# Mass Spectrometry in Structural and Stereochemical Problems. CCXXVIII.[1] Application of Ion Cyclotron Resonance for Differentiation between Tautomers: Vinylthiol and Thioacetaldehyde[2]

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Abstract: The base peak in the mass spectrum of pentyl thiovinyl ether, m/e 60, $C_2H_4S \cdot^+$, arising predominantly *via* hydrogen transfer from position 2 of the pentyl chain with elimination of C_5H_{10}, has two possible structures, the thioacetaldehyde ion b or the vinyl thiol ion c. Utilizing ion cyclotron resonance and pulsed double resonance spectroscopy, the two tautomers are distinguishable on the basis of their ion–molecule reactions. By deuterium labeling the ion–molecule reactions of the $C_2H_4S \cdot^+$ ions formed *via* hydrogen transfer from each carbon are investigated and compared with those found for the $C_2H_4S \cdot^+$ ions of known structure. It is found that when hydrogen is transferred from position 2 the $C_2H_4S \cdot^+$ ion has the thioacetaldehyde structure b while hydrogen transfer from positions 3 and 4 leads to $C_2H_4S \cdot^+$ ions possessing primarily the vinylthiol structure c.

I n a recent publication from this laboratory,[3] it was observed that alkyl vinyl ethers underwent random hydrogen transfer from the alkyl chain with formation of an m/e 44 peak (a) (eq 1). This fragmentation was

$$\xrightarrow{-C_7H_{14}} C_2H_4O \cdot^+ \qquad (1)$$

a, m/e 44
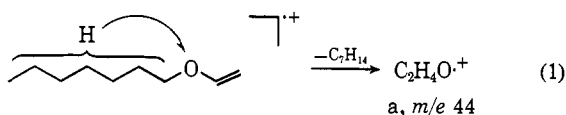
observed to decrease in importance upon lowering the ionizing voltage. Since completely nonspecific hydrogen transfer was observed, it was proposed that a had an ionized vinyl alcohol structure, a suggestion consistent with earlier appearance potential data.[4]

Alkyl thiovinyl ethers were observed[3] to undergo similar hydrogen transfer from the alkyl chain with formation of an analogous peak at m/e 60 (eq 2). In

$$\xrightarrow{-C_7H_{14}} C_2H_4S \cdot^+ \qquad (2)$$
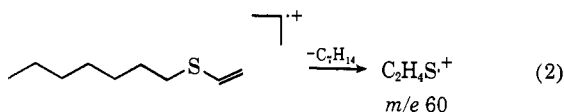
m/e 60

contrast to the alkyl vinyl ethers, however, the alkyl thiovinyl ethers displayed site-specific hydrogen transfer from C-2 and C-3. Also, in contrast to the alkyl vinyl ethers, the m/e 60 peak was the base peak at both 70 and 12 eV ionizing energy. Since the characteristics of this fragmentation process were in strong contrast to that observed for alkyl vinyl ethers, it was suggested that the ion of mass 60 had an ionized thioacetaldehyde structure b rather than an ionized vinylthiol structure c.

Several years ago we initiated a program which utilizes ion cyclotron resonance spectroscopy in elucidating the structure of ions created upon electron impact.[5] It was felt that this technique based on char-

b   c

acteristic ion–molecule reactions could be applied to the problem of the structure of the ion of mass 60 in the mass spectra of alkyl thiovinyl ethers, since the ion cyclotron resonance spectrometer has the ability to record mass spectra at sufficiently long lifetimes to observe gas-phase ion–molecule reactions, and the pulsed double resonance technique makes possible verification of reactant and product ions in all reaction sequences. The principles, theory, instrumentation, applications, and other techniques concerned with ion cyclotron resonance spectroscopy have been previously described in considerable detail and will not be elaborated upon further.[6]

Results and Discussion

Due to volatility problems encountered with the inlet system of the commercially available ion cyclotron resonance spectrometer, pentyl thiovinyl ether (Ia) was utilized as the precursor for the mass 60 ion (Figure 1).
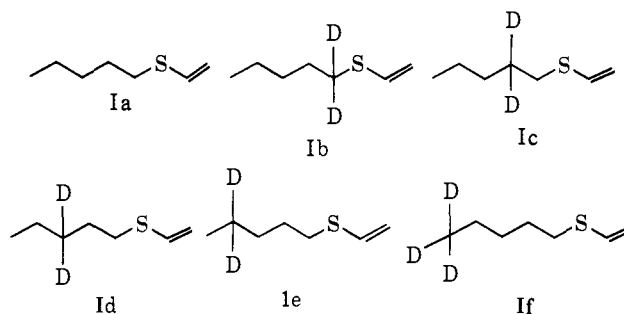
The per cent deuterium transferred from the carbons of the pentyl chain is given in Table I. As with heptyl thiovinyl ether, the major source of hydrogen is C-2.
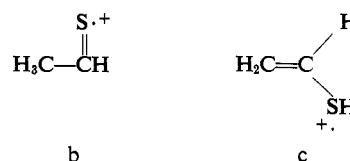
(1) For the preceding paper, see K. B. Tomer, S. Hammerum, and C. Djerassi, *Tetrahedron Lett.*, 915 (1973).

(2) Financial assistance from the National Institutes of Health (Grant No. AM 04257) is gratefully acknowledged.

(3) M. Katoh, D. A. Jaeger, and C. Djerassi, *J. Amer. Chem. Soc.*, **94**, 3107 (1972).

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

(5) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **91**, 2069 (1969); G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, **92**, 6205 (1970).

(6) J. D. Baldeschwieler, *Science*, **159**, 262 (1968); J. L. Beauchamp and J. T. Armstrong, *Rev. Sci. Instrum.*, **40**, 123 (1969); J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
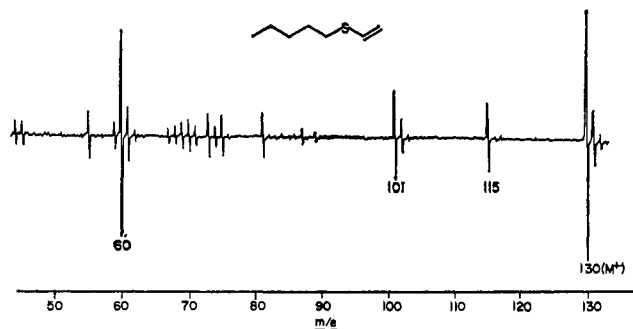
Figure 1. Ion cyclotron resonance spectrum of *n*-pentyl thiovinyl ether, 20 eV, 1.5 × 10⁻⁶ Torr.

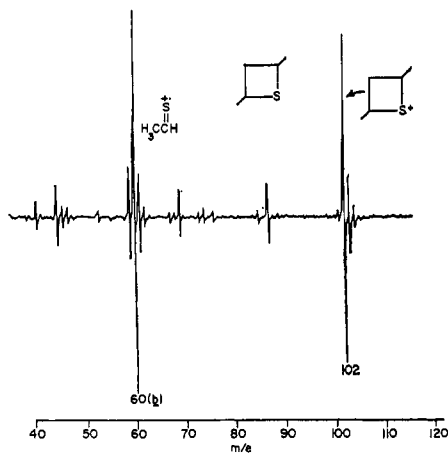Figure 2. Ion cyclotron resonance spectrum of 2,4-dimethyl-thietane, 20 eV, 2.5 × 10⁻⁶ Torr.

Table I. Per Cent Deuterium Transferred in Formation of m/e 60 Peak in Pentyl Thiovinyl Ethers[a]

	Position				
	1 (Ib)	2 (Ic)	3 (Id)	4 (Ie)	5 (If)
Mass spectrometry					
70 eV	4	47	29	14.5	2
15 eV	4	59	23	4	2.5
Ion cyclotron resonance					
20 eV	6.5	56.8	16	11	4

[a] Per cent deuterium transferred is corrected for the unlabeled mass 61 ions present.

It should be noted that this also applies to the 15-eV spectra where C-2 and C-3 are the most significant sources of hydrogen. The numbers do not add up to 100%, presumably due to deuterium isotope effects. Under the conditions found in the ion cyclotron cell the majority of hydrogen transferred is again from the C-2 position. It is not expected that there would be a perfect correlation between the mass spectral and ion cyclotron resonance percentages since there is a distinct possibility that differences in reactivity of the ions in ion–molecule reactions and slightly different ion residence times would lead to significantly different H/D ratios.

In order to study the ion–molecule reactions of the two isomeric $C_2H_4S \cdot^+$ ions they must be generated
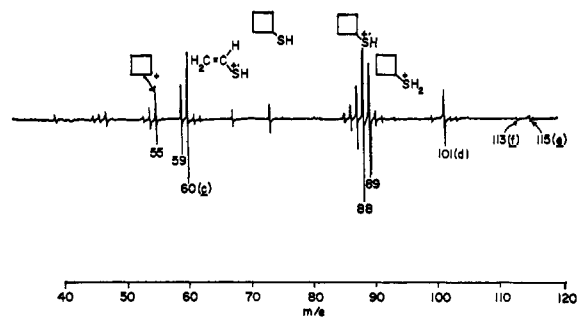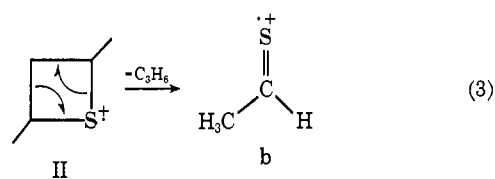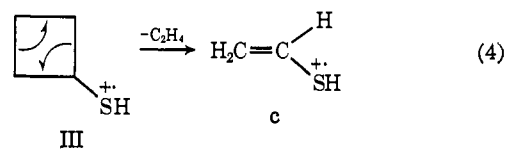
Figure 3. Ion cyclotron resonance spectrum of cyclobutanethiol, 20 eV, 3 × 10⁻⁶ Torr.

readily and unambiguously. Trost has reported that 2,4-dimethylthietane (II) eliminates C_3H_6 upon electron impact.[7] Therefore, II was chosen as a precursor for b (eq 3). The ion cyclotron resonance spectrum

$$ \text{II} \xrightarrow{-C_3H_6} \text{b} \tag{3} $$

(Figure 2) of II shows the peak at m/e 60 as the most intense one.

In analogy to the fragmentation of cyclobutanols,[5] cyclobutanethiol (III) was chosen as a likely precursor for the vinylthiol ion c (eq 4). Upon electron impact

$$ \text{III} \xrightarrow{-C_2H_4} H_2C=C \overset{H}{\underset{SH}{}} \tag{4} $$

III was found to give ion c as the most abundant one. The peak at m/e 60 was also observed to be a prominent peak in the ion cyclotron resonance spectrum (Figure 3) of III. Ion–molecule reactions are observed at m/e 101, 113, and 115 which arise by reaction of m/e 55, 59, and 60 ions with cyclobutanethiol (III), respectively (see eq 5–7 for "formal representation"). The structure of the m/e 101 ion is ambiguous and is, therefore, not indicated. The pentyl thiovinyl ethers (Ia–g) show fragment ions in the m/e 115–118 region precluding the use of the ion–molecule reaction leading to the m/e 115 as a distinguishing reaction.

In earlier papers[5] it had been observed that an ion with a vinyl alcohol structure donates a proton to a neutral acceptor while the isomeric keto ion does not. It was hoped that the two sulfur-containing tautomers, b and c, could be differentiated in an analogous manner. This approach was abandoned, however, when it was observed that both ions b and c donated a proton to a wide variety of neutral acceptors such as ketones, aldehydes, nitriles, and alcohols.

If, however, the proton transferred by b in an ion–molecule reaction could be differentiated from the proton transferred by c in its ion–molecule reaction, the two structures could be distinguished by deuterium

(7) B. M. Trost, W. L. Schinski, F. Chen, and I. B. Mantz, *J. Amer. Chem. Soc.*, **93**, 676 (1971). We wish to thank Dr. D. A. Jaeger for referring us to this article and for kindly donating a sample.
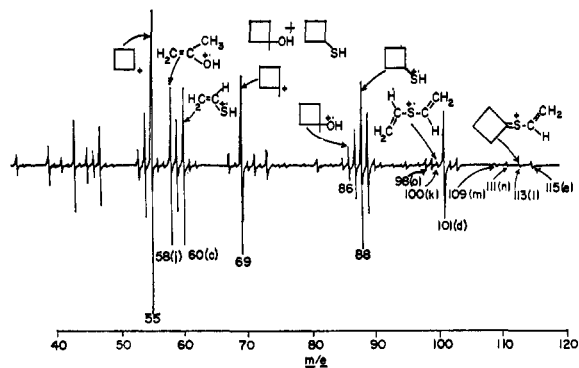
Figure 4. Ion cyclotron resonance spectrum of a mixture of 1-methylcyclobutanol and cyclobutanethiol, 20 eV, 8 × 10⁻⁶ Torr.
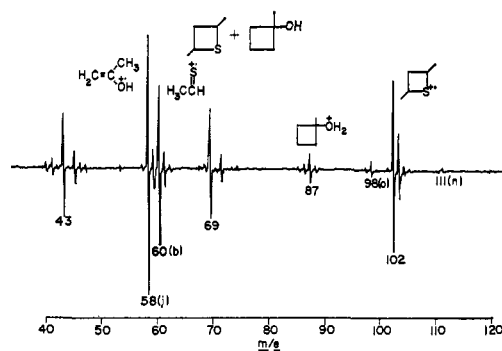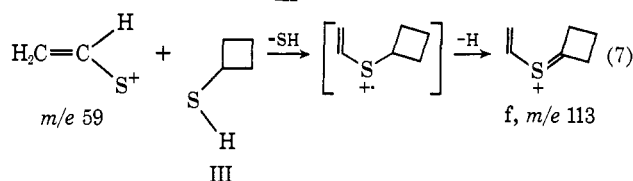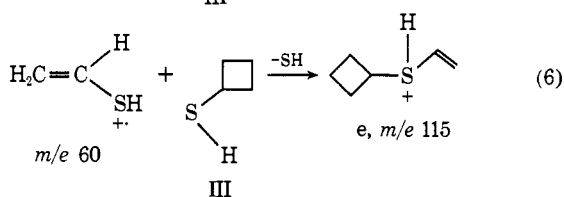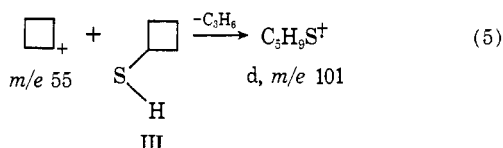

Figure 5. Ion cyclotron resonance spectrum of a mixture of 1-methylcyclobutanol and 2,4-dimethylthietane, 20 eV, 4 × 10⁻⁶ Torr.


(5)

(6)

(7)

labeling. Since the hydrogen transferrred in the formation of c would end up on the sulfur, the proton transfer reaction between cyclobutanethiol-S-d_1 (IV) (60% d_1, 40% H) and 4-heptanone (V) was investigated (eq 8). It was found by pulsed double resonance that


(8)

(9)
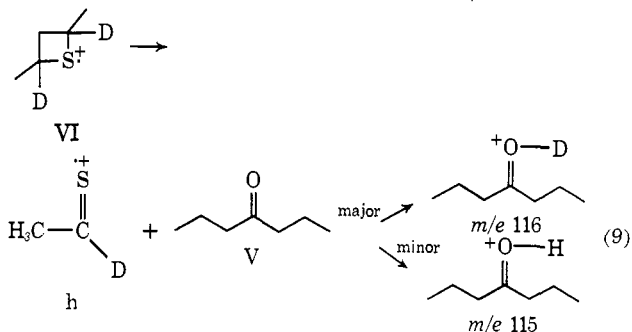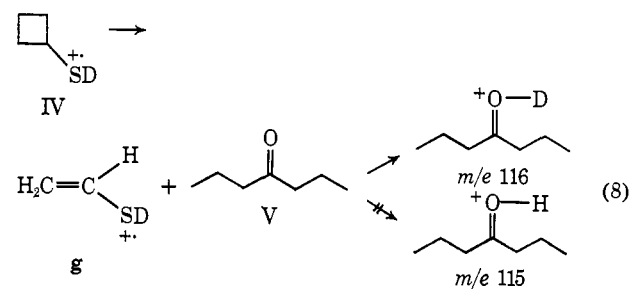
the ion g, vinylthiol-S-d_1, from IV transferred only deuterium to V. The proton transfer reaction (eq 9) of ionized thioacetaldehyde-1-d_1 (h), generated from

2,4-dideuterio-2,4-dimethylthietane (VI) with 4-heptanone, was then investigated. Pulsed double resonance demonstrated that the C-1 deuterium is transferred to a significant extent while the C-2 hydrogens are transferred to only a minor extent.[8]

The absence of any pulsed double resonance signal for proton transfer from ion g indicates that there is no tautomerization between thione b and thiol c on the icr time scale. This is analogous to the lack of tautomerization between the acetone molecular ion i and the 2-propenol ion j observed in earlier work.[5]
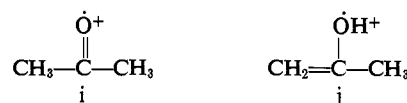
Since the itinerant hydrogen involved in the formation of b from Ia is probably transferred to C-2′, the two possible structures b and c for the mass 60 ion from I should be differentiable on the basis of proton transfer reactions in the appropriately labeled precursors (eq 10).

(10)
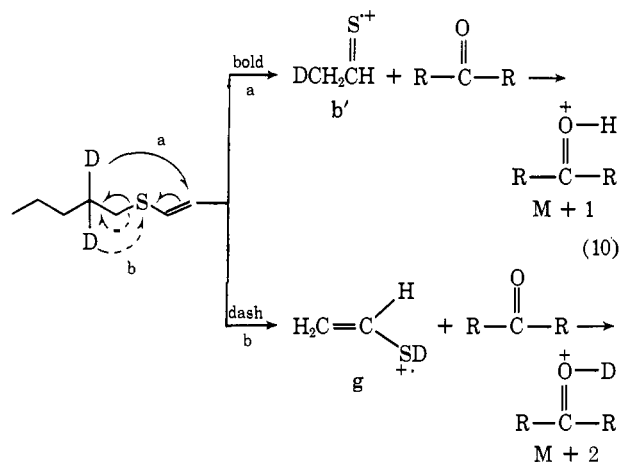
Earlier investigations[5] indicated that vinyl alcohols condense (vide infra) with 1-methylcyclobutanol (VII), while the keto tautomer does not. In an analogous manner, the ion cyclotron resonance spectrum of a mixture of VII and III (Figure 4) does reveal new peaks, albeit very small ones, at m/e 100 and 109 and an increase in intensity of the m/e 113 peak. The pulsed

(8) A small pulsed double resonance signal for hydrogen transfer from C-2 was observed and may also be due to a small amount of $C_2H_5S^+$ being present.
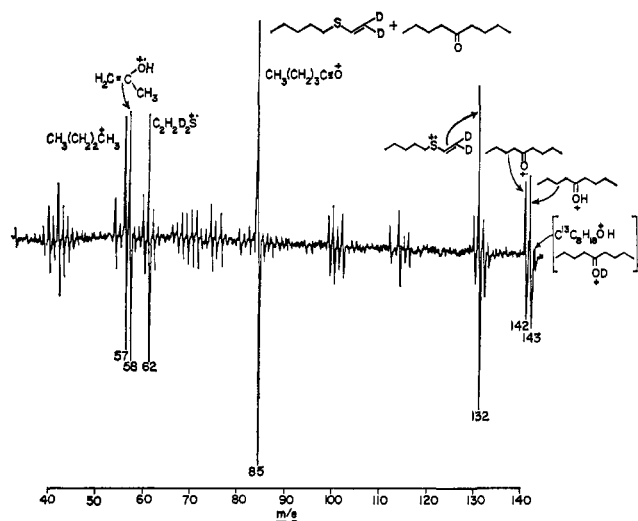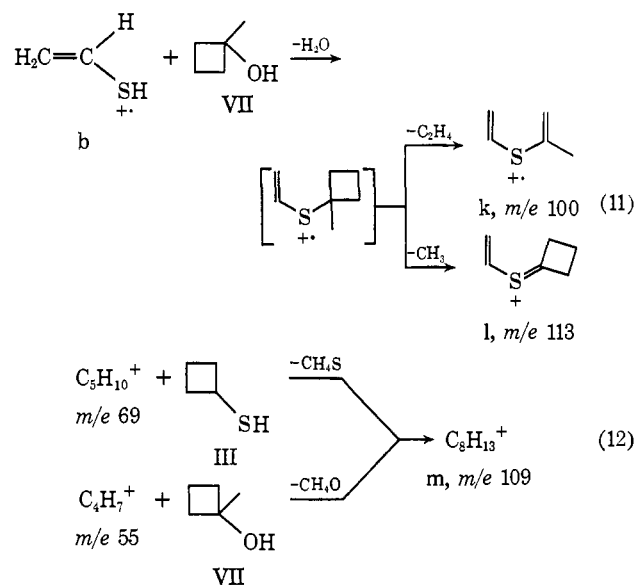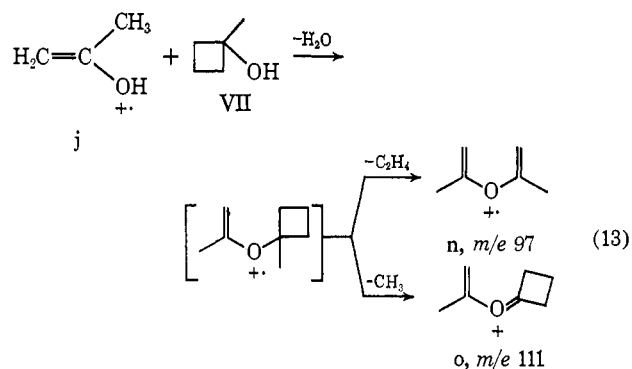
Figure 6. Ion cyclotron resonance spectrum of a mixture of n-pentyl thiovinyl-$2',2'$-d_2 ether and 5-nonanone, 20 eV, 1 × 10^{-6} Torr.

double resonance spectrum of the m/e 100 and 113 peaks revealed that the mass 60 ion (c) is a precursor for both peaks (eq 11). The pulsed double resonance signal for


the mass 59 ion as precursor to the m/e 113 peak is no longer observed. The pulsed double resonance spectrum of the m/e 109 peak indicates that the mass 69 and 55 ions are the precursors (eq 12). The icr spectrum of II and VII (Figure 5) did not, however, exhibit peaks at mass 100 and 113. Thus, these condensation reactions constitute a second method for distinguishing between b and c.

The mechanism (eq 11) proposed for the formation of these ions is analogous to that proposed for the condensation of 2-propenol and VII (eq 13). This mechanism was verified by the icr spectrum of III and VII, both of which had been partially exchanged with D₂O. The pulsed double resonance spectra of the mass 100 and 113 ions indicate that labeled vinylthiol g contributes to the formation of unlabeled k and l and that the ratio of mass 60 and 61 ions in the pulsed double resonance spectrum of the mass 100 ion is the same as

the ratio of mass 60 and 61 ions in the single resonance spectrum.

A third possible mechanism for formation of the mass 60 ion entails hydrogen transfer to C-1 of the vinyl moiety with formation (eq 14) of the molecular ion of
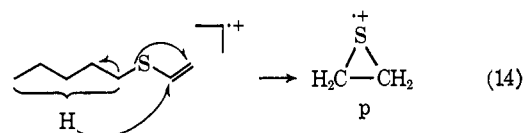
ethylene sulfide (p). If the reaction does proceed by mechanism 14 the hydrogens involved in any subsequent proton transfer reactions would have an equal probability of originating from C-1 or C-2 of the vinyl moiety (eq 15). To eliminate this possibility, pentyl
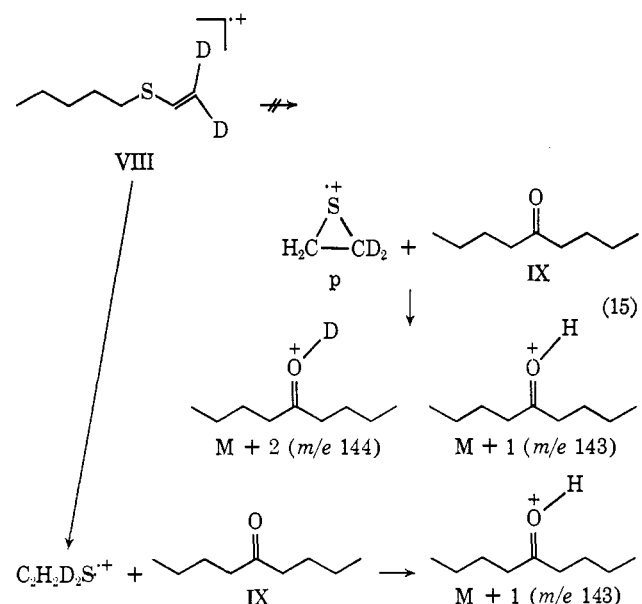
thiovinyl-$2,2$-d_2 ether (VIII) was prepared and the ion cyclotron resonance spectrum of a mixture of VIII and 5-nonanone (IX) was run (Figure 6). The pulsed double resonance spectrum of the protonated molecular ion of IX (Figure 7a) indicates substantial proton transfer from the mass 62 ion of VIII while the pulsed double resonance signal of the deuterated molecular ion of IX (Figure 7b) indicates negligible deuterium transfer.[9] Thus the formation of the mass 60 ion in I does not occur through a mechanism such as (14) in which the vinyl carbons become equivalent.

(9) The pulsed double resonance signal for deuterium transfer from m/e 62 is smaller than that for transfer from m/e 58 which is due to proton transfer to the ¹³C containing molecular ions of the ketone and it is also most likely due to proton transfer to the isotope containing molecules of the neutral ketone.

$$
C_5H_9D_2\overset{+}{S}CH=CH_2 \quad
\begin{array}{l}
\xrightarrow{a} \; \overset{\overset{+\cdot}{S}}{DH_2C\overset{\|}{C}H} \; + \; R'-\overset{\overset{O}{\|}}{C}-R \;\longrightarrow\; R'-\overset{\overset{+}{OH}}{\underset{\|}{C}}-R \\
\qquad\quad b' \qquad\qquad\qquad\qquad\qquad\qquad\qquad M+1 \\[4pt]
\xrightarrow{b} \; H_2C=\underset{\underset{+}{SD}}{\overset{H}{C}} \; + \; R'\overset{O}{\overset{\|}{C}R} \longrightarrow R'\overset{\overset{O-D}{+}}{\overset{\|}{C}R} \\
\qquad\qquad\qquad\qquad\qquad\qquad M+2 \\
\qquad\qquad\qquad g
\end{array}
$$

IX, R = R' = CH$_3$(CH$_2$)$_3$
X, R = R' = CH$_3$CH$_2$CD$_2$
XI, R = CH$_3$; R' = CH$_3$(CH$_2$)$_3$

(16)
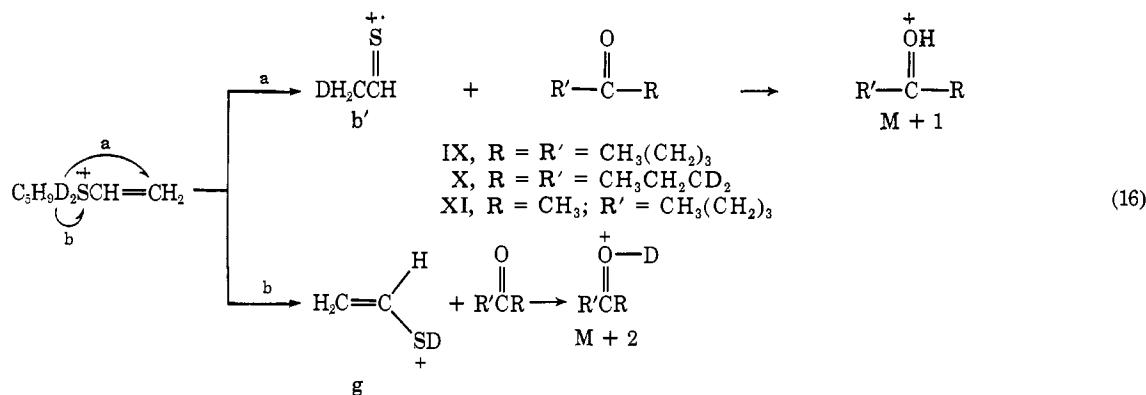
The ion–molecule reactions (eq 10 and 11) which have been found to distinguish between the tautomers, b and c, for the mass 60 ion from Ia permit the facile determination of the structure of the mass 60 ion arising *via* hydrogen transfer from each carbon atom by examining the five labeled pentyl thiovinyl ethers (Ib–f).

The relative contributions of the mass 60 and 61 ions to the M + 1 and M + 2 ions of ketones are presented in Table II (eq 16). One should not attach quantitative

Table II. Relative Contributions[a] of the Mass 60 and 61 Ions from the Pentyl Thiovinyl Ethers to the M + 1 and M + 2 Ions of Ketones

	d_0 (Ia)	1,1-d_2 (Ib)	2,2-d_2 (Ic)	3,3-d_2 (Id)	4,4-d_2 (Ie)	5,5,5-d_3 (If)
	Pulsed Double Resonance on M + 1					
m/e 60	100	100	100	100	100	100
m/e 61[b]	33	22	95	15	28	20
Neutral acceptor	X	X	XI	IX	X	IX
	Pulsed Double Resonance on M + 2					
m/e 60		100	25	60	70	100
m/e 61[b]		55	100	100	100	62
Neutral acceptor		X	XI	IX	X	IX

[a] ±5% for M + 1, ±10% for M + 2. [b] The contribution from the mass 61 ion is partially due to the presence of mass 61 ions resulting from double hydrogen trassfer.[10]

significance to the ratio of m/e 60/61 observed in proton transfer (after correcting for undeuterated 61 ions present), since the observed ratio may reflect differences in reactivity as well as in ion abundances. However, inspection of Table II indicates that only Ic shows significant hydrogen transfer for m/e 61 above that expected for the undeuterated mass 61 ion.[10] The data for deuterium transfer are extremely difficult to interpret since under ideal circumstances there should be no double resonance peak for mass 60. However, it is obvious that both Ic, Id, and Ie exhibit some deuterium transfer. Since ion b has been shown to donate some protons from C-2, it is possible that the double resonance peak for m/e 61 in Ic is due to deuterium transfer from an ion of structure b'. The peak may also be due to the presence of some ions of structure c from Ic.

Based on the proton transfer spectra, one may conclude that hydrogen transfer from C-3 and C-4 forms

(10) A significant peak at m/e 61 is observed in the mass spectrum of pentyl thiovinyl ether and is due to double hydrogen transfer. The pulsed double resonance peak at m/e 61 in the d_0 compound (Ia) for proton transfer is due to this ion.
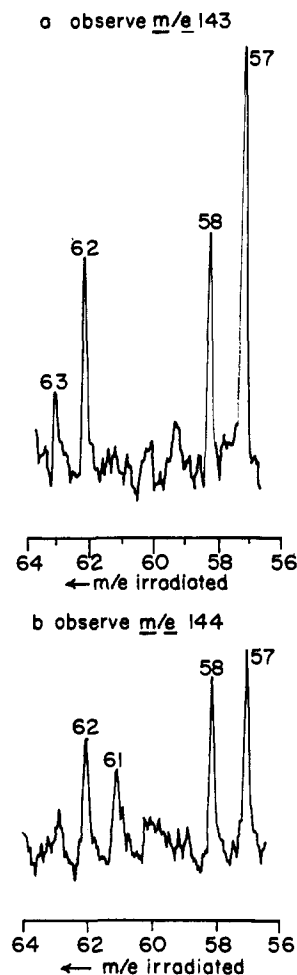

Figure 7. (a) Pulsed double resonance spectrum of the M + 1 (m/e 143) ion of 5-nonanone with the irradiating voltage = 0.06 V, phase = 180°, and other conditions identical with those under which Figure 6 was recorded. (b) Pulsed double resonance spectrum of the M + 2 (m/e 144) ion of 5-nonanone with the irradiating voltage = 0.06 V, phase = 180° and other conditions identical with those under which Figure 6 was recorded.

vinylthiol ions (c) *while hydrogen transfer from C-2 forms predominantly, if not exclusively, thioacetaldehyde ions* (b). As a check on these results, mixtures of the labeled pentyl thiovinyl ethers (Ib–f) and 1-methyl-cyclobutanol (VII) were run (eq 17) and the pulsed double resonance spectra of the mass 100 and 113 ions were examined. Table III shows the relative contributions of mass 60 and 61 ions from Ib–f to the formation of the mass 100 and 113 ions. This table indicates that Id does, in fact, yield a significant amount of mass

$$ (17) $$

h, m/e 100   l, m/e 113
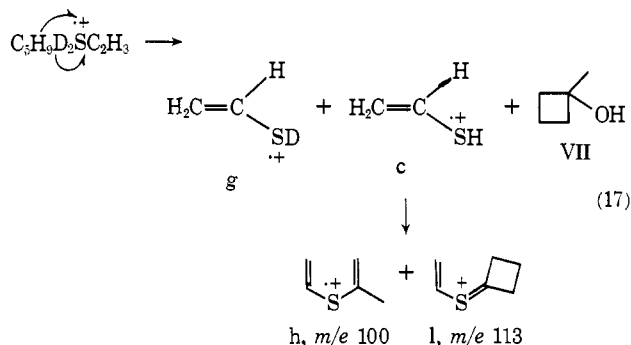
Table III. Relative Contributions[a] of m/e 60 and 61 Ions from Specifically Labeled Pentyl Thiovinyl Ethers to the Formation of the Mass 100 and 113 Ions in a Mixture of 1-Methylcyclobutanol (VII) and the Labeled Pentyl Thiovinyl Ethers (Ib–g)[b]

	Position					
	1 (Ib)	2 (Ic)	3 (Id)	4 (Ie)	5 (If)	4,5 (Ig)
	Pulsed Double Resonance on Mass 100					
m/e 60	100	100	100	100	100	60
m/e 61		15	73			100
	Pulsed Double Resonance on Mass 113					
m/e 60	100	100	100	100	100	100
m/e 61		15	50			90

[a] ±5% for mass 100, ±10% for mass 113. [b] No contribution was observed for unlabeled m/e 61 to mass 100 and 113 ions in Ia.

60 ion with a vinylthiol structure (c). On the other hand, Ic contributes only to a minor extent (approximately 13%) to the ions of structure c. Again compounds Ib, e, and f do not form ions of structure c, or if they do, the abundances are too low to be observable against the background noise.

However, the data for Ib–f in Table III raise another problem in that the origins of all the ions of structure c had not been established since only about 50% of the ions of structure c are accounted for by transfer of deuterium from C-2 and C-3. As noted earlier, a deuterium isotope effect is noticed in this system since the total per cent of deuterium transferred from all five carbons is not 100% (see Table I). It is possible, therefore, that in Id significantly more hydrogen is transferred from C-4 than in Ie. Conversely, less hydrogen may be transferred from C-3 in Id than in Ia. This also could be true for hydrogen transfer from C-5. To check this possibility, pentyl-3,3,4,4-d_4 thiovinyl ether (Ig) (77% d_4, 23% d_3) was prepared and the ion cyclotron resonance spectrum of a mixture of Ig and V was investigated (eq 18).

$$ (18) $$

k, m/e 100   l, m/e 113
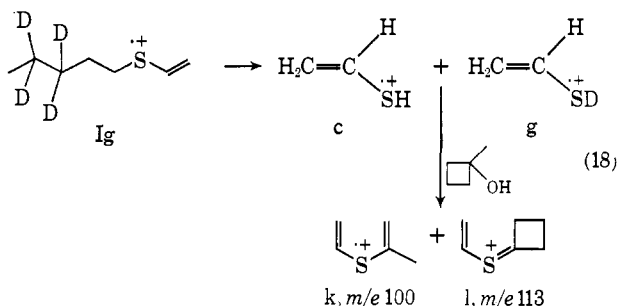
The results from the pulsed double resonance spectra of the m/e 100 and 113 peaks are given in Table III.

Comparison of the results for Ig and Id indicates that the m/e 61 peak has increased significantly relative to the m/e 60 peak. These data indicate that there is some hydrogen transfer from C-4 to sulfur resulting in the formation of ions of structure c. Since the ratios of m/e 60 and 61 indicated as precursors to the mass 100 peak accurately reflect the ratios of single resonance peaks (vide supra), Table III indicates that, within experimental error, the origins of the ions of structure c have been accounted for.

These results show that hydrogen transfer from C-2 of Ia to form the mass 60 ion occurs predominantly with transfer to carbon and formation of an ionized thioacetaldehyde structure b (eq 19). Hydrogen trans-

$$ (19) $$

$$ (20) $$

$$ (21) $$
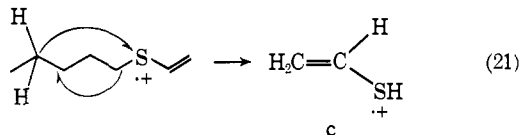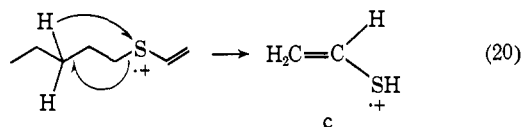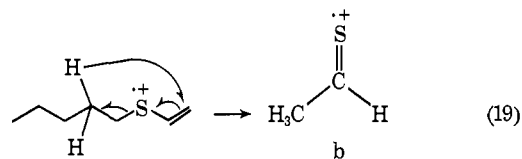
fer from C-3 occurs to sulfur with formation of an ionized vinylthiol ion c (eq 20). Although the small amount of hydrogen transfer from C-4 makes it difficult to determine the mechanism, our results indicate that hydrogen transfer to sulfur with formation of c is implicated (eq 21). If it is assumed that hydrogen transfer from C-1 and C-5 in addition to that from C-3 and C-4 leads to vinylthiol ions, c, and that the contribution from C-2 leading to vinylthiol ions is 13% of the total (Table III), it can be calculated that only 10% of the hydrogen transferred from C-2 is to sulfur while 90% is transferred to carbon with the formation of thioacetaldehyde ions, b. This translates to approximately a 1:1 ratio of ions with thioacetaldehyde structure and vinylthiol structure resulting from hydrogen transfer in pentyl thiovinyl ether.

These data indicate that the size of the transition state leading to the two possible products is the determining factor as to which product is formed. Thus, ionized thioacetaldehyde is formed by hydrogen transfer from C-2 through a six-membered transition state while ionized vinylthiol is formed by a five-membered transition state with hydrogen transfer from C-3 and by a six-membered transition state when hydrogen is transferred from C-4. Several factors may influence the predominant transfer from C-2 in contrast to the random transfer in the oxygen analog. One may be the greater stabilizing effect of sulfur over oxygen on an adjacent positive charge.[11] This effect should lower the energy of —X—C+—Ċ relative to —X+—C=C to a greater extent when X = S than when X = O. It is also possible that ionized thioacetaldehyde may be more stable relative to ionized vinylthiol than ionized acetaldehyde is relative to ionized vinyl alcohol.

(11) R. W. Taft, R. H. Martin, and F. W. Lampe, J. Amer. Chem. Soc., 87, 2490 (1965).

In summary, ion cyclotron resonance spectroscopy has again proven itself well suited to the determination of the structure of organic ions. In this case it has proven itself capable of the detection of mechanistically different pathways giving rise to ions of identical mass but different structure.

Experimental Section[12]

n-Pentyl Thiovinyl Ether (Ia). The sodium salt of 2-mercaptoethanol, prepared by treatment of 2-mercaptoethanol with sodium hydride in dry DMF, was heated with 1 equiv of *n*-pentyl bromide for 2 hr. The solution was cooled and the solvent removed by distillation. Water was added and the mixture was extracted with ether. The ether layer was dried over sodium sulfate and the ether removed *in vacuo*. The crude product in ether was refluxed overnight with excess phosphorus tribromide. Water was added and the ether layer was separated. The ether layer was washed with water and sodium bicarbonate solution, dried, and evaporated. An ether solution of 2-*S*-(*n*-pentyl)mercaptoethyl bromide was treated overnight at 25° with a 4 molar excess of 1,5-diazabicyclo-[4.3.0]non-5-ene. The reaction mixture was extracted with excess saturated sodium bicarbonate and dried over sodium sulfate and the ether evaporated *in vacuo*. *n*-Pentyl thiovinyl ether was purified by preparative glc.

Deuterium Labeled *n*-Pentyl Thiovinyl Ethers: *1,1-d₂* (Ib); *2,2-d₂* (Ic); *3,3-d₂* (Id); *4,4-d₂* (Ie); *5,5,5-d₃* (If). *n*-Pentyl-*1,1-d₂*, -*2,2-d₂*, -*3,3-d₂*, and -*4,4-d₂* alcohols were previously described.[1] *n*-Pentyl-*5,5,5-d₃* alcohol was prepared by reduction of acetic acid-*d₄* with lithium aluminum hydride. The bromide was prepared by reaction with triphenylphosphine and bromine.[13] Alkylation of the ethyl-*2,2,2-d₃* bromide thus formed with sodio diethyl malonate followed by saponification and decarboxylation yielded butyric-*4,4,4-d₃* acid. Reduction of the acid with lithium aluminum hydride and formation of the bromide as above yielded the labeled butyl bromide, which was converted by carbonation of its Grignard complex to valeric-*5,5,5-d₃* acid. Reduction with lithium aluminum hydride

then formed *n*-pentyl-*5,5,5-d₃* alcohol. Treatment of the labeled alcohols with phosphorus tribromide formed the labeled bromides. The latter were transformed into the labeled *n*-pentyl thiovinyl ethers as described above for the preparation of unlabeled *n*-pentyl thiovinyl ether. Per cent deuterium incorporation (compound, position, per cent): Ib, 1, 92.5% *d₂*, 7.5% *d₁*; Ic, 2, 100% *d₂*; Id, 3, 97% *d₂*, 3% *d₁*; Ie, 4, 91.5% *d₂*, 8.5% *d₁*; If, 5, 95% *d₃*, 5% *d₂*.

n-Pentyl-*3,3,5,5-d₄* Thiovinyl Ether (Ig). Methylmalonic acid was exchanged with deuterium oxide and decarboxylated thermally to yield propionic-*2,2-d₂* acid. Reduction of the acid with lithium aluminum deuteride yielded 1,1,2,2-tetradeuteriopropanol. Treatment of the alcohol with triphenylphosphine and bromine[13] yielded 1-bromo-1,1,2,2-tetradeuteriopropane which was homologated with sodio diethyl malonate. The 3,3,5,5-tetradeuteriopentanol was transformed to *n*-pentyl-*3,3,5,5-d₄* thiovinyl ether (Ig) as previously described for the labeled pentyl thiovinyl ethers (Ib–f). Mass spectral analysis showed an isotopic composition of 77% *d₄* and 23% *d₃*.

Cyclobutanethiol (III).[14] Cyclobutanone was reduced with lithium aluminum hydride to yield cyclobutanol which was transformed into cyclobutyl tosylate by the procedure of Brown and Han.[15] The tosylate and thiourea were refluxed in ethanol overnight to form the thiouronium salt. Treatment of the thiouronium salt with aqueous sodium hydroxide yielded cyclobutanethiol which was purified by glc.

2,4-Dideuterio-2,4-dimethylthietane (VI). Acetylacetone was reduced with sodium borodeuteride to yield 2,4-dideuterio-2,4-pentanediol.[16] The cyclic carbonate of the diol was prepared by heating the diol with diethyl carbonate and a catalytic amount of sodium. Heating the cyclic carbonate with potassium thiocyanate[7] at 165° under nitrogen yielded 2,4-dideuterio-2,4-dimethylthietane (92% *d₂*, 8% *d₁*) which was purified by glc.

n-Pentyl Thiovinyl-*2′,2′-d₂* Ether (VIII). Reaction of the sodio salt of ethyl 2-mercaptoacetate with *n*-pentyl bromide in DMF yielded ethyl 2-*S*-(*n*-pentyl)mercaptoacetate which was reduced with lithium aluminum deuteride to yield 2-*S*-(*n*-pentyl)mercapto-ethyl-*2,2-d₂* alcohol. Conversion of this alcohol to *n*-pentyl thiovinyl-*2′,2′-d₂* ether (VIII) through the corresponding bromide followed the procedures for Ia.

The preparations of 1-methylcyclobutanol and heptan-4-one-*3,3,5,5-d₄* were described in an earlier paper.[5] Cyclobutanethiol-*S-d₁* was prepared in the inlet system of the icr spectrometer by exchange with D₂O.

(12) The basic spectrometer used in this study is the Varian V-5900 spectrometer fitted with a dual inlet system. The spectrometer, the method, and applications of single and double resonance have been described.[6] Mass spectra were run on an MS-9 mass spectrometer by Mr. R. Ross. We wish to thank Mr. John Garcia for technical assistance with the icr spectrometer.

(13) G. A. Wiley, A. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964).

(14) H. E. Gunning, U. S. Patent 3230161 (1966).

(15) H. C. Brown and G. Han, *J. Amer. Chem. Soc.*, **78**, 2735 (1956).

(16) J. Dale, *J. Chem. Soc.*, 910 (1961).

Bridging in β-Chloroalkyl Radicals by Electron Spin Resonance

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Abstract: Chlorine bridging in alkyl radicals is examined by esr for a series of methyl substituted β-chloroethyl radicals in solution. The criterion for bridging in these radicals is considered as restricted rotation about the C_α–C_β bond and distortion at C_β which places the eclipsed chlorine atom closer to the p orbital at the radical center. Analysis of isotropic esr *g* values and temperature-dependent chlorine-35 and proton hyperfine splittings indicates that all these β-chloroalkyl radicals exist in stable conformations consisting of chlorine in asymmetric bridges. Bridging is promoted by methyl groups, but counteracting steric effects prevent the tetramethyl analog from achieving a symmetric bridged structure. The facile 1,2 migration of chlorine in the β-chloroisobutyl radical to the tertiary isomer is reported.

S tabilization of alkyl radicals and stereoselectivity in homolytic reactions due to bridging and anchimeric

assistance by heteroatom substituents are subjects which have been discussed at length and are of current