Phosphorylation of Organic Compounds by Phosphoric Anhydride. Part 1. Phosphorylated Benzanilides

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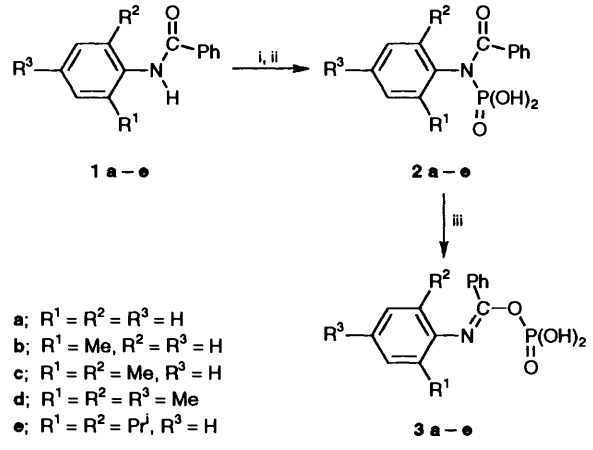
Phosphoric anhydride has been shown to react readily with benzanilides **1** to give initially N-phosphorylated benzanilides **2**, which rearrange to *E* and *Z* O-phosphorylated imidates **3** in the presence of protic compounds.

The methods available for the phosphorylation of organic compounds have been extended considerably over the past decade, primarily due to the need to synthesize biologically active phosphates. The acid chlorides are usually considered as the most powerful reagents and are widely used for the synthesis of monoesters and diesters.[1,2] On the other hand, methods which involve phosphoramidites and phosphoramidates are used for the synthesis of unsymmetrical diesters.[3] Phosphorylated compounds are also required for a range of industrial applications such as extractants, surfactants, and various additives. With respect to the latter, phosphorylated cyclic amines have been prepared as potential modifiers for silver halide crystallisation.[4] Phosphoric anhydride (P_4O_{10}) was found to be a convenient phosphorylating agent in the case of various primary and secondary amines.[5] Although this is not a commonly used reagent it has been postulated that phosphoric anhydride was probably responsible for the formation of the initial organic phosphates required for the evolution of life on this planet.[6] A range of primary amides has been phosphorylated mainly by phosphoryl chlorides.[7a]



Scheme 1 *Reagents and conditions:* i, P_4O_{10}; ii, moist Et_2O; iii, EtOH

In this report we show that phosphoric anhydride in trichloromethane reacts readily with the benzanilides **1a–e** to give phosphorylated products in 65–95% yield (Scheme 1).[7b] The dimethyl- and trimethyl-substituted anilides were the most reactive, a spontaneous and slightly exothermic reaction occurring. The other anilides required heating in trichloromethane under reflux for 20 minutes before any reaction was observed. Although the phosphoric anhydride is insoluble, the products dissolved in the hot medium.

† On sabbatical leave from St. Petersburg Institute of Cinema and Television.

Table 1 ^{31}P NMR chemical shifts of polyphosphates and phosphate esters

Compound	^{31}P NMR chemical shift, ppm	Ref.
1,5-μ-Oxotetrapolyphosphate (P_4O_{11})	−36.5	8*b*
Tetrametaphosphate (P_4O_{12})	−23.6	8*c*
Middle groups of polyphosphates	−21.5	8*c*
End groups of polyphosphates	−6 to −11	8*a*
Monoesters of phosphoric acid	−3 to 4	8*a*

Results and Discussion

The phosphorylation of the benzanilides was followed by phosphorus-31 NMR spectroscopy, and a similar sequence of signals was observed in all cases. The ^{31}P NMR spectra of the initial reaction mixtures gave signals in the −40 ppm region which soon were replaced by spectra containing two complex groups of signals in the regions of −25 to −27 ppm and the other at −12 to −13 ppm (see Fig. 1*a*).

Polyphosphates give signals across a wide range of phosphorus chemical shifts according to the connectivities and steric constraints of the phosphorus atom (see Table 1). Thus, the initial signals at −40 ppm are assigned to the bridging bicyclic phosphate groups such as those in intermediate **4**. The set of signals centred at −26 ppm are assigned to polyphosphate middle groups which occur in potential intermediates **5** and **6**,[8a] whilst the signals near −13 ppm are attributable to polyphosphate end groups as well as to the presence of some amidophosphate groups (see below). P–O–P Spin–spin couplings would contribute to the multiplicity of lines throughout.

Upon trituration of the reaction product with diethyl ether the spectra slowly simplified as the pyrophosphate groups were selectively hydrolysed through the action of atmospheric moisture.‡ The intensity of the set of signals at high field (−25 ppm) gradually decreased whilst several signals at −12 ppm gained in intensity and these were eventually transformed into essentially one signal. The products with chemical shifts at −12 to −13 have been isolated and were shown to be the N-phosphorylated amides **2a–e**. Thus the IR spectra showed the absence of the NH group and the presence of an amide group—

‡ The diethyl ether was distilled off. The trituration caused gentle hydrolysis of the polyphosphate groups remaining from the phosphoric anhydride structure. Evaporation of the ether produced cooling and condensation of atmospheric moisture.

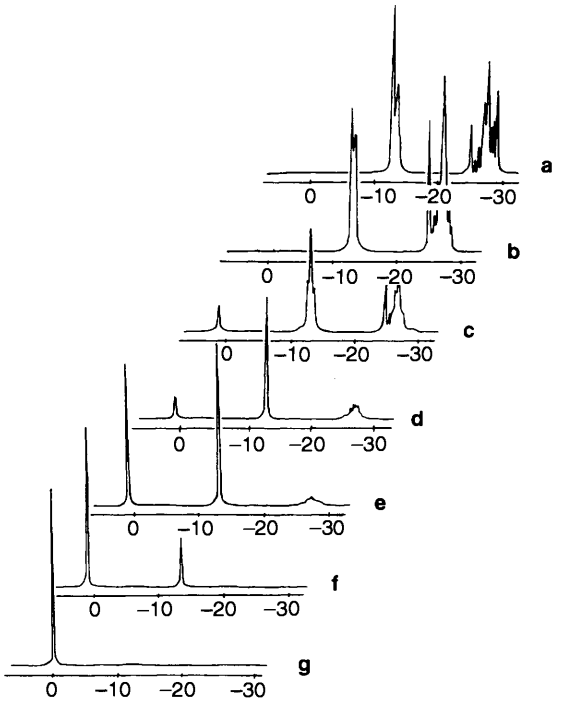
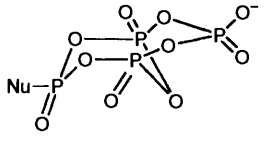


Fig. 1 ^{31}P NMR spectra of products from the reaction of phosphoric anhydride and benzanilide. (*a*) Initial product consisting of a mixture of polyamidophosphates; (*b*) and (*c*) changes induced by traces of hydrochloric acid 15 and 30 min later; (*d*) mainly N-phosphorylated benzanilide **2a** 60 min later; (*e*) and (*f*) changes induced by longer treatment by dil. hydrochloric acid, for 90 and 120 min; (*g*) final O-phosphorylated benzanilide after 180 min.



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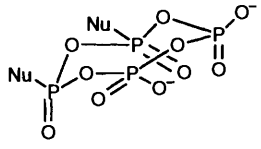

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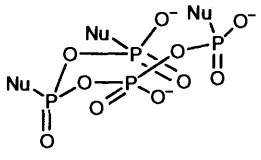

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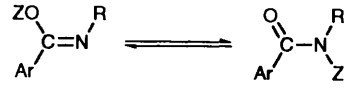
the latter being confirmed by the presence of ^{13}C NMR carbonyl signal in the region δ_C 163–173 (see Table 2). The compounds had insufficient solubility in NMR solvents such as $(CD_3)_2SO$ to allow us to detect the expected doublet due to the one-bond spin–spin coupling in a ^{15}N NMR spectrum.* Amidophosphates give ^{31}P NMR chemical shifts in the range 0–17 ppm,[8a] the position of the signals being strongly dependent on pH. N-Phosphorylated benzimidazole resonates at ~ −16 ppm.[8d] Thus the signals in the −12 to −13 ppm region are attributed to polyphosphate end groups in the earlier stages and amidophosphate **2a–e** in the latter stages of the reaction. It is believed that the N-phosphorylation proceeds by reaction of the anhydride with the imidolate tautomer of the benzanilides. Continued phosphorus-31 NMR monitoring of the reaction, induced by traces of dil. hydrochloric acid or the addition of a protic solvent such as ethanol, showed the development of one broadened signal as in Fig. 1[8a] or (more usually) two signals in the region 2 to −2 ppm which increase in intensity at the expense of the higher field signal. The chemical shifts are in accord with monoesters of phosphoric acid (see Table 1) and the signals are attributed to the presence of O-phosphorylated imidates **3a–e**. For each product the amide region of the IR spectrum was markedly changed and in the ^{13}C spectrum the amide carbonyl signal at δ_C ~ 170 had been replaced by new signal (quaternary carbon) in the region δ_C 134–143 which is attributed to the N=C–OPO_3H_2 group (see Table 2). The IR spectra of the products (Table 3) contained a band at ~ 1250 cm^{-1}, due to the phosphoryl group, which is broad in most cases, possibly due to hydrogen bonding. Two strong bands also appear in the region 1030–1000 cm^{-1} which is assigned to the C–O–P groups of *E* and *Z* isomers. The presence of isomers was confirmed by the NMR spectra of the products from benzanilides which were methylated in the aniline ring. Thus the ^{31}P NMR spectra of the O-phosphorylated product **3c**



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derived from 2,6-dimethylaniline and the product **3d** derived from 2,4,6-trimethylaniline gave two signals near δ_P 0 ppm in their ^{31}P NMR spectra, and their ^1H and ^{13}C NMR spectra contained two sets of signals for the *ortho*-orientated methyl groups. The ratio of the two isomers was approximately 1 : 0.5 and 1 : 0.8 respectively for the phosphates **3c** and **3d**, these ratios remaining constant across quite a wide range of polar solvents (acetone, ethanol, methanol, Me_2SO). As expected, the ^1H and ^{13}C chemical shifts of the *ortho* methyl groups were more sensitive to the *E* and *Z* geometries than were those of the *para*-orientated methyl group in compound **3d**. The other O-phosphorylated products probably also exist as a mixture of *E* and *Z* isomers as indicated by the occasional presence of two partially resolved phosphorus signals in the δ_P 0 ppm region. Hindered rotation of the aryl rings would be expected for the *ortho*-substituted products. However, the occurrence of two different stable rotamers for either the *E* or *Z* isomers of phosphates **3** appears most unlikely. Furthermore, two sets of signals (or broadened signals) were also observed for the non-*ortho*-substituted product **3a**.

There was no evidence for the presence of an equilibrium between N- and O-phosphorylated isomers and the latter products were always formed irreversibly. This can be attributed to the much higher stability of P–O bonds over P–N bonds compared with the loss of stability for the change from C=O to C=N and to the development of conjugation between the two aryl rings. Molecular mechanics modelling (COSMIC) indicated a larger degree of coplanarity of the C=N bond with the aryl rings in phosphates **3** compared with the coplanarity between the C=O bond and the aromatic ring in amidophosphates **2**. The N-phosphorylated products were quite difficult to isolate in a pure state, and small amounts of the O-phosphorylated isomer were usually present. If the N-phosphorylated products (from reactions using a 2 : 1 molar ratio of amide to phosphorylating agent) are not isolated rapidly following work-up with moist diethyl ether, further hydrolysis occurs with the formation of the initial amide in addition to rearrangement to the O-phosphorylated products.

Solid-state ^{31}P and ^{13}C NMR spectroscopy of a dry crystalline sample of the products from the phosphorylation of benzanilide also showed the presence of a mixture of two

* The SERC NMR facility at Warwick University is acknowledged for performing the ^{15}N NMR investigation.

Table 2 Carbon and phosphorus NMR chemical shifts of amide and imide groups

	^{13}C Chemical shifts				^{31}P Chemical shifts	
	N–C=O		N=C–O		$N-PO_3H_2$	$=C-O-PO_3H_2$
Compound	$[^2H_6]$Acetone-d_6	$(CD_3)_2SO$	$[^2H_6]$Acetone	$(CD_3)_2SO$	$[^2H_6]$Acetone	$[^2H_6]$Acetone
1a	166.72	166.50[a]				
2a	171.25	173.43[a]			−13.06	
3a			142.30	141.43[a]		2.81, 3.70
1b	166.50	163.57				
2b	168.79	170.27			−12.25	
3b			135.40	137.74		2.83
1c	168.07	163.06				
2c	173.47	162.99			−12.92	
3c			137.80	134.13		1.88, 2.56
1d	166.43	163.06				
2d	173.22	170.28			−13.19	
3d			138.70	135.24		1.62, 2.51
1e	166.90[a]	169.16				
2e	167.60[a]	169.56			−12.65	
3e			140.70[a]	137.95		2.02, 2.42

[a] The solvent was $CDCl_3$.

Table 3 Characteristic IR wavenumbers, ν_{max}/cm^{-1}

Compound	ν_{N-H}	$\nu_{P=O}$	ν_{P-O-C}	ν_{OH}
1a	3290			
2a		1255		3300–3000
3a	3280w	1275, 1255	1010, 1000	3100–2900
		1200		
1b	3220			
2b		1270		3400–3000
3b	3220w	1270	1020br	3300–2900
1c	3220w			
2c		1205		3400–2950
3c	3240w	1265–1250	1015, 1000	3100–2900
1d	3230			
2d		1230		3250–2950
3d	3230w	1240, 1210	1025, 1005	3300–3100
1e	3250			
2e		1265		3400
3e	3240w	1225, 1190	1020, 995	3200–2900

isomers **2a** and **3a**.* UV irradiation of a dry sample raised the intensities of the signals assigned to phosphoric monoester **3a** at the expense of the signals attributed to the phosphoramidic acid **2a**. The ^{13}C NMR spectrum of the irradiated crystalline product contained one additional signal at δ_C 141.9 (COP).

The rearrangement of the imidate **7** (Z = Ph) to amide **8** (Z = Ph) was first described in 1900.[9] Later Mumm[10] and Chapman[11] reported the migration of aryl and benzyl groups from oxygen to nitrogen for the imidate–amide system (**7** ⇌ **8**). Over recent years the variety of migrating groups has been extended to include alkyl,[12–14] benzoyl,[15,16] chloro,[17] and nitro groups.[18,19] Some authors have included studies of the stereochemistry,[12,13] the kinetics[12,20] and the mechanism of the reaction.[19,21] Only two migratory groups, Z = Cl[17] and Z = R_3Si,[22] exhibit a reversible reaction (*i.e.*, migration from nitrogen to oxygen as well as the reverse).

The mechanism of the rearrangement of the N-phosphorylated product to the O-phosphorylated product will be interesting to establish. The involvement of a protic solvent suggests a bimolecular mechanism such as the tentative mechanism shown in Scheme 2. Whilst we have no direct evidence that alcohol acts as a nucleophile the phosphoric acid group is well positioned to act as an intramolecular acid catalyst for the ethanolysis of the amide group. However, solid-state phosphorus-31 NMR spectroscopy showed that UV irradiation of a sample induced the rearrangement, although the involvement of trace amounts of water cannot be ruled out. The mechanism does not involve hydrolysis of the P–N bond, followed by secondary O-phosphorylation, since the anilides were not phosphorylated by partially hydrolysed phosphoric anhydride under the experimental conditions used in the work-up.

Conclusions.—In conclusion, phosphoric anhydride is readily available, easy to handle, and is an efficient N-phosphorylating agent for compounds such as the benzanilides, and with the ease of N-to-O phosphotropy the reaction is a convenient route to the preparation of stable O-phosphorylated amides.

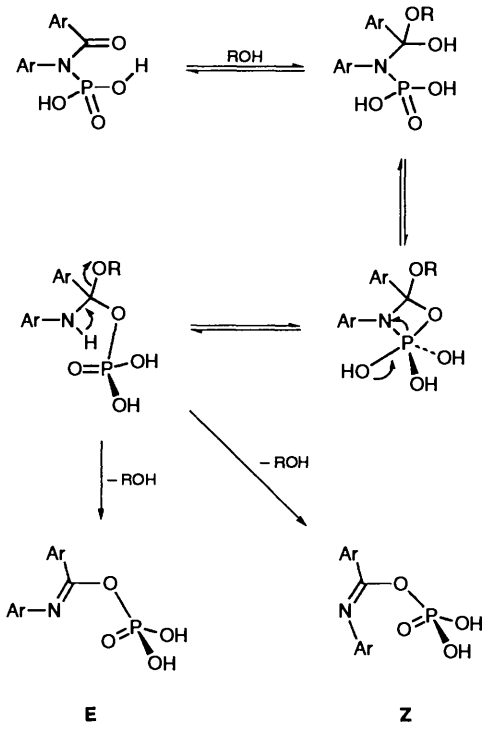
Experimental

IR spectra were determined for samples as KBr discs on a Pye Unicam SP3-200 instrument. NMR spectra were determined on JEOL FX90Q, GSX270 and Bruker 100 instruments (the latter being used for the solid-state measurements) and the products were dissolved in $[^2H_6]$acetone except where indicated otherwise. The ^{13}C NMR chemical shifts obtained on saturated $(CD_3)_2SO$ solutions were referenced to the solvent chemical shift, which resonated at δ_C 37.74 relative to $SiMe_4$. Whilst the chemical shift of the Me_2SO is influenced by the solute to some extent the relative order of the signals appeared to be the same in all solvents. *J* Values are given in Hz.

Benzanilides **1**.—The various benzanilides were prepared from the appropriate anilines and aroyl chlorides,[23] recrystallised from ethanol, and dried *in vacuo* at 50 °C for 3 h.

N-Aryl-N-benzoylphosphoramidic Acids **2**.—The normal phosphorylation procedure involved heating a heterogeneous mixture of the appropriate benzanilide (0.02 mol) and phosphoric anhydride (P_4O_{10}; 0.01 mol) in trichloromethane (distilled from phosphoric anhydride; 25 cm^3) for 3 h. As the trichloromethane developed a yellow colour ^{31}P NMR spectroscopy showed the presence of phosphorylated products.

* Solid-state NMR spectra were determined at the Institute of High Molecular Compounds, St Petersburg. Solid-state NMR parameters were as follows: **2a** δ_C 121.6, 128.4, 134.67, 162.8 and 169.98; δ_P −1.16 (minor component), −14.10 (major component) and for **3a** δ_C 121.6, 128.6, 134.95, 141.9, 162.30 and 169.44; δ_P −2.15 (major component), −10.40 (minor component).



Scheme 2 Proposed mechanism for phosphorus migration from N to O

In the case of the 2',6'-diisopropylbenzanilide **1e** the colour was pink. When the reaction was complete all the amide had reacted, leaving a small amount of unchanged anhydride. After evaporation of the solvent a sticky residue was obtained, which was triturated repeatedly with diethyl ether until the *N*-aryl-*N*-benzoylphosphoramidic acid was obtained as a yellow or pink powder.

N-Benzoyl-*N*-phenylphosphoramidic acid **2a** was obtained from benzanilide **1a**, by the above procedure, as a yellow powder (5.1 g, 92%), m.p. 56–57 °C (decomp.); ν_{max}/cm^{-1} 3300–3000, 1650, 1605 and 1255; δ_H 6.86–7.91 (m, Ph); δ_C 130.0–140.8 (m, Ph) and 171.25 (CO); δ_P −13.06.

N-Benzoyl-*N*-(2-methylphenyl)phosphoramidic acid **2b** was obtained from anilide **1b**, by the above procedure, as a yellow powder (4.8 g, 83%), m.p. 69–70 °C (decomp.); ν_{max}/cm^{-1} 3400–3000 and 1270; δ_H 2.32 (3 H, s, Me) and 7.15–7.97 (9 H, m, ArH); δ_C 16.4 (Me), 124.6–135.4 (m, Ar) and 168.79 (s, CO); δ_P −12.25.

N-Benzoyl-*N*-(2,6-dimethylphenyl)phosphoramidic acid **2c** was obtained from the anilide **1c**, by the above procedure, as a yellow powder (5.7 g, 93%), m.p. 75 °C (decomp.); ν_{max}/cm^{-1} 3400–2950, 1636 and 1205; δ_H 2.19 (6 H, s, Me) and 6.96–7.80 (8 H, m, ArH); δ_C 19.9 (Me), 127.0–132.3 (m, Ar) and 173.47 (CO); δ_P −12.92.

N-Benzoyl-*N*-(2,4,6-trimethylphenyl)phosphoramidic acid **2d** was obtained from the anilide **1d**, by the above procedure, as a yellow powder (6.0 g, 94%), m.p. 44 °C (decomp.); ν_{max}/cm^{-1} 3250–2950, 1655, 1610 and 1230; δ_H 2.01 (6 H, s, Me), 2.14 (3 H, s, Me) and 6.7–7.7 (7 H, m, ArH); δ_C 22.37, 24.12 (Me), 129.1–141.3 (m, Ar) and 173.22 (CO); δ_P −13.19.

N-Benzoyl-*N*-(2,6-diisopropylphenyl)phosphoramidic acid **2e** was obtained from the anilide **1e**, by the above procedure, as a pink powder (4.6 g, 64%), m.p. 43–44 °C (decomp.); ν_{max}/cm^{-1} 3400, 1640 and 1265; $\delta_H(Me_2SO)$ 1.71 (12 H, d, Me), 3.79 (2 H, sept, J_{HH} 8, CH) and 7.25–7.92 (8 H, m, ArH); $\delta_C(Me_2SO)$ 21.44 (Me), 26.14 (CH), 118.47–142.34 (m, Ar) and 169.56 (CO); δ_P −12.65.

N-Arylbenzimidoyl Phosphoric Anhydrides.—The normal rearrangement procedure involved treatment of the *N*-aryl-*N*-benzoylphosphoramidic acid with ethanol, which partially dissolved the acid. After 10 to 15 min fine yellow crystals began to separate. Most of the solvent was allowed to evaporate off. The crystalline solid was separated by filtration and dried *in vacuo* to give the hydrolytically stable products described below.

N-Phenylbenzimidoyl phosphoric anhydride **3a** was obtained from phosphoramidic acid **2a**, by the method described above, as a powder (3.9 g, 76%), m.p. 140–143 °C (decomp.); ν_{max}/cm^{-1} 3100–2900, 1675, 1600, 1590, 1275, 1255, 1200, 1010 and 1000; δ_H 6.95–7.79; δ_C 121.3–140.6 (m, Ar) and 142.3 (br, COP); δ_P 3.7 and 2.8 (Found: C, 56.5; H, 4.1; N, 5.1; P, 11.2. $C_{13}H_{12}NO_4P$ requires C, 56.32; H, 4.33; N, 5.05; P, 11.19%).

N-(2-Methylphenyl)benzimidoyl phosphoric anhydride **3b** was obtained from phosphoramidic acid **2b**, by the method described above, as a yellow powder (3.1 g, 64%), m.p. 113–115 °C (decomp.); ν_{max}/cm^{-1} 3300–2900, 1270 and 1020br; δ_H 2.83 (3 H, s, Me) and 7.16–8.03 (9 H, m, ArH); δ_C 16.8 (Me), 124.8–135.0 (m, Ar) and 135.4 (d, J_{CP} 11.7, COP); δ_P 2.83 (Found: C, 57.8; H, 4.7; N, 4.9; P, 10.5. $C_{14}H_{14}NO_4P$ requires C, 57.73; H, 4.81; N, 4.81; P, 10.65%).

N-(2,6-Dimethylphenyl)benzimidoyl phosphoric anhydride **3c** was obtained from phosphoramidic acid **2c**, by the method described above, as a powder (5.2 g, 91%), m.p. 126–128 °C (decomp.); ν_{max}/cm^{-1} 3100–2900, 1635, 1265–1250, 1015 and 1000; δ_H* 1.99 (3 H, s, Me), 2.62 (3 H, s, Me) and 6.88–7.73 (8 H, m, ArH); δ_C 19.8 (Me), 21.10 (Me), 123.8–132.6 (m, Ar) and 137.8 (d, J_{CP} 19, COP); δ_P 2.56 and 1.88 (Found: C, 59.0; H, 5.3; N, 4.7; P, 10.0. $C_{15}H_{16}NO_4P$ requires C, 59.02; H, 5.25; N, 4.59; P, 10.16%).

N-(2,4,6-Trimethylphenyl)benzimidoyl phosphoric anhydride **3d** was obtained from phosphoramidic acid **2d**, by the method described above, as a yellow powder (5.8 g, 97%), m.p. 165–168 °C (decomp.); ν_{max}/cm^{-1} 3300–3100, 1640, 1605, 1595, 1240, 1210, 1025 and 1005; δ_H* 1.92 and 2.15 (6 H, 2 s, Me), 2.21 and 2.27 (3 H, 2 s, Me) and 6.76–7.70 (7 H, m, ArH); δ_C 19.5, 20.1, 21.0, 21.2 (Me), 129.1–144.8 (Ar) and 138.7 (d, J_{CP} 24, COP); δ_P 2.51 and 1.62 (Found: C, 60.0; H, 5.8; N, 4.3; P, 9.6. $C_{16}H_{18}NO_4P$ requires C, 60.19; H, 5.64; N, 4.39; P, 9.72%).

N-(2,6-Diisopropylphenyl)benzimidoyl phosphoric anhydride **3e** was obtained from phosphoramidic acid **2e**, by the method described above, as a yellow (3.0 g, 65%), m.p. 256–257 °C (decomp.); ν_{max}/cm^{-1} 3200–2900, 1600, 1225, 1190, 1020 and 995; $\delta_H(Me_2SO)$ 1.73 (12 H, d, J_{HH} 7, Me), 3.79 (2 H, sept, J_{HH} 7, CH), 7.79–8.67 (8 H, m, ArH); $\delta_C(Me_2SO)$ 21.64 (Me), 26.34 (CH), 121.14–144.34 (m, Ar) and 137.95 (br, COP); δ_P 2.42 and 2.02 (Found: C, 62.9; H, 6.80; N, 3.7; P, 8.40. $C_{19}H_{24}NO_4P$ requires C, 63.16; H, 6.65; N, 3.88; P, 8.59%).

Acknowledgements

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* The NMR proton spectra of acids **3c** and **3d** exhibited fine structure.

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