Trimethylsilyl Migration from Nitrogen to Carbon in a Silicon–Nitrogen–Phosphorus Compound

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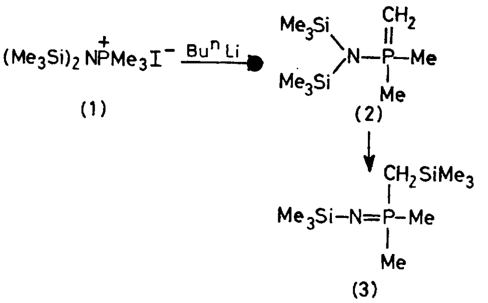
Summary In a process which involves migration of a Me_3Si group from nitrogen to carbon, the phosphonium salt $[(Me_3Si)_2NPMe_3]I$ is dehydrohalogenated by Bu^nLi to form the phosphine imine, $Me_3SiNP(CH_2SiMe_3)Me_2$.

Currently there is considerable interest in the synthesis[1] and stereochemistry[2] of compounds containing the silicon–nitrogen-phosphorus linkage. Many of these compounds are fluxional as a result of the lability of silyl substituents towards intramolecular rearrangements.[3] In a recent study[4] of the preparation and oxidation reactions of $(Me_3Si)_2NPMe_2$ we observed three examples of the migration of Me_3Si groups: from phosphorus to nitrogen, from nitrogen to nitrogen, and from nitrogen to oxygen. Similar processes had been reported previously for trimethylsilylated anilides,[5] sulphinic amides,[6] thioamides,[7] and phosphoramidates.[8]



We now report what appears to be the first instance of the ready migration of a silyl substituent from nitrogen to carbon. The silylaminophosphonium salt (**1**) reacts smoothly with Bu^nLi to form the phosphine imine (**3**) rather than the isomeric phosphorus ylide (**2**).

In a typical experiment, Bu^nLi (9 ml of a 2·4M hexane solution) was added at 0 °C to a stirred solution of (**1**) (13·0 mmol), prepared[4] from $(Me_3Si)_2NPMe_2$ and MeI, in methylene chloride (20 ml) under dry nitrogen. The mixture was allowed to warm to room temperature and stirred for 3·5 h. After filtration and solvent removal, distillation afforded (**3**) as a colourless liquid (1·94 g, 63% yield, b.p. 65—66 °C at 2·5 Torr); ν_{max} (neat liquid): 2830m, 2805w, 1415m, 1310s, 1290s, 1255s, 1130m, 950m, 860vs,br, 785m, 750m, and 720m cm^{-1}. Satisfactory C and H analyses were obtained.

Table. ^1H and ^{13}C n.m.r.[a] data for (**3**)

Signal	$\delta(^1H)$	$\delta(^{13}C)$	J_{PH}	J_{PC}
$(CH_3)_3SiC$	−0·21	0·47	0·0	2·93
$(CH_3)_3SiN$	0·02	4·17	0·0	4·15
PCH_2Si	0·91	23·44	17·0	69·9
$(CH_3)_2P$	1·25	22·18	13·0	64·7

[a] Chemical shifts, δ, in p.p.m. downfield from Me_4Si; coupling constants, *J*, in Hz.

The ^1H and ^{13}C n.m.r. data confirm the molecular structure of the reaction product to be that of the phosphine imine (**3**) and not the ylide (**2**). The chemical shift and J_{PCH} value of the methylene protons are in excellent agreement with data reported for other (trimethylsilyl)methyl-substituted phosphorus compounds.[9] The doublet upfield from Me_4Si, characteristic of the $P{=}CH_2$ unit,[9,10] is not observed. Moreover, the ylide structure (**2**) cannot account for the observation of nonequivalent Me_3Si groups unless hindered rotation about the N–P bond is postulated. This possibility can be ruled out, however, because many structurally related compounds such as $(Me_3Si)_2NR$ [R = PMe_2, $P(S)Me_2$, and $PMe_3{}^+I^-$] exhibit only a single resonance in the Me_3Si region of the ^1H or ^{13}C n.m.r. spectrum.[4]

Finally, it is interesting that n.m.r. spectra obtained on the crude reaction product clearly indicate that the structural rearrangement ($\mathbf{2} \rightarrow \mathbf{3}$) occurs at or below room temperature and is not a result of heating during the final distillation.

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