Collision-Induced Dissociations of Deprotonated Phosphorus Esters. Specific Proton Transfer Accompanying Fragmentation

Richard A. J. O'Hair* and John H. Bowie
Department of Organic Chemistry, University of Adelaide, South Australia, 5001
Roger N. Hayes
Department of Chemistry, University of Nebraska-Lincoln, Lincoln. NE 68588-0362, USA

The collision-induced dissociations of deprotonated phosphorus esters are dominated by elimination of neutral species from the alkoxy groups with accompanying proton rearrangement. For example, $[(MeO)_2P(CH_2)(O)]^-$ eliminates CH_2O and CH_2 with specific proton transfer to carbon to produce, respectively, $(MeO)(Me)PO^-$ and $(MeO)(Me)PO_2^-$, whilst $[(EtO)_2P(CH_2)(O)]^-$ similarly eliminates MeCHO and C_2H_4. The loss of C_2H_4 from this ion occurs by the competitive losses of $CH_2{=}CH_2$ and MeCH; both losses form the product ion $Me(EtO)PO_2^-$. Thus neutral eliminations are accompanied by specific proton transfer to carbon.

We have reported[1] the formation of a variety of multiply bonded phosphorus species related to bismethylene metaphosphite $[P(CH_2)_2]^-$ and trimethylene metaphosphate $[P(CH_2)_3]^-$ anions.[2] For example, the reaction of HO^- with trimethylphosphine and trimethylphosphine oxide produces the precursor ions shown in equations (1) and (2), and these latter, upon collision activation in the mass spectrometer, yield the product ions shown in equations (3)–(6).

$$HO^- + Me_3P \longrightarrow (Me_2PCH_2)^- + H_2O \quad (1)$$

$$HO^- + Me_3PO \longrightarrow (Me_2PO_2)^- + CH_4 \quad (2)$$

$$(Me_2PCH_2)^- \nearrow [P(CH_2)_2]^- + CH_4 \quad (3)$$

$$(Me_2PCH_2)^- \searrow [P(CH_2)_3]^- + H_2 \quad (4)$$

$$(Me_2PO_2)^- \longrightarrow (CH_2PO_2)^- + CH_4 \quad (5)$$

In this paper we extend the investigation to an examination of deprotonated phosphorus esters. Our initial plan was to find perhaps better ways of generating ions like those shown in equations (3)–(5). In the event, such species were found, but the dominant reactions are those which involve proton transfer followed by elimination of a neutral species.

Results and Discussion

Collision-activation mass spectra [(CA) MS/MS] were measured with a VG ZAB 2HF mass spectrometer; collision activation MS/MS/MS experiments were performed with a Kratos MS 50-TA instrument. Full details of the procedures are provided in the Experimental section. The studied ions are listed in column 3 of Table 1. They were prepared by deprotonation reactions (see columns 1–3, Table 1), with the exception of three ions the syntheses of which are summarised in equations (6)–(8). The collisional activation mass spectra of all listed ions are either recorded in Table 1 or illustrated in Figures 1 and 2.

$$Me_2(MeO)PO + MeO^- \longrightarrow Me(MeO)PO_2^- + C_2H_6 \quad (6)$$

$$Me_2(CD_3O)PO + CD_3O^- \longrightarrow Me(CD_3O)PO_2^- + MeCD_3 \quad (7)$$

$$(EtO)_3PO + HO^- \longrightarrow (EtO)_2PO_2^- + EtOH \quad (8)$$

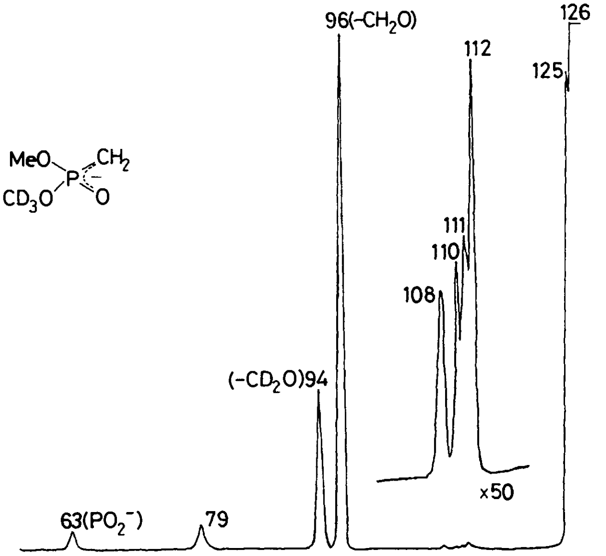


Figure 1. Collision-activation mass spectrum of $[(MeO)(CD_3O)P(CH_2)(O)]^-$ (placing a voltage of +1 000 V on the collision cell indicates that the losses of CH_2 and CD_2 are completely collision-induced, *i.e.* both peaks are completely shifted from their original positions).

The spectra are best divided into two categories, *viz.* (*i*) those of ions containing MeO groups, and (*ii*) those containing EtO or higher homologues. Let us consider the spectrum (Table 1) of $[(MeO)_2P(CH_2)(O)]^-$: all other ions containing a methoxy group behave similarly. The interpretation of this spectrum is aided by those of the three deuteriated derivatives; data from two are given in Table 1, while the spectrum of the third is reproduced in Figure 1. Our initial aim was to improve procedures for making small multiply bonded ions such as PO_2^-, PO^-, and CH_2PO^- *etc*, however this was not realised since these ions are only formed in small abundance (Table 1). Instead, $[(MeO)_2P(CH_2)(O)]^-$ undergoes competitive losses of $H^\cdot$, $CH_3^\cdot$, CH_2 and CH_2O; all processes involving the methoxy group.† The simple cleavage reactions are straightforward, but,

---

† In the case of an ion which has both a methyl and an alkoxy substituent, $[(CH_2)_2PO]^-$ is formed in small yield *e.g.*

$$[Me(MeO)P(CH_2)(O)]^- \longrightarrow [(CH_2)_2PO]^- + MeOH \quad \text{(see Table 1).}$$

Table 1. Collision-activation mass spectra (MS/MS) of deprotonated phosphorus esters [loss or formation; relative abundance (%)].

			Loss								
Neutral reactant	Reactant ion	Product ion	$H^\bullet$	$D^\bullet$	CH_2	CD_2	$Me^\bullet$	$CD_3^\bullet$	C_2H_4	$C_2H_2D_2$	C_2HD_3
$Me_2(MeO)PO$	NH_2^-	$Me(MeO)P(CH_2)(O)^-$	8		6		7				
$Me_2(CD_3O)PO$	NH_2^-	$Me(CD_3O)P(CH_2)(O)^-$	10	3		2	1	6			
$Me_2(MeO)PO$	MeO^-	$Me(MeO)PO_2^-$	63		5		26				
$Me_2(CD_3O)PO$	CD_3O^-	$Me(CD_3O)PO_2^-$	32	23		6	9	7			
$Me(MeO)_2PO$	NH_2^-	$(MeO)_2P(CH_2)(O)^-$	29		4		3				
$CD_3(MeO)_2PO$	DO^-	$(MeO)_2P(CD_2)(O)^-$	12	9	3		2				
$Et(MeO)_2PO$	NH_2^-	$(MeO)_2P(CHMe)(O)^-$	6		4		3				
$Me_2(EtO)PO$	NH_2^-	$Me(EtO)P(CH_2)(O)^-$	11						86[b]		
$Me(MeO)(EtO)PO$	NH_2^-	$MeO(EtO)P(CH_2)(O)^-$	15						95[c]		
$Me(EtO)_2PO$	NH_2^-	$(EtO)_2(CH_2)(O)^-$	18						100[d]		
$CD_3(EtO)_2PO$	DO^-	$(EtO)_2P(CD_2)(O)^-$	12						100[e]		
$Me(CD_3CH_2O)_2PO$	NH_2^-	$(CD_3CH_2O)_2P(CH_2)(O)^-$	10							39[f]	72[f]
$Me(EtO)(CD_3CH_2O)PO$	NH_2^-	$(EtO)(CD_3CH_2O)P(CH_2)(O)^-$	12						100[f]	100[f]	49
$Et(EtO)_2PO$	NH_2^-	$(EtO)_2P(CHMe)(O)^-$	14						100[g]		
$Me(EtO)(Pr^iO)PO$	NH_2^-	$(EtO)(Pr^iO)P(CH_2)(O)^-$	18						52[h]		
$CD_3(EtO)(Pr^iO)PO$	DO^-	$(EtO)(Pr^iO)P(CD_2)(O)^-$	15[j]	15[j]					51[k]		
$Me_2(Pr^iO)_2PO$	NH_2^-	$Me(Pr^iO)P(CH_2)(O)^-$	8								
$(MeO)_3PO$	NH_2^-	$(MeO)_2PO_2^-$	100		1		8				
$(EtO)_3PO$	NH_2^-	$(EtO)_2PO_2^-$(l)	8						100[m]		

[a] Both loss of 30 amu. [b] Composite peak (dish-shaped plus Gaussian), width at half height = 162 ± 3 volts. [c] Composite peak, unresolved; overlaps with Gaussian peak produced by loss of CH_2O. [d] Composite peak, width at half height = 160 ± 3 volts. [e] Composite peak; width at half height = 161 ± 3 volts. [f] Composite peak, not resolved. [g] Composite peak. [h] Composite peak, width at half height = 166 ± 3 volts. [i] Peak corresponding to loss of C_3H_6 is composite, *i.e.* usual Gaussian peak superimposed on dish (see *e.g.* Figure 2). However in this case, an additional Gaussian peak due to

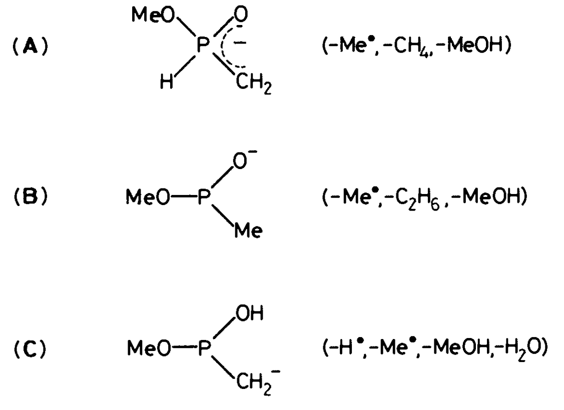
in contrast, the neutral eliminations are most unusual and we will concentrate on these in this paper.

The base peak of the spectrum is produced by the loss of formaldehyde. A pronounced isotope effect (H/D = 3.2) is observed (see Figure 1) for this process, *i.e.* CH_2O is lost more readily than CD_2O. This indicates that the H-transfer step is rate-determining. The only two possible analogies that we know to this reaction are in the ion chemistry of methoxyboranes[3] and deprotonated anisoles.[4] The first example is of hydride-ion donation by the methoxy group* to boron, to form a borohydride anion [equation (9)]. The second example is of proton transfer, followed by loss of CH_2O [equation (10)].

$$(MeO)_4B^- \longrightarrow (MeO)_3BH^- + CH_2O \qquad (9)$$

$$\begin{aligned} NH_2^- + PhOMe \longrightarrow \\ (C_6H_4)^-OMe \rightleftharpoons PhOCH_2^- \\ \downarrow \qquad \\ C_6H_5^- + CH_2O \qquad (10) \end{aligned}$$

Hydride transfer seems a less likely proposition in a phosphorus system than for electron-deficient borane ions. Nevertheless there are three possible structures which could be formed by loss of CH_2O from the phosphorus ester anions and these are shown in Scheme 1. Hydride rearrangement would form (**A**), while the two possible H-transfers to C and O would form (**B**) and (**C**) respectively. The fragmentations of (**A**), (**B**), and (**C**) can be predicted from a knowledge of earlier phosphorus[1] and cognate[3,7] studies. These predicted fragmentations are indicated in parentheses in Scheme 1.



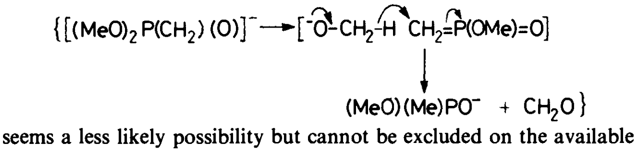
Scheme 1.

The consecutive collisional activation spectra (MS/MS/MS) of the product ions produced by the respective losses of CH_2O from $[(MeO)_2P(CH_2)(O)]^-$ and a labelled derivative are shown in Table 2. The former eliminates $Me^\bullet$, C_2H_6 and MeOH, thus identifying the product as (**B**) (Scheme 1). We suggest formation of (**B**) as shown in equation (11);† its collision-induced dissociations are summarised in equations (12)–(14). We represent the elimination of neutral species as stepwise reactions since, to date, we have only authenticated one concerted ion reaction in organometallic negative ion chemistry.[8]

---

* The methoxide ion is an ambident species in the gas phase, being able to react through both O and H.[5,6]

† The alternative hydride ion transfer, *i.e.*



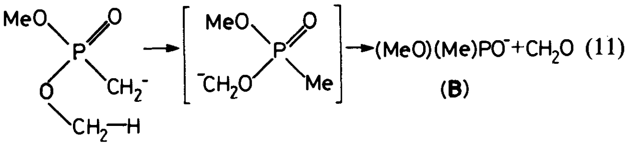
$$\{[(MeO)_2P(CH_2)(O)]^- \longrightarrow [^-O\text{-}CH_2\text{-}H\ CH_2{=}P(OMe){=}O] \downarrow (MeO)(Me)PO^- + CH_2O\}$$

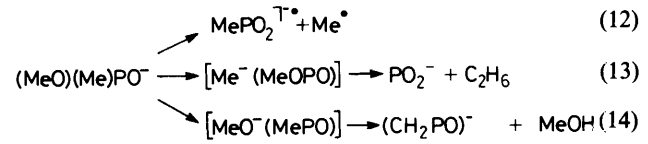
seems a less likely possibility but cannot be excluded on the available evidence.

Loss (*contd.*)										Formation			
CH_2O	CD_2O	MeOH	CD_3OH	C_3H_6	MeCHO	CD_3CHO	EtOH	Me_2CO	Pr^iOH	PO_3^-	PO_2^-	CH_2PO^-	PO^-
100		6									1	1	0.5
	100		8								2	2	1
37[a]		100								37[a]	18		
	100		47							22	10		
100										2	1	0.2	
100										2	1	0.1	
100										1	1		
					100		6						
100					56					12	2		
					63					13	2		
					92					8	2		
						100				6	2		
					77	68				7	2		
					53					1	1		
				100[i]	16[i]			34		10	1		
				100[i]	16[i]			31		12	1		
				31				100	4	1	1		
										10	2		
					2					26			

loss of CH_3CHO is superimposed on the low mass maximum of the C_3H_6 dish-shaped peak, thus making the composite peak unsymmetrical. [j] Unresolved. [k] Composite peak. [l] This spectrum is a unimolecular spectrum (*i.e.* no collision gas in the cell). In the presence of collision gas, the shape of the peak due to loss of C_2H_4 is masked by a pronounced peak due to loss of $C_2H_5^{\cdot}$. [m] Dish-shaped peak-width at half height = 138 ± 3 volts.

The possibility of concerted elimination reactions for equations (11), (13), and (14) cannot, however, be excluded on the available evidence.

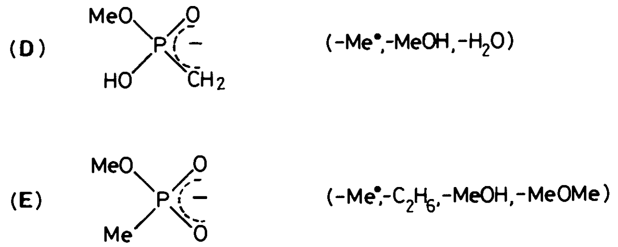




$$(MeO)(Me)PO^- \longrightarrow \begin{cases} MePO_2^{-\cdot} + Me^{\cdot} & (12) \\ [Me^-(MeOPO)] \longrightarrow PO_2^- + C_2H_6 & (13) \\ [MeO^-(MePO)] \longrightarrow (CH_2PO)^- + MeOH & (14) \end{cases}$$

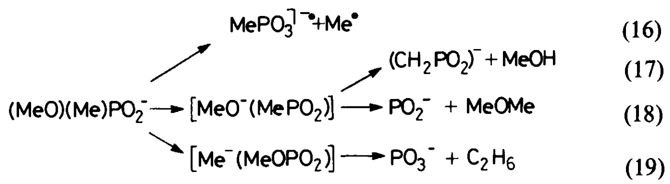
The loss of CH_2 from a methoxy group is unique in negative ion chemistry. It is a high energy process in so far as it is completely collision-induced with no unimolecular fraction (see legend to Figure 1). Figure 1 shows an isotope effect (H/D) of 2.0 in favour of CH_2 loss. In this case there are only two plausible structures for the product ion. These are shown in Scheme 2 as (**D**) and (**E**). The expected fragmentations of the two ions are indicated in parentheses. The CA MS/MS/MS data for both the unlabelled and D_3-labelled product ions shown in Table 2 clearly identify the product ion as (**E**).* The overall process is shown in equation 15; the collision-induced dissocations of the product ions are summarised in equations (16)–(19).

The spectra of ethyl and higher esters are recorded in Table 1 or Figure 2. There are two dominant proton transfer reactions, best illustrated for $[(EtO)_2P(CH_2)(O)]^-$ (Table 1 and *cf.* Figure 2). The first is loss of acetaldehyde, a reaction directly analogous to the loss of CH_2O from a methoxy group [see equation (11)]. This process has an overall deuterium-isotope effect (H/D) of 3.7, indicating that the proton transfer is involved in the rate-determining step.



Scheme 2.

$$[(MeO)_2P(CH_2)(O)]^- \rightarrow (MeO)(Me)P(O)OCH_2^- \rightarrow (MeO)(Me)PO_2^- + CH_2 \quad (15)$$



$$(MeO)(Me)PO_2^- \longrightarrow \begin{cases} MePO_3^{-\cdot} + Me^{\cdot} & (16) \\ [MeO^-(MePO_2)] \longrightarrow \begin{cases} (CH_2PO_2)^- + MeOH & (17) \\ PO_2^- + MeOMe & (18) \end{cases} \\ [Me^-(MeOPO_2)] \longrightarrow PO_3^- + C_2H_6 & (19) \end{cases}$$

The second loss involves the elements of C_2H_4. The data in Table 1 and Figures 2 and 3(*a*) show that there are two processes operating, which result in the formation of a composite peak; *i.e.* a sharp central Gaussian peak superimposed on a broad dish-shaped peak. The dish-shaped peak is very wide [see Figure 3(*a*)], indicating that this process has a large reverse activation energy.[9] The spectrum (Table 1 and Figure 3(*b*) of the labelled ion $[(CD_3CH_2O)_2P(CH_2)(O)]^-$ shows losses of CD_3CH and CH_2=CD_2. This is best illustrated in Figure 3(*b*), where loss of CD_3CH gives the Gaussian peak at *m/z* 126 superimposed on the dish-shaped peak (centred at *m/z* 127) for the loss of CH_2=CD_2. The product ion studies outlined

---

* $(MeO)_2PO_2^-$ has no carbanion site but loses CH_2 to a minor extent [1% of the base peak (Table 1) and *cf.* ref. 9]. In this case it seems that oxygen is the recipient site for H transfer, *i.e.*

$$(MeO)_2PO_2^- \longrightarrow (MeO)(HO)PO_2^- + CH_2.$$

$Me(CD_3O)PO_2^-$ also loses CD_2 (Table 1): whether this reaction is preceded by proton transfer $[Me(CD_3O)PO_2^- \longrightarrow [(CD_3O)(HO)P(CH_2)(O)]^- \longrightarrow CH_2D(HO)PO_2^- + CD_2]$ or whether H transfers to O is not known.

Table 2. CA MS/MS/MS data for product ions.

Precursor ion (*m/z*)	Product ion (*m/z*)	Spectra of product ions [*m/z* (loss) abundance]
$[(MeO)_2P(CH_2)(O)]^-$ (123)	$[123 - CH_2]$ (109)	94 ($CH_3^{\cdot}$) 11, 79 (C_2H_6) 26, 77 (MeOH) 100, 63 (MeOMe) 12
$[(MeO)_2P(CD_2)(O)]^-$ (125)	$[125 - CH_2]$ (111)	96 ($CH_3^{\cdot}$) 8, 79 ($C_2H_4D_2$, MeOH) 85, 78 (MeOD) 100, 63 ($MeOCHD_2$) 14
$[(MeO)_2P(CH_2)(O)]^-$ (123)	$[123 - CH_2O]$ (93)	78 ($CH_3^{\cdot}$) 100, 63 (C_2H_6) 12, 61 (MeOH) 6
$[(MeO)(CD_3O)P(CH_2)(O)]^-$ (126)	$[126 - CH_2O]$ (96)	78 ($CD_3^{\cdot}$) 100, 63 ($C_2H_3D_3$) 8, 61 (CD_3OH) 4
$[(MeO)_2P(CD_2)(O)]^-$ (125)	$[125 - CH_2O]$ (95)	80 ($CH_3^{\cdot}$) 100, 63 ($C_2H_4D_2$, MeOH) 14[a], 62 (MeOD) 4[a]
$[(EtO)_2P(CH_2)(O)]^-$ (151)	$[151 - C_2H_4]$[b] (123)	108 ($CH_3^{\cdot}$) 22, 95 (C_2H_4) 100, 79/78[a] (28), 63 (C_3H_8) 3
$[(EtO)(CD_3CH_2O)P(CH_2)(O)]^-$ (154)	$[154 - CD_3CH]$[b] (123)	108 ($(CH_3)^{\cdot}$) 16, 95 (C_2H_4) 100, 79/78[a] (30), 63 (C_3H_8) 3

[a] Not fully resolved. [b] The CA MS/MS spectrum of $Me(EtO)PO_2^-$ is 108 ($CH_3^{\cdot}$) 22, 95 (C_2H_4) 100, 79/78[a] (26), and 63 (C_3H_8) 3.

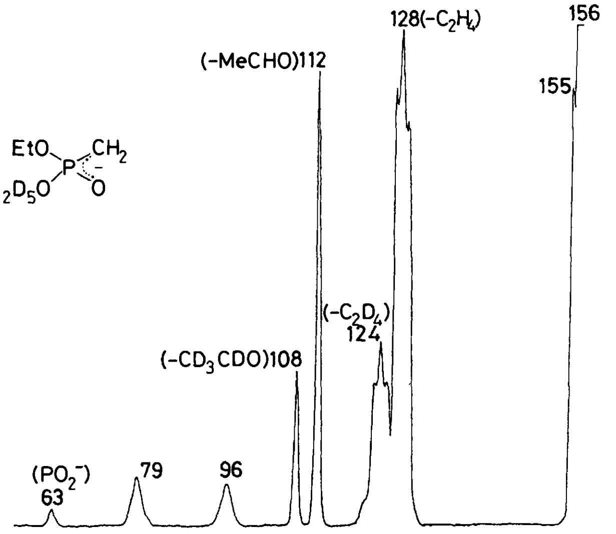


Figure 2. Collision-activation mass spectrum of $[(EtO)(C_2D_5O)P(CH_2)(O)]^-$.

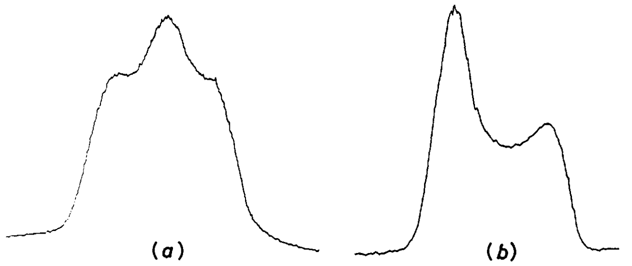
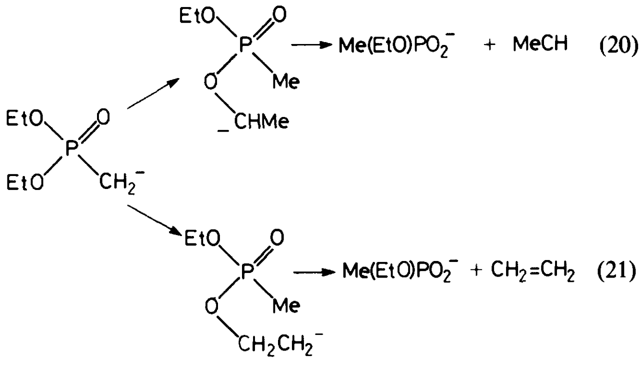


Figure 3. (*a*) Composite peak for loss of C_2H_4 from $[(EtO)_2P(CH_2)(O)]^-$. Sharp central peak loss of MeCH, dish-shaped peak loss of $CH_2{=}CH_2$. Width of peak at half height = 161 ± 3 volts; (*b*) peak profile for losses of $CH_2{=}CD_2$ and CD_3CH from $[(CD_3CH_2O)_2P(CH_2)(O)]^-$. Large Gaussian peak at *m/z* 126 (loss of CD_3CH) superimposed on dish-shaped peak at *m/z* 127 (loss of $CH_2{=}CD_2$).

in Table 2, show that losses of both MeCH and $CH_2{=}CH_2$ from $[(EtO)_2P(CH_2)(O)]^-$ yield the same ion $Me(EtO)PO_2^-$; *i.e.* both H-transfer reactions occur to carbon, not oxygen. Thus the two competing reactions occur as shown in equations (20) and (21). The loss of MeCH is directly analogous to the loss of CH_2 from a methoxy group [*cf.* equation (11)], while the loss of ethene proceeds through a six-centre state and is directly analogous to similar losses from carbonyl enolate ions[10] and deprotonated *N*-ethyl amides,[11] all of which give either broad or dish-shaped peaks.



In conclusion, deprotonated phosphorus esters $[(R^2(RO)P(CH_2)(O)]^-$ (R^2 = alkyl or alkoxy; R = alkyl), on collision-activation, undergo competitive neutral eliminations from alkoxy groups, *viz.* (*i*) elimination of an aldehyde (*e.g.* CH_2O and MeCHO when R = Me and Et respectively), or a ketone (*e.g.* Me_2CO when R = Pr^i), (*ii*) a carbene (*e.g.* CH_2 and MeCH when R = Me and Et respectively), and (*iii*) an alkene (*e.g.* $CH_2{=}CH_2$ when R = Et). All of these reactions involve specific H-transfer to the carbanion centre.

Experimental

Full experimental details for the operation of the ZAB 2HF spectrometer[12] have been given previously.[10] The specific conditions for the collisional activation MS/MS spectra are as follows: chemical ionization slit in the source, ion source temperature 150 °C, electron energy 70 eV, and accelerating voltage 7 kV. All phosphorus esters were introduced through the septum inlet which was maintained at 150 °C and source pressure 5×10^{-7} Torr.* The reactant ions are as shown in Table 1; NH_2^- (from NH_3), DO^- (from D_2O), and MeO^- (or CD_3O^-) from MeONO (or CD_3ONO)[13] (NH_3, D_2O, or MeONO pressure 1×10^{-5} Torr). The estimated total source pressure was 10^{-1} Torr. Helium pressure in the second collision cell [unless indicated to the contrary, *cf.* $(EtO)_2PO_2^-$ (Table 1)] measured 2×10^{-7} Torr; there was a 10% reduction in the main beam. The electric sector scan mode was used. The measured isotope effects are a mean of 10 individual scans and, the overall experimental error is ±5%.

Collision-activation (CA) MS/MS/MS experiments were performed with a Kratos MS 50-TA instrument[14] with the following conditions: chemical ionisation Mark IV source, ion source temperature 100 °C, electron energy 280 eV, emission current 500 μ A, and accelerating voltage 8 kV. MeO^- was used as the reactant ion (MeONO pressure 1×10^{-6} Torr), phosphorus ester pressure 2×10^{-5} Torr, estimated source pressure 10^{-1} Torr. Helium was present in both collision cells at a measured pressure of 2×10^{-6} Torr; there was a 30% reduction in the main beam.

---

* 1 Torr = 133.322 Pa.

Table 3. Experimental data on labelled compounds.

Compound	Literature reference	% Yield	B.p./°C (mmHg)	% Deuterium incorporation	δ_P(ppm)[a]	δ_H[b]
$CD_3(MeO)_2PO$	23	77	64–66 (12)	99% D_3	−33.9	3.98 (6 H, d)
$CD_3(EtO)_2PO$	23	72	78–80 (12)	67% D_3	−31.2	1.39 (6 H, t), 4.19 (4 H, m)
$Me(MeO)(CD_3O)PO$	24	15	68–70 (13)	99% D_3	−33.8	1.50 (3 H, d), 4.00 (4 H, d)
$Me(CD_3CH_2O)_2PO$	24	42	108–110 (25)	98% D_6	−31.2	1.42 (3 H, d), 4.00 (4 H, d)
$Me(EtO)(CD_3CH_2O)PO$	24	22	103–106 (20)	98% D_3	−31.2	1.30 (3 H, t), 1.35 (3 H, d), 4.03 (4 H, m)
$Me(EtO)(C_2D_5O)PO$	24	13	88–90 (15)	99% D_5	−31.1	1.32 (3 H, t), 1.45 (3 H, d), 4.08 (2 H, m)
$Me_2(CD_3O)PO$	24	10	64–66 (14)	99% D_3	−54.5	1.49 (6 H, d)
$Me_2(CD_3CH_2)PO$	24	14	80–83 (12)	98% D_3	−52.7	1.55 (6 H, d), 4.08 (2 H, d)

[a] $CDCl_3$ solution, 95% H_3PO_4 internal standard. [b] $CDCl_3$ solution, $SiMe_4$ internal standard.

Synthesis of Phosphorus Esters.—The following esters are known: $Me(MeO)_2PO$,[15] $Et(MeO)_2PO$,[16] $Me(EtO)_2PO$,[17] $Et(EtO)_2PO$,[18] $Me(MeO)(EtO)PO$, $Me(EtO)(Pr^iO)PO$,[19] $Me_2(MeO)PO$,[20] $Me_2(EtO)PO$,[21] and $Me_2(Pr^iO)PO$.[22] $(MeO)_3PO$ and $(EtO)_3PO$ are commercial samples.

Labelled Compounds.—All labelled compounds were prepared by standard procedures and the details are listed in Table 3.

Acknowledgements

This work was supported with the aid of a grant from the Australian Research Council. R. N. H. acknowledges the support of the Midwest Center for Mass Spectrometry, which is an N.S.F. instrument facility.

References

1 R. A. J. O'Hair, J. C. Sheldon, and J. H. Bowie, *J. Chem. Soc., Dalton Trans.*, 1988, 2837.
2 A. Rajca, J. E. Rice, A. Streitwieser, and H. F. Schaefer, *J. Am. Chem. Soc.*, 1987, **109**, 4189.
3 R. N. Hayes, J. H. Bowie, and J. C. Sheldon, *Organometallics*, 1986, **5**, 162; G. J. Currie, K. M. Downard, J. C. Sheldon, and J. H. Bowie, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1973.
4 J. C. Kleingeld and N. M. M. Nibbering, *Tetrahedron*, 1983, **39**, 4193; P. C. H. Eichinger, J. H. Bowie, and R. N. Hayes, *Aust. J. Chem.*, in the press.
5 S. Ingemann, T. C. Kleingeld, and N. M. M. Nibbering, *J. Chem. Soc., Chem. Commun.*, 1982, 1009.
6 J. C. Sheldon, J. H. Bowie, and R. N. Hayes, *Nouv. J. Chim.*, 1984, **8**, 79; J. C. Sheldon, G. J. Currie, J. Lahnstein, R. N. Hayes, and J. H. Bowie, *Nouv. J. Chim.*, 1985, **9**, 205.
7 R. A. J. O'Hair, J. H. Bowie, and G. J. Currie, *Aust. J. Chem.*, 1988, **41**, 57, and references cited therein.
8 J. C. Sheldon, J. H. Bowie, and P. C. H. Eichinger, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1263.
9 S. Meyerson, D. J. Harvan, J. R. Hass, F. Ramirez, and J. F. Marecek, *J. Am. Chem. Soc.*, 1984, **106**, 6877.
10 M. B. Stringer, J. H. Bowie, and J. L. Holmes, *J. Am. Chem. Soc.*, 1986, **108**, 3888.
11 M. J. Raftery and J. H. Bowie, *Int. J. Mass Spectrom. Ion Proc.*, 1988, **85**, 167.
12 V. G. Instruments, Wythenshawe, Manchester, UK; Model ZAB 2HF.
13 D. P. Ridge and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1974, **96**, 3595.
14 D. J. Burinsky, R. G. Cooks, E. K. Chess, and M. L. Gross, *Anal. Chem.*, 1982, **54**, 295; M. L. Gross, E. K. Chess, P. A. Lyon, F. W. Crow, S. Evans, and H. Tudge, *Int. J. Mass Spectrom. Ion Phys.*, 1982, **42**, 243.
15 S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 1953, 2224.
16 V. R. Jentzsch, P. Schneider, and G. W. Fischer, *J. Prakt. Chem.*, 1975, **317**, 733.
17 A. H. Ford-Moore and J. H. Williams, *J. Chem. Soc.*, 1947, 1465.
18 B. C. Saunders, G. J. Stacey, F. Wild, and I. G. E. Wilding, *J. Chem. Soc.*, 1948, 699.
19 H. S. Aaron, R. T. Uyeda, H. F. Frack, and J. I. Miller, *J. Am. Chem. Soc.*, 1962, **84**, 617.
20 H. Reihoudt, D. Bianchi, and D. Moelle, *Chem. Ber.*, 1957, **90**, 1656.
21 G. M. Kosolapoff and R. M. Watson, *J. Am. Chem. Soc.*, 1951, **73**, 5466.
22 O. A. Raevskii, M. M. Gilyazov, and Y. A. Levin, *Zh. Obshch. Khim.*, 1983, **53**, 1720.
23 R. Engel, 'Synthesis of Carbon Phosphorus Bonds,' CRC press, Boca Raton, Florida, 1988; A. H. Ford-Moore and B. J. Perry, *Org. Synth.*, 1963, **4**, 325.
24 Z. Pelchowicz, *J. Chem. Soc.*, 1961, 238.

Paper 9/02775K
Received 29*th June* 1989
Accepted 21*st September* 1989