Generation and Some Reactions of the Bis(trimethylsilyl)aminyl Radical

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Summary The radical $(Me_3Si)_2N\cdot$, generated by u.v. photolysis of $(Me_3Si)_2NN(SiMe_3)_2$ or of $(Me_3Si)_2NOSiMe_3$, readily abstracts hydrogen from hydrocarbons, adds to ethylene, to phosphorus(III) compounds, and to t-butyl isocyanide, and is hence much more reactive than the dimethylaminyl radical.

There is considerable interest at present in the changes in properties of organic compounds which are brought about by substitution of silicon for carbon atoms at key positions in the molecule.[1] Dialkylaminyl radicals are less reactive than alkoxyl radicals. For example, dimethylaminyl radicals abstract hydrogen from C–H groups much less readily than do alkoxyl radicals,[2] and this difference can be associated in part with the weaker N–H bond (398 kJ mol^{-1}) in Me_2NH compared with the O–H bond in ROH (439 kJ mol^{-1} in MeOH).[3] We now report that the bis(trimethylsilyl)aminyl radical (**1**) exhibits reactivity similar to that of an alkoxyl radical and different from that of $Me_2N\cdot$.

The radical (**1**) was generated by u.v. photolysis of tetrakis(trimethylsilyl)hydrazine[4] (TTH) [equation (1)] or (along with the trimethylsiloxyl radical) of tris(trimethylsilyl)hydroxylamine[5] (**2**).†

$$(Me_3Si)_2NN(SiMe_3)_2 \xrightarrow{h\nu} \underset{(\mathbf{1})}{2(Me_3Si)_2N\cdot} \qquad (1)$$

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† The mercury compound $[(Me_3Si)_2N]_2Hg$ also underwent photochemical cleavage to give (**1**), although this source was generally less convenient than TTH or (**2**).

The reactions of (**1**) were studied by monitoring the e.s.r. spectra of the radical products formed during continuous photolysis of solutions of TTH in cyclopropane containing the co-reactant. The results are summarised in the Table.

TABLE. Radicals detected by e.s.r. spectroscopy during reactions of the bis(trimethylsilyl)aminyl radical derived from TTH.

Reactant	Temp. range (K)	Product radicals[a]
$CH_2{=}CH_2$	150—230	$(Me_3Si)_2NCH_2\dot{C}H_2$[b]
$MeCH{=}CH_2$	170—270	$\cdot CH_2CH{=}CH_2$
Cyclopentane	150—230	Cyclopentyl
Me_3CH	170—270	$Me_2CH\dot{C}H_2 + Me_3C\cdot$
EtOH	170—250	$Me\dot{C}HOH$
EtOEt	170—200	$Me\dot{C}HOEt$
$(EtO)_3P$	170—230	$(EtO)_3\dot{P}N(SiMe_3)_2$[c]
Et_3P	150—230	$Et\cdot$
Bu^tNC	170—300	$Bu^tN{=}\dot{C}N(SiMe_3)_2$[d]

[a] The concentrations of simple alkyl radicals were lower than when di-t-butyl peroxide replaced the TTH. [b] $a(2H_\alpha)$ 21·8, $a(2H_\beta)$ 30·5, a(N) 2·5 G, g 2·0025 at 230 K. [c] At 230 K the ethyl radical, produced by β-scission of the phosphoranyl radical, was also detected. [d] $a(Si_2N)$ 11·5, $a(^{13}C_\alpha)$ 95·2 G, g 2·0017 at 170 K; many further small splittings, from the protons and probably from the other nitrogen nucleus, were apparent.

Repetition of these experiments when tetramethyltetrazene (as a photochemical source of dimethylaminyl radicals[6]) replaced the TTH gave rise to the spectrum of $Me_2N\cdot$, and no radical reaction products could be detected. Photolysis of TTH alone in cyclopropane afforded only the spectrum of the cyclopropyl radical, even at low temperatures (140 K), and evidently (**1**) readily abstracts hydrogen from cyclopropane in which the C–H bonds are relatively strong[3] [equation (2)] [D(C–H) 421 kJ mol^{-1}].‡

$$\underset{(\mathbf{1})}{(Me_3Si)_2N\cdot} + \overline{CH_2CH_2CH_2} \rightarrow (Me_3Si)_2NH + \cdot\overline{CHCH_2CH_2} \quad (2)$$

Photolysis of TTH in the presence of triethyl phosphite gave rise to a spectrum which is ascribed to the phosphoranyl radical (**3**) [a(P) 841·5, a(N) *ca.* 2 G, g 2·0022 at 170 K§] [equation (3)].

$$\underset{(\mathbf{1})}{(Me_3Si)_2N\cdot} + (EtO)_3P \longrightarrow \underset{(\mathbf{3})}{(EtO)_3\dot{P}N(SiMe_3)_2} \quad (3)$$

An identical spectrum was obtained during photolysis of diethyl peroxide in the presence of $(EtO)_2PN(SiMe_3)_2$. When TTH was replaced by (**2**), the spectrum of $(EtO)_3P\cdot OSiMe_3$ was detected in addition to that of (**3**). The radical (**1**) also adds to ethylene to give the 2-bis(trimethylsilyl)aminoethyl radical, but abstraction of hydrogen to form the allyl radical is more rapid than addition to the double bond in propene. The relatively persistent (approximately first order decay; $t_{\frac{1}{2}}$ *ca.* 90 s at 250 K) imidoyl radical (**4**) is formed by addition of (**1**) to t-butyl isocyanide [equation (4)], and the magnitude of $a(^{13}C_\alpha)$ for (**4**) (95·2 G) suggests that the electronegativity of the $(Me_3Si)_2N$ group is only slightly less than that of the Bu^tO group.[7]

$$\underset{(\mathbf{1})}{(Me_3Si)_2N\cdot} + Bu^tN{=}C{:} \rightarrow \underset{(\mathbf{4})}{Bu^tN{=}\dot{C}N(SiMe_3)_2} \quad (4)$$

The reaction of (**1**) with isobutane is of particular interest since the isobutyl radical is the major product. The concentration ratio $[Bu^{i}\cdot]:[Bu^{t}\cdot]$ was given by 0·28 exp-$(3830/RT)$ where $R = 8{\cdot}31$ J mol^{-1} K^{-1}, and at 170 K $[Bu^{i}\cdot]:[Bu^{t}\cdot]$ was 4·2 : 1. The t-butyl radical is the major product when t-butoxyl radicals react with isobutane, and at 170 K $[Bu^{i}\cdot]:[Bu^{t}\cdot]$ was *ca.* 0·02 : 1. This difference in selectivity is probably steric in origin, a consequence of the large bulk of the trimethylsilyl groups on the nitrogen radical centre.

Reaction (2) is probably at least thermoneutral and may well be exothermic, indicating[3] that D(N–H) in hexamethyldisilazane is $\geqslant 421$ kJ mol^{-1}. As a result of interaction between the nitrogen lone pair and the vacant d-orbitals on silicon, the radical (**1**) should be more electrophilic than $Me_2N\cdot$, accounting in part for the more rapid addition of (**1**) to ethylene.[8] It is possible that (**1**), unlike $Me_2N\cdot$ which is a π-radical, is a σ-radical in which the nitrogen lone pair is in a π-orbital.[9]

TTH is readily soluble in hydrocarbons, fairly stable to moisture, and provides a very convenient photochemical source of (**1**) for e.s.r. studies. Preliminary results show that bis(trimethylsilyl)bromamine, $(Me_3Si)_2NBr$, acts as a free-radical chain brominating agent for hydrocarbons and that the radical (**1**) is the chain-carrier. For example, the bromamine reacts with toluene at 353 K in the presence of azoisobutyronitrile and t-butylethylene (as a bromine atom scavenger) to form benzyl bromide and hexamethyldisilazane.[10]

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‡ We have not yet succeeded in detecting the e.s.r. spectrum of (**1**). The precursor of (**1**) will always supply a source of abstractable hydrogen even in an inert solvent.

§ These parameters refer to the predominant isomer in which the nitrogen ligand is equatorial. Line shape effects indicate that rapid exchange takes place with the isomer in which the amino group is apical.

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