Alkoxysulfonium Salts from Dimethyl Sulfoxide and Epoxides. Preparation, Characterization, Reactions, and Mechanistic Studies[1]

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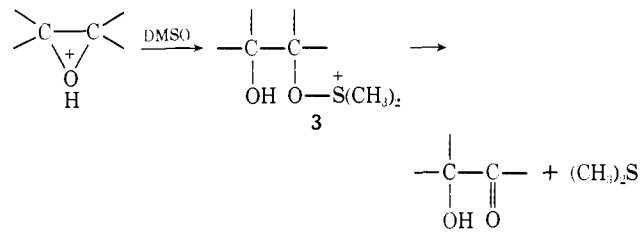
Abstract: Crystalline vicinally substituted hydroxysulfonium salts (**3**) have been prepared (40–80% yield) and characterized from aliphatic primary, secondary, tertiary, and allylic epoxides, benzylic epoxides, diepoxides, and epoxycyclohexane by reaction with DMSO and 2,4,6-trinitrobenzenesulfonic acid. Reaction of **3** with nucleophiles (methanol, water, DMSO-d_6) has also been examined. Reaction of methanol with primary and secondary aliphatic alkoxysulfonium salts is *exclusively* on *sulfur*, but with a tertiary salt attack is *exclusively* on *carbon*. In the benzylic salt from styrene oxide, major attack (75%) occurs on the benzylic carbon atom and minor attack (25%) on sulfur. Water reacts with the salts to yield 1,2-glycols usually in high yields. DMSO ring opening of the epoxides proceeds with clean inversion. Thus, from *cis*- and *trans*-9,10-epoxystearic acids, *threo*- and *erythro*-9,10-dihydroxystearic acids, respectively, are obtained stereospecifically. Complete absence of DMSO-d_6 exchange is observed with the aliphatic primary and secondary salts but benzylic, allylic, and tertiary salts undergo facile solvolysis to displace DMSO. Results are especially interesting with the salt from butadiene monoepoxide, and a detailed study has been conducted with that salt. Some salt thermolyses and reactions with triethylamine have also been conducted. Mechanistic interpretations of the various reactions have been proposed. A new compound, the 2:1 salt of DMSO and trinitrobenzenesulfonic acid, is a convenient source of anhydrous acid.

Publications on the ring-opening reactions of 1,2-epoxides (oxiranes) with nucleophiles are abundant[2,3] but the use of dimethyl sulfoxide (DMSO) as an electron-donor species in acid-catalyzed ring-opening reactions is relatively unexplored.[1,4–7]

Reaction of epoxides with DMSO was first reported by Cohen and Tsuji[6] who obtained fair to good yields of 1,2-hydroxy ketones (α-ketols) from cyclohexene oxide (**1**), 1,2-epoxy-1-phenylethane (styrene oxide) (**2**), and an epoxy steroid on reaction with DMSO using boron fluoride as catalyst. Subsequently, Tsuji[7] reported that the oxidative conversion of epoxides to 1,2-hydroxy ketones by DMSO could also be accomplished without boron fluoride if air was passed through the reaction mixture or if a catalytic amount of *tert*-butyl hydroperoxide was present. Tsuji concluded that an ionic mechanism prevailed if boron fluoride was the catalyst but a free-radical mechanism was applicable in the presence of air or hydroperoxide. In our detailed investigation[5] of these and related reactions we showed that a dichotomy of mechanism does *not* exist and under all the reported conditions a single ionic mechanism applied in which an alkoxysulfonium salt (**3**) is the key intermediate obtained by acid-catalyzed ring opening of epoxides by DMSO. The role of air or hydroperoxide was shown unequivocally to be that of an oxidizing agent to convert a small proportion of the DMSO to methanesulfonic and/or sulfuric acid which are the actual ring-opening catalysts.[5,8] Our evidence for the intermediacy of **3** was limited and was based largely on nmr spectra of solutions of **2** in acidified DMSO[5a] and the isolation of one crystalline alkoxysulfonium salt in low yield, the alkoxysulfonium trifluoroacetate from **1**, DMSO, and trifluoroacetic acid.[5b]



Since their initial preparation by Meerwein and coworkers,[9,10] many alkoxysulfonium salts have been isolated[11–18] but none contains a hydroxyl group vicinal to the oxysulfonium moiety, with the exception of the one reported from our laboratory.[5b] Since our published mechanism for the acid-catalyzed reaction of DMSO with epoxides required the intermediacy of alkoxysulfonium salts, we initiated a multiphase program as follows: (a) preparation, isolation, and characterization of vicinally substituted hydroxyoxysulfonium salts from aliphatic primary, secondary, tertiary, and allylic epoxides, benzylic epoxides, di-

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(8) Details of this oxidation and other occult acid-catalyzed reactions of DMSO will be submitted for publication shortly.
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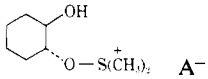
Table I. Alkoxysulfonium Salts from Epoxides, DMSO, and N_3phSOH (4)[a]

Epoxide	Product(s)[b]		Mp, °C	Yield, %	Neut. equiv Calcd	Neut. equiv Found
Styrene oxide (2)	$C_6H_5CH(OS^+(CH_3)_2\ A^-)—CH_2OH$	(5)	172–174	65–75	491	492
Cyclohexene oxide (1)		(6)	172–174	65–83	469	468
2,3-Epoxybutane (7) (*cis* + *trans*)	$CH_3—CH(OH)—CH(O—S^+(CH_3)_2\ A^-)—CH_3$ (*threo* + *erythro*)	(8)	139–140	60–80	443	441
1,2-Epoxybutane (9)	$CH_3CH_2CH(OH)—CH_2OS^+(CH_3)_2\ A^-$	(10)	120–121	48	443	447
	$CH_3CH_2CH(O—S^+(CH_3)_2\ A^-)—CH_2OH$	(11)	143–144	12	443	447
Isobutylene oxide (12)	$(CH_3)_2C(O—S^+(CH_3)_2\ A^-)—CH_2OH$[c]	(13)	197–199	43	443	452
Butadiene monoepoxide (14)	$CH_2=CH—CH(O—S^+(CH_3)_2\ A^-)—CH_2OH$	(15)	106 (dec)	70	441	448
anti-1,2,3,4-Diepoxybutane (16)	$CH_2(O)—CH(OH)—CH(OH)—CH_2(O)$ with $^+S(CH_3)_2$ and $^+S(CH_3)_2\ 2A^-$	(17)	168–170			

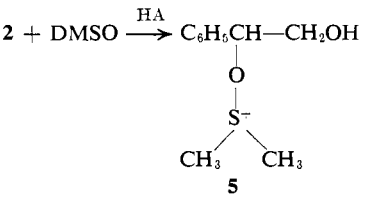
[a] See Experimental Section for explicit procedures. [b] A^- = N_3phSOH$^-$. [c] Unstable compound neat or in DMSO; prompt analysis is required to obtain correct results.

epoxides, and cyclohexene oxide (**1**); (b) reaction of selected salts with nucleophiles (water, methanol, hexadeuteriodimethyl sulfoxide (DMSO-d_6)); (c) determination of the site of nucleophilic attack (whether on carbon and/or sulfur); (d) isolation and/or identification of the reaction products of the salts (**3**) with nucleophiles; (e) determination of the stereochemistry of the ring-opening process and products (where relevant); (f) thermolysis and reactions of **3** with base; and (g) in selected cases, definition of mechanistic pathways in the preparation and further reactions of **3**.

Results and Discussion

Preparation of Alkoxysulfonium Salts (3). The room temperature reaction of epoxides with excess DMSO in the presence of equivalent quantities of various strong acids was initially studied by nmr; primary objectives were extent of reaction, structural information on products and by-products, and the isolation of pure crystalline **3** in good yield. For exploratory purposes, styrene oxide (**2**) was chosen as the model epoxide and the acids examined were those combining high acidity with low nucleophilicity of their anions (nitric,[19] trifluoroacetic, methanesulfonic, *p*-toluenesulfonic, *p*-nitrobenzenesulfonic, and 2,4,6-trinitrobenzenesulfonic acids) to minimize reaction of the protonated epoxide with the anion of the acid instead of with DMSO. Solutions of **2** in dry DMSO in the absence of acid are stable at room temperature; all nmr signals are assignable to the starting materials and no new signals appear.

With all of the strong acids, the nmr signals of the epoxide protons of **2** quickly disappear and the new spectral patterns observed are consistent with attack of DMSO predominantly at the benzylic carbon to yield



5

A^- (anion corresponding to acid used)

salts **5**. With nitric and methanesulfonic acids, some reaction also occurs between the protonated epoxide and the anions of the acids but such reactions are not observed with the other acids. With the disappearance of the epoxide proton signals, two new singlets appear at about δ 3.35 and 3.5 (TMS = 0). These are attributed to the magnetically nonequivalent SCH_3 groups as the alkoxysulfonium group is attached to a chiral carbon atom. A methine triplet whose signal area is exactly one-sixth that of the SCH_3 singlets also appears at δ 5.77 along with a methylene doublet at δ 3.93 whose area is exactly one-third that of the SCH_3 singlets. Whereas the methylene and methine protons of **2** exhibit an ABX pattern of three doublets, the new signals assignable to the methylene and methine protons are a doublet and triplet, respectively.

All the strong acids listed cause almost immediate disappearance of **2** with concomitant salt formation (**3**) but only 2,4,6-trinitrobenzenesulfonic acid (N_3phSOH) (**4**) yields a stable, crystalline salt (**5**), mp 172–174°, isolable in 65–75% yield by precipitation with ether, ethyl acetate, or ether–ethyl acetate. No products of attack of the anion on protonated epoxide are detectable. Therefore, **4** was chosen as the strong acid in reactions of DMSO with all the other epoxides and no attempt was made to find other strong acids that might yield crystalline salts. In almost all cases, crystalline, analytically pure **3** are obtained (Table I). As Table I shows, salts

(19) To maintain anhydrous conditions, nitric acid was used as its crystalline complex with DMSO (ref 5b).

are obtained in 40–80% yields. No attempt has been made to optimize the yields; with an excess of epoxide over N_3phSOH yields of salts increase substantially.

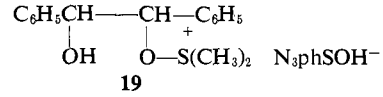
With styrene oxide (**2**), the only salt observed in solution is **5**, the product of benzylic attack by DMSO on protonated epoxide. The SCH_3 groups are magnetically nonequivalent for the reason already noted. Cyclohexene oxide (**1**) also reacts rapidly with DMSO–N_3phSOH to yield salt **6** (65–83%). Nmr analysis shows two singlets for the SCH_3 groups. (*cis* + *trans*)-2,3-Epoxybutane (**7**) yields the expected mixture of threo and erythro salts (**8**), mp 139–140° (60–80%), characterized in the usual way. The nmr spectrum of the mixed salts (**8**) shows four singlets for the SCH_3 groups as expected from a mixture of threo and erythro diastereomers. The methyl and methine protons of **8** attached to the carbon atom bearing the alkoxysulfonium groups are slightly downfield of the corresponding protons on the hydroxyl-bearing carbon atom.

1,2-Epoxybutane (**9**) yields a 2:1 mixture of positionally isomeric salts resulting from attack of DMSO at both the terminal carbon atom (**10**) (major product) and the nonterminal carbon atom (**11**) of the oxirane group. The product ratio is calculated from the area ratios of the SCH_3 groups in **10** and **11** in the reaction solution. The salts are readily separated by selective solution in acetone and, as Table I shows, **10**, mp 120–121°, is isolated in 48% yield and **11**, mp 143–144°, in 12% yield. Salt **11** shows two SCH_3 singlets (oxysulfonium group attached to the chiral carbon atom) but **10** shows one SCH_3 singlet.

Isobutylene oxide (**12**) reacts to give salt **13**, mp 197–199°, exclusively. The SCH_3 groups show only one singlet at δ 3.22 and one singlet for the CCH_3 groups at δ 1.40. Salt **13** is not stable and must be analyzed and studied promptly. It is also very unstable in DMSO and undergoes facile elimination to yield isobutyraldehyde (see later discussion). The instability probably accounts for the relatively low yield (43%) of analytically pure salt.

Butadiene monoepoxide (**14**) gives salt **15**, mp 106° (dec) (70% yield), exclusively as the initial reaction product; the oxysulfonium moiety is attached to the secondary carbon atom and no product of double bond attack is observed (solvolysis–rearrangement of this salt is discussed later). The SCH_3 groups appear as two singlets at δ 3.25 and 3.30. *anti*-1,2,3,4-Diepoxybutane (**16**) yields a di(alkoxysulfonium) salt (**17**), mp 168–170° in which DMSO attacks exclusively at the terminal carbon atoms of the oxirane groups, a result consistent with earlier literature reports on the reaction of **16** with other nucleophiles.[20,21] Salt **17** is difficult to obtain in analytically pure form owing in part to its low solubility in various solvents (benzene, chloroform, methylene chloride, dioxane, acetone, acetonitrile, nitromethane, and dimethylformamide), although it can be precipitated from a mixed solvent system of DMSO–acetone–ether. The crystallized product is usually contaminated with the N_3phSOH–2DMSO adduct (**18**) (described shortly) but after multiple precipitations pure **17** can be obtained in low yield. The product shows one singlet for the SCH_3 groups.

trans-Stilbene oxide was also treated with DMSO and N_3phSOH. The nmr spectrum of the solution immediately after mixing the reactants shows the formation of alkoxysulfonium salt (**19**) and stilbene glycols



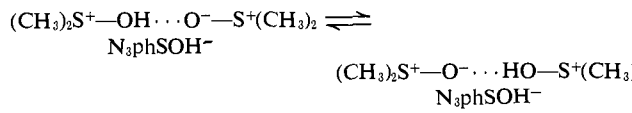
19

(**20**) in a 2:1 ratio. Salt **19** shows two singlets at δ 3.10 and 3.22 for SCH_3 groups on a chiral carbon atom and two doublets at δ 5.17 and 5.70 due to two different methine protons. The downfield doublet is attributed to the proton on the carbon atom bearing the oxysulfonium group. When the usual salt precipitation technique was employed, salt **18** was isolated in over 75% yield. After work-up of the solution the final product consisted only of a mixture of *meso*- and *dl*-stilbene glycols (**20**)[22] (50% yield) and none of salt **19**. Since N_3phSOH is a hydrate and we wished to avoid water in the acidic reaction mixture, we used the N_3phSOH–2DMSO adduct (**18**) as the source of anhydrous acid. Nmr now shows that salt **19** is in fact the *exclusive* product but after work-up the same mixture of glycols as before, but none of salt **19**, is obtained. As will be discussed later, benzylic, tertiary, and allylic sulfonium salts are readily hydrolyzed and solvolyzed. Salt **19** is not only benzylic but the second phenyl group may be anchimerically assisting hydrolysis. We conclude that water present in or picked up by the solvents as well as that used in the work-up causes facile hydrolysis of salt **19** to the glycols.

(*cis* or *trans*)-9,10-Epoxystearic acids form noncrystalline alkoxysulfonium salts which could not be purified completely but are readily hydrolyzed stereospecifically to (*threo* or *erythro*)-9,10-dihydroxystearic acid in good yield as already reported by us.[1] *anti-cis,cis*-9,10,12,13-Diepoxystearic acid also yields oily di(alkoxysulfonium) salts which can be hydrolyzed to a 2:1 mixture of *threo,threo,threo*- and *threo,erythro,threo*-9,10,12,13-tetrahydroxystearic acids in over 80% yield.[23]

In the absence of epoxides, N_3phSOH forms an interesting new compound (**18**) with DMSO in 75–85% yield. This adduct (**18**), mp 112–114°, is readily obtained by dissolving N_3phSOH in DMSO at 60°, cooling the solution to room temperature, and then precipitating **18** with ethyl acetate. The adduct has the composition 1 N_3phSOH–2DMSO and it is an excellent source of anhydrous N_3phSOH (N_3phSOH itself is a hydrate). Although we assume that the proton source in the reaction of epoxides with DMSO is N_3phSOH, the actual proton donor may in fact be the adduct **18**.

Equivalent weight and elemental analysis indicate that **18** has the composition shown; the nmr spectrum of **18** in CD_3NO_2 shows four equivalent methyl groups at δ 2.97 (s, 12 H), an acidic proton at 10.25 (s, 1 H), and aromatic protons at 8.54 (s, 2 H). A possible structure



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for **18** in solution is one in which the proton of N_3phSOH is *bound* to the oxygen atom of one DMSO and

(20) P. W. Feit, *Ber.*, **93**, 116 (1960).
(21) W. F. Beech, *J. Chem. Soc.*, 2483 (1951).
(22) "Sadtler Standard Spectra," NMR No. 6303m.
(23) Details of the work with *anti-cis,cis*-9,10,12,13-diepoxystearic acid will be reported elsewhere.

hydrogen bonded to the oxygen atom of a second, and the proton *rapidly* exchanges between the two DMSO molecules. A similar explanation has been proposed recently to rationalize the ir spectrum of methanesulfonic acid in DMSO.[24]

The formation of alkoxysulfonium salts (**3**) can be rationalized as a "borderline SN2 mechanism," as has been shown in acid-catalyzed ring-opening reactions of epoxides with other nucleophiles.[2-4] This pathway predicates backside attack of DMSO with inversion at the carbon atom which can provide the most developing carbonium ion character in the transition state. DMSO attacks exclusively at the nonterminal carbon atom of the oxirane ring in all of the previously described cases, except 1,2-epoxybutane (**9**) which yields the two isomeric salts **10** and **11** in a 2:1 ratio, a result consistent with studies of the reaction of **9** with other nucleophiles.[25]

The location of the oxysulfonium group can be shown by its SCH_3 signal(s) in the nmr spectra of the salts.[17] Attachment of the SCH_3 groups of the oxysulfonium moiety to a chiral carbon atom produces two distinguishable singlets (salts **5**, **6**, **8**, **11**, **15**, and **19**) whereas attachment to a nonchiral carbon atom produces only one singlet (salts **10**, **13**, **17**, and others). Similar results have been reported when an isopropyl or isopropoxy group is attached to a chiral or nonchiral carbon atom.[26] The SCH_3 signals of alkoxysulfonium salts (**3**) appear downfield (δ 3.2–3.5) from those of DMSO (δ 2.6) because of the greater deshielding effect on the salts of the sulfur atom bearing a formal positive charge.

The products obtained from alkoxysulfonium salts by hydrolysis, methanolysis, or reaction with base show that they are O-alkylated, not S-alkylated. S-Alkylated salts are very unreactive toward hydrolysis and methanolysis.[11] The isolation of alkoxysulfonium salts from so many structurally different epoxides upon reaction with DMSO and acid suggests that in all previously reported acid-catalyzed reactions, DMSO reacts by an ionic pathway exclusively[5] and not by a free-radical one.[7] Support for this conclusion will be reported separately.[5b]

Reaction of Alkoxysulfonium Salts with Nucleophiles. (a) Methanol. The hydrolysis of certain aliphatic alkoxysulfonium salts occurs by attack of water *exclusively* or *predominantly* at sulfur.[12,13,27-32] However, the site of attack (on sulfur and/or carbon) in hydrolysis or methanolysis[33] of salts in which the oxysulfonium group is attached to a benzylic, tertiary, or allylic carbon atom is not clear. Therefore, we directed our attention first to ascertaining the distribution between sulfur and carbon attack by methanol on alkoxysulfonium salts (**3**) of various structural types.

(24) J. M. Williams and J. Kreevoy, *J. Amer. Chem. Soc.*, **89**, 5499 (1967).
(25) L. Smith and S. Skyle, *Acta Chem. Scand.*, **5**, 1514 (1951).
(26) G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 2628 (1964).
(27) K. W. Buck, A. B. Foster, A. R. Perry, and J. M. Webber, *Chem. Commun.*, 433 (1965).
(28) H. Hogeveen, G. Maccagneni, and F. Montanari, *J. Chem. Soc. C*, 1585 (1966).
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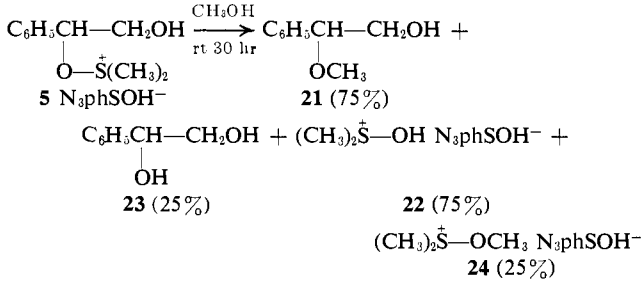
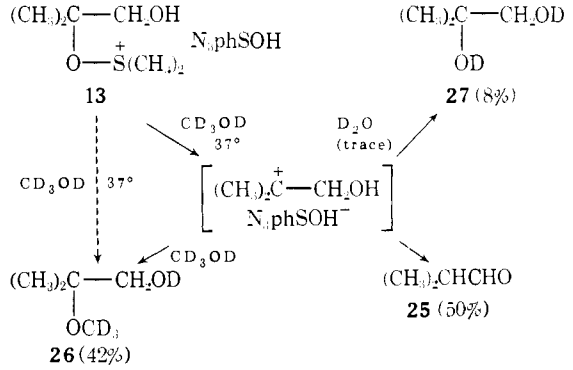
(30) M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc. C*, 572 (1970).
(31) D. R. Dalton and V. P. Dutta, *J. Chem. Soc. B*, 85 (1971).
(32) D. R. Dalton and D. G. Jones, *Tetrahedron Lett.*, 2875 (1967).
(33) S. G. Smith, Ph.D. Dissertation, University of California at Los Angeles, 1959.

Salt **5** (from styrene oxide and DMSO), in which the oxysulfonium group is attached to a benzylic carbon atom, was selected for initial study. In the methanolysis of **5** at room temperature for 30 hr, major attack (75%) is on the benzylic carbon atom, *not* at sulfur, with displacement of the oxysulfonium moiety (DMSO) to form 2-methoxy-2-phenylethanol (**21**) and the 1:1 salt of DMSO–N_3phSOH (**22**). Minor attack (25%) occurs on sulfur to yield 1-phenyl-1,2-ethanediol (styrene glycol) (**23**) and methoxy dimethyl sulfonium-2,4,6-trinitrobenzenesulfonate (**24**) (Scheme I). In all probability, attack at the benzylic carbon atom (major) involves a solvolytic (SN1-like) process whereas attack at sulfur (minor) may be a typical SN2 process or may involve the formation of an unstable, tetracovalent neutral, sulfur intermediate. In contrast, attack on sulfur is the *exclusive* process in reaction of primary and secondary aliphatic alkoxysulfonium salts (**8**, **10**, and **11**) with methanol under similar conditions to yield glycols and **24**, but attack on carbon (by methanol) is the *exclusive* process in the reaction of **13**, a tertiary salt obtained from isobutylene oxide (**12**) and DMSO. In the latter case, methanol-d_4 was used to aid in the nmr interpretation of the reaction course and product identification. With tertiary salt **13**, at the end of 5 hr nmr signals assignable to isobutyraldehyde (**25**) (50%), 2-methoxyisobutanol-d_4 (**26**) (42%), isobutylene glycol-d_2 (**27**) (8%), and the DMSO–N_3phSOH 1:1 salt (**22**) (100%) are observed. If attack on sulfur had also occurred, product **24**-d_3 should have been obtained. The formation of these products can be rationalized (Scheme II) by assuming a solvolytically formed carbonium ion or a tight ion pair as a common intermediate although some direct nucleophilic displacement of the alkoxysulfonium group by methanol-d_4 cannot be totally ignored. Direct displacement, shown in Scheme II by a broken vertical arrow, is considered to be a minor or negligible process.

Scheme I



Scheme II

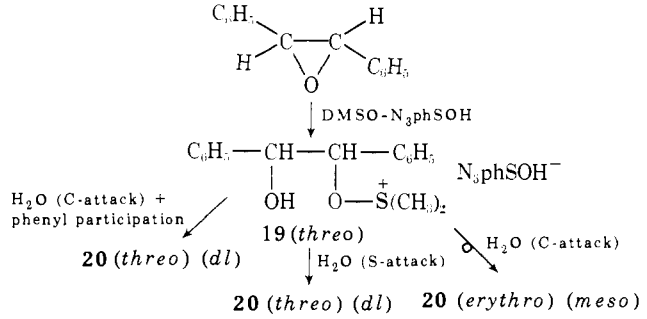


(b) Water. Reaction of salts **5** and **6** with excess D_2O and $NaHCO_3$ for 20–30 min on the steam bath yields styrene glycol-d_2 (**23**-d_2) and *trans*-1,2-cyclohexanediol-d_2 (**28**-d_2), respectively, as the sole products. Tertiary salt **13** (from isobutylene oxide, DMSO, and N_3phSOH) reacts completely with D_2O (no base present) within 5 min on the steam bath; products are isobutylene glycol-d_2 (**27**) (50%), isobutyraldehyde (**25**) (5%), and the 1:1 DMSO–N_3phSOH salt (**22**). Failure to obtain a better material balance in this case is caused by loss of **25** as its water azeotrope, bp 59°.[34a]

The exclusive formation of **28** from cyclohexene oxide (**1**) (no *cis*-1,2-cyclohexanediol could be detected or isolated) leads to the conclusion that the initial attack of DMSO on the protonated oxirane group occurs with clean inversion followed by attack of D_2O *exclusively* on sulfur, a result to be expected with all primary and secondary aliphatic epoxides. To check this conclusion, we examined the reaction of *cis*- and *trans*-9,10-epoxystearic acids (**29** and **30**, respectively) with DMSO–N_3phSOH followed by hydrolysis.[1] If inversion occurs on ring opening only and water attacks solely on sulfur in the alkoxysulfonium salts, the cis isomer **29** should yield exclusively *threo*-9,10-dihydroxystearic acid (**31**) and the trans isomer **30** should yield exclusively *erythro*-9,10-dihydroxystearic acid (**32**). In each case 65–70% yield of the predicted isomer is obtained.

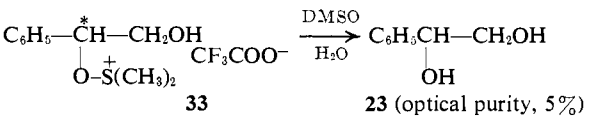
The results with *trans*-stilbene oxide on reaction with DMSO–N_3phSOH, in which only a mixture of *meso*- and *dl*-glycols (**20**) are isolated but nmr monitoring of the reaction mixture shows that intermediate alkoxysulfonium salts **19** do indeed form, can now be readily understood (Scheme III). The epoxide reacts with

Scheme III



DMSO–N_3phSOH presumably with retention (phenyl participation) to yield salt **19**, formulated as all threo.[3,34b] This salt, a benzylic species, should undergo facile C-attack with phenyl participation to yield *threo* (*dl*)-**20**; direct C-attack with inversion (no phenyl participation) should yield *erythro* (*meso*)-**20**. S-attack should also yield *threo* (*dl*)-**20** (no inversion) since the asymmetric carbon is uninvolved. An alternate route to mixed *meso*- and *dl*-glycols is ionization of **19** to an intermediate carbonium ion or intimate ion pair which should also yield a mixture of glycols.

(c) DMSO. One goal of this study was to rationalize certain mechanistic uncertainties in earlier published work by Barili and coworkers.[35] These investigators assumed that the trifluoroacetic acid catalyzed hydrolysis of optically active styrene oxide in DMSO at 25° proceeded by way of the intermediate alkoxysulfonium trifluoroacetate (**33**) by repeated displacement of the oxysulfonium group by DMSO to yield glycol (**23**) with



an optical purity of only 5%. Displacement processes of this type (DMSO displacing DMSO) were first suggested by Torsell[17] in aliphatic systems at higher temperatures.

Instead of **33** we used the crystalline trinitrobenzenesulfonate (**5**) and found that in DMSO-d_6 solution at the nmr probe temperature of 37°, DMSO-d_6 directly replaces DMSO. After 2–3 hr the signals of the $S(CH_3)_2$ group at δ 3.30 and 3.43 completely disappear and a new singlet at δ 2.57 first observed after 10 min corresponding to liberated DMSO remains constant; other peaks assignable to phenylacetaldehyde (**34**) are also observed. The concentrations of salt **5**, **5**-d_6 (**35**), and **34** are shown in Table II. When the DMSO-d_6 reaction is complete, **5** is converted to almost equal quantities of **34** and **35**. Thus, elimination competes effectively with displacement of DMSO suggesting that an SN1-like (or a tight ion pair) solvolysis mechanism is operative rather than direct, multiple SN2 displacements in which elimination products would not be found. Such a solvolytic pathway in which planar intermediates form readily explains the racemization of optically active styrene oxide, *via* salt **33**, reported by Barili and coworkers.[35]

Table II. Solvolysis of **5** in DMSO-d_6 at 37°

Time, min	**5**, %	**5**-d_6 (**35**), %	Phenylacetaldehyde, % (**34**)
10	89	11	
30	74	15	11
50	42	44	14
70	32	47	21
90	21	49	30
110	15	50	35
130	10	48	42
150	10	46	44
170	4	50	45

The results we obtained with the tertiary salt **13** (from isobutylene oxide–DMSO–N_3phSOH) on treatment with DMSO-d_6 can also be explained by an SN1-like solvolytic mechanistic pathway (Table III). The

Table III. Solvolysis of **13** in DMSO-d_6 at 37°

Time, min	**13**, %	**13**-d_6 (**36**), %	Isobutyraldehyde, % (**25**)
15	39	16	47
35	16	10	73
55	5	9	85
75	2	6	89
95	1	5	93
115	1	1	96

(34) (a) H. J. Hagemeyer and G. C. Decroes, "The Chemistry of Isobutyraldehyde and Derivatives," Tennessee Eastman Co. Technical Bulletin, Kingsport, Tenn., 1953, p 5; (b) G. Berti and F. Bottari, *J. Org. Chem.*, 25, 1286 (1960).

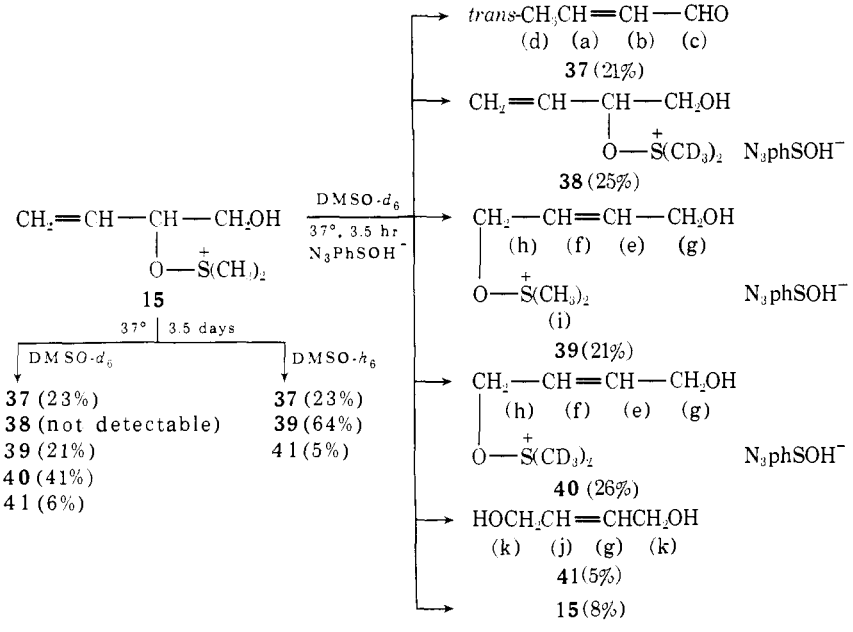
(35) L. Barili, G. Berti, B. Macchia, F. Macchia, L. Monti, and D. Tei, *Chimi. Ind. (Milan)*, 51, 1391 (1969).

Table IV, Solvolysis of **15** in DMSO-d_6 at 37°

Time, min	**15**, %	**15**-d_6 (**38**), %	**39**, %	**39**-d_6 (**40**), %	**37**, %	**41**, %	**15**-h_6 + d_6, %[a]	**39**, h_6 + d_6, %
10	92	8[b]	3	3				
30	61	24[b]	8	6	1	11	85[c]	14
50	49	36	11	10	4		85	21
70	37	36	13	10	10	1.5	73	23
90	29	36	17	15	12	1.5	64	32
110	22	38	17	16	16	1.6	60	33
130	18	38	18	17	17	2.0	56	35
150	13	37	19	21	18	2.5	50	40
170	11	36	20	20	18	3.0	47	40
190	9	31	21	22	20	3.5	40	43
210	8	25	21	26	21	5	33	47
4680 (78 hr)			21	41	23	6		62

[a] Calculated from methine proton. Material balances are estimated to be correct to ±10%. [b] % **38** was calculated from liberated DMSO-h_6 at δ 2.55 (DMSO-d_5 H contaminant in the DMSO-d_6 was subtracted from the integration); in all other cases by difference. [c] Calculated by adding **15**-h_6 and **15**-d_6 (**38**).

Scheme IV



reaction is extremely rapid and is virtually complete in slightly over 1 hr. The nmr signals for the $S(CH_3)_2$ and $C(CH_3)_2$ groups at δ 3.22 and 1.40, respectively, decrease rapidly and, concurrently, a singlet at δ 2.57 (DMSO) and a doublet at 1.04 (isobutyraldehyde) (**25**) increase. In the salt, the $S(CH_3)_2$ group signal disappears more rapidly than that of the $C(CH_3)_2$ group implying that salt **13** is not converted directly to **25** but a portion of it is first converted to **13**-d_6 (**36**) and then to final product. After 1.5–2 hr, 93–96% conversion of **13** to **25** is obtained.

Of special significance is the *complete* absence of DMSO-d_6 exchange in the aliphatic primary and secondary salts **6**, **8**, **10**, **11**, **17**, and **24**, as shown by the absence of nmr spectral changes in solutions of those salts in DMSO-d_6 at 37°. Stability of the primary alkoxysulfonium salts is additional evidence for ruling out any SN2 displacement reactions by DMSO under the mild conditions employed. No attempt was made to force the reactions.

Solvolysis of salt **15** (from butadiene monoepoxide–DMSO–N_3phSOH) with DMSO-d_6 is an especially interesting case (Scheme IV) and requires separate discussion (Table IV). Solvolysis of salt **15** in DMSO-d_6 for 210 min (3.5 hr) at the nmr probe temperature of 37° yields five products all of which can be distinguished by nmr (decoupling experiments to be described later confirmed proton assignments discussed here). Scheme IV summarizes the results and also shows those obtained after solvolysis of **15** for 3.5 days both in DMSO-d_6 and DMSO. Solvolysis in DMSO was an important control in product identification and material balance.

The products in Scheme IV were characterized solely by nmr. *trans*-Crotonaldehyde (**37**, 21–23% yield in 3.5 hr to 3.5 days) shows a doublet of quartets for H_a from δ 6.80 to 7.42 (1 H, J_{ab} = 15 Hz, J_{ad} = 7 Hz); a quartet of quartets for H_b from δ 5.9 to 6.2 (1 H, J_{ba} = 15 Hz, J_{bc} = 8 Hz, J_{bd} < 1 Hz); a doublet for H_c at δ 9.42 (1 H, J_{cb} = 8 Hz); and a doublet of doublets for H_d at δ 1.98 and 2.02 (3 H, J_{da} = 7 Hz, J_{db} < 1 Hz). The nmr spectrum is identical with that of an authentic sample.[36] Formation of **37** is readily explained by solvolytic elimination from **15** and **38** followed by acid-catalyzed isomerization.

Except for the absence of signals due to the $S(CH_3)_2$

(36) "Varian High Resolution NMR Spectra Catalog," Vol. 1, Spectrum No. 60.

group, salt **38** (25% yield in 3.5 hr) has the same nmr spectrum as the starting salt **15**; no difficulty is experienced in characterizing it. After 3.5 days, however, salt **38** cannot be detected, a result with useful mechanistic implications.

The nmr spectrum of the mixture of salts **39** and **40** (21 and 26% yields, respectively, after 3.5 hr) shows two olefinic protons H_e and H_f (the starting material **15** has three olefinic protons, two of which are terminal) as four triplets (close examination shows four triplets of triplets but because of small long-range coupling, only four triplets with shoulders are normally observed). Two of the triplets are centered at δ 6.21 and 6.36 (1 H, J_{ef} = 15 Hz, J_{eg} = 3.5 Hz, J_{eh} < 1 Hz) and the other two triplets are centered at δ 5.63 and 5.77 (1 H, J_{fe} = 15 Hz, J_{fh} = 7 Hz, J_{fg} < 1 Hz). The large J value of 15 Hz for the olefinic protons H_e and H_f clearly shows that they are trans. Each olefinic proton further couples with two different pair of methylene protons, H_g and H_h, respectively, thus accounting for the observation of two triplets for each olefinic proton. Two doublets centered at δ 4.78 (2 H, J_{hf} = 7 Hz, J_{he} < 1 Hz) and δ 4.10 (2 H, J_{ge} = 3.5 Hz, J_{gf} < 1 Hz) are assigned to the two different pairs of methylene protons H_h and H_g. A singlet at δ 3.78 (H_i) suggests the presence of an $S(CH_3)_2$ attached to a nonchiral (primary) carbon atom, although the unexpectedly high downfield position of the signal suggests the possibility of a direct C–S bond rather than a C–O–S bond. In alkoxysulfonium salts the $S(CH_3)_2$ signals usually appear farther upfield at approximately δ 3.3–3.4.

After 3.5 days, however, conversion of **15** to **39** + **40** is 62%, as compared to only 47% after 3.5 hr, and integration of the signals assigned to **39** and **40** shows that the olefinic:methylene:$S(CH_3)_2$ proton ratio is 2:4:2, respectively, which suggests that one-third of the final salt mixture is **39** and two-thirds is the deuterated salt **40**. These conclusions (yield of **39** + **40** and their proportions) were confirmed by conducting the solvolyses of **15** in DMSO; yield of **39** was 64% and the olefinic:methylene:$S(CH_3)_2$ proton ratio was 2:4:6.

Proton assignments in **39** and **40** were made on the following lines of reasoning. In structures **39** and **40** the methylene absorption downfield (δ 4.78, H_h) has been assigned to the protons on the carbon atom bearing the oxysulfonium group because of the earlier observation that the methylene signal in the $(CH_3)_2S^+$–O–CH_2– group in salt **10** appears farther downfield than the methylene signal in the HO–CH_2 group in salt **11**. In further confirmation of the assignments, the methylene protons in the HO–CH_2– group in both salts **39** and **40** have almost the identical chemical shift (δ 4.10) as that of the methylene protons (H_k, δ 4.18) in the HO–CH_2– group of 1,4-butenediol (**41**).[37]

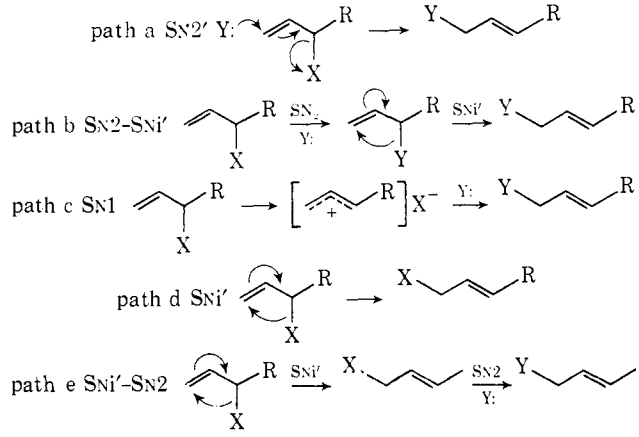
The downfield olefinic proton signals at δ 6.21–6.36 in the mixture of salts **39** and **40** are assigned to H_e and those upfield at δ 5.63–5.77 to H_f on the basis of coupling constants and double irradiation studies. When protons H_h of one methylene group [$(CH_3)_2S^+$–O–CH_2–] at δ 4.78 are irradiated, the signal of the H_f proton centered at δ 5.70 collapses to a broad doublet from the original doublet of triplets because it is now coupled only to protons H_e (J_{fe} = 15 Hz) and protons H_g (J_{fg} < 1 Hz). When protons H_g of the other methylene group (–CH_2OH) are irradiated at δ 4.10, the signal of the H_e proton centered at δ 6.28 collapses to a broad doublet from its original doublet of triplets as it is now coupled only to protons H_f (J_{ef} = 15 Hz) and H_h (J_{eh} < 1 Hz). When proton H_e (δ 6.28) is irradiated the expected methylene signal of protons H_g (δ 4.10) collapses to a singlet from a doublet; when proton H_f (δ 5.70) is irradiated the methylene signal of protons H_h (δ 4.78) also collapses to a singlet.

1,4-Butenediol (**41**) (5% yield in 3.5 hr or 3.5 days) was characterized by its nmr spectrum (δ 5.74–5.84, m, olefinic protons H_j; 3.98–4.08, m, methylene protons H_k), identical with that of an authentic sample.[37]

Salts **39** and **40** presumably form by allylic rearrangement from **15** and **38**, respectively, whereas *trans*-crotonaldehyde (**37**) can be formed as an elimination product from either **15** or **38**. The glycol **41** is assumed to form by hydrolysis of **39** or **40** by traces of water present. Its yield never exceeds 5–6%.

Proposed Reaction Pathways. A number of pathways have been proposed for allylic rearrangements (Scheme V); the subject has recently been reviewed.[38,39]

Scheme V



In the current study the solvolysis–rearrangement of salt **15** to salts **38**, **39**, and **40** in the highly polar solvent DMSO-d_6 is described (Scheme IV). If conversion of **15** to **40** had taken place by paths a and c, **40** should have been the predominant (exclusive?) product with very little, if any, **39**, on the basis of the relative proportions of DMSO-d_6 to -h_6. Since yields of **39** and **40** are 21 and 26%, respectively, after 3.5 hr, paths a and c can be disregarded. Path e can also be ruled out as conversion of **39** to **40** is not observed even after 3.5 days. If, however, **39** is the more stable S-alkylated product, its conversion to **40** would also be unlikely.

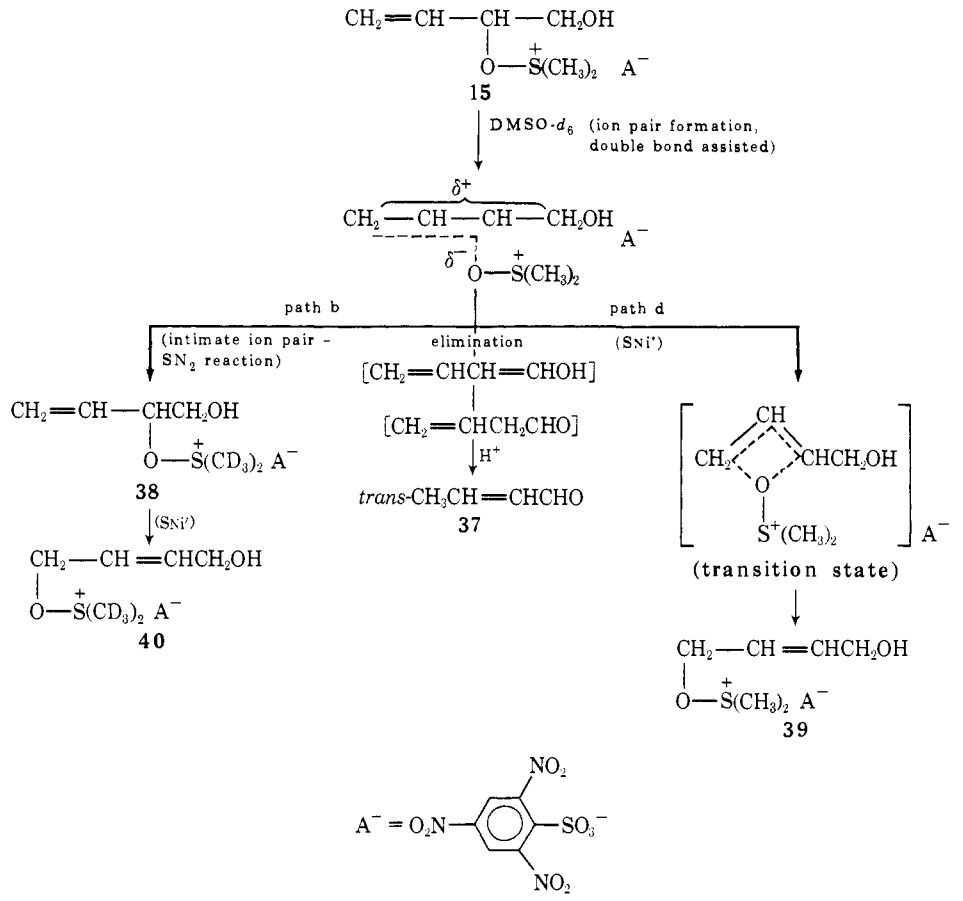
We propose that paths d (SNi′) and b (SN2–SNi′) are operative in the formation of **38**, **39**, and **40** from **15** (Scheme VI). This conclusion is consistent with the recent work of Sneen[39] who has properly pointed out that an "ion pair" is not simply a pair of ions; considerable polarization of the electron density of the anionic component toward the cationic component must exist. Sneen suggests that an alternative to "ion pair" might be "extended covalent bond" or better perhaps "an extended bond with considerable ionic character." It is clearly unlikely in view of the high

(37) "Sadtler Standard Spectra," NMR No. 6511m.

(38) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

(39) R. A. Sneen, *Accounts Chem. Res.*, **6**, 46 (1973), and references therein.

Scheme VI



polarity of the reaction medium that conversion of **15** to **38** (Schemes IV and VI) proceeds by SN2 displacement. In view of Sneen's[39] results and also Bordwell's work with tertiary allylic halides,[40] we prefer to view the formation of **38** as an intimate ion pair–SN2 reaction or possibly a double bond assisted displacement reaction with considerable SN1 character (Scheme VI). Salt **39** derives then from **15**, and **40** from **38**, respectively, by SNi' reactions (path d) (where X = O–S$^+$–$(CH_3)_2$ or O–S$^+$–$(CD_3)_2$). As Table IV shows the *initial* rate of formation of solvolytic product **38** is about three times greater than that of the internal return product **39**. This result helps rationalize the ratio of final products (3.5 days) **39** and **40** and the absence of **38**. The combined yield of **39** + **40** after 3.5 days agrees almost perfectly with that of **39** in the solvolysis of **15** in DMSO.

Additional literature is also available lending support to path b in allylic rearrangement reactions.[41–46] Path d was proposed many years ago to explain internal return products.[47]

Miscellaneous Reactions. (a) Thermolysis in DMSO. Thermolysis of **5** in DMSO-d_6 at 100° for 1 hr yields phenylacetaldehyde (90%) (**34**), determined by nmr. The reaction may involve reformation of styrene oxide (**2**) followed by acid-catalyzed isomerization or by a direct elimination process (E2 if DMSO assisted or E1 if solvolytic). Under similar conditions, **8** yields methyl ethyl ketone.

(b) With Triethylamine. Stirring a suspension of **5** in acetone with an equivalent quantity of triethylamine at room temperature yields phenacyl alcohol (60% by nmr; 40% isolated yield) and triethylammonium 2,4,6-trinitrobenzenesulfonate (**42**) (98%), plus unidentified minor products. The ylide intermediate mechanism proposed by Fenselau and Moffatt[48] is probably operative here.

Experimental Section

Nmr spectra were obtained using Varian A-60A and XL-100-15 spectrometers; tetramethylsilane was usually used as an internal standard (δ 0) but in a few cases DMSO (δ 2.6) was used. Ir spectra were determined using a Perkin-Elmer Infracord spectrometer, Model 137B. Glc was performed on a Varian Aerograph Model A90-D3 instrument equipped with a thermal conductivity detector; a 5 ft × 0.25 in. o.d. stainless steel column packed with 20% methylsilicone polymer (SE-30) coated on Chromosorb W (60–80 mesh) with helium as carried gas was employed. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Del. 19808.

Materials. DMSO (reagent grade) was distilled under vacuum over calcium hydride and then stored under a nitrogen atmosphere;

(40) F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, **94**, 2119, 5829 (1972).
(41) R. D. Kepner, S. Winstein, and W. E. Young, *J. Amer. Chem. Soc.*, 71, 115 (1949).
(42) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C43 (1951).
(43) P. D. de la Mare, "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1951, pp 62–68.
(44) B. D. England and E. D. Hughes, *Nature (London)*, **168**, 1002 (1951); *J. Chem. Soc.*, 1615 (1955).
(45) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).
(46) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 855–857.
(47) W. G. Young, S. Winstein, and H. C. Goering, *J. Amer. Chem. Soc.*, 73, 1958 (1951).
(48) A. H. Fenselau and J. G. Moffatt, *J. Amer. Chem. Soc.*, **88**, 1762 (1966).

it is difficult to keep anhydrous and it should be checked periodically. 1,2-Epoxy-1-phenylethane (styrene oxide) (Aldrich), 1,2-epoxycyclohexane (Columbian Carbon), 1,2-epoxybutane (Aldrich), 2,3-epoxybutanes (Pfaltz and Bauer), and butadiene diepoxide (Research Organic/Inorganic) were purified by distillation. A Nester/Faust stainless steel spinning band column was used. Oleic and linoleic acids were purified by repeated urea fractionation of reagent grade materials from methanol following by reduced pressure distillation.[49] Epoxidation was conducted in the usual way with peroxyacetic acid.[50,51] 2,4,6-Trinitrobenzenesulfonic acid (Pierce), *p*-nitrobenzenesulfonic acid (Eastman), *p*-toluenesulfonic acid (Eastman), methanesulfonic acid (Eastman), trifluoroacetic acid (Eastman), isobutylene oxide (Pfaltz and Bauer), butadiene monoepoxide (Aldrich), *trans*-1,2-cyclohexanediol (Pfaltz and Bauer), and phenacyl alcohol (Eastman) were used without further purification. The best quality, anhydrous solvents were used without purification including the deuterated analogs CD_3OD (Marshallton). DMSO-d_6 (Aldrich, Norell), and CD_3NO_2 (Diaprep).

General Method of Preparation of Crystalline Salts from DMSO–N_3phSOH (4)–Epoxides. DMSO (5 ml, 61.5 mmol) was warmed to 60° in a three-necked flask fitted with an addition funnel, thermometer, condenser, and magnetic stirrer. 2,4,6-Trinitrobenzenesulfonic acid (N_3phSOH) (**4**) (3.6 g, 12.3 mmol) was added in one portion with stirring and the resulting yellow solution was cooled to room temperature. The appropriate epoxide (12.3 mmol) was then added dropwise with stirring over 5–10 min and the solution was stirred for an additional 10–15 min to ensure complete reaction. The DMSO solution was poured into an excess of cold ethyl acetate (100–150 ml) or ethyl acetate–ether (1:2) and the resulting mixture was stirred for 30 min in an ice bath. The crude precipitated salts were filtered, washed several times with cold ether, dried, and weighed. Each salt was purified as described below under the individual cases; yields, melting points, and neutralization equivalents are listed in Table I. All of the salts are new compounds.[52]

We were unable to obtain crystalline salts with nitric,[19] trifluoroacetic, methanesulfonic, *p*-toluenesulfonic, and *p*-nitrobenzenesulfonic acids, DMSO, and styrene oxide. However, in all of these cases nmr showed that the anticipated DMSO ring-opening process had occurred very rapidly with some minor competing reactions, as already discussed. Therefore, all the work reported in this paper deals with N_3phSOH salts. Additional details of work with the other acids can be found in the Ph.D. dissertation.[1]

Preparation of N_3phSOH–DMSO Adduct (1:2) (18). N_3phSOH (3.6 g, 12.3 mmol) was dissolved in DMSO (5 ml, 61.5 mmol) at 60° and the solution was cooled to room temperature and then poured into ethyl acetate (100–200 ml) with stirring. The precipitate of crude salt was filtered and washed with cold ethyl acetate followed by cold ether; yield, 4.6 g (83%), mp 100–105°. A further quantity of **18** was isolated from the filtrate by addition of ether. The combined crude salts were purified by dissolution in acetone and precipitation by addition of ether: yield of analytically pure **18**, mp 112–114°, 75%; nmr (CD_3NO_2) δ 2.97 [$(CH_3)_2S^+$, s, 12 H], 8.54 (aromatic anion, s, 2 H), 10.25 (acidic H, s, 1 H); neut. equiv 454 (calcd, 449).

Styrene Oxide–N_3phSOH–DMSO Salt (5). The crude salt prepared by the general method was precipitated from acetone by ether to give the analytically pure salt as colorless flakes, mp 172–174°, in 65% yield. When the mole ratio of epoxide:N_3phSOH was increased to 1.5:1, yield of pure salt increased to 75%: nmr (DMSO-d_6) δ 3.30 and 3.43 [$(CH_3)_2S^+$, 2 s, 6 H], 3.90 ($-CH_2-$, d, 2 H), 5.58 (–CH, t, 1 H), 7.47 (aromatic, s, 5 H), 8.85 (aromatic anion, s, 2 H).

1,2-Epoxycyclohexane–N_3phSOH–DMSO Salt (6). The pure salt was obtained in 65% yield as a colorless solid, mp 172–174°, from acetone solution by ether precipitation; the yield was 83% when the mole ratio of epoxide:N_3phSOH was increased to 1.5:1: nmr (DMSO-d_6) δ 0.98–2.32 [$-(CH_2)_4-$, b, 8 H], 3.32 and 3.37 [$(CH_3)_2S^+$, 2 s, 6 H], 3.48 (–CH, m, 1 H), 4.15 (CH, m, 1 H), 8.89 (aromatic anion, s, 2 H).

2,3-Epoxybutanes (7)–N_3phSOH–DMSO Salts (8). Crude salts, mp 100–130°, were obtained in 82% yield by precipitation with ethyl acetate–ether. They consisted predominantly of a mixture of threo and erythro isomers (by nmr) contaminated with a small quantity (*ca.* 5%) of **18** as an impurity. The impurity was removed by washing the crude salts with ethyl acetate and filtering and washing the filter cake with ether. The analytically pure mixture of threo and erythro salts, mp 139–140°, was obtained in 60–80% yield from an acetone solution of the crude salts by ether precipitation: nmr (DMSO-d_6) δ 1.02, 1.07, 1.20, and 1.25 (CH_3, 4 d, 6 H), 3.23, 3.25, 3.26, 3.28 [$(CH_3)_2S^+$, 4 s, 6 H], 3.75 (CH, m, 1 H), 4.35 (CH, m, 1 H), 8.80 (aromatic anion, s, 2 H).

1,2-Epoxybutane (9)–N_3phSOH–DMSO Salts (10, 11). Crude salts, mp 112°, were obtained in 77% yield by precipitation with ethyl acetate–ether. A mixture of pure salts **10** and **11**, mp 120–122°, was obtained in 60% yield from an acetone solution of the crude salts by ether precipitation; the yield was 66% when the epoxide:acid ratio was 1.5:1. The pure salts were separated by selective solution of **10** in acetone in which **11** is relatively insoluble. Salt **10**, mp 120–121°, was obtained in 48% yield and **11**, mp 143–144°, in 12% yield: nmr (DMSO-d_6) **10**, δ 0.7–1.70 (CH_3CH_2, m, 5 H), 3.27 [$(CH_3)_2S^+$, s, 6 H], 3.60 (–CH, m, 1 H), 4.28 ($-CH_2-$, m, 2 H), 8.83 (aromatic anion, s, 2 H); **11**, δ 0.66–1.83 (CH_3CH_2, m, 5 H), 3.25 and 3.28 [$(CH_3)_2S^+$, 2 s, 6 H], 3.55 ($-CH_2-$, m, 2 H), 4.38 (–C*H*, m, 1 H), 8.87 (aromatic anion, s, 2 H).

Isobutylene Oxide (12)–N_3phSOH–DMSO Salt (13). Salt **13** is quite unstable in DMSO, and must be prepared, isolated, and analyzed promptly; its instability accounts for the low yield. The pure salt, mp 197–199°, was obtained in 43% yield by two consecutive precipitations from acetone solution. The nmr spectrum of **13** in DMSO-d_6 always showed the presence of isobutyraldehyde (**25**) which could be obtained in virtually quantitative yield by elimination, as described later (see also Table III): nmr (DMSO-d_6) **13**, δ 1.40 (CH_3, s, 6 H), 3.22 [$(CH_3)_2S^+$, s, 6 H], 3.53 ($-CH_2-$, s, 2 H), 8.8 (aromatic anion, s, 2 H); **25**, δ 1.04 (CH_3, d, 6 H), 2.43 (–CH, m, 1 H), 9.60 (–C(O)H, d, 1 H).

Butadiene Monoepoxide (14)–N_3phSOH–DMSO Salt (15). The pure salt, mp 106° (dec), was obtained in 70% yield from acetone solution by ether precipitation: nmr (DMSO-d_6) δ 3.25 and 3.30 [$(CH_3)_2S^+$, 2 s, 6 H], 3.36–3.86 ($-CH_2-$, m, 2 H), 5.06 (–C*H*, m, 1 H), 5.3–6.1 (olefinic, m, 3 H), 8.8 (aromatic anion, s, 2 H).

***anti*-1,2,3,4-Diepoxybutane (16)–N_3phSOH–DMSO Salt (17).** The crude salt, mp 134–135°, was obtained in 75% yield by precipitation with ethyl acetate–ether and was contaminated with **18**. The pure salt, **17**, mp 168–170°, was obtained in low yield by three consecutive ether precipitations from a DMSO–acetone solution (4 g of **17** dissolved in 12 ml of DMSO followed by 40 ml of acetone): nmr (DMSO-d_6) δ 3.32 [$(CH_3)_2S^+$, s, 12 H], 3.35–4.52 ($-CH_2-$ + –CH + OH, m, 8 H), 8.7 (aromatic anion, s, 2 H).

***trans*-Stilbene Oxide–N_3phSOH–DMSO Reaction.** The nmr spectrum of the solution immediately after mixing the reactants showed the formation of salt **19** and stilbene glycols (**20**) in a 2:1 ratio. When the reaction mixture was poured into excess ethyl acetate–ether, the only product that precipitated, however, was the N_3phSOH–DMSO 1:2 adduct (**18**) (75% yield). After filtration and solvent evaporation, the yellow liquid residue was treated with 10% aqueous NaCl solution (to dissolve excess DMSO) and the aqueous system was extracted three times with ether. The combined ether extracts were washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. A semisolid residue (2.80 g from 2.90 g of *trans*-stilbene oxide) was obtained which was dissolved in hot ethanol and cooled to 0°. The crystalline product (1.55 g) was shown by nmr to be a mixture of *meso*- and *dl*-stilbene glycols (**20**) (50% yield). When the N_3phSOH–DMSO 1:2 adduct was used instead of N_3phSOH hydrate, salt **19** was the *exclusive* reaction product (nmr) but after work-up the same mixture of glycols was obtained as before.

Reaction of Salts (3) with Nucleophiles. (a) Methanolysis of 5 (Scheme I). Salt **5** (1.0 g, 2 mmol) and anhydrous methanol (40 ml) were stirred at room temperature until the reaction mixture became homogeneous (30 hr). The methanol was evaporated under vacuum and a small portion of the residue was dissolved in DMSO-d_6 for a preliminary determination of its composition by nmr.[53] The remainder of the residue was extracted with ether (8 × 20 ml, 5 min stirring with each portion of solvent) and the combined ether extracts were evaporated under vacuum to yield a yellow oil. It was shown to be a 3:1 mixture of **21** (carbon attack) and

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(52) All new compounds had acceptable elemental analyses; see paragraph at end of paper regarding supplementary material.

(53) Details of nmr spectra and the arguments employed in deducing compositions of mixtures and structures of products can be found in the Ph.D. Thesis of M. A. K. (ref 1). Only the most pertinent details are given in this paper.

23 (sulfur attack). The ether-insoluble residue was shown to be a mixture of **22** and **24**, also in a 3:1 ratio. Pure salt **22** was isolated, mp 197–198°, by solution of **22** + **24** in acetone and precipitation of **22** by ether: nmr (CD_3NO_2) δ 3.1 (s, 6 H), 8.7 (s, 2 H); neut. equiv 376 (calcd for $C_8H_9N_3O_{10}S_2$, 371).

Compounds **21**, **23**, and **24** were characterized by preparation of authentic samples by well-established methods and observation of the anticipated nmr peak enhancements by addition of these authentic compounds to the appropriate solutions being examined by nmr.

(b) Methanolysis of 8 (Erythro + Threo). Salt **8** (1.0 g, 2 mmol) was stirred with methanol (100 ml) at room temperature until a homogeneous solution was obtained (14 hr). Evaporation of the methanol under vacuum followed by nmr (DMSO-d_6) examination of the residue showed that 67% of **8** had decomposed to (*dl* + *meso*)-2,3-butanediols and **24** exclusively (100% sulfur attack). Ether extraction of the residue (6 × 20 ml, 5 min stirring with each portion of solvent) followed by vacuum evaporation of the combined ether extracts yielded a yellow liquid residue shown by nmr to be a mixture of (*dl* + *meso*)-2,3-butanediols (overall yield 66%) (comparison with authentic material).[54] The ether-insoluble fraction was shown by nmr (DMSO-d_6) to contain **24** and **8** in a 2:1 ratio. Pure **24**, mp 168–170°, was isolated in 66% yield from an acetone solution of the mixture by precipitation with ether; no depression in melting point was found on admixture with authentic **24**.

(c) Methanolysis of 10 and 11. The mixture of salts **10** and **11** (1.0 g, 2.3 mmol) was treated with methanol (100 ml), as described above. Nmr analysis of the residue showed that 72% of the starting materials had decomposed to 1,2-butanediol (70%) and salt **24** (70%). The ether-soluble portion of the residue consisted exclusively of 1,2-butanediol (overall yield 70%). The ether-insoluble part was shown by nmr to be a mixture of **24** and (**10** + **11**) in a 3:1 ratio. Pure **24**, mp 168–170°, was isolated in 70% yield as described above: nmr (DMSO-d_6) δ 3.3 [$(CH_3)_2S^+$, s, 6 H], 4.0 CH_3O, s, 3 H), 8.8 (aromatic, s, 2 H).

(d) Methanolysis of 13 (Scheme II). Salt **13** (0.15 g, 0.34 mmol) was dissolved in methanol-d_4 (0.5 ml) in an nmr tube and the reaction course was followed spectrally at 37°. At the end of 4 hr **13** had completely decomposed; the nmr spectrum showed the formation of isobutyraldehyde (**25**) (50%), 2 methoxyisobutanol-d_4 (**26**) (42%), isobutylene glycol-d_2 (**27**) (8%), and the DMSO–N_3phSOH salt (**22**) (100%).

(e) Hydrolysis of 5. In an nmr tube, a suspension of salt **5** (0.076 g, 0.155 mmol) was heated for 30 min on the steam bath with a solution of $NaHCO_3$ in D_2O (0.013 g, 0.000155 mol in 0.5 ml). The nmr spectrum[53] indicated the formation of styrene glycol-d_2 (**23**-d_2) and [$(CH_3)_2S^+$-OD N_3phSOH$^-$] (**22**-d_1) as the exclusive products in 100% yield. Confirmation of structure and yields of product were obtained by peak enhancements using authentic samples.

(f) Hydrolysis of 6. Salt **6** was hydrolyzed with D_2O–$NaHCO_3$ for 20 min as described in (e). The nmr spectrum[53] showed the formation of *trans*-1,2-cyclohexanediol-d_2 (**28**-d_2) and **22**-d_1 as the sole products. The complete absence of methine signals at δ 3.75 and the presence of methine signals at δ 3.38,[55] coupled with appropriate peak enhancements by the use of authentic **28**, confirmed the exclusive formation of *trans*-glycol. The same result was obtained on a preparative scale (1.1 g of **6**, 0.21 g of $NaHCO_3$, and 10 ml of H_2O); hexane extraction of the aqueous solution yielded exclusively *trans*-1,2-cyclohexanediol, mp 103–104°.[56]

(g) Hydrolysis of 13. The hydrolysis of **13** (0.15 g, 0.34 mmol) with D_2O was conducted in an nmr tube without $NaHCO_3$; hydrolysis was complete within 5 min at steam bath temperature. Products were isobutylene glycol-d_2 (**27**) (50%), isobutyraldehyde (**25**) (5%), and the 1:1 DMSO–N_3phSOH salt (**22**). Considerable **25** was lost as its water azeotrope.[34]

(h) Hydrolysis of the N_3phSOH–DMSO Salts of *cis*- and *trans*-9,10-Epoxystearic Acids (29 and 30, Respectively). This has already been reported.[1] The cis isomer **29** gave *threo*-glycol **21** (9,10-dihydroxystearic acid, mp 95°) exclusively, and the trans isomer gave *erythro*-glycol **32** (9,10-dihydroxystearic acid, mp 130°) exclusively in 65–70% yields.

(i) Hydrolysis of the N_3phSOH–DMSO Salt (19) of *trans*-Stilbene Oxide (Scheme III). This has been described above under the attempted preparation and isolation of **19**.

(j) DMSO Solvolysis of 5 (Table II). Salt **5** (0.15 g, 0.3 mmol) was dissolved in DMSO-d_6 (0.5 ml) in an nmr tube and solvolysis was followed at 37°. The first nmr scan was taken after 10 min and then at 20-min intervals. After 170 min signals attributable only to **5**-d_6 (**35**) (50%), phenylacetaldehyde (**34**) (45%), and unreacted **5** (5%) were found.[53]

(k) DMSO Solvolysis of 13 (Table III). As described under (j), **13** (0.15 g, 0.35 mmol) was allowed to react with DMSO-d_6 (0.5 ml) in an nmr tube at 37°. Reaction was extremely rapid; at the first nmr scan (15 min reaction time) about 60% of **13** had already been converted to **13**-d_6 (**36**) (16%) and isobutyraldehyde (**25**) (47%). Within 2 hr, **13** and **13**-d_6 were barely detectable (1%) and conversion to **25** was 96%.[57]

(l) DMSO Solvolysis of 15. As described under (j), **15** (0.15 g, 0.34 mmol) was allowed to react with DMSO-d_6 in an nmr tube at 37°. Results are summarized in Scheme IV; the course of the reactions (by nmr monitoring) is shown in Table IV. All five reaction products could be distinguished by nmr; decoupling experiments, already described, confirmed proton assignments. A control study to aid in product characterization was conducted using DMSO. Yields of products were calculated from integration of nmr peak areas and suitable equations.[53]

(m) DMSO Solvolysis of Salts 6, 8, 10, 11, 17, and 24. No change was observed in the nmr spectra of these salts in DMSO-d_6 at 37°.

Thermolysis of Salts. Salt **5** (0.15 g, 0.3 mmol) was heated in DMSO-d_6 (0.5 ml) for 1 hr at 100° in an nmr tube. The sole decomposition product observed was phenylacetaldehyde (**34**) (90% yield).[58] On similar treatment, **8** (*erythro* + *threo*) yielded methyl ethyl ketone exclusively.

Reaction of 5 with Triethylamine (TEA). To a suspension of **5** (1.23 g, 2.5 mmol) in dry acetone (25 ml), an equivalent quantity of freshly distilled TEA (0.253 g, 2.5 mmol) in dry acetone (5 ml) was added. The brown homogeneous solution that resulted was stirred for an additional 15 min, followed by addition of ether (150 ml) and then cooling to 0°. The precipitated triethylammonium 2,4,6-trinitrobenzenesulfonate (**42**), mp 182–183°, was filtered and washed with cold ether (0.93 g, 95% yield). Evaporation of the combined ether filtrates under vacuum yielded a solid residue from which an additional quantity of **42** (0.03 g) was isolated by addition of cold ether (total yield of **42**, 98%): nmr (DMSO-d_6) δ 1.25 (CH_3, t), 3.68 ($-CH_2-$, m), 8.83 (aromatic, s).

The ether solutions were combined and evaporated to dryness under vacuum to yield a yellow, solid residue which was then extracted with hot *n*-hexane (4 × 5-ml portions). The combined extracts were cooled to 0° overnight and the precipitate of phenacyl alcohol was filtered, washed with a small quantity of cold hexane, and dried (0.134 g, mp 75°, 40% yield): nmr [$(CD_3)_2CO$] δ 4.93 ($-CH_2-$, s, 2 H), 7.33–7.75 (aromatic, m, 2 H), 7.91–8.71 (aromatic, m, 3 H). Enhancement of the nmr peaks was observed with an authentic sample.

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Supplementary Material Available. Elemental analysis of the new compounds will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8393.

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