Studies of Cyclic Acetals. Part XV.[1] Use of Alkyl Substituents as Pseudoisotopic Labels: Influence of a 4-Hydroxy-substituent upon the Electron-impact Mass Spectrum of Alkylated Derivatives of 3,6,8-Trioxabicyclo[3.2.1]octane

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Low-resolution, electron-impact mass spectra are tabulated for derivatives of the title compound having methyl substitutions in the following positions: 4,5 (1); 1,5 (2); 1,4,4 (3); 1,4,4,5 (4); 4,4,5,7,7 (5), for 5-methyl-3,6,8-trioxabicyclo[3.2.1]octan-4-ol (6) and its analogues in which the hydroxy-group is replaced by OMe (8), OEt (10), $OCMe_3$ (11), and OAc (12), and for 4,5-dimethyl-3,6,8-trioxabicyclo[3.2.1]octan-4-ol (7) and its 4-OMe analogue (9). A substantial portion of the decomposition subsequent to electron impact is rationalized according to a few, common fragmentation pathways, which are identified by analysis of mass-number shifts caused by changes in substitution; variations in relative abundance of major fragments as a function of substitution are consistent with conventional considerations of carbonium-ion stability. The presence of an oxygenated substituent at C-4 of these trioxabicyclo-octanes provides two additional fragmentation modes, whose relative prominence is also rationalized on the basis of general principles of stabilization of charges.

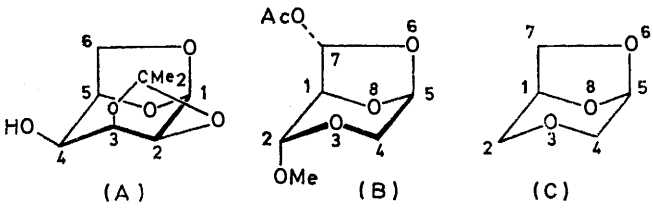
FRAGMENTATION subsequent to electron impact has been elucidated in detail for the heterobicyclic molecule 1,6-anhydro-2,3-*O*-isopropylidene-β-D-talopyranose [2] (A) and for the 3,4-*O*-isopropylidene [3] isomer by the combined techniques of data-reduced, high-resolution

[1] Part XIV, P. Calinaud, J. Gelas, and S. Veyssières-Rambaud, *Bull. Soc. chim. France*, 1973, 2769; for preceding, related paper, see ref. 2.

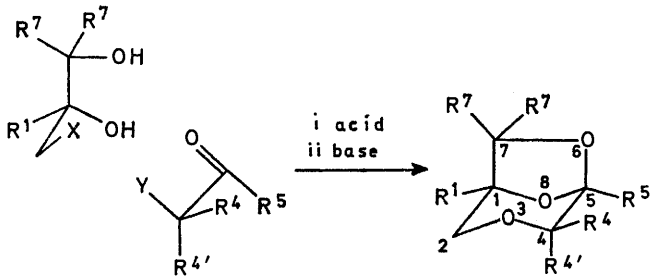
[2] D. Horton, E. K. Just, and J. D. Wander, *Org. Mass Spectrometry*, 1972, **6**, 1121.

[3] D. Horton, J. S. Jewell, E. K. Just, J. D. Wander, and R. L. Foltz, *Biomedical Mass Spectrometry*, 1974.

mass spectrometry and specific isotopic labelling.[4] The structurally related, bicyclic triacetal (1*S*,2*S*,7*S*)-7-acetoxy-2-methoxy-3,6,8-trioxabicyclo[3.2.1]octane [5] (B) has been subjected to detailed physical characterization,[6] although the electron-impact mass spectrum of this compound suffers from such an abundance of prominent fragments that only the molecular weight and the identity of the two substituents can be readily deduced.



As variously substituted examples of the 3,6,8-trioxabicyclo[3.2.1]octane ring system are readily available [7] by a two-step process effecting condensation [8] of appropriately alkylated derivatives of glycolaldehyde and glycerol (Scheme 1), the placement of substituents

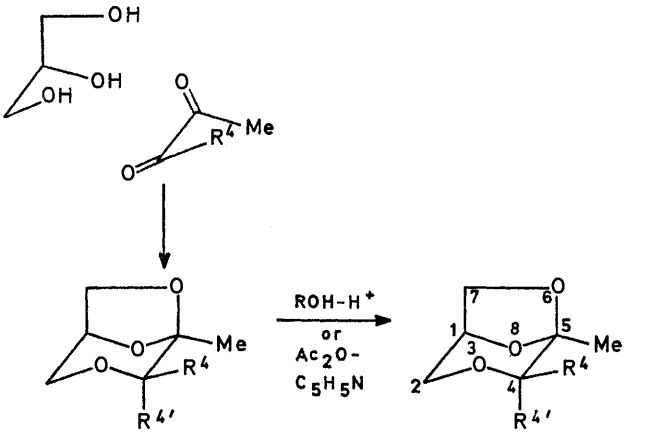


X,Y = OH or OAc, Cl

(1) $R^1 = R^{4'} = R^7 = H, R^4 = R^5 = Me$
(2) $R^4 = R^{4'} = R^7 = H, R^1 = R^5 = Me$
(3) $R^5 = R^7 = H, R^1 = R^4 = R^{4'} = Me$
(4) $R^7 = H, R^1 = R^4 = R^{4'} = R^5 = Me$
(5) $R^1 = H, R^4 = R^{4'} = R^5 = R^7 = Me$

SCHEME 1

in compounds (1)—(5) is, for the purpose of identifying fragmentation modes, equivalent to an isotopic labelling procedure if no new decomposition pathways are introduced by the substituents. Introduction of a hydroxy-group at the 4-position of the bicyclic ring system (C) is accomplished [9] by direct, equimolar condensation of butanedione or pyruvaldehyde with glycerol, as illustrated in Scheme 2; the methyl acetals (8) and (9) were prepared from (6) and (7), respectively, by acid-catalysed condensation with methanol, and (6) was converted into the ethyl and t-butyl acetals (10) and (11), respectively, by similar treatment with the appropriate alcohols under acidic conditions. The acetate (12) of (6) was formed by the action of acetic anhydride in dry pyridine. This report (a) generalizes the behaviour under electron impact of five racemic, methylated derivatives (1)—(5) of 3,6,8-trioxabicyclo[3.2.1]-octane in terms of fragmentation pathways that appear to be common to all five examples and to account for all the high-mass fragments plus many of the smaller ones, and (b) derives the major decomposition modes



(6) $R^4 = H, R^{4'} = OH$
(7) $R^4 = Me, R^{4'} = OH$
(8) $R^4 = H, R^{4'} = OMe$
(9) $R^4 = Me, R^{4'} = OMe$
(10) $R^4 = H, R^{4'} = OEt$
(11) $R^4 = H, R^{4'} = OBu^t$
(12) $R^4 = H, R^{4'} = OAc$

SCHEME 2

common to the 5-methyl-3,6,8-trioxabicyclo[3.2.1]-octan-4-ol derivatives (6)—(12), noting differences in the fragmentation processes brought about by the presence of the exocyclic oxygen atom.

RESULTS AND DISCUSSION

Relative intensities of selected ions observed in the 70 eV electron-impact mass spectrum of 4,5-dimethyl-3,6,8-trioxabicyclo[3.2.1]octane (1) and its 1,5-dimethyl (2), 1,4,4-trimethyl (3), 1,4,4,5-tetramethyl (4), and 4,4,5,7,7-pentamethyl (5) analogues are arranged in Table 1 in such a way as to highlight homologies that relate identified fragments.* In all five examples, the ion at largest mass number is the molecular ion ($M^{+\cdot}$). This ion is relatively abundant for the lower members (1)—(3) of this series, but is rather substantially decreased in intensity with increasing methylation. A very weak ion is observed 15 daltons below $M^{+\cdot}$; this may be attributed to the apparently disfavoured pro-

* Structures assigned to fragment ions are based on plausible mechanistic steps, but the possibility of isomeric structures is not excluded, especially for the smaller ions.

[4] D. Horton, J. S. Jewell, E. K. Just, and J. D. Wander, *Carbohydrate Res.*, 1971, **18**, 49; R. C. Dougherty, D. Horton, Kerstin D. Philips, and J. D. Wander, *Org. Mass Spectrometry*, 1973, **7**, 805; D. L. Corina and J. E. G. Barnett, *Adv. Carbohydrate Chem. Biochem.*, 1972, **27**, 128.

[5] R. J. Yu and C. T. Bishop, *Canad. J. Chem.*, 1967, **45**, 2195.

[6] J. Gelas, D. Horton, and J. D. Wander, *J. Org. Chem.*, in the press.

[7] P. Calinaud and J. Gelas, unpublished results; P. Calinaud, Thèse de 3e cycle No. 345, Clermont-Ferrand, 1973.

[8] E. G. Hallonquist and H. Hibbert, *Canad. J. Research*, 1933, **8**, 129; N. Baggett, J. M. Duxbury, A. B. Foster, and J. M. Webber, *J. Chem. Soc.* (*C*), 1966, 208; J. Gelas, *Bull. Soc. chim. France*, 1970, 3721, 4046.

[9] J. Gelas and A. Thiallier, *Carbohydrate Res.*, 1973, **30**, 21

cess of loss of a methyl group to generate, at least initially, a strained, bicyclic oxonium ion.

The most abundant fragment of higher mass number corresponds to the expulsion of a neutral carbonyl species from $M^{+\cdot}$; three different fragments might be

TABLE 1

Intensities * of major fragments † in the electron-impact mass spectra of the methylated 3,6,8-trioxabicyclo-[3.2.1]octanes (1)—(5)

m/e	(1)	(2)	(3)	(4)	(5)	Assignment
186					1	
172				1·5		$M^{+\cdot}$
158			9	0·1		
144	4	16				
171					0·6	
157				0·2		$M^{+\cdot} - CH_3$
143			1	0·1		
129	0·3	0·1		0·1		
142				0·7		
128			1		[24] ‡	*a*
114	0·2	[19] ‡				
128					24 ‡	
114		19 ‡		26		*b*
100	52		38		0·1	
102		2				
101		4			0·1	
87	0·4	6	3	4	2	
86	1	0·7	2	2	26	
72	5	75	55	100 ¶	3	*d*
58	28	3	9	2	1	
113	0·1	0·1	0·5	0·5	4	
99	0·2	2	2	4	0·3	
85	4	4	10	3	29	*g*
71	20	15	38	12	18	
57	16	15	57	7	8	
43	100 ¶	100 ¶	36	82	60	*e*
29	6	6	10	3	4	
84	28	6		1	1	*h*
69	4	2	2	5	10	
68	0·1	3	0·4	2	100 ¶	
54	1	10	36	10	0·3	*f*
40	2·5	2	3	1	2	
59	0·8	1	100 §	14	9	$Me_2\overset{+}{C}OH$
45	9	3	4			
31	3	1	8	1		
55	11	5	21	5	2	
41	18	14	15	6	12	
39	5	8	18	18	5	

* Expressed as percentage of the base peak. † Except where significant for the discussion, peaks having intensities <0·4% of the base peak are not recorded. ‡ The number in square brackets indicates the lesser of two isomeric species contributing to the ion current at the mass number in question. ¶ *Ca.* 30% of the net ionization >*m/e* 39. § *Ca.* 20% of the net ionization >*m/e* 39.

eliminated, and each elimination gives rise to a different product ion. Loss of O-6, C-7, and both R^7 groups would produce a species formulated as the 1,3-dioxanyl radical-cation *a*; similar expulsion of O-3 and C-4, together with R^4 and $R^{4'}$, would generate the 1,3-dioxolanyl radical-cation *b*; excision of O-3 and C-2 (as formaldehyde in all five examples) would lead to the analogous 1,3-dioxolanyl structure *c*. Ions *b* and *c* are both capable of tautomerization into the alternative structures, *b'* and *c'*, respectively, which may influence the relative stabilities of these ions.

The systematic variations in the numbered R groups in (1)—(5) are analogous to labelling the compound specifically at C-2, C-4, and C-7, because both the neutral carbonyl fragment and the odd-electron ion generated by decomposition of $M^{+\cdot}$ according to one of these pathways will exhibit substituent retention patterns characteristic of the particular pathway. Accordingly, the observation of a very prominent ion corresponding to loss of formaldehyde from (2), acetaldehyde from (1), and acetone from (3)—(5) specifies that fragment *b* (or its tautomeric allyl acetate form *b'*) is the principal charged product of this process; a lesser mode to form fragment *a* is revealed by minor ions corresponding to loss of formaldehyde from (1), (3), and (4) [the same loss from (2) is ambiguous] and of acetone (also degenerate with formation of *b*) from (5). The remaining fragment *c* may be excluded from consideration because no evidence is present for loss of formaldehyde from (5).

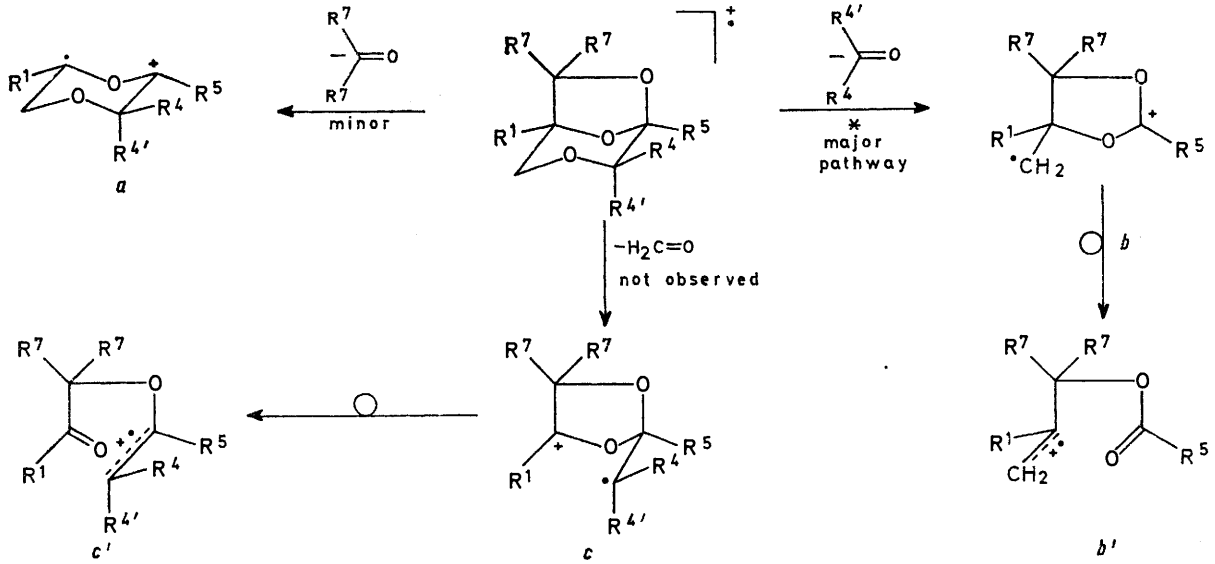
The allyl acetate radical-cation *b'* appears to be also an intermediate in the formation of some prominent smaller fragments (Scheme 4). Loss of keten from (1), (2), (4), and (5) or carbon monoxide from (3) produces the corresponding alcohol ion *d*, which constitutes the base peak for (4), whereas retention of the proton and the charge by the carbonyl portion produces the acylium ion *e*, which is the base peak for (1) and (2); the comparatively low abundance of *m/e* 43 in the spectrum of (3) presumably arises through another pathway discussed later. A third decomposition of *b'* is by loss of R^5CO_2H to produce the hydrocarbon ion *f*, which is relatively minor for the less substituted examples but appears as the base peak in the spectrum of (5).

A methylene-homologous series proceeding down wards from *m/e* 113 contributes a modest portion of the net ion-current. Evidence by which this series may be defined is relatively scarce and ambiguous. However, the structures *g* and *g'* (or isomers thereof) may be proposed (Scheme 5) to account for a portion of the ion current at *m/e* 85 in the spectrum of (1) and (3) because of the apparent shifts of this fragment to *m/e* 113 in the spectrum of (5), which indicates retention of both R^7 groups, and to *m/e* 99 in the spectrum of (2) and (4), in which both R^1 and R^5 are methyl groups.

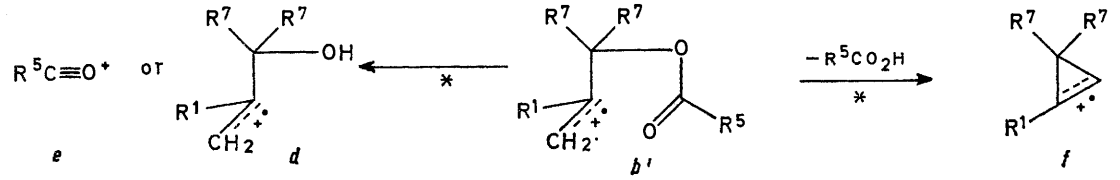
Protonated acetone (*m/e* 59) is a relatively abundant fragment in the spectra of (4) and (5), and is the base peak for (3). It may be observed that (3), which has a proton replacing the methyl group at the cationic centre of *b*, exhibits *m/e* 59 as the base peak of its spectrum, whereas in the remaining four examples this peak is at least an order of magnitude less important. This observation may indicate that this ion is formed initially in competition with *b*. A related process, in which a methyl group is lost rather than a proton captured, is presumably responsible for part of the ion current at *m/e* 43, especially in the spectrum of (3).

The relatively prominent ion at *m/e* 84 in the spectrum

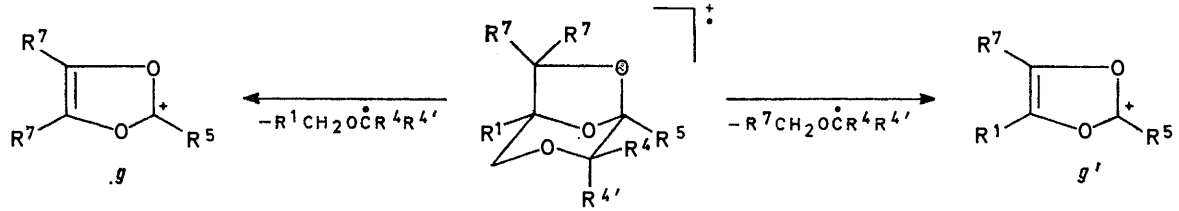
of (1) and (2) is evidently formed directly from $M^{+\cdot}$; a plausible mechanism for this process, for which metastable evidence (Table 2) is found in both spectra, would involve concerted loss of C-5 and three of its substituents, together with 4-H as acetic acid, to generate the tetrahydrofurylium ion *h*, as illustrated in Scheme 6. The absence of a proton on C-4 of (3)—(5) may account for the insignificance of this fragment



SCHEME 3



SCHEME 4



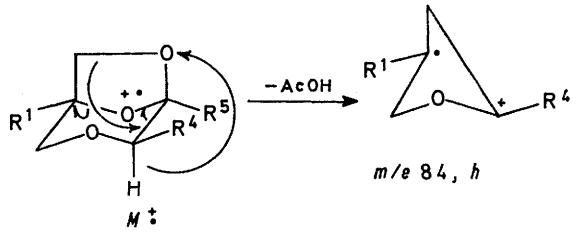
SCHEME 5

TABLE 2

Prominent metastable fragments observed in the electron-impact mass spectra of (1)—(5)

m/e Obs.	*m/e* Calc.	Process	Compound
90·5	90·25	$M^{+\cdot} \longrightarrow b$	(2)
66·0	66·05	$(70 \longrightarrow 68)$	(5)
50·8	50·52	$(143 \longrightarrow 85)$	(3)
49·0	49·00	$M^{+\cdot} \longrightarrow 84$	(1), (2)
45·5	45·47	$b \longrightarrow d$	(2)—(4)
36·1	36·20	$b \longrightarrow f$	(5)
33·8	33·64	$b \longrightarrow f$	(1)
29·3	29·43	$(171 \longrightarrow 71)$	(5)
28·3	28·50	$b \longrightarrow 57$	(2), (3)
25·7	25·68	$d \longrightarrow 43$	(1), (2)
24·2	24·36	$(69 \longrightarrow 41)$	(5)
18·4	18·49	$b \longrightarrow e$	(1)

(or methylene-homologues thereof) in the decomposition products from these three examples.



SCHEME 6

A complete identification of the remaining, smaller ions is not supported by obvious patterns of mass-

number dependence upon substitution. Nonetheless, it has been shown that the decomposition of (1)—(5) is, in the main, exceedingly simple and that the single species *b* and its secondary fragments account for almost all the ions formed subsequent to electron impact. This behaviour is in sharp contrast to that of the 7-acetoxy-2-methoxy-analogue (B),[5] whose mass spectrum [6,10] displays a plethora of ions of comparable prominence.

(7), the acetals (8)—(11), and the ester (12) are presented in Table 3 in an array that indicates homologous relationships in the larger fragments. A number of metastable ions, which were of assistance in the elucidation of several of the fragmentation processes to be discussed, were observed and are recorded in Table 4.

In distinct contrast with the rather stable molecular ions derived from the methylated trioxabicyclo-octanes (1)—(5), molecular ions derived from (6)—(12) are

TABLE 3

Intensities * of principal fragments † in the electron-impact mass spectra of 3,6,8-trioxabicyclo[3.2.1]octane derivatives (6)—(12)

m/e	(6)	(8)	(10)	(11)	(7)	(9)	(12)	Assignment
202				0·04				
188								
174			0·03			0·01		$M^{+\cdot}$
160		0·02						
146	1							
187				0·5				
173								
159			0·05			2		$M^{+\cdot} - \cdot CH_3$
145		[0·4] ‡			0·05			
131	0·5							
173				0·3				
159								
145			[5] ‡					$M^{+\cdot} - \cdot CHO$ (?)
131								
117	[18] ‡							
159					0·01	2		*i*
145		0·4 ‡	5 ‡	52			4	
143					0·1	12		*k*
129	4	2	9	21	0·3		6	
117	18 ‡	0·8	0·4	1	2	0·5	0·2	*j*
116				3			2	
115	7							
103	2							
101				8	10			
100	60	36	30	12	9 ‡	32 ‡	26	*b*
89		3						
87	4	7	0·8	3		9	1	
100					[9] ‡	[32] ‡		*l*
86	7	0·6	0·5	3			2	
85	6	1	0·8	1	0·5	0·8	1	*g*
75		3	1			7		$C_3H_7O_2^+$
73	14	8	10	10	1·5	4	6	*m*
61	19	5	3	3	2	2	4	*n*
58	35	11	13	8	4	14	13	*d*
57	42	15	12	33 ¶	11	12	15	$C_3H_5O^+$
43 §	100	100	100	100	100	100	100	CH_3CO^+

*, † See Table 1. ‡ Two fragments contribute to the net ion current at this mass number; the number is placed to identify the more important contributor. ¶ The Me_3C^+ ion undoubtedly contributes to the ion current at *m/e* 57 in (11). § This ion represents 30 (6), 75 (7), 50 (8), 50 (9), 55 (10), 40 (11), and 55% (12) of the net ion current > *m/e* 42.

Alterations in the fragmentation modes of (1) (caused by the introduction of a single oxygenated group at C-4) were determined for the hemiacetal 5-methyl-3,6,8-trioxabicyclo[3.2.1]octan-4-ol (6), its methyl (8), ethyl (10), and t-butyl (11) acetal analogues, and its acetic ester (12), all of which correspond to replacement of R^4 by the oxygenated group, and for the hemiacetal 4,5-dimethyl-3,6,8-trioxabicyclo[3.2.1]octan-4-ol (7) and the analogous methyl acetal (9), both of which correspond to introduction of the oxygenated function with retention of the 4-methyl group. Relative intensities of the principal ions observed in the 70 eV electron-impact mass spectrum of the hemiacetals (6) and either very weak or are not observed at all, and no systematic dependence upon substitution is in evidence. A very minor process forming the $M^{+\cdot} - 15$ ion is presumed to be analogous to the formation of the similarly minor $M^{+\cdot} - 15$ ion postulated as a bicyclic oxonium ion in the decomposition of (1)—(5). The mass spectrum of (11) exhibits a weak ion presumably formed by loss of 29 daltons (Et· or ·CHO) from $M^{+\cdot}$, although no other definite evidence was observed to support or identify this process.

Principal decomposition modes of these derivatives appear to be directed by the exocyclic, oxygenated

[10] D. Horton and J. D. Wander, unpublished data.

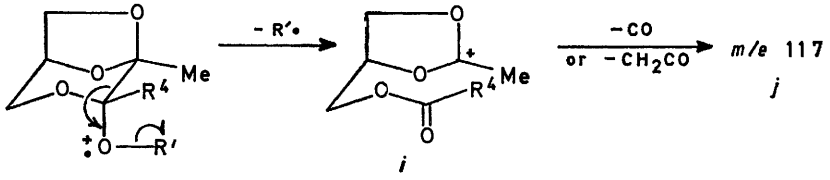
substituent. The largest-mass ion of any prominence is formed from $M^{+\cdot}$ by scission of the O–R′ bond within

TABLE 4

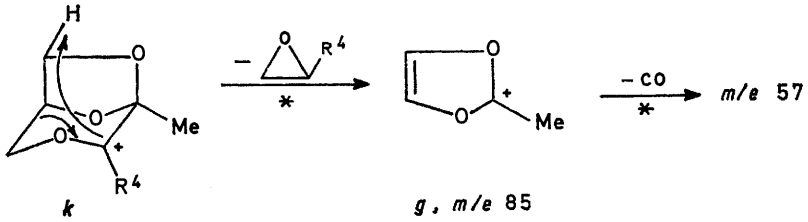
Prominent metastable fragments observed in the electron-impact mass spectra of 3,6,8-trioxabicyclo[3.2.1]-octane derivatives (6)—(12)

Obs.	Calc.	Process	Compound
57·2	57·33	$k \longrightarrow l$	(6)
56·2	56·01	$k \longrightarrow g$	(6), (7), (11)
52·9	53·29	$b \longrightarrow m$	(10)
43·2	43·32	$C_3H_7O_2^+ \longrightarrow C_3H_5O^+$	(12)
38·3	38·22	$g \longrightarrow C_3H_5O^+$	(7)
37·2	37·21	$b \longrightarrow n$	(8), (10), (11)
33·7	33·64	$b \longrightarrow d$	(8), (10)
30·2	30·31	$n \longrightarrow CH_3CO^+$	(12)
25·2	25·33	$m \longrightarrow CH_3CO^+$	(8), (10), (11)
22·3	22·41	$i \longrightarrow C_3H_5O^+$	(11)
18·4	18·49	$b \longrightarrow CH_3CO^+$	(6)—(12)
14·6	14·33	$k \longrightarrow CH_3CO^+$	(10)
12·7	12·75	$i \longrightarrow CH_3CO^+$	(11)
11·7	11·63	$(M^{+\cdot} - 15) \longrightarrow CH_3CO^+$	(10)

$R^{4\prime}$, with presumed concurrent rupture of the C-4–C-5 bond to generate the dioxolanium cation *i*, as depicted in Scheme 7. The intensity of *i* appears to be determined by the stability of the radical R′· that is eliminated when *i* is formed. Subsequent loss from *i* of carbon monoxide [(6), (8), (10)—(12)] or of keten [(7), (9)] is presumed to lead to the corresponding alcohol *j*. The ion current at *m/e* 117 in the spectrum of (1) may arise also partly from the loss of a formyl radical from $M^{+\cdot}$, although no obvious mechanism is evident to account for its particular prominence in the spectrum of (1). More extensive fragmentation of *i* leads to *m/e* 57 ($C_3H_5O^+$), for which a number of plausible structures may be envisaged, and to *m/e* 43 ($CH_3C{\equiv}O^+$), which is in all instances the most abundant fragment. Metastable ions verify both these processes.



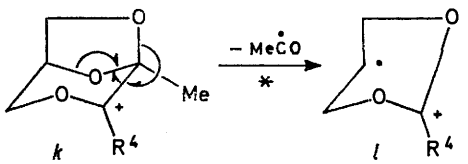
SCHEME 7



SCHEME 8

Cleavage of the C-4–OR′ bond is an initial fragmentation of $M^{+\cdot}$ that is more generally significant, presumably because of the lower degree of strain anticipated for the resulting oxonium ion *k*; the relative abundance of this ion appears to reflect the extent of steric relief obtained by loss of OR′. Further decomposition of *k* by loss of C-2, O-3, and C-4 as an epoxide derivative to form *m/e* 85, presumably the 2-methyl-1,3-dioxolylium ion (Scheme 8) already postulated as *g*, is verified by a metastable ion, as is the subsequent loss of carbon monoxide from a presumably rearranged form of *g* to produce one of the ions contributing to the ion current at *m/e* 57. One further descendant of *k* may arise by expulsion of C-5 and O-8 as an acetyl radical to produce the odd-electron ion *l* (Scheme 9).

The most important single mode of fragmentation from $M^{+\cdot}$ is cleavage of the C-2–O-3 and C-4–C-5 bonds to excise the neutral ester fragment R^4CO_2R' ($R^4COR^{4\prime}$) and generate the odd-electron ion *b* at *m/e* 100. This reaction, which is exactly analogous to the principal decomposition step of the alkylated 3,6,8-trioxabicyclo-[3.2.1]octanes (1)—(5), appears to be in direct competition with the formation of *i*, because the abundance of *b* decreases with increasing stability (and size) of $R^{4\cdot}$, in direct contrast with the behaviour of *i*. The actual prominence of *b* as a product of decomposition of $M^{+\cdot}$ far exceeds the ion current measured at *m/e* 100, as attested by very substantial metastable ions heralding further decompositions of *b*, presumably by loss of the hydrocarbon fragments $C_2H_3^\cdot$ and $C_3H_3^\cdot$, by loss of keten, and by loss of a neutral C_3H_5O radical,

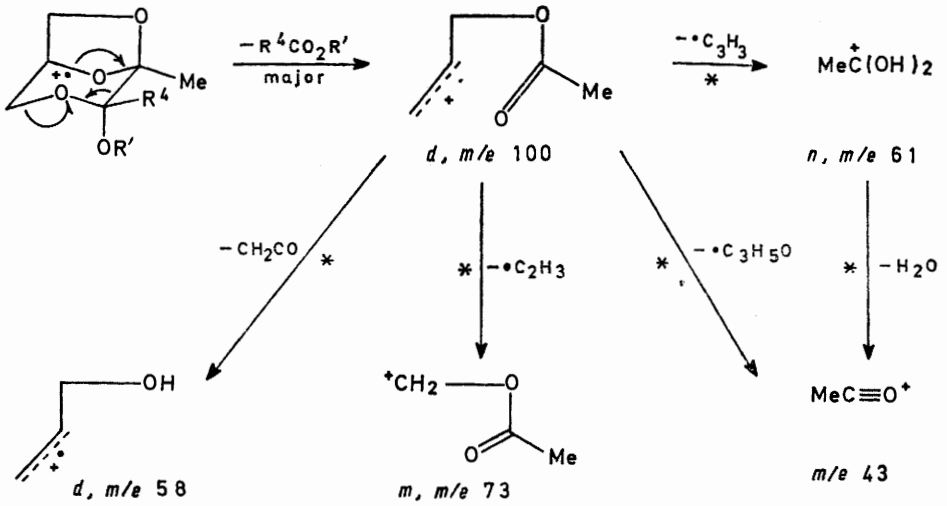


SCHEME 9

to form the acetoxymethyl cation *m*, protonated acetic acid *n*, the allyl acetate radical-cation *d*, and the acetylium ion (*m/e* 43), respectively (Scheme 10). Although the relative prominence of the ion *b* is essentially unaffected by the oxygenated substituent at C-4, the somewhat greater tendency of this ion to fragment further in the mass spectra of (6)—(12) suggests a

possible difference in the internal energy of *b* as a function of original substitution.

Substantial contributions to the acetylium ion (*m/e* 43) peak are also seen (Table 4) to originate from the $M^{+\cdot} - 15$ ion and from *k*, *m*, and *n*. The degree to which the fragmentation of (6)—(12) is dominated by this ion appears to be determined by the extent of availability of other, favoured processes. Thus, (6) forms *b* in greater amounts than the others and (11) produces a very substantial amount of *i*, whereas (7) generates no other prominent cations, owing perhaps to the presence of the incipient acetyl residue present in the C-4 substitution; the comparative unimportance of *m/e* 43 in the decomposition of the acetate (12) suggests that initial fragments formed from (12) are sufficiently stable to support competition with the acetyl group for the positive charge.



SCHEME 10

EXPERIMENTAL

Mass spectra of (1)—(5), (8), (10), and (11) were determined on a DuPont 21–490 mass spectrometer; samples of (8), (10), and (11) were introduced through a direct insertion probe and ionized at a source temperature of 170° with 70 eV ionizing potential. Samples of (1)—(5) were purified on a ¼ in (o.d.) column of SE-30 on Chromosorb W at a column temperature of 110° and a helium flow rate of 60 cm^3 min^{-1}, and introduced through a single-stage jet separator into the source, which was kept at 170°. Uniformity of the eluate was verified by the acquisition of several scans over the width of the gas chromatographic peak. Spectra of (6), (7), (9), and (12) were determined on an A.E.I. MS-9 double-focusing mass spectrometer at a source temperature of 150°, 70 eV ionizing potential, and an accelerating potential of 8 kV. The shorter flight-path in the DuPont instrument appears to enhance the population of metastable ions. Spectra were recorded by C. R. Weisenberger and R. Patterson.

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