Mass Spectral Study of Alkyl Alkanesulfonates[1]

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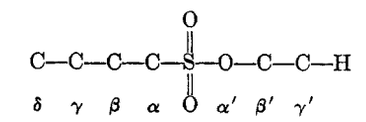
The mass spectra of several methyl and ethyl alkanesulfonates have been recorded and studied. Deuterium-labeling experiments have also been conducted. There is evidence for a number of interesting hydrogen-transfer reactions. Methyl methanesulfonate shows simple α cleavage (CS) to give $[CH_3]^+$ and $[SO_2CH_3]^+$, *m/e* 95, and simple α' cleavage ($SOCH_3$) to give $[CH_3SO_2]^+$, *m/e* 79, and $[OCH_3]^+$, *m/e* 31. However, there are ions at *m/e* 80, $[CH_3SO_2H]^+$, and *m/e* 30, $[OCH_2]^+$, owing to α' cleavage with transfer of a β' hydrogen. Methyl alkanesulfonates with α and β hydrogens transfer a β hydrogen with α cleavage to give an olefin and *m/e* 96, $[HOSO_2CH_3]^+$. Those methyl esters with α, β, and γ hydrogens transfer a β and a γ hydrogen with α cleavage to give an allyl radical and *m/e* 97, $[(HO)_2SOCH_3]^+$. If two sets of β hydrogens are available, two β hydrogens are transferred with α cleavage to give an allyl radical and *m/e* 97. Ethyl esters transfer a β' and a γ' hydrogen with β' cleavage to give a vinyl radical and *m/e* 97, $[CH_3SO(OH)_2]^+$. The mechanistic implications of these data are discussed in terms of five-membered and bicyclic transition states.

Mass spectral studies of diaryl sulfones have been adequate,[2] but other tri- and tetracoordinated sulfur compounds, *e.g.*, alkyl sulfones and sulfoxides, have received little attention.[3,4] A number of general features have been outlined in the spectra of diaryl sulfones.[2] Three fragmentation paths are defined by the prominent peaks. The first path accounts for the great abundance of arylsulfinyl and aryloxy ions in the spectra of all the compounds studied, and presumably involves rearrangement of the parent ion to an aryl arenesulfinate followed by cleavage of the S–OAr bond. The second path involves loss of OH or H_2O followed by loss of SO; this mode is found only in the spectra of *o*-methylated sulfones. Evidence seems to indicate that the *o*-methyl loses two hydrogens to a sulfone oxygen, which is lost as water, followed by insertion of the resulting carbene into the ring. Loss of SO to give a fluorene ion is analogous to loss of CO from cyclic aromatic ketones.[5] Species with *o*-methyl groups in both rings lose a methyl group by a third path, which has not yet been well defined.

In a brief study by Madsen and co-workers,[4] it has been shown that some diaryl and aryl alkyl sulfides show peaks, in the range 2–26% relative abundance, at $(M - S)^+$, $(M - HS)^+$, $(M - H_2S)^+$, and $(M - H_3S)^+$. Disulfides lose S, HS, S_2, and even CH_2S in the case of dibenzyl disulfide. Dibenzyl sulfoxide gives $(M - SO)^+$ in the amount of 30% relative abundance, and diphenyl sulfone shows $(M - SO_2)^+$ in 5% relative abundance. The mechanisms of these eliminations have not been elucidated.

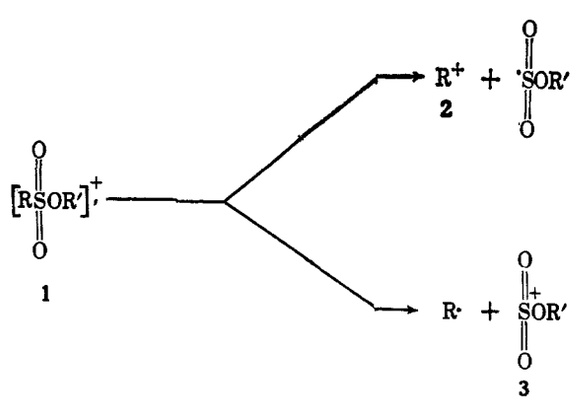
The present study concerns sulfonate esters, particularly methyl alkanesulfonates, and the fragmentations and rearrangements, which result under mass spectral conditions. These rearrangements can be explained by mechanisms, which have been established by the use of deuterium-labeled analogs. In referring to various bonds undergoing cleavage in the fragmentation of these materials the following scheme will be used. α cleavage will mean cleavage of the C–S bond,



β cleavage refers to the C_α–C_β bond, α' cleavage refers to the S–OR bond, *etc.* A substituent referred to as an α substituent will be borne on the α carbon. The convention proposed by Budzikiewicz, Djerassi, and Williams[6] for denoting electron shifts will be used. A fishhook ($\curvearrowright$) will indicate the movement of a single electron; an arrow ($\rightharpoonup$) will denote the movement of an electron pair.

Results

Unlike the diaryl sulfones, the parent ions of most of the alkyl alkanesulfonates (**1**) are scarce; usually they occur in about 1–3% abundance relative to the base (most abundant) peak. In general, the most abundant ions in the spectra are those arising from the alkyl group (**2**) obtained upon α cleavage. These fragmentation patterns are quite similar to those of most related alkyl structures, and are treated elsewhere.[7] Suffice it to say, all the esters show simple α cleavage to give alkyl ion (**2**) and, to a varying degree, the complementary $(SO_2OR')^+$ (**3**). Also $(R - 1)^+$



and especially $(R - 2)^+$ ions appear in the spectra of higher methyl esters. In methyl methanesulfonate, **2** (*m/e* 15) is the base peak of the spectrum (Figure 1);

(1) Abstracted from the Ph.D. Theses of R. W. C. and G. D. M., Purdue University, Lafayette, Ind., 1966, which should be consulted for the complete spectra of those esters which are not presented here. Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(2) S. Meyerson, H. Drews, and E. K. Fields, *Anal. Chem.*, **36**, 1294 (1964).

(3) S. Meyerson and J. D. McCollum, Division of Physical Chemistry, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1959; A. Quayla *Chimia* (Aarau), **8**, 259 (1959).

(4) J. Madsen, C. Nolde, S. Lawesson, G. Scholl, J. H. Bowie, and D. H. Williams, *Tetrahedron Letters*, 4377 (1965).

(5) J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959).

(6) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p xii.

(7) See, for example, ref 6, Chapters 1–7 and 9.

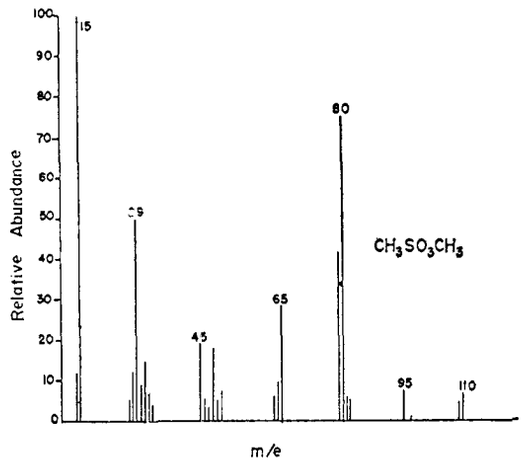


Figure 1.—Methyl methanesulfonate.

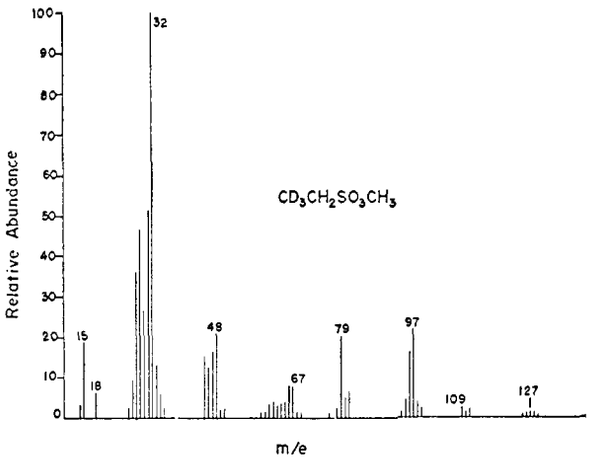


Figure 3.—Methyl ethane-2,2,2-d_3-sulfonate

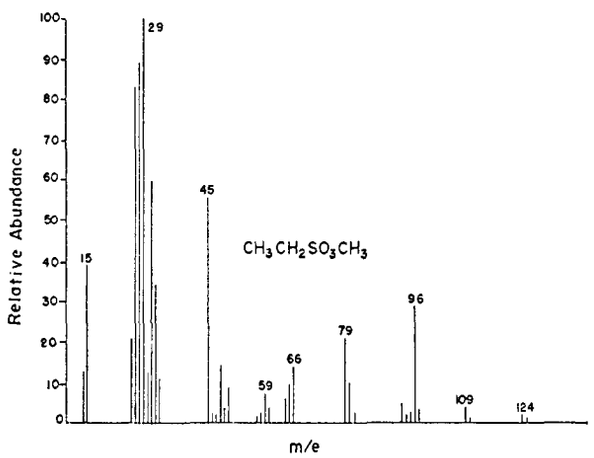


Figure 2.—Methyl ethanesulfonate.

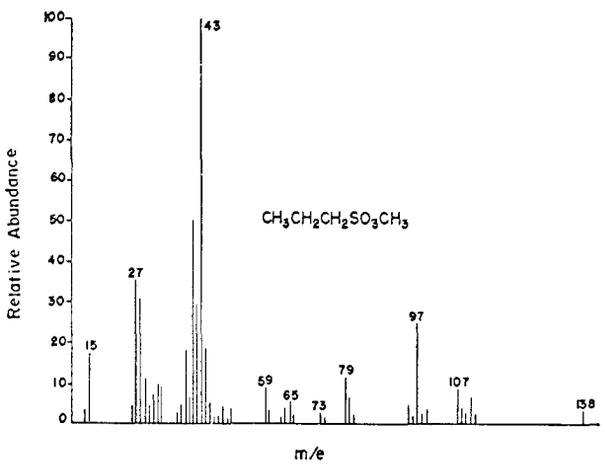


Figure 4.—Methyl 1-propanesulfonate.

3 (*m/e* 95) is present in about 10% relative abundance. In the partially mono-α-deuterated analog, **3** (*m/e* 95) amounts to about 18% relative abundance. Methyl ethanesulfonate has a spectrum (Figure 2) with *m/e* 29 as the base peak. Certainly part of this is due to HCO^+ (derived from CH_3O or $CH_2{=}O$), but the ethyl group also appears at *m/e* 29. This is shown by a significant increase in *m/e* 30 in the spectrum of methyl ethane-1-d_1-sulfonate (**1**, R = CH_3CHD; R′ = CH_3), and further by the fact that *m/e* 32, $(CD_3CH_2)^+$, is the base peak in the spectrum (Figure 3) of methyl ethane-2,2,2-d_3-sulfonate. The undeuterated and mono-α-deuterated compounds also give significant $(R - H)^+$ ions at *m/e* 28 and *m/e* 29, respectively. The tri-β-deuterated material gives a significant $(R - D)^+$ ion at *m/e* 30, but the *m/e* 31 ion is practically unchanged in intensity in this spectrum *vs.* the undeuterated and mono-α-deuterated esters; this indicates that there is little $(R - H)^+$ ion in the spectrum of the tri-β-deuterated ester. Also in the spectrum of methyl ethanesulfonate, the intensity of *m/e* 95 has been greatly reduced, while an ion (*m/e* 96) has appeared in about 30% relative abundance; *m/e* 96 also appears in the spectrum of the mono-α-deuterated ester. In the tri-β-deuterated ester this ion appears at *m/e* 97 [the *m/e* 96 ion in the tri-β-deuterated analog is probably the $(M - 31)^+$ ion, which appeared at *m/e* 93 in the undeuterated and at *m/e* 94 in the mono-α-deuterated esters]. Quite clearly then, a β hydrogen is being transferred from the ethyl group to the sulfonate group with concurrent cleavage to give $(R - H)^+$ and $(HOSOOCH_3)^+$ ions.

In methyl 1-propanesulfonate (**1**, R = $CH_3CH_2CH_2$; R′ = CH_3; Figure 4) and higher straight-chain homologs all of which have α, β, and γ hydrogens, the ions at *m/e* 95 and *m/e* 96 become much less important, whereas *m/e* 97 appears and becomes more intense as the chain becomes longer. Also, α deuterium does not appear in the *m/e* 97 ion.

There is yet another rearrangement which occurs in the alkyl portion of methyl alkanesulfonates. Two β hydrogens are transferred if two sets of β hydrogens are available. This is shown in methyl 2-propanesulfonate [**1**, R = $(CH_3)_2CH$; R′ = CH_3; Figure 5], which gives abundant *m/e* 41 and *m/e* 97 ions. Deuterium labeling has shown that α deuterium atoms are not transferred, but that two β deuterium atoms (Figure 6) are. It is unlikely that both deuteriums come from the same carbon since methyl ethanesulfonate does not transfer two hydrogens.

The spectrum of only one compound with two sets of β hydrogens and one set of γ hydrogens has been recorded. Such a compound should transfer two hydrogens and undergo cleavage of the C–S bond to give an ion, *m/e* 97; this ion occurs in about 12% relative abundance in the spectrum of methyl 2-butanesulfonate [**1**, R = $CH_3CH_2(CH_3)CH$; R′ = CH_3], and α deuterium is not incorporated. Labeling of the

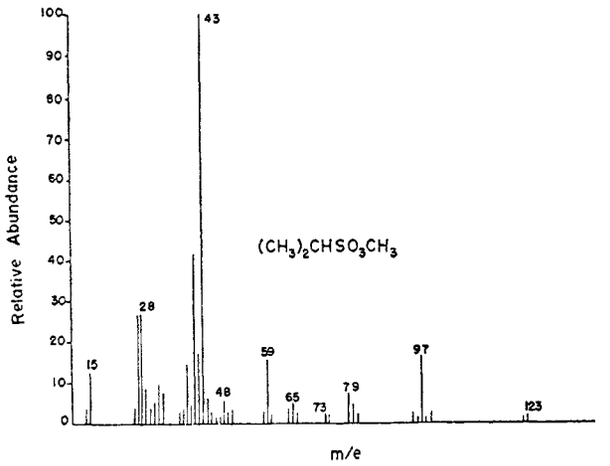


Figure 5.—Methyl 2-propanesulfonate.

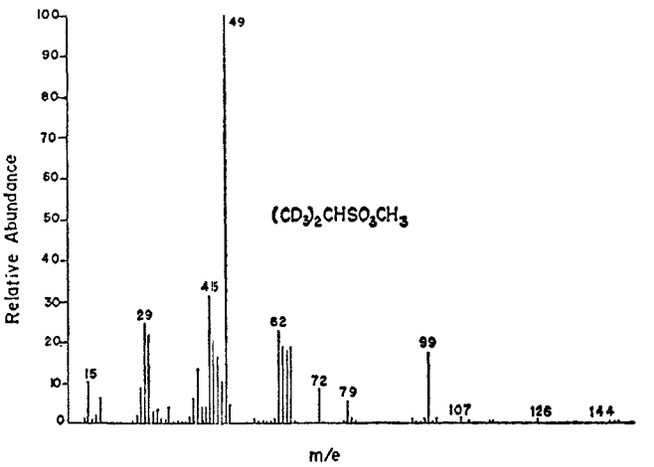
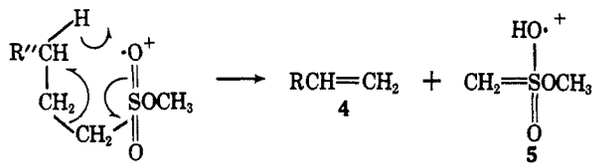


Figure 6.—Methyl 2-propane-1,1,1,3,3,3-d_6-sulfonate.

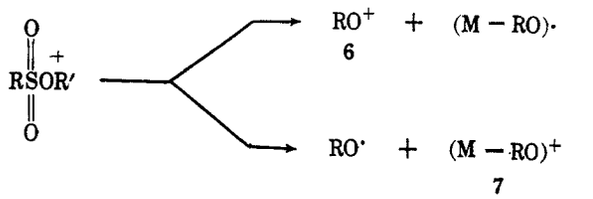
β carbons shows that one β hydrogen and one γ hydrogen (m/e 98, 12%) are transferred more often than two β hydrogens (m/e 99, 4%).

2-Propenesulfonate (**1**, R = CH_2=$CHCH_2$; R′ = CH_3) shows none of the hydrogen transfers discussed above; m/e 95 is the only ion of any significance in that portion of the spectrum. This indicates that available β or γ hydrogens on olefinic carbons are not transferred as readily as from saturated carbon.

Another rearrangement common to the methyl alkanesulfonates from propane through octane is a γ-hydrogen transfer with β cleavage to produce an olefin (**4**) and an ion, m/e 110 (**5**), which is electronically analogous to an oxosulfonium ylide. α deuterium is retained in this ion.



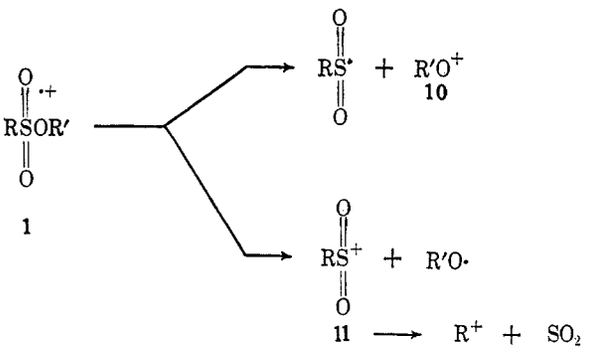
Another ion common to most of the spectra is that corresponding to an alkoxy ion (**6**) derived from the alkane group of the sulfonate ester (this ion was observed in 26 out of 32 ester spectra which were recorded). This must be a rearrangement ion. The complementary (M − OR)$^+$ ion (**7**) for the methyl alkanesulfonates corresponds to m/e 79, and this ion



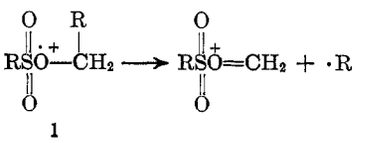
occurs in all of the spectra. In those spectra where it occurs, the rearranged RO$^+$ ion (**6**) has an average relative abundance of approximately 10–25%. If the alkane group in the ester contains deuterium, the label is retained in 6. Compare, for example, $CH_3CH_2SO_3CH_3$, $CH_3CHDSO_3CH_3$, and $CD_3CH_2SO_3CH_3$; these compounds show peaks at m/e 45, $(CH_3CH_2O)^+$, m/e 46, $(CH_3CHDO)^+$, and m/e 48, $(CD_3CH_2O)^+$, respectively.

Neither ethyl methanesulfonate (**1**, R = CH_3; R′ = CH_3CH_2; Figure 7) nor any of its deuterated analogs shows an (M − 31)$^+$ ion (m/e 93). Methyl ethyl sulfite (**9**, R = CH_3CH_2; R′ = CH_3) shows an (M − 31)$^+$ ion (m/e 93) and an (M − 45)$^+$ ion (m/e 79). All of the methyl esters (**1**, R′ = CH_3) give a peak at m/e 31; however, not all of them give an (M − 31)$^+$ ion. Generally, those esters derived from secondary, benzylic, or allylic sulfonic acids do not show such an ion.

Those esters having radical-stabilizing substituents on the carbon attached to sulfur (**1**, R = $C_6H_5CH_2$ and CH_2=$CHCH_2$), when labeled with α deuterium atoms, show no ions containing deuterium other than the molecular ion and hydrocarbon fragments. Presumably, α cleavage is so energetically favorable that no rearrangements can compete. Most of the other esters show some evidence of simple α' cleavage, but the low intensity of **11** seems to indicate facile decom-



position of this ion, except where R = CH_3. Furthermore, these esters undergo some γ' cleavage, which is common to compounds containing an alkoxy group.[7] The methyl esters lose one hydrogen, while ethyl methanesulfonate preferentially loses a methyl group, which is shown by deuterium labeling to be due to γ' cleavage. The second most abundant peak in the



R = H, CH_3, and CD_3

spectrum of methyl methanesulfonate is m/e 80 (78% of the base peak, m/e 15). In the α deuterated ester this peak appears at m/e 81. Even though the ester

was only partially mono-α-deuterated, the approximately equal ratios of parent ions, m/e 110:111, and icns, m/e 80:81, show that the fragment in question has the same percentage deuterium as the starting mixture, indicating that a β' hydrogen is transferred to a sulfonyl oxygen with α' cleavage to give $(CH_3SO_2H)^+$, m/e 80. In the higher methyl alkanesulfonates, this mode of fragmentation does not compete well with other paths, as evidenced by very low intensities of RSO_2H^+ ions.

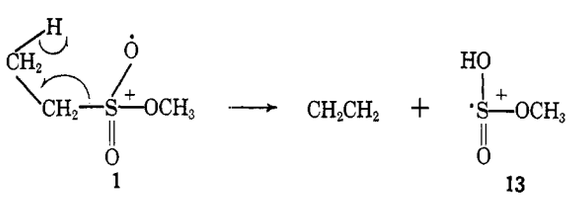
Only two ethyl sulfonate esters have been investigated. Ethyl methanesulfonate (**1**, R = CH_3; R′ = CH_3CH_2) shows evidence of a double-hydrogen transfer with concurrent β' cleavage upon electron bombardment. The parent ester gives a peak at m/e 97 in approximately 20% relative abundance; the mono-α-deuterated ester shows incorporation of the deuterium to give m/e 98. The tri-β-deuterated ester gives the same ion at m/e 98.

Many of the methyl esters (**1**, R′ = CH_3) show ions corresponding to $(RSO_2OR')^+ \rightarrow (R + CH_2O)^+$, **8**. For example, the spectrum of methyl methanesulfonate gives a peak at m/e 45 of nearly 20% relative abundance. High resolution measurements[8] have shown that this particular ion is due 82% to $(C_2H_5O)^+$ and 18% to $(CHS)^+$. Deuterium labeling shows that the m/e 59 ion in the spectrum of methyl ethanesulfonate is $(C_3H_7O)^+$; the ion occurs at m/e 60, $(C_3H_6DO)^+$, in the mono-α-deuterated ester and at m/e 62, $(C_3H_4D_3O)^+$, in the tri-β-deuterated ester. Obviously a rearrangement must be occurring.

Discussion

The results outlined above involve several interesting rearrangements. However, in certain instances a clear-cut distinction cannot be made between alternate mechanisms on the basis of the present evidence.

There are two reasonable pathways which can account for the transfer of a β hydrogen in methyl ethanesulfonate to give an m/e 96 ion. The most straightforward involves transfer of a β hydrogen with concurrent α cleavage to give ethene and **13**, which is the parent ion of methyl bisulfite. A possible analogy for



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this fragmentation is the pyrolysis of sulfoxides to olefins,[9] as illustrated by the pyrolysis at 80° of phenyl 1,2-diphenyl-1-propyl sulfoxide (**14**) to give methyl-*trans*-stilbene (**15**). The elimination proceeds through a five-membered-ring transition state (**16**) (Scheme I). However, five-membered-ring transition states are not very common in mass spectral fragmentations.[10] Four and six-membered-ring transition states are quite common, presumably because there can be an uninterrupted cyclic movement of electrons in such rings, whereas

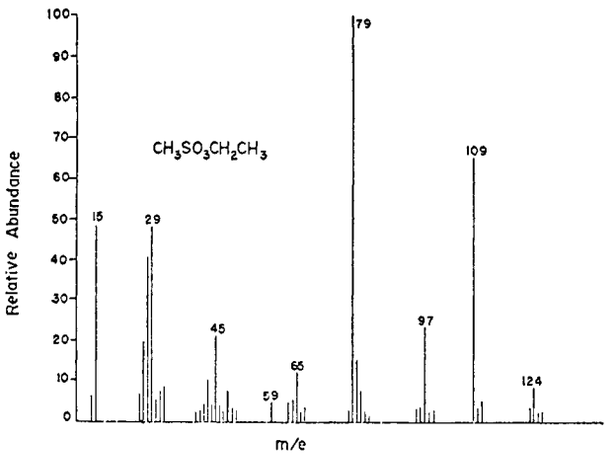
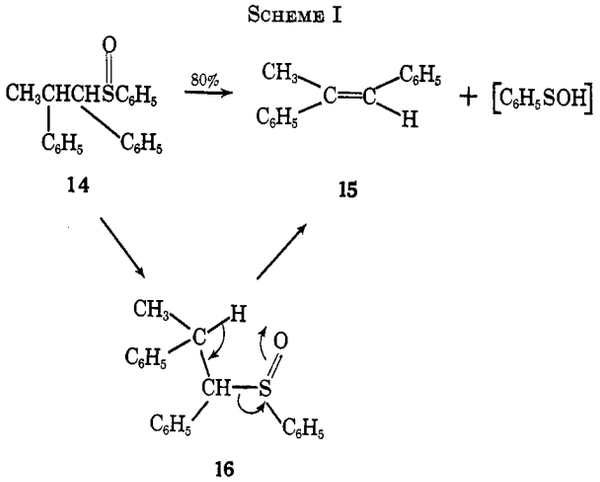
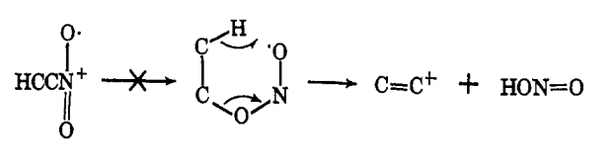


Figure 7.—Ethyl methanesulfonate.

SCHEME I



this is not normally the case in five-membered rings. However, in the proposed rearrangement–fragmentation for the sulfonate parent ion through the five-membered ring, the alkyl group is oxidized to olefin while the sulfur undergoes a reduction. This change in oxidation state of sulfur accommodates a smooth transition of electrons through a five-membered ring. Other heteroatoms, which can exist in various oxidation states, should show similar behavior, for example nitrogen or phosphorus. Indeed, it has been shown that tertiary aliphatic nitro compounds readily lose HNO_2 to give olefins;[11] although such a five-membered transition was not suggested by the authors, it can account for the observed ions (Scheme II). *E.g.*, 2,4-dimethyl-2-nitropentane (**17**) shows peaks which are attributed to a combination of the spectra of 2,4-dimethyl-1-pentene (**18**) and 2,4-dimethyl-2-pentene (**19**). Rearrangement of the nitro compounds to nitrite esters has been excluded, thereby eliminating the possibility of a six-membered-ring transition state (**20**) to transfer a hydrogen with concurrent β cleavage.



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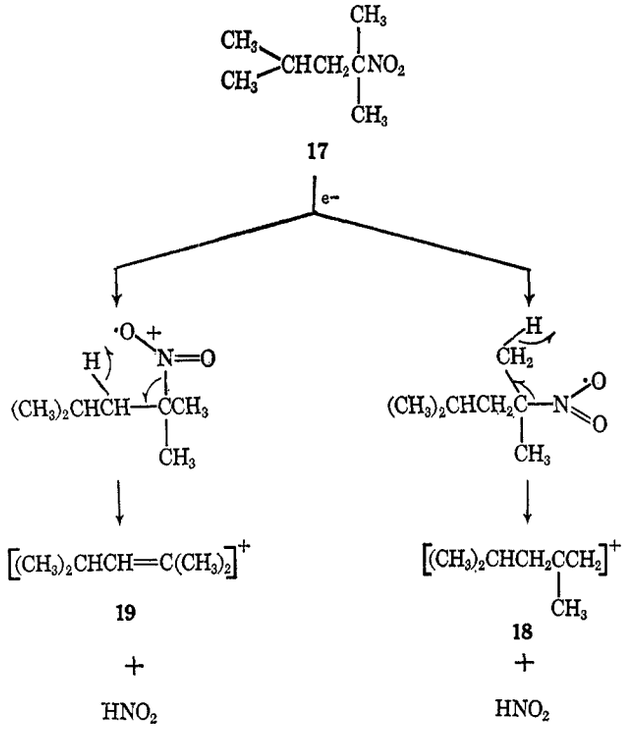
(8) Performed by D. S. Weinsey, Phillips Petroleum Co., Bartlesville, Okla.

(9) C. A. Kingsburg and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960).

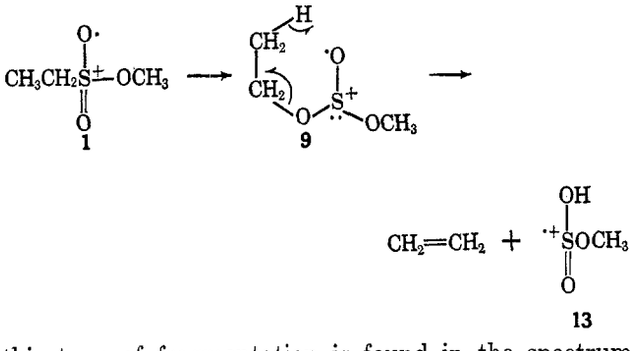
(10) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, Chapter 7.

(11) R. T. Alpin, M. Fischer, D. Becher, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 4888 (1965).

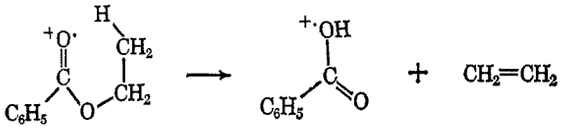
SCHEME II



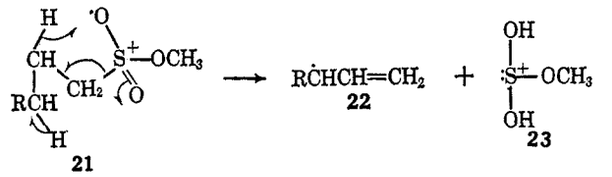
The alternate pathway for transfer of an original β hydrogen in methyl ethanesulfonate would then require rearrangement to methyl ethyl sulfite (**9**) followed by transfer of what has become a γ hydrogen with simultaneous C–O bond cleavage. Precedent for



this type of fragmentation is found in the spectrum of ethyl benzoate,[12] where there is evidence for β' cleavage with transfer of a γ' hydrogen to give ethene and benzoic acid. There are again two reasonable

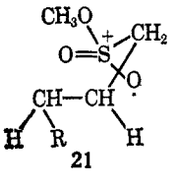


pathways for the apparent transfer of a β and a γ hydrogen in methyl 1-propanesulfonate. The first pathway occurs with α cleavage while the two hydrogens are transferred through a 3,2,1 bicyclic transition state (**21**) to give an allyl radical (**22**) and the parent



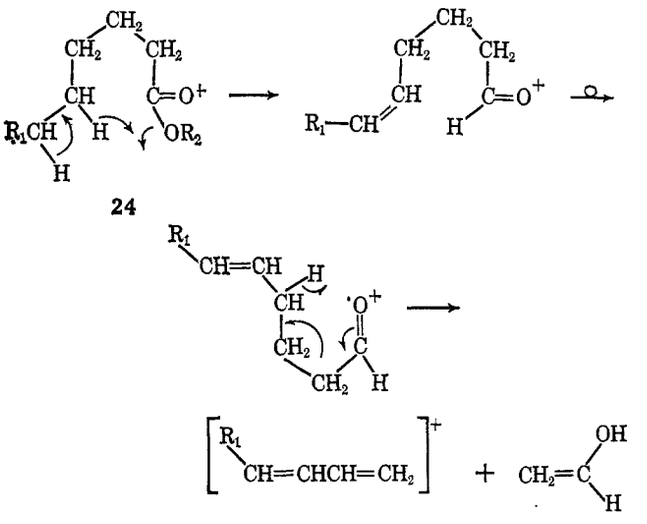
(12) F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959).

ion of protonated methyl bisulfite (**23**). Molecular models show that the geometry for this transformation is quite favorable, and, furthermore, as R becomes longer this conformation becomes more probable because of steric interference of R with the sulfonate

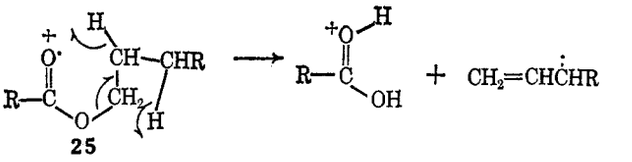


group. Although this type of 3,2,1 bicyclic double-hydrogen rearrangement seems to be unprecedented in the mass spectral literature, other bicyclic pathways have been proposed in mass spectral fragmentations.[13,14] For example, a 3,3,1 bicyclic doubly hydrogen-bridged transition state (**24**) has been proposed for the loss of methanol and CH_2=CHOH, *i.e.*, $(M - 76)^+$, from 6-substituted aliphatic methyl esters[15] (Scheme III).

SCHEME III

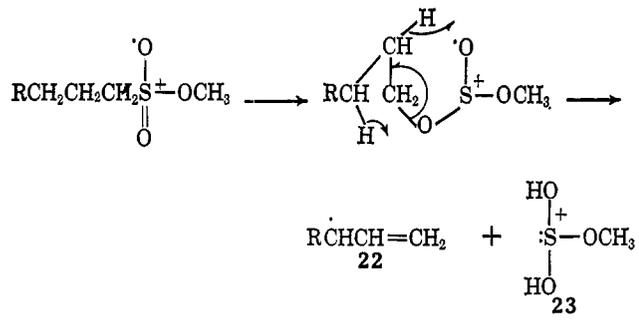


A 3,2,1 bicyclic transition state (**25**) has been proposed for the transfer of two hydrogens in propyl and higher esters of aliphatic and aromatic carboxylic acids.[12] Djerassi and Fenselau have shown that the itinerant hydrogens come mostly, but not entirely, from C-2 and C-3 in the butyl esters.[13] This study

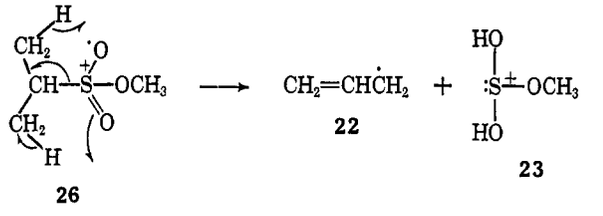


provides precedent for the second possible pathway for formation of **22** and **23** in the methyl sulfonates containing three or more carbons in the alkyl chain. As before, prior rearrangement to methyl alkyl sulfite would be required. This molecule could then undergo the same transformation as the carboxylic esters.

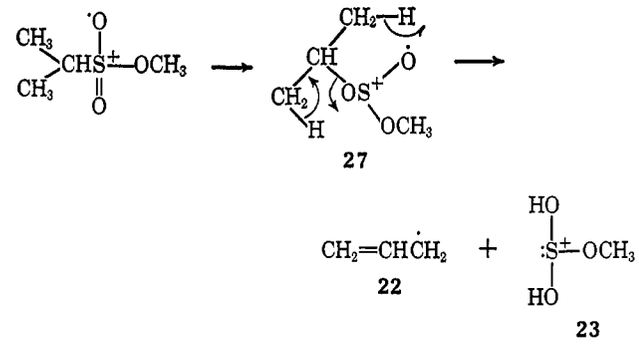
(13) C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, **87**, 5756 (1965).
(14) S. Meyerson and L. C. Leitch, *ibid.*, **88**, 56 (1966).
(15) Spectrum from American Petroleum Institute, Research Project 44, Serial No. 390, Aug 31, 1949.

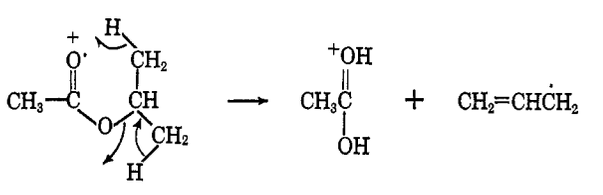


The same two mechanistic pathways, with appropriate modifications, can explain the *m/e* 97 ion in methyl 2-propanesulfonate. The first would proceed through a 3,3,0 bicyclic transition state (**26**) to give α cleavage and a β,β double-hydrogen transfer. Models show these two five-membered rings as being sound sterically.



The second mechanism requires transfer of one γ hydrogen to sulfinyl oxygen and one γ hydrogen to isopropoxy oxygen with β cleavage after rearrangement of the sulfonate to sulfite [**9**, R = $(CH_3)_2CH$; R′ = CH_3]. The hydrogen transfers would occur through a 4,2,0 bicyclic transition state (**27**). Although conclusive proof has not been given, the *m/e* 61 ion in isopropyl acetate[15] is presumably protonated acetic acid arising from a rearrangement similar in form to that above.

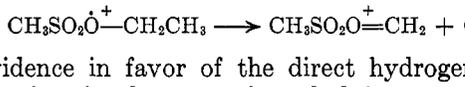




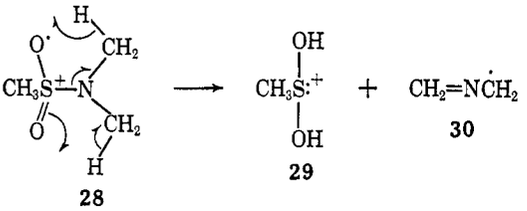
There is no positive evidence to allow an absolute choice between double-hydrogen transfer with α cleavage and rearrangement to sulfite followed by double-hydrogen transfer with β cleavage. We prefer the first path over the second for several reasons. As has been pointed out the *m/e* 97 ion becomes increasingly abundant in the higher esters, but the alkoxy ion, $(RCH_2CH_2CH_2O)^+$, becomes less abundant. Furthermore, if methyl alkyl sulfites are produced, then loss of groups from the carbon attached to oxygen should be common, since this is a favored reaction in most compounds containing the RCO group.[7] Loss of methyl does occur in methyl ethanesulfonate (**1**, R = CH_3CH_2; R′ = CH_3) to the extent of about 5% relative abundance (*m/e* 109). Deuterium labeling has shown that

$$CH_3CH_2SO_3CH_3 \xrightarrow{e^-} CH_3^+ + (M - CH_3)^+$$

it is the methyl originally in the ethyl group that is lost. Methyl 2-propanesulfonate loses a methyl from isopropyl to the extent of 2% relative abundance. Methyl 1-propanesulfonate loses ethyl to the extent of about 3% relative abundance (*m/e* 109). The only other methyl ester which gives a similar fragmentation is methyl 2-chloroethanesulfonate, whose spectrum shows *m/e* 109, $(M - CH_2Cl)^+$, in nearly 30% relative abundance; this certainly is prompted by the stabilizing effect of chlorine on the fragment produced. These results are to be contrasted to the much more prominent loss of methyl from the ethyl group in ethyl methanesulfonate (**1**, R = CH_3; R′ = CH_3CH_2). This ion occurs in 70% relative abundance.

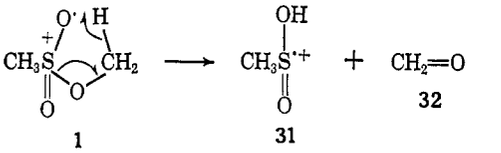


Evidence in favor of the direct hydrogen transfer mechanism in the case of methyl 2-propanesulfonate may be found in the spectrum of N,N-dimethyl methanesulfonamide (**28**). Simple α' cleavage occurs to give *m/e* 79, $(CH_3SO_2)^+$, in about 12% relative abundance. There is also a peak at *m/e* 81 in nearly 10% relative abundance, which corresponds to $(CH_3SO_2 + 2H)^+$. Since it has been shown that α hydrogens are not involved in the transfers occuring in sulfonate esters, it is reasonable to assume that the same is true in this case; consequently the itinerant hydrogens originate in the N,N-dimethyl groups. Any sort of rearrangement in this portion of the molecule seems rather unlikely, and, therefore, the most plausible explanation is the direct transfer of two β' hydrogens through a 3,3,0 bicyclic transition state, with concurrent α' cleavage, to give protonated methanesulfinic

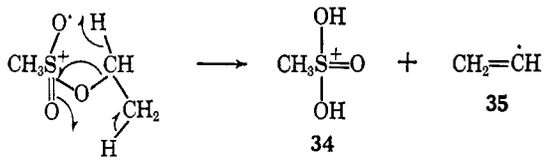


acid (**29**) and a highly stabilized radical derived from N-methylformaldimine (**30**) (which is also recorded at *m/e* 42).

The most unambiguous instance of a five-membered ring transition state for the transfer of a hydrogen in sulfonate esters is given by methyl methanesulfonate (**1**, R = R′ = CH_3). Clearly, the peak *m/e* 80 is due to the ion resulting from transfer of a β' hydrogen with



α' cleavage to give the parent ion of methanesulfinic acid (**31**) and formaldehyde (**32**). A mechanism consistent with the spectra of the ethyl esters would require transfer of a β' and a γ' hydrogen with β' cleavage, through a 3,2,1 bicyclic transition state (**33**) to give protonated methanesulfonic acid (**34**, electronically similar to a sulfoxonium ion) and a vinyl radical (**35**). This transition state would differ from



33 **34** **35**

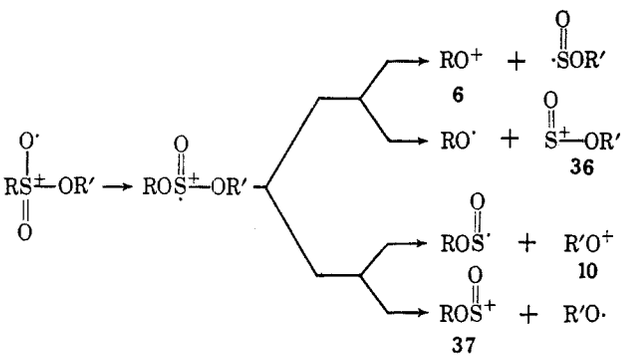
that proposed for the fragmentation of methyl 1-propanesulfonate and higher homologs involving β,γ double-hydrogen transfer with α cleavage only in the position of cleavage (β' instead of α). Vinyl radical have been postulated in the mass spectral fragmentation of some β-hydroxy ethers.[16]

$$(RCH_2CH_2OCH_2CH_2OH)\cdot^+ \longrightarrow$$

$$RCH{=}\dot{C}H + HOCH_2CH_2\overset{+}{O}H_2$$

The occurrence of RO^+ (**6**) is most easily explained by assuming that **1** rearranges to dialkyl sulfite (**9**), which may then fragment to give **6** (ion or radical) and **36** (radical or ion), or **10** (ion or radical) and **37** (radical or ion) (Scheme IV). This rearrangement would be

SCHEME IV



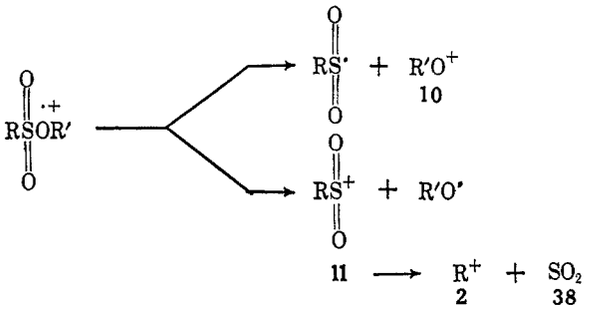
somewhat analogous to that given by diaryl sulfones.[2] It is interesting to note that neither ethyl methanesulfonate (**1**, R = CH_3; R′ = CH_3CH_2) nor any of its deuterated analogs gives an $(M - 31)^+$ ion, (m/e 93), whereas methyl ethyl sulfite (**9**, R = CH_3CH_2; R′ = CH_3) has an ion at $(M - 31)^+$ in 15% relative abundance. This would seem to indicate that a methyl group cannot migrate, and that the migrating group must carry at least one substituent to stabilize it as either a radical or a carbonium ion. Further, it is unlikely that a carbonium ion would migrate to an electron-deficient oxygen. Such a scheme would account for the appearance of **6**, **36** (m/e 79 for R′ = CH_3), and **10** (m/e 31 for R′ = CH_3) in most of the spectra. However, as has been pointed out previously, not all the esters give **37**, $(M - 31)^+$ for R′ = CH_3. This might be due to rapid decomposition of **37** to R^+ (**2**) and sulfur dioxide (**38**). The rate of decomposition of **37** might be expected to depend upon the stability of **2** as a carbonium ion. Such a dependence would explain the fact that methyl sulfonate esters derived from secondary, benzylic and allylic sulfonic acids do not show significant $(M - 31)^+$ peaks, since these ions (**37**) would be expected to fragment rapidly to SO_2 and the stable carbonium ion. Such a fragmentation to give a primary carbonium ion would not be as facile, and, consequently, $(M - 31)^+$ should be recorded for methyl esters derived from primary sulfonic acids. This is indeed the case.

$$ROS{=}\overset{+}{O} \longrightarrow R^+ + SO_2$$

37 **2** **38**

The production of $R'O^+$ (**10**, m/e 31 for R′ = CH_3) and $(M - OR')^+$ involves simple α' cleavage to **10** (ion or radical) and alkanesulfonyl radical or ion (**11**). Rapid decomposition of **11** would explain the absence of $(M - 31)^+$ in those methyl esters which yield a stabilized carbonium ion **2** (Scheme V).

SCHEME V

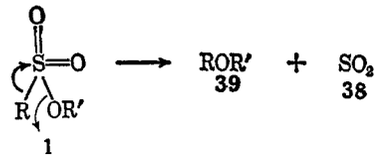


Neither of the schemes above accounts for the formation of $(R + CH_2O)^+$ ions (**8**), which also appear in the spectra of those compounds showing RO^+ ions (**6**). An ion–molecule recombination reaction, such as an alkyl group (**2**) attacking the formaldehyde (**32**) which

$$R^+ + CH_2O \longrightarrow RO{=}\overset{+}{C}H_2$$

2 **32**

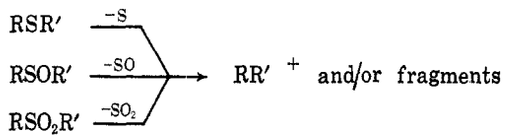
is produced from the methyl esters, is unlikely because mass spectra are generally run at very low sample pressures to virtually eliminate second-order reactions. In fact, the relative abundance of the $[R + CH_2O]^+$ peak is not proportional to the square of the sample pressure, thereby precluding a second-order ion–molecule reaction. Those ion–molecule reactions which do occur usually involve attack on un-ionized parent molecules which are the most abundant (>90%) species present. Another possible scheme would involve a three-centered rearrangement of sulfonate (**1**) to an ether (**39**) with the expulsion of sulfur dioxide



1 **39** **38**

(**38**). This decomposition is quite similar to those studied by Madsen and co-workers[4] who showed that expulsion of sulfur from sulfides, SO from sulfoxides, and SO_2 from sulfones can occur.

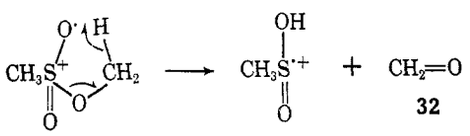
(16) F. W. McLafferty and W. J. Beard, ASTM E-14 Meeting on Mass Spectrometry, New York, N. Y., 1957, p 29.



Summary

The spectra of nearly 30 methyl alkanesulfonates and two ethyl alkanesulfonates, along with the spectra of various deuterium-labeled analogs of these compounds, have been recorded and studied. There is evidence in these spectra for a number of distinct but similar cyclic and bicyclic transition states for the transfer of one or two hydrogens to the sulfonyl oxygens accompanied by cleavage of the molecule.

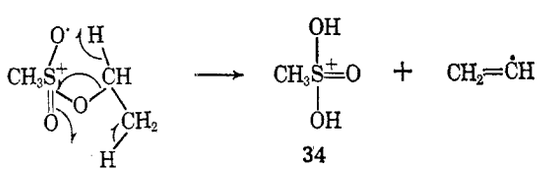
Undoubtedly, methyl methanesulfonate transfers a methoxy (β') hydrogen with concurrent α' cleavage to give m/e 80, the parent ion of methanesulfinic acid (**31**). This transfer involves an uncommon five-



31 32

membered transition state. Most of the esters show simple α' and γ' cleavages.

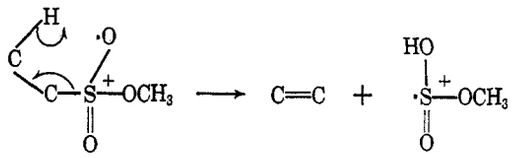
Ethyl methanesulfonate also undergoes β' cleavage with transfer of a β' and γ' hydrogen to give protonated methanesulfonic acid (**34**). This probably occurs through a 3,2,1 bicyclic transition state (**33**).



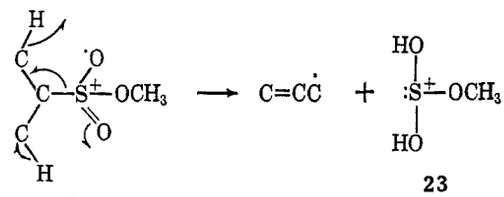
33 34

The alkyl group attached to sulfur gives various rearrangements depending upon the availability of β and/or γ hydrogens on saturated carbon atoms. With no such hydrogens, simple α cleavage occurs. α cleavage is observed in all the spectra, but it is greatly diminished when β or γ hydrogens are available. In general, two mechanistic pathways are plausible for the hydrogen transfers involved. The first involves direct transfer through a five-membered transition state or through two five-membered transition states or a five- and a six-membered transition state. The second involves prior rearrangement of the sulfonate ester to a sulfite followed by transfers using six- or six- and five-membered transition states. Although these two pathways would be extremely difficult to distinguish experimentally (such a distinction cannot be made with the present evidence), the former pathway is preferred by these authors because of the data concerning alkoxy ions discussed in the text and because of the demonstrated possibility for a five-membered transition state in the fragmentation of methyl methanesulfonate. Consequently, only those mechanisms following the first pathway will be summarized.

When one set of β hydrogens is available, a β hydrogen is transferred with α cleavage to give an olefin and the molecular ion of methyl bisulfite (**13**, m/e 96).

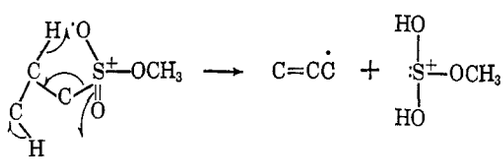


With two sets of β hydrogens, two β hydrogens are transferred through a 3,3,0 bicyclic transition state (**26**) with α cleavage to give an allyl radical and protonated methyl bisulfite (**23**, m/e 97).



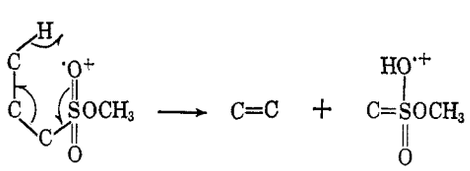
26 23

When a β and a γ hydrogen are available, transfer of these through a 3,2,1 bicyclic transition state with α cleavage gives an allyl radical and protonated methyl bisulfite (**23**).



If two sets of β hydrogens and one set of γ hydrogens are available, deuterium labeling indicates that the double-hydrogen transfer occurs through both the 3,3,0 and the 3,2,1 bicyclic transition states, but that the latter is preferred.

A rearrangement involving a six-membered ring also occurs with those molecules possessing γ hydrogens.



Experimental Section

Most of the sulfonate esters were prepared by the interaction of the sulfonyl chloride, the alcohol, and triethylamine in benzene, and the general procedure is given below. The α-deuterated esters were prepared in the same manner using the deuterated alcohol; this procedure has been shown to give a mixture of undeuterated esters and mono-α-deuterated esters.[17] The mixtures contained approximately 30–60% of the deuterated esters. The preparations of the β-deuterated esters are given below. The purity of the compounds was checked by nmr and glpc and when necessary the esters were either redistilled or purified by glpc before analysis; the esters studied are listed in Table I. Mass spectra were recorded on an Hitachi RMU-6A instrument using a heated inlet, an ionization energy of 70 ev, an inlet temperature of 185°, and a source temperature of 160°.[18] Nmr spectra were recorded on a Varian A-60 spectrometer in deuteriochloroform with (tetramethylsilane TMS) = 0.

General Procedure for the Preparation of Alkyl Alkanesulfonates.—To a solution of 0.13 mole of triethylamine and 0.13 mole of alcohol in 200 ml of benzene contained in a dry, 500-ml, three-necked flask equipped with an addition funnel, nitrogen inlet, calcium chloride drying tube, and a magnetic stirrer was slowly added with cooling and stirring a solution of 0.10 mole of the sul-

(17) R. W. Campbell, Ph.D. Thesis, Purdue University, 1966.

(18) We are indebted to Dr. F. W. McLafferty and Dr. M. M. Bursey and their staff for these spectral determinations.

TABLE I

ALKYL ALKANESULFONATES, $RSO_2Cl + R'OH\ RSO_3R'$

R	R'	X	Bp (mm), °C	R	R'	X	Bp (mm), °C
CH_3	CH_3	Cl[a]	78 (10)	$CH_3(CH_2)_5$	CH_3	Cl[e]	82–86 (0.5)
CH_2D	CH_3	Cl[a]	75 (8)	$(CH_3)_3CCH_2CH_2$	CH_3	Cl[b]	60–61 (0.15)
CH_3CH_2	CH_3	Cl[a]	80 (9)	*c*-C_6H_{11}	CH_3	Cl[d]	73.5–76 (0.4)
CH_3CHD	CH_3	Cl[a]	78 (8)	$CH_3(CH_2)_6$	CH_3	Cl[e]	93–95 (0.8)
CD_3CH_2	CH_3	Br[b]	99 (16)	$CH_3(CH_2)_7$	CH_3	Cl[e]	100–106 (0.4
$CH_3(CH_2)_2$	CH_3	Cl[a]	62 (2)	$ClCH_2CH_2$	CH_3[f]	..	109.5–106 (5.5)
CH_3CH_2CHD	CH_3	Cl[a]	42 (0.08)	$C_6H_5CH_2CH_2$	CH_3	Cl[e]	108–110 (0.15)
$(CH_3)_2CH$	CH_3	Cl[c]	74 (7.5)	CH_2=$CHCH_2$	CH_3	Cl[g]	87–89 (9)
$(CH_3)_2CD$	CH_3	Cl[c]	72–73 (7.0)	CH_2=$CHCHD$	CH_3	Cl[g]	86–88 (8)
$(CD_3)_2CH$	CH_3	Cl[b]	82–86 (7.5)	$C_6HC_5H_2$	CH_3	Cl[a]	Mp 60–67
$CH_3(CH_2)_3$	CH_3	Cl[a]	57–59 (0.5)	C_6H_5CHD	CH_3	Cl[a]	Mp 59–61
$CH_3CH_2(CH_3)CH$	CH_3	Cl[d]	88–90 (6)	CH_3	CH_3CH_2	Cl[a]	78 (7.5)
$CH_3CH_2(CH_3)CD$	CH_3	Cl[d]	82–86 (5.5)	CH_2D	CH_3CH_2	Cl[a]	78 (7.5)
$CH_3CD_2(CD_3)CH$	CH_3	Cl[b]	84.5–86 (6)	CH_3	CD_3CH_2	Cl[a]	85–86.5 (9)
$(CH_3)_2CHCH_2$	CH_3	Cl[e]	79–82 (4)	*p*-$CH_3C_6H_4$[f]	CH_3CH_2	..	109–112 (0.25)
$CH_3(CH_2)_4$	CH_3	Cl[e]	77–78 (0.5)	CH_3CH_2[h]	C_6H_5	..	94–96 (0.3)

[a] Eastman. [b] Preparation given below. [c] V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **74**, 5285 (1952). [d] G. Berti, *ibid.*, **76**, 1213 (1954). [e] C. Ziegler and J. M. Sprague, *J. Org. Chem.*, **16**, 621 (1951). [f] W. D. Emmons and A. F. Ferris, *J. Am. Chem. Soc.*, **75**, 2257 (1953). [g] M. A. Belons and I. V. Postovskii, *Zh. Obshch. Khim.*, **20**, 1701 (1950). [h] D. Klamann, *Ann.*, **583**, 63 (1953).

fonyl chloride in 50 ml of benzene. The mixture was stirred overnight under nitrogen, and the precipitated triethylamine hydrochloride was filtered. The filtrate was washed several times with dilute hydrochloric acid and dried over sodium sulfate, and then the solvent was removed under reduced pressure. The resulting ester was then distilled *in vacuo* through a 10-cm Vigreux column.

Ethanol-2,2,2-d_3.[19,20]—A solution of 104 g (1.0 mole) of malonic acid (Mallinckrodt), 50 g of deuterium oxide (Columbia Organic Chemicals, 99.7%), and 100 ml of dioxane (distilled from sodium) was stirred for 48 hr at room temperature. The solvent was then removed at room temperature *in vacuo*, and the residue was dried *in vacuo* over phosphorus pentoxide. This procedure was repeated for a total of three times. This product was then decarboxylated by heating with stirring at 145° until the evolution of CO_2 stopped (about 24 hr). The crude acetic acid-d_4 was then taken up in 100 ml of Ansul ether 141 (distilled from $LiAlH_4$) and slowly added with stirring to a cooled slurry of 38.0 g (1.0 mole) of lithium aluminum hydride in 600 ml of Ansul ether 141 contained in a 2-l., three-necked, round-bottom flask equipped with a stirrer, addition funnel, and a condenser mounted with a $CaCl_2$ drying tube. The mixture was stirred overnight, and then excess methyl carbitol (about 200 ml) was added. The product was then distilled from the reaction mixture until the temperature at the distilling head reached 150°. This material was then redistilled to give 35.0 g of ethanol-2,2,2-d_3, bp 78–80°.

Ethyl-2,2,2-d_3 Bromide.—Phosphorus tribromide (54.4 g, 0.2 mole, 19.1 ml) was slowly added to a solution of 26.6 g (0.544 mole) of ethanol-2,2,2-d_3 in 50 ml of bromobenzene with stirring at −15° in a 200-ml, three-necked flask equipped with a stirrer, addition funnel, and a Dry Ice condenser sealed with a $CaCl_2$ drying tube. The mixture was stirred overnight at 0°, and the product was distilled from the reaction mixture, bp 37–40°. After washing with cold, dilute NaOH and cold water, the crude material weighed 18.7 g (30.8%).

Ethane-2,2,2-d_3-sulfonyl Bromide.[21]—Ethyl-2,2,2-d_3 bromide (18.7 g, 0.167 mole) was refluxed with 42.0 g (0.17 mole) of $Na_2S_2O_3 \cdot 5H_2O$ in 200 ml of 50% aqueous methanol for 3 hr. After concentrating the mixture *in vacuo* to 30 ml, it was taken up in 100 ml of water and 75 ml of acetic acid. This solution was cooled to 0° and chlorine was bubbled slowly through the solution with vigorous stirring. The mixture first became yellow, then orange, and finally yellow-green, whereupon the addition was stopped. A dark layer of the sulfonyl bromide had formed; this material was extracted with ether; and the ether layer was washed with dilute $NaHSO_3$, and then several times with cold water. The ether solution was then dried ($CaCl_2$) and distilled *in vacuo*. Ethane-2,2,2-d_3-sulfonyl bromide, bp 85–86° (18 mm), was collected in the amount of 16.0 g (55%).

Methyl Ethane-2,2,2-d_3-sulfonate.—To a solution of 10.1 g (0.1 mole) of triethylamine and 3.2 g (0.1 mole) of methanol in 100 ml of benzene was slowly added a solution of 16.0 g (0.091 mole) of ethane-2,2,2-d_3-sulfonyl bromide in 25 ml of benzene. The mixture was stirred for 5 hr, and then it was worked up as usual to give a mixture as shown by the nmr spectrum which was assumed to be ester and sulfonyl bromide. The mixture was distilled through a 10-cm Vigreux column to give the following fractions: bp 82–87° (16 mm), 97–99° (16 mm), and 99° (16 mm). The high-boiling fraction was shown by vpc to be a mixture, but it was separated by vpc, and pure methyl ethane-2,2,2-d_3-sulfonate was collected for an nmr spectrum and for mass spectral analysis (8-ft SE-30 silicone rubber column, T = 145°, flow = 70 ml of helium/min, the ester came off last). Nmr showed δ 3.12 (m) area 2, 3.88 (s) area 3.

2-Propanol-1,1,1,3,3,3-d_6.[22]—To a stirred slurry of 2.5 g (0.0625 mole) of $LiAlH_4$ in 125 ml of Ansul ether 141 (distilled from $LiAlH_4$) contained in a 500-ml, three-necked, round-bottom flask equipped with a stirrer, addition funnel, and a condenser with a $CaCl_2$ drying tube was slowly added 10.0 g (0.173 mole) of acetone-d_6 (Merck Sharp and Dohme of Canada, 99%). The mixture was stirred for 4 hr, and then methyl carbitol (200 ml) was added to decompose the excess $LiAlH_4$ and the salt of the product. The apparatus was arranged for distillation, and 9.2 g of material, bp 80–95°, was distilled. This material was redistilled to give 7.89 g (76.5%) of 2-propanol-1,1,1,3,3,3-d_6.

2-Bromopropane-1,1,1,3,3,3-d_6.—Phosphorus tribromide (21.0 g, 0.0789 mole) was added dropwise to 7.89 g (0.119 mole) of 2-propanol-1,1,1,3,3,3-d_6 at −10° under nitrogen with stirring. After standing overnight, the product was distilled from the reaction mixture, bp 55–60°. This material was washed twice with cold, concentrated H_2SO_4 and dried over potassium carbonate to yield 9.5 g (57.5%) of 2-bromopropane-1,1,1,3,3,3-d_6.

2-Propane-1,1,1,3,3,3-d_6-sulfonyl Chloride.—A mixture of 8.6 g (0.0667 mole) of 2-bromopropane-1,1,1,3,3,3-d_6 and 55 ml of saturated aqueous Na_2SO_3 was refluxed until the temperature of the reflux vapors was nearly 100°. The solvent was evaporated at the water aspirator, and the residue was extracted with 80% aqueous ethanol. The ethanol was evaporated *in vacuo*, and the sodium sulfonate was dried *in vacuo* at room temperature and then in an oven at 140° for 24 hr to give 12.2 g of white solid. This material was suspended in 50 ml of DMF in a 300-ml, three-necked flask equipped with a stirrer, an addition funnel, and a condenser with a $CaCl_2$ drying tube, and then 16.6 g (0.14 mole) of thionyl chloride was added with stirring over a 30-min period. The mixture was stirred for 0.5 hr more, and poured into 300 ml of ice–water. A dark oil separated. The mixture was extracted with ether (three 75-ml portions), and the combined extracts were washed with water (two 150-ml portions) and dried (Na_2SO_4). The ether was distilled, and the residue was distilled *in*

(19) V. J. Shiner, Jr., and M. L. Smith, *J. Am. Chem. Soc.*, **80**, 4095 (1958).

(20) R. F. Nystrom, W. H. Yanko, and W. G. Brown, *ibid.*, **70**, 441 (1948).

(21) T. B. Johnson and J. M. Sprague, *ibid.*, **58**, 1351 (1936).

(22) See Table I, footnote *c*.

vacuo to give 6.30 g (63.5%) of the sulfonyl chloride, bp 68.5–72° (13 mm).

Methyl 2-Propane-1,1,1,3,3,3-d_6-sulfonate.—To a dry solution of 5.12 g (0.047 mole) of triethylamine and 1.49 g (0.047 mole) of methanol in 150 ml of benzene was slowly added a benzene solution of 6.30 g (0.0424 mole) of 2-propane-1,1,1,3,3,3-d_6-sulfonyl chloride. The mixture was stirred overnight, and then it was filtered. Usual work-up yielded a liquid which was distilled *in vacuo* to give four fractions, bp 63.5–68°, 69–70.5°, 71–81°, and 82–86° (all at 7.5 mm), with a total weight of 0.72 g. From the nmr spectra, the purity of the first three fractions was questionable, but the fourth fraction was shown to be pure material: $n^{28.5}$D 1.4229; nmr δ 3.29 (m) area 1 and 3.89 (s) area 3.

2-Butanol-1,1,1,3,3-d_5.[20,23]—A mixture of 36 g (0.5 mole) of 2-butanone, 75 ml of deuterium oxide, and a trace of K_2CO_3 was refluxed for 24 hr, and then the 2-butanone–water azeotrope was distilled, bp 75–90°, and dried (K_2CO_3). This equilibration was repeated for a total of four times. The azeotrope from the last equilibration was diluted with ether and separated, and the ether layer was dried (K_2CO_3). The ether solution was filtered and distilled, and the deuterated 2-butanone was collected at bp 78–80° in the amount of 30.8 g (80%). According to the nmr spectrum this material was 97% α deuterated; it was slowly added to a slurry of 4.56 g (0.12 mole) of $LiAlH_4$ in 200 ml of Ansul ether 141 with stirring under nitrogen. The mixture was stirred for 5 hr at room temperature, and then it was left to stand overnight. At the end of this time, approximately 75 ml of methyl carbitol was slowly added, and the apparatus was rearranged for distillation. 2-Butanol-1,1,1,3,3-d_5 was distilled, bp 90–96°, in the amount of 23.8 g (75.5%).

2-Bromobutane-1,1,1,3,3-d_5.—To cold, stirred 2-butanol-1,1,-1,3,3-d_5 (37.3 g, 0.472 mole) was slowly added 46.9 g (0.173 mole) of phosphorus tribromide. After standing overnight, the mixture was distilled *in vacuo;* the fraction, bp 40–50° (110 mm), was collected, washed with cold, concentrated H_2SO_4 (two 25-ml portions), and shaken with 10 g of anhydrous K_2CO_3. The liquid was filtered and distilled, and the 2-bromobutane-1,1,1,-3,3-d_5, bp 84–88°, was collected in the amount of 49.0 g (73.4%).

2-Butane-1,1,1,3,3-d_5-sulfonyl Chloride.[24]—A mixture of 19.6 g (0.139 mole) of 2-bromobutane-1,1,1,3,3-d_5, 10.55 g (0.139 mole) of thiourea, and 35 ml of ethanol was stirred and heated at 100° for 8 hr. Then the solvent was evaporated at the water aspirator, and the residual oil was taken up in acetone and brought out of solution by adding ether. The oil was dissolved in water, and 10% NaOH was added until no more cloudiness formed. The thiol was then extracted with ether. The ether was distilled, and then the thiol–water azeotrope was distilled, bp 65–70°. The thiol was suspended in 50 ml of acetic acid and 150 ml of water. The mixture was stirred very vigorously and cooled to 0°; a stream of chlorine was slowly passed through the mixture while holding the temperature at 0–5°. The addition was continued until the mixture remained yellow. The sulfonyl chloride was extracted with ether, and the combined extracts were washed with dilute $NaHSO_3$, water, dilute $NaHCO_3$, and finally with water. The ether layer was dried ($CaCl_2$) and evaporated *in vacuo*, and the residue was distilled *in vacuo*. The product was collected, bp 69–72° (5.0 mm), in the amount of 9.53 g (42.4% yield from 2-bromobutane-1,1,1,3,3-d_5).

Methyl 2-Butane-1,1,1,3,3-d_5-sulfonate.—To a solution of 9.53 g (0.059 mole) of 2-butane-1,1,1,3,3-d_5-sulfonyl chloride and 2.24 g (0.07 mole) of methanol in 100 ml of benzene was slowly added 7.07 g (0.07 mole) of triethylamine. The mixture was stirred overnight, and then it was worked up as usual. The ester was distilled *in vacuo*, bp 84.5–86° (6 mm), and collected in the amount of 3.05 g (32.4%): n^{23}D 1.4331; nmr δ 1.05 (s) area 3, 3.05 (s) area 1, and 3.86 (s) area 3.

3,3-Dimethyl-1-butanesulfonyl Chloride.—A mixture of 36.2 g (0.3 mole) of 3,3-dimethyl-1-chlorobutane and 250 ml of saturated, aqueous Na_2SO_3 was stirred and refluxed for 2 weeks; the solution was then cooled and filtered. The white solid so obtained was recrystallized from water and dried in an oven at 140° for 3 days. This material was obtained in the amount of 28.75 g. To a suspension of 20.6 g of this salt (0.1 mole assuming the sodium sulfonate to be the monohydrate) in 150 ml of DMF was slowly added 12.0 g (0.10 mole) of thionyl chloride. The mixture was left to stand overnight, and then it was poured into ice water. The resulting solid was filtered and recrystallized from hexane, mp 43.5–45°; the product was obtained in the amount of 5.12 g (65% based on thionyl chloride).

Methyl 3,3-Dimethylbutanesulfonate.—To a solution of 5.12 g (0.0278 mole) of 3,3-dimethylbutanesulfonyl chloride and 1.28 g (0.04 mole) of methanol in benzene was slowly added 3.69 g (0.036 mole) of triethylamine. The mixture was stirred for 6 hr and then worked up as usual. The product was distilled *in vacuo*, bp 60–61° (0.15 mm), to give 3.02 g (60.4%) of methyl 3,3-dimethylbutanesulfonate: nmr δ 0.95 (s) area 9, 1.70 (m) area 2, 3.08 (m) area 2, and 3.85 (s) area 3.

N,N-Dimethylmethanesulfonamide.—Dimethylamine (100 g, 2.22 moles) was slowly bubbled into a cold, stirred solution of 114.5 g (1.0 mole) of methanesulfonyl chloride in 300 ml of benzene; the mixture was stirred for 3 hr and then filtered. The benzene was evaporated at the water aspirator, and the residue was twice recrystallized from 95% ethanol and vacuum dried to give 30.7 g (25% yield) of N,N-dimethylmethanesulfonamide: mp 48–50°; nmr δ 2.79 (s) area 3 and 2.86 (s) area 6.

Methyl Ethyl Sulfite.[25]—To 130 g (1.1 moles) of thionyl chloride contained in a 300-ml, three-necked flask equipped with a stirrer, addition funnel, and a drying tube was slowly added 32 g (1.0 mole) of methanol. The mixture was allowed to stand for 48 hr; the methyl chlorosulfite was distilled *in vacuo* through a 50-cm Vigreux column, bp 35–36° (65 mm). Then 11.4 g (0.10 mole) of this material was slowly added to a mixture of 4.6 g (0.10 mole) of ethanol and 9.5 g (0.12 mole) of pyridine in 100 ml of ether which had been cooled to 0°. The mixture was stirred for 1 additional hr and filtered. The filtrate was washed with dilute HCl, water, and dilute $NaHCO_3$, and dried ($MgSO_4$). The ether was evaporated, and the residue was distilled, bp 55–58° (24 mm), to give 1.8 g (14.5%) of methyl ethyl sulfite: nmr δ 1.32 (t) area 3, 3.61 (s) area 3, and 4.05 (q) area 2.

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(23) V. J. Shiner, Jr., and S. Cross, *J. Am. Chem. Soc.*, **79**, 3599 (1957).

(24) J. M. Sprague and T. B. Johnson, *ibid.*, **59**, 1837 (1937).

(25) See Table I, footnote *d*.