sulfene rearrangement product 16. Thus olefin

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[32] R. Hoffmann and R. B. Woodward, Accounts Chem. Res. 1, 17 (1968).

formation from 15, and conceivably 2, to yield ethenesulfonyl chloride (11) is favored over formation of the sulfene g or b. The analysis was performed by chemical ionization (methane) gc mass spectrometry.

It was thought that 16 may have been formed by simple exchange and not via g. To test this, ethenesulfonyl chloride (11) was stirred in benzene containing triethylamine·HBr and triethylamine. Little exchange occurred. A 50/1 mixture of 11/16 was recovered. These experiments indicate that a 1,3-sigmatropic rearrangement may be occurring in Scheme III. It must be noted that the d orbitals of bromine are of lower energy than those of chlorine. To properly test Scheme II for a 1,3-sigmatropic rearrangement it would be necessary to use isotopically labeled 2, $^{37}ClCH_2CH_2SO_2Cl$.

CONCLUSIONS

2-Chloroethanesulfonyl chloride (2) or ethenesulfonyl chloride (11) when added to benzene containing ethanol-d and triethylamine produce undeuterated (14) and some α-monodeuterated ethyl ethenesulfonate (14'). The sulfene [$CH_2=C=SO_2$] (c) from 11, and possibly [$ClCH_2CH=SO_2$] (b) from 2, account for the α-monodeuterated ester. There is circumstantial evidence for the 1,3-sigmatropic rearrangement of b to give 11. The reaction of 2-bromoethanesulfonyl chloride (15) with base shows that olefin formation to give 11 is greatly favored over sulfene formation, [$BrCH_2CH=SO_2$](g). The sulfene c, and the suspected sulfene b may collapse with triethylamine·HCl to give an undeuterated ester or be trapped by ethanol-d to give an α-monodeuterated ester. The fact that a mixture of esters are produced means that no one process is operating exclusively in Scheme II.

EXPERIMENTAL

Boiling points are uncorrected. Infrared spectra were recorded on a Beckmann IR10 spectrometer, proton nmr spectra on a Varian Associates T60 spectrometer, and mass spectra on either an AEI MS902 or Hewlett Packard 5930A spectrometer.

Ethenesulfonyl chloride (11). 2,6-Lutidine (107.2 g, 1 mol) in isopropyl ether (200 ml) was added over 15 minutes to 2-chloroethanesulfonyl chloride (2) (163.0 g, 1 mol) in isopropyl ether (600 ml) at -40°. The mixture was stirred for 1 hour and allowed to warm to 20°. Additional ether (600 ml) was added and the salt was filtered. Additional salt precipitated out of the filtrate and a second filtration was required. The filtrate was concentrated under vacuum at 25°. THF (600 ml) was added to precipitate the remaining salt. The filtrate was concentrated under vacuum at 25° to yield 95.0 g of a 6/1 mixture of 11 and 2, as determined by nmr. Distillation gave pure 11 (65.0 g, 52% yield) b.p. 44-56°/7 mm (Lit.[33] b.p. 52-56°/10 mm). Selected spectral data: ir(neat) 3.20 and 3.25 microns (m, CH_2=CH), 6.20 (w, C=C), 7.25 and 8.55 (s, SO_2), 10.15 and 10.60 (s, m, C=CH_2). nmr(neat) δ7.3-6.2 (m, CH_2=CH). ms (relative intensity) 91.0 (78) CH_2=$CHSO_2$, 36.0 (21), 27.0 (100) CH_2=CH.

Ethyl ethenesulfonate (14,14'). General Procedure. The sulfonyl chloride (0.4 mol) in benzene (500 ml) was added to benzene (800 ml) containing triethylamine (10% excess) and ethanol-d (0.4 or 0.8 mol) over 15 minutes. The reaction temperature was maintained at 20° by an ice bath. The ice bath was removed and the mixture stirred for 30 minutes. The salt was filtered and washed with benzene (100 ml). The filtrate was concentrated under vacuum and the residue distilled to give 14,14', b.p. 86-88°/5 mm (Lit.[26] b.p. 73.5-74.0°/3 mm). Deuterium incorporation was determined by mass spectrometry, but could not be detected by ir nor nmr. Selected spectral data for undeuterated standard: ir(neat) 7.35 and 8.5 microns (s, SO_2). nmr(neat) δ6.9-6.1 (m, 3H, CH_2=CH), 4.4-4.0 (q, 2H, $O\underline{CH_2}CH_3$), 1.5-1.2 (t, 3H, $CH_2\underline{CH_3}$). ms (relative intensity) 135.0 (1) P-1, 121.0 (64) CH_2=$CHSO_3CH_2$, 109.0 (16) $SO_3CH_2CH_3$, 91.0 (100) CH_2=$CHSO_2$, 45.0 (12) OCH_2CH_3, 29.0 (52) CH_2CH_3.

[33] E. F. Landau, J. Amer. Chem. Soc. 69, 1219 (1947).

2-Bromoethanesulfonyl chloride (15). Thionyl chloride (100.0 g, 0.72 mol) was added to 2-bromoethanesulfonic acid sodium salt (91.0 g, 0.43 mol) in DMF (300 ml) over 30 minutes. The temperature was maintained at 25° by an ice bath. The mixture was stirred for 30 minutes, then poured into ice water. The product was extracted with ether and the ether extract washed with ice water. The ether was dried with $MgSO_4$ and the ether removed under vacuum. The residue was distilled to give 15 (60.0 g, 67% yield), b.p. 105-110°/18 mm (Lit.[33] b.p. 82°/5 mm). Selected spectral data: ir(neat) 7.30 and 8.65 microns (s, SO_2). nmr ($CDCl_3$) δ4.3-3.6 (m).

Ethenesulfonyl bromide (16). 2-Bromoethanesulfonyl chloride (15) (40.0 g, 0.19 mol) in benzene (250 ml) was added to triethylamine (22.9 g, 0.21 mol) in benzene (200 ml) over 20 minutes. The temperature was maintained at 25° by an ice bath. The salt was filtered and washed with benzene. The filtrate was concentrated under vacuum and the residue distilled. A low boiling fraction (8.0 g, b.p. 64-80°/18 mm) was determined by chemical ionization (methane) gc mass spectrometry to be a 0.61/0.31/0.07 mixture of 11, 15, 16.

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