Mass Spectrometry in Structural and Stereochemical Problems. CCXII.[1] Electron Impact Induced Triple Hydrogen Rearrangements and Other Fragmentations of Alkyl Vinyl Ethers and Thioethers[2,3]

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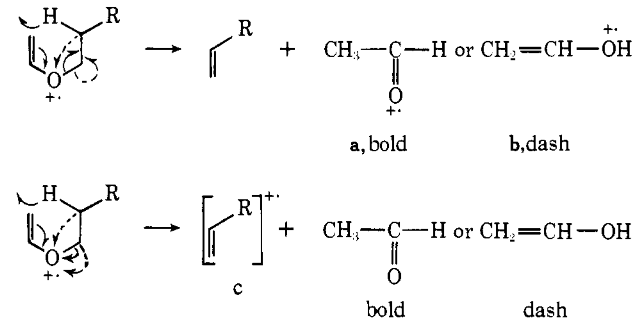
Abstract: The mass spectrometry of alkyl vinyl ethers has been examined in detail because of some unusual mechanistic aspects. Important fragmentations of the molecular ion were triggered by hydrogen transfer and included loss of methyl radical and of ethanol. Both processes involved the interesting intermediacy of ionized 2-methyl-substituted cyclic ethers and single and triple hydrogen transfers, respectively. It was concluded that the important ion of mass 44 is ionized vinyl alcohol (b) resulting from a nonspecific hydrogen transfer rather than ionized acetaldehyde (a). The mass spectrometry of alkyl thiovinyl ethers was also investigated and was found to display fragmentations resulting from generally analogous hydrogen transfers. However, the mass 60 ion, which corresponds to the ion of mass 44 (ionized vinyl alcohol) of alkyl vinyl ethers, is probably ionized thioacetaldehyde (rather than vinyl mercaptan) and is produced by a site-specific McLafferty rearrangement. Special attention has been paid in this study to the occurrence and nature of the otherwise rare triple hydrogen migration.

Part A

In an early study[6] of the mass spectrometry of alkyl vinyl ethers, despite the lack of definitive deuterium-labeling experiments, the origin of the important mass 44 ion was explained in terms of a "McLafferty rearrangement" yielding ionized acetaldehyde (a) (Scheme I, bold). However, on the basis of appearance potential data Meyerson and McCollum[7] suggested that the ion of mass 44 corresponded to ionized vinyl alcohol (b) arising from hydrogen transfer to oxygen (Scheme I, dash). Audier[8] investigated the charge retention ratio between the mass 44 ion and the corresponding ionized olefin (c), which was assumed to result from hydrogen abstraction from C-2 of the alkyl chain.

Scheme I



With the use of deuterium labeling, low ionizing voltage spectra, and scanning in the metastable mode, the mass spectrometry of alkyl vinyl ethers has been investigated in detail. In view of the interesting results, the hitherto uninvestigated sulfur analogs (alkyl thiovinyl ethers) were also included in order to determine the effect of changes in the heteroatom upon the course of electron impact induced decomposition.

Alkyl Vinyl Ethers. In the 70-eV spectra (Figures 1 and 3) of alkyl vinyl ethers, oxygen-containing peaks were generally less significant than hydrocarbon peaks except for the molecular (M), M − 15, *m/e* 44, and *m/e* 45 peaks. In the 15- or 12-eV spectra (Figures 2 and 4), hydrocarbon ions produced *via* secondary decomposition were depressed, and the molecular, M − 15, M − 44 (alkyl chain ≤5; see Figures 1 and 2), and M − 46 (alkyl chain >5; see Figures 3 and 4) ions were enhanced. Scanning the metastable mode with *n*-heptyl vinyl ether (II) confirmed that the latter ions were the result of primary processes, whereas the depressed ions originated from secondary ones; metastable transitions from the molecular ion were found only for the M − 44, M − 46, and M − 72 ions. A metastable transition for M → M − 15 was observed in the normal mass spectrum. The following discussion deals mainly with primary fragmentations.

M − 15 Peaks. This important peak escaped the attention of former investigators[6-8] even though in 12-eV spectra it is the base peak for C_4–C_6 *n*-alkyl vinyl ethers (I, III, and IV) and the second or third highest for the C_7–C_{10} homologs (II, V, VI, and VII). Deuterium labeling of various positions of *n*-butyl vinyl ether (I) (Table I) demonstrated that the M − 15 peak does not originate simply by loss of a terminal methyl group (Scheme II). Rather, the major pathway involves loss of the terminal methylene group following abstraction of a hydrogen atom from the C-3 position of the *n*-butyl chain (Scheme III). The validity of

$R—O—CH=CH_2$

I, R = n-C_4H_9
II, R = n-C_7H_{15}
III, R = n-C_5H_{11}
IV, R = n-C_6H_{13}
V, R = n-C_8H_{17}
VI, R = n-C_9H_{19}
VII, R = n-$C_{10}H_{21}$

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(1) For preceding paper see G. Eadon, S. Popov, and C. Djerassi, *J. Amer. Chem. Soc.*, **94**, 1282 (1972).

(2) Financial assistance from the National Institutes of Health (Grants AM 12758 and AM 04257) is gratefully acknowledged.

(3) Some of these results have been published in preliminary communications: (a) M. Katoh and C. Djerassi, *J. Chem. Soc. D*, 1385 (1969); (b) *J. Amer. Chem. Soc.*, **92**, 731 (1970).

(4) Postdoctoral Fellow, 1968–1970, on leave from Mitsubishi Chemical Industries, Tokyo, Japan.

(5) National Science Foundation Postdoctoral Fellow, 1970–1971.

(6) F. W. McLafferty, *Anal. Chem.*, 31, 2072 (1959).

(7) S. Meyerson and J. D. McCollum, *Advan. Anal. Chem., Instrum.*, 2, 211 (1963).

(8) H. E. Audier, *Org. Mass Spectrom.*, 2, 283 (1969).

Fig.1

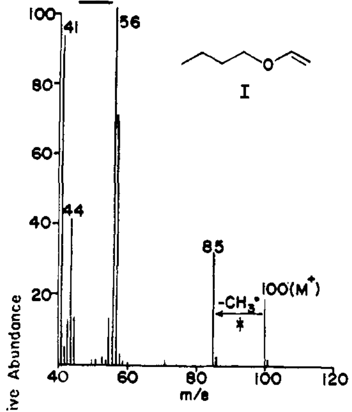


Fig.2

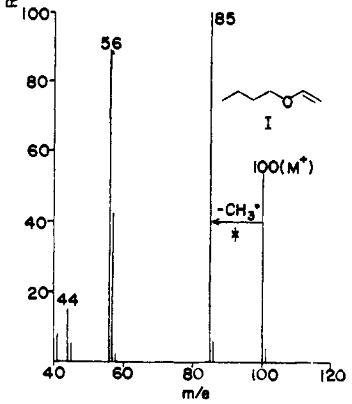
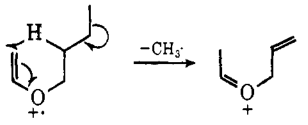
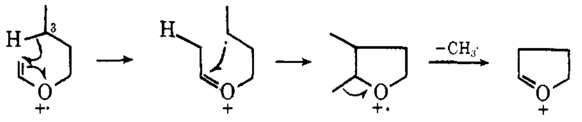


Figure 1. Mass spectrum (70-eV) of *n*-butyl vinyl ether (I).
Figure 2. Mass spectrum (12-eV) of *n*-butyl vinyl ether (I).

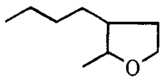
Scheme II



Scheme III

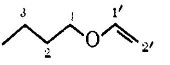


Scheme III was substantiated by the observation of a significant M − 15 peak in the mass spectrum of 2-methyl-3-*n*-butyltetrahydrofuran (VIII) (Figure 5).



VIIIa, *cis*-2,3
VIIIb, *trans*-2,3

Table I. M − CH_3 Loss in *n*-Butyl Vinyl Ether (I) at 70 eV[a,b]



I

Ion	1-d_2 (Ia)	2-d_2 (Ib)	3-d_2 (Ic)	4-d_3 (Id)	2'-d_2 (Ie)
M − CH_3	98.2	98.2	46.3	75.1	17.3
M − CH_2D	1.8	1.8	53.7	6.4	
M − CHD_2					82.7
M − CD_3				19.5	

[a] Only minor changes were noted at low voltage (nominal 15 eV).
[b] All values are per cent.

Fig.3

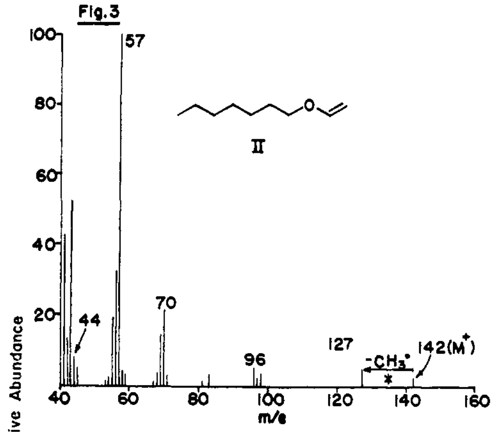


Fig.4

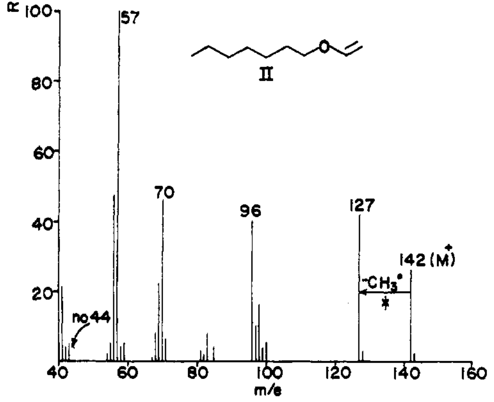
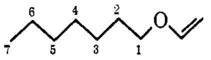


Figure 3. Mass spectrum (70-eV) of *n*-heptyl vinyl ether (II).
Figure 4. Mass spectrum (15-eV) of *n*-heptyl vinyl ether (II).

With *n*-heptyl vinyl ether (II) deuterium labeling (Table II) showed that the loss of methyl was initiated by hydrogen abstraction from the C-4 position through an eight-membered transition state (Scheme IV).

Table II. M − CH_3 Loss in *n*-Heptyl Vinyl Ether (II) at 70 eV[a,b]

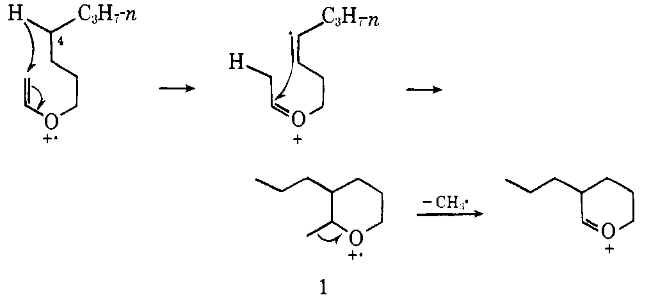


II

Ion	1-d_2 (IIa)	2-d_2 (IIb)	3-d_2 (IIc)	4-d_2 (IId)	5-d_2 (IIe)	6-d_2 (IIf)	7-d_3 (IIg)
M − CH_3	100	100	98	19.2	96	98	100
M − CH_2D			2	80.8	4	2	

[a] Only minor changes were noted at low voltage (nominal 15 eV).
[b] All values are per cent.

Scheme IV



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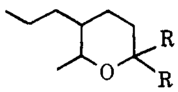
As in the case of the lower homolog I, this scheme was validated by a significant M − 15 peak in the mass spectrum (Figure 6) of the proposed intermediate 2-methyl-3-*n*-propyltetrahydropyran (IX).[9] The difference in mass spectral behavior between I and II is clearly associated with the absence of a more reactive secondary hydrogen atom at C-4 of the *n*-butyl chain of I.[10]



IXa, R = H, *cis*-2,3
IXb, R = H, *trans*-2,3
IXc, R = D, *trans*-2,3

M − 46 Peaks. Triple Hydrogen Transfer. In the mass spectral fragmentation of alkyl vinyl ethers (*e.g.*, II) with an alkyl chain of greater than five carbons, the elements of ethanol were lost from the molecular ion (see Table VII).[11] As mentioned above, this fragmentation is a primary process, and the hypothetical sequence M → M − C_2H_4O → M − C_2H_6O or M → M − CH_3 → M − C_2H_6O was not detected by scanning in the metastable mode (see Table VI).[11] Since deuterium labeling demonstrated that the vinyl group was lost in the fragmentation, it followed that three hydrogen atoms had to migrate from the alkyl chain. Such a unidirectional triple hydrogen transfer is virtually unique and has so far been encountered in only one other instance.[12]

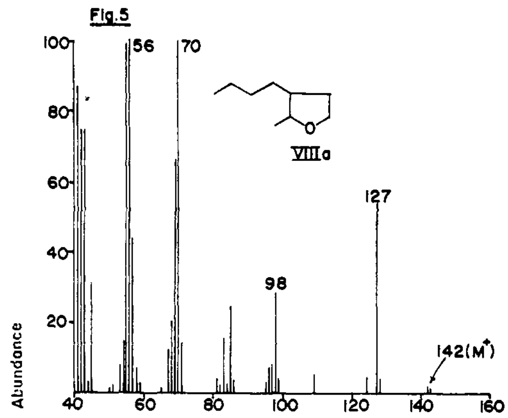
With *n*-heptyl vinyl ether (II) (Table III), the triggering reaction is envisioned as the hydrogen transfer from C-4 (Scheme IV) with concomitant cyclization to yield ionized 2-methyl-3-*n*-propyltetrahydropyran (**1**). As outlined in Scheme V, hydrogen transfer from C-5 to C-1′ then yields ionized ethyl 4-*n*-heptenyl ether (**2**), and subsequent hydrogen transfer to oxygen from C-3 or C-6 (minor) accompanied by cleavage yields ethanol and radical ion d or e, respectively. Alternatively, Scheme VI might be operative in the generation of d through a hydrogen transfer from C-3 to C-1′ in **1** involving a favorable six-membered transition state.

Table III. Origin of Hydrogen Transfer in M − C_2H_6O Fragment in *n*-Heptyl Vinyl Ether (II) at 70 eV[a,b]

II

Ion	1-d_2 (IIa)	2-d_2 (IIb)	3-d_2 (IIc)	4-d_2 (IId)	5-d_2 (IIe)	6-d_2 (IIf)	7-d_3 (IIg)
M − C_2H_6O	99	96	32	47	28	61	97
M − C_2H_5OD	1	4	63	53	62	37	1
M − $C_2H_4OD_2$			5		11	2	1

[a] Only minor changes were noted at low voltage (nominal 15 eV). [b] All values are per cent.



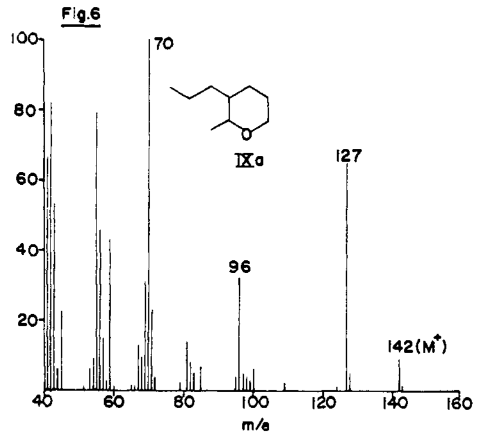
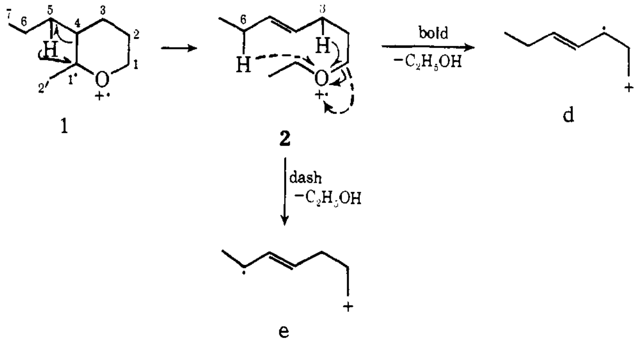


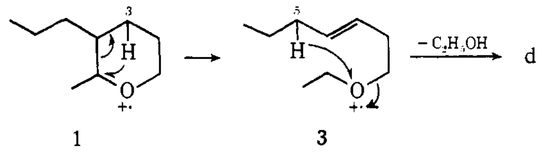
Figure 5. Mass spectrum (70-eV) of *cis*-2-methyl-3-*n*-butyltetrahydrofuran (VIIIa).

Figure 6. Mass spectrum (70-eV) of *cis*-2-methyl-3-*n*-propyltetrahydropyran (IXa).

Scheme V

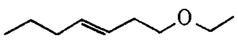


Scheme VI



Mass spectra of the proposed intermediate 2-methyl-3-*n*-propyltetrahydropyran (IX) (Figure 6) displayed a pattern about the C-7 hydrocarbon region very similar to that (Figures 3 and 4) of II. Furthermore, the mass spectra of the specially synthesized ethyl *cis*-4-*n*-heptenyl ether (X) and ethyl *trans*-3-*n*-heptenyl ether (XI) exhibited an M − 46 peak corresponding to loss of ethanol from the molecular ion.

X



XI

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(9) See also H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 253.

(10) C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, **87**, 5747 (1965).

(11) This table is included in Part B; see footnote 15.

(12) (a) S. Meyerson, I. Puskas, and E. K. Fields, *Chem. Ind. (London)*, 1845 (1968); (b) J. Cable and C. Djerassi, *J. Amer. Chem. Soc.*, **93**, 3905 (1971).

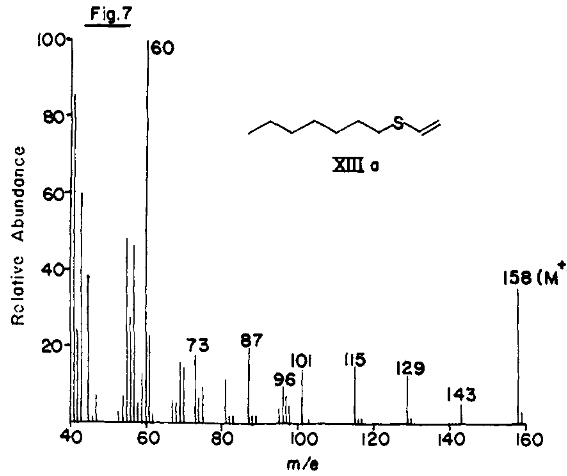
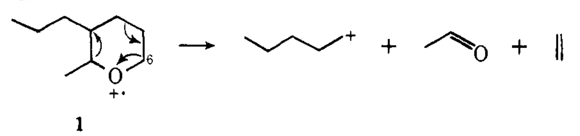


Figure 7. Mass spectrum (70-eV) of *n*-heptyl thiovinyl ether (XIIIa).

***m/e* 70 in *n*-Heptyl Vinyl Ether (II).** This peak was the result of a primary fragmentation process, but it also arose by a secondary fragmentation of an *m/e* 98 precursor. Because of satellite peaks which were shifted by deuterium labeling, precise identification of this peak was not possible. However, in the mass spectra of the *1-d*$_2$ (IIa) and *2-d*$_2$ (IIb) analogs, the highest peak in the satellite group was at *m/e* 70, whereas with the other labeled analogs (IIc–g) the highest ones were at *m/e* 71, 72, and 73. Also, in the spectrum of *trans*-2-methyl-3-*n*-propyltetrahydropyran-*6,6-d*$_2$ (IXc), no deuterium was included in the ion of mass 70. It is proposed that the *m/e* 70 peak corresponds to ionized pentene produced as outlined in Scheme VII.

Scheme VII



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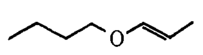
***m/e* 44.** From the pertinent isotopic labeling results for *n*-butyl vinyl ether (I) summarized in Table IV, it can be concluded that a completely nonspecific hydrogen transfer operated in the formation of the ion of mass 44. In contrast to earlier assumptions,[6,8] hydrogen abstraction from C-2 was not significantly favored over that from other positions; it seems likely, therefore, that the mass 44 ion should be depicted as ionized vinyl alcohol (b) rather than ionized acetaldehyde (a) (Scheme I). The generation of ionized acetaldehyde requires hydrogen migration to C-2′, and hydrogen of C-2 would be expected to be predominantly involved in such a process.

Table IV. Hydrogen Transfer in *m/e* 44 and M − 44 Ions of *n*-Butyl Vinyl Ether (I) at 70 eV[a,b]

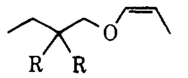
Ion	*1-d*$_2$ (Ia)	*2-d*$_2$ (Ib)	*3-d*$_2$ (Ic)	*4-d*$_3$ (Id)
m/e 44 (C_2H_4O)	83.2	74.7	78.5	67.8
m/e 45 (C_2H_3DO)[c]	16.8	25.3	21.5	32.2
M − C_2H_4O	89.6	72	58.5	91.8
M − C_2H_3DO	10.4	28	41.2	8.2

[a] Only minor changes were noted at low voltage (nominal 15 eV). [b] All values are per cent. [c] Statistically random distribution would be 22.2% for d_2 and 33.3% for d_3 analogs.

In the 70- and 12-eV mass spectra of *n*-butyl *cis*- and *trans*-propenyl ether (XIIb, XIIa) strong peaks were



XIIa

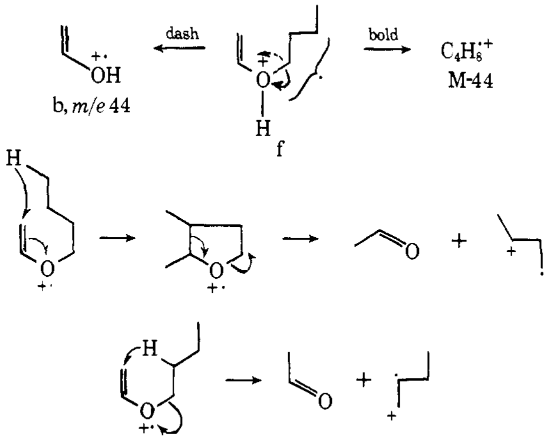


XIIb, R = H
XIIc, R = D

observed at *m/e* 58 ($CH_3CH{=}CHOH\cdot^+$). With *n*-butyl-*2,2-d*$_2$ *cis*-propenyl ether (XIIc), hydrogen transfer from C-2 was not selective in yielding *m/e* 58; only 24.2% D was included in *m/e* 58, whereas the value for completely random extraction out of nine *n*-butyl hydrogens is 22.2%. Hence, here also virtually complete randomization occurred.

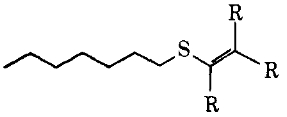
M − 44 Peaks. Since the second and fourth rows of Table IV are not identical, the M − 44 ion in the mass spectrum of *n*-butyl vinyl ether (I) did not result solely from the partitioning of a common intermediate radical ion[8] such as f between *m/e* 44 and M − 44 (Scheme VIII). Other pathways (see Scheme VIII) also must have generated M − 44, most likely as the result of initial hydrogen transfer to C-2′.

Scheme VIII



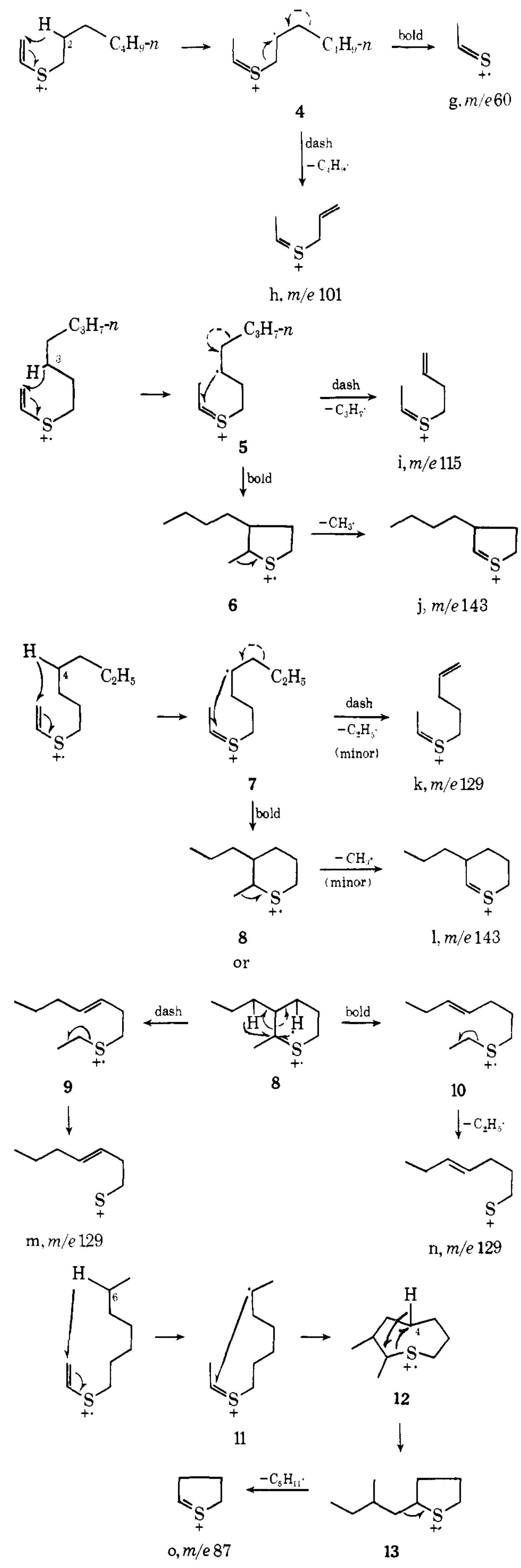
Alkyl Thiovinyl Ethers. The mass spectra of alkyl thiovinyl ethers are characterized by (1) ions resulting from the loss of alkyl radicals, (2) hydrocarbon ions, and (3) a strong *m/e* 60 peak.

Loss of Alkyl Radicals. The 70-eV mass spectra of *n*-alkyl thiovinyl ethers *n*-$C_nH_{2n+1}SCH{=}CH_2$ (n = 4–8) displayed significant M − C_mH_{2m+1} (m = 1, 2, . . ., n) ions. Scanning in the metastable mode (Table VIII)[11] with *n*-heptyl thiovinyl ether (XIIIa) (Figure 7) detected metastable transitions from the molecular ion for peaks corresponding to the loss of methyl, ethyl, propyl, butyl, and hexyl. Furthermore, for *n*-heptyl thiovinyl ether (XIIIa), with the vinyl labeled analog XIIIb, it was shown that some of the eliminated alkyl groups contained a part of, or the entire vinyl group, and some contained no part. Eliminated methyl con-



XIIIa, R = H
XIIIb, R = D

Scheme IX



tained $=CH_2$; ethyl, 80%-$CH=CH_2$; propyl, no vinyl part; butyl, 40% -$CH=CH_2$; pentyl, -$CH=CH_2$; and hexyl and heptyl, no vinyl part. Therefore, the M − C_mH_{2m+1} peaks were not the result of simple carbon–carbon bond cleavages. Deuterium labeling of *n*-heptyl thiovinyl ether (XIII), summarized in Table V, elucidated the mechanistic pathways outlined in Scheme IX. The loss of methyl to give M − 15 involved the methylene group and one hydrogen atom from the *n*-heptyl chain. The loss of ethyl yielding M − 29 was more favorable than loss of methyl, and the triggering reaction is visualized as a hydrogen transfer from C-4 through an eight-membered transition state, M → **7**. The proposed mechanism embodies a sequence analogous to that for the triple hydrogen transfer with alkyl vinyl ethers, M → **7** → **8** → **9** or **10**. The paths from **9** and **10** to m and n, respectively, are supported by the known[13] cleavage of the carbon–sulfur bond in mass spectral fragmentation of thioethers.

Terminal alkyl groups were lost to different extents: almost no methyl loss; small ethyl (k) and pentyl loss; significant propyl (i) and butyl (h) loss. The peak at *m/e* 87 is very interesting and is proposed to be ion o generated as formulated.

Hydrocarbon Ion Peaks. With alkyl thiovinyl ethers n-$C_nH_{2n+1}SCH=CH_2$, the butyl (XIV) and pentyl (XV) analogs displayed the highest C_n hydrocarbon peak at C_nH_{2n}, and the hexyl (XVI), heptyl (XIII), and octyl (XVII) homologs at C_nH_{2n-2} (M − C_2H_6S) (Table IX).[11] For *n*-heptyl thiovinyl ether (XIIIa), with the vinyl-labeled analog XIIIb, it was shown that the C_7 hydrocarbon ion group did not contain the vinyl group. Furthermore, for *n*-heptyl thiovinyl ether (XIII) the highest peak among the C_7 hydrocarbon group was *m/e* 98 for *1-d*$_2$ (XIIIc), *2-d*$_2$ (XIIId), and *6-d*$_2$ (XIIIh); *m/e* 97 for *3-d*$_2$ (XIIIe), *4-d*$_2$ (XIIIf), and *5-d*$_2$ (XIIIg); and *m/e* 99 for *7-d*$_3$ (XIIIi). Therefore, three hydrogens were extracted from C-3, C-4, and C-5 and lost with the vinyl group. These facts suggest the operation of a triple hydrogen transfer resulting in the loss of thioethanol analogous to the triple hydrogen transfer with alkyl vinyl ethers resulting in the loss of ethanol. Other lower hydrocarbon peaks were depressed in low voltage spectra.

R—S—CH=CH$_2$
XIV, R = n-C_4H_9 XVI, R = n-C_6H_{13}
XV, R = n-C_5H_{11} XVII, R = n-C_8H_{17}

***m/e* 60 and 61 Peaks.** In contrast to the behavior of alkyl vinyl ethers, site specificity of hydrogen transfer was observed in the formation of the mass 60 ion, which corresponds to *m/e* 44 for the oxygen analogs. Hydrogen migrated from C-2 to a significantly higher extent (49%) than from the other positions although a contribution from C-3 (14%) was also detected (see Table X).[11] These facts are intriguing because alkyl vinyl ethers, alkyl phenyl ethers,[14] and alkyl thiophenyl ethers[14] exhibit nonspecific rearrangements. The *m/e* 60 peak may be produced through three pathways but mainly through the first two (Scheme X).

The *m/e* 61 peak originates from double hydrogen migration from C-2 and C-3 (see Table X)[11] followed by cleavage. Among possible mechanistic pathways

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(13) S. D. Sample and C. Djerassi, *J. Amer. Chem. Soc.*, 88, 1937 (1966).

(14) J. K. MacLeod and C. Djerassi, *ibid.*, 88, 1840 (1966).

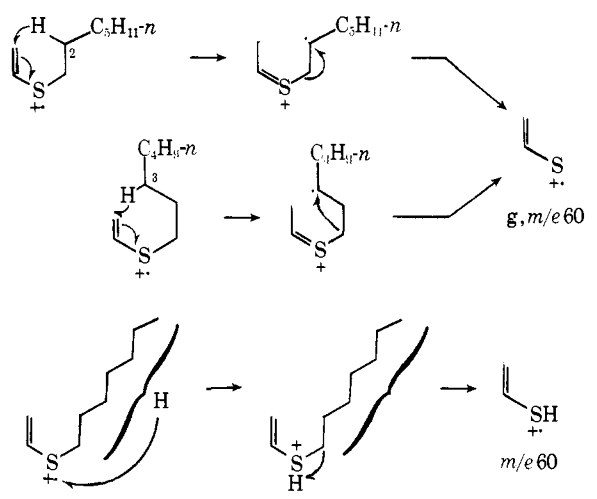
Table V. M − C_mH_{2m+1} Loss in *n*-Heptyl Thiovinyl Ether (XIII) at 70 eV[a,b]

XIII

Ion	*1*-d_2 (XIIIc)	*2*-d_2 (XIIId)	*3*-d_2 (XIIIe)	*4*-d_2 (XIIIf)	*5*-d_2 (XIIIg)	*6*-d_2 (XIIIh)	*7*-d_3 (XIIIi)
M − CH_3	100	100	40	81	100	100	100
M − CH_2D			60	19			
M − C_2H_5	100	100	80	35	62	56	68
M − C_2H_4D			20	65	38	27	16
M − $C_2H_3D_2$						17	0
M − $C_2H_2D_3$							16
M − C_3H_7	100	100	100	100	7	7	0
M − C_3H_6D					16	7	5
M − $C_3H_5D_2$					77	86	10
M − $C_3H_4D_3$							85
M − C_4H_9	100	100	85	28	13	5	5
M − C_4H_8D			15	17	20	16	5
M − $C_4H_7D_2$				55	67	79	10
M − $C_4H_6D_3$							80
M − C_5H_{11}	100	100	70	10	14	5	0
M − $C_5H_{10}D$			20	65	21	15	11
M − $C_5H_9D_2$			10	25	65	80	10
M − $C_5H_8D_3$							79

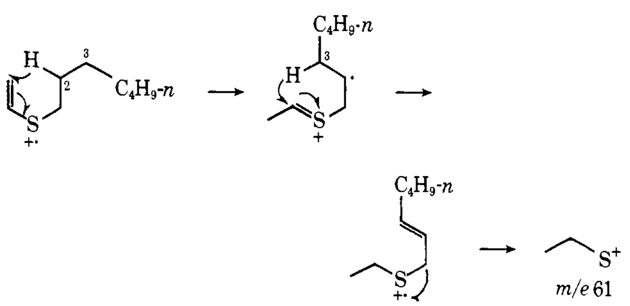
[a] Only minor changes were noted at low voltage (nominal 15 eV). [b] All values are per cent.

Scheme X



the following is attractive (Scheme XI). The first two steps involve favored six-membered transition states, and in the second the hydrogen transferred is also activated by the adjacent radical site. The well-known[13] carbon–sulfur fission, which has no significant counterpart among ethers,[10] is particularly favored in the present instance because of allylic activation.

Scheme XI



In summary, the mass spectrometry of alkyl vinyl ethers and of alkyl thiovinyl ethers is characterized by interesting mechanistic pathways involving unique hydrogen transfers and cyclizations of intermediate radical ions. The observed differences between the two classes of compounds are, in part, associated with the lability of the carbon–sulfur bond in thioethers.[13,15]

Experimental Section[16]

n-Butyl Vinyl Ether (I).[17] To a solution of 7.0 ml (20 g, 74 mmol) of phosphorus tribromide in 200 ml of ether at 0° was added dropwise 11.8 g (92 mmol) of 2-*n*-butoxyethanol (Eastman). The reaction mixture was refluxed for 2 hr and poured onto ice. The ether layer was washed twice with water, dried over magnesium sulfate, and rotary-evaporated to yield 15.2 g (91%) of 2-*n*-butoxyethyl bromide. Unless noted otherwise, this general method was employed throughout for conversion of alcohols to the corresponding bromides. A solution of *ca.* 300 mg of the above bromide in 2 ml of benzene was distilled from 500 mg of sodium hydroxide. The distillate was dried and preparative glc yielded *n*-butyl vinyl ether (I).

n-Butyl-*1,1*-d_2 Vinyl **Ether** (Ia). The reduction of methyl butyrate with lithium aluminum deuteride in ether yielded *n*-butyl-*1,1*-d_2 alcohol. To a suspension of 100 mg of sodium hydride in THF was added 300 mg (3.94 mmol) of this alcohol, followed by 668 mg (3.94 mmol) of ethyl bromoacetate. The mixture was refluxed for 3 hr and after work-up yielded crude ethyl *n*-butoxy-*1,1*-d_2-acetate. This material was reduced with lithium

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(15) As an experiment, this paper has been divided into Parts A and B. Part A contains the salient features of the complete paper and consists of the above and the Experimental Section. Part B contains further discussion and will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-3107. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

(16) Mass spectra were obtained by Mr. R. G. Ross and Mr. R. Conover on Atlas CH-4 and AEI MS-9 mass spectrometers. Most samples were introduced by direct insertion and the remainder by the heated inlet system. Nuclear magnetic resonance (nmr) spectra were measured with Varian HA-100, A-60, and T-60 instruments in the indicated solvent with tetramethylsilane (TMS) as internal standard. Infrared (ir) spectra were recorded on a Perkin-Elmer Model 700 spectrophotometer. Elemental analyses were performed by Messrs. E. Meier and J. Consul. The lithium aluminum deuteride and deuterium oxide employed contained >98% D, and, in general, deuterated compounds contained >95% D as indicated. Where necessary, mass spectra of these compounds were corrected for incomplete deuteration.

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aluminum hydride in ether, and isolation by preparative glc gave 2-(*n*-butoxy-*1,1*-d_2)ethanol, which was converted to Ia using procedures given above for I.

***n*-Butyl-*2,2*-d_2 Vinyl Ether (Ib).** The reduction of methyl propionate with lithium aluminum deuteride in ether yielded *n*-propyl-*1,1*-d_2 alcohol. This material was converted to *n*-propyl-*1,1*-d_2 bromide, and carbonation of the corresponding Grignard reagent in ether with carbon dioxide yielded *n*-butyric-*2,2*-d_2 acid. Reduction of *n*-butyric-*2,2*-d_2 acid with lithium aluminum hydride in ether yielded *n*-butyl-*2,2*-d_2 alcohol, which was converted to Ib using procedures given above for Ia.

***n*-Butyl-*3,3*-d_2 Vinyl Ether (Ic).** The reduction of *n*-pentyl acetate with lithium aluminum deuteride in ether yielded a mixture of ethyl-*1,1*-d_2 alcohol and *n*-pentyl alcohol. Treatment of this mixture with a 10% (w/v) solution of phosphorus tribromide in ether at 25° gave after work-up an ether solution of ethyl-*1,1*-d_2 bromide and *n*-pentyl bromide. Ether and ethyl-*1,1*-d_2 bromide were distilled and added to 400 mg of magnesium. Grignard formation was induced with the addition of a few drops of methyl iodide, and after it was complete, excess ethylene oxide was bubbled through the mixture. The reaction mixture was hydrolyzed with saturated aqueous ammonium chloride and filtered. The layers were separated, and the aqueous layer was continuously extracted with benzene. The combined benzene and ether solutions were dried and yielded crude 2-*n*-butoxy-*3,3*-d_2-ethanol, which was purified by preparative glc and converted to *n*-butyl-*3,3*-d_2 vinyl ether (Ic) using procedures above for I.

***n*-Butyl-*4,4,4*-d_3 Vinyl Ether (Id).** In standard fashion 6.4 g (0.10 mol) of acetic-d_4 acid was converted to acetyl-d_3 chloride with phosphorus tribromide. Treatment of this material with *n*-pentyl alcohol in benzene gave *n*-pentyl acetate-d_3, which was converted to *n*-butyl-*4,4,4*-d_3 vinyl ether (Id) using the procedures outlined above for Ic, except that lithium aluminum hydride instead of deuteride was employed.

***n*-Butyl Vinyl-*2′,2′*-d_2 Ether (Ie).** The treatment of *n*-butoxyacetic acid[18] with thionyl chloride followed by methanol yielded methyl *n*-butoxyacetate. Reduction of 1.5 g (0.01 mol) of methyl *n*-butoxyacetate with lithium aluminum deuteride in ether yielded 2-*n*-butoxyethanol-*1,1*-d_2. From a mixture of 500 mg of this material and an excess of *N,N′*-dicyclohexylcarbodiimide, *n*-butyl vinyl-*2′,2′*-d_2 ether (If) was distilled (oil bath, 150°). The crude product was diluted with ether, dried over magnesium sulfate, and isolated by preparative glc.

***n*-Pentyl Vinyl Ether (III).[19]** From *n*-pentyl alcohol, *n*-pentyl bromide was prepared, which was converted to 2-*n*-pentoxyethanol with sodium ethylene glycoxide in benzene. Conversion of 2-*n*-pentoxyethanol to *n*-pentyl vinyl ether (III) followed the analogous procedures employed for I.

***n*-Hexyl,[20] *n*-Heptyl,[21] *n*-Octyl,[17] and *n*-Nonyl[20] Vinyl Ether (IV, II, V, VI).** These compounds were prepared simultaneously in one reaction as follows. In a solution of 6.2 g (0.10 mol) of ethylene glycol in 150 ml of benzene was dissolved 2.3 g (0.10 g-atom) of sodium. Then 0.025 mol each of *n*-hexyl, *n*-heptyl, *n*-octyl, and *n*-nonyl bromide was added to the well-stirred suspension, and the mixture was refluxed overnight and filtered. Dilution of the filtrate to 200 ml with benzene was followed by the addition of 7.0 ml (20 g, 74 mmol) of phosphorus tribromide during 1 hr. After standing overnight, the reaction mixture was poured onto ice, and the benzene solution was separated, washed with aqueous sodium bicarbonate, and dried. Rotary evaporation of benzene yielded a crude mixture of the 2-*n*-alkoxyethyl bromides. To a suspension of ~500 mg of potasssium *tert*-butoxide in THF was added 2.0 g of the above bromide mixture, and the reaction mixture was refluxed for 2 hr, filtered, and concentrated. The retention times (R_T) of *n*-pentyl (III) and *n*-decyl vinyl ether (VII) were determined on glc, and using a linear relationship between the length of the *n*-alkyl chain and log R_T,[22] *n*-hexyl (IV), *n*-heptyl (II), *n*-octyl (V), and *n*-nonyl vinyl ether (VI) were identified by interpolation and preparatively collected and gave consistent mass spectra (M^+).

Deuterium-Labeled *n*-Heptyl Vinyl Ethers (IIa–g). The same procedure was employed for preparation of IIa–g. A mixture of 25 mg of deuterium-labeled *n*-heptyl alcohol, 10 mg of mercuric acetate, and 30 mg of oxalic acid in 3.0 ml of ethyl vinyl ether (MCB) was stirred at 25° for 1 hr. Volatile material was then flash distilled at 25 mm into a receiver at −78°, and the *n*-heptyl vinyl ether was isolated by preparative glc.

***n*-Heptyl-*1,1*-d_2 Alcohol.** Reduction of methyl *n*-heptanoate with lithium aluminum deuteride in ether gave *n*-heptyl-*1,1*-d_2 alcohol.

***n*-Heptyl-*2,2*-d_2 Alcohol.** To a solution of 10.1 g (50 mmol) of dimethyl *n*-pentylmalonate[23] in 250 ml of anhydrous ether was added 2.8 g (0.12 g-atom) of sodium, and the mixture was refluxed for 1 hr, followed by the addition of 0.92 g (20 mmol) of absolute ethanol. The mixture was refluxed for 72 hr, and 50 ml of deuterium oxide was added to the mixture at 0°. After distillation of volatile material, the residue was dried under vacuum, and an additional 50 ml of deuterium oxide was added. Then 19 g (0.14 mol) of phosphorus trichloride was added cautiously to the mixture at 0° during 1 hr, and it was refluxed overnight. The resulting *n*-heptanoic-*2,2*-d_2 acid was extracted with ether and reduction with lithium aluminum hydride yielded *n*-heptyl-*2,2*-d_2 alcohol.

***n*-Heptyl-*3,3*-d_2 Alcohol.** Reduction of methyl valerate with lithium aluminum deuteride in ether yielded *n*-pentyl-*1,1*-d_2 alcohol, which was converted to *n*-pentyl-*1,1*-d_2 bromide. In standard fashion, alkylation of sodio diethyl malonate with *n*-pentyl-*1,1*-d_2 bromide gave diethyl *n*-pentyl-*1,1*-d_2-malonate, which was hydrolyzed with aqueous 8% sodium hydroxide. Without isolation, sulfuric acid catalyzed decarboxylation of the resulting *n*-pentyl-*1,1*-d_2-malonic acid yielded *n*-heptanoic-*3,3*-d_2 acid. Reduction of this material with lithium aluminum hydride gave *n*-heptyl-*3,3*-d_2 alcohol.

***n*-Heptyl-*4,4*-d_2 Alcohol.** Using procedures employed for *n*-heptyl-*2,2*-d_2 alcohol, diethyl *n*-propylmalonate[24] yielded *n*-pentyl-*2,2*-d_2 alcohol, which was converted to *n*-pentyl-*2,2*-d_2 bromide. This material gave *n*-heptyl-*4,4*-d_2 alcohol with the procedures for *n*-heptyl-*3,3*-d_2 alcohol.

***n*-Heptyl-*5,5*-d_2 Alcohol.** The lithium aluminum deuteride reduction of methyl propionate yielded *n*-propyl-*1,1*-d_2 alcohol, which was converted to *n*-propyl-*1,1*-d_2 bromide. Alkylation of sodio diethyl malonate with *n*-propyl-*1,1*-d_2 bromide yielded diethyl-*n*-propyl-*1,1*-d_2-malonate. Hydrolysis and decarboxylation as above for *n*-heptyl-*3,3*-d_2 alcohol gave *n*-pentyl-*3,3*-d_2 alcohol. This alcohol was converted to *n*-pentyl-*3,3*-d_2 bromide and then to *n*-heptyl-*5,5*-d_2 alcohol using the procedures employed for *n*-heptyl-*3,3*-d_2 alcohol.

***n*-Heptyl-*6,6*-d_2 Alcohol.** Using the procedure employed for *n*-heptyl-*2,2*-d_2 alcohol, dimetnyl methylmalonate yielded *n*-propyl-*2,2*-d_2 alcohol, which was converted to *n*-propyl-*2,2*-d_2 bromide. Two alkylations with sodio diethyl malonate as above effected the homologation resulting in *n*-heptyl-*6,6*-d_2 alcohol.

***n*-Heptyl-*7,7,7*-d_3 Alcohol.** Carbonation of the Grignard reagent of *n*-hexyl-*6,6,6*-d_3 bromide[25] with carbon dioxide yielded *n*-heptanoic-*7,7,7*-d_3 acid. Reduction of this material with lithium aluminum hydride gave *n*-heptyl-*7,7,7*-d_3 alcohol.

Isobutyl Vinyl Ether (XVIII).[21] Using a procedure analogous to that employed above for II and IV–VI, isobutyl bromide and monosodium ethylene glycoxide in benzene yielded 2-isobutoxyethanol. Conversion of this material to isobutyl vinyl ether (XVIII) through the corresponding bromide followed the procedures for I.

2-Methylbutyl[26] and Isopentyl[21] Vinyl Ether (XIX, XX). The corresponding bromides of 2-methylbutyl alcohol and isopentyl alcohol were prepared and converted to 2-methylbutyl vinyl ether (XIX) and isopentyl vinyl ether (XX), respectively, using the procedures employed for XVIII.

Ethyl *trans*-3-Heptenyl Ether (XI).[27] To a mixture of 409 mg (3.58 mmol) of *trans*-3-hepten-1-ol (Aldrich), 2 ml of benzene, and 2 drops of absolute ethanol was added 140 mg (3.58 mg-atoms) of potassium. The mixture was refluxed under nitrogen until all potassium dissolved, and then 4.1 g (38 mmol) of ethyl bromide was added. The mixture was refluxed for 5 hr and added to 3 ml of water. The mixture was extracted with ether three times, and the

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combined extracts were dried over sodium sulfate and rotary-evaporated to yield crude ethyl *trans*-3-heptenyl ether. Preparative glc (10 ft × 0.25 in. aluminum column packed with 15% Carbowax 20M on 80–100 mesh acid-washed Chromosorb W) gave pure XI.

The ir spectrum (neat) of XI displayed intense bands at 1055 (COC) and 965 cm^{-1} (C=C).

Ethyl *cis*-4-Heptenyl Ether (X). Using the procedure of Wood and Horning[28] *cis*-3-hexen-1-ol (Aldrich) was converted to 1-bromo-3-hexene, bp 49–50° (20 mm). In standard fashion the Grignard reagent of 4.04 g (24.8 mmol) of 1-bromo-3-hexene was prepared in ether. Carbon dioxide (bone dry) was vigorously bubbled through the Grignard solution at −78° for 10 min and then until the reaction mixture reached 25°. The mixture was hydrolyzed with 10% sulfuric acid and extracted four times with ether. The combined ether extracts were combined and extracted three times with aqueous 5% sodium bicarbonate. Then the combined aqueous extracts were acidified with dilute sulfuric acid and extracted with ether. The extracts were dried over sodium sulfate and yielded 1.37 g (44%) of *cis*-4-heptenoic acid. Reduction of *cis*-4-heptenoic acid in ether with lithium aluminum hydride gave *cis*-4-hepten-1-ol, and using the procedure for XI, this material was converted to ethyl *cis*-4-heptenyl ether (X). Preparative glc as for XI yielded X, which was further purified by glc (10 ft × 0.25 in. aluminum column packed with 10% SE-30 on 80–100 mesh acid-washed Chromosorb W) to give an analytical sample.

Anal. Calcd for $C_9H_{18}O$: C, 75.99; H, 12.76. Found: C, 76.21; H, 12.58.

***n*-Butyl *cis*- and *trans*-Propenyl Ether[29] (XIIb, XIIa).** Bromomethyl *n*-butyl ether[30] was converted to *n*-butyl propenyl ether (XII) *via* the Wittig reaction.[31] Preparative glc separated *n*-butyl *cis*-propenyl ether (XIIb) and *n*-butyl *trans*-propenyl ether (XIIa).

***n*-Butyl-*2,2-d*$_2$ *cis*- and *trans*-Propenyl Ether (XIIc, XIId).** Using the procedure for *n*-heptyl-*2,2-d*$_2$ alcohol, diethyl ethylmalonate yielded *n*-butyl-*2,2-d*$_2$ alcohol, which was converted to 1-chloropropyl *n*-butyl-*2,2-d*$_2$ ether with hydrogen chloride and propionaldehyde.[30] A solution of 0.50 g (3.3 mmol) of 1,5-diazabicyclo[5.4.0]-undec-5-ene (Aldrich) in 5 ml of ether was added during 10 min to 0.50 g (3.3 mmol) of 1-chloropropyl *n*-butyl-*2,2-d*$_2$ ether in 10 ml of ether. The reaction mixture was stirred for 30 min and filtered to remove the resultant white precipitate. Preparative glc yielded *n*-butyl-*2,2-d*$_2$ *cis*-propenyl ether (XIIc), but the trans isomer XIId was contaminated by an impurity of molecular weight (M$^+$) 98, probably 2-methyl-2-penten-1-one (aldol condensation product of propionaldehyde).

***cis*- and *trans*-2-Methyl-3-*n*-butyltetrahydrofuran (VIIIa, VIIIb).** To a suspension of 2.5 g (0.10 ml) of sodium hydride in 220 ml of THF was added 12.8 g (0.10 mol) of 2-acetylbutyrolactone (Aldrich). Then 15.5 g (0.12 mol) of *n*-butyl bromide was added, and the mixture was refluxed overnight. After the addition of saturated aqueous sodium sulfate, THF was rotary-evaporated, and the mixture was extracted with ether. The combined extracts were dried over sodium sulfate and rotary-evaporated to leave a residue which was fractionally distilled to give 11.2 g (61%) of 2-acetyl-2-*n*-butylbutyrolactone, bp 78–84° (2 mm). A mixture of 9.2 g of this material and 20 ml of concentrated hydrochloric acid was refluxed overnight and extracted with ether. The combined extracts were washed with water, dried, and yielded 3-(2-chloroethyl)-2-heptanone. Reduction of this material in absolute ethanol with sodium borohydride yielded 3-(2-chloroethyl)-2-heptanol, which was cyclized to *cis*- and *trans*-2-methyl-3-*n*-butyltetrahydrofuran (VIIIa and VIIIb) in a suspension of sodium hydride in refluxing THF. Preparative glc separated VIIIa and VIIIb.

The longer retention time component was assigned as the trans isomer VIIIb. The nmr spectrum (carbon tetrachloride) of VIIIb displayed a complex multiplet from δ 3.4 to 4.1 (CHO and CH_2O, 3 H), and a complex multiplet from δ 0.7 to 2.3 (15 H) including a doublet at δ 0.97, $J = 7$ Hz (2-CH_3), and a broad singlet at δ 1.2. Irradiation of the 2-methyl doublet yielded $J_{H\text{-}2,H\text{-}3} = 11$ Hz, which corresponds to axial–axial coupling. The ir spectrum (neat) of VIIIb exhibited an intense band at 1050 cm^{-1} (C–O).

Anal. Calcd for $C_9H_{18}O$: mol wt, 142. Found: (M$^+$), 142.

The cis isomer VIIIa gave a mass spectrum identical with that of VIIIb.

***cis*- and *trans*-2-Methyl-3-*n*-propyltetrahydropyran (IXa, IXb).[32]** A mixture of 2.05 g (13.4 mmol) of 3-acetylenanthonitrile[33] and 24 ml of 6 *N* hydrochloric acid was refluxed for 31 hr, diluted with water, and extracted with ether. The combined ether extracts were dried over sodium sulfate and yielded 2.07 g (90%) of 4-acetylenanthic acid, which was reduced following the procedure of House, *et al.*[34] To a suspension of 280 mg (7.4 mmol) of sodium borohydride in 2.0 ml of 0.2 *N* sodium hydroxide solution at 0° was added a solution of 2.07 g (12.0 mmol) of 4-acetylenanthic acid and 1.0 g of sodium hydroxide in 15 ml of water. The reaction mixture was stirred at 25° for 30 hr and cooled to 0°; 10 ml of 6 *N* hydrochloric acid was added. The mixture was stirred at 25° for 48 hr and extracted with ether. The combined extracts were dried over sodium sulfate and yielded 1.82 g (97%) of crude *cis*- and *trans*-δ-caprolactone. The reduction of the mixture of *cis*- and *trans*-δ-caprolactone to *cis*- and *trans*-2-methyl-3-*n*-propyltetrahydropyran (IXa and IXb) employed sodium borohydride–boron trifluoride etherate in THF.[35] The cis and trans isomers, IXa and IXb, respectively, were separated by preparative glc and yielded almost identical mass spectra.

The longer retention time component was assigned as the trans isomer IXb. The nmr spectrum (carbon tetrachloride) of IXb displayed a complex multiplet from δ 2.7 to 4.1 (CHO and CH_2O, 3 H) and another complex multiplet from δ 0.7 to 2.1 (15 H) including a doublet at δ 1.01, $J = 7$ Hz (2-CH_3). Irradiation of the 2-methyl doublet yielded $J_{H\text{-}2,H\text{-}3} = 11$ Hz, which corresponds to axial-axial coupling. The ir spectrum (neat) of IXb exhibited an intense band at 1100 cm^{-1} (C–O).

The nmr spectrum (carbon tetrachloride) of the cis isomer IXa displayed a complex multiplet from δ 2.7–4.1 (CHO and CH_2O, 3 H) and a complex multiplet from δ 0.7–2.1 (15 H) including a doublet at δ 1.10, $J = 7$ Hz (2-CH_3). The ir spectrum (neat) of IXa exhibited an intense band at 1100 cm^{-1} (C–O).

***trans*-2-Methyl-3-*n*-propyltetrahydroyran-*6,6-d*$_2$ (IXc).** The preparation of *trans*-2-methyl-3-*n*-propyltetrahydropyran-*6,6-d*$_2$ (IXc) followed that for IXb above with the substitution of sodium borodeuteride for sodium borohydride.

***n*-Butyl,[17] *n*-Pentyl, *n*-Hexyl,[36] *n*-Heptyl, and *n*-Octyl[17] Thiovinyl Ether (XIV, XV, XVI, XIII, XVII).** These compounds were prepared by the same procedure given for *n*-heptyl thiovinyl ether (XIII). Under nitrogen 1.2 g (52 mg-atoms) of sodium was dissolved in 100 ml of THF containing 0.5 ml of absolute ethanol and 6.0 g (50 mmol) of ethyl 2-mercaptoacetate. Then 8.9 g (50 mmol) of *n*-heptyl bromide was added, and the mixture was refluxed overnight, followed by the addition of 10 ml of water. The THF was rotary-evaporated, and the residue was extracted with ether. The combined extracts were dried over Drierite and yielded ethyl 2-*S*-*n*-heptylmercaptoacetate. This material was reduced with lithium aluminum hydride in ether to 2-*S*-*n*-heptylmercaptoethanol, which was converted to 2-*S*-*n*-heptylmercaptoethyl bromide. To an ether solution of 2-*S*-*n*-heptylmercaptoethyl bromide was added a 4 molar excess of 1,5-diazobicyclo[5.4.0]undec-5-ene. The reaction mixture was stirred overnight at 25°, diluted with ether, extracted with excess aqueous 5% sodium bicarbonate, and dried over sodium sulfate. Rotary evaporation of ether yielded *n*-heptyl thiovinyl ether (XIII) which was purified by preparative glc.

Anal. Calcd for $C_9H_{18}S$ (XIII): mol wt, 158. Found: (M$^+$), 158. Calcd for $C_7H_{14}S$ (XV): mol wt, 130. Found: (M$^+$), 130.

***n*-Pentyl-*2,2-d*$_2$ and *n*-Pentyl-*4,4-d*$_2$ Thiovinyl Ether (XVa, XVb).** These materials were prepared with the *n*-pentyl-*2,2-d*$_2$ alcohol and *n*-pentyl-*4,4-d*$_2$ alcohol following the above described procedures for the unlabeled *n*-alkyl thiovinyl ethers.

Deuterium-Labeled *n*-Heptyl Thiovinyl Ethers: *1,1-d*$_2$ (XIIIa), *2,2-d*$_2$ (XIIIb), *3,3-d*$_2$ (XIIIc), *4,4-d*$_2$ (XIIId), *5,5-d*$_2$ (XIIIe), *6,6-d*$_2$ (XIIIf), *7,7,7-d*$_3$ (XIIIg). These compounds were prepared using the deuterium-labeled *n*-heptyl alcohols described above and the procedure for the unlabeled *n*-alkyl thiovinyl ethers.

***n*-Heptyl Thiovinyl-*1′,2′,2′-d*$_3$ Ether (XIIIh).** The preparation of

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n-heptyl thiovinyl-*1′,2′,2′-d*$_3$ ether (XIIIh) followed that for protio thioether XIII through ethyl 2-*S*-*n*-heptylmercaptoacetate. Two exchanges of the latter material in ethanol-*O-d*[37] containing 0.3 *M* potasium ethoxide at reflux gave ethyl 2-*S*-*n*-heptylmercaptoacetate-*2,2-d*$_2$ which was reduced with lithium aluminum deuteride in ether to yield 2-*S*-*n*-heptylmercaptoethyl-*1,1,2,2-d*$_4$ alcohol. Conversion of 2-*S*-*n*-heptylmercaptoethyl-*1,1,2,2-d*$_4$ alcohol to *n*-heptyl thiovinyl-*1′,2′,2′-d*$_3$ ether (XIIIh) through the corresponding bromide followed the procedures for XIII.

cis- **and** *trans*-**2-Methyl-3-*n*-butyltetrahydrothiophene (XXIa, XXIb).** The preparation of *cis*- and *trans*-2-methyl-3-*n*-butyltetrahydrothiophene (XXIa, XXIb) employed a procedure similar to that of Naylor.[38] Under nitrogen a mixture of 0.80 g of phosphorus pentasulfide, 1.5 g of sand, and 200 mg of a crude mixture of *cis*- and *trans*-2-methyl-3-*n*-butyltetrahydrofuran (VIIIa, VIIIb) was held at 100° for 3.5 hr. The reaction mixture was slurried several times in ether, and the combined extracts were dried over sodium sulfate. Rotary evaporation of ether yielded 309 mg of an oil containing *cis*- and *trans*-2-methyl-3-*n*-butyltetrahydrothiophene (XXIa, XXIb). By glc (10 ft × 0.25 in. aluminum column packed with 10% SE-30 on 80–100 mesh acid-washed Chromosorb W) the ratio of isomers was 4:1, and they were preparatively separated and yielded almost identical mass spectra.

Anal. Calcd for $C_9H_{18}S$: mol wt, 158. Found: (M^+), 158.

The nmr spectrum (deuteriochloroform) of a mixture of XXIa and XXIb displayed a complex series of signals from δ 0.65 to 3.18 with doublets at δ 1.15, J = 7 Hz, and δ 1.30, J = 7 Hz (2-methyl protons).

cis- **and** *trans*-**2-Methyl-3-*n*-propyltetrahydrothiopyran (XXIIa, XXIIb).** The preparation of *cis*- and *trans*-2-methyl-3-*n*-propyltetrahydrothiopyran (XXIIa, XXIIb) from a crude mixture of *cis*- and *trans*-2-methyl-3-*n*-propyltetrahydropyran (IXa, IXb) employed the procedure of Naylor[38] as modified above for XXI. By glc conditions employed for XXI the ratio of isomers in the crude XXII was ~10:1; the major isomer was preparatively collected.

Ethyl *cis*-4-Heptenyl Thioether (XXIIIa). The conversion of *cis*-4-hepten-1-ol, prepared above, to 1-bromo-4-heptene followed the procedure of Wood and Horning.[28] Under nitrogen, 300 mg (7.68 mg-atoms) of potassium was dissolved in a solution of 4.2 g (67.5 mmol) of ethanethiol in 20 ml of anhydrous ether. Then 562 mg (3.18 mmol) of 1-bromo-4-heptene was added, and the mixture was refluxed overnight, added to water, and extracted with ether. The combined extracts were dried over sodium sulfate and yielded crude ethyl *cis*-4-heptenyl thioether. Preparative glc (10 ft × 0.25 in. aluminum column packed with 15% Carbowax 20M on 80–100 mesh acid-washed Chromosorb W) gave pure XXIIIa.

Anal. Calcd for $C_9H_{18}S$: C, 68.28; H, 11.46. Found: C, 68.55; H, 11.42.

The nmr spectra (deuteriochloroform) of XXIIIa displayed a complex multiplet from δ 5.01 to 5.78 (vinyl protons, 1.90); a complex multiplet from δ 0.89 to 2.85 (16.1 H) containing two triplets at δ 0.97, J = 7.0 Hz, and δ 1.12, J = 7.0 Hz (4-heptenyl and ethyl methyl protons, respectively); and a quartet at δ 2.26, J = 7.0 Hz, overlapping with a triplet at δ 2.27, J = 7.0 Hz.

Ethyl-*2-d* *cis*-4-Heptenyl Thioether (XXIIIb). The preparation of ethyl-*2-d* *cis*-4-heptenyl thioether followed the procedure for the protio material XXIIIa through *cis*-4-hepten-1-ol. Using the procedure of Smith and Williams,[39] *cis*-4-hepten-1-ol was converted to *cis*-4-heptenyl tosylate. Under nitrogen 150 mg (6.52 mg-atom) of sodium was dissolved in a solution of 2 ml of absolute ethanol and 10 ml of THF. Then 0.77 g (6.41 mmol) of ethyl 2-mercaptoacetate was added followed by 1.16 g (4.32 mmol) of *cis*-4-heptenyl tosylate. The reaction mixture was refluxed for 2 hr and stirred overnight at 25°, and 10 ml of water was added. The THF was removed by rotary evaporation, and the residue was extracted with ether. The combined extracts were dried over sodium sulfate and yielded 0.784 g of a mixture of 2-*S*-(*cis*-4-heptenyl) mercaptoacetate and ethyl 2-mercaptoacetate. This mixture was reduced with lithium aluminum hydride in ether to give 480 mg of 2-*S*-(*cis*-4-heptenyl)mercaptoethanol, which was converted to 562 mg (86%) of 2-*S*-(*cis*-4-heptenyl)mercaptoethyl bromide. Reduction of this material with lithium aluminum deuteride in ether at reflux yielded ethyl-*2-d* *cis*-4-heptenyl thioether (XXIIIb) which was purified by preparative glc as was XXIIIa.

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(38) R. F. Naylor, *J. Chem. Soc.*, 1106 (1947).

(39) G. A. Smith and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 5254 (1969).

Mass Spectrometry in Structural and Stereochemical Problems. CCXIV.[1] Electron Impact Induced Fragmentation of Simple Acetylenes[2]

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Abstract: The mass spectra of a series of isomeric nonynes and decynes have been intestigated with the aid of deuterium labeling, metastable analysis, and metastable defocusing. Although the spectra indicate retention of identity of the individual alkynes to a large extent under electron bombardment, evidence is presented which is consistent with some triple bond migration prior to the formation of some fragments. Hydrogen scrambling is extensive in the ions which arise by multiple fragmentation pathways. Most of the simple cleavage modes which occur in the straight-chain alkynes are suppressed in their branched-chain isomers, where the McLafferty rearrangement and β-fission processes become dominant.

The use of mass spectrometry as a routine analytical probe for structure determination demands retention of the identity of the molecule under investigation subsequent to electron impact and prior to fragmentation. Although simple olefinic hydrocarbons have been extensively investigated,[5] mechanistic interpretation of decomposition pathways is often seriously complicated by ubiquitous 1,2- and 1,3-hydrogen transfers, and consequent double bond migration, prior to

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(1) For preceding paper see S. Popov, G. Eadon, and C. Djerassi, *J. Org. Chem.*, 37, 155 (1972).

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