Sulfur-containing Radicals: From EPR Spectroscopic Studies to Synthetic Methodology

A Thesis Presented to the University of London in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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“I believe a leaf of grass is no less than the journey-work of the stars.”

Walt Whitman
This thesis is dedicated to my late Auntie, Doreen Latter.

1930-2001
ABSTRACT

A variety of novel homochiral silanethiols have been prepared and investigated as polarity-reversal catalysts for the enantioselective hydrosilylation of a prochiral alkene. The enantiomeric excesses of the products were disappointingly small. A computer modelling procedure, based on molecular mechanics, was applied in order to understand the results and quantitative agreement with experiment was reasonably good.

Silanethiols have been oxidised to the corresponding disulfides and these have been investigated as photochemical sources of silanethiyl radicals. Electron paramagnetic resonance (EPR) spectroscopy has been used to study the reactivity of these silanethiyl radicals and the results have been compared with the known chemistry of alkanethiyl radicals. Competitive hydrogen-atom abstraction from, and thiy radical addition to, propene and cyclopentene, together with addition to phosphines, alkyl isocyanides and the $\text{S}_2\text{H}2$ dealkylation of trialkylboranes have all been studied.

The radical-chain isomerisation of allyl silyl ethers takes place on heating in the presence of an initiator and an arenethiol as a protic polarity-reversal catalyst. Various thiols were tested and pentafluorothiophenol was found to be particularly effective in this role. It has been shown that thermodynamic equilibrium between isomers is established under the conditions used for these experiments. This methodology has also been applied to the isomerisation of allyl alkyl ethers to alkyl vinyl ethers.

As a model for the corresponding reactions of thiy radicals, EPR spectroscopy has been used to determine the relative molar rate constants for abstraction of allylic and benzylic hydrogens from cyclic and acyclic acetals by tert-butoxyl radicals using competition experiments. Absolute rate constants and Arrhenius activation parameters for $\beta$-scission of $\text{R}^1\text{O}(\text{R}^2\text{O})\text{CR}^3$ have been determined by a steady-state EPR method and the results can be understood in terms of angle-strain and stereoelectronic effects. Calculations using density functional theory have been carried out in support of this work and the agreement between computed and experimental results is remarkably good.
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ABBREVIATIONS

AIBN azobis(isobutyronitrile)
DBPB 2,2-di-tert-butyldiroyoxybutane
DBPC 1,1-di-tert-butylperoxyxycyclohexane
DLP dilauroyl peroxide
DMF N,N-dimethylformamide
ee enantiomeric excess
EPR electron paramagnetic resonance
ether diethyl ether
FBT 4-fluorothiophenol
FMTP 4-(trifluoromethyl)thiophenol
HPLC high-performance liquid chromatography
LDA lithium diisopropylamide
petroleum petroleum spirit, b.p. 40-60 °C
PFTP pentafluorothiophenol
PRC polarity-reversal catalysis
NMR nuclear magnetic resonance
RT retention time
TDT tert-dodecanethiol
TBHN di-tert-butyl hyponitrite
THF tetrahydrofuran
tlc thin layer chromatography
ZPVE zero-point vibration energy
CHAPTER 1
GENERAL INTRODUCTION: THE CHEMISTRY OF THIYL RADICALS

Free radicals are highly versatile reaction intermediates which allow many transformations to be carried out under relatively mild conditions.¹ Sulfur radicals are especially important because of their role in biological processes and play an important role in organic synthesis.² The most important types of sulfur radicals are thiyl radicals (RS*), sulfinyl radicals (RS*O) and sulfonyl radicals (RS*O₂). Thiyl radicals are the most common and their chemistry is reviewed in this chapter.

1.1 Generation of thiyl radicals

Since thiols have relatively weak S-H bonds (MeS-H, 365 kJ mol⁻¹)³ compared with C-H bonds (CH₃CH₂-H, 421 kJ mol⁻¹),³ the thiyl radical 1 can be produced efficiently by reaction of a thiol with a simple alkyl radical [eqn. (1.1)]. The ease of this reaction explains why thiols can inhibit radical-chain reactions by hydrogen transfer.

\[
R^* + XSH \rightarrow RH + XS^* \quad (1.1)
\]

Another common route to generate thiyl radicals is by photolysis of a disulfide or by radical displacement reactions on disulfides [eqns. (1.2) and (1.3)].⁴

\[
RSSR \xrightarrow{hv} 2RS^* \quad (1.2)
\]

\[
X^* + R'SSR' \rightarrow XSR' + R'S^* \quad (1.3)
\]

\(X^* = \text{e.g. } RS^*, R_3Sn^*, R_3Si^*, R_3C^*\)

Fava et al.⁵ have shown that thiyl radicals can be generated from the reaction between a thiol and oxygen, which can be used to initiate a free radical chain process leading to isotopic exchange between thiols and disulfides.

\[
\begin{align*}
C_6H_5SH + O_2 & \rightarrow C_6H_5S^* + HO_2^* \\
C_6H_5S^* + C_6H_5S'SC_6H_5 & \rightarrow C_6H_5S-SC_6H_5 + ^7SC_6H_5 \\
^7SC_6H_5 + C_6H_5SH & \rightarrow C_6H_5S^*H + C_6H_5S^*
\end{align*}
\]

SCHEME 1.1
1.2 **Hydrogen-atom abstraction by thiyl radicals**

Although hydrogen-atom abstraction is a common reaction of an alkoxyl radical, the corresponding reaction of a thiyl radical is usually relatively slow although hydrogen-atom abstraction by a thiyl radical can be observed in the presence of a good hydrogen-atom donor to suppress the reverse reaction. For example, Huyser and Kellogg demonstrated that hydrogen-atom abstraction by thiyl radicals takes place in the radical-chain reaction of β-hydroxysulfides with thiols to give ketones (Scheme 1.2).

\[
\begin{align*}
RS^* + HO\,SR & \rightarrow RSH + HO\,SR \\
HO\,SR & \xrightarrow{\text{FAST}} RS^* + \text{R' C=CCH}_2
\end{align*}
\]

**Scheme 1.2**

Hydrogen-atom abstraction by a thiyl radical is also involved in the thiol-catalysed decarbonylation of an aldehyde (see Section 1.5) and in the reactions that are reported in this thesis.

1.3 **Addition of thiyl radicals to carbon-carbon multiple bonds**

The free radical addition of a thiol to carbon-carbon multiple bonds is a well-established reaction. It represents one of the most useful methods of synthesising sulfides under mild conditions and has been the subject of many reviews. These reactions were originally initiated by thermal decomposition of peroxides or azocompounds, by UV irradiation or by radiolysis but, more recently, organoboranes have been used as initiators [eqn (1.3)]. Traces of oxygen are required for the initiator process which involves initial formation of a peroxyborane \( \text{Et}_2\text{BOOEt} \) followed by its reaction with \( \text{Et}_3\text{B} \) to produce ethoxyl and ethyl radicals.

\[
\text{HOCH}_2\text{CH}_2\text{C}≡\text{CH} + \text{PhSH} \xrightarrow{\text{Et}_3\text{B}/\text{O}_2, 25^\circ\text{C}} \text{HOCH}_2\text{CH}_2\text{C}≡\text{CHH} \quad \text{(1.3)}
\]

91% \((Z : E = 1 : 1.5)\)
The reversibility of the addition of a thyl radical to an alkene plays an important role in the overall thiol-alkene addition reaction. The exothermic addition step [eqn. (1.4)] is reversible and the values of $k_1$ can be large compared to $k_1$ and $k_2$. As discussed above, step (1.5) is also exothermic because the dissociation energy of a C-H bond is generally greater than that of an S-H bond, which explains the ready addition of thiols to alkenes without telomer formation.\(^9\)

\[
\begin{align*}
RS^* + \text{C} = \text{C} & \rightleftharpoons k_1 \text{RS} - \text{C} - \text{C}^* \quad (1.4) \\
\text{RS} - \text{C} - \text{C}^* + \text{RSH} & \rightarrow k_2 \text{RS} - \text{C} - \text{C}^* + \text{RS}^* \quad (1.5)
\end{align*}
\]

Because of the reversibility of reaction (1.4), the photochemical reactions of terminal alkenes with disulfides gives very poor yields. However, the reaction of disulfides with terminal acetylenes gives good yields, because the addition of a thyl radical to the alkyne is much less reversible than its addition to an alkene [eqns. (1.6) and (1.7)].\(^10\)

\[
\begin{align*}
\text{R'C}=\text{CH}_2 + \text{RSSR} & \rightarrow h_n \text{R'S}=\text{CH}_2\text{SR} \quad (1.6) \\
\text{R'C}=\text{CH} + \text{RSSR} & \rightarrow h_n \text{R'=CH=CHSR} \quad (1.7)
\end{align*}
\]

The addition of a radical to a terminal double bond in an alkyl allyl sulfide can indirectly generate an alkylthyl radical, because alkyl radicals with β-C-S bonds undergo β-scission readily. As an example of this, Keck and co-workers\(^11\) have shown that the phenylthyl radical carries the chain reaction of allyl phenyl sulfide with hexabutylditin and an alkyl halide (Scheme 1.3). The tributyltin radical, generated by reaction of PhS\(^*\) with the hexabutylditin, reacts with alkyl halide to form R\(^*\) which reacts with the allyl sulfide to give the allylation product.
1.4 Reactions of alkylthiyl radicals at coordinatively unsaturated centres

Alkylthiyl radicals add to a number of coordinatively unsaturated elements to give hypervalent intermediates (e.g. attack at phosphorus) or transition states in which the coordinate number of the element is increased (e.g. attack at boron).

### 1.4.1 Phosphorus(III) compounds

Although alkanethiols do not react with phosphorus(III) compounds under ionic conditions, they are quantitatively converted into alkanes under the influence of ultraviolet light or in the presence of an initiator. Walling and his co-workers have shown that alkylthiyl radicals react with trialkyl phosphites to undergo desulfurisation via β-scission of an intermediate phosphoranyl radical to give the corresponding alkyl radicals (Scheme 1.4).

**SCHEME 1.4**

1.4.2 Trialkylboranes

Trialkylboranes undergo facile photochemical reactions with disulfides leading to the production of monosulfides (Scheme 1.5).
1.4.3 Isocyanides

Electron paramagnetic resonance (EPR) spectroscopy has shown that alkylthiyl radicals add to the terminal carbon of an alkyl isocyanide at low temperatures to give an imidoyl radical (RN=CSX), that may undergo various subsequent transformations (see Section 3.1.3).

1.5 Thiols as protic polarity-reversal catalysts

The concept of polarity-reversal catalysis (PRC) is based on the exploitation of polar factors that influence the reactions of electrically-neutral radicals. Barrett and Waters reported that thiols catalyse the radical-chain decarbonylation of aldehydes [eqns. (1.8) and (1.9)]. In the general discussion that followed this paper, F. R. Mayo suggested an explanation for the catalysis based on polar effects. Mayo pointed out that the chain-propagating abstraction of hydrogen from an aldehyde by an alkyl radical [eqn. (1.9)] does not benefit from favourable charge transfer (polar effects) in the transition state, because both the alkyl radical and the acyl radical are nucleophilic. Mayo proposed that the catalysis of the overall hydrogen transfer reaction (1.9), through the cycle of reactions [eqns. (1.10) and (1.11)], could be understood because the thiol radical is electrophilic. This phenomenon has been generalised and christened polarity-reversal catalysis (PRC); in this case the thiol is acting as a protic polarity-reversal catalyst that promotes overall hydrogen-atom transfer from the aldehyde to the nucleophilic carbon-centred radical produced by decarbonylation.

\[
\begin{align*}
R\dot{C}=O & \rightarrow R^* + CO \quad (1.8) \\
R^* + RCHO & \rightarrow RH + R\dot{C}=O \quad (1.9) \\
R^* + XSH & \rightarrow RH + XS^* \quad (1.10) \\
XS^* + RCHO & \rightarrow XSH + R\dot{C}=O \quad (1.11)
\end{align*}
\]

Several other instances of PRC have been identified. For example, the radical-chain hydrosilylation of alkenes using trialkysilanes is not very useful in
synthesis because the hydrogen-atom abstraction step [eqn. (1.12)] is relatively slow at moderate temperatures and competing telomerisation of the alkene can also be a problem.\textsuperscript{18, 19} Hydrogen-atom transfer from silicon in a trialkylsilane to a non-conjugatively stabilised alkyl radical is usually exothermic and it has been argued that the slowness of this reaction can be attributed to unfavourable polar effects which operate in the transition state for abstraction of electron-rich hydrogen by a nucleophilic alkyl radical (Scheme 1.7).\textsuperscript{20, 21}

\[
\text{R}^* + \text{SiR}_3 + \text{R}_3\text{SiH} \rightarrow \text{H} + \text{SiR}_3
\] (1.12)

\[\text{stable} \quad \text{unstable} \quad \text{unstable} \quad \text{stable}\]

**SCHEME 1.7**

Our group has shown that this reaction is promoted by thiols which act as protic polarity-reversal catalysts, such that the slow direct abstraction is replaced by the cycle of relatively rapid reactions (1.13) and (1.14), both of which benefit from favourable polar effects, because the thyl radical is electrophilic and the sulfhydryl hydrogen atom is electron-deficient.\textsuperscript{22} Polar effects facilitate the hydrogen transfer reaction (1.12) by stabilising the transition state (Scheme 1.8).

\[
\text{R}^* + \delta-\delta+ \quad \text{YSH} \quad \text{FAST} \quad \text{RH} + \text{YS}^* \] (1.13)

\[
\text{YS}^* + \delta+\delta- \quad \text{Et}_3\text{SiH} \quad \text{FAST} \quad \text{YSH} + \text{Et}_3\text{Si}^* \] (1.14)

\[\text{stable} \quad \text{stable}\]

**SCHEME 1.8**
Success of this method depends on the reversibility of the addition of the thyl radical to the alkene, while the corresponding addition of the silyl radical is rapid and irreversible. This results in only slow loss of the thiol catalyst by addition to the alkene.

For example, a good isolated yield (85%) of the triethylsilane adduct 3 can be obtained by hydrosilylation of diethyl allylmalonate 2 at 60 °C using tert-dodecanethiol as protic polarity-reversal catalyst [eqn. (1.15)].

\[
\begin{align*}
\text{(EtO}_2\text{C)}_2\text{C} & \quad \text{Et}_3\text{SiH} \\
\text{H} & \quad \text{t-C}_{12}\text{H}_{25}\text{SH cat.} \\
\underline{2} & \quad \rightarrow \\
\text{(EtO}_2\text{C)}_2\text{C} & \quad \text{SiEt}_3 \\
\text{H} & \\
\underline{3}
\end{align*}
\]

This catalytic cycle has been applied to the enantioselective radical-chain hydrosilylation of prochiral alkenes using optically active thiol catalysts (see Section 2.1.2.3) and thiols have also been used as protic polarity-reversal catalysts in several classes of radical-chain reaction such as the hydroacylation of alkenes, reductive carboxyalkylation of alkenes, and epimerisation of 1,2-diols.
1.6 REFERENCES


CHAPTER 2
SYNTHESIS OF SILANETHIOLS AND THEIR APPLICATIONS AS POLARITY-REVERSAL CATALYSTS

2.1 INTRODUCTION
Although silicon is immediately beneath carbon in the Periodic Table, replacement of a key carbon atom in an organic molecule by a silicon atom can often bring about significant changes in properties. Silicon is more electropositive than carbon; its atoms are larger and have energetically-accessible 3d orbitals that can participate in dπ-pπ bonding. For example, a trialkysilanol R₃SiOH is more acidic than the corresponding alcohol R₃COH, because of stabilisation of the siloxide anion A by electron donation from oxygen to silicon. Trialkysiloxy radicals (R₃SiO•) behave rather more like hydroxyl radicals (HO•) than alkoxyl radicals (R₃CO•). Whilst dialkylaminyl radicals of the type (R₃C)₂N• are relatively unreactive, the bis(trimethylsilyl)aminyl radical (Me₃Si)₂N• is a highly-reactive abstractor of hydrogen from CH groups in organic molecules, a property that can be attributed to donation of the nitrogen lone pair into the vacant silicon 3d orbitals (see structure B). For these reasons, it was of considerable interest to investigate silanethiyl radicals X₃SiS• as second-row congeners of the well-known alkanethiyl radicals X₃CS•.

2.1.1 Preparation of organosilanethiols
2.1.1.1 Preparation of silanethiols by a heterolytic mechanism
Silanethiols can be synthesised by a variety of methods, some of which are illustrated in Scheme 2.1.

---

* The radical B may have a quasi-linear structure.

---
Alkylsilanethiols can be prepared by reaction of a trialkylchlorosilane with lithium hydrosulfide\(^5\) and arenesilanes readily react with elemental sulfur to give arenesilanethiols.\(^6\) Wojnowski \textit{et al.}\(^7\) have shown that \((\text{Bu}'\text{O})_3\text{SiSH}\) can be made by reaction of the alcohol \(\text{Bu}'\text{OH}\) with \(\text{SiS}_2\).

2.1.1.2 Preparation of silanethiols by a radical-chain mechanism

Silanethiols can also be generated by a radical-chain reaction between silanes and triphenylphospine sulfide\(^8\) or carbonyl sulfide\(^9\) (see Section 3.1.5).

2.1.2 Applications of organosilanethiols

2.1.2.1 Silanethiols as \( \text{H}_2\text{S} \) equivalents

Triphenylsilanethiol can function as an \( \text{H}_2\text{S} \) equivalent for the synthesis of alkanethiols and thioesters, when C-S bond formation is accomplished by a radical pathway. The triphenylsilyl radical generated thermally [azobis(isobutyronitrile), initiator] or photochemically in the presence of an olefin yields the \textit{anti}-Markovnikov \( \text{H}_2\text{S} \) adduct after deprotection by trifluoroacetic acid (TFA) (Scheme 2.2).\(^{10}\)

\[
\begin{align*}
\text{R} & \quad + \quad \text{Ph}_3\text{SiSH} \quad \xrightarrow{1. \text{Radical initiator}} \quad \text{R} - \text{SH} \\
& \quad \xrightarrow{2. \text{TFA}} \\
\end{align*}
\]

\textbf{SCHEME 2.2}

Triisopropylsilanethiol can also function as an \( \text{H}_2\text{S} \) equivalent for the synthesis of alkanethiols, unsymmetrical dialkyl sulfides and thioacetals, when C-S bond formation is accomplished by a heterolytic pathway (Scheme 2.3).\(^2\) The triisopropylsilyl group provides remarkable resistance toward hydrolytic cleavage of the Si-S bond as well as protection for the thiol moiety in Grignard reactions.
2.1.2.2 Silanethiols as reducing agents

The silanethiols (Me3Si)3SiSH and (Me3Si)2MeSiSH have been used as homolytic reducing agents for alkyl halides.11 In the presence of an initiator, they rearrange which allows the hydrogen donating ability of a thiol to be combined with the halogen abstracting ability of the silyl radical [see Scheme 2.4 for reaction of (Me3Si)3SiSH]. These silanethiols are a cleaner alternative to tin hydrides which suffer from the disadvantage that it is often difficult to separate the tin residues from the desired product and from the toxicity of organotin compounds.

2.1.2.3 Silanethiols as protic polarity-reversal catalysts

Silanethiols [in particular Ph3SiSH and (Bu'O)3SiSH] have been used as protic polarity-reversal catalysts to promote the overall abstraction of electron-rich hydrogen by one nucleophilic radical to produce a second nucleophilic radical. Of particular relevance to this work, silanethiols have been used in the hydrosilylation of alkenes (Section 1.5) and have been found to be good catalysts.12
The principle of polarity-reversal catalysis has been applied to make the hydrosilylation process enantioselective when a prochiral alkene is used in conjunction with an optically active thiol catalyst (Scheme 2.5).

\[
\text{R}^\bullet \text{SiH} \quad \text{R}^\bullet \text{SH} \quad \text{R}^\bullet \text{Si} \text{CHR}^1 \text{R}^2 \quad \text{XSH}
\]

Scheme 2.5

The stereogenic centre in the final adduct is generated by hydrogen-atom transfer (step b) from the thiol to the β-silylalkyl radical, formed by addition of a silyl radical to the prochiral alkene (step a). Enantioselective atom transfer, mediated by a prochiral radical and a closed-shell homochiral molecule, is generalised in eqn. (2.1). Here, the homochiral reagent R^*SH is able to attack at the Re and Si faces of the prochiral radical and hence create the enantioselectivity. It proceeds through the diastereoisomeric pair of transition states C and D, and it is the energy difference between these two structures that determines the enantioselectivity of the transfer of the hydrogen-atom.

\[
\begin{align*}
\text{R}^2 \text{CH}_2 \text{SiR}_3 + \text{R}^\bullet \text{SH} & \rightarrow \text{R}^\bullet \text{Si} \text{CHR}^1 \text{R}^2 \text{CH}_2 \text{SiR}_3 \text{R}^\bullet \text{S}^* \quad (2.1)
\end{align*}
\]

Results using a number of homochiral thiols have showed that catalytic amounts can be used to mediate enantioselective hydrosilylation of prochiral alkenes giving functionalised organosilanes in good yield and moderate enantiomeric purity. The
hydrosilylation of the prochiral methylenelactones 1 and 2 with triphenylsilane (Scheme 2.6) in the presence of different carbohydrate-derived thiols gave high chemical yields and the enantiomeric excesses (ee) of the product varied depending on the nature of the thiol. The highest enantiomeric purities were obtained from the lactone 2 using a 1-thio-β-D-glucopyranose and 1-thio-β-D-mannopyranose thiol (ca. 86 %) and a β-mannose thiol (ca. 95%). The optically active adducts formed can be oxidatively desilylated to provide a variety of useful silicon-free organic compounds.

![Scheme 2.6](image.png)

2.1.3 Aims of the project

The hydrosilylation of a variety of prochiral alkenes, has been investigated in our group and it was found that the steric bulk around the radical centre helped to raise the ee. Taking an overview, a high enantiomeric excess in the adduct has only been found when bulky substituents are present on both alkene and the silane. We reasoned that sterically bulky homochiral silanethiols might be used as catalysts in the radical-chain hydrosilylation of prochiral alkenes to induce high enantiomeric purities in the product.

In this work, a variety of novel homochiral silanethiols are prepared and tested for their capacity to mediate enantioselective hydrosilylation reactions.
2.2 RESULTS AND DISCUSSION

To begin with some achiral silanethiols were synthesised which showed some advantages over use of triphenylsilanethiol 3 as a catalyst. *tert*-Butyldiphenylsilanethiol 4 and *tri-ortho*-tolysilanethiol 5 were thought to be more stable to water compared to 3 which is highly moisture sensitive. These silanethiols were tested as catalysts for the hydrosilylation of the methylenelactone 1 by triphenylsilane (Scheme 2.7), using the typical procedure described in Section 2.4.2.5.

\[ \text{XSH, TBHN, 1,4-dioxane, 60 }^\circ\text{C, 2 h} \]

\[ \begin{align*}
1 & \rightarrow \text{X} & \\
\text{Ph}_3\text{SiH} & \text{SiPh}_3
\end{align*} \]

\[ X = \text{Ph}_3\text{Si 3, Bu}^\prime\text{Ph}_2\text{Si 4, (o-MeC}_6\text{H}_4)_2\text{Si 5} \]

**SCHEME 2.7**

The silanethiols 3-5 were found to be excellent polarity-reversal catalysts, giving high conversions (> 95%, see Table 2.1) and silanethiols 4 and 5 showed that they could be good alternatives to triphenylsilanethiol 3.

Bulky homochiral thiols were synthesised by modifying the procedure used by Wojnowski *et al.* to prepare (Bu′O)₃SiSH, by reacting sterically bulky alcohols (*e.g.* L-menthol) with SiS₂ and the silanethiols 7-12 were successfully synthesised using this method. It was thought that the large alkoxy groups would produce a “cup-shaped” pocket around the S-H group, which might make these thiols able to deliver the hydrogen enantioselectively to a prochiral alkyl radical.
Although the silanethiols 7-12 were found to be excellent polarity-reversal catalysts for hydrosilylation, giving high chemical conversions (> 95%, see Table 2.2), the enantiomeric excesses were disappointingly low. Molecular modelling of the silanethiols (Section 2.2) showed that these compounds may be too conformationally flexible and that the substituent groups RO present too "uniform" an environment around the SH group. In the light of this, the thiol 13 was synthesised, replacing a bornyl group with a phenyl ring in order to make the surroundings of the SH group less symmetrical. Unfortunately, this thiol also gave a low ee (Table 2.2).

\[
\text{Si(Ph)SH}
\]

13

2.2.1 Effect of Lewis acids on enantioselective hydrosilylation

Enantioselectivity in the hydrosilylation of the methylenelactone 1 using organosilanethiols as catalysts might be improved by making use of lanthanide based Lewis acid complexation. Here, the oxophilic Lewis acid might bridge reversibly between the thiol and the β-silylalkyl radical radical to give a loose complex, thus rendering hydrogen-atom transfer effectively intramolecular and thereby increasing enantioselectivity.

Preliminary experiments with methylenelactone 1, Ph₃SiH and silanethiol 7 in the presence of various Lewis acids (Table 2.3) showed high conversions (> 90%), but little change in ee.
CHAPTER TWO

Table 2.1: Hydrosilylation of methylenelactone 1\textsuperscript{a} by triphenylsilane initiated with TBHN (5 mol%) in 1,4-dioxane solvent at 60 °C for 2.5 h using different silanethiol catalysts

<table>
<thead>
<tr>
<th>Thiol\textsuperscript{b}</th>
<th>Conversion\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph\textsubscript{3}SiSH 3</td>
<td>90</td>
</tr>
<tr>
<td>Bu'Ph\textsubscript{2}SiSH 4</td>
<td>&gt; 95</td>
</tr>
<tr>
<td>(o-Tolyl)\textsubscript{3}SiSH 5</td>
<td>&gt; 95</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 1 mmol; solvent volume 2.5 cm\textsuperscript{3}. \textsuperscript{b} 5 mol% based on alkene. \textsuperscript{c} Determined by \textsuperscript{1}H NMR spectroscopy.

Table 2.2: Enantioselective hydrosilylation of methylenelactone 1\textsuperscript{a} initiated with TBHN (5 mol%) in refluxing 1,4-dioxane for 2.5 h using different homochiral alkoxysilanethiols as catalysts

<table>
<thead>
<tr>
<th>Thiol\textsuperscript{b}</th>
<th>Conversion\textsuperscript{c}</th>
<th>Product ee (%)\textsuperscript{d,e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>&gt; 95</td>
<td>9, 9</td>
</tr>
<tr>
<td>8</td>
<td>&gt; 95</td>
<td>-9</td>
</tr>
<tr>
<td>9</td>
<td>&gt; 95</td>
<td>-6, -7</td>
</tr>
<tr>
<td>10</td>
<td>&gt; 95</td>
<td>-3</td>
</tr>
<tr>
<td>11</td>
<td>&gt; 95</td>
<td>0.3</td>
</tr>
<tr>
<td>12</td>
<td>&gt; 95</td>
<td>0.4</td>
</tr>
<tr>
<td>13</td>
<td>&gt; 95</td>
<td>1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 1 mmol; solvent volume 2.5 cm\textsuperscript{3}. \textsuperscript{b} 5 mol% based on alkene. \textsuperscript{c} Determined by \textsuperscript{1}H NMR spectroscopy. \textsuperscript{d} Determined by chiral-stationary-phase HPLC analysis using a Daicel Chemical Industries Chiralcel-OD column. \textsuperscript{e} A positive ee indicates the (R)-enantiomer of 6 in excess; a negative ee indicates the (S)-enantiomer is in excess.
Table 2.3: Enantioselective hydrosilylation of methylenelactone 1\textsuperscript{a} initiated with TBHN (5 mol\%) in refluxing 1,4-dioxane for 2.5 h using 7\textsuperscript{b} as catalyst in the presence of various Lewis acids (10 mol\%)

<table>
<thead>
<tr>
<th>Lewis Acid</th>
<th>Product ee (%)\textsuperscript{c,d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(OTf)\textsubscript{2}</td>
<td>8</td>
</tr>
<tr>
<td>Mg(OTf)\textsubscript{2}</td>
<td>7</td>
</tr>
<tr>
<td>Sc(OTf)\textsubscript{3}</td>
<td>7</td>
</tr>
<tr>
<td>Y(OTf)\textsubscript{3}</td>
<td>8</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 1 mmol; solvent volume 2.5 cm\textsuperscript{3}. \textsuperscript{b} 5 mol\% based on alkene. \textsuperscript{c} Determined by chiral-stationary-phase HPLC analysis using a Daicel Chemical Industries Chiralcel-OD column. \textsuperscript{d} A positive ee indicates the (R)-enantiomer of 6 in excess; a negative ee indicates the (S)-enantiomer is in excess.
2.2.2 Computer-assisted design of homochiral thiols as catalysts for enantioselective hydrogen-atom transfer reactions

It was thought that molecular modelling might provide an insight into why these homochiral thiol catalysts gave low enantiomeric excesses and what criteria are needed for more effective catalysts. The thiol-catalysed hydrosilylation reaction of the methylenelactone 1 with $\text{Ph}_3\text{SiH}$ to give 6 was modelled in this investigation.

\[
\begin{array}{c}
\text{1} + \text{Ph}_3\text{SiH} \\
\rightarrow \\
\text{6}
\end{array}
\]

2.2.2.1 The molecular mechanics method

The basis of the molecular mechanics method is that a good estimate of the geometry of the molecule or transition state can be obtained by taking into account all the forces between the atoms, calculated using a classical mechanical approach. For example, bonded atoms are treated as if they are held together by forces that behave as mechanical springs and non-bonded interactions are taken to be made up of attractive and repulsive forces that together produce the typical van der Waals curve. To optimise the geometry of a molecule, the total energy that arises from these forces or stresses, is minimised by computational methods. The parameters used to derive the minimised total energies are based on experimental data and molecular mechanics calculations are sometimes referred to as 'empirical force field calculations'. A force field is required for all molecular mechanical calculations in order to compute the most stable geometry of the molecule. This force field is a collection of atom types (used to define the atoms in a molecule), equilibrium parameters (e.g. bond lengths, angles, torsions etc), force constants and equations to calculate the total energy of the molecule.

There are usually no problems associated with the optimising of 'ordinary' organic molecules, as all the parameters required would normally be present in the force field of most molecular modelling software. However, a common problem associated with the modelling of transition states is the insufficiency of parameterisation of force fields, because most force fields of modelling software are deficient in parameters for partial bonds.
2.2.2.2 Parameterisation of the force field

The MMX force field of the commercial program PCMODEL\textsuperscript{15} has been further parameterised by Gurdeep Nandra (1999), so as to give an accurate account of the transition state for the hydrogen-atom transfer from silanethiols to alkyl radicals. A set of parameters applicable to the transition state for hydrogen-atom abstraction from silanethiol (H\textsubscript{3}SiSH) by the methyl radical was established for transition state 14 using \textit{ab initio} molecular orbital methods.

In order to apply molecular mechanical procedures to system 14, the transition state was treated as a normal molecule which possesses all real vibrational modes. Given that the \textit{ab initio} computed S--H\textsuperscript{*}--C angle in 14 was very close to 180°, the energy required to move H\textsuperscript{*} by small amounts above and below the S---C vector would be very small and therefore the S--H\textsuperscript{*}--C moiety could be represented by a linear bond. By fixing the S---C distance to 2.977Å (corresponding to the S---C bond length in 14) and performing further \textit{ab initio} calculations gave rise to the structure 15, which possessed all real vibrational frequencies. The parameterisation was adjusted so that, apart from H\textsuperscript{*}, the geometry of 15 was identical to the geometry obtained for 14 and these parameters were incorporated into the MMX forcefield.
### Calculation of enantiomeric excess

#### Scheme 2.8

The GMMX conformational searching method of PCMODEL was used to obtain global energy minimum structures. Minimisation of the energies of the diastereoisomeric transition states (Scheme 2.8), leading to the (S)- and (R)- optically active products, were computed and the differences in these energies were taken as equal to the difference in the activation energies \( E_S - E_R \) for the reactions yielding the (S)- and (R)- products.\(^*\) The pre-exponential factors \( A \) were assumed to be equal for the two reactions and the Arrhenius equation was used to find the ratio of the rates constants \( k_R/k_S \) for the reactions leading to each enantiomer [eqns. (2.2) and (2.3)]. The ratios of the rate constants were then used in conjunction with eqn. (2.4) to obtain the enantiomeric excesses for the hydrogen transfer reactions.

\[
\begin{align*}
    k_S &= A \exp(E_S/RT) \\
    k_R &= A \exp(E_R/RT) \\
    k_R/k_S &= \exp((E_S - E_R)/RT) \\
    \%\text{ee} &= [(1 - k_S/k_R)/(1 + k_S/k_R)] \times 100
\end{align*}
\]

To predict the ee arising from the use of homochiral silanethiol catalysts in hydrosilylation reactions, the transition states for abstraction of hydrogen by \( 6a \) from thiols 7, 9, 10, 11 and 13 were computed and the results are shown in Table 2.4.

\(^*\) The transition states that lead to the formation of the (S)- and (R)-enantiomers of the hydrosilylation product of 6 were termed the \( (S')- \) and \( (R')- \)transition states, respectively.
2.2.2.4  Modelling of hydrogen transfer reactions using homochiral silanethiols

The typical orientation of the alkoxy groups found in all the trialkoxysilanethiols is shown in Figure 2.1 and, indeed, the large alkoxy groups generate a cup-shaped pocket around the S-H group. This discriminating in their reaction at the Re and Si faces of an approaching alkyl radical.

The results obtained from modelling the hydrogen-atom transfer from the homochiral silanethiols 7, 9, 10, 11 and 13 to 6a are shown in Table 2.4.

The mmx-minimised diastereoisomeric transition states for hydrogen-atom transfer between 6a and 7 are shown in Figures 2.2 and 2.3; the energy difference between these transition states is 2.43 kJmol\(^{-1}\). This energy difference translates to a predicted enantiomeric excess of 41% with a preference for the (R)-enantiomer of 6. The predicted result is of the same order as the experimental ee of 9% and the predicted major enantiomer is the same as that found experimentally. The predicted result is considered within any computational error that may had arisen due to insufficiencies in the modelling of experimental conditions (e.g. dielectric properties of the solvent) and this initial result gave a good indication that the modified force field was performing fairly satisfactorily.

The predicted ee from the transition states for hydrogen-atom transfer from the menthoxy silanethiols 9 and 10 to 6a, again, shows broad agreement with values obtained experimentally. Modelling the hydrogen-atom transfer from the
bornylsilanethiols 11 and 13 to 6a gave much higher predicted enantiomeric excesses than the experimental values and the reason for this discrepancy is unclear at present.
Figure 2.1: GMMX optimised structure of the silanethiol 7
Figure 2.2: GMMX optimised structure of the ($R'$)-transition state for hydrogen-transfer between 7 and 6a

The C=S bond in the "stretched sulfide" model of the transition state.
Figure 2.3: GMMX optimised structure of the (S')-transition state for hydrogen-transfer between 7 and 6a
Table 2.4: Comparison of enantiomeric excesses (ee) predicted computationally and those obtained by experiment for the addition of Ph$_3$SiH to the methylenelactone 1, using various silanethiol catalysts

<table>
<thead>
<tr>
<th>Silanethiol</th>
<th>Transition States</th>
<th>MMX $E$ kJ mol$^{-1}$</th>
<th>$(E_S-E_R)$ kJ mol$^{-1}$</th>
<th>$k_S/k_R$</th>
<th>Product ee (%)*</th>
<th>Experimental ee (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>tri-(1$R$,2$S$,5$R$)-menthoxy silanethiol</td>
<td>7+6a $S'$</td>
<td>250.8</td>
<td>2.43</td>
<td>0.42</td>
<td>41</td>
<td>9.1</td>
</tr>
<tr>
<td>tri-(1$S$,2$R$,5$R$)-menthoxy silanethiol</td>
<td>7+6a $R'$</td>
<td>248.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tri-(1$S$,2$S$,5$R$)-menthoxy silanethiol</td>
<td>9+6a $S'$</td>
<td>267.9</td>
<td>-1.47</td>
<td>1.70</td>
<td>-26</td>
<td>-7.2</td>
</tr>
<tr>
<td>tri-(1$S$,2$S$,5$R$)-menthoxy silanethiol</td>
<td>9+6a $R'$</td>
<td>269.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tri-[[(1$S$)-endo]-boronylsilanethiol</td>
<td>10+6a $S'$</td>
<td>280.4</td>
<td>-2.09</td>
<td>2.13</td>
<td>-36</td>
<td>-3</td>
</tr>
<tr>
<td>tri-[[(1$S$)-endo]-boronylsilanethiol</td>
<td>10+6a $R'$</td>
<td>282.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>di-[[(1$S$)-endo]-boronyloxy]phenylsilanethiol</td>
<td>11+6a $S'$</td>
<td>473.0</td>
<td>9.16</td>
<td>0.04</td>
<td>93</td>
<td>0.3</td>
</tr>
<tr>
<td>di-[[(1$S$)-endo]-boronyloxy]phenylsilanethiol</td>
<td>11+6a $R'$</td>
<td>463.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>di-[[(1$S$)-endo]-boronyloxy]phenylsilanethiol</td>
<td>13+6a $S'$</td>
<td>425.6</td>
<td>-2.80</td>
<td>2.75</td>
<td>-47</td>
<td>0.4</td>
</tr>
<tr>
<td>di-[[(1$S$)-endo]-boronyloxy]phenylsilanethiol</td>
<td>13+6a $R'$</td>
<td>428.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* A positive ee indicates the (R)-enantiomer of 6 in excess; a negative ee indicates the (S)-enantiomer is in excess.
2.2.2.5 Problems with this approach

During the course of the modelling, it became apparent that energy minimisation of the transition states was problematic. It was clear that obtaining the global minimum conformation for systems that contained a large number of rotatable bonds was difficult, because the number of local energy minima increased rapidly with the number of rotatable bonds and there were many different structures of very similar energy. The GMMX method was not always successful in finding the global minimum structure for a large system and the structures obtained were often of higher energy than could be obtained by repeated manual rotation of bonds. Single-point minimisations and manual re-orientation of groups within the transition state and the user's chemical experience proved to be a better method for obtaining the global minimum energy structures.

2.3 Conclusion

The current study has shown that the homochiral silanethiols chosen for study give products of low ee when used as polarity-reversal catalysts for the hydrosilylation of the methylenelactone 1. The modified force field for modelling the transition states for reactions of menthoxysilanethiols with the prochiral alkyl radical 6a, gave results comparable to experimental observations. Experimental enantiomeric excesses obtained for the silanethiols and those predicted computationally suggest that having bulky substituents on the catalysts may not be the only criteria for generating greater enantioselectivity. We suggest that other interactions, such as electrostatic and dipole-dipole interactions, may also contribute to the enantioselectivity observed experimentally. A possible approach may be to design thiol catalysts that mimic the interactions present in enzymes and on chiral chromatographic columns, so that there is a "lock and key" matching between the thiol and the prochiral radical. Further work would need to look at these other interactions that operate in the transition state and to develop further refinement of the force field.
2.4 EXPERIMENTAL

2.4.1 General procedures

$^1$H NMR spectra were recorded using a Varian VXR-400, Bruker AC 300 or a Bruker AC 500 instrument; the solvent was CDCl$_3$. Chemical shifts are quoted relative to residual protons in deuteriated chloroform ($\delta$$_H$ 7.24). Coupling constants $J$ are given in Hz and the use of [multipet] indicates an apparent multiplet associated with an averaged coupling constant and an asterisk is used to indicate a tentative assignment.

Infrared (IR) spectra were recorded on a Nicolet 205 FT-IR spectrometer as liquids films or KBr discs; only the major peaks are reported (in cm$^{-1}$). Mass spectra were obtained using electron impact ionisation (EI) or fast atom bombardment (FAB) on a Micromass ZAB 2SE instrument at University College London.

Elemental analyses were performed by the University College Chemistry Department Microanalytical Service. Melting points were determined using a Reichert hot-stage apparatus and are uncorrected.

Optical rotations were measured on an AA Series Polaar 2000 polarimeter (Optical Activity Ltd.) using a 1 dm cell and are given in units of 10$^{-1}$ deg cm$^2$ g$^{-1}$.

Determination of enantiomeric excess (ee) by high-performance liquid chromatography (HPLC) was carried out using Chiralcel-OD column (4.6 mm x 250 mm; Daicel Chemical Industries Ltd.) in conjunction with hexane-isopropyl alcohol eluent composition (flow rate 1 cm$^3$ min$^{-1}$).

Flash chromatography was performed by using silica gel (40-63 μm mesh) and thin-layer chromatography was performed on Merck Kieselgel 60 F$_{254}$ aluminium-backed pre-coated plates.

All reactions were performed using oven-dried glassware under an atmosphere of nitrogen, unless otherwise stated.

2.4.2 Materials

Commercial materials were generally obtained from Aldrich or Fluka and were used as received.

2.4.2.1 Di-tert-butyl hyponitrite (TBHN)$^{16}$

NaONa$\rightarrow$NONa$\stackrel{Bu^1Br,ZnCl_2,\text{ZnCl}_2}{\longrightarrow}$Bu$^1$ON=NOBu$^1$
CHAPTER TWO

Under a stream of dry nitrogen, sodium hyponitrite (2.13 g, 20.1 mmol) was added to a mixture of excess 2-bromo-2-methylpropane (13.02 g, 95.0 mmol) and anhydrous zinc chloride (2.60 g, 19.1 mol) in dry diethyl ether (11 cm$^3$) at 0 °C. The mixture was stirred for 30 minutes at 0 °C and stored in a freezer at 4 °C overnight. After removal of the precipitated NaBr by filtration through Celite, the filtrate was washed with ice water (2 x 10 cm$^3$), with satd. brine (10 cm$^3$) and dried over Na$_2$SO$_4$. The solvent and most of the 2-bromo-2-methylpropane was removed by rotary evaporation at room temperature and the residual semi-solid was recrystallised from methanol -20 °C (in a freezer) to afford the product as a white crystalline solid (1.11 g, 38%).

M.p. 80-81 °C (lit. m.p. 82 °C).

$\delta_H$: 1.36 (18H, s, Bu$'$).

$\delta_C$: 27.8 and 81.1.

2.4.2.2 4,4-Dimethyl-5-oxohexanenitrile$^{17}$

To a stirred solution of 3-methylbutan-2-one (21.5 g, 0.25 mol), $t$-butyl alcohol (2.2 g, 0.03 mol) and 30% KOH in MeOH solution (6.0 cm$^3$) under an atmosphere of nitrogen, acrylonitrile (15.9 g, 0.3 mol) was added dropwise over 30 min, ensuring the reaction did not exceed 40 °C (using an ice-bath). The reaction mixture was stirred for a further 4 h at room temperature, then was purified by distillation under reduced pressure to afford the product as a colourless oil (21.4 g, 62%).

B.p. 70 °C at 0.2 Torr (lit. b.p. 126-127 °C at 15.0 Torr).

$\delta_H$: 1.16 (6H, s, CMe$_2$), 1.82-1.87 (2H, m, CH$_2$CMe$_2$), 2.12 (3H, s, CH$_3$), 2.20-2.25 (2H, m, CH$_2$CN).
2.4.2.3 4,4-Dimethyl-5-oxohexanoic acid\textsuperscript{17}

A stirred mixture of the ketonitrile (21.4 g, 0.15 mol) and potassium hydroxide pellets (29.0 g, 0.53 mol) in water (140 cm\textsuperscript{3}) was heated under reflux for 2-3 h until evolution of ammonia had ceased. After cooling, the reaction mixture was washed with ether (75 cm\textsuperscript{3}), to remove any organic impurities and then acidified with conc. HCl and extracted with ether (3 x 75 cm\textsuperscript{3}). Combined ether extracts were dried over MgSO\textsubscript{4} and the solvent was removed under pressure to afford the product as a white solid (23.5 g, 99\%).

M.p. 46-47 °C (lit.\textsuperscript{12} m.p. 46-47 °C).

\(\delta_H: 1.13 (6H, s, CMe_2), 1.81-1.87 (2H, m, CH_2CM&), 2.13 (3H, s, C &), 2.22-2.58 (2H, m, CH_2CO_2).\)

\[\text{4,4-Dimethyl-5-oxohexanoic acid}

\[\begin{array}{c}
\text{CN} \\
\text{KOH} \\
\text{H}_2\text{O} \\
\text{CO}_2\text{H}
\end{array}
\]

2.4.2.4 5,5-Dimethyl-6-methylenetetrahydropyran-2-one \textsuperscript{13b}

The ketoacid (20.0 g, 0.13 mol), isopropenyl acetate (38.0 g, 0.038 mol) and conc. H\textsubscript{2}SO\textsubscript{4} (1-2 drops) were placed in a flask which was arranged for distillation and fitted with a short vigreux column. The mixture was stirred and heated so that slow distillation occurred and the material boiling at 55-62 °C was collected over 2.5 h. Solid NaHCO\textsubscript{3} was added to neutralise the solution and then the solution was filtered through Celite. The filtrate was transferred to a high vacuum distillation apparatus and the crude product was distilled to give the product 1 as a colourless oil (12.5 g, 70\%).

B.p. 42-44 °C at 0.1 Torr (lit.\textsuperscript{13b} b.p. 95-96 °C at 10 Torr).

\(\delta_H: 1.20 (6H, s, CMe_2), 1.68 (2H, t, J 7.2, CH_2CMe_2), 2.64 (2H, t, J 7.2, CH_2CO),\)
4.34 (1H, d, J 2.0, CH\textsubscript{vinyl}), 4.62 (1H, d, J 2.0, CH\textsubscript{vinyl}).

δ\textsubscript{C}: 25.9, 27.1, 31.8, 32.6, 91.2, 163.2 and 167.8.

MS (El) m/z: 140 (M\textsuperscript{+}, 52), 112 (M\textsuperscript{+}-CO, 36), 96 (M\textsuperscript{+}-CO\textsubscript{2}, 50), 70 (58), 44 (CO\textsubscript{2}\textsuperscript{+}, 100).

2.4.2.5 Typical procedure for hydrosilylation

\begin{center}
\begin{tikzpicture}
\node[draw, shape=rectangle] (a) at (0,0) {1};
\node[draw, shape=rectangle] (b) at (1,0) {6};
\draw (a) -- node[midway, above] {\text{silanethiol, TBHN,}} (b);
\node at (0.5,-0.5) {1,4-dioxane, 60 °C, 2h};
\end{tikzpicture}
\end{center}

A stirred solution of the methylenelactone 1 (0.42 g, 3.0 mmol), TBHN (27 mg, 0.05 mmol), triphenylsilane (0.86 g, 1.1 mmol), silanethiol (0.05 mmol) and 1,4-dioxane (4 cm\textsuperscript{3}) were placed in a 10 cm\textsuperscript{3} round-bottomed flask fitted with a short reflux condenser, equipped at the top with a silicone rubber septum inlet and a nitrogen by-pass bubbler. The flask was immersed in an oil bath equilibrated at 60 °C and left for 2 h. It was then allowed to cool to room temperature, the solvent was evaporated under reduced pressure and the \textsuperscript{1}H NMR spectrum of the crude product was recorded. The crude product was purified by flash-chromatography [eluent: petroleum-ether (9 : 1), followed by petroleum-ether (6 : 1), followed by petroleum-ether (3 : 1)] to afford the adduct as a white solid (0.28 g, 67%).

M.p. 115-116 °C (lit.\textsuperscript{13b} value 114-116 °C).

δ\textsubscript{H}: 0.92 (3H, s, CCH\textsubscript{A}), 1.00 (3H, s, CCH\textsubscript{B}), 1.58 (3H, m, CCH\textsubscript{2} and SiCH\textsubscript{A}), 1.79 (1H, dd, J 15.0 and 11.5, SiCH\textsubscript{B}), 2.40 (2H, m, CH\textsubscript{2}CO\textsubscript{2}), 4.11 (1H, dd, J 11.5 and 2.4, CHO) 7.38 (9H, m, Ph), 7.59 (6H, m, Ph).

δ\textsubscript{C}: 15.0, 19.3, 26.6, 27.4, 33.1, 34.0, 84.6, 127.8, 129.5, 134.5, 135.9 and 170.9.

MS (El) m/z: 400 (M\textsuperscript{+}, 1), 323 (M\textsuperscript{+}-Ph, 96), 259 (Ph\textsubscript{3}Si\textsuperscript{+}, 100), 199 (96), 181 (27), 105 (24), 41 (24).

The ee was determined using the Chiralcel-OD column (eluent: 10% isopropyl alcohol, t\textsubscript{R} 8 and 11 min); the (R)-(−)-enantiomer was eluted first.\textsuperscript{13b}
Hydrogen sulfide (8.9 cm$^3$, 6.20 g, 181.9 mmol) was condensed into a glass trap of known volume and bubbled through dry tetra-hydrofuran (THF, 300 cm$^3$) at -78 °C contained in a 500 cm$^3$ round-bottomed flask fitted with a condensor. Butyl lithium (1.6 M in hexane) (85.4 cm$^3$, 8.74 g, 136.4 mmol) was then added dropwise over 15 minutes at -78 °C. The solution was allowed to warm to 0 °C over a period of 40 minutes, re-cooled to -78 °C and then tert-butylchlorodiphenylsilane (25 cm$^3$, 26.4 g, 96.1 mmol) was added dropwise over 30 minutes. After the addition was complete, stirring was continued at -78 °C for 1 h, then 1 h at 0 °C and a further 2 h at room temperature. Water (100 cm$^3$) and pentane (100 cm$^3$) were added and, after separation, the organic phase was washed with water (3 x 80 cm$^3$) and dried over MgSO$_4$. Care was taken to avoid unnecessary water contact because of the possible moisture sensitivity of this compound. The solvent was removed by rotary evaporation and the crude product was passed through a short column of silica, eluting with hexane and then distilled under reduced pressure to give tert-butyldiphenylsilanethiol 4 (17.9 g, 68%).

B.p. 120-122 °C at 0.03 Torr.

IR (cm$^{-1}$, liq. film): 2560 (br) (S-H str).

$\delta_h$: 0.08 (1H, s, SH), 1.11 (9H, s, Bu'), 7.36-7.40 (6H, m, Ph), 7.68-7.73 (4H, m, Ph).

$\delta_c$: 20.1, 27.1, 127.7, 129.8, 133.8 and 135.6.

MS (El) $m/z$: 272 (M+, 2), 215 (100), 137 (67), 77 (47).

Found: C, 70.3; H, 7.3. C$_{16}$H$_{20}$OSSi requires C, 70.5; H, 7.4%.

2.4.2.7 Tri-ortho-tolylsilane$^{18}$

To a stirred mixture of magnesium (17.5 g, 0.72 mol) in dry ether (50 cm$^3$) was
added 2-bromotoluene (100.3 g, 0.59 mol) in dry ether (250 cm\(^3\)), dropwise over 3 h, so that gentle refluxing took place; a few crystals of iodine were added to initiate the reaction. After the addition was complete, trichlorosilane (9.9 cm\(^3\), 13.2 g, 97.6 mmol) was added dropwise at 0 °C over 15 minutes. The solution was heated under reflux for 88 h and then hydrolysed with 10% w/v solution of NH\(_4\)Cl (100 cm\(^3\)) at 0 °C, added dropwise over 30 minutes. The crude product was filtered through Celite, the filtrate was extracted with diethyl ether (3 x 100 cm\(^3\)) and the combined extracts were washed successively with water (2 x 100 cm\(^3\)) and satd. brine (2 x 100 cm\(^3\)) and dried over MgSO\(_4\). The solvent was evaporated under reduced pressure and the crude product was recrystallised from hexane to afford tri-ortho-tolylsilane as a white solid (20.7 g, 70 %). M.p. 89-90 °C (lit.\(^{18}\) value 89-90 °C).

\[ \delta_H: 2.23 \text{ (9H, s, } 3\text{C}_7\text{H}_3\text{)}, 5.77 \text{ (1H, s, SiH)}, 7.09 \text{ (3H, d, J 7.6, H-3)}, 7.13 \text{ (3H, t, J 7.4, H-4)}, 7.29 \text{ (3H, t, J 7.5, H-5)}, 7.53 \text{ (3H, d, J 7.3, H-6)}. \]

\[ \delta_C: 22.0, 125.0, 129.6, 130.3, 133.9, 135.3 \text{ and 143.9}. \]

MS (EI) \(m/z\): 302 (M\(^+\), 23), 210 (100), 195 (26), 119 (43).

### 2.4.2.8 Tri-ortho-tolylsilanethiol \(5^{19}\)

A stirred solution of tri-ortho-tolylsilane (9.72 g, 32.2 mmol) and sulfur (1.30 g, 40.6 mmol) in decalin (50 cm\(^3\)) was heated under reflux for 150 h. The solvent was removed by reduced pressure distillation and the crude product passed through a column of silica eluting with hexane. Recrystallisation from hexane gave tri-ortho-tolylsilanethiol \(5\) as a white solid (3.71 g, 33%). M.p. 109 °C.

\[ \delta_H: 0.54 \text{ (1H, s, SH)}, 2.31 \text{ (9H, s, } 3\text{C}_7\text{H}_3\text{)}, 7.14 \text{ (3H, t, J 7.4, H-4)}, 7.20 \text{ (3H, d, J 7.6, H-3)}, 7.34 \text{ (3H, t, J 7.5, H-5)}, 7.44 \text{ (3H, d, J 7.3, H-6)}. \]

\[ \delta_C: 23.6, 125.0, 130.2, 130.4, 132.8, 136.3 \text{ and 144.4}. \]

MS (EI) \(m/z\): 335 (M\(^+\), 3), 301 (94), 285 (40), 242 (100), 208 (100).

Found: C, 75.0; H, 6.7. \(\text{C}_{21}\text{H}_{22}\text{OSiS}\) requires C, 75.4; H, 6.6%. 

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2.4.2.9 Tri-(1R,2S,5R)-menthoxysilanethiol 7

Silicon disulfide (Alfa Aesar) was crushed to a powder using a dry stainless steel pestle and mortar enclosed in a polythene bag filled with nitrogen. Powdered silicon disulfide (1.30 g, 95% pure, 14.1 mmol) was charged into a 100 cm$^3$ round-bottomed flask containing a robust stirrer bar and equipped with a reflux condenser. (1R,2S,5R)-Menthol (L-menthol, 10.53 g, 67.4 mmol) was added and the mixture was stirred and heated (oil bath at 95 °C) under nitrogen for 72 h. The cooled reaction mixture was filtered through Celite to remove unreacted silicon disulfide and the filter cake was washed with a little dichloromethane. Excess menthol was removed from the filtrate by sublimation at 60 °C under reduced pressure (0.02 Torr) and the residual oil was passed through a column of silica gel eluting with hexane to give tri-(1R,2S,5R)-menthoxysilanethiol 7 (2.91 g, 39%) as a colourless oil that solidified on standing. M.p. 44-46 °C.

IR (cm$^{-1}$, KBr): 2540 (br) (S-H str).

$\left[\alpha\right]_D^{20} = -82.2$ (c 1.97, CHCl$_3$).

$\delta_H$: 0.01 (1H, s, SH), 0.74 (9H, d, J 6.9, 3CH$_3^A$), 0.78-0.94 (6H, m, H$^{ax}$-4 and H$^{ax}$-3), 0.87 (9H, d, J 6.4, 3CH$_3^B$), 0.88 (9H, d, J 7.0, 5-CCH$_3$), 1.04 (3H, q, J 12.2, H$^{ax}$-6), 1.17 (3H, dddd, J 12.7, 9.8, 3.0 and 3.0, H$^{ax}$-2), 1.38-1.42 (3H, m, H$^{ax}$-5), 1.54-1.65 (6H, m, H$^{eq}$-3, H$^{eq}$-4), 2.03 (3H, br. d, J 11.5, H$^{eq}$-6), 2.18 (3H, sept[d], J 7.0 and 2.5, CHMe$_2$), 3.70 (3H, td, J 10.5 and 4.3, 1-H).$^{20}

$\delta_C$: 15.8, 21.2, 22.2, 22.7, 25.3, 31.6, 34.4, 44.7, 49.6 and 74.0.

MS (EI) $m/z$: 527 (M$^+$, 3), 492 (85), 441 (32), 138 (100), 95 (68), 81 (97), 69 (61), 55 (44).

Found: C, 68.4; H, 11.2. C$_{30}$H$_{58}$O$_2$SiS requires C, 68.4; H, 11.1%.

Tetra-(1R,2S,5R)-menthyl orthosilicate$^{21}$ was also formed as a by-product (thiol : silicate = 3 : 1).

M.p. 96-97 °C (lit.$^{21}$ 93-96 °C).
[\alpha]_D^{20} = -83.15 (c 2.67, CHCl_3).

\(\delta_H\): 0.71 (9H, d, J 6.9, 3CH_3_A), 0.77-0.94 (6H, m, H^ax-4 and H^ax-3), 0.86 (9H, d, J 6.9, 3CH_3_B), 0.92 (9H, d, J 6.9, 5-CCCH_3), 1.00 (3H, q, J 11.0, H^eq-6), 1.15 (3H, dddd, J 12.7, 9.8, 3.1 and 3.0, H^ax-2), 1.26-1.38 (3H, m, H^ax-5), 1.54-1.60 (6H, m, H^eq-4 and H^eq-3), 2.05 (3H, br. d, J 11.5, H^eq-6), 2.26 (3H, sept[d], J 7.0 and 2.4, CHMe_2), 3.63 (3H, t[d], J 10.5 and 4.2, 1-H).^{20}

\(\delta_C\): 15.8, 21.2, 22.2, 22.7, 25.3, 31.6, 34.4, 44.7, 49.6 and 73.2.

MS (El) m/z: 649 (M+, 54), 563 (52), 509 (48), 139 (100), 83 (100).

Found: C, 74.2; H, 12.0. C_{40}H_{64}O_4Si requires C, 74.0; H, 11.8%.

### 2.4.2.10 Tri-(1S,2R,5S)-menthoxyasilanethiol 8

[Image of a molecular structure diagram showing the reaction of menthol with silicon disulfide to form tri-(1S,2R,5S)-menthoxyasilanethiol 8.]

Silicon disulfide (Alfa Aesar) was crushed to a powder using a dry stainless steel pestle and mortar enclosed in a polythene bag filled with nitrogen. Powdered silicon disulfide (1.31 g, 95% pure, 14.2 mmol) was charged into a 100 cm^3 round-bottomed flask containing a robust stirrer bar and equipped with a reflux condenser. (1S,2R,5S)-Menthol (D-menthol, 8.80 g, 56.4 mmol) was added and the mixture was stirred and heated (oil bath at 95 °C) under nitrogen for 48 h. The work-up described previously for 7 was used to give tri-(1S,2R,5S)-menthoxyasilanethiol 8 (2.32 g, 31%) as a colourless oil.

[\alpha]_D^{20} = +86.0 (c 1.76, CHCl_3).

\(\delta_H\): 0.01 (1H, s, SH), 0.74 (9H, d, J 6.9, 3CH_3_A), 0.77-0.99 (6H, m, H^ax-3 and H^ax-4), 0.87 (9H, d, J 6.5, 3CH_3_B), 0.88 (9H, d, J 7.1, 5-CCCH_3), 1.02 (3H, q, J 11.9, H^eq-6), 1.15-1.25 (3H, dddd, J 12.3, 10.0, 2.9, 3.0, H^ax-2), 1.28-1.42 (3H, m, H^ax-5), 1.49-1.64 (6H, m, H^eq-4 and H^eq-3), 2.05 (3H, br. d, J 12.1, H^eq-6), 2.19 (3H, sept[d], J 7.0 and 2.4, CHMe_2), 3.70 (3H, t[d], J 10.5 and 4.4, 1-H).^{20}

\(\delta_C\): 15.8, 21.2, 22.2, 22.7, 25.3, 31.6, 34.4, 44.7, 49.6 and 74.0.

MS (El) m/z: 527 (M^+, 3), 492 (81), 441 (43), 138 (100), 95 (50), 81 (87).
2.4.2.11 Tri-(1S,2R,5R)-menthoxysilanethiol 9

Silicon disulfide (Alfa Aesar) was crushed to a powder using a dry stainless steel pestle and mortar enclosed in a polythene bag filled with nitrogen. Powdered silicon disulfide (1.32 g, 95% pure, 14.3 mmol) was charged into a 100 cm$^3$ round-bottomed flask containing a robust stirrer bar and equipped with a reflux condenser. (1S,2R,5R)-Menthol (isomenthol, 10.55 g, 67.5 mmol) was added and the mixture was stirred and heated (oil bath at 95 °C) under nitrogen for 48 h. The work-up described previously for 7 was used to give tri-(1S,2R,5R)-menthoxysilanethiol 9 (2.24 g, 30%) as a colourless oil.

$[$α$]_D^{20} = +21.5$ (c 2.20, CHCl$_3$).

δ$_H$: -0.02 (1H, s, SH), 0.83 (9H, d, J 6.7, 3CH$_3^A$), 0.86 (9H, d, J 7.1, 3CH$_3^B$), 0.88 (9H, d, J 7.0, 5-CCH$_3$), 1.10-1.28 (6H, m, H$_{ax}$-3 and H$_{ax}$-2), 1.34-1.41 (6H, m, H$_{eq}$-3 and H$_{eq}$-4), 1.43-1.52 (3H, m, H$_{ax}$-6), 1.55-1.64 (6H, m, H$_{eq}$-6 and H$_{eq}$-4), 1.84 (3H, d[sept], J 6.8 and 6.8, CHMe$_2$), 1.87-1.99 (3H, m, H$_{eq}$-5), 4.18 (3H, t[d], J 6.6 and 3.3, 1-H).$^{20}$

δ$_C$: 18.9, 20.1, 20.6, 21.1, 25.9, 27.3, 30.2, 39.0, 48.4 and 70.7.

MS (El) $m/z$: 527 (M$^+$, 5), 492 (58), 441 (35), 138 (100), 95 (50), 81 (67).

Found: C, 68.7; H, 11.1. C$_{30}$H$_{58}$O$_5$SiS requires C, 68.4; H, 11.1%.

Tetra-(1S,2R,5R)-menthyl orthosilicate was also formed as a by-product (thiol : silicate = 6 : 1) and was not isolated.
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2.4.2.12 Tri-(1S, 2S, 5R)-menthylxysilanethiol 10

Silicon disulfide (Alfa Aesar) was crushed to a powder using a dry stainless steel pestle and mortar enclosed in a polythene bag filled with nitrogen. Powdered silicon disulfide (1.31 g, 95% pure, 14.2 mmol) was charged into a 100 cm³ round-bottomed flask containing a robust stirrer bar and equipped with a reflux condenser. (1S, 2S, 5R)-Menthol (neomenthol, 10.53 g, 67.4 mmol) was added and the mixture was stirred and heated (oil-bath at 95 °C) under nitrogen for 48 h. The work-up described previously for 7 was used to give (1S,2S,5R)-trimenthyloxysilanethiol 10 (2.61 g, 35%) and tetra-(1S,2S,5R)-menthyl orthosilicate (thiol : silicate = 4 : 1) which could not be separated by column chromatography.

δH: -0.05 (1H, s, SH), 0.83 (9H, d, J 6.8, 3CH₃), 0.76-1.99 (complex, 27H), 0.86 (9H, d, J 7.1, 3 CH₃), 0.88 (9H, d, J 7.1, 5-CCH₃), 4.39-4.41 (3H, m, 1-H).²⁰

2.4.2.13 Tri-[(1S)-endo]-bornyloxysilanethiol 10

Silicon disulfide (Alfa Aesar) was crushed to a powder using a dry stainless steel pestle and mortar enclosed in a polythene bag filled with nitrogen. Powdered silicon disulfide (1.31 g, 95% pure, 14.2 mmol) was charged into a 100 cm³ round-bottomed flask containing a robust stirrer bar and equipped with a reflux condenser. [(1S)-endo]-(-)-Borneol (9.03 g, 58.5 mmol) and toluene (3.6 cm³) were added and the mixture was stirred and heated (oil bath at 95 °C) under nitrogen for 48 h. The cooled reaction mixture was filtered through Celite to remove unreacted silicon disulfide and the filter
cake was washed with a little dichloromethane. The solvent was removed by rotary evaporation and the excess alcohol by sublimation at 60 °C under reduced pressure (0.02 Torr). The residual oil was passed through a short column of silica gel eluting the hexane to give tri-[(15)-endo]-borylsilanethiol 10 (2.21 g, 30%) as a colourless oil. M.p. 146-147 °C.

IR (cm⁻¹, KBr): 2535 (br) (S-H str).

\[ \alpha_0^{20} = -33.8 \text{ (c 2.18, CHCl}_3) \]

$\delta_H$: -0.03 (1H, s, SH), 0.82 (9H, s, 7-C-3CH₃), 0.83 (9H, s, 7-C-3CH₃), 0.83 (9H, s, 1-C-3CH₃), 1.06 (3H, dd, $J$ C-4 and 3.3, H₅-3), 1.12-1.26 (6H, m, H₆x-5 and H₆x-6), 1.59 (1H, dd, $J$ 4.5 and 4.5, H-4), 1.63-1.73 (3H, m, H₅l-5), 1.98 (3H, ddd, $J$ 12.3, 9.5 and 4.8, H₅l-6), 2.20 (3H, dddd, $J$ 13.2, 9.7, 4.6 and 3.2, H₅l-3), 4.22 (3H, dddd, $J$ 19.7, 3.1 and 2.0, H₅l-2).

$\delta_C$: 13.5, 18.8, 20.2, 26.3, 28.2, 38.8, 45.2, 47.4, 49.7 and 78.7.

MS (EI) m/z: 521 (M⁺, 7), 383 (39), 137 (100), 121 (63), 109 (88), 95 (86), 81 (82), 69 (57).

Found: C, 69.2; H, 10.2. C₃₀H₆₂O₄SiS requires C, 69.2; H, 10.1%.

Tetra-[(15)-endo]-tribornyl orthosilicate was also formed as a by-product (thiol : silicate = 3 : 1).³²

M.p. 289-290 °C (lit. ²² 290-291 °C).

$\alpha_0^{20} = -40.5$ (c 1.85, CHCl₃)

$\delta_H$: 0.81 (9H, s, 7-C-3CH₃), 0.82 (9H, s, 7-C-3CH₃), 0.82 (9H, s, 1-C-3CH₃), 1.03 (3H, dd, $J$ 13.2 and 3.3, H₅x-3), 1.08-1.24 (6H, m, H₆x-5 and H₆x-6), 1.63-1.73 (3H, m, H₅l-5), 2.01 (3H, ddd, $J$ 12.3, 9.4 and 4.7, H₅l-6), 2.13-2.22 (3H, m, H₅l-3), 4.15 (3H, ddd, $J$ 9.7, 3.1 and 2.0, H₅l-2).

$\delta_C$: 13.5, 18.6, 20.2, 26.3, 28.2, 38.9, 45.2, 47.4, 49.7 and 78.6.

MS (EI) m/z: 641 (M⁺, 7), 137 (93), 109 (78), 95 (100), 82 (54).

Found: C, 74.7; H, 11.0. C₄₀H₆₈O₄SiS requires C, 74.9; H, 10.7%.
2.4.2.14 Di-[(15)-endo]-bornyloxyphenylchlorosilane

To a stirred solution of phenyltrichlorosilane (7.5 cm$^3$, 10.09 g, 47.7 mmol) in diethyl ether (70 cm$^3$), [(1S)-endo]-(-)-borneol (14.35 g, 93.0 mmol) in ether (30 cm$^3$) and pyridine (7.36 g, 93.0 mmol) was added dropwise over 2 h at 0 °C (ice/water bath) under nitrogen. After the addition was complete, the solution was stirred at room temperature for 22 h. Next, the solution was filtered through Celite under nitrogen, washing the filter cake with hexane and then the solvent was removed by rotary evaporation. Solid appeared (possibly pyridinium hydrochloride) and the crude product was taken up in hexane and, again, filtered through Celite and solvent removed by rotary evaporation. The crude product was placed under high vacuum for 10 h to give di-[(1S)-endo]-bornyloxyphenylchlorosilane (16.3 g, 76%) as a cloudy, viscous oil. No further purification procedures were undertaken owing to the likely moisture sensitivity of this compound.

$\delta_H$: 7.36-7.44 (3H, m, Ph), 7.70-7.71 (2H, m, Ph).

$\delta_C$: 127.5, 130.4, 131.8 and 133.7.

Bomyl A: 0.80 (9H, s, 7-C-3CH$_3^A$), 0.84 (9H, s, 7-C-3CH$_3^B$), 0.85 (9H, s, 1-C-3CH$_3$), 1.09 (1H, dd, $J$ 13.4 and 3.3, H$ax$-$3$), 1.15-1.30 (2H, m, H$ax$-$5$ and H$ax$-$6$), 1.60 (1H, dd, $J$ 4.7 and 4.7, H-$4$), 1.65-1.73 (1H, m, H$eq$-$5$), 2.04-2.09 (1H, m, H$eq$-$6$), 2.01-2.08 (1H, dddd, $J$ 13.2, 9.7, 4.7, 3.3, H$eq$-$3$), 4.35 (1H, ddd, $J$ 9.7, 3.1, and 1.9, H$eq$-$2$).

$\delta_C$: 13.0, 18.4, 19.7, 25.9, 27.8, 38.1, 44.7, 47.0, 49.4 and 78.7.

Bomyl B: 0.81 (9H, s, 7-C-3CH$_3^A$), 0.85 (9H, s, 7-C-3CH$_3^B$), 0.87 (9H, s, 1-C-3CH$_3$), 1.15 (1H, dd, $J$ 13.4 and 3.3, H$ax$-$3$), 1.15-1.30 (2H, m, H$ax$-$5$ and H$ax$-$6$), 1.62 (1H, dd, $J$ 4.7 and 4.7, H-$4$), 1.65-1.73 (1H, m, H$eq$-$5$), 2.04-2.09 (1H, m, H$eq$-$6$), 2.21 (1H, dddd, $J$ 13.2, 9.7, 4.7, 3.3, H$eq$-$3$), 4.35 (1H, ddd, $J$ 9.7, 3.1 and 1.9, H$eq$-$2$).

$\delta_C$: 13.1, 18.4, 19.7, 25.9, 27.8, 38.5, 44.7, 47.1, 49.4 and 78.8.
2.4.2.15 Di-[(1S)-endo]-bornyloxyphenylsilanethiol 12

Hydrogen sulfide (1.5 cm³, 1.05 g, 30.9 mmol) was condensed into a glass trap of known volume and bubbled through dry tetra-hydrofuran (THF, 100 cm³) at -78 °C contained in a 500 cm³ round-bottomed flask fitted with a condenser. Butyllithium (9.7 cm³, 15.4 mmol) was then added over 10 minutes via a syringe. The solution was allowed to warm to 0 °C over a period of 1 h. Next, di-[(1S)-endo]-bornyloxyphenylchlorosilane (6.90 g, 15.4 mmol) and diethyl ether (2 cm³) was added at 0 °C over 10 minutes using a syringe. The solution was stirred at room temperature for 5 h. The solvent was removed by rotary evaporation and then pentane (30 cm³) was added and the solution filtered through Celite under nitrogen. Again, the solvent was removed on a rotary evaporator, and then the crude product was passed through a column of silica gel eluting with hexane-diethyl ether (200 : 1) and recrystallised from light petroleum (b.p. 40-60 °C)-diethyl ether to give di-[(1S)-endo]-bornyloxyphenylsilanethiol 12 (4.21 g, 61%) as a white solid. M.p. 69-71 °C.

IR (cm⁻¹, KBr): 2555 (br) (S-H str). 

[α]D20 = -33.4 (c 0.69, CHCl₃).

δH: 0.12 (1H, s, SH), 7.35-7.43 (3H, m, Ph), 7.70-7.73 (2H, m, Ph).

δC: 127.8, 130.4, 134.2 and 134.9. 

Bornyl A: 0.79 (9H, s, 7-C-3CH₃A), 0.82 (9H, s, 7-C-3CH₃B), 0.83 (9H, s, 1-C-3CH₃), 1.05 (1H, dd, J 13.2 and 3.3, Hα-3), 1.15-1.27 (2H, m, Hα-5 and Hα-6), 1.59 (1H, dd, J 4.6 and 4.6, H-4), 1.64-1.73 (1H, m, Hβ-5), 2.04-2.09 (1H, m, Hβ-6), 2.18 (1H, ddd, J 12.3, 9.5, 4.8, 3.3, Hβ-3), 4.30 (1H, ddd, J 9.7, 3.3 and 2.0, Hβ-2).* 

δC: 13.6, 18.8, 20.2, 26.4, 28.3, 39.0, 45.2, 47.4, 49.9 and 78.7.* 

Bornyl B: 0.83 (9H, s, 7-C-3CH₃A), 0.84 (9H, s, 1-C-3CH₃B), 0.84 (9H, s, 7-C-3CH₃B), 1.10 (1H, dd, J 13.2 and 3.3, Hα-3), 1.15-1.27 (2H, m, Hα-5 and Hα-6), 1.61 (1H, dd, J 4.6 and 4.6, H-4), 1.64-1.73 (1H, m, Hβ-5), 2.04-2.09 (1H, m, Hβ-6), 2.20 (1H, ddd, J 13.2, 9.7, 4.6, 3.3, Hβ-3), 4.34 (1H, ddd, J 9.7, 3.2 and 1.9, Hβ-2).*
Silicon disulfide (Alfa Aesar) was crushed to a powder using a dry stainless steel pestle and mortar enclosed in a polythene bag filled with nitrogen. Powdered silicon disulfide (1.32 g, 95% pure, 14.3 mmol) was charged into a 100 cm$^3$ round-bottomed flask containing a robust stirrer bar and equipped with a reflux condenser. (1R,2R,3R,5S)-(−)-Isopinocamphol (10.08 g, 65.3 mmol) was added and the mixture was stirred and heated (oil bath at 95 °C) under nitrogen for 48 h. The work-up described previously for 7 was used to give tri-(1R,2R,3R,5S)-isopinocampheyloxysilanethiol 11 (1.98 g, 28 %) as a colourless oil.

IR (cm$^{-1}$, liq. film): 2560 (br) (S-H str).

$[\alpha]_D^{20} = -37.0$ (c 1.32, CHCl$_3$).

δH: 0.08 (1H, s, SH), 0.91 (9H, s, 3CH$_3$), 1.08-1.13 (3H, m, H$^A$-7), 1.11 (9H, d, J 7.4, 2-C-3CH$_3$), 1.19 (9H, s, 3CH$_3$), 1.76 (3H, td, J 5.8 and 2.0, H-2), 1.83-1.88 (3H, m, H$^{a,b,c}$-1), 1.86-2.01 (3H, m, H-5), 2.04-2.10 (3H, m, H-1), 2.28-2.34 (3H, m, H$^B$-7), 2.44-2.50 (1H, dddd, J 10.0, 9.27, 3.2, 2.4, H$^{a,b,c}$-4'), 4.36 (1H, ddd, J 9.5, 5.0 and 4.8, H-3).

δC: 20.5, 23.9, 27.7, 34.0, 38.3, 38.7, 41.8, 46.8, 47.9 and 73.4.

MS (EI) m/z: 280 (M$^+$, 2), 137 (94), 93 (50), 81 (100).

Found: C, 73.9; H, 10.6. C$_{36}$H$_{54}$O$_2$SiS requires C, 73.7; H, 10.7%.

Tetra-(1R,2R,3R,5S)-isopinocamphey orthosilicate was also formed as a by-product (thiol : silicate = 3 : 1) and was not isolated.
2.5 REFERENCES


    (b) J. Darszewski, J. Lusztyk, M. Degueil, C. Navarro and B. Maillard,  


CHAPTER THREE
GENERATION AND REACTIONS OF SILANETHIYL RADICALS STUDIED
BY EPR SPECTROSCOPY

3.1 INTRODUCTION

3.1.1 Addition of alkanethiyl radicals to alkenes

It has been observed by electron paramagnetic resonance (EPR) spectroscopy that alkanethiyl radicals (RS*) add readily to carbon-carbon double bonds. For example, a series of β-mercaptoalkyl radicals have been generated by photolysis of a dialkyl disulfide in the presence of ethene, propene or isobutylene. The isotropic hyperfine coupling constants for the β-protons were unusually small and showed marked temperature dependence, increasing with increasing temperature. The results were interpreted in terms of hindered internal rotation about the Cα-Cβ bond and a preferred conformational orientation in which the sulfur atom is eclipsed with the p-orbital at the trigonal centre. The particularly low values of a(Hβ) (e.g. 14.50 G for MeSCH2CH2 at 200 K) were thought to imply a tilt of the heteroatom towards the radical centre (bridging hypothesis) with the β-hydrogens displaced away from tetrahedral positions towards the nodal plane. More recently M. Guerra has computed the structural parameters for β-substituted ethyl radicals HnM-CH2-CH2* (HnM = H3C, H2N, HO, F, H3Si, HS and Cl) using ab initio molecular orbital calculations and found that the low values of a(Hβ) in the eclipsed conformation can be explained by a sizeable reduction in spin density at Hβ with increasing electronegativity of the heteroatom, without the need for any “bridging”.

Placucci et al. have described an EPR study of the radical adduct 1 formed by the addition of the methanethiyl radical (MeS*) to cyclopentene. They also reported that abstraction of hydrogen to give the cyclopentenyl radical 2 occurred competitively. They reported that the spectrum of the adduct was generated at 173 K but, on raising the temperature to 213 K, the spectrum of this radical “disappears”, and between 273 and 293 K only the spectrum of the cyclopentenyl radical 2 is observed. However, close inspection of Placucci’s paper fails to reveal what was observable between 213 and 273 K and whether or not the spectra vary with sample photolysis time.
3.1.2 Thiophosphoranyl radicals

Roberts et al. have studied the EPR spectra of a series of thiophosphoranyl radicals generated in solution by addition of thyl radicals (RS*, from photolysis of RSSR or H₂S) to phosphorus(III) compounds. Although it was concluded that isotropic EPR parameters alone were not sufficient to determine the configuration of acyclic phosphoranyl radicals, it was thought that trigonal bipyramidal (TBP, C₂ᵥ) and σ⁺ (S*, C₃ᵥ) configurations represent limiting structures and the geometry between these two extremes adopted by a particular radical appears to depend upon the nature of the ligands. They suggested that the configuration is related to the ease of heterolytic dissociation of the P-ligand bonds and their conclusions are illustrated in Scheme 3.1.

\[ \text{SCHEME 3.1} \]

σ⁺ Electronic configurations have also been assigned to selenuranyl radicals of the type [R₂Se-X]* (R = alkyl or aryl, X = CF₃, R'CO, and Me₃SiO*). ⁵

3.1.3 The reactions of thyl radicals with trialkylboranes

The reaction of alkanethiyl radicals with trialkylboranes has been studied using EPR spectroscopy. ⁶ If the disulfides RSSR (R = Ph, Bu' or Bu) are photolysed in the
presence of tributyl-, triisobutyl- or tri-sec-butyl- borane ($R'_3B$), the EPR spectrum of
the appropriate displaced butyl radical ($R^*$) can be observed [eqns. 3.1 and 3.2]).

\[ R_{SSR} \xrightarrow{\text{hv}} 2R^* \]  

(3.1)

\[ RS^* + BR'_3 \rightarrow RSBR'_2 + R'^* \]  

(3.2)

Absolute rate constants for the reactions of the tert-butylthiyl radical with
trialkylboranes have been measured using a combination of laser flash photolysis and
product studies.\(^7\) Reactions with boranes are extremely rapid with rate constants in the
range $10^{-8}$ to $10^{-9}$ M$^{-1}$ s$^{-1}$ at 298 K and, by contrast, the addition to oct-1-ene is ca. 100 times
less rapid.

### 3.1.4 Addition of alkanethiyl radicals to alkyl isocyanides

Electron paramagnetic resonance (EPR) spectroscopy has shown that alkanethiyl
radicals add to the terminal carbon of alkyl isocyanides at low temperatures to
give imidoyl radicals [eqns. (3.3)].\(^8\)

\[ RS^* + R'\text{N}=C \rightarrow R'\text{N}=C=SR \]  

(3.3)

The imidoyl radicals exhibit $g$-factors of 2.0014, less than the free-spin value
(2.0023), which is consistent with the formation of a "$\sigma$-type" radical.\(^9\) The spectra of
several other types of imidoyl adduct $RN=\overline{C}X$ were reported and an increase in the
deviation from linearity at $C_\alpha$ was observed [as judged by the magnitude of $\alpha(\overline{13}C_\alpha)$] as
the electronegativity of the substituent $X$ increased. The magnitude of $\alpha(N_\beta)$ was also
found to be markedly dependent upon the nature of $X$.\(^8\)

### 3.1.5 Radical-chain reactions involving silanethiyl radicals

Silanes react with triphenylphosphine sulfide by a radical-chain mechanism to
give the corresponding silanethiols in good yield.\(^10\) Silanethiols are also formed when
silanes react with tert-dodecanethiol.\(^10\) Addition of the silyl radical to $R_3P=S$ gives an
intermediate thiophosphoranyl radical [$R_3SiS-PR_3]^*$, $\alpha$-scission of which generates the
phosphine and a silanethiyl radical (Scheme 3.2; $M = PR_3$). Similarly, silanes react by a
radical-chain mechanism with carbonyl sulfide to give silanethiols and carbon
monoxide in good yield when the other groups attached to silicon are alkyl or aryl
(Scheme 3.2; $M = CO$).\(^11\)
3.1.6 Aims of the research

To generate silanethiyl radicals $X_3\text{SiS}^*$, by UV photolysis of the corresponding disulfides $X_3\text{SiSSiX}_3$, and to use EPR spectroscopy to investigate the chemical properties of these radicals. In particular, the properties of $X_3\text{SiS}^*$ are to be compared with those of the corresponding alkanethiyl radicals $X_3\text{CS}^*$. 
3.2 RESULTS AND DISCUSSION

3.2.1 Preparation of \(X_3\text{SiSSSiX}_3\)

\[
X_3\text{SiSH} \xrightarrow{1. \text{NaH}} X_3\text{SiSSSiX}_3 \quad (3.4)
\]

\[
X = \text{Pr}'^3 \quad 3 \\
= \text{Bu}'^0 \quad 4 \\
= \text{Bu}'^\text{Ph}_2 \quad 5
\]

The disulfides 3-5 were prepared by oxidation of the appropriate thiol with iodine as shown in eqn. (3.4).\(^\text{12}\) Silanethiyl radicals were generated via the photolysis of the disulfides \(X_3\text{SiSSSiX}_3\) [eqn. (3.5)].

\[
X_3\text{SiSSSiX}_3 \xrightarrow{\text{hv}} 2X_3\text{SiS}^* \quad (3.5)
\]

3.2.2 UV/Visible spectra

The UV/visible data for bis(triisopropylsilyl) disulfide 3 and bis( tri-tert-butoxysilyl) disulfide 4 are shown below in Table 3.1. Bis(triisopropylsilyl) disulfide 3 is canary yellow and has an absorption band that stretches into the visible region (Figure 3.1), suggesting that visible as well as UV irradiation may generate silanethiyl radicals.

Table 3.1: Optical spectra of disulfides in heptane

<table>
<thead>
<tr>
<th>Disulfide</th>
<th>(\lambda_{\text{max}}/\text{nm})</th>
<th>(e_{\text{max}}/\text{M}^2\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Pr}'^3\text{SiSSSiPr}'^3)</td>
<td>220</td>
<td>4131</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>182</td>
</tr>
<tr>
<td>((\text{Bu}'^0\text{SiSSSi(0Bu')})_3)</td>
<td>218</td>
<td>1639</td>
</tr>
<tr>
<td></td>
<td>259</td>
<td>489</td>
</tr>
</tbody>
</table>

3.2.3 Addition of silanethiyl radicals to ethene

\[
\begin{align*}
\text{Pr}'^3\text{Si} & & \quad \text{Bu}'^\text{PhSi}\text{Si} \\
\text{H} & & \quad \text{H} \\
\text{H} & & \quad \text{H}
\end{align*}
\]

6          7          8

EPR spectroscopy was used to monitor the radicals present during continuous UV irradiation of liquid samples positioned in the microwave cavity of the
Figure 3.1: UV/Visible spectrum of Pr$_3$SiSSiPr$_3$ 3 (0.00055 M, insert 0.018 M) in heptane
spectrometer, as described in Section 3.4.1. Photolysis of the disulfides 3-5 provides a source of silanethiyl radicals and these were found to add readily to ethene.

UV irradiation of a cyclopropane solution containing bis(triisopropylsilyl) disulfide 3 (0.24 M) and ethene (4.17 M) at 180 K afforded a spectrum of 6 which was analysed in terms of coupling to two α-protons to give a triplet (21.41 G) and to two equivalent β-protons to give a triplet (13.81 G). The centre point of this multiplet corresponds to $g = 2.0023$.

Similar results were obtained when the experiment was repeated using bis(tert-butoxysilyl) disulfide 4 and bis(tert-butyldiphenylsilyl) disulfide 5 and all EPR parameters are given in Table 3.2. The average value of $a(2H_β)$ for 6, 7 and 8 was found to increase with increasing temperature indicating, that the preferred conformation has the S-C₆ bond eclipsing the axis of the SOMO. The hyperfine splitting will increase with increasing temperature towards a free-rotation value ($\frac{1}{2}B$) at infinite temperature (see EPR Section 6.3.2). It was found that the value varied by $\sim 1.7$ G over a temperature change of 70 K, which indicates that the silanethiyl group can rotate relatively easily. The values of the coupling constants for the β-protons are of the same magnitude as alkanethiyl adducts (13-14 G) which adopt a similar conformation.

The EPR spectra were strong, even after prolonged photolysis, indicating that the quantum yield of silanethiyl radicals from the disulfide is high. When the experiments were repeated for disulfides 3 and 5 using a pyrex glass filter in the light beam virtually no difference in the spectra were observed indicating that UV light of $\lambda \geq 300$ nm is effective for the formation of silanethiyl radicals from the disulfides.

In all cases weak spectra of other radicals can be observed alongside those of the alkene adducts. In particular, at 200 K the spectra obtained from bis(tert-butoxysilyl) disulfide 4 showed a well-resolved triplet (10.50 G) of doublets (17.73 G) whose centre was $g = 2.0046$ (see Figure 3.2). This was not present initially, but appeared after some minutes of photolysis and remained at higher temperatures. It is thought that this radical is generated as a result of a reaction of the adduct radical with the disulfide to yield a product which undergoes hydrogen-atom abstraction by a silanethiyl radical (see Scheme 3.3).
CHAPTER THREE

\[
\begin{align*}
(Bu'\text{O})_3\text{SiSCH}_2\text{CH}_2 & \\
\downarrow & \\
(Bu'\text{O})_3\text{SiSSi}(\text{OBu}')_3 & \\
\downarrow & \\
(Bu'\text{O})_3\text{SiSCH}_2\text{CH}_2\text{SSi}(\text{OBu}')_3 & + (Bu'\text{O})_3\text{SiS}^* \\
\downarrow & \\
(Bu'\text{O})_3\text{SiSCH}_2\text{CH}_2\text{SSi}(\text{OBu}')_3 & + (Bu'\text{O})_3\text{SiSH}
\end{align*}
\]

SCHEME 3.3

Table 3.2: EPR parameters for radical adducts of ethene in cyclopropane

<table>
<thead>
<tr>
<th>Radical</th>
<th>(T/\text{K})</th>
<th>(g)-Factor(^b)</th>
<th>(a(2\text{H}_a))</th>
<th>(a(2\text{H}_b))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr(^3)SiSCH(_2)CH(_2^*) (6)</td>
<td>166</td>
<td>2.0023</td>
<td>21.48</td>
<td>13.35</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>-</td>
<td>21.55</td>
<td>13.83</td>
</tr>
<tr>
<td></td>
<td>199</td>
<td>-</td>
<td>21.48</td>
<td>14.25</td>
</tr>
<tr>
<td></td>
<td>218</td>
<td>-</td>
<td>21.50</td>
<td>14.68</td>
</tr>
<tr>
<td></td>
<td>237</td>
<td>-</td>
<td>21.48</td>
<td>15.05</td>
</tr>
<tr>
<td>(Bu'O(_3))SiSCH(_2)CH(_2^*) (7)</td>
<td>179</td>
<td>2.0023</td>
<td>21.18</td>
<td>12.00</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>-</td>
<td>21.20</td>
<td>12.52</td>
</tr>
<tr>
<td></td>
<td>222</td>
<td>-</td>
<td>21.25</td>
<td>13.25</td>
</tr>
<tr>
<td></td>
<td>239</td>
<td>-</td>
<td>21.25</td>
<td>13.50</td>
</tr>
<tr>
<td>Bu'Ph(_2)SiSCH(_2)CH(_2^*) (8^c)</td>
<td>230</td>
<td>2.0024</td>
<td>21.38</td>
<td>14.25</td>
</tr>
<tr>
<td></td>
<td>259</td>
<td>-</td>
<td>21.42</td>
<td>14.55</td>
</tr>
</tbody>
</table>

\(^a\) Estimated error ± 0.05 G. \(^b\) Estimated error ± 0.0001. \(^c\) Fluorobenzene solvent.
Figure 3.2: EPR spectra of (Bu'O)₃SiSCH₂CH₂ 7 and (Bu'O)₃SiSCCH₂SSi(OBu')₃
(lines marked *, tentative assignment) in cyclopropane at 200 K

5.0 G
3.2.4 Reaction of silanethiyl radicals with cyclopentene

![Structure 1](image1)

The work of Placucci et al.\(^3\) (Section 3.1) was repeated and extended by the use of di-tert-butyl disulfide to generate Bu'S\(^+\) and disulfides 3 and 4 to produce silanethiyl radicals; the results are given in Tables 3.3-3.5. In all cases a fresh sample was used for each temperature and the results are taken from the first spectrum recorded.

Contrary to the work of Placucci et al.,\(^3\) we found that the adduct radical 1 was detectable in the temperature range 213-273 K. UV/visible photolysis of dimethyl disulfide (0.73 M) in the presence of cyclopentene (1.88 M) in the temperature range 202 to 260 K showed that the adduct radical 1 dominates, but at higher temperatures (≥ 273 K) the cyclopentenyl radical 2 is the major radical that can be observed (≥ 90%).

The experiment was repeated using an increased concentration of cyclopentene (3.76 M) and at 260 K a slight increase in the concentration of the adduct 1 was observed (80 : 20), compared to the 70 : 30 ratio observed at the lower cyclopentene concentration of 1.88 M. Placucci et al.\(^3\) did not publish the concentrations of their reagents.

We also observed the concentration of the cyclopentenyl radical 2 to increase with photolysis time, the concentration of the adduct radical 1 decreased with time (see Figure 3.3 and Section 3.2.5 for explanation).

Repeating the experiment using di-tert-butyl disulfide (0.52 M) at 202 K, gives rise mainly to the adduct 9 along with the allylic radical 2, the concentration ratio favouring the adduct 10 : 90. On raising the temperature to 260 K, the ratio is reversed in favour of the cyclopentenyl radical 2, 80 : 20.

UV/visible photolysis of bis(tri-tert-butoxysilyl) disulfide 4 (0.22 M) in the presence of cyclopentene at 201 K gives rise mainly to the adduct 10, along with the allylic cyclopentenyl radical 2, the ratio favouring the adduct 15 : 85. On raising the temperature to 260 K, the ratio reversed in favour of the cyclopentenyl radical 2, 90 : 10. With bis(triisopropylsilyl) disulfide 3 (0.24 M), the cyclopentenyl radical was detected in the range 200 to 259 K, with the adduct radical 11 remaining in low concentration (ratio 90 : 10).
Table 3.3: EPR parameters for thyl radical adducts 1, 9-11 of cyclopentene in cyclopropane solvent

<table>
<thead>
<tr>
<th>Radical</th>
<th>T/K</th>
<th>g-Factor$^b$</th>
<th>a(1H$_x$)</th>
<th>a(1H$_y^1$)</th>
<th>a(1H$_y^3$)</th>
<th>a(1H$_y^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>202</td>
<td>2.0030</td>
<td>21.72</td>
<td>22.52</td>
<td>30.36</td>
<td>39.72</td>
</tr>
<tr>
<td>1</td>
<td>230</td>
<td>21.10</td>
<td>22.74</td>
<td>31.10</td>
<td>39.10</td>
<td>38.34</td>
</tr>
<tr>
<td>1</td>
<td>260</td>
<td>20.82</td>
<td>23.63</td>
<td>31.92</td>
<td>38.34</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>202</td>
<td>2.0030</td>
<td>21.08</td>
<td>26.28</td>
<td>31.60</td>
<td>38.48</td>
</tr>
<tr>
<td>9</td>
<td>230</td>
<td>20.92</td>
<td>26.40</td>
<td>32.10</td>
<td>37.74</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>260</td>
<td>20.48</td>
<td>26.60</td>
<td>32.72</td>
<td>37.50</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td>2.0028</td>
<td>19.46</td>
<td>19.46</td>
<td>29.25</td>
<td>40.54</td>
</tr>
<tr>
<td>10$^c$</td>
<td>231</td>
<td>19.40</td>
<td>22.40</td>
<td>29.30</td>
<td>40.10</td>
<td></td>
</tr>
<tr>
<td>10$^c$</td>
<td>259</td>
<td>19.30</td>
<td>22.50</td>
<td>29.60</td>
<td>39.80</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>201</td>
<td>2.0028</td>
<td>19.56</td>
<td>19.56</td>
<td>29.12</td>
<td>40.24</td>
</tr>
<tr>
<td>11</td>
<td>229</td>
<td>19.50</td>
<td>20.50</td>
<td>29.50</td>
<td>40.40</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>260</td>
<td>19.49</td>
<td>20.40</td>
<td>29.32</td>
<td>40.20</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Estimated error ± 0.05 G. $^b$ Estimated error ± 0.0001. $^c$ Less accurate values, because the cyclopentenyl radical dominates the spectrum.
Table 3.4: Ratio of \([\text{cyclopentenyl}] : [\text{adduct radical}]\) formed by either hydrogen-atom abstraction from or thiyl radical addition to cyclopentene (1.88 M) in cyclopropane solvent

<table>
<thead>
<tr>
<th>X in XSSX</th>
<th>T/K</th>
<th>[cyclopentyl] : [adduct radical]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>202</td>
<td>5 : 95</td>
</tr>
<tr>
<td>Me</td>
<td>230</td>
<td>10 : 90</td>
</tr>
<tr>
<td>Me</td>
<td>260</td>
<td>30 : 70</td>
</tr>
<tr>
<td>Bu'</td>
<td>202</td>
<td>10 : 90</td>
</tr>
<tr>
<td>Bu'</td>
<td>230</td>
<td>30 : 70</td>
</tr>
<tr>
<td>Bu'</td>
<td>260</td>
<td>80 : 20</td>
</tr>
<tr>
<td>Pr'Si</td>
<td>200</td>
<td>95 : 5</td>
</tr>
<tr>
<td>Pr'Si</td>
<td>231</td>
<td>90 : 10</td>
</tr>
<tr>
<td>Pr'Si</td>
<td>259</td>
<td>90 : 10</td>
</tr>
<tr>
<td>(Bu'O)3Si</td>
<td>201</td>
<td>15 : 85</td>
</tr>
<tr>
<td>(Bu'O)3Si</td>
<td>229</td>
<td>70 : 30</td>
</tr>
<tr>
<td>(Bu'O)3Si</td>
<td>260</td>
<td>90 : 10</td>
</tr>
</tbody>
</table>

Table 3.5: EPR parameters for the cyclopentenyl radical 2 generated from hydrogen atom abstraction by tert-butoxyl radicals in cyclopropane

<table>
<thead>
<tr>
<th>T/K</th>
<th>g-Factor$^a$</th>
<th>Hyperfine splittings /G$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a$(2H$^1$)</td>
</tr>
<tr>
<td>202</td>
<td>-</td>
<td>14.40</td>
</tr>
<tr>
<td>230</td>
<td>2.0027</td>
<td>14.31</td>
</tr>
<tr>
<td>260</td>
<td>-</td>
<td>14.20</td>
</tr>
</tbody>
</table>

$^a$ Estimated error ± 0.05 G. $^b$ Estimated error ± 0.0001.
Figure 3.3: Plot of total peak height for the cyclopentenyl and adduct radicals versus duration of the photolysis of dimethyl disulfide in the presence of cyclopentene (1.88 M) in cyclopropane solvent at 230 K.
3.2.5 Addition of silanethiyl radicals to propene

Experiments were carried out in a similar way using propene (2.77 M) and the EPR parameters are presented in Table 3.6. The average value of \(2H_{\beta}\) was found to increase with increasing temperature indicating that the preferred conformation of 12 and 13 has the S-C\(\beta\) bond eclipsing the axis of the SOMO. The couplings to the \(\beta\)-methyl protons was essentially temperature independent, and this was expected because the methyl groups can freely rotate (see EPR Section, Figure 6.10, page 220). The \(g\)-values (2.0028) were higher than those of the radical adducts formed from ethene.

In this case the silanethiyl radical can abstract an allylic hydrogen atom to generate the allyl radical \([a(1H) \ 4.10 \text{ G}, \ a(2H_{\text{exo}}) \ 14.80 \text{ G}, \ a(2H_{\text{endo}}) \ 13.90 \text{ G} \text{ and } g \ 2.0027 \text{ at } 222 \text{ K}]{^13}\) as well as add to the alkene. We found when using both bis(triisopropylsilyl) disulfide 3 and bis(tri-tert-butoxysilyl) disulfide 4 that the adduct radical dominates the spectra between 180 and 260 K (~80%). The allyl radical can only be observed in low concentration, although its concentration was found to increase with time. A plot of radical concentration versus time for the photolysis of 4 in the presence of propene is displayed in Figure 3.4.

We tentatively interpret this time dependence in the following way. When silanethiyl radicals abstract hydrogen from propene they generate thiol \([\text{eqn. (3.7)}]\) in a reversible process. Hydrogen can also be abstracted from the thiol by the adduct radical 12 or 13 to regenerate a silanethiyl radical \([\text{eqn. (3.8)}]\), but now the reaction is irreversible. The consequence of this will be that the concentration of the adduct radical will decrease as the concentration of the thiol increases as photolysis progresses. The concentrations of the allyl radical, thiol and thyl radical would be expected to change during the reaction towards equilibrium between the four species shown in eqn. (3.7). These conclusions are thus in accord with the experimental results displayed in Figure 3.3, where total peak height will be proportional to radical concentration, the line widths for the allyl and adduct radicals were very similar.
\[ X_3\text{SiSSiX}_3 \xrightarrow{h_0} 2X_3\text{SiS}^* \]

\[ X_3\text{SiS}^* + \xrightarrow{k_1} X_3\text{SiS} \]

\[ X_3\text{SiS}^* + \xrightarrow{k_2} X_3\text{SiSH} + \]

\[ X_3\text{SiS} + X_3\text{SiSH} \xrightarrow{k_3} X_3\text{SiS}^* \]  

(3.6)

(3.7)

(3.8)

**Table 3.6:** EPR parameters for radical adducts 12 and 13 in cyclopropane

<table>
<thead>
<tr>
<th>Radical</th>
<th>( T/K )</th>
<th>( g )-Factor(^a )</th>
<th>( a(1\text{H}_\alpha) )</th>
<th>( a(3\text{H}_\beta) )</th>
<th>( a(2\text{H}_\beta) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pr}^\text{t}_3\text{SiSCH}_2\text{C}^*(\text{Me})\text{H} \ 12 )</td>
<td>180</td>
<td>2.0028</td>
<td>20.80</td>
<td>23.90</td>
<td>11.20</td>
</tr>
<tr>
<td></td>
<td>199</td>
<td>-</td>
<td>20.80</td>
<td>23.72</td>
<td>11.48</td>
</tr>
<tr>
<td></td>
<td>219</td>
<td>-</td>
<td>20.80</td>
<td>23.92</td>
<td>12.00</td>
</tr>
<tr>
<td></td>
<td>239</td>
<td>-</td>
<td>20.88</td>
<td>24.00</td>
<td>12.40</td>
</tr>
<tr>
<td>( (\text{Bu}^\text{t})_3\text{SiSCH}_2\text{C}^*(\text{Me})\text{H} \ 13 )</td>
<td>181</td>
<td>2.0028</td>
<td>20.72</td>
<td>23.60</td>
<td>10.30</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>-</td>
<td>20.74</td>
<td>23.66</td>
<td>10.76</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>-</td>
<td>20.70</td>
<td>23.62</td>
<td>11.32</td>
</tr>
<tr>
<td></td>
<td>239</td>
<td>-</td>
<td>20.76</td>
<td>23.60</td>
<td>11.50</td>
</tr>
<tr>
<td></td>
<td>259</td>
<td>-</td>
<td>20.70</td>
<td>23.40</td>
<td>11.55</td>
</tr>
</tbody>
</table>

\(^a\) Estimated error ± 0.05 G. \(^b\) Estimated error ± 0.0001.
**Figure 3.4:** Plot of total peak height for the allyl and adduct radicals versus duration of the photolysis of bis(tri-tert-butoxysilyl) disulfide 4 in the presence of propene (2.77 M) in cyclopropane solvent at 240 K
3.2.6 Abstraction of weakly-bound hydrogen

\[ \text{X}_3\text{SiS}^* + \text{RH} \rightleftharpoons \text{X}_3\text{SiSH} + \text{R}^* \]

Hydrogen-atom abstraction by thiy radicals is reversible and to an extent governed by the relative strengths of the R-H and S-H bonds. We have found that the thiy radicals, MeS*, (Bu'O)₃SiS*, Pr₃SiS* and Bu'Ph₂SiS* abstract hydrogen from 2-phenyl-1,3-dioxolane in the temperature range 230 to 300 K (fluorobenzene solvent) to generate the 2-phenyl-1,3-dioxolanyl radical which is detectable by EPR spectroscopy, showing that the equilibrium is to the right. For 2-vinyl-1,3-dioxolane, the radical \( \text{R}^* \) may again be detected by EPR spectroscopy (220 to 300 K); EPR parameters for all radicals are given in Table 5.10 (page 170).

In the case of 2-vinyl-1,3-dioxolane the adduct to the double bond was not detected, although it is thought that this adduct radical may be formed, but abstracts hydrogen from the silanethiol also produced such that in this case the equilibrium favours \( \text{X}_3\text{SiS}^* \) (see Scheme 3.4).

\[ \text{X}_3\text{SiSSiX}_3 \xrightarrow{\text{hv}} 2\text{X}_3\text{SiS}^* \]

\[ \text{X}_3\text{Si}^* + \text{CH}_2=\text{CH-CH}_3 \xrightarrow{\text{hv}} \text{X}_3\text{SiSH} + \text{X}_3\text{Si}^* \]

\[ \text{X}_3\text{Si}^* + \text{CH}_2=\text{CH-CH}_2\text{SiS}\text{X}_3 \xrightarrow{\text{hv}} \text{X}_3\text{SiSH} + \text{X}_3\text{Si}^* \]

SCHEME 3.4

3.2.7 Addition of silanethiyl radicals to triethyl phosphite

Photolysis of bis(triisopropylsilyl) disulfide 3 (0.22 M) in the presence of triethyl phosphite (0.78 M) in cyclopropane solvent at 198 K afforded a strong spectrum which was analysed in terms of coupling to \(^{31}\text{P} \) \( (I = \frac{1}{2}) \) to give a doublet \([d(^{31}\text{P})] = 828.8 \text{ G}\); the \( g \)-factor is \( g = 2.0087 \) (corrected for higher order effects). A central singlet \((g = 2.016)\) was also observed (for an explanation, see Section 3.2.9), but no other spectra were present. Similar spectra were recorded using bis(tri-tert-butoxy)silyl) disulfide 4 (see Table 3.7).
The isotropic phosphorus hyperfine splitting for phosphoranyl radical 14 is larger than for 15 and this presumably results from an increase in the proportion of P-3s character in the orbital of the unpaired electron on phosphorus, because of the greater electronegativity of the SSi(OBu') group as compared to the SSi(Pr') group.

It is difficult to assign a configuration to the phosphoranyl radical adducts based on EPR evidence alone. In the light of other results obtained in this work (see Sections 3.2.8 and 3.2.9), it is probable that the radicals have a \( \sigma^* \) structure as shown above, with a (2-centre : 3-electron) PS bond.

A similar conclusion was reached for the methanethiyl radical adduct of triethyl phosphite, which has been reported previously. In this case above ca. 195 K, the radical MeSP\(^{\cdot}\)(OEt)\(_3\) \([a(31P) 753.1 \text{ G}]\) underwent rapid \( \beta \)-scission to give methyl radicals and only the phosphoranyl MeP\(^{\cdot}\)(OEt)\(_3\) was detected.
### Table 3.7: EPR parameters for phosphoranyl radical adducts of triethyl phosphite in cyclopropane

<table>
<thead>
<tr>
<th>Radical</th>
<th>$T$/K</th>
<th>g-Factor$^{a,b}$</th>
<th>$^{31}$P Hyperfine splittings /G$^{a,c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bu'O)$_3$SiSP'OEt$_3$ 14</td>
<td>242</td>
<td>2.0073</td>
<td>863.5</td>
</tr>
<tr>
<td></td>
<td>198</td>
<td>2.0071</td>
<td>864.7</td>
</tr>
<tr>
<td>Pr'SiSP'OEt$_3$ 15</td>
<td>240</td>
<td>2.0091</td>
<td>828.1</td>
</tr>
<tr>
<td></td>
<td>197</td>
<td>2.0088</td>
<td>828.8</td>
</tr>
</tbody>
</table>

$^a$ Corrected for higher order effects using Preston's program ESRLSQ. $^b$ Estimated error ± 0.0002. $^c$ Estimated error ± 0.5 G.
3.2.8 Reactions of silanethiyl radicals with tributylphosphine

Photolysis of bis(tri-tert-butoxysilyl) disulfide 4 (0.22 M) in the presence of tributylphosphine (1.52 M) in cyclopropane solvent at 199 K afforded a strong spectrum assigned to the \( \sigma^* \) silanethiylphosphoranyl radical 16. It was analysed in terms of coupling to \( ^{31}\text{P} \) \( (I = \frac{1}{2}) \) to give a doublet \([\alpha(^{31}\text{P}) 614.23 \text{ G}]\) and coupling to six equivalent protons to give a septet \([\alpha(6\text{H}_a) 3.25 \text{ G}]\); the \( g \)-factor is \( g = 2.0077 \) (corrected for higher order effects). Two other phosphoranyl radicals were also observed, both showing larger values of \( \alpha(^{31}\text{P}) \), these relative concentrations depended on whether or not the phosphine had been distilled prior to use, which indicates that these radicals probably arise from impurities. A central singlet \((g = 2.015)\) was also observed (for a possible explanation, see Section 3.2.8).

Interestingly, the spectrum of 16 could be observed up to 302 K and no spectrum of the butyl radical was detected. The latter radical would be formed as a result of \( \alpha \)-scission of 16. It is thought the \( \sigma^* \) structure (local \( C_{3v} \) symmetry) of 16, in which the unpaired electron resides in the P-S bond \( \sigma^* \) orbital, accounts for the absence of fragmentation. In comparison, the corresponding tert-butoxy adduct 18 is too unstable with respect to \( \alpha \)-scission to be detected even at 173 K and gives the butyl radical \([\alpha(2\text{H}_a) 22.08 \text{ G}, \alpha(2\text{H}_b) 28.44 \text{ G}, \alpha(2\text{H}_c) 0.74 \text{ G} \) and \( g = 2.0027 \) at 200 K] extremely readily. This is thought to be because 18 exists in a “trigonal bipyramidal” (local \( C_{2v} \) symmetry) and such a structure would be expected to undergo very ready loss of a butyl radical from the apical site.

If the radicals 16 and 17 existed in a trigonal bipyramidal form we would expect different hyperfine splittings from the butyl groups in the apical and equatorial sites, and thus coupling to six equivalent protons further supports the assignment to a \( \sigma^* \) radical.

Similar spectra were produced using bis(trisopropylsilyl) disulfide 3 and EPR parameters for 16 and 17 are displayed in Table 3.8.

In order to support the assignment, we attempted to generate 16 by another route. Di-tert-butyl peroxide was photolysed in the presence tributylphosphine sulfide.
and tri-tert-butoxysilane in cyclopropane solvent, with the aim of inducing (Bu'0)2Si• to add to the sulfur atom of the P=S group. This indeed generated a phosphoranyl radical, but one showing $a^{(31)P} = 704.7$ G and $g = 2.0037$ at 200 K. The spectra were not clean, and other phosphoranyl radicals were present having $^{31}P$-coupling constants of ca. 332 G. The butyl radical $[a(2H_a) = 22.08$ G, $a(2H_p) = 28.44$ G, $a(2H_y) = 0.74$ G and $g = 2.0027$ at 200 K] was also clearly visible. A similar result was obtained using triisopropylsilane, but now a very weak spectrum of the expected $\sigma^\ast$ radical 17 could also be observed. Similar spectra were obtained when di-tert-butyl peroxide (15 % v/v) was photolysed in the presence of tributylphosphine sulfide in trimethylsilane or triethylsilane as solvent. Control experiments with no silane failed to produce any phosphoranyl radicals.

Comparison with spectra obtained from the photolysis of di-tert-butyl peroxide in the presence of tributylphosphine in cyclopropane at 200 K showed that a phosphoranyl radical having $a^{(31)P} = 703.9$ G is also generated (see Tables 3.9 and 3.10). It is thought that the silyl radical adds to the P=S double bond and the thiophosphoranyl radical formed then undergoes reversible $\alpha$-scission with cleavage of the P-S bond to give a silanethiyl radical and tributylphosphine.\textsuperscript{10} tert-Butoxy radicals then add to the phosphine and tert-butoxydealkylation leads to the secondary-product phosphoranyl radical observed (see Scheme 3.5).\textsuperscript{16}

\begin{center}
\textbf{SCHEME 3.5}
\end{center}
### Table 3.8: EPR parameters for silanethiyl radical adducts of tributylphosphine

<table>
<thead>
<tr>
<th>Radical</th>
<th>$T$/K</th>
<th>$g$-Factor$^{a,b}$</th>
<th>$a^{31}P$</th>
<th>$a(6H_d)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(Bu'O)_3SiSP'Bu_3$ 16</td>
<td>199</td>
<td>2.0077</td>
<td>614.2</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>2.0079</td>
<td>612.7</td>
<td>3.10</td>
</tr>
<tr>
<td>$Pr'SiSP'Bu_3$ 17</td>
<td>200</td>
<td>2.0099</td>
<td>566.2</td>
<td>$d$</td>
</tr>
<tr>
<td></td>
<td>239</td>
<td>2.0099</td>
<td>561.9</td>
<td>2.80</td>
</tr>
</tbody>
</table>

$^a$ Corrected for higher order effects using Preston’s program ESRLSQ. $^b$ Estimated error $\pm$ 0.0002. $^c$ Estimated error $\pm$ 0.5 G. $d$ Unresolved splitting.

### Table 3.9: EPR parameters for the photolysis of tert-butyl peroxide in the presence of tributylphosphine sulfide and silane in cyclopropane solvent.

<table>
<thead>
<tr>
<th>Silane</th>
<th>$T$/K</th>
<th>$g$-Factor$^{a,b}$</th>
<th>$a^{31}P$ /$G^{a,c,d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(Bu'O)_3SiH$</td>
<td>200</td>
<td>2.0037</td>
<td>704.7</td>
</tr>
<tr>
<td>$Pr'SiH$</td>
<td>202</td>
<td>2.0036</td>
<td>704.5</td>
</tr>
</tbody>
</table>

$^a$ Corrected for higher order effects using Preston’s program ESRLSQ. $^b$ Estimated error $\pm$ 0.0002. $^c$ Estimated error $\pm$0.5 G. $^d a(4H) = ca. 2.1$ G at 240 K; splitting poorly resolved.

### Table 3.10: EPR parameters for the phosphoranyl radical $Bu_2P'(OBu')_2$ produced by the photolysis of tert-butyl peroxide in the presence of tributylphosphine in cyclopropane solvent.

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$g$-Factor$^{a,b}$</th>
<th>$a^{31}P$ /$G^{a,c,d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2.0037</td>
<td>703.9</td>
</tr>
</tbody>
</table>

$^a$ Corrected for higher order effects using Preston’s program ESRLSQ. $^b$ Estimated error $\pm$ 0.0002. $^c$ Estimated error $\pm$ 0.5 G. $^d a(4H) = ca. 2.1$ G at 240 K; splitting poorly resolved.
3.2.9 Addition of silanethiyl radicals to tris(dimethylamino) phosphine

\[
\begin{align*}
\text{Me}_2\text{N} & \quad \text{Me}_2\text{N} \quad \text{Me}_2\text{N}^\text{P} \quad \text{SiX}_3 \\
\end{align*}
\]

\[X = \text{OBu}^\prime_3 \quad 19 \]
\[= \text{Pr}^\prime_3 \quad 20\]

Photolysis of bis(tri-tert-butoxysilyl) disulfide 4 (0.22 M) in the presence of tris(dimethylamino) phosphine (1.5 M) in cyclopropane solvent at 201 K afforded the spectrum shown in Figure 3.5. This was analysed in terms of coupling to \( ^{31}\text{P} \) \( (I = \frac{1}{2}) \) to give a doublet (762.0 G) and coupling to three equivalent \(^{14}\text{N} \) atoms \( (I = 1) \) to give a \( 1 : 3 : 6 : 8 : 6 : 3 : 1 \) septet (6.25 G) at 201 K; the g-factor is 2.0075. A central singlet can also be observed at \( g = 2.015 \) (see later for an explanation). No spectrum of the dimethylamino radical was detectable, suggesting that the phosphoranyl radical adopts a \( \sigma^* \) configuration, like that of 16. If the radical were to exist in a trigonal bipyramidal structure we would expect different hyperfine splittings from the apical and equatorial \(^{14}\text{N} \) nuclei and the presence of three equivalent nitrogen atoms supports the assignment to a \( \sigma^* \) radical. Similar spectra were obtained using bis(triisopropylsilyl) disulfide 3 (see Table 3.11).

It was observed that the lifetime of these samples was very short (yielding EPR spectra for ca. 8 minutes). When the concentration of bis(tri-tert-butoxysilyl) disulfide 4 was increased the sample depleted at an even faster rate. Care was taken when preparing the EPR tube to ensure that the phosphine and the disulfide did not mix and react thermally before photolysis. No radicals were observed at 253 K before any photolysis.

It appears that the reagents are rapidly consumed during UV irradiation of the sample. Analysis of a \(^1\text{H} \) NMR spectrum of a solution of tris(dimethylamino) phosphine (0.10 M) and bis(triisopropylsilyl) disulfide 3 (0.27 M) in benzene-\( d_6 \) (0.8 cm\(^3\)) at room temperature showed only a small amount of reaction between (Me\(_2\)N)\(_3\)P and the disulfide, possibly initiated by room light. However, when the experiment was repeated, exposing the solution to UV light (500 W mercury discharge lamp) for 5 minutes, the \(^1\text{H} \) NMR spectrum now showed considerable depletion in both reagents. It seems likely that the initially-formed phosphoranyl radical (Me\(_2\)N)\(_3\)P\(^*\)SX\(_3\) will have a low ionisation energy, because of the presence of the three amino groups, and thus
Figure 3.5: EPR spectrum of (Bu'O)₃Si(SP(NMe₂)₃ 19 in cyclopropane at 200 K

[Graph showing the EPR spectrum.]
### Table 3.11: EPR parameters for silanethiy radical adducts of tris(dimethylamino)-phosphine in cyclopropane

<table>
<thead>
<tr>
<th>Radical</th>
<th>T/K</th>
<th>g-Factor(^a,b)</th>
<th>(a(^{31}\text{P}))</th>
<th>(a(^{14}\text{N}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{Bu}^t\text{O})_3\text{SiSP}^*(\text{NMe}_2)_3) 19</td>
<td>201</td>
<td>2.0075</td>
<td>762.0</td>
<td>6.25</td>
</tr>
<tr>
<td>(\text{Pr}^t_3\text{SiSP}^*(\text{NMe}_2)_3) 20</td>
<td>197</td>
<td>2.0094</td>
<td>705.7</td>
<td>6.49</td>
</tr>
</tbody>
</table>

\(^a\) Corrected for higher order effects using Preston’s program ESRLSQ.\(^{16}\)  \(^b\) Estimated error ± 0.0002.  
\(^c\) Estimated error ± 0.5 G.
could readily transfer an electron to the silyl disulfide. The disulfide radical anion so formed would then break down to give a silanethiyl radical, leading to chain reaction which would be responsible for the rapid deletion of the reagents, (see Scheme 3.6).

\[
\text{SCHEME 3.6}
\]

The disulfide radical anion may give rise to the singlet mentioned before, which is observed in the EPR spectrum and the \( g \)-value of 2.015 is certainly consistent with this assignment [\( g \approx 2.014 \) for CH\(_3\)SSCH\(_3\)]\(^+\). The singlet decays in a similar way to the phosphoranyl radical at 200 K, further supporting the hypothesis illustrated in Scheme 3.6.

### 3.1.10 The reactions of silanethiyl radicals with trialkylboranes

Photolysis of bis(tri-tert-butoxysilyl) disulfide 4 (0.24 M) in cyclopropane solvent at 192 K afforded the spectrum of the butyl radical [\( a(2H_a) 22.08 \text{ G}, a(2H_b) 28.44 \text{ G}, a(2H_c) 0.70 \text{ G} \) and \( g = 2.0027 \) at 280 K]. Interestingly, a second, four line spectrum (\( g = 2.012, \text{peak separation 2.0 G} \)) appears over time at 192 K and at low temperatures (ca. 161 K) this was the dominate radical. The four lines had equal intensity and could therefore arise from hyperfine coupling to \( ^{11}\text{B} \) (\( I = 3/2 \)). It is thought that this maybe due to a \( \sigma^* \) disulfide radical 21 generated by reaction of a silanethiyl radical with \((\text{Bu'O})_3\text{SiSBBu}_2\) as shown in Scheme 3.7.
A similar result was obtained using triethylborane and bis(triisopropylsilyl) disulfide 3, when a four-line spectrum with a line spacing of 1.98 G and $g = 2.012$ could readily be observed at 181 K. Again, this splitting could arise from coupling to $^{11}$B ($I = 3/2$, natural abundance 80%) in a $\sigma^*$ sulfuranyl radical analogous to 21.

For (Bu'O)$_3$SiS* and Pr'$_3$SiS*, the relative rates of addition of the silanethiyl radicals to ethene and their S$_2$H2 reactions with triethylborane were measured at temperatures where only the ethyl radical and $\beta$-thioethyl radical could be observed (see Scheme 3.8 and Figure 3.6). Under the conditions used (200 K, [ethene] = 2.0 M), it has been shown that the reversibility of alkanethiyl radicals to ethene may be neglected. Since silanethiyl radicals are generally similar in reactivity to alkanethiyl radicals (vide infra), reversibility has been neglected in this study.

\[
\begin{align*}
X'S' + CH_2=CH_2 &\xrightarrow{k_A} XSC(\cdot)CH_2 \\
X'S' + Et_3B &\xrightarrow{k_B} Et^* + Et_2BSX \\
\left[ XSC(\cdot)CH_2 \right] / \left[ Et^* \right] &= k_A / k_B \times \left[ CH_2=CH_2 \right] / \left[ Et_3B \right] \\
k_B / k_A &= \left[ Et^* \right] / \left[ XSC(\cdot)CH_2 \right] \times \left[ CH_2=CH_2 \right] / \left[ Et_3B \right]
\end{align*}
\]

SCHEME 3.8

For both silanethiyl radicals, the S$_2$H2 reaction with triethylborane was faster than silanethiyl radical addition to ethene (see Table 3.12).
Table 3.12: Relative rates of addition of silanethiyl radicals to ethene (2.0 M) and their $S_{H2}$ reactions with triethylborane

<table>
<thead>
<tr>
<th>Silanethiyl radical</th>
<th>$T/K$</th>
<th>$(k_{S_{H2}}/k_{addition})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(Pr')_3SiS^*$</td>
<td>200</td>
<td>12.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.3$^a$</td>
</tr>
<tr>
<td>$(Bu'O)_3SiS^*$</td>
<td>220</td>
<td>5.6</td>
</tr>
</tbody>
</table>

$^a$Concentration of ethene (3.76 M) approximately doubled.

Figure 3.6: Composite EPR part spectrum of the ethyl radical (lines marked *) and adduct radical $(Bu'O)_3SiSCH_2CH_2^*$ at 193 K
3.2.11 Addition of silanethiyl radicals to isocyanides

When a solution of tert-butyl isocyanide, di-tert-butyl disulfide in cyclopropane at 180 K solvent was irradiated with high intensity UV light whilst the sample was in the cavity of the spectrometer, a strong 1:1:1 triplet EPR spectrum \( g(1^4\text{N}) = 5.0 \text{ G} \) was observed. A weak spectrum of the tert-butyl radical was also evident and at higher temperatures (280 K) only the spectrum of the later radical could be seen. The \( g \)-value of 2.0013 (less than the free-spin value of 2.0023) is as expected for the imidoyl radical \( \text{22} \).

\[
\begin{align*}
\text{Bu}^t\text{S}\text{•} & \quad \text{Bu}^t\text{N}=\text{C} & \rightarrow & \quad \text{Bu}^t\text{N}=\text{C}-\text{S}\text{Bu}^t \\
\text{22} & & & \\
\text{Bu}^t\text{N}=\text{C}-\text{S}\text{Bu}^t & \rightarrow & \quad \text{Bu}^t\text{N}=\text{C}=\text{S} & + & \quad \text{Bu}^t\text{•} \ (3.10)
\end{align*}
\]

This result is analogous to the addition of the tert-butoxyl radical to tert-butyl isocyanide and the subsequent \( \beta \)-scission of the imidoyl adduct \( \text{Bu}^t\text{N}=\text{COBu}^t \), as described by Blum and Roberts.\(^8\) It has been shown that in this case \( \beta \)-scission involves C-O cleavage to give isocyanate and the tert-butyl radical\(^8\) and it is reasonable that radical \( \text{22} \) will similarly fragment along the C-S bond as shown in eqn (3.10).

The experiment was repeated using our silyl disulfides as sources of silanethiyl radicals, and this gave rise to strong three-line EPR spectra of the corresponding imidoyl adducts [eqn. (3.11) and Table 3.13]. No spectra of any other radicals were detected even at high temperatures (323 K).

\[
\begin{align*}
\text{R}_3\text{SiS}\text{•} & \quad \text{Bu}^t\text{N}=\text{C} & \rightarrow & \quad \text{Bu}^t\text{N}=\text{C}-\text{SiR}_3 \\
\text{3.11} & & & \\
\end{align*}
\]

Although imidoyl radicals of the type \( \text{Bu}^t\text{N}=\text{CSR} \) undergo irreversible \( \beta \)-scission along the relatively weak S-C bond to generate alkyl radicals [eqn. 3.10], for \( \text{Bu}^t\text{N}=\text{C} \) \text{SSiR}_3, \( \beta \)-scission along the stronger S-Si is evidently reversible with the equilibrium favouring the imidoyl radical [eqn (3.12)].

\[
\begin{align*}
\text{Bu}^t\text{N}=\text{C}-\text{SiR}_3 & \quad \rightarrow & \quad \text{Bu}^t\text{N}=\text{C}=\text{S} & + & \quad \text{SiR}_3 \text{•} \\
\text{3.12} & & & \\
\end{align*}
\]

Silyl radicals add to tert-butyl isocyanide to generate the imidoyl radical \( \text{Bu}^t\text{N}=\text{CSiR}_3 \), which undergoes \( \beta \)-scission to give the tert-butyl radical via C-N bond
cleavage at low temperature [eqns. (3.13) and (3.14)]. Interestingly, the imidoyl radicals Bu'N=CSSiR₃, do not fragment along the C-N bond even at higher temperature (323 K).

\[ \text{R₃Si}^* + \text{Bu'N=C} \rightarrow \text{Bu'N=Si}^* \text{SiR₃} \quad (3.13) \]

\[ \text{Bu'N=C-SiR₃} \rightarrow \text{R₃Si≡C} + \text{Bu'N}^* \quad (3.14) \]

Cleavage of the C-N bond in eqn. (3.14) involves less structural reorganisation on going from Bu'N=CSSiR₃ to N≡CSiR₃ (both contain linear NCSi structures) than for C-N cleavage of Bu'N=CSSiR₃ in which the NCS group is strongly bent.

The values of \( a(^{14}\text{N}) \) for Bu'N=CSSiR₃ (ca. 2.7 G) are lower than the alkanethiyl analogues Bu'N=CSR (ca. 4.4-5.0 G). The reasons for this are difficult to analyse because there are three factors governing the value of \( a(^{14}\text{N}) \), namely spin polarisation of the N-C \( \sigma \)-bond, spin polarisation of the C-N \( \pi \)-bond and changes in overlap between the non-bonding orbitals on N and C as a result of variation of the angles \( \theta \) and \( \phi \) (Scheme 3.10). The angle \( \theta \) would be expected to increase as electronegativity of SX increases and it has been found that when the value of \( a(C\alpha) \) for imidoyl radicals is large \( a(^{14}\text{N}) \) is very small. Therefore, the greater electronegativity of SSiR₃ compared to SR may be responsible for the lower value of \( a(^{14}\text{N}) \) for Bu'N=CSSiR₃.

Silanethiyl radicals were also found to add to methyl isocyanide, and the resulting imidoyl radicals showed no evidence of fragmentation up to 331 K (Table 3.14). Interestingly, the \(^{14}\text{N}\) hyperfine splittings are substantially larger (ca. 11.5 G) than those for the tert-butyl analogue (ca. 2.7 G). In the case of MeN=CSSiR₃ it is
likely that there is larger overlap between the orbital of the unpaired electron on \( C_\alpha \) with that of the lone pair on \( N_\beta \) (pseudo-\( \pi \) overlap), resulting in a larger value of \( a^{(14N_\beta)} \) (Scheme 3.10). This could be because in \( Bu'N=CSSiR_3 \) the angle \( \phi \) is increased as a result of a steric effect, leading to smaller orbital overlap.
Table 3.13: EPR parameters for imidoyl radicals generated by addition of X* to tert-butyl isocyanide (Bu'NC)

<table>
<thead>
<tr>
<th>X*</th>
<th>T/K</th>
<th>Solvent</th>
<th>g-Factor$^b$</th>
<th>a(14N)/G$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu'S*</td>
<td>180</td>
<td>CP</td>
<td>2.0013</td>
<td>5.02$^d$</td>
</tr>
<tr>
<td>Bu'S*</td>
<td>210</td>
<td>CP</td>
<td>-</td>
<td>4.83$^d$</td>
</tr>
<tr>
<td>Bu'S*</td>
<td>280</td>
<td>CP</td>
<td>-</td>
<td>d</td>
</tr>
<tr>
<td>(Bu'O)$_3$SiS*</td>
<td>280</td>
<td>CP</td>
<td>2.0008</td>
<td>2.83</td>
</tr>
<tr>
<td>(Bu'O)$_3$SiS*</td>
<td>293</td>
<td>CP</td>
<td>2.0009</td>
<td>2.84</td>
</tr>
<tr>
<td>(Bu'O)$_3$SiS*</td>
<td>273</td>
<td>FB</td>
<td>2.0008</td>
<td>2.66</td>
</tr>
<tr>
<td>(Bu'O)$_3$SiS*</td>
<td>293</td>
<td>FB</td>
<td>2.0008</td>
<td>2.65</td>
</tr>
<tr>
<td>(Bu'O)$_3$SiS*</td>
<td>323</td>
<td>FB</td>
<td>-</td>
<td>2.65</td>
</tr>
<tr>
<td>Pr$_3$SiS*</td>
<td>280</td>
<td>CP</td>
<td>2.0008</td>
<td>2.71</td>
</tr>
<tr>
<td>Pr$_3$SiS*</td>
<td>293</td>
<td>CP</td>
<td>2.0008</td>
<td>2.68</td>
</tr>
<tr>
<td>Pr$_3$SiS*</td>
<td>273</td>
<td>FB</td>
<td>2.0008</td>
<td>2.55</td>
</tr>
<tr>
<td>Pr$_3$SiS*</td>
<td>293</td>
<td>FB</td>
<td>-</td>
<td>2.60</td>
</tr>
<tr>
<td>Pr$_3$SiS*</td>
<td>323</td>
<td>FB</td>
<td>-</td>
<td>2.60</td>
</tr>
</tbody>
</table>

$^a$ CP = cyclopropane and FB = fluorobenzene. $^b$ Estimated error ± 0.0001. $^c$ Estimated error ± 0.05 G. $^d$ The tert-butyl radical [a(9H) 22.75 G and g 2.0027 at 280 K] was observed.
Table 3.14: EPR parameters for imidoyl radicals generated by addition of $X'$ to methyl isocyanide (MeNC)

<table>
<thead>
<tr>
<th>$X'$</th>
<th>$T/K$</th>
<th>Solvent$^a$</th>
<th>$g$-Factor$^b$</th>
<th>$a^{(14N)}$</th>
<th>$a^{(3H)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bu'O)$_3$Si$'$</td>
<td>200</td>
<td>CP</td>
<td>-</td>
<td>11.61</td>
<td>1.31</td>
</tr>
<tr>
<td>(Bu'O)$_3$Si$'$</td>
<td>228</td>
<td>CP</td>
<td>-</td>
<td>11.63</td>
<td>1.33</td>
</tr>
<tr>
<td>(Bu'O)$_3$Si$'$</td>
<td>259</td>
<td>CP</td>
<td>-</td>
<td>11.65</td>
<td>1.34</td>
</tr>
<tr>
<td>(Bu'O)$_3$Si$'$</td>
<td>280</td>
<td>CP</td>
<td>2.0006</td>
<td>11.77</td>
<td>1.31</td>
</tr>
<tr>
<td>(Bu'O)$_3$Si$'$</td>
<td>291</td>
<td>CP</td>
<td>2.0006</td>
<td>11.75</td>
<td>1.25</td>
</tr>
<tr>
<td>(Bu'O)$_3$Si$'$</td>
<td>260</td>
<td>FB</td>
<td>-</td>
<td>11.52</td>
<td>1.33</td>
</tr>
<tr>
<td>(Bu'O)$_3$Si$'$</td>
<td>280</td>
<td>FB</td>
<td>2.0007</td>
<td>11.50</td>
<td>1.32</td>
</tr>
<tr>
<td>(Bu'O)$_3$Si$'$</td>
<td>301</td>
<td>FB</td>
<td>-</td>
<td>11.50</td>
<td>1.31</td>
</tr>
<tr>
<td>(Bu'O)$_3$Si$'$</td>
<td>331</td>
<td>FB</td>
<td>-</td>
<td>11.66</td>
<td>1.31</td>
</tr>
<tr>
<td>Pr'Si$'$</td>
<td>260</td>
<td>FB</td>
<td>-</td>
<td>11.42</td>
<td>1.33</td>
</tr>
<tr>
<td>Pr'Si$'$</td>
<td>280</td>
<td>FB</td>
<td>2.0007</td>
<td>11.50</td>
<td>1.32</td>
</tr>
<tr>
<td>Pr'Si$'$</td>
<td>301</td>
<td>FB</td>
<td>-</td>
<td>11.51</td>
<td>1.34</td>
</tr>
<tr>
<td>Pr'Si$'$</td>
<td>331</td>
<td>FB</td>
<td>-</td>
<td>11.55</td>
<td>1.33</td>
</tr>
</tbody>
</table>

$^a$ CP= cyclopropane and FB= fluorobenzene. $^b$ Estimated error ± 0.0001. $^c$ Estimated error ± 0.05 G.
3.2.12 Addition of silyl radicals to isothiocyanates

Photolysis of di-tert-butyl peroxide in the presence of triisopropylsilane (as a source of the triisopropylsilyl radical) and tert-butyl isothiocyanate, in either cyclopropane or fluorobenzene solvent, gave strong EPR spectra of the imidoyl adduct 23 in the temperature range 280-323 K. The EPR parameters were the same as for the radical generated previously by addition of silanethiyl radicals to tert-butyl isocyanide, confirming the assignment in both cases [eqn. (3.15)].

\[
\text{Pr}_3\text{Si}^* + \text{Bu}^\prime\text{N}=\text{C}=\text{S} \rightarrow \text{Bu}^\prime\text{N}=\hat{\text{C}}\text{SSiPr}_3
\]  

(3.15)

Similar results were found for the addition of tri-tert-butoxysilyl radicals to the isothiocyanate, and all EPR parameters are displayed in Table 3.15.
### Table 3.15: EPR parameters for imidoyl radicals generated by addition of silyl radicals to tert-butyl isothiocyanate (Bu'NCS)

<table>
<thead>
<tr>
<th>Silyl radical</th>
<th>T /K</th>
<th>Solvent$^a$</th>
<th>g-Factor$^b$</th>
<th>$a^{(14}\text{N})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$_3$Si$^*$</td>
<td>280</td>
<td>CP</td>
<td>2.0008</td>
<td>2.70</td>
</tr>
<tr>
<td>Pr$_3$Si$^*$</td>
<td>293</td>
<td>CP</td>
<td>-</td>
<td>2.77</td>
</tr>
<tr>
<td>Pr$_3$Si$^*$</td>
<td>273</td>
<td>FB</td>
<td>2.0008</td>
<td>2.63</td>
</tr>
<tr>
<td>Pr$_3$Si$^*$</td>
<td>293</td>
<td>FB</td>
<td>-</td>
<td>2.59</td>
</tr>
<tr>
<td>Pr$_3$Si$^*$</td>
<td>323</td>
<td>FB</td>
<td>-</td>
<td>2.62</td>
</tr>
<tr>
<td>(Bu'O)$_3$Si$^*$</td>
<td>280</td>
<td>CP</td>
<td>2.0008</td>
<td>2.86</td>
</tr>
<tr>
<td>(Bu'O)$_3$Si$^*$</td>
<td>302</td>
<td>CP</td>
<td>2.0008</td>
<td>2.87</td>
</tr>
</tbody>
</table>

$^a$ CP= cyclopropane and FB= fluorobenzene. $^b$ Estimated error $\pm 0.05$ G. $^c$ Estimated error $\pm 0.0001$. $^d$ Estimated error $\pm 0.05$ G.
3.3 Conclusion

EPR spectroscopic studies have provided some understanding of the chemistry of silanethiyl radicals. It was found that their behaviour is similar to that of alkanethiyl radicals, in their capacity to add to unsaturated molecules, abstract allylic and benzylic hydrogen atoms and add to co-ordinatively unsaturated elements to give hypervalent intermediates. Hydrogen-atom abstraction from propene and from cyclopentene gave EPR spectra that showed the concentration of the allylic radical increasing with time relative to that of the adduct radical, which is interpreted in terms of the build-up of thiol formed in the hydrogen abstraction process. The silanethiophosphoranyl radicals observed were believed to have $\sigma^*$ configurations, based in part on the observation that they did not undergo $\alpha$-scission even at relatively high temperatures. Silanethiyl radicals add to isocyanides to give imidoyl radicals. $\text{BuN}=\text{CSSiR}_3$ was found not to undergo $\beta$-scission along the Si-S bond compared to $\text{BuN}=\text{CSR}$, which fragments along the weaker C-S bond to afford $\text{R}^*$. 
3.4 EXPERIMENTAL

3.4.1 EPR Spectroscopy

The solution samples for EPR spectroscopic work were prepared in either under nitrogen capped tubes or were sealed under vacuum, when low boiling substances were involved. In the latter case, samples were flame-sealed in evacuated Suprasil quartz tubes (3 mm i.d., 0.5 mm wall); and narrower tubes (2 mm i.d., 0.5 mm wall) were used for samples which had a high dielectric constant. Quartz tubes (Wilmad 707 SQ) (3 mm i.d., 0.5 mm wall), and narrower tubes (2.4 mm i.d., 0.75 mm wall) for work using fluorobenzene, were sealed with a plastic cap and Nescofilm. In these "open" tubes, samples were made up by weight (solids) or volume (liquids) using microsyringes and were degassed by bubbling nitrogen through the solution for about a minute via a drawn-out Pasteur pipette; the tube was then sealed under a nitrogen atmosphere. For flame-sealed sample tubes, the low-boiling reagent and/or solvent were condensed into the tube using a calibrated vacuum line.

Spectra were obtained using Varian E-109 or Bruker ESP-300 instruments operating at 9.1-9.4 GHz and equipped for in situ UV-irradiation of the samples. The light source was a 500 W mercury discharge lamp (Osram HBO 500 W/2) in an Oriel 1 kW housing equipped with an f 0.7 Aspherab fused silica condensing lens. The slightly-converging beam from this was focussed using a fused silica lens (focal-length 10 cm, diameter 7.5 cm) and directed onto the sample through a 3 cm path length water-cooled cell filled with an aqueous solution containing NiSO$_4$$^\cdot$7H$_2$O (0.38 M), CoSO$_4$$^\cdot$7H$_2$O (0.07 M) and sulfuric acid (0.04 M)\textsuperscript{19}.

The temperature of the sample during photolysis was measured using a digital thermometer (Comark) connected to a thermocouple, positioned about ca. 4 cm down the dewar insert alongside the sample tube. The insert thermocouple has been calibrated against a second thermocouple contained in a sample tube filled with cyclopentane. The temperature increment due to sample heating as a result of UV irradiation was added to obtain the actual sample temperature during photolysis, and at full light intensity this varies between 5 and 7 K depending on conditions.\textsuperscript{20}

$g$-Factors were determined by measurement of the microwave frequency (using an E.I.P. Autohet microwave counter, model 331) and the magnetic field at the centre of the spectrum (using a Varian NMR gaussmeter).\textsuperscript{21} The difference in field between the gaussmeter probe and the sample was determined by measuring the $g$-factor of the pyrene radical anion, generated by the reduction of pyrene with sodium in THF, which
is accurately known to be 2.002710.\textsuperscript{22} The true field at the sample was found to be \textit{ca.} 0.21 G smaller than at the gaussmeter probe. The unknown \textit{g}-factor was calculated using the resonance condition shown in equation (3.13), where \((h/\mu_0) = 0.7144835 \text{ G MHz}^{-1}\) and \(v_0\) and \(B_0\) are the microwave frequency (in MHz) and the applied magnetic field at the centre of the spectrum (in G), respectively.

\[
g = (h/\mu_0) \times (v_0/B_0)
\]

(3.13)

Relative radical concentrations were determined by double integration of appropriate lines in each spectrum and confirmed by computer simulation of the composite spectrum, unless otherwise stated. Concentration ratios were extrapolated to zero UV irradiation time when necessary to overcome the effects of sample depletion and care was taken to avoid selective saturation of the spectra. Computer simulations were obtained using a modified version of ESRSPEC\textsuperscript{2},\textsuperscript{23} extended to handle composite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with \(I > \frac{1}{2}\), and lineshapes continuously variable between 100% Gaussian and 100% Lorentzian. The experimental methods for determination of relative rate constants using the EPR method have been described in detail previously.\textsuperscript{24}

### 3.4.2 Materials

The solvents cyclopropane (Union Carbide) and oxirane (Fluka) were freeze-thaw degassed and stored on the vacuum line in a 1 L glass globe or using a sample vessel fitted with a greaseless stop-cock, respectively, until all uncondensable gas was removed. Fluorobenzene was used as received.

\textit{Di-tert}-butyl peroxide (98%, Aldrich) was washed with 5% w/v aqueous potassium iodide containing 2% w/v sulfuric acid, until no more iodine was liberated. It was then washed successively with water, saturated aqueous sodium hydrogen carbonate and saturated brine, before being dried (MgSO\textsubscript{4}), passed down a column of basic alumina (activity 1) and finally distilled under nitrogen (b.p. 33 °C at 40 Torr).

Trimethylsilane was freeze-thaw degassed using a vacuum line and stored under vacuum in a sample tube fitted with a greaseless stop-cock. Triethylsilane was distilled and stored under nitrogen (b.p. 107-108 °C at 760 Torr).

\textit{tert}-Butyldiphenylsilanethiol was prepared as described in Section 2.4.2.6.
3.4.2.1 Triisopropylsilanethiol$^{25}$

Hydrogen sulfide (12.7 cm$^3$, 8.90 g, 260 mmol) was condensed into a glass trap of known volume and bubbled through dry tetrahydrofuran (THF, 300 cm$^3$) at -78 °C, contained in a 500 cm$^3$ round-bottomed flask fitted with a condenser. Butyllithium (1.6 M in hexane, 122.5 cm$^3$, 12.5 g, 122 mmol) was then added drop-wise over 15 minutes at -78 °C. The solution was allowed to warm to 0 °C over a period of 40 minutes, recooled to -78°C and then chlorotriisopropylsilane (27.7 cm$^3$, 25.0 g, 130 mmol) was added dropwise over 30 minutes. After the addition was complete, stirring was continued at -78 °C for 1 h, then 1 h at 0 °C and a further 2 h at room temperature. Water (100 cm$^3$) and pentane (200 cm$^3$) were added and, after separation, the organic phase was washed with water (3 x 100 cm$^3$) and dried over MgSO$_4$. The solvent was removed by rotary evaporation and the crude product was distilled under reduced pressure to give triisopropylsilanethiol (23.5 g, 95%).

B.p. 65 °C at 2.0 Torr (lit.$^{25}$ b.p. 70-75 °C at 2.1 Torr).

$^\delta_H$ -0.52 (1H, s, SH), 1.11 (18H, d, $^3$J 6.5, 3CH(CH$^3$)$_2$), 1.16 (3H, d, $^3$J 6.9, 3CH(CH$^3$)$_2$).

$^\delta_C$: 13.4 and 18.2.

3.4.2.2 Bis(triisopropylsilyl) disulfide $^3$$^{12}$

Triisopropylsilanethiol (10.00 g, 52.5 mmol) in benzene (50 cm$^3$) was added dropwise over 20 minutes to sodium hydride (60% in mineral oil, 2.57 g, 64.2 mmol) and the resulting suspension was allowed to stir for 10 minutes under nitrogen. A solution of iodine (8.13 g, 0.032 mmol) in benzene (100 cm$^3$) was added until a red/brown colour remained. The suspension was filtered through Celite and the solvent removed under reduced pressure to yield a red/brown oil. Recrystallisation of the crude
product from hexane gave bis(triisopropylsilyl) disulfide 3 as a canary yellow solid (5.12 g, 51%).

M.p. 37-38 °C (lit. 38 °C).

δ_H: 1.14 (36H, d, J 7.3, 6CH(CH_3)_2), 1.35 (6H, d, J 6.9, 6CH(CH_3)_2).

δ_C: 13.0 and 18.7.

MS (EI) m/z: 378 (M^+, 46), 157 (100), 115 (77), 87 (42), 73 (47), 59 (83).

3.4.2.3 Tri-tert-butoxysilanethiol

Silicon disulfide (Alfa Aesar) was crushed to a powder using a dry stainless steel pestle and mortar enclosed in a polythene bag filled with nitrogen. Powdered silicon disulfide (20.23 g, 95% pure, 0.22 mol) was charged into a 100 cm^3 round-bottomed flask containing a robust stirrer bar and equipped with a reflux condenser. tert-Butyl alcohol (60.10 g, 0.81 mol) was added and the mixture was stirred and heated under reflux (oil-bath at 95 °C) under nitrogen for 48 h. The cooled reaction mixture was filtered through Celite to remove unreacted silicon disulfide and the filter cake was washed with a little dichloromethane. Excess alcohol and dichloromethane were removed from the filtrate by rotary evaporation and the residual oil was distilled to give tri-tert-butoxysilanethiol (18.29 g, 30%) as a colourless oil.

B.p. 95 °C at 15 Torr (lit. 115 °C at 35 Torr).

δ_H: 0.18 (1H, s, SH), 1.34 (27H, s, 3Bu').

δ_C: 31.4 and 74.4.

MS (EI) m/z: 280 (M^+, 1), 157 (38), 57 (100), 41 (45), 29 (25).

3.4.2.4 Bis(tri-tert-butoxysilyl) disulfide 4

4
Tri-tert-butoxysilanethiol (6.00 g, 21.4 mmol) in benzene (10 cm$^3$) was added dropwise over 10 minutes to sodium hydride (60% in mineral oil, 1.28 g, 32.1 mmol) and the resulting suspension was allowed to stir for 10 minutes under nitrogen. A solution of iodine (4.08 g, 16.1 mmol) in benzene (100 cm$^3$) was added until a red/brown colour remained. The suspension was filtered through Celite and the solvent removed under reduced pressure to yield a red/brown oil. Recrystallisation of the crude product from hexane at 0 °C gave bis(tri-tert-butoxysilyl) disulfide 4 as a white solid (3.51 g, 58%).

M.p. 36 °C.

$\delta_H$: 1.34 (54H, s, 2Bu').

$\delta_C$: 31.5 and 74.2.

MS (EI) $m/z$: 558 (M$^+$, 37), 135 (100), 95 (16), 79 (67), 57 (100).

3.4.2.5 Bis(tert-butyldiphenylsilyl) disulfide 5

tert-Butyldiphenylsilanethiol (3.02 g, 11.1 mmol) in benzene (15 cm$^3$) was added dropwise over 10 minutes to sodium hydride (60% in mineral oil, 0.62 g, 15.4 mmol) and the resulting suspension was allowed to stir for 10 minutes under nitrogen. A solution of iodine (1.95 g, 7.7 mmol) in benzene (80 cm$^3$) was added until a red/brown colour remained. The suspension was filtered through Celite and the solvent removed under reduced pressure to yield a red/brown oil. Recrystallisation of the crude product from benzene/hexane gave bis(tert-butyldiphenylsilyl) disulfide 3 as a pale yellow solid (1.86 g, 62%).

M.p. 132-133 °C.

$\delta_H$: 0.98 (18H, s, 2Bu'), 7.30 (8H, t, J 7.4, Ph$^{meta}$), 7.39 (4H, t, J 7.6, Ph$^{para}$), 7.58 (8H, d, J 7.9, Ph$^{ortho}$).

$\delta_C$: 21.1, 28.0, 127.7, 129.7, 131.8 and 136.5.

MS (EI) $m/z$: 542 (M$^+$, 4), 351 (25), 259 (100), 239 (25), 197 (100), 135 (100), 105 (28).

Found: C, 70.8; H, 7.1. C$_{32}$H$_{38}$Si$_2$S$_2$ requires C, 70.8; H, 7.0%.
3.4.2.6 Tributylphosphine sulfide\textsuperscript{28}

Sulfur (1.91 g, 59.6 mmol) was added in three portions over 30 minutes to a stirred solution of tributylphosphine (10.00 g, 49.4 mmol) in benzene (13.2 cm\textsuperscript{3}) at room temperature under nitrogen. A rise in temperature upon each addition was observed which was checked using an ice bath. The solution was then refluxed for 1 h and then distilled under reduced pressure to give tributylphosphine sulfide (10.3 g, 89%).

B.p. 108 °C at 0.02 Torr (lit.\textsuperscript{28} 129-130 °C at 0.5 Torr).

\( \delta \)\textsubscript{H}: 0.92 (9H, t, J 7.3, 3CH\textsubscript{3}), 1.37-1.42 (6H, m, CH\textsubscript{2}CH\textsubscript{3}), 1.51-1.55 (6H, m, OCH\textsubscript{2}CH\textsubscript{2}), 1.76-2.11 (6H, m, OCH\textsubscript{2}).

\( \delta \)\textsubscript{C}: 13.2, 23.4, 23.5, 23.9, 24.0, 29.9 and 30.4.

MS (EI) \textit{m/z}: 234 (M\textsuperscript{+}, 26), 178 (33), 122 (100), 41 (20), 29 (27), 18 (29).

Found: C, 61.8; H, 11.5; S, 13.5%. C\textsubscript{12}H\textsubscript{27}PS requires C, 61.5; H, 11.6%; S, 13.7%.
3.5 REFERENCES


23. P.J. Krusic, *QCPE program no. 210*, Chemistry Department, Indiana University, USA.


CHAPTER 4
ISOMERISATION OF ALLYL SILYL ETHERS TO SILYL ENOL ETHERS
UNDER CONDITIONS OF POLARITY-REVERSAL CATALYSIS

4.1 INTRODUCTION

4.1.1 Preparation of silyl enol ethers

The most common preparative methods for silyl enol ethers involve O-silylation of an enolate ion or hydrosilylation of an α,β-unsaturated carbonyl compound in the presence of a transition metal catalyst. A third route involves the rearrangement of an allyl silyl ether again under the influence of a transition metal catalyst.

4.1.1.1 Preparation from enolates

Silyl enol ethers can be prepared by base treatment of a ketone (converting it to its corresponding enolate) followed by addition of a trialkylchlorosilane [e.g. eqn. (4.1)]. Both strong bases [e.g. lithium diisopropylamide (LDA)] and weaker bases [e.g. Et₃N] have been used for this purpose. The reaction can also be applied to aldehydes by the use of potassium hydride as base in 1,2-dimethoxyethane.²

![Reaction Scheme](image)

Conditions have been found under which either the (E)- or the (Z)-isomer of the silyl enol ethers of simple dialkyl ketones are produced with high selectivity. The isomer that contains the more highly substituted double bond is thermodynamically more stable, but the compound with the less substituted double bond is formed more rapidly (more acidic α-C-H group deprotonated) and is the product of kinetic control at low temperatures (Scheme 4.1).³
4.1.1.2 Preparation from hydrosilanes

The 1,4-addition of hydrosilanes to \(\alpha,\beta\)-unsaturated carbonyl compounds is promoted by a variety of catalysts such as chloroplatinic acid, platinium on alumina, and nickel.\(^4\) Tris(triphenylphosphine)chlororhodium(I) has been found to be an extremely effective catalyst for the hydrosilylations of \(\alpha,\beta\)-unsaturated ketones and aldehydes \[e.g., eqn. (4.2)].\(^5\)

\[
\begin{align*}
\text{C}_6\text{H}_5\text{(CH}_3)\text{2SiH} & \quad \text{Ph}_3\text{P}_3\text{RhCl} \\
\text{O} & \quad \text{C}_6\text{H}_5
\end{align*}
\]

(4.2)

Chiral rhodium catalysts have been found to induce asymmetric hydrosilylation, producing silyl enol ethers of 1.4 to 15.6% optical yield (72-94% chemical yield).\(^6\)

4.1.1.3 Preparation by transition-metal catalysed rearrangement of an allyl silyl ether

Double bond migration in allylic compounds under the influence of transition-metal catalysts to give the corresponding vinylic isomers have been studied by many groups.\(^7\) Sasson and Rempel\(^8\) have reported the conversion of allylic alcohols to aldehydes and ketones by ruthenium hydride complexes. Suzuki \textit{et al.}\(^9\) found that treatment of allyl silyl ethers with ruthenium hydride complexes resulted in selective migration of the double bond and gave the corresponding silyl enol ethers as the sole product \[eqn. (4.3)].\) They found a thermodynamic equilibrium mixture was produced with the \((Z)\)-enol isomer predominating to the extent of 55-68%.

\[
\begin{align*}
\text{R} \quad \text{R} \quad \text{R} \quad \text{R} & \quad \text{O} & \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \\
\text{R} & \quad \text{O} & \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} & \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \\
\text{R} & \quad \text{R} \quad \text{R} & \quad \text{O} & \quad \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \\
\end{align*}
\]

(4.3)

Recently, a degree of stereoselectivity has been obtained under conditions of kinetic control. Miyaura \textit{et al.}\(^10\) found that a cationic iridium complex, prepared \textit{via} the hydrogenation of \([\text{Ir(cod)}_2]\text{PF}_6-2\text{PPr}_3\) is an excellent catalyst for the stereoselective isomerisation of primary allyl silyl ethers to \((E)\)-enol ethers and secondary allyl ethers to \((Z)\)-enol ethers. For example, the primary allyl silyl ether 1 was converted almost exclusively to its \((E)\)-enol ether 2 \[eqn. (4.4)] in acetone solvent at room temperature.
4.1.2 Uses of silyl enol ethers

Silyl enol ethers are important reagents for organic synthesis, when they provide a source of nucleophilic carbon for C-C bond formation, for example in their reactions with carbonyl electrophilies in the presence of Lewis acid catalysts.

Lithium enolates are readily prepared by reaction of silyl enol ethers with methyllithium. Alkylations of these enolates (Scheme 4.2) have been used in the regiospecific preparation of hindered ketones.

\[
\text{SCHEME 4.2}
\]

Carbonyl compounds, powerfully activated by titanium(IV) chloride toward nucleophilic attack, react readily with silyl enol ethers to give crossed-aldol addition products in good yield [eqn. (4.5)]. The reaction is regiospecific, and selective reaction can occur when two different carbonyl functionalities appear in the same molecule.

When \(\alpha,\beta\)-unsaturated ketones and esters are subjected to reaction conditions identical to those used for the aldol reactions described above, good yields of 1,5-dicarbonyl compounds are obtained [eqn. (4.6)]. This acid-catalysed Michael reaction takes place under very mild conditions and offers tremendous advantages over the base-catalysed route.
4.1.3 Aims of research

We reasoned that allyl silyl ethers should isomerise by a radical-chain mechanism, in the presence of an appropriate thiol which would act as a protic polarity reversal catalyst (Section 1.5) to promote the overall abstraction of hydrogen from the electron-rich allylic H-CO bond in \( 3 \) by the chain-carrying nucleophilic allylic radical \( 4 \) (Scheme 4.3). The direct abstraction of hydrogen from \( 3 \) by \( 4 \) would be expected to be slow because of adverse polar effects in the transition state.

![SCHEME 4.3](image)

In this work we explore this methodology as a potentially useful route to silyl enol ethers derived from readily available allylic alcohols.
CHAPTER FOUR

4.2 RESULTS AND DISCUSSION

4.2.1 Isomerisation of \( \text{tert-butyl} \text{diphenyl(2-methylallyloxy)silane} \) \( 5 \)

\[ \text{OSiPh}_2\text{Bu}^t \xrightarrow{\text{AEBN, } 10 \text{ mol} \%} \text{OSiPh}_2\text{Bu}^t \]

**SCHEME 4.4**

Initial experiments were carried out with the 2-methylallyloxy silane \( 5 \) and conversion to the silyl enol ether \( 6 \) (Scheme 4.4) was monitored by \(^1\text{H} \) NMR spectroscopy. When a solution of \( 5 \) (1 mmol) and azobis(isobutyronitrile) (AIBN, 10 mol\%) in dry benzene (1.5 cm\(^3\)) was heated under reflux under nitrogen for 2.5 h, the allyl silyl ether was unchanged and no silyl enol ether was detectable. However, when the experiment was repeated in the additional presence of pentafluorothiophenol (PFTP, 10 mol\%), clean and complete conversion of \( 5 \) to \( 6 \) took place. The same result was obtained when the AIBN was replaced by different initiators as shown in Table 4.1, whereas without any initiator but in the presence of thiol, no conversion to silyl enol ether was observed. Choice of the thiol catalyst proved to be critical since, under otherwise identical conditions, thiophenol, \( \text{tert-dodecanethiol (TDT)}, \) tri-\( \text{tert-butoxysilanethiol} \) and triphenylsilanethiol gave conversions to \( 6 \) of 21, 5, 17 and 61%, respectively (see Table 4.2). Use of dilauroyl peroxide (DLP) as initiator with thiophenol or TDT as catalysts also gave low yields (Table 4.3).

Many thiols were investigated as catalysts using our most forcing conditions (refluxing octane), sometimes varying the initiator procedure, as shown in Table 4.4, but pentafluorothiophenol was the only thiol which achieved complete conversion of \( 5 \) to \( 6 \). Unexpectedly, triphenylsilanethiol which is thought to have a relatively strong SH bond and as a result not likely to be a good catalyst (Section 4.2.3), gave a high conversion (89%) compared to a far lower yield with tri-\( \text{tert-butoxysilanethiol} \) (15%). This result was supported by the observation that \( \text{tert-butyl} \text{diphenylsilanethiol} \) and tri-\( \text{ortho-tolylsilanethiol} \) also gave relatively high conversions (55-70%).

4.2.2 Inhibitor studies

Although these results point strongly to a radical-chain mechanism for the isomerisation of \( 5 \) to \( 6 \), in principle, some form of acid-catalysed process might be
Table 4.1: Isomerisation of tert-butyldiphenyl(2-methylallyloxy) silane 5
catalysed by pentafluorothiophenol (PFTP)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Conversion\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refluxing octane (b.p. 126 °C; oil bath 140 °C).</td>
<td>&gt;98</td>
</tr>
<tr>
<td>Initiator 2,2-di(tert-butyldi peroxy)butane.</td>
<td></td>
</tr>
<tr>
<td>Refluxing benzene (b.p. 80 °C; oil bath 95 °C).</td>
<td>&gt;98</td>
</tr>
<tr>
<td>Initiator dilauroyl peroxide.</td>
<td></td>
</tr>
<tr>
<td>Dioxane at 80 °C (oil bath 80 °C). Initiator dilauroyl peroxide.</td>
<td>&gt;98</td>
</tr>
<tr>
<td>Benzene at 60 °C (oil bath at 60 °C). Initiator TBHN.</td>
<td>&gt;98</td>
</tr>
<tr>
<td>Refluxing benzene (b.p. 80 °C; oil bath 95 °C).\textsuperscript{c}</td>
<td>&gt;98</td>
</tr>
<tr>
<td>Initiator AIBN.\textsuperscript{d}</td>
<td></td>
</tr>
<tr>
<td>Refluxing benzene (b.p. 80 °C; oil bath 95 °C).\textsuperscript{e}</td>
<td>0</td>
</tr>
<tr>
<td>No initiator</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Unless stated otherwise, reactions were carried out on the 1 mmol scale in 1.5 cm\textsuperscript{3} of solvent under reflux for 2.5 h with PFTP (5 mol\%) and initiator (5 mol\%) added at the start of the reaction with another addition of both (5 mol\%) after 40 minutes. \textsuperscript{b} Determined by \textsuperscript{1}H NMR spectroscopy. \textsuperscript{c} PFTP (10 mol\%) added at the start of the reaction. \textsuperscript{d} AIBN (10 mol\%) added at the start of the reaction.

Table 4.2: Results of isomerisation reactions initiated with AIBN (10 mol\%) in refluxing benzene (1.5 cm\textsuperscript{3}) for 2.5 h using different thiols

<table>
<thead>
<tr>
<th>Allyl Silyl Ether\textsuperscript{a}</th>
<th>Thiol\textsuperscript{b}</th>
<th>Conversion\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{2}=CH(Me)CH\textsubscript{2}OSiPh\textsubscript{2}Bu\textsuperscript{f}</td>
<td>Thiolphenol</td>
<td>21</td>
</tr>
<tr>
<td>TDT</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Pentafluorobenzenethiol</td>
<td>&gt;98, 26\textsuperscript{d}</td>
<td></td>
</tr>
<tr>
<td>Tri-tert-butoxy silanethiol</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Triphenylsilanethiol</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>No thiol</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} 1 mmol. \textsuperscript{b} 10 mol\%. \textsuperscript{c} Determined by \textsuperscript{1}H NMR spectroscopy. \textsuperscript{d} 2,4,6-collidine (10 mol\%).
**Table 4.3:** Isomerisation of \( \text{CH}_2=\text{CH}(\text{Me})\text{CH}_2\text{OSiPh}_2\text{Bu} \)\(^a\) initiated with dilauroyl peroxide\(^b\) in refluxing benzene (1.5 cm\(^3\)) for 2.5 h

<table>
<thead>
<tr>
<th>Thiol(^c)</th>
<th>Conversion(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiolphenol</td>
<td>14</td>
</tr>
<tr>
<td>TDT</td>
<td>12</td>
</tr>
</tbody>
</table>

\(^a\) 1 mmol. \(^b\) Peroxide (5 mol\%) added at the start of the reaction with another addition (5 mol\%) after 40 minutes. \(^c\) Thiol (5 mol\%) added at the start of the reaction with another addition (5 mol\%) after 40 minutes. \(^d\) Determined by \(^1\)H NMR spectroscopy.

**Table 4.4:** Isomerisation of \( \text{CH}_2=\text{CH}(\text{Me})\text{CH}_2\text{OSiPh}_2\text{Bu} \)\(^a\) initiated with 2,2-di(tert-butylperoxy)butane\(^b\) in refluxing octane (1.5 cm\(^3\)) for 2.5 h

<table>
<thead>
<tr>
<th>Thiol(^c)</th>
<th>Conversion(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiolphenol</td>
<td>31</td>
</tr>
<tr>
<td>( p )-Thiocresol</td>
<td>17</td>
</tr>
<tr>
<td>2,6-dimethylthiophenol(^e)</td>
<td>11</td>
</tr>
<tr>
<td>4-Methoxythiophenol</td>
<td>6</td>
</tr>
<tr>
<td>4-(Trifluoromethyl)thiophenol</td>
<td>91</td>
</tr>
<tr>
<td>Pentafluorothiophenol</td>
<td>&gt;98 (87), &gt;98(^f)</td>
</tr>
<tr>
<td>TDT(^g)</td>
<td>39</td>
</tr>
<tr>
<td>Methyl thioglycolate (MeO(_2)CCH(_2)SH)</td>
<td>50</td>
</tr>
<tr>
<td>( tert )-butyloxysilanethiol</td>
<td>13, 15</td>
</tr>
<tr>
<td>Triphenylsilanethiol</td>
<td>86, 89</td>
</tr>
<tr>
<td>( tert )-Butyldiphenylsilanethiol</td>
<td>68</td>
</tr>
<tr>
<td>Tri-( ortho )-tolylsilanethiol</td>
<td>55</td>
</tr>
<tr>
<td>(4-Trifluoromethyl)-2-pyrimidinethiol</td>
<td>0</td>
</tr>
<tr>
<td>2-Nitrothiophenol(^g)</td>
<td>72</td>
</tr>
<tr>
<td>2-4-Dinitrothiophenol(^g)</td>
<td>87</td>
</tr>
<tr>
<td>( tert )-Butylphenylphosphinothioic acid(^g)</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^a\) 1 mmol. \(^b\) Peroxide (5 mol\%) added at the start of the reaction with another addition (5 mol\%) after 40 minutes. \(^c\) Thiol (5 mol\%) added at the start of the reaction with another addition (5 mol\%) after 40 minutes. \(^d\) Determined by \(^1\)H NMR spectroscopy; isolated yields given in parentheses. \(^e\) 3 mol\% of peroxide and thiol added at the beginning of the reaction with two further additions at 20 minute intervals. \(^f\) 2,4,6-collidine (10 mol\%) present. \(^g\) Both peroxide and thiol (10 mol\%) added at the start of the reaction.
involved, the acid being generated (probably from the thiol) *in situ* during the reaction. Pentafluorothiophenol is itself a relatively strong acid (pKₐ ca. 2.7) because of the presence of the electronegative ring-fluorine atoms. The low conversion of 5 to 6 in the presence of collidine is probably a result of protonation of collidine by the acidic thiol (Table 4.2).

In order to test whether these isomerisations could be acid-catalysed an identical reaction was performed replacing PFTP with *para*-toluenesulfonic acid monohydrate (10 mol%) for conversion of 5 to 6. After 2.5 h heating in refluxing benzene, conversion of 5 to 6 was ca. 40% (Table 4.5) which indicates that the reactions can be acid-catalysed to some extent. In order to prove a radical-chain mechanism when using thiols, two identical reactions A and B (10 mol% each of PFTP and AIBN) were run side by side and samples were withdrawn from both for NMR analysis after 15 min. At the same time, the isolable aryloxyl radical galvinoxyl 7 (10 mol%) was added to flask B. As evidenced by the rapid colour change of the solution from dark brown to pale yellow, galvinoxyl reacts immediately with PFTP, presumably by abstraction of hydrogen to give the phenol monohydrogalvinoxyl that must also act as a radical scavenger to inhibit the radical-chain process. After 15 min heating, conversion of 5 to 6 was 48% in reaction A and 45% in reaction B, while after 2.5 h heating conversion was complete in reaction A but still only 45% in the inhibited reaction B (Table 4.6). 2-6-Di-tert-butyl-4-methylphenol also inhibited the isomerisation, although less effectively (Table 4.7).

These results strongly support a radical-chain mechanism for the isomerisation process. Repeating the inhibitor experiment using triphenylsilanethiol and DBPB in refluxing octane showed no evidence for an acid-catalysed mechanism (Table 4.8).
### Table 4.5: Results of isomerisation reactions with acid in refluxing benzene (1.5 cm$^3$) for 2.5 h

<table>
<thead>
<tr>
<th>Allyl Silyl Ether$^a$</th>
<th>Thiol$^b$</th>
<th>Conversion$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$=CH(Me)CH$_2$OSiPh$_2$Bu$^t$</td>
<td><em>para</em>-Toluenesulfonic acid monohydrate</td>
<td>49, 34</td>
</tr>
<tr>
<td>2,4,6-Collidine <em>para</em>-toluenesulfonate</td>
<td>0, 0</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 1 mmol. $^b$ 10 mol%. $^c$ Determined by $^1$H NMR spectroscopy.

### Table 4.6: Inhibited isomerisation of tert-butylidiphenyl(2-methylallyloxy)silane 5 using PFTP (10 mol%) and AIBN (10 mol%) in refluxing benzene (1.5 cm$^3$)

<table>
<thead>
<tr>
<th>Time</th>
<th>Conversion$^a$ for Flask A</th>
<th>Conversion$^a$ for Flask B$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 minutes</td>
<td>48</td>
<td>45</td>
</tr>
<tr>
<td>2.5 hours</td>
<td>&gt;98</td>
<td>45</td>
</tr>
</tbody>
</table>

$^a$ Determined by $^1$H NMR spectroscopy. $^b$ Galvinoxyl free radical (10 mol%) added after 15 minutes.

### Table 4.7: Inhibited isomerisation of tert-butylidiphenyl(2-methylallyloxy)silane 5 using PFTP (10 mol%) and AIBN (10 mol%) in refluxing benzene (1.5 cm$^3$)

<table>
<thead>
<tr>
<th>Time</th>
<th>Conversion$^a$ for Flask A</th>
<th>Conversion$^a$ for Flask B$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 minutes</td>
<td>45</td>
<td>44</td>
</tr>
<tr>
<td>2.5 hours</td>
<td>&gt;98</td>
<td>54</td>
</tr>
</tbody>
</table>

$^a$ Determined by $^1$H NMR spectroscopy. $^b$ 2,6-Di-tert-butyl-4-methylphenol (10 mol%) added after 15 minutes.

### Table 4.8: Inhibited isomerisation of tert-butylidiphenyl(2-methylallyloxy)silane 5 using triphenylsilanethiol (10 mol%) and 2,2-di(tert-butylnperoxy)butane (10 mol%) in refluxing octane (1.5 cm$^3$)

<table>
<thead>
<tr>
<th>Time</th>
<th>Conversion$^a$ for Flask A</th>
<th>Conversion$^a$ for Flask B$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 minutes</td>
<td>61</td>
<td>63</td>
</tr>
<tr>
<td>2.5 hours</td>
<td>89</td>
<td>63</td>
</tr>
</tbody>
</table>

$^a$ Determined by $^1$H NMR spectroscopy. $^b$ Galvinoxyl free radical (10 mol%) added after 15 minutes.
4.2.3 Pentafluorothiophenol as catalyst

\[
\text{XS}^* + \overset{\text{a}}{\text{D}} \rightarrow \overset{\text{b}}{\text{XS} \text{H}} + \overset{\text{c}}{\text{D}} \rightarrow \overset{\text{d}}{\text{XS}^*} + \overset{\text{e}}{\text{D}}
\]

**SCHEME 4.5**

In order for effective thiol-catalysed conversion of an allylic molecule to a more stable vinylic isomer (Scheme 4.5, D = electron-donating substituent), both reactions a and c must be rapid. Furthermore, removal of thiol by radical addition to the double bonds in the reactant or product must be minimised, by making addition of XS* to the C=C bonds highly reversible and/or retarded by the steric bulk of the thiyl radical. Both reactions a and c will be favoured for more electrophilic thiyl radicals but, since the activation energy for a reaction cannot be less than its endothermicity, the strength of the S-H bond should be such that neither reaction is significantly endothermic. Although reaction a will be very rapid with alkane- or silane-thiols as catalysts, reaction c (and reaction b) is likely to be appreciably endothermic and therefore relatively slow, with the equilibrium favouring the allylic radical. Because of the weaker S-H bond in thiophenol reaction c will be faster, while reaction a is still evidently fast enough, and this thiol is a more efficient catalyst. The S-H bond in PFTP is likely to be stronger than in thiophenol, the presence of electronegative substituents on the ring would be expected to strengthen the SH bond, compared with that in thiophenol, leading to a still more favourable balance between reactions a and c. The presence of the ring-fluorine atoms in PFTP will also maximise favourable polar effects for the abstraction of hydrogen by the especially electrophilic thiyl radical C₆F₅S*, to give the nucleophilic siloxyallyl radical (reaction a), as well as for abstraction of hydrogen from the thiol by the latter radical (reaction c).

Hence, arenethiols with electron-withdrawing substituents other than fluorine such as the nitrothiophenols and 4-(trifluoromethyl)thiophenol also act as polarity reversal-catalysts (Table 4.4).

4.2.4 Electron paramagnetic resonance spectroscopy of siloxyallyl radicals

EPR spectroscopy was used to monitor the radicals present during continuous UV irradiation of liquid samples positioned in the microwave cavity of the spectrometer, as described previously in Section 3.4.1. The EPR spectrum of the
trimethylsiloxyallyl radical \(9^{14}\) was observed during photolysis of a number of precursors of hydrogen-abstracting radicals \(X^*\) in the presence of allyloxytrimethylsilane 8 in cyclopropane solvent. In addition to di-tert-butyl peroxide (DTBP), which provides a photochemical source of the tert-butoxyl radical [eqn. (4.7; \(X^* = \text{Bu}^\text{tO}^*\)], bis(triisopropylsilyl) disulfide [\(X^* = ((\text{CH}_3)_2\text{CH})_3\text{SiS}^*\)], bis(tributoxysilyl) disulfide [\(X^* = (\text{Bu'O})_3\text{SiS}^*\)] and dimethyl disulfide [\(X^* = \text{MeS}^*\)] were also used.

\[
\text{X-X} \xrightarrow{h\nu} 2X^* \quad (4.7)
\]

diagram.

syn- and anti-Isomers 9S and 9A of the siloxyallyl radical were detected; spectroscopic parameters are given in Table 4.9 and the assignments of coupling constants follow those established previously for 9 and for other simple allylic radicals.\(^{15}\) Figure 4.1 shows a typical EPR spectrum and lines from the syn- and anti-isomers of 9 are marked. Since the line widths and shapes appeared the same, the isomer ratios were determined by peak height measurement and confirmed by computer simulation; the results are given in Table 4.10.

If we assume that 9S and 9A are removed by diffusion-controlled radical-radical reactions which have equal rate constants,\(^{16}\) then the relative steady-state concentrations 9S and 9A will be proportional to the relative rates of their formation, provided that syn- and anti-isomers do not interconvert within their life-times (ca. 1 ms) under the experimental conditions. The barriers associated with this type of isomerisation of monosubstituted allyl radicals are relatively large\(^{15b,d,e}\) and rotation about the \(C^1-C^2\) bond in 9 would not be expected to have any measurable effect on the observed value of \([9S]/[9A]\) at the temperatures investigated in this work.

Inspection of Table 4.10 shows that the value of \([9S]/[9A]\) varies slightly depending on the nature of the abstracting radical \(X^*\), it also increases with decreasing temperature. Two conformations of the allyl silyl ether need to be considered with respect to rotation about the \(\text{CH-CH}_2\text{OSiR}_3\) bond; these are 3a and 3b, in which
either the C-O bond or a C-H bond eclipses the double bond. It is most likely that 3a reacts with X* to give 9S, while 3b gives 9A. The temperature dependence of [9S]/[9A] will reflect the composite temperature dependencies of the rate constants for abstraction of hydrogen and the conformational equilibrium constant (K). In the conformation 3a there are two C-H bonds which make a relatively small dihedral angle of 30° with the C-2p\(_x\) orbitals of the double bond, while in 3b there is only one such C-H bond; the other is orthogonal to the \(\pi\)-system and allylic delocalisation of the unpaired electron will be available in the transition state for abstraction from this C-H bond only after rotation about the CH-CH\(_2\)OSiMe\(_3\) bond in the original allyl silyl ether. Thus, for stereoelectronic reasons the increase in [9S]/[9A] as the temperature decreases probably reflects mainly the lower activation energy for abstraction from 3a than from 3b, although changes in the conformational equilibrium constant K could also contribute.

The dependence of [9S]/[9A] on the nature of the abstracting radical X* could be a result of steric differences between the two abstracting species (all X* are similarly electrophilic).

Similar results were obtained using allyl silyl ethers 1, 5 and 10 (Table 4.9 and 4.10). It was also found that the methanethiyl radical (MeS*) and the tri-tert-butoxysilanethiyl radical [(Bu'\(\text{O}\))\(_3\)SiS*] predominately add to \(\text{H}_2\text{C}=\text{CHCH}_2\text{OSiMe}_3\) 8 at 199 and 223 K (Table 4.11), which may partly explain why (Bu'\(\text{O}\))\(_3\)SiSH does not act as a good polarity-reversal catalyst for the isomerisation of allyl silyl ethers to silyl enol ethers (see Table 4.4).

\[
\begin{align*}
\text{3a} & \quad \text{H} \quad \text{OSiR}_3 \\
\text{3b} & \quad \text{H} \quad \text{OSiR}_3
\end{align*}
\]

\[
\begin{align*}
\text{1 R}_3\text{Si} & = \text{Me}_2\text{Bu'Si} \\
\text{10 R}_3\text{Si} & = \text{Ph}_2\text{Bu'Si}
\end{align*}
\]
Figure 4.1: EPR spectrum of the trimethylsiloxyl radicals 9A and 9S (R = Me) at 223 K in cyclopropane solvent
Table 4.9: EPR parameters for syn- and anti-isomers of siloxyallyl radicals

\[ \text{[H}_2\text{C} = \text{CR'}\text{CHO}_3\text{SiR}_3\text{]}^+ \] in cyclopropane at 223 K

<table>
<thead>
<tr>
<th>R\textsubscript{3}Si</th>
<th>Isomer</th>
<th>( H^1_{\text{syn}} )</th>
<th>( H^1_{\text{anti}} )</th>
<th>( R^j )</th>
<th>( H^3_{\text{syn}} )</th>
<th>( H^3_{\text{anti}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me\textsubscript{3}Si</td>
<td>syn</td>
<td>14.36</td>
<td>3.10 (1H)</td>
<td>13.45</td>
<td>13.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anti</td>
<td>13.65</td>
<td>3.75 (1H)</td>
<td>13.20</td>
<td>14.25</td>
<td></td>
</tr>
<tr>
<td>Me\textsubscript{2}Bu'\textsubscript{Si}</td>
<td>syn</td>
<td>14.43</td>
<td>3.12 (1H)</td>
<td>13.44</td>
<td>13.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anti</td>
<td>13.65</td>
<td>3.75 (1H)</td>
<td>13.20</td>
<td>14.38</td>
<td></td>
</tr>
<tr>
<td>Ph\textsubscript{2}Bu'\textsubscript{Si}</td>
<td>syn</td>
<td>14.60</td>
<td>3.17 (1H)</td>
<td>13.40</td>
<td>14.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anti</td>
<td>13.65</td>
<td>3.75 (1H)</td>
<td>13.20</td>
<td>14.40</td>
<td></td>
</tr>
<tr>
<td>Ph\textsubscript{2}Bu'\textsubscript{Si}</td>
<td>syn\textsuperscript{c}</td>
<td>14.67</td>
<td>2.74 (3H)</td>
<td>12.78</td>
<td>13.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anti</td>
<td>13.30</td>
<td>2.74 (3H)</td>
<td>12.78</td>
<td>14.72</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} The \( g \)-values of all radicals are 2.0030 ± 0.0001.  \textsuperscript{b} Generally ± 0.05 G.  \textsuperscript{c} A third radical was also observed in the presence of both DTBP and disulfide and was not assigned coupling constants due to the dominance of other spectra obscuring lines. It is thought to arise by abstraction of hydrogen from the allylic CH\textsubscript{3} group.
### Table 4.10: syn : anti Isomer ratios for the siloxyallyl radicals formed by hydrogen-atom abstraction from various allyl silyl ethers in cyclopropane solvent

<table>
<thead>
<tr>
<th>Allyl Silyl Ether</th>
<th>Abstracting Radical X*</th>
<th>T / K</th>
<th>[9S]/[9A]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{C}=\text{CHCH}_2\text{OSiMe}_3 )</td>
<td>Bu'O*</td>
<td>180</td>
<td>5.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>5.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>3.79</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}=\text{CHCH}_2\text{OSiMe}_3 )</td>
<td>Pr(_3)SiS*</td>
<td>180</td>
<td>5.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>4.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>4.09</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}=\text{CHCH}_2\text{OSiMe}_3 )</td>
<td>(Bu'Ph(_2)_3SiS*)</td>
<td>260</td>
<td>4.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280</td>
<td>3.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>302</td>
<td>3.23</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}=\text{CHCH}_2\text{OSiMe}_2\text{Bu}' )</td>
<td>Bu'O*</td>
<td>180</td>
<td>7.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>4.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>2.75</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}=\text{CHCH}_2\text{OSiMe}_2\text{Bu}' )</td>
<td>Pr(_3)SiS*</td>
<td>180</td>
<td>5.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>4.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>3.52</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}=\text{CHCH}_2\text{OSiPh}_2\text{Bu}' )</td>
<td>Bu'O*</td>
<td>180</td>
<td>7.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>4.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>3.21</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}=\text{CHCH}_2\text{OSiPh}_2\text{Bu}' )</td>
<td>Pr(_3)SiS*</td>
<td>180</td>
<td>5.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>4.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>2.78</td>
</tr>
<tr>
<td>( \text{H}_2\text{C}=\text{CHCH}_3\text{CH}_2\text{OSiPh}_2\text{Bu}' )</td>
<td>Bu'O*</td>
<td>200</td>
<td>9.12</td>
</tr>
</tbody>
</table>

\(^a\) Fluorobenzene solvent.
Table 4.11: EPR parameters for the thiyl radical adducts of allyloxytrimethylsilane 8

<table>
<thead>
<tr>
<th>Radical</th>
<th>$T$ / K</th>
<th>g-Factor</th>
<th>Hyperfine splitting/G$^a$</th>
<th>adduct : allylic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$1H_\alpha$</td>
<td>$2H_\beta^b$</td>
</tr>
<tr>
<td>$(Bu'O)_3SiS^*$</td>
<td>199</td>
<td>-</td>
<td>20.80</td>
<td>10.50</td>
</tr>
<tr>
<td>$(Bu'O)_3SiS^*$</td>
<td>223</td>
<td>2.0028</td>
<td>20.53</td>
<td>11.15</td>
</tr>
<tr>
<td>MeS$^*$</td>
<td>199</td>
<td>-</td>
<td>21.20</td>
<td>12.52</td>
</tr>
<tr>
<td>MeS$^*$</td>
<td>223</td>
<td>2.0029</td>
<td>20.81</td>
<td>12.64</td>
</tr>
</tbody>
</table>

$^a$ Generally ± 0.05 G. $^b$ CH$_2$SX. $^c$ Predominantly adduct (> 95%) observed.
4.2.5 Isomerisation of other primary allyl silyl ethers

After 2.5 h in refluxing benzene under the usual conditions, with PFTP as catalyst and DLP as initiator, 90% of the allyl silyl ether 10 was converted to the isomeric silyl enol ethers 11E and 11Z with an E : Z ratio of 1 : 3.0. However, isomerisation was complete in refluxing toluene with 1,1-di-tert-butylperoxycyclohexane (DBPC, 10 mol%) as initiator or in refluxing octane with 2,2-di-tert-butylperoxybutane (DBPB, 10 mol%) as initiator; the E : Z ratio was 1 : 2.8 in both cases. Simple distillation afforded 11E and 11Z in 85% total isolated yield. The E- and Z-isomers were readily distinguished on the basis of the coupling constants between the vinylic protons.

The radical-chain mechanism for the isomerisation of allyl silyl ethers to silyl enol ethers is illustrated in Scheme 4.7 and the function of the thiol is to act as a protic polarity-reversal catalyst to promote the overall abstraction of allylic hydrogen from the allyloxysilane by the allylic radical 4, a reaction that is slow in the absence of thiol because of the lack of favourable charge-transfer stabilisation of the transition state. The allylic radical 4 exists in syn and anti forms, as detected by EPR spectroscopy at low temperature (Section 4.2.4), and trapping of 4-anti by the thiol presumably gives E-isomer of the silyl enol ether, while trapping of 4-syn will give the Z-isomer.
Similar experiments using PFTP were carried out on the primary allyl silyl ethers 1, 8 and 12-15 and the results are summarised in Tables 4.12-4.14. It was found that the optimal conditions were 10 mol% of both initiator and pentafluorothiophenol and the typical procedure is described in Section 4.4.4.

\[
\begin{align*}
\text{1} & \quad \text{R}_3\text{Si} = \text{Me}_2\text{Bu}^\prime\text{Si} \\
\text{8} & \quad \text{R}_3\text{Si} = \text{Me}_3\text{Si} \\
\text{13} & \quad \text{Ph}^{\prime}\text{CH} = \text{CHOSiMe}_2\text{Bu}^\prime \\
\text{14} & \quad \text{R}_3\text{Si} = \text{Me}_2\text{Si} \\
\text{15} & \quad \text{R}_3\text{Si} = \text{Ph}_2\text{Bu}^\prime\text{Si}
\end{align*}
\]

Isomerisation of the prototypical allyloxytrimethylsilane 8 took place readily either in refluxing toluene or in the neat silane as solvent (Table 4.12). In the latter case, the silyl enol ether could be isolated easily by simple distillation of the reaction mixture.

The allyl silyl ether 12 gave slightly lower conversions (91%) than usual, most likely because of the greater thermodynamic stability of 12, which has a triply substituted double bond, relative to the isomeric enol ether. It is possible that an equilibrium mixture of allyl silyl ether and silyl enol ether is formed (see Section 4.2.8). The allyl silyl ether 13 failed to isomerise in refluxing toluene which is probably due to the stability of the highly delocalised radical intermediate 13a making the equilibrium favour reaction d, Scheme 4.5.

\[
\begin{align*}
\text{13} & \quad \text{OSiMe}_2\text{Bu}^\prime \\
\text{13a} & \quad \text{OSiMe}_2\text{Bu}^\prime
\end{align*}
\]

4.2.6 Isomerisation of Z-1-tert-butyldiphenylsiloxypropene 11Z to show thermodynamic control

\[
\begin{align*}
\text{11Z} & \quad \text{OSiPh}_2\text{Bu}^\prime
\end{align*}
\]
4.2.8 Isomerisation of 16 to show thermodynamic equilibrium with 14

Isomerisation of the allyl silyl ether 14 (Scheme 4.10) was not complete in refluxing octane (94%) with a 16E : 16Z : 14 ratio of 10.7 : 2.3 : 1.0. It was thought a possibility that the allyl silyl ether 14 could be at thermodynamic equilibrium with its silyl enol ethers 16E/16Z under these conditions. If this is correct, heating of 16E/16Z in refluxing octane under our typical conditions would produce a thermodynamic equilibrium mixture of 14 and 16E/16Z. To test this hypothesis, simple distillation followed by chromatography on silica gel yielded a sample of enol ether consisting of predominately the E-isomer (16E : 16Z = 5.2 : 1.0), from which 14 was absent. This was then heated under reflux in octane for 2.5 h in the presence of PFTP and DBPB (10 mol% of each) when isomerisation of the allyl enol ether took place to give a mixture in which the 16E : 16Z : 14 ratio was 10.8 : 2.4 : 1.0, confirming that thermodynamic equilibrium between 16E, 16Z and 14 is established under the conditions used to convert 14 to 16E and 16Z.
Table 4.12: Results of isomerisation reactions catalysed by pentafluorothiophenol under different reaction conditions

<table>
<thead>
<tr>
<th>Allyl Silyl Ether</th>
<th>Solvent</th>
<th>Initiator</th>
<th>Conv.</th>
<th>E : Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂C=CHCH₂OSiMe₃</td>
<td>Toluene</td>
<td>AIBN</td>
<td>35</td>
<td>1 : 2.5</td>
</tr>
<tr>
<td></td>
<td>DBPC</td>
<td>72</td>
<td></td>
<td>1 : 2.5</td>
</tr>
<tr>
<td>H₂C=CHCH₂OSiMe₂Bu</td>
<td>Benzene</td>
<td>AIBN</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Benzene</td>
<td>DLP</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>DBPC</td>
<td>95</td>
<td>1 : 2.6</td>
</tr>
<tr>
<td></td>
<td>Octane</td>
<td>DBPC</td>
<td>&gt;98 (82)</td>
<td>1 : 2.3</td>
</tr>
<tr>
<td>H₂C=CHCH₂OSiPh₂Bu</td>
<td>Toluene</td>
<td>DBPC</td>
<td>&gt;98 (80)</td>
<td>1 : 2.8</td>
</tr>
</tbody>
</table>

* Unless stated otherwise, reactions were carried out on the 1 mmol scale in 1.5 cm³ of solvent under reflux for 2.5 h, in the presence of PFTP and initiator (both 10 mol%). † Determined by ¹H NMR spectroscopy; isolated yields given in parentheses. ‡ Neat allyloxytrimethylsilane 8 (15.54 mmol) heated in an oil bath at 110 °C for 1.5 h. § 1 mol%. ¶ 5 mmol. ‡‡ 25 mmol scale in octane (25 cm³). ‡§ 20 mmol scale in octane (20 cm³). ‡¶ Oil bath at 60 °C.

<table>
<thead>
<tr>
<th>Allyl Silyl Ether</th>
<th>Thiol</th>
<th>Solvent</th>
<th>Initiator</th>
<th>Conv.</th>
<th>E : Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂C=CHCH₂OSiMe₂Bu</td>
<td>PFTP</td>
<td>Toluene</td>
<td>DBPC</td>
<td>91</td>
<td>1 : 1.2</td>
</tr>
<tr>
<td></td>
<td>PFTP</td>
<td>Octane</td>
<td>DBPB</td>
<td>91</td>
<td>1 : 1.4</td>
</tr>
<tr>
<td>Me₂C=CHCH₂OSiPh₂Bu</td>
<td>PFTP</td>
<td>Toluene</td>
<td>DBPC</td>
<td>88</td>
<td>1 : 1.4</td>
</tr>
<tr>
<td></td>
<td>Ph₃SiSH</td>
<td>Toluene</td>
<td>DBPC</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TDT</td>
<td>Toluene</td>
<td>DBPC</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PFTP</td>
<td>Octane</td>
<td>DBPB</td>
<td>87</td>
<td>1 : 1.4</td>
</tr>
</tbody>
</table>

* Unless stated otherwise, reactions were carried out on the 1 mmol scale in 1.5 cm³ of solvent under reflux for 2.5 h, in the presence of PFTP and initiator (both 10 mol%). † Determined by ¹H NMR spectroscopy. ‡ Thiol (5 mol%) and DBPC (5 mol%) added at the start of the reaction with further additions of both (5 mol% of each) after 40 minutes.
Table 4.14: Results of isomerisation reactions catalysed by pentafluorothiophenol under different reaction conditions

<table>
<thead>
<tr>
<th>Silyl Enol Ether</th>
<th>Solvent</th>
<th>Initiator</th>
<th>Conv.</th>
<th>$E : Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>Benzene</td>
<td>AIBN</td>
<td>96</td>
<td>4.2 : 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DBPC</td>
<td>95 (78)</td>
<td>4.4 : 1</td>
</tr>
<tr>
<td>15</td>
<td>Octane</td>
<td>DBPB</td>
<td>94</td>
<td>4.7 : 1</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>DBPC</td>
<td>98</td>
<td>4.8 : 1</td>
</tr>
<tr>
<td></td>
<td>Benzene</td>
<td>AIBN</td>
<td>96 (81)</td>
<td>4.6 : 1</td>
</tr>
</tbody>
</table>

Unless stated otherwise, reactions were carried out on the 1 mmol scale in 1.5 cm$^3$ of solvent under reflux for 2.5 h, in the presence of PFTP and initiator (both 10 mol%). $^b$ Determined by $^1$H NMR spectroscopy; isolated yields given in parentheses. $^c$ Neat 14 (8.9 mmol) heated in an oil bath at 110 °C.

Table 4.15: Results of isomerisation reactions catalysed by pentafluorothiophenol under different reaction conditions

<table>
<thead>
<tr>
<th>Silyl Enol Ether</th>
<th>Solvent</th>
<th>Initiator</th>
<th>Initial</th>
<th>Reaction</th>
<th>$E : Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCH=CHO$^b$SiPh$_2$Bu$^c$</td>
<td>Octane</td>
<td>DBPB</td>
<td>1 : 3.4</td>
<td>1 : 2.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Octane</td>
<td>DBPB</td>
<td>0 : 1</td>
<td>1 : 2.8</td>
<td></td>
</tr>
</tbody>
</table>

Unless stated otherwise, reactions were carried out on the 1 mmol scale in 1.5 cm$^3$ of solvent under reflux for 2.5 h, in the presence of PFTP and initiator (both 10 mol%). $^b$ Determined by $^1$H NMR spectroscopy.

Table 4.16: Results of isomerisation reactions catalysed by pentafluorothiophenol under different reaction conditions

<table>
<thead>
<tr>
<th>Silyl enol ether</th>
<th>Solvent</th>
<th>Initiator</th>
<th>Initial</th>
<th>Reaction</th>
<th>$16E : 16Z : 14$</th>
<th>$16E : 16Z : 14$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$16E$ and $16Z$</td>
<td>Octane</td>
<td>DBPB</td>
<td>5.2 : 1 : 0</td>
<td>10.8 : 2.4 : 1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Unless stated otherwise, reactions were carried out on the 1 mmol scale in 1.5 cm$^3$ of solvent under reflux for 2.5 h, in the presence of PFTP and initiator (both 10 mol%). $^b$ Determined by $^1$H NMR spectroscopy.
4.2.9 Isomerisation of secondary allyl silyl ethers

The secondary allyl silyl ether 17 underwent isomerisation somewhat less readily than the primary analogue \( \text{H}_2\text{C} = \text{CHCH}_2\text{OSiPh}_2\text{Bu}^f \) 10. Thus, in refluxing benzene with AIBN and PFTP (both 10 mol%), conversion was 77% after 2.5 h (18E : 18Z = 1 : 1.9), although the conversion was increased to 86% when the AIBN was replaced by DLP (Table 4.17, Scheme 4.11). In refluxing toluene (DBPC initiator) or refluxing octane (DBPB initiator) conversion was >98% (18E : 18Z = 1 : 1.6 in both cases). Geometrical isomers were identified on the basis of NOE experiments.

A number of other secondary allyl silyl ethers 19-21 were isomerised to silyl enol ethers under similar conditions and the results are summarised in Table 4.17-4.19.

The lower reactivity of secondary allyloxysilanes seems likely to be mainly a stereoelectronic effect, arising from the fact that the single allylic CH bond is positioned close to the nodal plane of the double bond in the preferred conformation of the starting material, such that the allylic hydrogen atom is abstracted relatively slowly by a thiy radical (see Figure 4.2). Steric effects may also play a role, particularly in the case of 21 which has a bulky isopropyl group attached to the radical centre (see Figure 4.3).

The quantitative conversion of 20 to the corresponding silyl enol ether (Table 4.18) was reduced to almost zero when the PFTP was replaced by tert-dodecanethiol, again emphasising the importance of the choice of thiol catalyst. The low efficiency of the alkanethiol is presumably a consequence of the low rate of reaction c (Scheme 4.5), because of the effective stabilisation of the phenyl-substituted allylic radical intermediate involved in this isomerisation.
### Table 4.17: Results of isomerisation reactions under different reaction conditions

<table>
<thead>
<tr>
<th>Allyl Silyl Ether</th>
<th>Thiol</th>
<th>Solvent</th>
<th>Initiator</th>
<th>Conv.</th>
<th>$E : Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$=CHCH(Me)OSiMe$_2$Bu$^t$</td>
<td>PFTP</td>
<td>Benzene</td>
<td>AIBN</td>
<td>35</td>
<td>1 : 2.0</td>
</tr>
<tr>
<td>PFTP</td>
<td>Benzene</td>
<td>DLP</td>
<td>62</td>
<td>1 : 2.1</td>
<td></td>
</tr>
<tr>
<td>PFTP</td>
<td>Octane</td>
<td>DBPB</td>
<td>&gt; 98</td>
<td>1 : 2.0</td>
<td></td>
</tr>
<tr>
<td>CH$_2$=CHCH(Me)OSiPh$_2$Bu$^t$</td>
<td>PFTP</td>
<td>Benzene</td>
<td>AIBN</td>
<td>77, 26$^c$, 26$^c$</td>
<td>1 : 1.9</td>
</tr>
<tr>
<td>PFTP</td>
<td>Benzene</td>
<td>DLP$^d$</td>
<td>86</td>
<td>1 : 1.8</td>
<td></td>
</tr>
<tr>
<td>FMTP$^e$</td>
<td>Benzene</td>
<td>DLP$^d$</td>
<td>54</td>
<td>1 : 1.7</td>
<td></td>
</tr>
<tr>
<td>PFTP</td>
<td>Octane$^f$</td>
<td>DBPB</td>
<td>&gt; 98</td>
<td>1 : 1.6</td>
<td></td>
</tr>
<tr>
<td>PFTP</td>
<td>Toluene$^f$</td>
<td>DBPC</td>
<td>&gt; 98</td>
<td>1 : 1.6</td>
<td></td>
</tr>
<tr>
<td>TDT</td>
<td>Toluene</td>
<td>DBPC</td>
<td>2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ph$_3$SiSH</td>
<td>Toluene</td>
<td>DBPC</td>
<td>38</td>
<td>1 : 1.6</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Unless stated otherwise, reactions were carried out on the 1 mmol scale in 1.5 cm$^3$ of solvent under reflux for 2.5 h, in the presence of PFTP and initiator (both 10 mol%). $^b$ Determined by $^1$H NMR spectroscopy. $^c$ 2,4,6-Collidine (2 mol%). $^d$ Thiol (5 mol%) and DLP (5 mol%) added at the start of the reaction with further additions of both after 45 minutes. $^e$ 4-(Trifluoromethyl)thiophenol. $^f$ 1.5 hours.

### Table 4.18: Results of isomerisation reactions under different reaction conditions

<table>
<thead>
<tr>
<th>Allyl Silyl Ether</th>
<th>Thiol</th>
<th>Solvent</th>
<th>Initiator</th>
<th>Conv.</th>
<th>$E : Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$=CHCH(Ph)OSiMe$_2$Bu$^t$</td>
<td>PFTP</td>
<td>Toluene</td>
<td>DBPC</td>
<td>96</td>
<td>1 : 13</td>
</tr>
<tr>
<td>FBT$^c$</td>
<td>Toluene</td>
<td>DBPC</td>
<td>11</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ph$_3$SiSH</td>
<td>Toluene</td>
<td>DBPC</td>
<td>&lt; 2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>TDT</td>
<td>Toluene</td>
<td>DBPC</td>
<td>&lt; 2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PFTP</td>
<td>Octane</td>
<td>DBPB</td>
<td>&gt; 98</td>
<td>1 : 10</td>
<td></td>
</tr>
<tr>
<td>1-Octanethiol</td>
<td>Octane</td>
<td>DBPB</td>
<td>&lt; 2</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

(83)

$^a$ Unless stated otherwise, reactions were carried out on the 1 mmol scale in 1.5 cm$^3$ of solvent under reflux for 2.5 h, in the presence of PFTP and initiator (both 10 mol%). $^b$ Determined by $^1$H NMR spectroscopy; isolated yields given in parentheses. $^c$ 4-Fluorothiophenol.
Table 4.19: Results of isomerisation reactions catalysed by pentafluorothiophenol under different reaction conditions\textsuperscript{a}

<table>
<thead>
<tr>
<th>Allyl Silyl Ether</th>
<th>Solvent</th>
<th>Initiator</th>
<th>Conv.\textsuperscript{b}</th>
<th>E : Z\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}C=CHCH[CH(CH\textsubscript{3})\textsubscript{2}]OSiMe\textsubscript{3}</td>
<td>Octane</td>
<td>DBPB</td>
<td>31</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Octane</td>
<td>DBPB\textsuperscript{c}</td>
<td>61</td>
<td>1 : 3.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Unless stated otherwise, reactions were carried out on the 1 mmol scale in 1.5 cm\textsuperscript{3} of solvent under reflux for 2.5 h, in the presence of PFTP and initiator (both 10 mol%). \textsuperscript{b} Determined by \textsuperscript{1}H NMR spectroscopy. \textsuperscript{c} Thiol (10 mol\%) and DBPB (10 mol\%) added at the start of the reaction with further additions of both after 40 minutes.
Figure 4.2: B3LYP/6-31G(d,p) optimised structures for allyl silyl ethers 8 and 22

Secondary allyl silyl ether

Primary allyl silyl ether
Figure 4.3: B3LYP/6-31 G(d,p) optimised structure for 21

Secondary allyl silyl ether

21

hydrogen to be abstracted
(in an unfavourable position)
4.2.10 Density functional calculations

Density functional calculations at the (U)B3LYP/6-31G(d,p) level of theory predict that the E- and Z-isomers of Me₃SiOCH=CHMe are lower in energy than the most stable conformation of allyloxytrimethylsilane 8 by 29.7 and 33.0 kJmol⁻¹ (ΔG at 25 °C), respectively, while the syn-isomer of the allylic radical 9S (R = Me) is more stable than the anti-isomer 9A by 1.4 kJmol⁻¹ (Table 4.20). The appreciably greater stability of the silyl enol ether compared with the allyl silyl ether accords with the effectively complete isomerisation observed by experiment and the predicted equilibrium E : Z ratio is ca. 1 : 2.8 at 115 °C, in excellent agreement with the result obtained in refluxing toluene (1 : 2.2).

![Chemical Structures](https://example.com/structures.png)

4.2.11 Photochemically initiated isomerisation of allyloxy-tert-butyldiphenylsilane 10

Initial experiments were carried out with the allyloxy-tert-butyldiphenylsilane 10 and conversion to the silyl enol ethers 11E and 11Z (Scheme 4.6) was monitored by ¹H NMR spectroscopy. When a solution of 10 (2 mmol) and 2-hydroxy-2-methylpropiophenone (eqn. 4.8, 20 mol%) in dry cyclohexane (3.0 cm³) was irradiated through quartz with light from a 160 W mercury lamp under nitrogen for 6 h at 25 °C, the allyl silyl ether was unchanged and no silyl enol ether was detectable. However, when the experiment was repeated in the additional presence of pentafluorothiophenol (PFTP, 10 mol%), 32% conversion of 10 to 11E and 11Z took place (Table 4.21). When 2-hydroxy-2-methylpropiophenone was replaced with di-tert-butyl peroxide (eqn. 4.9) conversion of 10 to 11E and 11Z increased to 58% (E : Z = 1 : 3.7).
Table 4.20: Results of density functional calculations at the (U)B3LYP/6-31G(d) level

<table>
<thead>
<tr>
<th>Molecule</th>
<th>6-31G(d) opt. energy (hartree)</th>
<th>ZPVE (kJ mol(^{-1}))</th>
<th>(E (0,K)) (hartree)</th>
<th>Thermal corr. to (H) (hartree)</th>
<th>(H^{298-H_0}) (kJ mol(^{-1}))</th>
<th>(H^{298}) (hartree)</th>
<th>(H^{rel.}) (kJ mol(^{-1}))</th>
<th>Thermal corr. to (G) (hartree)</th>
<th>(G^{298}) (hartree)</th>
<th>(G^{rel.}) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>9E</td>
<td>-601.863991</td>
<td>489.6</td>
<td>-601.677513</td>
<td>0.200241</td>
<td>36.1</td>
<td>-601.663750</td>
<td>-28.9</td>
<td>0.147085</td>
<td>-601.716906</td>
<td>-29.7</td>
</tr>
<tr>
<td>9Z</td>
<td>-601.864628</td>
<td>490.1</td>
<td>-601.677959</td>
<td>0.200404</td>
<td>36.1</td>
<td>-601.664224</td>
<td>-30.2</td>
<td>0.146459</td>
<td>-601.718169</td>
<td>-33.0</td>
</tr>
<tr>
<td>8</td>
<td>-601.853071</td>
<td>490.5</td>
<td>-601.666250</td>
<td>0.200347</td>
<td>35.5</td>
<td>-601.652724</td>
<td>0.0</td>
<td>0.147484</td>
<td>-601.705587</td>
<td>0.0</td>
</tr>
<tr>
<td>9S</td>
<td>-601.218964</td>
<td>454.5</td>
<td>-601.045854</td>
<td>0.186608</td>
<td>35.4</td>
<td>-601.032356</td>
<td>0.6</td>
<td>0.133561</td>
<td>-601.085403</td>
<td>1.4</td>
</tr>
<tr>
<td>9A</td>
<td>-601.219341</td>
<td>455.1</td>
<td>-601.046003</td>
<td>0.186764</td>
<td>35.2</td>
<td>-601.032577</td>
<td>0.0</td>
<td>0.133412</td>
<td>-601.085929</td>
<td>0.0</td>
</tr>
</tbody>
</table>

1 Hartree = 2625.5 kJ mol\(^{-1}\). Values for enol ethers 9E and 9Z are relative to 8 and values for allylic radical 9S are relative to 9A.
A sample of silyl enol ethers $11E$ and $11Z$ ($E:Z = 1:37$) was subjected to the same experimental conditions, some isomerisation took place to give a final $E:Z$ ratio of $1:12$ (Table 4.22). This result can be compared with the $E:Z$ ratio of $1:3.7$ obtained from isomerisation of the allyl silyl ether, indicating that thermodynamic equilibrium between $11E$ and $11Z$ is not established under the conditions used. However, some interconversion of $E$ and $Z$ isomers does take place indicating that it will be very difficult to obtain kinetically-controlled isomers ratios, even with photochemical initiation at low temperature.
Table 4.21: Isomerisation of $\text{H}_2\text{C}=$CHCH$_2$OSiPh$_2$Bu$^\dagger$ 10 catalysed by PFTP under photochemical conditions in cyclohexane$^a$

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Conv.$^b$</th>
<th>$E : Z^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Hydroxy-2-methylpropiophenone</td>
<td>32</td>
<td>1 : 4</td>
</tr>
<tr>
<td>Di-tert-butyl peroxide$^c$</td>
<td>58</td>
<td>1 : 3.7</td>
</tr>
</tbody>
</table>

$^a$Unless stated otherwise, reactions were carried out on the 2 mmol scale in 3 cm$^3$ of solvent for 6 h at 25 °C, in the presence of PFTP (10 mol%) and initiator (20 mol%). $^b$Determined by $^1$H NMR spectroscopy. $^c$4 Equivalents based on allyl silyl ether.

Table 4.22: Isomerisation of silyl enol ethers 11$E$ and 11$Z$ catalysed by PFTP under photochemical conditions$^a$

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Initial $E : Z^b$</th>
<th>Final $E : Z^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-tert-butyl peroxide</td>
<td>1 : 37</td>
<td>1 : 12</td>
</tr>
</tbody>
</table>

$^a$Reactions were carried out on the 2 mmol scale in 3.0 cm$^3$ of solvent for 6 h at 25 °C, in the presence of PFTP (10 mol%) and initiator (4 eq.). $^b$Determined by $^1$H NMR spectroscopy.
4.2.11 Isomerisation of allyl alkyl ethers to alkyl vinyl ethers

After 2.5 h in refluxing benzene under the usual conditions, using PFTP as catalyst and AIBN as initiator, 91% of the allyl alkyl ether 23 was converted to an isomeric mixture of the vinyl allyl ethers 24E and 24Z with an E : Z ratio of 1 : 1.5. Isomerisation was complete in refluxing octane (DBPB initiator) to give the same E : Z ratio of 1 : 1.5. Under identical conditions allyl phenyl ether 25, isomerised less readily (Table 4.23) presumably because the transition state is less effectively stabilised by charge transfer (polar effects) of the type [RS⁻ H⁺ R⁺] because the lone pair on oxygen is less available. The secondary allylic ether, acrolein diethyl acetal 26, gave a poor conversion (35%), most likely because of stereoelectronic and/or steric effects (see Section 4.2.9). 2-Vinyl-1,3-dioxolane 27, 2-vinyl-1,3-dioxane 28 and 4-vinyl-1,3-dioxolan-2-one 29 all failed to isomerise, again, possibly because of stereoelectronic and/or steric effects (see also Section 5.2.3, page 175).

Allyl butyrate 30, allyl acetate 31 and 2-methyl-2-propene-1,1-diol diacetate 32 all failed to isomerise under the standard conditions. Allyl butyrate also failed to isomerise with triphenylsilane thiol, TDT, 4-(trifluoromethyl)thiophenol and thiophenol as catalysts. It is thought that hydrogen-atom abstraction by the thiyli radical (step a, Scheme 4.5) is slow because the transition state is less effectively stabilised by charge transfer when an ester oxygen is present.

---

**SCHEME 4.11**

After 2.5 h in refluxing benzene under the usual conditions, using PFTP as catalyst and AIBN as initiator, 91% of the allyl alkyl ether 23 was converted to an isomeric mixture of the vinyl allyl ethers 24E and 24Z with an E : Z ratio of 1 : 1.5. Isomerisation was complete in refluxing octane (DBPB initiator) to give the same E : Z ratio of 1 : 1.5. Under identical conditions allyl phenyl ether 25, isomerised less readily (Table 4.23) presumably because the transition state is less effectively stabilised by charge transfer (polar effects) of the type [RS⁻ H⁺ R⁺] because the lone pair on oxygen is less available. The secondary allylic ether, acrolein diethyl acetal 26, gave a poor conversion (35%), most likely because of stereoelectronic and/or steric effects (see Section 4.2.9). 2-Vinyl-1,3-dioxolane 27, 2-vinyl-1,3-dioxane 28 and 4-vinyl-1,3-dioxolan-2-one 29 all failed to isomerise, again, possibly because of stereoelectronic and/or steric effects (see also Section 5.2.3, page 175).

---

**CHART 4.11**

After 2.5 h in refluxing benzene under the usual conditions, using PFTP as catalyst and AIBN as initiator, 91% of the allyl alkyl ether 23 was converted to an isomeric mixture of the vinyl allyl ethers 24E and 24Z with an E : Z ratio of 1 : 1.5. Isomerisation was complete in refluxing octane (DBPB initiator) to give the same E : Z ratio of 1 : 1.5. Under identical conditions allyl phenyl ether 25, isomerised less readily (Table 4.23) presumably because the transition state is less effectively stabilised by charge transfer (polar effects) of the type [RS⁻ H⁺ R⁺] because the lone pair on oxygen is less available. The secondary allylic ether, acrolein diethyl acetal 26, gave a poor conversion (35%), most likely because of stereoelectronic and/or steric effects (see Section 4.2.9). 2-Vinyl-1,3-dioxolane 27, 2-vinyl-1,3-dioxane 28 and 4-vinyl-1,3-dioxolan-2-one 29 all failed to isomerise, again, possibly because of stereoelectronic and/or steric effects (see also Section 5.2.3, page 175).

Allyl butyrate 30, allyl acetate 31 and 2-methyl-2-propene-1,1-diol diacetate 32 all failed to isomerise under the standard conditions. Allyl butyrate also failed to isomerise with triphenylsilane thiol, TDT, 4-(trifluoromethyl)thiophenol and thiophenol as catalysts. It is thought that hydrogen-atom abstraction by the thiyli radical (step a, Scheme 4.5) is slow because the transition state is less effectively stabilised by charge transfer when an ester oxygen is present.
Isomerisation of the ethyl allyl ether 33 (Scheme 4.12) was not complete in refluxing octane (83%) with an $34E : 34Z : 33$ ratio of 3.9 : 0.92 : 1.0. Simple distillation followed by chromatography on silica gel yielded a sample consisting of predominately the $E$-isomer $34E$ ($34E : 34Z : 33 = 10 : 1.0 : 0$). This was subsequently heated under reflux in octane for 2.5 h in the presence of PFTP and DBPB (10 mol% of each) when isomerisation of the alkyl vinyl ethers took place to give a $34E : 34Z : 33$ ratio of 4.5 : 1.3 : 1.0 (Table 4.24), indicating that thermodynamic equilibrium between these three compounds is being approached under the conditions used originally to convert 33 to $34E$ and $34Z$.

![Scheme 4.12](image-url)
### Table 4.23: Isomerisation of alkyl allyl ethers catalysed by pentafluorothiophenol

<table>
<thead>
<tr>
<th>Alkyl Allyl Ether</th>
<th>Solvent</th>
<th>Initiator</th>
<th>Conv.</th>
<th>E : Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂=CHCH₂OBu</td>
<td>Benzene</td>
<td>AIBN</td>
<td>91</td>
<td>1 : 1.5</td>
</tr>
<tr>
<td>CH₂=CHCH₂OBu</td>
<td>Toluene</td>
<td>DBPC</td>
<td>70</td>
<td>1 : 1.5</td>
</tr>
<tr>
<td>CH₂=CHCH₂OBu</td>
<td>Octane</td>
<td>DBPB</td>
<td>&gt; 98</td>
<td>1 : 1.5</td>
</tr>
<tr>
<td>CH₂=CHCH₂OPh</td>
<td>Toluene</td>
<td>DBPC</td>
<td>52</td>
<td>1 : 2.2</td>
</tr>
<tr>
<td>CH₂=CHCH₂OPh</td>
<td>Octane</td>
<td>DBPB</td>
<td>70</td>
<td>1 : 2.3</td>
</tr>
<tr>
<td>CH₂=CHCH(OEt)₂</td>
<td>Toluene</td>
<td>DBPC</td>
<td>35</td>
<td>-</td>
</tr>
<tr>
<td>Myrtenyl methyl ether 33</td>
<td>Octane</td>
<td>DBPB</td>
<td>83</td>
<td>4.2 : 1</td>
</tr>
<tr>
<td>Myrtenyl methyl ether 33</td>
<td>Octane</td>
<td>DBPB³³</td>
<td>83</td>
<td>4.2 : 1</td>
</tr>
<tr>
<td>Myrtenyl methyl ether 33</td>
<td>Octane</td>
<td>DBPB³³</td>
<td>83</td>
<td>3.2 : 1</td>
</tr>
</tbody>
</table>

*Unless stated otherwise, reactions were carried out on the 1 mmol scale in 1.5 cm³ of solvent under reflux for 2.5 h, in the presence of PFTP and initiator (both 10 mol%). Determined by 'H NMR spectroscopy. ³² Nitrothiophenol. ³³ Thiol (10 mol%) and initiator (10 mol%) added at the start of the reaction with further additions of both after 45 minutes.*

### Table 4.24: Isomerisation of ethyl vinyl ethers 34E/34Z catalysed by pentafluorothiophenol

<table>
<thead>
<tr>
<th>Ethyl Vinyl Ether</th>
<th>Solvent</th>
<th>Initiator</th>
<th>Initial Ratio</th>
<th>Final Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>34E/34Z</td>
<td>Octane</td>
<td>DBPB</td>
<td>10 : 1 : 0</td>
<td>4.5 : 1.3 : 1</td>
</tr>
</tbody>
</table>

*Reactions were carried out on the 1 mmol scale in 1.5 cm³ of solvent under reflux for 2.5 h, in the presence of PFTP and initiator (both 10 mol%). ¹ Determined by 'H NMR spectroscopy.*
4.2.12 Alternatives to thiols as polarity-reversal catalysts

It is has been shown that phenolic hydrogen atoms involved in intramolecular, non-linear, hydrogen bonds, as in 2-methoxyphenol 35, can be abstracted relatively readily by free radicals. This contrasts with phenolic hydrogen atoms involved in intermolecular, linear, hydrogen bonds, as in other phenols (e.g. 36) that cannot be abstracted by attacking radicals because of steric blocking of the phenolic hydrogen. The bond strength of some phenols (2-methoxyphenol, 347 kJ mol⁻¹) is similar to that of thiols (thiolphenol, 349 kJ mol⁻¹) and it was thought that such phenols might be useful as polarity-reversal catalysts.

The standard experiment (Section 4.4.4) was repeated using various phenols (2-methoxyphenol 35, 2-fluorophenol 37, 2,4-difluorophenol 38, pentafluorophenol 39 and 3-acetyl-4-hydroxybenzonitrile 40), all of which have a hydrogen bond accepting substituent, such as methoxy, at the ortho position (see Scheme 4.14). Unfortunately, it was found that the phenols did not act as polarity-reversal catalysts.
4.3 Conclusion

The PFTP-catalysed isomerisation of primary allyl silyl ethers can provide a very convenient source of silyl enol ethers that might be less accessible from the appropriate aldehydes by O-silylation of their enolates. Thus, the terpenoid (1R)-(−)-myrtenol, a primary allylic alcohol that is readily available from the chiral pool, can be silylated under standard conditions to give the silyl ethers 14 and 15. Isomerisation of both compounds took place readily in refluxing benzene (or in the neat state for ease of product isolation), to give the silyl enol ethers as predominately the E-isomers, presumably because of steric destabilisation of the Z-isomers (Table 4.14).
CHAPTER FOUR

4.4 EXPERIMENTAL

4.4.1 General procedures

General procedures used in this work are described in Section 2.4.1.

The photochemical experiments were carried out using a quartz flask held in a water bath (quartz container) maintained at a constant temperature (25 °C) using ice with a water-cooled 160W medium-pressure mercury discharge lamp (quartz envelope) positioned 3 cm away from the reaction vessel.

4.4.2 Materials

Dry solvents (benzene/cyclohexane/octane/toluene) and all other commercial materials were generally obtained from Aldrich or Fluka and were used as received. Allyl phenyl ether 25 (b.p. 192 °C) and acrolein diethyl acetal 26 (b.p. 125 °C) were distilled under nitrogen before use.

4.4.3 Preparation allyl silyl ethers and allyl alkyl ethers

4.4.3.1 tert-Butyl-(2-methylallyloxy)diphenylsilane 5

\[
\text{OH} + \text{Bu}^\prime \text{Ph}_2\text{SiCl} \underset{\text{imidazole}}{\text{imidazole}} \text{CH}_2\text{Cl}_2 \rightarrow \text{OSiPh}_2\text{Bu}^\prime
\]

A stirred solution of 2-methylprop-2-en-1-ol (5.02 g, 69.6 mmol), tert-butylchlorodiphenylsilane (15.0 cm³, 15.88 g, 57.8 mmol) and imidazole (5.90 g, 86.7 mol) in dry dichloromethane (50 cm³) was heated under reflux under nitrogen for 5 h. The cooled reaction mixture was filtered through a short column of silica gel eluting with hexane to remove the imidazole salt and unreacted imidazole. The solvent was then removed using a rotary evaporator and residual oil distilled under reduced pressure to give tert-butyl-(2-methylallyloxy)diphenylsilane 5 as a colourless oil (14.8 g, 82%).

B.p. 115 °C at 0.1 Torr.

\[\delta_H:\ 1.05\ (9H,\ s,\ Bu') ,\ 1.54\ (3H,\ s,\ Me),\ 4.06\ (2H,\ s,\ CH_2O),\ 4.84\ (1H,\ s,\ CH^\beta\ vinyl),\ 5.12\ (1H,\ s,\ CH^\beta\ vinyl),\ 7.35-7.41\ (6H,\ m,\ Ph),\ 7.66-7.69\ (4H,\ m,\ Ph).\]

\[\delta_C:\ 19.0,\ 19.3,\ 26.8,\ 67.3,\ 109.2,\ 127.6,\ 129.6,\ 133.8,\ 135.5\ and\ 144.2.\]
MS (El) m/z: 310 (M⁺, 3.5), 253 (M⁺ -Bu', 100), 199 (33), 183 (17), 175 (56), 28 (23).

4.4.3.2 Allyloxy-tert-butyldiphenylsilane 10

A stirred solution of allyl alcohol (3.03 g, 52.2 mmol), tert-butylchlorodiphenylsilane (11.2 cm³, 11.83 g, 43.0 mmol) and imidazole (3.80 g, 56 mol) in dry dichloromethane (40 cm³) was heated under reflux under nitrogen for 5 hours. The work-up described previously for 5 was used. The product 10 was obtained as a colourless oil (10.5 g, 82%).

B.p. 103-104 °C at 0.07 Torr.

δH: 1.05 (9H, s, Bu'), 4.20 (2H, d, J 8.0, CH₂O), 5.12 (1H, dd[t], J 10.7, 1.9 and 1.8 CH₃vinyl), 5.38 (1H, dd[t], J 17.1, 2.0 and 2.0, CH₃vinyl), 5.91 (1H, dd[t], J 17.1, 10.5 and 4.3, CH₃vinylCH₂), 7.35-7.41 (6H, m, Ph), 7.66-7.69 (4H, m, Ph)

δC: 19.3, 26.8, 64.6, 113.9, 127.6, 129.6, 133.7, 135.5 and 137.0.

MS (FAB) m/z: 296 (M⁺, 4), 257 (20), 239 (100), 197 (35), 183 (40), 161 (95), 135 (78), 115 (40), 99 (37).

4.4.3.3 tert-Butyl(3-methylbut-2-enyloxy)diphenylsilane 12

A stirred solution of 3-methylbut-2-en-1-ol (5.04 g, 58.5 mmol), tert-butylchlorodiphenylsilane (12.6 cm³, 13.30 g, 48.4 mmol) and imidazole (4.94 g, 72.6 mol) in dry dichloromethane (50 cm³) was heated under reflux under nitrogen for 5 hours. The work-up described previously for 5 was used. The product 12 was obtained as a colourless oil (13.5 g, 86%).

B.p. 75 °C at 0.02 Torr.
\[ \delta_H: 1.03 (9H, s, Bu'), 1.44 (3H, s, Me), 1.83 (3H, s, Me), 4.18 (2H, d, J 6.4, CH\_2-O), 5.36 (1H, t[sept], J 6.4 and 1.4, CH\_\text{vinyl}-CH\_2), 7.34-7.42 (6H, m, Ph), 7.67-7.70 (4H, m, Ph). \]
\[ \delta_C: 17.9, 19.2, 25.7, 26.9, 61.1, 123.2, 127.6, 129.5, 133.8, 134.2 \text{ and } 135.6 \]
\[ \text{MS (FAB) } m/z: 323 (M^+ - 1, 5), 267 (16), 199 (100), 135 (29), 75 (40). \]

4.4.3.4 1-tert-Butyldimethyl(3-phenylallyloxy)silane 13

![Chemical structure of 1-tert-Butyldimethyl(3-phenylallyloxy)silane 13](image)

A stirred solution of cinnamyl alcohol (5.00 g, 37.3 mmol), tert-butylchlorodimethylsilane (6.18 g, 41.0 mmol) and imidazole (4.19 g, 61.5 mol) in dry dichloromethane (50 cm\(^3\)) was heated under reflux under nitrogen for 5 hours. The work-up described previously for 5 was used. The product 13 was obtained as a colourless oil (7.1 g, 77%).

B.p. 84-86 °C at 0.04 Torr (lit.\(^{26}\) b.p. 90-92 °C at 0.3 Torr).

\[ \delta_H: 0.10 (6H, s, 2Me), 0.90 (9H, s, Bu'), 4.33 (2H, d, J 5.1, CH\_2-O), 6.27 (1H, d[t], J 15.8 \text{ and } 5.0, CH\_\text{vinyl}-CH\_2), 6.57 (1H, d, J 15.8, CH\_\text{vinyl}-Ph), 7.22 (1H, t, J 7.26, Ph\_\text{para}), 7.29 (2H, t, J 7.27, Ph\_\text{meta}), 7.37 (2H, d, J 7.2, Ph\_\text{ortho}). \]

\[ \delta_C: -5.1, 18.5, 26.0, 63.9, 126.4, 127.3, 128.5, 129.2, 129.5 \text{ and } 137.2. \]

\[ \text{MS (EI) } m/z: 249 (M^+ + 1, 1), 248 (6), 191 (89), 117 (100), 105 (30), 77 (36), 75 (76). \]

4.4.3.5 [(1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylmethoxy]trimethylsilane 14

![Chemical structure of [(1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylmethoxy]trimethylsilane 14](image)

A stirred solution of (1R)-(+-)-myrtenol (10.5 cm\(^3\), 10.00 g, 65.7 mmol), chlorotrimethylsilane (8.56 g, 78.8 mmol) and imidazole (5.81 g, 85.3 mmol) in dry dichloromethane (25 cm\(^3\)) was heated under reflux under nitrogen for 5 hours. The
work-up procedure described previously for 5 was used and the product 14 was obtained as a colourless oil (11.96 g, 81%).

B.p. 54 °C at 0.75 Torr.

$[\alpha]_D^{20} = -35.19$ (c 2.16, CHCl$_3$).

$\delta_H$: 0.1 (9H, s, 3Me), 0.69 (3H, s, Me$^A$), 1.18 (3H, s, Me$^B$), 1.18 (1H, d, $J$ 8.5, CHCH$^A$CH), 1.98 (1H, t[d], $J$ 5.7 and 1.2, CCHCMe$_2$), 2.03-2.10 (1H, m, CH$_2$CH/CH$_2$), 2.20, 2.28 (2H, ABq, $J$$_{AB}$ 17.6, CH$_2$CH$_{vinyl}$), $^*2.35$ (1H, d[t], $J$ 8.5 and 5.6, CHCH$^B$CH), 3.92, 3.96 (2H, ABq, $J$ 13.9, CH$_2$O), $^#5.40$-5.42 (1H, m, CH$_{vinyl}$).

$\delta_C$: -0.5, 20.9, 26.1, 31.0, 31.4, 37.9, 41.0, 43.0, 65.1, 116.1 and 147.1.

MS (El) m/z: 224 (M$^{++}$ 1), 135 (49), 119 (30), 107 (37), 92 (33), 91 (94), 79 (80), 75 (37), 73 (89), 43 (39), 41 (43).

Found: C, 69.5; H, 11.0. C$_{13}$H$_{24}$OSi requires C, 69.6; H, 10.8%.

4.4.3.6 [(1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-ylmethoxy]-tert-butylidiphenyl-silane 15

![Diagram]

A stirred solution of (1R)-(−)-myrtenol (7.00 g, 46.0 mmol), tert-butylchlorodiphenylsilane (10.0 cm$^3$, 10.53 g, 38.3 mmol) and imidazole (3.39 g, 49.8 mmol) in dry dichloromethane (25 cm$^3$) was heated under reflux under nitrogen for 5 hours. The cooled reaction mixture was than passed through a column of silica gel eluting with hexane to remove impurities and the solvent removed using a rotary evaporator to obtain 15 as a colourless oil (12.89 g, 86%).

$[\alpha]_D^{20} = -19.20$ (c 0.88, CHCl$_3$).

$\delta_H$: 0.70 (3H, s, Me$^A$), 1.05 (9H, s, Bu$^i$), 1.18 (3H, s, Me$^B$), 1.19 (1H, d, $J$ 8.5, CHCH$^A$CH), 1.97 (1H, t[d], $J$ 5.8 and 1.3, CCHCMe$_2$), 2.08-2.13 (1H, m, CH$_2$CH/CH$_2$), 2.56, 3.34 (2H, ABq, $J$$_{AB}$ 17.5, CH$_2$CH$_{vinyl}$), $^*2.35$ (1H d[t], $J$ 8.6 and 5.6,

$^*$ A further small (2.5-2.6 Hz) apparent quintet splitting was evident on each of the four lines.

$^#$ A further small (2.0-2.2 Hz) apparent quartet splitting was evident on each of the four lines.
CHCH\(^6\)CH), 4.01, 4.06 (2H, ABq, \(J_{AB} 14.0, CH_2O\)), \(^* 5.52-5.58\) (1H, m, CH\(_{vinyl}\)), 7.34-7.43 (6H, m, Ph), 7.67-7.72 (4H, m, Ph).

\(\delta_C\): 19.3, 21.0, 26.2, 26.8, 31.1, 31.4, 38.0, 41.1, 42.9, 66.2, 115.9, 127.6, 129.5, 133.8, 133.9, 135.5 and 147.1.

MS (El) \(m/\ell\): 390 (M\(^+\), 4), 333 (62), 255 (45), 199 (100), 91 (81).

Found: C, 80.0; H, 8.9. \(C_{26}H_{34}O\) requires C, 79.9; H, 8.8%.

### 4.3.3.7 \((1R)-2,(EthoxymethyI)-6,6-dimethylbicyclo[3.1.1]hept-2-ene 33\(^28\)

![Diagram](image)

To a suspension of NaH (10.52 g, 60% in mineral oil, 262.7 mmol) in dry \(N,N\)-Dimethylformamide (DMF, 250 cm\(^3\)) was added dropwise a solution of \(1R\)-(-)-myrtenol (26.2 cm\(^3\), 25.00 g, 164 mmol) in DMF (50 cm\(^3\)). When the evolution of \(H_2\) had ceased, ethyl bromide (19.6 cm\(^3\), 28.63 g, 263 mmol) was added dropwise at room temperature and the mixture stirred overnight at room temperature. The mixture was then transferred to a separating funnel, quenched with water (50 cm\(^3\)) and extracted with ether (2 x 80 cm\(^3\)). The organic layer was then washed successively with 10% aq. HCl solution, water and satd. brine and dried over MgSO\(_4\). The solvent was removed by rotary evaporator and the residual oil was then distilled under reduced pressure to give \((1R)-2,(ethoxymethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene 33\) (21.8 g, 74%).

B.p. 81 °C at 4.0 Torr (lit. \(^{28}\) 30 °C at 0.018 Torr).

\(\alpha\)\(_{D}\)\(^{20}\) = -28.8 (c 2.40, CHCl\(_3\)).

\(\delta_H\): 1.17 (3H, t, \(J 7.0, CH_2CH_3\)), 0.82 (3H, s, Me), 1.16 (1H, d, \(J 7.0, CHCH^6CH\)), 1.26 (3H, s, Me), 2.05-2.09 (1H, m, \(CH_2CHCH_2\)), 2.13 (1H, d[t], \(J 5.8 \text{ and } 1.2, CCHCM_2\)), 2.21, 2.29 (2H, ABq, \(J 16.0, CH_2CH_{vinyl}\)), \(^{\dagger} 2.37\) (1H, d[t], \(J 9.6 \text{ and } 5.6, CHCH^6CH\)), 3.42 (2H, q, \(J 7.0, CH_2CH_3\)), 3.79, 3.82 (2H, ABq, \(J 12.6, CH_2O\)), \(^{\ddagger} 5.44-5.47\) (1H, m, \(CH_{vinyl}\)).

\(\delta_C\): 15.0, 20.9, 26.1, 31.1, 31.4, 37.9, 40.7, 43.2, 65.0, 73.3, 119.2 and 145.5.

\(^*\) A further small (2.1 Hz) apparent quartet splitting was evident on each of the four lines.

\(^{\dagger}\) Additional multiplicity was observed on each of the four lines.

\(^{\ddagger}\) A further small (1.5-1.7 Hz) apparent quartet splitting was evident on each of the four lines.
CHAPTER FOUR

MS (EI) m/z: 180 (M⁺, 15), 133 (23), 91 (27), 79 (27), 59 (17), 41 (22).

4.4.3.8 tert-Butyl(1-methylallyloxy)diphenylsilane 17

A stirred solution of 3-buten-2-ol (5.01 g, 69.5 mmol), tert-butylchlorodiphenylsilane (15.0 cm³, 15.88 g, 57.8 mmol) and imidazole (5.90 g, 86.7 mmol) in dry dichloromethane (50 cm³) was heated under reflux under nitrogen for 5 h. The work-up described previously for 5 was used and the product 17 was obtained as a colourless oil (15.1 g, 84%).

B.p. 119-120 °C at 0.1 Torr.

δH: 1.05 (9H, s, Bu'), 1.11 (3H, d, J 6.3, Me), 4.28 (1H, q[d], J 12.6 and 6.3, CHO), 4.93 (1H, d, J 4.93, CHA_vinylic), 5.07 (1H, d, J 17.2, CHB_vinylic), 5.81 (1H, ddd, J 17.1, 10.4 and 5.4, CH_vinylicMe), 7.32-7.38 (6H, m, Ph), 7.64-7.67 (4H, m, Ph).

δC: 19.3, 24.0, 27.0, 70.4, 112.7, 127.5, 129.5, 134.3, 134.6, 135.9 and 142.5.

MS (FAB) m/z: 310 (M⁺, 2), 309 (6), 253 (90), 199 (100), 175 (40), 135 (68), 75 (40), 55 (29).

4.4.3.9 tert-Butyl(1-methylallyloxy)dimethylsilane 19

A stirred solution of 3-buten-2-ol (5.04 g, 69.9 mmol), tert-butylchlorodimethylsilane (8.71 g, 57.8 mmol) and imidazole (5.90 g, 86.7 mol) in dry dichloromethane (50 cm³) was heated under reflux under nitrogen for 5 hours. The work-up described previously for 5 was used. The product 19 was obtained as a colourless oil (15.1 g, 84%).

B.p. 55-56 °C at 20 Torr (lit.31 b.p. 56 °C at 20 Torr).
\[ \delta_H: 0.02 (6H, s, 2Me), 0.83 (9H, s, Bu'), 1.15 (3H, d, J 6.3, Me), 4.22-4.3 (1H, m, CHO), 4.91 (1H, d, J 6.3, \text{CH}^a_{\text{vinyl}}), 5.13 (1H, d, J 17.1, \text{CH}^b_{\text{vinyl}}), 5.83 (1H, ddd, J 17.0, 10.4 and 5.2, \text{CH}_{\text{vinyl}}\text{CH}) \]

\[ \delta_C: -4.9, 18.3, 24.2, 25.9, 69.5, 112.4 \text{ and } 142.8. \]

MS (EI) \( m/z \): 186 (M\(^+\), 7), 147 (33), 129 (100), 75 (46), 28 (20).

4.4.3.10 \textit{tert}-Butyldimethyl(1-phenylallyloxy)silane 21\(^{32} \)

A stirred solution of \( \alpha \)-vinylbenzyl alcohol (5.01 g, 37.3 mmol), \textit{tert}-butylchlorodimethylsilane (5.8 cm\(^3\), 6.18 g, 41.0 mmol) and imidazole (4.19 g, 61.5 mmol) in dry dichloromethane (50 cm\(^3\)) was heated under reflux under nitrogen for 5 h. The work-up described previously for 5 was used. The product 20 was obtained as a colourless oil (6.4 g, 69\%).

B.p. 76-78°C at 0.02 Torr.

\[ \delta_H: 0.05 (6H, s, 2Me), 0.91 (9H, s, Bu'), 5.04 (1H, d, J 10.21, \text{CHPh}), 5.14 (1H, d, J 5.8, \text{CH}^a_{\text{vinyl}}), 5.24 (1H, d, J 17.01, \text{CH}^b_{\text{vinyl}}), 5.90 (1H, ddd, J 16.9 and 10.2 and 5.8, \text{CH}_{\text{vinyl}}\text{CH}), 7.18-7.25 (2H, m, Ph), 7.27-7.32 (3H, m, Ph) \]

\[ \delta_C: -4.1, -3.9, 18.3, 25.9, 75.9, 113.3, 126.0, 127.0, 128.2, 141.8 \text{ and } 143.8 \]

MS (EI) \( m/z \): 248 (M\(^+\), 2), 191 (8), 117 (100), 75 (23).

4.4.3.11 \textit{Preparation of 4-methylpent-1-en-3-ol}\(^{33} \)

To a stirred solution of vinylmagnesium chloride (1.6 M in THF, Aldrich) (99.4 cm\(^3\), 13.80 g, 159 mmol) in diethyl ether (100 cm\(^3\)), isobutyraldehyde (17.3 cm\(^3\), 13.8 g, 192 mmol) was added dropwise over 30 minutes at 0°C (ice/water bath) under nitrogen. After the addition the solution was stirred at 0°C for 1 h at room temperature.
The solution was then treated with aqueous ammonium chloride (30 g in 100 cm³), poured into a separating funnel and extracted with ether (3 x 50 cm³). The combined organic layers were washed with satd. brine (3 x 50 cm³) and then dried over MgSO₄. Diethyl ether was removed by distillation at atmospheric pressure because of the low boiling point of the product and the residual oil was distilled to afford the colourless product (10.5 g, 66%).


δH: 0.89 (1H, d, J 6.8, Me), 0.91 (1H, d, J 6.7, Me), 1.71 (1H, sept, J 6.3, CHMe₂), 3.39 (1H, d, J 6.5, OH), 3.84 (1H, t, J 6.2, CHOH), 5.13 (1H, ddd, J 10.5, 1.5 and 1.5, CH⁺ vinyl), 5.21 (1H, ddd, J 17.2, 1.4 and 1.4, CH⁻ vinyl), 5.84 (1H, ddd, J 17.2, 10.5 and 6.5, CH⁻ vinylCH).

δC: 17.7, 18.1, 33.5, 78.2, 115.5 and 139.4.

MS (El) m/z: 99 (M⁺-1, 4), 83 (100), 71 (50), 53 (80).

4.4.3.12 (1-Isopropylallyloxy)trimethylsilane 21^{10}

A stirred solution of 4-methyl-pent-1-en-3-ol (6.03 g, 60.2 mmol), chlorotrimethylsilane (7.81 g, 71.9 mmol) and imidazole (5.3 g, 77.9 mmol) in dry dichloromethane (50 cm³) was heated under reflux under nitrogen for 5 hours. The work-up described previously for 5 was used. The product 21 was obtained as a colourless oil (7.6 g, 74%).

B.p. 64 °C at 51 Torr.

δH: 0.08 (9H, s, 3Me), 0.83 (3H, d, J 6.8, Me³), 0.87 (3H, d, J 6.4, Me⁸), 1.57-1.65 (1H, m, CHCHO), 3.72-3.74 (1H, m, CHO), 5.04 (1H, d, J 10.4, CH⁺ vinyl), 5.10 (1H, d, J 17.2, CH⁻ vinyl), 5.75 (1H, ddd, J 17.2, 10.4 and 6.4, CH⁻ vinylCH).

δC: 0.3, 18.1, 18.4, 34.2, 79.1, 114.7 and 140.1.

MS (El) m/z: 169 (M⁺-3, 2), 135 (38), 129 (41), 105 (78), 91 (28), 77 (69), 73 (100), 61 (36), 55 (47), 49 (25).

Found: C, 77.9; H, 9.2. C₁₄H₂₁O₃Si requires C, 78.1; H, 8.9%.
4.4.4 Preparation of silyl enol ethers

These isomerisation reactions followed the same basic procedure and were carried out on a 1 mmol scale (unless otherwise stated) of allyl silyl ether. The thiol, initiator and solvent were varied as shown in Results and Discussion (Section 4.2). The typical procedure using pentafluorothiophenol and DBPB in refluxing octane is described below for 6.

4.4.4.1 tert-Butyl(2-methylpropenyloxy)diphenylsilane 6

A solution of tert-butyl(2-methylallyloxy)diphenylsilane 5 (1.0 mmol), pentafluorothiophenol (13.3 µL, 0.1 mmol) and 2,2-di-tert-butylperoxy butane (DBPB; 54 µL of a 50% w/w solution in mineral oil, 0.1 mmol) in dry octane (1.5 cm$^3$) was stirred and heated under reflux under nitrogen for 2.5 hours. The solvent was removed under reduced pressure and tert-butyl(2-methylpropenyloxy)diphenylsilane 6 (0.27 g, 87%) was isolated by chromatography on silica gel (petroleum, b.p. 40-60 °C, eluent) as a colourless oil that solidified on standing (m.p. ca. 30 °C).

$\delta^H$ 1.09 (9H, s, Bu'), 1.35 (3H, s, Me$^A$), 1.66 (3H, s, Me$^B$), 6.07 (1H, m, CH$\text{ vinyl}$), 7.24-43 (6H, m, Ph), 7.86 (4H, d, $J = 6.6$, Ph)

$\delta^C$: 15.0, 19.2, 26.6, 29.7, 113.0, 127.7, 129.7, 133.3, 133.7 and 135.4.

MS (EI) $m/z$: 310 (M$^+$, 16), 254 (21), 253 (100), 199 (27), 183 (78), 175 (16).

Found: C, 77.3; H, 8.2. C$_{20}$H$_{26}$OSi requires C, 77.4; H, 8.4%.

4.4.4.2 (E)/(Z)-(1-tert-Butyldimethylsiloxy)propene$^{10}$

The silyl enol ethers were prepared using the procedure for 6 on a 25 mmol scale and reduced pressure distillation of the reaction solution gave silyl enol ethers as a colourless oil (2.9 g, 67.4%).
B.p. 48 °C at 20 Torr.

**(E)-isomer**

δ\textsubscript{H}: 0.10 (6H, s, 2Me), 0.88 (9H, s, Bu'), 1.49 (3H, dd, \(J = 6.7\) and \(J = 1.6\), \(CH\textsubscript{3}CH\)), 4.95 (1H, d[q], \(J = 11.9\) and \(J = 6.8\), \(CH\textsubscript{vinyl}CH\textsubscript{3}\)), 6.21 (1H, d[q], \(J = 11.8\) and \(J = 1.6\), \(CH\textsubscript{vinyl}O\)).

δ\textsubscript{C}: -3.6, 12.1, 18.3, 26.7, 105.7 and 140.5.

**(Z)-isomer**

δ\textsubscript{H}: 0.11 (6H, s, 2Me), 0.91 (9H, s, Bu'), 1.5 (3H, dd, \(J = 6.7\) and \(J = 1.7\), \(CH\textsubscript{3}CH\)), 4.49 (1H, d[q], \(J = 6.7\) and \(J = 5.9\), \(CH\textsubscript{vinyl}CH\textsubscript{3}\)), 6.17 (1H, d[q], \(J = 5.8\) and \(J = 1.8\), \(CH\textsubscript{vinyl}O\)).

δ\textsubscript{C}: -5.3, 8.9, 18.3, 26.1, 104.8 and 139.2.

**MS (FAB) m/z:** 172 (M\textsuperscript{+}, 4), 131 (15), 115 (15), 75 (30), 73 (100).

Found: C, 62.8; H, 11.8. C\textsubscript{9}H\textsubscript{12}O\textsubscript{2}Si requires C, 62.7; H, 11.7%.

### 4.4.4.3 

**(E)/(Z)-(tert-Butyldiphenylsiloxy)propene 11E and 11Z**

![Reaction Scheme](image)

The silyl enol ethers were prepared using the procedure for 6 on a 20 mmol scale and reduced pressure distillation of the reaction solution gave silyl enol ethers as a colourless oil (5.0 g, 85%).

B.p. 98 °C at 0.02 Torr.

**(E)-isomer**

δ\textsubscript{H}: 1.05 (9H, s, Bu'), 1.43 (3H, dd, \(J = 6.8\), \(J = 1.7\), \(CH\textsubscript{3}CH\)), 5.09 (1H, d[q], \(J = 11.9\), \(J = 6.8\), \(CH\textsubscript{vinyl}CH\textsubscript{3}\)), 6.22 (1H, d[q], \(J = 11.9\), \(J = 1.6\), \(CH\textsubscript{vinyl}O\)), 7.35-7.42 (6H, m, Ph), 7.66-7.69 (4H, m, Ph).

δ\textsubscript{C}: 12.1, 19.2, 26.6, 106.0, 127.7, 129.8, 133.1, 135.4 and 140.6.

**(Z)-isomer**

δ\textsubscript{H}: 1.07 (9H, s, Bu'), 1.72 (3H, dd, \(J = 6.7\), \(J = 1.8\), \(CH\textsubscript{3}CH\)), 4.50 (1H, d[q], \(J = 6.7\), \(J = 5.9\), \(CH\textsubscript{vinyl}CH\textsubscript{3}\)), 6.18 (1H, d[q], \(J = 5.8\), \(J = 1.8\), \(CH\textsubscript{vinyl}O\)), 7.36-7.40 (6H, m, Ph), 7.65-7.67 (4H, m, Ph).

δ\textsubscript{C}: 9.2, 19.3, 26.6, 104.7, 127.7, 129.8, 133.0, 135.4 and 139.4.

**MS (EI) m/z:** 296 (M\textsuperscript{+}+1, 4), 239 (100), 183 (45), 117 (8), 105 (7).

Found: C, 77.1; H, 8.2. C\textsubscript{10}H\textsubscript{25}O\textsubscript{2}Si requires C, 77.2; H, 7.9%.
4.4.4.4 (E)/(Z)-1-Trimethylsiloxypropene

\[
\begin{align*}
\text{O} & \text{SiMe}_3 \\
\text{DBPB, PFTP} & \\
\text{Octane reflux} & \\
\end{align*}
\]

The silyl enol ethers were prepared using the procedure for 6 using neat allyloxytrimethylsilane (15 mmol) and reduced pressure distillation of the reaction solution gave silyl enol ethers as a colourless oil (1.62 g, 82%).

B.p. 24-25 °C at 37 Torr (lit. 34 100-101 °C at atmospheric pressure).

(E)-isomer

\[\delta_\text{H}: 0.04 (9\text{H, s, 3Me}), 1.49 (1\text{H, dd, } J=6.8, J=1.6, \text{CH}_2\text{CH}), 4.96 (1\text{H, d[q], } J=12.0, J=6.8, \text{CH}_\text{vinyiCH}_3), 6.19 (1\text{H, d[q], } J=12.0, J=1.7, \text{CH}_\text{vinyiO}).\]

\[\delta_\text{C}: -1.0, 12.1, 106.1 \text{ and } 139.9.\]

(Z)-isomer

\[\delta_\text{H}: 0.16 (9\text{H, s, 3Me}), 1.55 (1\text{H, dd, } J=6.7, J=1.8, \text{CH}_2\text{CH}), 4.52 (1\text{H, d[q], } J=6.7, J=6.6, \text{CH}_\text{vinyiCH}_3), 6.14 (1\text{H, d[q], } 5.9, J=1.7, \text{CH}_\text{vinyiO}).\]

\[\delta_\text{C}: -0.6, 8.9, 105.6 \text{ and } 138.5.\]

MS (El) \text{m/z}: 130 (M^{+}, 6), 103 (44), 75 (100), 57 (26).

4.4.4.5 (E)/(Z)-1-tert-Butyl-3-methyldiphenylsiloxy-1-butene

\[
\begin{align*}
\text{O} & \text{SiPh}_2\text{Bu}^t \\
\text{DBPB, PFTP} & \\
\text{Octane reflux} & \\
\end{align*}
\]

The silyl enol ethers were prepared using the procedure for 6 and the silyl enol ethers were obtained as a colourless oil (0.26 g, 80%).

(E)-isomer

\[\delta_\text{H}: 0.87 (6\text{H, d, } J=6.7, 2\text{Me}), 0.98 (9\text{H, s, Bu}^t), 2.09-2.15 (1\text{H, m, CHMe}_2), 4.31 (1\text{H, dd, } J=12.0 \text{ and } 8.0, \text{CH}_\text{vinyiCH}), 6.26 (1\text{H, dd, } J=12.0 \text{ and } 1.0, \text{CH}_\text{vinyiO}), 7.34-7.41 (6\text{H, m, Ph}), 7.64-7.68 (4\text{H, d, } J=6.6, \text{Ph}).\]

\[\delta_\text{C}: 19.2, 23.8, 26.6, 27.1, 27.6, 119.8, 127.7, 129.6, 133.1, 135.6 \text{ and } 138.7.\]

NOE: Irradiation at the vinylic proton (CH\text{vinyiO}, 6.26 ppm) showed a strong correlation with CHMe\text{z} (2.09-2.15 ppm).
(Z)-isomer

\[ \delta_H: 1.03 \ (6H, d, J 6.8, 2Me), 1.05 \ (9H, s, Bu'), 2.95-3.04 \ (1H, m, CHMe_2), 4.31 \ (1H, dd, J 8.8 and 5.8, CH_{\text{vinyl}}CH), 6.10 \ (1H, dd, J 5.8 and 1.1, CH_{\text{vinylO}}), 7.24-7.42 \ (6H, m, Ph), 7.65-7.67 \ (4H, d, J 6.6, Ph). \]

\[ \delta_C: 19.0, 23.2, 23.5, 26.6, 27.07, 118.2, 127.7, 129.8, 135.2, 135.7 \text{ and } 137.1. \]

NOE: Irradiation at the vinylic proton (CH_{\text{vinylO}}, 6.10 ppm) showed a strong correlation with CH_{\text{vinyl}}CH (4.31 ppm). No correlation with CHMe_2 (2.95-3.04 ppm) was observed.

MS (El) \( m/z: 324 \ (M^+, 3), 199 \ (100), 139 \ (42), 75 \ (37). \)

Found: C, 77.6; H, 8.5. \( C_{21}H_{28}OSi \) requires C, 77.7; H, 8.7%.

4.4.4.6 \( (E)/(Z)[(1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-ylidene-methoxy]trimethylsilane \ 16E/16Z \)

The silyl enol ethers were prepared using the procedure for 6 using neat allyl \(^{1}A\)-silyl ether (8.9 mmol) and reduced pressure distillation of the reaction solution gave silyl enol ethers as a colourless oil (1.57 g, 78%).

B.p. 62 °C at 0.15 Torr.

\((E)\)-isomer

\[ \delta_H: 0.14 \ (9H, s, 3Me), 0.69 \ (3H, s, Me^A), 1.18 \ (3H, s, Me^B), 1.31 \ (1H, d, J 9.6, CHCH^A\text{CH}), 1.79-1.84 \ (2H, m, CHCH_2CH_2), 1.89-1.94 \ (1H, m, CH_2CHCH_2), 2.22 \ (1H, t, J 5.6, CCHCM^2), 2.27 \ (1H, ddd, J 17.6, 9.1 \text{ and } 3.0, CCH^A\text{CH}_2), 2.31 \ (1H, d[t], J 9.6 \text{ and } 6.1, CCH^B\text{CH}), 2.40 \ (1H, d[t]d, J 18.1, 6.9 \text{ and } 1.9, CCH^B\text{CH}_2), 5.85-5.87 \ (1H, m, CH_{\text{vinyl}}). \]

\[ \delta_C: -0.5, 17.0, 22.0, 23.5, 26.0, 28.3, 40.9, 41.0, 46.6, 125.6 \text{ and } 130.4. \]

NOE: Irradiation at the vinylic proton (5.85-5.87 ppm) showed a strong correlation with CCHCM^2 (2.22 ppm).

\((Z)\)-isomer*

* The Z-isomer could not be satisfactory separated and some chemical shifts are approximate due to the dominance of the spectrum from the E-isomer.

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\[ \delta_H: 0.11 (9H, s, 3Me), 0.72 (3H, s, Me^A), 1.24 (3H, s, Me^B), 1.41 (1H, d, J 9.8, \text{CHCH}^A\text{CH}), \sim 1.73 - 1.78 (2H, m, \text{CHCH}_2\text{CH}_2), \sim 1.85 - 1.88 (1H, m, \text{CH}_2\text{CHCH}_2), 1.99 - 2.24 (1H, dd[t], J 16.2, 8.8, 1.2, \text{CHCH}^B\text{CH}), 2.28 - 2.45 (1H, m, \text{CHCH}^B\text{CH}), 2.25 - 2.30 (1H, m, \text{CHCH}^B\text{CH}), 2.94 (1H, t, J 5.6, \text{CHCH}_2\text{Me}_2), 6.05 - 6.07 (1H, m, \text{CH}_viny). \]
\[ \delta_C: -0.48, 19.1, 21.6, 23.8, 26.0, 26.1, 40.9, 41.1, 42.4, 124.0 \text{ and } 130.8. \]

MS (El) m/z: 224 (M\(^+\), 4), 181 (11), 155 (53), 73 (100), 41 (12).

Found: C, 70.0; H, 10.8. \( \text{C}_{13}\text{H}_{25}\text{OSi} \) requires C, 69.6; H, 10.8%

NOE: Irradiation at the vinylic proton (6.05 - 6.07 ppm) showed a strong correlation with \( \text{CHCH}^A\text{CH} \) (1.99) and \( \text{CHCH}^B\text{CH} \) (2.28 - 2.45).

### 4.4.4.7. \((E)/(Z)\)-tert-Butyl-\(((1R,5S)\)-6,6-dimethyl-bicyclo[3.1.1]hept-2-ylidenemethoxy)\(\text{diphenylsilane}\)

The silyl enol ethers were prepared using the procedure for 6 and the silyl enol ethers were obtained as a colourless oil (0.316 g, 81%).

---

\[ \delta_H: 0.70 (3H, s, Me^A), 0.84 (9H, s, Bu^t), 1.14 (3H, s, Me^B), 1.32 (1H, d, J 9.6, \text{CHCH}^A\text{CH}), 1.85 - 1.90 (2H, m, \text{CHCH}_2\text{CH}_2), 1.91 - 1.98 (1H, m, \text{CH}_2\text{CHCH}_2), 2.14 (1H, t, J 5.5, \text{CHCH}_2\text{Me}_2), 2.24 (1H, dd[t], J 9.6 \text{ and } 5.8, \text{CHCH}^B\text{CH}), 2.42 (1H, ddd, J 17.5, 8.2 \text{ and } 2.9, \text{CHCH}^B\text{CH}), 2.61 (1H, d[t]d, J 18.3, 6.0 \text{ and } 1.8, \text{CHCH}^B\text{CH}), 5.93 - 5.94 (1H, m, \text{CH}_viny), 7.35 - 7.40 (6H, m), 7.66 - 7.67 (4H, m).
\]

\[ \delta_C: 17.2, 19.3, 22.1, 23.6, 25.9, 26.6, 28.4, 41.0, 41.1, 46.3, 124.2, 127.7, 129.7, 131.3, 133.4 \text{ and } 135.5. \]

---

\[ \delta_H: 0.77 (3H, s, Me^A), 0.89 (9H, s, Bu^t), 1.29 (3H, s, Me^B), 1.50 (1H, d, J 9.8, \text{CHCH}^A\text{CH}), \sim 1.85 - 1.90 (2H, m, \text{CHCH}_2\text{CH}_2), \sim 1.80 - 1.82 (1H, m, \text{CHCH}^B\text{CH}), \sim 1.88 - 1.92 (1H, m, \text{CH}_2\text{CHCH}_2), 2.37 - 2.42 (1H, m, \text{CHCH}^B\text{CH}), \sim 2.58 - 2.61 (1H, m, \text{CH}_viny). \]

---

* The Z-isomer could not be satisfactorily separated and some chemical shifts are approximate due to the dominance of the spectrum from the \(E\)-isomer.
CCH₃CH₂), 3.19 (1H, t, J 5.6, CCHCM₂), 6.11-6.12 (1H, m, CHvinyl), 7.35-7.36 (6H, m, Ph), 7.65-7.67 (4H, m, Ph).

δc: 19.1, 19.3, 21.8, 23.8, 25.3, 25.8, 26.3, 41.0, 41.3, 42.6, 122.5, 127.6, 131.8, 133.4, 133.5 and 135.5.

MS (El) m/z: 391 (M⁺, 4), 199 (50), 197 (34), 135 (100), 75 (12).

Found: C, 80.1; H, 8.9. C₂₆H₃₄O₂Si requires C, 79.9; H, 8.8%.

### 4.4.4.8 (E)/(Z)-1-Methyl(tert-butyldiphenylsiloxy)prop-1-ene 21 and 22

The silyl enol ethers were prepared using the procedure for 6. The products 18E and 18Z were obtained as a colourless oil (0.23g, 74%).

(E)-isomer

δh: 1.01 (9H, s, Bu'), 1.35 (3H, d, J 6.9, MeC), 1.70 (3H, s, MeCO), 4.51 (1H, q, J 6.9, CHvinyl), 7.17-7.40 (6H, m, Ph), 7.69-7.74 (4H, m, Ph).

δc: 12.0, 19.0, 22.8, 26.5, 102.0, 127.6, 129.7, 134.8, 135.5 and 147.9.

(Z)-isomer

δh: 1.05 (9H, s, Bu'), 1.48 (3H, s, MeC), 1.58 (3H, d, J 6.6, MeCO), 4.39 (1H, q, J 6.6, CHvinyl), 7.17-7.40 (6H, m, Ph), 7.69-7.74 (4H, m, Ph).

δc: 10.7, 17.3, 19.5, 26.6, 102.3, 127.5, 129.6, 133.9, 135.5 and 148.0.

NOE: Irradiation at the vinylic proton (CHvinyl, 4.39 ppm) showed a strong correlation with both sets of methyl protons attached to the double bond (1.48 and 1.58 ppm).

MS (El) m/z: 311 (M⁺, 6), 310 (15), 253 (100), 233 (7), 199 (67), 183 (42), 123 (25).

Found: C, 77.4; H, 8.4. C₂₅H₃₂O₂Si requires C, 77.4; H, 8.4%.

### 4.4.4.9 (E)/(Z)-1-Methyl(tert-butyldimethylsiloxy)prop-1-ene

The silyl enol ethers were prepared using the procedure for 6. The products 18E and 18Z were obtained as a colourless oil (0.23g, 74%).
CHAPTER FOUR

The silyl enol ethers were prepared using the procedure for 6 and the products were obtained as a colourless oil (0.149 g, 80%).

(E)-isomer

\[ \delta_{H}: 0.14 (6H, 2\text{MeBu}'), 0.94 (9H, s, \text{Bu}'), 1.74 (3H, s, \text{Me}), 3.51 (3H, d, J 7.7, CH\text{CH}_2\text{vinyl}), 4.64 (1H, q, J 6.9, CH\text{vinyl}). \]

\[ \delta_{C}: -4.4, 12.1, 17.3, 22.7, 25.7, 101.8 \text{ and } 148.2. \]

(Z)-isomer

\[ \delta_{H}: 0.11 (6H, 2\text{MeBu}'), 0.90 (9H, s, \text{Bu}'), 2.03 (3H, s, \text{Me}), 4.00 (3H, d, J 8.0, CH\text{CH}_2\text{vinyl}), 4.44 (1H, q, J 6.7, CH\text{vinyl}). \]

\[ \delta_{C}: -3.9, 10.7, 18.2, 22.7, 25.8, 102.4 \text{ and } 147.5. \]

MS (El) m/z: 186 (M^+ 4), 145 (9), 73 (100), 57 (17), 43 (14).

Found: C, 64.2; H, 12.2. C_{10}H_{22}OSi requires C, 64.5; H, 11.9%.

4.4.4.10 (E)/(Z)-1-Phenyl(tert-butyldimethylsiloxy)propene

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Bu}' & \quad \text{DBPB, PFP} \quad \text{Octane reflux} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

The same procedure was used as for 5. The products were obtained as a colourless oil (0.27 g, 83%).

(E)-isomer

\[ \delta_{H}: 0.05 (6H, s, 2\text{Me}), 0.87 (9H, s, \text{Bu}'), 1.69 (3H, d, J 7.3, \text{MeCH}), 5.06 (1H, q, J 7.0, CH\text{vinyl}), 7.25-7.33 (3H, m, Ph), 7.39-7.42 (2H, m, Ph). \]

\[ \delta_{C}: -4.8, 10.1, 13.1, 30.3, 104.9, 125.9, 127.5, 128.4, 138.7 \text{ and } 150.0. \]

(Z)-isomer

\[ \delta_{H}: -0.05 (6H, s, 2\text{Me}), 0.97 (9H, s, \text{Bu}'), 1.71 (3H, d, J 6.9, \text{MeCH}), 5.06 (1H, q, J 7.0, CH\text{vinyl}), 7.25-7.33 (3H, m, Ph), 7.39-7.42 (2H, m, Ph). \]

\[ \delta_{C}: -4.0, 11.8, 18.4, 25.9, 105.9, 125.7, 127.3, 127.9, 139.8 \text{ and } 150.2. \]

MS (El) m/z: 248 (M^+ 2), 207 (44), 133 (32), 105 (100), 75 (90).

NOE: Irradiation at the vinylic proton (CH\text{vinyl}, 5.06 ppm) showed a strong correlation with ortho-protons on the phenyl ring (7.45-7.48 ppm) and the methyl protons attached to the double bond (1.71 ppm).
Found: C, 72.3; H, 9.7. C\textsubscript{13}H\textsubscript{24}OSi requires C, 72.5; H, 9.7%.

4.4.4.11 \((E)/(Z)-1\)-Isopropyl(\textit{tert}-butyldimethylsiloxy)prop-1-ene \textit{21}\textsuperscript{35}

The silyl enol ethers were prepared using the procedure for \textit{6}. The products were not isolated. 

\((E)\)-isomer
\[ \delta_{HH} \] = 0.03 (9H, 3Me), 0.90 (3H, d, \textit{J} 6.4, Me\textsubscript{A}), 0.92 (3H, d, \textit{J} 6.7, Me\textsubscript{B}), 1.50 (3H, d, \textit{J} 6.7, CH\textsubscript{3}CH\textsubscript{2}vinyl), 2.70 (1H, sept, \textit{J} 6.8, CHMe\textsubscript{2}), 4.45 (1H, q, \textit{J} 6.8, CH\textsubscript{2}vinyl).

\((Z)\)-isomer
\[ \delta_{HH} \] = 0.09 (9H, 3Me), 0.83 (3H, d, \textit{J} 6.8, Me\textsubscript{A}), 0.87 (3H, d, \textit{J} 6.8, Me\textsubscript{B}), 1.57 (3H, d, \textit{J} 6.9, CH\textsubscript{3}CH\textsubscript{2}vinyl), 2.60 (1H, sept, \textit{J} 6.9, CHMe\textsubscript{2}), 4.51 (1H, q, \textit{J} 6.7, CH\textsubscript{2}vinyl).

4.4.5 Preparation of alkyl vinyl ethers

4.4.5.1 \((E)/(Z)-\textit{tert}-Butoxypropene \textit{24E} and \textit{24Z}\textit{36}

The alkyl vinyl ethers were prepared using the procedure for \textit{6} and were not isolated. 

\((E)\)-isomer
\[ \delta_{HH} \] = 0.85-0.90 (3H, t, \textit{J} 7.3, CH\textsubscript{2}CH\textsubscript{3}), 1.32-1.40 (2H, m, CH\textsubscript{2}CH\textsubscript{3}), 1.50-1.62 (2H, m, OCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 1.49 (3H, dd, \textit{J} 6.8 and 1.6, CH\textsubscript{2}CH\textsubscript{2}vinyl), 3.60 (2H, t, \textit{J} 6.5, OCH\textsubscript{2}CH\textsubscript{2}), 4.74 (1H, d[q], \textit{J} 12.8 and 6.6, CH\textsubscript{2}vinylCH\textsubscript{3}), 6.20 (1H, d[q], \textit{J} 12.5 and 1.6, CH\textsubscript{2}vinylO).
(Z)-isomer
\[ \delta_\text{H}: 0.85-0.90 \text{ (3H, t, J 7.3, CH}_2\text{CH}_3\text{)}, 1.32-1.40 \text{ (2H, m, CH}_2\text{CH}_3\text{), 1.50-1.62} \text{ (2H, m, OCH}_2\text{CH}_2\text{CH}_3\text{)}, 1.55 \text{ (3H, dd, J 6.7, J 1.8, CH}_3\text{CH}_\text{vinyl}\text{)}, 3.70 \text{ (2H, t, J 6.7, OCH}_2\text{CH}_2\text{)}, 4.35 \text{ (1H, d[q], J 6.7, J 6.6, CH}_\text{vinyl}\text{CH}_3\text{)}, 5.92 \text{ (1H, d[q], J 6.2, J 1.6, CH}_\text{vinyl}\text{O)}.\]

4.4.5.2 (E)/(Z)-1-Phenoxypropene

\[ \xrightarrow{DBPB, PFTP \text{ Octane reflux}} \]

The alkyl vinyl ethers were prepared using the procedure for 6. The products were not isolated.

(E)-isomer
\[ \delta_\text{H}: 1.65 \text{ (3H, dd, J 7.0 and J 1.7, CH}_3\text{CH}_\text{vinyl}\text{)}, 5.36 \text{ (1H, dq, J 12.0 and 6.8, CH}_\text{vinyl}\text{CH}_3\text{)}, 6.40 \text{ (1H, d[q], J 12.0 and 1.7, CH}_\text{vinyl}\text{O)}, 6.90-7.03 \text{ (3H, m, Ph)}, 7.21-7.30 \text{ (2H, m, Ph)}.\]

(Z)-isomer
\[ \delta_\text{H}: 1.70 \text{ (3H, dd, J 6.9 and J 1.7, CH}_3\text{CH}_\text{vinyl}\text{)}, 4.85 \text{ (1H, dq, J 6.7 and 6.8, CH}_\text{vinyl}\text{CH}_3\text{)}, 6.35 \text{ (1H, dq, J 5.9 and 1.7, CH}_\text{vinyl}\text{O)}, 6.90-7.03 \text{ (3H, m, Ph)}, 7.21-7.30 \text{ (2H, m, Ph)}.\]

4.4.5.3 1,1-Diethoxypropene

The alkyl vinyl ethers were prepared using the procedure for 6. The products were not isolated.
\[ \delta_\text{H}: 1.28 \text{ (3H, t, J 7.0, CH}_2\text{CH}_3^{A}\text{)}, 1.30 \text{ (3H, t, J 7.0, CH}_2\text{CH}_3^{B}\text{)}, 1.57 \text{ (3H, d, J 6.3, CH}_3\text{CH}_\text{vinyl}\text{)}, 3.73 \text{ (2H, q, J 7.0, CH}_2^{A}\text{CH}_3\text{)}, 3.92 \text{ (2H, q, J 7.0, CH}_2^{B}\text{CH}_3\text{)}, 4.15 \text{ (1H, q, J 6.3, CH}_\text{vinyl})\text{).} \]
4.4.5.4 (E)/(Z)-(1R,5S)-2-Ethoxymethylene-6,6-dimethylbicyclo[3.1.1]heptane

The ethyl vinyl ethers were prepared using the procedure for 6 using neat allyl ethyl ether 33 (9.3 mmol) and reduced pressure distillation of the crude products gave a colourless oil (1.26 g, 75.4%).

B.p. 36 °C at 0.02 Torr.

(E)-isomer

\[ \delta_H: 0.71 (3H, s, Me^A), 1.18 (3H, s, Me^B), 1.21 (1H, t, J = 7.0, CH₂CH₃), 1.31 (1H, d, J = 9.7, CHCH^A(CH)), 1.80-1.85 (2H, m, CH₂CH₂CH₂), 1.89-1.95 (1H, m, CH₂CH₂CH₂), 2.20 (1H, t, J = 5.6, CCHMₑ₂), 2.26 (1H, ddd, J = 18.0, 8.6 and 3.0, CCH^B(CH₂), 2.32 (1H, d[t], J = 9.0 and 5.8, CHCH^B(CH₂)), 2.40 (1H, d[t]d, J = 18.0, 6.1 and 1.7, CCH^B(CH₂), 3.65-3.74 (2H, m, CH₂CH₃), 5.63-5.68 (1H, m, CH_viny).

\[ \delta_C: 15.3, 17.0, 22.0, 23.5, 26.0, 28.4, 40.9, 41.1, 46.6, 67.1, 121.4 and 137.2.

NOE: Irradiation at the vinylic proton (5.63-5.68 ppm) showed a strong correlation with CCHMₑ₂ (2.20 ppm) and CH₂CH₃ (3.65-3.74 ppm).

(Z)-isomer

\[ \delta_H: 0.74 (3H, s, Me^A), 1.24 (3H, s, Me^B), 1.17 (1H, t, J = 7.0, CH₂CH₃), 1.43 (1H, d, J = 9.8, CHCH^A(CH)), 1.74-1.81 (2H, m, CH₂CH₂CH₂), 1.87-1.89 (1H, m, CH₂CH₂CH₂), 1.97 (1H, d[t], J = 16.1, 8.7 and 1.2, CCH^A(CH₂), 2.28-2.31 (1H, m, CHCH^B(CH)), 2.36-2.42 (1H, m, CCH^B(CH₂), 2.91 (1H, t, J = 5.5, CCHMₑ₂), 3.63 (2H, q, J = 7.0, CH₂CH₃), 5.81-5.83 (1H, m, CH_viny).

\[ \delta_C: 19.1, 19.2, 21.5, 23.8, 28.4, 28.5, 29.9, 42.7, 48.8, 66.8, 120.7 and 137.9.

MS (FAB) m/z: 180 (M⁺, 23), 149 (40), 133 (30), 33 (24), 81 (41), 69 (45), 55 (45), 43 (52), 41 (51).

Found: C, 79.9; H, 11.4. C₁₂H₂₀O requires C, 79.9; H, 11.2 %.

* The Z-isomer could not be satisfactorily separated and some chemical shifts are approximate due to the dominance of the spectrum from the E-isomer.
4.4.6 Preparation of 4-cyanophenyl acetate

A solution of 4-hydroxybenzonitrile (5.00 g, 42.0 mmol), pyridine (9.6 cm$^3$, 9.40 g, 118.7 mmol) and acetic anhydride (4.9 cm$^3$, 5.35 g, 52.4 mmol) was stirred under nitrogen for 10 h at room temperature. The solution was then extracted with diethyl ether (3 x 30 cm$^3$) then washed successively with water (2 x 30 cm$^3$) and satd. brine (2 x 30 cm$^3$) and dried over MgSO$_4$. The solvent was removed by evaporation under reduced pressure and the crude product was recrystallised from hexane to afford the product (4.9 g, 72%).

M.p. 58 $^\circ$C (lit. 56-57 $^\circ$C).

$\delta_H$: 2.31 (3H, s, Me), 7.21-7.26 (2H, AA'BB', H-2 and H-6), 7.70-7.78 (2H, AA'BB', H-3 and H-5).

$\delta_C$: 21.0, 109.8, 118.2, 122.7, 133.6, 153.9 and 168.4.

MS (FAB) $m/z$: 161 (M$^+$+1, 100), 120 (63), 43 (27).

4.4.7 Preparation of 3-acetyl-4-hydroxybenzonitrile

A intimate mixture of 4-cyanophenyl acetate (4.99 g, 31.0 mmol) and anhydrous aluminium chloride (12.59 g, 94.5 mmol) was heated on an oil-bath at 180-185 $^\circ$C for 3 h under nitrogen. The cooled mixture was finely powdered and decomposed with ice-water (85 g) and conc. hydrochloric acid (12.5 cm$^3$), then extracted with diethyl ether (3 x 30 cm$^3$). The combined extracts were washed successively with water (2 x 30 cm$^3$) and satd. brine (2 x 30 cm$^3$) and dried over MgSO$_4$. The solvent was removed
by evaporation under reduced pressure and the crude product was recrystallised from ethanol to afford the product 41 (2.3 g, 46%).

M.p. 98 °C (lit. m.p. 100-101 °C).

δ_H: 2.65 (3H, s, Me), 7.00 (1H, d, J 8.8, H-6), 7.63 (1H, dd, J 8.7 and 2.0, H-5), 8.01 (1H, d, J 2.0, H-3), 12.7 (1H, s, OH).

δ_C: 26.6, 102.7, 118.1, 119.8, 120.0, 135.7, 138.7, 165.4 and 203.5.

MS (FAB) m/z: 162 (M^+ +1, 100), 120 (11), 43 (20).

4.4.8 Preparation of 2,4-dinitrothiophenol

A stirred solution of 1-chloro-2,4-dinitrobenzene (7.00 g, 34.6 mmol) and thiourea (3.16 g, 41.5 mmol) and ethanol (24 cm^3) was heated at reflux for 6 h. After addition of sodium hydroxide (5.3 g, 133 mmol) dissolved in water (20 cm^3), the mixture was boiled under reflux for one hour and poured into water (22 cm^3). The solution was then filtered through Celite to remove the precipitate, and the filtrate was acidified with 18% HCl (v/v) to pH 4. The compound was next extracted with diethyl ether (3 x 30 cm^3) and the combined extracts were washed successively with water (2 x 30 cm^3) and satd. brine (2 x 30 cm^3) and dried over MgSO_4. The solvent was evaporated under reduced pressure and the crude product was recrystallised from petroleum, b.p. 40-60°C/benzene to afford the product as a brown solid (4.2 g, 61%).

M.p. 132-133 °C (lit. m.p. 131 °C).

δ_H: 4.26 (1H, s, br, SH), 7.51 (1H, d, J 8.8, H-6), 8.15 (1H, dd, J 8.7, J 2.4, H-5), 9.01 (1H, d, J 2.4, H-3).

δ_C: 121.8, 127.2, 129.0, 131.6, 132.8 and 142.5.

MS (FAB) m/z: 200 (M^+ +1, 5), 147 (20), 124 (17), 73 (100), 45 (16).
4.5 REFERENCES


5.1 INTRODUCTION

5.1.1. Radical-chain deoxygenation of alcohols, diols and related compounds

Research in our group has been concerned with the application of polarity-reversal catalysis\(^1\) (PRC) by thiols to mediate the radical-chain deoxygenation of alcohols, diols and related compounds.\(^2\) For example, in the presence of an initiator and a thiol catalyst, an acetal 1 formally derived from two alcohols \(R^1\text{OH}\) and \(R^2\text{OH}\) (or from the diol \(\text{HOR}^1\text{R}^2\text{OH}\)) can undergo a radical-chain redox reaction that affords a reduced product \(R^1\text{H}\) and an ester of \(R^2\text{OH}\), as shown in eqn. (5.1). In the case of a cyclic acetal derived from a diol, the two product functional groups are joined, such that the overall reaction represents a redox rearrangement process.

\[
\begin{align*}
R^1\text{O} - R^2\text{O} - R^3 & \rightarrow R^1\text{H} + R^2\text{O} - R^3 \\
& (5.1)
\end{align*}
\]

The propagation stage of the mechanism is shown in Scheme 5.1 and abstraction of hydrogen from the acetal by the thyl radical (step a) and \(\beta\)-scission of dialkoxyalkyl radical 2 (step b) are key elementary processes that must both be rapid if the overall reaction is to be effective; step c is uniformly fast for abstraction of hydrogen from thiols by simple alkyl radicals.

![Scheme 5.1](image_url)
For example, the benzylidene acetal 3 can undergo an efficient ring-opening redox rearrangement to give 3-methylbutyl benzoate 4 (conversion ≥ 99%) in the presence of a peroxide initiator and a thiol catalyst [eqn. (5.2)].

\[ \text{Ph} \quad \text{3} \quad \text{BzO} \quad \text{4} \]

(5.2)

5.1.2 Aims of research

In general, to plan successful radical-chain reactions it is necessary to understand the factors that are important in determining the rates of the elementary steps involved. With this aim in mind an EPR spectroscopic study of hydrogen-atom abstraction by tert-butoxyl radicals from acyclic and cyclic acetals to form the corresponding dialkoxyalkyl radicals was undertaken and the absolute rates of β-scission for selected dialkoxyalkyl radicals (Scheme 5.1, step b) were determined. Although tert-butoxyl radicals abstract hydrogen much more rapidly from CH groups than do thiol radicals, both species are electrophilic and their reactivity patterns should be qualitatively similar.
5.2 RESULTS AND DISCUSSION

5.2.1 Reaction kinetics

Relative rate constants were determined using well-established kinetic EPR methods,\(^5\)\(^7\) in which transient radical intermediates are generated continuously and their steady-state concentrations are monitored directly. Di-tert-butyl peroxide (DTBP) was subjected to photolysis with high-intensity UV light in the presence of an acetal hydrogen-atom donor RH and, if appropriate, a reference hydrogen donor SH to permit the determination of the relative reactivity of RH. The relevant reactions are generalised in Scheme 5.2, where hydrogen abstraction from RH may take place at two sites to give radicals A\(^*\) and B\(^*\), respectively, and the radical B\(^*\) is transformed (by β-scission) into the radical C\(^*\). It is assumed that all the radicals present in detectable concentrations are removed at the diffusion-controlled rate by self- and cross-reactions with other such radicals with rate constants \(2k_i\) and \(k_i\), respectively, which are independent of the nature of the radicals involved; it is further assumed that \(2k_i = k_i\).\(^5\)\(^7\)

It is now well established that the bimolecular self-reactions of all simple carbon centred radicals proceed at the diffusion-controlled limit. Usually the rate constants decrease with increasing viscosity, which is considered as evidence for rate determination by diffusive encounters. Furthermore, Fischer et al.\(^7\) have that shown that rates can be predicted from classical theory using estimates of diffusion coefficients and reaction distances. Under these conditions, eqns. (5.3) and (5.4) apply to the steady-state radical concentrations determined by EPR spectroscopy.

\[
\frac{k_1}{k_2} = \frac{[A^*]}{([B^*] + [C^*])} \tag{5.3}
\]
In the absence of SH, the rate constant for $\beta$-scission of $B^*$ can be determined relative to $2k_i$ using eqn. (5.5). The value of $2k_i$ for all the transient radicals is taken as equal to the corresponding value for the tert-butyl radical in the same solvent at the same temperature, obtained from the reliable measurements reported by Schuh and Fischer who generated the tert-butyl radical via photolysis of di-tert-butylketone and measured the rate using a rotating-sector experiment. For cyclopropane (CP) and fluorobenzene (PhF) solvents, experimental values of $2k_i(Bu'^*)$ are not available and the published data for heptane (HP) solvent were scaled using solvent viscosities. It is known that rate constants correlate with solvent viscosities, as shown in eqn. (5.6), where $T$ is the absolute temperature and $\eta$ is solvent viscosity. At a given temperature, it follows that equations (5.7)-(5.10) will hold ($C$ is a constant).

$$2k_i \propto \frac{T^{1/2}}{\eta} \quad (5.6)$$

$$2k_i(Bu'^*)_{HP} = C/\eta_{HP} \quad (5.7)$$

$$2k_i(Bu'^*)_{Solvent} = C/\eta_{Solvent} \quad (5.8)$$

$$2k_i(Bu'^*)_{Solvent} = 2k_i(Bu'^*)_{HP} \times \frac{\eta_{HP}}{\eta_{Solvent}} \quad (5.9)$$

$$\log_{10} 2k_i(Bu'^*)_{Solvent} = \log_{10} 2k_i(Bu'^*)_{HP} + \log_{10} \eta_{HP} - \log_{10} \eta_{Solvent} \quad (5.10)$$

For example, plotting literature data for $\log_{10} \eta$ as a function of temperature for both heptane and fluorobenzene gave good straight lines corresponding to eqns. (5.11) and (5.12) (see Appendix 1, Tables 5.1-5.2 and Figures 5.1-5.2). Using these equations

$$\log_{10}(\eta/mPa.s)_{PhF} = -1.743 + 443.6/T \quad (5.11)$$

$$\log_{10}(\eta/mPa.s)_{HP} = -1.808 + 418.9/T \quad (5.12)$$

it was possible to interpolate the values of $\log_{10} \eta_{HP}$ and $\log_{10} \eta_{PhF}$ at a desired temperature. Using values of $\log 2k_i(Bu'^*)_{HP}$ calculated from the Arrhenius relationship for heptane [eqn. (5.13), $\theta = 2.303RT \text{kJ mol}^{-1}$] derived by Schuh and Fischer,$^9$
it was then possible to calculate $\log_k(\text{Bu}^*_{\text{PhF}})$. A plot of $\log_k(\text{Bu}^*_{\text{PhF}})$ as a function of temperature (see Appendix 1, Table 5.4 and Figure 5.3) gave the Arrhenius relationship [eqn. (5.14)] for fluorobenzene solvent. The corresponding relationship for cyclopropane (see Appendix 1, Table 5.3, 5.5 and Figures 5.4-5.5) is given in eqn. (5.15). Schuh and Fischer\cite{10} have reported experimental values for $k_t(\text{Bu}^*)$ in 3-methylpentan-3-ol (3MP) and their results in the temperature range 330-370 K (see Appendix 1, Table 5.6 and Figure 5.6), appropriate for this work, conform to the Arrhenius relationship shown in eqn. (5.16). The Arrhenius relationship for $k_t$ obtained in a similar way by Walton\cite{12} for tert-butylbenzene solvent is given in eqn. (5.17).

5.2.2 β-Scission of acyclic dialkoxyalkyl radicals

Previous work in our group on acyclic dialkoxyalkyl radicals has confirmed that it is radicals derived from the acetal CH rather than the O-alkyl groups that undergo β-scission [eqn (5.18)]. For tert-butoxy(methoxy)methane 6 even at 293 K, there was no EPR evidence for the β-Scission of Bu'OCH₂OCH₂ 18 to give Bu'OCH₂.

\[
\text{CH₃OCH₂OBu}^+ + \text{Bu'O}^* \rightarrow \text{CH₃CHO} + \text{Bu}^* \quad (5.17)
\]

This was substantiated by similar experiments with MeOCH₂OMe, only the spectra of MeOCHOMe and MeOCH₂OCH₂ were observed up to 345 K; in particular MeOCH₂ was not detected, supporting the conclusion that β-scission of 18 to give Bu'OCH₂ and
formaldehyde must be very much slower than the cleavage of 17 to give Bu′ and methyl formate.  

5.2.3 Relative molar rate constants for abstraction of hydrogen from cyclic and acyclic acetals by tert-butoxyl radicals

The relative molar rate constants for abstraction of hydrogen from cyclic and acyclic acetals by tert-butoxyl radicals were determined by competition experiments at 229 K in fluorobenzene solvent. One of the two competing acetals was always either 1,3-dioxolane 9 or 2-methyl-1,3-dioxolane 10 (see spectra shown in Figures 5.7 and 5.8), chosen to avoid line overlap with the radicals(s) derived from the second acetal. Stock mixtures of the two compounds were made up by weight and aliquots were mixed with DTBP (15-20% v/v) and diluted with fluorobenzene; the total acetal concentration was ca. 1.5 M. The sample was cooled in an ice bath, to avoid evaporative loss, in a standard Suprasil quartz EPR tube and de-oxygenated by bubbling a fine stream of argon through the liquid. EPR spectra were monitored during continuous UV irradiation of samples positioned in the variable-temperature inset of the spectrometer and relative radical concentrations were determined by double integration of appropriate lines and by computer simulation of the spectra.

For example, in the case of dimethoxymethane 5 [eqn. (5.19 and 5.20)] a preliminary EPR experiment with a sample made up of 1,3-dioxolane 9 (standard, 30%), and dimethoxymethane 5 (70%) showed only the spectrum of the radical derived from the standard at 229 K, indicating that dimethoxymethane 5 is much less reactive toward hydrogen abstraction than 1,3-dioxolane 9. Therefore a solution was prepared using a concentration of dimethoxymethane 5 much greater than 1,3-dioxolane 9, 0.384 M dimethoxymethane 5 and 0.031 M standard, which gave strong spectra of radicals derived from both substrates at 229 K and 262 K (see Figures 5.9-5.10). EPR

\[
\begin{align*}
\text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{Bu}^\circ & \rightarrow \text{CH}_3\text{OCHOCH}_3, \quad \text{(5.19)} \\
\text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{Bu}^\circ & \rightarrow \text{CH}_2\text{OCH}_2\text{OCH}_3, \quad \text{(5.20)}
\end{align*}
\]

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Figure 5.7: EPR spectra of the 1,3-dioxolanyl radical 22 at 229 K

Figure 5.8: EPR spectra of the 2-methyl-1,3-dioxolanyl radical 23 at 280 K
CHAPTER FIVE

Figure 5.9: EPR spectrum of CH$_3$OCHOCH$_3$ 15 and CH$_2$OCH$_2$OCH$_3$ 16 at 229 K

Figure 5.10: EPR spectrum of the CH$_3$OCHOCH$_3$ 15, CH$_2$OCH$_2$OCH$_3$ 16 and 1,3-dioxolanyl radical 22 at 262 K
spectra were taken on three identical samples at 229 and 261 K. Non-overlapping lines in the spectra were integrated [the two central lines of the quintet from the dioxolanyl radical 22 (standard), the central lines of the two septets for MeOCHOMe 15 and one of the triplets for MeOCH₂OCH₂ 16, as marked in Figure 5.10]. Relative rates for hydrogen-atom abstraction were then calculated using eqn. 5.4; the results are included in Tables 5.7 and 5.8. It was found that at 229 K dimethoxymethane 5 is 1/0.055 times less reactive towards hydrogen-atom abstraction than 1,3-dioxolane 9 and, in particular, abstraction from the acetal CH and O-methyl groups are 0.027 and 0.028 times less reactive than 1,3-dioxolane 9, respectively. At 261 K dimethoxymethane 5 is 1/0.145 less reactive towards hydrogen-atom abstraction than 1,3-dioxolane 9 and abstraction from the acetal CH and O-methyl groups occurs 0.063 and 0.081 times less rapidly than from 1,3-dioxolane 9.

Relative rates of hydrogen-atom abstraction from the acetals 5-14 to give the radicals 15-27 (see overleaf) were determined and the results are summarised in Table 5.9 (examples of EPR spectra are shown in Figures 5.11-5.14). The radicals 28-38 (see overleaf) were also generated in this work, either by hydrogen abstraction from the parent acetals or by β-scission of the derived dialkoxyalkyl radicals, and the EPR parameters of all radicals are collected in Table 5.10.

The temperature-dependence of the rate constant \( k_3 \) for hydrogen-atom abstraction from 2-methyl-1,3-dioxolane 10 by tert-butoxy radicals has been measured by Malatesta and Scaiano\(^\text{13}\) using the laser-flash photolysis method and the Arrhenius relationship obtained is given in eqn. (5.21). Our EPR results show that abstraction of hydrogen from 10 takes place exclusively from C(2) and so the value of \( k_3 \) at 229 K (4.34 x 10\(^6\) M\(^{-1}\) s\(^{-1}\)) obtained from eqn.(5.21) can be used to put our relative data on to an absolute basis; these results are included in Table 5.9.
### Table 5.7: Integration data for competitions between dimethoxymethane 5 and 1,3-dioxolane 9 for reaction with tert-butoxyl radicals

<table>
<thead>
<tr>
<th>Run</th>
<th>$T/K$</th>
<th>Mean$^a$ INT$^b \times 10^6$ for</th>
<th>Mean$^a$ INT$^b \times 10^6$ for</th>
<th>Mean$^a$ INT$^b \times 10^6$ for</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MeOCHOME 15</td>
<td>MeOCH$_2$OCH$_2$ 16</td>
<td>1,3-dioxolanyl radical</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>229</td>
<td>3.57</td>
<td>4.16</td>
<td>9.9</td>
</tr>
<tr>
<td>2</td>
<td>229</td>
<td>3.61</td>
<td>3.86</td>
<td>13.6</td>
</tr>
<tr>
<td>3</td>
<td>229</td>
<td>4.73</td>
<td>4.26</td>
<td>12.8</td>
</tr>
<tr>
<td>4</td>
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<td>4.80</td>
<td>5.90</td>
<td>6.7</td>
</tr>
<tr>
<td>5</td>
<td>261</td>
<td>3.65</td>
<td>4.70</td>
<td>4.8</td>
</tr>
<tr>
<td>6</td>
<td>261</td>
<td>4.65</td>
<td>6.20</td>
<td>5.3</td>
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$^a$ Mean value for whole of spectrum. $^b$ INT = Integral.

### Table 5.8: Relative rate constants for hydrogen abstraction from dimethoxymethane 5 by tert-butoxyl radicals in fluorobenzene at 229 and 261 K

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>229</td>
<td>0.029</td>
<td>0.027</td>
<td>0.033</td>
<td>0.028</td>
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<tr>
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<td>0.023</td>
<td>0.028</td>
<td>0.045</td>
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<tr>
<td>3</td>
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<td>0.027</td>
<td>0.057</td>
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</tr>
<tr>
<td>4</td>
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<td>0.063</td>
<td>0.071</td>
<td>0.081</td>
</tr>
<tr>
<td>5</td>
<td>261</td>
<td>0.062</td>
<td>0.079</td>
<td>0.141</td>
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<tr>
<td>6</td>
<td>261</td>
<td>0.070</td>
<td>0.094</td>
<td>0.164</td>
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</table>
### Table 5.9: Relative and absolute rate constants for hydrogen abstraction from acetals by tert-butoxyl radicals in fluorobenzene at 229 K

<table>
<thead>
<tr>
<th>Entry</th>
<th>Acetal</th>
<th>Site of reaction</th>
<th>$k$(relative)</th>
<th>$k$(absolute)$^b$/M$^{-1}$ s$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>(MeO)$_2$CH$_2$ 5</td>
<td>CH$_2$</td>
<td>(1)</td>
<td>5.2 x 10$^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH$_3$O</td>
<td>1.0</td>
<td>5.2 x 10$^4$</td>
</tr>
<tr>
<td>2</td>
<td>Bu'O(MeO)CH$_2$ 6</td>
<td>CH$_2$</td>
<td>1.5</td>
<td>7.8 x 10$^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH$_3$O</td>
<td>0.6</td>
<td>3.1 x 10$^4$</td>
</tr>
<tr>
<td>3</td>
<td>(MeO)$_2$CHMe 7</td>
<td>CHMe</td>
<td>3.4</td>
<td>1.8 x 10$^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH$_3$O</td>
<td>1.6</td>
<td>8.4 x 10$^4$</td>
</tr>
<tr>
<td>4</td>
<td>(MeO)$_2$CHPh 8</td>
<td>CHPPh</td>
<td>6.5</td>
<td>3.4 x 10$^5$</td>
</tr>
<tr>
<td>5</td>
<td>1,3-Dioxolane 9</td>
<td>C(2)H$_2$</td>
<td>37</td>
<td>1.9 x 10$^6$</td>
</tr>
<tr>
<td>6</td>
<td>2-Methyl-1,3-dioxolane 10</td>
<td>C(2)HMe</td>
<td>83</td>
<td>(4.3 x 10$^6$)</td>
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<tr>
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<td>2-Phenyl-1,3-dioxolane 11</td>
<td>C(2)HPh</td>
<td>40</td>
<td>2.1 x 10$^6$</td>
</tr>
<tr>
<td>8</td>
<td>2-Phenyl-1,3-dioxane 12</td>
<td>C(2)HPh</td>
<td>48</td>
<td>2.5 x 10$^6$</td>
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<tr>
<td>9</td>
<td>2-Vinyl-1,3-dioxolane 13</td>
<td>C(2)HVin</td>
<td>69</td>
<td>3.6 x 10$^6$</td>
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<tr>
<td>10</td>
<td>2-Vinyl-1,3-dioxane 14</td>
<td>C(2)HVin</td>
<td>92</td>
<td>4.8 x 10$^6$</td>
</tr>
</tbody>
</table>

$^a$ Rate constants are not statistically corrected on the basis of the number of equivalent abstractable hydrogen atoms. $^b$ Obtained by taking the rate constant for abstraction from 2-methyl-1,3-dioxolane to be 4.34 x 10$^6$ M$^{-1}$ s$^{-1}$ at 229 K.
<table>
<thead>
<tr>
<th>Radical</th>
<th>Solvent</th>
<th>T/K</th>
<th>$g$-Factor$^a$</th>
<th>Hyperfine splitting/G$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>PhF</td>
<td>223</td>
<td>2.0031</td>
<td>12.9 (1H$_a$), 0.81 (6H$_p$)</td>
</tr>
<tr>
<td>16</td>
<td>PhF</td>
<td>223</td>
<td>2.0032</td>
<td>18.3 (2H$_a$), 0.78 (2H$_p$)</td>
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<tr>
<td>17</td>
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</tr>
<tr>
<td>18</td>
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<tr>
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<tr>
<td>20</td>
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</tr>
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<td>25</td>
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</tr>
<tr>
<td>32</td>
<td>PhBu$^i$</td>
<td>229</td>
<td>2.0029</td>
<td>6.14 (1H$_p$), 4.96 (2H$_a$), 1.55 (2H$_m$), 1.15 (2H$_p$)</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
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Cont. Table 5.10

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<th>Solvent</th>
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<th>g-Factor$^a$</th>
<th>Hyperfine splitting/G$^b$</th>
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<td>PhBu$'$</td>
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<td>2.0031</td>
<td>14.94 (1H), 14.15 (1H), 2.27 (1H), 1.26 (2H)</td>
</tr>
<tr>
<td>37$^f$</td>
<td>PhBu$'$</td>
<td>229</td>
<td>2.0029</td>
<td>14.14 (1H), 13.50 (1H), 2.64 (1H), 1.03 (2H)</td>
</tr>
<tr>
<td>38$^i$</td>
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<td>2.0032</td>
<td>6.47 (1H$\nu$), 5.25 (2H$\alpha$), 1.70 (2H$\beta$)</td>
</tr>
</tbody>
</table>

Footnotes for Table 5.10

$^a$ Estimated error ± 0.0001. $^b$ Generally ± 0.05 G, except where the lines were relatively broad. However, simulations of the spectra of allylic and benzylic radicals were often very sensitive to the exact relationships between the coupling constants. $^c$ Ref. 19. $^d$ Relatively broad lines. $^e$ syn- and anti-Isomers were detectable; the coupling constants for the major (65%) isomer are given. The minor isomer (35%) showed 14.99 (1 H), 14.01 (1 H), 2.28 (1 H), 0.91 (2 H). $^f$ The EPR spectra of the syn and anti-isomers, assuming that both are present, could not be resolved within the line-width.
Figure 5.11: EPR spectrum of the 2-phenyl-1,3-dioxolanyl radical 24 at 229 K

Figure 5.12: EPR spectra of the 2-phenyl-1,3-dioxolanyl radical 24 and 1,3-dioxolanyl radical 22 (*) at 229 K
Figure 5.13: EPR spectra of the $\text{H}_2\text{COCH}_2\text{OBu}'$ 18 and tert-butyl radical (*) at 247 K

* Only the two central lines (with second-order line structure) of the tert-butyl radical are shown.

Figure 5.14: EPR spectra of $\text{H}_2\text{COCH}_2\text{OBu}'$ 18, tert-butyl radical (*) and 2-methyl-1,3-dioxolanyl radical 23 at 261 K
Abstraction of hydrogen from 5-7 takes place competitively from the acetal CH and O-methyl groups and the relative reactivities of 5 and 6 are essentially as expected on statistical grounds (Table 5.9, entries 1 and 2). The methyl group attached to the acetal carbon atom in 7 (entry 3) exerts a significant activating effect on abstraction of the remaining tertiary hydrogen atom. The effect of the phenyl group at the acetal carbon atom in 8 (entry 4) is even more activating towards abstraction of the tertiary hydrogen and it was not possible to measure the much lower reactivity of the O-methyl groups.

Cyclic and acyclic dialkoxyalkyl radicals in which hydrogen or an alkyl group is attached to the trivalent carbon atom are strongly pyramidal at this centre. Norman and co-workers have shown that values of $a(\alpha-\text{H})$ and $a(\alpha-\text{C})$ are greater than values for the planar methyl radical indicating a deviation from planarity (see EPR section 6.3). Correlation of $a(\alpha-\text{C})$ and $a(\alpha-\text{H})$ with $^1\text{H}$ NMR data confirmed their findings. However, if an $\alpha$-phenyl group is present then the radical centre is believed to be effectively planar. The pattern of ring-proton splittings (Table 5.10) is exactly as expected for a planar geometry at the radical centre [analogous to the planar $\pi$-type
species benzyl, phenoxy, etc.] rather than that obtained when the ring is attached to a bent radical centre [e.g. in C₆H₅S'O₂]. Such planarity allows full benzylic delocalisation of the unpaired electron on to the phenyl group (as indicated by the ring-proton hyperfine splittings), but this comes at the expense of frustrating the inherent pyramidalising effect of the two α-oxygen substituents. Thus, the activating effect of the phenyl group in 8 is not as large as might be expected by comparison with molecules in which the product radical centre is naturally close to planar.

The high reactivity of the hydrogen atom attached to the acetal carbon C(2) in 1,3-dioxolane 9 (entry 5) is probably mainly a consequence of stereoelectronic effects. It is generally observed that relatively small dihedral angles (ca. 30°) for C-H bonds adjacent to oxygen are responsible for a pronounced stereoelectronic effect which produces high rates of hydrogen-atom abstraction. Thus, the C(2)-H bonds subtend a relatively small and fixed dihedral angle with the lone pairs on the adjacent oxygen atoms and the transition state is effectively stabilised by charge transfer (polar effects) of the type [RO⁻ H⁺ CH(OR)]^+. The activating effect of the 2-methyl group in 10 (entry 6) is similar to that found for the acyclic analogue 7 in comparison with 5.

The relatively low reactivities of the C(2)-H groups in the benzylidene acetals 11 and 12 (entries 7 and 8), compared with that in 2-methyl-1,3-dioxolane 10, is surprising at first, in view of the fact that the benzylic CH group in 8 is more reactive than that in 7. However, the radical centres in the cyclic benzylic radicals 24 and 25 are both planar (see Table 5.10 and the computational section), which introduces angle strain into the 5- and 6-membered rings when the hydrogen is abstracted from C(2) in their protic parents. In contrast, the OCO angle in the acyclic analogue 21 derived from 8 is free to open to ca. 120°.

The allylic CH groups in the 2-vinyl-substituted acetals 13 and 14 (entries 12 and 13) show reactivities similar to those of the benzylic CH groups in the 2-phenyl analogues 11 and 12 and both sets of results can be rationalised on a similar basis, as described above. The relatively low reactivities of 13 and 14 towards hydrogen-atom abstraction at C(2) accords with the failure of these acetals to isomerise to the corresponding enol ethers observed under radical-chain conditions (Section 4.2.11). Both results can be seen as a consequence of the strain developed in the rings when C(2) becomes a planar, sp²-hybridised centre.
5.2.4 Absolute rate constants and Arrhenius activation parameters for $\beta$-scission of $R'\text{O}(R^2\text{O})\text{CR}^3$

The $\beta$-scission processes shown in eqns. (5.22)-(5.27) were examined. Samples usually consisted of the acetal (ca. 15% v/v) and DTBP (ca. 20% v/v) in fluorobenzene, tert-butyl benzene or 3-methylpentan-3-ol as solvent. Values of $k_\beta$ over a range of temperatures, for which EPR spectra of both the parent radical and its $\beta$-scission product were detectable, were obtained using eqn. (5.5), in conjunction with appropriate value of $2k_t$ derived from eqns. (5.14, 5.16 or 5.17).
For example, photolysis of di-tert-butyl peroxide (20% v/v) in the presence of 2-phenyl-4,4-dimethyl-1,3-dioxane 3 in tert-butylbenzene in the temperature range 305-336 K gave the spectra of both radicals 32 and 33 [eqn. (5.28)]. It is apparent [eqn. (5.5)] that the absolute concentration of radical 33 needs to be measured to obtain \( k_B \). Absolute radical concentrations were determined using the method described in Section 5.4. It was found that lines from the 2-phenyl-4,4-dimethyl-1,3-dioxan-2-yl radical 32 were difficult to integrate so the value of \( A \) at 310 K [eqn. (5.29)] was used to scale the peak height ratio \( h_B/h_A \) at other temperatures to obtain \([B]/[A]\). The calculated results are displayed in Table 5.11 and a line of best-fit for a plot of \( \log_{10}[k_B(32)/M^{-1}s^{-1}] \) versus \( 1/T \) (displayed in Figure 5.15) was used to obtain the Arrhenius relationship [eqn (5.30)] for the \( \beta \)-scission of the 2-phenyl-4,4-dimethyl-1,3-dioxan-2-yl radical 32.

When the concentration of \( A^* \) and \( B^* \) are equal (at a temperature \( T_{equal} \)) eqn. (5.5) simplifies to eqn. (5.31),

\[ k_B = 2k_t \]

which is sometimes useful to obtain the approximate value of \( k_B \) at \( T_{equal} \), since the radical concentration in all experiments of this type is about \( 5 \times 10^{-7} \text{ M} \). The value of \( T_{equal} \) for \( \beta \)-scission of 32 was obtained by interpolation (Figure 5.16) and was estimated to be 311 K. The value of \( 2k_t \) is \( 5.15 \times 10^6 \text{ M}^{-1}s^{-1} \) and the value of \( [B] \) obtained by interpolation is \( 1.28 \times 10^3 \text{ s}^{-1} \) and hence \( k_B \) at 311 K can be estimated to be \( \text{ca. } 1.32 \times 10^3 \text{ s}^{-1} \). The value of \( k_B \) at 311 K derived from the Arrhenius relationship given in eqn. (5.30) is \( 1.45 \times 10^3 \text{ s}^{-1} \), showing that values of \( T_{equal} \) can indeed be used as a reliable guide to the rate of \( \beta \)-scission, even when the quality of the EPR spectra does not permit a full kinetic analysis.
Table 5.11: Arrhenius data for the β-scission of the 2-phenyl-4,4-dimethyl-1,3-dioxan-2-yl radical 32 in tert-butylbenzene

<table>
<thead>
<tr>
<th>T/K</th>
<th>H(A)</th>
<th>H(B)</th>
<th>H(B)/H(A)</th>
<th>INT(B)</th>
<th>x (256/30)</th>
<th>[B]/[A]</th>
<th>[B]</th>
<th>k_p/2k_t</th>
<th>log k_p/2k_t</th>
<th>log 2k_t (Bu')</th>
<th>1000/T</th>
<th>log k_p</th>
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<tr>
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<td>92.5</td>
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<td>0.24</td>
<td>1.14E+06</td>
<td>9.73E+06</td>
<td>0.61</td>
<td>9.80E-08</td>
<td>1.57E-07</td>
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<td>9.66</td>
<td>3.28</td>
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<td>1.36E+07</td>
<td>0.60^d</td>
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<td>9.70</td>
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<td>0.77</td>
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<td>3.41</td>
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<td>1.01</td>
<td>1.63E+06</td>
<td>1.39E+07</td>
<td>2.51</td>
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<td>1.37E+07</td>
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<td>1.67</td>
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<td>-6.02</td>
<td>9.89</td>
<td>2.98</td>
<td>3.87</td>
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^a H = height of peak.  INT = Integral.  ^d Obtained using [B]/[A] = A x h_B/h_A [eqn. 5.29], A = 2.49.  ^d Obtained from integrals of both A and B.
Figure 5.15: Arrhenius plot for the $\beta$-scission of the 2-phenyl-4,4-dimethyl-1,3-dioxan-2-yl radical 32 in tert-butylbenzene.

Figure 5.16: Plot of $[B^*/[A^*]]$ versus temperature for the $\beta$-scission of the 2-phenyl-4,4-dimethyl-1,3-dioxan-2-yl radical 32 in tert-butylbenzene.
The Arrhenius plots for radicals 17, 28 and 30 are shown in Figures 5.17-5.21 and the linear regression lines correspond to the activation parameters given in Table 5.12. For dialkoxyalkyl radicals 17, 30, 32 and 34 in which the alkoxy substituents differ, only cleavage of the weaker C-O bond to give the more-stabilised tertiary alkyl radical was observed. For the dioxolanyl and dioxanyl radicals 22-27 without substituents on the alkoxy carbon atoms, β-scission was not detectable by EPR spectroscopy up to ca. 390 K.

β-Scission of the tert-butoxy(methoxy)methyl radical 17 to give the tert-butyl radical (entry 1) is very rapid above room temperature, in accord with our demonstration that tertiary alcohols can be successfully deoxygenated via thiol-catalysed radical-chain decomposition of their methoxymethyl ethers.² The activation parameters for the β-scission of 17 are very similar to those obtained previously¹⁹ for the corresponding cleavage of the di-tert-butoxymethyl radical 39 (entry 2), when the latter are recalculated using revised values for log₁₀(2Δt) and Eₐ applicable to cyclopropane as solvent [eqn. (5.15) and see Table 5.12] and consistent with the values used in the present work.

Our quantitative kinetic data for the ring opening of the dioxolanyl radical 28 (entry 3) support the previous qualitative conclusion¹⁹ that this cyclic radical undergoes β-scission much less readily than analogous acyclic dialkoxyalkyl radicals such as 17

and 39. The transition states for this type of β-scission process are product-like (see computational section) and the rate difference can be attributed in part to the angle strain that develops at C(2) in the transition structure for β-scission of the cyclic radical, as a result of planarisation at this centre. Perkins and Roberts¹⁹ have found that the value of a(Hα) for the dioxolanyl radical 28 is close to zero except at very low temperatures. This is thought to result from the near equality of the positive
Figure 5.17: Arrhenius plot for the β-scission of the tert-butoxy(methoxy)methyl radical 17 in fluorobenzene

Figure 5.18: Arrhenius plot for the β-scission of the 4,4,5,5-tetramethyl-1,3-dioxolan-2-yl radical 28 in tert-butylbenzene
Figure 5.19: Arrhenius plot for the β-scission of the 4,4,5,5-tetramethyl-1,3-dioxolan-2-yl radical 28 in 3-methylpentan-3-ol

Figure 5.20: Arrhenius plot for the β-scission of the 2-phenyl-4,4-dimethyl-1,3-dioxolan-2-yl radical 30 in tert-butylbenzene
Figure 5.21: Arrhenius plot for the $\beta$-scission of the 2-phenyl-4,4-dimethyl-1,3-dioxolan-2-yl radical 30 in 3-methylpentane
Table 5.12: Arrhenius parameters for β-scission of dialkoxyalkyl radicals

<table>
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<tr>
<th>Entry</th>
<th>Dialkoxyalkyl radical</th>
<th>Product radical</th>
<th>Solvent</th>
<th>Log₁₀(A₀/²⁻¹)(^a)</th>
<th>(E_a/²) kJ mol(^⁻¹)</th>
<th>(k_b(298 K)/²⁻¹)</th>
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</thead>
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<td></td>
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<tr>
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<td>39 Bu'' c-C⁵H₁₂</td>
<td></td>
<td></td>
<td>12.2(^c,d)</td>
<td>36.4(^c,d)</td>
<td>6.7 x 10⁵</td>
</tr>
<tr>
<td>3</td>
<td>28 PhBu'</td>
<td></td>
<td></td>
<td>14.5</td>
<td>66.1</td>
<td>8.3 x 10²</td>
</tr>
<tr>
<td>4</td>
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<td>63.4</td>
<td>1.6 x 10³</td>
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<tr>
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<td>13.1</td>
<td>62.0</td>
<td>1.7 x 10²</td>
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<tr>
<td>6</td>
<td>30 3MP</td>
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<td>13.4</td>
<td>62.4</td>
<td>2.9 x 10²</td>
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<tr>
<td>7</td>
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<td></td>
<td></td>
<td>13.2</td>
<td>59.8</td>
<td>5.3 x 10²</td>
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</tbody>
</table>

\(^a\) Estimated error ± 0.3. \(^b\) Estimated error ± 1.0 kJ mol\(^⁻¹\). \(^c\) Values of log₁₀(A₀/²A₀) and (Eₐ-Eₜ) taken from ref. 19. \(^d\) Taking log₁₀(2k₉/M⁻¹ S⁻¹) = 11.19 - 4.19/θ in cyclopropane solvent, calculated from viscosity data as described in the text. \(^e\) log₁₀(k₉/M⁻¹ S⁻¹) = 13.0 - 66.9/θ (k₉ = 19 M⁻¹ S⁻¹ at 298 K) is recommended in ref. 21.
(non-planarity) and negative (spin-polarisation) contributions to the splitting constant, which indicates a greater degree of non-planarity at the radical centre than in the acyclic dialkoxyalkyl radicals whose predominant coupling mechanism is spin-polarisation giving rise to a net negative coupling constant.

Stereoelectronic factors may also play a part in determining the rate of β-scission, because the need to achieve maximum overlap between the OCMe₂ bond undergoing cleavage and the orbital of the unpaired electron is frustrated by the constraints imposed by the cyclic nature of the transition state. It is thought that an important factor controlling the rates of scission of the cyclic radicals is the relatively small degree of overlap between the (approximately) 2pₚ orbital of the unpaired electron and the antibonding σ orbital of the β-O-C bond. The transition state for β-scission will be formed by overlap of the 2pₚ orbital of the unpaired electron with the σ* orbital on the adjacent oxygen, and this will be maximised in a conformation such as that shown in Scheme 5.3 in which the axis of the 2pₚ orbital and the Cα-O and O-Cγ bonds are coplanar. Such a conformation can be achieved in an acyclic dialkoxyalkyl radical, but in a cyclic 1,3-dioxanyl radical the σ* and 2pₚ orbitals are closer to being orthogonal.²⁹

β-Scission of alkoxyl radicals [eqn. (5.32)] is facilitated by polar solvents, particularly by hydrogen-bond donor solvents, that stabilise the transition state more than the ground state.²⁰ The influence of solvent polarity can be accounted for as a dipole-dipole interaction of the transition state for β-scission with solvent medium. Hence, the solvent should more strongly stabilise the transition state, and the activation energy for β-scission should decrease with a solvent polarity increase.²⁰

\[
\begin{align*}
|R\equiv\text{alkyl} & \quad [\delta^+\quad \delta^-]^{\ddagger} \quad \text{R}^* + \quad \text{O} = \text{O} \quad (5.32) \\
\text{C-O} & \quad [\text{C} = \text{O} \quad \delta^+\quad \delta^-]^{\ddagger} \quad \text{C} = \text{O} + \quad \text{R}^* \quad (5.33)
\end{align*}
\]
an alkoxyalkyl radical [eqn. (5.33)] is a closely related process and so the ring opening of 28 to give the β-formloxyalkyl radical 29 was also studied in 3-methylpentan-3-ol as solvent (entry 4). Although the rate of β-scission was greater in the alcohol solvent, the increase was relatively small.

The β-scission of the 2-phenyl-1,3-dioxolanyl radical 30 in tert-butylbenzene solvent (entry 5) has been studied previously by Ingold and co-workers.\(^{21,22}\) Our results indicate that ring opening of 30 to give the β-benzoyloxyalkyl radical 31 is rather more rapid than reported previously and the difference is attributable mainly to the lower activation energy determined in the present work. β-Scission of the benzylic radical 30 is only about 6 times slower at 298 K than opening of the unsubstituted analogue 28, which would be expected to cleave twice as fast as 30 simply on statistical grounds.

The geometry at C(2) is planar in 30, as it is in the product ester radical 31, while in 28 it is strongly pyramidal and this centre has to become planar in the product. Thus, there is less structural reorganisation on going to the transition structure for cleavage of 30 compared with the situation for 28. As found for β-scission of 28, there is only a modest increase in the rate of ring opening on moving from tert-butylbenzene to 3-methylpentan-3-ol as solvent (entry 6).

β-Scission of 32 [eqn. (5.26), (entry 7)], the six-membered-ring analogue of 30, takes place more readily than cleavage of the latter. The ring opening of 32 is calculated to be more exothermic by 5 kJ mol\(^{-1}\) than β-scission of 30 (see computational section) and, since the transition states are product-like, this is likely to be the most important factor controlling the relative rates. The observed rate difference may also be partly stereoelectronic in origin, because the presence of the larger ring permits better overlap of the β-OCMe\(_2\) bond with the orbital of the unpaired electron on moving to the transition state (compare structures 32a and 30a).
The spirocyclic radical \(34\) was included in this study because we have shown previously that constraining the bond angles at the nascent radical centre can have a major effect on the rate of ring opening of carbohydrate-derived 2-phenyl-1,3-dioxan-2-yl radical of the type \(40\). It is thought to be the reason why the \(\text{OMe}\) \(40\) \(\text{P-scission}\) of these compounds affords primary radicals in preference to secondary radicals. Unfortunately, because of the broad (and therefore weak) EPR signals from both \(34\) and from the radical \(35\) produced by its \(\text{P-scission}\) it was not possible to obtain quantitative kinetic data. However, the temperature at which the concentration of \(34\) is approximately equal to that of \(35\) is ca. 20 K lower than that (ca. 311 K) at which \([32] = [33]\), implying that the spirocyclic \(35\) undergoes \(\text{P-scission}\) more rapidly than its 4,4-dimethyl analogue \(32\). Using eqn. (5.31) we can obtain an approximate value of \(k^\text{P}\) at ca. 290 K at which \([34] = [35]\). The concentration of \([B^*]\) was taken to be the same value as for \(33\) (1.28 x 10^{-7} \text{ M}) which gives a value for \(k^\text{P}\) of 8.7 x 10^2 s^{-1} at 290 K.

No EPR spectroscopic evidence was found for \(\text{P-scission}\) of the benzylic radical \(38\) and its spectrum was still readily detectable at 400 K in tert-butylbenzene. Although other effects may also be operative, the slow \(\text{P-scission}\) of \(38\) is likely to be mainly stereoelectronic in origin, in that the ring system will be quite rigidly planar thus preventing overlap of the \(\text{P-O-CMe}_2\) bond with the SOMO. Likewise, no EPR evidence was found for \(\text{P-scission}\) of the allylic radicals 2-vinyl-1,3-dioxolan-2-yl \(36\) or
2-vinyl-1,3-dioxan-2-yl 37 and their spectra were still observable at 400 K, some 15 K above the highest temperature at which the 2-phenyl analogues 30 and 32 were detectable. This implies that 36 and 37 undergo β-scission more slowly than the 2-phenylated analogues. However, ring opening of 36 and 37 would yield radicals that contain acrylate ester functions and it would be difficult to obtain quantitative kinetic data for radicals of this type, because of the ease of alkyl radical addition to acrylates.

5.2.5 Density functional molecular orbital calculations

To aid interpretation of the experimental results, a number of molecular calculations were carried out at the UB3LYP/6-31G(d,p) level of density functional theory, using GAUSSIAN 98 package of programs. Ground-state radicals and transition structures were fully optimised with respect to all geometrical variables with no symmetry constraints. The set of normal harmonic frequencies was computed for each structure, first in order to confirm it as a local minimum or a transition state and then to obtain the zero-point vibrational energy (ZPVE), third-law entropy and thermal contribution to the enthalpy at 298 K. In addition to selected examples of the β-scission processes studied experimentally, the prototypical reactions shown in eqns. (5.30) and (5.35) were examined computationally. The reactions investigated proceed via the transition structures 43-48 and the results are presented in Table 5.13. The ring-opening β-scission of the unsubstituted 1,3-dioxolan-2-yl radical 23, along with cleavage of its 2-methyl and 2-trifluoromethyl analogues, has been examined theoretically previously by Zipse as part of a study of the 1,2-acyloxy rearrangement that takes place for β-acyloxyalkyl radicals.
Calculated activation parameters and rate constants were obtained using eqns. (5.36) and (5.37), in which \( k_B \) is Boltzmann's constant; the transmission constant (\( k \) in classical transition state theory) is taken to be unity and the temperature is 298 K throughout. The computed activation parameters and rate constants are given in Table 5.14.

\[ A^\beta = (k_B T e/h) \exp(\Delta S^\beta / R) \]  \hspace{1cm} (5.36)

\[ E_a^\beta = \Delta H^\ddagger + R T \]  \hspace{1cm} (5.37)

In agreement with the conclusions based on their EPR spectra, the parent benzylic or allylic 1,3-dioxolanyl and 1,3-dioxanyl radicals are all predicted to be effectively planar at C(2) (angle sums \( \geq 358^\circ \), see Figure 5.22 and 5.23): the configuration at C(2) in all the transition states 43-48 is also planar (angle sum \( > 359.5^\circ \), see Figure 5.24 and 5.25). The configuration at the nascent alkyl radical centre in the transition structure is strongly flattened in comparison with that centre in the starting radicals (compare Figure 5.22 with Figure 5.24). The developing C=O bond is relatively short (1.263-1.276 Å) and the rupturing C-O bond is relatively long (1.894-1.953 Å), structural features which suggest that the transition states should be regarded as "product-like". The computed lengths of the C=O bonds in the product radicals 31 and 33 are 1.218 and 1.217 Å, respectively. The developing C=O bond is shorter and the C-O bond undergoing cleavage is longer in the 6-membered transition structure 44, as compared with the 5-membered analogue 43. Within the series of 6-membered transition states, the developing C-O bond distance varies very little, while the length of the rupturing C-O bond increases with increasing methylation of the new radical centre.
Table 5.13: Results of density functional molecular orbital calculations at the UB3LYP/6-31G(d,p) level\(^d\)

<table>
<thead>
<tr>
<th>Radical</th>
<th>Electronic energy/hartree</th>
<th>Number of imag. freqs. (cm(^{-1}))</th>
<th>(r(\text{C-O}))^b</th>
<th>(r(\text{C}=\text{O}))^c</th>
<th>ZPVE(^d,e) /kJ mol(^{-1})</th>
<th>(H(298 \text{ K}))^e</th>
<th>(S(298 \text{ K}))^f</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>-577.425324</td>
<td>0</td>
<td>1.433</td>
<td>1.368</td>
<td>567.6</td>
<td>-577.196291</td>
<td>452.4</td>
</tr>
<tr>
<td>TS 43</td>
<td>-577.399773</td>
<td>1 (-729.5)</td>
<td>1.894</td>
<td>1.276</td>
<td>560.2</td>
<td>-577.173400</td>
<td>457.4</td>
</tr>
<tr>
<td>31</td>
<td>-577.434344</td>
<td>0</td>
<td>1.218</td>
<td>562.0</td>
<td>-577.205958</td>
<td>507.0</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>-616.738966</td>
<td>0</td>
<td>1.462</td>
<td>1.362</td>
<td>644.2</td>
<td>467.9</td>
<td></td>
</tr>
<tr>
<td>TS 44(^i)</td>
<td>-616.714120</td>
<td>1 (-536.7)</td>
<td>1.953</td>
<td>1.264</td>
<td>636.1</td>
<td>-616.457826</td>
<td>477.9</td>
</tr>
<tr>
<td>33</td>
<td>-616.749305</td>
<td>0</td>
<td>1.217</td>
<td>637.5</td>
<td>-616.491079</td>
<td>527.0</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>-694.156809</td>
<td>0</td>
<td>1.467</td>
<td>1.360</td>
<td>741.2</td>
<td>-693.859921</td>
<td>496.5</td>
</tr>
<tr>
<td>TS 45</td>
<td>-694.134808</td>
<td>1 (-549.5)</td>
<td>1.940</td>
<td>1.267</td>
<td>734.1</td>
<td>-693.840648</td>
<td>494.5</td>
</tr>
<tr>
<td>25(^g)</td>
<td>-498.779591</td>
<td>0</td>
<td>1.437</td>
<td>1.365</td>
<td>422.1</td>
<td>-498.608834</td>
<td>416.0</td>
</tr>
<tr>
<td>TS 46</td>
<td>-498.750911</td>
<td>1 (-842.7)</td>
<td>1.921</td>
<td>1.265</td>
<td>414.1</td>
<td>-498.583331</td>
<td>420.3</td>
</tr>
<tr>
<td>27</td>
<td>-384.439491</td>
<td>0</td>
<td>1.437(^h)</td>
<td>1.365(^c)</td>
<td>372.2</td>
<td>-384.289209</td>
<td>361.1</td>
</tr>
<tr>
<td>TS 47</td>
<td>-384.403444</td>
<td>1 (-658.8)</td>
<td>1.955</td>
<td>1.262</td>
<td>362.5</td>
<td>-384.256671</td>
<td>366.8</td>
</tr>
<tr>
<td>TS 48</td>
<td>-384.402531</td>
<td>1 (-686.4)</td>
<td>1.949</td>
<td>1.261</td>
<td>362.1</td>
<td>-384.255841</td>
<td>367.7</td>
</tr>
</tbody>
</table>

\(^a\) 1 Hartree = 2625.5 kJ mol\(^{-1}\). \(^b\) Length of the C-O single bond that will undergo cleavage or is undergoing cleavage in the transition state. \(^c\) Length of the C-O single bond that will become a C=O double bond in the product, or the length of the developing carbonyl C=O bond in the transition state or length of the C=O bond in the product radical. \(^d\) Negative vibrational frequencies are ignored in the calculation of ZPVE. \(^e\) Low frequency normal modes are treated as vibrations, rather than rotations. Any errors caused by his approximation are expected to be small. \(^f\) See Figure 5.25. \(^g\) Effective \(C_s\) symmetry. \(^h\) Both non-equivalent bonds are the same length. \(^i\) Length of the cis-C-O bond is 1.364 Å, that of the trans-C-O bond is 1.366 Å.
Table 5.14: Calculated activation parameters for β-scission of cyclic dialkoxyalkyl radicals in the gas phase at 298 K.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^\ddagger$ (298 K)</th>
<th>$\Delta S^\ddagger$ (298 K)</th>
<th>$E_a^\beta$</th>
<th>$\log_{10}(A^\beta s^{-1})$</th>
<th>$k_{\text{calc}}/s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>/kJ mol$^{-1}$</td>
<td>/J mol$^{-1}$ K$^{-1}$</td>
<td>/kJ mol$^{-1}$</td>
<td>at 298 K$^a$</td>
<td></td>
</tr>
<tr>
<td>30→31</td>
<td>60.1</td>
<td>+ 5.0</td>
<td>62.6 (62.0)</td>
<td>13.5 (13.1)</td>
<td>3.3 x 10$^2$ (1.7 x 10$^2$)</td>
</tr>
<tr>
<td>32→33</td>
<td>57.9</td>
<td>+ 10.0</td>
<td>60.4 (59.8)</td>
<td>13.8 (13.2)</td>
<td>1.5 x 10$^3$ (5.3 x 10$^2$)</td>
</tr>
<tr>
<td>34→35</td>
<td>50.6</td>
<td>- 2.0</td>
<td>53.1</td>
<td>13.1</td>
<td>6.6 x 10$^3$</td>
</tr>
<tr>
<td>25→41</td>
<td>74.2</td>
<td>+ 4.3</td>
<td>76.7</td>
<td>13.5$^b$</td>
<td>1.0</td>
</tr>
<tr>
<td>27→42$^c$</td>
<td>85.4</td>
<td>+ 5.7</td>
<td>87.9</td>
<td>13.6</td>
<td>1.3 x 10$^2$</td>
</tr>
</tbody>
</table>

$^a$ Experimental values determined in tert-butylbenzene given in parentheses. $^b$ The statistical factor of 2, because there are two equivalent β-C-O bonds, has not been included. $^c$ Via transition state 47 to give the s-trans-acrylate ester.
Figure 5.22: UB3LYP/6-31G(d,p)-Optimised structure of 2-phenyl-4,4-dimethyl-1,3-dioxolan-2-yl radical 28

Figure 5.23: UB3LYP/6-31G(d,p)-Optimised structure of the 2-phenyl-4,4-dimethyl-1,3-dioxan-2-yl radical 30
Figure 5.24: UB3LYP/6-31G(d,p)-Optimised structure of the transition state 43

Figure 5.25: UB3LYP/6-31G(d,p)-Optimised structure of the transition state 44
CHAPTER FIVE

The computed structures of 43 and 44 are shown in Figures 5.24 and 5.25 and these typify the stereochemical and geometrical features of all the transition states.

Ring-opening of 30 to give 31 is computed to be appreciably exothermic ($\Delta H = -25.4$ kJ mol$^{-1}$) and, as expected, the associated entropy change is large and positive ($\Delta S = + 54.6$ J mol$^{-1}$ K$^{-1}$). Ring opening of 32, the 6-membered-ring analogue of 30, to give 33 is more favourable ($\Delta H = -29.4$ kJ mol$^{-1}$, $\Delta S = + 59.1$ J mol$^{-1}$ K$^{-1}$). The reverse of these ring openings, namely 6-endo-trig-cyclisation of the benzoyloxyalkyl radicals 31 and 33, is thus predicted to be relatively unfavourable (e.g. $\Delta H^\ddagger = + 87.3$ kJ mol$^{-1}$, $\Delta S^\ddagger = + 69.1$ J mol$^{-1}$ K$^{-1}$ for the cyclisation of 33 to give 32).

The computed activation entropies for ring opening are small and positive, corresponding to Arrhenius pre-exponential factors a little greater than $10^{13.4}$ s$^{-1}$. The agreement between the calculated and experimental activation parameters, where the latter are available, is very gratifying and gives credence to both sets of values.

The spirocyclic 1,3-dioxan-2-yl radical 34 is predicted to undergo $\beta$-scission to give the tertiary radical 35 at a rate similar to that for cleavage of the non-spirocyclic analogue 32, in accord with the experimental results. The allylic 1,3-dioxan-2-yl radical 27 is predicted to undergo $\beta$-scission significantly less readily than its benzylic analogue 25, consistent with the experimental observation that similarly-substituted derivatives of these two prototypes show the same trend. $\beta$-Scission of 27 is predicted to take place preferentially via the anti-transition state 47 to give the trans-acrylate radical 42; the activation energy via the syn-transition state 48 is calculated to be greater by 2.2 kJ mol$^{-1}$. 
5.3 Conclusion

EPR spectroscopic studies, augmented by density functional calculations, can provide a basis for understanding the rates of the elementary reactions involved in the deoxygenation of alcohols and diols by way of their acyclic and cyclic acetals derivatives. For the β-scission processes studied by both experiment and by theory, agreement between the two approaches is remarkably good. The results obtained from this work should provide valuable information to aid the development of a more complete understanding of the contra-thermodynamic control of the β-scission of certain bicyclic 1,3-dioxan-2-yl radicals that has been observed during the radical-chain redox ring opening of carbohydrate-derived benzylidene acetals.\textsuperscript{4,26}
5.4 EXPERIMENTAL

EPR spectra were obtained during continuous UV irradiation of samples positioned in a standard variable temperature insert in the microwave cavity of a Varian E-109 or a Bruker ESP-300 spectrometer as described in Section 3.4.1.27

Relative radical concentrations were determined by double integration of appropriate lines in each spectrum and confirmed by computer simulation of the composite spectrum. Concentration ratios were extrapolated to zero UV irradiation time when necessary to overcome the effects of sample depletion and care was taken to avoid selective saturation of the spectra. Computer simulations were obtained using a modified version of ESRSPEC2,28 extended to handle composite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with I > \( \frac{1}{2} \), and lineshapes continuously variable between 100% Gaussian and 100% Lorentzian. The experimental methods for determination of relative rate constants using the EPR method have been described in detail previously.27,29

Absolute radical concentrations were determined by comparison with the EPR signal obtained from a standard solution of 2,2,4,4-tetramethylpiperidine-N-oxyl (TEMPO, Aldrich) in fluorobenzene, using the signal from a piece of synthetic ruby fixed to the inside wall of the microwave cavity as a sensitivity reference. Spectra were recorded under conditions such that the signal was not saturated (normally 1-2 mW) and the magnetic field sweep was chosen so that the peak widths were sufficiently broad so as to make manual analogue integration easy. After recording the spectrum of the radical at the desired temperature, the signal from the ruby was recorded under the same conditions with the light still on. Next the spectrum from TEMPO was recorded at room temperature using the same microwave power and modulation amplitude that was used for the radical being measured. After recording the spectrum of the standard, the spectrum from the ruby was recorded again as before. By comparison of the double integrals for the complete spectrum of the radical (\( I_{\text{rad}} \)) with that of the double integral of the standard (\( I_{\text{std}} \)), the concentration of the former could be determined. The height of the ruby signal (\( h^R \)) is used as a measure of the spectrometer sensitivity to scale between the spectrum of the radical and that of the standard. The ruby is outside the variable-temperature insert and its spectrum is always measured at room temperature. However, the spectra of the radical and of the standard were measured at different temperatures and corrections have to applied for this, since the intensity of an EPR signal increases as the temperature decreases. It is adequate to assume that the strength
of an EPR signal is proportional to $1/T$, where $T$ is the absolute temperature. Hence, a scaling factor $(T_{\text{rad}}/T_{\text{std}})$ is applied in the calculation of the unknown radical concentration. The experimentally determined integrated intensity ($I$) of an EPR signal is proportional to the square of the scan width ($SW$) used when recording the first-derivative spectrum. Hence, to relate the concentration of a radical to that of the standard, the value of $(I_{\text{rad}}/I_{\text{std}})$ is multiplied by $(SW_{\text{rad}}/SW_{\text{std}})^2$. For a digital spectrometer such as Bruker ESP300,

$$[\text{Rad.}] = [\text{Std.}] \times (I_{\text{rad}}/I_{\text{std}}) \times (SW_{\text{rad}}/SW_{\text{std}})^2 \times (h_{\text{rad}}/h^R_{\text{std}}) \times (T_{\text{rad}}/T_{\text{std}}) \times (\text{Gain}_{\text{rad}}/\text{Gain}_{\text{std}}) \times (\text{Conv.}_{\text{rad}}/\text{Conv.}_{\text{std}})$$  \hspace{1cm} (5.36)

where $\text{Conv.}$ is the conversion time used to record the spectrum i.e. the time the digitiser dwells at each data point.

NMR spectra were recorded for samples in CDCl$_3$ using a Bruker ADVANCE 500 instrument (500 MHz for $^1$H, 125.7 MHz for $^{13}$C). Chemical shifts are reported relative to Me$_4$Si, $J$ values are quoted in Hz and the use of [multiplet] indicates an apparent multiplet associated with an averaged coupling constant.

Further experimental procedures are described in Section 2.4.1.

### 5.4.5 Materials

Di-tert-butyl peroxyde (98%, Aldrich) was washed repeatedly with 5% w/v aqueous sodium iodide containing 2% w/v sulfuric acid, until no more iodine was liberated. It was then washed successively with water, saturated aqueous sodium hydrogen carbonate, and saturated brine, before being dried (MgSO$_4$), passed down a column of basic alumina (activity 1) and finally distilled (b.p. 46-47 °C at 76 Torr); it was stored under argon at 4 °C. Fluorobenzene and tert-butylenzene were distilled from calcium hydride and stored under argon; 3-methylpentan-3-ol was distilled from sodium and stored similarly.

The acetals 5, 7, 8, 9, 10, 11 and 13 were commercial products (Aldrich) and were used as received. The compounds described below were available within the group.

$\text{tert}$-Butoxy(methoxy)methane$^{30}$ 6 was prepared by the reaction of chloromethyl methyl ether with potassium $\text{tert}$-butoxide in dimethyl formamide at 0 °C; b.p. 100-101 °C at atmospheric pressure. 2-Phenyl-1,3-dioxane $^{31}$ 12, 2-phenyl-
4,4-dimethyl-1,3-dioxolane\textsuperscript{32} and 2-phenyl-5,5-dimethyl 1,3-dioxolan-4-one\textsuperscript{33} were prepared from benzaldehyde and the corresponding diol or hydroxy acid in the presence of \textit{p}-toluenesulfonic acid catalyst and with azeotropically removal of water, as described in the literature. 2-Vinyl-1,3-dioxane \textsuperscript{14} and 2-vinyl-4,4-dimethyl-1,3-dioxolane\textsuperscript{35} were prepared in a similar way from acrolein and the appropriate diol, using pyridinium \textit{p}-toluenesulfonate as catalyst. 4,4,5,5-Tetramethyl-1,3-dioxolane\textsuperscript{36} was prepared from pinacol and paraformaldehyde using syrupy phosphoric acid as catalyst.

The 1,3-dioxanes that have not been reported previously are described below; they were prepared from benzaldehyde or acrolein and the appropriate 1,3-diol in benzene, in the presence of pyridinium \textit{p}-toluenesulfonate as catalyst, by azeotropic removal of water using a Dean and Stark separator.\textsuperscript{31}

\subsection{5.4.1.1 Preparation of 2-phenyl-4,4-dimethyl-1,3-dioxane 3}

\begin{center}
\centerline{\includegraphics[width=0.5\textwidth]{reaction_scheme.png}}
\end{center}

A mixture of 3-methyl-1,3-butanediol (13.5 g, 130 mmol), benzaldehyde (11 cm\textsuperscript{3}, 180 mmol) and \textit{para}-toluenesulphonic acid (0.38 g, 2.0 mmol) in benzene (200 cm\textsuperscript{3}) was distilled azeotropically using a Dean-stark apparatus, for 4 hours until no more water was collected. At this point, the mixture was washed with 1 M NaOH (50 cm\textsuperscript{3}), sat. brine (50 cm\textsuperscript{3}) and dried over MgSO\textsubscript{4}. After removal of the solvent under reduced pressure the crude material was distilled under reduced pressure to afford the product as a colourless oil (12.5 g, 60%).

B.p. 77-78 °C at 0.1 Torr.

$\delta_H$: 1.34 (3H, s, CH\textsubscript{3}), 1.40 (1H, d[t], J 13.5 and 2.0, H\textsuperscript{eq}-5), 1.43 (3H, s, CH\textsubscript{3}), 2.02 (1H, ddd, J 13.4, 10.4 and 8.1, H\textsuperscript{ax}-5), 4.07 (2H, m, H-6), 5.71 (1H, s, PhCH), 7.28-7.37 (3H, m, Ph), 7.47-7.49 (2H, m, Ph).

$\delta_C$: 21.4, 31.7, 35.9, 63.5, 72.1, 95.2, 126.2, 128.1, 128.5 and 139.2.

MS (EI) \textit{m/z}: 192 (M\textsuperscript{+}, 58), 191 (M\textsuperscript{+}-1, 67), 123 (23), 105 (68), 77 (42), 69 (100), 55 (36).

Found: C, 74.9; H, 8.7. \(\text{C}_{12}\text{H}_{16}\text{O}_2\) requires C, 75.0; H, 8.4%. 

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5.4.1.2 Preparation of 2-phenyl-4,4-spiropentyl-1,3-dioxane 25

This compound was prepared via a three-step synthesis. The first step was a Reformatsky reaction as described by Carr and Whittaker. Subsequent reduction of the \( \beta \)-hydroxyester with lithium aluminium hydride gave the diol, which was converted to the spirocyclic acetal by reaction with benzaldehyde in the presence of an acid catalyst.

5.4.1.3 Preparation of ethyl \( \alpha \)-(1-hydroxycyclopentyl)acetate 49

\[
\text{\text{C}}\text{O} + \text{Br} \text{CO}_2\text{Et} \xrightarrow{\text{Zn}} \text{CH}_2\text{CO}_2\text{Et} \quad \text{Zn} \quad \text{benzene/toluene} \quad \text{OH} \quad \text{49}
\]

Part \((50 \text{ cm}^3)\) of a mixture of cyclopentanone \((12.6 \text{ g}, 0.15 \text{ mol})\), ethyl bromoacetate \((26.5 \text{ g}, 0.158 \text{ mol})\), benzene \((120 \text{ cm}^3)\) and toluene \((100 \text{ cm}^3)\), was added to zinc powder \((10.3 \text{ g}, 0.157 \text{ mol})\) in a \(500 \text{ cm}^3\) three-necked round bottomed flask, equipped with condenser, stirrer, and dropping funnel. The contents were heated to \(100 \degree \text{C}\), whereupon a vigorous reaction set in. The rest of the solution was run in to maintain reflux. When addition was complete the mixture was refluxed for a further \(2 \text{ h}\). After cooling, the solution was acidified with dilute \(\text{H}_2\text{SO}_4\) and the organic layer separated, dried (\(\text{MgSO}_4\)), and concentrated under reduced pressure. Distillation of the residual oil obtained gave the acetate \(49\) \((14.82 \text{ g}, 59\%)\).

B.p. 52-55 \degree \text{C}\) at 0.05 Torr \((\text{lit} 77-79 \degree \text{C}\) at 0.05 Torr).  
IR \(\text{cm}^{-1}\), liq. film): 3465 (OH), 1712 (C=O) and 1239 (C-O).  
\(\delta\text{H}: \ 1.21 (3\text{H}, \text{t}), \ 1.47-1.84 (8\text{H}, \text{m, ring CH}_2), \ 2.53 (2\text{H}, \text{s, CH}_2\text{CO}_2\text{Et}), \ 3.26 (1\text{H}, \text{br s, OH}), \ 4.14 (2\text{H}, \text{q, CH}_2\text{CH}_3)\).

5.4.1.4 Preparation of 1-(2-hydroxyethyl)cyclopentanol 50

\[
\text{CH}_2\text{CO}_2\text{Et} \xrightarrow{\text{LiAlH}_4} \text{CH}_2\text{CH}_2\text{OH} \quad \text{diethyl ether} \quad \text{50}
\]
LiAlH₄ (7.7 g, 0.20 mol) was placed in a round-bottomed flask equipped with a condenser and dropping funnel. Ether (200 cm³) was added and the mixture cooled in an ice bath. A mixture of ethyl α-(1-hydroxycyclopentyl)acetate (14.82 g, 0.09 mol) and ether (50 cm³) was then added dropwise. The mixture was warmed with a water bath for 30 minutes and then refluxed for 2 hours. The mixture was hydrolysed with water and 15% NaOH to give a granular solid. The liquid layer was decanted and solvent removed under reduced pressure to give a viscous oil (9.93 g, 88%)

B.p. 67-70 °C at 0.05 Torr (lit 100 °C at 0.4 Torr).

δH: 1.68-1.88 (8H, m), 1.92 (2H, t, CH₂CH₂OH), 2.76 (1H, br s, OH), 3.99 (2H, t, CH₂OH).

5.4.1.5 2-Phenyl-4,4-spiropentyl-1,3-dioxane 25

A mixture of 1-(2-hydroxyethyl)cyclopentanol 50 (3.8 g, 0.03 mol), benzaldehyde (2.5 g, 0.024 mol) and pyridinium p-toluenesulphonate (0.1 g, 0.40 mmol) in benzene (50 cm³) was distilled azeotropically using a Dean-Stark apparatus until no more water was collected. At this point, the mixture was washed with 1 M NaOH (20 cm³), sat. brine (20 cm³) and dried over MgSO₄. After removal of the solvent using a rotary evaporator the crude material was distilled under reduced pressure to afford the product as colourless oil (2.14 g, 42%).

B.p. 69-70 °C at 0.4 Torr.

δH: 1.43 (1H, d[t], J 13.3 and 1.9, H₅₋₅), 1.57-1.97 (7H, m, CH₂), 2.19 (2H, m, CH₂), 4.01 (1H, ddd, J 13.0, 11.5 and 2.4, H₆₋₆), 4.15 (1H, ddd, J 11.5, 5.3 and 1.5, H₅₋₅), 5.64 (1H, s, PhCH), 7.33 (3H, m, Ph), 7.50 (2H, m, Ph).

δC: 23.1, 24.4, 32.9, 34.9, 41.6, 64.9, 84.0, 96.3, 126.0, 128.1, 128.5 and 139.3.

MS (EI) m/z: 218 (M⁺, 20), 217 (M⁺-1, 12), 105 (83), 95 (100), 77 (60), 67 (60), 55 (100), 41 (53).

Found: C, 76.7; H, 8.3. C₁₄H₁₈O₂ requires C, 77.0; H, 8.3%.
A mixture of 3-methyl-1,3-butanediol (5.6 g, 54 mmol), acrolein (7.2 cm$^3$, 108 mmol) and pyridinium para-toluene sulphonate (0.27 g, 1.08 mmol) in benzene (80 cm$^3$) was distilled azeotropically using a Dean-Stark apparatus, for 2.5 hours until no more water was collected. At this point, the mixture was washed with 1 M NaOH (40 cm$^3$), sat. brine (40 cm$^3$) and dried over MgSO$_4$. After removal of the solvent under reduced pressure the crude material was distilled under reduced pressure to afford the product 51 as a colourless liquid (3.8 g, 50%).

B.p. 56 °C at 12 Torr.

δ$_{H}$: 1.26 (3H, s, CH$_3^A$), 1.29 (1H, d[t], $J$ 13.3 and 1.9, H$^{eq}$-5), 1.32 (3H, s, CH$_3^B$), 1.87 (1H, ddd, $J$ 13.4, 12.8 and 5.9, H$^{ax}$-5), 3.90 (1H, ddd, $J$ 13.0, 11.7 and 2.4, H$^{eq}$-6), 3.96 (1H, ddd, $J$ 11.7, 5.8 and 1.4, H$^{ax}$-6), 5.13 (1H, d, $J$ 4.8, vinylCH), 5.22 (1H, dd, $J$ 10.6 and 1.2, CH$_2^A$vinyl), 5.40 (1H, dd, $J$ 17.4 and 1.2, CH$_2^B$vinyl), 5.79 (1H, ddd, $J$ 17.4, 10.6 and 4.8, CHCH$_2$vinyl).

δ: 21.6, 31.4, 35.7, 62.9, 71.8, 94.4, 118.2 and 135.5.

MS (El) m/z: 142 (M$^+$, 14), 141 (M$^+$-1, 6), 122 (100), 89 (42), 71 (59), 59 (100), 43 (84).

Found: C, 67.8; H, 9.9. C$_8$H$_{14}$O$_2$ requires C, 67.6; H, 9.9%.
5.5 REFERENCES

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Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayaala, Q. Cui, K.
Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.
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USA.
1986, 51, 4711.
APPENDIX 1

Table 5.1: Viscosity data at different temperatures for fluorobenzene

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$10^3 / T$ (K$^{-1}$)</th>
<th>$\eta$ (mPa.s)</th>
<th>$\log_{10}(\eta/mPa.s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>3.66</td>
<td>0.749</td>
<td>-0.125</td>
</tr>
<tr>
<td>293</td>
<td>3.41</td>
<td>0.598</td>
<td>-0.223</td>
</tr>
<tr>
<td>298</td>
<td>3.56</td>
<td>0.550</td>
<td>-0.260</td>
</tr>
<tr>
<td>313</td>
<td>3.19</td>
<td>0.478</td>
<td>-0.321</td>
</tr>
<tr>
<td>323</td>
<td>3.09</td>
<td>0.423</td>
<td>-0.374</td>
</tr>
<tr>
<td>333</td>
<td>3.00</td>
<td>0.389</td>
<td>-0.410</td>
</tr>
<tr>
<td>348</td>
<td>2.87</td>
<td>0.338</td>
<td>-0.471</td>
</tr>
<tr>
<td>353</td>
<td>2.83</td>
<td>0.329</td>
<td>-0.483</td>
</tr>
<tr>
<td>373</td>
<td>2.68</td>
<td>0.275</td>
<td>-0.561</td>
</tr>
</tbody>
</table>

Table 5.2: Viscosity data at different temperatures for heptane

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$10^3 / T$ (K$^{-1}$)</th>
<th>$\eta$ (mPa.s)</th>
<th>$\log_{10}(\eta/mPa.s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>248</td>
<td>4.03</td>
<td>0.757</td>
<td>-0.121</td>
</tr>
<tr>
<td>273</td>
<td>3.66</td>
<td>0.523</td>
<td>-0.021</td>
</tr>
<tr>
<td>290</td>
<td>3.45</td>
<td>0.461</td>
<td>-0.336</td>
</tr>
<tr>
<td>293</td>
<td>3.41</td>
<td>0.409</td>
<td>-0.388</td>
</tr>
<tr>
<td>298</td>
<td>3.36</td>
<td>0.387</td>
<td>-0.412</td>
</tr>
<tr>
<td>313</td>
<td>3.19</td>
<td>0.341</td>
<td>-0.467</td>
</tr>
<tr>
<td>323</td>
<td>3.09</td>
<td>0.301</td>
<td>-0.521</td>
</tr>
<tr>
<td>343</td>
<td>2.92</td>
<td>0.262</td>
<td>-0.582</td>
</tr>
<tr>
<td>348</td>
<td>2.87</td>
<td>0.243</td>
<td>-0.614</td>
</tr>
</tbody>
</table>

Table 5.3: Viscosity data at different temperatures for cyclopropane

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$10^3 / T$ (K$^{-1}$)</th>
<th>$\eta$ (mPa.s)</th>
<th>$\log_{10}(\eta/mPa.s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>209</td>
<td>4.79</td>
<td>0.185</td>
<td>-0.73</td>
</tr>
<tr>
<td>224</td>
<td>4.46</td>
<td>0.170</td>
<td>-0.77</td>
</tr>
<tr>
<td>240</td>
<td>4.17</td>
<td>0.155</td>
<td>-0.81</td>
</tr>
<tr>
<td>255</td>
<td>3.92</td>
<td>0.140</td>
<td>-0.85</td>
</tr>
</tbody>
</table>
Table 5.4: Calculated values for \( \log_{10} 2k(Bu^\dagger) \) in fluorobenzene solvent

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( 10^3/T )</th>
<th>( \log_{10} \eta_{PF} )</th>
<th>( \log_{10} \eta_{HP} )</th>
<th>( \log_{10} 2k(Bu^\dagger)_{HP} )</th>
<th>( \log_{10} 2k(Bu^\dagger)_{PF} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>203</td>
<td>4.93</td>
<td>0.442</td>
<td>0.255</td>
<td>9.151</td>
<td>8.964</td>
</tr>
<tr>
<td>206</td>
<td>4.85</td>
<td>0.410</td>
<td>0.225</td>
<td>9.187</td>
<td>9.002</td>
</tr>
<tr>
<td>209</td>
<td>4.78</td>
<td>0.379</td>
<td>0.196</td>
<td>9.222</td>
<td>9.039</td>
</tr>
<tr>
<td>209</td>
<td>4.78</td>
<td>0.379</td>
<td>0.196</td>
<td>9.222</td>
<td>9.039</td>
</tr>
<tr>
<td>215</td>
<td>4.65</td>
<td>0.320</td>
<td>0.140</td>
<td>9.289</td>
<td>9.109</td>
</tr>
<tr>
<td>217</td>
<td>4.61</td>
<td>0.301</td>
<td>0.122</td>
<td>9.311</td>
<td>9.132</td>
</tr>
<tr>
<td>219</td>
<td>4.57</td>
<td>0.283</td>
<td>0.105</td>
<td>9.332</td>
<td>9.154</td>
</tr>
<tr>
<td>222</td>
<td>4.50</td>
<td>0.255</td>
<td>0.079</td>
<td>9.363</td>
<td>9.187</td>
</tr>
<tr>
<td>227</td>
<td>4.41</td>
<td>0.211</td>
<td>0.037</td>
<td>9.413</td>
<td>9.239</td>
</tr>
<tr>
<td>229</td>
<td>4.37</td>
<td>0.194</td>
<td>0.021</td>
<td>9.432</td>
<td>9.259</td>
</tr>
<tr>
<td>234</td>
<td>4.27</td>
<td>0.153</td>
<td>-0.018</td>
<td>9.480</td>
<td>9.309</td>
</tr>
</tbody>
</table>

Table 5.5: Calculated values for \( \log_{10} 2k(Bu^\dagger) \) in cyclopropane solvent

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( 10^3/T )</th>
<th>( \log_{10} \eta_{CP} )</th>
<th>( \log_{10} \eta_{HP} )</th>
<th>( \log_{10} 2k(Bu^\dagger)_{HP} )</th>
<th>( \log_{10} 2k(Bu^\dagger)_{CP} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>195</td>
<td>5.12</td>
<td>-0.681</td>
<td>0.340</td>
<td>9.049</td>
<td>10.07</td>
</tr>
<tr>
<td>209</td>
<td>4.79</td>
<td>-0.729</td>
<td>0.196</td>
<td>9.222</td>
<td>10.147</td>
</tr>
<tr>
<td>224</td>
<td>4.46</td>
<td>-0.773</td>
<td>0.062</td>
<td>9.383</td>
<td>10.218</td>
</tr>
<tr>
<td>240</td>
<td>4.14</td>
<td>-0.815</td>
<td>-0.063</td>
<td>9.533</td>
<td>10.285</td>
</tr>
</tbody>
</table>

Table 5.6: Termination rate constants for tert-butyl radical in 3-methylpentan-3-ol

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( 10^3/T )</th>
<th>( \log_{10} 2k(Bu^\dagger)_{3MP} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>3.10</td>
<td>9.83</td>
</tr>
<tr>
<td>339</td>
<td>2.95</td>
<td>9.96</td>
</tr>
<tr>
<td>356</td>
<td>2.81</td>
<td>10.12</td>
</tr>
<tr>
<td>367</td>
<td>2.72</td>
<td>10.20</td>
</tr>
<tr>
<td>380</td>
<td>2.63</td>
<td>10.27</td>
</tr>
</tbody>
</table>

*Values of \( \log_{10} 2k(Bu^\dagger)_{3MP} \) taken from ref. 10.
**Figure 5.1:** Plot of $\log \eta_{HP}$ versus $1000/T$

**Figure 5.2:** Plot of $\log \eta_{PF}$ versus $1000/T$
Figure 5.3: Plot of $\log 2k_0(\text{Bu}^*\text{phF})$ versus $1000/T$

Figure 5.4: Plot of $\log \eta_{CP}$ versus $1000/T$
Figure 5.5: Plot of $\log k_i(Bu^*_{\text{CP}}$ versus $1000/T$

Figure 5.6: Plot of $\log k_i(Bu^*_{\text{3MP}}$ versus $1000/T$
6.0 ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

Electron paramagnetic resonance (EPR) spectroscopy is the study of molecules containing unpaired electrons by observing the magnetic fields at which they come into resonance with monochromatic electromagnetic radiation.¹

In this chapter the theoretical principles of electron paramagnetic resonance spectroscopy are discussed in brief. Through EPR spectroscopy, information such as the gross chemical structure and the detailed conformation of a radical can be obtained and unpaired electron populations at various positions in delocalised radicals may also be deduced. By measuring relative and absolute radical concentrations and by determining radical lifetimes, it is possible to obtain detailed information concerning the reaction mechanisms of free radicals. The sensitivity of the technique is such that radicals can be detected in concentrations of ≥ 10⁻⁸ M.

6.1 Principles of EPR spectroscopy

The isolated electron has an intrinsic "spin" angular momentum and, because it is also a charged particle, it possesses a magnetic moment. When placed in an externally-applied magnetic field there are two observable spin states it can adopt. The electronic magnetic moment can be aligned parallel ($m_s = -1/2$, the $\beta$ spin state) or antiparallel ($m_s = +1/2$, the $\alpha$ spin state) to the applied field and the difference in energy between these two states is given by equation (6.1), in which $g$ is a proportionality constant (known as the g-factor), $\mu_B$ is the Bohr magneton, and $B$ is the strength of the applied magnetic field (or, more precisely, the magnetic flux density) (see Figure 6.1).

$$\Delta E = g\mu_B B$$

(6.1)

Initially, there is a Boltzmann distribution of unpaired electrons between the two spin states, with more electrons in the lower energy level ($m_s = -1/2$). The ratio of the numbers of electrons in the two energy states at thermal equilibrium is given by equation (6.2), in which $n_\beta$ and $n_\alpha$ are the numbers in the lower and higher energy states, respectively, and $k$ is Boltzmann's constant. On supplying the sample of radicals with electromagnetic radiation at a fixed frequency $\nu_0$, resonance will occur at an applied magnetic field $B_0$ such that the resonance condition [eqn. (6.3)] is satisfied (see Figure 6.1).

$$n_\beta/n_\alpha = \exp (\Delta E/kT) = \exp (g\mu_B B_0/kT)$$

(6.2)
CHAPTER SIX

P.E. of the unpaired electron

\[ n_\alpha = \text{ca. } 4.996 \times 10^{13} \quad (300 \text{ K}) \]

\[ m_s = +\frac{1}{2} \quad (\alpha \text{ state}) \]

\[ \Delta E = \hbar \nu_0 = g \mu_B B_0 \]

\[ n_\beta = \text{ca. } 5.004 \times 10^{13} \]

(if \(10^{14}\) radicals in sample)

Figure 6.1: Diagram showing the energies and state-population’s for unpaired electrons in an applied magnetic field

\[ \hbar \nu_0 = g \mu_B B_0 \quad \text{(6.3)} \]

The Boltzmann factor \((n_\beta/n_\alpha)\) and the lifetimes of transient radicals both increase with decreasing temperature and so, in general, lower temperatures lead to stronger EPR signals. The act of observing an EPR spectrum tends to equalise the populations of the two spin states and could rapidly lead to saturation (i.e. \(n_\alpha = n_\beta\)) and lead to loss of the signal. However, various mechanisms of relaxation exist which tend to restore the system to Boltzmann equilibrium and permit the EPR spectrum to be observed continuously.

In practice, an EPR spectrometer uses a magnetic field of approximately 330 mT (3300 G) and the corresponding value of \(\nu_0\) is ca. 9.2 GHz, in the X-band microwave region of the electromagnetic spectrum. It is usually arranged so that the frequency is kept constant and the magnetic field is varied to achieve resonance. The applied field is modulated by application of a small magnetic field oscillating at 100 KHz; the amplitude of this modulation field is generally 0.1-1.0 G. The output from the detector is thus also oscillating at the modulation frequency and this output is applied to a phase-sensitive amplifier that only amplifies signals oscillating in-phase with and at the same frequency as the modulation field. If the modulation amplitude is small in comparison with the linewidth, the output from the phase-sensitive amplifier will be the first-derivative of the normal output with respect to applied field. The net effect of field
modulation coupled with phase-sensitive detection is noise reduction and enhanced resolution.

6.2 Characteristics of EPR spectra

An EPR spectrum from a radical in fluid solution is characterised by three basic parameters: the g-factor, the linewidths and the hyperfine splitting constants.

6.2.1 g-Factor

The g-factor is characteristic of the radical type and reflects the variable amount of orbital magnetism possessed by the unpaired electron, in addition to its spin magnetism.

In a free atom, an unpaired electron may have orbital angular momentum in addition to its spin angular momentum, but when this electron is in a polyatomic radical its orbital motion is usually quenched by the “ligand field” (strength $\Delta$). However, spin-orbit coupling can restore a small amount of orbital magnetism to the electron and this causes it to have an effective magnetic moment marginally different from that of the free electron which, in turn, causes the g-factor to deviate from the spin-only value ($g = 2.00232$). The spin-orbit constant ($\zeta$) for an atom increases rapidly with increasing atomic number and thus $g$ is dependent on the nature of the atoms with which the unpaired electron is associated. For example, a purely carbon centred alkyl radical ($g = 2.0026$) can be distinguished readily from an $\alpha$-alkoxyallyl radical ($g = 2.0033$), in which the unpaired electron is delocalised between carbon and oxygen (see Table 6.1). The sign of $\delta g$ is dependent on the detailed electronic configuration and orbital energies of the radical, and is positive for most types of organic radicals, although it can be negative especially for certain $\sigma$ radicals e.g. acyl radicals. The magnitude of $\delta g$ depends on the size of ($\zeta/\Delta$), although the major variation between radicals is in $\zeta$ rather than $\Delta$ (see Table 6.2).
Table 6.1: Table showing variation in $g$-factor from spin-only value for a selection of radicals

<table>
<thead>
<tr>
<th>Radical</th>
<th>$g$-Factor</th>
<th>$\delta g$</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{C}^*$</td>
<td>2.0026</td>
<td>+ 0.0003</td>
<td>C-centred,</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}-\text{OH}$</td>
<td>2.0033</td>
<td>+ 0.0010</td>
<td>C,O-centred,</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}-\text{F}$</td>
<td>2.0045</td>
<td>+ 0.0022</td>
<td>C,F-centred,</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}-\text{Cl}$</td>
<td>2.006</td>
<td>+ 0.0037</td>
<td>C,Cl-centred,</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}-\text{Br}$</td>
<td>2.014</td>
<td>+ 0.0117</td>
<td>C,Br-centred,</td>
</tr>
<tr>
<td>$\text{Me}_2\text{N}^*$</td>
<td>2.0047</td>
<td>+ 0.0024</td>
<td>N-centred,</td>
</tr>
<tr>
<td>$\text{Me}-\text{C}=\text{O}$</td>
<td>2.0006</td>
<td>- 0.0017</td>
<td>C-centred,</td>
</tr>
<tr>
<td>$\text{Me}_3\text{CO}-\text{C}=\text{O}$</td>
<td>2.0011</td>
<td>- 0.0012</td>
<td>C-centred,</td>
</tr>
</tbody>
</table>

Table 6.2: Table showing variation in $\zeta$ with atomic number

<table>
<thead>
<tr>
<th>Atom</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>17</td>
<td>35</td>
</tr>
<tr>
<td>$\zeta / \text{cm}^{-1}$</td>
<td>29</td>
<td>76</td>
<td>151</td>
<td>270</td>
<td>586</td>
<td>2460</td>
</tr>
</tbody>
</table>

6.2.2 Line-widths and dynamic EPR spectroscopy

Chemical and physical processes that lead to exchange of the unpaired electron between different radical sites can give rise to lineshape effects in the EPR spectra. Such processes include hindered rotation around bonds, tumbling of the radical in a viscous liquid, interactions with other paramagnetic species and chemical reactions (e.g. acid-base equilibria and electron-transfer reactions). Dynamic EPR spectroscopy refers to the study of these exchange processes undergone by radicals on the EPR time-scale.
If the processes are slow with respect to this time-scale, lines may be assignable to distinct species, while if the rate of exchange is fast, a weighted average spectrum consisting of sharp lines will be seen. However, if exchange takes place at an intermediate rate on the EPR time-scale, line-broadening will occur and these lineshape effects can be analysed to estimate the rate constant for the exchange process.

6.2.3 Hyperfine splitting constants

The most useful information derivable from an EPR spectrum is obtained from the hyperfine splitting, which usually enables identification of the radical and also its detailed structure to be determined. The origin of the observed splittings is the interaction between the unpaired electron and the magnetic moments of neighbouring magnetic nuclei within the radical. The interaction with \( n \) equivalent nuclei of spin \( I \) results in \((2nI + 1)\) lines and the distance between each of these lines is (to first-order) equal to the hyperfine splitting constant. Since \(^{12}\text{C}\) has no magnetic moment, proton hyperfine couplings dominate EPR spectra of neutral and ionic hydrocarbon radicals.

The interactions of the unpaired electron with \( n \) equivalent protons (or other \( I = 1/2 \) nuclei) give rise to signal splitting into \((n + 1)\) lines and, furthermore, the relative intensities of these lines are given by the coefficients of the binomial expansion of \((1+x)^n\), which can be found readily from Pascal's triangle. Although the natural abundance of \(^{13}\text{C} \ (I = 1/2)\) is only ca. 1.1%, several other common elements have magnetic isotopes that are present in high abundance. These include \(^{10}\text{B} \ (I = 3)\) ca. 19.8\%, \(^{11}\text{B} \ (I = 3/2)\) ca. 80.2\% and \(^{14}\text{N} \ (I = 1)\) ca. 99.6\%.

6.3 Origins of hyperfine splitting

In solution, classical magnetic dipolar interactions between the unpaired electron and a magnetic nucleus are averaged to zero by the rapid random Brownian movement of the radicals and no coupling results via this interaction, which is only important for immobile radicals in the solid state. The isotropic hyperfine splittings observed for radicals in solution are only observed if the unpaired electron has a finite probability of being at the magnetic nucleus in question. This is usually referred to as the Fermi contact interaction. It is found that it is necessary for the singly-occupied molecular orbital (SOMO) to have some \( s \)-orbital character for hyperfine splitting to arise from the Fermi contact interaction, since only then will there be a finite electron density at the
nucleus in question. Experimental results for three-co-ordinate carbon-centred radicals show that the value of $\alpha^{(13}_C$ increases as the radical centre becomes increasingly pyramidal, because then the $\text{C}_\alpha^2\text{s}$ atomic orbital contributes progressively more to the SOMO. For example, along the series $\text{H}_3\text{C}$: $\text{H}_2\text{CF}$, $\text{HCF}_2$ and $\cdot\text{CF}_3$ the radicals become increasingly pyramidal as the degree of fluorination increases. This change in structure is paralleled by a steady increase in $\alpha^{(13}_C$ from 38.6 G for the planar $\text{H}_3\text{C}$ to the quasi-tetrahedral 271.6 G for $\cdot\text{CF}_3$.

### 6.3.1 $\alpha$-Proton splitting

In planar $\pi$-radicals such as methyl and benzyl, the $^1\text{H}$ and any $^{13}_C$ atoms are in the nodal plane of the SOMO and one might therefore expect to see zero coupling to these nuclei. Spin-polarisation is the mechanism that is responsible for the coupling to $\alpha$-$\text{H}$ and $\alpha^{13}_C$ nuclei that is actually in this situation; it can be illustrated by reference to the methyl radical $\text{H}_3\text{C}$, as shown below in Figure 6.2.

**Figure 6.2:** Schematic representation of the spin-polarisation mechanism

Structure A is more stable than structure B (Hund’s rules). Therefore, considering the two electrons occupying the C-H $\sigma$ bonding molecular orbital, the electron with the same spin as that in the $\pi$ SOMO spends more time close to carbon than to hydrogen and vice versa. Induced unpaired spin in the C-2s orbital is in the same sense as that in the SOMO and thus $\alpha^{(13}_C$ is positive. Conversely, the net
unpaired spin in the H-1s orbital is in the opposite sense from that in the SOMO and thus \( a(H_\alpha) \) is negative.

McConnell\(^4\) has shown for \( \pi \)-radicals containing fragment of the type C that the unpaired spin induced in the H\(_{\alpha} \)-1s orbital is approximately proportional to the unpaired spin population on the adjacent carbon atom \( \rho^\pi_{C\alpha} \). This can be expressed by equation (6.4) in which \( Q \) is a proportionality constant, which has a value between -20 and -30 G, depending on the particular type of radical; for the methyl radical \( [a(3H) = (-)23 \text{ G}] \) it is by definition -23.0 G.

\[
a(H_\alpha) = Q \rho^\pi_{C\alpha}
\]

(6.4)

6.3.2 \( \beta \)-Proton splitting

\( \beta \)-Protons are not, in general, in the nodal plane of C\(_{\alpha} \)-2\( p^\pi \) orbital and the H\(_{\beta} \)-1s orbital can contribute to the SOMO; spin-polarisation is relatively unimportant because of the greater distance between C\(_{\alpha} \) and H\(_{\beta} \), as compared with C\(_{\alpha} \) and H\(_{\alpha} \). The accepted major mechanism for \( \beta \)-proton coupling is hyperconjugation, which allows some of the unpaired spin population on C\(_{\alpha} \) to appear at the \( \beta \)-proton, producing a positive coupling constant. This is illustrated by the valence-bond model shown in Figure 6.3.

![Figure 6.3: Valence bond canonical forms for the ethyl radical](image)
In terms of molecular orbital theory, the \( H_\beta 1s \), \( C_\beta 2s/2p \) and \( C_\alpha 2p \) will all contribute to the SOMO (Figure 6.4). This interaction follows a \( \cos^2 \theta \) law, as given by the semi-empirical Heller-McConnell equation (6.5), in which \( A \) is a spin-polarisation parameter of small value (ca. 1 G), often neglected, and \( B \) is the hyperconjugation parameter of value 58.5 G. The angle \( \theta \) is defined as the dihedral angle between the \( C_\alpha 2p_\pi \) orbital and the C-H bond (Figure 6.5), and \( \rho_{C\alpha}^\pi \) is the unpaired electron population in the \( C_\alpha 2p_\pi \) orbital. The coupling constant to a \( \beta \)-proton is at a maximum when it is in the same plane as the axis of the \( C_\alpha 2p_\pi \) orbital, i.e. when \( \theta \) is zero.

\[
a(H_\beta) = (A + B \cos^2 \theta) \rho_{C\alpha}^\pi
\]

\( (6.5) \)

![Schematic diagram illustrating the mechanism of \( \beta \)-proton hyperfine coupling in molecular orbital terms](image)

**Figure 6.4**: Schematic diagram illustrating the mechanism of \( \beta \)-proton hyperfine coupling in molecular orbital terms
The form of the Heller-McConnell equation is supported by molecular orbital calculations. Thus, Fermi contact integrals (FI) obtained from ab initio MO calculations using the UMP2 /G311G* basis set correspond to hyperfine coupling constants which are in good agreement with experiment. A plot of FI for H* [which is proportional to $a(H^*)$] against $\cos^2 \theta$ gives a perfect straight line that passes almost through the origin, indicating that $A$ is very close to zero (Figure 6.6). This approach has also been used to show that, even for alkyl radicals in which the radical centre is somewhat non-planar, the Heller-McConnell equation can provide a good basis for semi-quantitative discussion.

A good example of the application of the Heller-McConnell equation is seen by considering the cyclohexyl radical, for which calculation predicts dihedral angles of ca. 11° and ca. 71° for the axial and equatorial $\beta$-protons, respectively (Figure 6.7). By experiment, the splitting constants are found to be 41.5 G and 5.3 G, and the ratio of these (0.13) is close to the value of $(\cos^2 71)/(\cos^2 11) = (0.11)$.

**Figure 6.5:** Schematic diagram defining $\theta$

**Figure 6.7:** Schematic diagram showing dihedral angles of axial and equatorial protons for cyclohexane
Figure 6.6: Plot of Fermi contact integral against $\cos \theta$
The equilibrium conformations and barriers to hindered rotation about Cα-Cβ bonds of substituted ethyl radicals of the type CX₂-CH₂-Y, which is of relevance to this research, can be obtained from the temperature dependence of the β-proton coupling constants and also from line-width effects. When there is hindered internal rotation about the Cα-Cβ bond, the cos²θ term in the Heller-McConnell equation is an average over the hindered rotation (equation 6.5). If different conformations have different energies, the observed β-coupling can exhibit a marked temperature dependence as the conformational population changes with temperature.

$$a(H_β) = (A + B \langle \cos^2 \theta \rangle) \rho^p_{Cα}$$  \hspace{1cm} (6.5)

For substituted ethyl radicals that are planar or near-planar at Cα, requires that the low-temperature equilibrium conformations correspond to one of the forms shown below (Figure 6.8).

![Diagram showing low-temperature equilibrium conformations of substituted ethyl radicals](image)

Figure 6.8: Diagram showing low-temperature equilibrium conformations of substituted ethyl radicals

According to the Heller-McConnell equation the low-temperature limits of \(a(H_β)\) are \((1/4B)\) for structure 1 and \((3/4B)\) for structure 2.  

As the temperature increases, the amplitude of torsional motion about the Cα-Cβ bond will increase until, in the hypothetical limit of infinite temperature, free rotation will be approached. Thus, \(a(H_β)\) for radicals for which the "eclipsed" equilibrium conformation 1 is preferred will increase with increasing temperature towards a free-rotation value of \((1/2B)\). When the "staggered" conformation 2 is preferred the value of \(a(H_β)\) will decrease with increasing temperature towards a free-rotation value of \((1/2B)\), as shown in Figure 6.10.
If the radical is not symmetrically substituted at $C_\alpha$ (e.g., Structure 3) then there will be a second structure of equal energy (4) corresponding to rotation by $\phi$.

![Diagram 6.9: Non-symmetrical conformations of substituted ethyl radicals](image)

**Figure 6.9:** Diagram showing non-symmetrical conformations of substituted ethyl radicals

(180-2\(\phi\)) about the $C_{\alpha}$-$C_\beta$ bond. The two $\beta$-protons in 3/4 are now non-equivalent and give rise to different coupling constants. Interconversion between 3 and 4 exchanges $H^A$.

![Diagram 6.10: Variation of $a(H_\beta)$ with temperature](image)

**Figure 6.10:** Diagram showing variation of $a(H_\beta)$ with temperature for equilibrium conformations of substituted ethyl radicals
and $H^B$. When rotation about the $C_\alpha$-$C_\beta$ is slow on the EPR time-scale the spectrum will consist of a doublet of doublets, as shown in Figure 6.11a. When rotation is fast on the EPR time-scale the spectrum will appear as shown in Figure 6.11c and the line spacing of the $1:2:1$ triplet will be equal to $(a(H^A) + a(H^B))/2$; here $H^A$ and $H^B$ are magnetically equivalent. In the intermediate region, when exchange between $H^A$ and $H^B$ takes place at a rate comparable with $[a(H^A) - a(H^B)]$ expressed in frequency units, the spectrum will appear as shown in Figure 6.11b. The wing lines will remain sharp, but the central component will be broadened. When the two inner lines in the slow exchange spectrum have just coalesced to form a single broad line, the rate constant for exchange between 3 and 4 is $\left(\frac{\pi}{\sqrt{2}}\right)[a(H^A) - a(H^B)] \times (2.8 \times 10^6) \text{ s}^{-1}$. For rates of interconversion between 3 and 4 at other temperatures, the spectrum can be computer simulated to give the rate constant for the exchange process.

**Figure 6.11:** Diagram illustrating change in line positions for two unequal equivalent $\beta$-protons
6.3.3 Long-range proton splitting

Long-range hyperfine interactions with γ and δ protons are usually rather small, and positive and negative contributions to them often cancel each other. They are very dependent on stereochemistry and an extensive review of this subject has been given by King. Ellinger et al. have given theoretical analyses of long-range hyperfine interactions in both simple aliphatic and bicyclic free radicals. Figure 6.12

![Diagram of protons](image)

Figure 6.12: “W” and “anti-W” protons

illustrates the so called “W” and “anti-W” rules. The former type of interaction leads to the larger value of $a(H_y)$ because contributions from spin-delocalisation and spin-polarisation are both positive, whereas they tend to cancel for the latter.

6.4 Second-order effects

In the spectra of the ethyl, $t$-butyl, and trifluoromethyl radicals, additional lines are seen which are the result of so called second-order effects. The analysis of hyperfine splitting which has been presented above is valid only in cases where the 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 as a result of removal of the degeneracy of certain Zeeman levels. For X-band EPR spectroscopy, second-order splittings become significant for coupling constants above ca. 20 G. Furthermore, lines can be shifted from the positions predicted by simple theory. Line shifts from the first-order positions are of the order $(a^2/4B_0)$, where $a$ is the hyperfine coupling constant and $B_0$ is the applied magnetic field at the centre of the spectrum.
CHAPTER SIX

For example, in the case of the trifluoromethyl radical, the coupling of the unpaired electron with three equivalent fluorines actually gives rise to the splitting pattern shown below (Figure 6.13) rather than the simple 1 : 3 : 3 : 1 quartet.

\[
\begin{array}{cccc}
\text{First-order} & 1 & 3 & 3 & 1 \\
\text{Second-order} & & & & \\
\text{Intensity} & 1 & 1 & 2 & 1 & 2 & 1 & 1 \\
\text{Downfield shift from first-order position in units of} (\alpha^2/4B_0) & 3 & 7 & 1 & 7 & 1 & 3
\end{array}
\]

Figure 6.13: Diagram showing second-order splittings for a radical with three equivalent \( I = 1/2 \) nuclei

In the present research a number of phosphoranyl radicals were detected by EPR spectroscopy. For such radicals the \( ^{31} \)P hyperfine splitting is very large (typically 600-900 G) in relation to the applied field (typically 3300 G) and the lines shifts for the “first-order” positions are very large, as shown in Figure 6.14.

\[
\text{First-order spectra} \quad a^{(31\text{P})} \quad \text{field corresponding to true } g\text{-value} \quad > a^{(31\text{P})} \quad \text{Actual line positions}
\]

Figure 6.14: Diagram showing second-order splittings for a phosphoranyl radical

The low field line shifts downfield from the first-order position by more than the high field line and thus the spacing between the two experimentally observed lines is greater than \( a^{(31\text{P})} \) and the centre of these lines no longer corresponds to the \( g \)-value. A
full analysis needs to be conducted in order to extract \( a^{(31P)} \) and \( g \) and, in this work, values were computed using Preston's program ESRLSQ.\(^{13}\)

This program carries out an exact calculation of \( a \) and \( g \), by numerical matrix diagonalisation and is applicable to coupling to nuclei of \( I > \frac{1}{2} \) and to more than one nucleus coupling. When \( a \) and \( g \) are overdetermined experimentally, a least-squares fit to the data is produced. For the case of coupling to one \( I = \frac{1}{2} \) nucleus, as here, \( a \) and \( g \) may also be obtained by solution of the Breit-Rabi equation.\(^{14}\)
6.5 REFERENCES