The Mechanism of Alkyl Radical Loss from Ionised Pentenyl Methyl and Hexenyl Methyl Ethers: the Importance of a 1,2-Hydrogen Shift to the Radical Site of a Distonic Ion

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The crucial step in alkyl radical loss from various ionised pentenyl and hexenyl methyl ethers is shown by collision-induced dissociation experiments to involve a 1,2-H shift at the radical site of a distonic ion, followed by γ-cleavage of the resultant ionised enol ether.

The behaviour of $C_nH_{2n}O^{+\cdot}$ species has fascinated organic chemists and mass spectroscopists for at least thirty years.[1] One class of $C_nH_{2n}O^{+\cdot}$ ions that have received very little attention is ionised alkenyl methyl ethers. Recently, it has been shown that expulsion of an alkyl radical from such radical-cations does not always proceed *via* simple σ-cleavage.[2,3] Instead, rearrangements involving distonic[4,5] ions and ionised methoxycyclopropanes sometimes permit the formation of a more stable oxonium ion than those accessible by σ-cleavage.[3]

This unexpected route (σ'-cleavage) can be formulated in terms of fission of the bond connecting the β-carbon atom to an alkyl substitutent in a distonic ion. This mechanism predicts that elimination of $CH_3^{\cdot}$ from $CH_3CH=C(CH_3)CH_2OCH_3^{+\cdot}$,

$1^{+\cdot}$, and $(CH_3)_2C=CHCH_2OCH_3^{+\cdot}$, $2^{+\cdot}$, should give rise to $CH_3CH=CHCH=O^+CH_3$ and $CH_2=C(CH_3)CH=O^+CH_3$, respectively, Scheme 1.

An alternative explanation for the σ'-cleavage process involves a 1,2-H shift at the radical site of the appropriate distonic ion, followed by fission of the bond between the alkyl substituent and the γ-carbon atom of the resultant ionised enol ether. The 1,2-H shifts to the radical centres are denoted by bold type in the Schemes to distinguish them from 1,2-H shifts to cationic centres which are shown in italic type. This mechanism predicts that loss of $CH_3^{\cdot}$ from $1^{+\cdot}$ and $2^{+\cdot}$ should give $CH_2=C(CH_3)CH=O^+CH_3$ and $CH_3CH=CHCH=O^+CH_3$, respectively, Scheme 2.

The contrasting specificities predicted by Schemes 1 and 2

Table 1 CID spectra of $C_5H_9O^+$ ions[a]

| m/z	[M − CH₃]⁺ from 1	[M − CH₃]⁺ from 2	[M − C₂H₅]⁺ from 3[b]	[M − C₂H₅]⁺ from 4[b]	[M − CH₃]⁺ from 5	[M − CH₃]⁺ from 6	[M − C₂H₅]⁺ from 7	[M − C₂H₅]⁺ from 8
83	4	2	1	5	1	6	2	5
70	5	7	6	5	4	3	2	5
69	23	53	57	24	43	19	24	26
68		3	3		1		1	
59				1	1		1	1
57	2	2	1	3	2	2	5	3
56	2	1	2	5	2	2	3	4
55	100	84	76	100	70	100	100	100
54	6	9	9	6	5	5	6	4
53	36	61	59	27	49	27	25	33
52	3	4	4	3	3		1	2
51	7	9	9	6	6	4	5	6
50	4	6	6	4	4	4	2	3
45	23	43	42	15	39	21	19	17
43	17	8	5	12	26	14	11	11
42	9	15	16	10	14	5	9	8
41	45	54	55	56	61	45	47	51
40	5	8	7	7	7	4	4	6
39	78	100	100	87	100	77	79	74
38	7	9	10	8	9	5	7	7
37	2	3	3	3		2	1	1
33	2	4	4		3		1	
31	2	3	3	2	2	3	2	1
29	36	43	44	43	38	30	41	40
28	9	11	11	10	6	10	9	10
27	29	43	42	29	45	31	29	30
26	6	9	8	5	10	3	3	6
15	13	18	17	14	17	11	15	13

[a] Spectra were measured on a Kratos Analytical CONCEPT II HH four-sector mass spectrometer. The collision cell was floated at 4 kV above ground potential; the collision gas was helium, and the precursor ion beam was attenuated to 70% of its initial intensity. Quoted data are averaged spectra, compiled from 15 individual scans, normalised to a value of 100 units for the most abundant fragment ion. These spectra are essentially free from contributions from the dissociation of ions which have not been energised by collision. [b] Apart from complications caused by dissociation of ions which have not been energised by collision, these spectra are in excellent qualitative agreement with those (ref. 11) reported previously for these ions.
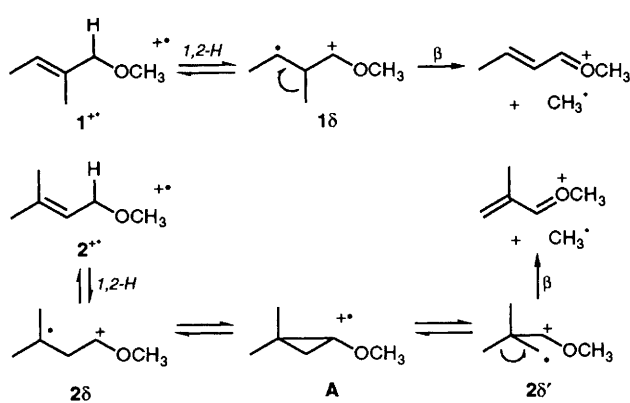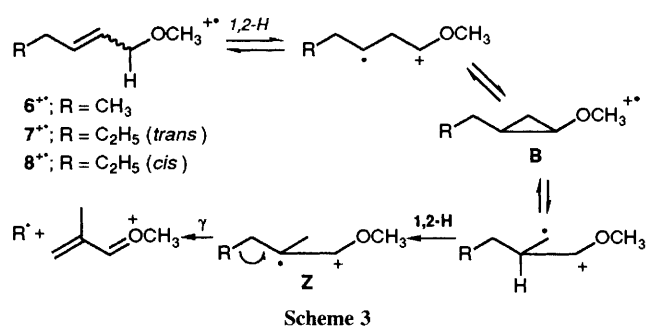

Scheme 1

Scheme 2

have been tested by determining the structures of the $C_5H_9O^+$ ions by measuring the collision-induced dissociation (CID) mass spectra of the $[M - CH_3]^+$ ions in the conventional spectra of **1** and **2**. The CID spectra of authentic $CH_3CH=CHCH=O^+CH_3$ and $CH_2=C(CH_3)CH=O^+CH_3$ were obtained by examining the $[M - C_2H_5]^+$ ions in the mass spectra of $CH_3CH=CHCH(C_2H_5)OCH_3$, **3**, and $CH_2=C(CH_3)CH(C_2H_5)OCH_3$, **4**, respectively. Analysis of these CID spectra reveals that Scheme 1 predicts the opposite specificity to that observed. In contrast, Scheme 2 does account for the experimental facts.

In addition, Scheme 2 correctly predicts that elimination of $CH_3\cdot$ from $CH_2=C(CH_3)CH_2CH_2OCH_3^{+\cdot}$, **5⁺·**, should give $CH_3CH=CHCH=O^+CH_3$. In this case, formation of the distonic ion, **1δ**, requires a 1,4-H shift in **5⁺·**. An analogous mechanism also explains the formation of
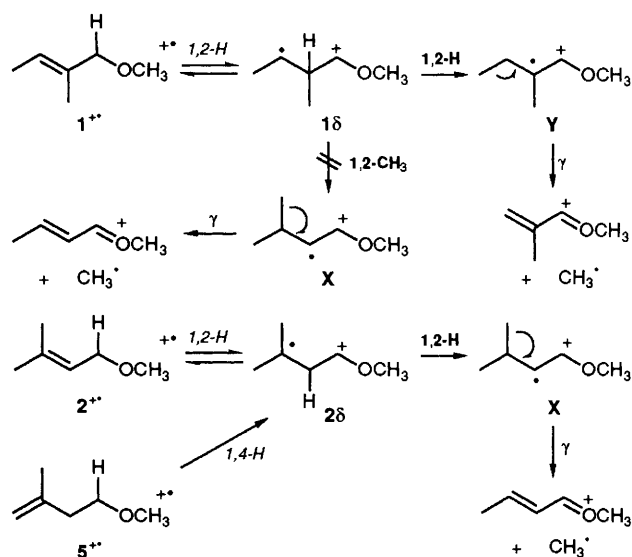
$CH_2=C(CH_3)CH=O^+CH_3$ by $CH_3\cdot$ loss from *cis*-$CH_3CH_2CH=CHCH_2OCH_3^{+\cdot}$, **6⁺·**, or by $C_2H_5\cdot$ loss from either *cis*- or *trans*-$CH_3CH_2CH_2CH=CHCH_2OCH_3^{+\cdot}$, **7⁺·** and **8⁺·**, Scheme 3. In these systems, reorganisation of the carbon chain, *via* distonic ions and ionised alkylmethoxy-cyclopropanes, **B**, precedes the crucial 1,2-H shift that leads to **Z**. Some of the steps (but not the 1,2-H shifts to radical centres) may be at least partially reversible, and are shown as such in the Schemes.

Scheme 3

Thus, a unifying explanation of the σ'-cleavage process is provided by mechanisms (Schemes 2 and 3) in which a 1,2-H shift at the radical site of a distonic ion leads to an ionised enol ether (**X**, **Y** or **Z**) which then fragments *via* γ-cleavage. The key step in these mechanisms is the 1,2-H shift. If such behaviour is general, then alkyl radical loss from ionised allylic alkenyl methyl ethers is even less simple than previously supposed.[3] Such 1,2-H shifts are known to be less facile than the corresponding processes at cationic centres.[6–9] Moreover, 1,2-shifts at radical centres have been shown to be of profound significance in the dissociation of ionised carboxylic acids.[8]

Two conclusions stem from this work. First, β-cleavage of distonic ions such as **1δ** involves an appreciable additional critical[10] energy, thus rendering this process unfavourable compared to rearrangement and eventual γ-cleavage. The reverse reaction in all probability proceeds *via* the same mechanism, but in the opposite direction, to that found for the forward process. Therefore, the reverse reaction (addition of an alkyl radical to a methyl cationated enal) should proceed *via* attachment of the alkyl group to the γ-carbon atom [conjugate addition, eqn. (1)] in preference to binding to the β-carbon atom [eqn. (2)]. Secondly, a 1,2-H shift at the radical centre takes place more readily than a 1,2-alkyl shift. Indeed, there is no evidence that 1,2-alkyl shifts of this kind occur in
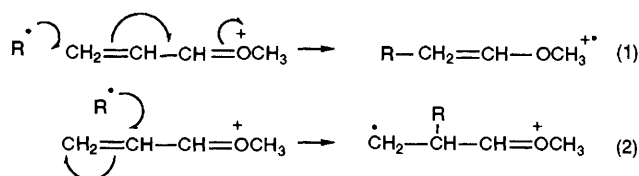
these systems; their occurrence would result in the formation of the same products as those accessible *via* β-cleavage [*e.g.* **1$^{+\cdot}$** → **1δ** → **X** → CH$_3$CH=CHCH=O$^+$CH$_3$, Scheme 2].

References

1 For an overview, see: G. Bouchoux, *Mass Spectrom. Rev.*, 1988, **7**, 1: 1988, **7**, 203.
2 R. D. Bowen, A. D. Wright, S. R. Thomas, K. R. Jennings and A. Maccoll, *Org. Mass Spectrom.*, 1991, **26**, 421.
3 R. D. Bowen and A. D. Wright, *J. Chem. Soc., Chem. Commun.*, 1991, 1055.
4 B. F. Yates, W. J. Bouma and L. Radom, *J. Am. Chem. Soc.*, 1984, **106**, 5808.
5 S. Hammerum, *Mass Spectrom. Rev.*, 1988, **7**, 123.
6 S. Hammerum, *Acta Chem. Scand.*, 1984, **38B**, 707.
7 H. Schwarz, T. Weiske, K. Levsen, A. Maquestiau, R. Flammang, *Int. J. Mass Spectrom. Ion Phys.*, 1982, **45**, 367.
8 T. Weiske and H. Schwarz, *Chem. Ber.*, 1983, **116**, 323; T. Weiske, H. Halim and H. Schwarz, *Chem. Ber.*, 1985, **118**, 495.
9 L. L. Griffin, K. Holden, C. E. Hudson and D. J. McAdoo, *Org. Mass Spectrom.*, 1986, **21**, 175; C. E. Hudson and D. J. McAdoo, *Tetrahedron*, 1990, **46**, 331.
10 A. Maccoll, *Org. Mass Spectrom.*, 1980, **15**, 109.
11 G. Bouchoux, Y. Hoppilliard and P. Jaudon, *Org. Mass Spectrom.*, 1987, **22**, 98.