

Thermal [1,3] Carbon Sigmatropic Rearrangements of Vinylcyclobutanes

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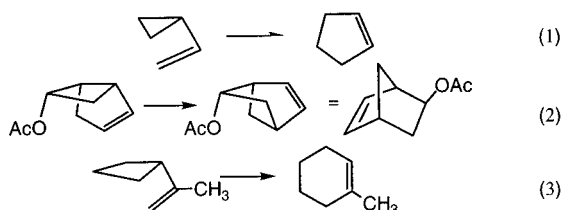
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ABSTRACT

Stereochemical, kinetic, and theory-based studies of the [1,3] carbon sigmatropic rearrangements of bicyclo[2.1.1]hex-2-enes, bicyclo[3.2.0]hept-2-enes, and monocyclic vinylcyclobutanes support the judgment that such reactions involve transient diradical structures traversing relatively flat potential energy surfaces.

Thermal [1,3] Carbon Shifts

The thermal isomerization of vinylcyclopropane to cyclopentene was reported in 1960 (eq 1).¹ A substituted bicyclo[3.2.0]hept-2-ene was isomerized to the related bicyclo[2.2.1]hept-2-ene in 1962 (eq 2).² Isopropenylcyclobutane was converted at 300 °C to 1-methylcyclohexene in 1963 (eq 3).³ These transformations exemplified a new type of chemical reaction, a thermally activated intramolecular [1,3] migration of carbon across an allylic π system.



A kinetic study of the vinylcyclopropane rearrangement⁴ found $E_a \approx 50$ kcal/mol, some 12 kcal/mol lower than E_a for thermal *cis*, *trans* equilibrations of deuterium- or alkyl-substituted cyclopropanes or cyclobutanes or for retro-[2 + 2] reactions of cyclobutanes. The difference was attributed to stabilization of the transition structure

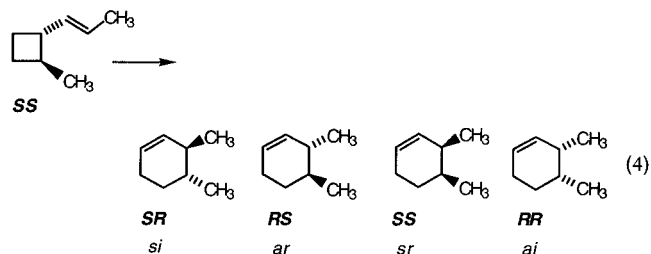
Phyllis A. Leber received a B.S. in Chemistry from Albright College in 1976 and a Ph.D. from the University of New Mexico in 1981. After a one-year visiting appointment at Pomona College, she joined the faculty at Franklin and Marshall College in 1982. Her research interests include not only probing the mechanistic variables affecting [1,3] sigmatropic rearrangements but also elucidating the biochemical role of plant cholinesterase.

John E. Baldwin was graduated from Dartmouth College with an A.B. degree in 1959; he received his Ph.D. from the California Institute of Technology with J. D. Roberts in 1963. He was a faculty member at the University of Illinois and the University of Oregon before moving to Syracuse University in 1984. His major research interests now relate to the kinetic, mechanistic, and stereochemical aspects of selected thermal reactions.

through allylic resonance. In an authoritative 1966 review Frey suggested that ring expansion reactions of vinylcyclopropanes and vinylcyclobutanes involve “allylically stabilized diradicals”.⁵ These reactions were viewed as stepwise, diradical-mediated processes.⁶

By 1965 when the seminal publications on the conservation of orbital symmetry appeared, [1,3] carbon shifts were already well-known and mechanistically characterized. The initial Woodward and Hoffmann considerations of “sigmatropic rearrangements” dealt primarily with hydrogen shifts. In 1969, in a summarizing recapitulation of orbital symmetry theory and representative applications, the [1,3] carbon shifts such as those shown in eqs 1–3 were classified as [1,3] sigmatropic carbon migrations. They were treated explicitly in light of the stereochemical specifications afforded by the Woodward–Hoffmann rules.⁷

Four distinct pathways for a [1,3] carbon shift are possible. The migrating carbon may migrate with inversion or retention of configuration, and the allylic π system may be utilized suprafacially or antarafacially. The stereochemistry of the migration, defined by the relative stereochemistry of starting material and product, may be suprafacial–inversion (*si*), suprafacial–retention (*sr*), antarafacial–retention (*ar*), or antarafacial–inversion (*ai*), as exemplified in the reactions shown in eq 4. The “allowed” pathways for thermal [1,3] carbon shifts are *si* and *ar*, while the *sr* and *ai* processes are “forbidden”.⁷

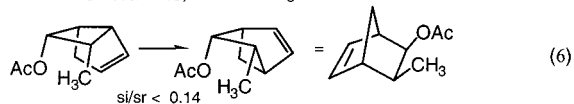
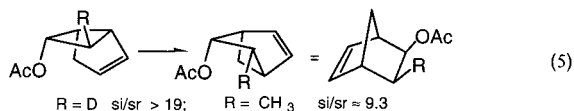


Investigators interested in [1,3] carbon shifts were not slow to recognize the significance of these theoretical insights. In 1967 6-*endo*-acetoxy-7-*exo-d*-bicyclo[3.2.0]hept-2-ene was found to isomerize with predominant inversion of configuration at the migrating carbon (eq 5, R = D),⁸ an outcome considered inconsistent with a stepwise mechanism. The observed *si* product was taken as evidence that the reaction took place in a concerted orbital-symmetry-controlled fashion. Studies on 6-*endo*-acetoxybicyclo[3.2.0]hept-2-enes reported in 1970 using C7-methyl-labeled analogues found that stereochemical preferences depended on the stereochemistry of the starting material.⁹ The 7-*exo*-methyl system preferred to isomerize with inversion (*si*/*sr* \geq 9.3; eq 5, R = CH₃), while the 7-*endo*-methyl substrate favored retention (*sr*/*si* \geq 7.2; *si*/*sr* < 0.14; eq 6). The dominant “forbidden” *sr* shift prompted consideration of theoretical constructs allowing

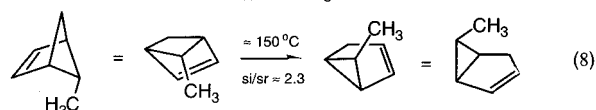
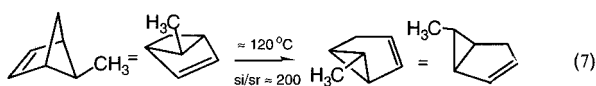
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reaction stereochemistry to be guided by subjacent orbital control.¹⁰



In 1969 the thermal isomerization of bicyclo[2.1.1]hex-2-ene to bicyclo[3.1.0]hex-2-ene was reported,¹¹ and Roth showed that 5-*exo*-methylbicyclo[2.1.1]hex-2-ene isomerized almost exclusively ($si/sr \approx 200$) to 6-*exo*-methylbicyclo[3.1.0]hex-2-ene (eq 7).¹² The 5-*endo*-methyl isomer, however, gave a mixture of both 6-*exo*- and 6-*endo*-methylbicyclo[3.1.0]hex-2-enes ($si/sr = 2.3$) as well as some 4-*endo*-methylbicyclo[3.1.0]hex-2-ene (eq 8). The *exo* isomer reacts with a high stereoselectivity agreeing perfectly with the dictates of orbital symmetry theory, but the *endo* isomer reacts through both *si* and *sr* paths to comparable extents.



Later that year Frey found that ΔS^\ddagger for the bicyclo[2.1.1]hex-2-ene-to-bicyclo[3.1.0]hex-2-ene isomerization is approximately zero,^{13,14} a result supportive of a concerted mechanism. He emphasized that “on the basis of orbital symmetry correlations such a process will only be allowed if inversion occurs at the migrating center.”

This work was covered in depth some 30 years ago in two important review articles.^{15,16} Experimental and theoretical work on thermal [1,3] carbon shifts since then have extended and in some details modified the mechanistic understandings of that time. This Account revisits the earlier work, with particular emphasis on the [1,3] carbon shifts shown by three sorts of vinylcyclobutanes: bicyclo[2.1.1]hex-2-enes; bicyclo[3.2.0]hept-2-enes; monocyclic vinylcyclobutanes. Yet other facile thermal processes often contribute significantly to the thermal chemistry such systems exhibit, and they must be considered.

Thermal Reactions of Vinylcyclobutanes

The only observable thermal process available to cyclobutane is thermal decomposition to yield two ethylene molecules. The reaction involves a tetramethylene diradical able to adopt numerous conformations along a broad flat potential energy surface (PES) before the second C–C bond is broken.^{17–19} Heating 1,2-*d*₂-cyclobutanes leads to *d*₀-, *d*₁-, and *d*₂-ethylenes and to *cis*, *trans* isomerizations.^{20–22} Stereospecifically labeled 1,2,3,4-*d*₄-cyclobutanes behave similarly, showing one- and two-centered

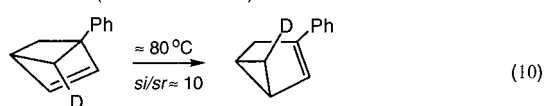
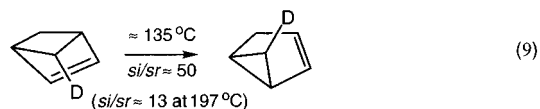
stereomutations as well as statistical fragmentations to *cis*- and *trans*-1,2-*d*₂-ethylene.²³ The evidence provided by these thermal stereomutation reactions for reversible bond fission is remarkable, for it suggests that a flexible tetramethylene diradical may re-form the cyclobutane ring despite the inherent ring strain and an unfavorable entropy.

Vinylcyclobutane rearranges to cyclohexene and also fragments to 1,3-butadiene and ethylene.^{24,25} Introduction of either a *cis*-2-alkyl or *cis*-2-vinyl substituent may lead to competing retro-ene reactions or Cope rearrangements. The *cis* isomer of 2-ethyl-1-vinylcyclobutane, for example, forms (2*Z*,6*E*)-octadiene as a major product²⁶ just as the *cis* isomer of 2-methyl-1-vinylcyclopropane gives 1,4(*Z*)-hexadiene.²⁷ The Cope rearrangement, a [3,3] sigmatropic process, is extremely facile in *cis*-divinylcyclobutanes: *cis*-divinylcyclobutane is converted to 1,5-cyclooctadiene much as *cis*-divinylcyclopropane is isomerized to 1,4-cycloheptadiene.

Detailed studies of [1,3] carbon shifts shown by substituted bicyclo[2.1.1]hex-2-enes, bicyclo[3.2.0]hept-2-enes, and vinylcyclobutanes, in combination with parallel work on vinylcyclopropanes, have provided complementary insights. Recent theoretical treatments of this reaction have also served to clarify the mechanistic variables that affect [1,3] carbon shifts.^{28–31}

Isomerizations of Bicyclo[2.1.1]hex-2-enes to Bicyclo[3.1.0]hex-2-enes

In 1984 Carpenter and Newman-Evans reported that 5-*endo-d*-bicyclo[2.1.1]hex-2-ene undergoes rearrangement to 6-*d*-bicyclo[3.1.0]hex-2-ene with a high degree of stereoselectivity at 135 °C ($si/sr \approx 50$; eq 9).³² At 197 °C, migration with retention became more significant, and the si/sr ratio fell to 13. This temperature-dependent reaction stereochemistry was attributed to the existence of two parallel competing reaction pathways. The rearrangement of 1-phenyl-5-*endo-d*-bicyclo[2.1.1]hex-2-ene gave 3-phenyl-6-*d*-bicyclo[3.1.0]hex-2-enes with $si/sr \approx 10$ (eq 10). The thermal chemistry of the 2-phenyl system was more complex, but it was possible to deduce that the [1,3] shift leading to 1-phenyl-6-*d*-bicyclo[3.1.0]hex-2-enes took place with $si/sr \approx 7$.



The 1- and 2-phenyl-substituted systems showed no observable temperature dependence in reaction stereoselectivity over a temperature range greater than 60 °C. A diradical process was proposed: “the primary evidence in favor of a nonpericyclic mechanism is *experimental* (the lack of temperature dependence of the product ratio).”²⁸

Despite the indirect evidence for diradical-mediated thermal rearrangements of 1- and 2-phenylbicyclo[2.1.1]hex-2-ene, the strong preferences for inversion at the CHD migrating group ($si/sr \approx 10$ for 1-phenyl and ≈ 7 for 2-phenyl reactants) were difficult to rationalize using standard least motion, steric, or electronic arguments. The possibility that dynamic control of “not-obviously-concerted” [1,3] carbon shifts could lead to a high degree of stereoselectivity, especially in relatively rigid bicyclic molecules, was raised.³³

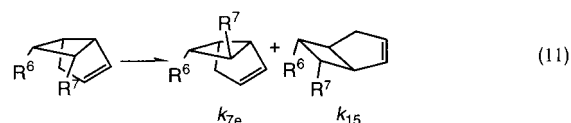
Isomerizations of Bicyclo[3.2.0]hept-2-enes to Bicyclo[2.2.1]hept-2-enes

The thermal isomerization of bicyclo[3.2.0]hept-2-ene to norbornene³⁴ was studied stereochemically in 1988 by two groups using analogues stereoselectively labeled with deuterium at C6 and C7.^{35,36} These reactants were converted to 5,6-*d*₂-norbornenes, which in turn cleaved to 1,2-*d*₂-ethylenes and cyclopentadiene. Migration with inversion was the dominant process, but there was a substantial retention component. Baldwin and Belfield observed (76 ± 4)% inversion ($si/sr \approx 3$) at 276 °C whereas Klärner and co-workers reported 89% inversion ($si/sr \approx 8$) at 312 °C. Klärner attributed the lack of complete inversion to a competition between a diradical pathway and a concerted process.

On the basis of extensive direct dynamic calculations on both the parent bicyclo[3.2.0]hept-2-ene system and the 7-*exo*-methyl and 7-*endo*-methyl analogues, Carpenter concluded that the stereoselectivity observed in [1,3] carbon migrations is dynamic in origin and is not dependent on conservation of orbital symmetry factors.²⁹ The dynamic model yields a local minimum corresponding to a diradical intermediate for the bicyclo[3.2.0]hept-2-ene-to-norbornene conversion. Yet conservation of angular momentum predicts predominant inversion of configuration in the direct trajectories between reactant and product. The simulations showed a direct retention pathway as well as a direct inversion pathway for the 7-*exo*-methyl analogue and predicted that the si/sr ratio would be lower than seen in the deuterium-labeled parent system. He also speculated that the 7-*exo*-methyl compound would show higher si/sr ratios at higher temperatures. That expectation assumed a competition between an extended statistical diradical pathway and a nonstatistical, direct, concerted or diradical pathway.

A recent study of the [1,3] carbon shifts from 7-*exo*-methylbicyclo[3.2.0]hept-2-ene to 5-methylbicyclo[2.2.1]hept-2-enes (5-methylnorbornenes) has tested these predictions.³⁷ The 7-*exo*-methyl epimer exhibited predominant inversion, $si/sr \approx 7$, a ratio somewhat higher than or comparable to the two experimental determinations of this ratio for the parent hydrocarbon, $si/sr \approx 3$ and $si/sr \approx 8$, made at different temperatures. The si/sr ratio was invariant from 250 to 300 °C, a fact considered consistent with a diradical intermediate.³⁸ The 7-*endo*-methyl isomer isomerized exclusively with retention at the migrating carbon.³⁷

The observation of a thermal isomerization from the endo to the exo isomer of 7-methylbicyclo[3.2.0]hept-2-ene at a rate competitive with its [1,3] shift prompted two further studies of appropriately labeled racemic bicyclo[3.2.0]hept-2-enes.^{39,40} Either a C1–C5 two-center epimerization (skeletal inversion) or a one-center epimerization at C7 might account for the observed process.³⁹ Kinetic studies of thermal reactions of 6-*endo-d*- and 7-*endo-d*-bicyclo[3.2.0]hept-2-ene provided reliable rate constants for both a one-center epimerization (k_{7e}) and for skeletal inversion (k_{15}) reactions.⁴⁰ There is a fair agreement between the rate constant for conversion of 7-*endo*-methyl to 7-*exo*-methylbicyclo[3.2.0]hept-2-ene, $6.3 \times 10^{-7} \text{ s}^{-1}$, and $k_{7e} = 5 \times 10^{-7} \text{ s}^{-1}$ for the labeled parent hydrocarbon. More tellingly, k_{7e} in a deuterium-labeled bicyclo[3.2.0]hept-2-ene, reflecting a reaction contingent upon C1–C7 cleavage, is significantly larger than k_{15} , a process implicating a diradical intermediate from C1–C5 homolysis (eq 11).



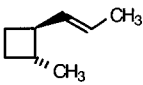
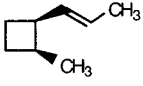
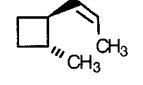
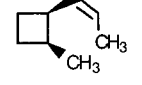
The endo-to-exo epimerization for the 7-*endo*-methyl system plays an appreciable role in the chemistry observed. The sum of the rate constants for epimerization and fragmentation is almost 50% of the overall rate of decay of the starting material, which differs only modestly from the decay rate observed for the exo epimer.³⁷ This evidence clearly indicates that a 1-(2-cyclopentene-4-yl)prop-2-yl diradical intermediate is accessible from the 7-*endo*-methyl system.

Isomerizations of Monocyclic Vinylcyclobutanes to Cyclohexenes

An important early study based on racemic *cis* and *trans* isomers of 1-propenyl-2-methylcyclobutanes provided rate constants for the two “allowed” pathways ($si + ar$) and the two “forbidden” routes ($sr + ai$).²⁶ The $(si + ar)/(sr + ai)$ ratio depended on the stereochemistry of the propenyl group and on the disposition of the 2-methyl substituent (Table 1). In all cases the more stable *trans*-1,2-dimethylcyclohexene was the major product.

A complete definition of reaction stereochemistry for [1,3] carbon shifts shown by monocyclic vinylcyclobutanes may be disentangled if suitable labels are present and if proper allowances for all other relevant reactions taking place simultaneously are made. Just one early study satisfied these criteria, work by Berson and Dervan^{41,42} on nonracemic *trans*-1,2-dipropenylcyclobutanes. At 146.5 °C the (1*R*,2*R*) stereoisomer of 1,2-bis(*E*-propenyl)cyclobutane gave a mixture of the symmetry-“allowed” (56%) and -“forbidden” (44%) pathways, with a strong preference for the suprafacial over the antarafacial modes of π -system participation (Table 2). The (1*R*,2*R*) enantiomer of the diastereomer having one *E*- and one *Z*-propenyl substituent gave mostly 3-methyl-4-((*Z*)-propenyl)cyclohexenes. The overall preference for “allowed” versus “forbidden”

Table 1. Stereochemistry of [1,3] Shifts for Racemic 1-Propenyl-2-methylcyclobutanes to 3,4-Dimethylcyclohexenes at 286 °C²⁶

reactant	products (%)		trans/ cis	(si+ar)/ (sr+ai)
	trans	cis		
	65	35	1.9	1.9
	68	32	2.0	0.5
	87	13	6.7	0.15
	90	10	9.0	9.0

products ($si > sr$ and $ar > ai$) was small, while enantiomeric products were formed in more unequal proportions, for suprafacial outcomes were greatly favored over the antarafacial alternatives.

The early work on racemic cis and trans isomers of 1-propenyl-2-methylcyclobutanes²⁶ has recently been extended through studies of the optically active systems, monitoring the time dependence of chiral vinylcyclobutanes and chiral reaction products⁴³ using capillary GC employing chiral stationary phases.⁴⁴ The thermal reactions of (1*S*,2*S*)-*trans*-1-((*E*)-propenyl)-2-methylcyclobutane at 275 °C (Table 2) show a stereochemical outcome very similar to the pattern reported for the [1,3] carbon shifts shown by a chiral *trans*-1,2-bis((*E*)-propenyl)cyclobutane: $si > sr > ar \approx ai$. The (*E*)-propenyl function that does not participate in the [1,3] shift contributes stereochemically much like a methyl group.

Both *trans*-1,2-bis((*E*)-propenyl)- and 1-((*E*)-propenyl)-2-methyl-substituted cyclobutanes give direct [1,3] rearrangements through four stereochemically distinct paths, two "allowed" and two "forbidden," as well as other thermal reactions such as fragmentations and epimerizations thought to involve diradicals. The *trans*-1,2-dipropenylcyclobutanes exhibit less fragmentation and epimerization and form higher yields of [1,3] shift products. This difference can be attributed to the different temperatures required for reactions: 146.5 °C for the dipropenyl reactants versus 275 °C for *trans*-1-propenyl-2-methylcyclobutanes. Yet even for *trans*-1,2-dipropenylcyclobutanes, fragmentation and epimerization processes represent almost 40% (by relative rate constants) of all the thermal reactions observed.^{41,42} This figure rises to over 70% for *trans*-1-propenyl-2-methylcyclobutanes.⁴³ It seems likely that diradical structures are involved in all of the various pathways, yet the stereochemical distributions of [1,3] shift products are not statistical. Any transient, conformationally flexible diradicals formed preserve the cisoid or transoid stereochemistry of the allylic unit, and relatively short diradical lifetimes could be sufficient to rule out complete conformational equilibrations of other sorts.

Moreover, there could be rotational biases modulated by substituents.

The [1,3] shifts from (1*S*,2*R*)-*cis*-1-((*E*)-propenyl)-2-methylcyclobutane at 275 °C gave a markedly different stereochemical distribution: $sr > ai \approx si > ar$.⁴³ This same pattern has been observed when a cyano group rather than a methyl is on the migrating carbon (Table 2).⁴⁵ In particular, the "allowed" ($si + ar$) to "forbidden" ($sr + ai$) ratios are clustered around 2 for the trans isomers and around 0.4 for the cis isomers. The dominant product in each case is the more stable *trans*-3,4-disubstituted cycloalkene. Remarkably similar product distributions across the four stereochemical pathways are seen with *trans*-1-((*E*)-propenyl)-2-methylcyclopropane⁴⁶ and the corresponding cis and trans isomers of 1-((*E*)-propenyl)-2-cyanocyclopropane.⁴⁷

Two important observations can be drawn from the data in Table 2 for monocyclic vinylcyclobutanes:

The $(sr + si)/(ar + ai)$ ratio is always greater than 1; as C1–C2 of the vinylcyclobutane is cleaved the allylic moiety is predisposed to react suprafacially. The $(sr + si)/(ar + ai)$ ratio is sensitive to the size of the migrating group. When there is a less sterically demanding substituent such as cyano on the migrating carbon, the $(sr + si)/(ar + ai)$ ratio is lower.

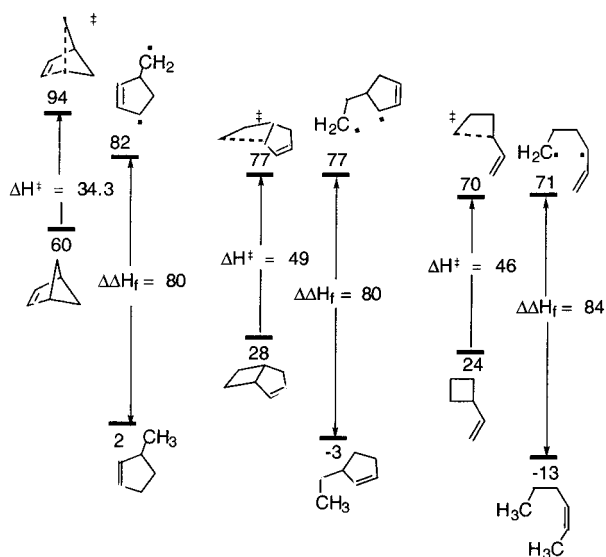
In [1,3] carbon shifts from monocyclic *trans*-2-substituted vinylcyclobutanes the si/sr ratio is always greater than 1. This ratio is lower for the monocyclic compounds than for the bicyclic systems considered above. It seems quite sensitive to the relative flexibility of the π -system. The *cis*-2-substituted vinylcyclobutanes have si/sr ratios much smaller than 1; both cis and trans diastereomers favor *trans*-3,4-disubstituted cyclohexene products.

Cross-System Comparisons

Considerations of ΔH_f data and simple thermochemical additivity relationships permit one to compare the energetics of the three systems just examined. In all three cases the [1,3] shift products are substantially favored thermodynamically over the reactants. Bicyclo[2.1.1]hex-2-ene is the most reactive, though the isomerization to bicyclo[3.1.0]hexene is not the most exothermic. The markedly high ΔH_f value of the [2.1.1] system, some 60 kcal/mol, almost certainly accounts for its greater reactivity. Following a simple additivity approach,²⁵ one can estimate ΔH_f for a presumed diradical intermediate; this energy may be compared with ΔH_f for a reactant plus ΔH^\ddagger for the [1,3] shift process. If the two values are the same or nearly the same, the simple diradical model approximates the real transition structure. For isomerizations of [3.2.0] and vinylcyclobutane structures good agreements between these values are found. For the isomerization of bicyclo[2.1.1]hex-2-ene, however, ΔH_f (exp) for the transition structure is more than 10 kcal/mol higher in energy than ΔH_f (calc) for the related conformationally relaxed diradical; an early transition state for the isomerization, one that still retains more than 10 kcal/mol of strain energy, is implied (Figure 1).

Table 2. Stereochemistry of [1,3] Shifts in 1-(*E*)-Propenyl-2-(substituted)-cyclobutanes to *cis*- and *trans*-3-Methyl-4-(substituted)-cyclohexenes

reactant	temp (°C)	<i>si</i> (%)	<i>ar</i> (%)	<i>sr</i> (%)	<i>ai</i> (%)	<i>si</i> / <i>sr</i>	<i>s/a</i>	(<i>si</i> + <i>ar</i>)/(<i>sr</i> + <i>ai</i>)	ref.
	147	49	3	48	0	1.0	32	1.1	42
	147	50	6	41	3	1.2	10	1.3	42
	275	58	5	33	4	1.8	10	1.7	43
	198	48	20	27	6	1.8	3	2.1	45
	275	18	11	51	20	0.35	2	0.4	43
	198	13	5	66	16	0.20	4	0.2	45

**FIGURE 1.** Thermochemical comparisons contrasting estimated energies of transition structures, from ΔH_f^\ddagger of reactants and ΔH_f^\ddagger values from kinetic data, with $\Delta\Delta H_f^\ddagger$ gaps between alkenes and related diradicals. All values (from cited references and standard reference works) are in kcal/mol.

Bicyclo[3.2.0]hept-2-ene and vinylcyclobutane are similar with respect to ΔH_f^\ddagger and ΔH_f^\ddagger values. Both systems have been studied kinetically at 275 °C, facilitating direct comparisons of reactivity. The [3.2.0] hydrocarbon isomerizes to norbornene, which is thermally unstable at the temperatures required to effect the [1,3] shift, whereas vinylcyclobutane gives cyclohexene, a stable molecule under the reaction conditions. Both systems fragment and suffer epimerizations as well as show [1,3] carbon shifts at competitive rates, while bicyclo[2.1.1]hex-2-enes exhibit only [1,3] shifts at the relatively low temperatures (120–180 °C) they require for thermal isomerizations.

Complete stereochemical data for all three systems substituted with a methyl group on the migrating carbon are available (Table 3). The *si*/*sr* ratios for 5-*exo*-methyl [2.1.1], 7-*exo*-methyl [3.2.0], and *trans*-1-(*E*)-propenyl-2-methylcyclobutane reactants decrease in the order $\approx 200/7/2$; the more rigid the system the higher the *si*/*sr* preference. Conformational flexibility favors less stereochemical selectivity.

The experimental *si*/*sr* ratios for 5-*endo*-methyl, 7-*endo*-methyl, and *cis*-2-methyl substituted versions of the three systems provide another telling correlation (Table 3). They reveal an unusually strong preference for migration with retention in 7-*endo*-methylbicyclo[3.2.0]hept-2-ene.

There may be a preferred rotation about C7–C6 in the bicyclo[3.2.0]hept-2-ene skeleton as C1–C7 is cleaved.^{29–31,48} If unmodulated through substitution it would lead to inward rotation of the 7-*endo*-methyl group during bond cleavage, a process that could be “blocked”, favoring by default the alternative rotation about C7–C6. This would place C7 under the five-membered ring in position to either re-form the [3.2.0] framework with a 7-*exo*-methyl group or produce the [1,3] shift product with net retention. The epimerization and [1,3] shift-with-retention products are formed at nearly equal rates. Epimerization and [1,3] migration may be linked mechanistically in 7-*endo*-methylbicyclo[3.2.0]hept-2-ene through a common diradical intermediate. The epimerization process cannot proceed in a concerted fashion.

The reactivity of 7,7-dimethylbicyclo[3.2.0]hept-2-ene is not significantly greater than the parent hydrocarbon. It decays through all reaction channels at a rate comparable to total isomerization and fragmentation rates observed for unsubstituted and mono-C7-methyl-substituted [3.2.0] reactants, but steric effects inhibit [1,3] migration: the [1,3] shift product is not observed.⁴⁹

Table 3. Stereochemistry of [1,3] Shifts in Epimeric Methyl-Substituted Bicyclo[2.1.1]hex-2-enes, Bicyclo[3.2.0]hept-2-enes, and Vinylcyclobutanes

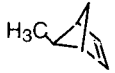
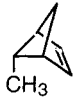
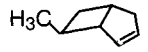

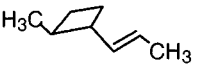
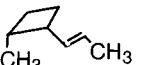

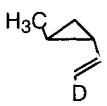
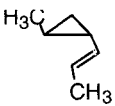
reactant	<i>si</i> (%)	<i>sr</i> (%)	<i>si</i> / <i>sr</i>	reactant	<i>si</i> (%)	<i>sr</i> (%)	<i>si</i> / <i>sr</i>	ref.
	99.5	0.5	200		69	31	2.2	10
	87	13	6.8		1	99	0.01	37
	64	36	1.8		26	74	0.35	43

Table 4. Methyl Substituent Effects on Stereochemistry of [1,3] Shifts in Vinylcyclopropanes

reactant	temp (°C)	<i>si</i> (%)	<i>ar</i> (%)	<i>sr</i> (%)	<i>ai</i> (%)	<i>si</i> / <i>sr</i>	<i>s/a</i>	(<i>si</i> + <i>ar</i>)/(<i>sr</i> + <i>ai</i>)	ref.
	300	40	13	23	24	1.7	2	1.1	55
	285	55	15	18	13	3.0	3	2.3	57
	297	65	8	22	5	3.0	7	2.7	46

Although the [1,3] migration still persists in 1-vinyl-2,2-dimethylcyclobutane, the relative importance of the [1,3] shift is much diminished.⁵⁰ The predominance of fragmentation in both [3.2.0] and vinylcyclobutane reactants substituted with two methyl groups on the potentially migrating carbon, along with far lesser amounts of retroene products, is consistent with the assumption that these thermal reactions are mediated by diradical structures.

Substituent Effects

The most common stereochemistry-defining substituent examined in [1,3] carbon shift reactions is methyl, which appears to exert a significant steric effect. This strong effect is evident in the stereochemical outcomes observed for the [1,3] shifts summarized in Table 3. When the methyl substituent on the migrating carbon in [2.1.1] or [3.2.0] reactants is exo, migration with inversion is clearly the dominant pathway, but the relative contribution of the *si* path decreases as the flexibility of the π -system increases. The decrease in the *si*/*sr* ratio is still more pronounced for *trans*-1-(*E*)-propenyl-2-methylcyclobutane. The trends for the epimeric endo or cis methyl-substituted reactants are more irregular, but the methyl enhances the *sr* contribution in all cases.

Data revealing that methyl substitution is not stereochemically innocent are available for vinylcyclopropanes (Table 4). Substituting a *trans* methyl for a deuterium at the migrating carbon increases the *si* pathway at the expense of *sr* and *ai*. An additional enhancement of the

si contribution occurs with corresponding decreases in both antarafacial components when deuterium is replaced by a methyl at the migration terminus. The close similarity between the overall reaction stereochemistry of the [1,3] shift for *trans*-1-(*E*)-propenyl-2-methylcyclobutane⁴³ and *trans*-1-(*E*)-propenyl-2-methylcyclopropane⁴⁶ makes this comparison appropriate.

Theoretical Work on [1,3] Carbon Shifts

A theoretical study of [1,3] shifts for bicyclo[3.2.0]hept-2-ene concluded that a temperature-independent *si*/*sr* ratio is consistent with a diradical mechanism.³⁸ More recently, Houk has applied CASSCF computational methods to the bicyclo[3.2.0]hept-2-ene-to-norbornene interconversion.⁴⁸ The results implicate diradical structures on a PES having a broad plateau. The preferred *si* pathway is approximately 1 kcal/mol lower in energy than the *sr* pathway. At 275 °C this difference in activation energy translates to a predicted *si*/*sr* ratio of 2.5, a value very close to that found experimentally,³⁵ *si*/*sr* \approx 3.

Shock tube kinetic experiments on 1-vinyl-*cis*-2,3-*d*₂-cyclobutane⁵¹ demonstrated that fragmentation to butadiene and ethylene results in complete loss of stereochemical integrity in the mixture of 1,2-*d*₂-ethylenes generated. The 1-hepten-3,7-diyl diradical is presumed to be an intermediate in this retro-[2 + 2] process. The same intermediate may well be involved in the vinylcyclobutane-to-cyclohexene rearrangement.

The only direct modeling studies of the [1,3] carbon shift in a monocyclic system have been conducted on the vinylcyclopropane-to-cyclopentene rearrangement. Both Davidson and Gajewski⁵² and Houk and co-workers⁵³ found through CASSCF calculations for this rearrangement that cleaving C1–C2 led to a diradical on a broad flat PES, one having no local energy minimum. All four stereochemically possible paths were accessible through conformational variations within a 2–3 kcal/mol range.

Direct dynamics computations by Houk and Doubleday⁵⁴ mirrored the experimental data for the four stereochemical contributions to the vinylcyclopropane-to-cyclopentene rearrangement.⁵⁵ The fixed-energy trajectories displayed mode selectivities, as noted for trimethylene. Doubleday, in a more detailed direct dynamics study, showed that the experimental stereochemical data and the computational results are consistent with a mechanism involving four competing direct reactions.⁵⁶ Short-lived trajectories afford a measure of stereoselectivity thanks to nonstatistical dynamics. As a result, *si* emerges as the modestly dominant path at lower temperatures. Similar theoretical work should be applicable to the isomerizations of vinylcyclobutane but would of course be substantially more complicated, for diradical structures would have more conformational options within a narrow band of energies.

Conclusions

The [1,3] carbon shifts observed for a variety of systems show a strong correlation between the *si/sr* ratio and the relative flexibility of the π system. In [2.1.1] reactants the *si/sr* ratio is quite large (50–200), depending on the nature and stereochemical disposition of substituents and in some cases on the temperature. The *si/sr* ratio assumes a more modest range (3–10) in [3.2.0] bicycloheptenes, where the π bond is less rigidly constrained. Finally, in monocyclic vinylcyclobutanes the *si/sr* ratio falls to less than 2.

The fact that the *si/sr* ratio increases on going from the parent to the corresponding 5-*exo*- or 7-*exo*-methyl substituted systems is consistent with an element of product stability control. For [2.1.1] reactants the *si/sr* ratio increases by a factor of at least 4. The greater thermodynamic stability of 6-*exo*-methylbicyclo[3.1.0]hex-2-ene compared to the endo epimer parallels this greater *si* bias. The *si/sr* ratio at 275 °C doubles in [3.2.0] reactants on replacing a deuterium at C7 with a 7-*exo*-methyl. This differential can be readily accommodated by the greater thermodynamic stability of 5-*exo*-methylbornene relative to the endo product.

For monocyclic *trans*-2-substituted vinylcyclobutanes the size of the substituent on the migrating carbon also plays a role in the stereochemical distribution, affecting particularly the *s/a* ratio. When there is a methyl or propenyl substituent on the migrating carbon, the *s/a* value is at least 10. It falls to 3 when a cyano substituent resides on the migrating carbon (Table 2).

Thermal processes kinetically competitive with [1,3] carbon shifts such as fragmentations and stereomutations are almost certainly mediated by more or less conformationally dextrous diradical structures. A consistent mechanistic framework would dictate that [1,3] shifts also involve intermediate diradicals.

The observed stereochemistry of the [1,3] shift in [2.1.1] and [3.2.0] reactants when the migrating carbon is labeled with methyl can be rationalized by assuming diradical intermediates constrained by relatively rigid molecular frameworks. Carpenter²⁹ predicted a substantial barrier to torsion in [2.1.1] reactants until after bond cleavage has occurred. If the resultant diradical just formed from 5-*exo*-methylbicyclo[2.1.1]hex-2-ene is a conformationally puckered species generated in an early transition state, steric interactions between that methyl on the migrating carbon and the *exo* H on C6 could strongly promote outward rotation to yield 6-*exo*-methylbicyclo[3.1.0]hex-2-ene directly (*si/sr* \approx 200), without relaxation of the diradical transition structure. In 5-*endo*-methylbicyclo[2.1.1]hex-2-ene the outward rotation may still be modestly favored due to nonbonded repulsion of the hydrogen on the migrating carbon and the *exo* H at C6. As a result inversion may still be favored over retention, but much less significantly so (*si/sr* = 2.2).

Both Carpenter³⁸ and Houk⁴⁸ have predicted that the preferred rotation about the C6–C7 bond in [3.2.0] systems rotates the *exo* C7-substituent away from the H at C1. This preferred rotation moves the migrating carbon C7 under the five-membered ring. In the case of the 7-*exo*-methyl reactant, this rotational bias favors [1,3] migration with inversion. When the C7-methyl is *endo*, however, the otherwise preferred rotation would result in a steric obstruction. The alternative rotation is now advantaged by default; the diradical formed can proceed to give either net epimerization or a [1,3] shift with retention.

Experimental and theoretical work concerned with [1,3] sigmatropic carbon shifts over the past 25 years has provided a wealth of information on this “not obviously concerted” reaction. It now appears to involve cleavage of a C–C bond to form a diradical structure or family of conformationally related structures on a relatively flat PES. Such diradicals may be extremely short-lived or in some circumstances persist a while, giving rise to product distributions indicative of more or less stereochemical promiscuity. We look forward to an experimental definition of the stereochemical characteristics of the parent vinylcyclobutane-to-cyclohexene isomerization, accessible through kinetic studies of suitable isotopically labeled analogues, and to theory-based clarifications of reaction dynamics for this prototypical conversion. Recent progress gained through studies of thermal [1,3] carbon shifts shown by various bicyclo[2.1.1]hex-2-enes, bicyclo[3.2.0]hept-2-enes, and substituted vinylcyclobutanes and of vinylcyclopropane-to-cyclopentene isomerizations bodes well for those endeavors.

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