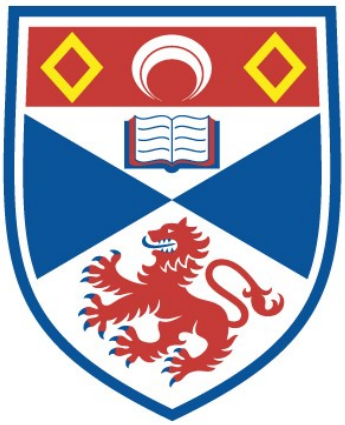
HOMOLYTIC RING FISSION IN SMALL, STRAINED BICYCLIC MOLECULES

Charles Roberts

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1984

HOMOLYTIC RING FISSION IN SMALL, STRAINED BICYCLIC MOLECULES.

by

Charles Roberts

A thesis presented to the University of St. Andrews in application for the degree of Doctor of Philosophy.

February 1984

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To my parents

DECLARATION

I hereby declare that the work in this thesis is a record of the experiments carried out by me in the Chemistry Department of the University of St. Andrews, that it is my own composition and that it has not been previously submitted for a higher degree.

February 1984

Charles Roberts

CERTIFICATE

I hereby certify that Charles Roberts , B.Sc., has completed twelve terms at research work under my supervision, has fulfilled the conditions of the Resolution of the University Court, 1967 No 1, and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research

UNIVERSITY CAREER

I entered St. Andrews University in October 1976 and graduated with an Upper Second Class Honours Degree in July 1980.

In October 1980 I was awarded a Science Research Council studentship, and have up until September 1983 carried out the work presented in this thesis.

ACKNOWLEDGEMENTS

I would like to thank Dr. J.C. Walton for his advice and encouragement throughout the period of this work.

I would also like to thank Professor P.A.H. Wyatt for the use of research facilities in the Chemistry Department of the University of St. Andrews.

Similarly I would like to thank the staff and technicians of the aforementioned department for their help during my years at St. Andrews University.

Finally, but not least I would like to thank my friends both in, and outwith, the Chemistry Department for putting up with me for so long.

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SUMMARY

The homolytic ring fission of strained bicycloalkyl radicals was investigated by E.S.R. spectroscopy. These bicycloalkyl radicals provided examples of cycloalkyl-, cyclopropylmethyl-, and cyclobutylmethyl- type radicals in which the preferred mode, and rate of β-scission could be studied. Three types of compounds were investigated; i.e. (i) bicyclo[n.1.0]alkanes, where n = 3-6; (ii) spiro[2.n]alkanes, where n = 3,4; and (iii) spiro[3.3]heptanes. Observations on the corresponding radicals enabled the influence of; (a) ring size (and consequent ring strain), and (b) the orientation of the SOMO on the rearrangement to be assessed.

The series of bicyclo[n.1.0]alk-2-yl radicals, where n = 3-6, were found to undergo β-scission of the outer cyclopropane bond to give the corresponding cycloalkenylmethyl radical. Ring fission was very rapid, and only the rearranged radicals could be detected in the accessible temperature range. In contrast, the first two members of the series (n = 1,2) rearranged by fission of the internal cyclopropane bond to give cycloalkenyl radicals. The conformations of the rearranged cycloalkenylmethyl radicals were determined from the temperature dependance of the β-hydrogen h.f.s., and were interpreted in terms of steric effects. The geometries of the radical species, their enthalpies of activation, and the enthalpies of reaction were calculated by semi-empirical MNDO computations. Photobromination of the n = 3 and n = 4 bicycloalkanes was carried out. The major products were identified and analysed. The main process in each case

was homolytic displacement by bromine atoms with consequent fission of the outer cyclopropane bond. This S_H2 reaction showed a clear parallel to the β-scission in the series of radicals. However, the change in the mode of fission from internal to outer cyclopropane bond with increasing ring size was less clear cut.

Hydrogen abstraction from the spiro[2.n]alkanes gave spiro[2.n]alk-4-yl radicals which ring open in one mode only to give cycloalkenylethyl radicals. The rate of β-scission increased greatly from the n = 2 to the n = 3 to the n = 4 member of the series. With spiro[2.3]hex-4-yl radicals both unrearranged and rearranged radicals were detectable. The Arrhenius parameters for the rearrangement were determined from measurements on the concentrations of the two species. The conformations of the ring opened cycloalkenylethyl radicals were deduced from the temperature dependance of the β-hydrogen h.f.s. The photobromination of spiro[2.3]hexane gave mainly 1-bromo-1-(2-bromoethyl)cyclobutane and 1,1-bis(bromomethyl)--cyclobutane from the S_H2 attack of bromine atoms at the cyclopropane carbon atom. Semi-empirical MNDO calculations were carried out to predict the enthalpies of activation, and the enthalpies of reaction for the rearrangements.

Bromine abstraction from 2-bromomethylspiro[3.3]heptane gave rise to a cyclobutylmethyl like radical, namely the spiro--[3.3]heptane-2-methyl, radical. This radical rearranged via β-scission to a 1-(prop-2-enyl)cyclobutylmethyl radical. Both unrearranged and rearranged radicals were detectable. As with spiro[2.3]hex-4-yl radicals the Arrhenius parameters for the

rearrangement were determined. The enthalpy of activation, and the enthalpy of reaction were also calculated by semi-empirical MNDO computations. The conformation of the unrearranged radical was determined from the temperature dependance of the β-hydrogen h.f.s.

Attempts to generate spiro[3.3]hept-1-yl radicals from spiro[3.3]heptane were unsuccessful due to the failure to prepare spiro[3.3]heptane. The spiro[3.3]hept-2-yl radical was however observed. This radical did not undergo β-scission.

With the cyclobutylmethyl-, and cyclopropylmethyl like radicals β-scission was observed to occur in a stereoelectronically allowed manner.

Overall this study has confirmed that the major influence in the ring fission of cycloalkylmethyl radicals is the stereoelectronic effect. Thus orbital interaction, through maximised overlap, is a prerequisite to β-scission of both cyclopropylmethyl- and cyclobutylmethyl- like radicals. The study of spiro[2.n]alkanes revealed that ring size may affect the rate of ring fission by way of a conformational effect.

Chapter 1

INTRODUCTION

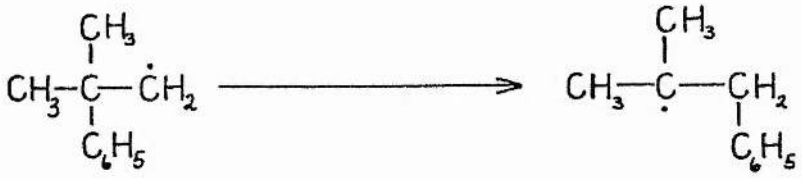
1.1 General History

Free-radical rearrangements have been the topic of many fine review articles. The first such review of major importance was that of Walling.[1] This has been followed by the works of Friedlina,[2] Wilt,[3] and, most recently, Beckwith and Ingold.[4]

What, though, is a free-radical rearrangement?

Perhaps the most concise, and most accurate description of what is entailed by the term "free-radical rearrangement" was that used by de Mayo[5] in the introduction to "Molecular Rearrangements." There he stated that a rearrangement should describe "any change in atomic disposition in the molecule (with concomitant bond cleavage, σ and π, and reformation)." As a short reply to the posed question, this is probably still the best answer.

The first free-radical rearrangement to be observed was the, now famous, neophyl rearrangement reported by Urry and Kharasch[6] (see scheme). This rearrangement displays a 1,2-phenyl migration. Since

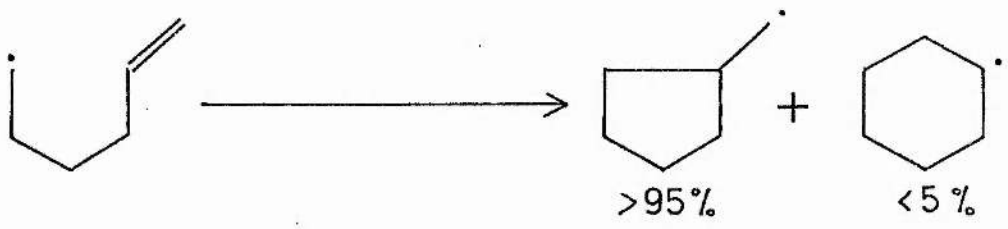


this first documented observation the number, and variety of free-radical rearrangements has increased many-fold, and continues to increase. However, despite the multitude of possible rearrangements, any observed free-radical rearrangement will generally fall into one

of three broad based categories. These being :

i)Group Transfer Processes : in this type, rearrangement occurs via the migration of an atom, or group of atoms from one centre to a second centre. The migration can be of carbon, or heteroatom, to carbon, or heteroatom. This category is very broad, and is generally further subdivided according to which atom, or atoms, migrate. Normally those migrations involving transfer of hydrogen, halogen, or heteroatom centred groups are covered by separate processes. The neophyl rearrangement mentioned earlier belongs to this category, and is an example of a 1,2-aryl migration.

ii)Ring Closure Processes : in this type, rearrangement occurs via the cyclisation of an alkenyl radical. This entails the addition of a radical centre to an unsaturated centre. The cyclisation of the 5-hexenyl radical is an example of this process.



iii)Bond Fission Processes : in this type, rearrangement occurs via the fission of an alkyl bond. In particular cycloalkyl ring opening (fission) involves the fission of a $\beta-\gamma$ bond (this is termed β-scission). An example of this process is the ring opening of the cyclopropylmethyl radical.

These categories cover most of the free-radical rearrangements observed. However, some rearrangements involve rotation, or inversion, and thus belong to different categories.

It is not the purpose of this work to examine the nature of all of these modes of free-radical rearrangement. Hence the reader who wishes a fuller examination is asked to consult one of the excellent aforementioned review articles[1-4] and the references therein.

It can be seen that, though dealt with as separate categories, ring closure and ring opening processes are related, and an examination of one almost necessitates a look at the other. This work is solely concerned with the ring opening aspect. However, the theory as to why radicals do ring open cannot be discussed without due reference to the ring closure reaction of radical species.

Rearrangement of a radical species, it may be thought, occurs because the product radical is thermodynamically more stable than the initial unrearranged radical species. In many cases this observation holds true. This is particularly so in those rearrangements involving group transfers. The neophyl rearrangement involves a primary radical rearranging to a more stable tertiary radical. (The order of radical stability being ; tertiary > secondary > primary.) However there are many rearrangements which result in the formation of products which are thermodynamically less favoured.

Why should this be?

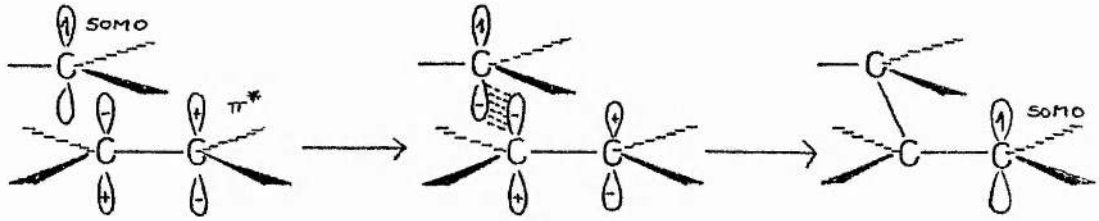
Thermodynamic control of free-radical rearrangement breaks down because it fails to take into account the steric, and polar effects found in the molecule. These effects can be demonstrated by examining a model of the addition of a methyl radical to ethylene.[7] The transition state for the addition is represented as being slightly dipolar. This electronic effect is a result of the interaction of the

semi-occupied molecular orbital (SOMO) of the methyl radical with the π^* anti-bonding orbital of the ethylene moiety. This in turn results in the creation of an allyl like transition state in which there are three electrons in three molecular orbitals ; one bonding (doubly filled), one non-bonding (singly filled), and one anti-bonding (empty).[7] Substituents on either, or both moieties affect the transition state, but do not alter the picture of orbital interaction.

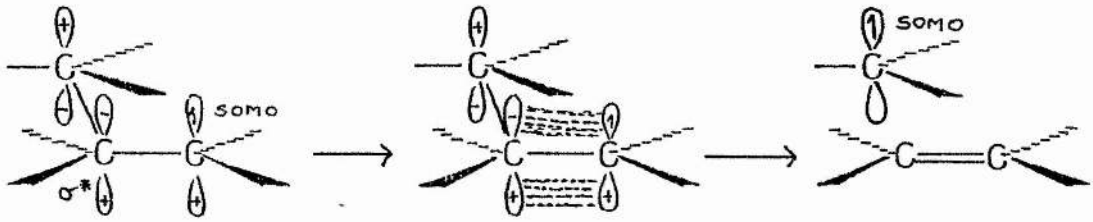
This addition reaction can be seen to rationalise radical cyclisation, as this is only a special case of radical addition to an unsaturated centre.

If ring closure of a radical species is identified as attack on an unsaturated centre by a radical, then the ring opening process is seen as the disruption of a radical species such that an unsaturated centre is developed along with the creation of a new radical centre. Thus ring opening and ring closure are opposite reactions progressing through the same transition state.

In the ring closure process the initial requirement is the interaction of the radical p orbital (SOMO) with the π^* anti-bonding orbital of the unsaturated centre. This leads to disruption of the π bonding of the unsaturated system, with concurrent σ bond formation (see scheme).



In the ring opening process the initial requirement is the interaction of the radical p orbital (SOMO) with the σ^* anti-bonding orbital of the $\beta-\gamma$ bond. This results in the formation of a π bonding system between the α and β atoms, with disruption of the σ bond between the β and γ atoms and creation of a new radical centre on, what was, the γ atom (see scheme).



It is seen therefore that both processes will be aided by the interacting orbitals adopting conformations which are beneficial to the process, whether this is cyclisation or fission. Thus the degree of overlap between interacting orbitals is maximised. The degree of orbital overlap will be influenced by steric factors within the radical species. In fact this is why the 5-hexenyl radical ring closes to the thermodynamically less favoured cyclopentylmethyl radical rather than a cyclohexyl radical.[4] Beckwith et al[8] state that for ring closure reactions, not only must there be maximised overlap of SOMO and π^* in the initial state of the rearrangement but that in the final state there must be overlap of the newly formed σ^* and SOMO. Correspondingly ring fission necessitates the maximised interaction (overlap) of SOMO and σ^* initially and overlap of the newly generated π^* and SOMO in the stage following the transition state. This rationale for both cyclisation, and ring fission of radical species is commonly referred to as the "stereoelectronic effect", and has been used by Beckwith[8,9] to explain the ring closure/fission reactions observed in free-radical rearrangements.

This stereoelectronic effect will be much used in subsequent sections in discussing the mode of β-scission observed for the radicals under investigation.

1.2 Background

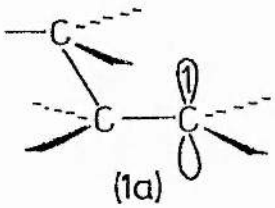
This study was undertaken with a view to elucidating the means by which homolytic ring fission occurs in small, strained cyclic compounds. Initially the study concerned a series of bicyclo[n.1.0]alkanes. This later developed into a study of spiro[2.n]alkanes, and also spiro[3.3]heptane.

Why, then are these compounds of interest?

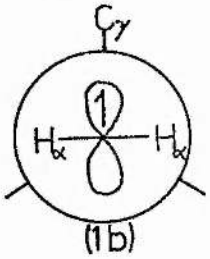
These compounds provide series of reasonably easily prepared molecules in which steric effects will alter as the value of n is increased, i.e. the ring size increases. This change in steric condition will be regular as n increases, with the difference between successive compounds not being so great as to completely alter the behaviour of the compound. Therefore, due to this systematic change in steric condition, the effect of this change on the mode of homolytic ring fission can be observed. It was anticipated that these observations would enable the mode of β-scission to be interpreted in terms of the different controlling factors of ring fission. This is of course of particular relevance in those compounds where more than one mode of β-scission is possible. It was a major objective to determine the effect of ring size on the mode of β-scission. Similarly, an increase in ring size may alter the rate of β-scission. In this case how, and why does the size of the ring affect the rate of ring opening?

These questions will be answered in the subsequent discussion.

The homolytic ring fission of cycloalkyl radicals by means of β-scission is interpreted as occurring most readily in those radical species in which the SOMO overlaps effectively with the β-γ bond,[4] as was discussed earlier. This conformation is desirable since it results in the greatest possible interaction of the SOMO with the σ* anti-bonding orbital of the β-γ bond. This, as shown earlier, comprises the stereoelectronic effect which is generally taken to be a prerequisite to β-scission, and is shown by (1a,b).



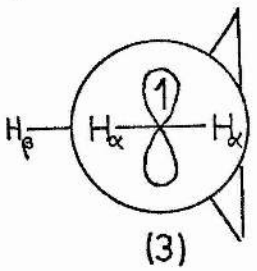
(1a)



(1b)

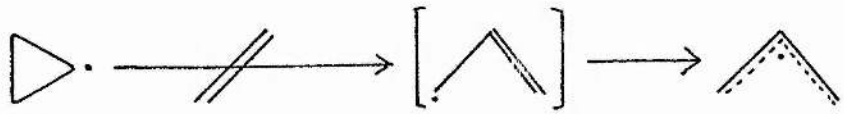
This stereoelectronic effect explains the relatively facile ring fission observed with cyclopropylmethyl radicals (2). At temperatures greater than 133K radical (2) ring opens to give but-3-enyl radicals.[10,11] The stable conformation of radical (2) is the eclipsed form (3).[10]

(2)



(3)

therefore expected. Cyclopropyl radicals (5) however do not ring open to give prop-2-enyl radicals in solution,[12,13] although ring fission can be observed at high temperatures. Because the rearrangement is



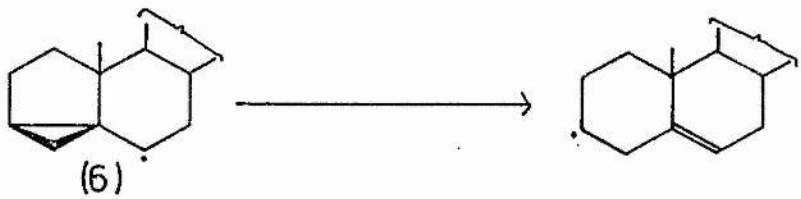
(5)

favoured thermodynamically, this cannot be the controlling effect. The stereoelectronic effect must take precedence. What, then is the stereoelectronic explanation for the slow rate of β-scission of the cyclopropyl radical (5)?

The cyclopropyl radical (5) possesses an anomalously low value for the α-hydrogen hyperfine splitting constant, $a(H_\alpha)$. The value of $a(H_\alpha)$ being $\underline{ca}$ 6.6G, c.f. the generally expected value of $\underline{ca}$ 21G for $a(H_\alpha)$ in alkyl radicals. This low value of $a(H_\alpha)$ reflects the fact that the radical centre is not planar. That is, the SOMO does not behave as a 'p' orbital perpendicular to the plane of the sp^2 hybridised carbon orbitals. Rather, the SOMO has appreciable 's' character and thus the cyclopropyl radical is a σ radical. With

this being the case the SOMO of radical (5) cannot overlap to any significant degree with the β-γ bond, as shown in the diagram above. Hence the absence of β-scission. Thus, since the stereoelectronic requirement necessary for β-scission is not met, the cyclopropyl radical is relatively stable to rearrangement via β-scission.

Similarly, the stereoelectronic effect explains why the product of β-scission is frequently that one, which in thermodynamic terms, is the less stable.[4,14,15] The simple explanation for this observation is that the $\beta-\gamma$ bond which breaks is that one which is more effectively overlapped by the SOMO. This explains the rearrangements, via β-scission, of examples (6-8).[14,15] In each of these examples



(6)

(7)

(8)

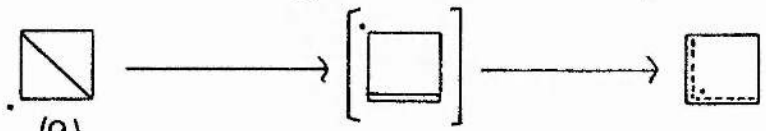
the $\beta-\gamma$ bond which breaks is that one with which the SOMO overlaps more effectively. The cyclohexyl radical generated by β-scission of (6) is more stable than the cyclopentylmethyl radical generated from radical (7). Thermodynamic factors therefore favour β-scission of the cyclopropane bond in radicals (6) and (7) to give a cyclohexyl radical. However, if molecular models of radicals (6) and (7) are constructed, it is observed that different cyclopropane bonds are overlapped more effectively by the SOMO.[14] In both radicals (6) and (7) β-scission of the $\beta-\gamma$ bond which is more effectively overlapped gives the observed products.[14] This observation is important as it

indicates that the conformation of a radical is very influential in determining the pathway of β-scission found in that radical.

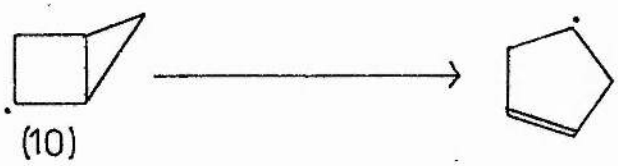
The stereoelectronic effect is therefore observed to be the major factor in the β-scission process.

However the question arises as to whether there exist examples of β-scission, in radical species, which are not governed by the aforementioned stereoelectronic effect.

Examples of radicals undergoing β-scission in a contrastereo--electronic manner do exist. Examples (9) and (10) show the ring opening of two bicycloalkyl radicals in a contrastereoelectronic



(9)



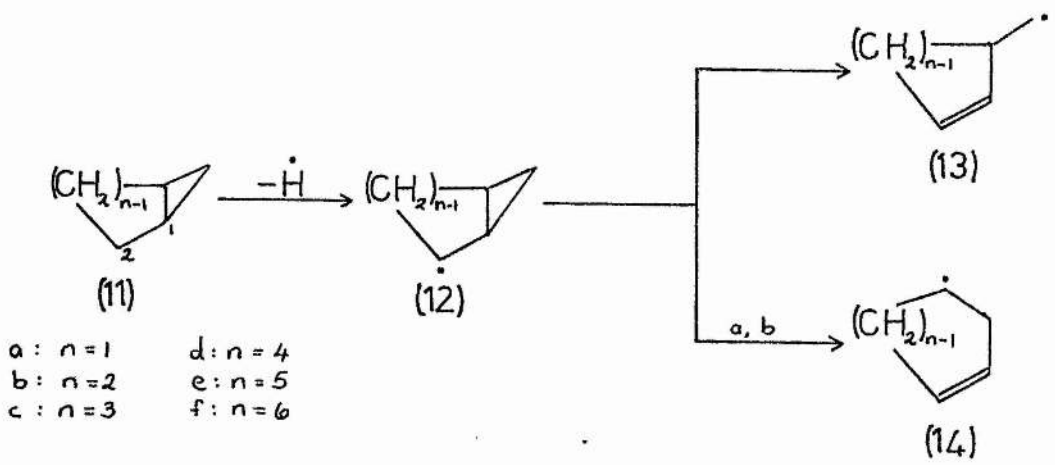
(10)

manner. Bicyclo[1.1.0]but-2-yl radicals (9), and bicyclo--[2.1.0]pent-2-yl radicals (10) undergo β-scission of the β-γ bond which is orthogonal to the SOMO,[16-18] i.e. the internal cyclopropane bond. The reason for this contrastereoelectronic ring opening lies, most probably, in ring strain effects which overcome the favourable stereoelectronic effect to external cyclopropane bond fission.

The bicyclo[n.1.0]alkanes (11) and the bicyclo[n.1.0]alk-2-yl radicals (12) derived from them, provide a series of cyclopropylmethyl like radicals in which the ring strain, and the degree of overlap of the SOMO, will change as n increases. [Hereafter radicals (9) and (10) are referred to as radicals (12a) and (12b) respectively.] Since the change in ring strain, and stereoelectronic effects will be systematic as n increases, the effect of either, or both, factors can be determined for the series. Since the result of β-scission was known for the first two members of the series, i.e. (12a,b), the higher members were studied, i.e. the species where n = 3-6. The results from the whole series, n = 1-6, are combined and discussed with a view to explaining the mode of β-scission adopted by any one member of the series.

Bicyclo[n.1.0]alkanes (11) will, on ^{1}H abstraction, provide a series of bicyclo[n.1.0]alk-2-yl radicals (12) which can undergo β-scission in one of two different modes (see Scheme 1). For radicals (12a,b) the mode of β-scission is known, but what of those radicals (12) where n $\geqslant$ 3?

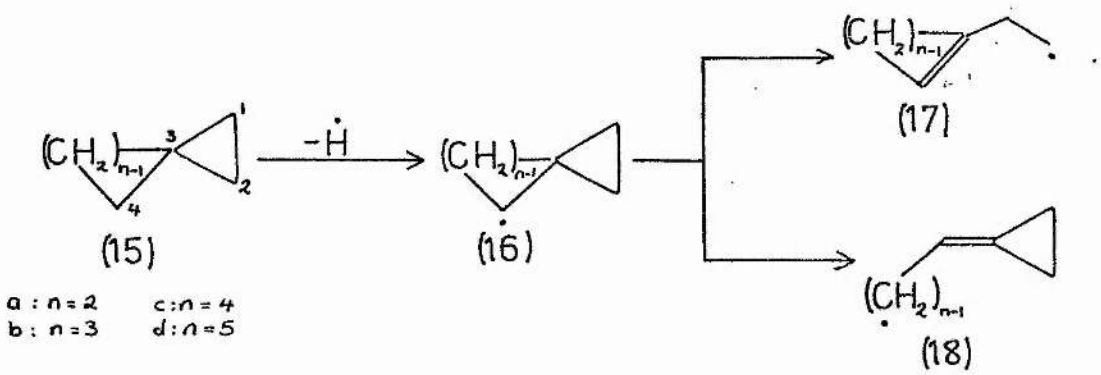
Scheme 1



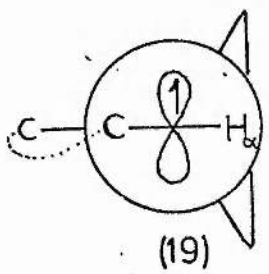
The study of the series of bicyclo[n.1.0]alkanes (11) and bicyclo[n.1.0]alk-2-yl radicals (12), where $n \geqslant 3$, is reported and discussed in Chapter 2 of this work.

The second series of compounds investigated was the spiro[2.n]alkanes (15) and the associated spiro[2.n]alk-4-yl radicals (16). These compounds provide a second series of cyclopropylmethyl like radicals which can ring open by β-scission (see Scheme 2).

Scheme 2

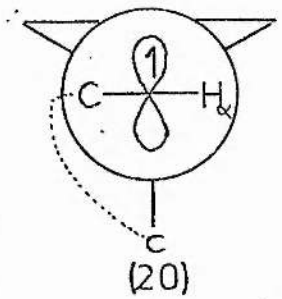


Spiro[2.n]alk-4-yl radicals (16) can therefore, in theory, undergo one of two modes of β-scission, either (i) or (ii). However route (ii) is unlikely by analogy with the cyclopropyl radical (5). The geometry of spiro[2.n]alk-4-yl radicals (16) is also more rigidly fixed, the radical having a conformation shown by (19). [N.B. The spiro[2.2]pent-4-yl radical (16a) does not adopt conformation (19) due to it possessing a non-planar radical centre, as is discussed later.]



(19)

This conformation (19) is however thought not to be conducive to β-scission. Kochi has indicated that β-scission is favoured by the adoption of conformation (20).[10] However, the rigid geometry of



(20)

radicals (16) would appear to preclude the adoption of this conformation. However, the β-scission of radicals (16) has been reported.[19] This is thought to indicate that though beneficial to β-scission the adoption of conformation (20) is not essential. Suzuki et al[19] observed that in the rearrangement of radicals (16c) and (16d) the greater yield of rearrangement products came from radical (16c), the spiro[2.4]hept-4-yl radical, than from the spiro[2.5]oct-4-yl radical (16d), which was unexpected. They felt that the larger ring radical (16d) could deform into conformation (20) more easily, than radical (16c), due to the more flexible ring.

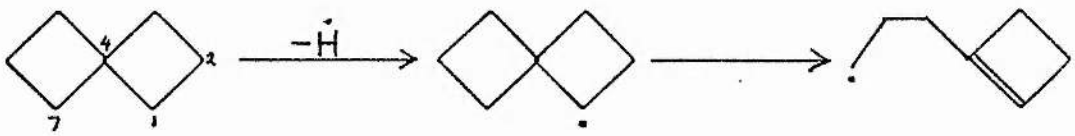
The first member of the series, spiro[2.2]pentane (15a), on generation of the spiro[2.2]pent-4-yl radical (16a), does not undergo β-scission readily.[20] The spiro[2.2]pent-4-yl radical, like the cyclopropyl radical (5), possesses an anomalously low value for $a(H_\alpha)$, i.e. ca 60. The small $a(H_\alpha)$ term indicates that radical (16a), like radical (5), is a σ radical. The SOMO possessing appreciable 's' character, and hence the radical centre is not planar. This prevents appreciable overlap between the SOMO and the β-γ bonds, and thus

explains the relative stability of radical (16a) to β-scission. Radical (16a) behaves more like a cyclopropyl radical (5) than a cyclopropylmethyl radical (2).

The work on spiro[2.n]alkanes is reported and discussed in Chapter 3.

Arising from the work on spiro[2.n]alkanes (15) attempts were made to observe the ring fission of spiro[3.3]heptane (21). Generation of the spiro[3.3]hept-1-yl radical (22) provides a cyclobutylmethyl like radical, which can ring open via β-scission (see Scheme 3). Cyclobutylmethyl radicals also ring open in a stereo-

Scheme 3



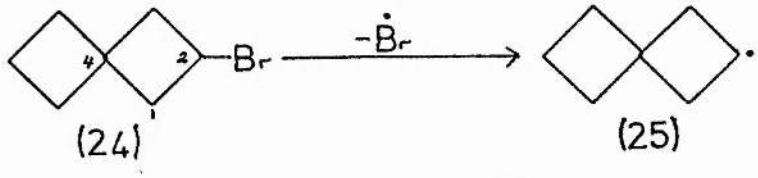
(21) (22) (23)

-electronically governed manner.[4] Compound (8) on page 11 showed an example of this. Ring fission of cyclobutylmethyl radicals however is much slower than that of cyclopropylmethyl radicals (2). The rate of β-scission of the cyclobutylmethyl radical has been determined.[21] At temperatures greater than ca 250K the cyclobutylmethyl radical undergoes β-scission, c.f. the cyclopropylmethyl radical which ring opens at temperatures greater than 133K. Assuming that cyclobutylmethyl like radicals, e.g. (22), behave in a similar manner, there is a greater likelihood of measuring the ring opening of

such radicals, e.g. (22), than of measuring that for cyclopropylmethyl like radicals.

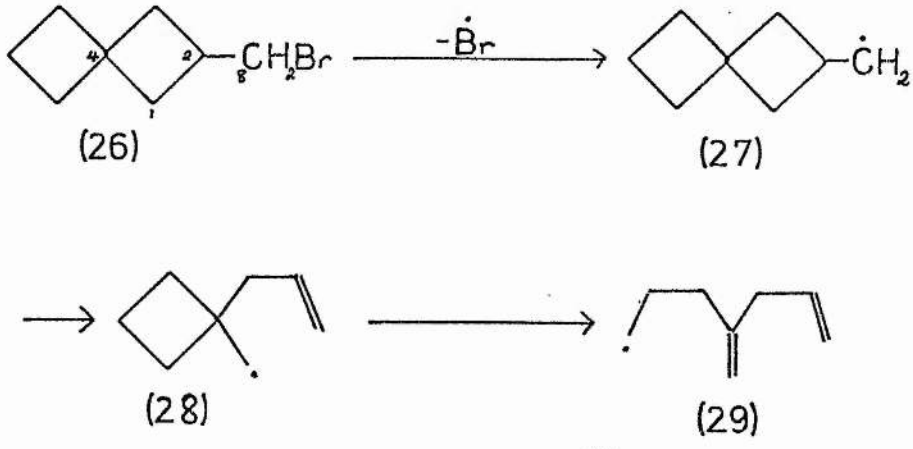
The preparation of spiro[3.3]heptane gives 2-bromo--spiro[3.3]heptane (24) as a synthetic precursor. Using tri-alkyl--tin radicals, bromine is abstracted to give the spiro[3.3]--hept-2-yl radical (25) (see Scheme 4). Radical (25) was observed. Naturally, radical (25) does not undergo β-scission, not being a cycloalkylmethyl type radical.

Scheme 4



Similarly <u>en route</u> to spiro[3.3]heptane (21), 2-(bromomethyl)--spiro[3.3]heptane (26) was prepared. Bromine abstraction from (26) gives a cyclobutylmethyl like radical (27) which can therefore ring open by β-scission to give radical (28) (see Scheme 5). Radical (28) is also a cyclobutylmethyl like radical and therefore can, in theory, undergo further β-scission to give radical (29).

Scheme 5



As these spiro[3.3]heptane derived products provide cyclobutylmethyl like radicals, and not cyclopropylmethyl like radicals, the work on them is reported and dicussed in a separate section, namely Chapter 4.

Chapter 5 of this work reports the synthetic details of the preparation of the compounds under investigation. A breakdown of the experimental results, including product identification, is also included in Chapter 5.

The work in Chapters 2-4 is divided into sections. Each section covers one particular aspect of the study of the compounds dealt with by that chapter.

The various aspects of the sections are discussed in the following text.

As stated initially, this work was aimed at observing the homolytic ring fission reaction, or reactions of bicyclo--[n.1.0]alkanes. This was later extended to encompass spiro[2.n]--alkanes, and spiro[3.3]heptane, plus associated compounds. The ring fission of a few of these compounds has been reported from the results

of product analysis studies. Such studies aim to determine the mode of ring fission by observing the products obtained. However, this method is far from ideal since the observed product mixtures are, in many cases, quite complex. This can lead to incomplete resolving of components. This in turn results in uncertainties in the identification of the components. Also, the possibility exists that a product is formed by more than one reaction mechanism. This again brings uncertainty.

To remove doubts as to the nature of the β-scission process, the radicals present were observed using the e.s.r. technique. In principle this allows the observation of any radical generated, or any radical resulting from rearrangement of the initial radical. In theory radical species are detectable by e.s.r. in concentrations as low as 10^{-8} mol l^{-1}. In practice this limit is, perhaps, too low as the signal to noise ratio of the e.s.r. spectrometer will limit the sensitivity obtainable for very low radical concentrations. The observation of the unrearranged radical species, aside from concentration requirements, necessitates that the ring fission process is sufficiently slow that the radical has an appreciable lifetime. This requires the radical to undergo rearrangement at a temperature greater than the minimum temperature at which spectra can be observed. The minimum temperature being just higher than that at which the sample freezes. In this work no spectra were recorded at temperatures lower than ca 90K, since no solvent system was accessible which would allow a lower operating temperature.

The e.s.r. technique allows positive identification of the product of β-scission, provided of course that such a product is detectable. It also enables the configuration, and conformation of the observed radical to be determined.

Accordingly the initial section of each discussion chapter covers a study of ^{1}H abstraction from the appropriate compounds. In this section the recorded e.s.r. spectra are shown, where relevant. Computer drawn simulations are also shown. For symmetrical radical spectra only the low-field half of the e.s.r. spectrum is shown. Complete e.s.r. spectra are shown if the recorded spectrum was unsymmetrical. Unless otherwise indicated the scan width was 100G. The hyperfine splittings (h.f.s.) determined from the spectra are tabulated in the appropriate text, all h.f.s. parameters being quoted in Gauss. The rearrangement of the generated radical species is discussed by examining the conformation of the unrearranged radical species. The ring opening is assessed in terms of the stereoelectronic effect known to govern β-scission. The rearrangement is also discussed in terms of relief of ring strain.

For those rearrangements where both unrearranged and rearranged radicals were observed the initial e.s.r. section is followed by a section reporting the results of a kinetic e.s.r. experiment.

The kinetic e.s.r. technique used was that developed by Ingold *et al.*[22-24] In this method discrete lines of the e.s.r. spectrum of both rearranged (R) and unrearranged (U) radicals are observed over a series of temperatures. this temperature range covers from when only radical (U) is detected, up to the temperature when only radical (R) is detected. The operating conditions of the e.s.r. spectrometer, temperature excepted, are maintained at the same values throughout. At each temperature point a ruby signal was also recorded. This measurement takes into account the effect of temperature on line height. Ideally this effect is negligible. In practice however, it is found that line height is slightly affected by temperature. A ruby sample, which gives a constant signal was therefore utilised at each temperature for normalisation. Using the same sample tube as was used in the kinetic e.s.r. experiment the signal of a known concentration of a persistent radical species was recorded. In the kinetic work covered here the radical used was 2,2-diphenyl-1-picrylhydrazyl (DPPH) in benzene solution. Finally an accurate calibration of the temperature control guage of the e.s.r. spectrometer was carried out. The signals recorded for the radical species, (R) and (U), and the signal recorded for the DPPH radical were doubly integrated by hand. The data so obtained was used to calculate values for the concentration of the unrearranged, [U], and rearranged, [R], radicals at each temperature using expression (1). This expession uses radical (U) as an example, the equation being analagous for radical (R).

$$[U] = [DPPH] \cdot \frac{w_u}{w_{DPPH}} \cdot \frac{G_{DPPH}}{G_u} \cdot \frac{(0.1)^2}{(1)^2} \cdot \frac{R_{DPPH}}{R_u} \cdot \frac{T_u}{T_{DPPH}} \cdot c_u \qquad (1)$$

where [U] is the concentration of radical (U) in mol l^{-1}

[DPPH] is the concentration of DPPH in mol l^{-1}

w is the weight of the doubly integated e.s.r. signal

G is the gain set on the e.s.r. spectrometer

R is the height of the ruby signal

T is the temperature at which the signal was recorded

c is a constant term which is used to allow for the fact that the line of the e.s.r. spectrum which was recorded was only a fraction of the whole spectrum

The subscripts refer to which radical the above terms apply to.

Thus, using epression 1, values of [R] and [U] are calculated for each of the observed temperatures.

Within the reaction sample radicals, (U) and (R), are removed by the reaction pathways shown below.

$$U \xrightarrow{k_r} R$$

$$\left.\begin{array}{ll} 2\ U \xrightarrow{2k_t} & \\ U + R \xrightarrow{2k_t} & \\ 2\ R \xrightarrow{2k_t} & \end{array}\right\} \text{non radical products}$$

Using the steady-state approach,[23,24] and assuming $2k_t$ is the same for all three termination reactions, these reaction processes are combined to give expression (2).

$$k_r/2k_t = \{[R]^2/[U]\} + [R] \quad (2)$$

Thus, for each temperature reading values of $k_r/2k_t$ are determined. The value of $2k_t$ for the radical termination reactions undergone by the radicals, (U) and (R), in the sample is unknown. However, a general value for $2k_t$ is assumed. For the kinetic e.s.r. experiments investigated the value of $2k_t$ is assumed to be equal to the value of $2k_t$ calculated for the n-pentyl radical.[21] This value of $2k_t$ is given by expression (3).

$$\log(2k_t/dm^3mol^{-1}s^{-1}) = (12.3 \pm 0.7) - (10.5 \pm 3.0/kJmol^{-1})/2.3RT \quad (3)$$

Using expression (3) values of $2k_t$ are calculated for each temperature reading. Hence the values of k_r are determined for each temperature reading. The values of k_r and T are plotted on a graph of $\log(k_r)$ against 1/T. This plot gives a straight line of the general form shown by expression (4).

$$\log(k_r) = c + m/T \quad (4)$$

where c is the intercept

m is the gradient

Using a least squares fit analysis the values of c and m are determined.

However, the kinetic rate equation for the rearrangement of radical (U) is given by expression (5).

$$k_r = A\, e^{-E/RT} \qquad (5)$$

where A is the pre-exponential (Arrhenius) factor, and E is the activation energy for the rearrangement

Expression (5) however can also be given by expression (6).

$$\log(k_r/s^{-1}) = \log A + (-E/2.3RT) \qquad (6)$$

Expression (6) is therefore a particular example of the general expression (4) in which c is equivalent to log A, and m is equivalent to -E/2.3R.

Therefore, from the least squares fit analysis values of c and m, the values of A and E for the rearrangement are determined. The least squares fit analysis of the $\log(k_r)$ against 1/T data also gives a correlation coefficient for the fit of the experimental data to the calculated straight line.

The next section in each chapter reports the findings of semi-empirical SCF-MO calculations carried out on the parent hydrocarbon, the unrearranged radicals, and the rearranged radicals. For the rearrangement reaction the calculations were used to determine

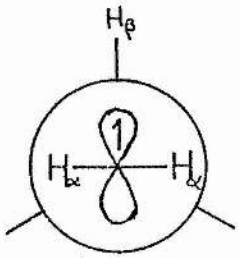
the enthalpy of activation, $\Delta H^{\ddagger}$, and the enthalpy of reaction, ΔH°.

The calculations were carried out using the MNDO method of Dewar and Thiel,[25,26] and the MINDO/3 method of Dewar *et al.*[27,28] This latter method is reported to possess certain advantages in the study of radicals.[18,25] Using the MNDO derived geometries, the conformations of the unrearranged radicals were examined.

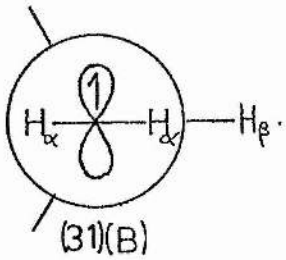
The next section describes the experimental determination of the conformations and barriers to internal rotation of the cyclo--alkylmethyl and cycloalkylethyl radicals.

The β-hydrogen hyperfine splitting, $a(H_\beta)$, of alkyl radicals is known to be temperature dependant. From the behavior of $a(H_\beta)$ with respect to temperature, i.e. $da(H_\beta)/dT$, the conformation of a radical can be determined.[29]

For an alkyl radical with a single β-hydrogen, a large absolute magnitude of $a(H_\beta)$, and a negative sign to $da(H_\beta)/dT$ proves that the radical adopts the eclipsed conformation (30)(E) preferentially. Similarly a small absolute magnitude of $a(H_\beta)$, and a positive sign to $da(H_\beta)/dT$ proves that the radical adopts the bisected conformation (31)(B) preferentially.

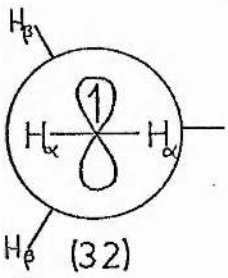


(30)(E)

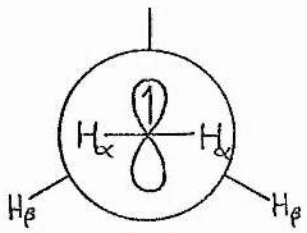


(31)(B)

For alkyl radicals in which there are two β-hydrogens the case is slightly different. Here a large absolute magnitude of $a(H_\beta)$, and a negative sign to $da(H_\beta)/dT$ proves that the radical adopts conformation (32) preferentially. A small absolute magnitude of $a(H_\beta)$, and a positive sign to $da(H_\beta)/dT$ proves that the radical adopts the perpendicular conformation (33) preferentially.



(32)



(33)

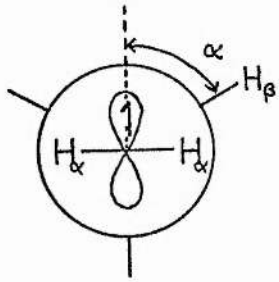
In the absence of $da(H_\beta)/dT$ data, the absolute magnitude of $a(H_\beta)$ is often sufficient to indicate the conformation adopted.

These examples all show two α-hydrogens. Where substitution of H_α occurs the change in steric condition can affect the conformation adopted. However, in this study all of the radicals for which conformations are determined possess two α-hydrogens.

In general a value of $a(H_\beta)$ greater than ca 27G indicates the adoption of conformations (30) or (32), whereas a value of $a(H_\beta)$ less than ca 27G indicates conformations (31) or (33) are adopted. This cut-off point of ca 27G is found since in the case where free rotation

about C-C is observed, i.e. the ethyl radical, the value of $a(H_\beta)$ is found to be ca 26.9G.[30]

Therefore, there exists a direct connection between the conformation of the radical and the magnitude of $a(H_\beta)$. In fact the magnitude of $a(H_\beta)$ is related to the dihedral angle, α, between the SOMO and the C_β-H_β bond. The relationship between $a(H_\beta)$ and α is given by expression (7).



$$a(H_\beta) = A + B\cos^2\alpha \qquad (7)$$

where both A and B are constants

In general A is found to be zero, or slightly positive in value, ca 2-3G.

Logic dictates that $a(H_\beta)$ is minimised when $\alpha = 90^\circ$, i.e. $\cos^2\alpha = 0$. In this conformation $a(H_\beta)$ is given by A. The minimum value of $a(H_\beta)$ is expected at $\alpha = 90^\circ$ because in this situation the C_β-H_β bond lies in the nodal plane of the SOMO. As a result the interaction between the SOMO and the C_β-H_β bond is slight. Correspondingly $a(H_\beta)$ is maximised at $\alpha = 0^\circ$, i.e. $\cos^2\alpha = 1$, in which case $a(H_\beta)$ is given by A + B. This conformation results in the eclipsing of the C_β-H_β bond by the SOMO, and hence results in maximum interaction between the SOMO and the C_β-H_β bond. As a result $a(H_\alpha)$ is maximised.

For the ethyl radical, in which free rotation about $\dot{C}-C_\beta$ is assumed the value of $a(H_\beta)$ is ca 26.9G.[30] This is given by A + 1/2B, where A is assumed to be zero and B is calculated to be ca 53.8G.

The ethyl radical is however a special case. In general alkyl radicals with two α-hydrogens display a two-fold barrier to rotation about $\dot{C}-C_\beta$, as shown by Figure 1.

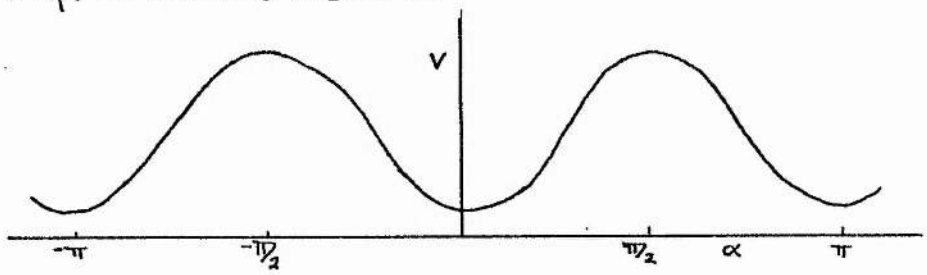


Figure 1 : The two-fold rotational barrier about $\dot{C}-C_\beta$.

The barrier to rotation is measured by V. For the two-fold barrier shown in Figure 1, V is calculated by using expresssion (8).

$$V_\alpha = V_o/2\ (1-\cos 2\alpha) \qquad (8)$$

where V_α is the value of V at angle α.

V_0 is the value of V when $\cos 2\alpha = 1$, i.e. the potential minimum.

α is the dihedral angle between the SOMO and the $C_\beta-H_\beta$ bond.

The radical species will populate the discrete, allowed energy levels, within the potential wells shown in Figure 1, following a Boltzmann distribution of energy levels. Using this Boltzmann distribution of energy level population it is possible to calculate the average value of $a(H_\beta)$ using expression (9).

$$\langle a(H_\beta)\rangle = \frac{\sum_{i=0}^{\infty} a(H_\beta).\exp(-V/kT)}{\sum_{i=0}^{\infty} \exp(-V/kT)} \qquad (9)$$

By introducing $\alpha = \theta + \theta_o$, where θ_o is the phase angle, and by combining expressions (7) and (8) into expression (9), a new expression (10) is derived.

$$\langle a(H_\beta)\rangle = \frac{\sum_{i=0}^{\infty} (A+B\cos^2(\theta+\theta_o)).\exp(-V_o(1-\cos 2(\theta+\theta_o))/2kT)}{\sum_{i=0}^{\infty} \exp(-V_o(1-\cos 2(\theta+\theta_o))/2kT)} \qquad (10)$$

Expression (10) is the form arrived at by using a quantum mechanical approach. Using this method Fessenden[31] predicted the V_o values for a number of alkyl radicals. However, this procedure is extremely cumbersome, and the evaluation of it requires considerable time. This is mainly because, before the Boltzmann distribution can be evaluated, the allowed energy levels must themselves be calculated using quantum theory. Thus, a more accessable form of (10) would be advantagous in calculating V values.

A different approach to the problem assumes that, instead of discrete, allowed energy levels, the energy difference between levels tends to zero such that an infinite number of energy levels is possible. Thus an energy continuum is achieved. In this continuum all energy levels between the minimum and maximum are permissible, and consequently all values of the dihedral angle are permissible. This approximation is used in the classical limit approach as detailed by Kochi.[29,32] Using this method expression (11) is derived.

$$\langle a(H_\beta)\rangle = \frac{\int_{-\pi}^{\pi} (A+B\cos^2(\theta+\theta_o)) \exp(-V_o(1-\cos 2(\theta+\theta_o))/2kT)\, d\theta}{\int_{-\pi}^{\pi} \exp(-V_o(1-\cos 2(\theta+\theta_o))/2kT)\, d\theta} \qquad (11)$$

Expression (11) reduces to the analytical expression (12).[33]

$$a(H_\beta) = A + 1/2B + 1/2B\cos 2\theta_0[I_1(\lambda)/I_0(\lambda)] \qquad (12)$$

where I_1 and I_0 are modified (hyperbolic) Bessel functions.

$\lambda = V_0/kT$

θ_0 is the dihedral angle at the potential minimum.

A and B are constants, A being zero or slightly positive.

Using expression (12), and by choosing appropriate values for A, B, and V_0, the experimental values of $a(H_\beta)$ are fitted to curves drawn from calculated values of $a(H_\beta)$. The values of A, B, and V_0 being altered such that the best possible fit is achieved.

The barrier, V_0, can also be calculated by semi-empirical calculations using the INDO method of Pople and Beveridge.[34]

The final sections of Chapters 2 and 3 report the results of the photobromination of the appropriate compounds.

Homolytic ring fission of cyclopropanes can be brought about by a displacement reaction with halogens,[35,36] i.e. a bimolecular homolytic substitution (S_H2) reaction.

The iodination of bicyclo[1.1.0]butane (11a) resulted in the exclusive formation of 1,3-di-iodocyclobutane via internal cyclopropane bond fission.[37] Chlorination and bromination reactions gave more complex product mixtures.[37] Similarly the bromination of bicyclo[2.1.0]pentane (11b) gave products which came mainly from almost exclusive fission of the internal cyclopropane bond.[17]

Photochlorination of spiro[2.2]pentane (15a) gave 1,1-bis-(chloromethyl)cyclopropane from the S_H2 reaction.[19] Applequist and Landgrebe[38] showed that the photochlorination of spiro[2.3]hexane (15b) gave products from both the S_H2 reaction of (15b) and from the β-scission of the spiro[2.3]hex-4-yl radical (16b). Similar studies on spiro[2.4]heptane (15c) gave products predominantly from the β-scission of the spiro[2.4]hept-4-yl radical (16c).[39]

In Chapter 2 the results of the photobromination of bicyclo[3.1.0]hexane (11c) and bicyclo[4.1.0]heptane (11d) are reported. Chapter 3 includes the results of the photobromination of spiro[2.3]hexane (15b).

Chapter 2

BICYCLO[n.1.0]ALKANES

and

BICYCLO[n.1.0]ALK-2-YL RADICALS

A Study of Homolytic Ring Fission

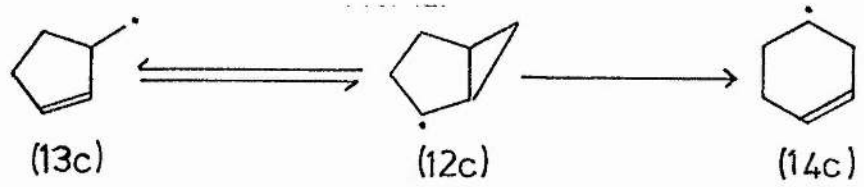
2.1 Introduction

As stated previously in Chapter 1 bicyclo[n.1.0]alkanes (11) and the associated bicyclo[n.1.0]alk-2-yl radicals (12) derived from (11) provide a series of cyclopropylmethyl like radicals in which the ring strain, and degree of overlap between the SOMO and the $\beta-\gamma$ bonds vary in a systematic manner, as the value of n is increased.

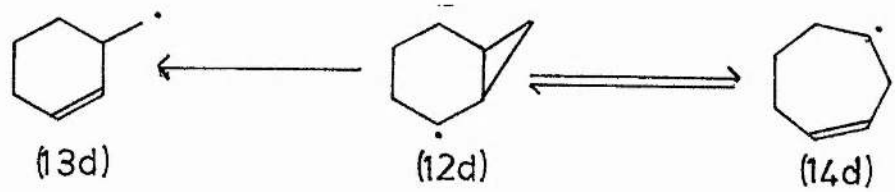
There exists in the literature a considerable body of work in which the radical rearrangements of bicyclo[n.1.0]alk-2-yl radicals (12) have been studied. These studies have been mainly carried out on the bicyclo[3.1.0]hex-2-yl (12c), and bicyclo[4.1.0]hept-2-yl (12d) radicals, and have all been of a reaction product analysis type. There has been no detailed examination of bicyclo[n.1.0]alk-2-yl radicals (12) and their rearrangement by the e.s.r. technique.

Freeman *et al*[39] showed that the chlorination of bicyclo[3.1.0]hexane (11c) results in products in which little, if any, rearrangement had occurred. However, they also reported that in the radical chloroformylation of (11c) a considerable degree of rearrangement occurred, with approximately equal amounts of products resulting from β-scission of the internal, and external cyclopropane bonds. Similarly Friedrich and Holmstead[40] reported that generation of radicals (12c) and (12d) by tri-n-butyl tin hydride reduction of the corresponding bicyclo[n.1.0]alkyl chlorides, resulted in products which were mainly derived from external cyclopropane bond fission. In much earlier work, Slaugh[41] had reasoned that the rearrangement of

cyclopentenylmethyl radicals (13c) to cyclohexenyl radicals (14c) occurred via a bicyclo[3.1.0]hex-2-yl radical (12c) intermediate,[41] his findings being shown by the scheme below. Rearrangement of



radical (14c) was not found.[40] Both Freeman[39] and Friedrich[40] used this scheme to rationalise their respective observations. Friedrich[40] also showed that cycloheptenyl radicals (14d) rearrange to cyclohexenylmethyl radicals (13d) through a bicyclo[4.1.0]hept-2-yl radical (12d) intermediate, but the reverse rearrangement does not occur.



Similar patterns of rearrangement of the radical species (12c) and (12d) have been reported by Dauben *et al*[42] in their study of the photoreduction of the corresponding bicyclo[n.1.0]alkan-2-ones, and in the reduction of the bicyclo[n.1.0]alkan-2-ols. In the photoreduction of bicyclo[n.1.0]alkan-2-ones (n = 3,4) Dauben *et al* found no trace of any product which came from internal cyclopropane bond fission, rather they noted that β-scission was confined exclusively to the external cyclopropane bond. In the reduction of the corresponding bicyclo[n.1.0]alkan-2-ols, they observed that bicyclo--[4.1.0]heptan-2-ol gave mainly products resulting from a

cyclohexenylmethyl radical. Whereas, though the reduction of bicyclo[3.1.0]hexan-2-ol gave mainly products from a cyclopentenylmethyl radical at ambient temperatures, an increase in temperature resulted in approximately equal amounts of products from both cyclopentenylmethyl and cyclohexenyl radicals. No analogous temperature effect was observed with bicyclo[4.1.0]heptan-2-ol.

From these studies it would appear that the bicyclo[n.1.0]alk-2-yl radicals (12), where $n > 3$ rearrange by β-scission of the external cyclopropane bond to give cycloalkenylmethyl radicals (13), though the case for $n = 3$, i.e. (12c), is perhaps more ambiguous in that fission of both internal and external cyclopropane bonds can occur giving radicals (14c) and (13c) respectively. This latter observation may conceal a temperature effect, whereby formation of radical (14c) is favoured at increased temperatures.

It was with these observations in mind that this study was instigated. Furthermore, this work on the bicyclo[n.1.0]alkanes, where $n \geqslant 3$ built upon that already carried out on the $n = 1,2$ members of the series. Both bicyclo[1.1.0]but-2-yl radicals (12a)[16] and bicyclo[2.1.0]pent-2-yl radicals (12b)[17,18] have been shown to rearrange via β-scission of the internal cyclopropane bond, as shown in Chapter 1 (p. 12). Radicals (12a) and (12b) undergo β-scission in a contrastereoelectronic manner. Hence the interest in those radicals (12) where $n \geqslant 3$. The effect of ring size on the β-scission of radicals (12) is therefore observed, with a view to observing if the subsequent members of the series, i.e. radicals (12) where $n \geqslant 3$,

undergo β-scission in a stereoelectronically governed manner.

It was felt that bicyclo[n.1.0]alk-2-yl radicals (12) could be generated quite easily from the corresponding hydrocarbon (11) as Freeman *et al*[39] showed that for hydrocarbon (11c) ^{1}H abstraction at C(2) is favoured.

As part of the study the intention was to generate radical (12c) via chlorine abstraction from 2-chlorobicyclo[3.1.0]hexane using trialkyltin, or trialkylsilyl radicals. These attempts however met with failure as is reported in the experimental section (p. 124). No e.s.r. signals were detectable.

Similarly it had been hoped to observe both radicals (12) and the rearranged radical, either (13) or (14). In this case a kinetic e.s.r. experiment would be possible. This was however not possible as will be seen subsequently.

2.2 Results and Discussion

(a) The E.S.R. Study of ^{1}H Abstraction from Bicyclo[n.1.0]alkanes (11)

Samples of bicyclo[n.1.0]alkane (11) along with di-tert-butyl peroxide (DTBO) were thoroughly degassed, for samples which were to be used at T < 240K cyclopropane, or n-propane was added as the hydrocarbon solvent. For T > 240K neat DTBO acted as the solvent. The degassed samples were sealed and photolysed within the cavity of

the e.s.r. spectrometer using a medium pressure Hg arc. All spectra were recorded at ca. 9.4GHz.

^{1}H abstraction from a sample of bicyclo[3.1.0]hexane (11c) at 220K resulted in the observation of the spectrum shown in Figure 2. The spectrum consists of a doublet of triplets with hyperfine splittings (h.f.s.) arising from two α-hydrogens and a single β-hydrogen. Each component shows further fine structure, which is not fully resolved, from γ-, and possibly δ-hydrogens. The h.f.s.

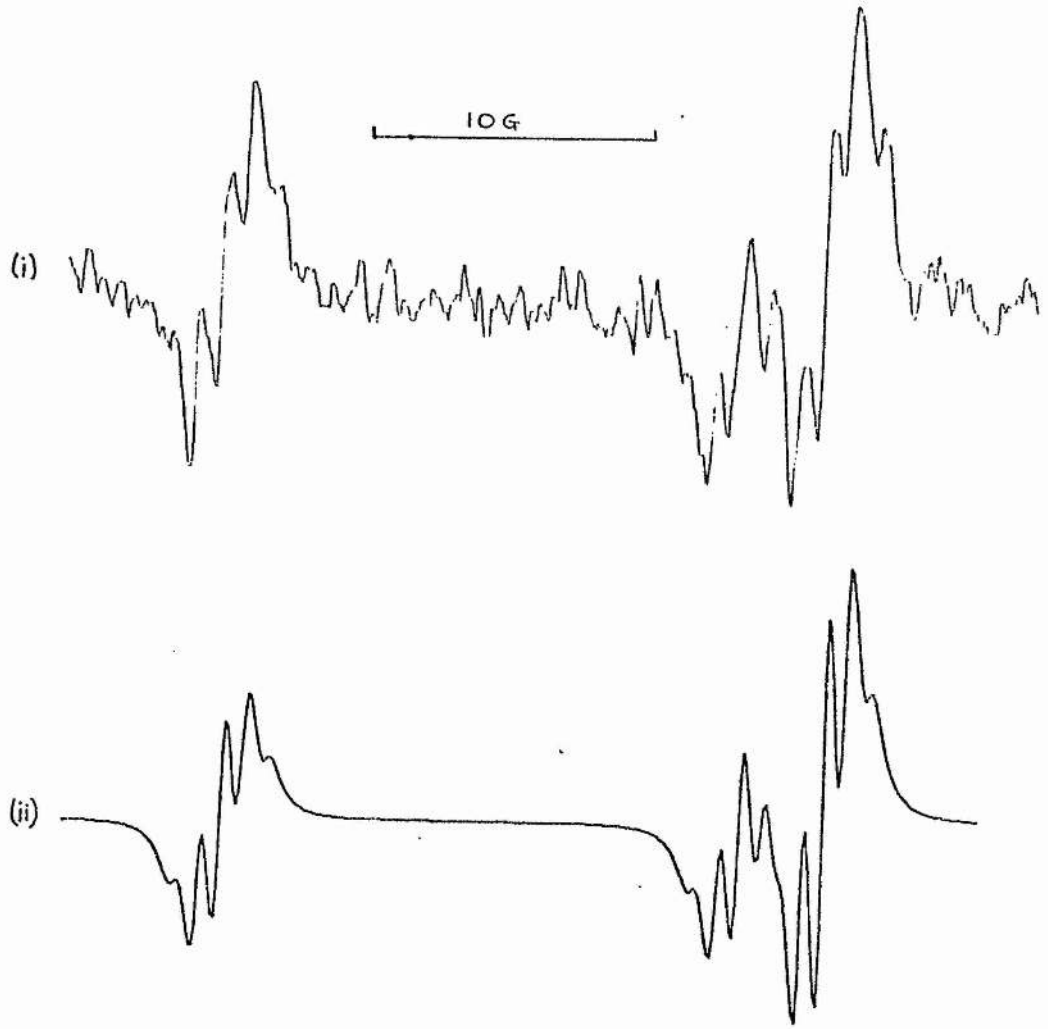


Figure 2. Low field half spectra of cyclopentenylmethyl radicals (13c) at 9.4GHz. (i)observed at 220K, (ii)simulation

parameters are given in Table 1. The computer simulation was drawn using these parameters. The h.f.s. values derived from the spectrum are very similar to those found for the cyclopentylmethyl radical.[33] Accordingly the spectrum was assigned to the cyclopentenylmethyl radical (13c). This was the only spectrum observed down to ca 160K, below which no radicals were detected.

^{1}H abstraction from bicyclo[4.1.0]heptane (11d) at 150K gave the spectrum shown in Figure 3. This spectrum consists of a doublet of triplets with h.f.s. arising from two α-hydrogens and a single β-hydrogen. At temperatures below 160K the fine structure was fully

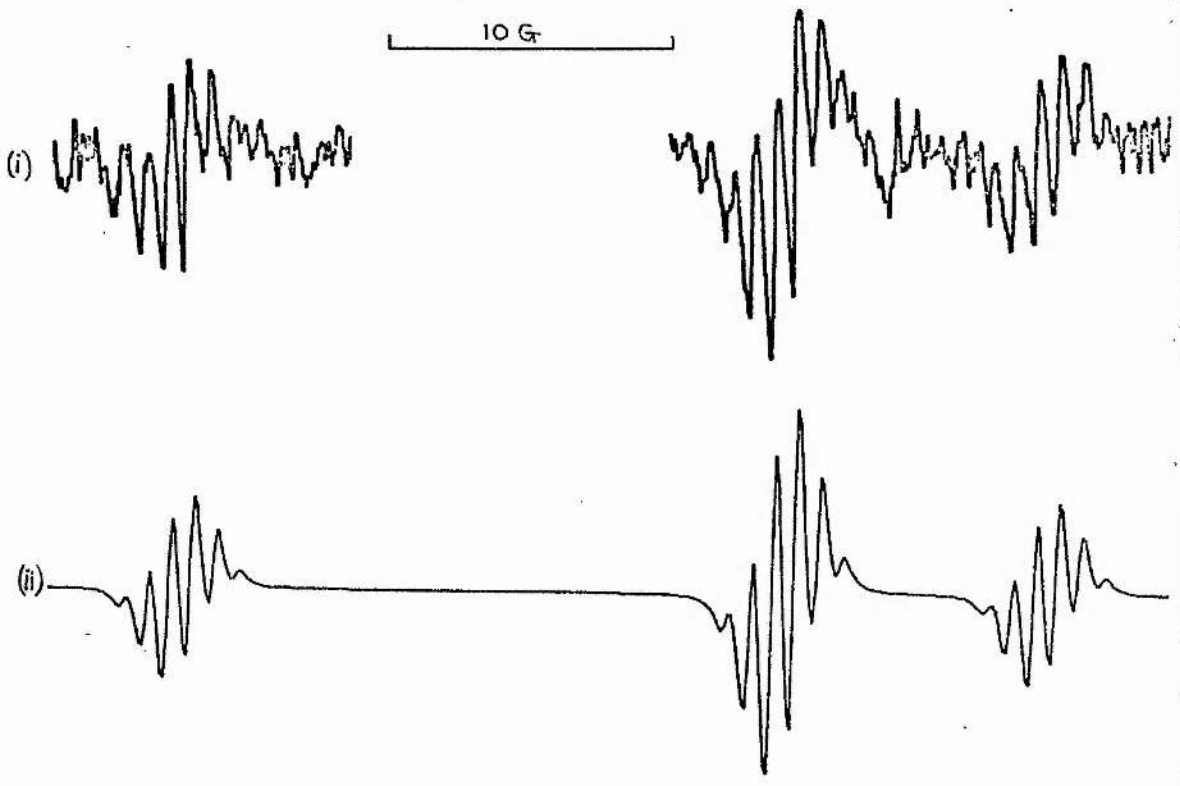


Figure 3. Low field half spectra of cyclohexenylmethyl radicals (13d) at 9.4GHz. (i)observed at 150K, (ii)simulation

resolved and arose from the coupling to five γ -, and δ - hydrogens. The h.f.s. parameters measured are given in Table 1. The computer simulation was drawn using these parameters. The h.f.s. values recorded are very similar to those of the cyclohexylmethyl radical.[33] The spectrum was thus assigned to the cyclohexenylmethyl radical (13d)

Table 1

E.s.r. derived h.f.s. parameters for cycloalkenylmethyl radicals (13)

Radical	T/K	h.f.s. /G
13c	220	($2H_\alpha$) 21.5 , (H_β) 18.5 , (>4H) 0.8
13d	150	($2H_\alpha$) 21.6 , (H_β) 30.8 , (5H) 0.8
13e	240	($2H_\alpha$) 21.5 , (H_β) 28.4
13f	230	($2H_\alpha$) 21.5 , (H_β) 31.4

The unusual resolving of the δ-hydrogens h.f.s. confirms this assignment as this is also observed in the structurally related but-3-enyl radical.[29] Davies *et al*[43] report that ^{1}H abstraction from the 2-trimethyl-stannyloxy derivative of (11d) at *ca* 186K resulted in an e.s.r. spectrum consisting of a doublet of triplets with h.f.s. parameters of ; a($2H_\alpha$) 21.5G and a(H_β) 25.7G : a small h.f.s. of a(3H) 0.7G was also noted. This spectrum was assigned to the trimethyl-stannyloxy derivative of the cyclohexenylmethyl radical. This observation by Davies *et al*[43] gives further weight to the assignment made earlier for the cyclohexenylmethyl radical (13d). This was the only radical observed down to *ca* 110K, below which no radicals were detected.

On ^{1}H abstraction from samples of bicyclo[5.1.0]octane (11e) and bicyclo[6.1.0]nonane (11f) the spectra of the cycloheptenylmethyl (13e) and cyclo-octenylmethyl (13f) radicals were observed. The h.f.s. parameters for both radicals are given in Table 1. Both of these spectra were very weak, and the presence of other radical species, though not radicals (14e) or (14f), was noted.

It was therefore seen that the bicyclo[n.1.0]alkanes (11), where $n \geqslant 3$ gave rise, on ^{1}H abstraction, to bicyclo[n.1.0]alk-2-yl radicals (12) which undergo rapid β-scission of the external cyclopropane bond to give cycloalkenylmethyl radicals (13). No bicyclo[n.1.0]alk-2-yl radicals were detected. This is the reason why the kinetic e.s.r. experiment was not possible. Similarly, for the radicals (12), where $n \geqslant 3$, the presence of cycloalkenyl radicals (14) was not detected. This observation does not rule out the presence of minor amounts of radicals (14). Rather, this only reflects the poor nature of the signal to noise ratio of the e.s.r. spectrometer which does not allow detection of minor component radicals. Davies *et al*[43] drew a similar conclusion, and did not rule out the possibility of *ca* 10% cycloalkenyl radicals.

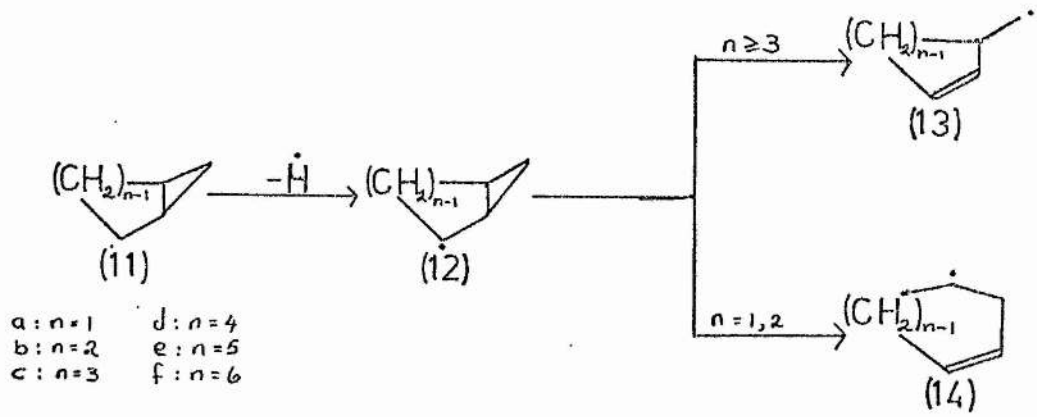
The findings of the e.s.r. experiment are therefore very much in agreement with those of Friedrich and Holmstead,[40] in that the bicyclo[n.1.0]alk-2-yl radicals (12), where $n \geqslant 3$, rearrange by β-scission of the external cyclopropane bond to give cycloalkenylmethyl radicals (13) as the major product. Their observation of small amounts of cycloalkenyl radical (14) products is

not in disagreement with the e.s.r. findings. This reflects rather on the inability of the latter to detect minor component radicals.

Thus the behaviour of those radicals (12) where $n \geq 3$ has been observed. How then, does this behaviour compare with that of radicals (12) where n = 1,2 , i.e (12a) and (12b)? As stated earlier, the ring opening of these radicals (12a,b) has been studied quite extensively. These studies show that both radicals (12a) and (12b) undergo β-scission of the internal cyclopropane bond to give cycloalkenyl radicals (14).[16,17,18,44]

Thus the behavior of radicals (12a,b) contrasts significantly with that of radicals (12c-f). There exists a sharp division between n = 2 and n = 3 radicals (12) as to which $\beta - \gamma$ bond is broken in the ring opening process. Thus Scheme 1 from page 13 can be amended to Scheme 6.

Scheme 6



Thus a change in the mode of β-scission occurs. Why does this change occur?

An examination of the conformation of the radicals (12) will allow the determination of which $\beta-\gamma$ bond overlaps more effectively with the SOMO of radical (12).

In order that this could be carried out, it was assumed that the conformation of the bicyclo[n.1.0]alk-2-yl radical (12) is not wholly dissimilar to that of the corresponding bicyclo[n.1.0]alkane (11).

Bicyclo[3.1.0]hexane (11c) is known to adopt a boat like conformation preferentially.[45,46,47] In this conformation the SOMO is found to overlap with both $\beta-\gamma$ bonds to a similar degree, though with perhaps greater overlap with the external cyclopropane bond. If the degree of puckering of the cyclopentyl ring is reduced, i.e. distorted into a more planar form, the degree of overlap with the external cyclopropane bond increases. This is perfectly feasible as the cyclopentyl ring of radical (12c) is likely to be less puckered than in the alkane (11c) due to the planar radical centre. Bicyclo[4.1.0]heptane (11d) is known to adopt a chair,[40] or "semi-chair"[46] conformation of the cyclohexane ring. With these conformations the SOMO is found to overlap more effectively with the external cyclopropane bond. Both bicyclo[n.1.0]alkanes (11e) and (11f), are assumed to adopt chair like conformations, though the exact conformation will be somewhat less rigidly fixed than is the case with (11d). This conformation of (11e) and (11f) again results in greater

overlap between the external cyclopropane bond and the SOMO. Bicyclo[1.1.0]butane (11a) adopts a "butterfly-wing" type conformation,[48] which results in greater overlap between the SOMO and the external cyclopropane bond. Bicyclo[2.1.0]pentane (11b) adopts a "semi-boat" conformation.[49,50] This conformation results in greater overlap between the SOMO and the external cyclopropane bond. Only with bicyclo[n.1.0]alkanes, where $n \geqslant 4$, can the SOMO be made to overlap more effectively with the internal cyclopropane bond, and this is only found in the less preferred boat conformation. Thus for all bicyclo[n.1.0]alkanes (11) it is evident that the conformation of the bicyclo[n.1.0]alk-2-yl radical (12) indicates that the external cyclopropane bond overlaps more effectively with the SOMO. This of course assumes the same, or similar, conformations of radicals (12) and the corresponding hydrocarbons (11). Therefore, from a stereoelectronic point of view the external cyclopropane bond should be broken by ring opening. For those radicals (12) where n = 3 and/or n = 4 this feature of orbital overlap has been used by Freeman,[39] Friedrich,[40] Dauben,[42] and Davies[43] to explain the mode of ring opening observed.

This leads to another conclusion though ; why, if all the bicyclo[n.1.0]alk-2-yl radicals adopt conformations which favour external cyclopropane bond fission , does this not occur with those radicals (12) where n = 1,2? Why do these radicals, (12a,b), undergo β-scission in a contrastereoelectronic manner? What other factor influences the β-scission process, and why is there a change in behaviour between bicyclo[n.1.0]alk-2-yl radicals where n = 2 and n = 3?

The answer to these questions may be found in an examination of the ring strain (RS) energies of the bicyclo[n.1.0]alk-2-yl radicals (12), and the RS energies of both possible rearrangement products, i.e. radicals (13) and (14).

The exact value of the RS energy of these radical species is unknown. However it is generally assumed that such energies are somewhat less than the RS energy of the corresponding hydrocarbon, the RS energies of which are known.[51]

In Table 2 the RS energies calculated for the associated hydrocarbon are used to determine the relief of ring strain resulting from both modes of β-scission.

Table 2

Relief of ring strain in β-scission of bicyclo[n.1.0]alk-2-yl radicals (12) RS values in $kJmol^{-1}$

Radical	RS(12)-RS(13)	RS(12)-RS(14)
12a	56	155
12b	107	206
12c	112	131
12d	115	98
12e	101	99
12f	105	89

The ring strain of each radical is assumed to be equal to that of the corresponding hydrocarbon : all values are calculated from ref. 51.

For radicals (12a) and (12b) internal cyclopropane bond fission results in ca 100 $kJmol^{-1}$ greater relief of ring strain than external cyclopropane bond fission. For radical (12c) internal cyclopropane bond fission is only ca 20 $kJmol^{-1}$ greater in relief of ring strain. For each of the other radicals (12d,e,f) external cyclopropane bond fission results in greater relief of ring strain. Thus for the radicals (12), where n = 1,2 , the much greater relief of ring strain realised by β-scission of the internal cyclopropane bond is such that this is sufficient to outweigh the unfavourable stereoelectronic effect involved in this mode of β-scission. For radical (12c) this difference is only ca 20$kJmol^{-1}$, and as such is not thought to be large enough to overcome the favourable stereoelectronic effect for external cyclopropane bond fission. For those radicals (12), where $n > 3$, the relief of ring strain and stereoelectronic effects promote β-scission of the external cyclopropane bond.

Therefore, the RS energies provide a reason as to why a change in the mode of β-scission occurs between radicals (12b) and (12c). It can be concluded that in the absence of any major effect, the governing factor in β-scission of bicyclo[n.1.0]alk-2-yl radicals (12) is the degree of overlap between the SOMO and the β-γ bond which is observed to break ; which in bicyclo[n.1.0]alk-2-yl radicals (12) where $n \geqslant 3$ is the external cyclopropane bond. Though the external cyclopropane bond is more effectively overlapped by the SOMO in radicals (12a) and (12b), this bond does not break. For these radicals (12a,b) the relief in ring strain resulting from internal cyclopropane bond fission is very much greater than that from external

cyclopropane bond fission. Thus, the stereoelectronic effect is overcome and consequently β-scission follows a contrastereoelectronic route.

The fact that this stereoelectronic effect is so predominant in β-scission reactions explains why the products are frequently thermodynamically less stable than those obtained by contrastereoelectronic β-scission.

Overall these observations lead to the conclusion that the β-scission of bicyclo[n.1.0]alk-2-yl radicals (12), where $n \geqslant 3$, is a kinetically controlled process. In contrast for those radicals (12) where n = 1,2 kinetic and thermodynamic factors favour internal cyclopropane bond fission.

(b) Semi Empirical SCF-MO Calculations on Bicyclo[n.1.0]alkanes.

Semi-empirical SCF-MO calculations cannot give a quantitative measurement of the degree of overlap between the SOMO and those orbitals which make up the β-γ bonds. For cycloalkylmethyl and bicycloalkyl radicals the fully optimised molecular geometry shows a decrease in the α-β bond lengths, along with a corresponding increase in β-γ bond lengths compared to those values calculated for the parent hydrocarbon.[18] Ab initio calculations show similar features for alkyl radicals.[52] This increase in the β-γ bond length can be

used as an indication of the weakening of this bond, which may result from overlap between this bond and the SOMO of the radical centre.

As stated in Chapter 1 these calculations are also used to determine the magnitudes of the enthalpies of formation (ΔH^{o}), and of activation ($\Delta H^{\neq}$). These values are then used in establishing the relative merits of kinetic and thermodynamic factors in controlling the rearrangement.

SCF-MO calculations were carried out on the rearrangement of radicals (12c) and (12d) using the MNDO technique of Dewar and Thiel.[25,26] Calculations on hydrocarbons (11c) and (11d), and on radicals (12c) and (12d), were also carried out using the MINDO/3 technique of Dewar *et al.*[27,28] Full optimisation of the geometry with respect to all variables was carried out. These variables were; bond lengths, bond angles, and dihedral angles. The enthalpies of reaction, and of activation, were calculated by taking a series of increasing $\beta-\gamma$ bond lengths and fully optimising all the other variables for each value.

Using the calculated fully optimised geometries of the bicyclo[n.1.0]alkanes, (11c) and (11d), and of the bicyclo[n.1.0]alk-2-yl radicals (12c) and (12d) the $\beta-\gamma$ bond extensions were calculated. These extensions measure the increase in the $\beta-\gamma$ bond length of the radical as compared to the same $\beta-\gamma$ bond in the parent bicycloalkane. These extensions are shown in Table 3. Both MNDO and MINDO/3 methods predict the radical to be essentially planar in configuration. From Table 3 the predicted

extensions in the β-γ bond lengths are approximately the same for

Table 3

β-γ bond extensions predicted by MNDO and MINDO/3 methods for bicylo[n.1.0]alk-2-yl radicals

Reaction	Internal fission[a]		External fission[b]	
	MNDO	MINDO/3	MNDO	MINDO/3
12c→14c	0.02	0.02		
12c→13c			0.02	0.02
12d→14d	0.02	0.02		
12d→13d			0.02	0.02

a: increase in internal cyclopropane bond relative to parent hydrocarbon. b: increase in external cyclopropane bond relative to parent hydrocarbon.

both internal and external cyclopropane bonds, from both MNDO and MINDO/3 methods. These extensions are minor compared to those found for bicyclo[1.1.0]but-2-yl radicals (12a),[44] and are similar to those observed in cycloalkylmethyl radicals.[33] As a result of the small degree of the predicted β-γ extension, and because the predicted extensions are the same for both β-γ bonds, it follows that these observations are of little use in predicting the mode of β-scission through β-γ bond weakening.

The plots of enthalpy of formation against β-γ bond length for radicals (12c) and (12d) are shown in Figures 4a and 4b respectively. Both plots show the two modes of β-scission of the respective radical. Using these plots the values of $\Delta H^{\ddagger}$ and ΔH^{o} were

determined, the results are shown in Table 4 (page 49).

In both 4a and 4b △ represents internal cyclopropane bond fission, i.e. radical 12⟶14, and ⊡ represents external cyclopropane bond fission, i.e. radical 12⟶13.

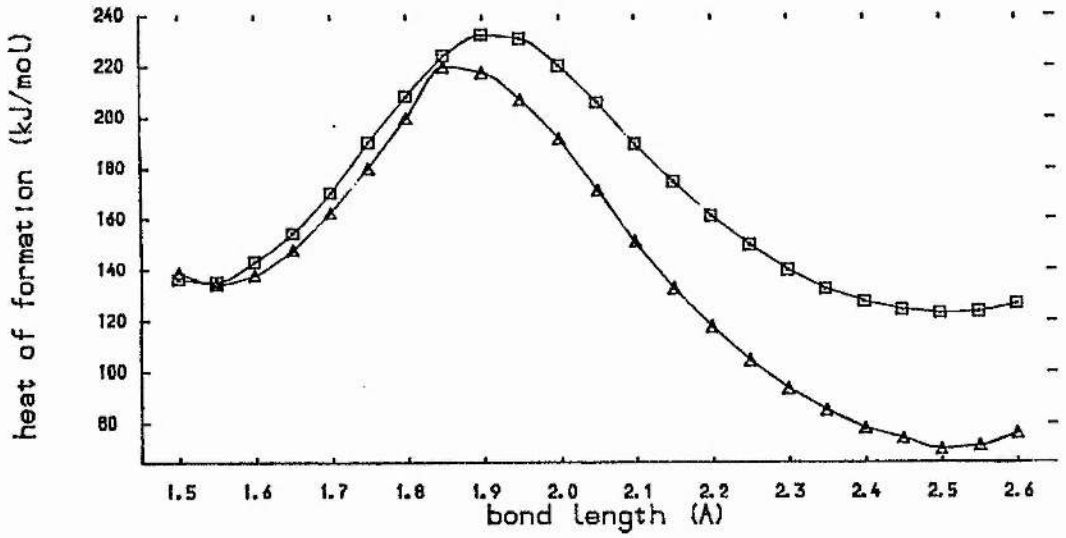


Figure 4a. Plot of heat of formation against $\beta-\gamma$ bond length for the β-scission of bicyclo[3.1.0]hex-2-yl radicals.

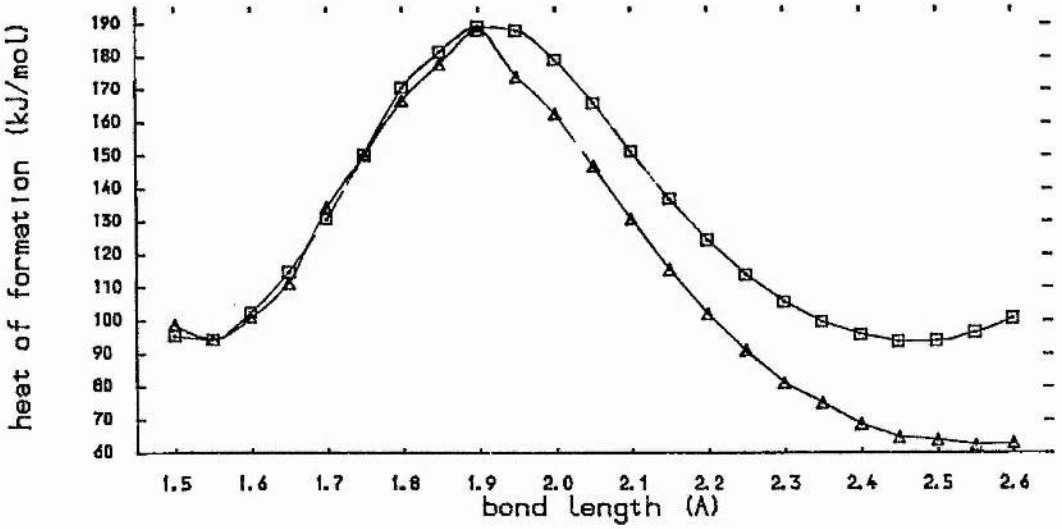


Figure 4b. Plot of heat of formation against $\beta-\gamma$ bond length for the β-scission of bicyclo[4.1.0]hept-2-yl radicals.

Table 4

ΔH^{o} and $\Delta H^{\neq}$ values calculated from Figures (4a) and (4b) using MNDO calculated ΔH_f values.

Reaction	ΔH^{o}/kJmol^{-1}	$\Delta H^{\neq}$/kJmol^{-1}
12c→13c	-13	98
12c→14c	-66	87
12d→13d	- 1	95
12d→14d	-32	94

From Table 4 for radicals (12c) and (12d), the MNDO calculations predict β-scission of the internal cyclopropane bond to be more exothermic. This is not altogher unexpected as the larger ring resulting from this mode of β-scission should be thermodynamically more stable, than that resulting from external cyclopropane bond fission. The ΔH^{o} values are hence of little use in predicting the manner of ring opening. The $\Delta H^{\neq}$ values for the two modes of β-scission are seen to be approximately equal for both bicyclo[n.1.0]alk-2-yl radicals, (12c) and (12d). Hence the $\Delta H^{\neq}$ values are also of limited use in predicting the mode of β-scission, since MNDO predicts approximately equal barriers for both internal and external cyclopropane bond fission.

Experimental results indicate that the activation energy of the ring fission is < 25 kJmol^{-1}. Thus the MNDO calculations overestimate this barrier by a factor of ca 4.

Using the optimised geometries calculated by the MNDO method, the conformations of the bicyclo[n.1.0]alk-2-yl radicals (12c,d) were studied. Figure 5 shows a computer drawn plot using these geometries, bicyclo[3.1.0]hex-2-yl (12c) being shown by 5a, bicyclo[4.1.0]hept-2-yl (12d) by 5b. In these plots only the relevant atoms are shown, namely the radical centre C(2), and the cyclopropane ring carbons. The hydrogen atoms attatched to these carbons are also shown. The aspect of view is along the C(2)-C(1) bond, with the C(2) foremost. From both plots in Figure 5 the SOMO is seen to overlap

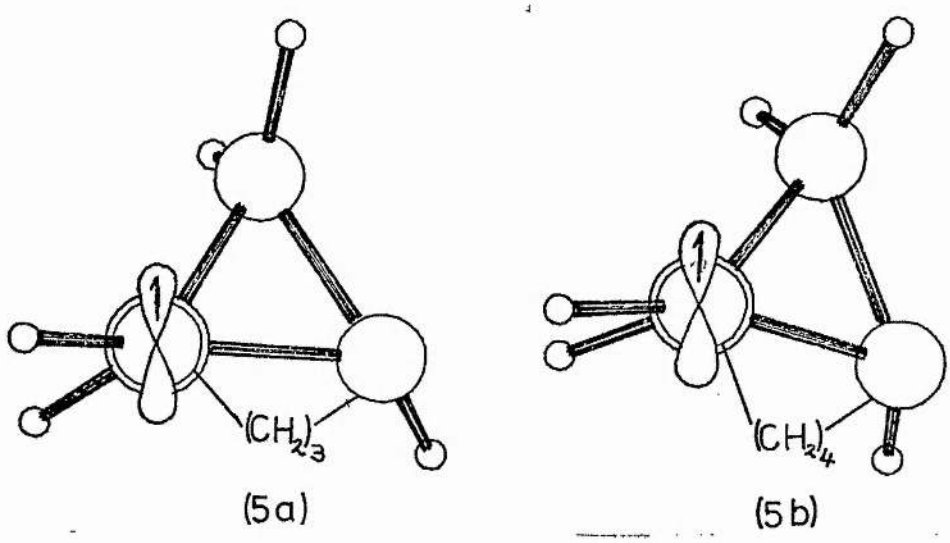


Figure 5. Geometry of bicyclo[3.1.0]hexyl (5a), and bicyclo[4.1.0]heptyl (5b) radicals from MNDO calculations.

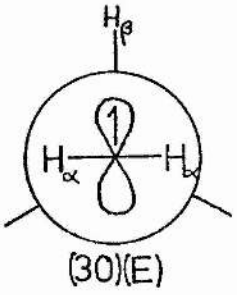
more effectively with the external cyclopropane bond. A similar result was deduced earlier (p. 41) by using molecular models of the bicyclo[n.1.0]alk-2-yl radicals (12). This further confirms that if β-scission is to follow a stereoelectronic effect, then the external cyclopropane should break, such that cycloalkenylmethyl radicals (13) are produced, as was observed.

(c) The Conformation of Cycloalkenylmethyl Radicals , and the Barrier to Internal Rotation about $\dot{C}-C_\beta$.

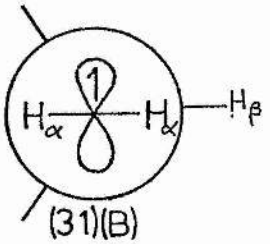
The temperature dependence of the β-hydrogen hyperfine splitting, $a(H_\beta)$ was discussed in Chapter 1. Similarly the method by which the barrier to internal rotation is determined was also discussed earlier.

For cyclopentenylmethyl (13c) and cyclohexenylmethyl (13d) radicals the value of $a(H_\beta)$ was measured at a series of temperatures. The results are shown graphically in Figure 6.

From the absolute magnitude of $a(H_\beta)$ for the cyclopentenylmethyl radical (13c) and from the fact that $da(H_\beta)/dT$ is positive, it follows that this radical adopts the bisected conformation (31)(B). Similarly, the absolute magnitude of $a(H_\beta)$ for the cyclohexenylmethyl radical (13d), and the fact that $da(H_\beta)/dT$ is negative is proof that this radical adopts the eclipsed conformation (30)(E). For both cycloheptenylmethyl (13e), and cyclo-octenylmethyl (13f) radicals the absolute magnitude of $a(H_\beta)$ is proof that these radicals adopt an eclipsed conformation.



(30)(E)



(31)(B)

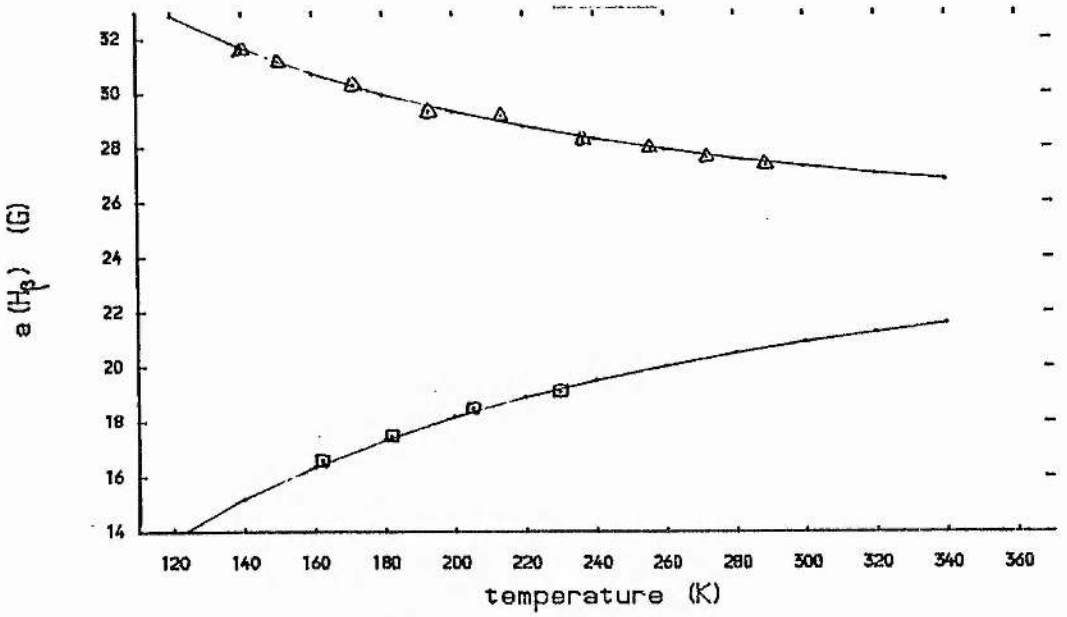


Figure 6. Plot of $a(H_\beta)$ against temperature for radicals (13c,d). ⊡ represents radical (13c), △ represents radical (13d)

The change in preferred conformation between cyclopentenylmethyl and cyclohexenylmethyl radicals, parallels that observed in cycloalkylmethyl radicals,[33] and the reason for the change can be accounted for in a similar manner.

The conformation adopted by an alkyl radical is most probably determined by steric effects manifested between the hydrogens of the radical centre, H_α, and those hydrogens on the nearest neighbouring carbon atoms, i.e. H_β and H_γ. The degree of steric interaction found between these hydrogens is most easily assessed by determining the interatomic separations between H_α-H_β, and H_α-H_γ in both bisected (31) and eclipsed (30) conformations. This calculation however, is not as easy as would at first appear. There are a number of imponderables, the action of which brings a degree of uncertainty into the results. These uncertainties are found in ; i) the exact $\dot{C}$-C_β bond length, ii) the degree of puckering of the cycloalkene ring, iii)

the precise configuration of the radical centre in the eclipsed conformation (30) (there exists evidence which shows that the configuration deviates from planarity in conformation (30)[53,54]).

In Table 5 the most important, i.e. shorter, hydrogen-hydrogen separations are shown. These were calculated using the "rationalised geometries" adopted in previous work.[33] This approach assumes a planar radical centre in both conformations, and assumes that $\dot{C}$-H_α 1.08, $\dot{C}$-C_β 1.48, C_β-H_β 1.12Å, and $\angle H_\alpha \dot{C} H_\alpha$ 120°. The rest of the radical structure is taken from the fully optimised MNDO geometry.

Table 5

The shorter H-H separations , in Å , for radicals (13c) and (13d) as calculated by MNDO theory.

	cyclopentenylmethyl (13c)		cyclohexenylmethyl (13d)	
	E (30)	B (31)	E (30)	B (31)
H_α-H_β	2.77	2.38	2.76	2.34
H_α-H_β	2.77	3.11	2.76	3.08
H_α-$H_{\gamma'}$	3.99	3.54	3.77	3.29
H_α-H_γ	2.42	3.40	2.67	3.35
H_α-H_γ	3.36	3.84	2.73	3.64
H_α-$H_{\gamma'}$	2.70	3.32	2.48	3.04
H_α-H_γ	3.61	2.70	3.60	2.68
H_α-H_γ	4.27	3.84	3.90	3.34

γ' refers to the single γ alkenic hydrogen.

From the values shown in Table 5 it can be seen that the steric effects which influence the conformation of radicals (13) are similar to those which influence the conformation of cycloalkylmethyl radicals[33], a not unexpected observation. In the bisected conformation (31) of both radicals, (13c) and (13d), the shortest, i.e. most repulsive, H-H separation is the unique H_α-H_β distance of 2.34-2.30Å, resulting from the eclipsing of H_β by one of the H_α. In the cyclohexenylmethyl radical (13d) this single term is thought to dominate all other repulsions and results in radical (13d) adopting an eclipsed conformation (30). For the larger ring cycloalkenylmethyl radicals (13e,f) this repulsive term is felt to be dominant, hence the preference for conformation (30). For the cyclopentenylmethyl radical (13c) the steric considerations appear to be similar for both conformations (30) and (31). However, it appears that the combined effect of two H_α-H_γ interactions of 2.42 and 2.70Å, when taken with two H_α-H_β repulsions of 2.77Å in the eclipsed conformation (30), are sufficient to overcome the unique H_α-H_β repulsion of 2.34Å, combined with the H_α-H_γ repulsion of 2.70Å found in the bisected conformation (31). Hence radical (13c) adopts the bisected conformation. The single difference between radicals (13) and the related cycloalkylmethyl radicals lies in the presence of a single allylic γ'-hydrogen in the former. In the eclipsed conformation of radicals (13) this γ'-hydrogen is found to be quite close to one of the α-hydrogens. Whilst this fact does not appear to influence the conformation adopted by the cycloalkenylmethyl radical, it may be that it affects some other property of the radical (13). This may possibly be the barrier to internal rotation about $\dot{C}$-C_β for radicals (13)

which may, because of the γ-hydrogen be larger than those found in cycloalkylmethyl radicals.

In Chapter 1 the method by which the barrier to internal rotation about $\dot{C}-C_\beta$ in alkyl radicals was discussed (see p. 27). The observed values of $a(H_\beta)$ are fitted to curves of calculated $a(H_\beta)$ values derived from expression (12). Expression (12) was used to calculate values of $a(H_\beta)$ which are shown by the curves in Figure 6. These curves can be seen to give an excellent fit with the experimental values of $a(H_\beta)$. The values of A, B, and V_o used to generate

$$a(H) = A + 1/2B + 1/2B\cos 2\theta_o[I_1(\lambda)/I_o(\lambda)] \qquad (12)$$

these curves are shown in Table 6. For comparison the V_o values for the corresponding cycloalkylmethyl radicals are also shown in parenthesis.

Table 6

Barrier to rotation about C-C for cycloalkenylmethyl radicals (13).

Radical	θ_o°	A	B	$V_o/kJmol^{-1}$	$(V_o/kJmol^{-1})$
13d	0	0	46	1.9	(1.6)
13c	90	2	50	2.5	(2.0)

The values of A and B found for radicals (13c) and (13d) are the same as those calculated for the corresponding cycloalkylmethyl radical.[33] The V_o values found for radicals (13c) and (13d) are seen to be greater than those found for the corresponding cycloalkylmethyl radical. This increase in the V_o term is most probably due to a

combination of steric and electronic effects, one of which may be the H_{α}-H_{γ}' repulsion that was noted earlier (p. 54).

Previous work has shown that for cycloalkylmethyl radicals MNDO calculations cannot predict the preferred conformation, but that INDO[34] calculations successfully predict the preferred conformation.[33] For cycloalkenylmethyl radicals (13) MNDO calculations do not predict the correct conformations. However, for radicals (13c) and (13d) INDO calculations also failed to predict the preferred conformation. INDO calculations did however predict approximately the correct barrier to rotation, V_o , as found experimentally.

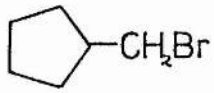
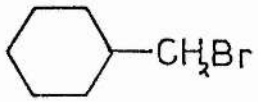
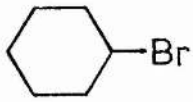
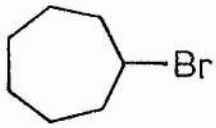
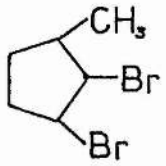
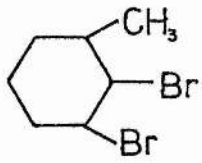
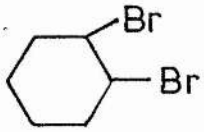
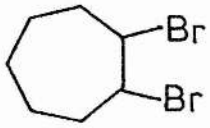
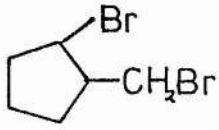
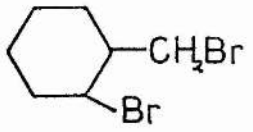
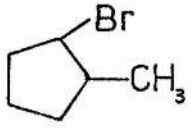
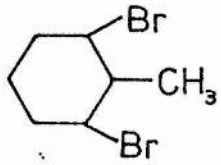
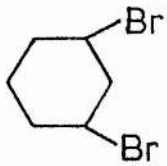
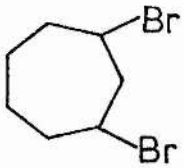
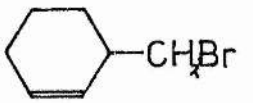
The energy difference between the conformations (30) and (31) however, is thought to be too small for either MNDO or INDO methods to differentiate between them. Hence the failure of both techniques to identify the preferred conformation.

(d) The Photobromination of Bicyclo[n.1.0]alkanes (11c) and (11d).

The reaction of bicyclo[3.1.0]hexane (11c) with molecular bromine in CCl_4 solution at room temperature proceeds rapidly upon illumination, and is complete in ca 1-2 minutes. The analogous reaction of bicyclo[4.1.0]heptane (11d) is somewhat slower, but is complete after ca 20 minutes. The major products are shown in Table 7, along with the percentage yields as established by quantitative g.l.c. analyses.

Table 7

Products , and yields obtained from the photobromination of (11c) and (11d) in CCl_4 solution at 20°C.

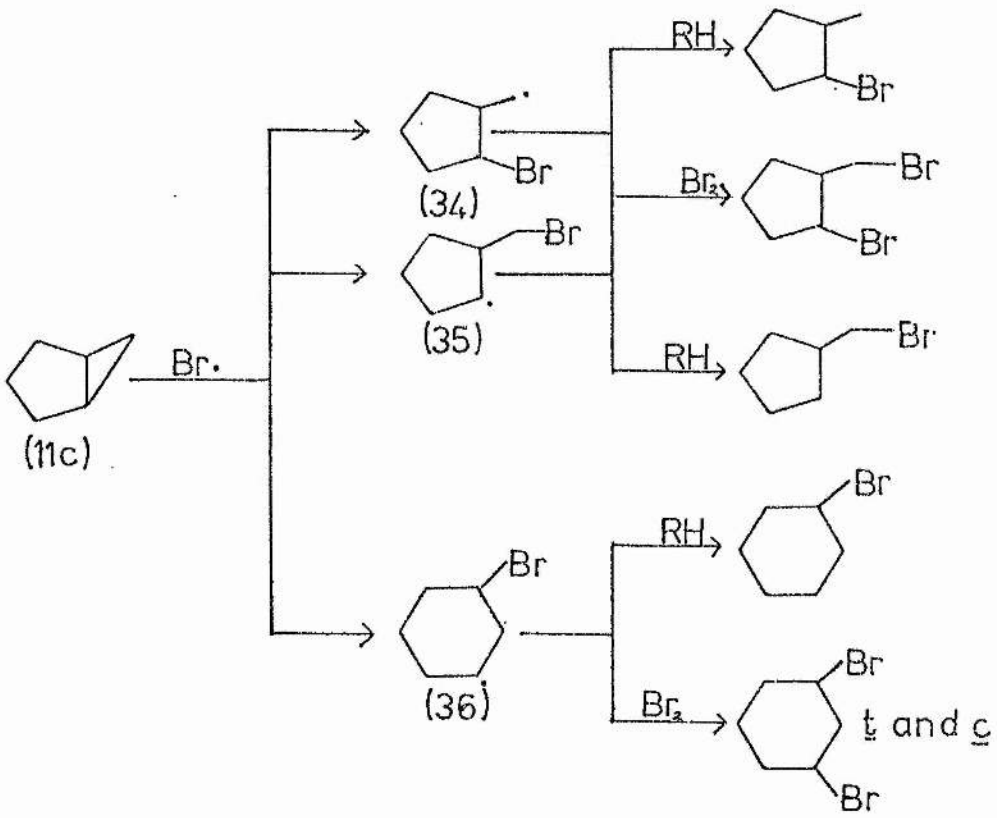
(11c)		(11d)	
product	%yield[a]	product	%yield[a]
	9·0		8.1
	17·7		1.4
	4.1[b]		42·5[b]
	3·7[c]		5·6[c]
	17·8[b]		17·0[b]
	8·7[b]		18·8[b]
	t 20.0 c 18.7		5·6[b]
			0.9

[a]Yields are mol % relative to the total products. [b]Mixture of isomers. [c]*trans*-Isomer.

The photobromination of (11c) gave rise to a different product mixture than that observed in the electrophilic reaction,[55] and the small yield of t-1,2-dibromocyclohexane is thought to come from an electrophilic reaction concurrent with the main radical process.[33,56] The t-1,2-dibromocycloheptane may come from the analogous reaction of (11d). The main products result from bimolecular homolytic substitution reactions, S_H2, between (11c,d) and bromine atoms. The main reaction, S_H2, mechanisms for (11c) are shown in Scheme 7, (11d) will undergo analogous reactions.

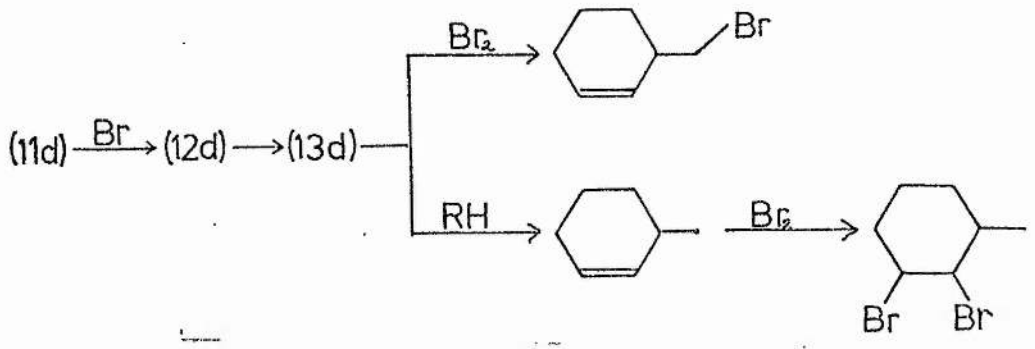
Scheme 7

S_H2 reaction mechanisms of (11c) with bromine atoms.



Attack by bromine atoms at the methylene carbon of the cyclopropane ring gives rise to radical (35), and at the bridgehead carbon to give radical (34) by fission of the external cyclopropane bond. Radical (36) results from bromine atom attack at the bridgehead carbon causing internal cyclopropane bond fission. These radicals can hence either abstract bromine from molecular bromine, or hydrogen from the substrate (or from HBr produced in solution) to give the mono- and di-bromo compounds shown. Radical (36) gives rise to 1,3-dibromocyclohexanes with a trans to cis ratio of ca 1.1. The photobromination of bromocyclohexane was shown to give 1,3-dibromocyclohexanes with a trans to cis ratio of ca 1.3.[57] This result gives credence to the proposed mechanism (see Scheme 7) by which 1,3-dibromocyclohexane is formed in the reaction of (11c) with molecular bromine. The 1,2-dibromo-3-methylcycloalkanes and 3-(bromomethyl)cyclohexene present in the product mixture indicates the ^{1}H abstraction at C(2) by bromine atoms to give radicals (12c,d). These radicals (12) then undergo β-scission of the external cyclopropane bond to give cycloalkenylmethyl radicals (13). Radicals (13) can hence abstract bromine or hydrogen, with subsequent addition of bromine by the methylcycloalkenes to give the observed products, see Scheme 8 for the mechanisms. The high yield of 1,2-dibromo-3-methylcyclohexane(c.f. 42.5%) indicates that this mechanism is of increasing importance as the ring size increases. The absence of any 1,2-dibromo-3-(bromomethyl)cycloalkane does not rule out the formation of such products, rather this indicates the failure of the analytical procedures in identifying minor quantities of

Scheme 6



tribrominated products. The g.l.c.-mass spectral data hinted at the presence of tribromides, but this was not verified. The g.l.c. analyses did not show any major peak which could be assigned to a tribromide. However the retention times of such compounds would be quite long, and it is therefore feasible that such products would come off the column as very long timed, low intensity peaks. If this were so, such peaks would , almost certainly, go unrecognized.

The chlorination of (11d) gave a complex product mixture,[58] however the main reaction mechanisms are analogous to those proposed for the bromination of (11d).

The degree of bromine attack at the bridgehead carbon relative to attack at the cyclopropane ring methylene carbon cannot be determined, since attack at either site can give 1-bromo-2--(bromomethyl)cycloalkane as the product (see Scheme 7). For bicyclo[2.1.0]pentane (11b) attack by bromine atoms results in the exclusive fission of the internal cyclopropane bond.[9] With bicyclo[3.1.0]hexane (11c) fission of both internal and external cyclopropane bonds was observed, and for bicyclo[4.1.0]heptane (11d) fission occurs mainly of the external cyclopropane bond. The amount

of products resulting from fission of the internal, or external cyclopropane bond can be determined from the product yields. Hence the ratio of external to internal cyclopropane bond fission can be determined. For (11c) this ratio is calculated to be ca 0.6, whereas for (11d) this becomes ca 6.3 (c.f. (11b) where the figure is 0.0). Thus the results of the bromination of bicyclo[n.1.0]alkanes (11) ties in well with the previous observations, in that as n increases a change in the manner of cyclopropane bond fission occurs, from internal β-scission when n = 2, to external β-scission when n = 4. The case for n = 3 (11c) showing intermediate behaviour in the bromination experiment. Thus for bromination of bicyclo[n.1.0]alkanes (11) the changeover point for ring fission is less abrupt. The nature of the products obtained from bromination of (11c,d) are similar to those recorded by Freeman et al,[39] and by Friedrich and Holmstead,[40] in that for (11c) both cycloalkenylmethyl and cycloalkenyl derived products are found, whereas with (11d) the products were mainly derived from cycloalkenylmethyl radicals.

Overall this change in the mechanism of the S_H2 reaction may reflect the effect of ring strain. From earlier discussion (p. 43) it was seen that as ring size increased the relief of ring strain resulting from internal cyclopropane bond fission decreases, whilst that from external cyclopropane bond fission increases slightly.

2.3 Conclusions

The study of bicyclo[n.1.0]alkanes (11) has revealed that for the members of this series, where $n \geqslant 3$, the bicyclo[n.1.0]alk-2-yl radical (12) derived from (11) undergoes β-scission of the external cyclopropane bond to yield cycloalkenylmethyl radicals (13). This behaviour contrasts with that of the radicals (12) where $n = 1,2$, which undergo β-scission of the internal cyclopropane bond to give cycloalkenyl radicals (14). Examination of the conformation of radicals (12) confirmed that for all members of the series n = 1-6, the stereoelectronic effect favours β-scission of the external cyclopropane bond. However, for those radicals (12) in which the relief of ring strain released by internal β-scission is much greater than that obtained by external β-scission, the stereoelectronic effect is overcome. Thus these radicals (12a,b) undergo β-scission in a contrastereoelectronic manner.

Thus it is concluded that the stereoelectronic effect is the main factor influencing β-scission. It will control β-scission in all cases, except those in which another factor is of importance, such as the relief of ring strain effect observed in radicals (12a) and (12b).

The preferred conformations of the cycloalkenylmethlyl radicals (13c,d) were determined. It was found that cycloalkenylmethyl radicals (13) adopt the same conformations as the corresponding cycloalkylmethyl radicals. The barriers to internal rotation of radicals (13c) and (13d) were calculated, and found to be greater than those determined for the corresponding cycloalkylmethyl radicals, though the values of the A and B terms were the same for both radical species.

Photobromination of (11c) and (11d) resulted in products arising from both internal, and external cyclopropane bond fission, though the latter is of greater importance in the larger ring system (11d).

Chapter 3

SPIRO[2.n]ALKANES

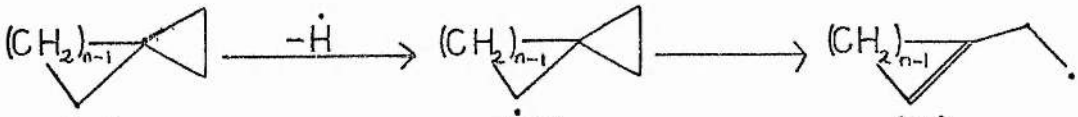
and

SPIRO[2.n]ALK-4-YL RADICALS

The Kinetic E.S.R. Study of the Rearrangement of a Cyclopropylmethyl Radical

3.1 Introduction

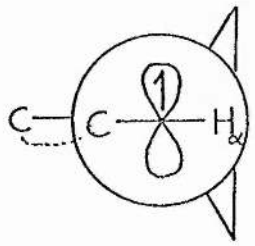
Spiro[2.n]alkanes (15) and the spiro[2.n]alk-4-yl radicals (15) derived from (15) provide a second series of cyclopropylmethyl like radicals, as noted in Chapter 1. However, unlike the bicyclo[n.1.0]alk-2-yl radicals (12) discussed in Chapter 2, these radicals (16) can only ring open, through β-scission, in one manner. There exists the possibility of a second mode of β-scission, however as discussed in Chapter 1 (p. 14) this second mode is unlikely.



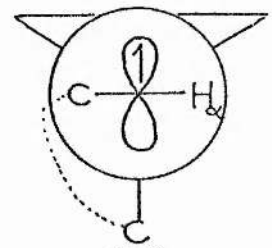
(15) a: n=2 c: n=4
b: n=3 d: n=5

(16) (17)

Radicals (16) are also 'locked' into a quite rigid geometry. Radicals (16) adopt the conformation shown by (19). [N.B. The spiro[2.2]pent-4-yl radical (16a) does not adopt conformation (19) due to the SOMO of the radical possessing 's' character.] Conformation (19) is thought not to be conducive to β-scission,[4] this being



(19)



(20)

favoured by conformation (20).[10] However, the adoption of a bisected conformation (19) does not appear to prevent the β-scission of radicals (16), where n = 4,5 , since this has been reported.

Unlike bicyclo[n.1.0]alkanes (11), spiro[2.n]alkanes (15) have not been studied in such detail. The main works on spiro[2.n]alkanes have been those of Applequist,[38] Suzuki,[19] and Walton.[20]

Applequist and Landgrebe reported that the vapour phase chlorination of spiro[2.3]hexane (15b) gave 1-(2-chloroethyl)--cyclobutene in ca 10% yield. This product can only result from the ^{1}H abstraction at C(4) of (15b) to give the spiro[2.3]hex-4-yl radical (16b), which then ring opens to give a cyclobutenylethyl radical (17b) which subsequently abstracts chlorine.[38] The presence of up to 20-25% 4-chlorospiro[2.3]hexane was also noted. This results from ^{1}H abstraction at C(4) to give radical (16b) which then abstracts chlorine. The formation of these two products was competitive. However Applequist and Landgrebe did not determine whether the relative ratio of the products was influenced by the partial pressure of chlorine.

Similar work on spiro[2.4]heptane (15c) gave a complex product mixture. However, 1-(2-chloroethyl)cyclopentene was observed in ca 17% yield.[38]

Thus both radicals (16b) and (16c) were observed to undergo β-scission to give the corresponding cycloalkenylethyl radical (17).

This observation of spiro[2.4]hept-4-yl radicals (16c) was reinforced by the work of Suzuki et al.[19] In their work they generated the spiro[2.4]hept-4-yl (16c) and spiro[2.5]oct-4-yl (16d) radicals

from the corresponding azo compounds. Both of these radicals (16c,d) undergo β-scission to give the expected cycloalkenylethyl radical (17c,d). However, radical (16c) found to give much more rearranged products. This was unexpected since the rigid geometry of radical (16c) will hold it in the unfavourable bisected conformation (19). Radical (16d), due to the larger ring, was thought to be able to adopt a conformation more favourable to β-scission. These observations were interpreted by Suzuki et al as being the result of ring strain effects.[19]

Walton et al[20] in the study of spiro[2.2]pentane (15a) found that the spiro[2.2]pent-4-yl radical (16a) did not ring open until above 370K. As mentioned earlier (Ch 1, p. 15) radical (16a) possesses an anomalously low value of $a(H_\alpha)$, ca 6G. This value is similar to that observed for cyclopropyl radicals. Hence radical (16a) was thought, like cyclopropyl radicals, to be a σ radical, i.e. the SOMO has appreciable 's' orbital character. Hence, the radical centre is non-planar. This prevents any significant degree of overlap between the SOMO and the β-γ bonds. The reaction is also probably only slightly exothermic (see Table 9, p. 77). As a result radical (16a) does not undergo β-scission to give cyclopropenylethyl radicals (17a).

The following sections report and discuss the findings of the work on the spiro[2.n]alkanes (15), where n = 3,4.

3.2 Results and Discussion

(a) The E.S.R. Study of ^{1}H Abstraction from Spiro[2.n]alkanes (15).

The e.s.r. samples were prepared in a similar manner to that described in Chapter 2 (p. 35). For spectra recorded between 140K and 90K CF_2Cl_2 was used as solvent. All spectra were recorded at ca 9.4GHz.

^{1}H abstraction from spiro[2.3]hexane (15b) at 141K gave the spectrum shown in Figure 7 (p. 68). This spectrum consists of a triplet of doublets arising from a single α-hydrogen and two β-hydrogens. Each component shows further fine structure of seven lines arising from six γ-hydrogens. The central lines of the triplets are reduced in intensity due to a second order splitting. The h.f.s. parameters are shown in Table 8 (p. 70). The simulated spectrum was drawn using these values. The e.s.r. spectrum was assigned to the spiro[2.3]hex-4-yl radical (16b). Radical (16b) has a single α-hydrogen and two β-hydrogens, and also six γ-hydrogens. The equivalence of all these six hydrogens was unexpected. The value of $a(H_\alpha)$ is seen to be somewhat smaller than that value normally expected for an alkyl radical, i.e. ca 21-2G. This slight decrease in the value of $a(H_\alpha)$ may indicate that the radical centre deviates from planarity. The size of this devation should be small. The structurally related cyclobutyl radical has a planar radical centre, with $a(H_\alpha)$ ca 21.3G.[10,59]

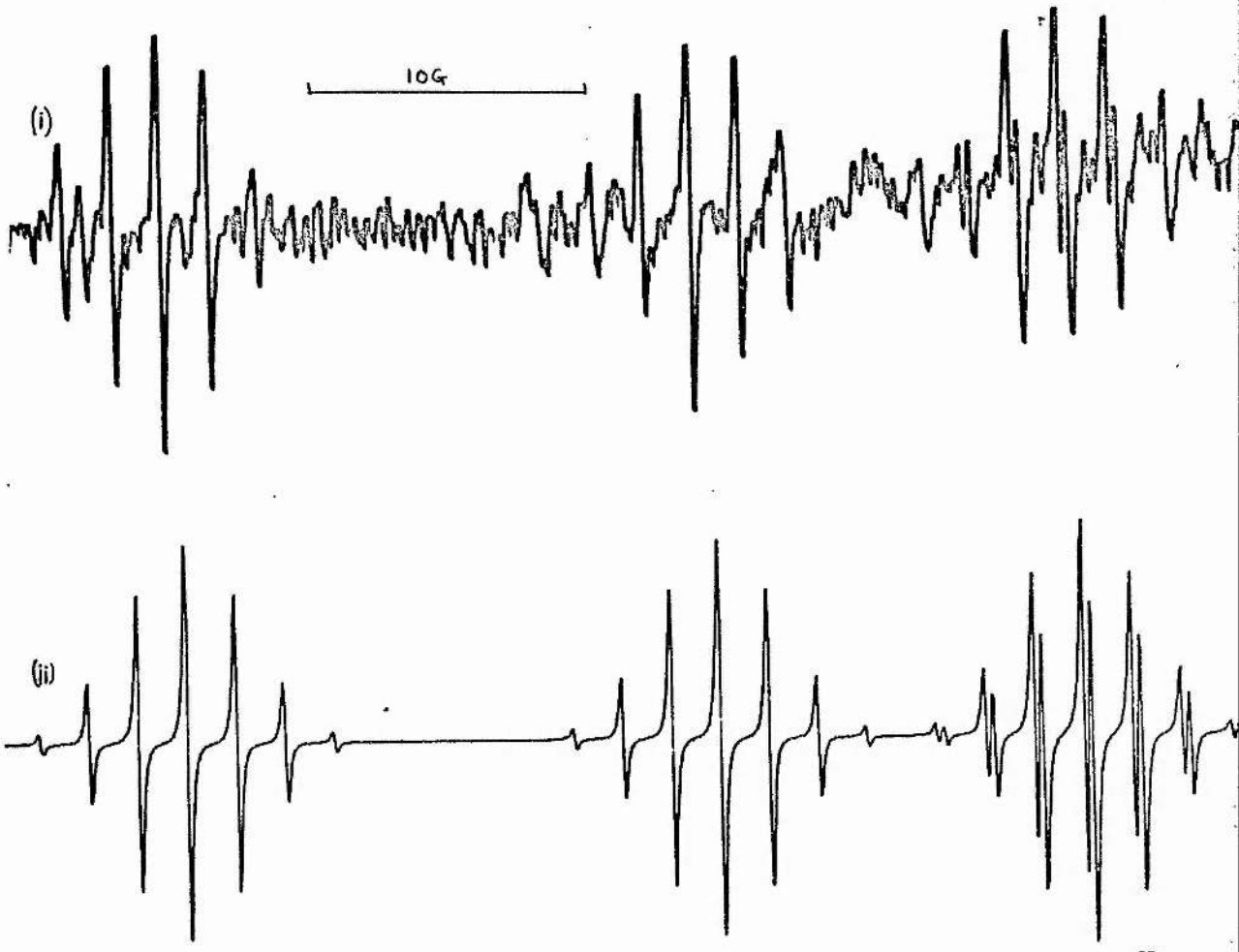


Figure 7. Low field half spectrum of spiro[2.3]hex-4-yl radicals (16b) at ca 9.4GHz. (i) observed at 141K, (ii) simulation

On warming the e.s.r. sample from 140K the spectrum of radical (16b) was observed to decrease in intensity. Simultaneously the appearance of new signals, which could only arise from a second radical species, were detected. Finally, at T > 175K the spectrum of radical (16b) could no longer be detected. At temperatures above 175K the observed spectrum was that shown in Figure 8. This spectrum consists of a triplet of triplets arising from two α-hydrogens and

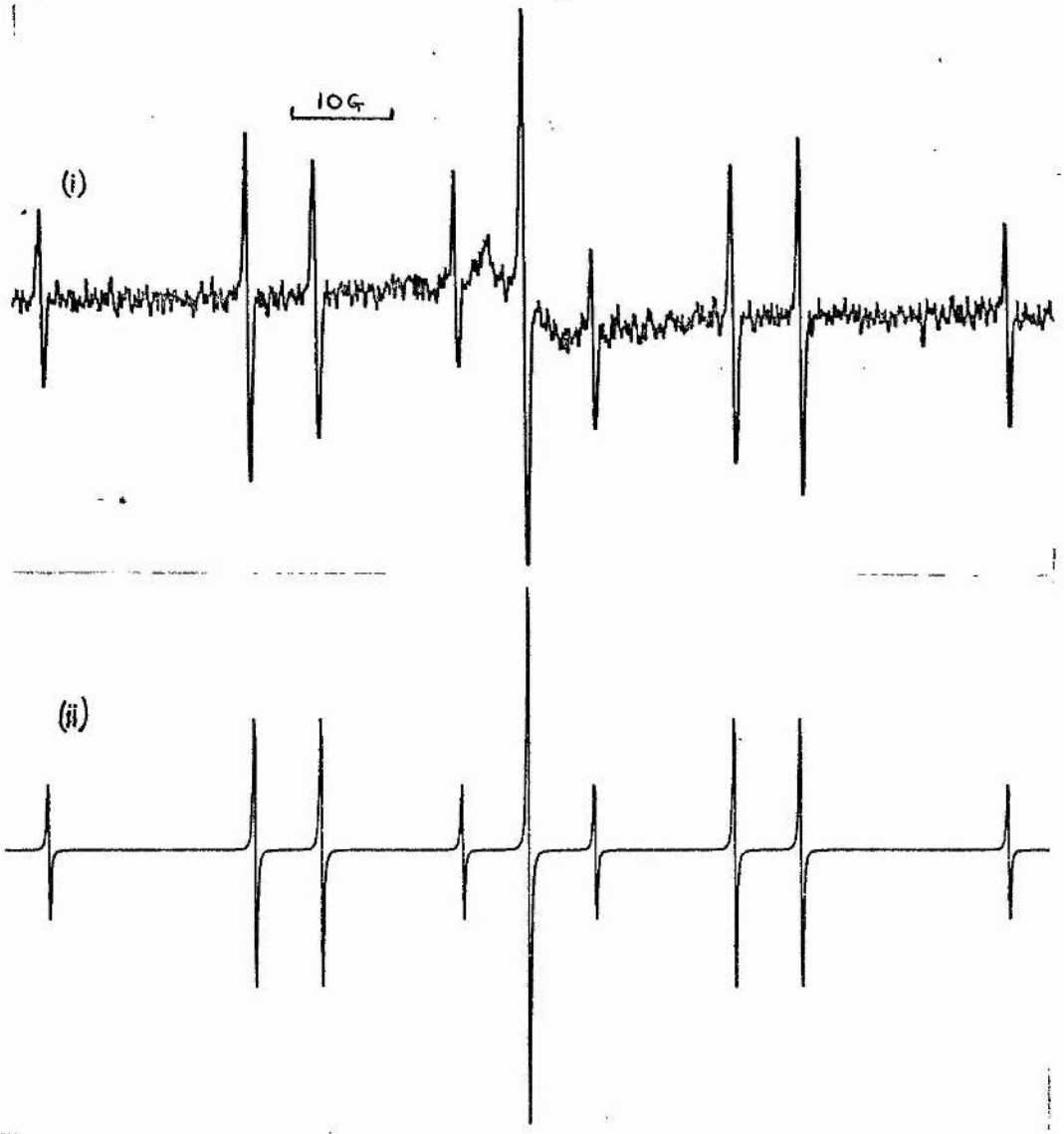


Figure 8. Whole spectrum of cyclobutenylethyl radical (17b) at ca 9.4GHz, 200G scan. (i) observed at 176K, (ii) simulation

two β-hydrogens. The h.f.s. parameters are given in Table 8. The simulation being drawn using these values. This radical was identified as the cyclobutenylethyl radical (17b). Radical (17b) is the product of β-scission of the spiro[2.3]hex-4-yl radical (16b).

The observation of both rearranged (17b) and unrearranged (16b) radicals allowed a kinetic e.s.r. experiment. The results of this are dealt with in section 3.2 (b), i.e. the following section.

Table 8

E.s.r. derived parameters for radicals (16b), (17b), and (17c).

Radical	T/K	h.f.s. /G
16b	141	$a(H_\alpha)$ 19.6; $a(2H_\beta)$ 33.0; $a(6H_\gamma)$ 1.8
17b	175	$a(2H_\alpha)$ 21.6, $a(2H_\beta)$ 28.2
17c	251	$a(2H_\alpha)$ 21.6; $a(2H_\beta)$ 27.2

^1H abstraction from spiro[2.4]heptane (15c) at 251K gave the spectrum shown in Figure 9 (p. 71). This spectrum consists of triplet of triplets arising from two α-hydrogens and two β-hydrogens. The h.f.s. parameters are shown in Table 8, these values were used to draw the computer simulation. The spectrum was assigned to the cyclopentenylethyl radical (17c). On decreasing the temperature no other radicals were detected. Even at 90K only radical (17c) was detected. No temperatures below 90K could be attained, as was mentioned earlier in the introduction (Ch 1, p. 19). Thus, even at ca 90K the spiro[2.4]hept-4-yl radical (16c) has ring opened to the cyclopentenylethyl radical (17c).

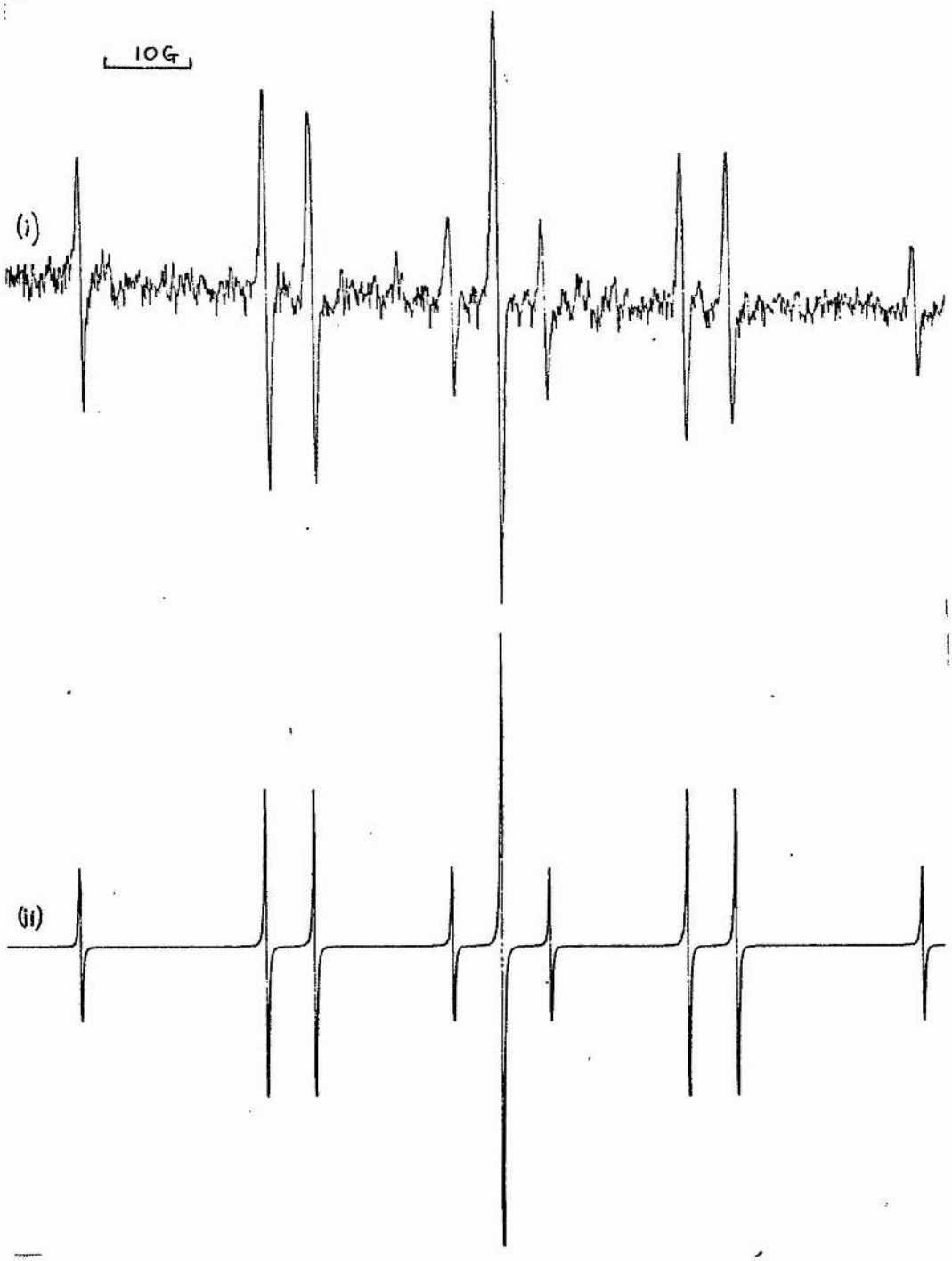


Figure 9. Whole spectrum of cyclopentenylethyl radicals (17c) at ca 9.4GHz, 200G scan. (i) observed at 251K, (ii) simulation

As reported previously spiro[2.2]pent-4-yl radicals are stable with respect to β-scission up to ca 370K.[20]

Therefore, between radicals (16a) and (16b), where n = 2 and n = 3, a change in behaviour occurs. The former, radicals (16a), do not rearrange via β-scission readily, whilst the latter, radicals (16b), do undergo β-scission to give cyclobutenylethyl radicals (17b).

Why does this change in behaviour occur?

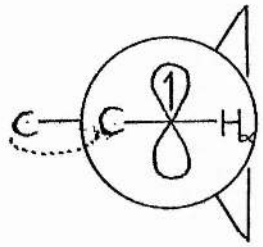
Secondly, why does radical (16c) ring open so much more readily than radical (16b)?

As discussed earlier, the spiro[2.2]pent-4-yl radical (16a) does not rearrange via β-scission due to the lack of interaction between the SOMO and the β-γ bond. This lack of interaction is due to the fact that radical (16a) is a σ radical, i.e. the SOMO has appreciable 's' character. As a result the radical centre is non-planar.

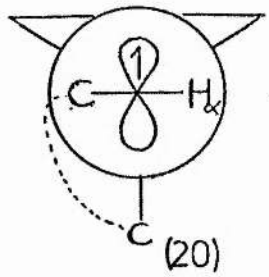
The spiro[2.3]hex-4-yl radical (16b) is assumed to have, what is, essentially, a planar radical centre, i.e. the SOMO behaves as a mainly 'p' character orbital. The slight decrease in magnitude of $a(H_\alpha)$ is probably the result of only a slight deviation from planarity at the radcial centre, c.f. radical (16a) where this deviation is ca 35°.[20] Thus radical (16b) is assumed to be virtually planar, like the

related cyclobutyl radical.[10,59]

The rather rigid geometry of spiro[2.3]alkanes means that radical (16b) adopts conformation (19). This conformation is thought not to favour β-scission.[10] Rather, this is favoured by conformation (20).[10]

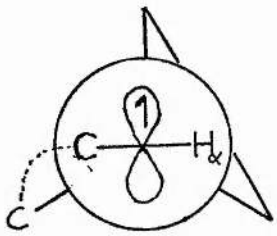


(19)



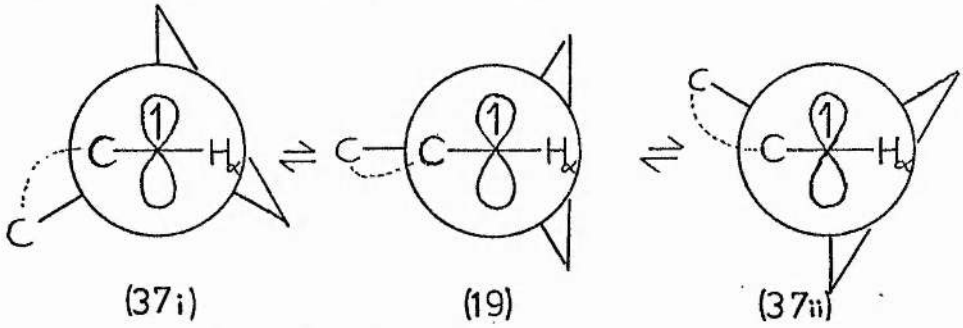
(20)

The rigidity of the cyclobutyl ring effectively prevents conformation (20) being adopted. However, a bending of the cyclobutyl ring would enable radical (16b) to adopt conformation (37). In this conformation



(37)

the overlap of the β-γ bond and the SOMO is maximised. Furthermore two possible conformations (37) are possible. In this conformational exchange conformation (19) can be seen as an intermediate form. If

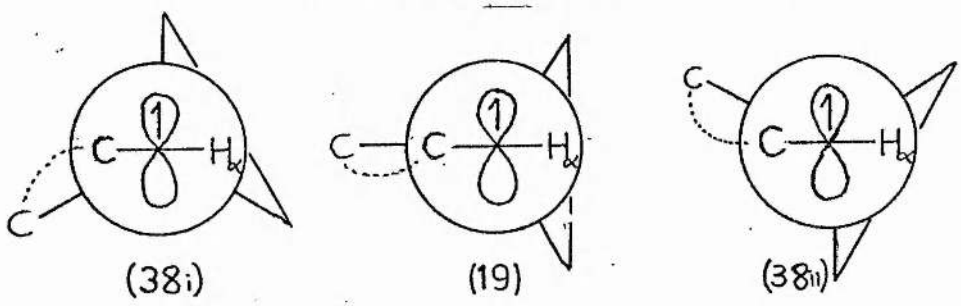


(37i) (19) (37ii)

this exchange between (37i) and (37ii) is rapid, the average effect will be conformation (19). Thus, if the exchange is too fast for the e.s.r. time scale the average effect, i.e. conformation (19), will

be detected. Hence the equivalence of both β-hydrogens and all six γ-hydrogens. This equivalence would not necessarily be expected for conformation (37). The necessity for radical (16b) to 'deform' before β-scission can occur may explain why radical (16b) does not ring open below 140K. At this temperature radical (16b) may adopt conformation (19) preferrentially, and hence does not undergo β-scission. As the temperature is increased the cyclobutyl ring may possibly become less fixed, with conformation (37) being encountered more often, and hence β-scission can occur.

The spiro[2.4]hept-4-yl radical (16c) has a planar radical centre. Again the radical adopts conformation (19), which is unfavourable to β-scission. However, puckering of the cyclopentane ring of radical (16c) would enable a similar conformational exchange to that proposed for radical (16b) to be set up. The puckering of the



(38i) (19) (38ii)

cyclopentane ring such that conformation (38) is achieved is more likely than the same degree of puckering of the cyclobutane ring. This is due to the greater flexibility of the larger ring. For conformation (38) to be achieved the cyclopentane ring must adopt a conformation in which four carbon atoms lie in a plane with the fifth carbon atom lying either above, or below this plane. This arrangement is not unexpected, since the cyclopentyl radical displays such a puckered ring conformation, four carbon atoms lie in a plane whilst the fifth is above, or below this plane.[59] The identity of this lone

carbon is not fixed, rather the cyclopentyl radical, like cyclopentane itself, exhibits a 'pseudo-rotating' puckered ring.[60] If the cyclopentane ring of radical (16c) displayed similar behaviour then the puckering necessary to achieve conformation (38) would be easily attained. Puckering of the cyclopentane ring should be easier than puckering of the cyclobutane ring due to the greater flexibility of the larger ring. As stated earlier the lack of ring opening of radical (16b) below 140K was attributed to the radical adopting the unfavourable conformation (19). Radical (16c) however, due to the larger, and hence more labile ring is more likely to adopt conformations, (38), favourable to β-scission. Hence the rapid β-scission of radical (16c), as observed. It is feasible that radical (16c) may also adopt the unfavourable conformation (19). However, this must occur below 90K from the experimental evidence.

If the proposals that ring puckering influences the β-scission of radicals (16b) and (16c) are valid, they are seen to give a rationale as to the varying rates of β-scission between radicals (16b) and (16c). The latter radical, (16c), can adopt conformations favourable to β-scission more readily, i.e. at lower temperatures, and hence ring opens much faster than radical (16b). Radical (16b) only adopts conformations favourable to β-scission at higher temperatures.

Thus the stereoelectronic effect, thought to be so important in β-scission can be used to explain the ring fission of spiro[2.n]alk-4-yl radicals. Using the proposals outlined previously the stereoelectronic effect is aided by the cyclobutane, and cyclopentane rings of radicals (16b) and (16c) respectively bending

out of a planar conformation into a puckered ring.

However, though explained by the stereoelectronic effect the ring opening of radicals (16b,c) may also be affected by the relief of ring strain. Accordingly a study of the relief of ring strain in the rearrangement of radicals (16) may lead to a clearer understanding of the β-scission process, as was the case with bicyclo-[n.1.0]alk-2-yl radicals (12).

As with bicyclo[n.1.0]alk-2-yl radicals no accurate thermodynamic data exists for radicals (16). Hence the ring strain (RS) energies used will be those for the parent hydrocarbon (15). Furthermore, accurate data for the hydrocarbons does not always exist, the exception being spiro[2.2]pentane for which accurate thermodynamic data is available. To overcome this problem the RS energy used for the spiro[2.n]alk-4-yl radicals (16b,c,d) is the sum of the RS energies of the two component rings. For spiro[2.2]pentane a similar summation results in a RS energy which is ca. 35kJmol^{-1} less than the tabulated RS energy of (15a).[51] Thus for the ring opening of radicals (16b-d) the RS energies used are only a lower limit, the actual figure may be greater. This limiting factor should not affect the results too adversely, and the error will probably be similar in each result. The relief of ring strain obtained by β-scission of radicals (16) is shown in Table 9.

Table 9

Radical	RS(16)-RS(17)/kJmol^{-1}
16a	41[a]
16b	102
16c	117
16d	109

a : the figure for radical (16a) uses the accurate thermodynamic data for the parent hydrocarbon. All data from ref 51.

From the values shown in Table 9 it is obvious that the relief of ring strain increases quite dramatically between radicals (16a) and (16b). The small value of the relief of ring strain gained by β-scission of radical (16a) to radical (17a) is purely due to the formation of the highly strained cyclopropenyl ring in radical (17a). This small relief of ring strain is probably a contributing factor in the relative stability of the spiro[2.2]pent-4-yl radical, (16a), even though this is a highly strained compound. From the bicyclo[n.1.0]alk-2-yl radicals (12) it has already been noted that ring opening may occur against the prevailing stereoelectonic effect, when the relief of ring strain is great. The other spiro[2.n]alk-4-yl radicals, (16b-d), result in similar relief of ring strain on β-scission, i.e. > 100kJmol^{-1}. The differences in the energy values may explain some of the observations made earlier. Namely the greater relief of ring strain resulting from β-scission of radical (16c) may partly explain the faster ring opening of radical (16c). Similarly the slightly greater relief of ring strain obtained by β-scission of

radical (16c) as compared to that obtained from β-scission of radical (16d) may, in part, explain why Suzuki *et al*[19] observed more rearrangement products from spiro[2.4]hept-4-yl radicals (16c) than from spiro[2.5]oct-4-yl radicals (16d). This observation being the opposite to that anticipated, a fact which they thought may be due to ring strain effects.[19]

Thus for spiro[2.n]alk-4-yl radicals (16) the rearrangement, via β-scission, to cycloalkenylethyl radicals (17) is favoured thermo-dynamically. Note that for radical (16a) the relief of ring strain gained by rearrangement is not all that great, being only *ca* $40 kJmol^{-1}$. This, along with the unfavourable stereoelectronic effect, explains the relative stability of radical (16a). For the other members of the series, radicals (16b-d), rearrangement is favoured both by thermodynamic and stereoelectronic effects. The relative merits of either in determining the rate of β-scission, or even whether β-scission occurs at all, cannot be identified. Perhaps the most that can be stated is that the thermodynamic factor may influence the rate of the rearrangement. It is also probably true to state that the stereoelectronic effect is the major influence in the β-scission of spiro[2.n]alk-4-yl radicals (16).

(b) The Kinetic E.S.R. Study of the Rearrangement of Spiro[2.3]hex-4-yl Radicals.

In the previous section it was reported that at temperatures below 140K only the spiro[2.3]hex-4-yl radical (16b) was detected. Between 140K and 175K both radical (16b) and the rearranged cyclobutenylethyl radical (17b) were detected. Above 175K only radical (17b) was detected. Since both unrearranged and rearranged radicals could be detected, a kinetic e.s.r. experiment, using the method of Ingold *et al*,[22-24] was carried out. The technique used was described in detail in Chapter 1, (p. 21). Using expression (1) the values of [U] and [R] were calculated. The terms used in expression

$$[U] = [DPPH] \cdot \frac{W_u}{W_{DPPH}} \cdot \frac{G_{DPPH}}{G_u} \cdot \frac{(0.1)^2}{(1)^2} \cdot \frac{R_{DPPH}}{R_u} \cdot \frac{T_u}{T_{DPPH}} \cdot C_u \quad (1)$$

(1) were explained on p. 22. The value of c for the unrearranged radical (16b) was 8, whilst a value of 25.6 was used for the rearranged radical (17b). The values of [U] and [R] calculated by use of (1) are shown in Table 10. From these values of [R] and [U], and by using expression (2) (p. 23), values for $k_r/2k_t$ were calculated. These values are also shown in Table 10. As stated in Chapter 1

$$k_r/2k_t = \{[R]^2/[U]\} + [R] \quad (2)$$

(p. 23) the value of $2k_t$ is assumed to be equal to that of the n-pentyl radical. Hence, by using the rate equation for the

termination reaction of n-pentyl radicals, i.e. expression (3), values of $2k_t$ were calculated. Using these values of $2k_t$ and the values of $k_r/2k_t$

$$\log(2k_t) = (12.3 \pm 0.7) - (10.5 \pm 3.0)/2.3RT \qquad (3)$$

derived from (2), values of k_r for the rearrangement were determined. These values are also shown in Table 10. The calculated values of k_r were plotted on an Arrhenius graph of $\log(k_r)$ against 1/T. This plot is shown by Figure 10 (p. 81).

Table 10

Data from the kinetic e.s.r. experiment

Temp/K	$[U]^a$/mol l^{-1}	$[R]^a$/mol l^{-1}	$k_r/2k_t$ [a,b]	k_r/s^{-1}
170	1.21	4.07	17.8	209
	1.37	3.99	15.6	183
	1.30	3.90	15.6	183
165	1.58	3.26	9.99	93.7
	2.07	3.13	7.86	73.7
	1.50	2.85	8.27	77.6
159.5	1.89	2.60	6.18	44.5
	3.43	2.08	3.34	24.0
	1.59	1.47	2.83	20.4
154	2.34	1.68	2.89	15.7
	3.85	1.37	1.86	10.1
	1.52	1.08	1.85	10.0
149	4.55	1.08	1.34	5.5
	2.21	0.64	0.83	3.4
143	2.05	0.37	0.44	1.3

a : all values $\times 10^8$, b: in mol dm^{-3}.

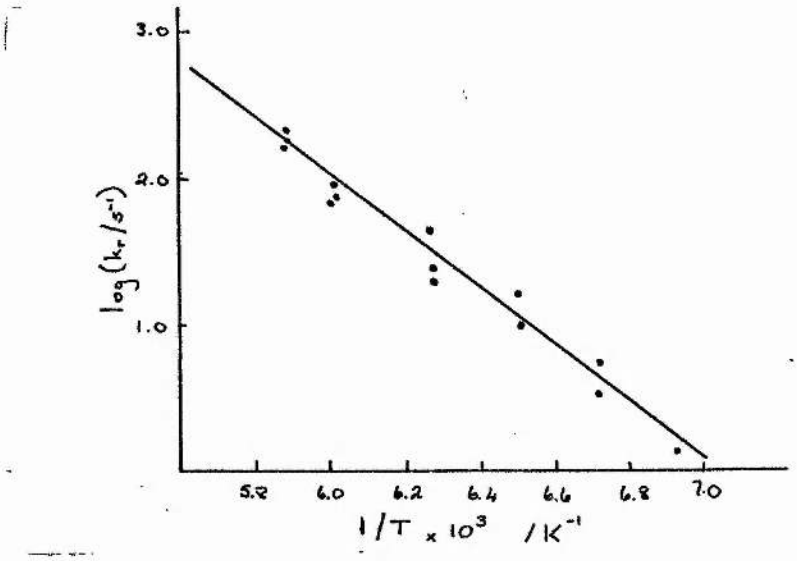


Figure 10. Arrhenius plot of $\log(k_r)$ against $1/T \times 10^3$ for the rearrangement of radical (16b).

Using a least squares fit analysis of the experimental values the following were calculated :-

Intercept = 13.17 ± 0.13

Gradient = -1.862 ± 0.097

The experimental data gave a correlation coefficient of 0.965 with the line drawn by the least squares fit analysis.

In the introduction (Ch 1, p. 24) it was shown that for this plot, $\log(k_r)$ against 1/T, the intercept is equal to the logarithm of the pre-exponential (Arrhenius) factor, A, and that the gradient is equal to -E/2.3R, where E is the activation energy of the rearrangement. Thus the following are obtained :-

$\log A = 13.2 \pm 0.1$

$E = 35.6 \pm 1.9$ kJmol^{-1}

Thus, for the rearrangement of spiro[2.3]hex-4-yl radicals (16b) to cyclobutenylethyl radicals (17b), the rate equation is :-

$$\log(k_r/s^{-1}) = (13.2 \pm 0.1) - (35.6 \pm 1.9\ kJmol^{-1})/2.3RT$$

The Arrhenius factor is ca 10^{13}, which is the order of magnitude expected for this type of reaction. The value of E for the rearrangement of cyclopropylmethyl radicals has been calculated to be ca $25.4kJmol^{-1}$.[11] Thus radical (16b) possesses a greater activation energy than the cyclopropylmethyl radical. This is expected since the latter radical ring opens at a lower temperature, i.e. ca 133K compared to ca 143K for radical (16b).

As discussed earlier no kinetic work was possible on the spiro[2.4]hept-4-yl radical (16c), as only the rearranged cyclopentenylethyl radical (17c) was observed. The activation energy for the rearrangement of radical (16c) is estimated to be $< 20kJmol^{-1}$. Similarly, the value of E for the rearrangement of spiro[2.2]pent-4-yl radicals (16a) is estimated to be $> 55kJmol^{-1}$.

Thus, as n is increased a steady decrease in the activation energy of rearrangement is observed for radicals (16a-c).

This links in with the stereoelectronic rationale to ring opening which suggests that β-scission can occur more readily as n increases, i.e. the thermodynamic barrier to ring puckering, the activation energy, decreases as n increases.

(c) Semi-Empirical SCF-MO Calculations on Spiro[2.n]alkanes.

The limitations of semi-empirical calculations were discussed earlier (Ch 2, p. 45).

Again these calculations can be used to give an indication of the weakening of the $\beta-\gamma$ bond by calculating the extension of these bonds in the radicals (16) as compared to the parent hydrocarbon (15). Table 11 shows the calculated $\beta-\gamma$ bond extensions for radicals (16a-c). From Table 11 it can be seen that a small degree of

Table 11

$\beta-\gamma$ bond extensions for radicals (16a-c).

Reaction	Bond extension / Å	
	MNDO	MINDO/3
16a →17a		0.01[a]
16b→17b	0.02	0.02
16c→17c	0.03	0.02

a : from ref 20.

weakening of the $\beta-\gamma$ bonds occurs. As with bicyclo[n.1.0]alk-2-yl radicals (12) the degree of weakening indicated by bond extensions is slight.

Similarly, as with radicals (12) the β-scission of radicals (16b,c) was followed by calculating the heat of formation at each point along a series of increasing β-γ bond lengths. The results of these calculations are shown in Figures 11a,b (p. 85). Figure 11a shows the ΔH_f against β-γ bond length plot for spiro[2.3]hex-4-yl radicals, whilst Figure 11b shows the analogous plot for spiro[2.4]hept-4-yl radicals. From these plots the values of the enthalpies of reaction, ΔH^o, and of activation, $\Delta H^{\neq}$, were determined. These values are given in Table 12.

Table 12

ΔH^o and $\Delta H^{\neq}$ values calculated from Figures 10a,b using MNDO calculated ΔH_f values.

Reaction	$\Delta H^{\neq}$/kJmol^{-1}	ΔH^o/kJmol^{-1}
16b→17b	102	0
16c→17c	87	-23

From Table 12 it can be seen that the $\Delta H^{\neq}$ values are approximately three to four times the experimental values. [N.B. The $\Delta H^{\neq}$ values for bicyclo[n.1.0]alk-2-yl radicals were also approximately four times the experimental result.] As observed in Chapter 2 the MNDO method overestimates the barrier to reaction, $\Delta H^{\neq}$, quite considerably.

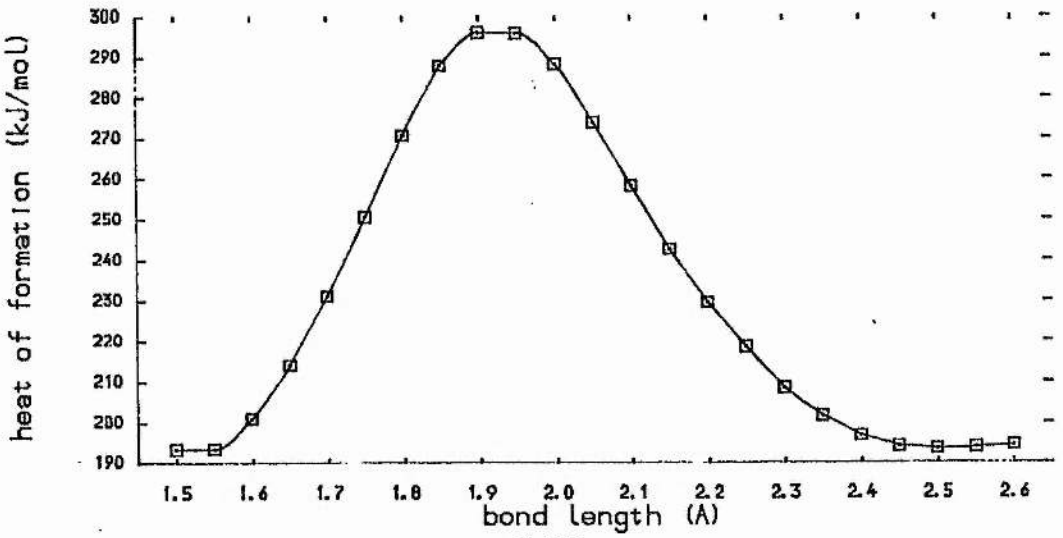


Figure 11a. Plot of heat of formation against β-γ bond length for the spiro[2.3]hex-4-yl radical (16b).

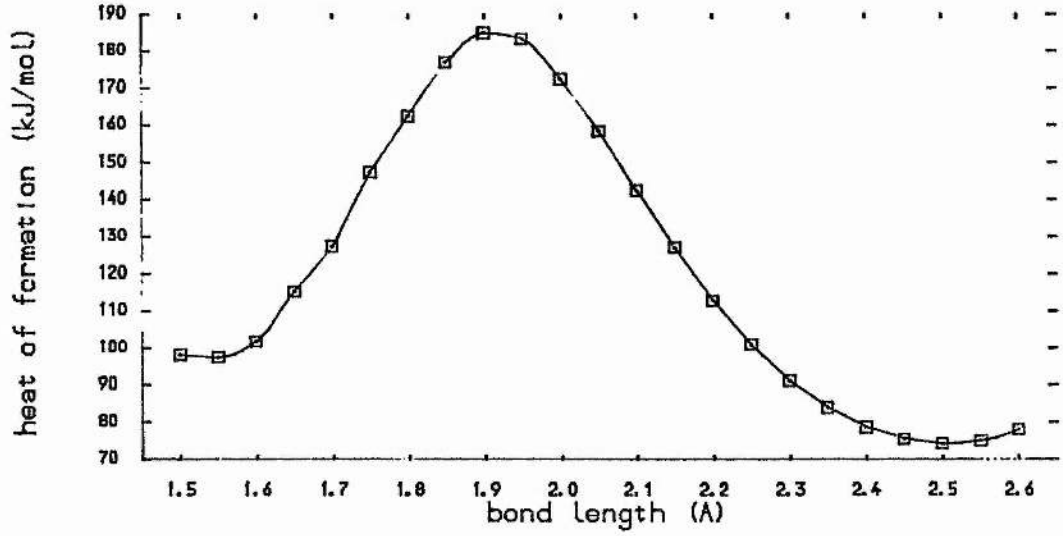


Figure 11b. Plot of heat of formation against β-γ bond length for the spiro[2.4]hept-4-yl radical (16c).

Also from Table 12 the ΔH° values for the rearrangement indicate that the β-scission of radical (16b) is, overall, a thermoneutral reaction. This contrasts significantly with the earlier discussed ring strain effects which showed that rearrangement of radical (16b)

to radical (17b) resulted in considerable relief of ring strain. This should mean that the rearrangement of (16b) to (17b) is exothermic. Similarly, MNDO predicts that the rearrangement of radical (16c) to radical (17c) is slightly exothermic. Relief of ring strain for this rearrangement is considerable, $> 100 kJmol^{-1}$, and therefore it is expected that this reaction would be quite exothermic.

Thus, it would appear that MNDO not only overestimates the activation energy for the rearrangement, but also considerably underestimates the overall enthalpy of reaction.

Using the MNDO calculated geometries, plots of the spiro[2.3]hex-4-yl (16b), and spiro[2.4]hept-4-yl (16c) radicals were drawn. These are shown by Figures 12a and 12b respectively. Only the

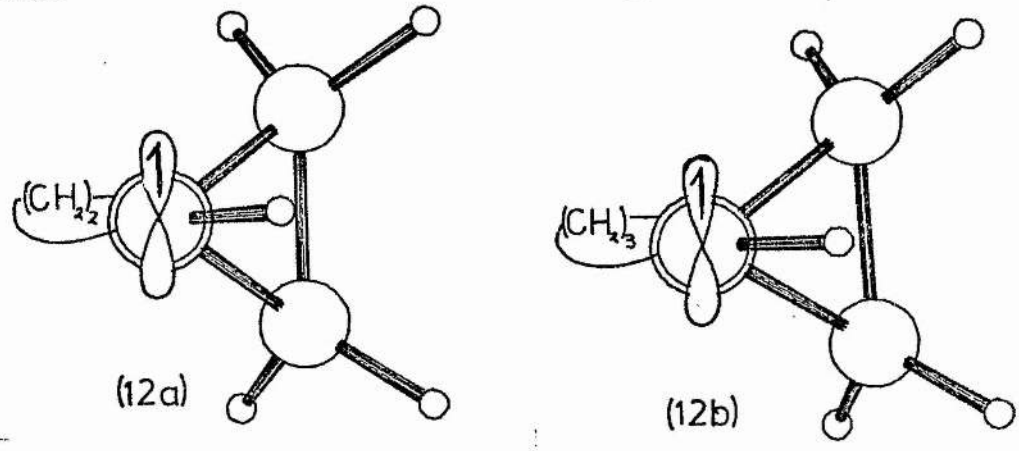


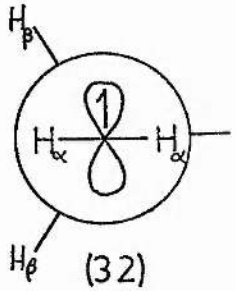
Figure 12. Geometry of spiro[2.3]hex-4-yl (12a), and spiro[2.4]-heptyl (12b) radicals from MNDO calculations.

relevant carbon atoms and associated hydrogens are shown. The aspect of view is along the C(4)-C(1) bond, with the C(4) foremost. The plots are very similar, both showing the radical to have adopted

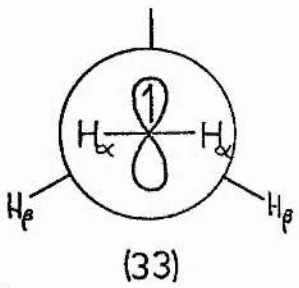
conformation (19). As stated previously this conformation is thought to be unfavourable to β-scission. However, in section 3.2 (a) it was suggested how, through ring puckering, a conformation more favourable to β-scission could be attained.

(d) The Conformation of Cycloalkenylethyl Radicals, and the Barrier to Internal Rotation about $\dot{C}$-C_β.

In the introduction (Ch 1, p. 25) the method by which the conformation of an ethyl like radical could be identified was outlined. There are two possible conformations for an alkyl radical which possesses two α-hydrogens and two β-hydrogens. These are the perpendicular conformation (33), or the unsymmetric conformation (32). The absolute magnitude, and the temperature dependance of $a(H_\beta)$ proves which conformation is adopted (Ch 1, p. 25).



(32)



(33)

Figure 13 shows the plot of $a(H_\beta)$ against temperature for cyclobutenylethyl (17b) and cyclopentenylethyl (17c) radicals. Both radicals, (17b) and (17c) have large absolute magnitudes for $a(H_\beta)$ and show a negative sign for $da(H_\beta)/dT$. Hence, both radicals adopt conformation (32) preferrentially.

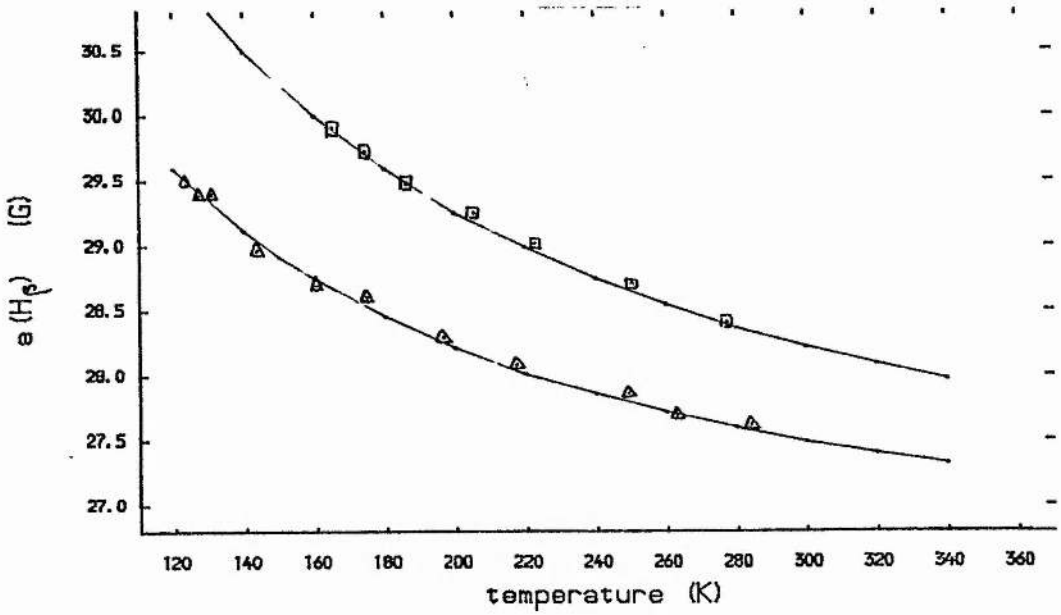


Figure 13. Plot of $a(H_\beta)$ against temperature for radicals (17b,c) ⊡ represents radical (17b), △ represents radical (17c).

As with cycloalkenylmethyl radicals the conformation adopted is probably influenced by steric factors. Again these steric effects can be most easily assessed by examining the interatomic separations between the α-hydrogens and their nearest neighbours. As before, 'rationalised geometries' are used whereby $\dot{C}$-H_α 1.08, $\dot{C}$-C_β 1.48, C_β-H_β 1.12Å and $\angle H_\alpha\dot{C}H_\alpha$ 120°. The other parameters coming from the fully optimised MNDO geometry. Thus, the shortest, and hence most important interatomic separations were calculated for both conformations, (32) and (33), of radicals (17b) and (17c). The results are shown in Table 13. The same uncertainties which were discussed previously (Ch 2, p. 52) should still be borne in mind.

Table 13

The shorter interatomic separations, in Å, for radicals (17b) and (17c) as calculated by MNDO theory.

	cyclobutenylethyl		cyclopentenylethyl	
	(32)	(33)	(32)	(33)
$H_\alpha-H_\beta$	2.98	2.47	2.94	2.45
$H_\alpha-H_\beta$	2.99	3.09	2.98	3.09
$H_\alpha-C_\beta$	2.71	3.12	2.72	3.12
$H_\alpha-H_\beta$	2.57	3.13	2.54	3.06
$H_\alpha-H_\beta$	2.59	2.48	2.58	2.46
$H_\alpha-C_\beta$	3.53	3.12	3.53	3.12

From the H-H separations shown in Table 13 it is seen that the most important, i.e. shortest, H-H separations are the two $H_\alpha-H_\beta$ repulsions of ca 2.45-2.48Å found in the perpendicular conformation (33) of both radicals (17b) and (17c). These repulsive terms appear to result in the adoption of conformation (32) by both cycloalkenylethyl radicals (17b) and (17c). Strangely MNDO predicts conformation (33) to be more stable for both radicals. However, the energy difference between the conformations is slight, ca 1kJmol^{-1}, and, as stated earlier, it is outwith the scope of the technique to correctly predict the adopted conformation.

The barrier to internal rotation about C-C , V_0, was calculated for both radicals (17b,c) using the method discussed earlier (Ch 1, p. 28). Figure 13 shows the plot of the experimental data, along with the curves drawn from calculated values of a(H). The latter being calculated by equation (12). The values of A, B, and

$$a(H_\beta) = A + 1/2B + 1/2B\cos 2\theta_0[I_1(\lambda)/I_0(\lambda)] \qquad (12)$$

V_0 were altered such that the best possible fit was obtained. Table 14 shows the values of A, B, and V_0 calculated.

Table 14

Radical	θ^o_0	A	B	V_0/kJmol^{-1}
17b	30	1.0	50	1.7
17c	30	1.0	50	1.1

From Table 14 it is seen that the A and B values for both radicals are identical. The barrier to internal rotation, V_0, for radical (17b) is slightly greater than that for radical (17c) The exact reason for this is unknown. Approximately the same barriers to rotation were determined by the INDO technique, though this failed to predict the correct conformation.

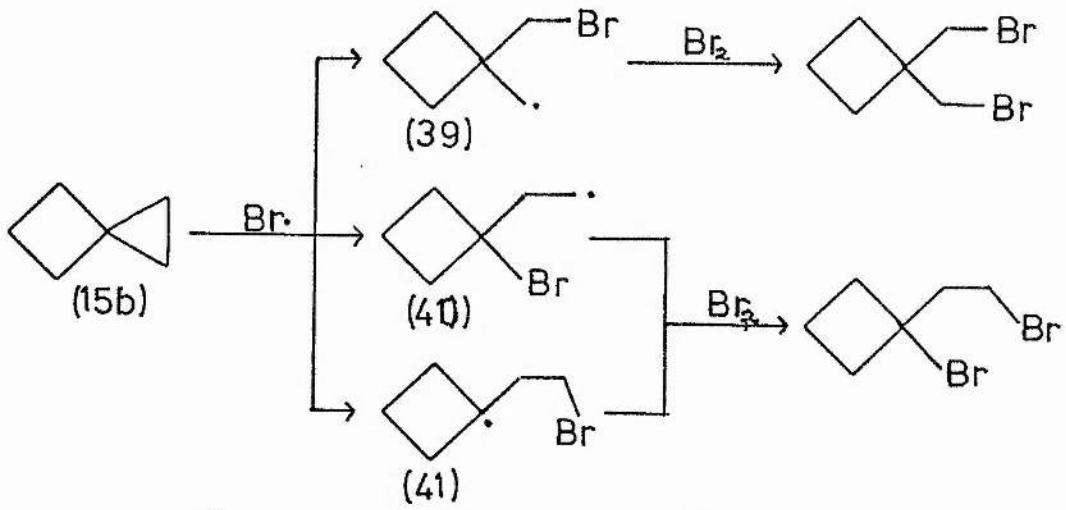
(e) The Photobromination of Spiro[2.3]hexane (15b).

The reaction of spiro[2.3]hexane (15b) with molecular bromine in CCl_4 solution, at 20°C, proceeds rapidly on illumination with complete removal of bromine colouration in ca 5 minutes. G.l.c. analysis of the reaction mixture showed two major components, along with some minor components and unreacted (15b). Retention time measurements identified 1,1-bis(bromomethyl)cyclobutane as one of the major reaction products. The second major product was identified as 1-bromo-1-(2-bromoethyl)cyclobutane by ^1H n.m.r. G.l.c. mass-spectrometry confirmed these products, and also identified the presence of mono-brominated products in the reaction mixture. The exact nature of these however could not be ascertained, but it is likely that 1-bromomethyl-1-methylcyclobutane was present. Similarly bromoethylcyclobutane may also have been present. No products resulting from rearrangement of radical (16b), spiro[2.3]hex-4-yl, were identified. Similarly no bromospiro[2.3]hexane was detected.

The result of a quantitative g.l.c. analysis showed the reaction products to be ca 80% 1,1-bis(bromomethyl)cyclobutane and ca 19% 1-bromo-1-(2-bromoethyl)cyclobutane. Mono-brominated products amounted to ca 1% of the total.

The reaction of (15b) with molecular bromine is shown in Scheme 9. Though this only shows the dibrominated products, the formation of

Scheme 9



monobromides can be seen to occur by hydrogen abstraction, from the substrate, by the intermediate radicals. Attack by bromine at the methylene carbon of the cyclopropane ring can give rise to radicals (39) and (41) by fission of the appropriate cyclopropane bond. These radicals henceforth abstract bromine to give the observed dibromo-products. Radicals (39) and (41) may also abstract hydrogen to give the monobromo- product. However, due to the small amount of monobrominated products obtained this route must be minor. Attack by bromine at the central carbon can give radical (40) by cyclopropane bond fission. This radical can then abstract bromine to give 1-bromo-1-(2-bromoethyl)cyclobutane as shown. Alternatively, radical (40) may abstract hydrogen, but as with radicals (39) and (41) this can only be a minor pathway due to the small yield of monobrominated

material.

The high yield of 1,1-bis(bromomethyl)cyclobutane in the bromination of spiro[2.3]hexane (15b) resembles the result of the bromination of spiro[2.2]pentane (15a). In this reaction the major product was 1,1-bis(bromomethyl)cyclopropane.[20] The photobromination of (15b) does not give products resulting from hydrogen abstraction at C(4), unlike the chlorination reaction in which such products were reported.[38]

3.3 Conclusions

The study of spiro[2.n]alkanes (15), where n = 3,4 , has shown that both the spiro[2.3]hex-4-yl (16b) and spiro[2.4]hept-4-yl (16c) radicals undergo β-scission of a cyclopropyl bond to give cyclobutenylethyl (17b) and cyclopentenylethyl (17c) radicals respectively. This contrasts with the behaviour of spiro[2.2]pent-4-yl radicals (16a), which are anomalously stable to β-scission. Radical (16b) and (16c) also ring open at different rates. The latter radical, (16c), was observed to have ring opened at temperatures as low as ca 90K. In contrast radical (16b) was observed only to ring open at temperatures greater than ca 140K. As a consequence of this a kinetic e.s.r. experiment on the rearrangement of radical (16b) was possible. This was carried out and as a result the energy of activation for the rearrangement was calculated to be ca 35kJmol^{-1}. This corresponds to the estimated values of the activation

energy for radicals (16a) and (16c) of $> 55 kJmol^{-1}$ and $< 20 kJmol^{-1}$ respectively. Thus for radicals (16) the activation energy for the rearrangement via β-scission is observed to decrease in a fairly regular manner as n increases from 2 to 4.

The β-scission of radicals (16b) and (16c) can be explained by use of the stereoelectronic effect, though this effect may be aided by the cyclobutane ring of (16b), or the cyclopentane ring of (16c) adopting a puckered conformation. This may also explain the difference in the rate of β-scission between radicals (16b) and (16c). Ring strain effects will promote β-scission in both radicals (16b,c). However, since, for radicals (16b) and (16c), the difference in relief of ring strain obtained is not great, the exact effect of ring strain on the ring opening of radicals (16b,c) cannot be determined.

The barrier to internal rotation about $\dot{C}-C_\beta$, and the preferred conformations of radicals (16b) and (16c) were determined. Both cycloalkenylethyl radicals (17b) and (17c) were found to adopt unsymmetric conformations (32). The barriers to internal rotation of both radicals were similar, both radicals having the same A and B factors. The V_0 terms were slightly different, radical (17b) possessing the greater value.

The photobromination of spiro[2.3]hexane gave two major products, i.e. 1,1-bis(bromomethyl)cyclobutane and 1-bromo-1-(2-bromoethyl)--cyclobutane. Monobrominated products amounted to ca 1% of the total reaction product. No products arising from hydrogen abstraction at C(4) were detected.

Chapter 4

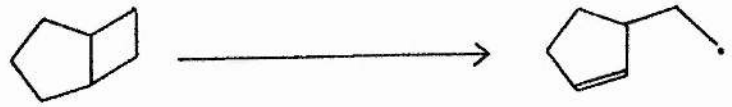
SPIRO[3.3]HEPTANES

A Study of Cyclobutylmethyl Radical Analogues

4.1 Introduction

Cyclobutylmethyl radicals (42), like cyclopropylmethyl radicals, are known to undergo β-scission in a stereoelectronically governed manner to give pent-4-enyl radicals.[4] Similarly cyclobutylmethyl like radicals also ring open in a stereoelectronically governed manner.

(42)



(8)

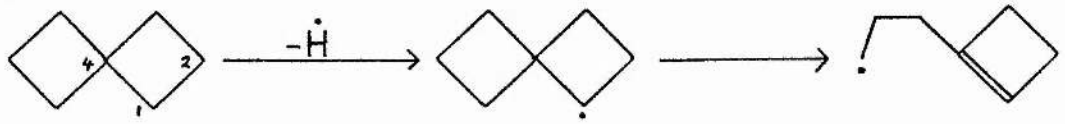
Example (8) from page 11 (shown above) demonstrates such behaviour.[15] The β-scission of cyclobutylmethyl radicals (42) has been studied, and the Arrhenius parameters for the rearrangement have been determined.[21] Radical (42) was observed to undergo rearrangement at a significantly higher temperature than that at which cyclopropylmethyl radicals (2) rearrange, i.e. ca 250K for radical (42) compared to ca 130K for radical (2). The activation energy for the rearrangement of radical (42) is also greater than that for radical (2). Therefore, the ring opening of cyclobutylmethyl radicals is much slower than the ring opening of cyclopropylmethyl radicals. Thus, assuming that cyclobutylmethyl like radicals behave in a similar manner to that of (42), there is a greater probability that the rearrangement of these radicals can be observed. In turn, if the rearrangement is more likely to be observed, then the chance of measuring the rate of

rearrangement increases.

Furthermore, the study of cyclobutylmethyl like radicals builds upon previous work carried out on cyclopropylmethyl like radicals. In particular this work follows on from that already carried out on spiro[2.n]alkanes (Ch. 3).

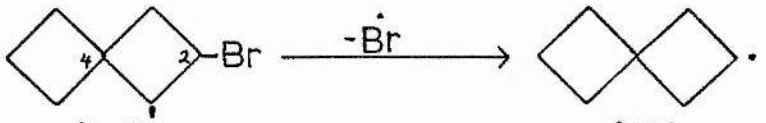
In Chapter 1 it was stated that this chapter was to cover three particular areas of work. These being :

i)Spiro[3.3]hept-1-yl radicals (22) generated from spiro[3.3]heptane (21).



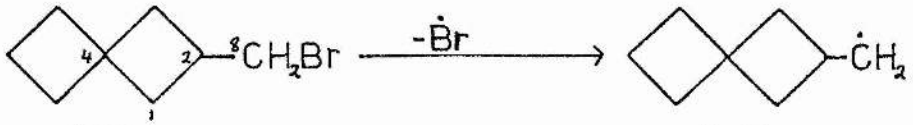
(21) (22) (23)

ii)Spiro[3.3]hept-2-yl radicals (25) generated from 2-bromospiro--[3.3]heptane (24).



(24) (25)

iii)Spiro[3.3]heptane-2-methyl radicals (27) generated from 2-bromo--methyspiro[3.3]heptane (26)



(26) (27)

(28) (29)

Of these three systems, only (i) and (iii) give cyclobutylmethyl like radicals. The spiro[3.3]hept-2-yl radical (25) is not a cyclobutylmethyl like radical, and as a result does not undergo rearrangement via β-scission in the accessible temperature range. It is also seen that ring opening of radical (27) yields a second cyclobutylmethyl like radical (28), which can potentially undergo a second β-scission to give radical (29).

Unfortunately spiro[3.3]heptane could not be prepared. Two different synthetic methods were attempted, one of these repeatedly, but no spiro[3.3]heptane was obtained.

4.2 Results and Discussion

(a) The E.S.R. Study of Bromine Abstraction from 2-Bromospiro--[3.3]heptane (24).

Samples of 2-bromospiro[3.3]heptane (24) along with DTBO and triethylsilane were prepared. Cyclopropane was added as the hydrocarbon solvent, and the samples were thoroughly degassed. The samples were sealed, and photolysed within the cavity of the e.s.r. spectrometer. All spectra were recorded at ca 9.4GHz.

On bromine abstraction from a sample of 2-bromospiro[3.3]heptane at ca 145K the spectrum shown in Figure 13 was recorded. This spectrum consists of a doublet of quintets with h.f.s. arising from a

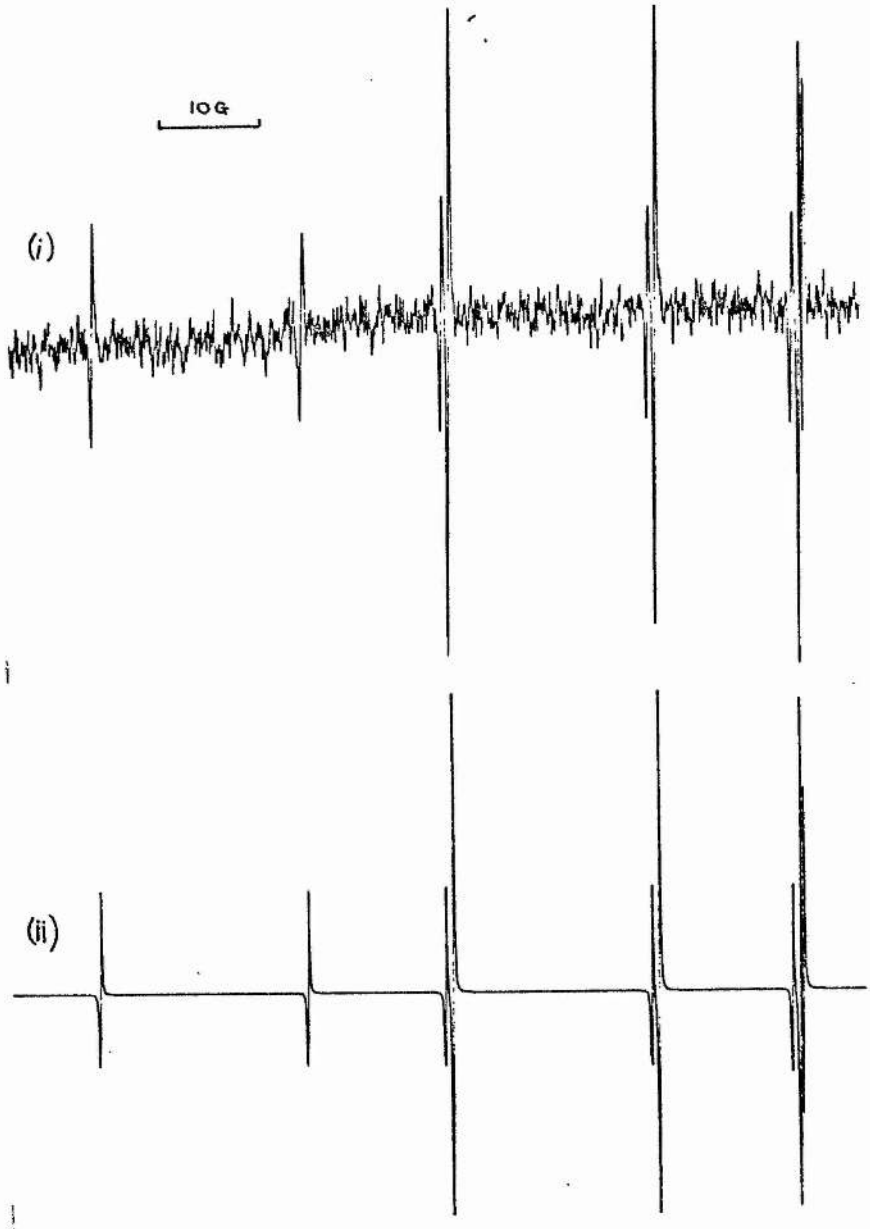


Figure 13. Low field half spectrum of spiro[3.3]hept-2-yl radicals (25) at 9.4GHz, 200G scan. (i)observed at 145K, (ii)simulation

single α-hydrogen and from four equivalent β-hydrogens. The h.f.s. parameters were found to be ; $a(H_\alpha)$ 21.6G, $a(4H_\beta)$ 36.5G. The simulated spectrum was drawn using these values. The h.f.s. parameters of radical (25) are very similar to those of the structurally similar cyclobutyl radical,[10] as would be expected. From Figure 13 it can be seen that the e.s.r. spectrum of radical (25) displays a resolved second order effect. In Figure 14 an expanded scale (10G sweep width) spectrum of the central line of the quintet is shown. Figure 14a shows the first derivative spectrum, 14b shows the second derivative spectrum of the same multiplet.

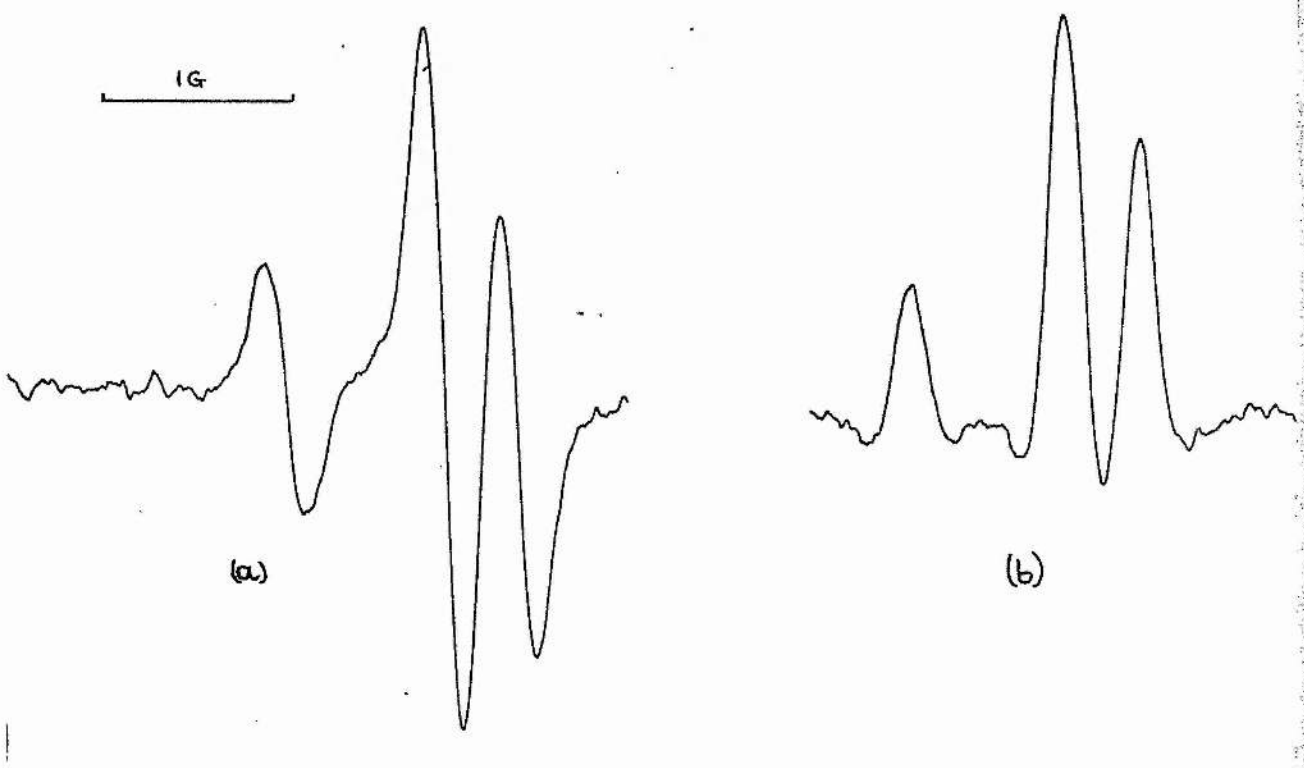


Figure 14. Expanded scale spectra (10G sweep width) of central line of quintet.

(b) The E.S.R. Study of Bromine Abstraction from 2-Bromomethylspiro--[3.3]heptane (26).

Samples of 2-bromomethylspiro[3.3]heptane (26), DTBO, and triethylsilane with cyclopropane as hydrocarbon solvent were prepared as in the previous section. For the kinetic e.s.r. experiment at T > 240K the samples were prepared from (26), DTBO, and hexamethyl-ditin using tert-butylbenzene as the solvent. All samples were thoroughly degassed, sealed and photolysed within the cavity of the e.s.r. spectrometer. All spectra were recorded at ca 9.4GHz.

On bromine abstraction from a sample of 2-bromomethylspiro[3.3]--heptane (26) at ca 143K the spectrum shown in Figure 15 (p. 101) was recorded. This consists of a doublet of triplets arising from the h.f.s. of two α-hydrogens and a single β-hydrogen. Each component is further split into a triplet by the h.f.s. of two γ-hydrogens. The h.f.s. parameters were found to be ; $a(2H_\alpha)$ 21.8G, $a(H_\beta)$ 10.2G, and $a(2H_\gamma)$ 1.65G. The simulation was drawn using these values. A close examination of the spectrum of radical (27) shows that the outer lines of the major triplet show partly resolved fine structure. This is not apparent on the central lines. In Figure 16a (p. 102) the second derivative spectrum of line x of the spectrum in Figure 15 is shown. This clearly shows the fine structure, though the exact nature of this cannot be fully made out. Figure 16b (p. 102) shows an expanded scale spectrum (10G sweep width) of this multiplet. This shows the fine structure to consist of seven lines, arising from the

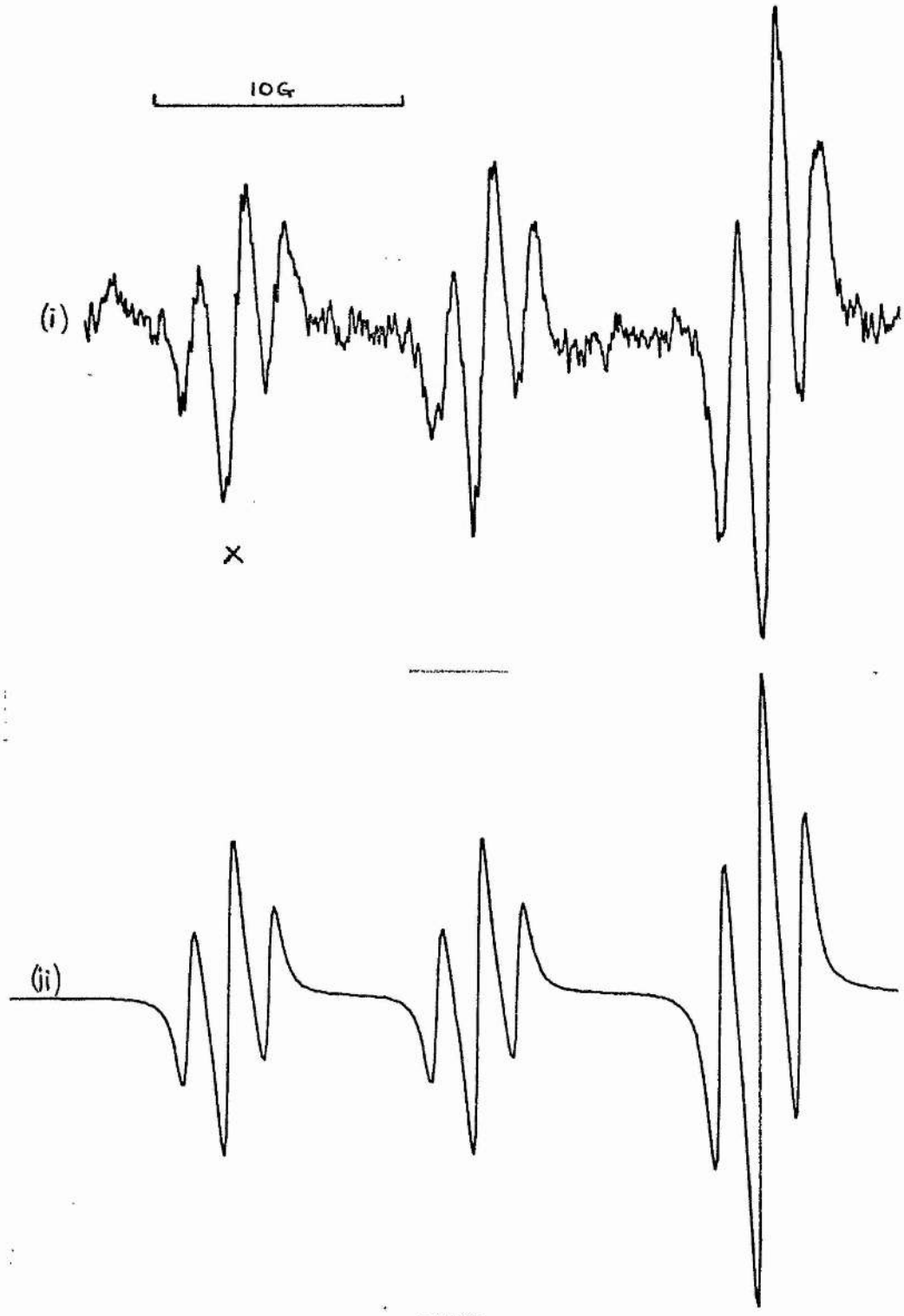


Figure 15. Low field half spectrum of spiro[3.3]heptane-2-methyl radicals (27) at 9.4GHz. (i)observed at 143K, (ii)simulation

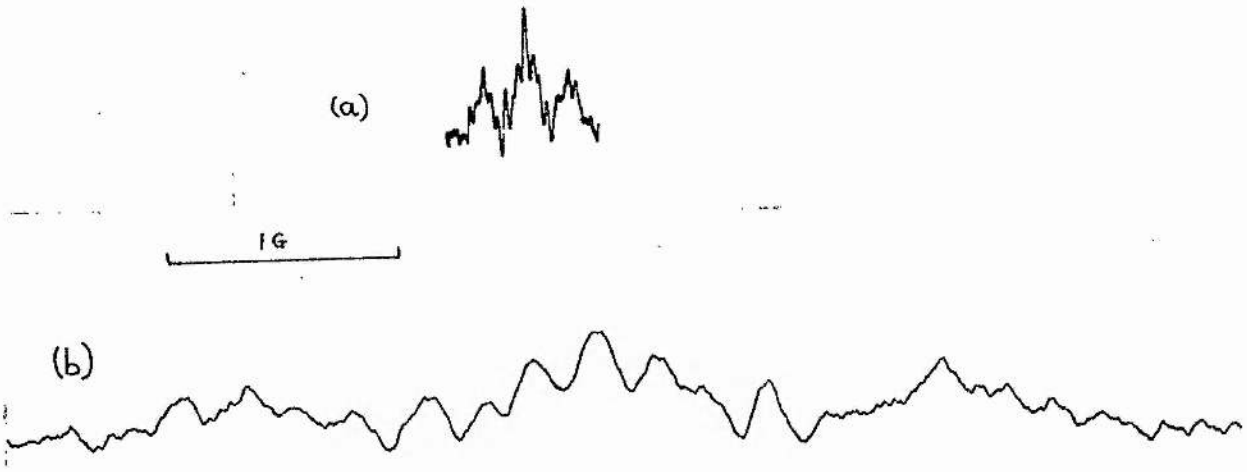


Figure 16. (a) Second derivative spectrum of line x in Figure 15, (b) expanded scale (10G sweep width) of same line.

h.f.s. of six equivalent hydrogens. Of these six hydrogens, two are γ'-hydrogens and the other four are ε-hydrogens. The h.f.s. was found to be ca 0.27G. Radical (27) possesses four γ-hydrogens, of these two give rise to the triplet splitting, whilst the other two, γ', along with the four ε-hydrogens on the second cyclobutyl ring give rise to the fine structure. The most probable reason as to why two different h.f.s arise from the γ-hydrogens is that the structure of the radical is such that the two γ'-hydrogens are orientated away from the SOMO. This most probably entails their position being on the opposite side of the plane of the cyclobutyl ring to the SOMO. As a result, the interaction between the SOMO and these γ'-hydrogens will be slight, hence the very small h.f.s.

The spectrum of radical (27) remained unchanged on warming, a(H) excepted, up to ca 245K. Above this temperature the signal intensity began to weaken, this being accompanied by the emergence of new radical signals. Above ca 275K radical (27) could no longer be detected, rather only the signals from the new radical species were observed. In Figure 17 the spectrum recorded at ca 270K is shown. The signals marked o arise from radical (27). The second radical spectrum consists of a triplet of triplets with h.f.s. arising from two α-hydrogens and two γ-hydrogens. The h.f.s. parameters were measured to be ; $a(2H_\alpha)$ 21.6G, $a(2H_\gamma)$ 1.2G. The simulation was drawn using these values. This spectrum was assigned to the rearrangement product of radical (27), namely the 1-(prop-2-enyl)cyclobutylmethyl radical (28). The rearrangement of radical (27) through to radical

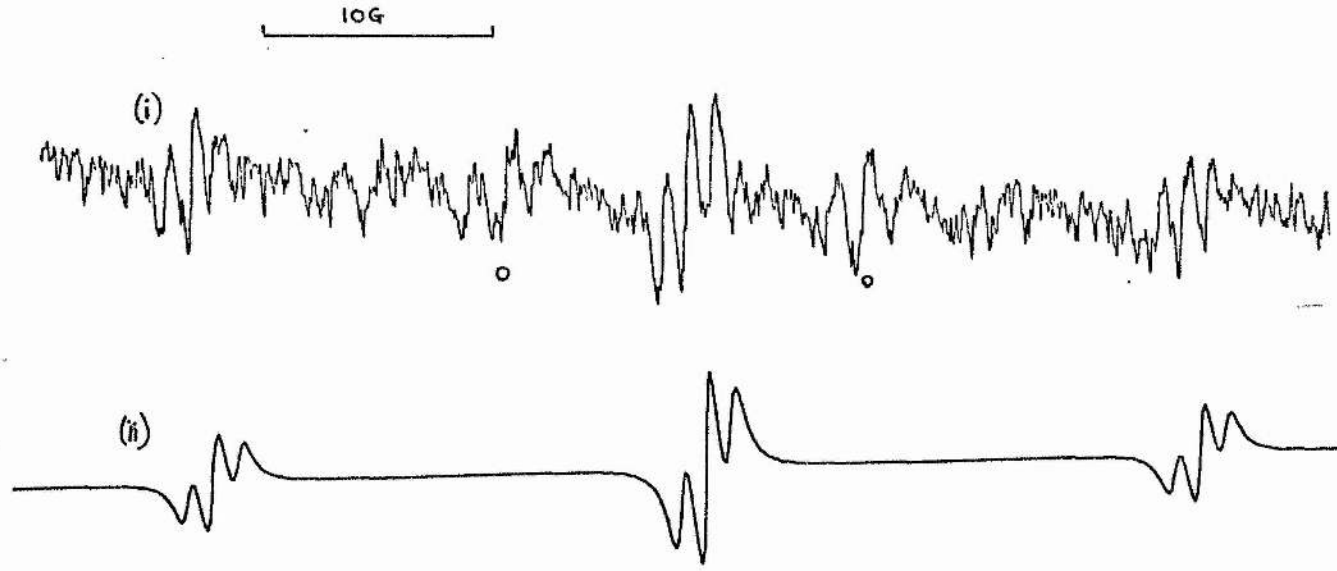


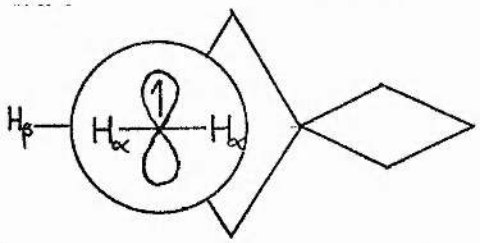
Figure 17. Whole spectrum of radical (28) at ca 9.4GHz (o denotes signals due to radical (27)). (i)observed at 270K, (ii)simulation

(28) was followed by a kinetic e.s.r. experiment, the results of which are discussed in the following section (4.2 (c)).

In the introduction it was stated that since radical (28) is itself a cyclobutylmethyl like radical, it can undergo β-scission to give radical (29) (see p. 96). From Figure 17 it can be seen that the signals from radical (28) were very weak. As a result, radical (29) could not be detected. However, the results of the kinetic e.s.r. experiment suggest that this second rearrangement does occur. This will be discussed more fully discussed in section 4.2 (c).

In the previous chapters it was shown that the conformations of the cyclopropylmethyl like radicals studied therein can, and do, influence the rearrangement. The same holds true for cyclobutylmethyl like radicals.

From the small absolute magnitude of $a(H_\beta)$ for the spiro[3.3]heptane-2-methyl radical (27) it follows that this radical adopts a bisected conformation (shown below). The cyclobutylmethyl



radical also adopts this conformation.[21] It can be seen that in this conformation there will be considerable overlap, and hence interaction, between the SOMO and the orbitals that comprise the

$\beta-\gamma$ bonds. Thus the rearrangement of radical (27) is favoured by stereoelectronic considerations. Hence β-scission should occur. At the same time however the rearrangement of radical (27) through β-scission will also be favoured by thermodynamic factors. The relief of ring strain in rearranging from radical (27) to radical (28) will be quite considerable, since this rearrangement results in the disruption of a cyclobutyl ring.

Thus the β-scission of the spiro[3.3]heptane-2-methyl radical (27) is favoured by both stereoelectronic and thermodynamic effects.

(c) The Kinetic E.S.R. Study of the Rearrangement of Spiro[3.3]--heptane-2-methyl Radicals (27).

In the previous section it was stated that between ca 245K and ca 275K both rearranged (28) and unrearranged (27) radical species could be detected. As a result a kinetic e.s.r. experiment was carried out using the procedure of Ingold et al.[22-24] This technique has been described in detail in Chapter 1 (p. 21). Using expression (1) the values of [U] and [R] were calculated. The value of c for the rearranged radical was 4, whilst a value of 2 was used for the

$$[U] = [DPPH] \cdot \frac{w_u}{w_{DPPH}} \cdot \frac{G_{DPPH}}{G_u} \cdot \frac{(0.1)^2}{(1)^2} \cdot \frac{R_{DPPH}}{R_u} \cdot \frac{T_u}{T_{DPPH}} \cdot \frac{c_u}{} \quad (1)$$

unrearranged radical. The values of [U] and [R] calculated are shown

in Table 15. From these values of [U] and [R] values of $k_r/2k_t$ were calculated using expression (2). These values are also shown in

$$k_r/2k_t = \{[R]^2/[U]\} + [R] \qquad (2)$$

Table 15. As stated in Chapter 1 (p. 23) the value of $2k_t$ is assumed to be equal to that for the n-pentyl radical. Hence, by using expression (3) values of $2k_t$ were calculated. Using the values of

$$\log(2k_t) = (12.3 \pm 0.7) - (10.5 \pm 3.0)/2.3RT \qquad (3)$$

$2k_t$ so determined, values of k_r were calculated. These are also shown in Table 15.

Table 15

Temp/K	$[U]^a$/mol l^{-1}	$[R]^a$/mol l^{-1}	$k_r/2k_t$ [a,b]	k_r/s^{-1}
246	7.31	1.21	1.41	165
251	6.92	1.74	2.14	276
254	5.51	2.01	2.74	375
257	4.00	1.60	2.24	327
260	5.01	3.37	5.64	869
262	5.05	2.35	3.44	550
265	4.92	2.33	3.43	580
267	3.30	2.37	4.07	724
273	3.04	1.97	3.25	631
276	2.36	2.36	4.72	963

a: all values $\times 10^8$, b: in mol dm^{-3}.

The values of k_r were plotted on an Arrhenius plot of $\log(k_r)$ against 1/T. This plot is shown by Figure 18.

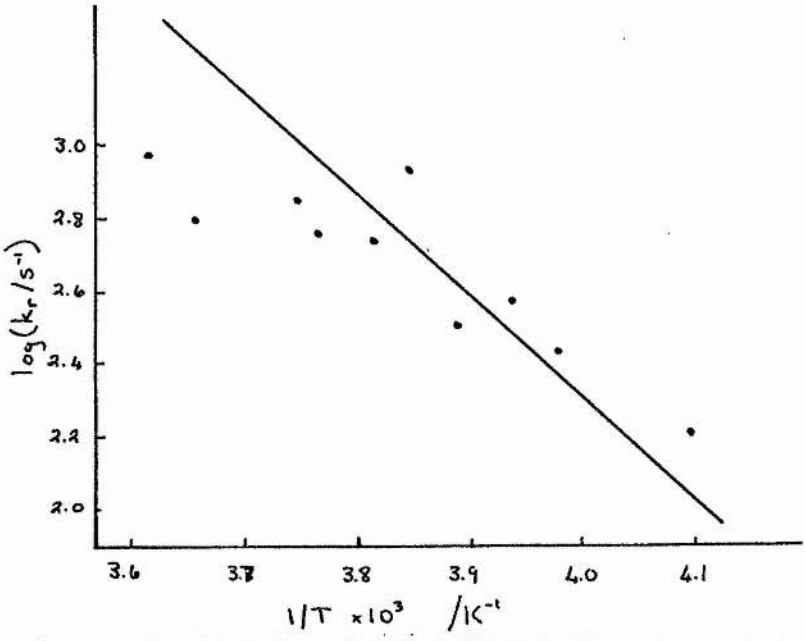


Figure 18. Arrhenius plot of $\log(k_r)$ against $1/T \times 10^3$ for the rearrangement of radical (27).

Using a least squares fit of all the experimental data resulted in the determination of an A factor of ca 10^9 for the rearrangement. This result is far too low, the expected value should lie in the range 10^{12}-10^{13}. Therefore the experimental data was checked and recalculated. The checked results still gave an A factor of ca 10^9. By plotting the experimental data on a large scale plot of $\log(k_r)$ against 1/T, it was found that the first five points, i.e. in the temperature range 246-260K inclusive, gave a straight line which yielded an A factor of ca 10^{13}. The other points, i.e. $T \geqslant 262K$, were seen to curve away from this straight line. Using a least squares fit analysis of these first five points the following were

obtained :-

Intercept = 13.4 ± 0.1

Gradient = -2.77 ± 0.8

The correlation coefficient was 0.81.

As stated previously the intercept is quivalent to log A, and the gradient is equivalent to -E/2.3R. Thus from the above results, the following were obtained :-

$$\log A = 13.4 \pm 0.1$$

$$E = 53.0 \pm 14.9 \text{ kJmol}^{-1}$$

Thus, for the rearrangement of spiro[3.3]heptane-2-methyl radicals (27) to radical (28) the rate equation is :-

$$\log(k_r/s^{-1}) = (13.4 \pm 0.1) - (53.0 \pm 14.9 \text{ kJmol}^{-1})/2.3RT$$

For the rearrangement of cyclobutylmethyl radicals the rate equation is[21] :-

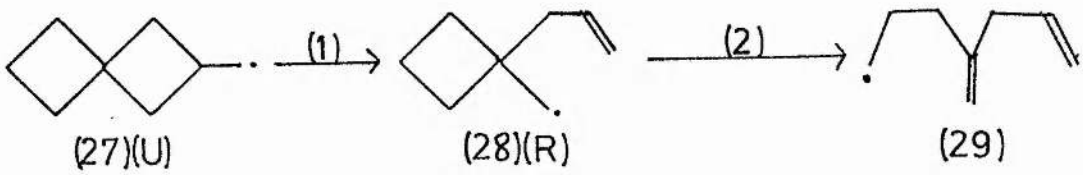
$$\log(k_r/s^{-1}) = (13.1 \pm 1.4) - (49.8 \pm 7.5 \text{ kJmol}^{-1})/2.3RT$$

As can be seen the A and E factors for these two rearrangements are very similar, which is not unexpected, since radical (27) is seen to be only a substituted cyclobutylmethyl radical. Also radical (27) ring opens at T > 245K, c.f. the cyclobutylmethyl radical which rearranges at T > 250K. The rearrangement of these two radicals is therefore very similar.

Also the fact that these two are so alike in A and E factors validates the use of only the first five experimental points.

However, the question as to why the other five experimental points do not fit in with the first five remains. Why are they seen to curve away from the straight line drawn through the first five points?

As mentioned earlier, the rearrangement product of radical (27), i.e. radical (28), is itself a cyclobutylmethyl like radical. Hence, this radical can also rearrange via β-scission to give radical (29) (see scheme).



If radical (28) were to rearrange to radical (29) within the temperature range of the kinetic e.s.r. experiment, the effect would be to reduce the concentration of the rearranged radical (28) from that level which would be found if this second rearrangement did not occur. That is, if rearrangement (2) occurs the value of [R] observed will be smaller than it should be. It was noted that at $T \geqslant 262K$ the experimental points started to fall away from the straight line calculated. Thus, radical (28) may start to rearrange to radical (29) at $T > 260K$. If this were so, the values of [R] determined for $T > 260K$ will be too small. As a result the values of $k_r/2k_t$, and consequently k_r, will also be too low, i.e. smaller than would be the

case if rearrangement (2) did not occur. Also as the temperature increases the rate of rearrangement (2) will increase. Hence radical (28) will be depleted more, even though since the rate of rearrangement (1) has also increased there will be more of radical (28) in the system. The result of this would be to make the calculated value of [R] even smaller, and hence produce smaller $k_r/2k_t$ and k_r values. This would result in the points at higher temperatures varying more from the straight line than those at lower temperatures, as is observed.

Therefore, although there is no direct evidence of rearrangement (2) occurring, there exists enough indirect evidence to point to it taking place. Inclusion of the sixth kinetic e.s.r. point (T = 262K) into the least squares fit analysis results in an A factor of ca. 10^{12}. Since the first five points give such a good result, i.e. very similar to that obtained with cyclobutylmethyl radicals, it is therefore acceptable to use only these five points. Though close to the straight line the point at T = 262K is outwith the experimental error, and therefore there must be some valid reason as to why it does not fit in with those points for $T \leqslant 260K$. This would tend to reinforce the arguement for the rearrangement of radical (28) to radical (29) at T > 260K.

Thus the kinetic e.s.r. experiment for radical (27) has shown that this radical undergoes β-scission to give radical (28) with similar A and E factors to those measured for the rearrangement of cyclobutylmethyl radicals. The kinetic e.s.r. experiment has also shown that radical (28) probably undergoes rearrangement at T > 260K

to give radical (29). Though this second rearrangement was not directly observed, it was deduced to have occurred by close examination of the experimental data.

Thus, as anticipated, radical (27) ring opens to radical (28), which then ring opens itself to radical (29).

(d) Semi-Empirical SCF-MO Calculations on Spiro[3.3]heptane-2-methyl Radicals.

The limitations of these MNDO calcuclations were discussed earlier in Chapter 2 (p. 45).

Unlike the previous examples in Chapters 2 and 3, no data as to the bond extensions found in the radical (27) relative to the same bonds in the parent hydrocarbon (26) were determined. Considering the inconclusive nature of this data in Chapters 2 and 3, it is unlikely that this data would shed any light on the β-scission process.

In Figure 19 the plot of heat of formation against β-γ bond length is shown for the rearrangement of radical (27) through to radical (28). From this plot values of the enthalpy of activation ($\Delta H^{\ddagger}$), and the enthalpy of reaction (ΔH^{o}) were calculated. These were found to be :-

$$\Delta H^{\ddagger} = 153 \text{ kJmol}^{-1}$$

$$\Delta H^{o} = 80 \text{ kJmol}^{-1}$$

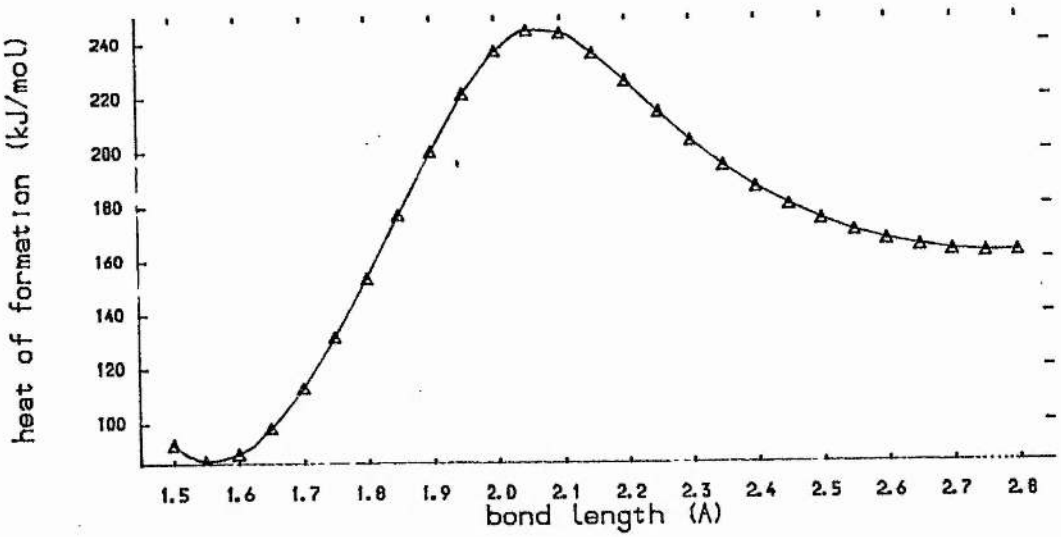


Figure 19. Plot of heat of formation against β-γ bond length for radical (27).

The value of $\Delta H^{\ddagger}$ calculated from the MNDO results is appoximately three times that value derived from the kinetic e.s.r. experiment. [N.B. The MNDO derived $\Delta H^{\ddagger}$ values for the rearrangement of bicyclo[n.1.0]alk-2-yl , and spiro[2.n]alk-4-yl radicals were three to four times that value determined from experimental results.] Therefore, as has been noted earlier, MNDO calculations considerably overestimate energy of activation barriers to rearrangement via β-scission.

The value of ΔH^{o} found by MNDO calculations varies quite considerably from that which is expected. As stated earlier, the rearrangement of radical (27) to radical (28) involves the ring opening of a cyclobutyl ring. This will result in considerable relief of ring strain (>100 $kJmol^{-1}$). From this it would be anticipated that the rearrangement of radical (27) to radical (28) would be an exothermic process. However, the MNDO calculations indicate that this

reaction is endothermic, and hence not favoured thermodynamically. However, it has been noted previously that MNDO calculations considerably underestimate the enthalpy of reaction for the rearrangement process.

In Figure 20 the plot of the MNDO calculated geometry of radical (27) is shown. As before only the relevant carbon atoms, and associated hydrogen atoms are shown. The aspect of view is along the C(8)-C(2) bond, with the radical centre, C(8), foremost.

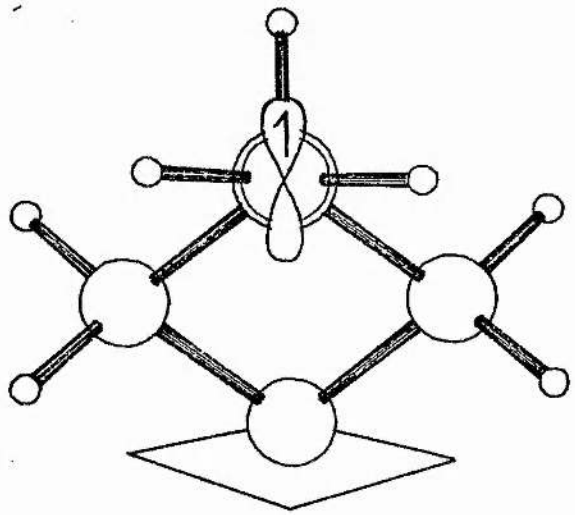


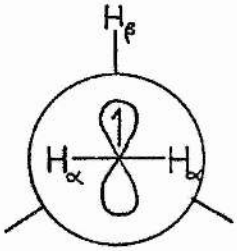
Figure 20. Geometry of spiro[3.3]heptane-2-methyl radical (27) from MNDO calculations.

As can be seen, MNDO predicts radical (27) to have adopted an eclipsed conformation, i.e. the SOMO eclipses the β-hydrogen. This is in contradiction to the experimental evidence, the magnitude of $a(H_\beta)$ indicates that radical (27) adopts a bisected conformation, i.e. the β-hydrogen is eclipsed by one of the α-hydrogens. [N.B. In Chapters 2 and 3 it was seen that MNDO could not predict the

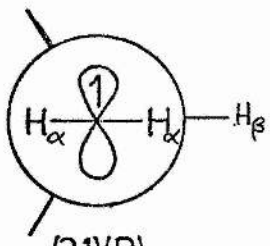
correct conformation of cycloalkenylmethyl and cycloalkenylethyl radicals.] Thus, the predicted MNDO geometry is incorrect, in terms of conformation. However, even though the predicted geometry is incorrect, it can be seen that by means of a small rotation about $\dot{C}$-C_β, i.e. C(8)-C(2), the SOMO can be made to eclipse the β-γ bond of the cyclobutyl ring. This can result in a considerable interaction between the SOMO and the σ^* orbital of the β-γ bond, and hence the stereoelectronic conditions necessary for ring opening are met.

(e) The Conformation of the Spiro[3.3]heptane-2-methyl Radical and the Barrier to Internal Rotation about $\dot{C}$-C_β.

In the introduction (Ch. 1, p. 25) the means by which the conformations of cycloalkylmethyl radicals are determined were discussed. Two possible conformations exist, these being the eclipsed form (30)(E), and the bisected form (31)(B). From the absolute magnitude of $a(H_\beta)$ and the temperature dependence of $a(H_\beta)$ the preferred conformation can be determined.



(30)(E)



(31)(B)

Figure 21 shows the plot of $a(H_\beta)$ against T for radical (27), the solid curve represents theoretical values. From this it is seen that $da(H_\beta)/dT$ has a positive sign, and this combined with the small absolute magnitude of $a(H_\beta)$ proves that radical (27) adopts the bisected conformation (31)(B). The related cyclobutylmethyl radical also adopts a bisected conformation.[21,33]

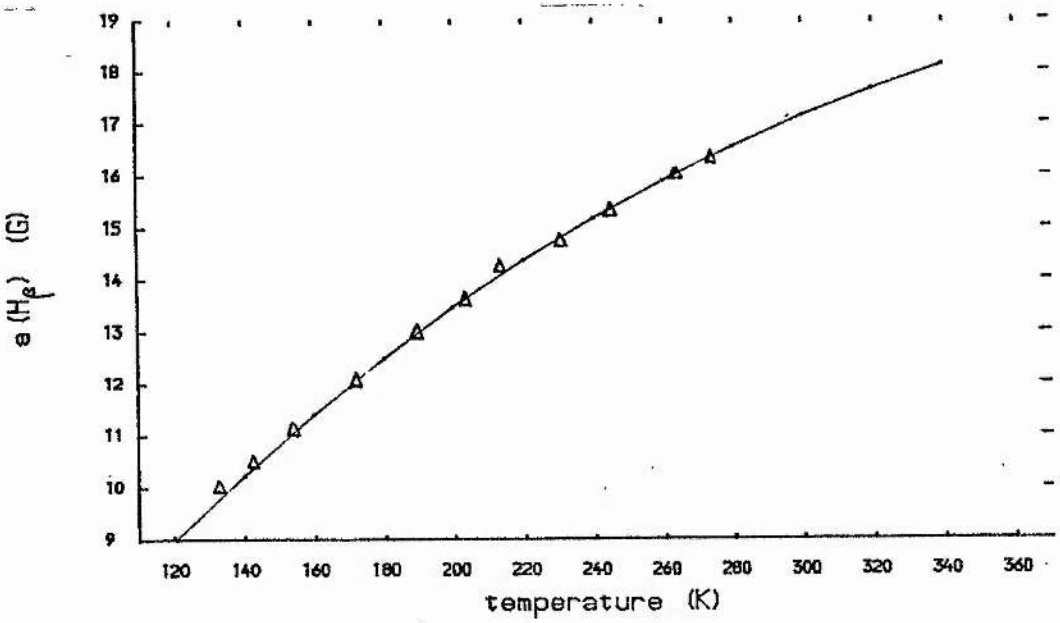


Figure 21. Plot of $a(H_\beta)$ against temperature for the spiro[3.3]heptane-2-methyl radical (27).

As stated in earlier chapters, the conformation of cycloalkylmethyl radicals will most probably be determined by steric effects found in the radical. These effects will be manifested between the H_α and the nearest neighbouring hydrogens, i.e. H_β and H_γ. The degree of interaction between these hydrogens is most readily assessed by determining the interatomic separation between H_α-H_β and H_α-H_γ in both conformations, (30) and (31). The same uncertainties as

were stated on p. 52 should still be borne in mind. In Table 16 the most important, i.e. shorter, hydrogen-hydrogen separations are shown. These were derived from the MNDO calculated geometry using the 'rationalised geometries' stated earlier, i.e. $\dot{C}$-H_α 1.08, $\dot{C}$-C_β 1.48, C_β-H_β 1.12Å, and $\angle H_\alpha C H_\alpha$ 120°.

Table 16

The shorter H-H separations, in Å, for radical (27) as calculated by MNDO theory.

	conformation	
	(30)(E)	(31)(B)
H_α-H_β	2.75	2.36
H_α-H_β	2.75	3.09
H_α-H_γ	3.70	3.61
H_α-H_γ	4.35	4.02
H_α-H_γ	2.66	3.61
H_α-H_γ	3.52	4.01
H_α-H_γ	2.66	2.79
H_α-H_γ	3.53	3.91
H_α-H_γ	3.70	2.78
H_α-H_γ	4.35	3.90

From Table 16 it can be seen that the shortest, and therefore most repulsive H-H interaction is the single H_α-H_β separation of 2.36A found in the bisected conformation (31)(B). There are no terms of a similar repulsive nature found in the eclipsed conformation. Thus, from interatomic separations, i.e. steric effects, it would be

assumed that radical (27) should adopt an eclipsed conformation. However, this is not the case, radical (27) is seen to adopt a bisected conformation. Walton *et al*[33] found that steric considerations predicted that the cyclobutylmethyl radical should adopt an eclipsed conformation. However, this radical adopts the bisected conformation.[21,33] This observation is interpreted in terms of an electronic effect, namely hyperconjugation involving the radical centre and the C_β-C_γ bonds of the cyclobutyl ring.[33] It is thought that in cyclobutane rings the C-H bonds possess greater 's' character, whilst the C-C bonds possess greater 'p' character. Thus hyperconjugation with the C_β-C_γ bonds is favoured due to their π character, whilst hyperconjugation with C_β-H_γ is disfavoured. This results in the bisected conformation being preferred.

A similar situation can be imagined with radical (27), which is only a substituted cyclobutylmethyl radical. Thus, radical (27) adopts a bisected conformation as a result of hyperconjugation between the radical centre, $\dot{C}$, and the C_β-C_γ bonds of the cyclobutyl ring. This electronic effect is sufficient to overcome the unfavourable steric effect found in the bisected conformation. This electronic effect may also affect the barrier to internal rotation, V, about $\dot{C}$-C_β for radical (27).

In Chapter 1 the method of determining the barrier to internal rotation about $\dot{C}$-C_β was discussed (p. 27). The observed values of $a(H_\beta)$ are fitted to a curve drawn from calculated values such the best possible fit is obtained. These values being calculated by expression (12).

$$a(H_\beta) = A + 1/2B + 1/2B\cos 2\theta_0[I_1(\lambda)/I_0(\lambda)] \qquad (12)$$

The curve shown in Figure 21 was drawn using values calculated by (12). The values of A, B, and V_0 used to calculate the curve were :-

$A = 2, \quad B = 50, \quad V_0 = 4.3\ kJmol^{-1}, \quad \theta_0 = 90^\circ$

These values of A, B, and θ_0 are the same as those found for the cyclobutylmethyl radical.[33] The value of V_0 for cyclobutylmethyl radicals was found to be 4.5 $kJmol^{-1}$,[33] the value for radical (27) is seen to be very similar to this.

For both radical (27) and cyclobutylmethyl radicals the value of V_0 is significantly greater than is normally found for cycloalkylmethyl radicals. This high barrier to internal rotation is a result of the electronic effect discussed earlier, i.e. the hyperconjugation between $\dot{C}$ and the C_β-C_γ bonds.

4.3 Conclusions

The spiro[3.3]hept-2-yl radical (25) was observed and gave an interesting spectrum in that it showed a fully resolved second order splitting.

The spiro[3.3]heptane-2-methyl radical (27) was observed, and also gave an interesting spectrum which showed fine structure due to γ'-, and ε - hydrogens. Radical (27) was observed to ring open at T > 245K to give radical (28). This rearrangement was studied by a kinetic e.s.r. experiment. From the results of this, the Arrhenius parameters for the rearrangement of radical (27) to radical (28) were calculated. These were found to be very similar to those calculated for the rearrangement of cyclobutylmethyl radicals. This result is not unexpected since radical (27) is a derivative of the cyclobutylmethyl radical. Some of the kinetic data were found to lie outwith the possible experimental error, and this was interpreted as indicating the rearrangement of radical (28) to radical (29). From the data obtained it is thought that this rearrangement [(28)$\longrightarrow$(29)] occurs at T > 260K. Thus radical (27), at T > 245K, rearranges to radical (28), this rearrangement being complete at ca 276K. However, at T > 260K, radical (28) itself rearranges to radical (29).

From the behaviour of $a(H_\beta)$ with temperature, and the absolute magnitude of $a(H_\beta)$, radical (27) was shown to adopt a bisected conformation. Steric effects favour adoption of an eclipsed conformation. However, like cyclobutylmethyl radicals, it is thought that hyperconjugation between the radical centre and the C_β-C_γ bonds of the cyclobutyl ring result in the radical assuming a bisected conformation.

The barrier to internal rotation was calculated. Radical (27) was found to possess the same A and B factors as the cyclobutylmethyl radical. The V_0 value was found to be slightly smaller than the V_0 value for cyclobutylmethyl radicals.

Chapter 5

EXPERIMENTAL

Experimental

^{1}H n.m.r. spectra were recorded on a Druker WP 80 instrument using $CDCl_3$, or $CDCl_3/CCl_4$ as solvent with tetramethylsilane as the internal reference. ^{13}C n.m.r. were recorded on a Varian CFT 20 instrument in $CDCl_3$ solution. All spectra were recorded at room temperature. Mass spectra were obtained on an AEI MS902 instrument , and g.l.c. mass spectra were obtained on this instrument used in conjunction with a Pye 104 g.l.c. chromatograph. G.l.c analyses were carried out on a modified Griffin and George D6 instrument , on Pye 104 and 105 instruments , and on a Pye PU4500 instrument. Preparative g.l.c. work was carried out on a Pye 105 instrument. A number of columns were employed for g.l.c. work , these were : (i) 7ft 10% Silicone Oil , (ii) 7ft 12% tritolylphosphate(TTP) , (iii) 7ft 10% SE30 , (iv) 12ft 10% Carbowax, and (v) 15ft 10% SE30. All column packings used Chromosorb as the solid support. The e.s.r. spectra were recorded on a Druker ER 200D instrument. E.s.r. samples were degassed using the 'freeze-thaw' technique , sealed in spectrosil quartz tubes , and photolysed directly within the cavity of the e.s.r. spectrometer using a 500 watt medium pressure Hg arc.

Preparation of Bicyclo[n.1.0]alkanes (11a-f)

The series of bicyclo[n.1.0]alkanes were prepared using either a straight Simmons-Smith reaction[61] , or by using the modified method of LeGoff.[62] Initially a readily prepared Zn/Cu couple was used , this however gave poor product yields , and subsequently the Zn/Cu couple was freshly prepared from granulated Zn and copper(II)acetate.[62] The yields from the latter were much improved and were of a similar size

to those quoted in the literature.[61,62] The crude product was fractionally distilled. However, the distillate was found to be slightly impure, and accordingly was further purified by means of prep-g.l.c. using column (i). The collected material was found to be >99% pure and the identity was confirmed by ^{1}H n.m.r. ; the spectra recorded agreeing with those quoted in the literature.[59,63]

Bromination of Bicyclo[3.1.0]hexane (11a)

Bromine (60µl) in deaerated CCl_4 (250µl) was added slowly to a deaerated solution of bicyclohexane (0.2g) in CCl_4 (250µl) at 20°C. On illumination with a tungsten lamp a vigorous reaction occurred resulting in the almost immediate disappearance of the bromine colour. G.l.c. analysis, using column (ii), showed the presence of eight major products, some of which were not completely resolved. Prep-g.l.c., using column (ii), was used to separate the products, which were then examined by ^{1}H n.m.r. The results of the separation and n.m.r. examination were as follows : peak 1 was found to be bromomethylcyclopentane, the n.m.r. agreeing with that of an authentic sample[33] ; peak 2 was found to be bromocyclohexane, the n.m.r. agreeing with that of an authentic sample ; peak 3 gave δ_H 1.0-1.2(3H, two d, J 7Hz), 2.5-3.6(5H, m), and 4.2-4.7(2H, m) and was identified as a mixture of 1,2-dibromo-3-methylcyclopentane isomers ; peak 4 was found to be 1,2-dibromocyclohexane, the n.m.r. agreeing with that in the literature[57] ; peak 5 gave δ_H 1.5-2.5(7H, m), 3.55 (2H, d, J 7Hz), and 3.9(1H, m) and was identified as 1-bromo-2-(bromomethyl)cyclopentane ; peak 6 gave δ_H 1.05(3H, d, J 7Hz), 1.3-2.3(8H, m), and 4.0-4.4(1H, m) and was identified as 1-bromo-2-methylcyclopentane ; peaks 7 and 8 were

identified as trans- and cis-1,3-dibromocyclohexanes respectively, the n.m.r. spectra agreeing with those in the literature.[57,64a,b] G.l.c.-mass spectrometry was carried out and gave further evidence as to peak identification. Peaks 1,2,4,7 and 8 were confirmed by carrying out retention time comparisons with authentic samples. The results of the quantitative g.l.c. analyses are shown in Table 7.

Bromination of Bicyclo[4.1.0]heptane (11d)

Bromine (60μl) in deaerated CCl_4 (250μl) was added slowly to a deaerated solution of bicycloheptane (0.2g) in CCl_4 (250μl) at 20°C. On illumination with a tungsten lamp a reaction occurred which resulted in the disappearance of the bromine colour after ca 20mins. G.l.c. analysis, using column (iii), showed the presence of eight major peaks, some of which were not completely resolved. Prep-g.l.c., using column (iii), was used to separate the products which were examined by ^1H n.m.r. The results of the separtion and n.m.r. examination were as follows : peak 1 was found to be bromomethylcyclohexane, the n.m.r. agreeing with that of an authentic sample[33]; peak 2 was found to be bromocycloheptane, the n.m.r. agreeing with that of an authentic sample; peak 3 gave δ_H 1.22(3H, d, J 7Hz), 1.3-2.5(9H, m), and 3.73(1H, dq) and was identified as 1-bromo-2-methylcyclohexane; peak 4 gave δ_H 1.6-2.4(m), 3.35(d, J 7Hz), and 5.6-6.0(m) and was identified as 3-(bromomethyl)cyclohex-1-ene; peak 5 was identified as being trans-1,2-dibromocycloheptane; peak 6 gave δ_H 1.05(3H, d, J 7Hz), 1.4-2.6(7H, m), and 3.6-4.2(2H, m) and was identified as containing isomers of 1,2-dibromo-3-methylcyclohexane; peak 7 gave δ_H 1.2-2.3(m), 3.70(d, J 7Hz), and 4.1-4.8(m) and was identified as

1-bromo-2-(bromomethyl)cyclohexane , peak 8 was identified as containing trans-, and cis-1,3-dibromocycloheptanes , the n.m.r. agreeing with that in the literature.[57] G.l.c.-mass spectrometry was carried out and gave further evidence as to product identity. Peaks 1,2,5 and 8 were confirmed by carrying out retention time comparisons with authentic samples. The results of the quantitative g.l.c. analyses are shown in Table 7.

Preparation of Bicyclo[3.1.0]hexan-2-ol

Bicyclohexanol was prepared from cyclopent-1-en-3-ol and di-iodomethane using the procedure of Dauben et al.[65] The crude product was distilled and the identity checked by ^1H n.m.r. The n.m.r. showed the presence of an impurity due to di-iodomethane. This impurity could not be removed by distillation. However , since the bicyclohexanol was only required as a precursor to the desired product it was decided not to attempt further purification , but rather to use the impure material in the following synthesis.

Preparation of 2-Chlorobicyclo[3.1.0]hexane

Using the method of Freeman et al[66] , 2-chlorobicyclo[3.1.0]hexane was prepared by the reaction of bicyclo[3.1.0]hexan-2-ol with thionyl chloride. The crude material was distilled and the identity checked by ^1H n.m.r. The n.m.r. was found to agree with that in the literature[7] , but showed the presence of an impurity , which was identified as di-iodomethane. Careful distillation of the product did not succeed in removing this impurity , and it was therefore decided to purify the material by prep-g.l.c. This was carried out and the collected material was examined by ^1H n.m.r. The n.m.r. recorded

however was not that of 2-chlorobicyclo[3.1.0]hexane. Instead the spectrum gave δ_H 1.6-2.8(6H, m), 4.05-4.40(1H, m), and 5.40-5.85(2H, m). The ^{13}C n.m.r. gave peaks at 24.09, 32.09, 35.48, 56.47, 123.94, and 126.54 p.p.m. Eventually, by using ^1H spin decoupling of the ^1H n.m.r. spectrum the compound was identified as 1-chloro-3-methylene-cyclopentane. It is felt that the 2-chlorobicyclohexane undergoes a decomposition with a rearrangement somewhere within the g.l.c., whether this occurs on the column itself or at the injection, or collection ports is unknown. As a result of this no purification was possible, and it was decided to use the impure material for the e.s.r. experiment. This was decided upon for two reasons; (a) the impurity was <10% of the mixture, and (b) since the bicyclo[3.1.0]hex-2-yl radicals were to be generated by chlorine abstraction by tri-n-butyl radicals, which preferentially abstract chlorine, it was thought that the presence of a small di-iodomethane impurity would not affect the e.s.r. experiment too adversely. On photolysis, samples of the 2-chlorobicyclo[3.1.0]hexane, hexa-n-butyl-ditin, or triethylsilane, and di-t-butyl peroxide in cyclopropane no spectra could be positively identified. At this stage it was decided to end this particular line of investigation as it was felt that the possible results did not justify the expenditure of time that was entailed.

Preparation of Cyclobutane-1,1-dimethanol (43)

Using the procedure of Mariella and Raube[57], diethyl-1,1-cyclo-butanedicarboxylate was prepared from 1-bromo-3-chloropropane and diethylmalonate. This was reduced to the dimethanol (43) by a $LiAlH_4$ reduction using the method of Schubert and Leahy.[60]

Preparation of 1,1-bis(Hydroxymethyl)cyclobutanereditosylate (44)

This was prepared from (43) by the reaction of (43) with p-toluene--sulphonylchloride in dry pyridine, following the procedure of Buchta and Geibel.[69] The crude product was recrystallised from methanol.

Preparation of 1,1-bis(Bromomethyl)cyclobutane (45)

Using the method of Buchta and Merck[70], (45) was prepared by the reaction of (44) with LiBr in acetone. The crude product was distilled and the identity confirmed by ^{1}H n.m.r.

Preparation of Spiro[2.3]hexane (15b)

Using the method of Buchta and Merck[70], (15b) was prepared from (45) by reaction with Zn dust in an ethanol/water mixture. The crude product was separated and distilled. The identity was confirmed by ^{1}H n.m.r.[38] For the e.s.r. work samples of >99% purity were obtained by prep-g.l.c. using column (iii).

Preparation of Spiro[2.4]heptane (15c)

Using the method of Wilcox and Craig[71] spiro[2.4]hepta-4,6-diene was prepared from freshly distilled cyclopentadiene, 1,2-dibromoethane and sodium amide. The crude product on work up was not purified, though the identity was checked by ^{1}H n.m.r.[38] The crude product was used to prepare (15c) by hydrogenation over a platinum (IV) oxide catalyst. The crude product was distilled, and the identity, i.e. the presence of (15c), confirmed by ^{1}H n.m.r.[38] G.l.c. analysis showed the presence of (15c) and two impurities. Prep-g.l.c. using column (iv) was carried out to obtain pure, >99%, samples for the e.s.r. work.

The two impurities were identified as being; (i)ethylcyclopentane, the ^1H n.m.r. showed δ_H 1.25(3H, t, J 7Hz), 1.5-1.8(9H, m) and 3.55(2H, q, J 7Hz), and (ii)1,1-dimethylcyclopentane the ^1H n.m.r. showed δ_H 2.0(6H, s) and 2.2-2.8(8H, m).

Bromination of Spiro[2.3]hexane (15b)

Bromine (60μl) in deaerated CCl_4 (250μl) was added slowly to a deaerated solution of spirohexane (20μl) in CCl_4 (250μl) at 20°C. On illumination with a tungsten lamp a reaction occurred which resulted in the removal of the bromine colour after ca 10mins. G.l.c. analysis of the reaction mixture, using column (iii), showed the presence of unreacted (15b) and two major products. Retention time comparisons with an authentic sample showed one of these products to be 1,1-bis(bromomethyl)cyclobutane (45). The ^1H n.m.r. spectrum of the reaction mixture showed peaks attributable to (15b) and (45) by comparison with authentic samples. The other product was identified as 1-bromo-1-(2-bromoethyl)cyclobutane from the ^1H n.m.r. spectrum, this gave δ_H 2.3-2.8(8H, m) and 3.4-3.6(2H, m). G.l.c.-mass spectrometry confirmed these assignments, and also revealed the presence of mono-brominated products in trace amounts.

Preparation of Spiro[3.3]heptane-2-carboxylic Acid (48)

Using the method of Buchta and Geibel[69], (44) was converted to diethyl-2,2-spiro[3.3]heptane-dicarboxylate (46). The HCl/H_2O hydrolysis method of Cason and Allen[72] was used to convert (46) to spiro[3.3]heptane-2,2-dicarboxylic acid (47). The crude diacid (47) was removed and dried. No purification was attempted. The diacid (47) was converted to the mono-acid (48) by pyrolysis following the

method of Buchta and Geibel.[69] The crude mono-acid was disilled and the identity checked by ^{1}H n.m.r.

Preparation of 2-Bromomethylspiro[3.3]heptane (26)

The mono-acid (48) was converted to spiro[3.3]heptane-2-methanol by a $LiAlH_4$ reduction. This was then converted to the tosylate by reaction with p-toluenesulphonylchloride. Reaction of the tosylate with LiBr in acetone gave (26). The crude product was distilled and the identity confirmed by ^{1} n.m.r. This gave δ_H 3.4(2H, d, J 7Hz), 2.55(1H, m) and 1.55-2.30(10H, m). ^{13}C n.m.r. gave peaks at 16.44, 35.06, 35.49, 38.96, 39.48, and 40.14 p.p.m. Mass spectrum gave : 162(12),160(12), 109(52), 95(16), 93(12), 91(4), 81(100*), 80(100*), 79(60), 77(12), 68(92), 67(100*), 55(28), 53(52), 41(92), 40(64), 39(84);(* peaks off scale). The molecular ion would give peaks at 190,188; no such peaks were detected. Pure samples, >99%, for the e.s.r. work were obtained by prep-g.l.c. using column (v).

Preparation of 2-Bromospiro[3.3]heptane (24)

Using the modified Hunsdiecker reaction of Cason and Walba[73] (48) was converted to (24). The crude product was distilled and the identity confirmed by ^{1}H n.m.r. This gave δ_H 4.4(1H, quin, J 7Hz), 2.25-2.85(4H, m), and 1.7-2.2(6H, m). ^{13}C n.m.r. gave peaks at 16.84, 34.58, 34.98, 36.18, 38.18, and 48.11 p.p.m. Pure samples, >99%, for the e.s.r. work were obtained by prep-g.l.c. using column (v).

Attempted Preparation of Spiro[3.3]heptane (21)

Initially this was attempted by the following the procedure of

Wienstein *et al*[74] starting from (48). However this met with failure, no product (21) being isolated. It was felt that the initial preparation of 2-iodospiro[3.3]heptane was unsatisfactory and therefore in subsequent synthetic attempts it was decided to prepare (24) and to treat this with tri-n-butyltin hydride and azobisisobutyronitrile using the method of Della and Patney.[75] This method was attempted, and did work. However the quantity of (21) obtained was insufficient for the experimental requirements. The synthesis was repeated, but again negligible spiroheptane was obtained.

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