LEWIS ACID-COMPLEXED-5-ACYLPENTAMETHYLCYCLOPENTADIENES

THE FORMATION AND THE FIVE-FOLD DEGENERATE REARRANGEMENT OF LEWIS ACID-COMPLEXED-5-ACYL-1,2,3,4,5-PENTAMETHYLCYCLOPENTADIENES

By

MAUNG ZEYA, B.Sc. (Hons.)

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TO MY PARENTS AND PHYU.

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TITLE: The Formation and the Five-Fold Degenerate Rearrangement of Lewis Acid-Complexed-5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes

AUTHOR: Maung Zeya, B.Sc. Hons. (Arts and Science University, Rangoon, Burma)

SUPERVISOR: Professor R. F. Childs

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SCOPE AND CONTENTS:

This thesis describes the preparation of some bicyclo[3.1.0]-hexenyl cations with different substituents at C_6 and a study of their degenerate rearrangements. The preparation of both isomers of 6-ethyl-1,2,3,4,5,6-hexamethylbicyclo[3.1.0]hexenyl cation was achieved by the photoisomerization of 1-ethyl-1,2,3,4,5,6-hexamethylbenzenonium ion. A new cation, 1,1,2,3,4,5-hexamethylbenzenonium ion was prepared and characterized.

The preparation of a series of 5-acyl-1,2,3,4,5-pentamethylcyclopentadienes has been developed in an attempt to generate bicyclo-[3.1.0]hexenyl cations with the hydroxy group at C_6. The protonation of 5-acyl-1,2,3,4,5-pentamethylcyclopentadienes results in the formation of dications which have been characterized by p.m.r. and uv spectroscopy. These dications are stable below 0° but at higher temperatures undergo a fragmentation reaction where protonated pentamethylcyclopentadiene is generated. This provides a convenient synthetic route for pentamethylcyclopentadiene.

5-Acyl-1,2,3,4,5-pentamethylcylopentadienes react with various Lewis acids to generate σ-complexes in which the Lewis acid is bonded to the carbonyl group. The zwitterions have been characterized using infrared and nuclear magnetic resonance spectroscopy.

The Lewis acid-complexed-5-acyl-1,2,3,4,5 pentamethylcyclopentadienes exhibit temperature dependent p.m.r. spectra. The averaging can best be explained in terms of a five-fold degenerate rearrangement in which the Lewis acid-complexed ketone group migrates around the periphery of the five-membered ring. The rates of circumambulation were determined by comparing the experimental and calculated p.m.r. spectra. The rate of automerization is dependent upon the nature of the acyl group as well as the Lewis acids used. A linear free energy relationship exists between the rates of circumambulation of $AlCl_3$-complexed aromatic ketones and the para-substituent constant, σ^+, the magnitude of the reaction constant ρ being 4.64 (correlation coefficient 0.999).

These results have been discussed in terms of a mechanism which involves a bicyclic zwitterion as the transition state for the degenerate rearrangement. The possibility of a homoconjugative interaction between the electron-deficient C_6 and the occupied π orbitals of cyclopentadiene is discussed.

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

It has been known for a long time that certain reactions and molecular rearrangements take place by pathways involving cyclic transition states.[1] Over the past ten years, the importance of the conservation of orbital symmetry during a chemical reaction has been recognized and used to explain these reactions. The rapid acceptance of these concepts was due in no small part to the contribution of Woodward and Hoffmann.[2] The idea of orbital symmetry has brought order to a large body of chemistry, opened up a new research area, and led to the discovery of new reactions.

The importance of orbital symmetry was recognized as early as 1954 by Fukui.[3] In the Frontier Orbital Theory developed by Fukui, the transition state in a bimolecular reaction is considered as a perturbation between the reactants. The activation energy for the reaction can be given by second-order perturbation theory. Calculations show that only the interaction between the highest occupied molecular orbital, HOMO, of one reaction partner and the lowest unoccupied molecular orbital, LUMO, of another is important. The magnitude of the interaction between the HOMO and the LUMO is determined by the difference in energy between them.

Longuet-Higgins and Abrahamson[4] and Woodward and Hoffmann[5] independently suggested the use of correlation diagrams. Orbitals of reactants and products can be classified symmetric or unsymmetric with respect to a mirror plane, σ, or a two-fold axis of symmetry, C_2.

The molecular wavefunction must conform to the symmetry of the molecular orbitals and can either be symmetric or asymmetric with respect to σ or C_2. The states of reactants and products can be correlated by plotting the energy of each state against a suitable reaction coordinate. If there is a correlation between the excited state of the product and the ground state of the reactant, then the reaction is energetically unfavourable. If, however, a correlation exists between the symmetries of reactant and product in the ground state and excited states, then the reaction will be favoured. Simply, it means that orbital symmetry is conserved in concerted reactions. Numerous reviews have been written on this intriguing subject.[6]

These concerted reactions, also known as "pericyclic reactions" as their transition states are of cyclic in nature, also include such well-known reactions as the Claisen[7] and Cope[8] rearrangements. From a synthetic viewpoint, reactions such as the Diels-Alder cycloaddition[9] are important in that two or more bonds are made in a single concerted reaction. The three main categories of concerted reactions are

(i) Intramolecular cycloaddition reactions (Electrocyclic reactions)

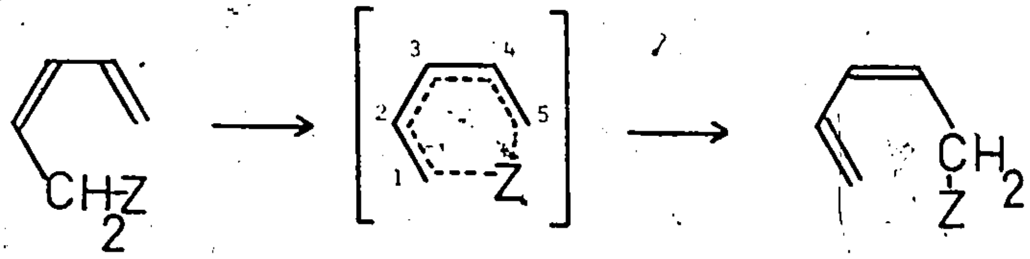
(ii) Intermolecular cycloaddition reactions

(iii) Sigmatropic rearrangements.

These reactions are largely unaffected by solvent changes or by catalysts and involve no electrophilic or nucleophilic reagents. The only initiation required to effect these reactions is light or heat and the reactions proceed with very high stereoselectivity. This thesis will be largely concerned with one of the three categories of concerted reactions, namely sigmatropic rearrangements.

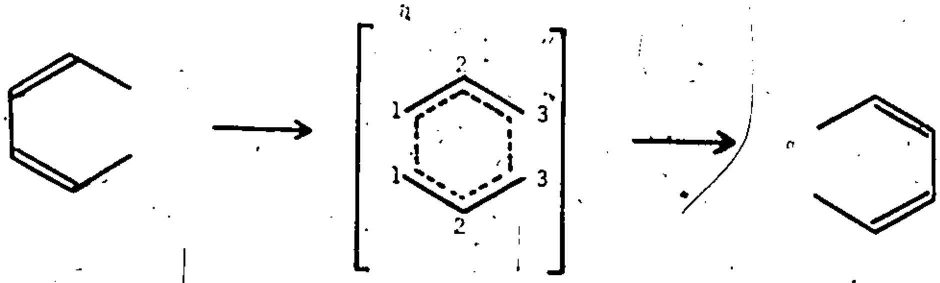
1. Sigmatropic Migrations

A sigmatropic migration is one which involves the migration of a σ bond flanked by one or more π electron systems, to a new position within the molecule, in an uncatalysed intramolecular process. If the migrating centre Z is detached from C_1 and migrated to C_j of the carbon framework, such that the bonding is through the same atomic centre within Z, then the process is the sigmatropic migration of the order [1,j]. Equation (1) illustrates a 1,5 shift.



1   2   3   1

However, when Z contains a π system of its own, the centre detached from C_1 may not be the atom which becomes bonded to C_j. If Z becomes bonded to C_j through its i^{th} atom (numbering from the terminus of Z originally bonded to C_1)., then the sigmatropic migration is of the order [i,j]. Equation (2) illustrates a 3,3 sigmatropic rearrangement.

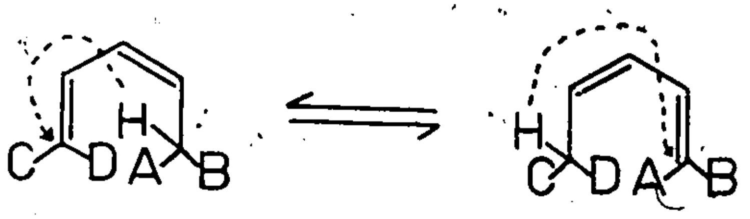


4 5 4′

2

There are various stereochemical results of a sigmatropic shift. For example, the two distinct pathways along which 1,5 hydrogen shift can take place are illustrated in Equation (3).

Suprafacial 1,5 migration



3(a)

Antarafacial 1,5 migration

3(b)

In both cases, the migrating hydrogen atom is bonded to both ends of the pentadienyl system during the rearrangement. In the suprafacial migration, the hydrogen atom is bonded to the same face of the migration framework. In the antarafacial process, the hydrogen atom, which was originally bonded to one face of the π system, becomes bonded to the opposite face.

For a sigmatropic migration, the orbital symmetry requirements are most readily deduced by assuming that the migration may be likened to the intimate interaction of a pair of radicals, namely $Z^{\cdot}$ and the framework radical. The most important bonding interactions will be between the highest occupied molecular orbitals on $Z^{\cdot}$ and the framework radical. In electrically neutral systems, the framework radical will always possess an odd number of carbon nuclei in conjugation and is therefore an odd alternant radical. The highest occupied molecular orbital of the framework radical in the ground state will be non-bonding, and the wavefunction will be characterized by nodes at even numbered carbon nuclei. The sign alternation of π components of the non-bonding orbital of a polyenyl radical containing j conjugated carbon atoms is shown in Fig. 1.

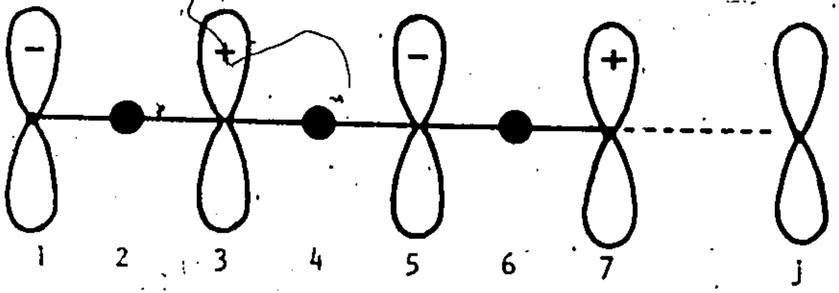


Figure 1 Sign Alternation of the π Components in the Non-Bonding Orbital of a Polyenyl Radical.

For a sigmatropic shift to be concerted, there must be a bonding interaction between the highest occupied molecular orbitals of the migrating group and the termini in the framework between which the migration occurs. For example the thermal 1,5 hydrogen shift is shown in Fig. 2a.

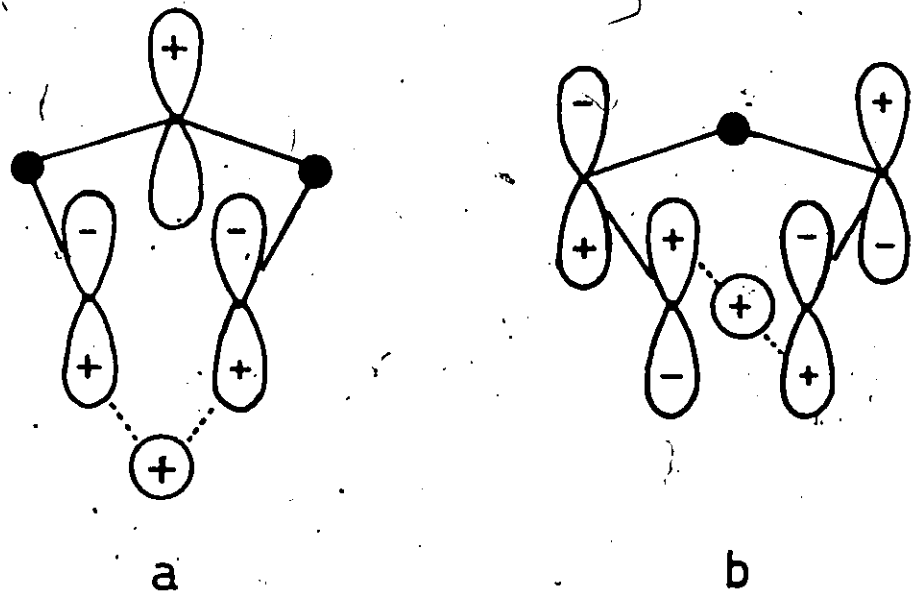


Figure 2 The (a) Thermally and (b) Photochemically Induced 1,5 Hydrogen Migration.

In photochemical reactions, the electron from the framework radical is promoted to the first excited state and the mode of migration will be determined by the symmetry characteristics of ψ_4. The 1,5 hydrogen migration will now be antarafacial, eg. Fig. 2b.

The migrating group can also use a 'p' orbital to achieve a bonding interaction with those of the framework during the rearrangement. There are two possible ways for this atomic orbital to migrate, either using one lobe or two lobes of the p orbital, Fig. 3.

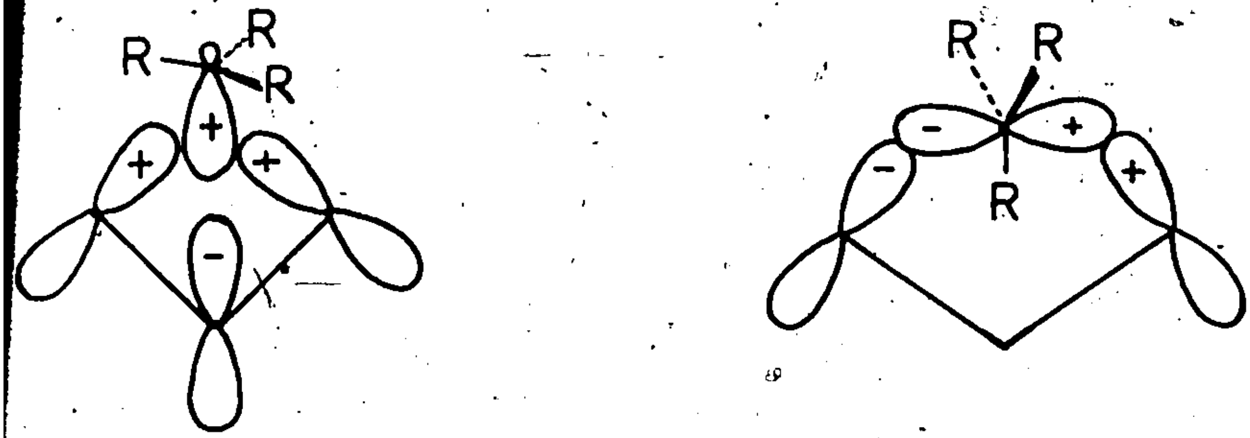


Figure 3 Possible Routes for Suprafacial 1,3 Alkyl Migration

Similar considerations for more complex systems lead to a series of selection rules for sigmatropic shifts which may be summarized as follows:

TABLE I The Selection Rules for Sigmatropic Shifts

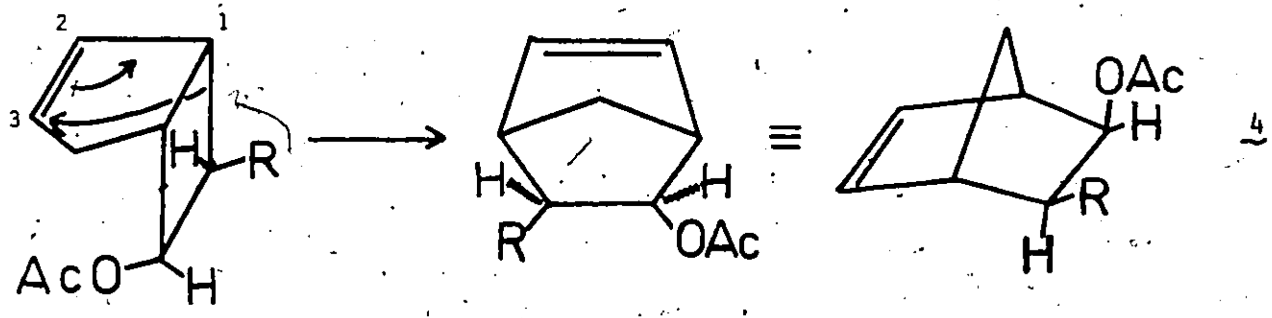
i + j	Ground State	Excited State
4n	antara-supra supra-antara	supra-supra antara-antara
4n + 2	supra-supra antara-antara	antara-supra supra-antara

More simply, it may be stated that the (s-s) or (a-a) combination is allowed under thermal control if (4n + 2) electrons are involved in the change. The (s-s) interaction for 4 electron system is allowed under photochemical control.

The stereochemistry of concerted reactions almost always follows the selection rules predicted by the Principle of the Conservation of Orbital Symmetry.[2] Numerous examples have been found in support of these rules. A limited number of examples of the application of these selection rules will be discussed in more detail.

(a) 1,3 Sigmatropic Rearrangements

In accord with the Principle of the Conservation of Orbital Symmetry, thermally induced suprafacial 1,3 sigmatropic migrations must take place with inversion of configuration at the migrating centre.[2] Very few thermal 1,3 migrations are known. One example, recently reported by Berson and Patton,[10] is the thermal isomerization at 300° of endobicyclo[3.2.0]heptenyl acetate (6) to exo-2-norbornenyl acetate 7.



6 7

The inversion of configuration at C_7 during the rearrangement was later proved[11] by replacing the trans hydrogen atom at C_7 with a deuterium atom [R = D]. The rearrangement product exo-3d norbornenyl acetate contained the deuterium atom and the acetoxy group cis to each other. This shows that, inversion of configuration at C_7 has taken place and that the orbital symmetry rules were obeyed.

(b) 1,5 Sigmatropic Rearrangements

Numerous examples of 1,5 hydrogen shifts have been observed.[12] Orbital symmetry considerations predict that migrations must be suprafacial ~~if~~ thermally induced. Suprafacial 1,5 hydrogen shifts in substituted 1,3 pentadienes have been investigated by Roth and König.[13] The structure of the transition state in 1,5 hydrogen migration in 1,3 pentadiene was proposed by Winstein et.al.[14] The migrating hydrogen is situated above the plane of the pentadienyl system and a plane through the two terminal carbon atoms approximately perpendicular to the first plane.

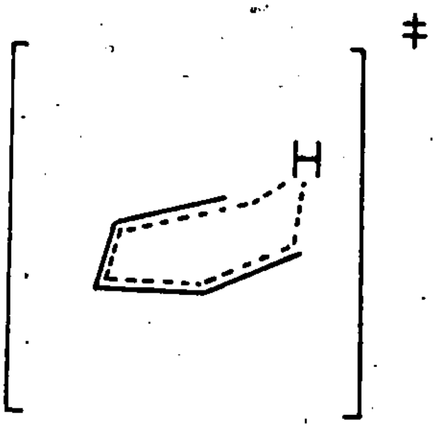
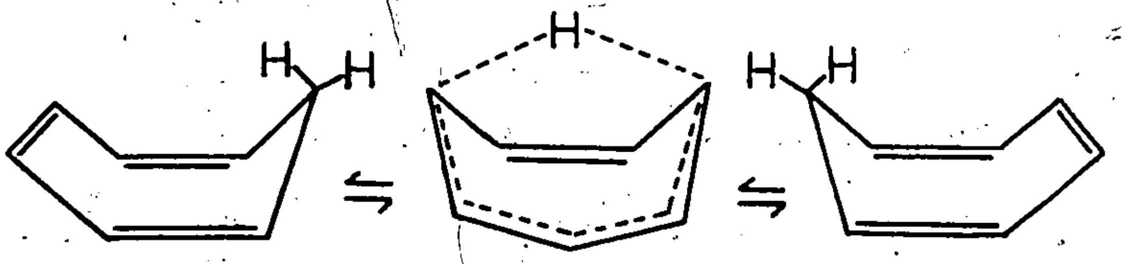


Figure 4. The Transition State for the 1,5 Hydrogen Migration in 1,3 Pentadiene

1,5 Hydrogen shifts are also observed in unsubstituted and substituted cycloheptatrienes.[15] The third double bond does not participate in the rearrangement[16] and the transition state was proposed as having the structure shown. The presence of a highly symmetrical transition state was suggested by the negative entropy of activation for the reactions and the magnitude of the primary kinetic isotope effects.[15]



5

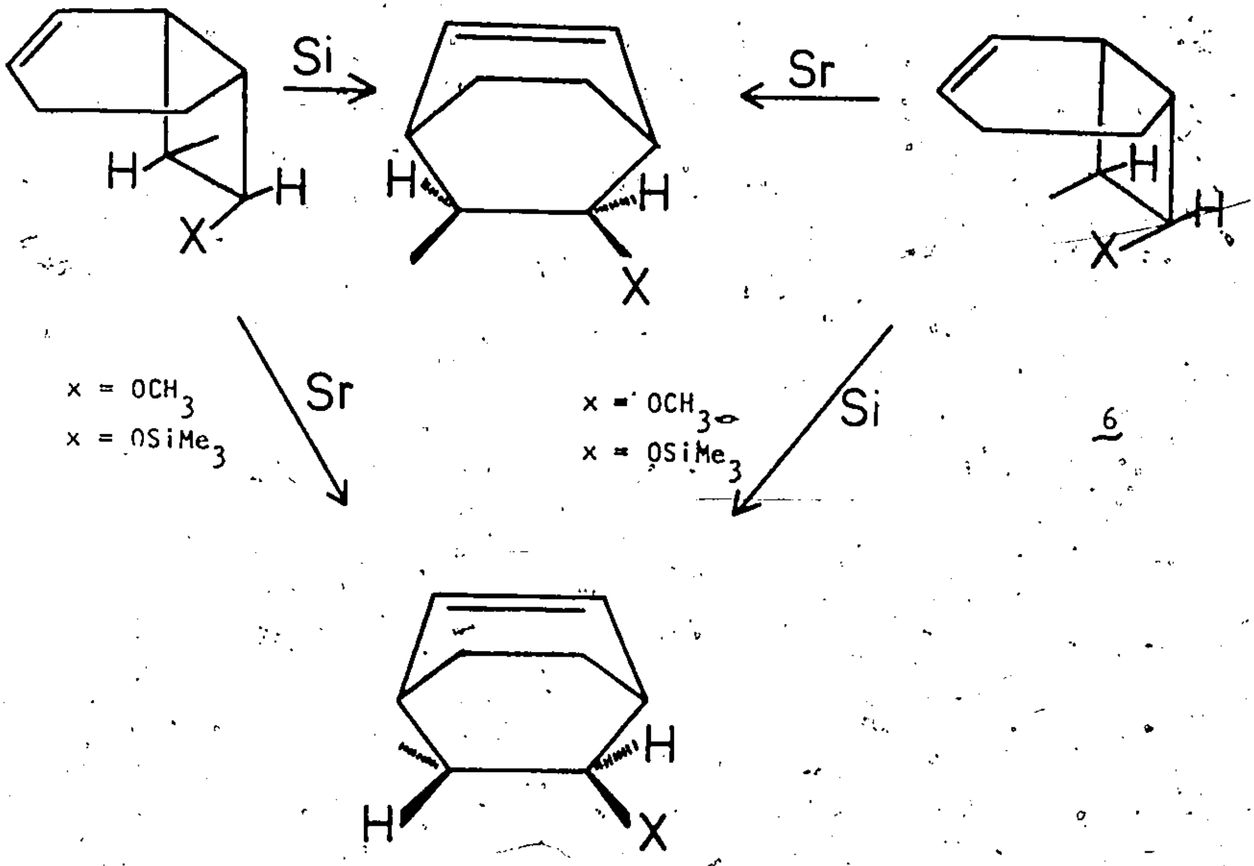
8 9 10

Numerous other examples can be provided to illustrate the feasibility of sigmatropic migrations. Thermal [1,7],[17] [3,4],[18] [3,3],[19] [5,5][20] sigmatropic shifts as well as photochemical [1,7][21] and [3,5][22] migrations are also known.

3. Failures of Orbital Symmetry Rules

Orbital symmetry selection rules, are not absolute. They are known to break down in a few extreme cases and the reverse stereochemistry to that predicted is then found.

Such a case is observed with the [1,3] migrations in bicyclo[4.2.0]octenyl cations where the product derived from retention of the configuration can predominate.[23]



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Depending upon the stereochemistry of the migrating group, the ratio of the product derived from inversion of configuration to that from retention, $\frac{s_i}{s_r}$, ranges from 2.2 to 0.065.

If the migration is stepwise having a diradical as the transition state, then the energy of transition state will be comparable to that of the non-interacting allyl and p orbitals. The migration of C_8 following the orbital symmetry pathway will result in a significant lowering of the energy of the transition state due to the strong interaction between the non-bonding allyl orbital and asymmetric p orbital.[6]

However, the interaction of the p orbital with the allyl radical in the forbidden geometry can also lead to a lowering of the transition state energy.[24] This results from an interaction of the p orbital of the migrating group with the subjacent orbital of the framework orbital, Fig. 5b. Moreover, theoretical calculations show that there is a substantial overlap between the migrating p orbital and the orbital in the centre of the allyl system which will further stabilize the transition state.

Subjacent control of the transition state geometry becomes important only when steric interactions render the operation of the orbital symmetry allowed pathway difficult. The transition state formed from bicyclo[3.2.0]heptenyl system is quite rigid and has an ideal geometry for overlap with both lobes of the p orbitals of the migrating carbon atom. In the [4.2.0] system the extra methylene makes the allowed pathway a more difficult process as the geometry of the molecule prevents the ready asymmetric overlap of the p orbital of the migrating carbon. The products resulting from subjacent orbital control are now seen to compete with the orbital symmetry allowed products. The subjacent interaction during the transition state in bicyclo[3.2.0]heptenyl system is minimal. The extra methylene group in bicyclo[4.2.0]octenyl system makes the overlap of the relevant orbital at C_2 and the migrating atom more feasible, giving rise to the products derived from orbital symmetry disallowed pathway.

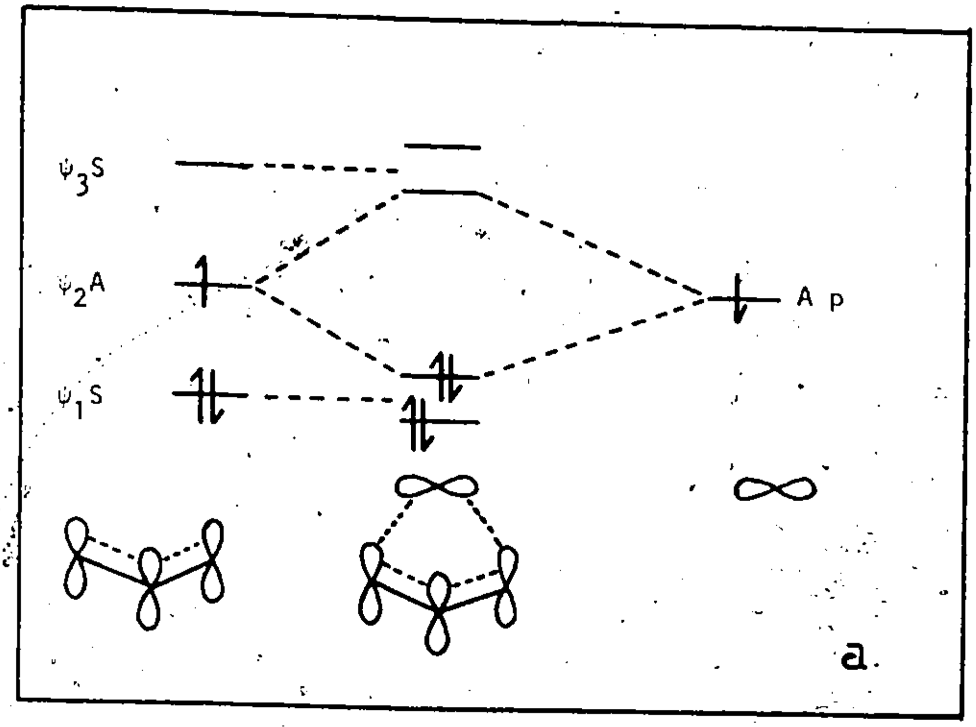
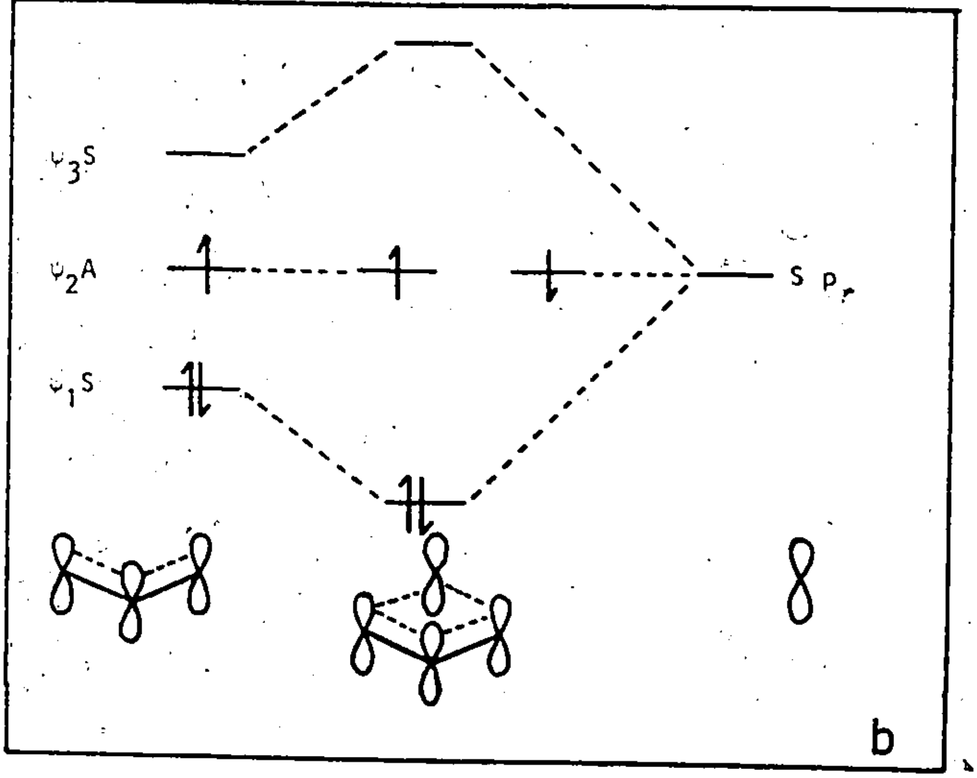


Figure 5 Schematic Diagram of Orbital Energies and Topologies of Three Different Suprafacial 1,3 Sigmatropic Rearrangement Transition States Derived by Interaction of an Alkyl Unit with a Carbon p orbital (a) Allowed, (b) Forbidden, (c) Diradical



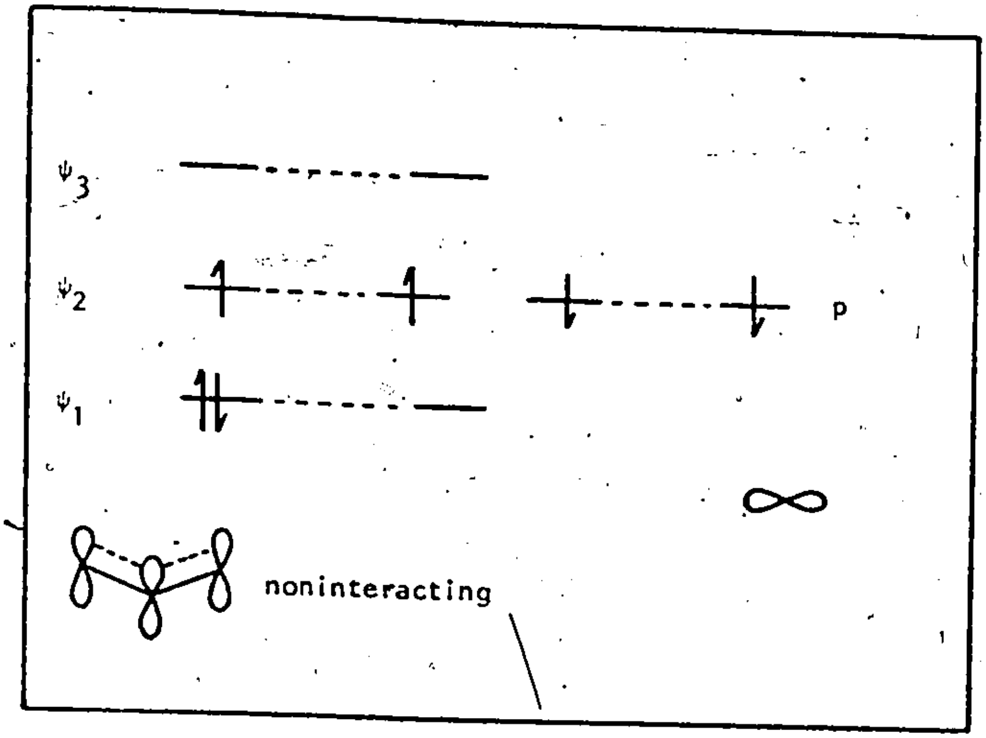


Figure 5(c)

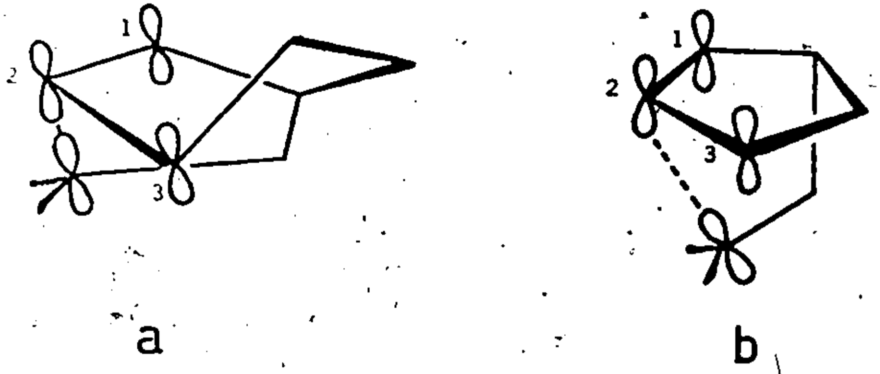


Figure 6 Suprafacial 1,3 migration in (a) bicyclo[4.2.0]octenyl and (b) bicyclo[3.2.0]heptenyl systems.

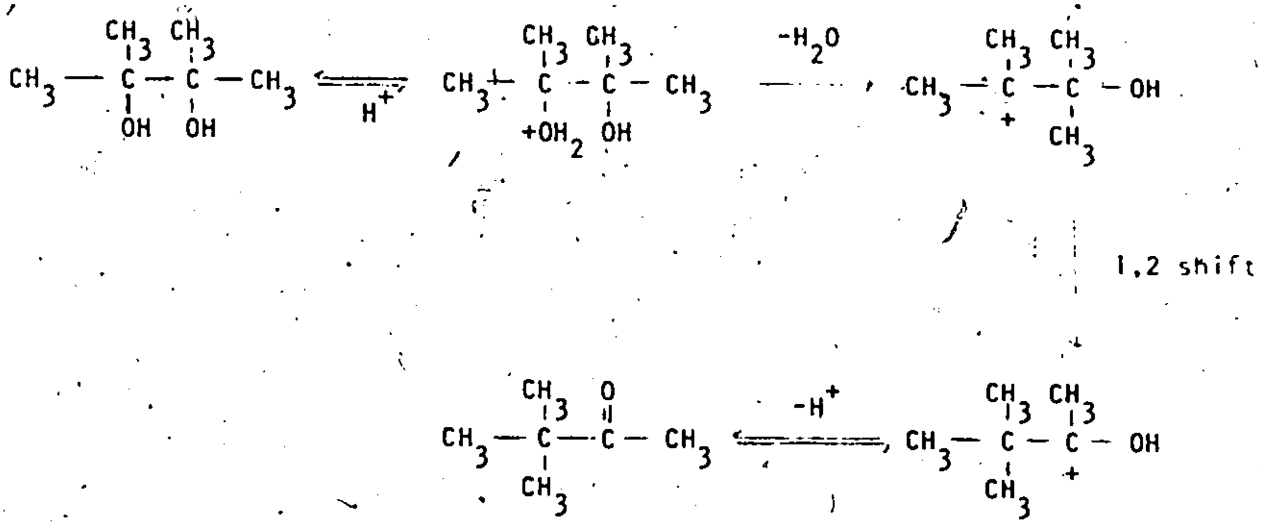
Recently, the existence of symmetry forbidden concerted reactions have been discussed by Baldwin[25] and notably Epiotis.[26] Configuration interaction between the highest occupied M.O. and the lowest unoccupied M.O. in certain systems is predicted to result in the violation of orbital symmetry rules. Numerous theoretical calculations have been done but there is yet little experimental data. A few cases of symmetry forbidden concerted reactions have been reported.[27]

It is of paramount importance, however, to note that the number of these extreme cases are few compared to the cases where orbital symmetry rules are rigidly obeyed.

4. Ionic Sigmatropic Migrations

(a) 1,2 Sigmatropic Shifts

Orbital symmetry allowed sigmatropic shifts can also occur in ionic species. For example, the well-known pinacol-pinacolone rearrangement involves a 1,2 methyl shift in the intermediate cation[28] (Equation 7)



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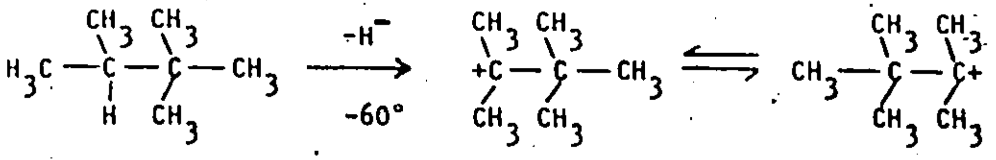
The dissolution of 2,2,3-trimethylbutane in $HFSO_3$-SbF_5/SO_2ClF mixture at low temperatures (ca -60°) results in the formation of dimethyl-t-butylcarbonium ion[29] (Equation 8).



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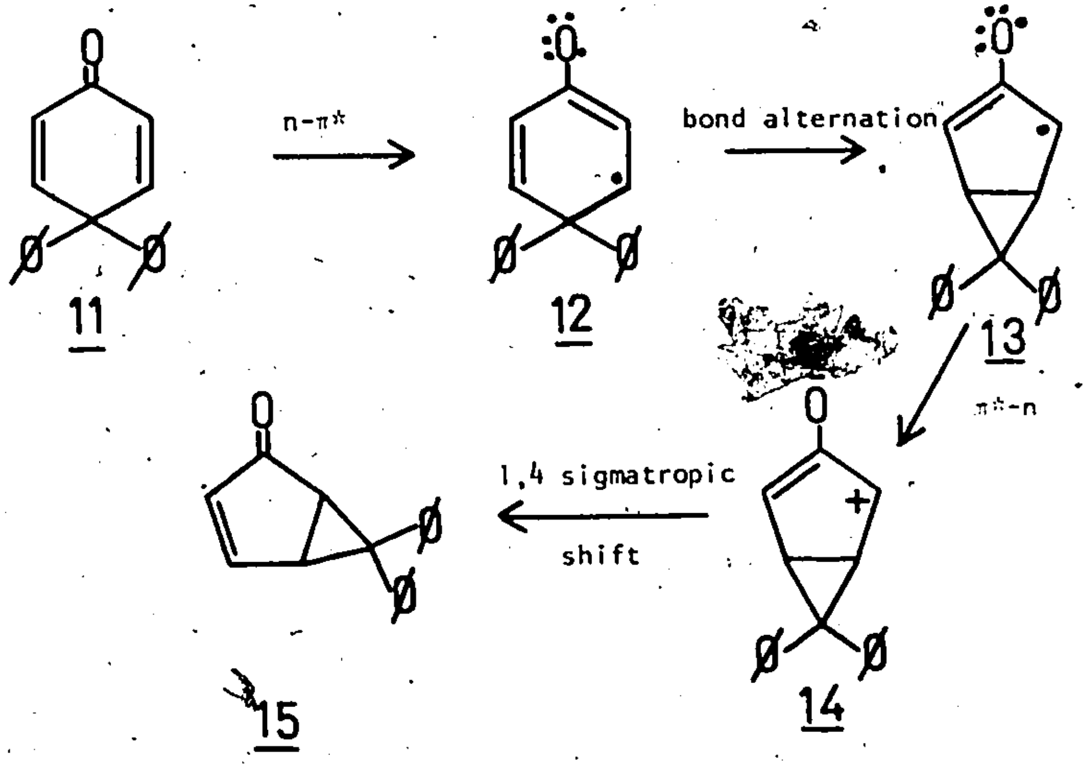
The p.m.r. spectrum of the resulting two cations showed only one signal, showing that the rate of equilibration between two cations due to methyl migration is very rapid compared to the nmr time scale. These cations are also degenerate (vide infra) and therefore the stereochemistry of 1,2 methyl migration cannot be determined.

(b) 1,4 Sigmatropic Shift

A 1,4 sigmatropic rearrangement in the bicyclo[3.1.0]hexenyl ions was first suggested by Zimmerman to account for the products of the photochemistry of 4,4-diphenylcyclohexa-2,5-dienone (11).[30] This mechanistic interpretation involving the zwitterionic intermediate was widely accepted, particularly because such a migration has been shown to occur in electron deficient species such as 14.[31]



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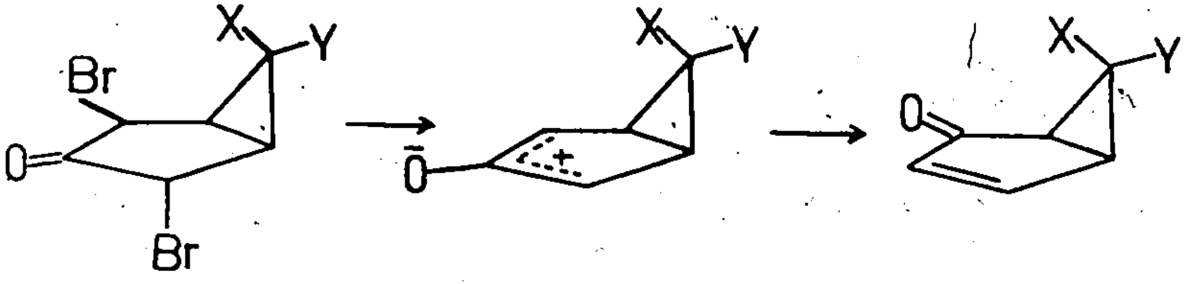
A very similar zwitterion was generated independently by Brennen and Hill,[32] and Zimmerman and Crumrine,[33] by a non-photochemical route, Equation (10). Isolation and identification of the products led these workers to conclude that a rapid 1,4 sigmatropic migration had taken place.



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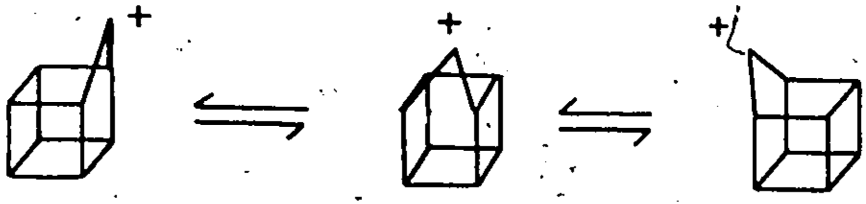
16 17 18

5. Degenerate Sigmatropic Shifts

A molecule (or cation) displaying degeneracy can be defined as a system which can rearrange, through a series of sequential sigmatropic shifts, accompanied by a definite energy barrier, in such a fashion as to generate the same gross structure as that of the starting material. In this rearrangement, both the molecular formula and the structural formula of the starting material is conserved. These migrations can be observed by loss of the optical activity,[34] isotopic label scrambling[35] and temperature dependent nmr spectra.[36]

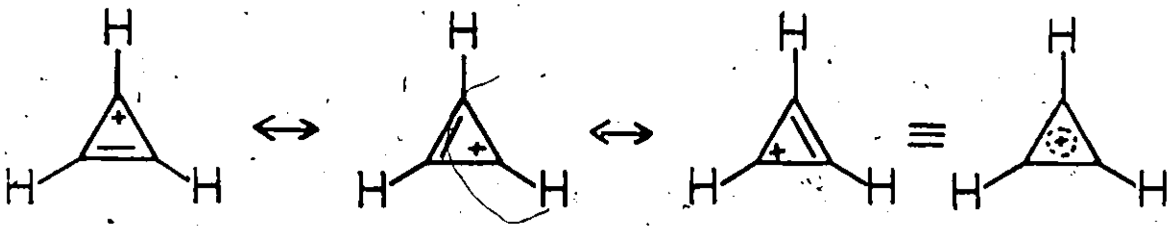
Degeneracy is distinctly different from aromaticity.[37] At any stage during the rearrangement, a degenerate system can be represented by drawing a discrete structure, whereas the structure of an aromatic system at any stage is the average of all the canonical forms that can be written. For example, the homocubyl cation[38] consists of a series of identical cations in equilibrium. The chemistry of the system can be adequately described in terms of a structure such as 20. However, the structure of the aromatic cyclopropenium cation cannot be represented as either of its resonance forms but only as the sum of them.[29]



11

20 20′ 20″

A Degenerate Cation



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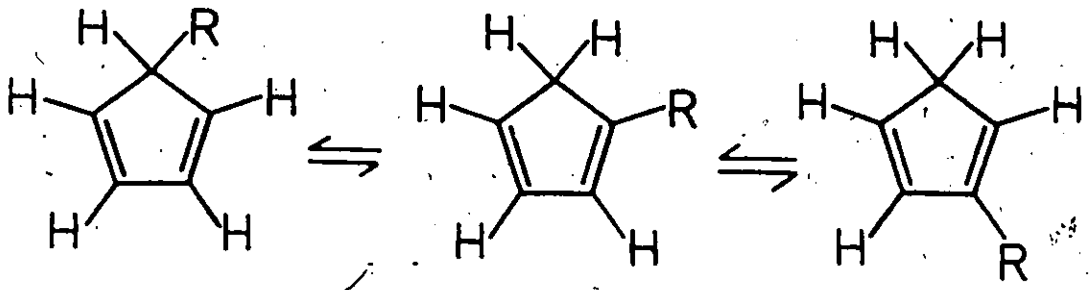
21 21 21 21

An Aromatic Cation

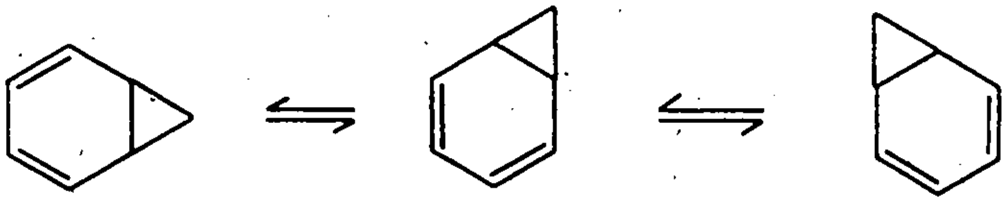
Degenerate 1,5 hydrogen migrations can occur thermally in cyclopentadienes (22). This degenerate rearrangement has not been observed directly, however, substituents bonded to carbon atoms enable the migration to be observed,[40] (Equation 13).



23 24 25

13

The possibility of a 1,5 degenerate rearrangement in the bicyclo-[4.1.0]heptadienyl system was suggested by Berson and Willcott.[41] The stepwise migration of cyclopropane would result in a new molecule having the same gross structure (Equation 14).

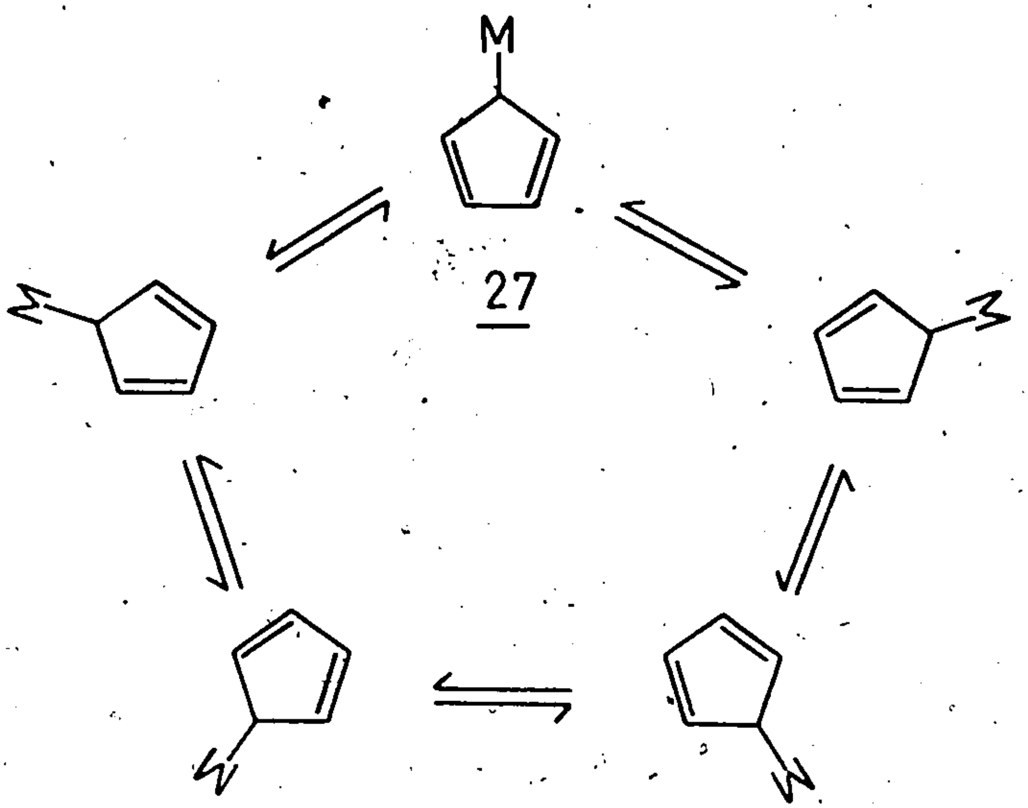


26 26′ 26″

14

The products of the thermal rearrangement of 3,7,7-trimethyltropylidine were consistent with the rearrangement in which cyclopropane undergoes 1,5 migration.

An intriguing sigmatropic (metallotropic[42]) rearrangement is demonstrated by σ bonded cyclopentadiene metal compounds.[43] This involves a series of degenerate 1,5 shifts, erroneously termed 1,2 shift[44] by many authors.



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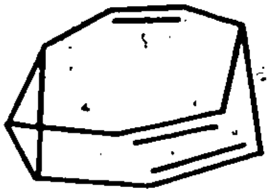
Other atoms or groups might be bonded to the metal atom which can either be a main group element (Si,Sn) or a transition element, e.g., Fe, Ti, etc. The fluxional behaviour[45] is also displayed by compounds having methyl substituents on the cyclopentadiene ring.[46]

The migration in these stereochemically non-rigid systems is evidenced by temperature dependent p.m.r. spectrum. The signals corresponding to ring hydrogen (or methyl groups) collapse to give a statistically averaged singlet as the temperature is raised. The range of the temperature at which such a rearrangement can be observed is dependent upon the energy barrier of migration. For compounds such as $C_5H_5Si(CH_3)_3$ with a high activation energy[44] the averaging is only observed on heating. In contrast the rearrangement in $C_5H_5HgC_2H_5$ requires a very low activation energy so that only the averaged singlet for the ring hydrogen atom can be observed at the lowest temperature attainable in an nmr experiment.[47]

Infrared studies by Cotton have shown that the systems which cannot be frozen are indeed fluxional molecules.[48]

From theoretical calculations, Ustynyuk and Shchembelov[49] have suggested that during the transition state in these migrations, there is an overlap between vacant p or d orbitals of the metal atom and occupied π orbitals of the cyclopentadiene ring.

This section could not be closed without mentioning the degenerate rearrangement shown by the legendary bullvalene (28). It was predicted by Doering[45] that a series of Cope rearrangements in this amazing compound could give rise to 10^6 structures.



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Bullvalene has since been synthesized by Schröder[50] and the compound shows a single p.m.r. resonance at 100°, the result of these rapid [3,3] sigmatropic shifts.

More examples of hydrocarbon degenerate rearrangements have been discussed in an excellent review by Gajewski.[51]

6. Ionic Degenerate Sigmatropic Shifts

Carbonium ions are particularly prone to rearrangements[52] and many examples of degeneracy can be found within this class of intermediates. On the basis of atoms and groups undergoing interchange, degenerate cation rearrangements can be classified as follows:

(a) Degeneracy resulting from hydrogen migration;

(b) Degeneracy resulting from carbon atom migration;

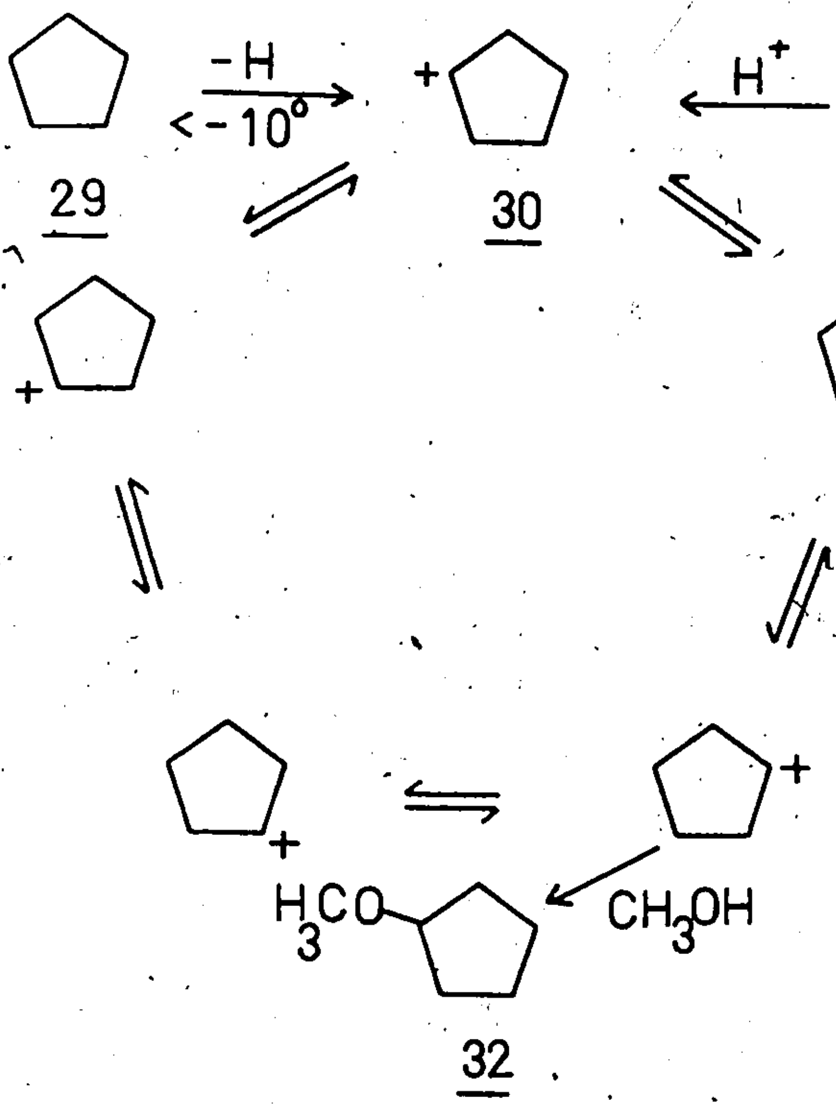
(c) Degeneracy resulting from both carbon and hydrogen migrations.

(a) Hydrogen Migration

Degenerate hydrogen migration involves the interchange of hydrogen atoms while the carbon framework remains fixed. Generally these hydride shifts are orbital symmetry controlled. Although the interchange and equivalence of all hydrogen atoms on the surface of the molecule can occur, partial hydrogen degeneracy of hydrogen atoms has also been observed. Complete degeneracy of the hydrogen atoms result in a single p.m.r. signal provided the rate of migration is faster than the nmr time scale. Many of these systems have been generated in highly acidic media, the conditions under which the p.m.r. spectrum can be observed directly.

Olah and Lukas[53] investigated the cyclopentyl cation generated in acidic solvents. Cyclopentane (29) was dissolved in a super acid (SbF_5-$HFSO_3$ or HF-SbF_5) diluted with SO_2ClF. The cyclopentyl cation (30) which was formed by hydride abstraction, was well characterized.[54] Quenching the acidic solution in methanol produced cyclopentyl methyl ether (32).

The cation exhibited a single peak in p.m.r. and the spectrum remained unchanged as the temperature was lowered to -130°. This was taken to indicate that the cyclopentyl cation was undergoing a



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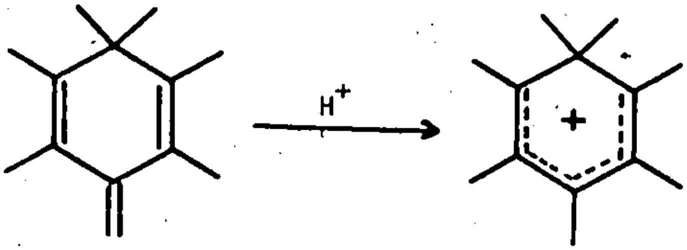
series of very rapid sequential 1,2 hydride shifts, resulting in complete hydrogen degeneracy. A number of other such examples exist.[55]

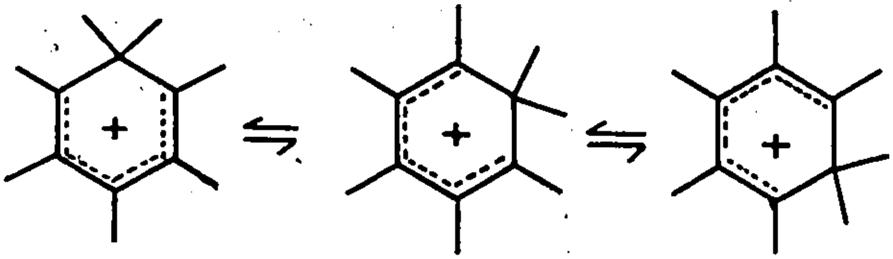
(b) Carbon Atom Migration

This type of rearrangement involves the migration of a carbon atom together with its substituents bonded to it. Complete degeneracy due to carbon migration involves an interchange of all the carbon atoms in the molecule. Theoretically such a degenerate rearrangement can be detected by the scrambling of the ^{13}C atom within the ion.

One of the earliest degenerate cations to be studied was heptamethylbenzenonium ion generated by the protonation of 3-methylene 1,2,4,5,6,6-hexamethylcyclohexa-1,4-diene (33).[56] The resulting stable cation exhibited a characteristic 1:2:2:2 p.m.r. spectrum with the three peaks at lower field corresponding to the methyl groups bonded to the sp^2 hybridized carbon atoms. At higher temperatures, the signals broadened, collapsed and at still higher temperatures became a singlet.

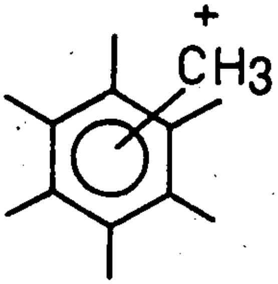


33 34 17



34 34′ 34″ 18

The changes in the p.m.r. spectra showed that the migration could occur via 1,2 (or 1,6) sigmatropic shifts. Another possibility is that the migration could be random, going through the transition state which resembles the π complex (35).



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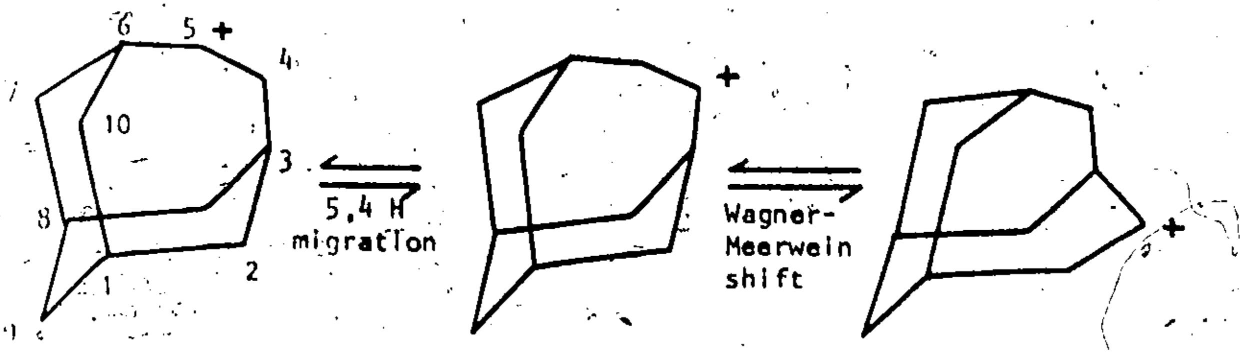
By the use of multiple resonance technique, Koptyug et. al.,[57] have established that such a random migration does not occur and that the methyl migration occurs in a series of discrete 1,2 shifts. Other benzenonium ions also show degenerate rearrangements. Examples are hexamethylbenzenonium ion, durenonium cation, pentamethylbenzenonium cation,[58] etc.

The ^{13}C nmr data for hexamethylbenzenonium ion has been published recently.[59] However, the averaging process shown by this cation has not been studied by ^{13}C magnetic spectroscopy.

(c) The Carbon and Hydrogen Migration

The 4-homoadamantyl cation (36) as noted by Nordlander,[60] is capable of exhibiting a combined carbon and hydrogen degeneracy.



36 36a 36b

19

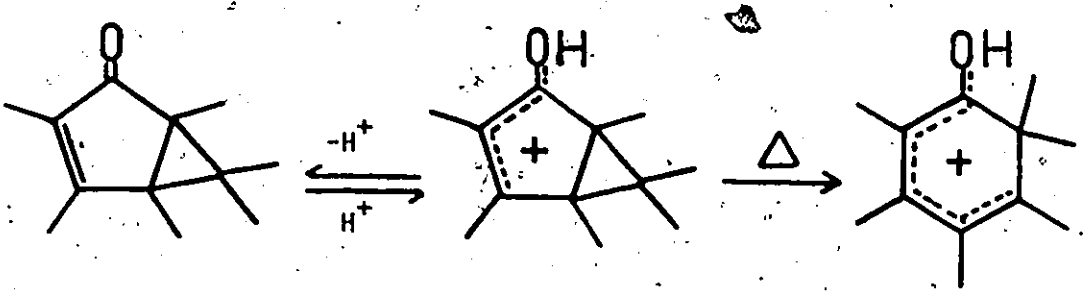
The two processes can be distinguished from each other by the deuterium label distribution. A D atom originally at C_4 in 36 would appear at C_5 in 36a and at C_3 in 36b. The combination of 1,2 hydride shifts and Wagner-Meerwein shifts causes the cation to be an eleven fold completely degenerate cation.

Further examples of degenerate cations have been discussed in the highly commendable review by Schleyer.[61]

7. Degenerate Circumambulatory Rearrangements

The bicyclo[3.1.0]hexenyl cation is particularly interesting in that it and many of its derivatives undergo a degenerate rearrangement. These rearrangements are particularly interesting as their stereoselectivity can be determined and the validity of the orbital symmetry rules tested.

One of the very first examples of this intriguing rearrangement was provided by Swatton and Hart.[62] A sulfuric acid solution of hexamethylbicyclo[3.1.0]hex-2-en-3-one upon quenching gave a nearly quantitative yield of 2,3,4,5,6,6-hexamethylcyclohexa-2-4-dienone.



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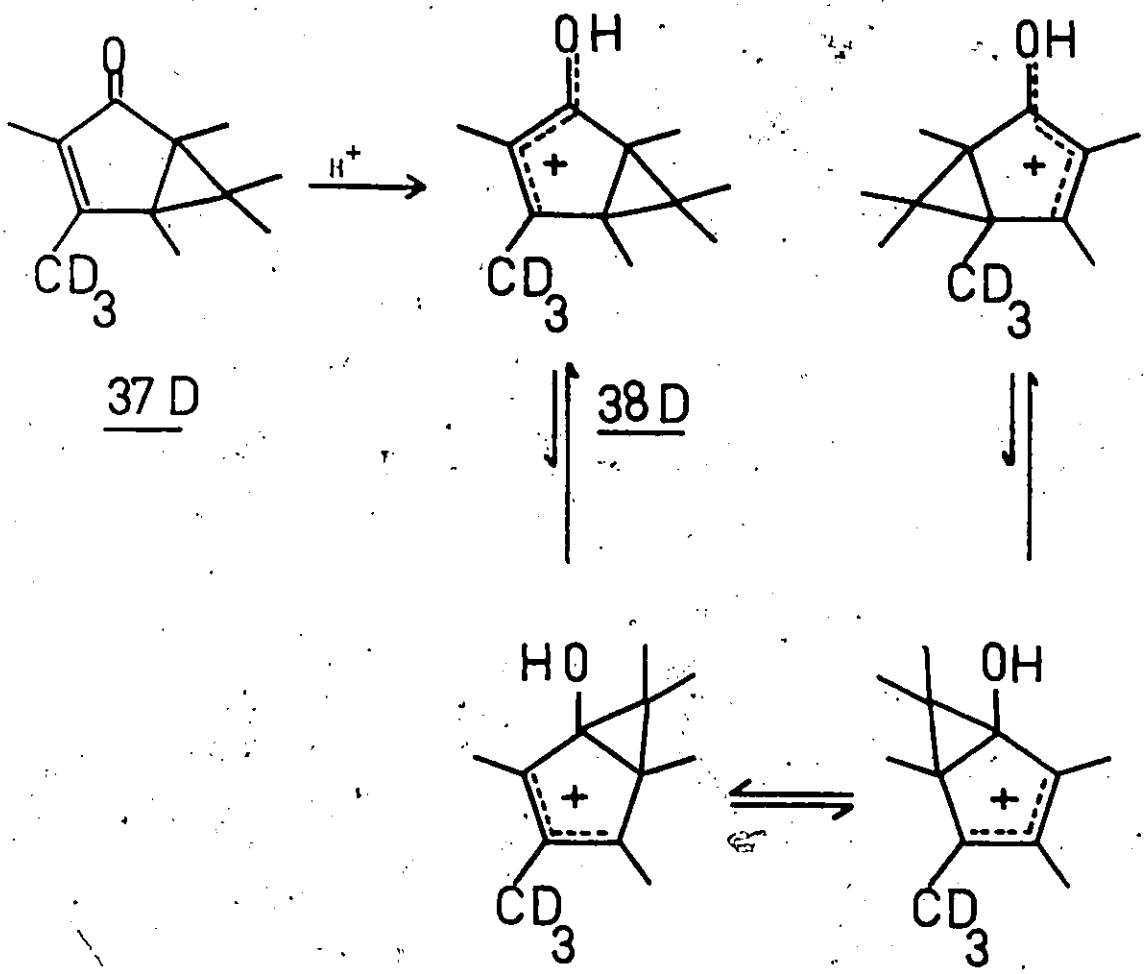
37 38 39

The intermediate, if any, in the rearrangement was not observed but labelling experiments indicated a mechanism involving the rapid degenerate migration of the cyclopropyl ring. An attractive mechanism would be the stepwise 1,4 sigmatropic migration of the cyclopropyl fragment so that the ring methyl groups will become equivalent and thus account for the scrambling of labelled CH_3 groups (Equation 21).

This behaviour was also observed in fluorosulfuric acid.[63]

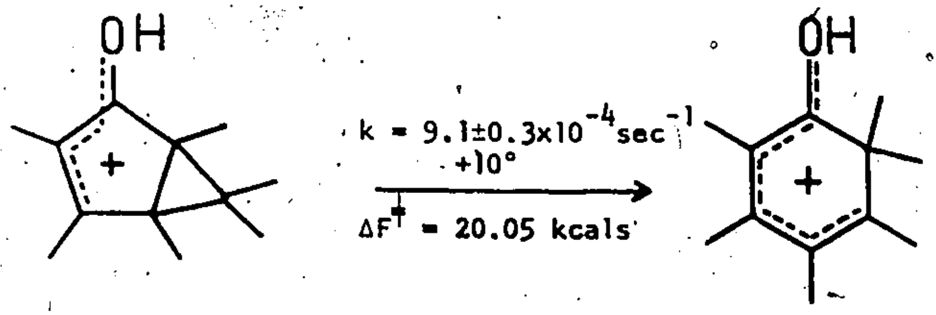
The rates of cyclopropyl migration and subsequent ring opening have been determined.



37 D

38 D

21



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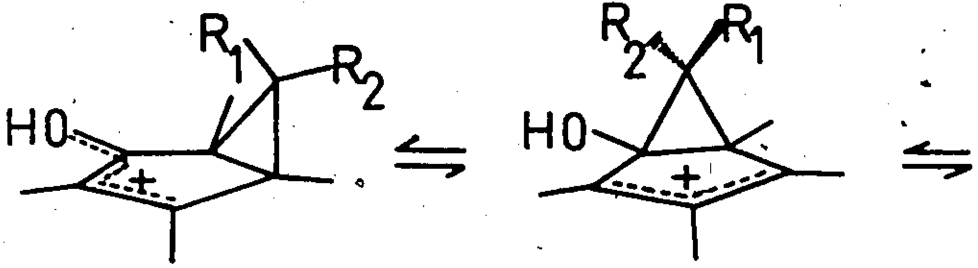
39

It was recognized[56] that this striking, perhaps, unique migration must have stereochemical consequences for the substituents at C_6. Migration in these rigid systems are bound to be suprafacial and when thermally induced must involve the inversion of configuration at the migrating centre viz., C_6, if symmetry is to be conserved.[2]

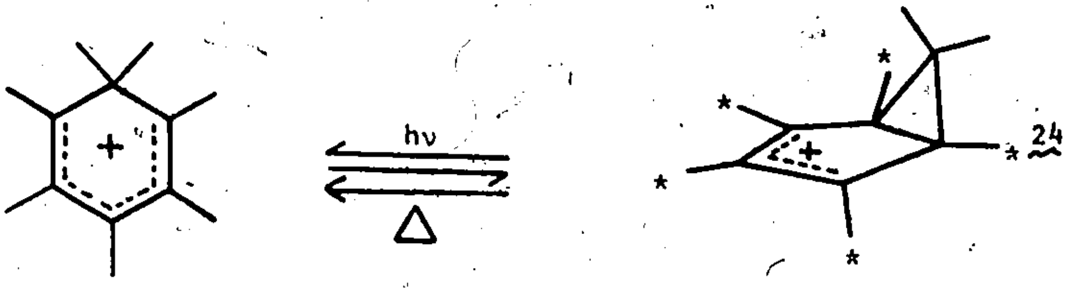
Hart, Rogers and Griffiths[64] later confirmed the stereochemistry of ring migration by using ethyl and methyl substituents at C_6. The rearrangement was confirmed by the scrambling of CD_3 groups bonded to C_4 of the five membered ring. Quenching at low temperature and identification of products showed that the orientation of substituents at C_6 remained unchanged, confirming that 1,4 sigmatropic migration must have occurred with an inversion of configuration at the migrating carbon atom.



23

$R_1 = CH_3$; $R_2 = C_2H_5$
$R_1 = C_2H_5$; $R_2 = CH_3$

Perhaps the best example of a cyclopropyl circumambulation on cyclopentenyl ion was provided by Childs and Winstein.[65] The 1,2,3,4,5,6,6-heptamethylbicyclo[3.1.0]hexenyl cation (40) was generated by the low temperature photoisomerization of heptamethylbenzenonium ion[66] (34) in fluorosulfuric acid.



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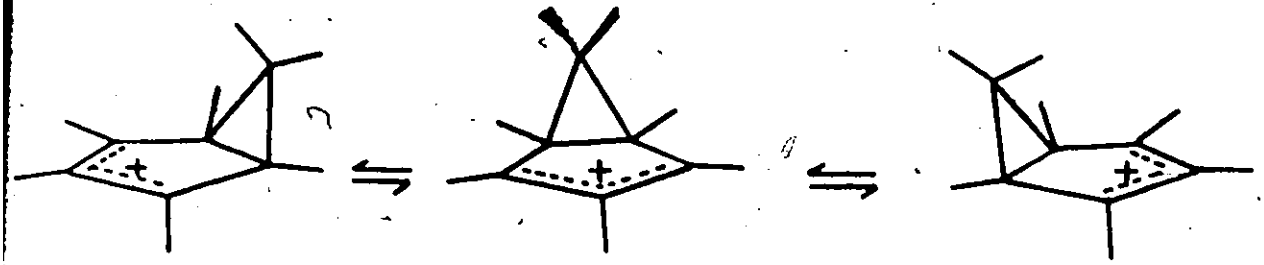
40

The bicyclic cation 40 was formed under such conditions that the nuclear magnetic resonance spectrum could be observed directly at varying temperatures. The signals of the low temperature p.m.r. spectrum were consistent with the bicyclic cation. At higher temperatures, the signals attributable to the ring methyls, marked by asterisks, broadened, coalesced and at still higher temperatures collapsed into a statistically averaged singlet. The other two signals, which gave distinct resonances, were unchanged throughout the averaging process. The original five line spectrum was recorded again upon cooling showing that the averaging process is reversible.

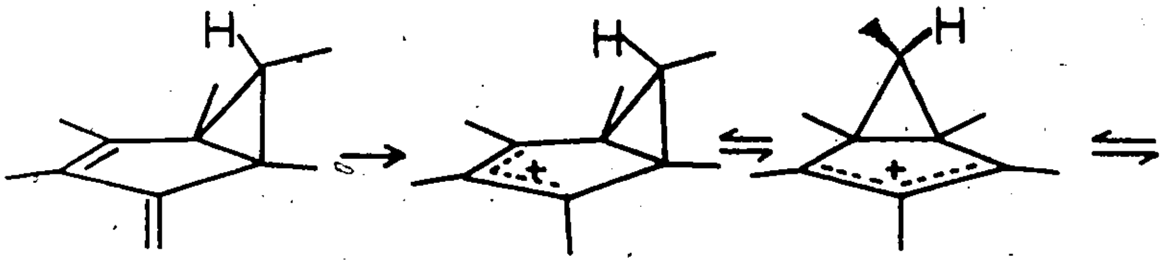
This behaviour can only be explained by the stepwise migration of the cyclopropane around the periphery of the cyclopentenyl ring as illustrated below.



40 40 40

25

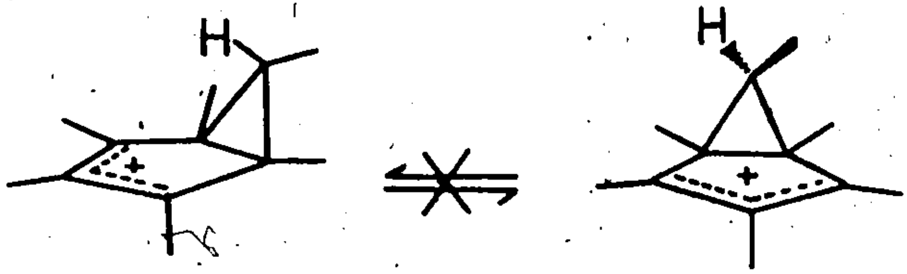
Suprafacial 1,4 sigmatropic cyclopropyl migration was also observed in *exo*hexamethylbicyclo[3.1.0]hexenyl cation[67] (42).



41 42 42′

26

The cation was generated by the protonation of homofulvene (41) and the orientation of the C_6 substituents is well characterized. The methyl doublet and the proton quartet remained unchanged during the averaging. The formation of *endo*hexamethylbicyclo[3.1.0]hexenyl cation (43) was not detected at any stage during the circumambulatory rearrangement.[68]

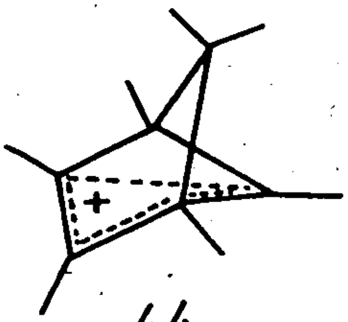


42 43

27

8. Mechanism of the Five Fold Degenerate Rearrangement

Any mechanism proposed for the thermally induced suprafacial sigmatropic rearrangements of the cyclopropane in the bicyclo[3.1.0]-hexenyl systems must account for the high degree of stereoselectivity that accompanies the migration. A one step process which can be classified as a suprafacial 1,4 sigmatropic shift[2] and stepwise migrations involving a series of thermally allowed 1,2 or 1,3 migrations meet this requirement. The intermediate in the stepwise migrations would be the bicyclo[2.1.1]hexenyl cation (44) which closely resembles the non-classical norbornenyl cation[69] (45).



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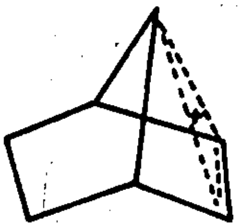

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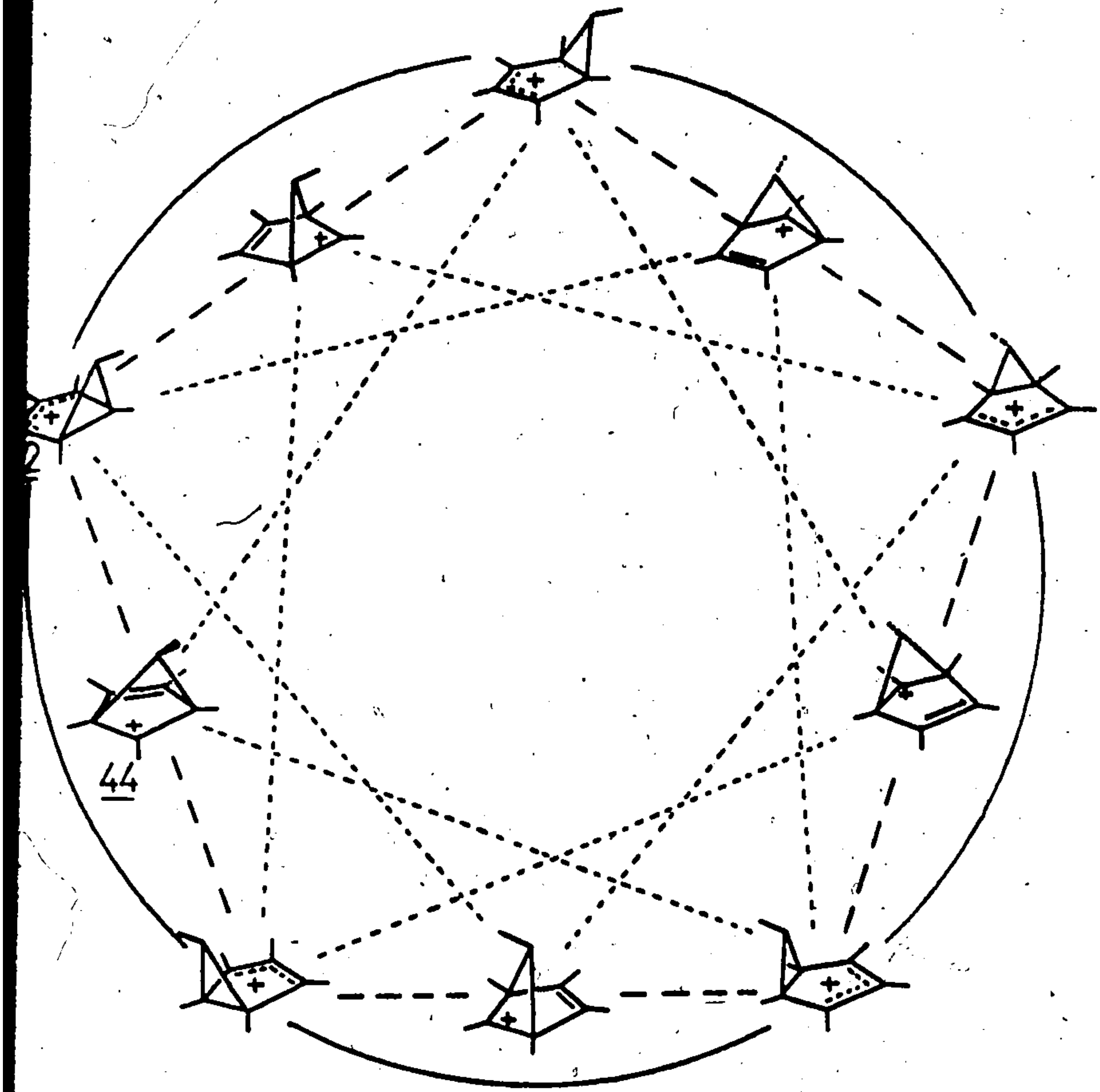
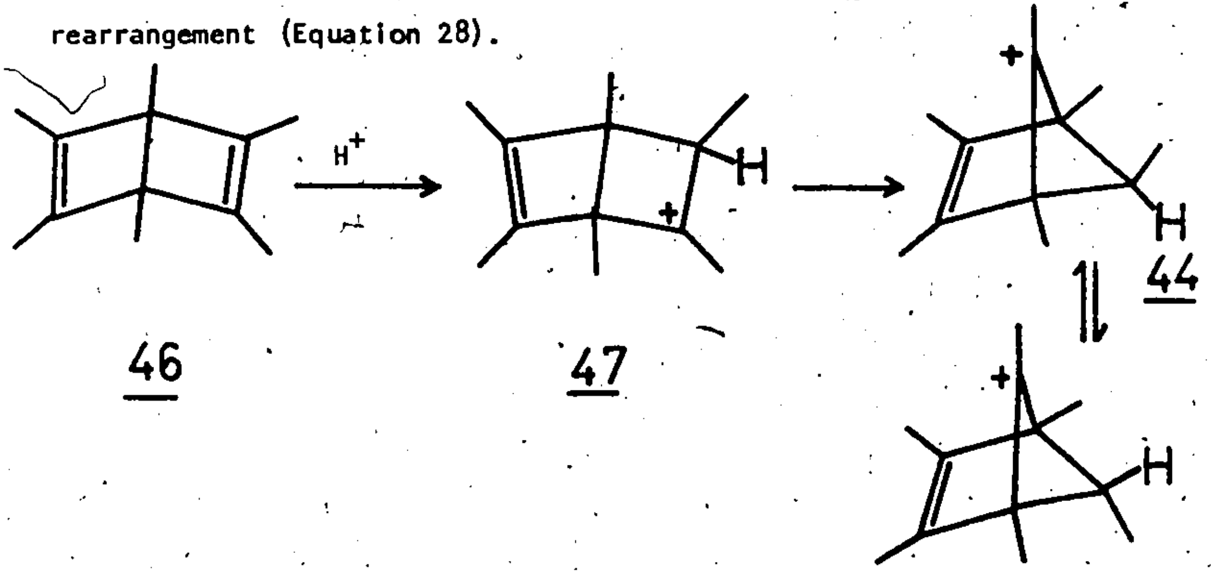
The possible 1,2, 1,3 and 1,4 sigmatropic migrations of hexamethyl bicyclo[3.1.0]hexenyl cation are illustrated in the following scheme.



eme I

Orbital symmetry predicts that suprafacial 1,4 and 1,3 sigmatropic migrations are allowed if there is an inversion of configuration during the migration. 1,2 Shifts are allowed only with the retention of configuration. Two successive 1,2 or 1,3 shifts would result in the same assemblage of the substituents at C_6, i.e. the *exo* group remaining *exo* and the *endo* group remaining *endo*. The net result will be the cation which will have the same arrangement as the cation resulting from a single 1,4 sigmatropic shift.

One of the attractive methods to distinguish the 1,4 sigmatropic migration from the stepwise 1,2 or 1,3 migrations would be to determine the stability of hexamethylbicyclo[2.1.1]hexenyl cation (44) under the conditions of the degenerate rearrangement. Indeed, the cation has been generated by Hogeveen[70a] and others[70b,c,d] by dissolving hexamethyldewarbenzene (46) in HF or BF_3-HF and subsequent rearrangement (Equation 28).



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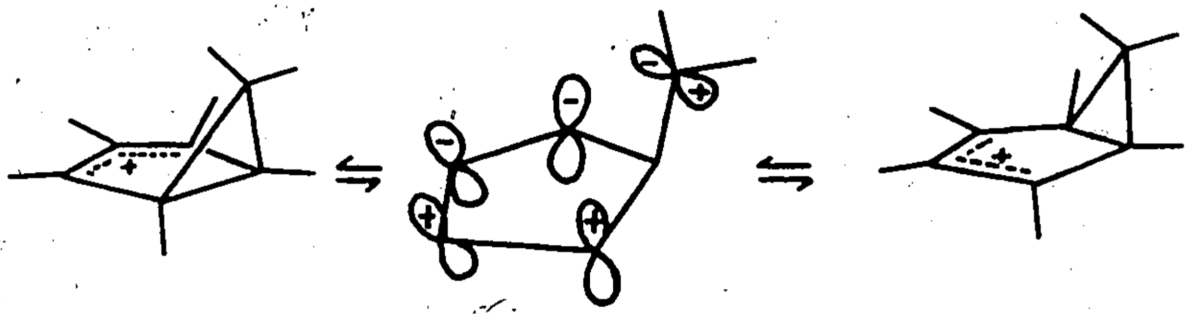
The hexamethylbicyclo[2.1.1]hexenyl cations (44), which rapidly interconvert are stable up to +20°. Above this temperature they isomerize to hexamethylbenzenonium ion (48). The same effect was observed when fluorosulfuric acid was used instead of $HF-BF_3$.[57]

9. Selectivity of the 1,4 Sigmatropic Migration

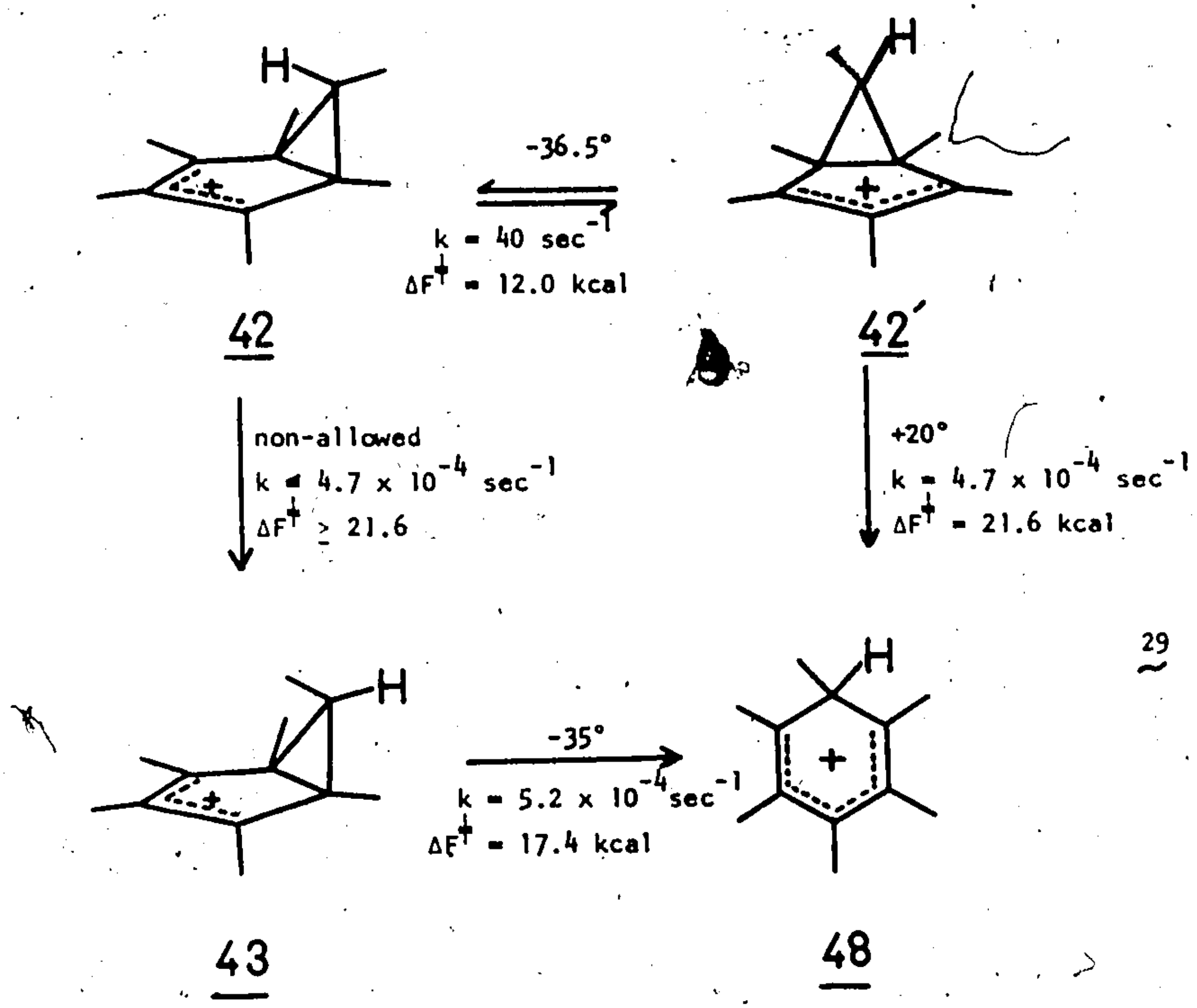
The five fold degenerate rearrangement in the bicyclo[3.1.0]hexenyl cations may be best viewed as a suprafacial 1,4 sigmatropic shift. The highest occupied molecular orbital of these systems (illustrated below) requires the inversion of configuration at C_6 in each migration. The result is that the arrangement of substituents at C_6 remained unchanged.



40 40a 40

25

It is of interest to note how facile the "allowed" pathway is compared to the "non-allowed" process in the 1,4 sigmatropic rearrangement. If exohexamethylbicyclo[3.1.0]hexenyl cation (42) rearranges in the "non-allowed" fashion, the endo hexamethylbicyclo[3.1.0]-hexenyl cation (43) will result. The endo isomer, however, was not observed in any stage during the migration of 42 .



It has been shown that the *exo* isomer 42 rearranges to hexamethylbenzenonium ion (48) with the rate constant of 4.7 x 10^{-4} sec^{-1} at 20°, corresponding to a free energy of activation of 21.6 kcal/mole. A similar thermal rearrangement of 43 also gives 48 with the free energy of activation for the rearrangement being 17.4 kcal/mole. If 43 is formed from 42 and if the rate of formation is slow compared to its ring opening to the hexamethylbenzenonium ion (48), then only 48 will be observed.

Since 48 is the only isomer detected from the rearrangement of 42, the rate constant for the "non allowed" isomerization to 43 must be less than 4.7×10^{-3} xec^{-1} at 20°; corresponding to the free energy of activation of ≥ 21.6 kcal/mole.

The difference in the free energies of activation between the "allowed" and the "non-allowed" process must be greater than or equal to 9.6 kcal/mole. Put in terms of the difference in rate constants at -36.5°, the temperature at which the 1,4 sigmatropic migration has the rate constant of 40 sec^{-1}, the rate constant for the "non-allowed" process will be ≤ 5.0×10^{-8} sec^{-1}, i.e., the "allowed" process is 8×10^{8} times faster than the "non-allowed" migration.

Although this amazing stereoselectivity can be considered as a startling validation of the orbital symmetry rules, it should be noted that a comparable stereoselectivity and the inversion of configuration at C_6 is also predicted by the Principle of Least Motion.[65]

10. The Effects of Substituents on C_6

The free energies of activation associated with the degenerate rearrangements of the bicyclohexenyl cations are summarized in Table II. It can be seen that the substituents on C_6 have a marked effect upon the energy barrier of this rearrangement.

TABLE II

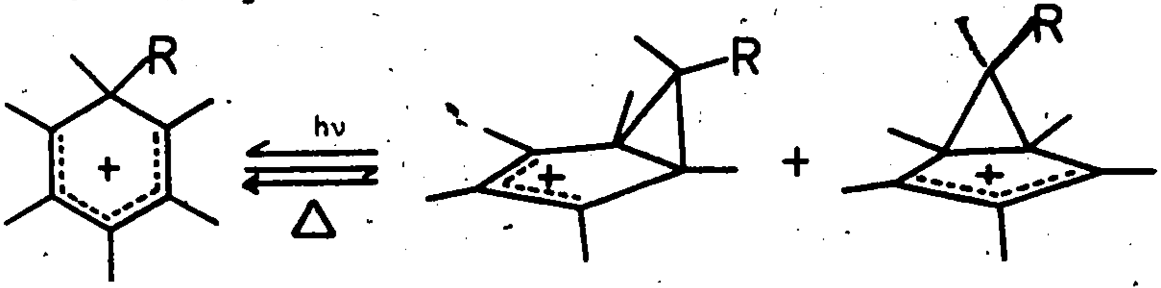
Activation Barriers for the Cyclopropyl Circumambulation

Compound	C_6 Substituents		$\Delta F^{\ddagger}$ kcal/mole
	exo	endo	
40	CH_3	CH_3	9.0
42	CH_3	H	12.0
43	H	CH_3	17.1
59	H	H	> 13.0
	H	H	> 18.6*

* 1,2,4,5-tetramethylbicyclo[3.1.0]hexenyl cation

It is of importance to note that the free energy of activation for the migration is greatly dependent upon the ability of the substituents on C_6 to stabilize a positive charge. For example, two methyl substituents on C_6 compared to two hydrogens, decreased the energy barrier of migration by more than 4 kcal/mole. This profound change in the energy barrier of the rearrangement shows that a considerable positive charge is developed at C_6 during the transition state.[65]

This conclusion that a partial positive charge being developed at C_6 during the migration has been confirmed by the work of Koptyug et al.[66] Bicyclo[3.1.0]hexenyl cations with various endo R groups [R = CH_3, Et, CH_2Cl] were generated photochemically and the influence of the nature of the exo C_6 substituents on the kinetic characteristics of the rearrangement studied.



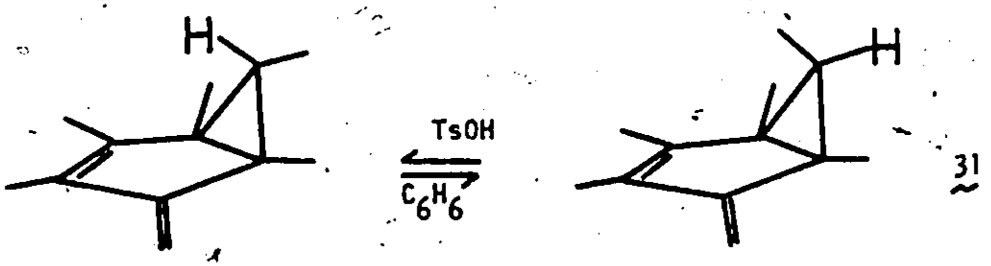
49 50 50a

30

Despite the limited number of compounds studied, Koptyug et. al., claimed that there was a linear correlation between log k of the reaction and σ^*. However, it should be noted that these workers arbitrarily selected only the rate of the exo ion (50a) and offered no explanation for the difference in the energy barrier of the two isomers. Quite clearly it is not just charge stability that is important to the system.

It might be noted that the energy barrier for the degenerate rearrangements is different in 42 and 43. This difference in free energies of activation could either be due to the difference in the ground state stabilities or the difference in energies associated with their respective transition states.

While the ground state stabilities of the exo and the endo hexamethylbicyclo[3.1.0]hexenyl cations cannot be compared easily, the homofulvenes are good models which closely resemble the bicyclic cations. The equilibration between the exo and the endo methyl isomers was reported by Criegee.[71] There is little difference in the ground state energies between 41 and 51. It is therefore most likely that the difference in energy barriers for the degenerate rearrangement in 42 and 43 must be due to a difference in the transition state energies.



41

51

This difference of the transition state energies for the migration of 43 and 42 cannot be due to the electronic effect of the C_6 substituent as the methyl group should be able to stabilize any partial positive charge equally well irrespective of its position. A very probable answer then is the effectiveness of the overlap of the electron deficient C_6 with the occupied π orbitals of the diene. The effectiveness of this overlap will be dependent upon the proximity of respective orbitals on C_6 and the diene. An examination of a molecular model shows that this distance can be reduced easily in the exo methyl system 42 but not in the endo methyl isomer 43. In this latter system a steric interaction between the C_6 endo substituent and the C_2C_3 carbons occurs. It is likely that this is being reflected in the differences in the rate of rearrangement in 42 and 43.

Therefore, it is valid to compare the ease of degenerate rearrangement of heptamethylbicyclo[3.1.0]hexenyl cation (40) with that of endo hexamethylbicyclo[3.1.0]hexenyl cation (43) since the steric effect of the endo substituent is the same in both cases. The difference in free energies of activation is 8.1 kcal/mole. If there is no interaction between the diene moiety and C_6, the difference in energies is expected to be 12-15 kcal/mole, as calculated from the data published by Olah[72] and Saunders.[73] The smaller difference observed must therefore be due to the overlap between electron deficient C_6 and the π orbitals of cyclopentadiene during the transition state even when the endo methyl prevents very close overlap. In other words, the degenerate rearrangement in all these systems proceeds with a continuous overlap of orbitals, which is the precise requirement for a symmetry allowed concerted reaction.

11. Relative Stabilities of Transition States and Ground States

It is evident from the work of Childs and Winstein[65] and Koptyug et.al.,[66] that C_6 becomes more electron deficient during the transition state in the 1,4 sigmatropic shifts of bicyclo[3.1.0]-hexenyl cations. The energy barrier of this rearrangement is lowered when electron donating groups are bonded to C_6. The lowest energy barrier associated with cyclopropyl migration yet measured for these bicyclo[3.1.0]hexenyl cations is 9.0 kcal/mole in <u>40</u> .

There is no reason why the energy barrier to migration could not be lowered still further by the appropriate choice of substituents. Indeed, in principle, the C_6 substituents could be chosen such that the potential energies of the ground state and the transition state might be comparable. At this point, the cyclopropyl fragment would be able to migrate with respect to cyclopentenyl ring with minimal energy of activation.

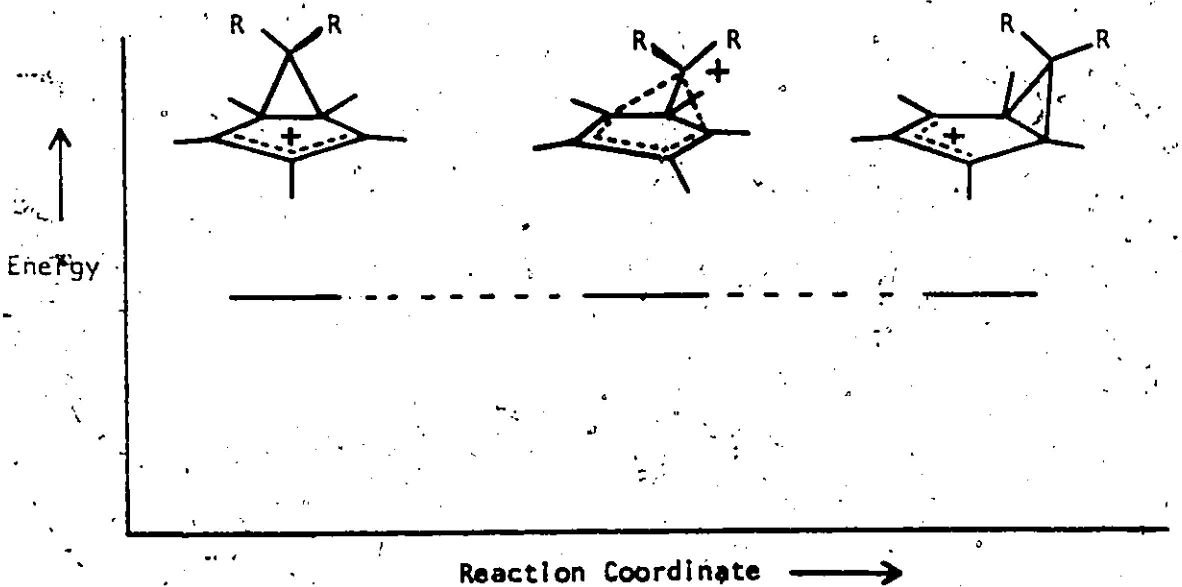


Figure 7. Relative Potential Energies of the Ground and the Transition States for the Cyclopropyl Circumambulation.

As the stabilizing groups upon C_6 further increases the transition state would be expected to become more stable than the bicyclohexenyl cation. In this situation, a degenerate migration of C_6 would still be anticipated. However, the cyclopentadiene-5-methyl cation would become ground state and bicyclohexenyl cation, the transition state or a high energy intermediate. At this point, the roles of the ground state and high energy intermediate or transition states will be inverted.

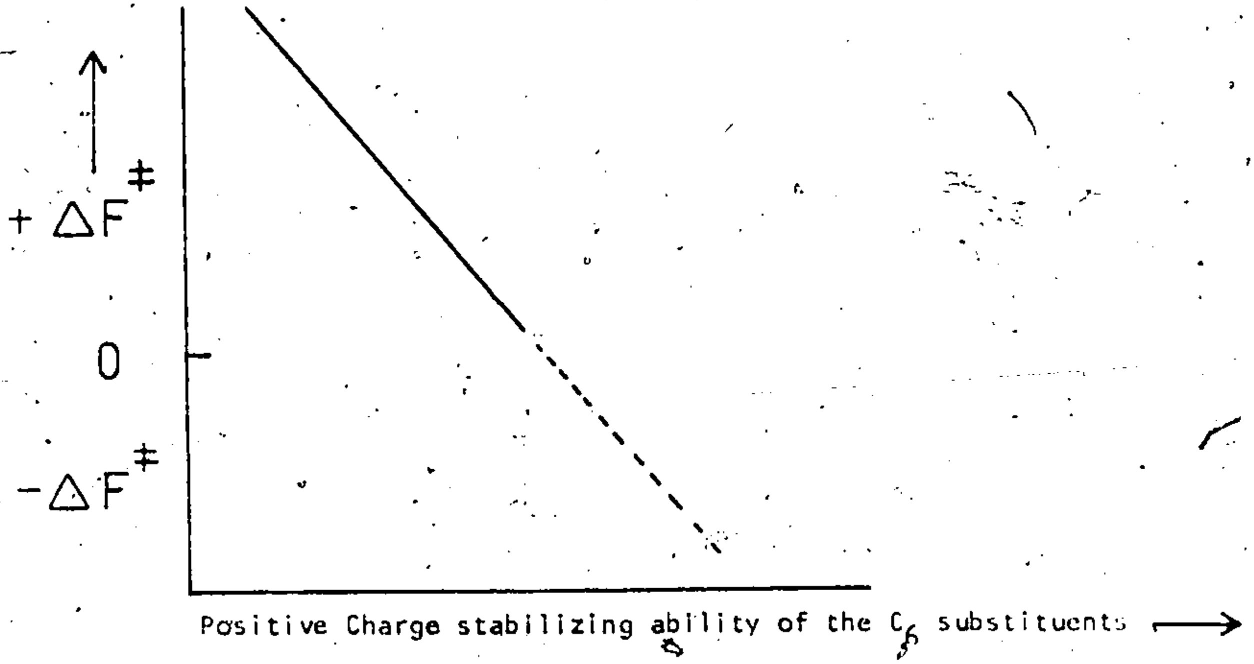


Figure 8 Activation Barrier as a Function of the Positive Charge Stabilizing Ability of the C_6 Substituents

It was the intent of this work to test this unprecedented phenomenon and to further probe the mechanism of the degenerate rearrangement by the synthesis of bicyclo[3.1.0]hexenyl cations with charge stabilizing groups as C_6 substituents. The degenerate rearrangements displayed by cations with various C_6 substituents, notably oxygen, will be discussed.

CHAPTER II

RESULTS AND DISCUSSION

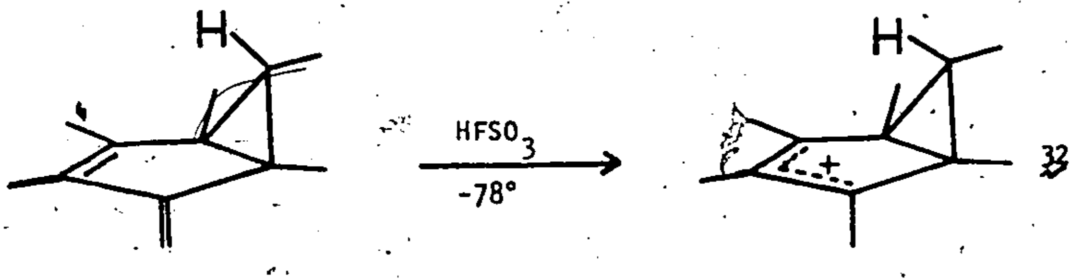
PART I

One of the aims of this research project was to synthesize the bicyclo[3.1.0]hexenyl cations with two different substituents at C_6 such that the effect of the orientation of the C_6 substituents on the circumambulatory rearrangement could be studied. The stereoselectivity of cyclopropyl migration could be investigated by determining the exo-endo isomer ratio during the rearrangement. As this thesis will be concerned with the mechanism of the thermal rearrangements of the bicyclo[3.1.0]hexenyl cations, it is appropriate to review how these cations can be synthesized.

1. Synthesis of Bicyclo[3.1.0]hexenyl Cations

(a) Direct Protonation of Homofulvenes and Related Materials

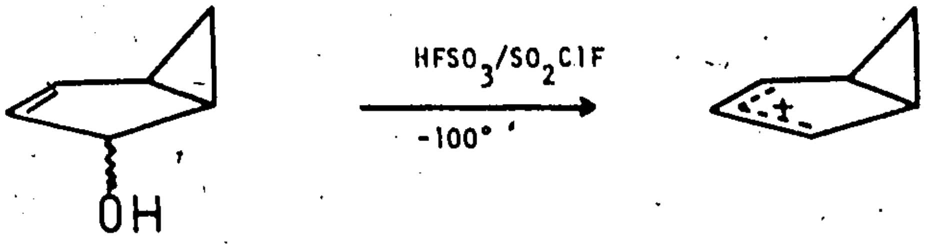
Dissolution of homofulvenes in strong acids results in the protonation of the exocyclic methylene group. The pentamethylhomofulvene (41), upon protonation with fluorosulfuric acid at low temperatures gives 42.[67]



41

42

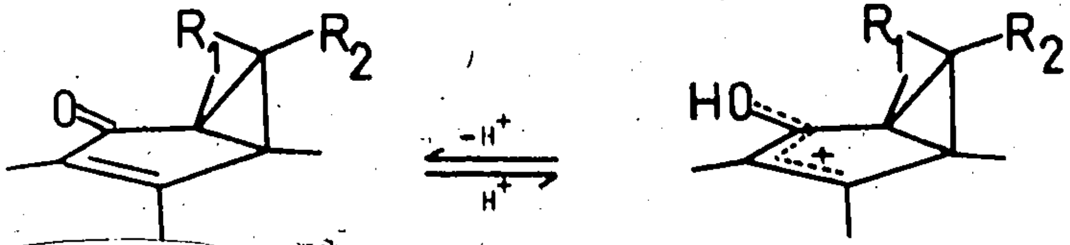
Protonation of bicyclo[3.1.0]hex-2-en-4-ol (52) with $HFSO_3/SO_2ClF$, results in the removal of the hydroxyl group and the formation of 53.[74] These ions have been suggested as intermediates in the photochemical isomerization of benzene in acidic media.[75,76,77]



52 53

33

Hydroxybicyclo[3.1.0]hexenyl cations have been generated by protonation of the corresponding bicyclic ketones at low temperatures.[62,64]



34

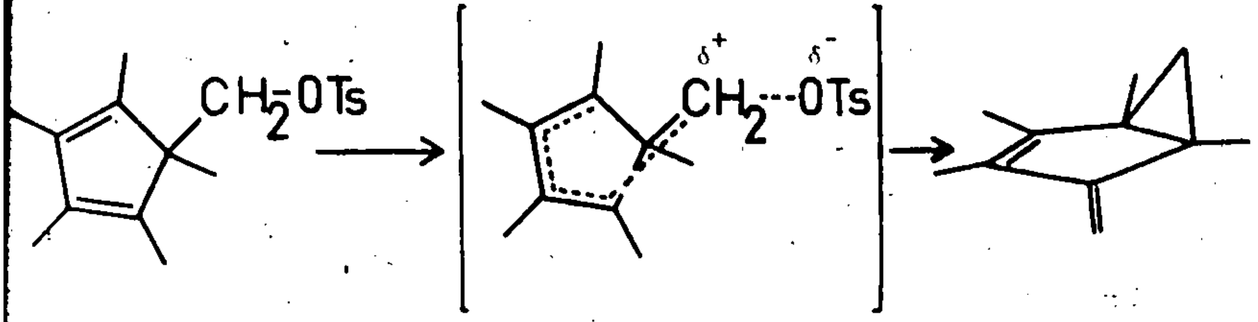
$R_1 = CH_3$ or C_2H_5

$R_2 = C_2H_5$ or CH_3

$R_1 = R_2 = CH_3$

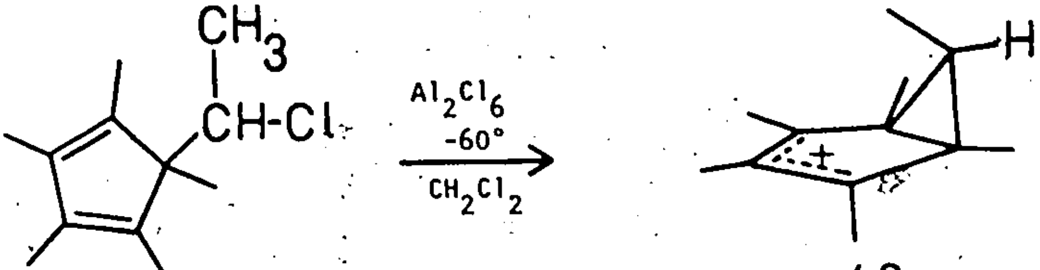
(b) Ionization of Cyclopentadiene-methyl Compounds

Winstein and Battiste[78] suggested the occurrence of homoallylic conjugation between the electron deficient C_6 and the π orbitals in pentamethylcyclopentadiene methyl tosylate (54). The formation of 59 as the intermediate in this solvolytic reaction was confirmed when tetramethylhomofulvene (55) was isolated as the kinetic product.



54 55 35

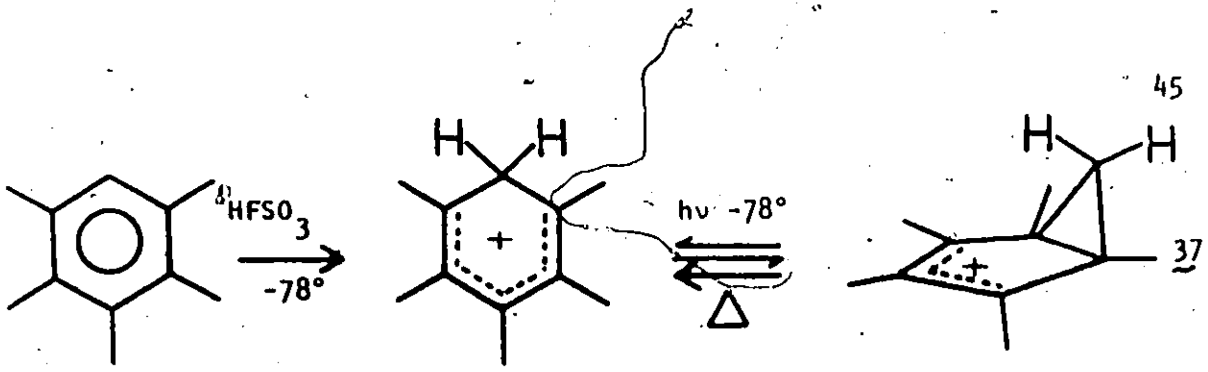
5-(α-Chloroethyl)-pentamethylcyclopentadiene (56) reacts with anhydrous Al_2Cl_6 in dry methylene chloride at -60° to produce 43 . There are two possible stereoisomers, one with the C_6 methyl group endo with respect to the cyclopentenyl ring, 43, and another with exo C_6 methyl substituent, 42 .. Koptyug[67a] and Criegee[79] independently reported the observation of only one isomer, namely 43 .



56 43 36

(c) Photochemical Isomerization

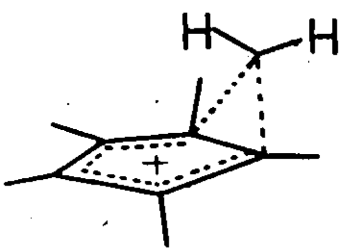
Childs and Winstein[65] were the first to investigate the photoisomerization of benzenonium cations in strong acids. Irradiation of the long wavelength absorption of benzenonium ions at low temperatures resulted in the formation of the corresponding bicyclo[3.1.0]hexenyl cations.



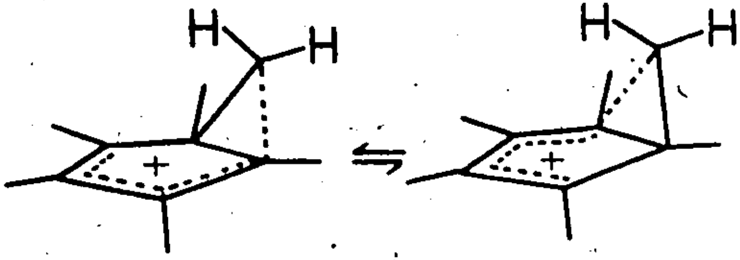
37

57 58 59

The simplest representation of the structure and the electron delocalization in 59 [and any other related bicyclo[3.1.0]hexenyl cations] is shown in 59b. This structure conforms to the symmetry required by its p.m.r. spectrum. The chemical shifts and coupling constants of C_6 hydrogens are also in agreement with the structure.[63]



59b



38

59c 59c

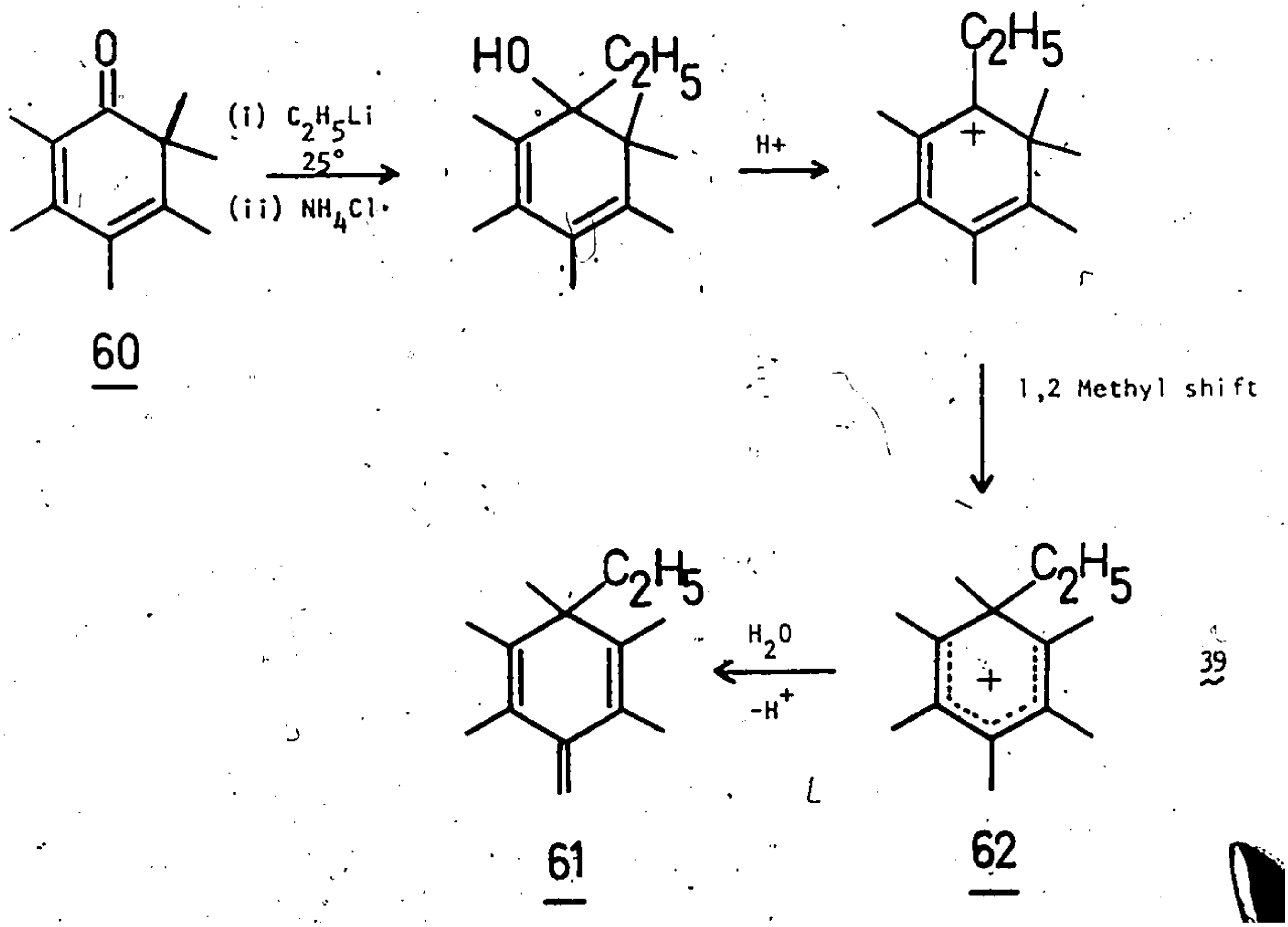
The same p.m.r. spectrum could also result from the rapidly equilibrating unsymmetrical homopentadienyl cations of the type 59c. However, cooling the solution of 59 in $HFSO_3/SO_2ClF$ to -120° caused no detectable freezing out of the spectrum of 59c.[63]

2. Synthesis of 6-Ethyl-1,2,3,4,5,6-Hexamethylbicyclo[3.1.0]hexenyl Cations

Photochemical isomerization of a benzenonium ion at low temperatures to a bicyclo[3.1.0]hexenyl cation would appear to be the most convenient method of synthesis. Accordingly, this synthetic procedure was attempted for the 6-ethyl-1,2,3,4,5,6-hexamethylbicyclo[3.1.0]hexenyl cation. The photochemical electrocyclic reaction is anticipated to produce both the exo and endo ethyl isomers, the ratio depending upon the relative ease of ring closure.

(a) Synthesis of 6-Ethyl-1,2,4,5,6-pentamethyl-3-methylene cyclohexa-1,4-diene (61)

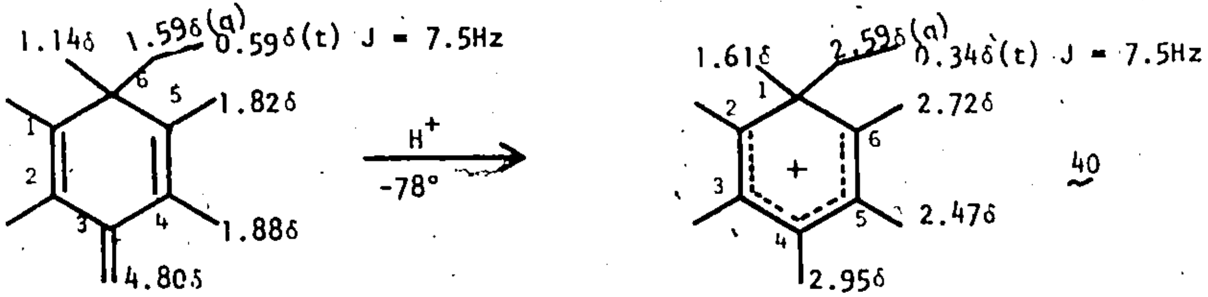
The synthesis of 2,3,4,5,6,6-hexamethylcyclohexa-2-4-dienone has been published.[80] Addition of ethyl lithium proceeded readily at room temperature to give the unstable tertiary alcohol. This, upon treatment with acid gave 62. Upon quenching with ice followed by neutralization the required triene 61 was obtained.



39

(b) Protonation of 6-Ethyl-1,2,4,5,6-pentamethyl-3-methylene cyclohexa-1,4-diene (61)

Addition of a proton to the exocyclic double bond at low temperature with fluorosulfuric acid results in the formation of 1-ethyl-1,2,3,4,5,6-hexamethylbenzenonium ion (62).



61 62 40

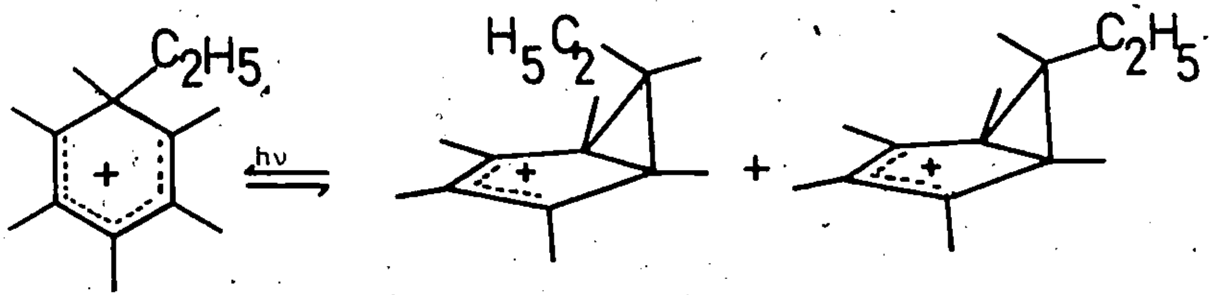
The structure of the benzenonium ion is clearly established from the change in p.m.r. spectrum when 61 is converted to 62. The spectrum now (equation 40) consists of four singlets at 1.61, 2.47, 2.72, and 2.95, a quartet at 2.59 and a triplet at 0.34 δ. The relative intensities of the peaks correspond to 3,6,6,3,2 and 3 hydrogen atoms, respectively, when normalized to a total of 23. The most significant change is the disappearance of the peak at 4.80δ corresponding to the exocyclic methylene group and its replacement by 2.95δ peak of a methyl group.

(c) Irradiation of 1-Ethyl-1,2,3,4,5,6-hexamethylbenzenonium Ion (62)

In the electronic spectrum of 62, the maximum absorption occurs at ca 398 nm. This is in agreement with the u.v. data recently published for polymethylated benzenonium ions.[81]

62 Was irradiated with light of wavelength > 320 nm at -90°. Low temperatures were used to prevent the reverse thermal

isomerization of the product cations. The products were identified as 63 and 64 on the basis of their p.m.r. spectra. Excellent agreement of the p.m.r. chemical shifts of the methyl group bonded to the cyclopentenyl ring reinforced the proposed structure of both cations. Stereochemical assignments have been made for cations 63 and 64 under the assumption that *endo* C_6 substituents are deshielded as compared to *exo* substituents in the bicyclo[3.1.0]hexenyl cations. The cations 63 and 64 were formed in a 2.5/1 ratio. It was not possible to completely isomerize 62 to 63 & 64. The maximum conversion achieved was 95%. Presumably the bicyclic cation can photoisomerize back to the benzenonium ion 62.



62 63 64

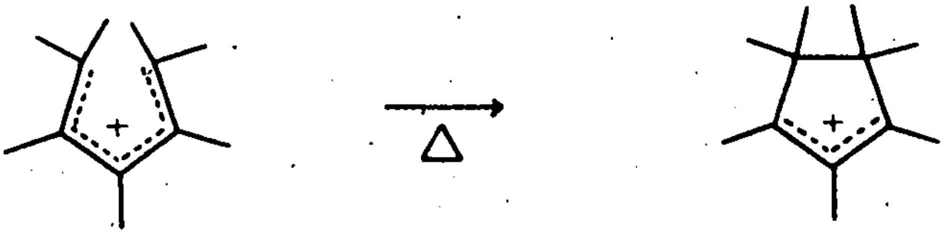
TABLE III

P.m.r. Data for 6-Ethyl-1,2,3,4,5,6-hexamethylbicyclo[3.1.0]hexenyl Cations

Cation	1&5CH_3	2&4CH_3	3CH_3	6CH_3	Others
63	1.74	2.59	2.11	1.56	0.81(t) 1.56(q) J = 7.5 Hz
64	1.74	2.59	2.11	1.19	0.94(t) 1.97(q) J = 7.5 Hz

(d) Mechanism of Photochemical Ring Closure

The thermally induced ring closure of substituted pentadienyl cations to the corresponding cyclopentenyl cations is a well-known rearrangement.[82] According to the Woodward and Hoffmann orbital symmetry rules, the electrocyclic ring closure must occur in a conrotatory manner.[2] The occurrence of the symmetry allowed conrotatory motion was confirmed by Sorenson[83] (Equation 42).



42

The ground state of the benzenonium ion 62 is inert to the thermal ring closure. The -C-MeEt- bridge which joins the terminals of the pentadiene cation prevents the conrotatory motion required for ring closure to the bicyclo[3.1.0]hexenyl cation. Such a motion will result in the product which has a trans cyclopropyl ring, which, even if formed, would likely open to give the starting material.

However, in its first excited state a disrotatory photochemical ring closure of benzenonium cations is allowed as is shown in Figure 9.

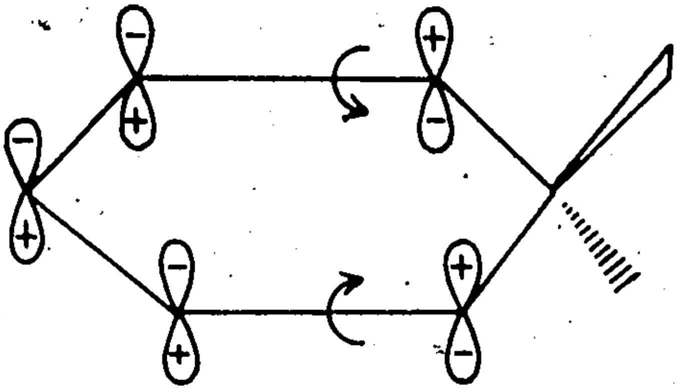
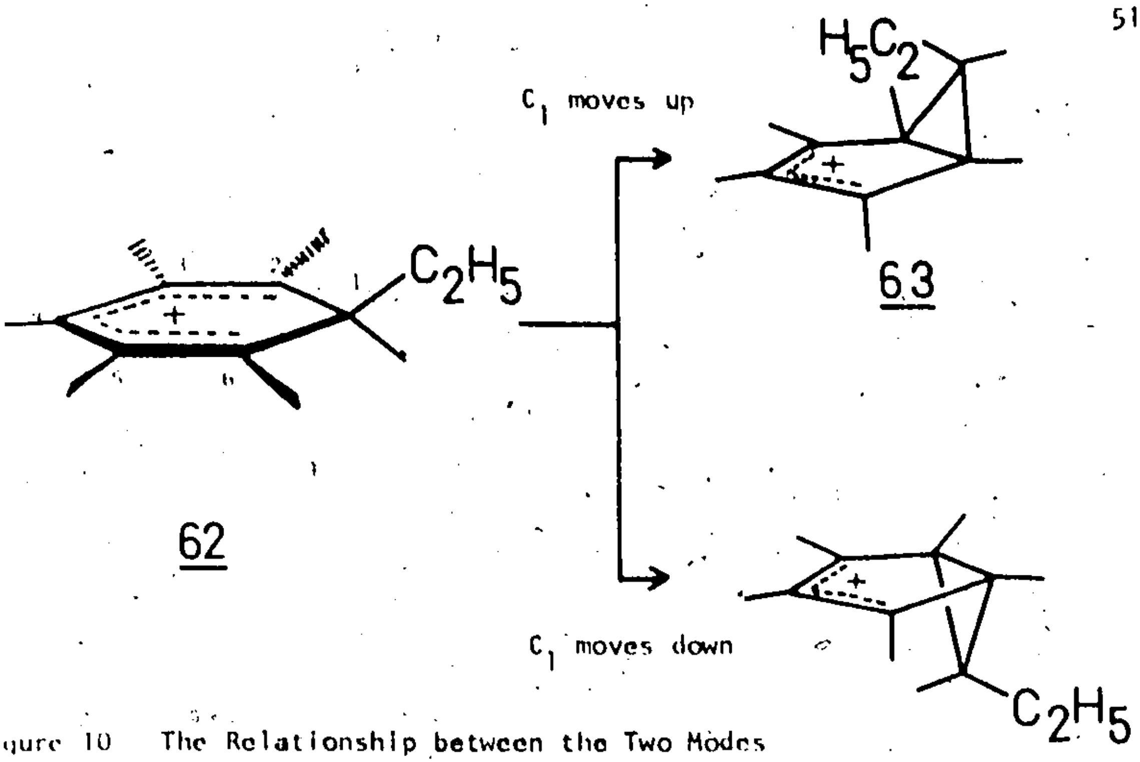


Figure 9 The Disrotatory Ring Closure of a Benzenonium Ion in its Excited State.

The Exo-Endo Isomer Ratio

In the photochemical ring closure of 62 to 63 and 64, the disrotatory motion permits C_1 to move either up or down. If C_1 moves up, placing the C_2H_5 group *endo*, then the CH_3 group on C_1 must pass through the horizontal plane between C_2 and C_6. The converse is true is C_1 moves down. When the repulsion between the C_1 substituents and the methyl groups on C_2 and C_6 are significant, and when one of the C_1 substituents has a greater steric requirement than the other, the product with the larger group in the *endo* position could be expected to predominate. This could explain why the *endo* hexamethylbicyclo[3.1.0]hexenyl cation is predominant in the photolysis of 48. Moreover, the hexamethylbenzenonium ion has been shown to be nonplanar and the C_1 methyl group is already in a pseudo axial position.



62

63

64

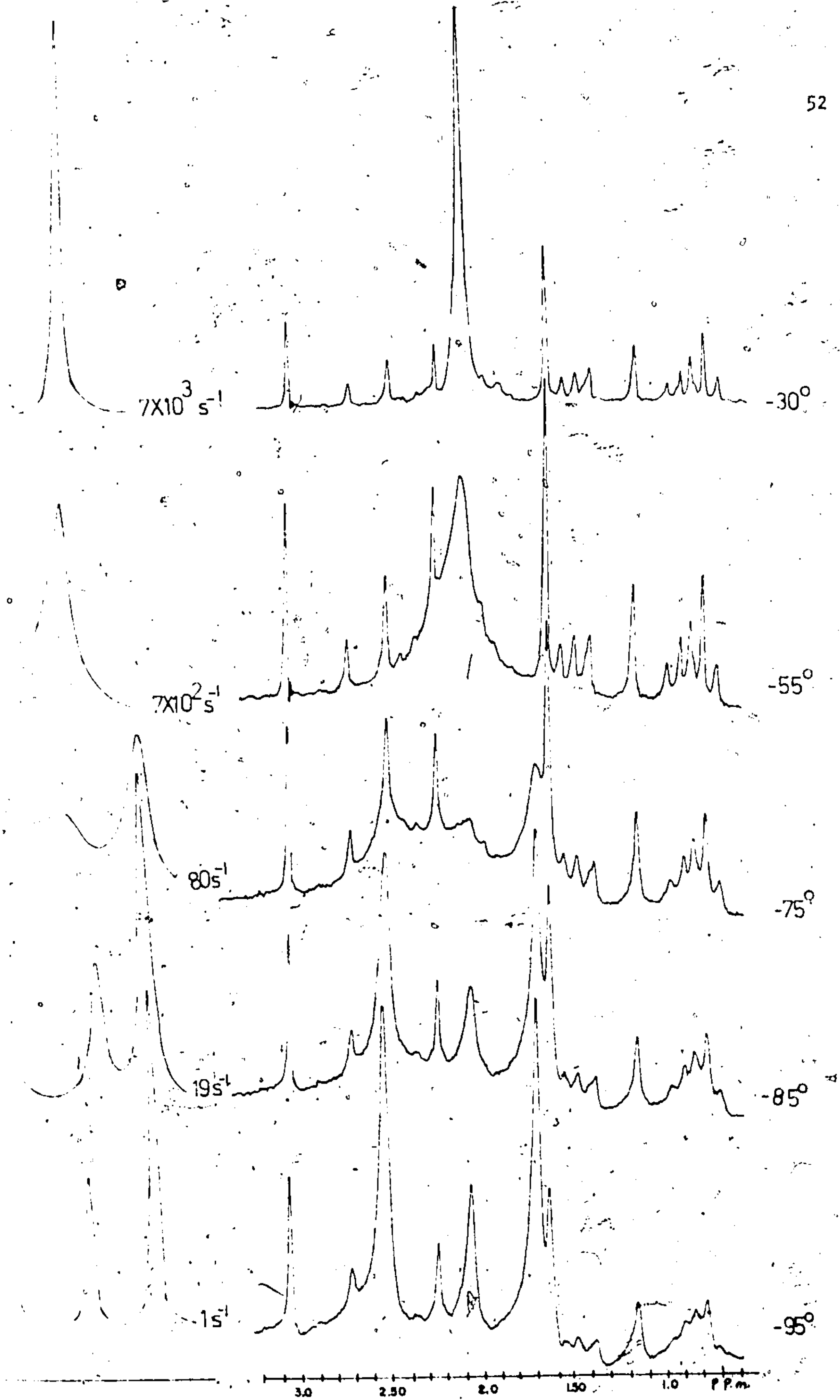
Figure 10 The Relationship between the Two Modes of Disrotatory Ring Closure of a Benzenonium Ion and the Resulting Bicyclic Cations

The small preference for 63 over 64 (2.5/1) probably reflects the similarity in size of the methyl and ethyl groups.[84] It is interesting that similar stereoselective ring closures have been found in the photoisomorization of the cyclohexadienones.[85-89]

3. Thermal Rearrangements of 6-Ethyl-1,2,3,4,5,6-hexamethyl bicyclo[3.1.0]-hexenyl Cations

The 6-ethyl-1,2,3,4,5,6-hexamethylbicyclo[3.1.0]hexenyl cations, like their electronically and structurally related heptamethyl analogue, display thermal rearrangements. Both 63 and 64 undergo a degenerate rearrangement where the cyclopropyl fragment migrates around the five-membered ring as well as an irreversible ring opening to benzenonium cation.

Figure 11 The Calculated and the Experimental Temperature Dependent P.m.r. Spectra of 6-Ethyl-1,2,3,4,5,6-hexamethylbicyclo[3.1.0]-hexenyl Cations

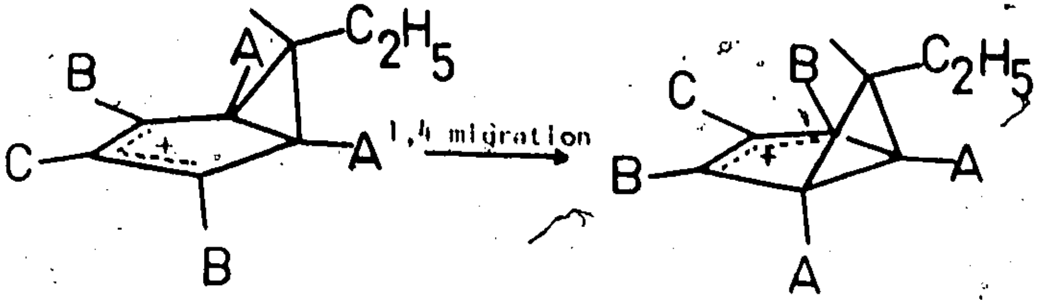

7X10^3 s^{-1}
-30°
7X10^{2}s^{-1}
-55°
80s^{-1}
-75°
19s^{-1}
-85°
1s^{-1}
-95°
3.0
2.50
2.0
1.50
1.0
P.P.m.

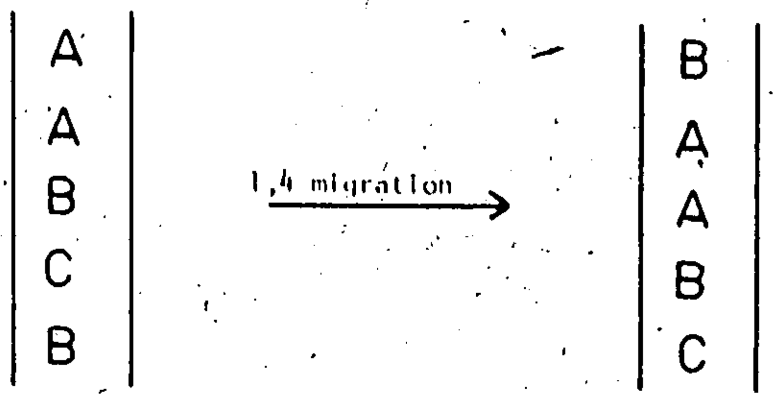
(a) Degenerate Circumambulatory Rearrangement

While the p.m.r. spectra of the photo products at -90° were consistent with the structures 63 and 64, at higher temperatures an averaging of the methyl signals of the cyclopentenyl ring was observed as shown in Fig. 11. At -80°, a significant broadening of the signals attributable to the ring methyls started to occur. At -75°, the signals corresponding to the 2, 3 and 4 methyl groups were transformed into a broad band while the signal for 1 and 5 methyl groups remained fairly sharp. The spectrum recorded at -55° showed that the signals for the five-ring methyl groups have coalesced into a broad singlet. At still higher temperatures, the resolution of the statistically averaged signal increased and at -20° it became a very sharp singlet.

The averaging process was reversible and the original spectrum was recorded when the sample was cooled to -90°. The quartets and the triplets of the ethyl group and the singlets for the methyl groups at C_6 of 63 and 64 remained sharp and non-averaged over the entire temperature range.

In order to explain the unsymmetrical collapse of signals corresponding to ring methyl groups, a careful observation must be made as to how the methyl groups are permuted among the three environments, A, B and C. This is illustrated symbolically as follows.





It will be noted that in one migration all methyl groups but one change environment. The consequence of this observation is that for 1,4 migration, the B and C resonances should collapse more rapidly since the averaging depends inversely on the lifetime of a nucleus in a given environment.[90]

A Saunders many site nmr line shape program[91] can be used to simulate the nmr line shapes of systems undergoing rearrangement with various rate constants. Knowing the line widths of the p.m.r. signals when the averaging process has been frozen out, the equilibrium populations of the various signals and the probabilities of migrations, the line shapes of the p.m.r. spectra averaging with various rate constants were calculated. Line shapes of p.m.r. spectra obtained experimentally and those simulated by the computer were compared to obtain the rate of the rearrangement.

The rate constants for the degenerate 1,4 sigmatropic shift and the temperatures at which the migration occurs are given in Table IV.

TABLE IV

Rate Constants for the Degenerate Rearrangement of 63 and 64.

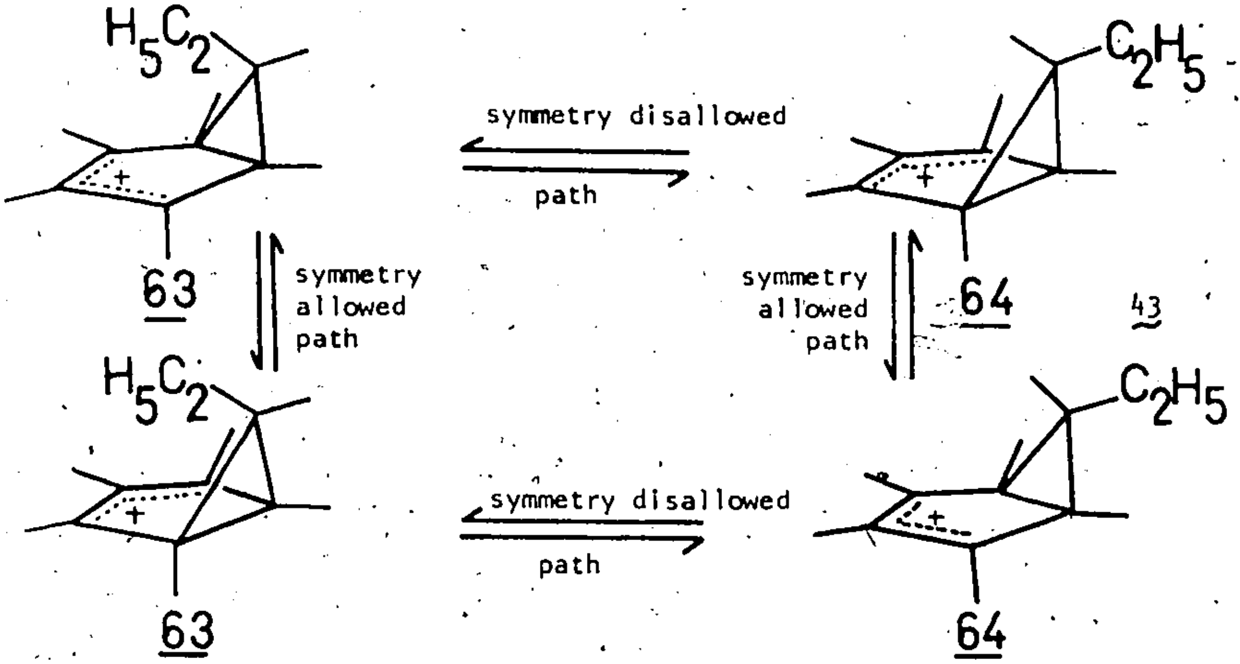
Rate Constant sec^{-1}	Temperature °C	$\Delta F^{\ddagger}$ kcals/mole
10	-90	9.6
80	-75	9.7
700	-55	9.7
7000	-30	9.8

No differences in the rate constants of migrations were detected for 63 and 64.

Stereoselectivity of Cyclopropyl Migration

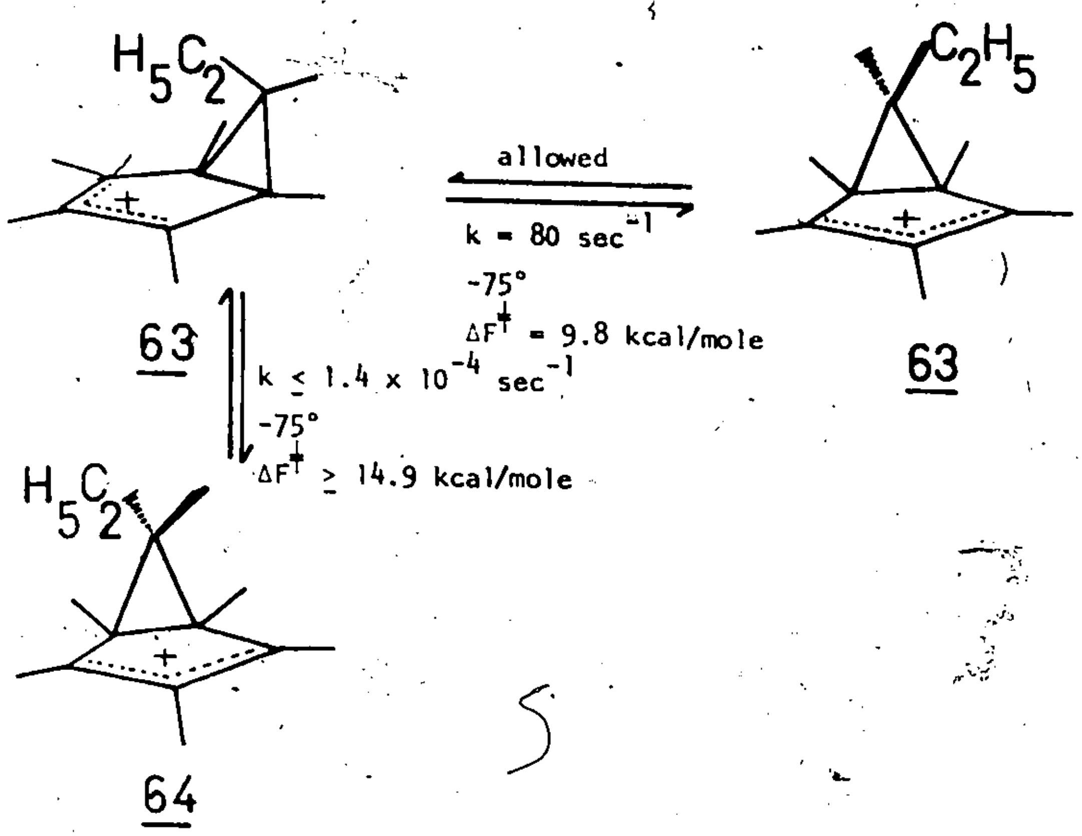
As in the cyclopropyl migrations of the *exo*-hexamethylbenzenonium ion, the degenerate circumambulatory rearrangements of 63 and 64 are highly stereoselective. The resonances of the substituents on C_6 remained sharp and showed no signs of averaging. It is clear that only the ring methyl groups were averaging. The ratio of *endo* to *exo* ethyl isomers remained constant at 2.5/1 throughout the averaging process.

In an allowed 1,4 sigmatropic migration, the orientation of the C_6 substituent would remain unchanged after each migration. If any fraction of, for example, the *endo* ethyl isomer would undergo the degenerate rearrangement by a symmetry disallowed process, the *exo* ethyl isomer would be formed. The reverse is true for the exo ethyl hexamethylbicyclo[3.1.0]hexenyl cation (64).



Individual resonances for the C_6 methyl signals were observed during the five-fold degenerate rearrangement exhibited by cations 63 and 64. Any interconversion between 63 and 64 would result in the broadening and eventual coalescence of the C_6 methyl resonances. A lower limit can be placed for orbital symmetry non-allowed interconversion of these isomers by determining the extent of line broadening during the circumambulatory rearrangement. The half widths of the C_6 methyl signals of 64 were examined and no broadening was found between -75° and -30°.

As a minimum broadening of 0.5Hz could be easily detected, using the slow exchange approximation,[90] the lower limit for the interconversion of 63 and 64 can be calculated. The free energy of activation for such an interconversion must be $\geq$ 14.9 kcal/mole.



44

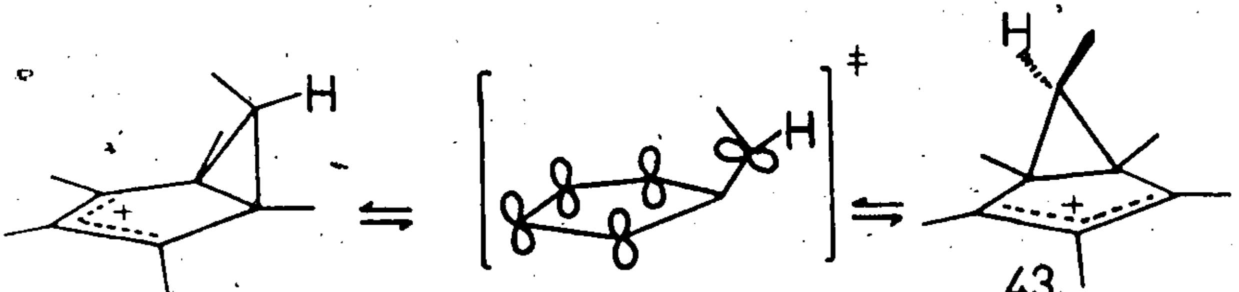
The difference between the allowed and the non-allowed rearrangement of 63 and 64 must then be equal to or greater than 14.9 - 9.8 $\geq$ 5.1 kcal/mole. In terms of the rate constants at -80°, the temperature at which the allowed 1,4 sigmatropic shift had a rate constant of 80 sec^{-1}, the rate constant for the non-allowed interconversion will be $k \leq 1.4 \times 10^{-4}\ sec^{-1}$. In short, it can be calculated that the orbital symmetry allowed suprafacial 1,4 sigmatropic shift was occurring at least 5.8×10^5 times faster than the non-allowed rearrangement.

Effects of C_6 Substituents on the Circumambulatory Rearrangement

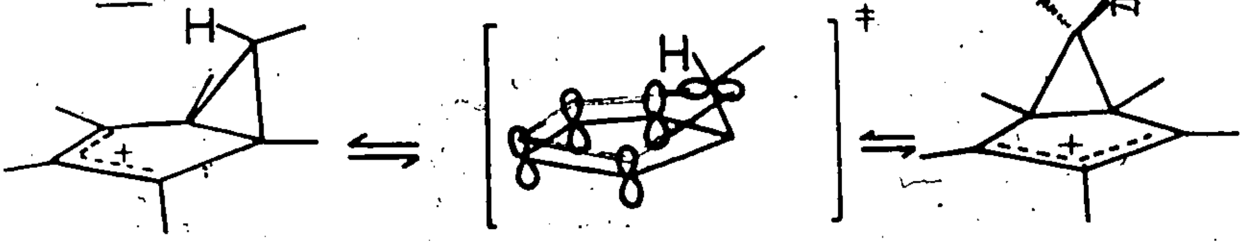
The difference in the barrier to the 1,4 sigmatropic rearrangement in heptamethylbicyclo[3.1.0]hexenyl ion (40) and 63 and 64 is 0.8 kcal/mole. This difference could be due to the abilities of methyl and ethyl groups to stabilize positive charge, the ethyl group being less effective than methyl. This is quite in agreement with the results published by Arnett,[92] Sorensen[93] and Olah[94] where those authors showed that a methyl group can stabilize positive charge better than an ethyl group.

It was also observed that both 63 and 64 displayed the same rate of line broadening during the degenerate rearrangement. There was no difference in the rate of the degenerate rearrangement depending on the orientation of the ethyl and methyl groups at C_6.

It will be recalled (page 38) that the rates of degenerate rearrangement displayed by cations 42 and 43 are different although the C_6 substituents are the same, *viz.* H and CH_3. It was suggested that the difference results from a steric factor and is not electronic in origin. In the transition state of the cyclopropyl migration, C_6 bearing the formally vacant p-orbital moves over towards C_1 and C_4 so that an effective overlap between the p orbital of C_6 and the occupied π-orbitals of the diene can occur. The exo hydrogen isomer 42 can move closer to the diene than the *endo* methyl isomer 43 for steric reasons.



43 43 45

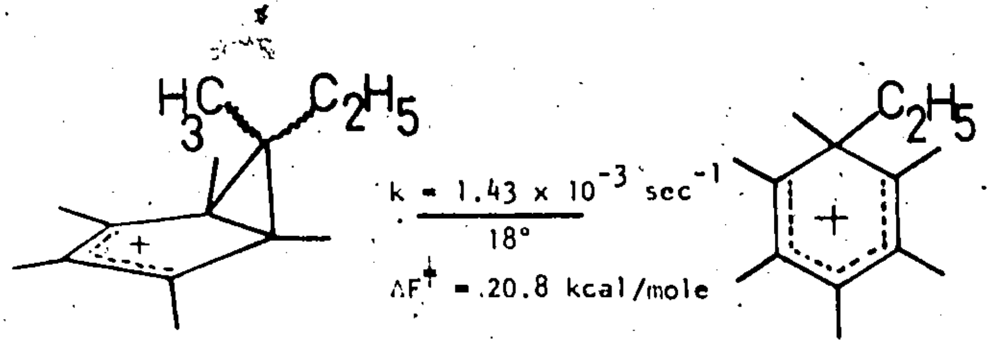


42 42 46

The results from the circumambulatory rearrangement of 63 and 64 confirm the above suggestion. The steric requirements of the ethyl and methyl groups are comparable[84] and therefore the electron deficient C_6 in the transition state will have a similar position in 63 and 64. No unexpected electronic factors seem to be operating in these systems.

(b) Thermal Ring Opening of Bicyclo[3.1.0]hexenyl Cations

When the FSO_3H solution of the cations 63 and 64 was warmed to 18°, the intensity of the averaged singlet at 2.10δ started to decrease and the signals attributable to the benzenonium ion 62 started to appear. The first order rate constant for the disappearance of the averaged signal (and hence the ring opening of bicyclic cations) was 1.43×10^{-3} sec^{-1}. At 18°, the energy barrier for the C_1-C_5 bond fission was 20.8 kcal/mole.



$$k = 1.43 \times 10^{-3}\ sec^{-1} \quad 18° \quad \Delta F^{\ddagger} = 20.8\ kcal/mole$$

63|64 62

47

The mechanism of this rearrangement can best be regarded as involving a concerted disrotatory motion which is forbidden thermally by orbital symmetry considerations.[95]

In view of the extent of interest recently shown in orbital symmetry forbidden reactions[25,26] it is important to note that activation energies associated with the rearrangements in cations are much lower than the corresponding neutral compounds. It is known that cations have longer wavelength electronic absorptions than their neutral counterparts.[96] Thus, for a charged system, there is a much lower lying excited state and configuration interaction between the HOMO and LUMO will facilitate the symmetry forbidden disrotatory ring opening.

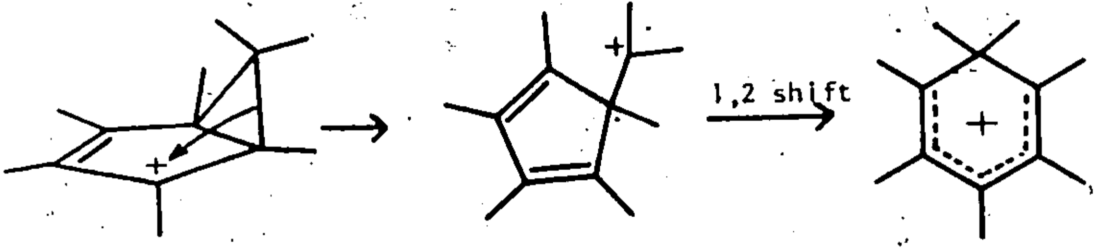
The rates of isomerization of bicyclo[3.1.0]hexenyl cations bearing different substituents on C_6 are given in the following table.

TABLE V Activation Barriers for the Irreversible Ring Opening of Bicyclo[3.1.0]hexenyl Ions

Cation	Exo	Endo	$\Delta F^{\ddagger}$ kcal/mole
<u>40</u>	CH_3	CH_3	19.8
<u>43</u>	H	CH_3	17.1
<u>42</u>	CH_3	H	21.6
<u>59</u>	H	H	17.4
<u>63</u>	CH_3	C_2H_5	20.8
<u>64</u>	C_2H_5	CH_3	20.8

The energies of activation required for the ring opening in the cations are quite comparable as long as the substituent in the <u>exo</u> position on C_6 remains the same. When the hydrogen atom at C_6 was replaced by a methyl group, the activation energy is increased by ∿ 2 kcals. The most plausible explanation for this observation is that the principal effect is steric in origin. The difference in activation energies of the ring opening between 43 and 42 can be attributed to the fact that only the hydrogen atom has to pass through the plane of C_1C_5 methyl groups on the cyclopentenyl ring in 43, whereas in 42 the methyl group has to pass through the same sterically congested plane.

Recently, it has been suggested[97] that the ring opening of these bicyclic cations involves the breakage of the C_5-C_6 bond to generate the cyclopentadienyl methyl cation 65 which subsequently undergoes a facile 1,2 shift to give the benzenonium ions. This is exemplified for the heptamethylbicyclo[3.1.0]hexenyl cation (40).



40 65 34 48

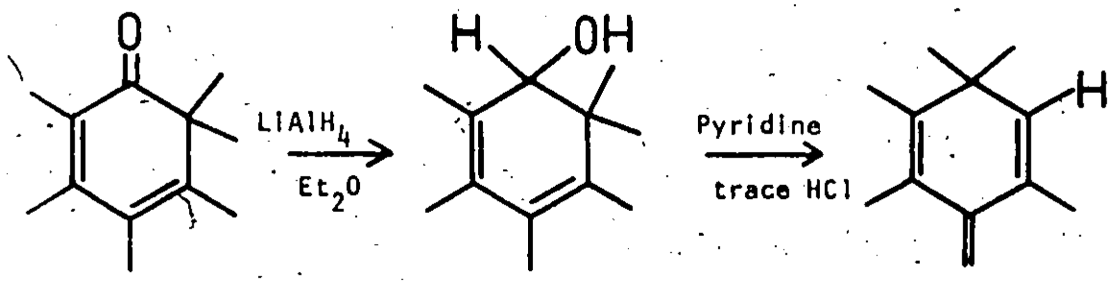
However, this mechanism can be rejected on the grounds that the alkyl substituents on C_6 would be expected to increase the stability of the cyclopentadienyl-methyl cation 65 leading to an increase in the rate of isomerization. The experimental observations contradict this proposed mechanism.

Perhaps one of the logical approaches to confirm this concerted yet symmetry forbidden rearrangement to the benzenonium ions is to study the rates of thermal cyclopropyl ring opening in bicyclo[3.1.0]-hexenyl cations where the C_1 and/or C_5 methyl substituents have been replaced by hydrogen atoms. Steric congestion will be less as compared to 40 and if the symmetry forbidden disrotatary motion takes place, its ease should be reflected in the rate of the thermal ring opening. It is for this reason that the synthesis of the 1,2,3,4,6,6 hexamethyl bicyclo[3.1.0]hexenyl cation was undertaken.

4. Synthesis of 1,2,3,4,6,6-Hexamethylbicyclo[3.1.0]hexenyl Cation

(a) Synthesis of 1,2,4,6,6 Pentamethyl-3-methylene cyclohexa-1,4-diene (67)

The reduction of hexamethylcyclohexa-2,4-dienone[80] (60) by a suitable reducing reagent would result in a secondary alcohol 66 which could eliminate water to give the triene 67.



60 66 67

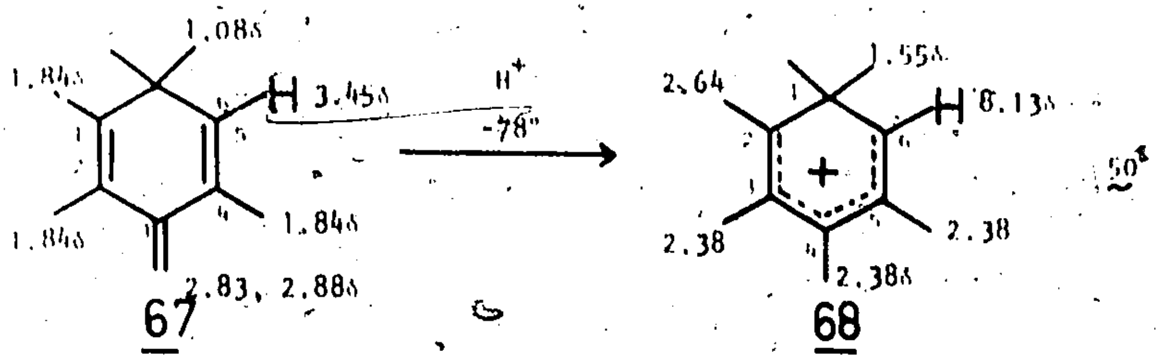
49

Sodium borohydride is a frequently used reagent for the reduction of αβ unsaturated ketones. However, in this case it did not give satisfactory results. Lithium aluminum hydride proved to be a better and a more efficient reducing reagent. The double bonds were not affected and the reaction was very clean.

The resulting secondary alcohol 66 was treated with pyridine containing a trace of hydrochloric acid to give 1,2,4,6,6-pentamethyl-3-methylenecyclohexa-1,4-diene[88] (67).

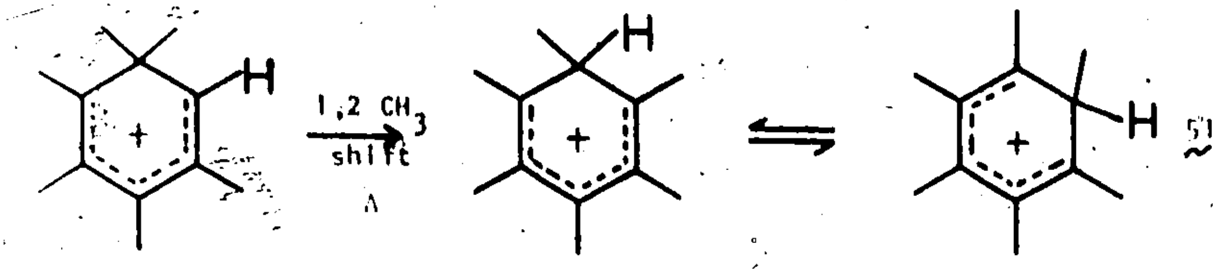
(b) Protonation of 1,2,4,6,6-Pentamethyl-3-methylenecyclohexa-1,4-diene

Proton addition to the exocyclic double bond of 67 can be achieved by the dissolution of 67 in HFSO$_3$ at -78°.



The p.m.r. spectrum of protonated 67 is consistent with 68. The vinyl proton resonance appeared at 8.13δ ppm. There were only six methyl resonances and these appeared at the positions expected for such a structure. Protonation of 67 was very clean and no other cations were detected in its p.m.r. spectrum.

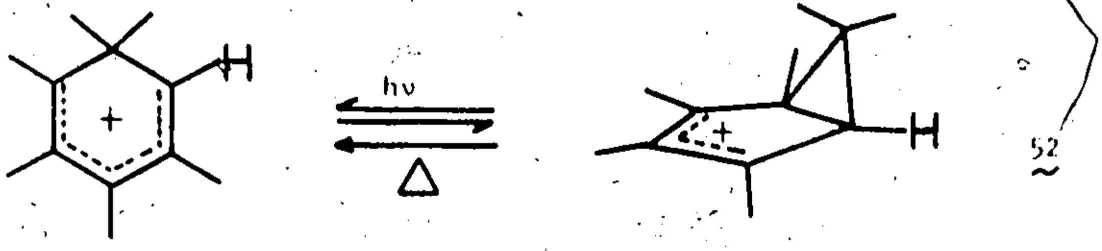
When the solution of 68 was warmed to -70°, a change in the p.m.r. spectrum was noted. The signals for the methyl groups coalesced and appeared as a broad singlet at -60°. Upon cooling to 75°, the p.m.r. spectrum recorded was consistent with that of hexamethylbenzenonium ion (48). This irreversible thermal isomerization serves as a proof for the structure of 68. A thermal 1,2 methyl migration in 68 should generate the more stable hexamethylbenzenonium ion (48) which would undergo a facile 1,2 hydride shift at temperatures higher than -70°.[98]



68 48 48

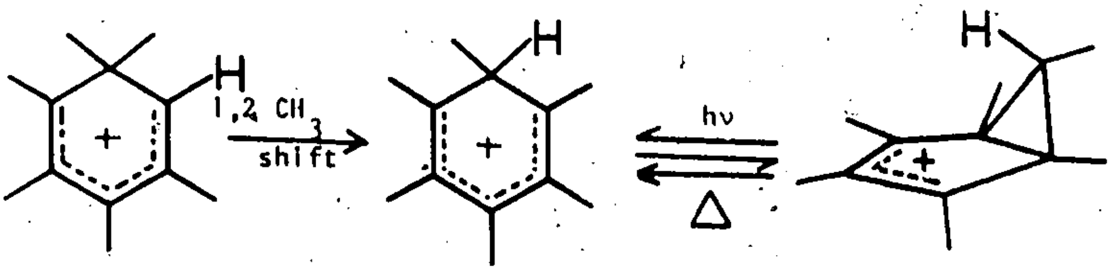
(c) U.V. Irradiation of 1,1,2,3,4,5-Hexamethylbenzenonium Ion (68)

It was expected that the irradiation of 68 would result in the formation of the 1,2,3,4,6,6-hexamethylbicyclo 3.1.0 hexenyl cation (69).



68 69

The $HFSO_3$ solution of 68 was irradiated for 2 hours at [illegible]°C. The p.m.r. spectrum was identical with that of endo hexamethylbicyclo[3.1.0]hexenyl cation (43), and hexamethylbenzenonium cation (48) and not that of the expected cation 69. Failure of 68 to isomerize to 69 is possibly due to a facile 1,2 methyl shift prior to photoisomerization. The intermediate cation 48 would then undergo a photochemical ring closure to 43 .



68 48 43 53

Alternatively, 69 may not be stable under the conditions where 68 was irradiated. In the light of results reported by Breslow et al.,[99] the difference between the polarities of the C_1 methyl and C_5 hydrogen might contribute towards the facile breaking of the C_1-C_5 bond in 69. The 1,2,3,5-tetramethylbicyclo[3.1.0]hexenyl cation[100] is another example where a similar effect could have contributed towards the rate of ring opening to the corresponding benzenonium ion.

5. Preparation of Systems with an Oxygen Substituent at C_6

As an oxygen atom is very effective at stabilizing a positive charge,[101] it was decided to attempt the preparation of the bicyclo[3.1.0]-hexenyl cations with a suitable oxygen group on C_6.

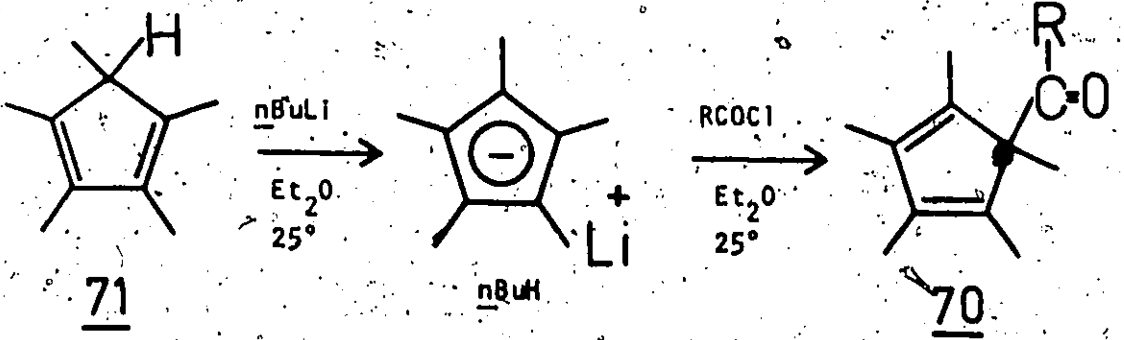
(a) Synthesis of 5-Acyl-1,2,3,4,5-Pentamethylcyclopentadienes

5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene 70a has been prepared previously[102] by the oxidation and subsequent rearrangement of hexamethyldewerbenzene. The preparation of ethyl-1,2,3,4,5-pentamethylcyclopentadiene-5-carboxylate (72) was reported by de Vries.[103] In this work, a general method for the preparation of 5-acyl-1,2,3,4,5-

TABLE VI P.m.r. Data for 5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes

Compound	Cyclopentadiene Ring Methyls			Other
	1,4	2,3	5	
70a	1.64	1.80	1.00	1.50
70b	1.63	1.80	1.02	0.78(t), 1.79(q) J = 7.5 Hz
70c	1.64	1.82	1.15	6.63-7.74, 3.76
70d	1.63	1.81	1.14	6.62-7.56, 3.98(q) 1.23(t), J = 7.5 Hz
70e	1.65	1.82	1.18	6.95-7.51, 2.28
70f	1.65	1.82	1.18	7.16-7.52, 1.25
70g	1.66	1.82	1.20	7.14-7.60
70h	1.63	1.79	1.17	7.12-7.47
70i	1.64	1.79	1.20	7.49-7.51

pentamethylcyclopentadienes was developed. Pentamethylcyclopentadiene[103] (71) reacts readily with strong bases such as nBuLi to give lithium pentamethylcyclopentadienide.[104] This organometallic compound was allowed to react with acyl chlorides to produce the corresponding 5-acyl-1,2,3,4,5-pentamethylcyclopentadienes (70) in good yields.



54

a, R = CH_3; b, R = C_2H_5; c, R = $pCH_3OC_6H_4$; d, R = $pC_2H_5OC_6H_4$; e, R = $pCH_3C_6H_4$; f, R = $ptBuC_6H_4$; g, R = C_6H_5; h, R = $pClC_6H_4$; i, R = $pCF_3C_6H_4$.

(b) Protonation of 5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene

5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene (70a) was protonated by extraction from methylene chloride solution into fluorosulfuric acid at -78°. The low temperature p.m.r. of the protonated ketone 73 is shown in Fig. 12. The complexity of p.m.r. resonances indicated that some reaction(s) in addition to oxygen protonation had occurred. Quenching the solution at -78° with diethyl ether/$NaHCO_3$ followed by water resulted in a 98% recovery of organic material. V.p.c. analysis showed that the product was $\geq$ 95% pure 70a. Clearly no rearrangement can have taken place upon the protonation of 70a at -78°.

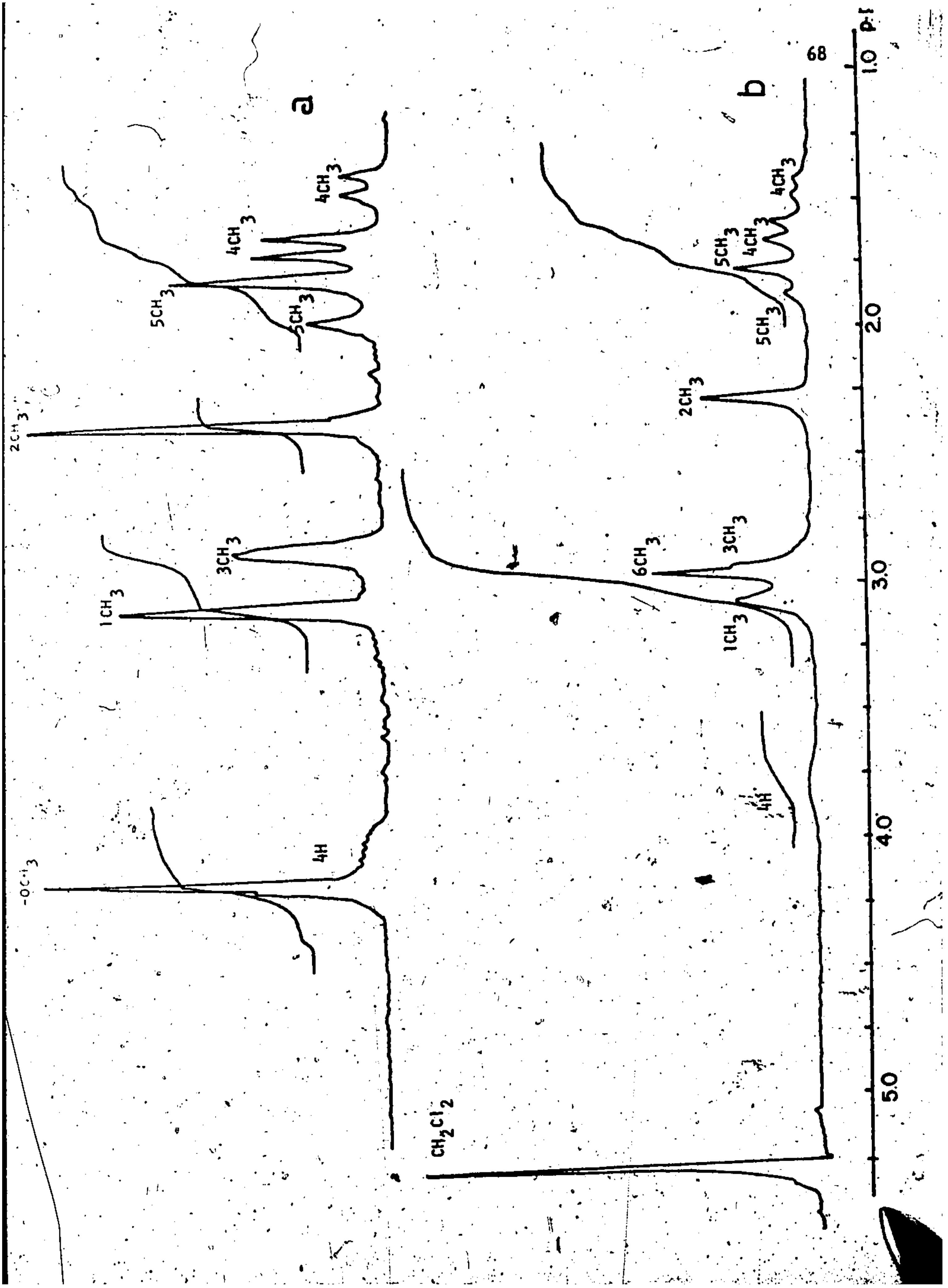
Figure 12 P.m.r. Spectra of 5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes in $HFSO_3$.

(a) R = $\underline{p}CH_3OC_6H_4$ (500 Hz sweep width)

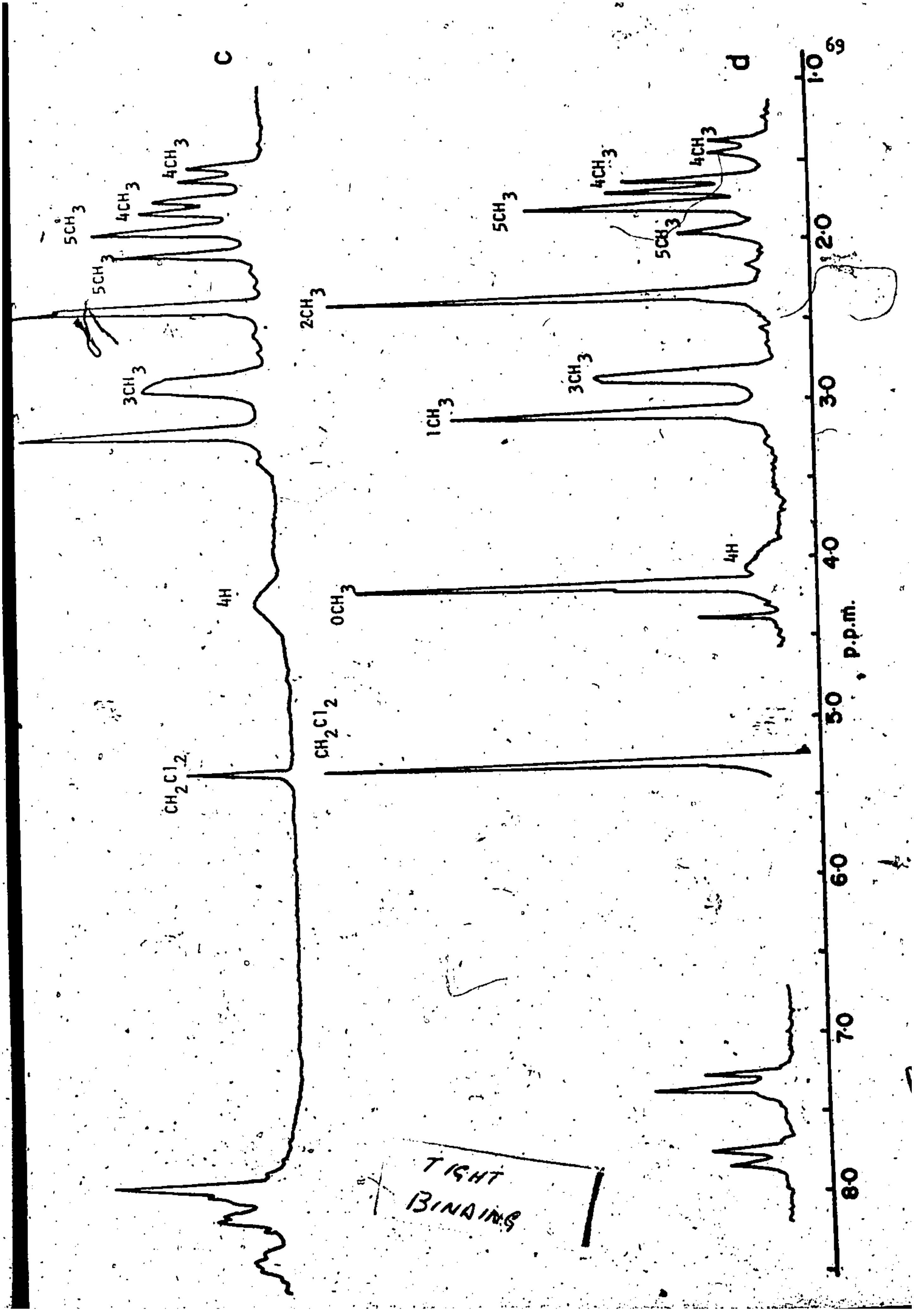
(b) R = CH_3 (500 Hz sweep width)

(c) R = C_6H_4 (1000 Hz sweep width)

(d) R = p-$CH_3OC_6H_4$ (1000 Hz sweep width)



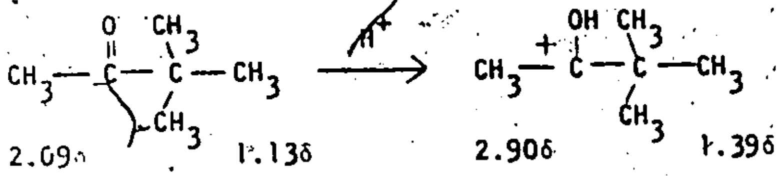
a
b
-OCH3
4H
1CH3
3CH3
2CH3
5CH3
5CH3
4CH3
4CH3
CH2Cl2
4H
1CH3
6CH3
3CH3
2CH3
5CH3
5CH3
4CH3
4CH3
68
5.0
4.0
3.0
2.0
1.0 p.p.m.



TIGHT BINDING

The first step in the analysis of the p.m.r. spectra of <u>73</u> was the identification of the C_6 methyl signal. This was done by the observation of the p.m.r. spectrum of related ketones, particularly 5-p-methoxybenzoyl-1,2,3,4,5-pentamethylcyclopentadiene (70c) in $HFSO_3$, Fig. 12b. It was found that the signal at 2.97 δ was absent in Fig. 12a, in addition, a signal at 4.19 δ ppm, attributable to the para methoxy group was present. It is clear that the singlet at 2.97 δ must belong to the C_6 methyl in protonated <u>70a</u>.

The position of the chemical shift of the C_6 methyl is quite consistent with a structure where protonation has occurred on the oxygen atom of <u>70a</u>. The structurally similar pinacolone (75) is a good model for the chemical shift of C_6 methyl in <u>70a</u>. Upon protonation, the resonance for the αCH_3 of pinacolone appeared at 2.90 δ.



55

<u>74</u> <u>75</u>

Model systems for the atomatic ketones were also chosen and protonated. The chemical shifts of these model ketones in $HFSO_3$ are given in the following table. This chemical shift data strongly supports the suggestion that protonation on the oxygen atom of <u>70a</u> and its related ketones has occurred.

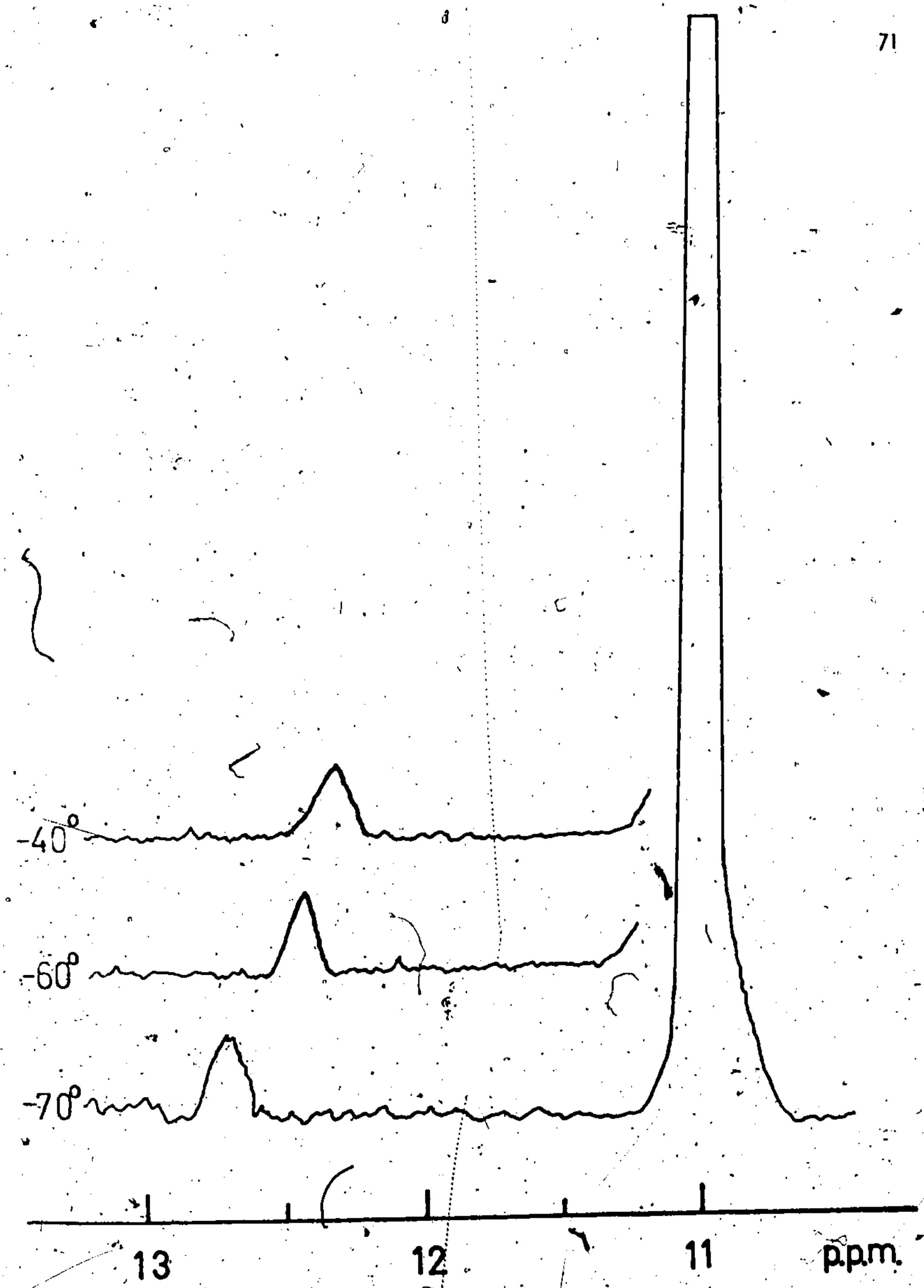


Figure 13 P.m.r. spectra of the Carbonyl Hydrogen in diprotonated 73c

TABLE VII

P.m.r. Data for Protonated 5-Benzoyl-1,2,3,4,5-pentamethylcyclopentadiene and their model compounds

Ketone	Chemical Shifts	
	Aromatic	OCH_3
Acetophenone	7.23-7.80	
Acetophenone protonated	7.71-8.64	
5-benzoyl-1,2,3,4,5-pentamethyl cyclopentadiene <u>70g</u>	7.14-7.60	
<u>70g</u> protonated	7.79-8.17	
p-methoxy-acetophenone	6.79-7.91	3.86
p-methoxy-acetophenone protonated	7.18-8.57	4.12
5-p-methoxy benzoyl-1,2,3,4,5-pentamethylcyclopentadiene <u>70c</u>	6.63-7.74	3.76
<u>70c</u> protonated	7.27-7.84	4.19

Further, an -OH resonance signal for the protonated <u>70c</u> was observed at 12.70 ppm. Similarly its p-ethoxy analogue <u>70d</u> in $HFSO_3$ displayed an -OH resonance at 12.68δ. The identification of these OH resonances was made by observing averaging between the solvent signal and the -OH resonance upon warming, Fig. 13.

The -OH signal was not observed for the protonated <u>70a</u>. The observation of the -OH signal[105-108] is possible only when the averaging caused by protonation and deprotonation is sufficiently slow. The less basic the ketone, the more drastic the conditions must be to be able to observe the -OH signal.[109]

The spectrum of the rest of the molecule is consistent with the protonated <u>70a</u> and was very similar to that of protonated pentamethylcyclopentadiene (76)[110,111] (Table VIII) where two isomers are always observed. It would appear that the protonation is also occurring

TABLE VIII Chemical Shifts of Pentamethylcyclopentadiene and its Related Compounds in $HFSO_3$ [a]

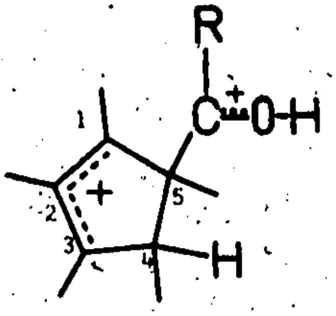
Cation	Chemical Shifts[b] $1CH_3$	$2CH_3$	$3CH_3$	$4CH_3$	$5CH_3$	4H	Others
76	2.89	2.22	2.89	1.50 d	1.50 d	3.56 m	
76a	2.89	2.22	2.89	1.43 d	1.43 d	3.56 m	
73a	3.07	2.29	2.94	1.63 d 1.46 d	1.77 d 1.87 d	3.79	
73b	3.06	2.27	2.93	1.59 d 1.16 d	1.75 1.85	3.74	2.98 q 1.32 t
73g	3.19	2.42	2.89	1.57 d 1.76 d	2.07 1.92	4.27	7.79-8.17
73c	3.12	2.40	2.88	1.68 d 1.45 d	1.83 1.98	4.10	4.19 7.27-7.84
73c D	3.13	2.42	2.94	1.74 1.49	1.89 2.03		4.19 7.27-7.84

---

[a] All chemical shifts measured from internal CH_2Cl_2 resonance signal taken at 5.30 δ.

[b] d = doublet, t = triplet, q = quartet; all coupling constants = 7.0 Hz.

upon the five-membered ring of the ketones giving rise to the structure of the type shown.



73

a, R = CH_3; b, R = C_2H_5; c, R = $pCH_3OC_6H_4$; d, R = C_6H_5

From the p.m.r. spectra of protonated ketones 73, it would appear that two isomers are being formed when ketones are protonated. The C_4 methyl groups appeared as a pair of doublets (J = 7.0 Hz) and the hydrogens bonded to C_6 appeared as broad signals. Double irradiation at the position of the C_4 hydrogen caused the C_4 doublets to collapse into singlets.

Replacement of the C_4 hydrogen with a deuterium atom by the use of deuterated fluorosulfuric acid caused the C_4 methyl resonances in both isomers to appear as singlets. Apart from the C_4 methyl and the loss of C_4-H signal, the p.m.r. spectrum of the ketone in $DFSO_3$ was identical with that of the corresponding protonated ketone.

Except for the resonance signals of the R group at C_6, the same pattern of p.m.r. spectra was observed for all the ketones in $HFSO_3$ [R = CH_3, C_2H_5, C_6H_5 and $pCH_3C_6H_4$-]. It must be stressed that in the spectra of 73c both the OH signal and the ring proton could be observed at the same time in the same spectrum. This means that the protonation of 70c results in the formation of a dication.[112-114]

As an alternative to p.m.r. spectroscopy in search for the evidence for carbonyl as well as dienyl protonation the uv spectra of these systems was examined. Electronic absorption spectrum of protonated ketones, particularly aromatic ketones, are well-established.[115] The existence of the protonated ketonic function as well as the dienylic cations in acidic solutions of 5-acyl-1,2,3,4,5-pentamethylcyclopentadienes was established by low temperature uv spectroscopy.

(c) U.V. Spectrum of 5-p-Methoxybenzoyl-1,2,3,4,5-pentamethylcyclopentadiene

5-p-Methoxybenzoyl-1,2,3,4,5-pentamethylcyclopentadiene (70c) was dissolved in $HFSO_3$ at -78° and its uv spectrum was taken at -50°C. Three intense absorption bands were recorded at 223 nm (log ε 4.84), 300 nm (log ε 4.70) and 375 nm (log ε 4.72). In contrast, in the unprotonated ketone only one strong band was observed at λ_{max} 268 nm and a weak $n-\pi^*$ band at 320 nm. The bands with the maxima at 223 nm and 375 nm can be attributed to the aromatic ring conjugated to the protonated carbonyl group. This conclusion was reached by the comparison of the uv spectrum of p-methoxy acetophenone in H_2SO_4. The latter spectrum contains two strong bands at λ_{max} 225 nm (log ε 4.00) and λ_{max} 336 nm (log ε 3.49).[116]

The absorption maximum at λ_{max} 300 nm must then arise from the electronic transition from cyclopentenyl part of the protonated species. A large number of cyclopentenyl, cyclohexenyl and other acyclic allylic cations have been extensively studied by Deno.[117] The structures and properties have been investigated thoroughly by means of p.m.r., ultraviolet spectroscopy and recovery experiments by various authors.[110,111,117]

A model system chosen for the allylic cation resulting from the protonation of ketone 70 is the hexamethylcyclopentenyl cation (77).[96] This shows a strong absorption at 301 nm which is directly comparable to that observed in 73c. Thus, both the p.m.r. and uv spectra of the $HFSO_3$ solutions of the 5-acylpentamethylcyclopentadienes are completely consistent with the formation of the dications of the structure 73.

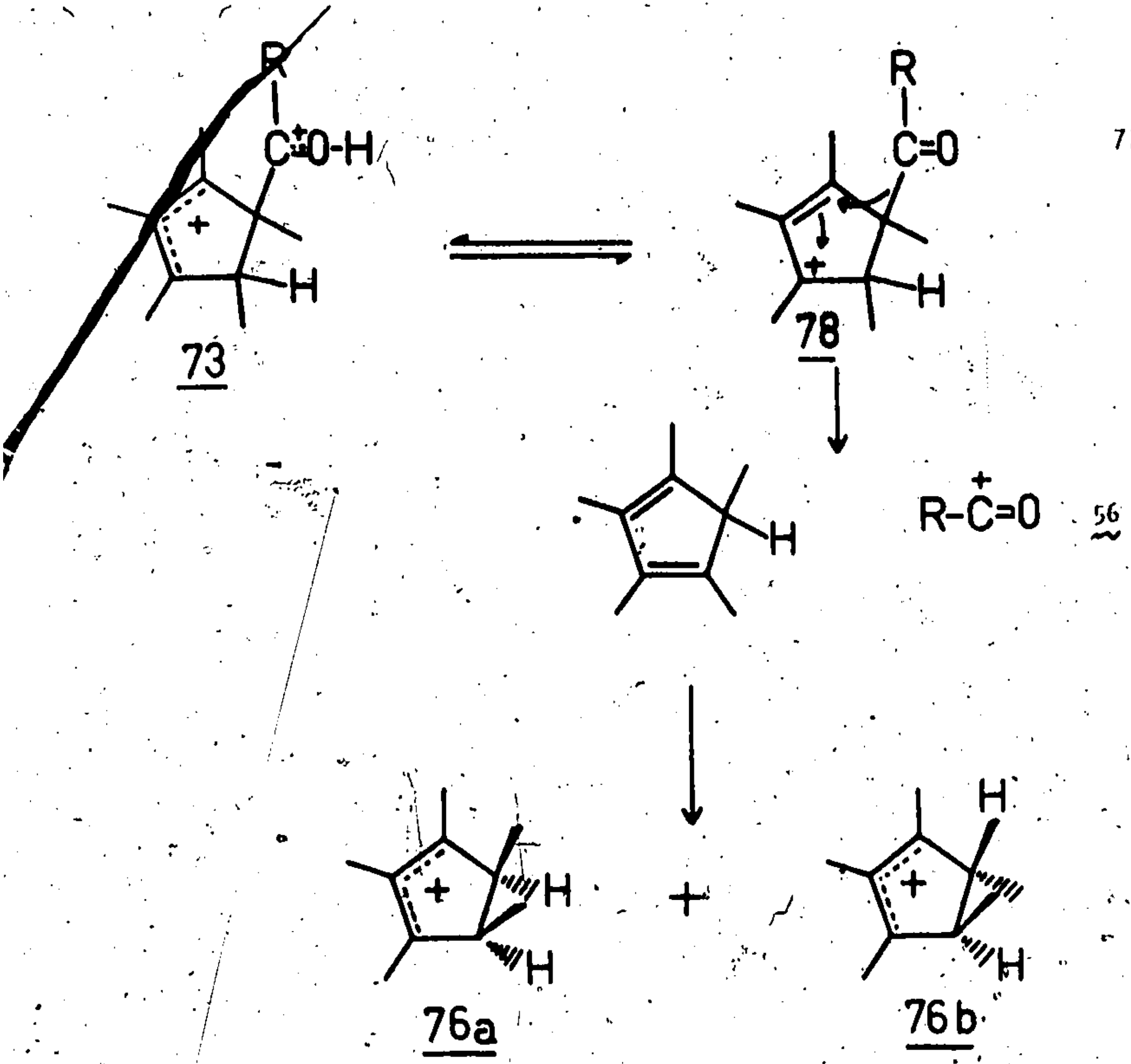
(d) Thermal Rearrangement of Diprotonated 5-Acyl-1,2,3,4,5-Pentamethylcyclopentadienes

The diprotonated 5-acyl-pentamethylcyclopentadienes were found to be thermally unstable. At temperatures above 0°, an irreversible rearrangement took place to give a product with p.m.r. spectrum identical with that of protonated pentamethylcyclopentadiene.[110,111] Quenching the solution in ether/HCO_3^-/H_2O resulted in the nearly quantitative recovery of pentamethylcyclopentadiene (71). The temperature at which the rearrangement occurred with a rate constant of ca. 1 x 10^{-3} sec^{-1} was dependent upon the nature of R (Table IX). A possible mechanism for this reaction is shown.

TABLE IX

Temperatures for the Thermal Fragmentation of the Dications.

Cation	Temp. °C
73a	15
73b	15
73c	60



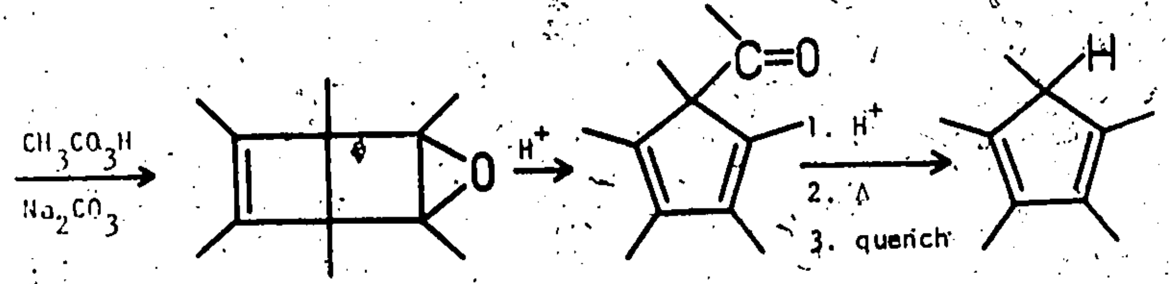
The cleavage of protonated carbonyl functional groups into an acylium ion has been reported for acids and esters in oleum,[118] $HFSO_3$-SbF_5,[119] and HF-BF_3[120] acid systems.

In the course of the thermal rearrangements of diprotonated 5-acyl pentamethylcyclopentadienes, the presence of the corresponding acylium ion was not detected at any stage. A cis/trans isomer ratio of 2,5/1 was observed for the protonated pentamethylcyclopentadiene.[110,111] This is in accord with the values reported by Brouwer[111] who reported that the preferential cis protonation of 71 took place.

A possible mechanism for this fragmentation reaction involves deprotonation and reprotonation. As such, the acidities of the solvents should affect its rate by altering the amount of the monoprotonated species 78. It was observed that when R = CH_3, $t_{\frac{1}{2}}$ of the cleavage reaction decreased significantly as the solvent was changed from $HFSO_3$ (30 mins) to 97% H_2SO_4 (15 mins) and to 80% H_2SO_4 (5 min) at 25°. In all cases a near quantitative recovery of 71 was achieved.

One result of this rearrangement is a convenient synthesis of pentamethylcyclopentadiene (71). The synthetic route currently being used, which was reported by de Vries,[103] involves a six step procedure that is long and tedious. It also involves an oxidation with active manganese dioxide[121] which renders a large scale preparation difficult. Hexamethyldewarbenzene (79) which is available commercially can be oxidized in acidic solution to give 5-acetyl pentamethylcyclopentadiene[101] (70a). Protonation and subsequent rearrangement of this ketone results in the formation of 71.

79



70

71

57

It is evident that the reaction of 70 with Bronsted Acids was a poor choice as a synthetic method to generate bicyclo[3.1.0]hexenyl cations with C_6 oxygen substituents. An ideal acid would be bonded to the carbonyl group without undergoing electrophilic attack on the double bonds. Lewis acids satisfy this requirement and the possibility of introducing an oxygen substituent on C_6 by the formation of Lewis acid-ketone complexes was further investigated.

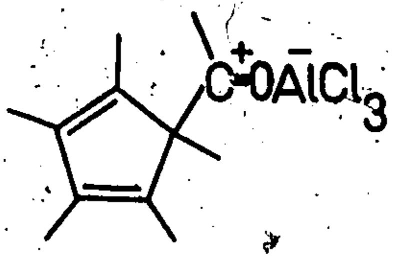
PART II 6. FORMATION OF ALUMINUM CHLORIDE-5-ACETYL-1,2,3,4,5-PENTAMETHYLCYCLOPENTADIENE COMPLEXES

5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene (70a) reacts with anhydrous Al_2Cl_6 in dry methylene chloride[122] to give a complex, as evidenced from the p.m.r. spectra shown in Fig. 14. The complex was made by adding a solution of 70a in methylene chloride to an equivalent amount of Al_2Cl_6 in CH_2Cl_2 kept at -78°. Stirring the solution at -78° resulted in a rapid formation of the complex. The addition of Al_2Cl_6 in methylene chloride to the ketone solution (i.e., the reverse addition) lead to the same complex.

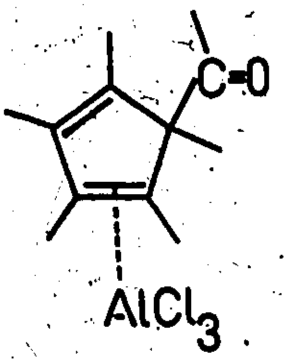
The low temperature p.m.r. spectra of the complex was significantly different from that of 70a. A four line p.m.r. spectrum was still recorded for the complex. However, one of the resonance signals, with relative area 1, moved downfield compared to the signals with relative intensity 2. The complex was stable at room temperature, it not undergoing any decomposition.

Quenching the CH_2Cl_2 solution of the complex in ice/water mixture and the subsequent extraction with ether resulted in a complete recovery of 70a. No other side products were detected when the sample was analysed on vpc. It was then concluded that no rearrangement in the carbon skeleton occurred due to the formation of the complex from 70a.

It is known that Lewis acids such as Al_2Cl_6 can form two types of complex, σ [123,124,125] and π complexes.[126,127] In the case of 70a, both types of complexes could be formed. Al_2Cl_6 could either react with a free electron pair from the oxygen atom to give a structure such as 80a, or form a charge transfer type π complex with the diene 81.

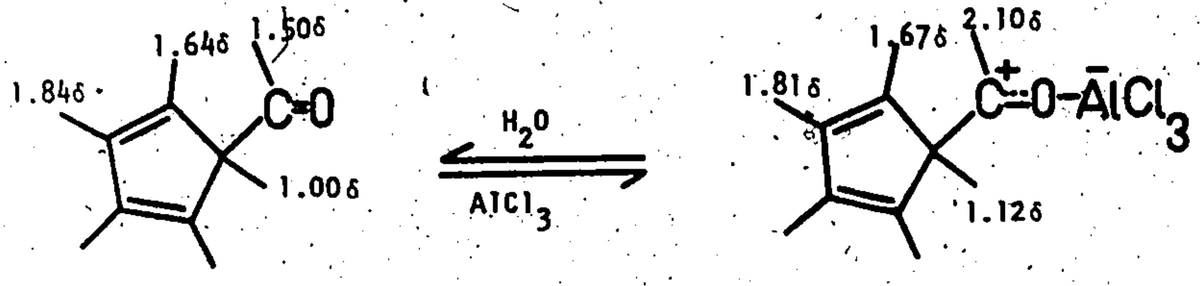


80a



81a

Several techniques[125,129] have been used in the investigation of the nature of ketone-Lewis acid adducts. One of the best methods to differentiate between the two structure is infrared spectroscopy.[130-132] The ir spectrum of the ketone 70a showed that there is a band attributable to the C-O stretching frequency at 1695 cm^{-1}. Upon complexation, the band at 1695 cm^{-1} disappeared and a new band was observed at 1570 cm^{-1}. No change in the stretching frequencies of the C=C bonds in the diene were observed. Clearly Al_2Cl_6 was complexed to the carbonyl oxygen and the structure can be considered as best represented at 80a.



70a   80a   58

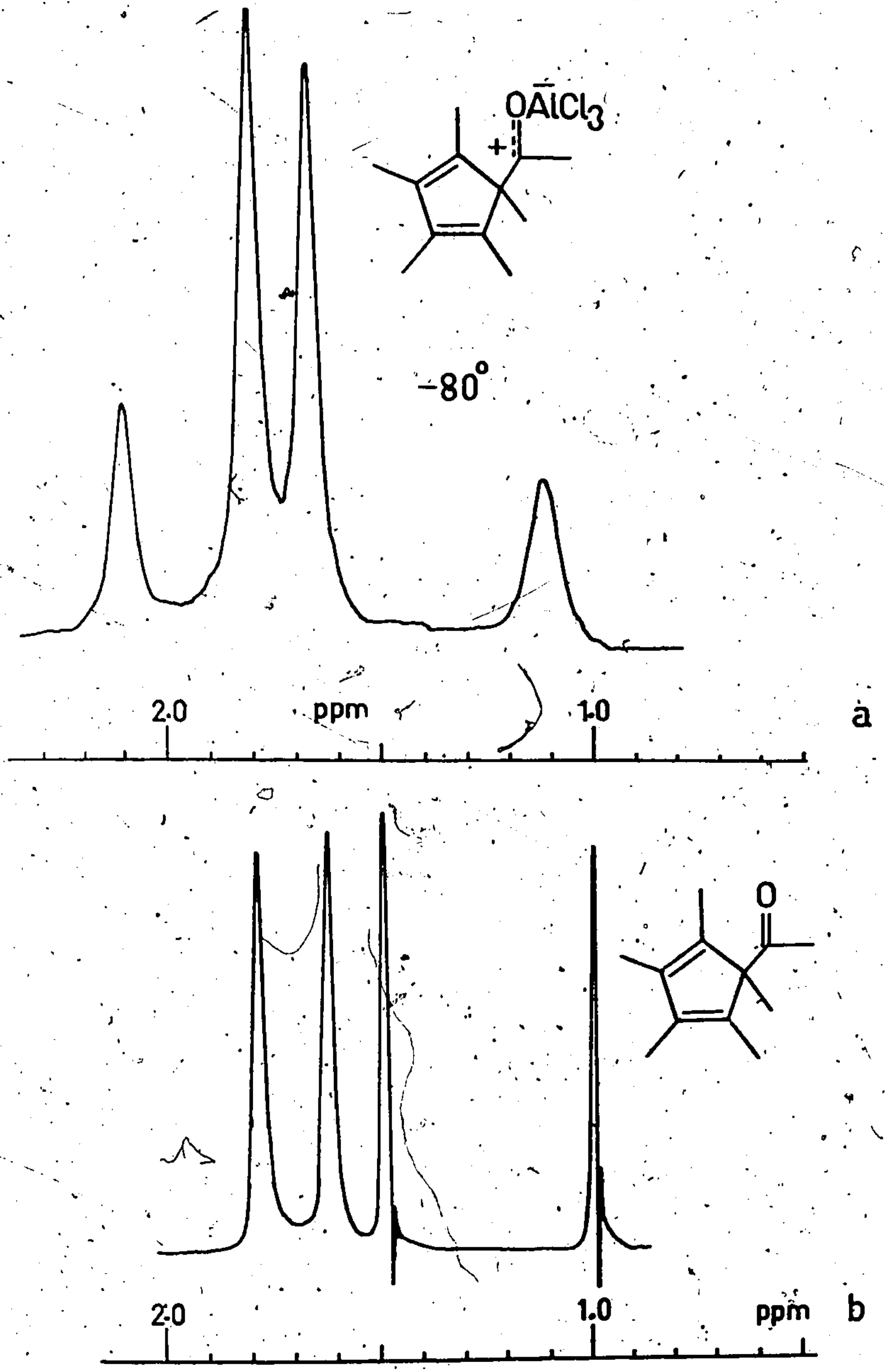


Figure 14 P.m.r. spectrum of (a) $AlCl_3$ complexed and (b) uncomplexed 5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene.

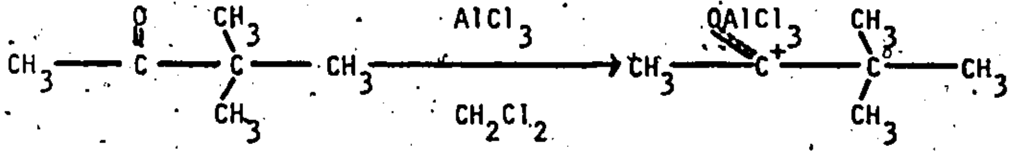
TABLE X P.m.r. Data for $AlCl_3$-complexed-5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes

Compound	Temp. °C	Cyclopentadiene Ring Methyls 1,4	2,3	5	Av[a] δ	Other
80a	-80	1.67	1.81	1.12	1.66	2.10
80b	-90	1.67	1.81	1.16	1.69	1.00(t), 2.28(q) J = 7.5 Hz
83	-10	1.71	1.71	1.28	--	1.33(t), 4.45(q) J = 7.5 Hz

[a] Position of averaged methyl resonances at higher temperature

In order to identify the resonances in the p.m.r. spectra of 80a, 5-propionyl-1,2,3,4,5-pentamethylcyclopentadiene (70b) was complexed with Al_2Cl_6 in CH_2Cl_2 at -78°. The low temperature p.m.r. spectrum of $AlCl_3$-complexed ethyl ketone (80b). Table X showed that the quartet and the methyl triplet of the C_2H_5 group appeared at 2.28δ and 1.00δ, respectively. By the comparison of the p.m.r. spectra of 80a and 80b it was concluded that the resonance signal at 2.10δ in the p.m.r. spectrum of 80a must belong to the C_6 methyl group, and the singlet at 1.12δ corresponds to the C_5 methyl.

The chemical shifts of the methyl resonances of $AlCl_3$ complexed 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene are consistent with the structure 80a, where Al_2Cl_6 is complexed to the carbonyl group. A large fraction of the positive charge resides on C_6, which is reflected in the chemical shift of the C_6 methyl group. An estimate of the magnitude of this deshielding when a complex has been formed between Al_2Cl_6 and a carbonyl oxygen can be obtained from the p.m.r. parameters of the sterically similar pinacolone (74) and its $AlCl_3$ complex (82).



$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow[CH_2Cl_2]{AlCl_3} CH_3-\overset{OAlCl_3}{C^+}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \qquad (59)$$

2.09δ 1.13δ 2.67δ 1.27δ

74 82

Δδ αCH_3 = 0.58 ppm

Δδ βCH_3 = 0.14 ppm

It will be noted that the extent of the deshielding suffered by the C_6 methyl of 80a is the same as that of the αCH_3 in pinacolone. Also, the downfield shift of C_5 methyl resonance is comparable to that of the βCH_3 in 82a.

The singlets at 1.67 and 1.81δ ppm correspond to the methyl groups on the sp^2 hybridized carbon atoms of the cyclopentadiene ring. The assignment of the ring methyls on the uncomplexed ketone 70a has been made.[102] The signal at 1.67δ was assigned to its C_1 and C_4 methyl groups and that at 1.81δ to the methyl groups on C_2 and C_3. Further evidence of this assignment has recently been published.[133]

7. Degenerate Rearrangement of the $AlCl_3$-complexed-5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes

The p.m.r. spectrum of 80a at -80° was consistent with the structure shown in equation 58.

As the temperature of the sample was raised, the signals for the methyl groups on the five-membered ring broadened, coalesced at -40°, and above that temperature appeared as a singlet at 1.66δ, Fig. 15. Upon cooling the sample again to -80°, the original three-line spectrum for the ring methyls was recorded. During the averaging process, the resonance signal attributable to the C_6 methyl group remained sharp and except for a viscosity effect, showed no sign of line broadening.

From the behaviour of the temperature dependent p.m.r. spectra, it was concluded that a degenerate rearrangement was occurring. The only possibility for this rearrangement is that $AlCl_3$ complexed ketone group, with its attendent substituent [C_6 methyl] was migrating with respect to the five-membered ring. A similar behaviour is exhibited by σ bonded cyclopentadienemetal compounds.[43,46,134]

As shown in Fig. 15, the resonance attributable to the methyl groups at C_2 and C_3 collapsed at half the rate of the other signals. This shows that the migration of C_6 was occurring with a definite sequence. A random migration would result in a symmetric collapse of the ring methyl resonances.[135] For a thermally induced sigmatropic shift in the present ring system, the migration must either be 1,3 or 1,5.[2] A differentiation between the two modes of rearrangement can be made from the observation of the pattern of collapse of the ring methyl signals. A single 1,5 migration of C_6 in 30a would result in the interchange of the ring methyls as shown below.

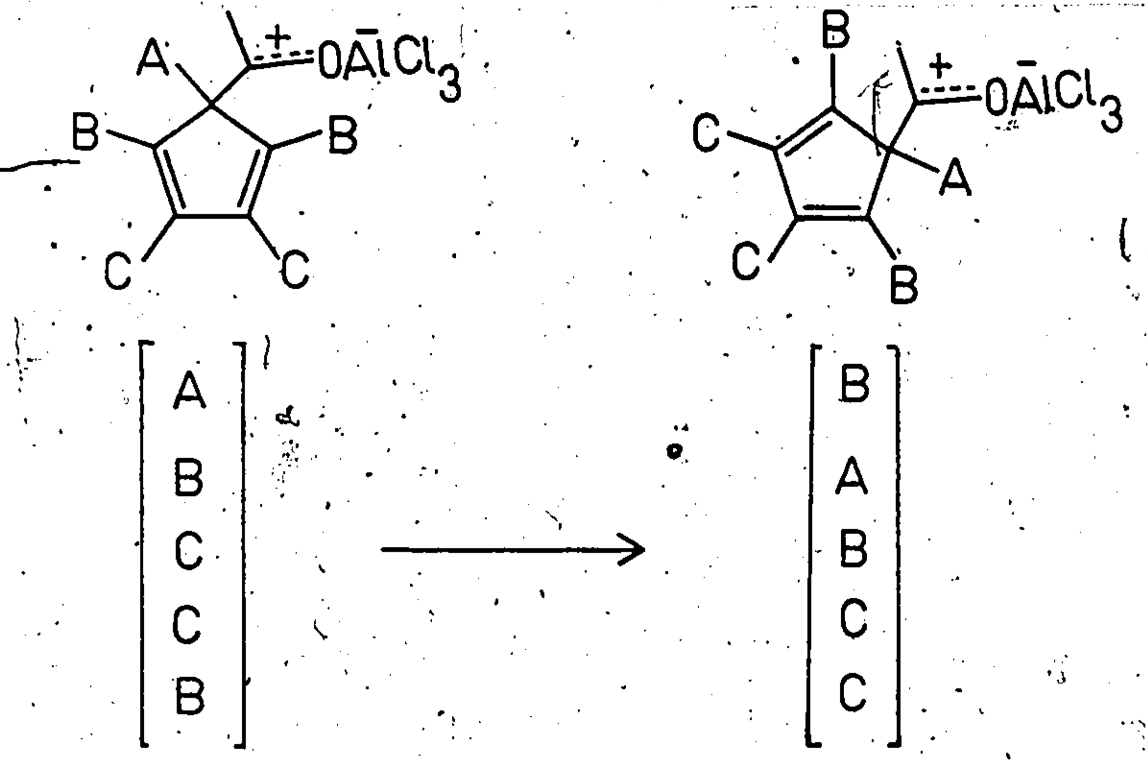
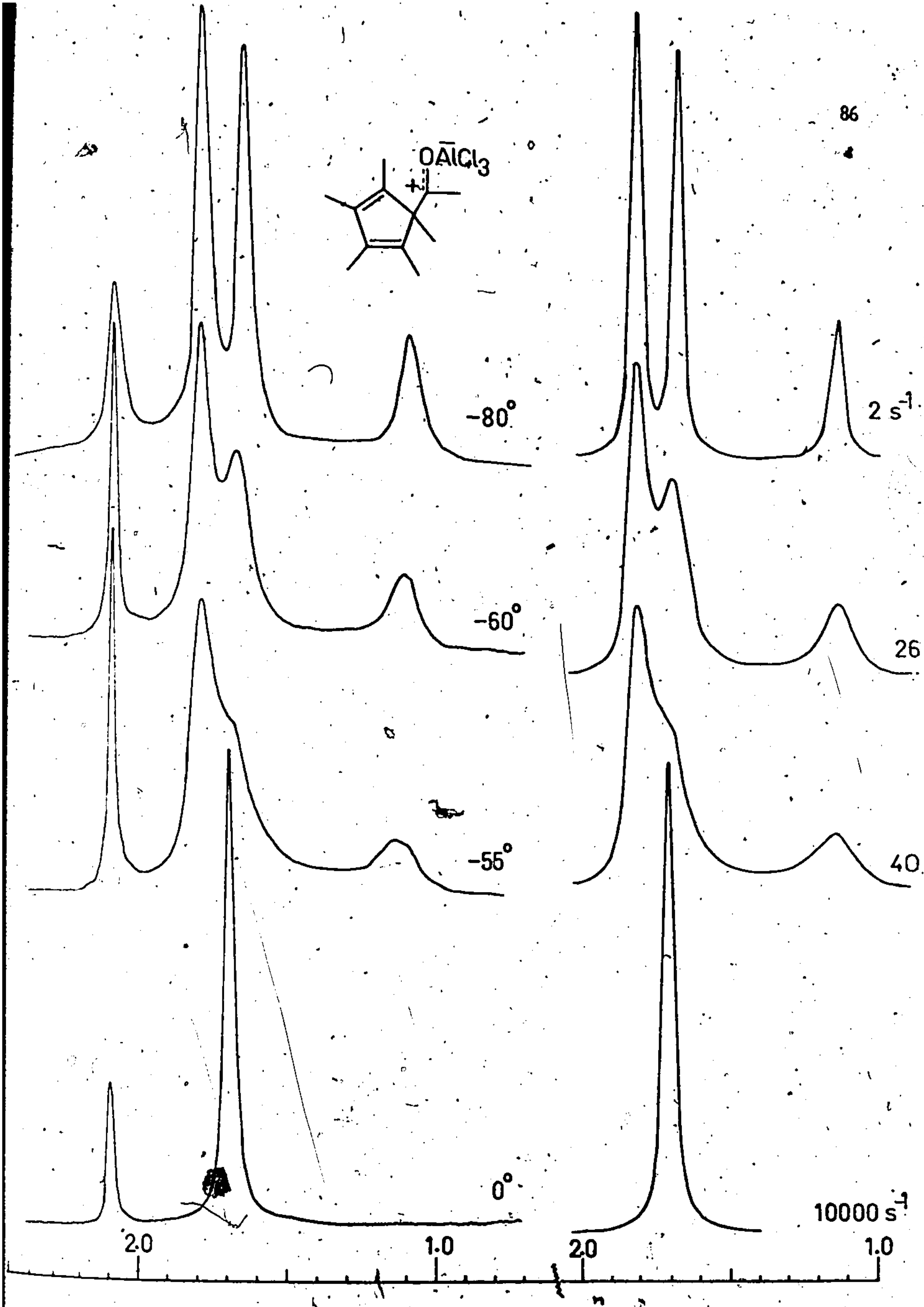
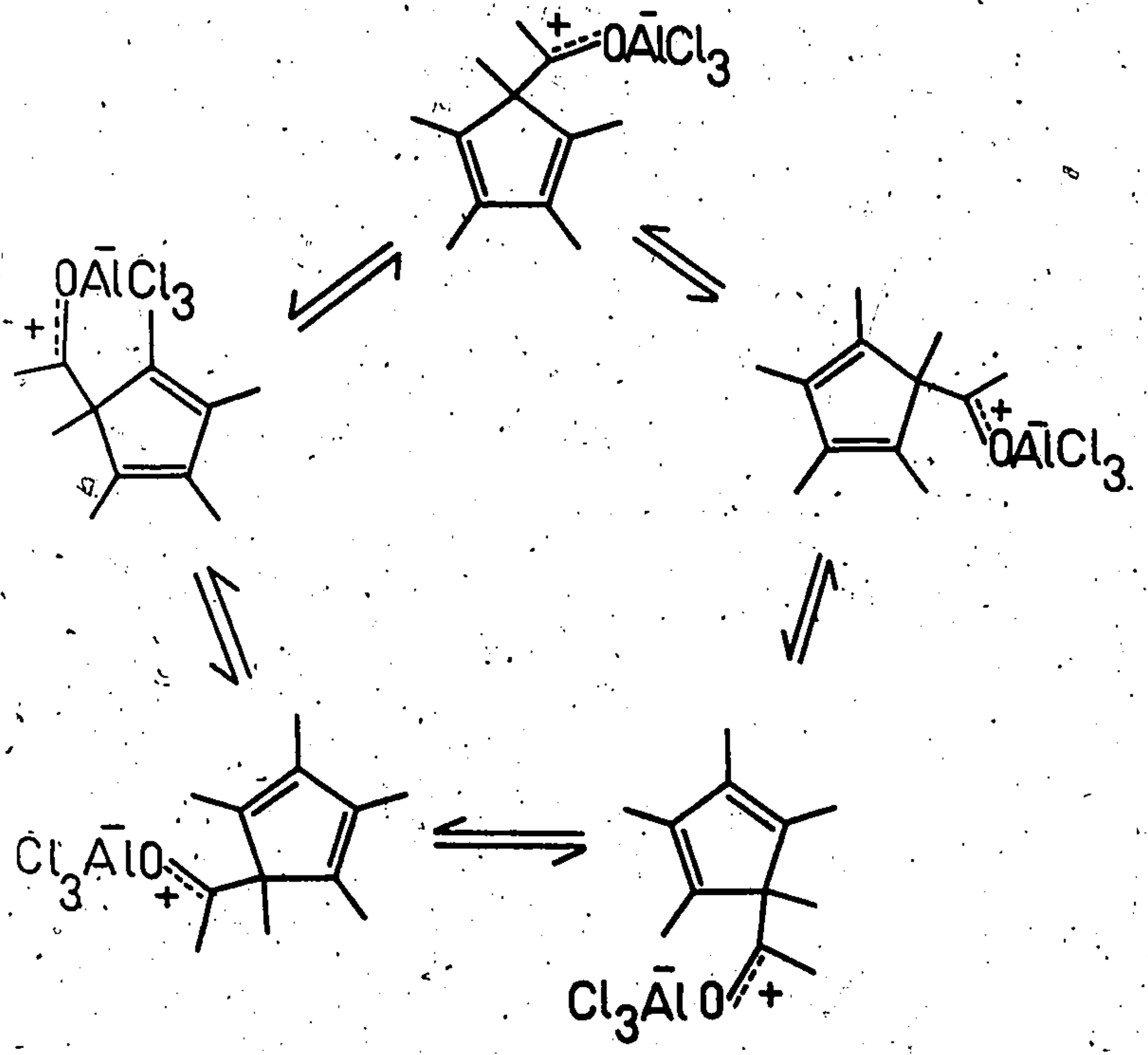


Figure 15 The Experimental and Calculated Temperature Dependent P.m.r. Spectra of $AlCl_3$-complexed-5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene


OĀlCl3
–80°
–60°
–55°
0°
2 s-1
26 s-1
40 s 1
10000 s-1
2.0
1.0
2.0
1.0

Due to a single 1,5 migration, there is an interchange of four methyl groups on the cyclopentadiene. The fifth methyl group, of type C, remained the same and this type of methyl signal will collapse at a slower rate than other ring methyls.

A similar argument made for a 1,3 migration of C_6 in 80a would lead to the conclusion that the methyl signal B would collapse more slowly than the other peaks. Experimentally, it was found that the resonance at 1.82δ attributed to C_3 and C_2, collapsed at a slower rate than the other ring methyl resonances. Clearly, the degenerate rearrangement of 80a must involve a series of 1,5 shifts as is shown in the following scheme.



From the limiting spectrum at -80°, the line widths of the signals of the ring methyl groups in the absence of exchange can be measured. The frequencies of the signals can also be determined. Using this information, the equilibrium population and exchange probabilities of these ring signals, the line shapes of the p.m.r. spectra with various rate constants were calculated with a Saunder's many site nmr line-shape program.[91]

The experimental temperature dependent p.m.r. spectra of 80a were compared with the computer simulated spectra. A visual fit was taken when the experimental spectra and the theoretical spectra were a replica of each other. The rate constants and the temperature at which the rearrangement took place are given in Table XI. The energy barrier to migration was calculated in the usual way.

The logarithmic functions of the rate constants log k_r correlate linearly with $\frac{1}{T}$.

Energy E_a and $\Delta S^{\ddagger}$ were calculated and the results are tabulated in Table XII.

TABLE XI

Rate Constants for Circumambulation

Zwitterion	R	rate $\sec^{-1}$	Temp. °C
80a	CH_3	2 ± .5 LS	-80
		26 ± 2 LS	-60
		40 ± 2 LS	-55
		10^4 LW	0
80b	C_2H_5	8 ± 2 LS	-90
		17 ± 2 LS	-85
		35 ± 2 LS	-82
		38 ± 2 LS	-80
		3.5×10^3 LW	-40
83	OC_2H_5	≤17 LW	70

Comparison of experimental and computer simulated p.m.r. spectra by line-shape analysis (LS) and estimated from line widths (LW).

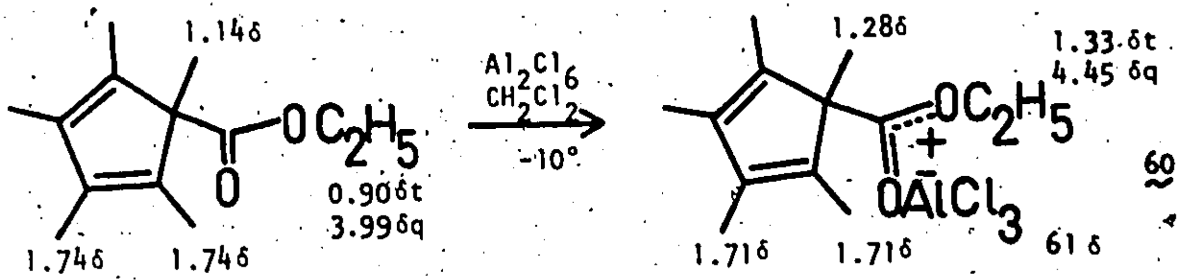
TABLE XII

Activation Parameters for Circumambulation

R	$\Delta F^{\ddagger}$ kcal/mole	E_a kcal/mole	log A	$\Delta S^{\ddagger}$ eu
CH_3	10.9 ± .3	10.1 ± .8	13.52	2.5 ± 5
C_2H_5	9.7 ± .3	11.8 ± 2.5	14.11	6.9 ± 4
OC_2H_5	$\geq$ 18.2			

Similar behaviour was exhibited by complex 80b. The rate constants of rearrangement and the free energy of activation associated with such a migration were calculated as described in the case of 80a. The energy barrier for the migration of C_6 in 80b was found to be 9.7 kcal/mole at -80°.

Ethyl-1,2,3,4,5-pentamethylcyclopentadiene-5-carboxylate (72) reacted with Al_2Cl_6 in CH_2Cl_2 to give a zwitterion whose strusture was assigned as 83.



72

83

In contrast to 80a and 80b, the zwitterion 83 showed no sign of a degenerate rearrangement, even when heated up to 70°. The C_5 methyl resonance and the singlet attributable to C_1, C_2, C_3 and C_4 methyl groups remained very sharp and no line broadening was observed. Using the slow exchange approximation,[90] a line broadening in these singlets could have been detected if the rearrangement occurred with a rate constant of 17 sec^{-1}. As no broadening of the signals was detected at 70°, the rate of the degenerate rearrangement must be $\leq$ 17 sec^{-1}.

At 70°, the free energy of activation associated with the rearrangement must be $\geq$ 17.6 kcal/mole.

A trend is observable for the dependence of the energy barrier for the rearrangement as the C_6 substituents are changed. When the CH_3 group at C_6 was replaced by the lesser charge stabilizing C_2H_5 group, the energy barrier decreased from 10.9 to 9.7 kcal. However, when the highly charge stabilizing substituent $-OC_2H_5$ was introduced on C_6, the energy barrier for the migration was raised to such an extent that no rearrangement was observed even at 70°. It would appear that the rate of the degenerate 1,5 migration of C_6 with its attendent substituents in the $AlCl_3$ complexed 5-acyl-1,2,3,4,5-pentamethylcyclopentadienes is very dependent upon the ability of its substituents on C_6 to stabilize positive charge.

8. Quantitative Correlation of the Rates of the Degenerate Rearrangement

To more systematically probe the effect of the C_6 substituents upon the energy barrier of its degenerate migration, a series of aromatic ketone complexes were prepared. As these differ only in their para substituent, the steric factors will be the same for all of them. The effect of a change of the para substituent on a reaction in aromatic systems is well-known.[136] P.m.r. spectral data of these complexes is given in Table XIII.

These zwitterions also undergo limiting spectra of all the complexes obtained except for the case where R = $\underline{p}CF_3C_6H_4$. The rate constants for the rearrangement and free energies of activation associated with 1,5-migration in each of the ketones were obtained as described in the previous section. Linear relationships between log k_r and $\frac{1}{T}$ as well as $\log(\frac{k_r}{T})$ vs $\frac{1}{T}$ were

TABLE XIII P.m.r. Spectra of $AlCl_3$-complexed-5-benzoylpentamethylcyclopentadienes

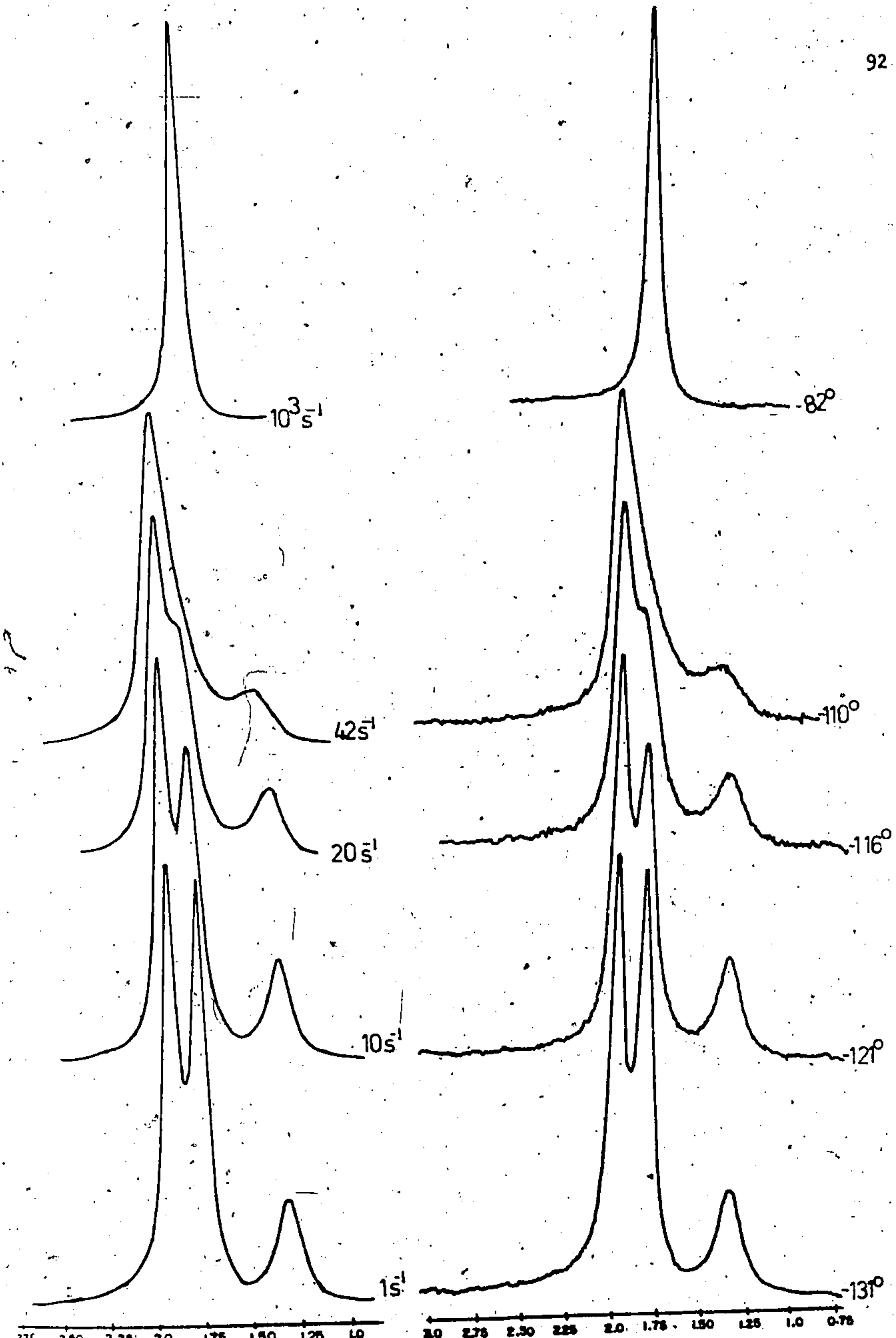
			Cyclopentadiene Ring Methyls				
Compound	R group	Temp.	1,4	2,3	5	Av[a]	Others
80c	$\underline{p}CH_3O_6H_4$	- 75	1.67	1.77	1.27	1.68	6.68-8.13, 3.88
80d	$\underline{p}C_2H_5OC_6H_4$	- 70	1.66	1.77	1.26	1.70	6.72-7.97, 4.03(q) 1.32(t)
80e	$\underline{p}CH_3C_6H_4$	- 93	1.71	1.81	1.33	1.69	7.13-7.87, 2.38
80f[b]	$\underline{p}tBuC_6H_4$	- 95	1.64	1.85	--	1.63	7.14-7.48, 1.24
80g	C_6H_5	-131	1.75	1.90	1.33	1.74	7.29-7.85
80h	$\underline{p}ClC_6H_4$	-140	1.71	1.87	1.25	1.69	7.30-7.65
80i[c]	$\underline{p}CF_3C_6H_4$	-115				1.73	7.75-7.77

[a] Position of averaged methyl resonances at higher temperatures.

[b] Obscured by t-butyl resonance.

[c] Frozen spectrum could not be obtained.

Figure 16 The Calculated and Experimental Temperature Dependent P.m.r. Spectra of $AlCl_3$-Complexed-5-benzoyl-1,2,3,4,5-pentamethyl-cyclopentadienes.


10³s⁻¹
42s⁻¹
20s⁻¹
10s⁻¹
1s⁻¹
2.75
2.50
2.25
2.0
1.75
1.50
1.25
1.0
-82°
-110°
-116°
-121°
-131°
3.0
2.75
2.50
2.25
2.0
1.75
1.50
1.25
1.0
0.75

observed. The rate constants for circumambulation and the activation parameters associated with each zwitterion are given in Table XIV.

To be able to obtain a meaningful correlation, the rate constants for the migration of C_6 must be compared at a constant temperature. The rate constants at -90° were calculated from the appropriate Arrhenius plots for the aromatic ketone complexes. The estimation of the rate constants at -90° was carried out because this temperature falls in the middle of the range of temperature used with these complexes. The rate constant for the rearrangement of (80i $R=p\text{-}CF_3C_6H_4$) was calculated by assuming $\Delta S^{\ddagger}$ value to be constant which is validated by the low $\Delta S^{\ddagger}$ value observed for these degenerate rearrangements.

Plotting the value of $\log k_{-90}$ against σ^+ for the substituents gave a straight line with a slope of 4.64 and correlation coefficient of 0.999.[137] The sign of the reaction constant ρ signifies that electron withdrawing substituents facilitate the rearrangement. This is obvious when the logarithmic function of the rate constants at -70° was compared for paramethoxy (0.82) and paratrifluoromethyl (5.65) substituents.

The magnitude of ρ, 4.64, is quite comparable with other reaction series where the electronic effect of substituents have a large effect upon the rate of reaction. For example, the reaction constant for the nucleophilic substitution reaction of substituted bromobenzenes with piperidine is 4.87.[138] The bromination of substituted nitrophenols where almost a full positive charge is being developed at the reaction site, has the reaction constant of 4.98.[139] The magnitude and sign of ρ would suggest then that in the transition state of the migration a very substantial amount of the positive charge is removed from C_6.

TABLE XIV Rate Constants for the Degenerate Rearrangement of the $AlCl_3$ Complexes of 5-Benzoylpentamethylcyclopentadienes

Cmpd.	Solv.	Temp. °C	k[a] sec^{-1}		ΔF‡ kcal/mole	Ea kcal/mole	log A	ΔS‡ eu
85	CH_2Cl_2	+ 70	≤.17		≥ 18.2			
80c	CH_2Cl_2	- 75	1.5±.5	LS		12.1±2.9	13.3	3 ± 14
		- 60	15 ± 2	LS				
		- 55	23 ± 2	LS	11.2±0.3			
		- 50	37 ± 2	LS				
		- 90[b]	0.15					
80d	CH_2Cl_2	- 70	1.0	LS		14.9±3.2	16.1	17.5±9
		- 65	2.0	LS				
		- 54	17 ± 2	LS				
		- 51	23 ± 2	LS				
		- 48	33 ± 2	LS	11.5±0.4			
80e	CH_2Cl_2	- 93	10 ± 2	LS		11.0±2.3	14.6	9.0±14
		- 90	17 ± 2	PH				
		- 85	100 ± 2	LS	9.8±0.3			
80f	CH_2Cl_2	- 95	10 ± 2	PH		9.7±8.2	11.8	- 3.8±7.0
		- 90	15 ± 2	LS				
		- 85	32 ± 2	PH	9.6±0.3			
		- 82	42 ± 2	LS				
		- 90[b]	16					
80g	$CHClF_2$	-131	1 ± .5	PH		8.2±1.3	12.7	0.7±10
		-126	2.5±.5	PH				
		-121	10 ± 2	LS				
		-116	20 ± 2	LS	8.0±0.3			
		-110	42 ± 2	LS				
		-103	60 ± 2	LS				
		- 91	10^3	E				
		- 90[b]	710					

TABLE XIV (Contd.)

Cmpd.	Solv.	Temp. °C	k^{a} sec^{-1}		$\Delta F^{\ddagger}$ kcal/mole	Ea kcal/mole	log A	$\Delta S^{\ddagger}$ eu
60n	$CHClF_2$	-130	4 ± .5	LS		6.4±0.8	10.4	-10 ± 7
		-127	8 ± 2	LS	8.3±0.3			
		-113	42 ± 2	LS				
		-108	60 ± 2	LS				
		- 90[b]	540	LS				
57i	$CHClF_2$	-152	60 ± 5	LS	5.0±0.6			
		- 90[c]	450,000					

[a] Comparison of experimental and computer simulated p.m.r. spectra by line-shape analysis (LS); peak-height (PH) and estimated from line widths (LW).

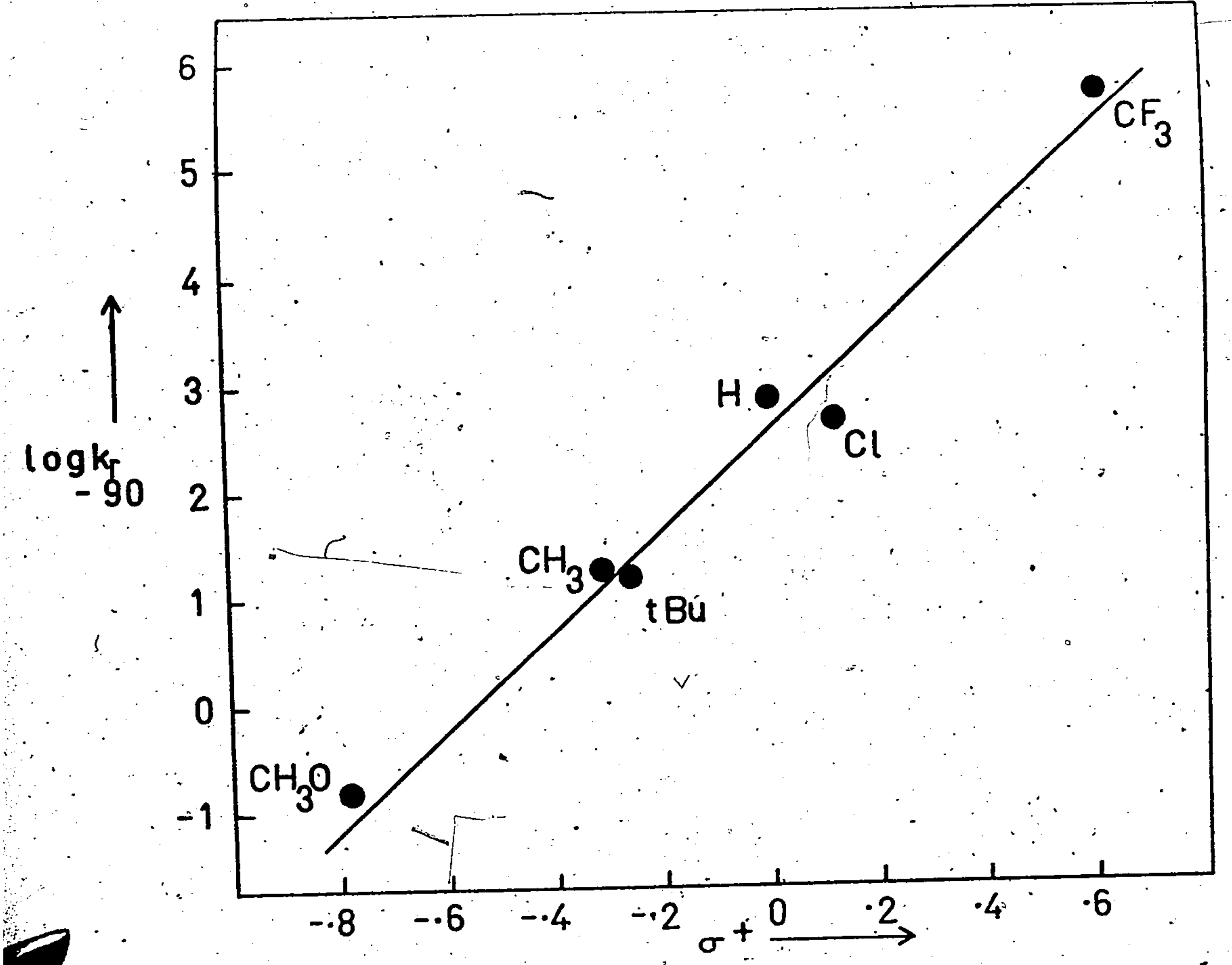
[b] Value at -90° obtained from Arrhenius plot.

[c] Value at -90° estimated assuming $\Delta F^{\ddagger}$ for the rearrangement is temperature independent.

[d] Error in the temperature measurements is taken to be ±5°; however, the relative errors in temperature is expected to be smaller.

[e] Activation parameters derived from Arrhenius plot may not be meaningful as the range of temperature is small.

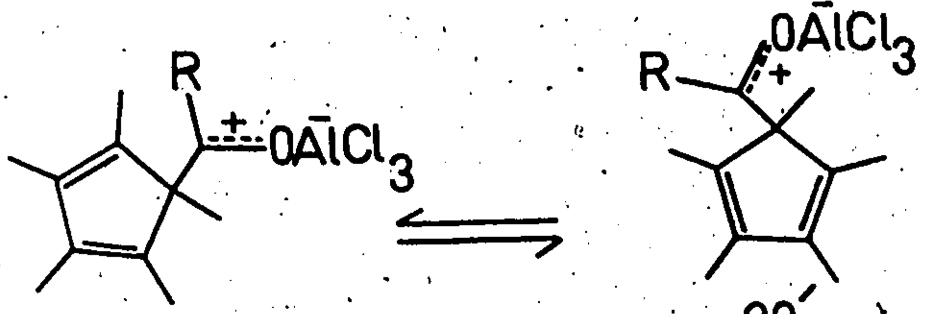
Figure 17. The Linear Free Energy Relationship between the Rates of Circumambulation and the para-Substituent Constants of the Aromatic Ketones. (A Reliable value of σ^+ for the ethoxy group is not available.)


log k_T -90
6
5
4
3
2
1
0
-1
-·8
-·6
-·4
-·2
0
·2
·4
·6
σ +
CF3
Cl
H
tBu
CH3
CH3O

9. Mechanism of the Degenerate Rearrangement

From Table XIV it is evident that electron withdrawing substituents facilitate the degenerate circumambulation of the complex 80 whereas highly electron donating groups render the migration more difficult.

Any mechanism that is proposed for this rearrangement must be able to satisfactorily account for this large inverse rate dependence. A simple 1,5 sigmatropic shift of C_6 is an attractive possibility but is difficult to see how substituent effect of this magnitude could be accounted by this process.



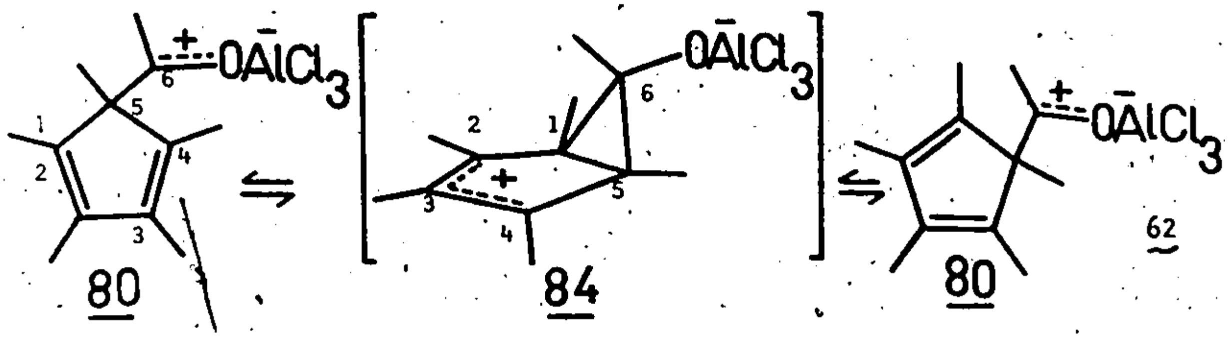
80

80′

61

A reaction mechanism in which a bicyclo[3.1.0]hexenyl ion occurs as a transition state or a high energy intermediate is completely consistent with these results. The exclusive 1,5 shift, as well as the large dependence of the rate on the structure, can be explained by this mechanism. The migration can occur by an asymmetric overlap of the formally vacant p orbital on C_6 with the filled π orbital of the cyclopentadiene ring. This overlap will result in the transfer of positive charge from C_6 onto the five-membered ring. The proposed mechanism of the rearrangement is illustrated in the following equation (equation 62).

The structure of the zwitterion at the halfway point during the migration can be represented as a bicyclo[3.1.0]hexenyl ion. Either one of the cyclopropane bonds could break giving back the complexed ketone 80. If the breakage of the C_1-C_6 bond occurs, the original zwitterion will result. However, the rupture of the C_6-C_5 bond will generate a zwitterion where the C_6 group has migrated to the adjacent carbon atom on the cyclopentadiene ring.



As in 84, the positive charge has been largely transferred onto the five-membered ring, the substituents on C_6 will then have a paramount effect on the rate of rearrangement of 80. The better the ability of the C_6 substituent to stabilize the positive charge, the lower will be the relative ground state energy of 80. In contrast, the substituent R will only have a small effect on the stability and energy of 84 as the stability of the allylic cation is affected mainly by the ring methyls and only to a small extent by the C_6 substituents. The difference in energies between 80 and 84 will be larger and the rate of rearrangement will be slower. Highly electron withdrawing groups such as p-$CF_3C_6H_4$ will increase the energy of 80 and the rate of the rearrangement will be faster as the energy barrier for the migration will be lower than the previous case.

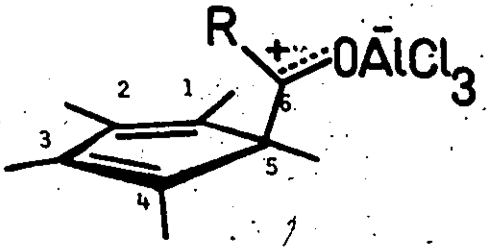
10. The Structure of the Zwitterions

As the zwitterions clearly resemble the transition state proposed for the degenerate "cyclopropyl merry-go-round" in the bicyclo[3.1.0]hexenyl cations, it is important that the structure of these complexes be examined in more detail. It will be noticed that the p.m.r. spectrum of the zwitterions, Table XIII, displayed a symmetry in which the C_1C_4 methyl signals appeared as a singlet and C_2 and C_3 methyl groups gave rise to another. Only one signal for the C_6 substituent could be detected at any temperature.

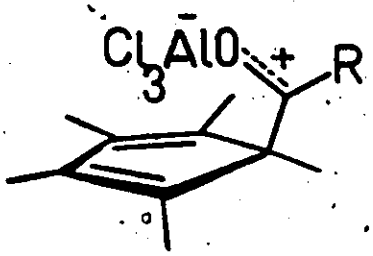
In order to account for the symmetry of the p.m.r. spectra, three alternatives must be considered.

(i) A rotation of the C_5C_6 bond could be occurring with a rate faster than the p.m.r. time scale. In this situation, only the averaged signal of C_6 will be observed at any time.

(ii) Another possibility is that the rotation is very slow and the principal rotomer can be written as either 85 or 86. In these structures, the C_6 substituents lie in the plane passing through the centre of the C_2-C_3 bond and through C_5 and C_6.

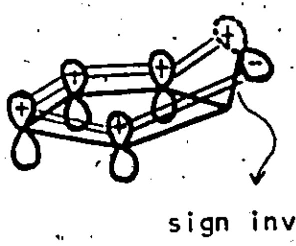


85

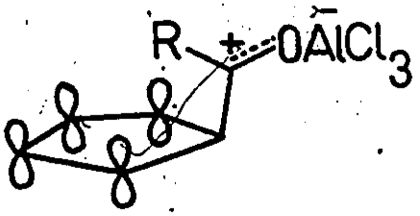


86

The stability associated with such a homo-conjugative interaction lies in the fact that the zwitterions fulfill all the requirements for Möbius Aromaticity.[140] A cyclic array of atomic p orbitals in which there are 4nπ electrons and an odd number of sign inversions as shown in the structure 87 has been calculated to be equal in energy to a conventional Hückel aromatic system.[141] However, it might be pointed out that in these conformations, there is a fairly severe eclipsing of one of the C_6 substituents and the C_5 methyl group. Moreover, the other C_6 substituent will prevent the formally vacant p orbital from approaching the π orbitals on C_1 and C_4 by interacting with C_2 and C_3 (Structure 88).

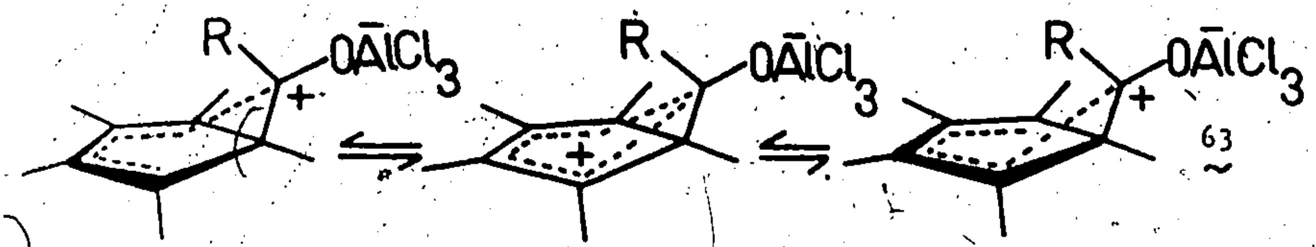


87



88

(iii) The third possibility would be two interconverting cations such as 89 and 89' in which homo-conjugation between the electron deficient C_6 and the occupied π orbitals of cyclopentadiene is present. Such a homo-conjugative interaction in cyclopentadienemethyl cations has been suggested by Winstein and Battiste.[78]



89 90 89

The halfway point in the interconversion 89 and 89' the zwitterion will resemble the structure 90 where C_6 is partially bonded both to C_1 and C_4. For the reasons given in the previous paragraph, 90 will be an energy maximum. At this point a slight motion of C_6 towards either C_1 or C_4 would result in the lowering of potential energy of 90 as shown in Figure 18.

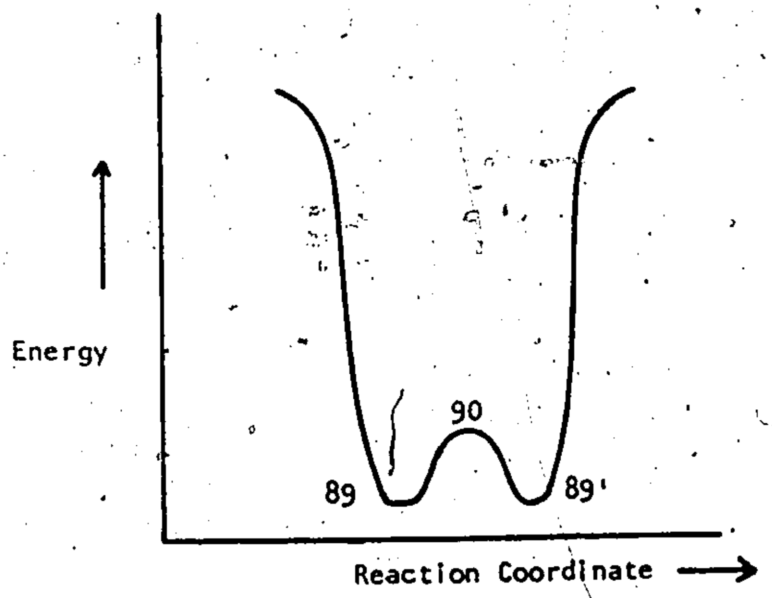


Figure 18 A possible Energy Profile for the Interconversion of 89 and 89'

In structures 89 and 89', the asymmetric overlap of C_6 with the π orbitals will ultimately lead to the formation of the transition state for the degenerate rearrangement. The increase in the magnitude of the overlap would enhance the formation of the transition state which would be reflected in the rate of circumambulation.

If either of these non-classical interactions were to occur, their effect would be more significant in systems where the charge stabilizing ability of R is the lowest.

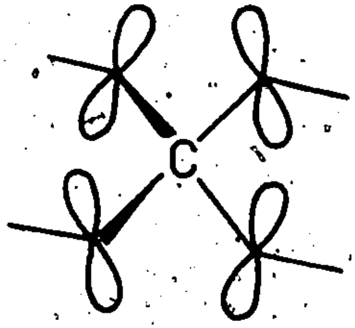
Upon a careful examination of the p.m.r. data in Table XIII. it will be noticed that there is a steady change in the resonance positions of the methyl groups on the cyclopentadiene ring.

As a result of the formation of the $AlCl_3$ complexes, the methyl substituent on C_5 is deshielded by 0.12 to 0.15 ppm over the entire series of aromatic ketones. When R = $\underline{p}CH_3OC_6H_4$, the C_2 and C_3 methyl resonances moved upfield by 0.05 ppm and moved downfield by 0.08 ppm when the electron withdrawing group [R = $\underline{p}ClC_6H_4$] is present. In a similar manner, the C_1 and C_4 methyl signals were deshielded by 0.05 ppm in <u>80c</u> (R = $\underline{p}CH_3OC_6H_4$) whereas in <u>80h</u> (R = $\underline{p}Cl_6H_4$) the signals moved downfield by 0.09 ppm. If it is assumed that the anisotropy of the phenyl group is constant in all the parasubstituted phenyl ketones, then this would seem to indicate that as the positive charge stabilizing ability of R decreases, the participation of the diene becomes more important.

While this data does not prove that homo-conjugative interaction is present in the zwitterions, it is highly suggestive that at least in the systems where the activation barrier is low, there could be some interaction.

11. Electronic Spectra of the Zwitterions

It was anticipated that homo-conjugative interaction between the electron deficient C_6 and the π orbitals of the five-membered ring would be reflected in the u.v. absorption of the diene. Such a change in the uv absorption may be likened to that observed for spiro conjugation.[142,143] When two π systems are held perpendicular to each other by a common atom of tetrahedral geometry, the overlap integral for the orbitals in the different planes is about 20% of the value for adjacent p orbitals in planar π electron molecules.



This type of delocalization was detected in spirotetrenes, where a red shift in the uv absorption of the diene was observed.[144] A similar behaviour was observed in the ketal of cyclopentadiene.[142]

Electronic spectra of Lewis acid adducts of carbonyl compounds have been reported by several authors.[130,145,146] In most of these reports,[130,146] the complexes were less sensitive towards humidity and anhydrous conditions need not be strictly imposed. Some data have been reported for the uv spectra of $AlCl_3$ adducts.[125,129]

The zwitterions for the uv measurements were prepared using a high vacuum technique. As the concentrations of the zwitterions were in the order of 10^{-4} M, a considerable number of difficulties were encountered. Although anhydrous conditions were maintained rigorously, consistent results were not obtained. Moreover, the equilibrium constants for the formation of the zwitterions at such high dilutions could not be accurately calculated. It is likely that the formation constant of the zwitterions will decrease considerably particularly when the solutions are very dilute.[147]

U.V. spectra of complexes 80a and 80h (R = pClC_6H_4) were recorded in CH_2Cl_2 solutions and the typical results given in Table XV.

TABLE XV

U.V. data for 5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes and their $AlCl_3$ Complexes

Zwitterion	R	λ_{max} (log ε)
80a	CH_3	253(3.60) 393(3.34)
	pClC_6H_4	262(3.70) 295(4.10) 390(2.70) 450(2.70)
	pClC_6H_4	262(3.50)
		262(3.80) 295(3.70) 385(2.10)
Uncomplexed Ketones		
70a	CH_3	258(3.40)
70h	pClC_6H_4	260(3.30) 315(2.30)

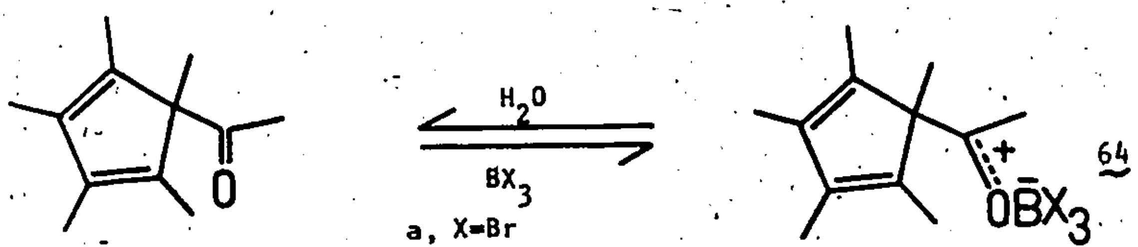
It is doubtful that the uv data can be attributed to that of the zwitterions since the solutions used for the uv experiments changed colour with time. In the light of inconsistencies and difficulties encountered, the data obtained are not meaningful.

^{13}C nmr would be another alternative to the ultraviolet spectroscopy for the determination of the homoallylic interaction in these zwitterions. The complexes are quite stable at room temperature, however, in the absence of a Fourier transform nmr machine, it was not possible to obtain the ^{13}C spectra with the concentrations of the zwitterions which could be prepared. The synthesis where incorporation of ^{13}C into the ring carbon atom of 5-acyl-pentamethylcyclopentadienes would be complex.

12. The Effect of the Change of Lewis Acids in Circumambulation

In order to further investigate the influence of positive charge upon the energy barrier of the degenerate rearrangement, 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene (70a) was complexed with other Lewis acids such as BCl_3, BBr_3 and BF_3 and the rearrangement of the complexes studied. The adducts were made by distilling the Lewis acid into a CH_2Cl_2 solution of 70a. Stirring at -78° resulted in the rapid formation of zwitterions 91.

The complexes were identified by recording the p.m.r. spectra at low temperatures. All three boron complexes displayed a 1:2:2:1 pattern of methyl resonances in the limiting spectra which was very similar to that of 80. Quenching the zwitterion solutions in ice/water resulted in the quantitative recovery of ketone 70a.



70a

a, X=Br
b, X=Cl
c, X=F

91

TABLE XVI

P.m.r. Data for Lewis acid-complexed-5-Acetyl-1,2,3,4,5-pentamethyl-cyclopentadienes

Compound	1,4CH$_3$	2,3CH$_3$	5CH$_3$	6CH$_3$	Averaged Signal	Deshielding in methyl signal
91a	1.79	1.93	1.40	2.55	1.79(1.77)	1.04
91b	1.72	1.84	1.22	2.38	1.66(1.66)	0.88
91c	1.62	1.77	1.02	1.97	1.67(1.67)	0.52
80a	1.67	1.81	1.12	2.10	1.66(1.61)	0.60

TABLE XVII

The Rate Constants and Free Energies of Activation for Circumambulation

Compound	Rate Const. sec^{-1}	Temp. °C	$\Delta F^{\ddagger}$ kcal/mole
91a	77 ± 2	-75	9.7 ± .3
91b	28 ± 2	-50	11.4 ± .3
91c	35 ± 2	4	14.2 ± .3
80a	26 ± 2	-60	10.9 ± .3

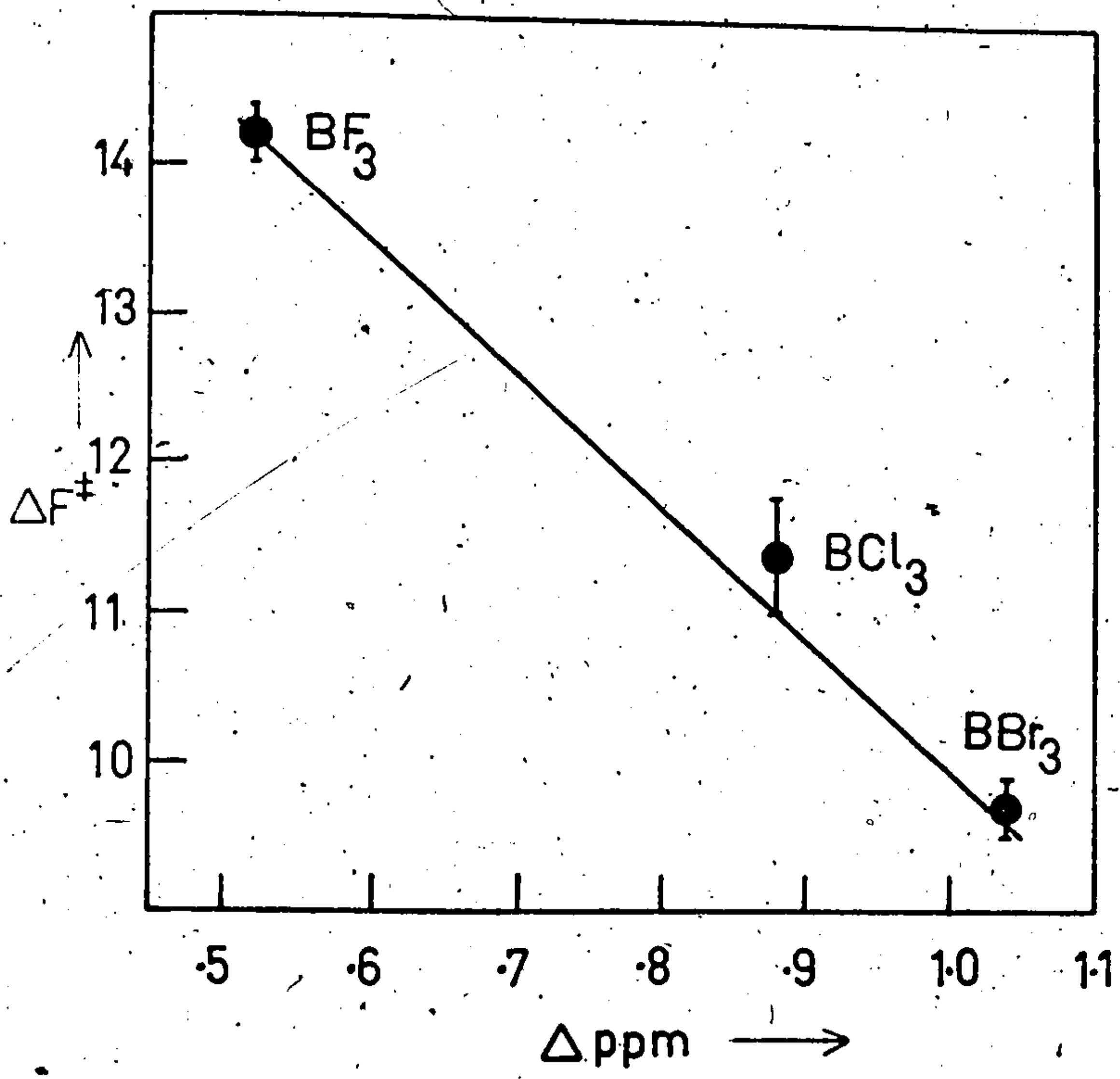


Figure 19 The Activation Barriers for the Five-Fold Degenerate Rearrangement of 91 as a Function of the Deshielding of the C_6 Methyl Signal.

The p.m.r. data of the zwitterions <u>91</u> are given in Table XVI. These zwitterions undergo degenerate circumambulation similar to <u>80</u>. The mode of rearrangement is identical with that of <u>80</u>. The rate constants and free energy of activation associated with the rearrangement were calculated as described in detail before, and are given in Table XVII. It is quite clear from the data in Table XVII that the rate of the degenerate rearrangement is dependent upon the Lewis acid used. As all the ketone was complexed, the difference in the energy barrier must be a function of the ability of the oxygen substituent to stabilize the positive change.

The deshielding of the C_6 methyl group in <u>91</u> relative to C_6 of <u>70a</u> (Δδ C_6 complex) could be a measure of the electron deficiency on the carbonyl group, assuming that the magnetic anisotropy of the Lewis acid remains the same. A linear correlation exists between the energy barrier $\Delta F^{\ddagger}$ and the magnitude of the positive charge on C_6 as measured by Δδ complex, Fig. 19. The number of points on the graph is limited to three since only the Lewis acids that form the same type of coordinate bond can be used. The magnetic anisotropies of Al_2Cl_6 and boron trihalides are different so that a comparison of Δδ complex between these Lewis acids cannot be made. The correlation of the rates of circumambulation at a constant temperature with the magnitude of the [illegible] charge on C_6 would be a better correlation. However, as the values of $\Delta S^{\ddagger}$ for these migrations are low, it can be assumed that the temperature dependence of $\Delta F^{\ddagger}$ is small so that the correlation shown in Fig. 19 is valid.

A quantitative scale of Lewis acidity for a limited number of Lewis acids has been published by Taft based on ^{19}F nmr studies.[148,149]

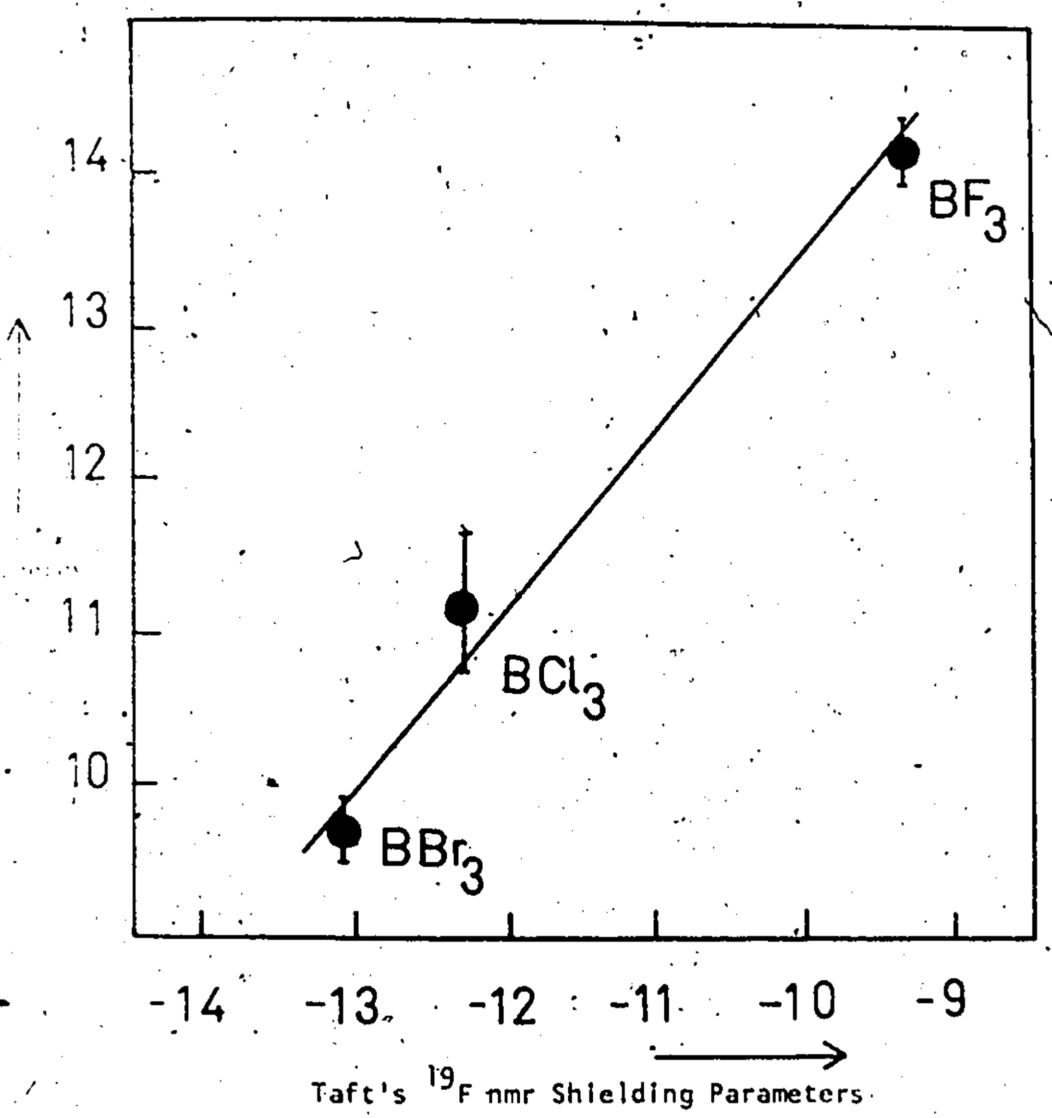
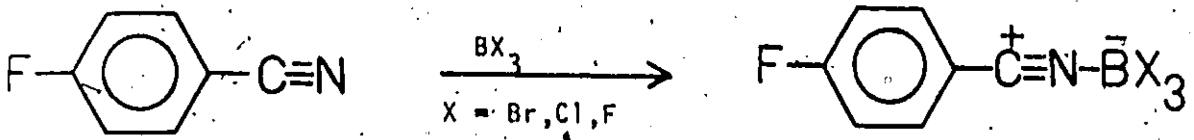


Figure 20 The Correlation between the Activation Barrier for Circumambulation in 91 and Taft's ^{19}F nmr Shielding Parameters.

It has been observed that the shielding of the ^{19}F nucleus in para-fluorophenyl derivatives $F-C_6H_4-X$ is highly sensitive towards the electron donating or withdrawing effect of X.[149]



92

93

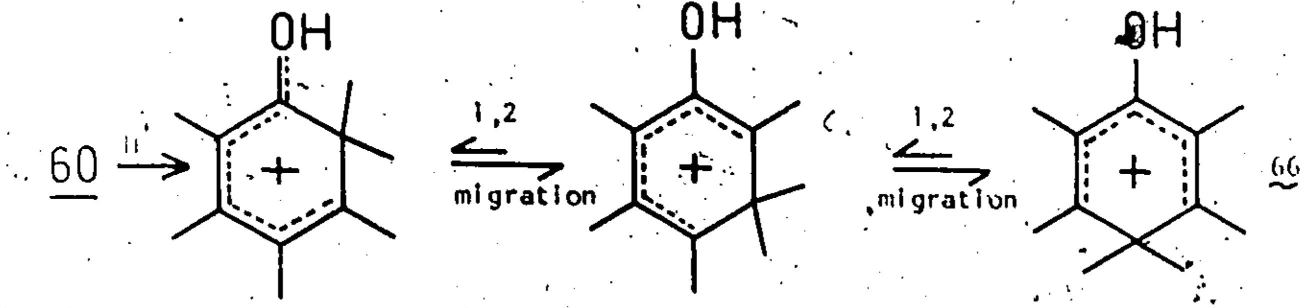
65

The magnitude of the difference in ^{19}F chemical shifts between 92 and 93 reflects the strength of the polarization of the bond between the cyano group and the Lewis acid. The chemical shift differences for BF_3, BCl_3 and BBr_3 were listed as -9.25, -12.30 and -13.10, respectively. A straight line correlation was obtained between Tafts' ^{19}F nmr shielding parameters and the energy barriers for the circumambulation of boron trihalide complexed-5-acetyl-1,2,3,4,5-pentamethylcyclopentadienes (91).

This correlation strengthens Taft's contention that the magnitude of the interaction between the electron donors and Lewis acids determines the extent of positive charge developed on the donor atom. It also reinforces the suggestion, made from the σ^+ vs log k_{-90} correlation made in the previous section, that the ease of migration of C_6 is determined by the magnitude of the positive charge being developed on it. Moreover, the results described in this thesis could enable a new scale for the acidity of Lewis acids to be set up.

13. The Effect of Lewis Acids on the Thermal Isomerization of Cyclohexadienones

The rearrangement of 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dienone (60) in fuming sulfuric acid has been used by Hart[150] to prepare the symmetrical 2,3,4,4,5,6-hexamethylcyclohexa-2,5-dienone (97). The same rearrangement was reported to have occurred in chlorosulfuric acid[151] and fluorosulfuric acid.[152] Deuterium labelling experiments have shown that 95 is a transient intermediate in this rearrangement.[151b]



94 95 96

The rearrangement of 94 to 96 can best be discussed in the light of the energy profile for the rearrangement. The rate determining step will depend upon the energy barrier associated with the isomerization to 95, which in turn is dependent upon the relative thermodynamic stabilities of 94 and 95. The electronic effect of the substituent on C_1 will play an important role in determining the relative stability of the cyclohexadienyl cation 94. The relative energies of 94 and 95 can be varied by changing the substituent on C_1 in 94.

A consideration of the resonance structures of 94 shows that electron donating substituents at C_1, such as protonated ketone group, will be expected to stabilize 94 relative to 95 (Figure 21a). The activation barrier associated with the isomerization will increase as 94 becomes more and more stable as compared to 95.

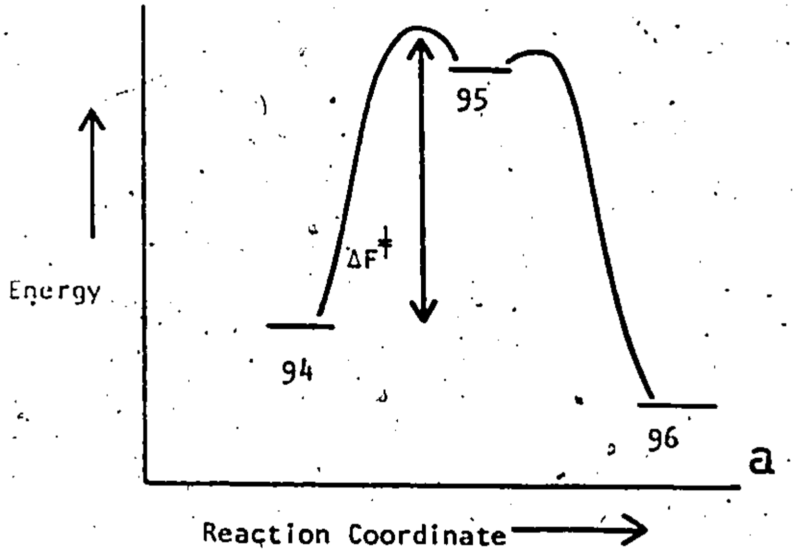
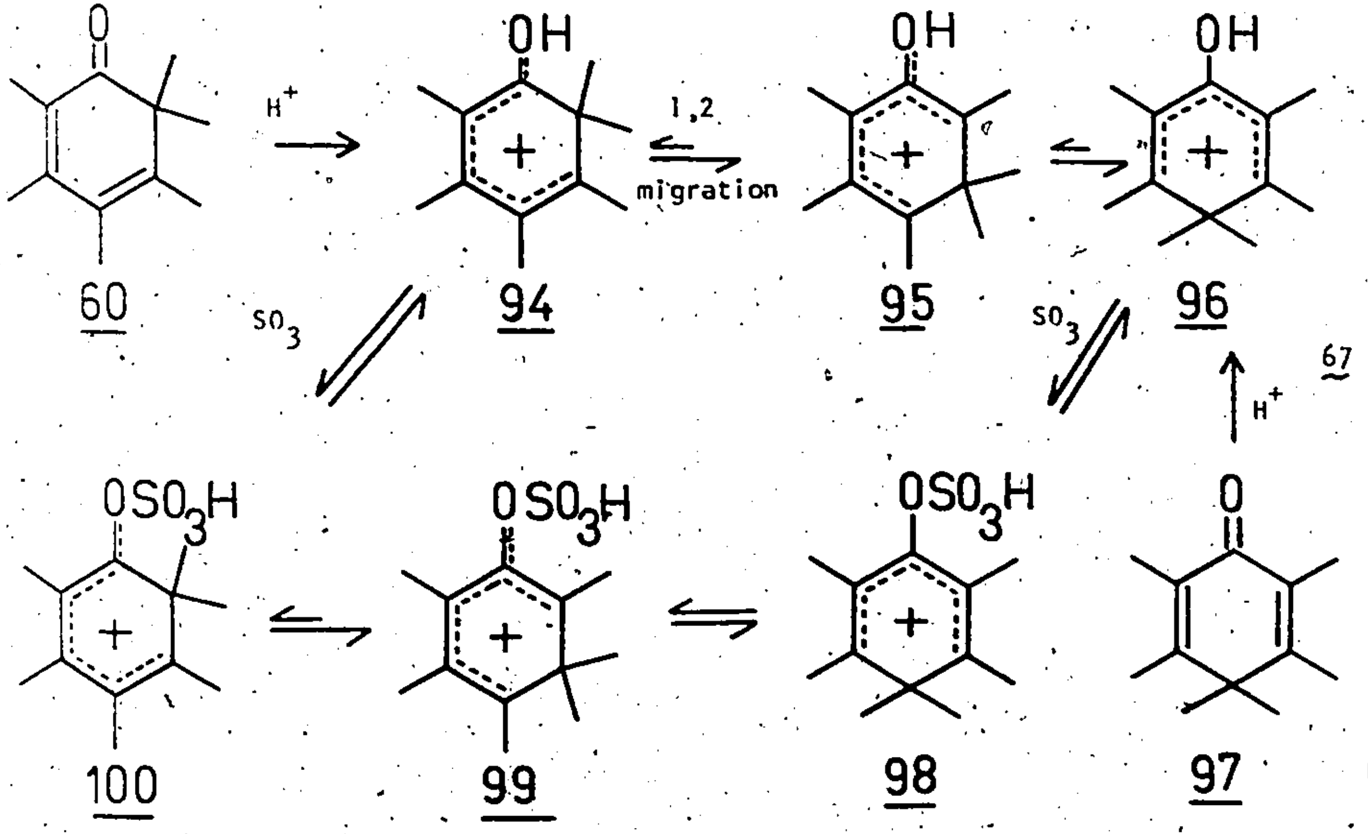


Figure 21 Reaction Profile for the Thermal Isomerization of Cyclohexadienones.



In contrast, electron withdrawing groups at C_1 will result in the increase in energy of 94. Although the electron withdrawing substituent will also cause an increase in the energy of 95,‡ the extent to which 94 is destabilized will be much more than the destabilization suffered by 95. The intermediate 95 would be expected to be more stable than 94 if the substituent on C_1 is electron withdrawing. The situation may be likened to the case where SO_3 was present in the $HFSO_3$ solution of 94. Coordination of SO_3 with the hydroxy group inhibits the electron-donating power of the -OH group to such an extent that 99 was observed as the only species in solution[152] (Figure 21b).

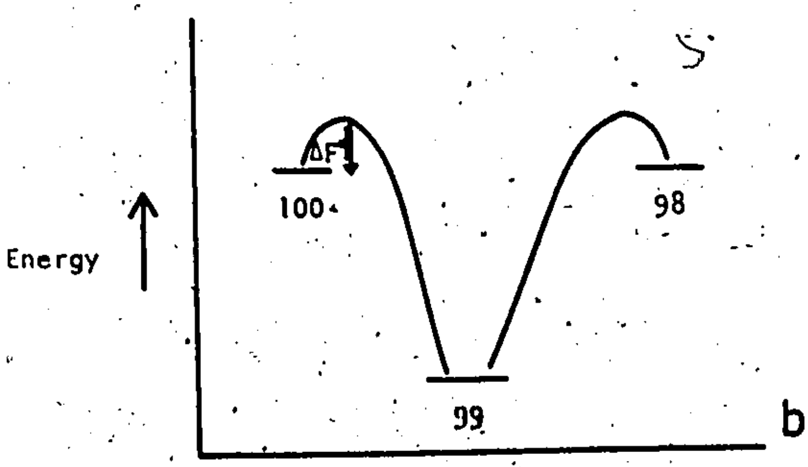
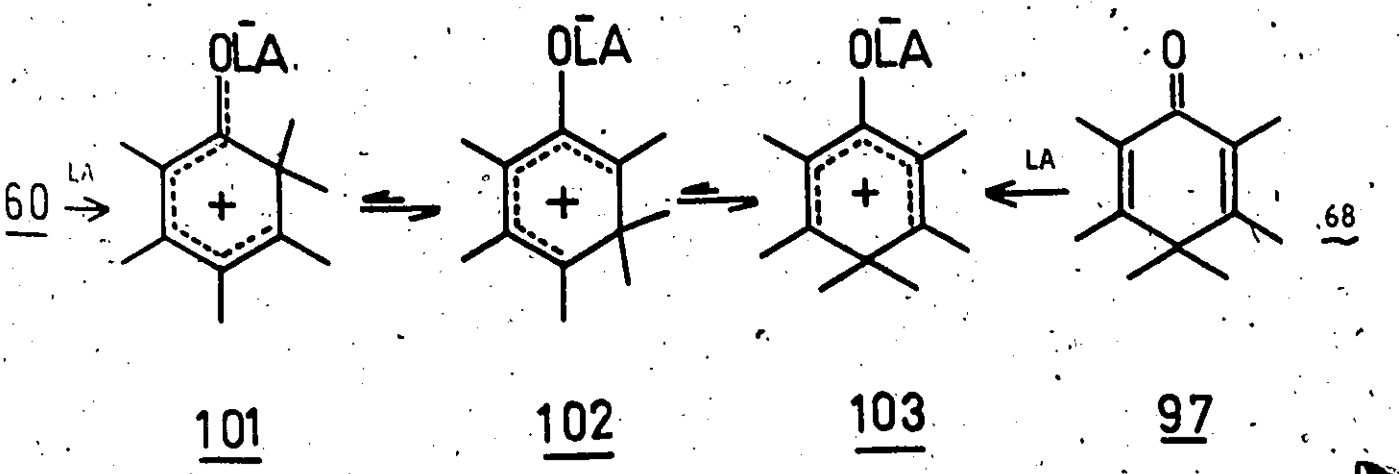


Figure 21



a, LA = $AlCl_3$; b, LA = BCl_3; c, LA = BF_3

However, if the electron-donating ability of the substituent at C_p is smaller than the protonated ketone group, the energy profile shown in Fig. 21c prevails. We have previously shown that the [illegible] oxygen Lewis acid adducts can stabilize positive charge to [illegible] extent depending upon the Lewis acid used. The difference [illegible] relative stabilities of 101 and 102 can then be considered [illegible] function of the positive charge stabilizing ability of the [illegible] oxygen Lewis acid adduct. The rates of isomerization of [illegible] will reflect the relative electron donating abilities [illegible] the various -OLA groups.

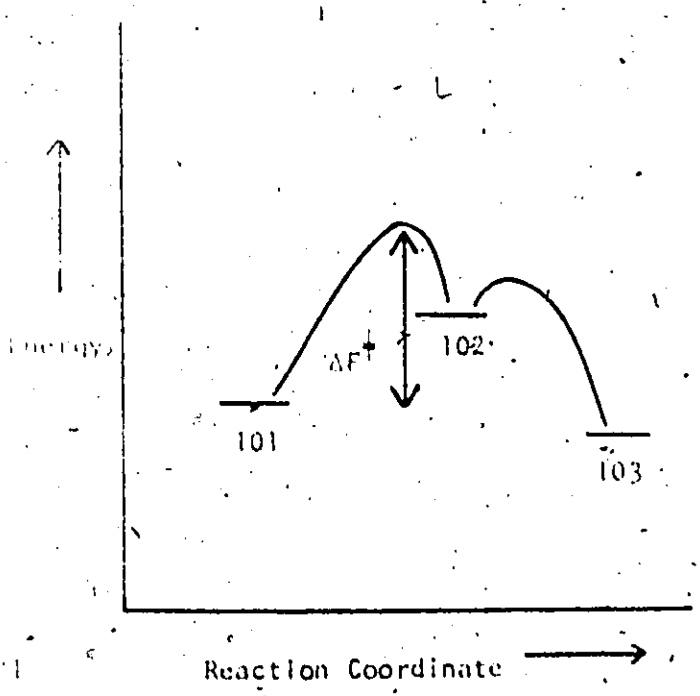


Figure 21

The complex between BCl_3 and 60 was made at -78° using CH_2Cl_2 as the solvent. The change in the p.m.r. spectrum of the sample shows that the complex was formed, and the low temperature p.m.r. spectrum was quite consistent with the structure 101.

TABLE XVIII

Chemical Shifts of the Lewis acid-complexed-hexamethylcyclohexadienones

LA	Compound	$2CH_3$	$3CH_3$	$4CH_3$	$5CH_3$	$6CH_3$
BCl_3	101	2.22	2.72	2.22	2.22	1.47
	103	2.20	2.38	1.39	2.38	2.20
BF_3	101	2.08	2.45	2.08	2.04	1.36
	103	2.06	2.20	1.27	2.20	2.06
$AlCl_3$	101	2.12	3.44	2.12	2.12	1.42
	103	2.15	2.29	1.36	2.29	2.15

TABLE XIX

Rates of the Thermal Isomerization of the Lewis acid-complexed-hexamethylcyclohexadienones

LA	Rate Constant sec^{-1}	Temperature °C	$\Delta F^{\ddagger}$ kcal/mole
H	$1.10 \pm .1 \times 10^{-3}$	61	24.1
BCl_3	$8.00 \pm .8 \times 10^{-4}$	-13	18.8
BF_3	$5.00 \pm .5 \times 10^{-4}$	70	25.3
$AlCl_3$	$1.22 \pm .1 \times 10^{-3}$	37	22.2

Upon warming, the complex 101 started to rearrange to 103. The identification of the product was achieved when the p.m.r. spectrum of 103 was compared with that of the authemtic sample. The kinetics of the reaction was followed by the decrease in the intensity of the signal of 6,6-methyl in 101. The intermediate 102 was not observed. $AlCl_3$ and BF_3 complexes of 60 also undergo the same rearrangement. The chemical shifts of the zwitterions and the rate data are given in Tables XVIII and XIX.

Attempts to quantitatively correlate the free energies of the cyclohexadienone isomerizations with those of the degenerate rearrangements in the Lewis acid complexed-5-acetyl-pentamethylcyclopentadienes failed to produce any meaningful result. Due to the instabilities of the zwitterions derived from the hexamethylcyclohexadienone (60) and other Lewis acids, the number of points in the correlation is limited.

CONCLUSION

It was suggested in Chapter I of this thesis that by synthesizing a bicyclo[3.1.0]hexenyl cation with substituents at C_6 carefully selected in terms of their charge stabilizing ability, the energies of the ground and transition states of the degenerate cyclopropyl rearrangement might be made equal. Substituents with a still higher ability to stabilize positive charge were predicted to cause inversion of the roles of the transition state and ground state. The results presented and discussed in Chapter II confirm these predictions.

As it was shown that the bicyclo[3.1.0]hexenyl cation and the 5-acyl-1,2,3,4,5-pentamethylcyclopentadiene Lewis acid complexes rearrange by the same mechanism, a qualitative correlation can be drawn where the barrier to migration is plotted against the positive charge stabilizing ability of the C_6 substituent, Figure 22. The line A on the graph represents the cyclopropyl migration of the bicyclo[3.1.0]hexenyl cations and B illustrates the automerization of the Lewis acid-complexed 5-acyl-1,2,3,4,5-pentamethylcyclopentadienes. As the same mechanism is involved in the rearrangement of these systems, the lines A and B must meet at a point where the mono and the bicyclic species have the same energy. At this point, there will be a minimal activation barrier for the degenerate rearrangement.

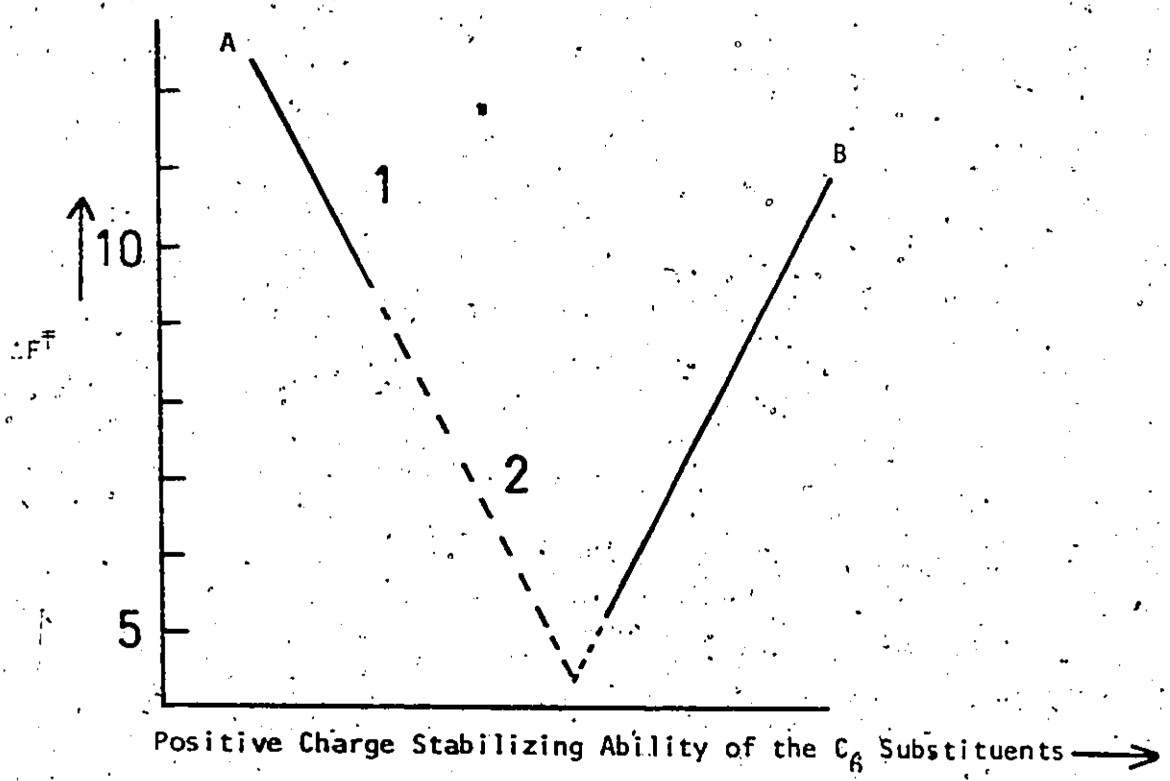


Figure 22 Activation Barrier for Migration as a Function of the Positive Charge Stabilizing Ability of the C_6 Substituents

The lowest value determined for the activation barrier associated with the migration of the zwitterions (line B) is 5.0 kcal/mole. No departure from linearity in line B was observed down to this point. It is evident that the energy barrier for the migration of C_6 when the two systems have the same energy must be well below 5 kcal/mole.

An interaction between the electron deficient C_6 and the filled orbitals of the diene becomes particularly interesting at this point. It has been shown that as the positive charge stabilizing ability of the C_6 substituent in the zwitterions decreases, the interaction between the diene moiety and the positive charge on C_6 increases. In other words, the non-classical interaction between the π electrons and C_6 becomes more pronounced as the electron withdrawing groups are bonded to C_6. If a Möbius type delocalization is present in these zwitterions it should become most pronounced and easily detected close to this point.

It was shown in the rearrangement of bicyclo[3.1.0]hexenyl cations that the very high stereoselectivity observed could be attributed to overlap of both lobes of the formally vacant p orbitals on C_6 with the diene. As the extent for this homoconjugative interaction will decrease as the C_6 substituent can more effectively stabilize charge, it is predicted that the migration will become less stereoselective. That is, on line A, the highest specificity should be observed in the region 1 and the lowest in area 2.

In view of the results obtained in this work, it is particularly interesting to consider the 1,5 migrations of the σ bonded cyclopentadienyl metal compounds.[43] The fluxional behaviour exhibited by these compounds can be considered to proceed via bicyclic species resulting from the overlap of an empty p or d orbital of the metal atom and the occupied π orbitals of the diene.[49] As such this proposed mechanism is directly comparable to that of the circumambulation of C_6 in the Lewis acid-complexed 5-acyl-1,2,3,4,5-pentamethylcyclopentadienes. It is particularly interesting that the structure of dimethyl (cyclopentadienyl) aluminum as derived from its electron scattering pattern corresponds to that required for a Möbius-type stabilization.[153]

CHAPTER III

EXPERIMENTAL

I. INSTRUMENTAL

(a) P.m.r. Spectra

P.m.r. spectra were obtained on Varian HA100, A60 and DP60IL spectrometers, all of which were equipped with variable temperature probes. The constant temperature of the probes on HA100 and A60 was maintained using Varian V4060 controllers and a V4540 was used on the DP60IL spectrometer. The practical range of the probes on the former two instruments was -100 to +200°. A somewhat wider range of temperature could be maintained on DP60IL spectrometer, the lowest temperature being -180° and the highest being 300°. These facilities were employed to observe the cations and the zwitterions in the range -160 to -10°, and kinetic studies at slightly higher temperatures.

The probe temperature was measured by a copper constantan wire thermocouple connected to a standardized potentiometer. Chemical shifts, all given in δ units, were measured relative to internal CH_2Cl_2 taken at 5.30 ppm. In all p.m.r. experiments performed on the HA100 or DP60IL spectrometers, the peak for $HFSO_3$, CH_2Cl_2 or the central peak of the triplet of $CHClF_2$ was used as the lock signal.

(b) Infrared Spectrometry

The infrared spectra of the compounds and zwitterions were recorded on Perkin-Elmer Model 337 grating spectrometer using NaCl or KBr cells. The calibration of the infrared spectra was carried out using the 1601 and 1984.5 cm^{-1} bands of polystyrene. All windows were polished before and after the ir spectra of the zwitterions were taken.

(c) Mass Spectrometry

A Consolidated Electrodynamics Corporation Model 21-110 high resolution, double focussing Mass Spectrometer was employed to determine the molecular weight of the ketones.

(d) Ultraviolet Spectrometry

The ultraviolet spectra were recorded with a Cary 14 spectrometer. Low temperature uv spectra were obtained using a special quartz Dewar fitted with four flat quartz windows through which the analyzing beam passed. The opening of the Dewar was fitted with a cork stopper bearing a nitrogen lead and gas exit. A variable voltage heater placed inside a large Dewar boiled off gaseous N_2 which was passed through the quartz Dewar containing the uv cell. The temperature of the sample was measured by a thermocouple connected to a standardized potentiometer.

(e) Vapor Phase Chromatography

Varian Aerograph 204 (analytical) and Aerograph Model A90-P3 (preparative) gas chromatographs were used. Helium was used as a carrier gas at 50-60 ml/min. The columns employed in conjunction with these instruments were 10 ft x 1/4" with 15% S.E. 30 on Chromosorb 60-80 and 8 ft x 1/8" with 15% S.E. 30 on Chromosorb 60-80.

(f) Analysis

Elemental analyses were performed by Galbraith Laboratories in

Knoxville, Tennessee. Liquid samples were purified using vapor phase chromatography before being sealed in clean 1/8" glass tubing. Solid samples were sublimed twice under vacuum and sent for analysis in clear vials.

2. REAGENTS

$HFSO_3$ was distilled from sodium fluoride (400 ml/gm). The first distillate was redistilled through a 12" glass column and stored as 1 ml aliquots in sealed glass ampoules. Antimony pentafluoride was distilled before use and kept in a teflon container. Reagent grade 96% H_2SO_4 was used as supplied. Aqueous H_2SO_4 solutions were prepared by dissolving an appropriate amount of 96% H_2SO_4 in distilled water. Reagent grade diethyl ether and methylene chloride for extraction purposes were used as supplied.

Methylene chloride, used as the solvent in the preparation of the zwitterions, was purified as described by Wood and Jones.[122] Reagent grade CH_2Cl_2 (500 ml) was refluxed with Al_2Cl_6 overnight and distilled. The distillate was washed with water (3 x 500 ml), dried ($CaCl_2$) and redistilled twice from P_2O_5.

Aluminum chloride (reagent grade) was sublimed twice <u>in vacuo</u>, the second sublimation being after the addition of an equal amount of Al powder.

Boron trihalides (BBr_3, BCl_3 and BF_3) were vacuum distilled twice before use. $CHClF_2$ (Freon 22) and sulfuryl chloride fluoride were used as supplied.

3. General Techniques

(a) Protonations

(i) Protonations were carried out by slowly adding the cation precursor in CH_2Cl_2 (20 mg in 0.2 ml) down the side of a clean dry nmr tube which contained $HFSO_3$ (0.5 ml) at -78°. Protonation was achieved when the organic base was extracted into the acid layer by agitating the sample with a precooled (liquid N_2) 2 mm quartz rod.

(ii) CH_2Cl_2 was excluded in the preparation of cations which were subsequently used for photochemical isomerizations. The cation precursor (usually a cyclohexadiene derivative) ca 20 mg was placed in a clean dry clear-walled nmr tube and cooled to -78°. A thin-walled capillary dropper used for introducing acid was cooled by alternatively withdrawing the cold $HFSO_3$ (-78°) from the ampoule into the dropper and expelling it back to the ampoule. After several repetitions, the precooled (-78°) acid was transferred to the nmr tube and the sample was agitated by means of a precooled 2 mm quartz rod. The dissolution of the precursor was usually slow as it was frozen at -78°. No attempt was made to warm the sample above that temperature. Protonation was usually complete after 10 mins.

(iii) Preparation of cations in H_2SO_4 was performed at -5°. H_2SO_4 (0.5 ml) in an nmr tube was cooled for 30 min., in a salt-ice mixture. The cation precursor ca 20 mg in 0.2 ml CH_2Cl_2 was introduced onto the acid through a long pipette. The extraction of the base into H_2SO_4 was done as described previously.

(b) Quenching of the Acid Solutions

The acid solution of the cation was added dropwise to the rapidly stirred mixture of sodium-bicarbonate (5 g) in ether (25 ml) kept at -78°. The dry ice-acetone bath was removed and the mixture was allowed to warm-up to 0°C. Ice water (10 ml) was added and the mixture was stirred for another 15 minutes, and filtered in vacuo. The ether layer was washed with saturated $NaHCO_3$ (2 x 25 ml) and dried ($MgSO_4$). Evaporation of the solvent lead to the recovery of the product which was analyzed using vapor phase chromatography.

(c) Cooling Apparatus

For the low temperature photoisomerizations of benzenonium ions, a cooling system capable of maintaining a constant temperature over the range -65° to -90° is required. The apparatus used consisted of a double-walled quartz tube which was fitted tightly onto a two-holed stopper which was secured on the mouth of a 2 gallon dewer of liquid nitrogen. An electrical lead from a 250 watt heater placed well below the level of liquid nitrogen, was placed through the second hole. This lead was connected to a rheostat. By heating the heater, gaseous nitrogen was boiled up through the inside of the quartz tube. The rate of the flow of nitrogen, and hence the temperature of the sample suspended inside the quartz tube, could be controlled by adjusting the power supply of the heater.

By means of this equipment, a stable temperature was maintained over a period of several hours. The temperature of the sample was measured by a thermocouple inserted into the sample which was covered with a glass tube to avoid corrosion. It was found that, depending upon the light source used, the temperature of the sample increased by 10-25° upon irradiation.

Ultraviolet Source

The light from a Philips SP-500 High pressure lamp in conjunction with a pyrex glass fitter was used for a preliminary investigation. A photoequilibrium was reached in 30 min. By the comparison of the peak areas for 2,6 dimethyl signals of the benzenonium ion and the peak areas for 1,5 dimethyl resonance of the bicyclic cations, it was found that the percentage isomerization was only 66%. A Toshiba 125 watt medium pressure Hg light source proved to be better. A 95% conversion was achieved in 3 hours. The Toshiba light source was used in all subsequent isomerizations.

(d) Preparation of the Zwitterions

METHOD (i)

Purified Al_2Cl_6 (ca 7.00 mg) was weighed out accurately in a clear-walled nmr tube and dissolved in anhydrous CH_2Cl_2 (1.0 ml). The sample had to be shaken occasionally to obtain a clear solution. The Al_2Cl_6 solution was then cooled to -78° for 15 min. An appropriate amount (0.9 equivalent) of a ketone dissolved in CH_2Cl_2 (0.2 ml) was added slowly to the solution of Al_2Cl_6. The mixture was agitated with a 2 mm quartz rod. A rapid formation of the zwitterion occurred. For the preparation of zwitterion solutions with higher concentrations, the required amount of Al_2Cl_6 was suspended in CH_2Cl_2 (1 ml) and the ketone added. The Al_2Cl_6 dissolved upon the formation of the zwitterion. The entire operation was performed in a dry box.

Vacuum Line Technique

Al_2Cl_6 (ca 25 mg) was weighed out accurately in a 20 ml reaction vessel containing a stirrer bar with an nmr tube attached to the side arm. The vessel was then attached to a high vacuum line and evacuated (30 min.). The appropriate solvent, CH_2Cl_2 or $CHClF_2$ (5 ml), was distilled into the vessel while it was cooled with liquid nitrogen. This mixture was warmed to -78° and stirred until solution of the Lewis acid occurred.

The vessel was then cooled in liquid nitrogen and the ketone ([illegible] of an equivalent) distilled in. An occasional warming of the ampoule containing the ketone was required. The reaction mixture was warmed to -78° and stirred for 10 min. The reaction vessel was detached from the vacuum line and placed in a large dewer containing a dry ice-acetone mixture so that the nmr tube and the side arm were kept at -78°. About 0.5 ml of the solution was transferred into the nmr tube by tilting the vessel. The nmr tube was then sealed under vacuum.

METHOD (ii)

When boron trihalides were used as Lewis acids, a reverse addition method was applied. The ketone (0.9 equivalent) was placed in the reaction vessel and the appropriate solvent, CH_2Cl_2 or $CHClF_2$ distilled in. The solution of the ketone was cooled in liquid nitrogen and the Lewis acid (1 equivalent) was distilled into the reaction vessel. The mixture was warmed to -78°, stirred and the solution transferred as described in the above method.

METHOD (iii) For U.V. Measurements

The zwitterions were prepared as in Method (i) except that a 200 ml reaction flask equipped with a stirrer bar and fitted with a side arm leading to a 2 mm quartz cuvette was used. CH_2Cl_2 was distilled three times from P_2O_5, the last two distillations being done on the vacuum line.

The uv spectra of the zwitterions were measured at 25°. The spectra were reproducible up to 12 hours, after which the colour of the sample turned brown and some precipitates were observed.

(e) Quenching the Zwitterions

A mixture of ice/water (20 ml) was stirred very rapidly using a magnetic stirrer. CH_2Cl_2 solution of the zwitterion was added dropwise on the rotating stirring bar so that an immediate mixing resulted. The mixture was warmed to +25°, ether (20 ml) was added and stirred for 15 min. The ether layer was separated, washed with saturated $NaHCO_3$ solution (2 x 20 ml), water (3 x 20 ml) and dried ($MgSO_4$). Evaporation of ether in vacuo resulted in the recovery of the product.

4. (a) Kinetic Studies

Studies of the rates of rearrangements were performed on p.m.r. samples by following the changes in the p.m.r. spectrum with time. All kinetic studies on cations undergoing irreversible isomerizations were carried out at least three times, the first study being exploratory in nature. The temperature of the probe was adjusted to ca -80°, the sample was taken out from a low temperature bath (-78°) and was inserted into the probe. The sample was warmed with an interval of 5° and the p.m.r. spectrum was recorded. The process was continued until a temperature was reached where the rate of isomerization was reasonably fast as judged from the change in p.m.r. spectrum. The temperature was noted.

The temperature of the probe was maintained at the selected temperature for at least 15 min. prior to the introduction of the second sample into the probe. The progress of thermal isomerization was followed by recording the decrease in the intensity of a p.m.r. signal attributable to the starting material with time. Rate constants for the reaction were calculated for each time interval from the corrected height of the signal that was being observed. Normally, the decrease in the intensity of a signal from the starting material was followed to about 4 half-lives. The rate constant was calculated from the first-order rate equation:

$$A = A_o e^{-kT} \tag{69}$$

so that

$$k = \frac{\ln(A_o - A)}{T}$$

where A_o = intensity of the signal at the time $t = 0$,

A = intensity of the signal at time t, and

T = time

The rate constant for the reaction k, was calculated as shown in equation

$$k = \frac{\Sigma k_i}{n}$$

n = number of k_i being determined.

The determination of the rate constant for isomerization was repeated until a consistant result was obtained. The average deviation (d) of the individual rate constants in each set of isomerizations was calculated as

$$d = \frac{\Sigma|k_i - k|}{n}$$

where d = average deviation

k_i = individual rate constants

k = average rate constant

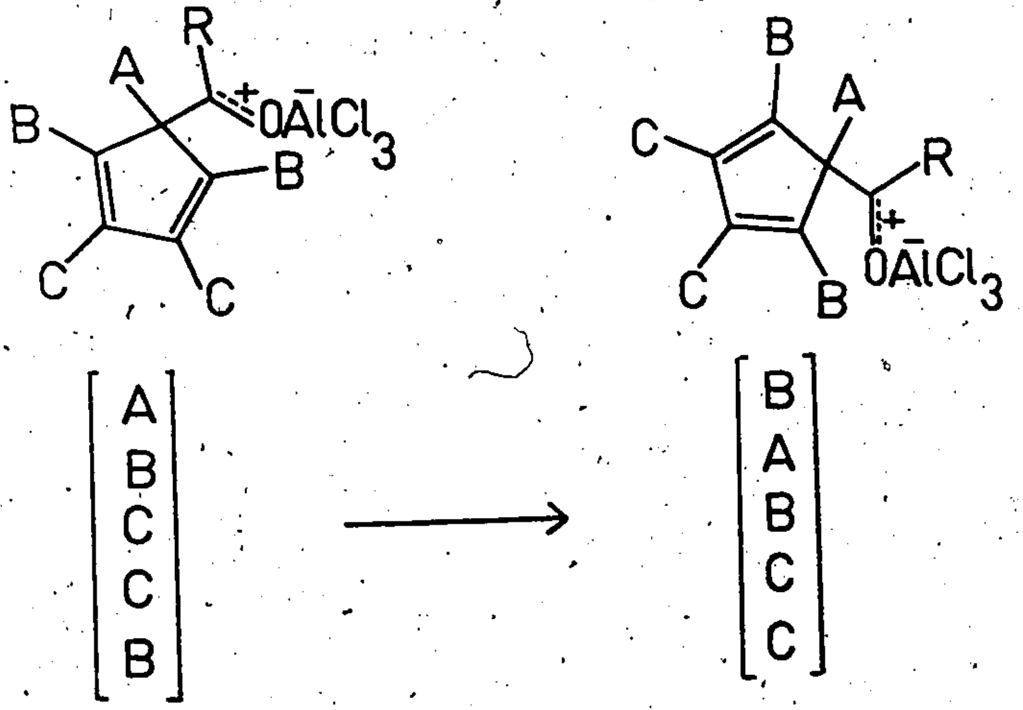
n = number of k_i being determined.

The temperature of the probe was measured before and after a kinetic run and the average value was taken.

(b) A Typical Line-Shape Calculation

A Saunders many site nmr line-shape program[91] was used for calculating line-shapes for the systems undergoing rapid exchange.

Consider the one-step migration of C_6 in the following system. The transformation affected on the substituents due to a single migration is shown below.



In this migration, the number of signals undergoing exchange was three, viz. A, B and C. When the averaging took place, an equilibrium population of the individual signals would be 0.2, 0.4 and 0.4, since their relative intensities were 1:2:2. From the above table, the signal for the substituent A is transformed to B with the transition probability 1.00. In contrast, B could either be transformed to C or to A. The transition probability is 0.50 in each case. Similarly, the signal for C could undergo two transitions. The transition could occur to another site C or to B, again with transition probabilities 0.50. Line widths of the p.m.r. signals in the absence of an exchange was determined from the limiting low temperature spectrum.

The above information was fed into the computer together with the frequencies at which the resonance signals appeared in the absence of exchange. The computer was then programmed to calculate the position and intensities of the p.m.r. signals undergoing averaging with a given rate constant.

A typical print-out from the computer consisted of a series of frequencies increasing with equal intervals over the prescribed range and another column consisting of relative intensities of the signals at each frequency value. Half-width and relative intensity of the maxima and minima of each peak was also given.

The rate of migration was established when a good agreement between the experimental and calculated spectra was obtained. The comparison was either made by a visual method (medium exchange rates), or by comparing peak heights (slow rates). The method employed in each case is given in the appropriate tables.

(c) A Typical Calculation of the Error Limits for Activation Barriers

The calculation of the error limits for the free energies of activation associated with the degenerate rearrangements discussed in this thesis was made taking into consideration that there is a propagation of errors. Relative errors are additive under the operations of multiplication and division while absolute errors are additive under addition and subtraction of the variable parameters.[154]

Thus in the degenerate rearrangement of $AlCl_3$-complexed-5-*p*-methoxybenzoyl-1,2,3,4,5-pentamethylcyclopentadiene (80c), the migration of C_6 occurs with a rate constant of 26 sec^{-1}, at -55°. A variation of 2 sec^{-1} in the rate constant was within the limits of detection. The temperature variation was ± 5°.

Rate = 23 ± 2 sec^{-1}, at -55 ± 5°.

The relative error in the rate constant $= \frac{\Delta k_r}{k_r} = \frac{2}{23}$

and the Relative error in the temperature $= \frac{\Delta T}{T} = \frac{5}{218}$

The error limit for the equilibrium constant $\Delta K^{\ddagger}$ can be calculated from

$k_r = \frac{kT}{h} K^{\ddagger}$, k_r = rate constant, k = Boltzmann's Constant,

h = Plancks Constant, T = temperature in °K.

$$K^{\ddagger} = \frac{k_r h}{kT}$$

$$\frac{\Delta K^{\ddagger}}{K^{\ddagger}} = \left[\left(\frac{\Delta k_r}{k_r}\right)^2 + \left(\frac{\Delta T}{T}\right)^2\right]^{\frac{1}{2}}$$

$$= [(0.0870)^2 + (0.0229)^2]^{\frac{1}{2}}$$

$$= [0.00761 + (0.000526)]^{\frac{1}{2}}$$

$$\frac{\Delta K^{\ddagger}}{K^{\ddagger}} = (0.00814)^{\frac{1}{2}}$$

$$= 0.0902$$

$$\Delta \ell_n K^{\ddagger} = \frac{\Delta K^{\ddagger}}{K^{\ddagger}}$$

The relative error for $\ell_n K^{\ddagger}$ will then be

$$\frac{\Delta \ell_n K^{\ddagger}}{\ell_n K^{\ddagger}} = \frac{\Delta K^{\ddagger}}{K^{\ddagger}} \times \frac{1}{\ell_n K^{\ddagger}}$$

$$= 0.0902 \times \frac{1}{26.01} \qquad \ell_n K^{\ddagger} = 26.01$$

$$= 0.00346$$

Relative error for the activation barrier $\frac{\Delta\Delta F^{\ddagger}}{\Delta F^{\ddagger}}$ will be the sum of the relative errors in the temperature and $\ell_n K^{\ddagger}$, since

$$\Delta F^{\ddagger} = -RT\ell_n K^{\ddagger}$$

$$\frac{\Delta\Delta F^{\ddagger}}{\Delta F^{\ddagger}} = \left[\left(\frac{\Delta \ell_n K^{\ddagger}}{\ell_n K^{\ddagger}}\right)^2 + \left(\frac{\Delta T}{T}\right)^2\right]^{\frac{1}{2}} = (0.000120 + 0.000526)^{\frac{1}{2}} = (0.00538)^{\frac{1}{2}}$$

70

$$\frac{\Delta\Delta F^{\ddagger}}{\Delta F^{\ddagger}} = 0.0232.$$

The error limit for the activation barrier of 87d = 0.0232 x 11.2

= 0.260 kcal.

Activation barrier for the degenerate rearrangement of 87d = 11.2 ± 0.3 kcal/mole.

(d) A Typical Calculation of the Error Limits for Activation Energies and the Entropies of Activation

The error limits for Ea and $\Delta S^{\ddagger}$ were calculated from Arrhenius Plots for the circumambulation of $AlCl_3$-complexed-5-acyl-1,2,3,4,5-pentamethylcyclopentadienes. The magnitudes of these error limits are large since the Arrhenius plots were made over a small range of temperature.

In the degenerate rearrangement of $AlCl_3$-complexed-5-p-methoxybenzoyl-1,2,3,4,5-pentamethylcyclopentadiene (80c), the rate constants estimated ranges from 1.5 ± 0.5 sec^{-1} at -75° to 37 ± 2 sec^{-1} at -50°.

The relative error in the rate constants can be calculated as shown below.

$$\frac{\Delta k_1}{k_1} = \frac{0.5}{1.5} = 0.333$$

and

$$\frac{\Delta k_2}{k_2} = \frac{2}{37} = 0.0541$$

$$\text{Relative error in the rates} = \left[\left(\frac{\Delta k_1}{k_1}\right)^2 + \left(\frac{\Delta k_2}{k_2}\right)^2\right]^{\frac{1}{2}}$$

$$= [0.00292 + 0.111]^{\frac{1}{2}}$$

$$= 0.337$$

$$\text{Relative error in } \log k = \frac{0.337}{\log k_2 - \log k_1} = \frac{0.337}{1.39} = 0.242$$

$$\text{Relative error in temperature} = \frac{\Delta T_1}{T_1} + \frac{\Delta T_2}{T_2} = \frac{990.0 + 1115.0}{223 \times 198} = 0.0476$$

The error limit in the slope can be calculated from the formula

$$\text{slope} = \frac{\Delta \log k}{\Delta T}$$

so that

$$\frac{\Delta Ea}{Ea} = [(\Delta\Delta \log k)^2 + (\Delta\Delta T)^2]^{\frac{1}{2}}$$

where $\frac{\Delta Ea}{Ea}$ = relative error for activation energy

$\Delta\Delta \log k$ = relative error in log k

$\Delta\Delta T$ = relative error in temperature

$$\therefore \frac{\Delta Ea}{Ea} = [(0.0476)^2 + (0.242)^2]^{\frac{1}{2}} = [0.002272 + 0.05856]^{\frac{1}{2}} = 0.246$$

Since Ea = 12.1 kcal/mole, we have

ΔEa = 2.9 kcal/mole

Using the same argument, the relative error for the intercept was calculated as ± 0.24. In the calculation of the entropy of activation, $\Delta S^{\ddagger}$, the following relationship was used.

$$A \simeq \frac{kT}{h} e^{\frac{\Delta S^{\ddagger}}{R}}$$

where k = Boltzmann's Constant

T = Temperature

h = Planck's Constant, and

R = Universal gas constant.

The two limits for the magnitude of the entropy of activation can be calculated using (i) the upper limit for log A and the lower limit for temperature and (ii) the lower limit for log A and the upper limit for temperature.

$$\log A = 13.3 \pm 3.2$$

(i) $\log A_1 = 16.5$ Temperature = 228°K

$$\frac{kT}{h} = \frac{1.38 \times 228 \times 10^{11}}{6.626}$$

$$= 4.75 \times 10^{12}$$

$$\log \frac{kT}{h} = 29.193$$

$$\frac{\Delta S_1^{\ddagger}}{R} = 2.303 \log A_1 - 2.303 \log \frac{kT}{h}$$

$$= (2.303 \times 16.5) - 29.193$$

$$= 8.81$$

$$\Delta S_1^{\ddagger} = 8.81 \times 1.983 \text{ eu}$$

$$= 17.5 \text{ eu}$$

Absolute error in $\Delta S^{\ddagger} = 17.5 - 3.2 = +14.5$ eu.

Similarly, $\Delta S_2^{\ddagger} = -11.3$ eu

Absolute error in $\Delta S^{\ddagger} = -11.3 - 3.2 = -14.5$ eu

Entropy of activation = 3.2 ± 14.5 eu.

6. Synthesis of 5-Acyl-pentamethylcyclopentadiene

Pentamethylcyclopentadiene (71) is an important intermediate in the synthesis of 5-acyl-pentamethylcyclopentadienes. A detailed procedure for the synthesis of 71 was not published by de Vries. However, in a report given to Professor S Winstein by de Vries, the synthesis of 71 was discussed in detail. A series of steps involved in the preparation of pentamethylcyclopentadiene as reported by de Vries is given below.

(a) Di(sec)-2-butenyl carbinol

Lithium ribbon (5 g), cut into small pieces, was stirred in dry ether (1 ℓ) by means of a mechanical stirrer. 2-Bromo-2-butene (50 g) was added dropwise over a period of 3 hours. Vigorous stirring was continued (2 hrs.) until all the lithium dissolved. Tiglaldehyde (30 g) was added at a rate sufficient to cause a mild reflux. After an additional stirring period (2 hours) the dark brown solution was decomposed by the addition of saturated ammonium chloride solution (500 ml). The light yellow ether layer was separated and the aqueous layer was extracted with ether (3 x 500 ml) and dried over anhydrous $MgSO_4$. Distillation yielded the required carbinol. Yield, 35 g, 70%, b.p. 44°/1.5 mm (reported 56°/1.5 mm). Ir (thin film) $\nu_{C=C}$ 1632, 3000 and ν_{O-H} 3500 cm^{-1} (reported 1632 cm^{-1}).

(b) Active Manganese Dioxide

Active manganese dioxide was prepared as reported by Attenburrow.[121]

(c) Di(sec)-2-butenyl Ketone

Di-2-butenyl carbinol (30 g) was stirred for 24 hr. with active manganese dioxide (210 g) in light petroleum ether (5 ℓ), b.p. < 45°. The solid MnO_2 was filtered off, and washed with light petroleum ether. The solvent was removed in vacuo without heating. Distillation of the residue yielded ~~the~~ the colourless di-2-butenyl ketone. Yield, 20 g, 68%, b.p. 50-52°/3 mm (reported 58°/4.2 mm). Ir (thin film) $\nu_{C=O}$ 1642 and $\nu_{C=C}$ 3000 cm^{-1} (reported 1642 cm^{-1}).

(d) 2,3,4,5-Tetramethylcyclopent-2-en-1-one

Di-2-butenyl ketone (20 g) was added slowly to a mixture of 85%

phosphoric acid (8 g) and 98% formic acid (26 g) kept at 85° under nitrogen. The mixture was stirred for 5 hr., by which time the colour had changed to greenish yellow. Upon cooling, the solution was added to ice-cold water (1 ℓ). The organic product was extracted with ether (4 x 100 ml), washed with 5% aqueous Na_2CO_3 solution (4 x 100 ml), water (4 x 100 ml) and dried over $MgSO_4$. Removal of ether <u>in vacuo</u> and distillation gave 2,3,4,5-tetramethylcyclopent-2-en-1-one. Yield, 19g, 95%, b.p. 40°/0.6 mm (reported 60-61°/3 mm). Ir (thin film) $\nu_{C=O}$ 1700, $\nu_{C=C}$ 1650 and 3000 cm^{-1} (reported 1700, 1650 cm^{-1}).

(e) 1,2,3,4,5-Pentamethylcyclopentenol

Tetramethylcyclopentenone (19 g) was dissolved in anhydrous ether (500 ml) in a two-necked flask equipped with a reflux condenser and a dropping funnel. Methyllithium (73 ml, 2.2 M solution in ether) was added dropwise. The stirring was continued for 2 hr when a saturated ammonium chloride solution (50 ml) was added. The ether layer was separated, washed with water (3 x 100 ml) and dried ($MgSO_4$). Removal of ether gave a pale yellow oil (20 g) which was used without further purification. Yield, 20g, 94%. Ir (thin film) ν_{O-H} 3400, $\nu_{C=C}$ 2950(m) cm^{-1}. Ir data for this compound not reported.

(f) 1,2,3,4,5-Pentamethylcyclopentadiene

Iodine (0.6 g) in small amounts was added to crude pentamethylcyclopentenol. The tertiary alcohol turned cloudy and droplets of water started to appear. Stirring was continued for 30 min when the reaction mixture was taken up in ether (100 ml). The ether layer was washed with acidified 5% sodium thiosulfate solution (2 x 25 ml), 5% sodium carbonate solution (2 x 25 ml), water (2 x 25 ml) and dried over $MnSO_4$. Removal of the ether and distillation gave pentamethylcyclopentadiene. Yield, 14.5 g, 82%, b.p. 60°/20 mm (reported 60-61°/20 mm). Ir (thin film) $\nu_{C=C-C=C}$ 1650(m) 1620 cm^{-1}(w) (reported 1653, 1620 cm^{-1}). P.m.r. (CCl_4) 1.10 (d, 3H, J=7.5), 1.80 (12 H), 2.57δ (m, 1H).

(g) General Method for the Preparation of 5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes

To pentamethylcyclopentadiene (1.36 g, 10 mmol) dissolved in anhydrous ether (100 ml), n-butyllithium (3 ml, 22% in n-hexane solution) was added gently at room temperature. An exothermic reaction occurred with the formation of a white precipitate of lithium pentamethylcyclopentadienide.[104] The appropriate acid chloride (10 mm) in ether was added dropwise at a rate sufficient to cause a gentle reflux. The mixture was stirred for 3 hours. Water (300 ml) was added, the organic layer separated, washed with saturated $NaHCO_3$ solution (3 x 50 ml) and water (2 x 50 ml). The ether solution was dried over anhydrous $MgSO_4$, the solvent was removed and the crude product chromatographed on a column of neutral alumina (activity I). The ketones were eluted with ether (5%) in pentane. The yields, ir data and the elemental analyses are given in Table XX.

6. Ethylpentamethylcyclopentadiene-5-carboxylate

Pentamethylcyclopentadiene (3.72 g) dissolved in ether (100 ml) was allowed to react with n-butyllithium (6 ml, 22% in n-hexane solution) as described previously.[104] Ethylchloroformate (2.82 g) in dry ether (25 ml) was added dropwise at such a rate to maintain a rapid reflux.

TABLE XX Properties and Analyses of 5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes[a]

				Analysis				
Compound	%	mp	$\nu_{C=O}$	Calc.		Found		m/e
	Yield	°C	cm^{-1}	C%	H%	C%	H%	
70b	65	b	1691	81.18	10.50	81.35	10.63	192
70c	66	136	1655	79.95	8.22	80.07	8.20	270
70d	70	124	1651	80.23	8.52	80.09	8.43	284
70e	60	b	1662	84.97	8.73	84.71	8.53	254
70f	71	97	1660	85.07	9.54	85.41	9.48	296
70g	68	b	1668	84.94	8.40	84.72	8.31	240
70h	69	126	1666	74.28	6.98	74.08	6.94	274
70i	58	b	1677	70.10	6.22	70.28	5.99	308

[a] P.m.r. spectra are given in Table VI

[b] Liquid

After an additional stirring period (2 hours), a saturated NH_4Cl solution (50 ml) was added, the ether layer separated, washed with water (2 x 50 ml) and dried ($MgSO_4$). Removal of the ether and distillation gave ethylpentamethylcyclopentadiene-5-carboxylate. Yield, 3.5 g, 83%, b.p. 60°/0.5 mm (reported 58-60°/0.5 mm). Ir (thin film) $\nu_{C=C}$ 3000, $\nu_{C=O}$ 1640 cm^{-1} (reported 1654 cm^{-1}). P.m.r. (CCl_4): 0.90 (t, 3H, J=7.5Hz); 3.99 (q, 2H, J=7.5Hz); 1.14(3H); 1.74δ(12 H).

7. Synthesis of 2,3,4,5,6,6-Hexamethylcyclohexa-2,4-dienone (60)

To an ice-cold solution of 30% H_2O_2 (21 ml) acetic anhydride (120 ml) and acetic acid (35 ml) was added. The mixture was stirred for 15 min., sulfuric acid (30 ml) was added slowly from a dropping funnel while the mixture was stirred very gently. The stirring was continued for 30 min. This solution was slowly added to the stirred solution of hexamethylbenzene (31.2 g) in methylene chloride (100 ml), acetic acid (300 ml) and sulfuric acid (200 ml) kept at 20°. The stirring was continued for 3 hr., after the addition was completed. The product was poured onto ice (300 g) and extracted with CH_2Cl_2 (8 x 100 ml). The extracts were combined and washed with saturated $NaHCO_3$ solution (2 x 500 ml) and water (2 x 50 ml) and dried (Na_2CO_3). The solvent was removed, absolute methanol (100 ml) added and the solution left in the ice-compartment overnight. Hexamethylbenzene was filtered off and the solvent was removed *in vacuo*. Distillation under vacuum gave 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dienone. Yield, 29.5 g, 86%, b.p. 60-62°/0.5 mm. Ir (thin film) $\nu_{C=O}$ 1645 and $\nu_{C=C}$ 1565 cm^{-1} (reported 1647 and 1567 cm^{-1}). P.m.r. (CCl_4): 1.11 (2H); 1.86 (3H) and 2.03δ (1H).

8. Synthesis of 6-Ethyl-1,2,4,5,6-pentamethyl-3 methylene-cyclohexa-1,4-diene

Lithium ribbon (0.15 g), cut into small pieces was stirred in dry ether (50 ml) while ethyl bromide (1.19 g) dissolved in ether (5 ml) was added slowly. The mixture was stirred until all the lithium pieces dissolved (approximately 45 min.). The above dienone 60 (1.78 g) was dissolved in ether (10 ml) and added dropwise at such a rate so as to maintain a mild refluxing. The mixture was refluxed for 1 hr., after the addition was completed. The excess lithium reagent was destroyed by the addition of saturated NH_4Cl solution (15 ml) and the ether layer separated and dried (Na_2CO_3). The ether was evaporated *in vacuo* and the residue dissolved in pentane. The product was extracted into conc. hydrochloric acid (3 x 20 ml) which was then poured onto ice (50 g), neutralized with solid $NaHCO_3$ and extracted again with pentane. The pentane solution was dried over anhydrous Na_2CO_3. Removal of pentane gave the required product. Yield, 1.8 g, 71%. Ir $\nu_{C=C}$ 3100 cm^{-1}, m/e (parent peak) = 178. P.m.r. (CCl_4): 0.59 (t, 3H, J=7.5Hz); 1.59 (q, 2H, J=7.5Hz); 1.14 (3H); 1.82 (3H); 1.88 (3H); 4.80δ (2H).

9. Synthesis of 1,2,4,6,6-Pentamethyl-3-methylenecyclohexa-1,4-diene (67)

To a suspension of lithium aluminum hydride (0.2 g) in ether (50 ml) a solution of 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dienone (1.78 g) in ether (5 ml) was added dropwise. The mixture was refluxed for 30 min., and the excess $LiAlH_4$ was destroyed by the addition of saturated ammonium chloride solution (15 ml). The secondary alcohol was extracted with ether (3 x 25 ml) and dried over anhydrous Na_2CO_3. After the removal of the solvent, the crude product was dissolved in dry pyridine (50 ml), 6 drops of conc. HCl was added and the resulting solution boiled for 30 min. The product was poured into water (300 ml) and extracted with ether (3 x 25 ml). The extract was washed with water and dried (Na_2CO_3). Removal of the ether gave 1,2,4,6,6-pentamethyl-3-methylenecyclohexa-1,4-diene. Yield, 15 g, 71%. Ir $\nu_{C=C}$ 1645 cm^{-1}, m/e (parent peak) = 162. P.m.r. (CCl_4): 1.08 (6H); 1.84 (9H); 2.83 (1H); 2.88 (1H); 3.45δ (1H).

10. The Characterization of the Product from the Thermal Rearrangement of 73a

The solution of 73a was made by extracting a solution of 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene (178 mg) in methylene chloride (1 ml) into $HFSO_3$ (2 ml) kept at -78°. The formation of the dication was confirmed by recording the low temperature p.m.r. spectrum. The sample was gradually warmed to 40° and kept for 2 hours.

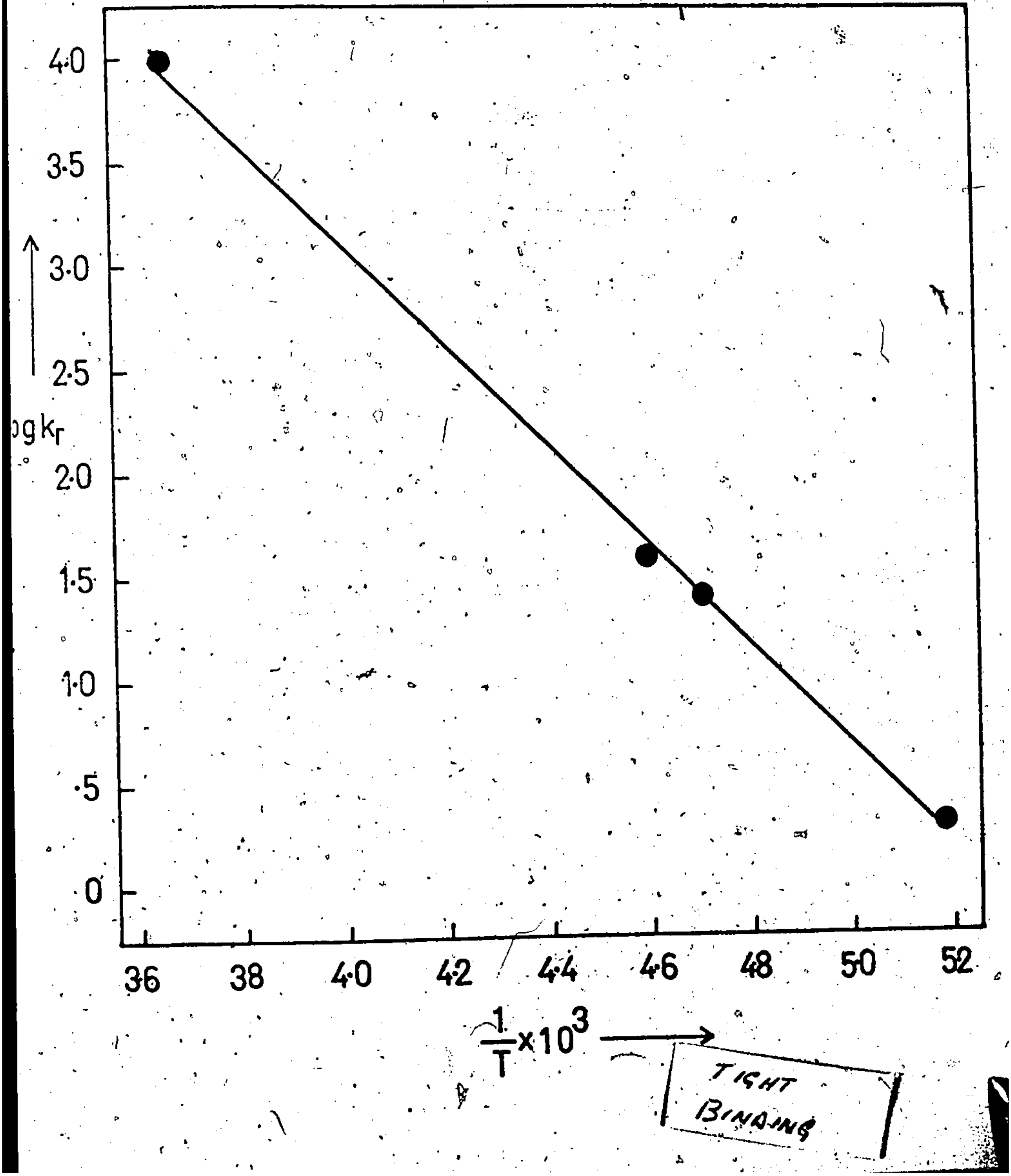
A suspension of sodium bicarbonate (5 g) in ether (25 ml) was stirred at -78° while the acid solution was added dropwise. The resulting mixture was warmed to 0°. Ice-water was added to the mixture and the stirring was continued for 15 min. The resulting solution was filtered *in vacuo* and the filtrate extracted with ether (3 x 25 ml). The extract was dried (Na_2CO_3) and evaporation of ether *in vacuo* yielded 148 mg of organic material.

The product was characterized as pentamethylcyclopentadiene by the comparison of its p.m.r. spectrum with that of an authentic sample. No other signal was observed in the p.m.r. spectrum of the product. Only two peaks were observed on the chromatogram when the product was subjected to vpc analysis using 8 ft x 1/8" 15% SE30 column as well as 8 ft x 1/8" 20% carbowax on chromasorb 60-80 columns.

The ratio of the peaks was determined by cutting the area under the peaks and weighing. The ratio of the amount of the major product to that of the minor was 19:1. The major product was collected and identified as pentamethylcyclopentadiene by the comparison of the p.m.r. spectra with an authentic sample.

Figure 23 Arhenius Plots for the Circumambulation of $AlCl_3$-Complexed 5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes.

Figure 23a Compound 80a



TIGHT BINDING

Figure 23b Compound <u>80b</u>

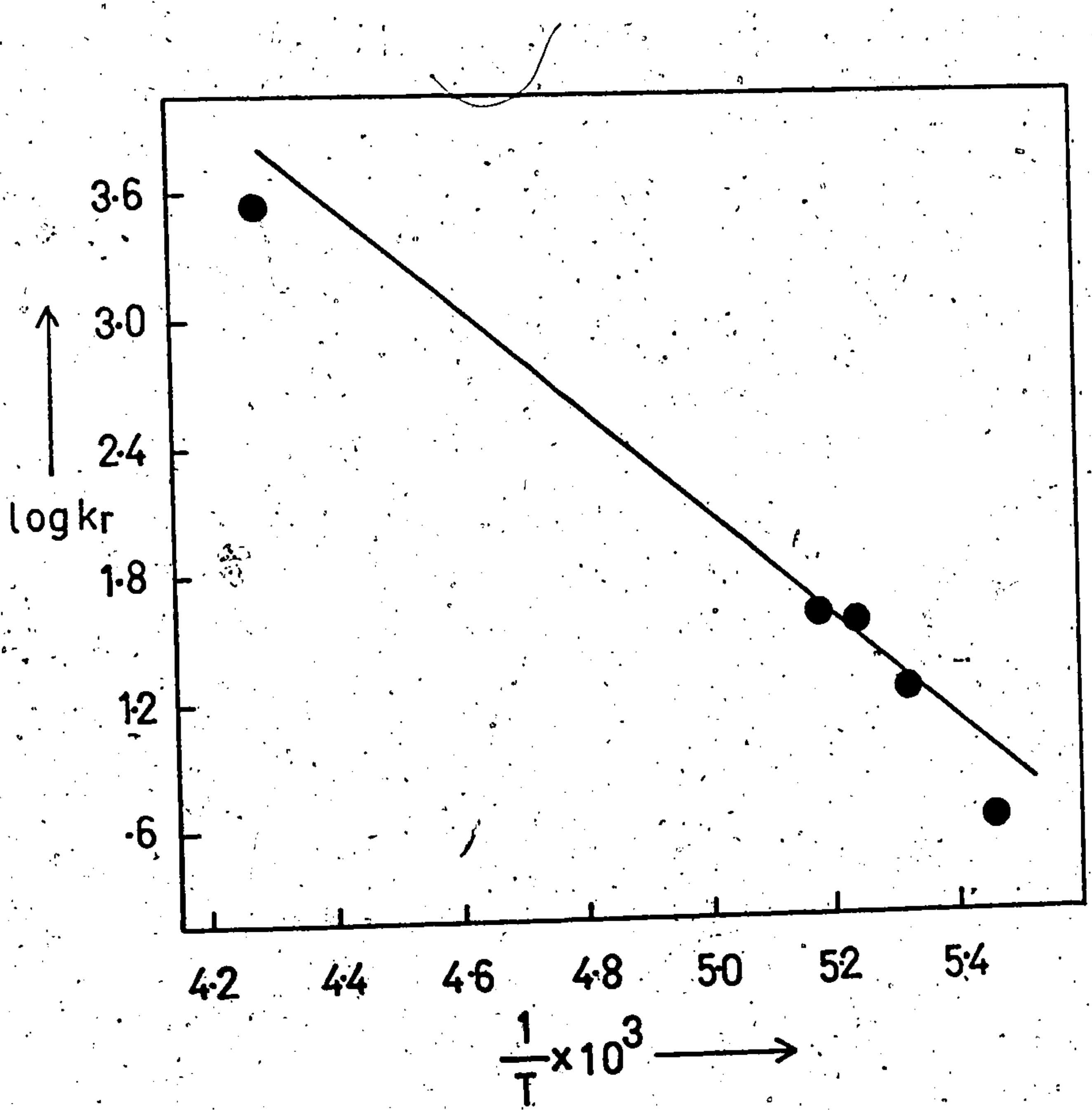


Figure 23c Compound <u>80c</u>

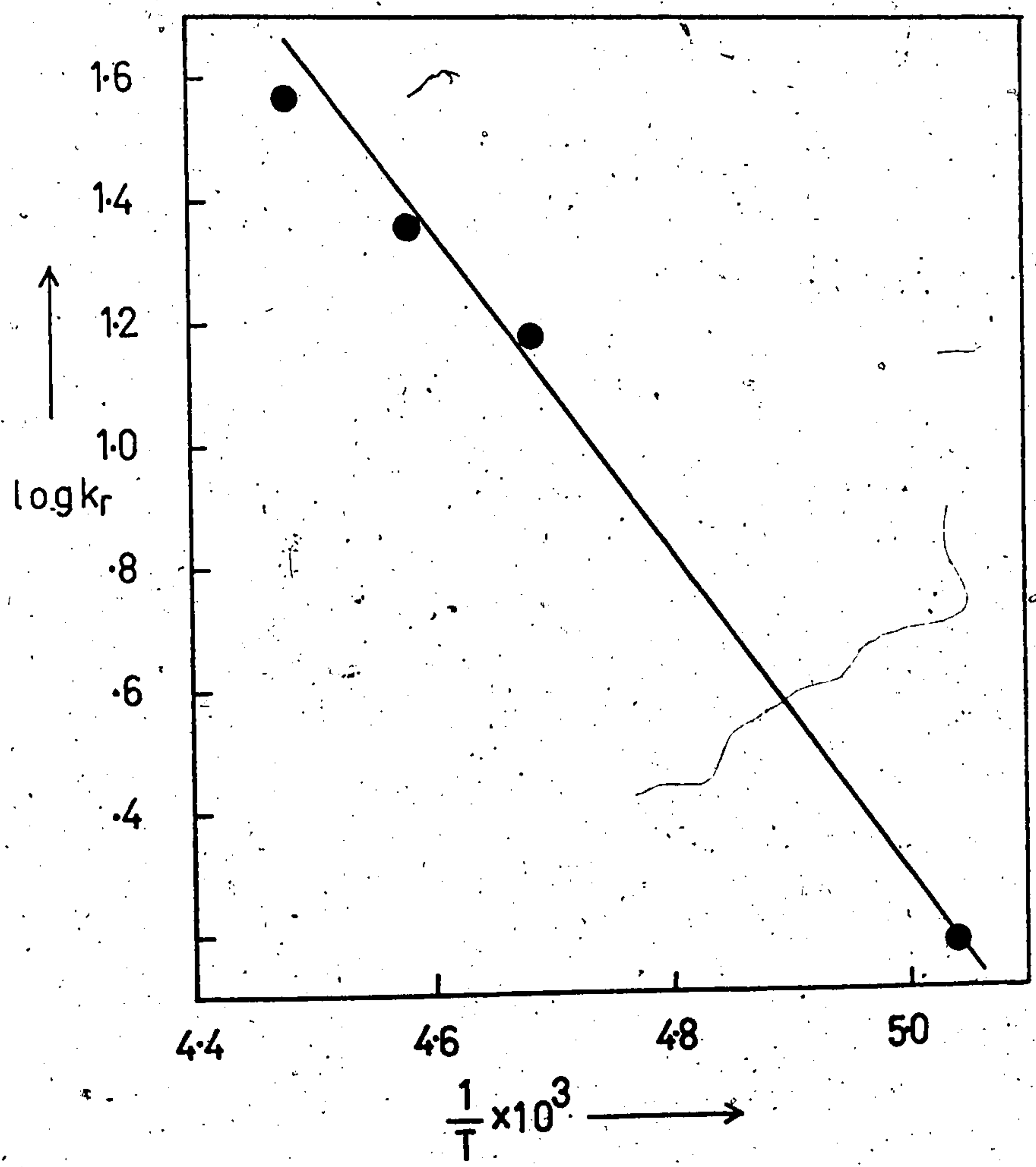


Figure 23d Compound 80d

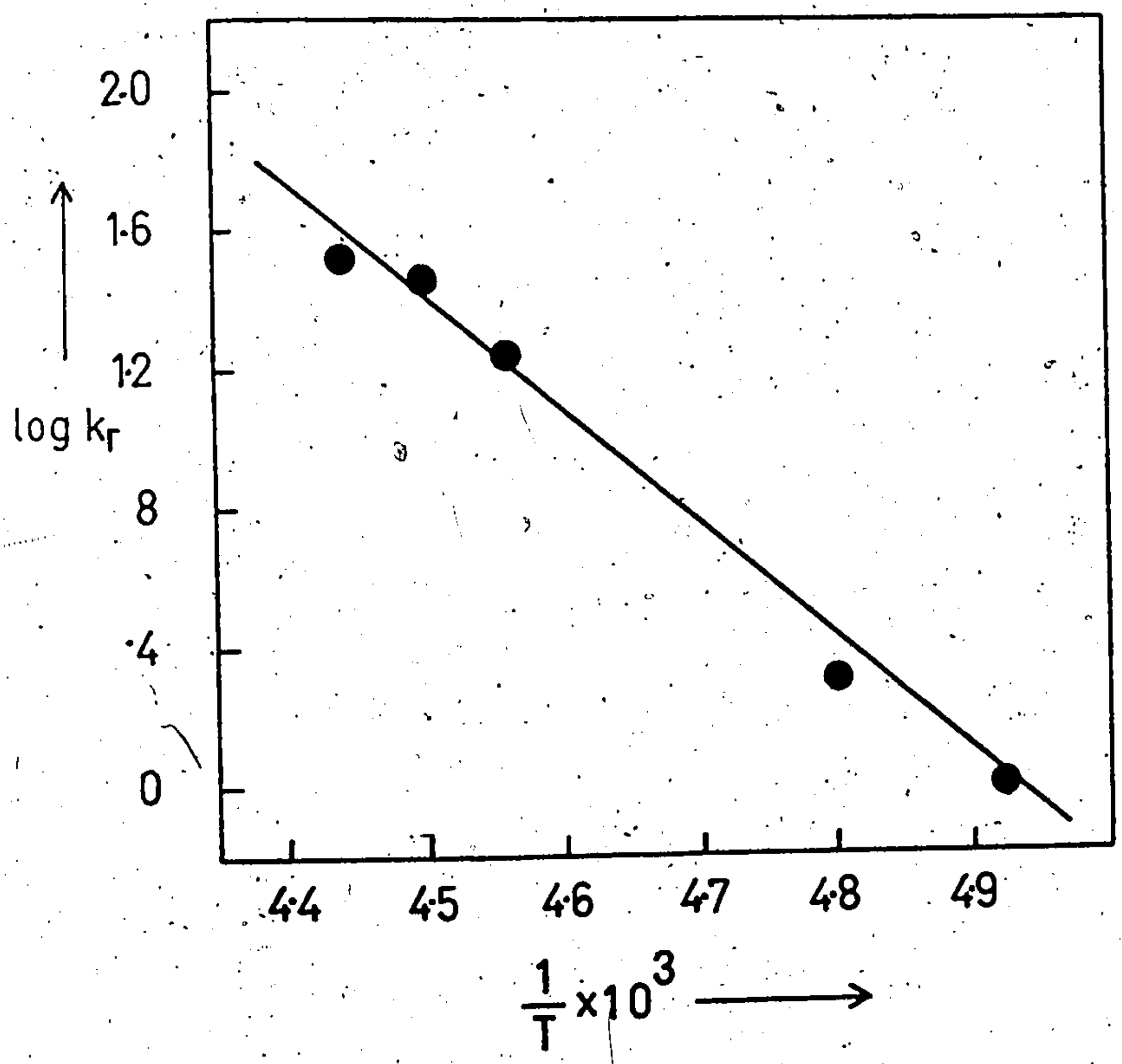


Figure 23e Compound 80e

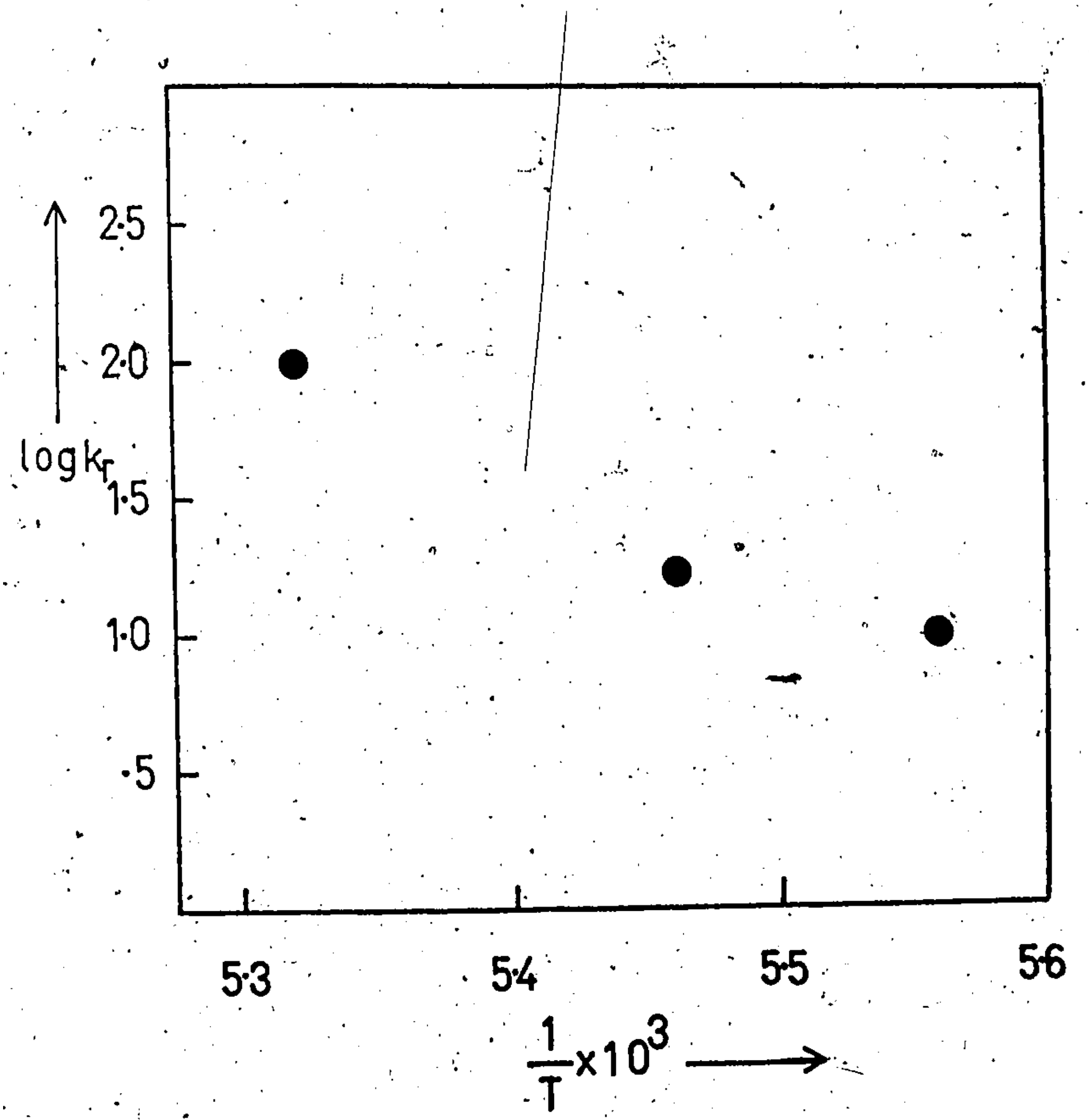


Figure 23f Compound 80f

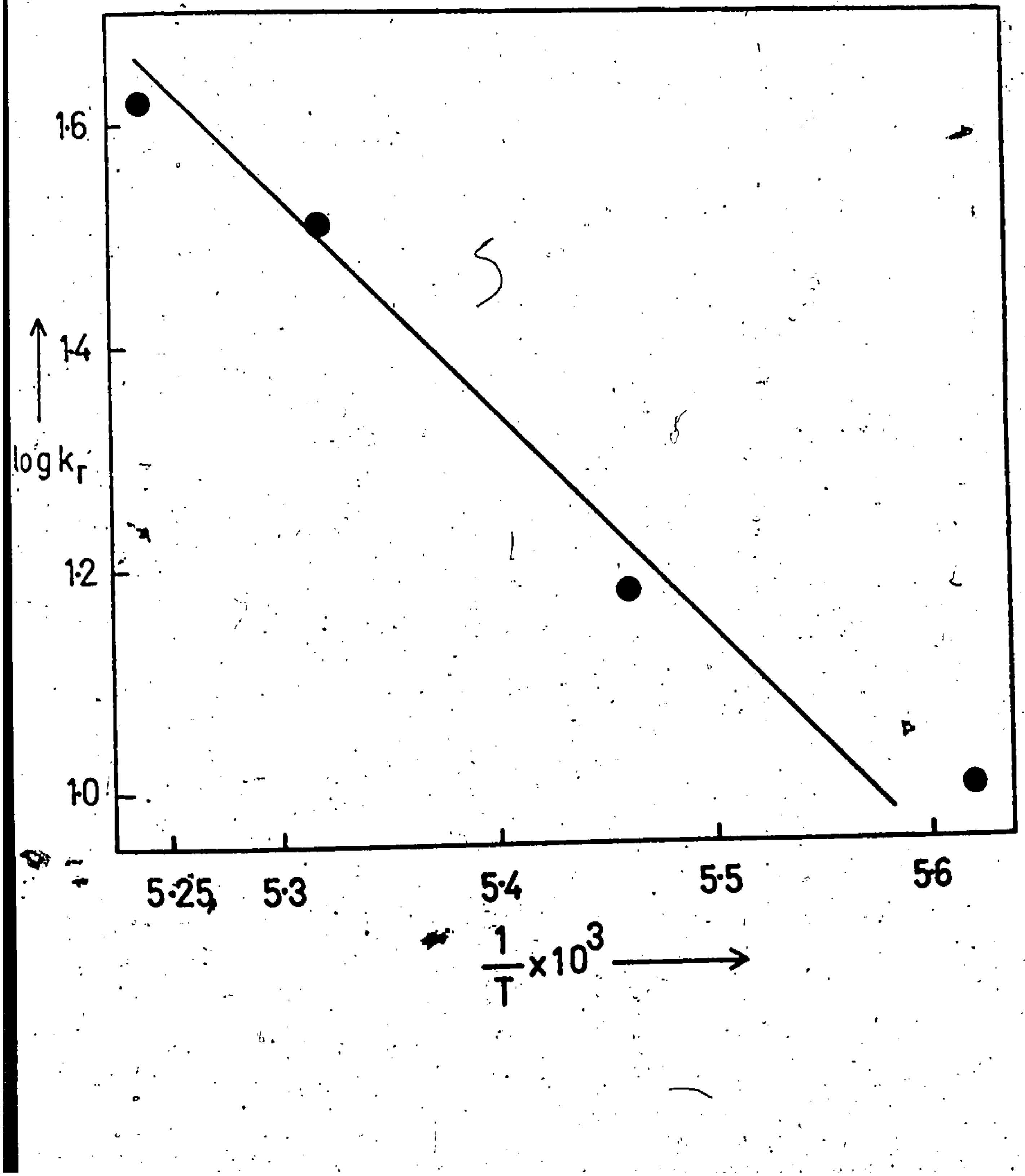


Figure 23g Compound 80g

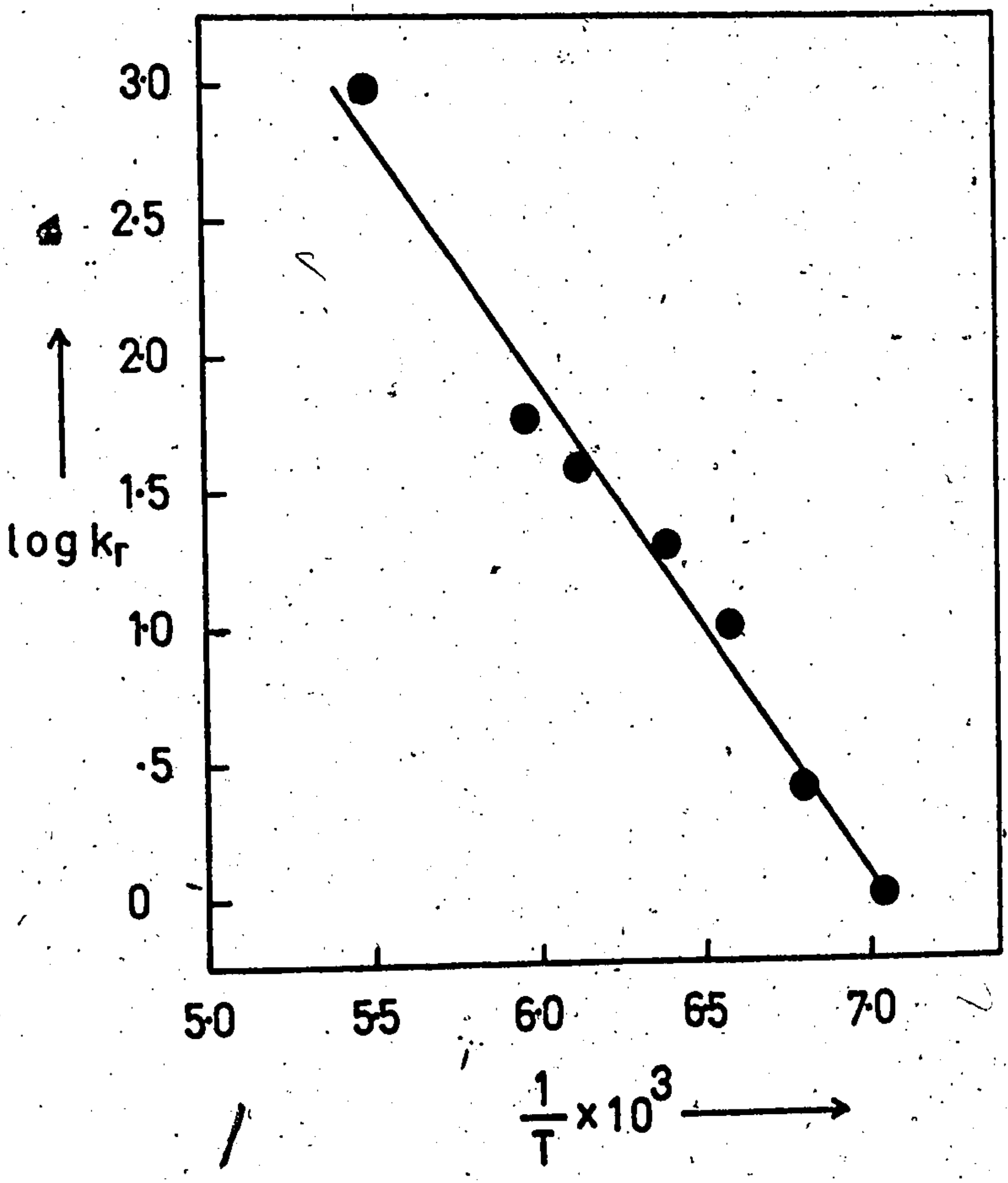
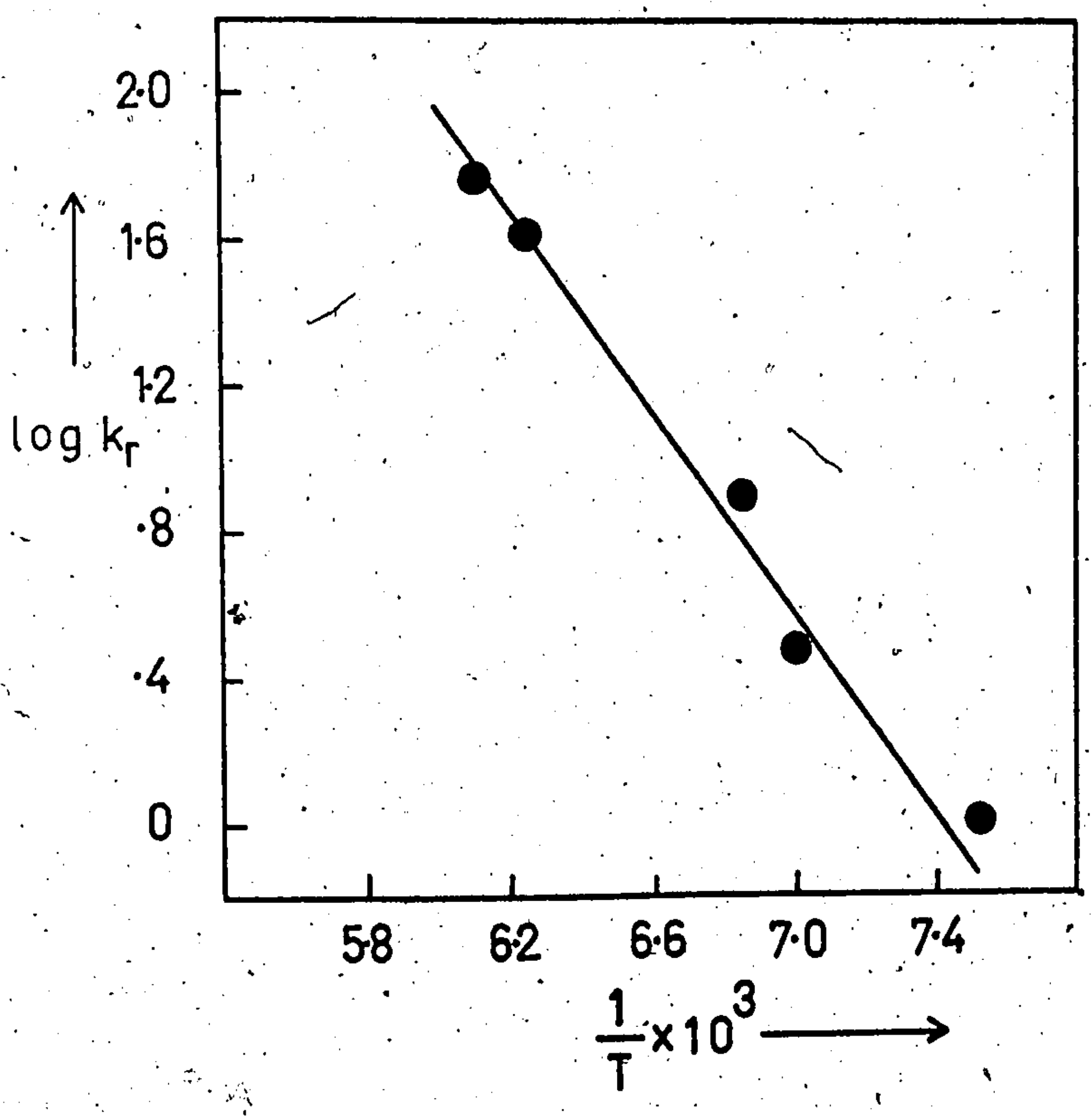


Figure 23h Compound 80h



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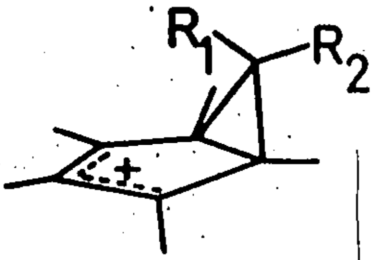
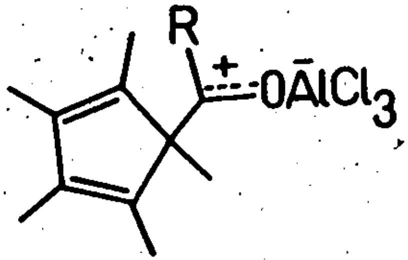
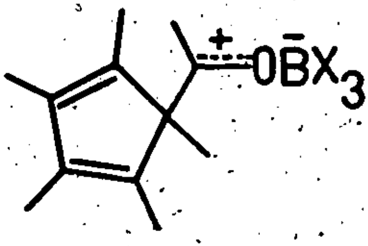


Compound	R_1	R_2
42	H	CH_3
43	CH_3	H
59	H	H
63	C_2H_5	CH_3
64	CH_3	C_2H_5



Compound	R
80a	CH_3
80b	C_2H_5
80c	$pCH_3OC_6H_4$
80d	$pC_2H_5OC_6H_4$
80e	$pCH_3C_6H_4$
80f	$ptBuC_6H_4$
80g	C_6H_5
80h	$pClC_6H_4$
80i	$pCF_3C_6H_4$



Compound	X
91a	Br
91b	Cl
91c	F