Photolysis of Phenylphosphinic Azides having *ortho* Alkyl Substituents: Intramolecular Nitrene Insertion into C–H Bonds

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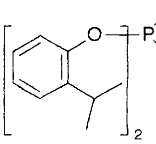
Dihydrobenzazaphosphole oxides (*e.g.* **6**) are important products in the photochemical reactions of phosphinic azides having *P*-mesityl or *P*-(2,4,6,-triisopropylphenyl) groups, suggesting that P^V nitrenes are not necessarily averse to intramolecular insertion.

Phosphoryl azides, $(RO)_2P(O)N_3$ (R = alkyl or aryl), decompose without rearrangement on photolysis, giving nitrenes that insert into solvent C–H bonds.[1,2] This intermolecular insertion is very efficient, and discrimination between different types of C–H bond is unusually small.[1,2] Nonetheless, attempts to functionalise unactivated alkyl groups by intramolecular insertion have met with little success. In particular, Breslow *et al.*[3] obtained a mere 3% of the cyclic phosphoramidate **2** on photolysis of the azide **1** in benzene, and none at all in cyclohexane, even though insertion into the C–H bonds of the solvent was clearly not a problem [$(ArO)_2P(O)NHC_6H_{11}$ formed in 70% yield].

For phosphinic azides, $R_2P(O)N_3$ (R = alkyl or aryl), the principal pathway of photochemical decomposition is a Curtius-like rearrangement (Scheme 1), and nitrene insertion is but a minor reaction.[4–7] It might therefore be thought that the search for intramolecular insertion is most unlikely to be successful with this type of phosphorus azide. In fact, however, the results now reported show that this is not necessarily the case.

Photolysis (254 nm) of dimesitylphosphinic azide **3** (Ar = 2,4,6-trimethylphenyl) in MeCN containing MeOH (10 mol equiv.) gave as the major product the methyl phosphonamidate **4** (Ar = mesityl) (51% isolated by chromatography) resulting from Curtius rearrangement, with migration of a mesityl group from phosphorus to nitrogen: *m/z* 331 (M^+, 100%), $\nu_{max.}$ (Nujol) 3070 cm^{-1} (NH), $\delta(CDCl_3)$ (in part) 6.85 (2 H, d, J_{PH} 4.5 Hz, PAr), 6.75 (2 H, s, NAr) and 3.57 (3 H, d, J_{PH} 12 Hz, OMe).† There was, however, a substantial amount of a second product, m.p. 160–162 °C, *m/z* 299 (M^+, 100%) having the same molecular formula as the nitrene **5** (Ar = mesityl). For this too the IR spectrum showed N–H absorption [$\nu_{max.}$ (Nujol) 3120 cm^{-1}], but the ^1H NMR spectrum ($CDCl_3$) revealed that only five of the original mesityl methyl groups remained [δ 2.36 (3 H, s), 2.32 (6 H, s), 2.27 (3 H, s) and 2.22 (3 H, s)], the sixth having been transformed into a deshielded methylene group [non-equivalent hydrogens, δ 4.68 (d, J_{gem} 14.5, J_{PH} 0 Hz) and 4.36 (dd, J_{gem} 14.5, J_{PH} 14.5 Hz)]. These features point to the dihydrobenzazaphosphole oxide **6** (Ar = mesityl) (19.5% isolated) that would result from intramolecular insertion of the nitrene into a C–H bond of one of the *ortho* methyl groups.



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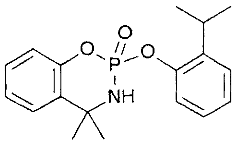

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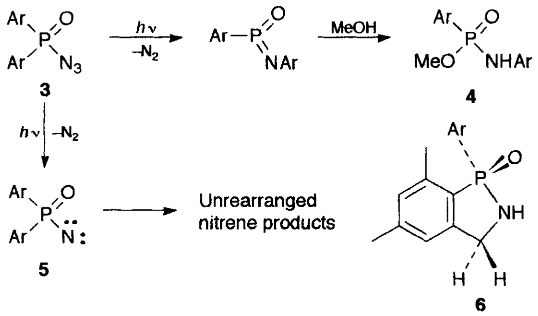
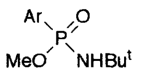
For an aryl group to migrate from phosphorus to nitrogen in the Curtius rearrangement, it seems likely that the p orbitals of the aromatic π system must be periplanar with respect to the azide P–N bond.[7] When the aryl group has *ortho* substituents, steric interactions with an especially bulky group on phosphorus could destabilise the effective P–aryl conformations and impede rearrangement, thus allowing intramolecular nitrene insertion to compete more effectively. The photolysis of *tert*-butyl(mesityl)phosphinic azide was therefore examined in MeCN–MeOH. Migration of the mesityl group was indeed much diminished, but migration of the *tert*-butyl group was important, and the rearrangement products **7** and **8** (Ar = mesityl) were isolated as a mixture (*ca.* 6:1, 32% yield) dominated by the *N*-*tert*-butyl compound **7** (purified by crystallisation): m.p. 113.5–115 °C, *m/z* 269 (M^+, 40%), $\delta(CDCl_3)$ (in part) 6.89 (2 H, d, J_{PH} 4 Hz, PAr), 3.60 (3 H, d, J_{PH} 11.5 Hz, OMe) and 1.29 (9 H, d, $J_{PH} < 1$ Hz, NBu^t). Now, however, intramolecular insertion was the equal of rearrangement, and the azaphosphole oxide **9** was isolated in 31% yield: m.p. 158–160 °C, *m/z* 237 (M^+, 5%) and 180 ($M^+ - Bu^t$, 100), $\delta(CDCl_3 + D_2O)$ (in part) 4.40 (1 H, dd, J_{gem} 14, J_{PH} 4 Hz), 4.23 (1 H, dd, J_{gem} 14, J_{PH} 8 Hz), 2.60 (3 H, s), 2.35 (3 H, s) and 1.16 (9 H, d, J_{PH} 16 Hz, Bu^t).

In bis(2,4,6-triisopropylphenyl)phosphinic azide **3** (Ar = 2,4,6-$Pr^i_3C_6H_2$) the P–aryl bonds will be conformationally more restricted than in the dimesityl compound. On photolysis in MeCN–MeOH, the Curtius rearrangement still played an important part, giving the phosphonamidate **4** (Ar = 2,4,6-$Pr^i_3C_6H_2$) in 28% yield: *m/z* 499 (M^+, 100%), $\delta(CDCl_3)$



Scheme 1



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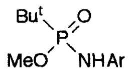

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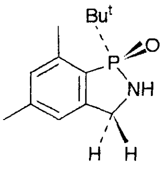

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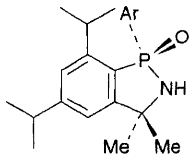

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† Phosphinic azides were prepared from phosphinic chlorides and NaN_3; they and their photolysis products were fully characterised by spectroscopy and elemental analysis or accurate mass measurement. CAUTION—Some P^v azides are highly toxic (F. L. Scott, R. Riordan and P. D. Morton, *J. Org. Chem.*, 1962, **27**, 4255; see also ref. 1). Photolyses were not taken to completion and 10–15% of the initial azide was recovered (chromatography); yields of products are based on the amount of azide consumed.

(in part) 7.11 (2 H, d, J_{PH} 4.5 Hz, PAr) 6.94 (2 H, s, NAr) and 3.68 (3 H, d, J_{PH} 11.5 Hz, OMe). Intramolecular insertion was, however, the principal pathway in this case, affording a 51% yield of the dihydrobenzazaphosphole oxide **10** (Ar = 2,4,6-$Pr^i_3C_6H_2$), m.p. 200.5–201.5 °C, *m/z* 467 (M^+, 100%), $\delta_H(C_6D_6)$ (in part) 3.41 (NH, d, J_{PH} 7 Hz), 1.57 (3 H, s) and 1.36 (3 H, s) (non-equivalent geminal Me groups on the azaphosphole ring), and 1.55–0.65 (30 H; a series of d, J_{HH} *ca.* 7 Hz, 5 × Me_2CH).‡

Breslow ascribed the paucity of intramolecular insertion by singlet phosphoryl nitrenes to their exceptionally high intermolecular reactivity; capture by the solvent at almost every collision leaves little opportunity for intramolecular reaction.[3] That being so, if our intramolecular reactions are indeed singlet nitrene insertions (rather than triplet abstraction–radical combination processes), then our nitrenes must be significantly less reactive.§ It could be that phosphinyl nitrenes in general are inherently less reactive than phosphoryl nitrenes, or it may be that the particular ones we have studied are so crowded that their intermolecular reactions are constrained by steric hindrance. Either way, it is clear that phosphinic azides can give the sought-for products of intramolecular insertion, in spite of the competition from Curtius rearrangement.

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‡ The ^{1}H NMR spectrum of **10** (Ar = 2,4,6-$Pr^iC_6H_2$) was complicated by slow rotation about the P–Ar bond, as evidenced by the appearance of five distinct isopropyl methine signals.

§ It is conceivable that our solvent system (MeCN–MeOH) is particularly resistant to nitrene attack. However, when Bu^t(Ar)-P(O)N_3 (Ar = mesityl) was photolysed in cyclo-C_6H_{12}–MeOH, intramolecular insertion was still an important reaction and very little (if any) intermolecular insertion into cyclo-C_6H_{12} was seen.