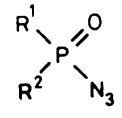
Influence of *ortho* Methyl and Isopropyl Substituents on the Reactivity of *N*-t-Butyl *P*-Arylphosphonamidic Chlorides with Isopropylamine and t-Butylamine: Steric Acceleration of Metaphosphonimidate Formation by an Elimination–Addition Mechanism; Contrasting Behaviour of *N,N*-Dimethyl *P*-Arylphosphonamidic Chlorides

Sally Freeman and Martin J. P. Harger
Department of Chemistry, The University, Leicester, LE1 7RH

The two types of phosphonamidic chloride $ArP(O)(Cl)NMe_2$ (**5**) and $ArP(O)(Cl)NHBu^t$ (**7**) have been prepared with Ar = Ph, *o*-MeC_6H_4, 2,4,6-$Me_3C_6H_2$, and 2,4,6-$Pr^i_3C_6H_2$. Both types give the expected phosphonic diamide substitution products with Pr^iNH_2 and Bu^tNH_2 in MeCN, but the two types display contrasting reactivity. With Bu^tNH_2 the NMe_2 substrates (**5**) become progressively less reactive as the degree of steric crowding increases, and although the decrease is quite small (70-fold overall) it seems consistent with an associative [$S_N2(P)$] mechanism. These substrates react ⩾100 times faster with Pr^iNH_2, than with Bu^tNH_2 and in Pr^iNH_2–Bu^tNH_2 competitive experiments they give almost exclusively (⩾99%) the product derived from the less hindered Pr^iNH_2. For the $NHBu^t$ substrates (**7**) with Bu^tNH_2, there is little difference in reactivity between the Ph and *o*-MeC_6H_4 compounds, and between the 2,4,6-$Me_3C_6H_2$ and 2,4,6-$Pr^i_3C_6H_2$ compounds, but remarkably the more crowded pair of substrates is the more reactive, by a factor of *ca.* 100. Also, in competitive experiments these substrates display relatively little preference for reaction with Pr^iNH_2. Here a dissociative elimination–addition mechanism, with a metaphosphonimidate intermediate, is seen to be important. A possible explanation of the steric acceleration is advanced. The ability of (**7**; Ar = Ph) to undergo substitution by elimination–addition makes possible the phosphonylation of unreactive nucleophiles such as Bu^tOH and Pr^i_2NH under mild conditions.

Metaphosphonimidates (**3**; R^1, R^2 = alkyl or aryl) contain a phosphorus atom that is formally quinquevalent yet has a co-ordination number of only 3. This property they share with monomeric metaphosphate.[1] They seem to be formed as short-lived intermediates in the photochemical rearrangements of phosphinic azides (**1**)[2] and in the base-induced rearrangements



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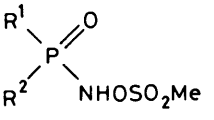

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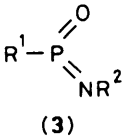

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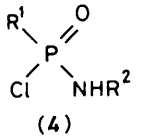


(**4**)

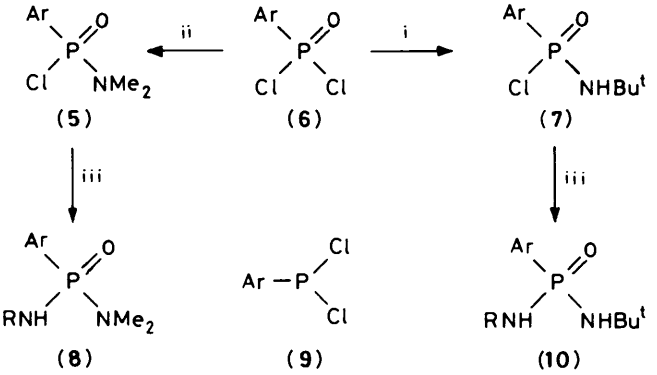
of the *N*-phosphinoylhydroxylamine derivatives (**2**).[3] For the particular case of *P*-aryl *N*-alkyl metaphosphonimidates (**3**; R^1 = aryl, R^2 = alkyl) these rearrangement pathways are of limited use. With alkylarylphosphinic azides (**1**; R^1 = alkyl, R^2 = aryl) the required alkyl migration does occur, but complications arise not only from competing aryl migration but also from radical and nitrene reactions.[4] With the corresponding hydroxylamine derivatives (**2**) alkyl migration does not occur at all; rearrangement proceeds with exclusive migration of the aryl group.[5]

In principle, *P*-aryl *N*-alkyl metaphosphonimidates should be accessible from the appropriate phosphonamidic chlorides (**4**; R^1 = aryl, R^2 = alkyl) by base-induced elimination of HCl.*

There have been few reports of the successful preparation of phosphonamidic chlorides containing an NH group, but encouraged by the results of a recent study of the *P*-alkyl compounds (**4**; R^1 = various alkyl, R^2 = Bu^t)[6] we turned our attention to related *P*-aryl compounds. In particular, we decided to attempt the preparation of the *P*-phenyl-, *P*-*o*-tolyl-, and *P*-mesityl-phosphonamidic chlorides (**7**) derived from t-butylamine. If successful, their behaviour could then be compared with that of the corresponding dimethylamine derivatives (**5**), where the lack of an NH group precludes the possibility of metaphosphonimidate formation.

Results and Discussion

The obvious way to make a phosphonamidic chloride is by treatment of the phosphonic dichloride with 2 mol equiv. of the appropriate amine (Scheme 1). Using t-butylamine in



(**5**) (**6**) (**7**) (**8**) (**9**) (**10**)

a; Ar = Ph b; Ar = *o*-MeC_6H_4 c; Ar = 2,4,6-$Me_3C_6H_2$
d; Ar = 2,4,6-$Pr^i_3C_6H_2$

Scheme 1. *Reagents:* i, 2 Bu^tNH_2 (−Bu^tNH_3Cl); ii, 2 Me_2NH (−Me_2NH_2Cl); iii, 2 RNH_2 (−RNH_3Cl)

* Phosphonamidic chlorides are distinguished from the better known phosphoramidic chlorides by the presence of a C–P bond.

Table. Reactions of phosphonamidic chlorides with Pr^iNH_2 and Bu^tNH_2 in acetonitrile at 0 °C. Rate constants (k) under first-order conditions (1.0M amine), ^{31}P n.m.r. chemical shifts (δ_P) of products, and product ratios (n^i/n^t) in competitive experiments (each amine 0.5M)[a]

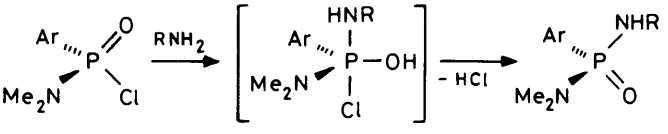
	ArP(O)(NMe$_2$)Cl (**5**)[b]			ArP(O)(NHBu^t)Cl (**7**)[c]		
	Phenyl	*o*-Tolyl	Mesityl	Phenyl	*o*-Tolyl	Mesityl
$10^4\ k^i/s^{-1}$	450	165	75	350	260	~7 000
$10^4\ k^t/s^{-1}$	3.45	1.15	0.71	107	70	~7 000
k^i/k^t	130	145	105	3.3	3.7	~1
δ_P^i/p.p.m.[d]	21.3	22.0	22.8	15.0	14.0	14.5
δ_P^t/p.p.m.[d]	19.6	20.6	21.8	13.9	13.3	13.2
n^i/n^t	≥100	≥100	≥100	3.3	3.2	1.65

[a] Superscripts i and t relate to reaction with Pr^iNH_2 and Bu^tNH_2 respectively. Uncertainty in values of k generally ≤ ±10%. [b] For Ar = 2,4,6-tri-isopropylphenyl: $10^4k^t = 0.050\ s^{-1}$. [c] For Ar = 2,4,6-tri-isopropylphenyl: 10^4k^t ~11 500; δ_P^i 15.1; δ_P^t 14.3; n^i/n^t 5.1. [d] Chemical shift in acetonitrile reaction mixture.

dichloromethane at 0 °C this approach worked well for the *P*-phenyl and *P*-*o*-tolyl compounds (**7a**) and (**7b**). For the *P*-mesityl compound, however, the product was very largely a mixture of the phosphonic diamide (**10**; R = Bu^t) and unchanged dichloride starting material; only *ca.* 3% of the required phosphonamidic chloride was evident in the ^{31}P n.m.r. spectrum. In this case it seems that the reactivity of the phosphonamidic chloride exceeds that of the phosphonic dichloride. Fortunately, the selective replacement of one chlorine atom was possible using the tervalent mesitylphosphonous dichloride (**9c**) and t-butylamine; oxidation of the resulting phosphonamidous chloride with dimethyl sulphoxide then afforded the required phosphonamidic chloride (**7c**). Like its phenyl and *o*-tolyl analogues, this proved to be a stable crystalline compound.* The *N*,*N*-dimethylaminophosphonamidic chlorides (**5a**—**c**) were obtained without difficulty from the phosphonic dichlorides and dimethylamine.

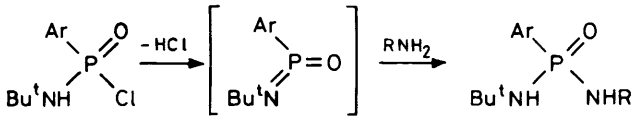
All of the phosphonamidic chlorides reacted cleanly with both isopropylamine and t-butylamine to give the expected phosphonic diamides (**8**) and (**10**) (R = Pr^i or Bu^t). The rates of the reactions were examined at 0 °C using a 10-fold excess of the amine as a 1.0M solution in acetonitrile. Samples were withdrawn at intervals and treated with a large excess of methanol [containing NaOMe in the case of the dimethylamino substrates (**5**)]. This converted unchanged phosphonamidic chloride into the corresponding methyl ester which was estimated by g.l.c. Linear first-order plots were obtained, and from them the rate constants (k) were deduced (Table). The mesityl compound (**7c**) was exceptional. It reacted so quickly (75% complete in 2 s) that only one sample could be taken; for it the values of k are necessarily very approximate. Competitive experiments were also carried out, under similar conditions. Each substrate was added to a large excess of an equimolar mixture of isopropylamine and t-butylamine in acetonitrile (1.0M total amine concentration) at 0 °C, and the NHPr^i/NHBu^t product ratio (n^i/n^t) was measured by ^{31}P n.m.r. spectroscopy (Table) and confirmed by g.l.c.

From the results it is clear that the NMe$_2$ substrates (**5**) react much more rapidly with isopropylamine than with t-butylamine ($k^i \geq 100\ k^t$), and under competitive conditions give practically none (< 1%) of the product derived from t-butylamine. Such high sensitivity to the bulk of the nucleophile is consistent with an associative $S_N2(P)$ mechanism proceeding through a five-co-ordinate intermediate or transition state (Scheme 2).[7] The



Scheme 2.

picture for the NHBu^t substrates (**7**) is quite different. In the case of the mesityl compound the rates of reaction with isopropylamine and t-butylamine are similar (although the values of k here are very approximate), and only a small preference for isopropylamine is evident under competitive conditions. These features point to a dissociative elimination–addition mechanism as shown in Scheme 3.† Here the amine acts as a base rather



Scheme 3.

than a nucleophile in the rate-limiting elimination of HCl, so its bulk will be of little consequence. And when nucleophilic attack does subsequently occur in the product-forming step, there will be little discrimination between competing nucleophiles because the metaphosphonimidate is highly reactive and sterically accessible. This type of mechanism is known to be important in the alkaline hydrolysis of some phosphoric acid derivatives having one or more NH groups attached to the

* Attempts to prepare *P*-arylphosphonamidic chlorides using other primary aliphatic amines have not been successful. Thus, for example, mesitylphosphonic dichloride gave a rather complex mixture of products with 2 mol equiv. MeNH$_2$ (^{31}P n.m.r. analysis), although with a large excess it was converted cleanly into *N*,*N*′-*dimethyl*-P-*mesityl*-*phosphonic diamide* [$\delta_P(CH_2Cl_2)$ 23.2; m.p. 137—140 °C; *m*/*z* 226 (M^+; 100%); Found: C, 58.5; H, 8.5; N, 12.7. $C_{11}H_{19}N_2OP$ requires C, 58.4; H, 8.5; N, 12.4%]. Significantly it was found that the diamide and the dichloride reacted together, and gave a similar mixture of products. In general, compounds of the type ArP(O)(NHR)Cl seem to be stable only if the nucleophilicity of the P(O)NHR moiety is reduced by a very bulky group R or, presumably, the P atom is exceptionally shielded from nucleophilic attack. Even PhP(O)(NHPr^i)Cl could not be prepared. [*N*-Aryl phosphonamidic chlorides such as PhP(O)(NHPh)Cl doubtless owe their stability to the nucleophilicity of the N atom being reduced by conjugation.]

† The picture presented in Scheme 3 is sufficient for our present purposes but is probably an oversimplification. In particular the elimination of HCl from the substrate probably involves formation and breakdown of the conjugate base.

phosphorus atom.[1] The phenyl and *o*-tolyl compounds show a somewhat greater preference for reaction with isopropylamine. A likely explanation is that with isopropylamine, but not the more hindered t-butylamine, the $S_N2(P)$ mechanism now competes effectively with elimination–addition. The rates observed with isopropylamine will then include the $S_N2(P)$ contribution, so they will be substantially greater than the rates with t-butylamine, while the mixtures formed in the competitive experiments will include some product derived directly from isopropylamine by the $S_N2(P)$ mechanism.

The two types of substrate (**5**) and (**7**) differ also in their response to the presence of *ortho* methyl substituents. The NMe_2 compounds (**5**) show the expected decline in reactivity as the *P*-aryl group changes from phenyl to *o*-tolyl to mesityl, although the change (1.5—3 fold per *ortho* Me group) is not as great as might have been anticipated for an $S_N2(P)$ mechanism. Examination of the phosphorane intermediate suggests an explanation (Figure 1). Given that the nucleophile (RNH_2)

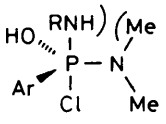


Figure 1.

enters apically and opposite to the leaving group (Cl),[7] the remaining ligands in the trigonal bipyramid must occupy equatorial positions. Because the lone pair of an equatorially bonded nitrogen atom has a marked preference for the equatorial plane,[7,8] the methyl groups of the Me_2N ligand will lie above and below that plane. Provided the plane of the aryl group (Ar) lies in the equatorial plane (and we know of no evidence that suggests it should not), *ortho* methyl substituents will give rise to only a small steric effect; the major steric interaction will be between the entering group (RNH) and a methyl group of the Me_2N ligand. Some support for this explanation can be found in the reactivity of phenylsulphonyl compounds. The transition state for substitution has a similar shape,[9] but in place of the Me_2N ligand it has just an oxygen atom. And now, significantly, *ortho* substituents do not retard substitution,[10] and may even accelerate it.[9,11]

For the NHBu^t substrates (**7**) the rate decreases very little ($\leqslant$1.5 fold) when phenyl is replaced by *o*-tolyl, and with mesityl it does not decrease at all. On the contrary it increases, and the increase (20—100 fold) is not small. Such steric acceleration of substitution at a phosphoryl centre seems to have no precedent.

We hoped to gain some information on the origin of the acceleration by examining the more crowded 2,4,6-tri-isopropylphenyl substrates (**5d**) and (**7d**). These were prepared in the same ways as the mesityl compounds, except that sulphuryl chloride was used in place of dimethyl sulphoxide to oxidise the *N*-t-butylphosphonamidous chloride. With t-butylamine the NMe_2 substrate (**5d**) reacted 14 times slower than its mesityl analogue ($10^4k^t = 0.050\ s^{-1}$ under the conditions of the Table). The magnitude of this difference seems compatible with the comments made earlier on the probable steric interactions in the five-co-ordinate $S_N2(P)$ intermediate. The NHBu^t substrate (**7d**) reacted at roughly the same rate as the mesityl analogue, and too fast for proper measurement. When it was made to compete with the mesityl compound for a limited amount of t-butylamine it was seen to be *ca.* 1.65 times more reactive. An isopropylamine–t-butylamine competitive experiment proved especially interesting, giving an NHPr^i/NHBu^t product ratio of 5.1. It seems inconceivable that $S_N2(P)$ plays any significant part here, in which case we must be witnessing discrimination on the part of the 2,4,6-tri-isopropylphenyl metaphosphonimidate. Such discrimination by a metaphosphonimidate is unusual but not too surprising: however great the intrinsic reactivity, a point must be reached where bulky substituents begin to moderate the observed reactivity towards sterically demanding nucleophiles.

Our rate measurements suggest that the NHBu^t substrates (unlike the NMe_2 ones) are influenced less by the overall crowding in the molecule than by whether or not both *ortho* positions are substituted: there is a sharp distinction between those substrates that have two *ortho* substituents [(**7c**) and (**7d**)] and those that do not [(**7a**) and (**7b**)], but otherwise the differences are small. With regard to the steric acceleration,[12] this may be a clue as to the nature of the interactions that destabilise the substrate relative to the metaphosphonimidate intermediate (strictly, of course, the metaphosphonimidate-like transition state). Of several possible explanations the one we find most satisfying contains the following postulates.

(i) Because one of the substituents on nitrogen is just a hydrogen atom, the NHBu^t group can avoid any substantial steric interaction with the Ar group in the substrate. Even if conjugation (p_π-d_π) imposes conformational restraints on the N–P bond that require the nitrogen p orbital to be aligned in a way that places one of the nitrogen substituents close to Ar, that substituent can always be the hydrogen atom. (The ability to form cyclic hydrogen-bonded dimers may be lost, but in a solvent like acetonitrile that should be of little consequence.[13])

(ii) There are two significant types of conformation for the Ar–P bond, which in the substrate links trigonal and tetrahedral centres;[14] these are shown in Figure 2 (A and B), where R is the

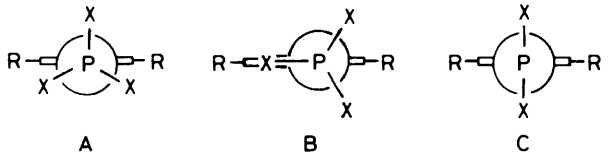


Figure 2.

ortho substituent and X = O, Cl, or NHBu^t. In A the separation between one of the ligands X and the two *ortho* positions (R) is maximised; in B the separation between two of the ligands X and one of the *ortho* positions is optimised. When the *ortho* positions carry only hydrogen atoms (Ar = phenyl) there is probably not much difference in energy (or population) between the two types of conformation. When one *ortho* methyl group is present (Ar = *o*-tolyl) the only change will be the loss of some conformational freedom as a result of the destabilisation of those type B conformations in which the methyl group eclipses X. When both *ortho* positions carry methyl groups all type B conformations will be adversely affected. Moreover, type A conformations will now also probably be destabilised, since any perturbation that would ease one of the *ortho*-Me/X gauche interactions will inevitably exacerbate the other. This is not the case when only one *ortho* substituent is present. It may therefore be that conformational factors cause significant destabilisation of the mesityl substrate while having little effect on the *o*-tolyl substrate.

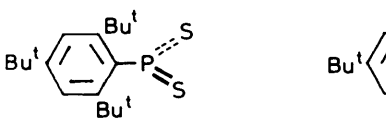
(iii) In the metaphosphonimidate the Ar–P bond joins two trigonal centres, so conformational strain can be relieved by adoption of a conformation (Figure 2, C) with a dihedral angle approaching 90°. The stable three-co-ordinate P^V species (**11**) and (**12**) are known to have dihedral angles of *ca.* 80° in the crystal.[15]

(iv) The major effect of changing the *ortho* substituents (R) from methyl to isopropyl will be a substantial reduction in conformational freedom about the R–Ar bonds. This restriction is due chiefly to the presence of the P atom, and will be almost as severe in the metaphosphonimidate as it is in the substrate. Any

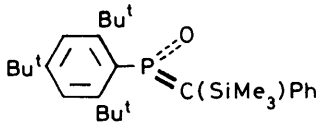
difference in $\Delta G^{\ddagger}$ for the mesityl and tri-isopropylphenyl substrates will therefore be small.

With these postulates it is possible to rationalise the ways in which the different *P*-aryl groups influence the reactivity of the NHBu^t substrates (**7**) in the elimination–addition mechanism. Of course other factors, notably solvation, may also be important.

Implicit in (iv) above is the absence of any substantial steric interaction between *ortho* isopropyl substituents in the *P*-aryl group and the other ligands on phosphorus. With *ortho* t-butyl substituents this could no longer be the case. Steric strain would be quite severe in the substrate, but much less so in the metaphosphonimidate. Enhanced steric acceleration would, therefore, be expected. Unfortunately, our attempts to prepare the phosphonamidic chloride (**7**) with Ar = 2,4,6-tri-t-butylphenyl have not been successful. The phosphonous dichloride is a known compound,[16] but we were unable to obtain (or at least to isolate) the phosphonamidic chloride by treatment with t-butylamine (2 mol equiv.) followed by oxidation. With sulphuryl chloride it gave the phosphonic dichloride (Scheme 4). This was understandably reluctant to



(**11**)



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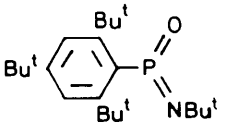
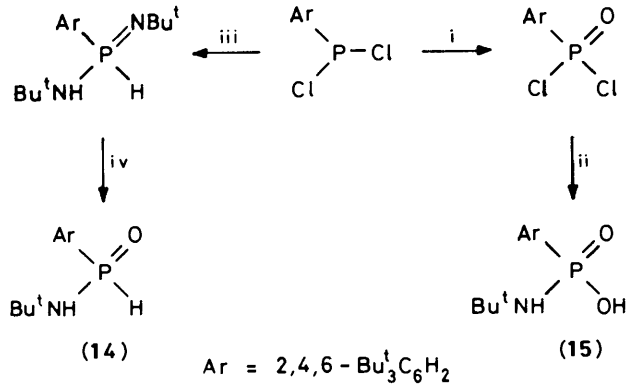


(**13**)

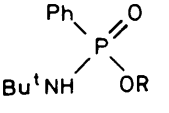
react with t-butylamine, although under extreme conditions (amine in large excess at 96 °C; no solvent) it did give the phosphonic diamide [presumably *via* the metaphosphonimidate (**13**)]. It reacted under mild conditions with methylamine (CH_2Cl_2 solution at room temperature) but gave only a mixture (1:1) of the diamide and unchanged starting material when just 2 mol equiv. of amine was used. The phosphonamidous acid (**14**) and the phosphonamidic acid (**15**) were also prepared (Scheme 4) but they did not give the phosphonamidic chloride



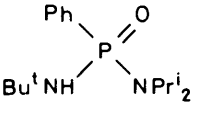
Scheme 4. *Reagents:* i, SO_2Cl_2 then H_2O; ii, Bu^{t}NH$_2$ + H_2O, then CF_3CO_2H; iii, Bu^{t}NH$_2$; iv, Me_2SO

with, respectively, sulphuryl chloride and oxalyl chloride. There was evidence of Ar–P bond cleavage in these reactions, giving rise to 1,3,5-tri-t-butylbenzene. Our failure to obtain the phosphonamidic chloride is all the more disappointing now that the metaphosphonimidate (**13**) has been produced by a different method, and shown to be stable as the monomer at 0 °C.[17]

An important consequence of the ability of NH-containing phosphonamidic chlorides to undergo substitution by elimination–addition is the ready occurrence of reactions that by $S_N2(P)$ would be very slow. Note, for example, that the NHBu^t substrate (**7d**; Ar = 2,4,6-tri-isopropylphenyl) reacted at least 2×10^5 times faster with t-butylamine than did the corresponding NMe_2 substrate (**5d**). Of practical significance, this high reactivity should allow molecules that for electronic or steric reasons are only weakly nucleophilic to be phosphonylated under mild conditions. The reactions of *N*-t-butyl-*P*-phenylphosphonamidic chloride (**7a**) with t-butyl alcohol, trifluoroethanol, hexafluoroisopropanol, and di-isopropylamine were therefore examined. They proceeded quite readily in dichloromethane, even at 0 °C, when 2,2,6,6-tetramethylpiperidine was added as base to generate the metaphosphonimidate. The products were the expected phosphonamidates [**16**; R = OBu^t, OCH_2CF_3, or $OCH(CF_3)_2$] and phosphonic diamide (**17**). It



(**16**)



(**17**)

might be noted that the phosphorylation of t-butyl alcohol is often considered diagnostic of the formation of monomeric metaphosphate,[18] and that di-isopropylamine does not react with $Ph_2P(O)Cl$ even under very forcing conditions.[19]

Experimental

Instrumentation for g.l.c., m.s., and n.m.r. was as previously described.[6] Chemical shifts are quoted relative to internal tetramethylsilane (δ_H) or external 85% H_3PO_4 (δ_P; positive values at low field). M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded with a Perkin-Elmer 298 instrument. Amines were dried over, and distilled from, potassium hydroxide. Acetonitrile was purified by distillation from calcium hydride. Light petroleum refers to the fraction b.p. 60—80 °C unless otherwise indicated.

Phosphonous Dichlorides.—Mesitylphosphonous dichloride (**9c**). The Grignard reagent from bromomesitylene (16.3 g, 82 mmol) and magnesium (3.95 g, 0.164 mol) in THF (40 ml) was added during 0.5 h to a stirred solution of bis(dimethylamino)chlorophosphine[20] (11.5 g, 75 mmol) in ether (70 ml) at −45 °C (bath temp.). After warming to room temperature the mixture was diluted with ether (100 ml) and filtered (N_2 atmosphere). The filtrate [δ_P 106.1; $ArP(NMe_2)_2$] was evaporated and the residue was extracted with light petroleum (130 ml). The extract was stirred at 0 °C and anhydrous hydrogen chloride (a slight excess) was introduced during *ca.* 1 h.[21] The solid (Me_2NH_2Cl) was filtered off (N_2 atmosphere) and the filtrate (δ_P 164.8) was evaporated, finally at 0.2 mmHg. Mesitylphosphonous dichloride (14.4 g, 87%) was obtained essentially pure, δ_P (CH_2Cl_2) 168.8; *m/z* 224, 222, 220 (M^+; 7, 42, 63%) and 187, 185 (33, 100); $\delta_H(CDCl_3)$ 6.84 (2 H, d, J_{PH} 4 Hz), 2.68 (6 H, d, J_{PH} 4 Hz), and 2.27 (3 H, s). It could be purified by distillation, b.p. 147 °C (oven temp.) at 0.5 mmHg (lit.,[22] 156—157 °C at 16 mmHg).

2,4,6-*Tri-t-butylphenylphosphonous dichloride*.[16] A solution of the aryl-lithium[23] in THF was prepared from 2,4,6-tri-t-butylbromobenzene[24] and butyl-lithium. This was maintained at −78 °C and phosphorus trichloride (1.5 mol equiv.) was added.[16] After a further 10 min at −78 °C the mixture was boiled under reflux for 1 h and filtered. Evaporation of the

filtrate gave the crude phosphonous dichloride δ_P (THF) 152.5. Attempts to purify it by distillation or crystallisation were unsuccessful.

2,4,6-*Tri-isopropylphenylphosphonous dichloride* (**9d**). Starting from 2,4,6-tri-isopropylbromobenzene a modification of the above procedure (3 mol equiv. PCl_3; no heating) gave the phosphonous dichloride (**9d**), δ_P 165.0, contaminated with *ca.* 25% of bis(2,4,6-tri-isopropylphenyl)phosphinous chloride (δ_P 88.3). This material was used without purification. A slightly different method might have given a purer product.[20]

Phosphonic Dichlorides.—o-*Tolylphosphonic dichloride* (**6b**). Diethyl *o*-tolylphosphonate, b.p. 109—110 °C at 0.2 mmHg (lit.,[25] 110 °C at 0.1—0.4 mmHg), $\delta_P(CHCl_2)$ 20.2, was prepared from *o*-bromotoluene and triethyl phosphite.[25] Treatment with phosphorus pentachloride[25] afforded *o*-tolylphosphonic dichloride (**6b**), b.p. 84—85 °C at 0.1 mmHg (lit.,[26] 273 °C at atmospheric pressure); $\delta_P(CH_2Cl_2)$ 35.5; $\delta_H(CDCl_3)$ 8.4—7.15 (4 H, m) and 2.73 (3 H, d, J_{PH} 1.5 Hz).

Mesitylphosphonic dichloride (**6c**). This was prepared in two ways. (*a*) The Grignard reagent obtained from bromomesitylene (17 g, 0.085 mol) and magnesium (4.0 g, 0.17 mol) in THF (20 ml) was added during 0.5 h to a stirred solution of diethyl chlorophosphate (22 g, 0.13 mol) in THF (30 ml) at 0 °C. After 0.5 h the mixture was diluted with ether and washed with aqueous acid. Distillation gave diethyl mesitylphosphonate (8.9 g, 41%), b.p. 118—122 °C at 0.4 mmHg (lit.,[27] 111—112 °C at 0.05 mmHg), $\delta_P(CH_2Cl_2)$ 20.4. Phosphorus pentachloride (18.6 g, 89 mmol) was added in portions and the mixture was heated at 100 °C overnight. Volatile matter was evaporated and ether was added. After filtration the ether was removed and the residue was crystallised from light petroleum to give mesitylphosphonic dichloride (**6c**) (5.5 g, 67%; overall 27%) which was further purified by distillation, b.p. 140 °C (oven temp.) at 0.1 mmHg, m.p. 87.5—88.5 °C; *m/z* 240, 238, 236 (M^+; 3, 17, 26%), and 119 (100); $\nu_{max.}$(Nujol) 1 270 cm^{-1}; $\delta_H(CDCl_3)$ 6.97 (2 H, d, J_{PH} 8 Hz), 2.72 (6 H, s), and 2.32 (3 H, s,); $\delta_P(CH_2Cl_2)$ 32.9. (*b*) A solution of mesitylphosphonous dichloride (1.85 g, 8.4 mmol) in tetrachloromethane (5 ml) was stirred at 0 °C while sulphuryl chloride (1.35 g, 10 mmol) was added during 7 min. After a further 0.5 h at room temperature the ^{31}P n.m.r. spectrum consisted of a single peak. Removal of all traces of volatile material at 0.1 mmHg afforded the pure solid dichloride (**6c**) (1.83 g, 92%).

2,4,6-*Tri-isopropylphenylphosphonic dichloride* (**6d**). The impure phosphonous dichloride was oxidised with sulphuryl chloride as in (*b*) above. The reaction mixture was filtered and volatile material evaporated. Addition of light petroleum to the residue gave the phosphonic dichloride (**6d**) (35%), m.p. 108—112 °C; $\nu_{max.}$(Nujol) 1 270 and 1 250 cm^{-1}; $\delta_H(CDCl_3)$ 7.13 (2 H, d, J_{PH} 8 Hz), 4.22 (2 H, septet, J_{HH} 7 Hz), 2.88 (1 H, septet, J_{HH} 7 Hz), 1.26 (12 H, d, J_{HH} 7 Hz), and 1.24 (6 H, d, J_{HH} 7 Hz); $\delta_P(CDCl_3)$ 33.7.

2,4,6-*Tri-t-butylphenylphosphonic dichloride.* The crude phosphonous dichloride (*ca.* 3.3 mmol) was dissolved in dichloromethane (10 ml) and oxidised by addition of sulphuryl chloride (0.54 g, 4.0 mmol). After 15 min at room temperature the ^{31}P n.m.r. spectrum consisted of a single peak (δ_P 85.5; presumably a complex). Volatile material was removed and the resulting oil was partitioned between light petroleum (30 ml) and iced water (20 ml). The organic layer was separated, washed with water (10 ml), and dried ($MgSO_4$). Removal of the solvent gave solid which was crystallised by dissolution in light petroleum (b.p. 40—60 °C) and cooling at −78 °C overnight. The resulting phosphonic dichloride (0.81 g, *ca.* 78%) was 95% pure by g.l.c. (3% OV 17 at 200 °C; R_t 6.9 min); m.p. 90—94 °C; $\nu_{max.}$(Nujol) 1 260 and 1 240 cm^{-1}; *m/z* 366, 364, 362 (M^+; 2, 12, 18%); 351, 349, 347 (M^+ − Me; 9, 54, 80), and 245 (100); $\delta_H(CDCl_3)$ 7.34 (2 H, d, J_{PH} 8 Hz), 1.52 (18 H, s), and 1.29 (9 H, s); $\delta_P(CDCl_3)$ 33.9.

Phosphonamidic Chlorides.—(a) N-*t-Butyl*-P-*phenylphosphonamidic chloride* (**7a**). A solution of t-butylamine (6.0 g, 82 mmol) in dichloromethane (60 ml) was added dropwise to a stirred solution of phenylphosphonic dichloride (8.0 g, 42 mmol) in ether (60 ml) at 0 °C. After 15 min the insoluble matter (Bu^tNH_3Cl) was filtered off and the filtrate was concentrated to afford a solid. Recrystallisation from light petroleum–ether afforded N-*t-butyl*-P-*phenylphosphonamidic chloride* (**7a**) (5.65 g, 58%), m.p. 94—95.5 °C; *m/z* 218 and 216 (M^+ − Me; 33, 100%) (M^+ not observed); $\nu_{max.}$(Nujol) 3 165 cm^{-1} (NH); $\delta_H(CDCl_3)$ 8.05—7.3 (5 H, m), 3.6 (br, NH), and 1.39 (9 H, s); $\delta_P(CH_2Cl_2)$ 29.0 (Found: C, 51.9; H, 6.5; Cl, 15.5; N, 5.9. $C_{10}H_{15}ClNOP$ requires C, 51.85; H, 6.5; Cl, 15.3; N, 6.05%).

The following were prepared from the appropriate phosphonic dichloride and the amine (2 equiv.) by methods similar to that described above.

N,N-*Dimethyl*-P-*phenylphosphonamidic chloride* (**5a**) (89%), b.p. 136 °C (oven temp.) at 0.15 mmHg (lit.,[28] 90 °C at 0.01 mmHg), solidified after keeping at −40 °C; *m/z* 205, 203 (M^+; 10, 30%) and 44 (100); $\delta_H(CDCl_3)$ 8.1—7.3 (5 H, m) and 2.68 (6 H, d, J_{PH} 14 Hz); $\delta_P(CH_2Cl_2)$ 41.7.

N-*t-Butyl*-P-o-*tolylphosphonamidic chloride* (**7b**) (52%), m.p. 74.5—76 °C; *m/z* 247, 245 (M^+; 5, 15%), and 232, 230 (33, 100); $\nu_{max.}$(Nujol) 3 150 cm^{-1} (NH); $\delta_H(CDCl_3)$ 8.15—7.1 (4 H, m), 3.3 (1 H, NH), 2.70 (3 H, d, $J_{PH} \leqslant 1$ Hz), and 1.41 (9 H, s); $\delta_P(CH_2Cl_2)$ 29.2 (Found: C, 54.3; H, 7.0; N, 5.8. $C_{11}H_{17}ClNOP$ requires C, 53.8; H, 7.0; N, 5.7%).

N,N-*Dimethyl*-P-o-*tolylphosphonamidic chloride* (**5b**) (86%), b.p. 144 °C (oven temp.) at 0.02 mmHg, m.p. 25—26 °C; *m/z* 219 and 217 (M^+; 33, 100%); $\delta_H(CDCl_3)$ 8.15—7.1 (4 H, m), 2.63 (3 H, d, J_{PH} 1 Hz), and 2.62 (6 H, d, J_{PH} 14 Hz); $\delta_P(CH_2Cl_2)$ 42.1 (Found: C, 49.7; H, 6.2; Cl, 16.5; N, 6.3. $C_9H_{13}ClNOP$ requires C, 49.7; H, 6.0; Cl, 16.3; N, 6.4%).

N,N-*Dimethyl*-P-*mesitylphosphonamidic chloride* (**5c**) (84%), b.p. 119—120 °C (oven temp.) at 0.2 mmHg, m.p. *ca.* 35 °C; *m/z* 247, 245 (M^+; 33, 100%); $\delta_H(CDCl_3)$ 6.90 (2 H, d, J_{PH} 5 Hz), 2.68 (6 H, d, J_{PH} 15 Hz), 2.61 (6 H, s), and 2.27 (3 H, s); $\delta_P(CH_2Cl_2)$ 38.7. Satisfactory elemental analysis could not be obtained. (Found: C, 52.7; H, 7.0; N, 5.4. $C_{11}H_{17}ClNOP$ requires C; 53.8; H, 7.0; N, 5.7%).

N,N-*Dimethyl*-P-(2,4,6-*tri-isopropylphenyl*)*phosphonamidic chloride* (**5d**) (68%), m.p. 121.5—122.5 °C; *m/z* 331, 329 (M^+; 21, 63%) and 286, 284 (33, 100); $\delta_H(CDCl_3)$ 7.08 (2 H, d, J_{PH} 5 Hz), 4.02 (2 H, septet, J_{HH} 7 Hz), 3.05—2.6 (1 H, m, largely hidden by signal at 2.75), 2.75 (6 H, d, J_{PH} 12 Hz), and 1.23 (18 H, d, J_{HH} 7 Hz); $\delta_P(CDCl_3)$ 39.5 (Found: C, 61.95; H, 8.8; Cl, 11.0; N, 4.2. $C_{17}H_{29}ClNOP$ requires C, 61.9; H, 8.9; Cl, 10.75; N, 4.25%).

(b) N-*t-Butyl*-P-*mesitylphosphonamidic chloride* (**7c**). A solution of t-butylamine (1.22 g, 16.7 mmol) in dichloromethane (8 ml) was added dropwise to a stirred solution of mesitylphosphonous dichloride (1.98 g, 8.96 mmol) in dichloromethane (10 ml) at 0 °C. After 0.5 h the resulting *N*-t-butyl-*P*-mesitylphosphonamidous chloride[29] (δ_P 111.9) was oxidised by dropwise addition of dimethyl sulphoxide (0.65 g, 8.34 mmol) at 0 °C. After 45 min at 30 °C the mixture was filtered and the filtrate was washed rapidly with water, dried, and concentrated. Addition of light petroleum to the residue precipitated N-*t-butyl*-P-*mesitylphosphonamidic chloride* (**7c**) (0.99 g, 40%) which was recrystallised from light petroleum–ether, m.p. 110—111 °C; *m/z* 275, 273 (M^+; 11, 33%) and 260, 258 (33, 100); $\nu_{max.}$(Nujol) 3 315 cm^{-1} (NH); $\delta_H(CDCl_3)$ 6.87 (2 H, d, J_{PH} 5 Hz), 3.24 (1 H, d, J_{PH} 15 Hz, NH), 2.67 (6 H, s), 2.26 (3 H, s), and 1.42 (9 H, s); $\delta_P(CH_2Cl_2)$ 25.8 (Found: C, 56.9; H, 7.7; Cl, 13.2; N, 5.0. $C_{13}H_{21}ClNOP$ requires C, 57.0; H, 7.75; Cl, 12.95; N, 5.1%).

(c) *N-t-Butyl-P-(2,4,6-tri-isopropylphenyl)phosphonamidic chloride* (**7d**). t-Butylamine (0.45 g, 6.16 mmol) was added to a solution of impure 2,4,6-tri-isopropylphenylphosphonous dichloride (*ca.* 3 mmol) in dichloromethane to give the *N*-t-butylphosphonamidous chloride (δ_P 115.2). This was oxidised by addition of sulphuryl chloride (1.0 g, 7.4 mmol). All volatile material was removed and the residue was dissolved in dichloromethane (10 ml). The solution was washed with water (2 × 3 ml), dried, and concentrated. Addition of light petroleum (b.p. 40—60 °C) gave pure *N-t-butyl-P-(2,4,6-tri-isopropylphenyl)phosphonamidic chloride* (**7d**) (0.263 g, *ca.* 25%), recrystallised from light petroleum (b.p. 40—60 °C), m.p. 121.5—122.5 °C; *m/z* 359, 357 (M^+; 10, 30%) and 303, 301 (33, 100); $\nu_{max.}$(Nujol) 3 245 cm^{-1} (NH); $\delta_H(CDCl_3)$ 7.08 (2 H, d, J_{PH} 5 Hz), 4.32 (2 H, septet, J_{HH} 7 Hz), 3.25 (1 H, d, J_{PH} 18 Hz, NH), 2.86 (1 H, septet, J_{HH} 7 Hz), 1.45 (9 H, s), 1.25 (12 H, d, J_{HH} 7 Hz), and 1.22 (6 H, d, J_{HH} 7 Hz); $\delta_P(CDCl_3)$ 25.4 (Found: C, 63.9; H, 9.3; Cl, 10.0; N, 3.85. $C_{19}H_{33}ClNOP$ requires C, 63.8; H, 9.3; Cl, 9.9; N, 3.9%).

Phosphonic Diamide Products from Reactions of Phosphonamidic Chlorides with Isopropylamine and t-Butylamine.—Most of the phosphonic diamides were prepared in the following way. A solution of isopropylamine or t-butylamine (8.8 mmol) in dichloromethane (3 ml) was mixed at 0 °C with a solution of the phosphonamidic chloride (**5**) or (**7**) (2.2 mmol) in dichloromethane (3 ml). When reaction was complete (usually ≤0.5 h at 0 °C) the mixture was washed twice with water, dried, and concentrated. The crude product was crystallised from light petroleum–ether. In the case of (**10d**; R = Pr^i) and (**10d**; R = Bu^t) the crude product was purified by chromatography [silica gel; eluant light petroleum (b.p. 40—60 °C)–ethyl acetate (7.5:1)] followed by crystallisation from aqueous methanol. The NMe_2 substrates (**5**) reacted relatively slowly with t-butylamine; in the preparation of (**8a**; R = Bu^t) and (**8b**; R = Bu^t) the reaction was allowed to proceed for 6 h at the reflux temperature; for the preparation of (**8c**; R = Bu^t) and (**8d**; R = Bu^t) it was more convenient to treat the NHBu^t substrate (**7c**) or (**7d**) with dimethylamine. The *N,N'*-di-t-butylphosphonic diamides (**10a**—**c**; R = Bu^t) could be prepared directly from the phosphonic dichlorides by treatment with an excess of t-butylamine.

The phosphonic diamides were characterised as follows. The ^1H n.m.r. spectra contained appropriate signals for all the structural elements present; the chemical shifts ($CDCl_3$) were in the ranges indicated below.

Phenyl	δ 7.9—7.2 (5 H, m)
o-MeC_6H_4	δ 8.0—7.0 (4 H, m) and 2.59—2.67 (3 H, s or d, J_{PH} 1—2 Hz)
2,4,6-$Me_3C_6H_2$	δ 6.81—6.85 (2 H, d, J_{PH} 4 Hz), 2.55—2.67 (6 H, s), and 2.25—2.35 (3 H, s)
2,4,6-$Pr^i_3C_6H_2$	δ 6.99—7.03 (2 H, d, J_{PH} 4 Hz), 4.41—4.47 [but 4.13 for (**8d**; R = Bu^t)] (2 H, septet, J_{HH} 7 Hz), 2.81—2.85 (1 H, septet, J_{HH} 7 Hz), and 1.21—1.25 (18 H, s)
NHBu^t	δ 1.26—1.35 (9 H, s) (also NH signal)
NHPr^i	δ 3.42—3.62 (1 H, m) and 1.03—1.20 (2 × 3 H, d, J_{HH} 7 Hz; Δδ 0.00—0.14 p.p.m.) (also NH signal)
NMe_2	δ 2.54—2.72 (6 H, d, J_{PH} 9—11 Hz)
NH	δ 2.3—2.7 (d, J_{PH} 6—12 Hz, or br)

The i.r. spectra (Nujol) included NH absorption (one or more maxima) in the range 3 450—3 150 cm^{-1}; for (**10d**; R = Bu^t) this was of exceptionally low intensity.

Diamide (**8a**; R = Pr^i), m.p. 87—89 °C, *m/z* 226 (M^+, 38%) and 168 (100) (Found: C, 58.1; H, 8.4; N, 12.35. $C_{11}H_{19}N_2OP$ requires C, 58.4; H, 8.5; N, 12.4%).

Diamide (**8a**; R = Bu^t), m.p. 82—84.5 °C, *m/z* 240 (M^+, 23%) and 168 (100) (Found: C, 59.6; H, 8.65; N, 11.25. $C_{12}H_{21}N_2OP$ requires C, 60.0; H, 8.8; N, 11.7%).

Diamide (**8b**; R = Pr^i), m.p. 55—57.5 °C, *m/z* 240 (M^+, 50%) and 182 (100) (Found: C, 60.0; H, 8.7; N, 11.6. $C_{12}H_{21}N_2OP$ requires C, 60.0; H, 8.8; N, 11.7%).

Diamide (**8b**; R = Bu^t), m.p. 119—120 °C, *m/z* 254 (M^+, 45%) and 182 (100) (Found: C, 61.5; H, 9.0; N, 11.0. $C_{13}H_{23}N_2OP$ requires C, 61.4; H, 9.1; N, 11.0%).

Diamide (**8c**; R = Pr^i), m.p. 97—99 °C, *m/z* 268 (M^+, 75%) and 210 (100) (Found: C, 62.7; H, 9.4; N, 10.6. $C_{14}H_{25}N_2OP$ requires C, 62.7; H, 9.4; N, 10.4%).

Diamide (**8c**; R = Bu^t), m.p. 88—89 °C, *m/z* 282 (M^+, 55%) and 210 (100) (elemental analysis not obtained).

Diamide (**8d**; R = Bu^t), m.p. 129.5—130.5, *m/z* 366 (M^+, 45%) and 249 (100) (Found: C, 68.9; H, 10.7; N, 7.6. $C_{21}H_{39}N_2OP$ requires C, 68.8; H, 10.7; N, 7.65%).

Diamide (**10a**; R = Pr^i), m.p. 134—136 °C, *m/z* 254 (M^+, 6%) and 239 (100) (Found: C, 61.5; H, 9.1; N, 10.9. $C_{13}H_{23}N_2OP$ requires C, 61.4; H, 9.1; N, 11.0%).

Diamide (**10a**; R = Bu^t), m.p. 187.5—189 °C (lit.,[30] 188—189 °C).

Diamide (**10b**; R = Pr^i), m.p. 141.5—142.5 °C, *m/z* 268 (M^+, 35%) and 253 (100) (Found: C, 62.9; H, 9.3; N, 10.35. $C_{14}H_{25}N_2OP$ requires C, 62.7; H, 9.4; N, 10.4%).

Diamide (**10b**; R = Bu^t), m.p. 154—155.5 °C, *m/z* 282 (M^+, 21%) and 154 (100) (Found: C, 64.2; H, 9.6; N, 10.0. $C_{15}H_{27}N_2OP$ requires C, 63.8; H, 9.6; N, 9.9%).

Diamide (**10c**; R = Pr^i), m.p. 117—118.5 °C, *m/z* 296 (M^+, 27%) and 224 (100) (Found: C, 65.0; H, 9.9; N, 9.5. $C_{16}H_{29}N_2OP$ requires C, 64.8; H, 9.9; N, 9.45%).

Diamide (**10c**; R = Bu^t), m.p. 112—113 °C, *m/z* 310 (M^+, 38%) and 182 (100) (Found: C, 66.2; H, 10.3; N, 8.7. $C_{17}H_{31}N_2OP$ requires C, 65.8; H, 10.1; N, 9.0%).

Diamide (**10d**; R = Pr^i), m.p. 70—72 °C, *m/z* 380 (M^+, 70%), 250 (90), and 249 (100) (Found: C, 69.6; H, 10.8; N, 7.2. $C_{22}H_{41}N_2OP$ requires C, 69.4; H, 10.9; N, 7.4%).

Diamide (**10d**; R = Bu^t), m.p. 90—92.5 °C, *m/z* 394 (M^+, 41%) and 321 (100) (Found: C, 69.5; H, 11.0; N, 6.9. $C_{23}H_{43}N_2OP$ requires C, 70.0; H, 11.0; N, 7.1%).

Rates of Reaction of Phosphonamidic Chlorides with Isopropylamine and t-Butylamine.—A 0.2M solution of the phosphonamidic chloride (*ca.* 10 mg) in acetonitrile [containing phenanthrene or *trans*-stilbene (*ca.* 2.5 mg) as g.l.c. standard] was mixed at 0 °C with an equal volume of a 2.0M solution of the amine in acetonitrile. Samples (10 μl) were withdrawn at intervals and added to MeOH (32 μl) [for NHBu^t substrates (**7**)] or NaOMe–MeOH (12 μl of 0.17M solution) [for NMe_2 substrates (**5**)]. Control experiments established that in this way formation of the diamide product [(**8**) or (**10**)] was effectively halted by the conversion of all the remaining phosphonamidic chloride into the corresponding methyl phosphonamidate. The samples were then examined by g.l.c. (3% OV 225 at 196 °C) and the amount of the amidate (R_t 2.6—4.8 min) (corresponding to unchanged substrate at the time of quenching) present in each was determined relative to the internal standard. The amount of diamide product (R_t 4.8—7.1 min) in each sample could also be determined but for deducing rate constants the disappearance of substrate was preferred. In general 4—8 samples were examined over a period of at least 3 half-lives. Plots of log[amidate] *vs.* time were linear ($r \geq 0.992$) and from them the rate constants *k* shown in the Table were deduced. The reactions of substrate (**7c**) were extremely fast. They were quenched after 2 s by addition of MeOH and the approximate values of *k* were deduced from the extent to which reaction was complete (*ca.* 75%) at that time. Substrate (**7d**) reacted even faster. A measure of its reactivity was obtained by making it compete with (**7c**) for

a limited amount of t-butylamine and comparing the extent to which the two substrates had reacted when all the amine had been consumed.

Competitive Reactions of Phosphonamidic Chlorides with 1:1 *Isopropylamine–t-Butylamine Mixture.*—The phosphonamidic chloride (*ca.* 70 mg) in acetonitrile was added at 0 °C to an equimolar mixture of isopropylamine and t-butylamine (20 mol equiv.) in acetonitrile giving a solution having a *total* amine concentration 1.0M. When reaction was complete, the mixture was concentrated and examined by ^{31}P n.m.r. spectroscopy with the aid of pure samples of both possible diamide products. The $NHPr^i/NHBu^t$ product ratio (n^i/n^t) was deduced directly from the relative areas of the peaks, *i.e.* it was assumed that because of their structural similarity the two products do not differ significantly in their ^{31}P n.m.r. response. The results are shown in the Table. Confirmation of the n.m.r. measurements was obtained by g.l.c. analysis; in every case the $NHBu^t$ product was eluted more quickly than the $NHPr^i$ product.

Reactions of N-*t-Butyl*-P-*phenylphosphonamidic Chloride with Less Nucleophilic Reagents.*—A solution of the phosphonamidic chloride (0.15 g, 0.64 mmol) in dichloromethane (1.3 ml) was added to a stirred mixture of the reagent (3.2 mmol) and 2,2,6,6-tetramethylpiperidine (3.2 mmol) in dichloromethane (1.3 ml) at 0 °C. When reaction was complete the volatile material was evaporated and ether was added. The mixture was filtered and the filtrate was washed with water. Evaporation of the solvent gave the crude product which was purified by crystallisation from light petroleum (b.p. 40—60 °C). The following reactions were carried out.

With t-butyl alcohol. This gave *t-butyl* N-*t-butyl*-P-*phenylphosphonamidate* (**16**; R = Bu^t) (70%), m.p. 136—137.5 °C; *m/z* 269 (M^+, <1%), 254 (M^+ − Me, 24), and 198 (100); $\nu_{max.}$(Nujol) 3 240 cm^{-1} (NH); $\delta_H(CDCl_3)$ 7.9—7.2 (5 H, m), 2.47 (1 H, NH), 1.41 (9 H, s), and 1.19 (9 H, s); $\delta_P(CH_2Cl_2)$ 15.3 (Found: C, 62.55; H, 9.0; N, 5.5. $C_{14}H_{24}NO_2P$ requires C, 62.4; H, 9.0; N, 5.2%), using a reaction time of 1.75 h (reaction appeared complete after 0.5 h).

With 2,2,2-*trifluoroethanol.* This gave 2,2,2-*trifluoroethyl* N-*t-butyl*-P-*phenylphosphonamidate* (**16**; R = CH_2CF_3) (82%), m.p. 76—78 °C; *m/z* 280 (M^+ − Me, 100%); $\nu_{max.}$(Nujol) 3 225 cm^{-1} (NH); $\delta_H(CDCl_3)$ 7.95—7.3 (5 H, m), 4.22 (2 H, m), 2.72 (1 H, d, J_{PH} 9 Hz, NH), and 1.28 (9 H, s); $\delta_P(CH_2Cl_2)$ 22.4 (Found: C, 49.1; H, 5.9; N, 4.8. $C_{12}H_{17}F_3NO_2P$ requires C, 48.8; H, 5.8; N, 4.7%), using a reaction time of 0.75 h.

With 1,1,1,3,3,3-*hexafluoropropan-2-ol.* This gave 1,1,1,3,3,3-*hexafluoro-2-propyl* N-*t-butyl*-P-*phenylphosphonamidate* [**16**; R = $CH(CF_3)_2$] (83%), m.p. 62.5—64 °C, b.p. 110 °C (oven temp.) at 0.5 mmHg; *m/z* 363 (M^+, <1%) and 348 (M^+ − Me, 100); $\nu_{max.}$(Nujol) 3 225 cm^{-1} (NH); $\delta_H(CDCl_3)$ 7.95—7.3 (5 H, m), 5.22 (1 H, d × septet, J_{PH} 12, J_{FH} 6 Hz), 2.81 (1 H, d, J_{PH} 10.5 Hz, NH), and 1.28 (9 H, s); $\delta_P(CH_2Cl_2)$ 24.6 (Found: C, 43.2; H, 4.5; N, 3.9. $C_{13}H_{16}F_6NO_2P$ requires C, 43.0; H, 4.4; N, 3.9%), using a reaction time of 0.5 h.

With di-isopropylamine. This gave after chromatography [silica gel, eluant ether–light petroleum (b.p. 40—60 °C) (4:1)] N,N-*di-isopropyl*-N′-*t-butyl*-P-*phenylphosphonic diamide* (**17**) (34%), m.p. 106.5—107 °C; *m/z* 296 (M^+, 9%) and 140 (100); $\nu_{max.}$(Nujol) 3 285 cm^{-1} (NH); $\delta_H(CDCl_3)$ 7.95—7.2 (5 H, m), 3.39 (2 H, m), 2.2 (1 H, NH), 1.27 (9 H, s), 1.24 (6 H, d, J_{HH} 7 Hz), and 1.03 (6 H, d, J_{HH} 7 Hz); $\delta_P(CH_2Cl_2)$ 19.2 (Found: C, 65.0; H, 9.8; N, 9.5. $C_{16}H_{29}N_2OP$ requires C, 64.8; H, 9.9; N, 9.45%), using a reaction time of 0.5 h.

Reactions of 2,4,6-*Tri-t-butylphenyl-phosphonous and -phosphonic Dichlorides.*—The following reactions were carried out in connection with the attempts to prepare 2,4,6-tri-t-butylphenylphosphonamidic chlorides.

(*a*) The crude phosphonous dichloride (0.55 g, 1.6 mmol) in dichloromethane (3 ml) was added to a stirred solution of t-butylamine (1.2 g, 16 mmol) in dichloromethane (3 ml). After 15 min, ^{31}P n.m.r. spectroscopy suggested that the phosphonous diamide (δ_P 41.3; *ca.* 80%) had been formed. The mixture was concentrated to 1 ml, mixed with dimethyl sulphoxide (1 ml), and left for 66 h. It was diluted with dichloromethane and the mixture washed with water and evaporated to give pure *N*-t-butyl-*P*-(2,4,6-tri-t-butylphenyl)phosphonamidous acid (**14**) (0.25 g, 43%), m.p. 185.5—188 °C (from light petroleum–toluene) (lit.,[31] 192—193 °C); *m/z* 365 (M^+, <1%), 293 (M^+ − $NHBu^t$, 20), 246 (ArH^+, 30), and 231 (100); $\nu_{max.}$(Nujol) 3 210 (NH), 2 430, 1 170, and 1 160 cm^{-1}; $\delta_H(CDCl_3)$ 8.16 (1 H, dd, J_{PH} 558, J_{HH} 6 Hz), 7.41 (2 H, d, J_{PH} 5 Hz), 1.59 (18 H, s), and 1.29 (18 H, s) (NH signal not located); $\delta_P(CDCl_3)$ 7.7 (Found: C, 72.7; H, 11.0; N, 3.8. Calc. for $C_{22}H_{40}NOP$: C, 72.3; H, 11.0; N, 3.8%).

(*b*) The phosphonic dichloride (58 mg, 0.16 mmol) in dichloromethane (1.2 ml) was added to a stirred solution of methylamine (0.10 g, 3.26 mmol) in dichloromethane (1 ml). After 1.5 h the solid ($MeNH_3Cl$) was filtered off and the filtrate was washed with water and dried. Evaporation of the solvent gave N,N′-*dimethyl*-P-(2,4,6-*tri-t-butylphenyl*)*phosphonic diamide* (47 mg, 83%) which was recrystallised from light petroleum–toluene; m.p. 194—195.5 °C; *m/z* 352 (M^+, <1%), 295 (M^+ − Bu^t, 100); $\nu_{max.}$(Nujol) 3 455 and 3 380 cm^{-1} (NH); $\delta_H(CDCl_3)$ 7.22 (2 H, d, J_{PH} 4 Hz), 2.39 (6 H, dd, J_{PH} 11, J_{HH} 5 Hz), 1.85 (2 H, NH), 1.45 (18 H, s), and 1.26 (9 H, s); $\delta_P(CDCl_3)$ 24.4 (Found: C, 68.0; H, 10.4; N, 7.9. $C_{20}H_{37}N_2OP$ requires C, 68.1; H, 10.6; N, 7.95%).

(*c*) The phosphonic dichloride (0.149 g, 0.41 mmol) was heated with t-butylamine (0.45 g, 6.16 mmol) at 96 °C for 35.5 h (δ_P 12.9, >90%). The excess of t-butylamine was removed and the resulting oil, dissolved in chloroform (3 ml), was washed with water. Crystallisation from methanol–water (3:1) gave N,N′-*di-t-butyl*-P-(2,4,6-*tri-t-butylphenyl*)*phosphonic diamide* (0.12 g, 67%), m.p. 100—101 °C; *m/z* 379 (M^+ − Bu^t, 100%) and 323 (M^+ − Bu^t − C_4H_8, 60); $\nu_{max.}$(Nujol) 3 435 cm^{-1} (NH; very low intensity); $\delta_H(CDCl_3)$ 7.17 (2 H, d, J_{PH} 4.5 Hz), 2.50 (2 H, d, J_{PH} 10 Hz, NH), 1.49 (18 H, s), 1.24 (9 H, s), and 1.13 (18 H, s); $\delta_P(CDCl_3)$ 13.7 (Found: C, 71.7; H, 11.2; N, 6.3. $C_{26}H_{49}N_2OP$ requires C, 71.5; H, 11.3; N, 6.4%).

(*d*) The phosphonic dichloride (6.9 g, 19 mmol) was stirred with t-butylamine (100 ml) containing water (0.51 g, 28.5 mmol) for 7 days. The precipitate (Bu^tNH_3Cl) was filtered off and the filtrate was evaporated. The residue was extracted with light petroleum and the extract was concentrated; the t-butylamine salt of the phosphonamidic acid (**15**) (5.79 g, 67%), δ_P(MeOH) 13.3, came out of solution. To obtain the free acid, a portion of the salt was treated with trifluoroacetic acid (0.95 mol equiv.) in ether. Insoluble material ($Bu^tNH_3OCOCF_3$) was filtered off and the filtrate was evaporated. The crude product was dissolved in methanol and water was immediately added to precipitate N-*t-butyl*-P-(2,4,6-*tri-t-butylphenyl*)*phosphonamidic acid* (**15**) (70%), m.p. 145—146.5 °C; $\nu_{max.}$(Nujol) 3 440 (NH), 2 700, 2 300, 1 700 (all br, OH), and 1 225 cm^{-1}; $\delta_H(CDCl_3)$ 7.22 (2 H, d, J_{PH} 4.5 Hz), 1.44 (18 H, s), 1.23 (9 H, s), and 1.14 (9 H, s) (OH and NH signals not located) (Found: C, 69.5; H, 10.6; N, 3.6. $C_{22}H_{40}NO_2P$ requires C, 69.25; H, 10.6; N, 3.7%). The free acid and its t-butylamine salt were both rather unstable (P–N bond cleavage) in solution. The acid was further characterised by treatment with diazomethane to give methyl *N*-t-butyl-*P*-(2,4,6-tri-t-butylphenyl)phosphonamidate,[17] m.p. 142.5—144 °C (from aqueous methanol); *m/z* 395 (M^+, <1%), 380 (M^+ − Me, 3), 338 (M^+ − Bu^t, 39), and 282 (M^+ − Bu^t − C_4H_8, 100); $\nu_{max.}$(Nujol) 3 180 cm^{-1} (NH); $\delta_H(CDCl_3)$ 7.28 (2 H, d, J_{PH} 4 Hz), 3.21 (3 H, d, J_{PH} 11 Hz), 2.65 (1 H, d, J_{PH} 11 Hz,

NH), 1.49 (18 H, s), 1.29 (9 H, s), and 1.25 (9 H, s); $\delta_P(CDCl_3)$ 22.2 (Found: C, 69.35; H, 10.7; N, 3.5. Calc. for $C_{23}H_{42}NO_2P$: C, 69.8; H, 10.7; N, 3.5%).

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