

Episulfonium Salts. I. Carbon vs. Sulfur Attack in the Reaction of Cyclooctene-S-methylepisulfonium Ion with Nucleophiles¹

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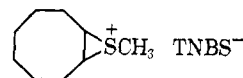
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Abstract: The reaction of cyclooctene-S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate (**1**) with a variety of nucleophilic reagents is shown to occur more often by attack at sulfur to give a sulfenyl compound and cyclooctene than on carbon to give a 1,2-disubstituted cyclooctane. The yields of cyclooctene, formed in the presence of excess cyclohexene, in most cases appear to correlate roughly with the relative "softness" of the attacking nucleophile as defined by the Pearson theory of hard and soft acids and bases.

The concept of an episulfonium ion intermediate has been important in the development of an understanding of organosulfur reaction mechanisms. Kinetic and stereochemical data on the addition of sulfenyl halides to olefins have established the possible intermediacy of episulfonium salts in this important class of reactions.⁴ A recent series of papers,⁵ which has dealt with the additions of various sulfenyl chlorides to substituted olefins and allenes, attempts to delineate the various steric and electronic factors which determine the direction of ring opening of the proposed episulfonium intermediate. Episulfonium salts also have been proposed as intermediates in the additions of sulfur dichloride⁶ and dialkylalkylthiosulfonium salts⁷ to alkenes. Furthermore, episulfonium salts are proposed to be involved in the rate accelerations observed in the solvolysis of β -halo thioethers.⁸

The importance of this concept to a wide variety of mechanistic interpretations of the chemistry of organosulfur compounds can be seen in the proposed intermediacy of episulfonium salts in a number of other systems.

The first physical evidence for the existence of a stable episulfonium salt was provided in 1958⁹ for cyclopentene-S-acetylepissulfonium *p*-toluenesulfonate, but an earlier report¹⁰ suggested that an episulfonium salt had been obtained by methylation of a terpene episulfide. More recently two other episulfonium salts have been prepared: *cis*-cyclooctene-S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate (**1**),⁷ which is the parent compound used in the present study, and a steroidal S-phenylepisulfonium hexafluoroantimonate.¹¹



1

TNBS⁻ = 2,4,6-trinitrobenzenesulfonate anion

It is interesting that reports concerning the reactions of a stable episulfonium salt with nucleophiles other than iodide, methyl mercaptide,^{7b} chloride, and tributylphosphine¹¹ have not been published. Thus, in light of the contribution of episulfonium salts to a variety of organosulfur reaction mechanisms, it was of importance to undertake a study of the reactions of **1** with a number of nucleophiles.

Results

The basis of this study was the nature of the products obtained when an episulfonium salt (**1**) was treated with various nucleophiles. The reaction conditions were such that nucleophilic attack at a carbon atom of the episulfonium ring yielded a different product than that which resulted from nucleophilic attack at the sulfonium sulfur atom.

Table I shows the products of the reaction of episulfonium salt **1** with nucleophiles in the presence of excess cyclohexene. These products may be classified under several categories, according to the nature of their origin.

a. Nucleophilic attack on carbon without involvement of cyclohexene (eq 1). Only two nucleophiles, pyridine and acetate ion, led to 2-substituted cyclooctyl thioethers, **2**. In the case of pyridine, very little cyclooctene (**3**) was found; but in the case of acetate ion, cyclooctene was the major terminus of the cyclooctyl ring system.

b. Nucleophilic attack on the sulfonium sulfur to yield a stable sulfenyl compound (eq 2). As shown in Table I, methyl mercaptide, thiourea, and tributylphosphine reacted with the episulfonium salt to form cyclooctene and a methanesulfenyl compound, **4**, via transfer of the methanesulfenyl group to the nucleophile.

c. Nucleophilic attack on sulfur to form a sulfenyl compound that added to cyclohexene (eq 3). Chloride and bromide ions and dimethyl sulfide led to cyclohexene adducts, **5**.

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(2) U. S. Public Health Service Environmental Science Trainee, 1967-1969.

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(4) N. Kharasch, Ed., "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p 382.

(5) (a) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **88**, 2866 (1966); (b) W. H. Mueller and P. E. Butler, *J. Org. Chem.*, **32**, 2925 (1967); (c) *ibid.*, **33**, 1533, 2111, 2642 (1968); (d) W. A. Thaler, W. H. Mueller, and P. E. Butler, *J. Am. Chem. Soc.*, **90**, 2069 (1968).

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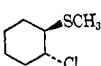
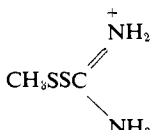
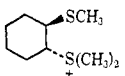
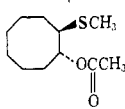
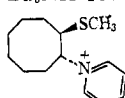
(8) See, for example: S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 828 (1948).

(9) L. Goodman, A. Benitez, and B. R. Baker, *ibid.*, **80**, 1680 (1958).

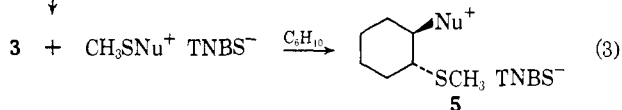
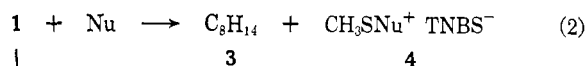
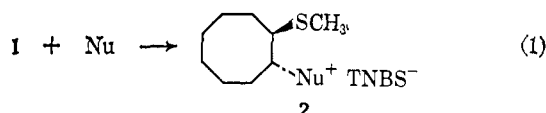
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Table I. Yields and Products for the Reactions of **1** with Nucleophiles

Nucleophile	% cyclooctene ^a	Other products %
I ^{-b}	100	CH ₃ SSCH ₃ (100) ^a + I ₂ (70)
Br ⁻	96	^c
Cl ⁻	98	 (102) ^a
F ⁻	44	
CH ₃ S ^{-b}	100	CH ₃ SSCH ₃ (100) ^a
Thiourea	99	 TNBS ^{-c} (75)
(CH ₃) ₂ S	76 (30 min) 99 (24 hr)	 TNBS ⁻ (62.5, 30 min)
CH ₃ COO ⁻	52	 (16) ^a
CH ₃ COOH	0	Starting material (91)
Bu ₃ P	100	CH ₃ SPBu ₃ TNBS ⁻ (61)
Bu ₃ N	88	Bu ₃ NH ⁺ TNBS ⁻ (60)
Pyridine	15	 TNBS ⁻ (75.7)

^a Yields obtained by gas chromatography. All other yields given are on analytical samples. ^b Reference 7b. ^c Inferred from other results. ^d Other products not identified. ^e TNBS⁻ = 2,4,6-trinitrobenzenesulfonate.



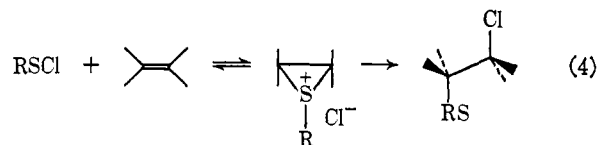
d. Nucleophilic attack on sulfur to form an unstable sulfenyl compound. The reaction of iodide ion with the episulfonium salt leads to dimethyl disulfide, but the process is categorically similar to c because methanesulfenyl iodide cannot be intercepted irreversibly by cyclohexene. Tributylamine, on the other hand, forms the tributylammonium salt by a process that might involve transfer of the methanesulfenyl group to nitrogen followed by decomposition of the product. Finally, fluoride ion yields cyclooctene as the only product that could be identified.

e. Unreactive nucleophiles. Acetic acid fails to react with the episulfonium salt under the reaction conditions chosen for this study.

Discussion

Mechanistic studies of the reaction between sulfenyl halides and alkenes have indicated the possibility of an equilibrium between starting materials and episulfo-

nium intermediate (eq 4).^{12,13} The presence of cyclohexene in large excess as part of the solvent system was, in fact, dictated by these published results.^{12,13} By this means, any methanesulfenyl chloride that might be formed in the reaction of **1** with chloride ion would be trapped by the cyclohexene to give 1-chloro-2-(methylthio)cyclohexane (**5**, where Nu⁺ = Cl). Similar results were found for bromide ion and dimethyl sulfide.



It was established that under the conditions chosen for the reactions, a potential reversibility of the second step of eq 4 was not involved in product control. When 1-chloro-2-(methylthio)cyclooctane (**2**, Nu⁺ = Cl) was dissolved in the reaction solvent in which cyclohexene was in great excess, no transfer of the elements of methanesulfenyl chloride was observed even after a 50-fold increase in reaction time over that employed for the nucleophilic reactions. It is also extremely unlikely that any 1,2-bisthioether (**2**, Nu⁺ = SCH₃) formed from carbon attack by methyl mercaptide ion would spontaneously decompose to dimethyl disulfide and cyclooctene under the reaction conditions employed. Thus any cyclooctene which is produced must arise from attack by the nucleophile at sulfonium sulfur. The fact that no reaction occurs between 1-chloro-2-(methylthio)cyclooctane and cyclohexene (*vide supra*) unequivocally demonstrates that the sulfonium sulfur of **1** is attacked much more rapidly by chloride ion than are the ring carbon atoms.

In order to test the possible effect of cyclohexene on some reactions in which no trapping of sulfenyl compound was observed, the reactions of **1** with pyridine, tributylamine, and tributylphosphine were studied in the same solvent system except that cyclohexene was substituted for cyclohexene. The nature and yields of products were comparable in each case.

The production of tributylammonium 2,4,6-trinitrobenzenesulfonate from tributylamine and **1** does not rule out nucleophilic attack on sulfur. Attempts to prepare the anticipated product, methylthiotributylammonium 2,4,6-trinitrobenzenesulfonate, from tributylamine and methanesulfenyl 2,4,6-trinitrobenzenesulfonate¹⁴ resulted in the production of the tributylammonium salt.

Of all the nucleophiles studied, tributylphosphine appears to be the only one capable of producing cyclooctene *via* a pathway which does not involve nucleophilic attack on the sulfur atom of **1**. Thus, tributylphosphine could react with **1** to produce the methyltributylphosphonium salt **6** and cyclooctene episulfide (**7**) (eq 5). Subsequently, the episulfide could be desulfurized¹⁵ and the final product, methylthiotributylphosphonium 2,4,6-trinitrobenzenesulfonate, could be produced in successive steps as shown in eq 6 and 7. The results cannot exclude this pathway. However,

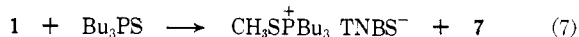
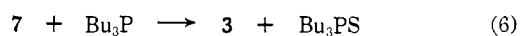
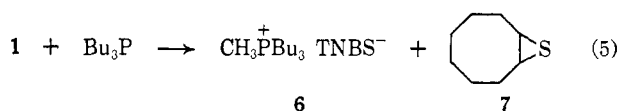
(12) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949).

(13) D. S. Campbell and D. S. Hogg, *J. Chem. Soc.*, 5887 (1965).

(14) G. K. Helmkamp, D. C. Owsley, W. M. Barnes, and H. N. Cassey, *J. Am. Chem. Soc.*, **90**, 1635 (1968).

(15) D. B. Denney and M. J. Boskin, *ibid.*, **82**, 4736 (1960).

the observation of Abikar¹¹ that tributylphosphine completely desulfurizes an S-phenylepisulfonium salt would lend credence to a mechanism in which sulfur is attacked directly by tributylphosphine.



It is interesting to note the insensitivity of **1** to acetic acid. This observation is consistent with the observations of other authors^{12,13,16} on the addition of sulfenyl halides to alkenes in glacial acetic acid. These reactions show the presence of very small amounts of acetate esters in the final products.

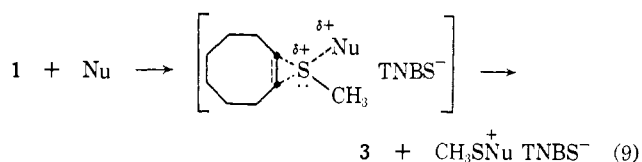
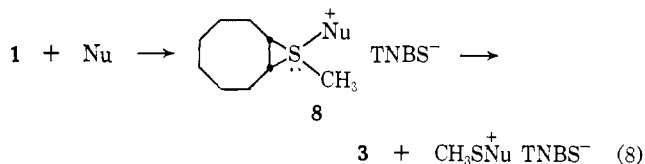
The results of this study are rather surprising. Table I shows that all nucleophilic reagents studied except acetic acid attacked the sulfonium sulfur of **1** to yield cyclooctene. These data indicate highly anomalous behavior on the part of a species that has been proposed as a highly reactive intermediate in a number of organosulfur reactions that proceed by nucleophilic attack on carbon in a product-forming step. Table I shows, furthermore, that all nucleophilic reagents in which the nucleophilic atom is of the third or higher rows of the periodic table attacked **1** to give quantitative yields of cyclooctene. Pyridine was the only nucleophile that opened the ring primarily as shown by the first example (eq 1).

The behavior of **1** that is depicted in Table I might be explained in terms of the empty 3d orbitals possessed by the sulfur atom. It is possible that the effect of both the positive charge¹⁷ and the strained ring of **1** may make the 3d orbitals of sulfur more energetically accessible for a bonding interaction with an attacking nucleophile. At the least, the sulfur atom of **1** must be highly polarizable.

Table I further reveals that it is generally true that the more highly polarizable nucleophiles give higher yields of cyclooctene, while the less polarizable nucleophiles give lower cyclooctene yields and also attack carbon to open the episulfonium ring. This observation is supported by the theory of hard and soft acids and bases as developed by Pearson,¹⁸⁻²⁰ in which it is shown that softer, *i.e.*, more polarizable, electrophilic centers prefer to interact with softer nucleophiles. Our system does demonstrate that the sulfonium sulfur of **1** is more highly polarizable than a ring carbon atom in the same salt. Furthermore, although the Pearson theory is mainly one in which correlations are best shown by kinetic treatments of "acid-base" reactions, the present study does show a rough correlation between the yields of cyclooctene and the relative softness of the nucleophilic reagents studied. Kice²¹ has found such a correlation in the kinetics of acid-catalyzed nucleophilic displacements at sulfenyl sulfur. Kinetic studies in

our system are now in progress to determine the relative rates of reaction of the various nucleophiles with **1**.

Two pathways seem to be the most probable for the desulfurization of **1** by nucleophilic reagents. The former pathway involves the formation of a stable intermediate containing a tetravalent sulfur atom (**8**) (eq 8), while the latter must be an "S_N2-like" displacement on sulfur (eq 9). Both of these proposed pathways are analogous to those proposed for nucleophilic displacements on silicon.²² Furthermore, the intermediate **8** would be isoelectronic about the sulfur atom with the well-known SF₄ molecule. Experiments are now in progress to ascertain which pathway may be taken by the various nucleophilic reagents in our system.



We have also found that *trans*-cyclooctene-S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate²³ reacts with iodide and methyl mercaptide ions to give quantitative yields of *trans*-cyclooctene. Thus, although it is not possible to generalize from our study to all reactions in which episulfonium salts are proposed as intermediates, our results indicate that a much closer study of such intermediates is warranted.

Experimental Section

Cyclooctene-S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate²⁴ was prepared by the method of Pettitt and Helmkamp.^{7b} All other starting materials were reagent grade and were used without further purification. Solvents were dried over molecular sieves. Diethyl ether was anhydrous, reagent grade and was used directly from the container.

Analyses for liquid products were performed on a 6-ft (1/8-in. diameter) stainless steel column packed with 10% SE-30 on 80-100 mesh Chromosorb W using a temperature-programmed F&M Model 700 gas chromatograph. Microanalyses were performed by C. F. Geiger, Ontario, Calif.; Elek Microanalytical Laboratories, Torrance, Calif.; and Galbraith Laboratories, Knoxville, Tenn. All melting and boiling points are uncorrected.

Tributylammonium TNBS. The solid product was isolated by addition of excess ether to an acetonitrile solution of 1.00 g (3.41 mmol) of 2,4,6-trinitrobenzenesulfonic acid and 0.78 g (4.2 mmol) of tributylamine. After recrystallization from acetonitrile by the successive addition of ether and methylene chloride, the product was collected as fine needles (0.97 g, 1.84 mmol, 54%), mp 193-194.5°.

Anal. Calcd for C₁₃H₂₀N₄O₆S: C, 45.18; H, 6.32; N, 11.70; S, 6.70. Found: C, 45.38; H, 6.42; N, 12.02; S, 6.63.

Methylthiotributylphosphonium TNBS. Methanesulfonyl TNBS¹⁴ (10 mmol) was filtered dropwise under nitrogen into a stirred solution of 4 ml of tributylphosphine in 25 ml of methylene chloride. After 30 min the mixture was added to 400 ml of ether to yield a red oil that crystallized after a few minutes. The product was

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(22) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(23) Preparation and reactions from unpublished results, G. K. Helmkamp and U. Zennhausern.

(24) The anion will be abbreviated as TNBS in the Experimental Section.

recrystallized slowly from a methylene chloride solution placed in an ether atmosphere to yield long spars, mp 107–108°. The product was somewhat air unstable, decomposing to a yellow, oily solid after 1 week.

Anal. Calcd for $C_{13}H_{22}N_3O_3PS_2$: C, 42.14; H, 5.96; N, 7.76; P, 5.72; S, 11.84. Found: C, 42.50; H, 6.65; N, 7.70; P, 5.40; S, 11.73.

1-Chloro-2-(methylthio)cyclooctane. A solution of 16.5 g (0.200 mol) of methanesulfonyl chloride²⁵ in 50 ml of methylene chloride was added to a well-stirred solution of 25.0 g (0.227 mol) of cyclooctene in 200 ml of methylene chloride. The reaction mixture was cooled to 0° with an ice bath. After the addition of the sulfonyl chloride was complete, the reaction mixture was allowed to stand overnight. The solution was dried over magnesium sulfate and the methylene chloride was removed on a rotary film evaporator. The remaining clear oil was distilled at 79–81° (2 mm) to yield 20.95 g (0.109 mol, 54%) of 1-chloro-2-(methylthio)cyclooctane.

Anal. Calcd for $C_8H_{17}ClS$: C, 56.08; H, 8.89. Found: C, 56.24; H, 8.88.

1-Chloro-2-(methylthio)cyclohexane. In a manner exactly analogous to that used for 1-chloro-2-(methylthio)cyclooctane, 16.5 g of methanesulfonyl chloride and 20.0 g (0.244 mol) of cyclohexene yielded 16.96 g (0.103 mol, 51%) of 1-chloro-2-(methylthio)cyclohexane, bp 61° (6 mm); lit.²⁶ 99° (13 mm).

2-(Methylthio)cyclooctyl Acetate. The addition of 963 g (0.0500 mol) of 1-chloro-2-(methylthio)cyclooctane to 8.34 g (0.0500 mol) of anhydrous silver acetate in a solution consisting of 100 ml of acetonitrile and 150 ml of glacial acetic acid yielded a silver chloride precipitate almost immediately. The solution was protected from light and stirred overnight at room temperature.

After silver chloride was separated from the solution by filtration, 500 ml of water was added. The aqueous solution was extracted twice with 200-ml portions of pentane. The pentane extracts were combined and washed twice with 50-ml portions of 10% sodium bicarbonate solution and three times with 50-ml portions of water. The pentane solution was then dried over magnesium sulfate and concentrated *in vacuo* on a rotary film evaporator. The resulting clear oil was distilled at 98–102° (1 mm) to yield 9.13 g (0.0445 mol, 89%) of 2-(methylthio)cyclooctyl acetate.

Anal. Calcd for $C_{11}H_{20}O_2S$: C, 61.07; H, 9.32. Found: C, 61.63; H, 9.15.

Reactions of Cyclooctene-S-methylepisulfonium TNBS with Nucleophiles. The reactions were carried out with equivalent amounts (0.25 mmol, unless otherwise noted) of the episulfonium salt **1** and nucleophile in a solvent mixture consisting of acetonitrile, cyclohexane, and methylene chloride (2:1:1, by volume). Solution samples were injected into the gas chromatograph and peak areas were compared with standard solutions to determine yields.

1. Chloride Ion. After 30-min reaction time with tetraphenylarsonium chloride, 0.245 mmol (98%) of cyclooctene and 0.255 mmol (102%) of 1-chloro-2-(methylthio)cyclohexane were found.

2. Bromide Ion. After 30-min reaction time with tetrabutylammonium bromide, 0.240 mmol (96%) of cyclooctene was found. Owing to its instability on the chromatographic column, 1-bromo-2-(methylthio)cyclohexane could not be detected.

3. Fluoride Ion. Because of insolubility of potassium fluoride, the mixture was stirred for 24 hr prior to gas chromatography; yield, 0.109 mmol (44%) of cyclooctene. Five minor products were detected but not identified.

(25) H. Brintzinger, K. Pfannstiel, H. Koddebusch, and K. E. Klug, *Ber.*, **83**, 87 (1950).

(26) H. Bohme, H. Bezenberger, and H. D. Stachel, *Ann.*, **602**, 114 (1957).

4. Dimethyl Sulfide. The reaction was carried out with 1.00 mmol of **1** and a 50% excess of dimethyl sulfide. After 30 min the chromatograph showed the presence of 0.764 mmol (76%) of cyclooctene; and after 24 hr the yield had risen to 0.99 mmol (99%). The reaction mixture was added to 400 ml of a 1:1 mixture of ether–pentane to yield 300 mg (62%) of 2-(methylthio)cyclohexyldimethylsulfonio TNBS, mp 140–142°. The product had melting point, mixture melting point, and nmr spectrum identical with those from an authentic sample.^{7a}

5. Thiourea. From a 30-min reaction of 1.00 mmol each of **1** and thiourea was obtained 0.99 mmol (99%) of cyclooctene. Filtration of the reaction mixture into 200 ml of a 1:1 mixture of ether–pentane yielded methylthioisothiuronium TNBS. The white solid was recrystallized from acetonitrile: yield, 280 mg (0.75 mmol, 75%); mp 184–186°; nmr spectrum δ 8.56 (singlet, 2 H) and 2.65 (singlet, 3 H).

Anal. Calcd for $C_8H_{11}N_3O_2S_2$: C, 23.13; H, 2.18; N, 16.86; S, 23.16. Found: C, 23.20; H, 2.29; N, 16.71; S, 23.29.

6. Acetic Acid. The episulfonium salt (449 mg, 1.00 mmol) was added to a solution consisting of 20 ml of acetonitrile, 10 ml of glacial acetic acid, and 10 ml of methylene chloride. After 30 min no cyclooctene was found in the reaction mixture. The addition of ether caused the precipitation of the starting material: recovery, 410 mg (91%).

7. Tributylphosphine. After 30 min, 1.00 mmol of **1** and a 50% excess of tributylphosphine gave a quantitative yield of cyclooctene. Addition of the reaction mixture to 200 ml of a 1:1 mixture of ether–pentane yielded crystalline methylthiotributylphosphonium TNBS. The product was recrystallized by placing a methylene chloride solution into a chamber whose atmosphere was saturated with ether vapor: yield, 330 mg (0.61 mmol, 61%). The melting point, mixture melting point, and nmr spectrum were identical with those of an authentic sample of the same material.

8. Tributylamine. After 30 min a 50% excess of tributylamine reacted with **1** to yield 88% of cyclooctene. Tributylammonium TNBS was precipitated by addition of the reaction mixture to 200 ml of a 1:1 mixture of ether–pentane. Recrystallization from acetonitrile–ether gave 60% yield of product, mp 194–194.3°. The melting point, mixture melting point, and nmr spectrum were identical with those of the previously described authentic material.

9. Butylamine. A 50% excess of butylamine reacted with **1** for 30 min to yield 56% of cyclooctene. The other products were red oils which could not be crystallized.

10. Pyridine. Equivalent amounts (1.00 mmol) of pyridine and **1** yielded 15% of cyclooctene in 30 min. The addition of 200 ml of 1:1 ether–pentane precipitated 2-(methylthio)cyclooctylpyridinium TNBS which was recrystallized from acetonitrile–ether: yield, 400 mg (0.75 mmol, 75%); mp 155–156°. The nmr spectrum of the product was compatible with its formulation.

Anal. Calcd for $C_{20}H_{24}N_4O_2S_2$: C, 45.44; H, 4.58. Found: C, 45.12; H, 4.15.

11. Acetate Ion. Due to the insolubility of sodium acetate, the reaction mixture was stirred for 12 hr; yield, 52% of cyclooctene and 16% of 2-(methylthio)cyclooctyl acetate. Three minor products were observed but not identified.

Reaction of Methanesulfonyl TNBS with Tributylamine. A solution of 10 mmol of methanesulfonyl TNBS¹⁴ in 30 ml of nitromethane was filtered dropwise under nitrogen into a stirred solution of 2.34 g (12.6 mmol) of tributylamine in 30 ml of methylene chloride. The deep purple solution was added to ether to precipitate the product. Slow evaporation of a methylene chloride solution of the product yielded pale yellow needles of tributylammonium TNBS, mp (and mixture melting point with an authentic sample) 193–194°. The nmr spectrum of the product was superimposable on that of the previously described samples.