A Thermal P^{III}-P^{V} Rearrangement Proceeding by a Radical Mechanism

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Summary The reaction between oximes and tervalent phosphorus compounds to give the corresponding alkylidenamide [$R^1_2P(O)N{=}CR^2R^3$] proceeds through the P^{III} isomer ($R^1_2PO{-}N{=}CR^2R^3$) which spontaneously rearranges (at least in part) by a radical-cage mechanism.

Although many rearrangements of phosphorus compounds are known, the mechanism of very few has been established. In particular the formation of strong phosphoryl bonds promotes a wide range of P^{III}–P^{V} rearrangements of which the Arbusov reaction is the best known. We present here evidence for a radical cage mechanism for an Arbusov-type reaction involving oximes and tervalent phosphorus compounds[1] (reaction 1).

$$\underset{}{R^1_2PX} + R^2R^3C{=}N{-}OH \rightarrow \underset{\text{(I)}}{R^2R^3C{=}N{-}OPR^1_2} \rightarrow \underset{\text{(II)}}{R^2R^3C{=}N{-}P({:}O)R^1_2} \qquad (1)$$

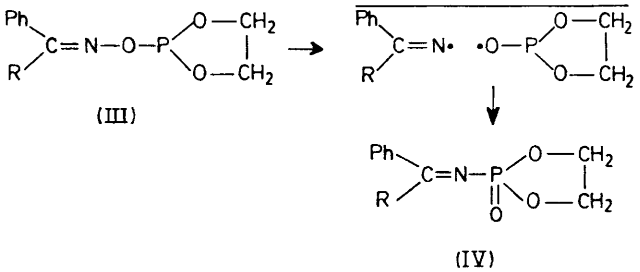
R^1 = alkoxy, aryl, or NMe_2;
R^2 and R^3 = aryl, alkyl, alkoxy, or NH_2;
X = halogen or NMe_2

This reaction proceeds at low temperatures and in general the P^{III} intermediate (I) cannot be isolated. However, treatment of benzophenone oxime with Ph_2PCl in the presence of Et_3N in diethyl ether–toluene at low temperatures (−60 °C) produced an immediate change in the ^{31}P n.m.r. spectrum.† The line at 80 p.p.m. (Ph_2PCl) was replaced by a low-field line at 115 p.p.m. attributed to the P^{III} species (I; $R^1 = R^2 = R^3$ = Ph). When the temperature of the reaction mixture was raised from −60 to −40 °C rearrangement was virtually complete after 20 min, with 94% conversion of (I) into a mixture of (II; $R^1 = R^2 = R^3$ = Ph) [m.p. 120—122 °C, 70%, ^{31}P 15·5 p.p.m.], the phosphinylated oxime, $Ph_2C{=}N{-}OP(O)Ph_2$, [9%, ^{31}P 33·6 p.p.m., identical with an authentic sample[4]], and 13% of an unknown product with a ^{31}P peak at 22·4 p.p.m.

At 0 °C in toluene, strong ^{31}P C.I.D.N.P. effects were observed, in particular a strong emission at 15 p.p.m. due to polarised (II). This changed to an absorption, and the normal spectrum was observed after 3 min. This suggests strongly that part of the reaction at least proceeds by a radical mechanism (2).

$$Ph_2C{=}N{-}O{-}PPh_2 \rightarrow \overline{Ph_2C{=}N\cdot\ \cdot O{-}PPh_2} \rightarrow Ph_2C{=}N{-}P({:}O)Ph_2 \qquad (2)$$

Application of Kaptein's rules to the above process, using the *g* value of 2·0033 for the iminyl radical[2] and 2·004 for the $Ph_2PO\cdot$ radical, which has a large positive phosphorus coupling constant,[3] predicts emission for the formation of (II) by radical cage recombination.



(III)

(IV)

a; R = Ph
b; R = Me

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† ^{31}P data are given in p.p.m. from 85% H_3PO_4, high frequency (low field) shifts being designated as positive, in accord with current (see for example, R. K. Harris, Senior Reporter, 'Nuclear Magnetic Resonance,' Specialist Periodical Reports, The Chemical Society, 1975, vol. 4, p. iv) convention.

The analogous reaction between benzophenone oxime and 2-chloro-1,3,2-dioxaphospholan is considerably slower than the reaction involving acyclic phosphorus compounds. Reaction at −60 °C produces a single isolable‡ species, ^{31}P 123·8 p.p.m., stable at this temperature, assigned structure (IIIa). When solutions of (IIIa) in toluene were heated to 60 °C, absorption at 123·8 p.p.m. corresponding to (IIIa) disappeared, being replaced by a peak at 18·8 p.p.m. due to (IVa), m.p. 139—140 °C.

Table

Rate of rearrangement of $Ph(Me)C{=}N{-}OP(OCH_2)_2$ (IIIb) at 34 °C

Solvent	$10^4k_1/s^{-1}$	Solvent	$10^4k_1/s^{-1}$
CCl_4	1·78	C_6D_6	1·41
$CDCl_3$	3·2 (3·0)[a]	CD_3CN	1·77

[a] Rate of appearance of product (IVb).

After 9 min at 60 °C, 70% conversion of (IIIa) into (IVa) was observed, with the formation of *ca.* 6% of unknown side product, ^{31}P 16·7 p.p.m. The reduced reactivity of (IIIa) relative to (I), (estimated to be *ca.* 10^2) is probably due to increased strain[5] in the dioxaphospholan radical, consequent on the delocalisation in the radical on formation of a 3-electron bond. Polarisation of the ^{31}P resonance of (IVa) was also observed when solutions of (IIIa) were heated at 60 °C in the n.m.r. probe.

The rearrangement of the corresponding acetophenone oxime derivative of 1,3,2-dioxaphospholan proceeds at a convenient rate at temperatures in the 30—60 °C range. The rate of rearrangement was calculated from the measured area of the (unpolarised§) ^1H n.m.r. peak corresponding to the CH_3 protons of the analogous P^{III} intermediate (IIIb) (^{31}P 120·9 p.p.m.) at δ 2·99 at discrete time intervals. In $CDCl_3$ the rate of appearance of the product (IVb) was also measured (Table) confirming the intermediacy of (IIIb). The first-order rate constant is almost independent of the nature of the solvent (Table), which is to be expected for a homolytic process of this type.[6]

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‡ The structure of the intermediate (I) rests mainly on the large low-field chemical shift and on its mode of formation. The structures of (IIIa) and (IIIb), which can be isolated, were confirmed by their ^1H and ^{13}C n.m.r. spectra. In particular the relatively large values for $|^3J_{PC}|$ for the iminyl carbon atoms [5·4 and 5·0 Hz respectively for (IIIa) and (IIIb)], establish the C=N–O–P part structure. The P^{III} nature of the intermediates is clearly established by the magnitude of the ^{31}P shift and confirmed by the large (8·8 and 9·3 Hz) $|^2J_{PC}|$ values for the CH_2 carbons of the dioxaphospholan ring, compared with the smaller values for the corresponding P^V products for (IVa) and (IVb) (*ca.* 1·0 and 0·0 Hz).

§ Work on the reaction of iminyl radicals of the acetophenone type in our laboratory has shown that strong polarisation of the CH_3 protons is neither to be expected on the basis of calculation of a_H values, nor found experimentally, even though polarisation of other nuclei in such systems may be observed.

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