Concerning the Electronic Stabilization of Sulfenes[1]

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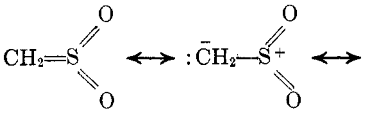
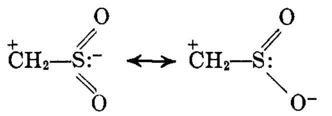
Sulfenes ($R_2C{=}SO_2$) are known to be capable of (2 + 2) π cycloaddition with activated olefins. Condensation occurs in the direction suggestive that the sulfur atom is electrophilic in nature. Molecular orbital calculations bear out this conclusion. Because stable sulfenes have not been prepared, attempts have been made to stabilize such intermediates by delocalization of the partial negative charge on carbon. Carbalkoxy groups and cyclopentadienyl substituents were employed for this purpose. Despite the fact that the derived sulfenes underwent "normal" cycloaddition, they were not stable in solution. The conclusion is reached that perhaps not only electronic delocalization but also simultaneous retardation of polymerization may be required for the ultimate isolation of a sulfene.

Earlier studies have shown that 1,2 elimination of hydrogen halide from primary and secondary sulfonyl chlorides and bromides can be readily achieved with trialkylamines. Under the usual reaction conditions, sulfenes (**1**) are believed to result;[4] however, the high reactivity and instability of these heterocumulenes has precluded their isolation and characterization. An attempt to prepare a stable sulfene has been reported by Opitz and his coworkers. Treatment of methanesulfonyl chloride with triethylamine in acetonitrile at −40° produces mesylsulfene (**2**) which is stable in this medium at −40° for several days (established by capture experiments), but which decomposes when warmed above −30°.[5a] Although **2** was not characterized, these workers did find that **2** could be isolated as a stable trimethylamine adduct.[5b]



1a **1b**



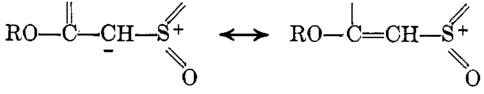
1c **1d**

$CH_3SO_2CH{=}SO_2$

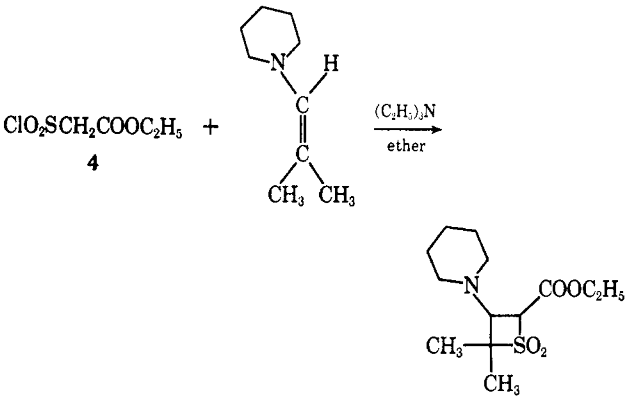
2

The normally observed reactivity of a sulfene is that corresponding to ylide structure **1b**, in which the sulfonyl group exhibits electrophilic character.[4] In the belief that the relationship between structure and stability of sulfenes would very likely obey the same rules as for other ylides,[6] we have attempted to prepare electronically stabilized sulfenes by several methods. Although success was not achieved, the uncovered information provides new insight into the sulfene question, and consequently our results are described at this time.

For the first part of this investigation, α-carbalkoxy groups were examined for their possible assistance in delocalization of the carbanionic character imparted to the α-sulfonyl carbon (**3**). Initially, it was deemed advisable to establish that such sulfenes display "normal" chemical behavior.[7] For this purpose, ethyl (chlorosulfonyl)acetate (**4**) was treated with 1-isobutenylpiperidine in the presence of ethereal triethylamine. The cycloaddition reaction gave **5** in 43% yield. Structural assignment to **5** follows from its spectral properties (see Experimental Section). The stereochemistry of **5** is a point of some interest. The large nmr coupling constant between the two thietane ring protons (9.3 Hz) suggests a dihedral angle between these protons of 0 or 180°.[8,9] The former angle can be achieved only in a planar thietane ring by a *cis* orientation of the bulky piperidino and carbethoxy groups; in this structure an all-eclipsed conformation is seen



3a **3b**



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[2] National Science Foundation Graduate Fellow, 1966–1968; American Chemical Society–Petroleum Research Fund Graduate Fellow, 1968–1969.

[3] NDEA Fellow, 1967–.

[4] For a recent review of sulfene chemistry, see G. Optiz, *Angew. Chem. Intern. Ed. Engl.*, **6**, 107 (1967).

[5] (a) G. Opitz, M. Kleeman, D. Bücher, G. Walz, and K. Rieth, *ibid.*, **5**, 594 (1966); (b) G. Optiz and D. Bücher, *Tetrahedron Lett.*, 5263 (1966).

[6] A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966.

[7] This question has been the subject of a limited amount of earlier work. Fusco, *et al.* [R. Fusco, S. Rossi, S. Maiorana, and G. Pagani, *Gazz Chim. Ital.*, **95**, 774 (1965)], for example, have observed that the action of triethylamine on phenacyl sulfonyl chloride in the absence of an electron-rich olefin results in the formation of a sulfene dimer. Ethyl(chlorosulfonyl)acetate (**4**) is claimed not to react with vinyl ethers, while phenacyl sulfonyl chloride gives (4 + 2) cycloadducts with these ethers as opposed to (2 + 2) adducts with enamines.[4]

[8] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

[9] Earlier work has shown that application of the Karplus correlation to the thietane dioxide ring system is reliable: L. A. Paquette, *J. Org. Chem.*, **29**, 2854 (1964); L. A. Paquette, M. Rosen, and H. Stucki, *ibid.*, **33**, 3020 (1968).

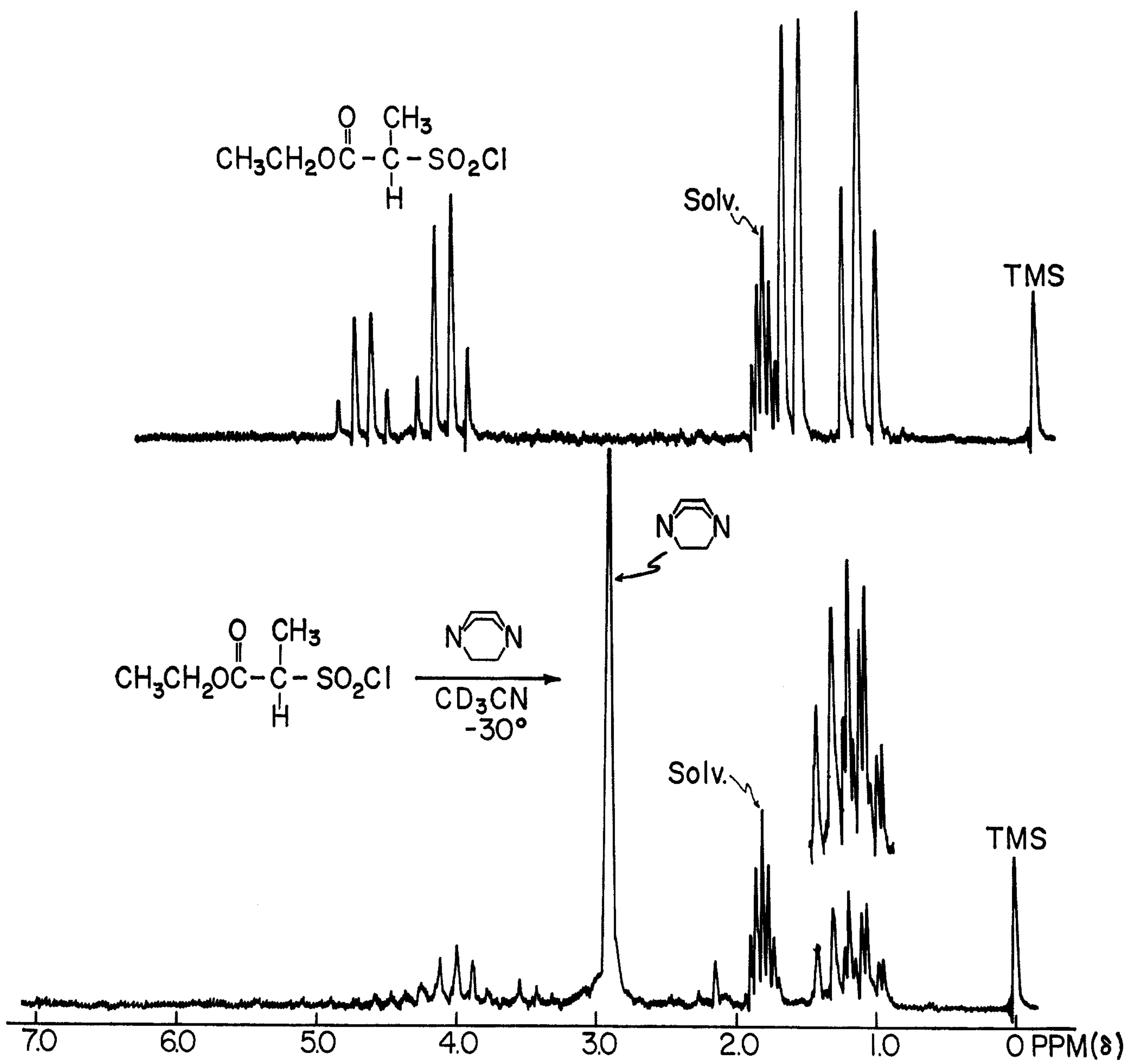
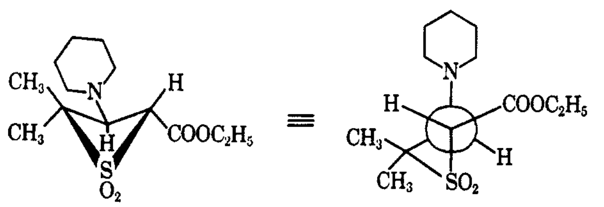


Figure 1.—60-MHz nmr spectrum of **7a** prior to, and subsequent to, the addition of DABCO (CD_3CN solution, −30°).

and thermodynamic instability relative to the *trans* isomer is to be expected. The 180° alignment can be attained only by *trans* substituents in a puckered thietane dioxide ring (**6**).[10] In this structure, a perfectly staggered conformation is present with pseudo-equatorial disposition of the two bulky ring substituents. To distinguish between these two alternatives, **5** was exposed to 0.02 mol equiv of sodium methoxide in methanol. After prolonged treatment, no epimerization was apparent; this observation is congruent with *trans* formulation **6**.



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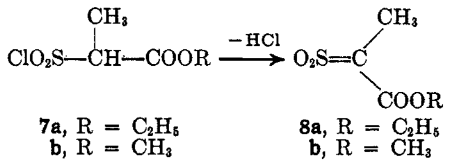
In view of this successful trapping of a carbalkoxysulfene, characterization of such an entity by nmr spectroscopy became the next goal. The possibility was considered that esters of 2-(chlorosulfonyl)propionate (**7**) would be best suited to our studies, since conversion to the corresponding sulfene was expected to result in collapse of the doublet methyl absorption of **7** (Figure 1) to a singlet. Addition of slightly greater than 1 equiv of 1,4-diazabicyclooctane (DABCO)[11] to a cold (−30°) acetonitrile-d_3 solution of ester **7a**,



$$\mathrm{ClO_2S{-}\overset{CH_3}{\overset{|}{C}}H{-}COOR \xrightarrow{-HCl} O_2S{=}C\begin{matrix}\diagup CH_3\\ \diagdown COOR\end{matrix}}$$

7a, R = C_2H_5
b, R = CH_3

8a, R = C_2H_5
b, R = CH_3

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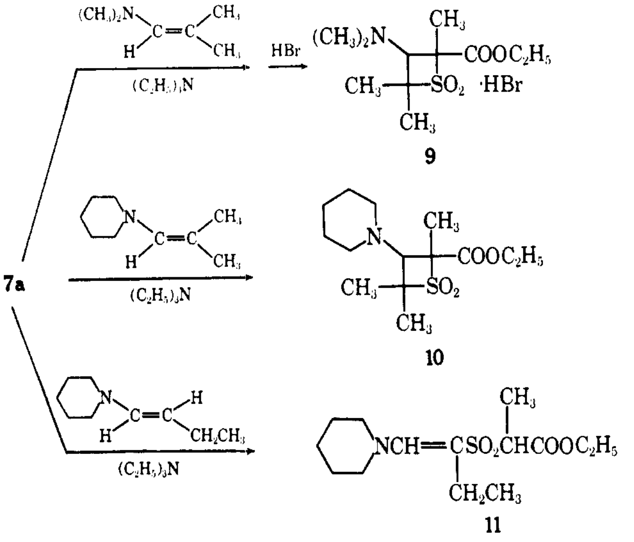
[10] For a review of the evidence in support of the puckered conformation for the thietane dioxide ring system, see L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, **89**, 4102 (1967), footnotes 17–21.

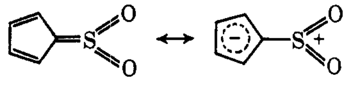
[11] DABCO has been chosen as the tertiary amine because of its exceedingly simple nmr spectrum (see Figure 1).

followed by rapid removal of the precipitated DABCO hydrochloride and nmr determination at this temperature, failed to give interpretable spectral information (Figure 1). The methyl ester **7b** behaved similarly, and the results could be reproduced consistently. The failure of these efforts seemed less surprising when it was discovered that, although **8a** behaved quite normally when generated in the presence of a suitable coreactant (Scheme I), no characterizable products could be isolated if the enamine was added some time (commonly 15–120 min) after the sulfene had been generated. The method of synthesis of **7a** and **7b** and full characterization of adducts **9–11** are described in the Experimental Section.

SCHEME I

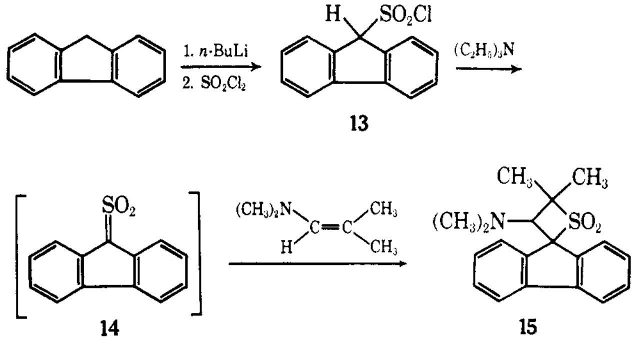


With the removal of carbalkoxy functions as sulfene substituents with sufficient stabilizing influence, attention was directed to a consideration of the sulfonylcyclopentadienes (**12**). This choice was predicated upon the recognized stabilizing capacity of a cyclopentadienyl substituent in ylide structures by virtue of negative charge delocalization in the five-membered ring. Notable examples are diazocyclopentadiene,[12] triphenylphosphonium cyclopentadienylide,[13] and 9-sulfinylfluorene.[14]



12a **12b**

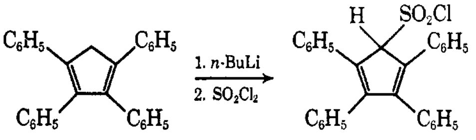
From the synthetic viewpoint, Opitz has generalized that the positioning of two phenyl groups α to a chlorosulfonyl function causes sulfur dioxide elimination, even at room temperature. Over 45 years ago, Wedekind and coworkers reported unsuccessful attempts to prepare 9-fluorenesulfonyl chloride (**13**) in apparent support of this generalization.[15] However, in our hands, fluorenyllithium has been observed to react with excess sulfuryl chloride in ether to afford **13**, mp 86–87.5°, in 32% yield. The structure of **13** was derived from its elemental analysis, its infrared spectrum, which exhibits sulfone stretching bands at 1370, 1180, and 1145 cm^{-1}, and its typical fluorene ultraviolet absorption [$\lambda_{\max}^{\text{isooctane}}$ 235 (ϵ 24,200) and 273 mμ (ϵ 10,000)]. In addition, the nmr spectrum of **13** consists of a one-proton singlet at δ 5.78 and an eight-proton multiplet at δ 7.80. With authentic **13** in hand, it was possible to demonstrate that the derived sulfene (**14**) readily undergoes the typical cycloaddition reaction with enamines. In the presence of N,N-dimethyl-1-isobutenylamine and triethylamine, for example, **13** was transformed into thietane dioxide **15** in 88% yield.



13 **14** **15**

Attempts to prepare stable solutions of **14** were, however, without success. Addition of triethylamine to ether solutions of **13** at various temperatures (−80–0°) in a nitrogen atmosphere resulted in the formation of a dark purple solution which, when filtered to remove amine hydrochloride, became dark yellow. Careful evaporation of the ether invariably afforded a bright yellow solid which was polymeric and which exhibited only very weak sulfone absorption in the infrared. Further, if **13** was exposed to an equimolar amount of triethylamine in the above fashion and N,N-dimethyl-1-isobutenylamine was added at a subsequent time (2–4 hr later), no cycloaddition product (**15**) was produced. Lastly, when a dilute (3.13×10^{-5} *M*) solution of **13** in isooctane was treated with 1 drop of triethylamine in a quartz cell, the ultraviolet absorption of **13** was noted to decay rapidly, and none of the spectral features exhibited by fluorenone or 9-sulfinylfluorene[14] was seen.

In order to examine the effect of phenyl substitution on the stabilizing capability of the cyclopentadiene ring, the preparation of tetraphenylcyclopentadienylsulfonyl chloride (**16**) was attempted. Reaction of tetraphenylcyclopentadienyl lithium with sulfuryl chloride in the predescribed manner gave an initial product which proved to be very labile. A solid was generally obtained whose composition varied from run to run and whose molecular weight (mass spectral analysis) was in the range of a dimeric substance. Further studies were not pursued.



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[12] W. von E. Doering and C. H. DePuy, *J. Amer. Chem. Soc.*, **75**, 5955 (1953).

[13] F. Ramirez and S. Levy, *ibid.*, **79**, 67 (1967).

[14] W. A. Sheppard and J. Dieckmann, *ibid.*, **86**, 1891 (1964).

[15] E. Wedekind and R. Stüsser, *Ber.*, **56**, 1557 (1923); E. Wedekind and D. Schenk, *ibid.*, **44**, 198 (1911).

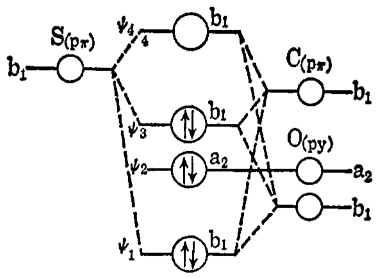
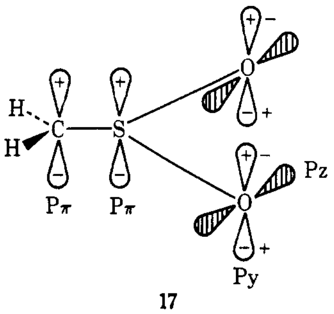


Figure 2.—Molecular orbitals in $CH_2{=}SO_2$.

Discussion

A sulfene molecule can logically be assumed to be planar in its ground state and to consist of sp^2-hybridized carbon and sulfur atoms.[16] If the oxygen atoms are typically sp hybridized, the molecular structure of sulfene is seen to be **17**, the point group of which is C_{2v}. As a result, $C_{(p\pi)}$ and $S_{(p\pi)}$ transform as b_1, while $O_{(py)}$ transforms as b_1, a_2. Assuming that the σ bonding orbitals are very stable and therefore that the σ antibonding orgitals have very high energy, we obtain the schematic energy diagram given in Figure 2. The relative energies of the atomic orbitals are based on the ionization potentials of the relevant atoms.[17] Since the $O_{(pz)}$ electrons are perpendicular to the y plane, they make no net contribution to the π molecular orbital. In view of the fact that only orbitals of like symmetry interact, $S_{(b_1)}$ will mix with $O_{(b_1)}$ and $C_{(b_1)}$, whereas $O_{(a_2)}$ will remain nonbonding. The molecular orbital seen in Figure 2 will then result. Sulfur d orbitals have not beeen considered, since they can be expected to contribute little as a result of their high energy content. It is particularly significant to note that ψ_3 is mostly carbon in nature and that the $C_{p\pi}$–$S_{p\pi}$ electron pair will therefore be polarized toward this atom.



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The above analysis suggests that the lowest ground-state molecular orbital of a sulfene exhibits appreciable negative character on carbon. Despite this fact, we have seen that attempts to stabilize a sulfene by delocalization of this electron pair in a classical sense were not successful. Perhaps the relationship between structure and stability is not dictated totally by such electronic stabilization, but rather is also a question of minimizing simultaneously the rate of polymerization. For this reason, the preparation of sterically hindered sulfenes should perhaps be undertaken.

Experimental Section[18]

2-Carbethoxy-4,4-dimethyl-3-piperidinothietane 1,1-Dioxide (5).—To a cold (−20°) solution of 6.07 g (0.060 mol) of triethylamine and 8.36 g (0.060 mol) of 1-isobutenylpiperidine[19] in 240 ml of anhydrous ether was added dropwise with stirring under nitrogen a solution of 11.2 g (0.060 mol) of ethyl (chlorosulfonyl)-acetate[20] in 75 ml of the same solvent. During the addition, the temperature was not allowed to rise above −15°. Stirring was continued at −16° to −10° for 2 hr and at room temperature for 5 hr. The precipitated triethylamine hydrochloride was separated by filtration and washed with ether. The combined washings and filtrate were evaporated under reduced pressure and the crude solid residue (12.0 g) was recrystallized from aqueous ethanol and dried to give 7.5 g (43%) of **5**, mp 92.5–94°. Further recrystallization from hexane gave an analytical sample: mp 93.5–94.5°; ir $\nu_{\max}^{CCl_4}$ 1742 (C=O), 1330, and 1200 cm^{-1} (SO_2); nmr $\delta_{TMS}^{CCl_4}$ 4.59 (d, $J = 9.3$ Hz, 1 H, CO–C**H**–SO_2), 4.23 (q, $J = 7$ Hz, 2 H, $OC\mathbf{H}_2CH_3$), 3.01 (d, $J = 9.3$ Hz, 1 H, C**H**–N), 2.25 (m, 4 H, α-piperidino protons), 1.4–1.7 with spikes at 1.53 and 1.50 (m, 12 H, remaining piperidino protons and ring methyl groups), and 1.32 ppm (t, $J = 7$ Hz, 3 H, $OCH_2C\mathbf{H}_3$).

Anal. Calcd for $C_{13}H_{23}NO_4S$: C, 53.96; H, 8.01; N, 4.84. Found: C, 54.25; H, 8.01; N, 4.77.

Potassium 1-Carbethoxyethanesulfonate.—To a freshly prepared oxygen-free aqueous solution of potassium sulfite (0.44 mol)[21] was added 76 g (0.42 mol) of ethyl 2-bromopropionate[22] and 70 ml of 95% ethanol. The inhomogeneous mixture was heated at reflux for 13 hr, at which point an additional 5 g of solid potassium sulfite was added and the mixture was refluxed for 2 hr. The mixture was cooled in an ice bath, the solid potassium bromide was filtered, and the filtrate was reduced to near dryness on the rotary evaporator. The residue was recrystallized from absolute ethanol with filtration of additional potassium bromide from the hot solution. Cooling of the filtrate gave a crystalline product (76.7 g, 83%). The material thus prepared still contained a trace of potassium bromide, as revealed by a positive silver nitrate test and a wide melting range (192–205°). Two additional recrystallizations from absolute ethanol produced bromide-free salt: mp 194–196° (lit.[23] mp 214°); ir $\nu_{\max}^{Nujol}$ 1720 (C=O), 1200, and 1040 cm^{-1} (SO_3^-); nmr $\delta_{TPSS}^{D_2O}$ 4.22 (q, $J = 6.8$ Hz, 2 H, $OC\mathbf{H}_2CH_3$), 3.91 (q, $J = 7.0$ Hz, 1 H, $CH_3C\mathbf{H}$), 1.49 (d, $J = 7.0$ Hz, 3 H, $C\mathbf{H}_3CH$), and 1.27 ppm (t, $J = 6.8$ Hz, 3 H, $OCH_2C\mathbf{H}_3$).

Anal. Calcd for $C_5H_9KO_5S$: C, 27.26; H, 4.12; S, 14.56. Found: C, 27.42; H, 4.04; S, 14.29.

Ethyl (2-Chlorosulfonyl)propionate (7a).—A 12.6-g (0.057 mol) sample of dry and finely pulverized potassium 1-carbethoxyethanesulfonate was thoroughly mixed with 14.35 g (0.069 mol, 20% excess) of granular phosphorus pentachloride. After the initial exothermic reaction had subsided, the mixture was heated for 1 hr on the steam bath and kept for 4 hr at room temperature. The resulting phosphorus oxychloride was removed by distillation at 80–90 mm. The residue was shaken with 100 ml of crushed ice and 150 ml of ether. After the aqueous layer was shaken with two additional portions of ether, the combined organic layers were shaken with saturated sodium chloride solution and dried. Distillation afforded 6.51 g (57%) of **7a**: bp 87–89° (0.9 mm); $n^{26}D$ 1.4555; ir $\nu_{\max}^{CCl_4}$ 1735 (C=O) 1380, 1365, 1190, and 1155 cm^{-1} (SO_2); for nmr, see Figure 1.

Methyl (2-Chlorosulfonyl)propionate (7b).—Treatment of 70.2 g (0.42 mol) of commercial methyl 2-bromopropionate with 0.42 mol of potassium sulfite as above resulted in the formation of 56 g (69%) of potassium 1-carbomethoxyethanesulfonate: mp 192–199° from ethanol; ir $\nu_{\max}^{Nujol}$ 1727 (C=O), 1195, and 1035

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(16) It may be contended that sulfenes are in fact nonplanar in view of what is known about the stereochemistry of α-sulfonyl carbanions. Obviously, this is a moot point in the case of nonstabilized sulfenes. However, if the sulfene carbon is substituted with a carbanion stabilizing group (with attendant charge delocalization), then the assumption of planarity for the sulfene is entirely plausible.

(17) H. B. Gray, "Electrons and Chemical Bonding," W. A. Benjamin, Inc., New York, N. Y., 1965, p 29. The following values are pertinent: O, 13.614 eV; C, 11.264 eV; S, 10.357 eV.

(18) Melting points are corrected while boiling points are uncorrected. The infrared spectra were obtained with a Perkin-Elmer Model 237 Infracord spectrometer. The microanalyses were determined by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The nmr spectra were determined with Varian A-60 or A-60A spectrometers. Ultraviolet measurements were made with a Cary Model 14 recording spectrometer.

(19) C. Mannich and H. Davidsen, *Ber.*, **69B**, 2106 (1936).

(20) R. Vieillefosse, *Bull. Soc. Chim. Fr.*, 351 (1947).

(21) H. F. Johnstone, *Inorg. Syn.*, **2**, 166 (1946).

(22) A. I. Vogel, *J. Chem. Soc.*, 644 (1948).

(23) R. Andreasch, *Monatsh. Chem.*, **46**, 639 (1925).

cm^{-1} ($\mathrm{SO_3}$); nmr $\delta_{\mathrm{TPSS}}^{\mathrm{D_2O}}$ 3.96 (q, J = 7.0 Hz, 1 H, $\mathrm{CH_3C\mathbf{H}<}$), 3.77 (s, 3 H, $\mathrm{OCH_3}$), and 1.50 ppm (d, J = 7.0 Hz, 3 H, $\mathrm{C\mathbf{H}_3CH}$).

Anal. Calcd for $\mathrm{C_4H_7KO_5S}$: C, 23.29; H, 3.42. Found: C, 23.03; H, 3.55.

Treatment of 51.6 g (0.25 mol) of this dry salt with 67.8 g (0.325 mol, 30% excess) of powdered phosphorus pentachloride in the predescribed manner afforded 19.9 g (43%) of **7b**: bp 75–78° (1.5 mm); $n^{29}\mathrm{D}$ 1.4607; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1750 (C═O), 1375, 1315, and 1180 cm^{-1} ($\mathrm{SO_2}$); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CD_3CN}}$ 4.84 (q, J = 6.9 Hz, 1 H, $\mathrm{CH_3C\mathbf{H}}$), 3.80 (s, 3 H, $\mathrm{OCH_3}$), and 1.75 ppm (d, J = 6.9 Hz, 3 H, $\mathrm{C\mathbf{H}_3CH}$).

2-Carbethoxy-3-dimethylamino-2,4,4-trimethylthietane 1,1-Dioxide Hydrobromide (**9**).—A solution of 4.0 g (0.02 mol) of **7a** in 20 ml of acetonitrile was added dropwise at −20° under nitrogen to a stirred solution of 2.0 g (0.02 mol) of triethylamine and 2.0 g (0.02 mol) of N,N-dimethyl-1-isobutenylamine[24] in 78 ml of the same solvent. Stirring was continued at −20° for an additional 1.5 hr and then at room temperature for 7 hr. After filtration of the triethylamine hydrochloride, the filtrate was reduced in volume to *ca.* 5 ml. When enough ether was added to return the solution to its original volume, more hydrochloride precipitated along with some yellow material. To the resultant filtrate was added ethereal hydrogen bromide solution until no further solid was produced. This solid was filtered and air dried to give 5.13 g (74%) of **9**: mp 177–178° (from ethanol); ir $\nu_{\max}^{\mathrm{Nujol}}$ 1727 (C═O), 1310, 1265, and 1210 cm^{-1} ($\mathrm{SO_2}$); nmr $\delta_{\mathrm{TPSS}}^{\mathrm{D_2O}}$ 5.18 (s, 1 H, $\overset{+}{\mathrm{N}}\mathrm{-C\mathbf{H}}$), 4.23 (q, J = 7.0 Hz, 2 H, $\mathrm{OC\mathbf{H}_2CH_3}$), 2.70 (br s, 6 H, $\mathrm{(CH_3)_2}\overset{+}{\mathrm{N}}$), 1.55 and 1.40 (s, 3 H and 6 H, respectively, ring methyl groups), and 1.28 ppm (t, J = 7.0 Hz, 3 H, $\mathrm{OCH_2C\mathbf{H}_3}$).

Anal. Calcd for $\mathrm{C_{11}H_{22}BrNO_4S}$: C, 38.38; H, 6.44; N, 4.07; S, 9.31. Found: C, 38.47; H, 6.45; N, 4.06; S, 9.54.

2-Carbethoxy-3-piperidino-2,4,4-trimethylthietane 1,1-Dioxide (**10**).—In a manner similar to that used in the preparation of **5**, 4.17 g (0.03 mol) of 1-isobutenylpiperidine and 6.00 g (0.03 mol) of **7a** were allowed to react in ether solution at −20° in the presence of triethylamine (3.03 g, 0.03 mol). Work-up of the reaction gave 7.49 g (83%) of crude **10**, mp 74–76°. Recrystallization from hexane afforded large white plates: mp 75–76.5°; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1735 (C═O), 1318, and 1250 cm^{-1} ($\mathrm{SO_2}$); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 4.24 (q, J = 7.1 Hz, 2 H, $\mathrm{-OC\mathbf{H}_2CH_3}$), 3.35 (s, 1 H, $\mathrm{N-C\mathbf{H}}$), 2.1–2.4 (m, 4 H, α-piperidino protons), 1.78 (s, 3 H, 2-methyl group), 1.60 and 1.55 (s, 3 H each, *gem*-dimethyl groups), 1.38–1.7 (m, 6 H, remaining piperidino protons), and 1.29 ppm (t, J = 7.1 Hz, $\mathrm{OCH_2C\mathbf{H}_3}$).

Anal. Calcd for $\mathrm{C_{14}H_{25}NO_4S}$: C, 55.42; H, 8.30; N, 4.62; S, 10.57. Found: C, 55.70; H, 8.30; N, 4.78; S, 10.53.

Addition of 1-Butenylpiperidine to 7a.—Treatment of 15.01 g (0.075 mol) of **7a** with a solution of 10.44 g (0.075 mol) of 1-butenylpiperidine[25] and 7.59 g (0.075 mol) of triethylamine in 340 ml of anhydrous ether at −10° as described above yielded 19.7 g (86%) of **11**: mp 41.5–43.0° from ethyl acetate–hexane; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1735 (C═O), 1304, and 1150 cm^{-1} ($\mathrm{SO_2}$); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 6.75 (s, 1 H, vinyl proton), 4.10 (q, J = 7.0 Hz, 2 H, $\mathrm{OC\mathbf{H}_2CH_3}$), 3.69 (q, J = 7.0 Hz, 1 H, $\mathrm{CH_3C\mathbf{H}}$), 3.34 (br, 4 H α-piperidino protons), 2.34 (q, J = 7.5 Hz, 2 H, $\mathrm{-C\mathbf{H}_2CH_3}$), 1.64 (br, 6 H, remaining piperidino protons), 1.40 (d, J = 7.0 Hz, 3 H, $\mathrm{C\mathbf{H}_3CH}$), 1.28 (t, J = 7.0 Hz, 3 H, $\mathrm{OCH_2C\mathbf{H}_3}$), and 1.10 ppm (t, J = 7.5 Hz, 3 H, $\mathrm{-CH_2C\mathbf{H}_3}$).

Anal. Calcd for $\mathrm{C_{14}H_{25}NO_4S}$: C, 55.42; H, 8.31; N, 4.62. Found: C, 55.52; H, 8.24; N, 4.65.

9-Fluorenylsulfonyl Chloride (**13**).—To a cold (0°) stirred solution of 12.5 g (0.075 mol) of fluorene in 150 ml of anhydrous ether was added under a nitrogen atmosphere 50 ml (0.08 mol) of 1.6 *M* *n*-butyllithium in hexane over a period of 15 min. The resulting yellow solution was added dropwise during 1 hr to 50 ml of cold (0°) sulfuryl chloride under nitrogen. The solvent and excess sulfuryl chloride were then evaporated *in vacuo*, methylene chloride (100 ml) was added, and the solution was washed twice with water (200 ml). The organic phase was dried, filtered, and evaporated, and the resultant yellow oil was refrigerated overnight. The crystalline product was triturated with pentane and filtered to yield 6.5 g (32.5%) of **13**. Further recrystallization from chloroform–pentane (1:1) gave pure **13**: mp 86–87.5° dec; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1370, 1180, and 1145 cm^{-1} ($\mathrm{SO_2}$); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.80 (m, 8 H, aromatic protons) and 5.78 ppm (s, 1 H, $\mathrm{C\mathbf{H}SO_2Cl}$); uv $\lambda_{\max}^{\mathrm{isooctane}}$ 235 (ϵ 24,200) and 273 mμ (ϵ 10,000).

Anal. Calcd for $\mathrm{C_{13}H_9ClO_2S}$: C, 59.00; H, 3.43; Cl, 13.42; S, 12.10. Found: C, 58.88; H, 3.49; Cl, 13.40; S, 12.17.

Addition of N,N-Dimethyl-1-isobutenylamine to 13.—To a cold (0°) stirred solution of 0.38 g (3.8 mmol) of N,N-dimethyl-1-isobutenylamine and 0.38 g (3.8 mmol) of triethylamine in 150 ml of anhydrous ether was added dropwise under nitrogen a solution of 1.0 g (3.8 mmol) of **13** in 50 ml of ether during 30 min. The slurry was filtered, the filter cake was washed with acetone, and the combined filtrates were evaporated to give 1.09 g (88%) of white solid. Recrystallization of this material from benzene–ethanol (1:1) afforded pure **15**: mp 179–180° dec; ir $\nu_{\max}^{\mathrm{KBr}}$ 1300, 1160, and 1125 cm^{-1} ($\mathrm{SO_2}$); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.50 (m, 8 H, aromatic prtons), 3.25 (s, 1 H, $\mathrm{N-C\mathbf{H}}$), 2.00 and 1.80 (s, 3 H each, $\mathrm{CH_3-N}$), and 1.73 ppm (s, 6 H, *gem*-dimethyl groups); mass spectrum *m/e* 327.

Anal. Calcd for $\mathrm{C_{19}H_{21}NO_2S}$: C, 69.70; H, 6.44; S, 9.79. Found: C, 69.41; H, 6.44; S, 9.77.

Registry No.— Potassium 1-carbethoxyethanesulfonate, 20449-08-5; potassium 1-carbomethoxyethanesulfonate, 20449-10-9; **5**, 20449-07-4; **7a**, 20449-09-6; **7b**, 20449-11-0; **9**, 20449-12-1; **10**, 20449-13-2; **11**, 20449-14-3; **13**, 20449-15-4; **15**, 20449-16-5.

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