Collision-induced Dissociations of Aryl-substituted Alkoxide Ions. Losses of Dihydrogen and Rearrangement Processes

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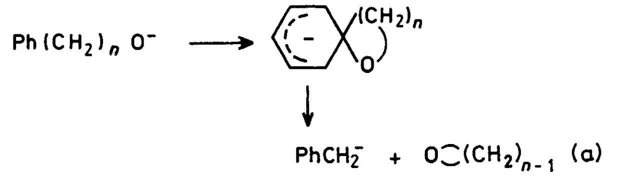
The ion $PhCH_2O^-$ undergoes competitive losses of H˙, H_2, CH_2O, and C_6H_6 upon collisional activation. The loss of H_2 occurs mainly to form $(C_6H_4)^-CHO$, and *ab initio* calculations suggest the reaction proceeds by the stepwise mechanism $PhCH_2O^- \longrightarrow [H^-(PhCHO)] \longrightarrow (C_6H_4)^-CHO + H_2$. The losses of CH_2O and C_6H_6 are accompanied (or preceded) by partial phenyl H–benzyl H interchange. The ion $Ph(CH_2)_3O^-$ undergoes many fragmentations including the losses of H_2O and, CH_2O and loss of H_2. The loss of H_2 occurs by both 1,2- and 1,3-eliminations. A number of minor fragmentations occur after partial interchange of phenyl hydrogens and hydrogens at position 2. The first example of a specific double proton transfer is noted, *viz.* $Ph(CH_2)_3O^- \longrightarrow C_6H_7^- + CH_2{=}CH{-}CHO$. Ions $Ph(CH_2)_nO^-$ (n = 2—5) all decompose to produce $PhCH_2^-$ ions: when n = 3—5 it is proposed that the reactions may involve Smiles intermediates, *i.e.* reaction (a).



(a)

The collision-induced dissociations of simple alkoxides[1–3] and more complex alkoxides (Wittig rearrangement products)[4,5] have been described. The 1,2-loss of dihydrogen from the ethoxide ion has been shown to be a stepwise process (i) in which both steps A and B are rate determining.[1] The methoxide ion, in contrast, undergoes a low-yield 1,1-elimination of dihydrogen [equation (ii)], in which steps C and D are both rate determining. In this reaction, step C, which is thought to be an equilibrium process, shows a pronounced deuterium isotope effect in spite of the fact that the activation energy for step C is considerably less than that of D.[3]

$$CH_3CH_2O^- \xrightarrow{A} [H^-(CH_3CHO)] \xrightarrow{B} [H_2(CH_2{=}CHO^-)] \longrightarrow CH_2{=}CHO^- + H_2 \quad \text{(i)}$$

$$CH_3O^- \xrightarrow{C} [H^-(H_2CO)] \xrightarrow{D} [H_2(H{-}\bar{C}{=}O)] \longrightarrow H{-}\bar{C}{=}O + H_2 \quad \text{(ii)}$$

We planned in the present study to study the loss of H_2 from alkoxide ions $Ph(CH_2)_nO^-$ (n = 1—5); in particular we were interested in determining whether $PhCH_2O^-$ undergoes 1,1-elimination like MeO^-. This paper addresses this problem, and also describes other fragmentations of these alkoxide systems.

Results and Discussion

Collision activation mass spectra (c.a. m.s.) were measured with a VG ZAB 2HF mass spectrometer. Collision activation mass spectra are recorded in Figures 2—4 and Tables 1—4. *Ab initio* calculations were carried out using GAUSSIAN 82[6] at the 3-21G level. The procedures adopted for these calculations have been described in full previously.[7]

(A) *Fragmentations of the Benzyl Oxide Ion.*—The c.a. mass spectra of $PhCH_2O^-$ (from $PhCH_2OD$) and the labelled derivatives $Ph^{13}CH_2O^-$, $PhCHDO^-$, $PhCD_2O^-$, $C_6D_5CH_2O^-$, and $C_6H_2D_3CD_2O^-$ are recorded in Table 1. Competitive losses from $PhCH_2O^-$ are H˙, H_2, CH_2O, and C_6H_6. The losses of CH_2O and C_6H_6 [equations (1) and (2)] do not involve carbon scrambling between the phenyl ring and the benzylic carbon, but a minor amount of scrambling of phenyl and CH_2 hydrogens is noted. We suggest that the hydrogen scrambling either occurs in the intermediate ion complex [equations (1) and

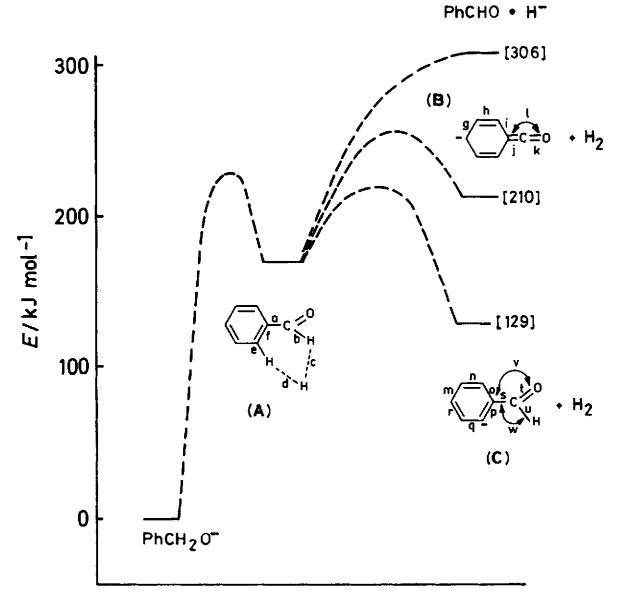
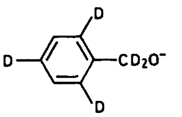


Figure 1. *Ab initio* calculations (3-21G) for the loss of H_2 from $PhCH_2O^-$. Geometries (Å, °) as follows: $PhCH_2O$, C–C 1.56, C–H 1.12, C–O 1.35; (**A**), a 1.46, b 1.09, c 2.10, d 2.02, e 1.08, f 1.39; (**B**), g 1.41, h 1.36, i 1.48, j 1.30, k 1.21, l 180; (**C**) m 1.40, n 1.37, o 1.40, p 1.42, q 1.43, r 1.38, s 1.46, t, 1.23, u 1.09, v 128, x 112. Energies (a.u.) $PhCH_2O^-$ −342.028 14, (**B**) −340.325 35, (**C**) −340.856 06, H_2 −1.122 96

Table 1. C.a. mass spectra of $PhCH_2O^-$ and labelled analogues

Initial ion	Loss $H^\bullet$	$D^\bullet$	H_2	HD	D_2	CH_2O	$^{13}CH_2O$	CHDO	CD_2O	C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_2D_4$	C_6HD_5
$PhCH_2O^-$	81		44			100				2				
$Ph^{13}CH_2O^-$	80		45				100			2				
$PhCHDO^-$	40	23[a]	23[a]	7		15		100		1.0	0.8			
$PhCD_2O^-$	55	5.5[a]	5.5[a]	8				26	100		0.4	0.04		
$C_6D_5CH_2O^-$	100	58[a]	58[a]	17	0.02	88		25					0.1	0.6
	18	6[a]	6[a]	5	2			13	100				0.3	0.02

[a] $D^\bullet$ and H_2 2 a.m.u.

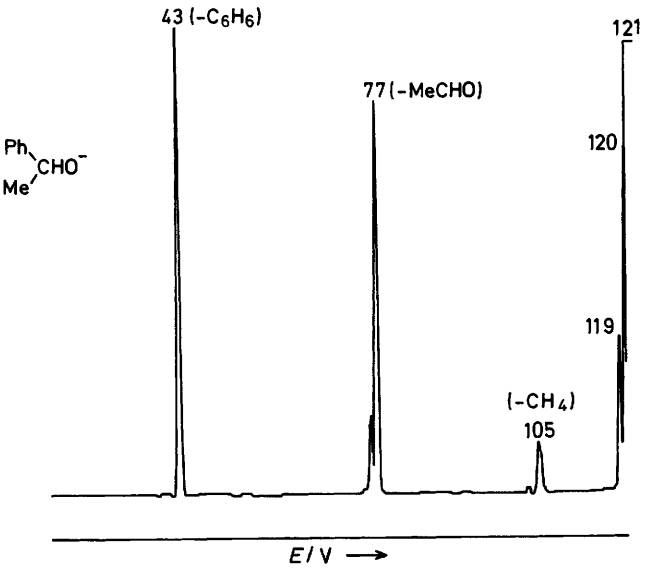


Figure 2. C.a. mass spectrum of $Ph(Me)CHO^-$. Experimental conditions, see Experimental section

Table 2. C.a. mass spectra of $PhCH_2CD_2O^-$ and $PhCD_2CH_2O^-$

Initial ion	Loss HD	H_2O	HOD	CH_2O	CD_2O
$PhCD_2CH_2O^-$	18		0.5	100	
$PhCH_2CD_2O^-$	24	2.2	0.7		100

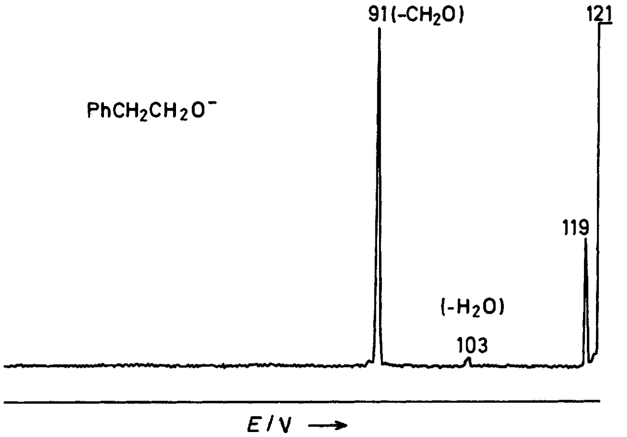
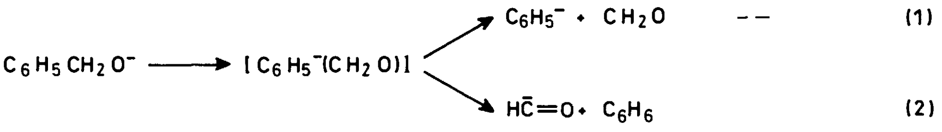
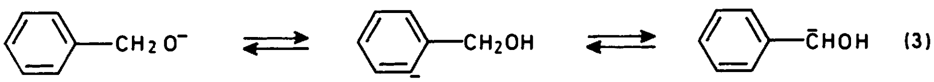


Figure 3. C.a. mass spectrum of $PhCH_2CH_2O^-$





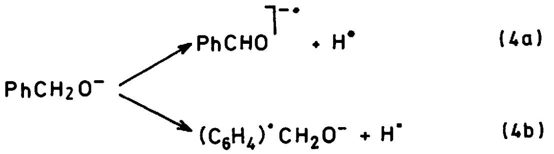


Table 3. C.a. mass spectra of $PhCH_2CH_2CH_2O^-$ and labelled analogues

Initial ion	Loss														Formation				
	H_2	HD	H_2O	HOD	$(H_2O + H_2)$	$(H_2O + HD)$	CH_2O	CD_2O	$(CH_2O + H^\cdot)$	$(CH_2O + D^\cdot)$	$(CD_2O + H^\cdot)$	$(CH_2O + H_2)$	$(CH_2O + HD)$	$(CD_2O + H_2)$	$C_7H_7^-$	$C_7H_6D^-$	$C_7H_5D_2^-$	$C_7H_3D_4^-$	$C_7H_2D_5^-$
$PhCH_2CH_2CH_2O^{-\,a}$	100		1.0		0.5		2.2		0.6			0.7			0.2				
$C_6D_5CH_2CH_2CH_2O^-$	100		1.2		0.2	0.4	2.9			1.6^b		1.6^b						0.05	0.2
$PhCD_2CH_2CH_2O^-$	100	8		0.5			2.7		0.2				0.2				0.1		
$PhCH_2CD_2CH_2O^-$	52	100	0.9	0.8		0.5^c	4.2		1.2	1.0^b		1.0^b	0.5		0.1	0.02			
$PhCH_2CH_2CD_2O^-$		100	1.2			0.4		2.5			0.9			0.6	0.2				

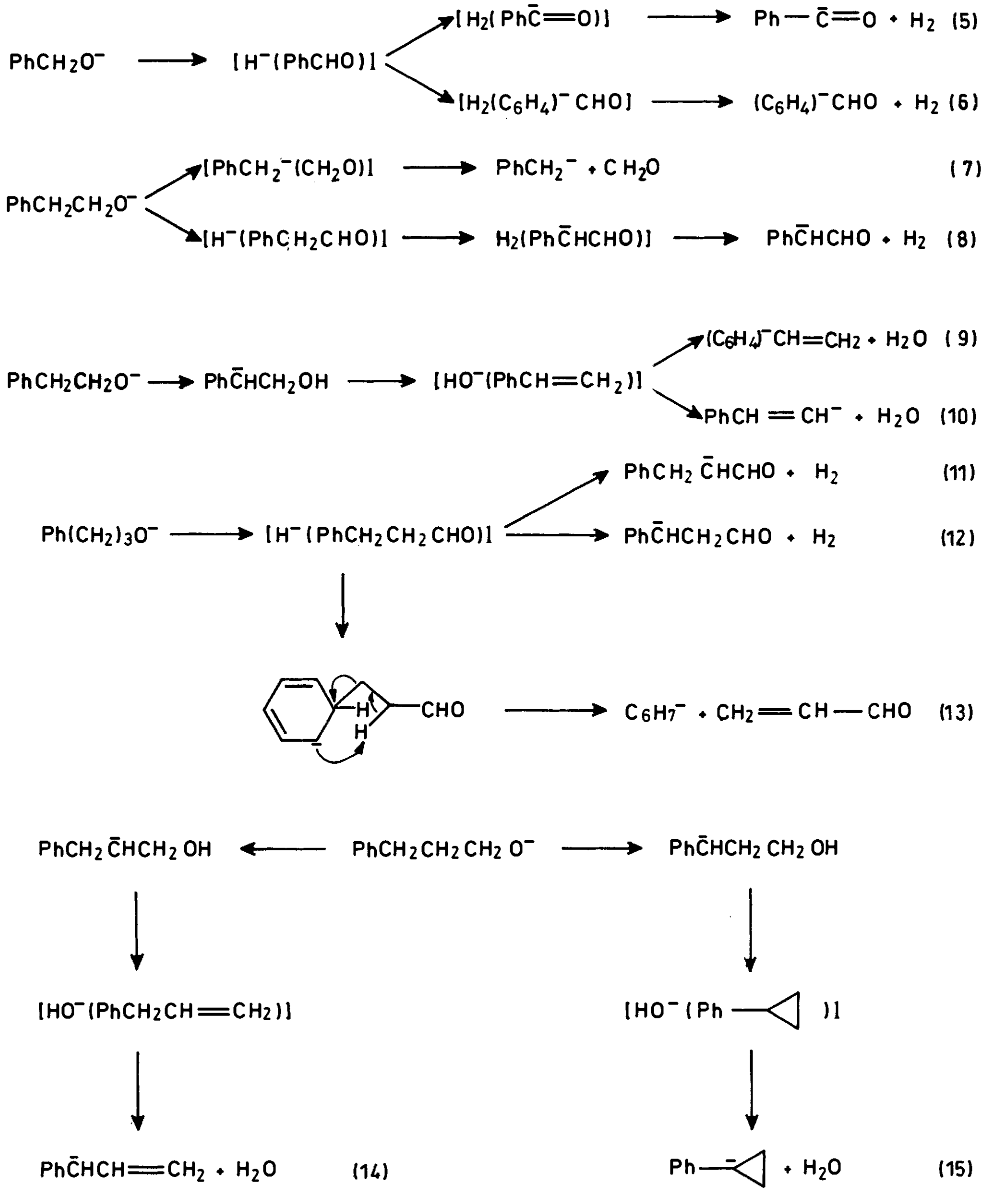
	Formation															
	$C_6H_7^-$	$C_6H_6D^-$	$C_6H_2D_5^-$	$C_6H_5^-$	$C_6H_4D^-$	$C_6H_2D_3^-$	$C_6HD_4^-$	$C_6D_5^-$	$C_3H_5O^-$	$C_3H_4DO^-$	$C_3H_3D_2O^-$	$C_2H_3O^-$	$C_2H_2DO^-$	$C_2HD_2O^-$	CHO^-	CDO^-
$PhCH_2CH_2CH_2O^{-\,a}$	1.0			1.6					1.9			2.5			0.1	
$C_6D_5CH_2CH_2CH_2O^-$			0.5			0.1	0.4	0.5	1.2	0.2		2.2			0.2	
$PhCD_2CH_2CH_2O^-$	0.6			0.7							0.8	2.0			0.1	
$PhCH_2CD_2CH_2O^-$		0.6		1.5	0.4					0.3	2.6		0.6	3.5	0.3	
$PhCH_2CH_2CD_2O^-$		0.6		0.7						2.2			2.7			0.1

[a] Ion formed from $PhCH_2CH_2CH_2OD$. [b] $(CH_2O + D^\cdot)$ and $(CH_2O + H_2)$ both 32 a.m.u. [c] This peak is a combination of $-(H_2O + HD)$ and $-(HOD + H_2)$.

Table 4. C.a. mass spectra of $Ph(CH_2)_3CH_2O^-$ and $Ph(CH_2)_4CH_2O^-$ and labelled derivatives

Initial ion	Loss													
	H_2	HD	H_2O	HOD	CH_2O	CD_2O	$(CH_2O + H_2)$	$(CH_2O + HD)$	$(CD_2O + H_2)$	C_2H_6O	C_2H_5DO	$C_2H_4D_2O$	C_3H_8O	C_3H_7DO
$Ph(CH_2)_3CH_2O^-$	100		0.8		0.4		0.6			1.2				
$PhCD_2(CH_2)_2CH_2O^-$	100		0.3	0.5	0.6			0.4			0.8			
$Ph(CH_2)_3CD_2O^-$	12	100	0.6			0.2			0.7			0.5		
$Ph(CH_2)_4CH_2O^-$	100		0.5		0.3		0.2						0.3	
$PhCD_2(CH_2)_3CH_2O^-$	100													

	Formation											
	$C_7H_9^-$	$C_7H_6D^-$	$C_7H_7D_2^-$	$C_7H_7^-$	$C_7H_5D_2^-$	$C_3H_3O_2^-$	$C_3H_5O^-$	$C_3H_4DO^-$	$C_2H_3O^-$	$C_2H_2DO^-$	HO^-	DO^-
$Ph(CH_2)_3CH_2O^-$	1.9			8.2					0.6		0.1	
$PhCD_2(CH_2)_2CH_2O^-$			1.1		9.0				0.7			0.1
$Ph(CH_2)_3CD_2O^-$		0.4		8.0						0.3	0.1	
$Ph(CH_2)_4CH_2O^-$				5.2		1.3	0.4					
$PhCD_2(CH_2)_3CH_2O^-$					5.5	1.0		0.5				



Scheme 1.

(2)] or by the processes shown in equation (3). Hydrogen transfer from benzylic to phenyl positions has been observed previously.[8]

Only qualitative statements can be made from the experimental data concerning H$^\cdot$ and H_2 loss since the data in Table 1 show (i) some H(D) scrambling may precede fragmentation, and (ii) pronounced deuterium isotope effects are observed for both losses. Since $PhCD_2O^-$ and $C_6D_5CH_2O^-$ both eliminate H$^\cdot$ preferentially, the loss(es) of H$^\cdot$ may be described as shown in equations (4a and b). Whether the product ions of equations (4a and b) equilibrate under the reaction conditions is not known.

Following our work on EtO^- [1] and MeO^-,[3] it seemed that the loss of H_2 from $PhCH_2O^-$ could take one of two courses, *viz.* to form Ph–C̄=O [equation (5)] or $(C_6H_4)^-CHO$ [equation (6)]. It is of interest in this context to note that Nibbering[9] has shown that both HO^- and NH_2^- remove H^+ and D^+ from PhCDO, while in contrast, ion complexes $[Me^-(C_6D_5CHO)]$ specifically decompose by loss of CH_3D.[4] The evidence in Table 1 can be summarised as follows: $PhCD_2O^-$ loses HD but no D_2, $C_6D_5CH_2O^-$ loses HD with a trace of D_2 but we cannot tell in this case whether H_2 is lost (the parent ion also loses D$^\cdot$), and $C_6H_2D_3CD_2O^-$ loses both HD and D_2 but again we do not know whether it loses H_2. Although we are unable to dismiss the possibility that some loss of H_2 occurs as shown in equation (5), we conclude that reaction (6) predominates, and that deprotonation of the phenyl ring by the incipient hydride ion either (i) occurs after scrambling of ring hydrogens, or (ii) can occur from *ortho*-, *meta*-, and *para*-positions. Aryl hydrogen scrambling has been observed previously in the negative mode,[4,8,10] but there are also cases where a loss involving an aryl hydrogen is specific.[11]

We have used *ab initio* calculations to investigate reactions (5) and (6), and the results are summarised in Figure 1. This is a large system for calculation and we have thus only been able to use a medium basis set (3-21G) for reactant, intermediate, and possible products. We have made no attempt to determine saddle points or barrier crests in this system. Even though the results should only be used in a qualitative sense, they are in accord with experiment.

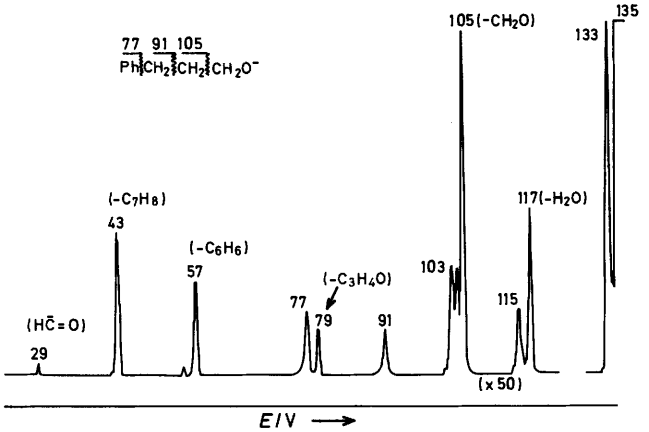
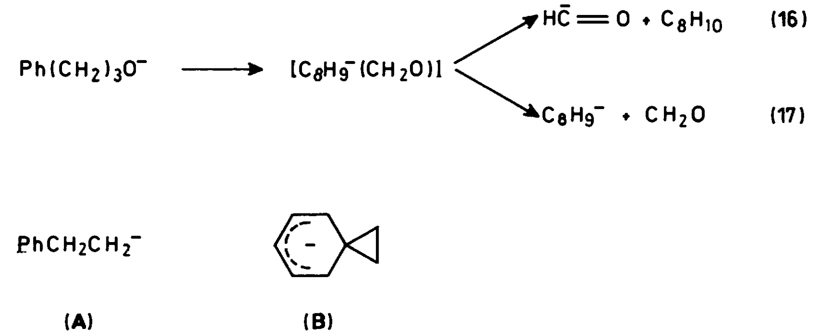


Figure 4. C.a. mass spectrum of $PhCH_2CH_2CH_2O^-$



Scheme 2.

The first step of the reaction involves lengthening of a benzylic C–H bond with initial formation of intermediate A, in which H^- is closer to an *ortho* hydrogen (2.02 Å) than it is to the formyl hydrogen (2.10 Å). Intermediate A can decompose in three ways, *viz.* (i) to H^- plus benzaldehyde; a reaction endothermic by 306 kJ mol⁻¹ (from $PhCH_2O^-$), (ii) by deprotonation of the formyl H to yield B [210 kJ mol⁻¹ endothermic, *cf.* equation (5)],* and (iii) by removal of an *ortho* proton to form C [129 kJ mol⁻¹ endothermic, *cf.* equation (6)]. The *ab initio* calculations suggest that C is the most likely product ion: reaction (6) is that which is observed experimentally.

(B) $PhCH_2CH_2O^-$ *and* $MeCH(PhO)^-$.—The c.a. mass spectra of $PhCH_2CH_2O^-$ and $MeCH(Ph)O^-$ are shown in Figures 2 and 3. Fragmentations are simple and characteristic of alkoxides (*cf.* ref. 4), and the spectra show how useful this method is as an analytical technique. The c.a. mass spectra of the labelled ions $PhCD_2CH_2O^-$ and $PhCH_2CD_2O^-$ are listed in Table 2. The ion $PhCH_2CH_2O^-$ undergoes three competitive fragmentations, losses of H_2, H_2O, and CH_2O. Loss of CH_2O may proceed through an ion complex [equation (7)] or by direct cleavage, while we believe loss of H_2 to be a stepwise process (8). The loss of H_2O is more complex and the labelling studies indicate two processes (9) and (10) with (9) predominating. This is yet another example of a negative ion elimination which is preceded by specific proton transfer.[12]

(C) $PhCH_2CH_2CH_2O^-$.—The fragmentations of $Ph(CH_2)_3O^-$ are the most complex of all the systems considered in this paper. Its c.a. mass spectrum is shown in Figure 4 and the fragmentations of four deuterium-labelled derivatives are recorded in Table 3.

The spectrum shown in Figure 4 is dominated by loss of H_2. The spectra of the labelled compounds (Table 3) suggest that this occurs by the two processes (11) and (12) (Scheme 1) with the former being the more pronounced. By analogy with earlier work, we suggest the reactive intermediate to be a hydride ion complex. Figure 4 shows a peak at *m/z* 79 ($C_6H_7^-$). This product is formed by a specific double H transfer; the first such reaction to be reported for negative ions. The transferred hydrogens come from the 1 and 2 positions, thus we propose that the reaction occurs through the hydride ion complex as shown in equation (13). The loss of water occurs by the two processes (14) and (15), with (14) predominating. Note that we suggest that these processes are initiated by 2- and 3-proton transfer respectively.

Perhaps the most interesting reactions are the loss of formaldehyde and the formation of the formyl anion [equation (16) and (17), respectively]. Two possible structures for the $C_8H_9^-$ ion are (**A**) and the spiro ion (**B**).† Ion (**A**) is the species that would be formed by 'direct' loss of CH_2O. It seems the less likely possibility, but it could be stabilised (to some extent) by negative hyperconjugation.[13]

Finally, there are four processes [suggested mechanisms are shown in equations (18)—(21), Scheme 3] which are preceded or accompanied by partial scrambling of phenyl hydrogens with the hydrogens at position 2. Such scrambling presumably occurs through the equilibria indicated in Scheme 3. We do not know what the structures of intermediates (**C**) and (**D**) are in reactions (18)—(21). Perhaps they are the normal ion complexes [*e.g.* $PhCH_2^-$ (ethylene oxide) for (20), (21)], or perhaps (**D**) corresponds to the Smiles[14] intermediate (**E**) (Scheme 3). We will return to this aspect later.

(D) $Ph(CH_2)_nO^-$ (*n* = 4 *and* 5).—The c.a. mass spectra of these ions and their labelled analogues are recorded in Table 4. There are similarities to the spectra discussed before. The loss of H_2 is principally a 1,2-elimination. Elimination of CH_2O presumably forms spiro ions analogous to (**B**) of Scheme 2. A double H transfer produces $C_7H_9^-$ [*cf.* equation (13), Scheme 1], and transfer of a benzylic hydrogen to O^- is noted [DO^-

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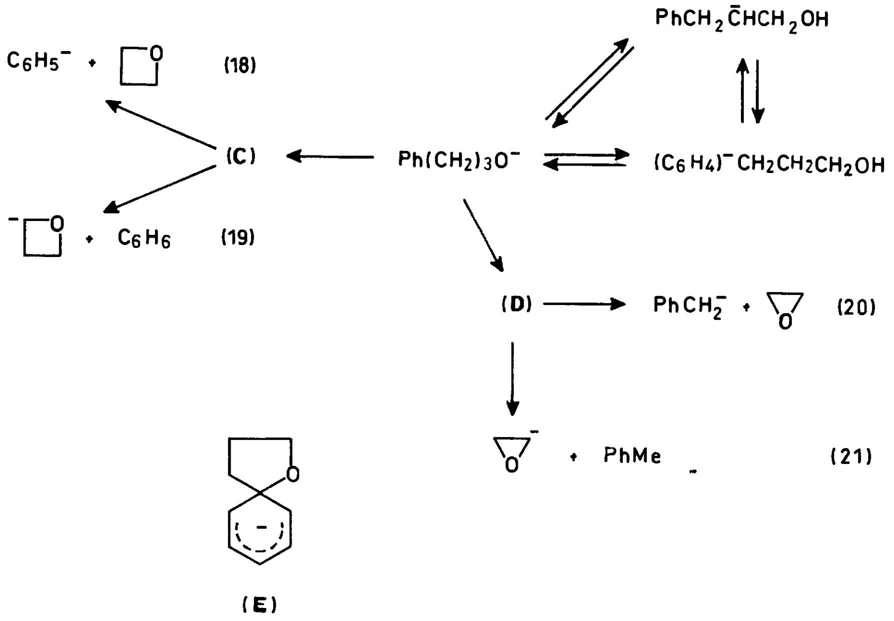
* The *ab initio* calculations show B is a symmetrical species with the charge residing mainly in the *para* position; it does not correspond to the benzoyl anion shown in equation (5)

† We have attempted, without success, to measure the c.a. mass spectrum of $C_8H_9^-$ (and its labelled analogues) by two techniques, *viz.* (i) by forming it in the first collision cell, transmitting the ion through the magnet ($m^* = m_2^2/m_1 = 105^2/135$) and collision-activating it in the second collision cell, (ii) using the m.s./m.s./m.s. capability of the Kratos TA 50 (EBE) spectrometer of the University of Nebraska, Lincoln (through the courtesy of Dr. R. N. Hayes). In neither case was the sensitivity sufficient to measure the desired spectrum.



Scheme 3.

is formed from $PhCD_2(CH_2)_3O^-$]. The most interesting fragmentation is the formation of $PhCH_2^-$. We have seen this product ion in the spectra of all ions $Ph(CH_2)_nO^-$ where n = 2—5; the relative abundances are 100, 0.2, 8, and 5% respectively. All four peaks are Gaussian with widths at half height of 29.5, 31.8, 35.6, and 39.4 ± 0.3 V, respectively. No fine structure is observed for any peak, so there is no evidence for the formation of $PhCH_2^-$ occurring by more than one process in any particular case. $PhCH_2^-$ is formed from $PhCH_2CH_2O^-$ by direct cleavage [equation (7)], but how is it formed in the other cases? In Scheme 3 we have suggested two possibilities. Either it is formed by S_Ni attack of O^- at the carbon β to the phenyl ring [*cf.* equation (20)] or it proceeds through nucleophilic aromatic substitution [*cf.* the Smiles spiro intermediate (E), Scheme 3]. In these cases we cannot differentiate between the two possibilities. We will investigate systems where we can prove (or disprove) the intermediacy of Smiles ions,* and will report our results later.

In conclusion, we define rules for the fragmentation of these alkoxide ions. The rules fall into a number of simple categories.

(i) 'Simple cleavage' forms an ion complex, which may either decompose by loss of the anion [*e.g.* equations (1) and (7)], or by the anion part of the complex effecting a number of reactions including deprotonation [equations (2), (6), (8), (11), (12)], and internal nucleophilic substitution or elimination [equations (13), (18), and (20)].

(ii) Specific proton transfer forms a carbanion which then undergoes 'cleavage' to form an ion complex. The ion complex then fragments as outlined in (i) above [equations (9), (10), (14), and (15)].

(iii) It is likely that certain fragmentations are initiated by internal aromatic nucleophilic substitution reactions [equations (16), (17), (20), and (21)].

(iv) A number of reactions [which fall into categories (i) and (ii) above] occur following partial phenyl–side chain hydrogen scrambling [equations (1)—(3), also Scheme 2]. Presumably these are slow reactions.

Experimental

C.a. mass spectra were recorded on a Vacuum Generators ZAB 2HF mass spectrometer operating in the negative chemical ionization mode.[15] All slits were fully open to obtain maximum sensitivity and to minimise energy-resolution effects.[16] The chemical ionisation slit was used in the ion source; ionising energy 70 eV (tungsten filament); ion source temperature 150 °C; accelerating voltage 8 kV. Alkoxide anions were generated by ^1H (or D) abstraction from the appropriate alcohols by HO^- (or H^- or $O^{-\bullet}$). Reactant negative ions were generated from H_2O using 70 eV electrons.[17] The indicated source pressure of H_2O was 5×10^{-4} Torr. The alcohol pressure (the alcohol was introduced through the septum inlet at 150 °C) was typically 5×10^{-7} Torr. The estimated total pressure within the source is 10^{-1} Torr. The pressure of He in the second collision cell was 2×10^{-7} Torr, measured by an ion gauge situated between the electric sector and the second collision cell. This produced a decrease in the main beam signal of *ca.* 10% and thus corresponds to essentially single-collision conditions.

Ab initio calculations were carried out using GAUSSIAN 82[6] at the 3-21G level. Procedures used have been outlined previously.[7]

Benzyl alcohol, 1-phenylethanol, 2-phenylethanol, 3-phenylpropanol, 4-phenylbutanol, and 5-phenylpentanol were commercial samples.

The Labelled Compounds. [1-^2H]*Benzyl Alcohol.*—Benzaldehyde (0.2 g) in anhydrous diethyl ether (5 ml) was added under nitrogen to a suspension of lithium aluminium deuteride (0.1 g) in anhydrous diethyl ether (7 ml) and the mixture was heated under reflux for 4 h. After cooling to 20 °C, water (0.1 ml), aqueous sodium hydroxide (10%, 0.1 ml), and water (0.3 ml) were added successively. The organic layer was dried (Na_2SO_4), and distillation gave [1-^2H]benzyl alcohol (0.095 g, 48%; $^2H_1$ 99%), b.p. 205—206 °C at 760 mmHg.

[1,1-$^2H_2$]*Benzyl Alcohol.*—Methyl benzoate (0.2 g) in anhydrous diethyl ether (5 ml) was added under nitrogen to a suspension of lithium aluminium deuteride (0.06 g) in

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* As an example, do the spectra of $PhOCH_2CH_2S^-$ and $PhSCH_2CH_2O^-$ both yield PhO^- and PhS^-, and if so can it be proved that the product ions are formed through a common spiro intermediate?

anhydrous diethyl ether (5 ml), and the mixture was heated under reflux for 24 h. Work-up as for [1-$^2H_1$]benzyl alcohol (above) gave [1-$^2H_2$]benzyl alcohol (0.15 g, 95%; $^2H_2$ 99%), b.p. 205—206 °C at 760 mmHg.

[$^2H_5$]Phenylmethanol was made from [$^2H_5$]phenylmagnesium bromide and paraformaldehyde by a reported method,[18] yield 44%, $^2H_5$ 99%.

[1-^{13}C]Benzyl alcohol was made by the reaction between [1-^{13}C]benzaldehyde (^{13}C 91%) and lithium aluminium hydride (see preparation of [1-^2H]benzyl alcohol), yield 52%, ^{13}C 91%.

([2,4,6-$^2H_3$]*Phenyl*)[1,1-$^2H_2$]*methanol*.—[2,4,6-$^2H_3$]benzoic acid (0.1 g; formed from [2,4,6-$^2H_3$]bromobenzene[19] by the Grignard reaction with CO_2) in anhydrous tetrahydrofuran (2 ml) was added to a suspension of lithium aluminium deuteride (0.03 g) in anhydrous tetrahydrofuran (2 ml), and the mixture was heated under reflux for 24 h. Work-up as for [1-^2H]benzyl alcohol gave ([2,4,6-$^2H_3$]phenyl)[1,1-$^2H_2$]methanol (0.08 g, 93%, $^2H_5$ 98%).

2-*Phenyl*[2,2-$^2H_2$]*ethanol*.—Phenylacetic acid (1.0 g), deuterium oxide (5 ml), and sodium deuterioxide (0.3 g) were heated in a sealed tube for 24 h at 120 °C. After cooling the solution was acidified (concentrated hydrochloric acid) and extracted with diethyl ether, dried (Na_2SO_4), the solvent removed, and the exchange procedure repeated to give phenyl[2,2-$^2H_2$]acetic acid ($^2H_2$ 98%). Phenyl[2,2-$^2H_2$]acetic acid (0.9 g) was dissolved in anhydrous tetrahydrofuran (10 ml), added to a suspension of lithium aluminium hydride (0.3 g) in tetrahydrofuran (12 ml), and the mixture was heated under reflux under nitrogen for 16 h. Work-up (as above) gave 2-phenyl[2,2-$^2H_2$]ethanol (0.55 g, 62%; $^2H_2$ 98%), b.p. 215—216 °C at 760 mmHg.

2-*Phenyl*[1,1-$^2H_2$]*ethanol*.—Reduction of phenylacetic acid with lithum aluminium deuteride (as above) gave 2-phenyl[1,1-$^2H_2$]ethanol, yield 70%, $^2H_2$ 99%.

3-([$^2H_5$]*Phenyl*)*propanol*.—To a solution of [$^2H_5$]phenylmagnesium bromide {from [$^2H_5$]bromobenzene (0.1 g)} in anhydrous diethyl ether (8 ml), under nitrogen, was added tetramethylene oxide (0.07 g) in anhydrous diethyl ether (1 ml), and the mixture was heated under reflux for 13 h. Aqueous ammonium chloride (saturated; 10 ml) was added, the organic layer separated, dried (Na_2SO_4), and the solvent removed. Vacuum distillation gave 3-([$^2H_5$]phenyl)propanol, b.p. 132—134 °C at 20 mmHg (0.09 g, 52%; $^2H_5$ 99%).

3-*Phenyl*[3,3-$^2H_2$]*propanol*.—[1,1-$^2H_2$]Benzyl alcohol was converted into [1,1-$^2H_2$]benzyl bromide by a reported procedure[20] in 80% yield. The Grignard reagent from [1,1-$^2H_2$]benzyl bromide was treated with ethylene oxide,[21] to give 3-phenyl[3,3-$^2H_2$]propanol in 36% yield ($^2H_2$ 99%).

3-*Phenyl*[2,2-$^2H_2$]*propanol*.—2-Phenyl[1,1-$^2H_2$]ethanol was converted into the bromide in 53% yield by a standard procedure.[20] The Grignard reagent from 2-phenyl[1,1-$^2H_2$]ethyl bromide was treated with dimethyl carbonate[22] to yield 3-phenyl[2,2-$^2H_2$]propanol in 30% yield ($^2H_2$ 99%).

3-*Phenyl*[1,1-$^2H_2$]*propanol*.—A solution of methyl 2-phenylpropanoate (0.1 g) in anhydrous diethyl ether (5 ml), under nitrogen, was added, at 20 °C, to a stirring suspension of lithium aluminium deuteride (0.05 g) in anhydrous diethyl ether. The mixture was heated under reflux, then work-up as for [1-^2H]benzyl alcohol gave 3-phenyl[1,1-$^2H_2$]propanol (0.08 g, 83%; $^2H_2$ 99%).

4-*Phenyl*[4,4-$^2H_2$]*butanol*.—This compound was produced in a similar manner to 3-phenyl[3,3-$^2H_2$]propanol, except that trimethylene oxide[23] was used instead of ethylene oxide, yield 36%, $^2H_2$ 98%.

4-*Phenyl*[1,1-$^2H_2$]*butanol*.—This was prepared by reduction of methyl 4-phenylbutanoate with lithium aluminium deuteride by the same method as used for the formation of [1,1-$^2H_2$]benzyl alcohol, yield 90%, $^2H_2$ 99%.

5-*Phenyl*[5,5-$^2H_2$]*pentanol*.—This compound was made by the same procedure as used for the preparation of 4-phenyl[4,4-$^2H_2$]butanol, except that phenyl[1,1-$^2H_2$]ethyl bromide was used instead of [1,1-$^2H_2$]benzyl bromide, yield, 30%, $^2H_2$ 98%.

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