Thermal [1,*j*] Sigmatropic Rearrangements

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Contents

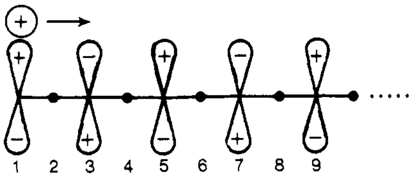
I. Introduction

Interest in the study of concerted processes in organic chemistry has increased markedly since the development of the general theory of the principles of orbital symmetry by Woodward and Hoffmann.[1] Consequently, application of the rules governing orbital symmetry control in electrocyclic reactions, sigmatropic rearrangements, cycloaddition reactions, and cheletropic processes has contributed much to our understanding of the nature of concerted reactions. Thermal and photochemical [*i*,*j*] sigmatropic rearrangement via either suprafacial or antarafacial pathways, and the resultant stereochemical consequences, is one of the more fascinating of these processes and has been the subject of several early reviews.[2-8] However, during the past 5 years a small army of workers has labored to demonstrate the wide applicability of orbital symmetry rules (or lack thereof) in sigmatropic processes in an even wider range of systems. Whereas not long ago sigmatropic migrations were unknown except for hydrogen, deuterium, and a few esoteric carbon examples, today not only are carbon migrations widely documented, but migrations of other functionalities (halogen, oxygen, nitrogen, organometallics, etc.) are being noted with ever increasing frequency.

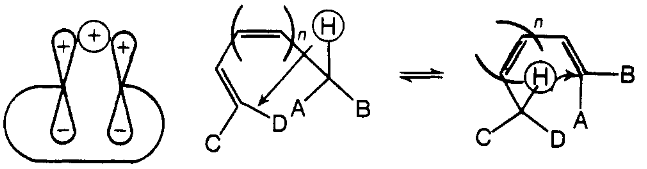
This review will be limited to thermal [1,*j*] sigmatropic migrations ($j = 3, 5, 7, 9$) in neutral molecules, but will cover all known migrating atoms or groups. Both cyclic and acyclic systems will be discussed and the literature coverage complete through the June 1974. Although several reviews during the past 5 years have discussed pericyclic reactions, sigmatropic processes have not been discussed in detail. In particular, it is now possible to review the process of sigmatropic migration in terms of energetics and the nature of the transition state from the wealth of kinetic data now available. It is realistic and feasible to discuss migratory aptitudes and competition between various possible allowed pathways, or between allowed and forbidden routes. Recently, it has also been recognized that conformation can affect the rates and also the product distributions of various thermal processes, and it is pertinent to extend this discussion to the interpretation of various aspects of sigmatropic migration. Finally, this review is an attempt to bring some order to the chaotic dispersion of information presently available so as to make it more useful and widely known.

II. Theoretical Aspects of Sigmatropic Migration

The elementary theoretical framework governing sigmatropic migration has previously been described in detail by Woodward and Hoffmann.[1] [1,*j*] hydrogen migration may be considered in terms of an interacting hydrogen atom and the HOMO of a polyene radical. The migrating H thus may participate in two possible transition-state geometries, if orbital symmetry is to be maintained. In suprafacial migration, the migrating H maintains contact at all times with the same face



Concerted Sigmatropic Suprafacial Pathway ($n = 1, 3, \ldots$)



Concerted Antarafacial Pathway ($n = 0, 2, 4, \ldots$)

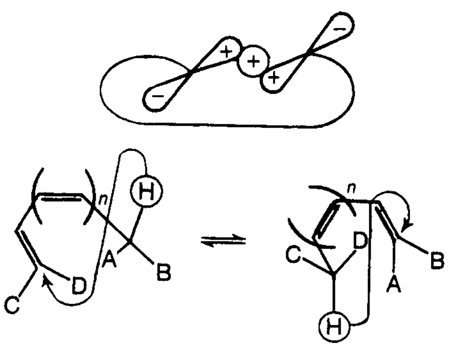


TABLE I. HOMO Selection Rules for [1,*j*] Sigmatropic Migration

j	Allowed	Forbidden
3	Antara-retention	Antara-inversion
	Supra-inversion	Supra-retention
5	Antara-inversion	Antara-retention
	Supra-retention	Supra-inversion
7	Antara-retention	Antara-inversion
	Supra-inversion	Supra-rentention

of the π system, while in an antarafacial process the hydrogen must maintain contact with both faces of the π system simultaneously. This requirement makes [1,3] antarafacial hydrogen migration extremely difficult, if not impossible.

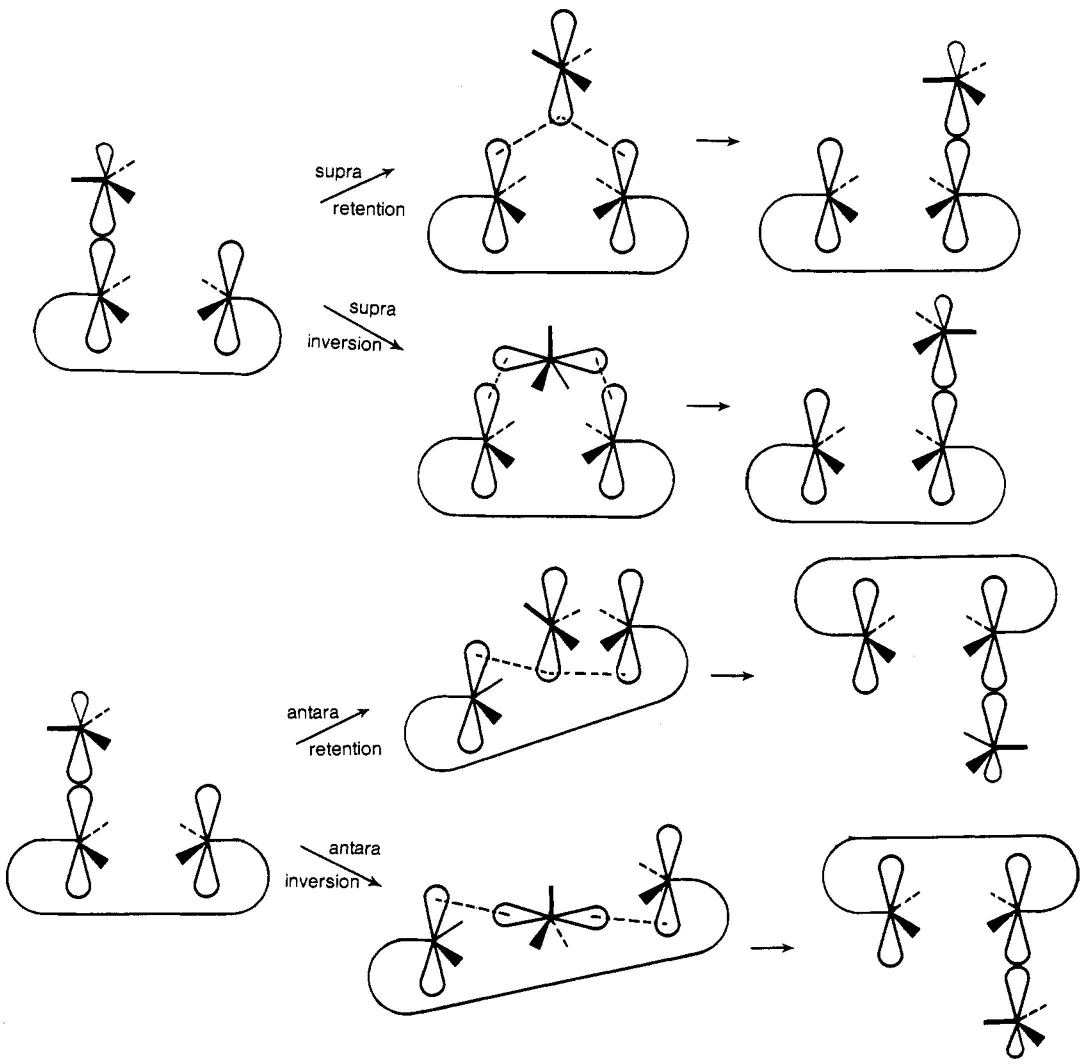
If the migrating atom is capable of undergoing stereochemical inversion, then the selection rules allow two distinct suprafacial or antarafacial routes with attendant retention or inversion at the migrating center (Scheme I). Thus for migrating groups other than hydrogen, [1,3] migrations become feasible. Selection rules for neutral [1,*j*] thermal migrations are summarized in Table I.

An alternative viewpoint of sigmatropic migration has been proposed by Zimmerman[9] and discussed also by Dewar.[10] Basically, this approach considers that thermal sigmatropic migration occurs via aromatic transition states. Cyclic transition states may be classified as either aromatic or antiaromatic depending on the number of π electrons involved and whether the polyene follows Hückel (zero or even number of twists in the cyclic array) or Möbius (odd number of twists) topology. Möbius transition states will be aromatic for 4*n* π electrons, with one sign inversion in the cycle, while Hückel transition states will be aromatic for (4*n* + 2) π electrons, with no sign inversions. Thus [1,3] hydrogen migration, involving 4 π electrons, can only occur via a Möbius array, an antarafacial pathway. [1,5] sigmatropic hydrogen migration, a (4*n* + 2) π array, follows a Hückel suprafacial pathway. The selection rules derived from application of the Hückel–Möbius concept are identical with those from the HOMO approach, but seem preferable to some workers because they avoid the necessity of knowing the individual symmetries of HOMOs (see Table II).

TABLE II. Selection Rules for Thermal [1,*j*] Sigmatropic Migrations

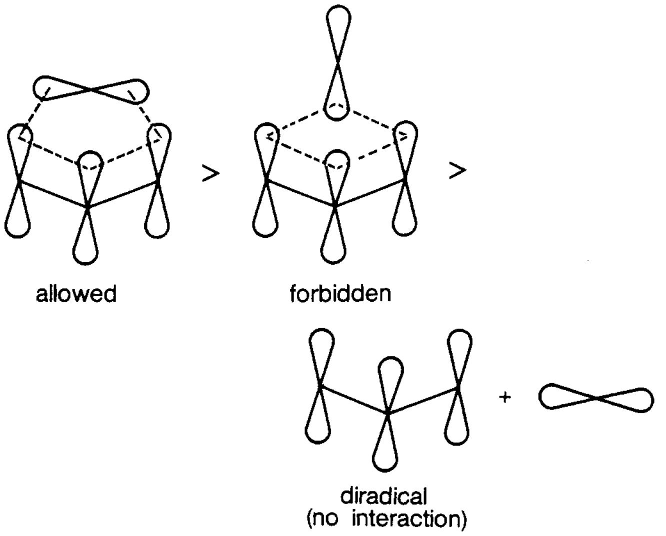
No. of electrons	System type	*j*	Allowed migration
4	Möbius	3	Antara-retention
			Supra-inversion
6	Hückel	5	Antara-inversion
			Supra-retention
4*n*	Möbius	(4*n* − 1)	Antara-retention
			Supra-inversion
4*n* + 2	Hückel	(4*n* + 1)	Antara-inversion
			Supra-retention

SCHEME I. Possible Pathways for Concerted [1,3] Migration



Various orbital interaction schemes have recently been devised which extend the above arguments. Fukui has reviewed[11] a method which considers the orbital interaction between the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) to predict the most favorable steric pathway. More recently, Goddard[12] has proposed the orbital phase continuity principle (OPCP), an ab initio method which asserts that certain phase relationships must occur between the orbitals of the reactants and products for the reaction to be allowed. The results generally agree with the Woodward-Hoffmann rules, and OPCP may also be applied to reactions involving no symmetry. Goddard's approach is based on a generalized valence-bond self-consistent field method and thus is the valence bond analog of the Woodward-Hoffmann MO approach. Finally Epiotis[13] has applied configuration interaction (CI) considerations in an effort to predict stereoselectivity in [1,3] and [1,5] shifts. Interestingly, he concludes that CI can affect [1,3] shifts and actually reverse stereoselectivity if groups of widely differing polarity are involved, but that [1,5] shifts are not affected. A generalization of this result is that CI is important for $4n$ processes, but not for $4n + 2$ aromatic arrays.

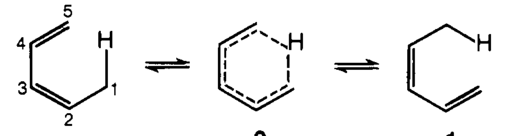
A topic of much recent concern centers on the question of the nature of a "forbidden" process. By carefully choosing the transition state geometry, one can envision symmetry-allowed concerted mechanisms for a great many reactions. However, other factors, such as ring strain or steric blockage may hinder or even preclude an "allowed" concerted process, even though it is probably true that in the absence of such constraints reaction will proceed through the allowed concerted route. If reaction nevertheless occurs, one must choose between a stepwise mechanism or a forbidden pathway. Berson and his coworkers[14,15] have recently discussed these problems in detail and have concluded that for [1,3] carbon migrations, and possibly other transition states as well, the order of preference can be allowed > forbidden > diradical. These workers point out that forbidden reactions may well be concerted and predictably stereoselective. The concertedness of the forbidden pathway becomes possible by interaction of the migrating carbon p orbital with a subjacent bonding allylic orbital. Berson thus refers to this electronic factor as Subjacent Orbital Control. These workers are careful to point out, however, that this effect does not assume importance unless steric factors argue against the allowed route. It would appear then that concerted forbidden processes can occur under the proper conditions, and it will be interesting to see if forbidden sigmatropic migrations of higher order ([1,5], [1,7], etc.) will be discovered in the future.



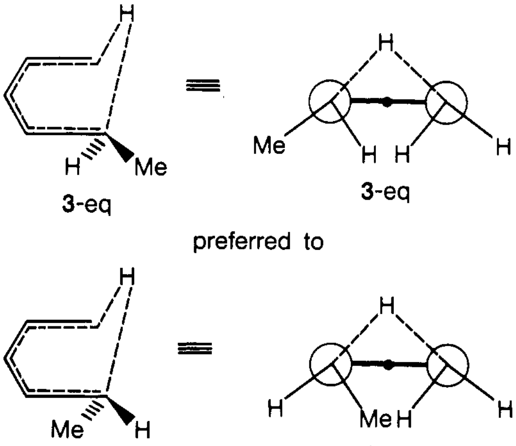
III. Nature and Conformation of Sigmatropic Transition States

A. Migration in Acyclic Systems

Concerted migration of a σ bond between the termini of a polyenylic π-electron system implies the formation of a cyclic transition state. Thus a [1,5] migration proceeds via a cyclic six-membered transition state with suprafacial (allowed) geometry. It has been recognized that a cis configuration about the C_2–C_3 π bond is a necessary prerequisite, as a trans orientation would dictate a highly strained transition state.[4] Substituent groups will tend to occupy preferentially the more stable pseudo-ring positions. Thus thermolysis of *cis*-1,3-hexadiene yields predominantly *cis,trans*-2,4-hexadiene, presumably via a transition state wherein the methyl group occupies a pseudo-equatorial position.[16] However, if there is little steric difference between two competing alkyl groups, Roth and coworkers[17] found that either may occupy the pseudo-equatorial position in the suprafacial transition state. Thus at 250° (*S*)-*cis,trans*-3-methyl-7-deuterio-4,6-octadiene yields a mixture of (*R*)-*trans,cis*-3-methyl-7-deuterio-3,5-octadiene and (*S*)-*cis,cis*-3-methyl-7-deuterio-3,5-octadiene (see Scheme II).



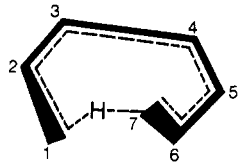
1 **2** **1**



3-eq **3-eq**

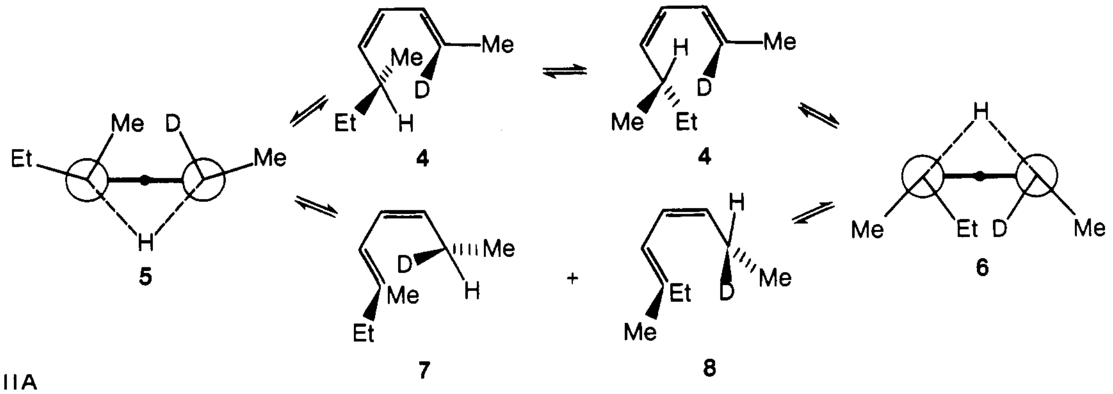
3-ax **3-ax**

One of the first reported examples of a thermal [1,7] shift is the interconversion of vitamin D and precalciferol.[18] If the migration follows a concerted path, the transition state must be coiled in a helical fashion to accommodate the antarafacial geometry. Structure **9** is an envisioned transition state for acyclic antarafacial [1,7] sigmatropic migration of hydrogen. In order to achieve this configuration, at least two double bonds must have the necessary cisoid configuration. If this condition is not met, then the more common [1,5] migration or some other pericyclic process may dominate (Scheme IIA).[19,20] It appears that [1,7] H migration is actually favored over [1,5] migration, all other factors being equal, with geometry being the deciding factor. The relative activation parameters for this competition will be discussed in a later section.

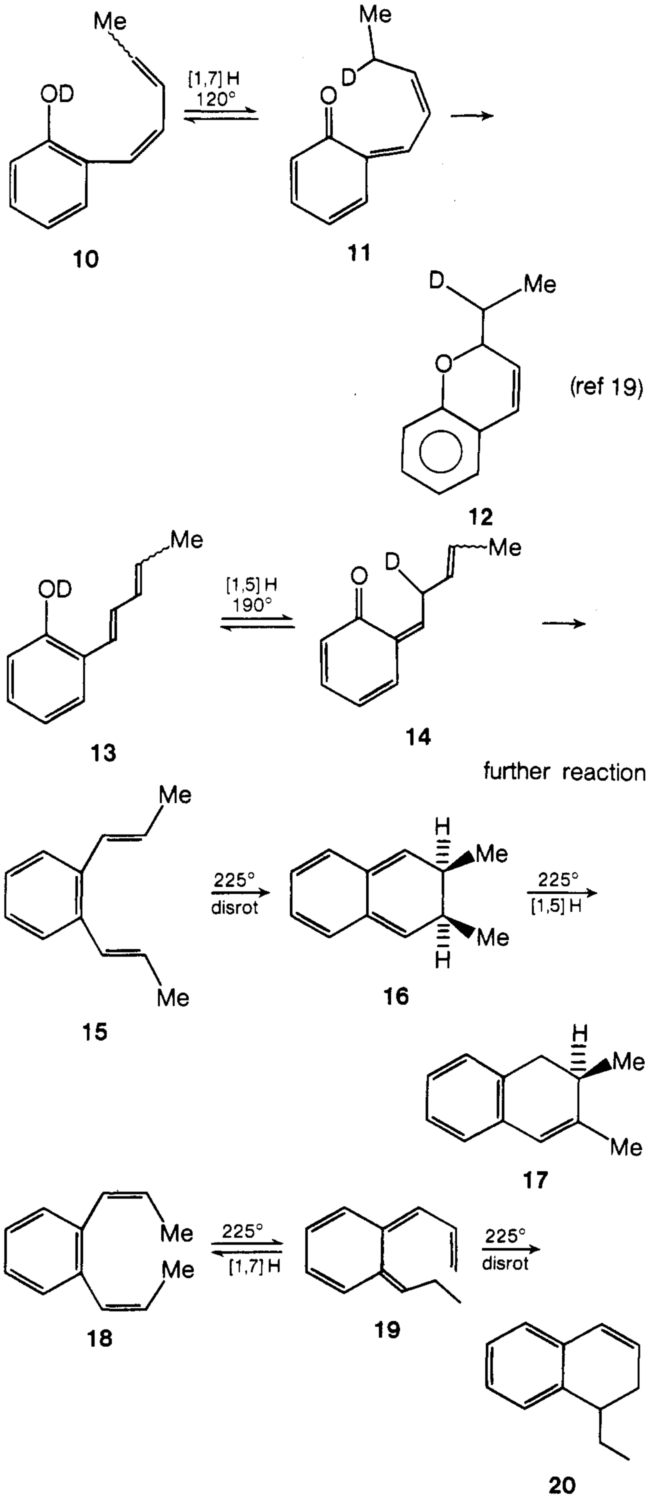


9

SCHEME II

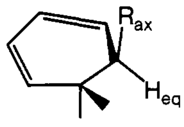


SCHEME IIA

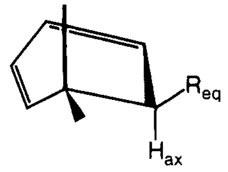


B. Migration in Cyclic Systems

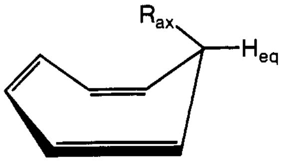
Thermal [1,5] sigmatropic migration in cyclic systems has been observed in a wide variety of systems and has been reviewed extensively in the literature up to 1970.[1-8] However, [1,3] and [1,7] H migration is not observed in small or medium sized rings owing to the unattainable geometry required for antarafacial migration. [1,3] migrations of carbon moieties, on the other hand, are not uncommon. Conformational effects are minimal in five-membered diene rings such as 1,3-cyclopentadiene and indene; however, in larger polyene rings the migrating atom or group can assume different conformational attitudes with respect to the π-electron system. For example, in either 1,3-cyclohexadiene or 1,3,5-cycloheptatriene, a migrating group can occupy either pseudo-axial or pseudo-equatorial positions. Kloosterziel and coworkers[21,22] first postulated that a group occupying a pseudo-axial position is more liable to participate in a concerted cyclic transition state than if it occupies a pseudo-equatorial position. Wolf and coworkers[23] also utilized this argument in suggesting that migration of hydrogen in preference to phenyl in 7-phenyl-1,3,5-cycloheptatriene was due mainly to the conformational preference of the phenyl group for the pseudo-equatorial position.



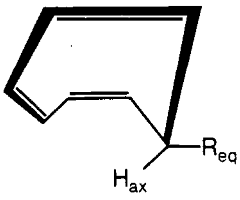
21-R_{ax}



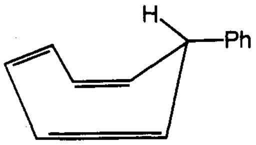
21-R_{eq}



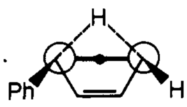
22-R_{ax}



22-R_{eq}



23



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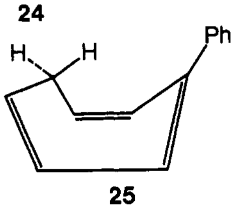
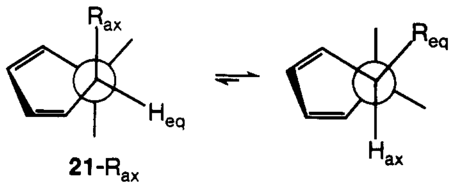


25

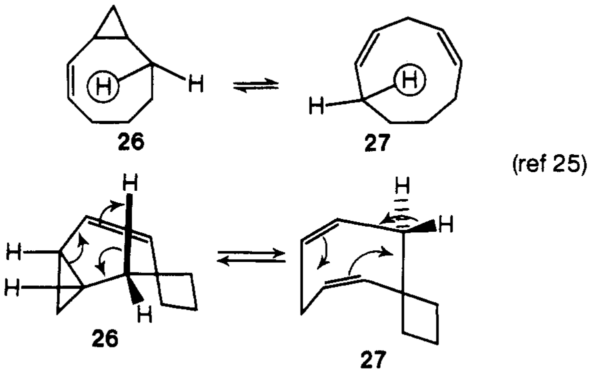
Spangler has recently reported that migration of hydrogen from C_5 of a 5-substituted-1,3-cyclohexadiene may also be conformation dependent.[24] In the range 300–350° in a fast flow system, 5-*tert*-butyl-1,3-cyclohexadiene rearranges faster than does the corresponding 5-methyl compound to yield 1-alkyl-1,3-cyclohexadiene. This behavior is ascribed to the pronounced preference of the *tert*-butyl group for the pseudo-equatorial position. Thus the rate of migration is enhanced when alkyl group bulk forces the C_5-H to maintain a predominantly axial conformation. These results indicate the possibility that relative migration rates, and also migratory aptitudes, may be controlled, to some extent, by ground-state conformation.



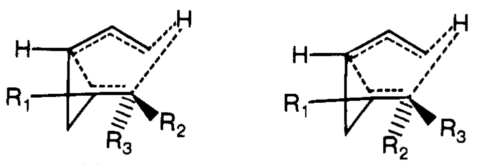
21-R_{ax} **21**-R_{eq}

C. Migrations Involving a Cyclopropane Ring

In 1966, Winstein and coworkers reported the apparent similarity between [1,5] H shifts in cyclic dienes and a shift across a homodiene wherein a cyclopropane ring replaced one of the double bonds of the diene system.[25] They suggested a transition state similar to the [1,5] sigmatropic transition state. Frey and Solly[26,27] studied similar migrations in acyclic analogs, in the gas phase, and extended this model of the transition state to allow for conformational preferences of substituent groups. In the thermolysis of 1,1-diethyl-2-vinylcyclopropane (R_1 = Et; R_2 = H; R_3 = Me), they found[26] a 1:1 product ratio of *trans,cis*-3-ethyl-2,5-heptadiene and *cis,cis*-3-ethyl-2,5-heptadiene. This product distribution indicates that the two possible transition states (A and B) are almost equivalent and that R_2 and R_3 occupy positions that are intermediate between axial and equatorial and thus have no preferred orientation. This result is striking when compared to the thermolysis of *cis*-1,3-hexadiene described above[16] where a 40:1 preference for a transition state having a pseudo-equatorial conformation was found. Frey and Solly also proposed[27] that a "boat"-like conformation might compete with the "chair" conformations depicted above. However, in the thermolysis of 1,1-dimethyl-2-vinylcyclopropane (**30**), only *cis*-2-methyl-1,4-hexadiene (**31**) is formed. These workers concluded that the "chair" transition state is probably at least 4.5 kcal/mol lower in energy than the "boat" form.

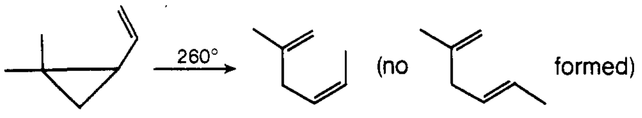


26 **27** **26** **27**

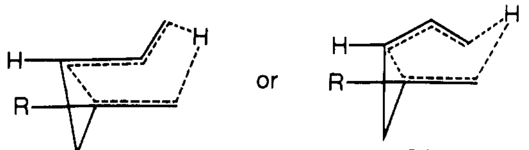


28
transition state A

29
transition state B



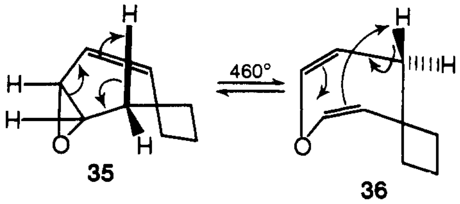
30 **31** **32**



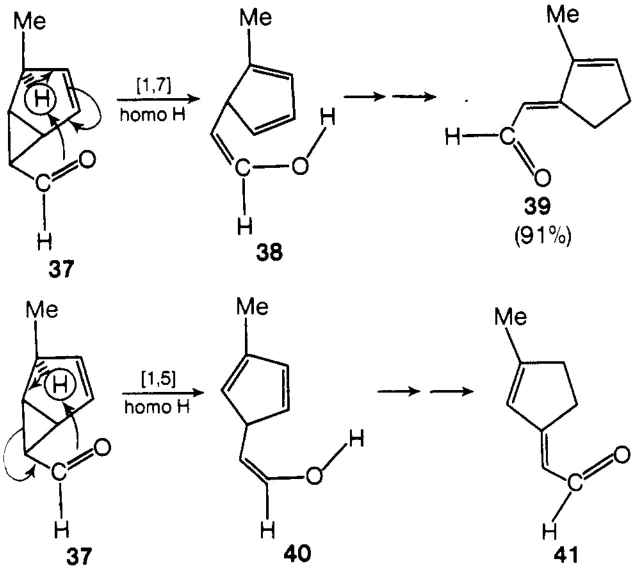
33
"boat" ⟶ *trans*

34
"chair" ⟶ *cis*

Crandall and Watkins proposed a similar transition state for the oxygen analog of a homodienyl shift in the thermolysis of 3,4-epoxycyclooctene (**35**).[28] More recently it has even been shown[29] that [1,5] and [1,7] homo migrations may compete with one another in the bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde system (**37**). As was also true for direct competition between [1,5] and [1,7] hydrogen shifts, the [1,7] homo shift dominates over the [1,5] homo shift if both are geometrically and conformationally allowed. This preference may be a measure of the greater stability of a homotrienyl vs. the homodienyl delocalization in the transition state.



35 **36**



37 **38** **39** (91%)

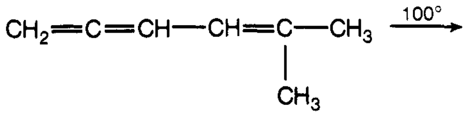
37 **40** **41** (9%)

IV. Specific Group Migrations

This section will discuss specific examples of group migrations with respect to product formation, reaction conditions, and reaction energetics. Activation parameters (log *A*, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$) for the various acyclic and cyclic systems and migration types which may be reasonably described as sigmatropic processes are tabulated under each separate heading. The Arrhenius activation energy (E_a) has been converted to $\Delta H^{\ddagger}$ by the relation $\Delta H^{\ddagger} = E_a - RT_m$, where T_m is the mean absolute temperature, so as to make direct data comparison easier. *The reader must realize that there are wide variations in the degree of proof of concertedness for many of the reactions discussed below.* While many authors have attempted to establish the sigmatropic nature of a particular rearrangement with experiments designed to demonstrate the unimolecularity and homogeneity of the process, others have done little more than claim a particular reaction as possibly being sigmatropic in nature. However, even these latter claims have been included in this review so as to document the extent to which sigmatropic migrations *may be involved* in organic rearrangements.

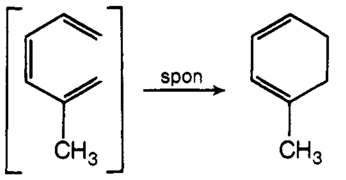
A. [1,*j*] Hydrogen and Deuterium Migrations

[1,5] sigmatropic hydrogen migration has been studied extensively during the past decade in a wide variety of systems and is perhaps the most widely known of all the sigmatropic processes. The suprafacial nature of this migration has been demonstrated conclusively by Roth et al.,[17] and early work in this area has been adequately reviewed.[1,3,4,6] In general, activation enthalpies for [1,5] migration in linear dienes will be in the range 30–36 kcal/mol, with activation entropies of ca. −10 eu. A particularly facile [1,5] H migration has been studied by Skattebol.[30] In the gas phase, 5-methyl-1,2,4-hexatriene (42) rearranges quantitatively to *cis*-2-methyl-1,3,5-hexatriene (43) which ring-closes to 1-methyl-1,3-cyclohexadiene (44) under the thermolytic reaction conditions. This [1,5] H migration to an allenic carbon proceeds at a reasonable rate (k (113°) = 2.73×10^{-4} sec^{-1}) at temperatures 100° *lower* than for comparable conjugated 1,3-dienes such as 2-methyl-1,3-pentadiene.[31] The activation enthalpy for this process (24 kcal) is the lowest for any known [1,5] H process in an open-chain system. Recently, Hansen, Schmid, and coworkers[32] have shown that *[1,5] H migration to an allenic carbon is indeed a suprafacial process,* and that the initial products (**46, 47**) derived from this migration may react further by other pericyclic processes. Activation parameters for specific examples of these and other [1,5] H shifts are shown in Table III.



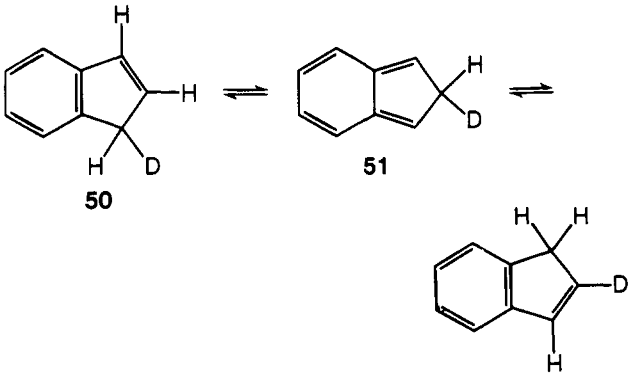
$$\underset{\textbf{42}}{CH_2{=}C{=}CH{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3} \xrightarrow{100°}$$

42



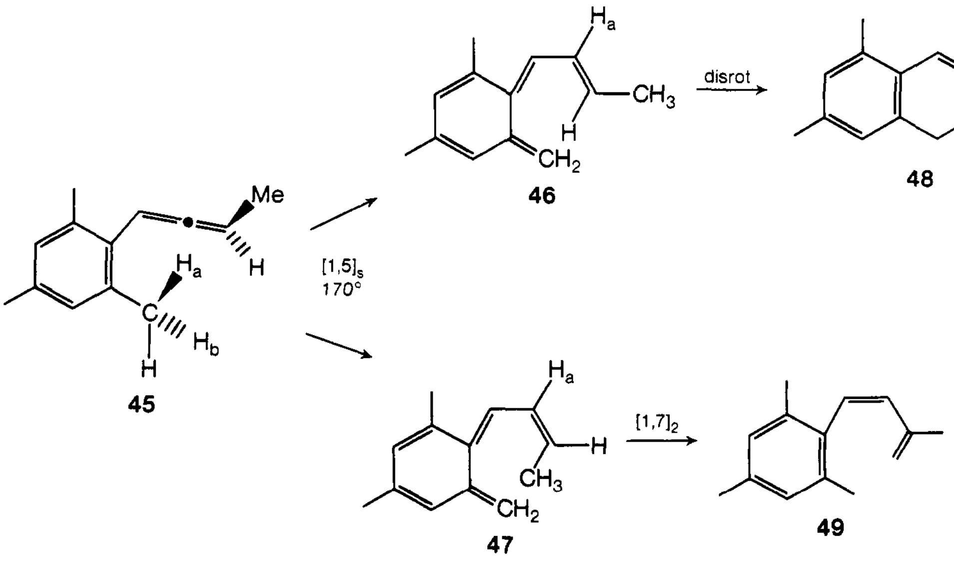
43 **44**

Many more examples of [1,5] H migration in cyclic molecules have been studied than the corresponding shifts in acyclic molecules. Roth[35a] established that thermal hydrogen migration in 1,3-cyclopentadiene and indene was indeed a concerted [1,5] process by substituting deuterium for hydrogen in appropriate positions, and following the migration process by NMR techniques. For example, indene (**50**) undergoes the following equilibrium proceeding through the isoindene intermediate **51**.[35b] Almy and Cram[36] established that migration in the indene system is a suprafacial, stereospecific process, and also showed a definite isotope effect that favored H migration over D migration. Alkyl substitution at C-5 (see Scheme III) lowers the activation enthalpy for migration of a C-5 H in cyclopentadiene,[37,38] while [1,5] H migration from C-5 in 5-[5-cyclopentadienyl]-1,3-cyclopentadiene occurs with particular ease.[39]



50 **51** **52**

[1,5] migration in the 1,3,5-cycloheptatriene system has been extensively studied. Kloosterziel and his coworkers[21,22,40–43] have demonstrated that hydrogen migration occurs in the following sequence. These workers have also demonstrated that migration rates from C-7 in **65** are dependent on the nature of X,[41,42] as are the final equilibrium compositions.[41] In general, migration in the cycloheptatriene system requires a greater activation energy than for the comparable 1,3-cyclopentadiene compound ($\Delta H^{\ddagger} \sim$ 25–35 kcal/



45 **46** **48** **47** **49**

SCHEME III

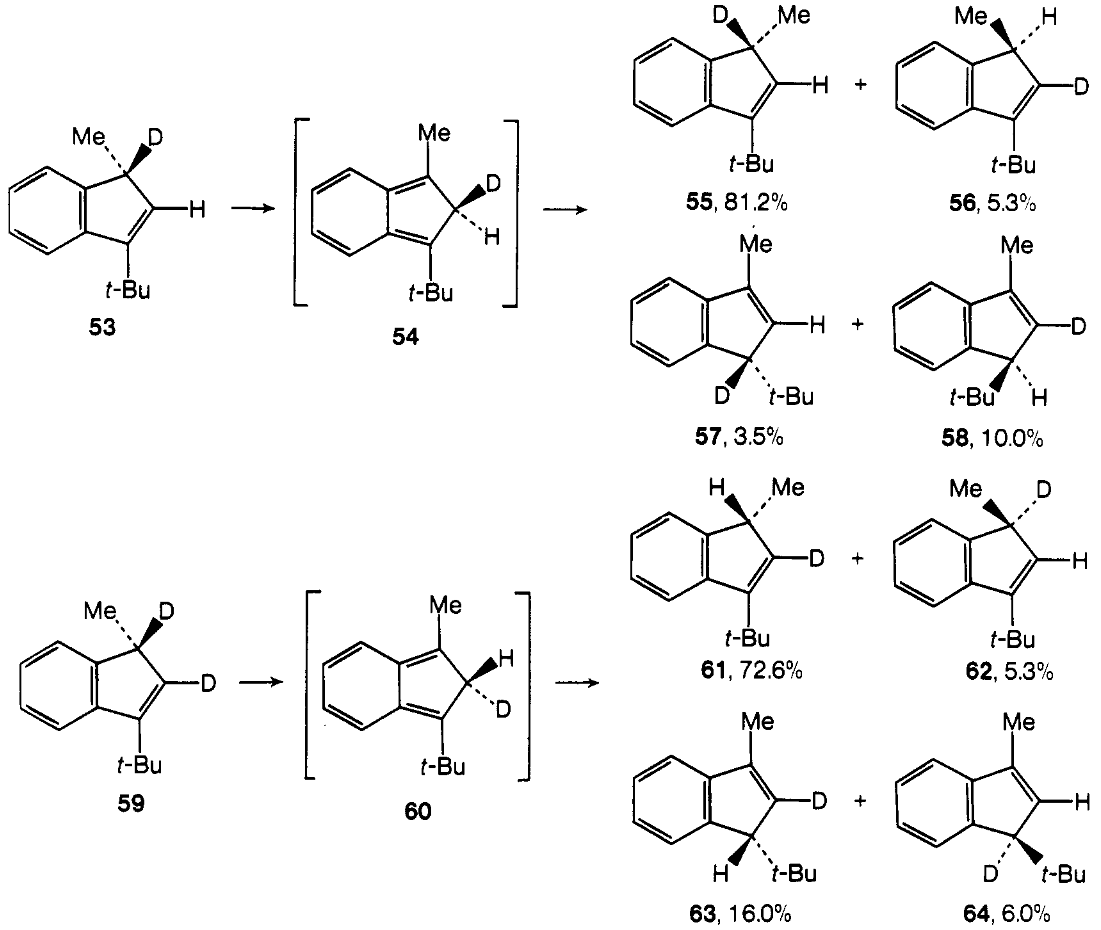
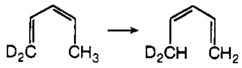
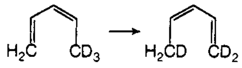
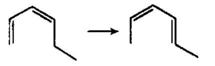
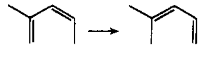
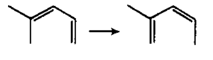
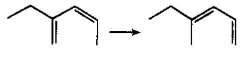
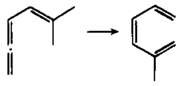
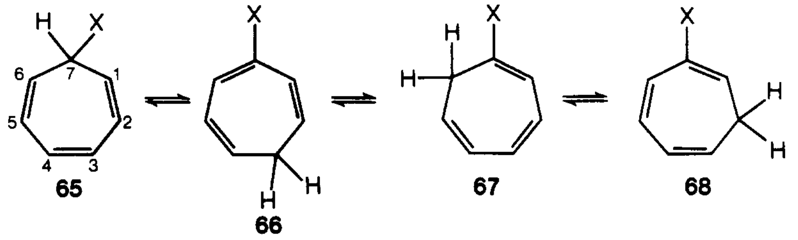


TABLE III. [1,5] Hydrogen Shifts in Acyclic Dienes

Reaction	Migrating group	*T* range, °K (medium)[a]	Log *A*, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	Ref
	H	458–478 (g)	11.93	35.4	−4.9[b]	33
	D	458–478 (g)	11.86	36.8	−5.2[b]	33
	H	475–518 (g)	10.80	31.5	−12.0	16
	H	473–677 (g)	11.24	31.6	−8.4[b]	31
	H	473–677 (g)	11.72	35.2	−6.3[b]	31
	H	463–523 (g)	10.77	30.6	−10.3[b]	34
	H	463–523 (g)	11.03	33.5	−9.1[b]	34
	H			24		30

[a] (g) indicates gas-phase reaction. [b] Calculated for T_m.



X = H, D, Me, C_6H_5, p-$Me_2NC_6H_4$, OMe, SMe, CN

TABLE IV. [1,5] Hydrogen Shifts in Cyclic Dienes and Trienes

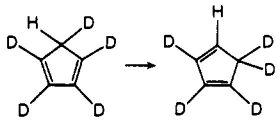
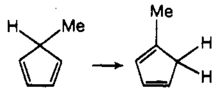
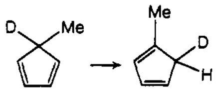
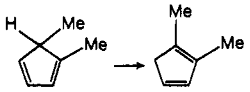
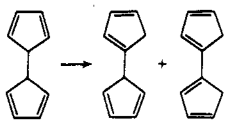
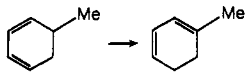
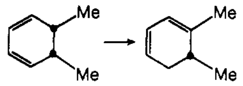
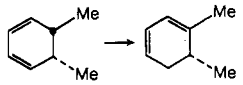
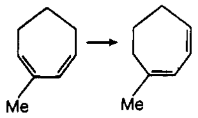
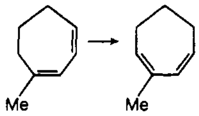
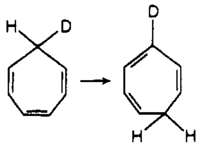
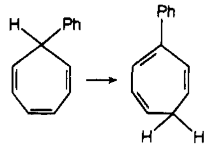
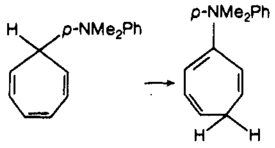
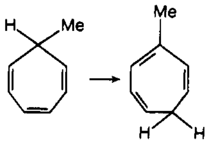
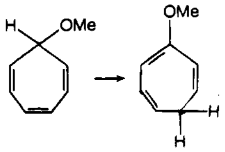
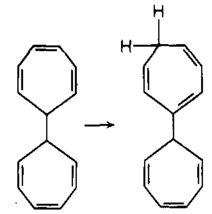
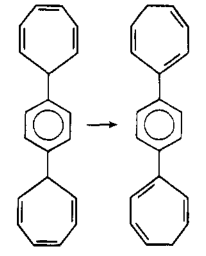
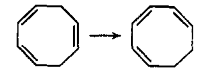
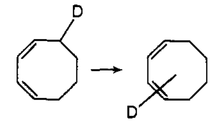
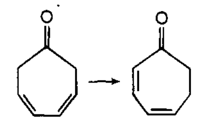
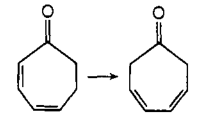
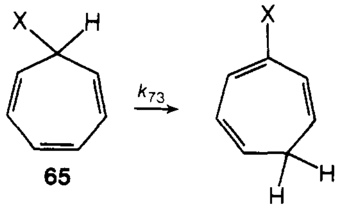
Reaction	Migrating group	T range, °K (medium)	Log A (sec^{-1})	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	Ref
	D	318–338 (CCl_4)	12.11	23.6	−3.3[b]	35
	H	279–298 (CCl_4)	10.87	19.3	−10.8	38
	D	292–313 (CCl_4)	11.88	21.7	−6.2	38
	H	303–327 (neat)		22.5	−4	37
	H	. . . (heptane)		18.6	−16	39
	H	573–634 (g)[a]	11.2	34.0	−10.7	46
	H	455–473 (hexane)		32.1	−7	48
	H	455–473 (hexane)		35.1	−3	48
	H	413–433 (g)[a]		29.5	−7.4	50, 51
	H	413–433 (g)[a]		28.6	−9.9	50, 51
	H	371–413 (neat)	10.9–11.5	30.2	−11.5	21
	H	353–393 (decane)	10.8	26.9	−11.7	22
	H	373–413 (neat)	11.3	27.6	−9.3	42
	H	402–499 (g)[a]	12.6	32.3	−4.9	54
	H	353–413 (neat)	10.0	25.7	−15.0	55

TABLE IV (Continued)

Reaction	Migrating group	*T* range, °K (medium)	Log *A* (sec^{-1})	$\Delta H^‡$, kcal/mol	$\Delta S^‡$, eu	Ref
	H	410–460 (neat)	13.3	32.8	−3.2	56
	H	398–428 (CDCl$_3$)	12.5	31.4	−3.9	57
	H	393–418 (g)	11.7	28.1	−5.6^b	52
	H	398–423 (neat)		29.3	−10.0	25
	H	333–374 (*n*-heptane)	11.5	25.8	−8.0	58
	H	333–374 (*n*-heptane)	11.5	26.2	−8.0	58

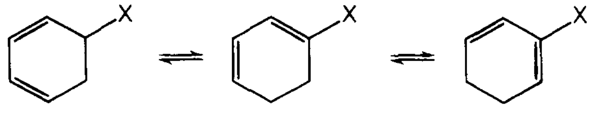
^{a} (g) indicates gas phase. ^{b} Calculated for T_m.

mol), whereas the similar negative entropies indicate that both systems have a highly ordered cyclic transition state ($\Delta S^‡ \sim -4$ to -15 eu). While relative rates have been determined for all of the competing H migrations in the 7-substituted-1,3,5-cycloheptatriene system, activation parameters are generally available only for the first step, abbreviated k_{73}.

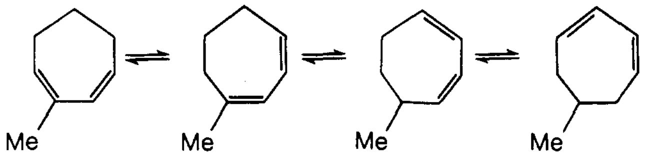


65 66

Kinetic data for migrations in six-, seven-, and eight-membered cyclic dienes are quite sparse. Spangler reported[44,45] that [1,5] H migration in the 1,3-cyclohexadiene system was fairly slow below 300 °C, but fast and reversible above 325°. van der Burg,[46] Marvell and coworkers,[47,48] and Kloosterziel [49] have all confirmed that [1,5] H migration is indeed much slower in the 1,3-cyclohexadiene system than in the case of 1,3-cyclopentadiene, and that the activation energies for the 1,3-cyclohexadiene systems are about 13–15 kcal/mol higher. Activation entropies are, however, in the same range as was observed for both the cyclopentadiene and cycloheptatriene systems. The reason for this large deviation is obscure, but it is easier for the migrating H in 1,3-cyclopentadiene to achieve the transition state commonly ascribed to the [1,5] migration. Whether conformation can account for all of this deviation, however, is open to argument. Mironov[50,51] and coworkers have determined that H migration in methyl-1,3-cycloheptadienes follows a predictable scheme with $\Delta H^‡$ for the conversion **72** → **73** midway between that of cyclopentadiene and cyclohexadiene (29 kcal/mol). The greater flexibility of the seven-membered ring allows for closer approach of the migration termini than is possible in 1,3-cyclohexadiene, thus providing further evidence for the conformational criteria previously discussed. Further increase in ring size does not appreciably lower the activation energy in either 1,3,6- or 1,3,5-octatriene,[52,53] and, indeed, conformational analysis of C$_8$ or larger dienic rings becomes increasingly difficult to interpret in terms of favorable confor-



69 70 71

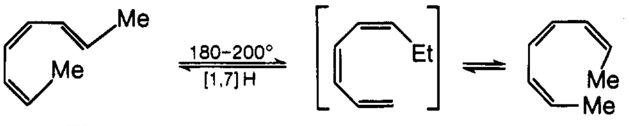


72 73 74 75

mations providing a driving force for sigmatropic migration. The activation parameters for hydrogen migration in the cyclic dienes and trienes discussed above are summarized in Table IV.

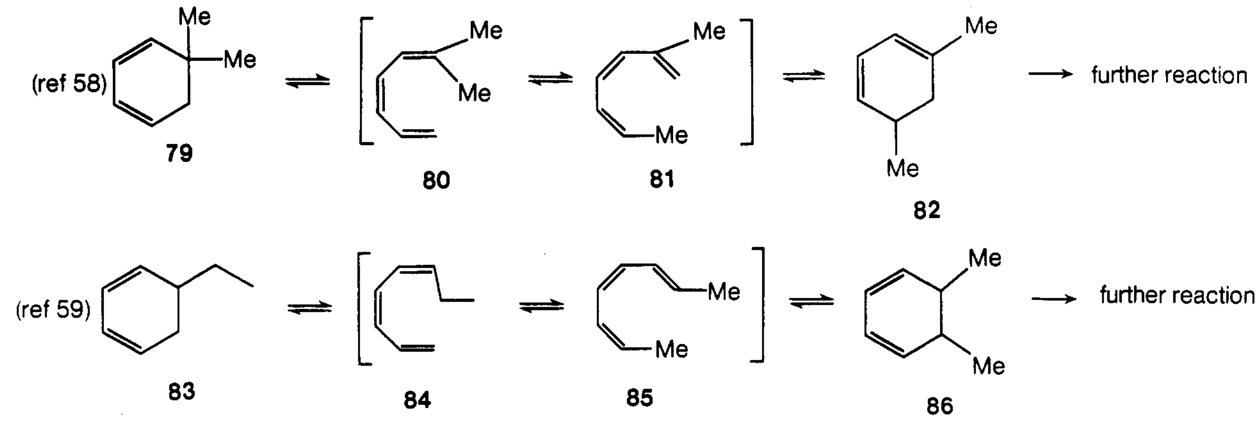
Although many early reviews categorize thermal [1,7] H shifts as rare, several recent reports indicate that [1,7] migration actually is preferable to [1,5] migration in systems where the two pathways are really competitive. The geometric requirements for an antarafacial transition state have been discussed previously (section III.A), and, if these requirements are met, activation enthalpies ($\Delta H^{\ddagger}$ ~ 15–27 kcal/mol) are considerably less than for the corresponding [1,5] process. The more numerous examples of [1,5] migration in the literature are more a reflection on the types of systems studied wherein [1,7] processes are discriminated against, usually because of the impossibility of attaining the necessary antarafacial geometry. The highly ordered [1,7] transition state is characterized by a highly negative entropy of activation (−15 to −25 eu), which also distinguishes it from the less ordered [1,5] state.

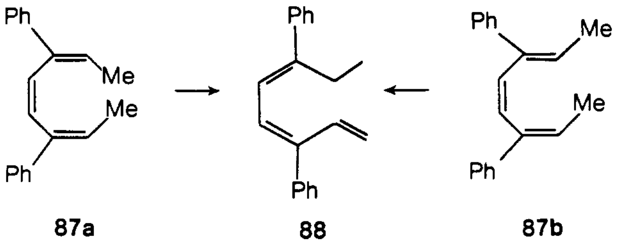
The simplest literature example[48] is the postulated [1,7] H shift in the reversible isomerization of 2,4,6-octatriene. The intermediary *cis,cis*-1,3,5-octatriene is not detectable under the reaction conditions. Similar shifts have been invoked to rationalize the observed thermolysis products obtained from 5-alkyl- and 5,5-dialkyl-1,3-cyclohexadienes[59,60] at 500° (Scheme IV). At the high temperature encountered in these rearrangements, other processes, such as [1,5] alkyl group migration and various radical-chain processes become possible, however, and this complication will be discussed in the section on carbon migrations. Courtot and Rumin[61,62] have studied an extremely facile [1,7] H migration, finding that either *cis,cis,cis*- or *cis,cis,trans*-3,6-diphenyl-2,4,6-octatriene rearranges to 3,6-diphenyl-1,3,5-octatriene (**88**) at room temperature.



76 77 78

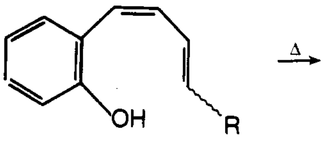
SCHEME IV



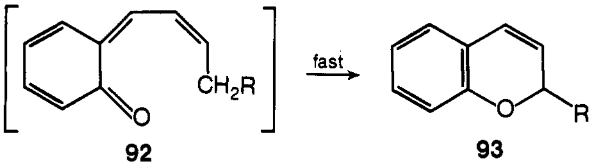


87a 88 87b

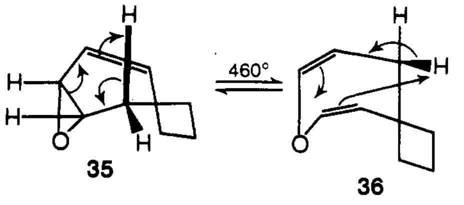
By far the most extensive investigation of the [1,7] migration process has been carried out by Hansen, Schmid, and coworkers.[20,63,64] The reversibility of the [1,7] H migration was confirmed by deuterium substitution, which also confirmed the [1,7] pathway as the main isomerization pathway (Schemes V and VI). A similar migration involves a [1,7] shift of hydrogen from oxygen to carbon in *o*-pentadienylphenols (**91**).[64,65] The [1,7] shift is also responsible for *cis–trans* isomerism in **91b**, and competes favorably with electrocyclic ring closure to **93**. Activation parameters for reactions involving a concerted [1,7] H shift are listed in Table V.



91a, R = H
b, R = Me

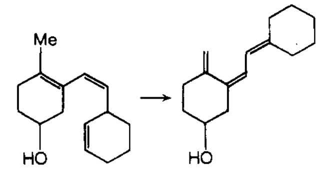
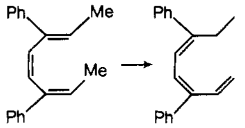
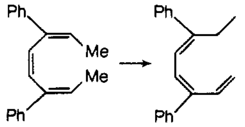
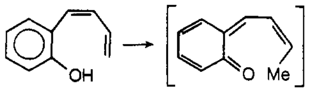
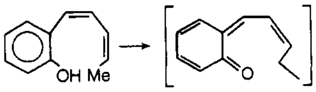
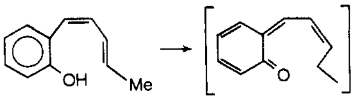


Homodienyl and homotrienyl hydrogen shifts have been recognized for many years as being related to [1,5] and [1,7] sigmatropic shifts in cyclic and acyclic polyenes, and the former has been the subject of a short early review.[25] In general, the activation parameters for [1,5] dienyl and [1,5] homodienyl migrations are similar. This degree of similarity carries over to [1,7] and [1,7] homodienyl shifts, even to the extent that [1,7] homodienyl shifts are preferred to [1,5] dienyl shifts when both are truly competitive.[29,66] For example, in the thermolysis of **94** (eq 1), the product of homo [1,7] migration, **99**, is preferred over the homo [1,5] product by 40:1. An epoxide ring may also function[28] as the "homo" portion of the diene, as in the reversible rearrangement of 3,4-epoxycyclooctene (**35**).

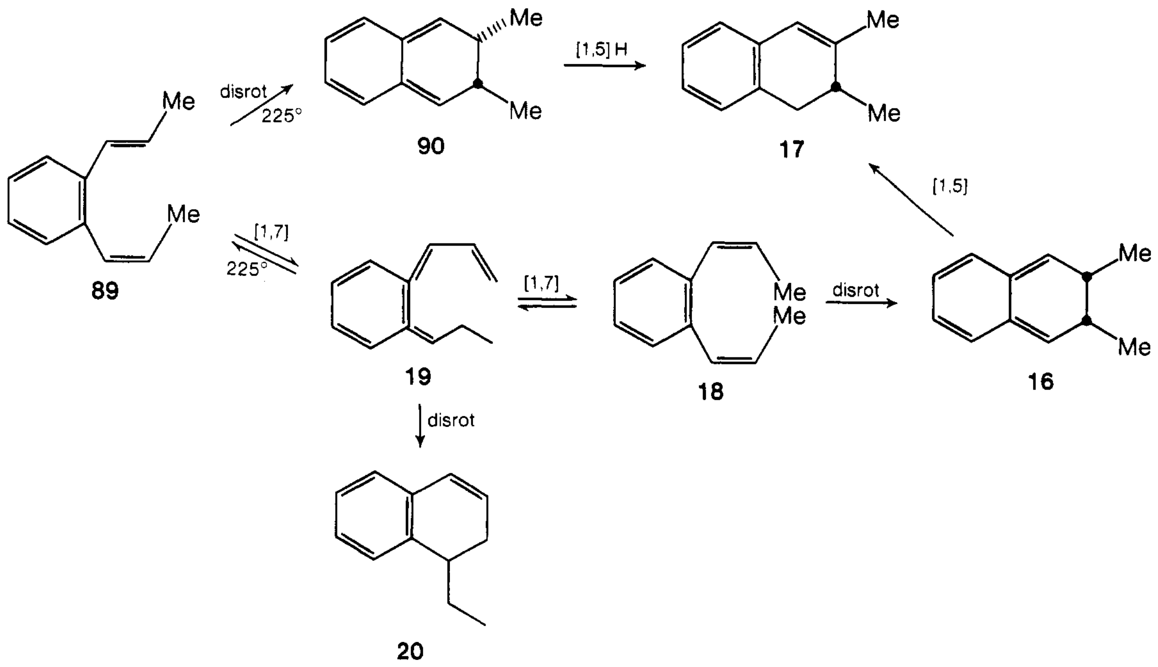


Berson and coworkers[67] proposed the intriguing rearrangement of bicyclo[4.2.1]nona-2,4,7-triene to bicyclo[4.3.0]nona-2,4,7-triene occurred through two successive al-

TABLE V. [1,7] Hydrogen Shifts in Various Systems

Reaction	*T* range, °K (medium)	Log *A* (sec^{-1})	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	Ref
	324–363 (decalin)		20.9	−17.2	18
	297–331 (CDCl$_3$)	9.5	18.5	−17.2	62
	278–318 (CDCl$_3$)	7.8	14.9	−25	61
	. . . ((CD$_3$)$_2$SO)		23	−17	65
	358–378 (octane)		24.9	−16	64
	358–378 (octane)		26.1	−15	64

SCHEME V



SCHEME VI

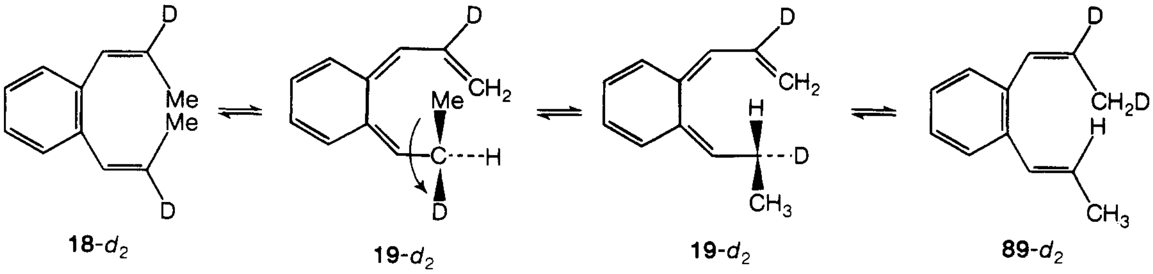


TABLE VI. [1,5] Homo and [1,7] Homo Hydrogen Shifts in Various Systems

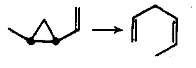
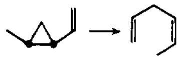
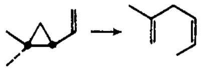
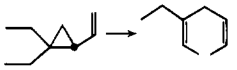
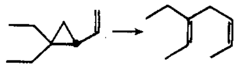
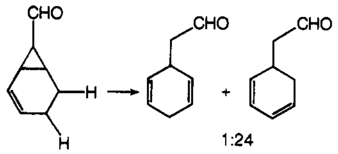
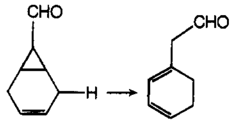
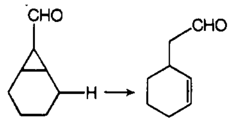
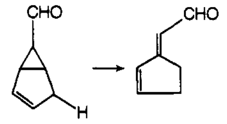
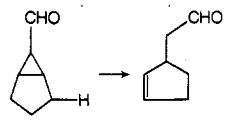
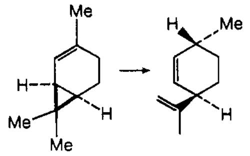
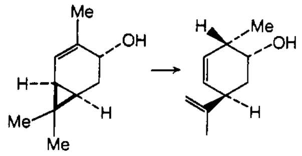
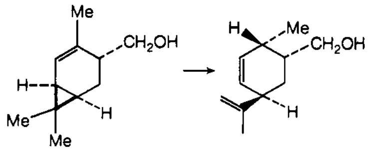
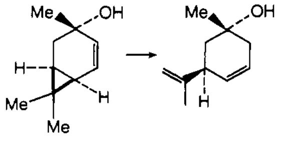
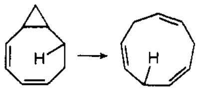
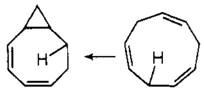
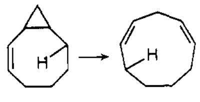
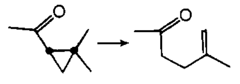
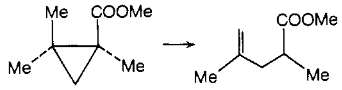
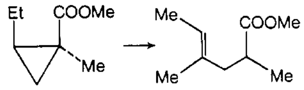
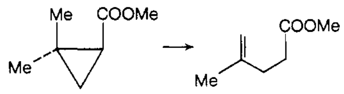
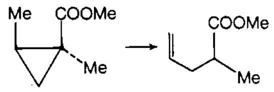
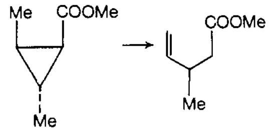
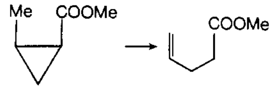
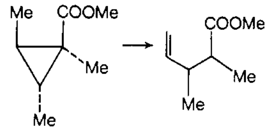
Reaction	*T* range, °K (medium)	Log *A* (sec^{-1})	$\Delta H^‡$, kcal/mol	$\Delta S^‡$, eu	Ref
	443–463 (g)[a]	10.95	30.2	−11	69
	439–493 (g)	11.03	30.3	−11.6	68
	473–533 (g)	11.41	32.5	−9.7	27
	468–523 (g)	11.26	32.5	−8.1[b]	26
	468–523 (g)	11.31	32.6	−7.8[b]	26
	373–423 (cyclohexane)		24.7	−11.5	66
	373–423 (cyclohexane)		27.8	−9	66
	373–423 (cyclohexane)		27.3	−7.2	66
	373–423 (cyclohexane)		28.3	−7.4	66
	373–423 (cyclohexane)		28.7	−9.4	66
	473–513 (g)		27.2	−17.2	70
	473–513 (g)		33.0	−8.8	70
	473–513 (g)		28.6	−6.5	70
	473–513 (g)		28	−6.7	70
			29.3	−7	25

TABLE VI (Continued)

Reaction	*T* range, °K (medium)	Log *A* (sec^{-1})	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	Ref
			32.1	−6	25
	424–443 (neat)		31.4	−6	25
	425–436 (neat)		29.9	−10	71
	513–532 (neat)		37.5	−8	72
	532–557 (neat)		33.9	−18	72
	532–557 (neat)		36.1	−14	72
	532–557 (neat)		30.2	−25	72
	532–570 (neat)		32.5	−22	72
	532–567 (neat)		35.9	−17	72
	532–570 (neat)		25.2	−37	72

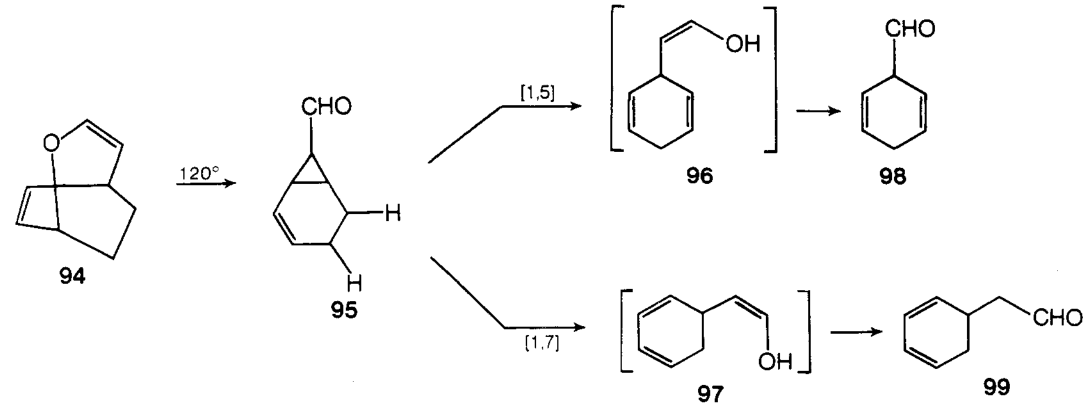
[a] (g) indicates gas-phase reaction. [b] Calculated for T_m.

lowed 1,5-homodienyl hydrogen shifts, which they termed the hydrogen "rebound" mechanism (Scheme VII). In order for the cyclopropane ring to participate in a concerted [1,5] or [1,7] homo migration, a cis orientation is required.[68,69] In the trans isomers, a diradical pathway is usually followed (Scheme VIII), and this is reflected in a much higher activation enthalpy and the appearance of products derived from the intermediary allylic radical.

A summary of activation parameters for [1,5] and [1,7] "homo" H migrations are listed in Table VI.

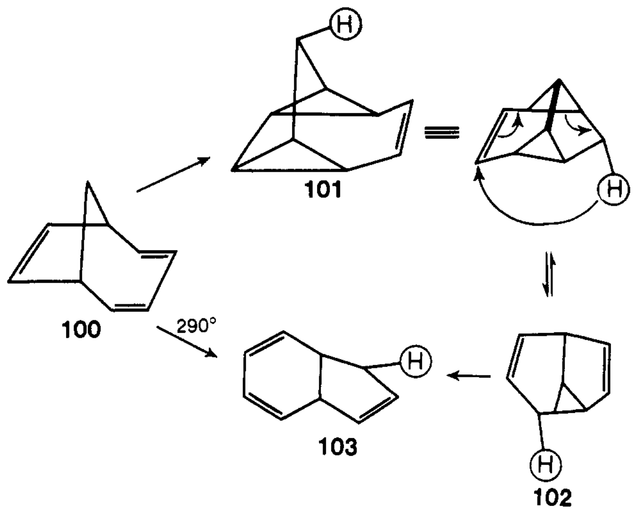
B. [1,*j*] Carbon Migrations

In the past 5 years intensive efforts have greatly increased our knowledge of group migrations other than hydrogen. In particular, the migration of carbon functionalities has attracted the greatest attention, and [1,3] and [1,5] sigmatropic processes involving alkyl, aryl, and more complex functional groups have been studied to attempt to describe the stereochemical consequences of the various carbon migration routes, both allowed and forbidden. In the following discus-

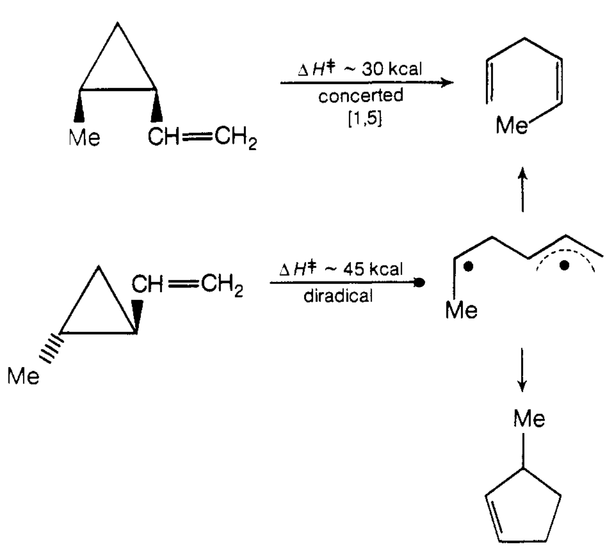


(I)

SCHEME VII



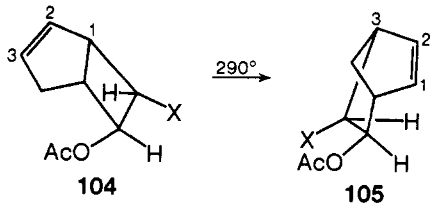
SCHEME VIII



sion, an attempt has been made to present these investigations in a coherent, but not necessarily chronological, fashion.

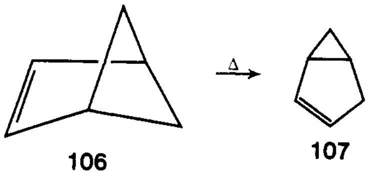
1. *Alkyl Groups. Migration of sp^3-Hybridized Carbon*

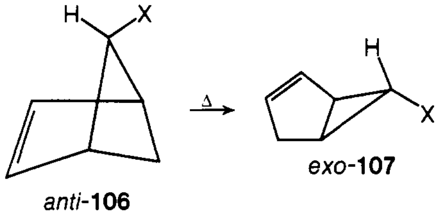
Two modes of [1,3] migration of sp^3 carbon are allowed according to orbital symmetry considerations, suprafacial migration with inversion of configuration of the migrating carbon or antarafacially with retention. Berson and Nelson described an elegant example in the bicyclo[3.2.0]hept-2-ene system (**104**) which demonstrates that inversion does occur for the suprafacial path.[73,74] Several workers[75-79] have studied the



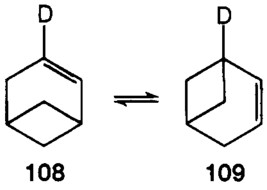
X = D, Me

similar thermal conversion of the bicyclo[2.1.1]hex-2-ene system (**106**) to the bicyclo[3.1.0]hexene system (**107**). Frey and Hopkins[75,76] showed that the reaction is quantitative in the gas phase (150–200°) and postulated a concerted [1,3] suprafacial migration of carbon. Roth and Friedrich[77] and Masamune et al.[78] demonstrated that the [1,3] shift definitely proceeds with inversion of the migrating group. Activation enthalpies are of the same order as [1,5] and [1,7] H migrations, ranging from 35 kcal for the parent hydrocarbon[76,77] to 25 kcal for the 5-*anti*-methoxy derivative.[79] A similar migration has also been postulated in the bicyclo[4.1.1]heptene system (**108**) by Dietrich and Musso,[80] a rearrangement which is degenerate in the parent hydrocarbon.

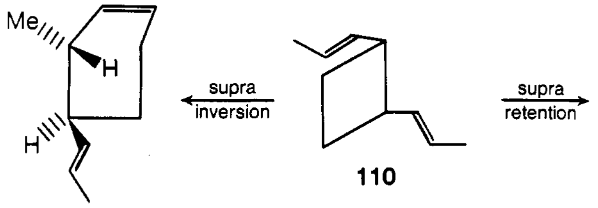




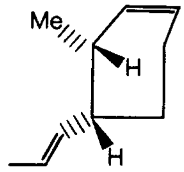
X = Me,[77] CH_3OCH_2COO-,[78] CH_3COO-,[78] MeO-,[79] N_3-[79]



Berson and coworkers[81,82] have recently been concerned with the contrasts between formally "allowed" and "forbidden" routes for carbon migration. These workers have found that forbidden routes can successfully compete with allowed routes in the *trans*-1,2-di(*trans*-propenyl)cyclobutanes (**110**). Although the allowed process dominates, as predicted, it is only slightly preferred. The supra retention pathway apparently is stabilized by overlap between the front lobe of the migrating carbon and the supra lobe of the allylic framework. This overlap, however, only assumes importance when the normal allowed supra-inversion pathway is partially or wholly blocked by geometric factors. An endo substituent interferes with the allowed geometry; consequently a large contribution from the forbidden s_r path is observed. The antarafacial routes in all of the above are very slow because of the unfavorable geometry (see Scheme IX).



111, 50.8%

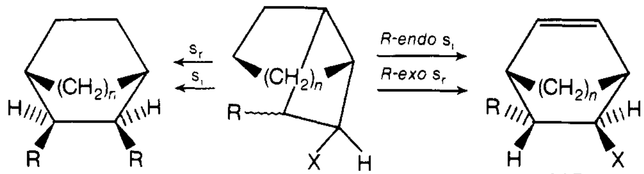


(ref 81)

112, 43.0%

There are relatively few reports of possible [1,3] antarafacial migrations with retention of configuration wherein there

SCHEME IX

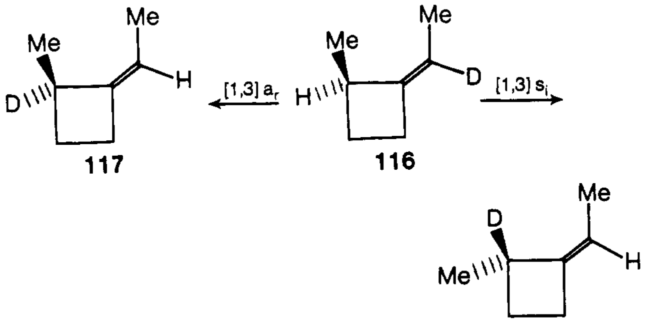


114 **113** **115**

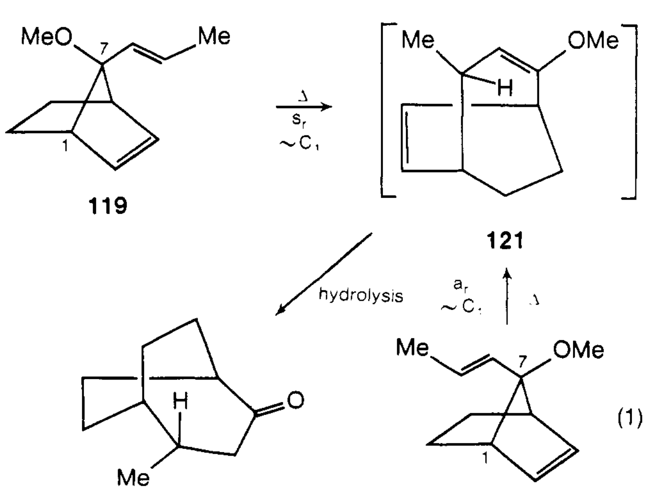
(ref 82)

n	R	X	s_r/s_i rate ratio
1	*exo*-Me	OAc	0.1
2	*exo*-Me	OAc	0.45
1	*endo*-Me	OAc	7
2	*endo*-Me	OAc	12

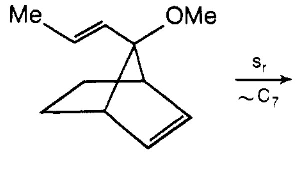
is a clear distinction between s_i and a_r pathways. Baldwin and Fleming[83] attributed the difference in the rates of deuterium scrambling and racemization in deuterium-labeled chiral *syn*-1-ethylidene-2-methylcyclobutane (**116**) to [1,3] antarafacial migration. Berson et al.[84] have pointed out that the two migration pathways differ only in the sense of torsional motion of the migration origin. The migrating group starts out *in the plane* of the migration framework, so that the steric difficulty of most other antarafacial processes is absent. These workers, in their most recent attempt,[84] forced retention of configuration on the migrating group by thermolyzing both *syn*-7-*trans*-propenyl-*anti*-7-methoxynorbornene and the corresponding anti,syn isomer. Both isomers produced *endo*-4-methylbicyclo[3.2.2]non-6-en-2-one (99% stereospecific), thus providing a formal [1,3] antarafacial migration with retention in the migrating group in **120** (eq 1). However, other evidence pointed to an alternative method involving migration of C_7 rather than C_1 (eq 2). It seems, therefore, that a really clear-cut example of [1,3] a_r migration has not yet been described. Clemans has recently described yet another different migration pathway in the norbornene system.[85] The migrating carbon follows a suprafacial path with inversion of configuration (eq 3 and 4).



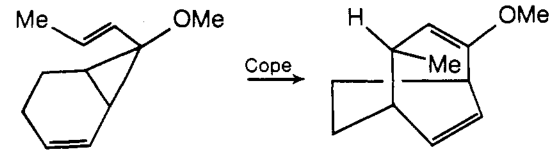
117 **116** **118**



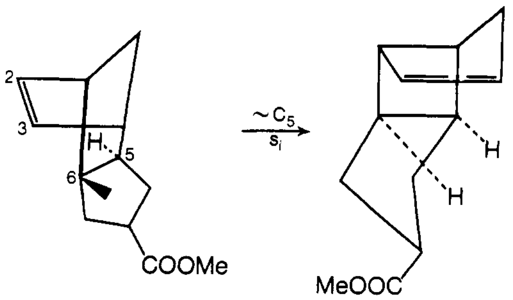
119 **121** **122** **120** (1)



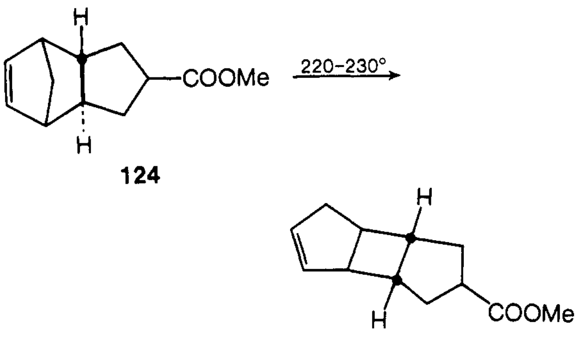
120



123 **121** (2)

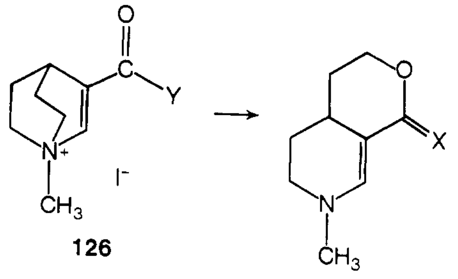


(3)



124 **125** (4)

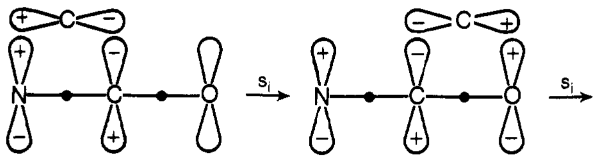
Several examples of [1,3] alkyl group migration from nitrogen to carbon have been studied recently, all of them following a suprafacial path with inversion in the migrating group. Hasselgren and coworkers[86,87] first reported the N to C type migration for the quinuclidine system. They postulated that rearrangement occurs via two consecutive [1,3] shifts,



126 **127**

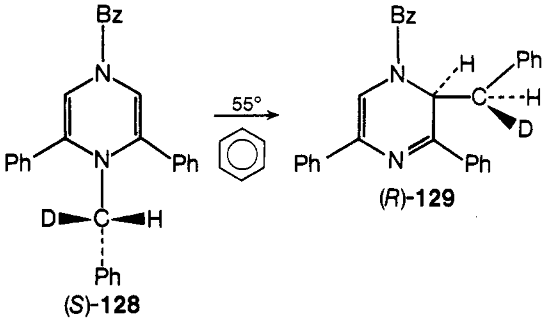
(a)[86] Y = OMe; X = O
(b)[87] Y = NR_2; X = NR_2, I^-

each resulting in inversion (eq 5). The first shift is from N to C, while the second is from C to O.

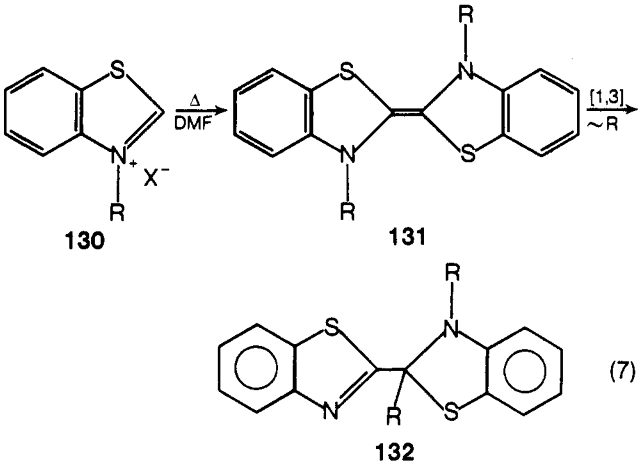


(5)

Lown and Akhtar[88,89] were able to analyze the stereochemistry of the migration of a chiral benzyl group from N to C in a 1,4-dihydropyrazine (eq 6). The [1,3] shift was predominantly suprafacial with inversion (88 ± 6%), the balance being ascribed to an intermolecular radical dissociation–recombination. Baldwin and Walker[90] have very recently found evidence for [1,3] benzyl and allylic migrations in the unstable dimers formed from the thermal decomposition of N-substituted benzothiazolium salts (eq 7). With allylic groups, there is a competing [3,3] migration which is favored at lower temperatures (eq 8). However, only [1,3] migration is observed for benzylic groups.



(6)



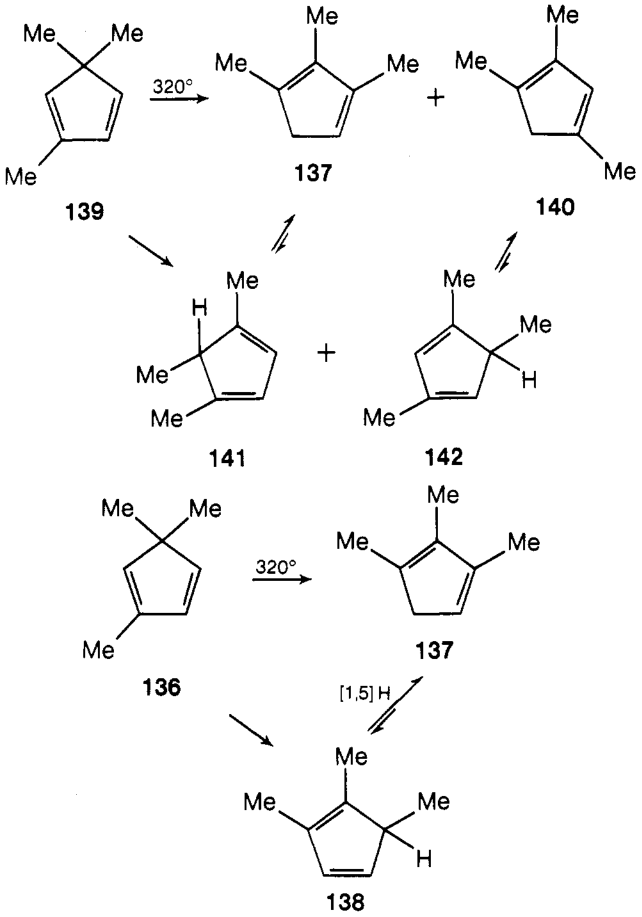
(7)

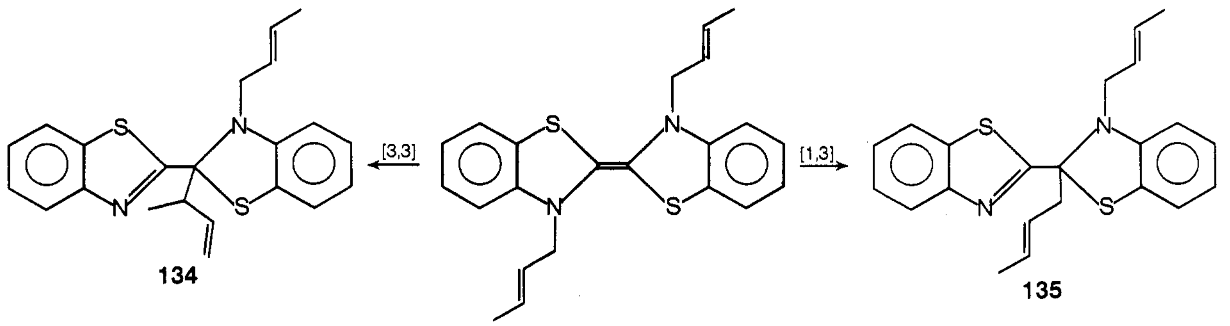
R = $-CH_2Ph$, $-CH_2CH{=\!=}CMe_2$, $-CH_2CH{=\!=}CHMe$

In Table VII is a summary of the activation parameters for [1,3] sp^3-hybridized carbon shifts.

[1,5] alkyl group migration is now well documented in several different cyclic dienic systems.[92–105] All of the well-studied reactions follow the allowed suprafacial route with retention of configuration in the migrating group. deHaan and Kloosterziel[92,93] reported the first unambiguous [1,5] alkyl shift in their studies of the thermal behavior of 1,5,5- and 2,5,5-trimethylcyclopentadienes. The mechanism may be formulated as an initial slow [1,5] methyl migration followed by rapid [1,5] H shifts eventually leading to a preponderance of the more stable trimethylcyclopentadienes (Scheme X). As

SCHEME X



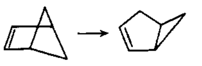
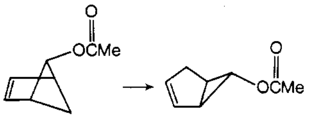
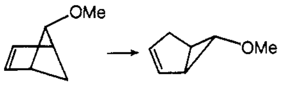
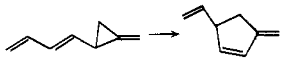
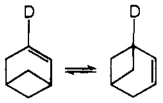


(8)

133

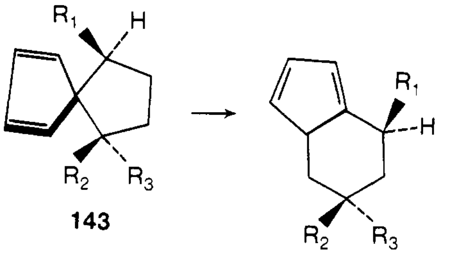
T, °C	% [3,3]
25	90
75	85
100	75

TABLE VII. [1,3] sp^3-Hybridized Carbon Shifts

Reaction	Migrating group	*T* range, °K (medium)	Log *A* (sec^{-1})	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	Ref
	$-CH_2-$ bridge	422–463 (g)[a]	13.95	34.29	−5.5[b]	75, 76
	$-CH_2-$ bridge	358–378 (*n*-dodecane)		27.5	−2	78
	$-CH_2-$ bridge	310–323 (CCl_4)		24.5	−0.5	79
	$-CH_2-$ bridge	303–330 (hexane)	9.6	19.4	−14.8[b]	91
	$-CH_2-$ bridge	500–510 (neat)		34.9		80

[a] (g) indicates gas-phase reaction. [b] Calculated for T_m.

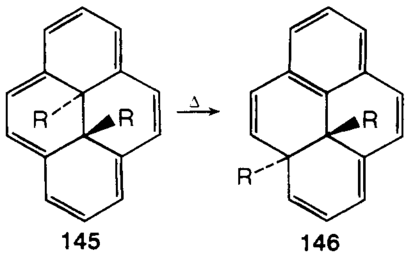
the [1,5] H shifts are both rapid and reversible with respect to the initial alkyl migration, the less stable intermediates are often difficult, if not impossible, to detect. The activation energy for methyl migration is approximately 20 kcal/mol higher than that for a similar [1,5] hydrogen migration.[93] Herndon and Manion[94] and McLean and Findlay[95] found similar activation parameters for [1,5] methyl migration in the cyclopentadiene system, and Mironov and coworkers[96-99] were able to establish that [1,5] methyl migration is indeed reversible in a series of studies of di-, tri-, and tetramethylcyclopentadienes. These latter workers also established[100] that reversible [1,5] migration of a *sec*-butyl group occurs without isomerization in the migrating group. Kloosterziel and coworkers[101,102] established the stereospecificity of alkyl migration in the rearrangements of *cis*- and *trans*-6,9-dimethylspiro[4,4]nona-1,3-diene (**143**), the migration occurring via a suprafacial pathway with retention of configuration in the migrating carbon.



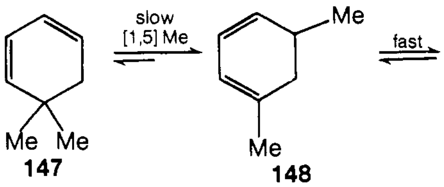
143 **144**

a, $R_1 = R_2 = Me$; $R_3 = H$
b, $R_1 = R_3 = Me$; $R_2 = H$

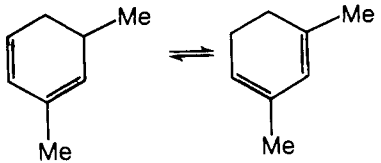
Boekelheide and Sturm[103] found an apparent [1,5] alkyl group migration in the thermal rearrangement of *trans*-15,16-dialkyldihydropyrenes (**145**), which is formally a [1,5] migration from C_5 of a 1,3-cyclohexadiene moiety. Although methyl migration required a temperature of 200°, ethyl and *n*-propyl migration occurred readily in boiling cyclohexane, the latter without isomerization. Mironov and coworkers[104] and Spangler and Boles[105] reported evidence for [1,5] methyl migration in the parent 5,5-dimethyl-1,3-cyclohexadiene (**147**), followed by rapid [1,5] hydrogen migration. Although at first this reaction seems to be analogous to the methyl migrations in cyclopentadiene,[92-96] the reaction is potentially more complicated. An alternate route to apparent methyl migration involves the following sequence: (a) electrocyclic ring-opening to *cis*-6-methyl-1,3,5-heptatriene, (b) [1,7] hydrogen migration to yield 2-methyl-1,3,5-heptatriene and (c) ring closure to give the product predicted for [1,5] methyl migration, 1,5-dimethyl-1,3-cyclohexadiene (**148**). Spangler and Boles[105] were unable to detect the presence of either **151** or **152** in any of their products over the product range



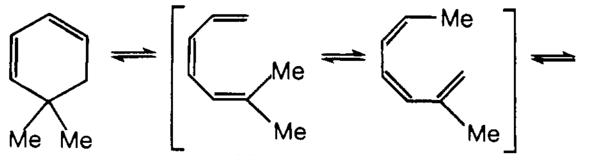
145 **146**
R = Me, Et, Pr



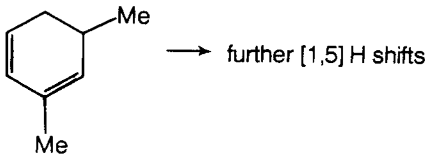
147 **148**



149 **150**

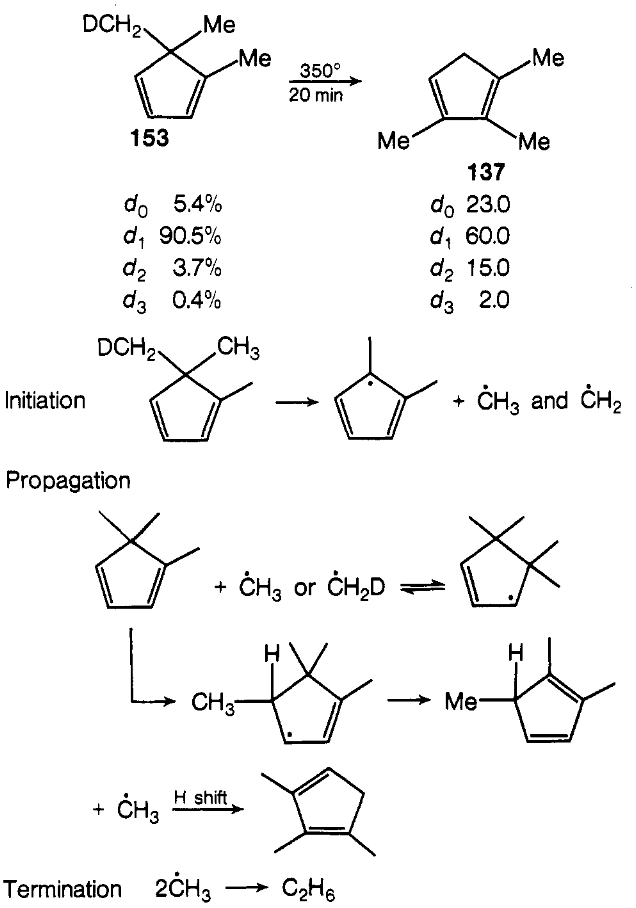


147 **151** **152**



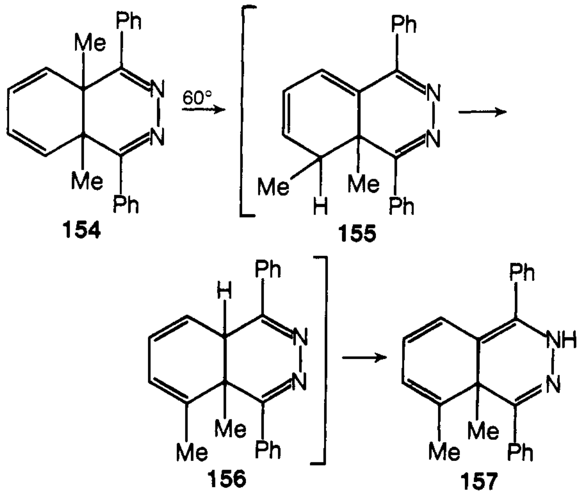
148

SCHEME XI

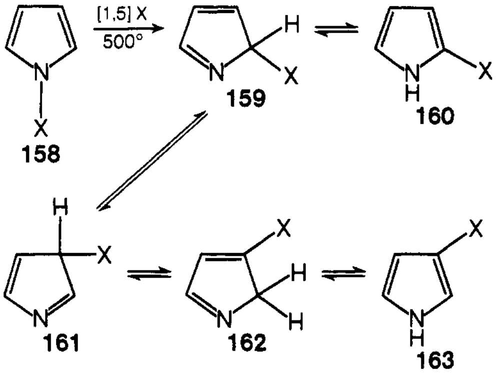


0.1–60% under fast flow conditions, and, in fact, [1,7] antarafacial migration in an open-chain triene has never been conclusively demonstrated, although Marvell and coworkers have postulated this as an isomerization route in 2,4,6-octatriene.[48] A further complication which has been emphasized recently is the possible intervention of a radical-chain process competitive with sigmatropic migration.[106,107] Willcott and Rathburn[107] thermolyzed a deuterium-substituted 1,5,5-trimethylcyclopentadiene under conditions similar to those employed by deHaan and Kloosterziel,[93] except for longer time periods, and on the basis of observed deuterium scrambling, these workers postulated a radical-chain process competitive with [1,5] sigmatropic methyl migration but with a higher activation energy (50–56 kcal vs. 42) (Scheme XI). Thus the radical-chain process would become more important at elevated temperatures, a result which had been previously suggested by McLean and Findlay.[95] It would thus appear that apparent [1,5] alkyl migrations must be analyzed carefully for cyclopentadiene and cyclohexadiene systems in order to separate out the two or three different possible mechanistic contributions. It is likely, however, that further studies directed toward the resolution of this problem will appear during the next few years.

[1,5] alkyl migration has been found in several heterocyclic dienes. Maier and coworkers[108] reported a [1,5] methyl shift at a temperature of 60° in a substituted dihydrophthalazine ring (eq 9). Patterson et al.[109] found that various allylic groups can undergo [1,5] shifts in pyrrole from N to C, with competition from a concurrent [3,3] migration (eq 10). In general, activation enthalpies ranged from 41 to 50 kcal/mol for the [1,5] shift as opposed to 32–43 kcal/mol for the [3,3] process.[109] This relative difference is in accord with that reported previously for competing [1,3] allyl vs. [3,3] rearrangement in the thermolysis of substituted benzothiazolium salts.[90] Sergio and coworkers[110,111] reported a particularly facile [1,5] alkyl shift from intermediary spiropyrazoles formed in the cycloaddition of disubstituted acetylenes to diazocyclopentadienes (Scheme XII). These [1,5] shifts are described as spontaneous and are in obvious contrast to the hydrocarbon analogs described by Kloosterziel[102] which rearrange at 280–380° (**143** → **144**).



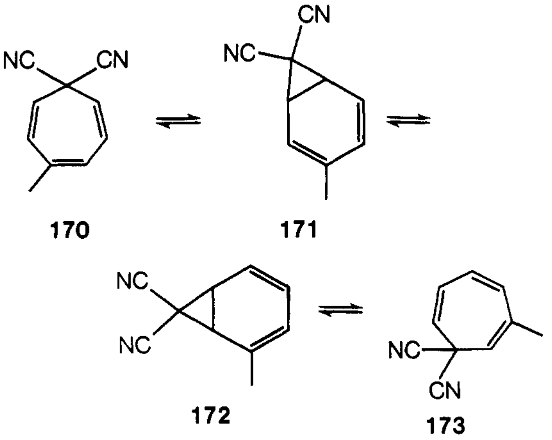
(9)



(10)

X = (a) α-methylallyl, (b) *trans*-crotyl, (c) *cis*-crotyl

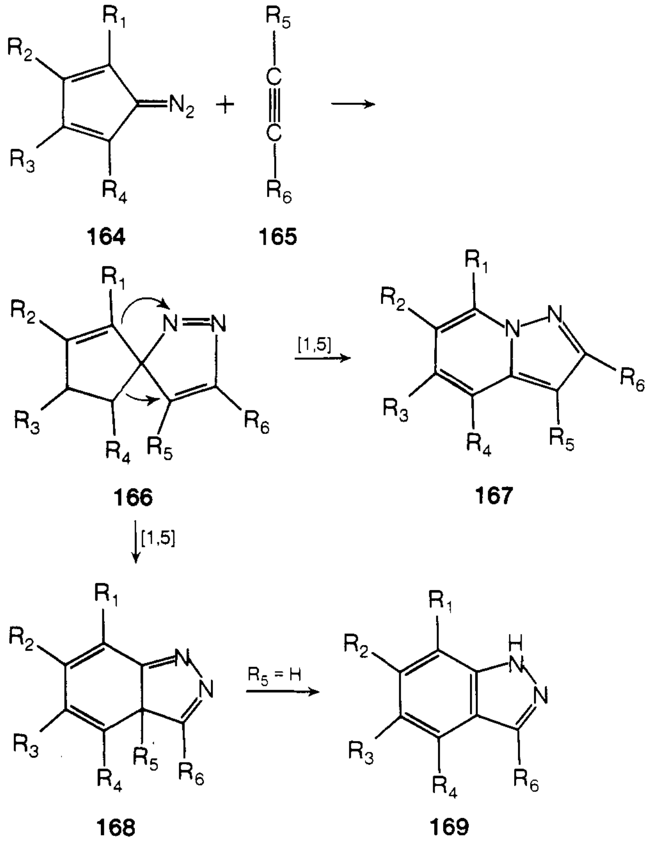
[1,5] alkyl migrations in 1,3,5-cycloheptatriene systems have been studied by Berson and coworkers,[112,113] and the results show that instead of simple [1,5] methyl migration in 3,7,7-trimethyl-1,3,5-cycloheptatriene,[112] a circumambulatory migration of ring carbon from an intermediary norcaradiene tautomer more readily explains the results. A similar path (eq 11) is followed for the 4-methyl-7,7-dicyanotropilidene, for which the dicyanonorcaradiene is a recognized valence isomer.[113]



(11)

Table VIII gives a summary of the activation parameters for [1,5] sp^3-hybridized carbon shifts.

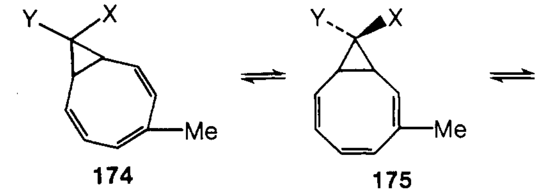
SCHEME XII



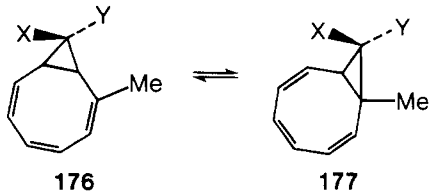
	R_1	R_2	R_3	R_4	R_5	R_6
a	Ph	Ph	Ph	Ph	COOMe	COOMe
b	Ph	H	H	Ph	CF	CN
c	(benzo)		Ph	Ph	CN	CN
d	(benzo)		(benzo)		H	H
e	Cl	Cl	Cl	Cl	H	Ph

Only one clear-cut example of [1,7] carbon migration has been studied. Klarner[114] was able to establish that each step in the circumambulatory mechanism proceeds with inversion of configuration at the migrating center, with free energies of activation of 29 kcal/mol. No endo-exo isomerization occurs (Scheme XIII).

SCHEME XIII



	174	175
$X = CH_3$ $Y = CN$	35%	33%
$X = CN$ $Y = CH_3$	34%	38%



176	177
21%	11%
24%	4%

2. *Aromatic Groups. Migration of sp^2-Hybridized Carbon*

The migration of phenyl groups to centers of positive charge leading to the formation of bridged phenonium ions is well known in many different systems, and it is perhaps surprising that sigmatropic migrations of phenyl and other aromatic groups have not been widely studied. Miller and coworkers[115,116] have studied the relative migration rates of hydrogen, phenyl, and methyl in the indene system (Scheme XIV), in diphenyl ether, and found migratory aptitudes wherein $H > C_6H_5 > CH_3$. McCullough and McClory[117] have more recently studied phenyl migration in the indene system to determine the effect of para substituents on the migration rate (aptitude). *p*-Bromo and *p*-methoxyl substitution had little effect

SCHEME XIV

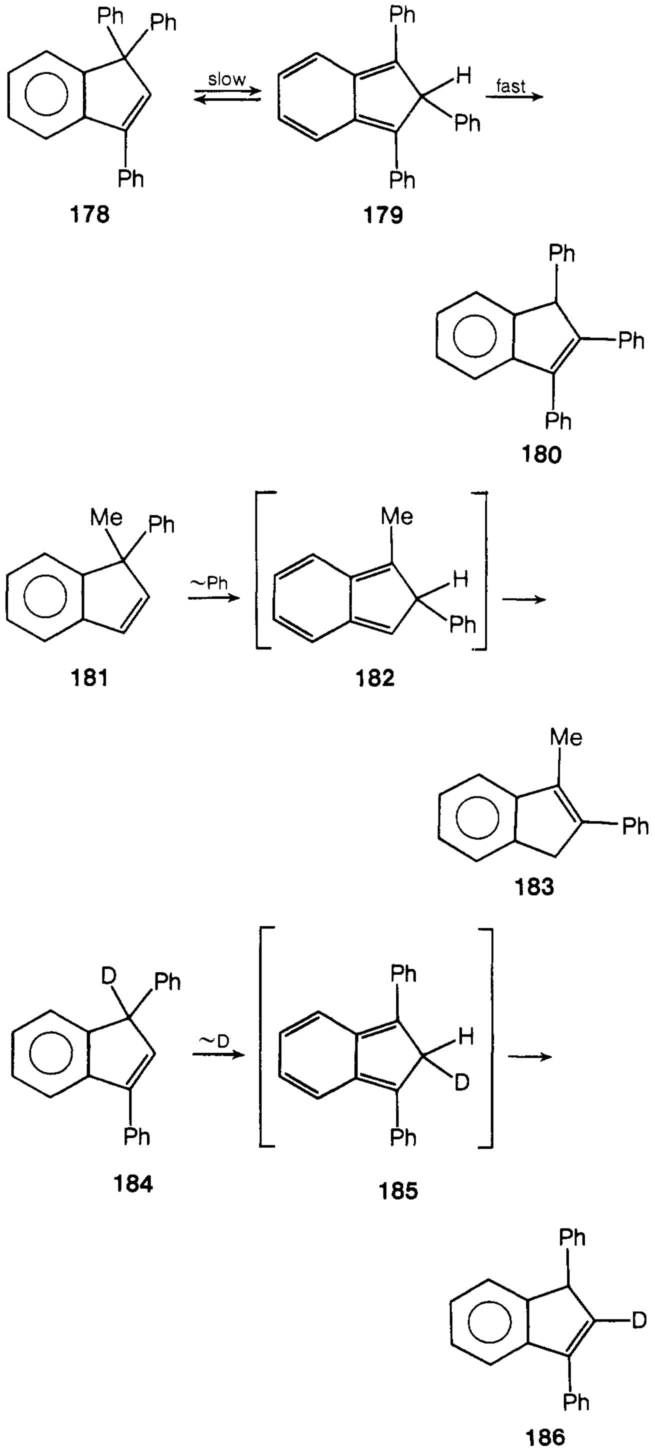
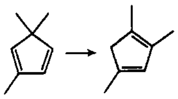
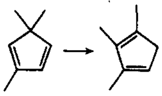
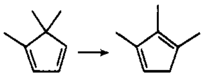
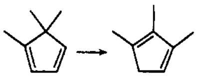
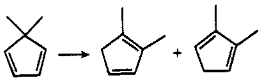
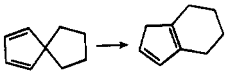
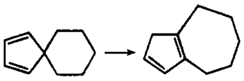
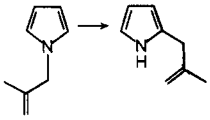
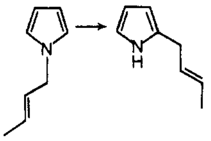
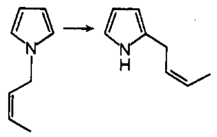
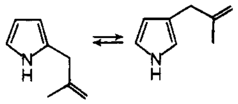
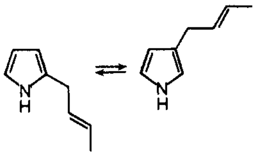
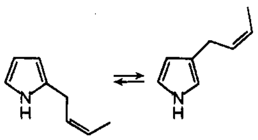
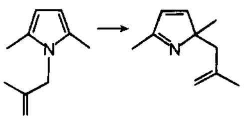
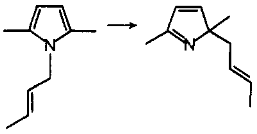
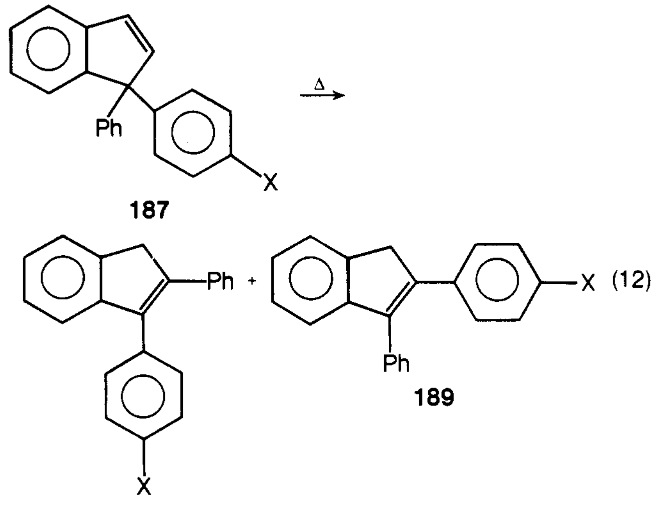


TABLE VIII. [1,5] sp^3-Hybridized Carbon Shifts

Reaction[a]	Migrating group	T range, °K (medium)	Log A (sec^{-1})	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	Ref
	Me	625–660 (g)[b]	13.9	44.2	+6	93
	Me	625–660 (g)	14.4	44.4	+3	93
	Me	625–660 (g)	14.6	40.3	−1	93
 + others	Me	608–702 (g)	13.7	43.8	+1	94
	Me	473–530 (g)	13.9	42.3	+3	95
	(–CH$_2$–)$_4$	553–653 (g)	13.3	34.6	−1	102
	(–CH$_2$–)$_5$	653–718 (g)	15.1	45.5	+6	102
	α-Methylallyl	739–823 (g)		43.0	−13.5	109
	*t*-Crotyl	739–823 (g)		46.7	−8.3	109
	*c*-Crotyl	739–823 (g)		48.1	−7.4	209
	α-Methylallyl	739–823 (g)		41.2 44.3	−15.5 −10.3	109
	*t*-Crotyl	739–823 (g)		41.8 44.2	−14.5 −10.1	109
	*c*-Crotyl	739–823 (g)		46.6 47.1	−8.3 −6.4	109
	α-Methylallyl	661–723 (g)		48.0	−4.0	109
	*t*-Crotyl	710–756 (g)		49.8	+0.7	109

[a] Reaction product shown as finally isolated after fast [1,5] H shifts. [b] (g) indicates gas-phase reaction.

on migratory aptitude, as might be expected for a simple [1,5] process (eq 12); however, *p*-cyano substitution greatly skews the migration process in favor of **189**. This was interpreted as indicating some radical character to the overall process, or transition state.



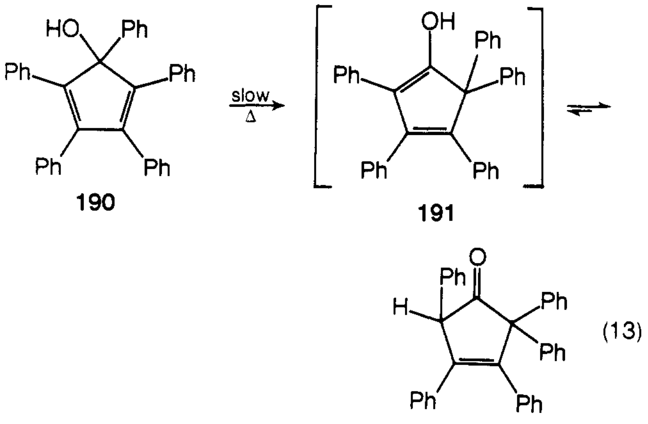
187

188

189

Substituent	% reaction	189:188
Br	100	50:50
OMe	100	52:48
CN	100	82:18

The only simple example of [1,5] phenyl migration in a cyclopentadiene ring has been described by Youssef and Ogliaruso.[118,119] Refluxing a solution of 1,2,3,4,5-pentaphenylcyclopentadienol in diphenyl ether produced 2,2,3,4,5-pentaphenyl-3-cyclopentenone, resulting from a slow [1,5] phenyl migration followed by tautomerization to the keto form. Beck and Schenker[120] have reported a possible [1,5] phenyl migration in a 1,3-cyclohexadiene system (eq 13), complicated, however, by an ionic route which is the dominant migration pathway (Scheme XV).



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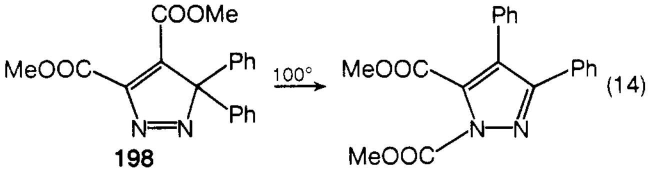
191

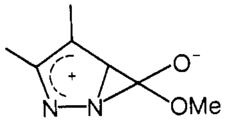
192

A [1,5] phenyl migration has also been postulated in the thermal rearrangement of a diphenyl, dicarbomethoxy pyrazole system (eq 14).[121] Bramley and coworkers interpreted this process as involving an initial [1,5] phenyl migration followed by two [1,5] COOMe migrations (or one [1,3] COOMe migration) to give the observed product. However, this rearrangement may also be envisaged as a two-step process via a dipolar aziridine intermediate, such as **200**. Sigmatropic



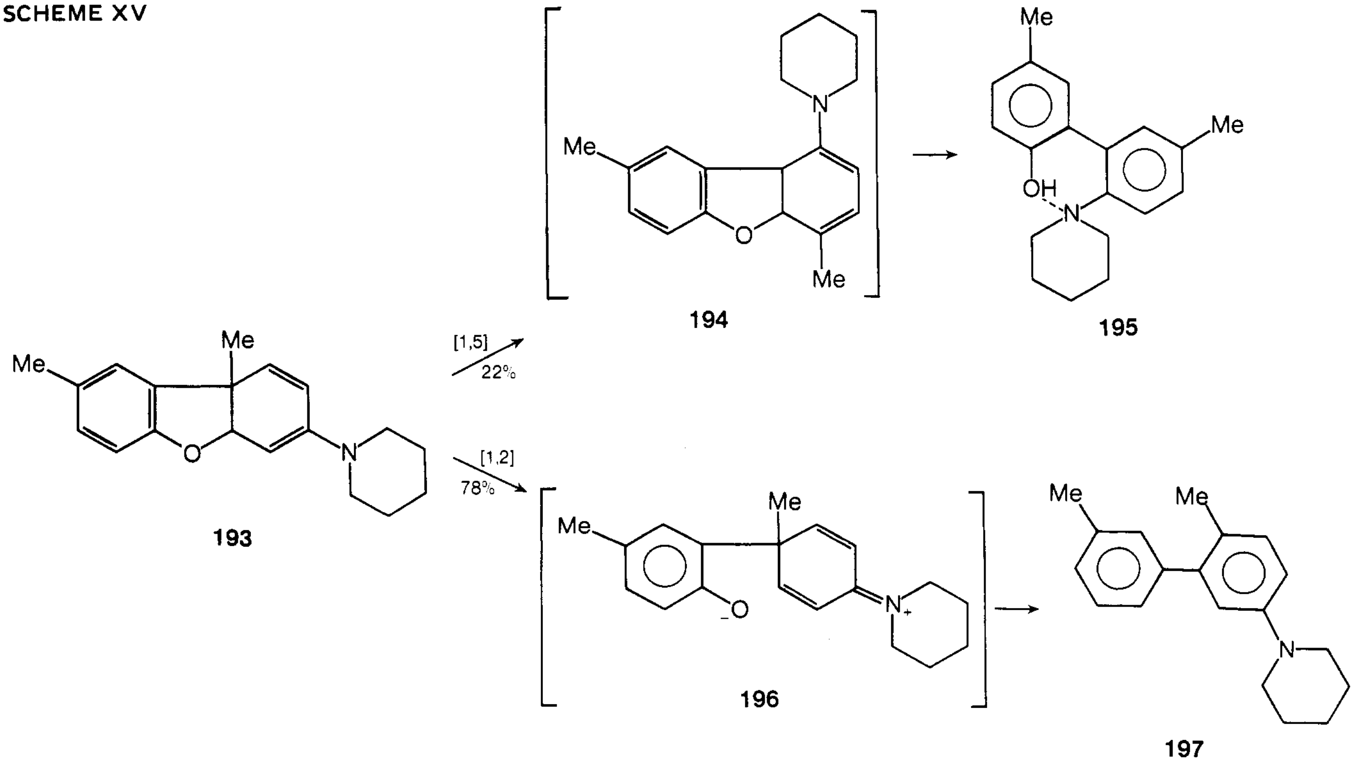
198

199



200

SCHEME XV



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196

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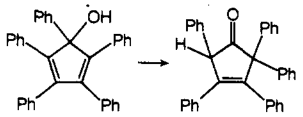
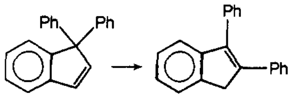
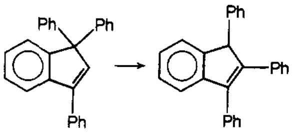
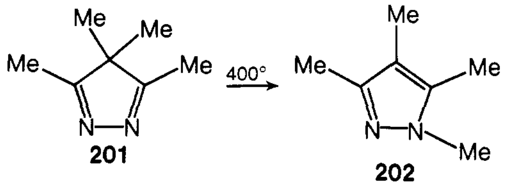
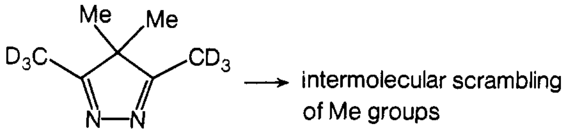
TABLE IX. [1,5] Migration of Phenyl Groups

Reaction	T range, °K (medium)	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	Ref
	446–473 (PhOPh)	35.3	−7.5	119
	523–553 (PhOPh)	27.2	−27.2	115
	493–509 (PhOPh)	26.7	−25.1	115

methyl migration has also been postulated in this system, although there is evidence that a competing radical pathway is also involved (eq 15 and 16).



201 202 (15)



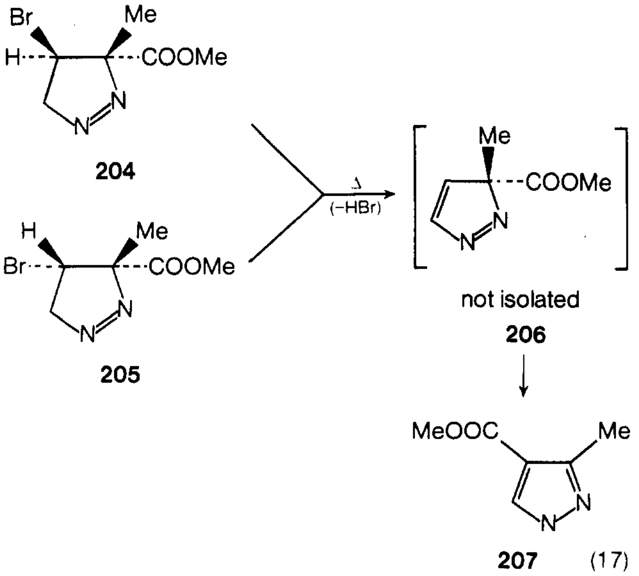
203 (16)

See Table IX for a summary of the activation parameters for [1,5] migration of phenyl groups.

3. Carbon Functional Groups

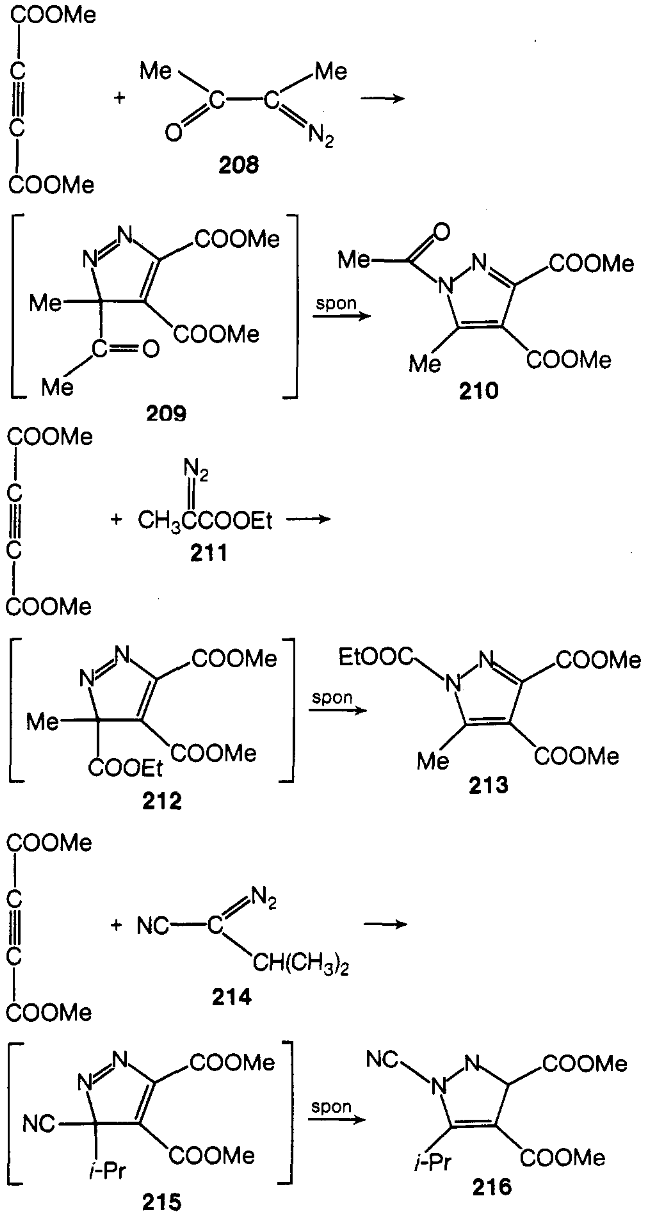
In the past few years there have been a surprising number of reports of apparent sigmatropic migration of carbon functional groups in five- and six-membered diene ring systems. With few exceptions, the migrating atom has been sp^2-hybridized, and the majority of reports have been concerned with carboalkoxy migration.

McGreer and Wigfield[122] probably were the first to observe [1,5] carboalkoxy shifts during the thermal dehydrobromination of 4-bromo-3-methyl-3-carbomethoxy-1-pyrazoline (eq 17). This migration is indeed similar to that observed by Bramley et al.,[121] which was discussed in the preceding section. Franck-Neumann and Buchecker[123] found that acetyl and cyano groups also undergo spontaneous [1,5] migration in the pyrazoline–pyrazole conversion during the condensation of acetylenedicarboxyate with α-diazo ketones, esters, and nitriles (Scheme XVI). In the analogous carbon system, cyclo-



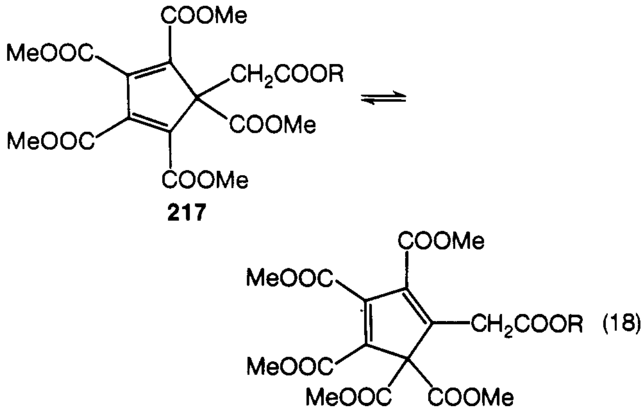
204 205 206 207 (17)

SCHEME XVI



208 209 210 211 212 213 214 215 216

pentadiene carboalkoxy migration requires greater activation. Thus Hoffmann and coworkers[124] found the [1,5] COOMe migration required 25–26 kcal/mol in cyclopentadienes with five ester substituents (eq 18).

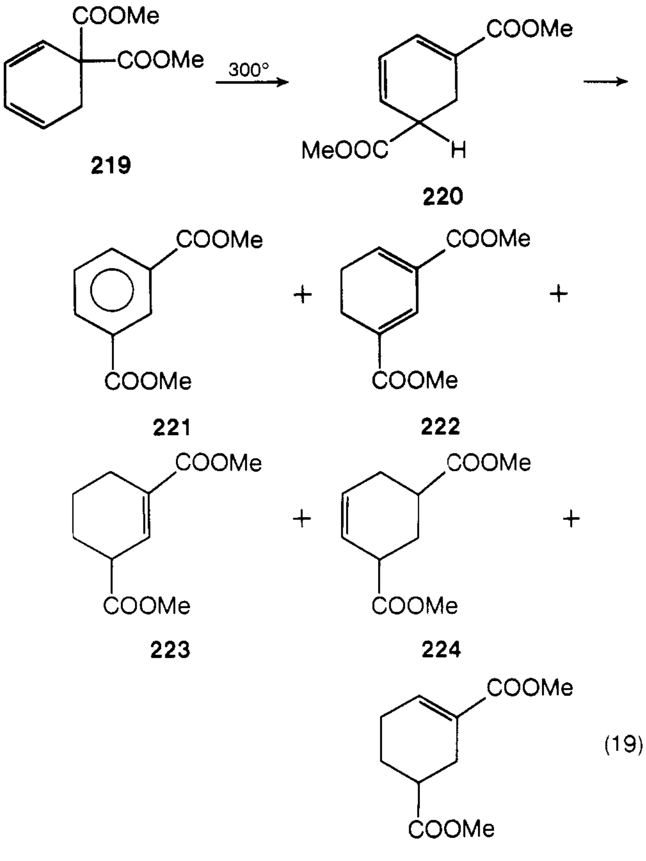


217

218

(18)

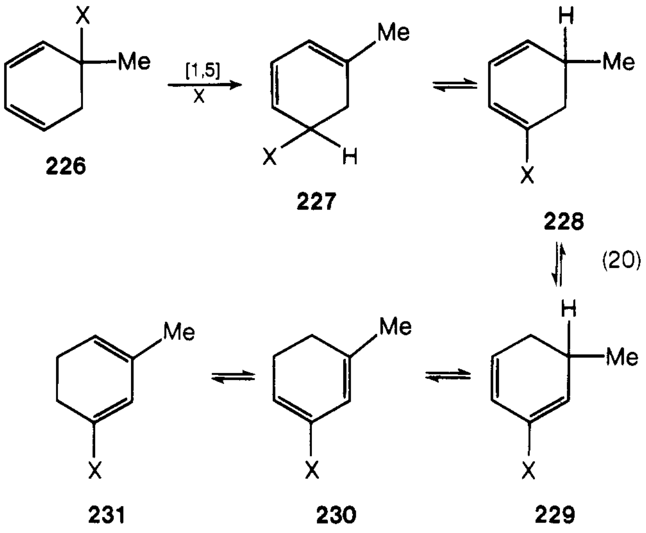
[1,5] carboalkoxy migration was postulated in the thermal rearrangement of 5,5-dicarboalkoxy-1,3-cyclohexadienes by Berson and Salomon[125] and also Baylouny.[126] The migration process, however, is complicated by the dehydrogenation–hydrogenation commonly found in high-temperature reactions of substituted 1,3-cyclohexadienes, resulting in a mixture of monoenes, dienes, and aromatic 1,3-diesters (eq 19).



219 220 221 222 223 224 225

(19)

Schiess and Fünfschilling[127,128] determined that acetyl and formyl groups, as well as carbomethoxy, also undergo [1,5] sigmatropic migration in the 1,3-cyclohexadiene system with activation energies ranging from 31 to 41 kcal/mol (eq 20). Relative rate studies show migratory aptitudes in the order CHO ≫ COMe > H > COOMe. Thus it follows that [1,5] migration of carbon functionalities in six-membered rings require greater activation than for five-membered rings, in accord with the previous results for [1,5] hydrogen and [1,5] alkyl migration.

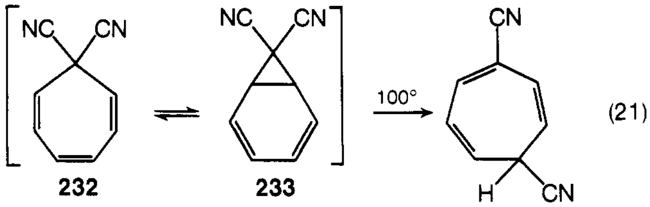


226 227 228 229 230 231

(20)

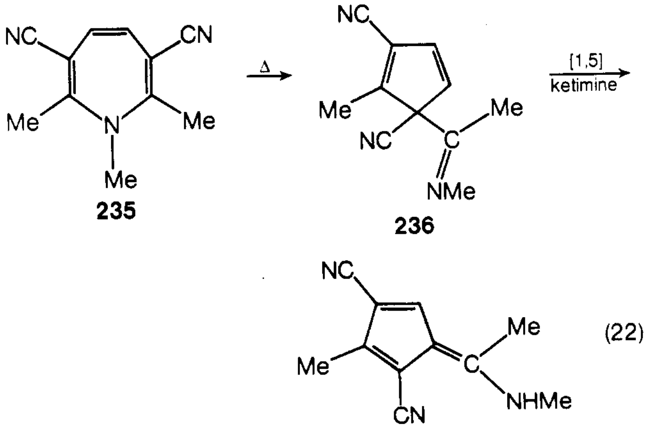
X = COOMe, COMe, CHO, H

In seven-membered rings, only two examples of a [1,5] migration of a carbon functional group have been studied. Ciganek found [1,5] CN migration occurred during the thermolysis of 7,7-dicyanotropylidine (eq 21),[129] and, in analogy to the migration of acetyl in both five- and six-membered rings, Mahendran and Johnson[130] postulated a [1,5] ketimine shift in the thermolysis of an 1*H*-azepine (eq 22). A summary of the known activation parameters for carbon functional group [1,5] migrations are given in Table X.



232 233 234

(21)



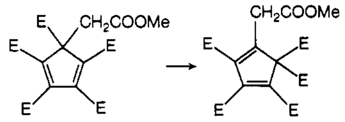
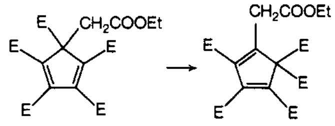
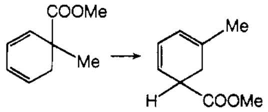
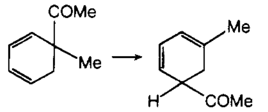
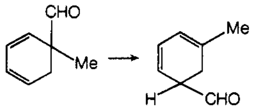
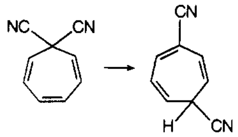
235 236 237

(22)

C. [*1,j*] Heteroatom Group Migrations

There are several well-scattered examples of [1,3] and [1,5] heteroatom migrations reported in the literature, which may roughly be divided into nonmetal and metal categories with respect to the atom directly involved in the migration.

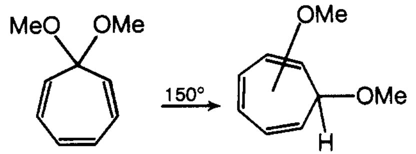
TABLE X. [1,5] Migrations of Carbon Functional Groups

Reaction	Migrating group	T range, °K (medium)	Log A (sec^{-1})	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
	E = COOMe	386–423 (PhCl)		25.3	−9.7	124
Reverse	COOMe	386–423 (PhCl)		25.1	−10.4	124
	COOMe	370–407 (PhMe)		25.3	−10.9	124
Reverse	COOMe	370–407 (PhMe)		26.9	−6.6	124
	COOMe	546–577 (heptane)	11.8	39.7	−5.9[a]	128
	COMe	473–513 (heptane)	12.1	34.9	−4.1[a]	128
	CHO	423–473 (heptane)	11.5	30.1	−7.8[a]	128
	CN	373–414 ($CDCl_3$)	10.8	27.6	−12.2	129

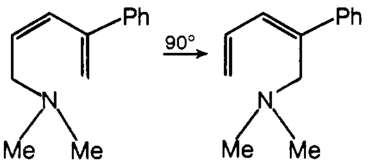
[a] Calculated for T_m.

This section will deal with the nonmetal category, while the following section will cover organometallic group shifts.

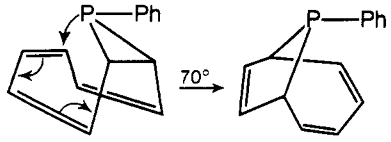
Hoffmann and coworkers[131] reported an apparent [1,5] methoxyl shift in a 7,7-dimethoxycycloheptatriene, which proceeds at a reasonable rate at 150° (eq 23). Migration of a dimethylamino group has also been reported[132] for a phenyl-substituted 1,3-pentadiene (eq 24), the driving force presumably coming from the greater conjugation in the product, as the migration is irreversible. A [1,5] P shift has been postulated[133] in the thermal (70°) conversion of 9-phenyl-9-phosphobicyclo[6.1.0]nonatriene to 9-phenyl-9-phosphobicyclo[4.2.1]nonatriene (eq 25).



238 239 (23)

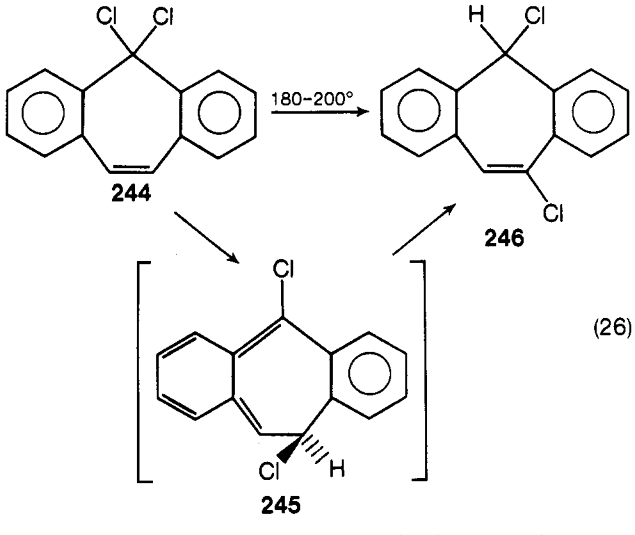


240 241 (24)

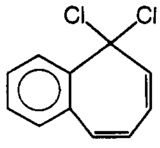


242 243 (25)

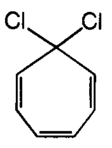
Looker[134] first reported a [1,5] halogen migration in the dibenzotropylidine system (eq 26). The apparent driving force for this migration is the relief of crowding between the equatorial substituent (Cl) and the peri-H atoms. Neither 5,5-dichloro-5*H*-benzocycloheptene (**247**) or 7,7-dichlorotropylidine (**248**) undergo this migration. However, Cl does migrate in the dibenzo derivative even when phenyl or a 1-naphthyl substituent replaces one of the chlorines in **244**. There have



244 245 246 (26)



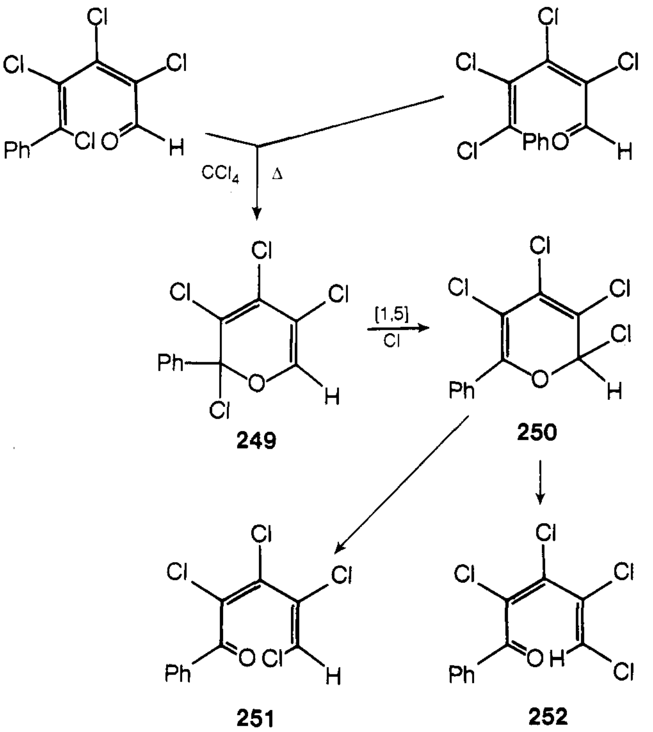
247



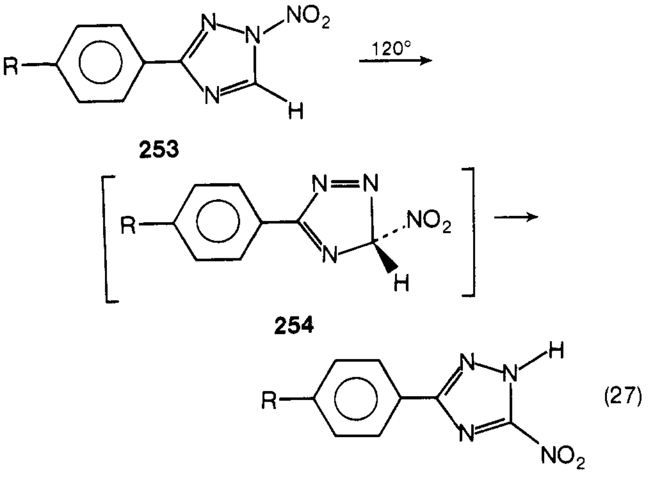
248

also been more recent reports of both [1,3] and [1,5] Cl migration. Roedig et al,[135] reported a rapid [1,5] Cl shift in a pentadienal isomerization occurring in boiling carbon tetrachloride, while Strohmeier and Eden[136] have interpreted the 3-chloro-1-butene/1-chloro-2-butene isomerization in dioxane at 75° as a [1,3] sigmatropic chlorine migration (Scheme XVII).

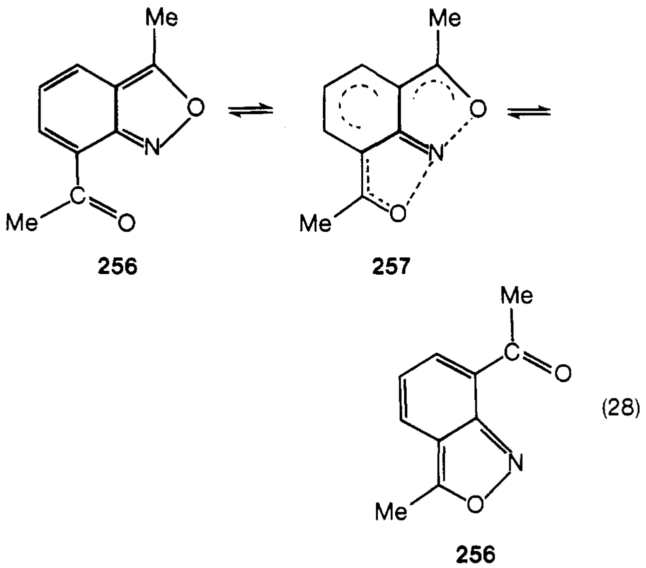
SCHEME XVII



There have been two reports of migration of sp^2-hybridized nitrogen. Habraken and Cohen-Fernandes[137] have found an apparent [1,5] *migration of a nitro group in the 1,2,4-triazole* system, which is followed by a rapid[1,5] hydrogen shift (eq 27). Parry and Rees[138] made an interesting study of a formal [1,9] sigmatropic migration of sp^2 nitrogen in a degenerate rearrangement. This is a ten-electron process proceeding via a suprafacial-retention pathway (eq 28). The rearrangement is detectable by NMR in Me_2SO or trichlorobenzene ($\Delta G^\ddagger$ = 23 kcal).



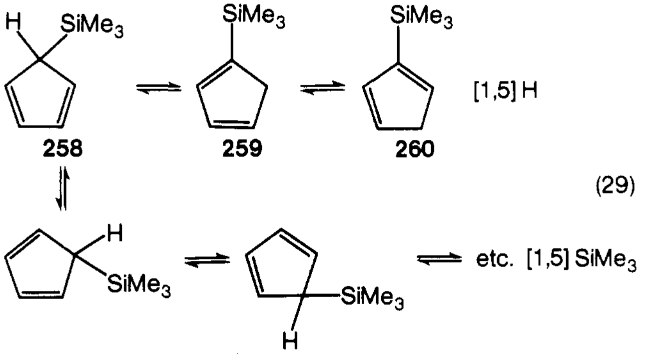
The relative paucity of clear-cut examples of heteroatom sigmatropic migration is curious. As is apparent from the *number of organometallic examples, there is no fundamental* reason why more examples have not been reported; however, this lack may merely represent the fact that little effort has yet been made to extend the search for further, or different, examples of heteroatom sigmatropic migration.



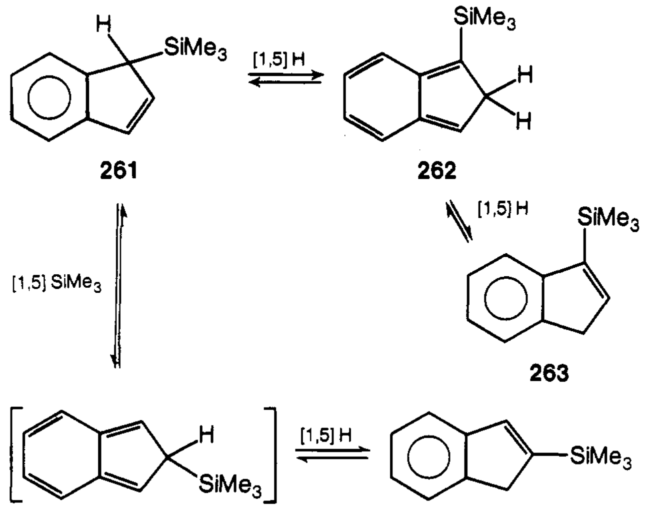
D. Organometallic Group Shifts

Sigmatropic migration of organometallic groupings has been investigated extensively over the past several years because of their remarkable mobility. Most of the work associated with these migrations has been directed toward determining if these exceedingly rapid shifts followed 1,2-least motion pathways or true [1,5] sigmatropic routes. Fritz and Kreiter[139] first demonstrated that trimethylsilyl shifts rapidly around a cyclopentadiene ring by observing the fluxional behavior of the NMR spectra of 5-trimethylsilylcyclopentadiene. Cotton and coworkers[140-142] quickly thereafter described similar rapid migrations in Fe, Cr, Ru, and Mo sandwich compounds, such as (π-C_5H_5)Fe(CO)$_2$(σ-C_5H_5). These workers referred to this process as "ring-whizzing" and proposed that the overall process was a series of very rapid 1,2 shifts. Part of the rationale for this argument is based on the fact that (π-C_5H_5)Fe(CO)$_2$(σ-1-indenyl) was found to be rigid up to about 70° by NMR spectroscopy. On this basis they concluded that 1,3-shifts were not occurring.

The [1,5] migration processes in 5-trimethylsilylcyclopentadiene may be considered as a competition between hydrogen and trimethylsilyl (eq 29). The temperature-dependent spectra of **258** could not be explained by the rate of [1,5] H migration, determined by Ashe[143] to be only 1.1 times the rate in pentadeuteriocyclopentadiene. Both Ashe[143] and McLean and Reed[144] estimated that the rate of H-averaging observed in the NMR spectra could only be consistent with a [1,5] $SiMe_3$ migration rate 10^6 *greater* than for [1,5] H migration. Davison and Rakita[145] similarly showed that trimethyl*germyl- and trimethylstannylcyclopentadiene, methylcyclo*pentadiene, and pentamethylcyclopentadiene also exhibited fluxional behavior by variable-temperature NMR.

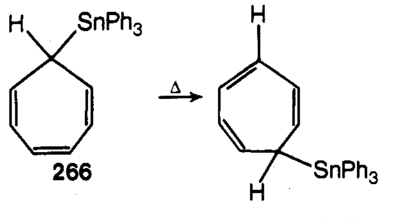


Trimethylsilyl migration in the indenyl system is complicated by the fact that [1,5] migration requires the intermediacy of an isoindenyl structure, **262**. Both Ashe[146] and Larrabee and Dowden[147] were able to trap the elusive isoindene intermediate with TCNE and maleic anhydride, respectively, and determined that [1,5] trimethylsilyl migration required an activation enthalpy of ca. 22 kcal/mol. This represents a $\Delta(\Delta G^\ddagger)$ of 8 kcal compared to 5-trimethylsilylcyclopentadiene, indicating the reluctance of **261** to form **264**. Heating **261** for several hours at 155° results in a gradual buildup of isomers resulting from [1,5] H migration, which is still much slower than $SiMe_3$ migration.[147] Larrabee and Dowden found similar behavior for 1-trimethylgermylindene.[147] Fluxional isomerization in the indenyl system has also been demonstrated for other organometallic groups, and trimethylstannyl, trimethylgermyl, dimethylphenylstannyl, and dimethylphenylsilyl all show fluxional behavior by variable-temperature NMR.[148,149] As the σ-bonded metal atom becomes more metallic in character, the temperature for the onset of fluxional behavior lowers. Me_3Sn, Me_3Ge, and Me_3Si are all static at −37°; however, fluxional behavior occurs at +49, +135, and +180°, respectively.[148] This greater ease of migration with increasing metallic character is exemplified by comparing the activation energies for stannyl groups (~14 kcal/mol) with those of silicon (~24 kcal/mol).[149]

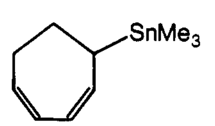


261 **262** **263** **264** **265** (30)

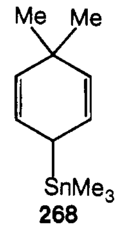
Several workers have disagreed on how best to label the above migrations, in that a 1,2-shift is indistinguishable from a [1,5] sigmatropic migration. However, in cycloheptatriene the least motion (1,2) path is quite different from the original [1,5] pathway which involves migration to the carbon furthest from the original point of attachment. Larrabee[150] found that triphenyl-7-cyclohepta-1,3,5-trienyltin (**266**) exhibits fluxional behavior with an activation energy similar to that of 1-trimethylstannylindenes[148,149] (10 vs. 14 kcal). The migration of the triphenylstannyl group occurred in a [1,5] fashion, not by the 1,2 least motion path. Curtis and Fink[151] also concluded that trimethylstannyl migration in 5-trimethylstannyl-1,3-cycloheptadiene (**267**) occurred via [1,5] shifts rather than by 1,2 or 1,3 pathways. These workers also determined that 1,1-dimethyl-4-trimethylstannyl-2,5-cyclohexadiene (**268**) did not exhibit fluxional behavior, since the [1,5] path is barred in this molecule. Ashe[152] made the surprising observation that in 7-trimethylsilylcycloheptatriene [1,5] H migration is actually faster than [1,5] trimethylsilyl migration (eq 31), a startling reversal of migratory aptitude compared to cyclopentadiene and indene derivatives. A possible explanation is that the large organometallic group cannot bridge the concave, nonplanar cycloheptatriene ring as well as it can for planar cyclopentadiene. However, this explanation is not consistent with the fluxional migration of triphenylstannyl in cycloheptatriene reported by Larrabee.[150] Apparently the more metallic groupings have no such conformational difficulty.



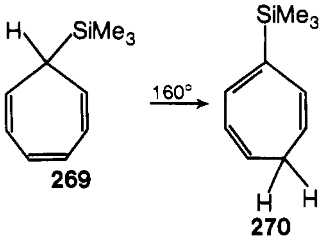
266



267
fluxional



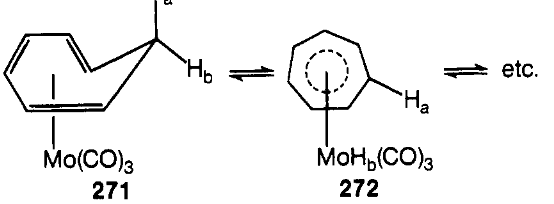
268
nonfluxional



269 **270** (31)

[1,5] H > [1,5] $SiMe_3$

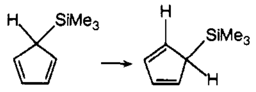
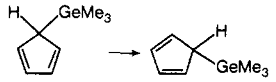
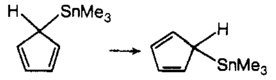
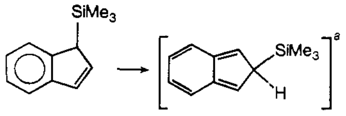
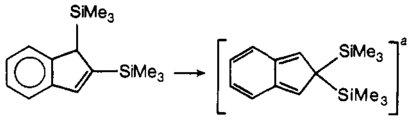
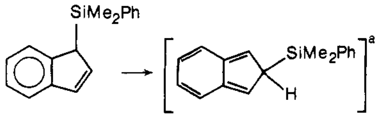
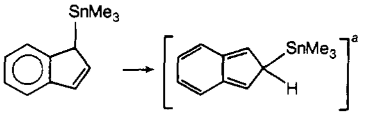
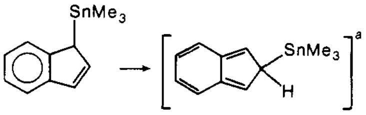
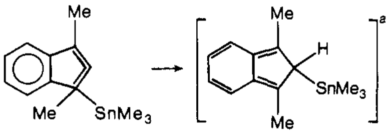
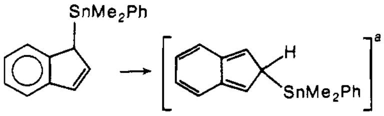
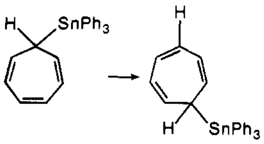
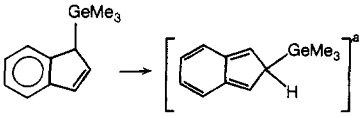
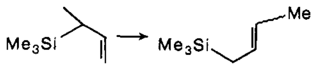
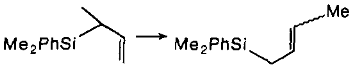
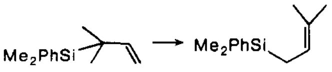
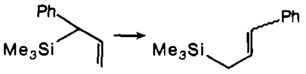
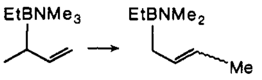
[1,5] hydrogen migration in cycloheptatriene-organometalloid complexes is not limited to Ashe's observation[152] in 7-trimethylsilylcycloheptatriene, as Roth and Grimme[153] found a conformational preference for migration of hydrogen in a cycloheptatriene–molybdenum tricarbonyl complex (eq 32). Interestingly, these workers postulated that the hydrogen occupying a pseudo-equatorial position undergoes migration exclusively, which is exactly opposite to the uncomplexed molecule. Pauson and coworkers[154,155] have confirmed this for the 7-*exo*- and 7-*endo*-phenylcycloheptatrienes complexed to $Mo(CO)_3$ and $Cr(CO)_3$. In both cases, only the exo isomer having a pseudo-equatorial hydrogen rearranges when heated. This reaction has been classified as a metal-assisted [1,5] sigmatropic hydrogen shift, although the mechanism of this "assistance" is still relatively obscure. The activation energy[155] for this process (24 kcal for 7-*exo*-methyl and 27 kcal for 7-*exo*-*p*-tolyl) compare favorably with [1,5] H migrations in the uncomplexed cycloheptatrienes (Table IV).



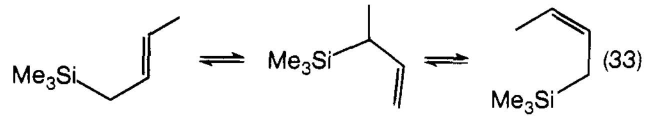
271 **272** (32)

There are few examples of [1,*j*] sigmatropic organometallic migrations in acyclic systems. Kwart and Slutsky[156] have studied the [1,3] shift of trisubstituted silyl groups in allylic frameworks and concluded that migration occurs probably via a suprafacial route with inversion at migrating silicon (eq 33). Activation parameters ($\Delta H^\ddagger$ ~ 47 kcal and $\Delta S^\ddagger$ ~ −7 eu) indicate the cyclic nature of the transition state, but there are no known [1,3] carbon shifts (e.g., *tert*-butyl) in simple

TABLE XI. [1,*j*] Migrations of Organometallic Groups

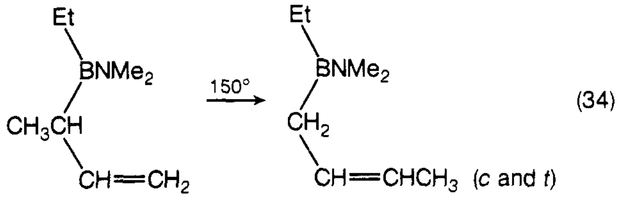
Reaction	Migrating group	T range, °K (medium)	Log A (sec^{-1})	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	Ref
	$SiMe_3$	243–293 (neat)	11.3	13.0	−9.2	158
	$GeMe_3$	251–398 (neat)	10.7	10.9	−11.0	159, 160
	$SnMe_3$	198–242 (neat)	12.6	6.8	−2.7	159, 160
	$SiMe_3$	313–333 (EtOAc)	12	22.5	−3.8[b]	146
	$SiMe_3$	295–473 (neat)	11.7	22.4	−6.9	160
	$SiMe_3$	371–448 (neat)	14.4	26.1	−6.7[b]	149
	$SiMe_2Ph$	304–461 (neat)	11.5	23.0	−6.4[b]	149
	$SnMe_3$	271–343 (neat)	11.7	13.2	−5.5[b]	161
	$SnMe_3$	233–413 (neat)	11.0	12.1	−10.5	160
	$SnMe_3$	256–321 (neat)	12.5	13.6	−1.4[b]	149
	$SnMe_2Ph$	250–325 (neat)	11.9	13.5	−4.2[b]	149
	$SnPh_3$	273–412 (C_2Cl_4)		9.5		150
	$GeMe_3$	288–473 (neat)	10.3	17.8	−13.7	160
	$SiMe_3$	779–840 (g)	12.3	46.1	−6.2	156
	$SiMe_2Ph$	773–845 (g)	12.2	45.6	−6.8	156
	$SiMe_2Ph$	789–850 (g)	12.3	46.0	−6.6	156
	$SiMe_3$	693–753 (g)	12.0	41.1	−7.4	156
	$BEtNMe_2$	374–421 (neat)		23.9	−20.6	157

[a] Isoindene intermediate not necessarily isolated. [b] Calculated for T_m.



273 **274** **275**

acyclic systems with which to compare these activation enthalpies. The transition state, in theory, should, however, be directly comparable to those discussed previously for [1,3] carbon migrations in simple cyclic systems. More recently, Hancock and Kramer[157] have described a fairly facile [1,3] sigmatropic boron migration (eq 34). The migration is apparently irreversible and crossover experiments indicate that the migration is indeed intramolecular.



276 **277**

Activation parameters for all of the [1,*j*] organometallic migrations discussed above are summarized in Table XI.

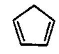
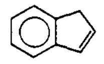
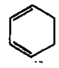
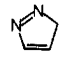
V. Migratory Aptitudes and the Influence of Substituents on Migration Rates

Migratory aptitudes in various sigmatropic migrations have been discussed briefly in the preceding sections. With the exception of the phenomenon of fluxional isomerization of organometallic groupings in certain systems, hydrogen migrates faster than any other functional group. This is in marked contrast to the more familiar shifts encountered in carbonium ion chemistry (1,2 shifts), wherein the favored migrating (or neighboring) group may usually be predicted by considering its bridging and charge-delocalization capabilities. Thus phenyl migrates in preference to hydrogen in such reactions as the pinacol rearrangement, and para substitution with electron-donating substituents enhances this preference, manifested by increasing migration rates. Rate differences for migration of deuterium compared to hydrogen are more properly considered as an isotope effect. Kloosterziel and ter Borg[53] reported a k_H/k_D of 5.0 for [1,5] migration in the cyclooctatriene system at 120°, while Roth and Konig found that $k_H/k_D = 1.15e^{-1400/RT}$ represented the isotope effect for migration in 1,3-pentadiene.[33] At 25°, $k_H/k_D = 12.2$ for 1,3-pentadiene, a value considerably higher than that found for 5-methylcyclopentadiene by McLean et al.[38] (7.67 at 7°, 5.75 at 27°, and 4.45 at 47°).

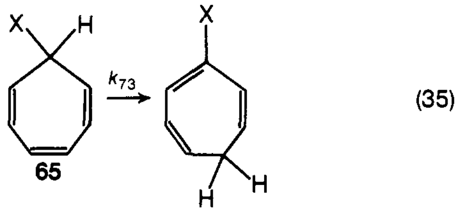
Several groups have recognized the problem of migratory aptitude in sigmatropic rearrangement, but most reported studies must still be considered fragmentary. A summary of these findings may be found in Table XII.

Another equally interesting facet of sigmatropic migration is the effect of substitution at a migrating center upon the overall migration rate. Kloosterziel and coworkers have studied this problem extensively in the 1,3,5-cycloheptatriene system[21,22,40-43] by considering the effect on k_{73} of various X groups (eq 35). Substitution of a strong activating (electron-donating) group on the para position of phenyl has very little effect on migration rate. Nozoe and Takahashi[55] confirmed that phenyl and methoxyl were equal in rate-enhancing capability and that both were faster than hydrogen. More recently Breslow and coworkers[162] have studied the effect of halogen substitution on [1,5] hydrogen migration in cyclopentadiene (eq 36). Halogen substitution *slows* the rate of hydrogen migration compared to the parent hydrocarbon (e.g., X = D) even though it stabilizes the reaction product. A considerable rate differential also exists between the different members of the halogen family, iodine being the slowest (H > Cl > Br > I). Breslow has rationalized this behavior as indicating that local positive charges on carbon must be involved in the [1,5] transition state. The fact remains that halogen is the only substituent which is known to retard sigmatropic hydrogen migration in a simple system uncomplicated by steric effects, and the mechanism of this retardation is still obscure and open to interpretation.

TABLE XII. Sigmatropic Migratory Aptitudes

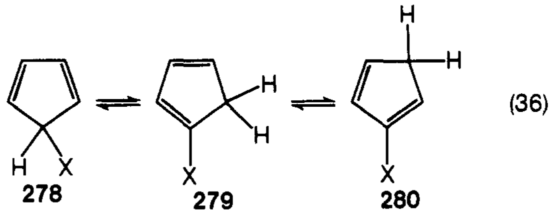
Migration type	System	Migratory aptitudes	Ref
[1,5]		H > D > Me,	33, 38, 39
[1,5]		H > C_6H_5 > Me	114, 115
[1,5]		CHO > $COCH_3$ > H > COOMe > Me[a]	127, 128
[1,5]		COOMe > Me	122
[1,5]		COOMe > C_6H_5	120

[a] Relative rates of group migration from 5-substituted-5-methyl-1,3-cyclohexadiene rather than direct competition.



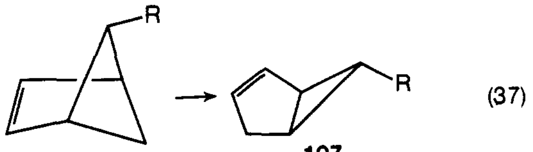
65 **66**

k_{73}: NMe_2 > OMe, C_6H_5, $p\text{-}Me_2NC_6H_4$ > CN > SMe > Me > H



278 **279** **280**

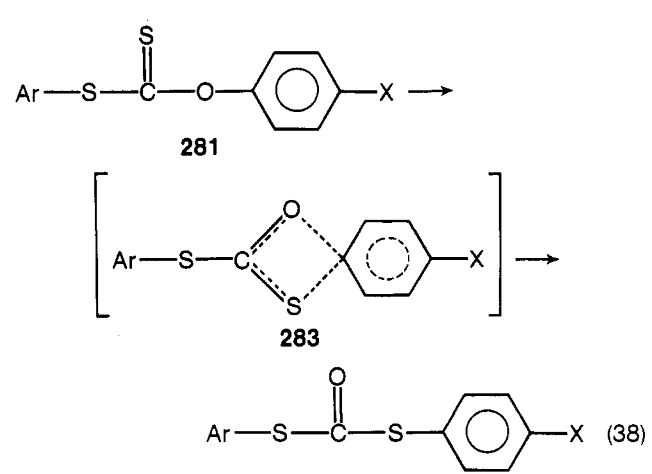
Substituent effects in [1,3] carbon migration have not been studied in any detail. In the conversion of anti 5-substituted bicyclo[2.1.1]hex-2-enes to exo-substituted bicyclo[3.1.0]hexenes, methoxyl and other similar substituents accelerate the conversion compared to the parent hydrocarbon (eq 37).[78,79]



106 **107**

NH_2 > N_3, CH_3O > CH_3COO > H

In an apparent [1,3] phenyl migration (from S to O, **281** → **282**), Araki[163] found that electron-donating groups retarded, and electron-withdrawing groups accelerated the rearrangement rate, presumably via a bridged intermediate, **283**. No studies have yet been directed toward establishing this effect for [1,5] carbon migrations. Similarly, no data are available on the possible effects of substituents on either [1,7] hydrogen or carbon migrations.



281 283 282 (38)

$NO_2 > CN > COCH_3 > Cl > H > CH_3 > OCH_3$

X	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
OCH_3	38.1	-6.5
H	37.2	-5.4
NO_2	33.6	-5.3

VI. Summary and General Trends in Current Research

In this review an attempt has been made to present an overview of the current state of our knowledge of thermal [1,*j*] sigmatropic migration. In particular, it is hoped that the discussion of differing viewpoints of the sigmatropic transition states and the collection of all available activation parameter data will enable others to further extend the theoretical framework. Several problems currently exist in the field and are actively being pursued by various research groups, and it is probable that important results will be reported in these areas during the next several years. I have attempted, in the following list, to identify the more important areas currently under study and readily admit a possible prejudice in the choice. (1) Continued efforts are being directed to find examples of all reasonably possible migration pathways for hydrogen and carbon. Likely candidates are [1,9] s hydrogen migration, [1,3] a_r, [1,5] a_i, and various [1,7] carbon migrations. (2) It is likely that more, and different, examples of groups that can thermally migrate via a sigmatropic transition state will be discovered, particularly via either [1,3] or [1,7] routes with inversion at migrating centers other than carbon. (3) Better theoretical predictions of activation parameters for various migration pathways need to be developed. Virtually all previous attempts to predict activation energies for [1,5] hydrogen migration are 7–10 kcal/mol[164–167] lower than the experimental value. (4) Another possible theoretical extension is an increased use of the principle of least motion (PLM)[164] in predicting the most probable [1,*j*] migration pathway. (5) A comprehensive study of migratory aptitude in various systems is needed in order to establish a frame-work of experimental data for future predictions. (6) A great deal of research is currently dealing with the problem of competition between allowed and forbidden migration routes, such as [1,3] s_r vs. [1,3] s_i and [1.3] a_r vs. [1,3] a_i, and these studies will probably be extended to [1,5] and [1,7] migration. (7) More research is necessary to elucidate the competition between various possible allowed routes, such as [1,5] s vs. [1,7] a hydrogen migration. (8) Much work remains to be done in order to establish the mechanism of rate enhancement or retardation by substituent groups. Dewar has already predicted,[166] for example, that electromeric substituents (CN, NMe_2) on piperylene may favor antiaromatic antara [1,5] hydrogen shifts. Such substituent control has already been demonstrated by Cookson and Kemp[168] in the thermal conversion of 3,3-dicyano-2-methyl-4-phenylpent-1-ene to 1,1-dicyano-2-methyl-4-phenylpent-1-ene by a [1,3] C shift with retention. Finally, an additional problem which has, to a large extent, been ignored by many workers is the determination of the degree of concertedness of many of the "sigmatropic" migrations discussed in this review. The possibility exists in any [1,*j*] migration that an alternate pathway involving radical dissociation–recombination (RDR) may compete to some extent with the concerted path. Baldwin and coworkers[169,170] have studied this competition in great detail for [2,3] sigmatropic processes, in a variety of systems, utilizing chemically induced dynamic nuclear polarization[171] (CIDNP) effects to detect paramagnetic species present during the migration course. While this technique is indeed useful, it remains to be seen if it will aid the detection and evaluation of RDR contributions to [1,*j*] migrations.

VII. Addendum

During the past year the rapid expansion of our knowledge concerning [1,*j*] sigmatropic rearrangements has continued unabated. Theoretical studies have included reviews on subjacent and superjacent orbital control,[172] substituent effects on subjacent orbital control,[173] a general discussion of the relationship of aromaticity and the generalized Woodward–Hoffmann rules,[174] and a discussion of the relative ease of various [1,3] sigmatropic pathways compared to calculated approximate reaction potential energy surfaces and orbital symmetry predictions.[175] Attempts have continued to develop transition-state models for sigmatropic migration. De Dobbelaere et al.[176] have extended their earlier work[167] on [1,5] hydrogen migration in cyclopentadiene to the 1,3-cyclohexadiene and 1,3,5-cycloheptatriene systems utilizing INDO calculations, while Dewar has published considerably on the use and value of MINDO/3 calculations in describing various pericyclic processes.[177]

Several interesting studies of [1,*j*] hydrogen migration have appeared. Schiess and Radimerski[178] have demonstrated that [1,5] hydrogen migration from C_1 in 2,4-pentadienal produces ketene intermediates at 500–600°. [1,7]-Sigmatropic hydrogen migrations in various alkyl-1,3,5-hexatrienes have been reported,[179] the most unusual being that of Hastings and coworkers[180] who report a suprafacial [1,7] hydrogen shift in an intermediate produced by heating (*E*)-2-benzylidene-(*Z*)-1-mesityl(phenyl)methyleneindan.

Migrations of carbon moieties have been of considerable interest during the past year. Krow and Reilly[181] reported a [1,3] carbon migration with retention of configuration (S_r) in the thermolysis of *N*-benzyl or *N*-carbomethoxy derivatives of 3-aza[3.3.2]deca-6,9-diene. Further studies on the possibility of [1,5] alkyl group migration in the 1,3-cyclohexadiene system have produced more evidence in favor of an alternative three-step process involving electrocyclic ring opening, [1,7] hydrogen migration, and electrocyclic ring closure.[182,183] In fact, Schiess and Dinkel[183] have demonstrated that at 300° [1,5] COOMe migration accounts for only 85% of the thermal rearrangement and the three-step process 15%. At 500° the percentage of [1,5] migration falls to 75%. For [1,5] phenyl migration, the [1,5] sigmatropic pathway accounts for only 4% at 550°. Dolbier and coworkers[184] have studied [1,5] methyl and ethyl migration in independently prepared isoindenes. In direct competition, ethyl migrates approximately seven times faster than methyl. Patterson and coworkers[185] reported further studies on the competition between [1,5] and [3,3] pathways for crotyl- and α-methallylpyrroles. Several workers have reported continuing studies of various [1,5] migrations in pyrazoles and spiropyrazoles involving sp^2-hybridized carbon.[186] The synthetic utility of these rearrangements is emphasized.

Sigmatropic migrations of carbon functional groups continue to be of considerable interest. Several [1,5] acyl shifts in a variety of systems have been noted, particularly in heterocyclic rings containing one or two nitrogens.[187] Further examples of [1,5] ester migrations have also been reported.[187b,188] Migration of oxygen functions have also received more attention and [1,5] OR migrations have been reported, from carbon to carbon[188a] and from nitrogen to carbon.[189] Finally [1,5] CHO migration in indenes has been shown to be faster than [1,5] H with $\Delta H^{\ddagger} = 22.08 \pm 0.75$ kcal/mol and $\Delta S^{\ddagger} = -11.41 \pm 2.21$ eu.[190] Studies of sigmatropic migration of noncarbon moieties have also been extended during the past year. Hartmann and Regitz have reported[191] sigmatropic migration of phosphoryl ($PO(OMe)_2$ and $POPh_2$) groups in phosphorylpyrazole synthesis, and Habraken and coworkers[192] have confirmed their earlier report[137] concerning [1,5] migration of nitro groups in pyrazole rings. Wiberg and Pracht have determined[193] that the relative rates of [1,3] sigmatropic SiX_3 migration increase in the order $X = Et < Me < OMe < Cl$. Ustynyuk and coworkers[194] have definitely confirmed that trimethylsilyl migration in the 1,3-cyclopentadiene system is [1,5] in nature and not [1,3] as some workers have previously suggested.

Finally, an excellent study of the influence of substituents on the rate of [1,5] Coome migration has recently been reported by Hoffmann and coworkers[195] for a series of 5-substituted pentamethoxycarbonyl cyclopentadienes. The relative rates (Me = 1.0) are MeS (0.28), Cl (0.33), C_6H_5 (1.9), $MeOOCCH_2$ (2.1), MeO (12.0), NC (15.5), C_6H_5NH (125), and Me_2N (260).

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