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MASS SPECTROMETRY OF ARALKYL COMPOUNDS WITH A FUNCTIONAL GROUP—III

SPECIFIC EXCHANGE BETWEEN SOME HYDROGEN ATOMS IN THE MOLECULAR ION OF γ-PHENYLPROPANOL[1]

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Abstract—The mass spectrum of γ-phenylpropanol has been compared with that of analogues, specifically deuterated in the aliphatic chain and in the Ph nucleus. It is shown, that in the molecular ion a mutual exchange takes place between the H atoms from the OH group, the γ-methylene group and in the *ortho*-positions of the aromatic ring.

INTRODUCTION

A study on the behaviour of aralkyl nitro compounds[2] upon electron impact furnished the opportunity to study the mass spectrum of γ-phenylpropanol obtained as synthetic precursor, specifically deuterated in the aliphatic chain and in the Ph nucleus.

From the spectra of γ-phenylpropanol and its deuterated analogues it appears that the loss of a molecule of water is much more complicated than one would expect from the investigations of deuterated aliphatic alcohols.[3,4] Furthermore, the mechanism for the formation of the fragment *m/e* 92 from this alcohol, previously suggested from the spectrum of the α-d_2 analogue only,[5] appears to be incomplete.

In the lower mass region of the spectra obtained in the present study, many diffuse peaks are found, corresponding to the well-known decomposition of ions from aromatic hydrocarbons, especially the loss of 26 mass units (C_2H_2), e.g. *m/e* 91 → 65, *m/e* 89 → 63, *m/e* 77 → 51 and *m/e* 65 → 39, etc. These have been omitted in the Appendix.

It is not possible to locate exactly the charge in the molecular ion from γ-phenylpropanol, as long as the ionization potential is not known. This should be borne in mind with regard to the Schemes A, B and C.

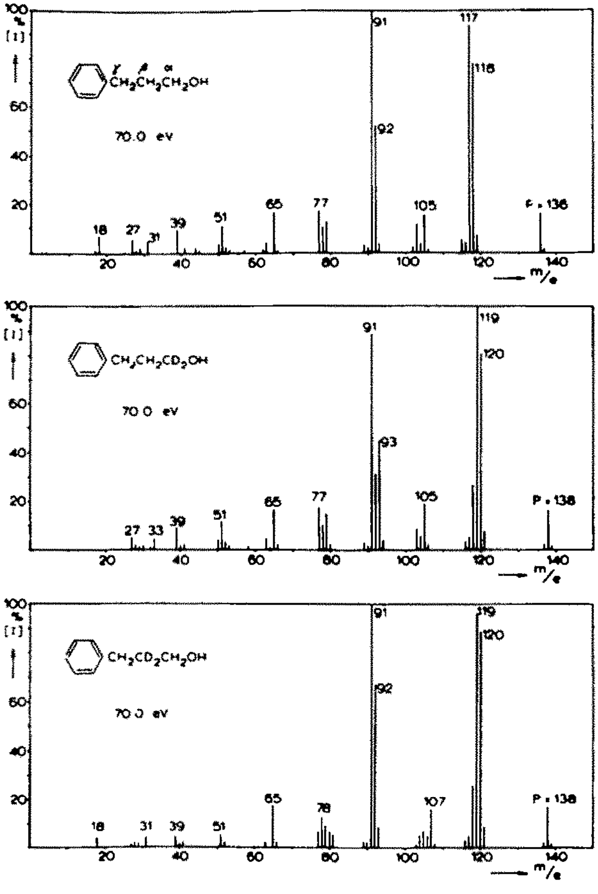
Fragmentation of γ-phenylpropanol, $C_6H_5CH_2CH_2CH_2OH$

Comparison of the standard spectrum with that of the α-d_2, β-d_2, γ-d_2, *ortho*-d_2, O-d_1 and *para*-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. (Figs 1 to 7, Appendix and Schemes A, B and C[6]).

1. *Elimination of water before and after mutual exchange between the hydroxyl-, γ- and* ortho-*hydrogen atoms in the molecular ion.* In the mass spectrum of undeuterated γ-phenylpropanol (P = 136) a large peak at *m/e* 118 corresponds with the loss of water (Fig. 1).

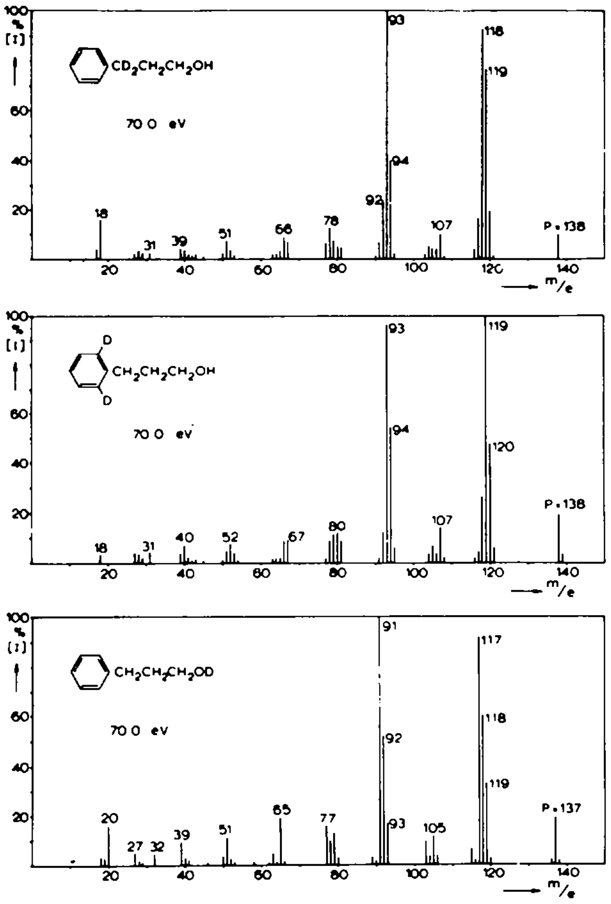
It has been shown, that the molecular ion of n-propanol loses water, involving a γ-hydrogen atom.[4]

The spectra of the specifically deuterated analogues and the observed *m/e*- and m_2/m_1-values for diffuse peaks, however, indicate a more complicated elimination from γ-phenylpropanol. (Figs 2 to 7 and Appendix, reaction No. 1).



Figs. 1, 2 and 3. Mass spectra of γ-phenylpropanol and its α-d_2 and β-d_2 analogues.

From the spectra we may calculate how much of the original deuterium is retained in the $(P - H_2O)^+$-ion, derived from the molecular ions of the deuterated alcohols. Although these calculations are complicated by the occurrence of the peak at *m/e* 117 in the spectrum of the unlabeled alcohol (Fig. 1),[7] a fair estimate can be made. The intensity of the $(P - H_2O)^+$-ion from the undeuterated and from all specifically deuterated γ-phenylpropanols is expressed as percentage of the sum of the intensities of all (corresponding) $C_9H_xD_y^+$-ions after correction for natural ^{13}C contribution (9·9%).[8] The value, obtained for the $(P - H_2O)^+$-ion from each deuterated alcohol, is then expressed as percentage of the corresponding value for the unlabeled alcohol. Finally a correction is made for incomplete labeling (Experimental). This leads to the values in Table 1.



FIGS. 4, 5 and 6. Mass spectra of γ-d_2, *ortho*-d_2 and O-d_1 analogues of γ-phenylpropanol.

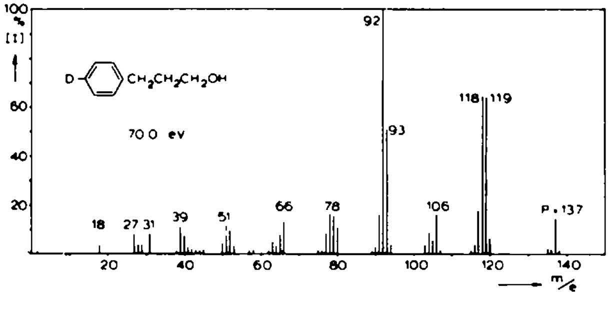


FIG. 7. Mass spectrum of the para-d_1 analogue of γ-phenylpropanol.

TABLE 1.

Label retentions* in $C_9H_{10}^+$ from deuterated γ-phenylpropanols (in %)

Ionization energy in eV	α-d_2	β-d_2	γ-d_2	*ortho*-d_2	O-d_1	*para*-d_1
70·0	97	106	18	57	45	110
15·0	93	96	21	42	45	103

* The last two columns refer to retention of one D, all other columns to retention of two D atoms.

From this Table it appears that the $C_9H_{10}^+$-ion derived from the *para*-d_1, α-d_2 and β-d_2 compounds retain nearly all the original deuterium. Apparently the molecular ions of these deuterated alcohols lose almost exclusively H_2O.

Surprising is the deuterium retention by loss of H_2O from the O-d_1 compound. The values, given in Table 1, imply a loss of H_2O as well as HDO from the corresponding molecular ion in about a 45:55 ratio. To account for this, an exchange between the OH hydrogen atom with another H atom in the molecular ion must be assumed, before a molecule of water is eliminated.

The almost exclusive loss of a molecule of H_2O from the parent-ions of the *para*-d_1, α-d_2 and β-d_2 alcohols (see above), shows that an α-, β- and/or *para*-H atom are not involved in this exchange process. We disregard the possibility of an exchange between the OH hydrogen atom and a *meta*-H atom, because the structural requirements for this exchange are unfavourable. Thus only γ- and/or *ortho* hydrogen atom remain available for this exchange.

The values in Table 1 given for the deuterium retentions after loss of water from the γ-d_2 and *ortho*-d_2 alcohols, somewhat varying with the applied ionization energies, indicate not only a loss of H_2O, but also an elimination of at least HDO from the corresponding molecular ions. The γ-H atoms are involved 2 to 3 times more than the *ortho* H atoms in the elimination of water.

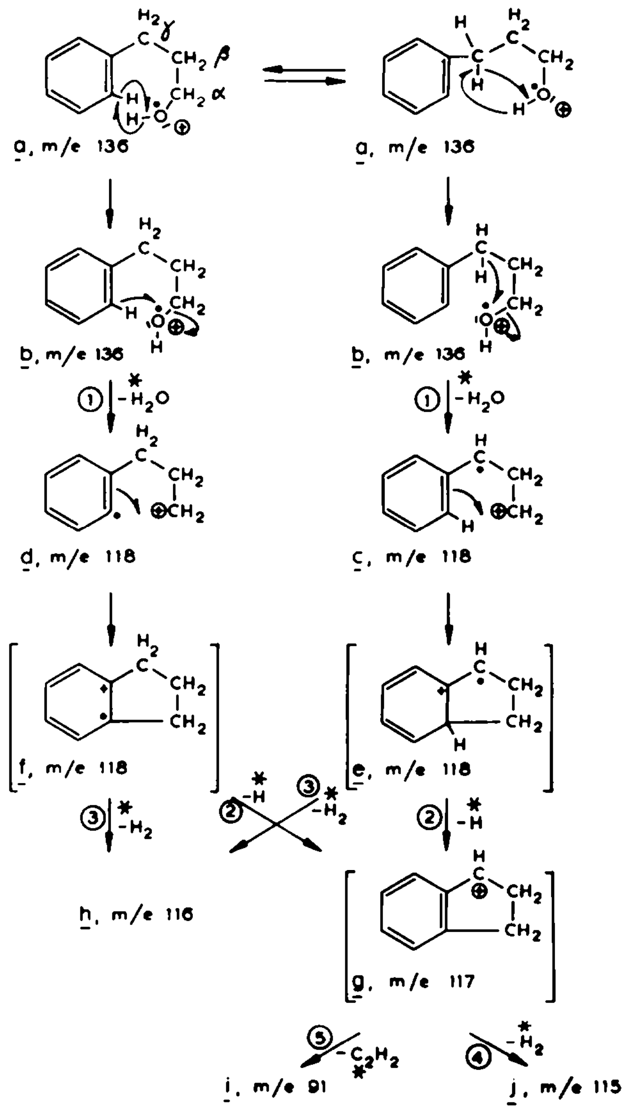
The few examples recorded in the literature on somewhat related aromatic ring-H participations are limited to the loss of OH from *o*-nitrobiphenyl,[9] the loss of an aromatic ring-H atom from compounds with the general formula $C_6H_5CH{=}CHCOR$ (as proved by deuteration)[10] and the loss of a Me radical from stilbene (also proved by deuteration).[11]

1.1. *Diffuse peaks corresponding with loss of* H_2O, HDO *and* D_2O *from γ-phenylpropanol* (*see Appendix*). Concerning the loss of a molecule of water from the parent ion, only one diffuse peak is observed in the spectrum of undeuterated γ-phenylpropanol and its *para*-d_1, α-d_2 and β-d_2 analogues, corresponding to the loss of H_2O. In the spectrum of the O-d_1 compound two diffuse peaks are found, corresponding to the elimination of H_2O and of HDO. Finally, in the spectra of the γ-d_2 and *ortho*-d_2 alcohols three diffuse peaks occur, indicating the loss of H_2O, HDO and D_2O.

From this it may be concluded that prior to the elimination of a water molecule the OH hydrogen atom exchanges with a γ-H atom as well as with an *ortho*-H atom in the molecular ion. An H atom from the γ-position may thus move to the *ortho*-position of the aromatic ring and *vice versa*.

Representing the —OH, γ- and *ortho*-H atoms by the symbols H, $\mathrm{H^{\gamma}}$ and $\mathrm{H^{o}}$, respectively, the molecular ion of γ-phenylpropanol can thus lose as a result of the exchanges $\mathrm{HH^{\gamma}O}$, $\mathrm{HH^{o}O}$, $\mathrm{H^{\gamma}H^{o}O}$, $\mathrm{H^{\gamma}_2O}$ and $\mathrm{H^{o}_2O}$. (Scheme A, sequences *a* → *b* → *d* and *a* → *b* → *c*).

SCHEME A



For the loss of D_2O from the parent ions of the γ-d_2 and *ortho*-d_2 alcohols, we calculate $m^* = 100{\cdot}96$ and observe within experimental error $m^* = 101{\cdot}02$ and $101{\cdot}00$, respectively. Yet these diffuse peaks could also be attributed to the transitions *m/e* 105 → 103 and/or *m/e* 107 → 104 ($m^*_{\mathrm{calc.}} = 101{\cdot}08$ and $101{\cdot}12$, respectively; cf Appendix reaction No. 6). Although these reactions may contribute to this diffuse peak, we still ascribe it to the elimination of D_2O from these molecular ions, because:

1. The measured m_2/m_1 values for this diffuse peak agree with the calculated value (see Appendix).

2. While in the spectra of the other labeled γ-phenylpropanols this diffuse peak disappears at lower ionization energy, it remains in the spectra of the γ-d_2 and *ortho*-d_2 alcohols, even at 7·0 eV, when the normal peaks have nearly vanished (see Figs 8 and 9, respectively).

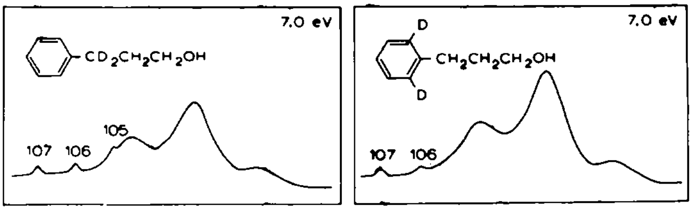


FIG. 8. FIG. 9.

Diffuse peaks, corresponding with the loss of H_2O, HDO and D_2O from the molecular ions of γ-d_2 and *ortho*-d_2 analogues of γ-phenylpropanol.

1.2. *Discussion of further degradations in* Scheme A. While the elimination of a water molecule from γ-phenylpropanol is well established, the structure of the resulting $C_9H_{10}^+$-ion (*m/e* 118) is uncertain. The preferential loss of an H atom from this ion, generating the peak at *m/e* 117 in the spectrum of the undeuterated γ-phenylpropanol (Fig. 1), resembles the behaviour of indane.[12] This resemblance is furthermore supported by common diffuse peaks, found in the spectrum of unlabeled γ-phenylpropanol for the decompositions of the $C_9H_{10}^+$-ion and the $C_9H_9^+$-ion (see Appendix).

Just like the parent- and the (parent-1)-ions of indane, the $C_9H_{10}^+$-ion loses H and H_2 and the $C_9H_9^+$-ion H_2 and C_2H_2.

Unfortunately, the diffuse peak, corresponding with the loss of C_2H_2 from the $C_9H_9^+$-ion, is not observed in the spectrum of any labeled alcohol. (Appendix, reaction Nos. 2, 3, 4 and 5 and Scheme A, sequences f, $e \rightarrow h$ and f, $e \rightarrow g \rightarrow i$, j.).

2. *Rearrangement of an α-hydrogen atom to one of the* ortho *positions of the phenyl ring* (Scheme B; $P - C_2H_4O$). In the mass spectra of undeuterated γ-phenylpropanol and its β-d_2 analogue a rather large peak is found at *m/e* 92 (see Figs 1 and 3). This peak shifts to *m/e* 94 in the spectra of the γ-d_2 and *ortho*-d_2 compounds and to *m/e* 93 in the spectrum of the *para*-d_1 analogue, suggesting that H atoms in these specific positions are not lost from the parent ion in forming *m/e* 92 (Figs 4, 5 and 7). In the spectrum of the O-d_1 alcohol this peak *m/e* 92 does not shift appreciably, whereas it shifts predominantly to *m/e* 93 in the spectrum of the α-d_2 analogue (see Figs 6 and 2, respectively).

These results can be explained—at least partly—by the transfer of an H atom from the α-position to one of the *ortho*-positions of the Ph-ring *via* a 6-membered transition state, resembling the well-known McLafferty rearrangement.[13] The same conclusion was reached previously by Meyerson[5] on the basis of the spectrum from the α-d_2 alcohol only.

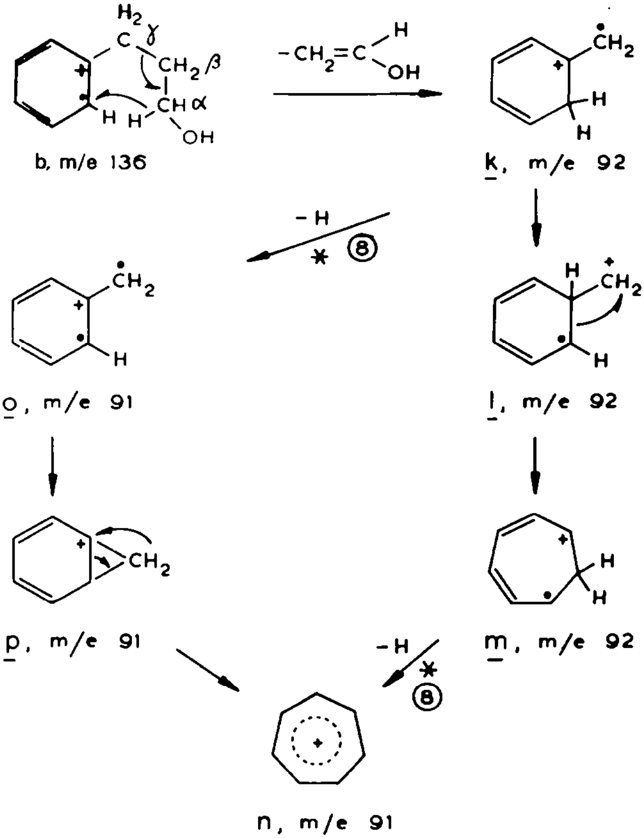
Yet, the occurrence of the peak at *m/e* 93 in the spectrum of the O-d_1 alcohol shows that more complicated processes must also be involved in the formation of the fragment *m/e* 92 from undeuterated γ-phenylpropanol:

1. As discussed above, prior to the McLafferty rearrangement of the α-H atom a mutual exchange between the —OH, γ- and *ortho*-H atoms in the molecular ion may take place.

2. The possibility cannot altogether be excluded that the OH hydrogen atom is transferred directly to one of the *ortho* positions of the Ph-ring, after which an ethylene oxide molecule may be split off.

Diffuse peaks show that the ion *m/e* 92 loses an H atom in a random fashion, resembling the behaviour of toluene[14] and thus generating the well-known tropylium ion *m/e* 91 (see Appendix, reaction No. 8). On this basis we suggest sequences *k* → *o* → *p* → *n* and *k* → *l* → *m* → *n*, as depicted in Scheme B.

SCHEME B

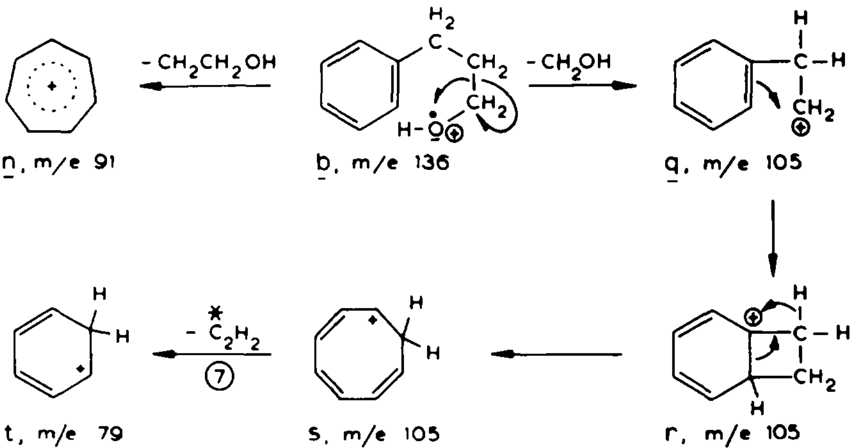


3. *Formation of the tropylium ion* (Scheme C). The strongest peak in the mass region *m/e* 90 to *m/e* 95 from all the spectra, obtained in the present study, can be explained by a simple C_β–C_γ cleavage, generating the well-known tropylium ion (Figs 1 to 7). Nevertheless, some of the tropylium ion could also be formed after a mutual exchange between the —OH, γ- and *ortho*-H atoms in the molecular ion, as discussed above (Scheme C, sequence *b* → *n*).

Two other possible modes for the generation of the tropylium ion have been given already in 1.2 and 2.

Because of the low intensity of the peak at *m/e* 93 in the spectrum of the β-d$_2$ alcohol, probably caused by the loss of C_2H_2 from the $C_9H_7D_2^+$-ion (see 1.2), the tropylium ion formation from this ion seems to be a minor process. This could also apply to the corresponding $C_9H_9^+$-ions from undeuterated and other deuterated γ-phenylpropanols.

SCHEME C



4. *Formation of the* $C_8H_9^+$*-ion* (m/e 105; Scheme C). In the spectra of the undeuterated γ-phenylpropanol and its α-d$_2$ analogue a peak is found at *m/e* 105. This peak shifts to *m/e* 106 and partly to *m/e* 106 in the spectra of the *para*-d$_1$ and O-d$_1$ compounds, respectively. In the spectra of the other deuterated analogues it shifts to *m/e* 107 (Figs 1 to 7).

This can all be explained by the loss of the terminal —CH_2OH-group before and after a mutual exchange between the OH, γ- and *ortho*-H atoms in the molecular ion (Scheme C, sequence *b* → *q*).

As indicated by the diffuse peaks, the resulting $C_8H_9^+$-ion loses a molecule of acetylene after extensive scrambling of all the H atoms in this ion (see Appendix, reaction No. 7).

This agrees with the almost complete scrambling of all H atoms in the $C_8H_9^+$-ions, derived from 1-bromo-2-phenylethane as well as from 1-bromo-1-phenylethane, appearing from comparisons of the spectra of these compounds with those of specifically deuterated analogues.[15]

Therefore, we propose an 8-membered ring structure for the $C_8H_9^+$-ion, possibly formed by the mechanism presented in Scheme C, sequence *q* → *r* → *s*. A series of consecutive 1–2 shifts of H in ion *s*, as suggested for toluene[14] and observed in the photoisomerization of cycloheptatriene,[16] and/or successive 1–5 shifts of H, observed in the thermal isomerization of cycloheptatriene,[17] explains the scrambling.

EXPERIMENTAL

Mass spectra were obtained with an A.E.I. MS2H- and an A.E.I. MS9 mass spectrometer. In the first instrument, samples were introduced through the heated inlet system at 200°. In the other instrument, samples were introduced from a glass vessel (±3 ml) fitted to the 4-way manifold since at the time of the experiments no heated inlet systems were available.

The spectra from both instruments were essentially the same. The maxima of diffuse peaks were derived from the MS9 spectra together with the m_2/m_1-values (Accuracy limit 0·5–1%), measured according to the method of Jennings,[18] using a scanning system similar to the one described by Sipma.[19] Only the circuit modification for use when m_2 is greater than $m_1/2$[18] was available.

All the samples were purified by preparative gas chromatography with a Wilkens Aerograph A-90-P instrument. The applied column was a 2 m/6 mm 20% Silicone Rubber SE-52, supported on kieselguhr and He gas was used as carrier gas. The retention time was 24 min at a column temp of 150°. After purification the compounds were checked by IR as well as by NMR, which established the structure, the D content and the purity.

The D content of the samples was also measured by Mass Spectrometry, using such a low ionization energy, that in the parent mass region from the spectrum of undeuterated γ-phenylpropanol the parent peak remained only. The parent mass regions from the deuterated analogues were then run under identical conditions.

The results of these measurements have been collected in Table 2.

TABLE 2. MEASUREMENTS OF DEUTERIUM CONTENT (%) OF LABELED γ-PHENYLPROPANOLS, $C_6H_5^{\gamma}CH_2^{\beta}CH_2^{\alpha}CH_2OH$

		By mass spectrometry Accuracy limit 0·1%			
Ionization energy	Site-specifically deuterated γ-phenylpropanol	d_2	d_1	d_0	By NMR Accuracy limit 1–2%
9·4 eV	α-d_2	88·3	11·1	·6	92·1
	β-d_2	88·0	11·3	·7	93·9
	γ-d_2	89·6	10·0	·4	94·8
	Ortho-d_2	96·0	4·0	—	—
	O-d_1	—	85·1	14·9	—
	para-d_1	—	90·0	10·0	—

Preparations of γ-phenylpropanol, specifically deuterated in the α-, β- and γ-positions. The syntheses of these compounds have been described earlier.[2]

Preparation of the O-d_1 *analogue from γ-phenylpropanol.* D_2O was introduced in the heated inlet system of the mass spectrometer and pumped away after a few min. This operation was repeated several times. Then γ-phenylpropanol, which was treated previously with an excess of D_2O, was introduced in the heated inlet system together with a fresh portion of D_2O.[20, 21]

Preparation of the ortho-d_2 *analogue from γ-phenylpropanol.* 100 g of *p*-nitrotoluene were heated with 520 g 90% D_2SO_4 (99·5 at % D) in a closed round-bottomed glass vessel for 24 hr at 90°.[22]

D_2SO_4 was synthesized from D_2O and SO_3.[23]

After two successive exchange reactions, 99·4 g *p*-nitrotoluene, specifically deuterated in the *ortho* positions with respect to the Me group and to the extent of 97–98% (NMR), were obtained. Reduction of the nitro group with Sn/HCl[24] and deamination[25, 26] yielded 37·6 g *ortho*-d_2 toluene. This was converted into 28·5 g benzoic acid, specifically deuterated in the *ortho* positions to the extent of about 98% (NMR), by oxidation with alkaline $KMnO_4$ at 90°.[27] Then, 18·5 g *ortho*-d_2 benzoic acid were reduced with LAH[28] to 15·8 g of *ortho*-d_2 benzylalcohol, which was converted in an overall yield of ±17% into the *ortho*-d_2 analogue from γ-phenylpropanol by use of the sequence of reactions, described earlier.[2]

Preparation of the para-d_1 *analogue from γ-phenylpropanol.* The Grignard compound was made from 50 g *p*-dibromobenzene to react with 30 g D_2O, yielding 21 g bromobenzene, deuterated in the *para*

APPENDIX. DIFFUSE PEAKS, OBSERVED IN THE MASS SPECTRA

Reaction No.	Metastable transitions	d_0		α-d_2		β-d_2	
		m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1
1	$C_9H_{12}O^+ \rightarrow C_9H_{10}^+ + H_2O$	102·44	0·866	—	—	—	—
1	$C_9H_{10}D_2O^+ \rightarrow C_9H_8D_2^+ + H_2O$	—	—	104·43	0·868	104·41	0·869
1	$C_9H_{10}D_2O^+ \rightarrow C_9H_9D^+ + HDO$	—	—	—	—	—	—
1	$C_9H_{10}D_2O^+ \rightarrow C_9H_{10}^+ + D_2O$	—	—	—	—	—	—
1	$C_9H_{11}DO^+ \rightarrow C_9H_9D^+ + H_2O$	—	—	—	—	—	—
1	$C_9H_{11}DO^+ \rightarrow C_9H_{10}^+ + HDO$	—	—	—	—	—	—
2	$C_9H_{10}^+ \rightarrow C_9H_9^+ + H$	116·08	0·988	—	—	—	—
2	$C_9H_8D_2^+ \rightarrow C_9H_7D_2^+ + H$	—	—	118·08	0·989	118·11	0·989
2	$C_9H_9D^+ \rightarrow C_9H_8D^+ + H$	—	—	117·02	0·985	117·04	0·986
3	$C_9H_{10}^+ \rightarrow C_9H_8^+ + H_2$	114·01	0·979	—	—	—	—
3	$C_9H_8D_2^+ \rightarrow C_9H_6D_2^+ + H_2$	—	—	116·04	0·979	116·07	0·980
3	$C_9H_9D^+ \rightarrow C_9H_7D^+ + H_2$	—	—	—	—	—	—
4†	$C_9H_9^+ \rightarrow C_9H_7^+ + H_2$	113·09	0·983	—	—	—	—
4†	$C_9H_7D_2^+ \rightarrow C_9H_5D_2^+ + H_2$	—	—	115·08	0·985	115·04	0·984
4†	$C_9H_7D_2^+ \rightarrow C_9H_6D^+ + HD$	—	—	113·10	0·980	113·11	0·981
4†	$C_9H_8D^+ \rightarrow C_9H_6D^+ + H_2$	—	—	114·06	0·981	114·08	0·981
4†	$C_9H_8D^+ \rightarrow C_9H_7^+ + HD$	—	—	112·05	0·979	112·07	0·977
5	$C_9H_9^+ \rightarrow C_7H_7^+ + C_2H_2$	70·81	0·775	—	—	—	—
5	$C_9H_8D^+ \rightarrow C_7H_6D^+ + C_2H_2$	—	—	—	—	72·0	0·774
6	$C_8H_9^+ \rightarrow C_8H_7^+ + H_2$	101·06	0·979	101·07	0·980	—	—
6	$C_8H_7D_2^+ \rightarrow C_8H_5D_2^+ + H_2$	—	—	—	—	103·07	0·985
6	$C_8H_7D_2^+ \rightarrow C_8H_6D^+ + HD$	—	—	—	—	101·11	0·973
6	$C_8H_8D^+ \rightarrow C_8H_6D^+ + H_2$	—	—	—	—	102·04	0·985
6	$C_8H_8D^+ \rightarrow C_8H_7^+ + HD$	—	—	—	—	—	—
7	$C_8H_9^+ \rightarrow C_6H_7^+ + C_2H_2$	59·45	0·751	59·46	0·751	—	—
7	$C_8H_7D_2^+ \rightarrow C_6H_5D_2^+ + C_2H_2$	—	—	—	—	61·37	0·757
7	$C_8H_7D_2^+ \rightarrow C_6H_6D^+ + C_2HD$	—	—	—	—	59·93	0·749
7	$C_8H_8D^+ \rightarrow C_6H_6D^+ + C_2H_2$	—	—	—	—	—	—
7	$C_8H_8D^+ \rightarrow C_6H_7^+ + C_2HD$	—	—	—	—	—	—
8	$C_7H_8^+ \rightarrow C_7H_7^+ + H$	90·03	0·991	—	—	90·03	0·986
8	$C_7H_6D_2^+ \rightarrow C_7H_5D_2^+ + H$	—	—	—	—	—	—
8	$C_7H_6D_2^+ \rightarrow C_7H_6D^+ + D$	—	—	—	—	—	—
8	$C_7H_7D^+ \rightarrow C_7H_6D^+ + H$	—	—	91·08	0·986	—	—

† Diffuse peaks from reaction No. 4 are flat-topped.[30]

OF SITE-SPECIFICALLY DEUTERATED $C_6H_5^{\gamma}CH_2^{\beta}CH_2^{\alpha}CH_2OH$

γ-d$_2$		*ortho*-d$_2$		O-d$_1$		*para*-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
—	—	—	—	—	—	—	—	102·45	0·868
104·44	0·869	104·42	0·866	—	—	—	—	104·43	0·870
102·69	0·863	102·67	0·860	—	—	—	—	102·69	0·862
101·02	0·857	101·00	0·853	—	—	—	—	100·96	0·855
—	—	—	—	103·44	0·866	103·39	0·868	103·44	0·869
—	—	—	—	101·68	0·860	—	—	101·70	0·861
116·05	0·989	—	—	116·13	0·991	116·05	0·987	116·07	0·992
118·05	0·991	118·06	0·987	—	—	—	—	118·08	0·992
117·13	0·990	117·07	0·985	117·19	0·992	117·03	0·987	117·08	0·991
—	—	—	—	114·02	0·981	—	—	114·08	0·983
116·05	0·980	116·05	0·978	—	—	—	—	116·09	0·983
115·07	0·983	—	—	—	—	115·04	0·979	115·09	0·983
—	—	—	—	113·04	0·981	113·08	0·978	113·07	0·983
—	—	115·09	0·980	—	—	—	—	115·09	0·983
113·14	0·971	113·12	0·975	—	—	—	—	113·12	0·975
114·09	0·978	114·09	0·975	114·02	0·981	114·10	0·982	114·08	0·983
112·10	0·980	112·16	0·979	—	—	112·07	0·978	112·11	0·974
—	—	—	—	70·85	0·776	—	—	70·82	0·778
—	—	—	—	—	—	—	—	71·78	0·780
—	—	—	—	101·06	0·980	101·05	0·973	101·08	0·981
—	—	—	—	—	—	—	—	103·09	0·981
101·02	0·972	101·00	0·970	—	—	—	—	101·12	0·972
—	—	—	—	102·03	0·981	102·09	0·982	102·08	0·981
—	—	—	—	—	—	100·15	0·973	100·12	0·972
—	—	—	—	59·43	0·750	59·48	0·750	59·48	0·752
61·37	0·757	61·40	0·755	—	—	—	—	61·37	0·757
59·91	0·749	59·88	0·747	—	—	—	—	59·86	0·748
—	—	—	—	60·40	0·752	60·42	0·754	60·42	0·755
—	—	—	—	—	—	58·93	0·750	58·92	0·745
—	—	—	—	90·07	0·989	—	—	90·06	0·989
92·08	0·987	92·09	0·984	—	—	—	—	92·07	0·989
90·05	0·976	90·04	0·980	—	—	—	—	90·09	0·979
91·08	0·986	—	—	91·08	0·989	91·03	0·986	91·06	0·989

position to the extent of about 92% (NMR). By reaction of its Grignard compound with CO_2,[29] 12·5 g *para*-d_1 benzoic acid were obtained. This acid was converted into the *para*-d_1 analogue from γ-phenylpropanol, as described above (overall yield ±14%).

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REFERENCES

[1] Part of the forthcoming thesis of N. M. M. Nibbering.

[2] N. M. M. Nibbering and Th. J. de Boer, *Some Newer Physical Methods in Structural Chemistry* (Edited by R. Bonnett and J. G. Davis) p. 47. United Trade Press, London (1967).

[3] W. Benz and K. Biemann, *J. Am. Chem. Soc.* **86**, 2375 (1964).

[4] S. Meyerson and L. C. Leitch, *Ibid.* **86**, 2555 (1964).

[5] H. M. Grubb and S. Meyerson, *Mass Spectrometry of Organic Ions* (Edited by F. W. McLafferty) Chap. 10; p. 510. Academic Press, New York (1963).

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

[7] See Ref. 5, Chap. 10; pp. 474 and 475.

[8] K. Biemann, *Mass Spectrometry* pp. 42–45. McGraw-Hill, New York (1962).

[9] S. Meyerson, I. Puskas and E. K. Fields, *J. Am. Chem. Soc.* **88**, 4979 (1966).

[10] J. Ronayne, D. H. Williams and J. H. Bowie, *Ibid.* **88**, 4980 (1966).

[11] R. A. W. Johnstone and B. J. Millard, *Some Newer Physical Methods in Structural Chemistry* (Edited by R. Bonnett and J. G. Davis) p. 28. United Trade Press, London (1967).

[12] *Catalog of Mass Spectral Data* Project 44; Serial Nos. 413 and 1214. American Petroleum Institute Research, Carnegie Institute of Technology, Pittsburgh, Pa.

[13] F. W. McLafferty, *Analyt. Chem.* **28**, 306 (1956).

[14] F. Meyer and A. G. Harrison, *J. Am. Chem. Soc.* **86**, 4757 (1964).

[15] To be published.

[16] A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chim.* **84**, 241 (1965).

[17] A. P. ter Borg, H. Kloosterziel and N. van Meurs, *Ibid.* **82**, 717 (1963).

[18] K. R. Jennings, *Some Newer Physical Methods in Structural Chemistry* (Edited by R. Bonnett and J. G. Davis) p. 105. United Trade Press, London (1967).

[19] G. Sipma, *Proceedings of the 5th Annual* MS9 *mass spectrometer users meeting.* To be published.

[20] See Ref. 8, Chap. 5.

[21] H. Budzikiewicz and C. Djerassi, *Chem. & Ind.* 1697 (1965).

[22] R. N. Renaud, D. Kovachic and L. C. Leitch, *Canad. J. Chem.* **39**, 21–30 (1961).

[23] P. Avinur, *Bull. Res. Counc. Israel* **7A**, 129 (1958).

[24] A. I. Vogel, *Textbook of Practical Organic Chemistry* (3rd Edition) p. 565.

[25] A. P. Best and C. L. Wilson, *J. Chem. Soc.* 242 (1946).

[26] See Ref. 24, p. 615.

[27] F. Ullmann and J. B. Uzbachian, *Ber. Dtsch. Chem. Ges.* **36**, 1798 (1903).

[28] R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.* **69**, 2548 (1947).

[29] See Ref. 24, p. 756.

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