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Thermal isomerizations of *cis*,*anti*,*cis*-tricyclo[6.4.0.0^{2,7}]dodec-3-ene to *trans*- and *cis*,*endo*-tricyclo[6.2.2.0^{2,7}]dodec-9-ene: diradical conformations and stereochemical outcomes in [1,3] carbon shifts

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Abstract—The gas-phase thermal isomerizations at 315 °C of *cis*,*anti*,*cis*-tricyclo[6.4.0.0^{2,7}]dodec-3-ene to *trans*-tricyclo[6.2.2.0^{2,7}]dodec-9-ene and to *cis*,*endo*-tricyclo[6.2.2.0^{2,7}]dodec-9-ene favor the former, the more geometrically strained product, by a ratio of 2.4:1. These products correspond to suprafacial inversion (*si*) and suprafacial retention (*sr*) stereochemical outcomes. The reaction stereochemistry shown by the 11-carbon homolog, *cis*,*anti*,*cis*-tricyclo[6.3.0.0^{2,7}]undec-3-ene, is strikingly different: the [1,3] carbon shift takes place to give only the 'forbidden' *sr* product. Two related bicyclic vinylcyclobutanes, 8-deuterio- and 8-*exo*-methylbicyclo[4.2.0]oct-2-enes, evidence contrasting reaction stereochemical predilections in [1,3] shifts, but the 12-carbon tricyclic system and the 8-*exo*-methyl bicyclic analog isomerize with the same *si*:*sr* ratio! These observations prompt fresh considerations of structural influences on conformational preferences available to the alkyl, allyl diradical reactive intermediates involved.

1. Introduction

Shortly after two groups reported in 1960 that vinylcyclopropane could be isomerized thermally to cyclopentene,[1] a vinylcyclobutane-to-cyclohexene rearrangement was encountered. In 1962 Berson and Patton exemplified this type of rearrangement as they communicated that 6-*endo*-acetoxybicyclo[3.2.0]hept-2-ene at 300 °C in decalin gave 5-*exo*-acetoxybicyclo[2.2.1]hept-2-ene in a 'largely if not completely stereospecific' manner.[2] In 1963 Ellis and Frey found a similar isomerization starting with isopropenylcyclobutane, a close relative of the unsubstituted system, vinylcyclobutane.[3]

In Woodward and Hoffmann's 1970 publication of *The Conservation of Orbital Symmetry*[4] such vinylcyclopropane and vinylcyclobutane isomerizations were formally classified as [1,3] carbon sigmatropic rearrangements. Selection rules for [1,3] carbon shifts were enunciated: *si* (suprafacial inversion) and *ar* (antarafacial retention) products were privileged as 'symmetry allowed' for monocyclic precursors, while products corresponding to *sr* (suprafacial retention) and *ai* (antarafacial inversion) paths were deemed to be 'forbidden'. For bicyclic vinylcyclobutanes geometrically unable to form *ar* or *ai* products, there would be only two possible paths, the symmetry-allowed *si* option and the symmetry-forbidden *sr* alternative.

The oft-neglected caveat to the dictate "Violations [to the Woodward–Hoffmann rules]—there are none!"[4] is that non-concerted reactions are exempt from the stereochemical limitations decreed by orbital symmetry theory. Thus the critical stereochemical and mechanistic issues raised by [1,3] carbon sigmatropic shifts hinge on the question of concertness. The energetics for these rearrangements are consistent with reactions involving a stepwise non-concerted mechanism and the intervention of diradical intermediates,[5] and yet measures of stereoselectivity have often been used as adequate surrogate probes for concertness. The sensible disclaimer that high stereoselectivity is a necessary but insufficient criterion for concert[6] has largely been ignored. For bicyclic vinylcyclobutanes, such as substituted bicyclo[3.2.0]hept-2-enes or bicyclo[2.1.1]hex-2-enes, the ratio of the rate of formation of the symmetry-allowed *si* product to that of the symmetry-forbidden *sr* product (the *si*/*sr* value) has long been taken as the default standard for assessing the degree of concert in [1,3] carbon shifts.

Keywords: [1,3] Carbon shifts; Alkyl, allyl diradical reactive intermediates.
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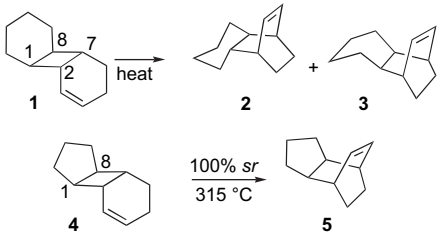
Many substituted bicyclo[3.2.0]hept-2-enes have been prepared and studied in attempts to elucidate the mechanism of the thermal [1,3] carbon sigmatropic shifts they display and to uncover reaction stereochemistry.[7] The thermal chemistry seen includes both *si* and *sr* [1,3] shift rearrangements, epimerizations at the migrating carbon, and fragmentations to cyclopentadienes and olefins. The parent hydrocarbon also gives a linear isomeric triene and undergoes a skeletal inversion, presumably through a diradical formed by cleavage of the C1−C5 bond. While the mixed stereochemical results found for thermal reactions of bicyclo[3.2.0]hept-2-enes have met with various interpretations,[7] recent experimental and theoretical investigations have suggested that these reactions are almost certainly mediated by short-lived, non-statistical diradical intermediates on a common shallow plateau on the potential energy surface.[8,9]

Few bicyclo[4.2.0]oct-2-ene hydrocarbons have been given comparable kinetic and stereochemical scrutiny.[10] The present work sought to learn from the thermal behavior of a tricyclic vinylcyclobutane, *cis*,*anti*,*cis*-tricyclo[6.4.0.0^{2,7}]-dodec-3-ene (**1**), which could conceivably isomerize to give two [1,3] carbon shift products, the *si* product **2** and the *sr* product **3** (Scheme 1). *cis*,*anti*,*cis*-Tricyclo[6.3.0.0^{2,7}]-undec-3-ene (**4**), the only similar tricyclic for which a thermal isomerization through a [1,3] carbon shift has been documented, isomerizes to give only one [1,3] shift outcome, the orbital symmetry theory 'forbidden' *sr* product **5** (Scheme 1).[11] The 12-carbon tricyclic **1** may be viewed as a bicyclo[4.2.0]oct-2-ene linked in a *cis*,*exo* fashion by a tetramethylene tether. Replacing the $-CH_2CH_2CH_2-$ moiety in **4** with this $-CH_2CH_2CH_2CH_2-$ tether was expected to allow the system more conformational flexibility at the diradical stage, but the manner in which that opportunity might be exploited could not be predicted.

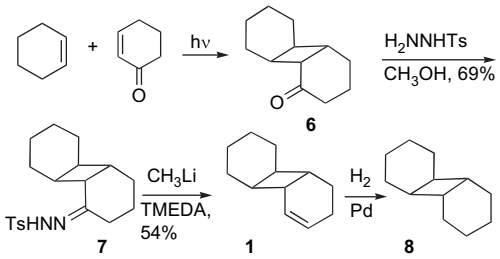


Scheme 1. Isomerizations through [1,3] carbon shifts for two tricyclic vinylcyclobutanes.

There is some indirect evidence in the literature to suggest that a *trans*-fused tricyclo[6.2.2.0^{2,7}]dodec-9-ene such as **2** would not be impossibly strained.[12] Moreover, energy minimization with Chem 3D Pro™ predicts that the **1**→**2** conversion would be exothermic by 2.9 kcal/mol and that the **1**→**3** isomerization would be exothermic by 9.4 kcal/mol; thus **2** would be 6.5 kcal/mol more strained than **3**. Accordingly **1**, in contrast to its 11-carbon homolog **4**, might enjoy a greater range of dynamic rotational possibilities as the C1−C2 bond is cleaved and could well form the less stable isomer **2**, the *si* product, through a kinetically competitive exothermic reaction. If so, it would permit an assessment of *si*/*sr* reaction stereochemistry in this particular and unusually restricted system.

2. Results and discussion

The complete tricyclic carbon skeleton of **1** was readily accessible through photochemical cycloaddition of cyclohexene and 2-cyclohexenone using a 450-W medium-pressure mercury lamp (Scheme 2).[13] The reaction was allowed to proceed to 80% conversion. Characterization of the ketone cycloadduct **6**, however, was complicated by the complexity of the product mixture. Attempted purification by column chromatography (elution from silica gel with 90:10 pentane/ether) gave **6** in sufficient purity (in a ca. 1:1:8 GC ratio of two minor earlier eluting isomers of ketone **6** as well as the desired product) to obtain an acceptable ^{13}C NMR spectrum: δ 214.9 (C=O), 48.0 (CH), 40.3 (CH_2), 38.6 (CH), 35.6 (CH), 35.2 (CH), 27.2 (CH_2), 26.6 (CH_2), 25.9 (CH_2), 22.6 (CH_2), 22.5 (CH_2), 22.3 (CH_2).

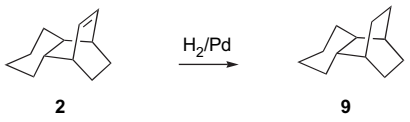


Scheme 2. Synthesis of *cis*,*anti*,*cis*-tricyclo[6.4.0.0^{2,7}]dodec-3-ene (**1**).

The tosylhydrazone derivative of **6** (**7**) was obtained as a white crystalline solid, mp 155–156 °C (dec). The Shapiro modification[14] of the Bamford–Stevens reaction gave compound **1**. Its structure was supported by ^{13}C NMR DEPT spectra: δ 130.3 (=CH), 126.4 (=CH), 38.9 (CH), 36.7 (CH), 33.9 (CH), 32.1 (CH), 28.9 (CH_2), 26.4 (CH_2), 23.4 (CH_2), 22.6 (CH_2), 22.4 (CH_2), 21.7 (CH_2). Definitive structure proof of **1** relied on its conversion to *cis*,*anti*,*cis*-tricyclo[6.4.0.0^{2,7}]dodecane (**8**), a known compound, by catalytic reduction. The multiple symmetry elements in **8** result in a simple ^{13}C NMR spectrum with only three signals: δ 34.3 (CH), 27.1 (CH_2), 23.1 (CH_2), in close agreement with literature values.[15] The NMR data confirm the *cis*,*anti*,*cis*-relationship in the tricycle because the *syn* isomer also affords a ^{13}C NMR spectrum with three signals, but at different chemical shifts.[15]

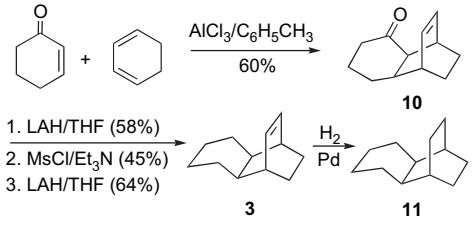
Exploratory thermal reactions of **1** were run to isolate and identify products; of particular interest was the possibility that both *si* and *sr* outcomes for [1,3] carbon shifts might be seen. Preparative GC separation of a flash-vacuum pyrolysis product mixture obtained by heating **1** at 350 °C gave **2** and **3**. The ^{13}C NMR spectrum of **2** consisted of 12 signals: δ 137.2 (=CH), 131.3 (=CH), 51.6 (CH), 45.0 (CH), 35.9 (CH), 35.8 (CH), 33.9 (CH_2), 32.4 (CH_2), 30.8 (CH_2), 28.2 (CH_2), 27.6 (CH_2), 17.6 (CH_2). Catalytic reduction of **2** to **9** completed the structure proof of **2** because the two-fold rotational symmetry axis in **9** implies that there will be only six nonequivalent carbons, as confirmed in its ^{13}C NMR spectrum: δ 46.1 (CH), 31.2 (CH_2), 30.4 (CH), 27.9 (CH_2), 27.8 (CH_2), 21.9 (CH_2) (Scheme 3).

An authentic sample of **3**, the possible *sr* product, was secured through the synthetic sequence outlined in Scheme 4.



Scheme 3. Forming the C_2-symmetric tricyclo[6.2.2.0^{2,7}]dodecane **9**.

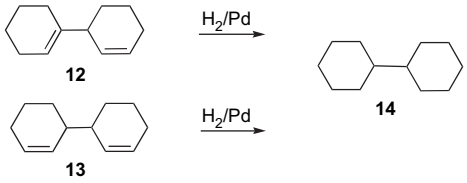
A Diels–Alder cycloaddition of 1,3-cyclohexadiene and 2-cyclohexenone using an aluminum trichloride catalyst afforded the known *endo* product **10**. The ^{13}C NMR chemical shifts for **10** matched those reported in the literature,[16] thus confirming the stereochemical assignment: δ 214.3 (C=O), 134.3 (=CH), 133.0 (=CH), 52.9 (CH), 42.1 (CH), 38.6 (CH_2), 35.7 (CH), 31.1 (CH), 29.5 (CH_2), 25.8 (CH_2), 23.9 (CH_2), 20.8 (CH_2). Although compound **3** was initially prepared only in low yield by Wolff–Kishner reduction of the hydrazone derivative of ketone **10**, a more efficient methodology—reduction with LAH, alcohol mesylation, and further reduction with LAH—was soon found to give more satisfactory yields.[11] The elimination side reaction noted earlier posed a less serious problem in the formation of **3** compared to its analog containing a five-membered ring.[11] The sample of **3** prepared through this three-step sequence of reactions gave a ^{13}C NMR spectrum with six peaks: δ 133.2 (=CH), 40.2 (CH), 36.2 (CH), 25.9 (CH_2), 25.2 (CH_2), 20.3 (CH_2). Catalytic reduction of **3** afforded the saturated analog **11**, a known compound[17,18] having six nonequivalent carbons: δ 37.0 (CH), 29.5 (CH), 27.6 (CH_2), 23.0 (CH_2), 21.0 (CH_2), 20.8 (CH_2).



Scheme 4. Preparation of **3** and the C_s-symmetric tricyclo[6.2.2.0^{2,7}]dodecane **11**.

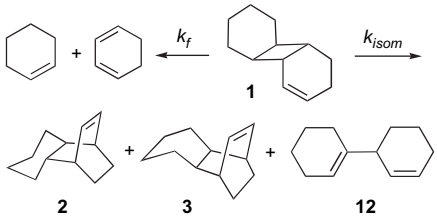
A minor thermal product **12** was tentatively identified as 1-(2-cyclohexen-1-yl)cyclohexene, available from **1** via a formal retro-ene reaction involving a 1,5-hydrogen shift from C8 to C4 and cleavage of C1−C2. That **12** shares the same bicyclic carbon skeleton as does 3,3′-bicyclohexenyl (**13**), which was made in one step by reacting 3-bromocyclohexene with its Grignard reagent, was confirmed when both **12** and **13** gave bicyclohexyl (**14**) upon catalytic hydrogenation. The ^{1}H and ^{13}C NMR spectra of **13** matched those reported in the literature,[19] and the ^{13}C NMR spectrum of **14** confirmed its enhanced symmetry, in agreement with literature data:[20] δ 43.5 (CH), 30.2 (CH_2), 26.9 (two overlapping peaks, CH_2). Coinjection of **13** with the thermal reaction mixture resulted in a peak eluting a mere 0.1 min earlier than did **12**. Further corroboration of the structure of **12** was predicated on the observation that both **12** and **13** give rise to a base peak in the mass spectrum at *m*/*z* 81 assigned to the cyclohexenyl allylic cation (Scheme 5).

The thermal reactions of **1**, as shown in Scheme 6, were followed kinetically at 315 °C using nitrogen as a bath gas in a gas-phase static reactor.[7h] Capillary GC analysis (Fig. 1)



Scheme 5. Bicyclohexadienes and bicyclohexane.

provided relative concentration versus reaction time data for **1**–**3** and **12**; all components were well-resolved and eluted in the order **2**, **3**, **1**, and **12**. The relative elution order for **2** and **3** is consistent with that previously reported[12] for **9** and **11** and with our own GC results for **9** and **11**. First-order rate plots obtained from four kinetic runs without an internal standard give a reliable overall rate constant for the three isomerizations: $k_{\text{isom}}=(k_{si}+k_{sr}+k_{15})=1.75(\pm0.06)\times10^{-5}$ s^{-1}. As isomerization products **2**, **3**, and **12** form irreversibly, their relative proportions remain essentially constant throughout the reaction. The rate constants for the reactions leading to them are, respectively, $k_{si}=k(\mathbf{1}\rightarrow\mathbf{2})=1.14\times10^{-5}$ s^{-1}, $k_{sr}=k(\mathbf{1}\rightarrow\mathbf{3})=0.47\times10^{-5}$ s^{-1}, and $k_{15}=k(\mathbf{1}\rightarrow\mathbf{12})=0.14\times10^{-5}$ s^{-1}. The *si*/*sr* value derived from k_{si} and k_{sr} is 2.4, and $k_{13}=(k_{si}+k_{sr})=1.61\times10^{-5}$ s^{-1}. When dodecane was employed as an internal standard, minor fractionations during vacuum line transfers led to a slightly less reliable rate constant for overall loss of **1**: $k_0=3.0(\pm0.2)\times10^{-5}$ s^{-1}, where $k_0=(k_{\text{isom}}+k_f)$. The rate of fragmentation determined by difference is $k_f\approx1.25\times10^{-5}$ s^{-1}. The relative order of importance of all kinetic processes is $k_{13}>k_f\gg k_{15}$.



Scheme 6. Thermal reactions of tricyclic **1**.

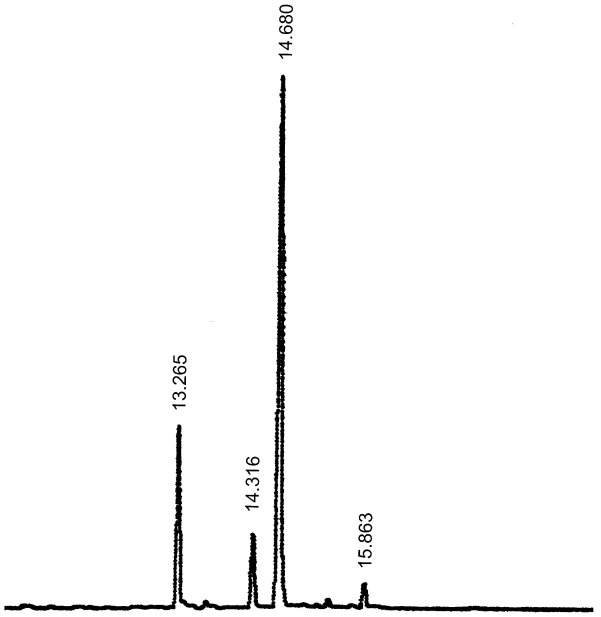
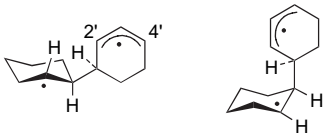


Figure 1. Capillary GC analysis of gas-phase thermal reaction mixture from **1** (without internal standard) after 6.5 h at 315 °C: **2**, **3**, **1**, and **12** (from left to right).

The lack of any significant retro Diels–Alder fragmentation of **2** and **3** to cyclohexene and 1,3-cyclohexadiene under the reaction conditions follows from both prior experimental work[11] and the invariance of the *si*/*sr* ratio at different reaction times. The simplest mechanistic explanation for the thermal behavior of **1** is homolytic cleavage of the C1−C2 bond to generate an alkyl, allylic diradical intermediate that partitions itself between three isomerization products and fragmentation. While the 1,5-hydrogen shift leading to **12** might be concerted, it is more likely a diradical-mediated process.

A summary of kinetic and stereochemical findings for the tricyclic vinylcyclobutanes **1** and **4**, and for four comparable bicyclic vinylcyclobutanes (**15**–**18**), is provided in Table 1. Neither the 12-carbon reactant **1** nor the 11-carbon tricycle **4** undergoes epimerization at the migrating carbon, while all four bicyclics do. For both bicycloheptenes and bicyclooctenes, a methyl substituent at the migrating carbon diminishes the importance of the one-center epimerization process relative to k_{13}.

Isomerization of **1** to give some [1,3] carbon shift product with inversion, when the related tricyclo[6.3.0.0^{2,7}]undec-3-ene **4** gives none, is not surprising. Breaking the C1−C2 bond of **4** would give a (2′-cyclohexenyl)cyclopentane-2,4′-diyl diradical locating the essentially planar cyclopentan-2-yl radical unit and the allylic radical moiety so that only the *sr* product would be geometrically feasible. And while the isomerization of **1** to **2** is exothermic, an *si* stereochemical outcome starting from **4** would correspond to an endothermic process. Nor is it unanticipated that the less stable of the two possible [1,3] carbon shift products from **1** is favored kinetically: it just suggests that the product-determining steps involve structures much like the diradical intermediates. The product ratio could be fixed at a time when the migrating carbon and the terminus of the shift are relatively far apart, the 2-substituted cyclohexyl radical and allylic cyclohexenyl radical substructures are relatively conformationally relaxed, and the difference in heats of formation of the two possible products could be of no significant importance as bond formations were initiated.[21,22] The product ratio, were this the case, would follow from the dynamic conformational characteristics of the diradical intermediates. It would be especially sensitive to axial versus equatorial conformational alternatives for the (2′-cyclohexenyl)cyclohexane-2,4′-diyl diradical and the dihedral angle defined by the C1−C8−C7−C2 segment of the starting material (the C2−C1−C1′−C2′ segment of **19** and **20**). Structures **19** and **20** provide schematic representations of such conformational forms for the diradical (Scheme 7). In **19** the cyclohexyl radical unit is more likely to form the *si* product **2**, while in **20** the more exposed face of the cyclohexyl radical moiety is positioned to favor formation of the *sr* product **3**.

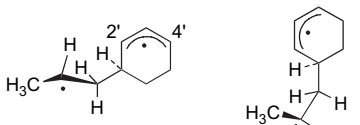


19 **20**

Scheme 7. Conformational isomers of the (2′-cyclohexenyl)cyclohexane-2,4′-diyl diradical reached through C1−C2 bond cleavage of **1**.

The totally unexpected result uncovered in the present study is that the tricyclic hydrocarbon **1** and *exo*-8-methylbicyclo[4.2.0]oct-2-ene (**18**) isomerize to [1,3] shift products with identical *si*/*sr* ratios—or perhaps with only very similar product ratios, recognizing that experimental uncertainties and slight variations in these ratios with temperature might contribute modestly to the observed *si*/*sr* values. At 315 °C, hydrocarbons **1** and **18** both give 70±1% inversion and 30±1% retention as [1,3] shift products are formed. While both **1** and **18** have an alkyl substituent in an *exo* disposition at the migrating carbon, the diradicals formed through C1–C2 or C1–C8 bond cleavages, from **1** or **18**, respectively, must have quite different geometrical constraints. These inherent differences, however, do not impact the *si*/*sr* ratios substantially.

This finding raises the possibility that these two reactants undergo ring openings to give diradical intermediates having similar conformational characteristics and they in turn lead to similar stereochemical preferences for ring closures. Diradical **21** would expose one face of the alkyl radical toward the cyclohexenyl allylic radical fragment, favoring the inversion product; the opposite face would be exposed in **22** and would favor the retention product (Scheme 8).

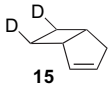
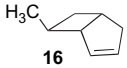
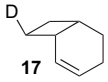
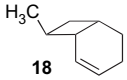
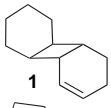
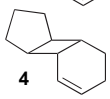


21 **22**

Scheme 8. Conformational isomers of the (2′-cyclohexenyl)propan-2,4′-diyl diradical reached through C1−C8 bond cleavage of 8-*exo*-methylbicyclo[4.2.0]oct-2-ene (**18**).

The enhanced potential for conformational flexibility in diradical intermediates formed from 8-*exo*-methylbicyclo[4.2.0]oct-2-ene (**18**), relative to the diminished

Table 1. Stereochemistry of [1,3] shifts for bicyclic and tricyclic vinylcyclobutanes

Compound	*T* (°C)	%*si*[a]	*si*/*sr*	k_{ep}/k_{13}[b]	Ref.
 **15**	276	76	3.2	0.1	7e,g,j
 **16**	275	87	6.8	0.07	7h
 **17**	300	58	1.4	7	10b
 **18**	275–315	71	2.4	3.5	10a
 **1**	315	71	2.4	0	This work
 **4**	315	0	0	0	11

[a] %*sr*=100−% *si*.
[b] k_{ep}=rate constant for one-way epimerization at the migrating carbon.

conformational space available to diradicals formed from **1**, does not substantially favor one or the other [1,3] shift stereochemical outcome. The differences in conformational flexibility and the experimental fact that both reactions isomerize with very similar or even identical *si*/*sr* ratios raise the possibility that the conformational preferences of the diradical intermediates involved are defined largely as the diradicals are formed. For 8-*exo*-methylbicyclo[4.2.0]oct-2-ene (**18**) the bevel rotation about the C6−C7 bond as the C1−C8 bond elongates could, just as the bond breaks, be accompanied by either of the two discrete relative senses of rotation about the C7−C8 bond. Similarly, tricyclo-[6.4.0.0^{2,7}]dodec-3-ene (**1**) could suffer bond cleavage through elongation of C1−C2 and a bevel rotation about C7−C8; with bond cleavage, a further rotation about C1−C8, in one relative sense or the other, could be stereochemically decisive. Were the [1,3] carbon shift paths of both reactants to favor marginally and to the same extent one sense of torsional rotation about the H−C2−C1−C1′ dihedral angle of the diradical intermediates as they were generated, identical or nearly identical initial diradical conformational ratios **19/20** and **21/22** could arise and very similar *si*/*sr* product ratios could result. This line of consideration applied to deuterium-labeled reactants **15** and **17**, which show more facile epimerization reactions and less stereoselectivity in kinetically controlled [1,3] shifts (Table 1), might lead one to suspect that the two senses of coupled rotations would be more evenly balanced when the migrating group was deuteriomethylene. Reaction with less selective stereochemical outcomes could be largely set as the diradical conformers were formed.

Were this line of conjecture supported by detailed theoretical studies it would move interpretations of [1,3] carbon migrations still further away from models based on competitions between orbital symmetry controlled versus 'forbidden' diradical-mediated reaction paths.

3. Conclusions

In summary, the 12-carbon tricyclic vinylcyclobutane **1** undergoes [1,3] sigmatropic rearrangements to give both *si* (**2**) and *sr* (**3**) products: the *si*/*sr* ratio is 2.4:1. This thermal behavior differs dramatically from the [1,3] shift stereochemistry shown by the 11-carbon homolog **4** (*si*/*sr*=0) but matches perfectly with the *si*/*sr* product ratio found for *exo*-8-methylbicyclo[4.2.0]oct-2-ene (**18**), quite an unforeseen outcome. The stereochemical preferences observed for [1,3] carbon sigmatropic shifts can be highly system dependent; the diradical intermediates involved most probably reflect a range of lifetimes, access to conformational space, and potential energy features within the high-energy caldera of the transition region. The present work provides another example illustrating that conformational and dynamic characteristics of diradical intermediates, not orbital symmetry considerations, control the thermal behavior of vinylcyclobutanes.

4. Experimental

4.1. General

Commercial reagents of high purity were used without further purification. To 1,3-cyclohexadiene was added 5 Å molecular sieves to each bottle once it had been opened. Triethylamine was distilled from CaH_2 just prior to use and stored over 5 Å molecular sieves. Toluene was dried over $CaCl_2$ and distilled prior to use. All reactions were performed under an argon or nitrogen atmosphere. Sigma–Aldrich 100–200 mesh silica gel was used for flash column chromatography. Mass spectra to confirm molecular formulas and to record fragment ions were determined using an Agilent Technologies 5973 mass selective detector and a 6890N Network GC System. NMR spectra were acquired on a Varian Unity 300 MHz or a Varian INOVA 500 MHz instrument. ^{13}C NMR hydrogen multiplicities for all compounds except one were obtained by DEPT pulse sequences; for compound **9**, APT pulse sequences gave better resolution. All GC analyses were acquired on an HP cross-linked methyl silicone column (50 m×0.2 mm i.d. ×0.10 μm film thickness). Purifications of samples for spectral characterization and for thermal reactions were accomplished by preparative GC on a 1/4 in×8 ft DC-710 column operating at 100 °C.

4.1.1. Catalytic hydrogenation. To a solution of an olefin in 5–10 mL of 95% ethanol, diethyl ether, or pentane was added a catalytic amount of 10% Pd/C; hydrogenation was accomplished in a Parr medium-pressure hydrogenation apparatus as the decrease in hydrogen pressure in the reaction vessel was monitored. The reaction mixture was filtered through sintered glass. When ethanol was used as the solvent, the resultant solution was diluted with water and extracted with pentane. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure.

4.1.2. Reductions with lithium aluminum hydride. A solution of the starting material (10 mmol), either ketone **10** or the mesylate precursor of **3** (Scheme 4), dissolved in 25 mL of anhydrous THF was cooled in an ice-water bath. To this solution was added 15 mL of 1 M LAH/THF over 30 min. After being stirred at ambient temperature overnight, the reaction mixture was again cooled to 0 °C and quenched with cold absolute ethanol. Neutralization was accomplished by sequential addition of 10 mL of cold satd aqueous NH_4Cl and 10 mL of cold 1 M HCl. After successive extractions with ether (3×25 mL), the organic layer was washed with water, 1 M HCl, water, satd aqueous $NaHCO_3$, water, and brine. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure.

4.1.3. Thermal reactions. Kinetic studies of gas-phase thermal reactions at 315.0 °C were performed in a pyrolysis system described elsewhere[7h] and analyzed by replicate analytical GC measurements. Retention times (min) obtained using a standard GC program (initial temperature of 100 °C held for 1 min to a final temperature of 180 °C with a temperature ramp of 3.0 °C/min) were as follows: **2** (13.27), **3** (14.32), **1** (14.68), **12** (15.86). For thermal reactions with dodecane as an internal standard, the initial temperature of 100 °C was held for 5 min, affording the following retention times (min): dodecane (13.53), **2** (15.31), **3** (16.57), **1** (17.01), **12** (18.40).

4.1.4. Kinetic data. For kinetic runs at 315.0 °C starting with **1** and no internal standard, with [**1**]+[**2**]+[**3**]+[**12**]= 100%, the (reaction time (h), mol percent **1**) data were 0 (100%), 2 (90.1%), 4 (80.2%), 6.5 (67.3%), and 8

(60.7%); the k_{isom} rate constant (Scheme 6) calculated from these data was $1.75(\pm0.06)\times10^{-5}$ s^{-1}. For kinetic runs at 315.0 °C starting with **1** and dodecane as an internal standard, the [**1**(*t*)]/[dodecane] GC intensity ratio equals a numerical constant times the mol percent of **1**(*t*); the (time (h), [**1**(*t*)]) data were 0 (100%), 2 (87.0%), 4 (68.4%), and 8 (42.7%). The rate constant for $k_0=(k_{isom}+k_f)$ (Scheme 6) was calculated to be $3.0(\pm0.2)\times10^{-5}$ s^{-1}.

4.2. Specific procedures

4.2.1. *cis*,*anti*,*cis*-Tricyclo[6.4.0.0^{2,7}]dodecan-3-one (6). A mixture of 150 mL of cyclohexene and 10 mL (9.9 g, 10 mmol) of 2-cyclohexen-1-one (Aldrich) was combined in a 500-mL photochemical reactor immersion well fitted with a thermometer and condenser. The reaction mixture was irradiated for a total of 16 h with a 450-watt Hanovia medium-pressure mercury lamp placed inside a Pyrex sleeve. Reaction progress was monitored by analytical GC: the concentration of 2-cyclohexenone decreased to 35% of its initial value after 10 h and to 20% after 16 h. Concentration of the reaction mixture under reduced pressure afforded in almost quantitative yield (based on the 2-cyclohexenone converted) a complex mixture of 95% C12-monoketone isomers and 5% C12-diketones. Compound **6**, a known compound,[13] accounted for almost 60% of the product mixture. A 4.2-g sample of the photochemical product mixture was partially purified by flash column chromatography (9:1 pentane/ether), affording 3.7 g of a colorless liquid obtained by combining and concentrating the cleanest column fractions. Analysis by GC and GC/MS showed a 1:1:8 mixture of isomeric ketones. IR (film): 2920, 1700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.56 (s, 2H), 2.32 (m, 1H), 2.19 (m, 1H), 2.00 (m, 1H), 1.85 (m, 1H), 1.78 (m, 1H), 1.70 (m, 2H), 1.58 (m, 1H), 1.54 (m, 1H), 1.47 (m, 1H), 1.41 (m, 2H), 1.32 (m, 1H), 1.24 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.9 (C=O), 48.0 (CH), 40.3 (CH_2), 38.6 (CH), 35.6 (CH), 35.2 (CH), 27.2 (CH_2), 26.6 (CH_2), 25.9 (CH_2), 22.6 (CH_2), 22.5 (CH_2), 22.3 (CH_2).

4.2.2. *cis*,*anti*,*cis*-Tricyclo[6.4.0.0^{2,7}]dodecan-3-one tosylhydrazone (7). To a solution of *p*-toluenesulfonylhydrazide (1.0 g, 5.37 mmol) in 10 mL of methanol was added 0.57 g (3.20 mmol) of ketone **6**. The white crystals that formed slowly were filtered and washed with 1:1 pentane/ether to yield **7** (0.76 g, 2.2 mmol, 69%). IR: 3210, 2925, 1625, 1600, 1310, 1190, 810 cm^{-1}; mp 155–156 °C (dec).

4.2.3. *cis*,*anti*,*cis*-Tricyclo[6.4.0.0^{2,7}]dodec-3-ene (1). Tosylhydrazone **7** (0.76 g, 2.2 mmol) was placed in a flame-dried apparatus. It was suspended in 13 mL of anhydrous TMEDA and cooled to −78 °C; CH_3Li (1.6 M in diethyl ether, 5.5 mL, 8.8 mmol) was added dropwise over 5 h. The reaction mixture was allowed to warm to rt and stirred overnight. Prior to workup the reaction mixture was cooled to −30 °C and quenched with 10 mL of cold water. The aqueous solution was extracted with pentane (3×25 mL) and the combined organic extracts were washed with water, 1 N HCl, water, satd $NaHCO_3$, water, and brine. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give **1** as a colorless oil (0.44 g, 2.7 mmol, 54% yield by GC). IR (film): 3015, 2920, 2850, 1645, 1450, 685 cm^{-1}; MS *m*/*z* (rel intensity): 162 (13) (calcd for $C_{12}H_{18}$, M^+ 162), 133 (17), 91 (19), 80 (100); ^1H NMR (300 MHz, $CDCl_3$): δ 5.79 (m, 2H), 2.42 (m, 1H), 2.28 (br s, 1H), 2.11 (m, 1H), 2.00 (m, 3H), 1.81 (m, 1H), 1.48 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.3 (=CH), 126.4 (=CH), 38.9 (CH), 36.7 (CH), 33.9 (CH), 32.1 (CH), 28.9 (CH_2), 26.4 (CH_2), 23.4 (CH_2), 22.6 (CH_2), 22.4 (CH_2), 21.7 (CH_2).

4.2.4. *cis*,*anti*,*cis*-Tricyclo[6.4.0.0^{2,7}]dodecane (8). A small sample of compound **1** was subjected to a standard catalytic hydrogenation procedure to give **8**,[15] which was purified by preparative GC. MS: 164 (11) (calcd for $C_{12}H_{20}$, M^+ 164), 82 (100), 80 (74), 67 (87); ^1H NMR (300 MHz, $CDCl_3$): δ 2.00 (br s, 4H), 1.60 (m, 4H), 1.40 (m, 8H), 1.20 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 34.3 (CH), 27.1 (CH_2), 23.1 (CH_2).

4.2.5. *trans*-Tricyclo[6.2.2.0^{2,7}]dodec-9-ene (2). A 50-μL sample of compound **1** was subjected to repetitive preparative flash-vacuum pyrolysis (ca. 1 Torr) at 350 °C through a column packed with glass helices that had been washed with 1 M potassium hydroxide and then oven dried before use. After at least 10 cycles there was a sufficient quantity of the major thermal products to permit isolation of **2** by preparative GC. The analytical GC proportions were 13.20 (**2**, 30%), 14.25 (**3**, 20%), 14.60 (**1**, 43%), and 15.80 min (**12**, 7%). For the preparative GC secured sample of **2**: MS 162 (25) (calcd for $C_{12}H_{18}$, M^+ 162), 133 (14), 91 (36), 80 (100), 79 (57); ^1H NMR (500 MHz, $CDCl_3$): δ 6.37 (t, 1H), 6.03 (t, 1H), 2.23 (br s, 1H), 2.19 (br s, 1H), 1.75 (m, 2H), 1.64 (m, 1H), 1.57 (m, 2H), 1.50 (m, 1H), 1.33 (m, 3H), 1.13 (d, 2H), 0.90 (m, 2H), 0.76 (t, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.2 (=CH), 131.3 (=CH), 51.6 (CH), 45.0 (CH), 35.9 (CH), 35.8 (CH), 33.9 (CH_2), 32.4 (CH_2), 30.8 (CH_2), 28.2 (CH_2), 27.6 (CH_2), 17.6 (CH_2).

4.2.6. *trans*-Tricyclo[6.2.2.0^{2,7}]dodecane (9). The ^1H NMR sample of compound **2** was diluted in 5 mL of diethyl ether and subjected to a standard catalytic hydrogenation procedure. The ^1H NMR was difficult to interpret due to the presence of a large water peak at δ 1.5 and the ether triplet at δ 1.2; between these two peaks were a series of small multiplets associated with compound **9**. ^1H NMR (500 MHz, $CDCl_3$): δ 1.77 (br m, 1H), 1.75 (br m, 1H), 1.54–1.23 (overlapping m, 12H), 1.15 (m, 1H), 1.13 (m, 1H), 0.83 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 46.1 (CH), 31.2 (CH_2), 30.4 (CH), 27.9 (CH_2), 27.8 (CH_2), 21.9 (CH_2). MS: 165 (13, $(M+1)^+$), 164 (100) (calcd for $C_{12}H_{20}$, M^+ 164), 135 (34), 121 (19), 94 (29), 82 (56), 81 (63), 67 (62).

4.2.7. *cis*,*endo*-Tricyclo[6.2.2.0^{2,7}]dodec-9-en-3-one (10).[16] A sublimation chamber was oven- and flame-dried under argon. After the addition of 100 mL of toluene, anhydrous aluminum chloride (1.0 g, 7.5 mmol), 2-cyclohexen-1-one (3.99 g, 41.5 mmol), and 1,3-cyclohexadiene (22.0 mL, 18.5 g, 231 mmol) were added sequentially. The chamber was flushed with argon and sealed. The reaction mixture, which was stirred at 40 °C for 144 h, turned orange as the reaction progressed. The reaction mixture was cooled to 0 °C, poured into 100 mL of ice water, and extracted with ether (3×50 mL). The organic extracts were washed with water and with brine and dried over $MgSO_4$. Ether was removed under reduced pressure; toluene was removed by

short-path distillation. Purification of the residue by flash chromatography (9:1 pentane/ether) gave compound **10** (4.39 g, 24.9 mmol, 60%). IR (film): 3040, 2920, 2865, 1700, 710; MS: 176 (17) (calcd for $C_{12}H_{16}O$, M^+ 176), 104 (10), 97 (43), 80 (100); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.26 (t, 1H), 6.12 (t, 1H), 3.09 (br s, 1H), 2.42 (m, 3H), 2.08 (m, 2H), 1.79 (m, 4H), 1.54 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.3 (C=O), 134.3 (=CH), 133.0 (=CH), 52.9 (CH), 42.1 (CH), 38.6 (CH_2), 35.7 (CH), 31.1 (CH), 29.5 (CH_2), 25.8 (CH_2), 23.9 (CH_2), 20.8 (CH_2).

4.2.8. *cis*,*endo*-Tricyclo[6.2.2.0^{2,7}]dodec-9-ene (3). A sample of ketone **10** (1.53 g, 8.69 mmol) was subjected to the standard LAH reduction to give an alcohol (0.90 g, 5.06 mmol, 58%). IR (film): 3400, 710. A solution of the crude alcohol in 25 mL of methylene chloride was cooled in an ice bath; triethylamine (2 mL) and then methanesulfonyl chloride (4.6 mL, 6.81 g, 5.94 mmol) were added. After being stirred at rt overnight, the reaction mixture was cooled to 0 °C, quenched with ca. 5 mL of cold 1 N HCl, and then extracted with methylene chloride (3×25 mL). The organic extracts were washed with water, 1 N HCl, water, satd $NaHCO_3$, water, and brine. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give a crude mesylate as a colorless oil (0.59 g, 2.3 mmol, 45%). IR (film): 1610, 1370, 1350, 1170, 730 cm^{-1}. The crude mesylate was converted to **3** (0.24 g, 1.5 mmol, 64%) using the standard LAH reduction method. MS: 162 (2) (calcd for $C_{12}H_{18}$, M^+ 162), 133 (1), 91 (10), 80 (100), 79 (20); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.17 (dd, 2H), 2.26 (br s, 2H), 1.69 (m, 2H), 1.50 (m, 6H), 1.29 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.2 (=CH), 40.2 (CH), 36.2 (CH), 25.9 (CH_2), 25.2 (CH_2), 20.3 (CH_2).

4.2.9. *cis*-Tricyclo[6.2.2.0^{2,7}]dodecane (11). A small sample of compound **3** was subjected to a standard catalytic hydrogenation procedure to give the known saturated tricyclic compound **11**,[12,17,18] which was purified by preparative GC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.55 (m, 2H), 1.43 (m, 2H), 1.25 (m, 8H), 1.10 (m, 8H) (compare Ref. 12); ^{13}C NMR (125 MHz, $CDCl_3$): δ 37.0 (CH), 29.5 (CH), 27.6 (CH_2), 23.0 (CH_2), 21.0 (CH_2), 20.8 (CH_2) (compare Ref. 18).

4.2.10. 1-(2-Cyclohexen-1-yl)cyclohexene (12). GC/MS analysis of the thermal reaction mixture gave MS data for **12**. MS: 162 (16) (calcd for $C_{12}H_{18}$, M^+ 162), 81 (100), 80 (88), 79 (79).

4.2.11. Bicyclohexenyl (13). Magnesium filings (0.40 g, 16.5 mmol) were suspended in a solution of 3-bromocyclohexene (1.0 mL, 1.4 g, 8.7 mmol) in 15 mL of anhydrous ether. The flask was gently warmed to initiate formation of the Grignard reagent. Additional 3-bromocyclohexene (2.3 mL, 3.2 g, 20 mmol) dissolved in 10 mL of ether was added dropwise to maintain reaction exothermicity. After being stirred for 2 h, the reaction mixture was cooled to 0 °C and quenched with cold 1 N HCl. After separation of the layers, the organic phase was washed with water (2×25 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a viscous oil. Purification by preparative GC gave pure **13**. MS: 162 (1) (calcd for $C_{12}H_{18}$, M^+ 162), 81 (100), 80 (77), 79 (31); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.72 (m, 2H), 5.53 (dd, 2H), 2.12 (br m, 2H), 1.96 (br s, 4H), 1.71 (m, 4H), 1.50 (m, 2H), 1.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.7/130.4 (=CH), 128.0/127.7 (=CH), 40.15/40.08 (CH), 26.04/25.95 (CH_2), 25.41/25.40 (CH_2), 22.28/22.21 (CH_2) (compare Ref. 19).

4.2.12. Bicyclohexyl (14). A small sample of **13** was dissolved in 85% ethanol and subjected to standard catalytic hydrogenation to give **14**. MS: 166 (9) (calcd for $C_{12}H_{22}$, M^+ 166), 83 (38), 82 (100), 67 (58); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.69 (t, 10H), 1.14 (m, 6H), 1.01 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 43.5 (CH), 30.2 (CH_2), 26.9 (2 overlapping peaks, CH_2). A sample of the flash-vacuum pyrolysis mixture containing compounds **1**–**3**, and **12** (Fig. 1) from which compound **2** had been removed by preparative GC was dissolved in pentane and subjected to a standard catalytic hydrogenation. This product mixture, and coinjection of authentic **14** with the saturated hydrocarbons from the reduction of the mixture of **1**, **3**, and **12**, gave three peaks, for **8**, **11**, and **14**.

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