The Reaction Between *N*-Methyl-*p*-toluohydroxamic Acid and Tervalent Phosphorous Compounds: a Thermal $P^{III} \longrightarrow P^{V}$ Rearrangement proceeding by a Radical Mechanism

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N-Methyl-*p*-toluohydroxamic acid (**6**) reacts rapidly with phosphorus compounds XYPCl (X = Ph, Y = OEt and X, Y = OCH_2CH_2O) at −60 °C in the presence of pyridine to give the P^{III} intermediates (**7**) which have been characterised by ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy. The intermediates decompose at ambient temperatures with homolysis of the N–O bond to give the isomeric *N*-phosphine oxides (**8**), accompanied by varying amounts of *O*-phosphonylhydroxamic acids (**9**) *N*-methyl-4-toluamide, (**4**) and phosphoryl-radical related products. Evidence for a radical-cage process (at least in part) is obtained from ^1H and ^{31}P CIDNP studies.

The Arbuzov reaction[1] is the best known example of the many rearrangements undergone by organophosphorus compounds involving the P^{III} to P^{V} change in oxidation state. The majority of these rearrangements proceed *via* the heterolysis of a C–O bond, which usually involves electrophilic catalysis. Similarly most of the classical rearrangements involving scission of N–O bonds proceed by ionic, polar, or concerted mechanisms and until recently there was little evidence to suggest that rearrangements of organophosphorus compounds might involve the homolysis of the N–O bond. However, such reactions do exist, *e.g.* Scheme 1(*a*),[2] and it is now evident that they form part of a much wider class of intramolecular rearrangements of hydroxylamine derivatives which proceed at low temperatures through radical pairs, *e.g.* Scheme 1(*b*).[2,3] Our recent work suggests

$$R^1R^2C{=}N{-}O{-}PX_2 \longrightarrow R^1R^2C{=}N^{\cdot}\ {}^{\cdot}OPX_2 \longrightarrow R^1R^2C{=}N{-}POX_2 \quad (a)$$

$$R_2N{-}O{-}SOR \longrightarrow R_2N^{\cdot}\ {}^{\cdot}OSOR \longrightarrow R_2N{-}SO_2R \quad (b)$$

Scheme 1.

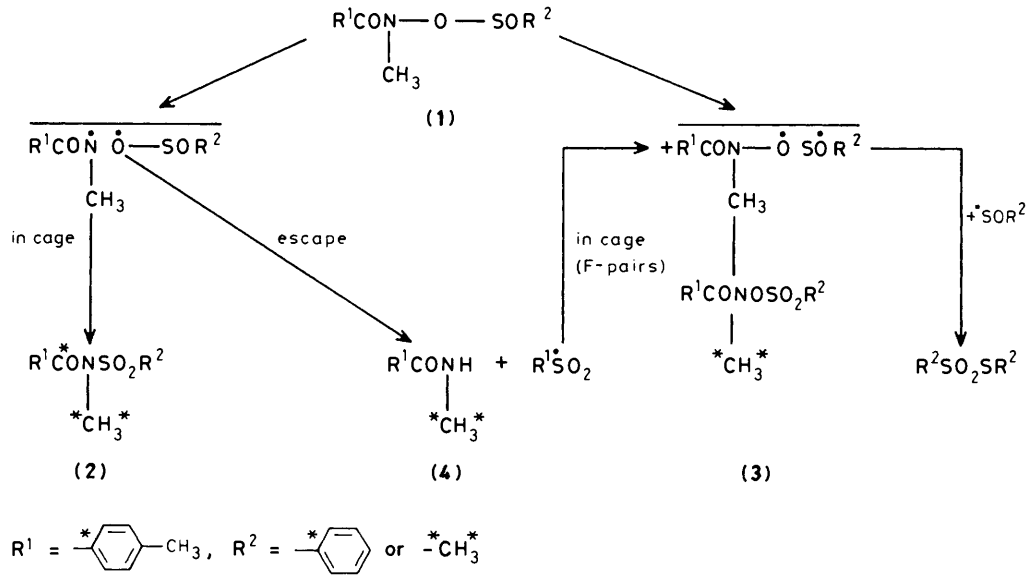
that simultaneous homolysis of both N–O and S–O bonds occurs during the rearrangement of *O*-sulphinylated *N*-methyl hydroxamic acids (**1**) (Scheme 2).[4] Experimental evidence has been found to support the hypothesis that the *N*-methyl-*N*-acyl sulphonamide, (**2**) and *N*-methyl-*O*-sulphonyl hydroxamic acid (**3**) are formed by in-cage and free-pair (F-pair) radical recombination, respectively. N.m.r. spectra (^1H and ^{13}C) show strong CIDNP effects in both the sulphonamide (**2**) and the *O*-sulphonylhydroxamic acid, (**3**). Strong CIDNP effects were also observed for the escaped product *N*-methyl-4-toluamide, (**4**). The CIDNP signals were analysed using Kaptein's equation[5] and were found to be entirely consistent with the mechanism proposed in Scheme 2. In addition, a strong e.s.r. signal was observed due to the persistent acylnitroxyl radical (**5**) (g = 2.0068, a^N 7.37 and a^{NCH_3} 8.10 G).[4] From the foregoing discussion it is of interest to see how the *N*-methyl-*O*-phosphinyl hydroxamic acid derivatives, (**7**) behave, *e.g.* Scheme 3. Indeed phosphonyl-radical formation should promote N–O bond homolysis since it appears that while fully oxidised leaving groups promote heterolytic rearrangement, *e.g.* Beckmann, Tiemann, and Lossen, which involve electron-deficient nitrogen or nitrenium ions,[6] reduced leaving groups promote homolytic rearrangement.[2] It is therefore a reasonable supposition that the nitrogen analogue of the Arbusov reaction *e.g.* Scheme 4 should proceed, at least in part, by a radical cage process. In this paper we investigate the mechanism of the reaction between *N*-methylbenzohydroxamic acid and various chlorides of tervalent phosphorus.

Results and Discussion

The *O*-phosphino hydroxamic acids (**7a–c**) were obtained in solution by treatment of *N*-methyl-4-toluohydroxamic acid[7] and pyridine in $CDCl_3$ under N_2 at −60 °C with the appropriate phosphorus chloride. N.m.r. evidence (^{31}P, ^1H, and ^{13}C) for the proposed structure of (**7a–c**) is presented in Table 1. ^{31}P Chemical shifts for (**7a–c**) lie in the region anticipated for P^{III} compounds (*ca.* δ 130–140).[8] In addition, the ^{13}C resonances of the carbonyl and *N*-methyl groups were observed at *ca.* δ 171.5 and *ca.* δ 40.7, respectively. These figures compare favourably with those found in the *N*-methyl-*O*-sulphinyl hydroxamic acids previously reported (*ca.* δ 171.7 and δ 42.0).[4] Further evidence to support the proposal comes from the intermediates implicated by Barrans[9] in the reactions of amidoximes with tris(dimethylamino)phosphine and 2-substituted 1,3,2-dioxaphospholanes (Scheme 5). Treatment of *N*-methyl-4-toluohydroxamic acid, (**6**) and pyridine in $CDCl_3$, at −50 °C, with X_2PCl (X = Ph, OEt) gave a single peak in the P^{III} region of the ^{31}P n.m.r. spectrum (Table 1). No signal corresponding to the phosphinyl chloride was observed, indicating the formation of (**7a–c**) to be very rapid. On warming the solution, the P^{III} resonances due to the intermediates (**7a**) and (**7c**) disappeared to be replaced by major peaks corresponding to the phosphine oxides (**8a, b**) accompanied by varying amounts of *O*-phosphonyl hydroxamic acids (**9a, b**), and phosphonyl-radical related products. (Table 2)

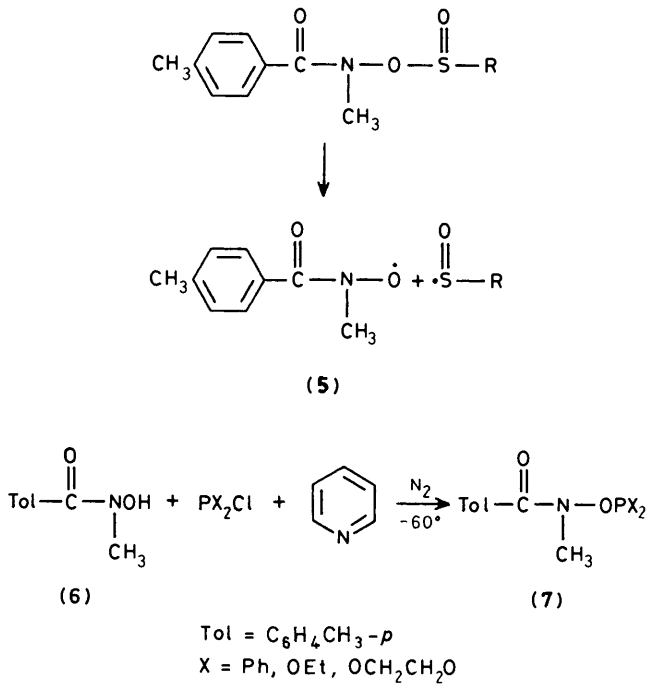
When this experiment was repeated using 2-chloro-1,3,2-dioxaphospholane at 30 °C the immediate product was (**7c**) (δ_P 133.15). However, within a few minutes the resonance at δ 133.15 began to diminish, to be replaced by two major peaks at δ 22.13 and 18.20 which are attributed to compounds (**8c**) and (**9c**). It took 120 min for the resonance at δ 133.15 to diminish to half of its original intensity.

When equivalent mixtures of (**6**) and pyridine in $CDCl_3$ at 25 °C were treated with X_2PCl (X = Ph, OEt) the major products, (**8a, b**) were accompanied by an increased quantity

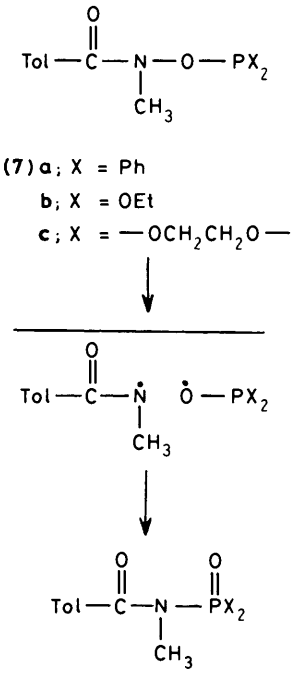


* Atoms which exhibited strong CIDNP phenomena are indicated by an asterisk *.

Scheme 2.



Scheme 3.



Scheme 4.

of by-products. Quantitatively, the rate of rearrangement decreased in the order $Ph_2 > (OEt)_2 > (CH_2O)_2P$. The structures of (**9a–c**) and (**4**) were confirmed by independent synthesis and comparison of the ^{31}P, ^{13}C, and ^{1}H n.m.r. spectra. Compounds (**9a–c**) were synthesised by treatment of the hydroxamic acid, (**6**) with the appropriate chlorophosphine oxide, (**10**) in the presence of 1 equiv. of base, Scheme 6.

Attempts to separate the reaction mixtures using medium pressure liquid chromatography (m.p.l.c.) were not very successful. Only three compounds were recovered from the column (Merck silica gel, 230–400 mesh; column dimensions 1.5 × 1 000 cm; solvent systems: cyclohexane–diethyl ether, solvent tradient 9:1 gradually changing to 1:9).

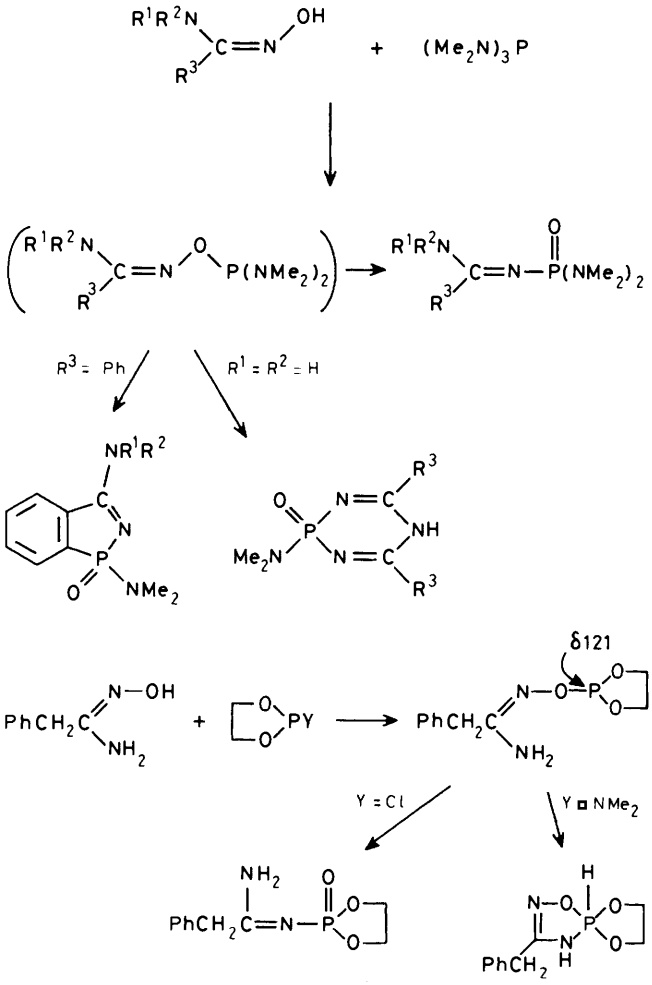
The compounds were identified as the following (in order of elution): *N*-methyl-*O*-phosphonyl hydroxamic acid (**9a–c**), *N*-methyl-4-toluamide (**4**), and diphenylphosphinic acid. *N*-Acyl-*N*-methyl phosphonamides, (**8a–c**) were not recovered, but given the amount of amide (**4**) and phosphinic acid recovered, it would seem that compound (**8**) has undergone hydrolysis. Attempts to deactivate silica by treatment with dichlorodimethylsilane, or Fluorosil as the stationary phase did not improve the situation.

The Reaction Mechanism.—Phosphine oxides (**8**) are clearly formed by a molecular rearrangement but the mode of formation of (**9**) is not obvious. By analogy with our previous work,[2–4] the *N*-methyl phosphine oxides, (**8a–c**) arise from

Table 1. N.m.r. spectral data (^1H, ^{13}C, and ^{31}P) for (**6**), (**7a–c**), (**8a–c**), (**9a–c**), and (**4**).

Compd.	δ_H[a] N–CH_3	δ_C[b,c] C=O	δ_C[b,c] N–CH_3	δ_P[d] X_2PCl	δ_P[d] P	δ_P[d] P=O	δ_P[d] O–P=O
(**6**)	3.31	167.34	38.41	—	—	—	—
(**7a**)	3.60	168.07	42.01	80.5	129.96	—	—
(**7b**)	3.40	171.24	40.91	164.0	139.62	—	—
(**7c**)	3.39	171.81	40.50	167.0	133.15	—	—
(**8a**)	3.44	168.6	38.8	—	—	31.1	—
(**8b**)	3.45	168.1	36.62	—	—	3.4	—
(**8c**)	3.29	168.4	36.53	—	—	22.1	—
(**9a**)	3.56	172.82	43.59	—	—	—	39.4
(**9b**)	3.55	172.52	41.45	—	—	—	−0.4
(**9c**)	3.52	172.58	41.74	—	—	—	18.20
(**4**)	2.94	168.19	26.75	—	—	—	—

[a] 100 MHz (continous wave) ^1H shifts relative to internal Me_4Si. [b] 50.3 MHz (Fourier transform), ^{13}C shifts relative to internal $SiMe_4$ at 25 °C. [c] Control experiment with (**7c**) showed no significant temperature effect on chemical shift. [d] 60 MHz (Fourier transform) ^{31}P shifts relative to external H_3PO_4. [e] Spectra run at −50 °C.



Scheme 5.

homolysis of the N–O bond Scheme 4. Geminate recombination of the resultant amidyl (**11**) and phosphoryl (**12**) radicals would give rise to *N*-methyl phosphine oxides (**8a–c**). The escaping amidyl radical (**11**) is responsible for the formation of *N*-methyl-4-toluamide (**4**) by an H-atom abstraction. This behaviour has been observed in previous studies.[4,10]

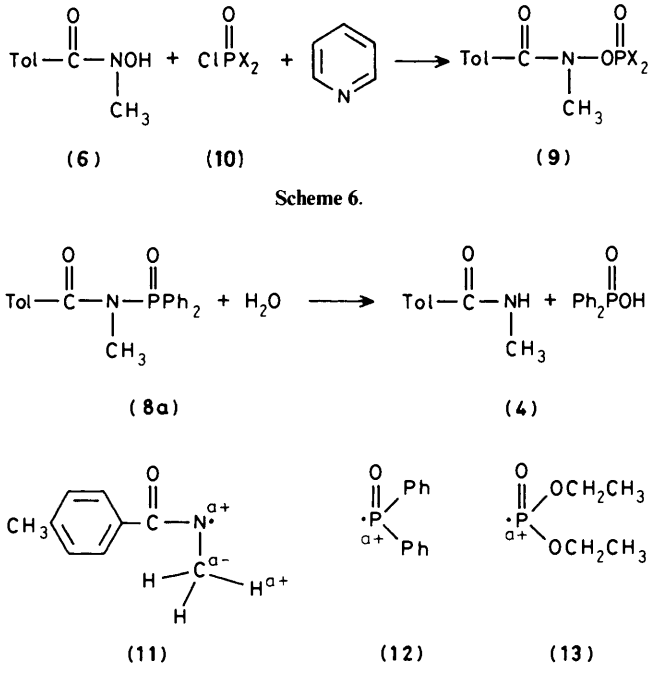
Table 2. % Yield of rearranged products from the thermolysis of *N*-methyl-*O*-phosphinylated hydroxamic acid (**7**).

(**7a**)[a]	(**7b**)	(**7c**)
40[b] (32)[c] (27)[d]	36	71
19 (27) (26)	13	10
34 (36) (40)	30	16

[a] % Yield based on NCH_3 ^1H n.m.r. signal. [b] Reactants mixed at −50 °C. [c] Reactants mixed at 25 °C. [d] Hydroxamic acid (2 mol dm^{-3})–phosphinylchloride (1 mol dm^{-3}) at −50 °C.

Table 3. CIDNP effects in the ^1H and ^{31}P n.m.r. spectra of the products from the thermolysis of *N*-methyl-*O*-phosphino hydroxamic acid (**7a, b**) at 30 °C (^1H) and 60 °C (^{31}P).

	^1H	^{31}P	
	N–CH_3	–P=O	–O–P=O
(**8a**)	E	A	—
(**8b**)	E	A	—
(**9a**)	A	—	E
(**9b**)	A	—	E
(**4**)	A	—	—



Scheme 6.

Direct evidence for these suggestions was obtained from the enhanced polarizations observed in both the ^1H and ^{31}P n.m.r. spectra when the reactions were carried out at 60 °C (^{31}P) (see Figure 1) and 30 °C (^1H) in the probe of an n.m.r. spectrometer. The ^1H CIDNP spectra of the reaction products from the thermolysis of (**7a, b**) showed polarizations which could be assigned to the *N*-methyl groups of (**8a**), (**9a**), and (**4**) (Tables 1 and 3). ^{31}P CIDNP spectra of the reaction products from the thermolysis of (**7a, b**) also showed strong polarizations which could be assigned to the phosphorus atom of both (**8a, b**) and (**9a, b**). These polarizations were analysed using the following sign equation for the net polarization Γ_{ne} equation (1). This

$$\Gamma_{ne} = \mu\varepsilon\Delta g a_i \qquad (1)$$

analysis is based on the diffusion model developed by Kaptein[5]

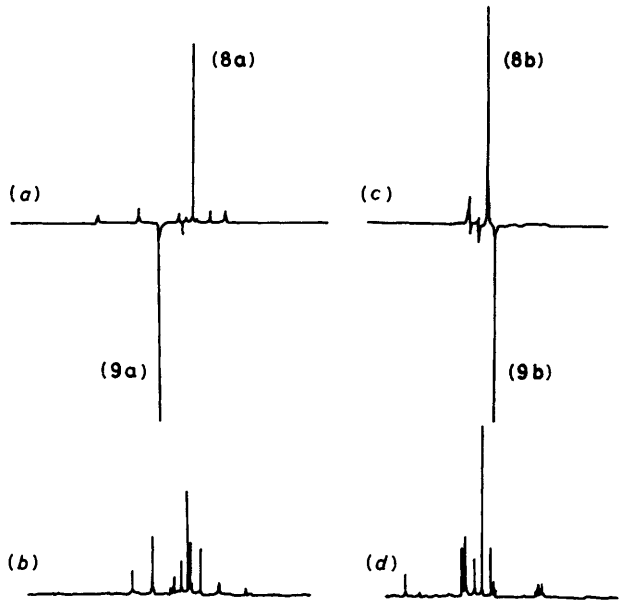


Figure. (*a*) ^{31}P N.m.r. spectrum of the thermolysis of *O*-diphenylphosphino-*N*-methyl-4-toluohydroxamic acid (**7a**) (10% w/v in $CDCl_3$) at 60 °C after *ca.* 90 s. (*b*) ^{31}P N.m.r. spectrum after 10 min, (*c*), (*d*) Analogous ^{31}P n.m.r. spectra for *N*-methyl-*O*-diethylphosphonyl-4-toluohydroxamic acid, (**7b**). All spectra are assigned with reference to Table 1.

where 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 observation. The net polarization, Γ_{ne} is positive when enhanced absorption is observed and negative when emission is observed, and has opposite values for cage recombination and for reaction outside the cage. The mechanistically significant parameter, ε, is positive for the former process (in cage) and negative for the latter (escape) and μ is negative for a singlet precursor produced by ground-stage homolytic fission.

The g value for the benzamidyl radical (**11**) is 2.0053[11] and the values for diphenylphosphinoyl (**12**) and diethylphosphonoyl (**13**) radicals are 2.035 and 2.0018, respectively.[12] Hyperfine splitting constants (a_i) for the amidyl radical (**11**) have been computed by the INDO method[10] and are shown in (**11**). A postive value for phosphorus is reported by Bentrude.[13] From these values it is possible to deduce the sign of ε for the phosphine oxides, (**8a, b**) and the amide (**10**). For example let us consider phosphine oxide (**8a**):

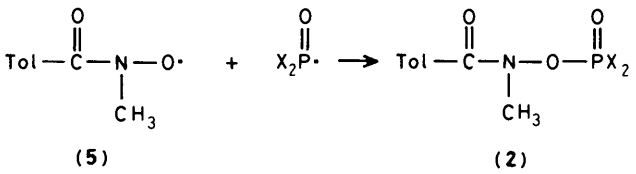
Compound	Observed effect		$\mu\ \varepsilon\ \Delta g\ a_i$
(**8a**) Γ_{NCH_3}	(−)	=	$-\ ?\ +\ +\ \therefore \varepsilon = +$
(**8a**) $\Gamma_{P=O}$	(+)	=	$-\ ?\ -\ +\ \therefore \varepsilon = +$
And for the amide (**4**)			
(**4**) Γ_{NCH_3}	(+)	=	$-\ ?\ +\ +\ \therefore \varepsilon = -$

These results indicate that the phosphine oxide (**8a**) is formed by, an in-cage recombination of a geminate radical pair, whereas amide (**4**) is formed by an out-of-cage process. Proton abstraction is such a process. Similar results are deduced for the thermolysis of (**7b**).

Phosphonoyl-radical-derived products, identified by ^{31}P n.m.r. spectroscopy, include chlorodiphenylphosphine oxide (**10**), 1,1,2,2-tetraphenyl-λ^5-phosphane 1,2-dioxide and diphenylphosphine oxide.[14]

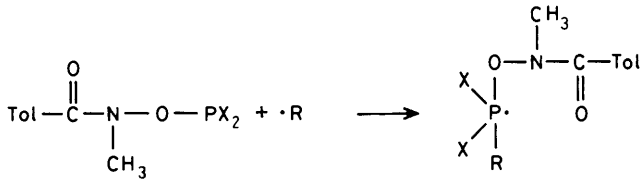
Chlorine and proton abstraction, and dimerization reactions are known in the literature.[15] Evidence for a radical mechanism was sought by carrying out thermolysis of (**7a, c**) in the probe of an e.s.r. spectrometer at 25 °C. The amidyl and phosphonoyl radicals, (**12**) and (**13**) were not noted but a persistent radical was observed which was identified as the acylnitroxyl radical (**5**). This radical is identical with the acylnitroxyl radical we recently reported[4] which was thought to come about by S–O bond homolysis during the thermolysis of *O*-sulphinyl-*N*-methyl hydroxamic acids. Clearly the bond energy of the P–O bond (360 kJ mol^{-1}; 86 kcal mol^{-1}) prohibits the homolysis of the P–O bond in a similar manner.

The origin of *O*-phosphinyl hydroxamic acids (**9**) is not known, but presumably involves the combination of phosphinyl and acylnitroxyl radicals. Since P–O bond homolysis is



(**5**) (**2**)

precluded because of the very large P–O bond energy, the acylnitroxyl radical could be produced by the intermediate formation of a phosphoranyl radical *viz.*, as axial bonds in five-



(**7**)

co-ordinated phosphorus compounds are very weak. Further work is required in order to substantiate this suggestion.

When the rearrangement is carried out at 25 °C rather than at a lower temperature, the yield of (**9a**) increases, as some phosphinyl radical is captured by acylnitroxyl derived directly from the starting material. It is significant that the yield of (**9a**) obtained under these conditions is equal to the yield obtained when an excess of hydroxamic acid was used (Table 2).

Experimental

Preparation of Starting Materials.—*N*-Methyl-4-toluohydroxamic acid (**6**) was prepared by a published method[7] involving the action of 4-toluoyl chloride (Aldrich) on *N*-methylhydroxylamine hydrochloride (Aldrich) in the presence of 2 equiv. of anhydrous sodium carbonate. Chlorodiphenylphosphine and diethyl chlorophosphite were obtained from Aldrich and distilled before use. The corresponding chlorophosphine oxides were obtained and treated similarly. 2-Chloro-1,3,2-dioxaphospholane and 2-chloro-1,3,2-dioxaphospholane 2-oxide were synthesised using the methods of Lucas[16] and Edmundson,[17] respectively.

Synthesis of O-*Diphenylphosphino*-N-*methyl*-4-*toluohydroxamic Acid* (**7a**).—To a stirred solution of *N*-methyl-4-toluohydroxamic acid (**6**) (1.0 g), and anhydrous pyridine (0.47 g) in $CDCl_3$ (20 cm^3) under oxygen-free nitrogen at −60 °C was added dropwise chlorodiphenylphosphine (1.33 g) in $CDCl_3$ (5 cm^3). The reaction mixture was stirred for 10 min and filtered under nitrogen into a precooled vial (−78 °C). ^1H, ^{13}C, and ^{31}P N.m.r. spectra were recorded immediately at −50 °C (see

Table 1). This procedure was used to prepare (**7b**). Compound (**7c**) could be prepared at 0 °C.

Unambiguous Synthesis of O-*Diphenylphosphinoyl*-N-*methyl*-4-*toluohydroxamic Acid* (**9a**).—To a stirred solution of *N*-methyl-4-toluohydroxamic acid (**6**) (1.0 g) and anhydrous triethylamine (0.61 g) in anhydrous diethyl ether (20 cm^3) at 0 °C, was added dropwise chlorodiphenylphosphine oxide (Aldrich) (1.43 g) in anhydrous diethyl ether (3 cm^3). The reaction mixture was stirred for 45 min at 0 °C, filtered, washed with ice-cold water, dried ($MgSO_4$), and evaporated to yield a colourless oil (1.9 g) which was crystallized from cyclohexane (1.6 g, 72%), m.p. 118 °C (Found: C, 69.0; H, 5.55; N, 8.82; P, 8.45; M^+, 365.118 07. $C_{21}H_{20}NO_3P$ requires C, 69.01; H, 5.82; N, 3.83; P, 8.48%; *M*, 365.118 08); $\delta_H(CDCl_3)$ 2.30 (3 H, s, $CH_3C_6H_4$), 3.56 (3 H, s, NCH_3), and 7.40–8.10 (14 H, br, ArH); $\delta_C(CDCl_3)$ 21.39 ($CH_3C_5H_4$), 43.58 (NCH_3), and 172.82 (C=O); $\delta_P(CDCl_3)$ 39.4 ppm (P=O); $\nu_{max.}$(thin film) 1 695 (C=O), 1 290 cm^{-1} (P=O).

This method was used to prepare the following:

O-*Diethylphosphonyl*-N-*methyl*-4-*toluohydroxamic acid* (**9b**), (78%), b.p. 160 °C at 0.7 mmHg (Found: C, 51.75; H, 6.7; N, 4.65; P, 10.15%; M^+, 301.107 90. $C_{13}H_{20}NO_5P$ requires C, 51.80; H, 6.69; N, 4.65; P, 10.28%; *M*, 301.107 91); $\delta_H(CDCl_3)$ 1.23 (3 H, t, *J* 7.08 Hz, OCH_2CH_3), 1.24 (3 H, t, *J* 7.08 Hz, OCH_2CH_3), 2.36 (3 H, s, CHC_6H_4), 3.55 (3 H, s, NCH_3), 4.27 (2 H, q, *J* 7.08 Hz, OCH_2CH_3), and 4.31 (2 H, q, *J* 7.08 Hz, OCH_2CH_3); $\delta_C(CDCl_3)$ 15.36 and 15.97 (OCH_2CH_3), 21.52 ($CH_3C_6H_4$), 41.45 (NCH_3), 65.23 and 65.47 (OCH_2CH_3), and 172.51 (C=O); $\delta_P(CDCl_3)$ −0.4 ppm (P=O); $\nu_{max.}$(thin film) 1 697 (C=O), 1 289 cm^{-1} (P=O).

N-*Methyl*-O-(2-*oxido*-1,3,2-*dioxaphospholan*-2-*yl*)-4-*toluohydroxamic acid* (**9c**): 91% (Found: C, 48.7; H, 5.1; N, 5.15; P, 11.35%; M^+, 271.2089. $C_{11}H_{14}NO_5P$ requires 48.71; H, 5.20; N, 5.16; P, 11.42%; *M*, 271.209); $\delta_H(CDCl_3)$ 2.44 (3 H, s, $CH_3C_6H_4$), 3.52 (3 H, s, NCH_3), 4.20–4.80 (4 H, m, $-OCH_2CH_2O-$), and 7.1–7.7 (br, 4 H, ArH); $\delta_C(CDCl_3)$ 21.52 ($CH_3C_6H_4$), 41.74 (NCH_3), 67.0 ($-OCH_2CH_2O-$), and 172.58 (C=O); $\delta_P(CDCl_3)$ 18.30 ppm (P=O); $\nu_{max.}$(thin film) 1 289 cm^{-1} (P=O).

E.S.R. Experiment.—A JEOL PE 1X e.s.r. spectrometer was employed. Solutions of (**7a**, **c**) were prepared (5%, w/v) as described for the synthesis of the *O*-diphenylphosphino-*N*-methyl hydroxamic acid (**7c**). The solutions in a precooled (−70 °C) e.s.r. tube were placed in the cavity of the spectrometer (25 °C). A strong signal due to the acylnitroxyl radical, (**5**) was observed within 60 s, which persisted for some 10 min (**7a**) and for at least 120 min (**7c**). The *g* value was measured using diphenylpicrylhydrazyl as the reference (*g* 2.0036).

CIDNP Experiments.—Solutions of (**7a**, **b**) (10 w/v in $CDCl_3$) were prepared as previously described at −70 °C and filtered into precooled 10 mm n.m.r. tubes and placed immediately in the preheated probe (60 °C) of a JEOL PFT-100 n.m.r. spectrometer.

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