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Bent bonds and the antiperiplanar hypothesis – a simple model to rationalize [1,3]-sigmatropic alkyl shifts†

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The bent bond/antiperiplanar (BBA) hypothesis has been applied to the analysis of [1,3]-sigmatropic alkyl shifts. These thermal rearrangements, for which there is evidence that they proceed through diradical intermediates, can be interpreted by considering their transient allyl radical structures. For the thermolysis of cyclic molecules, the preferred generation of pyramidal allyl radicals in staggered conformations is postulated on the basis of the BBA hypothesis. This accounts for the preference of suprafacial rearrangement pathways as well as the extent of inversion or retention of configuration at the migrating carbons.

Introduction

We reported[1] that using the Slater/Pauling bent bond model (tau-bonds, τ bonds)[2] instead of the usual Hückel σ–π model,[3] in combination with the antiperiplanar hypothesis and classic resonance concepts, provides a simple conceptual model to understand the conformation and reactivity of organic molecules containing double bonds and carbonyl groups (Fig. 1).[4] We refer to it as the bent bond/antiperiplanar (BBA) hypothesis.

Compared to the σ–π model, the bent bond model confers "tetrahedral character" to unsaturated carbons in olefins and carbonyl groups, allowing one to apply stereoelectronic principles normally associated with saturated systems. The preferred conformation and the various reactivities of these functional groups were well accounted for. The model even led to a simple rationalization of aromaticity, anti-aromaticity and electrocyclic reactions.

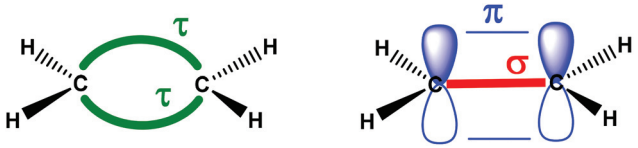

Fig. 1 Slater/Pauling τ-bond model (left) *vs.* Hückel sigma/pi model (right) of ethylene.

We also reported[5] that the BBA hypothesis could be applied to the Diels–Alder reaction by invoking the lowest energy singlet diradical (LESD) resonance structures for both diene and dienophile. This accounts for the reactivity, transition state geometry, regio- and stereoselectivity of a wide range of Diels–Alder reactions without invoking frontier molecular orbital (FMO) theory[6] or the Woodward–Hoffmann (W–H) symmetry rules.[7]

We now wish to report that sigmatropic alkyl shifts, for which there is evidence that they proceed through transient allyl diradical intermediates, can also be analyzed using the BBA hypothesis.

In the σ–π orbital model, the allyl radical is delocalized over three parallel p orbitals and both of its resonance structures are essentially planar (Fig. 2). In the corresponding τ bond model, the resonance structures have to be pyramidal in order for the radical to be antiperiplanar to one of the bent bonds and allow delocalization. The resonance forms can be interconverted by radical inversion (or by bond rotation) through an energy barrier. The rotational barrier for the allyl radical is known experimentally to be ≈15.7 kcal mol^{-1}, 14–14.5 kcal mol^{-1} of which is attributed to delocalization energy.[8] In the bent bond model, this reality implies that the inversion barrier for a pyramidalized allyl radical center must be quite higher than that of a typical primary or secondary carbon radical as the inversion would involve transient disruption of the resonance between the radical and its adjacent antiperiplanar bent bond. To compute the inversion barrier of an individual allyl radical resonance structure would require quantitative valence bond calculations on a bent bond orbital model. Of course, MO theory produces a largely planar structure for the allyl

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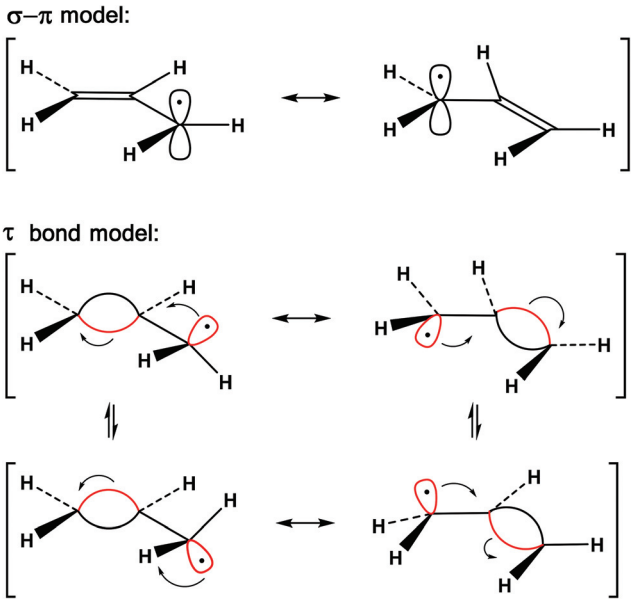


Fig. 2 Allyl radical resonance models.

radical with minimal pyramidalization at either carbon termini and a negligible inversion barrier (0.003 kcal mol^{-1}, B3LYP/6-31^{++}G**).

The τ bond model implies that an allyl radical produced from an optically active precursor could be trapped by reaction with another functional group prior to inversion, thus retaining its configuration in the product because of antiperiplanar delocalization. We note that antiperiplanar delocalization in the allyl radical resonance structures shown in Fig. 2 is reminiscent of the orbital symmetry of the corresponding allyl radical SOMO, to use MO parlance, while retaining tetrahedral character at the two termini. Interestingly, Messmer's computational studies on the allyl radical[9] showed that the bent bond model was favored over the σ–π model by 2.3 kcal mol^{-1}, using explicitly correlated *ab initio* VB wave functions, even with its geometry restricted to C_{2v} symmetry.

Overall, the consideration of resonance structures inherent to the bent bond model yields a new interpretive model for reactions involving allyl radical intermediates. It thus became pertinent to search for literature experiments that can support the validity of the τ bond model for reactions involving allyl radicals.

We wish now to report an analysis based on the Bent Bond Antiperiplanar (BBA) hypothesis of a series of 28 previously reported [1,3]-sigmatropic alkyl shifts, in most cases involving optically active molecules.

Sigmatropic [1,3]-alkyl shift

The [1,3]-alkyl shifts constitute a most interesting class of rearrangements that have generated much controversy over the years as to their adherence to the W–H rules.[10] Although concerted [1,3]-hydrogen shifts are disallowed according to the W–H rules, their [1,3]-alkyl counterparts are predicted to occur

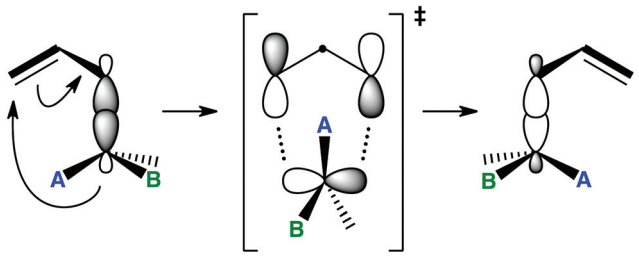


Fig. 3 Inversion of configuration in the suprafacial (*i.e. si*) thermal [1,3]-alkyl shift. Symmetry of allyl SOMO shown in the transition state.

only if the migrating group undergoes 180° rotation with concomitant inversion of configuration in order to match the antisymmetry of the allyl SOMO at the transition state (Fig. 3). Thus, the W–H rules predict only ***s***uprafacial migration with ***i***nversion of configuration at the migrating group (*i.e. si* label).

Thermal rearrangement of dipropenylcyclobutanes. In 1973, Berson reported a truly remarkable experimental study on the thermal rearrangements of optically active *trans*-1,2-*trans*–*trans*-dipropenylcyclobutane (+)-**1** and *trans*-1,2-*cis*–*trans*-dipropenyl-cyclobutane (−)-**4** (Fig. 4).[11] In both cases, the major products (>60%) were cyclohexene derivatives stemming from 1,3-rearrangements at 146.5 °C. Other products included the *cis* and the *trans* 3,4-dimethyl-*cis*–*cis*-cyclooctadiene isomers from the [3,3]-sigmatropic rearrangement as well as piperylene, and other minor unidentified products. One can attempt to rationalize the relative distributions of 1,3-rearrangement products using the W–H rules assuming that these rearrangement are concerted. Accordingly, and as described by Berson, the thermolysis of (+)-**1** should only lead to the formation of *trans* products (+)-**2** and (−)-**2** *via* ***a***ntarafacial/***r***etention (*ar*) and ***s***uprafacial/***i***nversion (*si*) pathways, respectively. Yet, almost 44% of cyclohexene products were the "forbidden" *cis* products (−)-**3** and (+)-**3**. A similar outcome was observed for the thermolysis of (−)-**4** where only products (+)-**5** and (−)-**5** were symmetry allowed, yet almost 48% of disallowed cyclohexene product (−)-**6** was formed. As all the major products stemmed from suprafacial reactions, Berson concluded that if only products (−)-**2**/(−)-**5** result from a concerted reaction (according to the W–H rules), then the formation of disallowed products (−)-**3**/(−)-**6** could be the result of some sort of diradical process. However, if one accepts a diradical process and that bond rotations can occur prior to bond formation, all the stereocenters could be effectively scrambled at 146.5 °C and the resulting intermediates would no longer be chiral. Yet the rearrangements of both (+)-**1** and (−)-**4** proceeded rather stereospecifically upon correction for any prior racemization, so the results seemed to indicate that these are not concerted reactions. The authors stated that "these results can be fitted by a biradical mechanism, but are more fruitfully interpreted as mainly the outcome of two competing concerted reactions, one allowed (suprafacial inversion) and one forbidden (suprafacial retention)". They also concluded that "at least, the present results provide an experimental basis for the refine-

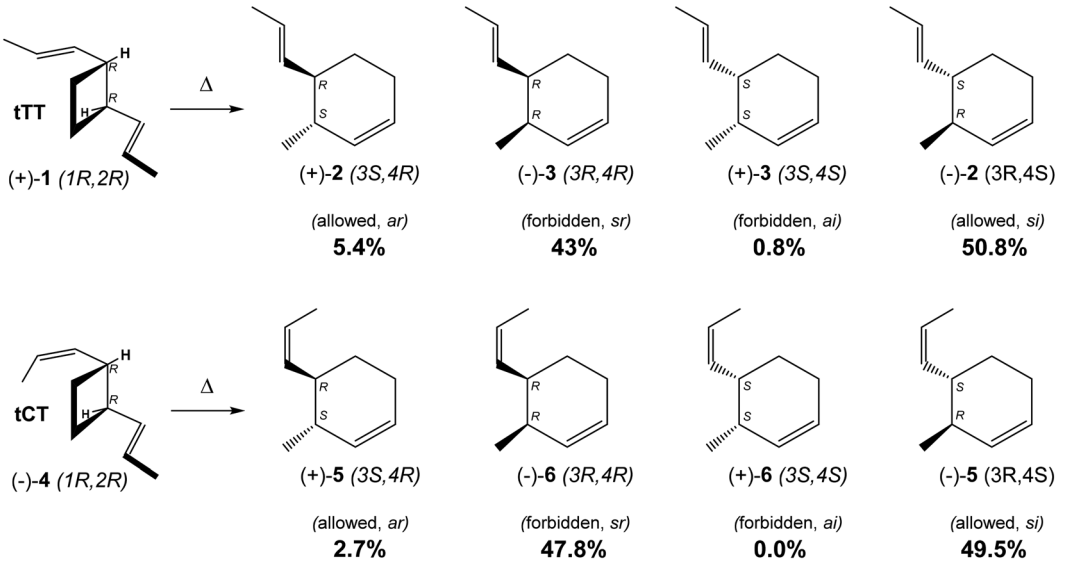


Fig. 4 Relative distribution of cyclohexene products from the thermolysis of dipropenyl-cyclobutanes (+)-**1** and (–)-**4** at 146.5 °C (extracted from ref. 11).

ment of the diradical theory".[11a] Of course, a possible explanation would be that allyl radicals obtained from the homolytic cleavage of organic molecules could be first produced in a pyramidal chiral form, in accordance with the BBA hypothesis.

Let us now re-examine the thermal homolytic cleavage of cyclobutane (+)-**1** using the BBA hypothesis. Because allyl radicals are postulated to retain pyramidal character, homolytic cleavage of the cyclobutane ring in chiral (+)-**1** produces three different diradical geometries (Fig. 5). Retention of configuration at both C1 and C2 during cleavage produces *S*,*S* diradical **7a**, inversion of configuration at only C2 (or C1) produces *S*,*R*/*R*,*S* diradical **8a**, while inversion at both C1 and C2 produces *R*,*R* diradical **9a**. Chiral diradicals **7a** and **9a** are C_2-symmetric. Note that both radicals in **7a** are initially generated in an eclipsed conformation with respect to their adjacent methylene group, and must be higher in energy than their staggered counterpart (*cf.* **8a** and **9a**: staggered radicals are indicated in red). The difference in energy between eclipsed and staggered ethane is 3 kcal mol^{-1}, whereas that of the ethyl anion is about 2.1 kcal mol^{-1} (B3LYP/6-31++G**). One can expect the energy difference between eclipsed and staggered ethyl radical conformers to be even smaller. For the allyl radical, quantitative valence bond calculations on the bent bond resonance structures would be required to evaluate the eclipsed *vs.* staggered conformational energy differences in allyl radical **7a** and its congeners.

If homolytic cleavage of (+)-**1** were to form **7a**, important conformational rotation of either of the allyl radical chains would be required to form cyclization conformer **7b** with the required geometric and stereoelectronic orientation to produce the minor product (+)-**2** (5.4%). Indeed, the geometry **7b** is consistent with antiperiplanar delocalization of one of the allyl radicals (as in Fig. 2) yielding the product (+)-**2** in a boat-like conformation with its two substituents in a *trans* diequatorial orientation. But in the end, we postulate that diradical **7a** has a higher kinetic propensity to reform (+)-**1** with full retention of chirality in light of its diradical geometry and alignment; the overall analysis is in agreement with the low observed yield of product (+)-**2**. It is known that singlet diradicals have little or no inherent enthalpic barrier to bond formation between radical centers.[12]

Now, homolytic opening of (+)-**1** but with concomitant inversion at C2 produces diradical **8a**, which can cyclize along conformations **8b** or **8c** to produce enantiomers (–)-**3** (43%) and (+)-**3** (0.8%), respectively. Note that cyclization to form the major enantiomer (–)-**3** involves a simple shearing motion (path **a**) leading to conformation **8b**, whereas the requisite cyclization to form minor enantiomer (+)-**3** involves a considerable conformational change (path **b**) to produce the corresponding cyclization geometry **8c**. Formation of the major isomer (–)-**3** *via* **8b** corresponds to a suprafacial attack with retention (*sr*), a symmetry forbidden process. Formation of the minor isomer (+)-**3** from **8c** corresponds to a symmetry forbidden *ai* rearrangement. Note here that direct recyclization of diradical **8a**, would require one radical inversion or near 180° rotation of one chain to produce the less stable *cis*-1,2-*trans*–*trans*-dipropenylcyclobutane. As a consequence, the proposed pathway from (+)-**1** to the enantiomers of **3** precludes any important degree of racemization, in accord with experiment.

Homolytic cleavage of (+)-**1** by a double inversion pathway (at C1 and C2) leads initially to allyl diradical **9a** with both radicals staggering their adjacent methylene group. Interestingly, the geometry of **9a** translates into cyclization conformer **9b** upon one bond rotation to only produce cyclohexene enantiomer (–)-**2** *via* the normally anticipated *si* pathway. Note that it is possible for diradical **9a** to form cyclobutane enantiomer (–)-**1** but only by 180° rotation of the two chains. This scenario is consistent with the experimental results as partial racemiza-

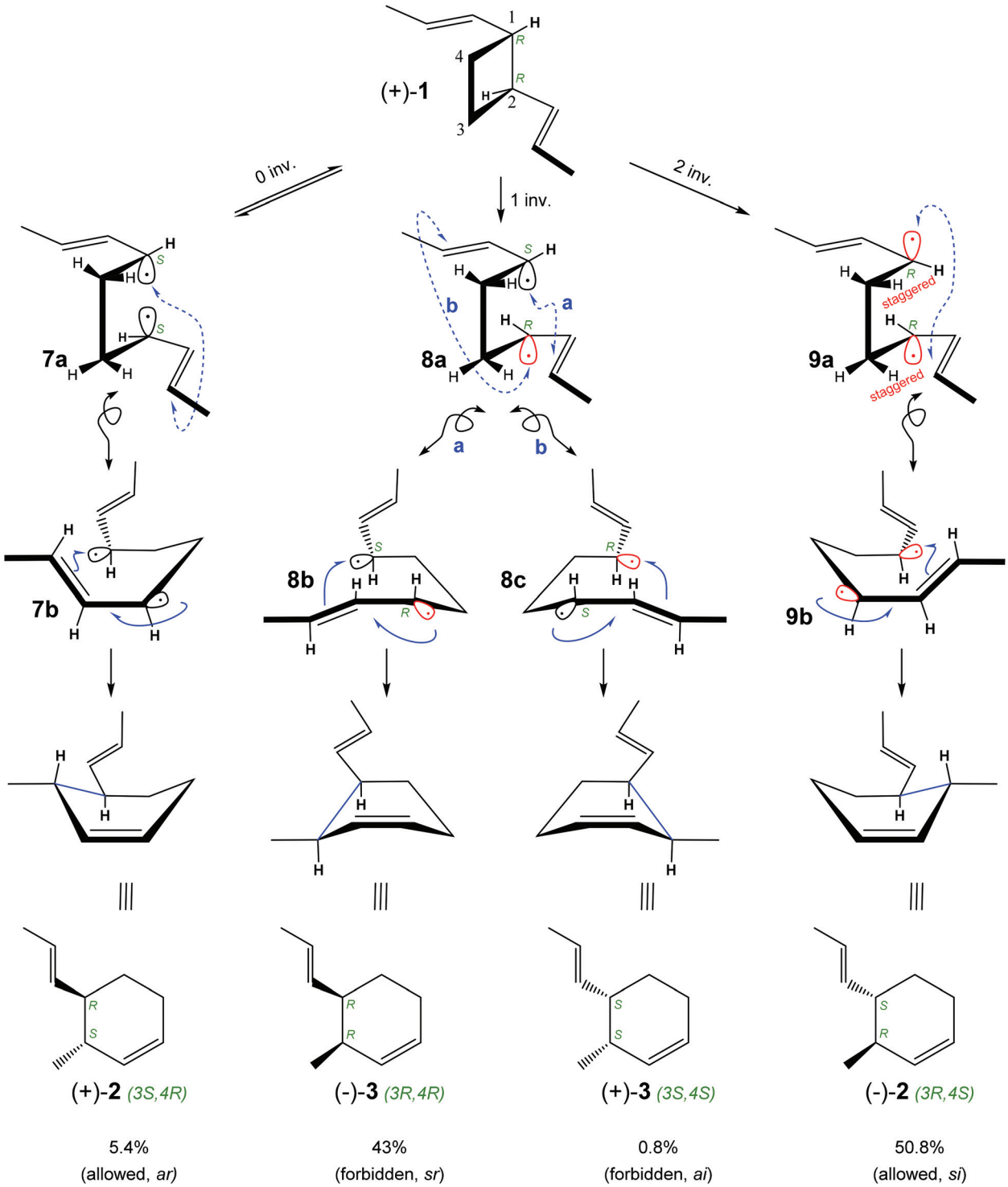


Fig. 5 Rationalizing the 1,3-sigmatropic rearrangement of (+)-**1**.

tion was observed during the thermolysis of (+)-**1**. The formation of a small amount of (−)-**1** may also contribute to the observed formation of 5.4% of (+)-**2**. The formation of (−)-**2** as a major product can be explained by the fact that **9a** is formed directly in the most stable staggered conformation for both radicals (*i.e.* about C1–C4 and C2–C3 bonds). By comparison, **8a** has one staggered and one eclipsed radical whereas the two radicals in **7a** are both eclipsed.

An important point to consider is the fate of the three possible chiral diradicals formed by homolytic opening of the cyclobutane ring. We postulated that diradical **7a** would always prefer to kinetically reform (+)-**1** from the predisposed radical

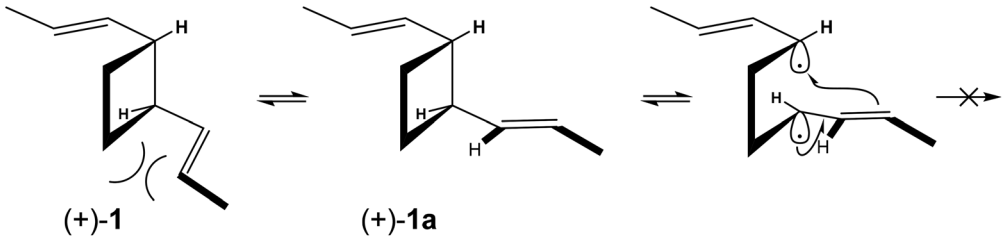


Fig. 6 Other propenyl chain conformers cannot cyclize.

orientation. For the processes involving single or double radical inversion there can, of course, be no facile return to starting material. For example, diradical **8a** can only lead to products (−)-**3** and (+)-**3**, the former being kinetically favoured. As for the double inversion case, diradical **9a** can only produce the major product (−)-**2** as well as some enantiomeric starting material *via* two bond rotations and ring closure, perhaps accounting for the small amount of observed racemization and formation of (+)-**2**.

It should be pointed out that other conformers of the propenyl chain of (+)-**1** such as (+)-**1a** (Fig. 6) need not be considered because thermolysis *via* the corresponding diradical would lead to a cyclohexene with a *trans* double bond. Compared to conformer (+)-**1a**, (+)-**1** is higher in energy due to its steric hindrance so steric decompression may contribute to its higher reactivity toward homolytic cleavage. Note also that the [3,3] rearrangement of such diradicals from (+)-**1a** could also lead to 3,4-dimethyl-*trans*–*cis*-cycloocta-1,5-dienes, which are also too high in energy to be observed in appreciable proportions.[11]

Examination of the thermolysis of the tCT isomer (−)-**4** (Fig. 4) leads to identical conclusions as those summarized for (+)-**1** (Fig. 5). As reported by Berson, the [1,3]-rearrangement of (−)-**4** gave almost exclusively migration products across the *trans*-propenyl chain. Indeed, for migration to occur across the *cis*-propenyl chain would force the terminal methyl of the *cis*-propenyl group to clash sterically with the 4-membered ring.

One can conclude that the experimental results from the thermal rearrangement of dipropenylcyclobutanes can be understood by invoking pyramidal allyl radicals based on the BBA hypothesis and classic arguments used by organic chemists. The next step was to test the generality of this concept by analyzing a variety of thermolysis reactions of other optically active molecules known to proceed *via* allyl radical intermediates.

Thermal rearrangement of methylpropenylcyclobutanes. Other intramolecular [1,3]-alkyl shift reactions have served as convenient model systems for studying the stereochemical outcome of this rearrangement.[10] To this effect, let us first re-examine the thermolysis of *cis* and *trans* 2-methyl-1-(*E*)-propenylcyclobutanes **10** and **11** studied by Baldwin and coworkers.[13] Summarized in Fig. 7, their results revealed distributions of product isomers that were simply inconsistent with the W–H rules. Note how the rearrangement of **10** yielded 33% of the symmetry forbidden *sr* product **13** while the rearrangement of **11** yielded 51% of its corresponding symmetry forbidden *sr* product **12**. Baldwin concluded that "the preference for *trans* isomers of products from either *cis* or *trans* isomers of the reactants are more plausibly explicated by postulating a common determinant: dynamic effects as conformationally flexible diradical intermediates seek exit channels from the caldera energetic plateau". Thus, all evidence pointed to a diradical mechanism where the W–H rules do not apply.

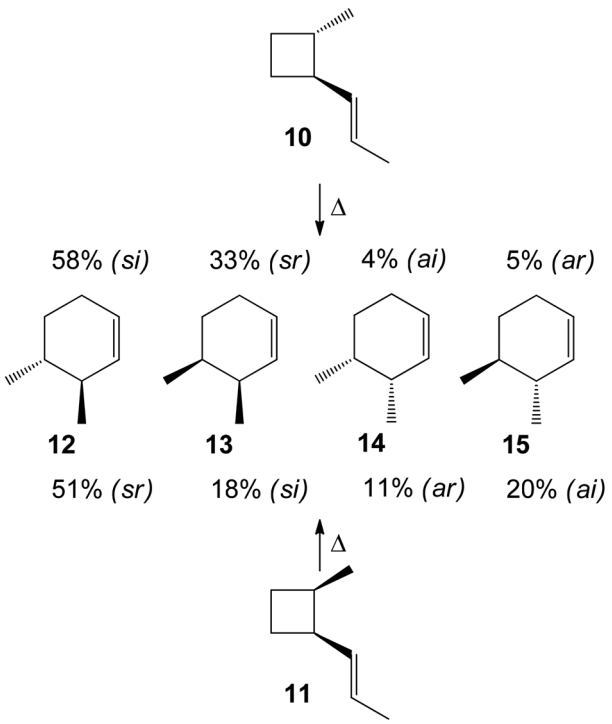


Fig. 7 Thermal rearrangement of 2-methyl-1-(*E*)-propenylcyclobutanes **10** and **11**.

According to the BBA hypothesis, *trans*-cyclobutane **10** can theoretically form four different diradicals from thermolytic cleavage (**16a–19a**, Fig. 8). For the ensuing analyses, and as discussed in the Introduction, the Walden-like inversion barrier for chiral allyl radicals is postulated to be considerably higher than that of secondary alkyl radicals. In addition, diradicals **16a**/**17a** should form more readily than diradicals **18a**/**19a** because their allyl radical component is formed in a staggered

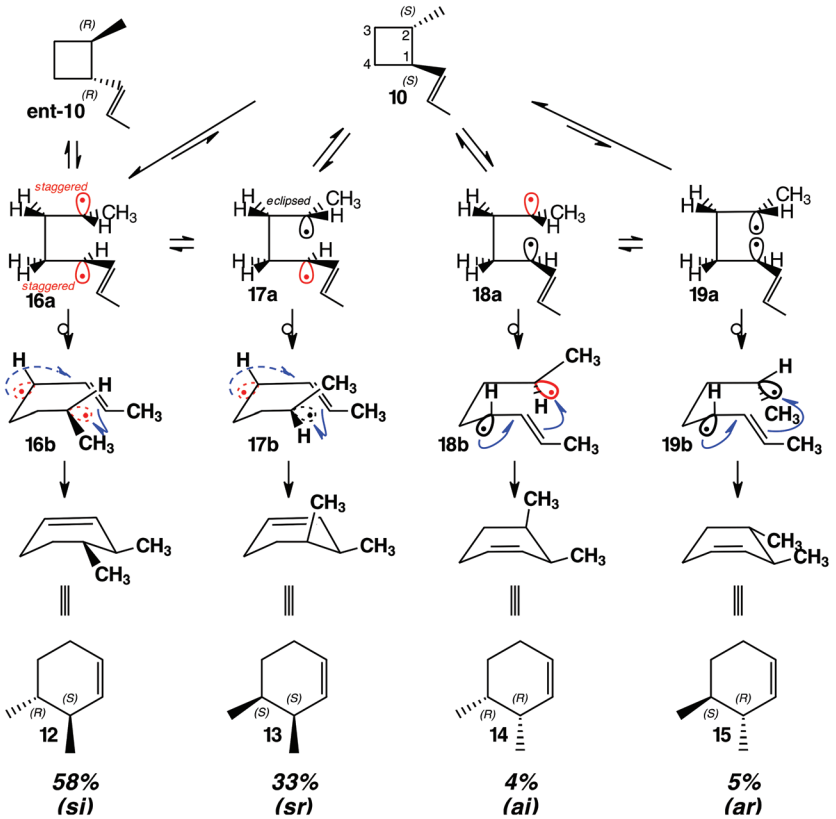


Fig. 8 BBAH analysis of *trans* 2-methyl-1-(*E*)-propenylcyclobutane **10**.

conformation with respect to their C1–C4 bond. Because of the much lower inversion barrier for secondary alkyl radicals, **16a**/**17a** should interconvert rapidly with a slight preference to form **16a** as its alkyl radical staggers the C2–C3 bond. This accounts for the formation of cyclohexenes **12** and **13**, with a higher percentage of the former (a symmetry allowed product) *via* a boat-like transition state corresponding to **16b** with *trans* diequatorial substituents. Diradical intermediates **18a**/**19a** both have the eclipsed allyl radical geometry at C1–C4. Again, **18a** and **19a** can rapidly equilibrate by Walden inversion of the secondary radical center to form cyclohexanes **14** and **15**. However, **19a** is expected to reform cyclobutane **10** rapidly due to the appropriate orbital orientation, removing some **18a**/**19a** from the reaction pool. The requisite cyclization geometries **18b**/**19b** also require considerable conformational reorganization of **18a**/**19a** in order to attain the appropriate stereoelectronic alignment for the [1,3]-rearrangement, both corresponding to antarafacial migration processes. In conclusion, and in agreement with the BBA hypothesis, the *si* and *sr* pathways leading to **12** and **13** account for 91% of the observed product isomers.

A similar analysis can be carried out for *cis* cyclobutane isomer **11** (Fig. 9). Once again, homolytic cleavage can produce four different diradicals (**20a–23a**). Diradicals **20a**/**21a** should predominate over **22a**/**23a** as their allyl radical component staggers the C1–C4 bond. Although diradical **20a** should form preferentially (staggered C2–C3 bond), it can easily equilibrate with **21a** by inversion at C2, aligning the radicals for cyclization *via* **21b** to form product **12** with both methyl groups pseudoequatorial; this can account for the greater proportion of **12** compared to **13**. As for diradicals **22a** and **23a**, each has an eclipsed allyl radical at C1 and can equilibrate by inversion of their secondary radical at C2. If formed, diradical **23a** is expected to reform cyclobutane **11** due to the appropriate orbital orientation and proximity, and can remove some of **22a**/**23a** from the reaction pool. In addition, the requisite geometry for the cyclization of **22b**/**23b** requires considerable conformational reorganization to attain the appropriate stereoelectronic alignment for the [1,3]-alkyl rearrangement. Consequently, the *si* and *sr* pathways, which yield products **12** and **13**, account for much of the cyclohexene isomers observed (69%). Overall, the experimental results correlate well with the BBA interpretation shown in Fig. 8 and 9.

An analogous study by Doering and co-workers with deuterium labelled racemic *cis* and *trans* 2-cyano-1-(*E*)-propenylcyclobutanes gave product distributions similar to those for the thermolysis of **10** and **11**.[14] The analysis of this work using the BBA hypothesis is described in the ESI.†

Thermal rearrangement of vinylcyclopropanes. Detailed studies on the thermal rearrangement of vinylcyclopropanes have also been carried out, in particular from the groups of Baldwin[15] and Doering.[16] Selected examples with the reported product distributions are reproduced in Fig. 10.

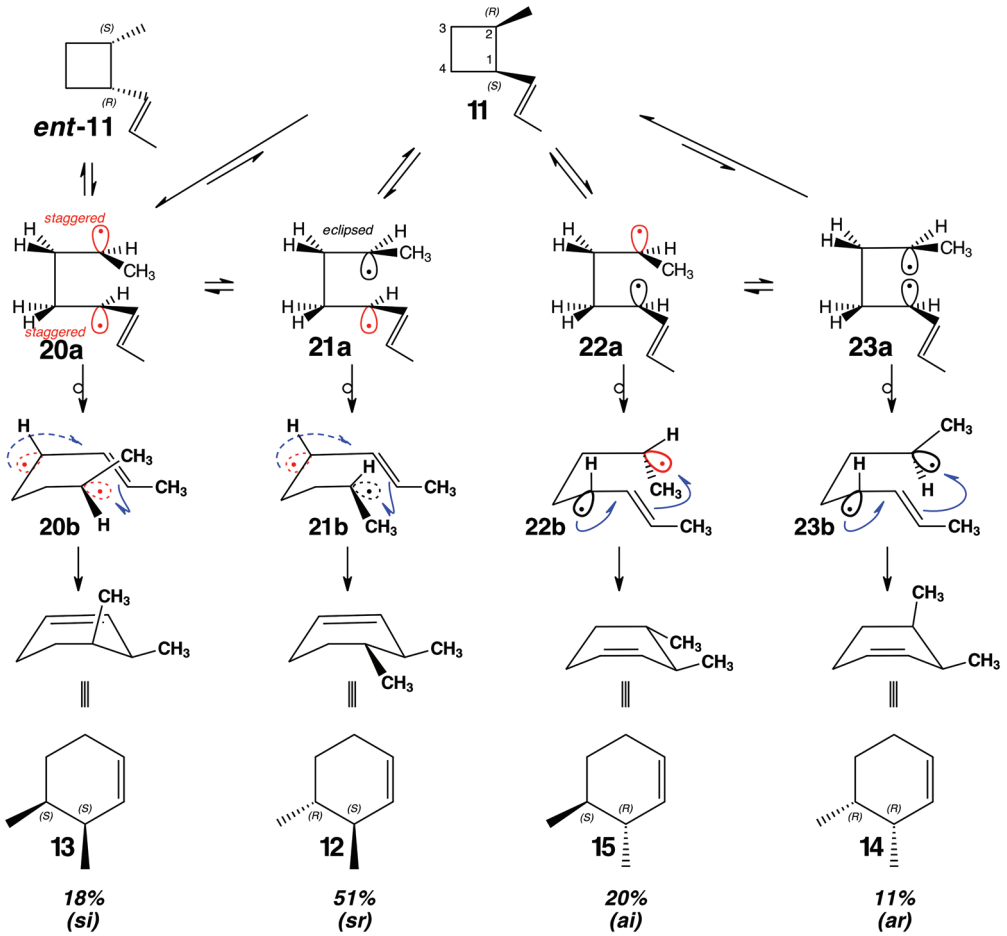
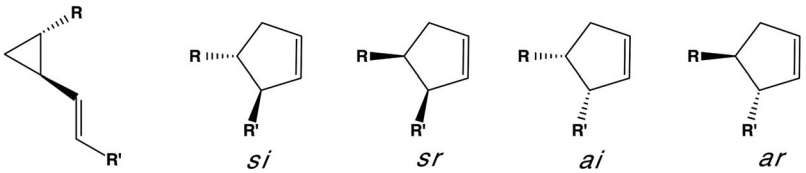


Fig. 9 BBAH analysis of *cis* 2-methyl-1-(*E*)-propenylcyclobutane **11**.

In all cases, the percentage sum of suprafacial rearrangement products (*si* + *sr*) is much higher than that of antarafacial rearrangement products (*ai* + *ar*) and the proportions of symmetry forbidden products (*sr* and *ai*) are non-negligible, results comparable to those for the cyclobutanes (Fig. 8 and 9).

Perhaps one of the more interesting studies from the Baldwin group concerns the thermal rearrangements of a family of trideuterated vinylcyclopropanes where the steric influence of the substituents is minimal (or absent). As shown in Fig. 11, heating trideuterated compound **24** resulted in the formation of all three possible products.[17] Note that, by symmetry, the *si* and *sr* rearrangement pathways yield the same product. Opening cyclopropane **24** *via* double inversion produces diradical **25a**, which can cyclize *via* **25b** to produce *si* product **29**. The same product (*i.e.* **30**) can be obtained by opening **24** with single inversion to produce diradical **26a**, which can cyclize *via* **26b** to produce *sr* product **30** (same as **29**) in 63% yield overall for both routes. Both **25a** and **26a** can be interconverted by Walden inversion at their primary alkyl center. The other possible diradical is **27a** (*i.e.* single inversion), which can cyclize *via* **27b** to produce *ai* product **31**. Of course, diradical **28a** is postulated to recyclize most readily to cyclopropane **24** or perhaps undergo primary radical inversion to produce **27a**. Overall, the BBA hypothesis does account for considerable amounts of *si* + *sr* product **29** (**30**) because the allyl radical in **25a** and **26a** is generated in the preferred staggered conformation.

The distinction between the *si* and *sr* routes cannot be made as both products are the same (**29** = **30**). Fortunately, the *cis* alkene isomer **33** was also prepared and subjected to thermolysis. Its analysis allows one to deconvolute the two mechanistic routes that lead to **29** and **30** (Fig. 12). First, we note that the total percentage of **29**/**30** from heating cyclopropane **24** is exactly the same as the percentage sum of **31** + **32** from heating cyclopropane **33**, while the percentage sum of **31** + **32** from heating cyclopropane **24** is exactly the same as the total percentage of **29**/**30** from heating cyclopropane **33**. In other words, the two series of experiments gave the same proportion of suprafacial over antarafacial products and permit the four reaction pathways to be deconvoluted. This is possible because **24** and **33** correspond to the same molecule except for the position of deuterium labels, which do not have a significant effect on the fragmentation pathways. Accordingly, we conclude that the percentages of product **29**/**30** from the rearrangement of **24** to be 40% and 23%, respectively. By the



R	R'	si	(si+sr)	sr	ai	(ai+ar)	ar
D	D	40	(63)	23	24	(37)	13
CH_3	D	55	(73)	18	13	(28)	15
CN	CH_3	54	(65)	11	22	(35)	13
CH_3	CH_3	65	(79)	22	5	(13)	8
CH_3	Ph	60	(79)	19	11	(21)	10
d5-Ph	D	58	(82)	24	10	(18)	8
Ph	CH_3	44	(69)	25	11	(31)	20
Ph	Ph	67	(64)	17	4	(16)	12

Fig. 10 Relative product percentages for the thermal rearrangement of selected vinylcyclopropane derivatives (extracted from ref. 15).

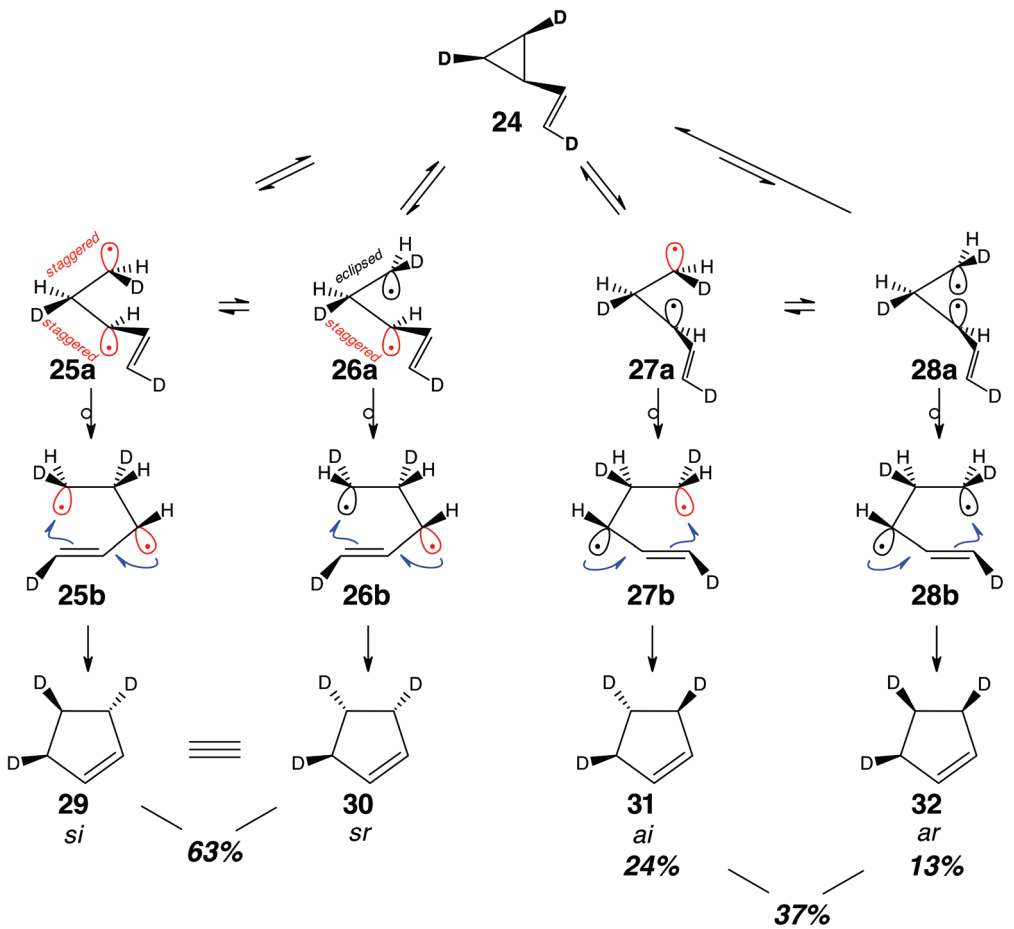


Fig. 11 Thermolysis of *trans* trideuterated vinylcyclopropane **24**.

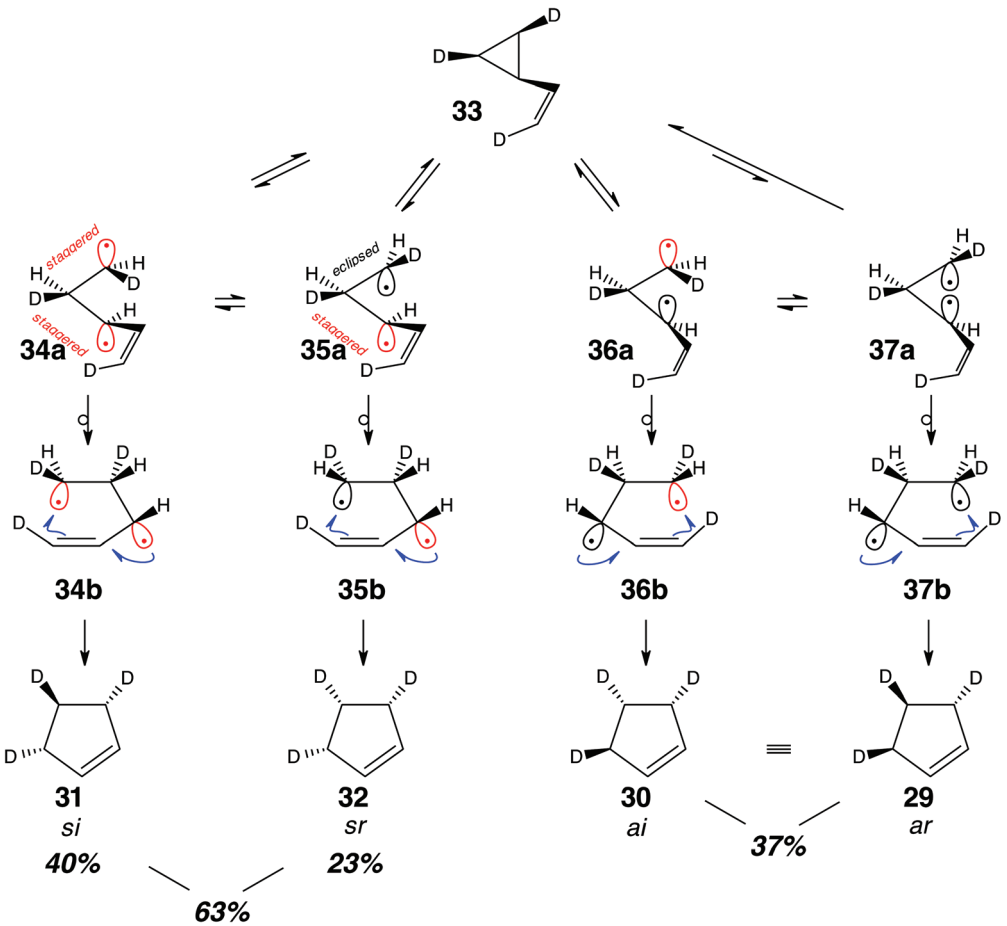


Fig. 12 Thermolysis of *cis* trideuterated vinylcyclopropane **33**.

same analysis, we conclude that the percentages of product **29**/**30** from the rearrangement of **33** to be 13% and 24%, respectively. Once again, the preferred diradical intermediates **34a**/**35a** (as well as **25a**/**26a**) are predicted to have a staggered allyl radical, and the *si*/*sr* product ratio is predicted by a slight preference for a staggered conformation about the primary radical center in **34a** (**25a**).

Thermal rearrangement of bicyclic derivatives. Other well-known studies of such [1,3]-alkyl shifts come from the classic thermal rearrangements of bicyclo[3.2.0]hept-2-ene, bicyclo [4.2.0]oct-2-ene, and bicyclo[2.1.1]hex-2-ene derivatives. These experiments were again carried out to test the W–H rules, which predicted that these thermolyses, if concerted, should take place *via* a suprafacial mode with inversion of configuration at the migrating carbon. Several of these compounds, including their *si*/*sr* rearrangement product ratios, are summarized in Fig. 13.

For instance, although the rearrangement of compound **38** (Fig. 14) in the *si* fashion (*si*/*sr* = 19) was viewed by some as another example of the W–H rules in action, the degree of inversion in other substituted derivatives suggests otherwise.[18–24] Indeed, all compounds having an *exo*-like CH_3 group (**40**, **42**, **44** and **46**) rearranged primarily *via* the suprafacial inversion pathway. On the other hand, the *endo*-like isomers **41** and **43** favored the suprafacial pathway with retention of configuration. For the thermolysis of **47**, the *si*/*sr* ratio was only 2.2. The thermolysis of *endo* **45** did take place but did not yield any of the *si* or *sr* rearrangement products.

Rationalizing this series of experimental results by the BBA hypothesis can be exemplified by considering *exo* and *endo* isomers **42** and **43** (Fig. 15) *via* their four respective pyramidalized diradicals. In the first mode, homolytic opening of **42** without inversion of configuration at C1 and C7 produces diradical **A**. But again, **A** is more readily disposed to recyclize to **42** due to the diradical geometry and the fact that both radical centers are eclipsed with respect to their adjacent CC bond (*i.e.* C5–C1 and C6–C7). In the second mode, bond cleavage with inversion of configuration at C7 would generate diradical **B**, which can only lead to *endo* isomer **43** by 180° rotation of the side-chain (*i.e.* C6–C7) unless Walden inversion to **A** were to occur. Regardless, we note that for both **A** and **B**, the allyl radical does not have the appropriate antiperiplanar orientation for the suprafacial [1,3]-rearrangement to the C3 position. In the third mode, **42** can produce diradical **C** by bond cleavage with inversion of configuration at C1, which does have the appropriate allyl radical configuration for the supra-

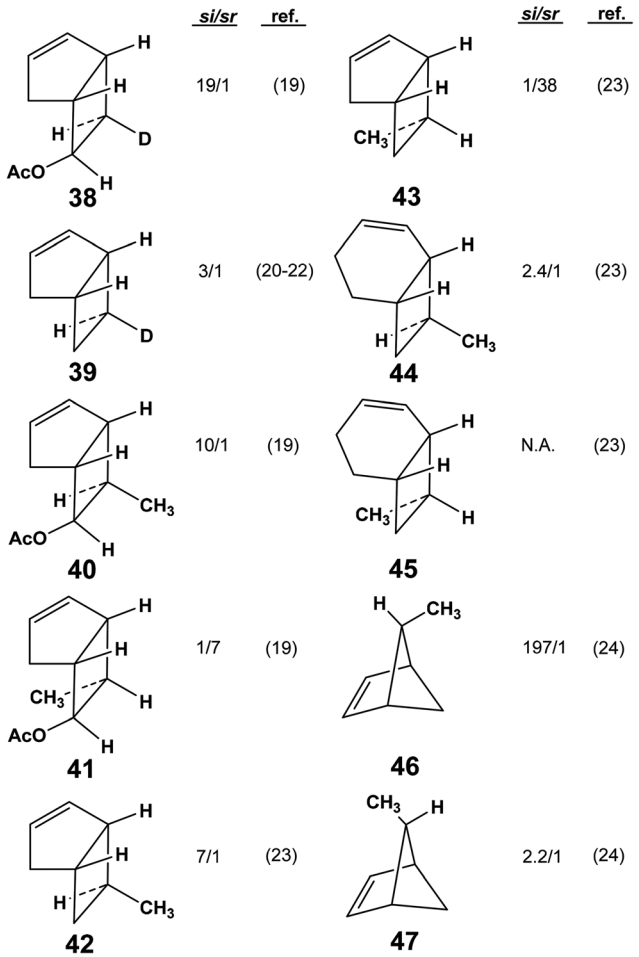


Fig. 13 Thermal rearrangement of bicyclic compounds.

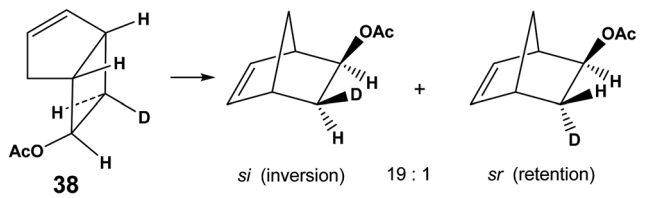


Fig. 14 Thermal rearrangement of compound **38**.

facial [1,3]-rearrangement by simple shearing motion of the side-chain to produce the *sr endo* product **48**. Finally, in the fourth mode, **42** can produce diradical **D** with inversion at both C1 and C7, staggering their adjacent CC bond (*i.e.* C5–C1 and C6–C7). Both **C** and **D** have the appropriate allyl radical geometry for the suprafacial [1,3]-rearrangement but **D** is more likely to form kinetically because the alkyl radical at C7 staggers the C6–C7 bond. Indeed, the *exo* compound **49** is the major product observed experimentally, corresponding to the pathway involving diradical **D**.

The thermolysis of the bicyclo[3.2.0]heptane isomer **43** containing an *endo*-like methyl group at C7 (Fig. 15) can now be examined bearing in mind that rearrangement occurs primarily with retention. We dismiss pathways **A** and **B** on the basis of their improper allyl radical geometry. The rearrangement of **43** *via* diradical **C** (eclipsed at C6–C7) would yield the *exo* product **50**. On the other hand, rearrangement *via* diradical **D** should be less favored because of severe steric repulsion between the endocyclic methyl group (R_1 = Me in **D**) and the ring. As a result, **43** should rearrange preferably *via* diradical **C** to yield the *exo* isomer **50**, in accord with experiment.

The rearrangement of **42** and **43** yielding the same *exo* product but through their respective *si* and *sr* pathways is summarized in Fig. 16. The preferred generation of staggered allyl radical **E** from compound **42** accounts for the *si* pathway, and formation of the *exo* product. For compound **43**, the corresponding staggered allyl radical **F** suffers from steric repulsion between the methyl group and the ring so the reaction transits to the eclipsed structure **G**, ultimately forming the same *exo* product.

Thermal rearrangement of tricyclic derivatives. Baldwin, Leber and co-workers[25] recently carried out the thermolysis of three tricycles containing a five-, a six- and, a seven-membered ring fused to the bicyclo[4.2.0]oct-2-ene, *i.e.* **54**, **57**, and **60**, and compared the results to those of 8-*exo*-methyl bicyclo [4.2.0]oct-2-ene **44** (Fig. 17). This could be coincidental but the *si*/*sr* product ratios are very similar for the thermolysis of **44**, **57**, and **60** (2.1 to 2.4) but no *si* product was obtained from **54**. Compound **57** with two six-membered rings fused to the cyclobutane ring can be analyzed by the BBA hypothesis (Fig. 18). There are again four different modes of producing pyramidalized diradicals. As before, we exclude the homolytic opening that does not invert any of the C1 or C2 configurations. However, **57** can form diradical **64** through two inversions, diradical **65** through inversion at C2, and diradical **66** by inversion at C1. Upon reclosure, **64** and **65** will lead to *trans* isomer **58** and *cis* isomer **59**, respectively. The *si*/*sr* ratio of 2.4 (*i.e.* **58**/**59**) is identical to that of the rearrangement of bicyclic **44** despite the fact that *trans* isomer **58** is estimated by calculation to be 6.4 kcal mol^{-1} higher in energy than the *cis* isomer **59**.[25] On the other hand, the *exo* and *endo*-methyl bicyclo [2.2.2]oct-2-ene isomers **52** and **53** resulting from the pyrolysis of compound **44** do not have such a large energy difference. The third mode of cleavage of tricyclic **57** leads to diradical intermediate **66** by inversion at C1[5] which fragments to cyclohexene and cyclohexadiene in 42% yield. There is also the possibility that **66** can reclose to form the *trans-cis–cis* epimer of **57** but this is not observed.

Compound **60** containing the 7-membered ring can be analyzed in the same manner. The *si*/*sr* ratio of 2.1 is close to that observed for **44** and **57** despite the fact that the *trans* isomer **61** is only 2.4 kcal mol^{-1} less stable than the *cis* isomer **62**.[25]

One can note also that the third diradical which arises from inversion at C1, leads to fragmentation (18%) and to the corresponding *cis–cis-trans* isomer **63** by recyclization, the C8 epimer of tricycle **60** (49%). It was also found[25] that isomer does not go back to the *cis* isomer **60** upon heating but undergoes fragmentation instead. This process could occur through

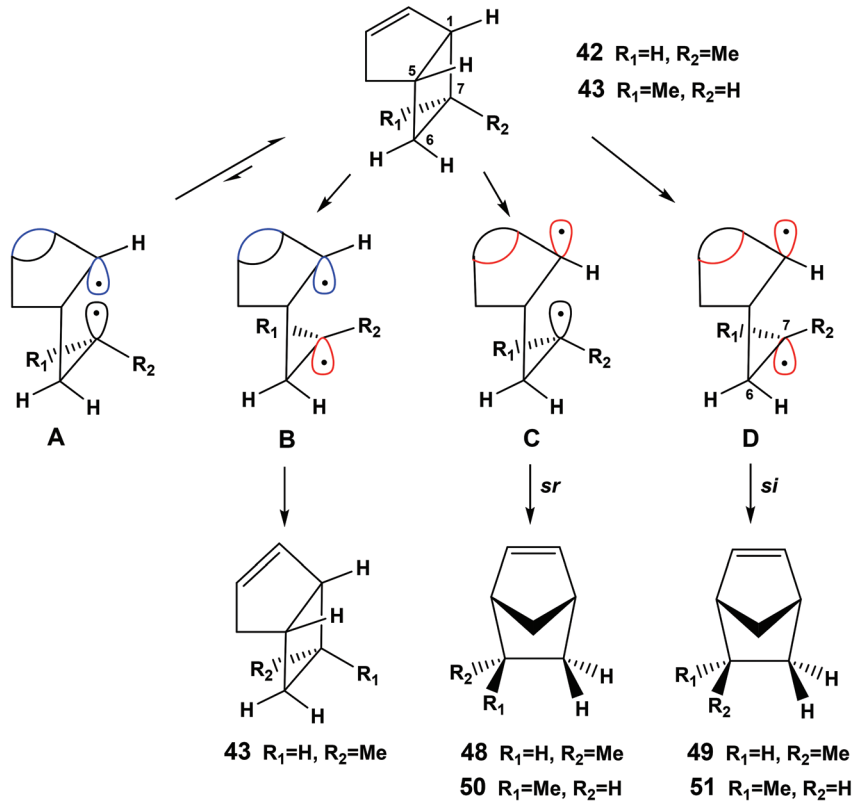


Fig. 15 BBAH analysis of thermolysis of *exo*-**42** and *endo*-**43**.

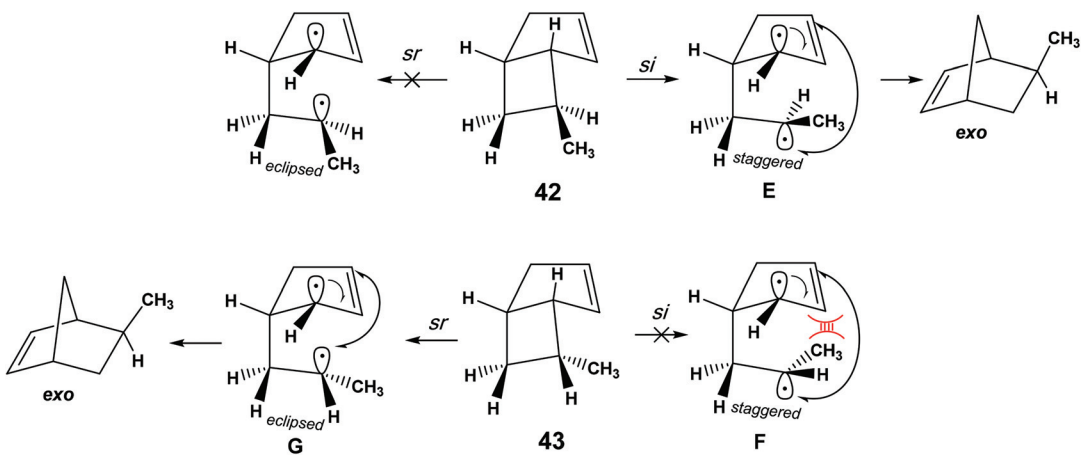


Fig. 16 Rearrangement of **42** and **43** to the *exo* isomer.

diradical **67** (*via* two inversions) which could then rotate to the more stable conformer **68** in order to fragment to *cis*-cycloheptene and 1,3-cyclohexadiene (Fig. 19).

It remains to analyze tricycle **54**, which contains a five-membered ring, in a similar manner. Two inversions at C1 and C2 will produce a diradical that cannot produce tricycle **55** because of the *trans* junction at the five-membered ring. Isomer **55** is calculated to be 23 kcal mol^{-1} higher in energy than the *cis* isomer **56**.[25] If this diradical is produced, it will certainly invert preferably at C1 to yield *cis* isomer **56** instead. Of course, **54** can produce a diradical with one inversion at C2 to form *cis* isomer **56** in 32% yield. This explains why the *si*/*sr* ratio is zero. The 68% of fragmentation to cyclopentene and 1,3-cyclohexadiene can also be explained through the third diradical due to inversion at C1 in a manner similar to that discussed for the tricycle **57** (*cf.* **66**).

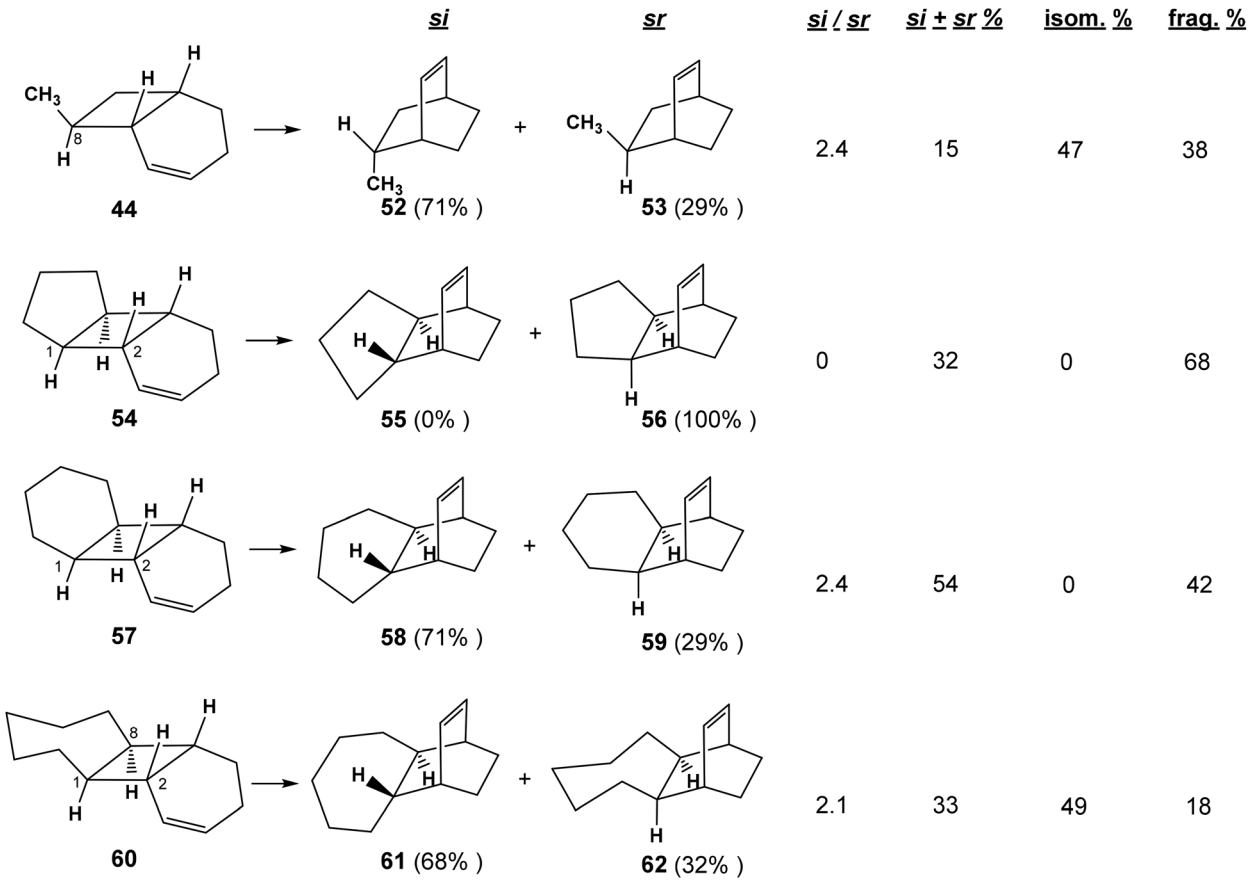


Fig. 17 Thermal rearrangement of bicyclic and tricyclic compounds.

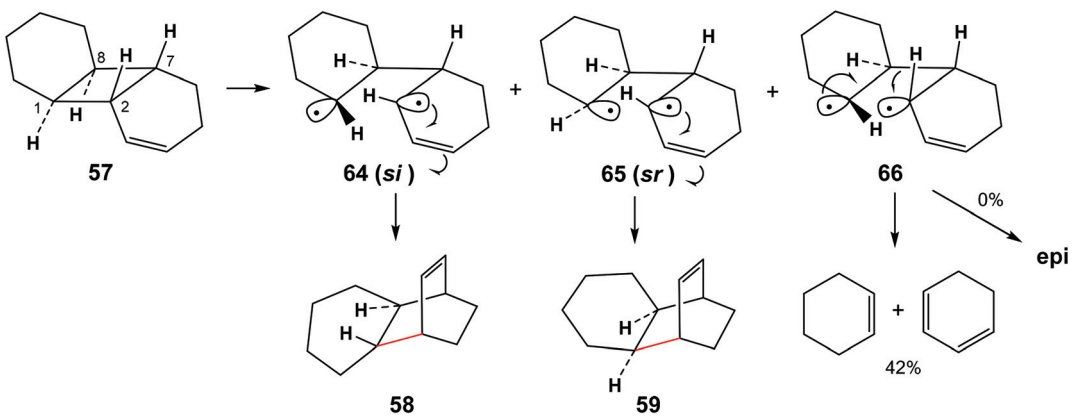


Fig. 18 BBA analysis of tricycle **57**.

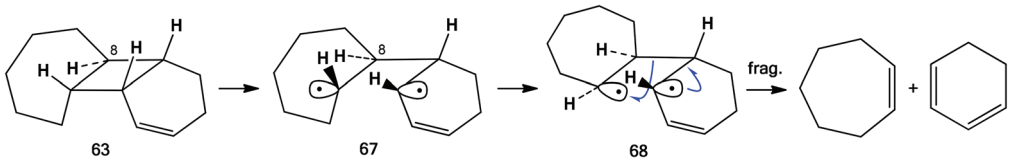


Fig. 19 Fragmentation of tricycle **63**.

Conclusion

The [1,3]-sigmatropic carbon rearrangements of dipropenylcyclobutanes, methylpropenylcyclobutanes, vinylcyclopropanes, bicyclo[3.2.0]hept-8-enes, bicyclo[4.2.0]oct-2-enes, bicyclo[2.1.1]hex-2-enes and tricyclic derivatives of bicyclo[4.2.0]oct-2-ene, which all involve allyl radical intermediates, have been analyzed using the BBA hypothesis. For these 28 thermolysis reactions, the generation of pyramidalized allyl and alkyl diradicals produced in staggered and/or eclipsed conformations accounts for the preference of suprafacial rearrangement pathways as well as the extent of inversion or retention of configuration at the migrating carbons.

Baldwin and Leber concluded:[25b] "recent experimental and theoretical investigation 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".[10b,25b,26–28] We conclude that the nature of the exit channel and the associated product distributions can be qualitatively accounted for by the BBA hypothesis. The BBA hypothesis has a strong and general predictive power for complex rearrangement pathways while invoking classic organic chemistry concepts; it should be useful to a broad audience of chemists due to its simplicity of application.

However, our analysis does assume that alkyl and particularly allyl radicals, when produced from chiral molecules, have a propensity to pyramidalize. This can be understood by postulating that the instantaneous allyl radical orbital has to be pyramidal in order to be oriented antiperiplanar to one of the bent bonds and to allow for delocalization to occur (Fig. 2).

The next step is to obtain additional experimental evidence that pyramidal allyl radicals can be produced and have a transient existence. Work in this direction is now in progress.

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