The Reaction of Sodium and Potassium with Dimethyl Sulfoxide. The Formation and Alkylation of Methanesulfenate[1]

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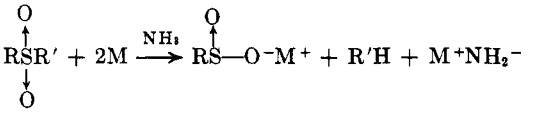
The reaction of sodium and potassium with excess dimethyl sulfoxide (DMSO) yields a mixture of the salts of methanesulfenate (I) and methylsulfinyl carbanion (II) along with methane and dimethyl sulfide. In the sodium–DMSO reaction there appear to be two primary reactions which are of about equal importance. One is reductive cleavage of the carbon–sulfur bond, which yields sodium methanesulfenate and, presumably, methylsodium (eq. 3), and the other is sulfur–oxygen bond cleavage, which yields dimethyl sulfide and, presumably, sodium oxide (eq. 5). The strong bases, methylsodium and sodium oxide, would react with DMSO to form sodium methylsulfinyl carbanion, methane, and sodium hydroxide (eq. 4 and 6). In the potassium–DMSO reaction carbon–sulfur bond cleavage greatly predominates. Sodium and potassium methanesulfenates are stable for several days at room temperature in the reaction mixture. Alkylation of methanesulfenate ions with alkyl bromides and iodides occurs readily to produce sulfoxides in good yields. No evidence of O-alkylated products was seen.

The reductive cleavage of sulfides[2-4] and sulfones[5,6] by alkali metals has been studied, but apparently the analogous reaction of sulfoxides with alkali metals has not previously been investigated.[7] Since sulfoxides are intermediate in oxidation state, their reactions with alkali metals are of considerable interest.

Both sulfones and sulfides are cleaved by alkali metals at the carbon–sulfur bond giving high yields of the products shown in eq. 1 and 2. In both, carbon–sulfur bond cleavage is the only significant process that occurs. We have now found that in sulfoxides a second process, sulfur–oxygen bond cleavage (reduction), also occurs.



$$R\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}R' + 2M \xrightarrow{NH_3} R\overset{\overset{O}{\uparrow}}{S}{-}O^-M^+ + R'H + M^+NH_2^- \qquad (1)$$

$$RSR' + 2M \xrightarrow{NH_3} R'S^-M^+ + RH + M^+NH_2^- \qquad (2)$$

As shown in eq. 1 and 2, cleavage reactions of sulfones and sulfides lead, respectively, to sulfinate and mercaptide salts which can be isolated as such or as their conjugate acids. A similar cleavage of sulfoxides, however, should lead to sulfenate salts which are considerably more elusive entities.[8] The only sulfenic acids that have been reported[9] are those derived from anthraquinone, which include 1-anthraquinonesulfenic acid and 1,4- and 1,5-anthraquinonedisulfenic acids. Alkanesulfenates have been postulated as intermediates in various reactions,[10-12] but their chemistry has not been studied. In this paper we present evidence that methanesulfenate is formed in the cleavage reaction, that it is stable in the reaction medium, and that it is alkylated by alkyl halides almost exclusively on sulfur to form sulfoxides.

Results and Discussion

The reactions of potassium and sodium with sulfoxides were studied by adding the alkali metal in small pieces to an excess of the sulfoxide. The reaction produces a hydrocarbon and an anionic mixture which was alkylated in order to identify its components.

The addition of sodium to neat DMSO at room temperature produced a slow, smooth reaction which required several hours to go to completion. The addition of potassium to neat DMSO at room temperature produced an extremely vigorous reaction which caused the solution to blacken. This latter reaction could be carried out smoothly using a 2:1 (v./v.) mixture of tetrahydrofuran (THF) and DMSO at <10°. Under these conditions a small piece of potassium was consumed in a few minutes. Methane was evolved during the reactions of both sodium and potassium with DMSO and the odor of dimethyl sulfide was quite pronounced during the work-up of the sodium–DMSO reaction. Lithium wire did not react with neat DMSO at temperatures up to 80°.

The resulting anionic mixture was alkylated with 1-bromopentane to give a mixture of sulfoxides which was analyzed quantitatively by gas chromatography (g.c.). The quantity of methane evolved was measured by trapping it in an inverted graduated cylinder. It was identified by its infrared spectrum and by its retention time on a g.c. column (alumina). The dimethyl sulfide was identified by conversion to its mercuric chloride salt, $2(CH_3)_2S \cdot 3HgCl_2$. The products obtained from these reactions after alkylation with 1-bromopentane are listed in Table I. Several other runs with both potassium and sodium gave essentially equivalent results.

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[1] Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

[2] F. E. Williams and E. Gebauer-Fuelnegg, *J. Am. Chem. Soc.*, **53**, 352 (1931); C. A. Kraus and G. F. White, *ibid.*, **45**, 768 (1923).

[3] W. E. Truce and J. J. Breiter, *ibid.*, **84**, 1621 (1962).

[4] R. C. Krug and S. Tocker, *J. Org. Chem.*, **20**, 1 (1955).

[5] R. E. Dabby, J. Kenyon, and R. F. Mason, *J. Chem. Soc.*, 4881 (1952).

[6] W. E. Truce, D. P. Tate, and D. N. Burdge, *J. Am. Chem. Soc.*, **82**, 2872 (1960).

[7] Recently, A. Ledwith and N. McFarlane [*Proc. Chem. Soc.*, 108 (1964)] reported that DMSO reacts with sodium to form methylsulfinyl carbanion, hydrogen, and dimethyl sulfide. However, our findings are at variance with theirs. We found no evidence for the formation of hydrogen. We found that methane is formed and suspect that they mistakenly identified methane as hydrogen. They apparently failed to detect that methanesulfenate is also formed.

[8] See N. Kharasch, S. J. Potempa, and H. J. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946), for a review of the pertinent literature.

[9] (a) K. Fries, *Chem. Ber.*, **45**, 2965 (1912); (b) T. C. Bruice and R. T. Markiw, *J. Am. Chem. Soc.*, **79**, 3150 (1957); (c) W. Jenny, *Helv. Chim. Acta*, **41**, 317, 326, 331 (1958).

[10] A. Levi, L. A. Warren, and S. Smiles, *J. Chem. Soc.*, 1490 (1933).

[11] A. S. F. Ash, F. Challenger, and D. Greenwood, *ibid.*, 1877 (1951); 2792 (1952).

[12] T. J. Wallace and A. Schriesheim, *Tetrahedron Letters*, 1131 (1963).

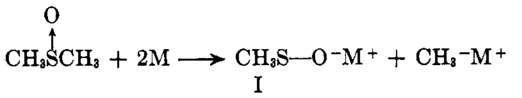
TABLE I

PRODUCTS OF REACTION OF DIMETHYL SULFOXIDE WITH ALKALI METALS[a]

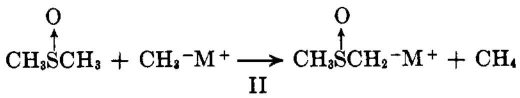
Run	Metal (0.1 mole)	Solvent (ml.)	Alkyl halide, RX	CH_3SO^- (as $CH_3S(O)R$), mole	$CH_3S(O)CH_2^-$ (as $CH_3S(O)CH_2R$), mole	CH_3SCH_3, mole	CH_4, mole
1	Sodium	DMSO (25)	$C_5H_{11}Br$	0.025	0.052	0.010	0.027
2	Sodium	DMSO (100)	$C_5H_{11}I$	0.024	0.050	0.0051	0.025
3[b]	Sodium	DMSO (100)	$C_{12}H_{25}Br$	80%		...	...
4[c]	Potassium	DMSO (60) Ether (40)	$C_5H_{11}Br$	0.049	0.037	0.001	0.056
5	Potassium	DMSO (100) THF (100)	$C_5H_{11}I$	0.050	0.055	...	0.042

[a] Reaction sequence: 0.1 mole of alkali metal was added to excess DMSO; after metal was consumed, alkyl bromide was added to reaction mixture. [b] The two homologs were not separated; the total yield was 80% of theoretical (assuming 0.05 mole of each homolog as theoretical). Methane and dimethyl sulfide were not determined. Methyl dodecyl sulfide (0.0065 mole) and dodecene (0.0035 mole) were also obtained. [c] This mixture formed two phases shortly after the reaction began; almost all of the reaction occurred in the lower layer where the DMSO was concentrated.

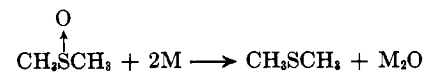
The products formed in the sodium–DMSO reaction very probably arise from the reactions shown in eq. 3–7.



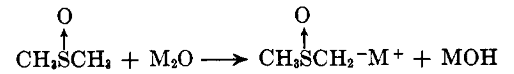
$$CH_3\overset{\overset{O}{\uparrow}}{S}CH_3 + 2M \longrightarrow \underset{I}{CH_3S{-}O^-M^+} + CH_3^-M^+ \qquad (3)$$



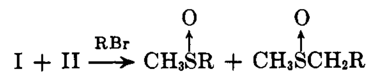
$$CH_3\overset{\overset{O}{\uparrow}}{S}CH_3 + CH_3^-M^+ \longrightarrow \underset{II}{CH_3\overset{\overset{O}{\uparrow}}{S}CH_2^-M^+} + CH_4 \qquad (4)$$



$$CH_3\overset{\overset{O}{\uparrow}}{S}CH_3 + 2M \longrightarrow CH_3SCH_3 + M_2O \qquad (5)$$



$$CH_3\overset{\overset{O}{\uparrow}}{S}CH_3 + M_2O \longrightarrow CH_3\overset{\overset{O}{\uparrow}}{S}CH_2^-M^+ + MOH \qquad (6)$$



$$I + II \xrightarrow{RBr} CH_3\overset{\overset{O}{\uparrow}}{S}R + CH_3\overset{\overset{O}{\uparrow}}{S}CH_2R \qquad (7)$$

The methane formed arises from the reaction sequence shown in eq. 3 and 4. The process shown in eq. 3 should give rise to a quantity of I equal to the quantity of methane formed; subsequent reaction of I with an alkyl bromide could then lead to the observed sulfoxide. The fact that within experimental error equal quantities of methane and pentyl methyl sulfoxide are formed is compelling evidence for the reaction sequence shown in eq. 3 and 4.

Our data further indicate that alkylation of the ambident sulfenate anion (I) occurred essentially exclusively on sulfur. Since the formation of I requires the formation of an equimolar quantity of methane, the fact that equal amounts of methane and pentyl methyl sulfoxide were obtained indicates that I must alkylate almost exclusively on sulfur. If a significant amount of O-alkylation had occurred, the yield of methane would have been measurably greater than that of pentyl methyl sulfoxide. All of our attempts to isolate pentyl methanesulfenate from this reaction mixture failed, but this failure does not preclude the formation of trace quantities of it. Although there is very little information available concerning sulfenates, that which is available indicates that alkylation on sulfur should be expected. Thus Fries[9] found that sodium α-anthraquinonesulfenate reacts with methyl iodide to form the sulfoxide, and Levi, Warren, and Smiles[10] obtained a sulfoxide by treating with methyl iodide a compound that was very probably sodium *o*-acetamidobenzenesulfenate. Similarly, the alkylation of sulfinates occurs on sulfur to produce sulfones rather than on oxygen to produce sulfinate esters.[13] Thus, the available evidence indicates that sulfur–oxygen ambident anions alkylate on sulfur, and our results are in accord with this.

In the sodium–DMSO reaction, the quantities of methane and pentyl methyl sulfoxide formed account for roughly half of the sodium consumed. It seems quite probable that a major part of the rest of the sodium reacts as shown in eq. 5. Substantial quantities of dimethyl sulfide (DMS) were isolated and must arise from sulfur–oxygen bond cleavage (reduction). Such a reduction apparently does not occur in the analogous reaction of sulfones with alkali metals; however, it is not surprising that sulfoxides and sulfones behave differently in this respect, since sulfoxides are easily reduced by a variety of reagents,[14] while sulfones are exceedingly difficult to reduce even with powerful reagents.[15]

The amount of DMS isolated was not quantitative and furthermore was found to be variable from one run to another. In every run in which the attempt to recover DMS was made, some of it was obtained, but the nonreproducibility of the amount formed suggested that it might be reacting further. One such reaction that it could undergo is that shown in eq. 8. This possibility was tested by treating a sodium–DMSO reaction mixture with bromododecane (run 3). After isolation of the solid product, a mixture of dodecyl and tridecyl methyl sulfoxides in 80% yield, the liquid residue was distilled to yield 3.5% of dodecene and 6.5% of dodecyl methyl sulfide. The most probable route by which dodecyl methyl sulfide could be formed is that shown in eq. 8, followed by alkylation of the methyl mercaptide. This result shows that some DMS is lost by further reaction, but the quantity consumed in this manner hardly accounts for all of the discrepancies in DMS yields. It seems probable that the basic difficulty was simply that our method of recovery was not quantitative.

$$CH_3SCH_3 + 2Na \longrightarrow CH_3S^-Na^+ + CH_3^-NA^+ \qquad (8)$$

The other major product of the sodium–DMSO reaction, II, is produced by the reaction with DMSO of the strong bases formed in the primary processes (eq. 3 and 5). In each of the cleavage reactions a stronger base

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(13) C. M. Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 667.

(14) H. H. Szmant, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, p. 159.

(15) F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **73**, 2251 (1951).

than II is formed. DMSO is known to react with sodamide and sodium hydride to form II,[16] and it would surely react in a similar manner with methylsodium. In independent experiments it was shown that sodium oxide reacts with DMSO to form II (see Experimental), which verified that eq. 6 was possible.

The course of the potassium–DMSO reaction was different from the sodium–DMSO reaction in only one important respect: whereas with sodium, reactions 3 and 5 occurred to about the same extent, with potassium, reaction 3 greatly predominated. The combined quantities of I and II (measured as the sulfoxides) account for essentially all of the potassium used. As in the sodium–DMSO reaction, methane and I were formed in equimolar quantities. Furthermore, very little DMS was obtained. It thus appears that the major difference between the two reaction systems is that in the potassium–DMSO reaction the carbon–sulfur bond cleavage process is very much faster than the reduction process, whereas in the sodium–DMSO reaction, the two processes occur at about equal rates.

Considered in the light of what is known about the reaction of sulfides and sulfones with alkali metals, the reactions discussed in this paper are not particularly surprising. What is novel and somewhat unexpected is that the alkali metal salt of methanesulfenate which is formed is stable for at least several days at room temperature in the reaction mixture. This system offers for the first time a means whereby the reactions of simple alkanesulfenates may be studied. Up to now anthraquinonesulfenates[9] were the only sulfenates which had been stable enough to study. The remarkable stability in the present instance is very probably due to the anion being dissolved in the aprotic DMSO solvent and further protected by II from contact with small amounts of proton sources. It is quite likely that in an alcohol or other protic solvent, I would be protonated and the resulting sulfenic acid would then undergo disproportionation. In the past, sulfenates and sulfenic acids have been regarded as quite unstable materials, but our results indicate that it is only the acids which are unstable while the sulfenate anions themselves are quite stable.

Experimental

Dimethyl sulfoxide (Crown Zellerbach) was dried over 4A Molecular Sieve and was distilled *in vacuo* from calcium hydride. The sodium, potassium, bromopentane, and iodopentane were reagent grade obtained from Matheson Coleman and Bell and were used as received. Two gas chromatographic columns were used to analyze the mixture of sulfoxides. One was a 5-ft., 0.25-in. diameter column packed with 10% Apiezon L on Fluoropak; the other was a 5-ft., 0.25-in. diameter column packed with 10% silicone fluid (SF-96) on Fluoropak. Use of Fluoropak as the support is important. Nonpolar stationary phases on other supports, such as Chromosorb, give much more pronounced tailing with the sulfoxides. Both the SF-96 and the Apiezon L columns gave the same percentages of isomers. The column temperatures used were normally around 140° and the injection port temperatures were around 200°. The elemental analyses were done by the Procter and Gamble Analytical Services Laboratory.

Reaction of Sodium with Dimethyl Sufoxide.—Dimethyl sulfoxide (DMSO, 100 ml.) was placed in a flask which had previously been swept with nitrogen. Then, 4.6 g. (0.2 g.-atom) of sodium in small pieces (*ca.* 0.25-in. cubes) was added at room temperature. The temperature rose to 42° after 10 min., and the mixture was maintained at 30–40° during the several hours required for the sodium to be consumed. Throughout the reaction there was a slow evolution of gas, the quantity of which, after passage through a drying tube, was measured in a graduated cylinder by displacement of water. The total volume of gas evolved was 1340 cc. (0.0545 mole). An infrared spectrum of the gas was essentially identical with that of an authentic sample of methane. Analysis of the gas by a mass spectrometer and by g.c. on an alumina column also indicated the presence of methane.

Then the reaction mixture was treated with 30.2 g. (0.20 mole) of 1-bromopentane and was stirred for an hour. An aspirator vacuum was applied through a Dry Ice trap to the reaction flask in order to remove dimethyl sulfide from the reaction mixture. The contents of the Dry Ice trap were taken up in ethanol and were added to an ethanolic solution of mercuric chloride, from which there was obtained 9.25 g. of $2(CH_3)_2S \cdot 3HgCl_2$, m.p. 157–158° (lit.[17] m.p. 158–159°), which corresponded to a yield of 1.22 g. (0.019 mole) of dimethyl sulfide. The original reaction mixture was then taken up in ether in order to precipitate the inorganic salts (*e.g.*, sodium bromide) present. Ether addition was continued until no further precipitate formed. The ether extracts were filtered, and the ether was evaporated to yield 79.5 g. of residue. Gas chromatographic (g.c.) analysis of the residue indicated the presence of three major components: DMSO (83.3 mole %), pentyl methyl sulfoxide (5.3 mole %), and hexyl methyl sulfoxide (11.4 mole %), which corresponded to a yield of 6.5 g. (0.049 mole) of pentyl methyl sulfoxide and 15.6 g. (0.105 mole) of hexyl methyl sulfoxide. The 79.5-g. residue was distilled through a 2-ft. spinning-band column to yield a 4.8-g. sample of pentyl methyl sulfoxide, b.p. 61° (0.35 mm.).

Anal. Calcd. for $C_6H_{14}OS$: C, 53.7; H, 10.43; S, 23.8. Found: C, 54.0; H, 10.9; S, 23.6.

A second cut from the distillation of the residue was hexyl methyl sulfoxide, b.p. 68.5° (0.23 mm.).

Anal. Calcd. for $C_7H_{16}OS$: C, 56.7; H, 10.9; S, 21.6. Found: C, 56.5; H, 11.1; S, 21.4.

The other sodium–DMSO runs in Table I were carried out in the same manner.

Identification of an Alkyl Methyl Sulfide from the Reaction of Dimethyl Sulfoxide with Sodium.—In another run, a reaction of 100 ml. of DMSO with 2.3 g. (0.1 g.-atom) of sodium was carried out as described above and was then treated with 25.0 g. (0.10 mole) of 1-bromododecane. After the reaction mixture was stirred overnight, it was poured into 300 ml. of water and extracted with ethyl acetate. The extracts were dried over magnesium sulfate, and the ethyl acetate was evaporated. The solid residue was recrystallized from hexane to yield 17.4 g. of a mixture of dodecyl and tridecyl sulfoxides. The filtrate was evaporated to yield a 5.0-g. residue. Distillation of the residue gave 0.6 g. of dodecene, b.p. 30–40° (0.7 mm.), and 1.5 g. (0.007 mole) of dodecyl methyl sulfide, b.p. 90–105° (0.7 mm.). The dodecyl methyl sulfide was identified by comparison of its g.c. retention time and its n.m.r. spectrum with those of an authentic sample of dodecyl methyl sulfide.

Reaction of Potassium with Dimethyl Sulfoxide.—To a stirred mixture of 60 ml. of DMSO and 40 ml. of diethyl ether at $<10°$ was added 3.9 g. (0.1 g.-atom) of potassium (*ca.* 0.25-in. cubes). The reaction proceeded rapidly and it was necessary to maintain the temperature at $<10°$ to prevent the potassium from undergoing an uncontrolled reaction which resulted in carbonization. There was evolved 1280 cc. (0.052 mole) of methane (identified by infrared spectra). The dimethyl sulfide formed was collected and identified as described above; the yield was 0.10 g. (0.0016 mole) of dimethyl sulfide [0.8 g., $2(CH_3)_2S \cdot 3HgCl_2$]. Then 15.1 g. (0.1 mole) of 1-bromopentane was added to the reaction mixture at room temperature and the mixture was stirred overnight. The reaction mixture was worked up as described above and most of the DMSO solvent was distilled to leave a 14.9-g. residue, which was determined by g.c. to consist of 41.5 mole % DMSO, 32.4 mole % pentyl methyl sulfoxide, and 26.1 mole % hexyl methyl sulfoxide. Small additional amounts of pentyl methyl sulfoxide and hexyl methyl sulfoxide were present in the DMSO distillate. The combined yields were 0.049 mole of pentyl methyl sulfoxide and 0.037 mole of hexyl methyl sulfoxide. This reaction was quite difficult to duplicate because as soon as some potassium reacted, the ether and DMSO separated into two layers. With

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[16] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

[17] F. Challenger, "Aspects of the Organic Chemistry of Sulfur," Academic Press Inc., New York, N. Y., 1959, p. 18.

the DMSO concentrated in one layer, the reaction is difficult to control. The procedure given below, however, is easily reproducible.

Reaction of Potassium with Dimethyl Sulfoxide in a 2:1 Tetrahydrofuran–DMSO Mixture.—To a stirred mixture of 50 ml. of DMSO and 100 ml. of tetrahydrofuran (THF) at <10° was added 2.0 g. (0.05 g.-atom) of potassium (*ca.* 0.25-in. cubes). The reaction proceeded smoothly and was complete within an hour. The gas evolved (515 cc., 0.021 mole) was collected in a graduated cylinder by allowing it to displace water from the cylinder. When the reaction was complete, 10.0 g. (0.05 mole) of 1-iodopentane was added at room temperature and the reaction mixture was stirred for 3.5 hr. The THF was stripped off to leave a residue of 63.9 g., which still contained *ca.* 2.5 g. of THF and which was assumed to contain 8.4 g. (0.05 mole) of potassium iodide, since none had been recovered. Analysis by g.c. indicated that the residue contained 0.025 mole of pentyl methyl sulfoxide and 0.0276 mole of hexyl methyl sulfoxide. No attempt was made to recover dimethyl sulfide.

Reaction of Sodium Oxide with Dimethyl Sulfoxide.—To 100 ml. of DMSO was added 6.2 g. (0.1 mole) of sodium oxide (Alfa Inorganics, Inc.), and the mixture was heated at 50° for 18 hr. The mixture was cooled to room temperature, 15.1 g. (0.1 mole) of 1-bromopentane was added, and stirring was continued for 3 hr. The mixture was filtered to remove the unreacted sodium oxide, and the filtrate was poured into water, extracted with ethyl acetate, and dried over magnesium sulfate. The solvent was evaporated, and the residue was identified as being primarily hexyl methyl sulfoxide by g.c. analysis. The yield was around 25%. The low yield was probably due to the poor solubility of sodium oxide and/or to formation of a coating of sodium hydroxide on the surface of the sodium oxide.

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Stereochemistry of the Addition of Dialkylalkylthiosulfonium Salts to Alkenes and Alkynes[1,2]

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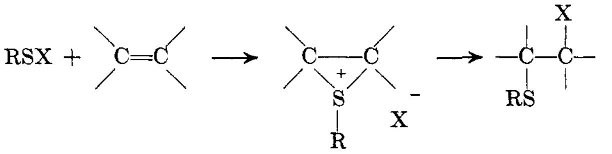
trans-2-Butene reacts with dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate (**1**) to form *dl-erythro*-1-dimethylsulfonio-2-methylthiobutane 2,4,6-trinitrobenzenesulfonate (**2**). Alkylation of **2** with trimethyloxonium trinitrobenzenesulfonate yielded 2,3-bis(dimethylsulfonio)butane 2,4,6-trinitrobenzenesulfonate (**3**). The direction of addition of **1** to the alkene was established as *trans* by comparing **3** with a product formed in the following sequence: (a) conversion of (*S*,*S*)-2-butene episulfide to (2*S*:3*R*)-3-methylthio-2-butanethiol (**5**); (b) monoalkylation of **5** to yield optically inactive (hence *meso*) 2,3-bis(methylthio)butane (6); and (c) exhaustive alkylation of either **5** or **6** to yield a compound identical with **3**. Similarly, the compound formed when **1** reacts with acetylene has n.m.r. and infrared spectra consistent with a *trans* arrangement of protons.

Dialkylalkylthiosulfonium salts react with alkenes and alkynes[3] in much the same way as do sulfenyl halides[4,5] to form 1:1 adducts. The proposed mechanism of addition of sulfenyl halides to olefins involves initial transfer of a sulfenium group to the double bond to form an episulfonium intermediate (eq. 1).[6]

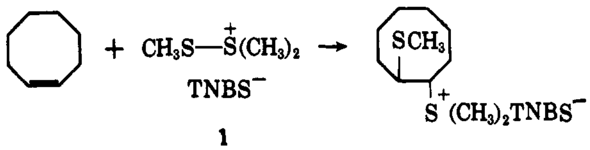


(1)

Nucleophilic attack by halide ion subsequently collapses the intermediate to produce the adduct. In dry acetic acid the reaction follows second-order kinetics.[6] In addition, observations of a positive salt effect and enhanced rates in polar solvents support a transition state that is more polar than the reactants.

The addition reaction between olefins and sulfenyl halides has been shown to be stereospecific. Addition to *cis* and *trans* olefin pairs gives nonidentical products.[7] The supposition that *trans* addition is involved is suggested by the nature of the products obtained from the solvolyses of the two butene adducts.[8] Assignment of stereochemistry is based on the reasonable assumption that the episulfonium intermediate opens *trans*.

Preliminary data on the reaction of alkylated disulfides with olefins indicated that the process was *trans* and stereospecific. Addition of dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate (**1**) to *cis*-cyclooctene affords the same product (eq. 2) as that



(TNBS = 2,4,6-trinitrobenzenesulfonate)

obtained by the reaction of cyclooctene S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate with dimethyl sulfide,[3] which indicates that the postulation of an episulfonium salt as a reaction intermediate is not unreasonable. The episulfonium salt of cyclooctene must have the *cis* configuration since it is prepared either by the reaction of *cis*-cyclooctene with methanesulfenyl 2,4,6-trinitrobenzenesulfonate[9] or by alkylation of *cis*-cyclooctene episulfide.[10] Furthermore, treatment of the salt with iodide or mercaptide ion regenerated *cis*-cyclooctene.[10] Thus, by analogy

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[2] Presented at the 1964 Pacific Southwest Regional Meeting of the American Chemical Society, Costa Mesa, Calif., Dec. 1964.

[3] G. K. Helmkamp, B. A. Olsen, and D. J. Pettitt, *J. Org. Chem.*, **30**, 676 (1965).

[4] N. Kharasch, H. L. Wehrmeister, and H. Tigerman, *J. Am. Chem. Soc.*, **69**, 1612 (1947).

[5] N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949).

[6] W. L. Orr and N. Kharasch, *ibid.*, **75**, 6030 (1953).

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

[8] A. J. Havlik and N. Kharasch, *ibid.*, **78**, 1207 (1956).

[9] D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **29**, 2702 (1964).

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