Episulfonium Ion Intermediates in an Addition Reaction of Cyclooctene

DAVID J. PETTITT AND GEORGE K. HELMKAMP

Department of Chemistry, University of California, Riverside, California

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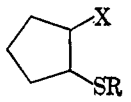
Stable episulfonium salts have been isolated from the reaction of alkanesulfenyl 2,4,6-trinitrobenzenesulfonates with cyclooctene. The salts could also be prepared by the alkylation of cyclooctene sulfide with oxonium salts or with a tertiary halide and silver 2,4,6-trinitrobenzenesulfonate.

Episulfonium ions have been proposed as intermediates resulting from neighboring group participation by divalent sulfur and in the reaction of sulfenyl compounds with olefins. In a recent review,[1] it was noted that "well-defined, stable episulfonium salts have not been prepared."

Spectral evidence for the existence of cyclopentene S-acetylepisulfonium *p*-toluenesulfonate (**2a**) was reported,[2] but full characterization of **2a**, a brown, viscous oil, was not achieved. Treatment of the β-halo sulfide **1b** with silver *p*-toluenesulfonate[2] gave a polymer-like material that presumably formed by way of **2b**.



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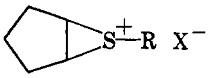

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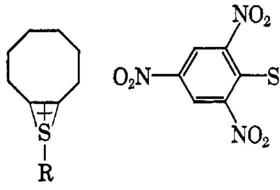
a, R = CH_3CO-
X = $p\text{-}CH_3C_6H_4SO_3-$
b, R = CH_3-
X = $Cl-$

In the reaction of sulfenyl chlorides and bromides with olefins, a *trans*, ionic addition mechanism with initial formation of a cyclic sulfonium ion has been postulated on the basis of kinetic and stereochemical evidence.[1,3-5]

As part of the study of the alkylation of episulfides,[6,7] it was of interest to investigate the reaction between olefins and alkylsulfenyl compounds with the intention of isolating episulfonium intermediates. In a preliminary report[7] the preparation of cyclooctene S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate (**3a**) from cyclooctene sulfide and trimethyloxonium 2,4,6-trinitrobenzenesulfonate was described. The episulfonium trinitrobenzenesulfonate displayed high stability in the solid state and was easily purified by recrystallization under mild conditions. These properties suggested that **3a** and its homologs could be isolated from the reaction of cyclooctene with alkanesulfenyl 2,4,6-trinitrobenzenesulfonates.

When a solution of silver 2,4,6-trinitrobenzenesulfonate[8] in nitromethane was added to a slight excess of an alkanesulfenyl bromide in methylene chloride at −25 to 0°, an immediate precipitate of silver bromide formed. Simultaneously, the characteristic red color due to the sulfenyl bromide disappeared. Addition of a 1:1 mixture of pentane and chloroform to the supernatant solution resulted in precipitation of a yellow solid that decomposed rapidly on exposure to air. Purification of the product to the point where satisfactory elemental analyses were obtained was attempted but not achieved. However, on the basis of the material's origin and subsequent reaction with cyclooctene, it was assumed that the compound was a sulfenyl 2,4,6-trinitrobenzenesulfonate.

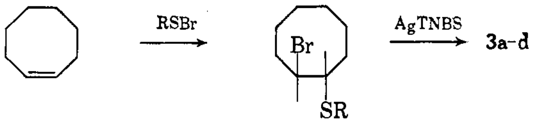
Upon addition of cyclooctene[9] to a solution of the sulfenyl 2,4,6-trinitrobenzenesulfonate, followed by evaporation of the solvent and addition of anhydrous ether, a moderate to high yield of the cyclooctene, S-alkylepisulfonium 2,4,6-trinitrobenzenesulfonate,[10] (**3a–d**) was obtained. One crystallization from warm nitromethane–ether or acetone–ether gave a pure product (Table I), yield 60–70%.



3a, R = CH_3
b, R = C_2H_5
c, R = $n\text{-}C_3H_7$
d, R = $n\text{-}C_4H_9$
e, R = $t\text{-}C_4H_9$

The structure proposed for the adducts **3** is supported by physical and chemical properties that would be inconsistent for compounds that might result from ring opening or transannular conversions. The retention of the three-membered ring is suggested by the presence of a weak infrared band at 3010 cm.$^{-1}$, characteristic of the C–H stretching frequency in that system. Strong bands at 1028 and 1057 cm.$^{-1}$, indicative of ionic sulfonate, and equivalent weights (Table I) also ruled out the possibility that ring opening had occurred.

An alternative route to **3a–d** was treatment of cyclooctene with alkanesulfenyl bromides, evaporation of the solvent, and additions of the crude 1-bromo-2-alkylthiocyclooctanes to a nitromethane solution of silver 2,4,6-trinitrobenzenesulfonate (AgTNBS in eq. 1). By



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[1] K. D. Gundermann, *Angew. Chem., Intern. Ed. Engl.*, **2**, 674 (1963).

[2] L. Goodman, A. Benitez, and B. R. Baker, *J. Am. Chem. Soc.*, **80**, 1680 (1958).

[3] N. Kharasch and A. J. Havlik, *ibid.*, **75**, 3734 (1953).

[4] N. R. Slobodkin and N. Kharasch, *ibid.*, **82**, 5837 (1960).

[5] D. J. Cram, *ibid.*, **71**, 3883 (1949).

[6] G. K. Helmkamp and D. J. Pettitt, *J. Org. Chem.*, **25**, 1754 (1960).

[7] D. J. Pettitt and G. K. Helmkamp, *ibid.*, **28**, 2932 (1963).

[8] Recrystallization of silver 2,4,6-trinitrobenzenesulfonate from acetonitrile–ether gave the silver salt containing three acetonitriles as solvent of crystallization. Loss of the acetonitrile occurred when the complex was heated at reduced pressure. Although the uncomplexed silver salt and the silver salt containing solvent of crystallization were both effective in the reactions to be described the latter was generally used because of its greater solubility in nitromethane.

[9] We are indebted to Cities Service Research and Development Co., New York 5, N. Y., for a generous donation of cyclooctene.

[10] Alternatively, these compounds could be named 9-alkyl-9-thioniabicyclo[6.1.0]nonane 2,4,6-trinitrobenzenesulfonates.

TABLE I

PHYSICAL DATA FOR EPISULFONIUM SALTS **3b–e**

Compd.	M.p., °C.	Calcd., % C	H	N	Found,[a] % C	H	N	Equiv. wt.[b] Calcd.	Found
3b	123–124	41.34	4.57	9.10	41.69	4.38	9.38	231	226
3c	116–117	42.76	4.85	8.80	42.98	5.15	8.93	238	231
3d	104–105	43.98	5.13	8.55	44.30	5.23	8.90	246	242
3e	110–111	43.98	5.13	8.55	44.11	5.39	8.86	246	243

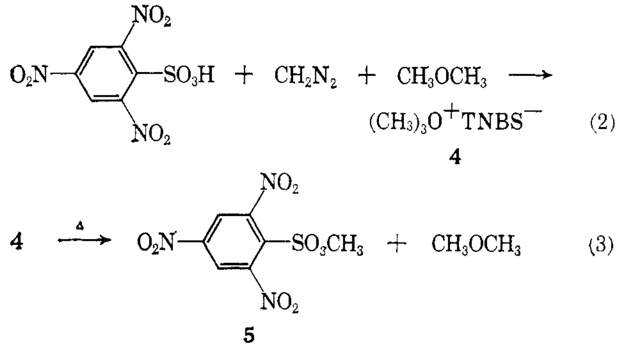
[a] Microanalyses were by C. F. Geiger, Ontario, Calif., and A. Elek, Los Angeles, Calif. [b] Determined with a Mechrolab Model 301A vapor pressure osmometer, with nitromethane solvent and trimethylsulfonium 2,4,6-trinitrobenzenesulfonate standard.

addition of ether, the episulfonium salts were isolated in high yields and pure form.

When **3a–d** were treated with sodium iodide in acetone or acetonitrile at room temperature, nearly quantitative amounts of iodine were rapidly produced. Cyclooctene and alkyl disulfide in the ratio of 2:1 were also formed,[7] as shown by gas chromatography. In the case of **3e**, rapid desulfurization by iodide ion required heating. This type of reaction is not characteristic of sulfonium salts in which ring strain is small or absent, for sulfonium iodides are commonly observed. Consequently, the [6.1.0]bicyclic system must still be intact, for a transannular process would lead to a system of reduced strain.[11] It is assumed that the reaction between the episulfonium salt and iodide ion took place by nucleophilic attack at sulfur, because an analogous reaction with sodium or lithium methyl mercaptide led to cyclooctene and alkyl disulfide. If attack in the latter case had been at carbon, stable bis-1,2-dialkylthio compounds[12] would have been formed. There still remains the possibility that iodide could attack at carbon, for a subsequent iodide-induced elimination reaction would have the same net stereochemical consequence.

Further verification of the structure of the episulfonium compound is based on syntheses by independent routes. Compounds **3a**[7] and **3b** were also prepared by the direct alkylation of cyclooctene sulfide with trimethyl and triethyl oxonium 2,4,6-trinitrobenzenesulfonates. The methyl ester of 2,4,6-trinitrobenzenesulfonic acid, which was obtained by heating trimethyloxonium 2,4,6-trinitrobenzenesulfonate, was also effective in converting cyclooctene sulfide to **3a**. Compound **3e** was prepared from the reaction between cyclooctene sulfide and the product of the reaction between silver 2,4,6-trinitrobenzenesulfonate and *t*-butyl chloride. The latter solution was assumed to contain the *t*-butyl ester of the sulfonic acid.

Trimethyloxonium 2,4,6-trinitrobenzenesulfonate (**4**) was prepared from the corresponding fluoborate[13] and 2,4,6-trinitrobenzenesulfonic acid, or, more conveniently, from the reaction of diazomethane with 2,4,6-trinitrobenzenesulfonic acid in methyl ether solvent.[7] The oxonium trinitrobenzenesulfonate was not hygroscopic and showed high stability in the solid state. After 4 months, storage in a desiccator at 5–10°, a sample of **4** showed about 10% decomposition, determined by measuring the amount of methyl ether produced when the salt was heated to 190°. Triethyloxonium 2,4,6-trinitrobenzenesulfonate, a stable, crystalline solid, was obtained by mixing solutions of the oxonium fluoborate[14] and 2,4,6-trinitrobenzenesulfonic acid.



Attempts were made to isolate episulfonium salts from the reaction of alkanesulfenyl 2,4,6-trinitrobenzenesulfonates with cyclohexene, but intractable tars were obtained.

Experimental[15]

2,4,6-Trinitrobenzenesulfonic Acid.—The preparation of the acid was based on that of Golumbic and Bergman.[16] To 100 g. (0.40 mole) of picryl chloride in 1000 ml. of absolute ethanol was added 100 g. (0.53 mole) of anhydrous sodium metabisulfite. The mixture was heated under reflux with vigorous stirring for 3 hr. and then cooled to below 5° and filtered. The crude sodium salt was washed with 100-ml. portions of cold, absolute ethanol until the wash solution was colorless.

After the tan solid was air-dried for 15 min., it was mixed with 300 ml. of reagent grade acetone; then 100 ml. of concentrated hydrochloric acid was added with swirling over a 5-min. period. The precipitated sodium chloride was removed by filtration and washed with 50 ml. of acetone. The acetone solvent and excess water were removed at reduced pressure with gentle heating on a water bath. At this point the light yellow product contained water of crystallization. Further heating at reduced pressure gave 102 g. (87%) of the anhydrous acid as a chalk-white solid, m.p. 193–195°. Although the anhydrous acid could be recrystallized from acetone–chloroform, a more satisfactory procedure was available for the dihydrate. The entire product from the synthesis was dissolved in 50–55 ml. of hot acetone and 50 ml. of chloroform was added. The dihydrate, which crystallized as long needles, was separated by filtration of the cold mixture, washed with 100 ml. of chloroform, and air-dried, melting at 85–87° with resolidification at 125–135° and remelting at 193–195°. The anhydrous acid was obtained by heating the hydrate for 2–3 hr. at 80° and 1-mm. pressure over phosphorus pentoxide, yield 94 g., 80%, m.p. 193–195°.

Boron Trifluoride Dimethyl Etherate.—The procedure of Laubengayer and Finlay[17] was employed. The product was distilled under nitrogen through a short Vigreux column, b.p. 73° (63 mm.).

Trimethyloxonium Fluoborate.—The salt was prepared according to the reported procedure,[13] yield 80–90%, m.p. 174–

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[11] A. C. Cope and J. I. Hecht, *J. Am. Chem. Soc.*, **84**, 4873 (1962).

[12] T. C. Whitner, Jr., and E. E. Reid, *ibid.*, **43**, 638 (1921).

[13] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil, *J. prakt. Chem.*, **147**, 257 (1937).

[14] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and E. Willfang, *ibid.*, **154**, 83 (1939).

[15] Analyses were performed by F. Geiger, Ontario, Calif., and A. Elek, Los Angeles, Calif.

[16] C. Golumbic and M. Bergman, *J. Org. Chem.*, **11**, 519 (1946).

[17] A. W. Laubengayer and G. R. Finlay, *J. Am. Chem. Soc.*, **65**, 884 (1943).

177° dec. The reported yield was 98% and the melting point was 124.5°.

Trimethyloxonium 2,4,6-Trinitrobenzenesulfonate from the Fluoborate.—Freshly dried, anhydrous 2,4,6-trinitrobenzenesulfonic acid (35.4 g., 0.12 mole) was dissolved in 75 ml. of hot, anhydrous acetonitrile. The solution was cooled to 10–15° and added in one portion with stirring to 14.8 g. (0.10 mole) of trimethyloxonium fluoborate in 30 ml. of reagent grade nitromethane at 5°. After 2–3 min., 200 ml. of anhydrous ethyl acetate then 50 ml. of pentane were added. The solid product was collected by filtration and washed with 100 ml. of ethyl acetate and 50 ml. of pentane. When most of the solvent had been removed, the salt was quickly transferred to a large tube and dried under vacuum over phosphorus pentoxide. The yield of white solid was 25–27 g. (71–76%), m.p. 181–183°. When the product was heated rapidly, it melted with vigorous effervescence at about 115–125°, then resolidified, and melted again at 181–183°.

Anal. Calcd. for $C_9H_{11}N_3O_{10}S$: C, 30.60; H, 3.14; N, 11.90. Found: C, 30.88; H, 3.30; N, 12.06.

The oxonium salt was placed in a desiccator over phosphorus pentoxide and stored in a refrigerator. After 4 months at 5–10°, a sample of the product gave an 84% yield of methyl ether when heated above 125°, indicating only about 10% decomposition during that time.

Trimethyloxonium 2,4,6-Trinitrobenzenesulfonate from Diazomethane, Acid, and Ether.—A mixture of 200 ml. of methyl ether and 14.7 g. (0.050 mole) of dry 2,4,6-trinitrobenzenesulfonic acid was cooled to −35° in a Dry Ice–isopropyl alcohol bath. During the subsequent reaction, the mixture was stirred vigorously and the temperature was maintained at −40 to −30°.

Diazomethane was added by bubbling methyl ether through a xylene solution of diazomethane[18] and passing the gases into the reaction flask with the delivery tube about 1 in. above the ether solution. The diazomethane solution, prepared from 20 g. of nitrosomethylurea with 100 ml. of supernatant xylene, was kept cold until methyl ether was passed through the xylene solution for 1–2 min. At this point the ice bath was replaced by a water bath at 25°. When a faint yellow color persisted in the reaction mixture (addition time, 20–50 min.), the delivery tube was removed and 200 ml. of absolute ethyl acetate was added. The product was isolated immediately by filtration and washed with 100 ml. of ethyl acetate and 50 ml. of petroleum ether (b.p. 60–70°) in rapid succession. When most of the solvent had been removed, the salt was quickly transferred to a beaker and dried in a vacuum desiccator. The yield of white powder was 12–14 g. (68–79%). The product showed the same melting point characteristics as that prepared from the fluoborate.

Methyl 2,4,6-Trinitrobenzenesulfonate. Thermal Decomposition of Trimethyloxonium 2,4,6-Trinitrobenzenesulfonate.—A sample of 1.41 g. (0.0040 mole) of the oxonium salt was placed in a flat-bottomed glass tube which was connected to a gas collection buret. The sample was heated in an oil bath to 190°. Gas evolution was first observed at 110–115°. The total amount of gas at standard conditions was 84.2 cc. (94%). Gas chromatography of the volatile product on a 15-ft. column of 25% by weight of silicone oil (GE SF-96) on firebrick revealed a single component, with a retention identical with that of methyl ether.

The brown solid residue (1.23 g.) was purified by dissolving it in a minimum amount of nitromethane at room temperature and adding ether until crystallization began. After three recrystallizations, 0.2 g. of a white solid was obtained; m.p. 180–181°; mol. wt., 294 found, 307 calcd. The methyl 2,4,6-trinitrobenzenesulfonate structure was assigned to the product on the basis of elemental analysis and molecular weight.

Anal. Calcd. for $C_7H_5N_3O_9S$: C, 27.37; H, 1.64; N, 13.68. Found: C, 27.76; H, 1.94; N, 13.42.

Triethyloxonium 2,4,6-Trinitrobenzenesulfonate.—Triethyloxonium fluoborate was prepared by the literature procedure[14] and was converted quickly to the trinitrobenzenesulfonate because of its hygroscopic nature. A solution of 10.0 g. (0.034 mole) of trinitrobenzenesulfonic acid was dissolved in 75 ml. of hot, absolute ethyl acetate, and the solution was cooled to 10°. To this was added in one portion 5.7 g. (0.030 mole) of triethyloxonium fluoborate in 10 ml. of nitromethane. The mixture was cooled and swirled for 5 min., then poured into 100 ml. of anhydrous ether. The precipitated product was collected by filtration and washed with 25 ml. of ether followed by 25 ml. of pentane. After removal of most of the solvent, the solid was dried in a vacuum desiccator, yield 10.1 g. (85%). The white salt melted at 88–89° with vigorous effervescence, resolidified, and melted again at 138–140°. The product was recrystallized by adding ether to a nitromethane solution at room temperature until crystallization began and cooling the mixture to 0°. One recrystallization gave a product with satisfactory elemental analysis, m.p. 88–89° and 142–144°.

Anal. Calcd. for $C_{12}H_{17}N_3O_{10}S$: C, 36.45; H, 4.34; N, 10.63. Found: C, 36.82; H, 4.68; N, 10.58.

1,2-Dithiocyanocyclooctane.—Thiocyanogen was prepared from 78 g. (0.24 mole) of lead thiocyanate and 32 g. (0.20 mole) of bromine in 1.5 l. of anhydrous acetic acid according to the method of McGhie, *et al.*[19] To this solution was added 22.0 g. (0.20 mole) of cyclooctene in one portion. The mixture was stirred overnight at room temperature. After dilution with three parts of water and filtration, the product was isolated by extraction with methylene chloride. Evaporation of the solvent left 39 g. of a yellow oil. Chromatography of a 20-g. sample on 100 g. of neutral alumina and elution with 1:1 ether–petroleum ether gave a nearly colorless oil with a strong carbonyl absorption band at 1740 cm.$^{-1}$ as well as a thiocyanate band at 2145 cm.$^{-1}$. Three crystallizations of the chromatographed product from petroleum ether (b.p. 60–70°) gave a white solid, m.p. 43–44°, which showed no carbonyl absorption band but which retained the thiocyanate band. The elemental analysis agreed with that expected for 1,2-dithiocyanocyclooctane. The thiocyanate groups are presumably *trans*.[19]

Anal. Calcd. for $C_{10}H_{14}N_2S_2$: C, 53.01; H, 6.23. Found: C, 53.29; H, 6.40.

Cyclooctene Sulfide.—The method reported by Youtz and Perkins[20] was modified somewhat. A solution of the crude 1,2-dithiocyanocyclooctane in 75 ml. of methanol was added to sodium sulfide prepared by dissolving 48 g. (0.20 mole) of sodium sulfide nonahydrate in 40 ml. of water and adding 70 ml. of methanol. The mixture was heated by a water bath at 60–65° with stirring for 45 min. and poured into 200 ml. of water. The product was extracted with two 50-ml. portions of ether, and, after drying over magnesium sulfate, was isolated by distillation through a Vigreux column; yield of colorless oil, 11.6 g. , 41% from cyclooctene; b.p. 71° (2 mm.); m.p. 25–26°; $n^{25}D$ 1.5287; λ_{max} 259 mμ (ϵ 46.6 for 3.10×10^{-2} *M* solution in pentane); principal infrared bands in carbon tetrachloride at 1038 (strong) and 1140 cm.$^{-1}$ (medium). The ultraviolet[21] and infrared[22] absorption characteristics parallel those of reported episulfides.

Anal. Calcd. for $C_8H_{14}S$: C, 67.52; H, 9.92. Found: C, 67.33; H, 9.99.

Disulfides.—The disulfides were prepared from the corresponding thiols according to the procedure of Fogel[23] and were purified by distillation.

Sulfenyl Bromides.—These compounds were prepared by a procedure similar to that reported for the synthesis of methanesulfenyl bromide.[24] Dryness of solvents, reagents, and glassware was essential to the success of the synthesis.

A solution of disulfide (0.011 mole) in 25 ml. of dry methylene chloride (distilled over phosphorus pentoxide) was cooled to − 25° in a Dry Ice–isopropyl alcohol bath. With moderate stirring, 1.60 g. (0.10 mole) of bromine in 25 ml. of methylene chloride was added dropwise over a 30-min. period in the absence of light. The mixture was stirred with cooling for an additional 30 min., and was kept at −25 to −20° until needed.

Silver 2,4,6-Trinitrobenzenesulfonate.—A solution of 13.5 g. (0.080 mole) of silver nitrate in 20 ml. of warm water was added in one portion to 17.6 g. (0.060 mole) of 2,4,6-trinitrobenzenesulfonic acid in 20 ml. of warm water. The mixture was cooled and the product was collected by filtration and washed with two 50-ml. portions of cold 95% ethanol and one 50-ml. portion of ether.

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[18] F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

[19] F. McGhie, W. A. Ross, F. J. Julietti, and B. E. Grimwood, *J. Chem. Soc.*, 4638 (1962).

[20] M. A. Youtz and P. P. Perkins, *J. Am. Chem. Soc.*, **51**, 3508 (1929).

[21] R. E. Davis, *J. Org. Chem.*, **23**, 216 (1958).

[22] N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **81**, 578 (1959).

[23] A. I. Fogel, "Practical Organic Chemistry," 3rd. Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 498.

[24] E. Schneider, *Ber.*, **84**, 911 (1951).

The silver salt was recrystallized from hot acetonitrile–ether and washed with two 50-ml. portions of ether. As soon as most of the solvent was removed, the solid was dried at reduced pressure and room temperature over phosphorus pentoxide. The yield of white, lusterous flakes was 22–24 g. (70–76%). When excess ether was added to the filtrate, an additional 4–6 g. of product was obtained. The compound melted at 88–89° and resolidified at 170–180°. The second solid did not melt but decomposed vigorously at temperatures above 355°.

When 11.8 g. of the product was heated at 80° and reduced pressure, 2.7 g. of acetonitrile was liberated. The residue again showed vigorous decomposition at 355–358°. Based on the amount of recovered acetonitrile and elemental analysis, the silver salt crystallized from acetonitrile contained three molecules of solvent of crystallization.

Anal. Calcd. for $C_{12}H_{11}AgN_6O_9S$: C, 27.54; H, 2.12; Ag, 20.61. Found: C, 27.14; H, 2.24; Ag, 20.52.

Attempted Characterization of Methanesulfenyl 2,4,6-Trinitrobenzenesulfonate.—A solution of 4.0 g. (0.0076 mole) of silver 2,4,6-trinitrobenzenesulfonate–acetonitrile complex in 20 ml. of 1:1 nitromethane–methylene chloride was cooled to 5°. A cold solution of 0.010 mole of methanesulfenyl bromide was added in the presence of dry nitrogen. Silver bromide precipitated and the red color of the sulfenyl bromide simultaneously disappeared. After the precipitate was removed by filtration, a 1:1 chloroform–pentane mixture was added and a light yellow solid was isolated. The solid was dried at reduced pressure, yield 2.2 g. (85% based on metathesis structure), m.p. 130–132° dec. The product decomposed rapidly in air to yield methyl disulfide and a nitromethane-insoluble solid. Attempts were made to purify the product by recrystallization, but satisfactory analyses were never achieved because of its instability.

Addition of 0.34 g. (0.0010 mole) of the crude product to 0.17 g. (0.015 mole) of cyclooctene in 10 ml. of nitromethane, followed by the addition of 25 ml. of ether, gave 0.20 g. of a white solid, m.p. 122–123°. The mixture melting point of the product with an authentic sample of cyclooctene S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate was undepressed.

Similar observations were made with the products from *n*-propane- and *n*-butanesulfenyl bromide and silver 2,4,6-trinitrobenzenesulfonate.

Cyclooctene S-Alkylepisulfonium 2,4,6-Trinitrobenzenesulfonates from Alkanesulfenyl 2,4,6-Trinitrobenzenesulfonates.—A solution of 7.9 g. (0.051 mole) of silver 2,4,6-trinitrobenzenesulfonate–acetonitrile complex in 20 ml. of nitromethane was added in one portion with stirring to 0.020 mole of alkanesulfenyl bromide in 50 ml. of methylene chloride at −25°. After 10 min., a solution of 2.5 g. (0.022 mole) of cyclooctene in 25 ml. of methylene chloride was added dropwise with stirring over a 10-min. period. The cooling bath was then removed, and the reaction mixture was warmed to 20–25° by a water bath. The precipitated silver bromide was removed by filtration and washed with 10 ml. of nitromethane. The filtrate was concentrated to 20–30 ml. at 20–25° and reduced pressure, leaving an orange residue. The addition of 200 ml. of ether gave a white or cream-colored solid which was collected by filtration of the cold mixture, washed rapidly with 25 ml. of ether and 25 ml. of pentane, and dried at reduced pressure.

The episulfonium compounds began turning orange when heated 2–3° below their melting points and an orange-red melt was formed. The melting points were somewhat dependent on the rate of heating. The reported values are those obtained by heating the sample rapidly to 5–10° below the anticipated melting point and heating slowly thereafter. The products displayed no apparent tendency to decompose when stored in closed containers at room temperature.

Cyclooctene S-Methylepisulfonium Trinitrobenzenesulfonate.—The crude yield was 5.2 g. (77%), m.p. 122–123°. One recrystallization from warm (30–40°) nitromethane–ether gave cream-colored prisms (4.5 g., 67%), with no increase in melting point.

Anal. Calcd. for $C_{15}H_{19}N_3O_9S_2$: S, 14.27. Found: S, 13.79. See also the data presented in Table I.

Cyclooctene S-Ethylepisulfonium Trinitrobenzenesulfonate.—The salt was obtained in 70% yield (4.9 g.) and showed a melting point of 121–123°. One recrystallization from nitromethane–ether gave white needles, 4.3 g., 62%, m.p. 123–124°.

Cyclooctene S-Propylepisulfonium Trinitrobenzenesulfonate.—The salt was isolated in 83% yield (6.05 g.), m.p. 102–104°. The product crystallized from nitromethane–ether as white needles, 4.2 g., 58%, m.p. 116–118°.

Cyclooctene S-Butylepisulfonium Trinitrobenzenesulfonate.—The salt was isolated as a white solid, 4.7 g., 64%, m.p. 104–105°. Recrystallization from acetone–ether did not result in an increase in the melting point.

Cyclooctene S-Alkylepisulfonium 2,4,6-Trinitrobenzenesulfonates from Cyclooctene Sulfide and Oxonium Salts. A. Preparation of 3a.—A solution of 4.3 g. (0.012 mole) of trimethyloxonium 2,4,6-trinitrobenzenesulfonate in 50 ml. of nitromethane was prepared. To this was added 1.4 g. (0.010 mole) of cyclooctene sulfide in 50 ml. of nitromethane with vigorous stirring over a period of 30 min. The solution was stirred for an additional 30 min. and then poured into 200 ml. of absolute ether. The mixture was cooled in an ice bath and the precipitated solid was washed successively with ether and pentane. After most of the solvent had been removed, the product was dried at reduced pressure over phosphorus pentoxide, yield 3.60 g. (80%), m.p. 121–122°. One crystallization from nitromethane–ether gave cream-colored prisms; 3.0 g., 67%; m.p. 122–123°; equiv. wt., 220 (calcd. 224); infrared bands in potassium bromide at 3010 (three-membered ring C–H), 1028, and 1057 cm.$^{-1}$ (ionic sulfonate).

Anal. Calcd. for $C_{15}H_{19}N_3O_9S_2$: C, 40.15; H, 4.26; N, 9.35. Found: C, 40.42; H, 4.50; N, 8.92.

Preparation of 3a from Cyclooctene Sulfide and Methyl 2,4,6-Trinitrobenzenesulfonate (5).—To 0.32 g. (0.0010 mole) of **5** in 3 ml. of nitromethane, 0.14 g. (0.0010 mole) of cyclooctene sulfide in 7 ml. of nitromethane was added in small portions with swirling. The addition took about 5 min. After 30 min., the reaction mixture was poured into 75 ml. of absolute ether and the product was isolated and purified as described above, yield 0.26 g. (58%), m.p. 122–123°.

B. **Preparation of 3b.**—With a procedure similar to that described for **3a**, a 47% yield of S-ethylepisulfonium 2,4,6-trinitrobenzenesulfonate was obtained after one recrystallization. The mixture melting point of the product with a sample of **3b** from cyclooctene and ethanesulfenyl 2,4,6-trinitrobenzenesulfonate was undepressed.

Cyclooctene S-Butylepisulfonium 2,4,6-Trinitrobenzenesulfonate from 1-Bromo-2-Butylthiocyclooctane.—Cyclooctene (1.1 g., 0.010 mole) in 20 ml. of methylene chloride was added in portions with swirling to 0.010 mole of butanesulfenyl bromide in 25 ml. of methylene chloride at 0°. The reaction mixture turned colorless. Removal of the solvent at reduced pressure left a colorless oil. The crude product was dissolved in 15 ml. of methylene chloride and added in one portion to 4.0 g. (0.076 mole) of silver 2,4,6-trinitrobenzenesulfonate–acetonitrile complex in 10 ml. of nitromethane. After 5 min., the silver bromide was separated and the filtrate was poured into 100 ml. of absolute ether. The white, crystalline product was collected and dried, 2.80 g. (74%), m.p. 104–105°. There was no change in melting point on recrystallization from acetone–ether, and the mixture melting point with **3d** from cyclooctene and butanesulfenyl-2,4,6-trinitrobenzenesulfonate was undepressed.

Cyclooctene S-methyl-, S-ethyl-, and S-propylepisulfonium 2,4,6-trinitrobenzenesulfonates were prepared on a small scale by a similar procedure for identification purposes.

Cyclooctene S-*t*-Butylepisulfonium 2,4,6-Trinitrobenzenesulfonate.—Cyclooctene sulfide (1.4 g., 0.010 mole) and freshly distilled *t*-butyl bromide (1.40 g. 0.010 mole) were added to 50 ml. of methylene chloride. During vigorous stirring, 3.70 g. (0.071 mole) of silver 2,4,6-trinitrobenzenesulfonate–acetonitrile complex in 50 ml. of nitromethane was added dropwise over a 30-min. period. The reaction mixture was kept at 5° for 1 hr. and then centrifuged. The supernatant liquid was decanted from the silver bromide into 200 ml. of 1:1 ether–pentane. A yellow oil separated which crystallized on cooling. Recrystallization from acetone–ether yielded white needles, 1.95 g. (57%), m.p. 110–111°.

Alternatively, **3e** was prepared by the addition of 1.4 g. (0.010 mole) of cyclooctene sulfide in 50 ml. of nitromethane to 0.010 mole of *t*-butyl 2,4,6-trinitrobenzenesulfonate. The ester was prepared as a suspension by the addition of 1.5 g. of *t*-butyl bromide to 50 ml. of methylene chloride containing 4.0 g. (0.010 mole) of silver 2,4,6-trinitrobenzenesulfonate. After the addition was complete, the silver bromide was removed by filtration, and the filtrate was treated as in the first preparation.

Desulfurization of Episulfonium Salts 3a–d with Sodium Iodide.—In a typical procedure, 0.0040 mole of episulfonium salt was dissolved in 20 ml. of dry acetonitrile, and 1.5 g. (0.010 mole of sodium iodide in 30 ml. of acetonitrile was added in one portion. After 5 min. at room temperature, the reaction mixture was titrated with 0.10 *N* sodium thiosulfate. Yields of iodine varied from 80–100%.

The titrated solutions from **3a** and **3c** were poured into 200 ml. of water and extracted with 100 ml. of pentane. Gas chromatographic analysis of the extract (10-ft. column of GE SF-96 silicone oil on Fluoropak at 110°) revealed only two components other than solvent. These corresponded in retention volume to cyclooctene and alkyl disulfide in a molar ratio of 2:1. The product from **3a** that corresponded to cyclooctene was trapped from the exit gases. Its refractive index, n^{22}D 1.4692, and infrared spectrum were identical with those of an authentic sample of cyclooctene.

Desulfurization of 3e with Sodium Iodide.—To 1.2 g. (0.0080 mole) of sodium iodide in 10 ml. of acetone was added 2.0 g. (0.0040 mole) of the episulfonium salt. As the compound dissolved, a second solid phase separated and the characteristic red color of the trinitrobenzenesulfonate–iodide ion complex[25] appeared, but the more intense red color of iodine was not apparent until after the mixture stood overnight. To ensure complete reaction the mixture was heated under reflux for 1 hr. The cold material was then poured into 100 ml. of water and titrated with sodium thiosulfate. The yield of iodine was 70%. The mixture was extracted with 10 ml. of pentane and chromatographed. Cyclooctene and *t*-butyl disulfide were detected in the ratio of 2:1.

Desulfurization of 3a with Lithium Methyl Mercaptide.—Butyl lithium (1.5 ml. of 15% solution in hexane) was added slowly to 0.5 g. of methyl mercaptan in 15 ml. of acetonitrile. The resulting suspension was added to 0.45 g. (0.0010 mole) of **3a** in 10 ml. of acetonitrile. After 20 min. the mixture was poured into 50 ml. of water, and extracted and analyzed as before for products. A 1:1 ratio of cyclooctene–methyl disulfide was detected.

Reaction of Cyclohexene with Ethanesulfenyl 2,4,6-Trinitrobenzenesulfonate.—A solution of 0.076 mole of ethanesulfenyl 2,4,6-trinitrobenzenesulfonate was prepared by adding 4.0 g. of silver 2,4,6-trinitrobenzenesulfonate in 15 ml. of nitromethane to 0.010 mole of ethanesulfenyl bromide in 25 ml. of methylene chloride at −25°. To this was added 0.90 g. (0.011 mole) of cyclohexene in 20 ml. of methylene chloride. The mixture began turning black immediately. After 5 min. the solid was removed by filtration and the filtrate was evaporated to near dryness at reduced pressure. The addition of 100 ml. of ether resulted in the separation of a viscous black oil. Attempts to crystallize the oil failed. Similar observations were made with the methane- and butanesulfenyl salts and cyclohexene.

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[25] When sodium iodide in acetone or acetonitrile was mixed with trinitrobenzenesulfonic acid or its salts, a red solution was formed. The red color was discharged immediately by the addition of water.

The Chlorination of Active Hydrogen Compounds with Sulfuryl Chloride.
II. Esters, Nitriles, Nitro Compounds, and Aldehydes

DONALD P. WYMAN, PAUL R. KAUFMAN, AND WILLIAM R. FREEMAN

Mellon Institute, Pittsburgh 13, Pennsylvania

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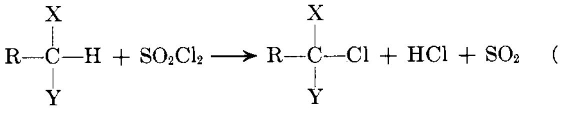
The following compounds were inert to sulfuryl chloride at room temperature: chloroacetonitrile, ethyl phenylacetate, ethyl chloroacetate, methylene chloride, acetonitrile, nitroethane, 1-chloro-1-nitroethane, ethyl acetate, and ethyl propionate. Acetoacetate reacted very vigorously, but only tars were isolated. Aldehydes also reacted very rapidly, but the yields of chlorinated derivatives were low, and polymers formed by acid-catalyzed polymerization were the major products. Ethyl cyanoacetate in a 1:1 molar reaction with sulfuryl chloride yielded predominantly ethyl dichlorocyanoacetate, whereas ethyl acetoacetate and diethyl malonate under the same conditions gave mainly monochloro derivatives, ethyl α-chloroacetoacetate and diethyl chloromalonate, respectively. Competitive chlorinations established that ethyl acetoacetate was more reactive than acetone or diethyl malonate and about as reactive as chloroacetone. Similar competitions showed that acetone also was more reactive than diethyl malonate. Acid-catalyzed ionic mechanisms differing somewhat from those used to explain acid-catalyzed chlorination with chlorine are proposed to explain the experimental results.

In a previous paper[1] in this series the ease with which a variety of ketones possessing α-hydrogen atoms were chlorinated by reaction with sulfuryl chloride was described. As a logical extension of that study, we have investigated the same kind of chlorination with a number of different compounds containing active methyl, methylene, and/or methine protons. The over-all reaction is shown in eq. 1. A large variation



$$\text{R}-\overset{\overset{\text{X}}{|}}{\underset{\underset{\text{Y}}{|}}{\text{C}}}-\text{H} + \text{SO}_2\text{Cl}_2 \longrightarrow \text{R}-\overset{\overset{\text{X}}{|}}{\underset{\underset{\text{Y}}{|}}{\text{C}}}-\text{Cl} + \text{HCl} + \text{SO}_2 \qquad (1)$$

in the nature of X, Y, and R was investigated with respect to their relative ability to enhance the chlorination.

It was evident from the experimental results that keto groups, $\overset{\overset{\text{O}}{\|}}{-\text{C}-}$, strongly favor the reaction shown in eq. 1 and that chlorinations of this kind are different (in several ways) from similar chlorinations performed with molecular chlorine. The details of this investigation along with tentative explanations of the differences between chlorinations with chlorine and sulfuryl chloride are presented in this paper.

Results

The products obtained from the chlorination of several active hydrogen compounds with sulfuryl chloride are listed in Table I. Ethyl cyanoacetate when treated with sulfuryl chloride (1:1 molar) at about room temperature yielded[2] mainly the dichloro derivative, ethyl dichlorocyanoacetate (67%), along with ethyl chlorocyanoacetate (21%). Ethyl acetoacetate and

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[1] D. P. Wyman and P. R. Kaufman, *J. Org. Chem.*, **29**, 1956 (1964).

[2] In all cases the per cent yields are based on the conversion of sulfuryl chloride to products. Thus, for example, a 1:1 molar reaction of sulfuryl chloride with ethyl cyanoacetate which gave a 67% yield of ethyl dichlorocyanoacetate means that 67% of the available sulfuryl chloride was used in the formation of this product, but, obviously, only 33.5% of the available ethyl cyanoacetate.