

ELECTRON SPIN RESONANCE STUDIES OF
RADICALS DERIVED FROM PRIMARY AMINE-BORANES
IN SOLUTION

A thesis submitted in partial fulfilment of the requirements for the
degree of Doctor of Philosophy undertaken at the University of London

by

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I am also indebted to the technical staff of the department whose services have been invaluable.

Abstract

The reactions of photochemically generated t-butoxyl radicals with primary amine-boranes ($\text{RNH}_2 \rightarrow \text{BH}_3$) were studied by electron spin resonance (e.s.r.) spectroscopy. Primary amine-boranes are isoelectronic analogues of the alkanes (RCH_2CH_3).

Much research has been carried out with carbon-centred radicals, the present work set out to investigate the similarities and differences in structures and chemical reactions between these species and the radicals derived from primary amine-boranes.

t-Butoxyl radicals abstract hydrogen atoms from $\text{RNH}_2 \rightarrow \text{BH}_3$ to form, initially, the nucleophilic amine-boryl radical $\text{RNH}_2 \rightarrow \dot{\text{B}}\text{H}_2$, which subsequently abstracts hydrogen from the parent to give the more stable isomeric aminyl-borane radical $\text{RNH} \rightarrow \dot{\text{B}}\text{H}_3$. The amine-boryl radicals can be intercepted by alkyl bromides or chlorides or by nitriles, with which they react by halogen atom abstraction or by addition to the CN group to give iminyl radicals, respectively. The e.s.r. spectra of $\text{RNH} \rightarrow \dot{\text{B}}\text{H}_3$ show the presence of extensive hyperconjugative delocalization of the unpaired electron onto the BH_3 group [$a(3\text{BH})$ 64-66 G]. Monoalkylaminyl-borane radicals react rapidly with alkenes with arenes and with conjugated or cumulated dienes to transfer a β -hydrogen atom from boron to give alkyl, cyclohexadienyl, or allyl radicals, respectively. Hydrogen-atom transfer to alkenes from the electrophilic $\text{MeNH} \rightarrow \dot{\text{B}}\text{H}_3$ takes place with high regioselectivity to give the more stable alkyl radical when two adducts are possible; the rate of transfer increases as the ionization potential of

the alkene decreases along the series $\text{CH}_2=\text{CH}_2 < \text{MeCH}=\text{CH}_2 < \text{Me}_2\text{C}=\text{CH}_2 \approx \text{Me}_2=\text{CHMe} < \text{Me}_2\text{C}=\text{CMe}_2$. The absolute rate for reduction of propene by $\text{MeNH}\dot{\rightarrow}\text{BH}_3$ was determined to be *ca.* $2.0 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ at 282 K. Competition experiments have been carried out to determine the relative rates of various reactions undergone by $\text{RNH}_2\dot{\rightarrow}\text{BH}_2$ and $\text{RNH}\dot{\rightarrow}\text{BH}_3$. The results are interpreted with the aid of *ab initio* molecular orbital calculations at the 6-31** level for $\text{RNH}_2\dot{\rightarrow}\text{BH}_2$, $\text{RNH}\dot{\rightarrow}\text{BH}_3$, $\text{RNH}_2\dot{\rightarrow}\text{BH}_3$, and $\text{RNH}=\text{BH}_2$ (R = H or Me), together with similar calculations for the isoelectronic counterparts.

It was found that the Si-Si bond was cleaved by the same type of reagents that cleave the C—C π -bond and that aminyl-borane radicals transferred a hydrogen atom to hexamethyldisilane (HMDS) by displacement of $\text{Me}_3\text{Si}\cdot$.

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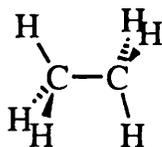
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CHAPTER 1

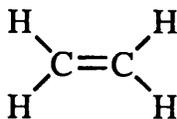
Introduction

1.1 ISOELECTRONIC RELATIONSHIPS

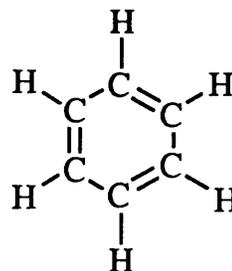
Boron and nitrogen are positioned either side of carbon in the Periodic Table. Because of this relationship, molecules in which a CC group is replaced by a BN moiety are isoelectronic, and the organic parent and its BN counterpart can show similar chemical and physical properties. Comparison of the properties of such isoelectronic pairs can increase our understanding of both families of compounds. Some of the best known examples of these isoelectronic pairs are those shown in (1.1) - (1.3).



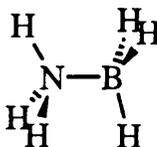
Ethane
(1.1a)



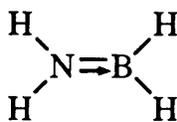
Ethene
(1.2a)



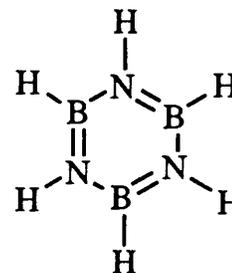
Benzene
(1.3a)



Ammonia-borane
(1.1b)



Aminoborane
(1.2b)



Borazine
(1.3b)

Both the size and electronegativity of carbon are intermediate between the corresponding values for boron and nitrogen, as detailed in Table 1.1.¹ While the organic compounds (1.1a) - (1.3a) have no dipole moment, the BN analogues are usually polar compounds. Ammonia-borane contains a formal dative σ bond between nitrogen and boron; the

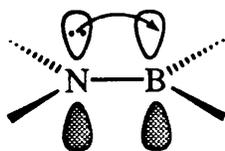
Table 1.1. Properties of boron, carbon, and nitrogen.

| Atom | B | C | N |
|--------------------------------|-----|-----|-----|
| Number of valence electrons | 3 | 4 | 5 |
| covalent single bond radius/pm | 88 | 77 | 70 |
| Pauling electronegativity | 2.0 | 2.5 | 3.0 |

molecule is highly polar in the sense $\text{H}_3\text{N}\rightarrow\text{BH}_3$ and the dipole moment is 5.22 D.² However, aminoborane is much less polar with $\mu = 1.84$ D.³ Even though aminoborane contains a formal $\text{N}\rightarrow\text{B}$ dative π linkage, because the electronegativity of nitrogen is much greater than that of boron there is compensating σ electronic transfer back from boron to nitrogen resulting in an overall small dipole moment [see structure (1.4)]. Of course for reasons of symmetry borazine has no dipole moment.

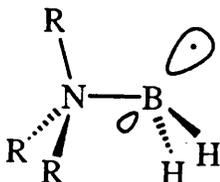
Since the substance of this thesis is concerned with free radical

chemistry and, in particular, with comparisons of the properties of

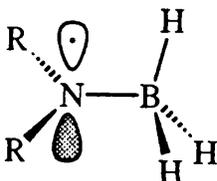


(1.4)

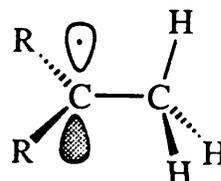
amine-boryl and aminyl-borane radicals (1.5) and (1.6), respectively, with those of the isoelectronic alkyl radicals (1.7), it is appropriate to describe relevant previous work on boron-, nitrogen-, and carbon-centred radicals.



(1.5)



(1.6)

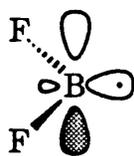


(1.7)

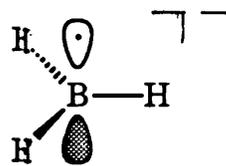
1.2 BORON-CENTRED RADICALS

Complexation of $X_2B\cdot$ with a Lewis base produces a boron-centred radical which is isoelectronic with a generally more familiar alkyl radical (e.g. the pairs $H_3B\cdot/H_3C\cdot$, $H_3N\rightarrow\dot{B}H_2/H_3C-\dot{C}H_2$, and $H_3P\rightarrow\dot{B}H_2/H_3Si-\dot{C}H_2$) are related in this way. The boryl radical itself ($H_2B\cdot$) has been characterised in the gas phase by optical absorption spectroscopy and is non-linear. The difluoroboryl radical $F_2B\cdot$ has been generated by γ -irradiation of BF_3 in an argon matrix at 4.2 K and characterised by e.s.r.

spectroscopy [$\alpha(^{11}\text{B})$ 295.0, $\alpha(2\text{F})$ 190 G, and g 2.0012],⁴ showing it to be also a σ -radical [structure (1.8)]. The FBF angle was calculated to be 112°.⁴



(1.8)



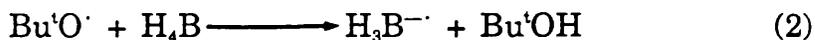
(1.9)

The borane radical anion (1.9) may be regarded as a complex between H_2B^\cdot and a hydride ion and it is isoelectronic with the methyl radical H_3C^\cdot . Isotropic spectra of H_3B^- , produced by γ -irradiation of potassium⁵ or tetramethylammonium⁶ borohydride in rigid matrices, have been recorded and these indicate that the borane radical anion is effectively planar in these environments [structure (1.9)].

Generation of F_3B^- by γ -irradiation of boron trifluoride in a tetramethylsilane matrix⁷ afforded an isotropic e.s.r. spectrum consistent with this radical being appreciably pyramidal [$\alpha(^{11}\text{B})$ is 153 G as compared to 19.9 G for H_3B^-]. The deviation from planarity when fluorine atoms replace hydrogen is paralleled by the isoelectronic carbon-centred radicals H_3C^\cdot and F_3C^\cdot .

The borane radical anion [$\alpha(^{11}\text{B})$ 19.9, $\alpha(3\text{H})$ 15.2 G, and g 2.0023] has also been generated in fluid solution by reaction of photochemically-produced t-butoxyl radicals with tetra-n-butylammonium borohydride [equations (1) and (2)].⁸ The cyanoborane radical anion⁹ $\text{H}_2\dot{\text{B}}\text{CN}^-$ has been generated in an analogous fashion from $\text{Bu}_4\text{N}^+\text{H}_3\text{BCN}^-$. The extent

of delocalisation of the unpaired electron onto nitrogen was found to be



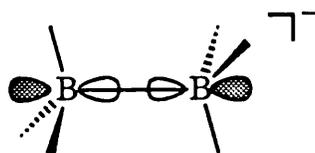
be similar to that for the isoelectronic cyanomethyl radical $\text{H}_2\dot{\text{C}}\text{CN}^-$.

Trialkylborane radical anions, resulting from reduction of the parent trialkylborane by sodium-potassium alloy in ether, show larger ^{11}B hyperfine splittings than $\text{H}_3\text{B}^{\cdot-}$ [$\text{Bu}_3\text{B}^{\cdot-}$ has $a(^{11}\text{B})$ 38.5 G].¹⁰ It was noted that the relative increase in going from $\text{H}_3\text{B}^{\cdot-}$ to $\text{R}_3\text{B}^{\cdot-}$ is larger than that found for $a(^{13}\text{C})$ on going from H_3C^\cdot to R_3C^\cdot , suggesting that boron-centred radicals are more easily pyramidalised than their carbon counterparts.

A well-resolved spectrum of the diborane radical anion has been recorded in solution following reaction of $\text{Bu}^t\text{O}^\cdot$ with tetrabutylammonium heptahydroborate¹¹ [equation (3)] [$a(^{211}\text{B})$ 10.88, $a(6\text{H})$ 0.75 G, and g



2.0024. This radical anion was believed to adopt structure (1.10), which has a one-electron B—B σ bond. The ^{11}B splitting (46.3 G) for the



(1.10)

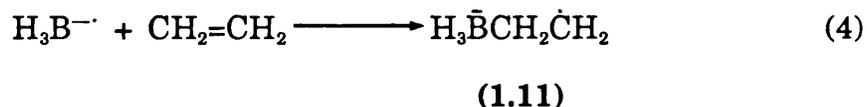
radical anion of the trimethylborate dimer¹² $[(\text{MeO})_3\text{B}-\text{B}(\text{OMe})_3]^-$ much larger than for (1.9) indicating that the $(\text{MeO})_3\text{B}$ groups are appreciably more pyramidal than BH_3 moieties in (1.9).

1.2.1 Reactions of Boryl Radicals and Borane Radical Anions

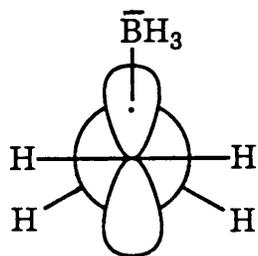
A variety of reactions of H_3B^- and $\text{H}_2\dot{\text{B}}\text{CN}^-$ have been studied in solution by e.s.r. spectroscopy. However, there are no known reactions of X_2B^\cdot .

Addition to Alkenes and Arenes

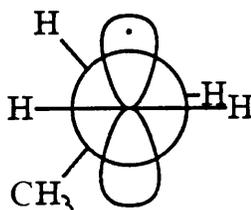
The borane radical anion has been shown to undergo addition to ethene to give the β -substituted ethyl radical¹³ (1.11) [equation (4)]; the



hyperfine splittings and their temperature dependences indicate that the eclipsed conformation (1.12) is preferred. In contrast, the isoelectronic propyl radical (1.13) and the radical $\bar{\text{O}}\text{CH}_2\dot{\text{C}}\text{H}_2$ ¹⁴ adopt a staggered



(1.12)

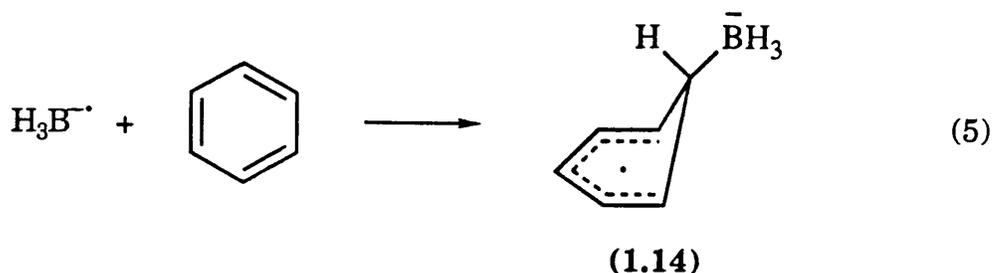


(1.13)

conformation. Methyl radicals do not add to ethene sufficiently rapidly

to permit the spectrum of the propyl radical to be detected under the same conditions. However, both $\text{H}_3\text{Si}^\cdot$ and $\text{Me}_3\text{Si}^\cdot$ add readily to ethene¹⁵ and the eclipsed conformation analogous to (1.12) is preferred. Similarities between the behaviour of H_3B^\cdot and silyl radicals are often seen and might be expected because of the diagonal relationship between boron and silicon in the Periodic Table.

In the presence of benzene, H_3B^\cdot gave the non-planar cyclohexadienyl radical adduct (1.14) [equation (5)]. No addition of H_3C^\cdot



to benzene was found under similar conditions, but addition of $\text{Me}_3\text{Si}^\cdot$ ¹⁶ occurs readily to give an adduct analogous to (1.14).

Reactions with Alkyl Halides

Both H_3B^\cdot and $\text{H}_2\text{BCN}^\cdot$ rapidly abstract halogen from alkyl bromides and chlorides as judged by e.s.r. spectroscopy. In the presence of RBr , the spectrum of either borane radical anion was replaced by that of the alkyl radical R^\cdot at 170 K. The borane radical anion also reacts with $\text{Pr}^\text{n}\text{Cl}$ (1.0 M) at this temperature, but the spectrum of $\text{H}_2\text{BCN}^\cdot$ remains unquenched.¹³ Alkyl radicals abstract halogen rapidly from alkyl iodides, but not from bromides or chlorides; again the reactivity of H_3B^\cdot

is closer to that of $R_3Si\cdot$ than $R_3C\cdot$.

Addition to Alkyl Cyanides

The borane radical anion adds rapidly to acetonitrile [equation (6)] even at 185 K. At this temperature $H_2\dot{B}CN^-$ did not add, as judged



by e.s.r. spectroscopy, although above 220 K the spectrum of the iminyl adduct was detected.

At higher temperatures the spectra of the iminyl radicals were replaced by those of alkyl radicals resulting from β -scission [equation (7)]. Thus, in e.s.r. studies of the reaction of $H_3B^{\cdot-}$ with EtCN, only the



spectrum of the ethyl radical was detected above 288 K. When $H_3B^{\cdot-}$ was generated in the presence of Bu^tCN , no iminyl radical could be detected, even at 170 K, and only the spectrum of $Bu^t\cdot$ was observed between 170 and 295 K.¹⁷ The methyl radical does not add to alkyl cyanides under similar e.s.r. conditions.

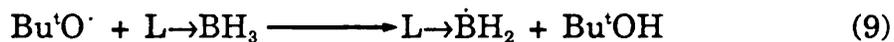
1.2.2. Ligated Boryl Radicals

As mentioned before, the borane radical anion may be considered to be the simplest ligated boryl radical, since it can formally be regarded

as a complex of H_2B^\cdot and the hydride ion [equation (8; $\text{L} = \text{H}^-$)]. A wide variety of ligated boryl radicals can be envisaged in which Lewis bases such as amines, phosphines, and sulphides are attached to the electron



deficient H_2B^\cdot . A large number of such species have now been generated by hydrogen atom abstraction from the parent borane complexes [equation (9; $\text{L} = \text{R}_3\text{N}$, R_2NH , R_3P or R_2S)] and their properties have been

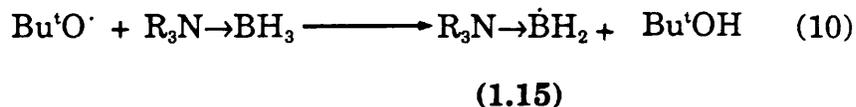


investigated using e.s.r. spectroscopy.

1.2.3. Amine-Boryl Radicals

Amine-boranes are of particular interest because of their relationship to organic compounds in which the CC moiety has been replaced by an isoelectronic NB linkage. Thus, ammonia-borane is isoelectronic with ethane, and the radicals formed by hydrogen atom abstraction from ammonia-borane will be isoelectronic with the ethyl radical.

The ammonia-boryl radical (1.15; $\text{R} = \text{H}$) has been generated by reaction of either $\text{Bu}^\cdot\text{O}^\cdot$ [equation (10)]^{18a} or $(\text{Me}_3\text{Si})_2\text{N}^\cdot$ ^{18b} with ammonia-borane. The spectroscopic parameters for (1.15; $\text{R} = \text{H}$) are $a(^{11}\text{B})$ 42.3, $a(2\text{H}_\alpha)$ 11.0, $a(3\text{H}_\beta)$ 11.0, $a(^{14}\text{N})$ 1.4 G, and g 2.0023 at 269 K. The



isoelectronic ethyl radical shows $a(3\text{H}_\beta)$ 26.9, $a(2\text{H}_\alpha)$ 22.4,^{19a} $a(^{13}\text{C}_\alpha)$ 39.1, $a(^{13}\text{C}_\beta)$ 13.6 G, and g 2.0024 at 95 K.^{19b} The magnitudes of the ^{11}B and 2H_α splittings for ammonia-boryl show it to be pyramidal at boron, whilst the ethyl radical is effectively planar at the radical centre.

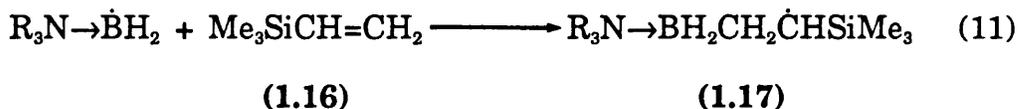
The trimethylamine-boryl (1.15; $\text{R} = \text{Me}$) and the triethylamine-boryl (1.15; $\text{R} = \text{Et}$) radicals have been generated by similar routes and have e.s.r. parameters in accord with a pyramidal equilibrium geometry at boron.²⁰ Discussion of the difference in structure at boron between $\text{H}_3\text{B}^{\cdot-}$ and $\text{R}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$ considered changes in the hybridization of the bonds to boron and in the composition of the SOMO arising from the replacement of the H^- in $\text{H}_3\text{B}^{\cdot-}$ by the much more electronegative R_3N group. Attention was also drawn to the steric and torsional effects which appear to be important in determining the pyramidal geometry of the *t*-butyl radical as compared with the planar equilibrium geometry of the methyl radical.²¹

1.2.4. Reactions of Amine-Borane Radicals

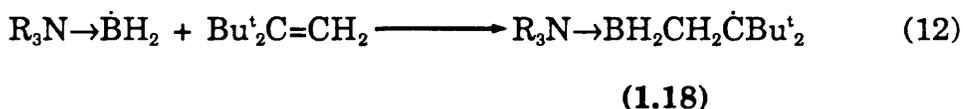
The reactions of amine-boryl radicals show many similarities to those of the borane radical anion, as might be predicted. Again, a general similarity to the reactions of silyl radicals is seen.

Addition to Alkenes and Arenes

Tertiary amine-boryl radicals and the ammonia-boryl²⁰ radical have been shown by e.s.r. spectroscopy to add to the relatively electron deficient trimethyl(vinyl)silane (1.16) [equation (11)]. The ammonia-boryl



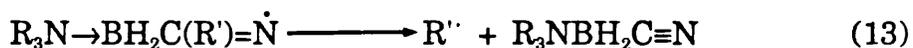
radical also adds to 1,1-di-*t*-butylethene to give a β -substituted alkyl radical (1.17) [equation (12)], which is relatively long-lived because of



steric protection afforded to the radical centre by the bulky *t*-butyl groups. As with borane radical anion adducts, the B—C $_{\beta}$ bonds eclipse the C $_{\alpha}$ —2p $_{\pi}$ orbital in the preferred conformation. Addition to ethene has not been reported.

Addition to Nitriles

The amine-boryl radicals R₃N→BH₂ (R = Me or H) add rapidly to alkyl cyanides to give iminyl radicals, which can undergo subsequent β -scission at higher temperatures [equation (13)].²² The rate of β -scission



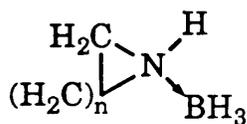
increases with decreasing strength of the R'—C bond in the order R' = Me < Et < Prⁱ < Bu^t. Addition of R₂NH→BH₂ could not be detected under similar conditions because of its rapid intermolecular rearrangement to R₂N→BH₃ (see later).

Reaction with Alkyl Halides

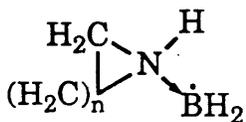
Both ammonia- and trialkylamine-boryl radicals abstract halogen rapidly from alkyl bromides and, less readily, from alkyl chlorides.²⁰ In this sense their reactivity is much greater than that of an alkyl radical and more comparable with a trialkylsilyl radical²³⁻²⁵ or H₃B[•]. The amine-boryl radicals are here exhibiting 'metalloidal' properties, probably due to both polar and thermodynamic factors.

β-Scission of Amine-Boryl Radicals

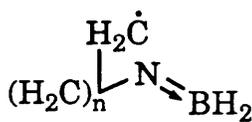
Hydrogen atom abstraction from aziridine- and azetidione-borane (1.19; *n* = 1 or 2) does not give rise to a spectrum of the corresponding amine-boryl radical (1.20), but instead to one of the ring opened radicals



(1.19)



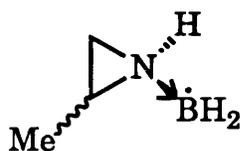
(1.20)



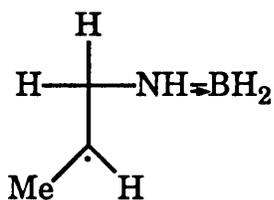
(1.21)

(1.21; *n* = 1 or 2).^{20,26} The aziridine-boryl radical thus resembles the isoelectronic cyclopropylmethyl radical, which undergoes ring opening β-scission to give the but-3-enyl radical.²⁷

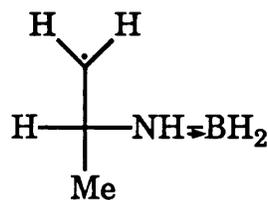
The regioselective ring opening of the 2-methylaziridine-boryl radical has also been studied.²⁸ The *cis*-isomer of (1.22) undergoes ring opening to give mainly the secondary alkyl radical, (1.23), while the *trans*-isomer gives mainly the less stable primary alkyl radical (1.24). The 2-methylaziridine-boryl radical therefore behaves like the isoelectronic *cis*- and *trans*-2-methylcyclopropylmethyl radicals.²⁹



(1.22)

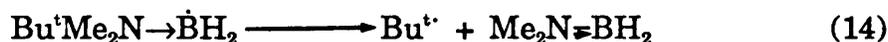


(1.23)



(1.24)

The acyclic *t*-butyldimethylamine-boryl radical²⁰ (1.25) undergoes rapid β -scission to give *t*-butyl radicals [equation (14)]. The process also occurs for $\text{Pr}^t_2\text{EtN} \rightarrow \dot{\text{B}}\text{H}_2$, but the latter cleavage is 3.7 times slower than



(1.25)

the former at 221 K, and absolute rate coefficients for these β -scission processes have been determined by laser flash photolysis e.s.r. techniques.³⁰ Both of the acyclic amine-boryl radicals undergo β -scission more slowly than the aziridine-boryl radical undergoes ring opening.

The high rate of β -scission of amine-boryl radicals compared with the corresponding cleavage of alkyl radicals can be traced to the former

process being highly exothermic, because of the large difference in energies between the N→B single bond and the N=B double bond. This arises because a weak σ bond is replaced by a strong σ bond and a relatively weak π bond. In contrast, the difference in energies between the carbon-carbon single and double bonds is much smaller, because now a strong σ bond is replaced by a strong σ bond and a relatively weak π bond. In accord with this analysis the β -scission of saturated acyclic alkyl radicals is appreciably *endothermic*, even when a tertiary alkyl radical is eliminated from a quaternary carbon atom,³¹ (e.g. loss of Bu^t· from Bu^tMe₂C— \dot{C} H₂ is endothermic by ca. 61.8 kJ mol⁻¹). Consequently such β -scissions are very much slower than analogous cleavage of the isoelectronic amine-boryl radicals.

1.2.5. Phosphine-Boryl Radicals

Several phosphine-boryl radicals (X₃P→BH₂; X = MeO, CF₃CH₂O, Me₂N, Et, Buⁿ, Bu^t) have been generated in solution by hydrogen atom abstraction from the parent phosphine-borane [equation (15)].³² The e.s.r.



parameters show that these radicals are close to planar at the boron radical centre, in distinct contrast to the amine-boryl radicals [e.g. (MeO)₃P→BH₂ shows $a(^{11}\text{B})$ 14.5, $a(2\text{H}_a)$ 16.6, $a(^{31}\text{P})$ 44.1 G, and g 2.0019 at 175 K]. This difference in geometry was attributed to delocalisation of the unpaired electron into vacant π orbitals associated with the X₃P

ligand, which will be greatest when the radical centre is planar. The phosphine-boryl radicals are less reactive than H_3B^\cdot and the amine-boryl radicals, failing to add to ethene, trimethyl(vinyl)silane, and benzene. They do abstract halogen from alkyl bromides, but not in general from alkyl chlorides.

The reaction of t-butoxyl radicals with secondary phosphine-boranes ($\text{R}_2\text{PH}\rightarrow\text{BH}_3$; R = Me, Et, or Ph) gives rise to the phosphinyl-borane radical ($\text{R}_2\dot{\text{P}}\rightarrow\text{BH}_3$) rather than to phosphine-boryl radicals.³³

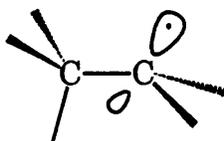
1.2.6. Sulphide-Boryl Radicals

Hydrogen-atom abstraction from a dialkyl sulphide-borane ($\text{R}_2\text{S}\rightarrow\text{BH}_3$; R = Me or Et) gives the corresponding dialkyl sulphide-boryl radical $\text{R}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$.³⁴ As for the phosphine-boryl radicals, the ^{11}B and H_α splittings indicate a near-planar boron radical centre [$\text{Me}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$ shows $a(^{11}\text{B})$ 23.2, $a(2\text{H}_\alpha)$ 16.6 G, and g 2.0017 at 149 K]. Similar factors to those involved in inducing planarity for the phosphine-boryl radical would account for the configuration of $\text{R}_2\text{S}\rightarrow\dot{\text{B}}\text{H}_2$.

1.3. CARBON-CENTRED RADICALS

The shapes of carbon-centred radicals have aroused considerable interest and some controversy in recent years. The configurational preference of alkyl radicals would be expected to be less strong than that of the planar carbocations (R_3C^+) and the pyramidal carbanions (R_3C^-). The methyl radical has a planar equilibrium geometry with the

unpaired electron in a C-2p_x orbital perpendicular to the molecular plane. All the higher alkyl radicals are pyramidal, although the deviation from planarity can be very small, and the barriers to inversion at the radical centre are usually very low. For example, the slightly non-planar geometry of the ethyl radical (1.26) is determined by torsional



(1.26)

and hyperconjugative effects; inversion at the radical centre is coupled to rotation about the C_α—C_β bond. Similar factors are responsible for the more pronounced non-planar equilibrium geometry of the isopropyl and t-butyl radicals.²¹

E.s.r. spectroscopy has been of much use in determining the shapes of carbon-centred radicals, and has the distinct advantage that the spectrum of the radical in its electronic ground state is recorded. Hyperfine splitting from an α-¹³C nucleus affords important information and is a particularly sensitive measure of non-planarity,³⁵ since it depends directly on the C_α-2s character of the SOMO. The hyperfine splittings for the methyl radical and fluorinated methyl radicals are shown in Table 1.2, along with the percentage unpaired electron occupation of the C-2s atomic orbital computed from $a(^{13}\text{C}_\alpha)$. The splitting corresponding to one unpaired electron in a pure C-2s orbital is 1115.4 G³⁶ and hence the ¹³C splitting for the methyl radical corresponds

Table 1.2 Hyperfine splittings of methyl and fluorinated methyl radicals.³⁵

| Radical | Hyperfine splitting (G) | | | Unpaired electron population of C _α -2s atomic orbital (%) |
|--------------------|-------------------------|---------------------|-------|---|
| | a(H) | a(¹³ C) | a(F) | |
| ·CH ₃ | 23.0 | 38.5 | — | 3.4 |
| ·CH ₂ F | 21.1 | 54.8 | 64.3 | 4.9 |
| ·CHF ₂ | 22.2 | 148.8 | 84.2 | 13.3 |
| ·CF ₃ | — | 271.6 | 142.4 | 24.4 |

to 3.4% population of the C-2s atomic orbital, whereas for F₃C· this rises to 24.4%. The hyperfine splittings for C_α and H_α in the methyl group arise by spin-polarisation, and are proportional to the spin density on C_α: a(H_α) is given by the McConnell equation (16)^{37,38} where Q is a proportionality constant (equal to 23.0 G³⁸ for the methyl radical) and

$$a(H_{\alpha}) = Q\rho_{c\alpha}^{\pi} \quad (16)$$

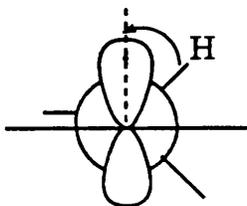
$\rho_{c\alpha}^{\pi}$ is the π unpaired electron spin population on C_α.

The magnitude of the β -proton splitting in π radicals is often greater than that of the α -splitting. Spin-polarisation makes only a small contribution to this splitting, the principal mechanism being hyperconjugative delocalization in which a small amount of the unpaired

electron is transferred from the SOMO to the β -C—H bond, leading to a positive spin density at the β -proton. The β -proton splitting can be described by the Heller-McConnell equation^{39,40} (17) in which A and B are constants relating to spin-polarization and hyperconjugative

$$a(H_\beta) = (A + B \cos^2\theta)\rho_{ca}^* \quad (17)$$

mechanisms respectively (A is *ca.* 1.0 G and B is *ca.* 56 G and θ is the dihedral angle shown in (1.27). This type of interaction is most effective when the β -C—H bond is perpendicular to the nodal plane (*i.e.* it eclipses the SOMO) and $\cos^2\theta = 1$.



(1.27)

Increasing methylation of the α -carbon atom also causes distortion from planarity at the radical centre. Thus the *t*-butyl radical is quite strongly pyramidal, and each CH_3 —C bond is calculated to be 22.1° out of the plane of the remaining $\text{C}_2\text{C}'$ moiety.²¹ The pyramidalization of the radical simultaneously maximises hyperconjugative stabilization and minimises torsional interactions between the methyl groups and the radical centre.²¹

1.3.1. Reactions of Alkyl Radicals

Addition Reactions

Alkyl radicals add to a variety of unsaturated compounds including alkenes, alkynes, aromatic molecules, and carbonyl compounds. Enthalpic, polar and steric effects are responsible for determining the rate and orientation of the addition of alkyl radicals to alkenes.^{42,43} An overview of these effects can be obtained by considering addition of the unhindered nucleophilic methyl radical, the more nucleophilic but hindered t-butyl radical, and the electrophilic trifluoromethyl radical to ethene and to monosubstituted or 1,1-disubstituted ethenes carrying electron donating or electron withdrawing groups. Table 1.3 gives the rate coefficients for representative addition reactions.

From Table 1.3 the influence of polar and steric effects can be seen. In all reactions addition takes place preferentially at the unsubstituted end of the double bond, which can be attributed to steric repulsion. Polar effects also influence the rate of addition, thus the electrophilic $F_3C\cdot$ adds more rapidly to alkenes with electron donating alkyl substituents. In tri- and tetra-substituted ethenes, steric effects are pre-eminent, but where polar and steric effects are in opposition, polar effects may be decisive, influencing rate and magnitude of the orientation ratio.

For addition of the nucleophilic t-butyl radical to a wide variety of alkenes a good correlation exists between the electron affinity of the alkene and the logarithm of the rate constant,⁴⁴ indicating that the SOMO-LUMO interaction is dominant and the activation energy

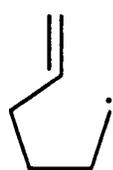
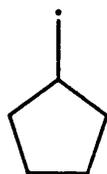
Table 1.3 Relative rates of addition alkyl radicals to alkenes at 282 K.

| | Me ^a | Bu ^b | F ₃ C ^c |
|--------------------|-----------------|-----------------|-------------------------------|
| Ethene | 1.03 | 1.20 | 0.26 |
| Fluoroethene | — | 26 | 0.09 |
| 1,1-difluoroethene | — | 538 | 0.01 |
| Propene | 1.00 | 1.00 | 1.00 |
| 2-Methylpropene | 2.14 | 0.86 | 4.66 |
| t-Butylethene | — | 0.16 | — |
| Tetramethylethene | 0.18 | 0.04 | — |

^a Data taken from C. J. Ctevenovic and R. J. Irwin, *J. Chem. Phys.*, 1967, **46**, 1694. ^b Data taken from K. Munger and H. Fischer, *Int. J. Chem. Kinetics*, 1985, **17**, 809; ^c Data taken from H. C. Low, J. M. Tedder, and J. C. Walton, *Int. J. Chem. Kinetics*, 1978, **10**, 325.

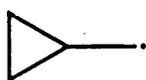
decreases as the LUMO energy decreases.

The hex-5-enyl radical (**1.28**) undergoes irreversible⁴⁵ cyclisation to give mainly the cyclopentylmethyl radical^{49,50} (**1.29**), along with a trace of cyclohexyl radical (**1.30**) [yield (**1.29**)/yield (**1.30**) = 72 at 298 K⁵²].

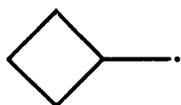
**(1.28)****(1.29)****(1.30)****(1.31)**

The stereoelectronic⁵³ requirements of the transition state for addition to a C=C bond can be more readily accommodated if 1,5-*exo* rather than 1,6-*endo* cyclisation takes place and the transition state for 1,5-*exo* cyclisation is thought to have the chair-like structure (1.31).

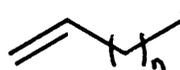
The β -scission of (1.29) and of higher cycloalkylmethyl radicals (the reverse of the cyclisation) to give ring opened products is endothermic.⁵⁰ However, cyclopropylmethyl (1.32) and cyclobutylmethyl (1.33) radicals undergo relatively rapid ring opening to relieve ring strain



(1.32)



(1.33)



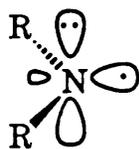
(1.34)

strain, and give ω -alkenyl radicals. Cyclopropylmethyl radicals have been shown by e.s.r. spectroscopy to undergo ring opening even at 133 K,⁵² whereas opening of the cyclobutyl ring is much slower and the radical (1.34; $n = 2$) was not detected below about 250 K.⁵³

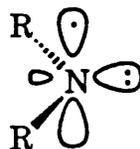
1.4. NITROGEN-CENTRED RADICALS

Many different types of nitrogen-centred radicals are known. Aminium cation radicals ($X_3N^{+\cdot}$) are isoelectronic counterparts of borane radical anions ($X_3B^{-\cdot}$) and neutral alkyl radicals (X_3C^{\cdot}). Much attention has been directed to determining the structure and electronic configurations of the neutral aminyl radicals (X_2N^{\cdot}), because the radical

centre must accommodate both lone pair and unpaired electron, making two electronic ground states feasible these are a σ radical (1.35) with an



(1.35)

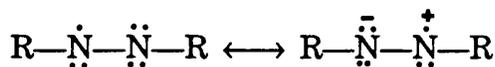


(1.36)

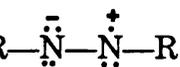
approximately sp^2 hybrid SOMO and $2p_x$ lone pair, or a $2p_x$ SOMO and an sp^2 orbital containing the lone pair (1.36).

1.4.1. Aminyl Radicals

Aminyl radicals may be generated by u.v. irradiation of a hydrazine⁵⁴ or a tetrazine⁵⁵ or by photolysing di-t-butyl peroxide in the presence of a dialkylaminophosphane.⁵⁶ Most aminyl radicals are relatively short-lived and can be observed by e.s.r. spectroscopy only at low temperatures. Stability may be increased dramatically by steric shielding of the radical centre; bis(pentachlorophenyl)aminyl $(C_6Cl_5)_2N\cdot$ is stable indefinitely,⁵⁷ and $Bu^tNPr\cdot$ is relatively persistent. Mesomeric stabilisation is possible when the atom in the α -position is able to delocalize the unpaired electron. Examples of this type include hydrazyl (1.37) and alkoxyaminyl radicals (1.38).



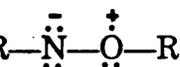
(1.37a)



(1.37b)



(1.38a)



(1.38b)

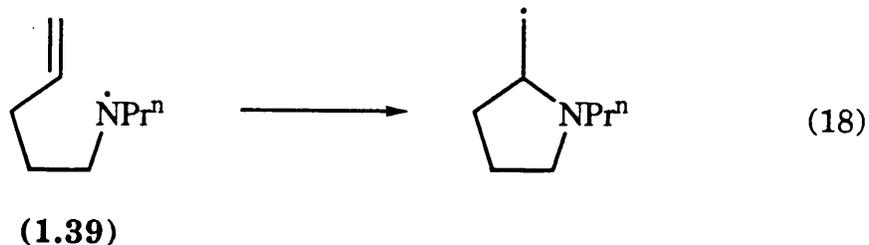
Table 1.4. E.s.r. parameters for selected nitrogen-centred radicals.

| Radical | Solvent ^a | T/K | a(N) | a(H _β) | g |
|-----------------------------------|----------------------|-----|-------|--------------------|--------|
| H ₂ N· ^b | A | 118 | 15.2 | — | 2.0046 |
| Me ₂ N· ^c | B | 183 | 14.78 | 27.36 | 2.0044 |
| Me ₂ NH· ^d | C | 304 | 19.28 | 34.27 | 2.0036 |
| Me ₃ N· ^e | D | 300 | 20.55 | 28.56 | 2.0036 |
| Me ₂ N—O· ^f | E | 300 | 15.90 | 13.48 | 2.0060 |

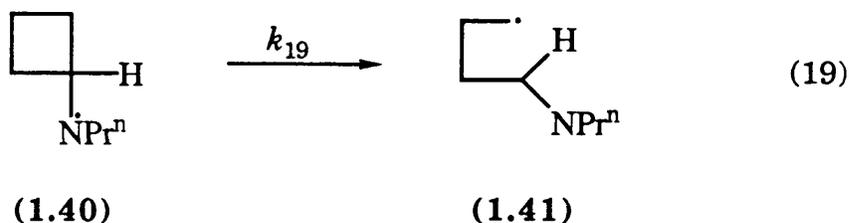
^a Solvent: A = gas phase, B = cyclopropane, C = HClO₄, pH 1, D = MeOH. ^b Data from D. R. Smith and W. A. Seddon, *Can. J. Chem.*, 1970, **48**, 1938. ^c Data from W. C. Danen and T. T. Kensler, *J. Am. Chem. Soc.*, 1970, **92**, 5235. ^d Data from ref. 59. ^e Data from R. W. Fessenden and P. Neta, *J. Phys Chem.*, 1972, **76**, 2857. ^f Data from C. Darne and J. Pariot, *Intern. J. Radiation Phys. Chem.*, 1972, **4**, 11.

Most aminyl radicals have a π electronic ground state (1.36), as confirmed by the nitrogen splitting which usually has a value between 10 and 20 G. Table 1.4 gives parameters for a number of nitrogen-centred radicals. Rearrangements of dialkylaminyl radicals akin to those observed with carbon-centred radicals are known.

In contrast to the rapid cyclisation of the hex-5-enyl radical, it was found that the pentenylaminyl radical (1.39) did not undergo cyclization [equation (18)] as judged by e.s.r. spectroscopy.⁵⁸ Both cyclopropyl- and cyclobutyl-aminyl radicals undergo rapid ring opening rearrangement. With the former species, the ring-opened radical could



be detected by e.s.r. spectroscopy even at the lowest attainable temperature (133 K). However, the aminyl radical (1.40) underwent ring opening more slowly and between 170 and 270 K both (1.40) and the acyclic radical (1.41) could be detected by e.s.r. spectroscopy, enabling the rate coefficient for ring cleavage [equation (19)] to be measured. The



temperature dependence of k_{19} is given by $\log (k_{19}/\text{s}^{-1}) = (12.8 \pm 1.5) - (43.9 \pm 6.0)/2.3RT \text{ kJ mol}^{-1}$ and at 282 K the value of k_{19} is $5.06 \times 10^4 \text{ s}^{-1}$.⁵⁹

1.4.2. Aminium Radical Cations

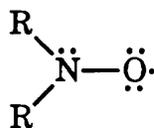
Transient dialkylaminium radical cations may be generated by the photolysis of *N*-chlorodialkylamine in sulphuric acid^{60,61} and many have been studied by e.s.r. spectroscopy.

The nitrogen splitting for $\text{R}_2\dot{\text{N}}\text{H}^+$ is larger than that for the

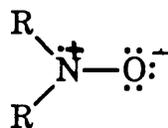
corresponding aminyl radical, for example the values of $a(\text{N})$ for $\text{Me}_2\text{N}^\cdot$ and $\text{Me}_2\text{NH}^{+\cdot}$ are 14.78 and 19.28 G, respectively. Aminium radicals are planar⁶² at nitrogen with an N-2p_x SOMO, according to both experimental and molecular orbital calculation. The methyl proton coupling in $\text{Me}_2\text{NH}^{+\cdot}$ (34.27 G)⁶¹ is significantly larger than $a(\text{H})$ for $\text{Me}_2\text{N}^\cdot$ (27.36 G).⁶¹ This difference has been explained in terms of more effective $\beta\text{-C-H}$ hyperconjugation in the aminium radical, because of better energetic matching between the N-2p_x SOMO and the filled $\beta\text{-CH}_3$ group π orbital. In the charged radical, the CNC bond angle is calculated to be 9° larger than in the neutral radical.⁶³

1.4.3. Nitroxide Radicals

Nitroxide radicals are isoelectronic with aminyl-borane radicals, for example dimethyl nitroxide ($\text{Me}_2\ddot{\text{N}}-\dot{\text{O}} \equiv \text{Me}_2\overset{+}{\text{N}}-\overset{-}{\text{O}}^\cdot$) is isoelectronic with dimethylaminyl-borane ($\text{Me}_2\dot{\text{N}}\rightarrow\text{BH}_3$). Nitroxide radicals which possess no α - or β -hydrogen atoms are very persistent, unlike the aminyl-boranes, and show no tendency to dimerize, react with oxygen or undergo β -scission. Their persistence is attributable to an inherently stable electronic configuration about the nitrogen and oxygen atoms. Two



(1.42)

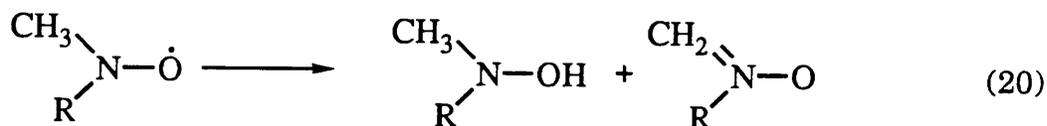


(1.43)

canonic structures (1.42) and (1.43) may be drawn to represent the three-

electron bonding arrangement. The values of $a(\text{N})$ (ca. 13 - 14 G) indicate that nitroxides must be close to planar at nitrogen. Their g values (ca. 2.0060) are significantly greater than those of $\text{Me}_2\dot{\text{N}}\text{H}^+$ (2.0034) and $\text{Me}_2\text{N}^\cdot$ (2.0047) and reflect the delocalisation of the unpaired electron onto the oxygen atom.

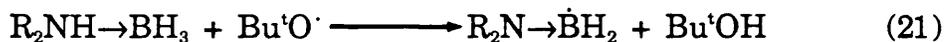
Nitroxides which contain $\beta\text{-C-H}$ bonds are relatively short lived and undergo disproportionation to give hydroxylamine and a nitron [e.g. equation (20)].



1.4.4. Radicals Derived From Secondary Amine-Boranes

The reaction of $\text{Bu}^t\text{O}^\cdot$ with dimethylamine-borane in solution has been shown to give the dimethylaminyl-borane radical $\text{Me}_2\dot{\text{N}}\text{-BH}_3$ [$a(3\text{H})$ 46.4, $a(6\text{H})$ 23.2, $a(^{14}\text{N})$ 17.4, $a(^{11}\text{B})$ 11.6 G, and g 2.0039 at 175 K]⁶⁴; the corresponding aminyl-borane radicals were also obtained from the reaction of $\text{Bu}^t\text{O}^\cdot$ with $\text{Et}_2\text{NH}\text{-BH}_3$ and $\text{Pr}^i_2\text{NH}\text{-BH}_3$. It was proposed²⁰ that t-butoxyl radicals initially abstract hydrogen from the BH_3 group to give the amine-boryl radical, (1.44) as the kinetically controlled product [equation (21)], but that this very rapidly isomerises by abstracting a hydrogen from nitrogen in the parent to give the aminyl-borane radical (1.45) [equation (22)] as the thermodynamically controlled product. The

initial formation of the amine-boryl radical, rather than the more stable aminyl-borane radical, was ascribed to polar effects which operate in the



transition state for reaction (21). The t-butoxyl radical is strongly electrophilic and thus prefers to abstract electron-rich hydrogen from boron, rather than electron deficient hydrogen from nitrogen.

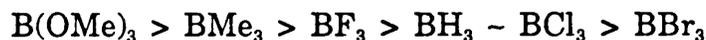
1.5 PREPARATION OF AMINE-BORANES

The stability of an amine-borane complex depends on the groups attached to both nitrogen and boron. The $\text{p}K_a$ of the protonated amine must exceed 5.0⁶⁵ for the borane complex to have reasonable stability and all aliphatic amines have greater basicities than this. In general, aromatic amines do not form stable complexes, although *N,N*-dimethylaniline⁶⁵ and pyridine⁶⁵ ($\text{p}K_a$ 5.1 and 5.2, respectively) are borderline and the borane complexes have been isolated.

The stability of an aliphatic amine-borane is reduced when one or more bulky groups is attached to nitrogen. Thus, the borane complexes of sterically hindered complexes such as Bu^tNH_2 and Et_3N are essentially completely dissociated in the vapour phase, and are useful hydroborating agents in solution.⁶⁶

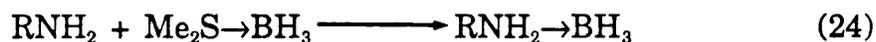
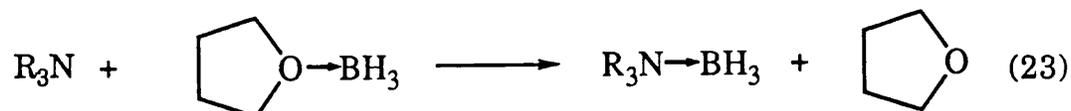
In principle, electron withdrawing groups on boron should increase

the strength of the nitrogen-boron dative bond, but often the lone pairs of electrons associated with such groups engage in π bonding to the vacant 2p orbital on boron, making it a weaker Lewis acid. Thermodynamic and qualitative observations indicate that the stability of the N \rightarrow B bond, with respect to a given nitrogen donor, increases in the following series.⁶⁷



The position of BH_3 has been determined by estimates of the bridge dissociation energy of diborane.⁶⁸ It should be noted that BF_3 forms relatively weakly bound complexes, since fluorine has a significant tendency to form π bonds with boron.

Amine-borane complexes containing the BH_3 group are very easily synthesised by displacement of an oxygen^{69,70} or sulphur⁷¹ base from the BH_3 moiety [*e.g.* equations (23) and (24)]. For these starting materials,



the hydrogen-bridged bonds in diborane have already been broken symmetrically by the base and these routes to amine-boranes were adopted throughout most of the present work.

Another well-established procedure involves elimination of dihydrogen from an amine-hydrochloride and metal borohydride^{72,73} [equation (25)]. Lithium borohydride is often used as it is more soluble



in diethyl ether, tetrahydrofuran, and 1,2-dimethoxyethane than sodium borohydride. The reaction is based upon the fact that the N—H bond in the amine hydrochloride is sufficiently acidic and the hydrogen in the borohydride sufficiently hydridic to make dihydrogen elimination favourable.

The direct reaction of a primary amine or, especially, of ammonia with diborane often leads to an ionic compound of the type $\text{H}_2\text{B}(\text{NR}_3)_2^+\text{BH}_4^-$ ⁷⁴ through asymmetric cleavage of the hydrogen bridge in diborane and, consequently, the indirect method is usually used. Primary and secondary amine-boranes have a tendency to lose hydrogen to give an aminoborane which then further reacts to give a cyclic dimer or trimer [equation (26)].



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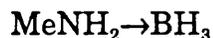
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CHAPTER 2

Radicals Derived From Primary Amine Boranes

2.1 METHYLAMINE-BORANE

E.s.r. spectra were recorded during continuous u.v. irradiation ($\lambda = 240 - 340$ nm) of static liquid samples positioned directly inside the microwave cavity of the spectrometer. The usual primary source of radicals was di-*t*-butyl peroxide [DTBP, equation (1)]. The reaction of *t*-butoxyl radicals with methylamine-borane (2.1) was examined in a



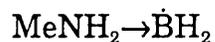
(2.1)

variety of solvents including cyclopropane, oxirane, dimethyl ether, methanol, benzene, *t*-butyl alcohol, and *t*-pentyl alcohol (*t*-pentyl = Pe^t) either singly or as binary mixtures; the amine-borane was insoluble in neat cyclopropane. In each case the system was examined at the lowest accessible temperature; the temperature was then increased in *ca.* 20 K increments to *ca.* 285 K. Most spectra were weak, and use of Bu^tOH-Pe^tOH either as a 3:1 or a 1:1 (v/v) mixture at 282 K gave the highest quality spectra (below 282 K Bu^tOH crystallised out of solution). When

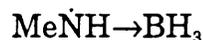
oxirane was the solvent, a narrower tube (2 mm i.d.) was used to reduce dielectric loss. A further improvement in spectrum quality was obtained by replacing $\text{MeNH}_2 \rightarrow \text{BH}_3$ containing natural abundance boron with material enriched to 97.5 atom% ^{11}B [natural abundance boron contains ^{10}B ($I = 3$) 19.8% and ^{11}B ($I = 3/2$) 80.2%, $\gamma^{10}\text{B}/\gamma^{11}\text{B} = 0.335$].

The spectra shown in Figure 2.1(a) and 2.1(b) were obtained when a sample containing $\text{MeNH}_2 \rightarrow \text{BH}_3$ (1.7 M) and DTBP (15% v/v) in $\text{Bu}^t\text{OH}/\text{Pe}^t\text{OH}$ (3:1 v/v) was irradiated at 282 K. Due to the poor signal to noise ratio, a number of spectra were taken and the splittings averaged as shown in Table 2.1.

The spectrum was computer simulated on the basis of $a(3\text{H})$ 63.87, $a(3\text{H}')$ 24.05, $a(1\text{H})$ 19.44, $a(^{14}\text{N})$ 15.36, $a(^{11}\text{B})$ 13.28 G; it is asymmetric about the centre due to a second-order splitting of *ca.* 1.4 G on the intensity three lines of the BH_3 quartet. The splittings are not in accord with expectation for the methylamine-boryl radical^{1,2} (2.2), however, they are very reasonable for the methylaminyl-borane radical (2.3). The



(2.2)



(2.3)

larger proton splitting is assigned to the BH_3 group and its magnitude shows that hyperconjugative delocalisation of the unpaired electron from nitrogen is much more efficient than delocalisation onto the *N*-methyl group. This is presumably a consequence of the lower electronegativity of boron (2.0) compared with that of nitrogen (3.0) which leads to a closer energetic match between the $\text{N-}2p_x$ orbital and the filled π group

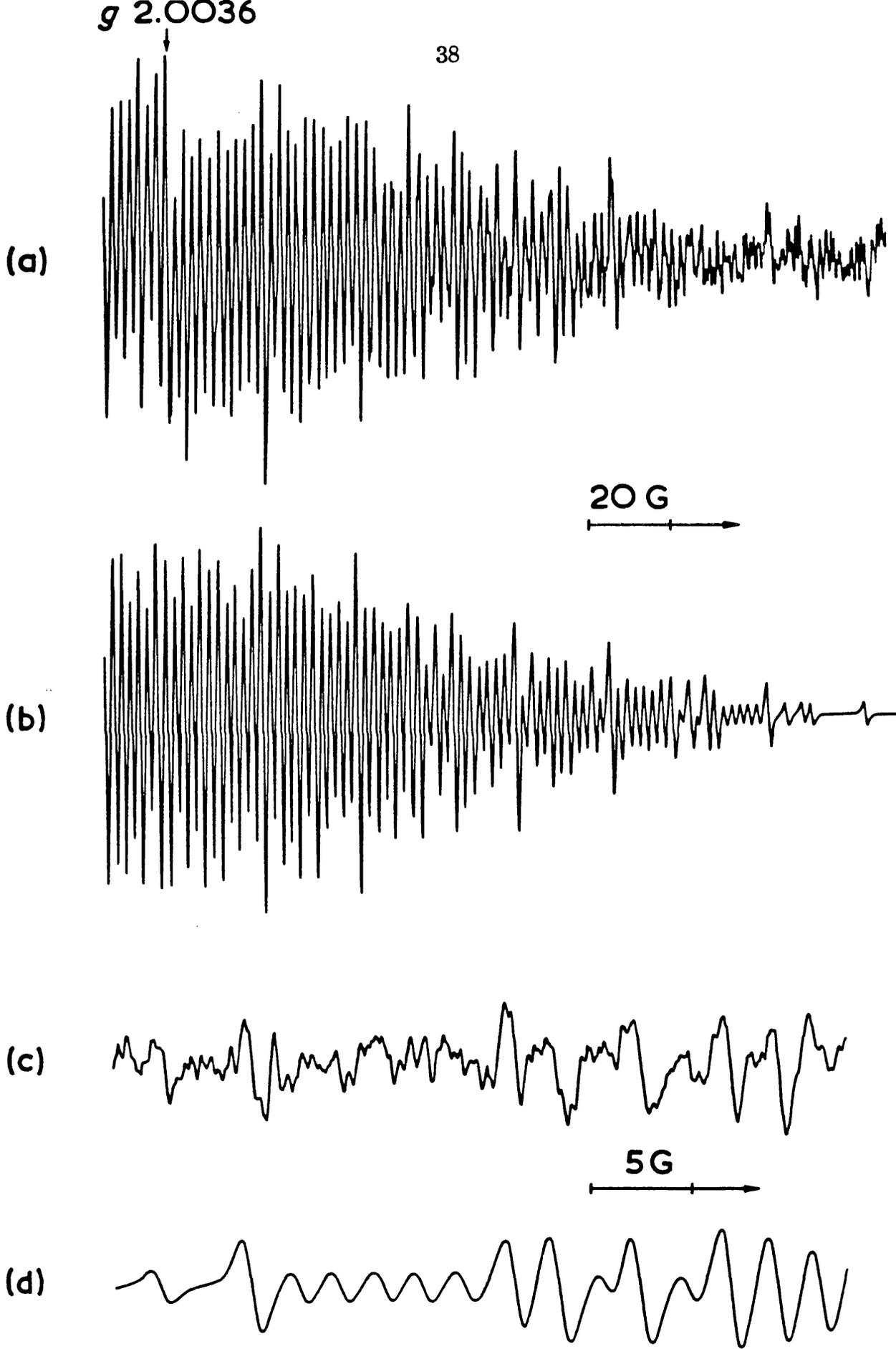


Figure 2.1

Legend to Figure 2.1

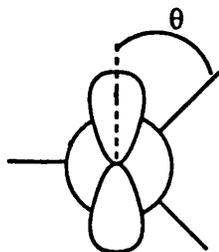
(a) High field half of the e.s.r. spectrum of the methylaminyborane radical (**2.3**) (97.5 atom% ^{11}B) in $\text{Bu}^t\text{OH-Pe}^t\text{OH}$ (3:1 v/v) at 283 K. (b) Computer simulation of (a) using the following splitting constants: 63.87 (3H), 24.05 (3H'), 19.44 (1H), 13.28 (^{11}B), and 15.36 (^{14}N). The linewidth is 1.0 G and the lineshape is 80% Lorentzian (20% Gaussian). (c) Low field region of the spectrum of (**2.3**), beginning with line 4, at 262 K. (d) Computer simulation of (c) using the same data as for (b).

Table 2.1. Measured hyperfine splittings (in G) from eleven experimental spectra.

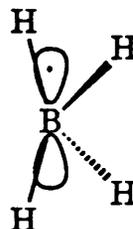
| $a(^{11}\text{B})$ | $a(^{14}\text{N})$ | $a(1\text{H})$ | $a(3\text{H}')$ | $a(3\text{H})$ |
|------------------------|--------------------|----------------|-----------------|----------------|
| 13.30 | 15.60 | 19.48 | 24.12 | 64.19 |
| 13.29 | 15.30 | 19.20 | 23.93 | 63.67 |
| 13.47 | 15.44 | 19.40 | 24.15 | 63.71 |
| 13.25 | 15.20 | 19.24 | 24.00 | 63.73 |
| 13.28 | 15.39 | 19.17 | 23.93 | 64.10 |
| 13.40 | 15.05 | 19.28 | 24.10 | 63.77 |
| 13.40 | 15.05 | 19.28 | 24.10 | — |
| 13.20 | 15.27 | 19.50 | 23.97 | — |
| 13.31 | 15.55 | 19.48 | 24.28 | — |
| 13.38 | 15.17 | 19.33 | 23.98 | — |
| 13.29 | 15.50 | 19.42 | 24.08 | — |
| mean 13.32 | 15.32 | 19.34 | 24.06 | 63.86 |
| std. deviation 0.08 | 0.19 | 0.12 | 0.11 | 0.22 |

orbital of an attached MH_3 substituent when $M = \text{B}$ than when $M = \text{C}$. Assuming free rotation about the $\text{N} \rightarrow \text{B}$ bond in (2.3) and the usual $\cos^2\theta$ [see structure (2.4)] dependence of the β -proton splitting on the dihedral angle, the proton in an eclipsed $\text{B}-\text{H}$ bond would give rise to a splitting of *ca.* 128 G, corresponding to a 25% H-1s contribution to the SOMO.

In fact, the aminyl-borane radicals may legitimately be regarded as derivatives of the perboryl radical H_4B^\cdot (2.5) [$a(2\text{H})$ 107 and $a(2\text{H}')$ 7 G], in which one of the strongly coupled protons has been replaced by an



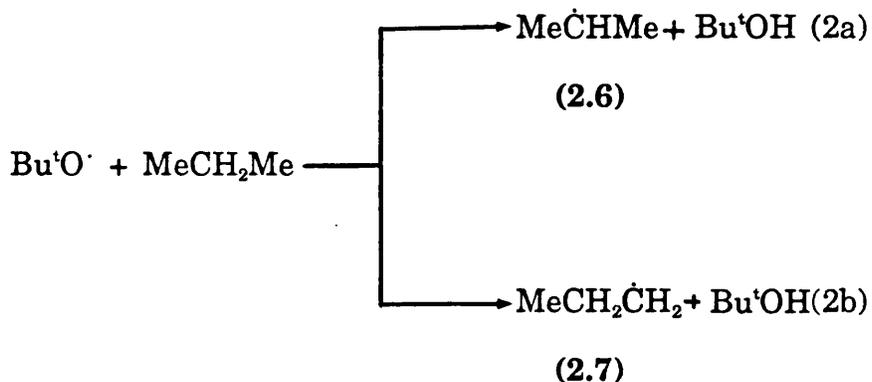
(2.4)



(2.5)

amino group, accompanied by distortion of the remaining BH_3 moiety.

When t-butoxyl radicals are generated in the presence of propane,⁴ the isopropyl radical is produced predominantly [equation (2)], in



preference to the n-propyl radical (2.7), which is less stable than (2.6) by 7-15 kJ mol^{-1} by recent estimates.⁵

When n-propyl bromide was present alongside methylamine-borane and DTBP, only the spectrum of (2.7) (Figure 2.2) was recorded at 282

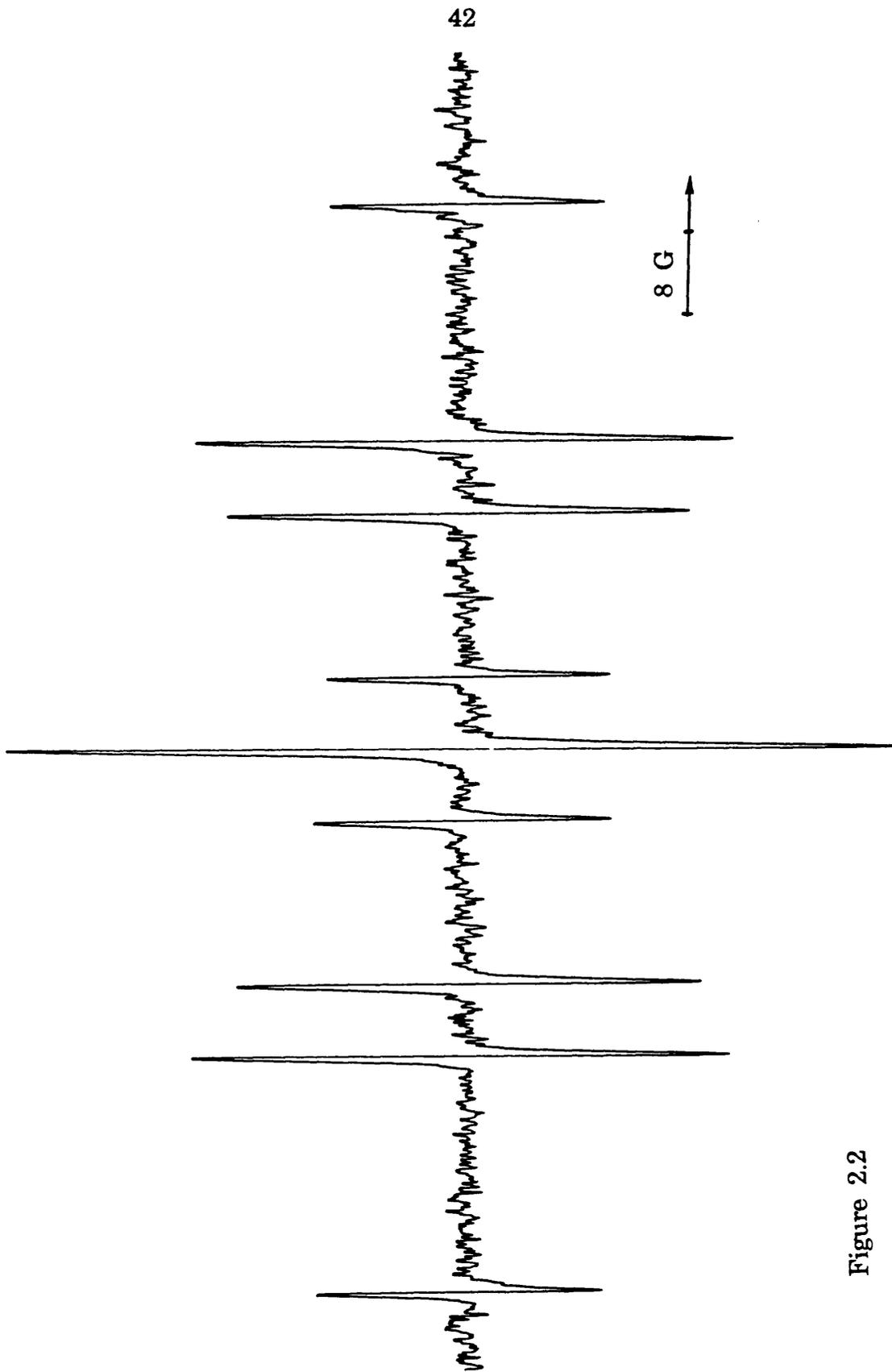


Figure 2.2

Legend to Figure 2.2.

E.s.r. spectrum of the n-propyl radical [$a(2H_a)$ 21.7, $a(2H_b)$ 28.5 G, g 2.0027] obtained by bromine atom abstraction from n-propyl bromide (1.0 M) by $\text{MeNH}_2 \rightarrow \dot{\text{B}}\text{H}_2$ in Bu'OH-Pe'OH (3:1 v/v) at 282 K.

K, and that of (2.3) was not seen. It has been shown previously⁶ that dialkylaminyl-borane radicals do not react with alkyl bromides to give alkyl radicals at significant rates under similar conditions. Hence it is the methylamine-boryl radical which must be intercepted by the n-propyl bromide [equation (3)].



This interpretation was supported by competition experiments using mixtures of n-propyl bromide and t-butyl bromide, which showed that the relative rate of generation of $\text{Bu}^t\cdot$ and $\text{Pr}^n\cdot$ was typical of their formation *via* halogen abstraction by an amine-boryl radical⁶. Making the usual assumptions,⁷ the value of k_4/k_3 was found to be 2.0 at 282 K in $\text{Bu}^t\text{OH-Pe}^t\text{OH}$ (3:1 v/v). In oxirane solvent the value of k_4/k_3 was similar (2.2), but it decreased with decreasing temperature to become 0.77 at 188 K. Methylamine-borane is known⁸ to associate in solution, but the similar value of k_4/k_3 obtained in protic and aprotic solvents suggests that any association of the radical (2.2) with the parent amine-borane does not influence its selectivity appreciably. The inversion of relative rates which takes at low temperature was unexpected, it is probably related to the very rapid nature of the bromine abstraction, to the different steric requirements of the tertiary and primary halides, and to the large degree of electron transfer from the ligated boryl moiety to the alkyl halide in the transition state. Table 2.2 gives details of the

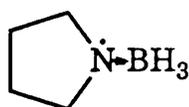
Table 2.2 Relative reactivities of t-butyl and n-propyl bromides towards halogen atom abstraction by ligated boryl radicals ($L \rightarrow \dot{B}H_2$).

| L | Solvent ^a | T/K | $\frac{k_{t-BuBr}}{k_{n-PrBr}}$ | Ref. |
|---------------------------------|----------------------|-----|---------------------------------|----------|
| MeNH ₂ | A | 282 | 2.0 | <i>b</i> |
| MeNH ₂ | B | 282 | 2.2 | <i>b</i> |
| Bu ^t NH ₂ | B | 188 | 0.7 | <i>b</i> |
| H ⁻ | C | 203 | 1.2 | <i>c</i> |
| CN ⁻ | C | 203 | 5.1 | <i>c</i> |
| NH ₃ | D | 261 | 1.5 | <i>e</i> |
| Me ₂ NH | D | 260 | 1.3 | <i>d</i> |
| Me ₃ N | D | 261 | 1.5 | <i>e</i> |
| Et ₃ N | E | 246 | 1.2 | <i>f</i> |
| Bu ₃ P | F | 240 | 5.6 | <i>g</i> |
| Me ₃ Si [•] | C | 203 | 3.4 | <i>h</i> |

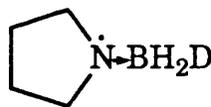
^a Solvent: A = Bu^tOH-Pe^tOH (3:1 v/v), B = oxirane, C = Me₂O-Pe^tOH, (1.3:1 v/v), D = Bu^tOH-Me₂O (4:1 v/v), E = cyclopropane-THF (3:1 v/v), F = cyclopropane. ^b This work. ^c Data from ref. 11. ^d Data from ref. 6. ^e Data from ref. 9. ^f Data from ref. 1. ^g Data from ref. 12. ^h Data from A. Hudson and R. A. Jackson, *Chem. Commun.*, 1969, 699.

relative rates of bromine atom abstraction from Bu^tBr and Pr^nBr for various ligated boryl radicals and for the trimethylsilyl radical.

Previous experiments in which DTBP was photolysed in the presence of *N*-deuteriated pyrrolidine-borane at 258 K gave rise to an e.s.r. spectrum which was completely superimposable on that obtained from the undeuteriated material under the same conditions and assigned to (2.8). This spectrum is sufficiently different from that predicted for the mono-*B*-deuteriated radical (2.9), by assuming that one *B*-proton



(2.8)



(2.9)

splitting is replaced by a deuteron splitting of 0.154 ($= \gamma_D/\gamma_H$) in magnitude, to be confident that the *B*-deuteriated aminyl-borane radical is not formed from the *N*-deuteriated amine-borane. These results show that the aminyl-borane radical is not formed by a 1,2-hydrogen atom shift from N to B following hydrogen atom abstraction from boron by $\text{Bu}^t\text{O}^\cdot$. It was concluded that the dialkylaminyl-borane radical detected by e.s.r. spectroscopy when DTBP is photolysed in the presence of $\text{R}_2\text{NH}\rightarrow\text{BH}_3$ is formed indirectly by the sequence of reactions (5) and (6).

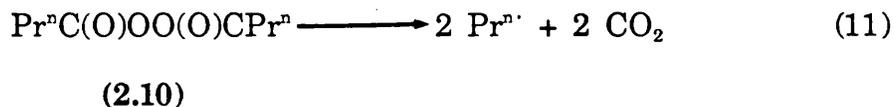


Pe^tOH solvent at 282 K with [PrⁿCl] fixed at 0.96 M, the value of [(2.3)]/[Pr^{n•}] (obtained by computer simulation of the spectrum and extrapolation to zero irradiation time) was measured as a function of [(2.1)] (0.47 - 1.57 M). If equal rate coefficients are assumed for the radical-radical reactions removing Pr^{n•} and (2.3),⁷ it can be shown that

$$k_8/k_9 = [(2.3)][Pr^nCl]/[Pr^{n•}][(2.1)] \quad (10)$$

equation (10) should hold, and indeed all values of k_8/k_9 thus obtained fell within the region 1.7 ± 0.3 . This result provides strong support for the proposal that (2.3) is formed indirectly by reaction (8) when t-butoxyl radicals are generated in the presence of methylamine-borane. It also indicates that the aminyl-borane radical (2.3) does not react with n-propyl chloride to produce n-propyl radicals under the conditions of the experiment.

Photolysis of dibutanoyl peroxide (2.10) (0.8 M) [equation (11)] in the presence of methylamine-borane (1.57 M) at 282 K afforded only a



strong spectrum of the n-propyl radical and (2.3) was not detected ($[(2.3)]/[Pr^{n•}] < 0.1$), showing that the alkyl radical does not react with the amine-borane to generate either (2.2) or (2.3) under experimental conditions.

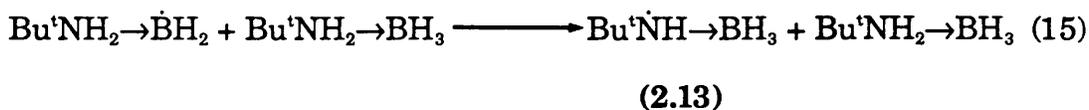
In previous work it was shown that reaction (6) is extremely rapid at low temperatures and n-propyl bromide was needed to intercept a secondary amine-boryl radical [equation (12)]. At 173 K in oxirane-cyclopropane (2.5:1 v/v) the value of k_6/k_{12} is 0.7 ± 0.1 .⁶ It is reasonable



to assume that the rate of halogen atom abstraction from a given alkyl halide should be the same for primary and secondary amine-boryl radicals and, if we further assume that the value of k_6/k_{12} will be little different at 282 K, it follows that reaction (6) is much faster than reaction (8) under the same conditions. This would be expected since progressive methylation at nitrogen will lead to a weakening of the N—H bond in $\text{Me}_n\text{NH}_{3-n}\rightarrow\text{BH}_3$ along the series $n = 0 > 1 > 2$ while having little effect on the strength of the B—H bond, (see Chapter 3 for relevant M.O. calculations).

It was not possible to observe the e.s.r. spectrum of $\text{MeNH}_2\rightarrow\text{BH}_2$ (2.2) at low temperatures in oxirane, even when relatively low concentrations of (2.1) (0.5 M) were present. However, the spectrum of (2.2) could be difficult to detect because of high multiplicity and relatively broad lines which would be expected.^{1,2}

reaction producing (2.13) [equation (15)].



The poor quality of the spectrum of (2.13) is evidently a consequence of its high multiplicity which in turn arises from a significant splitting from the γ -protons of the t-butyl group. This problem was overcome by using [$^2\text{H}_9$]-t-butylamine-borane (containing ^{11}B and ^{10}B in natural abundance) and at 237 K the spectrum shown in Figure 2.3(a) was obtained. This spectrum can be computer simulated using $a(3\text{H})$ 65.9, $a(1\text{H})$ 19.1, $a(^{14}\text{N})$ 15.1, $a(^{11}\text{B})$ 13.5 G and undoubtedly arises from t- $\text{C}_4\text{D}_9\dot{\text{N}}\text{H} \rightarrow \text{BH}_3$; the contribution from the ^{10}B containing radical [$a(^{10}\text{B})$ 4.52 G] is clearly evident. The magnitude of the ^{14}N splitting and the appreciable hyperconjugative delocalisation onto the BH_3 group indicate that this radical is essentially planar at the radical centre. The spectroscopic parameters for the aminyl-boranes (2.3) and (2.13) are compared with those for the isoelectronic alkyl radicals and related species in Table 2.3. As with methylamine-borane, the spectrum of the appropriate alkyl radical was observed in the presence of an alkyl bromide, indicating that the amine-boryl radical (2.12) was abstracting a halogen atom. Competition experiments showed that $\text{Bu}^{\cdot}\text{Br}$ is 0.7 times as reactive as $\text{Pr}^{\cdot}\text{Br}$ towards (2.12) at 186 K in oxirane solvent. The selectivity of (2.12) is thus very similar to that of (2.2) under similar conditions.

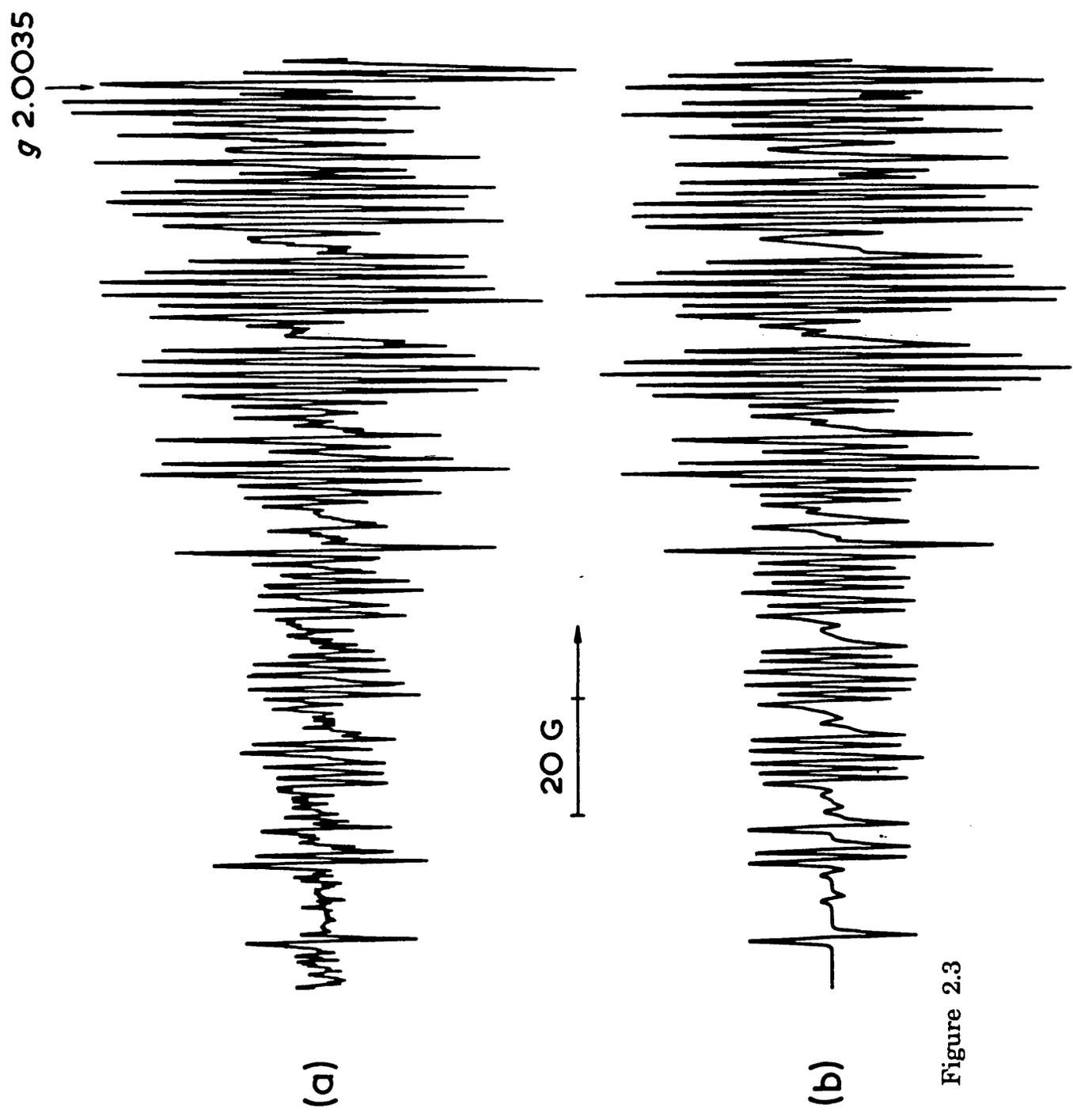


Figure 2.3

Legend to Figure 2.3

(a) Low field half of the e.s.r. spectrum of the [$^2\text{H}_9$]-t-butylaminyborane radical (2.13) containing ^{11}B and ^{10}B in natural abundance in cyclopropane-oxirane (1:1 v/v) at 237 K (b) Computer simulation of (a) using the following splitting constants: 65.9 (3H), 19.1 (1H), 15.1 (^{14}N), 13.5 (^{11}B), [4.52 (^{10}B)]. The linewidth is 1.0 G and the lineshape is Gaussian.

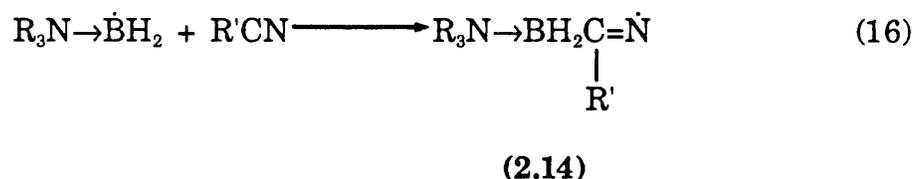
Table 2.3. E.s.r. parameters for aminyl-borane radicals and related species.

| Radical | Solvent ^e | T/K | g factor ^b | $a(^{14}\text{N})$ | $a(^{11}\text{B})$ | Hyperfine splittings (G) | |
|---|----------------------|-----|-----------------------|--------------------|--------------------|---------------------------------------|--|
| | | | | | | Others | |
| $\text{Me}\dot{\text{N}}(\text{H})\rightarrow\text{BH}_3$ (2.1) | A | 283 | 2.0036 | 15.4 | 13.3 | 63.9 (3 BH), 24.1 (3 CH), 19.4 (NH) | |
| $\text{Bu}^t\dot{\text{N}}(\text{H})\rightarrow\text{BH}_3$ (2.13) ^c | B | 225 | 2.0035 | 15.1 | 13.5 | 65.9 (3 BH), 19.1 (NH) | |
| $\text{Me}_2\dot{\text{N}}\rightarrow\text{BH}_3$ ^d | C | 175 | 2.0039 | 17.4 | 11.6 | 46.4 (3 BH), 23.2 (6 CH) | |
| $\text{MeN}_3\rightarrow\dot{\text{B}}\text{H}_2$ ^e | D | 280 | 2.0022 | 1.4 | 51.3 | 9.6 (2 BH), 1.4 (9 CH) | |
| $\text{Me}\dot{\text{C}}(\text{H})\text{Me}'$ | E | 273 | 2.0027 | 41.5 ^f | — | 24.7 (6 CH), 21.9 (1 CH) | |
| $\text{Bu}^t\dot{\text{C}}(\text{H})\text{Me}^h$ | E | 236 | 2.0027 | — | — | 25.1 (3 CH), 21.8 (1 CH), 0.56 (9 CH) | |
| $\text{Me}\dot{\text{N}}(\text{H})\rightarrow\text{O}^j$ | F | 298 | — | 13.8 | — | 13.8 (3 CH), 13.8 (1 NH) | |
| $\text{Bu}^t\dot{\text{N}}(\text{H})\rightarrow\text{O}^k$ | G | 298 | 2.0060 | 13.0 | — | 10.6 (NH) | |

^a A = Bu¹OH-Pe¹OH (3:1 v/v), B = cyclopropane-oxirane (1:1 v/v), C = cyclopropane-oxirane (1:2.5 v/v), D = Bu¹OH-Me₂O (4:1 v/v), E = cyclopropane, F = MeOH, G = toluene. ^b Corrected for second order effects. ^c Data for the [²H₉]Bu¹-containing radical. ^d Data from ref. 3. ^e Data from ref. 2. ^f Data from D. Griller and K. F. Preston, *J. Am. Chem. Soc.*, 1979, 101, 1975. ^g ¹³C-Splitting. ^h This work; generated by u.v. irradiation of DTBP (20% v/v) and Bu¹CH₂Me (20% v/v) in cyclopropane. ⁱ Data from J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, 45, 654. ^j The radicals are nitroxides; the BH₃ group is isoelectronic with an oxygen atom. ^k Data from Th. A. J. W. Wajer, A. Mackor, and Th. J. DeBoer, *Tetrahedron*, 1969, 25, 175.

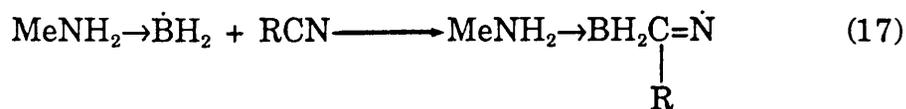
2.3 REACTION OF PRIMARY AMINE-BORYL RADICALS WITH NITRILES

When the trialkylamine-boryl radical^{1,10} ($R_3N \rightarrow \dot{B}H_2$) was generated in the presence of a nitrile (RCN ; $R = \text{alkyl}$) at 257 K the spectrum of the iminyl radical (2.14) was observed [equation (16)]. Likewise, the



ammonia-boryl radical ($R = H$) undergoes similar addition at 255 to 270 K, but under comparable conditions the secondary amine-boryl radical $Me_2NH \rightarrow \dot{B}H_2$ could not be trapped prior to its isomerisation to $Me\dot{N}H \rightarrow BH_3$ by abstraction from the parent amine-borane.⁶ Such isomerisation cannot take place for trialkylamine-boryl radicals. In the absence of a nitrile, the spectrum of ammonia-boryl radical was obtained, indicating that isomerisation to the aminyl-borane radical (if it occurs) is very slow compared with the self reaction of $H_3N \rightarrow \dot{B}H_2$.

Isomerisation of the primary amine-boryl radical is slower than that of the secondary amine-boryl radical (see before), and these species could be trapped by a variety of nitriles present in moderate concentrations [equation (17)]. The e.s.r. spectrum of (2.15; $R = 1\text{-Ad}$) was observed during u.v. irradiation at 282 K of a Bu^tOH/Pe^tOH (3:1 v/v) solution containing $MeNH_2 \rightarrow BH_3$ (1.2 M), DTBP (20% v/v), and 1-cyanoadamantane (*ca.* 0.5 M); no spectrum of the aminyl-borane radical



(2.15)

was detected. With acetonitrile (*ca.* 1.0 M) the spectrum of the adduct (2.15; R = Me) was observed and again the spectrum of (2.3) was not detected. The spectroscopic parameters of all iminyl radicals are collected in Table 2.3.

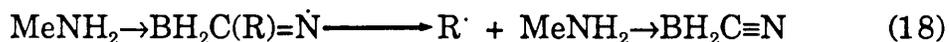
Table 2.3 Iminyl radicals $\text{L} \rightarrow \text{BH}_2\text{C}(\text{R})=\dot{\text{N}}$ derived from addition of $\text{L} \rightarrow \dot{\text{B}}\text{H}_2$ to nitriles.

| L | R | Solvent ^a | T/K | <i>g</i> Factor | $\alpha(^{14}\text{N})$ | $\alpha(^{11}\text{B})$ | Others |
|---------------------------------|-----------------|----------------------|-----|-----------------|-------------------------|-------------------------|--------------------------------------|
| MeNH ₂ | Me | A | 282 | 2.0025 | 9.5 | 22.5 | 2.7 3(H) ^b |
| | CD ₃ | A | 281 | 2.0025 | 9.5 | 22.6 | — |
| | 1-Ad | A | 283 | 2.0027 | 9.4 | 22.2 | — |
| Bu ^t NH ₂ | CD ₃ | A | 282 | 2.0025 | 9.4 | 22.5 | — |
| | Me | B | 234 | 2.0025 | 9.3 | 22.4 | — |
| | Et | B | 236 | 2.0027 | 9.5 | 22.4 | 2.8 (3H) |
| | Pr ⁱ | B | 234 | 2.0027 | 9.3 | 22.5 | 3.1 (1H) |
| | Bu ^t | B | 223 | 2.0026 | 9.3 | 20.9 | — |
| | 1-Ad | B | 234 | 2.0027 | 9.3 | 21.6 | 13.7 (¹³ C) ^c |

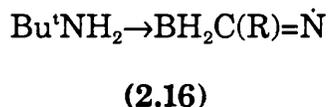
^a A = Bu^tOH-Pe^tOH (3:1 v/v), B = cyclopropane-oxirane (1:1 v/v). ^b Poorly resolved triplet splitting of *ca.* 0.6 G from the BH₂ protons also present. ^c Data for the iminyl radical from 1-Ad¹³CN.

In addition to the splitting of 2.7 G [absent for (2.15; R = CD₃)] from the C-methyl protons, (2.15; R = Me) also showed a poorly resolved splitting of *ca.* 0.6 G from the protons attached to boron. This last splitting was absent (as were lines due to the ¹⁰B-containing radical) when MeNH₂→¹¹BD₃ was used, resulting in a much more intense spectrum.

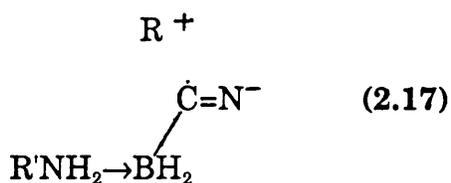
With *t*-butyl or isopropyl cyanide (1.5 M) in Bu^tOH-Pe^tOH (3:1 v/v) solvent at 282 K no iminyl radical was detected, but only the spectra of the alkyl radicals produced by their β-scission were observed [equation (18); R = Prⁱ or Bu^t].



In similar experiments with *t*-butylamine-borane (2.11) (1.2 M) at 282 K, the amine-boryl radical was trapped by CD₃CN (1.2 M) before it underwent β-scission and only (2.16; R = CD₃) was detected. Since (2.11) is more soluble than (2.1), the former was used to investigate the



the addition of amine-boryl radicals to nitriles over a range of temperatures. With methyl, ethyl, isopropyl, t-butyl or 1-adamantyl cyanides (RCN) at 234 K, only the spectrum of the iminyl adduct (2.16) was observed (see Table 2.3), but as the temperature was increased the spectrum of R \cdot produced by its β -scission¹⁴ also became evident for some of the nitriles [*cf.* equation (18)]. As judged from the intensities of the e.s.r. spectra of both (2.16) and R \cdot , the ease of β -scission increased along the series R = CH₃, 1-Ad \ll Et < Prⁱ < Bu^t, in parallel with decreasing strength of the R—C bond. At 245 K, only the spectrum of (2.16; R = Prⁱ) was detected, but the spectrum of Bu^t \cdot was present alongside that of (2.16; R = Bu^t). At *ca.* 255 K, the spectrum of Prⁱ \cdot became apparent and above *ca.* 275 only this radical was detected. The spectrum of (2.16; R = 1-Ad) is shown in Figure 2.4; no β -scission of this radical nor of (2.16; R = Me) was evident up to 306 K. 1-Adamantyl and methyl radicals are destabilized with respect to secondary and normal tertiary alkyl radicals, accounting for this result. Also charge separation of the type illustrated in (2.17) could be important in the transition state and



this would also disfavour β -scission when R is 1-adamantyl or methyl since the corresponding carbocations are highly destabilized.

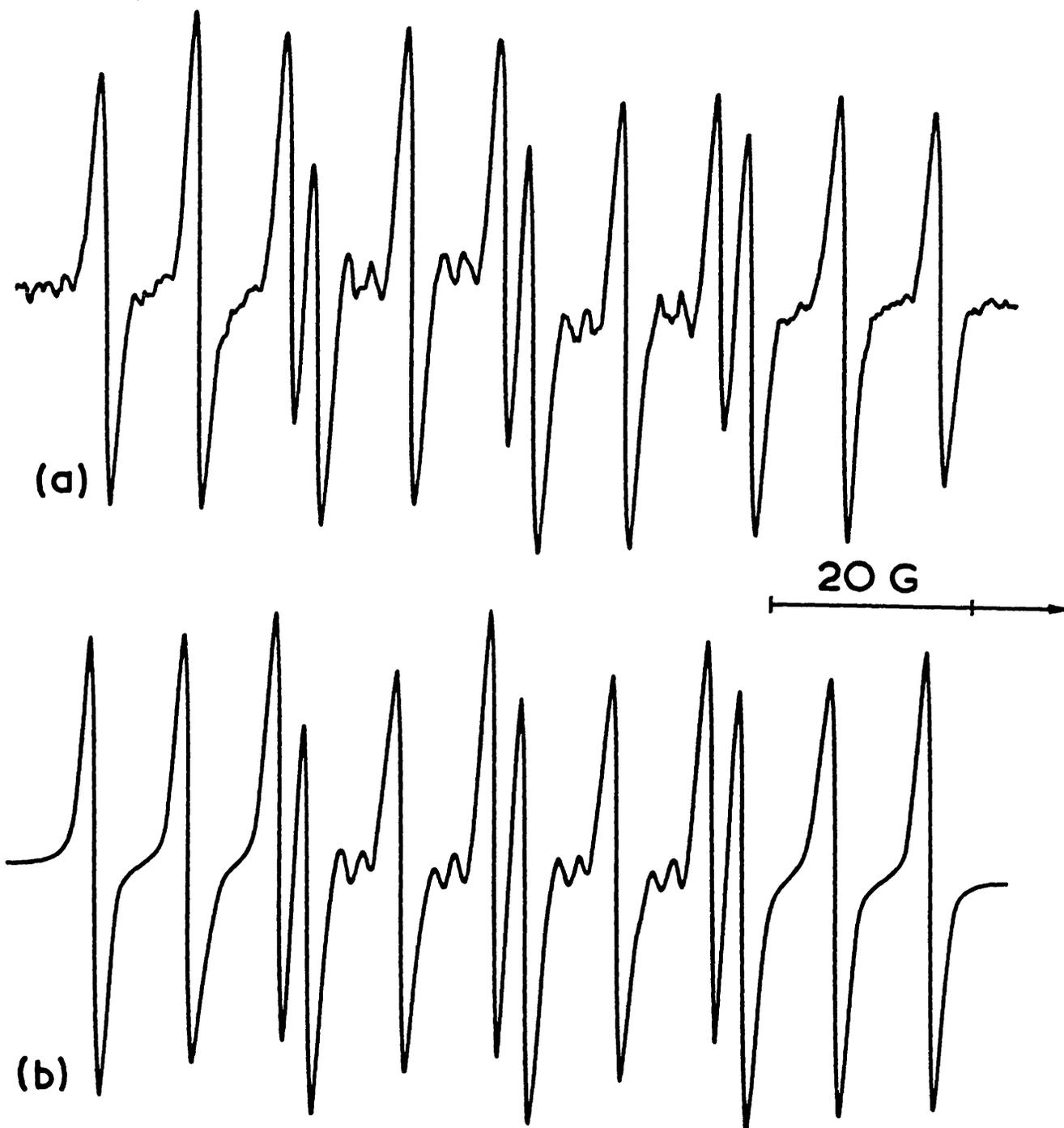


Figure 2.4

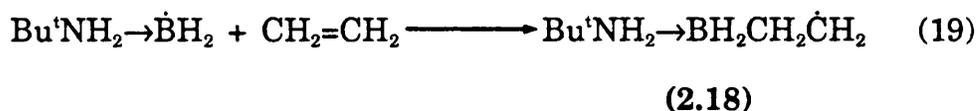
Legend to Figure 2.4

(a) E.s.r. spectrum of the iminyl radical (**2.16 R = 1-Ad**) containing ^{11}B and ^{10}B in natural abundance in cyclopropane-oxirane (1:1 v/v) at 237 K.

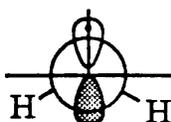
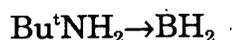
(b) Computer simulation of (a) using the parameters given in Table 2.3; the linewidth is 1.6 G and the lineshape is 65% Gaussian (35% Lorentzian).

2.4 ADDITION OF AMINE-BORYL RADICALS TO ALKENES

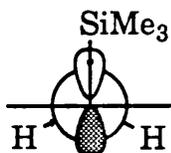
When a sample containing $\text{Bu}^t\text{NH}_2\rightarrow\text{BH}_3$ (0.97 M), DTBP (14% v/v), and ethene (3.48 M) in oxirane-cyclopropane (1:1 v/v) was u.v. irradiated at 190 K, a spectrum which is tentatively attributed to the β -borylethyl radical (2.18) was observed [equation (19)]. The spectrum was weak, but could be analysed in terms of $a(^{11}\text{B})$ 23.0, $a(2\text{H}_\beta)$ 17.2, $a(2\text{H}_\alpha)$ 20.4 G,



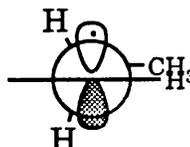
and g 2.0027. The magnitude of the ^{11}B splitting constant indicates an eclipsed conformation¹⁵ (2.19). Addition of trimethylsilyl radicals to ethene is known to give an adduct radical which also prefers the eclipsed conformation¹⁶ (2.20), while the *n*-propyl radical prefers a staggered



(2.19)



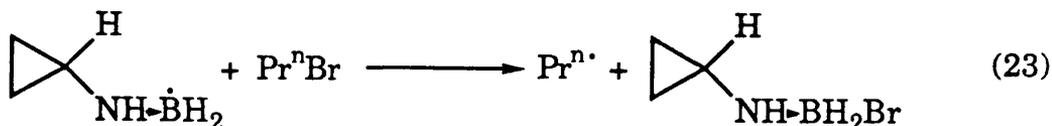
(2.20)



(2.21)

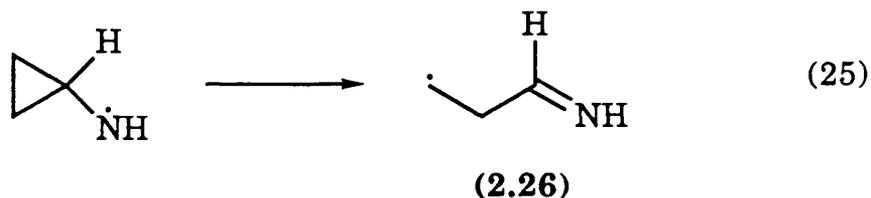
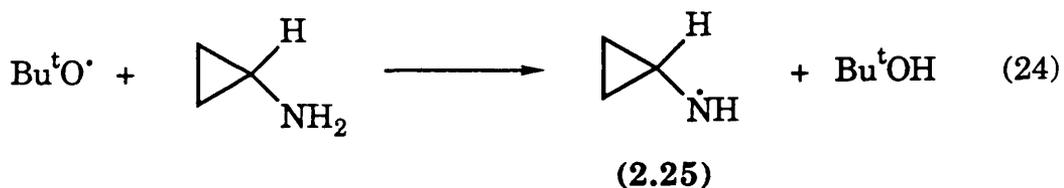
conformation¹⁶ (2.21). It is likely that an eclipsed conformation is preferred by the first two radicals because of an effective σ - π hyperconjugative interaction between the electrons forming the C—B or C—Si bonds and the unpaired electron formally centred on C_α . This stabilizing interaction would be maximized in the eclipsed conformation and would lead to transfer of spin density from C_α into the β -C—B sp^3

detected. Presumably the propyl radical is formed by halogen abstraction by the initially formed cyclopropylamine-boryl radical (2.22) [equation (23)]. When Pr^nBr was replaced by $\text{Me}_2\text{C}=\text{CMe}_2$ (1.1 M) (see Chapter 4),



spectra of both the alkyl radical (2.24) and $\text{Me}_2\text{CH}\dot{\text{C}}\text{Me}_2$ were obtained. This result is consistent with the occurrence of reactions (20) - (22) and shows that ring opening of (2.23) is competitive with H-atom transfer to $\text{Me}_2\text{C}=\text{CMe}_2$.

When cyclopropylamine-borane (1.2 M) and DTBP (*ca.* 20% v/v) in $\text{Bu}^t\text{OH}\text{-Pe}^t\text{OH}$ (3:1 v/v) was irradiated at 282 K, the spectrum shown in Figure 2.5 was again observed, but a second similar spectrum was also detected. This second spectrum alone was observed when DTBP was photolysed in the presence of cyclopropylamine (1.2 M) in $\text{Bu}^t\text{OH}\text{-Pe}^t\text{OH}$ (3:1 v/v) under the same conditions and it is assigned to the alkyl radical (2.26) formed by ring opening of the cyclopropylaminyl radical (2.25) [equations (24) and (25)].



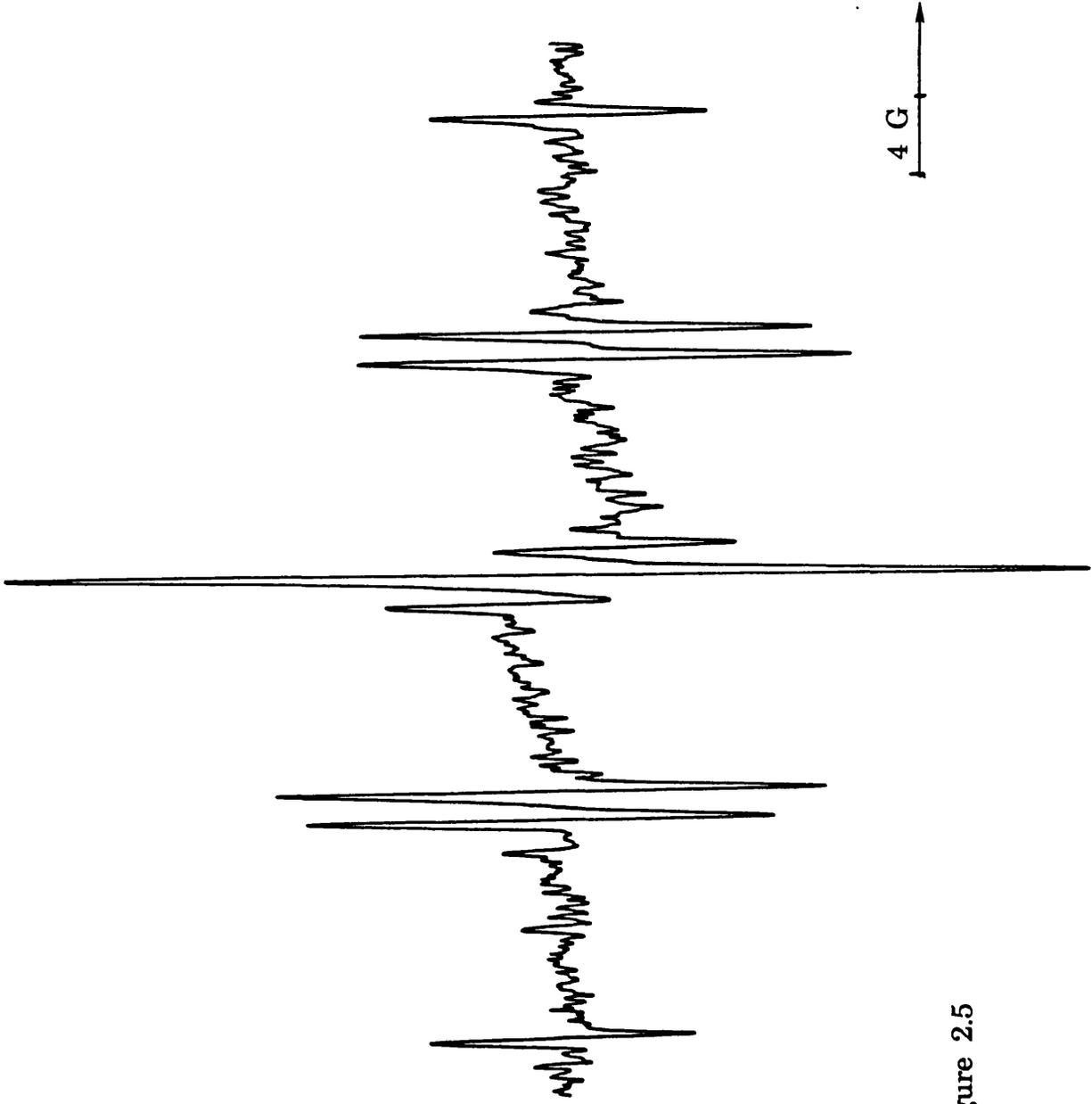


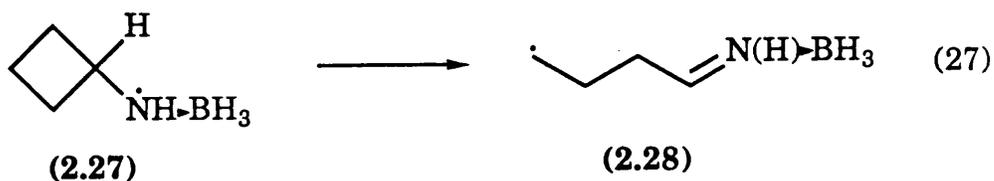
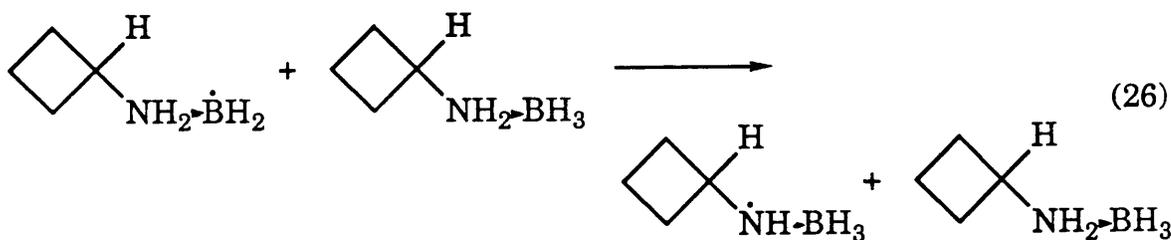
Figure 2.5

Legend to Figure 2.5.

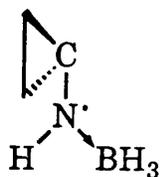
E.s.r. spectrum of (2.24) obtained by β -scission of the cyclopropylaminyloborane radical in cyclopropane-oxirane (1:1 v/v) at 282 K [$a(2H\alpha)$ 22.35, $a(2H\beta)$ 25.22 G, g 2.0026].

The stability of the amine-borane is probably considerably reduced when the amine has a small ring or bulky group¹⁸ attached to nitrogen, consequently at 282 K in protic solvent some decomposition of the amine-borane may occur to liberate the free amine. In aprotic cyclopropane-oxirane (1:1 v/v) at 239 K, a weaker spectrum was obtained which did not contain the lines due to (2.26). Reducing the temperature to 205 K in the latter solvent gave rise to the same spectrum but much weaker. However, at the lowest accessible temperature (180 K) no spectrum attributable to either the amine-boryl radical (2.22) or to the aminyl-borane radical (2.23) was observed. These spectra would be difficult to detect because of their high multiplicities and probably broad lines due to unresolved long-range couplings.

Photolysis of a solution containing cyclobutylamine-borane (1.0 M) and DTBP (*ca.* 20% v/v) in cyclopropane-oxirane (3:1 v/v) at 283 K afforded only a strong spectrum ascribed to the primary alkyl radical (2.28) formed by ring opening of the aminyl-borane radical (2.27) [equations (26) and (27)]; it was analysed in terms of $a(2H_a)$ 22.20 and $a(2H_b)$ 28.13 G (g 2.0026).

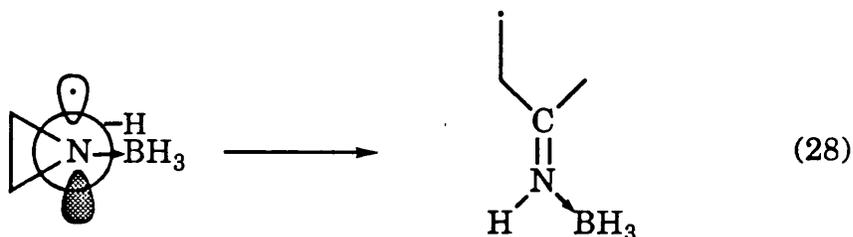


No further fine structure could be conclusively identified and no evidence for the presence of two configurational isomers of (2.24) or (2.28) could be found. Either only one isomer is present or if two isomers are formed they must have indistinguishable e.s.r. spectra. The cyclopropylaminyl-borane radical would be predicted to have to adopt the 'bisected' conformation [structure (2.29)] with the ring *anti* to the BH₃



(2.29)

for steric reasons and ring cleavage would be expected to yield the *trans* isomer specifically, as shown in equation (28). At 283 K in Bu^tOH-Pe^tOH (3:1 v/v) a much stronger spectrum of (2.28) was obtained (Figure



(28)

2.6), compared with that in cyclopropane-oxirane (1:1 v/v); no other lines were present. This spectrum was entirely quenched when the experiment was carried out in the presence of PrⁿBr (1.0 M) and only the spectrum of the n-propyl radical was recorded showing that (2.27) is trapped prior to isomerisation to (2.28) in an analogous fashion to the cyclopropylamine-boryl radical (2.22).

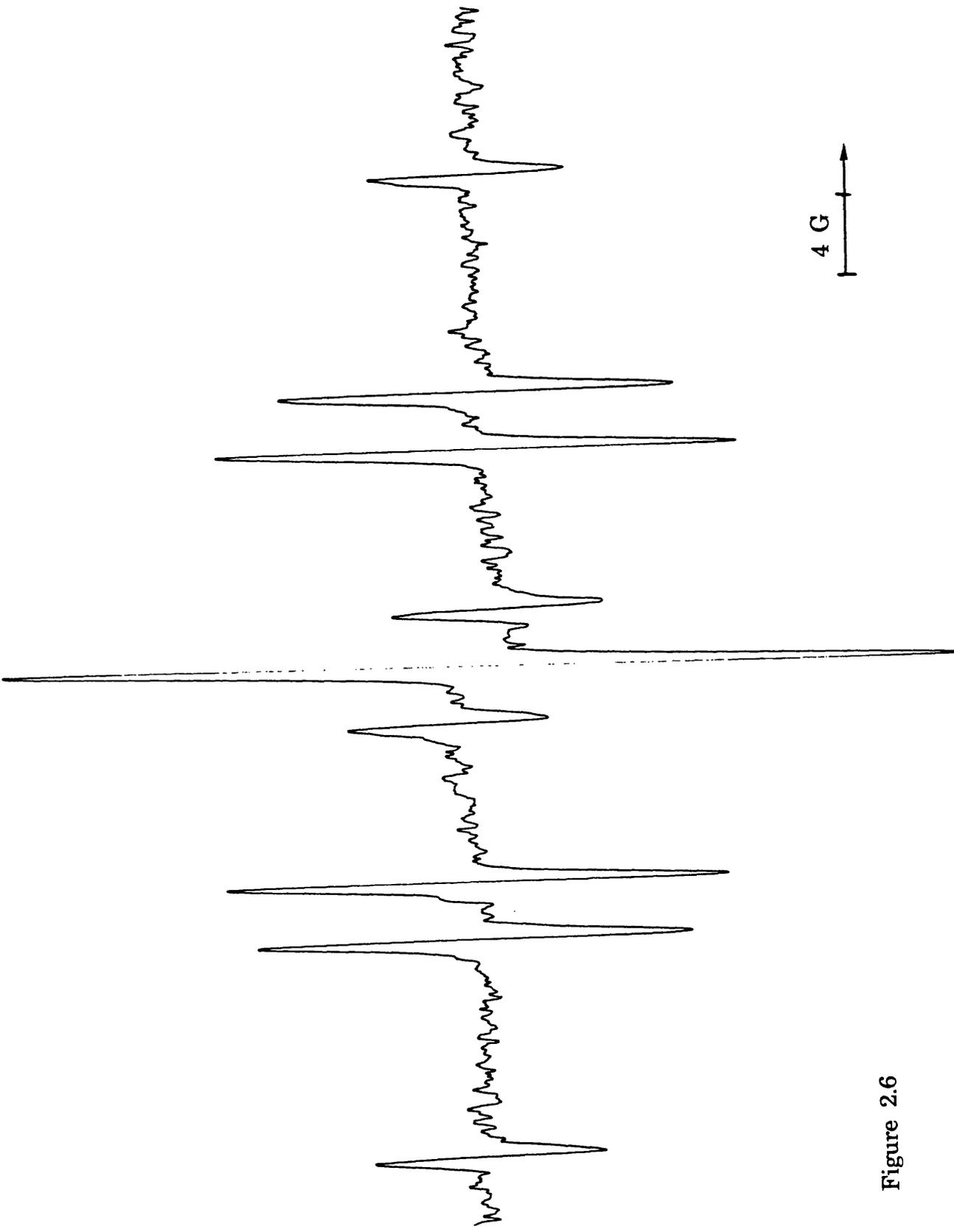
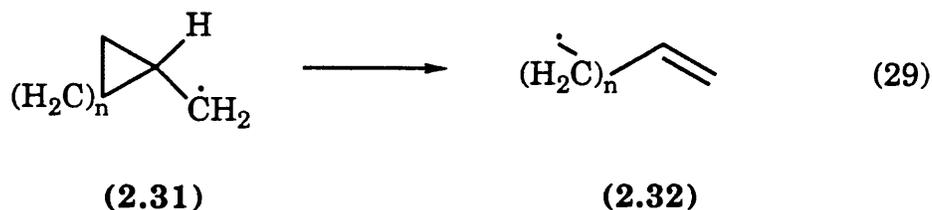


Figure 2.6

Legend to Figure 2.6.

E.s.r. spectrum of (2.28) derived from β -scission of the cyclobutylaminylborane radical in Bu^tOH-Pe^tOH (1:1 v/v) at 282 K [$a(2H_\alpha)$ 22.20, $a(2H_\beta)$ 28.13 G, g 2.0026].

Ring opening of the cyclobutylaminyl-borane radical is expected to be slower than that of the cyclopropylaminyl-borane radical, by analogy with the large differences in the rates for ring opening of the isoelectronic cyclopropyl- and cyclobutyl-methyl radicals, [equation (29)].



The radicals (2.30; $n = 1$) and (2.30; $n = 2$) undergo ring opening very readily to give (2.31; $n = 1$) and (2.31; $n = 2$), respectively. In e.s.r. experiments at 133 K,^{19,20} both (2.30; $n = 1$) and (2.31; $n = 1$) were present in equal concentrations; whereas the analogous ring opening of (2.30; $n = 2$) were not evident below 253 K²¹ and both (2.30; $n = 2$) and (2.31; $n = 2$) were present in equal concentration only at a much higher temperature (285 K).

When a sample containing cyclopentylamine-borane (1.1 M) and DTBP (*ca.* 16% v/v) in Bu^tOH-Pe^tOH (3:1 v/v) was irradiated at 282 K, no spectrum attributable to a ring-opened radical was detected, and β -scission did not occur even at 310 K. A very weak spectrum of the radical derived by H-atom abstraction from the free amine was observed after prolonged photolysis, the assignment being, confirmed by photolysing a sample containing cyclopentylamine instead of the amine-borane. When the above experiment with cyclopentylamine-borane was repeated in cyclopropane-oxirane at 282 K, the spectrum of the radical

derived from the free amine was not observed.

The rate coefficients for ring opening of cycloalkylaminyl-borane radicals are greater than those for opening of the corresponding cycloalkylcarbonyl radicals. The lower activation energies for ring opening of the aminyl-boranes also leads to a reduced difference in the rate coefficients for ring opening of cyclopropyl- and cyclobutyl-aminyl-borane radicals.

Polar factors should also be important in the transition states for ring opening of aminyl-boranes. For cycloalkylcarbonyl radicals, the SOMO-LUMO interaction is dominant, however for the aminyl-borane radicals the SOMO-HOMO interaction should become dominant because of a decrease in the energy of the SOMO for the nitrogen-centred species.

2.6 RADICALS DERIVED FROM AMMONIA-BORANE

Ammonia-borane is the simplest amine-borane and it is isoelectronic with ethane. It proved difficult to find a solvent in which ammonia-borane was completely soluble under the conditions of the e.s.r. experiments (typically 0.5 - 1.0 M at < 285 K). The most useful solvent system was Bu^tOH-Me₂O (4:1 v/v) and this binary mixture was used for most of the experiments; other solvents tried included Pe^tOH, dioxane, and 2,2,5,5-tetramethyltetrahydrofuran (TMTHF), used singly or as binary mixtures.

When a sample containing H₃N→BH₃ (1.1 M) and DTBP (ca. 20% v/v) in Bu^tOH-Me₂O (4:1 v/v) was u.v. irradiated at 282 K, a spectrum

of the ammonia-boryl radical (2.32) was obtained [equation (30)], in agreement with previous work.² No spectrum attributable^{to} aminyl-borane



(2.32)

was obtained, although some weak unidentified lines were present. This result contrasts sharply with the results obtained in similar experiments with primary and secondary alkylamine-boranes which yield only the spectrum of the aminyl-borane radical.

The M.O. calculations (Chapter 3, Table 3.1) indicate that $\text{H}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$ and $\text{H}_2\dot{\text{N}}\rightarrow\text{BH}_3$ are very similar in energy, with the latter being marginally more stable in the gas phase. However, the dipole moments of these radicals are large and solvation effects could be decisive in determining their relative stabilities in solution. In fact, it is probable that photolysis of DTBP in the presence of an amine-borane $\text{R}_n\text{H}_{3-n}\rightarrow\text{BH}_3$ ($n = 0 - 2$), under the normal conditions of the e.s.r. experiment, could afford amine-boryl and aminyl-borane radicals in something approaching their equilibrium concentrations [equation (31)]. Such equilibration should be least rapid for ammonia-borane, since conversion of the aminyl-



initially formed amine-boryl radical would be slow because the N—H bond in $\text{H}_3\text{N}\rightarrow\text{BH}_3$ is stronger than if the nitrogen is methylated.

When the ammonia-boryl radical was generated in the presence

of Pr^nBr (1.0 M) at 282 K in dioxane or dioxane-TMTHF, a strong spectrum of the n-propyl radical was obtained, arising from trapping of the ammonia-boryl radical [equation (32)]. It was noted that when



dioxane was used as part solvent a small amount of competitive abstraction took place from it.

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CHAPTER 3

Molecular Orbital Calculations

Because of the paucity of experimental thermodynamic data for amine-boranes, aminoboranes, and for the derived radicals, within the framework of which to discuss their chemistry, a number of *ab initio* molecular-orbital calculations for these species have been carried out using the GAUSSIAN 82 series of programs.^{1,2} In addition to the molecules containing nitrogen-boron bonds, the isoelectronic carbon-carbon bonded analogues were investigated for comparative purposes.

Equilibrium geometries were optimised, within any imposed symmetry constraints, at the Hartree-Fock level using the standard 6-31G** basis set; the spin restricted (RHF) and spin unrestricted (UHF) methods were used for closed-shell molecules and for radicals, respectively. The nature of each stationary point was determined by computing the set of normal harmonic vibrational frequencies and zero-point vibrational energies (ZPVEs) were evaluated. Electron-correlation energies were calculated for the Hartree-Fock equilibrium geometries using Møller-Plesset perturbation theory taken to third-order (MP3); core electrons were included. Total energies (E_0) and reaction energies ΔE_0 at 0 K were obtained using equation (1), in which the ZPVE is scaled by

$$E_0 = E(\text{MP3}/6\text{-}31\text{G}^{**}/\text{HF}/6\text{-}31\text{G}^{**}) + 0.9\text{ZPVE} \quad (1)$$

a factor of 0.9 to allow for over estimation of vibrational frequencies at this level of theory.² The values of ΔE_0 will differ only slightly from the corresponding reaction enthalpies at 298 K.³ Calculated energies, dipole moments, and ionisation potentials are given in Table 3.1 and equilibrium geometries are shown in Figure 3.1. It should be emphasised that these energies and geometries refer to *isolated* molecules in the *gas phase*. Many of the boron containing species investigated in this work, particularly those incorporating a formal N→B dative single bond, possess substantial dipole moments and consequently molecular association and solvation effects should be taken into account when relating the calculations to experimental observations made in condensed phases. Of course, it is precisely the electronegativity differences between boron and nitrogen which is basically responsible for the variety of structural and chemical differences observed when a CC linkage in an organic molecule is replaced by a NB moiety.

As reported previously,^{4,5} both e.s.r. experimental data and calculations show that the amine-boryl radicals are pyramidal at the boron-centre, although the vibrationally averaged structures observed in solution by e.s.r. spectroscopy appear to be appreciably less pyramidal than the computed gas phase minima. Experiment and theory concur that aminyl-boranes are much closer to planar at the nitrogen radical centre. The β -B—H bonds which eclipse the N-2p_x orbital in the aminyl-borane (3.1) and methylaminyl-borane (3.2) radicals are appreciably longer (by *ca.* 0.018 Å) than the other two B—H bonds, suggesting the existence of a significant hyperconjugative interaction

Table 3.1 Properties calculated using GAUSSIAN 82 in conjunction with the 6-31G** basis set

| Molecule | Imposed Symmetry | Total Energy / Hartree ^a | ZPVE ^b / kJ mol ⁻¹ | E_0 Hartree ^a | $\mu_{\text{calc.}}$ ($\mu_{\text{expt.}}/D$) | $E_{1 \text{ calc.}}^c$ ($E_{1 \text{ expt.}}^c$)/eV |
|---|------------------|-------------------------------------|--|----------------------------|---|--|
| $\text{H}_3\text{N} \rightarrow \dot{\text{B}}\text{H}_2^d$ | C_s | -81.986170 | 162.9 | -82.234878 | 5.69 | 6.63 |
| $\text{H}_2\dot{\text{N}} \rightarrow \text{BH}_3^d$ (3.1) | C_s | -81.990908 | 148.0 | -82.238890 | 5.15 | 11.09 |
| $\text{H}_2\text{N} \rightleftharpoons \text{BH}_2$ | C_{2v} | -81.499210 | 133.4 | -81.749065 | 1.81 (1.84) ^f | 11.79 (11.36) ^g |
| $\text{H}_3\text{N} \rightarrow \text{BH}_3^h$ (3.3) | C_{3v} | -82.624973 | 194.0 | -82.892921 | 5.54 (5.22) ^f | 11.16 (9.44) ^f |
| $\text{MeNH}_2 \rightarrow \dot{\text{B}}\text{H}_2$ (3.5) | C_s | -121.017405 | 244.4 | -121.397565 | 5.65 | 6.50 |
| $\text{Me}\dot{\text{N}}\text{H} \rightarrow \text{BH}_3$ (3.2) | C_1 | -121.031500 | 229.1 | -121.409670 | 5.52 | 10.81 |
| $\text{MeNH} \rightleftharpoons \text{BH}_2$ | C_s | -120.527022 | 213.7 | -120.908749 | 1.83 | 10.85 |
| $\text{MeNH}_2 \rightarrow \text{BH}_3$ (3.6) | C_s | -121.655887 | 275.2 | -122.055247 | 5.52 (5.19) ^m | 11.02 (9.66) ^f |
| $\text{H}_3\text{C}-\dot{\text{C}}\text{H}_2^a$ | C_s | -78.605526 | 165.2 | -78.857994 | 0.21 | 9.55 (8.51) ^f |

| Molecule | Imposed Symmetry | Total Energy / Hartree ^e U(R)HF | MP3(full) | ZPVE ^{b/} kJ mol ⁻¹ | E_0 Hartree ^e | $\mu^{\text{calc.}}$ ($\mu_{\text{expt.}}$)/D | $E_1^{\text{calc.}}$ ($E_1^{\text{expt.}}$)/ eV |
|------------------------------------|------------------|---|-------------|--|-------------------------------|--|---|
| H ₂ C=CH ₂ | D _{2h} | -78.038841 | -78.349913 | 143.1 | -78.300859 | 0 | 10.16 (10.51) ^f |
| H ₃ C-CH ₃ | D _{3d} | -79.238235 | -79.583016 | 208.0 | -79.511715 | 0 | 13.24 (12.1) ^f |
| MeCH ₂ -CH ₂ | C _s | -117.642816 | -118.111411 | 246.5 | -118.026913 | 0.21 | 9.50 (8.1) ^f |
| MeCH-Me | C _s | -117.646908 | -118.115933 | 245.9 | -118.031640 | 0.17 | 8.85 (7.69) ^f |
| MeCH=CH ₂ | C _s | -117.081614 | -117.551847 | 223.1 | -117.475370 | 0.32 (0.37) ^f | 9.71 (9.73) ^f |
| MeCH ₂ Me | C _{2v} | -118.276159 | -118.780683 | 288.4 | -118.681822 | 0.06 (0.08) ^f | 12.91 (11.5) ^f |
| Me [•] | D _{3h} | -39.564457 | -39.715003 | 81.0 | -39.687237 | 0 | 10.43 (9.84) ^f |
| H [•] | | -0.498233 | -0.498233 | 0 | 0.498233 | 0 | 13.56 (13.60) ^f |

^a 1 Hartree = 2625.5 kJ mol⁻¹. ^b Zero-point vibrational energy computed at the U(R)HF/6-31G^{**} level; all vibrational frequencies were positive for every structure. ^c Calculated vertical ionisation potential is the negative of the HOMO for a closed-shell molecule or the negative of the most loosely bound α electron for a radical. ^d See also reference 5. ^e Compare J. D. Dill, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 3402. ^f Gas phase M. Sugie, M. Takeo, and C. Matsumura, *Chem. Phys. Lett.*, 1979, **64**, 573. ^g N. P. C. Westwood and N. H. Werstiuk, *J. Am. Chem. Soc.*, 1986, **108**, 891. ^h Compare J. S. Binkley and L. R. Thorne, *J. Chem. Phys.*, 1983, **79**, 2932. ⁱ Gas phase; R. D. Suenram and L. R. Thorne, *Chem. Phys. Lett.*, 1981, **78**, 157. ^j D. R. Lloyd and N. Lynaugh, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 947. ^k The BH₃ and CH₃ rotations appear to be essentially free. No significant gain in stability was achieved when the constraint on the dihedral angles H'BN' and H'CN' was removed and the optimisation begun from very different starting points. ^l Compare R. Bonaccorsi, P. Palla, R. Cimiraglia, and J. Tomasi, *Int. J. Quantum Chem.*, 1983, **24**, 307. ^m In benzene solution; H. Nöth and H. Beyer, *Chem. Ber.*, 1960, **93**, 939. ⁿ Compare J. Pacansky and M. Dupuis, *J. Chem. Phys.*, 1978, **68**, 4276. ^o F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1979, **101**, 4067. ^p G. Bieri, F. Burger, E. Heilbronner, and J. P. Maier, *Helv. Chim. Acta*, 1977, **60**, 2213. ^q Compare J. Pacansky and M. Dupuis, *J. Chem. Phys.*, 1979, **71**, 2095; T. A. Claxton and A. M. Graham, *J. Chem. Soc., Faraday Trans. 2*, 1988, **84**, 121. ^r F. A. Elder, C. Giese, B. Steiner, and M. Inghram, *J. Chem. Phys.*, 1962, **36**, 3292. ^s Compare J. Pacansky and M. Yoshimine, *J. Phys. Chem.*, 1987, **91**, 1024. ^t *Handbook of Chemistry and Physics*, ed. R. C. Weast, 55th edn., CRC Press, Cleveland, 1974.

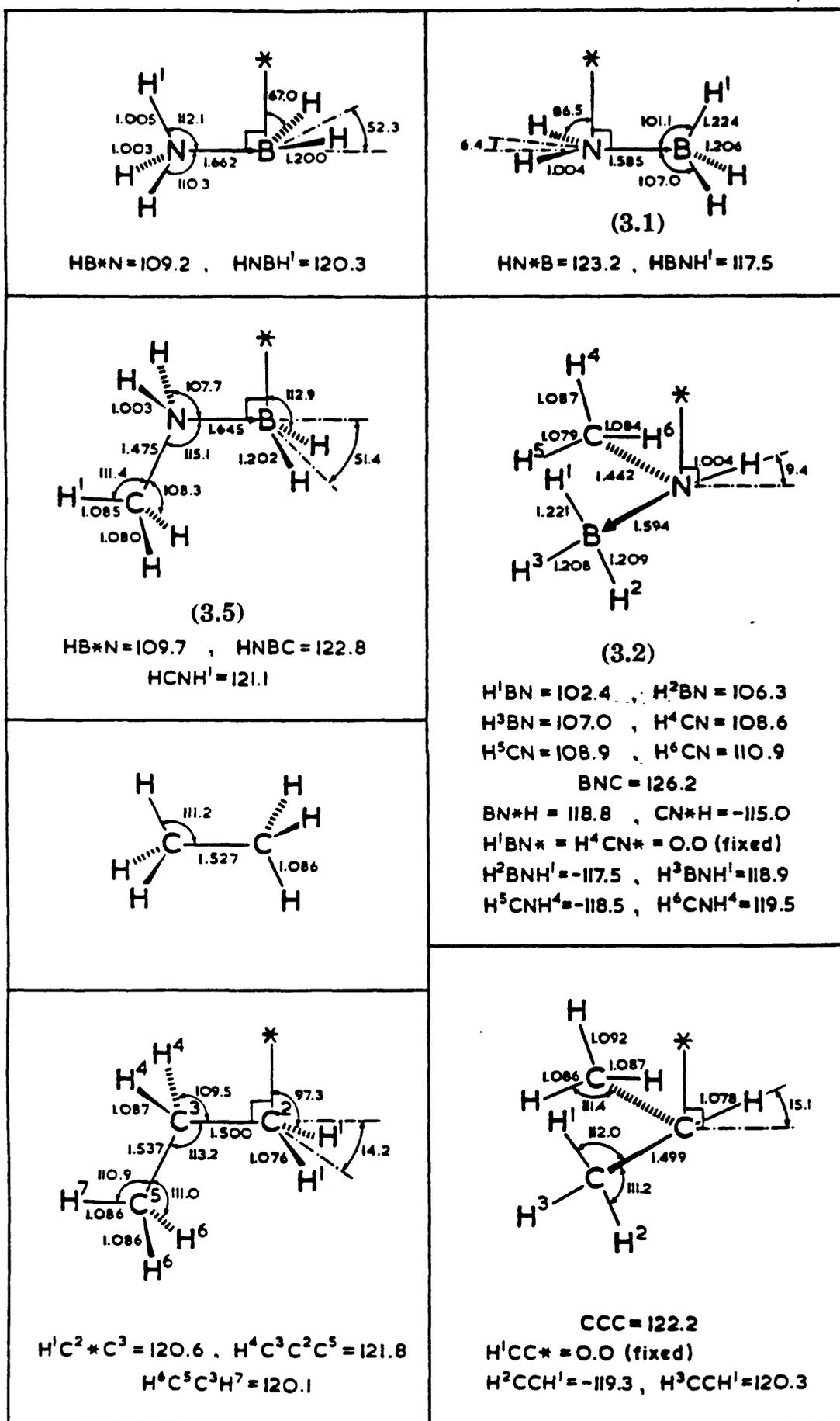


Figure 3.1

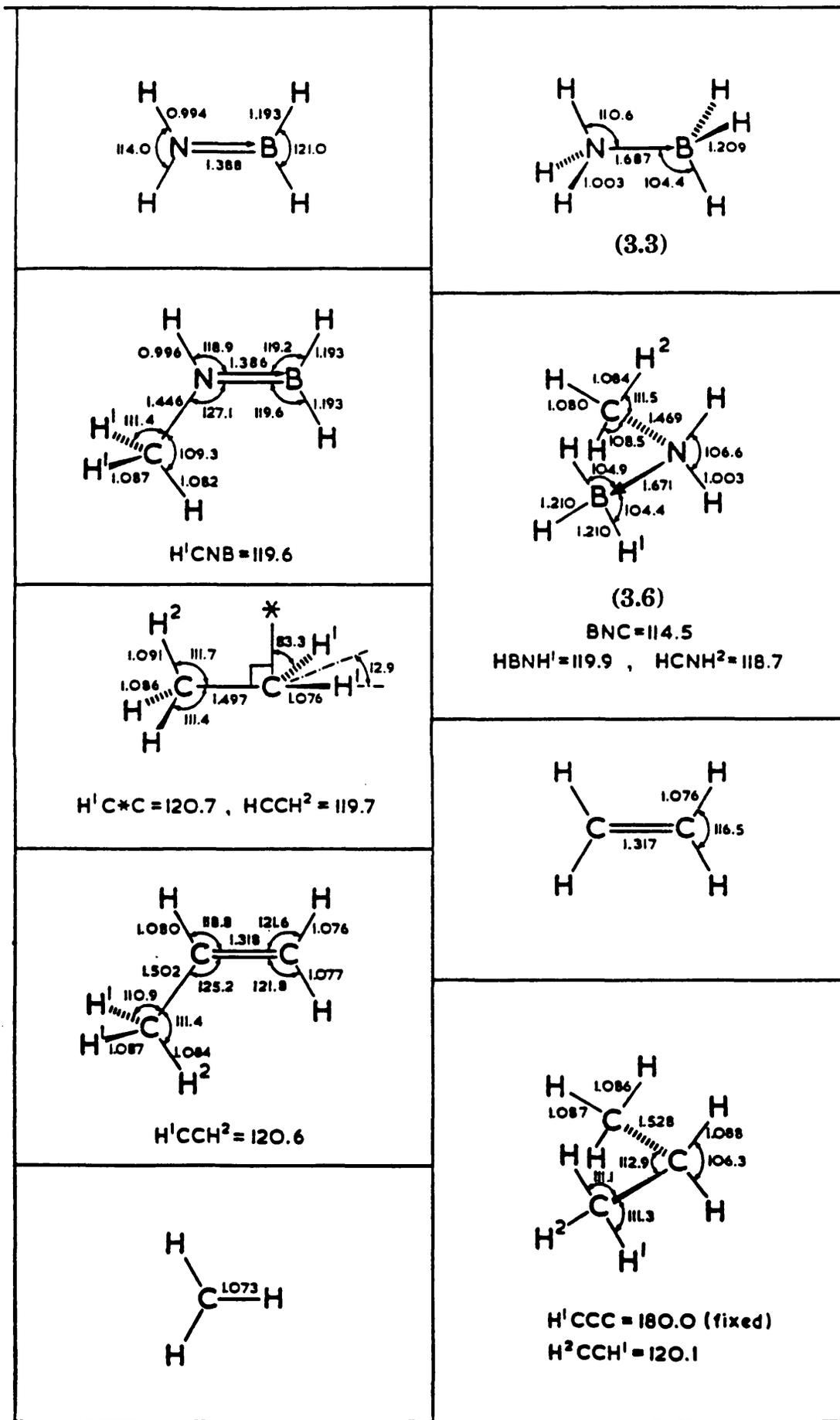
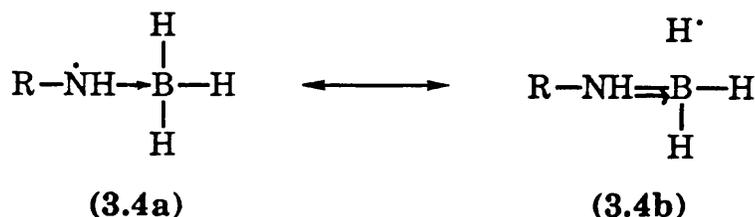


Figure 3.1 continued

Legend to Figure 3.1.

Optimised geometries for the molecules listed in Table 3.1. Bond lengths are given in Å and bond angles in degrees; ABCD is the dihedral angle between the planes ABC and BCD. The asterisk represents a dummy atom used to help define molecular geometry. In structure (3.2) the dummy atom is positioned such that the N* vector is perpendicular to the CNB plane. In structure (3.3) the NH₂ plane is constrained to be perpendicular to the BNC plane and H¹ and H² are constrained to lie in the BNC plane.

between the eclipsing bond and the unpaired electron, as accounted for by inclusion of canonical structures such as (3.4b). For the methyl-



aminyl-borane radical (3.2) in solution this hyperconjugative interaction is evidently stronger than for the computed structure in the gas phase, since the average values of $a(3BH)$ calculated for the equilibrium geometry by the *ab initio* [(+)29.6 G] and INDO [(+)29.2 G] methods are much smaller than the observed value [(+)63.9 G]. The remaining calculated splittings [*ab initio*, INDO, and observed (in gauss)] are $a(^{14}\text{N})$ +33.0, +16.9, (+)15.4, $a(^{11}\text{B})^*$ -14.9, -10.9, (-)13.3, $a(\text{NH})$ -43.9, -19.9, (-)19.4, and $a(3\text{CH})$ +25.5, +21.7, (+)24.1. The INDO results are in generally good agreement with experiment; the *ab initio* results are, as expected,⁷ less good. The calculated ionisation potentials for the aminyl-boranes $\text{H}_2\dot{\text{N}}\rightarrow\text{BH}_3$ (3.1) and $\text{Me}\dot{\text{N}}\text{H}\rightarrow\text{BH}_3$ (3.2) are over 4 eV greater than for the respective isomeric amine-boryls. Amine-boryl radicals are strongly nucleophilic species, while aminyl-boranes must be regarded as much more electrophilic.

The isopropyl radical is calculated to be more stable than n-propyl by 12.4 kJ mol⁻¹, compared with experimental difference in their standard

*A scaling factor of 720.8 G per ¹¹B-2s electron was used in the INDO calculations.

enthalpies of formation⁹ of 7-15 kJ mol⁻¹. Aminyl-borane is calculated to be more stable than ammonia-boryl by 10.5 kJ mol⁻¹, and methylation at nitrogen increases the relative stability of the nitrogen-centred isomer such that MeNH→BH₃ is now 31.8 kJ mol⁻¹ more stable than MeNH₂→BH₂. These results are consistent with the detection by e.s.r. spectroscopy of H₃N→BH₂ when Bu'O· is generated in the presence of H₃N→BH₃ (see later),¹⁰ but of MeNH→BH₃ when the alkoxy radical is generated in the presence of MeNH₂→BH₃.

The strengths of the B—H and N—H bonds in H₃N→BH₃ and MeNH₂→BH₃ may be estimated by consideration of the isodesmic reactions (2) and (3). The computed values of ΔE₀(2) and ΔE₀(3) are +11.3 and



(3.5)

+7.3 kJ mol⁻¹, respectively, which when combined with $DH^\circ(\text{RCH}_2\text{—H})$ for ethane and propane (419.7 and 417.1 kJ mol⁻¹, respectively^{9b}) lead to values of $DH^\circ(\text{B—H})$ for H₃N→BH₃ and MeNH₂→BH₃ of 431 and 424 kJ mol⁻¹, respectively.** When the relative stabilities of the aminyl-borane and amine-boryl radicals are taken into account, the computed value of $DH^\circ(\text{N—H})$ for H₃N→BH₃ and MeNH₂→BH₃ are 421 and 392 kJ mol⁻¹,

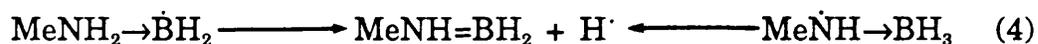
**The computed value of ΔE₀ for simple homolytic cleavage of R—H to give R· and H· are 408 (R = Et), 411 (R = Prⁿ), and 399 (R = Prⁱ) kJ mol⁻¹ in remarkably good agreement with the experimental bond dissociation energies.

respectively.

Both $\text{H}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$ and $\text{H}_2\dot{\text{N}}\rightarrow\text{BH}_3$ are calculated to be unstable with respect to $\text{H}\cdot + \text{H}_2\text{N}\rightleftharpoons\text{BH}_2$, by 32.6 and 22.1 kJ mol^{-1} , respectively. The transition states for these β -scission processes have been located previously⁵ and at present level of theory including ZPVEs, the activation energy for unimolecular loss of $\text{H}\cdot$ are 73.8 kJ mol^{-1} from $\text{H}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$ and -4.8 kJ mol^{-1} for $\text{H}_2\dot{\text{N}}\rightarrow\text{BH}_3$.

β -Scission of the ammonia-boryl radical, although more favourable thermodynamically, has a much higher activation energy. The activation energy for β -scission of $\text{H}_2\dot{\text{N}}\rightarrow\text{BH}_3$ becomes negative only after the inclusion of the correlation corrections for the *UHF optimised* structures; it is zero within the limitations of the computational method.

Unimolecular loss of a hydrogen from $\text{MeNH}_2\rightarrow\dot{\text{B}}\text{H}_2$ [equation (4)]



is calculated to be exothermic by 24.7 kJ mol^{-1} , while $\text{Me}\dot{\text{N}}\text{H}\rightarrow\text{BH}_3$ is slightly more stable (by 7.1 kJ mol^{-1}) than $\text{H}\cdot + \text{MeNH}\rightleftharpoons\text{BH}_2$. Although the transition states have not been investigated, it seems safe to assume that the activation energy for loss of a β -hydrogen atom from boron in $\text{Me}\dot{\text{N}}\text{H}\rightarrow\text{BH}_3$ will be much smaller than for β -cleavage of an N—H bond in $\text{MeNH}_2\rightarrow\dot{\text{B}}\text{H}_2$.

The methylamine-boryl radical (3.5) is calculated to be very unstable [by 101.7 kJ mol^{-1}] with respect to $\text{Me}\cdot + \text{H}_2\text{N}\rightleftharpoons\text{BH}_2$, accounting for the facility with which alkylamine-boryl radicals (including

$\text{Bu}^{\dot{\text{C}}}\text{NH}_2 \rightarrow \dot{\text{B}}\text{H}_2$, as described in chapter 2) undergo β -scission with loss of an alkyl radical from nitrogen.^{4,11}

In the absence of experimental thermochemical data, these results provide a suitable framework discussing the chemistry of aminyl-borane and amine-boryl radicals. In particular, the calculations indicate that the aminyl-borane radicals $\text{RNH}^{\dot{\text{C}}}\text{H} \rightarrow \text{BH}_3$ are much less stable relative to $\text{H}^{\cdot} + \text{RNH}^{\dot{\text{C}}}\text{H} \rightarrow \text{BH}_2$ than the isoelectronic alkyl radicals $\text{RCH}^{\dot{\text{C}}}\text{H}-\text{CH}_3$ are with respect to $\text{H}^{\cdot} + \text{RCH}=\text{CH}_2$.

References to Chapter 3

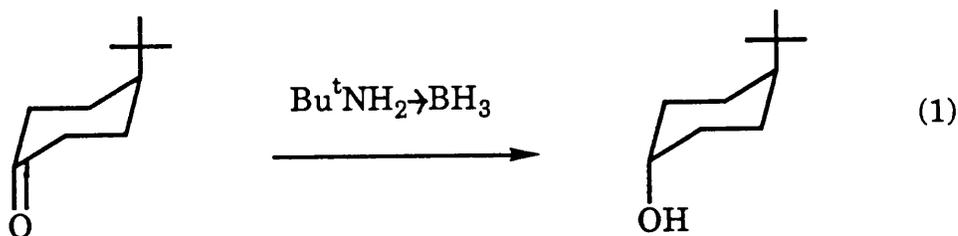
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CHAPTER 4

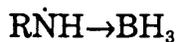
Hydrogen-Atom Transfer Reactions

4.1 REDUCTION OF ALKENES, ARENES, AND DIENES BY AMINYL-BORANE RADICALS

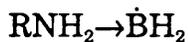
Amine-boranes have been shown previously to be mild, efficient and stereoselective reducing agents for aldehydes and ketones, in both protic and aprotic solvents with reactivity patterns different from diborane and sodium borohydride. However, no detailed mechanisms for these reductions have been put forward.¹ Secondary amine-boranes were found to be less reactive than primary amine-boranes and tertiary amine-boranes are unreactive. For example, reduction of cyclohexanone by $\text{Bu}^t\text{NH}_2\rightarrow\text{BH}_3$ took place with high chemoselectivity to give cyclohexanol as the only product [equation (1)] in high yield (87 %) at room temperature.²



The thermodynamic instability of aminyl-borane (4.1) and amine-boryl (4.2) radicals with respect to loss of a β -hydrogen atom suggests



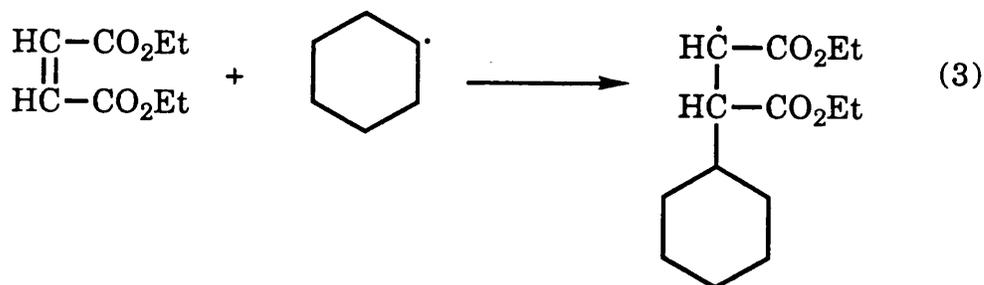
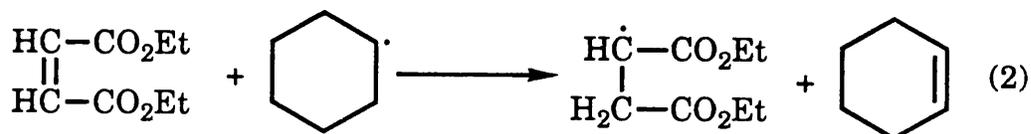
(4.1)



(4.2)

suggests that these species might function as efficient reducing agents by hydrogen-atom transfer to unsaturated substrates. The isoelectronic alkyl radicals are very much more stable with respect to analogous β -scission and prefer to add to alkenes *via* C_α rather than undergo β -H-atom transfer.³⁻⁵

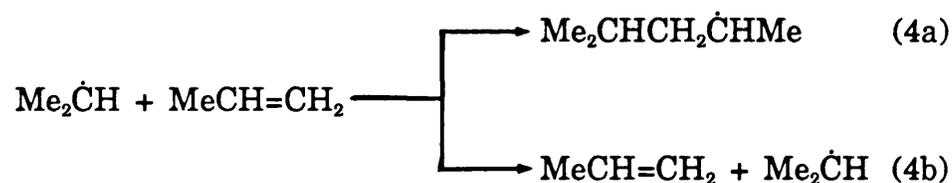
However, it has been shown recently that β -H-atom transfer from cyclohexyl radicals to an alkene (diethyl fumarate) occurs at elevated temperatures (between 520 and 670 K⁶) [equation (2)]. The radical derived from addition of the cyclohexyl radical to diethyl fumarate was also present, [equation (3)]. The ratio of diethyl oxalate



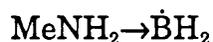
adduct to dimethyl oxalate (both formed by abstraction of hydrogen from the cyclohexane solvent) at 520 K was 22.9, indicating that even in this example the addition reaction is occurring predominantly. At higher

temperatures (670 K), the above product ratio was reduced to 11.3.

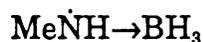
The relative rates of β -H-atom transfer and addition reflect the thermodynamics of the two processes. Addition of isopropyl radicals to propene [equation (4a)] is exothermic by 94 kJ mol⁻¹, whilst the degenerate H-atom transfer [equation (4b)] is, of course, thermoneutral. The methylamine-boryl (4.3) and methylaminyl-borane (4.4) radicals are



isoelectronic counterparts of the n-propyl and isopropyl radicals, respectively.^{7,8} Whilst MeCH₂ $\dot{\text{C}}\text{H}_2$ and Me₂ $\dot{\text{C}}\text{H}$ are more stable than MeCH=CH₂ and H \cdot by 138 and 145 kJ mol⁻¹, respectively, it was predicted on the basis of *ab initio* molecular orbital calculations that



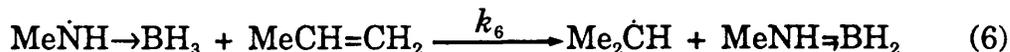
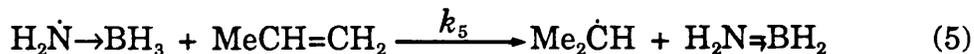
(4.3)



(4.4)

Me $\dot{\text{N}}\text{H} \rightarrow \text{BH}_3$ is more stable than MeNH \rightleftharpoons BH₂ + H \cdot by only 7 kJ mol⁻¹ and that MeNH₂ $\rightarrow \dot{\text{B}}\text{H}_2$ is *less* stable than these cleavage products by 25 kJ mol⁻¹.

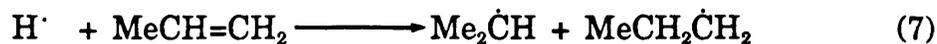
The β -H-atom transfer reactions [equations (5) and (6)] are calculated to be exothermic by 174.5 and 145.3 kJ mol⁻¹, respectively. These large exothermicities coupled with the availability of a low energy



pathway for β -H-atom transfer [as indicated by the effectively-zero activation energy calculated for β -scission of $\text{H}_2\dot{\text{N}}\rightarrow\text{BH}_3$ and the very large magnitudes of $\alpha(3BH)$ for $\text{Me}\dot{\text{N}}\text{H}\rightarrow\text{BH}_3$ and $\text{Bu}'\dot{\text{N}}\text{H}\rightarrow\text{BH}_3$] suggest that reactions (5) and (6) may proceed rapidly under mild conditions. Although β -H-atom transfer from the isomeric amine-boryl radical is thermodynamically somewhat more favourable, the corresponding indicators point to a less easy pathway. In contrast to the efficient hyperconjugative spin transfer to the β - BH_3 group which takes place for $\text{RNH}\rightarrow\text{BH}_3$, hyperconjugation is not very efficient for $\text{H}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$, as evidenced by the small value of $\alpha(3NH)$ (11.0 G).⁹

When a $\text{Bu}'\text{OH}-\text{Pe}'\text{OH}$ (3:1 v/v) solution containing $\text{MeNH}_2\rightarrow\text{BH}_3$ (1.0-1.5 M), DTBP (20% v/v), and propene (0.1-2.9 M) was irradiated with u.v. light at 282 K, the e.s.r. spectrum of the methylaminyl-borane radical was replaced by that of the isopropyl radical (see Figure 4.1) to an extent which increased with the concentration of the alkene. There was no evidence for the addition of amine-boryl or aminyl-borane radicals to propene and, with propene concentrations in excess of *ca.* 0.6 M, only the isopropyl radical could be detected. Even under very forcing instrumental conditions, it was not possible to detect with certainty the spectrum of the n-propyl radical and the value of $[\text{Pr}'\cdot]/[\text{Pr}^{\text{n}}\cdot]$ must be greater than *ca.* 30. Addition of thermalised hydrogen atoms to propene

[equation (7)] at 77 K, studied by e.s.r. spectroscopy using the rotating



cryostat technique, is reported to yield 98% isopropyl and 2% propyl radicals.¹⁰ The incomplete quenching of the spectrum of (4.4) when $[\text{MeCH}=\text{CH}_2]$ is < 0.6 M permitted the absolute rate coefficient for H-atom transfer to propene to be estimated. It was assumed that the isopropyl radical is removed only by self-reaction and cross-reaction with (4.4) and that these processes have the same (diffusion controlled)¹¹ rate coefficient ($2k_t$). Under these circumstances it may be shown that the equation (8) holds in which the ratio R ($= [\text{Pr}^\cdot]/[\text{Me}\dot{\text{N}}\text{H}\rightarrow\text{BH}_3]$) was

$$k_3 = 2k_t (R + 1)[\text{Pr}^\cdot]/[\text{MeCH}=\text{CH}_2] \quad (8)$$

obtained by computer simulation of the experimental spectra.

At 282 K in Bu^tOH-Pe^tOH (3:1 v/v) a constant value of $(R + 1)[\text{Pr}^\cdot]/[\text{MeCH}=\text{CH}_2]$ ($1.1 \pm 0.05 \times 10^6$) was obtained in three experiments in which the concentration of propene was varied between 0.15 and 0.38 M.* The previously measured¹² value of $2k_t$ for self-reaction of Prⁱ· in 3-methylpentan-3-ol at 282 K is 2.1×10^9 l mol⁻¹ s⁻¹ and this value was assumed to be appropriate for our solvent system.

*The propene concentrations have been calculated by assuming that 85% of the alkene is in solution (see Experimental Section).

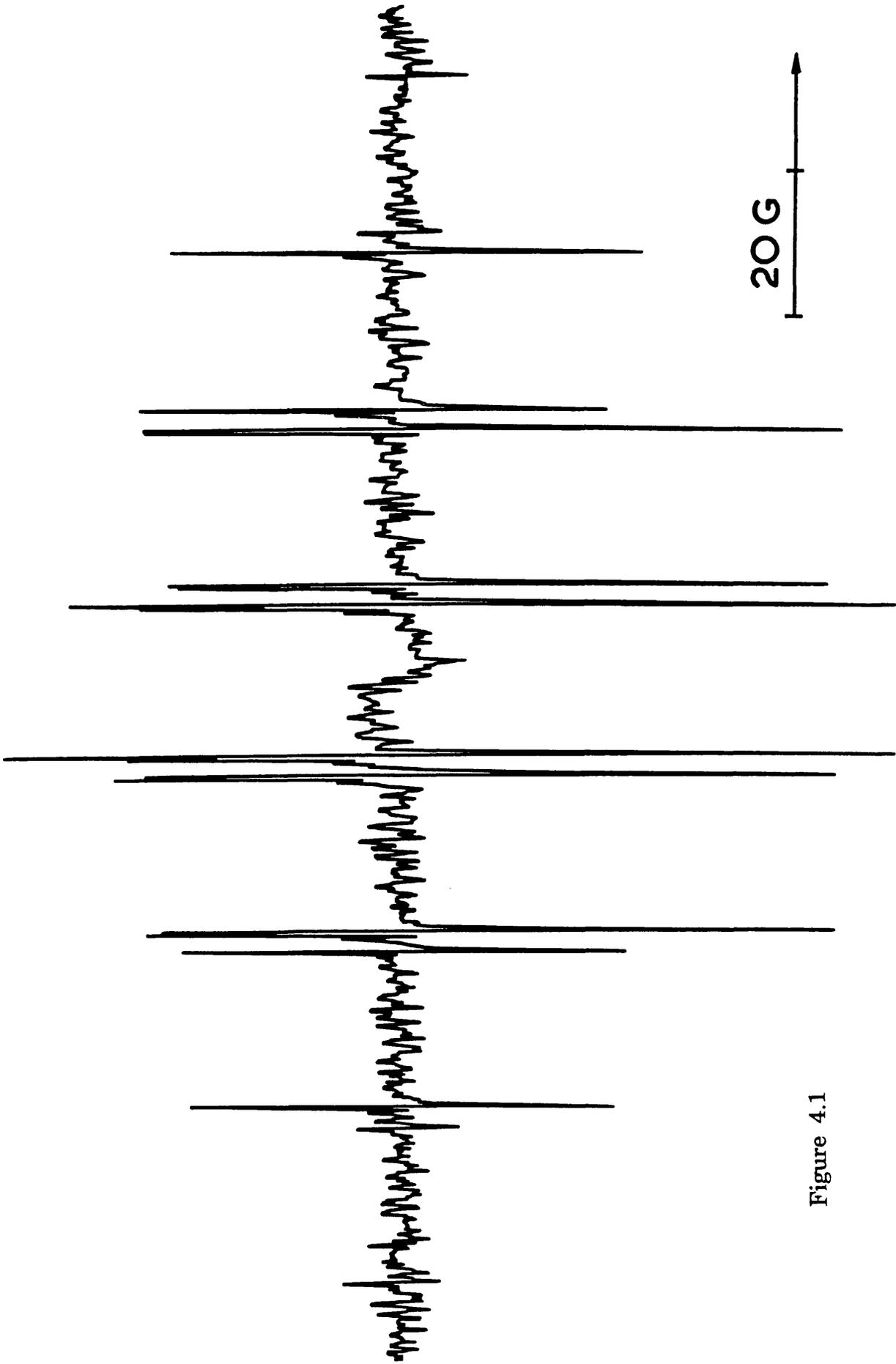


Figure 4.1

Legend to Figure 4.1

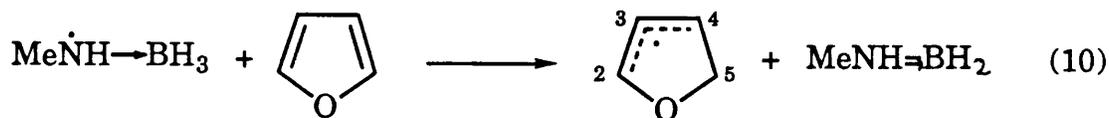
E.s.r. spectrum of the isopropyl radical obtained during u.v. irradiation of DTBP (20% v/v), $\text{MeNH}_2 \rightarrow \text{BH}_3$ (1.2 M), and propene (1.4 M) in Bu'OH-Pe'OH (3:1 v/v) at 282 K.

The value of k_3 thus obtained is $2.0 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ at 282 K.

It was found that a wide variety of alkenes can be reduced to alkyl radicals under similar conditions, the more stable radical being produced with high regioselectivity when two isomers are possible. For example, $\text{Me}_2\text{C}=\text{CH}_2$, $\text{Me}_2\text{C}=\text{CHMe}$ and $\text{Me}_2\text{C}=\text{CMe}_2$ yield Bu^\cdot , Pe^\cdot and $\text{Me}_2\text{CH}\dot{\text{C}}\text{Me}_2$, respectively. None of the less stable regioisomer was detected from the first two alkenes. β -H-Atom transfer to ethyl vinyl ether and to furan took place readily to give the corresponding α -alkoxyalkyl radicals [(4.5)¹³, Figure 4.2 and (4.6)¹⁴, Figure 4.3] [equations (9) and (10)]. The spectroscopic parameters for radicals formed by H-atom transfer from the methylaminyl-borane radical are given in Table 4.1. The allylic radical (4.6) has been generated previously by addition



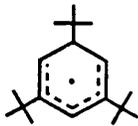
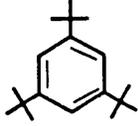
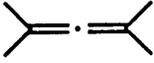
(4.5)



(4.6)

of hydrogen atoms (produced by radiolysis of water) to furan.¹⁵ When second-order effects^{16,17} are taken into account, the spectrum of (4.6) can be satisfactorily analysed in terms of equal splittings of 36.12 G from the two protons attached to C-5. This contrasts with the proposal by Ko *et al.*¹⁴ in which the splitting of *ca.* 0.4 G is taken to indicate non-equivalence of the two C-5 protons. The remaining parameters for (4.6) at 282 K are $a(1\text{H}^{2 \text{ or } 4})$ 13.37, $a(1\text{H}^{4 \text{ or } 2})$ 13.17, $a(1\text{H}^3)$ 2.14 G, and g

Table 4.1. Alkyl radicals produced by H-atom transfer from the methylaminyl-borane radical.

| Radical | Source | T/K | g Factor | $a(H_\alpha)$ | $a(H_\beta)$ | $a(H_\gamma)$ |
|---|---|-----|----------|-----------------------------------|---------------------------|--------------------------|
| $\text{Me}_2\dot{\text{C}}\text{H}$ | $\text{MeCH}=\text{CH}_2$ | 282 | 2.0026 | 21.9(1) | 24.7 | — |
| $\text{Me}_3\dot{\text{C}}$ | $\text{Me}_2\text{C}=\text{CH}_2$ | 282 | 2.0026 | — | 22.8 | — |
| $\text{Me}_2\dot{\text{C}}\text{CH}_2\text{Me}$ | $\text{Me}_2\text{C}=\text{CHMe}$ | 281 | 2.0026 | — | 22.9(6) 18.9(2) | 0.18 |
| $\text{Me}_2\dot{\text{C}}\text{CHMe}_2$ | $\text{Me}_2\text{C}=\text{CMe}_2$ | 282 | 2.0026 | — | 23.1(6) 11.8(1) | 0.3 |
| $\text{Me}\dot{\text{C}}\text{HCH}_2\text{Me}$ | <i>trans</i> - $\text{MeCH}=\text{CHMe}$ | 283 | 2.0026 | 21.7 | 24.7(3) 25.2(2) | — |
| $(\text{Me}_3\text{C})_2\dot{\text{C}}\text{Me}$ | $(\text{Me}_3\text{C})_2\text{C}=\text{CH}_2$ | 282 | 2.0026 | — | 22.5(3) | 0.4(18) |
| $\text{Me}_3\text{C}\dot{\text{C}}\text{Me}_2$ | $\text{Me}_3\text{C}(\text{Me})\text{C}=\text{CH}_2$ | 282 | 2.0026 | — | 22.8(6) | 0.4(9) |
|  |  | 282 | 2.0032 | 36.17 (2-C5) 2.14 (1-C3) | 13.37 (1-C4 or C2) | 13.17 (1-C2 or C4) |
|  |  | 305 | 2.0027 | 41.62 (2-C1) | 2.6 (2- C3/C5) | — |
|  |  | 305 | 2.0027 | 13.0 (6- <i>exo</i>) | 14.2 (6- <i>endo</i>) | 5.4 (1-C2) |
| $\text{EtO}\dot{\text{C}}\text{HCH}_3$ | $\text{EtOCH}=\text{CH}_2$ | 282 | 2.0027 | | | |

^a Solvent = Bu^tOH-Pe^tOH (3:1 v/v).

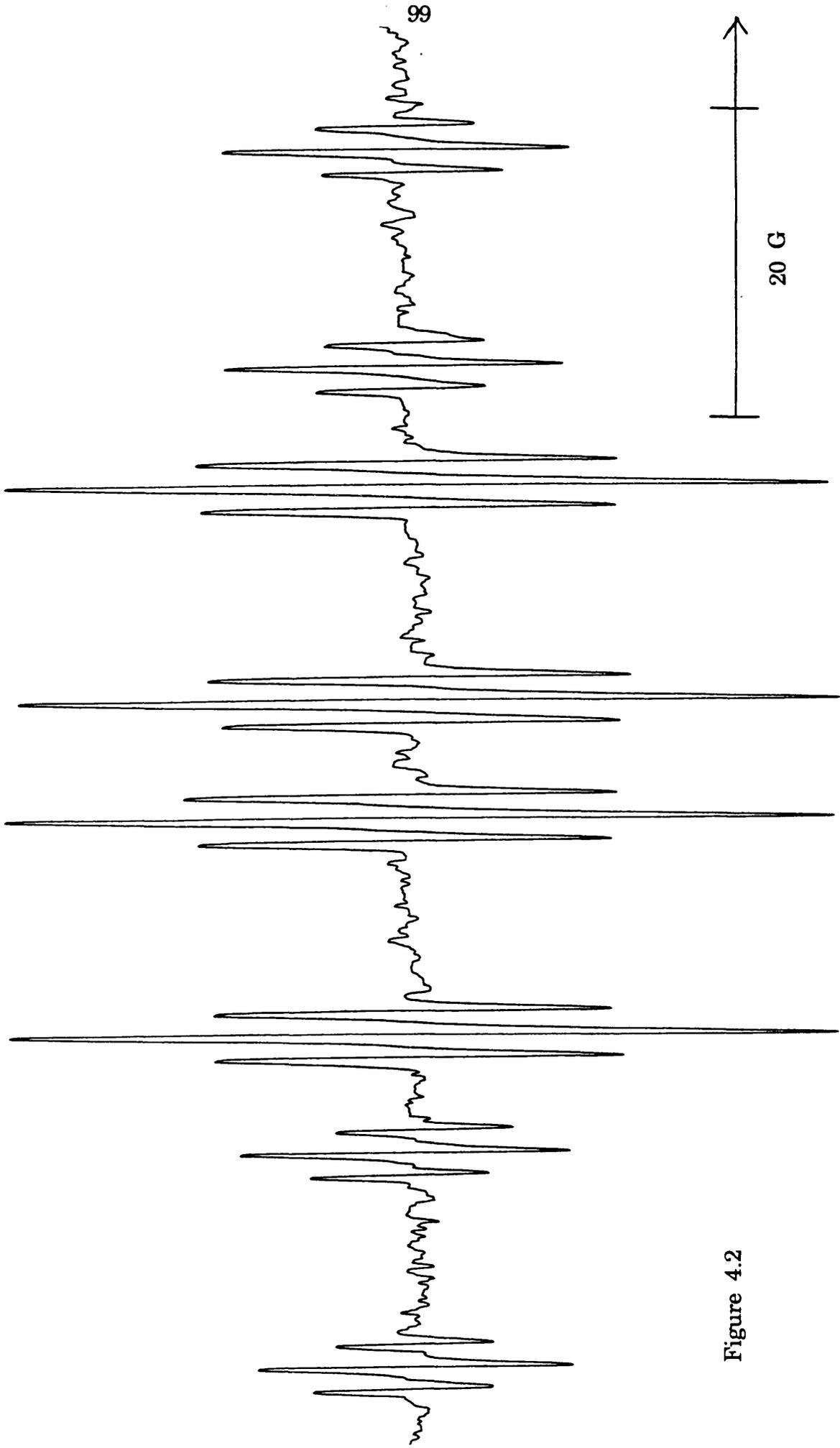


Figure 4.2

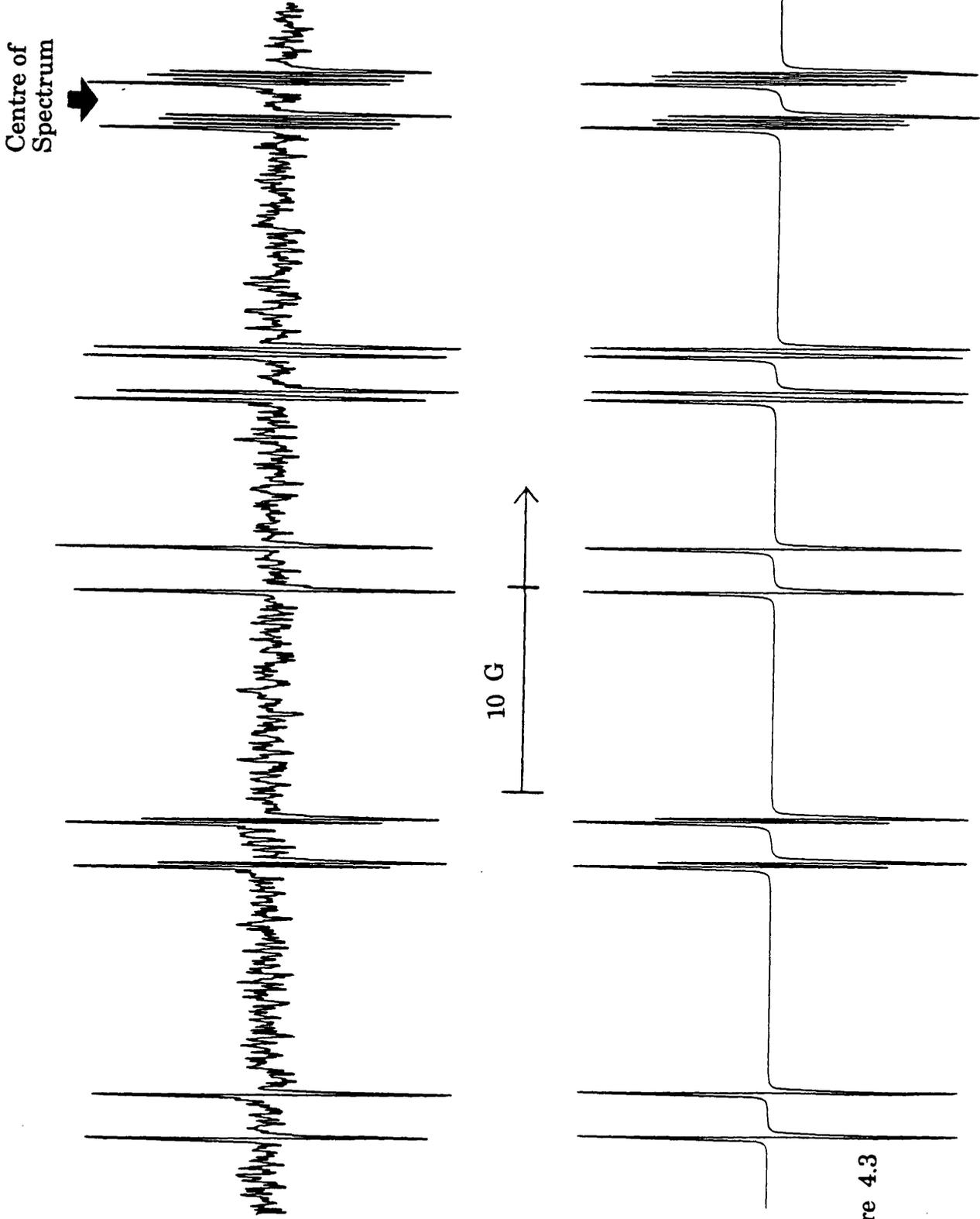


Figure 4.3

Legend to Figure 4.2

E.s.r. spectrum of the ethoxyethyl radical (4.5) in Bu^tOH-Pe^tOH (3:1 v/v) at 282 K.

Legend to Figure 4.3

E.s.r. spectrum of the oxacyclopentenyl radical (4.6) in Bu^tOH-Pe^tOH (3:1 v/v) at 282 K. (Low field half spectrum).

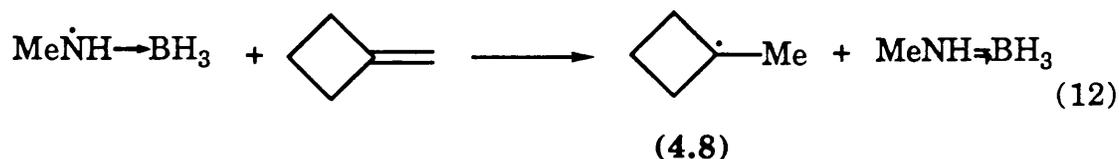
2.0032.

In an attempt to bring about β -H-atom transfer to an electron deficient alkene, trimethyl(vinyl)silane was examined. However, even when the concentration of the silane was low (*ca.* 0.2 M) and that of methylamine-borane was high (*ca.* 2.0 M) the major spectrum observed was that of the adduct (4.7) [$a(1H_\alpha)$ 18.6, $a(2H_\beta)$ 18.6, $a(^{11}B)$ 22.3 G, and g 2.0027 at 282 K] formed by the addition of the amine-boryl radical to the alkene [equation (11)]. Evidently the *nucleophilic* amine-boryl radical

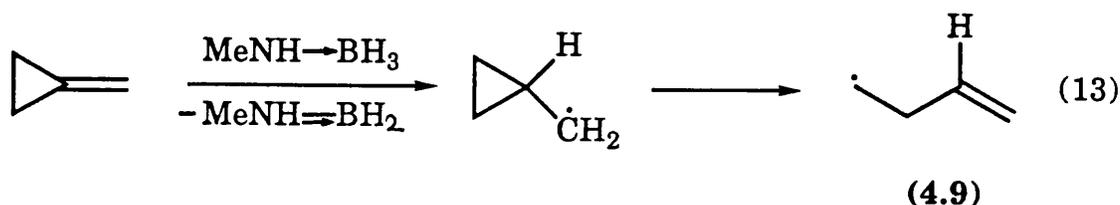


(4.3) is trapped by the electron deficient alkene before isomerisation to (4.4) can take place. Under these conditions other lines (not due to either $\text{Me}_3\text{Si}\dot{\text{C}}\text{HMe}$ or to $\text{Me}_3\text{SiCH}_2\dot{\text{C}}\text{H}_2$) were present; they were not present with higher silane and lower amine-borane concentrations. Possibly hydrogen-atom transfer is not the major reaction between (4.4) and the vinyl silane. The triethylamine-boryl¹⁸ and triethylsilyl¹⁹ radicals also undergo addition to trimethyl(vinyl)silane.

Hydrogen-atom transfer to methylenecyclobutane (*ca.* 1 M) at 282 K in Bu'OH-Pe'OH (3:1 v/v) afforded an e.s.r. spectrum which we ascribe to the 1-methylcyclobutyl radical (4.8) [equation (12)]; it could be



simulated in terms of $a(4H_\beta)$ 34.4, $a(3H_\beta)$ 23.2, $a(2H)$ 1.13 G, and g

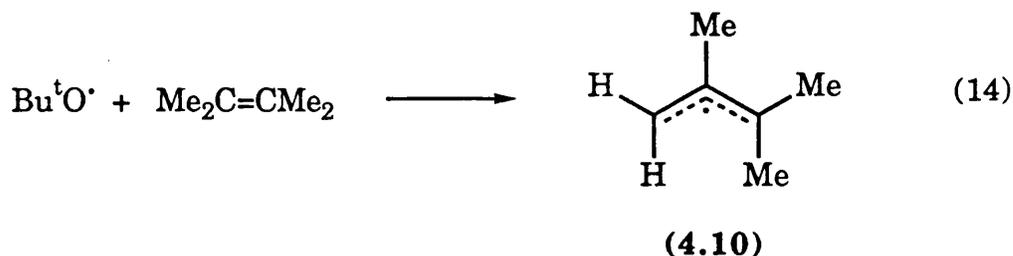


2.0027. In contrast, a similar experiment with methylenecyclopropane afforded the spectrum of the but-3-enyl radical¹⁶ (4.9) [equation (13)], presumably formed by H-atom transfer to the substituted end of the double bond²¹ followed by ring opening of the derived cyclopropylmethyl radical, along with lines derived from an unidentified radical. In previous studies²¹ of the addition of electrophilic radicals $\text{Bu}^{\cdot}\text{O}$, $\text{Bu}^{\cdot}\text{OH}^+$, and $\text{Me}_3\text{SiO}^{\cdot}$ and of the nucleophilic $\text{Me}_3\text{Si}^{\cdot}$ radical to methylenecyclopropane and -butane, it was found that all three electrophilic radicals added to the head (substituted) end of the double bond in methylenecyclopropane, whilst $\text{Me}_3\text{Si}^{\cdot}$ added to the tail end. With methylenecyclobutane, $\text{Me}_3\text{SiO}^{\cdot}$, $\text{Bu}^{\cdot}\text{OH}^+$, and $\text{Me}_3\text{Si}^{\cdot}$ added to the tail end. Addition to the head end for methylenecyclopropane could be favoured because, although this produces a primary radical (which undergoes rapid ring opening), in the transition state there is an increase in negative charge on the addendum and an increase in positive charge on the tail carbon. It is found that the cyclopropylmethyl cation is relatively stable, whilst the cyclopropyl cation (which is the relevant species when considering tail addition) is destabilised.²²

Ethene is also reduced by the aminyl-borane radical (4.4), although

this alkene appears to be relatively unreactive. Thus, generation of (4.4) in the presence of ethene (1.0 M provided all the alkene was in solution) at 282 K in Bu^tOH-Pe^tOH (3:1 v/v) yielded overlapping spectra of the ethyl radical, (4.4) and another radical which might possibly be the adduct radical, MeNH₂BH₂CH₂ĊH₂. The value of [Et[•]]/[(4.4)] was only *ca.* 0.2, indicating that ethene is a less avid acceptor of hydrogen than propene.

U.v. irradiation at 282 K of samples containing MeNH₂→BD₃ (0.5 - 1.7 M), DTBP (20% v/v), and Me₂C=CMe₂ (1.0-1.6 M) in Bu^tOH-Pe^tOH (3:1 v/v); 2,2,5,5-tetramethyltetrahydrofuran-dioxane (5:1 v/v), or dioxane, afforded the e.s.r. spectrum of Me₂CDĊMe₂, although Me₂CHĊMe₂ was also detected. However, the relative concentration of the protiated radical increased, initially rapidly, with the duration of photolysis and extrapolation indicated that Me₂CDĊMe₂ was the only radical present at zero irradiation time (Figure 4.4). This result demonstrates that it is the aminyl-borane radical (4.4) which is the active reducing agent and that the isomeric amine-boryl radical (4.3) is not involved, at least at *ca.* 282 K when the amine-borane concentration is > 0.5 M. It is noteworthy that no radicals resulting from abstraction from Me₂C=CMe₂ to give (4.10) [equation (14)] or from oxirane^{23,24} occurred, testifying to a high rate of H/D abstraction from boron in the amine-borane. A small



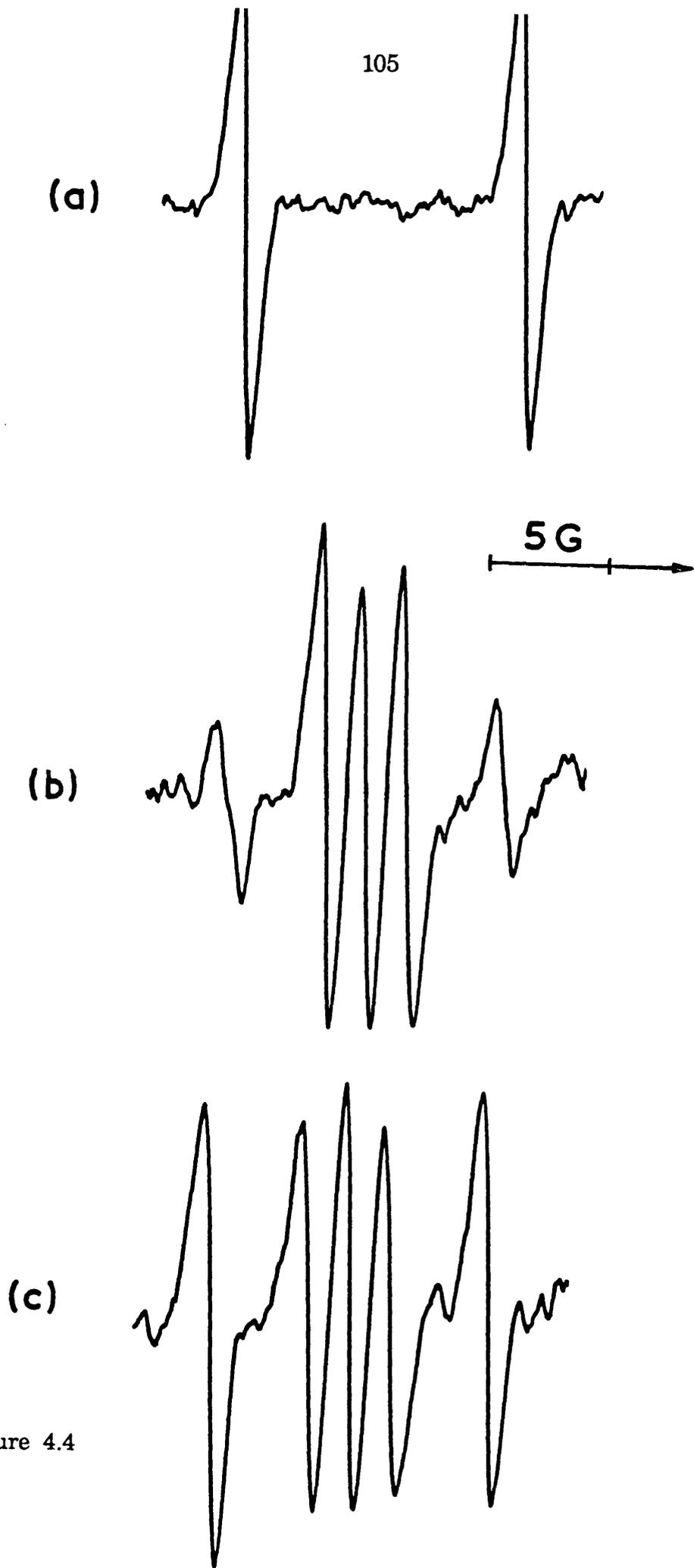


Figure 4.4

Legend to Figure 4.4.

E.s.r. spectrum of $\text{Me}\dot{\text{C}}\text{HMe}_2$ (lines 5 and 6) and $\text{Me}\dot{\text{C}}\text{CDMe}_2$ (lines 7,8 and 9) in $\text{Bu}^1\text{OH-Pe}^1\text{OH}$ (3:1 v/v) at 282 K, showing the development of $\text{Me}\dot{\text{C}}\text{CDMe}_2$ with time (*a*) was obtained using undeuteriated material, (*b*) is close to time zero and (*c*) is after 10 min.

amount of competitive H-atom abstraction from dioxane solvent was evident.

The extent to which protium is incorporated into $\text{MeNH}_2 \rightarrow \text{BD}_3$ with time was investigated by i.r. spectroscopy. In dioxane solution, $\text{MeNH}_2 \rightarrow \text{BH}_3$ gave rise to three resolved absorption bands in the 2200 - 2400 cm^{-1} region, at 2271, 2320, and 2356 cm^{-1} (Figure 4.5). By analogy with previous assignments for similar compounds, the last peak is ascribed to the BH_3 antisymmetric stretching mode,²⁵ and this peak was used to monitor the concentration of amine-borane by assuming the Beer-Lambert law to hold. The corresponding antisymmetric BD_3 stretching vibration of $\text{MeNH}_2 \rightarrow \text{BD}_3$ gave rise to a band at 1766 cm^{-1} which was broader than the 2356 cm^{-1} band for the protiated material. A single weak absorption band at 2330 cm^{-1} was also detected in the 2200 - 2400 cm^{-1} region and is attributed to a trace of $\text{MeNH}_2 \rightarrow \text{BD}_2\text{H}$, which arises because the primary source of deuterium (LiAlD_4) contained only 98 atom% D. Figure 4.5(a) and (b) shows i.r. spectra of $\text{MeNH}_2 \rightarrow \text{BD}_3$ and $\text{MeNH}_2 \rightarrow \text{BH}_3$, respectively. A series of solutions containing known concentrations of $\text{MeNH}_2 \rightarrow \text{BD}_3$ together with 0-50 mol% $\text{MeNH}_2 \rightarrow \text{BH}_3$ were examined and a plot of the optical density ratio (A_{2356}/A_{1766}) against $[\text{MeNH}_2 \rightarrow \text{BH}_3]/[\text{MeNH}_2 \rightarrow \text{BD}_3]$ gave a good straight line of slope 0.87 (Figure 4.6). Table 4.2 gives details of results obtained with eight samples.

Reaction mixtures containing $\text{MeNH}_2 \rightarrow \text{BD}_3$ were prepared and treated in exactly the same way as those used in e.s.r. spectra, except that the sample volumes were smaller to ensure that all of the solution

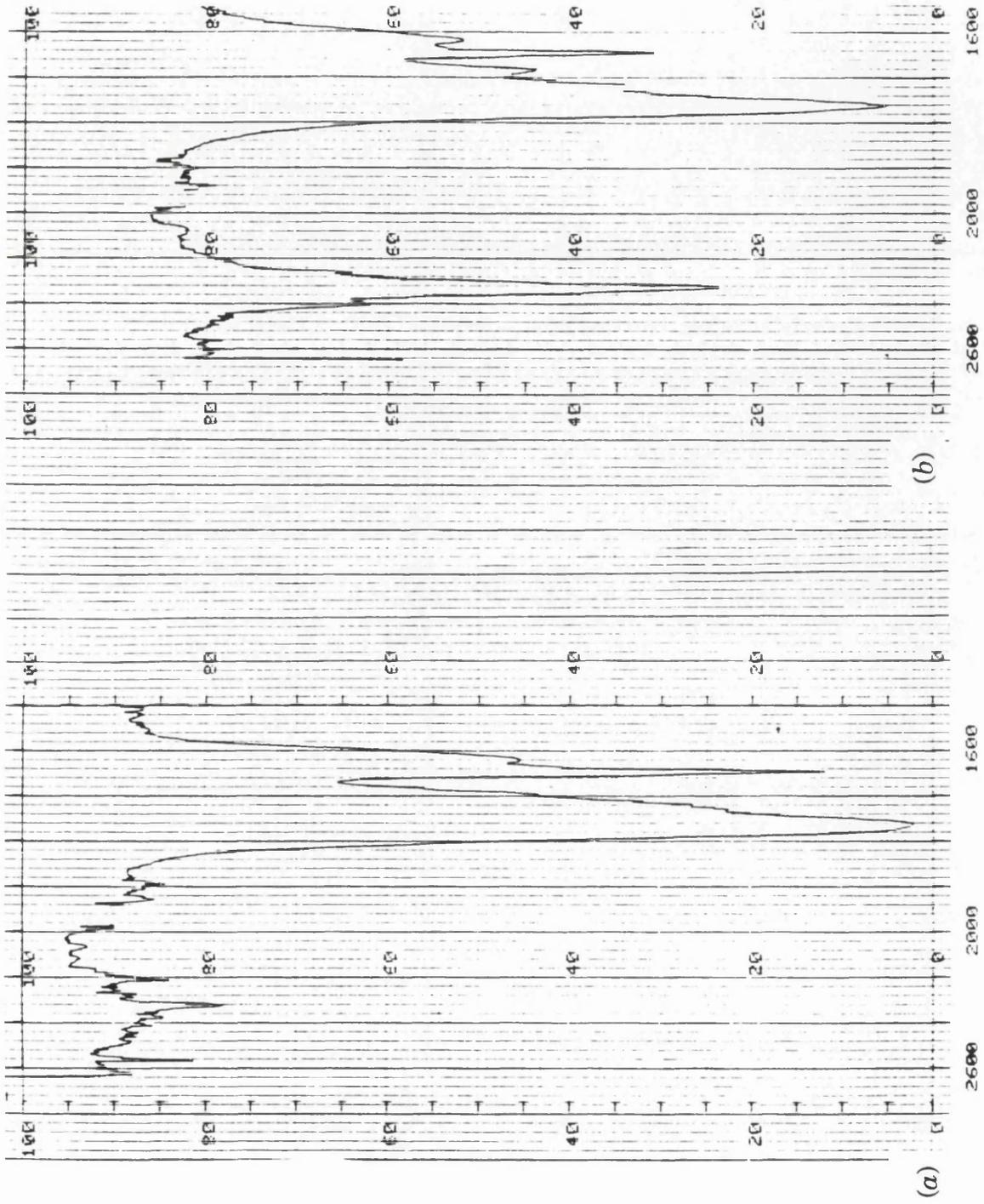


Figure 4.5

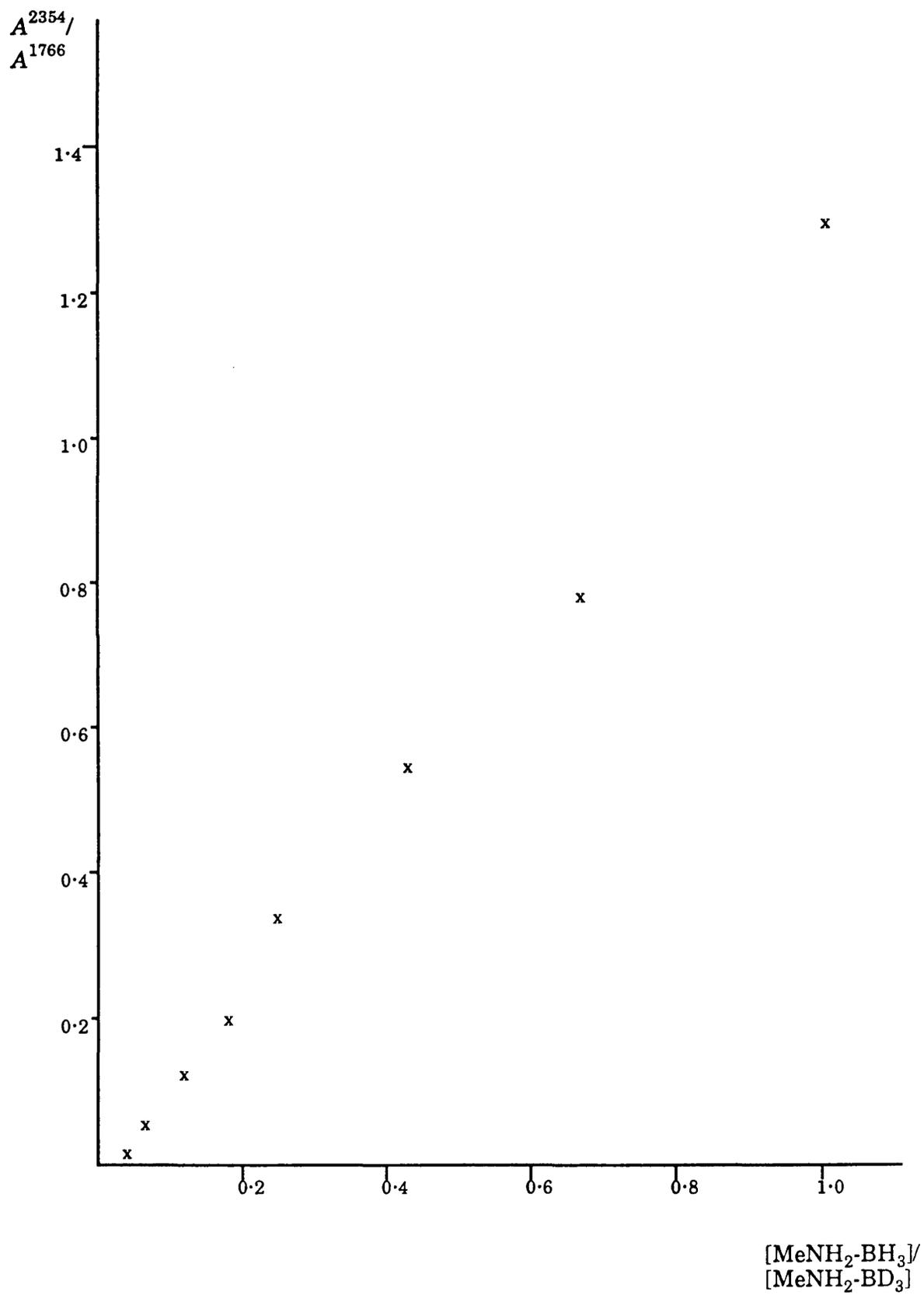


Figure 4.6

Legend to Figure 4.5

I.r. spectra of (a) $\text{MeNH}_2 \rightarrow \text{BD}_3$ and (b) $\text{MeNH}_2 \rightarrow \text{BH}_3$, both *ca.* 1.4 M in dioxane.

Legend to Figure 4.6

Graph of the optical density ratio (A_{2358}/A_{1766}) against $[\text{MeNH}_2 \rightarrow \text{BH}_3]/[\text{MeNH}_2 \rightarrow \text{BD}_3]$ obtained from i.r. measurements in dioxane solution.

Table 4.2. Relative molar extinction coefficients of $\text{MeNH}_2 \rightarrow \text{BD}_3$ and $\text{MeNH}_2 \rightarrow \text{BH}_3$.

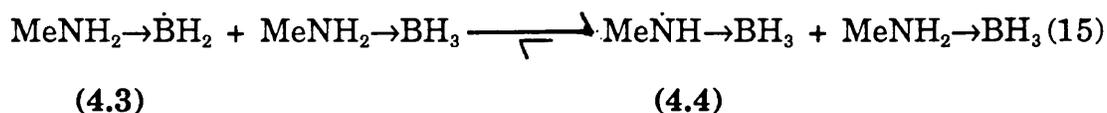
| $\frac{[\text{MeNH}_2 \rightarrow \text{BH}_3]}{[\text{MeNH}_2 \rightarrow \text{BD}_3]}$ | $A_{\text{BH}_3}^{2354}$ | $A_{\text{BH}_3}^{1766}$ | $\frac{A_{\text{BH}_3}^{2354}}{A_{\text{BD}_3}^{1766}}$ |
|---|--------------------------|--------------------------|---|
| 0.02 | 0.22 | 0.553 | 0.040 |
| 0.053 | 0.039 | 0.602 | 0.064 |
| 0.111 | 0.066 | 0.516 | 0.127 |
| 0.176 | 0.089 | 0.450 | 0.197 |
| 0.250 | 0.146 | 0.432 | 0.338 |
| 0.429 | 0.184 | 0.377 | 0.546 |
| 0.667 | 0.268 | 0.352 | 0.761 |
| 1.000 | 0.323 | 0.248 | 1.302 |

was positioned in the microwave cavity and thus received a similar dose of u.v. irradiation. After photolysis at 282 K, all volatiles were removed under reduced pressure and the residue (mainly amine-borane) was dissolved in dioxane and examined by i.r. spectroscopy. The recovered amine-borane showed a single band at 2330 cm^{-1} , which was more intense the longer the duration of photolysis; as before this band is assigned to the BH stretching vibration in $\text{MeNH}_2 \rightarrow \text{BD}_2\text{H}$ (Figure 4.7). The peak at 1766 cm^{-1} was used to monitor the residual $\text{MeNH}_2 \rightarrow \text{BD}_3$ and this band will include a contribution from the BD stretch for $\text{MeNH}_2 \rightarrow \text{BD}_2\text{H}$.

Samples containing $\text{MeNH}_2 \rightarrow \text{BD}_3$ (1.4 M) and DTBP (20% v/v) in

Bu¹OH-Pe¹OH (3:1 v/v) were irradiated for 0, 3, 10, and 20 min, after which the recovered amine-borane showed (A_{2330}/A_{1766}) values of 0.07, 0.13, 0.29, and 0.60, respectively. Using the same factor (0.87) which relates (A_{2330}/A_{1766}) to $[\text{MeNH}_2\rightarrow\text{BH}_3]/[\text{MeNH}_2\rightarrow\text{BD}_3]$, these relative optical densities correspond to 0.06, 0.11, 0.25, and 0.52 for $[\text{MeNH}_2\rightarrow\text{BD}_2\text{H}]/[\text{MeNH}_2\rightarrow\text{BD}_3] + [\text{MeNH}_2\rightarrow\text{BD}_2\text{H}] (\equiv P)$. In the presence of $\text{Me}_2\text{C}=\text{CMe}_2$ the corresponding values of P were 0.05, 0.06, 0.16, and 0.36 and, in the absence of DTBP the value of P was unchanged at 0.05 after 0, 10, and 20 min irradiation, similar to the value (0.04) for untreated $\text{MeNH}_2\rightarrow\text{BD}_3$ as prepared from 98 atom% D LiAlD_4 .

Accepting the uncertainties over the extinction coefficients for $\text{MeNH}_2\rightarrow\text{BD}_2\text{H}$ and the presence of reaction products in the recovered amine-borane, these results still show that substantial H/D exchange takes place rapidly under the conditions of the e.s.r. experiment. The smaller extent of isotopic exchange in the presence of alkene suggests that the isomerisation of (4.3) to (4.4) may be reversible to some degree [equation (15)] under the conditions of the experiment. When alkene is



present, (4.4) is efficiently trapped by β -H-atom transfer.

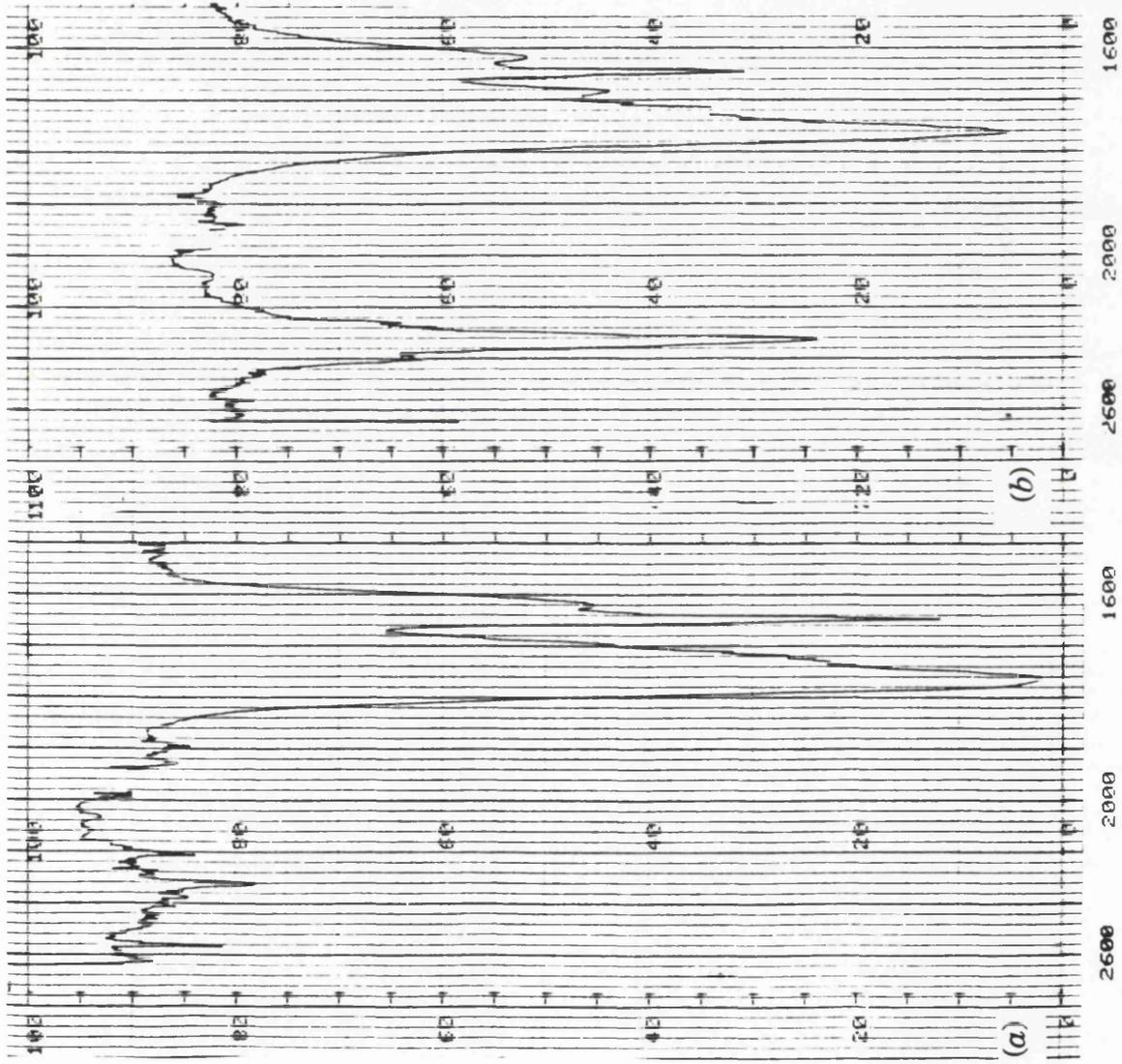


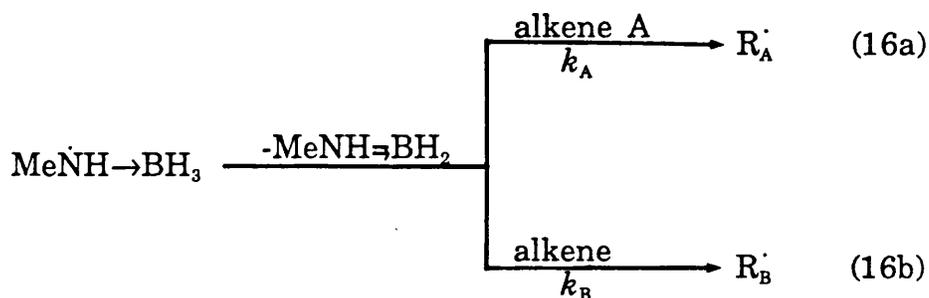
Figure 4.7

Legend to Figure 4.7

I.r. spectra of (a) $\text{MeNH}_2 \rightarrow \text{BD}_3$ prior to photolysis, and (b) $\text{MeNH}_2 \rightarrow \text{BD}_3$ after 20 min photolysis under the same conditions as the e.s.r. experiment.

Relative Rates of H-Atom Transfer To Alkenes

Relative rates of β -H-atom transfer from (4.4) to a number of alkenes at 282 K were measured in competition experiments [equation (16), making the usual assumptions¹¹ to relate stationary-state concentrations of radicals to their rates of formation. Provided that R_A



and R_B are removed only by self- and cross-reactions in diffusion-controlled processes which have the same rate coefficient, equation (17)

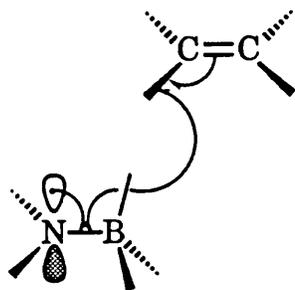
$$k_A/k_B = [R_A][\text{alkene B}]/[R_B][\text{alkene A}] \quad (17)$$

will hold. Selective removal of the product radicals by addition to either of the alkenes was unimportant under the experimental conditions, since the *relative* radical concentrations depended only on the relative amounts of alkenes and not their *total* concentration. The results are summarized in Table 4.3.

The relative rates of β -H-atom transfer to alkenes from (4.4) differ appreciably from those for addition of a free hydrogen atom in the gas phase at 298 K (see Table 4.3)²⁶

Initial attempts to compute meaningful transition state structures

for β -H-atom transfer to alkenes, by examining the prototype reaction between $\text{H}_2\dot{\text{N}}\rightarrow\text{BH}_3$ and $\text{CH}_2=\text{CH}_2$, have not proved successful, apparently because of the weakly-bound nature of aminyl-borane radicals in the gas phase. However, a transition state closely resembling (4.11) (or less likely a *cisoid*-conformation) would appear to be most reasonable.



(4.11)

Although the range of reactivities and ionization potentials is rather narrow, the two properties do appear to be correlated (Figure 4.8) providing support for predominance of the SOMO-HOMO interaction or, in more classical terms, for the importance of charge-transfer from the alkene to the aminyl-borane in the transition state. In particular, the more electron rich $\text{Me}_2\text{C}=\text{CMe}_2$ is more easily reduced than $\text{Me}_2\text{C}=\text{CH}_2$, although steric effects²⁷ should favour addition to the latter and a tertiary alkyl radical is produced from both alkenes. The double bond in an allylsilane is particularly electron rich for a mono-substituted ethene and the very high reactivity of allyl(trimethyl)silane in comparison with propene provides compelling evidence for the importance of polar effects in influencing the rate of H-atom transfer from the electrophilic (4.4).

Although aminyl-borane radicals have low SOMO energies (high

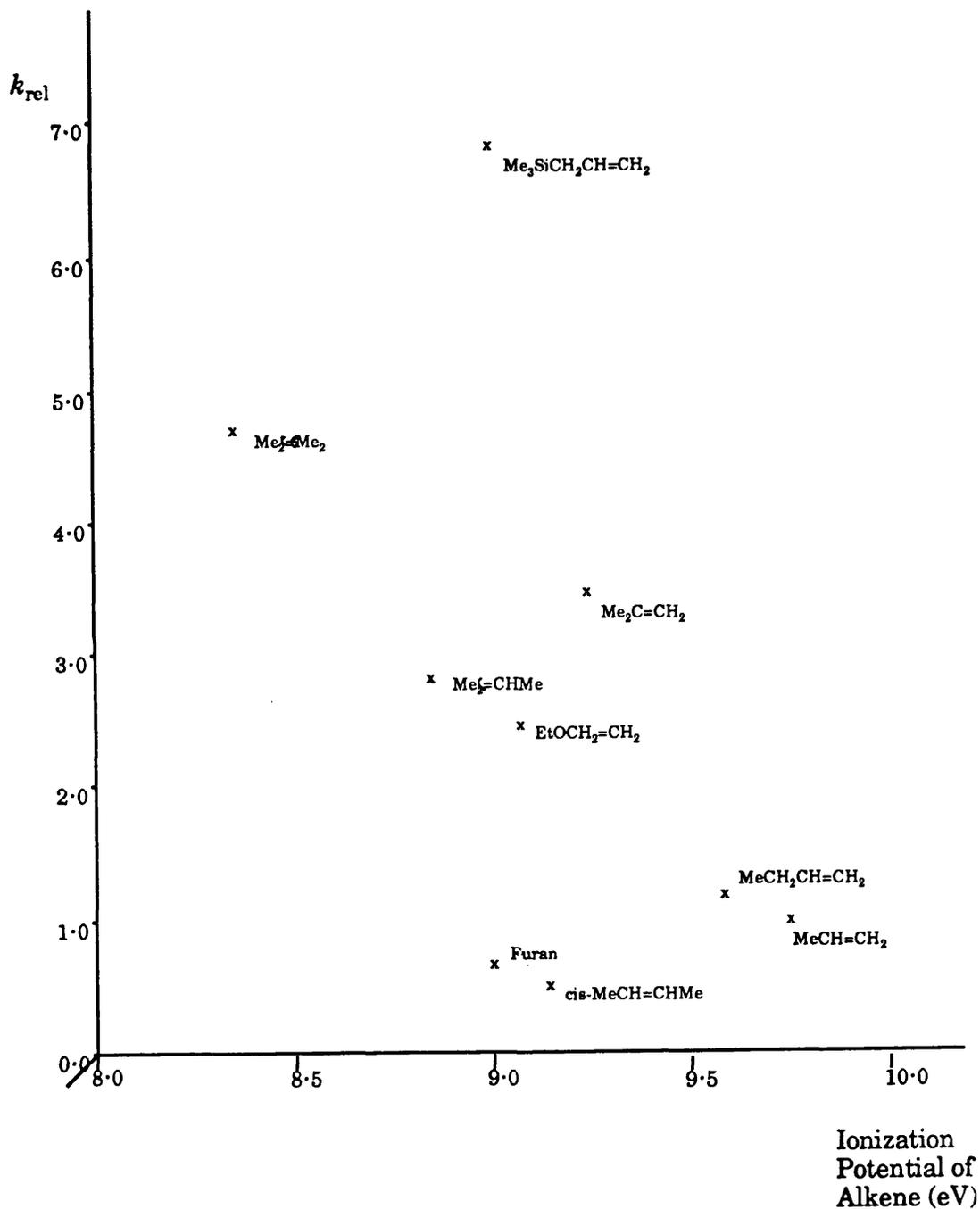
Table 4.3 Relative rates of hydrogen atom transfer to alkenes from the methylaminyl-borane radical (4.4) at 282 ± 1 K

| Alkene ^a | Solvent | k_{rel} | $k_{rel}(H)^b$ | Ionization potential of alkene (eV) |
|--|---------------------------------------|-----------|----------------|-------------------------------------|
| MeCH=CH ₂ | | (1.0) | (1.0) | 9.73 |
| MeCH ₂ CH=CH ₂ | | 1.2 | 1.03 | 9.63 |
| Bu ^t CH ₂ CH=CH ₂ | | 1.0 | | |
| Me ₂ C=CH ₂ | | 3.4 | 2.52 | 9.24 |
| <i>cis</i> -MeCH=CHMe | Bu ^t OH-Pe ^t OH | 0.5 | 0.47 | 9.12 |
| <i>trans</i> -MeCH=CHMe | (1:1 v/v) | 0.7 | 0.59 | 9.12 |
| Me ₂ C=CHMe | | 2.8 | 1.03 | 8.68 |
| Me ₂ C=CMe ₂ | | 4.7 | 0.84 | 8.27 |
| EtOCH ₂ =CH ₂ | | 2.4 | | 9.15 ^d |
| Me ₃ SiCH ₂ CH=CH ₂ | | 6.8 | | 9.00 |
| Furan | | 0.7 | | 8.99 ^c |
| MeCH=CH ₂ | | (1.0) | (1.0) | 9.73 |
| Me ₂ C=CH ₂ | | 3.3 | 2.52 | 9.24 |
| Me ₂ C=CHMe | Dioxane | 2.8 | 1.03 | 8.68 |
| Me ₂ C=CH ₂ | | 5.5 | 0.84 | 8.27 |

^a Competition experiments were carried out between propene and every other alkene and between 2-methylpropene and most other alkenes; all results were internally consistent to within experimental accuracy ($\pm 10\%$). ^b Data from ref. 39.

^c Data from G. Bieri, F. Burger, E. Heilbronner, and J. P. Maier, *Helv. Chim. Acta*, 1977, **60**, 2213 unless otherwise noted. ^d Data from H. Friege and M. Klessinger,

J. Chem. Research (S), 1977, 208. • Data from P. Linda, G. Marino, and S. Pignataro, *J. Chem. Soc. (B)* 1971, 1585.



Legend to Figure 4.8

Graph of relative rate of hydrogen atom transfer to alkenes from the methylaminy-borane radical against ionization potential of the alkenes.

i.p.s.), the hydrogen atoms attached to boron are relatively electron rich and interactions between *filled* molecular orbitals of the aminyl-borane radical and the LUMO of the alkene might also be important along with the SOMO-HOMO interaction in a frontier orbital analysis of β -H-atom transfer.

Furan displayed a fairly low reactivity towards (4.4), despite the allylic nature of the reaction product, and this is probably due to the loss of aromaticity upon addition of a hydrogen atom. Changing the solvent from protic Bu^tOH-Pe^tOH to aprotic dioxane has little influence on the rate of β -H-atom transfer from (4.4) and evidently any differences in the extent of solvation or association do not have large effects on the relative reactivities. In this context it is noteworthy that the calculated dipole moment of (4.4) is 5.5 D, while that of the aminoborane (4.12) is only 1.8 D.



(4.12)

The t-butylaminyl-borane radical also reduces alkenes in a qualitatively similar way to (4.4), although the spectrum of the t-butyl radical [produced by β -scission of (4.11)] was often observed [equation (18)].



(4.13)

β -Hydrogen-atom transfer from (4.13) at reduced temperatures was studied in cyclopropane-oxirane (1:1 v/v), or $\text{MeNH}_2 \rightarrow \text{BH}_3$ in oxirane, and DTBP (ca. 20% v/v). Relatively weak spectra of the alkyl radicals, Pr^\cdot , Bu^\cdot , or $\text{Me}_2\text{CH}\dot{\text{C}}\text{Me}_2$ were obtained with $\text{MeCH}=\text{CH}_2$, $\text{Me}_2\text{C}=\text{CH}_2$, and $\text{Me}_2\text{C}=\text{CMe}_2$, respectively.

With the dialkylaminyl-borane²⁴ $\text{Me}_2\dot{\text{N}} \rightarrow \text{BH}_3$, β -H-atom transfer to alkenes was found to occur much less readily than from (4.4) or (4.13). For example, u.v. irradiation of a $\text{Bu}^\cdot\text{OH}-\text{Pe}^\cdot\text{OH}$ (3:1 v/v) solution containing $\text{Me}_2\text{NH} \rightarrow \text{BH}_3$ (1.1 M), DTBP (ca. 20 % v/v) and one of the alkenes $\text{MeCH}=\text{CH}_2$, $\text{Me}_2\text{C}=\text{CH}_2$ or $\text{Me}_2\text{C}=\text{CMe}_2$ (1-3 M) afforded only relatively weak spectra of Pr^\cdot , Bu^\cdot , and $\text{Me}_2\text{CH}\dot{\text{C}}\text{Me}_2$, respectively, and quenching the spectrum of $\text{Me}_2\dot{\text{N}} \rightarrow \text{BH}_3$ was incomplete even with 3 M $\text{Me}_2\text{C}=\text{CMe}_2$. Reduction of propene was especially slow, as expected by comparison of the results obtained for (4.4) (Tables 4.3 and 4.4). The lower reactivity of the dialkylaminyl-borane radical parallels the smaller unpaired electron population on the β - BH_3 group, as evidenced by the appreciably smaller value of $\alpha(3\text{H})$ (46.4 G)²⁸ shown by $\text{Me}_2\dot{\text{N}} \rightarrow \text{BH}_3$. β -H-Atom transfer is probably also less favourable thermodynamically for $\text{Me}_2\dot{\text{N}} \rightarrow \text{BH}_3$ than for (4.4) or (4.13).

Generation of t-butoxyl radicals in the presence of an alkene, but in the absence of an amine-borane, afforded a spectrum of the allyl radical (Figure 4.9) derived from H-atom abstraction from the methyl group. Thus, photolysis of a solution containing propene (1.0 M) and DTBP (16% v/v) in $\text{Bu}^\cdot\text{OH}-\text{Pe}^\cdot\text{OH}$ (3:1 v/v) at 282 K afforded a spectrum of the allyl radical (4.14) [equation (19)] which could be analysed in

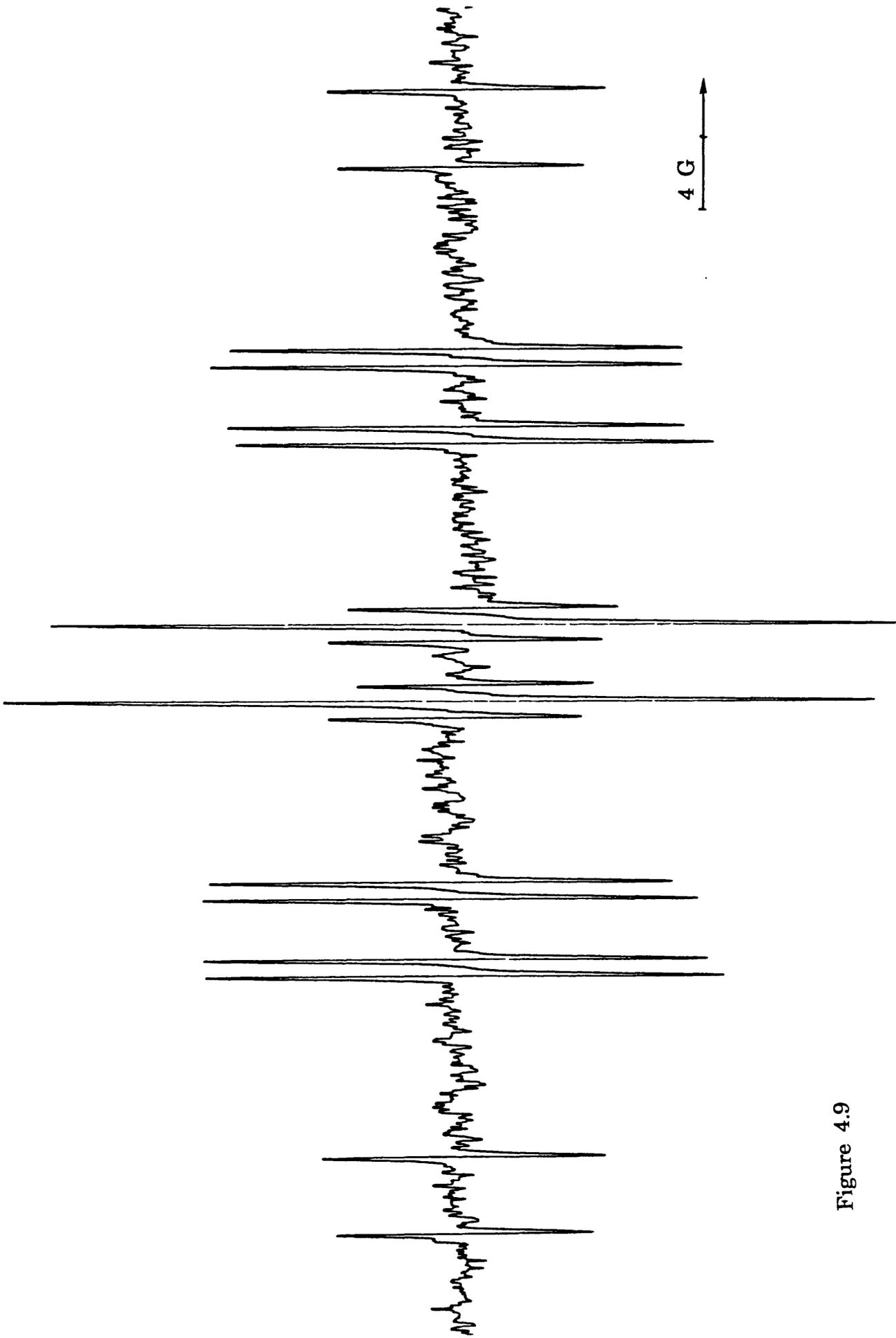
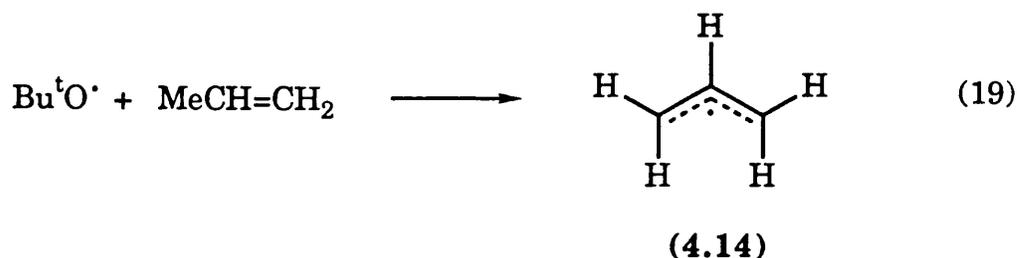


Figure 4.9

Legend to Figure 4.9.

E.s.r. spectrum of the allyl radical [$a(2H^1)$ 14.8, $a(2H^2)$ 14.0, $a(1H)$ 4.2 G, g 2.0026] derived by H-atom abstraction from propene (1.0 M) in Bu^tOH-Pe^tOH (3:1 v/v) at 282 K.

terms of $a(2H^1)$ 14.8, $a(2H^2)$ 14.0, $a(1H)$ 4.2 G, and g 2.0026.



It was noted that during u.v. irradiation of samples containing primary amine-boranes gas evolution occurred when the stationary state concentration of the aminyl-borane radical was high. A similar observation had been made previously when $\text{Me}_2\dot{\text{N}}\rightarrow\text{BH}_3$ was generated and the gas evolved was shown by Raman spectroscopy to be dihydrogen²⁸ [equation (20)]. When the steady-state concentration of the



aminyl-borane radical was low (for example in the presence of an alkene) no gas evolution was noted. It seems likely that self-reaction of aminyl-borane radicals can occur as shown in equation (20).

To probe the structure of the transition state for H-atom transfer to alkenes the competitive reduction of furan and tetramethylethene with different aminyl-boranes was investigated. Seven amine-boranes with widely differing *N*-alkyl groups were chosen. Apart from the nature of the amine-borane, the samples were identical to those used to obtain the data given in Table 4.3. The relative rates of reduction are shown in Table 4.4.

Table 4.4 Relative rates of hydrogen-atom transfer from $\text{RN}\dot{\text{H}}\rightarrow\text{BH}_3$ and from $\text{Me}_2\dot{\text{N}}\rightarrow\text{BH}_3$ to furan and tetramethylethene in $\text{Bu}^t\text{OH-Pe}^t\text{OH}$ (3:1 v/v) at 282 K.

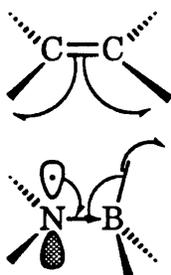
| R | k_{rel}^a |
|--|--------------------|
| H | 4.9 |
| Me | 6.8 |
| Bu ^a | 6.9 |
| Oct ^a | 7.1 |
| Bu ^t C(H)Me | 7.6 |
| Bu ^t ^b | 7.7 |
| $\text{Me}_2\dot{\text{N}}\rightarrow\text{BH}_3$ ^c | 7.0 |

^a Results were obtained by double integration of appropriate lines in the e.s.r. spectra; values are internally consistent to within experimental accuracy ($\pm 10\%$).

^b Bu^t from β -scission of $\text{Bu}^t\text{NH}_2\rightarrow\dot{\text{B}}\text{H}_2$ was also present. ^c A weak spectrum from $\text{Me}_2\dot{\text{N}}\rightarrow\text{BH}_3$ was also present.

Firstly, the dependence of k_{rel} on the nature of R in $\text{RN}\dot{\text{H}}\rightarrow\text{BH}_3$ shows that it is the aminyl-borane radical and not a free hydrogen-atom that is responsible for alkene reduction. Secondly, the relatively small dependence of k_{rel} upon the nature of R appears to be more consistent with the *transoid*-transition state (4.11) than with the alternative *cisoid*-structure (4.15), for which steric interactions between R and the alkene

would be expected to be more severe.



(4.15)

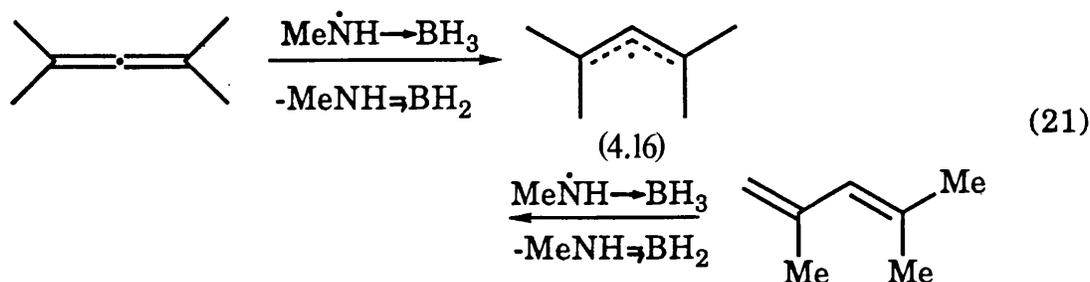
4.2 REACTION OF AMINYL-BORANE RADICALS WITH OTHER COMPOUNDS CONTAINING CARBON-CARBON MULTIPLE BONDS

Hydrogen-atom transfer to a number of other compounds containing carbon-carbon double bonds, including conjugated and cumulated double bonds and aromatic compounds have also been investigated.

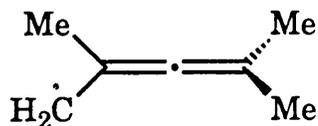
The 1,1,3,3-tetramethylallyl radical (4.16) was originally reported²⁹ to be formed by ring opening of the 2,2,3,3-tetramethylcyclopropyl radical, but this was later shown to be incorrect.³⁰ Although a number of 2-substituted derivatives, formed by radical addition to 2,4-dimethylpenta-2,3-diene (tetramethylallene), have been studied by e.s.r. spectroscopy,³¹ the spectrum of the parent radical has not yet been observed.

U.v. irradiation of a Bu^tOH-Pe^tOH (3:1 v/v) solution containing methylamine-borane (1.1 M), DTBP (ca. 20% v/v), and tetramethylallene or its conjugated isomer 2,4-dimethylpenta-2,4-diene (each 1.0 M) afforded

the same e.s.r. spectrum, shown in Figure 4.10, which is ascribed to the tetramethylallyl radical (4.16) [equation (21)].



The spectrum was simulated in terms of $a(6H^1)$ 14.2, $a(6H^2)$ 13.0, $a(1H)$ 5.4 G, and g 2.0027 at 301 K. These parameters do not indicate any sterically induced twisting of the allylic framework.³¹ Non-planarity is induced when a bulky substituent is present at C-2 in order to relieve steric strain. It is known³² that tetramethylallene is susceptible to H-atom abstraction by t-butoxyl radicals and to prove that this did not occur when methylamine-borane was present, a sample containing tetramethylallene (*ca.* 1.0 M), and DTBP (*ca.* 20% v/v) in Bu^tOH-Pe^tOH was u.v. irradiated at 306 K. The resultant spectrum, which is presumably due to (4.17), was different from that shown in Figure 4.9.



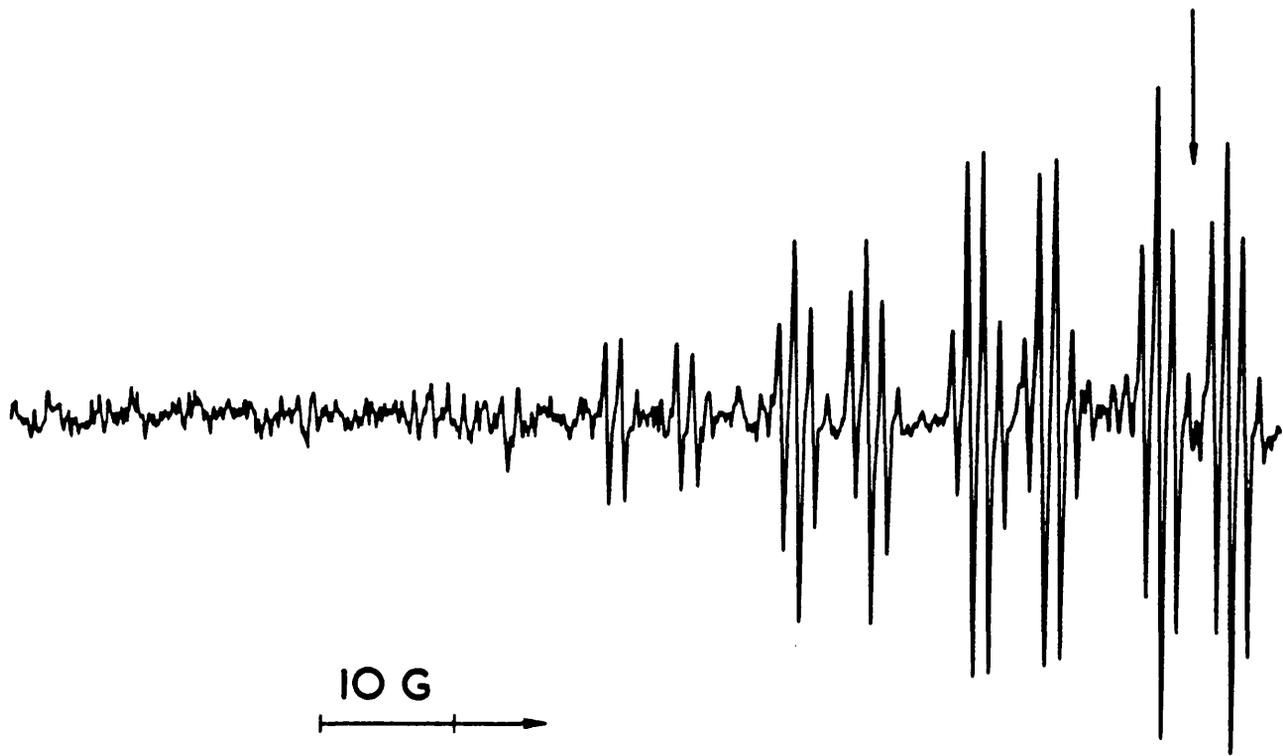
(4.17)

When the methylaminy-borane radical (4.4) was generated in the

Centre of Spectrum



(a)



10 G

(b)

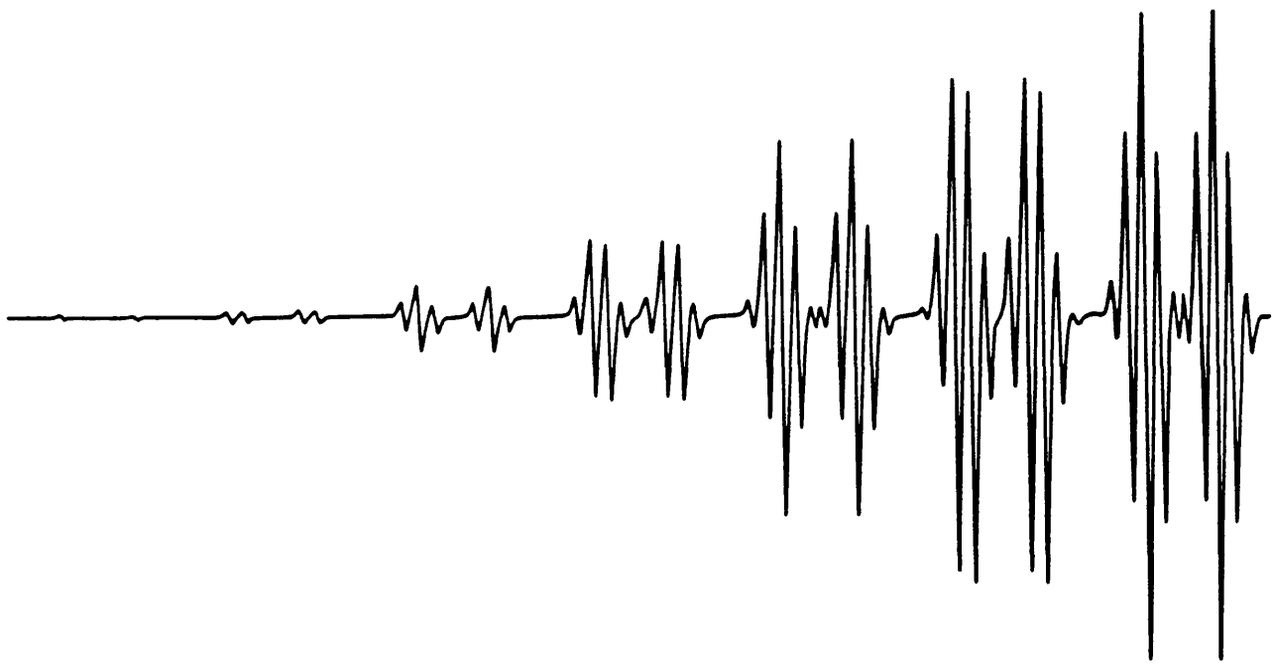
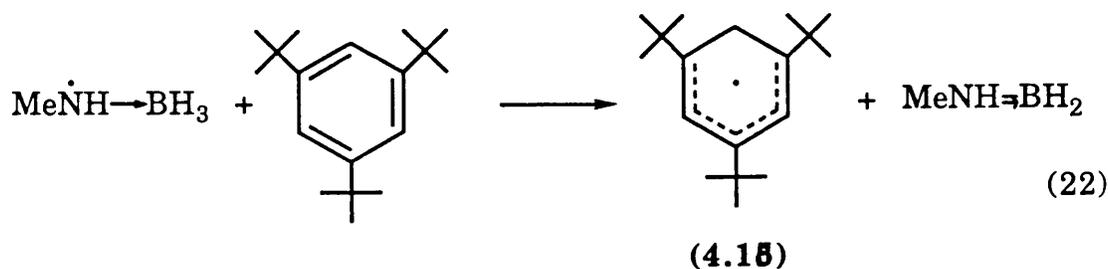


Figure 4.10

Legend to Figure 4.10

(a) Low field half spectrum of the tetramethylallyl radical (4.12) derived from 2,4-dimethylpenta-2,3-diene in Bu^tOH-Pe^tOH (3:1 v/v) at 300 K. (b) Computer simulation of (a) using the following splitting constants: 14.16 (6H), 12.98 (6H), and 5.40 G (1H). The linewidth is 0.4 G and the lineshape is 60% Lorentzian (40% Gaussian).

presence of benzene (1.0 M) the spectrum, of (4.4) was quenched and a very weak spectrum of what was probably the cyclohexadienyl radical (characterized by a triplet splitting of *ca.* 40 G) was present. To provide a more persistent cyclohexadienyl radical, which also had a simpler spectrum 1,3,5-tri-*t*-butylbenzene was chosen. Homolytic addition to this arene has been investigated previously; of the many addenda examined only pentafluorophenyl radicals gave an adduct detectable by e.s.r. spectroscopy.³³ Irradiation of a sample containing $\text{MeNH}_2 \rightarrow \text{BH}_3$ (1.2 M), 1,3,5-tri-*t*-butylbenzene (0.5 M), and DTBP (*ca.* 18% v/v) in $\text{Bu}^t\text{OH}-\text{Pe}^t\text{OH}$ (3:1 v/v) at 304 K afforded the spectrum of the cyclohexadienyl radical (4.18) [equation (22)] (Figure 4.11). It was relatively long-lived ($t = 0.5$ s at 304 K) in accord with expectation³³ for a cyclohexadienyl radical of this structure.



It has been shown previously that relatively persistent cyclohexadienyl radicals are also formed by homolytic addition to 1,3,5-tris(trimethylsiloxy)benzene³⁰ and hydrogen-atom transfer from (4.4) to this arene took place readily at 295 K in 2,2,5,5-tetramethyltetrahydrofuran solvent to yield the adduct (4.19) [$\alpha(2\text{H})$ 41.4, $\alpha(2\text{H}_{\text{meta}})$ 2.58 G and g 2.0028]. The e.s.r. spectrum (Figure 4.12) exhibited emission-enhanced

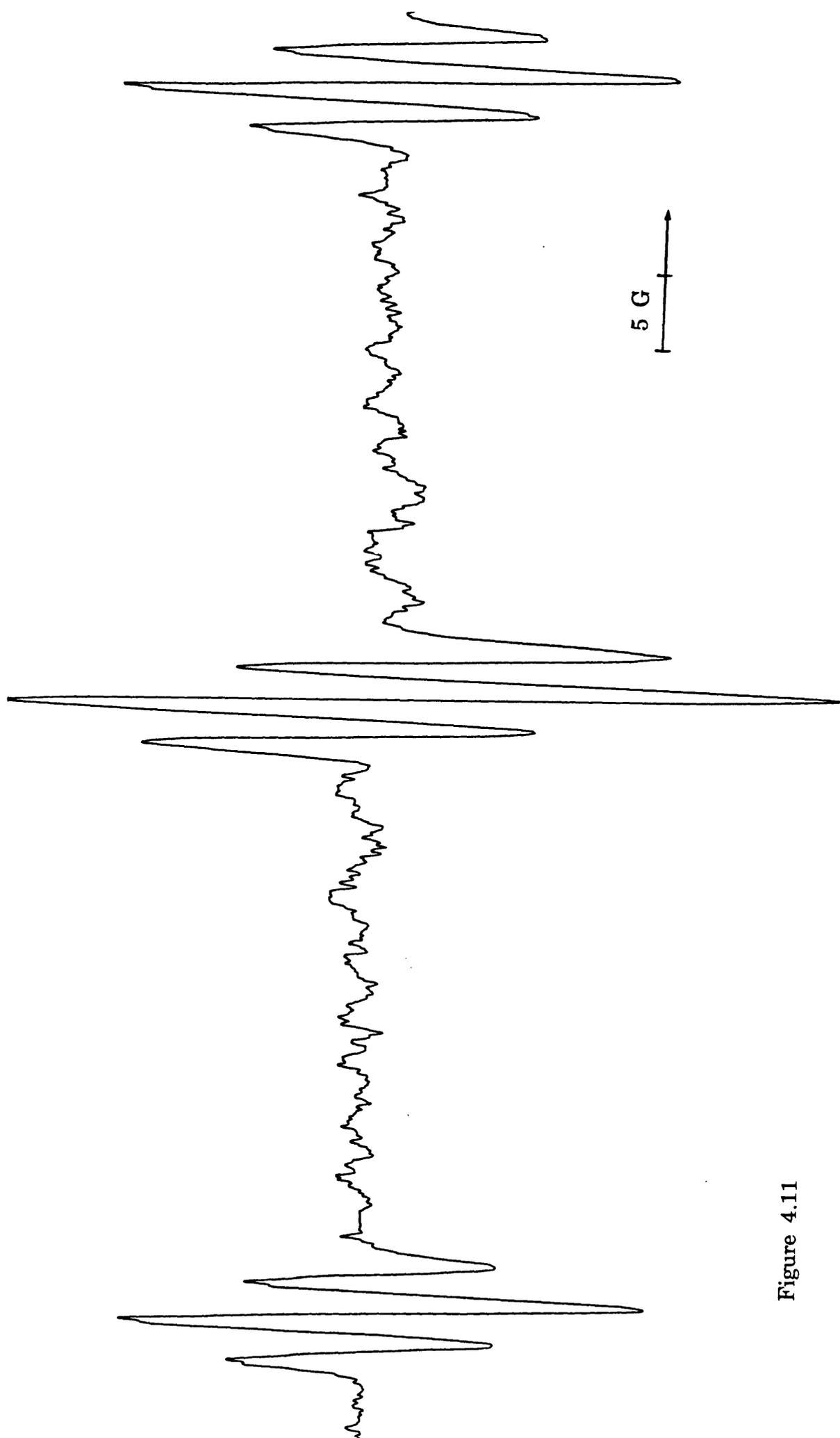


Figure 4.11

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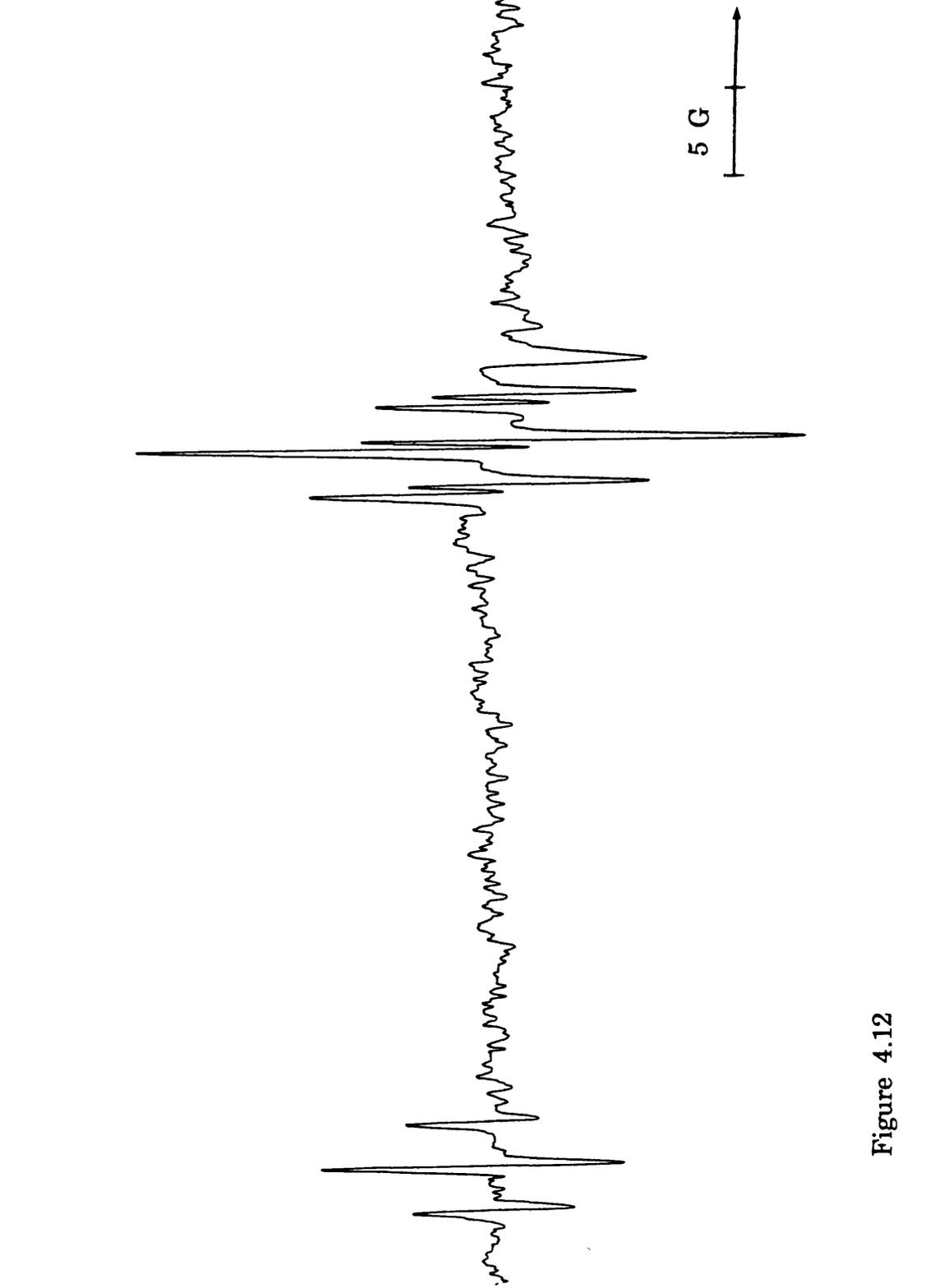


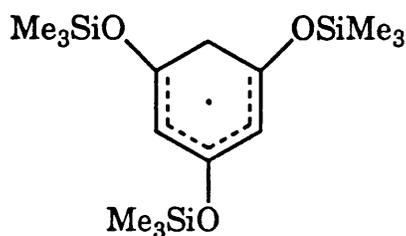
Figure 4.12

Legend to Figure 4.11

E.s.r. spectrum of the radical derived from H-atom transfer to tri-*t*-butylbenzene (0.5 M) at 304 K in Bu^tOH-Pe^tOH (3:1 v/v) [$a(2H)$ 41.6, $a(2H^{meta})$ 2.65 G, g 2.0027].

Legend to Figure 4.12

E.s.r. spectrum of the radical derived from H-atom transfer to tris(trimethylsiloxy)benzene (0.5 M) at 295 K in 2,2,5,5-tetramethyltetrahydrofuran [$a(2H)$ 41.4, $a(2H^{meta})$ 2.58 G, g 2.0026]. The broad line to high field of the central multiplet is due to electrons trapped in the quartz e.s.r. tube.



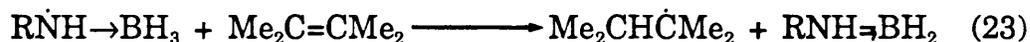
(4.19)

absorption polarization (see Figure 4.12).

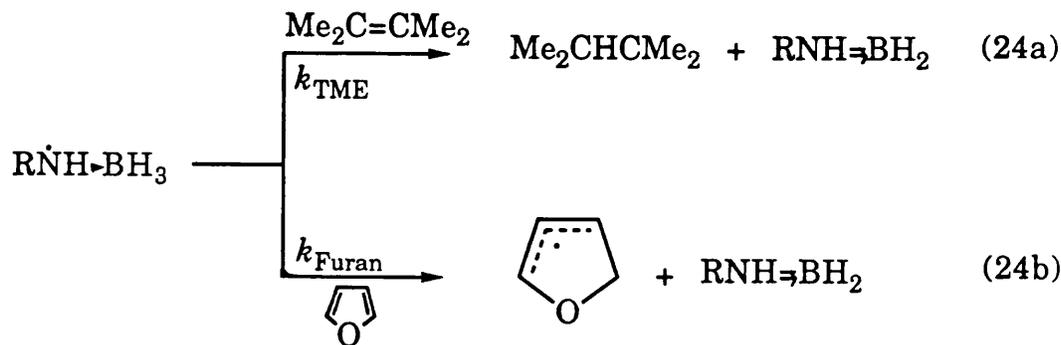
Methylamine-borane has the drawback of being insoluble in hydrocarbons, limiting its use to polar solvents. *t*-Butylamine-borane although more soluble, affords initially an amine-boryl radical which undergoes rapid β -scission at temperatures above *ca.* 270 K, thus preventing its conversion to the aminyl-borane. Therefore, a primary amine-borane was sought which would give rise to an aminyl-borane radical upon reaction with $\text{Bu}^{\bullet}\text{O}^{\bullet}$ and would also be soluble in hydrocarbons. With these aims in mind, *s*-butylamine-, *s*-octylamine-, and cyclopentylamine-boranes were investigated.

When a sample containing $\text{Bu}^{\bullet}\text{NH}_2 \rightarrow \text{BH}_3$ (1.1 M) and DTBP (*ca.* 18% v/v) in $\text{Bu}^{\bullet}\text{OH}-\text{Pe}^{\bullet}\text{OH}$ (3:1 v/v) or cyclopropane was photolysed at 282 K no e.s.r. spectrum could be identified with certainty, although some weak lines were present. The spectrum of the aminyl-borane radical would be difficult to detect because of the expected high multiplicity, broad lines, and temperature dependences. Replacing $\text{Bu}^{\bullet}\text{NH}_2 \rightarrow \text{BH}_3$ by $\text{Oct}^{\bullet}\text{NH}_2 \rightarrow \text{BH}_3$ afforded similar results. However, when *n*-propyl bromide (1.0 M) was included in the samples, experiments with either amine-borane afforded strong clean spectra of the *n*-propyl radical at 282 K.

When $\text{Me}_2\text{C}=\text{CMe}_2$ (1.0 M) was present along amine-borane and with DTBP (16% v/v), a strong spectrum of $\text{Me}_2\text{CH}\dot{\text{C}}\text{Me}_2$ was detected at 282 K in $\text{Bu}^t\text{OH}-\text{Pe}^t\text{OH}$ solvent. Here, the aminyl-borane radicals $\text{RNH}\dot{\rightarrow}\text{BH}_3$ ($\text{R} = \text{Bu}^t$ or Oct^t) are efficiently transferring a hydrogen atom to the alkene [equation (23)].



Hydrogen-atom transfer was next investigated at reduced temperatures in aprotic solvents. A sample containing $\text{Bu}^t\text{NH}_2\rightarrow\text{BH}_3$ (1.0 M) $\text{Me}_2\text{C}=\text{CMe}_2$ (1.0 M), and DTBP (ca. 40% v/v) in cyclopropane was u.v. irradiated at 250 K when the spectrum of $\text{Me}_2\text{CH}\dot{\text{C}}\text{Me}_2$ was slightly weaker than at 282 K in cyclopropane. Competitive H-atom transfer to furan and tetramethylethene [equation (24; $\text{R} = \text{Bu}^t$ or Oct^t)] gave the results shown in Table 4.5.



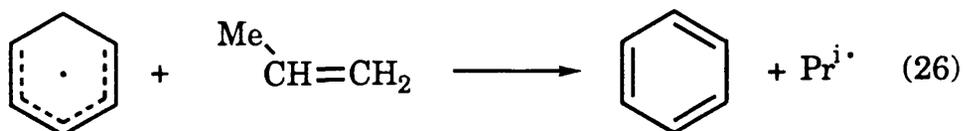
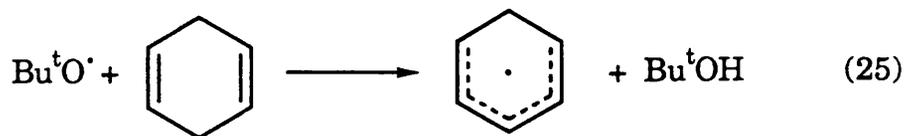
Finally, the possibility of H-atom transfer from the cyclohexadienyl radical to simple alkenes was investigated. When a sample containing cyclohexadiene (1.0 M) and DTBP (20% v/v) in $\text{Bu}^t\text{OH}-\text{Pe}^t\text{OH}$ (3:1 v/v)

Table 4.5 Competitive H-atom transfer to furan and tetramethylethene at reduced temperatures.

| Bu ^t NH→BH ₃ ^a | | Oct ^a NH ₂ →BH ₃ ^b | |
|---|---|--|---|
| T/K | <i>k</i> _{TME} / <i>k</i> _{Furan} | T/K | <i>k</i> _{TME} / <i>k</i> _{Furan} |
| 282 | 6.9 | 282 | 7.1 |
| 250 | 8.8 | 250 | 11.2 |
| 236 | 11.4 | 230 | 14.5 |
| 221 | 11.3 | | |

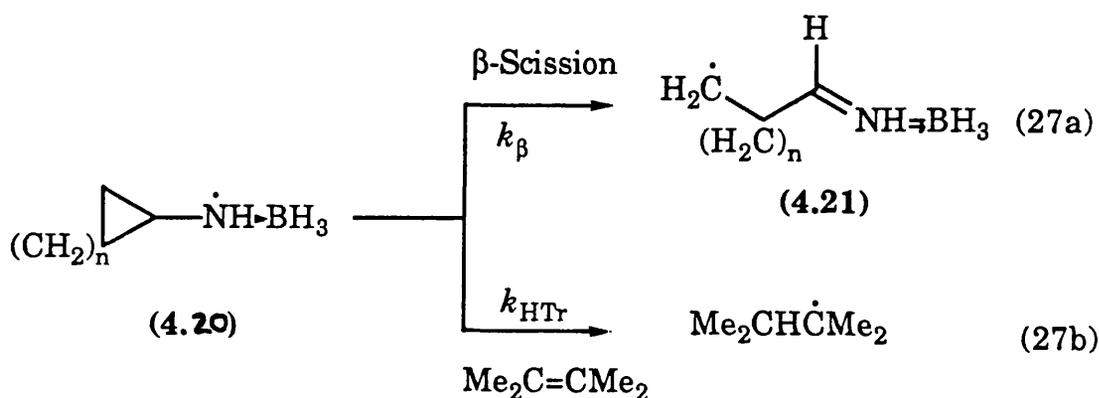
^aSolvent: cyclopropane-oxirane (6:1). ^bSolvent: cyclopropane.

was irradiated at 282 K, only a spectrum of the cyclohexadienyl radical was obtained [equation (25)]. Repetition of this experiment in the additional presence of either propene, 2-methylpropene, or tetramethylethene (*ca.* 1.0 M) gave rise only to a spectrum of the cyclohexadienyl radical in each case, and the reaction shown in equation (26) was not observed.



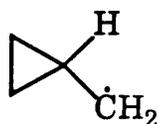
4.3 REACTIONS OF CYCLOALKYLAMINYL-BORANE RADICALS

It was reported in Chapter 2 that when a sample containing cyclopropylamine-borane (1.2 M) and DTBP (*ca.* 20%) v/v in cyclopropane-oxirane (1:1 v/v) was photolysed the spectrum of the primary alkyl radical (4.21; $n = 1$) [equation (27)] was obtained. It is well known that an intramolecular reaction can be used as a "clock" reaction to estimate the rate of a competing bimolecular reaction. When the above reaction was carried out in the presence of $\text{Me}_2\text{C}=\text{CMe}_2$ (0.74

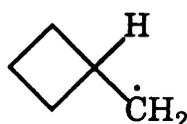


M) at 282 K, a spectrum of (4.21; $n = 1$) was obtained together with a much weaker spectrum of the hexyl radical [equation (27)]. The value of [(4.21; $n = 1$)]/[$\text{Me}_2\text{CH}\dot{\text{C}}\text{Me}_2$] was 7.6 and hence (k_β/k_{HTr}) is *ca.* 5.6 M. when $n = 1$. Similar competition experiments with (4.21 $n = 2$) gave a value of k_β/k_{HTr} of 2.7 M. With the assumption that the rate of H-atom transfer is the same for (4.21; $n = 1$ or 2) the value of the relative rate of β -scission for (4.21; $n = 1$)/(4.22; $n = 2$) is *ca.* 2.0. It follows from the rate of H-atom transfer to propene ($2.0 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$) and the data given in Table 4.3 that the value of k_β for ring opening of (4.21; $n = 1$) is *ca.* $2.0 \times 10^4 \text{ s}^{-1}$ and that for (4.21; $n = 2$) is *ca.* $1 \times 10^4 \text{ s}^{-1}$.

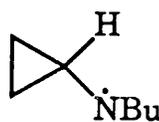
Such a small difference in the rates of ring opening of the cyclopropylaminyl- and cyclobutylaminyl-borane radicals would be very surprising in view of the fact that the cyclopropylmethyl radical (4.22) opens *ca.* 2×10^4 times more rapidly than the cyclobutylmethyl radical



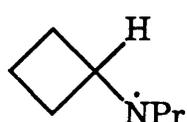
(4.22)



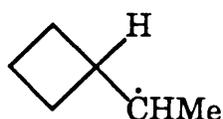
(4.23)



(4.24)



(4.25)

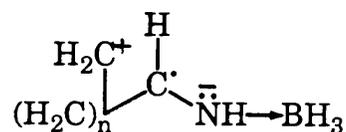


(4.26)

(4.23) at 282 K.^{31,32} The *N*-alkylated cyclopropylaminyl radical (4.24) undergoes ring opening approximately 50 times more rapidly than the comparable cyclobutylaminyl radical (4.25) at 323 K.³³ At 282 K the rate coefficient for ring opening of (4.25) ($4.7 \times 10^4 \text{ s}^{-1}$) is *ca.* 30 times greater than that for the ring opening of the 1-methylcyclobutylmethyl radical (4.26) (*ca.* $1.5 \times 10^3 \text{ s}^{-1}$),³⁴ which is the isoelectronic analogue of the aminyl-borane (4.20; $n = 2$). The rate coefficient for opening of (4.20 $n = 2$) is $1 \times 10^4 \text{ s}^{-1}$ at 282 K and hence a small difference in the rates of ring opening between (4.20; $n = 1$) and (4.20; $n = 2$) cannot be attributed to compression of the relative rates which will be observed as the absolute rate increases, implying that other factors must be

responsible. It seems likely that this anomaly is related to the exceptional nature of the three-membered ring³⁵ which makes (4.20; $n = 1$) an atypical primary aminyl-borane radical. Cyclopropylamine is less basic than other primary amines^{35a} and this should decrease the stability of cyclopropylamine-borane in protic media. The electronic configurations of aminyl-borane radicals are very sensitive to substituent effects and the unpaired electron distribution in the cyclopropylaminyl-borane radical (4.20; $n = 1$) could differ significantly from that in other aminyl-boranes. Thus, it is possible that (4.20; $n = 1$) 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 (4.27) in a valence bond



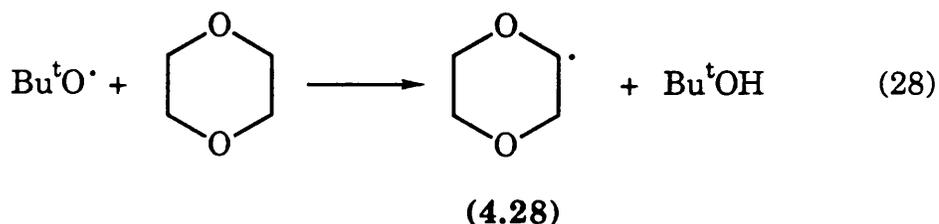
(4.27)

description of the transition state. For cycloalkylmethyl radicals charge separation in the transition state will clearly be less extensive (and probably in the opposite direction³¹).

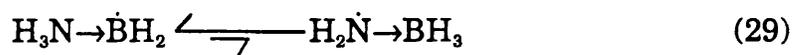
4.4 RADICALS DERIVED FROM AMMONIA-BORANE

Since $\alpha(3BH)$ increases significantly on going from $\text{Me}_2\dot{\text{N}}\rightarrow\text{BH}_3$ to $\text{Me}\dot{\text{N}}\text{H}\rightarrow\text{BH}_3$ (46.4 to 63.9 G), it is likely that $\text{H}_2\dot{\text{N}}\rightarrow\text{BH}_3$ would show a still larger value of $\alpha(3BH)$, probably paralleled by a greater thermodynamic instability towards β -scission. It is therefore possible that the lifetime of $\text{H}_2\dot{\text{N}}\rightarrow\text{BH}_3$ with respect to unimolecular loss of H^\cdot or bimolecular β -H-atom transfer to protic solvents or to parent ammonia-borane could be fairly short making this aminyl-borane difficult to detect.

To examine the possibility that $\text{H}_2\dot{\text{N}}\rightarrow\text{BH}_3$ could be produced along with $\text{H}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$ by the $\text{H}_3\text{N}\rightarrow\text{BH}_3 + \text{Bu}^t\text{O}^\cdot$ couple, the effect of adding $\text{Me}_2\text{C}=\text{CMe}_2$ was investigated. U.v. irradiation of a sample containing $\text{H}_3\text{N}\rightarrow\text{BH}_3$ (1.1 M), DTBP (*ca.* 17% v/v), and $\text{Me}_2\text{C}=\text{CMe}_2$ (1.5 M) in $\text{Bu}^t\text{OH}-\text{Me}_2\text{O}$ (4:1 v/v) at 282 K gave rise to a relatively strong spectrum of $\text{Me}_2\text{CH}\dot{\text{C}}\text{Me}_2$ and the spectrum of the ammonia-boryl radical was undetected. A similar result was obtained in $\text{Pe}^t\text{OH}-\text{Me}_2\text{O}$ (1:1 v/v) at 269 K with $\text{Me}_2\text{C}=\text{CMe}_2$ (1.1 M). In dioxane with $\text{H}_3\text{N}\rightarrow\text{BH}_3$ (1.1 M), $\text{Me}_2\text{C}=\text{CMe}_2$ (1.1 M), and DTBP (16% v/v) at 293 K, the spectrum of $\text{Me}_2\text{CH}\dot{\text{C}}\text{Me}_2$ was observed together with a weak spectrum of (4.28) derived by abstraction from dioxane [equation (28)]. When tetramethyl-



ethene was replaced by 2-methylpropene (1.4 M) in Bu^tOH-Me₂O (4:1 v/v) with H₃N→BH₃ (1.1 M) and DTBP (*ca.* 14% v/v) at 275 K, the spectrum of the ammonia-boryl radical was partially replaced by the t-butyl radical. When the experiment was repeated in the presence of propene (1.0 M) under the same conditions a weak spectrum of the isopropyl radical was observed together with the ammonia-boryl radical. These results accord with those obtained with MeNH₂→BH₃ in that the ease of reduction decreases in the order Me₂C=CMe₂ > Me₂C=CH₂ > MeCH=CH₂ and support the existence of a labile equilibrium between the ammonia-boryl and aminyl-borane radicals [equation (29)]. Use of H₃N→BD₃ in the



presence of Me₂C=CMe₂ gave rise to a spectrum of Me₂CD $\dot{\text{C}}$ Me₂ and to zero time showed this to be the only radical present.

In previous work²⁸ it proved possible to generate Me₂N $\dot{\text{N}}$ →BH₃ by H-atom abstraction from the NH group by cyclopropyl radicals [equation (30)]. However, this reaction does not occur sufficiently readily to be

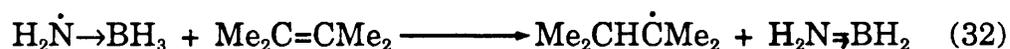
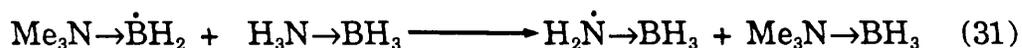


detected by e.s.r. spectroscopy with primary amine-boranes or ammonia-borane.

An alternate route for by-passing the aminyl-boryl radical and forming the aminyl-borane radical directly was to use a high

concentration of $\text{Me}_3\text{N}\rightarrow\text{BH}_3$, together with $\text{H}_3\text{N}\rightarrow\text{BH}_3$, ideally in the ratio of $\geq 10:1$ would be best. However, due to the low solubility of $\text{Me}_3\text{N}\rightarrow\text{BH}_3$ the maximum usable concentration ratio was 4:1. (It was assumed that the affinity of $\text{Bu}^{\cdot}\text{O}^{\cdot}$ towards both amine-boranes is the same).

When a sample containing $\text{Me}_3\text{N}\rightarrow\text{BH}_3$ (1.2 M), $\text{H}_3\text{N}\rightarrow\text{BH}_3$ (0.3 M), and DTBP (*ca.* 20% v/v) in $\text{Bu}^{\cdot}\text{OH}-\text{Me}_2\text{O}$ (4:1 v/v) was photolysed no spectrum of the ammonia-boryl radical was observed. When the experiment was repeated in the presence of $\text{Me}_2\text{C}=\text{CMe}_2$ (1.5 M), a relatively strong spectrum of $\text{Me}_2\text{CH}\dot{\text{C}}\text{Me}_2$ was obtained, suggesting that abstraction from the NH group of $\text{H}_3\text{N}\rightarrow\text{BH}_3$ by $\text{Me}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$ is occurring and that the aminyl-borane formed is able to undergo H-atom transfer to $\text{Me}_2\text{C}=\text{CMe}_2$ [equations (31) and (32)].



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CHAPTER 5

Hydrogen Atom Transfer From Aminyl-Borane Radicals To Hexamethyldisilane (HMDS)

Hydrogen atoms produced by pulsed mercury-photosensitised photolysis¹ of dihydrogen,² have been shown to react with hexamethyldisilane (HMDS) to give the trimethylsilyl radical and trimethylsilane according to equation (1). This reaction is particularly rapid in the gas phase at 295 K, and k_1 is $2.1 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$. Hydrogen



atoms react with alkanes by hydrogen atom abstraction³ [e.g. equation (2)] and $\text{S}_{\text{H}}2$ reaction at a carbon centre has never been observed. *t*-Butoxyl radicals react with HMDS by hydrogen-atom abstraction to give the radical (1)^{4,5} [equation (3)], rather than by $\text{S}_{\text{H}}2$ displacement from



(5.1)

silicon [cf. equation (1)], which in this case is calculated to be more exothermic by 100 kJ mol^{-1} .^{6,7} A value of $1.2 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ at 303 K

may be derived for k_3 based on the published relative and absolute rate coefficients.^{5,8}

Homolytic substitution at a multivalent atom centre becomes more favoured if there are low lying unoccupied orbitals available. Such reactions are particularly common for trialkylboranes and can become extremely rapid in favourable cases [e.g. equation (4)].³



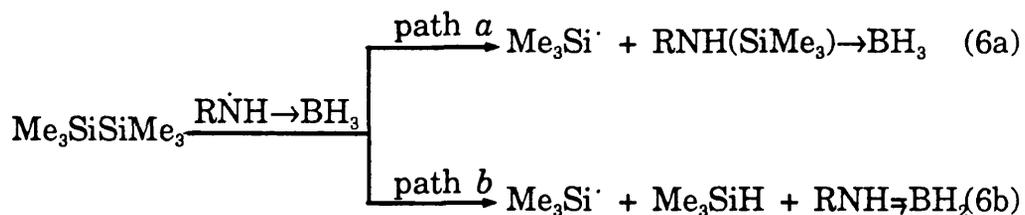
Molecular iodine also reacts with HMDS at elevated temperatures in the gas phase to yield trimethylsilyl iodide as the only product and this radical chain reaction also involves an $\text{S}_{\text{H}2}$ step at silicon, this time by an iodine atom [equation (5)].¹⁰ However, the extrapolated rate coefficient k_5 is only $1.8 \times 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$ at 295 K.



Since aminyl-boranes were found to transfer a β -H atom to alkenes quite efficiently, the possibility of a similar reaction taking place with HMDS was investigated. Disilanes and alkenes show many chemical similarities and the Si—Si σ bond and the C=C bond are cleaved by the same types of reagent.

Apart from abstracting hydrogen from the disilane, the aminyl-borane could cleave the Si—Si bond and displace $\text{Me}_3\text{Si}^\cdot$, in principle by two possible mechanisms [equation (6)]. Attack through nitrogen at

silicon (path *a*) would give a silylamine-borane as the diamagnetic



product, whereas trimethylsilane and an aminoborane would result from H-atom transfer from the BH_3 group to bring about cleavage of the Si—Si bond (path *b*).

As described in Chapter 2, the spectrum of methylaminyborane was observed when a solution containing $\text{MeNH}_2\rightarrow\text{BH}_3$ (1.1 M) and DTBP (ca. 15% v/v) in $\text{Bu}^t\text{OH-Pe}^t\text{OH}$ (3:1 v/v) was u.v. irradiated at 283 K. At 293 K, the aminylborane was again detected and its spectroscopic parameters were the same as those at 283 K. When the experiment was repeated in the presence of HMDS (0.28 M) only a spectrum of the methylaminyborane radical was observed initially, although the spectrum of $\text{Me}_3\text{Si}\cdot$ (Figure 5.1) grew in with time and after ca. 20 minutes photolysis it was quite intense. During this time the spectrum of the aminylborane radical decayed. Increasing the temperature to 306 K resulted in the detection of $\text{Me}_3\text{Si}\cdot$ immediately upon commencing photolysis when [HMDS] was (0.28 M); when the concentration of HMDS was increased to 1.0 M the spectrum of $\text{MeNH}\rightarrow\text{BH}_3$ was relatively weak initially and that of $\text{Me}_3\text{Si}\cdot$ was strong. It thus appears that the methylaminyborane radical reacts quite rapidly with HMDS by H-atom transfer to yield the trimethylsilyl radical by path *b*. The increase in

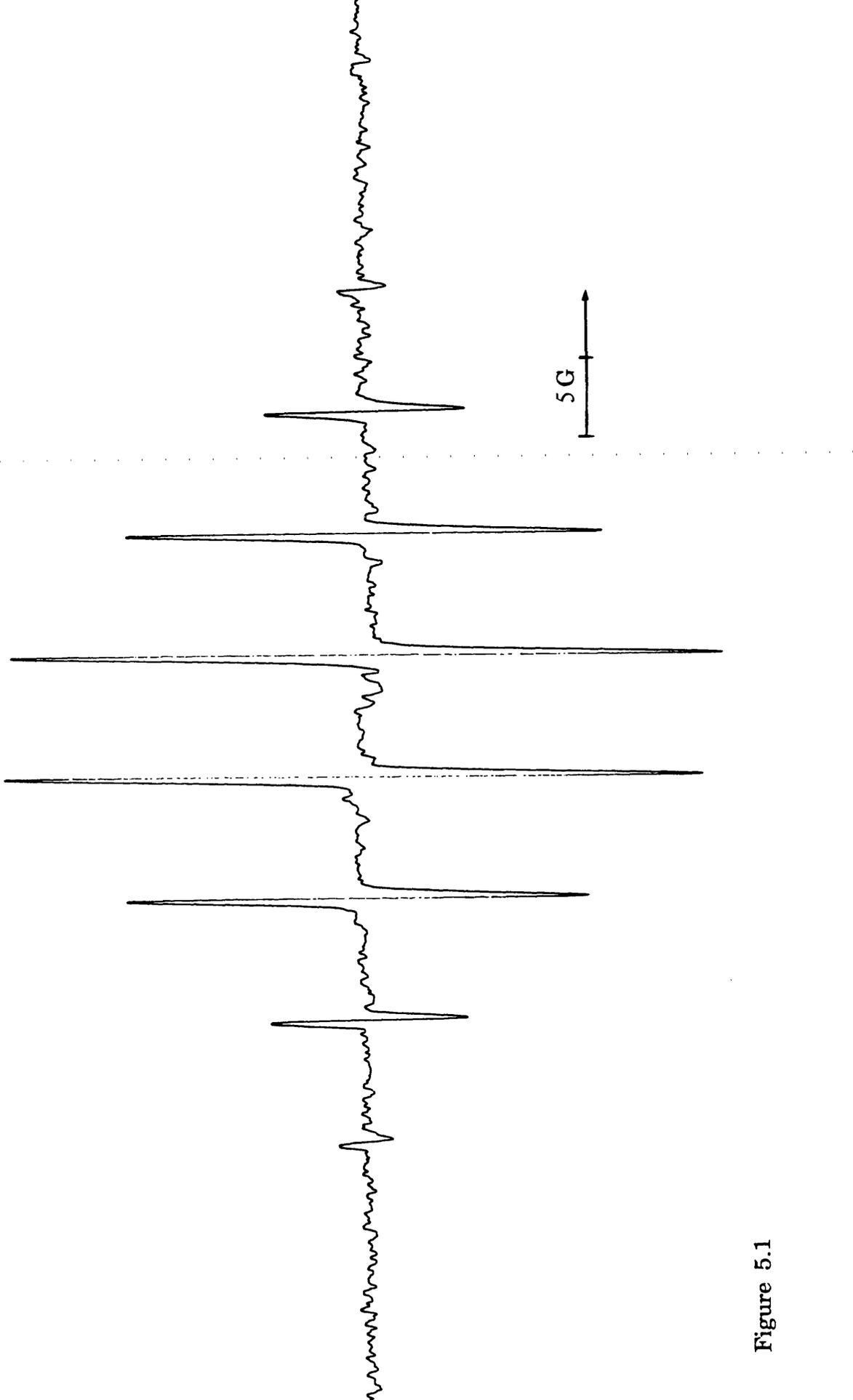


Figure 5.1

Legend to Figure 5.1

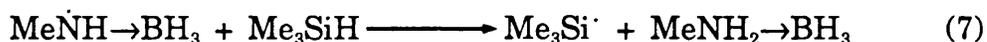
E.s.r. spectrum of the trimethylsilyl radical [$a(9H)$ 6.28 G, g 2.0032]
formed by reaction of $\text{Me}\dot{\text{N}}\text{H}\rightarrow\text{BH}_3$ with HMDS (1.0 M) in $\text{Bu}^t\text{OH}\text{-Pe}^t\text{OH}$
(3:1 v/v) at 293 K.

[Me₃Si·] with the duration of photolysis is probably a result of the build-up of the Me₃SiH produced by path *b*; hydrogen abstraction from the silane provides a second, more efficient, source of Me₃Si·. The radical (5.1) was not detected, showing that the t-butoxyl radical is scavenged by methylamine-borane before it can react with HMDS and that the aminyl-borane radical (5.2) does not abstract hydrogen from HMDS.

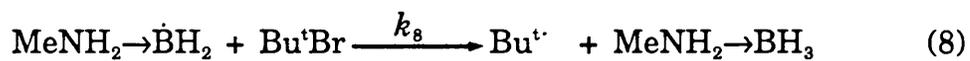
Changing R in RNH₂→BH₃ from Me to H or Bu[•] had little effect on the rate of the hydrogen atom transfer reaction, as judged from the intensities of the spectra of Me₃Si·. Dimethylaminyl-borane radicals were found to transfer a hydrogen atom to alkenes much less readily than the primary aminyl-borane radicals. Similarly, generation of Me₂N→BH₃ in the presence of HMDS (0.8 M) at 282 K gave rise only to a spectrum of the aminyl-borane radical.

Attack by an initially formed amine-boryl radical on HMDS was ruled out by photolysing a solution containing Me₃N→BH₃ (1.2 M), HMDS (1.0 M), and DTBP (16% v/v) in Bu[•]OH-Pe[•]OH (3:1 v/v) at 306 K. Only a spectrum of Me₃N→BH₂ was observed [characterised by a quartet splitting of *ca.* 50 G due to ¹¹B (*I* = 3/2)].

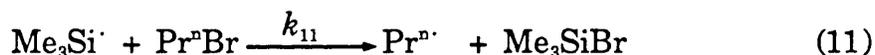
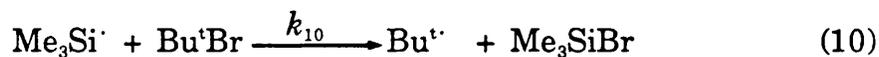
When a sample containing MeNH₂→BH₃ (1.1 M), Me₃SiH (1.3 M), and DTBP (16% v/v) in Bu[•]OH-Pe[•]OH (3:1 v/v) was photolysed at 292 K, the spectrum of Me₃Si· was detected, suggesting that abstraction of hydrogen from trimethylsilane by the aminyl-borane radical is occurring [equation (7)]. To confirm that MeNH→BH₃ rather than Bu[•]O· reacts with



Me_3SiH to produce $\text{Me}_3\text{Si}\cdot$, alkyl bromides were added to scavenge the amine-boryl radical precursor of the aminyl-borane. Irradiation of a solution containing $\text{MeNH}_2\rightarrow\text{BH}_3$ (1.1 M), $\text{Bu}^t\text{Br} + \text{Pr}^n\text{Br}$ (1:1 molar ratio, 0.79 M), and DTBP (ca. 16% v/v) in $\text{Bu}^t\text{OH}-\text{Pr}^n\text{OH}$ (3:1 v/v) at 282 K gave rise to e.s.r. spectra of both $\text{Bu}^t\cdot$ and $\text{Pr}^n\cdot$. The value of (k_8/k_9) was found to be 2.1, which is within experimental error of the value obtained



previously (see Chapter 2). When the experiment was repeated in the additional presence of Me_3SiH (0.79 M) the relative concentrations of $\text{Bu}^t\cdot$ and $\text{Pr}^n\cdot$ were unchanged. However, in the absence of amine-borane but in the presence of Me_3SiH (0.79 M) under the same conditions, the value of k_{10}/k_{11} was found to be 3.6. (It was noted that the spectrum of



the alkyl radicals decayed in intensity rapidly in the experiments with Me_3SiH . The problem was overcome by using separate samples for monitoring each radical, rapidly scanning a line from the alkyl radical spectrum and extrapolating back to time zero. The signal from a piece of synthetic ruby fixed in the microwave cavity was used to correct for

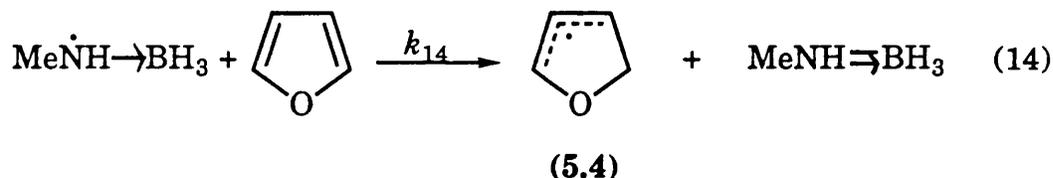
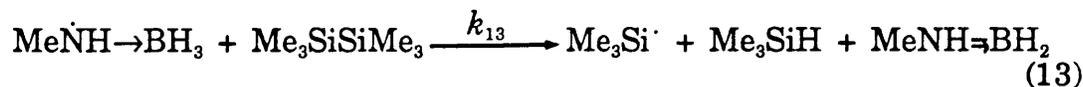
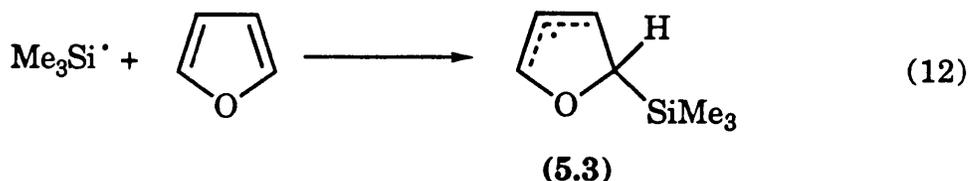
sensitivity changes between different samples.)

These results show that with the reagent concentrations employed, the t-butoxyl radical reacts preferentially with the amine-borane to give an amine-boryl radical and not with Me_3SiH to give $\text{Me}_3\text{Si}\cdot$. Since it is known that the amine-boryl radical goes on to give $\text{Me}\dot{\text{N}}\text{H}\rightarrow\text{BH}_3$ in the absence of bromide, $\text{Me}_3\text{Si}\cdot$ must be formed by the reaction of $\text{Me}\dot{\text{N}}\text{H}\rightarrow\text{BH}_3$ with Me_3SiH .

It was crucial to confirm that amine-boranes do not react directly with HMDS in $\text{Pe}^t\text{OH}-\text{Bu}^t\text{OH}$ solvent under the conditions of the e.s.r. experiments but in the absence of photolysis. Samples were made up with compositions identical to those used in e.s.r. experiments, although their total volumes were larger. When a sample containing $\text{Me}\dot{\text{N}}\text{H}_2\rightarrow\text{BH}_3$, DTBP, $\text{Me}_3\text{SiSiMe}_3$ and $\text{Bu}^t\text{OH}-\text{Pe}^t\text{OH}$ was studied by ^1H n.m.r. spectroscopy at room temperature after being kept in darkness for a period of 2 h the spectrum showed only the presence of solvents and starting materials; no Me_3SiH was detectable. When the experiment was repeated using $\text{Me}_3\text{N}\rightarrow\text{BH}_3$, again only the solvent and starting materials were detected. These results support the contention that the amine-borane does not react directly with HMDS over a much longer period than that of the e.s.r. experiments.

Hydrogen-atom transfer to HMDS from $\text{Me}\dot{\text{N}}\text{H}\rightarrow\text{BH}_3$ was judged to be much slower than similar transfer to alkenes. Trimethylsilyl radicals are known to add very rapidly to furan¹¹ [equation (12)] to give radical (5.3), and therefore it was possible to measure the relative rate of H-atom transfer to HMDS and to furan [equations (13) and (14)], using the

concentration of (5.3) as a measure of the rate of production of $\text{Me}_3\text{Si}\cdot$.



Photolysis of a sample containing $\text{MeNH}_2\rightarrow\text{BH}_3$ (1.10 M), HMDS (1.21 M), furan (0.19 M), and DTBP (14% v/v) in Bu'OH-Pe'OH (3:1 v/v) at 282 K afforded spectra of both (5.3) and (5.4) (Figure 5.2) from which (k_{14}/k_{13}) was determined to be 11.5. Furan has been shown to be 0.7 times as reactive as propene towards $\text{Me}\dot{\text{N}}\text{H}_2\rightarrow\text{BH}_3$ at 282 K (see Chapter 4) and thus H-atom transfer to HMDS is some 14 times slower than transfer to propene.

The partial quenching of the spectrum of the methylaminyborane radical in the presence of HMDS allowed the absolute rate coefficient k_{13} to be determined. Making the usual steady-state assumptions and also assuming that the rate coefficient for the self- and cross- reactions of $\text{Me}_3\text{Si}\cdot$ and $\text{Me}\dot{\text{N}}\text{H}\rightarrow\text{BH}_3$ are equal ($2k_t$), k_{13} given by equation (15) where

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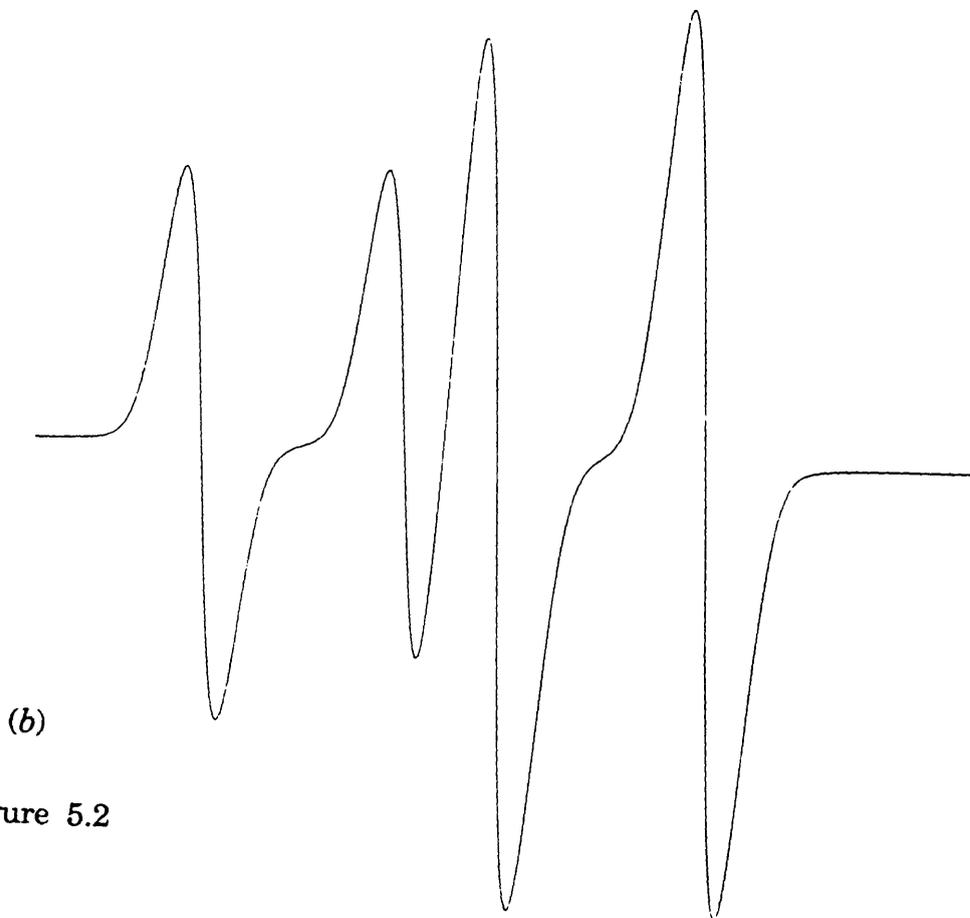
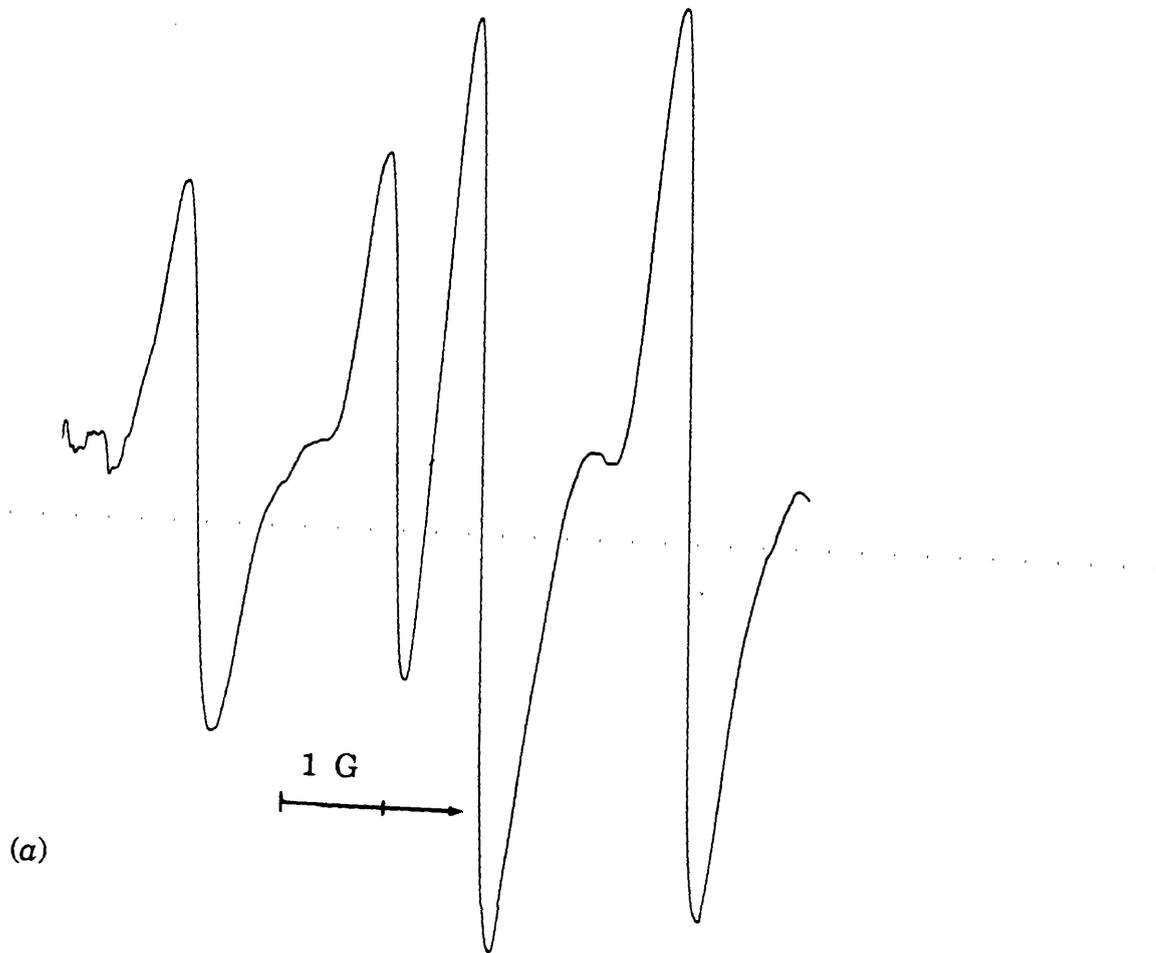


Figure 5.2

Legend to Figure 5.2

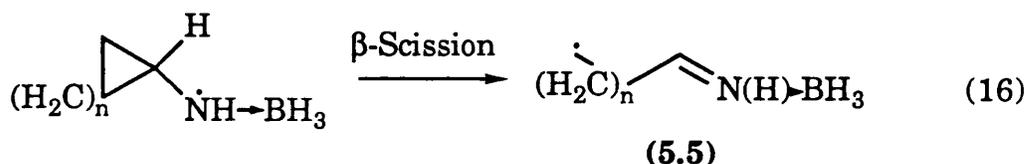
(a) Part e.s.r. spectra of (5.3) (lines 15 and 16) (5.4) (lines 25 and 26) derived from competitive H-atom transfer to HMDS (1.21 M) and furan (0.19 M) in Bu'OH-Pe'OH (3:1 v/v) at 282 K. The relative radical concentration [(5.3)]/[(5.4)] is 0.55.

(b) Computer simulation of (a) using the following splitting constants; for (5.3) $a(\text{H}^5)$ 41.4, $a(\text{H}^2 \text{ or } 4)$ 12.86, $a(\text{H}^4 \text{ or } 2)$ 12.30, $a(\text{H}^3)$ 2.1 G and for (5.4) $a(2\text{H}^5)$ 36.17, $a(1\text{H}^4 \text{ or } 2)$ 13.37, $a(1\text{H}^2 \text{ or } 4)$ 13.17 $a(1\text{H}^3)$ 2.1 G g 2.0032. The lineshape is 80% Gaussian (20% Lorentzian).

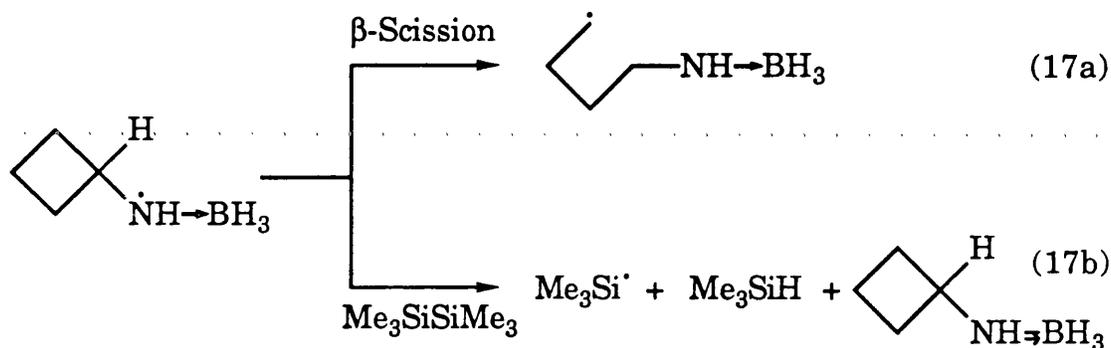
$$k_{13} = 2k_t (R + 1)[\text{Me}_3\text{Si}\cdot]/[\text{HMDS}] \quad (15)$$

$R = [\text{Me}_3\text{Si}\cdot]/[\text{MeNH}\rightarrow\text{BH}_3]$. To overcome the problems of build-up of $\text{Me}_3\text{Si}\cdot$ during the course of the experiment, a flow system was used such that the solution could be passed through the sample tube at 150-1000 $\mu\text{l min}^{-1}$. It was found that when a flow rate equal to or greater than of 150 $\mu\text{l min}^{-1}$ was used, the relative intensities of $\text{Me}_3\text{Si}\cdot$ and $\text{MeNH}\rightarrow\text{BH}_3$ remained constant. At 291 K when $\text{HMDS} = 0.70 \text{ M}$ the measured values of $[\text{Me}_3\text{Si}\cdot]$ and $[\text{Me}_3\text{Si}\cdot]/[\text{MeNH}\rightarrow\text{BH}_3]$ were $5.3 \times 10^{-8} \text{ M}$ and 2.56×10^{-2} , respectively. If $2k_t$ for $\text{Me}_3\text{Si}\cdot$ is taken to be $2.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ at 291 K, the same as $2k_t$ for the isopropyl radical in 3-methylpentan-3-ol at this temperature,¹² the value of k_{12} may be calculated to be $1.9 \times 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$.

Cyclopropylaminy- and cyclobutylaminy-borane radicals undergo ready β -scission at temperatures above 282 K, the former more rapidly (see Chapter 2). U.v. irradiation of a sample containing cyclo- $\text{C}_3\text{H}_5\text{NH}_2\rightarrow\text{BH}_3$ (1.1 M), HMDS (0.7 M), and DTBP (16% v/v) in $\text{Bu}^t\text{OH-Pe}^t\text{OH}$ (3:1 v/v) at 282 K gave rise only to the spectrum of (5.5; $n = 1$) [equation (16)]. When cyclopropylamine-borane was replaced by cyclobutylamine-borane, again only the β -scission product (5.5; $n = 2$) was



obtained. However, when the concentration of HMDS was increased to 3.1 M, a weak spectrum of $\text{Me}_3\text{Si}^\cdot$ was observed initially alongside that of (5.5) and $\text{Me}_3\text{Si}^\cdot$ increased in concentration as the photolysis proceeded. Under the latter conditions, β -scission of the cyclobutylaminyl-borane radical competes with H-atom transfer to HMDS [equation (17)].

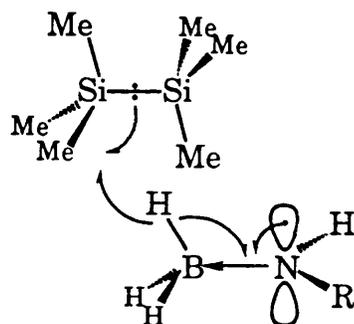


The cyclopentylaminyl-borane radical which showed no tendency to undergo the ring-opening reaction (Chapter 2) gave a strong spectrum of $\text{Me}_3\text{Si}^\cdot$ when a sample containing cyclo- $\text{C}_5\text{H}_9\text{NH}_2 \rightarrow \text{BH}_3$ (1.1 M), HMDS (0.7 M), and DTBP (16% v/v) in $\text{Bu}^t\text{OH-Pe}^t\text{OH}$ (3:1 v/v) was photolysed at 282 K.

The activation energies for $\text{S}_{\text{H}2}$ attack by H^\cdot at Si in disilanes are very small and comparable to the value for H-atom addition to ethene.¹³ The A-factors for attack at disilanes are smaller by an order of magnitude, indicating that the transition state is tighter than for addition to alkenes.

Frontier molecular orbital theory¹⁴ suggests that the interaction between the electrophilic $\text{MeNH} \rightarrow \text{BH}_3$ and HMDS can be reduced to an interaction between the singly-occupied molecular orbital (SOMO) and

the highest occupied molecular orbital (HOMO) of the disilane. The HOMO is an energetically high-lying Si—Si σ orbital with predominant p, less s, and very little d orbital contributions.¹⁵ The energetic position of the Si—Si σ orbital is very similar to that of the filled π orbital of an alkene. The SOMO-HOMO interaction will lead to frontside attack with the retention of configuration at silicon due to the greater localisation of the Si—Si σ orbitals between the two silicon centres. The transition state for hydrogen-atom transfer to the disilane will probably have a structure close to that depicted in (5.6).



(5.6)

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CHAPTER 6

Experimental

6.1 ELECTRON SPIN RESONANCE (E.s.r.) SPECTROSCOPY

E.s.r. spectra were recorded using a Varian E-109 spectrometer operating in the microwave region at *ca.* 9.1 GHz. The spectrometer was equipped for *in situ* u.v. irradiation of samples. The light source was an Osram HBO 500 W/2 mercury discharge lamp in an Oriel Universal 1 kW housing equipped with an *f*/0.7 Aspherab fused silica condensing lens. The slightly converging beam from this was focussed onto the sample, using a fused silica lens (focal length 10 cm, diameter 7.5 cm). The intensity of the incident radiation could be varied by placing gauze screens (nominally 3, 10, and 30% transmittance in the light path). Most of the infrared and much of the visible radiation was removed by passage of the beam through an aqueous solution filter (path length 3 cm) containing NiSO₄·7H₂O (0.38 M), CoSO₄·7H₂O (0.07 M), and H₂SO₄ (0.04 M). The light reaching the sample was mainly in the range 240-340 nm and the heating effect of irradiation was reduced to 6-7 °C at full intensity.

The temperature of the sample in the cavity was controlled by a flow of pre-cooled nitrogen using a standard variable temperature unit (Varian) and was measured by a thermocouple placed alongside the e.s.r.

tube about 2-3 cm from the top of the cavity insert; it was displayed on a digital thermometer (Comark). The insert thermocouple had been calibrated previously against a second thermocouple contained in a sample tube filled with cyclopentane.

The heating effect of the u.v. irradiation on the sample has been measured previously by utilising the temperature dependence of $a(H_\beta)$ for the isobutyl radical (generated by photolysis of DTBP in the presence of triethylsilane and isobutyl bromide) as a function of light intensity. The relationship between $a(H_\beta)$ (in gauss) and the sample temperature is given in equation (1).^{1,2} Extrapolation to zero intensity gives the

$$T(^{\circ}\text{C}) = 2.70394[a(H_\beta)]^2 - 198.419[a(H_\beta)] + 3490.41 \quad (1)$$

heating effect and actual sample temperatures during photolysis are given by the sample temperature in the dark plus this heating correction. For all temperatures quoted in this thesis, the heating effect of the radiation has been accounted for.

6.2 HYPERFINE COUPLING CONSTANTS

Hyperfine coupling is the interaction between the unpaired electron and the magnetic nuclei contained in the radical. The interaction with n equivalent nuclei of spin I results in $(2nI + 1)$ lines and the distance between each of these lines is (to first order) equal to the hyperfine coupling constant. Since ^{12}C has no magnetic moment, the proton hyperfine couplings dominate e.s.r. spectra of hydrocarbon radicals. The

interaction of the unpaired electron with n equivalent protons ($I = 1/2$) gives $(n + 1)$ lines and, furthermore, the relative intensities of these lines are given by the coefficients of the binomial expansion of $(1 + x)^n$, which can be found readily from Pascal's triangle. Although the natural abundance of ^{13}C ($I = 1/2$) is only *ca.* 1.1%, other elements have high abundance non-zero spin isotopes. These include ^{10}B ($I = 3$) *ca.* 19.8%, ^{11}B ($I = 3/2$) 80.2%, ^{14}N ($I = 1$) 99.6%, ^{31}P ($I = 1/2$) 100%.

6.2.2 Second-Order Effects

The above description of hyperfine coupling is valid only in cases where the hyperfine coupling energy is very much smaller than the electronic Zeeman energy. When hyperfine coupling constants are very large or the applied magnetic field is very small, additional splittings can occur which arise from the removal of the degeneracy of the appropriate Zeeman energy levels. Furthermore, lines can be shifted from the positions predicted by simple theory. These phenomena are referred to as second-order effects, since the energies of the levels may be calculated to second order using perturbation theory.³ Line shifts from the first-order positions are of the order (a^2/B_0) , where a is the hyperfine coupling constant and B_0 is the applied magnetic field at the centre of the spectrum.

For example, to second order, coupling of the unpaired electron to three equivalent protons actually gives rise to the splitting pattern shown in (a) rather than to a simple 1:3:3:1 quartet. Although to second order no splittings arise for the coupling to a single nucleus, the shifts of the

(a)

| | | | | |
|-------------|---|---|---|---|
| First order | | | | |
| Intensity | 1 | 3 | 3 | 1 |

| | | | | |
|--|---|-----|-----|---|
| Second order | | | | |
| Intensity | 1 | 1 2 | 1 2 | 1 |
| Shift from first order position in units of $(a^2/4B_0)$ | 3 | 7 1 | 7 1 | 3 |

(b)

| | | | | |
|---|------|------|------|------|
| First order | | | | |
| M_1 | +3/2 | +1/2 | -1/2 | -3/2 |
| Intensity | 1 | 1 | 1 | 1 |
| Second order | | | | |
| Intensity | 1 | 1 | 1 | 1 |
| Shifts from first order position in units of $(a^2/4B_0)$ | 3 | 7 | 7 | 3 |

$(2I + 1)$ lines resulting from coupling to such a nucleus increases rapidly as I increases. For coupling to ^{11}B ($I = 3/2$), the second-order shifts are shown in (b).

6.2.3 The g -Factor

The resonance condition for microwave energy absorption by a free radical in a magnetic field is given by equation (2) in which ν_0 is the

$$h\nu_0 = g\mu_B B_0 \quad (2)$$

fixed microwave frequency, h is Planck's constant, μ_B is the Bohr magneton, and B_0 is the applied magnetic field at the centre of the spectrum. The g -factor is a dimensionless proportionality constant and for an electron with only spin angular momentum has the value 2.00232. In a free radical, the unpaired electron can also possess residual orbital angular momentum, which can couple with the spin angular momentum with the result that the g -factor will deviate from the spin-only value. The g -factor is therefore governed by the environment of the unpaired electron in the radical. Though differences in g -factors are small, the g -factor for a particular type of radical is sufficiently distinctive so as to provide a reasonable means of identification. In this work g -factors were determined by measurement of the microwave frequency (using an E.I.P. Autohet microwave counter, model 331) and the magnetic field at the centre of the spectrum (using a Varian n.m.r. gaussmeter). The difference in the field between the magnetic probe and the sample was determined by measuring the g -factor of the pyrene radical anion

(2.00271), generated by the reduction of pyrene with sodium in THF.⁴ The unknown g -factor was calculated using the resonance condition shown in equation (2).

The g -factors and hyperfine splittings for the aminyl and iminyl radicals generated in Chapter 2 were determined from line positions and microwave frequencies using Preston's program ESRLSQ, which employs an exact solution of the isotropic Hamiltonian and an iterative least squares fitting procedure.⁵

Computer simulations of spectra were obtained using a modified version of ESRSPEC2,⁶ extended to handle composite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with $I > 1/2$, and lineshapes continuously variable between 100% Gaussian and 100% Lorentzian.

6.3 MEASUREMENT OF RADICAL CONCENTRATIONS

Absolute radical concentrations were determined by double integration of spectra and comparing with the signal from a known concentration of *N,N*-diphenyl-*N*-picrylhydrazyl (DPPH) in carbon tetrachloride. It was assumed that the strength of an e.s.r. signal is proportional to $1/T$, and that the integrated intensity is proportional to the square of the scan width used when recording the derivative spectrum. The e.s.r. signal from a small piece of synthetic ruby permanently fixed within the cavity of the spectrometer was used as an internal standard to compensate for changes in instrument sensitivity.

Relative Reactivities of Alkenes Towards The Methylaminy-Borane Radical

Mixtures of alkenes were prepared using a standard calibrated vacuum line, and sample tubes were back-filled with *ca.* 400 Torr of nitrogen before being flame sealed, leaving the minimum dead space. Within experimental error ($\pm 5\%$) at the pressures employed (20 - 30 Torr), the alkenes behaved as ideal gases. This was shown by weighing the alkene condensed from the vacuum line into a glass bulb equipped with a greaseless stopcock and a finger which could be cooled in liquid nitrogen. Because of the low boiling point of propene it was considered possible that a proportion of this alkene could remain in the gas phase in the sealed tubes at the temperatures employed. To check for this, a Bu'OH-Pe'OH (3:1 v/v) solution containing propene and furan was prepared in an n.m.r. tube and sealed with a dead space similar to that in the samples used in the e.s.r. experiments. The ^1H n.m.r. spectrum of this mixture was recorded at 282 K using a continuous-wave spectrometer (100 MHz, Jeol PS-100) and the vinylic resonances were integrated to obtain the relative concentrations of propene and furan in solution. Assuming that all of the furan originally condensed from the line was in solution, this showed that $85 \pm 5\%$ of the propene was in solution under these conditions.

6.4 MATERIALS

N.m.r. spectra (C_6D_6 solvent) were obtained with a Varian XL200 instrument (200 MHz for 1H) using tetramethylsilane as an internal standard (1H) or $Et_2O \cdot BF_3$ as an external standard (^{11}B). I.r. spectra of methylamine-borane and the *B*-deuteriated complexes were recorded on a Perkin-Elmer PE 983 instrument using *ca.* 0.1 M solutions in dioxane.

Preparations and manipulations of boron-containing compounds were carried out under an atmosphere of dry argon. Commercially available solvents and reagents which are liquids at room temperature were dried and distilled before use. Oxirane (Fluka), cyclopropane (Argo International), and dimethyl ether (Fluka) were used as received, as were the gaseous alkenes.

Purification of DTBP.

DTBP (Aldrich 99%, 250 ml) was washed with aqueous $AgNO_3$ (250 ml, 0.2 M) and water (2 x 250 ml), then dried with magnesium sulphate. The dried peroxide was passed down a column packed with activity 1 basic alumina, and distilled under reduced pressure (b.p. 33 °C at 40 Torr).

Methylamine-Borane

Methylamine (Fluka, 9.2 ml, *ca.* 0.18 mol) was condensed from a cylinder into a graduated trap cooled in a solid CO_2 -acetone slush bath, then allowed to evaporate into a stirred solution of dimethyl sulphide-borane (0.08 M) in diethyl ether (10 ml), cooled in a bath at -40 °C.

When the addition was complete (*ca.* 1 h), the mixture was allowed to warm to room temperature and was then stirred for a further 2 h. The ether, dimethyl sulphide, and excess amine were removed under reduced pressure and collected in a trap cooled in CO₂-acetone slush. The residual methylamine-borane was dissolved in diethyl ether (*ca.* 20 ml) at room temperature, the solution was filtered, and the product precipitated by addition of cyclohexane (*ca.* 25 ml), yield (3.1 g, 86%).

¹¹B-Enriched Methylamine-Borane

The procedure used to prepare the isotopically enriched complex was the same as that used to prepare the natural abundance material.

¹¹B-Enriched Borane-Methyl Sulphide Complex.⁸

A slurry of LiAlH₄ (5.0 g, 0.13 mol) in dry 1,2 dimethoxyethane (DME) (60 ml, dried over CaH₂ and distilled from LiAlH₄) was stirred at room temperature. A solution of ¹¹BF₃OMe₂ (Centronics Ltd, 22.5 g, 18.5 ml, 0.197 mol) in DME (40 ml) was added dropwise over a period of 3 h such that the temperature never exceeded 30 °C. The ¹¹B₂H₆ so formed was passed in a stream of argon through a trap cooled to -78 °C into stirred excess of dimethyl sulphide (17 ml, 14.4 g, 0.23 mol) cooled to -78 °C. After addition of the ¹¹BF₃OMe₂, the reaction mixture was heated to 70 °C for 1 h to complete the production of diborane. Excess Me₂S was removed from the trapped diborane using a water pump and a trap cooled in a solid CO₂-acetone slush bath.

B-Deuteriated Methylamine-Borane⁷ (MeNH₂→¹¹BD₃)

The ¹¹BD₃-labelled complex was prepared according to the above procedure, except that LiAlD₄ (Aldrich, 98 atom% D) was used instead of LiAlH₄.

Other amine-borane complexes, including isotopically enriched ones were prepared by the reaction of the appropriate amine with dimethyl sulphide-borane or -trideuterioborane, as described above. Ammonia-borane (Aldrich) was used either as received or after vacuum sublimation with indistinguishable results from the synthesised material. Properties of these complexes are given in Table 6.1

t-Butylamine-Borane

t-Butylamine (5.1 g, 0.070 M) in hexane (10 ml) was added dropwise to a stirred solution of dimethyl sulphide-borane (0.065 mol) in hexane maintained at *ca.* 20 °C. After the addition was complete, the mixture was stirred for a further 2 h at room temperature, before the precipitated t-butylamine-borane (5.1 g, 90%) was removed by filtration and dried under reduced pressure.

d₉-t-Butylamine-Borane

The method used to prepare the borane complex was the same as that used for the protiated material. d₉-t-Butylamine (2.32 g, 0.283 mol) gave 2.36 g of complex, yield 88%.

Table 6.1 Properties of Amine-Boranes $\text{RNH}_2 \rightarrow \text{BH}_3$

| R | M.pt. | Elemental composition | | | δ_{B}^a ($^1\text{J}_{\text{BH}}/\text{Hz}$) |
|-------------------------------------|-----------------|-----------------------|------------------|----------------|--|
| | | C | H | N | |
| Found % (Calc %) | | | | | |
| H | — | — | 19.76 (19.60) | 45.7 (45.4) | -22.2 (94) |
| Me | 56 ^b | 27.0 (26.8) | 17.8 (18.0) | 31.5 (31.2) | -17.6 (97) |
| Bu ^a | 18 | 55.1 (55.2) | 16.6 (16.2) | 16.0 (16.1) | -20.1 (97) |
| Oct ^a | — | 67.5 (67.2) | 15.5 (15.8) | 9.5 (9.8) | -19.7 (94) |
| Bu ^t | 96 ^c | 54.9 (55.2) | 16.3 (16.2) | 16.2 (16.1) | -22.4 (96) |
| Bu ^t CH(Me) | 98 | 62.3 (62.6) | 15.8 (15.8) | 12.1 (12.2) | -18.4 (96) |
| cyclo-C ₃ H ₅ | 44-45 | 50.8 (50.8) | 14.2 (14.1) | 19.5 (19.7) | -19.8 (97) |

Elemental composition

| R | M.pt. | Found % (Calc %) | | N | δ_B^a ($^1J_{\text{HF}}/\text{Hz}$) |
|---|-------|------------------|----------------|----------------|--|
| | | C | H | | |
| <i>cyclo</i> -C ₄ H ₉ | 67-68 | 56.5 (56.5) | 14.1 (14.2) | 16.3 (16.5) | -20.6 (98) |
| <i>cyclo</i> -C ₅ H ₉ | 78 | 60.7 (60.7) | 14.5 (14.5) | 14.2 (14.2) | -19.1 (94) |

^a In C₆D₆ solvent. ^b Lit. m.pt. 56 °C (data taken from H. Noth and H. Beyer, *Chem. Ber.*, 1960, 93, 928). ^c Lit 96 °C (data taken from H. Noth and H. Beyer, *Chem. Ber.*, 1960, 93, 928).

***d*₉-*t*-Butylacetamide⁶**

To stirred *d*₁₀-*t*-butyl alcohol (Aldrich, 5.0 g, 0.06 mol), acetonitrile (4.54 g, 0.11 mol), and deuteriated concentrated sulphuric acid, (9.17 g, 0.09 mol) were added simultaneously without external cooling. After 2 h the reaction mixture was poured into water (40 ml) then neutralised and saturated with potassium carbonate whilst cooling in an ice-bath. Most of the product precipitated and was removed by filtration, the remainder was extracted with ether. The combined product was recrystallised from dry hexane to yield 4.09 g (55%) of *N*-*d*₉-*t*-butylacetamide.

***d*₉-*t*-Butylamine.**

To a flask fitted with a condenser carrying a bubbler containing dilute HCl, *d*₉-*t*-butylacetamide (4.09 g, 0.033 mol), potassium hydroxide (10.67 g), and diethylene glycol (50 ml) were added. The solution was heated under reflux for 5 days. The deuteriated amine (2.1 g) was then distilled directly from the mixture (b.p. 46 °C). From the bubbler, more product was obtained. The contents of the bubbler dilute HCl was removed and saturated with sodium hydroxide pellets; distillation yielded 0.18 g of deuteriated amine. The product was combined and redistilled, yield (2.36 g, 87%).

Purification of Alkylamine-Borane Complexes

Complexes were purified by one of three methods.

(i) **Sublimation.** The impure material was placed in the bottom of the apparatus and heated in an oil bath under high vacuum (0.05 Torr).

Sublimation was often slow and some decomposition occurred. The method was used for $\text{MeNH}_2 \rightarrow \text{BH}_3$ and $\text{Bu}^i\text{NH}_2 \rightarrow \text{BH}_3$.

(ii) Precipitation. The complex was dissolved in the minimum volume of ether at room temperature, any insoluble material was removed by filtration, and cyclohexane was added dropwise to the stirred filtrate. The precipitated complex was removed by filtration and dried under high vacuum (0.05 Torr) for at least 2 h at room temperature. This method was used for $\text{MeNH}_2 \rightarrow \text{BH}_3$, $\text{cyclo-C}_3\text{H}_5\text{NH}_2 \rightarrow \text{BH}_3$, $\text{cyclo-C}_4\text{H}_7\text{NH}_2 \rightarrow \text{BH}_3$, $\text{cyclo-C}_5\text{H}_9\text{NH}_2 \rightarrow \text{BH}_3$.

(iii) Recrystallisation. Hot (*ca.* 50°C) solvent (hexane or cyclohexane) was added to the amine-borane complex, any insoluble material was removed by filtration of the hot solution, the filtrate was allowed to cool, and, the product was recovered by filtration and dried under high vacuum (0.05 Torr). This method was used for $\text{cyclo-C}_3\text{H}_5\text{NH}_2 \rightarrow \text{BH}_3$.

Dibutanoyl Peroxide^{6,9}

A mixture of pyridine (11.0 ml, 11.6 g, 0.14 mol) and ether (7.5 ml) was cooled to -10 °C and hydrogen peroxide (4.8 ml, 60%) was added slowly such that the temperature did not exceed 10 °C. The mixture was rapidly stirred so that the two phase system was finely dispersed. Butanoyl chloride (7.3 ml, 7.5 g, 0.07 mol) was added dropwise keeping the temperature between -5 and -10 °C. The reaction mixture was stirred for a further 2 h at 0 °C and carefully neutralised with chilled aqueous sulphuric acid. Ether (10 ml) was added and the peroxide was extracted. Throughout this and subsequent operations the temperature

was not allowed to warm to above 0 °C. The aqueous solution was extracted further with pentane (3 x 10 ml). The ether and pentane extracts were combined and washed with chilled aqueous sulphuric acid (10 ml, 2 M), then with sodium carbonate solution (10 ml, 2 M) and finally with water (10 ml), and dried (NaSO₄). Pentane and ether were removed using a rotary evaporator, while the flask was kept chilled by rotating it in an ice-water bath. The yield of peroxide was 92%, δ_{H} 0.70 (t, 6H, *J* 7.4 Hz), 1.42 (sextet, 4H, *J* 7.3 Hz), and 1.95 (t, 4H, *J* 7.3 Hz) ppm.

Tris(trimethylsiloxy)benzene¹⁰

Phloroglucinol hydrate (25 g), was dried by dissolving it in benzene and heating under reflux in a vessel equipped with a Dean and Stark apparatus until no more water collected. Benzene was removed under reduced pressure. Dry phloroglucinol (24.5 g, 0.19 mol) was dissolved in pyridine (47 ml) and ether (20 ml). Trimethylchlorosilane (74.0 ml, 63.3 g, 0.58 mol) was added dropwise with vigorous stirring whilst cooling in an ice-bath. The precipitated pyridine hydrochloride was removed by filtration under nitrogen, the solvent was removed from the filtrate under reduced pressure, and the product distilled under high vacuum b.p.102 – 104 °C.

Tetramethylallene was a gift from Dr. P. J. Garratt.

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