Skeletal Rearrangements in the Negative Ion Mass Spectrum of an Ylide

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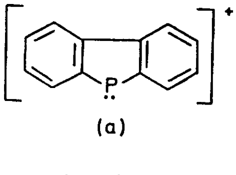
Summary The 70 eV negative ion mass spectrum of (diacetylmethylene)triphenylphosphorane contains skeletal rearrangement ions complementary to those observed in positive ion studies; this behaviour is rationalised in terms of the reduction of phosphorus from the penta- to the ter-valent state.

THE numerous examples of bond formation *via* skeletal rearrangement in positive ion mass spectra have few analogies in negative ion spectra.[1] The positive ion spectra of phosphines, keto-phosphoranes, and phosphine oxides exhibit an abundance of rearrangement ions,[2–5] the most significant being due to the formation of the phosphofluorenyl cation (a) or P–O bonds.



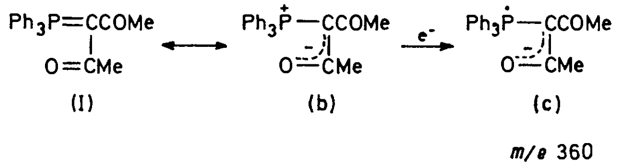
(a)

The latter process has been observed for β keto and ester alkylidene phosphoranes[3,4] and has been attributed to the dipolar nature of the compounds[6,7] where the ionic forms contribute to their ground state structure. We have investigated the 70 eV negative ion mass spectra of diketophosphoranes such as (I) (Table).

TABLE

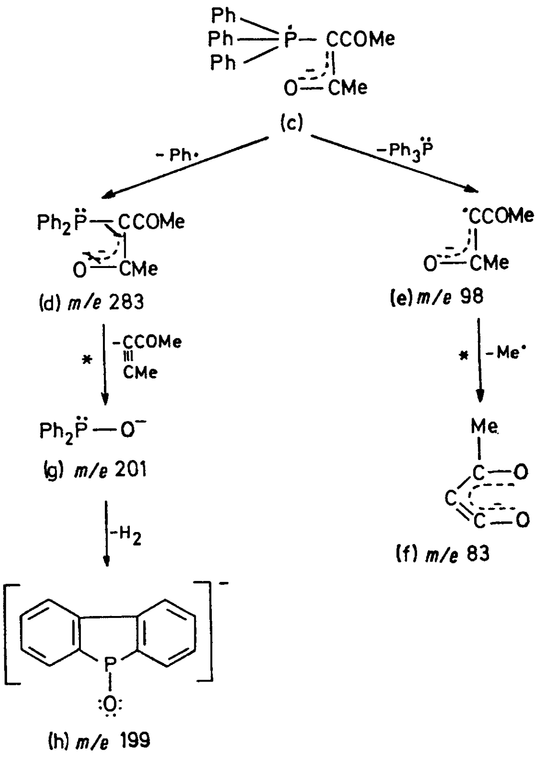
m/e	Relative intensity	Assignment
360	0·2	$M^{-\cdot}$
283	100·0	$[M\text{-Ph}]^-$
201	34·2	$[Ph_2PO]^-$
183	0·2	$[\overline{C_6H_4PC_6H_4}]^-$
98	11·1	$[C(COMe)_2]^{-\cdot}$
83	97·4	$[C(COMe)CO]^-$

Four metastable ion peaks were observed corresponding to the processes *m/e* 283 → 241 (205·2), 283 → 201 (142·7), 201 → 175 (152·3), and 98 → 83 (70·3). That at *m/e* 142·7 was particularly intense. Rearrangement ions similar to those observed in the positive examples involving P–O bond and phosphofluorenyl ion formation were indicated by ions at *m/e* 201 and *m/e* 183 respectively.



Molecular ion formation (c) may be rationalised as electron attachment at the positive centre of the zwitterionic form (b) of the resonance hybrid of (I). The resulting singly-occupied phosphorus orbital can achieve greater stability *via* radical loss, producing a stable tervalent phosphorus atom and the ions (d) and (e). (d) is more abundant than (e) since the latter readily loses a radical to give the more stable even electron ion (f). The intense metastable ion peak at *m/e* 142·7 confirms decomposition from $[M-\text{Ph}]^-$ to the rearrangement ion *m/e* 201, (g), involving P–O bond formation. This is a significant ion in the spectrum and, in a manner similar to the positive ion studies, exhibits hydrogen molecule loss to yield the cyclic ion *m/e* 199 (h) (0·3%). The ion (g) also fragments to *m/e* 175 (acetylene loss) as evidenced by the metastable ion peak at *m/e* 152·3. The peak observed at *m/e* 205·2 results from CH_2CO loss from the $[M-\text{Ph}]^-$ ion, in which a four- or six-membered (McLafferty-type) transition state could be involved.

The phosphofluorenyl anion (*m/e* 183) is observed but is of low intensity. No metastable ion evidence is noted for its formation or subsequent decomposition.



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