Collision-induced Dissociations of Substituted Benzyl Negative Ions in the Gas Phase. The Elimination of C_4H_4

Graeme J. Currie, John H. Bowie, Ralph A. Massy-Westropp, and Gregory W. Adams
Department of Organic Chemistry, University of Adelaide, South Australia, 5001

The major collision-induced dissociations of $\mathrm{Ph\bar{C}Et_2}$ involve the losses of $H^{\bullet}$, H_2, and CH_4. Loss of $H^{\bullet}$ occurs from the phenyl ring, H_2 is eliminated principally by the process $\mathrm{Ph\bar{C}Et_2} \longrightarrow \mathrm{PhC(Et){=}CHCH_2^-} + H_2$, while methane is lost by the stepwise process $\mathrm{Ph\bar{C}Et_2} \longrightarrow \{\mathrm{Me^-[Ph(Et)C{=}CH_2]}\} \longrightarrow \mathrm{(C_6H_4)^-C(Et){=}CH_2} + CH_4$, in which the second step (deprotonation) is rate-determining. The characteristic fragmentation of both Ph_2CH^- and Ph_3C^- is loss of C_4H_4. This loss occurs without atom randomisation and Dewar benzene intermediates are proposed. The ion Ph_3C^- also loses C_6H_6; this is a slow process which is preceded or accompanied by both intra- and inter-ring hydrogen scrambling.

The benzyl/tropylium cation story is one of the most researched in gas-phase ion chemistry.[1] The tropylium cation is the more stable of the two ions and its formation from the benzyl cation is accompanied or preceded by hydrogen (H) and carbon (C) randomisation. Randomisation reactions also occur for simpler aromatic systems, *e.g.* the benzene[2] and pyridine[3] radical cations, where H and C scrambling occur by different mechanisms,[2,3] with H scrambling being the faster reaction.[4]

The structure and reactivity of $C_7H_7^-$ species are also of interest. There are (at least) three discrete $C_7H_7^-$ ions; $PhCH_2^-$, cyclo-$C_7H_7^-$ (from deprotonation of cycloheptatriene), and a third isomer formed by deprotonation of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene).[5–7] The three isomers may be distinguished by their exchange reactions with MeOD ($PhCH_2^-$ and cyclo-$C_7H_7^-$ incorporate up to two and seven deuteriums respectively),[5] and by their infra-red photochemistry.[6] Cyclo-$C_7H_7^-$ rearranges to $PhCH_2^-$ when HO^- is allowed to react with cycloheptatriene, and it is suggested that the rearrangement proceeds through the intermediacy of a $C_7H_7^-(H_2O)$ complex.[7]

Aryl H scrambling reactions are not as well known (or understood) for negative ions as they are for positive ions. The first observation was for ions $(Ph)_nX^{-\bullet}$ ($n = 3, X = $ As and $n = 4$, $X = $ Si);[8] more recently for benzoyl enolate anions[9] and ions $\mathrm{PhO\bar{C}HR}$ (R = alkyl, allyl, or aryl).[10] However there are also cases where a loss involving an aryl hydrogen is specific, *e.g.* from the molecular anions of fluoroacetanilides[11] and benzil monoxime,[12] and from arylthiophenoxide anions.[13] Finally, the methylene hydrogens of $PhCH_2^-$ retain their positional identity during ion molecule reactions, as evidenced by the reaction shown in equation (1).[14]

$$C_6H_5CD_2^- + MeONO \longrightarrow C_6H_5CD{=}NO^- + MeOD \qquad (1)$$

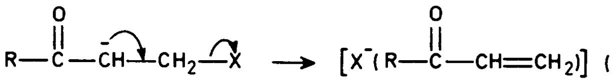
The collision-induced mass spectrum of a polyatomic negative ion is often a structural fingerprint of that ion.[15] Unfortunately, the benzyl anion only eliminates $H^{\bullet}$ and H_2, and these losses are not particularly diagnostic. In this paper we describe the collision-induced dissociations of the substituted benzyl systems $\mathrm{Ph\bar{C}(Et)_2}$, $\mathrm{Ph_2\bar{C}H}$, and $\mathrm{Ph_3\bar{C}}$. We address two questions:

(i) what are the characteristic fragmentations of alkyl- and aryl-substituted benzyl negative ions, and

(ii) does hydrogen or carbon scrambling occur prior to or during these fragmentations?

Results and Discussion

Collisional-induced (activation) mass spectra (c.a. mass spectra) were measured using a VG ZAB 2HF mass spectrometer operating in the chemical ionisation mode. Both mass-analysed ion kinetic energy spectra and linked scan (E, B) techniques were used as appropriate. Deprotonation of the hydrocarbons was effected using either HO^- or DO^- reagent ions. Collisional activation was achieved using He in the second collision cell. Full experimental details are recorded in the Experimental section. The c.a. mass spectra are either shown in Figures 1—3 or listed in Tables 1 and 2. Compounds used for this study are numbered (**1**)—(**15**).


(2)

$$\mathrm{R{-}C({=}O){-}\bar{C}H{-}CH_2{-}X} \longrightarrow [\mathrm{X^-(R{-}C({=}O){-}CH{=}CH_2)}] \qquad (2)$$

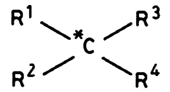
Stabilised enolate negative ions fragment through the intermediacy of ion (orbiting) complexes [equation (2)], from which the incipient anion X^- may either be displaced, or effect deprotonation, nucleophilic displacement, or elimination.[15] We will show that the majority of fragmentations of $\mathrm{Ph\bar{C}Et_2}$ may also be explained in terms of ion complexes. The c.a. mass spectrum of this ion together with those of its labelled derivatives are listed in Table 1.

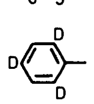
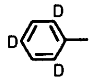
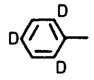
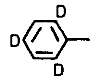
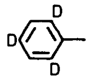
The symmetrical ion $\mathrm{Ph\bar{C}Et_2}$ was chosen for study in order that appropriate fragmentations of the side-chain can be investigated using intramolecular isotope effects. Fragmentations are complex and are summarised in Scheme 1. The major fragmentation involves loss of a phenyl hydrogen atom as shown in equation (3). Whether this $H^{\bullet}$ is lost randomly from the ring, or whether it originates from a specific position following H randomisation, is not known. Whatever the mechanism, there is a pronounced deuterium kinetic isotope effect [H/D > 4, *cf.* spectra (**1**) and (**6**) (Table 1)] operating for the process. Apart from this process and the minor formation of $C_6H_5^-$ [equation (4)], all other fragmentations may be rationalised as proceeding through ion complexes. The c.a. spectra of (**3**) and (**4**) (Table 1) show that loss of H_2 occurs through (*a*) by two specific 1,2-elimination reactions [equations (5) and (6)]. Of the two processes, that shown in equation (5) is by far the major contributor. Similar eliminations have been described before; they are considered to be stepwise processes.[16] Other processes may proceed through methyl anion complex (*b*), which may decompose to Me^- [equation (7)], cause deprotonation of the aromatic ring [equation (8)], or

Table 1. C.a. mass spectra of $Ph\bar{C}(Et)_2$ and labelled analogues

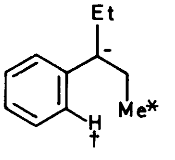
	(1) $Ph\bar{C}Et_2$[a]	(2) $Ph\bar{C}(Et)(CH_2{}^{13}Me)$	(3) $Ph\bar{C}(Et)(CH_2CD_3)$	(4) $Ph\bar{C}(Et)(CD_2Me)$	(5) $C_6D_5\bar{C}Et_2$	(6) $(C_6H_2D_3)\bar{C}Et_2$
Loss						
$H^\bullet$	100	100	100	100		100
$D^\bullet$			*b*	20[c]	100[c]	42[c]
H_2	26	25	*b*	20[c]	100[c]	42[c]
HD				8		
CH_4	57	29.0	28.0	51	3	45
$^{13}CH_4$		28.9				
CH_3D			24.9		18	18
CD_3H						
C_2H_4	2	*b*	*b*	*b*	2	2
C_2H_3D						
$C_2H_5^\bullet$	9	4.0	6.1	5	8	6
$^{12}C^{13}CH_5^\bullet$		3.8				
$C_2H_3D_2^\bullet$				3.5		
$C_2H_2D_3^\bullet$			2.7			
C_3H_8	4			2.5	3	4
$^{12}C_2{}^{13}CH_8$		3				
$C_3H_6D_2$				1.8		
$C_3H_5D_3$			3			
Formation						
$C_6H_5^-$	2	1	1	2		
$C_6D_5^-$					1	
$C_6H_2D_3^-$						0.5
CH_3^-	2	1.1	1.5	2	3	3
CD_3^-			1.0			
$^{13}CH_3^-$		1.0				

[a] The peak widths at half height are as follows [loss (volts ±0.2) *m/z*]: $H^\bullet$ (38.8) 146, H_2 (not resolved) 145, CH_4 (61.0) 131, $C_2H_5^\bullet$ (not resolved) 118, C_3H_8 (76.2) 103, C_5H_{10} (52.5) 77, and $C_{10}H_{12}$ (22.4) 15. [b] Small not resolved. [c] $D^\bullet = H_2 = 2$ a.m.u.



	R^1	R^2	R^3	R^4	*C
(1)	Ph	H	Et	Et	12
(2)	Ph	H	Et	$CH_2{}^{13}Me$	12
(3)	Ph	H	Et	CH_2CD_3	12
(4)	Ph	H	Et	CD_2Me	12
(5)	C_6D_5	H	Et	Et	12
(6)		H	Et	Et	12
(7)	Ph	H	H	Ph	12
(8)	Ph	H	H	Ph	13
(9)	Ph	D	D	Ph	12
(10)	C_6D_5	H	H	Ph	12
(11)		H	H	Ph	12
(12)	Ph	H	Ph	Ph	12
(13)	Ph	H	Ph	Ph	13
(14)	C_6D_5	H	Ph	Ph	12
(15)		H			12

effect the six-centre elimination reaction shown in equation (10).*



(16)

*[H/D = 1·12 ± 0·01; $^{12}C/^{13}C$ = 1·00 ± 0·01]

† H/D = 3·75 ± 0·2

The loss of CH_4 [equation (8)] is a major fragmentation of $Ph\bar{C}Et_2$; the ^2H and ^{13}C isotope effects derived from the spectra of ions from the labelled compounds (2)—(6)† for this process are listed alongside formula (16). The deprotonation step is clearly rate-determining, but the first step [the formation of (*b*)] shows no ^{13}C isotope effect. Interestingly, the spectrum (Table 1) of $C_6D_5\bar{C}Et_2$ shows loss of both CH_3D and CH_4 in the abundance ratio 18:3. Thus the pronounced deuterium isotope effect operating for the second step in equation (8) allows the operation of a second (and minor) loss of methane [see equation (9)], not observed in the other spectra.

The c.a. mass spectra of the diphenylmethane anion and of its labelled derivatives are listed in Table 2; these are spectra produced by electric sector (E) scans. The c.a. linked scan (E, B)

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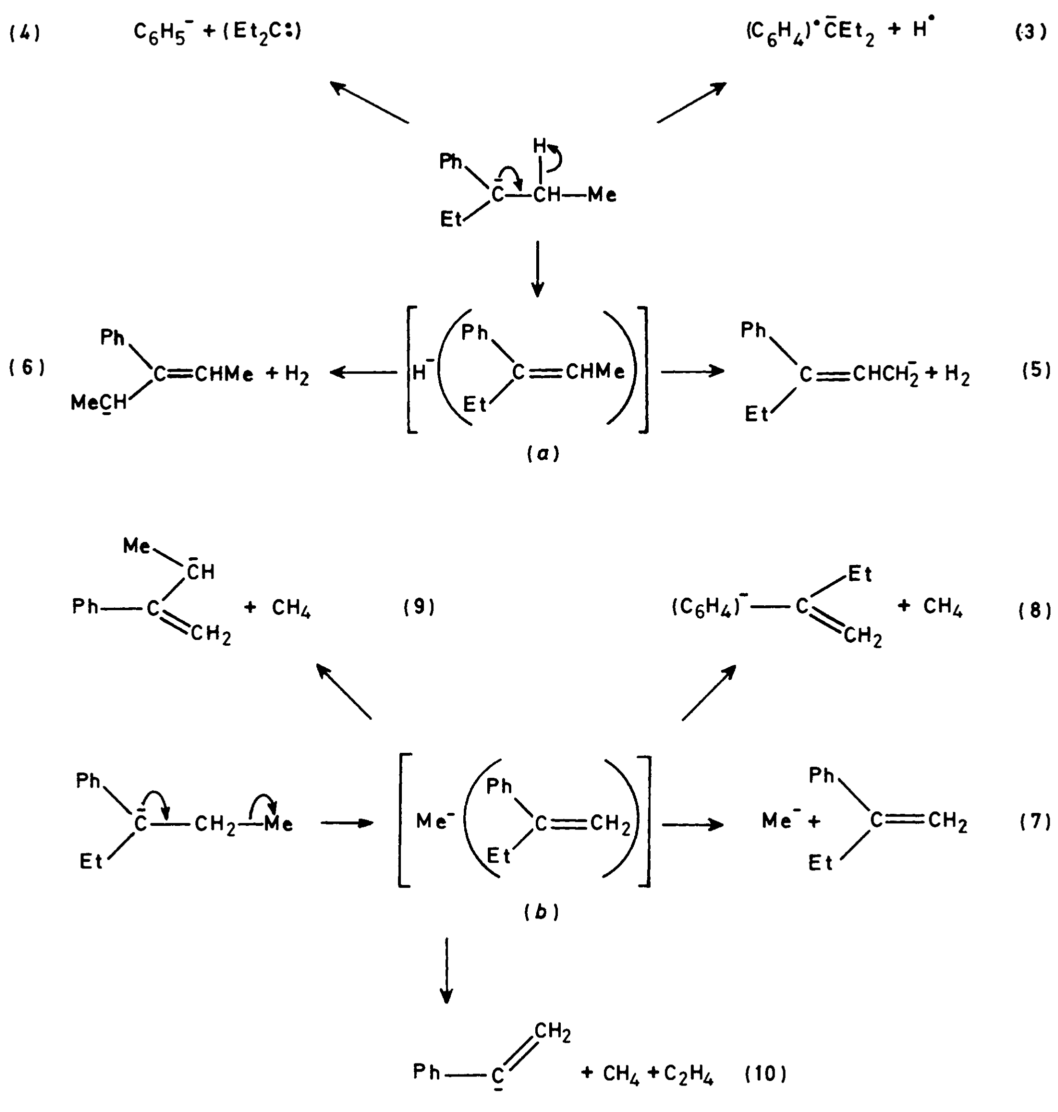
* The alternative S_Ni reaction yielding $Ph\bar{C}{=}CH_2 + C_3H_8$ seems a less likely possibility.

† The H/D value from (6) is obtained by assuming statistical randomisation of H and D on the phenyl ring. In qualitative terms, the large H/D effect is apparent merely by comparing the relative losses of CH_4 and CH_3D from $Ph\bar{C}Et_2$ and $C_6D_5\bar{C}Et_2$ (see Table 1).



Scheme 1.

Table 2. C.a. mass spectra of Ph_2CH^- and labelled derivatives

		Loss										Formation		
Compd.	Ion	$H^{\bullet}$	$D^{\bullet}$	H_2	HD	C_4H_4	$C_4H_2D_2$	C_4D_4	$C_6H_5^{\bullet}$	$C_6H_2D_3^{\bullet}$	$C_6D_5^{\bullet}$	$C_6H_5^-$	$C_6H_2D_3^-$	$C_6D_5^-$
(7)	Ph_2CH^-	100		84		2			0.5			0.2		
(8)	$Ph_2{}^{13}CH^-$	100		80		1.5			0.2			0.2		
(9)	Ph_2CD^-	100	75[a]	75[a]		2			0.3			0.1		
(10)	$Ph(C_6D_5)CH^-$	100	36[a]	36[a]	12	1.01[b]	0.70[b]		0.16[c]		0.15[c]	0.05	0.05	
(11)	$Ph(C_6H_2D_3)CH^-$	100	17[a]	17[a]	13	1.13[b]	0.94[d]		0.20[e]	0.18[e]		0.05		0.05

[a] Both H_2 and $D^{\bullet}$ = 2 a.m.u. [b–e] An average of 10 individual scans.

spectra of the trityl anion and labelled derivatives are shown in Figures 1—3. In these cases the c.a. spectra showed unresolved peaks, and linked scan spectra were required to achieve the appropriate resolution. Certain fragmentations are common to both systems. The major fragmentations of $Ph_2\bar{C}H$ are losses of $H^{\bullet}$ and H_2, and for Ph_3C^-, loss of H_2. The loss of H_2 is preceded or accompanied by hydrogen scrambling within each phenyl ring, and the process has an isotope effect H/D of close to 3 (see Table 2 and Figures 1—3). We propose that fluorenyl anions [equation (11), R = H or Ph] are product ions of these reactions. The cleavage reactions shown in equations (12) and (13) are minor processes; in the case of Ph_3C^- process (13) co-occurs with inter-ring H transfer (see later).

The most characteristic fragmentation of the two systems is loss of C_4H_4. This reaction is specific; there is neither evidence of the benzylic carbon inserting into phenyl rings nor of intra- or inter-ring hydrogen scrambling. Both $Ph_2{}^{13}CH^-$ and $Ph_3{}^{13}C^-$ eliminate C_4H_4; Figure 2 shows specific losses of C_4H_4 and C_4D_4, Figure 3, loss of $C_4H_2D_2$. Isotope effects H/D of 1.45 and 1.32 (correction has been made for statistical factors where appropriate) are noted for the losses of C_4H_4 and C_4D_4 from $Ph(C_6D_5)CH^-$ (Table 2) and $Ph_2(C_6D_5)C^-$ (Figure 2)

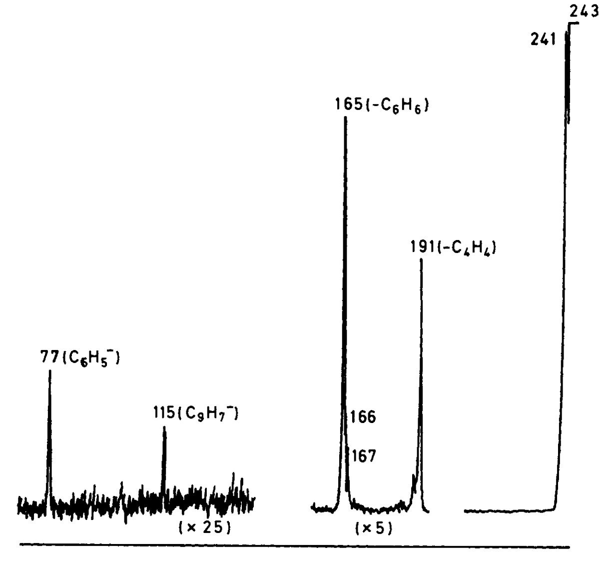
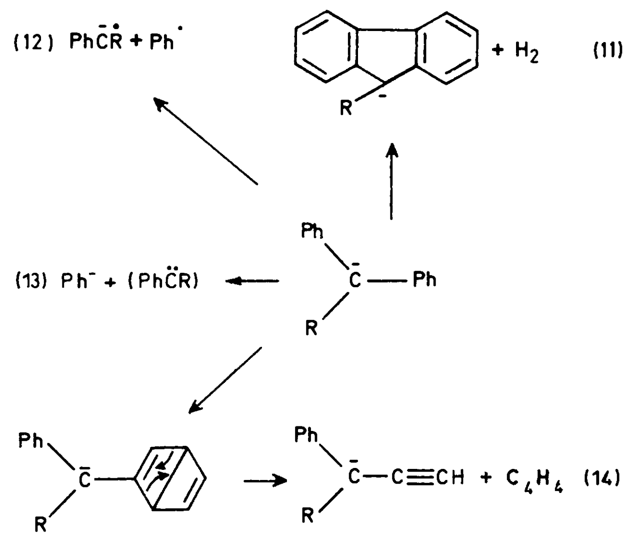
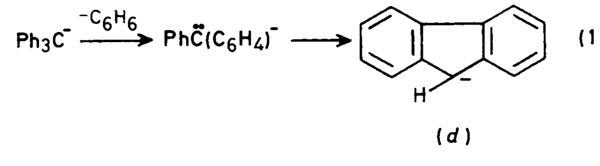


Figure 1. C.a. mass spectrum of Ph_3C^- [major peaks in the c.a. mass spectrum of $Ph_3{}^{13}C^-$ are: m/z (loss) % 242 (H_2) 100, 192 (C_4H_4) 11, 168 (C_6H_4 3, 167 ($C_6H_5^{\bullet}$) 4, and 166 (C_6H_6) 22]



Scheme 2.

respectively. We propose that this fragmentation occurs through Dewar benzene intermediates (*c*) (R = H or Ph) and that overall sequence occurs as shown in equation (14) (Scheme 2). We have reported earlier[17] the specific loss of C_4H_4 from PhS^-, but at that time offered no mechanism for the reaction because of the multitude of complex decompositions noted for this system. It is probable that this decomposition of PhS^- is directly analogous to that shown in equation (14).



(15)

(*d*)

Other fragment ions observed for Ph_3C^- are m/z 167, 166, 165, 115, and 77 (Figure 1) formed respectively by losses of C_6H_4, $C_6H_5^{\bullet}$, C_6H_6, (C_6H_4 + C_4H_4), and $C_{13}H_{10}$. The spectrum of $Ph_3{}^{13}C^-$ (see legend to Figure 1) shows that no fragmentation involves insertion of ^{13}C into a phenyl ring to effect carbon scrambling. All of these fragmentations are interrelated: consider first the loss of C_6H_6 (to form m/z 165) and the formation of $C_6H_5^-$ (m/z 77). The complex nature of these fragmentations can be seen in Figures 2 and 3. We propose that the loss of C_6H_6 forms the fluorenyl anion (*d*), and a possible simplified mechanism is shown in equation (15). If $Ph_2(C_6D_5)\bar{C}$ loses C_6H_6, C_6H_5D, and C_6HD_5, peaks at m/z 170, 169, and 165 would be observed in Figure 2. However, peaks are observed at m/z 170, 169, 168, 166, and 165 corresponding to losses of C_6H_6, C_6H_5D, $C_6H_4D_2$, $C_6H_2D_4$, and C_6HD_5. In addition, Figure 2 shows the formation of ions $C_6H_5^-$, $C_6H_4D^-$, $C_6HD_4^-$, and $C_6D_5^-$. There is therefore a process in which a single hydrogen (deuterium) is being transferred from one ring to another. We suggest this occurs as shown in Scheme 3.

Ion (*e*) may transfer an *ortho* H^+ or D^+ to form (*f*) and (*g*); these ions transfer H^+ or D^+ across rings to form (*h*) and (*i*), each of which may form (*j*). Assuming statistical elimin-

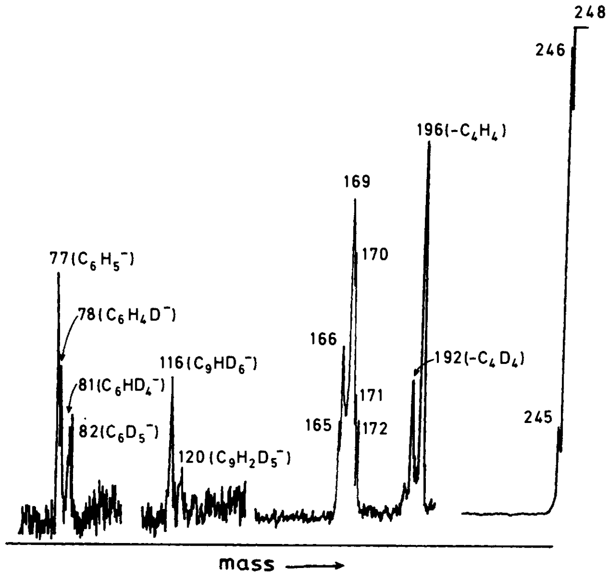


Figure 2. C.a. mass spectrum of $Ph_2(C_6D_5)C^-$

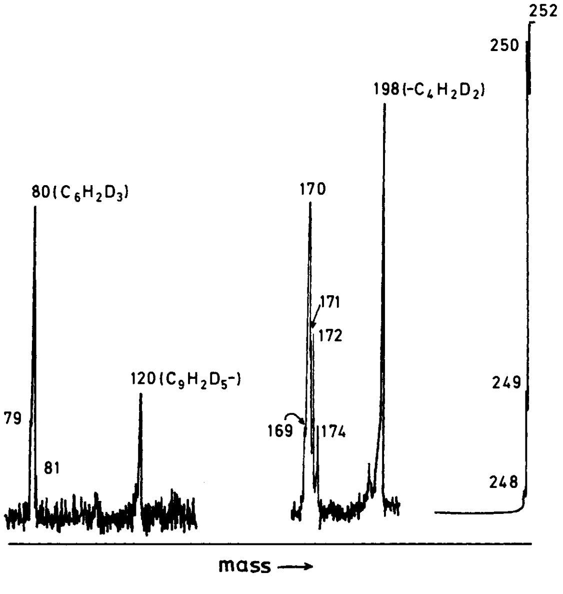
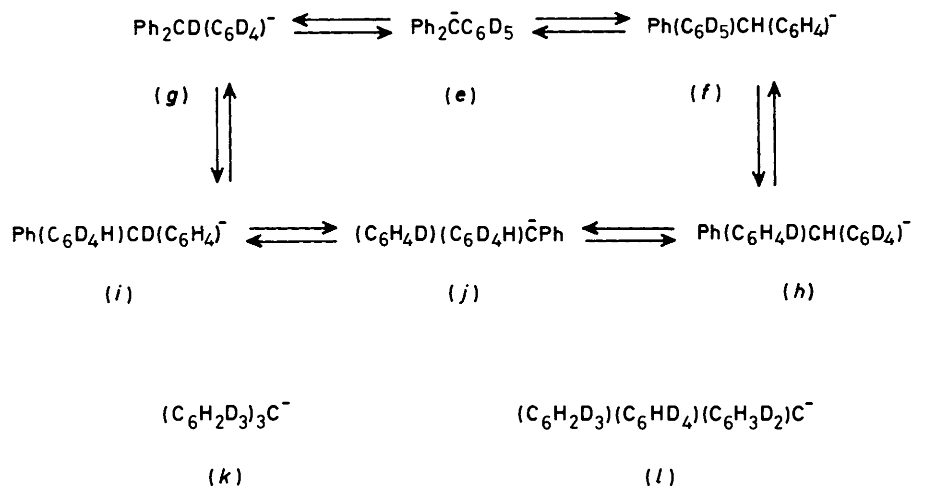


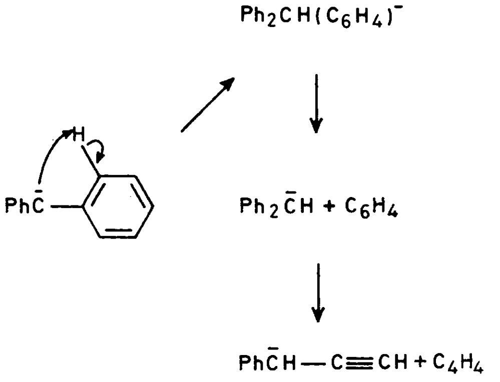
Figure 3. C.a. mass spectrum of $(C_6H_2D_3)_3C^-$



Scheme 3.

ation, a 1:2 ratio of (*e*) to (*j*) gives the following ratios: $C_6H_5^-:C_6H_4D^-:C_6HD_4^-:C_6D_5^- = 100:50:50:50$, and *m/z* 165:166:168:169:170 = 15:20:20:100:26. Examination of Figure 2 shows a rough correlation with these figures, but that there is an appreciable deuterium isotope effect operatiing (*e.g.* see the abundances of *m/z* 166 and 170). A similar treatment for $(C_6H_2D_3)_3C^-$ (Figure 3) will give only *m/z* 170 and 171 if no intra-ring H/D scrambling occurs. The presence of *m/z* 169 ($-C_6HD_5$) shows that the loss of C_6H_6 from Ph_3C^- involves both intra-ring H scrambling as well as specific H transfer between rings.

The loss of $C_6H_5^{\bullet}$ from Ph_3C^- yields *m/z* 166 (Figure 1), but the data in Figures 2 and 3 do not indicate whether this reaction occurs following H scrambling. However, the positions of ring hydrogens remain intact during loss of C_6H_4, as evidenced by specific losses of C_6D_4 and $C_6H_2D_2$ shown in Figures 2 and 3 respectively.* This process must involve *ortho* H transfer as shown in equation (16). Finally, the formation of $C_9H_7^-$ (*m/z* 115, Figure 1) occurs by specific losses of (C_6H_4 + C_4H_4). The sequence of this consecutive process is not known; one possibility is shown in equation (17)



(16)

(17)

In conclusion, this study answers the questions posed in the introduction:

(i) the characteristic fragmentation of $Ph\bar{C}Et_2$ is β-cleavage to the anion site to form $\{Me^-[Ph(Et)C{=}CH_2]\}$ which then undergoes a number of subsequent reactions. Phenyl-substituted benzyl anions eliminate C_4H_4; Ph_3C^- in addition loses C_6H_6;

(ii) examples have been discovered where fragmentation of aromatic systems occur with the hydrogen skeleton of the ion remaining intact, *e.g.* losses of C_4H_4 and C_6H_4 from Ph_3C^-. In contrast, there are slow processes which involve both inter-ring H transfer and intra-ring H scrambling, *e.g.* loss of C_6H_6 from Ph_3C^-.

Experimental

C.a. mass spectra were recorded on a Vacuum Generators ZAB 2HF mass spectrometer operating in the negative chemical ionization mode. All slits were fully open to obtain maximum sensitivity and to minimise energy resolution effects.[18] The chemical ionisation slit was used in the ion source; ionising energy 70 eV (tungsten filament), trap current 100 μA, ion source temperature 180 °C, accelerating voltage 8 kV. Liquids (**1**)—(**6**) were introduced through the septum inlet which was maintained at 180 °C. Solids (**7**)—(**15**) were introduced *via* the direct probe assembly, compounds (**7**)—(**11**) at 100 and compounds (**12**)—(**15**) at 150 °C. Ions from (**1**)—(**8**) and (**10**)—(**15**) were generated by H^+ abstraction by HO^- (or H^- or $O^{-\bullet}$) or from (**9**) by D abstraction with DO^- (or D^- or $O^{-\bullet}$). Reactant negative ions were generated from either H_2O or D_2O (injected through the septum inlet system) by 70 eV electrons.[9,19] The indicated source gauge pressure (of H_2O or D_2O) was typically 2×10^{-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. The same pressure was used in the first collision cell for linked scan experiments. C.a. mass spectra were measured with He in the second cell and by scanning the electric sector. C.a. linked scan mass spectra were measured with He in the first cell and by simultaneously scanning (E/B) the magnetic and electric sectors. Compounds (**1**), (**7**), and (**12**) were commercial products.

The Labelled Compounds.—All liquid hydrocarbon products were distilled in a small glass T-tube (90 °C/30 mmHg) and then further purified by preparative gas chromatography [20% F.F.A.P. on Chromasorb A (60—80 mesh) using a 6 mm diameter × 2 m glass column, N_2 flow rate 40 ml min^{-1}, and

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* This indicates that the intra-ring H scrambling which co-occurs with C_6H_6 loss is concomitant with process $(i) \longrightarrow (j)$ (Scheme 3), not process $(e) \longrightarrow (g)$.

column temperature 170 °C]. Solids were crystallised as indicated. Label incorporation was determined by positive-ion spectrometry.

Compounds (**2**)—(**4**) were made by a standard procedure using the commercial ethyl iodides, $^{13}CH_3CH_2I$, CD_3CH_2I, and $MeCD_2I$ respectively ($^{13}C = 65.1\%$, deuterium incorporation >99.5%). The unlabelled compound illustrates the method. The Grignard reaction[20] between propiophenone and ethylmagnesium iodide produced 3-phenylpentan-3-ol, which was dehydrated with potassium hydrogen sulphate followed by hydrogenation over Pd/C[21] to yield 3-phenylpentane in 80% overall yield.

Compounds (**5**) and (**6**) were made as for (**2**)—(**4**), except that the first step involves the Grignard reactions of pentan-3-one with [$^2H_5$]phenylmagnesium bromide and [2,4,6-$^2H_3$]phenylmagnesium bromide[22,23] respectively [(**5**; $^2H_5 > 99.5\%$); (**6**; $^2H_3 = 98\%$)].

Compounds (**8**)—(**11**) were available from a previous study.[22]

[^{13}C]*Triphenylmethane* (**13**). The Grignard reaction[24] between methyl benzoate (carbonyl group labelled with ^{13}C, $^{13}C = 61.5\%$) and phenylmagnesium bromide gave [^{13}C]-triphenylmethan-1-ol [97% yield, m.p. 159—161 °C from light petroleum (b.p. 40—60 °C)] which was reduced with sodium borohydride in trifluoroacetic acid by a standard method[25] to yield [^{13}C]triphenylmethane [81% yield, m.p. 93—94 °C from light petroleum (b.p. 40—60 °C), $^{13}C = 61.5\%$].

([$^2H_5$]*Phenyl)diphenylmethane* (**14**). (a) [$^2H_5$]Bromobenzene (1.43 g) in anhydrous tetrahydrofuran (THF) (3 cm^3) was added to a stirred mixture of magnesium (0.22 g) in THF (6 cm^3), and the mixture was then stirred under nitrogen, and at reflux for 30 min. Benzophenone (1.66 g) in THF (6 cm^3) was added, the mixture heated under reflux for 2.5 h, cooled to 0 °C, aqueous sulphuric acid (10%; 25 cm^3) was added, and the mixture extracted with diethyl ether (3 × 15 cm^3). The ethereal extract was washed with aqueous sodium hydrogencarbonate (saturated; 25 cm^3) and water (20 cm^3), and dried (Na_2SO_4). Removal of the solvent gave a colourless solid which was crystallised from light petroleum (b.p. 40—60 °C) to give ([$^2H_5$]phenyl)diphenylmethanol (1.40 g, 59%) as colourless crystals, m.p. 160—161 °C.

(b) Reduction[25] as in the case of (**13**) (above) gave ([$^2H_5$]phenyl)diphenylmethane [75% yield, m.p. 93—94 °C from light petroleum (b.p. 40—60 °C), $^2H_5 > 99.5\%$].

Tri([2,4,6-$^2H_3$]*phenyl)methane* (**15**). A standard Grignard reaction[26] between diethyl carbonate and [2,4,6-$^2H_3$]phenylmagnesium bromide gave tri([2,4,6-$^2H_3$]phenyl)methanol [yield 88%, m.p. 160—161 °C from light petroleum (b.p. 40—60 °C), $^2H_9 = 97\%$] which was reduced[25] to yield tri([2,4,6-$^2H_3$]phenyl)methane [yield 70%, m.p. 92—94 °C from light petroleum (b.p. 40—60 °C), $^2H_9 = 97\%$].

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References

1 T. W. Bentley, Mass Spectrometry Specialist Reports, Chemical Society (London), 1979, **5**, 81; Dunbar, R. C., in 'Gas Phase Ion Chemistry,' ed. M. T. Bowers, Academic Press, New York, 1979, volume 2, p. 202; F. W. McLafferty and F. M. Bockhoff, *J. Am. Chem. Soc.*, 1979, **101**, 1783.

2 J. H. Beynon, R. M. Caprioli, W. O. Perry, and W. E. Baitinger, *J. Am. Chem. Soc.*, 1972, **94**, 6828 and references cited therein; H. M. Rosenstock, J. Dannacher, and J. F. Liebman, *Radiat. Phys. Chem.*, 1982, **20**, 7.

3 R. J. Dickinson and D. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1363 and references cited therein.

4 E. Kluft and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Proc.*, in the press.

5 C. H. DePuy and V. M. Bierbaum, *Acc. Chem. Res.*, 1981, **14**, 146.

6 C. A. Wight and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1981, **103**, 6499; L. R. Thorne and J. L. Beauchamp, in 'Gas Phase Ion Chemistry,' ed. M. T. Bowers, Academic Press, New York, 1984, volume 3, p. 85.

7 R. L. White, C. L. Wilkins, J. J. Heitkamp, and S. W. Shaley, *J. Am. Chem. Soc.*, 1983, **105**, 4868.

8 J. H. Bowie and B. Nussey, *Chem. Commun.*, 1970, 17; *Org. Mass Spectrom.*, 1970, **3**, 933.

9 M. B. Stringer, D. J. Underwood, J. H. Bowie, J. L. Holmes, A. A. Mommers, and J. E. Szulejko, *Can. J. Chem.*, 1986, **64**, 764.

10 P. C. H. Eichinger, J. H. Bowie, and T. Blumenthal, *J. Org. Chem.*, 1986, **51**, 5078.

11 J. H. Bowie, *Aust. J. Chem.*, 1971, **24**, 989.

12 J. H. Bowie and S. Janposri, *Org. Mass Spectrom.*, 1976, **11**, 1290.

13 J. H. Bowie and M. B. Stringer, *Org. Mass Spectrom.*, 1985, **20**, 138.

14 G. Klass, V. C. Trenerry, J. C. Sheldon, and J. H. Bowie, *Aust. J. Chem.*, 1981, **34**, 519.

15 J. H. Bowie, *Mass Spectrom. Rev.*, 1984, **3**, 161; J. H. Bowie, M. B. Stringer, R. N. Hayes, M. J. Raftery, G. J. Currie, and P. C. H. Eichinger, *Spectrosc Int. J.*, 1987, in the press.

16 R. N. Hayes, J. C. Sheldon, J. H. Bowie, and D. E. Lewis, *J. Chem. Soc., Chem. Commun.*, 1984, 1431; *Aust. J. Chem.*, 1985, **38**, 355; M. B. Stringer, J. H. Bowie, and J. L. Holmes, *J. Am. Chem. Soc.*, 1986, **108**, 3888.

17 J. H. Bowie and M. B. Stringer, *Org. Mass Spectrom.*, 1985, **20**, 138.

18 P. C. Burgers, J. L. Holmes, J. E. Szulejko, A. A. Mommers, and J. K. Terlouw, *Org. Mass Spectrom.*, 1983, **18**, 254.

19 J. H. J. Dawson, Th. A. M. Kaandorp, and N. M. M. Nibbering, *Org. Mass Spectrom.*, 1977, **11**, 330; A. L. C. Smit and F. H. Field, *J. Am. Chem. Soc.*, 1977, **99**, 6471.

20 R. C. Huston and I. A. Kaye, *J. Am. Chem. Soc.*, 1942, **64**, 1576; A. Klages, *Chem. Ber.*, 1903, **36**, 3688.

21 N. V. Ioffe and B. V. Stolyarov, *Neftekhimiya*, 1964, **4**, 361 (*Chem. Abstr.*, 1965, **61**, 11912h).

22 J. H. Bowie, P. Y. White, and T. K. Bradshaw, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1966.

23 A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 1961, 241.

24 A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, New York and Toronto, 3rd edition, 1956, p. 259.

25 G. W. Gribble and R. M. Leese, *Synthesis*, 1977, 172.

26 A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, New York and Toronto, 3rd edition, 1956, p. 258.

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