Water Loss from Molecular Protonated Ions of Benzyl 2-Phenylethyl Ether and Derivatives

Eric E. Kingston[†] and James S. Shannon

School of Chemistry, University of New South Wales P.O. Box 1, Kensington N.S.W. 2033, Australia

Michael J. Lacey

CSIRO Division of Entomology, G.P.O. Box 1700, Canberra A.C.T. 2601, Australia

The skeletal rearrangement for water loss is the dominant ion reaction in the chemical ionization mass spectrum of benzyl 2-phenylethyl ether. Isotopic distributions obtained for this reaction with specifically labelled derivatives have been interpreted in terms of competing five- and six-centred skeletal rearrangements. Chemical substitution of the alternative aromatic rings strongly influences the balance of the competition.

INTRODUCTION

Skeletal rearrangements of molecular protonated ions MH^+ in a chemical ionization (CI) source are more pronounced as reaction pathways than skeletal rearrangements of molecular ions M^{++} in an electron ionization (EI) source. This accentuation arises because even-electron $[MH]^+$ ions are inherently more stable than odd-electron M^{++} ions; because the excess internal energies of molecular parent ions are usually lower in CI than in EI; and because residence times are generally an order of magnitude greater for CI sources than EI sources.

Skeletal rearrangements of molecular protonated ions formed by CI have been reviewed.¹ Some of the gasphase reorganizations reflect well known acid-catalysed reactions in solution, such as the pinacol rearrangement² and the Wagner-Meerwein rearrangement,³ and it is quite possible that novel solution reactions may be predicted from studies of CI skeletal rearrangements.

Competing losses of CH_2O and H_2O are important primary reactions of MH^+ ions of dibenzyl ether, and we have previously elucidated the mechanisms of these particular skeletal rearrangements by isotopic labelling and substituent effects.⁴ The mechanisms we proposed on the basis of these data involved isomeric molecular parent ions that were either ring-protonated (CH_2O loss) or oxygen-protonated (H_2O loss).

When we extended the investigation to the skeletal rearrangements for homologues of dibenzyl ether, we observed that CH_2O loss from $[MH]^+$ ions of benzyl 2-phenylethyl ether, di-2-phenylethyl ether and benzyl 3-phenylpropyl ether does not occur at all, which further supports the ring-closure mechanism proposed previously by us.⁴ However, H_2O loss is enhanced greatly over that observed for dibenzyl ether (Table 1). It may be inferred from these observations that H_2O loss is facilitated for the homologues of dibenzyl ether because six-centred and seven-centred mechanisms are now possible. These preliminary considerations led us to

† Present address: BHP Melbourne Research Laboratories, P.O. Box 264, Clayton, Victoria 3168, Australia.

0030-493X/87/010030-06\$05.00 © 1987 by John Wiley & Sons, Ltd. assess by isotopic labelling the proposition that H_2O loss from [MH]⁺ ions of benzyl 2-phenylethyl ether involves competition between a five-centred rearrangement and a six-centred rearrangement (Scheme 1).

RESULTS AND DISCUSSION

Integrity of reagent proton

Previous studies have shown that the reagent proton is involved extensively in water loss from $[MH]^+$ ions of dibenzyl ether.⁴ The positional integrity of the reagent proton in water loss from the homologous ethers was assessed from their CI (D₂) mass spectra but the results (Table 2) demonstrate a greater dilution of the reagent proton with other hydrogen atoms in these cases.

Hydrogen atoms involved in water loss

Methylene hydrogen atoms do not participate in water loss from $[MH]^+$ ions of dibenzyl ether.⁴ Similarly, we find exclusive loss of D₂O from $[MD]^+$ ions of C₆D₅CH₂OCH₂CH₂C₆D₅ (ion source and first field-free region (1st FFR)), confirming that only the reagent proton and aromatic hydrogen atoms are involved in the reaction.

Model for isotopic distributions

Consider the alternative reaction intermediates illustrated in Scheme 1. Let x be the proportion of the

Table 1.	$[MH - H_2O]^+$	as percentage o	of total ion	current (260I)
	for source rea	ctions		

Compound	CI(H ₂)	CI(iso-C ₄ H ₁₀)
Dibenzyl ether	4	3
Benzyl 2-phenylethyl ether	46	92
Benzyl 3-phenylpropyl ether	22	37
Di(2-phenylethyl) ether	12	36

Received 28 May 1986 Accepted (revised) 14 July 1986



Scheme 1

six-centred rearrangement. Let y and z be the proportion of the proton on the oxygen atom [(oxygen)-proton] that originated from the phenylethyl ring and benzyl ring, respectively. Let i be the primary kinetic isotope effect in the water loss.

Using benzyl 2-phenyl- d_5 -ethyl ether as an example, there are principally four structures (i)-(iv) that can be considered as intermediates for water loss from [MH]⁺ ions:



A primary kinetic isotope effect is possible for H_2O loss from intermediate (iii) and HOD loss from intermediate

Table	2.	Isotopic	distribution	for	water	loss	from	[MD] ⁺	ions
		of ethers	(1st FFR)						

Compound	[MD-HOD] ⁺	[MD – H ₂ O] ⁺
Dibenzyl ether	70	30
Benzyl 2-phenylethyl ether	30	70
Benzyl 3-phenylpropyl ether	31	69
Di(2-phenylethyl) ether	37	63

(iv). Thus, relative losses of $H_2O:HOD:D_2O$ from $[MH]^+$ ions of $C_6H_5CH_2OCH_2CH_2C_6D_5$ are $i(1-x) \times (1-y):[x(1-y)+iy(1-x)]:xy$.

Similarly, it can be shown that relative losses of $H_2O:HOD:D_2O$ [MH]⁺ of from ions $C_6D_5CH_2OCH_2CH_2C_6H_5$ are $ix(1-z):[ixz+(1-x)\times$ (1-z)]:(1-x)z,while relative losses of [MH] of $H_2O:HOD:D_2O$ from ions $C_6D_5CH_2OCH_2CH_2C_6D_5$ are 0:(1-y-z):(y+z).

Observed and calculated isotopic distributions for benzyl 2-phenylethyl ether

The isotopic distributions observed for water loss from $[MH]^+$ ions of specifically labelled benzyl 2-phenylethyl ether are shown in Table 3. Distributions for reactions in the 1st FFR were essentially independent of the reagent gas (H₂ or iso-C₄H₁₀), and therefore only the 1st FFR results for iso-C₄H₁₀ are reported, since the metastable peaks were more abundant with the latter.

There is good agreement between the calculated and observed distributions for various experimental conditions (Table 3). The results support the proposition that a six-centred rearrangement for water loss far outweighs the alternative five-centred rearrangement $(x \sim 0.90)$. Further, the reagent proton is the preferred source for the (oxygen)-proton subsequently lost as water.

Contribution to the (oxygen)-proton from the aromatic hydrogen atoms occurs from both rings but preferably with the 2-phenylethyl ring. Since we conclude that the separate identity of the aromatic labels is preserved before skeletal rearrangement, it is evident that a process of fast inter-ring proton transfer, as observed with several ω -phenylalkyl benzenium ions,⁵⁻⁸ is not applicable in the present case. Finally, a small isotope effect is evident for 1st FFR reactions.

As an extension to these results for benzyl 2-phenylethyl ether, the effects of chemical substitution of the alternative aromatic rings on the balance of the competition were investigated. Thus, substituent effects on the relative proportions of the five- and six-centred

Observed Calculated											
Ether	Conditions	H ₂ O	HOD	D ₂ O	x	Y	z	i	H ₂ O	HOD	D_2O
Benzyl, 2-phenylethyl	H ₂ , source iso-C ₄ H ₁₀ , source	100									
Benzyl-d ₅ , 2-phenylethyl)	83	15	2					84	15	1
Benzyl, 2-phenyl-d ₅ -ethyl	H ₂ , source	4	57	39	0.91	0.43	0.08	1.0	{ 5	56	29
Benzyl-d5, 2-phenyl-d5-ethyl	J	3	47	50					ίo	49	51
Benzyl-d ₅ , 2-phenyl-ethyl)	77	21	2					{ 78	21	1
Benzyl, 2-phenyl- <i>d</i> 5-ethyl	$iso-C_4H_{10}$, source	10	70	20	0.87	0.22	0.10	1.0	{ 10	71	19
Benzyl-d ₅ , 2-phenyl-d ₅ -ethyl		2	67	31					{ o	68	32
Benzyl, 2-phenylethyl	iso-C ₄ H ₁₀ , 1st FFR	100									
Benzyl-d ₅ , 2-phenylethyl)	80	20	0					80	19	1
Benzyl, 2-phenyl- <i>d</i> 5-ethyl	$iso-C_4H_{10}$, 1st FFR	11	69	20	0.90	0.23	0.14	1.5	{ 11	69	20
Benzyl-d ₅ , 2-phenyl-d ₅ -ethyl]	0	63	37					lo	63	37

Table 3. Observed and calculated isotopic distributions for water loss from [MH]⁺ ions of benzyl 2-phenylethyl ether

rearrangements in mono substituted derivatives were explored by analysing the isotopic distributions obtained after deuterium labelling of the unsubstituted aromatic ring. In the absence of results for reciprocal labelling of the substituted ring, two assumptions were made, on the basis of the results for benzyl 2-phenylethyl ether, to reduce the number of unknowns for the calculated distributions. These assumptions were that the kinetic isotope effect was negligible for the source reactions and that the parameters for source and 1st FFR reactions in CI(iso-C₄H₁₀) were similar except for the mediation of an isotope effect.

Observed and calculated isotopic distributions for benzyl d_5 2-(methylphenyl) ethyl ethers

The ring-activating methyl substituent on the phenylethyl aromatic ring would be expected to favour the competition for the six-centred rearrangement compared with the unsubstituted ether. The observed and calculated distributions for water loss from the three isomers are summarized in Table 4.

The results are consistent with the predictions. The presence of a methyl group as an *ortho*, *meta* or *para* substituent of the 2-phenylethyl ring enhances the sixcentred rearrangement for water loss over that observed in the unsubstituted benzyl 2-phenylethyl ether.

Observed and calculated isotopic distributions for methoxybenzyl 2-phenyl-d₅-ethyl ethers

In contrast to the results favouring the six-centred rearrangement after methyl substitution of the phenylethyl ring, we expected to find that the alternative five-centred rearrangement would be promoted by the presence of activating groups on the benzyl ring. Results were obtained for the 2- and 3-methoxybenzyl derivatives (Table 5), but water loss was an insignificant ion reaction for the 4-methoxy substituted ether, both in the source and the 1st FFR. The low values of x for the calculated distributions support the prediction that the five-centred rearrangement is relatively more favoured than the sixcentred rearrangement, compared with the unsubstituted ether.

The calculations indicate that the relative proportion of the six-centred rearrangement in the case of the 2methoxy substituted ether is significantly higher than that for the 3-methoxy substituted ether. We interpret this result in terms of proton solvation by the 2-methoxy substituent, which counteracts its inductive effect and restores the competition in favour of the six-centred rearrangement (Scheme 2). An analogous proton solvation has been proposed previously by us to explain the



Table 4.	Observed and	calculated isotopic	distributions f	for water loss	s from [MH] ⁺	ions of b	enzyl-d ₅	2-(methylphen	yl)ethyl ethers ^a

	Observed								Calculated		
Ether	Conditions	H ₂ O	HOD	D20	x	z	i	H₂O	HOD	D_2O	
Benzyl-d ₅ , 2-(2'-methylphenyl)ethyl	iso-C ₄ H ₁₀ , source	86	12	2	0.95	0.09	1.0	86	13	1	
Benzyl-d ₅ , 2-(2'-methylphenyl)ethyl	H ₂ , source	89	10	1	0.94	0.05	1.0	89	11	0	
Benzyl-d ₅ , 2-(2'-methylphenyl)ethyl	iso-C ₄ H ₁₀ , 1st FFR	84	16	0	1.0	0.16	1.5	84	16	0	
Benzyl-d ₅ , 2-(3'-methylphenyl)ethyl	iso-C₄H ₁₀ , source	82	16	2	0.94	0.12	1.0	83	17	1	
Benzyl-d ₅ , 2-(3'-methylphenyl-ethyl	H ₂ , source	83	16	1	0.94	0.12	1.0	83	17	1	
Benzyl-d ₅ , 2-(3'-methylphenyl)ethyl	iso-C₄H ₁₀ , 1st FFR	90	10	0	1.0	0.10	1.5	90	10	0	
Benzyl-d ₅ , 2-(4'-methylphenyl)ethyl	iso-C ₄ H ₁₀ , source	86	12	2	0.95	0.09	1.0	86	13	1	
Benzyl-d ₅ , 2-(4'-methylphenyl)ethyl	H ₂ , source	86	13	1	0.95	0.09	1.0	86	13	1	
Benzyl-d ₅ , 2-(4'-methylphenyl)ethyl	iso-C ₄ H ₁₀ , 1st FFR	83	17	0	1.0	0.17	1.5	83	17	0	

	Ubserved						Calculated				
Ether	Conditions	H₂O	HOD	D_2O	x	Y	i	H ₂ O	HOD	D20	
2-methoxybenzyl, 2-phenyl- <i>d</i> 5-ethyl	iso-C₄H ₁₀ , source	25	59	16	0.68	0.22	1.0	25	60	15	
2-methoxybenzyl, 2-phenyl-d ₅ -ethyl	H ₂ , source	30	56	14	0.63	0.20	1.0	30	57	13	
2-methoxybenzyl, 2-phenyl-d ₅ -ethyl	iso-C₄H ₁₀ , 1st FFR	31	53	16	0.68	0.22	1.5	32	54	14	
3-methoxybenzyl, 2-phenyl-d ₅ -ethyl	iso-C ₄ H ₁₀ , source	41	48	11	0.49	0.22	1.0	40	49	11	
3-methoxybenzyl, 2-phenyl- <i>d</i> 5-ethyl	H ₂ , source	31	49	20	0.49	0.40	1.0	31	49	20	
3-methoxybenzyl, 2-phenyl- <i>d</i> 5-ethyl	iso-C₄H ₁₀ , 1st FFR	53	42	5	0.43	0.22	1.5	52	41	7	
4-methoxybenzyl, 2-phenyl- <i>d</i> 5-ethyl	Water loss insignificant										
See footnote to Table 4											

Table 5. Observed and calculated isotopic distributions for water loss from $[MH]^+$ ions of methoxybenzyl 2-phenyl- d_5 -ethyl ethers^a

striking contrast in results for water loss from 2- and 3-methoxy substituted dibenzyl ethers.⁴

Observed and calculated isotopic distributions for water loss from benzyl- d_5 -2-(methoxyphenyl)ethyl ethers

As was observed for methyl substitution, we expected that the presence of an activating methoxy substituent on the phenylethyl ring, particularly in the 2- and 4positions, would favour the six-centred rearrangement. However, it was possible that the isotopic distributions for the 2-methoxy derivative could reflect some contribution from the five-centred rearrangement because of proton solvation, through a mechanism analogous to Scheme 2.

The observed results and calculated distributions for the 2- and 4-methoxy derivatives (Table 6) demonstrate that the six-centred rearrangement is favoured almost exclusively and that the five-centred rearrangement is not being promoted for the 2-methoxy derivative. It is possible that proton solvation is not a factor for the 2-methoxy derivative because it would involve a 7membered ring intermediate, whereas Scheme 2 involves a six-membered ring for the proton-methoxy interaction.

The observed distributions for the 3-methoxy derivative (Table 6) were surprising since they demonstrated that competition from the five-centred rearrangement is more pronounced than for the unsubstituted ether. We interpret this substituent effect as a curtailment of the six-centred rearrangement rather than a promotion of the five-centred rearrangement. Resonance delocalization of the positive charge in the reaction intermediate for the six-centred rearrangement by the 3-methoxy group will inhibit the dissociation step for water loss, relative to the unsubstituted ether (Scheme 3).

Observed and calculated isotopic distributions for water loss from bromobenzyl 2-phenyl- d_5 -ethyl ethers

The presence of a ring-deactivating bromo substituent on the benzyl ring, particularly in the 2- and 4-positions, would be expected to reduce the contribution from the five-centred rearrangement and thereby favour the sixcentred rearrangement. Unfortunately, the results for the bromo derivatives, particularly for the 1st FFR, were obscured by competing ion reactions. However, water loss from $[MH]^+$ ions overwhelmed the competition in the case of source reactions in CI(iso-C₄H₁₀) and therefore the present analysis of distributions was confined to these experimental conditions.

The observed distribution for water from $[MH]^+$ ions (⁸¹Br isotope) of 2-bromobenzyl 2-phenyl- d_5 -ethyl ether was 0:68:32 (H₂O:HOD:D₂O), which is matched by the calculated distribution for an exclusively six-centred rearrangement (x = 1.0, with y = 0.32 and i = 1.0). Similarly, the observed distribution for the 4-bromo derivative was 0:82:18 (H₂O:HOD:D₂O), which is identical to the calculated distribution for x = 1.0, y = 0.18 and i = 1.0.

The resonance stabilizing effect of a 3-bromo substituent on the benzyl ring would be expected to counteract the substituent's inductive effect and hence the isotopic distribution for water loss should reflect some contribution from the five-centred rearrangement. The observed distribution for losses of $H_2O:HOD:D_2O$ from [MH]⁺ ions of 3-bromobenzyl 2-phenyl- d_5 -ethyl

Table 6. Observed an	nd calculated isotopic	distributions for wate	r loss from [MH]⁺	ions of ben	nzyl-d ₅ 2-(met)	hoxyphenyl)ethyl	ethers*
----------------------	------------------------	------------------------	-------------------	-------------	-----------------------------	------------------	---------

	Observed							Calculated			
Ether	Conditions	H₂O	HOD	D20	x	z	i	H₂O	HOD	D20	
Benzyl- <i>d</i> 5, 2-(2′-methoxyphenyl)ethyl	iso-C₄H₁₀, source	95	5	0	1.0	0.04	1.0	95	5	0	
Benzyl-d ₅ , 2-(2'-methoxyphenyl)ethyl	H ₂ , source	82	15	3	0.92	0.10	1.0	83	16	1	
Benzyl-d ₅ , 2-(2'-methoxyphenyl)ethyl	iso-C ₄ H ₁₀ , 1st FFR	98	2	0	1.0	0.02	1.4	98	2	0	
Benzyl-d ₅ , 2-(3'-methoxyphenyl)ethyl	iso-C₄H ₁₀ h source	68	28	4	0.74	0.07	1.0	69	29	2	
Benzyl-d ₅ , 2-(3'-methoxypehnyl)ethyl	H ₂ , source	72	25	3	0.80	0.09	1.0	73	25	2	
Benzyl-d ₅ , 2-(3'-methoxyphenyl)ethyl	iso-C₄H ₁₀ , 1st FFR	65	31	4	0.67	0.10	1.4	66	31	3	
Benzyl-d ₅ , 2-(4'-methoxyphenyl)ethyl	iso-C₄H ₁₀ , source	92	8	0	1.0	0.08	1.0	92	8	0	
Benzyl-d ₅ , 2-(4'-methoxyphenyl)ethyl	H ₂ , source	84	15	1	0.91	0.08	1.0	84	15	1	
Benzyl- <i>d</i> 5, 2-(4'-methoxypehnyl)ethyl	iso-C ₄ H ₁₀ , 1st FFR	93	7	0	1.0	0.07	1.4	93	7	0	
See footnote to Table 4.											



ether was 10:70:20. The calculated distribution for x = 0.88 (similar to that for the unsubstituted ether), y = 0.24 and i = 1.0 is 9:70:21.

Structures of daughter ions

The electron shifts shown in Schemes 1 and 2 are merely illustrative and are not intended to be pre-emptive of other daughter ion structures. Nevertheless, it is possible to adduce from fragmentation patterns that the [MH-H₂O]⁺ daughter ions formed by five- and six-centred rearrangements of benzyl 2-phenylethyl ether (Scheme 1) are different. The expected products for the five- and six-centred rearrangements were generated by water loss from the $[MH]^+$ ions of 2-(2'-phenylethyl) benzyl alcohol and 2-(2'-benzyl) phenylethyl alcohol, respectively. The spectra of daughter ions formed in the 1st FFR by fragmentation of the selected $[MH - H_2O]^+$ parent ions (constant parent ion spectra) were similar for benzyl 2-phenylethyl ether and 2-(2'-benzyl) phenylethyl alcohol and distinguishable from that of 2-(2'phenylethyl) benzyl alcohol (see Experimental). This observation reinforces the conclusion that the sixcentred rearrangement is dominant for benzyl 2-phenylethyl ether.

EXPERIMENTAL

Chemical ionization mass spectra were obtained on an AEI MS902 mass spectrometer fitted with a CIS 2 ion source (Scientific Research Instruments), under conditions described previously.⁴ Reagent gases were hydrogen (CIG, Ultra High Purity, 99.99%), deuterium (Norsk Hydro, 99.7 atom % D) and isobutane (Matheson, 99.5%). Source pressures were maintained at 130 Pa for H₂ and D₂ and 70 Pa for isobutane. The labelling of the reagent proton was achieved by adding sufficient D₂O to the D₂ to exchange any water adventitiously present in the source⁹ but insufficient to cause deuterium exchange with the aromatic rings.¹⁰ Relative peak heights for daughter ions (Tables 1–6) are averaged values from at least five scans for main-beam reactions

(corrected for natural isotopic contributions) and at least three scans for 1st FFR reactions.

Daughter ions formed in the 1st FFR by fragmentation of a selected parent ion were assessed by a microprocessor-controlled¹¹ linked scan of the magnetic field *B* and electric sector voltage *E* at constant B/E and constant accelerating voltage (8 kV). The energy resolution was adjusted to at least 1200 at the beta slit (full width at half maximum height). In some cases where unexpected distributions of the labelled daughter ions were obtained, the distributions were reproduced using a VG 70-70 mass spectrometer by generating the required linked scans with a VG 11-250 data system.

Measurements of deuterium incorporation in labelled derivatives were carried out on an AEI MS12 mass spectrometer under electron ionization conditions at low eV values. High resolution mass spectra were obtained on the AEI MS902 mass spectrometer by a method described previously.¹²

Preparative gas chromatography was carried out on a Varian 712 chromatograph, using either a 10% OV225 on Chromsorb W column (80/100 mesh, 0.95 cm × 183 cm) or a 20% SE-30 on Chromsorb W column (80/100 mesh, 0.95 cm × 198 cm). Preparative short column chromatography was carried out using Merck Keiselgel H.

Deuterium-labelled starting materials were prepared as indicated previously.⁴ 2-(Phenyl-2',3',4',5',6'- d_5)ethyl alcohol (95% d_5 , 5% d_4) was prepared by the reaction of the Grignard compound from bromobenzene-2,3, 4,5,6- d_5 with ethylene oxide in ether solution at approximately -10 °C. The crude product was purified by short column chromatography.

The unlabelled and labelled ethers were prepared by a modification¹³ of the Williamson ether synthesis and purified by preparative gas chromatography. The molecular structures and homogeneity of the unlabelled compounds were validated by NMR, mass spectrometry and elemental analysis. Examination of the molecular ions of the labelled ethers (EI, 12–15 eV) confirmed that deuterium was not lost during the ether synthesis.

2-(2'-Phenylethyl)benzyl alcohol (Aldrich) was used as received. 2-(2'-Benzyl)phenylethyl alcohol was synthesized by the following procedure.¹⁴ 2-Benzylbenzoic acid (Aldrich) was converted to the acid chloride and treated with diazomethane to form the α diazoketone. The *tert*-butyl ester of (2-benzyl)phenyl acetic acid was obtained by dissolution of the α diazoketone in *tert*-butyl alcohol and reaction with silver benzoate and triethylamine, and was reduced (LiAlH₄) to yield the desired product.

The constant parent ion spectra (1st FFR) for the $[MH-H_2O]^+$ ions of m/z 195 from benzyl 2-phenylethyl ether and the model compounds were: benzyl 2-phenylethyl ether (m/z of daughter ion, RI%)-193,70; 180,76; 179,81; 178,61; 167,40; 166,20; 165,38; 118,20; 117,100; 91,50. 2-(2'benzyl)phenylethyl alcohol

 E. E. Kingston, J. S. Shannon and M. J. Lacey, Org. Mass Spectrom. 18, 183 (1983).

- G. L. Glish and R. G. Cooks, J. Am. Chem. Soc. 100, 6720 (1978).
 R. Wolfschütz, W. Franke, N. Heinrich, H. Schwarz, W. Blum
- and W. J. Richter, Z. Naturforsch. 37B, 1169 (1982).
- E. E. Kingston, J. S. Shannon, V. Diakiw and M. J. Lacey, Org. Mass Spectrom. 16, 428 (1981).
- D. Kuck, W. Bäther and H-F. Grützmacher, J. Am Chem. Soc. 101, 7154 (1979).
- 6. D. Kuck, Int. J. Mass Spectrum. Ion Phys. 47, 499 (1983).
- W. Bäther, D. Kuck and H-F. Grützmacher, Org. Mass Spectrom. 20, 589 (1985).

(m/z of daughter ion, RI%) - 193,75; 180,70; 179,50; 178,50; 167,25; 166,12; 165,25; 118,20; 117,100; 91,35. 2-(2'-phenylethyl)benzyl alcohol <math>(m/z of daughter ion, RI%) - 193,83; 180,100; 179,50; 178,17; 167,8; 166,5; 165,8; 118,3; 117,30; 91,5.

Acknowledgements

The authors are grateful for the invaluable advice and assistance of Dr J. J. Brophy, Dr V. Diakiw, Mr Derek Nelson and Mr Peter Gore. This study was supported financially by the Australian Research Grants Scheme. EEK acknowledges the receipt of an Australian Post-graduate Research Award.

REFERENCES

- D. Kuck, W. Bäther and H-F. Grützmacher, Int. J. Mass Spectrom. Ion Processes 67, 75 (1985).
- V. Diakiw, R. J. Goldsack, J. S. Shannon and M. J. Lacey, Org. Mass Spectrom. 13, 462 (1978).
- 10. D. F. Hunt and S. K. Sethi, *J. Am Chem. Soc.* **102**, 6953 (1980). 11. J. J. Brophy, E. E. Kingston, J. T. Morgan and D. Nelson, *Int. J.*
- Mass Spectrom. Ion Phys. 35, 319 (1980).
- J. J. Brophy, D. Nelson, R. J. Goldsack, R. O. Lidgard and D. P. Melley, *Lab. Pract.* 28, 615 (1979).
- 13. J. J. Brophy, Aust. J. Chem. 29, 2445 (1976).
- 14. M. Lorch and H. Meier, Chem. Ber. 114, 2382 (1981).