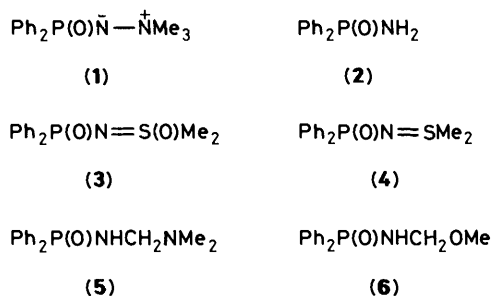# Photochemical Reactions of Trialkylammonio-*N*-diphenylphosphinoylimides: Rearrangement to *N*-Phosphinoyl Aminals and the Formation of Diphenylphosphinic Amide [1]

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The photolysis of the aminimide $Ph_2P(O)\bar{N}-\overset{+}{N}Me_3$ (**1**) in methanol gives the amide $Ph_2P(O)NH_2$ in high yield, but most of this is not formed from (**1**) directly *via* the nitrene; rather, it results from (solvolytic) decomposition of the phosphinoyl aminal $Ph_2P(O)NHCH_2NMe_2$ (**5**) formed from (**1**) by a photochemical rearrangement. With $Ph_2P(O)\bar{N}-\overset{+}{N}Et_3$ the corresponding rearrangement product $Ph_2P(O)NHCHMeNEt_2$ (an ethylidene aminal) is not observed, but this is probably just a consequence of very rapid decomposition. Although substrates bearing both Me and Et groups on the ammonium N atom appear to form only the rearrangement product (a methylene aminal) that results from involvement of a Me group, the yield is reduced substantially relative to the yield of (**5**) from (**1**). The size of the reduction is consistent with an Et group participating in the rearrangement about twice as readily as a Me group, but the product (an ethylidene aminal) that results suffering (much) more rapid decomposition to $Ph_2P(O)NH_2$.

The photochemical reactions of phosphinic azides, $R_2P(O)N_3$ (R = alkyl or aryl), are generally dominated by Curtius-like rearrangement,[2–5] and this limits their practical value as sources of phosphinoyl nitrenes. Relatively little is known about the photochemistry of phosphinic aminimides (ammonio-*N*-phosphinoylimides) but in as much as (**1**) is typical they seem not to undergo a comparable rearrangement.[4,6] In principle, therefore, they should be more attractive as photochemical sources of phosphinoyl nitrenes. However, while (**1**) does seem able to give substantial amounts of singlet-nitrene derived products such as (**3**) and (**4**), its photochemical reactions are characterised by remarkably high yields of the corresponding amide (**2**). In dimethyl sulphoxide (DMSO), for example, Kameyama *et al.*[6] obtained a 29% yield of the sulphoximine (**3**) but 51% of the amide (**2**). Also, the yield of the amide (28—30%)

$$Ph_2P(O)\bar{N}-\overset{+}{N}Me_3 \qquad Ph_2P(O)NH_2$$

$$(1) \qquad\qquad\qquad (2)$$

$$Ph_2P(O)N=S(O)Me_2 \qquad Ph_2P(O)N=SMe_2$$

$$(3) \qquad\qquad\qquad (4)$$

$$Ph_2P(O)NHCH_2NMe_2 \qquad Ph_2P(O)NHCH_2OMe$$

$$(5) \qquad\qquad\qquad (6)$$

exceeded that of the sulphilimine (**4**) (15—18%) in dimethyl sulphide (DMS),[7] and it was the only product isolated from a photolysis in methanol.[4] For comparison, photolysis of diphenylphosphinic azide in benzene–DMS (1:1) gave a 26% yield of the sulphilimine (**4**) (and only 9% of the amide) in spite of the competing Curtius rearrangement.[8]

Amides are generally regarded as triplet nitrene products, being formed by hydrogen abstraction, but there seems no obvious reason why the triplet state should be especially important when the nitrene precursor is an aminimide. Prompted by our continuing concern with the role of nitrenes in the reactions of phosphinic azides,[8] we have sought to learn more about the origin of the amide formed in the photochemical reactions of the aminimide (**1**).

Results and Discussion

Photolysis of the phosphinic aminimide (**1**)[6] in methanol solution (0.5M, 26 °C, 254 nm external illumination) was complete inside 4.5 h and gave the phosphinic amide (**2**) as the only substantial product (>90% by ^{31}P n.m.r. spectroscopy; 76% isolated). A minor product (<10%) was isolated by t.l.c., purified by crystallisation, and identified as the *N*-(methoxymethyl)amide (**6**), m/z 229 ($M^+ - MeOH$, 8%); $v_{max.}$ 3 175 cm^{-1} (NH); δ(CDCl$_3$) 8.0—7.25 (10 H, m), 4.42 (2 H, dd, J_{PH} 14, J_{HH} 8 Hz; simplifies to d, J 8 Hz, when ^{31}P irradiated), 4.4 (br, NH), and 3.27 (3 H, s). No other products were detected.

The photolysis was repeated but with interruption at *ca.* 70% completion (1.1 h). The ^{31}P n.m.r. spectrum of the reaction mixture showed the product to consist of comparable amounts of the amide (**2**) (δ_P 25.2) and an unknown compound (δ_P 26.4), with no more than a trace of (**6**). The unknown compound was unstable in methanol even in the absence of light, and decomposed on chromatography. Nonetheless, it was possible to isolate an almost pure (95%) sample by a series of careful extractions and precipitations, and to characterise it spectroscopically as the *N*-(dimethylaminomethyl)amide (**5**): m.p. 85—88 °C; $v_{max.}$(Nujol) 3 210 cm^{-1} (NH); δ(CDCl$_3$) 8.0—7.25 (10 H, Ph), 3.73 (2 H, dd, J_{PH} 9, J_{HH} 8 Hz; simplifes to d, J_{PH} 9 Hz, with D$_2$O), ~3.3br (1 H, m, NH), and 2.22 (6 H, s, NMe$_2$). The mass spectrum did not contain a peak for the molecular ion, but the highest-mass peak (m/z 229, 13%) corresponded to $Ph_2P(O)\overset{+\cdot}{N}=CH_2$ and the most abundant peak (m/z 44, 100%) to $\overset{+}{Me_2N}$. The structure (**5**) represents an *N*-phosphinoyl aminal, and intuitively one might expect it to have limited stability. We know of no previous reports of such compounds, and even acylated aminals have not been widely studied, albeit that they have attracted increased attention of late in connection with 'retro-inverso' peptides.[9] As confirmation of the aminal structure (**5**), it was found that spectroscopically identical material (m.p. 83—85 °C for an analytically pure sample) could be obtained in high yield by alkylation of diphenylphosphinic amide with $H_2C=\overset{+}{N}Me_2Cl^-$ (in CH_2Cl_2) and deprotonation of the resulting salt with base. This sample was additionally examined by f.a.b. mass spectrometry (glycerol matrix) and found to give the expected ($M + 1$) and ($M - 1$) peaks (m/z 275 and 273) in high abundance.
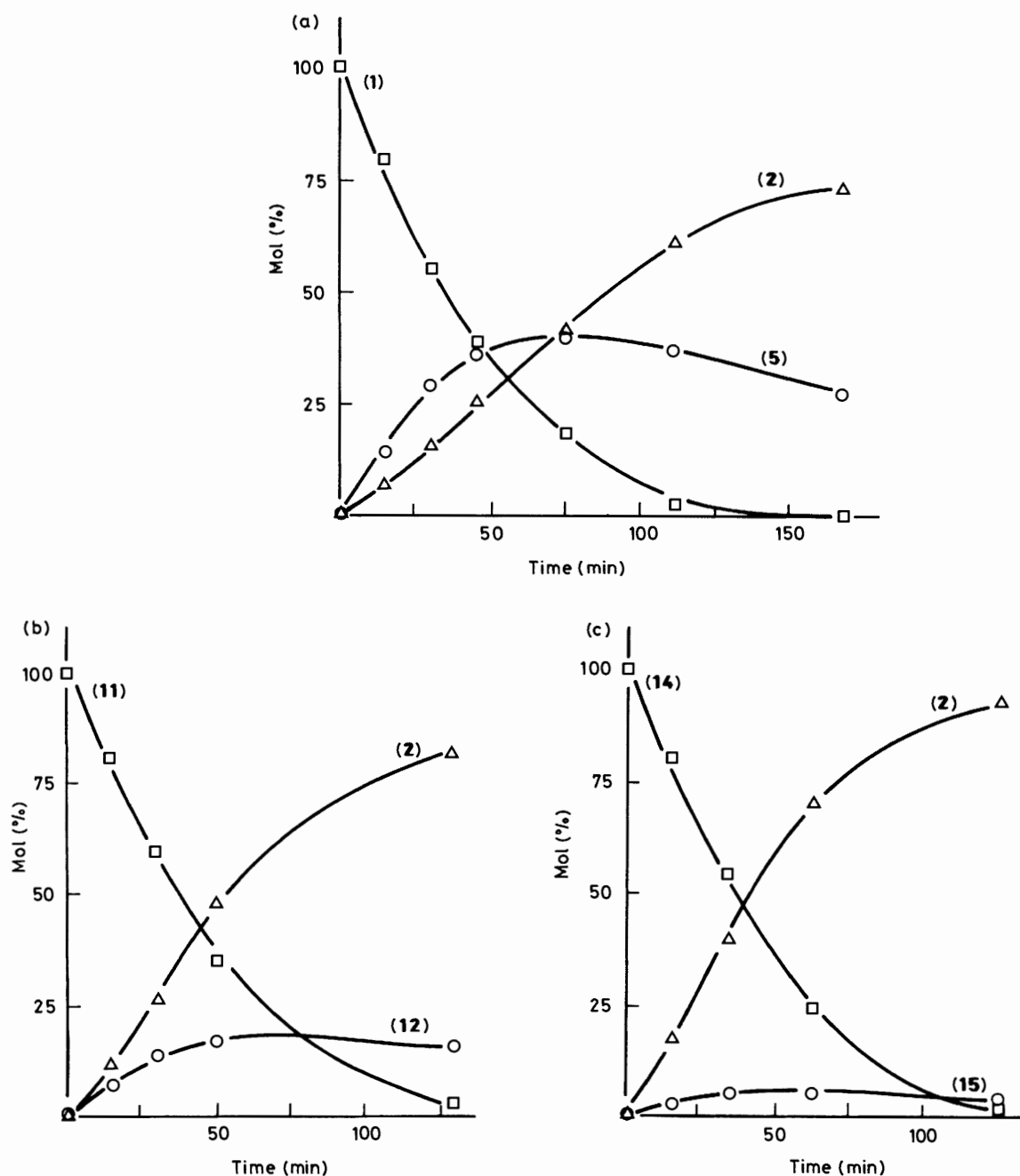
Figure. Photolysis of aminimides (0.15M) in methanol at 25 °C, λ 254 nm; composition of the reaction mixture for (a) $Ph_2P(O)\bar{N}-\overset{+}{N}Me_3$ (1), (b) $Ph_2P(O)\bar{N}-\overset{+}{N}Me_2Et$ (11), (c) $Ph_2P(O)\bar{N}-\overset{+}{N}MeEt_2$ (14)

A more detailed analysis of the photolysis of the aminimide (1) in methanol was carried out using ^{31}P n.m.r. spectroscopy to follow the course of the reaction, and a more dilute solution (0.15M) to reduce the time required to reach completion. As can be seen from the results in the Figure (a) the phosphinoyl aminal (5) now accounts for *ca.* 70% of the product in the early stages, and it is only in the late stages ($\geqslant 80\%$ completion) that the amide (2) becomes the major product. Clearly much of the amide must be formed indirectly by decomposition of the aminal, rather than directly by photolysis of the aminimide, a fact underlined by the continuing increase in the amount of amide even when all the aminimide has been consumed. Cessation of illumination did not halt the decay of the aminal to the amide, suggesting that even during the photolysis it was

occurring largely by a non-photochemical solvolysis mechanism. A control dark experiment with the authentic phosphinoyl aminal (5) showed that it had a half-life of *ca.* 100 min at 27 °C in methanol, and that the product was very largely the phosphinic amide (2) ($\geqslant 90\%$). Interestingly, the minor product was the *N*-(methoxymethyl)amide (6). The solvolysis probably proceeds as outlined in Scheme 1, where the left-hand pathway is essentially the same as that postulated for the hydrolysis of acylated aminals in non-acidic media.[9] Since a phosphinamide anion will presumably be a significantly better leaving group than a carboxamide anion, it does not seem unreasonable that this mechanism should proceed quite readily even in neutral methanol at room temperature. The observed rate of the non-photochemical solvolysis is sufficient to account
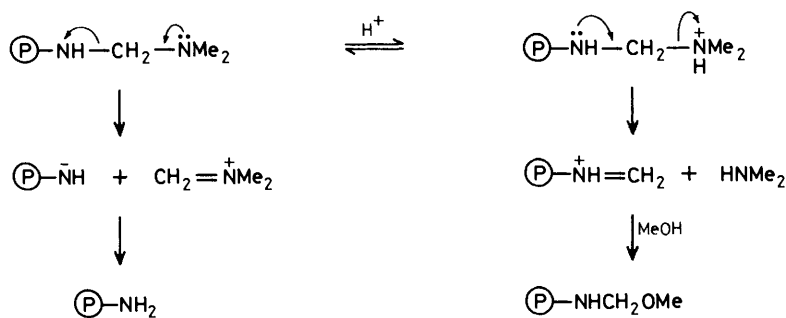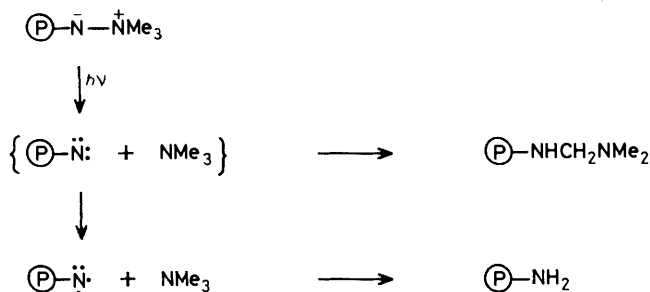
Scheme 1. [(P) = $Ph_2P(O)$]

for the decay of the aminal during the photolysis, but we do not exclude the possibility of some photochemical decomposition as well.

By working at lower temperatures (0 °C; 0.1M solution), so as to minimise solvolytic decomposition, it was possible to increase the proportion of the phosphinoyl aminal in the product in the earliest stages of photolysis to 75%, but some amide was always present. It therefore seems that ca. 25% of the aminimide goes directly to the amide on photolysis, and 75% to the aminal; this subsequently decomposes to the amide, together with a little of the N-(methoxymethyl)amide (6).

Having regard to the study of Kameyama et al.,[6] the aminimide (1) was also photolysed in DMSO (0.15M solution, 25 °C). The reaction was 3—4 times slower than in methanol and gave, as expected, the sulphoximine (3) (δ_P 15.4) as well as the amide (2) (δ_P 19.5). Here too, however, the principal product during the early stages of reaction was the phosphinoyl aminal (5) (δ_P 21.4) (not isolated but identified by ^1H and ^{31}P n.m.r. spectroscopic comparison with the authentic sample); it accounted for 48% of the product at 23% completion (0.75 h) and 47% at 50% completion (1.75 h), but only 24% at 90% completion (5.1 h). The amide content of the product increased from 26 to 58% during this time, while the sulphoximine amounted to ca. 20% throughout. Thus in DMSO, as in methanol, some 25% of the amide is formed directly from the aminimide, probably via the triplet nitrene as suggested[6] (Scheme 2), but most results from decomposition of the aminal. Control experiments showed that in DMSO the aminal decomposes only slowly in the absence of light ($t_{\frac{1}{2}}$ ~66 h at 25 °C), but is smoothly converted into the amide on irradiation.

Comparison of the results in DMSO and methanol shows that the sulphoximine is formed at the expense of the aminal. Accepting that the sulphoximine results from the singlet nitrene, it would be tempting to conclude that the aminal is derived from the same intermediate, by insertion into a C–H bond of NMe_3 (Scheme 2). Phosphoroyl nitrenes [from photolysis of $(RO)_2P(O)N_3$] are known to be very efficient at insertion into C–H bonds,[10] and formation of the aminal in this way would explain why the phosphinic aminimide (1) is not more efficient

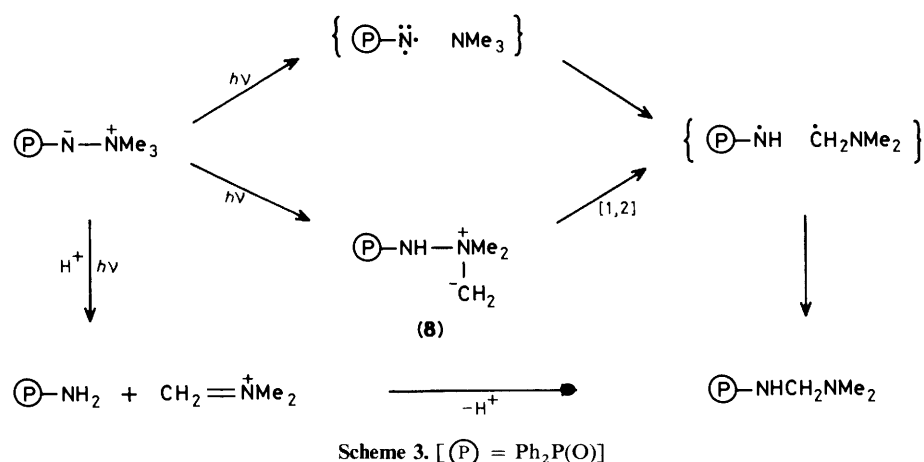**Scheme 2.** [(P) = $Ph_2P(O)$]

at forming other singlet-nitrene products. For the NMe_3 to be able to trap out more of the nitrene than does the DMSO solvent, it seems necessary to envisage the photolytic cleavage of the aminimide and the subsequent nitrene–NMe_3 reaction taking place within the same solvent cage. The fact that we observed none of the aminal (5) when the triethylammonium aminimide (7) was photolysed in methanol containing NMe_3 (10 mol equiv.) is consistent with this, but does not prove it.

$$Ph_2P(O)\bar{N}-\overset{+}{N}Et_3$$

(7)
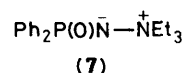
The inference that the phosphinoyl aminal is derived from the singlet nitrene rests on two assumptions: that the sulphoximine is a singlet-nitrene product, and that the basic photochemical behaviour of the aminimide is the same in methanol as it is in DMSO. The second of these assumptions is not easy to justify, and other possible mechanisms for the aminimide→aminal rearrangement must be considered. One such involves the nitrene in its triplet state. While the discovery of the alternative route to amide, via the aminal, removes the need to postulate that a remarkably high proportion of the aminimide forms the triplet nitrene on photolysis, it still remains a possibility: the aminal could be formed by collapse of the radical pair that would result from abstraction of a H atom from NMe_3 by the triplet nitrene (Scheme 3, top pathway). Essentially the same radical pair would also be an intermediate if the aminal were formed by (non-concerted) [1,2] sigmatropic rearrangement of the tautomeric form (8) of the aminimide (Scheme 3, middle pathway).* The initial tautomerism would be thermodynamically unfavourable for the ground state of the aminimide, but for the photoexcited state it may not be unreasonable. Evidence on this was sought by carrying out the photolysis of the aminimide in CH_3OD, halting the reaction at 70% completion and examining the remaining aminimide by mass spectrometry. Neither the molecular ion (m/z 274, 13%) nor the fragment m/z 58 ($Me_2\overset{+}{N}=CH_2$) showed any sign of D incorporation. Thus the tautomer, if it is formed in the photolysis, either does not revert to the aminimide, or does so by intramolecular proton transfer.

Amongst other possible routes to the aminal, alkylation of the amide (shown in outline in Scheme 3, bottom pathway) merits attention, given the success of a reaction of this type in the preparation of the authentic sample. A proton source would be available, even in an aprotic solvent, because the aminimide could not be obtained in a completely anhydrous state. No evidence for this was found, however, when the substituted aminimide (9; Ar = p-tolyl) was photolysed in methanol
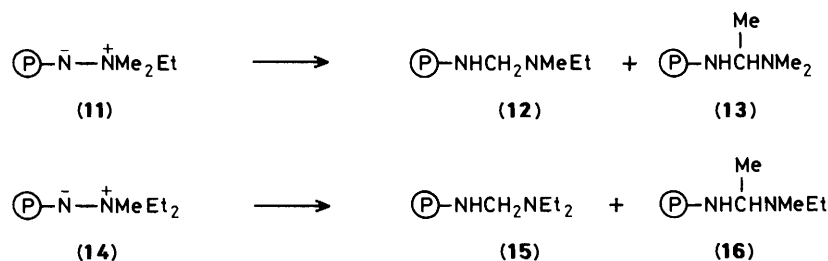
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* The term 'sigmatropic rearrangement' is used here in a purely structural sense, with no mechanistic connotation [Report from IUPAC Commission on Physical Organic Chemistry, ed. V. Gold, Pure Appl. Chem., 1983, 55, 1281 (see p. 1357)].

$$\{ \; (P)\text{-}\overset{\cdot\cdot}{N}\cdot \quad NMe_3 \; \}$$

$$(P)\text{-}\bar{N}\text{—}\overset{+}{N}Me_3 \xrightarrow{h\nu} \qquad \qquad \searrow \{ \; (P)\text{-}\dot{N}H \quad \dot{C}H_2NMe_2 \; \}$$

$$H^+ \downarrow h\nu \qquad \xrightarrow{h\nu} \qquad (P)\text{-}NH\text{—}\overset{+}{N}Me_2 \nearrow^{[1,2]}$$
$$\underset{-CH_2}{\overset{|}{}}$$
$$(8)$$

$$(P)\text{-}NH_2 \;+\; CH_2 =\overset{+}{N}Me_2 \xrightarrow{} \underset{-H^+}{} \xrightarrow{} (P)\text{-}NHCH_2NMe_2$$

Scheme 3. [(P) = $Ph_2P(O)$]

containing diphenylphosphinic amide: the aminal product consisted entirely of the substituted compound (10; Ar = *p*-tolyl) with none of the unsubstituted phenyl analogue (Ar=Ph) (^{31}P n.m.r. analysis).

$$Ar_2P(O)\bar{N}\text{—}\overset{+}{N}Me_3 \qquad\qquad Ar_2P(O)NHCH_2NMe_2$$
$$(9) \qquad\qquad\qquad\qquad\qquad (10)$$

It seemed possible that the photochemical behaviour of phosphinic aminimides having two different alkyl groups in the ammonium moiety would prove instructive; such compounds can, in principle, rearrange in two ways (Scheme 4), and the

prepared from $Ph_2P(O)NH_2$ and $H_2C=\overset{+}{N}Et\text{-}R$ Cl^- (R = Me or Et). The composition of the photolysis reaction mixtures at various times is shown in the Figure (b) and (c). No evidence was seen for the ethylidene aminal (13) or (16) which would result from involvement of an *N*-ethyl group in the rearrangement, and in the case of the triethyl substrate (7) there was no sign of any aminal at all—the amide was the only product detected, even when MeCN (aprotic) was used as solvent. The absence of ethylidene aminals was disappointing but not altogether unexpected; the solvolytic breakdown will inevitably proceed more readily when the iminium ion being formed is $MeCH=\overset{+}{N}R_2$ rather than $CH_2=\overset{+}{N}R_2$. It would be wrong to conclude that the ethylidene aminals are not formed

$$(P)\text{-}\bar{N}\text{—}\overset{+}{N}Me_2Et \xrightarrow{} (P)\text{-}NHCH_2NMeEt \;+\; (P)\text{-}NH\overset{\overset{Me}{|}}{C}HNMe_2$$
$$(11) \qquad\qquad\qquad\qquad (12) \qquad\qquad\qquad (13)$$

$$(P)\text{-}\bar{N}\text{—}\overset{+}{N}MeEt_2 \xrightarrow{} (P)\text{-}NHCH_2NEt_2 \;+\; (P)\text{-}NH\overset{\overset{Me}{|}}{C}HNMeEt$$
$$(14) \qquad\qquad\qquad\qquad (15) \qquad\qquad\qquad (16)$$

Scheme 4. [(P) = $Ph_2P(O)$]

balance between the competing pathways could be mechanistically revealing. To this end the 'mixed' aminimides (11) and (14) were required, together with the triethylammonium compound (7) for comparison. Adopting the approach employed for the simple trimethyl aminimide (1), the appropriate hydrazinium salts were prepared by alkylation of the hydrazides $Ph_2P(O)NHNR_2$ (R = Me or Et) with EtI or MeI. Not surprisingly, the reactions with EtI required relatively forcing conditions (large excess of EtI, no solvent, sealed vessel; 40 h at 80—90 °C for R = Me, 46.5 h at 100 °C for R = Et). The hydrazinium salts, dissolved in CH_2Cl_2, were then treated with aqueous NaOH to give the required aminimides. These were solids but, like the trimethyl compound, could not be obtained completely free of water.

The 'mixed' aminimides (11) and (14) were photolysed in methanol (0.15M solutions, 25 °C) under the conditions employed for the trimethyl compound (1) and the reactions were monitored by ^{31}P and ^{1}H n.m.r. spectroscopy. In both cases only two products were observed, the phosphinic amide (2) and the methylene aminal (12) or (15) resulting from involvement of an *N*-methyl group in the rearrangement. The identities of the aminals were confirmed by comparison with authentic samples

just because they were not detected. Unfortunately, we have not been able to devise a method for making authentic samples of the ethylidene aminals, and have therefore been unable to examine their stability in control experiments.

From the results in the Figure it can be seen that replacing one or two Me groups by Et has hardly any effect on the rate at which the aminimide reacts but a very significant effect on the extent to which the reaction proceeds *via* the methylene aminal: based on the composition of the products in the earliest stages of reaction the values for the different aminimides are *ca.* 70% for the NMe_3 compound, 35% for NMe_2Et, and 13% for $NMeEt_2$. This can be rationalised in terms of *ca.* 30% of the aminimide going directly to amide in each case while the rest rearranges to the aminals, with an Et group being involved in aminal formation in preference to a Me group, though only by a factor of 2 (a factor of 3 per C_α-H bond). A preference of this order would be reasonable for a mechanism involving singlet-nitrene insertion, given that the nitrene derived from $(EtO)_2P(O)N_3$ (and assumed to be in the singlet state) inserts into a secondary C-H in $CH_3CH_2CH(CH_3)_2$ only 4.3 times more readily than into a primary C-H bond.[10] It is more difficult to decide what to expect for the other possible mechanisms, although if an Et

group really does participate in the rearrangement in preference to a Me group the [1,2] sigmatropic rearrangement pathway (Scheme 3, middle) seems unlikely; the proton would surely be removed from Me rather than Et in the initial tautomerism. Of course the evidence here is largely circumstantial; it could be that Et groups do not participate in aminal formation, and that with the 'mixed' aminimides a (much) larger proportion of the substrate goes directly to the amide.

Conclusion

Most of the amide produced in the photochemical reactions of the phosphinic aminimide (1) is formed indirectly, by rearrangement to the phosphinoyl aminal (5) which subsequently decomposes. There is no need to postulate that an exceptionally large part of the aminimide reacts via the triplet nitrene. Nonetheless, some amide is formed directly from the aminimide, and this presumably involves the triplet nitrene. The singlet nitrene seems also to be involved, since adducts are formed with DMS and DMSO. The fact that no Curtius-like rearrangement occurs in any of the photochemical reactions of the aminimide implies that the nitrene—whether singlet or triplet—does not rearrange. That being so, it is difficult to see how the nitrene could be responsible for the Curtius rearrangement observed in the photolysis of diphenylphosphinic azide; by implication it seems that the Curtius rearrangement must be a concerted reaction of the photoexcited azide.

Experimental

M.p.s were determined using a Kofler hot-stage apparatus. I.r. spectra were recorded as Nujol mulls with a Perkin-Elmer 298 instrument, and ^{1}H n.m.r. spectra with a Varian EM 390 (or Bruker AM-300) spectrometer. ^{31}P N.m.r. spectra (^{1}H-decoupled) were recorded at 24.3 MHz with a JEOL JNM-FX60 spectrometer; positive chemical shifts are downfield from external 85% H_3PO_4. Routine mass spectra were obtained with a V.G. Micromass 16B instrument; f.a.b. spectra were recorded by PCMU Harwell. Light petroleum refers to the fraction b.p. 60—80 °C unless otherwise indicated. Tetra-alkyldiamino-methanes were prepared by adding an aqueous solution of the appropriate secondary amine (2 mol equiv.) to an ice-cold aqueous solution of formaldehyde;[11] N,N,N',N'-tetraethyl-diaminomethane [$\delta(CDCl_3)$ 3.02 (2 H, s), 2.53 (8 H, q, J 7 Hz), and 0.97 (12 H, t, J 7 Hz)] and N,N'-diethyl-N,N'-dimethylaminomethane [$\delta(CDCl_3)$ 2.84 (2 H, s), 2.43 (4 H, q, J 7 Hz), 2.19 (6 H, s), and 1.01 (6 H, t, J 7 Hz)] were used as isolated, without distillation.

Preparation of Trialkylammonio-N-phosphinoylimides (Phosphinic Aminimides) and their Precursors.—Phosphinic aminimides were dried in vacuo over phosphoric anhydride but could not be obtained in a completely anhydrous state; the m.p.s, i.r. maxima, and ^{31}P n.m.r. chemical shifts (in aprotic solvents) varied with the degree of hydration.

1,1-Diethyl-2-diphenylphosphinoylhydrazine.—A solution of diphenylphosphinic chloride (13.9 g, 58.9 mmol) in dichloromethane (10 ml) was added to a stirred mixture of 1,1-diethylhydrazine (**CAUTION***) (5.28 g, 60 mmol) and triethylamine (5.95 g, 58.9 mmol) in dichloromethane (25 ml) over 0.5 h. The reaction mixture was stirred overnight, filtered,

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* 1,1-Diethylhydrazine was prepared by reduction of N-nitrosodiethyl-amine with LiAlH$_4$; like others before, we found the induction period to be of variable length (up to 3 h) and the ensuing reaction extremely difficult to control.

and the solid (Et_3NHCl) washed with dichloromethane (85 ml). The resulting solution was washed with water (3 × 20 ml) and dried. Concentration afforded the title compound (15.8 g, 93%), m.p. 142—143 °C (from toluene); m/z 288 (M^+, 13%), 218 (100), and 216 (90); $v_{max.}$ 3 095 (NH), 1 205, and 1 190 cm^{-1}; $\delta(CDCl_3)$ 8.05—7.2 (10 H, m), 4.02 (1 H, d, J_{PH} 19 Hz, NH), 2.77 (4 H, q, J_{HH} 7 Hz), and 0.94 (6 H, t, J_{HH} 7 Hz); $\delta_P(CH_2Cl_2)$ 20.6 (Found: C, 66.8; H, 7.4; N, 9.7. $C_{16}H_{21}N_2OP$ requires C, 66.65; H, 7.3; N, 9.7%).

1,1-Dimethyl-2-(di-p-tolylphosphinoyl)hydrazine.—A solution of di-p-tolylphosphinic chloride[12] (8.6 mmol) in dichloromethane (6 ml) was added to a stirred solution of 1,1-dimethylhydrazine (1.3 g, 22 mmol) in dichloromethane (7 ml) at 0 °C. After 1.5 h at room temperature, the reaction was worked up as above to give the title compound (1.51 g, 61%), m.p. 142.5—144 °C (from toluene–light petroleum); m/z 288 (M^+, 5%) and 244 (100); $v_{max.}$ 3 090 (NH), 1 200, and 1 185 cm^{-1}; $\delta(CDCl_3)$ 7.72 (4 H, dd, J_{PH} 12, J_{HH} 8 Hz), 7.16 (4 H, dd, J_{PH} 3, J_{HH} 8 Hz), 3.75 (1 H, d, J_{PH} 17 Hz, NH), 2.54 (6 H, s, NMe$_2$), and 2.32 (6 H, s, ArMe); $\delta_P(CDCl_3)$ 22.4 (Found: C, 67.0; H, 7.4; N, 9.7. $C_{16}H_{21}N_2OP$ requires C, 66.65; H, 7.3; N, 9.7%).

Trimethylammonio-N-diphenylphosphinoylimide (**1**).[6]—1,1-Dimethyl-2-diphenylphosphinoylhydrazine (9.07 g, 35 mmol) was heated under reflux with methyl iodide (9.91 g, 70 mmol) in ethanol (18 ml) for 15 h. The volatile material was evaporated and the residue was dissolved in dichloromethane. Addition of ether precipitated 1,1,1-trimethyl-2-diphenylphosphinoyl-hydrazinium iodide, m.p. 164—166 °C; $v_{max.}$ 3 070 (NH) and 1 220 cm^{-1}; $\delta(CDCl_3)$ 8.66 (1 H, d, J_{PH} 7.5 Hz, NH), 8.05—7.3 (10 H, m), and 3.78 (9 H, s); $\delta_P(CDCl_3)$ 25.8. The hydrazinium salt was treated with 2M sodium hydroxide (25 ml) and the product was extracted into chloroform (4 × 25 ml). Concentration of the extracts and addition of ether gave trimethyl-ammonio-N-diphenylphosphinoylimide (**1**) (8.45 g, 88%) as a partial hydrate, m.p. 169—171 °C (lit.,[4,6] 172—174 °C or 178.3—178.5 °C); m/z 274 (M^+, 22%), 259 (25), and 201 (100); $v_{max.}$ ~3 450 (H_2O) and 1 170 cm^{-1}; $\delta(CDCl_3)$ 7.95—7.15 (10 H, m), 3.30 (9 H, s), and 3.13 (0.6 H_2O); $\delta_P(MeOH)$ 17.1.

Trimethylammonio-N-(di-p-tolylphosphinoyl)imide (**9**; Ar = p-tolyl).—Following the procedure described above, 1,1-dimethyl-2-(di-p-tolylphosphinoyl)hydrazine was heated with methyl iodide (reaction time 7 h) to give the hydrazinium iodide [$\delta_P(CDCl_3)$ 27.0, m.p. 175—176 °C] and this on treatment with sodium hydroxide afforded trimethylammonio-N-(di-p-tolyl-phosphinoyl)imide (**9**; Ar = p-tolyl) (80%) as a partial hydrate, m.p. 156—158 °C (from toluene); m/z 302 (M^+, 25%), 287 (30), and 229 (100); $v_{max.}$ ~3 350 (H_2O) and 1 175 cm^{-1}; $\delta(CDCl_3)$ 7.65 (4 H, dd, J_{PH} 11, J_{HH} 7.5 Hz), 7.06 (4 H, dd, J_{PH} 3, J_{HH} 7.5 Hz), 3.32 (9 H, s), 2.85 (s, H_2O), and 2.26 (6 H, s); $\delta_P(MeOH)$ 22.4 (Found: C, 66.8; H, 7.7; N, 9.2. $C_{17}H_{23}N_2OP\cdot0.2H_2O$ requires C, 66.7; H, 7.7; N, 9.2%).

Ethyldimethylammonio-N-diphenylphosphinoylimide (**11**).—A mixture of 1,1-dimethyl-2-diphenylphosphinoylhydrazine (1.84 g, 7.1 mmol) and an excess of ethyl iodide (6 ml) was heated in a closed vessel for 40 h at 80—90 °C. Excess of ethyl iodide was removed and the residue was dissolved in dichloromethane. Addition of ether precipitated 1-ethyl-1,1-dimethyl-2-diphenyl-phosphinoylhydrazinium iodide (2.46 g, 84%), m.p. 168—170 °C (from toluene–CH_2Cl_2); $v_{max.}$ 3 145 (NH) and 1 190 cm^{-1}; $\delta(CDCl_3)$ 8.5 (1 H, br, NH), 8.1—7.35 (10 H, m), 4.26 (2 H, q, J_{HH} 7 Hz), 3.64 (6 H, s), and 1.44 (3 H, t, J_{HH} 7 Hz); $\delta_P(CH_2Cl_2)$ 25.6 (Found: C, 46.2; H, 5.3; N, 6.7. $C_{16}H_{22}IN_2OP$ requires C, 46.2; H, 5.3; N, 6.7%).

Treatment of a solution of the hydrazinium iodide (0.55 g,

1.33 mmol) in dichloromethane (16 ml) with 1M aqueous sodium hydroxide (2 ml) gave the *title compound* (11) (0.37 g, 97%) as a partial hydrate, m.p. 110—112 °C [from light petroleum (b.p. 40—60 °C)]; m/z 288 (M^+, 2%), 273 (2), 259 (18), 216 (100), and 201 (95); $\nu_{max.}$ ~3 460 (H_2O) and 1 160 cm^{-1}; δ(CDCl$_3$) 7.95—7.15 (10 H, m), 3.48 (2 H, q, J_{HH} 7 Hz), 3.21 (6 H, s), 2.88 (s, H_2O), and 1.43 (3 H, t, J_{HH} 7 Hz); δ_P(MeOH) 20.6 (Found: C, 63.7; H, 7.4; N, 9.3. C$_{16}$H$_{21}$N$_2$OP·0.75H$_2$O requires C, 63.7; H, 7.5; N, 9.3%).

Diethylmethylammonio-N-*diphenylphosphinoylimide* (14).— Similarly, a mixture of 1,1-diethyl-2-diphenylphosphinoylhydrazine and methyl iodide (13 mol equiv.) was heated for 24 h at 50 °C. Excess of methyl iodide was removed and the resulting solid was crystallised from dichloromethane–ether (2:1) to give 1,1-*diethyl-1-methyl-2-diphenylphosphinoylhydrazinium iodide* (47%), m.p. 174—175.5 °C; $\nu_{max.}$ 3 150 (NH) and 1 195 cm^{-1}; δ(CDCl$_3$, 300 MHz) 8.5 [1 H, br, NH (d, J_{PH} 9 Hz at 90 MHz)], 8.05—7.5 (10 H, m), 4.24 (2 H, dq, J_{gem} 13, J_{HH} 7 Hz), 4.09 (2 H, dq, J_{gem} 13, J_{HH} 7 Hz), 3.52 (3 H, s), and 1.44 (6 H, t, J_{HH} 7 Hz); δ_P(CDCl$_3$) 26.2 (Found: C, 47.3; H, 5.6; N, 6.45. C$_{17}$H$_{24}$IN$_2$OP requires C, 47.45; H, 5.6; N, 6.5%).

The hydrazinium iodide was treated with sodium hydroxide as before and the crude product was triturated with light petroleum–ether (1:2) to give the *title compound* (14) (76%) as a hygroscopic partial hydrate, m.p. 77—80 °C; m/z 302 (M^+, 1.5%), 287 (2), 273 (21), and 216 (100); $\nu_{max.}$ ~3 410 (H_2O) and 1 145 cm^{-1}; δ(CDCl$_3$) 8.0—7.0 (10 H, m), 3.41 (4 H, q, J_{HH} 7 Hz), 3.07 (3 H, s), 3.02 (s, 0.5 H_2O), and 1.29 (6 H t, J_{HH} 7 Hz); δ_P(MeOH) 19.8.

Triethylammonio-N-*diphenylphosphinoylimide* (7).—A mixture of 1,1-diethyl-2-diphenylphosphinoylhydrazine (13.2 g, 45.8 mmol) and ethyl iodide (35.7 g, 229 mmol) was heated at 100 °C in a closed vessel for 46.5 h (after 1 h the mixture was homogeneous, at the end there was much precipitate). Removal of the volatile material and crystallisation from toluene–dichloromethane (1:1) gave 1,1,1-*triethyl-2-diphenyl-phosphinoylhydrazinium iodide* (12.6 g, 62%), m.p. 166—167 °C; $\nu_{max.}$ 3 070 (NH) and 1 180 cm^{-1}; δ(CDCl$_3$) 8.36 (1 H, d, J_{PH} 13 Hz, NH), 8.15—7.35 (10 H, m), 3.96 (6 H, q, J_{HH} 7 Hz), and 1.34 (9 H, t, J_{HH} 7 Hz); δ_P(CH$_2$Cl$_2$) 26.8 (Found: C, 48.5; H, 5.9; N, 6.4. C$_{18}$H$_{26}$IN$_2$OP requires C, 48.7; H, 5.9; N, 6.3%).

A portion of the hydrazinium iodide (3.10 g, 6.98 mmol) in dichloromethane (40 ml) was treated with 2M aqueous sodium hydroxide (7.0 ml). The organic layer was washed with water (8 ml), dried, and concentrated to give the *title compound* (7) as a semi-hydrate (2.22 g, 98%), m.p. 109—111 °C (from toluene); m/z 316 (M^+, 8%) and 287 (100); $\nu_{max.}$ ~3 400 (H_2O), 1 185 and 1 175 cm^{-1}; δ(CDCl$_3$) 8.0—7.1 (10 H, m), 3.40 (6 H, q, J_{HH} 7 Hz), 2.85 (s, 0.5 H_2O), and 1.25 (9 H, t, J_{HH} 7 Hz); δ_P(MeOH) 18.3 (Found: C, 66.6; H, 8.1; N, 8.55. C$_{18}$H$_{25}$N$_2$OP·0.5H$_2$O requires C, 66.4; H, 8.1; N, 8.6%).

Photochemical Reactions of Trialkylammonio-N-*phos-phinoylimides (Phosphinic Aminimides).*—The phosphinic aminimides generally contained some water (*ca.* 0.5 mol equiv.), allowance for which was made when calculating the weight to be used in each experiment. Photochemical reactions were carried out in quartz tubes illuminated externally with 254 nm lamps in a Rayonet reactor; the reaction temperature was generally 25—26 °C. Solvents were purified before use: methanol by distillation from its magnesium salt and DMSO by distillation under reduced pressure (first 20% discarded) and storage over 4A molecular sieves. Reaction products (and unchanged aminimide) that were not isolated were identified by n.m.r. spectroscopic comparison with authentic samples [^{1}H n.m.r. signals; enhancement of ^{31}P n.m.r. signals on addition of

authentic material (δ_P values varied considerably from one solution to another)].

(*a*) A 0.05M solution of the aminimide (1) (1.29 mmol) in methanol was irradiated for 4.5 h. The aminimide was completely consumed and only two products, δ_P 25.2 and 26.4 (ratio *ca.* 12:1), were observed in significant amounts (a little poorly defined polymeric material seemed also to be formed). The crude product was crystallised from benzene to give diphenylphosphinic amide (2) (183 mg), m.p. 159—161 °C (lit.,[13] 165—167 °C). The mother liquor was evaporated and the residue washed with CCl$_4$ to give more of the amide (2) (29 mg; total 212 mg, 76%). The CCl$_4$ extract was chromatographed on a layer of alumina (eluant 6% MeOH in ether) and the faster-moving material was collected and crystallised from CCl$_4$–ether to give a small sample of N-(*methoxymethyl*)*diphenylphosphinic amide* (6), m.p. 96—98 °C; m/z 229 (M^+ − MeOH, 8%) and 201 (100); $\nu_{max.}$ 3 175 (NH) and 1 190 cm^{-1}; δ(CDCl$_3$) 8.0—7.25 (10 H, m), 4.42 (2 H, dd, J_{PH} 14, J_{HH} 8 Hz; simplifes to d, J_{HH} 8 Hz when ^{31}P irradiated), 4.4br (1 H, NH), and 3.27 (3 H s). The spectra were identical with those of the authentic sample.

(*b*) A 0.15M solution of the aminimide (1) (1.37 mmol) in methanol was irradiated for 1.1 h. Some aminimide (31%) remained and two products δ_P 25.2 and 26.4 (unstable) (ratio 0.9:1) were observed. The crude product was dissolved in CH$_2$Cl$_2$ (1 ml) and ether (5 ml) was added. The precipitated aminimide was removed and the solution evaporated. The residue was dissolved in CH$_2$Cl$_2$ (2 ml) and the unstable product was isolated as detailed below, working rapidly and keeping everything ice-cold. The CH$_2$Cl$_2$ solution was extracted with 0.5M hydrochloric acid (1 ml) and then water (1 ml). The combined aqueous extracts (containing a protonated form of the unstable compound) were washed with CH$_2$Cl$_2$ (1 ml) and made basic with 2M aqueous NaOH (0.3 ml). They were then extracted with CH$_2$Cl$_2$ (2 × 1 ml) and the combined organic extracts were dried (Na$_2$SO$_4$). Concentration and addition of ether precipitated N-(*dimethylaminomethyl*)*diphenylphosphinic amide* (5), m.p. 85—88 °C; m/z 229 (M^+ − HNMe$_2$, 13%), 201 (93), and 44 (100); $\nu_{max.}$ 3 210 (NH), 1 195, and 1 175 cm^{-1}; δ(CDCl$_3$) 8.0—7.25 (10 H, m), 3.73 (2 H, dd, J_{PH} 9, J_{HH} 8 Hz; collapses to d, J_{PH} 9 Hz with D$_2$O; further simplifes to s when ^{31}P decoupled), ~3.3br (NH), and 2.22 (6 H, s). The ^{31}P n.m.r. spectrum revealed a small impurity [amide (2), 5%] but in all other respects the spectra were identical with those of the authentic sample. The CH$_2$Cl$_2$ solution remaining from the acidic extraction was diluted with ether to precipitate diphenylphosphinic amide (2), m.p. 163—165 °C (from benzene).

(*c*) A 0.15M solution of the aminimide (1) (2.7 mmol) in DMSO was irradiated and samples (1.1 ml) were withdrawn at intervals and examined immediately by ^{31}P n.m.r. spectro-scopy. Three products were observed together with unchanged aminimide, in the proportions shown below. The identity of the products was tentatively established by ^{31}P n.m.r. comparison with authentic samples.

Time (h)	0.75	1.25	1.75	2.5	3.5	5.13
Unchanged (1)	77	64.5	51	37	20	9%
(5) δ_P 21.4	11	16.5	23	25	25.5	22%
(2) δ_P 19.5	6	11.5	17	25.5	40.5	53%
(3) δ_P 15.4	6	7.5	9	12.5	14	16%

More positive identification of the products was obtained by irradiating a 0.10M solution of the aminimide for 1.2 h, at which point there was still some unchanged aminimide (15%) but a relatively large amount of the unstable product (δ_P 21.4, 29%). The DMSO was removed under reduced pressure and the residue was examined by ^{1}H n.m.r. spectroscopy: δ(CDCl$_3$) included 3.36 (s) for unchanged (1), 3.20 (s) for the product (3),

and 3.72 (dd, J_{PH} 9, J_{HH} 8 Hz; collapses to d, J_{PH} 9 Hz with D_2O) and 2.18 (s) (integral ratio 1:3) for the unstable product (5) [the amide product (2) did not give rise to any clearly assignable signals].

(d) A 0.15M solution of the aminimide (9; Ar = p-tolyl) in methanol containing diphenylphosphinic amide (2) (1 mol equiv.) was irradiated for 2.5 h. Analysis of the reaction mixture revealed no aminimide, much unchanged diphenylphosphinic amide (δ_P 25.1), and just two products, namely di-p-tolylphosphinic amide (δ_P 25.7) and N-(dimethylaminomethyl)-di-p-tolylphosphinic amide (10; Ar = p-tolyl) (δ_P 27.1) (ratio 6:1). N-(Dimethylaminomethyl)diphenylphosphinic amide (5) (δ_P 26.4) was shown to be absent.

(e) A 0.1M solution of the triethyl aminimide (7) in methanol was irradiated for 1 h. Analysis by ^{31}P n.m.r. spectroscopy showed the reaction to be 40% complete and diphenylphosphinic amide (2) (δ_P 25.1) to be the only product. After 5 h the aminimide was completely consumed and the amide (2) was still the only detectable product. When CD_3CN was used as solvent the amide (2) was again the only product that could be detected; there was no evidence (^1H and ^{31}P n.m.r.) for the presence of $Ph_2P(O)NHCHMeNEt_2$.

(f) A 0.15M solution of the triethyl aminimide (7) in methanol containing Me_3N (10 mol equiv.) was irradiated, and samples were withdrawn at intervals [extending over 4.75 h (98% completion)] and examined by ^{31}P n.m.r. spectroscopy. In all the samples diphenylphosphinic amide (2) was the only product; N-(dimethylaminomethyl)diphenylphosphinic amide (5) was shown to be absent.

(g) A 0.15M solution of the ethyldimethyl aminimide (11) in methanol was irradiated for 2.2 h (>95% completion), samples being withdrawn at intervals and analysed immediately. Two products were observed, diphenylphosphinic amide (2) (δ_P 25.6) and N-(ethylmethylaminomethyl)diphenylphosphinic amide (12) (δ_P 26.6), $\delta(CDCl_3)$ included 3.81 (dd, J_{PH} 9, J_{HH} 7 Hz; collapses to d, J_{PH} 9 Hz with D_2O), 2.49 (q, J_{HH} 7 Hz), 2.27 (s), and 0.97 (t, J_{HH} 7 Hz) (integral ratio 2:2:3:3) (cf. the authentic specimen). The composition of the reaction mixture at different times is shown in the Figure (b).

(h) A 0.15M solution of the diethylmethyl aminimide (14) in methanol was irradiated for 2.1 h (>95% completion). Samples were withdrawn at intervals and analysed immediately. The dominant product was diphenylphosphinic amide (2) (δ_P 25.3) but there was ^{31}P n.m.r. evidence for a small amount of N-(diethylaminomethyl)diphenylphosphinic amide (15) (δ_P 26.4) (cf. the authentic specimen). The composition of the reaction mixture at various times is shown in the Figure (c).

(i) Control experiments were carried out to test the stability of N-(dimethylaminomethyl)diphenylphosphinic amide (5). A 0.10M solution of (5) in methanol underwent solvolysis in the absence of light ($t_{\frac{1}{2}}$ ca. 1.7 h at 27 °C) to give a 9:1 mixture of diphenylphosphinic amide (2), m.p. 163—165 °C, and N-(methoxymethyl)diphenylphosphinic amide (6). A 0.15M solution of (5) in DMSO was largely unchanged after 13.3 h at 25 °C in the absence of light [13% conversion to the amide (2); $t_{\frac{1}{2}}$ ca. 66 h] but a similar solution on irradiation at 25 °C was almost completely converted into the amide (2) (94% by ^{31}P n.m.r.; no other product observed) after 12 h.

Authentic Samples of Products Formed in Aminimide Photochemical Reactions

Diphenylphosphinic amide (2),[12] di-p-tolylphosphinic amide,[12] and N-diphenylphosphinoyldimethylsulphoximine (3)[4] were prepared as previously described. The methods employed for other compounds are summarised below.

N-(Dimethylaminomethyl)diphenylphosphinic Amide (5).— N,N-Dimethylmethyleneammonium chloride (0.52 g, 5.5 mmol)

(prepared from $Me_2NCH_2NMe_2$ and CH_3COCl)[14] was added to a stirred suspension of (partially soluble) diphenylphosphinic amide (0.93 g, 4.3 mmol) in dry dichloromethane (7 ml). After 1 h reaction was complete [δ_P 26.4 for hydrochloride of (5)]. The mixture was diluted with dichloromethane (15 ml). The solution was added to ice-cold 1M NaOH solution (6.5 ml), the organic layer was separated, and the aqueous layer was extracted with chloroform (5 ml); the combined organic portions were then washed with water, dried, and evaporated. Addition of ether to the residue precipitated N-(dimethylaminomethyl)diphenylphosphinic amide (5) (0.87 g, 74%), m.p. 84—87.5 °C, m/z (f.a.b., glycerol matrix) 275 ($M^+ + 1$, 93%), 273 ($M^+ - 1$, 27), 230 ($M^+ - NMe_2$, 100), and 201 (52),* other spectroscopic data as for sample isolated from photolysis of (1); a sample recrystallised from $CHCl_3$–ether at -10 °C had m.p. 82.5—84.5 °C (Found: C, 65.4; H, 7.0; N, 10.2; P, 11.3. $C_{15}H_{19}N_2OP$ requires C, 65.7; H, 7.0; N, 10.2; P, 11.3%).

N-(Dimethylaminomethyl)di-p-tolylphosphinic Amide (10; Ar = p-tolyl).—This compound was prepared from di-p-tolylphosphinic amide in the same way (crystallised from ether–light petroleum) (24%); m.p. 96—99 °C (decomp.), m/z 257 ($M^+ - HNMe_2$, 4%), 245 ($M^+ - CHNMe_2$, 3), 244 ($M^+ - CH_2NMe_2$, 4), and 229 (100); $v_{max.}$ 3 220 (NH) and 1 175 cm^{-1}; $\delta_P(MeOH)$ 27.1; $\delta(CDCl_3)$ 7.66 (4 H, dd, J_{PH} 14, J_{HH} 8 Hz), 7.17 (4 H, dd, J_{PH} 3, J_{HH} 8 Hz), 3.69 (2 H, dd, J_{PH} 9, J_{HH} 7.5 Hz; simplifies to d, J_{PH} 9 Hz with D_2O), 3.3br (1 H, NH), 2.33 (6 H, s, p-Me), and 2.23 (6 H, s, NMe_2); a satisfactory elemental analysis could not be obtained (Found: C, 66.8; H, 7.6; N, 9.1. $C_{17}H_{23}N_2OP$ requires C, 67.5; H, 7.7; N, 9.3%).

N-(Diethylaminomethyl)diphenylphosphinic Amide (15).— This compound was prepared (57%) from diphenylphosphinic amide and N,N-diethylmethyleneammonium chloride (ex. $Et_2NCH_2NEt_2 + CH_3COCl$)[14] in the same way; recrystallised from ether–light petroleum, m.p. 99.5—102.5 °C; m/z (f.a.b., glycerol matrix) 303 ($M^+ + 1$, 10%), 301 ($M^+ - 1$, 5), 230 ($M^+ - NEt_2$, 6), 201 (9), and 86 ($H_2C=\overset{+}{N}Et_2$, 100);* $v_{max.}$ 3 165 (NH) and 1 190 cm^{-1}; $\delta_P(CDCl_3)$ 22.6; $\delta(CDCl_3)$ 7.95—7.3 (10 H, m), 3.96 (2 H, dd, J_{PH} 8.5, J_{HH} 7 Hz), 3.30 (1 H, m, NH), 2.60 (4 H, q, J_{HH} 7 Hz), and 0.96 (6 H, t, J_{HH} 7 Hz) (Found: C, 67.4; H, 7.5; N, 9.0. $C_{17}H_{23}N_2OP$ requires C, 67.5; H, 7.7; N, 9.3%).

N-(Ethylmethylaminomethyl)diphenylphosphinic Amide (12).—This compound was similarly prepared (87%) from diphenylphosphinic amide and N-ethyl-N-methylmethyleneammonium chloride (ex. $EtMeNCH_2NMeEt + CH_3$-COCl); it was obtained as an oil, m/z (f.a.b., glycerol matrix) 289 ($M^+ + 1$, 100%), 287 ($M^+ - 1$, 34), 230 ($M^+ - NEtMe$, 91), and 201 (94);* $v_{max.}$(film) 3 190 (NH) and 1 195 cm^{-1}; $\delta(CDCl_3)$ 7.95—7.3 (10 H, m), 3.86 (2 H, dd, J_{PH} 9, J_{HH} 7 Hz), 3.55 (1 H, m, NH), 2.50 (2 H, q, J_{HH} 7 Hz), 2.28 (3 H, s), and 0.98 (3 H, t, J_{HH} 7 Hz).

N-(Methoxymethyl)diphenylphosphinic Amide (6).—Attempts to replace the NMe_2 group in the phosphinoyl aminal (5) with a methoxy group, by quaternisation with MeI followed by nucleophilic displacement with MeOH, invariably gave a mixture of products (^{31}P n.m.r. monitoring implied a rather complex reaction). Chromatography on a layer of alumina (eluant 6% MeOH in ether) gave mainly diphenylphosphinic amide (R_F 0.2) but also some of the required product (6) (15%),

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* Ions having m/z < 80 were not recorded in the f.a.b. mass spectra; fragments corresponding to the most abundant ion (m/z 86) in the spectrum of (15) were therefore not seen in the spectra of the lower homologues (5) and (12), though presumably they were formed.

R_F 0.3, crystallised from CCl_4-ether, m.p. 97—99 °C; $\delta_P(CH_2Cl_2)$ 23.2; i.r., ^1H n.m.r., and mass spectra as for sample isolated from photolysis of (1) (Found: C, 63.9; H, 6.1; N, 5.4. $C_{14}H_{16}NO_2P$ requires C, 64.4; H, 6.2; N, 5.4%).

Acknowledgements

References

1 Preliminary communication: S. Freeman and M. J. P. Harger, *J. Chem. Soc., Chem. Commun.*, 1985, 241.
2 M. J. P. Harger and M. A. Stephen, *J. Chem. Soc., Perkin Trans. 1*, 1981, 736.
3 G. Bertrand, J.-P. Majoral, and A. Baceiredo, *Tetrahedron Lett.*, 1980, **21**, 5015; A. Baceiredo, J.-P. Majoral, and G. Bertrand, *Nouv. J. Chem.*, 1983, **7**, 255.
4 M. J. P. Harger and S. Westlake, *Tetrahedron*, 1982, **38**, 1511.
5 M. J. P. Harger and S. Westlake, *Tetrahedron*, 1982, **38**, 3073.
6 E. Kameyama, S. Inokumo, and T. Kuwamura, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1439.
7 S. Westlake, PhD. Thesis, Leicester University, 1981; M. J. P. Harger, unpublished observations.
8 M. J. P. Harger and S. Westlake, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2351.
9 G. M. Loudon, M. R. Almond, and J. N. Jacob, *J. Am. Chem. Soc.*, 1981, **103**, 4508, and references therein.
10 R. Breslow, A. Feiring, and F. Herman, *J. Am. Chem. Soc.*, 1974, **96**, 5937.
11 J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, 1957, **22**, 355.
12 M. J. P. Harger, *J. Chem. Soc., Perkin Trans. 2*, 1980, 154.
13 I. N. Zhmurova, I. Y. Voitsekhovskaya, and A. V. Kirsanov, *J. Gen. Chem. USSR (Engl. Transl.)*, 1959, **29**, 2052.
14 G. Kinsat and L.-F. Tietze, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 239; H. Böhme and K. Hartke, *Chem. Ber.*, 1960, **93**, 1305.