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ON THE LOSS OF A BENZYL RADICAL FROM THE MOLECULAR ION OF α,ω-DIBENZYLOXYALKANES

EVIDENCE FOR A BENZYL CATION TRANSFER IN AN S_{Ni}-TYPE REACTION, REVEALED BY A SIMULTANEOUS D- AND ^{18}O-LABELLING[a]

A. P. BRUINS and N. M. M. NIBBERING*
Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands

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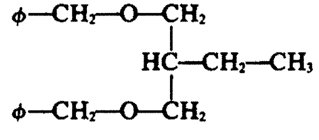
Abstract—The molecular ions of the title compounds appear to lose a benzyl radical, which must be due to the presence of two benzyloxy groups, as benzylalkyl ethers do not exhibit such an expulsion upon electron impact. The results of the partition of the labels deuterium and ^{18}O in the ions *m/e* 107 (protonated benzaldehyde) and [M-benzyl-benzaldehyde]$^+$ put forward evidence that this process is initiated by a successive migration of a benzylic H atom to the opposite ether function and transfer of the benzyl cation from this protonated O atom to the uncharged O atom in an S_{Ni}-type reaction (*cf* Scheme 5).

INTRODUCTION

Functional group interactions in gaseous ions are nowadays the subject of extensive studies in the conventional mass spectrometer[1] as well as in the I.C.R. instrument.[2]

In one of our previous papers we reported[3] that the molecular ion of



$$\begin{array}{l} \phi\text{—CH}_2\text{—O—CH}_2 \\ \qquad\qquad\quad | \\ \qquad\qquad \text{HC—CH}_2\text{—CH}_3 \\ \qquad\qquad\quad | \\ \phi\text{—CH}_2\text{—O—CH}_2 \end{array}$$

expels a benzyl radical—a very unusual reaction in view of the concept of charge localization. At that time the crucial step in this elimination was thought to involve a migration of one of the benzyl groups to the opposite O atom of the molecular ion.

Extensive D- and ^{18}O-labelling,* as well as variation in length of the chain between the benzyloxy groups, have now been performed to get a much deeper insight in the underlying mechanism of the [M-91]$^+$-ion formation and the further degradation to the ions *m/e* 107, [M-91-106]$^+$ and [M-91-108]$^+$.

RESULTS

The 70 eV spectra of α,ω-dibenzyloxyalkanes $\phi CH_2—O—(CH_2)_n—O—CH_2\phi$ with $n = 2$ to 5 are presented in Figs 1 to 4. They all show a weak molecular ion peak (<1%, omitted in the Figs). In the labelling experiments we focussed our attention especially on 1,4-dibenzyloxybutane (1). Compared with the other dibenzyl ethers, its mass spectrum gives least interference between relevant diffuse peaks and normal peaks. The relevant regions from the spectra of the following four labelled 1,4-dibenzyloxybutanes

$\phi CD_2—O—(CH_2)_4—O—CD_2\phi$ (2)
$\phi CH_2—O—(CH_2)_4—O—CD_2\phi$ (3)
$\phi CH_2—{}^{18}O—(CH_2)_4—{}^{16}O—CD_2\phi$ (4)
$\phi CH_2—O—CD_2(CH_2)_2CD_2—O—CH_2\phi$ (5)

are given in Table 2 (see experimental, calculations).

1°. *Loss of a benzyl radical.* The molecular ion of **2** appears to eliminate specifically a dideuterobenzyl radical (Table 2), the same being true for the other α,ω-dibenzyloxyalkanes, labelled with deuterium in both benzylic positions. The spectrum of **3** shows in addition that the expelled benzyl radical contains exclusively its original benzylic hydrogens, without an exchange of these atoms between the benzyl groups. However, a dideuterobenzyl radical is lost more easily than an unlabelled benzyl radical; the measured ratio [*m/e* 179]/[*m/e* 181] equals 1·4:1, typically pointing to an isotope effect of a hydrogen transfer in some stage of this reaction.

2°. *Formation of* m/e 107. Fragment *m/e* 107 appears to contain exclusively the original benzylic

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*This paper has been presented at the 6th International Conference on Mass Spectrometry, Edinburgh, 1973.

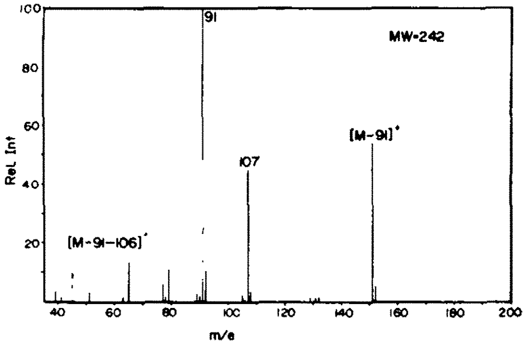

Fig 1.

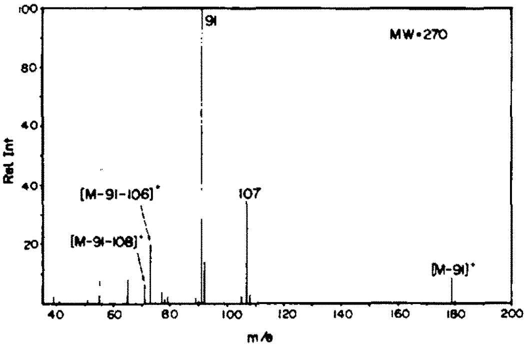

Fig 3.

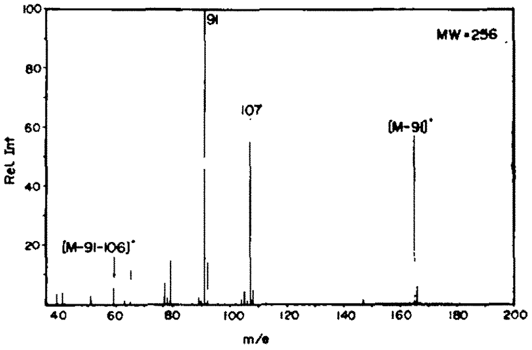

Fig 2.

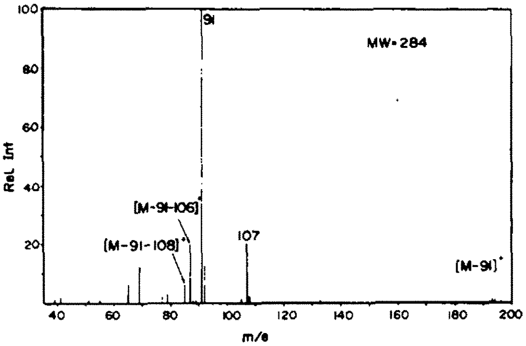

Fig 4.

hydrogens (compounds **2** and **3**, Table 2). The value 1·4:1 for the ratio [*m/e* 107]/[*m/e* 109] in the spectrum of **3** indicates again that a hydrogen isotope effect is operative. The combined deuterium and ^{18}O-labelling further shows that this ion has the composition of a benzyloxy group, containing its original labels. High resolution measurements on *m/e* 109 in this case reveal a ratio 1·4:1 for $[C_6H_5CH_2{}^{18}O]/[C_6H_5CD_2{}^{16}O]$. Also in the spectra of the other α,ω-dibenzyloxyalkanes, labelled with deuterium in both benzylic positions, a practically complete shift of *m/e* 107 to *m/e* 109 is observed.

It is noteworthy that intense first- and second-field free region metastables are observed for the reaction

$$[M\text{-}91]^+ \rightarrow m/e\ 107$$

on both the A.E.I. MS 902 and the Varian M.A.T. 711 double focussing mass spectrometers. A very weak indication for direct formation of *m/e* 107 from the molecular ion could only be found by use of the refocussing technique with the very sensitive Varian M.A.T. 711, having a long first field free region (±1 meter). The ratio of the intensities of the signals corresponding with the decompositions $M^{+\cdot} \rightarrow m/e$ 107 and $[M\text{-}91]^+ \rightarrow m/e$ 107 was 1:1,000. This does not mean that the same ratio is valid in the generation of *m/e* 107 in the ion source.

3°. *Loss of benzaldehyde from the* $[M\text{-}91]^+$*-ion.* The peak, resulting from this reaction, is found at *m/e* 73 (compound **1**). It shifts to *m/e* 74 in the spectrum of **2** and is partitioned over the masses 73 and 74 in the ratio 1·5:1 in the spectrum of **3** (Table 2), as a result of a hydrogen isotope effect in some stage of the successive fragmentations. The relevant peaks in the spectrum of **4** are *m/e* 73, 74 and 76. This mass region is somewhat complex, due to incomplete ^{18}O-labelling and interference with the expulsion of benzyl alcohol-^{16}O from the $[M\text{-}93]^+$-ion (see below), giving peak *m/e* 73. The following reactions can be expected:

$$[M\text{-}91]^+(m/e\ 183) \xrightarrow{-\phi CD^{16}O} m/e\ 76 \qquad (1)$$

$$\xrightarrow{-\phi CD^{18}O} m/e\ 74 \qquad (2)$$

$$[M\text{-}93]^+(m/e\ 181) \xrightarrow{-\phi CH^{18}O} m/e\ 73 \qquad (3)$$

$$\xrightarrow{-\phi CH^{16}O} m/e\ 75. \qquad (4)$$

Complete retention of the original O atom in the expelled benzaldehyde leads to reactions (1) and (3). Mixing of O atoms results in all four fragmentations and the occurrence of only (2) and (4) would be the consequence of a complete interchange of these atoms. It is obvious that the latter two possibilities are ruled out by the absence of *m/e* 75,[*] and that *m/e* 74 accompanies *m/e* 76 due to incomplete ^{18}O-labelling. Using the results of high resolution measurements on *m/e* 73 and correction for incomplete ^{18}O-labelling, a ratio of 1·5 : 1 is obtained for $[C_4H_9{}^{16}O]/[C_4H_8D^{18}O]$, again reflecting a hydrogen isotope effect (see Experimental for calculations).

The molecular ions of the other α,ω-dibenzyloxyalkanes, deuterated in both benzylic positions, appear to lose specifically a dideuterobenzyl radical, followed by mono-deuterobenzaldehyde.

4°. *Loss of benzyl alcohol from the* $[M\text{-}91]^+$*-ion.* This reaction is only observed for the dibenzyl ethers with n = 4 and n = 5. The position of the peaks, at *m/e* 71 and *m/e* 85 respectively, was unchanged after deuteration in both benzylic positions (compound **2**, Table 2). A shift however to *m/e* 74 is observed in the spectrum of **5**. This proves, at least in the case of n = 4, that the eliminated benzyl alcohol contains two benzylic hydrogens and one H atom from an aliphatic methylene group, adjacent to an O atom.

Upon combined deuterium- and ^{18}O-labelling, as performed in compound **4**, four reactions are possible:

$$[M\text{-}91]^+(m/e\ 183) \xrightarrow{-\phi CD_2{}^{16}OH} m/e\ 73 \quad (5)$$

$$\xrightarrow{-\phi CD_2{}^{18}OH} m/e\ 71 \quad (6)$$

$$[M\text{-}93]^+(m/e\ 181) \xrightarrow{-\phi CH_2{}^{18}OH} m/e\ 71 \quad (7)$$

$$\xrightarrow{-\phi CH_2{}^{16}OH} m/e\ 73. \quad (8)$$

Three cases can be considered:

(a) complete retention of the original oxygen in the expelled benzyl alcohol gives (5) and (7),
(b) complete mixing gives (5) to (8),
(c) complete interchange gives (6) and (8).

Unfortunately all these cases result in both *m/e* 71 and *m/e* 73, and the presence of incomplete ^{18}O-labelled material gives an additional contribution to *m/e* 71. The diffuse peaks, corresponding with reactions (5) to (8) are 29·12, 27·55, 27·85 and 29·44 respectively. In the 15 eV spectrum of the unlabelled compound, the only two diffuse peaks in this region are those arising from the loss of benzaldehyde and benzyl alcohol from the $[M\text{-}91]^+$-ion; interfering metastables from other reactions have disappeared. At this electron energy the diffuse peaks due to reactions (5) and (7) are not observed, but the one due to reaction (6) is found instead; the metastable from reaction (8) however coincides with that from reaction (3).

DISCUSSION

The results obtained clearly show that during the fragmentations mentioned in 1°, 2° and 3°, the atoms of one benzyloxy group do not mix with those of the other. The $[M\text{-}91]^+$ and *m/e* 107 ions could therefore be thought to arise from simple cleavages of a C—O bond in the molecular ion, although this would be in contradiction with the concept of charge localization, predicting *m/e* 91[†] and the ion $[M\text{-}107]^+$. The absence of $[M\text{-}91]^+$ and *m/e* 107 in benzylalkyl ethers is a strong argument against such an explanation[1a,4] and indicates that a functional group interaction in α,ω-dibenzyloxyalkanes should be considered. Moreover, the simple cleavage reactions cannot account for the hydrogen isotope effect observed in the formation of the ions described in 1°, 2° and 3° (Results).

Also the mechanism proposed by Hesse *et al.*[1b] for the loss of a radical R· from $R—NH—(CH_2)_4—NH—R$ induced by migration of an *aliphatic* H atom, as presented in Scheme 1, is incompatible with the observed isotope effect. Djerassi *et al.*[1a] discussed the formation of *m/e* 107 in a series of bifunctional benzyl ethers: $\phi—CH_2—O—(CH_2)_n—X$ with $—X = —CO_2CH_3$, $—CO_2H$, $—OH$, $—OCH_3$, $—N(CH_3)_2$, $—Br$ and $—OSi(CH_3)_3$. They concluded from deuterium labelling data that the structure of this ion was best represented as protonated benzaldehyde, produced *via* the route given in Scheme 2. Such a mechanism indeed explains an isotope effect in the fragmentation, discussed in 2°, as far as *m/e* 107 is formed directly from the molecular ion.

With Scheme 2 in mind, it is quite conceivable that the benzylic radical centre, generated after the reciprocal hydrogen transfer, attacks the opposite ether function, leading to expulsion of a benzyl radical and formation of oxygen-protonated 2-phenyl-1, 3 - dioxepane (Scheme 3). The structure of ion *a* indeed allows fragmentation to *m/e* 107 and *m/e* 73 (loss of benzaldehyde), as evidenced by an experiment on the pressure dependence of the ion cyclotron resonance spectrum[5] of 2 - phenyl - 1, 3 - dioxepane; the abundances of these ions increase on raising the pressure from 7×10^{-6} to 8×10^{-5} Torr, sufficiently high to produce the protonated cyclic acetal by ion–molecule collisions (Experimental). It would be highly improbable however, that the proton in ion *a* should not migrate from one O atom to the other, thereby introducing a complete equivalence of both O atoms in the degradation to *m/e* 107, *m/e* 73 and *m/e* 71. This

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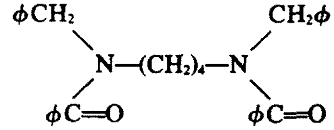
[*] *m/e* 75 is present for 1·0% after correction for natural ^{13}C contributions. The ratio *m/e* 75 : *m/e* 76 equals 0·11 : 1 (Table 2, compound **4**). A similar ratio is found for *m/e* 73 : *m/e* 74 (0·10 : 1) in the case of compound **2**. These incomplete shifts (see also calculations) can be explained by a minor scrambling between deuterium atoms and aromatic H atoms in some stage of the decompositions.

[†] *m/e* 91 is base peak in all 70 eV spectra, as a result of charge localization either in the phenyl ring or on an O atom; $[M\text{-}107]^+$ does not occur.

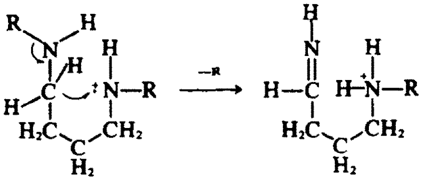
equivalence violates the results quoted in 2°, 3° and 4°. Ion *a* should further be expected to lose a benzene molecule, by protonation of the phenyl ring,* leading to a carbenium ion, highly stabilized by two adjacent O atoms. The corresponding ion, with mass 101, can indeed be generated from protonated 2 - phenyl - 1, 3 - dioxepane in the I.C.R. cell, but is completely absent in the mass spectrum of compound 1. All these arguments therefore reject the intermediacy of ion *a*.

The mechanism, quoted in the introduction, can explain the observed isotope effect, but introduces again an equivalence of O atoms with respect to the benzyl groups (Scheme 4).[3]

A mechanism, consistent with all present labelling results can be obtained when the first two steps in Scheme 4 are interchanged (Scheme 5). The rearrangement of *b* to *c* is an S_{Ni}-type reaction, essentially involving a benzyl cation transfer, and can be compared with the acidic ether cleavage in solution. The only clear example, as far as we know, of a benzyl cation transfer, but then to an amino function, was given by Hesse *et al.* in their study on the electron impact induced fragmentation of

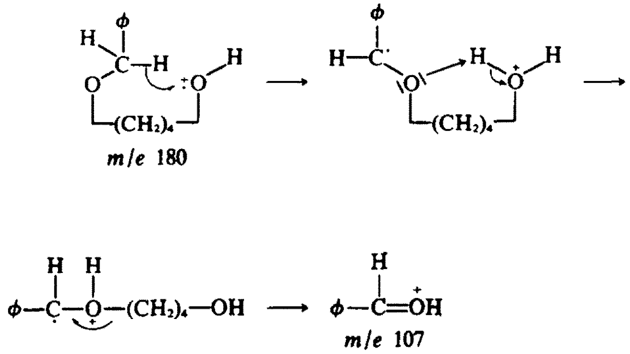


and related compounds.[1b]

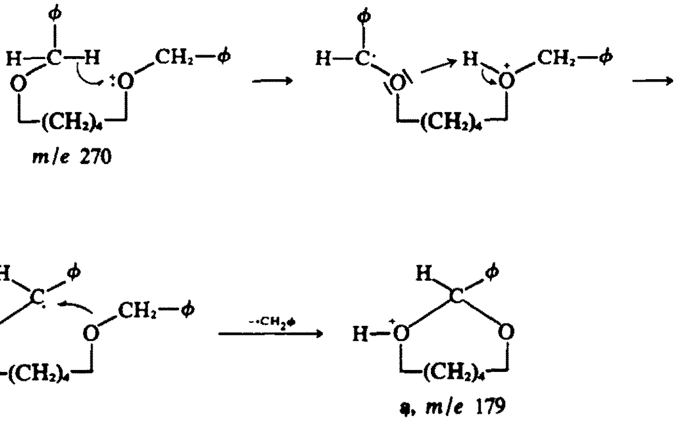


SCHEME 1. Loss of R˙ from N,N′-disubstituted 1,4-diaminobutanes, reported by Hesse *et al.*

The expulsion of benzaldehyde from ion *d* is then due to an attack of the OH group upon the methylene C atom adjacent to the positively charged O atom; the same attack, with an additional hydrogen transfer, leads to formation of *m/e* 107



SCHEME 2. Formation of protonated benzaldehyde from 4-benzyloxybutanol-1, reported by Djerassi *et al.*



SCHEME 3. A possible expulsion of a benzyl radical from 1,4-dibenzyloxybutane.

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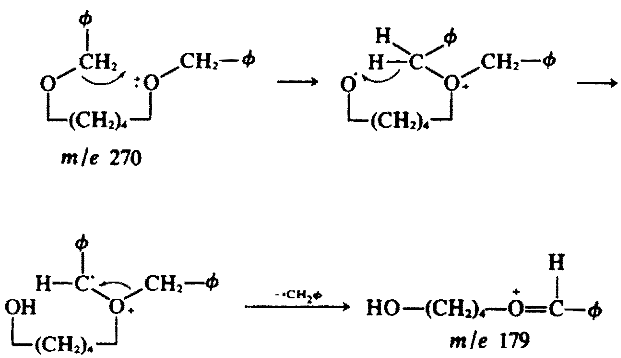
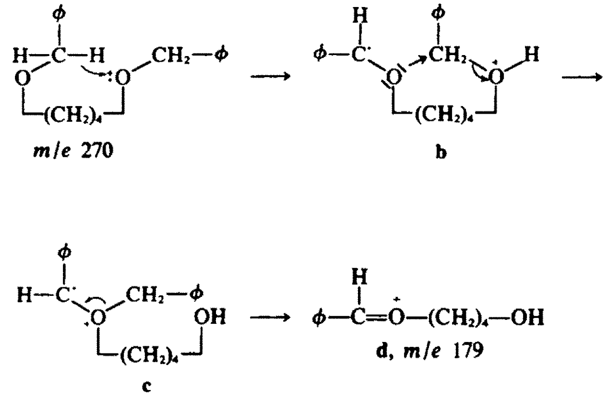
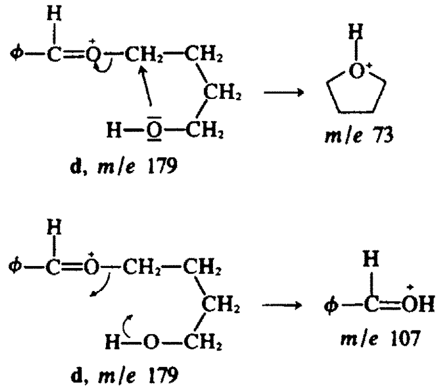
*This kind of reaction is observed in oxygen-protonated species, containing a phenyl ring.[6]



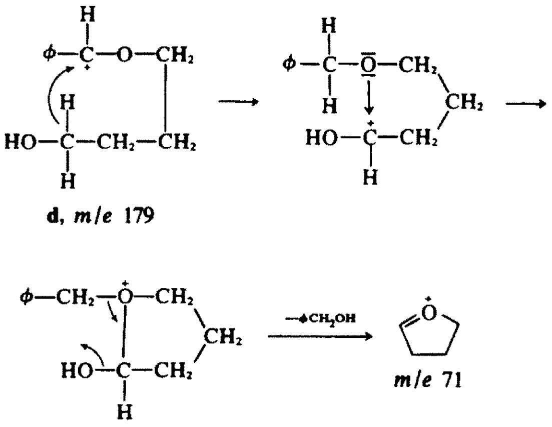
SCHEME 4. Loss of a benzyl radical as proposed in Ref 1.



SCHEME 5. Loss of a benzyl radical from the molecular ion of 1,4-dibenzyloxybutane, sustained by the performed labelling studies.



SCHEME 6. Decomposition of the $[M-91]^+$-ion to m/e 73 and m/e 107.



SCHEME 7. Loss of benzyl alcohol from the $[M-91]^+$-ion.

(Scheme 6). Ion *d* can also explain the loss of benzyl alcohol, initiated by a hydride transfer from the methylene C atom carrying the OH group. This is followed by ring closure and 1,2 elimination of benzyl alcohol, as depicted in Scheme 7.

The spectra of α,ω-dibenzyloxyalkanes with n = 2 to 5 (Figs 1 to 4) show that the further degradations of the $[M-91]^+$-ion, in particular to $[M-91-106]^+$ and $[M-91-108]^+$, are very sensitive to the length of the alkyl chain; the abundances of the latter two ions increase with the length of the alkyl chain, reflecting the relative instability of 3- and 4-membered heterocyclic ions with respect to 5- and 6-membered ones. The effect is even more pronounced when the electron voltage is lowered to 15 eV, see Table 1.

Table 1. Partial mass spectra[a,b] of the compounds $\phi CH_2O(CH_2)_nOCH_2\phi$

n	2		3		4		5	
	m/e	%	*m/e*	%	*m/e*	%	*m/e*	%
$M^{+\cdot}$	242	<0·1	256	<0·1	270	<0·1	284	<0·1
$[M\text{-}91]^+$	151	69·6	165	30·3	179	2·4	193	5·7
m/e 107		9·2		24·0		31·0		18·6
m/e 91		3·4		17·0		15·0		15·4
$[M\text{-}91\text{-}106]^+$	45	0·40	59	2·0	73	19·7	87	27·5
$[M\text{-}91\text{-}108]^+$	43	—	57	0·15	71	10·0	85	12·0

[a] Presented as percentages of the total ion current.

[b] Measured at 15 eV on the A.E.I. MS 902 instrument.

EXPERIMENTAL

Instruments. Mass spectra were measured at 70 eV on the Varian M.A.T. 711 and A.E.I. MS 902 double-focussing mass spectrometers. The spectra and label distributions from both instruments were essentially the same. 15 eV spectra were taken on the MS 902. The Varian M.A.T. 711 was directly coupled to the Varian Spectro System 100.

Samples were introduced into the M.A.T. 711 *via* the all-metal reference inlet system at 165° and into the MS 902 *via* the all-glass inlet system at 180°; ion sources were held at 180°. Close examinations of second field-free region metastables were best done on the MS 902, whereas high resolution measurements on *m/e* 73, 109 and 181 in the case of compound 4 were performed at a resolving power of 8,000, 16,000 and 27,000 respectively on the M.A.T. 711.

I.C.R. experiments on 2 - phenyl - 1, 3 - dioxepane were performed on a Varian V 5903 ion cyclotron resonance spectrometer, using marginal oscillator frequencies of 287·0, 140·0 and 76·78 kHz for the desired mass regions up to *m/e* 77, *m/e* 153 and *m/e* 280. The abundances of *m/e* 73, *m/e* 101, *m/e* 107 and *m/e* 179 increased in comparison with *m/e* 71, 105 and 178 ($M^{+\cdot}$) when the pressure was raised from 7×10^{-6} to 8×10^{-5} Torr. Observing *m/e* 73, 101 or 107 with the marginal oscillator, positive signals were obtained at double resonance frequencies corresponding to *m/e* 179, pointing to collision induced fragmentations[7] of *m/e* 179, the $[M+1]^+$-ion.

Syntheses of (un)labelled compounds

Synthesis of 1, 4 - dibenzyloxybutane as a typical example for the unlabelled and symmetrically labelled compounds: 1·05 g NaH (50% dispersion in oil, 22 mmole) was washed with dry pentane and covered by 25 ml dry DMF. 0·90 g 1, 4 - butanediol (10 mmole) was added and the mixture was stirred at 20° for 1 h. After addition of 2·39 ml benzyl bromide (3·42 g, 20 mmole) and stirring for 14 h at 20°, the mixture was diluted with 100 ml ether. NaBr precipitated and was removed together with DMF by washing with water. After evaporation of the solvent the raw product (1·8 g) was purified by GLC, using a 15% OV 1 column. IR and NMR spectra confirmed the structure.

The asymmetrically labelled 3 was prepared as follows:

$$HO{-}(CH_2)_4{-}OH \xrightarrow[\phi CH_2Br]{NaH} \phi CH_2O{-}(CH_2)_4{-}OH$$

$$\xrightarrow[CBr_4]{\phi_3P} \phi CH_2O{-}(CH_2)_4{-}Br$$

$$\xrightarrow[\phi CD_2OH]{NaH} \phi CH_2O{-}(CH_2)_4{-}OCD_2\phi$$

The mass spectrum of this compound showed a molecular ion peak at *m/e* 272; the absence of *m/e* 270 and 274 indicates that no ether cleavage, followed by recombination occurs during the last step of this reaction sequence, so that this route is useful for the combined D- and ^{18}O-labelling. It was performed by taking dideuterobenzyl bromide in the first, and benzyl alcohol-^{18}O in the last step of this sequence.

4 - Benzyloxybutanol - 1 was prepared in essentially the same way as the diethers from 10 g NaH (0·2 mole), 39 ml 1, 4 - butanediol (0·4 mole) and 24 ml benzyl bromide at 0°. The raw product was purified by distillation. The product, 16 g, was collected at 96–98°/0·2 mm Hg. GLC analysis indicated that the diether was absent after the distillation.

4 - Benzyloxybut - 1 - ylbromide (4·9 g, 68%) was prepared according to the method of Hooz and Gilay[8] from 5·4 g 4 - benzyloxybutanol - 1, 14·1 g CBr_4 and 9·4 g triphenylphosphine. The product was purified by distillation and collected at 92–94°/0·1 mm Hg.

Compound 3 was prepared from 0·48 g NaH, 1·05 ml benzyl alcohol-d_2 and 2·43 g (dideuterobenzyloxy) butyl bromide. The diether was separated from by-products by GLC.

Benzylalcohol-^{18}O was prepared by exchange of 0·5 ml (0·53 g, 5 mmole) of freshly distilled benzaldehyde with 1·0 ml $H_2{}^{18}O$ (50 mmole, 60% ^{18}O, purchased from Bio-Rad Laboratories), acidified with a trace of dry HCl gas. After shaking for 18 h at 20° and 6 h at 50°, the ^{18}O content was 50·6%. Reduction with LAH gave 0·46 g benzyl alcohol-^{18}O (84%).

Synthesis of 2 - phenyl - 1, 3 - dioxepane was performed by reaction of 1·06 g benzaldehyde with 1·08 g 1,4-butanediol and a trace of *p*-toluenesulfonic acid in toluene soln, according to standard methods.[9]

Calculations. The deuterium content of the compounds was 98·8%. The ^{18}O content of 4, measured from 10 scans of the molecular ion region was 52·5 ± 0·1%. No corrections were made for incomplete deuterium labelling.

The relevant regions from the mass spectra of the dibenzyloxybutanes are given in Table 2. The ratio of the intensities of the ions $[M\text{-}93]^+$ and $[M\text{-}91]^+$ in the spectrum of 3 is 8·9:6·4 = 1·39:1. The average of ten high resolution scans of *m/e* 181 in the case of 4 gave a ratio of 60:40 for $[C_{11}H_{15}{}^{16}O^{18}O]:[C_{11}H_{13}D_2{}^{16}O_2]$. The ratio [M-93]:[M-91] then becomes (0·6 × 7·4):3·5 = 1·26:1.

The ratio [*m/e* 107]:[*m/e* 109] for 3 is 42·3:30·9 = 1·37:1. Ten high resolution scans of *m/e* 109 in the spectrum of 4 gave an average ratio of 42:58 for $[C_6H_5CH_2{}^{18}O]:[C_6H_5CD_2{}^{16}O]$, which becomes (100/52·5 × 42):58 = 1·38:1 by correction for incomplete ^{18}O-labelling.

Table 2. Partial mass spectra[a, b, c] of 1,4-dibenzyloxybutanes[d]

Compound:	1	2	3	4	5
base peak:	m/e 91	m/e 93	m/e 93 (m/e 91:94%)	m/e 93 (m/e 91:94%)	m/e 91
m/e	%	%	%	%	%
71	6·7	10·6	18·1 (18·1)	13·6 (13·6)	—
72	0·3	0·6	1·0 (0·2)	1·0 (0·4)	—
73	19·9	2·1	27·3 ± 0·1 (27·2)	29·8 (29·8)	1·2
74	0·8	20·5	18·9 ± 0·1 (17·7)	9·5 (8·2)	7·1
75	—	0·9	0·8 (—)	1·4 (1·0)	0·6
76	—	—	—	8·8 (8·8)	4·1
77	3·9	0·9	3·4	4·2	25·4
78	1·3	0·7	1·5	1·7	1·5
79	6·2	1·0	4·9	5·6	5·7
80	0·3	1·1	1·3	1·4	0·9
81	—	2·6	2·3	2·5	—
104	0·7	—	0·5 (0·5)	0·6	—
105	2·4	1·0	2·9 (2·8)	2·9	4·0
106	0·9	0·4	1·2 (1·0)	1·4	3·1
107	33·6	0·8	42·4 ± 0·3 (42·3)	22·9	52·5
108	2·9	3·4	6·5 (3·2)	5·7	5·5
109	—	39·6	31·3 ± 0·3 (30·9)	55·2	1·1
110	—	3·3	2·6 (0·2)	4·7	—
111	—	—	—	—	—
179	8·6	—	8·9 ± 0·1 (8·9)	4·0 (4·0)	—
180	1·0	—	1·4 (0·4)	0·8 (0·3)	—
181	—	9·4	6·5 ± 0·06 (6·4)	7·5 (7·4)	—
182	—	1·2	0·8 (—)	1·1 (0·2)	1·0
183	—	—	0·4 (0·3)	3·6 (3·5)	5·9
184	—	—	—	0·4 (—)	0·7

[a] Given as percentages of the base peak, average of 8 runs.

[b] Intensities measured by the computer; ions with intensities below a threshold of 0·3% of the base peak are omitted by the computer.

[c] Figures in parentheses are corrected for natural ^{13}C contributions.

[d] 1: $\phi CH_2O(CH_2)_4OCH_2\phi$, 2: $\phi CD_2O(CH_2)_4OCD_2\phi$;
3: $\phi CD_2O(CH_2)_4OCH_2\phi$; 4: $\phi CD_2O(CH_2)_4{}^{18}OCH_2\phi$;
5: $\phi CH_2OCD_2(CH_2)_2CD_2OCH_2\phi$.

The ratio [*m/e* 73]:[*m/e* 74] for **3** is 27·2 : 17·7 = 1·54 : 1 when complications due to the incomplete shift (91%) of *m/e* 73 to *m/e* 74 in the spectrum of **2** are neglected. The nominal mass *m/e* 73 in the spectrum of **4** was divided into the contributions $C_4H_7{}^{18}O$ and $C_4H_9{}^{16}O$ in a ratio of 16:84 after ten high resolution scans. Incomplete ^{18}O-labelling fully accounts for the presence of *m/e* 74, having the composition $C_4H_8D^{16}O$. The ratio of the intensities of the ions $[C_4H_9{}^{16}O]^+$ (*m/e* 73) and $[C_4H_8D^{18}O]^+$ (*m/e* 76) is (0·84 × 29·8):8·8 = 25·0:8·8. Correction for incomplete ^{18}O-labelling gives 25·0:(1·90 × 8·8) = 1·49:1.

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