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MASS SPECTROMETRY OF ARALKYL COMPOUNDS WITH A FUNCTIONAL GROUP—IV

SPECIFIC EXCHANGE BETWEEN THE α- AND *ORTHO*-HYDROGEN ATOMS IN THE MOLECULAR ION OF γ-PHENYLPROPYLBROMIDE[1]

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Abstract—The mass spectrum of γ-phenylpropylbromide has been compared with that of analogues, specifically deuterated in the aliphatic chain and in the Ph ring. It is shown that in the molecular ion a mutual exchange takes place between the H atoms from the α-methylene group and in the *ortho*-positions of the aromatic ring. Moreover, it is demonstrated that the Br atom as well as an α-H atom are transferred to one of the *ortho*-positions of the Ph nucleus *via* a McLafferty rearrangement.

INTRODUCTION

IN A study on the mass spectral behaviour of aralkyl nitro compounds[2] γ-phenylpropylbromide, specifically deuterated in the side chain and in the aromatic ring, was obtained as synthetic precursor. The spectrum of γ-phenylpropylbromide is known from a systematic study of the mass spectral behaviour of undeuterated aromatic halogenated compounds.[3]

The availability of site-specifically deuterated γ-phenylpropylbromide furnished the opportunity to study its mass spectrum in more detail. It was shown earlier that in the molecular ion of γ-phenylpropanol a mutual "hydroxyl-γ- *ortho*"-exchange of H takes place.[4] The same is true for γ-phenylpropylbromide with respect to "α- and *ortho*-hydrogens".

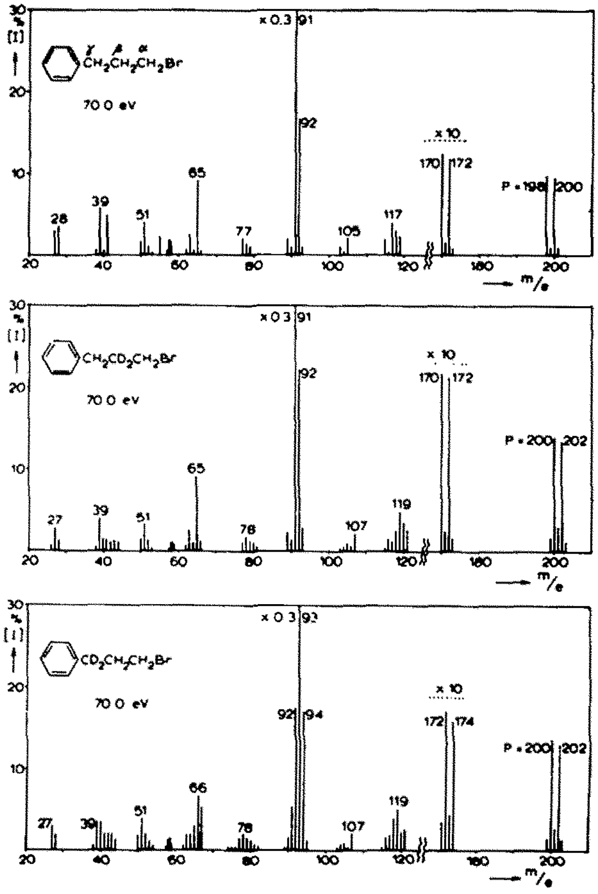
In the lower mass region of the spectra obtained in the present study, many diffuse peaks are found, corresponding to the well-known decomposition of ions from aromatic hydrocarbons, especially the loss of 26 mass units (C_2H_2), e.g. m/e 91 → 65, m/e 89 → 63, m/e 77 → 51, etc. These have been omitted in the Appendix. Also the decomposition of the $C_8H_9^+$-ion, generated by loss of the terminal —CH_2Br group from the parent ion, is not considered, because this has been described earlier.[4] It is not possible to locate exactly the charge in the molecular ion from γ-phenylpropylbromide, as long as the ionization potential is not known. This should be born in mind with regard to Scheme A.

Fragmentation of γ-phenylpropylbromide, $C_6H_5CH_2CH_2CH_2Br$

Comparison of the standard spectrum with that of the α-d_2, β-d_2, γ-d_2, *ortho*-d_2 and *para*-d_1 analogues together with the m/e- and m_2/m_1-values for diffuse peaks enable us to distinguish four reaction ways for the decomposition of the molecular ion (Figs 1 to 6, Appendix and Scheme A[5], respectively).

1. *Intramolecular bromine shift before and after exchange between the α- and* ortho-*hydrogen atoms in the molecular ion.* In the mass spectra of γ-phenylpropylbromide

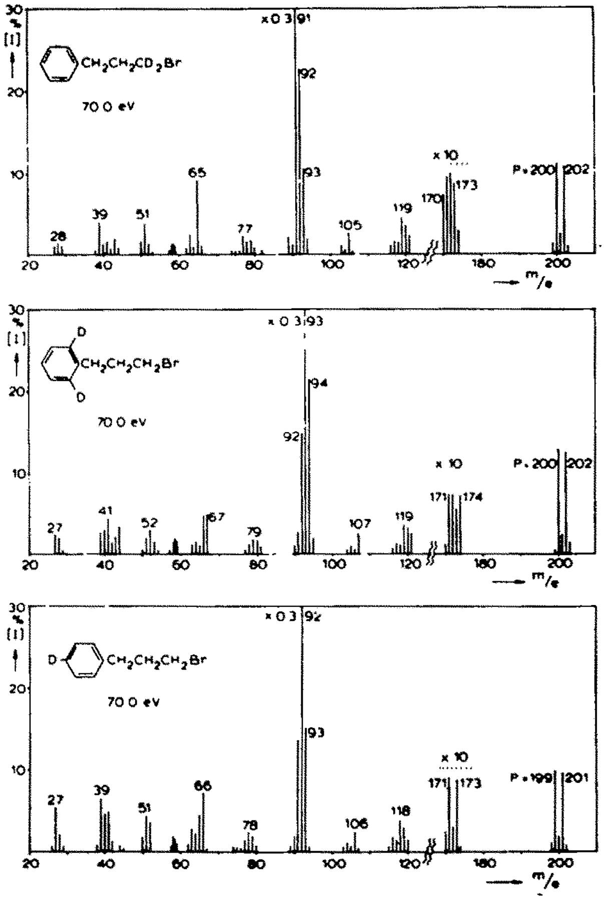
(P = 198, 200) and its β-d_2 analogue small peaks are found at *m/e* 170 and at *m/e* 172 (Figs 1 and 2). These peaks shift to *m/e* 172 and *m/e* 174 and to *m/e* 171 and *m/e* 173 in the spectra of the γ-d_2 and *para*-d_1 compounds, respectively (Figs 3 and 6).



FIGS. 1, 2 and 3. Mass spectra of γ-phenylpropylbromide and its β-d_2 and γ-d_2 analogues.

In the spectrum of the α-d_2 analogue four peaks are found at *m/e* 170, 171, 172 and 173. These peaks shift to the higher mass range with one mass unit in the spectrum of the *ortho*-d_2 derivative (Figs 4 and 5).

Apart from the peaks at *m/e* 171 and *m/e* 173 in the spectra of the α-d_2 and *ortho*-d_2 compounds, the observed shifts can be explained by assuming a transfer of the Br atom to one of the *ortho* positions of the Ph ring *via* a 6-membered transition state; in this reaction a C_2H_4 molecule is split off from the molecular ions of the γ-d_2, *ortho*-d_2 and *para*-d_1 analogues, whereas the corresponding molecular ions of the



Figs. 4, 5 and 6. Mass spectra of α-d$_2$, *ortho*-d$_2$ and *para*-d$_1$ analogues of γ-phenylpropyl-bromide.

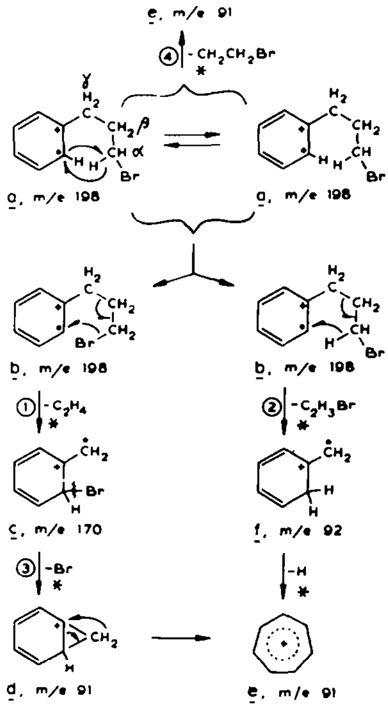
α-d$_2$ and β-d$_2$ compounds lose a $C_2H_2D_2$ molecule (Scheme A, sequence $b \rightarrow c$). This elimination resembles the well-known McLafferty rearrangement.[6]

From the occurrence of the peaks at *m/e* 171 and at *m/e* 173 in the spectra of both α-d$_2$ and *ortho*-d$_2$ bromides we may assume that at least one exchange between an α- and an *ortho*-H atom has taken place in the molecular ion before the Br atom rearranges to one of the *ortho*-positions of the Ph ring. As a consequence of this exchange these molecular ions eliminate also a C_2H_3D molecule during the re-arrangement of the Br atom (Scheme A, sequence $a \rightarrow b \rightarrow c$).

The elimination of these ethylene molecules with various deuterium content is supported by the corresponding diffuse peaks (Appendix, reaction No. 1).

Moreover, in the spectra of the α-d$_2$ and *ortho*-d$_2$ compounds diffuse peaks are observed, which correspond with the loss of a C_2H_4- and a $C_2H_2D_2$-molecule from the parent ions, respectively (Appendix, reaction No. 1).

SCHEME A



This can be explained by assuming that at least two successive exchanges between an α- and an *ortho*-H atom in the molecular ion have occurred prior to the intramolecular Br-shift.

Ion *c*, generated by the Br-rearrangement, loses Br as is substantiated by the observed diffuse peaks (Appendix, reaction No. 3). Further routes to the tropylium ion *e* follow an obvious pattern.

2. *Hydrogen shift before and after exchange between the α- and* ortho-*atoms in the molecular ion.* The peak at *m/e* 92 in the mass spectra of γ-phenylpropylbromide and its β-d_2 analogue shifts to *m/e* 93 in the spectra of the *para*-d_1 and α-d_2 compounds and to *m/e* 94 in the spectra of the γ-d_2 and *ortho*-d_2 derivatives (Figs 1 to 6).

This can all be explained by a McLafferty rearrangement[6] of an α-H atom to one of the *ortho* positions of the Ph ring (Scheme A, sequence *b* → *f*). During this rearrangement a C_2H_3Br molecule is eliminated from the molecular ions of the undeuterated, γ-d_2, *ortho*-d_2 and *para*-d_1 compounds. Accordingly, the β-d_2 and α-d_2 molecular ions lose a C_2D_2HBr- and a C_2H_2DBr-molecule, respectively.

This process is supported by the diffuse peaks, observed in the spectra (Appendix, reaction No. 2).

The observed diffuse peaks, however, indicate also the elimination of a C_2H_3Br molecule from the molecular ion of the α-d_2 analogue, thus generating the fragment *m/e* 94. This can be interpreted by assuming that prior to the intramolecular H shift from the α-C atom at least one exchange between an *ortho*- and an α-H atom in the molecular ion has occurred, as discussed in 1.

After this exchange the α-C atom possess a H as well as a D atom, which both can shift to one of the *ortho* positions of the Ph ring, thus yielding the fragments *m/e* 93 and *m/e* 94. Thus, the fragment *m/e* 93 in the spectrum of the α-d_2 compound can be formed before as well as after the "*ortho*-α"-exchange of hydrogens in the molecular ion (Scheme A, sequence $a \rightarrow b \rightarrow f$).

The last conclusion also applies to the fragment *m/e* 94 in the spectrum of the *ortho*-d_2 analogue. The generation of *m/e* 93 in this spectrum is similar to that of *m/e* 94 in the spectrum of the α-d_2 compound, although *m/e* 93 is also formed by a direct cleavage of the C_β—C_γ bond, as discussed in 3.

For the loss of an H atom from ion *f* we may refer to Part III[4].

3. *Formation of the tropylium ion before and after exchange between the* α- *and* ortho-*hydrogen atoms in the molecular ion.* The peak at *m/e* 91 in the spectra of the d_0, α-d_2 and β-d_2 compounds shifts to *m/e* 93 in the spectra of the γ-d_2 and *ortho*-d_2 analogues and to *m/e* 92 in the spectrum of the *para*-d_1 bromide. They form the base peaks in the spectra and arise from the corresponding molecular ions by a simple cleaveage of the C_β—C_γ bond, before an "α-*ortho*"-exchange of H in the molecular ion has occurred (Figs 1 to 6).

Except in the spectrum of the α-d_2 analogue, we observe diffuse peaks in the other spectra, supporting this reaction (Appendix, reaction No. 4). In the spectrum of the α-d_2 compound only diffuse peaks are found for the formation of *m/e* 92 ($C_7H_6D^+$) from the molecular ion.

It follows that generation of the tropylium ion by C_β—C_γ cleavage also takes place after at least one "α-*ortho*"-exchange of H.

4. *Loss of the bromine atom from the molecular ion before and after* "α-ortho"-*exchange of hydrogen.* The shift of the peak at *m/e* 119 in the spectrum of undeuterated γ-phenylpropylbromide to *m/e* 121 in the spectra of the α-d_2, β-d_2, γ-d_2 and *ortho*-d_2 analogues and to *m/e* 120 in the spectrum of the *para*-d_1 compound establish the loss of the Br atom from the molecular ion as further supported by diffuse peaks (Appendix, reaction No. 5).

The resulting $C_9H_{11}^+$-ion from the d_0 compound eliminates C_2H_4, generating the tropylium ion as supported by the diffuse peak, observed in the spectrum (Appendix, reaction No. 6).

The corresponding $C_9H_9D_2^+$-ion from the α-d_2, β-d_2 and γ-d_2 analogues loses C_2H_4, C_2H_3D as well as $C_2H_2D_2$, as indicated by the diffuse peaks (Appendix, reaction No. 6).

Finally, the $C_9H_9D_2^+$-ion from the *ortho*-d_2 compound eliminates C_2H_4 as well as C_2H_3D, whereas the $C_9H_{10}D^+$-ion from the *para*-d_1 analogue loses C_2H_4 only.

The elimination of a C_2H_3D molecule from the $C_9H_9D_2^+$-ion of the *ortho*-d_2 derivative may be explained by an "α-*ortho*"-exchange of H in the molecular ion prior to its fragmentation as discussed above.

From a study of the mass spectra of t-butylbenzene and its α-^{13}C[7] analogue and of the spectra from 3-phenylpentane and some of its *mono*-deuterated derivatives (in the side chain),[8] a phenylated cyclopropane structure for the $C_9H_{11}^+$-ion has been suggested.

This structure is also reasonable for the present $C_9H_{11}^+$-ion with the refinement of scrambling of the H atoms in the cyclopropane ring, as demonstrated by the loss of C_2H_4, C_2H_3D as well as $C_2H_2D_2$ from the $C_9H_9D_2^+$-ions of the α-d_2, β-d_2 and γ-d_2 γ-phenylpropylbromides (Appendix, reaction No. 6).

APPENDIX. DIFFUSE PEAKS, OBSERVED IN THE MASS SPECTRA

Reaction No.	Metastable transitions			d_0		γ-d_2	
				m^*	m_2/m_1	m^*	m_2/m_1
1	$C_9H_{11}{}^{81}Br^+$	$\rightarrow C_7H_7{}^{81}Br^+$	$+ C_2H_4$	147·83	0·856	—	—
1	$C_9H_{11}{}^{79}Br^+$	$\rightarrow C_7H_7{}^{79}Br^+$	$+ C_2H_4$	145·88	0·856	—	—
1	$C_9H_9D_2{}^{81}Br^+$	$\rightarrow C_7H_5D_2{}^{81}Br^+$	$+ C_2H_4$	—	—	149·78	0·859
1	$C_9H_9D_2{}^{79}Br^+$	$\rightarrow C_7H_5D_2{}^{79}Br^+$	$+ C_2H_4$	—	—	147·85	0·858
1	$C_9H_9D_2{}^{81}Br^+$	$\rightarrow C_7H_7{}^{81}Br^+$	$+ C_2H_2D_2$	—	—	—	—
1	$C_9H_9D_2{}^{79}Br^+$	$\rightarrow C_7H_7{}^{79}Br^+$	$+ C_2H_2D_2$	—	—	—	—
1	$C_9H_9D_2{}^{81}Br^+$	$\rightarrow C_7H_6D{}^{81}Br^+$	$+ C_2H_3D$	—	—	—	—
1	$C_9H_9D_2{}^{79}Br^+$	$\rightarrow C_7H_6D{}^{79}Br^+$	$+ C_2H_3D$	—	—	—	—
1	$C_9H_{10}D{}^{81}Br^+$	$\rightarrow C_7H_6D{}^{81}Br^+$	$+ C_2H_4$	—	—	—	—
1	$C_9H_{10}D{}^{79}Br^+$	$\rightarrow C_7H_6D{}^{79}Br^+$	$+ C_2H_4$	—	—	—	—
5	$C_9H_{11}{}^{81}Br^+$	$\rightarrow C_9H_{11}^+$	$+ {}^{81}Br$	70·79	0·598	—	—
5	$C_9H_{11}{}^{79}Br^+$	$\rightarrow C_9H_{11}^+$	$+ {}^{79}Br$	71·58	0·598	—	—
5	$C_9H_9D_2{}^{81}Br^+$	$\rightarrow C_9H_9D_2^+$	$+ {}^{81}Br$	—	—	72·57	0·602
5	$C_9H_9D_2{}^{79}Br^+$	$\rightarrow C_9H_9D_2^+$	$+ {}^{79}Br$	—	—	73·31	0·602
5	$C_9H_{10}D{}^{81}Br^+$	$\rightarrow C_9H_{10}D^+$	$+ {}^{81}Br$	—	—	—	—
5	$C_9H_{10}D{}^{79}Br^+$	$\rightarrow C_9H_{10}D^+$	$+ {}^{79}Br$	—	—	—	—
2	$C_9H_{11}{}^{81}Br^+$	$\rightarrow C_7H_8^+$	$+ C_2H_3{}^{81}Br$	42·34	—	—	—
2	$C_9H_{11}{}^{79}Br^+$	$\rightarrow C_7H_8^+$	$+ C_2H_3{}^{79}Br$	42·75	—	—	—
2	$C_9H_9D_2{}^{81}Br^+$	$\rightarrow C_7H_6D_2^+$	$+ C_2H_3{}^{81}Br$	—	—	43·81	—
2	$C_9H_9D_2{}^{79}Br^+$	$\rightarrow C_7H_6D_2^+$	$+ C_2H_3{}^{79}Br$	—	—	44·20	—
2	$C_9H_9D_2{}^{81}Br^+$	$\rightarrow C_7H_8^+$	$+ C_2HD_2{}^{81}Br$	—	—	—	—
2	$C_9H_9D_2{}^{79}Br^+$	$\rightarrow C_7H_8^+$	$+ C_2HD_2{}^{79}Br$	—	—	—	—
2	$C_9H_9D_2{}^{81}Br^+$	$\rightarrow C_7H_7D^+$	$+ C_2H_2D{}^{81}Br$	—	—	—	—
2	$C_9H_9D_2{}^{79}Br^+$	$\rightarrow C_7H_7D^+$	$+ C_2H_2D{}^{79}Br$	—	—	—	—
2	$C_9H_{10}D{}^{81}Br^+$	$\rightarrow C_7H_7D^+$	$+ C_2H_3{}^{81}Br$	—	—	—	—
2	$C_9H_{10}D{}^{79}Br^+$	$\rightarrow C_7H_7D^+$	$+ C_2H_3{}^{79}Br$	—	—	—	—
4	$C_9H_{11}{}^{81}Br^+$	$\rightarrow C_7H_7^+$	$+ C_2H_4{}^{81}Br$	41·44	0·457†	—	—
4	$C_9H_{11}{}^{79}Br^+$	$\rightarrow C_7H_7^+$	$+ C_2H_4{}^{79}Br$	41·83	0·457†	—	—
4	$C_9H_9D_2{}^{81}Br^+$	$\rightarrow C_7H_5D_2^+$	$+ C_2H_4{}^{81}Br$	—	—	42·86	—
4	$C_9H_9D_2{}^{79}Br^+$	$\rightarrow C_7H_5D_2^+$	$+ C_2H_4{}^{79}Br$	—	—	43·28	—
4	$C_9H_9D_2{}^{81}Br^+$	$\rightarrow C_7H_6D^+$	$+ C_2H_3D{}^{81}Br$	—	—	—	—
4	$C_9H_9D_2{}^{79}Br^+$	$\rightarrow C_7H_6D^+$	$+ C_2H_3D{}^{79}Br$	—	—	—	—
4	$C_9H_9D_2{}^{81}Br^+$	$\rightarrow C_7H_7^+$	$+ C_2H_2D_2{}^{81}Br$	—	—	—	—
4	$C_9H_9D_2{}^{79}Br^+$	$\rightarrow C_7H_7^+$	$+ C_2H_2D_2{}^{79}Br$	—	—	—	—
4	$C_9H_{10}D{}^{81}Br^+$	$\rightarrow C_7H_6D^+$	$+ C_2H_4{}^{81}Br$	—	—	—	—
4	$C_9H_{10}D{}^{79}Br^+$	$\rightarrow C_7H_6D^+$	$+ C_2H_4{}^{79}Br$	—	—	—	—
3	$C_7H_7{}^{81}Br^+$	$\rightarrow C_7H_7^+$	$+ {}^{81}Br$	48·18	0·533	—	—
3	$C_7H_7{}^{79}Br^+$	$\rightarrow C_7H_7^+$	$+ {}^{79}Br$	48·78	0·533	—	—
3	$C_7H_5D_2{}^{81}Br^+$	$\rightarrow C_7H_5D_2^+$	$+ {}^{81}Br$	—	—	49·79	0·537
3	$C_7H_5D_2{}^{79}Br^+$	$\rightarrow C_7H_5D_2^+$	$+ {}^{79}Br$	—	—	50·33	0·542
3	$C_7H_6D{}^{81}Br^+$	$\rightarrow C_7H_6D^+$	$+ {}^{81}Br$	—	—	—	—
3	$C_7H_6D{}^{79}Br^+$	$\rightarrow G_7H_6D^+$	$+ {}^{79}Br$	—	—	—	—
6	$C_9H_{11}^+$	$\rightarrow C_7H_7^+$	$+ C_2H_4$	69·60	0·764	—	—
6	$C_9H_9D_2^+$	$\rightarrow C_7H_5D_2^+$	$+ C_2H_4$	—	—	71·49	0·767
6	$C_9H_9D_2^+$	$\rightarrow C_7H_6D^+$	$+ C_2H_3D$	—	—	69·93	0·758
6	$C_9H_9D_2^+$	$\rightarrow C_7H_7^+$	$+ C_2H_2D_2$	—	—	68·43	0·751
6	$C_9H_{10}D^+$	$\rightarrow C_7H_6D^+$	$+ C_2H_4$	—	—	—	—

† Measured on the MS2H instrument by use of the method, described by W. Sonneveld and H. J. Hofman.[9,10]

OF SITE-SPECIFICALLY DEUTERATED $C_6H_5\overset{\gamma}{C}H_2\overset{\beta}{C}H_2\overset{\alpha}{C}H_2Br$

β-d$_2$		α-d$_2$		*ortho*-d$_2$		*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
—	—	—	—	—	—	—	—	147·87	0·856
—	—	—	—	—	—	—	—	145·91	0·858
—	—	149·83	0·858	149·76	0·856	—	—	149·84	0·861
—	—	148·02	0·852	147·97	0·854	—	—	147·88	0·860
146·38	0·849	146·14	0·852	146·13	0·854	—	—	146·40	0·851
144·40	0·847	144·40	0·849	144·41	0·847	—	—	144·44	0·850
—	—	148·02	0·856	147·97	0·853	—	—	148·11	0·856
—	—	146·14	0·854	146·13	0·850	—	—	146·16	0·855
—	—	—	—	—	—	148·81	0·858	148·86	0·861
—	—	—	—	—	—	146·88	0·856	146·90	0·859
—	—	—	—	—	—	—	—	70·91	0·595
—	—	—	—	—	—	—	—	71·62	0·601
72·53	0·602	72·52	0·603	72·49	0·601	—	—	72·59	0·599
73·31	0·602	73·33	0·603	73·24	0·601	—	—	73·32	0·605
—	—	—	—	—	—	71·64	0·599	71·75	0·597
—	—	—	—	—	—	72·44	0·599	72·47	0·603
—	—	—	—	—	—	—	—	42·38	0·460
—	—	—	—	—	—	—	—	42·80	0·465
—	—	43·85	—	43·77	—	—	—	43·81	0·466
—	—	44·25	—	44·18	—	—	—	44·25	0·470
41·81	—	—	—	—	—	—	—	41·95	0·456
42·28	—	—	—	—	—	—	—	42·37	0·460
—	—	42·81	—	42·86	—	—	—	42·88	0·461
—	—	43·23	—	43·25	—	—	—	43·31	0·465
—	—	—	—	—	—	43·03	—	43·09	0·463
—	—	—	—	—	—	43·44	—	43·52	0·468
—	—	—	—	—	—	—	—	41·45	0·455
—	—	—	—	—	—	—	—	41·87	0·460
—	—	—	—	—	—	—	—	42·88	0·461
—	—	—	—	—	—	—	—	43·30	0·465
—	—	41·91	—	41·96	—	—	—	41·95	0·456
—	—	42·36	—	42·35	—	—	—	42·37	0·460
40·91	—	—	—	—	—	—	—	41·04	0·451
41·42	—	—	—	—	—	—	—	41·45	0·455
—	—	—	—	—	—	42·13	—	42·16	0·458
—	—	—	—	—	—	42·55	—	42·59	0·463
48·17	0·532	48·17	0·533	—	—	—	—	48·21	0·529
48·81	0·537	48·82	0·533	—	—	—	—	48·78	0·536
—	—	—	—	49·80	0·535	—	—	49·78	0·535
—	—	—	—	50·30	0·541	—	—	50·36	0·541
—	—	49·20	0·535	49·12	0·534	48·98	0·533	49·00	0·532
—	—	49·20	0·535	49·80	0·534	49·56	0·538	49·57	0·538
—	—	—	—	—	—	—	—	69·62	0·765
71·56	0·767	71·48	0·767	71·46	0·765	—	—	71·52	0·769
69·92	0·759	69·95	0·759	69·93	0·758	—	—	69·99	0·760
68·42	0·752	68·43	0·752	—	—	—	—	68·46	0·752
—	—	—	—	—	—	70·50	0·764	70·57	0·767

EXPERIMENTAL

The mass spectra of undeuterated and site-specifically deuterated γ-phenylpropylbromides have been run under the same conditions as the corresponding undeuterated and deuterated γ-phenylpropanols,[4] from which the γ-phenylpropylbromides were synthesized, as described earlier.[2]

All the samples were purified by GLC, using a 3·5 m/6 mm 30% Silicone Oil column, operating at a temp of 150° (retention time: 56 min).

After purification the samples 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 at such a low ionization energy, that in the parent mass region from the spectrum of undeuterated γ-phenylpropylbromide the parent peak remained only (17·0 eV). The parent mass regions from the deuterated analogues were then run under identical conditions. The results of these measurements have been collected in Table 1.

TABLE 1. MEASUREMENT OF DEUTERIUM CONTENT (%) OF SITE-SPECIFICALLY DEUTERATED γ-PHENYLPROPYLBROMIDE, $C_6H_5\overset{\gamma}{C}H_2\overset{\beta}{C}H_2\overset{\alpha}{C}H_2Br$

	By mass spectrometry Accuracy limit 0·1%			By NMR Accuracy limit 1–2%
Labeled position	d_2	d_1	d_0	
α	88·6	10·9	0·5	93·6
β	88·6	10·9	0·5	93·8
γ	90·3	9·0	0·7	93·1
ortho	96·0	3·9	0·1	—
para	—	89·9	10·1	—

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