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MASS SPECTROMETRY OF ARALKYL COMPOUNDS WITH A FUNCTIONAL GROUP—VI[1]:

MASS SPECTRA OF 1-PHENYLETHANOL-1, 2-PHENYLETHANOL-1 AND 1-PHENYLPROPANOL-2*

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Abstract—Mass spectra of 1-phenylethanol-1 and its analogues, specifically deuterated in the aliphatic chain, suggest that the $[M - CH_3]^+$ ion is represented partly by an α-hydroxybenzyl fragment. Moreover, the molecular ion loses successively—after scrambling of all hydrogen atoms, except those of CH_3—a hydrogen atom and C_6H_6, generating the CH_3CO^+ ion.

Diffuse peaks, found in the spectra of 2-phenylethanol-1 and its analogues, specifically deuterated in the aliphatic chain and in the phenyl ring, show that the molecular ion loses C_2H_4O, possibly *via* a four-center mechanism, after an exchange of aromatic and hydroxylic hydrogens.

Mass spectra of 1-phenylpropanol-2 and its analogues, specifically deuterated in the aliphatic chain, demonstrate that in the molecular ion exclusively the hydroxyl hydrogen atom is transferred to one of the *ortho*-positions of the phenyl ring *via* a McLafferty rearrangement, generating the $[M - C_2H_4O]^+$ ion. Furthermore, an eight-membered ring structure is proposed for the $[M - CH_3]^+$ ion to explain the loss of H_2O and C_2H_2O from this ion after an extensive scrambling of hydrogen atoms.

INTRODUCTION

TO OBTAIN more insight into the mass spectral behaviour of aralkyl compounds with a functional group, we have studied the mass spectra of 1-phenylethanol-1, 2-phenylethanol-1 and of 1-phenylpropanol-2 by comparing the standard spectra with those of specifically deuterated analogues.

The mass spectrum of unlabelled 1-phenylethanol-1 has been reported in the literature.[2]

Mass spectra of 2-phenylethanol-1 and its O-d_1 analogue have shown earlier,[3] that the $[M - CH_2O]^+$ ion is formed *via* a McLafferty rearrangement[4] of the hydroxyl hydrogen atom to one of the *ortho*-positions of the phenyl ring. The availability of 2-phenylethanol-1, specifically deuterated in the aliphatic chain and in the phenyl ring,[5] provided an opportunity to study its mass spectrum in more detail.

As far as we know, the mass spectrum of unlabeled 1-phenylpropanol-2 has not been reported in the literature.

In the lower mass region of the spectra obtained in the present study many diffuse peaks are found, corresponding with the well-known decompositions of ions from aromatic hydrocarbons,[6] e.g. *m/e* 91 → 65, *m/e* 89 → 63, *m/e* 77 → 51, etc. These have been omitted in Appendices 1, 2 and 3. Moreover, it is not possible to locate exactly the charge in the molecular ions from 1-phenylethanol-1, 2-phenylethanol-1 and from 1-phenylpropanol-2, as long as the ionization potentials are not known. This should be borne in mind with regard to Schemes 1, 2, 3, 4 and 5.

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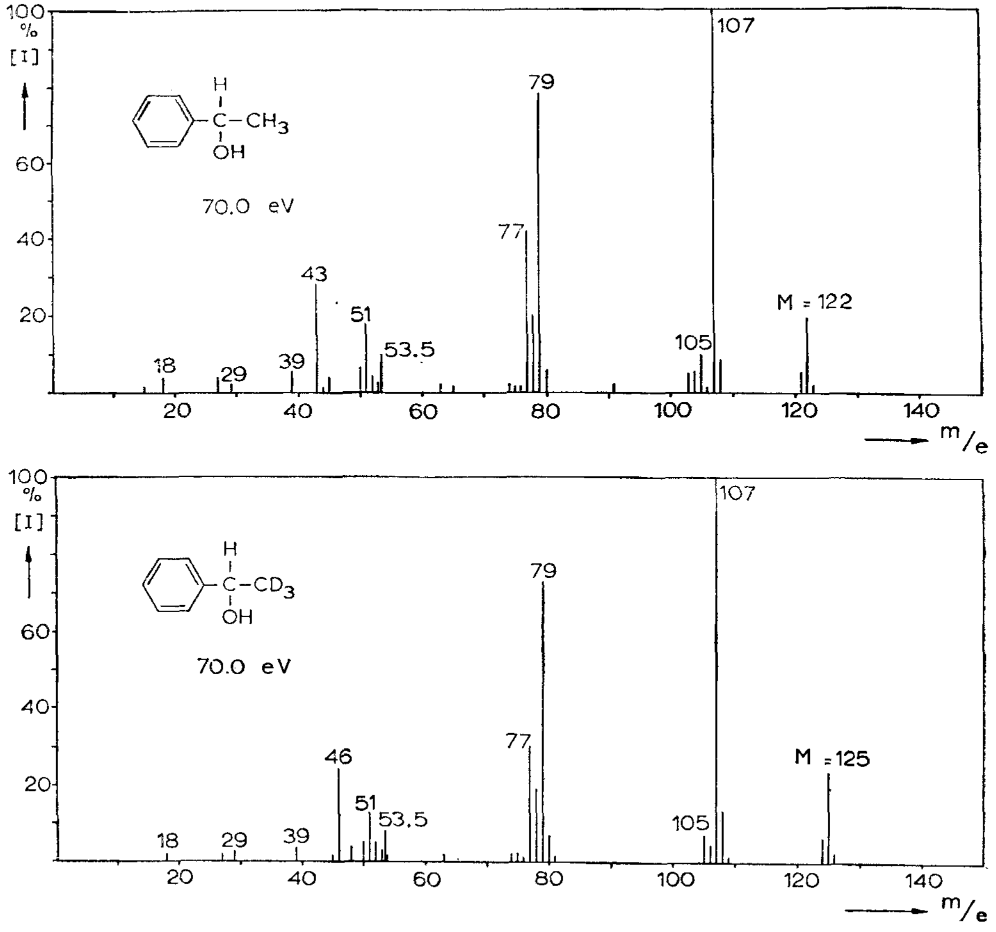
* Part of the forthcoming thesis of N. M. M. Nibbering.

Fragmentation of 1-*phenylethanol*-1, $C_6H_5\overset{\alpha}{C}H(OH)\overset{\beta}{C}H_3$.

Comparison of the standard spectrum with that of α-d_1, β-d_3 and O-d_1 analogues together with the *m/e* and m_2/m_1 values for diffuse peaks enable us to distinguish two main reaction paths for the decomposition of the molecular ion. (See Figs. 1 to 4, Appendix 1 and Scheme 1.*)

1. *Successive losses of* CH_3 *and* CO *from the molecular ion.* In the mass spectra of undeuterated 1-phenylethanol-1 (M = 122) and its β-d_3 analogue the base peak is



FIGS. 1 and 2. Mass spectra of 1-phenylethanol-1 and its β-d_3 analogue.

found at *m/e* 107 (Figs. 1 and 2). This peak shifts to *m/e* 108 in the mass spectra of the α-d_1 and O-d_1 compounds (Figs. 3 and 4).

This can be explained simply by loss of the CH_3 group from the molecular ion, which reaction is supported by corresponding diffuse peaks found in the spectra (Scheme 1, sequence $a \rightarrow b$ and Appendix 1, reaction no. 1).

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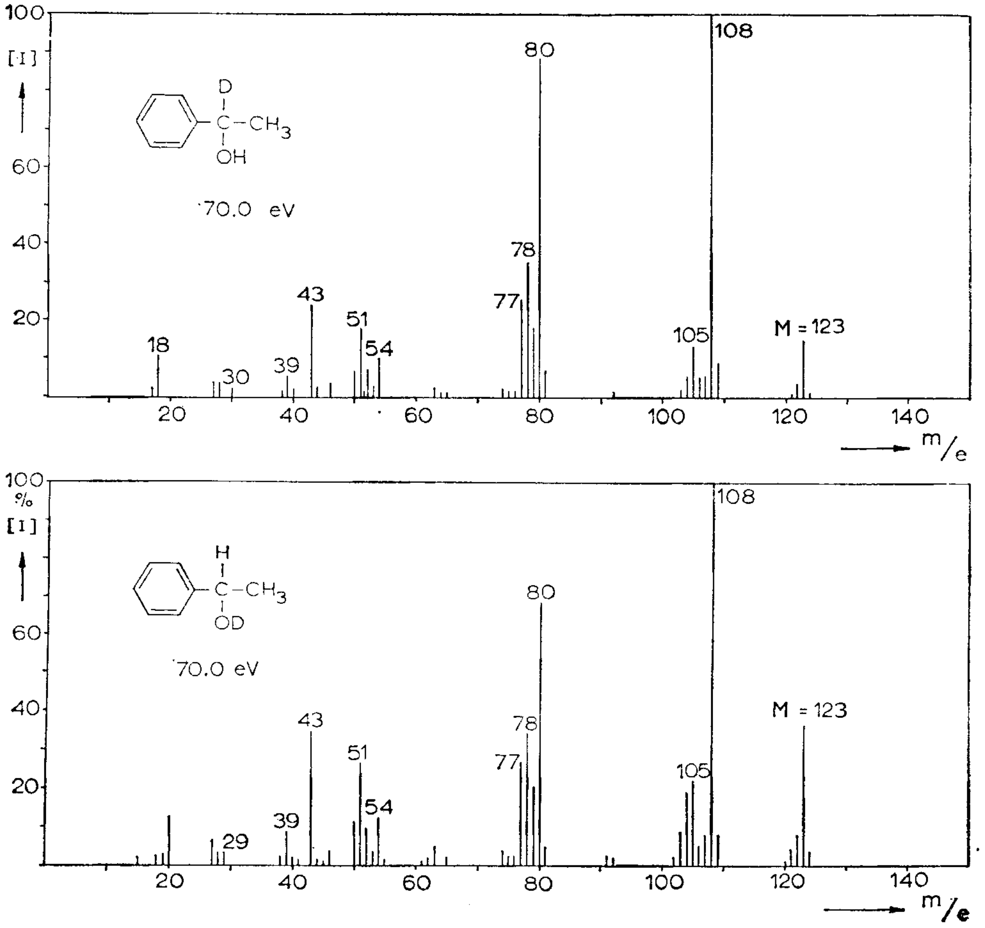
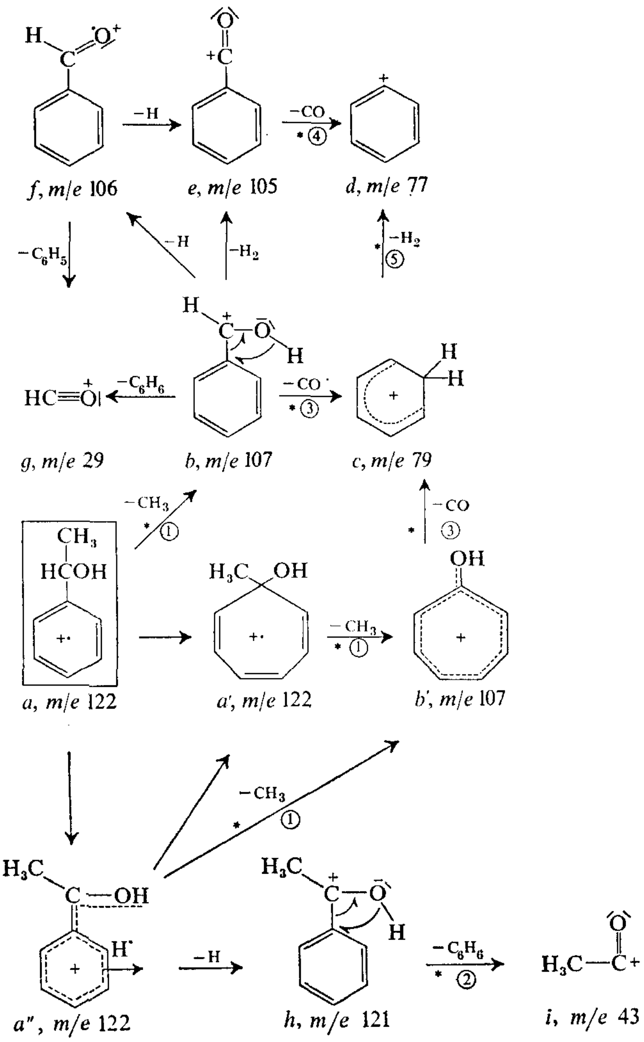
* Reactions for which corresponding diffuse peaks are observed are denoted by an asterisk. The numbers at the reactions correspond with the reaction numbers in Appendix 1.



FIGS. 3 and 4. Mass spectra of α-d_1 and O-d_1 analogues of 1-phenylethanol-1.

The structure of ion *b* however, generated in this reaction, is uncertain. Previously, deuterium labelling has indicated that after a nearly complete scrambling of all hydrogen atoms the molecular ion of benzylalcohol[7,8] loses a hydrogen atom, giving an ion with the same mass as ion *b* in the present study. Shannon[8] suggested this scrambling process to proceed *via* a π-complex before and after ring expansion of the phenyl ring to a seven-membered ring system and thus proposed an α-hydroxybenzyl- and a hydroxytropylium structure for the $[M - 1]^+$ ion from benzylalcohol. Apart from scrambling these structures are also reasonable for the fragment *m/e* 107 in the present case. Therefore, besides ion *b* (α-hydroxybenzyl) also ion *b'* (hydroxytropylium) has been included in Scheme 1. Just like the $[M - 1]^+$-ion from benzylalcohol[7,8] ions *b* and *b'* lose successively CO and H_2 generating ions *c* and *d* resp. (Scheme 1), possibly *via* the mechanisms proposed earlier.[8] This sequence of reactions is supported by corresponding diffuse peaks (Appendix 1, reaction no.'s 3 and 5, resp.).

Although the further decomposition of fragment *m/e* 107 from 1-phenylethanol-1 is analogous to that from benzylalcohol,[7,8] it is questionable whether all hydrogen atoms, except those of the CH_3 group, scramble and whether a ring expansion to a



SCHEME 1

seven-membered ring occurs in the molecular ion of 1-phenylethanol-1, as in the molecular ion of benzylalcohol.[8] This problem results in two possible structures for fragment *m/e* 107 [M − CH_3], presented by ions *b* and *b′* (Scheme 1), which could be formed before and/or after an extensive scrambling of all hydrogen atoms in the molecular ion, except those of the CH_3 group. Sequences $a \to a' \to b'$ and $a \to b$ correspond with the first-mentioned possibility. In ion *b* none of the hydrogen atoms have lost their original position, which could be supported by the following arguments:

(a) In all spectra the peak at *m/e* 105 is the most intense one in the mass region *m/e* 100 to *m/e* 110, apart from the base peaks due to loss of the CH_3 group from the molecular ions. The same phenomenon was observed in the mass spectrum of benzylalcohol by Eliel *et al.*[7] and because in that case the $[M - 1]^+$ ion (*m/e* 107) was formed by loss of one hydrogen atom from the molecular ion after a nearly complete scrambling of all hydrogen atoms, it could not be the precursor of fragment *m/e* 105. Therefore a different route to fragment *m/e* 105 was suggested,[7] viz:

$$\begin{array}{ccccc} C_6H_5CH_2OH^{+\cdot} & \xrightarrow{-H_2} & C_6H_5CHO^{+\cdot} & \xrightarrow{-H} & C_6H_5CO^+ \\ m/e\ 108 & & m/e\ 106 & & m/e\ 105 \end{array}$$

Analogous to this route the peak at *m/e* 105 in all spectra of the present study might be explained by the sequence:

$$\begin{array}{ccccc} C_6H_5CH(OH)CH_3^{+\cdot} & \xrightarrow{-H_2} & C_6H_5COCH_3^{+\cdot} & \xrightarrow{-CH_3} & C_6H_5CO^+ \\ m/e\ 122 & & m/e\ 120 & & m/e\ 105 \end{array}$$

This cannot be true, however, because the peak at *m/e* 120, corresponding with the molecular ion of acetophenone, is hardly visible and can therefore not account for the rather high intensity of the peak at *m/e* 105 (relative abundances of the fragments *m/e* 120 and *m/e* 105 in the mass spectrum of acetophenone[9] are 31·51% and 100%, respectively). A more probable formation of fragment *m/e* 105 would thus be the loss of a hydrogen molecule from ion *b*, but this implies that ion *b* has an α-hydroxybenzyl structure, in which the hydrogen atoms have not lost their original positions (Scheme 1, sequence *b* → *e*). This reaction corresponds with the transition of one even-electron carbonium ion (ion *b*) to an other even-electron carbonium ion (ion *e*).[10] This sequence may be more favourable than the sequence *b* → *f* → *e* (Scheme 1), involving an intermediary odd-electron system. Nevertheless, this last sequence could also be operative in generating ion *e*. Sequence *f* → *e* resembles the behaviour of benzaldehyde,[11] which loses specifically the aldehydic hydrogen atom upon electron impact, as proved by deuteration. Finally, ion *e* loses CO giving ion *d* as demonstrated by diffuse peaks (Appendix 1, reaction no. 4).

(b) In the mass spectrum of unlabelled 1-phenylethanol-1 a peak of low intensity at *m/e* 29 is observed (Fig. 1). This peak does not shift in the mass spectra of the β-d_3 and O-d_1 analogues, but shifts to *m/e* 30 in the mass spectrum of the α-d_1 compound (Figs. 2, 4 and 3, resp.). The same was found in the mass spectra of benzylalcohol[7] and its deuterated analogues and because no randomizing migration of hydrogens can have occurred in the formation of the fragment *m/e* 29 (CHO^+), the following reaction sequence has been suggested:[7]

$$\begin{array}{ccccc} C_6H_5CH_2OH^{+\cdot} & \xrightarrow{-H_2} & C_6H_5CHO^{+\cdot} & \xrightarrow{-C_6H_5} & CHO^+ \\ m/e\ 108 & & m/e\ 106 & & m/e\ 29 \end{array}$$

In the present study however, it is difficult to explain the formation of the fragment *m/e* 29 *via* such a mechanism. A more probable sequence would seem to be the elimination of a benzene molecule from ion *b* through a four-membered transition state[12] (arrows in ion *b*) to give ion *g*, although this ion *g* could also be generated *via* the sequence *b* → *f* → *g* (Scheme 1).

From these considerations it may be concluded, that fragment *m/e* 107 consists, at least partly, of an α-hydroxybenzyl structure, in which the hydrogen atoms have not lost their identity. Consequently, the molecular ion of 1-phenylethanol-1 must have partly a structure as represented by ion *a* in Scheme 1.

2. *Successive eliminations of* H *and* C_6H_6 *from a scrambled molecular ion.* In the mass spectra of undeuterated 1-phenylethanol-1 and its β-d_3 analogue small peaks are found at *m/e* 121 and at *m/e* 124, respectively. These agree with the loss of a hydrogen atom from the corresponding molecular ions (Figs. 1 and 2). In the mass spectra of the α-d_1 and O-d_1 compounds small peaks are observed at *m/e* 122 and at *m/e* 121, generated by loss of a hydrogen as well as a deuterium atom from the corresponding molecular ions (Figs. 3 and 4).

These observations suggest a non-specific loss of a hydrogen atom from the molecular ion and analogous to the behaviour of benzylalcohol[7,8] it may be assumed, that all hydrogen atoms except those of the CH_3 group scramble in the molecular ion, before a hydrogen atom is eliminated.

The $[M - 1]^+$-ion from unlabelled 1-phenylethanol-1 and from its β-d_3, α-d_1 and O-d_1 analogues is the precursor of the acetyl cation, containing the original CH_3 group, as indicated by diffuse peaks found in the spectra and in agreement with the shift of the peak at *m/e* 43 in the mass spectra of undeuterated 1-phenylethanol-1 and its α-d_1 and O-d_1 analogues to *m/e* 46 in the mass spectrum of the β-d_3 compound (Appendix 1, reaction no. 2 and Figs. 1 to 4). This reaction can be rationalized by assuming that all hydrogen atoms, except those of the CH_3 group, scramble in the molecular ion *via* a π-complex without alteration of the carbon skeleton, as proposed by Shannon[8] for the molecular ion of benzylalcohol. Loss of a hydrogen atom from this π-complex, represented by ion *a''*, could give ion *h*, from which a benzene molecule may be eliminated in a four-membered transition state[12] (arrows in ion *h*) to give the acetyl cation *i* (Scheme 1).

In relation to the discussions, given above, the following points can be made:

(a) The occurrence of the peak at *m/e* 43 in the mass spectra of unlabelled 1-phenylethanol-1 and its α-d_1 and O-d_1 analogues and of the peak at *m/e* 46 in the mass spectrum of the β-d_3 compound are not caused by the presence of acetophenone, which could in principle be formed by chemical dehydrogenation in the mass spectrometer or by a loss of a hydrogen molecule from the parent ion of 1-phenylethanol-1. A peak at *m/e* 120 in the mass spectra of the d_0, α-d_1 and O-d_1 compounds and a peak at *m/e* 123 in the mass spectrum of the β-d_3 compound, corresponding with the molecular ions of acetophenone and its β-d_3 analogue, are hardly observed and can therefore not account for the high intensity of the peak due to the acetyl cation in the spectra (Relative abundances of the fragments *m/e* 120 and *m/e* 43 in the mass spectrum of acetophenone[9] are 31·51% and 21·43%, resp.).

(b) Neither in section 1 nor in section 2 was a ring expansion of the molecular ion to a seven-membered ring system necessary to explain our results. Ring expansion could just as well occur during or after cleavage of a bond in the molecular ion, as depicted by the sequence $a'' \rightarrow b'$ in Scheme 1. This does not altogether exclude the possibility of an earlier ring expansion in the molecular ion itself before and/or after scrambling of hydrogen atoms. Naturally this would depend on the relative rates of scrambling and ring expansion (cf. sequences $a \rightarrow a'$ and $a \rightarrow a'' \rightarrow a'$ in Scheme 1).

In section 1 an unscrambled and in section 2 a scrambled molecular ion were assumed to interpret the spectra. This suggests that *loss of a methyl group is a very fast reaction whereas loss of hydrogen is very slow compared with the rate of hydrogen scrambling in the molecular ion.* Similar observations have been made earlier by Meyer and Harrison for ethylbenzene.[13]

Fragmentation of 2-*phenylethanol*-1, $C_6H_5\overset{\beta}{C}H_2\overset{\alpha}{C}H_2OH$

Comparison of the standard spectrum with that of α-d_2, β-d_2, *ortho*-d_2, *para*-d_1, O-d_1 and (*ortho*-d_2 + O-d_1) analogues together with the *m*/*e*- and m_2/m_1-values for diffuse peaks enable us to distinguish four reaction paths for the decomposition of the molecular ion (See Figs. 5 to 12, Appendix 2 and Schemes 2 and 3*).

1. *Elimination of vinylalcohol after exchange of aromatic and hydroxylic hydrogen atoms in the molecular ion* (*Fig.* 5, *Appendix* 2, *reaction no's* 2*a to* 2*h*, *and Scheme* 2). In the mass spectrum of undeuterated 2-phenylethanol-1 a diffuse peak of low intensity is found, corresponding with the loss of a C_2H_4O molecule from the molecular ion (M = 122). Clearly observable shifts of this diffuse peak in the mass spectra of the specifically deuterated analogues (Fig. 5) show, that the deuterium distribution in the eliminated C_2H_4O molecule is as follows:

para-d_1: C_2H_4O
ortho-d_2: C_2H_4O and C_2H_3DO
β-d_2: $C_2H_2D_2O$
α-d_2: C_2H_3DO
O-d_1: C_2H_4O
(*ortho*-d_2 + O-d_1): C_2H_4O and C_2H_3DO

Moreover, the relative heights of the diffuse peaks in the spectra of the *ortho*-d_2 and (*ortho*-d_2 + O-d_1) compounds indicate that C_2H_4O and C_2H_3DO are lost in a 2:1- and in a 1:1 ratio, respectively. These ratios can be explained by assuming that all aromatic hydrogen atoms and the hydroxylic hydrogen atom are involved statistically in the elimination of the C_2H_4O molecule from the molecular ion. This would imply that the O-d_1 and *para*-d_1 analogues also lose C_2H_3DO besides C_2H_4O from the molecular ions. An indication that this actually occurs is the just visible enhancement in the base lines of the spectra from the O-d_1 and *para*-d_1 compounds at positions, where we must expect a diffuse peak corresponding with the elimination of a C_2H_3DO molecule from the molecular ions of these compounds (Fig. 5).

Two mechanisms could account for these observations:

(a) The hydroxylic hydrogen atom could be captured by the π-orbital of the phenyl ring to give a π-complex (Scheme 2, sequence $a \rightarrow b$). After equilibration of this hydrogen atom with all aromatic hydrogens, which could be effected in the equilibrium $b \rightleftharpoons b'$, a hydrogen atom returns to oxygen (Scheme 2, sequence $b \rightarrow c$). From an infrared spectrometric study an OH-π-sextet interaction in 2-phenylethanol-1[14] has also been suggested, despite the essential difference between infrared and mass spectrometry.

(b) The hydroxylic hydrogen atom could be transferred to one of the *ortho* positions of the phenyl ring to give a σ-complex (Scheme 2, sequence $a \rightarrow b'$). In this σ-complex equilibration of the hydroxylic hydrogen atom with all aromatic hydrogens could be reached by a series of consecutive 1,2-shifts of hydrogen, as proposed for toluene.[13] Then, after equilibration, a hydrogen atom returns to oxygen (Scheme 2, sequence $b' \rightarrow c$).

Finally, from ion *c* a molecule of vinylalcohol may be eliminated *via* a four-membered transition state[12] (arrows in ion *c*) generating ion *d*.

The 'aromatic — hydroxylic'-exchange of hydrogens in the molecular ion of 2-phenylethanol-1 can only be deduced from observed diffuse peaks, because the peak at *m*/*e* 78 (ion *d*) in the mass spectrum of unlabeled 2-phenylethanol-1 does not shift clearly in the mass spectra of its deuterated analogues (see Figs. 6 to 12). Moreover, another route is also operative in the formation of ion *d* (see below).

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* Reactions, for which corresponding diffuse peaks are observed, are denoted by an asterisk. The numbers at the reactions correspond with the reaction numbers in Appendix 2.

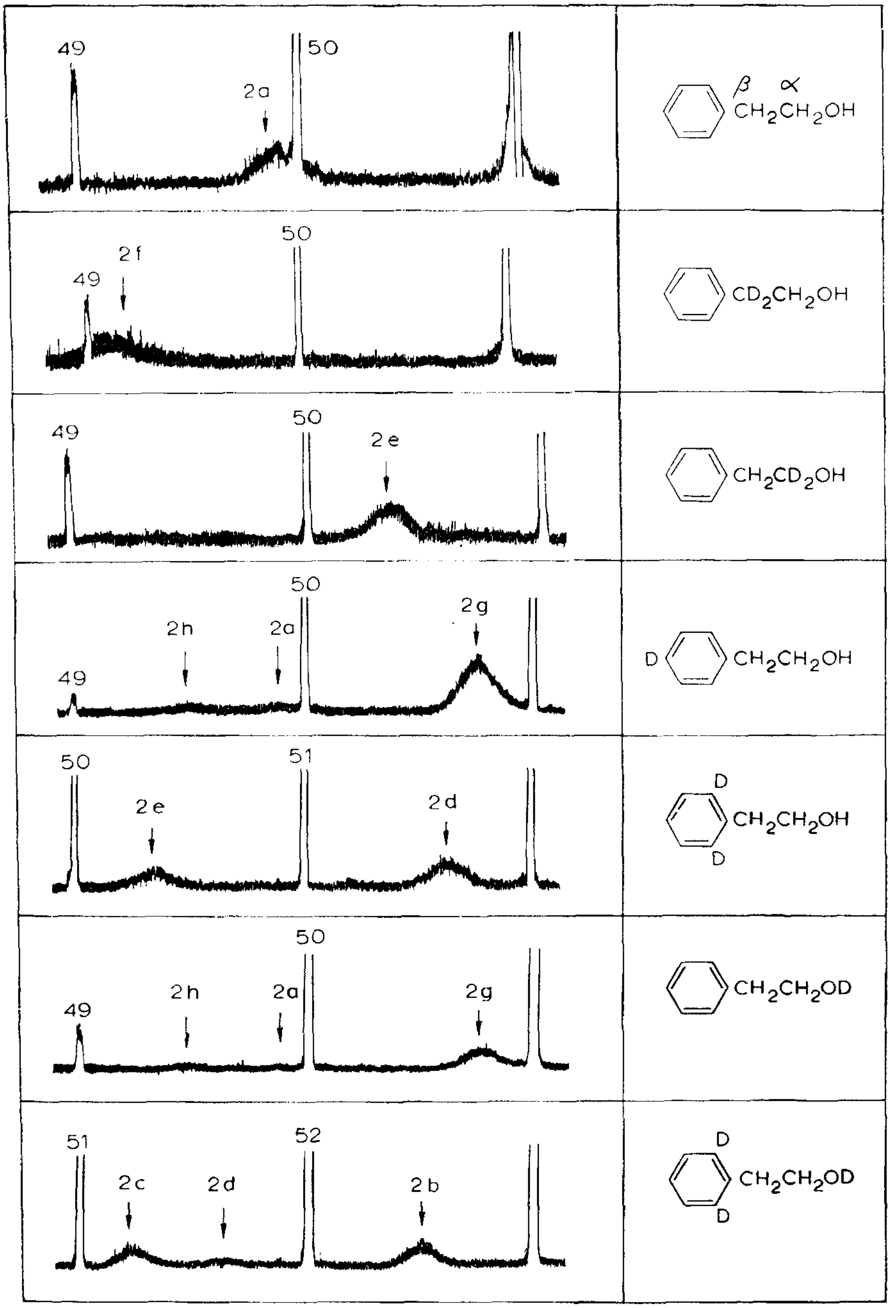
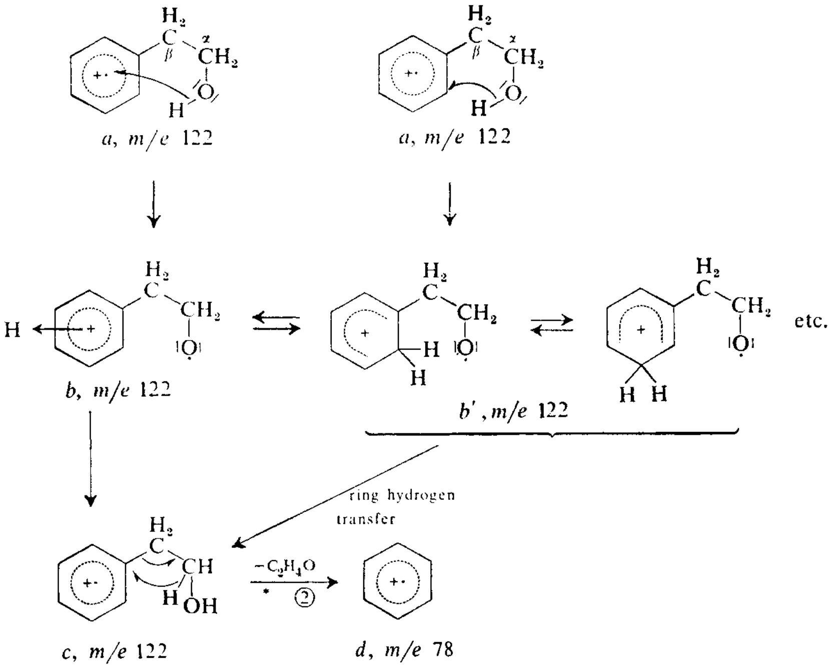


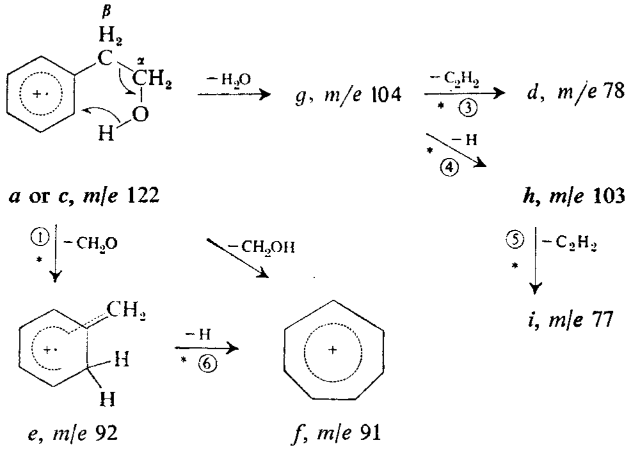
FIG. 5. Partial mass spectra of 2-phenylethanol-1 and its specifically deuterated analogues, obtained at 25–30 eV and with maximum gain of the electron multiplier. Code numbers 2a, 2b, etc. refer to reaction numbers in Appendix 2.



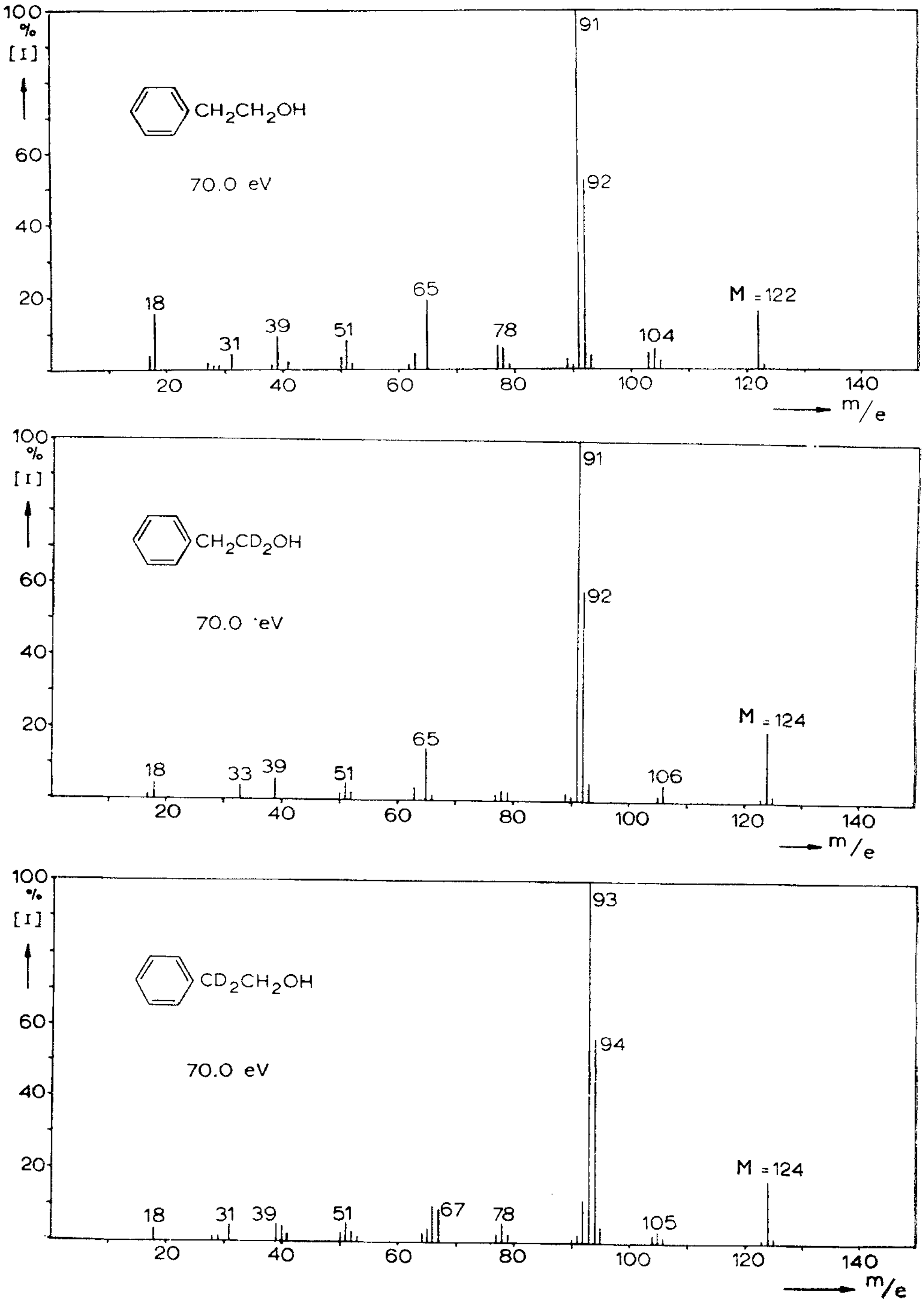
SCHEME 2

The suggested exchange contrasts with the behaviour of the molecular ions from γ-phenylpropanol,[5] γ-phenylpropylbromide[15] and benzoic acid,[16] in which specific '*ortho*-γ-hydroxylic'-, '*ortho*-α'- and '*ortho*-hydroxylic' exchanges of hydrogens have been found respectively.

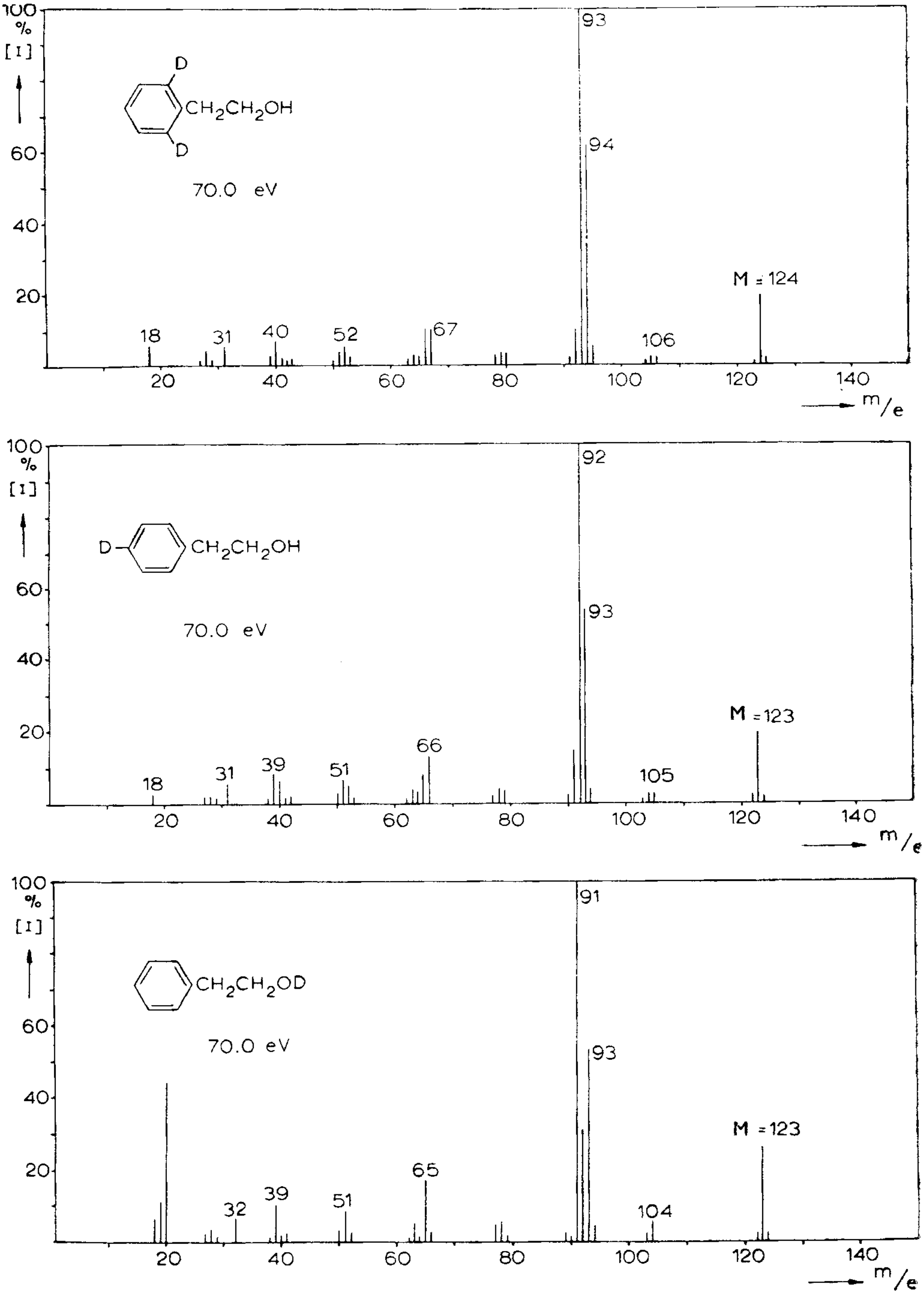
2. *Elimination of* H_2CO *from the molecular ion* (*Scheme* 3). In the mass spectra of undeuterated 2-phenylethanol-1 ($M = 122$) and its α-d_2 analogue a peak is found at *m/e* 92 (Figs. 6 and 7). This peak shifts to *m/e* 93 in the mass spectra of the O-d_1 and *para*-d_1 compounds, to *m/e* 94 in the spectra of the β-d_2 and *ortho*-d_2 analogues and to *m/e* 95 in the mass spectrum of the (*ortho*-d_2 + O-d_1) derivative (Figs. 8 to 12).



SCHEME 3



FIGS. 6, 7 and 8. Mass spectra of 2-phenylethanol-1 and its α-d_2 and β-d_2 analogues.



FIGS. 9, 10 and 11. Mass spectra of *ortho*-d_2, *para*-d_1 and O-d_1 analogues of 2-phenylethanol-1.

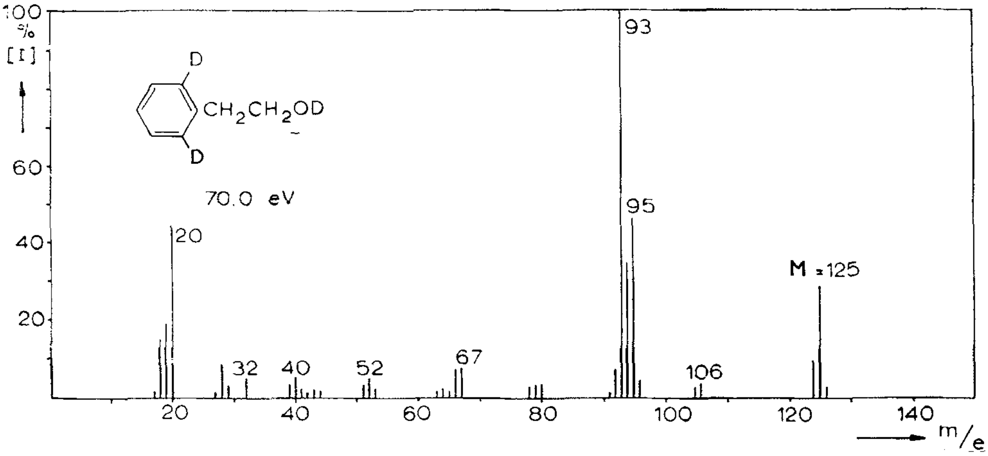


FIG. 12. Mass spectrum of the (*ortho*-d_2 + O-d_1) analogue of 2-phenylethanol-1.

This can all be explained by the elimination of a molecule of formaldehyde from the molecular ion *via* a McLafferty rearrangement[4] of the hydroxylic hydrogen atom to one of the *ortho* positions of the phenyl ring (Scheme 3, sequence *a* → *e*). Diffuse peaks support this reaction and indicate that the eliminated molecule of formaldehyde contains specifically the α-hydrogen atoms (Appendix 2, reaction no. 1).

The same conclusion was partly reached earlier by Gilpin,[3] who measured the mass spectra of unlabelled 2-phenylethanol-1 and of its O-d_1 analogue. He noted, however, that the peak at *m/e* 92 in the mass spectrum of the O-d_1 compound could not be explained completely by the presence of undeuterated 2-phenylethanol-1 and natural ^{13}C contribution of the peak at *m/e* 91. He therefore concluded that a hydrogen atom rearrangement also takes place (*m/e* 92), although to a minor extent as compared with the rearrangement of the deuterium atom (*m/e* 93).[3] This explanation for the peak at *m/e* 92 in the mass spectrum of the O-d_1 compound seems to us very unlikely, because the molecule of formaldehyde, lost from the molecular ion, would then not contain *both* α-hydrogen atoms, as found by us. An alternative explanation for the occurrence of the peak at *m/e* 92 in the mass spectrum of the O-d_1 compound can be given on the basis of the diffuse peaks, found in the spectra. These show a random loss of hydrogen from ion *e* to give the tropylium ion *f*, as found earlier[5] (Appendix 2, reaction no. 6).

Finally, it may be noted that prior to the McLafferty rearrangement of the hydroxylic hydrogen atom to one of the *ortho* positions of the phenyl ring, an 'aromatic — hydroxylic' -exchange of hydrogens in the molecular ion may have occurred, as discussed in 1 (Scheme 3, sequence *c* → *e*). This exchange process, however, has no influence on the elimination of a molecule of H_2CO from the molecular ion.

3. *Formation of the tropylium ion* (*Scheme* 3). The base peaks in all spectra can be explained by a simple C_α-C_β cleavage, generating the well-known tropylium ion, although this ion could possibly also be partly formed from an 'aromatic hydrogen-hydroxylic hydrogen'-exchanged molecular ion, as discussed in 1 (Figs. 6 to 12 and Scheme 3, sequence *a*, *c* → *f*). Another route to the tropylium ion *f* is the loss of a hydrogen atom from ion *e* (Scheme 2), as discussed in 2.

4. *Successive losses of* H_2O *and* C_2H_2 *from the molecular ion* (*Scheme* 3). In the mass spectra of 2-phenylethanol-1 and its O-d_1 analogue a small peak is observed at *m/e* 104. This peak shifts to *m/e* 105 in the mass spectra of the *para*-d_1 and β-d_2 compounds and to *m/e* 106 in the spectra of the *ortho*-d_2, α-d_2 and (*ortho*-d_2 + O-d_1) analogues (Figs. 6 to 12).

These observations can be explained by the loss of a molecule of water, containing a β-hydrogen atom, from the molecular ion (Scheme 3, sequence $a \rightarrow g$), although dehydration prior to electron impact could also happen. Moreover, just as noted in 2 and 3, loss of a molecule of water from an 'aromatic hydrogen-hydroxylic hydrogen'-exchanged molecular ion cannot be excluded altogether (Scheme 3, sequence $c \rightarrow g$).

After randomization of hydrogen atoms, ion *g* loses acetylene, as established by the diffuse peaks found in the spectra (Table 6, reaction no. 3).

The same is true for the loss of a hydrogen atom from ion *g*, which results in the formation of ion *h*, which also eliminates acetylene (Appendix 2, reaction no.'s 4 and 5, respectively).

This behaviour of ion *g* resembles that of styrene, for which an octatetraene ring with a random distribution of hydrogen atoms has been proposed earlier, based on the mass spectra of some specifically deuterated styrenes.[17]

Fragmentation of 1-*phenylpropanol*-2, $C_6H_5\overset{\beta}{C}H_2\overset{\alpha}{C}H(OH)\overset{\beta'}{C}H_3$

Comparison of the standard spectrum with that of α-d_1, O-d_1, β'-d_3, β, β'-d_5 and (β, β'-d_5 + O-d_1) analogues together with the *m/e* and m_2/m_1 values for diffuse peaks enable us to distinguish four main reaction paths for the decomposition of the molecular ion (See Figs. 13 to 18, Appendix 3 and Schemes 4 and 5†).

1. *Elimination of acetaldehyde from the molecular ion.* In the mass spectra of unlabelled 1-phenylpropanol-2 (M = 136) and its β'-d_3 and α-d_1 analogues the base peak is found at *m/e* 92 (Figs. 13 to 15). This peak shifts to *m/e* 93 in the mass spectrum of the O-d_1 compound (Fig. 16), to *m/e* 94 in that of the β, β'-d_5 compound (Fig. 17) and to *m/e* 95 in that of the (β, β'-d_5 + O-d_1) analogue (Fig. 18).

This can all be explained by a McLafferty rearrangement[4] of the hydroxylic hydrogen atom to one of the *ortho*-positions of the phenyl ring and the deuterium labelling indicates that transfer occurs exclusively from this functionality, even if other hydrogen atoms are available like those of the CH_3 group in the present study. This has been already noted earlier[18] from the mass spectra of O-d_1 analogues of compounds, closely related to 1-phenylpropanol-2. This phenomenon however, can be explained in two ways:

(a) The McLafferty rearrangement takes place in the molecular ion. Then we must conclude, that participation of the hydroxylic hydrogen atom in this rearrangement is energetically much more favourable than that of the hydrogen atom linked in the alkyl group (e.g. CH_3 group).

(b) The McLafferty rearrangement takes place in the fragment ion, formed from the molecular ion by loss of the CH_3 group. In that case a hydrogen atom from the CH_3 group cannot participate in this reaction. Diffuse peaks, found in the spectra, favour the first explanation (See Appendix 3, reaction no. 1). Thus we may conclude that the molecular ion of 1-phenylpropanol-2 loses a molecule of acetaldehyde *via* the process depicted in Scheme 4, sequence $a \rightarrow b$.

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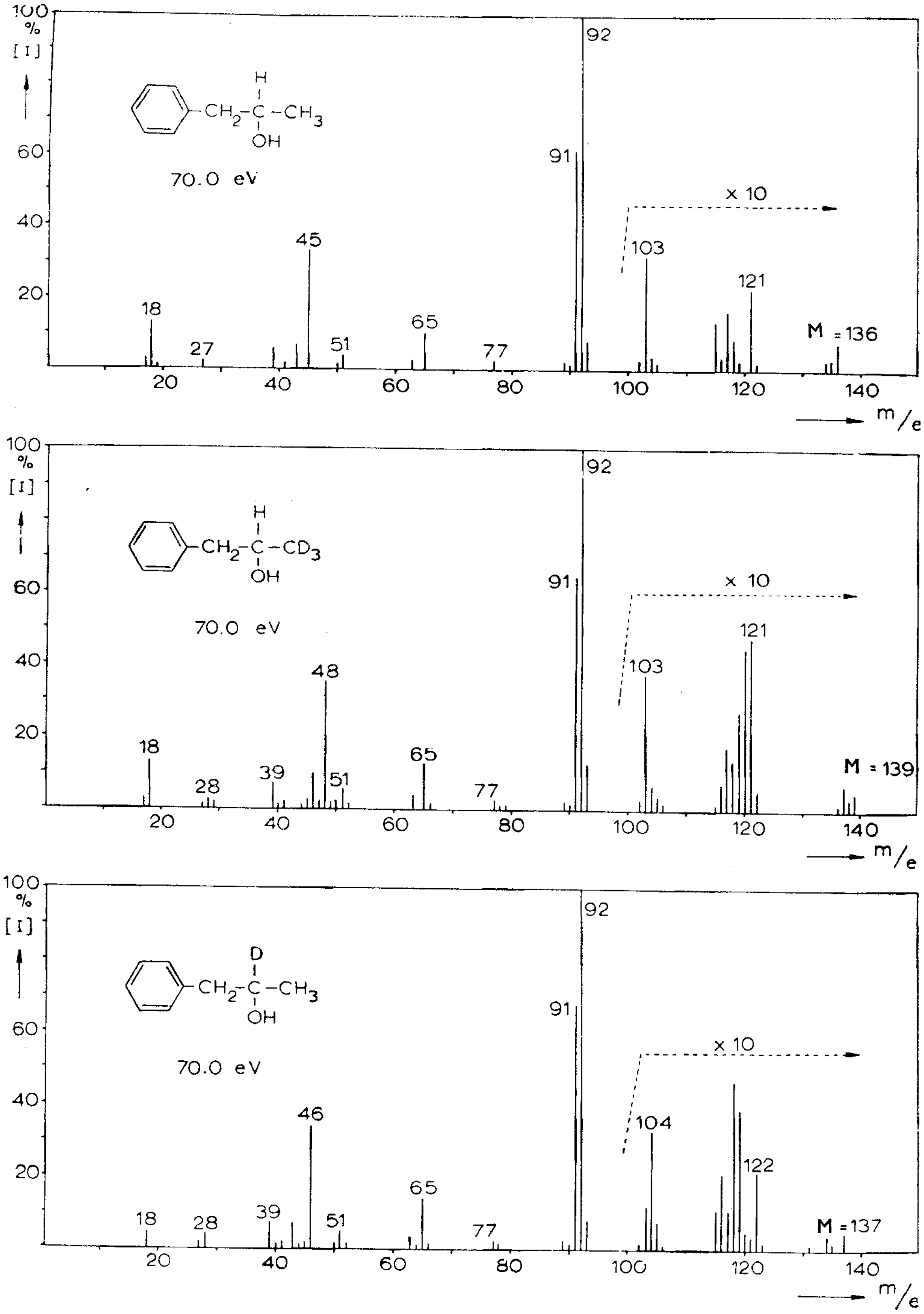
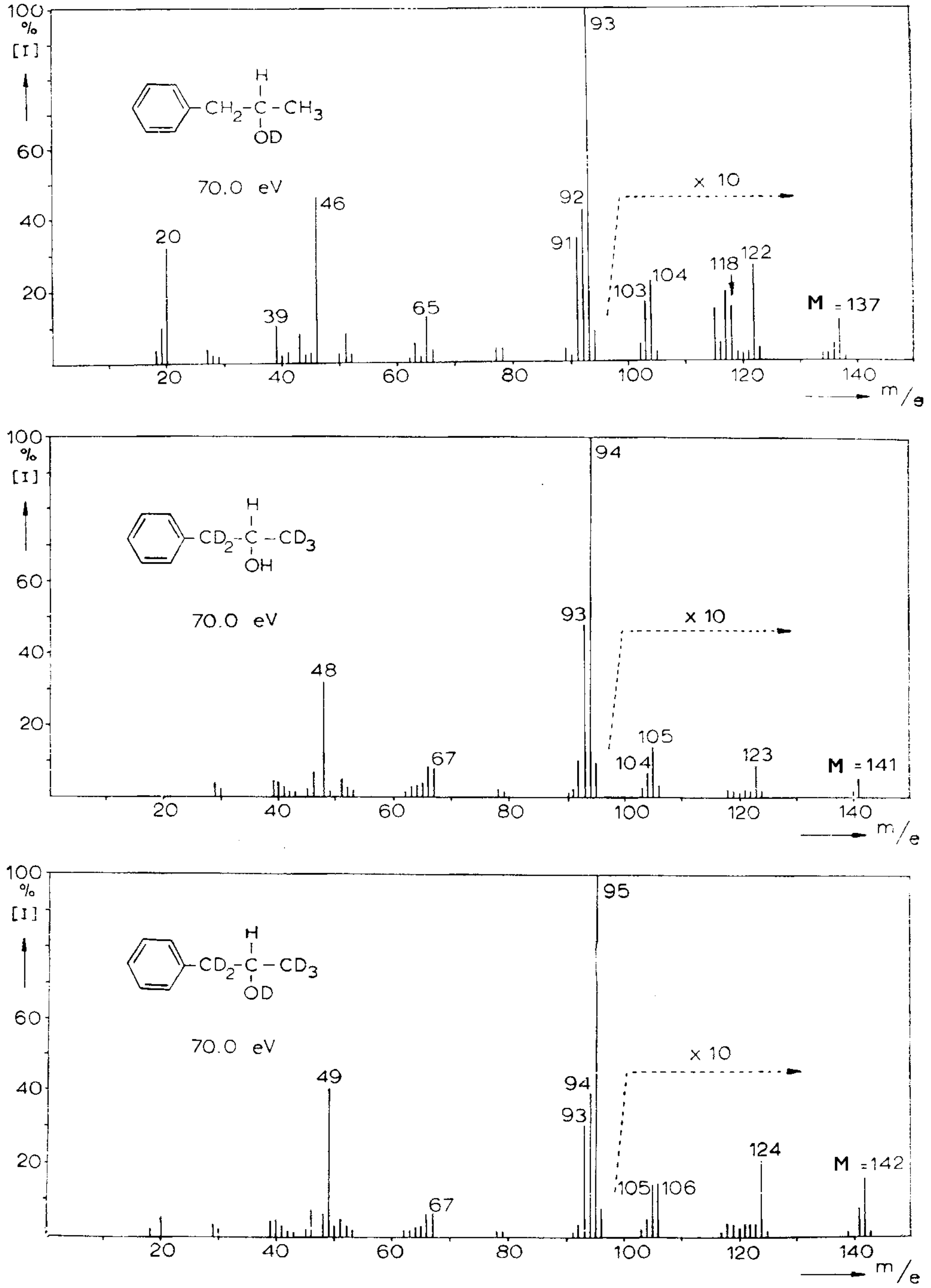
* Reactions, for which corresponding diffuse peaks are observed, are denoted by an asterisk. The numbers at the reactions correspond with the reaction numbers in Appendix 3.



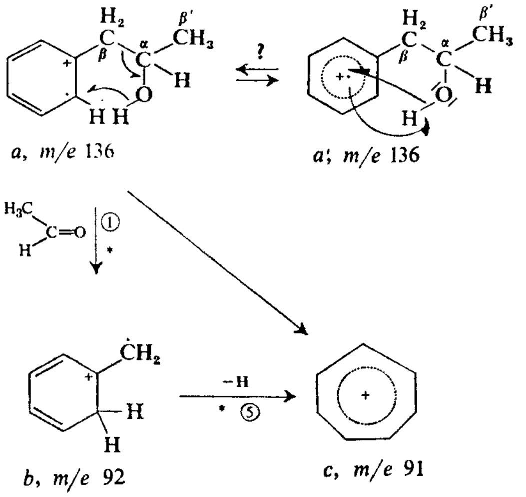
FIGS. 13, 14 and 15. Mass spectra of 1-phenylpropanol-2 and its β'-d_3 and α-d_1 analogues.



FIGS. 16, 17 and 18. Mass spectra of O-d_1, β, β'-d_5 and (β, β'-d_5 + O-d_1) analogues of 1-phenylpropanol-2.

Just as noted in 2-phenylethanol-1, prior to the McLafferty rearrangement an 'aromatic-hydroxylic'-exchange of hydrogens in the molecular ion may occur (Scheme 4, sequence *a'* → *a*). This however has no influence on the sequence *a* → *b*.

Diffuse peaks, observed in the spectra, indicate a random loss of a hydrogen atom from ion *b* to give the tropylium ion *c*, as found earlier[5] (Appendix 3, reaction no. 5). An other route to the tropylium ion *c* could be a simple C_β-C_α-cleavage in the molecular ion (Scheme 4, sequence *a* → *c*).



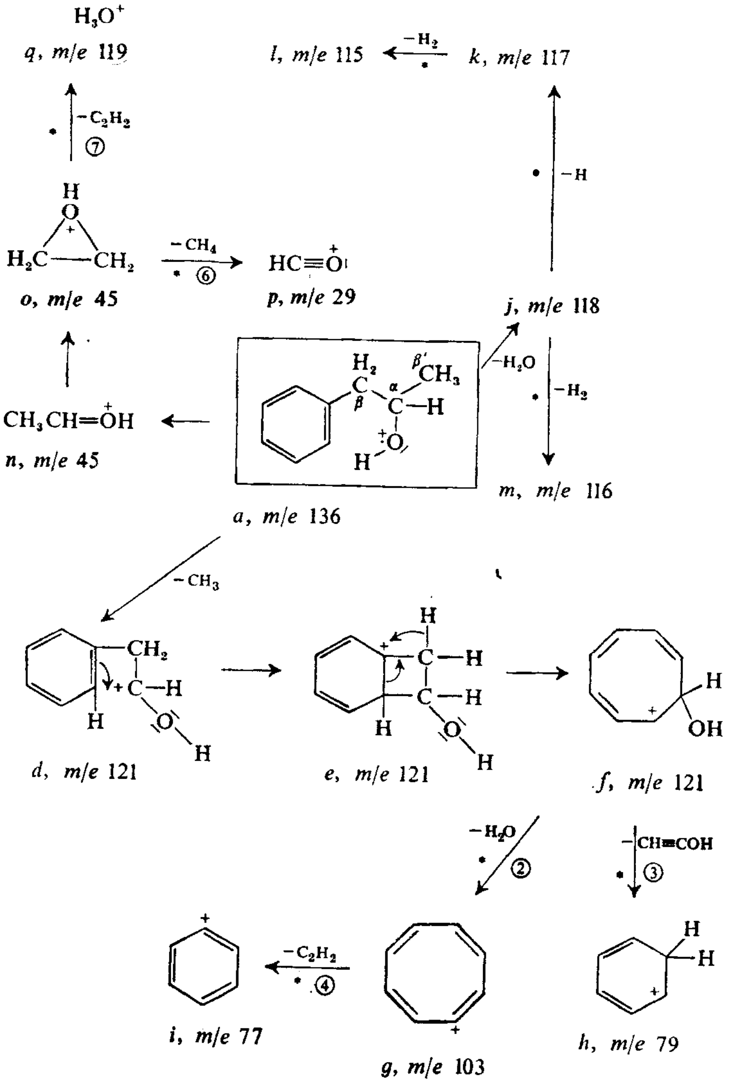
SCHEME 4

2. *Successive losses of* CH_3 *and* H_2O *or* C_2H_2O *from the molecular ion.* The shift of the peak at *m/e* 121 in the mass spectra of undeuterated 1-phenylpropanol-2 and its β'-d_3 analogue to *m/e* 122 in the mass spectra of the α-d_1 and O-d_1 compounds, to *m/e* 123 in the mass spectrum of the β, β'-d_5 analogue and to *m/e* 124 in the mass spectrum of the (β, β'-d_5 + O-d_1) derivative, corresponds with the loss of the CH_3 group from the molecular ion (Figs. 13 to 18 and Scheme 5, sequence *a* → *d*).

Ion *d* loses H_2O after an extensive scrambling of hydrogen atoms, as indicated by the diffuse peaks, found in the spectra (Appendix 3, reaction no. 2).

The extent of scrambling of hydrogen atoms in ion *d* could be estimated from retention of the original deuterium in the $[M - CH_3 - H_2O]^+$ ion, derived from corresponding ions *d* of the deuterated alcohols. To arrive at this, the intensity of the $[M - CH_3 - H_2O]^+$ ion from the undeuterated and from all specifically deuterated samples of 1-phenylpropanol-2 is expressed as percentage of the sum of the intensities of all corresponding $C_8H_xD_y^{\cdot+}$ ions after correction for natural ^{13}C contribution (8·8%). This leads to the values in Table 1.

From this Table retention of the original deuterium in the $[M - CH_3 - H_2O]^+$ ion can be calculated. This leads to the values in Table 2, which also contains values, expected after a complete scrambling of all hydrogen atoms in ion *d* (rows 'found' and 'Calc.' in Table 2, respectively).



Scheme 5

Table 1. Intensities of $C_8H_xD_y^+$ ions from deuterated 1-phenylpropanol-2 (in $\% \Sigma C_8H_xD_y^+$)

m/e	d_0	α-d_1	β'-d_3	O-d_1	β, β'-d_5	(β, β'-d_5 + O-d_1)
102	8·0	5·0	9·3	12·0	2·2	1·5
103	92·0	26·0	90·7	38·5	11·8	7·5
104	—	69·0	—	49·5	28·3	13·4
105	—	—	—	—	57·7	39·4
106	—	—	—	—	—	38·2

The underlined values refer to the $[M - CH_3 - H_2O]^+$ ion.

TABLE 2. LABEL RETENTIONS IN $C_8H_7^+$ FROM DEUTERATED 1-PHENYLPROPANOL-2 (IN %)

	α-d_1	O-d_1	β, β'-d_5	(β, β'-d_5 + O-d_1)
Found	75·0	53·8	62·7	41·5
Calc.	77·8	77·8	58·3	41·7

From this Table it appears, that scrambling of all hydrogen atoms in ion *d* is almost complete; however, it must be pointed out that:

(a) No corrections have been made for incomplete labelling, because the D-content of site-specifically deuterated 1-phenylpropanol-2 could not be measured by mass spectrometry (see Experimental). This is no objection, because the NMR spectra of the α-d_1, β'-d_3 and β, β'-d_5 analogues have shown a specific and an almost complete deuteration (see Experimental), whereas the peak at *m/e* 45 in the mass spectrum of the d_0 compound, due to the $CH_3CH(OH)^+$-ion, shifts to a very large extent to *m/e* 46 and to *m/e* 49 in the mass spectra of the O-d_1 and (β, β'-d_5 + O-d_1) analogues, respectively (see Figs. 13, 16 and 18).

(b) It has been assumed, that the $C_8H_7^+$-ion originates exclusively from ion *d*. Alternatively, the $C_8H_7^+$-ion could also be formed from the $[M - H_2O]^+$-ion by loss of the CH_3-group. If the $(M - H_2O)^+$-ion has a β-methylstyrene structure, then the importance as a precursor of the $C_8H_7^+$-ion is rather low (relative abundances of the fragments *m/e* 118 and *m/e* 103 in the mass spectrum of β-methylstyrene[19] are 76·5% and 10%, respectively).

Another indication for scrambling of hydrogen atoms in ion *d* is the loss of C_2H_2O from this ion, as substantiated by the diffuse peaks (Appendix 3, reaction no. 3). To explain the scrambling of hydrogen atoms in ion *d*, we propose an eight-membered ring structure for the $C_8H_9O^+$-ion, possibly formed by the mechanism presented in Scheme 5, sequence $d \rightarrow e \rightarrow f$, and analogous to that suggested for the $C_8H_9^+$-ion from γ-phenylpropanol.[5] After a series of successive 1-2- and/or 1-5 shifts of hydrogen[20] in ion *f*, H_2O as well as C_2H_2O (possibly hydroxyacetylene) are eliminated, generating ions *g* and *h* (Scheme 5).

Finally, from ion *g* a molecule of C_2H_2 is eliminated giving ion *i*, as supported by diffuse peaks (Appendix 3, reaction no. 4).

3. *Loss of a molecule of water from the molecular ion.* The peak at *m/e* 118 in the spectra of the d_0 and O-d_1 compounds shifts to *m/e* 119 in the mass spectrum of the α-d_1 analogue (Figs. 13, 15 and 16) and to *m/e* 121 in the spectrum of the β'-d_3 compound (Fig. 14; this peak coincides with that due to the $[M - CD_3]^+$ ion).

No clear shift of this peak is observed in the mass spectra of the β, β'-d_5 and (β, β'-d_5 + O-d_1) analogues (Figs. 17 and 18).

It is possible, that water is eliminated from the molecular ion in a rather complicated manner. Also the structure of the resulting ion *j* is unknown (Scheme 5). It can only be stated, that the loss of H and H_2 from this ion is analogous to that found for the $C_9H_{10}^+$ ion, derived from γ-phenylpropanol[5] (Scheme 5, sequences $j \rightarrow k \rightarrow l$ and $j \rightarrow m$).

4. *Formation and further degradation of the $C_2H_5O^+$ ion.* The peak at *m/e* 45 in the mass spectrum of the d_0 compound shifts to *m/e* 46 in the mass spectra of the α-d_1 and O-d_1 analogues, to *m/e* 48 in the spectra of the β'-d_3 and β, β'-d_5 compounds and to *m/e* 49 in the mass spectrum of the (β, β'-d_5 + O-d_1) derivative (Figs. 13 to

18). This can be explained by a simple C_β-C_α cleavage in the molecular ion with charge retention on the hydroxyl containing moiety (Scheme 5, sequence $a \rightarrow n$). It has been proposed earlier[21,22] that ion *n* isomerizes to ion *o*, from which a CH_4 and a C_2H_2 molecule are eliminated (Scheme 5, sequences $o \rightarrow p$ and $o \rightarrow q$ and Appendix 3, reaction nos 6 and 7). The diffuse peaks, corresponding with these reactions, indicate that all hydrogen atoms in ion *o* scramble in contrast with a previous study,[21] which has suggested no participation of the hydroxylic hydrogen atom in the scrambling process in ion *o*.

EXPERIMENTAL

Mass spectra were obtained with an AEI MS-2H and an AEI MS-9 mass spectrometer. Samples were introduced through a heated (Gallium) inlet system at 150°. The spectra from both instruments were essentially the same. The *m/e* and the m_2/m_1 values for diffuse peaks have been measured on the MS-9 instrument (Appendices 1, 2 and 3), as described earlier.[5]

TABLE 3. MEASUREMENT OF DEUTERIUM CONTENT (%) OF LABELLED 1-PHENYLETHANOL-1, $C_6H_5\overset{\alpha}{C}H(OH)\overset{\beta}{C}H_3$

	By mass spectrometry Accuracy limit 0·3%					By NMR Accuracy limit 1 to 2%
Ionization energy	Site-specifically deuterated 1-phenylethanol-1	d_3	d_2	d_1	d_0	
	α-d_1	—	—	95·9	4·1	95
9·0 eV	β-d_3	97·7	2·3	—	—	98
	O-d_1	—	—	93·7	6·3	1

All samples were purified by preparative gas chromatography with a Wilkens Aerograph A-90-P instrument. The applied columns were a 2·5 m/6 mm with 30% PEG 2000 for the undeuterated 1-phenylethanol-1 and its α-d_1 and β-d_3 analogues (column temp. 170°; retention time 30·2 min) and for unlabelled 1-phenylpropanol-2 and its α-d_1, β′-d_3 and β, β′-d_5 analogues (column temp. 158°; retention time 61·5 min) and a 2 m/6 mm with 20% Silicone Rubber SE-52 for 2-phenylethanol-1 and its α-d_2, β-d_2, *ortho*-d_2 and *para*-d_1 analogues (column temp. 150°; retention time 13·6 min). The supporting material was kieselguhr and helium was used as carrier gas. After purification IR and NMR spectra established the structure, the D content and the purity.

The D content of the specifically deuterated analogues from 1-phenylethanol-1 and 2-phenylethanol-1 was also measured by mass spectrometry, using such a low ionization energy, that in the parent mass regions from the spectra of the corresponding undeuterated compounds only the molecular ion peaks remained. The results of these measurements have been collected in Tables 3 and 4. The D content of the specifically deuterated analogues from 1-phenylpropanol-2 could not be measured by mass spectrometry because of the low intensity of the molecular ion peak and the presence of a $[M - 1]^+$ ion peak, not disappearing completely at lower ionization energy, in the mass spectrum of the corresponding unlabelled compound.

Preparation of the α-d_1 *analogue from* 1-*phenylethanol*-1. 9·3 g of acetophenone were reduced[23] with $LiAlD_4$ to 8·8 g of $C_6H_5CD(OH)CH_3$.

Preparation of the β-d_3 *analogue from* 1-*phenylethanol*-1. 12 g of acetophenone were heated with 10 g of D_2O and 100 mg of K_2CO_3 for 16 hr at 110°.[24,25] After exchange the deuterated compound was extracted with dry ether, the ether was removed and the residue subjected to the same procedure three more times. Then it was reduced with $LiAlH_4$ to 9·7 g of $C_6H_5CH(OH)CD_3$.

Preparations of the O-d_1 *analogue from* 1-*phenylethanol*-1. D_2O was introduced in the heated inlet system of the mass spectrometer and pumped away after a few minutes. This operation was repeated several times. Then 1-phenylethanol-1, previously treated with an excess of D_2O, was introduced in the heated inlet system together with a fresh portion of D_2O.[26,27]

Table 4. Measurement of deuterium content (%) of labelled 2-phenylethanol-1, $C_6H_5\overset{\beta}{C}H_2\overset{\alpha}{C}H_2OH$

	By mass spectrometry Accuracy limit 0·1%					By NMR Accuracy limit 1 to 2%
Ionization energy	Site-specifically deuterated 2-phenylethanol-1	d_3	d_2	d_1	d_0	
10·0 eV	α-d_2	—	94·4	5·6	—	96
	β-d_2	—	94·6	5·4	—	9
	ortho-d_2	—	95·4	4·6	—	—
	para-d_1	—	—	89·9	10·1	—
	O-d_1	—	—	92·8	7·2	—
	(*ortho*-d_2 + O-d_1)	73·3	25·0	1·7	—	—

Preparations of 2-*phenylethanol*-1, *specifically deuterated in the* α, β, ortho *and* para *positions.* The syntheses of these compounds have been described earlier.[5]

Preparations of the O-d_1 *analogues from* 2-*phenylethanol*-1 *and its* ortho-d_2 *derivative.* These compounds were obtained, as described above.

Preparations of 1-*phenylpropanol*-2 *and its* α-d_1 *analogue.* These compounds were obtained by reduction of phenylacetone with $LiAlH_4$ and $LiAlD_4$, respectively.[23] According to the NMR spectrum the α-d_1 analogue was deuterated specifically in the α-position and to the extent of 95%.

Preparation of the β′-d_3 *analogue from* 1-*phenylpropanol*-2. 50 g of propylenecarbonate (Fluka reagent) were reduced[28] with $LiAlD_4$ in diethylcarbitol to 9·4 g of CD_3OH with b.p. 61° to 64° and deuterated to the extent of 98% (NMR). This was converted into 32·7 g CD_3J.[29] The Grignard compound was made from 14·1 g of CD_3J to react with 11·6 g of phenylacetaldehyde, giving after hydrolysis and distillation 9·4 g of $C_6H_5CH_2CH(OH)CD_3$ with b.p. 90° to 91°/6 mm and deuterated to the extent of 97% (NMR).

Preparation of the β, β′-d_5 *analogue from* 1-*phenylpropanol*-2. 3 g of phenylacetone were exchanged twice with 12·5 g of D_2O and 200 mg of K_2CO_3 for 18 hr at 90°. The exchanged product was then reduced with $LiAlH_4$ in a standard procedure[23] to $C_6H_5CD_2CH(OH)CD_3$, which was deuterated specifically in the β- and β′-positions to the extent of 99% (NMR).

Preparations of the O-d_1 *analogues from* 1-*phenylpropanol*-2 *and its* β, β′-d_5 *derivative.* These compounds were obtained, as described above.

Acknowledgement—The authors are greatly indebted to Mr W. J. Rooselaar and Mr J. D. van Wageningen, who measured the mass spectra, to Miss M. Boomgaard for taking the NMR spectra and to Miss A. M. A. Schoff for the IR spectra.

APPENDIX 1. DIFFUSE PEAKS, OBSERVED IN THE MASS SPECTRA OF SITE-SPECIFICALLY DEUTERATED $C_6H_5\overset{\alpha}{C}H(OH)\overset{\beta}{C}H_3$

Reaction no.	Metastable transitions	d$_0$		β-d$_3$		α-d$_1$		O-d$_1$		Calc.	
		m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1
1†	$C_8H_{10}O^+ \rightarrow C_7H_7O^+ + CH_3$	93·83	·877	—	—	93·83	·878	93·82	·878	93·88	·877
1†	$C_8H_7D_3O^+ \rightarrow C_7H_7O^+ + CD_3$	—	—	91·56	·857	—	—	—	—	91·61	·856
1†	$C_8H_8D_2O^+ \rightarrow C_7H_7O^+ + CHD_2$	—	—	92·30	·857	—	—	—	—	92·35	·863
1†	$C_8H_9DO^+ \rightarrow C_7H_6DO^+ + CH_3$	—	—	—	—	94·82	·879	94·81	·879	94·87	·878
2	$C_8H_9O^+ \rightarrow C_2H_3O^+ + C_6H_6$	15·28	—	—	—	—	—	—	—	15·29	·355
2	$C_8H_6D_3O^+ \rightarrow C_2D_3O^+ + C_6H_6$	—	—	17·05	—	—	—	—	—	17·08	·371
2	$C_8H_8DO^+ \rightarrow C_2H_3O^+ + C_6H_5D$	—	—	—	—	15·17	—	15·14	—	15·16	·352
3	$C_7H_7O^+ \rightarrow C_6H_7^+ + CO$	58·41	·741	58·38	·741	—	—	—	—	58·38	·738
3	$C_7H_6DO^+ \rightarrow C_6H_6D^+ + CO$	—	—	—	—	59·34	·743	59·32	·744	59·32	·741
4	$C_7H_5O^+ \rightarrow C_6H_5^+ + CO$	56·48	·736	56·47	·736	56·49	·737	56·50	·737	56·51	·733
5	$C_6H_7^+ \rightarrow C_6H_5^+ + H_2$	75·07	·974	75·07	·974	—	—	75·05	·978	75·07	·975
5	$C_6H_6D^+ \rightarrow C_6H_4D^+ + H_2$	—	—	—	—	76·06	·975	76·05	·976	76·08	·975
5	$C_6H_6D^+ \rightarrow C_6H_5^+ + HD$	—	—	—	—	74·12	·963	74·10	·966	74·13	·962

† For reaction no. 1 isotope diffuse peaks have also been observed in the spectra; these have been omitted in the Appendix.

APPENDIX 2. DIFFUSE PEAKS, OBSERVED IN THE MASS SPECTRA

Reaction No.	Metastable transitions	d_0		α-d_2	
		m*	m_2/m_1	m*	m_2/m_1
1	$^{13}C_1{}^{12}C_7H_{10}O^+ \rightarrow {}^{13}C_1{}^{12}C_6H_8^+ + H_2CO$	70·30	—	—	—
1	$C_8H_{10}O^+ \rightarrow C_7H_8^+ + H_2CO$	69·37	0·757	—	—
1	$^{13}C_1{}^{12}C_7H_7D_3O^+ \rightarrow {}^{13}C_1{}^{12}C_6H_5D_3^+ + H_2CO$	—	—	—	—
1	$C_8H_7D_3O^+ \rightarrow C_7H_5D_3^+ + H_2CO$	—	—	—	—
1	$^{13}C_1{}^{12}C_7H_8D_2O^+ \rightarrow {}^{13}C_1{}^{12}C_6H_6D_2^+ + H_2CO$	—	—	—	—
1	$C_8H_8D_2O^+ \rightarrow C_7H_6D_2^+ + H_2CO$	—	—	—	—
1	$^{13}C_1{}^{12}C_7H_8D_2O^+ \rightarrow {}^{13}C_1{}^{12}C_6H_8^+ + D_2CO$	—	—	69·19	—
1	$C_8H_8D_2O^+ \rightarrow C_7H_8^+ + D_2CO$	—	—	68·26	0·744
1	$^{13}C_1{}^{12}C_7H_9DO^+ \rightarrow {}^{13}C_1{}^{12}C_6H_7D^+ + H_2CO$	—	—	—	—
1	$C_8H_9DO^+ \rightarrow C_7H_7D^+ + H_2CO$	—	—	—	—
1	$C_8H_9DO^+ \rightarrow C_7H_8^+ + HDCO$	—	—	68·80	0·744
2a	$C_8H_{10}O^+ \rightarrow C_6H_6^+ + C_2H_4O$	49·91	0·643	—	—
2b	$C_8H_7D_3O^+ \rightarrow C_6H_3D_3^+ + C_2H_4O$	—	—	—	—
2c	$C_8H_7D_3O^+ \rightarrow C_6H_4D_2^+ + C_2H_3DO$	—	—	—	—
2d	$C_8H_8D_2O^+ \rightarrow C_6H_4D_2^+ + C_2H_4O$	—	—	—	—
2e	$C_8H_8D_2O^+ \rightarrow C_6H_5D^+ + C_2H_3DO$	—	—	50·35	0·640
2f	$C_8H_8D_2O^+ \rightarrow C_6H_6^+ + C_2H_2D_2O$	—	—	—	—
2g	$C_8H_9DO^+ \rightarrow C_6H_5D^+ + C_2H_4O$	—	—	—	—
2h	$C_8H_9DO^+ \rightarrow C_6H_6^+ + C_2H_3DO$	—	—	—	—
3	$C_8H_8^+ \rightarrow C_6H_6^+ + C_2H_2$	58·52	0·754	—	—
3	$C_8H_6D_2^+ \rightarrow C_6H_4D_2^+ + C_2H_2$	—	—	60·36	0·755
3	$C_8H_6D_2^+ \rightarrow C_6H_5D^+ + C_2HD$	—	—	59·0	0·747
3	$C_8H_7D^+ \rightarrow C_6H_5D^+ + C_2H_2$	—	—	59·45	0·753
3	$C_8H_7D^+ \rightarrow C_6H_6^+ + C_2HD$	—	—	57·95	0·738
4	$C_8H_8^+ \rightarrow C_8H_7^+ + H$	102·0	0·987	—	—
4	$C_8H_6D_2^+ \rightarrow C_8H_5D_2 + H$	—	—	104·02	0·989
4	$C_8H_6D_2^+ \rightarrow C_8H_6D^+ + D$	—	—	102·06	0·979
4	$C_8H_7D^+ \rightarrow C_8H_6D^+ + H$	—	—	103·01	0·988
4	$C_8H_7D^+ \rightarrow C_8H_7^+ + D$	—	—	—	—
5	$C_8H_7^+ \rightarrow C_6H_5^+ + C_2H_2$	57·56	0·751	—	—
5	$C_8H_5D_2^+ \rightarrow C_6H_3D_2^+ + C_2H_2$	—	—	59·45	0·753
5	$C_8H_5D_2^+ \rightarrow C_6H_4D^+ + C_2HD$	—	—	57·95	0·738
5	$C_8H_6D^+ \rightarrow C_6H_4D^+ + C_2H_2$	—	—	58·54	0·749
6	$C_7H_8^+ \rightarrow C_7H_7^+ + H$	90·01	0·987	90·03	0·987
6	$C_7H_5D_3^+ \rightarrow C_7H_4D_3^+ + H$	—	—	—	—
6	$C_7H_5D_3^+ \rightarrow C_7H_5D_2^+ + D$	—	—	—	—
6	$C_7H_6D_2^+ \rightarrow C_7H_5D_2^+ + H$	—	—	—	—
6	$C_7H_6D_2^+ \rightarrow C_7H_6D^+ + D$	—	—	—	—
6	$C_7H_7D^+ \rightarrow C_7H_6D^+ + H$	—	—	—	—
6	$C_7H_7D^+ \rightarrow C_7H_7^+ + D$	—	—	—	—

† These diffuse peaks are just visible (see Fig. 5).

OF SITE-SPECIFICALLY DEUTERATED $C_6H_5\overset{\beta}{C}H_2\overset{\alpha}{C}H_2OH$

Reaction	O-d_1		β-d_2		ortho-d_2		para-d_1		(ortho-d_2 + O-d_1)		Calc.	
No.	m*	m_2/m_1	m*	m_2/m_1	m*	m_2/m_1	m*	m_2/m_1	m*	m_2/m_1	m*	m_2/m_1
1	—	—	—	—	—	—	—	—	—	—	70·37	0·756
1	69·38	0·757	—	—	—	—	69·37	0·757	—	—	69·43	0·754
1	—	—	—	—	—	—	—	—	73·20	—	73·22	0·762
1	—	—	—	—	—	—	—	—	72·21	—	72·27	0·760
1	—	—	72·26	—	72·23	—	—	—	72·21	—	72·27	0·760
1	—	—	71·30	0·760	71·25	0·759	—	—	71·26	—	71·32	0·758
1	—	—	—	—	—	—	—	—	—	—	69·24	0·744
1	—	—	—	—	—	—	—	—	—	—	68·30	0·742
1	71·26	—	—	—	—	—	71·27	—	71·26	—	71·32	0·758
1	70·35	0·758	70·33	0·760	70·30	0·758	70·31	0·758	70·31	—	70·38	0·756
1	—	—	—	—	—	—	—	—	—	—	68·86	0·748
2a	49·9†	0·640	—	—	—	—	49·9†	0·641	—	—	49·90	0·639
2b	—	—	—	—	—	—	—	—	52·51	0·650	52·53	0·648
2c	—	—	—	—	—	—	—	—	51·23	0·642	51·24	0·640
2d	—	—	—	—	51·64	0·647	—	—	51·6†	0·642	51·65	0·645
2e	—	—	—	—	50·34	0·640	—	—	—	—	50·36	0·637
2f	—	—	49·10	0·632	—	—	—	—	—	—	49·09	0·629
2g	50·79	0·645	—	—	—	—	50·77	0·646	—	—	50·78	0·642
2h	49·5†	0·640	—	—	—	—	49·5†	0·641	—	—	49·49	0·634
3	58·51	0·752	—	—	—	—	58·51	0·752	—	—	58·54	0·750
3	—	—	—	—	60·42	0·755	—	—	60·40	0·755	60·42	0·755
3	—	—	—	—	59·0	0·744	—	—	59·0	0·744	58·91	0·745
3	—	—	59·48	0·755	59·45	0·753	59·50	0·754	59·47	0·751	59·48	0·752
3	—	—	57·97	0·749	57·96	0·743	—	—	57·92	0·748	57·97	0·743
4	102·02	0·988	—	—	—	—	102·01	0·986	—	—	102·06	0·990
4	—	—	—	—	104·01	0·986	—	—	104·00	—	104·06	0·990
4	—	—	—	—	102·04	0·978	—	—	102·0	—	102·08	0·981
4	—	—	103·05	0·989	103·01	0·986	103·01	0·988	103·0	—	103·05	0·990
4	—	—	—	—	—	—	101·02	0·977	—	—	101·07	0·981
5	57·57	0·749	—	—	—	—	57·57	0·748	—	—	57·59	0·748
5	—	—	—	—	59·45	0·753	—	—	59·47	0·751	59·48	0·752
5	—	—	—	—	57·96	0·743	—	—	57·92	0·748	57·97	0·743
5	—	—	58·53	0·749	58·53	0·748	58·51	0·752	58·50	0·748	58·53	0·750
6	90·04	0·985	—	—	—	—	90·02	0·984	—	—	90·06	0·989
6	—	—	—	—	—	—	—	—	93·0	—	93·08	0·989
6	—	—	—	—	—	—	—	—	91·0	—	91·10	0·979
6	—	—	92·03	0·988	92·03	0·988	—	—	92·0	—	92·07	0·989
6	—	—	90·03	0·981	90·06	9·976	—	—	90·0	—	90·09	0·979
6	91·04	0·986	—	—	91·02	0·983	91·02	0·987	—	—	91·06	0·989
6	89·04	0·978	—	—	—	—	89·04	0·976	—	—	89·08	0·978

Appendix 3. Diffuse peaks, observed in the mass spectra of site-specifically deuterated $C\,\overset{\beta}{H_5}\overset{\alpha}{CH_2}CH(OH)\overset{\beta'}{CH_3}$

Reaction No.	Metastable transitions	d_0		β'-d_3		α-d_1		O-d_1		β,β'-d_5		(β,β'-d_5 + O-d_1)		Calc.	
		m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1
1	$C_9H_{12}O^+ \rightarrow C_7H_8^+ + C_2H_4O$	62·27	0·679	—	—	62·27	0·674	62·32	—	—	—	—	—	62·28	0·676
1	$C_9H_6D_6O^+ \rightarrow C_7H_5D_3^+ + C_2HD_3O$	—	—	—	—	—	—	—	—	—	—	63·59	0·670	63·60	0·669
1	$C_9H_7D_5O^+ \rightarrow C_7H_6D_2^+ + C_2HD_3O$	—	—	—	—	—	—	—	—	62·68	0·669	62·68	0·669	62·71	0·667
1	$C_9H_9D_3O^+ \rightarrow C_7H_8^+ + C_2HD_3O$	—	—	60·87	0·664	—	—	—	—	—	—	—	—	60·93	0·662
1	$C_9H_{10}D_2O^+ \rightarrow C_7H_8^+ + C_2H_2D_2O$	—	—	61·31	0·664	—	—	—	—	—	—	—	—	61·37	0·667
1	$C_9H_{11}DO^+ \rightarrow C_7H_8^+ + C_2H_3DO$	—	—	—	—	61·81	0·674	—	—	—	—	—	—	61·82	0·672
1	$C_9H_{11}DO^+ \rightarrow C_7H_7D^+ + C_2H_4O$	—	—	—	—	—	—	63·16	0·681	—	—	—	—	63·18	0·679
2	$C_8H_9O^+ \rightarrow C_8H_7^+ + H_2O$	87·71	0·853	87·72	0·852	—	—	—	—	—	—	—	—	87·72	0·851
2	$C_8H_6D_3O^+ \rightarrow C_8H_4D_3^+ + H_2O$	—	—	—	—	—	—	—	—	—	—	90·69	0·856	90·68	0·855
2	$C_8H_6D_3O^+ \rightarrow C_8H_5D_2^+ + HDO$	—	—	—	—	—	—	—	—	—	—	88·98	0·847	88·96	0·847
2	$C_8H_6D_3O^+ \rightarrow C_8H_6D^+ + D_2O$	—	—	—	—	—	—	—	—	—	—	87·18	0·843	87·27	0·839
2	$C_8H_7D_2O^+ \rightarrow C_8H_5D_2^+ + H_2O$	—	—	—	—	—	—	—	—	89·66	0·855	—	—	89·69	0·854
2	$C_8H_7D_2O^+ \rightarrow C_8H_6D^+ + HDO$	—	—	—	—	—	—	—	—	88·00	0·847	—	—	87·98	0·845
2	$C_8H_8DO^+ \rightarrow C_8H_6D^+ + H_2O$	—	—	—	—	88·59	0·853	88·60	0·853	—	—	—	—	88·71	0·852
2	$C_8H_8DO^+ \rightarrow C_8H_7^+ + HDO$	—	—	—	—	87·00	0·846	87·01	0·846	—	—	—	—	87·00	0·844
3	$C_8H_9O^+ \rightarrow C_6H_7^+ + C_2H_2O$	51·60	0·656	51·60	0·655	—	—	—	—	—	—	—	—	51·62	0·653
3	$C_8H_6D_3O^+ \rightarrow C_6H_4D_3^+ + C_2H_2O$	—	—	—	—	—	—	—	—	—	—	54·27	—	54·29	0·661
3	$C_8H_6D_3O^+ \rightarrow C_6H_5D_2^+ + C_2HDO$	—	—	—	—	—	—	—	—	—	—	52·98	0·655	52·96	0·653
3	$C_8H_7D_2O^+ \rightarrow C_6H_5D_2^+ + C_2H_2O$	—	—	—	—	—	—	—	—	53·37	—	—	—	53·40	0·659
3	$C_8H_7D_2O^+ \rightarrow C_6H_6D^+ + C_2HDO$	—	—	—	—	—	—	—	—	52·00	0·654	—	—	52·08	0·650
3	$C_8H_8DO^+ \rightarrow C_6H_6D^+ + C_2H_2O$	—	—	—	—	52·50	0·659	52·49	0·658	—	—	—	—	52·51	0·656
4	$C_8H_7^+ \rightarrow C_6H_5^+ + C_2H_2$	57·55	0·750	57·57	0·750	57·52	0·749	57·54	0·749	—	—	—	—	57·59	0·748
4	$C_8H_4D_3^+ \rightarrow C_6H_2D_3^+ + C_2H_2$	—	—	—	—	—	—	—	—	—	—	60·43	0·755	60·42	0·755
4	$C_8H_4D_3^+ \rightarrow C_6H_3D_2^+ + C_2HD$	—	—	—	—	—	—	—	—	—	—	58·99	0·750	58·91	0·745

† Diffuse peaks from reaction no. 6 are flat-topped[30].

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Appendix 3. (continued).

Reaction No.	Metastable transitions	d_0		β'-d_3		α-d_1		O-d_1		β,β'-d_5		(β,β'-d_5 + O-d_1)		Calc.	
		m*	m_2/m_1	m*	m_2/m_1	m*	m_2/m_1	m*	m_2/m_1	m*	m_2/m_1	m*	m_2/m_1	m*	m_2/m_1
4	$C_8H_5D_2^+ \rightarrow C_6H_3D_2^+ + C_2H_2$	—	—	—	—	—	—	—	—	59·44	0·754	59·46	0·750	59·48	0·752
4	$C_8H_5D_2^+ \rightarrow C_6H_4D^+ + C_2HD$	—	—	—	—	—	—	—	—	58·00	0·746	58·0	0·745	57·97	0·743
4	$C_8H_6D^+ \rightarrow C_6H_4D^+ + C_2H_2$	—	—	—	—	58·50	0·752	58·51	0·752	58·49	0·746	58·51	0·745	58·53	0·750
5	$C_7H_8^+ \rightarrow C_7H_7^+ + H$	90·03	0·988	90·03	0·987	90·04	0·988	90·03	0·984	—	—	—	—	90·06	0·989
5	$C_7H_5D_3^+ \rightarrow C_7H_4D_3^+ + H$	—	—	—	—	—	—	—	—	—	—	93·03	0·988	93·08	0·989
5	$C_7H_5D_3^+ \rightarrow C_7H_5D_2^+ + D$	—	—	—	—	—	—	—	—	—	—	91·07	0·980	91·10	0·979
5	$C_7H_6D_2^+ \rightarrow C_7H_5D_2^+ + H$	—	—	—	—	—	—	—	—	92·03	0·989	92·03	0·980	92·07	0·989
5	$C_7H_6D_2^+ \rightarrow C_7H_6D^+ + D$	—	—	—	—	—	—	—	—	90·06	0·980	90·07	0·976	90·09	0·979
5	$C_7H_7D^+ \rightarrow C_7H_6D^+ + H$	—	—	—	—	—	—	91·01	0·987	—	—	—	—	91·06	0·989
5	$C_7H_7D^+ \rightarrow C_7H_7^+ + D$	—	—	—	—	—	—	89·04	0·976	—	—	—	—	89·08	0·978
6†	$C_2H_5O^+ \rightarrow CHO^+ + CH_4$	18·69	—	—	—	—	—	—	—	—	—	—	—	18·68	0·644
6†	$C_2HD_4O^+ \rightarrow CDO^+ + CHD_3$	—	—	—	—	—	—	—	—	—	—	18·30	—	18·36	0·612
6†	$C_2HD_4O^+ \rightarrow CHO^+ + CD_4$	—	—	—	—	—	—	—	—	—	—	17·10	—	17·15	0·591
6†	$C_2H_2D_3O^+ \rightarrow CDO^+ + CH_2D_2$	—	—	—	—	—	—	—	—	18·73	—	—	—	18·74	0·624
6†	$C_2H_2D_3O^+ \rightarrow CHO^+ + CHD_3$	—	—	—	—	—	—	—	—	17·50	—	—	—	17·50	0·604
6†	$C_2H_4DO^+ \rightarrow CHO^+ + CH_3D$	—	—	—	—	18·26	—	18·29	—	—	—	—	—	18·27	0·630
7	$C_2H_5O^+ \rightarrow H_3O^+ + C_2H_2$	8·04	—	—	—	—	—	8·05	—	—	—	—	—	8·03	0·422
7	$C_2HD_4O^+ \rightarrow D_3O^+ + C_2HD$	—	—	—	—	—	—	—	—	—	—	9·92	—	9·90	0·449
7	$C_2HD_4O^+ \rightarrow HD_2O^+ + C_2D_2$	—	—	—	—	—	—	—	—	—	—	9·02	—	9·02	0·429
7	$C_2H_2D_3O^+ \rightarrow HD_2O^+ + C_2HD$	—	—	9·21	—	—	—	—	—	9·22	—	—	—	9·20	0·438
7	$C_2H_2D_3O^+ \rightarrow H_2DO^+ + C_2D_2$	—	—	8·35	—	—	—	—	—	8·35	—	—	—	8·34	0·417
7	$C_2H_4DO^+ \rightarrow H_2DO^+ + C_2H_2$	—	—	—	—	8·71	—	8·73	—	—	—	—	—	8·71	0·435
7	$C_2H_4DO^+ \rightarrow H_3O + C_2HD$	—	—	—	—	7·86	—	7·87	—	—	—	—	—	7·86	0·413

† Diffuse peaks from reaction no. 6 are flat-topped[30]

[30] J. H. Beynon, R. A. Saunders and A. E. Williams, Z. Naturforsch **20a**, 180 (1965).

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