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Gas-Phase Wittig Rearrangement of Carbanions Derived from Benzyl Ethers

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The CA mass spectra of ions PhC^-HOR and $Ph(R)CH{-}O^-$ (R = alkyl and phenyl) are very similar, suggesting that the Wittig rearrangement $PhC^-HOEt \rightarrow Ph(Et)CH{-}O^-$ occurs in the gas phase. Major fragmentations can be interpreted in terms of 1,2-elimination of groups from the Wittig product ion. For example, ^2H labeling of PhC^-HOEt and $Ph(Et)CH{—}O^-$ show that the major processes produce $Me{—}CH{=}CH{—}O^- + C_6H_6$ and $(C_6H_4)^-CHO + C_2H_6$, with the latter process involving prior scrambling of phenyl hydrogens. An analogous process, $Ph_2CH{—}O^- \rightarrow (C_6H_4)^-CHO + C_6H_6$ gives the major peak in the spectrum of "PhC^-HOPh".

Introduction

In recent years there have been significant advances in the analytical applications of negative ion mass spectrometry, particularly in the areas of negative ion chemical ionization and fast atom bombardment.[1] These techniques often yield $(M-H^+)^-$ ions, but since the ions are generally of low energy, they fragment little, thus providing sparse structural information. Collision-induced dissociations of $(M-H^+)^-$ ions can often provide this structural information together with fundamental information concerning ion behavior.[1-3]

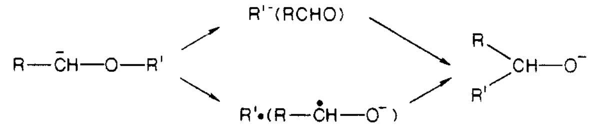
One of the better known carbanion rearrangements in the condensed phase is the Wittig rearrangement.[4] The rearrangement could, in principle, involve either of the intermediates shown in Scheme I, and to support such mechanistic proposals, it has been shown that aldehydes are often byproducts of the reaction.[5] The migratory aptitude of substituents R^1 is allyl ≈ benzyl > methyl > ethyl > phenyl in solution reactions.[5] Since the migratory aptitudes are in the order of free radical stabilities,[6] the radical pair mechanism for the reaction is favored.[7] Recent work[8-10] in this area includes analogous rearrangements of thioethers[9] and silyl ethers.[10]

In this paper we address the following question: Can the CA mass spectra of carbanions from benzyl ethers be interpreted in terms of Wittig rearrangements (Scheme I) or are the fragmentations typical solely of the precursor benzyl ether $(M-H^+)^-$ ions?

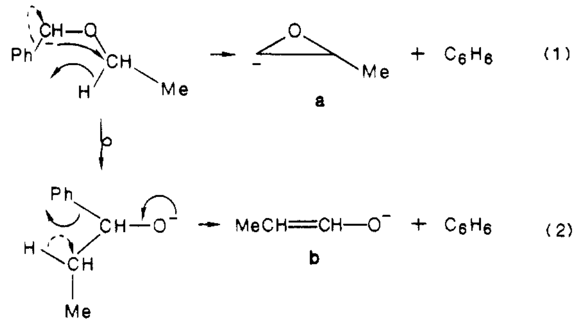
Results and Discussion

Full experimental details are provided in the Experimental Section. The compounds used for this study together with their spectra are listed in Tables I–IV. Two examples are illustrated in Figures 1 and 2.

Scheme I



Scheme II



We have chosen benzyl alkyl and benzyl phenyl ethers for this study since each can form only the substituted benzyl anion on deprotonation.[11] The spectra of benzyl ethers are listed in Table I and illustrated in Figure 1 and those of the appropriate secondary alcohols (the products in a Wittig rearrangement) in Table II and Figure 2.

(A) Benzyl Alkyl Ethers. The CA mass spectra of all benzyl alkyl ethers [except benzyl *tert*-butyl ether (X)] show analogous fragmentations. Our discussion will now be primarily confined to the ethyl ether (and its D-labeled derivatives) which we have chosen to represent this class of compound.

The spectra of PhC^-HOCD_2Me and $Ph(MeCD_2)CH{-}O^-$ are shown in Figures 1 and 2. Apart from *m/z* 106 ($-MeCD_2\cdot$) in Figure 1, the two spectra are identical. The peak widths (and thus the kinetic energy release) for *m/z* 105, 77, 76, and 58 are identical in both spectra (see legends to Figures 1 and 2). When the collision cell is maintained at −1 kV, it can be seen that the contribution to each process from unimolecular and collision-induced dissociations are similar in each spectrum (see legends to Figures 1 and 2). It seems likely that, apart from *m/z* 106 in Figure 1, other ions in both systems are being formed from a common intermediate. Certainly the results of D labeling are almost identical for the ether and alcohol systems.

A major fragment peak shown in Figures 1 and 2 is *m/z* 58; this corresponds to ions $C_3H_5O^-$ (*m/z* 57) in the spectra of the carbanions from unlabeled II and XVI (compounds together with numbers are listed in columns 1 of Tables

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(1) Bowie, J. H. *Mass Spectrom Rev.* **1984**, *3*, 161.

(2) Bowie, J. H.; Blumenthal, T.; Laffer, M. H.; Janposri, S.; Gream, G. E. *Aust. J. Chem.* **1984**, *37*, 1447. Bowie, J. H.; Stringer, M. B.; Duus, F.; Lawesson, S.-O.; Larsson, F. C. V.; Madsen, J. Ø. *Aust. J. Chem.* **1984**, *37*, 1619.

(3) Stringer, M. B.; Bowie, J. H.; Holmes, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 3338.

(4) Wittig, G. *Angew. Chem.* **1954**, *66*, 10. Zimmerman, H. E. In *Molecular Rearrangements*; de Mayo, P., Ed.; Interscience: 1963; Vol. 1, p 345. Baldwin, J. E.; DeBernardis, J.; Patrick, J. E. *Tetrahedron Lett.* **1970**, 353.

(5) Hauser, C. R.; Kantor, S. W. *J. Am. Chem. Soc.* **1951**, *73*, 1437; Cast, J.; Stevens, T. S.; Holmes, J. *J. Chem. Soc.* **1960**, 3521.

(6) Lansbury, P. T.; Pattison, V. A.; Sidler, J. D.; Bierber, J. B. *J. Am. Chem. Soc.* **1966**, *88*, 78. Schafer, H.; Schöllkopf, U.; Walter, D. *Tetrahedron Lett.* **1968**, 2809.

(7) Schöllkopf, U. *Angew, Chem., Int. Ed. Engl.* **1970**, *9*, 763.

(8) D'Orchymont, H.; Goeldner, M. P.; Biellmann, J. F. *Tetrahedron Lett.* **1982**, 1727.

(9) Biellmann, J. F.; Durep, J. B.; Schirlin, D. *Tetrahedron* **1980**, *36*, 1249. Ikehara, H.; Tanimoto, S. *J. Chem. Soc., Chem. Commun.* **1983**, 1316; *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2478. Davies, S. G.; Holman, N. J.; Laughton, C. A.; Mobbs, B. E.; *J. Chem. Soc., Chem. Commun.* **1983**, 1316.

(10) Reetz, M. T.; Greif, N. *Chem. Ber.* **1977**, *110*, 2958.

(11) We have therefore chosen substituents which have been shown to be poor migrating groups in the condensed phase.[5] If we had chosen, say benzyl allyl ethers, two carbanions may be formed initially, and this would complicate the interpretation of the spectra.

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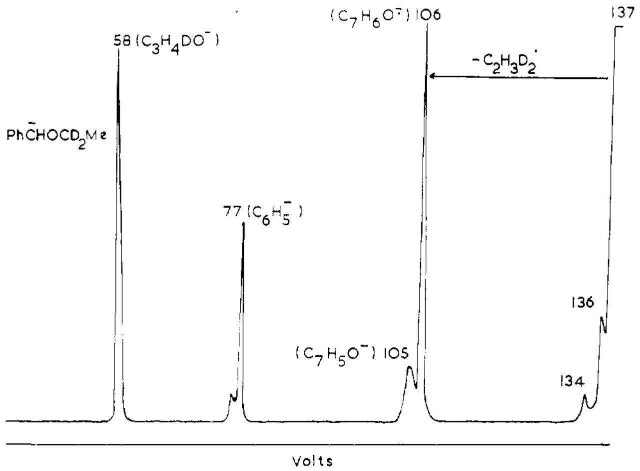


Figure 1. CA mass spectrum of PhC^-HOCD_2Me. For experimental conditions see Experimental Section. The voltages at half-height for peaks are [m/z (V, ±0.2)]: 106 (39.5), 105 (63.2), 77 (34.0), and 58 (31.6). When a voltage of −1 kV is applied to the collision cell, the following percentages of collision-induced:unimolecular decompositions are noted [m/z (collision induced:unimolecular)]: 106 (50:50), 105 (75:25), 77 (90:10), 76 (100:0), and 58 (44:56).

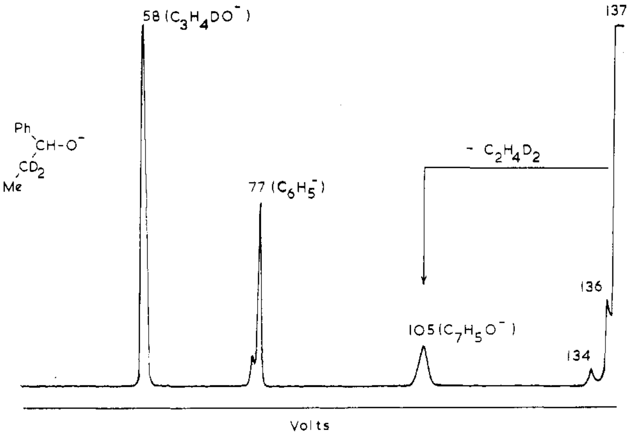
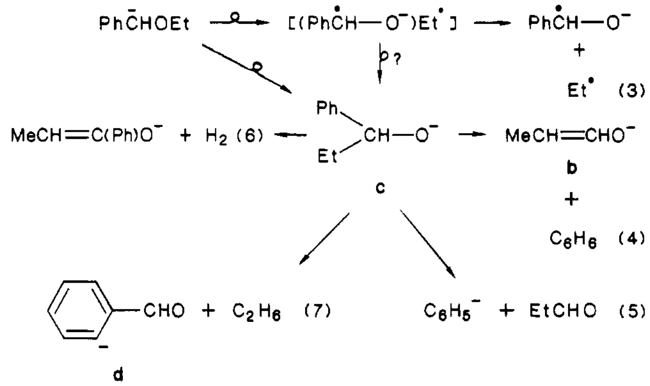


Figure 2. CA mass spectrum of $Ph(MeCD_2)CH—O^-$. For experimental conditions see Experimental Section. The voltages at half height for peaks are [m/z (V, ±0.2)]: 105 (62.8), 77 (33.9), and 58 (31.6). When a voltage of −1 kV is applied to the collision cell, the following percentages of collision-induced:unimolecular decompositions are noted [m/z (collision induced:unimolecular)]: 105 (70:30), 77 (86:14), 76 (100:0), and 58 (46:54).

I and II). Analogous peaks are observed in other benzyl alkyl ether spectra (Table I, column [$-(R^1 + H)$]); these become more pronounced with elaboration of the alkyl substituent. Figures 1 and 2 show that m/z 58 is formed by elimination of C_6H_5D; this is in accord with the absence of such a peak in the spectrum of PhC^-HO-*t*-Bu.

The formation of an ion $C_3H_5O^-$ directly from PhC^-HOEt seems most unlikely; a possibility might be production of the anion **a** as shown in eq 1 (Scheme II). In contrast, the elimination of C_6H_6 from the Wittig rearrangement ion should readily form the propionaldehyde enolate negative ion (**b**, eq 2). This type of fragmentation is directly analogous to other 1,2-elimination reactions of alkoxide anions studied previously.[12] The CA mass spectra of ions $C_3H_5O^-$ from II and XVI are identical; these are recorded in Table III. The charge reversal mass spectra[13] of the ions are also very similar (see Table IV). To attempt to identify the structure of this ion, we have compared its CA and charge reversal mass spectra with those of a number of $C_3H_5O^-$ anions, viz., those formed by deprotonation of propylene oxide,[14] propionaldehyde, allyl alcohol, and acetone (see Tables III and IV). Examination of Tables III and IV show that the $C_3H_5O^-$ ion does not correspond to those formed from propylene oxide or to $CH_2=CH—CH_2—O^-$ or $CH_2=C(Me)O^-$. However, its spectra are consistent with those of the propionaldehyde enolate anion $MeCH=CHO^-$.

Scheme III



The fragmentations of PhC^-HOEt are summarised in Scheme III. We suggest that all fragmentations [except the loss of Et· (eq 3)] are preceded by a carbanion Wittig rearrangement to **c** which decomposes (i) by two cleavage processes, viz., loss of H·[15] and the formation of $C_6H_5^-$ (eq 5) and (ii) by a number of 1,2-elimination processes (cf. ref 12) including the losses of C_6H_6 (eq 4), H_2 (eq 6), and C_2H_6 (eq 7).[16] The loss of Et· from PhC^-HOEt forms the benzaldehyde radical anion;[17] this could be formed directly

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[12] (a) The *tert*-butoxide anion undergoes specific and stepwise 1,2-elimination of methane to form $CH_2=C(Me)O^-$ (Tumas, W.; Foster, R. F.; Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 7464. Tumas, W.; Foster, R. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 4053). (b) The ethoxide anion undergoes stepwise 1,2-elimination of H_2 to form $CH_2=CHO^-$ (Hayes, R. N.; Sheldon, J. C.; Bowie, J. H.; Lewis, D. E. *J. Chem. Soc., Chem. Commun.* **1984**, 1431; *Aust. J. Chem.* **1985**, *38*, 1197.

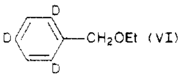
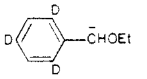
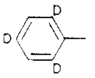
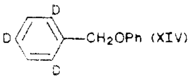
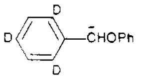
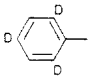
[13] Bowie, J. H.; Blumenthal, T. *J. Am. Chem. Soc.* **1975**, *97*, 2959. Howe, I.; Bowie, J. H.; Szulejko, J. E.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 99.

[14] The reaction of HO^- with propylene oxide has been reported (Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229), and it has been suggested that the deprotonated species is not a cyclic species but may correspond to $CH_2=C^-H—CH_2O^-$ or $CH_2=C(Me)O^-$. Deuterium-labeling studies were not carried out for this system, but the data in Tables III and IV eliminate structure $CH_2=CH—CH_2O^-$. Whatever the structure of this $C_3H_5O^-$ ion, it does not correspond to the ion formed from PhC^-HOEt or $Ph(Et)CHO^-$ (see Tables III and IV).

[15] The loss of H· comes exclusively from the phenyl ring (see Tables I and II, spectra V and XVIII. The spectra of VI and XIX show that H/D scrambling occurs prior to this fragmentation and that there is an isotope effect operating in these cases in favor of H· loss. Reports of aryl H scrambling in negative ions are rare (Bowie, J. H.; Nussey, B. *J. Chem. Soc., Chem. Commun.* **1970**, 17. Stringer, M. B.; Underwood, D. J.; Bowie, J. H.; Holmes, J. L. Mommers, A. A.; Szulejko, J. E. *Can. J. Chem.* **1986**, *64*, 764.

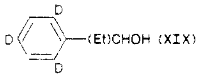
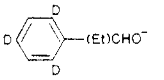
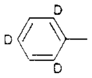
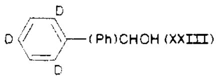
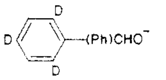
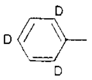
[16] (a) The formulation as **d** is nominal since we assume the phenyl H which is eliminated is an ortho hydrogen. Spectra V and XVIII (Tables I and II) show specific loss of a phenyl deuterium. Spectra VI and XIX show aryl H/D randomisation (cf. ref 15 above) and that there is an isotope effect (H/D) of ca. 2 in favor of loss of C_2H_6 (as opposed to loss of C_2H_5D). (b) If this reaction is stepwise like similar 1,2-eliminations (cf. ref 12), the intermediate will be [$C_2H_5^-(PhCHO)$]. It is interesting that the reaction product is *specifically* $C_6H_4^-CHO$ rather than the benzoyl anion $C_6H_5C^-=O$, since it has been shown that deprotonation of benzaldehyde by NH_2^- leads to *both* of the above ions (Kleingeld, J. C.; Nibbering, N. M. M. *Tetrahedron* **1984**, *40*, 2789). (c) It is likely that other reactions shown in Scheme III also proceed through the intermediacy of ion complexes, i.e., (4) and (5) through [$C_6H_5^-(EtCHO)$] and (6) through ($H^-[Ph(Et)C=O]$).

Table I. CA Mass Spectra of $R^1C^-(R^3)OR^2$ Ions[a]

compd (no.)	initial ion	R^1	R^2	R^3	$-H\cdot$	$-D\cdot$	$-H_2$	$-HD$	$-R^2\cdot$
$PhCH_2OMe$ (I)	PhC^-HOMe	Ph	Me	H	50 (120)		11 (119)		100 (106)
$PhCH_2OEt$ (II)	PhC^-HOEt	Ph	Et	H	40 (134)		5 (133)		100 (106)
$PhCD_2OEt$ (III)	PhC^-DOEt	Ph	Et	D	30 (135)	9 (134)[b]	9 (134)[b]		100 (107)
$PhCH_2OCD_2Me$ (IV)	PhC^-HOCD_2Me	Ph	CD_2Me	H	29 (136)			8 (134)	100 (106)
$C_6D_5CH_2OEt$ (V)	$C_6D_5C^-HOEt$	C_6D_5	Et	H		18 (138)[b]	18 (138)[b]		100 (111)
			Et	H	26 (137)	24 (136)[b]	24 (136)[b]		100 (109)
PhCH(Me)OEt (VII)	$PhC^-(Me)OEt$	Ph	Et	Me	27 (148)		8 (147)		36 (120)
$PhCH_2OPr$ (VIII)	PhC^-HOPr	Ph	Pr	H	50 (148)		10 (147)		27 (106)
$PhCH_2O$-*i*-Pr (IX)	PhC^-HO-*i*-Pr	Ph	*i*-Pr	H	33 (148)		3 (147)		24 (106)
$PhCH_2O$-*t*-Bu (X)	PhC^-HO-*t*-Bu	Ph	*t*-Bu	H	88 (162)				100 (106)
$PhCH_2OPh$ (XI)	PhC^-HOPh[d]	Ph	Ph	H	100 (182)		32 (181)		
$PhCD_2OPh$ (XII)	PhC^-DOPh	Ph	Ph	D	100 (183)	18 (182)[b]	18 (182)[b]		
$C_6D_5CH_2OPh$ (XIII)	$C_6D_5C^-HOPh$	C_6D_5	Ph	H	100 (187)	16 (186)[b]	16 (186)[b]	8 (185)	
			Ph	H	100 (185)	14 (184)[b]	14 (184)[b]	5 (183)	

[a] Spectra are listed as follows: the first figure is the relative abundance (%); the figure in parentheses refers to the *m/z* value of the ion. [b] Both H_2 and $D\cdot$ = 2 amu. [c] In this case (R^1 + D) = C_6H_5D is lost. [d] The peak widths at half-height in the CA mass spectrum of PhC^-HOPh

Table II. CA Mass Spectra of $(R^1)(R^2)(R^3)C{-}O^-$ Ions[a]

compd (no.)	ion	R^1	R^2	R^3	$-H\cdot$	$-D\cdot$	$-H_2$	$-HD$
Ph(Me)CHOH (XV)	$Ph(Me)CHO^-$	Ph	Me	H	55 (120)		21 (119)	
Ph(Et)CHOH (XVI)	$Ph(Et)CHO^-$	Ph	Et	H	30 (134)		11 (133)	
$Ph(CD_2Me)CHOH$ (XVII)	$Ph(CD_2Me)CHO^-$	Ph	CD_2Me	H	24 (136)			5 (134)
$C_6D_5(Et)CHOH$ (XVIII)	$C_6D_5(Et)CHO^-$	C_6D_5	Et	H		30 (138)[c]	30 (138)[c]	
			Et	H	18 (137)	15 (136)[c]	15 (136)[c]	
Ph_2CHOH (XX)[e,f]	Ph_2CHO^-	Ph	Ph	H	100 (182)		28 (181)	
Ph_2CDOH (XXI)	Ph_2CDO^-	Ph	Ph	D	100 (183)	20 (182)[c]	20 (182)[c]	
$C_6D_5(Ph)CHOH$ (XXII)	$C_6D_5(Ph)CHO^-$	C_6D_5	Ph	H	100 (187)	29 (186)[c]	29 (186)[c]	
			Ph	H	100 (185)	21 (184)[c]	21 (184)[c]	3 (183)

[a] Spectra are listed as follows: the first figure is the relative abundance (%); the figure in parentheses refers to the *m/z* value of the ion. [b] In this case, (R^1 + D) = C_6H_5D is eliminated. [c] Loss of either H_2 or $D\cdot$ = 2 amu. [d] $R^1 = R^2$ = Ph. [e] The peak widths at half-height in the CA mass spectrum of $Ph_2CH{-}O^-$ are [*m/z* (*V*, ±0.2)]: 153 (40.0), 105 (32.9), 77 (37.1), and 76 (45.8). When a voltage of −1 kV is applied to

Table III. CA Mass Spectra (*m/z*) of $C_3H_5O^-$ Ions

precursor	ion structure	56 ($-H\cdot$)	55 ($-H_2$)	41 ($-CH_4$)	29 ($-C_2H_4$)	27 ($-CH_2O$)
PhC^-HOEt[a]	$C_3H_5O^-$	100	70	12		3
$Ph(Et)CH{-}O^-$[a]	$C_3H_5O^-$	100	68	12		4
Propylene oxide	$C_3H_5O^-$[14]	100	92	16	28	45
propionaldehyde	$MeCH{=}CHO^-$	100	72	10		2
allyl alcohol	$CH_2{=}CH{-}CH_2{-}O^-$	100	34		6	24
acetone	$CH_2{=}CH(Me)O^-$	100	12	29		

[a] The $C_3H_5O^-$ ions studied here are produced in the CI source. It is assumed they have the same structure as those observed in the CA mass spectra.

Table IV. Charge Reversal (Positive Ion) Mass Spectra (*m/z*) of $C_3H_5O^-$ Ions

precursor	ion	56	55	54	53	43	42	41	40	39	38	37	31	30	29	28	27	26	25	15	14	13	12
PhC^-HOEt[a]	$C_3H_5O^-$	6	11	1	2	2	7	8	2	15	5	5			100	45	59	55	10	6	13	4	2
$Ph(Et)CH{-}O^-$[a]	$C_3H_5O^-$	5	12	2	2	2	8	9	2	15	6	6			100	43	62	56	11	6	14	4	2
propylene oxide	$C_3H_5O^-$[14]	11	41	3	7	2	14	13	4	34	16	12			100	46	83	56	14	3	7	2	1
propionaldehyde	$MeCH{=}CH{-}O^-$	6	11	2	2	2	5	7	2	12	5	5			100	49	61	53	10	5	11	3	1
allyl alcohol	$CH_2{=}CH{-}CH_2O^-$	7	28	3	5	...	6	10	4	26	10	8	8	12	100	54	99	67	18	2	7	3	1
acetone	$CH_2{=}C(Me)O^-$	...	3	1	3	36	100	31	12	30	14	12			36	13	34	24	7	14	22	7	2

[a] The $C_3H_5O^-$ ions studied here are produced in the CI source. It is assumed that they have the same structure as those observed in the CA mass spectra.

from PhC^-HOEt or indirectly via the intermediate of the radical Wittig rearrangement [eq 3 (Scheme III)]. Whether this (hypothetical) intermediate is able to rearrange to **c** is not known.

$-(R^2 + H)$	$-(R^2 + D)$	$-(R^1 + H)$	$-(R^1R^3CO) \rightarrow R^{2-}$	$-(R^2R^3CO) \rightarrow R^{1-}$	$-(R^2R^3CHO) \rightarrow (R^1\text{-}H)^{\bullet-}$	$-(R^2R^3CDO) \rightarrow (R^1\text{-}D)^{\bullet-}$	$-CO$	$-(CO + H_2)$	$-(CO + HD)$
20 (105)		84 (43)		21 (77)	2 (76)				
25 (105)		97 (57)		26 (77)	4 (76)				
24 (106)		82 (58)		18 (77)	2 (76)				
18 (105)		88 (58)[c]		48 (77)	6 (76)				
	28 (109)	89 (57)		24 (82)		1 (80)			
15 (108)	10 (107)	96 (57)		26 (80)	1 (79)	1 (78)			
100 (119)		48 (71)		5 (77)					
16 (105)		100 (71)		18 (77)		2 (76)			
10 (105)		100 (71)		18 (77)	2 (76)				
56 (105)		...		68 (77)	5 (76)				
78 (105)[e]		78 (105)[e]	30 (77)[e]	30 (77)[e]	6 (76)		2 (155)	14 (153)	
76 (106)[e]		76 (106)[e]	28 (77)[e]	28 (77)[e]	6 (76)		2 (156)	2 (154)	8 (153)
	25 (109)	48 (105)	15 (77)	13 (82)		2 (80)	2 (160)	5 (158)	4 (157)
18 (108)	19 (107)	48 (105)	18 (77)	16 (80)	1 (79)	1 (78)	2 (158)	6 (156)	5 (155)

are [*m*/*z* (*V*, ±0.2)]: 153 (38.8), 105 (33.0), 77 (36.9), and 76 (46.1). When a voltage of −1 kV is applied to the collision cell, the following collision-induced:unimolecular ratios are observed [*m*/*z* [*m*/*z* (c:u)]: 153 (20:80), 105 (45:55), 77 (90:10), and 76 (100:0). [e] $R^1 = R^2$.

$-(R^2 + H)$	$-(R^2 + D)$	$-(R^1 + H)$	$-(R^1R^3CO) \rightarrow R^{2-}$	$-R^2R^3CO \rightarrow R^{1-}$	$-(R^2R^3CHO) \rightarrow (R^1\text{-}H)^{\bullet-}$	$-(R^2R^3CDO) \rightarrow (R^1\text{-}D)^{\bullet-}$	$-CO$	$-(CO + H_2)$	$-(CO + HD)$
6 (105)		100 (43)		54 (77)	7 (76)				
4 (105)		100 (57)		33 (77)	6 (76)				
11 (105)		100 (58)[b]		52 (77)	7 (76)				
	3 (109)	100 (57)		32 (82)		4 (80)			
2 (108)	1.5 (107)	100 (57)		29 (80)	2 (79)	1.5 (78)			
80 (105)[d]		80 (105)[d]	27 (77)[d]	27 (77)[d]	8 (76)		2 (155)	16 (153)	
76 (106)[d]		76 (106)[d]	28 (77)[d]	28 (77)[d]	8 (76)		2 (156)	2 (154)	8 (153)
	42 (109)	72 (105)	28 (77)	25 (82)		6 (80)	2 (160)	7 (158)	6 (157)
20 (108)	21 (107)	51 (105)	20 (77)	18 (80)	2 (79)	2 (78)	2 (158)	7 (156)	5 (155)

the collision cell, the following collision-induced:unimolecular ratios are observed [*m*/*z* (c:u)]: 153 (25:75), 105 (50:50), 77 (90:10), and 76 (100:0). [f] The CA spectrum of $Ph_2{}^{13}CD\text{-}O^-$ [from $Ph_2{}^{13}CDOD$ (XXII)] is $-H\cdot$ (100%), −2 (22), $-{}^{13}CO$ (2), $-({}^{13}CO + H_2)$ (2), $-({}^{13}CO + HD)$ (8), $[(C_6H_4)^{-13}CDO \equiv (Ph_2{}^{13}CDO^- - C_6H_6)]$ (98), $C_6H_5^-$ (29), and $C_6H_4^{\bullet-}$ (7).

(B) Benzyl Phenyl Ether. The CA mass spectra of PhC^-HOPh and $Ph_2CH{-}O^-$ (and those of the appropriate pairs of labeled compounds) are identical in every respect (see Tables I and II). The peak abundances are the same, as are the width of the peaks at half-height. When the collision cell is floated at −1 kV, spectra XI and XX show, within experimental error, very similar contributions of unimolecular and collision-induced dissociations. Thus we believe that all fragmentations of PhC^-HOPh can be rationalized in terms of a Wittig rearrangement.

Certain of the fragmentations shown in Figure 3 are directly analogous to those outlined in Scheme III. These include the losses of $H^\cdot$, the formation of $C_6H_5^-$ (cf. eq **5**), and the elimination of C_6H_6 to form $(C_6H_4^-){-}CHO$ (cf. eq 7). The last of these fragmentations shows some interesting features. The spectrum of $Ph_2{}^{13}CD{-}O^-$ (footnote *f*, Table II) shows specific loss of C_6H_6—indicating no interchange of phenyl and benzylic carbons or hydrogens. The spectra of XIII (Table I) and XXII (Table II) show losses of C_6D_5H:C_6H_5D (48:25), and the deuterium isotope effect H/D = 1.92) shows the deprotonation step to be rate determining. In addition, the spectra of XIV (Table I) and XXIII (Table II) show H/D scrambling of individual phenyl rings and that H is lost more readily than D. We suggest the overall process is stepwise as shown in eq 8.

$$PhC^-HOPh \rightarrow Ph_2CH{-}O^- \rightarrow [Ph^-(PhCHO)] \rightarrow (C_6H_4)^-\text{-}CHO + C_6H_6 \quad (8)$$

The final fragmentations observed in these systems involve losses of CO and CH_2O respectively. Both reactions involve skeletal rearrangement. The spectrum of $Ph_2{}^{13}CDO^-$ shows losses of ^{13}CO and $^{13}CHDO$. The D_5 derivatives XIII (Table I) and XXII (Table II) show an isotope effect (H/D = 2.7) in favor of the loss of CH_2O against CHDO, and finally, the spectra of the D_3 derivatives XIV and XXIII show that H/D phenyl ring scrambling accompanies these fragmentations. Possible product ions for these reactions are shown in eq 9 and 10.

In conclusion, the CA mass spectra of benzylic carbanions derived from benzyl alkyl ethers and benzyl phenyl ether may be interpreted in terms of Wittig rearrangements.[18] Fragmentations principally involve characteristic

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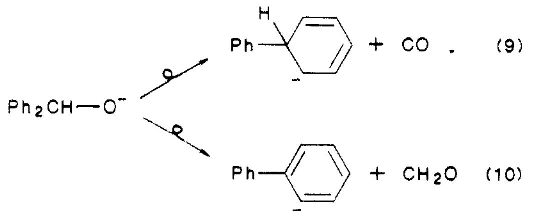
[17] A reviewer has questioned the proposed structure $Ph\dot{C}H{-}O^-$, since the electron affinity of benzaldehyde is likely to be low, and has asked whether there is an isomeric structure which may be more stable. As far as we are aware, the electron affinity of benzaldehyde is not known (see, e.g.; Ellison, G. B., Experimentally Determined Electron Affinities, Oct 1985, University of Colorado, Boulder), and we are thus not in a position to make a definitive statement on this matter.



1,2-elimination reactions of the Wittig products Ph(R)CH—O^-. From an analytical view point, only when *m/z* 106 is present in the CA spectrum of PhC^-HOR can this technique be used to distinguish ions PhC^-HOR and Ph(R)CHO^-.

Experimental Section

CA mass spectra and charge reversal mass spectra[13] were recorded on a Vacuum Generators ZAB-2HF mass spectrometer operating in the negative chemical ionization mode.[19] All slits were fully open to obtain maximum sensitivity and to minimize energy-resolution effects.[20] The chemical ionization slit was used in the ion source: ionizing energy, 70 eV (tungsten filament); trap current, 100 μA; ion source temperature, 150 °C; accelerating voltage, 8 kV. Carbanions were generated by ^1H abstraction from compounds I, II, IV–XI, and XII–XXIII by HO^- (or H^- or $O^{\bullet -}$) or from III and XII by ^2H abstraction by DO^- (or D^- or $O^{\bullet -}$). Reactant negative ions were generated from either H_2O or D_2O by 70-eV electrons.[21] The indicated source gauge pressure (of H_2O or D_2O) was typically 5×10^{-6} torr. The ether (or alcohol) pressure was typically 5×10^{-7} torr. The *estimated* total pressure within the source is 2×10^{-2} torr. (cf. ref 21c). 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.

All unlabeled benzyl ethers (I, II, VII–XI) are known and were prepared by the following general procedure. To the appropriate sodium alkoxide (50 mmol) in dry dimethylformamide (20 mL) at 0 °C under nitrogen was added benzyl bromide (8.55 g, 50 mmol) over a period of 15 min. The reaction mixture was stirred at 25 °C for 1 h and poured into water (100 mL); the product was extracted into diethyl ether (4 × 60 mL) which was washed with aqueous sodium chloride (saturated, 2 × 40 mL) and water (40 mL) and dried ($MgSO_4$). Removal of the solvent in vacuo followed by distillation (under reduced pressure) gave the benzyl ether in yields ranging from 70 to 93%.

The labeled compound IV was made by the general procedure (above) using $NaOCD_2Me$ [$^2H_2 > 99\%$, from $MeCD_2OH$, a commercial product]. Compounds III and XII were prepared from $PhCD_2Br$ ($^2H_2 > 99\%$, from methyl benzoate and $LiAlD_4$[22] followed by bromination with PBr_3) by the procedure outlined above.

The labeled compounds V and VI were prepared from [$^2H_5$]bromobenzene ($^2H_5 > 99\%$, from [$^2H_6$]benzene[23]) and [2,4,6-$^2H_3$]iodobenzene ($^2H_3 = 98\%$, from [2,4,6-$^2H_3$]aniline[23]), respectively, by the following method (cf. ref 24): Lithium (62.5 mg) was added to [$^2H_5$]bromobenzene (728.2 mg) in anhydrous diethyl ether (4 mL) under nitrogen and allowed to stir at 25 °C for 30 min. This solution was added to a precooled (0 °C) suspension of Cu^IBr (321 mg) in anhydrous diethyl ether (3.3 mL), the mixture allowed to stir at 0 °C for 30 min, and then iodomethyl ethyl ether (0.86 g) was added dropwise over a 10-min period. The reaction mixture was allowed to stir at 0 °C for 2 h, poured into water (10 mL), and extracted with diethyl ether (5 × 5 mL). The ethereal extract was washed with aqueous sodium chloride (saturated, 2 × 5 mL), aqueous sodium metabisulfite (5%, 2 × 5 mL), and water (5 mL) and dried (Na_2SO_4). Removal of the solvent followed by vacuum distillation gave [2,3,4,5,6-$^2H_5$]benzyl phenyl ether (497 mg, 78%; $^2H_5 > 99\%$), bp 78–79 °C (18 mmHg).

The phenyl methanols XV–XVII were made from the appropriate alkyl bromide [XV (methyl bromide), XVI (ethyl bromide), XVII ($MeCD_2Br$)] by a standard Grignard reaction between the alkylmagnesium bromide and benzaldehyde (yields 70–80%).

Compounds XVIII and XIX were made from [$^2H_5$]bromobenzene and [2,4,6-$^2H_3$]iodobenzene by a standard Grignard reaction between the appropriate phenylmagnesium halide and propional (XVIII, $^2H_5 > 99\%$, yield 81%; XIX, $^2H_3 = 98\%$, yield 54%).

The diphenylmethanol derivatives XX–XXIII were available from a previous study.[25]

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Registry No. I (carbanion), 104977-34-6; II (carbanion), 104977-35-7; III (carbanion), 104977-36-8; IV (carbanion), 104977-37-9; V (carbanion), 104977-38-0; VI (carbanion), 104977-39-1; VII (carbanion), 104977-40-4; VIII (carbanion), 104977-41-5; IX (carbanion), 104977-42-6; X (carbanion), 104977-43-7; XI (carbanion), 104977-44-8; XII (carbanion), 104977-45-9; XIII (carbanion), 104977-46-0; XIV (carbanion), 104977-47-1.

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(18) A reviewer has asked whether the carbanion Wittig rearrangement occurs on formation of PhC^-HOR or after collisional activation of the ion. Since some fragmentations show unimolecular components (legend to Figure 1; footnote *b*, Table I; footnote *e*, Table II) at least a portion of the rearrangement occurs *before* collisional activation (some ions must be formed in vibrationally excited states—for modes of formation see Experimental Section). This problem can also be studied by considering the charge reversal (positive ion) spectra of the two anions in question. If the charge reversal spectra of the two anions are significantly different, at least a proportion of the negative ion rearrangement is occurring *after* collisional activation.[21c] This situation pertains in the present case: the charge reversal spectra of $PhC^-HOEt/Ph(Et)CHO^-$ and PhC^-HOPh/Ph_2CHO^- show similar fragmentations, but abundances of certain peaks are significantly different for both pairs of ions.

(19) See, e.g. Terlouw, J. K.; Burgers, P. C.; Hommes, H. *Org. Mass Spectrom.* **1979**, *14*, 307.

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