Photochemical Reactions of Phenylphosphinic Azides having *ortho* Alkyl Substituents: Diminution of Curtius-like Rearrangement; Intramolecular Nitrene Insertion into C–H Bonds[1]

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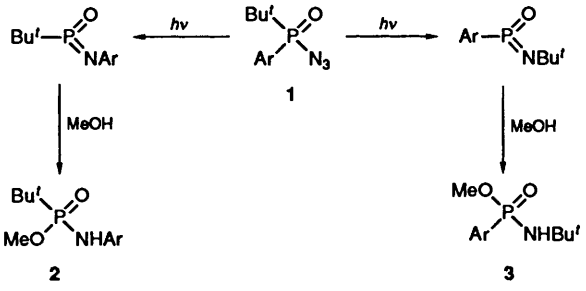
Two types of reaction are important for the photolysis of the phosphinic azides $Ar_2P(O)N_3$ (Ar = mesityl or 2,4,6-triisopropylphenyl) in MeCN–MeOH: Curtius-like rearrangement, giving ArP(O)(OMe)NHAr, and nitrene insertion into a C–H bond of an *ortho* substituent (Me or $CHMe_2$), giving a dihydrobenzazaphosphole oxide **11** or **12**. The behaviour of $Bu^tArP(O)N_3$ (Ar = mesityl) is similar except that two rearrangement products are formed (Bu^t or Ar migration; ratio 6:1). Extensive intramolecular insertion is unprecedented for photochemically-generated phosphorus(v) nitrenes. The exceptional behaviour of the present azides probably owes much to steric congestion. It may discourage rearrangement (Ar migration), relative to other phosphinic azides, so more nitrene is made available for insertion reactions; and it may encourage intramolecular reaction, relative to phosphoryl azides, by shielding the nitrene from external molecules (solvent) while ensuring that an internal C–H bond is held in close proximity.

Although rather high temperatures are needed to bring about the thermal decomposition of phosphorus(v) azides,[2] they eliminate N_2 quite readily when exposed to UV light. The principal photochemical reaction of a phosphoryl azide $[(RO)_2P(O)N_3]$ is formation of the nitrene, which then usually inserts into a solvent C–H bond.[3,4] For phosphinic azides $[R_2P(O)N_3]$ the dominant photochemical reaction is generally a Curtius-like rearrangement,[5–9] and nitrene insertion plays little part, if any. Two features of these photochemical reactions prompted the present investigation. First, for phosphoryl nitrenes, there is an apparent reluctance to undergo intramolecular C–H insertion, notwithstanding the efficiency of intermolecular insertion.[10] Second, for phosphinic azides, the migratory aptitude of different alkyl groups differs significantly when assessed by their ability to compete with phenyl migration $[RPhP(O)N_3]$, but not when measured in direct competition [*e.g.* $Bu^tMeP(O)N_3$].[8] It seemed possible that the photochemical behaviour of *tert*-butyl(mesityl)phosphinic azide **1** (Ar = mesityl) would shed light on both points. The *ortho*-methyl substituents in the aryl group might not only afford particularly attractive sites for intramolecular insertion but also, by virtue of steric interaction with the *tert*-butyl group, influence the propensity of the aryl group to migrate.

Results and Discussion

tert-Butyl(mesityl)phosphinic chloride was readily obtained, in good yield, by controlled hydrolysis of the complex ($ArBu^tPCl_2^+AlCl_4^-$) formed by reaction of $ArPCl_2$ (Ar = mesityl) with Bu^tCl and $AlCl_3$. In spite of the steric congestion at phosphorus, the phosphinic chloride reacted quite rapidly ($\leqslant$1 h) with NaN_3 in DMF (dimethylformamide) at room temperature to give the corresponding azide **1** (Ar = mesityl).

The photochemistry of the azide was examined by irradiating (254 nm; 160 min) a dilute MeCN solution, with MeOH (10 mol equiv.) present to trap out any metaphosphonimidate formed by Curtius-like rearrangement (Scheme 1). Chromatography of the reaction mixture gave two substantial product fractions, in addition to some unchanged azide (14%). The first of these fractions proved to be a mixture of two compounds [$\delta_P(CH_2Cl_2)$ 22.2 and 38.3; ratio ~6:1), but repeated crystallisation afforded a pure sample of the major component. For this, the ^1H NMR spectrum showed that the Ar group was still attached to



Scheme 1 Ar = mesityl

phosphorus (*meta* H atoms: δ 6.89, d, J_{PH} 4), but the Bu^t group was not (δ 1.29; $J_{PH} < 1$), and that a P–OMe group had been incorporated (δ 3.60; 3 H, d, J_{PH} 11.5). This clearly accords with the alkyl-migration product **3** (Scheme 1). The minor component was not obtained pure, but was seen to contain a P–Bu^t group (δ 1.26, d, J_{PH} 15). Moreover, it had exactly the same ^{31}P chemical shift and GLC retention time as an authentic sample of **2**, the alternative rearrangement product, prepared by sequential treatment of $Bu^tP(O)Cl_2$ with ArNHLi (Ar = mesityl) and NaOMe. It therefore seems that rearrangement is an important reaction pathway (**2** + **3**, 32%)† and, as with the phenyl azide **1** (Ar = Ph),[8] both possible rearrangement products are formed. Significantly, however, the *tert*-butyl:aryl migration ratio is substantially greater with Ar = mesityl (~6:1) then it is with Ar = phenyl (2.1:1). Previously, using a series of azides $PhRP(O)N_3$, the alkyl:phenyl migration ratio was seen to increase with the size of the alkyl group [1.2:1 (R = Me), 1.7:1 (R = Pr^i), 2.1:1 (R = Bu^t)], even though the inherent migratory aptitudes of *tert*-butyl and methyl seemed to differ little, as judged by the behaviour of $Bu^tMeP(O)N_3$.[8] We suggested, therefore, that the observed changes in the alkyl:phenyl migration ratio resulted from steric inhibition of phenyl migration. In particular, a more bulky alkyl group will tend to destabilise the conformation required for phenyl migration (Fig. 1) so that, whether rearrangement occurs in the excited state of the azide (as shown) or in the nitrene, migration

† All product yields refer to chromatographically isolated material and are based on the amount of azide actualy consumed (unrecovered).

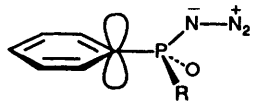
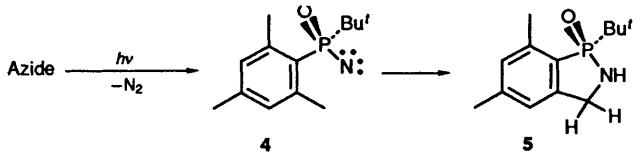


Fig. 1

of the Ph group will compete less effectively.[8] The behaviour now observed for the mesityl azide **1** (Ar = mesityl) seems to support that view. With Me groups at the *ortho* positions, in place of H atoms, the steric interactions between the alkyl and aryl groups will inevitably be more severe, the effect on aryl migration more serious, and the preference for alkyl migration more pronounced.

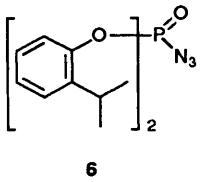
The other substantial product fraction from the photolysis of azide **1** (Ar = mesityl) consisted of a single compound, having a molecular formula corresponding simply to loss of N_2 (M^+ and elemental analysis). The lowfield position of the ^{31}P NMR signal (δ_P 61.9) suggested that both *tert*-butyl and mesityl groups were still attached to phosphorus, although the ^1H NMR spectrum showed the symmetry of the mesityl group to have been lost [non-equivalent H atoms in Ar: δ 6.99 (1 H, d, J_{PH} 4.5) and 6.91 (1 H, s)]. Most important, only two of the original Me groups remained intact (δ 2.61 and 2.35, both 3 H), the third having been transformed into a deshielded CH_2 group with non-equivalent H atoms (δ 4.40 and 4.23; both dd, J_{gem} 14, J_{PH} 3 or 8). This all points to the dihydrobenzazaphosphole oxide **5** (31%) that would result from intramolecular insertion of the nitrene **4** into an *ortho* methyl C–H bond (Scheme 2). From the



Scheme 2

isolated yields it would appear that intramolecular insertion and rearrangement are of equal importance, but this is rather misleading. In an analytical experiment, using GLC to follow the reaction, the insertion:rearrangement product ratio was found to decline appreciably as photolysis progressed [GLC peak area (uncalibrated) 1.35 at 20% completion (t = 10 min) and 1.25 at 60% (t = 45) but only 0.75 at 85% completion (t = 110)]. This implies that the intramolecular insertion product suffers quite extensive photochemical degradation (products observed by GLC but not identified), and that the yield in the preparative experiment (31% at *ca.* 85% completion) substantially understates the amount actually formed. As much as 50% of the azide probably reacts by intramolecular nitrene insertion.

To appreciate the significance of such extensive intramolecular insertion it is necessary to recall the behaviour of phosphoryl nitrenes. Phosphoryl azides do not rearrange on photolysis, but give nitrenes that insert efficiently into solvent C–H bonds.[3,4] Discrimination between different types of C–H bond (1°, 2° or 3°) is unusually small, suggesting that phosphoryl nitrenes are especially reactive towards insertion.[3,4] Nonetheless, attempts to harness this reactivity for the intramolecular functionalisation of alkyl groups have met with little success.[10] Even the azide **6**, with 3° benzylic C–H bonds, gave only 3% of the intramolecular



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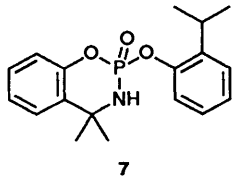

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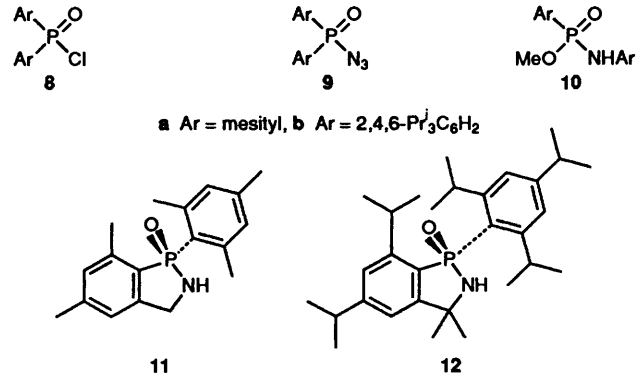
insertion product **7** when photolysed in benzene, and none at all in cyclohexane.[10] This, in spite of the fact that the nitrene is clearly well disposed towards C–H insertion, as evidenced by the high yield of the intermolecular insertion product $(ArO)_2P(O)NHC_6H_{11}$ (70%).[10] Against that background, the importance of intramolecular insertion in the case of our phosphinoyl nitrene **4** is surely rather remarkable.* Indeed, if the Curtius-like rearrangement is a concerted reaction of the photo-excited azide, and does not involve formation of the nitrene,[11] then such nitrene as is formed must be trapped rather efficiently by intramolecular insertion.

Diarylphosphinic Azides.—In looking for further examples of intramolecular insertion by phosphinoyl nitrenes, we hoped also to gain some understanding of why they should differ from phosphoryl nitrenes. It seemed possible that the azides **9a** and **9b** would prove rewarding.



8 **9** **10**

a Ar = mesityl, **b** Ar = 2,4,6-$Pr^i_3C_6H_2$

11 **12**

The preparation of the dimesityl azide from the known phosphinic chloride **8a** was not a problem, but for the bis(triisopropylphenyl) compound neither the phosphinic acid nor the chloride had previously been reported. In the event, addition of $POCl_3$ to the aryllithium (from ArBr + BuLi) at −70 °C followed by gradual warming to room temperature gave the phosphinic chloride **8b** as the dominant phosphorus-containing product (δ_P 47.0; ~70%). After chromatography only one impurity remained (δ_P 37.1; ~7%), and since this was apparently the phosphinic bromide (*m/z* 489.2 and 491.2, ratio 1:1; $M^+ - C_3H_7$) its presence was not a problem. We anticipated that the *ortho* Pr^i groups in **8b** would shield the P atom, and make nucleophilic attack quite difficult. Nonetheless, it was surprising to find that the phosphinic chloride could be recovered completely unchanged after 4 days in 2 mol dm^{-3} NaOMe solution. Fortunately, azide ion in DMF is such a powerful nucleophile that conversion of the chloride into the azide **9b** was almost complete after 52 h at 60 °C; the azide was then purified by crystallisation. In the ^1H NMR spectra of both **8b** and **9b** the 12 Me groups give rise to three distinct but equal signals (3 × 12 H, d, J_{HH} 6.5). The two *para* Pr^i groups are equivalent; within each the two Me groups are diastereotopic, but being so remote from the tetrahedral phosphorus centre they do not display magnetic non-equivalence. The four *ortho* Pr^i groups are also equivalent, but now the diastereotopicity

* It is conceivable that our reaction medium (MeCN–MeOH) is particularly resistant to nitrene attack, so that intramolecular reaction is particularly favoured. However, when the azide **1** (Ar = mesityl) was photolysed in cyclohexane saturated with MeOH, intramolecular insertion was still an important reaction and very little, if any, intermolecular insertion into cyclohexane was seen (GLC). [Cyclohexane is not our preferred solvent for photochemical work with phosphinic azides because of the low solubility of MeOH (required to trap the metaphosphonimidates resulting from rearrangement)].

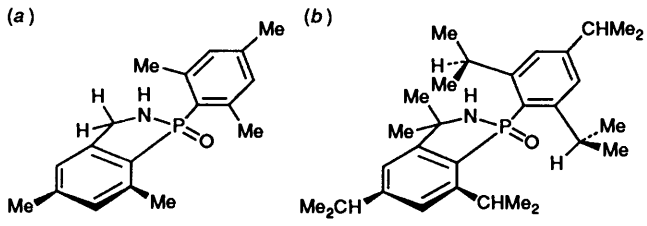


Fig. 2

Table 1 Dihydrobenzazaphosphole oxide **12**: ^{1}H NMR spectroscopic data (300 MHz) in C_6D_6 at 25 °C

	δ_H		
Entry	$CHMe_2$[a]	$CHMe_2$[b]	Assignment
1	5.864	1.570 and 1.487[c]	*ortho* (free ring)
2	3.324[d]	1.416 and 0.933	*ortho* (fused ring)
3	3.312[d]	1.093 and 0.663[c]	*ortho* (free ring)
4	2.752[e]	1.168 (6 H)	*para*
5	2.716[e]	1.157 (6 H)	*para*
6		1.572 and 1.362[f]	$>CMe_2$ (5-ring)[g]

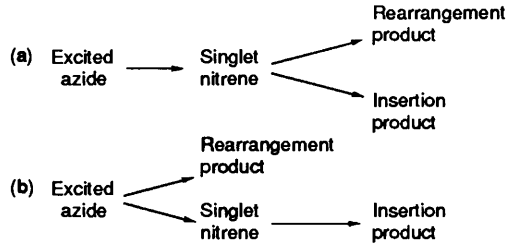
[a] 1 H; septet, J_{HH} 6–7 Hz. [b] 6 H or 2 × 3 H; d, J_{HH} 6–7 Hz. [c] Some broadening at 50 °C. [d] Methine signals in entries 2 and 3 should possibly be interchanged. [e] Methine signals in entries 4 and 5 should possibly be interchanged. [f] 2 × 3 H; s. [g] NH in 5-ring: δ 3.407; d, J_{PH} 7.3.

of the two Me groups within each is quite clearly reflected in magnetic non-equivalence.

For the azides **9a** and **9b** photolysis was again carried out in MeCN containing MeOH (10 mol equiv.). In each case chromatography afforded unchanged azide (*ca.* 10%) and two substantial products which were purified by crystallisation. These proved to be the rearrangement product **10a** (51%) or **10b** (28%) and the intramolecular insertion product **11** (19.5%) or **12** (51%). The ^{1}H NMR spectra (300 MHz) of the insertion products displayed some interesting features. For **11**, the five Me groups gave the anticipated four singlets (6 H, 3 × 3 H), but the one corresponding to the two *ortho* Me groups in the free (unfused) mesityl residue was noticably broad. It became sharp on warming to 50 °C, but on cooling it separated into two remarkably different signals [δ($CDCl_3$) 2.33 (6 H)→2.82 (3 H) and 1.81 (3 H) at −50 °C]. Apparently rotation about the mesityl–P bond is retarded at room temperature, and at −50 °C is sufficiently slow for the *ortho* Me groups to display magnetic non-equivalence. A model of the molecule shows there to be potentially serious steric interactions between the *ortho* substituents in the two benzenoid rings. These interactions will not be great for a conformation like that in Fig. 2(*a*), but much higher-energy conformations must be passed through if there is to be rotation about the mesityl–P bond.

For the triisopropylphenyl compound **12** the spectrum in $CDCl_3$ contained distinct signals for each of the four aromatic protons, implying that rotation about the aryl–P bond is slow, even at room temperature. Elsewhere the spectrum was complicated by overlap of signals, but this was not such a problem in C_6D_6. Then, with the aid of decoupling and variable temperature measurements, it was (more or less) possible to locate the signals for each of the Pr^i groups (Table 1). Because of the slow rotation, the two *ortho* Pr^i groups in the free (unfused) aryl ring are non-equivalent and give rise to four distinct methyl doublets (entries 1 and 3). These were sharp at room temperature but began to broaden on warming (beginnings of coalescence). One of them appeared at an unusually high field (entry 3), presumably because the Me group is positioned over, and is shielded by, the π electrons of the fused aromatic ring [Fig. 2(*b*)]. At the other extreme, one of the methine (CH) protons produced a signal at remarkably low field (entry 1). This proton is part of the other *ortho* Pr^i group, and its extreme deshielding must surely be due to the fact that it is forced close to the oxygen atom of the P=O group.[12]

Conclusions.—Insertion is generally considered a concerted reaction of the singlet nitrene, albeit that the same product can (in principle) be formed non-concertedly from the triplet, by abstraction–radical combination. In the case of phosphoryl nitrenes, the singlet concerted mechanism is supported by some sound experimental evidence[4a] (if not by theoretical considerations[11]) and we will therefore assume that our intramolecular insertion products are derived from the singlet nitrene. That being so, when the phosphinic azides are photolysed, there are two points at which the pathways for rearrangement and intramolecular insertion may diverge (Scheme 3). In (**a**), all the



Scheme 3

excited azide forms singlet nitrene which then undergoes either rearrangement or insertion. In this case intramolecular insertion diverts nitrene that would otherwise rearrange: it is a *cause* of non-rearrangement. In (**b**), some of the excited azide rearranges directly and some forms the singlet nitrene. In this case intramolecular insertion merely provides an outlet for the singlet nitrene arising from azide that forgoes rearrangement: it is a *consequence* of non-rearrangement, not a cause. On balance we favour picture (**b**), although the evidence is not conclusive. Compared to the *tert*-butyl mesityl azide **1** (Ar = mesityl), the dimesityl compound **9a** has more numerous sites for intramolecular insertion and the bis(triisopropylphenyl) compound **9b** has more reactive sites (3° *vs.* 1° C–H). Relative to rearrangement, however, intramolecular insertion is actually rather less important for **9a** and not much more important for **9b**. These variations in the rearrangement : insertion ratio can be accounted for by steric factors, in particular the influence they have on the ability of the excited azide to assume the geometry required for aryl migration (*cf.* Fig. 1).

Also, there is the question of hydrogen abstraction and amide formation. Amide was not isolated from the reactions of any of the present azides, and in the case of **1** (Ar = mesityl), having prepared an authentic sample of Bu^{t}ArP(O)NH_2, it was shown (GLC) that none at all had been formed. This is noteworthy because phosphorus(v) azides, including **1** (Ar = Ph) and **6**, do generally produce a modest amount of the corresponding amide (typically *ca.* 10%) on photolysis. Assuming that the triplet nitrene is responsible for hydrogen abstraction, it could be that the triplet is never formed in the present reactions, *i.e.* that the singlet nitrene undergoes intramolecular insertion too quickly for intersystem crossing to compete. If that is so, it seems unlikely that rearrangement is a reaction of the singlet nitrene; if it were, it would surely be suppressed by intramolecular insertion much more than is actually the case. Concerted rearrangement of the excited azide seems again to be more likely.

As to why intramolecular insertion should be important for our phosphinic azides, two points merit consideration. First, Breslow attributed the paucity of intramolecular insertion with

phosphoryl azides to the extreme reactivity of the nitrene: intermolecular reaction with the solvent at practically every collision leaves little opportunity for intramolecular reaction. Second, in a phosphoryl azide the alkyl or aryl groups are attached to phosphorus *via* an O atom. This provides a degree of geometrical freedom not present in a phosphinic azide. Thus, for example, the phosphoryl azide **6** may well have no difficulty getting into the geometry required for intramolecular insertion, but it is certainly not constrained to be there. The situation is quite different for our phosphinic azides. The nitrene, when it is formed, cannot avoid being close to at least one benzylic C–H bond. This will obviously encourage intramolecular insertion. Perhaps just as important, it will tend also to shelter the nitrene from reaction with a solvent molecule. We do not discount the possibility that phosphinoyl nitrenes are inherently less reactive (more stable) than their phosphoryl counterparts, but we think it likely that the special geometric and steric features present in our systems are largely responsible for the behaviour observed. Studies of phosphonoyl nitrenes—intermediate between phosphoryl and phosphinoyl—could prove particularly rewarding. Such work, however, should only be undertaken in full knowledge of the high toxicity of some phosphorus(v) azides.[13]

Experimental

CAUTION—Some phosphorus(v) azides are highly toxic.[13] No information is available for the phosphinic azides employed in the present work, but appropriate precautions were taken.

M.p.s were determined using a Kolfer hot-stage apparatus and are uncorrected. IR spectra were obtained on a Perkin-Elmer 298 instrument. ^{1}H NMR spectra were recorded at 90 MHz on a Varian EM 390 spectrometer or (where indicated) at 300 MHz on a Brucker AM-300 (Me_4Si internal standard; coupling constants given in Hz), and ^{31}P NMR spectra (^{1}H decoupled) were recorded at 36.2 MHz on a JEOL JNM-FX90Q spectrometer (positive chemical shifts downfield from external 85% H_3PO_4). Mass spectra were obtained in EI (70 eV) or CI (NH_3) mode using VG 12-253, 16-B or ZAB-E (high resolution) spectrometers. GLC analyses were carried out using either a 12 m × 0.53 mm i.d. fused silica column containing a 1.2 μ film of SE 54 (He carrier gas) or a 1.5 m × 4 mm i.d. glass column packed with 3% OV 225 coated on silanised 100–120 mesh diatomite C'Q' (N_2 carrier gas), and a flame-ionisation detector. Preparative chromatographic separations were carried out by elution from silica gel in the form of a column or a rotating circular layer (Chromatatron).

Acetonitrile was distilled from CaH_2, dimethylformamide (DMF) from P_2O_5 (reduced pressure), and methanol from its magnesium salt. Light petroleum refers to the fraction b.p. 60–80 °C unless otherwise indicated, and ether refers to diethyl ether.

Phosphinic Chlorides.—tert-*Butyl(mesityl)phosphinic chloride.* A solution of mesitylphosphonous dichloride (4.42 g, 20.0 mmol)[14] in CH_2Cl_2 (3 cm^3) (δ_P 165) was added during 10 min to a stirred suspension of $AlCl_3$ (2.66 g, 20.0 mmol) in CH_2Cl_2 (5 cm^3). Most of the solid dissolved. After 30 min, the mixture was cooled in ice while *tert*-butyl chloride (2.22 g, 24.0 mmol) was added dropwise during 10 min. Some $CHCl_3$ was added to facilitate stirring, and reaction was allowed to continue at room temperature for 40 min (δ_P 129). The reaction was quenched by addition to a mixture of crushed ice (30 g) and concentrated hydrochloric acid (7 cm^3). The organic layer was separated, the aqueous layer was extracted with $CHCl_3$ (2 × 10 cm^3), and the combined organic portions were dried (Na_2SO_4). After evaporation of the solvent, crystallisation from light petroleum gave tert-*butyl(mesityl)phosphinic chloride* (4.27 g, 83%), m.p. 90.5–92.5 °C; *m/z* 258, 260 (M^+, 21%, ratio 3:1) and 202, 204 ($M^+ - C_4H_8$, 100, ratio 3:1); ν_{max}(Nujol)/cm^{-1} 1225 and 1210 (P = O); $\delta_P(CH_2Cl_2)$ 73.0; $\delta_H(CDCl_3)$ 6.92 (2 H, d, J_{PH} 5), 2.67 (6 H, s), 2.26 (3 H, s) and 1.28 (9 H, d, J_{PH} 19) (Found: C, 60.6; H, 7.9. $C_{13}H_{20}ClOP$ requires C, 60.35; H, 7.8%).

Dimesitylphosphinic chloride. Following published procedures,[15] the phosphinic acid was prepared from mesitylmagnesium bromide and $POCl_3$ and was converted into the phosphinic chloride, $\delta_P(CH_2Cl_2)$ 46.4, by heating with $SOCl_2$.

Bis(2,4,6-triisopropylphenyl)phosphinic chloride. Butyllithium (7.35 mmol) in hexane (2.9 cm^3) was gradually added to a stirred solution of 2,4,6-triisopropylbromobenzene (1.98 g, 7.0 mmol) in THF (15 cm^3) at −70 °C. After a further 1.5 h at −70 °C, $POCl_3$ (1.61 g, 10.5 mmol) was added. The mixture was allowed to warm gradually to room temperature, and remain there for a further 1 h. All volatile material was evaporated off and the residue was extracted with light petroleum. Evaporation of the extract gave the crude phosphinic chloride as a viscous yellow oil (1.95 g); the ^{31}P NMR spectrum consisted of one substantial peak, $\delta_P(CDCl_3)$ 47.0, and several small byproduct peaks (~5% each); the ^{1}H NMR spectrum suggested substantial amounts of unchanged 2,4,6-triisopropylbromobenzene and 1,3,5-triisopropylbenzene. A part of this material was purified by chromatography on a column of silica gel. Elution with light petroleum containing ethyl acetate (4%) afforded *bis(2,4,6-triisopropylphenyl)phosphinic chloride* as a waxy solid, m.p. ~90 °C, still contaminated with one of the byproducts (δ_P 37.1, ~7%; probably the phosphinic bromide); *m/z* (EI) 445, 447 ($M^+ - C_3H_7$, 100%, ratio 3:1); ν_{max}(Nujol)/cm^{-1} 1220; $\delta_P(CDCl_3)$ 47.1; $\delta_H(CDCl_3)$ 6.96 (4 H, d, J_{PH} 5.5), 3.88 (4 H, septet, J_{HH} 6.5, *o*-C*H*Me$_2$), 2.82 (2 H, septet, J_{HH} 6.5, *p*-C*H*Me$_2$), 1.17 (12 H, d, J_{HH} 6.5, *p*-CH*Me*$_2$) and 1.02, 0.98 (both 12 H, d, J_{HH} 6.5, *o*-CH*Me*$_2$) [Found: M + H$^+$ (CI), 489.3053 (100%). $C_{30}H_{46}{}^{35}ClOP$ requires *M* + H, 489.3053].

Phosphinic Azides.—(a) *tert*-Butyl (mesityl)phosphinic chloride (1.04 g, 4.0 mmol) in DMF (10 cm^3) was added dropwise to a stirred suspension of NaN_3 (0.39 g, 6.0 mmol) in DMF (2 cm^3). Stirring was continued for a further 1 h, then the mixture was diluted with ether (30 cm^3), filtered, and concentrated. Distillation afforded tert-*butyl(mesityl)phosphinic azide* **1** (Ar = mesityl) (0.88 g, 83%), b.p. 140 °C (oven temp.) at 0.6 mmHg, solidifies on cooling, m.p. 46–48 °C; *m/z* 265 (M^+, 20%), 181 ($M^+ - N_2 - C_4H_8$, 100) and 180 ($M^+ - N_2 - C_4H_9$, 90); ν_{max}(Nujol)/cm^{-1} 2145 (N_3) and 1270; $\delta_P(CH_3Cl_2)$ 55.1; $\delta_H(CDCl_3)$ 6.88 (2 H, d, J_{PH} 4.5), 2.63 (6 H, s), 2.24 (3 H, s) and 1.16 (9 H, d, J_{PH} 18) (Found: C, 59.05; H, 7.5; N, 15.9. $C_{13}H_{20}N_3OP$ requires C, 58.9; H, 7.6; N, 15.8%).

(b) Dimesitylphosphinic chloride (1.61 g, 5.0 mmol) in MeCN (15 cm^3) was stirred with NaN_3 (0.48 g, 7.4 mmol) overnight. The mixture was diluted with ether (30 cm^3), filtered, and concentrated. Crystallisation from light petroleum gave *dimesitylphosphinic azide* **9a** (1.42 g, 87%), m.p. 127–128 °C; *m/z* 327 (M^+, 30%), 312 (M^+ − Me, 95), 299 ($M^+ - N_2$, 50), 285 (65), 284 (85) and 236 (100); ν_{max}(Nujol)/cm^{-1} 2140 (N_3), 1275 and 1210; δ_P(MeCN) 33.3; $\delta_H(CDCl_3)$ 6.82 (4 H, d, J_{PH} 4.5), 2.34 (12 H, s) and 2.24 (6 H, s) (Found: C, 66.3; H, 6.9; N, 13.1. $C_{18}H_{22}N_3OP$ requires C, 66.0; H, 6.8; N, 12.8%).

(c) Bis(2,4,6-triisopropylphenyl)phosphinic chloride (0.765 g, 1.57 mmol) and NaN_3 (0.15 g, 2.3 mmol) were stirred together in DMF (4.5 cm^3) at 60 °C for 52 h (sealed vessel; N_2 atmosphere). The mixture was cooled, diluted with ether (40 cm^3), and filtered, and volatile material was evaporated from the filtrate under reduced pressure. The residue was partitioned between light petroleum (50 cm^3) and water (40 cm^3). The organic portion was dried and concentrated to give the azide, $\delta_P(CDCl_3)$ 34.9, contaminated with some unchanged phosphinic chloride (δ 47.2; ~5%). Crystallisation from a small volume of methanol at 0 °C afforded pure *bis(2,4,6-triisopropylphenyl)phosphinic*

azide **9b** (0.622 g, 80%), m.p. 81–82.5 °C; *m/z* 467 ($M^+ - N_2$, 95%), 452 ($M^+ - C_3H_7$, 100) and 424 ($M^+ - N_2 - C_3H_7$, 75) (M^+ not observed); *m/z* (CI) 496 ($M + H^+$, 12%) and 469 ($M + NH_4^+ - C_3H_6$, 100); ν_{max}(Nujol)/cm^{-1} 2140 (N_3), 1270 and 1200; δ_P($CDCl_3$) 34.4; δ_H($CDCl_3$) 6.99 (4 H, d, J_{PH} 4.5), 3.80 (4 H, septet, J_{HH} 6.5, *o*-Me_2CH), 2.81 (2 H, septet, J_{HH} 6.5, *p*-Me_2CH), 1.17 (12 H, d, J_{HH} 6.5, *p*-Me_2CH) and 1.02, 1.00 (both 12 H, d, J_{HH} 6.5, *o*-Me_2CH) (Found: C, 72.1; H, 9.2; N, 8.2%; $M + H^+$, 496.3457. $C_{30}H_{46}N_3OP$ requires C, 72.7; H, 9.4; N, 8.5%; *M* + H, 496.3457).

Photochemical Reactions of Phosphinic Azides.—A 0.05 mol dm^{-3} solution of the appropriate phosphinic azide and MeOH (10 mol equiv.) in MeCN was placed in a quartz tube. The tube was flushed with N_2 and was then placed in a Rayonet reactor fitted with 254 nm lamps (air cooling).

(a) The reaction mixture from *tert*-butyl(mesityl)phosphinic azide **1** (Ar = mesityl) (531 mg, 2.00 mmol), after irradiation for 160 min, was chromatographed on a column of silica gel. Elution with light petroleum containing acetone (30%) gave unchanged phosphinic azide (76 mg, 14%), δ_P(CH_2Cl_2) 55.1, followed by a mixture of two products (146 mg), δ_P(CH_2Cl_2) 22.2 and 38.3, ratio ~6:1. Repeated crystallisation from light petroleum afforded a pure sample of the major component of the mixture, identified as *methyl* N-tert-*butyl*-P-*mesitylphosphonamidate* **3**, m.p. 113.5–115 °C; *m/z* 269 (M^+, 40%), 254 (M^+ – Me, 95), 213 ($M^+ - C_4H_8$, 40) and 197 (M^+ – NHBu^t, 100); ν_{max}(Nujol)/cm^{-1} 3190 (NH); δ_P(CH_2Cl_2) 22.2; δ_H($CDCl_3$; 300 MHz) 6.89 (2 H, d, J_{PH} 4), 3.60 (3 H, d, J_{PH} 11.5), 2.62 (6 H, d, J_{PH} 1.5), 2.50 (1 H, br, d, J_{PH} 10.5, NH), 2.28 (3 H, s) and 1.29 (9 H, d, J_{PH} 0.5) (Found: C, 62.6; H, 9.0; N, 5.1. $C_{14}H_{24}NO_2P$ requires C, 62.4; H, 9.0; N, 5.2%). The minor component of the mixture was not obtained pure, but ^{1}H NMR signals at δ 2.35 (s, mesityl *o*-Me groups) and 1.26 (d, J_{PH} 15, P-Bu^t) were consistent with it being methyl *P-tert*-butyl-*N*-mesitylphosphonamidate **2**. In support, an authentic sample of **2** was seen to enhance the ^{31}P NMR signal and the GLC peak (R_t 2.9 min on 3% OV 225 at 220 °C) of this component.

Elution with acetone containing EtOH (7%) afforded 5,7-*dimethyl*-1-tert-*butyl*-2,3-*dihydro*-1H-2,1-*benzazaphosphole* 1-*oxide* **5** (128 mg), crystallised from ethyl acetate–ether, m.p. 158–160 °C; *m/z* 237 (M^+, 5%) and 180 ($M^+ - C_4H_9$, 100); ν_{max}(Nujol)/cm^{-1} 3210 (NH); δ_P($CHCl_2$) 61.9; δ_H($CDCl_3$; 300 MHz) 6.99 (1 H, d, J_{PH} 4.5), 6.91 (1 H, s), 4.40 (1 H, dd, J_{PH} ~3, J_{gem} 14), 4.23 (1 H, dd, J_{PH} 8, J_{gem} 14), 3.37 (1 H, br, d, J_{PH} 10, NH; exchanged with D_2O), 2.61 (3 H, s), 2.35 (3 H, s) and 1.16 (9 H, d, J_{PH} 16) (Found: C, 65.9; H, 8.6; N, 5.8. $C_{13}H_{20}NOP$ requires C, 65.8; H, 8.5; N, 5.9%).

An intermediate fraction contained a trace product, δ_P(CH_2Cl_2) 44.6, that was not identified.

In a similar experiment, GLC (SE 54 at 185 °C) was used to monitor the disappearance of the azide (R_t 3.6 min) and the appearance of the phosphonamidates **3** (2.4 min) and **2** (3.1 min) and dihydrobenzazaphosphole oxide **5** (7.2 min). It was seen that the **5**:(**2** + **3**) peak area ratio declined from 1.35 at 20% completion (t = 10 min) to 1.25 at 60% (45 min) and 0.75 at 85% (110 min) as a result of the photochemical instability of **5** [degradation products, R_t 5.7 (minor) and 9.2 min (major), not identified]. No *tert*-butyl(mesityl)phosphinic amide was detected (R_t 5.1 min for the authentic sample).

(b) The reaction mixture from dimesitylphosphinic azide **9a** (655 mg, 2.00 mmol), after irradiation for 90 min, was chromatographed on a layer of silica gel. Elution with light petroleum containing ether (50–90%) gave unchaned azide (73 mg, 11%) followed by *methyl* N,P-*dimesitylphosphonamidate* **10a** (302 mg), crystallised from ethyl acetate, m.p. 163–164 °C; *m/z* 331 (M^+, 100%), 316 (M^+ – Me, 55), 197 (M^+ – NHAr, 50) and 134 ($ArNH^+$, 75); ν_{max}(Nujol)/cm^{-1} 3070 (NH); δ_P($CDCl_3$) 22.0; δ_H($CDCl_3$) 6.85 (2 H, d, J_{PH} 4.5), 6.75 (2 H, s), 4.05 br (1 H, d, J_{PH} 10, NH), 3.57 (3 H, d, J_{PH} 12), 2.58 (6 H, s), 2.26 (3 H, s) and 2.19 (9 H, s) (Found: C, 68.6; H, 7.9; N, 4.0. $C_{19}H_{26}NO_2P$ requires C, 68.9; H, 7.9; N, 4.2%).

Elution with ether containing MeOH (5%) afforded 1-*mesityl*-5,7-*dimethyl*-2,3-*dihydro*-1H-2,1-*benzazaphosphole* 1-*oxide* **11** (104 mg), crystallised from light petroleum, m.p. 160–162 °C; *m/z* 299 (M^+, 100%), 284 (M^+ – Me, 95) and 180 (M^+ – Ar, 40); ν_{max}(Nujol)/cm^{-1} 3120 (NH); δ_P($CDCl_3$) 38.9; δ_H($CDCl_3$; 25 °C; 300 MHz) 6.99 (1 H, s), 6.92 (1 H, d, J_{PH} 4.5), 6.87 (2 H, d, J_{PH} 4), 4.68 (1 H, d, J_{gem} 14.5), 4.37 (1 H, dd, J_{PH} 14.5, J_{gem} 14.5), ~3.5 (br, NH), 2.37 (3 H, s), 2.33 (6 H, br s), 2.27 (3 H, s) and 2.22 (3 H, s); at 50 °C the broad 6 H singlet at δ 2.33 became sharp, and at −50 °C it was replaced by two very broad 3 H singlets at δ 2.82 and 1.81 (also at −50 °C, δ 6.87 became very broad) (Found: C, 71.6; H, 7.4; N, 4.5%; M^+, 299.1441. $C_{18}H_{22}NOP$ requires C, 72.2; H, 7.4; N, 4.7%; *M*, 299.1439).

(c) The reaction mixture from bis(2,4,6-triisopropylphenyl)-phosphinic azide **9b** (500 mg, 1.01 mmol), after irradiation for 150 min, was chromatographed on a layer of silica gel. Elution with light petroleum–ether (1:1) then ether gave unchanged azide (50 mg, 10%) followed by *methyl* N,P-*bis*(2,4,6-*triisopropylphenyl*)*phosphonamidate* **10b** (131 mg), crystallised from light petroleum, m.p. 151–152 °C; *m/z* 499 (M^+, 100%), 456 ($M^+ - C_3H_7$, 40), 297 (35), 281 (M^+ – NHAr, 40), 219 (25) and 218 ($ArNH^+$, 50); ν_{max}(Nujol)/cm^{-1} 3140 (NH); δ_P($CDCl_3$) 22.6; δ_H($CDCl_3$; 300 MHz) 7.12 (2 H, d, J_{PH} 4.5), 6.94 (2 H, s), 4.15 (2 H, septet, J_{HH} 6.5), 4.08 (1 H, br, NH), 3.68 (3 H, d, J_{PH} 11.5), 3.53 (2 H, septet, J_{HH} 7), 2.91 (1 H, septet, J_{HH} 7), 2.84 (1 H, septet, J_{HH} 7) and 1.25, 1.23, 1.21, 1.16, 1.12, 1.03 (all 6 H, d, J_{HH} 6.5–7) (Found: C, 74.0; H, 9.9; N, 2.7. $C_{31}H_{50}NO_2P$ requires C, 74.5; H, 10.1; N, 2.8%).

Elution with ether containing MeOH (5%) gave 5,7-*diisopropyl*-3,3-*dimethyl*-1(2′,4′,6′-*triisopropylphenyl*)-2,3-*dihydro*-1H-2,1-*benzazaphosphole* 1-*oxide* **12** (219 mg), crystallised from light petroleum, m.p. 200.5–201.5 °C; *m/z* 467 (M^+, 100%), 452 (M^+ – Me, 40) and 424 ($M^+ - C_3H_7$, 45); ν_{max}(Nujol)/cm^{-1} 3220 (NH); δ_P($CDCl_3$) 34.3; δ_H($CDCl_3$; 300 MHz) 7.20 (br, 1 H), 7.04 (1 H, d, J_{PH} 5), 7.01 (br, 1 H), 6.96 (br, 1 H), 5. 18 (1 H, septet, J_{HH} 6.5) (most of spectrum complicated by overlap of signals); δ_H(C_6D_6) see Table 1 (Found: C, 77.2; H, 9.9; N, 2.9. $C_{30}H_{46}NOP$ requires C, 77.0; H, 9.9; N, 3.0%).

Authentic Samples of Potential Photolysis Products.—*Methyl* P-tert-*butyl*-N-*mesitylphosphonamidate* **2**. Butyllithium (12.5 mmol) in hexane (5 cm^3) was added to a stirred solution of 2,4,6-trimethylaniline (1.76 g, 13.0 mmol) in THF (3 cm^3) at 0 °C. After 10 min, the resulting solution (ArNHLi) was added dropwise with stirring to a solution of *tert*-butylphosphonic dichloride (1.06 g, 6.05 mmol) in THF (6.5 cm^3) at −50 °C. The mixture was quenched with CF_3CO_2H (1.71 g, 15 mmol) in THF (8 cm^3) and was then allowed to warm to room temperature. Volatile material was evaporated and the residue was partitioned between CH_2Cl_2 and water. The organic portion was dried (Na_2SO_4) and concentrated and the residue, after washing with ether–light petroleum, was crystallised from ether to give P-tert-*butyl*-N-*mesitylphosphonamidic chloride* (1.35 g, 82%), m.p. 182–184 °C; *m/z* 273, 275 (M^+, 40%, ratio 3:1), 237 (M^+ – HCl, 40), 181 ($M^+ - HCl - C_4H_8$, 70), 135 (30) and 134 ($ArNH^+$, 100); ν_{max}(Nujol)/cm^{-1} 3170 (NH); δ_P(CH_2Cl_2) 55.5; δ_H($CDCl_3$) 6.80 (2 H, s), 4.55 (1 H, br d, J_{PH} 14, NH), 2.32 (6 H, s), 2.20 (3 H, s) and 1.40 (9 H, d, J_{PH} 20) (Found: C, 57.1; H, 7.7; N, 5.0. $C_{13}H_{21}ClNOP$ requires C, 57.0; H, 7.7; N, 5.1%). A portion of the phosphonamidic chloride (135 mg, 0.49 mmol) in MeOH (2 cm^3) was treated with NaOMe (1.0 mmol) in MeOH. After 10 min the reaction was quenched (NH_4Cl), the solvent evaporated, and the residue partitioned between CH_2Cl_2 and water. The organic layer afforded *methyl* P-tert-

butyl-N-*mesitylphosphonamidate* **2** (111 mg, 84%), crystallised from light petroleum, m.p. 164–165 °C; *m/z* 269 (M^+, 50%), 135 (100) and 134 ($ArNH^+$, 70); ν_{max}(Nujol)/cm^{-1} 3170 (NH); δ_P(MeOH) 39.1; δ_H($CDCl_3$) 6.80 (2 H, s), 3.85 (1 H, br d, J_{PH} 11, NH), 3.57 (3 H, d, J_{PH} 10.5), 2.33 (6 H, s), 2.20 (3 H, s) and 1.26 (9 H, d, J_{PH} 15) (Found: C, 62.6; H, 8.9; N, 5.1. $C_{14}H_{24}NO_2P$ requires C, 62.4; H, 9.0; N, 5.2%).

tert-*Butyl*(*mesityl*)*phosphinic amide*. A solution of *tert*-butyl(mesityl)phosphinic chloride (588 mg, 2.16 mmol) in 8 mol dm^{-3} ethanolic NH_3 (large excess) was placed in a sealed vessel. After 65 h the volatile material was evaporated and the residue was partitioned between CH_2Cl_2 and water. The organic portion afforded pure tert-*butyl*(*mesityl*)*phosphinic amide* (479 mg, 93%), δ_P(CH_2Cl_2) 47.6; crystallised from toluene–light petroleum, m.p. 157–158.5 °C; *m/z* 239 (M^+, 25%), 183 ($M^+ - C_4H_8$, 90), 182 ($M^+ - C_4H_9$, 85) and 166 ($M^+ - C_4H_8 - NH_3$, 100); ν_{max}(Nujol)/cm^{-1} 3240 and 3120 (NH); δ_H($CDCl_3$) 6.81 (2 H, d, J_{PH} 3), 2.90 (2 H, br s, NH_2), 2.64 (6 H, s), 2.22 (3 H, s) and 1.13 (9 H, d, J_{PH} 15) (Found: C, 65.25; H, 9.3; N, 5.8. $C_{13}H_{22}NOP$ requires C, 65.25; H, 9.3; N, 5.85%).

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