Tetrahedron Vol. 38, No. 5, pp. 567 to 608, 1982
Printed in Great Britain.

0040-4020/82/050567-42$21.00/0
Pergamon Press Ltd.

TETRAHEDRON REPORT NUMBER 123

CIRCUMAMBULATORY REARRANGEMENTS

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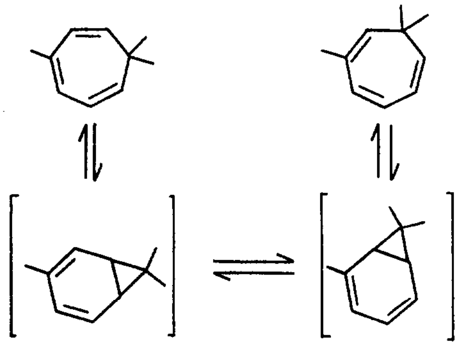
(*Received in U.S.A.* 27 *July* 1981)

CONTENTS

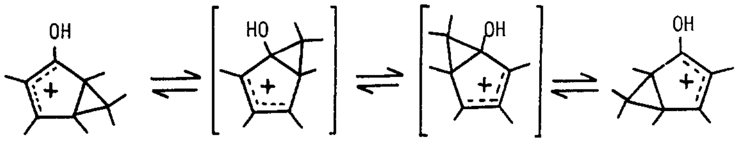
Despite contravening the principle of "least structural change",[1] molecular rearrangements are important in organic chemistry.[2] Some examples, such as the acid catalysed ring expansions of cyclic oximes in the preparation of nylon precursors,[3] are of practical consequence. Others have played an important role in the development of the theory of organic chemistry.[4] This latter role has been emphasized in recent years as the significance of orbital symmetry in organic reactions has been recognized.[5] The class of reactions which have become known as circumambulatory rearrangements has been particularly important in the latter role.

Although it was not the earliest example of a circumambulatory rearrangement, much stimulus for the rapid development of this area of chemistry goes back to the "bones" rearrangement reported by Berson and Willcott in 1965.[6] This skeletal rearrangement of 7,7-disubstituted cycloheptatrienes was suggested to proceed by the migration of the cyclopropyl group around the norcaradiene valence tautomer as is shown in eqn (1).



(1)

Another early and important example of a circumambulatory rearrangement was that provided by the cyclopropyl walk reactions of the bicyclo[3,1,0]hexenyl cations and zwitterions. This type of reaction formed one of the essential steps in the mechanism proposed by Zimmerman and Schuster from the "Type A" photo-rearrangements of 2,5-cyclohexadienones.[7] In 1967 Swatton and Hart[8] described a remarkable degenerate isomerization (eqn 2) which involved a sequence of three individual walk reactions. The following year a five-fold degenerate version of this type of circumambulation was reported by Childs and Winstein[9] which proceeded with a very high stereoselectivity in accord with the predictions of orbital symmetry (eqn 3). In the same year two independent reports appeared on the stereoselectivity of the 1,4 sigmatropic shift of bicyclo[3.1.0]hexenyl zwitterions.[10]



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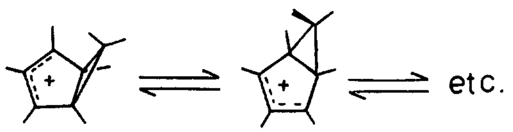


(3)

These early observations which were published in the period just following the introduction of orbital symmetry considerations,[11] provided some striking examples of the importance of these considerations in organic reactions. Following this period many other circumambulatory rearrangements have been reported and these will be reviewed systematically here.

DEFINITIONS

At the outset it is important to clarify what is meant by the term circumambulatory rearrangement. This term is but one of many which have been introduced into the literature to describe this type of reaction. Other more flamboyant descriptions include "merry-go-round", "ring walk", "ring runner" and "ring whizzer" as well as the more general fluxional or degenerate rearrangement.

In this review a *circumambulatory rearrangement is defined as a molecular rearrangement in which an atom or group of atoms migrates around the periphery of a ring in such a way that during a series of such reactions the atom or group of atoms can become bonded to any of the ring carbons.*

Four qualifications should be noted with respect to this definition:

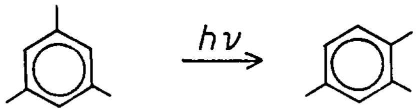
(a) It must be the same atom or group of atoms which migrates, or in principle can migrate, to each ring atom.

(b) The rearrangement does not have to be degenerate for it to be termed a circumambulatory rearrangement.

(c) No restriction is placed on the way or number of times that the migrating atom or group of atoms is bound to the ring atoms.

(d) No mechanistic pathway is implied in the definition.

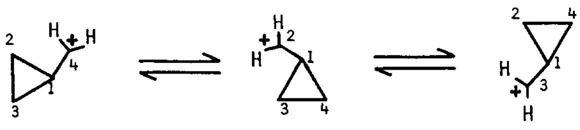
A good example of a circumambulatory rearrangement is provided by the sequence of reactions shown in eqn (3) for the heptamethylbicyclo[3.1.0]hexenyl cation.[9] In this cation it is possible for the migrating group ($C(CH_3)_2$) to become bonded to any adjacent pair of ring carbons. In such a process the ring carbons do not change their positions with respect to each other but remain in the same relative order. It is the $C(CH_3)_2$ group which migrates around the ring. This is an important point to stress in as much as it eliminates from consideration such reactions as the photochemical positional isomerization of benzenes (eqn 4). Carbon labeling experiments have shown that this reaction proceeds exclusively *via*



(4)

ring transposition and not methyl group migration.[12] Hence this type of reaction cannot be classified as a circumambulation.

A similar situation is encountered with the degenerate rearrangements of cyclopropylcarbinyl cations (eqn 5). In this case what appears at first glance to be an example of a circumambulation involves a more complex reaction in which an interchange of carbon atoms take place.[13]

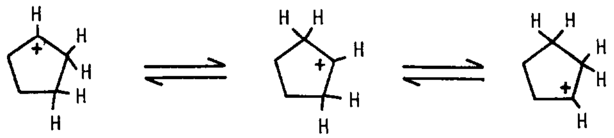


(5)

The heptamethylbicyclohexenyl cation can also be termed a fluxional molecule,[14] a term frequently used to describe similar rearrangements in organometallic systems.[15] The rearrangement (shown in eqn 3) can also be termed a degenerate rearrangement in as much as after isomerization a molecule with the same gross structure is produced.[16] Detection of such a reaction requires the use of isotopic labels or dynamic NMR techniques.[17,18] According to suggested IUPAC nomenclature,[18] the terms fluxional and degenerate rearrangement mean the same thing and only differ in a somewhat arbitrary manner based on the rate of the rearrangement. The term fluxional is usually employed to describe a degenerate rearrangement which is rapid on the NMR time scale.

A circumambulatory rearrangement does not have to be a degenerate rearrangement. Clearly all the steps of the isomerizations represented in eqns (2) and (3) are very similar and it would be a false distinction to term the degenerate rearrangement shown in eqn (3) a circumambulation and not include that indicated by the former equation.

It is important to stress in the definition of circumambulatory rearrangement used here that it must be a single migrating atom or group of atoms which moves around the ring. This restriction rules out from consideration the degenerate rearrangements occurring in species such as the cyclopentyl cation, (eqn 6).[19] It is not possible to attain this degeneracy by the migration of a single hydride around the ring. Instead a series of different hydrogen atoms must be involved.



(6)

The circumambulating group in these reactions does not have to be joined to the ring atoms by two σ bonds as has been shown so far in eqns (1)–(3). The group may be singly bound as is illustrated by the well known examples of the degenerate rearrangements of the cyclopentadienes. It is not necessary that the migrating group be joined to the ring formally be σ-bonds. There are many examples of circumambulations among the π-bonded organometallics.[20]

The last point to stress in these introductory remarks is that the definition of circumambulatory rearrangements given above does not limit the mechanistic varieties expected. Many reactions appear to proceed by concerted "sequential sigmatropic shifts"[21] but they could equally well involve pseudopericyclic reactions.[22] Alternatively the migrations might proceed via short lived intermediates which are haptotropically[23] related to the major equilibrium species. Dissociative mechanisms are also possible. The common feature behind all these mechanistic possibilities is the net effect of the reaction, namely the migration of the group around the ring.

CLASSIFICATION OF CIRCUMAMBULATING SYSTEMS

It is convenient to subdivide circumambulating systems in two ways. Firstly into three broad classes depending on the characteristics of the system and secondly on the basis of the size of ring around which the circumambulating group migrates. Nearly all the reported circumambulations appear to fall into one of three broad classes,

(A) *Unsaturated ring systems with a σ-bonded migrating group.*

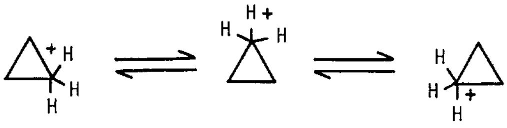
(B) *Unsaturated ring systems with a π-bonded migrating group.*

(C) *Fully saturated ring systems with a carbonium ion center* (i.e. *a pentavalent carbon atom*).

Examples of the first class of reaction have already been given (eqns 1–3) and this class of circumambulation will form the substance part of this review.

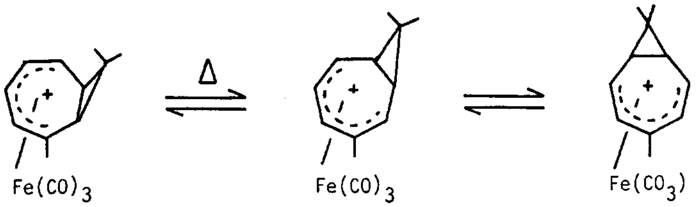
Class B circumambulations are often encountered in organometallic chemistry. As there are several reviews of these fluxional systems they will not be covered in depth here.[20]

The reactions of class C have not normally been considered to be examples of circumambulations. However, they fully meet the definition advanced earlier and should be included. A typical example of this type of reaction is encountered with corner protonated cyclopropane derivatives (eqn 7).[24] Saunders *et al.*[24] have reviewed this topic.



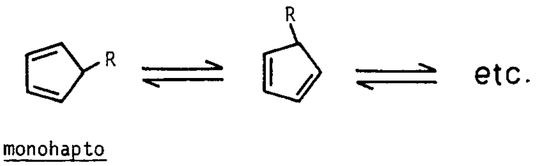
(7)

In addition to the three classes of rearrangements mentioned above there are one or two closely related reactions which do not easily fit into either group. These include, for example, the rearrangements of the oxocarbons.[25] It is also possible in principle to have a ring which bears two or more migrating groups that circumambulate in a cooperative manner (eqn 8).[26] Few examples of this type of joint circumambulation are known.



(8)

A further convenient way of organizing the various types of circumambulatory systems is on the basis of the size of the ring around which the walk process occurs. This approach is useful in as much as it can often show the interrelationships among what seem at first quite divergent types of rearrangement. For example with 5-membered rings it is possible in principle to get circumambulation of a group which is bonded once (eqn 9), twice (eqn 10), three (eqn 11) or even four times (eqn 12) to the ring atoms.



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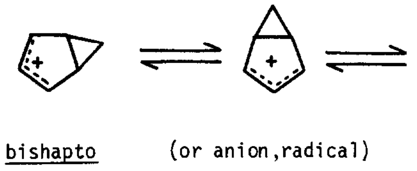

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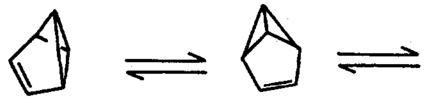
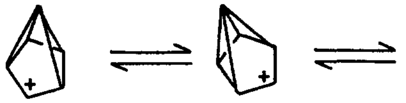


(11)

trishapto



(12)

tetrahapto (or anion, radical, dication)

In practice there is frequently a close relationship among these various possibilities. Thus, rearrangements of cyclopentadienes (eqn 9) can involve bicyclo[3.1.0]hexenyl species as transition states or reaction intermediates.

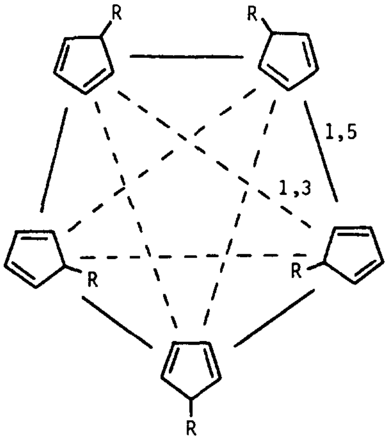
This review is organized firstly on the basis of the size of the ring around which the circumambulation occurs and then secondly for an individual ring, on the basis of the number of ring atoms to which the migrating group is bonded. Adopting the organometallic chemist's nomenclature, these are termed *monohapto, bishapto, trishapto*, etc. bound migrating groups, signifying bonding to one, two, three, etc. ring atoms.[27]

CIRCUMAMBULATIONS INVOLVING σ-BONDED GROUPS

Stereochemical considerations

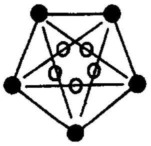
Before considering individual examples of circumambulating systems it is appropriate to take an overview of the ways in which a complete circumambulation can occur and the resulting stereochemical consequences. With a σ-bonded migrating group the circumambulation can formally be regarded as involving a series of suprafacial sigmatropic shifts and orbital symmetry has to be considered.[5,28] This is not to say the "dictates" of orbital symmetry will always be followed. Not all the reactions to be discussed involve concerted reactions and even where they are concerted other factors such as the principle of least motion[29] and subjacent orbital control need to be kept in mind.[30]

In those cases where the circumambulatory group is bonded to only one of the ring atoms (the *monohapto* case) a complete circumambulation could occur either by a series of steps in which the migrating group moves around the ring in a consecutive manner, or by a process in which it hops across the ring. Thus a circumambulation of a 5-membered ring could involve the migrating group becoming bonded successively to carbons 1, 2, 3, 4, 5 and then 1 (Scheme 1, solid lines). Each step in such a circumambulation could be regarded as a 1,5-sigmatropic shift. The reaction shown in Scheme 1 is very frequently encountered with σ-bonded organometallic systems. Most often in these cases it is erroneously termed a 1,2 shift. Alternatively, the same net circumambulation could be achieved by a series of 1,3-sigmatropic shifts. For this case the migrating group would be bonded in order to carbons 1, 3, 5, 2, 4 and then 1 (Scheme 1, dotted lines).



Scheme 1.

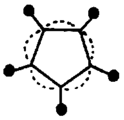
Attempts have been made to depict such consecutive transformations in somewhat less cumbersome form than the complete series of diagrams shown in Scheme 1. Muetterties[31] has suggested a topological approach to the question and has represented the 1,3 shift circumambulation of Scheme 1 as shown in Scheme 2. Similar formulations based on graph theory had been advanced by Balaban[32] and Plath and Has.[33] While this type of formalism of a circumambulatory process can convey a lot of information and in some of the more complex cases as used by Woodward and Hoffmann[34] look exceedingly elegant, they have not come into general use.



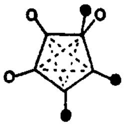
Scheme 2.

A second consideration involved with the circumambulation of a *monohapto* group is the stereochemistry of the migrating center itself. If each step of the circumambulation is concerted then it can be classed as a sigmatropic shift and might be expected to proceed in a stereoselective manner.[35]

For example if the thermally induced circumambulation of a cyclopentadiene (Scheme 1) were to proceed by concerted suprafacial 1,5 sigmatropic shifts, then the configuration of the migrating group should be retained, no matter how many circumambulations of the ring take place (Scheme 3). On the other hand, the same thermal circumambulation taking place by a series of 1,3 shifts would lead to racemization. After one complete circumambulation the starting compound could in principle be recovered with the opposite chirality. In practice racemization would be observed (Scheme 4). Similar effects should be observed with the other odd membered rings.



Scheme 3.

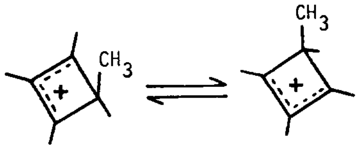


Scheme 4.

With even membered rings the situation can be more complicated. Depending on the type of sigmatropic shift occurring it is possible to envisage a complete circumambulation which could occur without the migrating-group becoming bonded to all of the ring atoms. For example, with the benzenium ions, rearrangement by successive 1,3 shifts would regenerate the starting cation after only three shifts, $C_1 \rightarrow C_3$; $C_3 \rightarrow C_5$; $C_5 \rightarrow C_1$. On the other hand the commonly encountered 1,2 or 1,6 shifts lead to a circumambulation in which the migrating group becomes bonded to each of the ring carbons in turn.

Another feature of circumambulations of a *monohapto* group around an even membered ring is an ambiguity which can result with the simple application of orbital symmetry to determine the stereochemical consequences of migration. With the cyclobutenyl cations, for example, the migration of a group onto the adjacent carbon (eqn 13) can be considered to be either a 1,2- or a 1,4-sigmatropic shift. The stereochemistry expected at the migrating group of such concerted reactions depends on how it is classified.

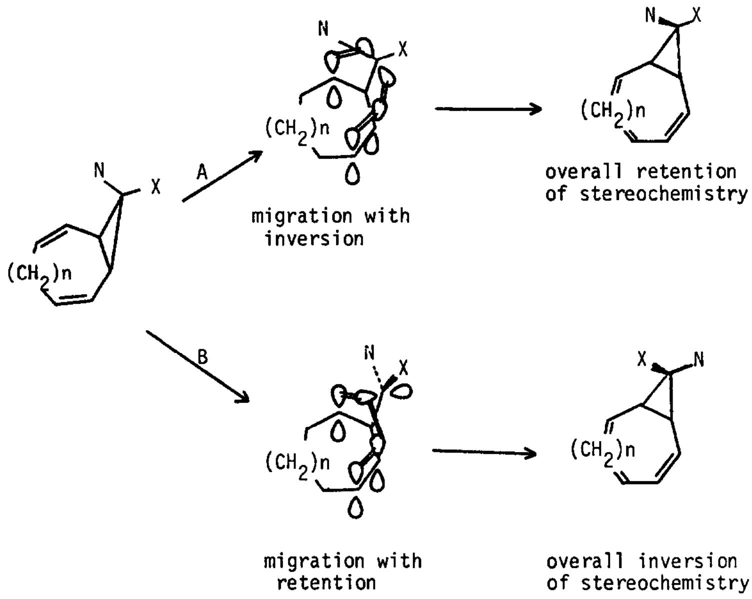
When the migrating group is bound to two ring carbons (the *bishapto* case) the question whether the migration proceeds with inversion or retention of configuration is of importance in determining the overall stereochemical result. With the most frequently encountered example of this type of circumam-



(13)

1,2 or 1,4?

bulation, the cyclopropyl walk reaction, there are two possible stereochemical results of a single migration. These are either migration with retention of configuration at the cyclopropyl carbon, which results in the overall interconversion of the exo and endo cyclopropane substituents, or migration with inversion at the cyclopropyl carbon, which results in the overall maintainance of the positions of the cyclopropane substituents. These two possibilities are shown in Scheme 5. Examination of the relative spatial movements involved in each of these possible pathways indicates that the reaction proceeding with inversion of configuration at the migrating carbon (path A, Scheme 5) is the least motion process for the 5 and larger membered rings. It is geometrically easy with these rings to slide the cyclopropyl carbon around the ring when the configuration at this carbon is inverted at each step (path A). On the other hand, migration with retention of configuration involves a pivoting type motion and a much larger movement, of the migrating carbon. The pivot is a non-least motion process for the five and larger membered rings.

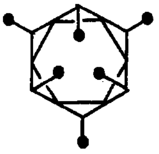


Scheme 5.

Whereas for all of these larger rings the principle of least motion predicts the same result, orbital symmetry predictions alternate depending on the number of electrons involved. Thus thermally induced circumambulations about a five-membered ring cation (the bicyclo[3.1.0]hexenyl cation, eqn (3)) involving 1,4 sigmatropic shifts should occur with inversion of configuration at the migrating carbon. In this case orbital symmetry and least motion considerations concur and circumambulations are generally facile.

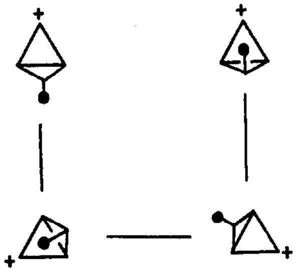
In the case of a cyclopropane migrating around a 6-membered ring by a series of 1,5 shifts (eqn 1) the exact opposite pertains. For a concerted ground state reaction the migration should occur with retention of configuration, the non-least motion pathway. This type of reaction is expected to be more difficult and the question arises as to what the steric outcome will be.

It will be noted in the case of the thermally induced migrations of the cyclopropyl around the 6-membered ring by consecutive 1,5 sigmatropic shifts, that the substituents on the cyclopropane are expected to switch from exo to endo and *vice versa* on each step. The net result of a complete circumambulation on the 6-membered ring and indeed any comparable pivot type migration on an even membered ring, is that the starting material is regenerated without epimerization (Scheme 6).[36]

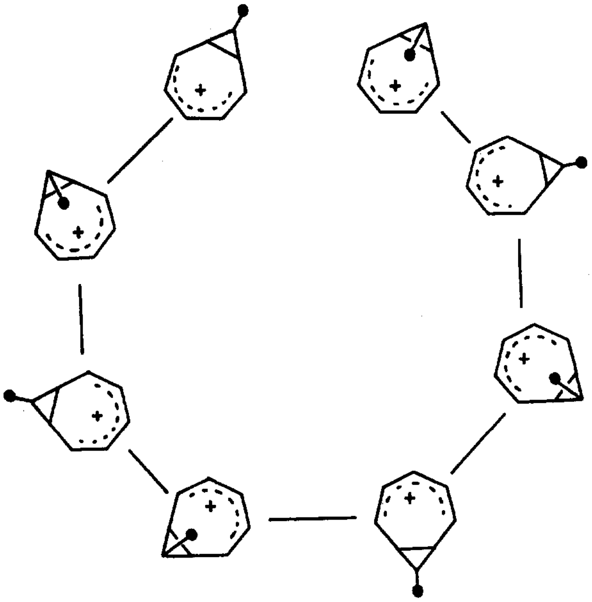


Scheme 6.

This situation does not hold with odd membered rings. Pivot type migrations are expected to occur for the thermal circumambulation of both the 3-and 7-membered rings. In each case a complete circumambulation is predicted (on the basis of orbital symmetry considerations) to regenerate the starting material with the opposite stereochemistry (Schemes 7 and 8).[37]

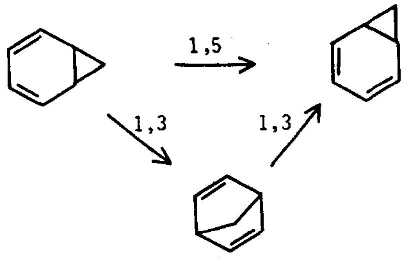


Scheme 7.



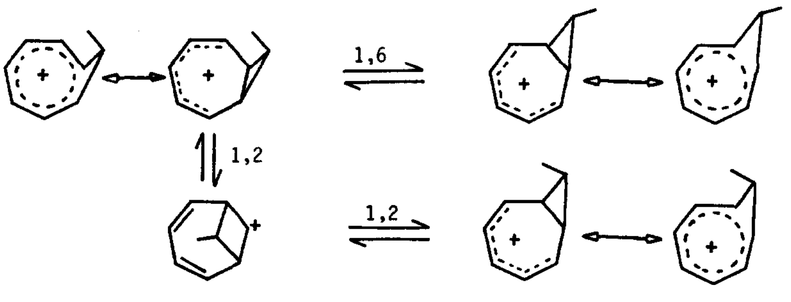
Scheme 8.

One other feature of these possible circumambulations of *bishapto* systems bears mention. This is the question of what the steric consequences will be if the cyclopropyl moves not by a single shift into the adjacent site but by a series of smaller shifts which eventually yield the same product. For example the walk reaction of a bicyclo[4.1.0]hexadiene could involve a 1,5 shift or could also take place by consecutive 1,3 shifts (eqn 14).



(14)

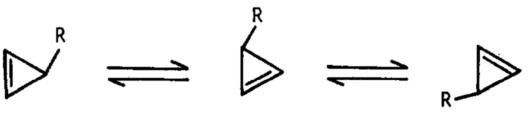
Woodward and Hoffmann have shown for even membered rings that the same general stereochemical result will hold for a series of smaller shifts as would be expected for the one step process.[36] This generalization does not hold true however with the migrations of a cyclopropyl around an odd membered ring as is illustrated in eqn (15) for the bicyclo[5.1.0]octadienyl cation. With odd membered rings each case must be considered separately.



(15)

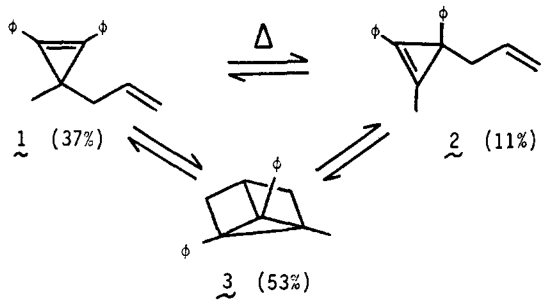
CIRCUMAMBULATIONS AROUND 3-MEMBERED RINGS

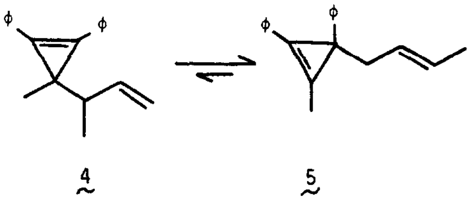
(a) *Monohapto cases.* This type of reaction could potentially occur with the migration of groups around cyclopropene (eqn 16). This reaction is formally a suprafacial 1,3-sigmatropic shift and if it were to follow orbital symmetry then it would proceed with inversion at the migrating group. When R=H such a circumambulation is formally forbidden and indeed there is no evidence for the degenerate rearrangement of cyclopropene itself.[38] Indeed thermally induced rearrangements of this type have not been reported for simply substituted cyclopropenes.



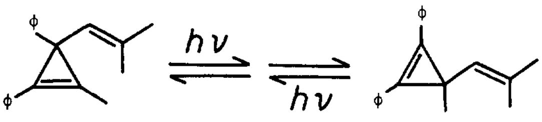
(16)

A more complex cyclopropene circumambulation involving a Cope rearrangement has been reported by Padwa and Blacklock.[39] Thus cyclopropene **1** is converted on heating to an equilibrium mixture of **1**, **2** and **3**. Evidence that the reaction involves a Cope-type rearrangement (3,3-sigmatropic shift) and not a simple 1,3 shift mechanism comes from the observed interconversion of **4** and **5**. These reactions, which involve compounds such as **3**, appear to be examples of the two step Cope reaction suggested by Doering[40] and Dewar.[41]

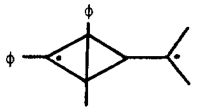




A photoinduced circumambulation around the 3-membered ring has been reported by Zimmerman and Hovey with vinylcyclopropenes.[42] The photochemistry of cyclopropenes is fairly complex and it will not be discussed in detail here.[43] However Zimmerman showed that one of the reactions occurring on the direct irradiation of compounds such as **6** is its conversion to **7**. This type of reaction, which is relatively inefficient, was detected with a range of similarly substituted cyclopropenes. Diradical species such as **8** are suggested as intermediates in these circumambulations.



6 **7**



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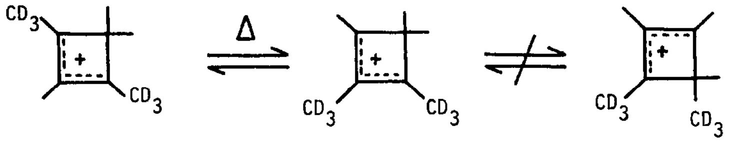
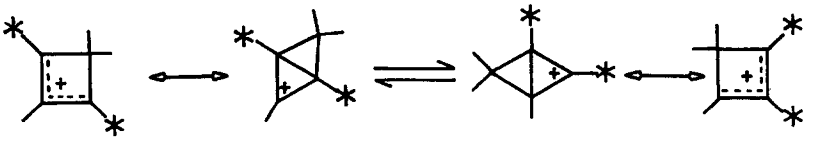
(b) ***Bishapto-cases***. An example of this type of circumambulation is provided by the degenerate rearrangement of the pentamethylcyclobutenyl cation, **9**, reported by Koptyug *et al.*[44] Cation **9** was generated with CD_3 groups at the C_1 and C_3 ring positions and a scrambling reaction observed in which the labeled groups became equilibrated between positions, 1, 2, and 3 *but not* 4 (eqn 17). The absence of incorporation of a CD_3 group at position 4 eliminates from consideration the obvious possibility of a simple methyl shift mechanism (potentially a *monohapto*-four ring circumambulation).



(17)

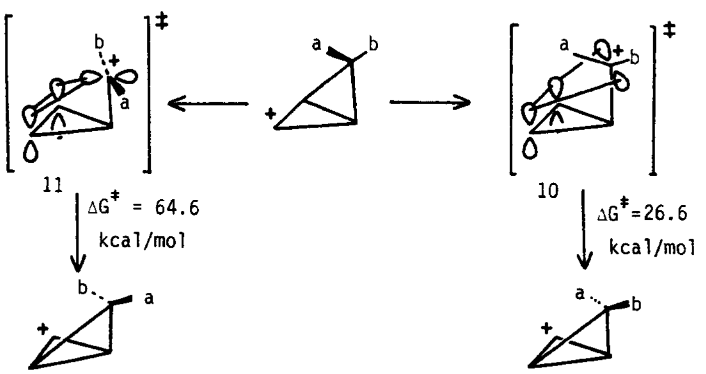
9

Since the first preparation of cyclobutenyl cations by Katz[45] there has been much discussion as to the importance of 1,3 overlap or the homocyclopropenyl nature of these cations.[46] In this present case it would appear that the degenerate rearrangement observed by Koptyug can best be regarded as the circumambulation of the cyclopropyl around the bicyclo[1.1.0]butyl cation form of **9** (eqn 18).



(18)

No experimental evidence is available as to the stereochemical consequences of this circumambulation. Devaquet and Hehre[47] have examined this type of rearrangement theoretically and come to the conclusion that the lowest energy pathway for this migration is the opposite to that predicted by orbital symmetry. The two possible transition states are shown in Scheme 9 along with the calculated energy differences from the starting bicyclic cation. It is clear that the so called "forbidden" transition state, **10**, is substantially lower in energy than the formally allowed one, **11**.



Scheme 9.

The reason for this apparent failure of orbital symmetry was attributed to the interaction of the asymmetric Walsh type orbital of the cyclopropene with the carbonium ion center on the migrating carbon in a comparable manner to that encountered in the cyclopropylcarbinyl cations.[48] This interaction provides an outstanding example of subjacent orbital control of a reaction.

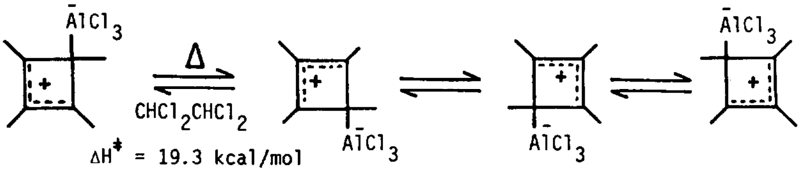
In practice it is doubtful whether this stereochemical prediction can be tested. The low energy path to the interconversion of the exo and endo substituents via the planar cyclobutenyl cation makes this type of experiment difficult and optically active cations would have to be generated.

CIRCUMAMBULATIONS AROUND 4-MEMBERED RINGS

(a) *Monohapto cases*

For this type of system the unsaturated portion of the 4-membered ring must be either an ionic or radical species. In previous sections reference has already been made to the absence of alkyl shifts in the cyclobutenyl cation **9**. Indeed this seems to be general and there appear to be no examples of degenerate alkyl shifts in these cations.[46] Eventually on heating, an irreversible ring expansion to cyclopentyl cations is observed and this limits the temperature to which cyclobutenyl cations can be heated in order to detect a walk reaction.[44]

One series of examples of this type of circumambulation has been reported when the migrating group is an aluminum species.[49–51] The cyclobutenyl cation, **12**, prepared by the reaction of 2-butyne with aluminum trichloride,[49] and whose structure has been confirmed by an X-ray diffraction study[52] undergoes a degenerate isomerization when heated to +80°. As both the methyl proton and ring carbon resonances in the ^{1}H and ^{13}C NMR spectra, respectively, of **12** are averaged when heated, it appears that the rearrangement can best be understood in terms of the migration of the $-\bar{A}lCl_3$ group around the ring (eqn 19). Double irradiation and line broadening experiments suggested that this migration occurs in a consecutive, stepwise manner indicating that intermolecular processes are not involved.[50] The exact mechanism of the circumambulation is not clear.



12

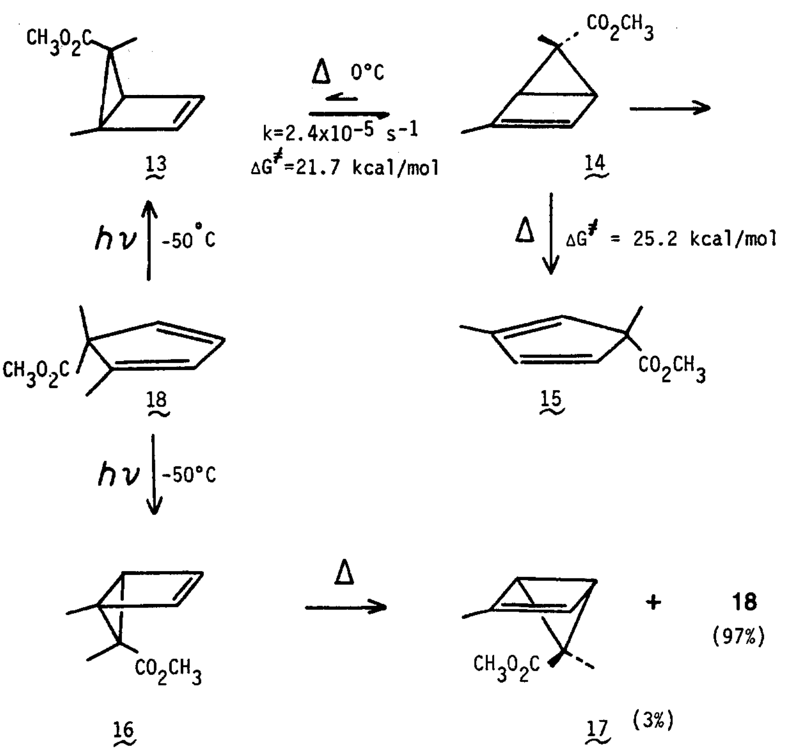
(19)

(b) *Bishapto cases*

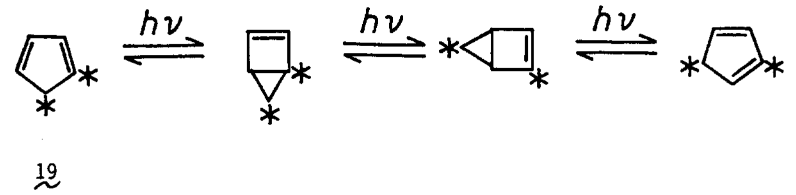
There are many examples of this type of circumambulation. The clearest, but not the earliest one is the recent report of Klärner and Adamsky[53] on the rearrangement of bicyclopentene **13** to **14**. The bicyclopentene **13**, prepared together with, and separated from its diastereomer **16** at low temperature, rearranged to **14** with high stereoselectivity. That this is a kinetically controlled stereochemical result is shown by the corresponding conversion of **16** to **17**. This circumambulation is occurring with inversion at the migrating cyclopropyl carbon and overall retention of stereochemistry. This result is in accord with orbital symmetry but contradicts the semi-empirical MO calculation reported by Schoeller.[54]

Bicyclo[2.1.0]pentenes lacking the electron withdrawing ester group on the cyclopropyl carbon do not appear to undergo comparable circumambulations but ring open to cyclopentadienes.[55,56] Even with two ^{13}C labels in the ring system it has not been possible to detect any thermally induced circumambulatory rearrangement.[56] It is tempting to attribute the effect of the electron withdrawing substituent to a strengthening of the internal cyclopropane bond.[57] However examination of the activation energies for the circumambulation and ring opening reactions as a function of the substituent on C_5, shows that it is the energy of the former reaction which is decreased by the electron withdrawing substituent. The activation energy for the breaking of the internal cyclopropane bond is relatively insensitive to the C_5 substituent.[53]

One possible exception to this general lack of ground state circumambulations of bicyclo[2.1.0]pentenes occurs during the photochemical isomerization of a dimethylindene.[58] There are however alternative reaction pathways which avoid circumambulation.



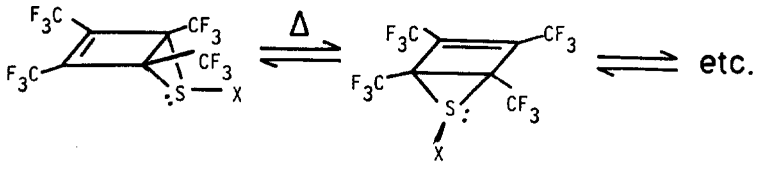
Circumambulation of a cyclopropane around a 4-membered ring can also be photochemically induced. Andrews and Baldwin[59] suggested the occurrence of this process to account for the scrambling of the doubly ^{13}C labeled cyclopentadiene **19** on irradiation (eqn 20).



(20)

While the number of examples of circumambulations with strictly carbocyclic bicyclo[3.1.0]pentenes are limited, they appear to occur much more frequently with heterocyclic systems. Indeed this type of walk reaction is often invoked to account for the photoisomerizations of the 5-membered ring heterocycles.[60]

Clear examples of this type of reaction are provided by the rearrangements of Dewar thiophen **20** and its S-oxide, **21**, reported by Lemal *et al.*[22a,61] (eqn 21). Both these molecules were shown by dynamic ^{19}F NMR spectroscopy to undergo a degenerate rearrangement in which the sulfur atom moves around the ring.

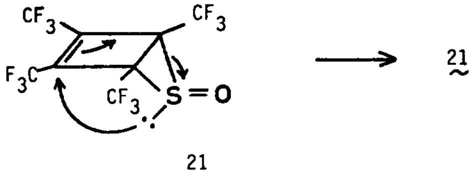


(21)

20, X = lone pair $\Delta G^{\ddagger}$ (20) = 22.1 kcal/mol.

21, X = O $\Delta G^{\ddagger}$ (21) = 6.7 kcal/mol.

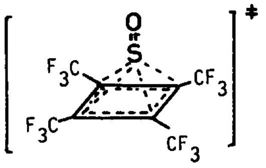
It is not known whether these reactions proceed via a stepwise migration of the sulfur atom or group around the ring. This is a pivotal question in terms of the various suggested mechanisms for these processes. Lemal *et al.* suggested that the circumambulation of **21** in particular has too low an activation energy for it to involve a 1,3-sigmatropic shift. Instead it was proposed that the reaction might involve the long pair of electrons on sulfur and a new term "pseudopericyclic" was introduced to describe this type of process (eqn 22).[22a] This proposal has not met with wide acceptance.[22b,62]



(22)

21

Other alternatives include a migration *via* a pyramidal transition state **22**,[22b,62,63] or an ion pair mechanism.[64]

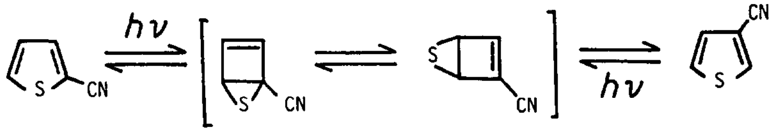


22

It is interesting that pertrifluoromethyl Dewar pyrrole does not appear to undergo comparable degenerate isomerizations.[65]

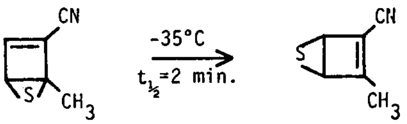
The trifluoromethyl substituted systems discussed above do not readily isomerize to the parent thiophene analogues. This stability which is typical of such fluorinated compounds,[66] does not generally extend to the simpler derivatives of Dewar thiophene. Thus while such circumambulations were frequently postulated to account for the phototransposition reactions of thiophens, until fairly recently there was little hard evidence for this. It should be noted that circumambulations of Dewar structures are not the only photochemical pathways open to these 5-membered heterocycles.[67,60]

Day *et al.*[68] have shown by trapping and labeling experiments that thiabicyclo[2.1.0]pentenes are involved in the phototranspositions of cyanothiophens (eqn 23). Direct evidence for circumambulation of sulfur around the 4-membered ring was obtained by the preparation of **23** and **24** by irradiation of



(23)

3-cyano-2-methylthiophen at low temperatures. At −35° the circumambulatory rearrangement of **23** to **24** was observed (eqn 24).[69]



(24)

23 24

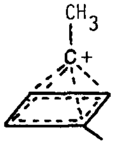
Similar sulfur walk reactions have been suggested to account for the rearrangements of thiophens under electron impact[70] and in glow discharges.[71]

Similar walk reactions have been proposed to account for some of the photorearrangements of pyrroles,[72] and other heterocyclic systems.[73] Circumambulatory rearrangements around a 4-membered ring are implicated in some of the photoisomerizations of protonated pyrones.[74]

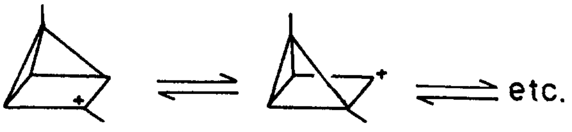
(c) *Trishapto cases*

To suggest that there might be some examples of circumambulation of a *trishapto* bound group around a 4-membered ring is of course an anathema to the devotees of pyramidal cations. There has, however, always been the possibility that such ions are better represented by rapid equilibration or circumambulation of less symmetric species.[75]

The attempted preparation of a range of pyramidal cations was prompted by theoretical predictions of Stohrer and Hoffmann.[76,77] For example, a dimethyl cation has been prepared by Masamune *et al.* and suggested to have the structure **25** on the basis of its ^{13}C and ^{1}H NMR spectra.[78] The elimination from consideration of rapidly equilibrating structures such as **26** or **27** was made on the basis of chemical shift arguments. Equilibration of a cation such as **26** can be classed as a circumambulation.



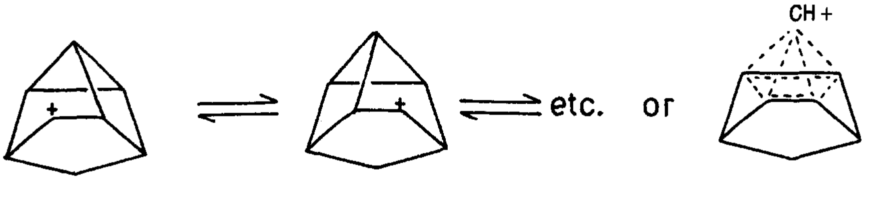
25



26 26

27 27

Similar arguments can be raised concerning the bishomopyramidal cations.[79,75] Here the four basal carbons of the pyramid are not all directly linked to each other but nevertheless this system again can formally be regarded as involving circumambulations around a four-membered ring (eqn 25).

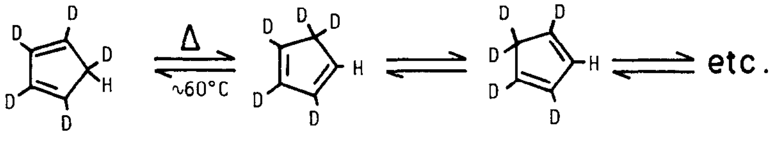


(25)

CIRCUMAMBULATIONS AROUND 5-MEMBERED RINGS

(a) *Monohapto cases*

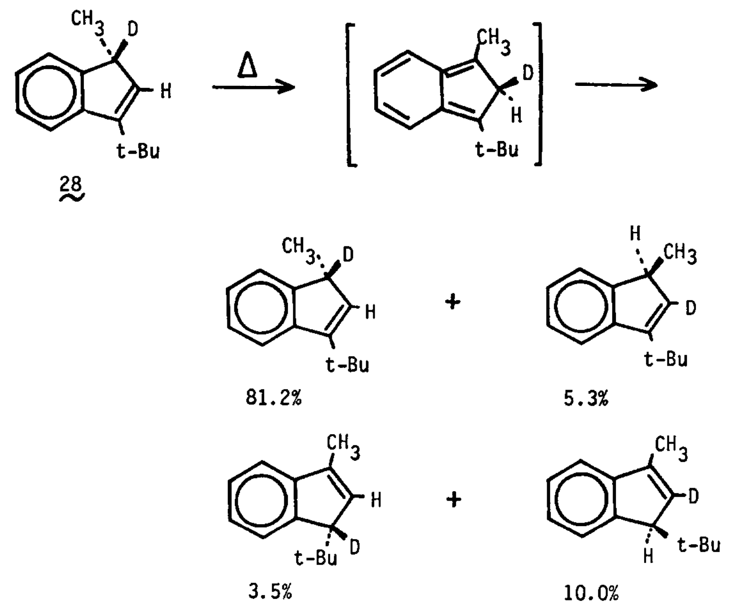
(i) *Thermal reactions.* The well established thermally induced hydride shifts of cyclopentadienes and related molecules provide good examples of this type of circumambulation (eqn 26).[80,35] Roth has



(26)

established using pentadeuterocyclopentadiene that these circumambulations proceed through consecutive 1,5 rather than 1,3-sigmatropic shifts.[81] This holds true even with the indenes where rearrangements involving 1,5 shifts necessitate the involvement of the less stable isoindenes.[82] Using the substituted indene **28**, Almy and Cram[83] have shown that these 1,5-hydride shifts are suprafacial (eqn 27).

This type of circumambulation is not limited to hydride as the migrating group. A wide variety of other types of groups can undergo comparable thermally induced migration. Alkyl group shifts generally have substantially higher activation energies than hydride shifts and, where there is a choice, hydride shifts preferentially (eqn 28).[84–86]



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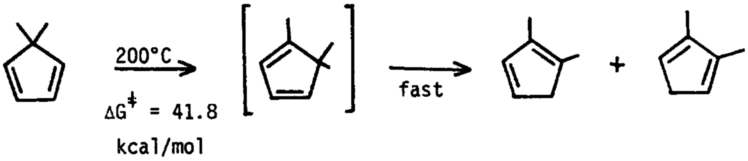
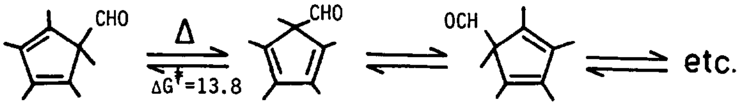
(27)



(28)

Alkyl groups other than methyl are known to migrate[87] and the 5-membered ring does not have to be strictly carbocyclic.[88] Kloosterizel *et al.*[89] have shown that this type of isomerization in a spirocyclic cyclopentadiene derivative occurs suprafacially with retention of configuration at the migrating centre. Caution has to be exercised however, in the tacit acceptance that all of these alkyl shifts take place by concerted 1,5 sigmatropic shifts. On the basis of a deuterium scrambling, Wilcott and Rathburn have suggested that a radical chain mechanism is also operative in the case of 1,5,5-trimethylcyclopentadiene.[90]

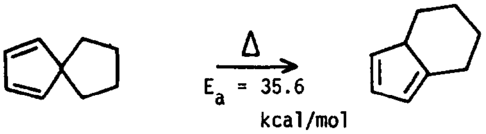
Whereas alkyl groups migrate less readily than hydrogen around a cyclopentadiene ring, unsaturated groups such as formyl, vinyl and related substituents migrate with exceptional ease.[91,92] For example, 5-formylpentamethylcyclopentadiene **29** exhibits a ^{1}H NMR spectrum which is largely averaged at room temperature.[91] The activation energy for this circumambulation is only 13.8 kcal/mol^{-1} (eqn 29).



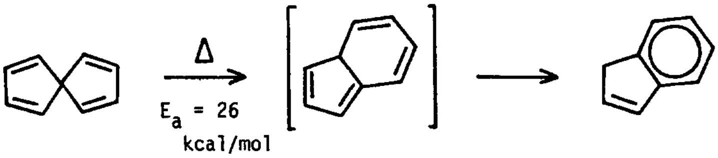
29

(29)

The marked difference in migratory aptitude of saturated and unsaturated groups is well exemplified by the recent reports on the 1,5 shifts of various spirocyclic cyclopentadiene derivatives (eqns 30, 31).[92]



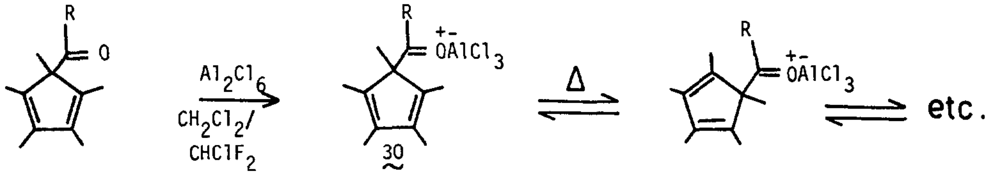
(30)



(31)

Related 1,5-acyl,[93] aryl,[94,95] and substituted vinyl group [94] migrations have been reported with indenes. Explanations based on secondary orbital interactions in the transition state of these migrations of unsaturated groups have been put forward to account for their facility.

While the formyl group of 5-formylpentamethylcyclopentadiene, **29** undergoes a facile circumambulation around the 5-membered ring, no comparable isomerizations of other acyl substituted pentamethylcyclopentadienes have been reported.[91] On the other hand, Childs and Zeya[96] have shown that such reactions become exceedingly easy when the acyl oxygen atom is complexed with a Lewis acid. These circumambulation were shown to proceed by the stepwise movement of the complexed acyl group around the ring (Scheme 10). The rates of this circumambulation were studied as a function of the substituent R of the acyl group and they were found to be very dependent upon the ability of R to stabilize or destabilize a positive charge. This is shown clearly by the three different phenyl substituted compounds **30c**, **d** and **e**. The rate of the circumambulation in **30e** is such that at −152° it was still not possible to freeze out completely its ^1H NMR spectrum.



30a R = CH_3 $\Delta G^{\ddagger} = 10.9$

30b R = OEt $\Delta G^{\ddagger} \geqslant 18.2$

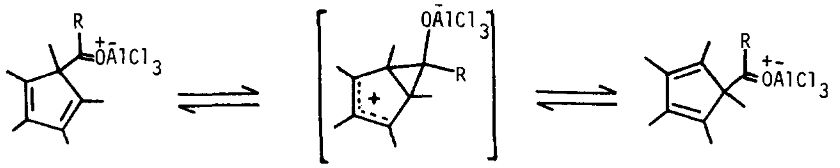
30c R = C_6H_5 $\Delta G^{\ddagger} = 8.0$

30d R = $pCH_3OC_6H_4$ $\Delta G^{\ddagger} = 11.2$

30e R = pCF_3-C_6H_4 $\Delta G^{\ddagger} = 5.0$

Scheme 10.

The very large dependence of the rate constants of these ring whizzers (circumambulation seems too pedestrian a term to adequately describe these zwitterions) on the substituent R, shows that in the transition state for the migration the positive charge is substantially removed from the acyl group. It was suggested that each step of the circumambulation proceeded through a bicyclic zwitterion such as **31**, rather than involving a "simple" 1,5 shift of the acyl group (eqn 32).



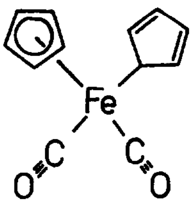
31

(32)

Alder and Grimme[97] have recently elaborated this suggestion to include the migration of unsaturated groups in general around a cyclopentadiene and have suggested that it is useful to view these reactions in terms of the timing of the bond making and breaking processes. In the case of **30**, bond making precedes bond breaking, and **31** could be involved. On the other hand with a methyl shift, bond making and breaking are suggested to be almost synchronous and the process viewed as a 1,5-sigmatropic shift. Alder and Grimme conveniently summarize their suggestion in terms of a More O'Ferrall–Jenks diagram.[98]

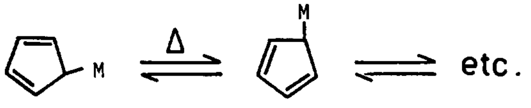
The proposal of bond making preceding bond breaking in the circumambulation of some of these *monohapto* cyclopentadienes is particularly useful in as much as it provides a link between the very similar reactions of the *bishapto* systems. The suggestion is also closely related to one proposed to account for the facile circumambulations encountered with *monohapto* cyclopentadienyl organometals.

The initial work with *monohapto* cyclopentadienyl organometals was that of Piper and Wilkinson[99] in 1956. In trying to account for the ^1H NMR spectrum of **32** these workers made the unprecedented suggestion that the *monohapto* cyclopentadiene ring was continuously shifting so averaging the proton resonances. Some ten years later this proposal was subsequently proved.[100]



32

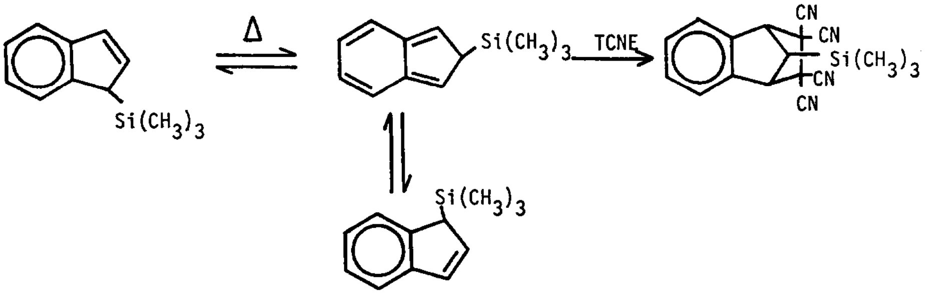
A very large number of examples of this type of circumambulation are known and many have been studied in detail. No attempt is made here to comprehensively review all of these circumambulatory systems. Some idea of the scope of this type of circumambulation can be gained from the non exhaustive listing below (Scheme 11) and from the excellent review by Cotton.[20]



M = $Si(CH_3)_3$[101,105,107,110]; $SiH(CH_3)$*i*-Pr[102]; $SiH(Cl)R$[103]; $SiCl(CH_3)_2$[106,107]; $SiCl_2(CH_3)$[104,106,107]; $SiCl_3$[106]; SiH_3[109]; $Ge(CH_3)_3$[105,107,110]; GeH_3[108]; $Ge(OCH_3)_3$[111]; $GeCl_3$[111]; $Sn(CH_3)_3$[103,105,107,110]; PF_2[114]; $HgCl$[112,113]; $HgCl$[112,113]; $HgBr$[112,113]; HgI[112,113]; HgC_5H_5[112,113]; $HgCH_3$[107]; $Fe(CO)_2(\eta^5\text{-}C_5H_5)$[100,107,108,115]; $Fe(CO)_2(\eta^5\text{-}C_5H_5)$[116]; $Mo(NO)(\eta^5\text{-}C_5H_5)_2$[117]; $Cr(NO)_2(\eta^5\text{-}C_5H_5)$[118]; $Ru(CO)_2(\eta^5\text{-}C_5H_5)$[115]

Scheme 11.

Detailed analyses of the temperature dependence of both ^{13}C and ^{1}H NMR spectra of many of these organometals have indicated that the circumambulations proceed by stepwise 1,5 shifts.[20] Recent work in this area using chiral groups has shown that the migrations occur by suprafacial 1,5 shifts with retention of configuration at the migrating atom.[102,116] In the case of 1-trimethylsilylindene, Ashe[119] has chemically trapped the isoidene form strongly indicating that even in a system where a 1,3 shift would avoid the formation of the unstable isoindene, the 1,5 shift process is still favored (eqn 33). The above example is instructive in another way as it shows that the migrating aptitude of $Si(CH_3)_3$ is greater than that of H. This is in fact general for Group IV substituents, as is shown in Table 1.



(33)

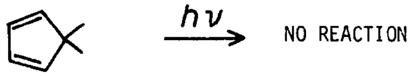
Table 1. Barriers to circumambulation of a group around cyclopentadiene

R	$\Delta G^{\ddagger}$	refs.
H	24.3^{a}	81
CH_3	41.8	84
$Si(CH_3)_3$	15.2	107,111
$Ge(CH_3)_3$	13.3	111
$Sn(CH_3)_3$	6.6	111

[a] value quoted is Ea.

There have been several discussions as to the origin of this effect and in particular over the question of the participation of d-orbitals in these migrations.[120] In particular Hoffmann *et al.*[23] have emphasized the close relationship among the *mono*, *bis*, *tris* and *pentahapto*-cyclopentadienyl systems and have presented the circumambulations in terms of changes in the coordination type of the migrating atom. This type of rearrangement, which has been termed a haptotropic shift, is very similar to that proposed by Childs and Zeya[96] to account for the migrations of the Lewis acid complexes of acetylpentamethylcyclopentadiene.

(ii) *Photoinduced circumambulations.* In contrast to the very large number of thermally induced circumambulations around a cyclopentadiene ring, there are few examples of comparable photo-initiated rearrangements. Alkyl substituted cyclopentadienes and indenes do not undergo direct alkyl group migrations when irradiated. For example McLean and Findlay[84] have shown that 5,5-dimethylcyclopentadiene is photochemically inert (eqn 34). 1,1-Dimethylindene, like indene itself, has been shown to undergo a photodimerization rather than alkyl shift (eqn 35).[121,122] In some photochemical reactions of cyclopentadienes alkyl shifts have been reported. These it would seem are the result of the photochemical isomerization of the five-membered ring to a bicyclo[2.1.0]pentene and a circumambulation of the cyclopropyl around the 4-membered ring. This type of reaction was discussed in an earlier section.



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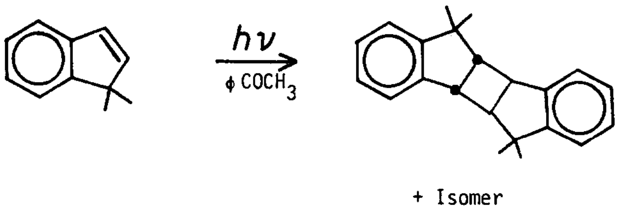
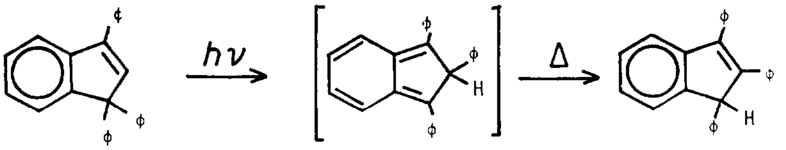


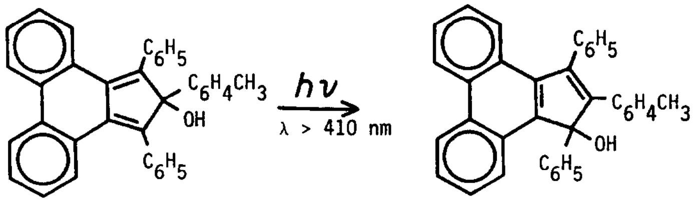
(35)

Photochemically induced aryl shifts have been observed with substituted indenes.[122,123] McCullough *et al.*,[124] have shown that these isomerizations proceed by a photochemical 1,5 shift of the aryl group to give isoindenes as observable intermediates (eqn 35). At normal temperatures the isoindenes undergo rapid thermal shifts to regenerate indenes. McCullough has pointed out that in contrast to alkyl shifts, photochemical suprafacial 1,5 shifts of aryl groups in these systems are consistent with orbital symmetry considerations.[121]



(36)

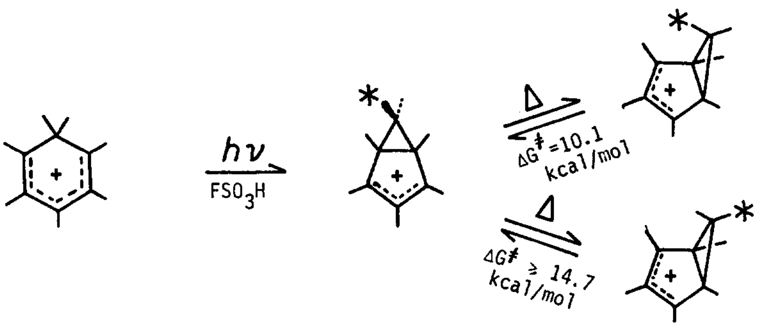
It has been reported that photoinduced hydroxy and alkoxy group migrations occur with some highly substituted cyclopentadienes (eqn 37).[125] These reactions appear to proceed by a dissociative pathway.



(37)

(b) *Bishapto cases*. There are a large number of examples of the circumambulation of a group which is bonded to two different ring atoms of a 5-membered ring. As might be expected, cationic examples are the most plentiful but in addition a radical case has been reported. While this type of circumambulation is nearly always thermally induced, it is frequently encountered as one of the steps in the photoisomerization of unsaturated 6-membered rings.

The most studied examples of this type of circumambulation involve the bicyclo[3.1.0]hexenyl cations. As was mentioned earlier, Swatton and Hart[8] were the first to propose this type of a circumambulation (eqn 2). The highly specific nature of the circumambulation became evident with the report of Childs and Winstein[9] on the properties of the haptamethylbicyclo[3.1.0]hexenyl cation. This cation undergoes a very low energy circumambulation ($\Delta G \neq 10.1$ kcal mol^{-1} [9]) which could be detected by an averaging of the resonances of the methyl groups on the 5-membered ring. During this circumambulation there was no interchange or averaging of the resonances of the C_6 methyl groups. The difference in energy between the circumambulation process which retains the overall stereochemistry at C_6 and the one which inverts this stereochemistry was found to be ≥ 4.6 kcal mol^{-1} (Scheme 12).

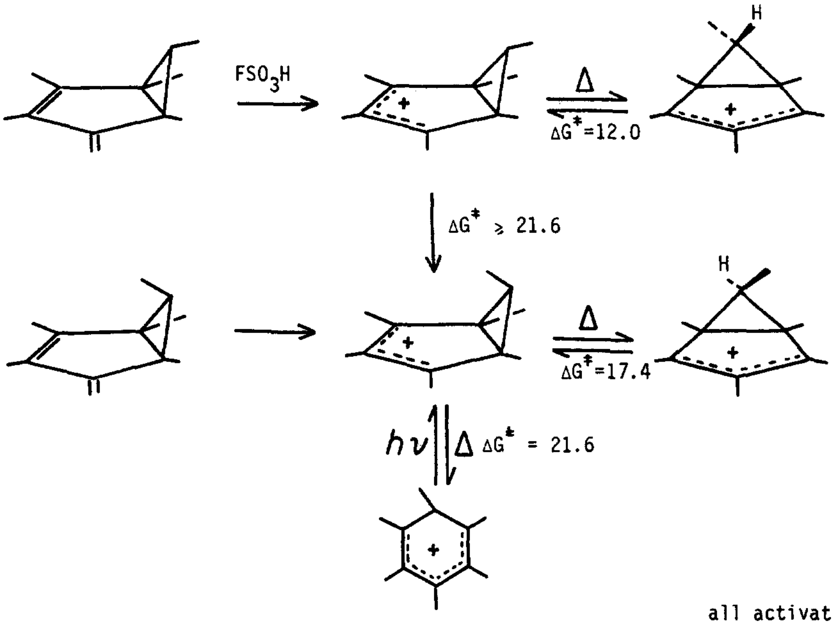


Scheme 12.

An even more remarkable stereoselectivity was observed with the corresponding hexamethylbicyclo[3.1.0]hexenyl cations.[96,127] Childs and Winstein[96] showed the difference in evergy ($\Delta\Delta G \neq$) between the circumambulatory pathway which retains the overall stereochemistry at C_6 and the one which interchanges the C_6-substituents to be at least 9.6 kcal mol^{-1}. This very high stereoselectivity corresponds to a difference in rate constants of the two processes of at least 8×10^8 at −36.5° (Scheme 13).

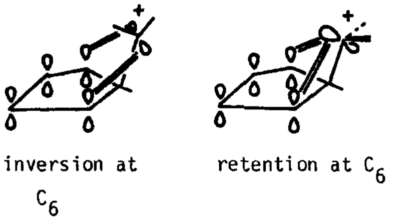
The obvious pathway for these circumambulations is one involving successive suprafacial 1,4-sigmatropic shifts. It is expected on the basis of orbital symmetry considerations that such a process should take place with inversion of configuration at C_6, the migrating carbon, and this would lead to the overall retention of stereochemistry. Hehre[128] has examined this type of rearrangement using molecular orbital theory and finds a substantial energy difference between the two possible transition states. It should be noted that the orbital symmetry allowed pathway is also the one preferred by least motion (Scheme 14).

While it is gratifying that the observed and predicted stereochemistries of these circumambulations agree it should not be assumed that they involve 1,4 shifts. A similar stereochemical outcome would be expected if the rearrangements were to involve the formation of bicyclo[2.1.1]hexenyl cations as transient intermediates (Scheme 15). In the case of the hexamethylbicyclo[3.1.0]hexenyl cation such a possibility was unequivocally ruled out by the independent synthesis of **33** and its C_6 isomer and the finding that these ions were stable under the conditions where the circumambulation of **34** is rapid.[129,96] Calculations of Hoffman *et al.*[23] suggest that the bicyclo[2.1.1]hexenyl cations should be less stable than the bicyclo[3.1.0]hexenyl cations. If this is the case then the observed stability of **34** must be attributed to kinetic barriers rather than ground state effects.

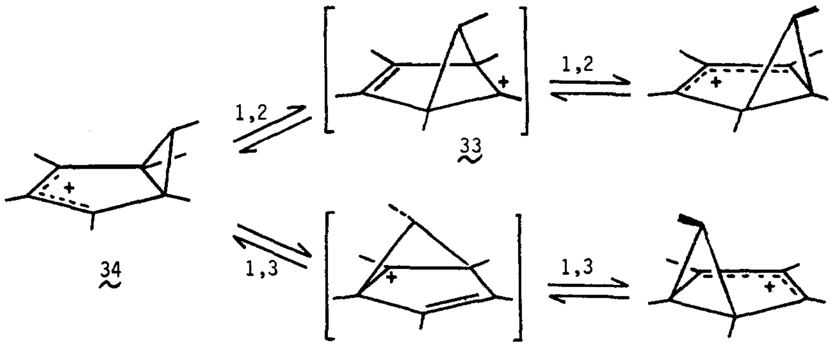


all activation energies in kcal/mol

Scheme 13.



Scheme 14.



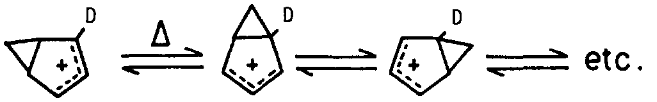
Scheme 15.

Experimentally, it has been found that there is considerable development of positive charge at C_6 of these bicyclo[3.1.0]hexenyl cations in the transition state of their circumambulations.[96] The importance of the C_6-substituents was also shown by the calculations of Hehre.[128] This sensitivity of the barrier to circumambulation of C_6 around the 5-membered ring can best be viewed as a balance between the bicyclo[3.1.0]hexenyl cation and cyclopentadienylcarbinyl cations. Charge stabilizing substituents at C_6 will have a greater effect on the relative energy of the cyclopentadienylcarbinyl structure than the closed system (eqn 38). As the substituents on C_6 become better at stabilizing a positive charge the relative energy difference between **35** and **36** should decrease. Indeed there is no limit to this in as much as when **36** becomes more stable than **35**, we have the situation of the migration of a *monohapto* group around a

35 36 (38)

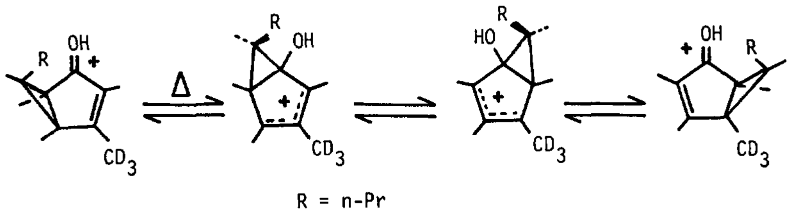
cyclopentadiene involving the *bishapto* system as a transition state. Such a case has of course been discussed previously with Lewis acid complexes of 5-acyl-pentamethylcyclopentadiene.

Berson *et al.*[130] have examined the circumambulatory rearrangements of the parent bicyclo[3.1.0]hexenyl cation. In this case rearrangement was slow on the NMR time scale and deuterium labels were necessary to detect the reaction (eqn 39). Again, a high stereoselectivity was found.



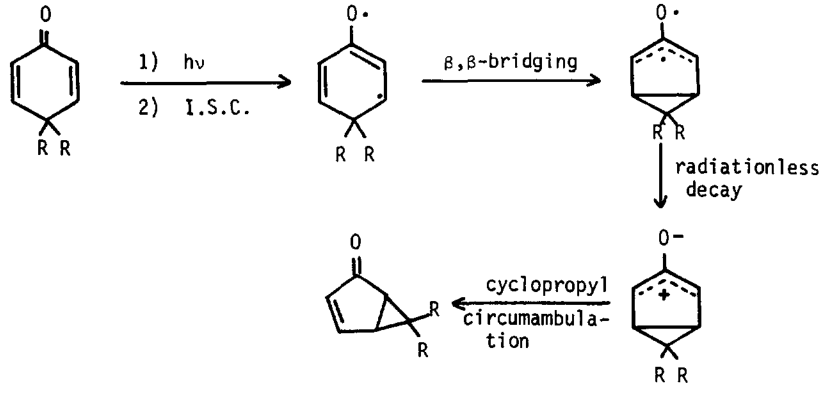
(39)

Turning to the hydroxy-substituted systems, Hart, Rodgers and Griffiths[131] have established that these circumambulations proceed with high stereoselectivity (eqn 40).



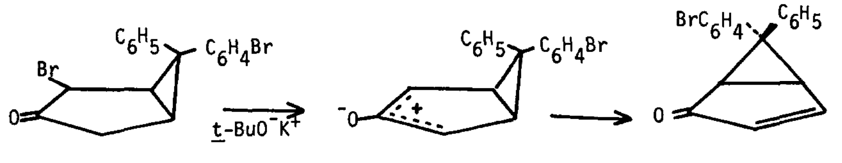
(40)

This reaction of the hydroxy systems is of particular interest in as much as closely related reactions have been invoked in the Type A photoreactions of cross conjugated cyclohexadienones.[132] The original mechanism proposed by Zimmerman and Schuster[7] for this type of reaction involved the cyclopropyl circumambulation of a ground state bicyclic zwitterion (Scheme 16).



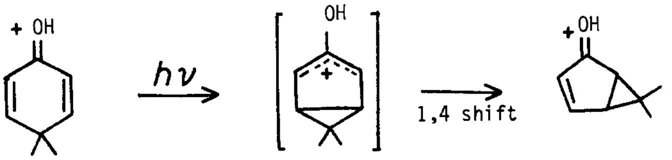
Scheme 16.

Trapping experiments have confirmed the intermediacy of a zwitterion in certain of these rearrangements.[133,134] Independent generation of bicyclo[3.1.0]hexenyl zwitterions has shown that they undergo rearrangement to the corresponding bicyclohexenones with inversion of configuration at the migrating cyclopropyl carbon (eqn 41).[135] Schuster *et al.*[136] have recently reported the photoisomerization of some chiral cyclohexadienones and showed that the photochemical reaction proceeds with this same stereochemical result. This conclusion has recently been confirmed by Samuel.[137]



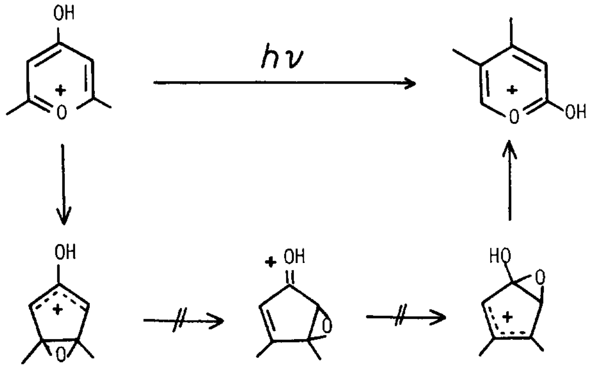
(41)

Protonated 2,5-cyclohexadienones undergo a comparable photoisomerization on irradiation to their neutral counterparts.[138] These reactions have been suggested to involve a cyclopropyl circumambulation, although definitive evidence is lacking (eqn 42). An extension of these reactions to *para*-protonated phenols has been reported.[139] Similar rearrangements have been found on irradiation of protonated cyclo-2,4-hexadienones.[138]



(42)

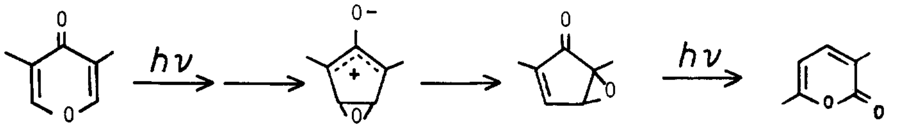
The circumambulation of an oxygen atom around a cyclopentenyl cation has been invoked to account for the photoisomerization of protonated 4-pyrones (Scheme 17).[74, 140] More recent studies by Barltrop *et al.*[141] suggest such an oxygen walk is not the major isomerization pathway but that a more complex route with solvent addition is involved.



Scheme 17.

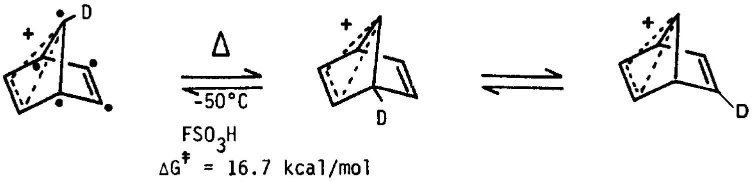
Circumambulations of oxygen or a nitrogen group could possibly be involved in the photo-reactions of pyrylium[142] and pyridinium cations.[143]

Pyrones themselves exhibit a variety of photochemical reactions.[144] In neutral solvents the observed phototransposition of 4-pyrones to 2-pyrones is thought to involve an oxygen circumambulation (eqn 43).[145]



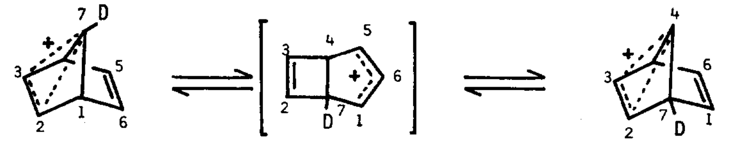
(43)

The examples presented so far in this section of circumambulations around a 5-membered ring have all involved cases where a single atom (CH_2; CR_2; O) is bonded twice to the ring. Circumambulations are not restricted to this type of situation and there are some well established examples where the circumambulating group is bonded by two different atoms to the five-membered ring. A case in point is the 5-carbon scrambling reactions of 7-norbornadienyl cations reported by Lustgarten, Brookhart and Winstein (eqn 44).[146]



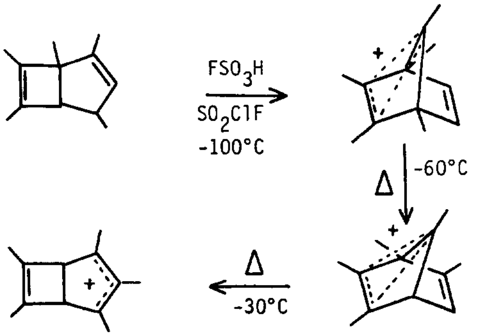
(44)

Using specifically deuterated cations, it was shown that the isomerization occurred by a stepwise circumambulatory motion of the two carbon bridge of the "bound" vinyl group around the five carbon ring (indicated by · in eqn 44). This circumambulation around the 5-membered ring was suggested to involve the intermediate formation of a bicyclo[3.2.0]heptadienyl cation and proceed by what the authors describe as an "inch worm, ratchet-like fashion" (eqn 45). Support for this suggestion came from the independent synthesis of the bicyclo[3.2.0]heptadienyl cations.



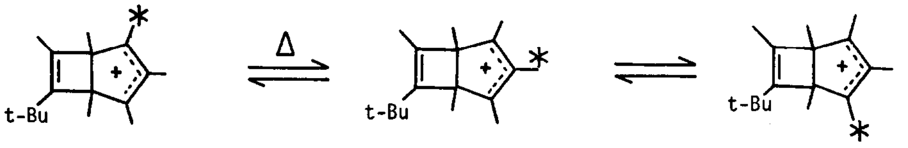
(45)

The relative difference in energy between the 7-norbornadienyl and bicyclo[3.2.0]heptadienyl cations is dependent on the positioning and nature of substituents.[146] Hogeveen and van Krutchen[147] have shown with the polymethyl substituted systems that the relative energies can be reversed in some cases. This is shown, for example, in the stepwise circumambulation of the pentamethyl cation (eqn 46). In this case successive steps require somewhat higher temperatures in order to proceed.



(46)

Hogeveen and van Krutchen[147] also generated the t-butyl substituted cation 37. NMR evidence indicated this ion exists as the bicyclo[3.2.0]heptadienyl cation. Labelling one of the 5-membered ring positions with a CD_3 group showed that the C_2-cyclobutene bridge circumambulates around the 5-membered ring. This reaction presumably involves the intermediacy of the now higher energy, and unobserved, norbornadienyl cations (eqn 47).

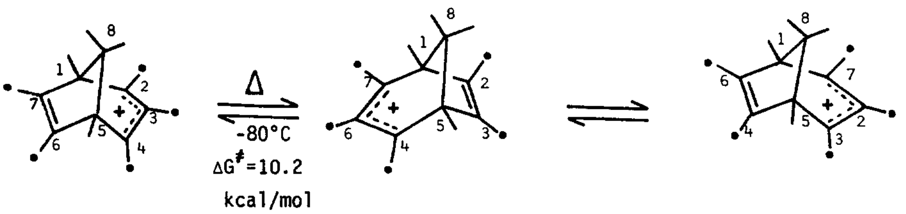


37

(47)

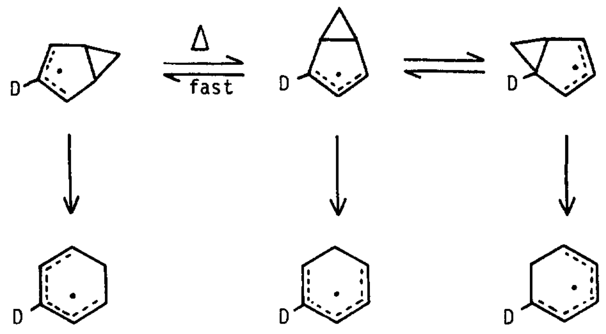
It is interesting that comparable circumambulatory rearrangements for the 7-norbornenyl and bicyclo[3.2.0]heptenyl cations appear to be more difficult than those of the 7-norbornadienyl and bicyclo[3.2.0]heptadienyl cations.[148]

Hart and Kuzuya[149] have reported a further example of a 5 carbon circumambulation with the polymethylbicyclo[3.2.1]hexadienyl cations. As is shown in eqn (48), carbons 1, 5, and 8 with their attendent methyl groups circumambulate around the remaining five carbons, C_2, C_3, C_4, C_6 and C_7. These five carbons can formally be considered to form a bishomocyclopentadienyl cation.



(48)

Circumambulations of *bishapto* groups around a 5-membered ring are not restricted to cations and related zwitterions. Sustmann and Lubbe[156] have reported that a circumambulation also occurs with the bicyclo[3.1.0]hexenyl radical (Scheme 18). This radical, when generated at −196° in adamantane matrix, was found to be stable up to −60°, when it isomerized to the cyclohexadienyl radical. Comparable isomerizations of specifically deuterated bicyclic radicals gave a mixture of deuterated cyclohexadienyl radicals, suggesting that circumambulation of the cyclopropyl ring around the cyclopentenyl radical is faster than the ring opening reaction.

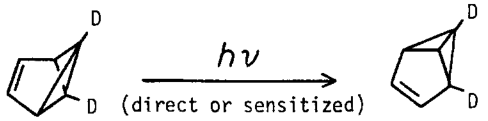


Scheme 18.

Comparable circumambulations of bicyclo[3.1.0]hexenyl anions do not appear to have been reported. Such anions are related by simple disrotatory electrocyclic reactions to the cyclohexadienyl anions.[151]

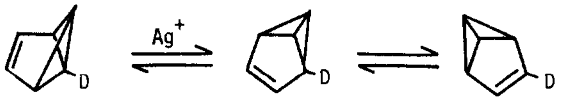
(c) *Trishapto cases.* Benzvalene provides an example of a molecule in which a potential migrating group is bound to three different ring atoms of a 5-membered ring. With the synthesis of specifically deuterated benzvalene,[152] both photochemical[153] and metal[15,155] catalysed degenerate rearrangements of benzvalene have been reported.

Katz, Turro *et al.*[153] have shown that either direct or sensitized excitation of 5,6-dideuterobenzvalene, **38**, leads to the formation of **39**. It was not reported whether any deuterium was also present at the vinyl sites. The conversion of **38** to **39** can be regarded as a circumambulation of C_6 around the 5-membered ring by what formally can be regarded as a 1,3-sigmatropic shift.



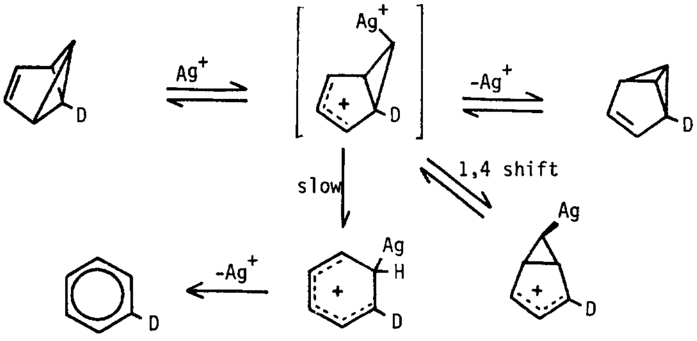
38 39

In the course of studies on the metal and metal ion catalysed isomerization of 5-deuterobenzvalene the recovered benzvalene was found to have extensive deuterium scrambling (eqn 49).[155] The mechanism



(49)

suggested for this circumambulation consists of the reversible addition of Ag^+ to one of the bicyclobutane bonds to give an 6-argentobicyclo[3.1.0]hexenyl cation. An additional possibility not considered

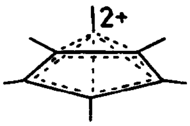


Scheme 19.

by the authors is a degenerate circumambulation of the bicyclohexenylcation comparable to those discussed in an earlier section (Scheme 19).

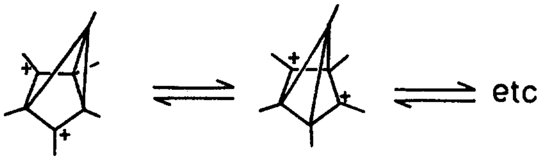
It is interesting that no thermally induced degenerate isomerizations of benzvalene have been detected in the absence of a metal or metal ion catalyst.[156] Such a reaction would formally involve suprafacial 1,3-sigmatropic shifts and within the geometric constraints of the molecule, be difficult to achieve.

Another possible example of a *trishapto* circumambulation around a 5-membered ring is provided by $(C(CH_3))_6^{2+}$ dication reported by Hogeveen and Kwant.[157] This ion has been formulated as the pyramidal dication **40**.[157,158]



40

An alternative possibility is that the dication consists of a rapidly equilibrating set of structures as shown in eqn (50). The ^1H NMR spectrum of the dication **40** is unchanged down to −140°. This means



(50)

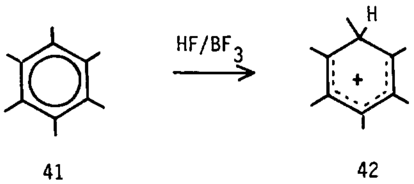
that if it does consist of a set of equilibrating structures then the barrier to the circumambulation must be less than 5 kcal mol.

CIRCUMAMBULATIONS AROUND 6-MEMBERED RINGS

(a) *Monohapto cases*

There are many examples of this type of circumambulation encountered with benzenium ions.[159] The development of strong acid solvents and consequent ability to study carbocations under long life time conditions have not only uncovered a large number of these reactions but also enabled their mechanisms to be studied in detail. It should also be noted that this type of circumambulation is also encountered under more conventional dilute acid conditions, as for example in the well known dienone/phenol rearrangements,[160] and as a competing reaction in the electrophilic substitutions of aromatic compounds.[161]

Hydrogen migrations are the most commonly encountered circumambulations. A good example of this type of rearrangement is provided by protonated hexamethylbenzene, **41**.[162,163] Evidence for the hydrogen migration comes from variable temperature NMR spectra of **42** in HF/BF_3 which show a "frozen" spectrum at temperatures below −80° and an averaged one at −20°.

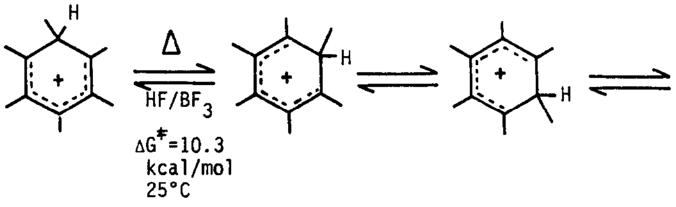


41 42

There are several mechanistic possibilities for the hydrogen shifts of a cation such as **42**.[159] The simplest one is an intermolecular exchange process with the proton pool. The rate of such a process is expected to be inversely related to increasing acid strength of the medium used and this has been used to check for this type of reaction. It has been found, for example, that an intermolecular exchange process takes place with protonated hexamethylbenzene in 96% H_2SO_4 or at 0° and above in HF/BF_3 medium.[162]

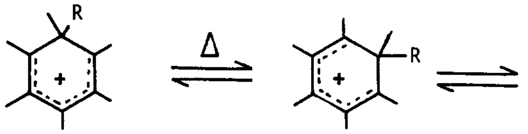
Intramolecular exchange is also possible. The rate of intramolecular exchange is expected to be independent of the strength of the acid used as solvent. Further evidence for this type of process is the persistence of a modified spin/spin coupling in the averaged spectrum. Thus at −20° in HF/BF_3, the ^1H NMR spectrum of **42** exhibits a high field doublet corresponding to 18 protons and lower field multiplet corresponding to the single added proton. The coupling constant observed of 2.1 Hz is the weighted mean of the coupling constants in the low temperature spectrum.[162]

There are a variety of different intramolecular shifts which in principle are possible with a cation such as **42**. These are 1,2, 1,3 or 1,4 shifts, or a combination of these. In addition there is what has been termed a "parachute" mechanism by Koptyug *et al.*[164] in which the migrating group can form a π-complex with the aromatic ring and then drop back to form a σ-bond to any of the ring carbons. With **42** and many other benzenium ions it has been shown that the hydrogen exchange occurs by successive 1,2 (or 1,6) shifts (eqn 51).[162,165]



(51)

Circumambulations around the 6-membered ring of a benzenium cation are not restricted to hydrogen as the migrating group. A wide range of other substituent groups are known to migrate (Scheme 20). The most extensively studied systems are based upon hexamethylbenzene and these are summarized in Scheme 20.[165] Line shape analyses, spin echo experiments, saturation transfer techniques and most recently, two dimensional NMR spectroscopy[166] have been used to examine the mechanism of these shifts. In most cases it would appear that the reactions are intramolecular and proceed *via* successive 1,2 shifts. No information about the stereochemistry at the migrating center is available.



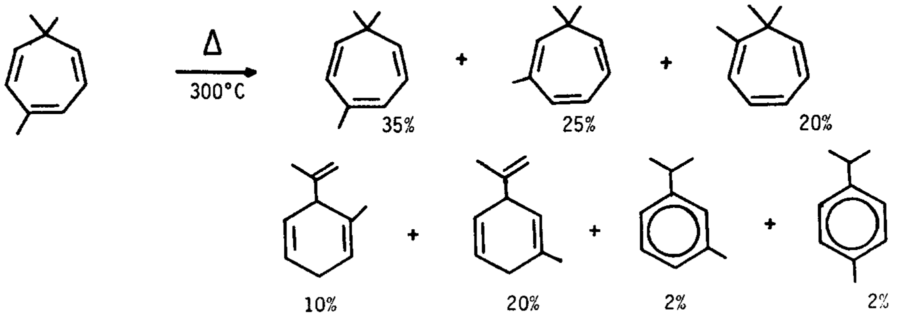
R	$\Delta G^{\ddagger}$ kcal/mol	reference.
H	10.6	162,163,164
CH_3	18.1	167,168
C_2H_5	16.0	168
$CH_2C_6H_5$	10.9	169
C_6H_5	17,2	170
$pC_6H_4CH_3$	16.0	171
pC_6H_4Cl	17.8	171
$pC_6H_4CF_3$	19.9	171
Cl	14.7	172
Br	9.2	173
NO_2	12.9	174

Scheme 20.

(b) *Bishapto cases*

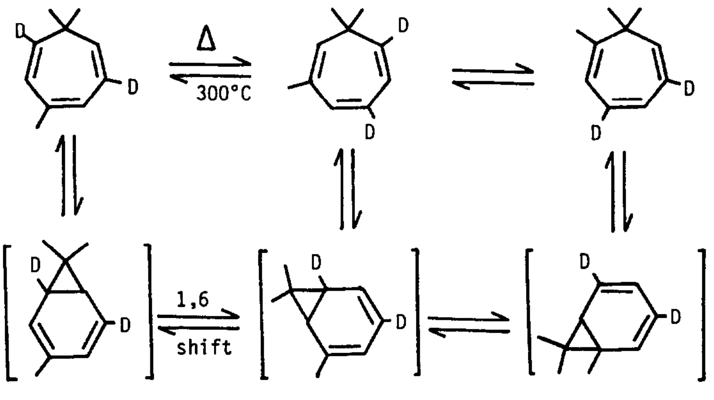
(i) *Thermally induced circumambulations.* As was mentioned at the outset of this review, a major impetus to the investigation of circumambulatory rearrangements came from the reports of Berson and Willcott on the thermally induced isomerizations of trimethylcycloheptatrienes (eqn 52).[6,175,176]

Using deuterated derivatives of these cycloheptatrienes, these workers were able to show that the interconversions of the three cycloheptatrienes involved skeletal rearrangements rather than hydride shifts.[175] It



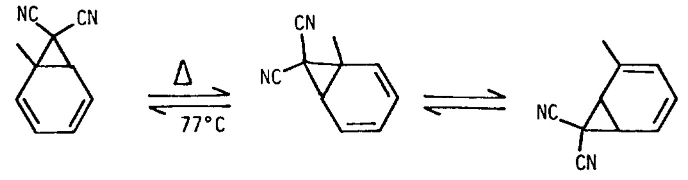
(52)

was suggested that the rearrangements could best be accounted for on the basis of a cyclopropyl circumambulation around norcaradiene valence tautomers of the cycloheptatrienes (Scheme 21).



Scheme 21.

Evidence supporting this suggested rearrangement pathway came from observations of the rearrangements of the 7,7-dicyanonorcaradienes. Ciganek has shown that two cyano groups at C_7 of a cycloheptatriene/noncaradiene system are sufficient to make the norcaradiene more stable than the cycloheptatriene form.[177] Thus it might be anticipated that rearrangements with the dicyanonorcaradiene might be considerably more facile than with cycloheptatrienes as the unfavorable pre-equilibrium step has been eliminated. Both Ciganek[178] and Berson *et al.*[179] showed that this was indeed the case (eqn 53).

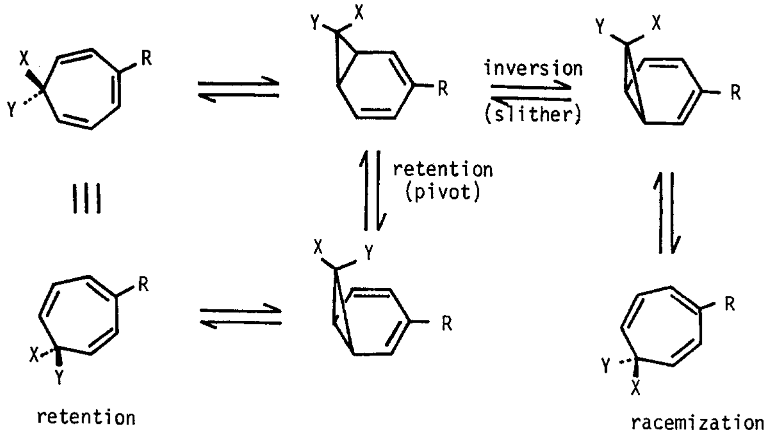


(53)

There has been considerable interest in the stereochemistry of the cyclopropyl walk step of these rearrangements of 7,7-disubstituted cycloheptatrienes. This walk reaction can be considered to be a suprafacial 1,5 sigmatropic shift. Orbital symmetry considerations suggest that such a concerted reaction should proceed with retention of configuration at the migrating cyclopropyl carbon. On the other hand such a reaction is the non-least motion pathway involving a 120° twist of the migrating carbon as compared to a 60° twist for the "forbidden", inversion path.[176] Calculations by Schoeller in fact suggest that subjacent orbital interaction is important in the disallowed pathway and that the two routes have very similar activation energies (inversion favored over retention by 1.4 kcal mol^{-1}.[180]

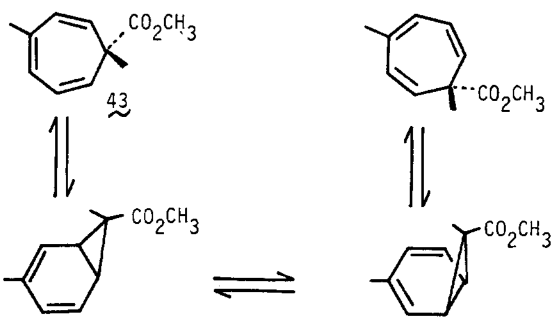
The experimental distinction between these two alternatives and other non-concerted pathways proved to be difficult, particularly as most systems exist preferentially in the cycloheptatriene form. Berson and Willcott pointed out that it was possible to differentiate between the various possibilities by using suitably labelled, optically active cycloheptatrienes.[175] Migration with retention would lead to no loss of optical activity whereas migration with inversion would lead to racemization (Scheme 22).

There have been several tests of the stereoselectivity of the cyclopropyl circumambulation and some conflicting claims. Klärner examined the thermal rearrangements of ester **43** and showed that the 1,5



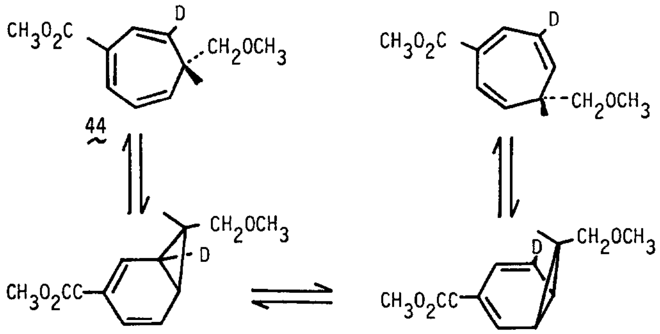
Scheme 22.

shift took place with inversion of configuration at the migrating center (Scheme 23).[181] The stereoselectivity of this orbital symmetry forbidden, least motion allowed migration was estimated to be in excess of 97.5%.

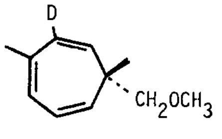


Scheme 23.

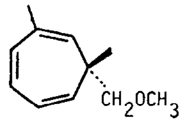
Hansen studied the thermolysis of optically active 1-deutero-3-methoxycarbonyl-7-methyl-7-methoxymethylcycloheptatriene, **44**, and found that racemization and deuterium scrambling took place at approximately the same rate (Scheme 24).[182] These results support the work of Klärner suggesting that the [1,5] shifts proceeds with inversion.



Scheme 24.



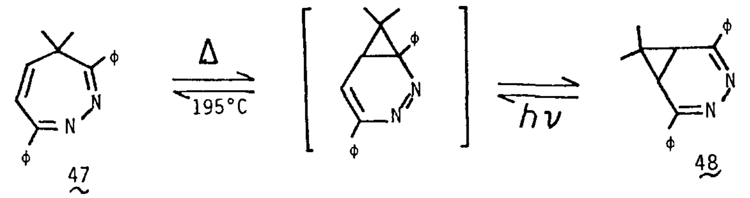
45



46

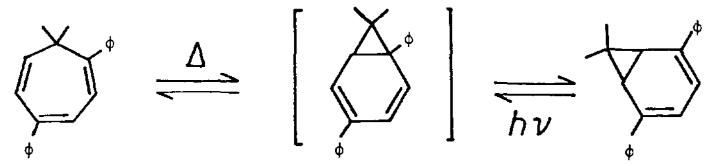
Baldwin and Broline have questioned these results as a result of a study of the rearrangement of **45**.[183] However, more recent work by Klärner and Brassel with the related ether **46** substantiates the claim that these reactions proceed with inversion of configuration in the 1,5 shift step.[184]

Heterocyclic 7-membered ring systems exhibit a variety of thermally induced isomerizations including circumambulatory rearrangements involving their bicyclo[4.1.0]hexadienyl type valence tautomers. For example Zimmerman and Eberback showed that the diazepine **47** was converted to the diazanorcaradiene **48** on heating at 195° (eqn 54).[185] Several closely related reactions have been reported.[186]



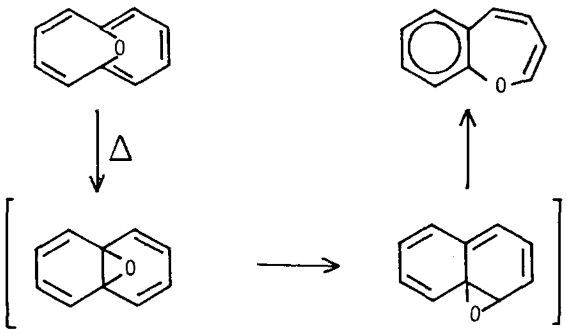
(54)

The positioning of conjugating substituents would appear to be important in determining this type of reaction. In the case quoted above the two phenyl groups stabilize the norcaradiene **48**.[187,188] As will be outlined below, this type of reaction is photochemically reversed. Paquette and Leichter have reported comparable reactions with a similarly substituted carbocyclic system, (eqn 55).[188]



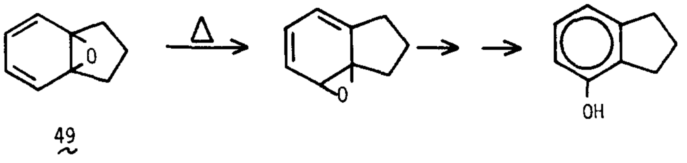
(55)

A heteroatom can be the atom or group in this type of circumambulation.[189] Oxepins appear to undergo oxygen walk reactions *via* their arene oxide valence tautomeric forms.[190,191] Vogel *et al.*[190] have reported that oxygen bridged cyclodecapentene is readily isomerized to benzoxepin by what would appear to be an oxygen circumambulation (eqn 56). Bruice, Jerina *et al.* have re-examined the conversion



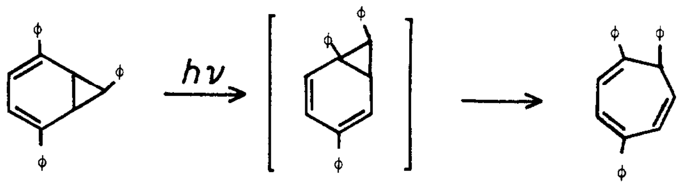
(56)

of the oxanorcaradiene **49** to indanol and concluded that under neutral conditions an oxygen walk process is the principle reaction pathway (eqn 57).[193,194]



(57)

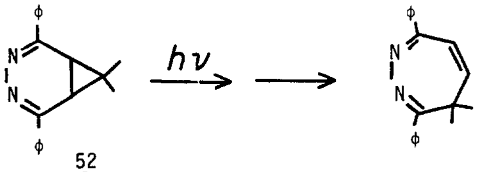
(II) ***Photochemically induced circumambulations.*** There are many examples of photochemically induced circumambulations of a three-membered ring around a cyclohexadiene. These are found in both "simple" norcaradiene systems and particularly with the benzosubstituted cases. In 1969 Mukai *et al.* reported the photochemical conversion of norcaradiene **50** to cycloheptatriene **51**.[195] They suggested, but did not prove, that a cyclopropyl walk reaction was involved (eqn 58). This type of reaction is a very general one of 2,5-diaryl substituted norcaradienes.[196] As was mentioned above Paquette and Leichter



50 51

(58)

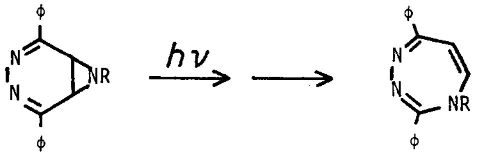
reported the comparable reaction for the 7,7-dimethyl-2,5-diphenylnorcaradiene (eqn 55).[188] Similarly Zimmerman and Eberbach showed that **52** was converted to **53** on irradiation (eqn 59).[185] This reaction



52 53

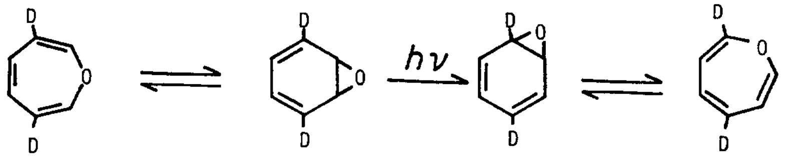
(59)

was studied in detail and it was established that the reaction proceeds by a cyclopropyl circumambulation. Saito *et al.* have reported a related nitrogen walk (eqn 60).[197]



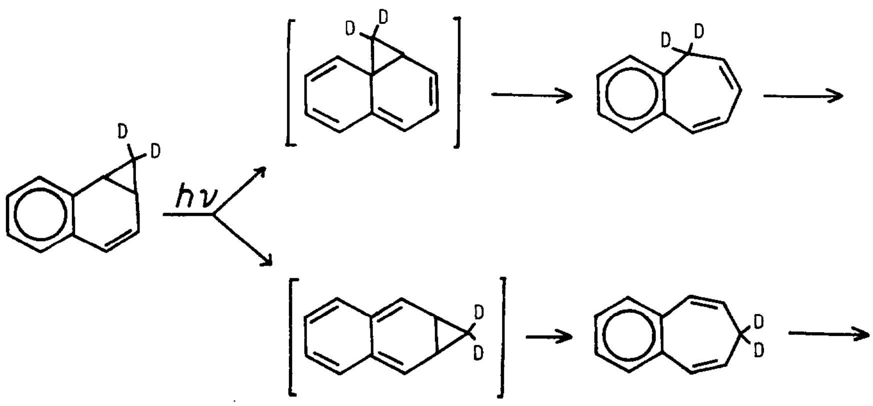
(60)

Arene oxides also have been shown to undergo photoinduced oxygen walk reactions. Thus benzene oxide/oxepin is converted photochemically to phenol.[190] Jerina and Chapman showed by using deuterated benzene oxide that in addition to the formation of phenol, deuterium scrambling occurred in recovered benzene oxide.[198] An oxygen circumambulation was proposed (eqn 61). Other arene oxides have been reported to undergo photoinduced oxygen walks.[191,199]



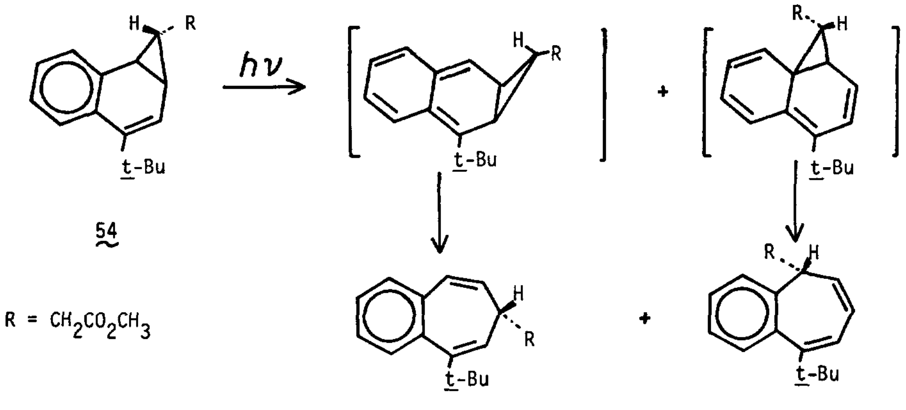
(61)

The photochemically induced circumambulations of benzonorcaradienes have received considerable attention.[178,200–204] The parent benzonorcaradiene, for example, undergoes a variety of photochemical reactions among which is the formation of the two benzocycloheptatrienes. Gruber and Pomerantz showed by using deuterium substituted compounds that both of these reactions appear to proceed via cyclopropyl circumambulations, Scheme 25.[201]



Scheme 25.

In a series of papers, Kato and colleagues have investigated the stereochemical course of these photoisomerizations of benzonorcaradienes.[202,203] Using the optically active ester **54**, it was shown that on direct irradiation both of the cyclopropyl circumambulations occur with inversion at the migrating center as would be anticipated on the basis of orbital symmetry considerations (Scheme 26).[203]

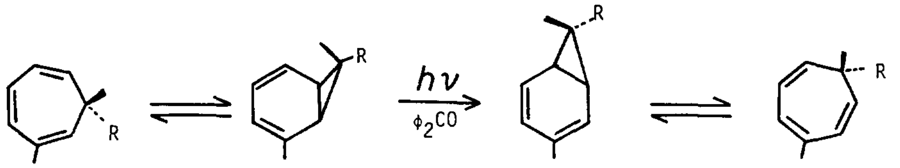


54

R = $CH_2CO_2CH_3$

Scheme 26.

Klärner and Yaslak[204] have examined the benzophenone sensitized circumambulations of **55** and **56** and have found that the reactions are stereoselective (92% for **55** and 96% for **56**). In each case the walk reactions occur with inversion at the migrating cyclopropyl carbons (eqn 62)).



(62)

55 ; R = CO_2CH_3

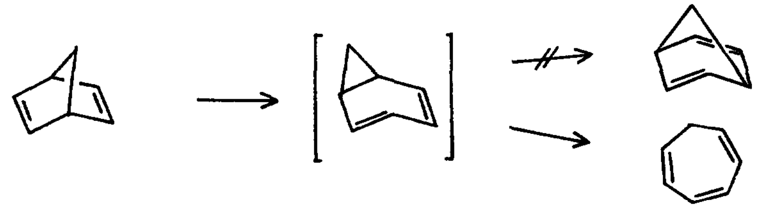
56 ; R = CN

It is interesting to note that all the circumambulations of norcaradiene type systems, whether they be thermally or photochemically induced, appear to proceed preferentially by the least motion preferred inversion process. Orbital symmetry seems not to be the dominant factor controlling the stereoselectivity of these reactions.

(c) *Other Bishapto systems*

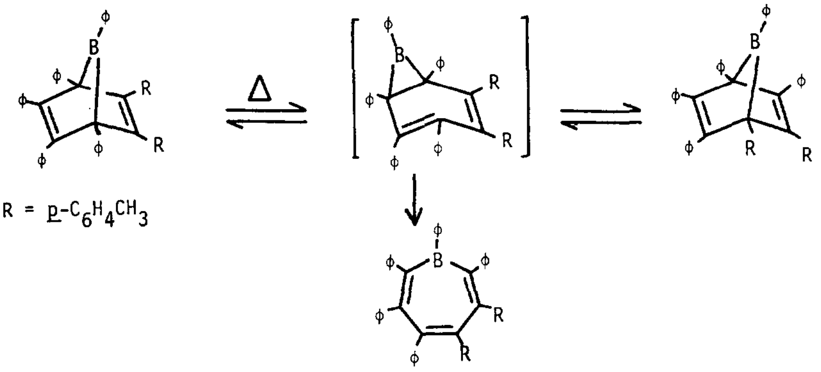
The circumambulations described in the previous sections have involved the migration of a cyclopropyl around a 6-membered ring. Other bridging possibilities exist but, it would seem, few examples of their circumambulations have been reported.

In principle it is possible to envisage a degenerate circumambulation of norbornadienes which could take place by successive 1,3 shifts (eqn 63). Norcaradiene would be an intermediate in such a reaction and this converts rapidly to the cycloheptatriene. There is no evidence that norcaradienes isomerize to norbornadienes. Rather on heating of norbornadienes to high temperatures, they isomerize to cycloheptatrienes.[205]



(63)

While circumambulations of carbocyclic bicyclo[2.2.1]heptadienes have not been reported, Eisch and Galle have reported such a reaction of the 7-boraderivatives.[206] The suggested mechanism involves two successive 1,3 shifts with the involvement of a 7-boranorcaradiene (Scheme 27). Other mechanisms are possible however, which would be more in line with the 5C and 7C scrambling reactions of the 7-norbornadienyl cations. Borepin is the ultimate thermal product.[207]

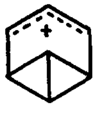


Scheme 27.

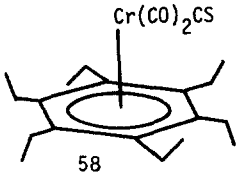
(d) *Tris- and higher hapto cases*

Little work has been reported in this area. The tricyclo$[4.1.0.0^{2,7}]$heptenyl cation, **57**, can be considered to be an example of a *trishapto* system. There is however, no evidence that **57** undergoes any circumambulations but rather converts to 7-norbonadienyl and bicyclo[3.2.0]heptadienyl cations.[208]

In passing it is of interest to note that circumambulations can be detected with *hexahapto* organometal derivatives of arenes.[209] For example a tripodal rotation of the $Cr(CO)_2CS$ grouping with respect to the coordinated hexaethylbenzene of **58** has been shown to have an activation energy of *ca.* 3 kcal mol^{-1}.[209b]



57

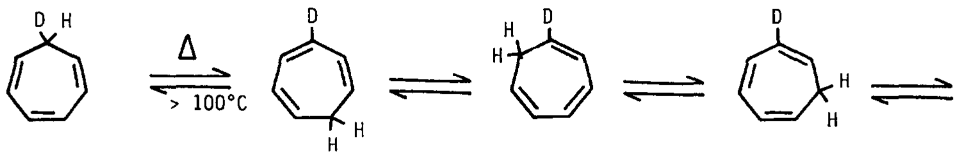


58

CIRCUMAMBULATIONS AROUND 7-MEMBERED RINGS

(a) *Monohapto cases*

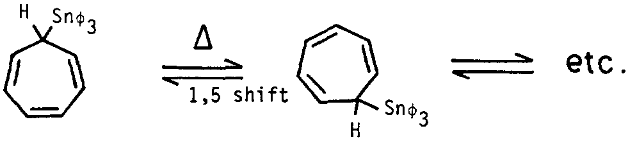
(i) *Thermal reactions.* Thermally induced circumambulations of cycloheptatrienes are frequently encountered. The best known example is provided by their facile hydride shifts.[35] Kloosterziel *et al.*[210] have shown by using deuterium labels that these circumambulations proceed by way of consecutive 1,5 shifts (eqn 64). This type of hydride shift occurs with a large variety of substituted cycloheptatrienes.[211-213]



(64)

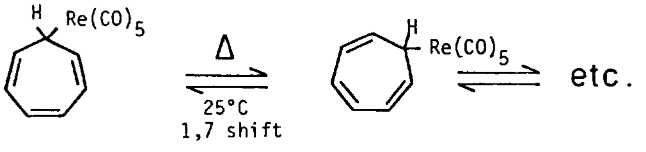
While there are many examples of circumambulations involving hydride shifts, there are few cases where other types of substituents are involved in these migrations. In general, at higher temperatures needed to induce migrations of alkyl and other groups, the "bones" rearrangements involving the norcaradiene valence tautomers come into play.[175-184] A 1,5-methoxy group migration has been reported by Hoffmann *et al.*[214]

Turning to monohapto-metallo cycloheptatrienes, there are two different types of migration encountered. With 7-triphenyltin cycloheptatriene, it has been shown that the tin group circumambulates around the 7-membered ring by a series of 1,5 shifts (eqn 65).[215]



(65)

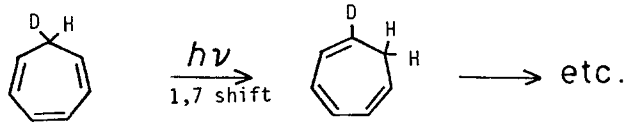
On the other hand the rhenium carbonyl substituted cycloheptatriene **59** appears to undergo a thermally induced circumambulation by a series of 1,7 shifts (eqn 66).[216] It is not clear at this point why there should be such a difference between these two systems.



59

(66)

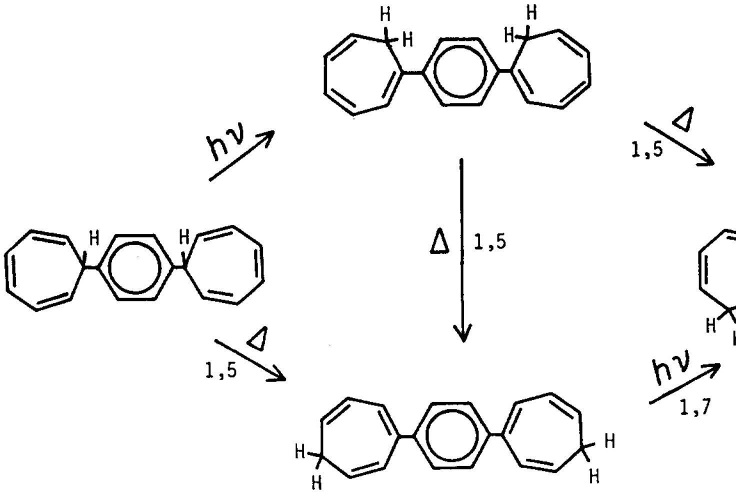
(ii) *Photochemical reactions.* At about the same time the nature of the thermally induced 1,5 hydride shifts were clearly delineated, there were a series of reports on photochemically induced hydride shifts of cycloheptatrienes.[217-219] In this case it was shown that the circumambulations proceed by way of the symmetry allowed 1,7 shifts (eqn 67).



(67)

The efficiency of this photochemical hydride shift was shown to be some five-hundred times greater than the competing electrocyclic closure to bicyclo[3.2.0]hepta-2,6-diene.[219,220] Comparable 1,7 hydride shifts have been encountered on irradiation of a wide variety of substituted cycloheptatrienes.[211,221] A particularly appealing set of these reactions described by Murray and Kaplan is shown in Scheme 28.[212]

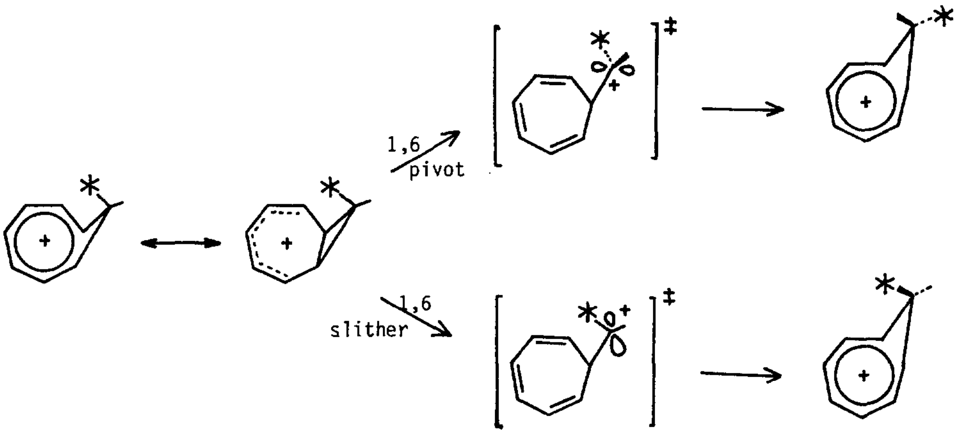
Photo-induced alkyl shifts have also been reported.[222]



Scheme 28.

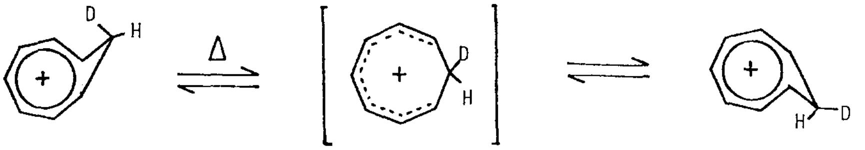
(b) *Bishapto cases*

(i) *Thermal reactions.* Considerable attention has been given to the possible occurrence of circumambulatory rearrangements of homotropylium cations. Until recently this search met with little success. Two factors combine to make circumambulatory rearrangements of homotropylium cations more difficult than the comparable rearrangements of the bicyclo[3.1.0]hexenyl cations discussed previously. Firstly, the homotropylium ions are homoaromatic and for the migration to occur the resulting stabilization must be lost.[223] A second factor comes from orbital symmetry considerations where it is expected that the allowed migration, which involves retention of configuration at C_8, is the non-least motion pathway. In other words the ground state of the homotropylium is stabilized as compared to the bicyclo[3.1.0]hexenyl cations whereas the "allowed" transition state for the homotropylium cation circumambulation is destabilized (Scheme 29).



Scheme 29.

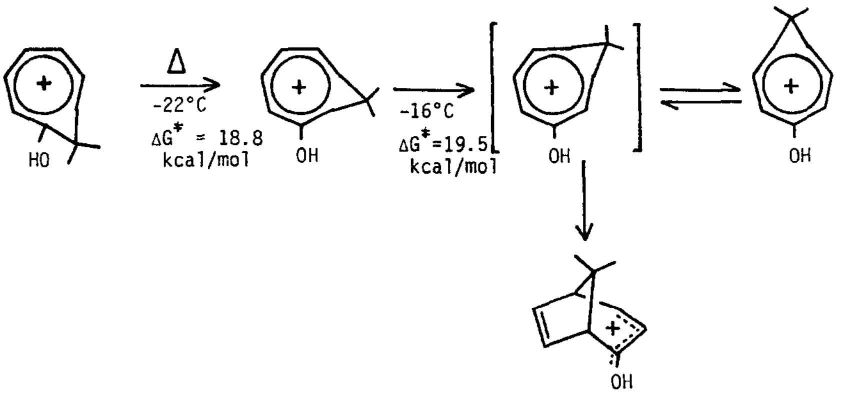
While the occurrence of an "allowed"pivot type circumambulation could account for the endo-exo equilibration of isotopic labels on C_8 of homotropylium cations,[224] in practice no such migration has been detected with simple homotropylium cations. This equilibration of C_8 isotopic labels has been examined with a variety of ring labeled homotropylium cations and in each case endo-exo interconversion occurs by a ring inversion process rather than by circumambulation (eqn 68).[225–227] The most complete study reported is that of Berson and Jenkins[225] who concluded that the barrier to circumambulation of the homotropylium cation itself must be at least 27 kcal mol⁻¹. Calculations by Hehre[128] for this migration suggest the barrier should be of the order of 43 kcal mol⁻¹.



(68)

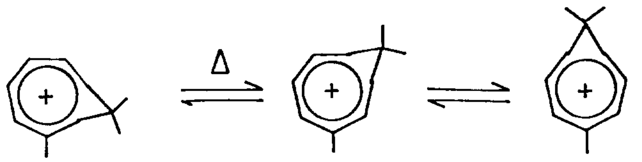
Just as with the circumambulations of the bicyclo[3.1.0]hexenyl cations, charge stabilizing substituents at C_8, the migration centre, facilitate these reactions. Hehre explored the effect of methyl substituents using molecular orbital theory and predicted that circumambulations of the 8,8-dimethylhomotropylium should be facile.[128] It was suggested that the activation energy for the forbidden, slither process should be of the order of 13 kcal mol⁻¹, some 15 kcal mol⁻¹ less than would be required for the allowed pivot route.

The first demonstration that 8,8-dimethyl substituted systems can circumambulate came from the report of Childs and Rogerson[227,228] on the rearrangement of the corresponding homotropone (Scheme 30). No information is available as to the steric course of this reaction. No comparable circumambulations of the mono-methyl cations and parent protonated homotropones have been detected.



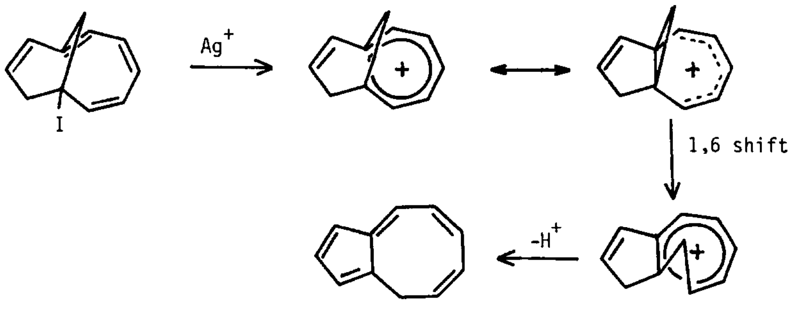
Scheme 30.

The parent 8,8-dimethylhomotropylium cation has been prepared.[229] It undergoes a facile rearrangement to isopropyltropylium cation at −50° which prevented the detection of any circumambulation using a line broadening technique. By labelling one of the ring carbons with a methyl substituent, it was possible to detect a slow circumambulation at −75° (eqn 69).



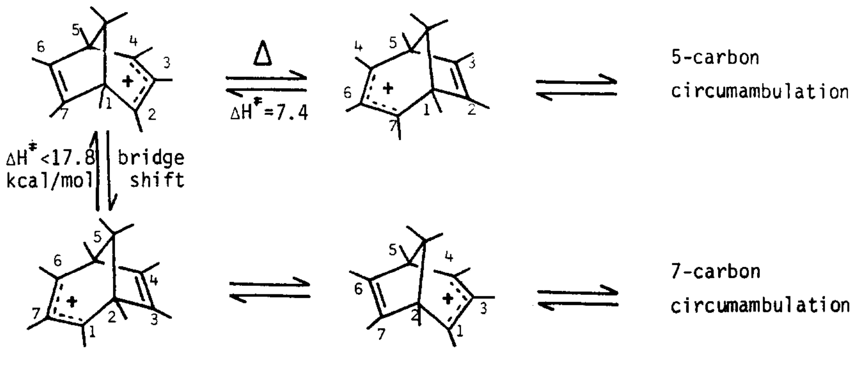
(69)

Scott and Brunsvold[230] have reported the circumambulation of an C_8 unsubstituted, but constrained homotropylium cation (eqn 70). It was suggested that in this case the three carbon bridge linkage acts to close C_1–C_7 bond, presumably decreasing the homoaromatic stabilization, and so facilitating the migration.



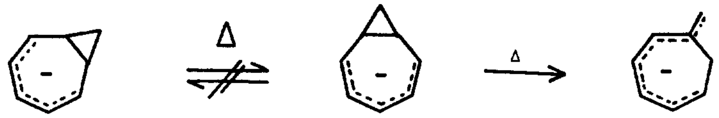
(70)

The bicyclo[3.2.1]octadienyl cations are structurally related to the homotropylium cations. This can be seen from Scheme 30, where the protonated 8,8-dimethyl homotropones eventually rearrange to the protonated bicyclo[3.2.1]octadienone. Hart and Kuzuya[149] have investigated the circumambulatory rearrangements of the polymethylbicyclo[3.2.1]octadienyl cations. As was stated earlier, at low temperatures a 5-carbon circumambulation was observed which interconverted C_2, C_3, C_4 ,C_6 and C_7. At higher temperatures they noted a seven-carbon circumambulation in which the bridging C_8 carbon effectively circumambulates around the 7-membered ring. It was suggested that this seven carbon circumambulation involves the 5-carbon shift process together with a slower bridge shift (Scheme 31).



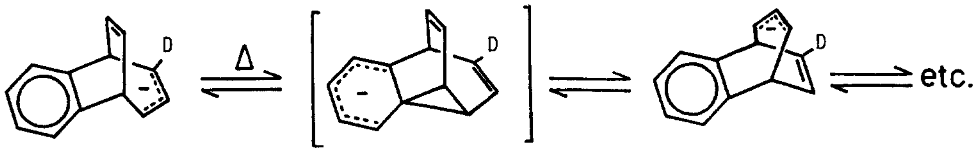
Scheme 31.

Turning to the anions, the bicyclo[5.1.0]octadienyl anion has been prepared.[231,233] This anion exhibits a temperature independent ^1H NMR spectrum over the range of −80 to −20°, indicating that any circumambulation is slow on the NMR time scale (eqn 71).[232] On irradiation bicyclo[5.1.0]octadienyl anions are interconverted with the cyclooctatrienyl anions.[233] In the absence of any ring labels it is not clear whether photochemically induced circumambulations are also occurring with these anions.



(71)

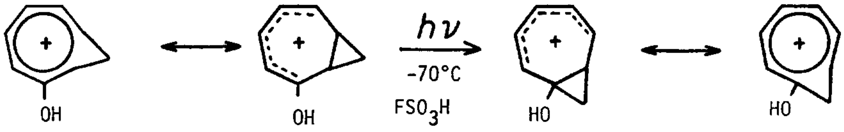
Grutzner *et al.*^{234} have detected a 7-carbon circumambulation of the bicyclic anion **59**. The circumambulation was suggested to involve intermediate cyclopropyl anions as shown in eqn (72).



59

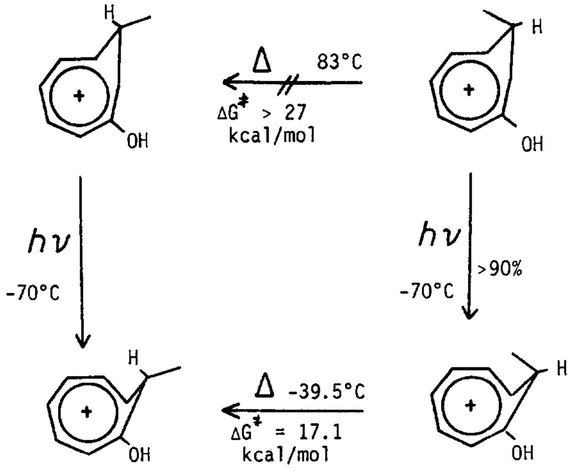
(72)

(ii) ***Photochemical reactions.*** Photochemically induced circumambulations have been reported with the 2-hydroxyhomotropylium cations by Childs and Rogerson.^{227} On irradiation these cations are converted to the corresponding 1-hydroxy ions (eqn 73). As is shown in Scheme 32, these reactions occur in a stereoselective manner by a slither movement. This process is both orbital symmetry and least motion allowed.



(73)

Circumambulations of *tris* and *higher hapto* bound groups around 7-membered rings do not appear to have been reported.



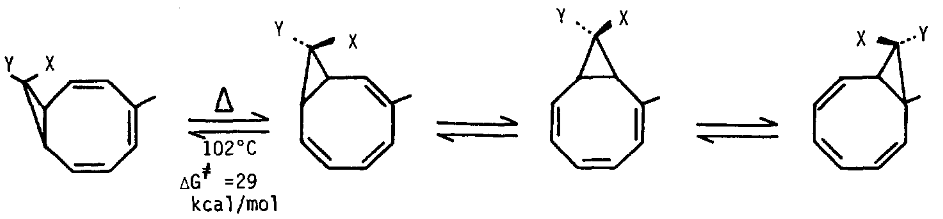
Scheme 32.

CIRCUMAMBULATIONS AROUND 8 AND 9-MEMBERED RINGS

There are relatively few reports of circumambulation with the larger membered ring systems. In principle circumambulations should still occur but in practice other rearrangements of these unsaturated rings frequently have lower activation energies.

With the 8-membered rings there appear to be no circumambulation reported of ***monohapto*** bound groups. The homotropylium cations, for example, do not exhibit 1,2 (1,8) hydride shifts^{223} and no comparable reactions have been reported for the cyclooctatrienyl anions.^{232,233}

The ***bishapto*** 8-membered ring systems provide a good example of the difficulty in detecting circumambulations in the presence of a variety of other possible isomerization pathways. Bicyclo[6.1.0]nona-2,4,6-trienes, which could undergo a cyclopropyl circumambulation, have been found to isomerize to *cis* and *trans*-dihydroindenes,^{235} bicyclo[5.2.0]nona-2,5,8-trienes and *cis, cis, cis, trans*-cyclononatetraenes,^{236} tricyclo[6,1,0.0^{2,6}]nona-3,5-dienes,^{237} and bicyclo[4,2,1]nona-2,4,7-trienes.^{238} Despite the propensity of the bicyclo[6.1.0]nonatrienes to rearrange to other ring systems, Klärner^{239} has been able to show that the 9-cyano-4,9-dimethyl systems **60** and **61** undergo a cyclopropyl circumambulation (eqn 74).



(74)

60	35%	33%	21%	11%
61	34%	38%	24%	4%

60; X = CH_3, Y = CN

61; X = CN, Y = CH_3

Both **60** and **61** undergo circumambulatory rearrangements. In each case a mixture of four isomers was obtained however there was no interconversion between the two series of compounds. In each case the circumambulations proceeded with an inversion at C_9 (the slither mechanism) with very high stereoselectivity. This reaction course is the one expected on the basis of both orbital symmetry and least motion considerations.

In terms of higher membered rings, Groves and Ma[240] have suggested a circumambulation of an ethylidene bridge around the 9-membered ring of the homobullvalenyl cation as one way in which the observed deuterium scrambling could be accommodated. It would appear that further reactions are necessary to fully account for their observations.

CONCLUSIONS

As is evident from the material in this review there are a large number of molecular rearrangements which can be classified as circumambulatory rearrangements. Indeed it was the size of the topic and the difficulty in locating the diverse material which led to the classification system used here for this class of rearrangement. It is hoped that this classification, which is based firstly on the size of the ring around which the circumambulation occurs and secondly on the number of ring atoms to which the migrating group is bonded, might be generally useful.

Not only are there a large number of examples of circumambulatory rearrangements but many of these have been important in the development of our understanding of the importance of orbital symmetry and least motion in sigmatropic shifts. A comparison of the cyclopropyl circumambulations about 4, 5, 6, 7 and 8-membered rings, for example is particularly instructive in this context. In each case the preferred migration pathway would seem to be that involving inversion at the migrating carbon, the slither movement. This is the least motion favored process for all but the 4-membered ring. Orbital symmetry is clearly not the all determinant factor although this would seem to play an important role in determining the barriers to circumambulation.

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