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DIMETHYLSULPHIDE AS A NITRENE TRAP IN THE PHOTOLYSIS OF SOME PHOSPHINIC AZIDES

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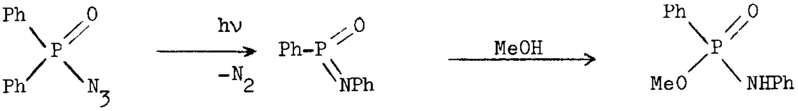
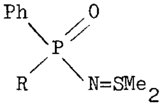
Summary. When $PhRP(O)N_3$ (R = Ph or t-Bu) is photolysed in dimethylsulphide substantial amounts (22 - 32%) of $PhRP(O)N{:}SMe_2$ and $PhRP(O)NHCH_2SMe$ are produced and rearrangement is less important than in benzene.

Phosphinic azides eliminate N_2 on photolysis. The major pathway in methanol involves rearrangement to a metaphosphonimidate which is trapped by the solvent e.g. azide (1) gives (3) via (2).[1,2] In benzene (1) gives a dimer of (2).[3] This rearrangement could be concerted or it might proceed via a nitrene intermediate. We now report an attempt to trap phosphinyl nitrenes with dimethylsulphide (DMS).



(1) (2) (3)

Diphenylphosphinic azide (1) (1 mmol) was irradiated in DMS (24 ml) containing a little methanol.[4] The nitrene adduct, sulphilimine (4, R = Ph), was isolated in 24% yield[5] by chromatography or by extraction into aqueous HCl; m.p. 160.5 - 162°C, M^+ 277, δ 7.9 - 7.2 (10 H, m) and 2.66 (6 H, s). Chromatography also afforded an isomer of (4) having m.p. 123 - 127°C, δ 8.0 - 7.3 (10 H, m), 4.05 (2 H, dd, J 11,8 Hz), 3.3 br (1H), and 2.21 (3 H, s); this was assigned structure (5, R = Ph). Monitoring the reaction by ^{31}P n.m.r.



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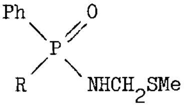

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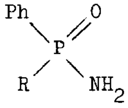
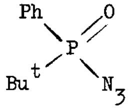


(6)

spectroscopy revealed that (5) is a primary product and does not arise by rearrangement of (4). Indeed, the yield of (5) is as great as that of (4) during the early stages of the photolysis but declines as a result of decomposition on continued irradiation. The rearrangement product (3) was also formed, but in only 27% yield (g.l.c.) compared with 70% for a similar experiment with benzene as solvent. The amide (6, R = Ph) was a significant minor product in both DMS (11%) and benzene (3%).

Clearly DMS inhibits rearrangement but does not completely stop it. The possibility that it occurs both by a nitrene mechanism which is suppressed, and a concerted mechanism which is not, caused us to examine the unsymmetrical azide (7) in which either phenyl or t-butyl can migrate.[2] In benzene[4] the rearrangement products (8) and (9) were formed in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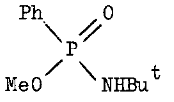
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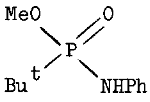
(9)

59% yield and a 2:1 ratio (g.l.c.). In DMS the yield was reduced to 25% while the ratio remained unchanged. Since the migratory aptitude of t-butyl relative to phenyl is unlikely to be exactly the same for both nitrene and concerted mechanisms, this suggests that rearrangement proceeds by a single mechanism which is only partially suppressed by DMS. Again two sulphur-containing compounds were produced, the sulphilimine (4, R = t-Bu) (32%), m.p. 128 - 130°C, M$^+$ 257, δ 7.9 - 7.2 (5 H, m), 2.64 (3 H, s), 2.60 (3 H, s) and 1.05 (9 H, d, J 15 Hz), and its isomer (5, R = t-Bu) ($\sim$ 22%), m.p. 143 - 145°C, δ 8.0 - 7.3 (5 H, m), 3.98 (2 H, m), 2.90 br (1H), 2.17 (3 H, s), and 1.12 (9 H, d, J 15 Hz), as well as the amide (6, R = t-Bu) (13% in benzene, 16% in DMS).

When the azides were photolysed in a mixture of DMS and benzene (1:7 v/v)[4] the sulphilimines (4) were still important products (17% for R = Ph, 24% for R = t-Bu) but their isomers (5) were much less prominent ($\sim$ 2%). Assuming that the sulphilimines arise by reaction of singlet nitrenes with DMS, it seems certain that their isomers (5) do not, albeit that they are formally the products of C-H insertion. In the case of azide (1) the sulphilimine is apparently formed at the expense of rearrangement, the yield of (3) (45%) being markedly lower than in benzene. This is what would be expected if rearrangement proceeds via a nitrene. For azide (7), however, the picture is less clear with the yield of (8) + (9) (55%) being only slightly lower than in benzene. Thus we cannot be certain that nitrenes are intermediates in the rearrangements even though they play a substantial part in the photochemistry of phosphinic azides.[6]

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References and Footnotes

1. J. Wiseman and F.H. Westheimer, J. Am. Chem. Soc., 1974, 96, 4262; M.J.P. Harger and M.A. Stephen, J. Chem. Soc., Perkin Trans. 1, 1981, 736.
2. M.J.P. Harger and S. Westlake, Tetrahedron, in the press.
3. G. Bertrand, J.-P. Majoral and A. Bacciredo, Tetrahedron Letters, 1980, 5015.
4. MeOH (10 mol. equiv.) was included in all reactions to trap metaphosphonimidates.
5. Yields are based on azide consumed. Reactions were followed by i.r. and g.l.c. and were taken to > 70% completion. Where significant product decomposition was observed [(5, R = Ph) and sometimes (3) and (9)] the yield shown is that at ca. 50% completion. The new compounds (4) and (5) gave satisfactory elemental analysis.
6. It is conceivable that DMS suppresses rearrangement in some way other than by the trapping of a nitrene (e.g. by interception of an excited state of the azide) and that this process is associated with the formation of (5) rather than (4).

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