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The Origin of the Amide formed in the Photochemical Reactions of Aminimides: Rearrangement of Trimethylammonio-*N*-diphenylphosphinoylimide to *N*-(Dimethylaminomethyl)diphenylphosphinic Amide

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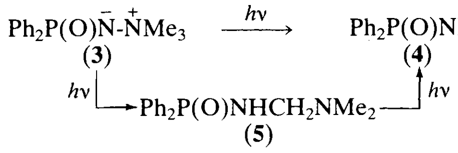
The principal photochemical reaction of $Ph_2P(O)\bar{N}\text{–}\overset{+}{N}Me_3$ in dimethyl sulphoxide or methanol is rearrangement to $Ph_2P(O)NHCH_2NMe_2$ which subsequently decomposes to give the amide $Ph_2P(O)NH_2$; rearrangement also occurs with $PhCO\bar{N}\text{–}\overset{+}{N}Me_3$ but is apparently not the major reaction pathway.

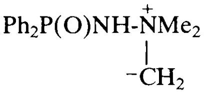
Aminimides[1] such as (**1**) and (**3**) have attracted attention as possible photochemical sources of nitrenes.[2—5] While they do seem able to produce significant amounts of singlet-nitrene derived products,[2,3] their photochemical reactions are characterised by remarkably high yields of the corresponding amides. Thus, for example, Kameyama *et al.*[3] found that photolysis of (**3**) in dimethyl sulphoxide (DMSO) gave 29% of the sulphoximine (**2**) but 51% of the amide (**4**). Amides are formally the products of hydrogen abstraction by triplet nitrenes, but it is not obvious why the triplet state should be especially important when aminimides are the nitrene precursors. Indeed, Lwowski[6] has made the point that some other (unspecified) intermediate might be responsible for the amide formed in these reactions. We now report that aminimides can undergo a photochemical rearrangement and that this, at least in the case of (**3**), is ultimately responsible for much of the final amide.

$PhCO\bar{N}\text{-}\overset{+}{N}Me_3$
(**1**)

$Ph_2P(O)N{=}S(O)Me_2$
(**2**)



$$\begin{tikzcd}
\underset{(\mathbf{3})}{Ph_2P(O)\bar{N}\text{-}\overset{+}{N}Me_3} \arrow[r, "h\nu"] \arrow[dr, "h\nu"'] & \underset{(\mathbf{4})}{Ph_2P(O)NH_2} \\
 & \underset{(\mathbf{5})}{Ph_2P(O)NHCH_2NMe_2} \arrow[u, "h\nu"']
\end{tikzcd}$$



$$Ph_2P(O)NH\text{-}\overset{+}{N}Me_2\ \big|\ {}^{-}CH_2$$
(**6**)

$Ph_2P(O)\bar{N}\text{-}\overset{+}{N}Et_3$
(**7**)

$(p\text{-}MeC_6H_4)_2P(O)\bar{N}\text{-}\overset{+}{N}Me_3$
(**8**)

$PhCONHCH_2NMe_2$
(**9**)

When the aminimide (**3**) was photolysed in DMSO (0.15 M solution, 25 °C, λ 254 nm) and the progress of the reaction followed by ^{31}P n.m.r. spectroscopy† it was seen that during the early stages the principal product was neither the amide (**4**) (δ_P 19.5 p.p.m.) nor the sulphoximine (**2**) (δ_P 15.4), but an unstable compound (δ_P 21.4) having a ^1H n.m.r. spectrum suggestive of the structure (**5**). On continued irradiation the proportion of this compound in the product declined (0.46 at 50% completion to 0.23 at 90% completion) while that of the amide increased (0.36 at 50% completion to 0.58 at 90% completion). The proportion of the sulphoximine remained essentially constant (~0.18) throughout.

In methanol the only substantial product of prolonged photolysis of (**3**) was the amide (**4**) [δ_P(MeOH) 25.1 p.p.m.] (isolated yield 76%), and, here too, much of it arose indirectly (Figure 1). In this case a sample of the unstable compound [δ_P(MeOH) 26.4] (m.p. 85—88 °C) was isolated in a sufficiently pure state (95%) for detailed spectroscopic examination: $\nu_{max.}$ (Nujol) 3210 cm^{-1}(NH); δ(CDCl$_3$) 8.0—7.25 (10H, m), 3.73 (2H, dd, J_{PH} 9, J_{HH} 8 Hz; simplifies to d, *J* 9 Hz, with D$_2$O), ~3.3 br. (1H, m, NH), and 2.23 (6H, s); *m/z* 229 [$Ph_2P(O)\overset{+}{N}{=}CH_2$, 14%]. Although there is no detectable molecular ion in the mass spectrum, these data are consistent with the phosphinoyl-aminal structure (**5**). We know of no other examples of this type of compound, but we feel confident that the structure is correct since spectroscopically identical material (m.p. 83—85 °C for an analytically pure sample) was obtained when the amide (**4**) was treated with $ClCH_2NMe_2$ in CH_2Cl_2 and the resulting salt deprotonated with base. Moreover control experiments showed that this substance undergoes solvolysis in methanol to give the amide (**4**) at a rate ($t_{\frac{1}{2}}$ ~ 90 min at 28 °C) comparable with the disappearance of the unstable product in the photolysis of the aminimide. In DMSO (**5**) is solvolytically much more stable, but photochemically it is smoothly converted into (**4**).

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† Positive ^{31}P n.m.r. chemical shifts are downfield relative to 85% H_3PO_4.

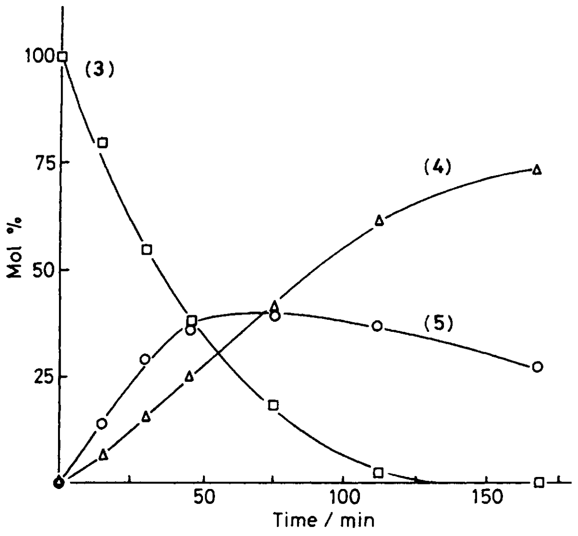

Figure 1. Photolysis of compound (**3**) (0.15 M) in methanol at 25 °C, λ 254 nm; composition of the reaction mixture.

The results shown in Figure 1 imply that some of the aminimide (**3**) goes directly to amide on photolysis, possibly *via* the triplet nitrene,[3] but most (65—70%) first rearranges to the phosphinoyl-aminal (**5**).‡ This transformation of the aminimide can be seen as insertion of the singlet nitrene into a C–H bond of Me_3N or as a [1,2] sigmatropic rearrangement of the tautomeric form (**6**). As yet we have no firm evidence, although we note that (**5**) is not formed when the aminimide (**7**) is photolysed in the presence of Me_3N [or when (**8**) is photolysed in the presence of amide (**4**)].

For comparison with (**3**), we have looked briefly at the aminimide (**1**). An earlier investigation found only benzamide and tarry material when (**1**) was photolysed in methanol,[4] but from photolysis of a 0.05 M solution taken to *ca.* 80% completion we have been able to isolate (flash chromatography on silica gel) not only benzamide (~ 70%) but also the rearranged compound, *N*-(dimethylaminomethyl)benzamide (**9**) (~ 20%); m.p. 57—59 °C (lit.,[7] 57—59 °C); spectra as for an authentic sample.[7] The results of monitoring the photolysis (h.p.l.c. or a combination of g.l.c. and ^1H n.m.r. spectroscopy) suggest that in this case most of the amide is formed directly (possibly *via* the triplet nitrene[5]); some 35% of the aminimide rearranges to (**9**) but solvolytically this is reasonably stable, and photochemically it is not converted cleanly into benzamide.

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‡ It is, of course, conceivable that the rearranged compound (**5**) is formed from and/or decomposes to the triplet nitrene but this does not invalidate the distinction between amide formed *via* (**5**) and amide derived 'directly' from the aminimide.

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