Electron-impact-promoted Hydrogen Transfer *via* an Eight-membered Transition State in Vinyl Ethers

By MASANOBU KATOH and CARL DJERASSI*

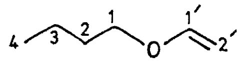
(*Department of Chemistry, Stanford University, Stanford, California,* 94305)

Summary The origin of the important $M - CH_3$ ion in vinyl ethers has been elucidated through deuterium labelling; when a secondary hydrogen atom is available for transfer, 8-membered transition states play the dominant role and other hydrogen transfers, previously thought to be site-specific, have now been shown to involve randomization.

THE importance of hydrogen transfers in organic mass spectrometry has been emphasized numerous times[1] and the vast majority of site-specific hydrogen migrations has been shown by isotopic labelling to involve six- or four-membered transition states.[1,2] We report the occurrence of a site-specific eight-membered transition state in the genesis of the important $M - CH_3$ ions of alkyl vinyl ethers. Interestingly enough, this favoured fragmentation mode (base peak in the 12 ev spectra of C_4—C_6 alkyl vinyl ethers) has escaped the attention of the few investigators[3-5] who have concerned themselves with the mechanistically intriguing reactions of this class of organic compounds after electron impact.

TABLE 1

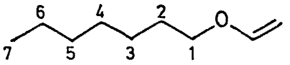
$M - CH_3$ loss in n-butyl vinyl ether



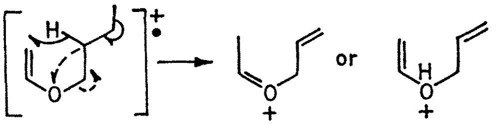
Ion	1-^2H_2	2-^2H_2	3-^2H_2	4-^2H_3	$2'\text{-}^2H_2$
$M - CH_3$	98·2%	98·2%	46·3%	75·1%	17·3%
$M - CH_2D$	1·8%	1·8%	53·7%	6·4%	
$M - CHD_2$					82·7%
$M - CD_3$				19·5%	

TABLE 2

$M - CH_3$ loss in n-heptyl vinyl ether

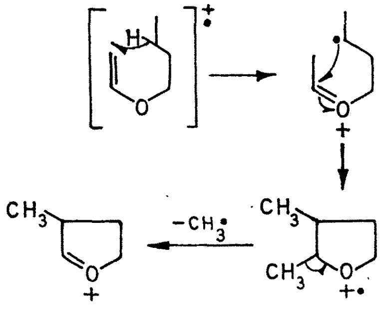


Ion	1-^2H_2	2-^2H_2	3-^2H_2	4-^2H_2	5-^2H_2	6-^2H_2	7-^2H_3
$M{-}CH_3$	100%	100%	98%	19·2%	96%	98%	100%
$M{-}CH_2D$			2%	80·8%	4%	2%	



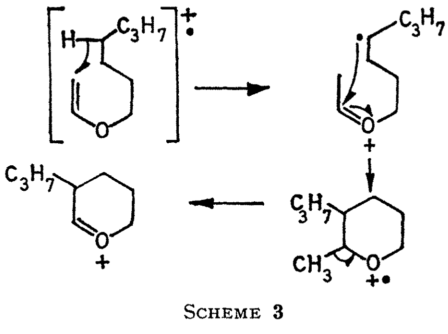
SCHEME 1

Deuterium labelling of various positions in n-butyl vinyl ether demonstrates (Table 1) that less than 20% of the methyl loss originates from the terminal methyl group (*e.g.* Scheme 1) and that over 80% involves the methylene grouping together with one hydrogen from the butyl chain. Furthermore, the data in Table 1 show that over 80% of the itinerant hydrogen atom arises from C-3 of the butyl chain, thus implicating a seven-membered transition state (Scheme 2).



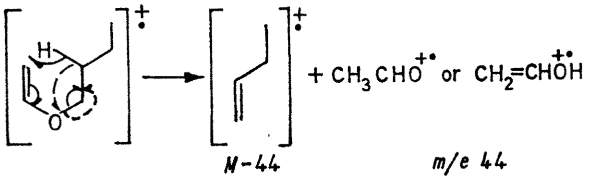
SCHEME 2

However, because of the well known preference of secondary over primary hydrogen transfer, we selected a second compound, n-heptyl vinyl ether, in which a larger number of secondary hydrogens were available for abstraction. The results summarized in Table 2 show a dramatic difference in that over 80% of the migrating hydrogen now originates from C-4—a result which is best accommodated by an eight-membered transition state (Scheme 3). The difference between the two compounds (Table 1 as opposed to Table 2) is clearly associated with the absence of a secondary hydrogen atom at C-4 of n-butyl vinyl ether.



SCHEME 3

Another noteworthy feature of Tables 1 and 2 is the virtual absence of hydrogen scrambling prior to electron impact. A similar site-specificity without hydrogen scrambling, but involving a six-membered[3] or four-membered[4] transition state, has been invoked in the genesis of the important *m/e* 44 ion (Scheme 4) of such alkyl vinyl ethers.



SCHEME 4

Our data summarized in Table 3 make such assumptions *untenable and* require prior randomization approaching statistical equilibration, which is not too surprising in view of our earlier results[6] with butyl phenyl ether. Furthermore, it has been implied[5] that the production of the *m/e* **44** species and the corresponding $M-44$ ion, in which the charge resides on the olefin moiety, arise by the same hydrogen transfer mechanism. If this were true, the figures in the second (*m/e* 45) and fourth ($M-45$) horizontal columns of Table 3 should be identical, which they are not. Full details and further aspects of the mass spectrometry of vinyl ethers will be recorded in a full paper.

TABLE 3

Hydrogen transfer in m/e 44 *and* M—44 *ions of n-butyl vinyl ether*

Ion	1-$^2H_2$	2-$^2H_2$	3-$^2H_2$	4-$^2H_3$
m/e 44 (C_2H_4O)	83·2%	74·7%	78·5%	67·8%
m/e 45 (C_2H_3DO)[a]	16·8%	25·3%	21·5%	32·2%
$M-C_2H_4O$	89·6%	72%	58·8%	91·8%
$M-C_2H_3DO$	10·4%	28%	41·2%	8·2%

[a] Statistically random distribution would be 22·2% for $^2H_2$ and 33·3% for $^2H_3$ analogues.

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