INVESTIGATIONS OF THE STRUCTURES

AND REACTIONS OF NEUTRAL FREE

RADICALS IN SOLUTION

A Thesis submitted for the Degree

of Doctor of Philosophy undertaken at

the University of London

by

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For

<u>Aryan Kshatriya's Surajwansh Kaushal Dynasty</u>

Rana Joginder Singh Kaushal

Rani Prem Kumari Kaushal

Rana Amar Deep Kaushal

Rana Kanwal Deep Kaushal

Rani & Rana Param Deep Kaushal

Kunwar Sanjay Kaushal

and

Kunwar Karan Kaushal

ACKNOWLEDGMENTS

Abstract

This thesis naturally falls into two sections.

Section A

Before this work, no <u>direct</u> evidence for cyclisation of the 2-(isocyanatocarbonyl)ethyl radical to give the succinimidyl radical existed, because the latter radical had never been generated from acyclic reagents. Using a combination of e.s.r. spectroscopic techniques and product analysis, the cyclisation of ω-(isocyanatocarbonyl)alkyl radicals derived from the ω-bromoalkanoyl isocyanates has been studied.

Imidyl radicals, generated by photolysis of, or halogen-atom abstraction from, <u>N</u>-halogenoimides, are efficiently trapped by $Bu^t_2C=CH_2$ to give relatively persistent adducts which have been characterised by e.s.r. spectroscopy. Bromine-atom abstraction from $BrCH_2CH_2C(O)NCO$ yields $H_2\overset{\bullet}{C}CH_2C(O)NCO$ which undergoes rapid 1,5-<u>endo</u>-cyclisation to give the succinimidyl radical. This cyclisation has been investigated using e.s.r. spectroscopy in conjunction with spin-trapping by $Bu^t_2C=CH_2$ and $Bu^tN=O$. The rate coefficient for cyclisation of $H_2\overset{\bullet}{C}CH_2C(O)NCO$ has been estimated to be 3.7 x 10^6 s^{-1} at 328 K in cyclohexane from analysis of the products from the radical-chain reaction between $BrCH_2CH_2C(O)NCO$ and triethylgermane.

E.s.r. and product-analysis studies show that $H_2\overset{\bullet}{C}CMe_2C(O)NCO$ cyclises, more rapidly than $H_2\overset{\bullet}{C}CH_2C(O)NCO$, to give the 2,2-dimethylsuccinimidyl radical, which subsequently undergoes ring opening to yield $Me_2\overset{\bullet}{C}CH_2C(O)NCO$. The overall rearrangement of $H_2\overset{\bullet}{C}CMe_2C(O)NCO$ to $Me_2\overset{\bullet}{C}CH_2C(O)NCO$

represents a 1,2-shift of the -C(O)NCO group $\underline{via}$ an intermediate imidyl radical. The glutarimidyl radical is formed by 1,6-$\underline{endo}$-cyclisation of $H_2\overset{\bullet}{C}CH_2CH_2C(O)NCO$.

It is proposed that the rapid cyclisation of ω-isocyanatoalkyl radicals provides strong evidence that the unpaired electron occupies a σ-orbital in the product imidyl radicals.

Section B

Polarity reversal catalysis (PRC) of hydrogen-atom abstraction reactions, in particular when the slow abstraction of electron deficient hydrogen by electrophilic t-butoxyl radicals was studied.

A number of amine-alkylboryl radicals have been generated in fluid solution, by hydrogen-atom abstraction from the corresponding amine-alkylborane complexes, using photochemically-produced t-butoxyl radicals, and studied by e.s.r. spectroscopy. The air-stabilities of the parent complexes have been investigated.

Amine-alkylboryl radicals abstract halogen rapidly from both alkyl bromides and chlorides. These radicals are highly nucleophilic and rapidly abstract an electron deficient α-hydrogen atom from esters, ketones, lactones, anhydrides, and imides. Because of this property of the derived boron-centred radicals, amine-alkylboranes act as polarity reversal catalysts for the net abstraction of electron deficient hydrogen atoms by the electrophilic t-butoxyl radical. Relative reactivities of alkyl bromides and of esters have been measured by e.s.r. spectroscopy using competition techniques.

CONTENTS

Section A: Imidyl Radicals

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CHAPTER 1

INTRODUCTION

1.1 Historical Background

Reactions of imidyl radicals (**1**) remained unrecognised until the importance of two factors became apparent. Firstly, the necessity to use solvents in which the solubility of the imidyl radical precursor, the N-halogenoimide (**2**), was sufficiently high and, secondly, the necessity to eliminate competitive chain
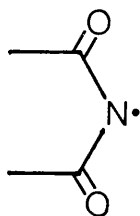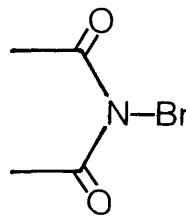
(**1**)   (**2**)

reactions carried by halogen atoms (X$^{\bullet}$), which could be accomplished by including alkenes to selectively scavenge X$^{\bullet}$ and X$_2$.

Radical reactions of N-halogenoimides have been known since 1942, when Ziegler et al. reported radical allylic brominations[1] [equation (**1.1**)] using N-bromosuccinimide (NBS) in CCl$_4$. A critical factor for success in these allylic brominations was use of CCl$_4$ as the reaction medium, a solvent in which NBS is only slightly soluble (ca. 10^{-3} M).

This reaction was first described by Bloomfield, without evidence, as a radical chain reaction involving the succinimidyl radical as the hydrogen

(NBS) $\quad$ (SH) $\qquad$ **(1.1)**
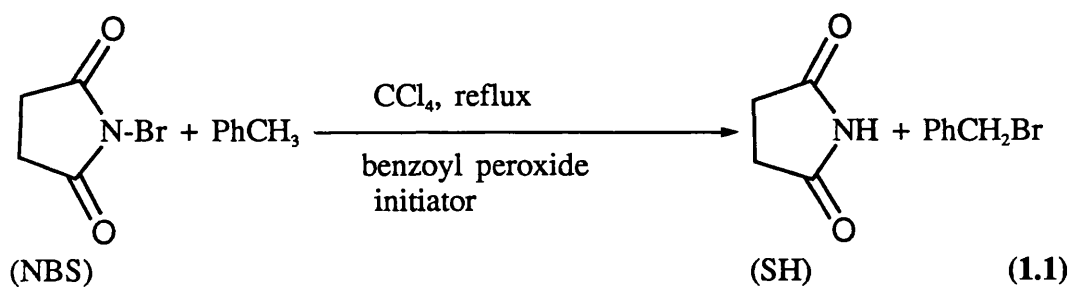
abstractor[2] [equations **(1.2)** and **(1.3)**]. Later, in 1953, it was shown by

$$S\cdot + CH_2=CHCH_2\text{-}R \longrightarrow SH + CH_2=CH\overset{\bullet}{C}H\text{-}R \qquad \textbf{(1.2)}$$

$$CH_2=CH\overset{\bullet}{C}H\text{-}R + NBS \longrightarrow CH_2=CHCHBr\text{-}R + S\cdot \qquad \textbf{(1.3)}$$
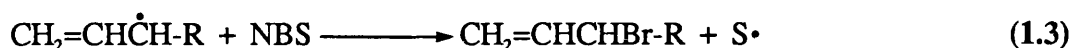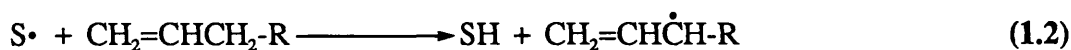
The Bloomfield mechanism

Goldfinger[3] that the bromine atom was in fact responsible for hydrogen abstraction under these (Ziegler) conditions [equations **(1.4)** - **(1.6)**]. In this

$$CH_2=CH\overset{\bullet}{C}H\text{-}R + Br_2 \longrightarrow CH_2=CHCHBr\text{-}R + Br\cdot \qquad \textbf{(1.4)}$$

$$Br\cdot + CH_2=CHCH_2\text{-}R \longrightarrow H\text{-}Br + CH_2=CH\overset{\bullet}{C}H\text{-}R \qquad \textbf{(1.5)}$$

$$HBr + NBS \longrightarrow SH + Br_2 \qquad \textbf{(1.6)}$$
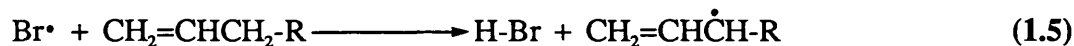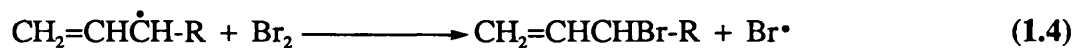
The Goldfinger mechanism

bromine-atom based mechanism, Goldfinger proposed that NBS reacted rapidly with HBr to generate a low concentration of bromine which was sufficient to maintain a Br• chain: NBS was infact acting simply as a source of molecular bromine.

The low solubility of NBS in CCl_4 is the crucial factor in precluding imidyl radical reactions under Ziegler conditions. In contrast, if a solvent is used in

3

which NBS has a higher solubility (e.g. acetonitrile or dichloromethane), NBS

can compete successfully with the small amounts of Br_2 in reactions with the

allylic radical intermediates [equation (1.7)]. When the concentration of NBS

$$CH_2=CHCHBr\text{-}R + S\bullet$$

$$CH_2=CH\overset{\bullet}{C}H\text{-}R \overset{NBS}{\underset{Br_2}{\diagdown}}$$

(1.7)

$$CH_2=CHCHBr\text{-}R + Br\bullet$$
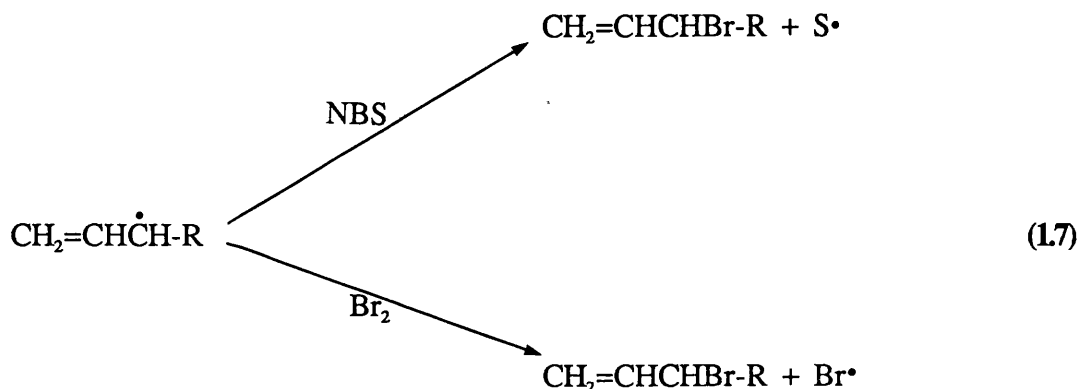
is high succinimidyl radicals are formed and, if the scavenging of Br_2 is

adequate, the chemistry is attributable totally to the imidyl radicals.

In 1974, Skell[4] showed $S\bullet$ to be the chain carrier when brominations are

carried out in dichloromethane or acetonitrile solvents particularly if $Br_2/Br\bullet$

scavengers, such as alkenes without allylic hydrogens are present to suppress the

bromine atom chain. Under these conditions Skell found that selectivity was the

same for N-chloro, N-bromo, and N-iodosuccinimides and the species responsible

for hydrogen atom abstraction must therefore be identified as the succinimidyl

radical rather than a halogen atom.

It was further proposed by Skell[4,5] that under different sets of reaction

conditions two different electronic states of $S\bullet$ could be formed, a ground state

π-radical ($S_{\pi}^{\bullet}$) and an excited state σ-radical ($S_{\sigma}^{\bullet}$) and that these two states had

different chemical properties. In the presence of bromine scavenging alkenes

(e.g. $Cl_2C=CH_2$) in dichloromethane, the concentration of Br_2 is vanishingly

small, the concentration of NBS is high, and the chain carrier was thought to

be $S_{\sigma}^{\bullet}$ [equations (1.8) and (1.9)]. Without alkene scavenger and in the presence

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$$Me_3C\overset{\bullet}{C}H_2 + NBS \xrightarrow[\underline{ca.}\ 30\ kJ\ mol^{-1}]{Exothermic\ by} Me_3CCH_2Br + S^{\bullet}_{\sigma} \qquad (1.8)$$

$$S^{\bullet}_{\sigma} + Me_4C \longrightarrow SH + Me_3C\overset{\bullet}{C}H_2 \qquad (1.9)$$
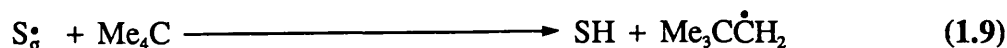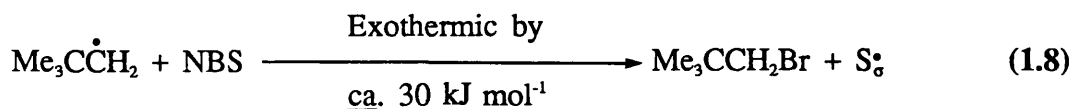
of added molecular bromine, when the concentrations of bromine and NBS are both large, the chain carrier was thought to be $S^{\bullet}_{\pi}$ [equations (1.10) - (1.12)].

$$Me_3C\overset{\bullet}{C}H_2 + Br_2 \longrightarrow Me_3CCH_2Br + Br^{\bullet} \qquad (1.10)$$

$$Br^{\bullet} + NBS \xrightarrow{Thermoneutral} S^{\bullet}_{\pi} + Br_2 \qquad (1.11)$$

$$S^{\bullet}_{\pi} + Me_4C \longrightarrow SH + Me_3C\overset{\bullet}{C}H_2 \qquad (1.12)$$
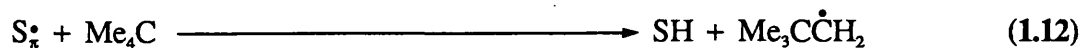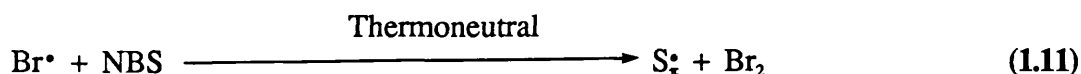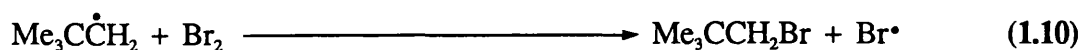
It is certainly reasonable that $S^{\bullet}_{\sigma}$ and $S^{\bullet}_{\pi}$ should have similar energies. In a dialkylaminyl radical (3) the unpaired electron resides in an N-2p π orbital and a pair of electrons occupies the lower energy $\underline{ca.}$ sp^2 hybrid σ-orbital. The σ radical (4) is an excited state of much higher energy. However, in the
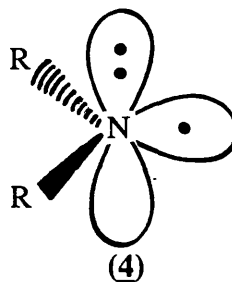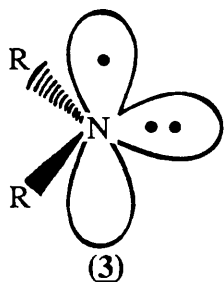
succinimidyl radical two carbonyl groups are attached to nitrogen and π delocalisation of a pair of electrons (5) will be more favourable energetically

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than delocalisation of a single electron (6). Thus, the difference in energy

between σ and π succinimidyl radicals should be much smaller than between σ

and π dialkylaminyl radicals and it is even possible that $S_\sigma^{\cdot}$ could be the
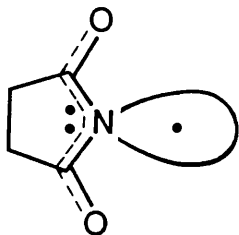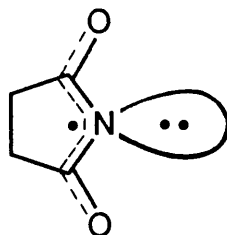
(5) $S_\sigma^{\cdot}$ (6) $S_\pi^{\cdot}$

ground state. Skell[4] proposed that $S_\pi^{\cdot}$ is the ground state which he considered

to be about 60 kJ mol^{-1} more stable than the more reactive $S_\sigma^{\cdot}$. The reaction

between Br• and NBS is approximately thermoneutral and can give only $S_\pi^{\cdot}$,

whereas bromine-atom abstraction from NBS by an alkyl radical is sufficiently

exothermic to yield $S_\sigma^{\cdot}$. It does not give rise to $S_\pi^{\cdot}$ because the transition

geometry (7), predicted on the basis of frontier molecular orbital control,

correlates with $S_\sigma^{\cdot}$ and the unpaired electron is in an orbital orthogonal to that

which it would occupy in $S_\pi^{\cdot}$. In order to explain his results, Skell[4] proposed

that the selectivity of $S_\sigma^{\cdot}$ in hydrogen abstraction was much greater than that

of $S_\pi^{\cdot}$, which was in turn more selective than Br• (see Table 1.1). Skell[5] further

proposed that $S_\sigma^{\cdot}$, but not $S_\pi^{\cdot}$, undergoes rapid and reversible ring opening to

(7)
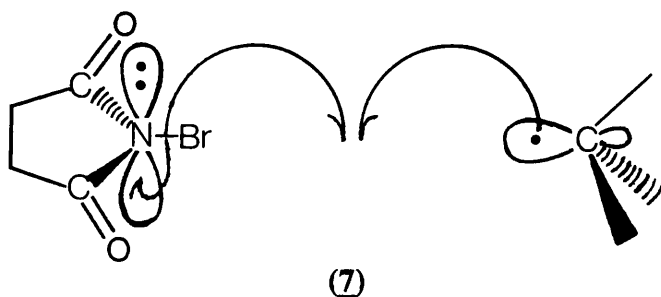
	$S_\sigma^\bullet$	$S_\pi^\bullet$	$Br^\bullet$
$\left(\dfrac{\text{Reactivity } Me_4C}{\text{Reactivity } CH_2Cl_2}\right)$ at 20 °C in CD_2Cl_2	102	6	0.6

Table 1.1 Selectivity of various radicals in hydrogen abstraction from neopentane and dichloromethane.

give the 2-(isocyanatocarbonyl)ethyl radical (8) [equation (1.13)]. This ring opening had been established previously by Johnson and Bublitz[6] who proposed it as a step in the radical chain isomerisation of NBS to 3-bromopropanoyl isocyanate (BPI) [equation (1.14)]. Skell's conclusion that only $S_\sigma^\bullet$ undergoes

(8)

$$\text{(1.13)}$$

$$\text{(1.14)}$$
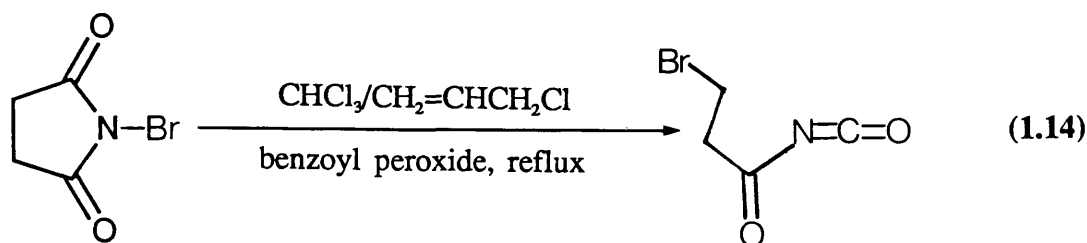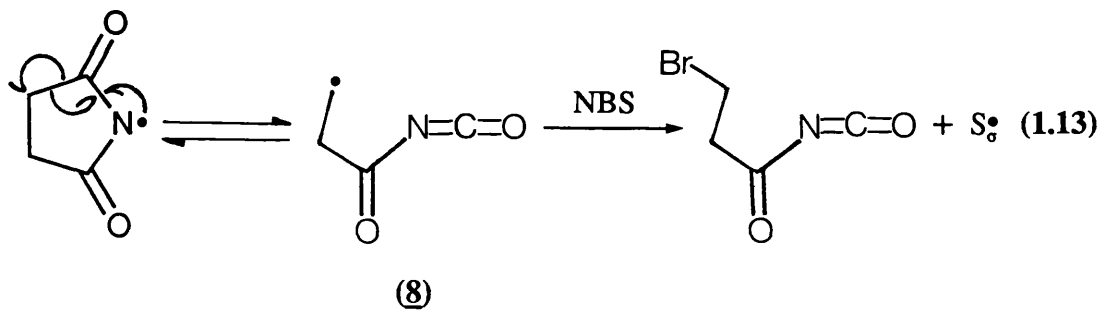
ring opening was based on his failure to detect BPI in reactions of NBS which he believed to proceed via $S_\pi^\bullet$ and on the theoretical argument, first presented by Koenig and Wielsek,[7] that only $S_\sigma^\bullet$ and not $S_\pi^\bullet$ correlates with (8) [equation

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(1.15)]. However, the experimental basis upon which Skell's elaborate and

$$(1.15)$$

$$(\underline{8})$$
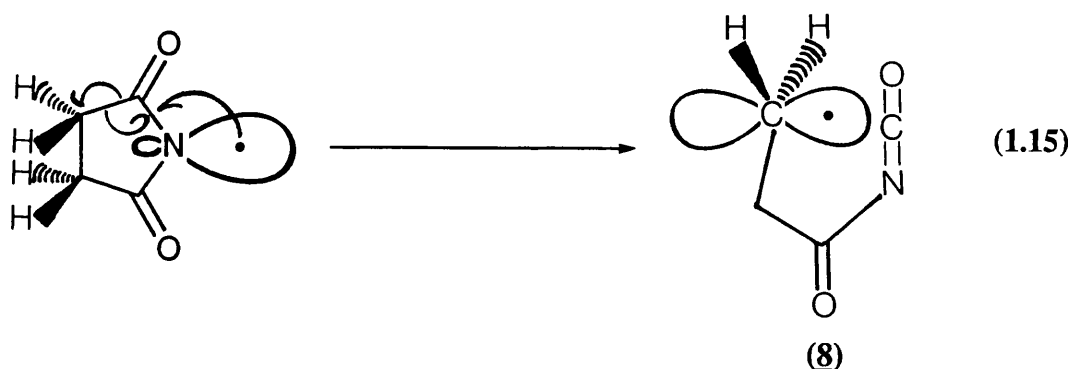
unprecedented proposals have been built has recently been shown to be flawed by a series of very careful studies by Tanner[8,9] and by Walling[10,11]. These authors have shown that BPI is produced in reactions of NBS under S_N^* conditions and further more they have shown that the reactivity attributed by Skell to S_N^* is really a superposition of the reactivities of Br• and the succinimidyl radical, which is the main chain carrier under "S_G^* conditions". There is only one succinimidyl radical chain carrier under all conditions and its electronic state, σ or π, is not yet known, except that according to Koenig and Wielesek[7] it should be a σ-radical since it ring opens readily to (8). Skell's evidence[5] for reversible ring opening of S• to (8) appears sound and involves cis / trans scrambling of deuterium in NBS during reactions proceeding via S• [equation (1.16)].

$$\text{via (8)}$$

$$(1.16)$$
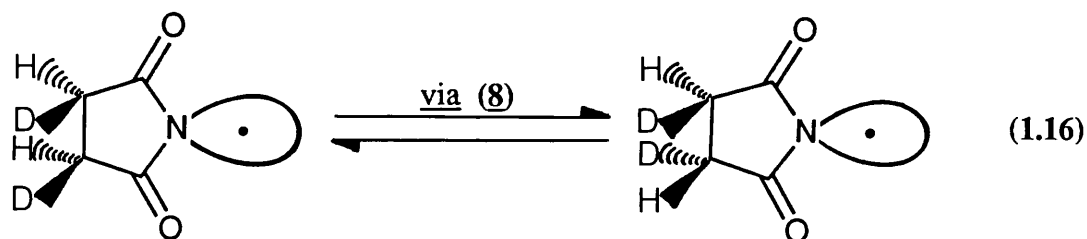
Ring opening was thought to be readily reversible with $\underline{k}_1 \simeq \underline{k}_{-1} \simeq 2 \times 10^7$ s^{-1} at around room temperature [equation (1.17)], although kinetic data obtained

$$\text{S}\bullet \quad \underset{\underline{k}_{-1}}{\overset{\underline{k}_1}{\rightleftharpoons}} \quad \overset{\bullet}{\underset{\parallel}{\underset{O}{\diagdown}}}\text{N}{=}\text{C}{=}\text{O} \qquad\qquad (1.17)$$
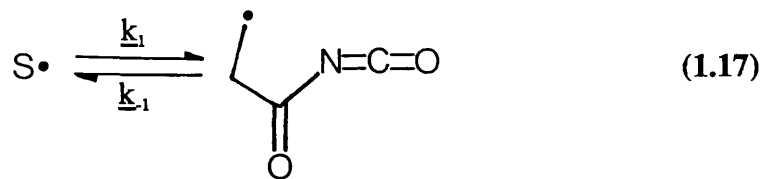
(8)

by Walling et al.[10] require that $\underline{k}_1 \leq 2 \times 10^4$ s^{-1} under similar conditions. While our own work was in progress, a further report from Skell's group appeared revising upwards his value of $\underline{k}_1$ to ca. 5×10^8 s^{-1} at 288 K and doubting the validity of his earlier conclusion that $\underline{k}_1$ and $\underline{k}_{-1}$ are approximately equal.[12]

Whilst no e.s.r. spectrum of S• (or indeed of any imidyl radical) in solution has ever been detected, one assigned to this radical trapped in a rigid matrix has been interpreted by Eberson and co-workers[13] in terms of an electronic ground state (S$_\pi$) in which the SOMO is anti-symmetric with respect to reflection in the plane containing the heavy atoms and in which the unpaired electron is centred mainly on nitrogen. This conclusion receives support from high-level ab initio MO calculations which predict S$_\pi$ to be the ground state, although this is separated from the excited state S$_\sigma$ by only 21.5 kJ mol^{-1}.[14]   † However, as has been mentioned already, the ring opening process shown in equation (1.17) is stereoelectronically allowed[7,16] only from S$_\sigma$ and it follows that cyclisation of (8) should lead to this electronic state. Dewar and Olivella[16] have calculated

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†Other recent theoretical work,[15] while agreeing that S$_\pi$ is the ground state, predicts the first excited state to be a σ-radical, less stable by 49.0 kJ mol^{-1}, in which the unpaired electron is centred mainly on the oxygen atoms (^{2}B$_2$ in C$_{2v}$). The ^{2}A$_1$ state (S$_\sigma$) was predicted to be less stable than S$_\pi$ by 66.9 kJ mol^{-1}.

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that the ring opening of $S_\sigma^\cdot$ to give (**8**) is exothermic by 30 kJ mol^{-1} and have estimated $\underline{k}_1$ to be $\underline{ca}$. 2.4 x 10^4 s^{-1} at 298 K, close to the maximum value proposed by Walling _et al._[10] (see above), although on the basis of these calculations endothermic cyclisation of (**8**) to give $S_\sigma^\cdot$ would be very slow under normal conditions. Symmetry forbidden ring opening of $S_\pi^\cdot$ was predicted to be extremely slow at ambient temperature[16] and it has even been suggested[17] that, whilst the electronic ground state is indeed $S_\pi^\cdot$, the reported chemistry of S$\cdot$ may be that of $S_\sigma^\cdot$. Of course, the calculations refer to isolated molecules in the gas phase and medium effects could be critically important since imidyl radicals are undoubtedly very polar species.

1.2   Reactions of Imidyl Radicals

The halogen scavenging recipe is useful for generating imidyl radicals from a variety of N-halogenoimides. Both the halogen and the imidyl residue can be varied.

1.2.1   Ring-Opening of Imidyl Radicals

An important reaction of N-halogenoimides is the ring-opening reaction to form halogenoacylisocyanates, which proceeds by a radical chain mechanism.[5] In the proposed pathway, the imidyl radical opens to form a carbon-centred radical with an ω-acylisocyanate function. This radical abstracts a halogen from the N-halogenoimide to form the product with regeneration of the chain propagating imidyl radical [equation (1.13)]. Ring opening is in competition with abstraction and addition reactions in the presence of suitable substrates such as alkanes,[5] alkenes,[5] or arenes.[18]

However, there were several important observations. Firstly, the yield of ring opened product is dependent on the N-halogenoimide concentration.[5] Secondly, NBS gives product derived from ring-opening while NCS does not.[5] Thirdly, the yields of isocyanates are larger if α-alkyl substituents are present on the N-halogenoimides.[5]

These facts suggested were interpreted in terms of reversibility of the ring-opening reaction, since halogen transfer from the N-halogenoimide to the ring-opened radical will be slower for N-chloroimides than for N-bromo-or N-iodoimides. Methyl substituents in the α-position increase the rate of ring-opening, e.g. 2,2-dimethyl-N-bromoglutarimide (22DMNBG) ring opens while 3,3-dimethyl-N-bromoglutarimide (33DMNBG) does not. Methyl substituents

11
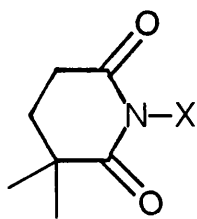
X=Br; 22DMNBG
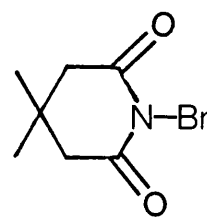
X=Cl; 22DMNCG

33DMNBG
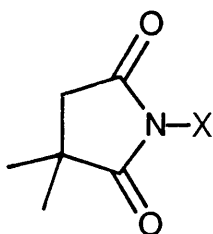
X=Br; 22DMNBS

X=Cl; 22DMNCS

also decrease the rate of ring closure by stabilizing the ring-opened radical (a tertiary radical instead of a primary radical).[5] Thus, even a chloro compound such as 22DMNCS produces isocyanate.[5] In benzene at 70 °C, 22DMNBS forms 72 % isocyanate, but NBS gives only 1 %, the remainder being consumed in the substitution reaction with benzene.[18]

N-Halogenoglutarimides undergo ring-opening less rapidly than the corresponding succinimides, a consequence of the difference in ring strain, and ring-opening has not been observed for the N-halogenophthalimides.

To summarize, the yield of ring-opened product is diminished by choosing N-chloroimides instead of N-bromoimides, increased by substituting the α-positions with methyl groups, and decreased by using N-halogenoglutarimides
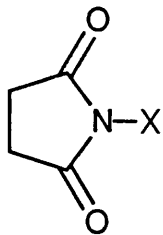
N-Halogenosuccinimide
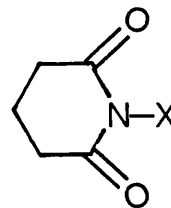
N-Halogenoglutarimide
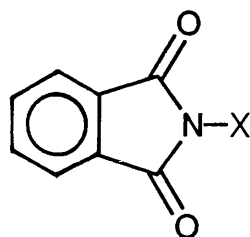
N-Halogenophthalimide

and N-halogenophthalimides rather than N-halogenosuccinimides.

1.2.2 Hydrogen Atom Abstraction Reactions of Imidyl Radicals

Hydrogen abstractions by imidyl radicals have been examined for a number of substrates RH, through the general chain sequence shown in equations (1.18) and (1.19). The problem of distinguishing between competitive halogen atom

$$\text{(imidyl)}N\bullet \quad + RH \longrightarrow \text{(imidyl)}NH + R\bullet \tag{1.18}$$

$$R\bullet + \text{(imidyl)}NX \longrightarrow RX + \text{(imidyl)}N\bullet \tag{1.19}$$
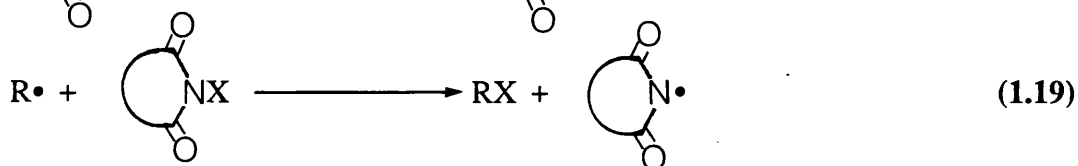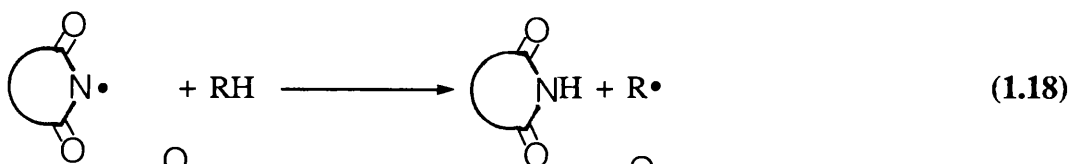
chains can be overcome by using substrates relatively unreactive to halogen atoms, for example neopentane, dichloromethane, t-butyl chloride or

2,2-dichloropropane are relatively unreactive towards bromine atoms.

1.2.3 Addition of Imidyl Radicals to Alkenes

If radical chain reactions with imidyl radicals are carried out under conditions of high alkene concentration 1:1-addition becomes the major reaction.[4,17,19] The imidyl radical adds to an alkene forming an adduct radical which then reacts with $\underline{N}$-halogenoimide to form the 1:1-addition product [equations (1.20a) and (1.20b)].

$$(1.20a)$$

$$(1.20b)$$
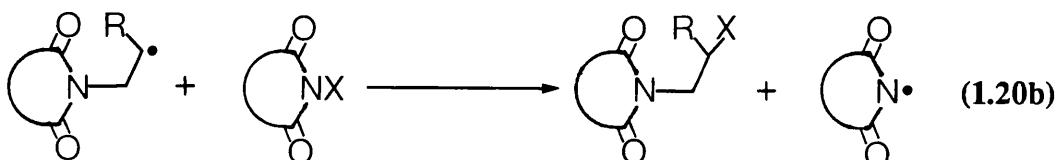
These addition reactions are remarkably clean, yields are good, and the chain lengths are high (up to 2000).[17] Imidyl radicals show electrophilic behavior and add rapidly to electron rich alkenes to form adduct radicals which are nucleophilic.[20] These adduct radicals abstract bromine from the $\underline{N}$-bromoimides, thus regenerating the chain carrier. The alternation between electrophilic imidyl and nucleophilic alkyl radicals explains the high yields of the addition reactions. This also explains why the addition reaction does not preclude polymerization of less electron rich alkenes such as 1,1-dichloro-

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ethylene, and why no addition product is obtained with electron poor alkenes such as fumarodinitrile, maleic anhydride or tetrachloroethylene.[17] Styrene provides an intramolecular competition between addition to the double bond and addition to the aromatic nucleus (see below), with the double bond being only twice as reactive as the benzene ring.[19]

1.2.4   Reactions of Imidyl Radicals with Arenes

Imidyl radicals also add to arenes. An addition/elimination sequence leads to substitution of the aromatic nucleus by an imidyl moiety. Imidyl radicals add to benzene with a rate similar to the rate of addition to alkenes,[17,18] forming a cyclohexadienyl radical. In marked contrast, the methyl radical strongly prefers addition to alkenes (ethylene by a factor of approximately 100).[4,21] The cyclohexadienyl radical abstracts a halogen atom from the N-halogenoimide to give a cyclohexadiene (isomers are possible), which then loses HX to give the substituted arene. The hydrogen halide is scavenged by the N-halogenoimide giving imide and halogen. To ensure halogen-free reaction conditions, these reactions [equations (1.21) - (1.24)] must be carried out with an alkene/N-halogenoimide ratio of at least 0.5. The intermediacy of a cyclohexadiene is indicated by the isolation of the tribromide formed by addition of Br_2,[22] especially noticeable when the scavenging by alkene is not efficient.

$$\text{(1.21)}$$

$$\text{(imide)}N\text{-}C_6H_5\text{•} + \text{(imide)}NX \longrightarrow \text{(imide)}N\text{-}C_6H_5\text{-}X + \text{(imide)}N\text{•} \qquad (1.22)$$

$$\text{(imide)}N\text{-}C_6H_5\text{-}X \longrightarrow \text{(imide)}N\text{-}C_6H_5 + HX \qquad (1.23)$$

$$HX + \text{(imide)}NX \longrightarrow X_2 + \text{(imide)}NH \qquad (1.24)$$
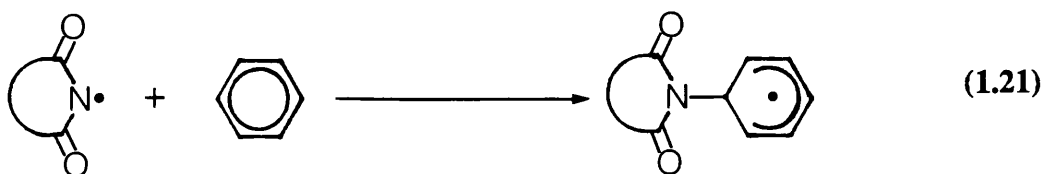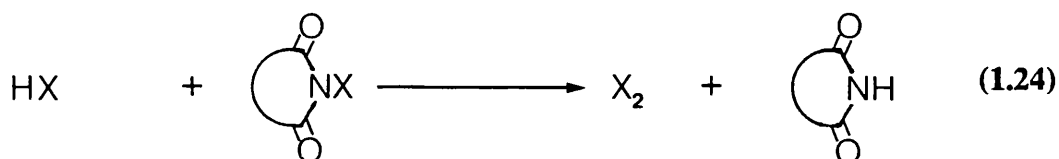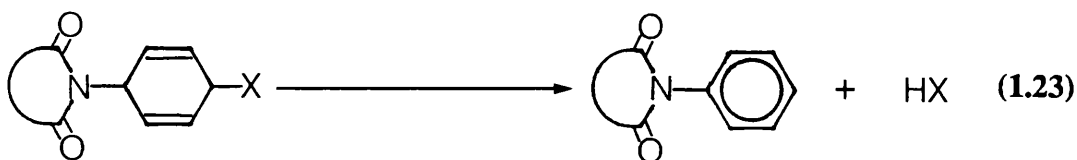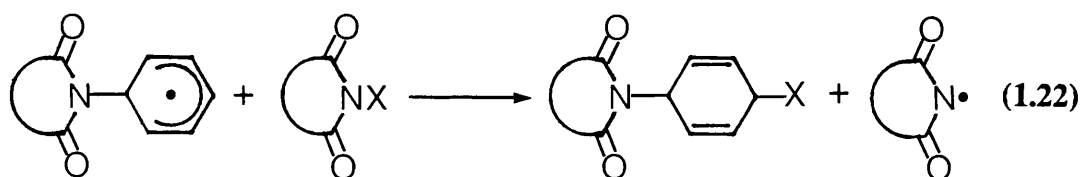
The <u>overall</u> rate of these benzene substitution reactions is small in comparison to alkene-additions or hydrogen abstractions. The slow step in the chain sequence must be the transfer of bromine from the bromoimide to the cyclohexadienyl radical, since the addition step is irreversible and is as fast as addition to alkenes.[17] The irreversibility of the addition to benzene is indicated by the non-dependence of the relative rate constants for additions to alkenes and benzene (direct competition) on the total concentrations of alkene and benzene or on the concentration of N-bromoimide.[17]

1.2.5   Reactions of Imidyl Radicals with Organotin Compounds

Davies, Roberts, and Smith[23] has shown that tetraalkylstannanes react with N-bromosuccinimide to give bromoalkane and N-trialkylstannylsuccinimide. In acetone solvent, this reaction proceeds by a radical chain mechanism involving bimolecular homolytic substitution (S_H2) by the succinimidyl radical at the tin

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atom [equations (1.25) and (1.26); R = alkyl or benzyl, X = Br]. $\underline{N}$-chloro- and

$$\text{(succinimidyl radical)} + R_4Sn \longrightarrow NSnR_3 + R\bullet \qquad (1.25)$$

$$R\bullet + \text{(N-X succinimide)} \longrightarrow RX + N\bullet \qquad (1.26)$$
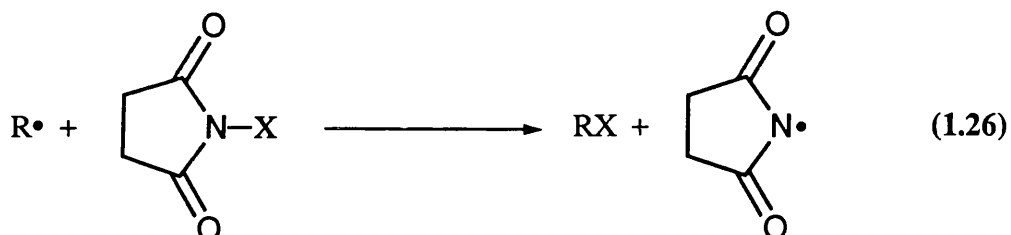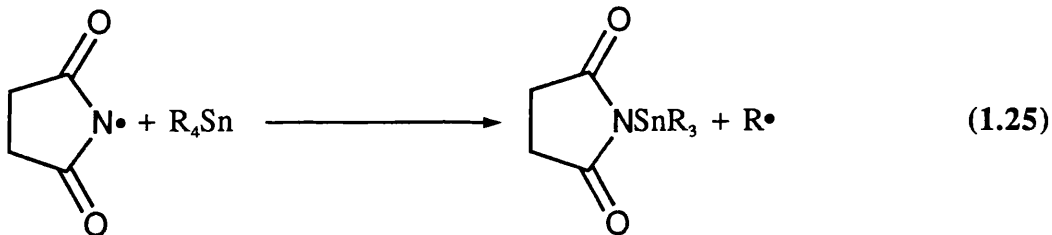
$\underline{N}$-iodosuccinimide react in a similar way (X = Cl or I).

Absolute rate coefficients for the S_H2 reaction (1.25) were obtained for a variety of alkyl groups, R, along with relative (and one absolute) rate constants for the halogen-abstraction reaction (1.26; X = Cl, Br, or I).[23] These were the first rate coefficients determined for reactions of imidyl radicals and selected values are given in Tables 1.2 and 1.3.

$\underline{N}$-Chlorosuccinimide also reacts with hexabutylditin[24] and the reaction proceeds quantitatively as shown in equation (1.27). Heptane, chloroform or

$$\text{(N-Cl succinimide)} + Bu_3SnSnBu_3 \longrightarrow \text{(N-SnBu}_3\text{ succinimide)} + Bu_3SnCl \qquad (1.27)$$
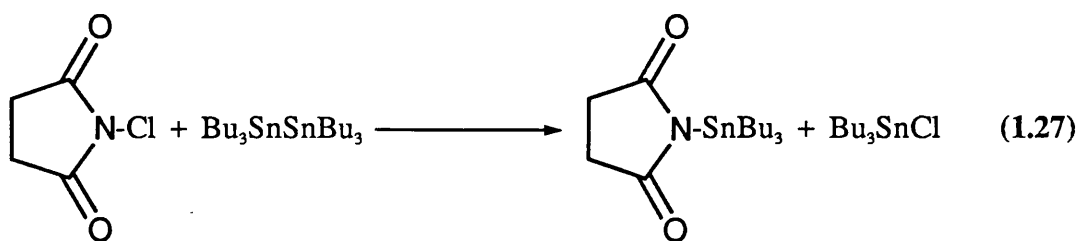
bromoform were used as solvents. $\underline{N}$-Bromosuccinimide reacted in the same way, but faster.

This reaction was also formulated as proceeding through a radical chain

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Table 1.2   Rate coefficients for reaction (**1.25**) at 35 °C in acetone solvent

R_4Sn	NXS	Rate coefficient / dm^3 $mol^{-1}s^{-1}$
Pr_4Sn^a	NBS	4×10^3
Bu_4Sn^a	NBS	8×10^3
$PhCH_2SnBu_3^a$	NBS	1.3×10^5
Me_4Sn^b	NIS	1.4×10^5
Et_4Sn^b	NBS	3.5×10^4
	NIS	4×10^4
Bu_4Sn^b	NBS	4×10^3
$Bu^s_4Sn^b$	NBS	8×10^2

a   By direct measurement, assuming the rate coefficient for the termination of two succinimidyl radicals to be 2×10^9 dm^3 $mol^{-1}s^{-1}$. b   By competition with Pr_4Sn, taking the rate coefficient for the reaction (**1.25**) where R = Pr to be 4×10^3 dm^3 mol^{-1} s^{-1}.

Table 1.3   Relative rate coefficients for reaction **(1.26)** at 35 °C in acetone solvent

R•	NCS	NBS	NIS
PhĊH$_2$	(1)	7.0[a]	22
Pr•	(1)	7.3	22

[a]   By direct measurement, taking rate coefficient for reaction **(1.26)** to be 5 x 10^5 dm^3 mol^{-1} s^{-1}.

pathway, again involving S_H2 attack by the succinimidyl radical at a tin centre [equations (1.28) and (1.29)].

$$\text{(succinimidyl radical) N} \cdot + Bu_3SnSnBu_3 \longrightarrow \text{(succinimide) NSnBu}_3 + Bu_3Sn^\bullet \qquad (1.28)$$

$$Bu_3Sn^\bullet + \text{(succinimide) NX} \longrightarrow Bu_3SnX + \text{(succinimidyl) N} \cdot \qquad (1.29)$$
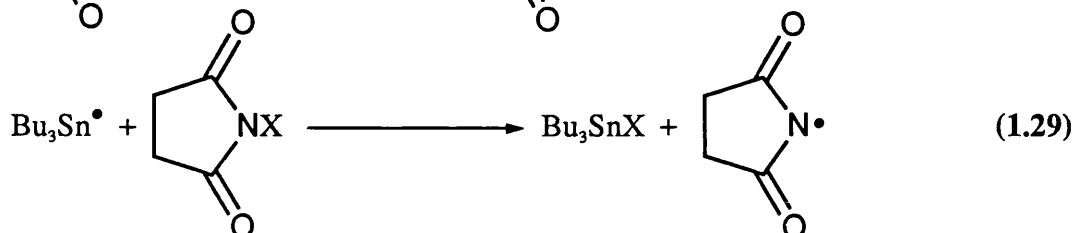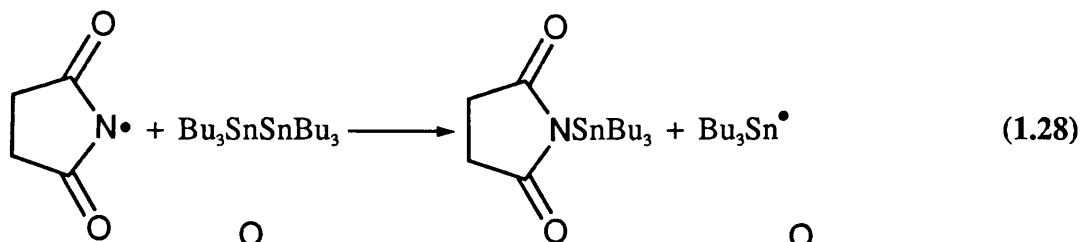
Against this background, we felt it was important to investigate the formation of imidyl radicals by cyclisation of ω-(isocyanatocarbonyl)alkyl radicals, thus avoiding some of the complications associated with the use of N-halogenoimides. Indeed, before this work no direct evidence for the cyclisation of the 2-isocyanatoethyl radical (8) existed because S· had never been generated from acyclic reagents. Thus, we set out to use a combination of electron spin resonance (e.s.r.) spectroscopic techniques and product analysis to study the cyclisation of ω-(isocyanatocarbonyl)alkyl radicals derived by bromine atom abstraction from the ω-bromoalkanoyl isocyanates (9) - (11).
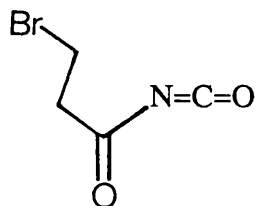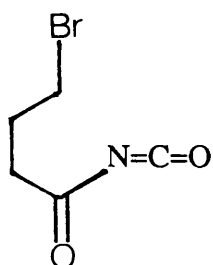
(9)   (10)
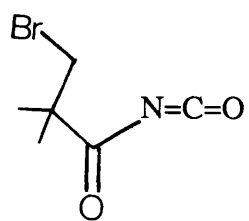
(11)

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CHAPTER 2

RESULTS AND DISCUSSION

2.1   **Syntheses**

3-Bromopropanoyl isocyanate (**1**) was prepared by treatment of 3-bromopropanoyl bromide with silver cyanate in the absence of solvent [equation (**2.1**)] by Johnson and Bublitz.[1] However, this reaction is heterogeneous and the

$$BrCH_2CH_2C(O)Br + AgNCO \longrightarrow BrCH_2CH_2C(O)NCO + AgBr \qquad (2.1)$$
$$(\underline{1})$$
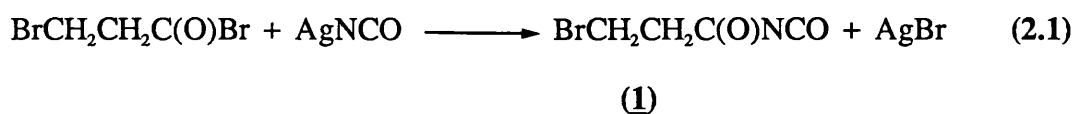
treatment had to be repeated four times to achieve complete conversion of the acid bromide. For the present work, various attempts were made to prepare (**1**) by alternative routes.

The reaction between tri-n-butyltin isocyanate and 3-bromopropanoyl chloride [equation (**2.2**)] gave no product. The reaction between silver

$$BrCH_2CH_2C(O)Cl + (C_4H_9)_3SnNCO \longrightarrow No\ (\underline{1})\ produced \qquad (2.2)$$
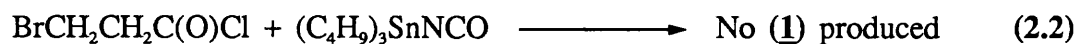
isocyanate and 3-bromopropanoyl bromide [equation (2.1)] in diethyl ether with sonication yielded ca. 60 % of the desired product, but a major impurity was detected by ^1H n.m.r. spectroscopy. This was shown to be ethyl 3-bromopropanoate (**2**), which presumably arises from the reaction between 3-bromopropanoyl bromide and diethyl ether catalysed by silver ion [equation

24

(2.3)].

$$BrCH_2CH_2C(O)Br + C_2H_5OC_2H_5 \xrightarrow{Ag^+} BrCH_2CH_2C(O)OC_2H_5 + C_2H_5Br \quad (2.3)$$

(2)
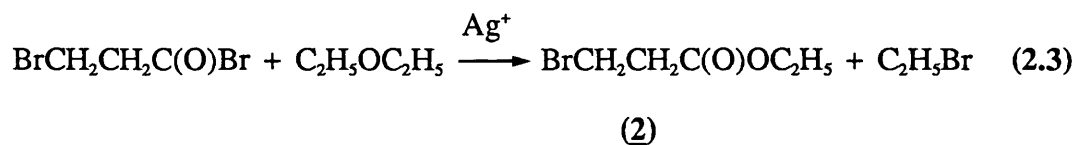
Depending on the stage at which the ether was added to the reaction mixture, different ratios of (1):(2) were obtained, as expected. After a number of trials, (1) was prepared in a single step using the reagents shown in equation (2.1) by ultrasonication of the reaction mixture in benzene. 4-Bromobutanoyl isocyanate (3) was prepared in low yield by a similar procedure in diethyl ether solvent, starting from 4-bromobutanoyl chloride.

Acyl isocyanates which do not have hydrogen attached at C-2 can be readily prepared from the corresponding amide and oxalyl chloride[2] [equation (2.4)] and this method worked well for synthesis of 3-bromo-2,2-dimethyl

$$RC(O)NH_2 + ClC(O)C(O)Cl \longrightarrow RC(O)NCO + CO + 2HCl \quad (2.4)$$
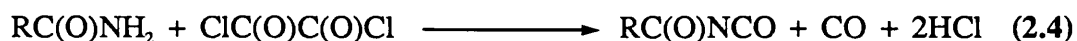
propanoyl isocyanate (4).

Various methods were tried to prepare propanoyl isocyanate. The reaction between propanoyl chloride and silver isocyanate in diethyl ether did not yield any of the desired product. The reaction between propanoic anhydride and trimethylsilyl isocyanate was attempted using two different catalysts, $SnCl_4$ and $AlCl_3$ [equation (2.5)].[3] However, in our hands with either catalyst,

$$[C_2H_5C(O)]_2O + Me_3SiNCO \xrightarrow[\text{or } AlCl_3]{SnCl_4} C_2H_5C(O)NCO + C_2H_5C(O)OSiMe_3 \quad (2.5)$$

25

$$C_2H_5C(O)NCO \xrightarrow{\text{>100 °C}} C_2H_5C{\equiv}N + CO_2 \qquad (2.6)$$
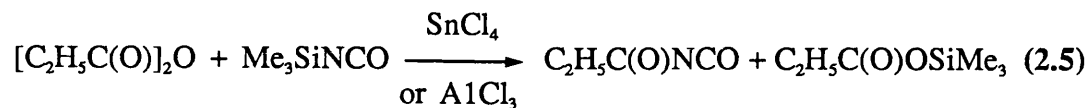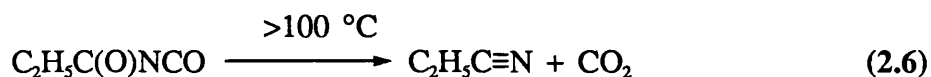
decarboxylation of the product occurred at the reaction temperature (ca. 100 °C) to give propanonitrile and carbon dioxide [equation (2.6)]. The reaction between propanamide and oxalyl chloride in 1,1,2,2-tetrachloroethane solvent according to a literature method[4] yielded only a ca. 1 % yield of the propanoyl isocyanate, even if the temperature during reaction was controlled carefully in an attempt to avoid decarboxylation. Propanoyl isocyanate was eventually prepared by the reaction between tri-n-butyltin isocyanate and propanoyl chloride, according to a published method[5] used previously to prepare similar compounds [equation (2.7)].

$$(C_4H_9)_3SnNCO + C_2H_5C(O)Cl \longrightarrow C_2H_5C(O)NCO + (C_4H_9)_3SnCl \qquad (2.7)$$
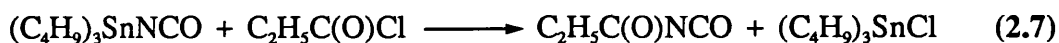
All acyl isocyanates were colourless liquids which were very sensitive to water and, especially in the case of (1), light sensitive and subject to

(1)   (3)   (4)
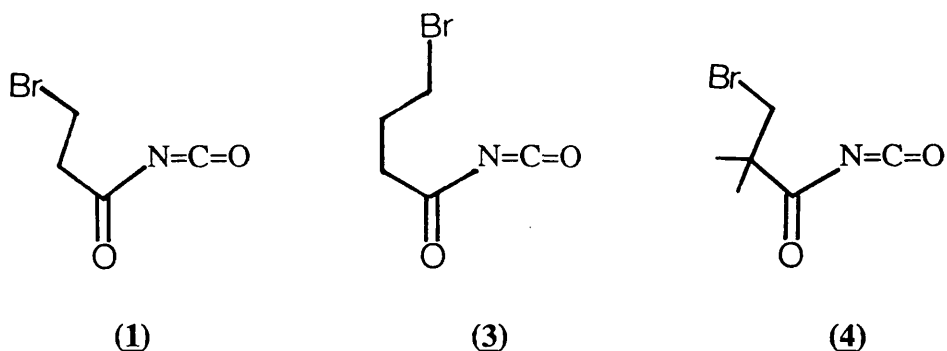
polymerisation during storage. In common with unsubstituted acyl isocyanates, they react smoothly with methanol in diethyl ether to give crystalline N-

acylurethanes [equation (2.8)], which were used for characterisation and

$$RC(O)NCO + MeOH \longrightarrow RC(O)NHCO_2Me \qquad (2.8)$$
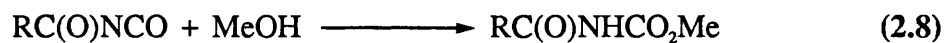
quantitative determination of these reactive compounds.

Authentic sources of imidyl radicals were provided by the N-halogenoimides (5 - 9; X = Cl or Br), which were prepared from the corresponding imides by reaction with Bu^{t}OCl in methanol or with bromine in aqueous sodium bicarbonate.
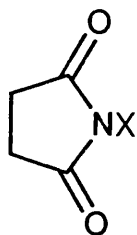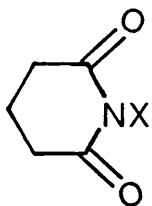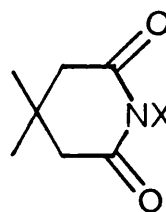
(5)   (6)   (7)
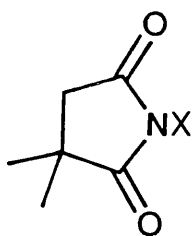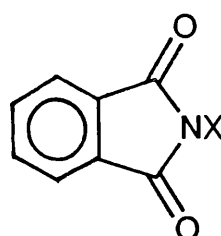
(8)   (9)

2.2   Spin-Trapping of Imidyl and Alkyl Radicals

2.2.1   Spin-Trapping with 1,1-Di-t-Butylethylene (DTBE)

$\underline{N}$-Halogenoimides undergo radical chain addition to simple alkenes (see Chapter 1), implying that the electrophilic imidyl radicals (Im$^{\bullet}$) add rapidly to the C=C bond.[6] Our initial approach was to use the technique of spin-trapping[7] to intercept imidyl radicals and convert them to relatively persistent adducts which would be readily detectable by e.s.r. spectroscopy. We reasoned[8] that 1,1-di-t-butylethylene[9] (DTBE) would function as a selective trap for Im$^{\bullet}$ [equation (2.9)] and that uncyclised ω-(isocyanatocarbonyl)alkyl radicals would

$$\text{Im}^{\bullet} + \text{Bu}^{t}_{2}\text{C=CH}_{2} \longrightarrow \text{Bu}^{t}_{2}\overset{\bullet}{\text{C}}\text{-CH}_{2}\text{Im} \qquad (2.9)$$

$$\underline{(10)}$$
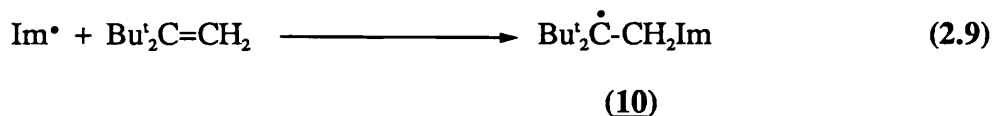
not undergo addition at a detectable rate.

Authentic imidyl adducts $\underline{(10)}$ were generated directly in the microwave cavity of an e.s.r. spectrometer[10] by u.v. photolysis of the $\underline{N}$-chloroimide ($\underline{ca}$. 0.2 $\underline{M}$) [equation (2.10)] in the presence of DTBE ($\underline{ca}$. 0.5 $\underline{M}$). The solvent was

$$\text{ImCl} \xrightarrow{\quad h\upsilon \quad} \text{Im}^{\bullet} + \text{Cl}^{\bullet} \qquad (2.10)$$
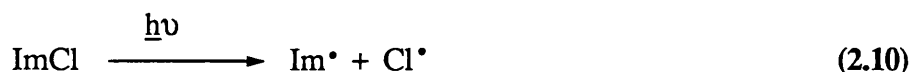
usually perdeuterioacetonitrile (CD_3CN), which gave rather better quality spectra than CH_3CN, although other solvents such as EtCN, Pr^{n}CN, and CH_2Cl_2 were also satisfactory. Under these conditions, the corresponding adduct[9] of the

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chlorine atom to DTBE was not readily detected.

Strong spectra of the adducts (10) were observed from all the N-chloroimides (5 - 9; X = Cl) (see Figures 2.1 and 2.2) in the temperature range 230-300 K; the spectroscopic parameters are collected in Table 2.1. All these spectra exhibited temperature-dependent line-broadening attributable to out-of-phase modulation of the splittings from instantaneously non-equivalent β-protons. Thus, the lines corresponding to $M_I(2H_\beta) = 0$ broadened selectively as the temperature was lowered. These lineshape effects were particularly pronounced for (10) derived from glutarimidyl or 3,3-dimethylglutarimidyl radicals and for the adduct derived from (7; X = Cl) at ca. 235 K, the central multiplet of the β-proton "triplet" was broadened almost beyond the limit of detection (see Figure 2.1a). Hindered rotation about the N-C_β bond is the probable cause of these lineshape effects[8] and the non-equivalence of the β-protons could be especially marked when the non-planar glutarimidyl moiety is present. Inspection of molecular models suggest that rocking of the imide ring between the two minima (11a) and (11b) is a possible cause of the selective line

(11a)   (11b)

29
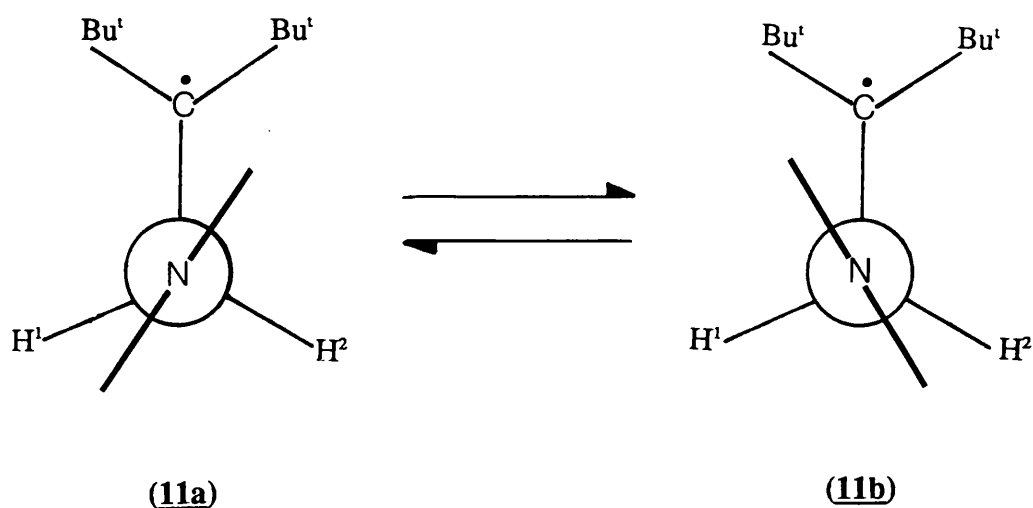
broadening exhibited by these sterically congested radicals (see Figure **2.3**). In common with other adducts of DTBE, the eclipsed conformation about the C_α-C_β bond shown in (**11**) is preferred for steric reasons.[9] Attempts to observe spectra of (**10**) in the slow-exchange region by working in CH_2Cl_2 at low temperatures were unsuccessful. When photolysis was interrupted at 263 K, decay of (**10**; Im = S) was approximately first-order ($t_{1/2}$ ca. 18 s).

Ring opening of the 2,2-dimethylsuccinimidyl radical (DMS•) to give a tertiary alkyl radical would be expected to be more favourable thermodynamically (gem-dimethyl effect) and more rapid than ring opening of S• . Despite this, u.v. photolysis of N-chloro-2,2-dimethylsuccinimide (**8**; X = Cl) in the presence of DTBE afforded very strong e.s.r. spectra of the
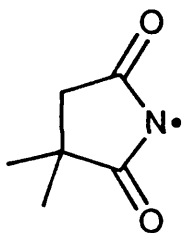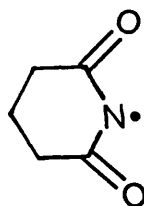
DMS•   G•

(admittedly quite persistent) adduct (**10**; Im = DMS).

There have been suggestions that photochemical generation of imidyl radicals from N-halogenoimides can give rise to excited species different from those generated in thermal reactions.[11] Imidyl adducts of the type (**10**) were also detected by e.s.r. spectroscopy when dibutanoyl peroxide (ca. 0.2 M) was decomposed thermally (320-340 K) in the presence of an N-chloroimide (ca. 0.2 M) and DTBE (ca. 0.5 M) in aceto- or butyro-nitrile solvent [equations (**2.11**) and (**2.12**)]. Once generated, the persistent adducts (**10**) could still be detected

Table 2.1

E.s.r. parameters for the adducts $Bu^t_2\dot{C}CH_2Im$ (**10**) in [$^2H_9$]acetonitrile

Im•	T/K	Hyperfine splittings (G)[a]		
		a(2H$_\beta$)	a(^{14}N$_\beta$)	a(18H$_\gamma$)
Succinimidyl	305	13.65	6.88	0.38
	259	13.56	6.95	0.38
2,2-Dimethylsuccinimidyl	290	13.50	6.88	0.38
	248	13.48	7.00	0.38
Glutarimidyl	332	15.38	5.25	0.34
	244	15.31	5.50	0.33
3,3-Dimethylglutarimidyl	324	15.00	5.40	0.33
	244	14.90	5.64	0.33
Phthalimidyl	330	13.63	7.28	0.38
	270	13.50	7.36	0.37

a All g-factors are 2.0025.

31

(a)

10 G

(b)

(c)

Figure 2.1

32
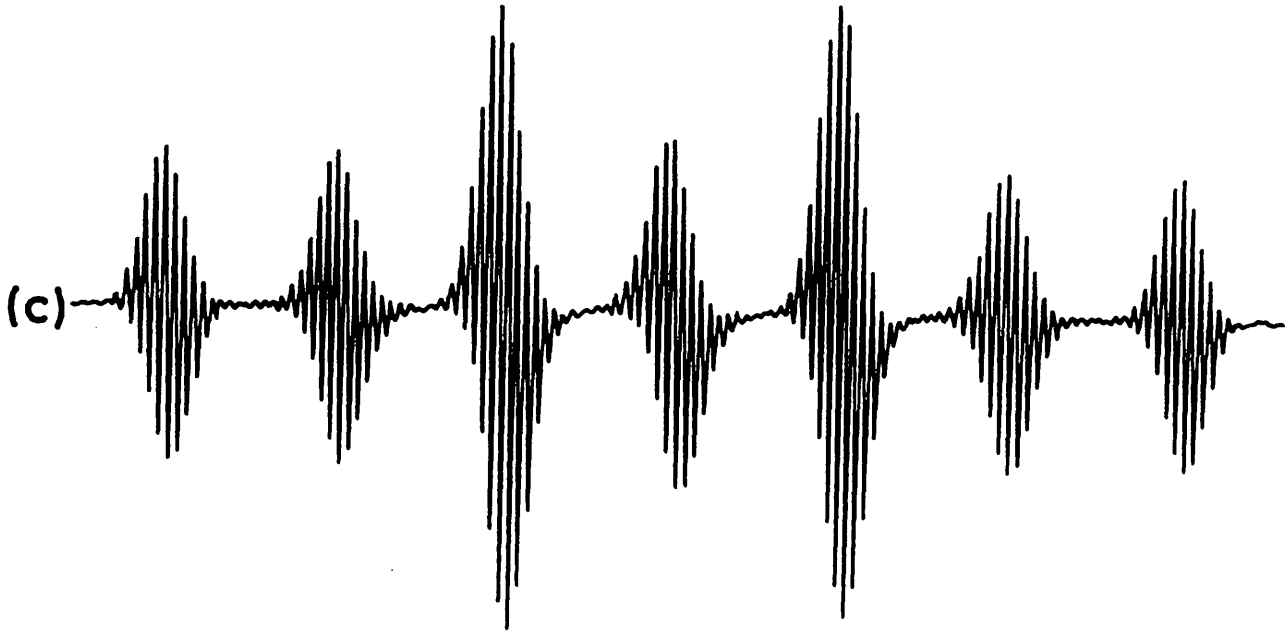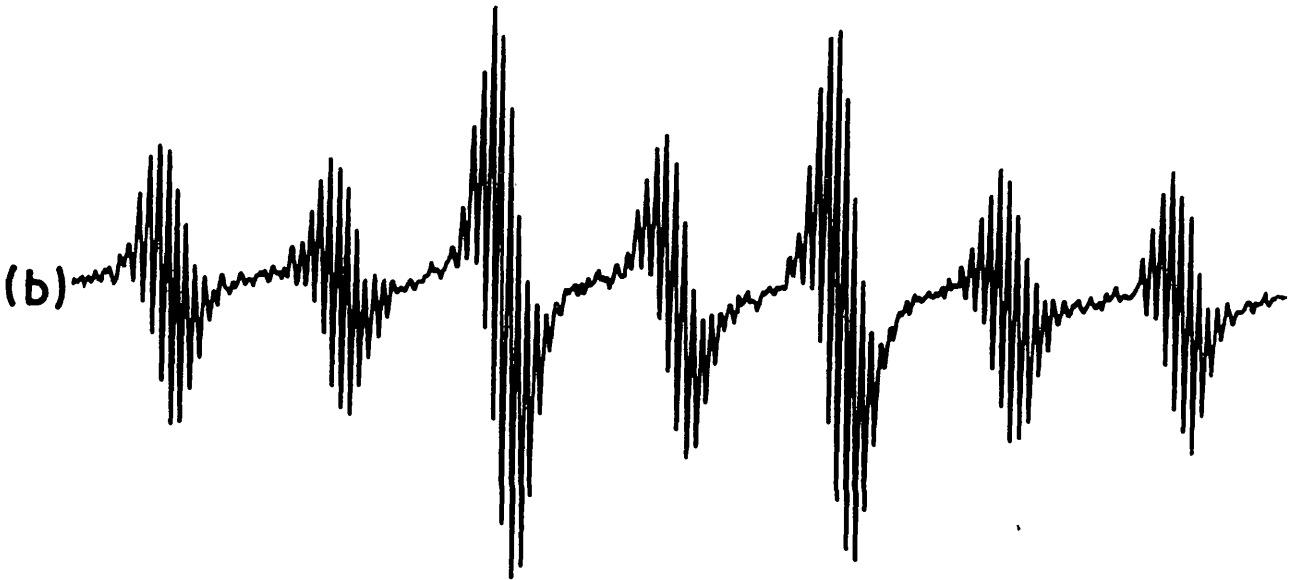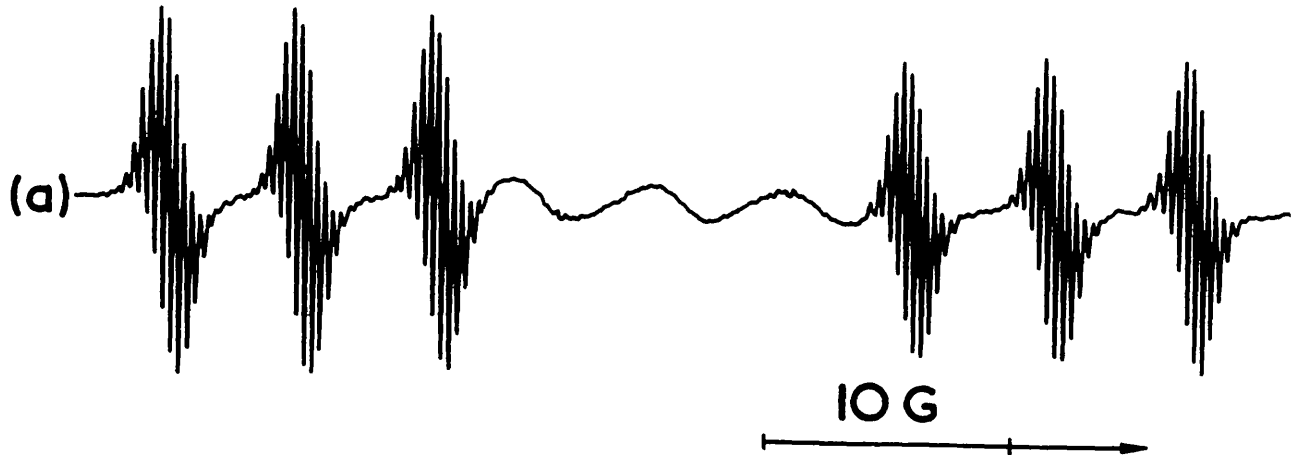
Figure captions

Figure 2.1   E.s.r. spectra of radicals (**10**) formed by addition of imidyl radicals to $Bu^t_2C=CH_2$ in CD_3CN.   (a) $Im^\bullet$ from photolysis of (**7**; X = Cl) at 245 K.   (b) $Im^\bullet$ from photolysis of (**8**; X = Cl) at 293 K.   (c) $Im^\bullet$ produced during thermolysis of TBHN in the presence of (**4**) and $Bu^n_3P{\rightarrow}BH_3$ at 294 K; the spectrum is essentially indistinguishable from that shown in (b).

(a)

10 G

(b)

(c)

Figure 2.2

34
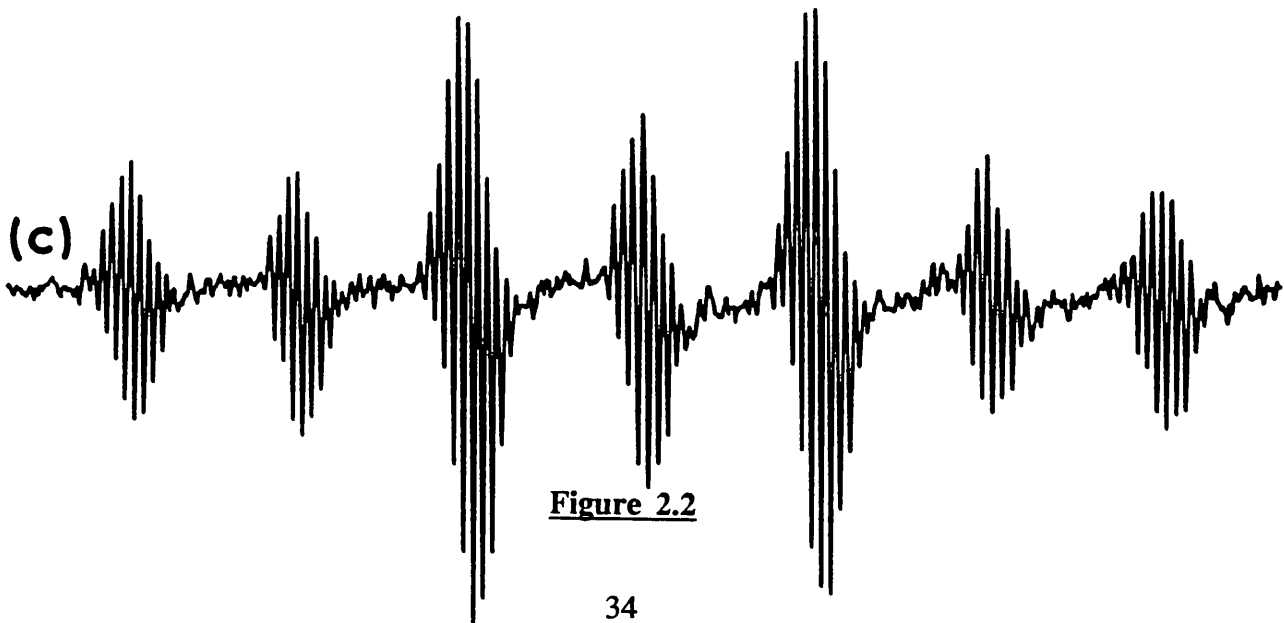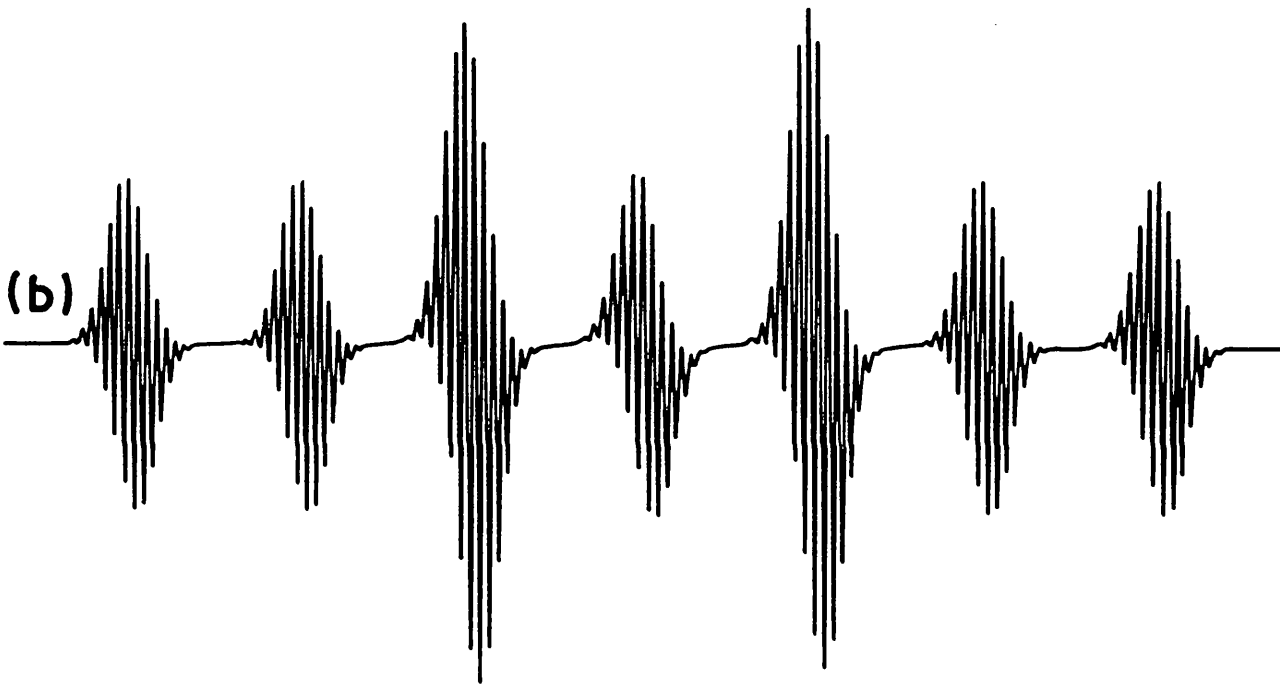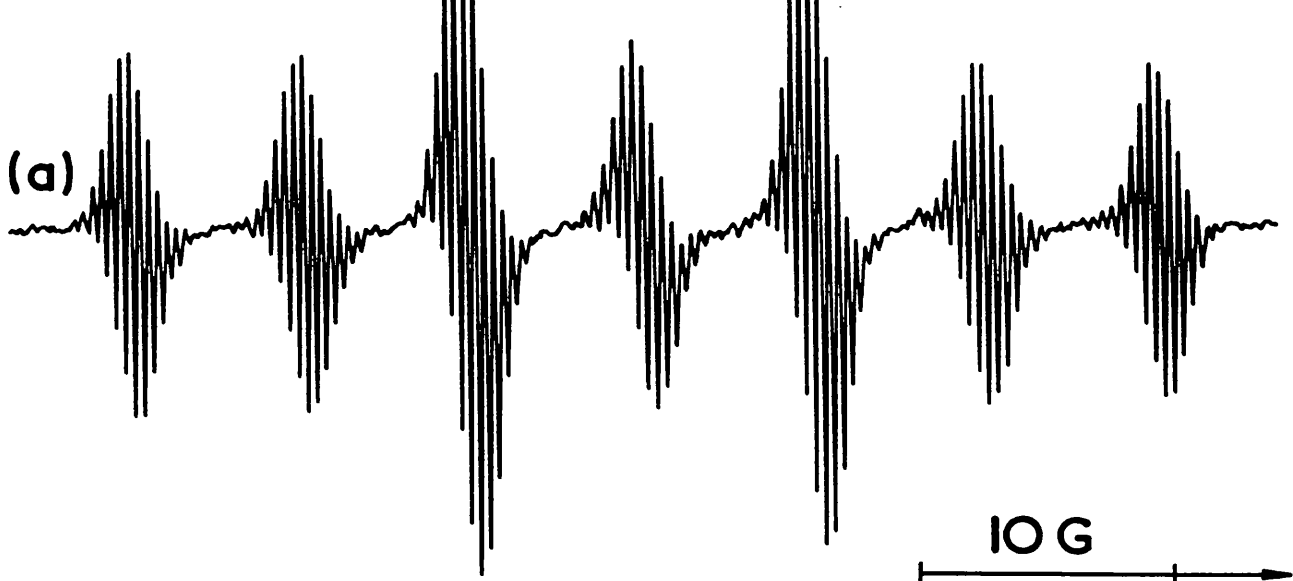
Figure captions

Figure 2.2 (a) E.s.r. spectrum of the radical ($\underline{10}$; Im = S) at 261 K obtained during u.v. irradiation of NCS and DTBE in CD_3CN. (b) Computer simulation of (a) using the splitting constants given in the text. The peak-to-peak widths of the lines associated with $M_I(2H_\beta)$ = 0 and ± 1 are 0.21 and 0.17 G, respectively. (c) E.s.r. spectrum of the radical ($\underline{10}$; Im = S) at 317 K obtained during thermolysis of TBHN in the presence of ($\underline{1}$), DTBE, and $Bu^n_3P{\rightarrow}BH_3$ in CD_3CN [$\underline{a}(2H_\beta)$ 13.71, $\underline{a}(N_\beta)$ 6.86, and $\underline{a}$ ($18H_\gamma$) 0.38 G].

35

$\underline{a}(H^1)$

$\underline{a}(H^2)$ $\underline{a}(H^2)$

Slow exchange limit
(low temperature)

Intermediate
exchange-rate region

$\dfrac{\underline{a}(H^1)+\underline{a}(H^2)}{2}$ $\dfrac{\underline{a}(H^1)+\underline{a}(H^2)}{2}$

Fast exchange limit
(high temperature)
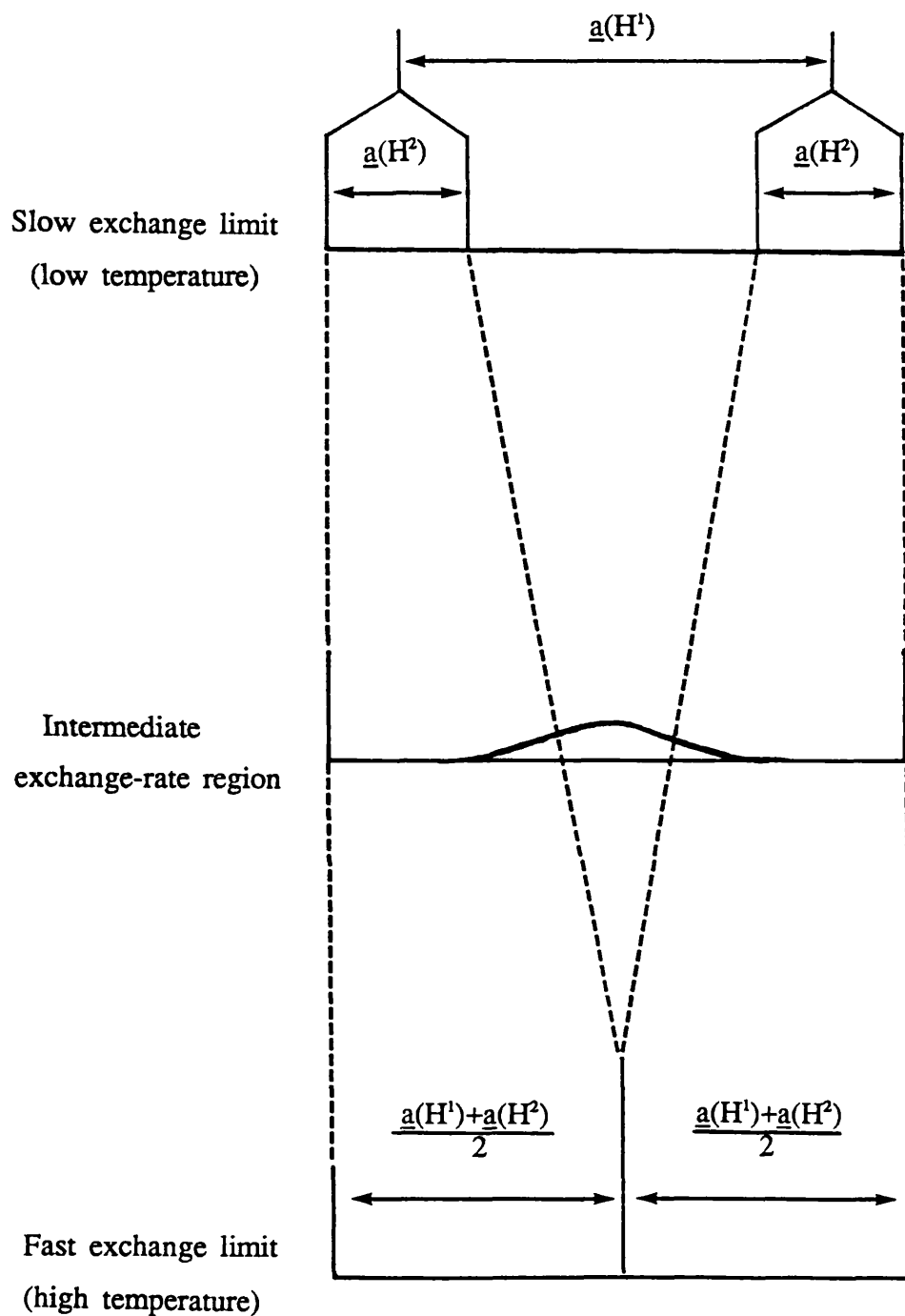
Figure 2.3   Diagram showing the lineshape changes that accompany modulation of the splittings from the β-protons H^1 and H^2 as a result of rotation about C_α-C_β bond.

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at lower temperatures and their spectra were indistinguishable from those of the adducts produced photochemically.

$$\text{Pr}^n\text{C(O)OOC(O)Pr}^n \xrightarrow{\text{heat}} 2\text{Pr}^{n\bullet} + 2\text{CO}_2 \qquad (2.11)$$

$$\text{Pr}^{n\bullet} + \text{ImCl} \longrightarrow \text{Im}^\bullet + \text{Pr}^n\text{Cl} \qquad (2.12)$$
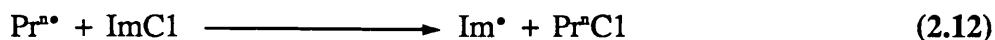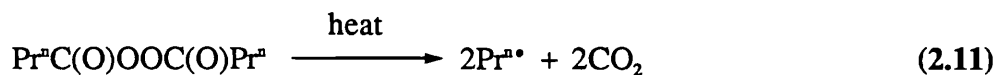
Spin-trapping experiments with the three ω-bromoalkanoyl isocyanates (**1**), (**3**) and (**4**) showed conclusively that the corresponding (isocyanato carbonyl)alkyl radicals undergo cyclisation to give imidyl radical. The most suitable halogen abstracting radical proved to be $\text{Bu}^n_3\text{P}{\rightarrow}\overset{\bullet}{\text{B}}\text{H}_2$ [equations (2.13) and (2.14)],[12] although trialkylstannyl and trialkylsilyl radicals were also

$$\text{Bu}^t\text{ON=NOBu}^t \xrightarrow{\text{heat}} 2\text{Bu}^t\text{O}^\bullet + \text{N}_2 \qquad (2.13)$$

$$\text{Bu}^t\text{O}^\bullet + \text{Bu}^n_3\text{P}{\rightarrow}\text{BH}_3 \longrightarrow \text{Bu}^n_3\text{P}{\rightarrow}\overset{\bullet}{\text{B}}\text{H}_2 + \text{Bu}^t\text{OH} \qquad (2.14)$$
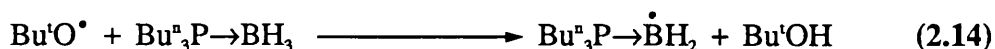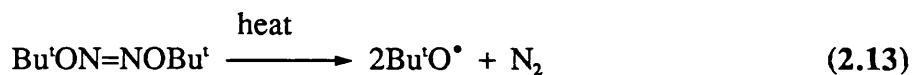
effective. When a CD_3CN solution containing tributylphosphine-borane[12] (ca. 0.4 M), DTBE (ca. 0.5 M), di-t-butyl hyponitrite[13] (TBHN) (ca. 0.1 M), and a bromoacyl isoyanate (ca. 0.8 M) was heated in darkness at 290-320 K, the e.s.r. spectrum of the appropriate imidyl adduct (**10**) was observed. Thus, (**1**), (**3**) and (**4**) afforded adducts of S• , the glutarimidyl radical (G•), and DMS• , respectively [e.g. equations (2.15) - (2.17)], and the spectroscopic parameters

$$\text{Bu}^n_3\text{P}{\rightarrow}\overset{\bullet}{\text{B}}\text{H}_2 + \text{BrCH}_2\text{CH}_2\text{C(O)NCO} \longrightarrow \overset{\bullet}{\text{C}}\text{H}_2\text{CH}_2\text{C(O)NCO} + \text{Bu}^n_3\text{P}{\rightarrow}\text{BH}_2\text{Br} \quad (2.15)$$

$$\overset{\bullet}{C}H_2CH_2C(O)NCO \; \rightleftharpoons \; S\bullet \qquad\qquad (2.16)$$

(12)

$$\overset{\bullet}{C}H_2CH_2CH_2C(O)NCO \; \longrightarrow \; G\bullet \qquad\qquad (2.17)$$
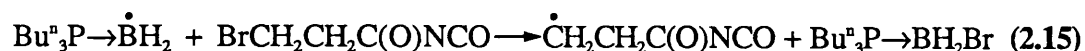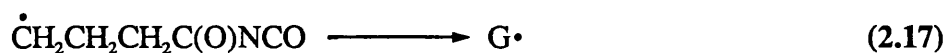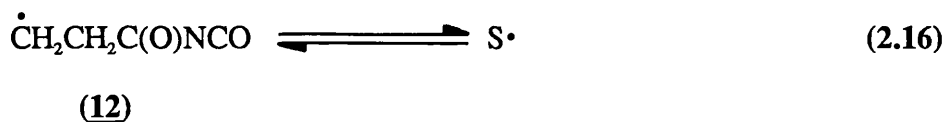
were the same, within experimental error, as those of the adducts derived from the N-chloroimides (see Figure 2.1C). Abstraction of bromine from (1) gives (12) [equation (2.15)], which would react only slowly with the phosphine-borane[12] and must cyclise relatively rapidly to give S• . Presumably[14,15] the initial product of cyclisation is $S_\sigma^\bullet$, even if this is not the electronic ground state. 2,2,5,5-Tetramethyltetrahydrofuran (TMTHF) was also used as a solvent for these trapping experiments with results similar to those obtained using nitriles.

2.2.2   Attempted Trapping of the Diacetylaminyl Radical with DTBE

U.v. photolysis of an acetonitrile solution containing N-chlorodiacetamide (ca. 1 M) and DTBE (ca. 0.7 M) at 241 K did not give rise to any spectrum; at 253 K a weak spectrum was observed but this could not be interpreted successfully.

The diacetylaminyl radical (13a), apart from being acyclic is very similar to S• and it was expected that both species would behave the same way. One possible explanation for the difference could be that, for steric reasons, the diacetylaminyl radical adopts the conformation shown,[16] rather than one analogous to that of S•. It is possible that (13a) could rearrange to the

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$$O=\overset{\overset{\displaystyle CH_3}{|}}{C}\!\!\diagdown\!\!\underset{\underset{\displaystyle O=\overset{\overset{\displaystyle}{|}}{C}\diagdown CH_3}{|}}{N^{\bullet}} \quad\longrightarrow\quad \overset{\overset{\displaystyle H_2}{\displaystyle C}}{\underset{}{}} \quad\longrightarrow\quad \overset{\overset{\displaystyle \overset{\bullet}{C}H_2}{|}}{C}\!\!\diagdown\!\!NH \quad (2.18)$$

(13a) (13b) (13c)
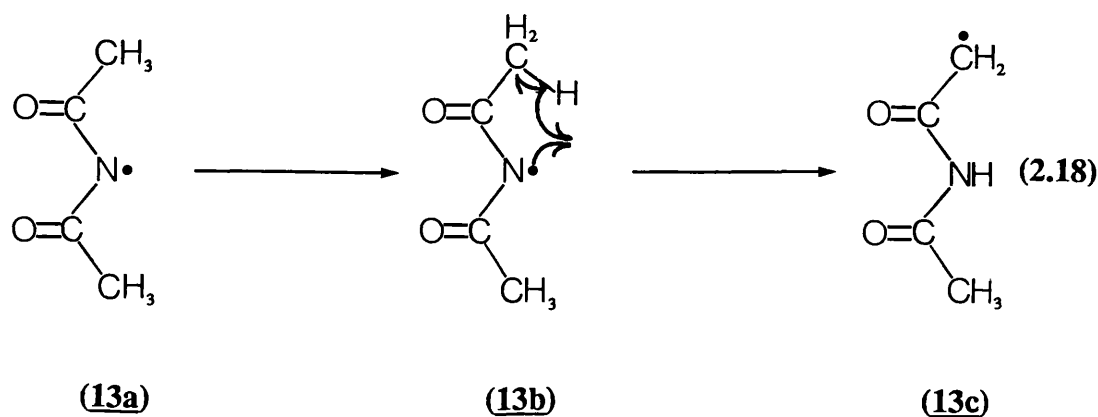
transient carbon-centred radical (13c) [equation (2.18)], which would probably not add to DTBE at a detectable rate.

2.2.3   Spin-Trapping with 2-Methyl-2-nitrosopropane (MNP)

This nitroso compound is known to form persistent adducts with both imidyl[17-19] and alkyl[7] radicals, although the nitroxides formed by addition of primary alkyl radicals are much shorter lived than those derived from tertiary radicals. Rate coefficients are available[20] for the trapping of alkyl radicals by MNP and we hoped initially to determine quantitative rates for cyclisation of ω-(isocyanatocarbonyl)alkyl radicals and ring opening of imidyl radicals.

Attempts were made to measure the rate coefficient for cyclisation of the radical (12) to S• using MNP (Scheme 1, in which M-H can be $Me_3N\rightarrow BH_3$, $Bu^n_3P\rightarrow BH_3$, or Et_3SiH) and k_{-1} is given by the equation (2.19). It would be reasonable to use the value of k_{trap} for a primary alkyl radical $R\overset{\bullet}{C}H_2$ at same

$$\left[\frac{\text{Rate of formation of } (14b)}{\text{Rate of formation of } (14a)}\right]_{t=0} = \frac{k_{-1}}{k_{trap}\,[\text{MNP}]} \qquad (2.19)$$

temperature.[20] All the other quantities in equation (2.19) can be measured and
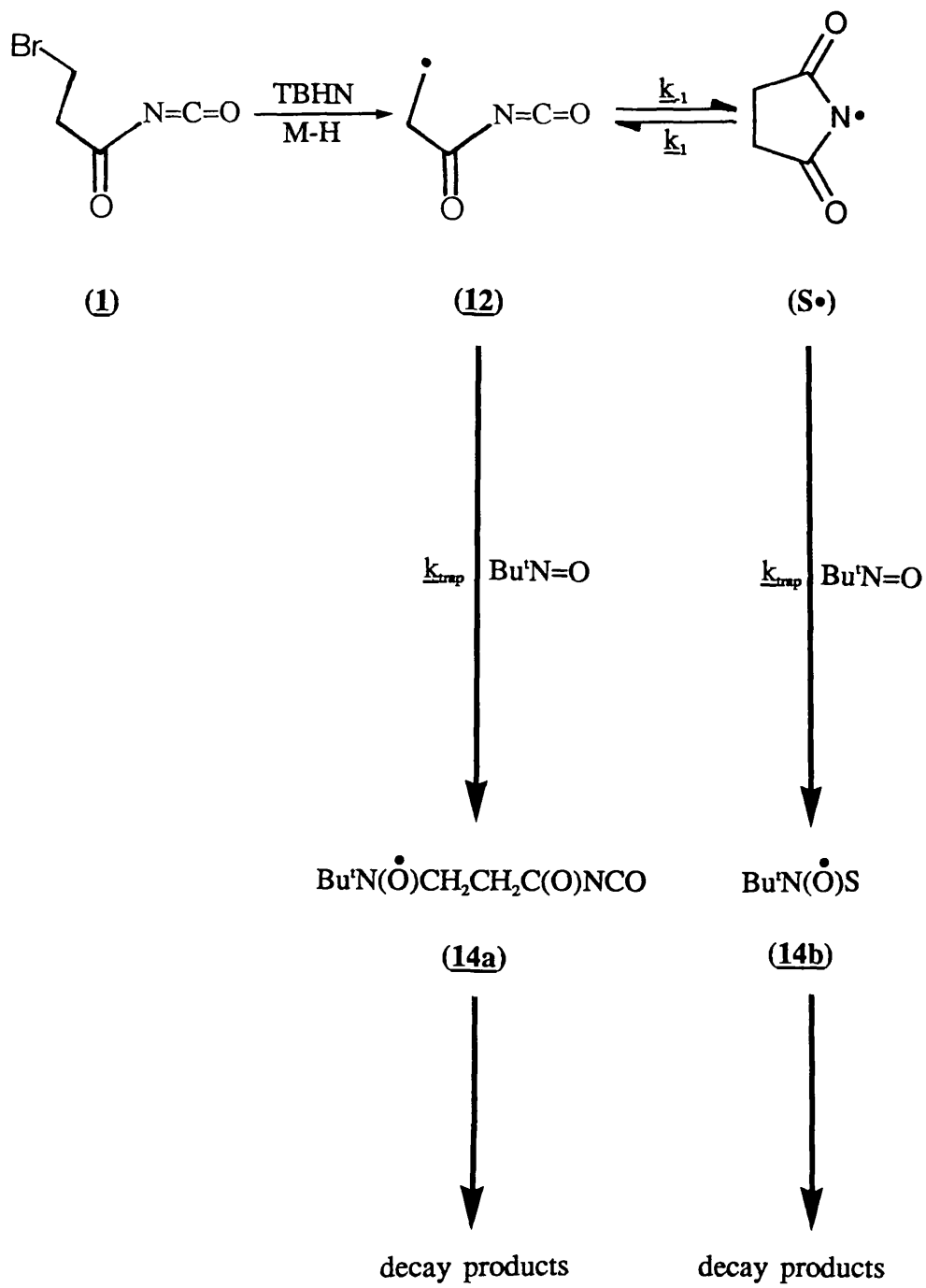
Scheme 1

the value of k_{-1} can be obtained.

In agreement with previous work,[17-19] irradiation with filtered light from a high-pressure mercury arc lamp † of a CD_3CN solution containing N-bromosuccinimide (NBS) (ca. 1.0 M) and MNP (ca. 0.04 M) at 290-315 K, afforded the e.s.r. spectrum of the nitroxide (15; Im = S). Other N-bromoimides

$$Im^\bullet \ + \ Bu^tNO \ \longrightarrow \ Bu^tN(\overset{\bullet}{O})Im \qquad\qquad (2.20)$$

$$\underline{(15)}$$
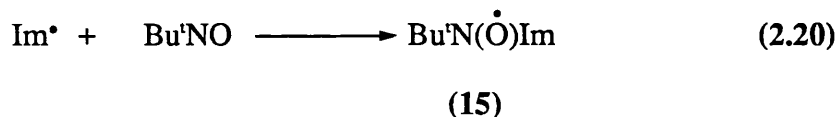
were more soluble than NBS and similar experiments could be carried out in TMTHF solvent. Glutarimidyl radicals undergo ring opening more slowly than succinimidyl radicals,[21] probably because the ring is larger and there is less bond angle strain, and both G$^\bullet$ and the 3,3-dimethylglutarimidyl radical were readily trapped by MNP during photolysis of (7; X = Br) in TMTHF. The e.s.r. parameters of all nitroxide spin-adducts are given in Table 2.2.

The amine-borane $Me_3N{\rightarrow}BH_3$ reacted exothermically on mixing with (1) in all the various solvents and was not studied further. Trial experiments were carried out to determine the optimum conditions for trapping of ω-(isocyanatocarbonyl)alkyl radicals using ethyl 3-bromopropanoate [$BrCH_2CH_2C(O)OEt$] as a model for the bromoacyl isocyanates. The phosphine-boryl radical $Bu^n_3P{\rightarrow}\overset{\bullet}{B}H_2$ abstracted bromine more slowly from the bromopropanoate than it added[22] to MNP under normal conditions.

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† The beam from the mercury discharge lamp used to generate transient radicals[10] was attenuated with a 3 % transmittance metal gauze screen and passed through a 4 mm thick sheet of Pyrex glass.

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Trimethylstannyl radicals (generated from hexamethylditin and TBHN) produced a mixture of nitroxide radicals, including the adduct derived from EtCN formed by hydrogen abstraction from the solvent.

The triethylsilyl radical, derived from Et_3SiH, proved to be the most suitable halogen abstractor. When CD_3CN or TMTHF solutions containing (**1**) (ca. 1.0 M), MNP (ca. 0.05 M), triethylsilane (ca. 1.2 M), and TBHN (ca. 0.05 M) were heated in darkness at temperatures between 290 and 315 K, an intense composite e.s.r. spectrum derived from two nitroxides was detected (see Figure **2.4a**). The stronger spectrum arises from (**15**; Im = S) [equations (**2.21**) -

$$Bu^tON=NOBu^t \xrightarrow{\text{heat}} 2Bu^tO^{\bullet} + N_2 \qquad (2.21)$$

$$Bu^tO^{\bullet} + Et_3Si\text{-}H \longrightarrow Et_3Si^{\bullet} + Bu^tOH \qquad (2.22)$$

$$Et_3Si^{\bullet} + BrCH_2CH_2C(O)NCO \longrightarrow {\overset{\bullet}{C}}H_2CH_2C(O)NCO + Et_3SiBr \qquad (2.23)$$
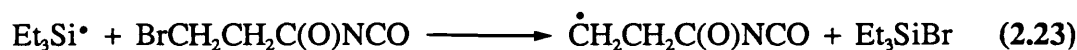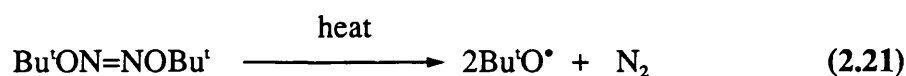
(**2.23**) and Scheme **1**] and the weaker three line spectrum [$a(N)$ 7.8 G, g 2.0067 in CD_3CN at 328 K] is assigned to an acyl t-butyl nitroxide, probably $Bu^tN(\overset{\bullet}{O})C(O)CH_2CH_2Br$ formed by trapping of the acyl radical (**16**) derived from a trace of 3-bromopropanoyl bromide present in (**1**) (cf. reference 23). No

$$BrCH_2CH_2C(O)Br \xrightarrow{Et_3Si^{\bullet}} BrCH_2CH_2\overset{\bullet}{C}(O) + Et_3SiBr \qquad (2.24)$$

$$(\underline{16})$$

spin-adduct of the uncyclised 2-(isocyanatocarbonyl)ethyl radical (**12**) was

detected, even when the concentration of MNP was increased to ca. 1.2 M, [++]

although we note that the resulting nitroxide would be expected to be much

shorter-lived than (15) under the same conditions. Since adducts of both

cyclised and uncyclised radicals could not be detected simultaneously, it is not

possible to measure the rate of cyclisation of (12) using this method.

In similar experiments with 3-bromo-2,2-dimethylpropanoyl isocyanate (4),

again no spectrum of the primary alkyl spin-adduct (17) was observed, but

neither could a signal from (15; Im = DMS) be conclusively identified. The

spectrum was dominated by an intense signal which we assign to the very

persistent di-t-alkyl nitroxide (18) (see Figure 2.4b), produced by trapping of the

t-alkyl radical formed by overall 1,2-shift of the C(O)NCO group following

$$Bu^tN(\overset{\bullet}{O})CH_2CMe_2C(O)NCO \qquad Bu^tN(\overset{\bullet}{O})CMe_2CH_2C(O)NCO$$

$$(17) \qquad\qquad\qquad\qquad (18)$$

abstraction of bromine from (4). Variation of the MNP concentration from ca.

0.04 to 1.2 M did not lead to the detection of nitroxides other than (18) [apart

from variable concentrations of $Bu^tN(\overset{\bullet}{O})OBu^t$]. Since (15; Im = DMS) would

be expected to be as persistent as the S• adduct, its absence is presumably

related to the greater rate of ring opening of the methylated imidyl radical.

Thus, for neither of the bromoacyl isocyanates (1) or (4) was it possible to

determine quantitative rates of cyclisation or ring opening using MNP.

[++] This would be the concentration of monomeric MNP if the dimer
dissociates fully in solution. The extent of dissociation will be solvent
dependent and will be smaller in CD$_3$CN than in TMTHF.

Table 2.2   E.s.r. parameters for t-butyl nitroxides $Bu^tN(\dot{O})Im$ **(15)** and $Bu^tN(\dot{O})R$

Nitroxide	Solvent	T/K	g-factor	Hyperfine splittings (G)	
				$\underline{a}$(N)	Others
(15); Im = succinimidyl)	CD_3CN	294	2.0058	16.38	1.81 (N_γ)
(15); Im = glutarimidyl)	CD_3CN	295	2.0059	15.88	1.91 (N_γ), 0.27 (nH)[a,b]
(15); Im = 3,3-dimethylglutarimidyl)	TMTHF	294	2.0058	15.63	1.85 (N_γ), 0.27 (nH)[b,c]
(18)	TMTHF	293	2.0060	15.30	0.53 ($2H_\delta$)[b]
$Bu^tN(\dot{O})CH_2CH_2CO_2Et$	TMTHF	294	2.0060	15.38	12.25 ($2H_\gamma$), 0.63 ($2H_\delta$)

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<u>a</u> Splitting into an even number (≥8) of lines spaced by 0.27 G.   <u>b</u> Splitting pattern unchanged, but better resolved, for the nitroxide

derived from [$^2H_9$]MNP.   <u>c</u> Splitting into an even number (≥10) of lines spaced by 0.27 G.

Figure 2.4

45
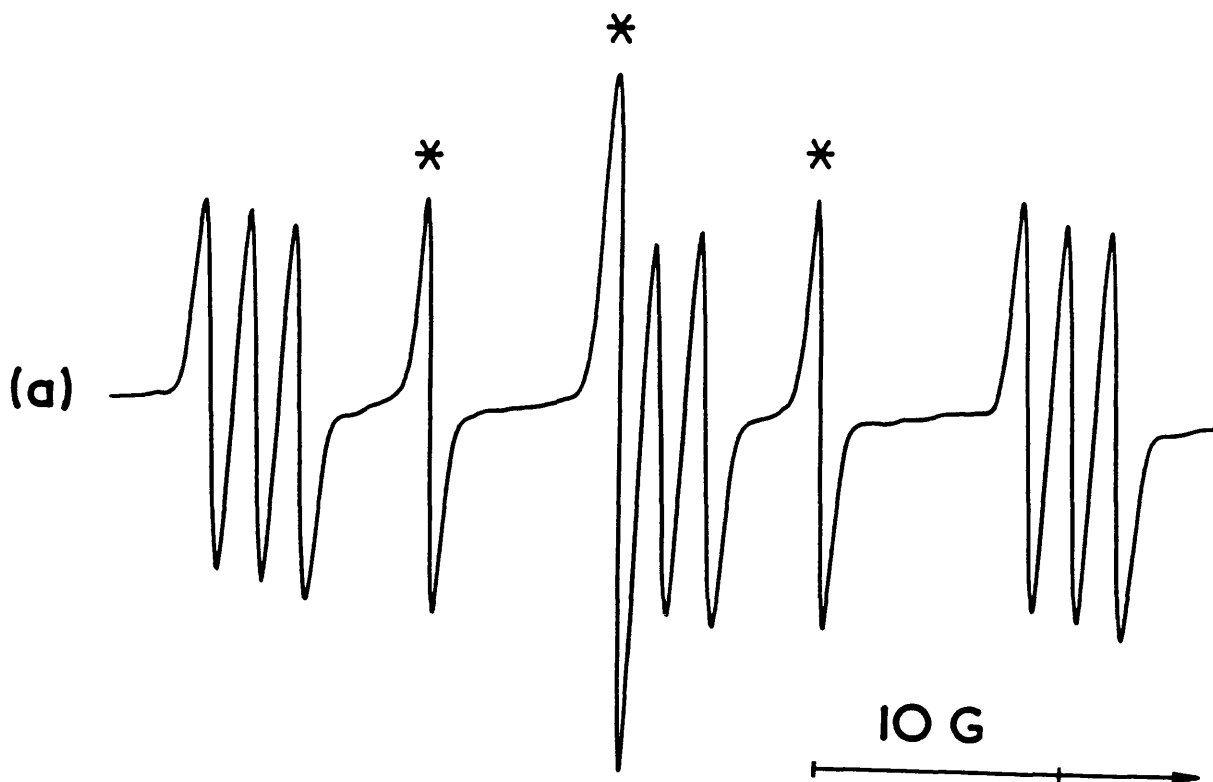
Figure 2.4 (a) E.s.r. spectrum of the nitroxide (**15**; Im = S) obtained during thermolysis of TBHN in the presence of (**1**), MNP, and Et_3SiH in CD_3CN at 328 K. The asterisks mark lines assigned to an acyl t-butyl nitroxide (see text). (b) E.s.r. spectrum of the nitroxide (**18**) obtained during thermolysis of TBHN in the presence of (**4**), [$^2H_9$]MNP, and Et_3SiH in TMTHF at 302 K.

2.3   Direct Detection of Imidyl and (Isocyanatocarbonyl)alkyl Radicals

Despite numerous attempts under a variety of conditions of solvent and temperature, it was not possible to detect any e.s.r. spectra attributable to imidyl radicals during u.v. irradiation of the N-halogenoimides (5 - 9; X = Cl or Br) either alone or in the presence of R_3SnSnR_3 (R = Me or Bu^n) which might scavenge halogen atoms more rapidly than imidyl radicals, especially at low temperatures. It is possible that the e.s.r. spectrum of Im• could be broadened in the presence of N-halogenoimide, if the thermoneutral exchange reaction (2.25) takes place on the e.s.r. timescale. If this exchange is slow, ^{14}N hyperfine

$$Im^{\bullet} \ + \ Im\text{-}X \ \longrightarrow \ Im^{\bullet}\text{-}X \ + \ Im^{\bullet} \qquad (2.25)$$
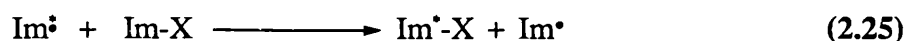
splitting will be observed, but if it is fast on the e.s.r. time scale the unpaired electron will see a rapidly inverting ^{14}N magnetic moment and no splitting will be detected. In the intermediate exchange region, line broadening will occur. Sometimes, very weak and poorly defined signals were detected, but these appeared to be associated with the formation of solid deposits in the sample tubes.

Phthalimidyl radicals(19) do not undergo detectable ring opening, which is understandable[6,24] because the product would be a highly unstable aryl radical [equation (2.26)]. Ring opening of the 3,3-dimethylglutarimidyl radical (20) is

$$(2.26)$$

(19)
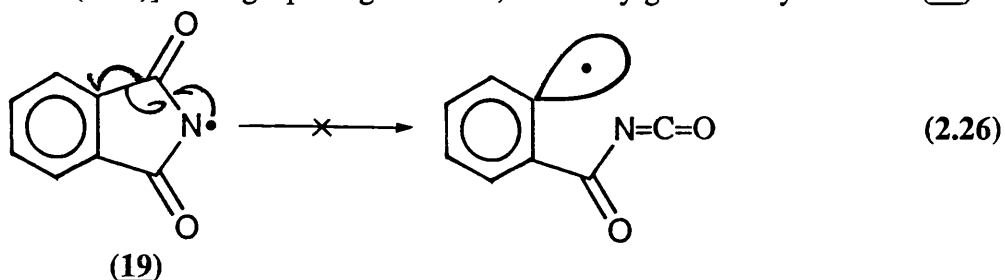
also relatively slow [equation (2.27)].[6,24] In contrast, the 2,2-dimethylglutarimidyl

radical (21) opens more rapidly,[6,24] since a stabilised tertiary alkyl radical is

formed [equation (2.28)]. However, even the N-halogenoimides (6), (7), and (9)

did not afford e.s.r. spectra attributable to the imidyl radicals (G•), (20), or (19),

$$\text{(20)} \quad \longrightarrow\!\!\times\!\!\longrightarrow \quad \text{N=C=O} \qquad (2.27)$$

$$\text{(21)} \quad \longrightarrow \quad \text{N=C=O} \qquad (2.28)$$
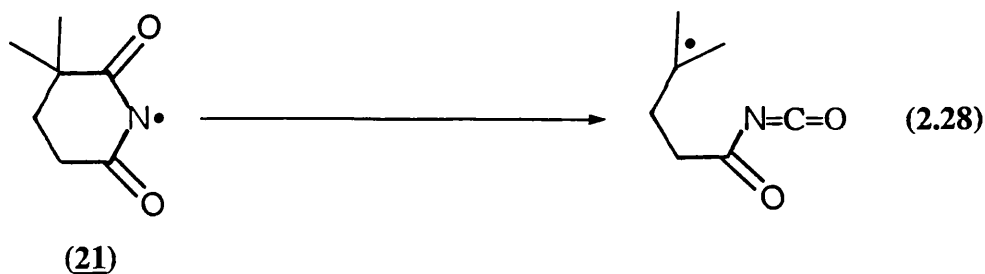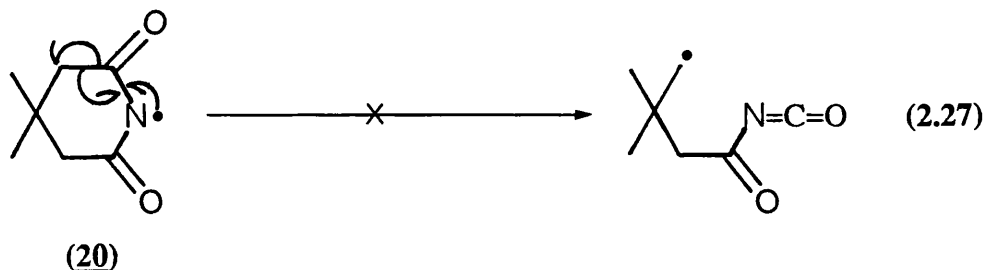
respectively. In particular, no spectra were obtained from most soluble N-

halogenoimides (7; X = Cl or Br) in CH_2Cl_2 even at 160 K.

E.s.r. spectra were detected during u.v. irradiation of cyclopropane

solutions containing di-t-butyl peroxide (DTBP) (ca. 15 % v/v), trimethyl- or

triethyl-silane (ca. 10 % v/v), and one of the bromoacyl isocyanates (1) or (4)

(ca. 1.0 M). This is a well-known method for the generation of specific alkyl

radicals for e.s.r. study[25] and involves bromine atom abstraction by a trialkylsilyl

radical [see equation (2.23)]. The experiments were technically difficult because

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of the high reactivities of (1) and (4) and the small quantities involved. We

were well aware that chemical modification of the NCO group (e.g. by

hydrolysis) might pass undetected and samples were prepared under stringently

anhydrous conditions; the reagents were frozen in layers at 77 K in the sample

tube and only allowed to mix at ca. 170 K in an ethanol slush bath immediately

before insertion into the microwave cavity.

No e.s.r. spectra attributable to imidyl radicals were observed from either

(1) or (4), although these radicals would abstract hydrogen from the silane

rapidly even at low temperatures leading to chain consumption of reagents (see

later). At ca. 165 K in cyclopropane, the e.s.r. spectrum obtained from (1) was

very weak and although an alkyl-type radical was probably present, it could not

be identified with any certainty.

When t-butoxyl radicals were produced photochemically from DTBP in

CD_3CN or thermally from TBHN (0.4 $\underline{M}$) in heptane, each containing (1) (0.8

$\underline{M}$) and $Bu^n_3P{\rightarrow}BH_3$ (0.4 $\underline{M}$), a chain reaction ensued, presumably because S•

abstracts hydrogen from the phosphine-borane [equation (2.32)]. Succinimide

(S-H) was isolated by h.p.l.c. in ca. 25 % yield [based on (1)] from the

products of thermal reactions at 328 K.

$$Bu^tO^{\bullet} + Bu^n_3P{\rightarrow}BH_3 \longrightarrow Bu^tOH + Bu^n_3P{\rightarrow}\overset{\bullet}{B}H_2 \quad (2.29)$$

$$Bu^n_3P{\rightarrow}\overset{\bullet}{B}H_2 + BrCH_2CH_2C(O)NCO \longrightarrow Bu^n_3P{\rightarrow}BH_2Br + \overset{\bullet}{C}H_2CH_2C(O)NCO \quad (2.30)$$

$$\overset{\bullet}{C}H_2CH_2C(O)NCO \longrightarrow S^{\bullet} \quad (2.31)$$

$$S^{\bullet} + Bu^n_3P{\rightarrow}BH_3 \longrightarrow S\text{-}H + Bu^n_3P{\rightarrow}\overset{\bullet}{B}H_2 \quad (2.32)$$
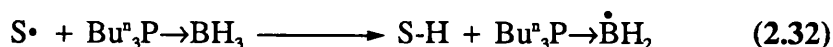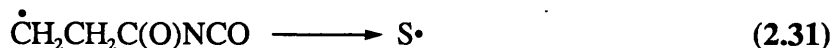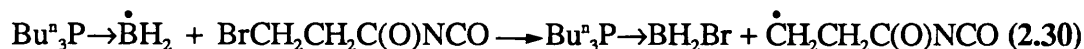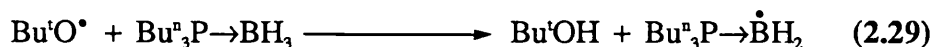
More definitive results were obtained from (4) and the spectrum recorded

4

during u.v. irradiation of DTBP, Me_3SiH, and (4) is reproduced in Figure 2.5. The spectrum can be analysed in terms of a 23.0 G splitting from six equivalent protons and a 14.0 G splitting from two protons, although the central lines of the triplets arising from the latter coupling are broadened relative to the wing lines, indicating the existence of a dynamic process which acts to exchange two instantaneously non-equivalent protons on the e.s.r. timescale.[26] Under conditions of higher resolution, it was possible to detect further splitting on the sharper lines which arises from a combination of second-order effects and long-range coupling of 0.51 G to [14]N. We assign this spectrum to the tertiary radical (23), produced by ring opening of DMS•, itself formed by cyclisation of the primary radical (22) [equation (2.33)]. The temperature range over which (23) could be detected was restricted at the lower end by reagent solubility and above ca. 150 K rapid consumption of reagents and precipitation of a white solid occured. The low value of $\underline{a}(2H_\beta)$ for (23) indicates[26] that the eclipsed conformation about the C_α-$CH_2C(O)NCO$ bond is preferred; the selective line-broadening probably arises because of hindered rotation about the CH_2-$C(O)$ bond.

$$\text{(22)} \quad \xrightleftharpoons[\underline{k}_{-2}]{\underline{k}_2} \quad \text{DMS•} \quad \xrightleftharpoons[\underline{k}_{-3}]{\underline{k}_3} \quad \text{(23)} \qquad (2.33)$$
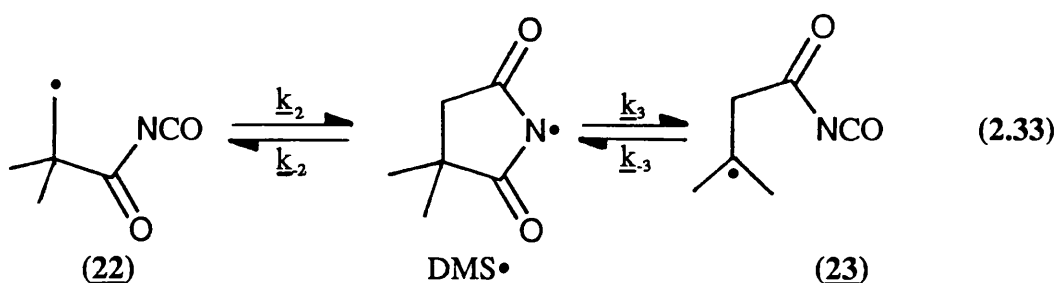
Detection of only (23) at 149 K implies[27] that both $\underline{k}_2$ and $\underline{k}_3$ are $> \underline{ca}$. 10^3 s^{-1} and that $(\underline{k}_3/\underline{k}_{-3}) \gg 1$ at this temperature; $(\underline{k}_3/\underline{k}_2)$ would be expected to be $> 1.$[6,11] If an $\underline{A}$-factor of 10^{11} s^{-1} applies to the unimolecular ring closure and

(a)

20 G

2 G

(b)

Figure 2.5

51
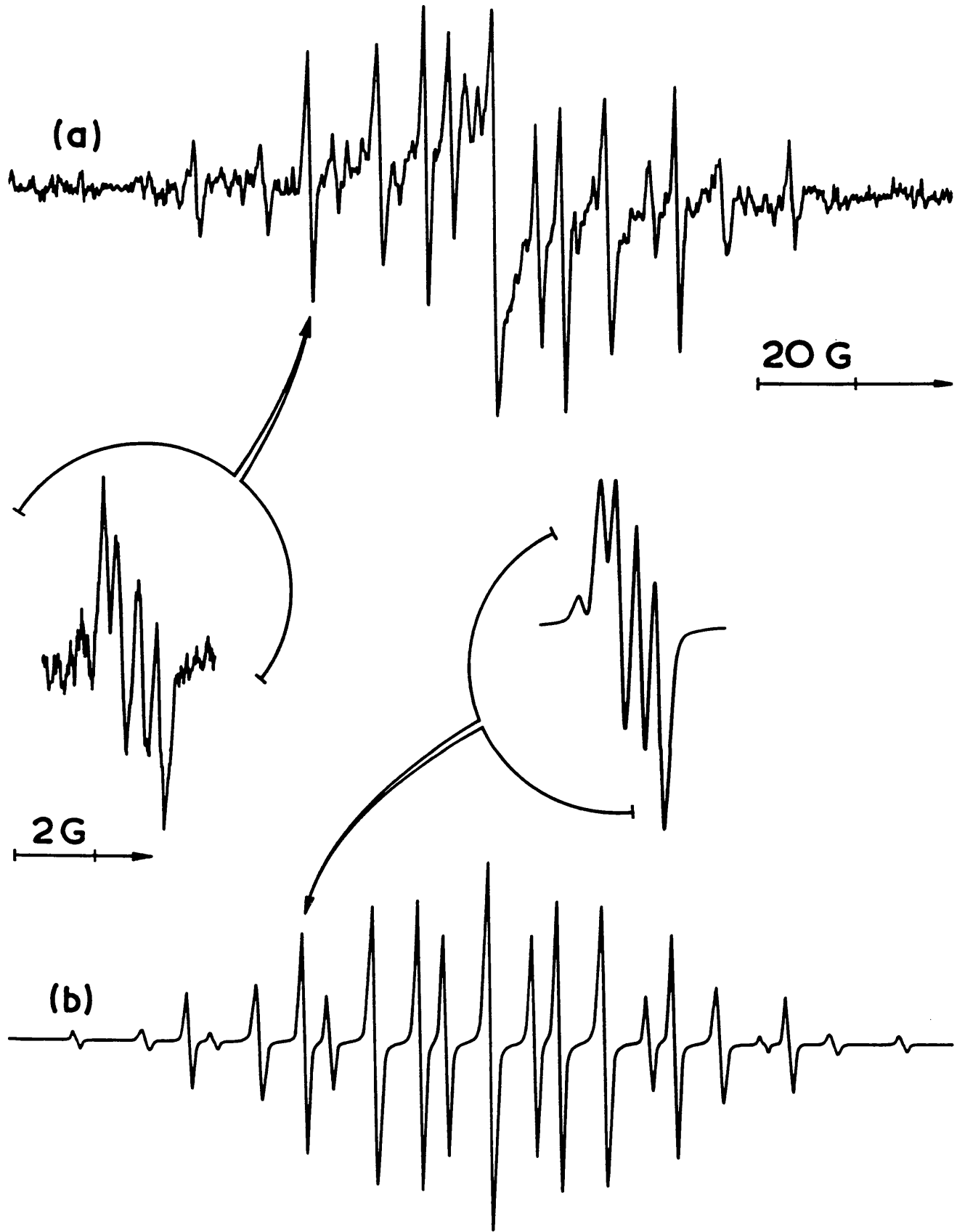
Figure captions

Figure 2.5 (a) E.s.r. spectrum of the alkyl radical (23) produced by photolysis of DTBP in the presence of (4) and Me_3SiH in cyclopropane at 149 K. The spectrum shows selective line broadening (see text); further fine structure due to nitrogen and second-order proton splittings is resolvable for the unbroadened "lines". (b) Computer simulation using the parameters given in Table **2.3**; ΔB_{p-p} for the lines corresponding to $M_I(2H_\beta) = 0$ is 1.08 G, for other lines it is 0.70 G.

opening, a rate coefficient of $> 10^3$ s^{-1} at 149 K implies an activation energy $<$ 23 kJ mol^{-1}.

For comparative purposes a number of related substituted alkyl radicals were generated by halogen atom abstraction from the corresponding bromides.[25] These radicals are shown in (24) - (27) and their e.s.r. parameters are included in Table 2.3. 3-Bromopropyl isocyanate[28] afforded the radical (27) and the
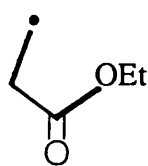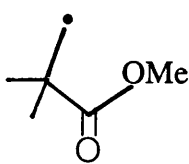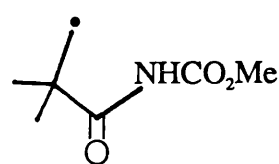
(24)   (25)   (26)
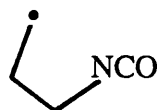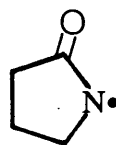
(27)   (28)

complications found with (1) and (4) were absent, such that a clean e.s.r. spectrum could be observed over a wide range of temperature. The same spectrum was detected when Et$_3$SiH was replaced with Bu^{i}SnMe$_3$ (cf. reference 29) and when the silane and DTBP were replaced with Me$_3$SnSnMe$_3$. Between 173 and 300 K the spectrum of (27) exhibited selective broadening of the lines associated with $M_I(2H_\beta) = 0$, indicating out-of-phase modulation of the β-proton splittings probably because of hindered rotation about the C_β-C_γ bond.[26] No

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spectroscopic evidence for cyclisation of (27) to give the amidyl radical (28) could be found up to 300 K, when the spectrum of (27) was still observed. The radical (27) was detectable for extended periods of time at high temperatures, indicating that the amidyl (28) was not being formed and removed by a fast reaction with silane or stannane which would result in chain consumption of reagents.

A number of possible reasons may be advanced to explain the slower cyclisation of (27) compared with 2-(isocyanatocarbonyl)alkyl radicals. Amidyl radicals similar to (28) are known to be π radicals[30] in their electronic ground states and any excited σ radical would be expected to be less close in energy than S_σ^* is to S_π^*. Cyclisation of (27) to (28) would thus be stereoelectronically forbidden if the heavy atoms are co-planar and even for non-planar rings the activation energy could still be relatively large. The same reasoning would account for the fact the β-scission of cyclic or acyclic amidyl radicals has never been observed. It is also possible that replacement of the CH_2NCO group in (27) by a $C(O)NCO$ moiety reduces strain in the transition state for ring closure or accelerates cyclisation because of polar effects which favour addition of nucleophilic alkyl radicals to acyl, as opposed to alkyl, isocyanates, in the same way as they favour analogous addition of nucleophilic alkyl radicals to acrylates as compared with simple alkenes.

Table 2.3   E.s.r. parameters for carbon-centred radicals derived from bromo compounds

Radical	Solvent	T/K	g-Factor	Hyperfine splittings (G)	
				$a(2H_\alpha)$	Others
(23)	Cyclopropane	149	2.0028	-	23.0 ($6H_\beta$), 14.0 ($2H_\beta$), 0.51 (1N)
(24)[a]	Cyclopropane	178	2.0028	22.5	31.3 ($2H_\beta$)
(25)	Cyclopropane	194	2.0027	22.1	0.53 ($6H_\gamma$)
(26)	Oxirane	195	2.0027	22.1	0.49 ($6H_\gamma$), 0.49 (1N), 0.49 (N$\underline{H}$)[b]
(27)	Cyclopropane	193	2.0027	22.3	27.5 ($2H_\beta$), 0.50 ($2H_\gamma$)

a   Previously reported by R.M. Haigh, A.G. Davies, and M.-W. Tse, J. Organomet. Chem., 1979, 174, 163.

b   Pattern of equally spaced lines with the predicted intensity distribution.

2.4 Product Analysis

In order to support and extend the conclusions reached from the e.s.r. spectroscopic studies, we have determined quantitatively the products from radical chain reductive debromination of (1) and (4) with triethylgermane in cyclohexane at 328 K. In the absence of spin-traps and provided that heterolytic processes do not intervene, (1) and (4) would be expected to react with a number of metal or metalloidal hydrides by radical chain mechanisms[31] to give the corresponding imide. If the hydride is also capable of donating a hydrogen atom sufficiently rapidly to an isocyanatocarbonyl(alkyl) radical, acyl isocyanate will be produced competitively. Quenching of the reaction mixture with methanol will convert any acyl isocyanates to the corresponding urethanes. The pertinent reactions for reductive debromination of (1) by triethylgermane are summarised in Scheme 2.

Triethylgermane was chosen as the reducing agent after a number of trial experiments. Tributylstannane reacted exothermically with (1) and with (4) upon mixing in cyclohexane at room temperature in the absence of initiator. Addition of the Sn-H function across the isocyanate group is probably involved, by analogy with the (slower) reaction which is known to take place between tin hydrides and alkyl or aryl isocyanates.[32] Radical chain debromination of (1) could be brought about by treatment with either $Bu^n_3P{\rightarrow}BH_3$ or Et_3SiH in the presence of TBHN at 320-330 K, but although succinimide was formed in moderate yield none of the urethane (31) was detected after quenching with methanol. As expected,[8,12,33] hydrogen atom abstraction from $Bu^n_3P{\rightarrow}BH_3$ or Et_3SiH is too slow to compete with cyclisation of (12) to give S• , even when these hydrides are present in relatively high concentration (1-2 $\underline{M}$). Alkyl
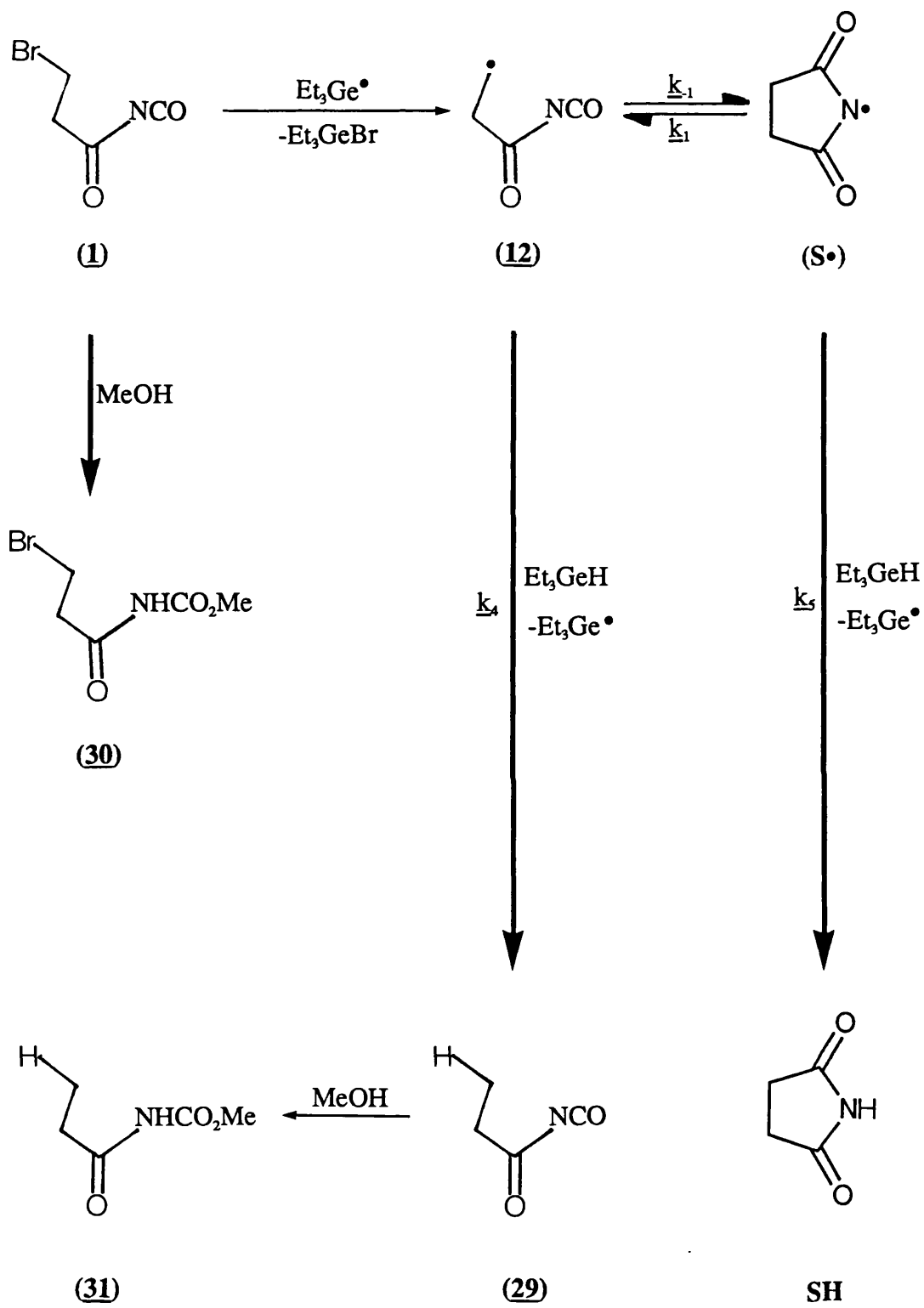
Scheme 2

radicals abstract hydrogen more rapidly from trialkylgermanes[34,35] and using

Et$_3$GeH small amounts of (31) were detected along with succinimide.

Triethylgermane was used in preference to Bu$^n{}_3$GeH because the greater

volatility of the former allowed it to be removed from the products immediately

after quenching with methanol, preventing any complication which might arise

because of subsequent reactions of the germane, such as reduction of the

bromourethane (30) (derived from any unreacted bromoacyl isocyanate) to form

(31) [equation (2.34)].

$$\text{BrCH}_2\text{CH}_2\text{C(O)NHCO}_2\text{Me} \xrightarrow[-\text{Et}_3\text{GeBr}]{\text{Et}_3\text{GeH}} \text{CH}_3\text{CH}_2\text{C(O)NHCO}_2\text{Me} \qquad (2.34)$$

(31)
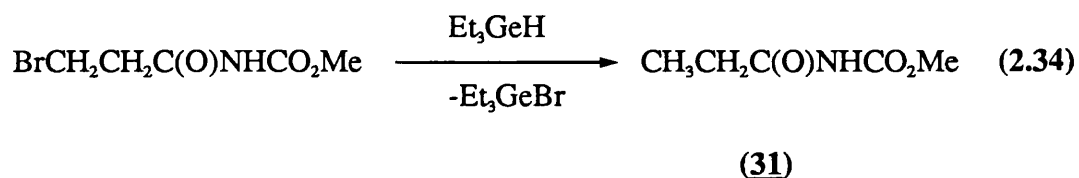
However, triethylgermane was also found to react with the acyl

isocyanates (1) and (29) at the C(O)NCO function, probably by addition of the

Ge-H group to give (32) and/or (33), products analogous to those formed

between tin hydrides and alkyl or aryl isocyanates.[32] Hence, propanoyl

isocyanate formed by the homolytic pathway shown in Scheme 2 will be

$$\text{RC(O)NCO} + \text{Et}_3\text{GeH}$$

RC(O)N(GeEt$_3$)CHO   (2.35a)
(32)

RC(O)NHC(O)GeEt$_3$ (2.35b)
(33)

58
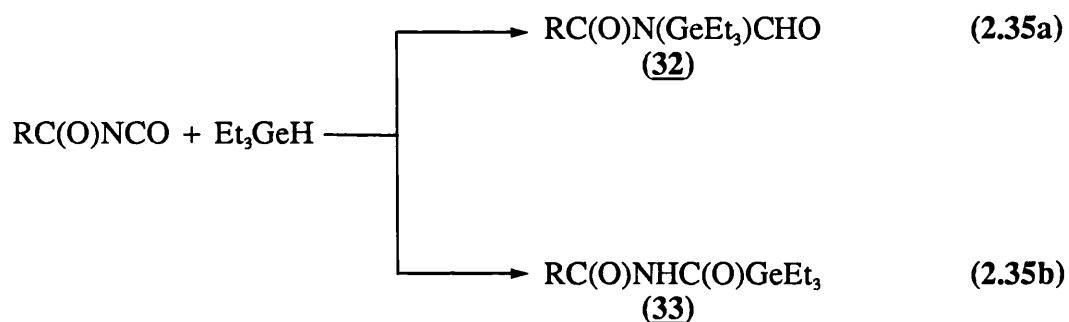
subsequently destroyed by reaction with Et_3GeH. It might also be argued that reaction of (1) with Et_3GeH at the $C(O)NCO$ group could give a product which might undergo homolytic debromination to give a compound capable of reacting with methanol to form the urethane (31). This would provide a source of (31) other than that from (29) produced from (12) via hydrogen abstraction from the germane. Whilst it is difficult to eliminate this alternative source completely, we believe it is very unlikely since (32) and (33) will probably react with methanol to give $\underline{N}$-formylamides $RC(O)NHCHO$.[36]

In a trial experiment with Bu^n_3SnH, when the reaction mixture was quenched with H_2O, which will convert propanoyl isocyanate (29) to propanamide [equation (2.36)], n.m.r. and h.p.l.c. analysis showed that only a very small amount of succinimide was present alongside the propanamide. As

$$CH_3CH_2C(O)NCO \quad \xrightarrow{\ H_2O\ } \quad CH_3CH_2CONH_2 + CO_2 \qquad (2.36)$$
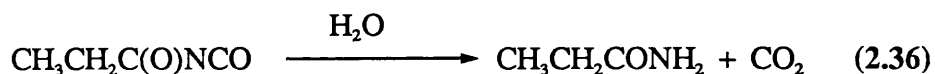
discussed above the probable reason for this result is that Bu^n_3SnH donates a hydrogen atom rapidly to (12) to give propanoyl isocyanate before the radical has a chance to cyclise to give S•. When the reaction was quenched with water it was difficult to remove excess H_2O completely before analysis of the reaction products. When MeOH was used to quench the isocyanates in the final experiments, the more volatile alcohol was removed much more easily.

When azobis(isobutyronitrile) (AIBN) was used as an initiator at $\underline{ca}$. 353 K with Bu^n_3GeH as a reducing agent, succinimide was formed in high yield, but (29) and/or (31) could not be detected with certainty. This might be because

the activation energy for the cyclisation of (12) to S• is higher than that for hydrogen atom abstraction from the hydride by (12). Alternatively, destruction of propanoyl isocyanate by the germane could be much faster at 353 K. In subsequent work a compromise temperature of 328 K was chosen in order to detect products from both cyclised and uncyclised radicals.

Despite all the technical problems encountered, by working at 328 K and by carrying out appropriate control experiments, we have obtained a value for k_{-1} in which we have reasonable confidence, although the precision will clearly not be as high as would be expected for rate coefficeints derived using similar techniques with simple systems.

A known amount of 3-bromopropanoyl isocyanate (1) was added quickly from a calibrated microsyringe to a rapidly stirred solution of Et_3GeH and TBHN in cyclohexane maintained at 328 ± 0.5 K. The reaction flask was equipped with a water-cooled condenser and a septum inlet and its contents were maintained under an atmosphere of dry argon. After a known time, the reaction was stopped by plunging the flask into an ice-water bath. An excess of methanol was added to convert acyl isocyanates into the N-acylurethanes (30) and (31) during 10 min. rapid stirring at 273 K, before all material volatile at room temperature was quickly pumped into a cold trap under reduced pressure (0.1 Torr). A known weight of methyl phenyl sulphone was added as internal standard to the residual solid and the mixture was dissolved in a $[^2H_8]$-tetrahydrofuran and examined by high field ^1H n.m.r. spectroscopy to determine product yields. However, the n.m.r. peaks for N-acylurethanes (30) and (31) were extremely small in comparison to the CH peak for succinimide. Hence, although the results obtained, either by cutting out and weighing the peaks or

by electronically integrating them were reasonable, the errors were large and a better technique for analysis of products was sought.

Yields were determined more accurately by reverse-phase h.p.l.c. analysis, using the methyl phenyl sulphone as internal standard; the results are collected in Table **2.4**. The cold trap contained mainly excess Et₃GeH, cyclohexane, and methanol.

The possibility that (**30**) might be reduced to (**31**) after the addition of methanol but <u>before</u> removal of the excess germane, was examined by quenching a reaction mixture which had been prepared as usual but maintained at 273 K (Table **2.4**, entry 3). Although a high yield of the bromourethane (**30**) was obtained, no (**31**) was detected and only a trace of succinimide was found. Since both (**1**) and (**29**) react with Et₃GeH at their C(O)NCO groups and because the conversion of isocyanates to urethanes might be somewhat less than quantitative, the final yield of (**31**) will be less than the total amounts of propanoyl isocyanate produced during the reaction (see before). A control experiment (entry 4) was carried out in which (**1**) was replaced with an equal quantity of (**29**) and the yield of (**31**) was determined after quenching with methanol in the normal way. Since the reaction between (**29**) and Et₃GeH is likely to be first-order in isocyanate, the value of [amount (**29**) taken/yield (**31**)] (**2.9**) obtained from this experiment was used to scale-up the yield of (**31**) obtained from (**1**) (entry 1). Comparison of entries 1 and 2 shows that increasing the reaction time from 10 to 30 min. leads to almost complete destruction of the product propanoyl isocyanate by reaction with excess germane.

The succinimidyl radical is a potent abstractor of hydrogen to yield succinimide, even abstracting a hydrogen atom from cyclopropane at a rate

Table 2.4

Products obtained from reactions of 3-bromopropanoyl and propanoyl isocyanates with triethylgermane in cyclohexane in the presence of TBHN[a]

Entry	T/K	Reaction time (min.)	Product yields[b] (mmol)		
			SH	(30)	(31)
1[c]	328	10	0.412	0.0273	0.0109
2	328	30	0.465	0.0015	0.0017
3	273	0[d]	0.0037	0.554	e
4[f]	328	10	e	e	0.227

a Reaction mixtures contained Et_3GeH (2.36 mmol), the acyl isocyanate (0.664 mmol), and TBHN (ca. 0.033 mmol) in cyclohexane (1.0 cm^3). For entries 1-3, $[Et_3GeH]_0$ is 1.63 $\underline{M}$, for entry 4 it is 1.64 $\underline{M}$. After reaction, isocyanates were converted to urethanes by addition of dry methanol (0.10 cm^3). b Obtained by h.p.l.c. analysis; those obtained by ^1H n.m.r. spectroscopy were similar but are considered rather less accurate. c Et_3GeH (1.3 mmol) was recovered by trap-to-trap distillation after reaction (see the text). d Reaction mixture was quenched with methanol immediately after addition of (1). e Not detected. f Reaction of propanoyl isocyanate with Et_3GeH.

sufficient to make halogenation of this hydrocarbon by $\underline{N}$-halogenosuccinimides a viable reaction.[11,37] It is therefore reasonable to assume that hydrogen atom transfer to the electrophilic $S\cdot$ from Et_3GeH will be extremely rapid, making the cyclisation of (12) effectively irreversible under our experimental conditions. At 300 K, the rate coefficient for abstraction of hydrogen from Bu^n_3GeH by t-butoxyl radicals[38] is $\underline{ca}$. 9×10^7 l mol^{-1} s^{-1}. Assuming that $Bu^tO^\bullet$ and $S\cdot$ are similarly reactive towards trialkylgermanes, it is likely that $\underline{k}_5$ is $\underline{ca}$. 10^8 l mol^{-1} s^{-1} at 328 K. Since $[Et_3GeH]$ is $\underline{ca}$. 1.5 $\underline{M}$ in our experiments, cyclisation of (12) will be effectively irreversible provided that $\underline{k}_1$ is $< \underline{ca}$. 10^8 s^{-1}. This would accord with our previous work[39] in which we have shown that tetra-alkylstannanes react with $\underline{N}$-halogenosuccinimides at 308 K by a radical chain mechanism [equations (2.37) and (2.38) to give $\underline{N}$-trialkylstannylsuccinimide and not products derived from ring opening of $S\cdot$, although $\underline{k}_6$ is only $\underline{ca}$. 10^4 l mol^{-1} s^{-1}.

$$S\cdot \; + \; R_4Sn \; \xrightarrow{\;\;\underline{k}_6\;\;} \; R_3SnS \; + \; R\cdot \qquad\qquad (2.37)$$

$$R\cdot \; + \; SHal \; \xrightarrow{} \; RHal \; + \; S\cdot \qquad\qquad (2.38)$$

Based on Scheme 2, it follows that after a reaction time $\underline{t}$ equation (2.39) will hold. Because of the difficulties with side reactions described previously,

$$d[SH]/d[(\underline{29})] \; = \; \underline{k}_{-1}/\underline{k}_4[Et_3GeH]_t \qquad\qquad (2.39)$$

it is only worthwhile to integrate equation (2.40) making the simple assumption

that the germane concentration remains constant at an "average" value of

$[Et_3GeH]_0 - 0.5[(\underline{1})]_0$, to obtain equation (2.40). The data from entry 1, taking

the yield of (29) to be 2.9 times the yield of (31), together with the value of

$$\text{Yield SH/Yield } (\underline{29}) \ = \ \underline{k}_{-1}/\underline{k}_4[Et_3GeH]_{av} \qquad (2.40)$$

$[Et_3GeH]_{av}$ (1.40 $\underline{M}$) lead to $(\underline{k}_{-1}/\underline{k}_4) = 18.2$ $\underline{M}$. The rate coefficient for hydrogen

atom abstraction from $Bu^n{}_3GeH$ by the primary hex-5-enyl radical (34) has been

measured[34] and, using the published Arrhenius parameters, we calculate it to be

2.04×10^5 1 mol^{-1} s^{-1} at 328 K. Assuming that (12) abstracts hydrogen from

Et_3GeH at a similar rate, we obtained $\underline{k}_{-1} = 3.7 \times 10^6$ s^{-1} at 328 K in

cyclohexane.

(2.41)

(34)
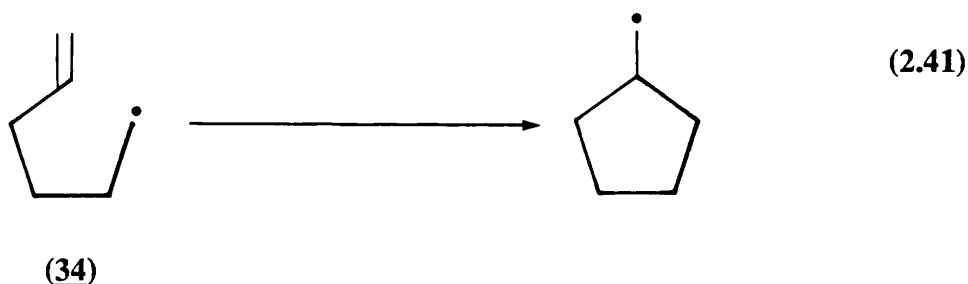
Our value for $\underline{k}_{-1}$ is considerably smaller than that recently proposed by

Skell and his co-workers[40] (5×10^8 s^{-1} at 288 K), which extrapolates to 8×10^8

s^{-1} at 328 K if we use the $\underline{A}$-factor ($10^{10.42}$ s^{-1}) determined for cyclisation of (34)

[equation (2.41)]. One contributing reason for this discrepancy could be the

invalidity of Skell's assumption that (12) and the cyclopropylmethyl radical both

abstract bromine from NBS at the same rate. Although both are primary alkyl radicals, the cyclopropylmethyl radical would be appreciably more nucleophilic than (12) (the cyclopropylmethyl cation is relatively stabilised) and polar effects could result in the former abstracting bromine more rapidly than (12) [equation (2.42)]. Taking our value for k_{-1}, extrapolated to 288 K assuming an A-factor

$$\overset{\bullet}{C}H_2CH_2C(O)NCO \ + \ SBr \ \xrightarrow{\ \underline{k_7}\ } \ BrCH_2CH_2C(O)NCO \ + \ S\bullet \qquad (2.42)$$

$$\underline{(12)} \qquad\qquad\qquad\qquad\qquad \underline{(1)}$$
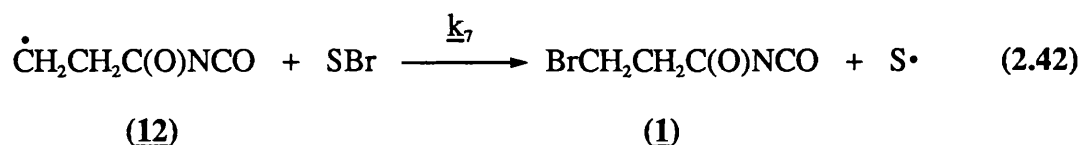
of $10^{10.42}$ s^{-1} in conjunction with Skell's value[40] of (k_{-1}/k_7) (0.035 $\underline{M}$ at 288 K) gives $\underline{k_7}$ = 3.1 x 10^7 1 mol^{-1} s^{-1} at 288 K, much smaller than the value proposed by Skell[40] (1.3-1.6 x 10^{10} 1 mol^{-1} s^{-1}). The lower value would be more in line with the rate coefficient for abstraction of bromine from NBS by the (albeit stabilised) benzyl radical obtained previously by us[39] (ca. 5 x 10^5 1 mol^{-1} s^{-1} at 308 K).

We have also examined the products from reaction between triethylgermane and 3-bromo-2,2-dimethylpropanoyl isocyanate (4) using the same techniques. After quenching the reaction mixture with methanol, the yields of DMSH and of the three N-acylurethanes (35) - (37) were determined by reverse-phase h.p.l.c.. The imide DMSH and the urethanes (36) and (37) arise because the initially formed radical (22) undergoes cyclisation to give DMS• which ring opens to (23) [equation (2.33)], all in competition with hydrogen abstraction from the germane. As mentioned before, cyclisation of (22) to DMS• is evidently much faster than the corresponding cyclisation of (12) to give S•, because of the presence of the two methyl groups on C-2 (gem-dimethyl

effect[41]). A similar acceleration of ring closure is brought about by 2,2-dimethylation of the hex-5-enyl radical [equation (2.41)].[42]

In cyclohexane at 328 K under the same conditions as described above for the reactions of (12) (entry 1, Table 2.4), (4) (0.679 mmol) and triethylgermane (2.36 mmol, initially 1.60 M) yielded, after quenching with methanol, DMSH (0.590 mmol), (36) (0.004 mmol), and (37) (0.062 mmol); the bromoacyl urethane (35) was not detected. In view of the complexity of the reaction kinetics and the number of unknown rate coefficients, we did not consider that any attempt to interpret the data quantitatively would be justified. However, the results serve to confirm that the (isocyanatocarbonyl)ethyl radical (22) undergoes rapid cyclisation to give DMS• which then readily opens to form the tertiary radical (23). Overall this represents a particularly rapid 1,2-shift of the C(O)NCO group by way of the intermediate cyclic imidyl radical. The

DMSH   (35)   (36)

(37)
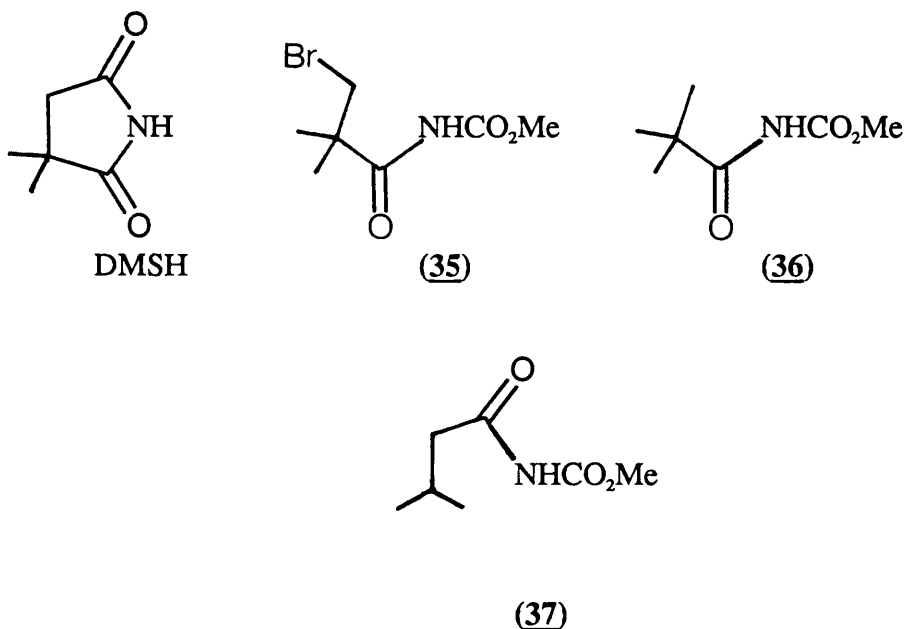
rearrangement contrasts with the 1,2-homolytic shift undergone by β-

acyloxyalkyl radicals such as (38) which are believed[43] to proceed in a concerted fashion, usually[44,45] through a five-membered cyclic transition state and not via

$$MeC(O)OCMe_2\dot{C}H_2 \longrightarrow Me_2\dot{C}CH_2OC(O)Me \qquad (2.43)$$

$$\underline{(38)}$$
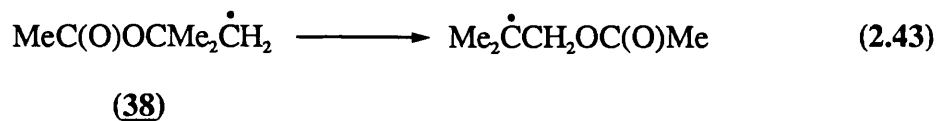
the stereoelectronically disfavoured pathway involving a discrete 1,3-dioxolanyl radical intermediate.

The very rapid cyclisation of the three ω-(isocyanatocarbonyl)alkyl radicals studied in this work to give imidyl radicals and the facility with which S• and DMS• undergo ring opening surely requires the involvement of σ imidyl radicals. It seems likely that these are the electronic ground states (at least under our conditions), but if not, then the σ state must be very close in energy to the π ground state for each radical.

Cyclisation of (isocyanatocarbonyl)alkyl radicals has potential in synthesis, since it represents an efficient method for increasing the length of a carbon chain by one atom, through reaction of bromoacyl isocyanates with reagents such as silanes, phosphine-boranes, germanes, and (probably) hexamethylditin.

References to Chapter 2

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CHAPTER 3

EXPERIMENTAL

3.1   E.S.R. Spectroscopy

The details of this technique, including the method for measuring hyperfine coupling constants and g-values are described in Chapter 7. Liquid samples were sealed under vacuum in Suprasil quartz tubes (either 3 mm i.d., 4 mm o.d. or 1.5 mm i.d., 2.5 mm o.d., the latter for samples which had a high dielectric constant).

Spectra were obtained using a Varian E-109 instrument operating at ca. 9.1 GHz. Computer simulations of spectra were obtained using a modified version of ESRSPEC2,[1] 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 % Lorentizian. The samples containing MNP were prepared and handled in darkness or subdued light.[2]

3.2   N.M.R. Spectroscopy

[1]H N.m.r. spectra were recorded using Varian XL-200 or VXR-400 instruments; the solvent was $CDCl_3$ and the internal standard was tetramethylsilane.

3.3   High-Performance Liquid Chromatography Analyses

Analyses were carried out using a Gilson binary gradient liquid

chromatograph with u.v. detection at 254 nm. The stationary phase was Spherisorb ODS2 (5 µm) and the eluting solvents were water-acetonitrile (90:10 v/v) for the reaction products from 2,2-dimethyl-3-bromopropanoyl isocyanate and water-methanol (90:10 v/v) followed by a linear gradient to 40 % methanol for the reaction products from 3-bromopropanoyl isocyanate. Mixtures containing known amounts of the reaction products were stirred with the eluting solvents for 30 min. (comparable with the time required for h.p.l.c. analysis) at room temperature, the solvents removed under reduced pressure, and the residue subjected to analysis. The relative product concentrations were unchanged within experimental accuracy by such treatment. I am grateful to Mr. S.T. Corker for carrying out the h.p.l.c. analyses.

3.4   **Materials**

Cyclopropane (Argo International), and oxirane (Fluka) were used as received. Di-t-butyl peroxide (Aldrich) was purified by washing successively with acidic potassium iodide solution, with water, with sodium metabisulphite solution, with water, with aqueous silver nitrate solution, and finally with water. The peroxide was then dried over anhydrous magnesium sulphate, run down a column of alumina [Brockman activity 1, alkaline (pH 9.3-9.7)], left to stand over potassium hydroxide pellets and finally distilled at reduced pressure (b.p. 46-47 °C/76 Torr).

The materials (mainly Aldrich) which were commercially available were all purified by distillation or recrystallisation. Preparations of other compounds are described below. All solvents were dried before use. All the isocyanates used in this work were very moisture sensitive and were prepared and handled

under an atmosphere of dry argon maintaining rigorously anhydrous conditions.

1,1-Di-t-butylethylene[3] and trimethyl(isobutyl)stannane[4] were prepared as described previously; [^{2}H$_9$]MNP was prepared as described by Holman and Perkins[5a] from [^{2}H$_9$]Bu^{t}NH$_2$, itself prepared[5b] from [^{2}H$_9$]Bu^{t}OD (Aldrich).

3.4.1   Di-t-butyl Hyponitrite (TBHN)[6]

An excess of t-butyl bromide (25.0 cm^3, 30.5 g, 0.22 mol; freshly distilled from P$_2$O$_5$), maintained between -15 to -5 °C using CO$_2$-meths bath, was stirred rapidly while dry silver hyponitrite (10.0 g, 0.04 mol) was added slowly (over 0.5 h) in small portions. The mixture was protected from light by wrapping the reaction flask in aluminium foil. Stirring was continued for a further 0.5 h. before the mixture was allowed to warm to room temperature, the silver bromide was filtered off, washed with dry ether and the volatiles were removed from the combined filtrate at room temperature under reduced pressure (ca. 10 Torr). The residue was recrystallised (solution temperature ≤ 0 °C) from absolute methanol at low temperature (-5 °C) and was dried by pumping under reduced pressure (0.1 Torr) at 0 °C for ca. 30 min.

3.4.2   Dibutanoyl Peroxide[7]

Aqueous hydrogen peroxide (3.97 cm^3, 60 % w/v, 70 mmol) was added dropwise to a stirred solution of pyridine (11.0 cm^3, 11.55 g, 137 mmol) in diethyl ether (3.5 cm^3), chilled initially to ca. -4 °C in an ice/meths bath, such that the temperature of the solution did not exceed 0 °C. Butanoyl chloride (7.30 cm^3, 7.49 g, 70 mmol) was then added over 30 min., keeping the temperature of the reaction mixture below 0 °C. The resulting solution was

stirred at -4 to 0 °C for a further 2 h. before addition of diethyl ether (10 cm³), followed by chilled aqueous sulphuric acid (20 cm³, 5 $\underline{M}$). The ether layer was separated and the aqueous layer was extracted with a further 10 cm³ ether. The combined ether extracts were washed successively with aqueous sulphuric acid (20 cm³, 2 $\underline{M}$), water, and saturated aqueous sodium bicarbonate solution, and was finally dried over sodium sulphate. Removal of ether using a rotary evaporator, followed by pumping at 0.01 Torr afforded 3.3 g of oily crude product. This was purified by passage through a 6.5 cm x 2.5 cm diameter column of silica gel (60-120 mesh) using dichloromethane as an eluant followed by removal of the solvent under vacuum. $\delta(^1H)$ 0.67 (t, 6H, $\underline{J}$ 7.34 Hz), 1.40 (sextet, 4H, $\underline{J}$ 7.39 Hz), and 1.91 (t, 4H, $\underline{J}$ 7.32 Hz).

3.4.3   Triethylgermane[8]

This compound was prepared using the procedure described for the preparation of tributylgermane.[9] Lithium aluminium hydride (0.99 g, 26 mmol) was placed in 33 cm³ diethyl ether at 0 °C and the mixture was stirred for $\underline{ca}$. 15 min. To this was added triethylgermanium chloride (Strem, 5.0 g, 26 mmol) over a period of $\underline{ca}$. 15 min. with vigorous stirring. The mixture was stirred at a bath temperature of 0 °C for 15 min., then at room temperature for 2 h. and finally, refluxed for 1 h. The mixture was cooled to 0 °C and hydrolysed slowly and cautiously with 30 cm³ of cold water. The mixture was filtered and the ether layer was washed with two 20 cm³ portions of ice-cold water and dried over magnesium sulphate. Ether was carefully removed at 10 Torr and the residue was distilled to yield 2.2 g (55 %) of triethylgermane, b.p. 121-122 °C at 760 Torr (lit.[10] b.p. 120-122 at 760 Torr). $\delta(^1H)$ (C_6D_6) 3.92 (septet,

6H) and 0.8-1.6 [m, $(C_2H_5)_3$]. Storage was in sealed ampoules bearing a minimum of air.

3.4.4   Methyl 3-Bromo-2,2-dimethylpropanoate[11]

3-Bromo-2,2-dimethylpropanoic acid (Riedel, 5.0 g, 28 mmol) was dissolved in a mixture of methanol (25 cm³) and benzene (25 cm³) in a 100 cm³ two-necked flask fitted with a condenser and an argon inlet. Concentrated sulphuric acid (0.2 cm³, as a catalyst) was added slowly and the mixture was heated under reflux for ca. 1 h. Methanol and benzene were then removed by distillation at atmospheric pressure using a short fractionating column and the residue was distilled under reduced pressure. The reaction yielded 3.5 g (64 %) of methyl 3-bromo-2,2-dimethylpropanoate, b.p. 55-57 °C at 5 Torr (lit.[11] b.p. 75-78 °C at 21 Torr). $\delta(^1H)$ 1.33 (s, 6H), 3.51 (s, 2H), and 3.73 (s, 3H). [lit.[11] $\delta(^1H)$ 1.30 (s, 6H), 3.45 (s, 2H), and 3.70 (s, 3H)].

3.4.5   2,2-Dimethylsuccinimide (8; X = H)[12,13]

This compound was prepared by a literature route.[12,13] 2,2-Dimethylsuccinic acid (10.0 g, 68 mmol) was placed in a 50 cm³ three-necked flask fitted with a water condenser, dropping funnel, and a magnetic stirrer. Ammonium hydroxide (28 % NH_3, specific gravity 0.880, 8.32 g, 238 mmol) was added very slowly from the dropping funnel while the mixture was stirred and cooled in an ice/water bath. The neutralisation was very exothermic and most of the acid dissolved forming a clear solution. The condenser was removed and replaced with a still-head and an air condenser. Distillation gave two fractions, the first was mainly water which distilled at 96-100 °C at

atmospheric pressure and the second was the product, 2,2-dimethylsuccinimide (7.0 g, 96 %), b.p. 140-149 °C at 0.5 Torr. The amide solidified at room temperature and was recrystallised from a mixture of benzene and hexane, m.p. 98-101 °C (lit.[12] m.p. 94-101 °C). δ(^{1}H) 1.35 (s, 6H), 2.61 (s, 2H), and 8.78 (br.s., 1H).

3.4.6   N-Chloroglutarimide (6; X = Cl)

This compound was prepared by a modification of the general method[14] used to synthesise N-chloroimides. t-Butyl hypochlorite[15] (2.00 g, 17 mmol) was added dropwise to a stirred solution of glutarimide (1.87 g, 17 mmol) in methanol (20 cm^3) cooled in an ice-bath. The temperature was allowed to rise to ambient and stirring was continued for 1 h. Removal of the methanol under reduced pressure left the crude product which was purified by flash chromatography on silica (pentane-ethyl acetate 2:1 v/v eluant) to yield N-chloroglutarimide (1.85 g, 76 %), m.p. 150 °C. (Found: C, 40.8; H, 4.0; N, 9.4; Cl, 23.9. C_5H_6 ClNO$_2$ requires C, 40.7; H, 4.1; N, 9.5; Cl, 24.0 %). δ(^{1}H) 2.03 (quintet, 2H, J 6.5 Hz) and 2.88 (t, 4H, J 6.5 Hz).

The N-chloroimides (5 - 9; X = Cl) which were not available commercially were prepared from the corresponding imides[12,16] and either t-butyl hypochlorite in methanol (or in water-t-butyl alcohol[14]).

3.4.7   N-Bromo-2,2-dimethylsuccinimide (8; X = Br)[12,17]

This compound was prepared according to a literature method.[17] 2,2-Dimethylsuccinimide (1.0 g, 7.87 mmol) was dissolved along with sodium bicarbonate (0.79 g, 9.4 mmol) in 65 cm^3 of water to yield a clear solution.

The solution was cooled to 3 °C in an ice/salt bath and a slight excess of bromine was added in small amounts with continuous vigorous stirring until the mixture retained a very pale orange-brown colour. The precipitate which formed was removed by filtration, washed quickly with cold water, and dried under reduced pressure (0.01 Torr) for ca. 1 h. at 30 °C. The crude product was recrystallised from hot water (80 °C) to yield 1.13 g (70 %) of N-bromo-2,2-dimethylsuccinimide, m.p. 156-158 °C (lit.[12] m.p. 155-157 °C). δ(¹H) 1.40 (s, 6H) and 2.77 (s, 2H) [lit.[12] δ 1.4 (s, 6H) and 2.75 (s, 2H)].

N-Bromo-3,3-dimethylglutarimide (7 ; X = Br)[16] was prepared the same way[17] from the corresponding imide (Aldrich).

3.4.8   3-Bromopropanoyl Isocyanate (1)

Silver cyanate[18] was thoroughly dried at 30 °C for 9 h. under reduced pressure (0.05 Torr) and then finely powdered. Silver cyanate (14.0 g, 93 mmol) was added in three approximately equal portions to mechanically stirred 3-bromopropanoyl bromide[19] (10.0 g, 46 mmol) cooled in an ice-water bath. After each addition, the flask was immersed in a water-filled ultrasonic cleaning bath (Decon FS200) and the contents was stirred and sonicated for 30 min. at room temperature. Benzene (10 cm³) was added after the second portion of silver cyanate in order to keep the reaction mixture mobile. After centrifugation, benzene was removed from the supernatant liquid under reduced pressure and the residual oil was distilled to yield 3-bromopropanoyl isocyanate (4.5 g, 55%), b.p. 69 °C at 10 Torr (lit.[19] 68-70 °C at 10 Torr). δ(¹H) 3.08 (t, 2H, J 6.5 Hz) and 3.56 (t, 2H, J 6.5 Hz). Preparations in which the benzene was replaced by diethyl ether were usually rather more successful, although

occasionally some ethyl 3-bromopropanoate was produced along with (1) (presumably by silver-assisted reaction of ether with residual acyl bromide) and the ester was difficult to remove by distillation.

3.4.9   Methyl N-(3-bromopropanoyl)carbamate (30)

Methanol (1.0 cm³) was added dropwise to a stirred solution of 3-bromopropanoyl isocyanate (0.20 g, 1.12 mmol) in diethyl ether (2 cm³) cooled in an ice bath.   After 15 min., the ether and excess methanol were removed under reduced pressure and the residual solid was recrystallised from methanol to give (30) (0.20 g, 85 %), m.p. 138-139 °C (lit.[19b] 137-138 °C). $\delta(^1H)$ 3.42 (t, 2H, J 6.5 Hz), 3.64 (t, 2H, J 6.5 Hz), 3.80 (s, 3H), and 7.60 (br.s, 1H). This general procedure was used to prepare N-acylurethanes from all acyl isocyanates; the solvent for recrystallisation differed for other compounds. Data for all urethanes are given in Table **3.1**; the ^1H n.m.r. spectra were in accord with expectation.

3.4.10   4-Bromobutanoyl Isocyanate (3)

This isocyanate was prepared from 4-bromobutanoyl chloride (Aldrich) (10.0 g, 54 mmol) and silver cyanate (16.2 g, 108 mmol) using the method described for (1) and adding diethyl ether to maintain mobility.   The acyl isocyanate was obtained in low yield (1.0 g, 10 %), b.p. 63 °C at 0.75 Torr. $\delta(^1H)$ 2.19 (quintet, 2H, J 6.7 Hz), 2.72 (t, 2H, J 7.1 Hz), and 3.48 (t, 2H, J 6.3 Hz).

3.4.11   3-Bromo-2,2-dimethylpropanoyl Isocyanate (4)

This compound was prepared in three steps from 3-bromo-2,2-dimethylpropanoic acid. Thionyl chloride (7.7 g, 65 mmol) was added dropwise to a stirred solution of 3-bromo-2,2-dimethylpropanoic acid (10.0 g, 55 mmol) in benzene (10 cm³) which was warmed in an oil bath maintained at 35-40 °C. The resulting mixture was heated under reflux for 30 min., allowed to cool, and the benzene and excess thionyl chloride were removed under reduced pressure to leave crude acid chloride.   This was added cautiously, dropwise to vigorously-stirred aqueous ammonia (55 cm³, specific gravity 0.880) contained in an open beaker surrounded by an ice-water bath.   After the addition was complete, the mixture was stirred for a further 30 min. before the precipitated amide was removed by filtration, washed with cold water, dried under reduced pressure (30 °C, 0.01 Torr), and recrystallised from benzene to yield 3-bromo-2,2-dimethylpropanamide, m.p. 117-118 °C (lit.[20] m.p. 113-115 °C). $\delta(^1H)$ 1.36 (s, 6H), 3.53 (s, 2H), and 5.82 (br.s, 2H).

Oxalyl chloride (4.9 g, 39 mmol) in 1,2-dichloroethane (10 cm³) was added dropwise to a stirred slurry of 3-bromo-2,2-dimethylpropanamide (5.0 g, 28 mmol) in 1,2-dichloroethane (10 cm³) cooled in an ice-water bath. The mixture was allowed to warm to room temperature and then stirred and heated under reflux for 24 h., during which time all the solid dissolved. The solvent was removed under reduced pressure and the residual oil was distilled to yield 3-bromo-2,2-dimethylpropanoyl isocyanate (4.7 g, 81 %), b.p. 60-61 °C at 5 Torr. $\delta(^1H)$ 1.34 (s, 6H) and 3.47 (s, 2H). The isocyanate was further characterised as the urethane after treatment with methanol (see Table **3.1**).   t-Butyl isocyanate[21] was prepared from 2,2-dimethylpropanamide using the same

procedure.

3.4.12   Propanoyl Isocyanate

Various methods were tried to prepare propanoyl isocyanate (see Chapter 2) and this compound was finally obtained by the reaction of tri-n-butyltin isocyanate with propanoyl chloride.[22]

Urea was dried at 0.01 Torr/70 °C for ca. 8 h. Bis(tri-n-butyltin) oxide (35.0 cm^3, 41.1 g, 69 mmol) was mixed with the finely powdered urea (8.6 g, 143 mmol) in a 250 cm^3 three-necked round bottom flask equipped with a magnetic stirrer, an air cooled condenser and a wide bore nitrogen inlet tube which reached just below the surface of the liquid. With a slow stream of nitrogen bubbling through the vigorously-agitated slurry, the temperature was slowly raised to 125 °C; then between 125-130 °C some foaming occured, indicating the evolution of ammonia. The temperature was maintained at 130-140 °C for 1 h., during which time a moderate stream of nitrogen was led through the agitated mixture in order to remove ammonia and water. The crude liquid product was purified by vacuum distillation to give 28 g (80 %) of tri-n-butyltin isocyanate, b.p. 100-102 °C at 0.01 Torr (lit.[23] 100-102 °C at 0.01 Torr). The infrared spectrum (liquid film) showed a strong absorption band at 2210 cm^{-1} (lit.[23] 2208 cm^{-1}) indicating the presence of the NCO group.

Propanoyl chloride (2.2 g, 24 mmol) was added to magnetically-stirred tributyltin isocyanate (10.0 g, 38 mmol) at room temperature. The mixture was heated slowly to 50 °C and stirred for 30 min. at this temperature. Distillation of the mixture yielded propanoyl isocyanate (1.0 g, 42 %), b.p. 44-46 °C at 100 Torr (lit.[24] 40-50 °C at 100-110 Torr). δ(^{1}H) 1.17 (t, 3H, $\underline{J}$ 7.4 Hz and 2.54 (q,

2H, $\underline{J}$ 7.4 Hz).

The same procedure was used to prepare 3-methylbutanoyl isocyanate from the corresponding acyl chloride and tri-n-butyltin isocyanate, b.p. 35 °C at 15 Torr (lit.[25] 52 °C at 40 Torr). $\delta(^1H)$ 0.99 (d, 6H, $\underline{J}$ 6.5 Hz), 2.20 (nonet, 1H, $\underline{J}$ 6.6 Hz), and 2.36 (d, 2H, $\underline{J}$ 6.8 Hz).

3-Bromopropyl isocyanate was prepared as described previously.[26]

3.4.13 N-<u>Chlorodiacetamide</u>[27]

This compound was prepared from diacetamide (Aldrich, 0.5 g, 5.0 mmol) and t-butyl hypochlorite (1.3 g, 11 mmol) in dichloromethane (8 cm^3) by the general method[27] used to synthesise $\underline{N}$-chloroamides (see above). (Found: C, 35.5; H, 4.6; N, 10.4; Cl, 26.0. $C_4H_6ClNO_2$ requires C, 35.4; H, 4.5; N, 10.3; Cl 26.1 %). $\delta(^1H)$ 2.57 (s, 6H).

Table 3.1   Melting points and analytical data for <u>N</u>-acylurethanes RC(O)NHCO₂Me

R	Solvent for recryst.	M.p. (°C)	Lit. m.p. (°C)	Ref.	Elemental analysis [found % (calc. %)]			
					C	H	Br	N
BrCH₂CH₂	Methanol	138-139	132-134.5 137-138	19ᵃ, 19ᵇ	28.5 (28.6)	3.7 (3.8)	37.8 (38.0)	
BrCH₂CH₂CH₂	Benzene	118-119			32.4 (32.2)	4.4 (4.5)	35.8 (35.7)	
BrCH₂CMe₂	Benzene	107-108			35.7 (35.3)	5.1 (5.1)	33.4 (33.6)	
Et	Benzene+ hexane	134-136	132-133	24	45.9 (45.8)	7.1 (6.9)		
Buⁱ	Benzene	97-98			52.5 (52.8)	8.4 (8.2)		
Buᵗ	Benzene	110-111			52.9 (52.8)	8.3 (8.2)		

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Section B: Polarity Reversal Catalysis

CHAPTER 4

INTRODUCTION

4.1   Polar Effects in Radical Reactions

Although the reactions of neutral free radicals are less subject to polar influences than ionic reactions, such factors can still strongly affect the courses of homolytic processes. The importance of polar effects in influencing the reactions of uncharged free radicals has been recognised for over forty years.[1] A striking illustration of the operation of polar effects can be seen in the phenomenon of alternating radical co-polymerisation. This is the property of certain monomer pairs, for example styrene and maleic anhydride, of forming a co-polymer in which the monomer units tend to alternate along the chain.[1]

It is also well-established that polar factors play an important role in determining the chemo- and regio-selectivities of hydrogen atom transfer reactions of the type (4.1).[1-4] In valence bond terms, the transition state for

$$A^{\bullet} + H\text{-}B \longrightarrow A\text{-}H + B^{\bullet} \qquad\qquad (4.1)$$

such direct atom transfer reactions can be represented as a hybrid of the canonical structures (1a-d) and the stability of the transition state will increase as the contribution from the ionic structures (1c) or (1d) increases. As a result, the activation energies for a series of similarly exothermic hydrogen atom abstraction reactions would be expected to decrease as the properties of the attacking and departing radicals become more mutually conducive to the parti-

$$[\text{A}^\bullet \ \text{H–B}] \longleftrightarrow [\text{A–H} \ \text{B}^\bullet] \longleftrightarrow [\text{A}^+ \ \text{H}^\bullet\text{B}^-] \longleftrightarrow [\text{A}^- \ \text{H}^\bullet\text{B}^+]$$

$\underline{\textbf{(1a)}}$ $\qquad\qquad$ $\underline{\textbf{(1b)}}$ $\qquad\qquad$ $\underline{\textbf{(1c)}}$ $\qquad\qquad$ $\underline{\textbf{(1d)}}$
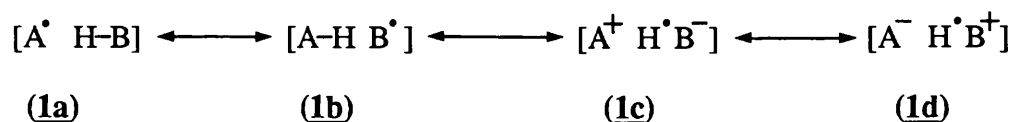
cipation of charge- transfer structures of the types $\underline{\textbf{(1c)}}$ or $\underline{\textbf{(1d)}}$. Thus, if $\text{Nuc}^\bullet$ and $\text{E1}^\bullet$ are nucleophilic and electrophilic radicals, respectively, polar effects will favour abstraction of hydrogen from H-Nuc by $\text{E1}^\bullet$ and from H-E1 by $\text{Nuc}^\bullet$, but abstraction of hydrogen from H-Nuc by $\text{Nuc}^\bullet$ or from H-E1 by $\text{E1}^\bullet$ will both be disfavoured.

Similar conclusions may be arrived at by consideration of frontier molecular orbital interactions in the reactants.[5] The unpaired electron in $\text{A}^\bullet$ is in a singly occupied molecular orbital (SOMO) which can interact with both the highest occupied molecular orbital (HOMO) and with the lowest unoccupied molecular orbital (LUMO) of the hydrogen donor HB, as shown in Figure **4.1**. Both of these interactions are net stabilising and the extent of stabilisation depends upon the reciprocal of the energy difference between the SOMO and the HOMO or LUMO of HB.

Radicals with a high-energy SOMO will react readily with molecules which have a low-energy LUMO, and radicals with a low-energy SOMO will react preferentially with molecules having a high-energy HOMO. This is illustrated by considering the reactions of the methyl radical and the chlorine atom with propanoic acid.[6] Methyl radicals preferentially attack hydrogen atoms on C-2 of the acid; on the other hand, chlorine atoms preferentially attack the hydrogen atoms attached to C-3. Quantitatively in the gas phase, methyl radicals attack an electron deficient α-hydrogen 7.8 times <u>faster</u> than a more electron rich β-hydrogen, whereas chlorine radicals attack an α-hydrogen 30 times <u>slower</u>
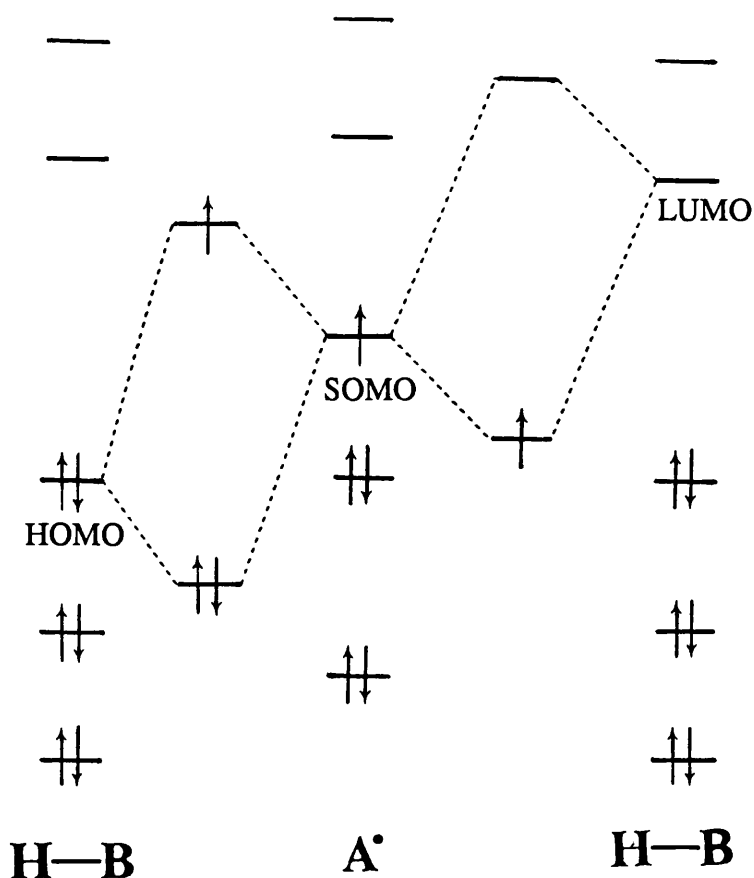
Figure 4.1   Schematic diagram showing the interactions between the frontier molecular orbitals of A° and H-B.

than a β-hydrogen. The methyl radical has a much higher energy SOMO (lower ionisation potential) than the chlorine atom. Because of the presence of the electron withdrawing carboxyl group, the C-2-H σ bonding orbital (the HOMO) and the σ* orbital (the LUMO) will be relatively low in energy. Conversely, the C-3-H σ and σ* orbitals will be relatively high in energy because the CO_2H group is more remote and the CH_2CO_2H group is a mild electron donor. The orbital interactions are therefore those shown in Figure

H—CH$_2$CH$_2$CO$_2$H

H—CHCO$_2$H
        |
       CH$_3$

$\dot{C}H_3$ SOMO

$\underline{C}$ $\underline{B}$ $\underline{D}$ $\underline{A}$

Cl$^{\bullet}$ SOMO

H—CH$_2$CH$_2$CO$_2$H

H—CHCO$_2$H
        |
       CH$_3$
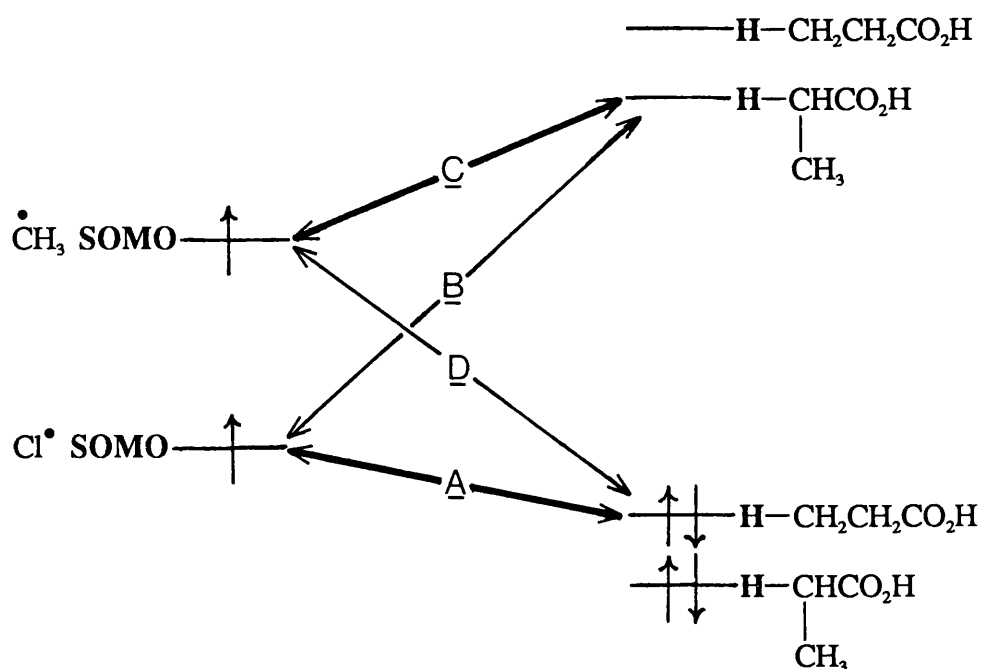
Figure 4.2   Schematic diagram showing the frontier orbital interactions for the attack of methyl and chlorine radicals on propanoic acid.

4.2. The interactions $\underline{A}$ for the chlorine atom and $\underline{C}$ for the methyl radical are more effective than $\underline{B}$ and $\underline{D}$, respectively, because the energy differences between the relevant orbitals are smaller. Thus, as from the valence bond analysis given before, we conclude that the hydrogen abstractions (4.2) and

El$^{\bullet}$ + H-Nuc $\longrightarrow$ H-El + Nuc$^{\bullet}$ (4.2)

Nuc$^{\bullet}$ + H-El $\longrightarrow$ H-Nuc + El$^{\bullet}$ (4.3)

El$^{1\bullet}$ + H-El^2 $\longrightarrow$ H-El^1 + El$^{2\bullet}$ (4.4)

Nuc$^{1\bullet}$ + H-Nuc^2 $\longrightarrow$ H-Nuc^1 + Nuc$^{2\bullet}$ (4.5)
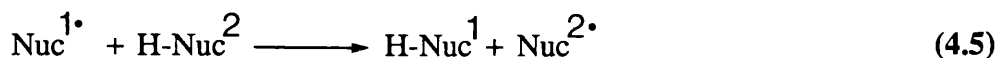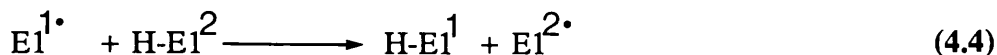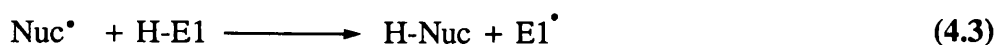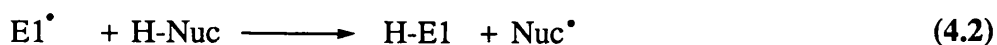
(4.3) will be favoured by polar effects while reactions (4.4) and (4.5) will not.

4.2 Polarity Reversal Catalysis (PRC)

The preceding analysis points to the concept of polarity reversal catalysis (PRC),[7-9] whereby the sluggish single step processes **(4.4)** and **(4.5)** are replaced by pairs of fast consecutive steps, as illustrated in equations **(4.6)** and **(4.7)** or **(4.8)** and **(4.9)**, respectively. Both steps of each catalytic cycle are now facilitated by favourable polar effects. We may refer to the molecules H-Nuc and H-E1 as "donor" and "acceptor" catalysts, respectively.

$$E1^{1\bullet} + \text{H-Nuc} \longrightarrow \text{H-E1}^{1} + \text{Nuc}^{\bullet} \qquad (4.6)$$

$$\text{Nuc}^{\bullet} + \text{H-E1}^{2} \longrightarrow \text{H-Nuc} + E1^{2\bullet} \qquad (4.7)$$

$$\text{Nuc}^{1\bullet} + \text{H-E1} \longrightarrow \text{H-Nuc}^{1} + E1^{\bullet} \qquad (4.8)$$

$$E1^{\bullet} + \text{H-Nuc}^{2} \longrightarrow \text{H-E1} + \text{Nuc}^{2\bullet} \qquad (4.9)$$
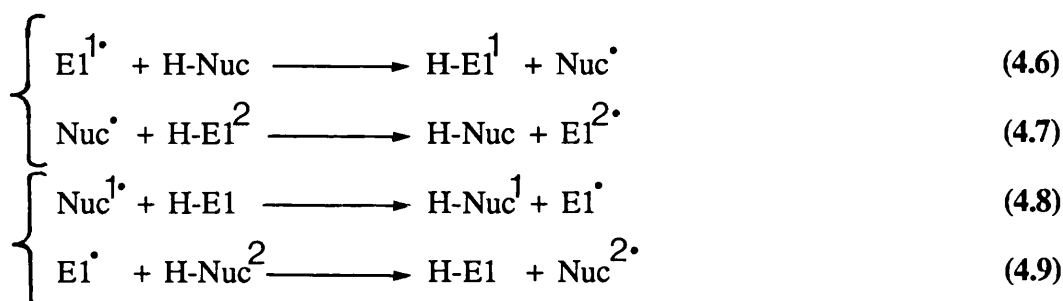
Alkoxyl radicals, such as the t-butoxyl radical, are highly electrophilic species[2-4] (the ionisation potential and electron affinity of $Bu^tO^{\bullet}$ are 12 and 1.89 eV, respectively) and as such their chemical reactivities are strongly influenced by polar factors.

$$Bu^tO^{\bullet} + \text{H-X} \longrightarrow Bu^tOH + X^{\bullet} \qquad (4.10)$$

$$[Bu^tO^{\bullet} \text{ H-X}] \longleftrightarrow [Bu^tO\text{-H} \ ^{\bullet}X] \longleftrightarrow [Bu^tO^- \text{ H}^{\bullet} \text{ X}^+]$$

$$\underline{(2a)} \qquad\qquad \underline{(2b)} \qquad\qquad \underline{(2c)}$$
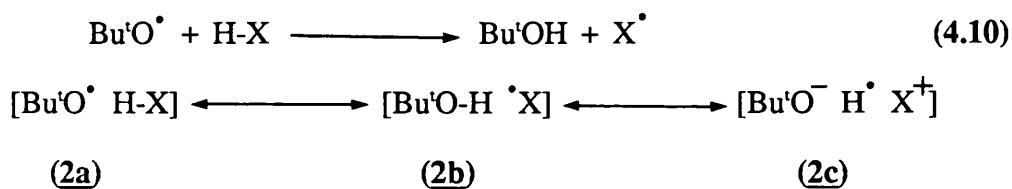
The rates of similarly exothermic hydrogen atom abstraction reactions **(4.10)** will thus increase with the extent of charge transfer stabilisation of the transition state **(2)**, as represented by the inclusion of structure **(2c)**. Thus the rate of reaction **(4.10)** will increase with increasing stability of the

cationic fragment X^+.

Abstraction of an electron deficient hydrogen (that is when X^+ is relatively unstable and X^- relatively stable) by $Bu^tO^\bullet$ should be susceptible to PRC using an appropriate donor catalyst and it has been shown[7,9] that such radicals are catalysed by amine-alkylborane complexes such as trimethylamine-thexylborane [trimethylamine-(1,1,2-trimethylpropyl)-borane]. In their presence the direct abstraction from $H^{\delta+}$-$X^{\delta-}$ is replaced by the catalytic cycle shown in equations (4.11) and (4.12). Both steps are facilitated by favourable polar effects, the

$$Bu^tO^\bullet + Me_3N{\rightarrow}BH_2R \xrightarrow{\hspace{3cm}} Bu^tOH + Me_3N{\rightarrow}\overset{\bullet}{B}HR \qquad (4.11)$$

$$Me_3N{\rightarrow}\overset{\bullet}{B}HR + H^{\delta+}\text{-}X^{\delta-} \xrightarrow{\hspace{3cm}} Me_3N{\rightarrow}BH_2R + X^\bullet \qquad (4.12)$$
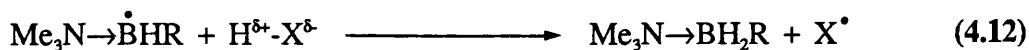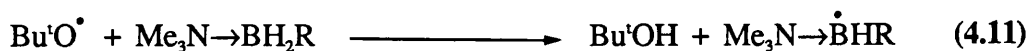
charge transfer structure (<u>3</u>) making an appreciable contribution to the transition state for reaction (4.12).

$$[Me_3N{\rightarrow}\overset{+}{B}HR \quad H^\bullet \quad X^-] \qquad\qquad (\underline{3})$$

The strengths of the H-El or H-Nuc bonds in acceptor or donor catalysts for hydrogen atom abstraction reactions is crucial. Idea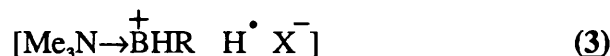lly, these should be such that the exothermicity of the uncatalysed reaction is split approximately equally between the two steps of the catalytic cycle, as illustrated for a donor catalyst in Figure 4.3. Sufficient is now known about substituent effects on radical stability for these to be used to modify bond strength in the required direction.

Donor catalysts will generally be built around metal(loid)-H bonds (as in $Me_3N{\rightarrow}BH_2R$), and steric or electronic substituent effects could be used to
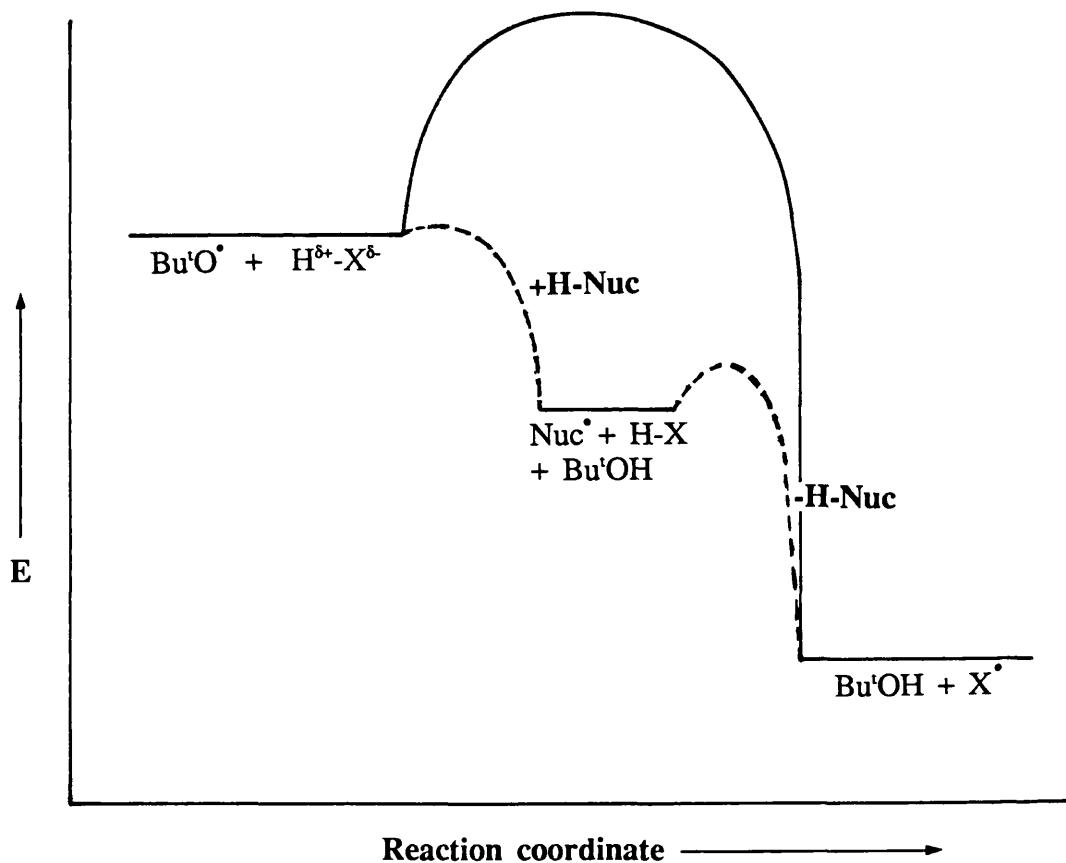
Figure 4.3   Schematic potential energy diagram to illustrate the principle of PRC.

modify their strengths and the selectivities of the derived metal(loid)-centred radicals.

In this section of the thesis we expand upon the concept of PRC. A number of amine-alkylborane complexes (**4**) - (**11**) have been prepared and investigated as "donor" catalysts for abstraction of electron deficient hydrogen atoms from a variety of organic molecules. The air-stabilities of these complexes have been studied and the reactivities of the amine-boryl radicals, derived from them by hydrogen atom abstraction, have been determined using e.s.r. methods.

$Me_3N{\rightarrow}BH_2Thx$

(4)

$Me_3N{\rightarrow}BH_2Bu^n$

(5)

$Me_3N{\rightarrow}BH_2Bu^i$

(6)

$Me_3N{\rightarrow}BH_2Bu^s$

(7)

$Me_3SiCH_2N(Me_2){\rightarrow}BH_2Thx$

(8)

$Me_3SiCH_2N(Me_2){\rightarrow}BH_3$

(9)

Me-$\underset{}{N}{\rightarrow}\overset{}{B}H$
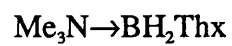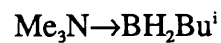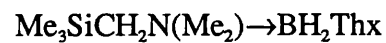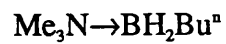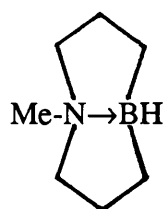
(10)
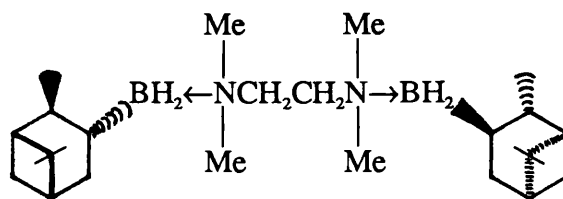
(TMEDA.2BH₂Ipc)

(11)

Since a knowledge of the properties of boron-centred radicals is important for understanding the application of ligated boranes as polarity reversal catalysts, a review of these properties is appropriate at this point.

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4.3 Borane Radical Anions

Studies of the complexes of boryl radicals $X_2B^\bullet$ with Lewis bases provides an interesting comparison with the more familiar isoelectronic alkyl radicals. The borane radical anions $X_3B^{\bullet-}$, which can be regarded as complexes between X^- and $X_2B^\bullet$, have been investigated previously; the simplest example is $H_3B^{\bullet-}$, which is isoelectronic with the methyl radical $H_3\overset{\bullet}{C}$. Isotropic e.s.r. spectra of $H_3B^{\bullet-}$, formed by γ-irradiation of alkali-[10] or tetramethylammonium-[11] borohydrides, have been detected in rigid matrices and the spectroscopic parameters were taken to indicate that the borane radical anion is effectively planar in these environments. This result was confirmed when $H_3B^{\bullet-}$ [$a(^{11}B)$ 19.9, a(3H) 15.2 G, and g 2.0023 at 253 K] was generated in solution by the reaction of photochemically produced t-butoxyl radicals with the borohydride anion [equations (4.13) and (4.14)].[12]

$$Bu^tOOBu^t \xrightarrow{\ h\upsilon\ } 2Bu^tO^\bullet \qquad (4.13)$$

$$Bu^tO^\bullet + H_4B^- \longrightarrow H_3B^{\bullet-} + Bu^tOH \qquad (4.14)$$

After γ-irradiation of boron triflouride in a tetramethylsilane matrix,[13] an isotropic e.s.r. spectrum of $F_3B^{\bullet-}$ was observed and the hyperfine splittings were consistent with this radical anion being appreciably non-planar at boron [$a(^{11}B)$ = 153 G]. This pyramidalisation at boron on substitution of fluorine for hydrogen in $H_3B^{\bullet-}$ paral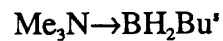lels the structural differences between the pair of isoelectronic carbon radicals $H_3\overset{\bullet}{C}$ and $F_3\overset{\bullet}{C}$,[14] and may be associated with the greater electronegativity of fluorine compared with hydrogen and with the

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presence of pairs of non-bonding electrons on the former atom.

Trialkylborane radical anions, resulting from reduction of the parent trialkylborane by sodium-potassium alloy in ether, show larger ^{11}B coupling constants than $H_3B^{\bullet-}$ [$Bu^t_3B^{\bullet-}$ has $\underline{a}(^{11}B)$ 38.5 G].[15] It was noted that the relative increase of $\underline{a}(^{11}B)$ on going from $H_3B^{\bullet-}$ to $R_3B^{\bullet-}$ is larger than that in $\underline{a}(^{13}C)$ for the progression $H_3\overset{\bullet}{C}$ to $R_3\overset{\bullet}{C}$, indicating that the boron-centred radicals are more easily pyramidalised than their carbon-centred counterparts.

4.4 Neutral Ligated Boryl Radicals

A wide variety of neutral ligated boryl radicals can be envisaged in which Lewis bases such as amines, phosphines, sulphides, and carbon monoxide are formally attached to the electron deficient $H_2B^{\bullet}$. In fact, a wide variety of ligated boryl radicals have now been generated by hydrogen atom abstraction from the parent borane complexes [equation (4.15); where $L = R_3N$, R_2NH, R_3P or R_2S] and the structures and reactivities of these have been investigated

$$L{\rightarrow}BH_3 \xrightarrow{\quad -H^{\bullet} \quad} L{\rightarrow}\overset{\bullet}{B}H_2 \qquad (4.15)$$
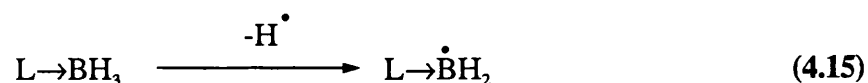
using e.s.r. spectroscopy.[16 - 19]

While the phosphine- and sulphide-boryl radicals are, like $H_3B^{\bullet-}$, essentially planar at the radical centre, the amine-boryl radicals are strongly pyramidal at boron. These differences have been explained in terms of the greater electronegativity of nitrogen compared with hydrogen and of the ability of the R_3P^{17} and R_2S^{19} ligands to delocalise the unpaired electron from boron, whereas little delocalisation occurs onto an R_3N donor.

4.4.1 Amine-Boryl Radicals

The amine-boranes and -boryl radicals are of particular interest because they afford a comparison with organic systems in which a C-C moiety is replaced by the isoelectronic $N{\rightarrow}B$ linkage. Ammonia-borane ($H_3N{\rightarrow}BH_3$) is isoelectronic with ethane (H_3C-CH_3), and the radicals formed by hydrogen atom abstraction from $H_3N{\rightarrow}BH_3$ will be isoelectronic with the ethyl radical.

t-Butoxyl radicals react with ammonia-borane or with primary, secondary,

or tertiary amine-boranes to give amine-boryl radicals [equations (4.16) and (4.17)].[20,21] The e.s.r. spectroscopic parameters for the ammonia-boryl radical

$$Bu^tOOBu^t \xrightarrow{\;h\upsilon\;} 2Bu^tO^\bullet \qquad (4.16)$$

$$Bu^tO^\bullet + R_3N{\rightarrow}BH_3 \xrightarrow{\hspace{2cm}} R_3N{\rightarrow}\overset{\bullet}{B}H_2 + Bu^tOH \qquad (4.17)$$
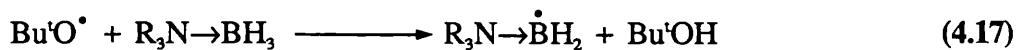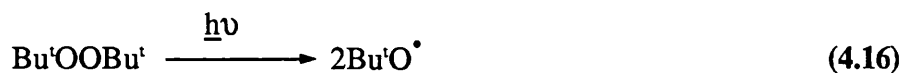
$$\underline{(12)}$$

(12; R = H) are $\underline{a}(^{11}B)$ 42.3, $\underline{a}(2H_\alpha)$ 11.0, $\underline{a}(^{14}N)$ 1.4, $\underline{a}(3H_\beta)$ 11.0 G, and $\underline{g}$ 2.0023 at 269 K in t-butyl alcohol-dimethyl ether (4:1 v/v). For comparison the ethyl radical shows $\underline{a}(2H_\alpha)$ 22.2 and $\underline{a}(3H_\beta)$ 26.9 G. The magnitudes of the ^{11}B and α-proton hyperfine coupling constants show that $H_3N{\rightarrow}\overset{\bullet}{B}H_2$ is clearly pyramidal at boron, unlike ethyl radical[22] which is effectively planar at the radical centre. The e.s.r. parameters for the trimethylamine-boryl radical (12; R = Me) and the triethylamine-boryl radical (12; R = Et) are indicative of a pyramidal equilibrium geometry.[16]

Secondary and primary amine-boryl radicals have been generated similarly and their chemical properties have been investigated. When the ligand is a secondary amine, although the amine-boryl radical (13) is the initial (kinetically controlled) product of the reaction with t-butoxyl radicals, (13) subsequently

$$Bu^tO^\bullet + R_2NH{\rightarrow}BH_3 \xrightarrow{\hspace{2cm}} R_2NH{\rightarrow}\overset{\bullet}{B}H_2 + Bu^tOH \qquad (4.18)$$

$$\underline{(13)}$$

$$R_2NH{\rightarrow}\overset{\bullet}{B}H_2 + R_2NH{\rightarrow}BH_3 \xrightarrow{\hspace{2cm}} R_2\overset{\bullet}{N}{\rightarrow}BH_3 + R_2NH{\rightarrow}BH_3 \qquad (4.19)$$

$$\underline{(14)}$$

abstracts hydrogen rapidly from the NH group of the parent amine-borane to

give the more stable isomeric aminyl-borane radical (**14**) [equations (**4.18**) and (**4.19**)].[21]

The work described in this section of the thesis was carried out in part to determine the effects of replacing an α-hydrogen atom in $R_3N{\rightarrow}\dot{B}H_2$ by an alkyl group and thus to compare the properties of $R_3N{\rightarrow}\dot{B}HR'$ with those of the isoelectronic secondary alkyl radicals $R_3C\text{-}\dot{C}HR'$.

4.4.2   Effects of α-Alkylation on the Structure and Reactivity of Carbon-Centred Radicals

The properties of carbon-centred radicals have been studied exhaustively and shown to depend to a large extent on the nature of the substituents attached to C_α.

The methyl radical has been shown by infra-red[23] and ultraviolet[24] spectroscopy to have a planar equilibrium geometry. E.s.r. data for $H_3\dot{C}$ are also in accord with a planar structure. The ethyl radical has been shown to have a non-planar equilibrium geometry (**15**) at the radical centre, although the deviation from planarity is small as is the barrier to pyramidal inversion.

(**15**)
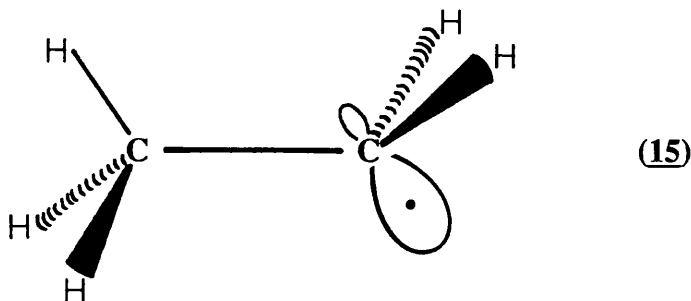
Inversion and rotation about the $C_\alpha\text{-}C_\beta$ bond are likely to be strongly coupled.[22,25] The isopropyl and t-butyl radicals are also non-planar at C_α, although the barriers to "umbrella" inversion are very small.[26-28] Pyramidalisation

upon replacement of H in $H_3\overset{\bullet}{C}$ by methyl groups has been attributed to the minimisation of torsional repulsions and the maximisation of hyperconjugative stabilisation by interaction of the unpaired electron with β-C-H bonds.[29,30] As the hydrogens on the methyl radical are successively replaced by methyl groups, i.e. going from primary to secondary to tertiary species, the radical becomes progressively more stabilised. This increase in the stability is usually attributed to hyperconjugative interaction between the unpaired electron and the alkyl group. An alternative explanation may be given in terms of the reduction in steric compression present in R-H on going to the radical $R^{\bullet}$;[31] probably both factors are important.

The vertical ionisation potentials of alkyl radicals decrease progressively along the series $Me^{\bullet} > R^{p\bullet} > R^{s\bullet} > R^{t\bullet}$. For example, the ionisation energies of $Me^{\bullet}$, $Et^{\bullet}$, $Pr^{i\bullet}$, and $Bu^{t\bullet}$ are 9.84, 8.51, 7.69, and 6.92 eV, respectively.[32] As a consequence of this trend, alkyl radicals become increasingly nucleophilic along the series $Me^{\bullet} < R^{p\bullet} < R^{s\bullet} < R^{t\bullet}$.[3]

4.5   Reactions of Borane Radical Anions and Ligated Boryl Radicals

Amine-boryl radicals have been invoked as intermediates in the reduction of 1,2-dichloroethane, CCl_4 and CCl_3Br by trimethylamine- or 4-methylpyridine-borane.[33-35] The reactions of trimethylamine- or 4-methylpyridine-borane with carbon tetrachloride at ca. 353 K to give the corresponding amine-chloroboranes are markedly accelerated by addition of small quantities of dibenzoyl peroxide. Ryschkewitsch and co-workers[33] have proposed a chain pathway with propagation steps as shown in equations (4.20) and (4.21).

$$Cl_3\dot{C} \ + \ R_3N{\rightarrow}BH_3 \ \longrightarrow \ CHCl_3 \ + \ R_3N{\rightarrow}\dot{B}H_2 \qquad (4.20)$$

$$R_3N{\rightarrow}\dot{B}H_2 \ + \ CCl_4 \ \longrightarrow \ R_3N{\rightarrow}BH_2Cl \ + \ Cl_3\dot{C} \qquad (4.21)$$
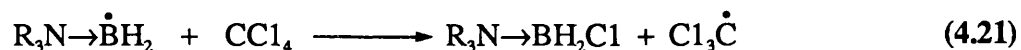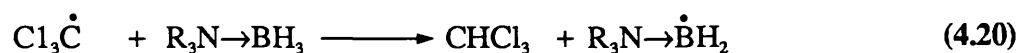
Similar, but more rapid, reactions take place with CCl_3Br to give exclusively the bromoborane adduct from 4-methylpyridine-borane, but a 2:3 mixture of $Me_3N{\rightarrow}BH_2Cl$ and $Me_3N{\rightarrow}BH_2Br$ results from trimethylamine-borane. Analogous mechanisms were proposed for the chlorination of amine-boranes at boron by antimony pentachloride,[34] sulphuryl chloride[34] and dimethylchloroamine.[35]

E.s.r studies have confirmed the ability of boron-centred radicals to abstract halogen from alkyl halides and have established a variety of other types of reactions.

4.5.1   Reactions with Alkyl Halides

The borane radical anion reacts rapidly with both alkyl chlorides and bromides to give alkyl radicals [equation (4.22)].[36] The amine-boryl radicals[16,37]

$$H_3B^{\bullet-} + RHal \longrightarrow H_3\bar{B}Hal + R^{\bullet} \qquad (4.22)$$
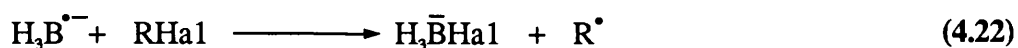
behave similarly, although they appear to be somewhat less reactive than $H_3B^{\bullet-}$. In these reactions, $H_3B^{\bullet-}$ and $R_3N{\rightarrow}\dot{B}H_2$ behave in a fashion similar to trialkylsilyl radicals,[38] rather than like their isoelectronic alkyl radical counterparts, reflecting the "diagonal" relationship between boron and silicon in the Periodic Table.

Both thermodynamic and polar factors are thought to be responsible for the higher reactivity of $R_3N{\rightarrow}\dot{B}H_2$ towards alkyl halides as compared with $R_3C\text{-}\dot{C}H_2$. It is likely that the transition state for dehalogenation of an alkyl halide by amine-boryl radical involves a large degree of charge transfer from $R_3N{\rightarrow}\dot{B}H_2$ to the halide and this will favour abstraction by the nucleophilic boron-centred radical [see (16a) and (16b)]. The bond to halogen is probably stronger in

$$[R_3N{\rightarrow}\dot{B}H_2 \quad R'\text{-Hal} \longleftrightarrow R_3N{\rightarrow}BH_2^+ \quad \dot{R}' \quad Hal^-]$$

(16a)   (16b)
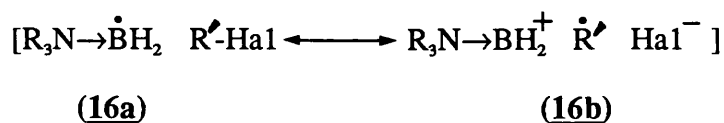
$R_3N{\rightarrow}BH_2Hal$ than in $R_3C\text{-}CH_2Hal$, because of the metalloidal character of boron. Generally, the abstraction of bromine by a ligated boryl radical from an alkyl bromide is faster than the abstraction of chlorine from an alkyl chloride.[39]

4.5.2 β-Scission

As stated above, in bimolecular processes the chemical reactivity of an amine-boryl radical (17) resembles that of a silyl radical more closely than that of the isoelectronic alkyl radical. However, whereas alkylsilyl radicals do not undergo ready unimolecular β-scission, the amine-boryls do [equation (4.23)]

$$R_3N{\rightarrow}\overset{\bullet}{B}H_2 \xrightarrow{\hspace{3cm}} \overset{\bullet}{R} + R_2N\overset{\_}{\rightleftharpoons}BH_2 \qquad (4.23)$$

(17)

and much more readily than even the isoelectronic alkyl radicals.[16]

The reactions of $Bu^tO^\bullet$ with aziridine- and azetidine-boranes (17; n = 1 or 2) have been examined previously[16,39,40] using e.s.r. spectroscopy and shown to lead ultimately to carbon-centred radicals (20), formed by the ring-opening

(18) (19) (20)

$$(4.24)$$

β-scission of intermediate amine-boryl radicals [equation (4.24)]. The aziridine-boryl radical thus resembles the isoelectronic cyclopropylmethyl radical, which undergoes ring opening to give the but-3-enyl radical.[41]

The acyclic t-butyldimethylamine-boryl radical (21) also undergoes rapid β-scission, now to produce $Bu^{t\bullet}$ [equation (4.25)].[16] The isoelectronic alkyl

$$Bu^tMe_2N{\rightarrow}\overset{\bullet}{B}H_2 \longrightarrow Bu^{t\bullet} + Me_2N \overset{\rightharpoonup}{\leftharpoondown} BH_2 \qquad (4.25)$$

(21)

radical $Bu^tMe_2C{-}\overset{\bullet}{C}H_2$ shows no sign of β-scission under similar conditions. β-

Scission also takes place rapidly for $Pr^i_2EtN{\rightarrow}\overset{\bullet}{B}H_2$, to give the isopropyl radical,

although the rate of cleavage is ca. 3.7 times slower than that of (21) at 221

K^{42} and both are slower than the ring opening of the aziridine-boryl radical.

The high rate of β-scission of amine-boryl radicals has been attributed to

the thermodynamic favourability of this process, which is reflected in much

lower activation energies for decomposition of the amine-boryls[42] as compared

with the isoelectronic alkyl radicals, β-scission of which is much less favourable

thermodynamically.

4.5.3   Spin-Trapping

"Spin-trapping" of carbon-centred radicals by C-nitroso compounds and by

nitrones, to give relatively persistent nitroxide adducts readily detectable by e.s.r.

spectroscopy, has become established as an important tool in mechanistic free

radical chemistry.[43] Spin-trapping of ligated boryl radicals can provide similarly

useful information. Transient amine-boryl radicals add rapidly to 2-methyl-2-

nitrosopropane (MNP), 2,4,6-tri-t-butylnitrosobenzene, or phenyl-N-t-butylnitrone

to produce persistent nitroxide radicals which may also be readily detected by

e.s.r. spectroscopy[37,44] [e.g. equation (4.26)]. Spin-trapping is sufficiently rapid

$$R_3N{\rightarrow}\overset{\bullet}{B}H_2 + Bu^tN{=}O \longrightarrow \begin{array}{c} R_3N{\rightarrow}BH_2 \\ \diagdown \\ \overset{\bullet}{N}{-}\overset{\bullet}{O} \\ \diagup \\ Bu^t \end{array} \qquad (4.26)$$
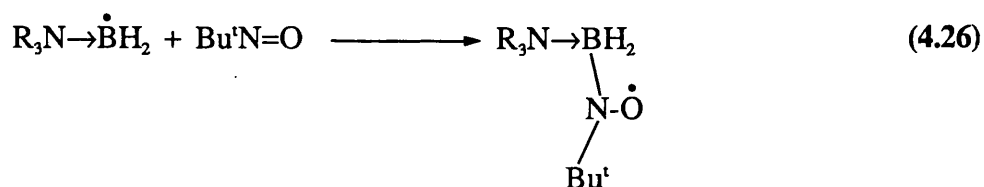
at 292 K that $Pr^i_2EtN{\rightarrow}\overset{\bullet}{B}H_2$ can be intercepted by MNP (ca. 0.02 M) before its

β-scission. With $Bu^tMe_2N{\rightarrow}\overset{\bullet}{B}H_2$, β-scission is more rapid and only di-t-butyl

nitroxide derived from addition of $Bu^{t\bullet}$ to MNP could be detected.

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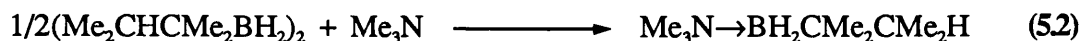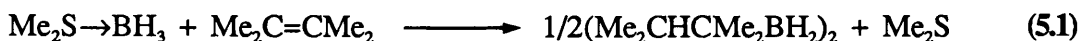
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CHAPTER 5

RESULTS AND DISCUSSION

5.1   Syntheses of Catalysts

Trimethylamine-thexylborane[1,2] (**1**) was prepared by the hydroboration of 2,3-dimethylbut-2-ene, using dimethyl sulphide-borane (BMS), followed by the addition of an excess of trimethylamine.

$$Me_2S{\rightarrow}BH_3 + Me_2C{=}CMe_2 \longrightarrow 1/2(Me_2CHCMe_2BH_2)_2 + Me_2S \qquad (5.1)$$

$$1/2(Me_2CHCMe_2BH_2)_2 + Me_3N \longrightarrow Me_3N{\rightarrow}BH_2CMe_2CMe_2H \qquad (5.2)$$

Trimethylamine-n-butylborane[3] (**2**) was prepared by reduction of n-butylboronic anhydride with lithium aluminium hydride in the presence of trimethylamine. The boronic anhydride was prepared[4] by dehydration of n-butylboronic acid, itself prepared by reaction of n-butylmagnesium bromide with trimethyl borate at low temperature.

$$(Bu^nBO)_3 \xrightarrow[\text{2. Me}_3\text{N}]{\text{1. LiAlH}_4} Me_3N{\rightarrow}BH_2Bu^n \qquad (5.3)$$
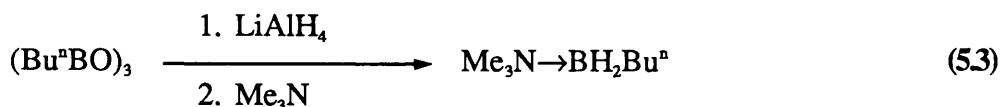
Trimethylamine-isobutylborane[3] (**3**) and trimethylamine-s-butylborane (**4**) were prepared similarly from isobutylboronic anhydride and s-butylboronic anhydride, respectively. It became increasingly difficult to distil, and hence to purify, the amine-alkylborane complexes as the butyl group became more highly

branched, probably because of a steric effect on the strength of the N→B bond.

N,N-Dimethyl(trimethylsilylmethyl)amine-thexylborane[1,2] (5) was prepared in a similar manner to (1). The amine $Me_3SiCH_2NMe_2$ was prepared[5,6] by heating chloromethyl(trimethyl)silane with an approximately threefold excess of dimethylamine for 24 h. in a sealed tube at 80 °C. Equimolar quantities of the amine and thexylborane dimer[7] were mixed in ether at 0 °C, followed by removal of the solvent to give $Me_3SiCH_2NMe_2$→BH_2Thx as a colourless liquid, which could not be distilled without decomposition. [1]H and [11]B N.m.r. spectroscopy showed that the crude product contained ca. 5 % of an impurity, which could not be removed by adding more dimethylamine. Column chromatography or preparative h.p.l.c. failed because the complex decomposed during attempted purification with evolution of gas (presumably hydrogen).

N,N-Dimethyl(trimethylsilylmethyl)amine-borane[8] (6) was synthesised by the reaction of $Me_3SiCH_2NMe_2$ with BMS in ether at 0 °C. The complex was purified by sublimation under reduced pressure to give (6) as an analytically pure, white crystalline solid.

1-Methyl-cis-1-azonia-5-boratobicyclo[3.3.0]octane (7) was synthesised from triethylamine-borane and diallylmethylamine, using a modification of the method reported for the preparation of 1,1-dimethyl-1,2-azaborolidine (8)[9-12] [equation (5.4)]. An equimolar mixture of triethylamine-borane and diallylmethylamine was refluxed in xylene for 5 h., after which time the xylene was removed by distillation at atmospheric presssure, followed by distillation of the product under reduced pressure (b.p. 53-54 °C at 1.8 Torr). Analytically pure product was obtained (see Chapter 6 for analytical data) as a colourless liquid, even though its boiling point is very close to that of xylene. However,

$$\text{Et}_3\text{N}{\rightarrow}\text{BH}_3 \;+\; \text{Me}_2\text{N}\diagdown\diagup\diagdown \;\; \xrightarrow[\text{-Et}_3\text{N}]{\text{Xylene}} \;\; \text{Me}_2\text{N}{\rightarrow}\text{BH}_3 \;\; \longrightarrow \;\; \text{Me}_2\text{N}{\rightarrow}\text{BH}_2 \quad (5.4)$$

<div align="center">(<u>8</u>)</div>

the yield of (<u>7</u>) was very low (<u>ca.</u> 5 %) and much sticky polymeric material was also formed.

The first step of the reaction presumably yields diallylmethylamine-borane (<u>9</u>), which then undergoes an intramolecular hydroboration to give the bicyclic product (<u>7</u>) [equation (5.5)].

$$\text{Et}_3\text{N}{\rightarrow}\text{BH}_3 \;+\; \text{Me-N} \qquad \xrightarrow[\text{-Et}_3\text{N}]{\text{Xylene}} \qquad \text{Me-N}{\rightarrow}\text{BH}_3 \qquad \longrightarrow \qquad \text{Me}{\blacktriangleright}\text{N}{\rightarrow}\text{B}{\blacktriangleleft}\text{H} \quad (5.5)$$

<div align="center">(<u>9</u>)   (<u>7</u>)</div>

Formation of (<u>8</u>) [equation (5.4)] is reported to take place at temperatures above 100 °C,[10] but it was found that temperatures of 140 °C or over are required for the bicyclisation of (<u>9</u>). These temperatures were achieved by removing the xylene at atmospheric pressure, rather than reduced pressure. Attempts were made to improve the yield of (<u>7</u>) by changing the reaction conditions. Neither increasing the reflux time to 18 h. in xylene or using trimethylamine-borane as a hydroborating agent instead of triethylamine-borane (5 h. reflux time) improved the yield significantly. Using toluene instead of xylene as solvent afforded large amounts of uncyclised amine-borane (<u>9</u>),

<div align="center">110</div>

presumably because of the lower temperatures involved.

A low yield of (7) was also obtained when it was prepared from diallylmethylamine and BMS. A slight molar excess of BMS in ether was added to diallylmethylamine in ether at -20 °C and, after stirring for a further 20 min. at -20 °C, the volatiles were removed under reduced pressure (10 Torr). The residual oil was then heated under reflux in xylene for 5 h. and (7) was isolated as described before, followed by a further trap-to-trap distillation under reduced pressure (0.1 Torr).

The structure of (7) was confirmed by ^{1}H, ^{11}B, and ^{13}C n.m.r. spectroscopy [see Figures **5.1** - **5.3**]. Chemical shifts were assigned to the protons and carbon atoms using a ^{1}H - ^{13}C 2-D correlated spectrum (see Chapter 6 for the chemical shifts and coupling constants). Both cis - and trans-isomers of bicyclo [3.3.0]octane (**10a**) and (**10b**) are known[13,14] and the former is thermodynamically more stable. Since the bicyclic amine-dialkylborane (7) is formed by high temperature intramolecular hydroboration, it seems likely that the thermodyna-
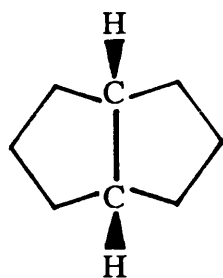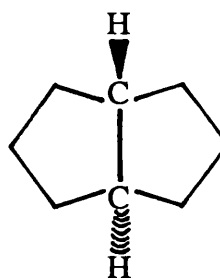
(10a)   (10b)

mically more stable isomer will be formed preferentially and molecular models indicate that, like the carbocyclic analogues, the cis-isomer (**11a**) will be more stable from the trans-(**11b**). That only one isomer is obtained is supported by

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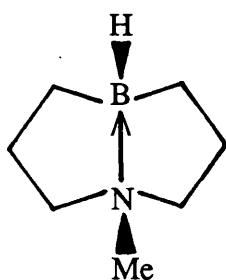
(11a)
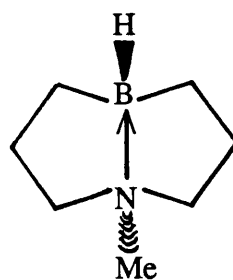
(11b)

the observation of only one set of resonances in the ^{13}C n.m.r. spectrum and by the fact that the product was homogeneous as judged by h.p.l.c.

The mass spectrum showed a strong peak at $(M-1)^+$ which is assigned to the complexed boronium ion (12), produced by loss of H· from the molecular ion.
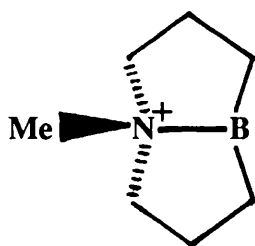
(12)

A major problem with the use trimethylamine-thexylborane (1) as a polarity reversal catalyst was that the complex was water sensitive and it reacted rapidly with the atmosphere to form an unstable solid of variable composition. This reactivity towards water and the partial decomposition of the complex upon distillation are related to the large bulk of the thexyl group, which results in a weak N→B bond [equation (5.6)]. The trimethylamine-butylboranes (2)-

$$Me_3N{\rightarrow}BH_2Thx \ \rightleftharpoons \ Me_3N \ + \ ThxBH_2 \ \xrightarrow[-2H_2]{H_2O} \ ThxB(OH)_2 \qquad (5.6)$$

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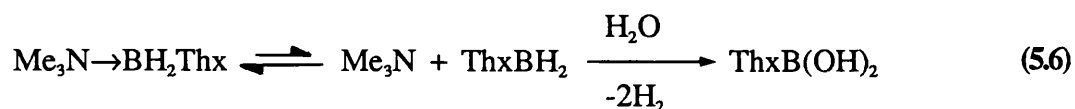
(**4**), which contain less bulky $\underline{B}$-alkyl groups, were synthesised in order to determine their usefulness as more air-stable catalysts [see Table **5.1**]. On the basis of the overall results, it was clear that the trimethylamine-n-butylborane (**2**) was the most suitable of the catalysts (**1**) - (**4**) in terms of its thermal and water stability.
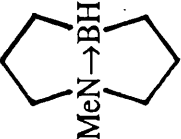
Another way to improve the stability of a complex $Me_3N{\rightarrow}BH_2R$ would be to replace the trimethylamine by an amine which is more basic, but not significantly more bulky, than Me_3N. Such an amine is $Me_3SiCH_2NMe_2$ in which one hydrogen atom in Me_3N has been replaced by a Me_3Si group.

Although $Me_3N{\rightarrow}BH_3$ is not an effective polarity reversal catalyst, because the radical $Me_3N{\rightarrow}\overset{\bullet}{B}H_2$ does not abstract from the α-C-H groups of esters and nitriles as readily as $Me_3N{\rightarrow}\overset{\bullet}{B}HR$, it was considered possible that $Me_3SiCH_2NMe_2{\rightarrow}BH_3$ (**6**) might be useful since the derived amine-boryl radical $Me_3SiCH_2NMe_2{\rightarrow}\overset{\bullet}{B}H_2$ should be more nucleophilic than $Me_3N{\rightarrow}\overset{\bullet}{B}H_2$ because the amine is a stronger Lewis base. Indeed, (**6**) turned out to be an air-stable crystalline solid which was reasonably effective as a polarity reversal catalyst, although it was not very soluble in organic solvents.

The β-C-Si bonding electrons in $Me_3SiCH_2NMe_2$ amine act as a powerful electron donor[6] and raise the energy of the lone pair of electrons on nitrogen, which should result in a stronger N$\rightarrow$B donor bond and hence disfavour hydrolysis. The complex $Me_3SiCH_2NMe_2{\rightarrow}BH_2Thx$ (**5**) turned out to be very difficult to purify and hence was not suitable as a catalyst.

A different approach was to increase the stability of the N$\rightarrow$B linkage by incorporating it into a ring system. The bicyclic amine-borane (**7**) had excellent thermal and air stability; it could withstand the high temperatures involved in

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Table 5.1   Properties of amine-alkylborane complexes

| Compound		Physical form at r.t. (b.pt./ or m.pt.)	$\delta(^{11}B)$/ppm^a ($\underline{J}_{B\text{-}H}$/Hz)	Effect of exposure to the atmosphere ^{b}
$Me_3N{\rightarrow}BH_2Thx$	(**1**)	Liquid (58-60 °C/0.05 Torr)	+ 1.8 (t) (98.8)	Obviously reacted; white solid produced. None of the original complex remained after 15 min. exposure to air, as judged by ^1H n.m.r. spectroscopy.
$Me_3N{\rightarrow}BH_2Bu^n$	(**2**)	Liquid (50 °C/0.45 Torr)	- 1.56 (t) (98.5)	No obvious change after 5 h. After 1.5 h. and 5 h., [ ]change was detected by ^1H n.m.r. spectroscopy.
$Me_3N{\rightarrow}BH_2Bu^i$	(**3**)	Liquid (45 °C/0.5 Torr)	- 2.21 (t) (97.5)	No obvious change after 1.5 h. After 1.5 h, no change was detected by ^1H n.m.r. spectroscopy.
$Me_3N{\rightarrow}BH_2Bu^t$	(**4**)	Liquid (60 °C/2.5 Torr)	+ 1.32 (t) (97.3)	No obvious change after 1.5 h. After 1.5 h, no change was detectable by ^1H n.m.r. spectroscopy.
$MeN{\rightarrow}BH$ (cyclic structure)	(**7**)	Liquid (53-54 °C/1.8 Torr)	+ 4.06 (d) (100.1)	No obvious change after 5 h. No change was detectable by ^1H n.m.r. spectroscopy after 5 h.
$Me_3SiCH_2N(Me)_2{\rightarrow}BH_3$	(**6**)	Crystalline solid (34-35.5 °C)	- 7.61 (q) (97.7)	No obvious change after 5 h. No change was detectable by ^1H n.m.r. spectroscopy after 1.5 h. and 5 h.
$TMEDA.2BH_2Ipc$	(**13**)	Crystalline solid (126-128 °C)	- 2.04 (t)^c (80.0)	No obvious change after 5 h. No change was detectable in ^1H n.m.r. spectroscopy after 1.5 h. and 5 h.

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<u>a</u> In C_6H_6 solvent with an external D_2O lock unless otherwise stated.

<u>b</u> A sample (<u>ca</u>. 50 μl or 50 mg) was left exposed to the atmosphere on a watchglass, but losely covered with a large beaker. The solvent for ^1H n.m.r. spectroscopy was C_6D_6 for (<u>1</u>) - (<u>6</u>) and $CDCl_3$ for (<u>13</u>).

<u>c</u> In $CHCl_3$ solvent with an external D_2O lock.

its synthesis (140 °C) and exposure to the atmosphere for prolonged periods.

The tetramethylethylenediamine complex of isopinocampheylborane, TMEDA. $2BH_2Ipc$ (**13**), is an optically active donor catalyst which can be prepared from optically pure (+)- or (-)-α-pinene.[15-17] The crystal structure of (**13**) has recently been reported.[17] It was planned to examine this complex to see if hydrogen-atom abstraction from appropriate molecules could be enantioselective. If this is so, then catalytic kinetic resolution of racemic mixtures should be possible, as well as enantioselective syntheses. Impurities in (**13**) (as supplied by Aldrich) made the amine-borane unstable when exposed to the atmosphere, but after purification by recrystallisation from diethyl ether, the complex appeared to be air stable and could be stored without apparent change for a long period of time (see Table **5.1**). The ^1H n.m.r. spectrum of (**13**) is shown in Figure **5.4**.

400 MHz ^{1}H n.m.r. spectrum of Me-N→BH in C_6D_6.

Figure 5.1

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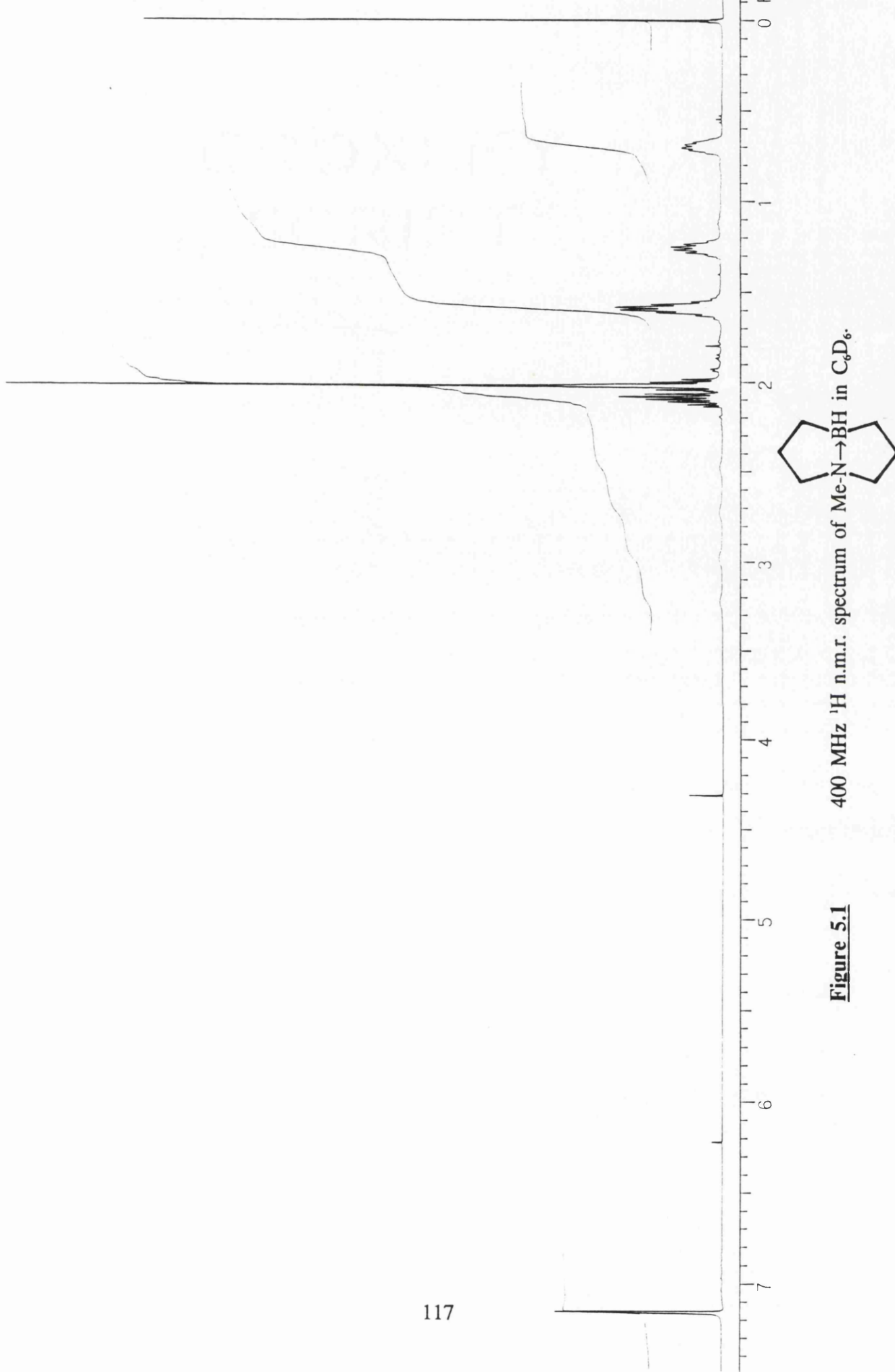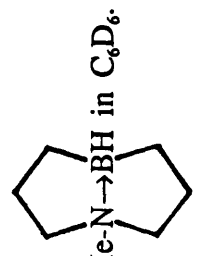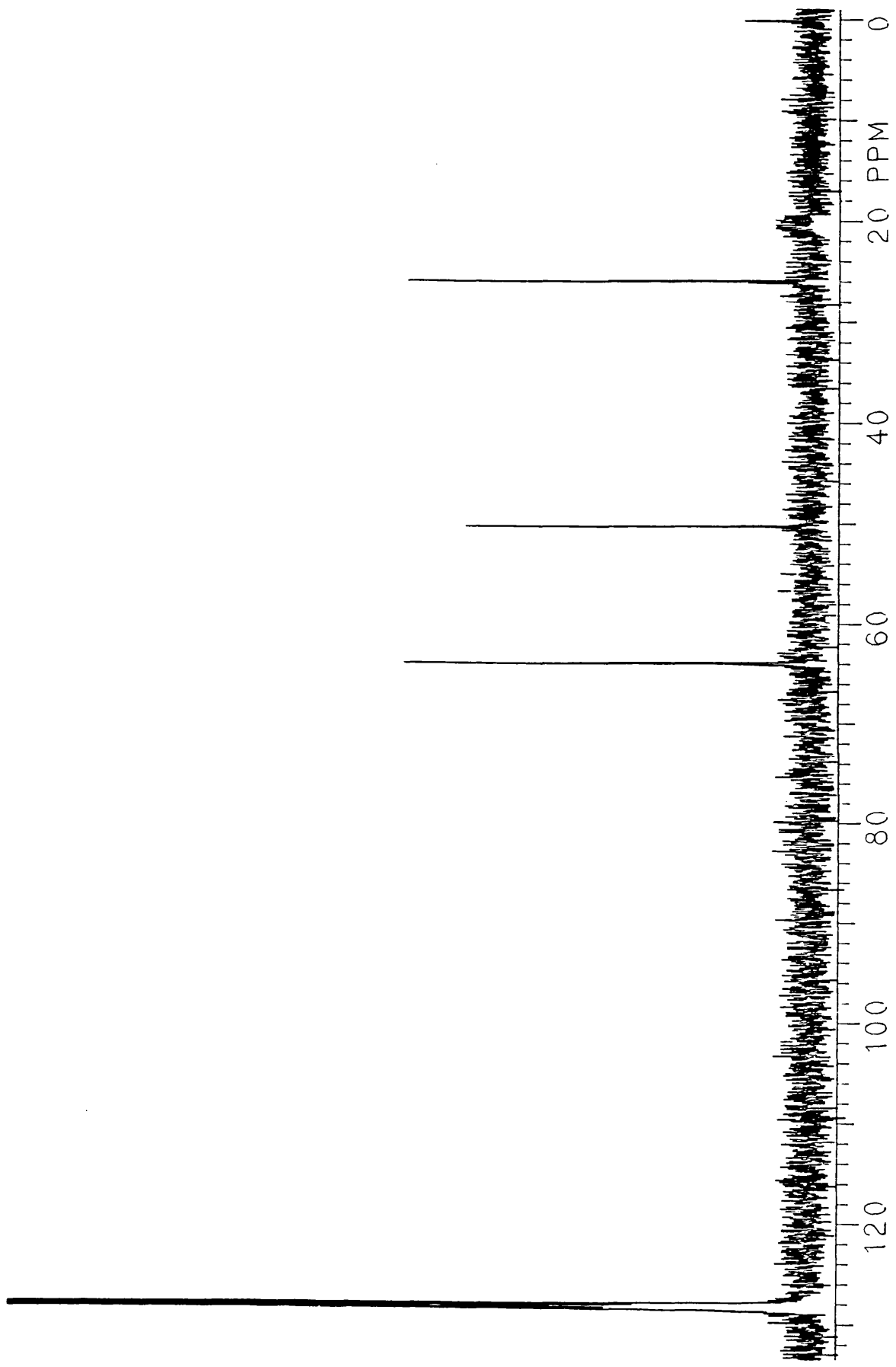
400 MHz ^{13}C n.m.r. spectrum of Me-N→BH in C$_6$D$_6$.

Figure 5.2

F2 (PPM)
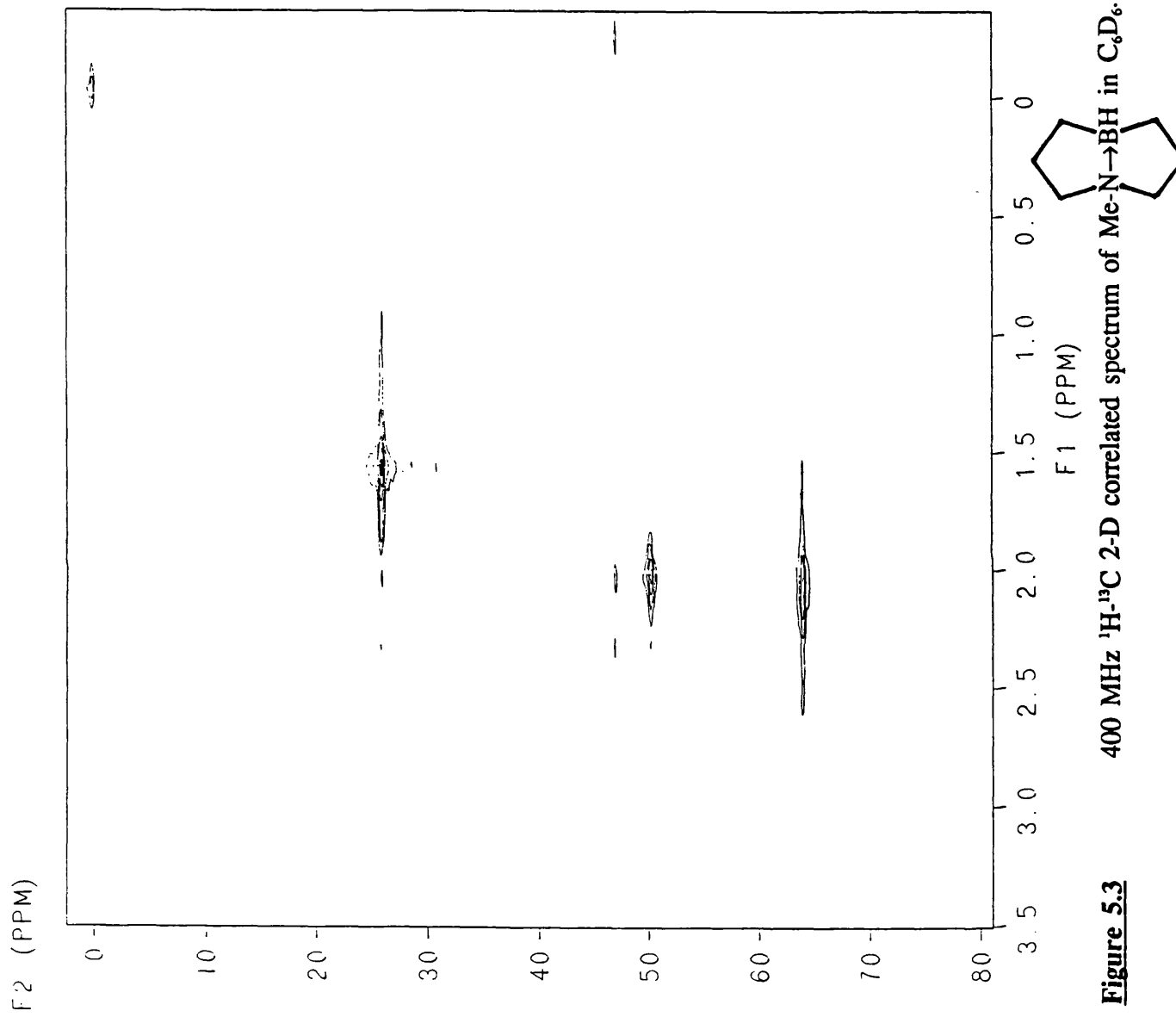
400 MHz ^{1}H-^{13}C 2-D correlated spectrum of Me-N→BH in C$_6$D$_6$.
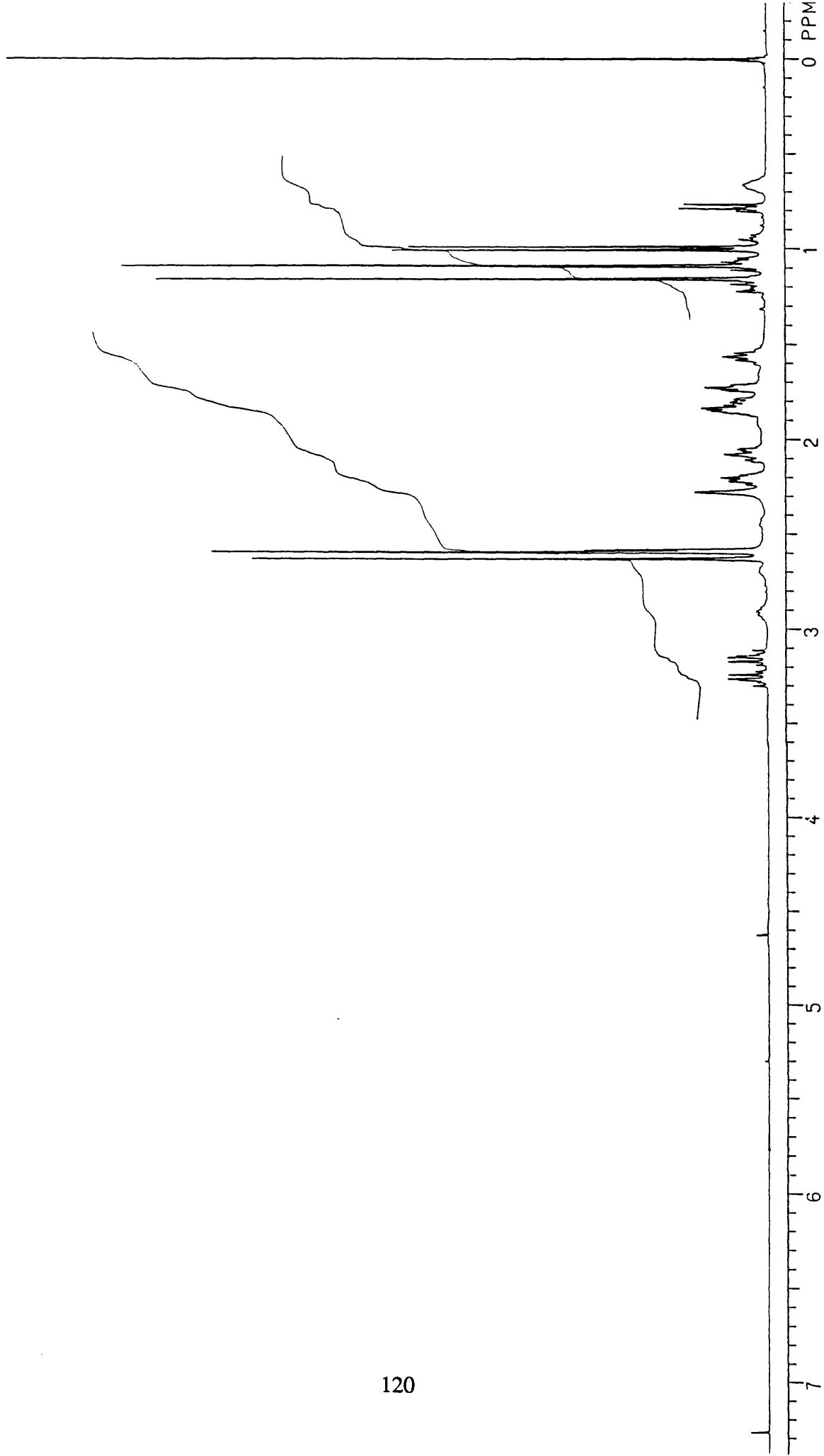
Figure 5.3
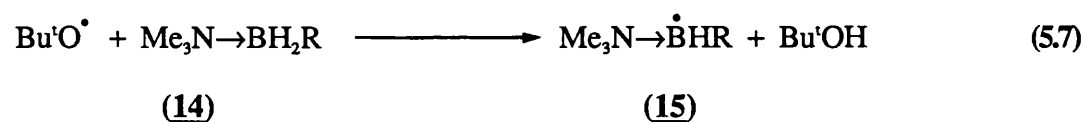
Figure 5.4   400 MHz ^{1}H n.m.r. spectrum of TMEDA.2BH$_2$Ipc [prepared from (+)-α-pinene] in CDCl$_3$.

5.2   Structures and Reactions of Amine-Alkylboryl Radicals

5.2.1   E.S.R. Spectra of Amine-Alkylboryl Radicals

U.v. photolysis of a cyclopropane solution containing trimethylamine-s-butyl borane (**14**; R = Bu^s; ca. 1 M) and DTBP (ca. 20 % v/v) gave rise to the spectrum shown in Figure **5.5** along with its computer simulation. This spectrum is assigned to the trimethylamine-s-butylboryl radical (**15**; R = Bu^s) formed by hydrogen atom abstraction from the ligated borane [equation (5.7)].

$$Bu^tO^{\bullet} + Me_3N{\rightarrow}BH_2R \xrightarrow{\hspace{3cm}} Me_3N{\rightarrow}\overset{\bullet}{B}HR + Bu^tOH \qquad (5.7)$$
$$\underline{(14)} \qquad\qquad\qquad\qquad \underline{(15)}$$

The spectrum can be analysed as a quartet of triplets which arise from coupling of the unpaired electron to ^{11}B (I = 3/2, natural abundance 80.2 %), to one α-hydrogen attached to boron, and to one β-hydrogen attached to carbon; the coupling to these two hydrogens is equal within the linewidth. The contribution from the radical containing ^{10}B [I = 3, natural abundance 19.8 %, $\gamma(^{10}B)/\gamma(^{11}B)$ 0.335] is small, but still the signals were strong enough to be detected [a(^{10}B) 19.3, a(1H$_{\alpha}$) 7.5, and a(1H$_{\beta}$) 7.5 G]. The spectra obtained from trimethylamine-n-butylborane and trimethylamine-isobutylborane (**14**; R = Bu^n or Bu^i, respectively) are similarly attributed to the corresponding amine-alkylboryl radicals. In both cases, a quartet of triplets of doublets was observed due to coupling of the unpaired electron to ^{11}B, to two equivalent β-hydrogens, and to one α-hydrogen, respectively.

The much smaller value of a(C-H$_{\beta}$) found for (**15**; R = Bu^s) compared

(a)

20 G

(b)

Figure 5.5

Figure 5.5   (a) E.s.r. spectrum of the trimethylamine-s-butylboryl radical (**15**; R = Bu^r) in cyclopropane at 261 K.   (b) Computer simulation of (a); the coupling constants are given in Table **5.2**, the linewidth is 5.0 G, and the lineshape is 50 % Gaussian.

with that for (<u>15</u>; R = Bu^n or Bu^i) is presumably a conformational effect. For

steric reasons, the average dihedral angle between the β-C-H bonds and the axis

of the orbital of the unpaired electron in (<u>15</u>; R = Bu^r) will be greater than

that for (<u>15</u>; R = Bu^n or Bu^i), as shown in the idealised Newman projections

(<u>16a</u>) and (<u>16b</u>). The average dihedral angle for (<u>15</u>; R = Bu^n or Bu^i) is

Me

H

B

H

Et

NMe₃

(<u>16a</u>)

Prⁿ

H

B

H

H

NMe₃

(<u>16b</u>)
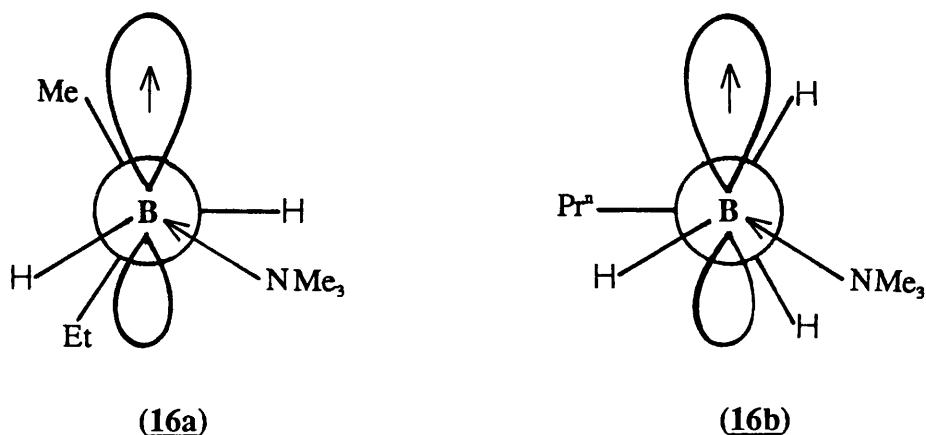
smaller than the value of 45° (corresponding to the free rotation) limit for

$Me_3N \rightarrow \dot{B}HMe$. E.s.r. parameters for the amine-alkylboryl radicals are given in

Table **5.2**, alongside data obtained previously[2,8] for $Me_3N \rightarrow \dot{B}HMe$, $Me_3N \rightarrow \dot{B}HBu^i$,

and for $Me_3N \rightarrow \dot{B}H_2$.

The equilibrium geometry[18] at boron in the trimethylamine-boryl radical

(<u>15</u>; R = H) has been shown to be pyramidal (see Chapter 4) on the basis of

the magnitudes and temperature dependencies of the ¹¹B and α-proton coupling

constants. The e.s.r. parameters for the amine-alkylboryl radicals are similarly

indicative of a non-planar configuration at the radical centre. The ¹¹B splittings

are large and correspond to 7.6 - 8.1 % unpaired electron population of the B-

2s atomic orbital,[19] compared with a B-2s contribution to the SOMO of only

2.8 % for the planar $H_3\dot{B}^-$ in which spin-polarisation is the major mechanism

for hyperfine coupling. The small decrease in $\underline{a}(^{11}B)$ with increasing temperature suggests that the time-average configuration of $Me_3N{\rightarrow}\dot{B}HR$ becomes more nearly planar at higher temperatures, as expected for a pyramidal equilibrium geometry and the associated double minimum potential function which would govern inversion at the radical centre.[20] The magnitudes of $\underline{a}(H_\alpha)$ for ($\underline{15}$; R = Bu^n, Bu^i or Bu^t) are similar to the values found previously for $Me_3N{\rightarrow}\dot{B}HMe$ and $Me_3N{\rightarrow}\dot{B}HBu^t$ ($\underline{15}$; Me or Bu^t) and appreciably smaller than that (15.2 G at 253 K) for the planar or nearly-planar borane radical anion $H_3\dot{B}^{\bullet-}$,[21] again in accord with a pyramidal geometry for the amine-alkylboryl radicals. The sign of $\underline{a}(H_\alpha)$ for ($\underline{15}$; R = alkyl) is almost certainly negative.

The ^{11}B splittings for ($\underline{15}$; R = Bu^n, Bu^i, or Bu^t) are 13-14 % larger than $\underline{a}(^{11}B)$ for ($\underline{15}$; R = H) under similar conditions, suggesting that the time average configuration of the former deviates more from planarity at boron. The value of $\underline{a}(^{13}C_\alpha)$ also increases, although to a lesser extent, upon progressive alkylation of a carbon radical centre: for example the values of $\underline{a}(^{13}C_\alpha)$ for $Me\dot{C}H_2$, $Me_2\dot{C}H$ and $Me_3\dot{C}$ are 39.4, 40.8, and 44.8 G, respectively, at $\underline{ca}$. 195 K.[22-24]

U.v. photolysis of a cyclopropane solution containing $\underline{N},\underline{N}$-dimethyl(trimethylsilylmethyl)amine-borane ($\underline{17}$; R = H; $\underline{ca}$. 0.3 $\underline{M}$) and DTBP ($\underline{ca}$. 20 % v/v) at the lowest accessible temperature, 237 K, gave rise to a spectrum which is assigned to the amine-boryl radical [$\underline{18}$; R = H; equation (5.8)]. A 1 : 1 : 1 : 1 quartet of binomial triplets was observed which could be

$$Bu^t\dot{O} + Me_3SiCH_2N(Me_2){\rightarrow}BH_2R \xrightarrow{-Bu^tOH} Me_3SiCH_2N(Me_2){\rightarrow}\dot{B}HR \qquad (5.8)$$

$$(\underline{17}) \qquad\qquad\qquad (\underline{18})$$
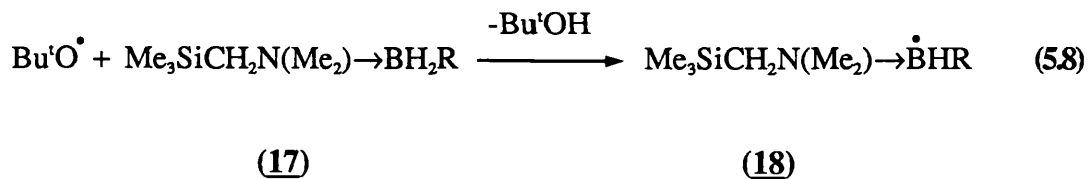
analysed in terms of the parameters given in Table **5.2**. At higher temperature,

β-scission of (18; R = H) gives rise to the trimethylsilyl(methyl) radical (19) [$\underline{a}(2H_\alpha)$ 20.93, $\underline{a}(9H_\gamma)$ 0.40 G, and $\underline{g}$ 2.0026 at 261 K], as shown in equation

$$\text{Me}_3\text{Si}\dot{\text{C}}\text{H}_2\text{---N}\text{---BHR} \longrightarrow \text{Me}_3\text{Si}\dot{\text{C}}\text{H}_2 + \text{Me}_2\text{N}{=}\text{BHR} \qquad (5.9)$$
$$(19)$$
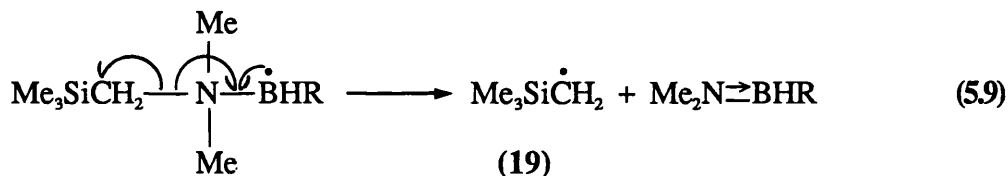
(5.9). In order to confirm the formation of $\text{Me}_3\text{Si}\dot{\text{C}}\text{H}_2$, the authentic radical was generated by u.v. photolysis of a cyclopropane solution containing trimethylsilyl(methyl) chloride (ca. 1.3 M), triethylsilane (ca. 1.3 M), and DTBP (ca. 20 % v/v), which afforded the same spectrum [$\underline{a}$ ($2H_\alpha$) 20.90, $\underline{a}$ ($9H_\gamma$) 0.43 G, and $\underline{g}$ 2.0026 at 261 K] as was obtained from (18; R = H).

At low temperature (ca. 237 K), β-scission is retarded and a stronger spectrum of the amine-alkylboryl radical (18; R = H) is observed, but at higher temperatures (ca. 261 K), β-scission is faster and the spectrum of $\text{Me}_3\text{Si}\dot{\text{C}}\text{H}_2$ becomes relatively strong. The e.s.r. parameters for (18; R = H) are similar to those for $\text{Me}_3\text{N}\rightarrow\dot{\text{B}}\text{H}_2$, implying a similarly pyramidal geometry at boron for both radicals.

A spectrum of $\text{Me}_3\text{Si}\dot{\text{C}}\text{H}_2$ was obtained between 179 and 236 K from dimethyl(trimethylsilylmethyl)amine-thexyl borane (17; R = Me$_2$CHCMe$_2$ = Thx). Rapid β-scission of the amine-alkylboryl radical is probably promoted by the bulky thexyl group because strain is relieved on going to the aminoborane.

$$\text{Me}_3\text{Si}\text{CH}_2\text{N}(\text{Me}_2)\rightarrow\dot{\text{B}}\text{HThx} \longrightarrow \text{Me}_3\text{Si}\dot{\text{C}}\text{H}_2 + \text{Me}_2\text{N}{=}\text{BHThx} \qquad (5.10)$$

Table 5.2 E.s.r. parameters for alkylamine-alkylboryl radicals in cyclopropane solvent

Radical	T/K	g-Factor[a]	Hyperfine splittings (G)[a] $\underline{a}$(^{11}B)	$\underline{a}$(1H$_\alpha$)	Others
Me$_3$N→$\dot{\text{B}}$HBu^n	236	2.0024	58.4	6.4	16.4 (2H$_\beta$)
	260	2.0022	58.3	6.4	16.2 (2H$_\beta$)
Me$_3$N→$\dot{\text{B}}$HBu^i	236	2.0023	58.3	6.4	16.4 (2H$_\beta$)
	260	2.0022	58.2	6.4	16.3 (2H$_\beta$)
Me$_3$N→$\dot{\text{B}}$HBu^t	237	2.0020	57.9	7.8	7.8 (1H$_\beta$)
	261	2.0020	57.8	7.8	7.8 (1H$_\beta$)
Me$_3$SiCH$_2$N(Me$_2$)→$\dot{\text{B}}$H$_2$	237	2.0025	54.7	10.4[b]	—
Me$_3$N→$\dot{\text{B}}$H$_2^{c,d}$	280	2.0022	51.3	9.6	1.4 (1N), 1.4 (9H$_\gamma$)
Me$_3$N→$\dot{\text{B}}$HMe^{e,f}	199	2.0020	61.6	6.1	14.8 (3H)
Me$_3$N→$\dot{\text{B}}$HBu^{t,f}	235	2.0020	60.2	9.0	—

a Corrected for second-order effects. The lines are broad for (**15**) and (**18**); splittings and g-factors are generally accurate to ± 0.2 G and ± 0.0001, respectively. b Two equivalent protons. c t-Butyl alcohol-dimethyl ether (4:1 v/v) solvent. d Data from reference 8. e Oxirane solvent. f Data from reference 2.

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The e.s.r. spectrum obtained during u.v. irradiation of a cyclopropane solution containing 1-methyl-cis-1-azonia-5-boratobicyclo[3.3.0]octane (7; ca. 0.5 M) and DTBP (ca. 20 % v/v) at 261 K was too weak to analyse with certainty, although its general form was as expected for the amine-alkylboryl (20) [see equation (5.11)].

$$\text{Bu}^t\text{O}^\bullet + \text{Me}\blacktriangleright\text{N}\rightarrow\text{B}\blacktriangleleft\text{H} \longrightarrow \text{Me}\blacktriangleright\text{N}\rightarrow\text{B}^\bullet + \text{Bu}^t\text{OH} \qquad (5.11)$$

$$(7) \qquad\qquad\qquad (20)$$
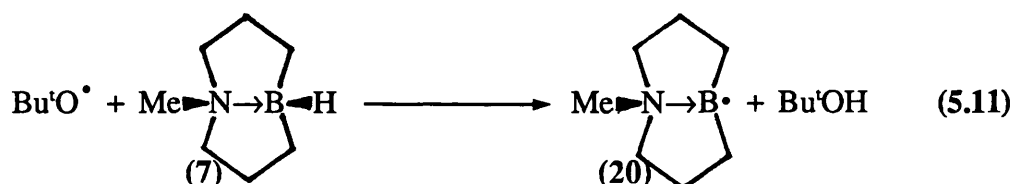
5.2.2   Spin-Trapping with 2-Methyl-2-nitrosopropane

It has been shown previously that ligated boryl radicals of the type $L\rightarrow\overset{\bullet}{\text{B}}\text{H}_2$ (L = R_3N or R_3P) undergo ready addition to 2-methyl-2-nitrosopropane (MNP) to afford nitroxides of the type (21).[25,26] Similar experiments were carried out

$$L\rightarrow\overset{\bullet}{\text{B}}\text{H}_2 + \text{Bu}^t\text{N=O} \longrightarrow L\rightarrow\text{BH}_2\text{N}(\text{Bu}^t)\text{-}\overset{\bullet}{\text{O}} \qquad (5.12)$$

$$(21)$$
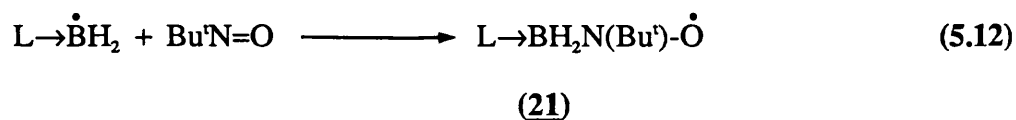
to determine whether amine-alkylboryl radicals could be similarly trapped by MNP.

Benzene solutions containing the amine-alkylborane, MNP, and di-t-butyl hyponitrite (TBHN) as a source of t-butoxyl radicals [equation (5.13)] were heated to ca. 300K in the microwave cavity of the spectrometer.

$$\text{Bu}^t\text{ON=NOBu}^t \xrightarrow{\Delta} 2\text{Bu}^t\text{O}^\bullet + \text{N}_2 \qquad (5.13)$$
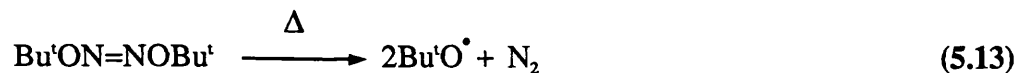
At 300 K, a benzene solution containing MNP (ca. 0.01-0.02 M),

trimethylamine-n-butylborane (ca. 0.5 M), and TBHN (ca. 0.02 M), afforded an

e.s.r. spectrum which we ascribe to a nitroxide of the type (22) [$a(^{14}N)$ 15.3,

a(2H) 10.2, a(2H) 0.50 G, and g 2.0060]. These e.s.r. parameters are very close

$$\overset{\bullet}{C}H_2CH_2R + Bu^tN\overset{\bullet}{O} \longrightarrow Bu^tN(\overset{\bullet}{O})CH_2CH_2R \qquad (5.14)$$

<center>(22)</center>
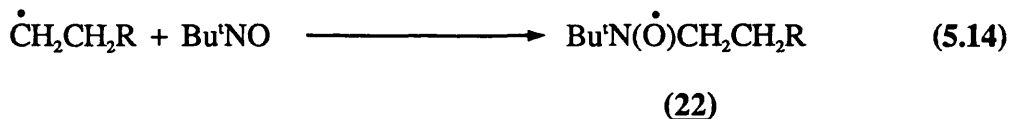
to those reported[26,27] for the nitroxide $Bu^tN(\overset{\bullet}{O})Bu^n$ [$a(^{14}N)$ 15.3, a(2H) 9.2, a(2H)

0.50 G, and g 2.0061 at 298 K]. The origin of the n-butyl radical adduct is not

clear. The blue colour of monomeric MNP persisted throughout these

experiments.

when trimethylamine-n-butylborane was replaced by the bicyclic amine-

borane (7) at 298 K, the e.s.r. spectrum obtained was again that of a nitroxide

of the type (22). It is possible that such a radical could arise from the addition
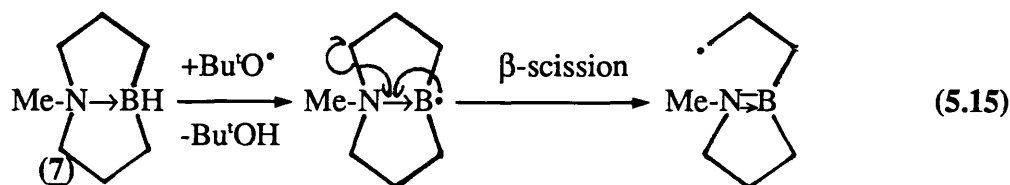
of radical [equation (5.15)] to MNP or, more likely, it could be formed by the

same (unknown) route followed from $Me_3N{\rightarrow}BH_2Bu^n$.

When a similar experiment was attempted with

dimethyl(trimethylsilylmethyl)amine-borane, a spectrum ascribed to the nitroxide

(23) was detected at 300 K [$a(^{14}N_\alpha)$ 11.6, $a(^{11}B)$ 5.9, $a(2H_\beta)$ 10.4, a(1N) 1.8 G,

<center>129</center>

$$\text{Me}_3\text{SiCH}_2\text{N}(\text{Me}_2){\rightarrow}\overset{\bullet}{\text{BH}}_2 \xrightarrow{\text{Bu}^t\text{NO}} \text{Me}_3\text{SiCH}_2\text{N}(\text{Me}_2){\rightarrow}\text{BH}_2\text{N}(\overset{\bullet}{\text{O}})\text{Bu}^t \quad (5.16)$$

$$\underline{(23)}$$
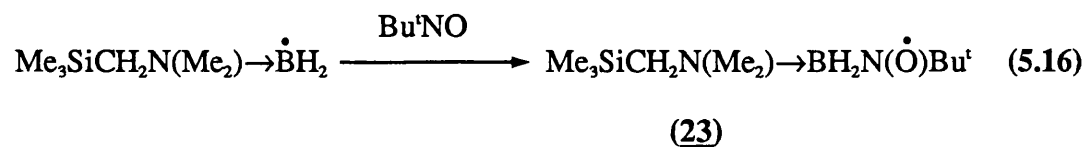
and g 2.0064]. The e.s.r. parameters of $\underline{(23)}$ agree well with those [$\underline{a}(^{14}\text{N}_\alpha)$ 12.3, $\underline{a}(^{11}\text{B})$ 5.8, $\underline{a}(2\text{H}_\beta)$ 10.2, $\underline{a}(1\text{N})$ 2.2 G, and g 2.0064] of $\text{Me}_3\text{N}{\rightarrow}\text{BH}_2\text{N}(\overset{\bullet}{\text{O}})\text{Bu}^t$ obtained by addition of $\text{Me}_3\text{N}{\rightarrow}\overset{\bullet}{\text{BH}}_2$ to MNP at 294 K.[26]

5.2.3 Reactions with Alkyl Halides

In common with the "primary" ligated boryl radicals $\text{L}{\rightarrow}\overset{\bullet}{\text{BH}}_2$ (L = R_3N, R_3P, or R_2S),[8,21,28-30] the ligated alkylboryl radicals rapidly abstract halogen from alkyl bromides [e.g. equation (5.17)]. Alkyl chlorides react less rapidly, whilst

$$\text{L}{\rightarrow}\overset{\bullet}{\text{BHR}} + \text{Pr}^n\text{Br} \longrightarrow \text{Pr}^{n\bullet} + \text{L}{\rightarrow}\text{BHRBr} \quad (5.17)$$
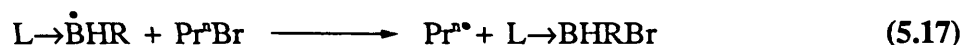
iodides appear to be most reactive. When n-propyl bromide (ca. 1.0 $\underline{\text{M}}$) was present along with ($\underline{14}$; R = Bu^n, Bu^i, or Bu^s), ($\underline{17}$; R = H, Thx), or ($\underline{7}$) and DTBP in cyclopropane at 175-217 K, the e.s.r. spectrum of the amine-boryl radical was not detected, but a strong spectrum of the n-propyl radical [$\underline{a}(2\text{H}_\alpha)$ 22.0, $\underline{a}(2\text{H}_\beta)$ 30.5, $\underline{a}(3\text{H}_\gamma)$ 0.3 G, and g 2.0025 at 196 K] was observed. Similar experiments with $\text{TMEDA}{\rightarrow}2\text{BH}_2\text{Ipc}$ in oxirane also resulted in a strong spectrum of n-propyl radical.

Even though alkyl chlorides would be expected to react less rapidly, a strong spectrum of $\text{Pr}^{n\bullet}$ was observed when n-propyl chloride (ca. 1.0 $\underline{\text{M}}$) was present along with ($\underline{7}$) (ca. 0.5 $\underline{\text{M}}$) and DTBP in cyclopropane at 175-257 K.

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In similar experiments with $Me_3N{\rightarrow}BH_2Bu^n$ and Bu^tCl or 1-chloroadamantane a strong spectrum of the corresponding alkyl radical was observed at 193 K. The detection of a strong, though complex, spectrum from the 1-adamantyl radical (**24**) [$\underline{a}(6H_\beta)$ 6.58, $\underline{a}(3H_\gamma)$ 4.66, $\underline{a}(3H_\delta^{cis})$ 0.80 and $\underline{a}(3H_\delta^{trans})$ 3.08 G, and $\underline{g}$ 2.0028 at 193 K] suggests that amine alkylboranes could usefully replace triethylsilane as a source of halogen-abstracting radical for the production of alkyl radicals from alkylhalides for e.s.r. studies. 1-Bromoadamantane afforded a weaker spectrum of the adamantyl radical under similar conditions.
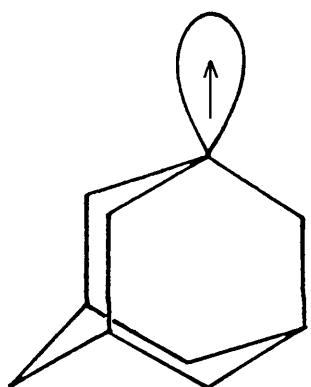
(**24**)

Quantitative competition experiments were carried out in order to determine the relative reactivities of t-butyl and n-propyl bromides towards amine-alkylboryl radicals. Provided that reactions (**5.17**) and (**5.18**) are the only sources of $\overset{\bullet}{R^1}$ and $\overset{\bullet}{R^2}$, and that these species are removed by diffusion-controlled radical-radical reactions, the relative reactivities of the competing halides will be given by equation (**5.19**). The relative radical concentrations, obtained by

$$L{\rightarrow}\overset{\bullet}{B}HR + R^1Hal \xrightarrow{\underline{k}_{5.17}} L{\rightarrow}BHRHal + \overset{\bullet}{R^1} \qquad (5.17)$$

$$L{\rightarrow}\overset{\bullet}{B}HR + R^2Hal \xrightarrow{\underline{k}_{5.18}} L{\rightarrow}BHRHal + \overset{\bullet}{R^2} \qquad (5.18)$$

131
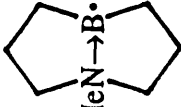
$$\underline{(k}_{5.17}/\underline{k}_{5.18}) = [\dot{R}^1][R^2Hal] \ / \ [\dot{R}^2][R^1Hal] \qquad\qquad (5.19)$$

double integration of suitable lines in the spectra, were extrapolated to zero photolysis time and the calculated values of $(\underline{k}_{5.17}/\underline{k}_{5.18})$ are given in Table 5.3 (also see Figure 5.6).

The selectivity with which the amine-alkylboryl radicals abstract bromine from t-butyl and n-propyl bromides is very similar to that reported for other amine-boryl radicals.[2] As concluded previously,[8] this low selectivity implies a high absolute reactivity, similar to that of $H_3\dot{B}^-$ but greater than that of $H_2\dot{B}CN^-$ and $R_3P{\rightarrow}\dot{B}H_2$. t-Butyl bromide is less reactive than n-propyl bromide towards the amine-alkylboryl radicals, but the two halides are almost equally reactive towards the "primary" amine-boryl radical $Me_3SiCH_2N(Me_2){\rightarrow}\dot{B}H_2$. The relative reactivity of t-butyl bromide towards the amine-alkylboryl radicals increases slightly with increasing temperature. Although the transition state for bromine atom abstraction by amine-alkylboryl radicals would be expected to be very "early", such that the activation energy will be insensitive to the strength of the C-Br bond being broken, steric effects are evidently still important in the transition state and will favour abstraction from the less encumbered primary bromide by the sterically demanding amine-alkylboryl radicals.

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Table 5.3   Relative reactivities of *t*-butyl bromide and *n*-propyl bromide towards various amine-alkylboryl radicals in cyclopropane

Amine-alkylboryl radical	T/K	Ligated borane conc / M	Total alkyl bromide conc / M	k_{Bu^tBr}/k_{Pr^nBr} [b]
$Me_3N{\rightarrow}\dot{B}HBu^n$ [a]	173	1.00	0.91	0.55
	217	1.00	0.91	0.67
$Me_3N{\rightarrow}\dot{B}HBu^i$	173	1.00	0.91	0.55
	217	1.00	0.91	0.69
$Me_3N{\rightarrow}\dot{B}HBu^t$	173	1.00	0.91	0.64
	217	1.00	0.91	0.70
$MeN{\rightarrow}\dot{B}\cdot$ (bicyclic structure)	173	0.30	1.03	0.53
	217	0.30	1.03	0.62
$Me_3SiCH_2N(Me_2){\rightarrow}\dot{B}H_2$	217	0.25	1.08	0.87
	235	0.25	1.08	0.98
$TMEDA{\rightarrow}2\dot{B}HIpc$ [c]	173	0.10	1.08	0.56
	217	0.10	1.08	0.56
$Me_3N{\rightarrow}\dot{B}H_2$ [d,e]	261	1.00	1.00	1.50
$Me_3N{\rightarrow}\dot{B}HMe$ [d]	217	1.00	1.00	1.10

Me₃N→ḂHBuᵗ ᵈ	173	1.00	1.00	0.70
	216	1.00	1.00	0.87
Me₃N→ḂHThx ᶠ	173	1.00	0.91	0.64
	217	1.00	0.91	0.80
Me₃N→ḂHThx ᵈ	173	1.00	1.00	0.67

a The concentration ratio [Bu^{t}Br] / [Pr^{n}Br] = 1.000

b Estimated error ± 10 %.

c Oxirane solvent.

d Data from reference 2.

e t-Butyl alcohol-dimethyl ether (4:1 v/v) solvent.

f Thx = CMe_2CHMe_2.

line 2 of Pr$^{n \bullet}$
rel. intensity 1/8

line 4 of Bu$^{t \bullet}$
rel. intensity 84/512

1 G
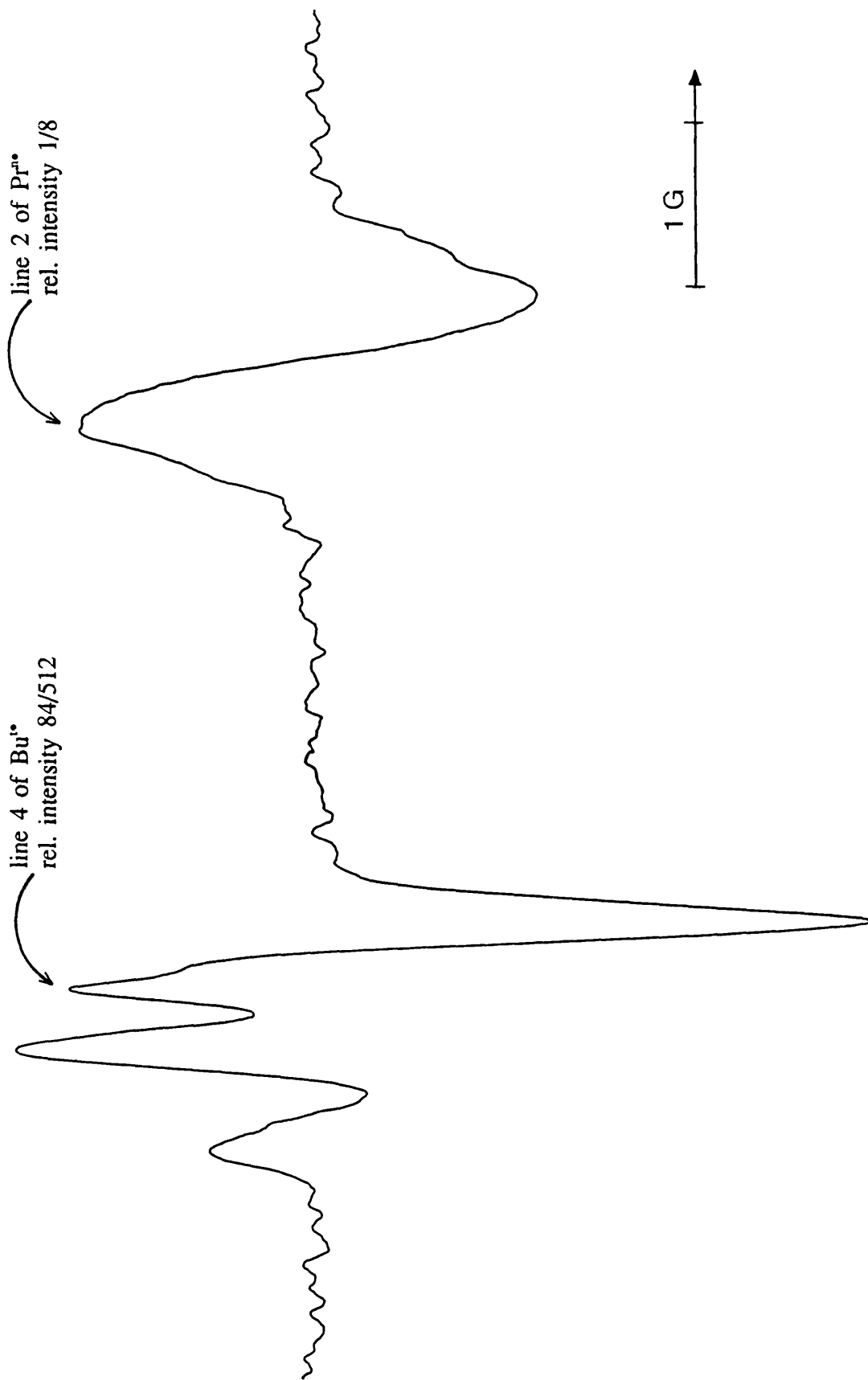
Figure 5.6   E.s.r. spectra in cyclopropane at 173 K of the radicals t-butyl and n-propyl obtained from a mixture of t-butyl and n-propyl bromide (ca. 1 $\underline{M}$) in the presence of Me$_3$N→BH$_2$Bu^t (ca. 1 $\underline{M}$) with DTBP (17 % v/v).

150 camphenyl bromu
p 116

5.3 Catalysed Hydrogen Atom Abstraction by t-Butoxyl Radicals

5.3.1 Hydrogen Atom Abstraction from Esters

Photolysis of an oxirane solution containing ethyl acetate (1.0 $\underline{M}$) and DTBP (20 % v/v) produced a spectrum of the oxiranyl radical (Figure **5.7a**). When the experiment was repeated in the presence of $TMEDA.2BH_2Ipc$ (**13**; $\underline{ca}$. 0.1 $\underline{M}$), a strong spectrum of the α-(ethoxycarbonyl)methyl radical (**25**)[31] [$\underline{a}(H_\alpha)$ 21.35, $\underline{a}(H_\alpha)$ 21.50, $\underline{a}(2H_\delta)$ 1.59 G, and $\underline{g}$ 2.0036 at 200K] was observed

$$CH_3CO_2Et + Bu^tO^\bullet \xrightarrow[\underline{(13)} \text{ Catalyst}]{TMEDA.2BH_2Ipc} H_2\overset{\bullet}{C}CO_2Et + Bu^tOH \qquad (5.20)$$
$$\underline{(25)}$$
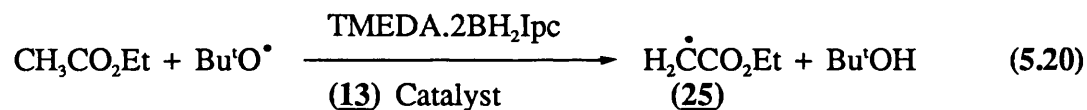
(Figure **5.7b**). The e.s.r. parameters for (**25**) are essentially the same as those reported previously.[31] Similar results were obtained when (**13**) was replaced by (**14**; R = Bu^n, Bu^i, or Bu^s), (**17**; R = H), or (**7**) at 179-261 K in cyclopropane.

The observation of different splittings from the α-hydrogens in $H_2\overset{\bullet}{C}CO_2Et$ is due to restricted rotation about the C-C(O) bond. Delocalisation of the unpaired electron from C_α onto the carbonyl group induces partial double bond character between the carbon atoms [see structures (**26a**) and (**26b**)] and barriers

(26a)   (26b)
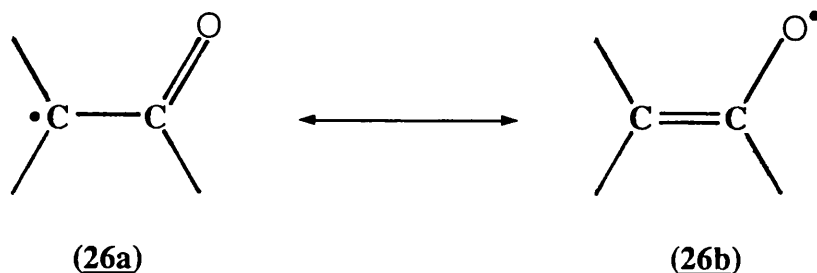
to rotation about the C-C(O) bond in such radicals have been shown to be

(a)

5G

(b)

2G

Figure 5.7

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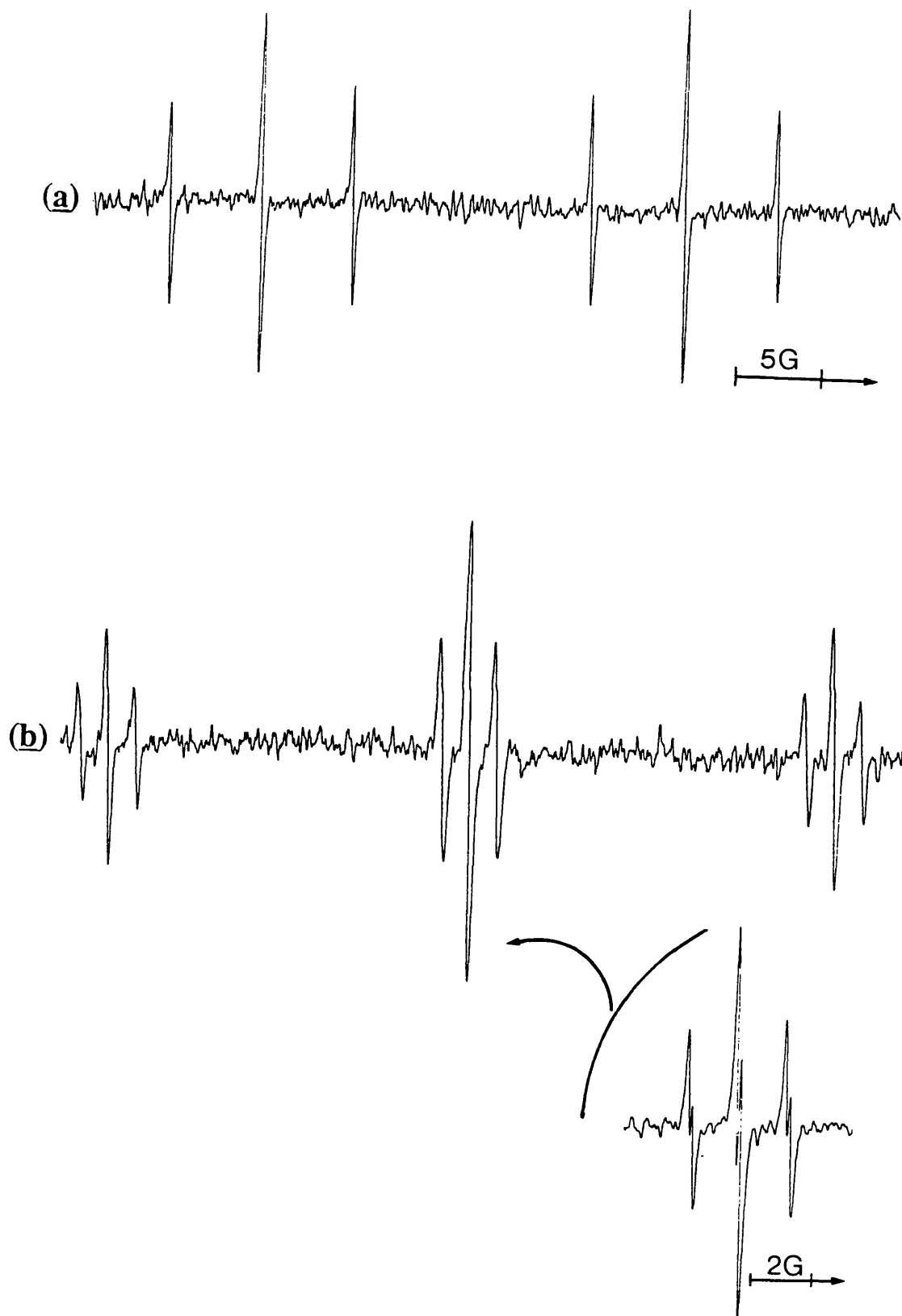
Figure 5.7   E.s.r. spectra in oxirane at 200 K.   (a) The radical $H_2\overset{\boxed{}\bullet}{\text{COCH}}$ produced in the absence of catalyst.   (b) The radical $H_2\overset{\bullet}{\text{C}}CO_2CH_2CH_3$ produced in the presence of $TMEDA.2BH_2Ipc$ (ca. 0.1 M).

<u>ca</u>. 40 kJ mol^{-1}, similar to those found for α-(alkylcarbonyl)alkyl radicals.[31]

The observation of the long-range coupling due to the methylene protons of the ethoxy group is attributable to delocalisation of the unpaired electron onto the alkoxy-oxygen atom [see structure (<u>27</u>)].

$$
\underset{(\underline{27})}{\overset{\displaystyle}{}}
$$
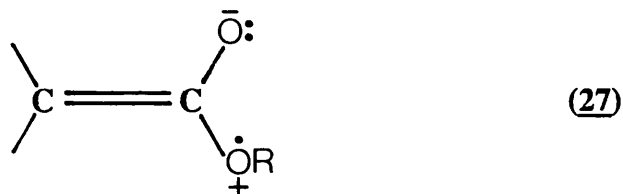
The spectrum of a secondary product radical became evident after samples had been u.v. irradiated for relatively short periods of time. The spectrum consisted of a doublet of triplets of smaller triplets and we assign this to the radical (<u>28</u>) [a(2H) 26.25, a(H) 21.00, and a(2H) 1.63 G at 200 K] produced by

$$
\underset{(\underline{25})}{2H_2\overset{\bullet}{C}CO_2Et} \longrightarrow EtO_2CCH_2CH_2CO_2Et \underset{-H^\bullet}{\longrightarrow} \underset{(\underline{28})}{EtO_2CCH_2\overset{\bullet}{C}HCO_2Et} \qquad (5.21)
$$
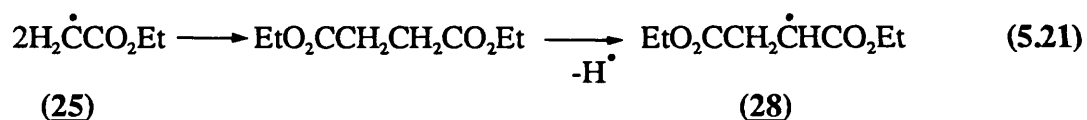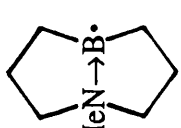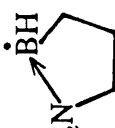
hydrogen abstraction from diethyl succinate, itself formed by dimerisation of (<u>25</u>). The same spectrum was obtained from authentic succinate[32] and the e.s.r. parameters agreed well.

The relative reactivities of ethyl acetate, propanoate, and 2-methylpropanoate towards different amine-alkylboryl radicals under conditions of PRC were determined and the results are summarized in Tables 5.4 and 5.5. The standard competition method[33] was used, making the assumption that the product radicals are removed by diffusion-controlled reactions which have equal rate coefficients. The reactivities are evidently governed by enthalpic, polar and steric factors. The results in Table **5.4** clearly indicate that the steric factors

Table 5.4 Relative reactivites of ethyl propanoate and ethyl acetate towards various amine-alkylboryl radicals in cyclopropane

Amine-alkylboryl radical	T/K	Catalyst conc/M	$[Me\dot{C}HCO_2Et]/[H_2\dot{C}CO_2Et]$[a,b]	$k_{propanoate}/k_{acetate}$	$(k_{propanoate}/k_{acetate})$ mean[c]
$Me_3N{\rightarrow}\dot{B}HBu$[a]	189	0.10	2.11	4.22 ⎤	
	189	0.20	2.00	4.00 ⎬	4.11
	218	0.20	2.79	5.58 ⎦	
$Me_3N{\rightarrow}\dot{B}HBu^i$	189	0.10	1.89	3.78 ⎤	3.88
	189	0.20	1.99	3.98 ⎦	
$Me_3N{\rightarrow}\dot{B}HBu^t$	189	0.10	2.42	4.84 ⎤	4.92
	189	0.20	2.50	5.00 ⎦	
$MeN{\rightarrow}\dot{B}{\cdot}$ (bicyclic)	189	0.13	2.58	5.16 ⎤	5.45
	189	0.26	2.87	5.74 ⎦	
$Me_3SiCH_2N(Me_2){\rightarrow}\dot{B}H_2$	218	0.11	5.25	10.50 ⎤	10.15
	218	0.22	4.90	9.80 ⎦	
$TMEDA.2\dot{B}HIpc$[d]	189	0.10	2.54	5.08 ⎤	5.76
	189	0.20	3.22	6.44 ⎦	
$Me_3N{\rightarrow}\dot{B}HThx$[e]	189	0.10	2.34	4.68 ⎤	4.55
	189	0.17	2.20	4.42 ⎦	
Me_2N...$\dot{B}H$ (cyclic)[e]	189	0.10	4.13	8.26 ⎤	8.33
	189	0.10	4.20	8.40 ⎦	

a The concentration ratio $[H_3CCO_2Et]/[MeCH_2CO_2Et] = 2.000$. b The total concentration of the esters was 1.2 $\underline{M}$. c Estimated error ± 10
d Oxirane solvent. e Data from reference 32.

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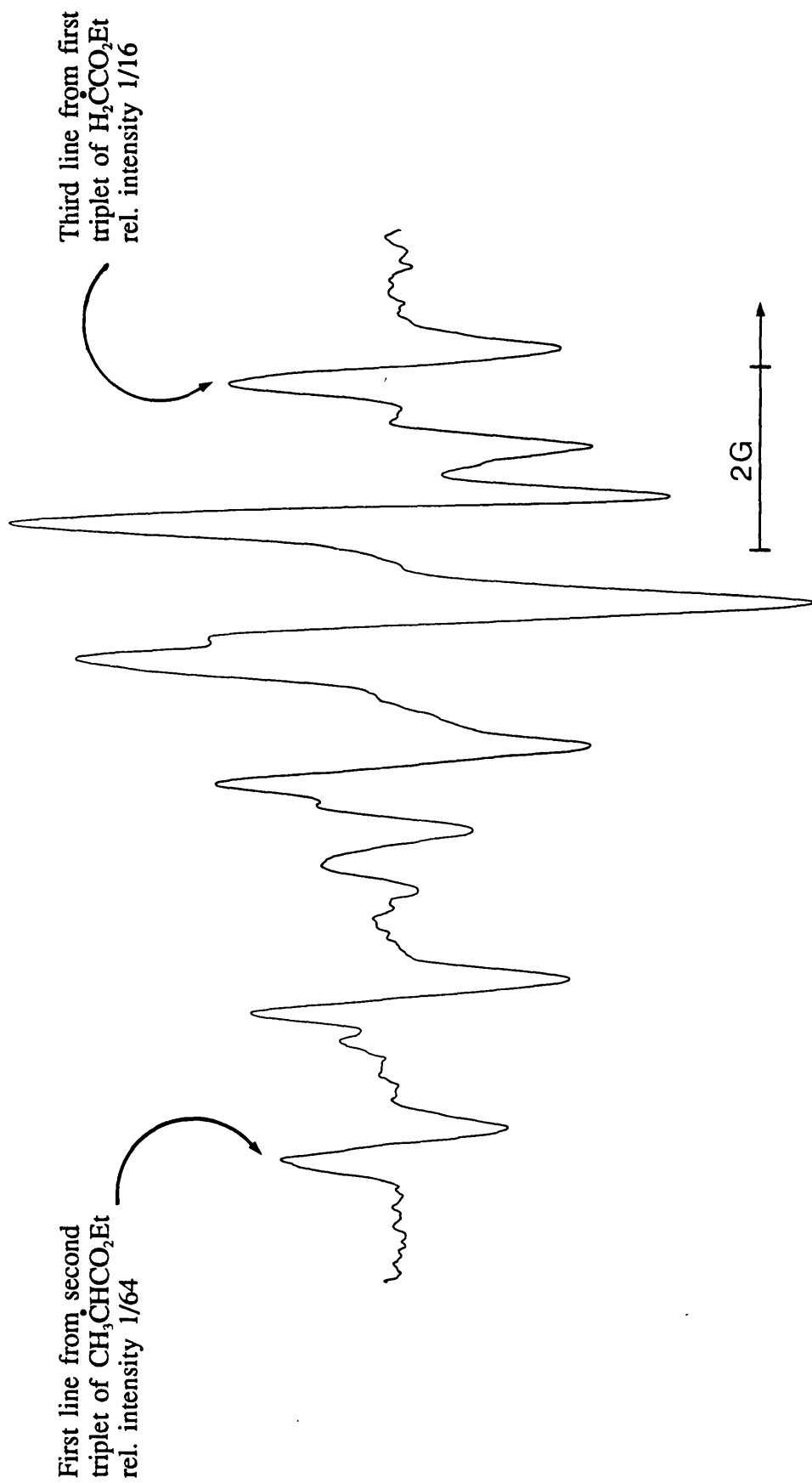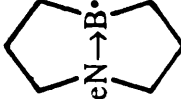
Figure 5.8 E.s.r. spectra in cyclopropane at 189 K of the radicals $H_2\dot{C}CO_2Et$ and $MeH\dot{C}CO_2Et$ produced in the presence of $Me_3N{\rightarrow}BH_2Bu^t$.

play an important part in determining reactivities. As steric crowding around the radical centre is reduced, for example going from $Me_3N{\rightarrow}\overset{\bullet}{B}HBu^s$ to $Me_3SiCH_2N(Me_2){\rightarrow}\overset{\bullet}{B}H_2$, the reactivity of ethyl propanoate increases relative to that of ethyl acetate.

During photolysis of a 2:1 molar mixture of ethyl acetate with ethyl propanoate, DTBP (18 % v/v), and (14; R = Bu^s) in cyclopropane at 189 K (see Figure 5.8), the trimethylamine-s-butylboryl radical was found to be 4.9 times more reactive towards ethyl propanoate than towards ethyl acetate, even though the hydrogen being abstracted in the former ester is presumably less electron deficient than in the latter. It would seem likely that the stability imparted to the transition state when a secondary radical is formed from ethyl propanoate outweighs any reduction in favourable polar effects. When the experiment was repeated using $Me_3SiCH_2N(Me_2){\rightarrow}BH_3$ rather than $Me_3N{\rightarrow}BH_2Bu^s$ ethyl propanoate was now found to be 10.2 times more reactive than the ethyl acetate, in accord with the smaller steric demands of the less bulky silylmethylamine-boryl radical.

Ethyl 2-methylpropanoate was found to be 2.1 times less reactive than ethyl propanoate towards $Me_3N{\rightarrow}\overset{\bullet}{B}HBu^s$ (see Table 5.5). It is proposed that steric rather than polar effects are now dominant and are responsible for the reduction in the reactivity of the 2-methylpropanoate, since the sterically demanding amine-s-butylboryl radical will favour abstraction from the less encumbered propanoate. Towards the less bulky amine-alkylboryl radicals $Me_3SiCH_2N(Me_2){\rightarrow}\overset{\bullet}{B}H_2$ and the bicyclic amine-boryl (20) the 2-methylpropanoate is much the more reactive ester.

Table 5.5 Relative rates of α-hydrogen abstraction from esters by amine-alkylboryl radicals in cyclopropane at 189 K

Amine-alkylboryl radical	Ester reactivity (per molecule)		
	CH_3CO_2Et	$MeCH_2CO_2Et$	Me_2CHCO_2Et
$Me_3N{\rightarrow}\dot{B}HBu^n$	(1)	4.11	3.26
$Me_3N{\rightarrow}\dot{B}HBu^i$	(1)	3.88	3.03
$Me_3N{\rightarrow}\dot{B}HBu^t$	(1)	4.92	2.40
$MeN{\rightarrow}\dot{B}\cdot$ (20)	(1)	5.45	5.92
$Me_3SiCH_2N(Me_2){\rightarrow}\dot{B}H_2$	(1)	10.15	15.38
$TMEDA.2\dot{B}HIpc$ [a]	(1)	5.76	1.35
$Me_3N{\rightarrow}\dot{B}HThx$	(1)	4.55	0.48
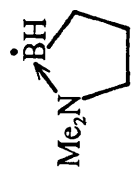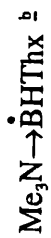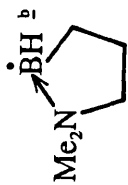
Me$_2$N→·BH (pyrrolidine)	(1)	8.33	9.36
Me$_3$N→·BHThx [b]	(1)	4.50	0.40
Me$_2$N→·BH [b] (pyrrolidine)	(1)	8.30	9.00

a Oxirane solvent.

b Data from V. Paul and B.P. Roberts, J. Chem. Soc., Perkin Trans. 2, 1989, 0000.

5.3.2 Hydrogen Abstraction from Ketones

The carbonyl group in a ketone is a powerful π-electron withdrawing substituent and, like that in an ester, should activate adjacent C-H groups towards abstraction by $Bu^tO^{\bullet}$ in the presence of "donor" polarity reversal catalysts.

Photolysis of a cyclopropane solution containing acetone (1.24 $\underline{M}$) and DTBP (36 % v/v) at 201 K in the absence of any catalyst, afforded a very weak spectrum of the α-carbonylalkyl radical ($\underline{29}$) (for e.s.r. parameters see

$$Bu^tO^{\bullet} + Me_2CO \xrightarrow{\text{slow}} Bu^tOH + MeCO\overset{\bullet}{C}H_2 \qquad (5.22)$$

$$(\underline{29})$$
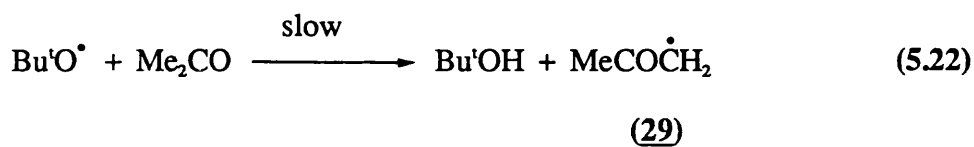
Table 5.6), along with other e.s.r. signals. The spectra of secondary product radicals also grew-in with time; these secondary species could be formed by photoreactions of the ketone, for example photoreduction, which would produce $CH_3\overset{\bullet}{C}(OH)CH_3$. In marked contrast, when the experiment was repeated in the presence of $Me_3N{\rightarrow}BH_2Thx$ ($\underline{1}$) (0.2 $\underline{M}$) as a polarity reversal catalyst, a very strong spectrum of ($\underline{29}$) alone was observed. The single step (5.22) has been replaced by the catalytic cycle (5.23) and (5.24).

$$Bu^tO^{\bullet} + Me_3N{\rightarrow}BH_2Thx \xrightarrow{\text{fast}} Bu^tOH + Me_3N{\rightarrow}\overset{\bullet}{B}HThx \qquad (5.23)$$

$$Me_3N{\rightarrow}\overset{\bullet}{B}HThx + Me_2CO \xrightarrow{\text{fast}} Me_3N{\rightarrow}BH_2Thx + MeCO\overset{\bullet}{C}H_2 \qquad (5.24)$$

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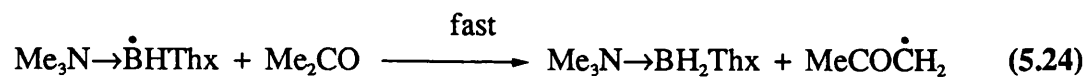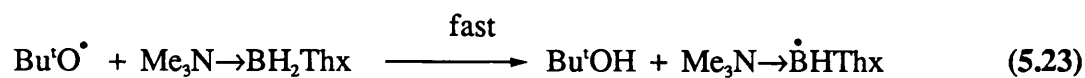
Restricted rotation about the C-C(O) bond in α-(alkylcarbonyl)alkyl radicals,[31] similar to that described before for α-(alkoxycarbonyl)alkyl radicals, is responsible for non-equivalence of the α-protons in MeCOĊH₂. Stabilisation of the α-carbonylalkyl radical by conjugative delocalisation of the unpaired electron onto oxygen is also responsible for the relatively high g-value of MeCOĊH₂ (2.0045) as compared with H₃Ċ (2.0026). CH bond weakening in acetone owing to delocalisation in (29) makes reaction (5.22) appreciably exothermic. Despite being necessarily less exothermic than reaction (5.22), reaction (5.24) proceeds much more rapidly, because the transition state will be strongly stabilised by polar effects. The transition state for reaction (5.24) can be represented as a resonance hybrid of structures (30a-c) and the ionic form (30c) would be expected to make a major contribution. The ionization potential of Me₃N→ḂHThx is probably very low (that calculated[32] for H₃N→ḂHMe is 6.4 eV) and the electron affinity of an α-carbonylalkyl radical

Me₃N→ḂHThx   H-CH₂COMe ⟷ Me₃N→BHThx-H   ĊH₂COMe

(30a)   (30b)

Me₃N→B⁺HThx   Ḣ   :C̄H₂COMe

(30c)
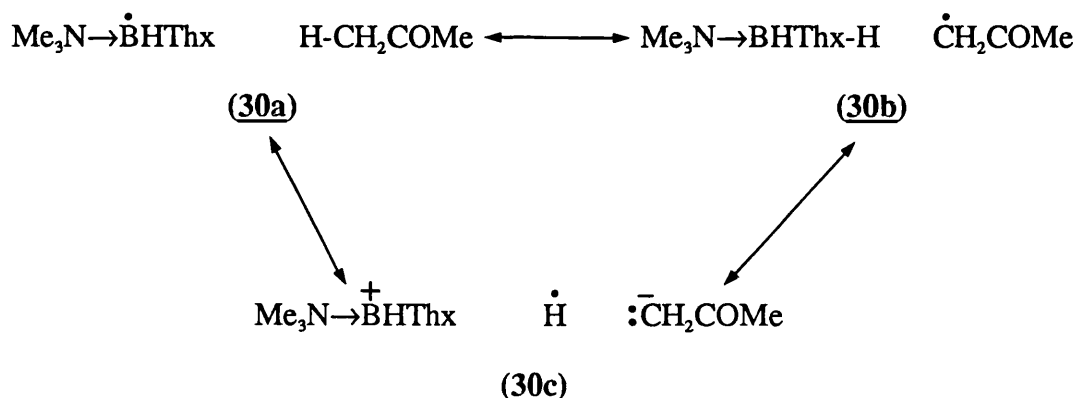
will be relatively large because of the high stability of the enolate ion produced by electron addition. For comparison, e.s.r. data for the substituted methyl radical derived in a similar way from 3-methylbutan-2-one are included in the

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Table **5.6.**

Photolysis of a cyclopropane solution containing cyclohexanone (0.88 $\underline{M}$) and DTBP (36 % v/v) afforded <u>mainly</u> the 2-oxocyclohexyl radical (<u>31</u>) along with other radicals. However, in the presence of (<u>1</u>) (0.2 $\underline{M}$), <u>only</u> a strong spectrum of (<u>31</u>) (see Figure **5.9**) was observed.
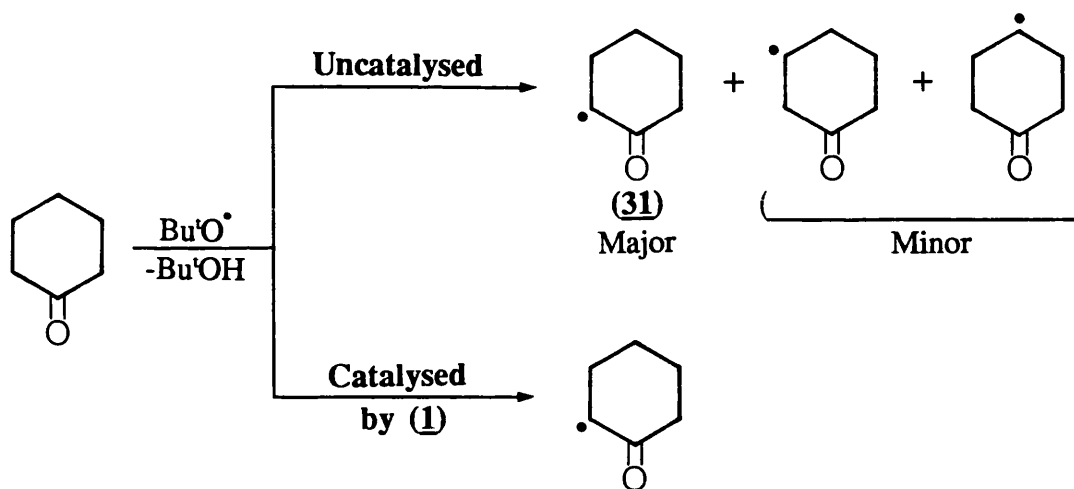
The 2-oxocyclohexyl radical is thought to exist in the half-chair conformation shown in structures (<u>32a</u> and <u>b</u>).[34] At low temperatures (147 K), $H_\beta{}^{ax}$ and $H_\beta{}^{eq}$ are magnetically non-equivalent because exchange resulting from

(<u>32a</u>)   (<u>32b</u>)
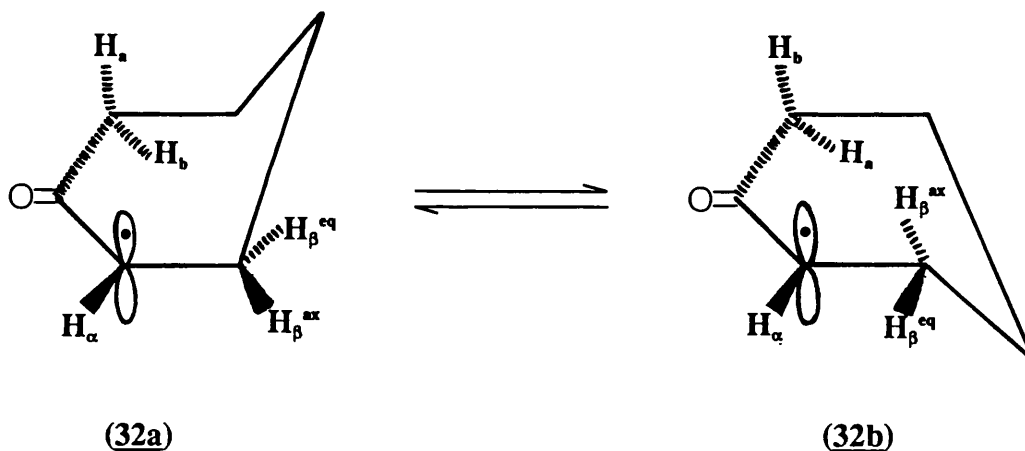
ring inversion is slow on the e.s.r. time scale.

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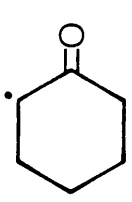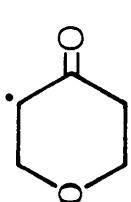
Hyperfine splitting from a β-hydrogen depends on the dihedral angle (θ) between the semi-occupied orbital of the unpaired electron and the β-C-H bond [as shown in (33)] and it is given by the Heller-McConnell equation (5.25), in which $\underline{A}$ (ca. 1 G) and $\underline{B}$ (ca. 58.5 G) are constants and $\rho^{\pi}c_{\alpha}$ is the π spin

(33)
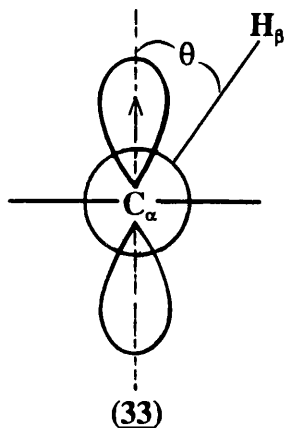
$$\underline{a}(H_{\beta}) = (\underline{A} + \underline{B}\text{Cos}^2\theta)\,\rho^{\pi}c_{\alpha} \qquad (5.25)$$

population on C_{α}. The mechanism of spin transmission is hyperconjugation, which is at a maximum when the dihedral angle is zero and vanishes when θ = 90°. The differences in the observed splittings for $\underline{a}(H_{\beta}^{\pi x})$ and $\underline{a}(H_{\beta}^{eq})$ in the radical (31) at low temperatures (147 K) arise because of the differences in the dihedral angles which each C-H bond makes with the orbital of the unpaired electron. As the temperature increases, interconversion between the two half-chair conformations (32a and b) to exchange the β-hydrogens becomes faster. The central line of the β-proton triplet ($M_I = 0$) is broadened when the inversion occurs at an "intermediate" rate, but as the temperature increases still further, the β-protons become magnetically equivalent and a 1:2:1 triplet is observed when the unpaired electron "sees" two protons in an "average" environment. For further discussion of this type of alternating line width effect see Chapter 2.

Table 5.6   E.s.r. parameters for radicals obtained by catalytic hydrogen abstraction from ketones in the presence of $Me_3N \rightarrow BH_2Thx$

Radical	T/K	Solvent [a]	g-Factor	Hyperfine coupling constants (G)
$\dot{C}H_2C(O)CH_3$	201	A	2.0045	20.04 (1H), 19.50 (1H), 0.1 (3H)
$\dot{C}H_2C(O)CHMe_2$ [b]	189	A	2.0044	19.93 (1H), 19.60 (1H), 0.66 (1H), 0.33 (6H)
	147	A	2.0046	43.38 ($1H_\beta^{ax}$), 23.62 ($1H_\beta^{eq}$), 17.84 ($1H_\alpha$), 1.31 ($1H_a$)
	179	B	2.0045	40.16 ($1H_\beta$), 28.40 ($1H_\beta$), 17.80 ($1H_\alpha$)

a   A = Cyclopropane.   B = Oxirane.
b   Data from ref. 32.

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Figure 5.9

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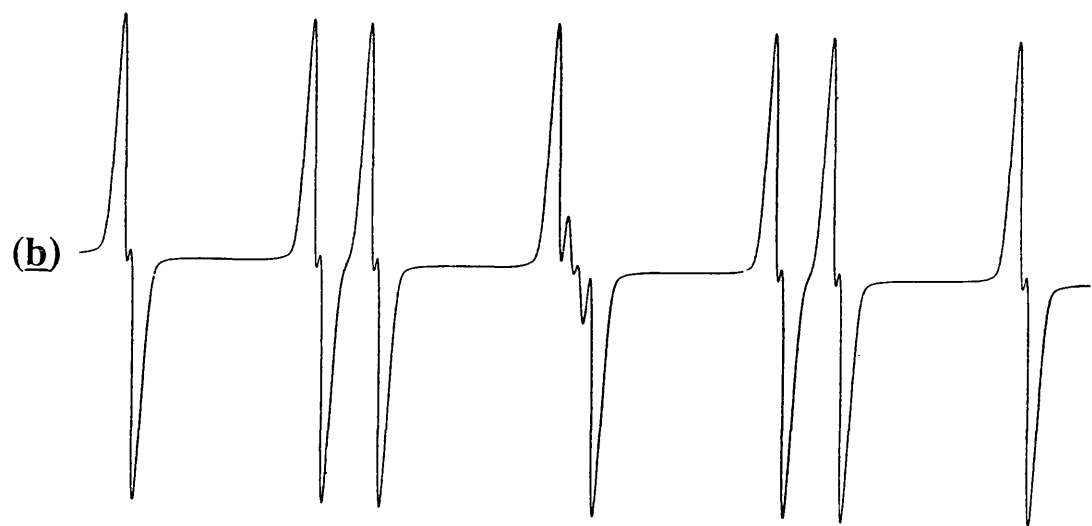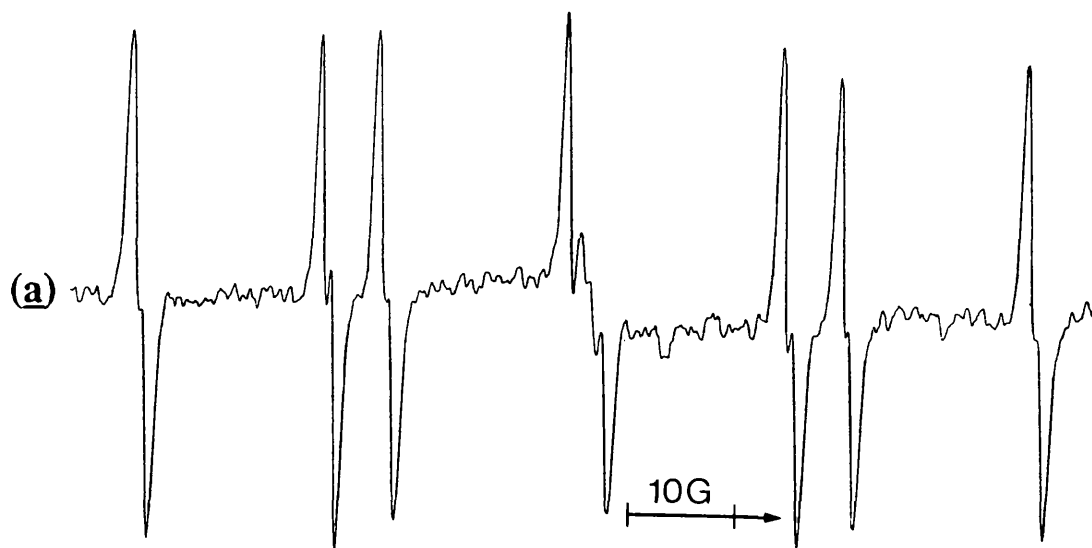
Figure captions

Figure 5.9 (a) E.s.r. spectrum of 2-oxocyclohexyl radical (**31**) in cyclopropane produced in the presence of $Me_3N \rightarrow BH_2Thx$ (0.2 **M**) at 147 K. (b) Computer simulation of (**31**).

Catalysed abstraction from tetrahydro-4H-pyran-4-one (0.98 M) afforded the radical (34a) at 179 K. The control of regioselectivity which may be exercised
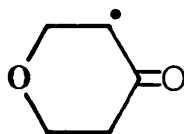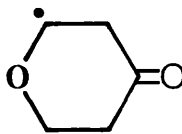
(34a)   (34b)

using PRC was strikingly illustrated here, because in the absence of $Me_3N{\rightarrow}BH_2Thx$ as catalyst (34b) was now formed almost to the exclusion of (34a). Lineshape effects resulting from conformational exchange were observed for both (34a) and (34b) and were similar to those observed for the 2-oxocyclohexyl radical (31). Analogous lineshape effects have been observed previously for numerous other radicals containing six-membered rings[35-39] and the rate constants and activation energies for ring inversion have been obtained in many cases.

Quantitative study of ring inversion for (34a) was undertaken using lineshape analysis. The rate constants (k/s^{-1}) at four different temperatures were obtained by computer simulation and the results are shown in Table 5.7. An Arrhenius plot of these data yielded an activation energy of 27.3 kJ mol^{-1} and a pre-exponential factor of 8.4×10^{13} s^{-1} for conformational exchange in (34a).

Radical (34a) contains two sp^2-hybridised carbon atoms in the ring and the activation energy for ring inversion may be compared with that for a similar diamagnetic molecule. Cyclohexanone has only one sp^2-carbon and the inversion barrier has not been measured for the molecule (35). Therefore, cyclohexene

150
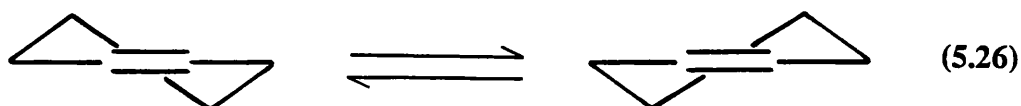
Table 5.7

The rate constants for an Arrhenius plot

T/K	$1/T$ /K^{-1}	k/s^{-1}	$\log_{10}(k/s^{-1})$
211	4.74×10^{-3}	1.48×10^{7}	7.17
238	4.20×10^{-3}	7.75×10^{7}	7.89
260	3.85×10^{-3}	2.68×10^{8}	8.43
265	3.78×10^{-3}	4.23×10^{8}	8.63
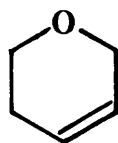
(35)

which has two sp^2 carbons was chosen. The preferred conformation is a half-chair in equilibrium with its mirror image [equation (5.26)], which is similar to

(5.26)

the conformation of the radical (34a) [see equation (5.27)]. Moreover, the

(5.27)
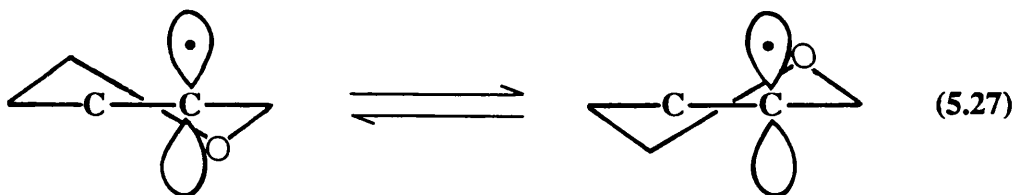
major canonical contributors for (34a) also resemble cyclohexene [see (36a and
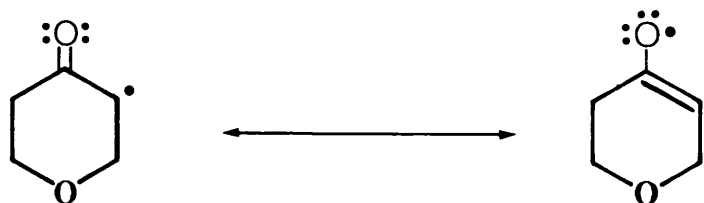
(36a)   (36b)

b)]. The barrier to ring inversion for cyclohexene is 22.2 kJ mol^{-1}, which is very similar to that obtained in this work for the radical (34a).

5.3.3   Hydrogen Abstraction from Lactones

U.v. irradiation of an oxirane solution containing β-propiolactone (ca. 1 M)

and DTBP (17 % v/v) between 169 and 261 K afforded a strong spectrum of

oxiranyl radical [$\underline{a}(1H_\alpha)$ 24.63, $\underline{a}(2H_\beta)$ 5.50 G, and $\underline{g}$ 2.0033] at all

temperatures. When the experiment was repeated in the presence of (1) (ca. 0.2

M), the spectrum of (37) was observed (see Table 5.8 for e.s.r. parameters).

$$\text{Bu}^t\text{O}^{\bullet} + \quad \underset{\text{catalyst}}{\overset{+\ (1)}{\xrightarrow{\hspace{3cm}}}} \quad \text{(37)} \quad +\ \text{Bu}^t\text{OH} \quad (5.28)$$
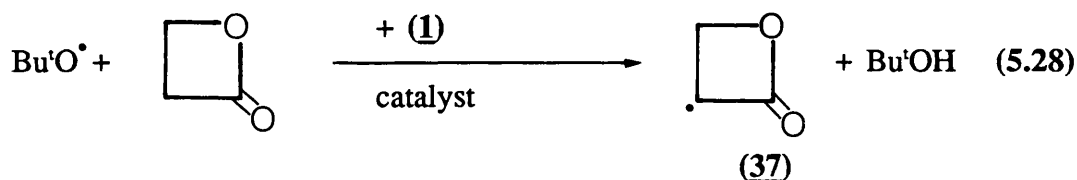
The spectrum appeared as a doublet of triplets, which results from coupling of

the unpaired electron with one α-proton and two β-protons, respectively. The

coupling to the β-protons is relatively large (24.88 G) because the average

dihedral angle subtended by each β-C-H bond is only ca. 30°. The π

conjugative interactions between the unpaired electron and the carbonyl group

and between the latter and the endocyclic oxygen atom should hold the ring in

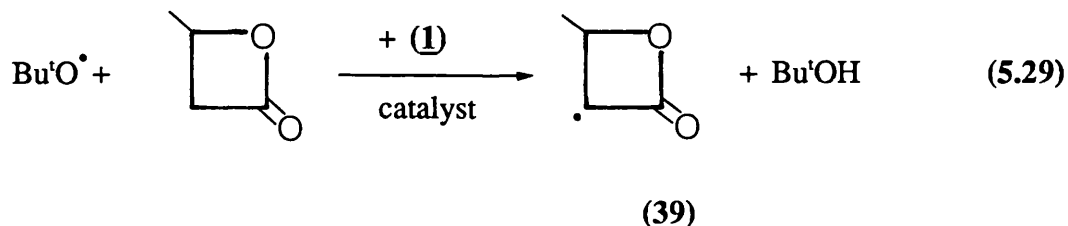a near-planar conformation, as shown in (38). The large value of $\underline{a}(H_\alpha)$ (21.88

(38)
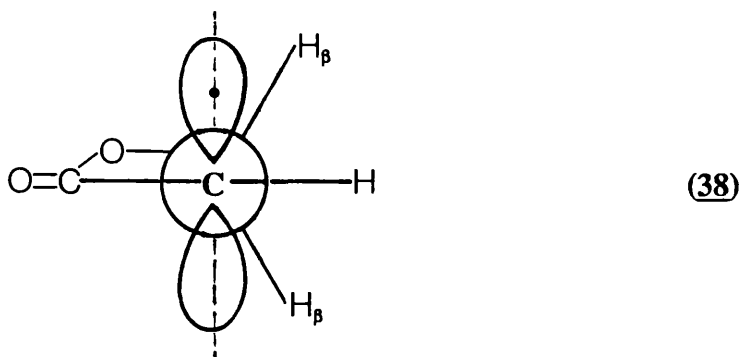
G), which is similar to the average value found for $\overset{\bullet}{C}H_2CO_2Et$ (21.43 G),

supports this conclusion.

In similar experiments with (±)-β-butyrolactone (ca. 1 M) in the presence

of (**1**) (0.2 **M**), the spectrum of (**39**) was observed (Figure **5.10**). The coupling

$$\text{Bu}^t\text{O}^{\bullet} + \quad \text{[}\beta\text{-lactone ring with =O]} \quad \xrightarrow[\text{catalyst}]{+\ (\mathbf{1})} \quad \text{[radical ring with =O]} \quad + \text{Bu}^t\text{OH} \qquad (5.29)$$

(**39**)

to the single β-proton is smaller than $\underline{a}(H_\beta)$ for the radical (**37**) derived from β-propiolactone. The dihedral angle subtended by the β-methyl group is probably less than 30°, for steric reasons, causing the β-C-H bond to subtend an angle greater than 30° and resulting in the reduction in $\underline{a}(H_\beta)$ [see structure (**40**)]. Some slight deviation from planarity of the ring would also probably be involved.

(**40**)
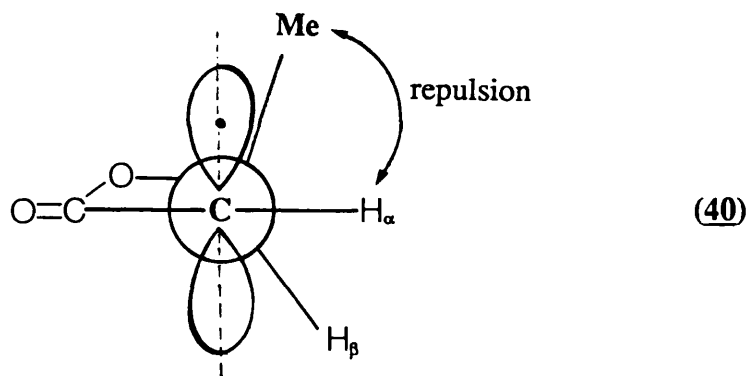
U.v. irradiation of an oxirane solution containing diketene (<u>ca.</u> 1 **M**) and DTBP (<u>ca.</u> 17 % v/v) at 169 K afforded an e.s.r. spectrum which we ascribe to a mixture of the oxiranyl radical and the allylic radical (**41**). The spectrum of (**41**) became relatively more intense at higher temperatures. In the presence of (**1**) (<u>ca.</u> 0.2 **M**) as a polarity reversal catalyst, only a strong spectrum of (**41**) was observed (Figure **5.11**).

The relatively high reactivity of diketene towards $\text{Bu}^t\text{O}^{\bullet}$ which results in the detection of (**41**) even in the absence of the catalyst is attributed to the
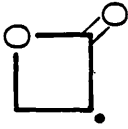
154

HB

HA—⟨ O

(41a)

HB

HA • ⟨ O

(41b)
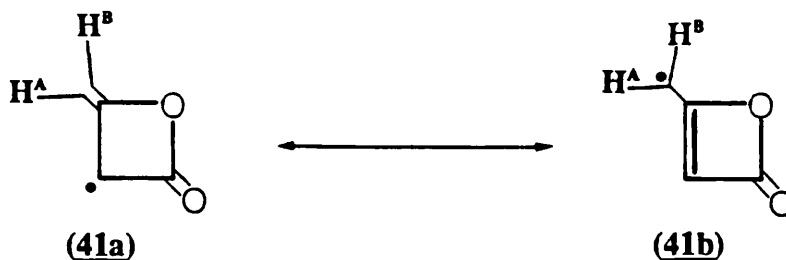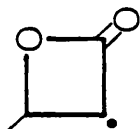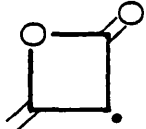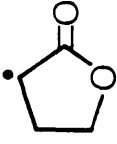
allylic nature of (41). Allylic delocalisation is also responsible for the relatively

large splittings (10.75 and 10.00 G) from the γ-protons H^A and H^B and for the

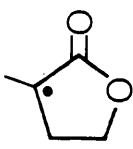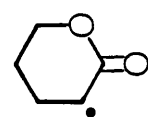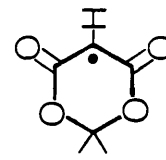relatively low value of $\underline{a}$(H$_\alpha$).

During photolysis of a solution containing α-methyl-γ-butyrolactone ($\underline{ca}$. 1.0

$\underline{M}$) and DTBP (18 % v/v) in oxirane between 169-260 K only a weak spectrum

ascribed to (42) was observed (no spectrum of the oxiranyl radical was seen

H   CH$_3$

H

O

O

(42)
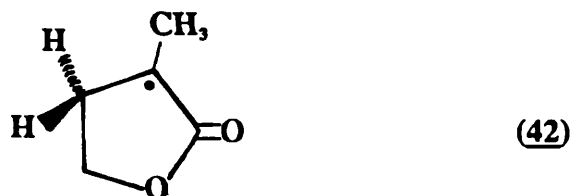
at any temperature). In the presence of (1) ($\underline{ca}$. 0.1 $\underline{M}$), a strong spectrum of

(42) was observed (Figure 5.12). The spectrum of (42) was analysed as triplet

of quartets of small triplets, which arise from coupling of the unpaired electron

with five β-protons (2+3) and two γ-protons. It seems likely that the five-

membered ring in (42) is close to planar and there will be free rotation about

the C$_\alpha$-CH$_3$ bond. If the dihedral angle θ in the Newman projection (42a) is

30°, a value of 32.5 G would be predicted for $\underline{a}$(2H$_\beta$) on the basis of the

Heller-McConnell equation (5.25). The experimental value is 5 G greater than

Table 5.8 E.s.r. parameters for radicals obtained by catalytic hydrogen abstraction from lactones and related compounds in the presence of $Me_3N{\rightarrow}BH_2Thx$

Radical	T/K	Solvent [a]	g-Factor	Hyperfine coupling constants (G)
(37)	169	A	2.0035	24.88 ($2H_\beta$), 21.88 ($1H_\alpha$)
(39)	166	A	2.0034	21.76 ($1H_\beta$), 21.74 ($1H_\alpha$), 0.31 ($3H_\gamma$)
(41)	169	A	2.0032	16.38 ($1H_\alpha$), 10.75 ($1H_\gamma$), 10.00 ($1H_\gamma$)
b	225	A	2.0035	41.35 ($2H_\beta$), 20.30 ($1H_\alpha$), 1.02 ($2H_\gamma$)

Compound				Hyperfine couplings
(42)	A	169	2.0037	37.50 (2H$_\beta$), 21.65 (3H$_\beta$), 0.73 (2H$_\gamma$)
(44)	B	249	2.0034	34.81 (2H$_\beta$)^c, 19.75 (1H$_\alpha$), 0.46 (2H$_\gamma$)
(46)	A	158	2.0045	19.38 (1H$_\alpha$)
(Bu^{t}CO$_2$)$_2$CH b	B	189	2.0039	20.40 (1H$_\alpha$)

Concentrations of lactones and related compounds were (ca. 1 M), Me$_3$N→BH$_2$Thx (ca. 0.1-0.2 M) and DTBP (15-18 % v/v).

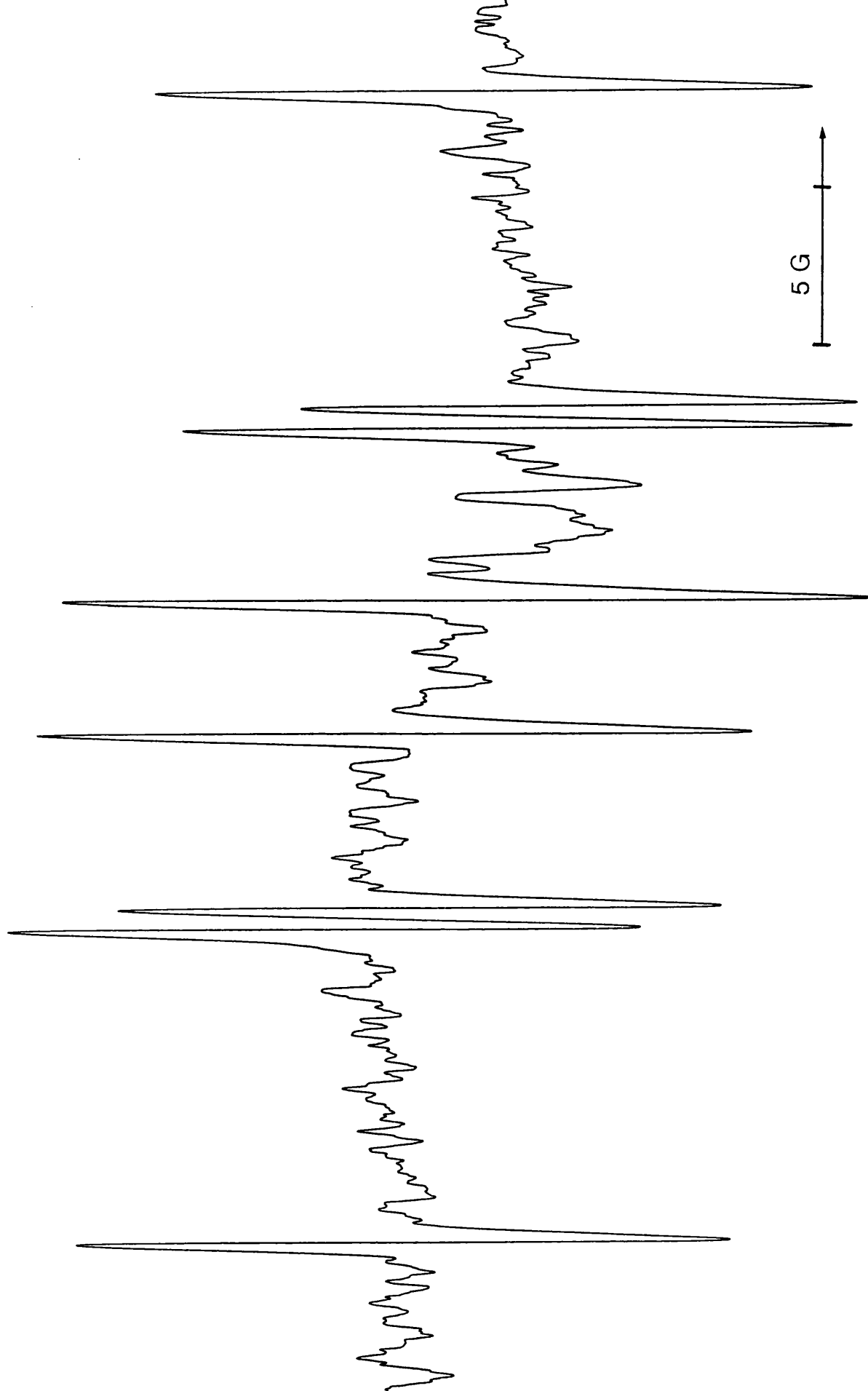a A = Oxirane; B = Cyclopropane.

b Data from Reference 32.

c a (2H$_\beta$).

156

(a)

5G

(b)

0·5G

0.5G

Figure 5.10

157
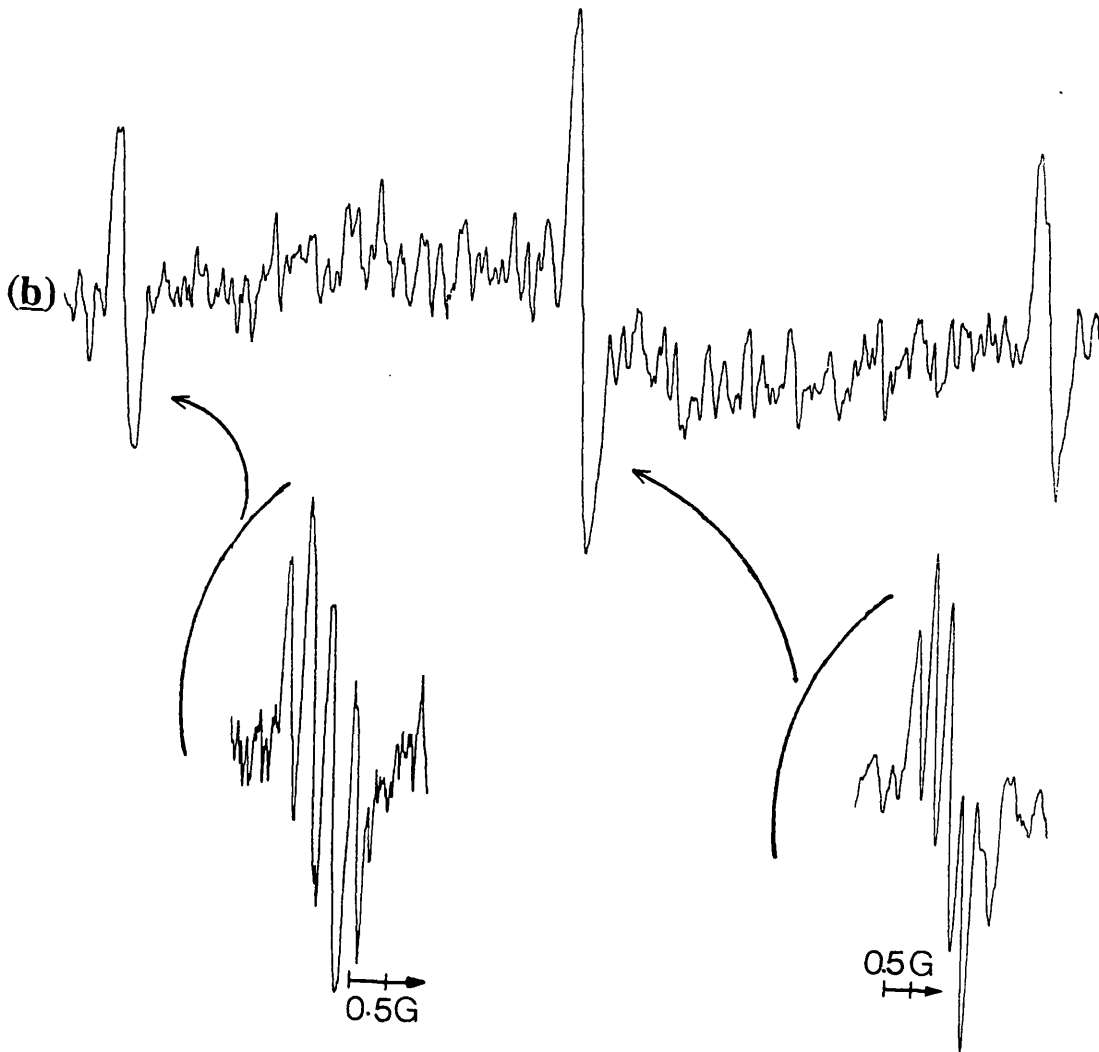
Figure captions

Figure 5.10   E.s.r. spectra in oxirane at 166 K.   (a)   The oxiranyl radical produced in the presence of (±)-β-butyrolactone (<u>ca</u>. 1 <u>M</u>) and DTBP.   (b)   The radical (<u>39</u>) produced from (±)-β-butyrolactone (<u>ca</u>. 1 <u>M</u>) in the presence of Me₃N→BH₂Thx (0.2 <u>M</u>).

Figure 5.11 E.s.r. spectrum of (**41**) produced by photolysis of diketene (ca. 1 $\underline{M}$) and DTBP in the presence of $Me_3N{\rightarrow}BH_2Thx$ (0.2 $\underline{M}$) in oxirane solvent.

159
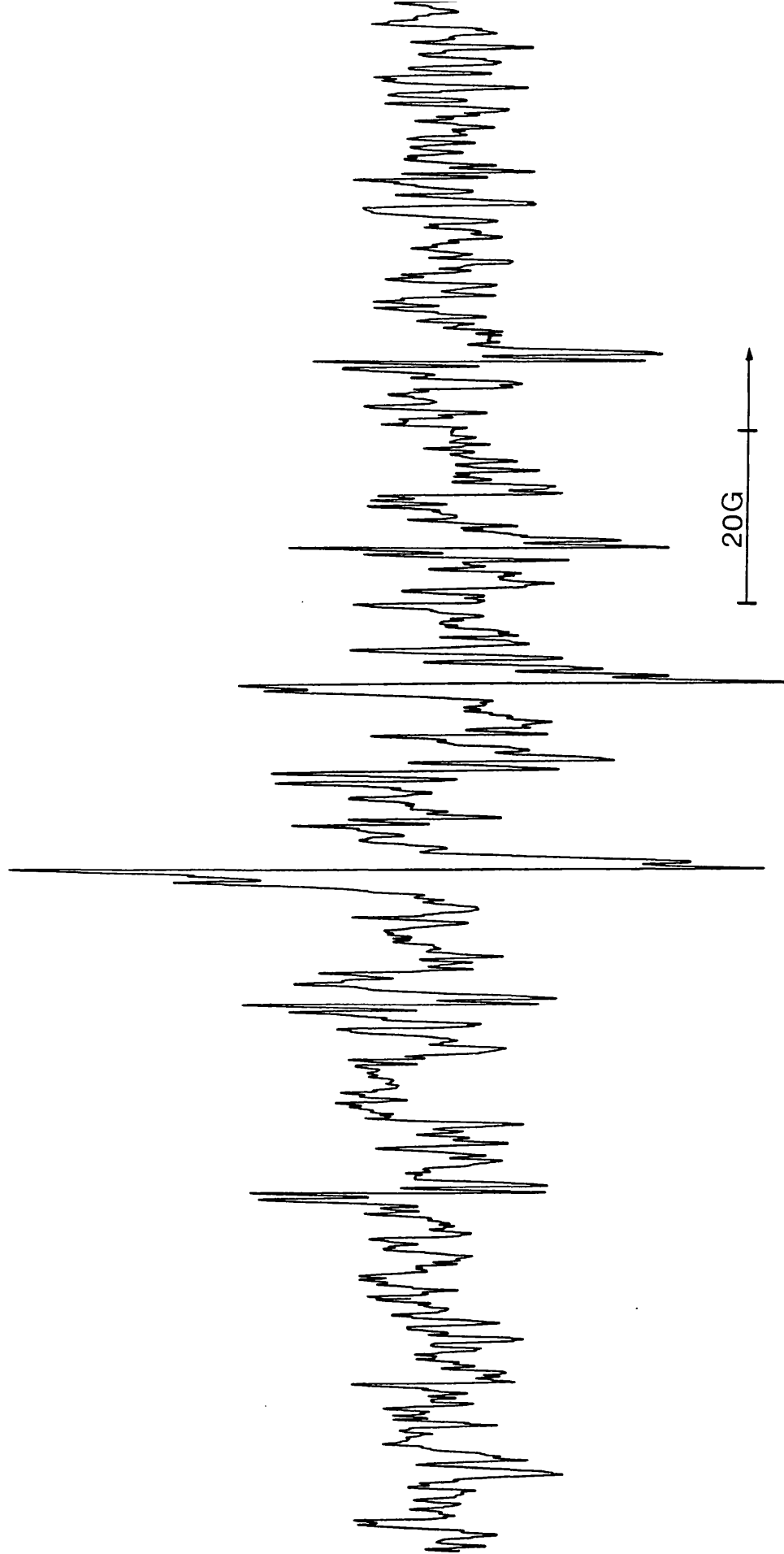
Figure 5.12 E.s.r. spectrum of (**42**) produced by photolysis of α-methyl-γ-butyrolactone (<u>ca.</u> 1 <u>M</u>) and DTBP in the presence of Me₃N→BH₂Thx (0.1 <u>M</u>) in oxirane solvent.

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this. Possibly θ is less than 30° (which would relieve angle strain in the ring) and/or spin population on the endocyclic oxygen atom gives rise to a contribution to $\underline{a}(2H_\beta)$.

(42a)
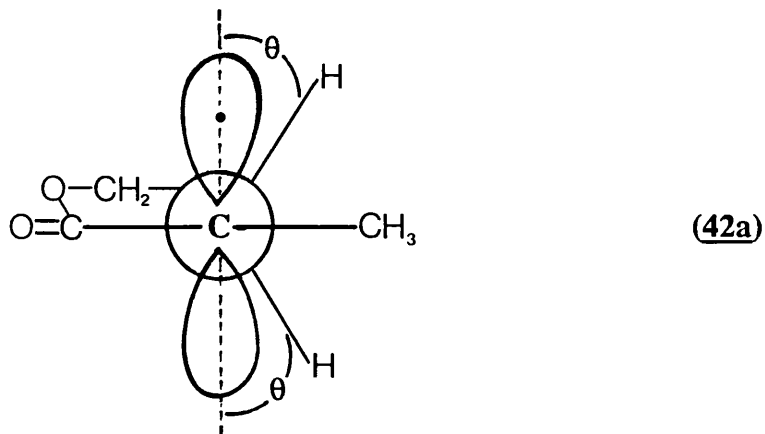
In a similar experiment with δ-valerolactone (<u>ca.</u> 1 <u>M</u>) and DTBP (15 % v/v) in the absence of catalyst, the spectrum observed showed the presence of a mixture of two radicals, one of which could be analysed in terms of $\underline{a}(2H_\beta)$ 27.75, $\underline{a}(1H_\alpha)$ 19.6, $\underline{a}(2H_\gamma)$ 0.28 G, and $\underline{g}$ 2.0030 at 249 K. This spectrum is ascribed to (<u>43</u>), and the other is attributed to the α-carbonyl-substituted radical
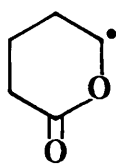

(<u>43</u>)
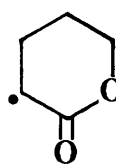
(<u>44</u>)

(<u>44</u>) (see Table **5.8** for its e.s.r. parameters). No spectrum due to the oxiranyl radical was seen at any temperature between 249 and 276 K. When the experiment was repeated in the presence of (<u>1</u>) (<u>ca.</u> 0.1 <u>M</u>), a strong spectrum of (<u>44</u>) was observed (Figure **5.13**). A 1:2:1 triplet was observed for (<u>43</u>)

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because of magnetic equivalence of the two β-protons at 249 K, while the central lines of the β-proton triplet were broadened beyond detectability for (44) at the same temperature [Figure **5.13** (a)]. It is possible that the barrier to ring inversion for (43) could be lower than that for (44). However, the mean value of $\underline{a}(2H_\beta)$ is much smaller (27.75 G) for (43) than for (44) (34.8 G), and hence the <u>difference</u> between the couplings from the two β-protons will probably be much greater for (44) than for (43). If this is so, then a greater rate of ring inversion would be required to average out the splittings from the β-protons in (44) than in (43).

The presence of two electron withdrawing carboalkoxy groups in 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) (45) should mean that the α-methylene hydrogens are highly reactive towards abstraction by a nucleophilic amine-alkylboryl radical. With (45) (<u>ca</u>. 1 <u>M</u>) between 158-260 K in the absence of catalyst only the spectrum of oxiranyl radical derived from the solvent was observed at low temperatures (158 K), but as the temperature was raised, a second spectrum appeared which is assigned to the radical (46). The

(46)
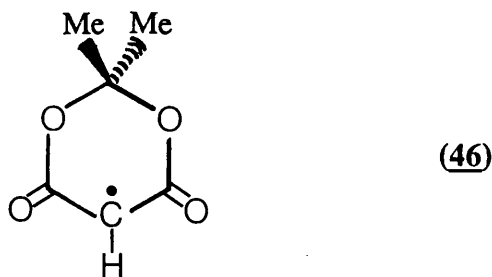
spectrum of oxiranyl radical only reapeared when temperature was lowered again. In the presence of (1) (0.2 <u>M</u>), the spectrum of (46) was observed and that of the oxiranyl radical was absent. However, the spectrum of an another radical (a single line at g 2.0045) was also evident. This second radical might

(a)

20 G

1G

(b)

1G
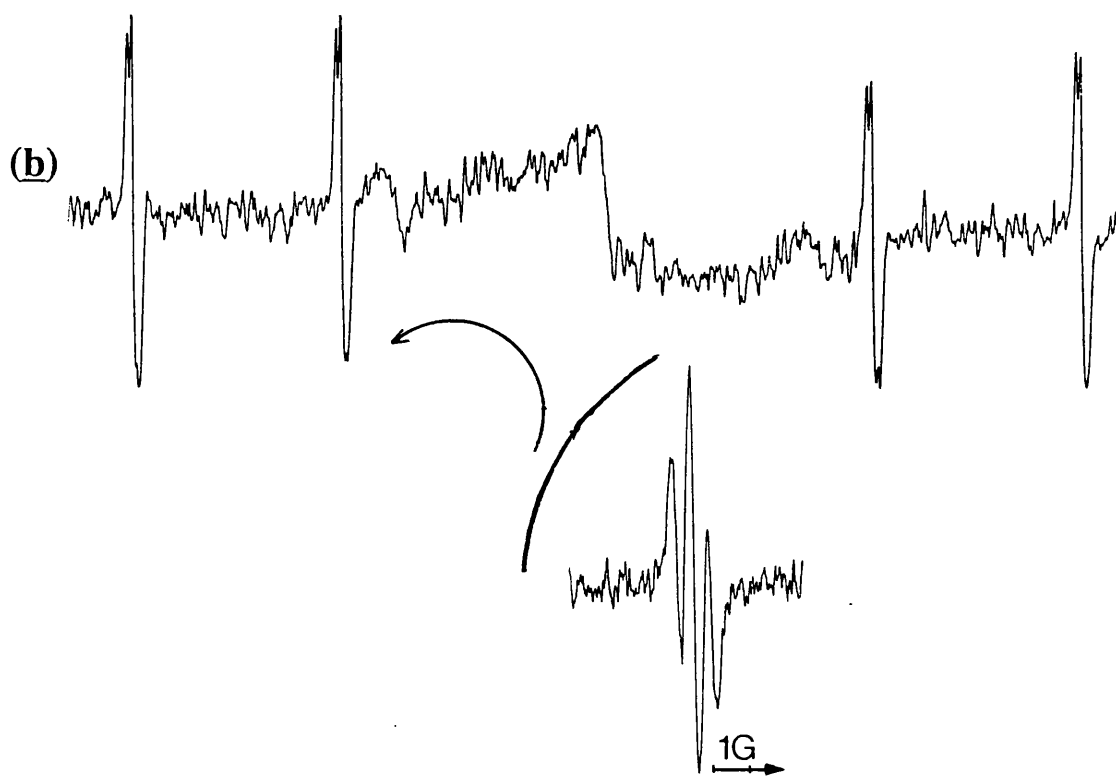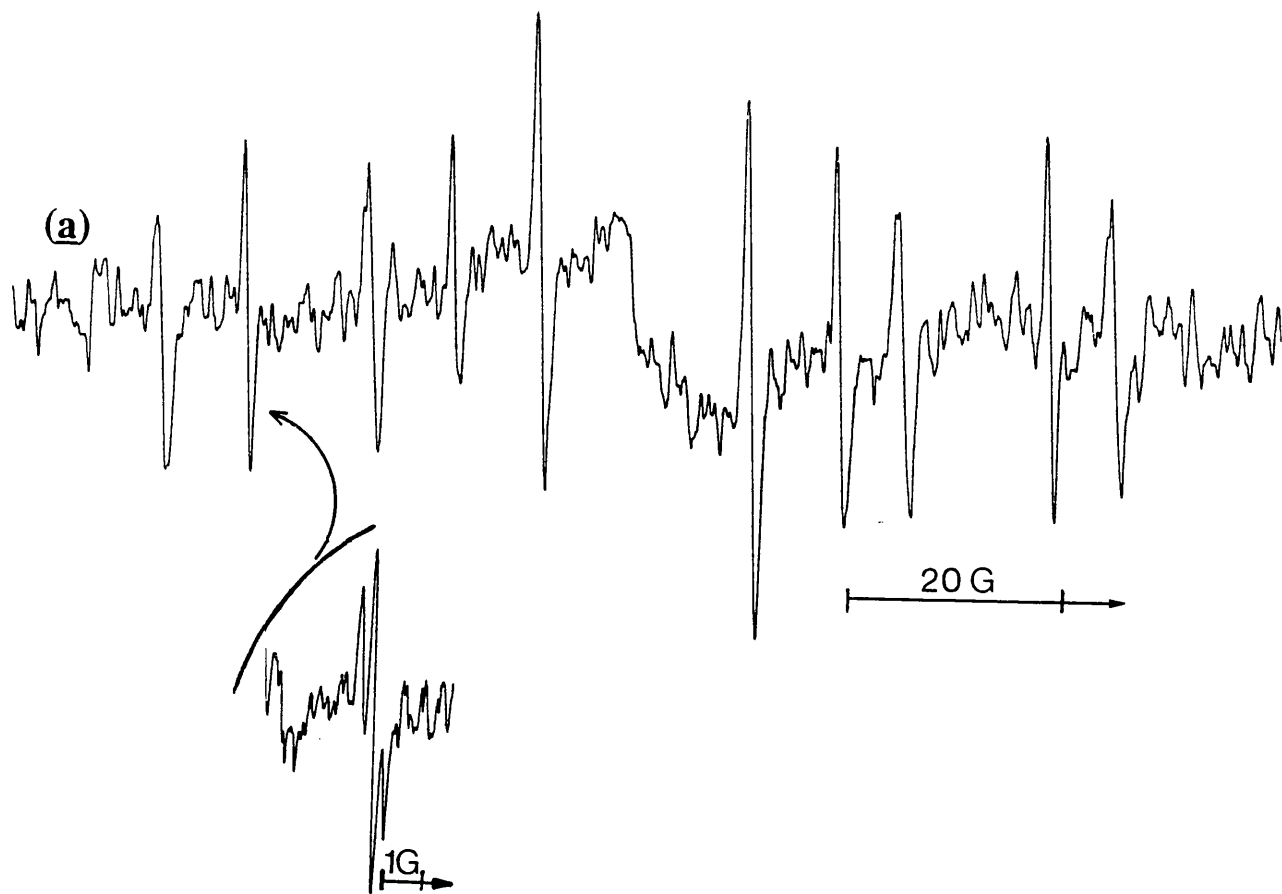
Figure 5.13

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## Figure captions

Figure 5.13   E.s.r. spectra in oxirane at 249 K.   (a) The radicals (**43**) and (**44**) produced from δ-valerolactone (ca. 1 **M**) in the absence of catalyst.   (b) The radical (**44**) produced from δ-valerolactone in the presence of $Me_3N{\rightarrow}BH_2Thx$ (0.1 **M**).   The central lines of the β-proton triplet for (**44**) are not observed owing to line broadening.

derive from a reaction product of Meldrum's acid with the catalyst (1) or it could be a secondary product radical formed by hydrogen abstraction from the dimer of (46) (cf. the results with acetates described in section 5.3.1). For comparison, e.s.r. parameters for the acyclic $(Bu^tCO_2)_2\overset{\bullet}{C}H$ are also included in Table **5.8**.

5.3.4   Hydrogen Abstraction from Anhydrides

The carbonyl groups in an anhydride, like those in lactones, ketones, or esters, should activate adjacent C-H groups towards amine-alkylborane catalysed abstraction by $Bu^tO^{\bullet}$.

Photolysis of an oxirane solution containing succinic anhydride (ca. 1 M) and DTBP (20 % v/v) at 169 K in the absence of catalyst, afforded only a spectrum of the oxiranyl radical; however at 261 K, a weak spectrum of (47) was also observed. When the temperature was lowered to 169 K, oxiranyl
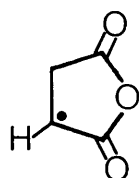
(47)

radicals were once again the only product. Photolysis of similar solution, but containing (1) (0.2 M), at 169 K afforded a strong spectrum of (47) without any contribution from the oxiranyl radical (see Figure **5.14**). The e.s.r. parameters are given in Table **5.9**. The spectrum of (47) appears as a triplet of doublets owing to coupling of the unpaired electron with two equivalent β-hydrogens and one α-hydrogen. The central "line" of the β-proton triplet is split into a doublet

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due to a second-order effects. This second-order splitting of 0.40 G is very close to the value $\{[\underline{a}(2H_\beta)]^2/B_0 = 0.36\ G\}$ predicted from the treatment of such effects given by Fessenden.[34]
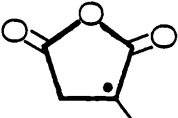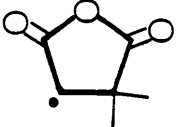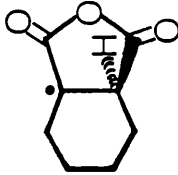
Succinic anhydride reacted visibly upon mixing with (**1**) at room temperature, so extreme care was taken to keep the temperature of the sample as low as possible prior to and during recording of the spectrum. Alongside the spectrum of (**47**), a 1:2:1 triplet was also observed at higher temperatures and at 261 K this spectrum was the only one observed. This triplet corresponded to $\underline{a}(2H)$ 6.65 G and $\underline{g}$ 2.0037 and assignment has not yet proved possible. When photolysis was conducted at 261 K, only the strong triplet was immediately apparent, but when the temperature was subsequently lowered to 169 K only a strong spectrum of (**47**) was observed. Either the triplet arises from a reaction product of succinic anhydride and $Me_3N{\rightarrow}BH_2Thx$ (**1**) at higher temperatures or it might possibly derive from a reaction of (**47**) which takes place at higher temperatures.

In similar experiments with ($\pm$)-methylsuccinic anhydride ($\underline{ca}$. 1 $\underline{M}$) in the absence of catalyst at 169 K, the oxiranyl radical was the major radical detected, but at 261 K a mixture of both oxiranyl and the radical (**48**) was detected. In

(**48**)

the presence of (**1**) (0.1 $\underline{M}$) at 169 K, the major spectrum is attributed to (**48**) (Figure **5.15**). A triplet of quartets is produced by coupling of the unpaired

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Table 5.9   E.s.r. parameters for radicals obtained by catalytic hydrogen abstraction from anhydrides in the presence of Me$_3$N→BH$_2$Thx in c

Radical	T/K	g-Factor	Hyperfine coupling constants (G)
(47)	169	2.0036	34.13 (2H$_\beta$), 20.63 (1H$_\alpha$)
(48)	169	2.0037	30.15 (2H$_\beta$), 22.10 (3H$_\beta$)
(50)	169	2.0035	20.40 (1H$_\alpha$), 0.82 (6H$_\gamma$)
(51)	169	2.0037	66.88 (H$_\beta^{1ax}$ + H$_\beta^{2ax}$), 1.25 (nine lines observed which arose from coupling with other hydrogen

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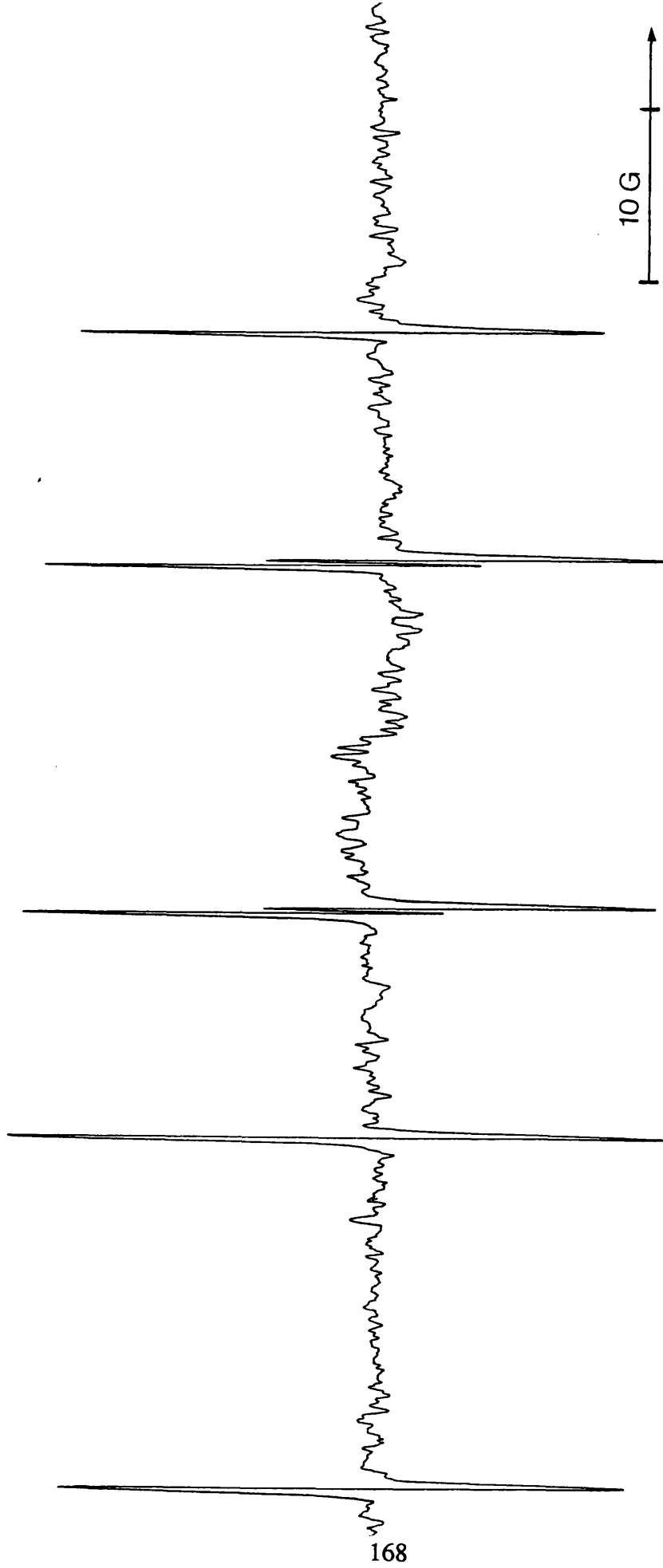
Figure 5.14 E.s.r. spectrum in oxirane of (47) produced from succinic anhydride (ca. 1 M) in the presence of DTBP and $Me_3N{\rightarrow}BH_2Thx$ (0.2 M) at 169 K.

168

(a)

(b)

10G

0.5G

0.5G

Figure 5.15

169
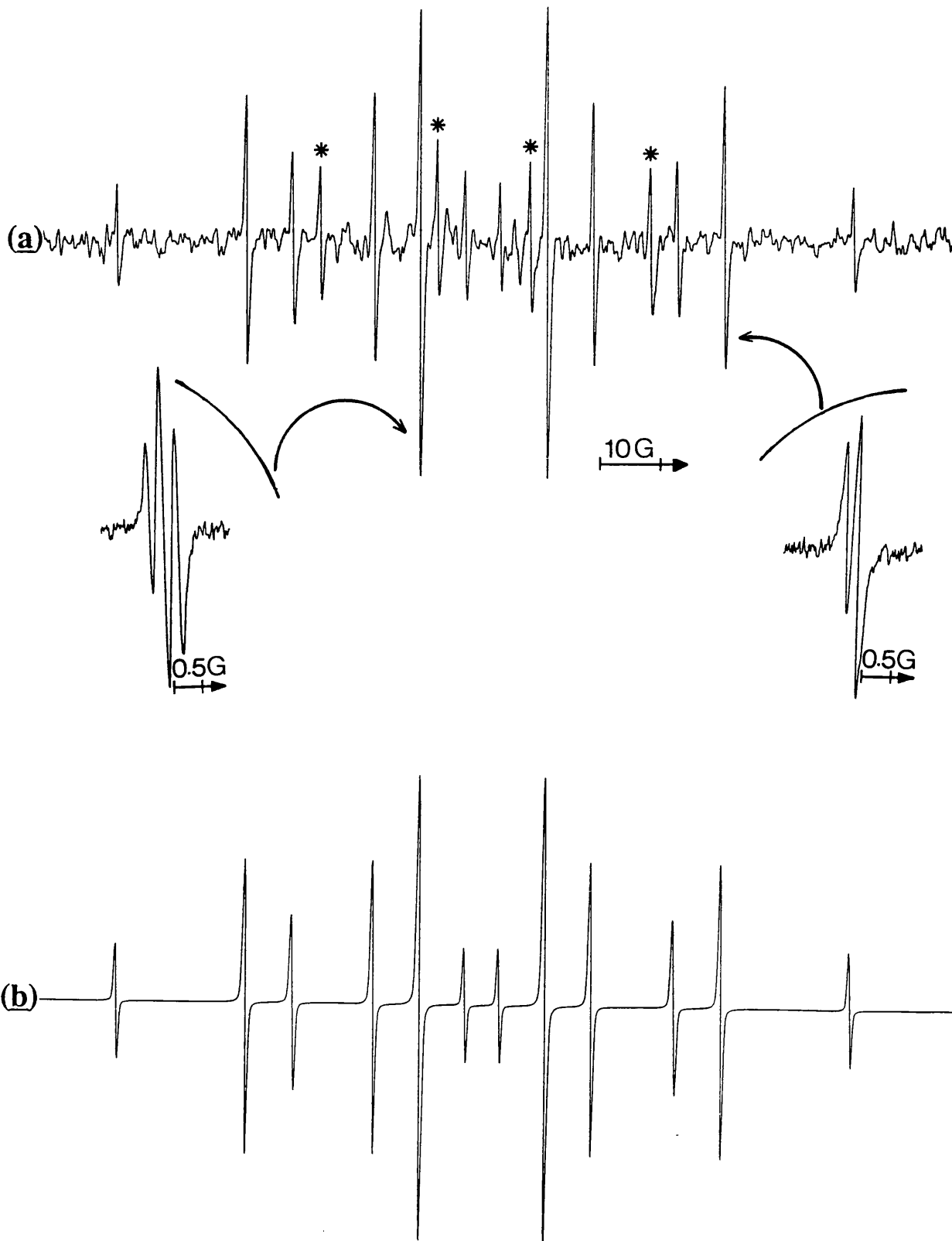
Figure captions

Figure 5.15   a) E.s.r. spectrum of radical (<u>48</u>) in oxirane at 169 K obtained from methylsuccinic anhydride (1 <u>M</u>) in the presence of $Me_3N{\rightarrow}BH_2Thx$ (0.1 <u>M</u>). Second-order effects are shown inset for two different lines. (b) Computer simulation of the spectrum of (<u>48</u>). The coupling constants are given in Table **5.9**; the linewidth is 0.50 G and the lineshape is 50 % Gaussian.

170

Figure 5.16

171
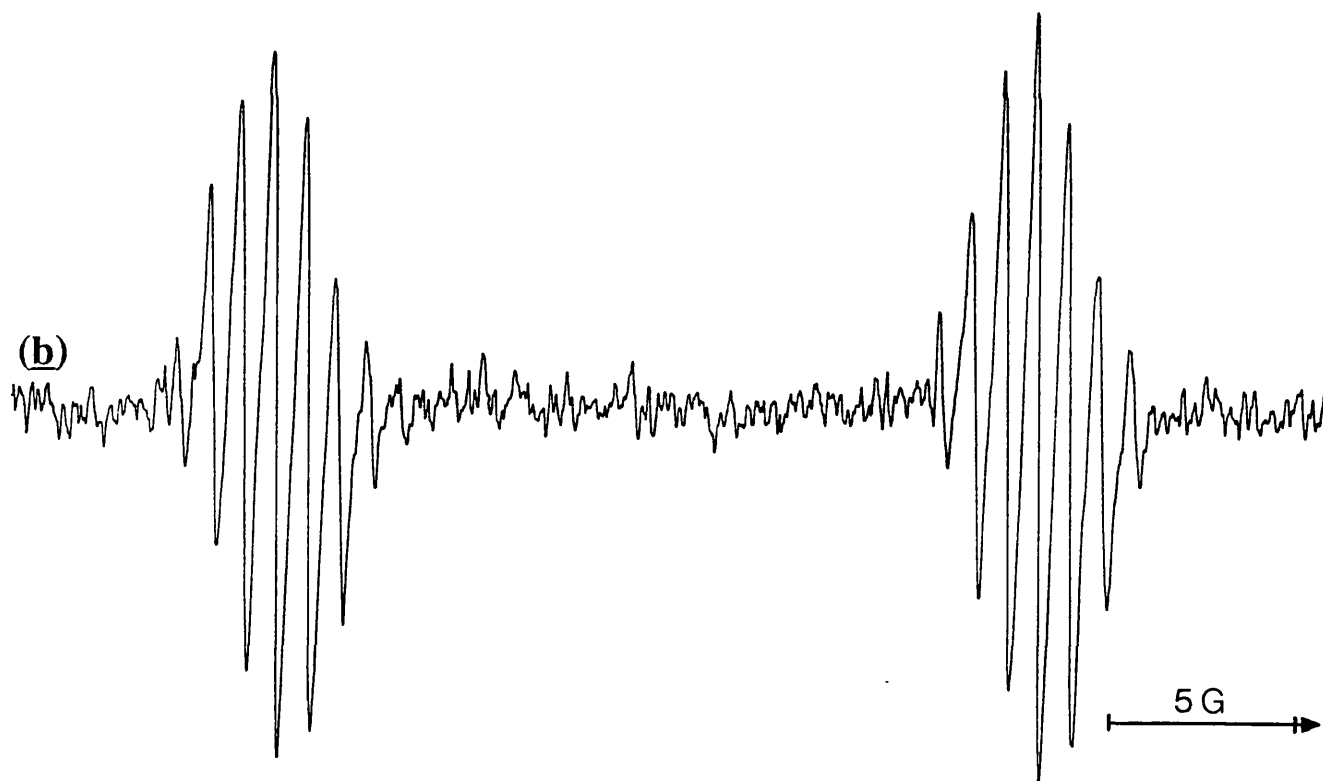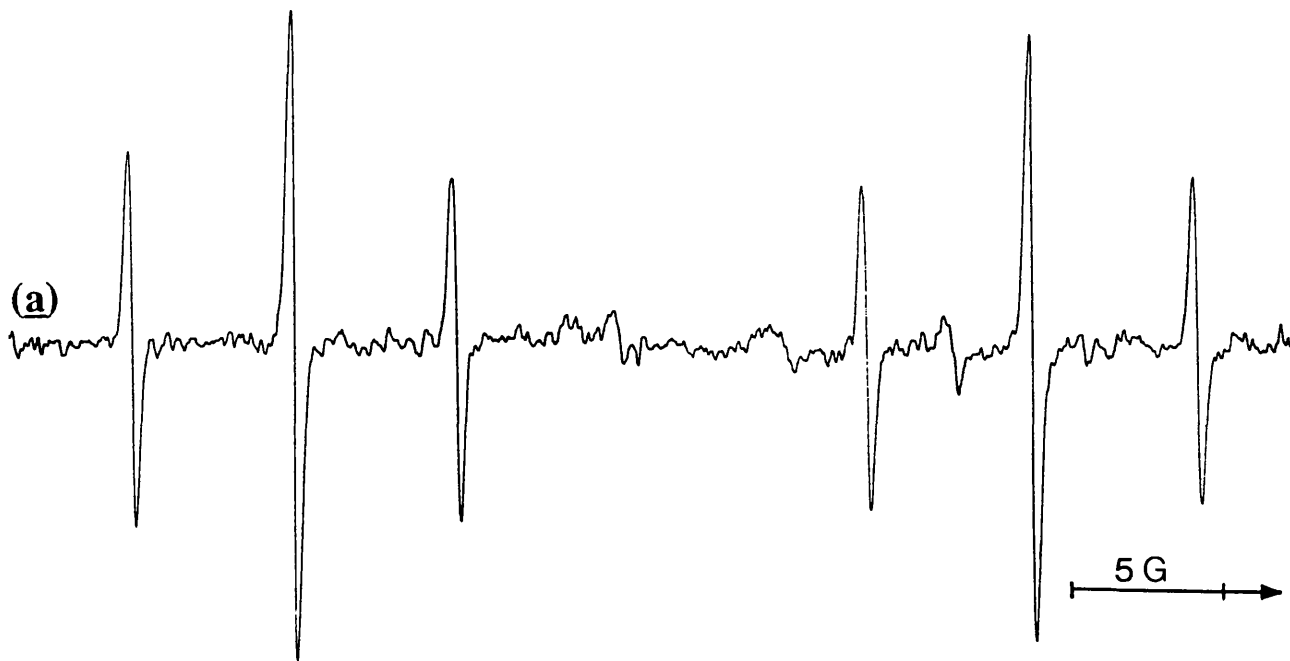
Figure captions

Figure 5.16 E.s.r. spectra in oxirane at 189 K. (a) The oxiranyl radical produced in the presence of 2,2-dimethylsuccinic anhydride (ca. 1 M) and DTBP. (b) The radical (50) produced from 2,2-dimethylsuccinic anhydride in the presence of Me$_3$N→BH$_2$Thx (0.1 M).

electron with two equivalent β-hydrogens (the ring is probably planar) and three methyl hydrogens. Second-order effects[34] were evident in the spectrum (see Figure **5.15a**).

A minor spectrum consisting of a doublet of doublets [$a(H^1)$ 36.50, $a(H^2)$ 20.50 G, and g 2.0037 at 169 K] was also observed and was at first thought to result from the isomeric radical (**49**). The amine-alkylboryl radical

(**49**)
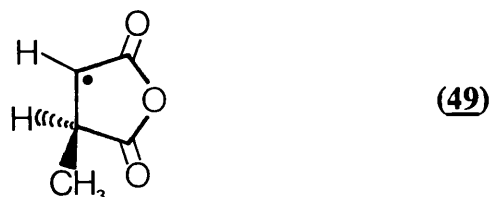
$Me_3N{\rightarrow}\overset{\bullet}{B}HThx$ derived from the catalyst (**1**) is very bulky and should prefer to abstract hydrogen from the least hindered α-C-H group in the molecule, to give rise to (**49**). By using a less hindered catalyst, namely $Me_3N{\rightarrow}BH_2Bu^n$, it was expected to obtain only the spectrum ascribed to (**48**). However, no change in radical concentration ratio was observed when $Me_3N{\rightarrow}BH_2Bu^n$ was used as a catalyst, suggesting that the second spectrum does not derive from (**48**).

As noted previously, acid anhydrides can react directly with amine-alkylboranes and it is possible that methylsuccinic anhydride reacted with (**1**) or (**2**) to give rise indirectly to the minor spectrum.

With 2,2-dimethylsuccinic anhydride (ca. 1 M) in the presence of (**1**) (0.1 M), a strong spectrum was obtained which is assigned to (**50**) (Figure **5.16**). In the absence of (**1**), only the oxiranyl radical derived from the solvent was detected at 169 K, but at higher temperature (261 K), a weak spectrum from (**50**) was also apparent.

(50)
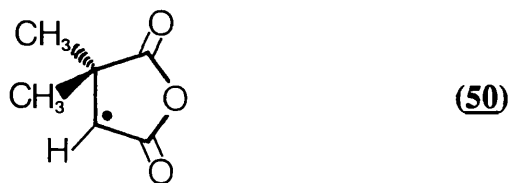
The e.s.r. parameters obtained for (50) (see Table 5.9) infact support the suggestion that the second radical derived from 2-methylsuccinic anhydride is, after all, (49).

Photolysis of an oxirane solution containing cis-1,2-cyclohexanedicarboxylic anhydride (ca. 1 M) and DTBP (17 % v/v) in the presence of (1) (0.2 M) gave rise to a spectrum which is assigned to the radical (51). Coupling of the

(51)
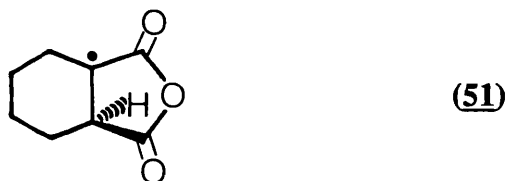
unpaired electron with two non-equivalent axial and equatorial β-hydrogens gives rise to a doublet of doublets further split by coupling with other hydrogens in the ring to give multiplets. A minor spectrum consisting of a doublet [a(H) 28.25 G and g 2.0034] was also observed at 169 K; it was also present when $Me_3N\rightarrow BH_2Bu^i$ was used as a catalyst. At higher temperature (260 K), the spectrum ascribed to (51) was absent and other signals, most likely from two radicals appeared (a 1:2:1 triplet and a 1:1 doublet). The spectra obtained at higher temperature probably have origins analogous to those discussed before for the other anhydrides.

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When dimethylether was used as a solvent instead of oxirane, similar results were obtained except that MeOĊH$_2$ was also detected.

5.3.5   Hydrogen Abstraction from Imides

U.v. photolysis of DTBP (20 % v/v) in the presence of succinimide (ca. 1 M) in oxirane solution gave rise to a strong spectrum of the oxiranyl radical between 169-209 K. However, when (1) (0.2 M) was also present, only the spectrum of (52) was observed at 169 K (Figure 5.17). The e.s.r. parameters are given in Table 5.10. The ring is almost certainly planar in (52). As

(52)
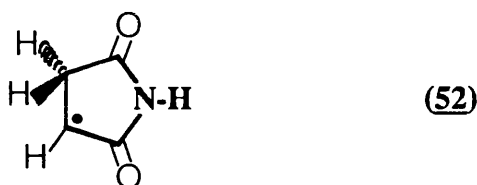
temperature was increased, a multiplet appeared in the centre of the spectrum and this multiplet was relatively strong at 209 K. The identity of the radical giving rise to this multiplet is not known.

In similar experiments with 3,3-dimethylglutarimide and with barbituric acid (each ca. 1 M) in the presence of (1) (0.2 M), only the corresponding radical

(53)

(54)

175
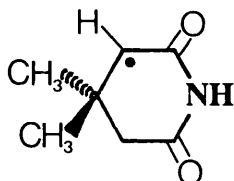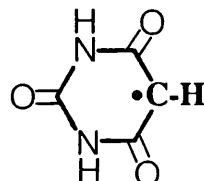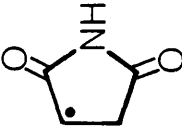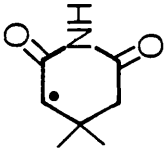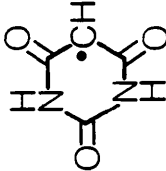
Table 5.10 E.s.r. parameters for radicals obtained by catalytic hydrogen abstraction from imides in the presence of $Me_3N \rightarrow BH_2Thx$ in oxira

Radical	T/K	g-Factor	Hyperfine coupling constants (G)
(52)	169	2.0043	30.84 ($2H_\beta$), 20.75 ($1H_\alpha$), 1.50 ($1H_\gamma$), 0.33 (N)
(53)	215	2.0042	20.10 ($1H_\alpha$), 1.17 (coupling with other hydrogens in the ri
(54)	175	2.0046	19.38 ($1H_\alpha$), 1.00 ($2H_\gamma$)

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Figure 5.17

177
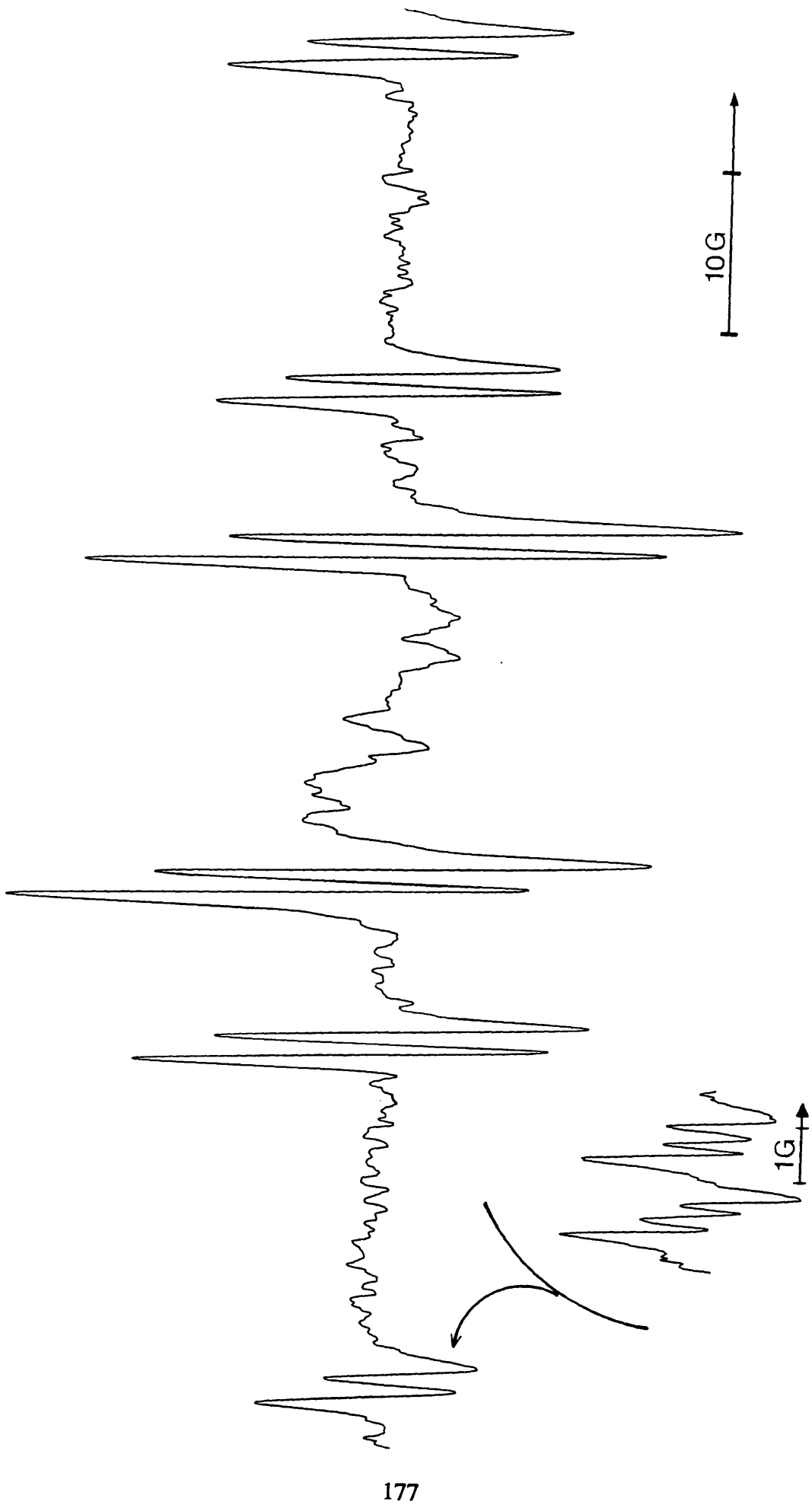
Figure 5.17   E.s.r. spectrum of (52) in oxirane solution at 164 K produced

from succinimide (ca. 1 M) in the presence of $Me_3N \rightarrow BH_2Thx$ (0.2 M).

derived by abstraction of hydrogen from an α-C-H group was detected. With barbituric acid at 175 K, a secondary-product radical (single line, g 2.0042) was also detected (cf. the result with Meldrum's acid). At still higher temperature (199 K), the secondary product radical dominated the spectrum and no spectrum due to (54) was detected. There is a remarkable similarity between the e.s.r. parameters of (54) and (46) (radical derived from Meldrum's acid, see Table 5.8), which might be expected since these radicals are structurally similar. The relatively high g-factor of (54) in comparision with the g-factors of (52) and (53) is ascribable to the greater extent of delocalisation of the unpaired electron onto oxygen in the case of the radical derived from barbituric acid.

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CHAPTER 6

EXPERIMENTAL

6.1   E.S.R. Spectroscopy

The techniques used to obtain e.s.r. spectra from samples in fluid solution were those described in Chapter 3. The experimental details, including the method for measuring hyperfine coupling constants and g-values are described in Chapter 7. The samples containing 2-methyl-2-nitrosopropane (MNP) were prepared and handled in darkness or subdued light.[1]

6.2   N.M.R. Spectroscopy

^{11}B, ^{1}H, and ^{13}C n.m.r. spectra were recorded using Varian XL-200 or VXR-400 instruments, with $BF_3.OEt_2$ (^{11}B) external or Me_4Si (^{1}H and ^{13}C) internal standards. ^{1}H n.m.r. of all the amine-boranes were recorded for solutions in C_6D_6 unless otherwise stated.

6.3   Materials

Cyclopropane (Argo International) and oxirane (Fluka) were used as received. The alkyl halides, ethyl acetate, ethyl propanoate, and ethyl isobutyrate (all Aldrich) were purified by distillation. For competition experiments, a stock mixture of the two reactants was made up by weight and portions of this were used for sample preparation. Di-t-butyl peroxide (DTBP, Aldrich) and MNP (Aldrich) were purified as described in Chapter 3. Di-t-butyl hyponitrite[2] (TBHN) was prepared as described in Chapter 3. The ketones,

lactones, anhydrides, amides, and imides used in this work were commercial materials (mainly Aldrich), which were all purified by distillation or recrystallisation, apart from those compounds whose preparations are described elsewhere in this thesis or given below.

6.3.1   2-Methylsuccinic Anhydride[3]

Methylsuccinic acid (Aldrich, 14.64 g, 110 mmol) was combined with acetyl chloride (13.20 cm^3) and thionyl chloride (1.40 cm^3) and the mixture was heated under gentle reflux for 3 h. The excess chlorides were removed under reduced pressure (10 Torr) and the residue recrystallized from a mixture of chloroform and petroleum ether (b.p. 80-100 °C) to yield 7.0 g (56 %) of 2-methylsuccinic anhydride, m.p. 32-34 °C (lit.[4] 33-35 °C). δ(^{1}H) (CDCl$_3$) 1.45 (d, J 7.3 Hz, Me), 2.64 (m, CHMe), and 3.18 (m, CH$_2$).

6.3.2   2,2-Dimethylsuccinic Anhydride[3,5]

This anhydride was prepared from 2,2-dimethylsuccinic acid (Aldrich, 5.0 g, 34.2 mmol), acetyl chloride (4.50 cm^3) and thionyl chloride (0.50 cm^3) using the method described for the methylsuccinic anhydride. The anhydride was purified by distillation, b.p. 83-84 °C/3 Torr (lit.[5] 114 °C/25 Torr); yield 3.5 g (80 %). δ(^{1}H) (C$_6$D$_6$) 0.63 (s, Me$_2$) and 1.80 (s, CH$_2$).

Preparation and manipulations of all boron-containing compounds were conducted under dry nitrogen or argon; all solvents were dried before use. Trimethylamine-thexylborane[6] and the isomeric trimethylamine-butylboranes[7] were prepared by the published methods. TMEDA.2BH$_2$Ipc (R-Alpine-Boramine; Aldrich) was purified by recrystallisation from diethyl ether. Syntheses of new

compounds or of compounds prepared by modification of literature procedures are described below.

6.3.3   Trimethylamine-n-butylborane[7]

Dry n-butyl bromide (254 g, 1.850 mol) in ether (600 cm^3) was added slowly over a period of 1.5 h. to magnesium turnings (45 g, 1.851 mol) in ether (200 cm^3) while the reaction mixture was stirred and allowed to reflux gently. After stirring for a further 0.5 h., the Grignard solution was allowed to cool to room temperature. The n-butylmagnesium bromide in ether (900 cm^3) was transferred to a dropping funnel and added dropwise during 3 h. with stirring to a solution of trimethyl borate (170 cm^3, 1.500 mol) in ether (300 cm^3), which was cooled in a solid CO$_2$-meths bath so that the internal temperature remained below -50 °C. The mixture was left to warm to room temperature overnight and then stirred for a further hour at room temperature before being hydrolysed by the dropwise addition during 2 h. of 1.5 $\underline{M}$ sulphuric acid (400 cm^3) with stirring and cooling in ice. Solid sodium chloride was then added to facilitate phase separation and the ether layer was separated. The solvent was removed under reduced pressure, toluene (150 cm^3) was added, and water was removed azeotropically using a Dean and stark trap. Most of the toluene was removed by distillation at reduced pressure and the residue was distilled through a 15 cm. vacuum jacked Vigreux column, to yield n-butylboronic anhydride,[8] the fraction b.p. 73-75 °C/0.2 Torr being collected; yield 63 g (50 %); (lit.[8] b.p. 108 °C/5.5 Torr). δ(^{1}H) 0.6-1.8 (m, C$_4$H$_9$). Only a trace (< 0.5 %) of oxidation product (δ 3.9, t, $\underline{J}$ 7.0 Hz) produced by reaction of this very air-sensitive compound with adventitious oxygen was detected.

Lithium aluminium hydride (9.0 g, 0.237 mol) was dissolved in ether (250 cm^3) by stirring under reflux for 1 h. The solution was cooled to 0 °C, the reaction flask was equipped with a condenser containing solid CO$_2$-acetone slush, and trimethylamine (30 cm^3, 0.340 mol) was allowed to evaporate into the mixture. The mixture was warmed under reflux and stirred during dropwise addition of n-butylboronic anhydride (15.0 g, 59.6 mmol) in ether (50 cm^3). Stirring under reflux was continued for a further 1 h., after which water (15.4 cm^3) was added cautiously to the reaction mixture immersed in a bath maintained at -10 °C. The mixture was filtered, the filtrate was dried (MgSO$_4$), the ether was removed under reduced pressure, and the residual oil was distilled to yield (15.5 g, 67 %) product, b.p. 50 °C/ 0.45 Torr (lit.[7] 72 °C/3 Torr). δ(^{1}H) 0.65 (br.t, BH$_2$CH$_2$), 1.16 (t, J 7.2 Hz, CH$_2$Me), 1.74 (br.m, CH$_2$CH$_2$), 1.87 (s, Me$_3$N), and 2.31 (q, J$_{BH}$ 96.8 Hz, BH$_2$).

6.3.4   Trimethylamine-isobutylborane[9,7]

This was prepared from the isobutylboronic anhydride as described for the n-butylborane complex and on half the scale. The reaction yielded 52 % of the amine complex which was purified by distillation b.p. 45 °C/0.5 Torr. δ(^{1}H) 0.57 (br.q, BH$_2$CH$_2$), 1.37 (d, J 6.6 Hz, Me$_2$CH), 1.84 (s, Me$_3$N), 2.07 (septet, J 6.6 Hz, Me$_2$CH) and 2.24 (q, J$_{BH}$ 92 Hz, BH$_2$). A small amount of impurity was detected by n.m.r. spectroscopy which could not be removed by stirring the distilled material with an excess of trimethylamine for 5 min. at room temperature. The unreacted amine was then removed at 0.5 Torr, but no changes were observed in the n.m.r. spectrum, indicating that the impurity was not (Bu^{i}BH$_2$)$_2$.

6.3.5 Trimethylamine-s-butylborane[10,7]

This amine complex was prepared from the s-butylboronic anhydride (b.p. 81-83 °C/2.5 Torr; lit.[10] 79.5-80.5 °C/2.5 Torr) by the method described for trimethylamine-n-butylborane. The complex was purified by distillation as before, b.p. 60 °C/2.5 Torr (lit.[7] b.p. 60 °C/2.5 Torr). δ(^{1}H) 0.47 (br, BH$_2$C$\underline{H}$), 1.32 (t, $\underline{J}$ 7.32 Hz, CH$_2\underline{Me}$), 1.36 (d, $\underline{J}$ 7.32 Hz, CH$\underline{Me}$), 1.64 (br.m, CH$_2$), 1.83 (s, Me$_3$N), 2.10 (q, $\underline{J}_{BH}$ 94.6 Hz, BH^a) and 2.18 (q, $\underline{J}_{BH}$ 94.6 Hz, BH^b).

6.3.6 N,N-Dimethyl(trimethylsilylmethyl)amine-borane

This compound was synthesised by the reaction of $\underline{N},\underline{N}$-dimethyl(trimethylsilylmethyl)amine[11,12] with Me$_2$S.BH$_3$. The amine was prepared from a mixture of chloromethyl(trimethyl)silane (9.8 g, 80 mmol) and the dimethylamine (ca. 13.9 cm^3; ca. 9.0 g; ca. 200 mmol) which was heated in a thick-walled sealed tube in an oil bath at 80 °C for 24 h. Precautions were taken to minimise the effect of any possible explosion. After being allowed to cool, the tube was further cooled in a solid CO$_2$-meths bath and opened. The contents were poured into 100 cm^3 of 10 % sodium hydroxide solution and the mixture was extracted with pentane (3 x 30 cm^3). The pentane extract was washed with water (50 cm^3), dried (MgSO$_4$), concentrated by distillation at atmospheric pressure, and finally the residue was distilled from calcium hydride to yield 7.0 g (67 %) of $\underline{N},\underline{N}$-dimethyl(trimethylsilylmethyl)amine, b.p. 110-111 °C (lit.[11] 110.1 °C/746 Torr).

Dimethyl sulphide-borane (2.3 cm^3, 1.83 g, 24 mmol of a 10 $\underline{M}$ solution in excess dimethyl sulphide) in ether (5 cm^3) was added dropwise to a stirred solution of the amine (3.50 g, 27 mmol) in ether (5 cm^3) cooled in an ice-water

bath.[13] After the addition was complete, the mixture was stirred for a further

1 h. at room temperature and all volatiles were removed under reduced pressure

to yield N,N-dimethyl(trimethylsilylmethyl)amine-borane (2.8 g, 72 %) as a

white crystalline solid, which was purified by sublimation (0.01 Torr, bath

temperature 35 °C), m.p. 34-35.5 °C. $\delta(^1H)$ 0.08 (s, Me$_3$Si), 1.97 (s, SiCH$_2$N),

2.17 (s, NMe$_2$), and 2.40 (q, J$_{BH}$ 95.3 Hz, BH$_3$). (Found: C, 49.7; H, 13.6; N,

9.5. C$_6$H$_{20}$BNSi requires C, 49.7; H, 13.9; N, 9.7 %).

6.3.7   N,N-Dimethyl(trimethylsilylmethyl)amine-thexylborane

Thexylborane dimer[14] was prepared from 2,3-dimethylbut-2-ene (12.0 cm^3,

100 mmol) which was added dropwise with stirring to dimethyl sulphide-borane

(10 cm^3 of a 10 M solution in excess dimethyl sulphide; 100 mmol) maintained

at ca -10 °C. After the addition was complete, the mixture was stirred for a

further 2 h. at 0 °C, before dimethyl sulphide was removed under reduced

pressure and collected in a trap cooled to -78 °C to leave essentially pure

thexylborane dimer. N,N-Dimethyl(trimethylsilyl)amine (4.0 g, 31 mmol) in

ether (10 cm^3) was added dropwise to thexylborane dimer (3.0 g, 31 mmol) in

ether (10 cm^3) at 0 °C. The mixture was stirred for a further 1 h. before the

volatiles were removed under reduced pressure. The product contained ca. 5

% of an unidentified impurity as judged by ^1H and ^{11}B n.m.r. spectroscopy.

$\delta(^1H)$ (CDCl$_3$) 0.18 (s, Me$_3$Si), 0.84 (s, CMe$_2$), 0.86 (d, J 6.5 Hz, CHMe$_2$), 1.4

(septet, J 7.5 Hz, CHMe$_2$), 2.5 (s, CH$_2$N) and 2.65 (s, Me$_2$N); $\delta(^{11}B)$ (C$_6$H$_6$) +

1.84 (t, J$_{BH}$ 100.4 Hz). The product could not be purified by adding more

dimethylamine, by low-temperature recrystallisation from pentane, by column

chromatography, or by preparative h.p.l.c.

6.3.8   1-Methyl-cis-1-azonia-5-boratobicyclo[3.3.0]octane

A solution of diallyl(methyl)amine   (PCR, 4.0 g, 36 mmol) and triethylamine-borane (4.13 g, 36 mmol) was stirred and refluxed in xylene (50 cm^3) for 5 h. under argon.   Xylene and triethylamine were then removed by distillation at atmospheric pressure.   The residue was distilled under reduced pressure to yield the bicyclic amine-dialkylborane complex[15-18] (ca. 0.2 g, 5 %), b.p. 53-54 °C/1.8 Torr. δ(^{1}H) 0.70 (br.m, 2H, H^{b}C$\underline{H}$·BH), 1.27 (m, 2H, $\underline{H}^b$CH·BH), 1.58 (m, 4H, CH$_2$C$\underline{H}_2$CH$_2$), 2.03 (s, 3H, MeN), 2.09 (m, 4H, C$\underline{H}_2$N) and 2.84 (q, 1H, J_{BH} 99.3 Hz, BH). δ(^{13}C) 19.8 (2C, $\underline{C}$H$_2$BH, also showed poorly resolved C-^{11}B splitting), 25.8 (2C, CH$_2\underline{C}$H$_2$CH$_2$), 50.3 (1C, MeN), and 63.9 (2C, $\underline{C}$H$_2$N). (Found: C, 67.8; H, 12.9; N, 11.1. C$_7$H$_{16}$BN requires C, 67.3; H, 12.9; N, 11.2 %).

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CHAPTER 7

THEORETICAL AND EXPERIMENTAL BACKGROUND

In this chapter we dwell briefly on the theoretical background of electron spin resonance (e.s.r.) spectroscopy. E.s.r. spectroscopy is by far the most useful method for radical detection. As will be apparent later, detailed analysis of an e.s.r. spectrum frequently makes it possible to deduce not only the gross chemical structure of the radical, but also its detailed conformation. Spin densities at various positions in delocalized radicals may also be obtained. The technique can be applied to the measurement of radical concentrations. E.s.r. spectroscopy is of particular value in that, by use of suitable methods of generation, short-lived radicals may be detected. The sensitivity of the method allows radical concentrations of 10^{-8} moldm^{-3} to be observed.

This chapter outlines some of the general principles underlying e.s.r. spectroscopy and is included because of the important part played by the technique in the research described in this thesis.

7.1 Principles of E.S.R. Spectroscopy

An unpaired electron possesses spin angular momentum and thus also possesses a magnetic moment. It can thus exist in two spin states, which are of equal energy in the absence of an external magnetic field. In the presence of an applied magnetic field the electron can align itself parallel or antiparallel to this field. The difference in energy of these states is given by equation (7.1).

$$\Delta E = g \, \mu_B \, \underline{B}_0 \qquad\qquad (7.1)$$

Here g is the Landé factor, which is a dimensionless proportionality constant and takes the value 2.002322 for a free electron, μ_B is the Bohr magneton, and B_0 is the strength of the applied magnetic field (magnetic flux density) at the centre of the spectrum. The frequency (ν_0) of the electromagnetic radiation required to induce transitions from one energy level to the other is thus given by equation (7.2), in which h is Planck's constant.

$$\nu_0 = \frac{g\ \mu_B\ B_0}{h} \qquad (7.2)$$

Initially, in a bulk sample there are more electrons in the lower ($M_s = -1/2$) energy level. Irradiation with electromagnetic radiation of frequency ν_0 results in transitions from the lower to the higher ($M_s = +1/2$) energy level. Non-emitting relaxation processes maintain the Boltzmann distribution of the two states and normally prevent saturation. The ratio of the numbers of spins in the two energy states at thermal equilibrium is given by equation (7.3), in which n_α and n_β are the numbers of spins in the lower and higher states, respectively, ΔE

$$n_\alpha/n_\beta = e^{\Delta E/kT} = e^{g\ \mu_B B_0/kT} \qquad (7.3)$$

is the energy difference between them, and k is Boltzman's constant. The sensitivity of the e.s.r. method is thus related to the strength of the applied magnetic field. It is imperative that this field be homogeneous if the absorption peak is not to be broadened with resultant obscuring of the hyperfine splitting, which is so important in determination of radical structures.

In general, for the study of organic free radicals, a magnetic field of

about 330 mT (3300 gauss) is employed. Resonance can be achieved either by variation of the irradiation frequency or of the field, but invariably the frequency is kept constant and the magnetic field varied. In contrast to n.m.r. spectrometers, e.s.r. spectrometers are arranged to record the first derivative of the absorption curve rather than the absorption curve itself. This gives somewhat greater sensitivity and also better resolution. The area under the absorption curve is proportional to the number of spins in the sample. Integration of the first derivative to give the absorption curve, followed by integration of this to obtain its area, enables one to determine radical concentrations by comparison of this area with that due to a known concentration of radicals. N, N-Diphenyl-N′-picrylhydrazyl (DPPH) is frequently used as a standard.

7.2   Methods of Radical Production for E.S.R. Studies

Radicals are generally transient species and hence special experimental techniques have to be devised to allow their observation within the cavity of an e.s.r. spectrometer.   There are three principal methods which are used.   (a) Radicals may be generated and immobilised in a matrix at very low temperatures.   (b) They can be produced by u.v. or electron irradiation of a solution of a suitable radical precursor in the cavity of the spectrometer.   (c) They may be formed and continuously introduced into the cavity by use of a flow system.

The lifetime of radicals generated in a matrix is very much greater than would be the case in solution because the slow rate of diffusion prevents or retards reactions of the radical.   The spectra of radicals produced in this way are complicated by anisotropic Zeeman and hyperfine interactions which are absent in the spectra of liquids, where the tumbling of the radicals averages out such interactions.

For the study of the e.s.r. spectra of specific radicals, the most useful procedure involves u.v. irradiation in the cavity of the spectrometer, and this is the method used here.   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 30, 10, and 3 % transmittance) in the light path. Most of the infrared and much of the visible radiation were removed by passage of the beam through an aqueous solution filter (path length 3 cm) containing $NiSO_4 \cdot 7H_2O$ (0.38 $\underline{M}$), $CoSO_4 \cdot 7H_2O$ (0.70 $\underline{M}$), and H_2SO_4 (0.04 $\underline{M}$). The light reaching the sample was mainly in the wavelength 240-340 nm and the heating effect of irradiation on the sample was reduced to $\underline{ca}$. 6-7 °C at full intensity.

The temperature of the sample in the cavity was controlled by a pre-cooled flow of 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, and 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 utilising the temperature dependence of $\underline{a}(H_\beta)$ 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 $\underline{a}(H_\beta)$ and the sample temperature is given in equation (7.4).[1] Extrapolation to zero intensity gives the heating effect, and actual sample

$$T(°C) = 2.70394[\underline{a}(H_\beta)]^2 - 198.419[\underline{a}(H_\beta)] + 3490.41 \qquad (7.4)$$

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

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7.3   Characteristics of E.S.R. Spectra

Electron spin resonance spectra are characterized[2] by three parameters: the g-factor, hyperfine splitting constants, and linewidths. A close study of these parameters enables much detailed structural information about the particular radical to be gleaned.

7.3.1   g-Factors

In a magnetic field an unpaired electron in a free radical possesses, in addition to its spin angular momentum, a small amount of unquenched orbital angular momentum as a result of spin-orbit coupling. This causes the electron to have a slightly different effective magnetic moment from that which a free electron would possess (g 2.00232). The g-factor of a polyatomic free radical as defined in [equation (7.5)] will thus deviate slightly from the spin-only value. Hence, for a given operating frequency, radicals with different g-factors resonate

$$\underline{h}\ \upsilon_0\ =\ \underline{g}\ \mu_B\ \underline{B}_0 \qquad\qquad (7.5)$$

at different applied field strengths. Differences in g-values are small, but are nevertheless significant and can give valuable information about the structure of a radical.

In this work g-values 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 field between the magnetic probe and the sample was determined by measuring the g-value of the pyrene radical anion (2.002710)

generated by the reduction of pyrene with sodium in THF.[3] The unknown g-value was calculated using the resonance condition shown in equation (7.5).

7.3.2   Hyperfine Splitting Constants

These are by far the most useful characteristics of e.s.r. spectra, both for elucidating the structure and also the shape of the radical under study. Hyperfine coupling arises from interaction between the unpaired electron and neighbouring magnetic nuclei (^{1}H, ^{11}B, ^{13}C, ^{14}N, ^{17}O, etc.) present in the radical. The interaction with $\underline{n}$ equivalent nuclei of spin $\underline{I}$ results in ($2\underline{n}\underline{I}$ + 1) lines and the distance between each of these lines is (to first-order) equal to the hyperfine splitting constant.   Since ^{12}C has no magnetic moment, proton hyperfine couplings dominate e.s.r. spectra of hydrocarbon radicals. The interaction of the unpaired electron with $\underline{n}$ equivalent protons ($\underline{I}$ = 1/2) gives ($\underline{n}$ + 1) lines and, furthermore, the relative intensities of these lines are given by the coefficients of the binomial expansion of (1 + X)$^{\underline{n}}$, which can be found readily from Pascal's triangle.   Although the natural abundance of ^{13}C ($\underline{I}$ = 1/2) is only $\underline{ca}$. 1.1 %, other elements have high abundance non-zero spin isotopes.   These include ^{10}B ($\underline{I}$ = 3) $\underline{ca}$. 19.8 %, ^{11}B ($\underline{I}$ = 3/2) $\underline{ca}$. 80.2 %, and ^{14}N ($\underline{I}$ = 1) 99.6 %.

E.s.r. spectra can be complex, in part because coupling with β-protons is frequently as great or greater than that with α-protons. For very complex spectra it is sometimes only possible to obtain the hyperfine splitting constants on the basis of a computer simulation.

7.4   Origins of Hyperfine Splitting

Isotropic hyperfine splitting results only from interaction of the unpaired electron at the magnetic nucleus in question. This is usually refered to as the Fermi contact interaction. Thus, coupling might be expected to be observable only when the electron is in an orbital with some s-character, since only then will there be a finite electron density at the nucleus. For π-radicals, no splitting would be expected, since the unpaired electron is in a p-orbital which has a node at the nucleus. Experimentally, it is found that though splitting for electrons in orbitals with s-character can be very large (506 G for the hydrogen atom), there is nevertheless also some splitting in π-radicals.

7.4.1 α-Proton Splittings*

Hyperfine interaction of this type can be best illustrated by the methyl radical $H_3\overset{\bullet}{C}$. Figure **7.1** shows schematically the spin polarization mechanism,

      (a)   (b)
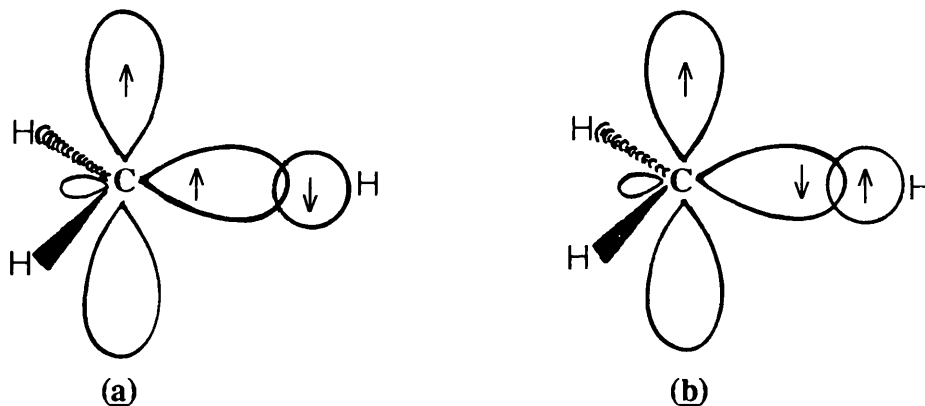
Figure 7.1   The spin polarization mechanism for the methyl radical.

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*Throughout this thesis, the common nomenclature used was for hydrogen positions with reference to atom X : $-CH_2-CH_2-\overset{\bullet}{X}-H$
                                                       γ β α

which is responsible for the α-hydrogen splitting. For the two possible arrangements of electron spins about the trigonal carbon, that shown in Figure **7.1(a)** is the more probable. The electrons in the σ bond are not perfectly paired due to exchange interaction, which causes the σ electron with the same spin as the $\pi(2p_z)$ electron to come closer to this electron than the σ electron of opposite spin [Figure **7.1(b)**].

McConnell[4] has shown for π-radicals that the unpaired spin induced in the H-1s orbital $\underline{a}(H_\alpha)$, is approximately proportional to the unpaired spin population on the adjacent carbon atom, $\rho^\pi c_\alpha$. This can be expressed by equation (**7.6**), in which $\underline{Q}$ is a proportionality constant with a value between -20 and -30 G.

$$\underline{a}(H_\alpha) = \underline{Q} \, \rho^\pi c_\alpha \tag{7.6}$$

The value of $\underline{Q}$ varies according to the particular type of radical.

The sign of the splitting $\underline{a}(^{13}C)$ is <u>positive</u> when the unpaired spin in C-2s orbital is in the <u>same</u> sense as that in the SOMO and sign of the splitting $\underline{a}(H_\alpha)$ is <u>negative</u> because the unpaired spin in the H-1s orbital is in the <u>opposite</u> sense.


7.4.2   β-Proton Splittings

Since spin polarization strongly depends on the distance between the unpaired electron and the interacting nuclei another mechanism must be operative in transferring spin density to a β-proton. As commonly accepted, this is the <u>hyperconjugation mechanism</u>, which allows some of the unpaired α-spin density to appear at the β-proton, producing a positive coupling constant [see

(1a)   **(1b)**
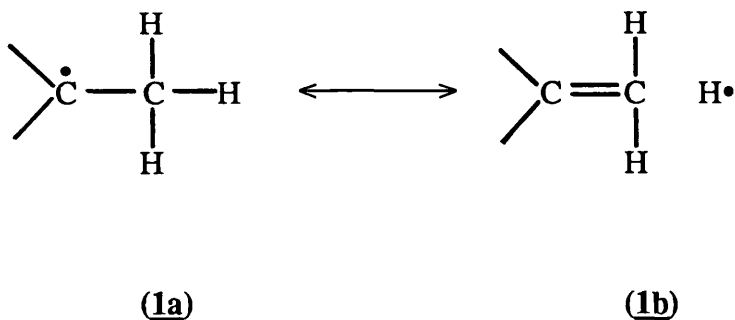
the canonical structure (**1b**)].

The hyperconjugation mechanism can be explained using simple molecular orbital theory, and can be visualized in Figure (7.2) for ethyl radical. The basic concept is that there must be overlap between one or more sigma C-H bonds
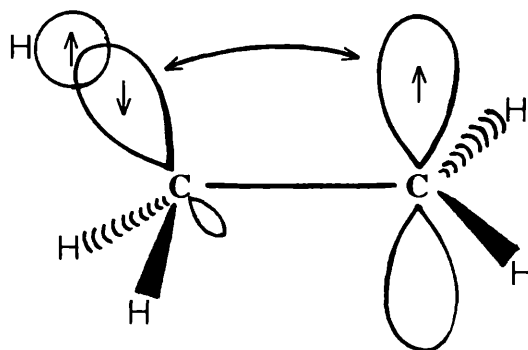

Figure 7.2   The hyperconjugation mechanism for the ethyl radical.

and the p-orbital containing the unpaired electron. This interaction follows a $\cos^2\theta$ law, as shown by the Heller-McConnell equation[5] (**7.7**), in which $\underline{A}$ is a spin-polarization parameter of small value (ca. 1 G), often neglected, and $\underline{B}$ is

$$\underline{a}(H_\beta) = (\underline{A} + \underline{B}\cos^2\theta)\ \rho^\pi c_\alpha \qquad\qquad (7.7)$$

a hyperconjugation parameter of value 58.5 G. The angle θ is defined as the

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dihedral angle between the C_α-2p orbital and the C-H bond [structure (2)]. The

(2)
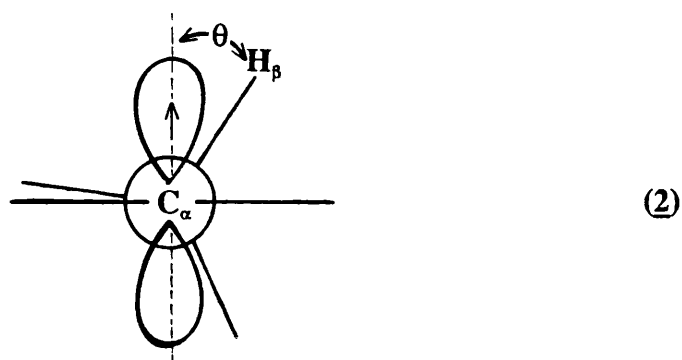
coupling constant with a β-proton is thus at a maximum when it is in the same

plane as that of the p-orbital i.e. when θ is zero.

7.4.3 Long-Range Proton Splittings

Long-range hyperfine interactions with γ and δ hydrogens are usually

rather small, and positive and negative contributions to them often cancel each

other. They are very dependent on stereochemistry. An extensive review of

this subject has been given by king.[6] Ellinger et al.[7] have given theoretical

analyses of long-range hyperfine interactions in both simple aliphatic and

bicyclic free radicals. Figure 7.3 illustrates the so-called "W" and "anti-W"
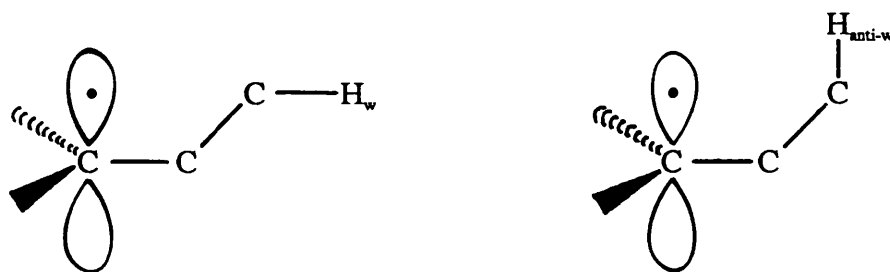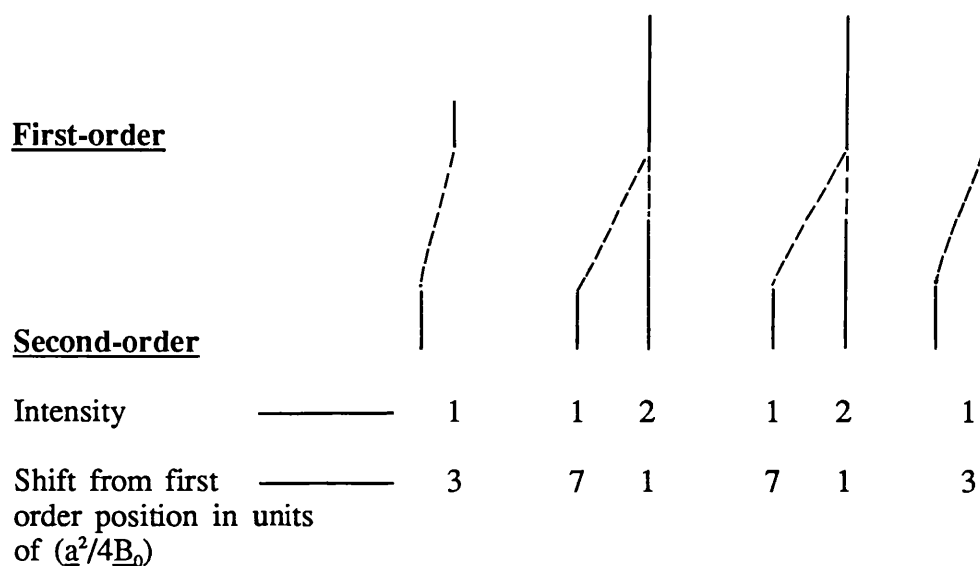
Figure 7.3   "W" and "anti-W" protons.

rules. The former type of interaction leads to the larger value of $\underline{a}(H_\gamma)$ because

contributions from spin delocalization and spin polarization are both positive.
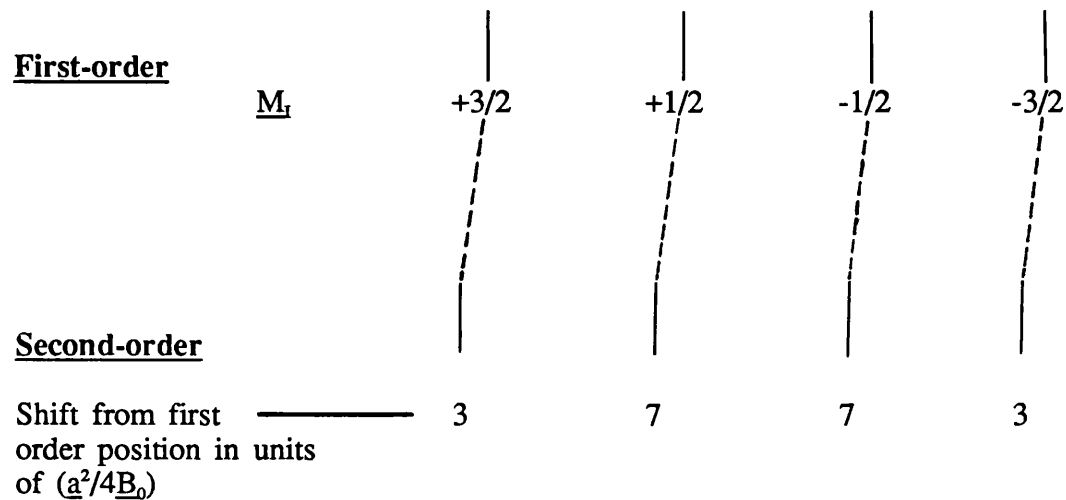
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7.5 Second-Order Effects

The analysis of hyperfine splittings which has been presented 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 due to 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.[8] 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 with three equivalent protons actually gives rise to the splitting pattern shown below rather than to a simple 1:3:3:1 quartet.

First-order						

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

Although to second-order no extra splittings arise for coupling to a single nucleus, the shifts of the $(2I + 1)$ lines resulting from coupling to such a nucleus increase rapidly as I increases. For coupling to ^{11}B ($I = 3/2$), the second-order shifts are shown below.

First-order

| M_I | +3/2 | +1/2 | -1/2 | -3/2 |

Second-order

Shift from first order position in units of $(a^2/4B_0)$

| | 3 | 7 | 7 | 3 |

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References to Chapter 7

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