# FRAGMENTATION OF ISOMERIC DIDEOXY DERIVATIVES OF 1,6-ANHYDRO-β-D-HEXOPYRANOSES UNDER ELECTRON IMPACT

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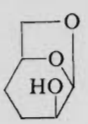
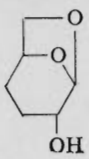
Electron impact mass spectra of all possible dideoxy derivatives of 1,6-anhydro-β-D-hexopyranoses and their sixteen specifically deuterium-labeled derivatives are reported. The spectra of positional isomers differ considerably making possible the reliable location of the hydroxyl group by mass spectrometry. The configuration of the hydroxyl group at $C_{(2)}$ and $C_{(4)}$ has only a negligible effect on the fragmentation pattern of stereoisomers. However, mass spectra of the $C_{(3)}$-configurational isomers differ sufficiently to permit a stereochemical assignment. The fragmentation paths were elucidated by means of deuterium labeling and metastable spectra.

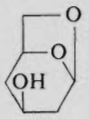
Derivatives of 1,6-anhydro-β-D-hexopyranoses are often found among degradation products of oligo- and polysaccharides[1]. Analyses of these complex mixtures can be conveniently conducted by gas chromatography-mass spectrometry techniques, provided the components are sufficiently volatile. If less volatile, the newly developped tandem mass spectrometry (MS–MS) technique could be employed[2]. In order to identify an unknown compound in a complex mixture it is necessary to have good reference spectra at hand or, alternatively, to understand thoroughly the fragmentation of closely related compounds. Hitherto only a few papers have appeared[3–5] dealing with the decomposition routes of fully functionalized 1,6-anhydro-β-D--hexopyranoses. The present paper is aimed at mapping and rationalizing the electron--impact mass spectra of a complete series of isomeric dideoxy derivatives *I–VI*, prepared earlier in this laboratory[6,7]. Since the compounds investigated provide examples of both positional isomerism and stereoisomerism we were also interested in the stereochemistry of ion decompositions. From a stereochemical point of view, the conformational mobility of the pyranose ring in *I–VI* is greatly reduced by the 1,6-anhydro bridging and it is known that in similar carbocyclic systems the mass spectra strongly depend on the hydroxyl group configuration[8]. On the other hand, it could be assumed that the acetal functionality in *I–VI* would induce a rapid ring cleavage, thus diminishing or even destroying the stereochemical effects of the hydroxyl group.



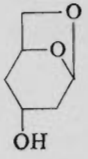
*I*
*Ia*: 2-$^2H_1$
*Ib*: 3,3-$^2H_2$



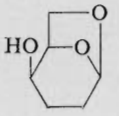
*II*
*IIa*: 2-$^2H_1$
*IIb*: 3,3-$^2H_2$
*IIc*: O$^2$H



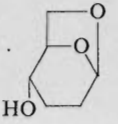
*III*
*IIIa*: 3-$^2H_1$
*IIIb*: 2,2,4,4-$^2H_4$
*IIIc*: O$^2$H



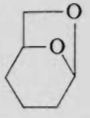
*IV*
*IVa*:3-$^2H_1$
*IVb*: 2,2,4,4-$^2H_4$



*V*
*Va*: 4-$^2H_1$
*Vb*: 3,3-$^2H_2$



*VI*
*VIa*: 4-$^2H_1$
*VIb*: 3,3-$^2H_2$
*VIc*: O$^2$H
*VId*: 2,3-$^2H_2$

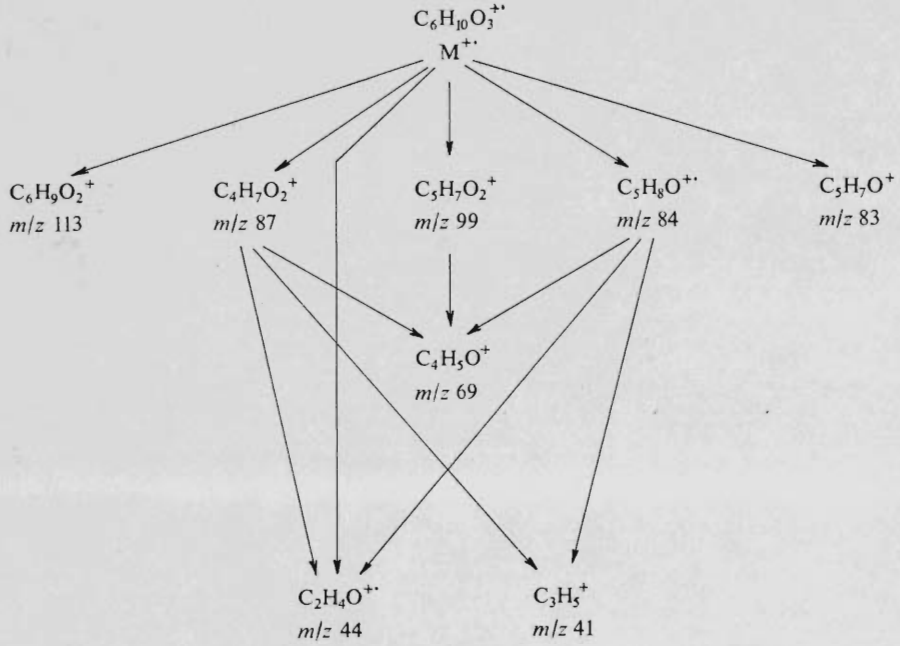


*VII*

The fragmentations induced by the acetal grouping can be traced in the mass spectrum of the "parent" compound 6,8-dioxabicyclo[3.2.1]octane (*VII*) (Table I). The spectrum can be interpreted assuming a primary cleavage of the $C_{(1)}$—$C_{(2)}$ bond, in analogy with other acetals[9]. The molecular ions further decompose by subsequent expulsion of ethylene (ions $C_4H_6O_2^{+\bullet}$, *m/z* 86) and the aldehyde group (ions $C_3H_5O^+$, *m/z* 57). In a competing reaction, both the $C_{(5)}$—$O_{(5)}$ and $C_{(6)}$—$O_{(6)}$ bonds are cleaved with loss of formic acid to generate $C_5H_8^{+\bullet}$ ions, *m/z* 68. Decomposition of metastable ions in the first field-free region (FFR) reveals that the $C_3H_5O^+$ and $C_3H_6O^{+\bullet}$ ions also originate directly from the molecular ions, probably because of a different kind of skeletal fission.

Introduction of a hydroxyl group at $C_{(2)}$ has a profound effect on the mass spectra of *I* and *II* (Table I). The origin of significant ions *m/z* 99 ($C_5H_7O_2^+$), 87 ($C_4H_7O_2^+$), 84 ($C_5H_8O^{+\bullet}$), 83 ($C_5H_7O^+$), 69 ($C_4H_5O^+$), 44 ($C_2H_4O^{+\bullet}$) and 41 ($C_3H_5^+$) was determined from their metastable spectra in the first FFR and is depicted in Scheme 1.

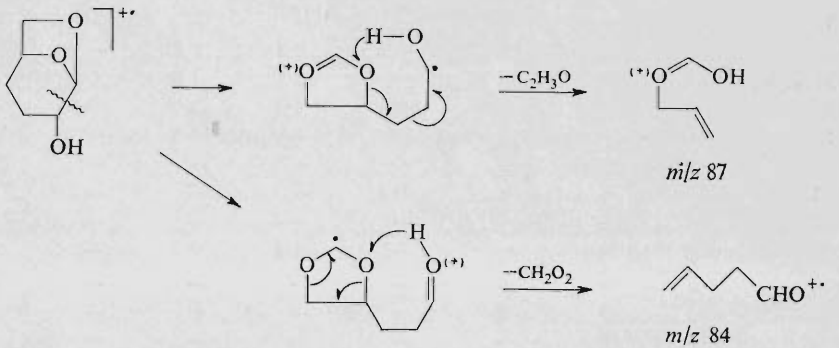
The loss of a $C_2H_3O$ radical from the molecular ion, leading to the *m/z* 87 ions is depicted in Scheme 2. The proposed mechanism is supported by the spectra of labeled compounds *Ia*, *Ib*, *IIa*, *IIb* and *IIc*. As documented in Table I, the deuterium from $C_{(3)}$ (compounds *Ib* and *IIb*) and $C_{(2)}$ (compounds *Ia* and *IIa*) is carried away in the neutral fragment, while the hydroxyl deuterium (compound *IIc*) is preserved in the ion.




SCHEME 1

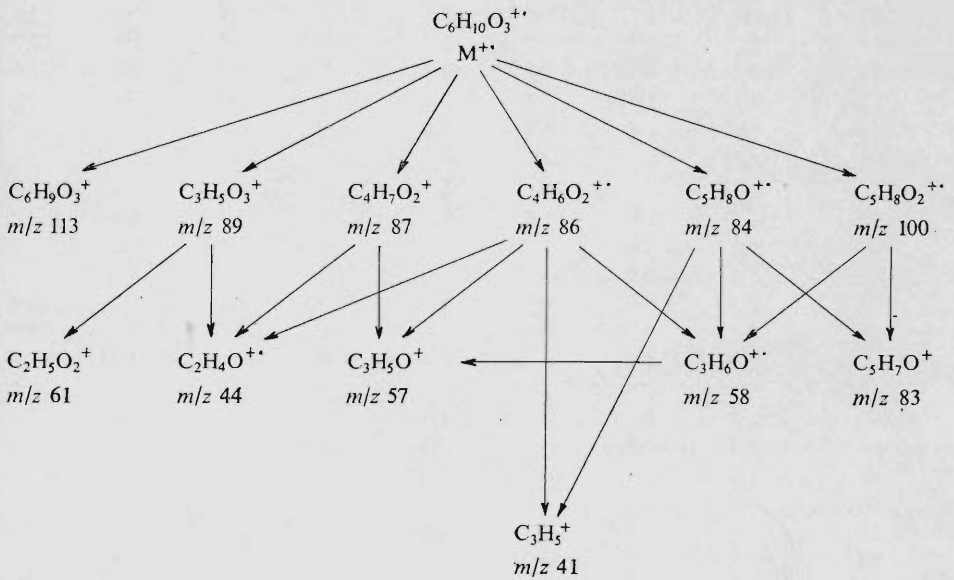
The formic acid elimination from the molecular ion, leading to $m/z$ 84, involves also transfer of the hydroxyl hydrogen (Scheme 2); however, a small (less than 10%) fraction loses the $C_{(2)}$ hydrogen instead (Table I, compounds *Ia*, *IIa*). Further decomposition of both $m/z$ 87 and $m/z$ 84 ions generates $C_3H_5^+$, $m/z$ 41. The spectra of the labeled compounds confirm that the latter ion species contain the $C_{(4)}$—$C_{(5)}$—$C_{(6)}$ segment and that they are formed by a simple fission of the $C_{(6)}$—$O_{(6)}$, $C_{(5)}$—$O_{(5)}$ and $C_{(3)}$—$C_{(4)}$ bonds, without complicating hydrogen migrations. Complementarily to ions $m/z$ 87 are formed the two-carbon fragments $m/z$ 44 and 43. The former ions originate by a clean cleavage of the $C_{(1)}$—$_{(2)}$ and $C_{(3)}$—$C_{(4)}$ bonds, as corroborated by appropriate mass shifts in the spectra of the labeled analogues ($m/z$ 44 to $m/z$ 45 for *Ia*, *IIa* and *IIc*, $m/z$ 44 to $m/z$ 46 for *Ib* and *IIb*; see Table I). On the other hand, the $C_2H_3O^+$ ions do not contain a hydroxyl hydrogen. Specificity of this hydrogen transfer could not be determined at 75 eV because of a competing loss of the hydrogen from $C_2H_4O^{+\cdot}$ ions. The 15 eV spectra of *I* and *II* are dominated by the $C_5H_8O^{+\cdot}$ and $C_2H_3O^+$ ions. The highly specific formation of the $C_5H_8O^{+\cdot}$ and $C_4H_7O_3^+$ ions is preserved also at 15 eV; in addition, the complementary specific formation of the $C_2H_3O^+$ ions is clearly discernible showing mass shifts $m/z$ 43 to $m/z$ 44 with *Ia* and *IIa*, $m/z$ 43 to $m/z$ 45 with *Ib* and *IIb* and the retention of $m/z$ 43 with *IIc*. The stereochemical effect of the hydroxyl group at $C_{(2)}$ on fragmentation

routes in *I* and *II* is negligible and, in fact, mass spectra of the pairs of isomers *I*–*II*, *Ia*–*IIa* and *Ib*–*IIb* are almost superimposible in the range 14–75 eV. This is probably caused by a very facile rupture of the $C_{(1)}$—$C_{(2)}$ bond which destroys the configurational identity of the hydroxyl group prior to fragmentation of the molecular ion.




SCHEME 2

By contrast, the 3-hydroxy derivatives *III* and *IV* differ slightly in relative intensities of several ion species. The origins of significant fragments are summarized in the fragmentation map (Scheme 3). Ions $C_3H_5O^+$, *m/z* 89, originate from the molecular




SCHEME 3

TABLE I

Mass spectra of compounds *I*, *Ia*, *Ib*, *II*, *IIa*, *IIb*, *IIc*, and *VII*

| *m/z* | relative intensity (% of base peak) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *I* | *Ia* | *Ib* | *II* | *IIa* | *IIb* | *IIc* | *VII* |
| 133 | — | — | 0·8 | — | — | — | — | — |
| 132 | 0·2 | — | 0·8 | — | 0·3 | 1·1 | — | — |
| 131 | 0·4 | 0·7 | 0·7 | — | 2·1 | 1·9 | 0·9 | — |
| 130 | 0·9 | — | 0·5 | 0·5 | 1·2 | 2 | 0·5 | — |
| 115 | 0·6 | — | 0·9 | — | — | 4·5 | — | 1·7 |
| 114 | — | — | — | — | — | — | — | 20·6 |
| 113 | — | — | — | 0·4 | — | — | — | 0·5 |
| 111 | 0·7 | — | — | — | — | — | — | — |
| 109 | 0·8 | — | — | — | 1·9 | 2·7 | — | — |
| 102 | — | — | 0·7 | — | — | — | — | — |
| 101 | — | — | 0·9 | — | — | — | — | — |
| 100 | — | 0·9 | — | — | — | — | — | — |
| 99 | 1·4 | — | — | 0·8 | — | — | — | — |
| 98 | 1 | — | — | — | — | — | — | — |
| 97 | 1·1 | — | — | — | 3·2 | 2·5 | 0·9 | — |
| 95 | 1·4 | 0·8 | — | 0·5 | 4·1 | 3 | 1·1 | 0·5 |
| 89 | — | — | — | — | — | — | 1·1 | — |
| 88 | 0·7 | 0·6 | 0·9 | 0·6 | 0·6 | — | 19·3 | — |
| 87 | 11·1 | 17·1 | 18·2 | 12·5 | 16·9 | 19·8 | 6·9 | 1·3 |
| 86 | 0·9 | 3·3 | 41·6 | 0·9 | 2·6 | 33·6 | 2·2 | 19·6 |
| 85 | 2·5 | 22·7 | 16·8 | 2·5 | 31·2 | 17·5 | 17·6 | 3·6 |
| 84 | 35 | 24·6 | 5·4 | 33·7 | 24·8 | 8·2 | 61·9 | 10·3 |
| 83 | 14·5 | 6·3 | 2·7 | 12·8 | 7·7 | 5·7 | 19·8 | 3·6 |
| 82 | 2·1 | 3·7 | 2·1 | 2 | 3·8 | 4·4 | 3·8 | 0·7 |
| 81 | 2·9 | 1·2 | 1·3 | 2·4 | 3·3 | 4·5 | 4 | — |
| 78 | 0·5 | — | — | — | — | — | — | 2·6 |
| 77 | 1·1 | — | — | — | 4·8 | — | — | — |
| 74 | — | 1·6 | 1·6 | — | 1·9 | 3·4 | 1·9 | — |
| 73 | 1·2 | 2·4 | 2 | 1·5 | 3·2 | 2·3 | 2·6 | — |
| 72 | 1·6 | 2·4 | — | 1·6 | 1·3 | — | 3 | — |
| 71 | 2·5 | 1·6 | 4·7 | 1·9 | 3·7 | 6·1 | 2·1 | 2·1 |
| 70 | 1·5 | 7·7 | 4·7 | 1·2 | 5·8 | 6·8 | 2 | 1·1 |
| 69 | 7·7 | 4·9 | 4 | 7·4 | 7·3 | 9·5 | 12·9 | 4·4 |
| 68 | — | 1·6 | 2 | — | 2·6 | 2·3 | — | 34·3 |
| 67 | 2·2 | 2·8 | 2·3 | 1·4 | 5·8 | 6·8 | 2·4 | 17·2 |
| 66 | 2·2 | 0·8 | — | 2·1 | 2·6 | — | 3·1 | 1·1 |
| 65 | 1·4 | — | — | 1·1 | 3·1 | 2·3 | — | 1 |
| 60 | — | — | 3·8 | 0·6 | — | 4·5 | 4 | — |
| 59 | 5·6 | 9·1 | 16 | 4·6 | 7·1 | 15·5 | 5·6 | 1·4 |
| 58 | 7·5 | 13·2 | 24·3 | 5·4 | 13·4 | 23·9 | 17·7 | 34·3 |

TABLE I
(*Continued*)

| *m/z* | relative intensity (% of base peak) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *I* | *Ia* | *Ib* | *II* | *IIa* | *IIb* | *IIc* | *VII* |
| 57 | 22·8 | 36·9 | 41·6 | 22·6 | 38·1 | 52·7 | 29·1 | 100 |
| 56 | 15 | 23 | 24·6 | 14·2 | 24·5 | 27·3 | 28·2 | 5·4 |
| 55 | 25·4 | 24·6 | 12·6 | 23·4 | 28·5 | 18·2 | 37·6 | 15 |
| 54 | 4 | 5·6 | 2·4 | 3·9 | 5·2 | 1·1 | 6·6 | 1·3 |
| 53 | 3·8 | 2·4 | 1·3 | 3·7 | 3·9 | 2·3 | 4 | 8·3 |
| 52 | 1 | 0·8 | 0·8 | 0·8 | — | 0·9 | 0·5 | 1·3 |
| 51 | 1·9 | 1·2 | 1·3 | 1·5 | 4·5 | 5·7 | 2·2 | 2·8 |
| 50 | 1·2 | — | — | 1 | — | — | 1·4 | 1·6 |
| 49 | — | — | — | — | — | — | 2·9 | — |
| 48 | — | 1·6 | — | — | — | — | — | — |
| 47 | 2 | 1·6 | 5·3 | 2·8 | 2·1 | 6·4 | 1·9 | 1·5 |
| 46 | — | 5·2 | 47 | — | 5·7 | 40·9 | 5·7 | — |
| 45 | 5·5 | 53·2 | 28·6 | 5·9 | 54·8 | 30·7 | 64·7 | 2·9 |
| 44 | 48·3 | 33·3 | 25·1 | 51·4 | 36·1 | 33 | 35·7 | 8·3 |
| 43 | 38 | 19 | 25 | 38·8 | 23·2 | 30·7 | 57·9 | 12·1 |
| 42 | 7 | 16·5 | 15 | 6·5 | 13·7 | 17·3 | 14·1 | 8·3 |
| 41 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 30 |
| 40 | 4·8 | 7·9 | 10·3 | 5 | 9·7 | 10·7 | 8·8 | 14·2 |
| 39 | 15·2 | 14·3 | 9·4 | 15·1 | 19·3 | 14·1 | 22·8 | 23·5 |
| 38 | 1·5 | 1 | — | 1·3 | 1·9 | — | 2 | 2·4 |

ions by the loss of $C_3H_5$ radical. As follows from the spectra of labeled analogues (Table II, compounds *IIIa,b,c* and *IVa,b*), the hydrogen atoms from $C_{(2)}$, $C_{(3)}$ and $C_{(4)}$ are lost within the neutral fragment while the hydroxyl hydrogen is retained in the ion. This can be simply accounted for by migration of the hydroxyl group to the dioxolane moiety followed by elimination of the $C_{(2)}$—$C_{(3)}$—$C_{(4)}$ fragment Scheme 4). The migrational propensity of the hydroxyl group is configurationally dependent, the axial hydroxyl group being transferred preferentially. The $C_3H_5O_3^+$ ions further decompose by losing carbon monoxide, producing ions $C_2H_5O_2^+$, *m/z* 61. This fragmentation implies considerable rearrangement of the original dioxolane ring in the $C_3H_5O_3^+$ ions of *III* and *IV*. It should be noted that the charged fragments $C_3H_5^+$, which are complementary by mass to ions *m/z* 89, arise mainly by a different fragmentation path. The mass shifts due to labeling (*m/z* 41 to *m/z* 43 with *IIIb* and *IVb* and the retention of *m/z* 41 with *IIIa*, *IIIc* and *IVa*) reveal that the formation of $C_3H_5^+$ ions can be explained by simple cleavage of the $C_{(3)}$—$C_{(4)}$, $C_{(5)}$—$O_{(5)}$ and $C_{(6)}$—$O_{(6)}$ bonds. In competition with the hydroxyl migration,

TABLE II

Mass spectra of compounds *III*, *IIIa*, *IIIb*, *IV*, *IVa* and *IVb*

| *m/z* | relative intensity (% of base peak) | | | | | | |
|---|---|---|---|---|---|---|---|
| | *III* | *IIIa* | *IIIb* | *IIIc* | *IV* | *IVa* | *IVb* |
| 134 | — | — | 2·2 | — | — | — | — |
| 133 | — | — | 4·8 | — | — | — | — |
| 132 | 0·3 | — | 2·4 | 1·3 | — | — | — |
| 131 | 1·1 | 3·7 | — | 13·2 | 1·2 | 1·4 | — |
| 130 | 4·4 | — | — | 3 | 1·1 | | — |
| 129 | 0·9 | — | — | — | 1·2 | — | — |
| 115 | — | 1·4 | 7·8 | — | — | 1·7 | 8·4 |
| 114 | — | 2 | — | — | 0·4 | 1·7 | — |
| 113 | 2·5 | 1·1 | — | 4·4 | 3·8 | — | — |
| 112 | 1·6 | — | — | 2·9 | 1·2 | — | — |
| 111 | 1 | — | — | 1·2 | 1·1 | — | — |
| 109 | 1 | — | — | — | — | 1·2 | 7·5 |
| 104 | — | — | 2·4 | — | — | — | 2·6 |
| 103 | — | — | — | — | — | — | 3·7 |
| 102 | — | — | 2·4 | — | — | — | 3·7 |
| 101 | 0·5 | 3·4 | — | 5·8 | 0·7 | 2 | — |
| 100 | 3·2 | — | — | 1·5 | 3·2 | — | — |
| 99 | — | — | — | — | 1·1 | — | — |
| 98 | 1·6 | — | — | — | — | — | — |
| 97 | 0·9 | 2·3 | 3·8 | 1·9 | 1·8 | 2·9 | — |
| 96 | 1·9 | — | 2·4 | 1·2 | 1 | — | — |
| 95 | 2 | 2·8 | 7·1 | 2·3 | 2·4 | 2·9 | 7·5 |
| 94 | 0·8 | — | — | 1·1 | 1·4 | — | — |
| 90 | — | — | 3·6 | 26·7 | 0·6 | — | 1·9 |
| 89 | 20·2 | 21·3 | 27·9 | 10·7 | 10·9 | 12·5 | 15 |
| 88 | 0·8 | 1·1 | 15 | 9 | 1·1 | 2·9 | 24·1 |
| 87 | 6 | 7·1 | 35·7 | 10·8 | 9·6 | 8·7 | 32 |
| 86 | 13·3 | 17 | 46·9 | 18·8 | 30·3 | 32·6 | 32 |
| 85 | 3·6 | 48·3 | 31 | 74·4 | 3·9 | 32·6 | 24·8 |
| 84 | 48·5 | 25·6 | 14·3 | 49 | 35·8 | 21·5 | 13·2 |
| 83 | 22·5 | 7·1 | 10·7 | 16·5 | 18·6 | 5·8 | 11·3 |
| 82 | 2·9 | 4·3 | 6 | 5·7 | 2·9 | 5·2 | 5·6 |
| 81 | 4·8 | 2·3 | 6 | 5·5 | 4·7 | 2·9 | 11·3 |
| 80 | — | — | 2·4 | — | — | — | — |
| 79 | 1 | — | 4·3 | 1·3 | 1·6 | — | — |
| 74 | — | 5·7 | 7·1 | 7·4 | — | 3·5 | 6·8 |
| 73 | 5·5 | 2·8 | 4·8 | 4·7 | 4·2 | 4·4 | 7·5 |
| 72 | 2·6 | 4·3 | 4·8 | 4·8 | 4·4 | 5·8 | 8·6 |
| 71 | 5·7 | 4·3 | 17·1 | 6·1 | 9·4 | 5·8 | 18·8 |
| 70 | 2·5 | 14·2 | 19·5 | 10·5 | 2·5 | 13·1 | 16·9 |

TABLE II
(*Continued*)

| *m/z* | relative intensity (% of base peak) | | | | | | |
|---|---|---|---|---|---|---|---|
| | *III* | *IIIa* | *IIIb* | *IIIc* | *IV* | *IVa* | *IVb* |
| 69 | 17·2 | 8·5 | 19 | 20·3 | 14·8 | 7·3 | 21 |
| 68 | 2·5 | 14·2 | 10·7 | 3·2 | 2·6 | 13·4 | 9·4 |
| 67 | 14·9 | 8·5 | 8·3 | 23·1 | 15 | 5·8 | 10·5 |
| 66 | 6·1 | 4 | 4·8 | 6·3 | 4 | 3·5 | — |
| 65 | 4·2 | — | 3·6 | 3·4 | 3 | — | — |
| 63 | 1·1 | — | 3·6 | 1·6 | 1·2 | — | 5·6 |
| 62 | 0·9 | — | 3·6 | 26·9 | — | — | 5·5 |
| 61 | 18·4 | 21·9 | 26·2 | 8 | 17·7 | 18 | 23·3 |
| 60 | 1·5 | 2 | 29·3 | 5·2 | 1·6 | 2 | 42·5 |
| 59 | 5 | 8 | 91·2 | 44·3 | 8·2 | 11·6 | 100 |
| 58 | 43·4 | 61·9 | 100 | 88·6 | 79·1 | 100 | 90·6 |
| 57 | 91·5 | 100 | 49·3 | 99·1 | 100 | 88·7 | 48·9 |
| 56 | 16·3 | 28·4 | 25·5 | 25·6 | 17·6 | 26·2 | 24 |
| 55 | 28·3 | 22·7 | 21·4 | 36·5 | 30·7 | 21·8 | 24·4 |
| 54 | 4·6 | 5·7 | 4·8 | 7·8 | 4·3 | 5·5 | 5·6 |
| 53 | 5·8 | 2·8 | 3·6 | 7·9 | 7·4 | 3·8 | 3·7 |
| 52 | 1·1 | 1·4 | — | 1·4 | 1·6 | — | — |
| 51 | 3·1 | 2·8 | 7·1 | 4·3 | 3·9 | 3·8 | 7·5 |
| 50 | 1·8 | — | — | 2·6 | 2·7 | — | — |
| 48 | — | — | 2·4 | — | — | — | — |
| 47 | 2·9 | 2·3 | 15·5 | 3·1 | 3·1 | 2·9 | 19·9 |
| 46 | — | 22·7 | 55·5 | 32·8 | 1·8 | 29·7 | 55·6 |
| 45 | 25·1 | 63·1 | 91·7 | 99·2 | 34·2 | 64 | 76·7 |
| 44 | 70 | 46·3 | 73·8 | 60 | 72·5 | 43·3 | 60·6 |
| 43 | 91·5 | 55·4 | 97·1 | 100 | 80·9 | 53·2 | 78·9 |
| 42 | 12·5 | 29·7 | 79·3 | 20·7 | 13·4 | 27·3 | 58·6 |
| 41 | 100 | 84·1 | 41·7 | 99·8 | 97·2 | 80·8 | 39·5 |
| 40 | 12·7 | 19·3 | 19·8 | 20·3 | 12·3 | 15·9 | 21·8 |
| 39 | 24·2 | 18·2 | 15·2 | 33·3 | 24·6 | 18·3 | 21·6 |
| 38 | 2·6 | — | — | 3·7 | 2·9 | — | — |

the molecular ions of *III* and *IV* undergo the loss of $C_2H_4O$ and $CH_2O_2$ molecules producing ions *m/z* 86 and *m/z* 84, respectively. The origin of the eliminated $C_2H_4O$ molecule cannot be established unambiguously using the available labeled compounds. Table II shows that both hydrogens from $C_{(3)}$ and the hydroxyl group are lost from the $(M-C_2H_4O)^{+\bullet}$ ions and also that the deuterium content in these ions (if generated from *IIIb* and *IVb*) decreases by two relative atom units. This means that the expelled $C_2H_4O$ molecule contains either the $C_{(2)}$—$C_{(3)}$ or $C_{(3)}$—$C_{(4)}$

TABLE III

Mass spectra of compounds *V*, *Va*, *Vb*, *VI*, *VIa*, *VIb*, *VIc*, *VId*

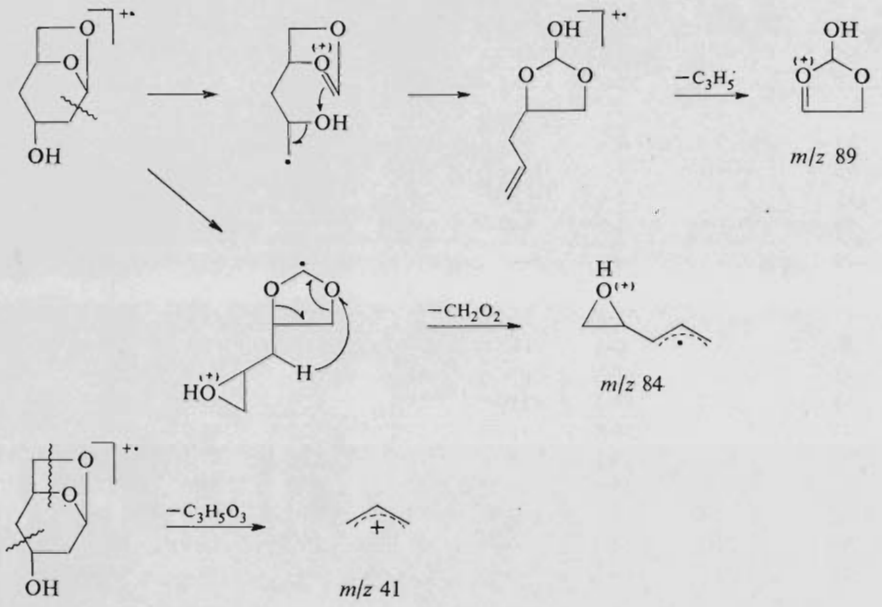
| *m/z* | relative intensity (% of base peak) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *V* | *Va* | *Vb* | *VI* | *VIa* | *VIb* | *VIc* | *VId* |
| 133 | — | — | — | — | — | — | — | 0·2 |
| 132 | — | — | — | — | 2·1 | 4·5 | 0·7 | 1·4 |
| 131 | 0·7 | 0·8 | — | 0·6 | 7·3 | — | 5·3 | 2 |
| 130 | 0·9 | 0·6 | — | 3·8 | — | — | 1·9 | 1 |
| 129 | 0·5 | — | — | — | — | — | — | 0·8 |
| 115 | 0·6 | — | — | — | 9·9 | — | — | — |
| 112 | 0·7 | 1·1 | — | — | — | — | — | — |
| 111 | — | — | — | — | 3·7 | — | — | — |
| 109 | — | 1·6 | — | — | 5·8 | — | — | — |
| 103 | — | 6·3 | 2·1 | 0·9 | 18·3 | 8·9 | 8·8 | 1·3 |
| 102 | 3·7 | 3 | 4·9 | 13·2 | 2·1 | 10·7 | 6·8 | 13·2 |
| 101 | 2·3 | 3·7 | 2·5 | 3·7 | — | 4·5 | 2·1 | 5·7 |
| 97 | 1 | — | — | — | 10·5 | — | — | 1·3 |
| 95 | 1·1 | 1·8 | — | — | 15·3 | — | — | 1·3 |
| 90 | — | — | 4·9 | — | — | 4·5 | — | 3·8 |
| 89 | 1·7 | 4·8 | 100 | — | 7·9 | 90·2 | 5·2 | 46·5 |
| 88 | 5 | 100 | 14·8 | 5 | 100 | 12·5 | 100 | 66 |
| 87 | 100 | 13·9 | 12 | 100 | 16·8 | 21·6 | 39·9 | 34 |
| 86 | 7 | 7 | 9 | 7 | 10·5 | 12·5 | 8·9 | 8·8 |
| 85 | 1·4 | 4·6 | 8·6 | 1·2 | 15·7 | 15·9 | 9·1 | 11·9 |
| 84 | 8·7 | 10·4 | 4·2 | 14·7 | 20·9 | 4·5 | 16·5 | 11·3 |
| 83 | 11·5 | 5·3 | 3·9 | 11·2 | 14·7 | 9·5 | 7·2 | 6·2 |
| 82 | 2·7 | 3·6 | 2·1 | 2 | 10·5 | 6·8 | 2·1 | 2·6 |
| 81 | 3·7 | 2·4 | 2·1 | 5 | 15·7 | 12 | 3·9 | 2·6 |
| 75 | — | 2 | — | — | 5·2 | — | 2·2 | — |
| 74 | — | 14·2 | 8·5 | 2·5 | 26·2 | 13·6 | 13·4 | 3·8 |
| 73 | 11·7 | 2·4 | 10·6 | 16·2 | 2·1 | 15·2 | 6·3 | 20·8 |
| 72 | — | 3·6 | 5·6 | 1·2 | 6·3 | — | 5·4 | 8·2 |
| 71 | — | 6 | 9 | 7·8 | 13·1 | 13·6 | 6·2 | 9·4 |
| 70 | 2 | 6·4 | 6·1 | 3·8 | 15·7 | 10·2 | 8 | 10 |
| 69 | 11·7 | 7·8 | 4·2 | 13·4 | 23·6 | 18·2 | 12 | 6·9 |
| 68 | — | 1·2 | — | 1·2 | 5·2 | — | — | 1·3 |
| 67 | 2·8 | — | 2·2 | 3·8 | 13·1 | — | 2·1 | 2·6 |
| 66 | 3·2 | — | — | 2·5 | 5·2 | — | 1·7 | — |
| 65 | 2·3 | — | — | 1·9 | 6·8 | 6·8 | 1·3 | 1·3 |
| 62 | — | — | — | — | — | — | 2·6 | — |
| 61 | 2·6 | 2·4 | 2·8 | 2·9 | — | 3·4 | 2 | 3·8 |
| 60 | — | 1·2 | 5·6 | 1·2 | — | 5·7 | 3 | 3·8 |
| 59 | 4 | 6 | 16·9 | 5 | 7·8 | 15·9 | 5·4 | 15·1 |
| 58 | 13·3 | 36·1 | 29·2 | 15 | 57·6 | 36·8 | 38·5 | 40·3 |

TABLE III
(*Continued*)

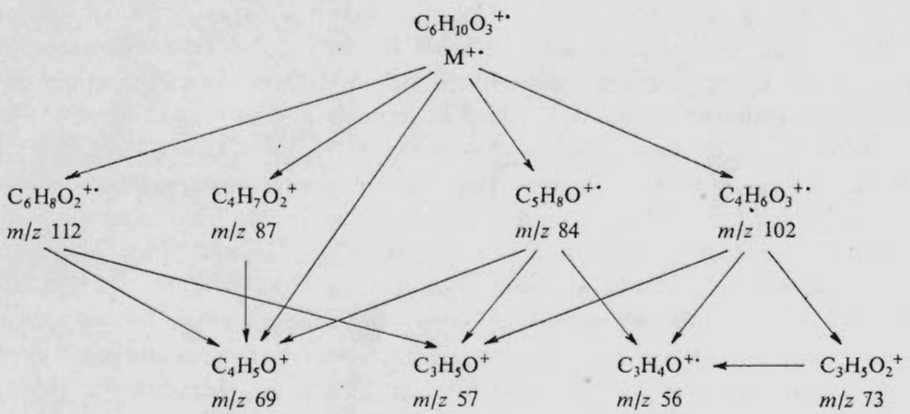
| *m/z* | relative intensity (% of base peak) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *V* | *Va* | *Vb* | *VI* | *VIa* | *VIb* | *VIc* | *VId* |
| 57 | 56 | 78·3 | 71·8 | 76·2 | 95·3 | 100 | 82·6 | 50·3 |
| 56 | 70 | 42·8 | 58·2 | 90 | 55 | 73·9 | 74·3 | 100 |
| 55 | 29 | 22·9 | 20·1 | 33·8 | 54·5 | 36·4 | 28·3 | 31·4 |
| 54 | 4·7 | 5·4 | — | 4 | 8·4 | — | 4 | 5 |
| 53 | 6 | 2·4 | — | 6·5 | 10·5 | — | 6·6 | 3·1 |
| 52 | — | 1 | — | — | — | 2·3 | — | 1·3 |
| 51 | 3 | 2·4 | 2·5 | 3 | 15·7 | 10·2 | 2·4 | 3·1 |
| 50 | 1·5 | 1·2 | — | 1·5 | 5·2 | 2·3 | 1·5 | 1·3 |
| 49 | — | — | — | — | 6·8 | 4·5 | — | — |
| 48 | — | 22·3 | — | — | 28·3 | — | 23·7 | 1·9 |
| 47 | 23·3 | 2·4 | 26·3 | 30 | 5·2 | 33·2 | 10·5 | 34·6 |
| 46 | — | 6·4 | 11 | — | 13·1 | 11·4 | 7·1 | 5 |
| 45 | 11 | 11·7 | 17·3 | 13 | 15·7 | 23·2 | 22·4 | 21·4 |
| 44 | 24·7 | 18·8 | 23·4 | 25·4 | 42·9 | 36·4 | 18·7 | 37·7 |
| 43 | 45·7 | 28·2 | 31·7 | 43·1 | 52·9 | 45·9 | 42 | 48·4 |
| 42 | 16 | 27·5 | 18·3 | 19·6 | 32·5 | 29·1 | 20·9 | 18·9 |
| 41 | 36·7 | 15·9 | 9·9 | 32·8 | 39·3 | 28·6 | 27·2 | 17·6 |
| 40 | 4·3 | 7·6 | 9·9 | 3·8 | 14·7 | 13·6 | 4·4 | 10 |
| 39 | 21·3 | 12 | 6·3 | 21·9 | 26·2 | 15·9 | 18·3 | 11·3 |
| 38 | 2·7 | — | — | 2·5 | — | — | 1·9 | 1·2 |

part of the skeleton. The same holds for the complementary $C_2H_4O^{+\cdot}$ ions (Table II). The formation of $(M-CH_2O_2)^{+\cdot}$ ions, *m/z* 84, involves a transfer of one hydrogen to the neutral fragment. The data in Table II confirm that both hydrogens from $C_{(3)}$ and the hydroxyl group remain in the $(M-CH_2O_2)^{+\cdot}$ ions. The origin of the hydrogen transferred cannot be established from the low resolution spectra of *IIIb* and *IVb* because of superposition of ion groups $C_5H_{8-x}{}^2H_xO$ and $C_4H_{6-x}{}^2H_xO_2$, resulting from imperfect labeling. The high resolution spectra show, however, that one deuterium atom is lost in the eliminated formic acid. The deuterium content in the $(M-CH_2O_2)^{+\cdot}$ ions from *IIIb* (31·0% $^2H_3$, 42·8% $^2H_2$ and 26·2% $^2H_1$) matches well the deuterium distribution in the molecular ions (30·3% $^2H_4$, 37·6% $^2H_3$, 29·4% $^2H_2$ and 2·7% $^2H_1$). This confirms that one deuterium atom either from $C_{(2)}$ or $C_{(4)}$ is lost clearly. Although these sites are not distinguished by present labeling, we tentatively suggest that the deuterium is transferred from $C_{(4)}$ (Scheme 4). The mass spectra of the last pair of isomers *V* and *VI* (Table III, Scheme 5) are dominated by $C_4H_7O_2^+$, *m/z* 87. Some of the possible routes leading to this ion can be eliminated

on the basis of the spectra of labeled analogues *Va,b* and *VIa–d* (Table III). As the deuterium atoms from the hydroxyl group, $C_{(4)}$, $C_{(3)}$ and $C_{(2)}$ remain in the $(M-C_2H_3O)^+$ ions, it is clear that their formation must involve a cleavage of the dioxolane moiety. By analogy[9,10] we assume that a fission of the $C_{(4)}$—$C_{(5)}$ bond is followed by loss of the $C_{(5)}$—$C_{(6)}$ fragment carrying either the $O_{(5)}$ or $O_{(6)}$ oxygen

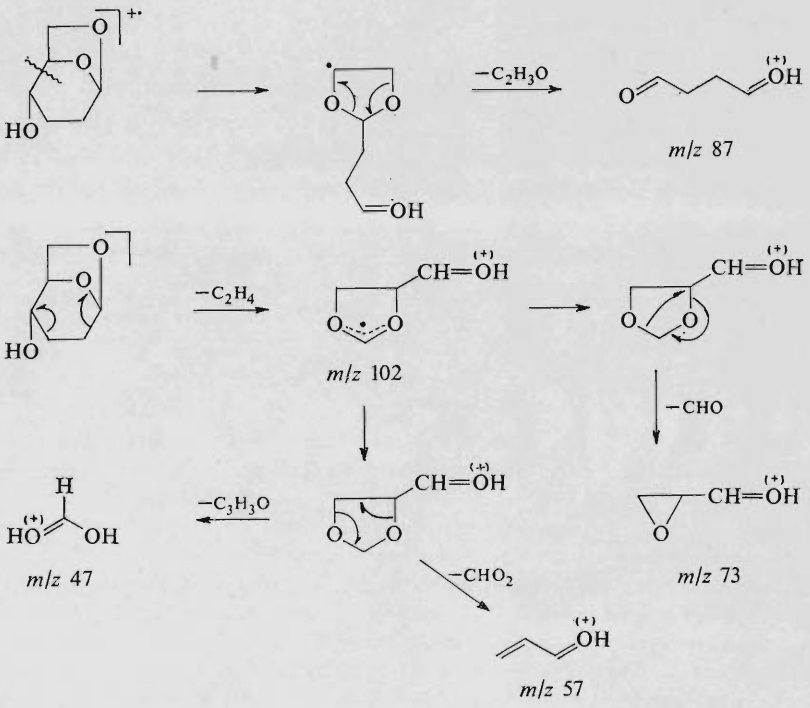



SCHEME 4




SCHEME 5

atom (Scheme 6). $C_3H_5O_2^+$, *m/z* 73, arises from $(M-C_2H_4)^{+\cdot}$ by loss of the aldehyde group. Of several possible routes by which these ions could be formed some can be ruled out by deuterium labeling. Table III shows that deuterium atoms both from the $C_{(4)}$ and the hydroxyl group (compounds *Va*, *VIa*, *VIc*) are retained in the charged fragments. This makes the loss of the $C_{(4)}$—$CO_{(4)}$ moiety improbable because it would require a clean stripping of the $C_{(4)}$ and hydroxyl hydrogen, followed by a clean transfer of another skeletal hydrogen back to the $C_{(4)}$—$O_{(4)}$ grouping.




SCHEME 6

The formation of $C_3H_5O_2^+$ ions can be better visualized as proceeding *via* cleavage of the dioxolane ring (Scheme 6). The origin of the eliminated oxygen atom ($O_{(5)}$ and/or $O_{(6)}$) remains yet unknown. Further decomposition of both $(M-C_2H_4)^{+\cdot}$ and $C_3H_5O_2^+$ ions furnishes the $C_3H_5O^+$ and $C_3H_4O^{+\cdot}$, *m/z* 57 and 56, respectively. Metastable transitions in the first FFR and the spectra of the labeled compounds show that the latter ions contain the $C_{(6)}$—$C_{(5)}$—$C_{(4)}$—$C_{(4)}$ part of the skeleton. Nevertheless, a small part of these ions is formed from the $(M-CH_2O_2)^{+\cdot}$ ions and some of the deuterium-containing $C_3H_5O^+$ and $C_3H_4O^{+\cdot}$ ions can be attributed

to this competing pathway. The formation of the $CH_3O_2^+$ ions, $m/z$ 47, was largely elucidated by deuterium labeling. Since only the $C_{(4)}$ and hydroxyl hydrogens are kept in the $CH_3O_2^+$ ions, two probable ways of their formation can be considered. In the first mechanism (Scheme 6), the $CH_3O_2^+$ ions contain the $O_{(5)}—C_{(1)}—O_{(6)}$ moiety and the hydrogens are transferred from $C_{(4)}$ and $O_{(4)}$. The second mechanism involves oxygen migration instead of hydrogen, so that the $CH_3O_2^+$ ions would contain the $O_{(4)}—C_{(4)}—O_{(5)}$ part. As these ions originate from the $(M-C_2H_4)^{+\cdot}$ ions by elimination of the $C_3H_3O$ radical, the first mechanism appears to be more probable.

When comparing the electron-impact mass spectra of *I – VI* it can be concluded that positional isomers are easily distinguished, while configurational assignment would be difficult. If the hydroxyl group is situated close to the dioxolane ring (*i.e.* at $C_{(2)}$ or $C_{(4)}$), the corresponding α(C—C) bonds in the molecular ions are rapidly cleaved and, consequently, configurational information is lost. Chemical ionization mass spectrometry may be useful in resolving these stereoisomers, as documented by the recent work on isomeric epoxides with 1,6-anhydroxy-β-D-hexopyranose skeleton[11].

## EXPERIMENTAL

*Mass spectra* were recorded on a JEOL JMS D-100 spectrometer operating at 14—75 eV. The samples were introduced either by direct inlet at 60°C or by a gas chromatograph — mass spectrometer coupling (SE-30, 3% on Chromosorb W, column temperature 70°C, injection chamber temperature 120°C, separator temperature 120°C). Decompositions of metastable ions in the first FFR were monitored by accelerating voltage scanning. The alcohols *I — VI* were prepared as described earlier[6,7]. The $[O^2H_1]$ derivatives *IIc*, *IIIc* and *VIc* were prepared by dissolving the corresponding alcohol (1 mg) in [O—$^2$H] methanol (14 μl). Aliquots of these solutions were introduced into the ion source through very thin glass capillaries at 40°C. The ion source was conditioned with deuterium oxide at $10^{-3}$ Pa for two hours before each measurement. The labeled alcohols *Ia*, *IIa*, *IIIa*, *IVa*, *Va* and *VIa* were prepared from the corresponding ketones[7], 1,6-anhydro-3,4-dideoxy-β-D-glycerohexopyranos-3-ulose, *VIII*, 1-6--anhydro-2,4-dideoxy-β-D-glycerohexopyranos-2-ulose, *IX*, and 1,6-anhydro-2,3-dideoxy-β-D--glycerohexopyranos-4-ulose, *X*, by reduction with lithium aluminium deuteride in ether. The deuterium content in these derivatives was assumed to be the same as in the reagent used (98% $^2H_1$, 2% $^2H_0$). The alcohols *Ib*, *IIb*, *IIIb*, *IVb*, *Vb* and *VIb* were prepared by reduction of the corresponding labeled ketones with lithium aluminium hydride in ether. The replacement of hydrogen by deuterium in *VIII* and *X* (deuterium oxide, lithium deuteroxide, tetrahydrofuran, triethylbenzylammonium chloride, 20°C, 48 hours) proceeded easily. The deuterium content in *Ib* and *IIb* (91·5% $^2H_2$, 5·8% $^2H_1$, 2·6% $^2H_0$) and *Vb*, *VIb* (92% $^2H_2$, 6% $^2H_1$, 2% $^2H_0$) was determined from the mass spectra of corresponding ketones. The deuteration of *IX* turned out to be difficult because it proceeded slowly and the ketone was simultaneously destroyed in alkaline medium. After two exchanges (with 40% material recovery) the following deuterium content was found: 30·3% $^2H_4$, 37·6% $^2H_3$, 29·5% $^2H_2$ and 2·6% $^2H_1$. This material was used for the preparation of *IIIb* and *IVb*. The 2,3-dideuterio derivative

*VId* was prepared by catalytical deuteration ($^2H_2$ gas, palladium, ethanol) of 1,6-anhydro-4-O-benzyl-2,3-dideoxy-β-D-erythro-hex-2-enopyranose[13]. The deuterium content in *VId*: 37% $^2H_2$, 38% $^2H_1$, 25% $^2H_0$.

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