Gas-phase Carbanion Rearrangements. Deprotonated Benzyl and Allyl Ethers

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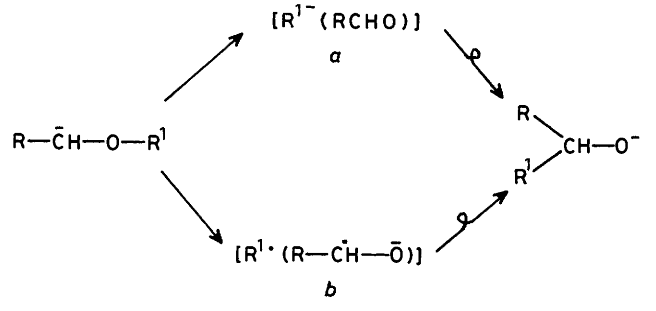
The following systems have been studied: (i) the ion $PhO\bar{C}Ph_2$ on collisional activation undergoes Wittig rearrangement to Ph_3CO^- before fragmentation; (ii) $PhO\bar{C}HCH{=}CH_2$ undergoes competing rearrangements, *viz.* Wittig rearrangement to $Ph(CH_2{=}CH)CHO^-$ and anionic Claisen rearrangement to (HO) deprotonated *o*-allylphenol, with the former reaction predominating; (iii) deprotonation of dibenzyl ether yields an unstable species which forms $PhCH_2^-$: no Wittig rearrangement is observed in the gas phase although it occurs in the condensed phase; and (iv) $PhCH_2OCH_2CH{=}CH_2$ deprotonates to form the two interconvertible anions $Ph\bar{C}HOCH_2CH{=}CH_2$ and $PhCH_2O\bar{C}HCH{=}CH_2$ of which the former is the more stable. Both ions give minor Wittig products, but the major process is loss of H_2O to form a deprotonated dihydronaphthalene. There is some analogy between gas-phase and condensed-phase reactions in this system. The condensed-phase reaction of allyl benzyl ether under forcing conditions (lithium di-isopropylamide/tetrahydrofuran–hexamethylphosphoramide) gives the products 1-phenylbut-3-en-1-ol, 1,2-dihydronaphthalene, and 1-(*o*-tolyl)prop-2-en-1-ol in the approximate ratio 4:3:1.

The Wittig rearrangement [1–3] can, in principle, involve either of the intermediates *a* or *b* shown in Scheme 1. In the condensed phase, aldehydes are often by-products of the reaction [4,5] and the migratory aptitude of substituents R^1 is allyl ≃ benzyl > methyl > ethyl > phenyl.[4,5] Since the migratory aptitude is in the order of free-radical stabilities,[6,7] it has been suggested [8] that the radical pair mechanism is the more likely.

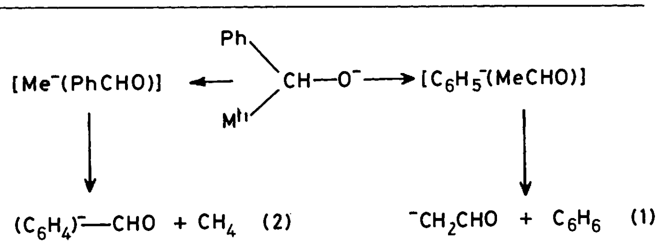


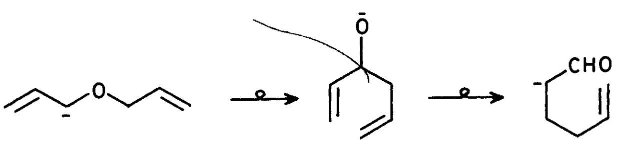
Scheme 1. $R = C_6H_5$ or $CH_2{=}CH–$, R^1 = allyl, benzyl, alkyl, or aryl

The collisional activation mass spectra of ions $Ph\bar{C}HOR$ and $Ph(R)CHO^-$ (R = alkyl and phenyl) are similar, suggesting that the Wittig rearrangement also occurs in the gas phase.[9] Major fragmentations are best interpreted in terms of the Wittig product ion. For example, $Ph\bar{C}HOMe$ is converted into $Ph(Me)CHO^-$ and the decompositions of this ion are rationalised as shown in equations (1) and (2), with the latter process involving prior scrambling of phenyl hydrogens. When R^1 is an alkyl group > Me, there is some doubt that *a* can be an intermediate [10] since the electron affinity of $R^1 \leqslant 0$.[11] When R^1 is alkyl, the collisional activation spectrum of $Ph\bar{C}HOR^1$ always shows pronounced loss of $R^{1\bullet}$, perhaps *via* the intermediacy of *b*.[9]

Finally, in the condensed phase, treatment of diallyl ether with $KNH_2–NH_3$ gives 1-vinylbut-3-en-1-ol by a Wittig rearrangement,[12,13] and on heating, this alcohol yields hex-5-en-1-al *via* an oxy-Cope rearrangement.[14] Analogous reactions occur in the gas phase. Collisional activation of *c* produces *e*, which is formed by 1,2- and 1,4-Wittig rearrangements (to *d*) followed by oxy-Cope rearrangement to *e*.[15]

In the present paper we extend our study of the gas-phase Wittig rearrangement to four new systems including (i) $PhO\bar{C}H–CH{=}CH_2$, which we expected to undergo both Wittig and anionic Claisen rearrangement, and (ii) allyl benzyl ether, a system which can, in principle, form two initial carbanions, $Ph\bar{C}HOCH_2CH{=}CH_2$ and $PhCH_2O\bar{C}H–CH{=}CH_2$.





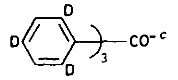
c *d* *e*

Results and Discussion

Collisional activation mass spectra are either illustrated in Figures 1—3 or listed in Tables 1, 2, 4, and 5. Charge reversal (positive ion) mass spectra of negative ions [16] are recorded in Tables 3 and 6.

(A) *Phenyl (Diphenylmethyl) Ether.*—Let us consider, first, decompositions of the ion $PhO\bar{C}Ph_2$. We chose this system for two reasons: *viz.* (i) the Wittig rearrangement in this case requires phenyl migration to a sterically hindered carbanion site (this is a reaction which occurs in the condensed phase [17]); and (ii) the Wittig product ion Ph_3CO^- should itself show interesting fragmentations. The collision activation (c.a.) mass spectra of $PhO\bar{C}Ph_2$ and Ph_3CO^- (and labelled analogues) are recorded in Table 1. Apart from the formation of a peak of small abundance in the spectrum of $PhO\bar{C}Ph_2$ corresponding to PhO^-, the spectra of $PhO\bar{C}Ph_2$ and Ph_3CO^- are very similar and suggest almost complete fragmentation through the Wittig ion. Fragmentations are summarised in Scheme 2.

Table 1. C.a. mass spectra of $PhO\bar{C}Ph_2$, Ph_3CO^-, and labelled analogues

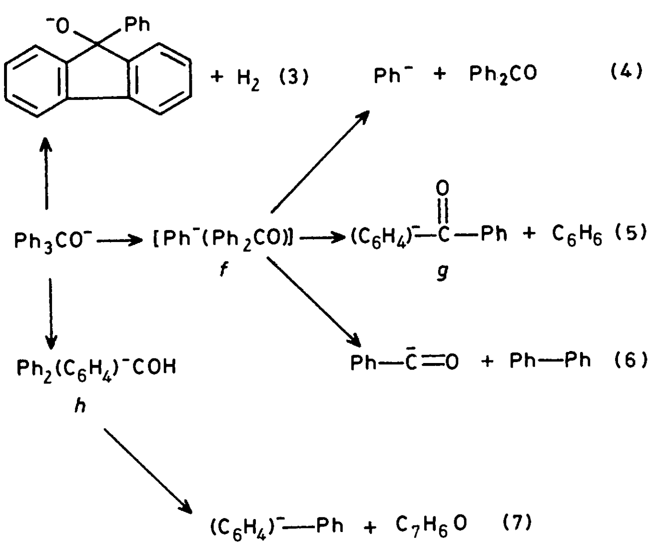
Parent ion	Loss																						
	$H^\cdot$	$D^\cdot$	H_2	HD	C_6H_6	C_6H_5-D	C_6H_3-D_3	C_6H_2-D_4	C_6D_5-H	C_7H_6-O	$C_6{}^{13}C$-H_6O	C_7H_5-DO	C_7H_3-D_3O	C_7H_2-D_4O	C_7H-D_5O	C_{12}-H_{10}	$C_{12}H_5$-D_5	$C_{12}H_4$-D_6	C_{13}-H_{10}	Ph_2-CO	Ph_2-^{13}CO	$Ph(C_6H_5)$-CO	$(C_6H_2D_3)_2$-CO
$PhO\bar{C}Ph_2$ [a]	100		22		55					5						2			3	12			
Ph_3CO^- [b]	100		24		57					5						2				13			
$Ph_3{}^{13}CO^-$	100		23		55						4					2					12		
$Ph_2(C_6D_5)CO^-$ [c]	100	48[d]	48[d]	15	20	14			20	2.1		1.3			3.0	1	1			3		8	
 [c]	100	39[d]	39[d]	8			23	30					1	3				2					10

[a] Formed by deprotonation of $PhOCHPh_2$. [b] Formed by deprotonation of Ph_3COH. [c] The c.a. mass spectra of the deuterium-labelled derivatives showed composite peaks for the various losses of C_6H_6, C_7H_6O, $C_{12}H_{10}$, $(C_6H_5)_2CO$, and labelled analogues. The ratios listed here were determined using the linked-scan (E/B) technique for ions decomposing in the first collision cell. [d] $D^\cdot$ and H_2 = 2 a.m.u.

Table 2. C.a. mass spectra of $C_6D_5O\bar{C}H$-$CH{=}CH_2$ and $Ph(CH_2{=}CH)CHO^-$ (and labelled derivatives)

Initial ion	Loss																	
	H_2	HD	H_2O	HOD	$C_2H_3^\cdot$	CO	CH_2O	CHDO	C_3H_4	C_3H_4O	C_3H_3DO	C_6H_6	C_6H_5D	$C_6H_2D_4$	C_6HD_5	PhCHO	PhCDO	C_6D_5CHO
$C_6D_5O\bar{C}HCH{=}CH_2$	66	100	7	8	2	2	3	2	1	9	3			2	6			0.1
$Ph(CH_2{=}CH)CHO^-$ [a]	100		10			4	4			21		10				0.1		
$C_6D_5(CH_2{=}CH)CHO^-$	83	100	9	9		4	5	3		32	3			1	13			0.2
$Ph(CH_2{=}CH)CDO^-$	100	93	28	4		10	4	5			38	19					0.3	
$Ph(CH_2{=}CD)CHO^-$	100	67		18		8	5	5			36		18			0.05		

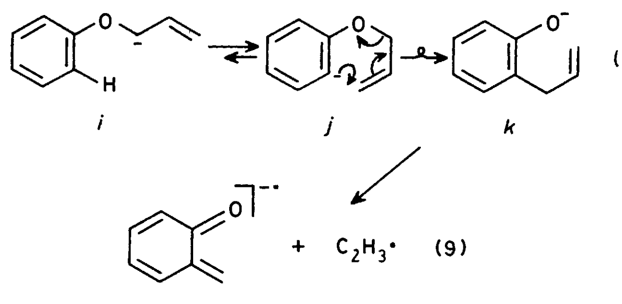
[a] Peak widths at half height [*m/z* (V ± 0.2) loss]: 55 (34.5) C_6H_6, 77 (39.4) C_3H_4O, 103 (45.2) CH_2O, 105 (53.9) C_2H_4, 115 (51.5) H_2O, and 131 (56.5) H_2. When a voltage of +1 000 V is applied to the collision cell the following collision-induced:unimolecular ratios are obtained: *m/z* (c:u) 55 (30:70), 77 (80:20), 103 (50:50), 105 (70:30), 115 (10:90), and 131 (70:30).



Scheme 2.

The major fragmentation involves loss of a phenyl hydrogen. Whether this H$^•$ is lost randomly from the ring or whether it originates from a specific position following H randomisation cannot be determined from available data. Aryl hydrogen scrambling has been noted previously for negative ions,[9,18,19] but there are also cases where a loss involving an aryl hydrogen is specific.[20–22] Loss of H_2 also occurs with H scrambling within each phenyl ring. There is also a pronounced isotope effect, *i.e.* no D_2 is lost from $(C_6H_2D_3)_3CO^-$ (see Table 1). We suggest the overall mechanism shown in equation (3). The majority of other fragmentations may be explained in terms of decomposition of ion complex *f* [equations (4)—(6)]. The formation of *g* [equation (5)] occurs with some phenyl H scrambling, but deprotonation occurs principally from *ortho* positions with an isotope effect H:D of 1.4. The product ion of equation (6) is shown as the benzoyl anion, but conversion of this ion into the more stable $(C_6H_4)^-CHO$ species cannot be excluded.[9,23] Finally, formation of $C_{12}H_9^-$ is rationalised as shown in equation (7). *ortho* H transfer (minor H scrambling is noted) plausibly produces *h* which fragments to products.

(B) *Allyl Phenyl Ether*.—The c.a. mass spectrum of deprotonated allyl phenyl ether is shown in Figure 1 while those of $C_6D_5O\bar{C}HCH{=}CH_2$, $Ph(CH_2{=}CH)CHO^-$, and its labelled derivatives are recorded in Table 2. We were interested in this system because here it is possible that an anionic Claisen rearrangement[24] could complete with the Wittig rearrangement. Specific proton-transfer reactions (as a prelude to fragmentation) are features of a variety of characteristic negative ion reactions,[19,25] and we wished to determine whether the Claisen rearrangement shown in equation (8) operates in this case.



Scheme 3.

Table 3. Charge reversal (positive ion) mass spectra of $Ph\bar{O}CH{-}CH{=}CH_2$ and $Ph(CH_2{=}CH)CHO^-$

m/*z* [% ion from $Ph\bar{O}CHCH{=}CH_2$, % ion from $Ph(CH_2{=}CH)CHO^-$]

132 (2, 2),	131 (12, 11),
115 (19, 18),	105 (52, 54),
103 (27, 25),	91 (14, 13),
89 (18, 18),	77 (100, 100),
75 (20, 21),	65 (12, 10),
63 (31, 28),	55 (16, 18),
51 (66, 66),	50 (55, 53),
39 (26, 24),	37 (15, 15),
29 (6, 7), and	27 (21, 20)

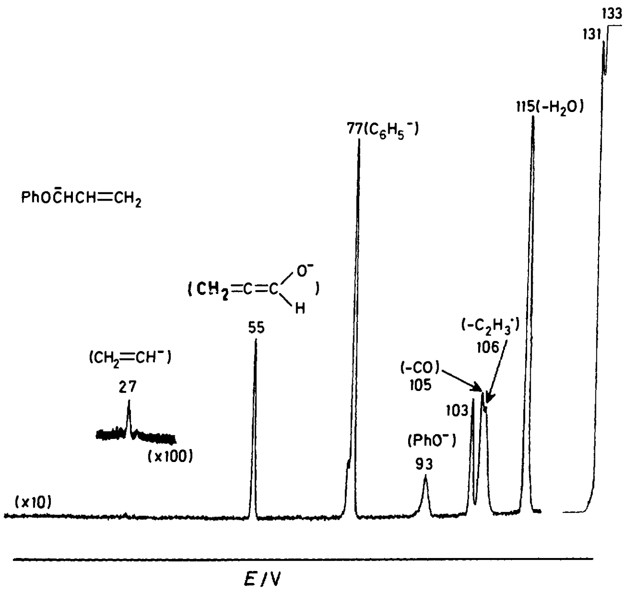
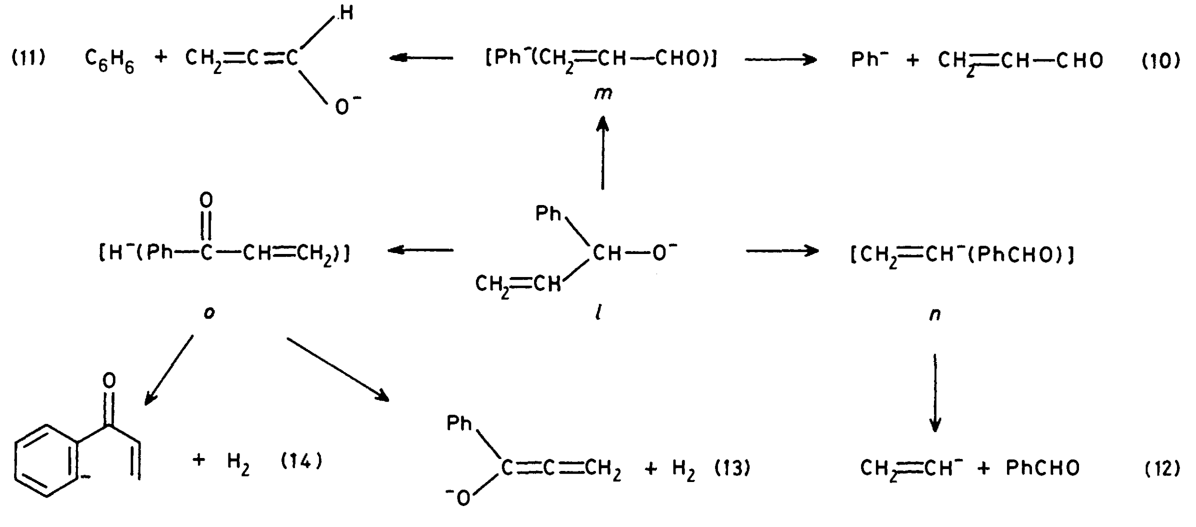


Figure 1. Collision activation mass spectrum of $Ph\bar{O}CHCH{=}CH_2$. For experimental conditions see Experimental section. Peak widths at half-height [*m*/*z* (V ± 0.2)]: 55 (35.7), 77 (39.1), 103 (44.8), 105 and 106 (not resolved), 115 (51.1), and 131 (56.0). When a voltage of +1 000 V is applied to the second collision cell, the following collision-induced:unimolecular ratios are obtained [*m*/*z* (collision-induced:unimolecular)]: 55 (40:60), 77 (70:30), 93 (95:5), 103 (50:50), 105 (80:20), 106 (100:0), 115 (10:90), 131 (65:35)

Comparison of the spectra (Figure 1, Table 2) of $Ph\bar{O}CHCH{=}CH_2$ and $Ph(CH_2{=}CH)CHO^-$ shows that the Wittig rearrangement, which will be described later, is the predominant rearrangement. However there are two peaks in Figure 1 which do not appear in the other spectrum. The first, *m*/*z* 93, corresponds to PhO^-, a cleavage product of the deprotonated ether. The second, *m*/*z* 106, is formed by loss of $C_2H_3^•$, a process which cannot occur directly from $Ph\bar{O}CHCH{=}CH_2$. Thus we prepared *k* [see equation (8)] by deprotonation of *o*-allylphenol and its c.a. mass spectrum shows only one fragmentation, pronounced loss of $C_2H_3^•$ [see equation (9)]. We propose that *m*/*z* 106 is formed through *k*. This minor process is energetically unfavourable (it is totally collision induced—see caption to Figure 1), in comparison with the Wittig rearrangement which has an appreciable unimolecular component.

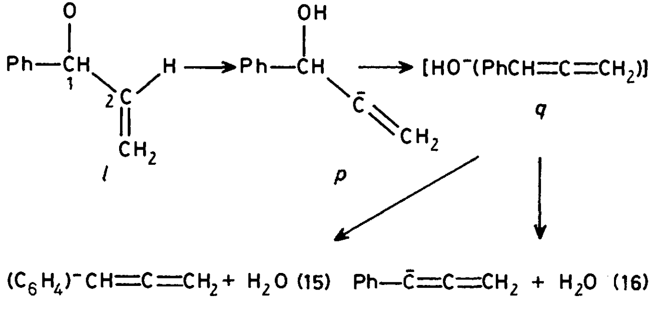
Consideration of the spectra in Figure 1 and Table 2 indicates that other product peaks in the spectrum of $Ph\bar{O}CH{\cdot}CH{=}CH_2$ are formed through Wittig ion *l* (Scheme 4). In particular, the widths of the peaks at half height are (within experimental error) the same in the spectra of $Ph\bar{O}CH{-}CH{=}CH_2$ and



Scheme 4.

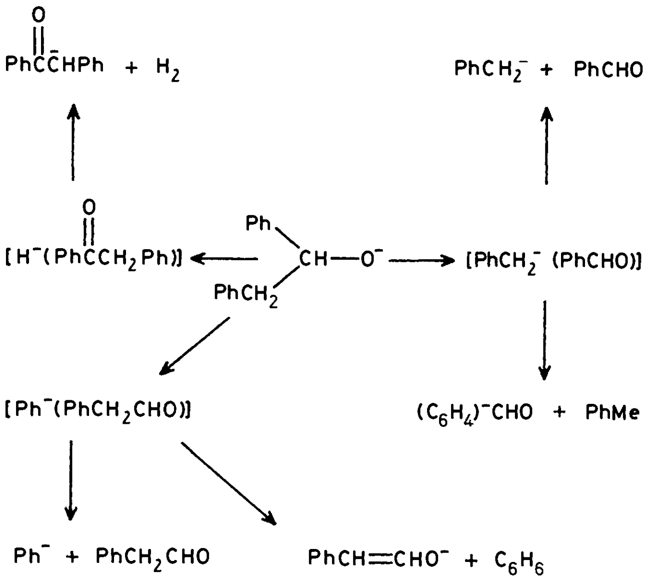
Ph(CH$_2$=CH)CHO$^-$. Most fragmentations follow normal trends.[9] We suggest that ion *l* (Scheme 4) fragments primarily *via* ion complexes *m*—*o*: labelling studies show that *m* fragments as summarised in equations (10) and (11), *n* as in equation (12). Fragmentation through the hydride ion complex *o* is of interest, since there are two specific losses of H_2. These are shown in equations (13) and (14), respectively. Ring deprotonation [equation (14)] is the favoured process; however, the likelihood of the operation of deuterium isotope effects for *both* processes allows only qualitative comparison to be made. The losses of CO and CH_2O shown in Figure 1 are exactly analogous to those described earlier for the diphenylmethoxide anion.[9]

Pronounced loss of H_2O from an alkoxide ion is most unusual.[9,26] In the present case loss of H_2O from *l* (Scheme 5) involves exclusive elimination of 2-H, with the second hydrogen coming mainly from the phenyl ring but partially from C-1. Thus there are two specific losses of water: both involve initial proton transfer $l \longrightarrow p$ (Scheme 5) followed by formation of ion complex *q* from which HO$^-$ mainly deprotonates the phenyl ring [equation (15)] with the minor process being loss of an allenic proton [equation (16)].



Scheme 5.

(C) *Dibenzyl Ether.*—Dibenzyl ether undergoes a Wittig rearrangement in the condensed phase,[4] but in the gas phase it forms no stable deprotonated form, and no Wittig rearrangement is noted. Reaction of dibenzyl ether with HO$^-$ gives only PhCH$_2^-$ formed presumably by dissociation of unstable $PhCH_2O\bar{C}HPh$. We have investigated the decompositions of the Wittig product Ph(PhCH$_2$)CHO$^-$ and its labelled species and since its fragmentations are of interest we summarise them in Scheme 6. Spectra are listed in Table 4.



Scheme 6.

(D) *The Gas-phase Rearrangements of Deprotonated Allyl Benzyl Ether.*—Allyl benzyl ether is the most complex system we have studied in this series. Not only can it form two deprotonated forms but the c.a. mass spectra indicate complex competing rearrangements.

The c.a. mass spectra of deprotonated allyl benzyl ether and of the two possible Wittig product ions Ph(CH$_2$=CH–CH$_2$)-CHO$^-$ and PhCH$_2$(CH$_2$=CH)CHO$^-$ are listed in Table 5. The allyl benzyl ether spectrum is dominated by loss of water, *a process not in this case proceeding* via *a Wittig rearrangement.* Other fragmentations are minor and may be rationalised in terms of the characteristic decomposition of the two product Wittig ions (see Table 2), although the relative abundances of peaks in the spectra do not correlate as well as those of the previous examples we have considered.

When PhCD$_2$OCH$_2$CH=CH$_2$ is allowed to react with DO$^-$, $(M - D^+)^-$ and $(M - H^+)^-$ ions are formed in the ratio 5:1; the c.a. mass spectra of these ions are reproduced in Figures 2 and 3. Consider first Figure 2. Apart from the various losses of H_2O (which we will consider later), other peaks are those expected from Wittig rearrangement ion Ph(CH$_2$=CH–CH$_2$)-CDO$^-$ (*cf.* Table 5). One ion, *m*/*z* 92 (PhCHD$^-$) can only be

Table 4. C.a. mass spectra of $Ph(PhCH_2)CHO^-$ and labelled analogues

Initial ion	Loss												
	H_2	HD	C_6H_6	C_6H_5D	C_7H_8	$C_7H_6D_2$	C_7HD_7	PhCHO	$Ph^{13}CHO$	$PhCH_2CHO$	$PhCH_2{}^{13}CHO$	$PhCD_2CHO$	$C_6D_5CD_2CHO$
$Ph(PhCH_2)CHO^-$	46		9		16			100		0.5			
$Ph(PhCH_2)^{13}CHO^-$	44		8		15				100		0.6		
$Ph(PhCD_2)CHO^-$		21		3		12		100				0.1	
$Ph(C_6D_5CD_2)CHO^-$		20		4			13	100					0.1

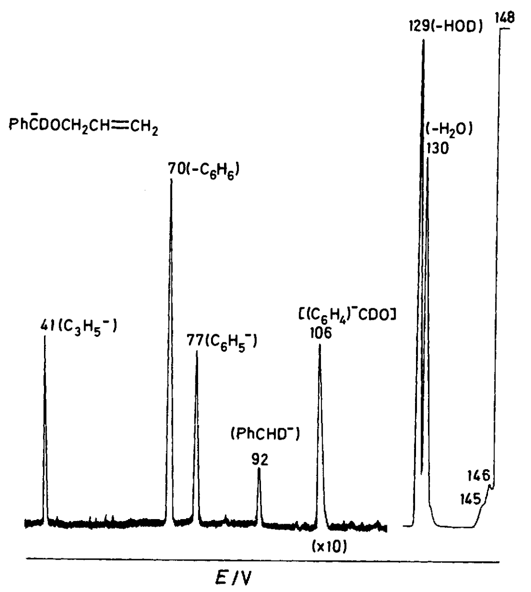


Figure 2. Collision activation mass spectrum of $\mathrm{Ph\bar{C}DOCH_2CH{=}CH_2}$

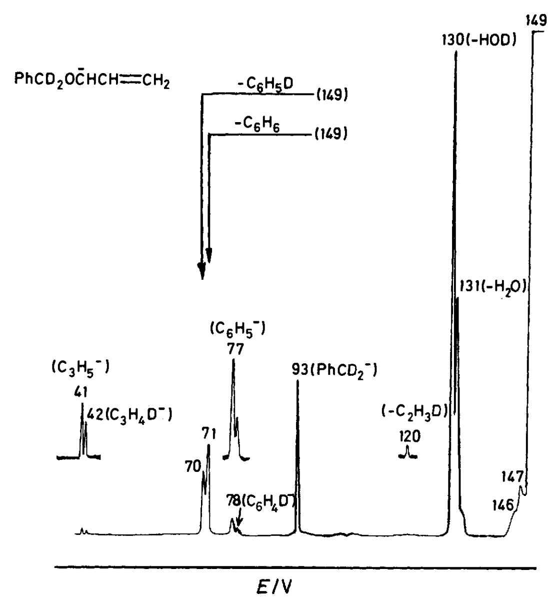
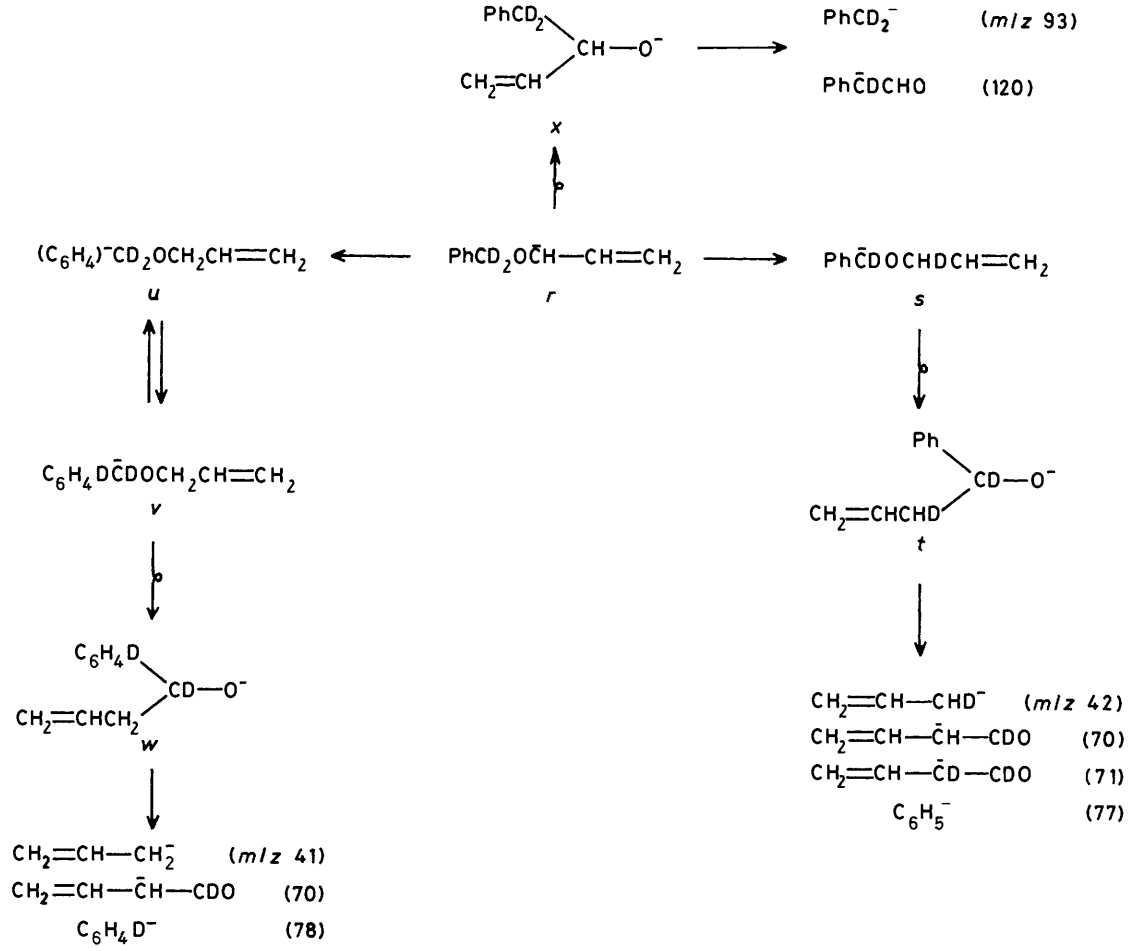


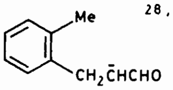
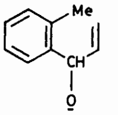
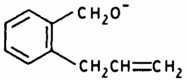
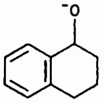
Figure 3. Collision activation mass spectrum of $\mathrm{PhCD_2O\bar{C}HCH{=}CH_2}$



Scheme 7.

produced following the proton transfer $\mathrm{Ph\bar{C}DOCH_2CH{=}CH_2} \longrightarrow \mathrm{PhCHDO\bar{C}HCH{=}CH_2}$, but since the peak is so small, the proton transfer must be a very minor process. In marked contrast, Figure 3 shows that $\mathrm{PhCD_2O\bar{C}HCH{=}CH_2}$ undergoes several proton–deuterium transfers prior to fragmentation. The peaks at *m*/*z* 42, 70, 71, and 77 are formed by characteristic fragmentations of the Wittig ion *t* (Scheme 7, *cf.* Table 5) following the deuterium transfer *r* ⟶ *s* (Scheme 7), whereas *m*/*z* 41 and 78 plausibly originate from Wittig ion *w*

Table 5. C.a. mass spectra of deprotonated allyl benzyl ether and various isomeric $C_{10}H_{11}O^-$ ions

	Loss												
Initial ion	$H^{\cdot}$	H_2	CH_4	H_2O	C_2H_4	CH_2O	C_3H_6	C_3H_4O	C_4H_6O	C_6H_6	C_7H_8	C_8H_8	PhCHO
$(PhCH_2OCH_2CH{=}CH_2{-}H^+)^{-a}$	3	7		100			1	2	2	19			4
$Ph(CH_2{=}CHCH_2)CHO^{-b}$	11	18		15			24		1	4			100
$PhCH_2(CH_2{=}CH)CHO^{-c,d}$	18	4		2	1			100			0.2		
$PhCH_2CH_2\bar{C}HCHO$								100					
 [28,29]	16	52	14	100			8	31				12	
 [28,29]	11	89	6	35	9			100			25		
	9	35	12	16	36	100		21					
	13	100		19									

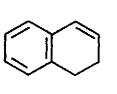
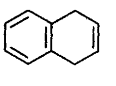
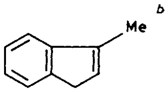
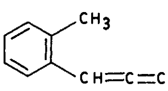
[a] Voltages of half height: [m/z (V ± 0.2) loss]: 145 (37.9) H_2, 129 (23.7) H_2O, 105 (42.6) C_3H_6, 91 (26.6) C_3H_4O, 77 (39.1) C_4H_6O, 69 (33.6) C_6H_6, 41 (21.7) PhCHO. When a voltage of +1 000 V is applied to the collision cell the following collision-induced:unimolecular ratio is observed [m/z (c:u)]: 145 (20:80), 129 (10:90), 105 (90:10), 91 (50:50), 77 (70:30), 69 (30:70), and 41 (10:90). [b] Voltages at half height [m/z (V ± 0.2) loss]: 145 (37.7) H_2, 129 (21.5) H_2O, 105 (42.7) C_3H_6, 77 (39.0) C_4H_6O, 69 (33.8) C_6H_6, 41 (21.8) PhCHO. When a voltage of +1 000 V is applied to the collision cell the following collision-induced:unimolecular ratio is observed [m/z (c:u)]: 145 (5:95), 129 (30:70), 105 (85:15), 77 (80:20), 69 (65:35), and 41 (10:90). [c] Voltages at half height [m/z (V ± 0.2) loss]: 145 (37.8) H_2, 129 (20.1) H_2O, 119 (45.5) C_2H_4, 91 (26.4) C_3H_4O, 55 (20.3) PhMe. When a voltage of +1 000 V is applied to the collision cell the following collision-induced:unimolecular ratio is observed [m/z (c:u)]: 145 (10:90), 129 (30:70), 119 (90:10), 91 (45:55), and 55 (10:90). [d] The c.a. mass spectrum of $PhCH_2(CH_2{=}CH)CDO^-$ is as follows [loss (abundance)]: $H^{\cdot}$ (6), $D^{\cdot}$ + H_2 (12), HD (2), H_2O (1.5), HOD (0.5), C_2H_4 (1), C_3H_3DO (100), and C_7H_8 (0.3).

formed after phenyl to allyl H^+ transfer ($r \longrightarrow u$), then benzyl to phenyl D^+ transfer ($v \longrightarrow w$). *Thus the allyl carbanion* r *is unstable with respect to the benzyl carbanion* (e.g. s) *under the reaction conditions.* Since the peaks at m/z 93 ($PhCD_2^-$) and 120 ($Ph\bar{C}DCHO$) show no counterparts at m/z 92 or 119, the normal Wittig rearrangement ($r \longrightarrow x$) of the allylic carbanion r (*cf.* Table 5) also occurs.

The major fragmentations of $Ph\bar{C}HOCH_2CH{=}CH_2$ and $PhCH_2O\bar{C}HCH{=}CH_2$ are losses of water. Comparison of Figures 2 and 3 show the major loss (perhaps even exclusive loss) proceeds through the benzylic carbanion. In our experience, loss of water of this magnitude originates either from a solvated ion $[R^-(H_2O)]$[27] or a cyclic species where loss of water effects increased conjugation (see earlier for $PhO\bar{C}HCH{=}CH_2$, also ref. 24). In Table 5 are listed the c.a. mass spectra of a number of deprotonated species which we believed could conceivably arise by rearrangement of deprotonated allyl benzyl ether. This list is without prejudice to the condensed-phase experiments described later. Comparison of these spectra with those of the deprotonated forms of allyl benzyl ether (Table 5, Figures 2 and 3) show that *none can be the precursor ion for loss of water.* Yet we must be careful here since the anion eliminating water may not necessarily correspond to the species formed by direct deprotonation of the neutral. For example deprotonation of *o*-allyl benzyl alcohol removes the acidic OH proton whereas the decomposing (or rearranging) species could perhaps be the allylic carbanion.

The c.a. and charge reversal[16] mass spectra of unknown $C_{10}H_9^-$ may give an insight into the structure of this ion provided the ions formed in the source and collision cell have the same structure. This seems very likely since the loss of water observed in the c.a. mass spectrum of allyl benzyl ether is almost exclusively unimolecular in origin (see footnote *a*, Table 5). Unfortunately, the c.a. mass spectrum of $C_{10}H_9^-$ shows only loss of H_2, a fragmentation which provides little structural information. The charge reversal mass spectrum of $C_{10}H_9^-$ is recorded in Table 6 together with those of deprotonated 1,2- and

Table 6. Charge reversal (positive ion) mass spectra of the $C_{10}H_9^-$ ion from deprotonated allyl benzyl ether and various $C_{10}H_9^-$ isomers [relative abundance (%)]

	m/z																				
Deprotonated form of	129	128	127	126	115	114	113	103	99	89	87	77	74	63	51	50	43	41	39	29	27
$PhCH_2OCH_2CH{=}CH_2$ [a]	54	100	33	2	17		8	35	4	20	11	37	25	34	40	36	3	6	20	2	6
 [a]	48	100	35	3	19		8	35	5	21	14	26	29	40	32	33	1	6	18	2	4
 [a]	46	100	37	4	20		9	27	5	18	13	21	25	38	25	27	1	4	16	1	5
 [b]	36	100	39	25	10	15	9	14	2	7	10	12	18	21	14	16			16		7
 [a]	42	100	51	18	14	13	8	16	2	11	13	18	24	34	32	33			16		3
$PhCH_2CH{=}C{=}CH_2$ [a]	20	100	46	16	8	8	6	16	2	11	7	21	18	26	25	24	11	29	24	14	12

[a] The c.a. mass spectrum shows only loss of H' and H_2. [b] The c.a. mass spectrum is as follows [m/z (abundance) loss]: 128 (100) H', 127 (10) H_2, 114 (0.05) Me', and 113 (0.1) CH_4.

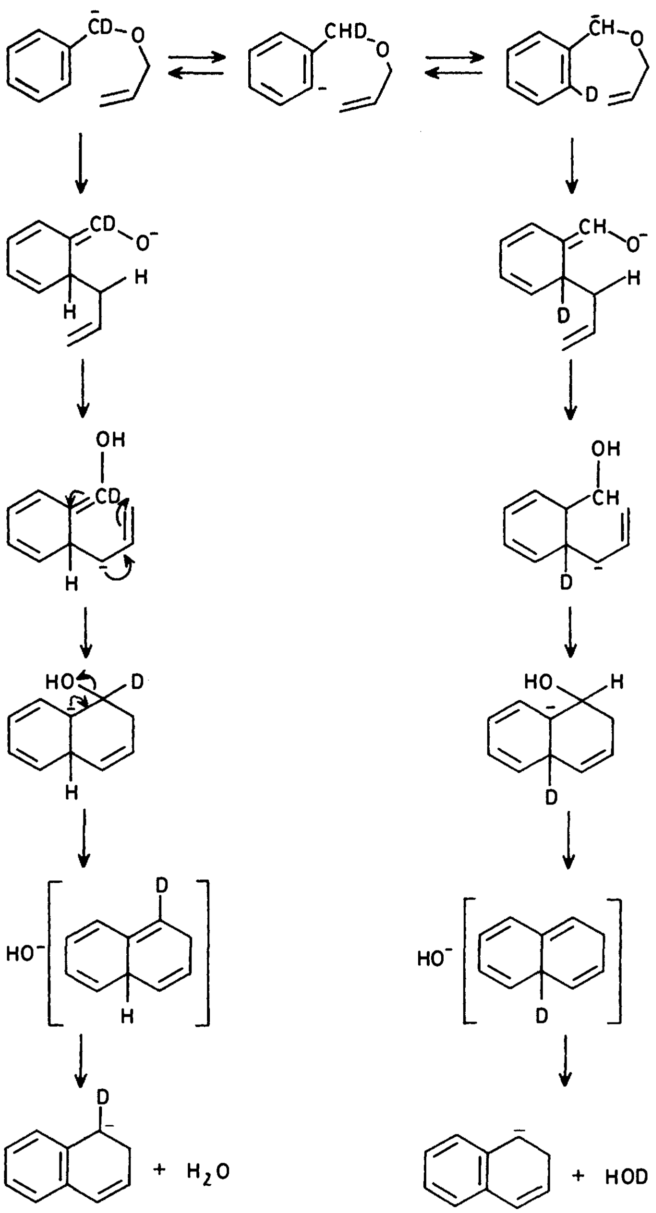
1,4-dihydronaphthalene and related systems. *The spectrum of the unknown is very similar to that of a deprotonated dihydronaphthalene: we suggest the product ion has such a structure.* The immediate precursor to such a species would be similar to a ring-deprotonated hydroxytetralin. The OH-deprotonated hydroxytetralin shown in Table 5 eliminates dihydrogen like an alkoxide;[30] loss of water (which requires proton transfer to oxygen) is less pronounced. A better analogy is afforded by the c.a. mass spectrum of deprotonated 1-methoxytetralin; this shows exclusive and pronounced elimination of methanol.

Taking collectively the above data, together with the fact that losses of both H_2O and HOD are observed in Figures 2 and 3, leads us to propose the mechanistic pathways shown in Scheme 8. The losses of H_2O and HOD demand benzylic–phenyl H–D transfer (*cf.* also Scheme 7): this is followed by the cyclisations and water eliminations as shown.

(E) *The Condensed-phase Rearrangements of Deprotonated Allyl Benzyl Ether.*—There are two reports of the reaction of allyl benzyl ether with strong base. These are summarised in Scheme 9. Reaction with KNH_2–NH_3[31] or Bu^tOK–DMSO[32] causes initial isomerisation of the double bond in poor yield, more forcing conditions[31] causes Wittig rearrangement of the isomerised compound. These results show little analogy with the gas-phase reactions described above. In particular, there is no report of the formation of a $C_{10}H_{10}$ hydrocarbon. This has led us to investigate the solution rearrangements of allyl benzyl ether under more forcing conditions, *i.e.* with lithium di-isopropylamide/tetrahydrofuran–hexamethylphosphoramide (LDA/THF–HMPA). Results are summarised in Scheme 9. Three products were isolated, and their structures were confirmed by g.c.–m.s., i.r. and ^1H n.m.r. The products, 1-phenylbut-3-en-1-ol (**1**), 1,2-dihydronaphthalene (**2**), and 1-*o*-tolylprop-2-en-1-ol (**3**) were formed in the approximate ratio 4:3:1.

The variety of products formed in the various solution reactions is interesting. In our system, Wittig species (**1**) is the major product and it is formed to the exclusion of the alternative product [*i.e.* $PhCH_2(CH_2{=}CH)CHOH$]. In the gas-phase reaction *both* Wittig product ions are detected (by their decompositions), but they are formed in small yield. 1,2-Dihydronaphthalene is a major product; if 1,4-dihydronaphthalene were formed it would certainly isomerise to 1,2-dihydronaphthalene under the reaction conditions. We have shown that a dihydronaphthalene ion is the major product in the gas-phase reaction, and we have proposed its mode of formation (Scheme 8). The alcohol (**3**) is a minor product; such rearrangements accompanied by alkyl group migration have been observed before.[28,29] Deprotonated (**3**) is not formed in the gas-phase reaction (see Table 5 for a comparison of the two spectra).

In conclusion, we have described four quite different ether systems: *viz.* (i) $PhO\bar{C}Ph_2$, which undergoes an exclusive Wittig rearrangement; (ii) $PhO\bar{C}HCH{=}CH_2$, which undergoes competing Wittig and anionic Claisen rearrangements; (iii) $PhCH_2$-$O\bar{C}HPh$, which surprisingly undergoes only simple cleavage to $PhCH_2^-$ in the gas phase; and (iv) $PhCH_2OCH_2CH{=}CH_2$, which forms two initial deprotonated forms which may interconvert, undergo other proton transfers, and minor Wittig rearrangement. The major rearrangement involves complex cyclisations followed by water loss to yield a deprotonated dihydronaphthalene.



Scheme 8.

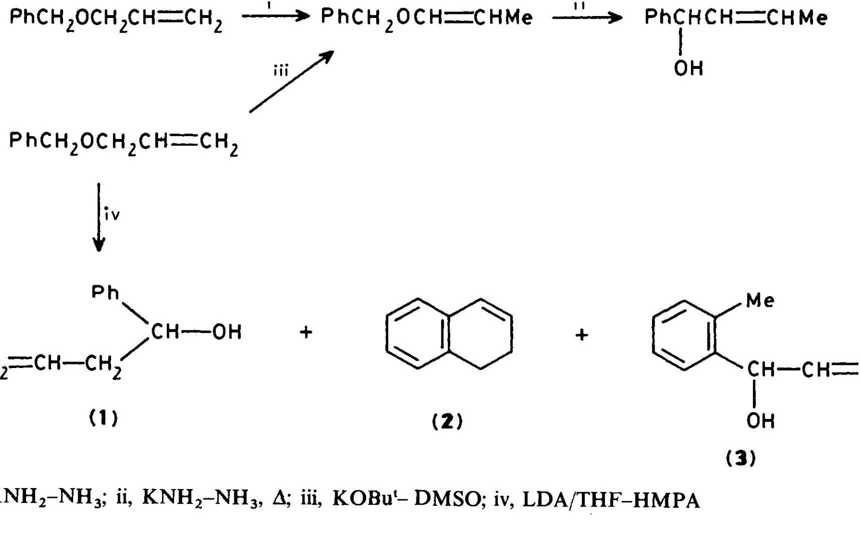
Experimental

C.a. mass spectra and charge reversal mass spectra[16] were recorded on Vacuum Generators ZAB-2HF mass spectrometer operating in the negative chemical ionisation mode.[33] All slits were fully open to obtain maximum sensitivity and to minimise energy-resolution effects. 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. Liquids were introduced through the septum inlet at 100 °C; solids through the direct probe at between 50 and 100 °C. Carbanions were generated by H^+ abstraction by HO^- (or H^- or $O^{-\bullet}$) or D^+ abstraction as appropriate by DO^- (or D^- or O^-). Reactant negative ions were generated from either H_2O or D_2O by 70 eV electrons.[19] The indicated source gauge pressure (of H_2O or D_2O) was typically 5×10^{-4} Torr. The substrate pressure 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.

Dibenzyl ether and 1-hydroxy-1,2,3,4-tetrahydronaphthalene were commercial products. The following compounds were prepared by reported procedures: diphenylmethyl phenyl ether,[34] allyl phenyl ether,[35] 1-phenylprop-2-en-1-ol,[36] allyl benzyl ether,[9] 1-phenylbut-3-en-1-ol,[37] 1-benzylprop-2-en-1-ol,[38] 4-phenylbutanal,[39] 3-(*o*-tolyl)propanal,[40] *o*-allylphenol,[41] 1-(*o*-tolyl)prop-2-en-1-ol,[42] 1-methoxy-1,2,3,4-tetrahydronaphthalene,[43] 1,2-dihydronaphthalene,[44] 1,4-dihydronaphthalene,[45] 3-methylindene,[46] and 1-benzylallene.[47]

o-*Allylbenzyl alcohol* was prepared by a reported technique,[48] but the product was impure and was purified by preparative gas chromatography (Pye Unicam 104) using a 5% SE 30 on Chromasorb A(40-60) 2.4 m × 7 mm column: column temperature 160 °C, flow rate 60 ml min^{-1}, retention time 6.45 mins. The compound is not particularly stable and its ^{1}H n.m.r. signals, when freshly prepared, are δ 2.42 (1 H, s), 3.46 (2 H, m), 4.65 (2 H, s), 5.13 (2 H br s), 5.66—6.42 (1 H, m), and 7.28 (4 H, br s) (Found: $M^{+\bullet}$, 148.0891. $C_{10}H_{12}O$ requires *M*, 148.0888).

1-(o-*Tolyl*)*allene* was prepared in 59% yield, by the reported method[49] used for phenylallene. It is a liquid, b.p. 82.5—84 °C at 16 mmHg. It is not particularly stable but when freshly prepared shows the following ^{1}H n.m.r. spectrum: δ 2.33 (3 H, s), 5.08 (2 H, m), 5.48 (1 H, m), and 7.12 (4 H, br s) (Found: $M^{+\bullet}$, 130.0783. $C_{10}H_{10}$ requires *M*, 130.0783).



Scheme 9. *Reagents:* i, KNH_2–NH_3; ii, KNH_2–NH_3, Δ; iii, KOBu^t– DMSO; iv, LDA/THF–HMPA

The Labelled Compounds.—The compounds Ph(PhCH$_2$)CHOH, Ph(PhCH$_2$)^{13}CHOH, Ph(PhCD$_2$)CHOH, and Ph(C$_6$D$_5$CD$_2$)CHOH were available from a previous study.[50] Similarly, Ph$_3$COH, Ph$_3$^{13}COH, Ph$_2$(C$_6$D$_5$)COH, and ([2,4,6-^{2}H$_3$]phenyl)$_3$COH were available from a previous study.[51]

[^{2}H$_5$]*Phenyl allyl ether* was made from C$_6$D$_5$OD (^{2}H$_6$ 98%) by a reported procedure[35] in 86% yield (^{2}H$_5$ > 99%).

1-([^{2}H$_5$]*Phenyl)prop-2-en-1-ol* was made from C$_6$D$_5$MgBr and acrolein by a standard method,[36] yield 62%, ^{2}H$_5$ > 99%.

1-*Phenyl*[1-^{2}H$_1$]*prop-2-en-1-ol* was made from phenylmagnesium bromide and [1-^{2}H$_1$]acrolein by a standard method,[36] yield 85%, ^{2}H$_1$ 99%. [1-^{2}H$_1$]Acrolein was prepared by Sarett oxidation[52] of 9,10-ethano[13-^{2}H$_2$]anthracen-11-ylmethanol[53] followed by pyrolysis,[54] overall yield 60%, ^{2}H$_1$ 99%.

1-*Phenyl*[2-^{2}H$_1$]*prop-2-en-1-ol* was made from phenylmagnesium bromide and [2-^{2}H$_1$]acrolein[55] by a standard method,[36] yield 58%, ^{2}H$_1$ 99%.

Base-catalysed Rearrangement of Allyl Benzyl Ether.—To a solution of di-isopropylamine (3.42 g) in anhydrous tetrahydrofuran (50 ml) maintained at −78 °C was added n-butyl-lithium (1.40M in hexane; 23.1 ml) dropwise. After stirring at −78 °C for 15 min, hexamethylphosphoramide (6.05 g) was added, followed by allyl benzyl ether (4.60 g) in anhydrous tetrahydrofuran (20 ml). The dark red solution was allowed to warm to 20 °C and stirred for 2 h at that temperature. The mixture was then poured into aqueous ammonium chloride (saturated; 300 ml), the organic layer separated and extracted with diethyl ether (5 × 40 ml), the combined ethereal extracts washed with aqueous hydrogen chloride (2M, 30 ml) and water (3 × 30 ml), and dried (Na$_2$SO$_4$). After removal of the solvent, the residue was distilled *in vacuo* to yield three discrete fractions. The first, b.p. range 76—94 °C at 10 mmHg, was 1,2-dihydronaphthalene (1.17 g), identified by comparison with authentic material[44] using i.r., ^{1}H n.m.r., and g.c.–m.s. The second fraction, b.p. range 74—92 °C at 2 mmHg, was 1-(*o*-tolyl)prop-2-en-1-ol (0.39 g) identified by comparison with an authentic specimen[42] by i.r., ^{1}H n.m.r., and g.c.–m.s. The third fraction, b.p. range 94—98 °C at 2 mmHg, 1-phenylbut-3-en-1-ol (1.46 g) was identical with authentic material,[37] as above.

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