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Homolytic Reactions of Ligated Boranes. Part 14. ESR Studies of Ring Opening of Cycloalkylaminyl–Borane Radicals and Reactions of Aminyl–Borane Radicals with Silicon-containing Compounds

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ESR spectroscopy has been used to characterise reactions of the aminyl–borane radicals $\mathrm{R\dot{N}H{\rightarrow}BH_3}$ (**2**) in solution. The relative rates of β-hydrogen-atom transfer from [**2**; R = H, Me, $\mathrm{Bu^s}$, $\mathrm{Bu^tC(H)Me}$, or $\mathrm{Bu^t}$] to 2,3-dimethylbut-2-ene and to furan depend on the nature of the group R, confirming that H-atom transfer is bimolecular and does not involve prior β-scission of (**2**) to give a free hydrogen atom. Because of favourable polar factors, β-H-atom transfers from (**2**) to the allylsilanes $\mathrm{Me_3SiCH_2CH{=}CH_2}$ and $\mathrm{Me_3SiCH_2CMe{=}CH_2}$ are particularly rapid. The cycloalkylaminyl–borane radicals (**2**; R = cyclo-$\mathrm{C_3H_5}$ or cyclo-$\mathrm{C_4H_7}$) undergo rapid ring opening at 282 K, while no spectroscopic evidence was found for opening of the cyclopentyl or cyclohexyl analogues. Alkylaminyl–borane radicals transfer a β-hydrogen atom to hexamethyldisilane to bring about homolytic Si–Si bond cleavage. These radicals also react with trialkylsilanes $\mathrm{R_3SiH}$ to give $\mathrm{R_3Si^\bullet}$. Approximate absolute rate coefficients for the reactions of (**2**) have been determined at 282 or 292 K. Of the primary amine–boranes investigated, s-butylamine– and cyclopentylamine–boranes appear to be the most suitable complexes for ESR spectroscopic work in liquid solution.

In Part 11 of this series,[2] we reported that UV photolysis of di-t-butyl peroxide (DTBP) in the presence of a primary amine–borane (**1**) affords aminyl–borane radicals (**2**) through the sequence of reactions (1)–(3). The radicals (**2**) were detected by ESR spectroscopy and their reactions with alkenes, alkadienes, and arenes were studied using the same technique.

$$\mathrm{Bu^tOOBu^t} \xrightarrow{h\nu} 2\,\mathrm{Bu^tO^\bullet} \qquad (1)$$

$$\mathrm{Bu^tO^\bullet} + \underset{(\mathbf{1})}{\mathrm{RNH_2{\rightarrow}BH_3}} \longrightarrow \mathrm{Bu^tOH} + \mathrm{RNH_2{\rightarrow}\dot{B}H_2} \qquad (2)$$

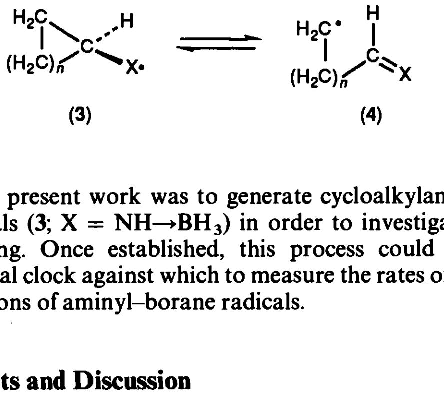
$$\mathrm{RNH_2{\rightarrow}\dot{B}H_2} + \mathrm{RNH_2{\rightarrow}BH_3} \rightleftharpoons \mathrm{RNH_2{\rightarrow}BH_3} + \underset{(\mathbf{2})}{\mathrm{R\dot{N}H{\rightarrow}BH_3}} \qquad (3)$$

Aminyl–borane radicals of the type (**2**; R = H or alkyl) react with alkenes by regioselective hydrogen-atom transfer to give alkyl radicals and the corresponding aminoborane [*e.g.* equation (4)].[2] In a search for further chemical transformations

$$\mathrm{R\dot{N}H{\rightarrow}BH_3} + \mathrm{RCH{=}CH_2} \longrightarrow \mathrm{R\dot{C}H{-}CH_3} + \mathrm{RNH \overset{\rightarrow}{=} BH_2} \qquad (4)$$

of (**2**), we have investigated the reactions of aminyl–borane radicals with a number of silicon-containing compounds. Two allylsilanes, hexamethyldisilane, and three trialkylsilanes have been examined on the grounds that the presence of the metalloidal silicon might render these molecules prone to attack by electrophilic[2] aminyl–borane radicals.

The equilibrium (5) lies to the right when $n = 1$ or 2 if the leading atom of the group X is carbon, nitrogen, or oxygen, and radicals of the type (**3**) usually undergo ready ring opening.[3–10] The aziridine– and azetidine–boryl radicals behave similarly.[11,12] When $n = 3$ or 4 the equilibrium (5) often lies to the left and cyclisation of (**4**) occurs readily. The rates of ring opening and closure can be understood in terms of enthalpic, polar, and stereoelectronic factors.[3] A primary aim of the present work was to generate cycloalkylaminyl–borane radicals (**3**; X = $\mathrm{NH{\rightarrow}BH_3}$) in order to investigate their ring opening. Once established, this process could serve as an internal clock against which to measure the rates of bimolecular reactions of aminyl–borane radicals.



(**3**) (**4**) (5)

Results and Discussion

Primary amine–boranes were prepared by the reaction of a small excess of amine with dimethyl sulphide–borane in diethyl ether.[2] Solutions containing the amine–borane (*ca.* 1 mol $\mathrm{dm^{-3}}$), DTBP (*ca.* 16% v/v), and any third reagent were irradiated with UV light (maximum intensity in the region 240–340 nm) while the sample was in the microwave cavity of an ESR spectrometer. The solvent was usually either cyclopropane–oxirane (1–3:1 v/v) or t-butyl alcohol–t-pentyl alcohol (3:1 v/v).†

As reported previously,[2] photolysis of DTBP in the presence of methylamine–borane (**5**) in tertiary alcohol at 282–292 K afforded the ESR spectrum of (**2**; R = Me), formed as shown in equations (1)–(3). t-Butylamine–borane (**6**) and DTBP in cyclopropane–oxirane at 225–250 K gives rise to the ESR spectrum of (**2**; R = $\mathrm{Bu^t}$).[2] Under similar conditions, ammonia–borane (**7**) affords the spectrum of the boron-centred radical $\mathrm{H_3N{\rightarrow}\dot{B}H_2}$,[13] although we have presented evidence that the isomeric aminyl–borane (**2**; R = H) is also present in low concentration in this system and will transfer a β-hydrogen atom to an added alkene.[2]

ESR spectra of the aminyl–borane radicals (**2**) are very com-

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† Throughout the remainder of the paper this mixed alcohol solvent is referred to simply as tertiary alcohol.

plex and difficult to interpret[2] and those derived from the other amine–boranes (**8**)–(**13**) investigated in this work are too weak to analyse, although their chemical behaviour leaves no doubt that the aminyl–borane radicals are indeed produced.

$MeNH_2 \rightarrow BH_3$

(**5**)

$Bu^tNH_2 \rightarrow BH_3$

(**6**)

$H_3N \rightarrow BH_3$

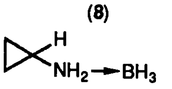
(**7**)

$Bu^sNH_2 \rightarrow BH_3$

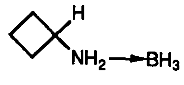
(**8**)

$Bu^tC(H)MeNH_2 \rightarrow BH_3$

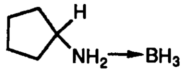
(**9**)



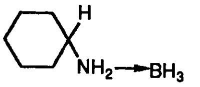
(**10**)



(**11**)

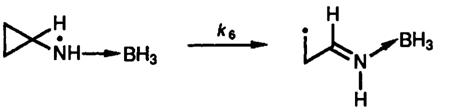


(**12**)



(**13**)

Ring Opening of Cycloalkylaminyl–Borane Radicals.—UV irradiation of a cyclopropane–oxirane solution (1:1 v/v) containing DTBP and cyclopropylamine–borane (**10**) at 200–285 K afforded an ESR spectrum as expected for a primary alkyl radical of the type $RCH_2\dot{C}H_2$ and which we ascribe to the species (**15**) produced by ring opening of the cyclopropylaminyl–borane radical (**14**). Ring fission is evidently very rapid and, although the spectrum of (**15**) is at this point very weak, it is still observable at the lowest temperature (200 K) attainable before crystallisation of the amine–borane. Only one set of lines with no clearly identifiable fine structure was observed and, although both *E*- and *Z*-isomers could be present (but have indistinguishable ESR spectra), for stereoelectronic[3] and steric reasons the *E*-isomer shown is expected to be the major product (*cf.* refs. 9 and 14). Cyclopropylamine–borane appeared to be relatively unstable in tertiary alcohol solvent at 282 K under the conditions used for the ESR experiments and, because of this, the complex was studied only in aprotic cyclopropane–oxirane.



(6)

(**14**) (**15**)

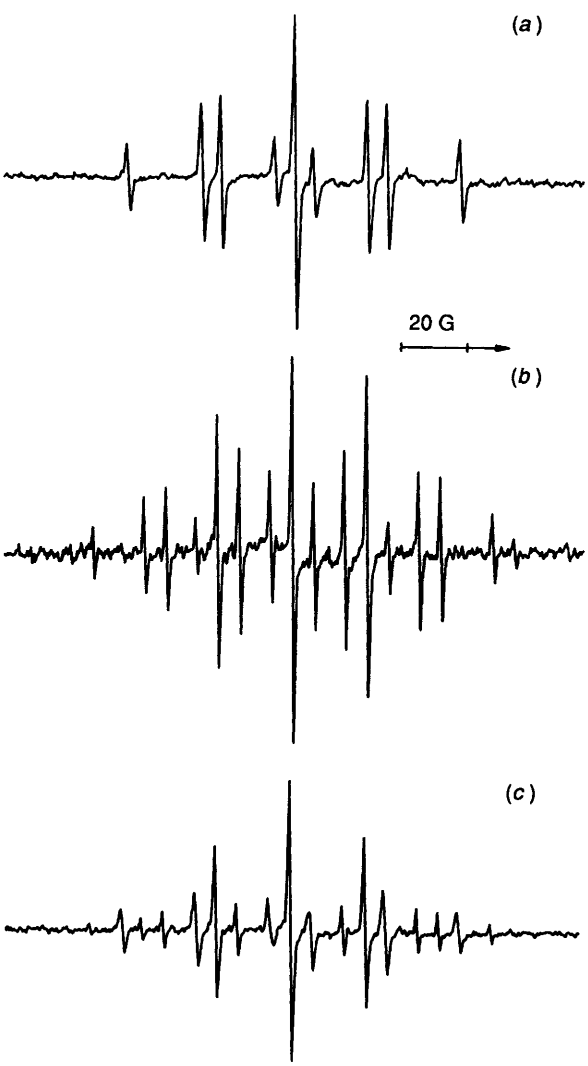
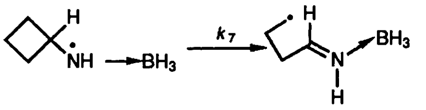


Figure 1. ESR spectra obtained at 282 K in tertiary alcohol. (*a*) The radical (**17**) formed by ring opening of the cyclobutylaminyl–borane radical. (*b*) The radical (**24**) formed by H-atom transfer to 2-methyl-3-trimethylsilylpropene. (*c*) The radicals (**17**) and (**24**) formed by competitive ring opening of (**16**) and H-atom transfer to the allylsilane.

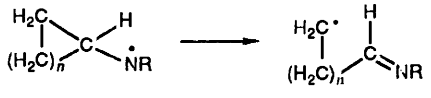
The cyclobutylaminyl–borane radical (**16**) underwent analogous ring opening to give (**17**) in tertiary alcohol at 282–292 K and in cyclopropane–oxirane (2:1 v/v) at 210–282 K. The spectrum of (**17**) is shown in Figure 1(*a*) and the ESR parameters for (**15**) and (**17**) are given in Table 1, which also includes data for related species (**18**; R = H or alkyl, n = 1 or 2) formed by ring opening of uncomplexed cycloalkylaminyl radicals. In similar experiments with cyclopentylamine–borane (**12**) and cyclohexylamine–borane (**13**), no primary alkyl radicals derived from ring opening of the corresponding alkylaminyl–borane radicals were detected, even at 310 K in tertiary alcohol solvent, showing that β-scission is much slower when it involves opening of the less strained five- or six-membered rings.



(7)

(**16**) (**17**)

When the experiments with the cycloalkylamine–boranes (**10**)–(**13**) were repeated in the presence of 1-bromopropane (0.5–1 mol dm^{-3}), only the ESR spectrum of the n-propyl radical was observed. In particular, the radicals (**15**) or (**17**) were not detected, confirming that these species are formed by ring opening of the aminyl–borane radicals (**14**) or (**16**). The alkyl bromide reacts very rapidly with the initially-formed amine–boryl radicals,[11] preventing their reaction with the parent amine–borane to produce the isomeric aminyl–borane radicals [equation (3)].[2]



(8)

(**18**)

Table 1. ESR parameters for the radicals (**15**) and (**17**) and for related species.

Radical	Solvent[a]	T/K	g Factor	Hyperfine splittings (G) $a(2\ H_\alpha)$	Hyperfine splittings (G) $a(2\ H_\beta)$	Ref.
$H_2\dot{C}CH_2CH{=}NHBH_3$ (**15**)	A	227	2.0026	22.3	25.4	*b*
		282	2.0026	22.3	25.1	
$H_2\dot{C}(CH_2)_2CH{=}NHBH_3$ (**17**)	A	227	2.0026	22.3	29.0	*b*
		282	2.0026	22.2	28.1	
	B	282	2.0027	22.1	28.0	
$H_2\dot{C}CH_2CH{=}NH$	A	282	2.0026	22.3	28.1	*b,c*
$H_2\dot{C}(CH_2)_2CH{=}NH$	B	282	2.0026	22.1	28.0	*b,d*
$H_2\dot{C}CH_2CH{=}NPr$	C	135–275	2.0027	22.1[e]	29.2[e]	*f*
$H_2\dot{C}(CH_2)_2CH{=}NPr$	C	270	2.0025	21.8	28.1	*f*

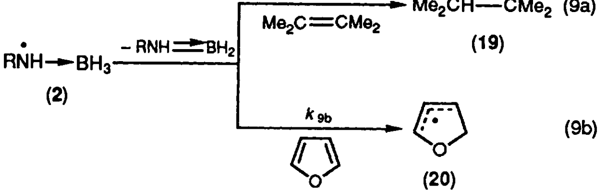
[a] A = cyclopropane–oxirane (2:1 v/v); B = tertiary alcohol; C = cyclopropane. [b] This work. [c] First reported by W. C. Danen and C. T. West, *J. Am. Chem. Soc.*, 1974, **96**, 2447. These authors generated the radical by photolysis of DTBP in the presence of cyclopropylamine; the same route was used in the present work. [d] Formed by ring opening of the cyclobutylaminyl radical, generated by photolysis of DTBP in the presence of cyclobutylamine (*cf.* ref. 4). The spectrum was weak and unidentified lines were also present. [e] The particular temperature at which the ESR parameters were measured was not quoted. [f] Data from ref. 4.

Table 2. Relative rates of hydrogen-atom transfer from $R\dot{N}H{\rightarrow}BH_3$ to 2,3-dimethylbut-2-ene (k_{9a}) and to furan (k_{9b}) in tertiary alcohol at 282 K.

R	(k_{9a}/k_{9b})[a]
H	4.9
Me	6.7
Bu^s	6.9
$Bu^tC(H)Me$	7.6
Bu^t[b]	8.1

[a] Usually the mean value obtained from three or four separate experiments; estimated error ±10%. [b] The ESR spectrum of the t-butyl radical, formed by β-scission of $Bu^tNH_2{\rightarrow}\dot{B}H_2$,[2] was also detected.

Reactions of Primary Aminyl–Borane Radicals with Allylsilanes and with other Alkenes.—Although the aminyl–borane (**2**; R = Me) is calculated to be only 7.1 kJ mol^{-1} more stable than $MeNH{\rightleftharpoons}BH_2$ and H$^•$,[2] we have concluded previously that aminyl–borane radicals reduce alkenes by bimolecular hydrogen-atom transfer, rather than by prior β-scission to give free H$^•$ followed by addition of this atom to the C=C bond.[2] Further confirmation of the bimolecular pathway has now been obtained from measurements of the relative rates of reduction of furan and 2,3-dimethylbut-2-ene by the $DTBP/RNH_2{\rightarrow}BH_3$ couple during UV irradiation [equation (9)]. If addition of free H$^•$ is involved, then the ratio of rate coefficients for the formation of (**19**) and (**20**) will be independent of the nature of the *N*-alkyl group in (**2**). Competition experiments were carried out with a number of different amine–boranes and the values of (k_{9a}/k_{9b}) were calculated in the usual way[2] from the relative concentrations of (**19**) and (**20**) during UV irradiation, together with the known concentrations of furan and 2,3-dimethylbut-2-ene. The results, which are given in Table 2, provide strong support for bimolecular H-atom transfer from (**2**). However, the differences in relative reactivities are rather small, in accord with the open transition state proposed earlier[2] and for which the different steric demands of R would exert only a small influence on selectivity.



Polar effects should be quite important for H-atom transfer from the strongly electrophilic aminyl–borane radical (**2**) to alkenes. Although steric and enthalpic factors must also be considered, the rate of H-atom transfer has been found to increase as the π ionisation potential of the alkene decreases.[2] In the terminology of frontier molecular-orbital theory, the reaction is controlled by the SOMO–HOMO interaction. The ionisation potentials of allylsilanes are relatively low, because the electron pair of the β-C–Si bond interacts with the C=C π orbital and thus raises its energy.[15] The allylsilanes (**21**) and (**23**) should thus be readily reduced to the corresponding β-silylalkyl radicals by the aminyl–borane radicals (**2**).

Figure 1(*b*) shows the ESR spectrum of the radical (**24**) recorded during UV irradiation of a tertiary alcohol solution containing 2-methyl-3-trimethylsilylpropene (**23**) (0.8 mol dm^{-3}), methylamine–borane (1.2 mol dm^{-3}), and DTBP (17% v/v) at 282 K, confirming that H-atom transfer from the aminyl–borane (**2**; R = Me) takes place rapidly. A similar result was obtained with 3-trimethylsilylpropene (**21**) and competition experiments[2,16] showed that (**21**) and (**23**) are respectively 9.4 and 16.0 times more reactive than furan towards the aminyl–borane radical (**2**; R = Me) at 282 K.* Relative and absolute rates of alkene reduction obtained in this work and previously

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* ESR spectra of the triethylsilyl analogue of (**22**)[17a] and the radical (**24**),[17b] generated by addition of trialkylsilyl radicals to propene and to 2-methylpropene, respectively, have been described previously. At 282 K in tertiary alcohol, (**22**) showed $a(H_\alpha)$ 20.9, $a(3\ H_\beta)$ 24.2, $a(2\ H_\beta)$ 17.7 G, and g 2.0026; (**24**) showed $a(6\ H_\beta)$ 22.2 $a(2\ H_\beta)$ 15.6 G, and g 2.0027.

Table 3. Relative and absolute rate coefficients for hydrogen-atom transfer from $\mathrm{Me\dot{N}H\rightarrow BH_3}$ (**2**; R = Me) to alkenes in tertiary alcohol at 282 K.

Alkene	$k^{\mathrm{rel}}_{\mathrm{H\text{-}transfer}}$	$k_{\mathrm{H\text{-}transfer}}$[a]/ $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$	Alkene ionisation potential/eV
$\mathrm{MeCH{=}CH_2}$	(1.0)	2.0×10^{3}[b]	9.73[c]
$\mathrm{Me_2C{=}CH_2}$	3.4[b]	6.8×10^{3}	9.24[c]
$\mathrm{Me_2C{=}CMe_2}$	4.7[b]	9.4×10^{3}	8.27[c]
$\mathrm{Me_3SiCH_2CH{=}CH_2}$ (**21**)	6.6	1.3×10^{4}	9.0[d]
$\mathrm{Me_3SiCH_2CMe{=}CH_2}$ (**23**)	11.2	2.2×10^{4}	*ca.* 8.5[e]
Furan	0.7[b]	1.4×10^{3}	8.99[f]

[a] Computed from the relative rate and $k_{\mathrm{H\text{-}transfer}}$ for reduction of propene taken from ref. 2. [b] Data from ref. 2. [c] G. Bieri, F. Burger, E. Heilbronner, and J. P. Maier, *Helv. Chim. Acta*, 1977, **60**, 2213. [d] U. Weidner and A. Schweig, *J. Organomet. Chem.*, 1972, **39**, 261. [e] Estimated from the ionisation potentials of (**21**), propene, and 2-methylpropene by assuming that substituent effects are additive. [f] P. Linda, G. Marino, and S. Pignataro, *J. Chem. Soc. B*, 1971, 1585.

are collected in Table 3. No ESR evidence was found for addition of aminyl–borane radicals through nitrogen to the allylsilanes.

$$\underset{}{\mathrm{R\dot{N}H\rightarrow BH_3}} + \underset{\textbf{(21)}}{\mathrm{H_2C{=}CHCH_2SiMe_3}} \longrightarrow \mathrm{RNH}\,\underline{\rightharpoonup}\,\mathrm{BH_2} + \underset{\textbf{(22)}}{\mathrm{H_3C\dot{C}HCH_2SiMe_3}} \quad (10)$$

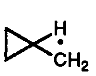
$$\mathrm{R\dot{N}H\rightarrow BH_3} + \underset{\textbf{(23)}}{\mathrm{H_2C{=}CMeCH_2SiMe_3}} \xrightarrow{k_{11}} \mathrm{RNH}\,\underline{\rightharpoonup}\,\mathrm{BH_2} + \underset{\textbf{(24)}}{\mathrm{Me_2\dot{C}CH_2SiMe_3}} \quad (11)$$

When reduction of (**23**) (0.56 mol dm^{-3}) was brought about by the cyclobutylaminyl–borane radical (**16**) at 282 K in tertiary alcohol solvent, competitive ring opening of (**16**) took place and superimposed spectra of (**17**) and (**24**) were observed [see Figure 1(*c*)]. If the self- and cross-reactions of (**17**) and (**24**) are assumed to be diffusion-controlled processes which have the same rate coefficients, then equation (12) should hold.[16] The value of

$$(k_7/k_{11}) = [\textbf{(23)}][\textbf{(17)}]/[\textbf{(24)}] \quad (12)$$

[(**17**)]/[(**24**)] was inversely proportional to [(**23**)] (0.44–0.96 mol dm^{-3}) and essentially independent of the amine borane concentration (0.58–1.13 mol dm^{-3}), which leads to a value for (k_7/k_{11}) of 2.7 mol dm^{-3} at 282 K. If the reasonable assumption is made that k_{11} is almost independent of the nature of the *N*-alkyl group, it follows from the data given in Table 3 that the value of k_7 for ring opening of (**16**) is *ca.* 6×10^4 s^{-1} at 282 K in tertiary alcohol. In cyclopropane–oxirane (2:1 v/v) solvent (k_7/k_{11}) was found to be *ca.* 4 times smaller (0.7 mol dm^{-3}).

Similar competition experiments with cyclopropylamine–borane gave (k_6/k_{11}) to be 1.5 mol dm^{-3} at 282 K in cyclopropane–oxirane (2:1 v/v). With the assumption that k_{11} is the same for (**14**) and (**16**), the value of (k_6/k_7) would be only *ca.* 2 under these conditions. Such a small difference in the rates of ring opening of the cyclopropylaminyl- and cyclobutylaminyl–borane radicals would be very surprising in view of the fact that the cyclopropylmethyl radical (**25**) opens *ca.* 2×10^4 times more rapidly than the cyclobutylmethyl radical (**26**) at 282 K.[7,10] The *N*-alkylated cyclopropylaminyl radical (**27**) undergoes ring opening approximately 50 times more rapidly than the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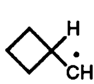
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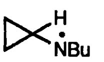
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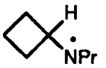
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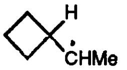
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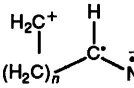
comparable cyclobutylaminyl radical (**28**) at 323 K.[18] At 282 K the rate coefficient for ring opening of (**28**) (4.7×10^4 s^{-1}) is *ca.* 30 times greater than that for opening of the 1-methylcyclobutylmethyl radical (**29**) (*ca.* 1.5×10^3 s^{-1}),[9] which is an isoelectronic analogue of the aminyl–borane (**16**). The rate coefficient for opening of (**16**) is 6×10^4 s^{-1} at 282 K and hence a small difference in rates of opening between (**14**) and (**16**) cannot be attributed to compression of the relative rates which will be observed as the absolute rates increase, implying that other factors must be responsible. It seems likely that this anomaly is related to the exceptional nature of the three-membered ring[19] which makes (**14**) an atypical primary aminyl–borane radical. Cyclopropylamine is less basic than other primary amines[19a] and this should decrease the stability of (**10**) in protic media (see above). The electronic configurations of aminyl–borane radicals are very sensitive to substituent effects[1,2] and the unpaired electron distribution in the cyclopropylaminyl–borane radical (**14**) could differ significantly from that in the other primary aminyl–boranes. Thus, it is possible that (**14**) undergoes ring opening more slowly and reduces alkenes more rapidly than a 'normal' primary aminyl–borane radical.

Polar effects would be expected to be relatively important for ring opening of cycloalkylaminyl–borane radicals. Fission should be facilitated by charge transfer from carbon to nitrogen, as represented by a significant contribution from the canonical form (**30**) in a valence-bond description of the transition state.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For cycloalkylmethyl radicals analogous charge separation in the transition state will clearly be less extensive (and probably in the opposite direction[7]).

Reactions of Aminyl–Borane Radicals with Hexamethyldisilane.—t-Butoxyl radicals react with hexamethyldisilane (HMDS) by hydrogen-atom abstraction to give the radical (**31**),[20] rather than by $\mathrm{S_H2}$ displacement of $\mathrm{Me_3Si^{\bullet}}$ from silicon [equation (14; X = $\mathrm{Bu^tO}$)] which is estimated to be more

$$\mathrm{Bu^tO^{\bullet}} + \underset{\text{HMDS}}{\mathrm{Me_3SiSiMe_3}} \xrightarrow{k_{13}} \underset{\textbf{(31)}}{\mathrm{Me_3SiSiMe_2\dot{C}H_2}} + \mathrm{Bu^tOH} \quad (13)$$

$$\mathrm{X^{\bullet}} + \mathrm{Me_3SiSiMe_3} \xrightarrow{k_{14}} \mathrm{Me_3Si^{\bullet}} + \mathrm{Me_3SiX} \quad (14)$$

exothermic[21,22] by *ca.* 100 kJ mol^{-1}. The $\mathrm{S_H2}$ reaction (14) is probably very sensitive to steric effects. A value of 1.7×10^6 dm^3 mol^{-1} s^{-1} at 295 K has been determined for k_{13} using laser-flash photolysis/optical detection techniques.[23] In contrast, iodine,[24] bromine,[25] and hydrogen[26,27] atoms react with HMDS preferentially at silicon. The $\mathrm{S_H2}$ reaction (14) is particularly rapid with hydrogen atoms and, in the gas phase at 295 K, k_{14} is 2.1×10^7 dm^3 mol^{-1} s^{-1} when X = H,[26c] whereas with X = I the extrapolated rate coefficient[24] is only 1.8×10^2 dm^3 mol^{-1} s^{-1}.

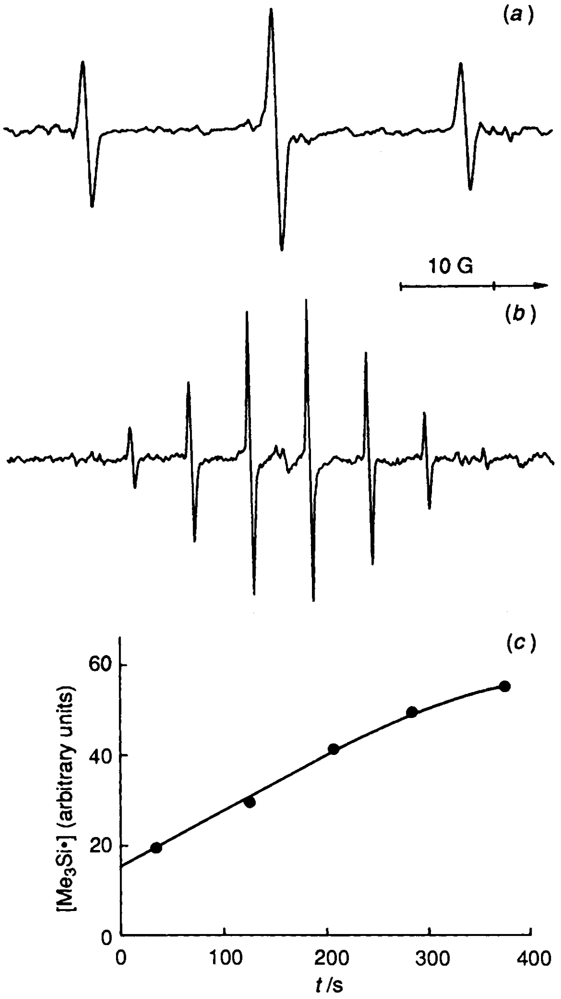


Figure 2. (*a*) ESR spectrum of the radical (**31**) in tertiary alcohol at 292 K. (*b*) ESR spectrum of the trimethylsilyl radical formed by reaction of (**2**; R = cyclo-C_5H_9) with HMDS in tertiary alcohol at 292 K. (*c*) Graph showing the increase in [$Me_3Si^•$] with the duration of UV irradiation of a static sample containing DTBP, HMDS, and cyclopentylamine–borane in cyclopropane–oxirane (3:1 v/v) at 292 K.

Disilanes and alkenes show many chemical similarities;[26c] in particular, the Si–Si σ bond and the C=C π bond are cleaved by similar reagents. Because aminyl–boranes of the type (**2**) readily donate hydrogen atoms to alkenes, we were led to investigate the reactions of (**2**) with HMDS.

Figure 2(*a*) shows the ESR spectrum of the radical (**31**) recorded at 292 K during UV irradiation of a tertiary alcohol solution containing HMDS (0.82 mol dm^{-3}) and DTBP (17% v/v). The spectrum of (**31**) is less well resolved than that obtained previously[20a] at much lower temperature. The trimethylsilyl radical[28] was not detected under these conditions. However, when the experiment was repeated in the presence of cyclopentylamine–borane (**12**) (0.48 mol dm^{-3}), the radical (**31**) was no longer detected but instead the spectrum of $Me_3Si^•$ was observed [see Figure 2(*b*)]. Similar results were obtained in aprotic cyclopropane–oxirane solvent and with the amine–boranes (**7**)–(**9**) and (**13**). We conclude that (**2**) reacts with HMDS according to equation (15) and that hydrogen-atom abstraction by (**2**) to give (**31**) does not compete. It is also evident that t-butoxyl radicals abstract hydrogen from the amine–borane in preference to HMDS under these conditions.

$$\underset{(\mathbf{2})}{\mathrm{R\dot{N}H{\rightarrow}BH_3}} + \mathrm{Me_3SiSiMe_3} \xrightarrow{k_{15}} \mathrm{Me_3Si^{\bullet}} + \mathrm{Me_3SiH} + \mathrm{RNH}\overset{\rightarrow}{=}\mathrm{BH_2} \quad (15)$$

With all amine–boranes, the steady-state concentration of $Me_3Si^•$ increases with the duration of photolysis [as is evident from Figure 2(*b*)] and the time dependence is shown graphically in Figure 2(*c*). We attribute the increase in radical concentration to the formation of $Me_3Si^•$ by reaction of (**2**) with the trimethylsilane produced in reaction (15) (see below) and this observation provides strong evidence against the S_H2 process shown in equation (16) being the primary source of $Me_3Si^•$.

$$\mathrm{R\dot{N}H{\rightarrow}BH_3} + \mathrm{Me_3SiSiMe_3} \nrightarrow \mathrm{Me_3Si^{\bullet}} + \mathrm{R}\underset{\mathrm{SiMe_3}}{\mathrm{N}}\mathrm{H{\rightarrow}BH_3} \quad (16)$$

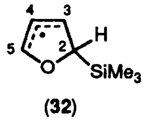
It was shown by use of ^1H and ^{11}B NMR spectroscopy that $MeNH_2{\rightarrow}BH_3$ (**5**) does not react directly with HMDS in tertiary alcohol solvent at 293 K in the presence or absence of DTBP without photolysis. Thus, for reagent concentrations similar to those used in the ESR experiments, there was no change in the ^1H or ^{11}B NMR spectra during 2 h and only unreacted $MeNH_2{\rightarrow}BH_3$ or HMDS could be detected as well as solvent and peroxide (if present).

The ESR spectrum of the methylaminyl–borane radical (**2**; R = Me) was observed when a tertiary alcohol solution containing $MeNH_2{\rightarrow}BH_3$ (1.3 mol dm^{-3}) and DTBP (16% v/v) was UV irradiated at 292 K. [At 283 K, *a*(N) 15.4, *a*(^{11}B) 13.3, *a*(3 B*H*) 63.9, *a*(3 C*H*) 24.1, *a*(N*H*) 19.4 G, and *g* 2.0036.[2] At 292 K the appearance of the spectrum was unchanged.] In the additional presence of HMDS (0.43–1.96 mol dm^{-3}), the spectrum of $Me_3Si^•$ was detected alongside a weakened spectrum of the aminyl–borane and the value of [$Me_3Si^•$]/[(**2**; R = Me)] (≡ *r*), extrapolated to zero UV irradiation time, was directly proportional to [HMDS]. The rate coefficient k_{15} was determined using equation (17), which is derived[2,16,29] by

$$k_{15} = 2k_t(r + 1)[\mathrm{Me_3Si^{\bullet}}]/[\mathrm{HMDS}] \quad (17)$$

assuming that self-reaction[30,31] of $Me_3Si^•$ and its reaction with (**2**; R = Me) are diffusion-controlled processes with the same rate coefficient ($2k_t$). If $2k_t$ is taken to be 2.6×10^9 dm^3 mol^{-1} s^{-1} (the rate coefficient for diffusion-controlled self-reaction of $Pr^{i•}$ in 3-methylpentan-3-ol at 292 K, extrapolated from the data reported by Lipscher and Fischer[32]), we obtain $k_{15} = 1.8 \times 10^2$ dm^3 mol^{-1} s^{-1} at 292 K. A similar value for k_{15} was obtained when the reaction mixture was allowed to flow slowly through the sample cell at a rate such that *r* was independent of the flow rate, thus removing the need for extrapolation to zero irradiation time. Because *r* was $\leqslant 1$ in these experiments, the trimethylsilyl radical will be removed almost exclusively by its reaction with (**2**).

The rate of reaction (15) was also measured relative to hydrogen-atom transfer from (**2**; R = Me) to furan [equation (9b)]. Trialkylsilyl radicals add very rapidly to furan[33] and thus the steady-state concentration of the adduct radical (**32**)* provides a direct measure of the rate of formation of $Me_3Si^•$ by reaction (15). From the relative concentrations of (**20**) and (**32**)



(**32**)

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* For (**32**) at 282 K in tertiary alcohol, *a*(H_2) 41.5, *a*(H_3) 12.2, *a*(H_4) 2.1, *a*(H_5) 12.9 G, and *g* 2.0033.

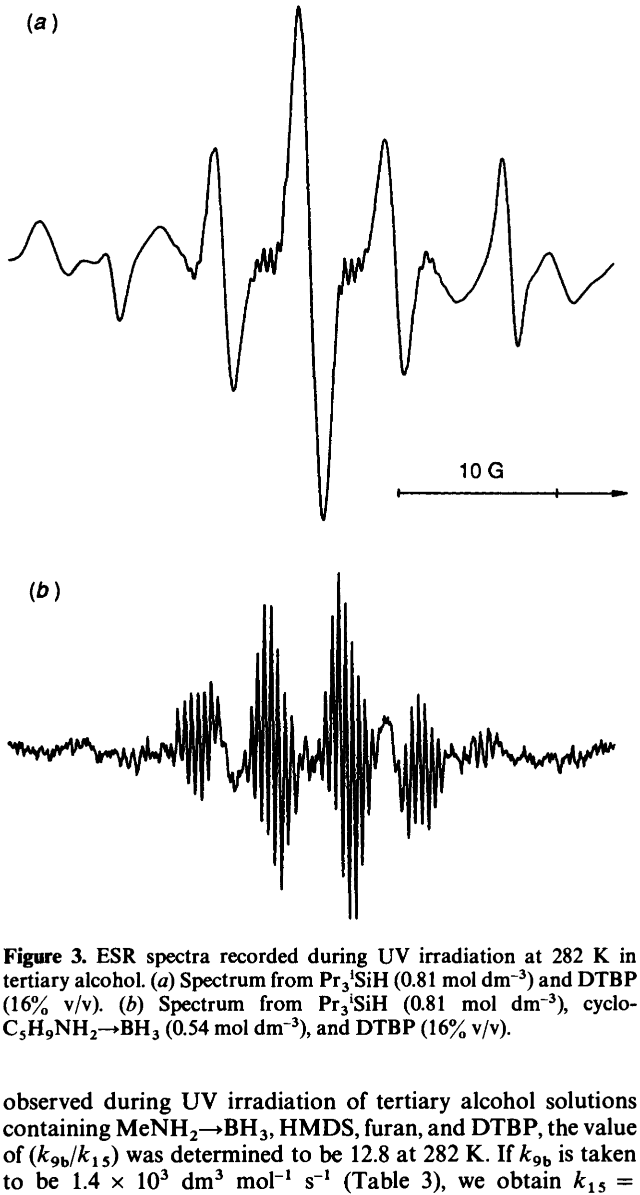

Figure 3. ESR spectra recorded during UV irradiation at 282 K in tertiary alcohol. (*a*) Spectrum from $Pr_3{}^iSiH$ (0.81 mol dm^{-3}) and DTBP (16% v/v). (*b*) Spectrum from $Pr_3{}^iSiH$ (0.81 mol dm^{-3}), cyclo-$C_5H_9NH_2\rightarrow BH_3$ (0.54 mol dm^{-3}), and DTBP (16% v/v).

observed during UV irradiation of tertiary alcohol solutions containing $MeNH_2\rightarrow BH_3$, HMDS, furan, and DTBP, the value of (k_{9b}/k_{15}) was determined to be 12.8 at 282 K. If k_{9b} is taken to be 1.4×10^3 dm^3 mol^{-1} s^{-1} (Table 3), we obtain $k_{15} = 1.1 \times 10^2$ dm^3 mol^{-1} s^{-1}, in good agreement with the value of k_{15} determined independently at 292 K.

Reactions of Aminyl–Borane Radicals with Trimethylsilane.—The increase in $[Me_3Si^\bullet]$ with photolysis time when (**2**) reacts with HMDS suggests that aminyl–borane radicals react with trimethylsilane to produce $Me_3Si^\bullet$ [equation (18)].

$$R\dot{N}H\rightarrow BH_3 + Me_3SiH \xrightarrow{k_{18}} \begin{cases} Me_3Si^\bullet + RNH_2\rightarrow BH_3 & (18a) \\ Me_3Si^\bullet + RNH\rightleftharpoons BH_2 + H_2 & (18b) \end{cases}$$

We have calculated the strength of the N–H bond[2] in $MeNH_2\rightarrow BH_3$ to be 392 kJ mol^{-1} and since[22,34] $E_{dis}(Me_3Si–H)$ is 378 kJ mol^{-1}, it follows that the abstraction reaction (18a) is probably exothermic by *ca.* 14 kJ mol^{-1}. From the computed strength[2] of a B–H bond in $Me\dot{N}H\rightarrow BH_3$ (7.1 kJ mol^{-1}) and the bond energy for dihydrogen (436 kJ mol^{-1}), the alternative β-H-atom transfer reaction (18b) is estimated to be substantially more exothermic (ΔH *ca.* −51 kJ mol^{-1}). Some gas, presumably dihydrogen,[35] was evolved during UV irradiation, but although this observation is suggestive of the H-atom transfer reaction (18b), it is not unequivocal evidence because other sources of H_2 can be envisaged. It would certainly not be unreasonable for the two reactions (18a) and (18b) to take place in competition.

UV irradiation of a tertiary alcohol solution containing cyclopentylamine–borane (**12**) (1.12 mol dm^{-3}), trimethylsilane (0.54 mol dm^{-3}), and DTBP (16% v/v) at 282 K afforded the ESR spectrum of $Me_3Si^\bullet$. Repetition of the experiment when the amine–borane was replaced by the allylsilane (**23**) (0.54 mol dm^{-3}) yielded a spectrum which we assign to the silyl radical adduct[*] (**33**), formed as shown in equations (19) and (20). When

$$Bu^tO^\bullet + Me_3SiH \xrightarrow{k_{19}} Me_3Si^\bullet + Bu^tOH \quad (19)$$

$$Me_3Si^\bullet + H_2C{=}CMeCH_2SiMe_3 \longrightarrow Me\dot{C}(CH_2SiMe_3)_2 \quad (20)$$
(33)

both amine–borane (1.12 mol dm^{-3}) and allylsilane (0.54 mol dm^{-3}) were present along with Me_3SiH (0.54 mol dm^{-3}), the spectrum of (**24**) was observed and that of (**33**) was not detected above the noise level. The amine–boranes (**5**), (**7**)–(**9**), and (**13**) behaved in a similar way. With both amine–borane and Me_3SiH present, without the allylsilane, the reaction of (**2**) with Me_3SiH must, therefore, be the source of $Me_3Si^\bullet$; effectively all the t-butoxyl radicals are scavenged by the amine–borane. In the presence of the allylsilane, (**2**) very rapidly donates a hydrogen atom to give (**24**) (see Table 3) in preference to reaction with trimethylsilane to give $Me_3Si^\bullet$.

The rate of reaction (18) for (**2**; R = Me) was measured relative to H-atom transfer from the aminyl–borane radical to furan [equation (9b)]. The steady-state concentration of the adduct (**32**) was taken to be a direct measure of the rate of production of the trimethylsilyl radical by reaction (18). Experiments were carried out in tertiary alcohol at 282 K with fixed concentrations of Me_3SiH (0.33 mol dm^{-3}) and furan (1.16 mol dm^{-3}). The value of [(**20**)]/[(**32**)] was 6.0 and was independent of the concentration of $MeNH_2\rightarrow BH_3$ in the range 0.75–1.50 mol dm^{-3}, which confirms that all the t-butoxyl radicals are trapped by the amine–borane and that the only source of $Me_3Si^\bullet$ is reaction (18). It follows that (k_{9b}/k_{18}) is 1.7 and hence that k_{18} is 2.4×10^3 dm^3 mol^{-1} s^{-1} at 282 K.

In accord with the explanation proposed for the time dependence of $[Me_3Si^\bullet]$ in the earlier experiments with HMDS, the aminyl–borane radical (**2**) reacts much more rapidly with Me_3SiH than with the disilane.

Reactions of Aminyl–Borane Radicals with other Trialkylsilanes.—When DTBP is photolysed in the presence of R_3SiH where R is a more complex alkyl group than methyl, ESR spectra of persistent carbon-centred radicals are usually observed alongside the spectrum of $R_3Si^\bullet$. For example, with triisopropylsilane the spectra of these very persistent secondary-product radicals are so intense that they almost obscure the spectrum of $Pr_3{}^iSi^\bullet$ [see Figure 3(*a*)].[37] Special instrumental techniques have been used to eliminate the spectra of the persistent radicals and reveal the spectrum of the transient $R_3Si^\bullet$.[37]

However, if cyclopentylamine–borane is included in the sample, at a concentration sufficient to trap all the t-butoxyl radicals and convert them to aminyl–borane radicals, the spectrum of $Pr_3{}^iSi^\bullet$ is now relatively clean [see Figure 3(*b*)].[†] Removal of persistent radicals was accomplished similarly for

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[*] For (**33**), $a(3\ H_\beta)$ 21.8, $a(4\ H_\beta)$ 15.3 G, and g 2.0026. The methylene protons are non-equivalent in pairs and give rise to different splittings at lower temperatures. This dynamic behaviour has been discussed by Sakurai and his co-workers.[36]

[†] For $Pr_3{}^iSi^\bullet$ at 282 K in tertiary alcohol, $a(3\ H_\beta)$ 4.58 and $a(18\ H_\gamma)$ 0.42 G.

triethylsilane in tertiary alcohol or cyclopropane–oxirane solvents. In the presence of amine–borane, it is the aminyl–borane (**2**) that reacts with the silane rather than the less selective t-butoxyl radical. The observation that persistent radicals are generated much more slowly in reactions of $\mathrm{Bu^tO^{\bullet}}$ with methylsilanes suggests that their formation may be indirectly attributed to the tendency[38,39] of $\mathrm{Bu^tO^{\bullet}}$ to abstract hydrogen relatively rapidly from the alkyl groups on silicon when these are more complex than methyl.

Rate of Hydrogen Abstraction From Amine–Boranes by t-Butoxyl Radicals.—The t-butyldimethylamine–boryl radical (**34**) undergoes very rapid β-scission at 282 K to give $\mathrm{Bu^{t\bullet}}$ [equation (21)].[11,12] Hence, the relative rates of hydrogen abstraction by $\mathrm{Bu^tO^{\bullet}}$ from $\mathrm{Bu^tMe_2N{\rightarrow}BH_3}$ and from $\mathrm{Bu^tOMe}$ could be determined in competition experiments, by monitoring the relative concentrations of t-butyl and t-butoxymethyl[40] radicals [equations (22) and (23)].[16] At 282 K in cyclopropane–oxirane (2:1 v/v), the value of (k_{22}/k_{23}) was found to be 50 and analogous competition experiments with $\mathrm{Me_3SiH}$ and $\mathrm{Bu^tOMe}$ gave (k_{19}/k_{23}) to be 6.2. These results may be compared with the absolute rate coefficients determined previously for H-atom abstraction by $\mathrm{Bu^tO^{\bullet}}$ from triethylsilane[23,38,41,*] and from t-butyl methyl ether[40] which are 3.8×10^6 and 5.8×10^5 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$, respectively, at 282 K. On this basis, (k_{19}/k_{23}) would be expected to be *ca.* 7.

$$\underset{(\mathbf{34})}{\mathrm{Bu^tMe_2N{\rightarrow}\dot{B}H_2}} \longrightarrow \mathrm{Bu^{t\bullet}} + \mathrm{Me_2N\overset{\rightarrow}{=}BH_2} \qquad (21)$$

$$\mathrm{Bu^tO^{\bullet}} + \mathrm{Bu^tMe_2N{\rightarrow}BH_3} \xrightarrow{k_{22}} \mathrm{Bu^tMe_2N{\rightarrow}\dot{B}H_2} + \mathrm{Bu^tOH} \qquad (22)$$

$$\mathrm{Bu^tO^{\bullet}} + \mathrm{Bu^tOMe} \xrightarrow{k_{23}} \mathrm{Bu^tO\dot{C}H_2} + \mathrm{Bu^tOH} \qquad (23)$$

We conclude that k_{22} is *ca.* 2.9×10^7 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at 282 K in cyclopropane–oxirane and that this rate coefficient may be considered typical for abstraction of hydrogen from the $\mathrm{BH_3}$ group of most amine–boranes. When DTBP is photolysed in the presence of a mixture of amine–borane and trimethylsilane, >90% of the t-butoxyl radicals will abstract hydrogen from the amine–borane provided that $[\mathrm{RNH_2{\rightarrow}BH_3}]/[\mathrm{Me_3SiH}]$ is > *ca.* 1.1.

Choice of Primary Amine–Borane for ESR Studies.—Hydrogen-atom transfer from primary aminyl–borane radicals to alkenes, dienes, and arenes provides a useful method for the generation of specific carbon-centred radicals for study by ESR spectroscopy in solution.[2] Primary alkylamine–boranes $\mathrm{R^pNH_2{\rightarrow}BH_3}$ are generally less stable thermally and more difficult to handle than $\mathrm{R^sNH_2{\rightarrow}BH_3}$ or $\mathrm{R^tNH_2{\rightarrow}BH_3}$.[42,43] The radical $\mathrm{R^tNH_2{\rightarrow}\dot{B}H_2}$, which is the initial product of reaction between $\mathrm{Bu^tO^{\bullet}}$ and a tertiary alkylamine–borane, undergoes β-scission to give $\mathrm{R^{t\bullet}}$ in competition with intermolecular isomerisation to give $\mathrm{R^t\dot{N}H{\rightarrow}BH_3}$ under normal conditions.[2] Secondary alkylamine–boranes are thus most useful for ESR studies of the reactions of aminyl–borane radicals.

Of the complexes used in this work, with tertiary alcohol or cyclopropane–oxirane solvents, the most suitable amine–boranes appear to be cyclopentylamine–borane (**12**) [which is more soluble than cyclohexylamine–borane (**13**)] and s-butylamine–borane (**8**). The amine–borane (**8**) is more soluble than (**12**), but it is a liquid at room temperature and somewhat more difficult to handle and purify. s-Octylamine–borane was investigated briefly as a potentially more soluble complex; it has relatively good solubility in cyclopropane alone and the derived aminyl–borane radical behaved in qualitatively the same way as (**2**; R = $\mathrm{Bu^s}$). However, like (**8**), it is a liquid at room temperature and not as easy to purify as (**12**).

Experimental

ESR spectra were recorded using a Bruker ESP-300 instrument operating at *ca.* 9.4 GHz. The arrangement for UV irradiation of samples in the microwave cavity was as described previously.[44] Samples were contained in Suprasil quartz tubes (2 or 3 mm i.d. depending on the dielectric properties of the solution) which were either flame sealed or closed with greaseless stopcocks.[2] Relative radical concentrations were determined by double integration of appropriate lines in each spectrum and the results were confirmed by computer simulation using a modified[44] version of Krusic's program ESRSPEC2.[45] Absolute radical concentrations were determined by comparison with the signal obtained from a solution of *N,N*-diphenyl-*N′*-picrylhydrazyl in $\mathrm{CCl_4}$, using the signal from a piece of synthetic ruby, fixed to an inside wall of the microwave cavity, to compensate for changes in spectrometer sensitivity.

Materials.—NMR spectra ($\mathrm{C_6D_6}$ or $\mathrm{CDCl_3}$ solvents) were obtained with a Varian XL-200 instrument (200 MHz for ^{1}H), using tetramethylsilane as internal standard (^{1}H) or $\mathrm{Et_2O{\rightarrow}BF_3}$ as external standard (^{11}B).

t-Butyl and t-pentyl alcohols were distilled from sodium metal; oxirane (Fluka) and cyclopropane (Argo International) were used as received. Di-t-butyl peroxide (Aldrich) was purified as described previously.[46] Furan, 2,3-dimethylbut-2-ene, 3-trimethylsilylpropene, hexamethyldisilane, triethylsilane, and tri-isopropylsilane were commercial products which were distilled under argon before use. Trimethylsilane (Petrarch Systems) was used as received.

2-Methyl-3-trimethylsilylpropene[15c,47] was prepared by a method similar to that used by Mayr *et al.*[15c,48] 3-Chloro-2-methylpropene (9.07 g, 0.10 mol) was added dropwise, intermittently during 7 h, to a stirred suspension of magnesium (3.7 g, 0.15 mol) in tetrahydrofuran (THF) (100 cm^3) containing chlorotrimethylsilane (9.24 g, 0.085 mol). During the addition, the reaction flask was immersed in ice-water contained in an ultrasonic cleaning bath (Decon FS200) and sonicated. The reaction flask and its contents were removed from the ultrasonic bath and stirred and heated in a bath at 45 °C for 8 h. The reaction mixture was hydrolysed with saturated aqueous ammonium chloride, the aqueous layer was extracted with ether (3 × 100 cm^3), and the combined organic layers were dried ($\mathrm{MgSO_4}$). Most of the ether and THF were removed by fractional distillation at atmospheric pressure; the residual liquid was washed with water (3 × 10 cm^3), dried ($\mathrm{MgSO_4}$), and distilled to give the allylsilane (**23**), b.p. 109–110 °C at 756 Torr.† $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 0.04 (9 H, s), 1.55 (2 H, d, *J* 1.3 Hz), 1.72 (3 H, dd, *J* 1.4, 0.7 Hz), 4.48 (1 H, m), and 4.59 (1 H, m). The product contained a small amount (*ca.* 4 mol%) of 2,5-dimethylhexa-1,5-diene (formed by allylic coupling). The 1,1,4-trimethylpent-4-enyl radical was generated by H-atom transfer to the pure diene (Aldrich) from (**2**), but this radical was not detected in reactions of the allylsilane containing the diene. The diene could be removed from (**23**) by preparative GLC and the pure allylsilane behaved indistinguishably from the material containing the diene.

The amine–boranes (**5**)–(**7**) were obtained as described previously.[2] The amine–boranes (**8**)–(**13**) were prepared by the reaction of a small excess of the corresponding amine with dimethyl sulphide–borane (Aldrich, 10 mol dm^{-3} solution in excess $\mathrm{Me_2S}$) in diethyl ether at 0 °C. Removal of all volatiles

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* The value quoted refers to abstraction from the Si–H group only.

† 1 Torr = 133.322 Pa.

Table 4. Properties of new primary amine–boranes $RNH_2 \rightarrow BH_3$.

			Elemental composition Found% (Calc%)		
R	M.p./°C	δ_B[a] ($^1J_{BH}$/Hz)	C	H	N
Bu^s	17–18	−20.1	55.1	16.6	16.0
		(96)	(55.2)	(16.2)	(16.1)
$Bu^tC(H)Me$	97–98	−18.4	62.4	15.8	12.1
		(95)	(62.7)	(15.8)	(12.2)
cyclo-C_3H_5	44–45	−19.8	50.8	14.1	19.5
		(97)	(50.8)	(14.2)	(19.8)
cyclo-C_4H_7	68–69	−20.6	56.5	14.1	16.3
		(98)	(56.6)	(14.2)	(16.5)
cyclo-C_5H_9	77–78	−19.1	60.7	14.5	14.2
		(94)	(60.7)	(14.3)	(14.2)
cyclo-C_6H_{11}	95–96	−19.3	63.6	14.2	12.2
		(95)	(63.8)	(14.3)	(12.4)

[a] C_6D_6 solvent.

under reduced pressure left the amine–borane in an almost pure state. The complexes (**9**)–(**13**) were purified by dissolution in the minimum volume of diethyl ether at room temperature, removal of any turbidity by filtration, and precipitation of the amine–borane by dropwise addition of cyclohexane. The complexes were separated by filtration and dried under reduced pressure (0.1 Torr) for 2 h at room temperature. The amine–borane (**8**) was purified by recrystallisation from diethyl ether–pentane at low temperature. The melting points, microanalytical data, and ^{11}B NMR parameters for (**8**)–(**13**) are given in Table 4.

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