The Structure and Mechanism of Formation of $C_5H_9O^+$ from Ionized Phytyl Methyl Ether

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The recent proposal that ionized phytyl methyl ether [$C_{16}H_{33}(CH_3)C=CHCH_2OCH_3^+$] undergoes an allylic rearrangement to ionized isophytyl methyl ether [$CH_2=CHC(C_{16}H_{33})(CH_3)OCH_3^+$] before elimination of an alkyl radical is discussed. Both literature precedent and new results in which the structure of the $[M - C_{16}H_{33}]^+$ fragment ion is established by comparison of its collision-induced dissociation mass spectrum with the spectra of isomeric $C_5H_9O^+$ ions of known structure are inconsistent with this proposal. The formation of $CH_3CH=CHCH=O^+CH_3$ by loss of a γ -alkyl substituent without skeletal isomerization rather than $CH_2=CHC(CH_3)=O^+CH_3$ after allylic rearrangement is explained in terms of a mechanism that involves two 1,2-H shifts, followed by σ -cleavage of the resultant ionized enol ether, $C_{16}H_{33}(CH_3)CH-CH=CHOCH_3^+$. (*J Am Soc Mass Spectrom* 1996, 7, 205–208)

The final article [1] in the last issue of *Organic Mass Spectrometry* is a letter that proposes that ionized phytyl methyl ether undergoes an allylic rearrangement to ionized isophytyl methyl ether before fragmentation via α -cleavage by expulsion of $C_{16}H_{33}$ (major channel) or CH_3 (minor channel) to give $C_5H_9O^+$ (m/z 85) and $C_{20}H_{39}O^+$ (m/z 295), respectively; Scheme I. The key step in this isomerization involves the cyclic distonic [2, 3] ion *b*, which may be derived from a 2,2-disubstituted oxetane by methyl cationization on oxygen and hydrogen atom abstraction from the 3-position. The facile participation of such a species is novel, especially in view of the well-known difficulty to form four-membered rings from acyclic precursors.

An alternative mechanism for the allylic rearrangement entails C–O bond cleavage to give an ion–neutral complex [4] that consists of a 1,1-disubstituted allylic cation and a methoxy radical. Recombination of the components with attachment of the oxygen atom to the more substituted carbon atom then leads to ionized isophytyl methyl ether; Scheme II. There is some literature precedent for this route in the analogous rearrangement steps observed in the reactions of ionized *n*-alkanols and long-chain alkyl esters of carboxylic acids [5, 6].

The similarity of the conventional electron impact ionization (EI) mass spectra of phytyl and isophytyl

methyl ethers was cited [1] as a reason to propose that allylic rearrangement preceded fragmentation of ionized phytyl methyl ether. However, the similarity of these spectra is purely coincidental: parallel trends have been reported previously for simpler related pairs of allylic alkenyl methyl ethers [7].

Thus, the 70-eV EI spectra of $CH_3CH=CHCH_2OCH_3$ and $CH_2=CHCH(CH_3)OCH_3$ both show intense fragment ion signals at m/z 71. Moreover, the only obvious differences between the spectra are the relative intensities of the signals at m/z 59, 45, and 43. Indeed, even the spectrum of the third allylic isomer of $C_4H_7OCH_3$ [$CH_2=(CH_3)CCH_2OCH_3$] can be distinguished only with care from those of $CH_3CH=CHCH_2OCH_3$ and $CH_2=CHCH(CH_3)OCH_3$ [7]. In all three cases, collision-induced dissociation (CID) studies establish that the same product ion [$CH_2=CHCH=O^+CH_3$] is formed [8]. These similarities persist in the low energy (12-eV), low temperature (350-K) EI spectra of the three isomeric ethers and in the 70- and 12-eV EI spectra of their $C_4H_7OCD_3$ analogs [7]. Furthermore, the reactions of metastable $C_4H_7OCH_3^+$ species generated from the isomeric ethers are closely similar: all three isomers show a strong preference for expulsion of a methyl radical (94–95% of the metastable ion current) [8]. These data could be taken to indicate that the three isomeric radical cations interconvert with one another before

Scheme I

Scheme II

dissociation through common transition states occurs. However, the behavior of their labeled analogs refutes such an explanation. Thus, for example, metastable $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OCD}_3^{+\cdot}$ and $\text{CH}_2=(\text{CH}_3)\text{CH}_2\text{OCD}_3^{+\cdot}$ lose CH_3 with high selectivity ($\sim 97\%$), but $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{OCD}_3^{+\cdot}$ eliminates CH_3 (66%), $\text{CH}_2\text{D}^{\cdot}$ (28%) and even a small proportion of $\text{CHD}_2^{\cdot}$ (6%) [8]. Consequently, although $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OCD}_3^{+\cdot}$ and $\text{CH}_2=(\text{CH}_3)\text{CH}_2\text{OCD}_3^{+\cdot}$ display apparently indistinguishable reactivities, $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{OCD}_3^{+\cdot}$ has a distinct and subtly different chemistry.

Parallel similarities are found in the spectra of isomeric $\text{C}_5\text{H}_9\text{OCH}_3$ and $\text{C}_6\text{H}_{11}\text{OCH}_3$ ethers. Thus, the 70-eV EI spectra of prenyl and isoprenyl methyl ethers [$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{OCH}_3$ and $\text{CH}_2=\text{CHC}(\text{CH}_3)_2\text{OCH}_3$, respectively] are quite similar [7]. The major differences are the greater relative intensity of the $\text{M}^{+\cdot}$ signal in the spectrum of prenyl methyl ether and the occurrence of a significant $[\text{M} - \text{C}_2\text{H}_3]^+$ ion in the spectrum of isoprenyl methyl ether. These differences persist on a much reduced scale in the spectra reported for phytyl and isophytyl methyl ethers; a weak $\text{M}^{+\cdot}$ signal at m/z 310 is quoted only for the former, but a weak $[\text{M} - \text{C}_2\text{H}_3]^+$ ion at m/z 283 is quoted only for the latter [1].

Despite the similarity of their spectra, the molecular ions of prenyl and isoprenyl methyl ethers do not equilibrate before loss of a methyl radical at either high or low internal energies. Thus, CID studies reveal that $[\text{M} - \text{CH}_3]^+$ in the EI spectrum of isoprenyl methyl ether has a different structure from the corresponding ion in the spectrum of prenyl methyl ether [9]. Moreover, metastable $\text{CH}_2=\text{CHC}(\text{CH}_3)_2\text{OCD}_3^{+\cdot}$ eliminates both CH_3 and CD_3 , whereas metastable

$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{OCD}_3^{+\cdot}$ loses CH_3 essentially exclusively (Bowen, R. D.; Suh, D.; Terlouw, J. K., unpublished work).

Schemes I and II both entail isomerization of the heavy atom skeleton of ionized phytyl methyl ether, with eventual formation of the conjugated oxonium ions $\text{CH}_2=\text{CHC}(\text{R})=\text{O}^+\text{CH}_3$ [$\text{R} = \text{CH}_3$ and $\text{C}_{16}\text{H}_{33}$, respectively] in which the methoxy group is attached to a carbon atom that carries two hydrocarbon substituents. In contrast, a comprehensive survey [9] of alkyl radical loss from ionized pentenyl and hexenyl methyl ethers in which the structure(s) of the resultant fragment ions were determined by measurement of their CID spectra interpreted elimination of a γ -alkyl group in allylic systems in terms of two consecutive 1,2-H shifts, followed by σ -cleavage of the resultant ionized enol ether; Scheme III. The first of these 1,2-H shifts (shown in *Italic type*) may be considered to terminate at a cationic center (i.e., a hydride anion migrates to a carbon atom that is part of an electron-deficient double bond). Such processes are facile and normally occur at the thermochemical threshold. However, the second 1,2-H shift (shown in **bold type**) must terminate at a radical center (i.e., a hydrogen atom migrates to the radical site of a distonic ion). Such steps involve additional energy barriers and do not normally occur in simple radicals [10], even in the gas phase in cases where they are energetically favorable [11]. Nevertheless, there is clear evidence from related research on distonic ions isomeric with ionized carboxylic acids [12, 13] and work on distonic ions derived from ionized alkenols [14] or ionized alkenyl methyl ethers [8, 9] that slow 1,2-H shifts to the radical site do occur in such systems. Each of these 1,2-H shifts to a spin center is usually the key step in the mechanism for dissociation. Typically, as in the present case, it leads to an ionized substituted alkene, which may fragment by γ -cleavage.

A direct 1,3-H shift in the ionized allylic alkenyl methyl ether would lead to the same ionized enol ether as that formed by two 1,2-shifts. These alternative descriptions cannot be distinguished purely on the basis of the present data. However, there are sound precedents for exclusion of such a 1,3-H shift, which is symmetry forbidden [15] and known to entail a substantial energy barrier in cationic systems [16]. Moreover, no evidence was found for 1,3-H shifts to radical

Scheme III

centers in distonic ions that are isomeric with ionized carboxylic acids, even though 1,2-H shifts were documented for these radical cations [12, 13].

The pathway that involves 1,2-H shifts for loss of a γ -substituent does not involve prior changes to the connectivity of the heavy atoms. Furthermore, it usually produces a different fragment ion from that given by allylic rearrangement followed by α -cleavage. Thus, the CID spectrum of the $[M - CH_3]^+$ ion formed from prenyl methyl ether is essentially the same as that of $CH_3CH=CHCH=O^+CH_3$ [generated by ionization and ethyl radical loss from $CH_3CH=CHCH(C_2H_5)OCH_3$], but distinct from those of $CH_2=CHC(CH_3)=O^+CH_3$ [formed by dissociative ionization of $CH_2=CHC(CH_3)_2OCH_3$ or $CH_2=CHC(CH_3)(C_2H_5)OCH_3$] and $CH_2=(CH_3)CCH=O^+CH_3$ [formed by dissociative ionization of $CH_2=(CH_3)CCH(C_2H_5)OCH_3$] [9]. These observations establish a strong precedent for interpretation of the facile loss of $C_{16}H_{33}$ from ionized phytol methyl ether by an analogous mechanism that leads to $CH_3CH=CHCH=O^+CH_3$, rather than $CH_2=CHC(CH_3)=O^+CH_3$, as would be required by Schemes I and II.

This hypothesis is subjected readily to experimental test. The CID spectrum of the $C_5H_9O^+$ ion formed from ionized phytol methyl ether is almost identical to

that of authentic $CH_3CH=CHCH=O^+CH_3$, but distinct from those of $CH_2=(CH_3)CCH=O^+CH_3$ and $CH_2=CHC(CH_3)=O^+CH_3$; Figure 1. These data refute the speculative proposal that involves allylic rearrangement via the cyclic distonic ion and also exclude the possibility of a skeletal isomerization analogous to that proposed in early work on ionized alkanols and esters.

These literature precedents and new results emphasize that the occurrence of similar spectra cannot always be regarded as sound evidence to propose that ionized allylic ethers obtained from isomeric precursors interconvert before fragmentation. In particular, ionized phytol methyl ether does not rearrange either reversibly or unidirectionally to ionized isophytol methyl ether. Instead, it dissociates independently via another mechanism, which almost certainly involves two 1,2-H shifts followed by γ -cleavage. The strong preference for expulsion of $C_{16}H_{33}$ in the final step probably reflects generic trends in the relative rates for loss of various alkyl radicals from distonic ions (loss of CH_3 occurs much more slowly than elimination of C_2H_5 and larger species) [12, 13]. Further work shows that alkyl radical loss from $R^1R^2C=CHCH_2OCH_3^{+\bullet}$ radical cations generally involves γ -cleavage (Bowen, R. D.; Clifford, P.; Gallagher, R. T., in preparation).

Figure 1. CID spectra of $C_5H_9O^+$ ions formed from (a) $CH_2=(CH_3)CCH(C_2H_5)OCH_3$, (b) $CH_2=CHC(CH_3)(C_2H_5)OCH_3$, (c) $CH_3CH=CHCH(C_2H_5)OCH_3$, and (d) phytol methyl ether. These spectra were recorded on a Kratos Analytical Ltd. (Manchester, U.K.) Concept II HH four-sector mass spectrometer with helium as the collision gas under the conditions reported previously [9].

References

1. Rontani, J.-F. *Org. Mass Spectrom.* **1994**, 29, 808.
2. Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, 106, 5805.
3. Hammerum, S. *Mass Spectrom. Rev.* **1988**, 7, 123.
4. Reviews: Morton, T. H. *Tetrahedron* **1982**, 38, 3195; van Baar, B. L. M.; Terlouw, J. K.; Akkok, S.; Zummack, W.; Schwarz, H. *Int. J. Mass Spectrom. Ion. Processes* **1987**, 81, 217; Heinrich, N.; Schwarz, H. In *Ion and Cluster Ion Spectroscopy*; Maier, J. P., Ed.; Elsevier: Amsterdam, 1988; p 329; McAdoo, D. J. *Mass Spectrom. Rev.* **1988**, 7, 363; Meyerson, S. *Org. Mass Spectrom.* **1989**, 24, 267; Hammerum, S. In *Fundamentals of Gas-Phase Ion Chemistry*; Jennings, K. R., Ed.; Kluwer: Dordrecht, 1990; p 379; Bowen, R. D. *Acc. Chem. Res.* **1991**, 24, 364; Longevialle, P. *Mass Spectrom. Rev.* **1992**, 11, 157; McAdoo, D. J.; Morton, T. H. *Acc. Chem. Res.* **1993**, 26, 295.
5. Meyerson, S. *Org. Mass Spectrom.* **1989**, 24, 653.
6. Bukovits, G. J.; Budzikiewicz, H. *Org. Mass Spectrom.* **1983**, 18, 219.
7. Bowen, R. D.; Wright, A. D.; Thomas, S. R.; Jennings, K. R.; Maccoll, A. *Org. Mass Spectrom.* **1991**, 26, 421.
8. Bowen, R. D.; Wright, A. D.; Colburn, A. W.; Derrick, P. J. *Int. J. Mass Spectrom. Ion Processes* **1992**, 116, 193.
9. Bowen, R. D.; Wright, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 96; Wright, A. D.; Bowen, R. D. *Can. J. Chem.* **1993**, 71, 1073.
10. Beckwith, A. J. L.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic: New York, 1980; Vol. 1, p 162.
11. Hammerum, S. *Acta Chem. Scand. Ser. B* **1984**, 38, 707.
12. Weiske, T.; Schwarz, H. *Chem. Ber.* **1983**, 116, 323; Weiske, T.; Halim, H.; Schwarz, H. *Chem. Ber.* **1985**, 118, 495.
13. Weiske, T.; Schwarz, H. *Tetrahedron* **1986**, 42, 6245.
14. Hudson, C. E.; McAdoo, D. J. *Tetrahedron* **1990**, 46, 331.
15. Woodward, R. B.; Hoffmann, R. *Angew. Chem. Int. Ed. Eng.* **1969**, 8, 781.
16. Bowen, R. D.; Colburn, A. W.; Derrick, P. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1274; Bowen, R. D.; Derrick, P. J. *Org. Mass Spectrom.* **1993**, 28, 1197.