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The Reaction Between Oximes and Tervalent Phosphorus Compounds: A Low-Temperature Radical Rearrangement Process

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Ketoximes react rapidly with X_2PCl compounds where X = Ph, Me_2N, EtO and X_2 = OCH_2CH_2O at low temperatures (−60 to −80 °C) in the presence of triethylamine to give a P^{III} intermediate **2**, which rearranges by a unimolecular process to the corresponding *N*-phosphinylated imine **3**. Free radicals, formed by capture of the initially produced phosphonyl radical, are detected by ESR spectroscopy, and evidence for a radical cage process is obtained from ^{31}P CIDNP studies. Where X_2 = OCH_2CH_2O, the P^{III} intermediate (**2d,e**) can be isolated, and the structure established from the ^{13}C NMR spectra. Kinetic measurements show compound **2e** to rearrange (30 – 60 °C) ca. 10 times more slowly than the open chain compound (X = OEt), and the negative activation entropy suggests that this particular system (**2e**) rearranges, in part, by a cyclic transition state.

Reaktion zwischen Oximen und dreiwertigen Phosphorverbindungen: Radikalische Umlagerung bei niedriger Temperatur

Ketoxime reagieren mit X_2PCl-Verbindungen (X = Ph, Me_2N, EtO, X_2 = OCH_2CH_2O) bei niedrigen Temperaturen (−60 bis −80 °C) in Gegenwart von Triethylamin zu einem P^{III}-Zwischenprodukt **2**, das unimolekular zum entsprechenden *N*-Phosphinylimin **3** umlagert. Freie Radikale, die durch Abfangen des im Anfangsschritt gebildeten Phosphonyl-Radikals entstanden sind, werden durch ESR-Spektroskopie nachgewiesen, und Hinweise auf einen Radikalkäfig-Prozeß werden von ^{31}P-CIDNP-Untersuchungen erhalten. Bei X_2 = OCH_2CH_2O kann die P^{III}-Zwischenstufe (**2d,e**) isoliert werden, deren Konstitutionen anhand der ^{13}C-NMR-Spektren zugeordnet werden. Nach kinetischen Messungen lagert **2e** bei 30 – 60 °C ca. 10mal langsamer um als die offenkettige Verbindung **2** mit X = OEt. Die negative Aktivierungs-Entropie zeigt, daß **2e** teilweise über einen cyclischen Übergangszustand umlagert.

Many rearrangements of organophosphorus compounds involve the change in oxidation state, P^{III}-P^{V}, of which the best known is the Arbusov reaction [1]. Most of these rearrangements, generally involving the scission of a C – O bond, proceed by heterolytic mechanisms, frequently through the action of electrophilic catalysts.

Similarly most of the classical rearrangements involving fission of the N – O bond proceed by ionic, polar or concerted mechanisms, and until recently there was little evidence that rearrangements of organophosphorus compounds might involve the homolytic fission of the N – O bond.

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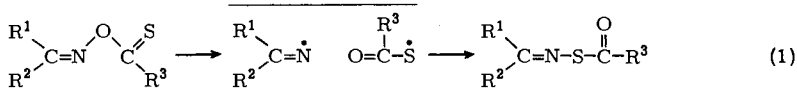
However, our work[2] has shown that a wide class of intramolecular rearrangements of derivatives of hydroxylamine proceed at low temperatures through radical pairs (see below).



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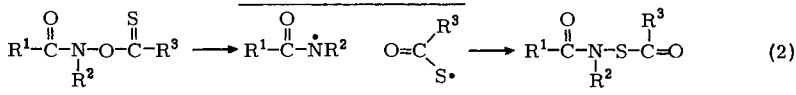

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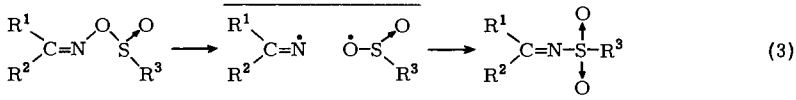

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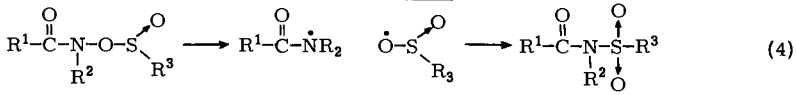

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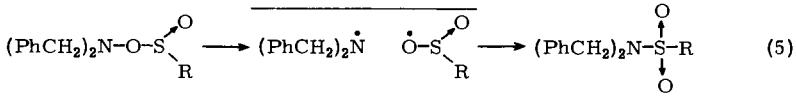
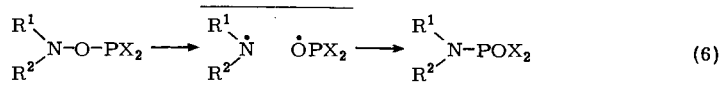


(5)

Under optimum conditions these reactions are essentially quantitative, and hence the radical nature of these processes is not immediately evident. More detailed investigations, however, reveal minor side products derived from escaped radicals, which can in some reactions be detected and characterised by ESR spectroscopy.

By analogy with (3) – (5) it is reasonable to assume that hydroxylamine derivatives of P^{III} rearrange in a similar manner. On closer examination it appears that while the fully oxidised leaving group promotes heterolytic rearrangement, e.g. *Beckmann, Tiemann* and *Lossen,* involving electron deficient nitrogen, or nitrenium ions[3], reduced leaving groups promote homolytic rearrangement.

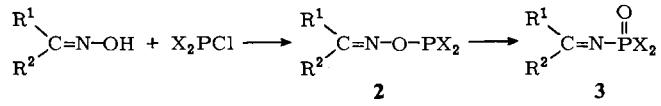
Accordingly, the nitrogen analogue of the Arbusov reaction should proceed by a radical cage process (6) and not by a heterolytic mechanism.



(6)

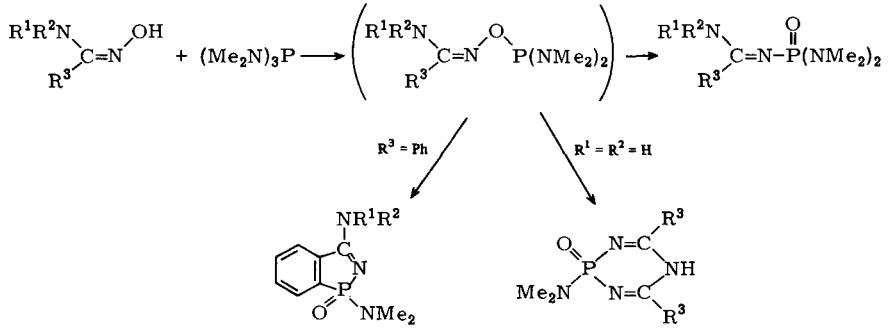
1

Compounds of the type **1** are, however, unknown, and oximes react with tervalent phosphorus compounds to give the oxidised product (**3**) directly. Evidence[4] for the formation of such intermediates, **2**, in the reaction between *O,O'*-diethyl phosphorous chloride (X = OEt) and oximes or acetohydroxamates (R^1 = Et, R^2 = Me; R^1 = Me, R^2 = OEt), comes from observation of the ^{31}P chemical shifts in the region anticipated for phosphite esters (134 – 143 ppm). The corresponding reaction with diphenylphosphinous chloride has been developed to give an amine synthesis and for the preparation of isothiocyanates[5].

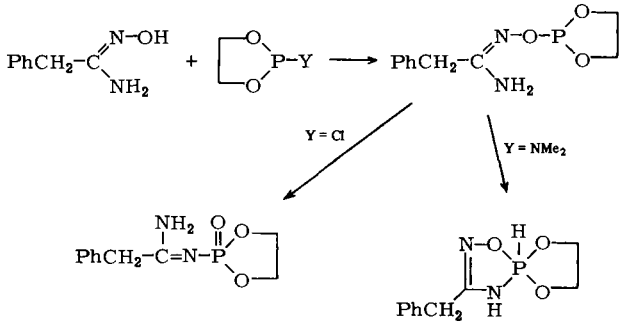


2 **3**

Amidoximes react in a similar manner with tris(dimethylamino)phosphane, although other final products are formed in this case[6]:



Further evidence for the structure of the intermediate, **2**, comes from the reaction of amidoximes with 2-substituted 1,3,2-dioxaphospholans. The N^2-[bis(dimethylamino)phosphinyl]-amidine is formed from 2-chloro-1,3,2-dioxaphospholan whereas a spiro-oxyphosphorane is formed in the reaction of 2-dimethylamino-1,3,2-dioxaphospholan. This presumably arises by cyclisation of the P^{III} intermediate, as reactions of this kind are common.



In the present work we have isolated and characterised by ^{13}C NMR spectroscopy two of these P^{III} intermediates formed from oximes and carried out an investigation into the mechanism of the rearrangement.

Results and Discussion

At room temperature the main product of the reaction between oximes and X_2PCl [X = Ph, OEt, NMe_2 and X_2 = OCH_2CH_2O] is the *N*-phosphylimine*), **3**. The reac-

*) The collective term phosphyl is used for the group $P(O)X_2$ as defined in a previous publication[7].

tion with diphenylphosphinous chloride and benzophenone oxime gives two major products, the first identified as the imine **3a** and the second as the phosphinylated oxime, **4** (Fig. 1), with minor, as yet unidentified, products ($\delta^{31}P$ = 29.1 and 21.2) starred in Fig. 1. By comparison with the chemical shift of triarylphosphane oxides[8] ($\delta^{31}P$ = 22 – 27), and by analogy with the cyclisation of the amidoxime observed by *Barrans*[6], these are attributed to products arising from phosphinylation of the aromatic ring (*vide infra*).

$$Ph_2C{=}N{-}OH + Ph_2PCl \longrightarrow \underset{\mathbf{3a}}{Ph_2C{=}N{-}\overset{\overset{O}{\|}}{P}Ph_2} + \underset{\mathbf{4}}{Ph_2C{=}N{-}O{-}\overset{\overset{O}{\|}}{P}Ph_2}$$

At low temperatures (−40 to −60 °C) equivalent mixtures of Ph_2PCl, benzophenone oxime, and triethylamine (in toluene/ether) gave a single peak in the P^{III} region ($\delta^{31}P$ = 115.0) attributed to the intermediate **2a** (X = Ph), see Table 1. No signal corresponding to the starting material was observed showing the formation of **2** to be rapid. On warming the mixtures, the ^{31}P absorption corresponding to **2a** disappeared and was replaced by the major peak corresponding to the imine **3a** with smaller peaks due to side products. Data for this and similar reactions are summarised in Table 1.

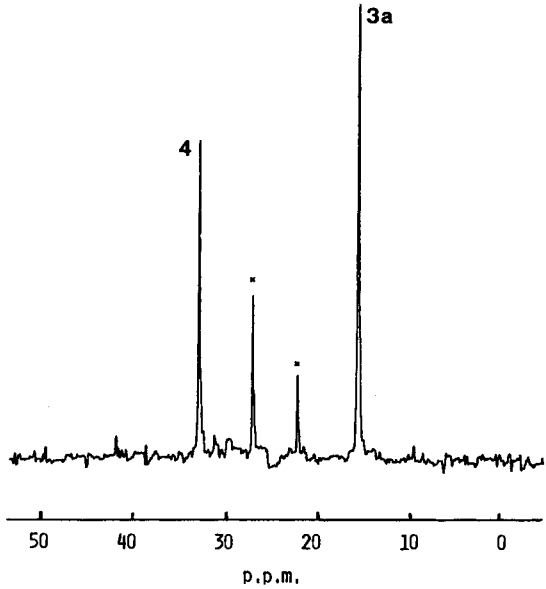


Fig. 1. Noise-decoupled $^{31}P\{^1H\}$ spectrum of the products **3a** and **4** from the reaction between diphenylphosphinous chloride and benzophenone oxime. Unidentified products are marked ×

In general, lower yields of **3** were obtained when the reaction was carried out at 25 °C, than when the initial reaction was carried out at −40 °C and the mixture warmed. Qualitatively, it was found that the rate of rearrangement decreased in the order $Ph_2P > (Me_2N)_2P \gg (EtO)_2P > (CH_2O)_2P$.

Table 1. ^{31}P NMR Data for the P^{III} intermediates **2** and the reaction products **3**

	Oxime	X_2PY	$\delta^{31}P$ (ppm) X_2PY	**2**	**3**	% Conversion to **3** (NMR)
a	$Ph_2C=N-OH$	Ph_2PCl	80.5	115.0	15.5	73 (50)[b]
b	$Ph_2C=N-OH$	$(Me_2N)_2PCl$	160	134.4	15.9	66
c	$Ph_2C=N-OH$	$(Me_2N)_3P$	122	120	15.9	67
d	$Ph_2C=N-OH$	$(CH_2O)_2PCl$	167	123.8	18.8	87
e	$Ph(Me)C=N-OH$[a]	$(CH_2O)_2PCl$	167	120.9	20.4	100
f	$Ph(Me)C=N-OH$[a]	$(EtO)_2PCl$	164	135.3	2.9	68 (47)[b]

[a] *E*-isomer. – [b] Reaction at 25 °C.

The rearrangement of **2a** proceeded rapidly at −40 °C ($t_{\frac{1}{2}} \approx 7$ min), whereas the rearrangement of **2f** could be followed conveniently at 25 °C (*vide infra*). The rate was reduced further by substituting the dioxaphospholan ring ($X_2 = OCH_2CH_2O$), and these intermediates, **2d** and **e**, were isolated by precipitation (see Exp. Part). Their structures were characterised by analysis of their ^{13}C NMR spectra (Table 2).

Table 2. $^{13}C\{^1H\}$ NMR Spectra of the intermediates **2d,e** and corresponding products **3d,e** isolated from the reaction of 2-chloro-1,3,2-dioxaphospholan with acetophenone oxime (A) and benzophenone oxime (B) (C-1, C-2 ... aromatic nuclei)

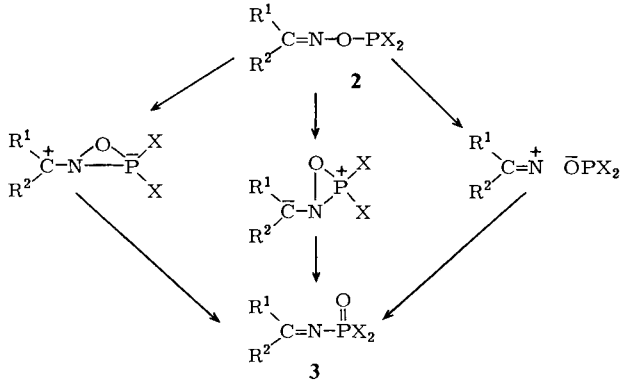
A	Chemical shift (ppm) **2e**[a]	Coupling (Hz)	Chemical shift (ppm) **3e**	Coupling (Hz)
CH_2CH_2	66.1 (d)	$^2J_{PC} = 9.3$	66.1 (s)	$^2J_{PC} \approx 0$
CH_3	13.7 (s)		24.6 (d)	$^3J_{PC} = 12.2$
C=N	161.7 (d)	$^3J_{PC} = 5.0$	183.3 (d)	$^2J_{PC} = 2.0$
C-1	135.2 (s)		137.6 (d)	$^3J_{PC} = 31.0$
C-2	126.3 (s)		(128.1) (s)	
C-3	128.5 (s)		(128.4) (s)	
C-4	129.9 (s)		133.0 (s)	
B	**2d**		**3d**	
CH_2CH_2	66.0 (d)	$^2J_{PC} = 8.8$	65.8 (d)	$^2J_{PC} = 1.0$
C=N	161.5 (d)	$^3J_{PC} = 5.4$	181.9 (d)	$^2J_{PC} = 2.4$
C-1	135.5 (s)		138.0 (d)	$^3J_{PC} = 20$
C-1′	132.2 (s)			
C-2	127.3 – 130.2[b] (complex)		129.5 (s)	
C-3			128.3 (s)	
C-4			132.0 (s)	

[a] *E*-isomer. – [b] Non-equivalent phenyl groups.

The downfield shifts in **3** relative to **2** and the large coupling constants J_{PC}, observed for the CH_3 and C-1 (aromatic) carbon atoms in the former, are consistent with the anisotropy of the P=O group with the change of oxidation state[9].

The difference in the chemical shifts of the C-1 and C-1′ (aromatic) nuclei for **2d** are produced by the configurational stability of the P^{III} compound, whereas the single absorption for **3d** is attributed to the fluxational behaviour of the phosphylated imine, with rapid inversion at nitrogen.

In discussing the mechanism of the P^{III}-P^{V} rearrangement several possible reaction paths have to be considered. In view of the high nucleophilic reactivity of phosphorus, an obvious mechanism is cyclisation to a phosphonium zwitterion followed by a β-elimination. Ionisation to a nitrenium ion is discounted since this would lead to a Beckmann rearrangement. Phosphorus is also strongly electrophilic and in view of the recent work of *Schmidpeter*[10] in which compounds of the type $PX_2Y_2^-$ were isolated, a route involving a carbonium ion is possible.



These heterolytic mechanism can be discounted on two grounds. First, substitution at the imino carbon atom ($R^1 = R^2 = Ph$; $R^1 = R^2 = Me$; $R^1 = Ph$, $R^2 = Me$) has little effect on the rate of rearrangement. Secondly, change of solvent[11] also has a negligible effect on the rate (Table 3). This insensitivity to changes of solvent is characteristic of homolytic rearrangements[2], and the significant rate increase in deuteriochloroform has been observed in other rearrangements proceeding through radical-pairs.

Table 3. Rate of rearrangement of **2e** at 34 °C

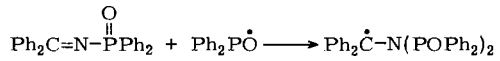
Solvent	$10^4\,k_1\,(s^{-1})$	Solvent	$10^4\,k_1\,(s^{-1})$
CCl_4	1.6	C_6D_6	1.41
$CDCl_3$	3.2 (3.0*))	CD_3CN	1.77

*) Measured by the rate of formation of **3e**.

We are therefore left with two mechanisms, the first involving homolytic fission and the second a 1,2 sigmatropic rearrangement.

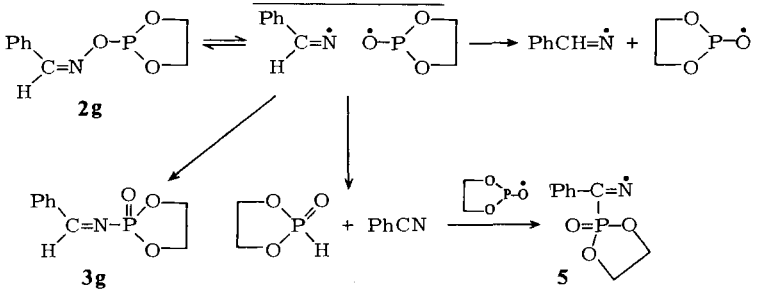
Evidence for free radicals is found by carrying out the reaction of benzophenone oxime and diphenylphosphinous chloride in the presence of triethylamine in the probe of an ESR spectrometer. Although iminyl and phosphonyl radicals are not observed, a persistent carbon based radical (g = 2.0024) with highly complex hyperfine splitting due to the aromatic protons and two equivalent phosphorus atoms is detected. This has so far not been analysed completely by computer simulation, but is probably formed by capture of the diphenylphosphonyl*) radical by the reaction product **3a**.

*) Phosphonyl is used as a collective term for X_2P-O where X = OR, NR_2, Alk, Ar.



3a

A definitive spectrum (Fig. 2) is however obtained in the reaction of benzaldoxime with 2-chloro-1,3,2-dioxaphospholan. In this reaction, nitrile is formed by elimination as a major product together with the phosphinylated imine **3g** (R^1 = Ph, R^2 = H). The nitrile acts as a trap for escaped phosphonyl radicals to give the iminyl, **5**, with g = 2.0044, a_N = 12.7, a_P = 32.2 G.



2g **3g** **5**

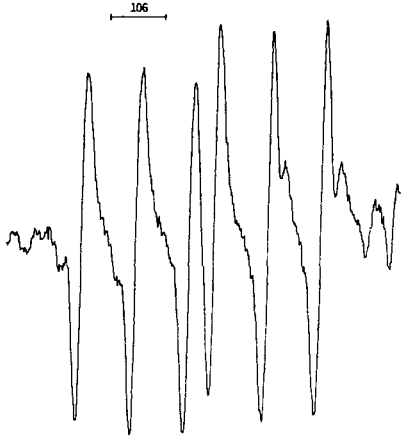
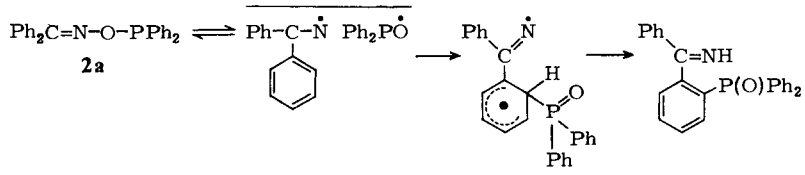


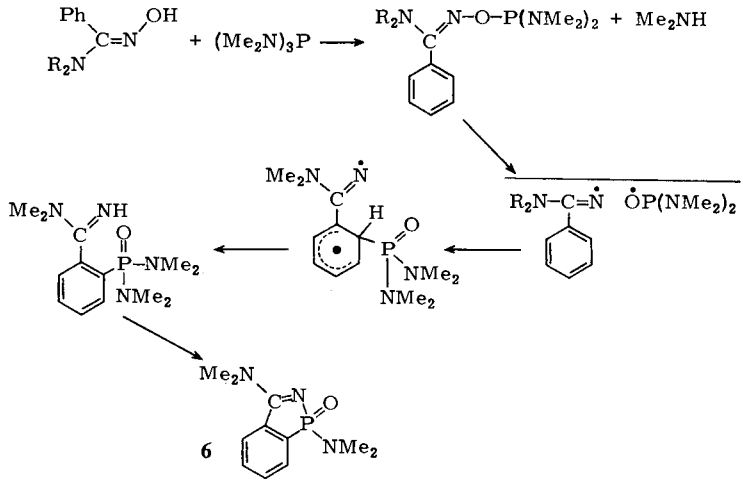
Fig. 2. Electron spin resonance spectrum of the iminyl radical **5**, showing splitting due to one nitrogen and one phosphorus atom

The reaction mixture of benzophenone oxime and diphenylphosphinous chloride polymerises styrene at −20 °C, and so it appears that phosphinyl radicals are very reactive towards mutiple bonds.

The absorptions at 21 and 29 ppm in the ^{31}P NMR spectrum in the reaction of benzophenone oxime with diphenylphosphinous chloride are attributed to addition of phosphonyl radicals to the aromatic nucleus.

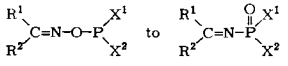


Intramolecular hydrogen atom transfers to iminyls have been observed by *Forrester* et al.[12], and such a process may account for the formation[6] of 1,3-bis(dialkylamino)-1*H*-2,1-benzazaphosphole 1-oxide (**6**) in the similar reaction of amidoximes with tris(dimethylamino)phosphane.



Direct evidence for the participation of a radical-cage process is obtained from ^{31}P CIDNP experiments observed when the reaction is carried out at temperatures such that the final product is formed within a few seconds*); residual polarisations in the ^{31}P nucleus are observed.

Table 4. ^{31}P CIDNP Spectra observed in the rearrangement of



R^1	R^2	X^1	X^2	$g(P\dot{O}X^1X^2)$[c]	$g(R^1R^2C=\dot{N})$[d]	δ(ppm)	Polarisation
Ph	Ph	Ph	Ph	2.0035 (6)	2.0033	15.5	E[a,b]
Ph	Me	Ph	Ph	2.0035 (6)	2.0030	17.9	E[a]
Me	Me	Ph	Ph	2.0035 (6)	2.0028	16.7	E[a]
Ph	Ph	Me_2N	Me_2N	2.0026	2.0033	15.9	A[b]
Ph	Me	OEt	OEt	2.0018	2.0030	2.9	A[b]
Ph	Ph	OCH_2CH_2O		(2.0018)	2.0033	18.8	A[b]
Ph	Me	OCH_2CH_2O		(2.0018)	2.0030	20.4	A[b]

[a] $CDCl_3$ as solvent. – [b] Toluene/ether as solvent. – [c] Reference[14]. – [d] Reference[17].

*) These vary from 0 to 90 °C depending on the phosphorus compound.

When diphenylphosphinous chloride was used, the enhanced emission decayed over a period of 2–3 min (Fig. 3). In other cases enhanced absorptions are obtained (Table 4), as for example in the formation of **3c** where strong enhanced absorption at 16.2 ppm is observed together with other, less intense, polarisation (Fig. 4).

Fig. 3

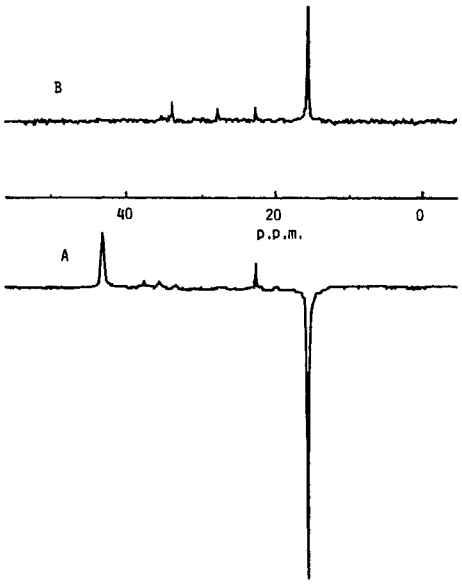


Fig. 4

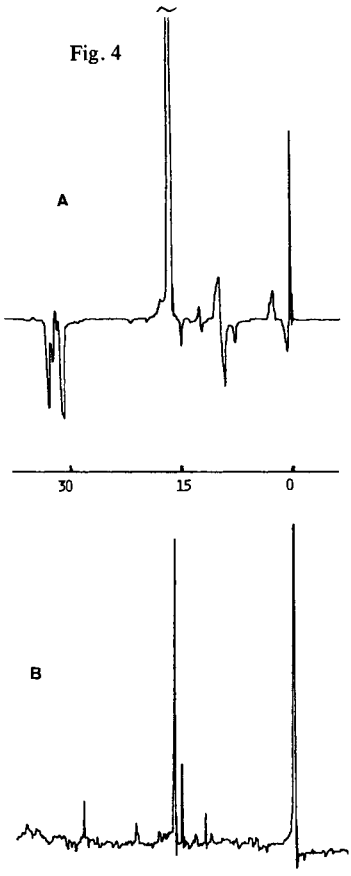


Fig. 3. Polarised (A) and unpolarised (B) noise-decoupled $^{31}P\{^1H\}$ spectra of the products of the reaction between diphenylphosphinous chloride and benzophenone oxime in the presence of NEt_3 taken (A) immediately after warming the mixture from −60 °C to room temperature, and (B) after standing at room temperature for several minutes

Fig. 4. Polarised (A) and unpolarised (B) noise-decoupled $^{31}P\{^1H\}$ spectra of the products of the reaction between $(Me_2N)_2PCl$ and benzophenone oxime in the presence of NEt_3

These polarisations can be analysed on the basis of the diffusion model developed by *Closs* and *Kaptein* [13], which leads to the following sign equation for the net polarisation, Γ_{ne},

$$\Gamma_{ne} = \mu\varepsilon\Delta g a_i$$

Here Δg is the difference in the g-values for the two radicals formed by homolysis, and a_i is the sign of the hyperfine coupling constant for the nucleus (i) under observa-

tion. The net polarisation Γ_{ne} is positive when absorption is observed and negative when emission is observed, and has opposite values for cage-recombination and for reaction outside the cage.

The parameter ε is positive for the former process and negative for the latter and μ is negative for a singlet precursor produced by ground-state homolytic fission.

Values of g for iminyls are well known and have been obtained[14] under the experimental conditions similar to those used in this work. There is, however, considerable confusion in the literature concerning the g-values of phosphonyl radicals, as values ranging from 2.0044 to 2.0019 have been recorded for dialkoxyphosphonyls[15]. The value of 2.0036 obtained for $Ph_2P\dot{O}$ in a crystal matrix by *Geoffroy* and *Lucken*[16] is close to the value in solution of 2.0035 given by *Roberts* and *Singh*[17], who also gave values of 2.0026 for $(Me_2N)_2P\dot{O}$ and 2.0018 for $(EtO)_2P\dot{O}$.

Using these values and a positive coupling constant a_i for the phosphorus nucleus in $X_2P\dot{O}$, the experimental data are analysed as follows:

	Γ_{ne}	$g_P - g_N$	a_P	ε
Ph_2P-	−	+	+	+
$(Me_2N)_2P-$	+	−	+	+
$(EtO)_2P-$	+	−	+	+
$(CH_2O)_2P-$	+	−	+	+

Although the polarisation changes from positive to negative as the substituent at phosphorus is changed, the value of ε is positive in all cases, showing that the net polarisation is produced in an in-cage process.

The magnitude of the polarisations however is low, as shown by values of 10 – 14 obtained by extrapolation to zero time. This indicates that perhaps only part of the reaction proceeds through the radical-cage, or alternatively part of the reaction may proceed by an out of cage process, e.g. by induced decomposition:

$$R_2C{=}N{-}OPX_2 + X_2P{-}\dot{O} \longrightarrow \underset{\displaystyle X_2P{=}O}{R_2\dot{C}{-}N{-}OPX_2} \longrightarrow R_2C{=}N{-}\overset{\displaystyle O}{\overset{\|}{P}}X_2 + X_2P\dot{O}$$

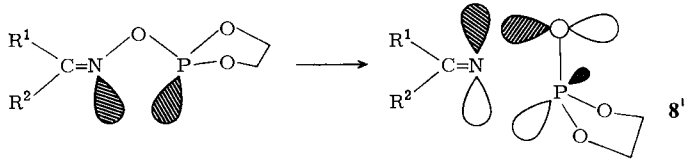
In previous work on other radical-cage rearrangements[2], we have used the values of activation entropies as measures of the extent of the radical-cage process. In all cases so far studied, ΔS^* is positive (ranging from 0 – 12 e.u.). With the isolation of the P^{III} intermediate derived from 1,3,2-dioxaphospholan, **2e**, unimolecular rate constants could be obtained at a series of temperatures (Table 6), to give $\Delta H^* = 21.1 \pm 1.3$ kcal/mol and $\Delta S^* = -7.3 \pm 6$ e.u.

Although these values are not precise the activation entropy is certainly not positive, suggesting that the major part of this particular reaction proceeds by a mechanism not involving a radical-cage. It is now generally accepted[18] that 1 – 2 and 1 – 3 homolytic rearrangements involve a spectrum of intermediates, the contribution of each depending on the structure of the radicals, solvent viscosity, and the temperature. Following an earlier suggestion of *Noyes*[19], the overall process can be represented as follows:

The initial homolysis gives an intimate (non-solvent separated) radical pair **7**, and a solvent separated cage pair **8** produced by diffusion requiring a time t, such that some spin inversion of the electrons can occur by a precessional motion under the influence of a strong magnetic field. This produces the CIDNP effect.

$$\underset{\mathbf{2}}{R_2C{=}N{-}OPX_2} \rightleftharpoons \underset{\mathbf{7}}{(R_2C{=}\dot{N}\ \ \dot{O}PX_2)} \rightleftharpoons \underset{\mathbf{8}}{\overline{R_2C{=}\dot{N}\ \ \dot{O}PX_2}} \rightleftharpoons R_2C{=}\dot{N} + \dot{O}PX_2$$

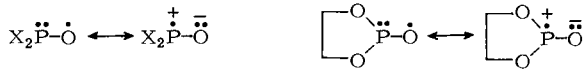
In the intimate radical-pair, the electrons will interact, either mutually or with molecular orbitals of the radicals (as in the so-called subjacent control[20]), and these interactions will control the observed stereochemistry, as in the *Stevens, Meisenheimer* and related rearrangements[18]. In the present case however the reaction product, **3**, is configurationally unstable due to rapid inversion at nitrogen and stereochemical techniques cannot be used. We suggest that the negative activation entropy is due to the combination of the two singly occupied orbitals as shown in **8'**.



8'

The initial lone pair repulsion is replaced by the symmetry allowed combination to give a weakly bonded complex, **8'**. This is essentially a cyclic transition state with extensive (almost complete) bond breaking.

On this basis, the rate of rearrangement can be explained in terms of the electronic stabilisation in the phosphonyl radical*). From the rate constants and activation energy given in Table 6 and from the half-life of the rearrangement of **2a** at $-40\,^{\circ}C$ it is found that **2a** rearranges ca. 10^5 times faster than **2b**. This is attributed to partial transfer of electrons from the P lone pair to oxygen as represented by the resonance structures.



This resonance decreases with the ionisation potential of phosphorus, i.e. by substitution of electron attracting groups[20] (e.g. $Ph_3P \approx 7.36$ eV, $(EtO)_3P \approx 8.4$ eV).

The dioxaphospholan ring reduces the rate by ca. 10 fold; which may be explained by increase in ring strain produced by the electron transfer since rate decreases between 5 and 200 have been obtained in nucleophilic reactions of dioxaphospholans[21].

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*) Approximate values of 27 and 32 kcal/mol are estimated for the $(EtO)_2P\dot{O}$ and $Ph_2P\dot{O}$ radicals from the present kinetic data and standard bond energies. The values for nitroxides are in the 35 – 40 kcal/mol range.

Experimental Part

Rearranged Products

N-(Diphenylmethylene)diphenylphosphinic amide (**3a**): Diphenylphosphinous chloride (5.0 g) in benzene (20 ml) was added slowly to a solution of benzophenone oxime (4.5 g) and triethylamine (0.23 g) in benzene (70 ml) with stirring, under nitrogen at 0 °C for 1 h. The amine hydrochloride was filtered off and the solvent removed slowly. The initial precipitate was filtered off and recrystallised from benzene to give 1.7 g (20%) *O*-(diphenylphosphinyl) benzophenone oxime (**2a**), m. p. 185 °C. Chloroform was added to the original solution to precipitate the product, which was recrystallised from toluene/*n*-hexane, m.p. 124 °C, yield 3.6 g (42%).

$C_{25}H_{20}NOP$ (381.4) Calcd. C 78.7 H 5.2 N 3.7 Found C 78.0 H 5.3 N 3.6

2-[(Diphenylmethylen)amino]-1,3,2-dioxaphospholan 2-oxide (**3d**): 2-Chloro-1,3,2-dioxaphospholan (4.9 g) was added slowly to a mixture of benzophenone oxime (7.0 g) and triethylamine (4.0 g) in toluene/ether (50 ml of 1:1 mixture), under nitrogen at 0 °C. The mixture was stirred for 30 min, the amine hydrochloride filtered off and the solution heated to 80 °C under nitrogen for 2.5 h. The solvent was removed and the product recrystallised from toluene, m.p. 138 – 140 °C, yield 8.3 g (76%).

$C_{15}H_{14}NO_3P$ (287.2) Calcd. C 62.7 H 4.9 N 4.9 Found C 62.5 H 4.7 N 4.9

The P^{III} intermediate, *O*-(1,3,2-dioxaphospholan-2-yl) benzophenone oxime (**2d**), was isolated by removing the solvent from the reaction mixture at 25 °C and washing the white solid several times with petroleum ether. It is unstable and very hygroscopic, but could be kept at −10 °C for several days. Satisfactory analyses were not obtained, but the structure was established by ^{13}C NMR analysis (see text).

2-[(1-Phenylethyliden)amino]-1,3,2-dioxaphospholan 2-oxide (**3e**): 2-Chloro-1,3,2-dioxaphospholan (6.5 g) was added slowly to a mixture of (*E*)-acetophenone oxime (6.9 g) and triethylamine (5.14 g) in toluene (50 ml) under nitrogen at 0 °C. The amine hydrochloride was filtered off, and the solution heated to 40 °C for 4 h. The solvent was removed and the oil dissolved in benzene (20 ml) and ether (50 ml) added. After 2 days at −10 °C a white solid precipitated, m.p. 46 – 47 °C, yield 4.3 g (40%).

$C_{10}H_{12}NO_3P$ (225.2) Calcd. C 53.3 H 5.3 N 6.2 Found C 51.0 H 5.2 N 6.2

The intermediate **2e** was prepared in the same way as for **2d** and characterised by ^{13}C NMR spectroscopy (Table 2).

N-(Diphenylmethylene)-N',N',N'',N''-tetramethylphosphoric triamide (**3c**) was prepared by the method of *Lopez* [6], and recrystallised from benzene/*n*-hexane, m.p. 108 – 109 °C, yield 52%).

$C_{15}H_{16}N_3OP$ (285.3) Calcd. C 64.8 H 7.3 N 13.3 Found C 64.6 H 7.1 N 13.4

NMR Spectra: The spectra were recorded on a JEOL PFT-100 instrument operating in the Fourier Transform mode at 40 MHz for ^{31}P, at 25.15 MHz for ^{13}C and 100 MHz for ^{1}H.

Except for the reactions of 2-chloro-1,3,2-dioxaphospholan the reactions were carried out at low temperatures (usually −40 °C) in the probe of the spectrometer. In a typical experiment, 20% solutions of the three reactants in toluene or toluene/diethyl ether mixtures were mixed at −60 °C and transferred rapidly to an 8 mm NMR tube which was then inserted in the preheated probe of the spectrometer. The ^{31}P NMR spectrum was taken at various time invervals after the mixing. The results obtained are shown in Table 5.

To follow the rearrangement of the product derived from 1,3,2-dioxaphospholan, 10% solutions in toluene were used and the $^{31}P\{^{1}H\}$-NMR spectrum recorded at various times at 50 °C. The peak of **2e** at δ_P = 120.9 decreases whereas the relative intensity of δ_P = 20.2 due to the product **3e** increases.

Tab. 5. Reaction of diphenylphosphinous chloride with benzophenone oxime

Temp. (°C)		Yields (%) Products observed*) with the chemical shifts (ppm) **2a** 115 (ppm)	34.8 (ppm)	27.4 (ppm)	22.5 (ppm)	**3a** 15.5 (ppm)
−60	3 min 50 s	93	7	–	–	–
−40	2 min 50 s	83	7	–	–	10
−40	22 min 10 s	6	9	–	12	73
25	10 min	–	15	5	8	65

*) Values obtained from the integrated peaks.

Kinetic Measurements: The rearrangement of **2e** was followed by ^{1}H NMR spectroscopy by observing the change in the intensity of the signal from the methyl protons at $\delta = 2.35$. The area under the peak was measured at known time intervals and first order rate constants calculated using the appropriate computer programme. At least 10 measurements were made in the determination of each rate constant, and the reaction was followed up to at least 80% completion.

Solutions were prepared in a series of solvents at concentrations of 0.5 M. In the reaction in $CDCl_3$, the rate constant was also found by measuring the increase in the signal from the methyl protons of the product, **3e**, at $\delta = 2.99$.

Table 6. Rearrangement of **2e** in carbon tetrachloride

Temp. (°C)	34	42.5	47.5	52.5
$10^4 k_1$ (s^{-1})	1.6 ± 0.3	3.32 ± 0.4	7.73 ± 0.4	1.11 ± 0.3
		$\Delta H^{\neq}$ = 21.1 ± 1.5 kcal/mol		
		$\Delta S^{\neq}$ = −7.3 ± 6 e.u.		

The progress of the reaction of **2f** was followed by ^{31}P NMR spectroscopy by measuring the decrease in the intensity of the peak at $\delta = 135.3$. The concentration was ca. 0.5 mol/litre obtained by mixing equimolar quantities of the reactants in toluene. The following results were obtained.

Temp. °C	23	33.5
$10^4 k_1$ (s^{-1})	5.53 ± 0.5	16.8 ± 0.9

ESR Experiments: Thoroughly degassed solutions (0.3 M) of the reactants were mixed in the probe of a JEOL PE 1X ESR spectrometer, and the signals observed after 1 – 2 min. The g values were measured, using diphenylpicrylhydrazyl as reference ($g = 2.0036$).

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