Infrared spectra of the two samples were nearly identical, varying only in the relative intensities of two bands in the vicinity of 1500 cm.$^{-1}$. Thompson[25] reported m.p. 197–198° for this compound. The 160° melting point is apparently that of a second crystalline modification; polymorphism is not uncommon in the tertiary amides.[25]

Reaction of Lithium Nitride with Acetyl Chloride.—The lithium nitride employed in this experiment was prepared by the method of Masdupuy and Gallais[28] as a black crystalline solid which was then ground to a fine powder in a mortar. Acetyl chloride (54 g., 0.23 mole) was added over 15 min. to a dispersion of 7.67 g. (0.22 mole) of lithium nitride in 50 ml. of diglyme. The mixture was stirred mechanically and warmed on a steam bath for 4 hr. The mixture was then filtered to remove lithium chloride and unchanged lithium nitride and the filtrate was cooled. A precipitate of 1.5 g. of diacetamide, m.p. 77–78°, was obtained and identified by its molecular weight and infrared spectrum. No triacetamide was observed.

In another experiment employing Foote Mineral lithium nitride,[27] 23.2 g. (0.25 mole) of acetyl chloride was added over a period of 2 hr. to 3 g. (0.086 mole) of lithium nitride in 5 ml. of diglyme. The mixture was stirred for 6 hr. and allowed to stand overnight, when an additional 5 g. of acetyl chloride was added without observable effect. To the mixture was added 100 ml. of 5% sodium hydroxide solution and the resulting mixture was extracted with ether. Removal of the ether by distillation left 0.8 g. of a dark red resinous material which melted over a range of 118–126° and appeared to be an aldol resin. Acidification of the aqueous layer produced a small amount of a precipitate which was assumed to be diacetamide but which was not investigated.

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[28] E. Masdupuy and F. Gallais, *Inorg. Syn.*, **4**, 1 (1953).

The Reaction of Alkyl Benzenesulfonates with Sodium Methoxide in Dimethyl Sulfoxide and Dimethylformamide. Scope and Stereochemistry.

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Benzenesulfonates of typical primary and secondary alcohols react rapidly at room temperature with sodium methoxide in dimethyl sulfoxide to give high yields of alkenes and/or alkyl methyl ethers. Except for cyclohexyl benzenesulfonate, the ether–alkene ratio is significantly higher in reactions with sodium methoxide than with potassium *t*-butoxide. Although 2-octyl benzenesulfonate reacts more slowly with sodium methoxide than with potassium *t*-butoxide in dimethylformamide, product ratios are essentially identical in both solvents. Mechanistic implications are discussed for the predominance of Hofmann elimination from 2-octyl benzenesulfonate and for the conversion of 2-octyl *p*-brosylate to 2-methoxyoctane of inverted configuration.

Aryl sulfonates have been shown to react readily with potassium *t*-butoxide in dimethyl sulfoxide (DMSO) to yield alkenes and alkyl *t*-butyl ethers.[1] Continued interest in the reaction has led to an investigation of other nucleophiles in DMSO and other aprotic media. Results of investigations involving both sodium methoxide[2] and dimethylformamide (DMF) are reported here.

Benzenesulfonate esters were treated with an excess of sodium methoxide in DMSO at 20–25° for 30 min. and the products were analyzed by gas chromatography as described previously.[1] Table I presents a comparison of results obtained in this investigation with corresponding results reported earlier for potassium *t*-butoxide. In Table II are results obtained in DMF for reactions of benzenesulfonates of a typical primary and secondary alcohol with both sodium methoxide and potassium *t*-butoxide.

Generally the data are consistent with a recent report that both *n*-octadecyl bromide and 2-mesitylethyl tosylate give a larger substitution–elimination ratio with sodium methoxide in refluxing methanol than with potassium *t*-butoxide in refluxing *t*-butyl alcohol.[3]

More specifically, predominant Hofmann elimination obtained with 2-octyl benzenesulfonate and potassium *t*-butoxide (65% Hofmann in DMSO; 66% in DMF) compared with this ester and sodium methoxide (59% and 57% Hofmann in DMSO; 56% and 55% in DMF) appears to be another example of the steric influence of the nucleophile in controlling the direction of elimination.[4]

Because isomerization of alkenes has been reported under conditions similar to these, a control experiment was run using 0.5 *M* 1-octene and 1.0 *M* potassium *t*-butoxide in DMSO at 20°. The observation of less than 4% isomerization to 2-octene, together with reported equilibrium constants, in a similar system but at 55°, of 7.83 and 25.9 for isomerization of 1-pentene to *cis*- and *trans*-2-pentene, respectively,[5] indicates almost exclusive kinetic control of alkene ratios here.

Predominantly Hofmann elimination observed in this study, even with methoxide anion, contrasts remarkably with predominantly Saytzeff elimination (58–59% Saytzeff in five runs) observed in the E2 elimination of 2-pentyl arenesulfonates with sodium ethoxide in ethanol.[6] In the present study similarities of product proportions in both DMSO and DMF suggest that the predominance of Hofmann elimination here may be due to a general solvent effect. A simple explanation is based on the inability of DMSO and DMF (but ability of ethanol) to solvate anions by hydrogen bonding. Thus, in Colter and Johnson's study, the solvent ethanol can stabilize the departing anion readily by hydrogen bonding in a *trans* elimination. In this work, however, hydrogen bonding to the sulfonate anion can occur only from alcohol *generated in the elimination itself.* The stabilization gained by hydrogen bonding of the generated anion with simultaneously generated alcohol may be a sufficient driving

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[1] C. H. Snyder and A. R. Soto, *J. Org. Chem.*, **29**, 742 (1964).

[2] D. H. Ball, E. D. M. Eades, and L. Long, Jr. [*J. Am. Chem. Soc.*, **86**, 3579 (1964)], have reported unusual stereochemical consequences of a reaction of sodium methoxide with carbohydrate mesyl esters in DMSO.

[3] P. Veeragau, R. T. Arnold, and E. W. Eigenmann, *ibid.*, **86**, 3072 (1964).

[4] H. C. Brown, I. Moritani, and Y. Okamoto, *ibid.*, **78**, 2193 (1956).

[5] A. Schriesheim, J. E. Hofmann, and C. A. Rowe, Jr., *ibid.*, **83**, 3731 (1961).

[6] A. K. Colter and R. D. Johnson, *ibid.*, **84**, 3289 (1962).

TABLE I

PRODUCTS OF THE REACTION OF ALKYL BENZENESULFONATES (0.5 M) WITH ALKOXIDES (1.0 M) IN DIMETHYL SULFOXIDE AT 20–25°

	Sodium methoxide		Potassium t-butoxide[a]	
Parent alcohol	% alkene	% ether	% alkene	% ether
1-Hexanol	Trace	89, 90[b]	20	69
2-Methyl-1-butanol	2.3	62, 65[b]	22	39
2-Octanol	26, 27[b] 1-octene	25, 28[b]	51 1-octene	Trace
	18, 20[b] 2-octenes		28 2-octenes	
Cyclopentanol	27, 33[b]	44, 44[b]	76	None
Cyclohexanol	85	5	83	Trace

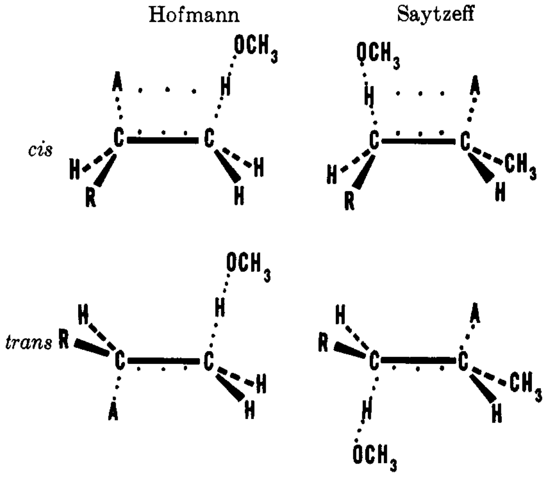
[a] See ref. 1. [b] Duplicate determinations.

TABLE II

PRODUCTS OF THE REACTION OF ALKYL BENZENESULFONATES (0.5 M) WITH ALKOXIDES (1.0 M) IN DIMETHYLFORMAMIDE AT 20–25°

	Sodium methoxide			Potassium t-butoxide		
Parent alcohol	% alkene	% ether	Time, hr.	% alkene	% ether	Time, hr.
1-Hexanol	None	90	0.5	17.5	68	1
2-Octanol	12.6 1-octene 9.8 2-octenes	14.3	0.5	57 1-octene 30 2-octenes	Trace	0.5
	30 1-octene 25 2-octenes	32	2			

force to produce a *cis* elimination[7] in DMF and DMSO. In such a *cis* elimination steric repulsions involving the attacking alkoxide and both the pentyl group (in 2-octyl esters) and the departing sulfonate in Saytzeff elimination would appear somewhat greater than those between the alkoxide and the departing anion alone in Hofmann elmination, and thus may be responsible for the observed results. An examination of molecular models suggests that this steric difference in nucleophilic environments may be somewhat greater in *cis* than in *trans* eliminations.



Similar reasoning may explain the disproportionately large amount of elimination from cyclohexyl benzenesulfonate with methoxide ion. The sulfonate moiety is predominantly in the equatorial conformation, restricting substitution to the small fraction in the axial conformation. However, *cis* elimination may occur about as readily from the equatorial conformer as *trans* elimination from the axial if the postulated hydrogen bonding is a sufficient driving force to compensate for the lack of complete coplanarity of the sulfonate moiety and an equatorial β-hydrogen in the transition state.

Alkoxide promoted elimination from sulfonate esters of *threo*- or *erythro*-3-*d*-2-alkanols and examination of the *cis*- and *trans*-2-alkenes for deuterium content should provide a convenient test for the postulated *cis* elimination.

Finally, the appreciable formation of 2-methoxyoctane in the reaction of 2-octyl benzenesulfonate with sodium methoxide has been used to gain an insight into the mechanism of the reaction.

The electronic character of the leaving group has been shown to exert only a very small influence (in terms of a parameter mathematically analogous to ρ) on the substitution–elimination ratio obtained with unbranched primary alkyl arylsulfonates.[1] The magnitude of the observed value may be explained by several mechanistic hypotheses. One possible route involves formation of both alkene and ether from the alkyl moiety *via* a common intermediate which does not incorporate the leaving group and in which the leaving group's electronic influence is weak or nonexistent, *e.g.*, a dissociated carbonium ion,[8] a carbene, or an alkoxydimethylsulfonium cation, $(CH_3)_2SOR^+$.[9,10] Incursion of the first two should produce extensive racemization of an optically active alkyl moiety, while the last, involving an over-all double displacement, should give net retention.[9]

Accordingly (+)-2-octyl p-brosylate, $[\alpha]^{27}\text{D}$ +7.12° (c 1.68, ethanol), lit.[11] $[\alpha]^{25}\text{D}$ +7.06° (c 1.84, ethanol), was prepared from p-bromobenzenesulfonyl chloride and (+)-2-octanol, $[\alpha]^{21}\text{D}$ +9.50° (neat), lit. $[\alpha]^{20}\text{D}$ +9.91°,[12] +9.93°[13], and reacted with sodium methoxide in dry DMSO to yield (−)-2-methoxyoctane, $[\alpha]^{28}\text{D}$ −7.28° (c 7, ethanol). Preparation of (+)-2-methoxyoctane from methyl iodide and the potassium salt of (+)-2-octanol by the method of Kenyon and

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[7] (a) N. A. LeBel, *et al.*, *J. Am. Chem. Soc.* **85**, 3199 (1963); (b) C. H. DePuy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1314 (1962); (c) S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957); (d) S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952); (e) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962); (f) A. J. Parker, *J. Chem. Soc.*, 1328 (1961).

[8] M. Cocivera and S. Winstein *J. Am. Chem. Soc.*, **85**, 1702 (1963).

[9] R. Fuchs, G. E. McCrary, and J. J. Bloomfield, *ibid.*, **83**, 4281 (1961).

[10] S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

[11] R. C. Cary, F. F. Vitcha, and R. L. Shriner, *J. Org. Chem.*, **1**, 280 (1937).

[12] J. B. M. Coppock and F. R. Gross, *J. Chem. Soc.*, 1789 (1939).

[13] H. Brauns, *Rec. trav. chim.*, **65**, 803 (1946).

McNicol[14] gave ether with $[\alpha]^{26}\mathrm{D}$ +7.42° (c 7, ethanol) and $[\alpha]^{29}\mathrm{D}$ +7.83° (c 7, ethanol) from two different preparations. The higher of these two values indicates 93% inversion and 7% racemization or about 96% inversion and 4% retention in the p-bromobenzenesulfonate reaction.[15]

The validity of these results depends on complete retention of the carbinol carbon's configuration in the Williamson reaction. Although Kenyon and McNicol recovered starting (+)-2-octanol of essentially unchanged activity from products of a similar reaction and the reaction itself involves materials and conditions presumably incompatible with racemization,[16] doubt has been expressed[17] concerning the stereochemical reliability of the reaction as applied to conversion of (+)-2-octanol to (+)-2-ethoxyoctane. Evidence for this doubt consists of a report,[18] whose relation to the reaction under consideration is not clear, and apparent variations in rotational ratios of ether and alcohol observed by independent workers. Unfortunately these observed ratios involved variations in temperature and wave length. Thus the small differences in observed ratios are not necessarily inconsistent with configurational purity.[19]

The high orders of inversion observed in this work eliminate the possibility of extensive carbonium ion, carbene, or alkoxydimethylsulfonium ion formation in reactions of secondary esters and indicate ether formation predominantly *via* a simple bimolecular displacement. It is tempting to extrapolate these results to primary systems in which absence of significant electronic effects has been noted.

Thus dissociation of a primary ester in DMSO to a carbonium ion should be less likely than similar dissociation of a secondary ester. Supporting this is the absence of any peak attributable to 2-methyl-2-butene in the chromatogram of products obtained from the reaction of 2-methyl-1-butyl benzenesulfonate with sodium methoxide in DMSO. 2-Methyl-2-butene and 2-methyl-1-butene are demonstrably resolvable on a Carbowax 20M column.

Similarly carbenes seem unlikely in the primary systems. Reaction of hexyl benzenesulfonate (0.5 M) with potassium t-butoxide in DMSO in the presence of cyclohexene (1.0 M) produced essentially unchanged yields of hexene (21%) and ether (73%). Recovery of cyclohexene (89%) was identical with that obtained from a synthetic reaction mixture.

However, alkoxydimethylsulfonium cations cannot be ruled out in reactions of primary esters. Observation of almost identical product ratios on reaction of hexyl benzenesulfonate with potassium t-butoxide in both DMSO and DMF suggests a similarity of reaction paths in both solvents but is inconclusive. Recovery of over 90% of hexyl p-bromo- and p-nitrobenzenesulfonates from attempted solvolyses of these esters in DMSO[1] indicates absence of extensive alkoxydimethylsulfonium ion formation under reaction conditions, but does not preclude preferential reaction of alkoxide with a small equilibrium concentration of this cation.

Finally, although the reaction of 2-octyl benzenesulfonate with sodium methoxide seems somewhat slower in DMF than in DMSO, the final ether–alkene ratio in DMF is equal to the average ratio obtained with this ester and methoxide in DMSO. More extensive comparison of the data in the tables suggests that solvent variations may produce significant variations in reaction rates with substantially unchanged product ratios.

Continued study of this reaction is in progress.

Experimental

Illustrative Reaction.—Except where noted, materials, conditions, and isolation and analytical procedures have been described.[1] A solution of 3.025 g. (12.5 mmoles) of 1-hexyl benzenesulfonate, $n^{20}\mathrm{D}$ 1.4955 (lit.[20,21] $n^{25}\mathrm{D}$ 1.4952), in 12.5 ml. of dimethyl sulfoxide was added to a stirred slurry of 1.35 g. (25 mmoles) of sodium methoxide in 12.5 ml. of dimethyl sulfoxide maintained at 20–25°. After the reaction mixture had been stirred 30 min. at this temperature, isolation and analysis indicated 90% methyl n-hexyl ether and traces of 1-hexene. Combination of heptane extracts of two identical reactions and distillation gave 0.670 g. (23%/reaction) of a series of fractions of methyl n-hexyl ether, b.p. 117–120° at 763 mm., $n^{20}\mathrm{D}$ 1.3960–1.3969 (lit.[22] b.p. 125–126° at 770 mm., $n^{20}\mathrm{D}$ 1.3972). This ether was demonstrated chromatographically identical (Carbowax 20M column and silicon oil column) with the presumed ether peak of the heptane extracts.

Ethers produced from other esters (except cyclohexyl benzenesulfonate) were condensed from chromatographic eluents of respective heptane extracts and characterized by refractive indices. Infrared spectra of all isolated ethers were consistent with assigned structures.

Reaction of (+)-2-Octyl *p*-Bromobenzenesulfonate.—To a stirred slurry of 1.35 g. (25 mmoles) of sodium methoxide in 12.5 ml. of dimethyl sulfoxide, distilled under vacuum from calcium hydride, was added a solution of 4.36 g. (12.5 mmoles) of the ester, m.p. 29–30° (lit.[11] m.p. 30°), prepared by the method of Carey, *et al.*,[11] in 12.5 ml. of similarly dried dimethyl sulfoxide. The temperature of the reaction mixture was maintained at 20–25° during addition and for 2 hr. thereafter. Standard isolation procedures, combination of heptane extracts of this and two additional preparations, and distillation gave a fraction containing both octenes and 2-methoxyoctane. Gas chroma-

TABLE III
REFRACTIVE INDICES OF METHYL ALKYL ETHERS
CONDENSED FROM GAS CHROMATOGRAPHIC ELUENTS

	Found	Lit.	
Alkyl moiety	nD (temp., °C.)	nD (temp., °C.)	Ref.
2-Methyl-1-butyl	1.3850 (20)	1.3849 (20.2)	*a*
2-Octyl	1.4082 (20)	1.4083 (20)	*b*
	1.4069 (25)	1.4071 (25)	*c*
		1.4068 (25)	*d*
Cyclopentyl	1.4200 (20)	1.4204 (20)	*e*

[a] P. Guye and L. Chavanne, *Bull. soc. chim. France*, [3] **15**, 275 (1896). [b] E. J. Corey and W. J. Wechter, *J. Am. Chem. Soc.*, **76**, 6040 (1954). [c] R. L. Letsinger, A. W. Schnitzer, and E. Bobko, *ibid.*, **73**, 5708 (1951). [d] W. von E. Doering and R. W. Young, *ibid.* **74**, 2997 (1952). [e] A. I. Vogel, *J. Chem. Soc.*, 1809 (1948).

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(14) J. Kenyon and R. A. McNicol, *J. Chem. Soc.*, **123**, 14 (1923).

(15) The observation[2] that a carbohydrate ester can give methyl ether of *retained* configuration may be due to a necessarily equatorial leaving group in the system studied. Backside displacement in that system should not be observed.

(16) (a) W. von E. Doering and T. C. Aschner, *J. Am. Chem. Soc.*, **71**, 838 (1949); (b) P. G. Stevens and S. A. V. Deans, *Can. J. Res.*, **B17**, 290 (1939); (c) P. G. Stevens, *J. Am. Chem. Soc.*, **54**, 3732 (1932); (d) W. Huckel and H. Naab, *Ber.*, **64**, 2137 (1931).

(17) A. Streitwieser, Jr., and A. C. Waiss, Jr., *J. Org. Chem.*, **27**, 290 (1962).

(18) See footnote 5 of ref. 17.

(19) W. Heller in "Technique of Organic Chemistry," Vol. I (part 3), A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 33, pp. 2306–2309, 2315–2316.

(20) F. L. M. Pattison and J. E. Mallington, *Can. J. Chem.*, **34**, 757 (1956).

(21) B. L. Emling, *J. Am. Chem. Soc.*, **74**, 4702 (1952).

(22) A. I. Vogel, *J. Chem. Soc.*, 616 (1948).

tographic fractionation gave ether with physical characteristics described elsewhere in this publication.

Preparation of (+)-2-Methoxyoctane.—(+)-2-Octanol was converted to (+)-2-methoxyoctane by the procedure of Kenyon and McNicol.[14] Distillation of the product under reduced pressure gave ether, b.p. 59–60° at 11 mm. (lit.[14] b.p. 76–77° at 44 mm.), n^{20}_D 1.4072, n^{25}_D 1.4065 (literature values are given in Table III).

Reactions in Dimethylformamide.—These were similar to those in dimethyl sulfoxide except that the solvent was dried overnight over a mixture of potassium hydroxide and barium oxide, filtered, and fractionally distilled before use.

The Addition of Dialkylalkylthiosulfonium Salts to Alkenes[1]

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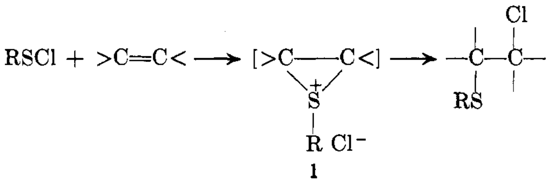
Alkylated disulfides in the form of dialkylalkylthiosulfonium trinitrobenzenesulfonates, RR′S⁺SR TNBS⁻, add to substituted ethylenes or acetylenes to yield 1-alkylthio-2-dialkylsulfonio derivatives. Acetylene itself is fairly unreactive, and the presence of electron-withdrawing substituents in alkenes leads to decreased reactivity. The addition is probably *trans*, for dimethylmethylthiosulfonium trinitrobenzenesulfonate adds to *cis*-cyclooctene to yield a product identical with that from the reaction of *cis*-cyclooctene S-methylepisulfonium trinitrobenzenesulfonate with dimethyl sulfide.

In the reaction of sulfenyl halides with alkenes, the proposed mechanism involves electrophilic addition initiated by transfer of a sulfenium group, RS⁺, to the substrate. The episulfonium intermediate, **1** (eq. 1), reacts with halide with net *trans* addition.[3-5]


(1)

1

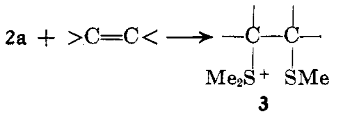
Other nucleophiles could be intercepted by the intermediate, and, indeed, other types of compounds could act as sulfenium transfer agents if an appropriate leaving group were present.

Recently we reported the formation of alkylated disulfides **2** from alkyl disulfides and oxonium salts of trinitrobenzenesulfonic acid[6] (eq. 2). These salts

$$\mathrm{RSSR + R'_3O^+ \longrightarrow R'_2O + RR'S^+SR} \qquad (2)$$

2a, R = R′ = Me
b, R = Et; R′ = Me
c, R = R′ = Et

had structural features that led to the prediction that they would transfer the sulfenium group to an alkene, for dimethyl sulfide seemed to represent a good leaving group. It was found that such a reaction was feasible, for a 1-alkylthio-2-dialkylsulfonioalkane (**3**) formed very readily with many alkenes (eq. 3).

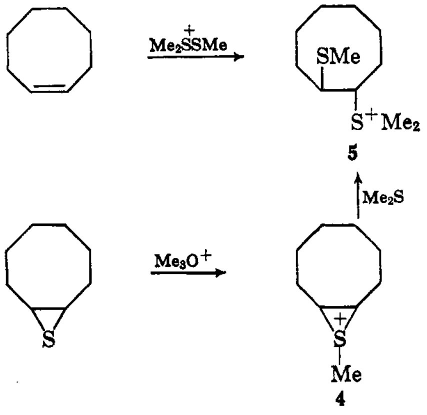


$$\mathbf{2a} + \mathrm{{>}C{=}C{<}} \longrightarrow \underset{\mathrm{Me_2S^+}}{-\overset{|}{\underset{|}{C}}}-\underset{\mathrm{SMe}}{\overset{|}{\underset{|}{C}}-} \qquad (3)$$

3

If cyclooctene were used as the alkene, the adduct **3** could be prepared by an alternate route. The stable cyclooctene S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate[7] (**4**) reacted readily with methyl sulfide to yield the same product, **5**, as that formed in the addition of dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate to cyclooctene (eq. 4).

Variations in the structure of the alkene had little influence on the reaction, as in the case of Kharasch's extensive survey of the addition of 2,4-dinitrobenzenesulfenyl chloride.[8] However, the presence of electron-withdrawing groups in the vinyl positions slows down or inhibits the addition. Neither isomer of 1,2-dichloroethylene was found to react under time and temperature conditions in which alkyl-substituted ethylenes reacted readily, but chalcone seemed to form a product slowly. Substituted acetylenes also reacted *via* monoaddition, but no catalytic process related to the sulfenyl chloride addition[9] to acetylene was investigated. The compounds included in the present work are described in Table I.



(4)

Abrupt limitations were encountered in the preparation of homologs of methylated methyl disulfide,[6] but it was possible to carry out additions with diethylethylthiosulfonium trinitrobenzenesulfonate (**6**), methylethylethylthiosulfonium trinitrobenzenesulfonate (**7**), and methylethylmethylthiosulfonium trinitrobenzenesulfonate (**8**) (Table II).

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[1] Supported in part by Grant GM 8185 from the National Institutes of Health, U. S. Public Health Service.

[2] Abstracted in part from the Ph.D. Thesis of D. J. Pettitt.

[3] N. Kharasch and A. J. Havlik, *J. Am. Chem. Soc.*, **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, H. N. Cassey, B. A. Olsen, and D. J. Pettitt, *J. Org. Chem.*, **30**, 933 (1965).

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

[8] See, for example, N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2725 (1949); N. Kharasch, C. M. Buess, and S. I. Strashun, *ibid.*, **74**, 3422 (1952).

[9] N. Kharasch and S. J. Assony, *ibid.*, **75**, 1081 (1963).