Hydrolysis of Diarylphosphinic Amides in Acidic Solution: Steric Inhibition and Mechanism [1]

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The pseudo-first-order rate constants for the hydrolysis of diphenylphosphinic amide $Ph_2P(O)NH_2$ and its di-*p*-tolyl, di-*o*-tolyl, and dimesityl analogues ($10^6k\psi$ 3 630, 2 340, 81.0, and 3.27 s^{-1} respectively with H^+ 0.0662M and *T* 30.2 °C) in water–dioxan (9 : 1 v/v) containing perchloric acid show that reaction is sterically hindered by *ortho*-methyl substituents in the *P*-aryl groups. Steric inhibition is as great, or greater, in the hydrolysis of the corresponding (*N*-phenyl)diarylphosphinic amides ($10^6k\psi$ 5 440, 4 470, 54.9, and 0.88 s^{-1} respectively with H^+ 1.36M and *T* 39.9 °C) and (*N*-*p*-nitrophenyl)diarylphosphinic amides ($10^6k\psi$ 724, 702, 6.57, and 0.098 s^{-1} respectively with H^+ 2.58M and *T* 39.9 °C) even though the departing amine is less nucleophilic. Such sensitivity to steric hindrance is consistent with associative (*A*2) mechanisms for the hydrolysis of all the substrates.

PHOSPHINIC ACIDS and their derivatives (1; R = alkyl or aryl) are generally disinclined towards reaction by dissociative $S_N1(P)$ mechanisms in which phosphinylium cations (2) would be intermediates.[2-5] Thus the paper

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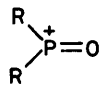

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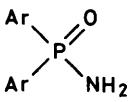
by Tomaschewski and Kühn,[6] in which an associative (*A*2) mechanism is favoured for the acid-catalysed hydrolysis of (*N*-phenyl)diphenylphosphinic amide (4a) in aqueous dioxan, is unexceptional. On the other hand, a thorough kinetic study led Haake and his co-workers [7,8] to conclude that the mechanism of the acid-catalysed hydrolysis of a diphenylphosphinic amide in water–dioxan (9 : 1, v/v) is dependent on the nucleophilicity of the departing amine. In particular, they deduced that hydrolysis is associative (*A*2) for the primary amide (3a) but dissociative (*A*1) for the *p*-nitroanilide (5a) with the anilide (4a) following an intermediate 'merged *A*1-*A*2' pathway.[8c]

Our work with alkylphenylphosphinic amides, PhRP(O)NHX, in aqueous methanol has shown that acid-catalysed hydrolysis is very sensitive to hindrance by bulky alkyl groups R attached to phosphorus, even



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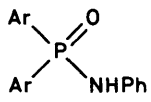

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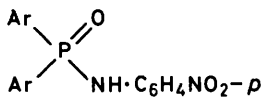

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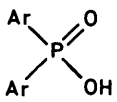
a; Ar = phenyl
b; Ar = *p*-tolyl
c; Ar = *o*-tolyl
d; Ar = mesityl



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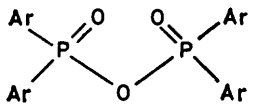
for the *p*-nitroanilides (X = $C_6H_4NO_2$-*p*).[9,10] This suggests that alkylphenylphosphinic amides hydrolyse by associative (*A*2) mechanisms, irrespective of the nucleophilicity of the departing amine. However, we would not expect a fundamental change of mechanism to result from the replacement of a *P*-phenyl group in $Ph_2P(O)NHX$ by an alkyl group, since conjugation between a tetrahedral phosphoryl centre and an unsaturated substituent like phenyl is of relatively little importance.[11] Our suggestion thus appears to be at variance with Haake's proposed spectrum of mechanisms. We have now tried to clarify the situation by examining the importance of steric hindrance in the acid-catalysed hydrolysis of diphenylphosphinic amides. Specifically, we have compared the hydrolysis reactions of the diphenylphosphinic amide (3a), anilide (4a), and *p*-nitroanilide (5a) with those of their di-*p*-tolyl (3b)—(5b), di-*o*-tolyl (3c)—(5c), and dimesityl (3d)—(5d) analogues.

RESULTS

Preparation of Diarylphosphinic Amides.—The diarylphosphinic acids (6a—d) are known compounds and were prepared by standard methods. They were converted into the corresponding phosphinic chlorides by heating with



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thionyl chloride, initially using benzene as solvent. Unexpected complications were encountered with the sterically hindered acids (6c) and (6d). Thus the product from di-*o*-tolylphosphinic acid (6c) was clearly a mixture of two compounds (δ_{Me} 2.42 and 2.20) in a ratio of *ca.* 2 : 1. The minor component (isolated after treating the mixture with aniline) was identified as the anhydride (7; Ar = *o*-tolyl) by ^1H n.m.r. and i.r. spectroscopy (especially $\nu_{max.}$ 920 cm^{-1}, P–O–P), mass spectrometry (M^+ 474), and elemental analysis. From dimesitylphosphinic acid (6d) the corresponding anhydride (7; Ar = mesityl) ($\nu_{max.}$ 970 and 960 cm^{-1}; M^+ 586) was the only compound obtained after recrystallisation of the initial reaction product. By carrying out the reactions of these acids in a large excess of thionyl chloride without additional solvent, the required phosphinic chlorides could be obtained free of contamination from anhydrides.

The reactions of diphenyl-, di-*p*-tolyl-, and di-*o*-tolylphosphinic chlorides with ammonia to give (3a—c), with aniline to give (4a—c), and with *p*-nitroaniline to give (5a—c) were straightforward, but steric hindrance was very evident in the case of dimesitylphosphinic chloride. With

ammonia reaction proceeded slowly at room temperature in ethanol, but nevertheless the amide (3d) was obtained in 61% yield after 6 days. Using forcing conditions, the anilide (4d) was prepared in 44% yield by heating dimesitylphosphinic chloride with aniline in pyridine at 170 °C for 65 h (sealed tube). In anticipation of the failure of the weakly nucleophilic *p*-nitroaniline to react with dimesitylphosphinic chloride, it was first converted into its sodium salt with sodium hydride. In this way, the *p*-nitroanilide (5d) was obtained in 72% yield.

Rates of Hydrolysis of Diarylphosphinic Amides.—The rates of hydrolysis were determined spectrophotometrically using dilute solutions (10^{-3}—10^{-5}M) in aqueous perchloric acid containing dioxan (9 : 1, v/v). For the primary amides (3) it was necessary to use a lower temperature (30.2 °C) and a much lower concentration of acid (0.066 2M) than were used for the much less reactive anilides (4) and *p*-nitroanilides (5) (*T* 39.9 °C; H^+ 1.36 or 2.58M). Also, because there are no wavelengths at which the u.v. spectra of the primary amide reaction mixtures change substantially as hydrolysis proceeds, accurate rates could not be obtained by direct monitoring. Samples were therefore removed, quenched, and worked up (see Experimental section) to separate the hydrolysis product (diarylphosphinic acid) from the unchanged phosphinic amide before spectrophotometric examination. It was then possible to follow not only the disappearance of starting material but also the appearance of product; the results were in excellent agreement.

For each substrate a linear first-order plot was obtained extending over the entire period examined, this being at least 4 × $t_{\frac{1}{2}}$ generally but only 3 × $t_{\frac{1}{2}}$ (28 days) for (4d) and 1.27 × $t_{\frac{1}{2}}$ (104 days) for (5d). The derived pseudo-first-order rate constants ($k\psi$) are shown in Table 1. The discrepancy between duplicate determinations can be accommodated by an uncertainty of ±3% although the maximum possible error in $k\psi$ is estimated to be ±5% generally and ±15% for (4d), because of some uncertainty in A_∞, and for (5d), because our data extends over only 1.27 × $t_{\frac{1}{2}}$.

Products of Hydrolysis of Diarylphosphinic Amides.—With the exceptions of dimesitylphosphinic anilide (4d) and *p*-nitroanilide (5d), the change in the u.v. spectrum accompanying hydrolysis of each of the substrates was consistent with the expected diarylphosphinic acid and amine (or ammonia) being the only products. Even with (4d) and (5d), deviations were conspicuous only when hydrolysis was conducted at temperatures higher than those used in the kinetic runs in attempting to obtain infinity spectra. The deviation was most marked in the case of (*N*-*p*-nitrophenyl)dimesitylphosphinic amide (5d), where the extreme slowness of the hydrolysis under the kinetic conditions ($t_{\frac{1}{2}}$ 81.8 days at 39.9 °C) required that a much higher temperature (90 °C) be used to obtain the infinity spectrum. Significantly, the u.v. spectrum of a solution of dimesitylphosphinic acid in the hydrolysis reaction medium was found to change markedly, suggesting decomposition, on heating at 90 °C.

Gas-liquid chromatography has also been used to examine the hydrolysis products. For each substrate, a hydrolysis reaction mixture such as that used in the kinetic study was extracted with chloroform and the extract treated with an excess of diazomethane. Analysis of the extract by g.l.c. (3% silicone–OV 17; 250 °C or, for Ar = mesityl, 270 °C) showed the presence of a compound having the same retention time as the product from the reaction of an authentic sample of the appropriate diarylphosphinic acid and diazomethane. Moreover, apart from a little unchanged amide in some cases, no other product could be detected (the amines remaining in the aqueous phase as their perchlorate salts). In particular, it was found that hydrolysis of the dimesitylphosphinic amides did not produce any mesitylene (0.5% would have been detected, using 3% OV 17 at 75 °C), nor the di-*o*-tolyl compounds any toluene (1% would have been detected, using 10% silicone E30 at 60 °C). The instability of dimesitylphosphinic acid was confirmed by heating a solution in aqueous dioxan containing 2.58M perchloric acid. After 6 days at 90 °C the area of the g.l.c. peak due to methyl dimesitylphosphinate in the diazomethane-treated chloroform extract had declined to less than 5% of its value before heating.

TABLE 1

Hydrolysis of diarylphosphinic amides in water–dioxan (9 : 1, v/v) containing perchloric acid

	$Ar_2P(O)NH_2$ [a]			$Ar_2P(O)NHC_6H_5$ [b]			$Ar_2P(O)NHC_6H_4NO_2$ [c]		
	Amide	$10^6k\psi/s^{-1}$	k_{rel}	Amide	$10^6k\psi/s^{-1}$	k_{rel}	Amide	$10^6k\psi/s^{-1}$	k_{rel}
Ar = phenyl	(3a)	3 630	100	(4a)	5 440	100	(5a)	724	100
Ar = *p*-tolyl	(3b)	2 340	64.5	(4b)	4 470	82.2	(5b)	702	97.0
Ar = *o*-tolyl	(3c)	81.0	2.23	(4c)	54.9	1.01	(5c)	6.57	0.91
Ar = mesityl	(3d)	3.27	0.090	(4d)	0.88	0.016	(5d)	0.098	0.014

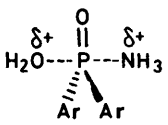
[a] $[HClO_4]$ = 0.0662M, *T* = 30.2 °C. [b] $[HClO_4]$ = 1.36M, *T* = 39.9 °C. [c] $[HClO_4]$ = 2.58M, *T* = 39.9 °C.

DISCUSSION

Each of the diarylphosphinic amides (3)—(5) (a—d) gives the corresponding phosphinic acid and amine (or ammonia) on hydrolysis in acid solution. When forcing conditions are used for the highly hindered dimesitylphosphinic anilide (4d) and *p*-nitroanilide (5d) the dimesitylphosphinic acid produced suffers some decomposition, but this apart, no unusual hydrolysis products were detected either spectrophotometrically or by gas-liquid chromatography. This in itself does not constitute evidence against *A*1 hydrolysis mechanisms since we have no reason to expect that phosphinylium cations would fragment if formed, although we note that complications can arise in the acid-catalysed hydrolysis of hindered arylsulphonic amides. Thus, for example, (*N*-phenyl)-2,4-dimethylphenylsulphonic amide gives *m*-xylene (9.4%) as well as the expected products while (*N*-phenyl)mesitylsulphonic amide gives mesitylene (89%) and no mesitylsulphonic acid.[12]

In common with Haake and Koizumi [7] we find that diphenylphosphinic amide (3a) hydrolyses rapidly under mildly acidic conditions ($t_{\frac{1}{2}}$ 3.2 min in 0.066M H^+ at 30 °C). Di-*p*-tolylphosphinic amide (3b) is somewhat less reactive (Table 1) but the difference is small. Apparently the electronic effects exerted by *para*-methyl

substituents in the *P*-phenyl groups have little influence on the rate of hydrolysis. In contrast, di-*o*-tolylphosphinic amide (3c) is 45-times less reactive than the diphenyl compound, suggesting that hydrolysis is hindered substantially by the steric effects of the *ortho*-methyl substituents. In the dimesityl compound (3d) each *P*-phenyl group carries two *ortho*-methyl substituents, and hydrolysis is now $>10^3$-times slower than for diphenylphosphinic amide. Such sensitivity to steric hindrance is readily understood in terms of a bimolecular (*A*2) hydrolysis mechanism for primary diarylphosphinic amides, whether it proceeds by direct displacement *via* an S_N2-like transition state resembling (8) or by a five-co-ordinate phosphorane intermediate such as (9). In either case, bulky groups attached to phosphorus would be likely to hinder attack by the water nucleophile.



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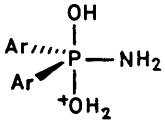

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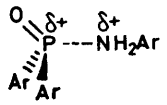
(*N*-Phenyl)diphenylphosphinic amide (4a) is less basic than the primary amide (3a) and in acid solution will exist to a much smaller extent in its reactive protonated form. No doubt this is why the hydrolysis of (4a) is *ca.* 10^2-times slower than that of (3a). In fact, once protonated (on nitrogen) the anilide will be more reactive than the primary amide with respect to P–N bond cleavage since aniline is less nucleophilic, and a better leaving group, than ammonia. As Haake and Tyssee [8a] have pointed out, the anilide should therefore be more disposed towards dissociative reaction. Nevertheless, we find (Table 1) that *ortho*-methyl substituents in the *P*-phenyl groups retard the hydrolysis of the anilide (4a) at least as much as they do the hydrolysis of the amide (3a).

Since *p*-nitroaniline is less nucleophilic than aniline, we might expect the hydrolysis of a *p*-nitroanilide to be both slower overall and more dissociative in character than is the hydrolysis of the corresponding anilide.[8c] The rate constants in Table 1 reveal that the *p*-nitroanilides (5) are indeed less reactive than the anilides (4) but they also show that hydrolysis is still liable to steric hindrance. We can account for our results in terms of an *A*1 mechanism only by supposing that bulky *P*-aryl



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groups inhibit solvation of a unimolecular dissociative transition state (10) and that the resulting destabilization far outweighs any gain accruing from relief of strain in the transition state. Conceivable though this may be, we note that the reduction in the rate of hydrolysis of the *p*-nitroanilides that accompanies the change in the *P*-aryl groups from phenyl to *o*-tolyl to mesityl is no less than it was for the amides and anilides. Surely it is more reasonable to suppose that the *p*-nitroanilides, like the amides and anilides, react by associative mechanisms in which formation of a bond between the water nucleophile and the phosphorus atom is important in the transition state. That being so, it is appropriate to consider the extent to which associative mechanisms can be reconciled with the results of other mechanistic investigations.

Substituent Effects.[6,8]—The observed rates of hydrolysis of *N*-phenyl-[6] and *N*-*p*-nitrophenyl-[8] diphenylphosphinic amides (4a) and (5a) are influenced in similar ways by *para*-substituents (NO_2, Cl, and MeO *etc.*) in *P*-phenyl groups. The influence is small [σ_1 −0.31 for (4a) and −0.55 for (5a)]; it reflects only the inductive effects of the substituents, and probably originates mainly in the initial protonation equilibrium. Substituents (NO_2 and MeO) in the *N*-phenyl group of (4a) have a much greater influence on rate,[8] but here also their effect is largely on the initial protonation. Because we cannot with confidence isolate the effects of substituents on the P–N bond-cleavage step, we do not feel that they provide a reliable means of distinguishing between *A*1 and *A*2 mechanisms.

Dependence of Rate on Acidity.[8]—For the *p*-nitroanilide (5a) and sulphuric acid as catalyst, log $k\psi$ has a linear dependence on H_0 but with a slope of only 0.59. Log $k\psi$ is also linearly related to H_A; now the slope is 1.0 and the Bunnett solvation parameters w [13] and ϕ,[14] being within experimental error of zero,[8] could be consistent with an *A*1 mechanism. With perchloric acid as catalyst, the plot of log $k\psi$ *vs.* H_0 gives a straight line of slope 0.56. In this case, Haake *et al.*[8] did not analyse the dependence of their values of $k\psi$ on H_A, presumably because the acidity function data were not then available. Using the values of Yates *et al.*[15] for H_A of perchloric acid, we find that log $k\psi$ is linearly dependent on H_A but the slope is only 0.64 and the values of w (*ca.* 2) and ϕ (*ca.* 0.6) are as expected for an associative (*A*2) mechanism.* The case for an *A*1 mechanism seems less secure.

Entropy of Activation.[8]—Hydrolysis of the *p*-nitroanilide (5a) has a large negative entropy of activation, $\Delta S^{\ddagger}$ −104 J K^{-1} mol^{-1}. While it has been suggested [8c] that this is not necessarily incompatible with an *A*1 mechanism, it is surely at least as consistent with an associative (*A*2) mechanism.

Solvent Isotope Effects.[8]—Comparison of values of $k\psi$ for reaction in D_2O and in H_2O gives k_D/k_H 1.3 for the amide (3a), 2.3 for the anilide PhMeP(O)NHPh, and 2.7 for the *p*-nitroanilide (5a), implying a progressive decline in the importance of nucleophilic participation by water in the rate-limiting P–N bond scission. We have no simple explanation for the apparent conflict between

* Ref. 8 explains the determination of w and ϕ using H_A and H_0 for the H_2SO_4-catalysed hydrolysis and H_0 for the $HClO_4$-catalysed hydrolysis. We have used the same method with H_A for the $HClO_4$-catalysed hydrolysis. The plots we obtain are poorly linear and their slopes, and hence w and ϕ, can be determined only very approximately. The significance of the values of w and ϕ may be limited in view of the poor linearity.

these results and our own steric hindrance measurements, with their implication that nucleophilic participation by water is important in the hydrolysis transition states for all three substrates.

Stereochemistry.—Departures from stereospecific inversion of configuration at phosphorus in the methanolysis of optically active (*N*-phenyl)methylphenylphosphinic amide, MePhP(O)NHPh, at higher acidities were originally attributed to the incursion of an *A*1 mechanism.[16] However, more recent work [17] suggests that the stereochemical results may be explained better by an *A*2 mechanism with some nucleophilic participation by the conjugate base of the acid catalyst.

Conclusion.—The acid-catalysed hydrolysis of diphenylphosphinic amide is retarded by substituents which sterically hinder attack at phosphorus, and the reactions of the anilide and *p*-nitroanilide are no less sensitive to steric hindrance. The situation is comparable with that found for alkylphenylphosphinic amides, anilides, and *p*-nitroanilides. Our results tell us nothing explicit about the extent to which the P–N bond is broken in the hydrolysis transition state, but they do suggest that formation of a bond between the water nucleophile and phosphorus is important in all cases. That being so, it seems inappropriate to describe the mechanism of hydrolysis of any of the substrates as *A*1 or dissociative.

EXPERIMENTAL

Instrumentation was as described previously.[10] Dioxan was purified by passage down a column of alumina and distillation. Chloroform used for extracting hydrolysis mixtures was AnalaR.

Diphenylphosphinic Acid.—This compound had m.p. 189—191 °C (lit.,[18] 195—196 °C) and was prepared by treating chlorodiphenylphosphine with alkaline hydrogen peroxide.[18]

Di-p-tolylphosphinic Acid.—Following the general procedure of Kosolapoff and Struck,[19] diethyl phosphite was allowed to react with *p*-tolylmagnesium bromide and the product was oxidised with bromine to give the acid, m.p. 128—130 °C (from ethyl acetate) (lit.,[20] 131—132°), δ (CCl_4) 12.5 (1 H, s), 7.42 (4 H, dd, J_{PH} 12, J_{HH} 8 Hz), 6.90 (4 H, dd, J_{PH} 4, J_{HH} 8 Hz), and 2.28 (6 H, s).

Di-o-tolylphosphine Oxide and Di-o-tolylphosphinic Acid.—Dibutyl phosphite (19.8 g, 0.103 mol) in ether (60 ml) was added during 30 min to a stirred, cooled solution of *o*-tolylmagnesium bromide (0.37 mol) in ether (150 ml), and the mixture left at room temperature overnight. With cooling, 3.5M-hydrochloric acid (150 ml) was slowly added, followed by water (150 ml). Ether was evaporated off together with *ca*. one third of the water, and the insoluble di-*o*-tolylphosphine oxide was collected by filtration. Attempted oxidation with alkaline hydrogen peroxide [21] gave unchanged phosphine oxide, m.p. 93—95 °C (lit.,[21] 94—95 °C), *m/e* 230 (M^+); δ ($CDCl_3$) 8.05 (1 H, d, J_{PH} 469 Hz), 7.8—6.9 (8 H, m), and 2.33 (6 H, s).

Di-*o*-tolylphosphine oxide (*ca*. one half of the above product) was mixed with 1.5M-aqueous sodium hydroxide (150 ml), bromine (12 g) was added, and the suspension stirred at 70 °C for 6 h. The cooled reaction mixture was then treated with sodium metabisulphite (to destroy the excess of bromine), acidified with concentrated hydrochloric acid, and extracted with chloroform. The residue remaining after evaporation of the chloroform was crystallised from ethanol to give di-*o*-tolylphosphinic acid (7.78 g, 0.032 mol, *ca*. 66%), m.p. 172—173 °C (lit.,[21] 175—177 °C), δ ($CDCl_3$) 12.3 (1 H, s), 8.0—7.5 (2 H, m), 7.4—6.8 (6 H, m), and 2.25 (6 H, d, J_{PH} <1 Hz).

Dimesitylphosphinic Acid.—This compound (16%) was prepared from mesitylmagnesium bromide and phosphorus oxychloride by the method of Fritzsche *et al*.[22] After crystallisation from ethanol it had m.p. 206—209 °C (lit.,[22] 210 °C), δ ($CDCl_3$) 10.8 (1 H, s), 6.73 (4 H, d, J_{PH} 4 Hz), 2.37 (12 H, d, J_{PH} <1 Hz), and 2.22 (6 H, s).

Diarylphosphinic Chlorides.—(*a*) The appropriate diarylphosphinic acid (5 mmol) and thionyl chloride (10 mmol) were heated in benzene (10 ml) for 2 h. Volatile material was evaporated under reduced pressure to give diphenylphosphinic chloride, which was used without purification, or di-*p*-tolylphosphinic chloride, b.p. (oven temp.) 170—175 °C at 0.3 mmHg, δ ($CDCl_3$) 7.63 (4 H, dd, J_{PH} 14, J_{HH} 8 Hz), 7.17 (4 H, dd, J_{PH} 4, J_{HH} 8 Hz), and 2.37 (6 H, s). The i.r. spectra of these compounds contained only very weak absorptions at *ca*. 950 cm^{-1} (P–O–P) suggesting that they were largely free of anhydrides. The product from di-*o*-tolylphosphinic acid absorbed strongly at *ca*. 930 cm^{-1} and its n.m.r. spectrum contained two methyl signals at δ (CCl_4) 2.42 and 2.20 in a ratio *ca*. 2 : 1. The minor component was subsequently isolated [see preparation of (*N*-phenyl)di-*o*-tolylphosphinic amide] and identified as *di-o-tolylphosphinic anhydride*, m.p. 194—196 °C from ethyl acetate, *m/e* 474 (M^+), $\nu_{max.}$ (Nujol) 920 cm^{-1}; δ ($CDCl_3$) 8.0—7.5 (4 H, m), 7.4—6.8 (12 H, m), and 2.20 (12 H, s) (Found: C, 70.7; H, 6.0. $C_{28}H_{28}O_3P_2$ requires C, 70.9; H, 5.95%). The product from dimesitylphosphinic acid consisted entirely of *dimesitylphosphinic anhydride*, m.p. 235—238 °C from benzene–petroleum (b.p. 60—80 °C) (1 : 1); *m/e* 586 (M^+); $\nu_{max.}$ (Nujol) 970 and 960 cm^{-1}; δ (CCl_4) 6.55br (8 H, s), 2.23 (24 H, s), and 2.17 (12 H, s) (Found: C, 73.9; H, 7.7. $C_{36}H_{44}O_3P_2$ requires C, 73.7; H, 7.6%).

(*b*) The appropriate diarylphosphinic acid (5 mmol) and thionyl chloride (5 ml) were heated without any additional solvent for 2 h. Volatile material was evaporated under reduced pressure to give *di-o-tolylphosphinic chloride*, b.p. (oven temp.) 150—160 °C at 0.08 mmHg, m.p. 65—66 °C (softens above 58 °C), *m/e* 266, 264 (ratio 1 : 3, M^+); $\nu_{max.}$ (Nujol) no absorption at 1 000—900 cm^{-1}; δ (CCl_4) 7.8—6.9 (8 H, m) and 2.42 (6 H, d, *J* 1 Hz), no signal at 2.20 (Found: C, 63.2; H, 5.4. $C_{14}H_{14}ClOP$ requires C, 63.5; H, 5.3%), or dimesitylphosphinic chloride, m.p 138—139 °C from cyclohexane (lit.,[23] 140.5—141 °C), $\nu_{max.}$ (Nujol) no appreciable absorption at 1 000—900 cm^{-1}; δ (CCl_4) 6.72 (4 H, d, J_{PH} 4 Hz), 2.37 (12 H, s), and 2.27 (6 H, s).

Diarylphosphinic Amides (3).—In a typical preparation, di-*p*-tolylphosphinic chloride (1.54 g, 5.82 mmol) in dichloromethane (10 ml) was added dropwise to a stirred, cooled mixture of 4M-ethanolic ammonia (8 ml) and dichloromethane (8 ml). Reaction was allowed to continue overnight at room temperature. Insoluble material (NH_4Cl) was removed by filtration and the solvent was evaporated from the filtrate. The residue was dissolved in chloroform (30 ml) and the solution washed with 5% aqueous potassium carbonate (10 ml) and water (10 ml). Evaporation of the chloroform and crystallisation of the resulting solid from ethyl acetate and from toluene afforded *di-p-tolylphosphinic amide* (0.94 g, 3.85 mmol, 66%), m.p. 187—188 °C, δ ($CDCl_3$)

7.65 (4 H, dd, J_{PH} 12, J_{HH} 8 Hz), 7.03 (4 H, dd, J_{PH} 3, J_{HH} 8 Hz), 3.22br (2 H, s), and 2.28 (6 H, s) (Found: C, 68.9; H, 6.6; N, 5.85. $C_{14}H_{16}NOP$ requires C, 68.55; H, 6.6; N, 5.7%).

The following amides were prepared in a similar manner from the appropriate diarylphosphinic chlorides.

Diphenylphosphinic amide, m.p. 165—166 °C from toluene (lit.,[24] 165—167 °C); *di-o-tolylphosphinic amide* (81%), m.p. 156.5—157.5 °C, δ ($CDCl_3$) 8.0—7.6 (2 H, m), 7.4—6.9 (6 H, m), 3.50br (2 H, s), and 2.32 (6 H, d, J_{PH} 1.5 Hz) (Found: C, 68.6; H, 6.7; N, 5.9. $C_{14}H_{16}NOP$ requires C, 68.55; H, 6.6; N, 5.7%); *dimesitylphosphinic amide* (61%), m.p. 225.5—226.5 °C, δ ($CDCl_3$) 6.73 (4 H, d, J_{PH} 4 Hz), 3.30br (2 H, s), 2.37 (12 H, s), and 2.23 (6 H, s) (Found: C, 71.8; H, 8.0; N, 4.7. $C_{18}H_{24}NOP$ requires C, 71.7; H, 8.0; N, 4.65%), using a reaction time of 6 days and a larger excess of ethanolic ammonia with no dichloromethane.

(N-*Phenyl*)*diphenylphosphinic Amide* (4a).—Diphenylphosphinic chloride (4.0 mmol) in tetrachloromethane (2 ml) was added dropwise to a solution of aniline (0.85 g, 9.15 mmol) in tetrachloromethane (10 ml) and stirring continued at room temperature for 24 h. After dilution with chloroform the reaction mixture was washed with very dilute aqueous hydrochloric acid and sodium hydroxide and then with water. After evaporation of the solvent, crystallisation twice from ethanol afforded (*N*-phenyl)diphenylphosphinic amide (0.534 g, 1.82 mmol, 46%), m.p. 237—239 °C (lit.,[8c] 239—241.5 °C). Further purification by chromatography on alumina (eluant 4% methanol in ether) and crystallisation from 1 : 1 chloroform–ether gave material, m.p. 238.5—239 °C.

(N-*Phenyl*)*di*-p-*tolylphosphinic amide* (4b) (48%), m.p. 215.5—216.5 °C after chromatography and crystallisation from ethyl acetate and from ethanol–ether (1 : 2) (lit.,[6] 216—216.5 °C), δ ($CDCl_3$) 7.65 (4 H, dd, J_{PH} 12, J_{HH} 8 Hz), 7.3—6.7 (9 H, m), 5.38 (1 H, d, J_{PH} 10 Hz), and 2.37 (6 H, s), was prepared by the above method using di-*p*-tolylphosphinic chloride and aniline.

(N-*Phenyl*)*di-o-tolylphosphinic Amide* (4c).—(*a*) The product from the reaction of di-*o*-tolylphosphinic acid (5.0 mmol) with thionyl chloride in benzene (see preparation of diarylphosphinic chlorides) was dissolved in tetrachloromethane (10 ml). Aniline (1.39 g, 15.0 mmol) and pyridine (0.5 ml) were added and the mixture was stirred and heated under reflux overnight. Volatile material was removed under reduced pressure and the residue dissolved in chloroform. The solution was washed with dilute hydrochloric acid and dilute aqueous sodium hydroxide and the solvent evaporated. Crystallisation twice from ethyl acetate afforded (N-*phenyl*)*di-o-tolylphosphinic amide* (0.60 g, 1.87 mmol, 36%), m.p. 186—187 °C, δ ($CDCl_3$) 7.7—6.7 (13 H, m), 5.13 (1 H, d, J_{PH} 11 Hz), and 2.55 (6 H, d, J_{PH} 1 Hz) (Found: C, 74.9; H, 6.4; N, 4.4. $C_{20}H_{20}NOP$ requires C, 74.8; H, 6.3; N, 4.4%).

The first crystallisation mother-liquor was evaporated and the residue extracted with hot benzene–petroleum (b.p. 60—80 °C) (1 : 1). On cooling, the extract deposited a solid (0.121 g) which was recrystallised from ethyl acetate to give di-*o*-tolylphosphinic anhydride (see preparation of diarylphosphinic chlorides).

(*b*) Di-*o*-tolylphosphine oxide (1.15 g, 5.0 mmol) was treated with phosphorus trichloride according to the method of Montgomery and Quin.[25] After removal of volatile material the crude di-*o*-tolylchlorophosphine was added to a stirred, cooled solution of aniline (1.0 ml) in benzene. Stirring was continued at room temperature for several days. Insoluble matter was filtered off and the filtrate was concentrated. The residue in dichloromethane (10 ml) was added slowly with stirring to 30% hydrogen peroxide (5 ml). After 1.3 h the organic layer was separated and the aqueous phase extracted with chloroform. The combined organic extracts were concentrated and crystallised from ethyl acetate to give (*N*-phenyl)di-*o*-tolylphosphinic amide (0.589 g, 1.83 mmol, 37%) having i.r. and n.m.r. spectra identical to those of the material prepared above.

(N-*Phenyl*)*dimesitylphosphinic Amide* (4d).—A mixture of dimesitylphosphinic chloride (0.80 g, 2.5 mmol) and aniline (1.16 g, 12.5 mmol) in pyridine (5 ml) was heated at 170 °C for 65 h in a sealed tube. Volatile material was removed under vacuum and the residue was dissolved in chloroform. Water was added, and then hydrochloric acid until the aqueous layer remained acidic. The organic layer was separated, washed with dilute aqueous sodium hydrogen carbonate, and concentrated. The resulting foam was chromatographed on alumina. Elution with ether afforded, after crystallisation from benzene–petroleum (b.p. 60—80°) (1 : 1), (N-*phenyl*)*dimesitylphosphinic amide* (0.41 g, 1.1 mmol, 44%), m.p. 167—169 °C, δ (CCl_4) 7.0—6.5 (9 H, m, including 6.60, *ca.* 4 H, d, J_{PH} 4 Hz), 5.52 (1 H, d, J_{PH} 11 Hz), 2.27 (12 H, s), and 2.20 (6 H, s) (Found: C, 76.6; H, 7.6; N, 3.9. $C_{24}H_{28}NOP$ requires C, 76.4; H, 7.5; N, 3.7%).

(N-p-*Nitrophenyl*)*diphenylphosphinic Amide* (5a).—Diphenylphosphinic chloride (6.0 mmol) in tetrachloromethane (3 ml) was added to *p*-nitroaniline (0.89 g, 6.5 mmol) in pyridine (12 ml) and the mixture was heated under nitrogen at 110 °C (bath temp.) for 24 h. Volatile material was evaporated under reduced pressure and the solid residue was washed with aqueous sodium hydrogen carbonate. Crystallisation twice from acetone gave (*N*-*p*-nitrophenyl)-diphenylphosphinic amide (0.583 g, 1.73 mmol, 29%), which, after further purification by chromatography on alumina (eluant 4% methanol in ether) and crystallisation from chloroform–ether (1 : 1) had m.p. 228—231 °C (lit.,[8c] 231.5—233.5°).

The following were similarly prepared from the respective diarylphosphinic chloride and *p*-nitroaniline.

(N-p-*Nitrophenyl*)*di*-p-*tolylphosphinic amide* (5b) (25%), m.p. 229—230 °C from acetone, δ ($CDCl_3$) 8.0—6.9 (12 H, m), 6.23 (1 H, d, J_{PH} 9 Hz), and 2.35 (6 H, s) (Found: C, 65.5; H, 5.3; N, 7.6. $C_{20}H_{19}N_2O_3P$ requires C, 65.6; H, 5.2; N, 7.65%).

(N-p-*Nitrophenyl*)*di-o-tolylphosphinic amide* (5c) (36%), m.p. 219—221 °C from ethyl acetate–acetone (1 : 1) and from ethanol (no chromatographic purification), δ ($CDCl_3$) 8.1—6.9 (12 H, m), 5.87 (1 H, d, J_{PH} 9 Hz), and 2.53 (6 H, d, J_{PH} <1 Hz) (Found: C, 65.6; H, 5.3; N, 7.7. $C_{20}H_{19}N_2O_3P$ requires C, 65.6; H, 5.2; N, 7.65%).

(N-p-*Nitrophenyl*)*dimesitylphosphinic Amide* (5d).—*p*-Nitroaniline (0.83 g, 6.0 mmol) was added to a stirred suspension of sodium hydride (0.144 g, 6.0 mmol) in tetrahydrofuran (20 ml) in an atmosphere of nitrogen. After 0.5 h, dimesitylphosphinic chloride (0.641 g, 2.0 mmol) was added and stirring continued at room temperature for 20 h. The reaction was quenched by addition of wet tetrahydrofuran and some of the solvent evaporated off. Water (25 ml), hydrochloric acid (sufficient to make the mixture acidic), and chloroform (20 ml) were added. The layers were separated and the aqueous phase extracted with chloroform (3 × 10 ml). The total organic extracts were

combined, concentrated, and chromatographed on alumina. Elution with ether gave *p*-nitroaniline, and with 10% methanol in ether gave a yellow solid. This was washed with ether and crystallised from ethyl acetate to give (N-p-*nitrophenyl*)*dimesitylphosphinic amide* (0.604 g, 1.43 mmol, 72%), m.p. 226—227°, δ ($CDCl_3$) 7.90 (2 H, d, J_{HH} 9 Hz), 7.03 (2 H, d, J_{HH} 9 Hz), 6.75 (4 H, d, J_{PH} 4 Hz), 5.77 (1 H, d, J_{PH} 12 Hz), 2.35 (12 H, s), and 2.23 (6 H, s) (Found: C, 68.2; H, 6.5; N, 6.6. $C_{24}H_{27}N_2O_3P$ requires C, 68.2; H, 6.4; N, 6.6%).

I.r. Spectra of Diarylphosphinic Amides.—The spectra were recorded for Nujol mulls; significant absorptions include the following.

$Ar_2P(O)NH_2$: 3 420—3 080 (3 or 4 maxima), *ca.* 1 570 (NH_2), and 1 190—1 160 cm^{-1} (P=O); $Ar_2P(O)NHPh$: *ca.* 3 150 (>1 maximum for Ar = Ph) and *ca.* 1 600 (NH), and 1 190—1 160 cm^{-1} (P=O); $Ar_2P(O)NHC_6H_4NO_2$: 3 240—3 110 (>1 maximum for Ar = Ph) and *ca.* 1 600 (NH), 1 515 and *ca.* 1 340 (NO_2), and 1 195—1 165 cm^{-1} (P=O).

Rates of Hydrolysis of (N-*Phenyl*)*diarylphosphinic Amides* (4).—(a) For (4a—c), a mixture of dilute aqueous perchloric acid (2.7 ml) and dioxan (0.25 ml) contained in a 10-mm silica cuvette was maintained at 39.9 °C in a spectrophotometer. A solution of the anilide in dioxan (0.05 ml) was added to give a reaction mixture having [$HClO_4$] = 1.36M and [anilide] as shown in Table 2. After thorough mixing

TABLE 2

Hydrolysis of diarylphosphinic amides: Initial concentration (c_0) of amide and wavelength at which absorbance monitored

Amide	10^4c_0/M	λ/nm
(3a)	7.90	266
(3b)	7.62	263
(3c)	3.65	271
(3d)	0.76	285
(4a)	0.48	230
(4b)	0.39	235
(4c)	0.48	227
(4d)	0.79	255
(5a)	1.13	335
(5b)	0.96	335
(5c)	0.93	340
(5d)	0.54	340

the decrease in the absorbance (A) with time was continuously monitored at a suitable wavelength (λ) (see Table 2) for a period $\geqslant 4 \times t_{\frac{1}{2}}$. The value of A_∞ was taken as the absorbance of the reaction mixture after a period $>8 \times t_{\frac{1}{2}}$; this was *ca.* 60% of the initial value (A_0). The spectra (210—300 nm) of these experimental infinity solutions were essentially the same as those of simulated infinity solutions containing the appropriate amounts of diarylphosphinic acid and aniline dissolved in the reaction medium. Plots of $\log_{10}(A - A_\infty)$ *vs.* time gave straight lines, from the slopes of which the values of $k\psi$ were deduced. Each value of $k\psi$ in Table 1 is the average of two determinations.

(b) For (4d), a reaction mixture was prepared as in (a) above but on a larger scale. Portions (3.5 ml) were sealed in glass ampoules in an atmosphere of nitrogen, and totally immersed in a bath thermostatted at 39.9 °C. A fresh ampoule was opened every fourth day, the contents transferred to a 10-mm silica cuvette which was flushed with nitrogen, and the spectrum (210—300 nm) recorded. The cell was then placed in the bath, and the spectrum was recorded again two days later. In this way, 7 ampoules gave a total of 15 readings at 2-day intervals over 28 days (*ca.* $3 \times t_{\frac{1}{2}}$). Samples of the reaction medium (containing no substrate) were also maintained at 39.9 °C and were used in the reference beam of the spectrophotometer. In an attempt to obtain an experimental infinity spectrum, a sample of the hydrolysis reaction mixture was heated at 50—55 °C for 28 days. The spectrum so obtained showed an optical density appreciably lower than that of the spectrum of a simulated infinity solution. This could be a consequence of partial decomposition of the dimesitylphosphinic acid product or crystallisation of some of it out of the reaction mixture. There was no indication of either process occurring during the kinetic run, but even a small loss of the phosphinic acid could lead to serious errors in measurements made at $\lambda < 240$ nm where the value of ε_{acid} is not much less than that of $\varepsilon_{substrate}$. It was therefore preferable to use absorbance measurements made at longer wavelengths, where ε_{acid} is small relative to $\varepsilon_{substrate}$ and any loss of the phosphinic acid will be less serious, even though this necessitated measuring small absolute values of A (the low solubility of both the substrate and the phosphinic acid in the reaction medium precluding the use of more concentrated solutions) with consequent reduction in precision. Using A_∞ from the simulated infinity spectrum, plots of $\log_{10}(A - A_\infty)$ *vs.* time were linear and gave at λ = 255 nm: $k\psi$ 8.79×10^{-7} s^{-1} ($\varepsilon_{substrate}$ 7 150; $\varepsilon_{product}$ 1 270); at λ = 265 nm: $k\psi$ 9.03×10^{-7} s^{-1} ($\varepsilon_{substrate}$ 4 110; $\varepsilon_{product}$ 1 270). The former value of $k\psi$ is considered the more reliable and is the one shown in Table 1.

Rates of Hydrolysis of (N-p-*Nitrophenyl*)*diphenylphosphinic Amides* (5).—For (5a—c) the rates of hydrolysis were determined as for the *N*-phenyl compounds above except that [$HClO_4$] = 2.58M and instead of monitoring continuously at a fixed wavelength the spectrum (250—500 nm) of the reaction mixture was scanned at regular intervals. For each *p*-nitroanilide at least 20 scans extending over *ca.* $4 \times t_{\frac{1}{2}}$ were recorded, as well as an infinity spectrum after $>8.5 \times t_{\frac{1}{2}}$. At the chosen wavelength (Table 2) the value of A_∞ was only 2—3% of the value of A_0. In each case a well-defined isosbestic point was observed at 281 nm. Each value of $k\psi$ in Table 1 is the average of two determinations.

For (5d) the rate of hydrolysis was determined as for the anilide (4d) except that [$HClO_4$] = 2.58M, and 13 ampoules were used to enable a total of 27 spectra (250—500 nm) to be recorded at 4-day intervals over a period of 104 days (*ca.* $1.27 \times t_{\frac{1}{2}}$). In an attempt to obtain an experimental infinity spectrum, a sample of the hydrolysis reaction mixture was heated at 90 °C for 15 days. The spectrum of the resulting solution differed greatly from that of a simulated infinity mixture consisting of dimesitylphosphinic acid and *p*-nitroaniline at the appropriate concentration in the hydrolysis reaction medium. In particular, the absorption maximum at 238 nm due to dimesitylphosphinic acid was absent and a very broad absorption increasing gradually in intensity from 500 to 225 nm was present. Although the spectrum of the simulated infinity mixture did not change over 105 days at room temperature, on heating at 90 °C it became like that of the experimental infinity mixture. For determining the value of $k\psi$, A_∞ was taken as the absorbance of the simulated infinity at 340 nm. Because ε_{acid} is only *ca.* 2.5% of $\varepsilon_{substrate}$ at 340 nm, any loss of dimesitylphosphinic acid by decomposition during the kinetic run would not of itself introduce large errors. However, the optical density of the experimental infinity solution at 340 nm was actually greater than that of the simulated infinity solution because of absorption by the products of decomposition. By

monitoring the smooth decrease in A at 300 nm during the kinetic run, it was established with reasonable confidence that the decomposition products did not contribute substantially to the measured value of A at 340 nm during the period studied ($1.27 \times t_{\frac{1}{2}}$) although errors would probably be serious at longer times.

Rates of Hydrolysis of Diarylphosphinic Amides (3).—There being no wavelengths at which the spectra of the reaction mixtures change substantially as hydrolysis proceeds, accurate rates could not be obtained by direct monitoring; the following procedures were adopted.

(*a*) *For* (3a—c). The amide in dioxan (1.7 ml) was added to a mixture of aqueous perchloric acid (76.5 ml) and dioxan (6.8 ml), maintained at 30.2 °C in a thermostatted bath, to give a reaction mixture having $[HClO_4] = 0.066$ 2M and [amide] as shown in Table 2. After thorough mixing, samples (*ca.* 4.2 ml) were withdrawn at intervals and quenched by addition of potassium carbonate (55 mg). Exactly 4.0 ml of each quenched sample was extracted with chloroform as described in (*c*) below.

(*b*) *For* (3d). Problems were encountered with the dimesitylphosphinic acid product crystallising out during hydrolysis and causing some of the amide substrate to crystallise out with it [*cf.* the behaviour previously noted for 1-methylcyclopropyl(phenyl)phosphinic amide [9]]. It was, therefore, necessary to use much more dilute hydrolysis mixtures than those employed for (3a—c) (Table 2). Immediately after mixing, portions (exactly 8.0 ml) of the reaction mixture were placed in glass tubes which were flushed with nitrogen, stoppered tightly, and immersed in the bath at 30.2 °C. Tubes were removed at intervals and reaction quenched by addition of potassium carbonate (100 mg). Each quenched sample was extracted with chloroform as described in (*c*) below.

(*c*) *For* (3a—d). Each quenched sample was shaken efficiently with chloroform (3.2 ml) and the layers were separated. Control experiments established that in this way the unchanged amide was largely extracted into the chloroform portion [*ca.* 91% for (3a) and >98% for (3b—d)] while the diarylphosphinic acid (as its potassium salt) was completely (>98%) retained in the aqueous portion.

For each substrate 15—18 samples were taken over a period $>4 \times t_{\frac{1}{2}}$ as well as an infinity sample after $>10 \times t_{\frac{1}{2}}$. From the spectra (240—330 nm) of the chloroform extracts the disappearance of the phosphinic amide could be followed. Plots of $\log_{10} A$ *vs.* time gave straight lines from which the values of $k\psi$ in Table 1 were deduced. The spectra of the aqueous residues allowed the appearance of the diarylphosphinic acid (as its potassium salt after quenching) to be followed. Plots of $\log_{10} (A_\infty - A)$ *vs.* time gave values of $k\psi$ which differed from those deduced from the disappearance of the substrate by <2%. Each kinetic experiment was performed in duplicate.

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