The Influence of Intramolecular Dynamics on Branching Ratios in Thermal Rearrangements

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1- and 2-phenylbicyclo[2.1.1]hex-2-enes-*5-d* undergo thermal rearrangement to give products, differing only in the location of the deuterium, in a ratio of about 9:1, but with identical activation enthalpies. Similarly, optically active *trans*-2-methyl-1-(*trans*-2-phenylethenyl)cyclopropane is found to rearrange to enantiomeric methylphenylcyclopentenes that are formed in a 5.9:1 ratio but with virtually identical activation enthalpies. Barring repeated coincidence, these results do not seem to be explicable within the framework of the statistical theories of unimolecular kinetics such as RRKM theory, transition state theory, and variational transition state theory. The possible influence of dynamic effects in these and other unimolecular reactions is discussed.

Studies that we originally designed to elucidate substituent effects in hydrocarbon rearrangements have lead, instead, to observations that appear to be difficult to reconcile with the commonly employed models for describing unimolecular reactions (RRKM theory, transition state theory, and variational transition state theory). This paper describes the details of the experimental work, highlights the apparent discrepancy with the expectations based on these kinetic models, and advances some tentative explanations for the observed behavior.

The reactions that have been investigated are of two classes: the first consists of rearrangements of derivatives of bicyclo[2.1.1]hex-2-ene-*5-d* (**1**) (a formal retrovinylcyclopropane rearrangement) and the second is a ring expansion of *trans*-2-methyl-1-(*trans*-2-phenylvinyl)cyclopropane (**2**) (a forward vinylcyclopropane rearrangement, see Scheme I).

Synthesis and Stereochemical Characterization of Reactants. Three bicyclo[2.1.1]hex-2-enes-*endo*-*5-d* were prepared: the parent and the 1- and 2-phenyl derivatives. In addition, compounds were synthesized with exo isotopic labels. The syntheses have been reported previously[1] and so will not be repeated here, although experimental details are given in the final section of this paper.

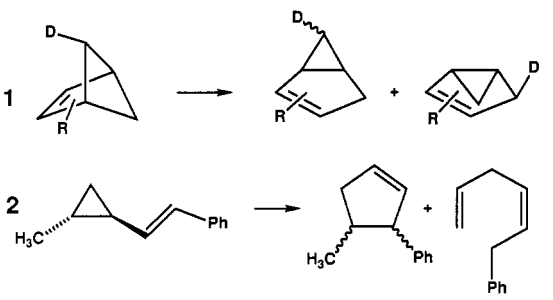
Stereochemical assignments are deducible from the synthetic sequences and were confirmed by lanthanide shift experiments on the bicyclo[2.1.1]hexan-2-one derivatives. In the ^2H NMR spectrum, the resonance assigned to the endo deuterium moved downfield at a rate 1.5 times higher than the resonance assigned to the exo deuterium, upon addition of increasing amounts of Eu(fod)$_3$.

Racemic **2** was easily prepared by reduction of *trans*-2-methylcyclopropanecarboxylic acid followed by Wittig reaction with benzylidenetriphenylphosphorane. This was not a satisfactory route to the optically active reactant, however, since *trans*-2-methylcyclopropanecarboxylic acid is very difficult to resolve. Two routes to optically active **2** were developed. While the second (Scheme III) was the more efficient, comparison of the two allowed confirmation of the absolute configuration of the reactant.

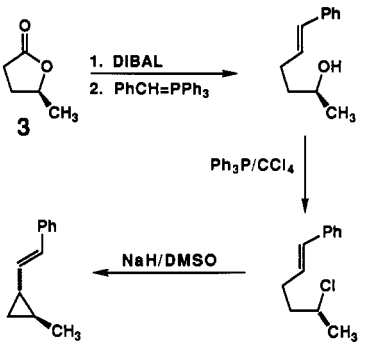
The optically active lactone **3**, of known absolute configuration, had been prepared previously.[2] In the final ring closure step of Scheme II only the desired product with the trans configuration about the cyclopropane ring is shown, although in fact the major product had the cis configuration (2.8:1 cis:trans).

The more efficient route shown in Scheme III employed the asymmetric Simmons–Smith reaction of Yamamoto.[3] The absolute configuration of the final product was predictable[3] but was confirmed by comparison with a sample prepared by the route in Scheme II.

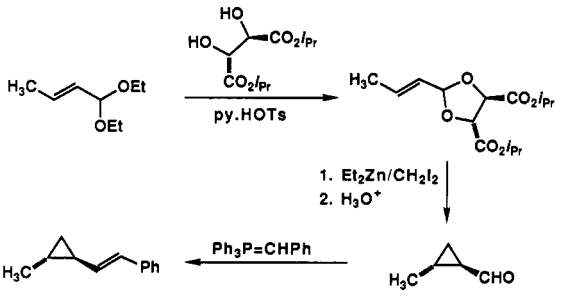
Scheme I



Scheme II



Scheme III



(1) Newman-Evans, R. H.; Carpenter, B. K. *Tetrahedron Lett.* **1985**, *26*, 1141. The preliminary results on the rearrangements have also been communicated: Newman-Evans, R. H.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 7994.

(2) Mori, K. *Tetrahedron* **1975**, *31*, 3011.

(3) Arai, I.; Mori, I.; Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 8254.

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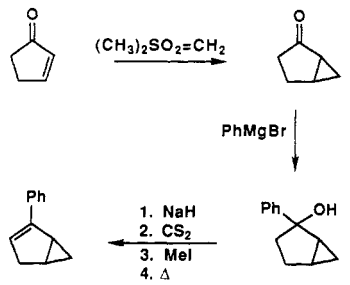
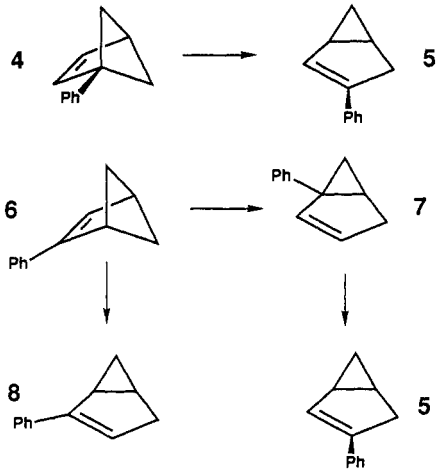
Scheme IV. Independent Synthesis of 2-Phenylbicyclo[3.1.0]hex-2-ene



Independent Synthesis and Stereochemical Characterization of Products. The thermal rearrangement of bicyclo[2.1.1]hexene has been studied previously.[4] The product is known to be bicyclo[3.1.0]hex-2-ene. The rearrangement of 1-phenylbicyclo[2.1.1]hexene (**4**) was found to yield only 3-phenylbicyclo[3.1.0]hex-2-ene (**5**), which was identified by the presence of only a single vinyl resonance in the ^{1}H NMR spectrum and differentiated from the 2-phenyl isomer (**8**) by the independent synthesis of **8** outlined in Scheme IV.

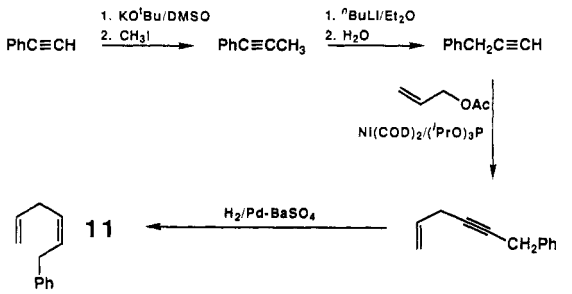


The rearrangement of 2-phenylbicyclo[2.1.1]hexene (**6**) was more complex. The major product was shown to be 1-phenylbicyclo[3.1.0]hex-2-ene (**7**) by the presence of two vinyl hydrogens in the ^{1}H NMR, one appearing as a doublet and the other as a doublet of multiplets. This compound was not stable to the reaction conditions, however, and slowly rearranged to 3-phenylbicyclo-[3.1.0]hex-2-ene (**5**), identified by comparison with the product of rearrangement of **4**. The minor product was identified as 2-phenylbicyclo[3.1.0]hex-2-ene (**8**) by independent synthesis (Scheme IV).

The endo and exo hydrogens on C6 of the various bicyclo[3.1.0]hexenes could be identified in the ^{1}H NMR spectrum by their coupling constants to the bridgehead hydrogens, following the analysis of Roth and Friedrich.[5] This, in turn, made it possible to identify the peaks in the ^{2}H NMR for the products of rearrangement of the deuterium-labeled bicyclo[2.1.1]hexenes.

Racemic **2** was found to give *cis*- and *trans*-4-methyl-3-phenylcyclopentenes (**9** and **10**, respectively) as well as (*Z*)-6-phenyl-1,4-hexadiene (**11**) upon pyrolysis. It was further discovered that **11** could be converted to **9** and **10** on extended heating, and so an independent synthesis of

Scheme V. Independent Synthesis of (*Z*)-6-Phenyl-1,4-hexadiene



the diene was sought. The one that worked best is shown in Scheme V.

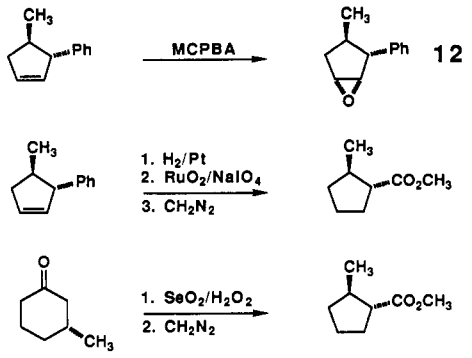
The stereoisomers **9** and **10** were identified by nuclear Overhauser experiments in the ^{1}H NMR. In particular, irradiation of the methyl resonance resulted in enhancement of the cis hydrogens on C3 and C5 in **10**, whereas compound **9** exhibited strong enhancement only for a hydrogen on C5 under similar circumstances. Comparison of the chemical shifts for the hydrogens in **9** and **10** with those reported for the cis and trans isomers of 3,4-dimethyl- and 4-*tert*-butyl-3-methylcyclopentenes[6] supported the stereochemical assignments.

Pyrolysis of optically active (1*R*,2*R*)-**2** resulted in formation of both enantiomers of **9** and **10**, as well as some of the diene **11** and the opposite enantiomer of **2**. Quantification of the enantiomers of **2** was achieved by use of the optically active mixed shift reagent Ag(fod)/Pr(hfc)$_3$ introduced by Offermann and Mannschrechk.[7] Addition of 1.3 equiv of this reagent to a $CDCl_3$ solution of the enantiomers of **2** resulted in splitting of the doublet for the hydrogen on the phenyl-bearing carbon into a pair of doublets in the ^{1}H NMR spectrum. Base-line resolution could be achieved if a Gaussian multiplier was applied to the FID. Concerns that this might introduce a systematic error into the integration were addressed by preparing a calibration curve of integration ratios vs enantiomer ratios using standard mixtures of racemic and (1*R*,2*R*)-**2**. The calibration curves were found to be independent of total concentration. Unfortunately, the mixed shift reagent was not effective at separating resonances for the enantiomers of the cyclopentenes. Chemical modification of the cyclopentenes by epoxidation or by conversion of the phenyl group into a benzoyl group (through ozonolysis and treatment with phenyllithium), followed by addition of the more common optically active shift reagent Eu(hfc)$_3$, were equally ineffective. Eventually it was discovered that an optically active capillary gas chromatography column (Chrompack liquid phase XE-60-s-Val-α-PEA) would allow separation of the enantiomers of the epoxide **12**, prepared from **10**. Unfortunately, no technique investigated would allow determination of the relative concentration of the enantiomers of **9** or its derivatives.

The absolute configurations of the enantiomers of **10** were determined by conversion to *trans*-2-methylcyclopentanecarboxylic acid methyl ester, which could be in-

(4) Frey, H. M.; Hopkins, R. E.; O'Neal, H. E.; Bond, F. T. *J. Chem. Soc. D* **1969**, 1069.
(5) Roth, W. R.; Friedrich, A. *Tetrahedron Lett.* **1969**, 2607.
(6) Hanselaer, M.; Samson, M.; Vandewalle, M. *Tetrahedron* **1978**, *34*, 2393.
(7) Offermann, W.; Mannschreck, A. *Tetrahedron Lett.* **1981**, *22*, 3227.

Scheme VI. Transformations Used for Assignment of Absolute Configuration and Determination of Optical Purity of *trans*-4-Methyl-3-phenylcyclopentene Products



dependently prepared from 3-methylcyclohexanone of known configuration, as shown in Scheme VI.

Kinetics and Stereochemistry of Rearrangements. The pyrolyses of bicyclo[2.1.1]hexene and its phenyl derivatives **4** and **6** were carried out in isooctane solution. The activation parameters for the parent compound were determined by capillary gas chromatographic analysis of reactions conducted at 130.1, 139.8, 144.6, 165.8, 170.4, and 175.3 °C. The results were: E_a = 35.68 ± 0.26 kcal/mol, log A = 14.24 ± 0.13, $\Delta H^{\ddagger}$ = 34.83 ± 0.26 kcal/mol, $\Delta S^{\ddagger}$ = 3.91 ± 0.61 cal/(mol K). These results are very similar to those reported by Frey[4] for the rearrangement of bicyclo[2.1.1]hexene in the gas phase, viz. E_a = 35.17 ± 0.14 kcal/mol, log A = 13.95 ± 0.07, $\Delta H^{\ddagger}$ = 34.29 ± 0.14 kcal/mol.

The pyrolysis of **4** was found to occur exclusively with the cleavage of the bonds to the phenyl-bearing carbon, affording 3-phenylbicyclo[3.1.0]hexene (**5**). The rate constants for this process were determined at 82.6, 92.2, 101.4, 109.7, 120.0, 125.2, and 133.5 °C. The results could be fit to the activation parameters: E_a = 29.60 ± 0.22 kcal/mol, log A = 13.32 ± 0.13, $\Delta H^{\ddagger}$ = 28.85 ± 0.23 kcal/mol, $\Delta S^{\ddagger}$ = −0.04 ± 0.60 cal/(mol K).

Analysis of the results from pyrolysis of **6** was complicated by the fact that products derived from C1–C5 and C4–C5 cleavage were observed, and that the major product (1-phenylbicyclo[3.1.0]hexene (**7**) from C4–C5 cleavage) was unstable to the reaction conditions, slowly rearranging to give the 3-phenyl isomer **5**. The rate constants for appearance of **7** + **5** and **8** were determined at 130.1, 139.8, 152.0, 160.2, 169.4, 175.4, and 181.4 °C, yielding the following activation parameters.

Formation of **7** + **5** (C4–C5 cleavage of **6**): E_a = 33.51 ± 0.23 kcal/mol, log A = 13.37 ± 0.12, $\Delta H^{\ddagger}$ = 32.66 ± 0.23 kcal/mol, $\Delta S^{\ddagger}$ = −0.05 ± 0.53 cal/(mol K). Formation of **8** (C1–C5 cleavage of **6**): E_a = 36.52 ± 0.28 kcal/mol, log A = 13.74 ± 0.14, $\Delta H^{\ddagger}$ = 35.67 ± 0.28 kcal/mol, $\Delta S^{\ddagger}$ = 1.64 ± 0.64 cal/(mol K).

The stereochemistry of the rearrangement was investigated for each compound by using the bicyclo[2.1.1]-hexene stereoselectively labeled with deuterium at C5. The products were analyzed by ^{2}H NMR, integration of which allowed quantification of the ratio of label isomers. The ratio of migration of labeled and unlabeled methano bridges could be used to deduce an intramolecular isotope effect. For those products derived from migration of the labeled bridge, the ratio of exo to endo deuterium could be used to calculate the retention:inversion ratio for the rearrangement. In each case reactants were recovered from partial reaction and analyzed by ^{2}H NMR to check for epimerization; none was detected. Again, compound **6** presented the most challenging analysis. The minor product (**8**) was formed in too small a quantity for the stereochemistry of its rearrangement to be determined. The major product (**7**) was found to undergo slow epimerization at C6 under the reaction conditions, and so the intrinsic stereochemistry of its formation had to be deduced by correcting for this secondary process. In fact the apparent epimerization is probably caused by reversible cleavage of the C1–C5 bond (weakend in this case by the attached phenyl group). A similar mechanism is postulated for isomerization of **7** to 3-phenylbicyclo[3.1.0]hexene (**5**). The bicyclo[3.1.0]hexenes derived from the deuterium labeled analogues of parent bicyclo[2.1.1]hexene and 1-phenylbicyclo[2.1.1]hexene were found to be stable to the reaction conditions.

Table I. Intramolecular Isotope Effects and Stereoselectivities for Rearrangement of Derivatives of Bicyclo[2.1.1]hexene-*5-d*

compound (isotope effect)	temp, °C	% retention
bicyclo[2.1.1]hexene (1.07 ± 0.03)	135.2	1.9 ± 0.4
	165.7	2.7 ± 0.3
	197.0	6.9 ± 0.5
1-phenylbicyclo[2.1.1]hexene (1.25 ± 0.05)	80.0	9.1 ± 0.3
	110.5	9.3 ± 0.4
	140.6	9.2 ± 0.4
	165.7	8.8 ± 0.3
2-phenylbicyclo[2.1.1]hexene (1.26 ± 0.05)	124.9	12.1 ± 0.3
	144.6	11.7 ± 0.6
	160.2	12.7 ± 0.7
	181.3	11.7 ± 0.3

Table II. Activation Free Energies for Conversion to Diene and Ring Expansion of Racemic *trans*-2-Methyl-1-(*trans*-2-phenylethenyl)cyclopropane

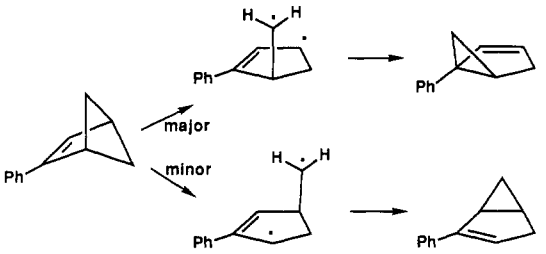
T, °C	$\Delta G^{\ddagger}_1$, kcal/mol	$\Delta G^{\ddagger}_2$, kcal/mol	$\Delta G^{\ddagger}_2 - \Delta G^{\ddagger}_1$, kcal/mol
218.8	40.6	43.4	2.8
220.4	40.8	43.6	2.8
228.9	40.9	43.7	2.8
231.8	40.7	43.5	2.8
240.1	40.7	43.6	2.9
243.6	40.8	43.6	2.8
249.9	40.8	43.7	2.9
256.1	40.8	43.7	2.9
259.5	40.9	43.7	2.8
274.0	40.9	43.7	2.8

The stereoselectivities of the rearrangement and the intramolecular isotope effect for each compound are summarized in Table I.

Pyrolysis of racemic **2** was carried out in sealed tubes in the gas phase. The activation free energies for conversion of **2** to the stereoisomeric cyclopentenes and to diene **11** (which was formed reversibly) were determined by nonlinear least-squares optimization. The results are summarized in Table II. In Table II, $\Delta G^{\ddagger}_1$ corresponds to the activation free energy for conversion of racemic **2** to the diene and $\Delta G^{\ddagger}_2$ corresponds to the activation free energy for conversion to the stereoisomeric cyclopentenes. The differences between the two is seen to be effectively temperature independent, corresponding to a difference in activation enthalpy of 2.5 ± 1.5 kcal/mol and a difference in activation entropy of 0.6 ± 2.9 cal/(mol K).

The activation enthalpy for conversion of **2** to diene **11** was found to be 39.1 ± 2.9 kcal/mol. The activation enthalpy for interconversion of enantiomers of optically active **2** was determined from kinetic measurements at 220.4, 228.9, 240.1, 249.9, and 259.5 °C, and found to be 39.7 ± 3.8 kcal/mol. The activation enthalpies for conversion of (1*R*,2*R*)-**2** to (3*R*,4*S*)-**10** and (3*S*,4*R*)-**10** were respectively 41.9 ± 3.8 and 42.7 ± 2.8 kcal/mol, determined over the

Scheme VII. Explanation of Preferred Regiochemistry for Rearrangement of 2-Phenylbicyclo[2.1.1]hexene



same temperature range. The mixture of enantiomers of **10** was converted to a mixture of enantiomers of *trans*-2-methylcyclopentanecarboxylic acid methyl ester by the route shown in Scheme VI. The ratio of rate constants for formation of the enantiomers of **10** was determined to be 5.9 ± 0.3 over the temperature range specified. The difference in activation enthalpies for the formation of the enantiomeric cyclopentenes determined from the temperature dependence of this ratio was 0.8 ± 1.5 kcal/mol. The uncertainty is lower than that quoted for the individual activation enthalpies because of covariance of errors.

Discussion

The rearrangement of bicyclo[2.1.1]hexene-*5-d* occurs with a strong, temperature-dependent preference for inversion of configuration at the labeled carbon. The stereochemistry is consistent with the results obtained for the 5-methyl analogues studied by Roth and Friedrich.[5] The traditional, and adequate, explanation of this result is that the path of lower activation enthalpy is the Woodward–Hoffmann-allowed [1,3] sigmatropic shift, which is forced to take place suprafacially and should therefore occur with inversion.[8] The pathway of higher activation enthalpy could be the nominally forbidden suprafacial retention [1,3] shift or it could be a nonpericyclic reaction occurring via a singlet biradical.[9]

The phenyl-substituted bicyclo[2.1.1]hexenes-*5-d* present much more of a problem of interpretation. The temperature-dependence studies indicate that if one wished still to invoke a competition between two mechanisms to explain the product ratios, then the pathways could have activation enthalpies that differed by no more than 100 cal/mol for the 1-phenyl isomer or 300 cal/mol for the 2-phenyl isomer. This seems like a rather implausible coincidence, especially given the fact that the overall effect of the phenyl substituent on the activation enthalpy is about 6 kcal/mol for the former and only 2 kcal/mol for the latter. It appears that one must invoke, in each case, a mechanism with a single rate-determining step and an intermediate that is capable of affording both stereoisomers of the product. The obvious choice is a mechanism occurring via a singlet biradical. The biradical mechanism has the added virtue of rationalizing the regiochemistry of rearrangement of **6**, which gives what would be expected to be the less stable isomer as the major product. A reasonable explanation would be that this is the product derived from the more stable biradical, i.e. the one in which the phenyl can stabilize an unpaired electron by delocalization (see Scheme VII).

The problem with the biradical mechanism, of course, arises when one tries to explain the stereochemistry of the rearrangement. If the biradical lived long enough to reach complete equilibrium, the product ratio should be very nearly 1:1, since the isomers differ only in the location of an isotopic label. The possibility that the product ratio reflects some hitherto unprecedented isotope effect can be dismissed because experiments conducted with exo labeled reactants were found to give inversion:retention ratios that were indistinguishable from those of the endo epimers.

So then, one must conclude that a biradical is involved but that it does not have time to explore all of its region of the potential energy surface before collapsing to products. Under these circumstances, what might determine the observed stereochemistry? A commonly invoked concept is the Principle of Least Nuclear Motion.[10] The argument underlying this principle is that one can treat a molecule as if it were an assembly of Hook's-Law springs. Since one knows that for such a spring the potential energy increases as the square of the displacement from the equilibrium position, one can argue that for a molecule the increase in potential energy upon going from reactant to transition structure will similarly depend on the displacements of the nuclei from their starting positions. The smaller the sum of squared displacements (weighted by appropriate force constants) the smaller the potential energy increase and hence the more favorable reaction. The key feature of the argument for the present purposes is that it is really an attempt to analyze barrier heights on the potential energy surface. As such, its effect ought to be seen primarily in the activation enthalpies of the competing reactions. But that cannot be the explanation for the current data. If the biradical had significantly different barrier heights for closure to the two products, the product ratio would be temperature dependent. The barrier height difference would need to be about 1.8 kcal/mol in order to explain the product ratio, and this is clearly not in agreement with the 0–0.3 kcal/mol difference determined experimentally.

The Principle of Least Nuclear Motion is not the only explanation so eliminated—none of the common steric or electronic arguments for restricted rotation or other selective behavior in biradicals can be used in this case because they are all statements about barrier heights on the potential energy surface.

An alternative explanation that merits examination is derived from variational transition-state theory.[11] In this theory it is recognized that the position of minimum flux (transition state) on a free energy surface need not coincide with the position of maximum potential energy along the reaction coordinate. In the case of certain biradicals it has further been pointed out that an intermediate that appears to have no potential energy barrier to decomposition can still be entropically bound.[12] The problem with using such arguments to explain the current data is that the *symmetry* of the free energy surface could differ from that of the potential energy surface only if there were a significant secondary isotope effect—a possibility that was excluded by comparison of the exo- and endo-labeled reactants. Thus changing the position or height of free energy barriers

(8) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.

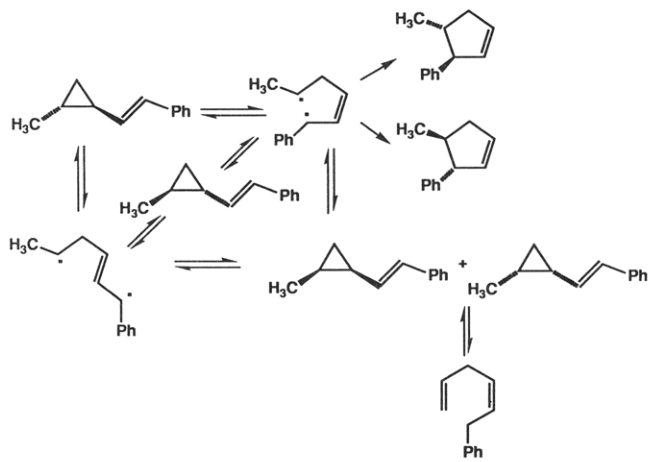
(9) For evidence suggesting that the forbidden pericyclic mechanism has lower activation energy than the biradical mechanism in [1,3] sigmatropic shifts, see: Berson, J. A.; Dervan, P. B.; Malherbe, R.; Jenkins, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5937 and references therein. For evidence suggesting the reverse, see: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; pp 139–140.

(10) Hine, J. *Adv. Phys. Org. Chem.* **1977**, *15*, 1.

(11) (a) Truhlar, D. G.; Garrett, B. C. *Acc. Chem. Res.* **1980**, *13*, 440. (b) Hase, W. L. *Acc. Chem. Res.* **1983**, *16*, 258.

(12) Doubleday, C., Jr.; Camp, R. N.; King, H. F.; McIver, J. W., Jr.; Mullhally, D.; Page, M. *J. Am. Chem. Soc.* **1984**, *106*, 447.

Scheme VIII. Proposed Mechanism for Rearrangement of (1*R*,2*R*)-2-Methyl-1-(*trans*-2-phenylethenyl)cyclopropane



with respect to the potential energy barriers is of no value in explaining these results.

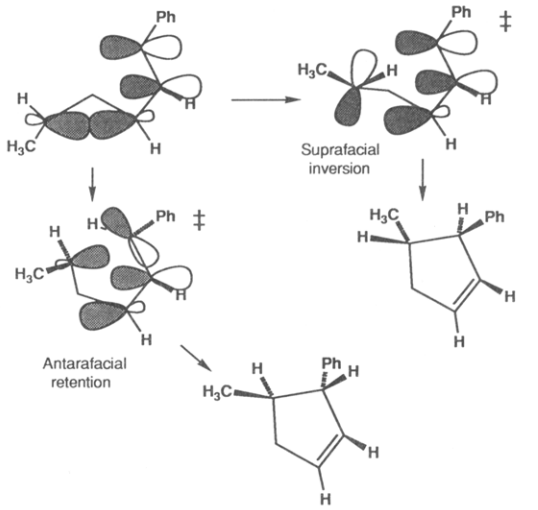
As will be discussed in more detail below, the most convincing explanation of these data, in the view of the present authors, is that the branching ratio in this reaction is largely dynamically determined and that activation parameters derived from statistically based theories like transition-state theory have no physical significance in such reactions.

A similar picture emerges from the vinylcyclopropane rearrangement of **2**. The interconversion of enantiomers of **2** presumably can occur either by the cis or trans biradical (see Scheme VIII). Conversion to diene **11**, which is preceded by a rate-determining trans–cis isomerization, presumably can occur via the same biradicals, and so the apparent activation enthalpy for the enantiomer interconversion and diene formation would be expected to be similar. This was found to be true experimentally, the values being 39.7 and 39.1 kcal/mol, respectively.

If the cyclopentenes were formed from a biradical, it could only be from the cis one, and so the apparent activation enthalpy for their formation need not be the same as that for the other two processes. Indeed, the experimental results suggested it was about 2.5 kcal/mol higher. The activation enthalpies for formation of two enantiomers of a cyclopentene should be the same, however, if the biradical mechanism were correct. Experimentally they differed by 0.8 ± 1.5 kcal/mol. In contrast, a concerted pericyclic mechanism for the formation of the two enantiomers of **10** would lead one to expect very different activation enthalpies since the transition states would have grossly different structures (see Scheme IX). The near identity of the activation enthalpies and the fact that they are close to (or even a little higher than) the activation enthalpy for the known biradical processes of enantiomer interconversion and trans–cis isomerization clearly suggest that this vinylcyclopropane rearrangement occurs via a biradical.

The biradical should be achiral in its equilibrium nuclear geometry, and yet the products are formed with a 5.9:1 ratio of enantiomers. Just as in the case of the phenylbicyclo[2.1.1]hexene rearrangements, then, it seems necessary to invoke a mechanism occurring by a biradical that does not live long enough to achieve its equilibrium nuclear configuration. Again, there is no value in invoking the Principle of Least Nuclear Motion, or any other factor that would provide barriers of different heights for reaction of the biradical, to explain the product ratio because it appears not to be enthalpically determined. Unfortunately,

Scheme IX. Transition Structures for Suprafacial-Inversion and Antarafacial-Retention Rearrangements of (1*R*,2*R*)-2-Methyl-1-(*trans*-2-phenylethenyl)cyclopropane



the inability to resolve the enantiomers of *cis*-cyclopentene **9** precludes determination of overall inversion:retention ratios for this reaction. It is possible, however, to conclude that the formal antarafacial-retention pathway is more favorable than the formal suprafacial-inversion pathway for this reactant. This result is to be contrasted with that for *trans*-1-methyl-2-propenylcyclopropane for which the suprafacial-inversion route is preferred.[13] It is conceivable that the introduction of the phenyl group has driven the reaction all the way over to a biradical mechanism in the case of **2**, whereas at least some components of the transformation are occurring by concerted pericyclic pathways for *trans*-1-methyl-2-propenylcyclopropane; without data on the temperature-dependence of the product ratios in this latter system there is no way to know.

How, then, can the temperature independence of the product ratios be explained for the reactions in the present study, and what is the reason for the preference for inversion of configuration in the rearrangement of the phenyl-substituted bicyclo[2.1.1]hexenes?

The explanation that currently holds favor with the authors is that the rarrangements of the phenyl-substituted bicyclo[2.1.1]hexenes and the vinylcyclopropane **2** involve biradical intermediates from which products are derived with a ratio that is largely under dynamic control. This hypothesis is clearly at odds with the classical (statistical) theories of unimolecular kinetics.

These statistical theories assume that intramolecular reorganization of the nonfixed energy of a molecule is much faster than the interconversion between the species at the various local minima on the potential energy surface for its reaction. This assumption, made most explicitly by the model of Rice, Ramsperger, and Kassel, as modified by Marcus (RRKM theory),[14] allows one to calculate rate constants for a reaction by assigning the nonfixed energy statistically to the various vibrational and rotational modes of a molecule and its transition structure (or critical con-

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figuration) for reaction. Since transition-state theory gives the same results as RRKM theory in the high-pressure limit,[14g] a similar assumption is implicit in it.

Substantial experimental effort has been devoted to the problem of determining whether the statistical approximation is valid. Experiments involving chemical activation and mode-selective laser excitation have, with just a few notable exceptions,[15-18] shown that, indeed, the mode of excitation of a molecule is irrelevant to its subsequent chemistry, apparently because intramolecular redistribution of energy is very fast, just as the RRKM and similar theories assume.[19] Why, then, should one suggest that intramolecular dynamics play such an important role here? There are three components to the answer.

First, most of the earlier experiments have centered on the comparison of some experimental rate constant with that predicted by RRKM theory. Since the theory can only be expected to give answers good to within about an order of magnitude, the test is inherently insensitive. A branching ratio for which symmetry factors allow precise prediction of product ratios, if RRKM theory is right, is a much more sensitive test of adherence to statistical behavior.

Second, the branching in the current reactions is hypothesized to occur at an intermediate of high potential energy (a singlet biradical). At this nuclear geometry, the molecule has quite low nonfixed energy—the kinetic energy having been sacrificed to overcome the potential energy difference between the intermediate and the starting material. Current theories suggest that the rate of reorganization of nonfixed energy depends on how much excess energy there is. At low levels of excitation the rate can apparently be quite small.[20]

Third, localization of nonfixed energy (typically by IR laser excitation in the earlier experiments) can only be expected to lead to non-RRKM behavior if the excited mode is identical with or strongly coupled to the reaction coordinate. In the present studies it is the working hypothesis that the biradical intermediates are produced with nonfixed energy localized in the mode corresponding to the reaction coordinate for their formation and that this mode is coupled with different strengths to the reaction coordinates for progress on to products. If the coordinate for formation of the intermediate were only weakly coupled to all of the exit channels (as may well be the case in many reactions), statistical selection of the channels, as predicted by RRKM theory, would be expected. It is hypothesized, however, that in the reactions studied here strong coupling of the coordinate for formation of the intermediate occurs to one of the exit channels.

The feature that is hypothesized to lead to strong coupling in the present reactions is the ability to conserve linear and angular momentum in the motion of the nuclei as the molecule passes through the transition structure leading to the intermediate and then on to the favored product. Classical trajectory calculations have been carried out on a potential energy surface in which such selective coupling is expected.[21] The results support this picture and serve to emphasize the most important feature of this phenomenon, namely that *the product distribution in a reaction involving dynamic control of branching ratios need not reflect the symmetry of the equilibrium nuclear geometry of the intermediate*. One could, for example, have a reaction occurring from an optically active reactant, via an achiral intermediate, and still observe optically active products. It appears that the ring expansion of **2** may be an example of such a phenomenon. The calculations further suggest that while there should be some temperature dependence of the product ratio, it is very weak and unlikely to be detectable with the normal experimental precision and accessible temperature range.

What, then, are the conditions that allow momentum conservation between coordinates for formation and reaction of an intermediate? In the case of the [1,*n*] sigmatropic shifts in rigid bicyclic molecules, all of which seem to show a preference for inversion of configuration at the migrating carbon when there is an energetically accessible biradical mechanism,[22] one can argue that conservation of momentum will favor inversion because it is the "continuation" of the motion that transformed the originally pyramidal tetracoordinate carbon of the reactant into the planar trigonal carbon of the biradical. In other words, the out-of-plane bending of the groups on the trigonal carbon of the intermediate is excited with a particular phase of motion that leads it to an inverted geometry as the first pyramidal configuration capable of product formation. In the case of the vinylcyclopropane rearrangement a more complex reaction coordinate is possible because there is more flexibility in the reactant and intermediate biradical. As a result the stereoselectivity is lower and the product ratio could be susceptible to changes in substitution pattern.

In more general terms, reactions for which there is a plausible single-stage mechanism leading all the way from reactant to one product are likely to be candidates for intervention from dynamic phenomena, if there exists a potential intermediate that could be derived by stepwise making or breaking of bonds and whose energy is estimated to be equal to or lower than that for the transition structure of the single-stage process. This is precisely the situation for the "not-obviously-concerted" reactions where there has been the most controversy about the existence or otherwise of biradical intermediates.[23] It would be very interesting to check the temperature dependence of the product ratios in these reactions (specifically those whose product ratios do not reflect the symmetry of an energetically accessible intermediate) to see whether they do show the behavior that has been identified in the present work as a clue to the intervention of dynamic effects.

The difficulties of rationalizing observed stereochemistry with a thermochemical mandate for a biradical mechanism led Doering to propose the "continuous diradical as transition state" in the stereomutation of a vinylcyclopropane derivative.[24] It is important to ask whether Doering's hypothesis is equivalent to the present proposal or whether it is sufficient to explain the present data. The answer to both questions is "no". The continuous diradical is en-

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visioned to be a structure that is not sitting in the local potential energy minimum expected for most intermediates, but is still at a branch point for collapse to a number of stereoisomeric products. It is thus completely characterizable as a feature of the potential energy surface, requiring no departure from the statistical theories of unimolecular kinetics (although it may be at variance with some later concepts that seek to describe allowable general shapes for potential energy surfaces).[25] The continuous diradical does not serve to explain the data in the present paper because, in common with any other model seeking to explain product ratios by modification of the potential energy surface, it does not resolve the fundamental conflict between the unsymmetrical nature of the product ratios and their temperature independence.

In order for the hypothesis of dynamically determined, branching ratios to be correct the reaction coordinate(s) must be relatively weakly coupled both to the other internal motions of the molecule and, in the case of reactions in solution, to the solvent. Were this not the case, there would be a randomizing effect on the reactive trajectories, due to exchange of nonfixed energy with other modes, that could serve to diminish or even eradicate the selectivity based on momentum conservation. With regard to the first part, coupling of the reaction coordinate to the other internal modes, there is now both theoretical[26] and experimental[27] evidence to suggest that the phase space for even large-amplitude vibration of molecules can be partitioned into regions that are not strongly coupled, and that the effective dimensionality of a reaction coordinate can thus be much lower than the full 3N-6. Recent theoretical work also suggests that, at least for hydrocarbon reactions in nonpolar solvents, exchange of energy between some vibrational modes of the solute and the solvent can occur on a time scale comparable to that of intramolecular vibrational energy transfer, again opening up the possibility of a low effective dimensionality for reactions coordinates under these circumstances.[28] It is not expected that this would necessarily be the case for charged or highly dipolar molecules, however, and so the dynamic phenomena suggested in the present work are not likely to be readily applicable to reactions involving such species.

If the hypothesis presented in this work is correct it raises a challenge for the mechanistic chemist to differentiate those phenomena that are due to the shape of the potential energy surface for a reaction from those that are due to dynamics. It poses an even bigger challenge to the theorist to develop a successor to the statistical theories that can incorporate dynamic effects without having to resort to full-scale trajectory calculations, which are impractical, even with modern supercomputers, for molecules of interest to organic chemists.

Experimental Section

General Techniques. Proton magnetic resonance (^{1}H NMR) spectra were recorded on a 60-MHz Hitachi/Perkin-Elmer R24B continuous wave (CW) spectrometer, 90-MHz Varian EM-390 CW spectrometer, 80-MHz Varian CFT-20 Fourier transform (FT) spectrometer, 200-MHz Varian XL-200 FT spectrometer, or 300-MHz Bruker WM-300 FT spectrometer. Absorptions are reported in parts per million (δ) downfield from tetramethylsilane. ^{2}H NMR spectra were recorder on the Bruker instrument. Proton-decoupled ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a 22.49-MHz JEOL FX-90Q FT spectrometer. Absorptions are reported in parts per million (δ) downfield from tetramethylsilane. Those ^{13}C NMR spectra which were proton coupled were collected in an off-resonance decoupling mode; therefore, accurate coupling constants were not obtained. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and were not corrected. Boiling points were noted during distillation and were not corrected. Analytical thin-layer chromatography (TLC) analyses were performed using Machery-Nagel Polygram Sil G/UV silica gel coated plates with fluorescent indicator. Preparative TLC was performed on Analtech 20 × 20 cm glass plates coated with 1 mm silica gel with fluorescent indicator. Column chromatography was performed by the method of medium pressure "flash chromatography" developed by Still,[29] using "silica gel 60 for chromatography" from EM Science (E. Merck). Analytical capillary gas chromatography was performed on a Hewlett-Packard 5880 series gas chromatograph equipped with a 12 m × 0.2 mm i.d. methyl silcone deactivated Carbowax-20 M column, flame ionization detector, and Hewlett-Packard 5880 series GC integrating printer. Chiral analyses were performed using a Chrompack 50 m × 0.22 mm WCOT fused silica column. The liquid phase was XE-60-S-VAL-S-α-PEA. Preparative gas chromatography was performed on a Varian Aerograph Series 200 gas chromatograph equipped with a thermal conductivity detector. High-performance liquid chromatography (HPLC) was performed on a Perkin-Elmer Series 3B solvent delivery system coupled to an LC-75 variable-wavelength detector with an Omniscribe B-5000 recorder. Solvents used were of the highest purity; distilled-in-glass, UV quality, or the equivalent and were filtered and degassed prior to use. The column used was a Perkin-Elmer Silica A 2.6 mm × 250 mm column or Pirkle-A. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Commercially available reagents were generally checked for purity (^{1}H NMR, melting point, etc.) prior to use and purified if necessary. Solvents used were commercially available ACS reagent grade, or the equivalent, and were used without purification unless otherwise noted. Tetrahydrofuran and benzene were distilled from sodium benzophenone ketyl immediately prior to use. Anhydrous diethyl ether and anhydrous ethanol were used without further purification. Dry hexanes were vacuum transferred from sodium benzophenone ketyl and tetraglyme immediately prior to use. Dimethoxyethane was distilled from lithium aluminum hydride first, then from sodium benzophenone ketyl. Dimethyl sulfoxide was distilled from barium oxide at reduced pressure. Dimethylformamide and pyridine were distilled from barium oxide.

Alkyllithium solutions were obtained from Alfa or Aldrich Chemical Co. and concentrations were determined from titration with 1,3-diphenylacetone *p*-tosylhydrazone.[30]

A standard lithium aluminum hydride quench refers to the method of Fieser.[31] The following general procedure was used: added dropwise to the solution of n grams of lithium aluminum hydride in ethereal solvent were n mL of H_2O, n mL of 15% aqueous NaOH, $3n$ mL of H_2O. The solution was then filtered, the salts were washed well with ether, and the solvent was dried and concentrated. A standard diisobutylaluminum hydride quench follows the procedure of Trost.[32] A small quantity of methanol or aqueous ammonium chloride was added to the solution. When the reaction had subsided, saturated Na_2SO_4 was added, followed by solid Na_2SO_4. After stirring for 10–15 min, the solution became gelatinous. Ether and additional solid Na_2SO_4 were added until the salts become granular. These were filtered through Celite and washed well with ether, which was dried and concentrated.

Ethereal solutions of diazomethane were prepared in the fol-

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lowing manner: an ice-cold two-phase mixture of ether and 5 M KOH was prepared in a non-ground-glass flask. Enough *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine (available from Aldrich) was added to make a 1 M solution of diazomethane in ether. The ether immediately turned yellow with the evolution of gasses. When the reaction was complete, the ether was decanted and the solution of diazomethane was used immediately. If transfer was necessary, polished Pasteur pipets were used. Excess diazomethane was destroyed upon addition of acetic acid until the yellow color disappeared. The esters were worked up in the usual manner.

Synthesis of Bicyclo[2.1.1]hex-2-ene Derivatives (See Ref 1 for a Summary of the Scheme). 3-Hydroxy-2-phenyl-4-pentenoic Acid. To a stirred solution of phenylacetic acid (40.0 g, 0.29 mol) in tetrahydrofuran (200 mL) was added isopropylmagnesium bromide (0.62 mol, 680 mL of a 1.1 M solution in tetrahydrofuran) while the flask was cooled at 0 °C. When addition was complete the solution was warmed to room temperature and stirred for 4 h. After cooling back down to 0 °C, a tetrahydrofuran (50 mL) solution of freshly distilled acrolein (24.4 g, 0.44 mol) was added, and stirring was continued for 30 min. Saturated, aqueous ammonium chloride (300 mL) was poured into the flask, followed by ether (200 mL), and the phases were separated. The aqueous phase was acidified to pH 3 with 6 M hydrochloric acid and extracted with ether (3 × 100 mL). The combined organic phases were washed with water (2 × 100 mL) and brine (1 × 100 mL), dired, filtered, and concentrated. The crude, viscous oil remaining was purified by flash chromatography (50% ethyl acetate/hexane) and yielded 33.8 g (61%) of a light yellow oil which was a mixture of diastereomers and sometimes was contaminated with small amounts of phenylacetic acid: ^{1}H NMR ($CDCl_3$) δ 3.40 (m, 1 H), 4.40 (m, 1 H), 4.95 (m, 2 H), 5.55 (m, 1 H), 7.20 (s, 5 H). The chemical shift of the alcohol and carboxylate protons was highly variable.

Methyl 3-hydroxy-2-phenyl-4-pentenoate was prepared by reaction of the acid with diazomethane, as described in the section on general techniques: ^{1}H NMR (CCl_4) δ 3.45 (m, 1 H), 3.60 (2 s, 3 H), 4.50 (m, 1 H), 5.05 (m, 2 H), 5.60 (m, 1 H), 7.15 (s, 5 H).

Methyl 2-Phenyl-3-(trimethylsiloxy)-4-pentenoate. To a stirred solution of methyl 3-hydroxy-2-phenyl-4-pentenoate (0.52 g, 2.5 mmol) and pyridine (0.22 g, 2.8 mmol) in tetrahydrofuran (20 mL) was added trimethylsilyl chloride (0.27 g, 2.5 mmol) in tetrahydrofuran (10 mL). This was stirred for 3.5 h. At this point the reaction mixture was gravity filtered and concentrated. The oil remaining was purified by flash chromatography (5% ethyl acetate/hexane) and yielded 0.17 g (29%) of material: ^{1}H NMR (CCl_4) δ −0.20 (s, 4.5 H), 0.10 (s, 4.5 H), 3.40 (m, 1 H), 3.60 (s, 3 H), 4.45 (m, 1 H), 5.20 (m, 2 H), 5.70 (m, 1 H), 7.20 (s, 5 H).

Methyl 3-(*tert*-Butyldimethylsiloxy)-2-phenyl-4-pentenoate. Methyl 3-hydroxy-2-phenyl-4-pentenoate (9.3 g, 45.1 mmol), *tert*-butyldimethylsilyl chloride (8.2 g, 54.2 mmol), and imidazole (7.7 g, 113 mmol) in dimethylformamide (200 mL) yielded 11.7 g (84%) of a viscous oil following flash chromatography (5% ethyl acetate/hexane): ^{1}H NMR (CCl_4) δ −0.40 (s, 1.5 H), −0.20 (s, 1.5 H), 0.00 (s, 1.5 H), 0.05 (s, 1.5 H), 0.70 (s, 4.5 H), 0.90 (s, 4.5 H), 3.50 (m, 1 H), 3.55 (s, 3 H), 4.55 (m, 1 H), 5.00 (m, 2 H), 5.60 (m, 1 H), 7.20 (s, 5 H).

3-(*tert*-Butyldimethylsiloxy)-2-phenyl-4-penten-1-ol. To a stirred solution of methyl 3-(*tert*-butyldimethylsiloxy)-2-phenyl-4-pentenoate (11.7 g, 37.1 mmol) in benzene (100 mL) was added diisobutylaluminum hydride (81.7 mmol, 81.7 mL of a 1.0 M solution in hexane). After being stirred for 1 h the solution was cooled to 0 °C, and methanol (5 mL) was added, followed by saturated aqueous sodium sulfate (8.8 mL). The reaction mixture was warmed to room temperature and stirred for 0.5 h, during which time large amounts of aluminum salts had precipitated. After vacuum filtration the filtrate was concentrated, and the oil that remained was purified by flash chromatography (25% ethyl acetate/hexane), affording 9.2 g (85%) of a clear oil: ^{1}H NMR (CCl_4) δ 0.00 (s, 6 H), 0.90 (s, 4.5 H), 0.95 (s, 4.5 H), 1.70 (b s, 1 H), 2.85 (m, 1 H), 3.90 (m, 1 H), 4.40 (m, 1 H), 5.05 (m, 2 H), 5.85 (m, 1 H), 7.15 (s, 5 H).

3-(*tert*-Butyldimethylsiloxy)-2-phenyl-4-pentenal. 3-(*tert*-Butyldimethylsiloxy)-2-phenyl-4-penten-1-ol (11.1 g, 38.0 mmol) was dissolved in methylene chloride (50 mL) and poured into a vigorously stirred slurry of pyridinium dichromate (36.0 g, 95.0 mmol) and methylene chloride (200 mL). After the solution had stirred for 60 h, ether (200 mL) was added, and the black suspension was vacuum filtered through Celite. The filtrate was forced through a short column of florisil, the column was washed with ether (200 mL), and the effluent was concentrated; 6.6 g (60%) of a yellow oil were obtained following flash chromatography (5% ethyl acetate/hexane): ^{1}H NMR (CCl_4) δ −0.10 (s, 1.5 H), −0.05 (s, 1.5 H), 0.05 (s, 1.5 H), 0.10 (s, 1.5 H), 0.80 (s, 4.5 H), 0.90 (s, 4.5 H), 3.80 (dd, J = 7.5, 3.0 Hz, 1 H), 4.70 (dd, J = 7.5, 7.5 Hz, 1 H), 4.95 (m, 2 H), 5.60 (m, 1 H), 7.20 (s, 5 H), 9.5 (d, J = 3.0 Hz, 1 H).

3-(*tert*-Butyldimethylsiloxy)-4-phenyl-1,5-hexadiene. To a solution of methyltriphenylphosphonium bromide (12.0 g, 33.6 mmol) in tetrahydrofuran (100 mL) was added *n*-butyllithium (24.7 mmol, 11.2 mL of a 2.2 M solution in hexane), while cooling at 0 °C. After being stirred for 10 min the solution was cooled to −78 °C, and 3-(*tert*-butyldimethylsiloxy)-2-phenyl-4-pentenal (6.6 g, 22.4 mmol) was dissolved in tetrahydrofuran (100 mL) and added dropwise. When addition was complete the solution was stirred for 0.5 h, warmed to room temperature, and poured onto ether–water. The phases were separated, and the organic phase was washed with water (2 × 50 mL) and brine (1 × 50 mL), dried, filtered, and concentrated. The remaining residue was taken up in hexane and filtered to remove triphenylphosphine oxide, and the filtrate was subjected to flash chromatography (2% ethyl acetate/hexane), which yielded 4.7 g (73%) of material: ^{1}H NMR (CCl_4) δ −0.10 (s, 3 H), 0.00 (s, 3 H), 3.35 (dd, J = 6.0, 6.0 Hz, 1 H), 4.30 (dd, J = 6.0, 6.0 Hz, 1 H), 5.10 (m, 4 H), 5.70 (m, 1 H), 6.20 (m, 1 H), 7.15 (s, 5 H).

4-Phenyl-1,5-hexadien-3-ol. Tetrabutylammonium fluoride (24.5 mmol, 24.5 mL of a 1.0 M solution in tetrahydrofuran) was added in one portion to 4-(*tert*-butyldimethylsiloxy)-3-phenyl-1,5-hexadiene (4.7 g, 16.3 mmol) in tetrahydrofuran (100 mL). The solution was stirred for 1.5 h, at which time it was poured onto ether–water and the layers were separated. The aqueous was extracted with ether (2 × 50 mL), and the combined organic phases were washed with water (1 × 50 mL) and brine (1 × 50 mL), dried, filtered, and concentrated. The remaining residue was purified by flash chromatography (25% ethyl acetate/hexane) and yielded 2.0 g (75%) of a colorless oil: ^{1}H NMR (CCl_4) δ 1.45 (b s, 1 H), 3.20 (m, 1 H), 4.15 (m, 1 H), 4.95 (m, 4 H), 5.70 (m, 2 H), 7.05 (s, 5 H).

3-Phenylbicyclo[2.1.1]hexan-2-one. Via the procedure described below for the preparation of bicyclo[2.1.1]hexan-2-one by the oxidation–photolysis sequence, 4-phenyl-1,5-hexadien-3-ol (0.80 g, 4.6 mmol) yielded 0.30 g of crude material that afforded, after flash chromatography (35% ethyl acetate/hexane), 31 mg (3.8%) of compound. This material had been tentatively assigned as 3-phenylbicyclo[2.1.1]hexan-2-one. See the procedure below for spectral data.

4-Phenyl-1,5-hexadien-3-ol Pyruvate Ester. The same procedure was used as described below for 1,5-hexadien-3-ol. 4-Phenyl-1,5-hexadien-3-ol (2.0 g, 11.5 mmol), pyruvoyl chloride (1.2 g, 11.5 mmol), and pyridine (1.0 g, 12.6 mmol) in benzene (50 mL) yielded 2.3 g (82%) of a colorless oil, after flash chromatography (25% ethyl acetate/hexane): ^{1}H NMR (CCl_4) δ 1.95 (s, 1.5 H), 2.35 (s, 1.5 H), 3.55 (m, 1 H), 5.10 (m, 3 H), 5.45 (m, 2 H), 5.95 (m, 2 H), 7.15 (s, 5 H).

3-Phenylbicyclo[2.1.1]hexan-2-one. The procedure described for bicyclo[2.1.1]hexan-2-one (pyruvate ester method) was used. 4-Phenyl-1,5-hexadien-3-ol (2.0 g, 11.5 mmol) afforded 70 mg (3.5%) of a yellow oil, after flash chromatography (35% ethyl acetate/hexane), which was tentatively assigned the structure of the title compound: ^{1}H NMR (CCl_4) δ 1.60 (m, 1 H), 1.80 (m, 1 H), 2.25 (m, 2 H), 3.10 (m, 2 H), 3.60 (m, 1 H), 7.25 (m, 5 H).

1,5-Hexadien-3-ol. Acrolein (12.9 g, 0.23 mol) was dissolved in tetrahydrofuran (50 mL) and added dropwise to a tetrahydrofuran solution of allylmagnesium chloride (0.23 mol, 192 mL of a 1.2 M solution) while cooling at 0 °C. The solution was stirred for 15 min before adding the saturated ammonium chloride solution (200 mL). The two phases were separated, and the aqueous phase was extracted with ether (3 × 50 mL). The combined organic phases were washed with water (2 × 50 mL) and brine (1 × 50 mL), dried, filtered, and concentrated. The remaining material was vacuum distilled, which afforded 14.7 g (65%) of a colorless liquid: bp 55–58 °C/(40 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.80 (s, 1 H), 2.35 (m, 2 H), 4.20 (m, 1 H), 5.15 (m, 4

H), 5.85 (m, 2 H); ^{13}C NMR ($CDCl_3$) 41.5 (t), 71.7 (d), 114.5 (t), 117.9 (t), 134.0 (d), 140.2 (d).

1,5-Hexadien-3-ol Pyruvate Ester. Pyruvoyl chloride (3.0 g, 28.6 mmol) was dissolved in benzene (40 mL) and added to a solution of 1,5-hexadien-3-ol (2.8 g, 28.6 mmol) and pyridine (2.3 g, 31.4 mmol) in benzene (100 mL) while the solution was cooled with cold tap water. After 15 min the mixture was gravity filtered to remove the pyridinium hydrochloride that had precipitated and then concentrated. The residue was taken up in carbon tetrachloride (50 mL), and after the solution had stood for 0.5 h was again gravity filtered and concentrated; 4.6 g (96%) of material was obtained, and it was used without further purification.

Bicyclo[2.1.1]hexan-2-one. Method 1: Pyruvate Ester Photolysis.[33] 1,5-Hexadien-3-ol pyruvate ester (17.1 g, 0.10 mol) was dissolved in benzene (500 mL), placed in a photoreactor, and purged with nitrogen for 1 h. When the purge was complete, the solution was photolyzed for 80 h. Most of the benzene was removed by careful distillation and then the remaining residue was vacuum distilled and yielded 1.2 g (12%) of colorless, volatile liquid: bp 60–63 °C/(40 mmHg). Spectral data appear with the alternative procedure described below.

Method 2: Oxidation–Photolysis. Chromium trioxide (28.7 g, 0.29 mol) was added in several portions to water (50 mL) with vigorous stirring. The solution was cooled to 0 °C and concentrated sulfuric acid (24.7 mL) was slowly and carefully added. While the solution was still ice cold, it was added dropwise to 1,5-hexadien-3-ol (22.6 g, 0.29 mol) in 1:1 acetone–benzene (150 mL) while the solution was mechanically stirred and cooled at 0 °C. The solution was stirred cold for 15 min and then warmed to room temperature. When the green suspension had reached room temperature, it was poured onto pentane (100 mL), and the layers were separated. The dark green aqueous phase was extracted with pentane (2 × 50 mL), and the combined organic phases were washed with brine (1 × 50 mL), dried, filtered, and diluted to a volume of 500 mL with more pentane. The resulting solution was placed in a photoreactor and irradiated through Pyrex glass for 24 h. After photolysis, the solvent was removed by careful distillation, and the residue left in the flask was vacuum distilled, providing 19.9 g (86%) of colorless, volatile liquid: bp 61–63 °C/(42 mmHg): ^1H NMR (CCl_4) δ 1.55 (m, 2 H), 2.05 (m, 2 H), 2.15 (m, 2 H), 2.75 (m, 2 H); ^{13}C NMR ($CDCl_3$) 35.5 (d), 40.5 (2t), 55.7 (d), 199.5 (s).

Bicyclo[2.1.1]hexan-2-one (*p*-Tolylsulfonyl)hydrazone. Bicyclo[2.1.1]hexan-2-one (7.25 g, 75 mmol) and (*p*-tolylsulfonyl)hydrazine (14.0 g, 75 mmol) were dissolved in methanol (120 mL) and refluxed for 8 h. The solution was then placed in a freezer overnight, which caused white crystals to form. The solid was vacuum filtered and washed with ice-cold methanol. The last traces of solvent were removed in vacuo, and this procedure left 13.0 g (68%) of white crystals, mp 192–194 °C. A quantitative yield could be recovered by concentration of the filtrate and recrystallization of the solid that remained from methanol: ^1H NMR (acetone-d_6) δ 1.25 (m, 2 H), 2.25 (m, 2 H), 2.35 (s, 3 H), 2.65 (m, 1 H), 2.80 (m, 2 H), 7.30 (d, J = 7.5 Hz, 2 H), 7.70 (d, J = 7.5 Hz, 2 H), 8.70 (b s, 1 H), one proton in the upfield region was obscured by the signal due to acetone-d_5; ^{13}C NMR (acetone-d_6) 19.8 (q), 34.8 (d), 39.3 (t), 39.5 (t), 54.8 (d), 127.0 (d), 128.2 (d), 135.7 (s), 142.3 (s), 204.5 (s).

Bicyclo[2.1.1]hex-2-ene. To a suspension of bicyclo[2.1.1]-hexan-2-one (*p*-tolylsulfonyl)hydrazone (3.0 g, 11.0 mmol) in ether (25 mL) was added methyllithium (28.0 mmol, 21.7 mL of a 1.3 M solution in ether) at room temperature. After 20 h the mixture was cooled to 0 °C, and water was carefully added until any exothermicity had ceased. Just enough water was added to dissolved the salts, and the layers were separated. The aqueous phase was extracted with ether (3 × 10 mL), and the combined organic phases were washed with saturated aqueous sodium bicarbonate (1 × 20 mL), dried, and filtered. All but about 1–2 mL of the ether were removed by careful distillation, and the remaining material was purified by preparative gas chromatography and yielded 0.35 g (39%) of pungent-smelling, volatile material: ^1H NMR (CCl_4) δ 2.25 (t, J = 1.0 Hz, 2 H), 2.50 (s, 4 H), 6.70 (t, J = 1.0 Hz); ^{13}C NMR ($CDCl_3$) 42.8 (d), 67.8 (t), 143.0 (d).

2-Phenylbicyclo[2.1.1]hexan-2-ol. Bromobenzene (50.0 g, 0.30 mol) was dissolved in tetrahydrofuran (50 mL) and added dropwise to magnesium turnings (7.7 g, 0.32 mol) and tetrahydrofuran (300 mL) at such a rate that the solution felt just warm, not hot, to the hand. When addition was complete the gray solution was refluxed for 1 h. The Grignard reagent was cooled to 0 °C, bicyclo[2.1.1]hexan-2-one (15.3 g, 0.16 mol) in tetrahydrofuran (50 mL) was added dropwise, and when addition was complete, aqueous saturated ammonium chloride solution (100 mL) was added. Ether (100 mL) was added, and after the phases were separated, the aqueous phase was washed with ether (2 × 50 mL). The combined organic layers were washed with water (2 × 50 mL) and brine (1 × 50 mL), dried, filtered, and concentrated. The residue was purified by flash chromatography (25% ethyl acetate/hexane) and yielded 22.3 g (81%) of material: IR (film) 3550 cm^{-1}; ^1H NMR (CCl_4) δ 1.15 (m, 1 H), 1.70 (m, 4 H), 1.90 (m, 1 H), 2.25 (m, 1 H), 2.45 (m, 1 H), 2.75 (m, 1 H), 7.25 (m, 5 H); ^{13}C NMR ($CDCl_3$) 37.5 (t), 38.4 (d), 40.4 (t), 43.8 (t), 49.9 (d), 81.1 (s), 126.5 (d), 127.1 (d), 128.3 (d), 146.7 (s).

2-Phenylbicyclo[2.1.1]hex-2-ene. Sodium hydride (34 mmol, 1.65 g of a 50% dispersion in oil) was added in a few portions to 2-phenylbicyclo[2.1.1]hexan-2-ol (3.0 g, 17 mmol) in ether (75 mL). This solution was stirred for 15 min before the addition of carbon disulfide (2.9 g, 38 mmol). The reaction mixture was refluxed for 0.5 h before the addition of methyl iodide (5.4 g, 38 mmol). The solution was refluxed for 12 h and then cooled to 0 °C, and water was carefully added until gas evolution had ceased. Enough water was then added to just dissolve the salts, and after the layers were separated, the aqueous phase was extracted with pentane (3 × 20 mL). The combined organic layers were washed with water (1 × 30 mL), brine (1 × 30 mL), dried, filtered, and concentrated. The crude residue was purified by flash chromatography (pentane) and afforded 1.2 g (50%) of clear oil that was unstable in air and polymerized on standing at room temperature. The hydrocarbon could be stabilized by addition of a few crystals of hydroquinone, and storing it in a degassed solution in a freezer: ^1H NMR (CCl_4) δ 2.45 (m, 2 H), 2.70 (m, 3 H), 3.15 (m, 1 H), 7.15 (m, 6 H); ^{13}C NMR ($CDCl_3$) 43.6 (d), 44.1 (d), 65.1 (t), 124.4 (d), 126.6 (d), 128.4 (s), 135.4 (d superimposed on s), 156.2 (s). Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.31; H, 7.83. The structure was further confirmed by ozonolysis as described below.

3-Benzoylcyclobutanecarboxaldehyde. 2-Phenylbicyclo-[2.1.1]hex-2-ene (27 mg, 0.17 mmol) was dissolved in methylene chloride (10 mL), and ozone was bubbled through the solution for 3 min while cooling at −78 °C. Dimethyl sulfide (5 mL) was added, and then the solution was allowed to warm to room temperature. Water was added, and the phases were separated. The organic phase was washed with water (1 × 5 mL), dried, filtered, and concentrated. The oil remaining was purified by flash chromatography (50% ethyl acetate/hexane) and yielded 25 mg (78%) of material: ^1H NMR ($CDCl_3$) δ 2.45 (m, 4 H), 3.15 (m, 1 H), 3.90 (m, 1 H), 7.40 (m, 3 H), 7.75 (m, 2 H), 9.55 (d, 1 H); ^{13}C NMR ($CDCl_3$) 25.1, 28.0, 38.0, 40.9, 127.1, 128.3, 128.7, 133.3, 199.5, 201.6.

1-Acetoxy-2-phenyl-2-propene. Selenium dioxide (80 g, 0.70 mol) was added in portions to a vigorously stirred solution of 2-phenylpropene (236.0 g, 2.0 mol), glacial acetic acid (103 mL), and acetic anhydride (158.0 g, 1.55 mol). This mixture was heated at 75 °C for 1 h and then at 125 °C for 2 h. During this time all the selenium dioxide had gone into solution, and selenium metal started to precipitate. After the reaction mixture was allowed to cool to room temperature it was filtered to remove the selenium metal. The acetic acid, acetic anhydride, and most of the 2-phenyl-1-propene was removed by bulb-to-bulb distillation (ambient temperature, 0.3 mmHg), and the residue was vacuum distilled, which afforded 75.0 g (61%) of a colorless, foul-smelling liquid: ^1H NMR (CCl_4) δ 2.05 (s, 3 H), 5.00 (s, 2 H), 5.40 (s, 1 H), 5.50 (s, 1 H), 7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) 20.7 (q), 65.5 (t), 115.0 (t), 125.8 (d), 127.9 (d), 128.1 (d), 128.3 (d), 128.7 (d), 137.8 (s), 142.4 (s), 170.5 (s).

2-Phenyl-2-propen-1-ol. Sodium hydroxide (17.9 g, 0.45 mol) was dissolved in water (200 mL) and added to 1-acetoxy-2-phenyl-2-propene (75.0 g, 0.43 mol). After the two-phase system was refluxed for 9 h, it was cooled to room temperature and extracted with ether (3 × 150 mL). The combined extracts were

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washed with water (2 × 100 mL), dired, filtered, and concentrated. The oil remaining was vacuum distilled, yielding 47.0 g (82%) of a faint yellow oil: bp 75–78 °C (0.2 mm Hg); ^{1}H NMR (CCl_4) δ 1.75 (b s, 1 H), 4.45 (s, 2 H), 5.25 (s, 1 H), 5.35 (s, 1 H), 7.30 (m, 5 H).

2-Phenyl-2-propenal. To a vigorously stirred slurry of pyridinium dichromate (84.0 g, 0.22 mol) and methylene chloride (300 mL) was added 2-phenyl-2-propen-1-ol (15.0 g, 0.11 mol) in methylene chloride (100 mL). The solution was stirred in the dark for 24 h, at which time ether (300 mL) was added and the suspension was vacuum filtered through Celite. The filtrate was forced through a 10 × 4 cm plug of florisil (with a vane pump, as in flash chromatography), and the florisil was washed well with ether. The effluent was concentrated, and the yellow liquid was used in the next reaction immediately, without further purification; 8.7 g of material was obtained, containing small amounts of methylene chloride and pyridine: IR (film) 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.10 (s, 1 H), 6.65 (s, 1 H), 7.35 (m, 5 H), 9.75 (s, 1 H).

2-Phenyl-1,5-hexadien-3-ol. To a solution of allylmagnesium chloride (65.0 mmol, 32.5 mL of a 2 M solution in tetrahydrofuran) was added 2-phenyl-2-propenal (8.7 g, 65.0 mmol) in tetrahydrofuran (50 mL) while cooling at 0 °C. When addition was complete, the mixture was stirred for 0.5 h, and then saturated aqueous ammonium chloride (100 mL) was added. The two phases were separated, and the aqueous phase was extracted with ether (2 × 100 mL). The combined organic phases were washed with water (2 × 50 mL) and brine (1 × 50 mL), dried, filtered, and concentrated. The residue was purified by flash chromatography (25% ethyl acetate/hexane) and yielded 7.2 g (63%) of material: ^{1}H NMR ($CDCl_3$) δ 2.00 (b s), 2.25 (dt, J = 7.5, 6.0 Hz, 2 H), 4.60 (t, J = 6.0 Hz, 1 H), 4.95 (m, 1 H), 5.10 (s, 1 H), 5.25 (s, 1 H), 5.30 (m, 1 H), 5.70 (m, 1 H), 7.25 (s, 5 H); ^{13}C NMR ($CDCl_3$) 40.4 (t), 72.3 (d), 112.7 (t), 118.2 (t), 126.8 (d), 127.6 (d), 128.3 (d), 134.2 (d), 139.9 (s), 151.0 (s).

2-Phenyl-1,5-hexadien-3-ol Pyruvate Ester. Pyruvoyl chloride (1.9 g, 17.8 mmol) in benzene (50 mL) was added dropwise to 2-phenyl-1,5-hexadien-3-ol (3.1 g, 17.8 mmol) in benzene (50 mL) while cooling with cold tap water. The mixture was allowed to stir for 15 min before it was gravity filtered and concentrated. The remaining residue was purified by flash chromatography (25% ethyl acetate/hexane) and afforded 4.3 g (98%) of colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.45 (m, 5 H), 4.90 (m, 1 H), 5.05 (m, 1 H), 5.30 (s, 2 H), 5.70 (m, 2 H), 7.20 (s, 5 H).

1-Phenylbicyclo[2.1.1]hexan-2-one. 2-Phenyl-1,5-hexadien-3-ol pyruvate ester (4.3 g, 17.6 mmol) was dissolved in benzene (500 mL), placed in a photoreactor, and purged with nitrogen for 1 h. The solution was then irradiated through Pyrex for 8 h. The reaction mixture was concentrated and afforded 1.33 g (44%) of a yellow solid, after flash chromatography (25% ethyl acetate/hexane): ^{1}H NMR ($CDCl_3$) δ 2.00 (dd, J = 5.0, 2.0 Hz, 2 H), 2.30 (m, 4 H), 2.75 (m, 1 H), 7.05 (m, 5 H); ^{13}C NMR ($CDCl_3$) 30.9 (d), 42.4 (t), 44.8 (t), 68.0 (s), 126.6 (d), 127.0 (d), 128.3 (d), 136.8 (s), 211.6 (s); IR (film) 1755 cm^{-1}.

1-Phenylbicyclo[2.1.1]hexan-2-one (*p*-Tolylsulfonyl)hydrazone. (*p*-Tolylsulfonyl)hydrazine (1.44 g, 7.7 mmol) and 1-phenylbicyclo[2.1.1]hexan-2-one (1.33 g, 7.7 mmol) were dissolved in methanol (50 mL), and this solution was refluxed for 8 h. After being cooled to room temperature, the solution was concentrated, resulting in a yellow solid which could be recrystallized from ether–hexane. This procedure left 2.36 g (90%) of a white solid: mp 170–171 °C; ^{1}H NMR (acetone-d_6) δ 1.85 (dd, J = 4.5, 1.5 Hz, 2 H), 2.20 (m, 2 H), 2.40 (s, 3 H), 2.50 (m, 2 H), 2.65 (m, 1 H), 7.20 (m, 9 H), 8.65 (b s, 1 H).

1-Phenylbicyclo[2.1.1]hex-2-ene. To a solution of 1-phenylbicyclo[2.1.1]hexan-2-one (*p*-tolylsulfonyl)hydrazone (2.3 g, 6.7 mmol) in tetrahydrofuran (50 mL) was added methyllithium (16.7 mmol, 12.1 mL of a 1.4 M solution in ether) while cooling at 0 °C. After the solution was stirred for 12 h at room temperature, it was cooled back to 0 °C and water was added dropwise until exothermicity of hydrolysis ceased. More water was added to just dissolve the salts, and the reaction mixture was extracted with ether (3 × 50 mL). The combined organic extracts were washed with saturated aqueous sodium bicarbonate (1 × 30 mL) and brine (1 × 30 mL), dried, filtered, and concentrated. The residue was subjected to flash chromatography (pentane) and yielded 0.37 g (38%) of a clear oil: ^{1}H NMR (CCl_4) δ 2.60 (m, 1 H), 2.70 (m, 4 H), 6.60 (dd, J = 4.5, 2.0 Hz, 1 H), 6.80 (dd, J = 4.5, 2.0 Hz, 1 H), 7.15 (s, 5 H); ^{13}C NMR ($CDCl_3$) 39.3 (d), 58.1 (s), 71.0 (t), 126.2 (2 d), 128.2 (d), 142.4 (s), 143.8 (d), 145.2 (d). Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.79.

1-Hexen-5-yn-3-ol. To a slurry of aluminum powder (7.9 g, 0.29 mol) and mercuric chloride (0.1 g) in tetrahydrofuran (100 mL) was added propargyl bromide (55.6 g of a 90% solution in toluene, 0.42 mol) in tetrahydrofuran (150 mL) over the course of 0.5 h. During the addition, and for 2 h afterwards, the solution was not allowed to warm past 30 °C. This required the intermitent use of a cold tap water bath. The solution was then cooled to −78 °C, and freshly distilled acrolein (27.0 g, 0.48 mol) was dissolved in tetrahydrofuran (50 mL) and added over 15 min. When addition was complete, the solution was warmed to 0 °C and then enough aqueous, saturated ammonium chloride was added to form two phases. The layers were separated, and the aqueous phase was extracted with ether (3 × 100 mL). The combined organic phases were washed with water (1 × 100 mL) and brine (1 × 100 mL), dried, filtered, and concentrated. The residue was vacuum distilled, which afforded 20.6 g (52%) of colorless, volatile liquid: bp 52–53 °C (20 mmHg); ^{1}H NMR (CCl_4) δ 1.90 (t, J = 3.0 Hz, 1 H), 2.35 (dd, J = 7.0, 3.0 Hz, 2 H), 2.70 (s, 1 H), 4.15 (dt, J = 7.0, 6.0 Hz, 1 H), 5.05 (dd, J = 10.0, 2.0 Hz, 1 H), 5.25 (dd, J = 18.0, 2.0 Hz, 1 H), 5.85 (ddd, J = 18.0, 10.0, 6.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 27.3 (t), 70.7 (d), 70.8 (d), 79.8 (s), 115.7 (t), 138.7 (d); IR (film) 3550, 3380, 2300 cm^{-1}.

1-Hexen-5-yn-3-ol-*6-d*. Bromoethane (35.0 g, 0.32 mol) was dissolved in ether (50 mL) and added dropwise to magnesium turnings (8.2 g, 0.34 mol) in ether (50 mL) at such a rate that a gentle reflux was maintained. When addition was complete, the mixture was heated at reflux for another 0.5 h. The solution was cooled to 0 °C, and 1-hexen-5-yn-3-ol (13.0 g, 0.14 mol) was dissolved in ether (100 mL) and added dropwise. When addition was complete, the solution was refluxed for another 1 h. The reaction mixture was then cooled to 0 °C, and deuterium oxide (22.2 g, 1.1 mol) was added. After 1 h saturated, aqueous ammonium chloride (200 mL) was introduced into the flask, which dissolved all the solids, other than left over magnesium. The phases were separated, and the aqueous phase was extracted with ether (3 × 20 mL). The combined organic phases were washed with brine (1 × 50 mL), dried, filtered, and concentrated. The oil left behind was vacuum distilled and afforded 12.2 g (90%) of material: bp 35–37 °C (6 mmHg); ^{1}H NMR (CCl_4) δ 2.35 (d, J = 7.0 Hz, 2 H), 2.70 (s, 1 H), 4.15 (dt, J = 7.0, 6.0 Hz, 1 H), 5.05 (dd, J = 10.0, 2.0 Hz, 1 H), 5.25 (dd, J = 18.0, 2.0 Hz, 1 H), 5.85 (ddd, J = 18.0, 10.0, 2.0 Hz, 1 H).

***cis*-1,5-Hexadien-3-ol-*6-d*.** 1-Hexen-5-yn-3-ol-*6-d* (12.2 g, 0.13 mol), pyridine (5.0 g, 63 mmol), and palladium on barium sulfate (0.5 g) were mixed with methanol (150 mL) and attached to a hydrogenation apparatus. The system was evacuated (water aspirator vacuum) and then refilled with hydrogen. The mixture was stirred for 6 h, at which time the requisite amount of hydrogen (2.9 L, 0.12 mol) had been taken up. After the reaction mixture was vacuum filtered through Celite, the filtrate was concentrated. The remaining material was vacuum distilled and yielded 8.1 g (65%) of colorless liquid: bp 50–55 °C (12 mmHg); ^{1}H NMR (CCl_4) δ 2.35 (m, 2 H), 3.35 (b s, 1 H), 4.20 (m, 1 H), 5.15 (m, 3 H), 5.85 (m, 2 H).

3-Propynal. This compound was prepared in 31% yield from propargyl alcohol according to a procedure described by Sauer.

1-Hexyn-5-en-3-ol. To a solution of 3-propynal (11.9 g, 0.22 mol) in ether (100 mL) was added allylmagnesium chloride (0.29 mol, 145 mL of a 2 M solution in tetrahydrofuran) while cooling at −78 °C. When addition was complete, the solution was allowed to warm to room temperature, and saturated, aqueous ammonium chloride (200 mL) was added. The two layers that had formed were separated, and the aqueous phase was extracted with ether (3 × 50 mL). The combined organic phases were washed with water (1 × 50 mL) and brine (1 × 50 mL), dried, filtered, and concentrated. The oil that remained was vacuum distilled, which afforded 17.0 g (81%) of material: ^{1}H NMR (CCl_4) δ 2.40 (m, 3 H), 3.40 (s, 1 H), 4.25 (m, 1 H), 5.10 (m, 2 H), 5.85 (m, 1 H); ^{13}C NMR ($CDCl_3$) 41.8 (t), 61.2 (d), 84.0 (s), 118.6 (t), 132.7 (d).

1-Hexyn-5-en-3-ol-*1-d*. Via the procedure described for the preparation of 1-hexen-5-yn-3-ol-*6-d*, 1-hexyn-5-en-3-ol (17.0 g,

0.18 mol) gave 12.5 g (72%) of material: bp 55–58 °C (25 mmHg); ^{1}H NMR (CCl_4) δ 2.40 (dd, J = 6.0, 5.0 Hz, 2 H), 3.10 (d, J = 6.0 Hz, 1 H), 4.25 (dt, J = 6.0, 5.0 Hz, 1 H), 5.10 (m, 2 H), 5.85 (m, 1 H).

***cis*-1,5-Hexadien-3-ol-*1*-*d*.** Via the same procedure described for the preparation of *cis*-1,5-hexadien-3-ol-*6*-*d*, 1-hexyn-5-en-3-ol-*1*-*d* (12.5 g, 0.13 mol) afforded 8.0 g (67%) of material: bp 55–56 °C (20 mmHg); ^{1}H NMR (CCl_4) d 2.35 (m, 2 H), 3.20 (s, 2 H), 4.20 (m, 1 H), 5.15 (m, 3 H), 5.85 (m, 2 H).

1:1 *exo*:*endo*-Bicyclo[2.1.1]hexan-2-one-*5*-*d*. The results of this reaction were the same whether *cis*-1,5-hexadien-3-ol-*1*-*d* or -*6*-*d* was used. Via the procedure for the preparation of bicyclo[2.1.1]hexan-2-one by Jones oxidation–photolysis, 5.7 g (72%, from 6-deuterio) or 6.2 g (76%, from 1-deuterio) of material was obtained: ^{1}H NMR (CCl_4) δ 1.55 (m, 1.5 H), 2.05 (m, 2 H), 2.15 (m, 1.5 H), 2.75 (m, 2 H); ^{2}H NMR (CCl_4) δ 1.55, 2.15, ratio of the two peaks was 1:1.

2-Phenyl-1-hexen-5-yn-3-ol. Propargylaluminum sesquibromide (0.26 mol) was prepared as described for the preparation of 1-hexen-5-yn-3-ol.1 2-Phenyl-2-propenal (crude material from the oxidation of 50.0 g of the corresponding alcohol) was dissolved in tetrahydrofuran (100 mL) and added over 20 min, while cooling at −78 °C. When addition was complete, the mixture was warmed to 0 °C, hydrolyzed, and worked up as described for the parent compound. The remaining syrup was purified by flash chromatography (20% ethyl acetate/hexane) and yielded 19.5 g (44% based on aluminum) of a light yellow oil: ^{1}H NMR (CCl_4) δ 1.50 (s, 1 H), 1.85 (m, 1 H), 2.30 (m, 2 H), 4.45 (t, 1 H), 5.15 (s, 1 H), 5.30 (s, 1 H), 7.50 (s, 5 H); ^{13}C NMR ($CDCl_3$) 26.6 (t), 71.0 (d), 71.4 (d), 80.5 (s), 113.5 (t), 126.8 (d), 127.8 (d), 128.4 (d), 139.3 (s), 149.6 (s); IR (film) 3380, 3300, 2330 cm^{-1}.

2-Phenyl-1-hexen-5-yn-3-ol-*6*-*d*. Via the procedure described for the preparation of 1-hexen-5-yn-3-ol-*6*-*d*, 2-phenyl-1-hexen-5-yn-3-ol (3.3 g, 19.2 mmol) afforded 3.1 g (94%) of compound: ^{1}H NMR (CCl_4) δ 1.50 (s, 1 H), 2.30 (m, 2 H), 4.45 (m, 1 H), 5.15 (s, 1 H), 5.30 (s, 1 H), 7.20 (s, 5 H).

***cis*-2-Phenyl-1,5-hexadien-3-ol-*6*-*d*.** The same procedure was followed that is described for the preparation of 1,5-hexadien-3-ol-*1*-*d* and -*6*-*d*. 2-Phenyl-1-hexen-5-yn-3-ol-*6*-*d* (3.1 g, 17.9 mmol) afforded 2.9 g (93%) of material: ^{1}H NMR (CCl_4) δ 2.00 (b s, 1 H), 2.25 (m, 2 H), 4.60 (m, 1 H), 5.10 (s, 1 H), 5.25 (s, 1 H), 5.30 (s, 1 H), 5.70 (m, 1 H), 7.25 (s, 5 H).

1:1 *exo*:*endo*-1-Phenylbicyclo[2.1.1]hexan-2-one-*5*-*d*. The procedure described for the preparation of 1-phenylbicyclo-[2.1.1]hexan-2-one via pyruvate ester photolysis was used. *cis*-2-Phenyl-1,5-hexadien-3-ol-*6*-*d* (3.3 g, 18.9 mmol) yielded 1.2 g (37% combined yield for both the esterification and photolysis) of a light yellow solid: ^{1}H NMR ($CDCl_3$) δ 2.00 (d, 1.5 H), 2.30 (m, 3.5 H), 2.75 (m, 1 H), 7.05 (m, 5 H); ^{2}H NMR (CCl_4) δ 2.00, 2.30. The two peaks in the deuterium NMR spectrum were in a ratio of 1:1.

1:1 *exo*:*endo*-Bicyclo[2.1.1]hex-2-ene-*5*-*d*. The synthesis of bicyclo[2.1.1]hex-2-ene-*5*-*d*, as well as that of the 1-phenyl and 2-phenyl derivatives, in which the 5-deuterium existed as a 1:1 mixture of endo/exo isomers, was performed exactly as described for the corresponding all protio derivatives, from the appropriate deuteriated bicyclic ketone. A listing of ^{1}H NMR and ^{2}H NMR spectral data for each bicyclo[2.1.1]hex-2-ene-*5*-*d* follows (the two important resonances in the ^{2}H NMR spectra were always in a 1:1 ratio). Bicyclo[2.1.1]hex-2-ene-*5*-*d*: ^{1}H NMR (CCl_4) δ 2.25 (m, 1.5 H), 2.50 (s, 3.5 H), 6.75 (m, 2 H); ^{2}H NMR (CCl_4) δ 2.25, 2.50. 1-Phenylbicyclo[2.1.1]hex-2-ene-*5*-*d*: ^{1}H NMR (CCl_4) δ 2.60 (m, 0.5 H), 2.70 (m, 3.5 H), 6.60 (m, 1 H), 6.80 (m, 1 H), 7.15 (s, 5 H); ^{2}H NMR ($CHCl_3$) δ 2.60, 2.70. 2-Phenylbicyclo[2.1.1]hex-2-ene-*5*-*d*: ^{1}H NMR (CCl_4) δ 2.45 (m, 1.5 H), 2.70 (m, 2.5 H), 3.15 (m, 1 H), 7.15 (m, 6 H); ^{2}H NMR ($CHCl_3$) δ 2.45, 2.70.

3-(Trimethylsiloxy)-1-hexen-5-yne. The procedure used has been described for the preparation of methyl-2-phenyl-3-(trimethylsiloxy)-4-pentenoate. 1-Hexen-5-yn-3-ol (15.3 g, 0.16 mol) afforded 11.4 g (75%) of a colorless liquid: bp 40–45 °C (45 mmHg); ^{1}H NMR (CCl_4) δ 0.05 (s, 9 H), 1.75 (t, J = 3.0 Hz, 1 H), 2.20 (dd, J = 7.0, 3.0 Hz, 2 H), 4.05 (dt, J = 7.0, 6.0, 1.0 Hz, 1 H), 4.90 (d, J = 12 Hz, 1 H), 5.10 (d, J = 18.0 Hz, 1 H), 5.70 (ddd, J = 18.0, 12.0, 6.0 Hz, 1 H); IR (film) 3350 cm^{-1}.

1-(Tri-*n*-butylstannyl)-4-(trimethylsiloxy)-1,5-hexadiene. Tri-*n*-butyltin hydride (12.4 g, 42.6 mmol) was added to 3-(trimethylsiloxy)-1-hexen-5-yne (7.3 g, 42.6 mmol), and the resulting mixture was irradiated with a sunlamp for 9 h. The crude material was purified by flash chromatography (1.5% ethyl acetate/hexane) and yielded 14.8 g (75%) of a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 0.90 (m, 27 H), 2.20 (m, 2 H), 3.95 (m, 1 H), 4.95 (m, 2 H), 5.70 (m, 2.6 H), 6.25 (m, 0.4 H); ^{13}C NMR ($CDCl_3$) 0.31, 9.5, 13.7, 27.3, 29.2, 46.7, 73.8, 113.6, 130.6, 141.2, 145.5.

1-(Tri-*n*-butylstannyl)-1,5-hexadien-4-ol. Method 1. To a solution of 1-(tri-*n*-butylstannyl)-4-(trimethylsiloxy)-1,5-hexadiene (14.3 g, 31.2 mmol) in tetrahydrofuran (100 mL) was added tetrabutylammonium fluoride (37.4 mmol, 37.4 mL of a 1 M solution in tetrahydrofuran), and the resulting solution was stirred for 2.5 h. Ether (100 mL) was then added, and the reaction mixture was washed with water (2 × 50 mL) and brine (1 × 50 mL), dried, filtered, and concentrated. The residue was purified by flash chromatography (15% ethyl acetate/hexane), which yielded 11.0 g (92%) of material. Spectral data appear below.

Method 2. Tri-*n*-butyltin hydride (78.4 g, 0.27 mol) was added to 1-hexen-5-yn-3-ol (23.5 g, 0.24 mol), and the two-phase mixture was vigorously stirred and irradiated with a sunlamp for 7 h, during which time the reaction mixture had become homogeneous. Flash chromatography (15% ethyl acetate/hexane) afforded 71.5 g (77%) of material: ^{1}H NMR (CCl_4) δ 1.10 (m, 28 H), 2.25 (m, 2 H), 4.05 (m, 1 H), 5.00 (d, 1 H), 5.15 (d, 1 H), 5.80 (m, 2.6 H), 6.40 (m, 0.4 H); ^{13}C NMR ($CDCl_3$) 9.5, 13.7, 27.3, 29.1, 45.8, 71.6, 114.5, 133.1, 140.3, 144.1; IR (film) 3380 cm^{-1}.

***endo*-5-(Tri-*n*-butylstannyl)bicyclo[2.1.1]hexan-2-one.** The oxidation–photolysis procedure described for the preparation of bicyclo[2.1.1]hexan-2-one was followed. 1-(Tri-*n*-butylstannyl)-1,5-hexadien-4-ol (30.0 g, 7.8 mmol) yielded 18.8 g (63%) of a colorles liquid, after flash chromatography (7% ethyl acetate/hexane): ^{1}H NMR ($CDCl_3$) δ 1.15 (m, 27 H), 1.90 (d, J = 7 Hz, 1 H), 2.10 (m, 2 H), 2.30 (m, 2 H), 2.85 (m, 2 H); ^{13}C NMR ($CDCl_3$) 9.1 (t), 13.6 (q), 27.3 (t), 29.1 (t), 40.8 (d), 41.5 (t), 42.7 (d), 60.8 (d), 215.3 (s); IR (film) 1770 cm^{-1}.

***syn*,*endo*-5-(Tri-*n*-butylstannyl)bicyclo[2.1.1]hexan-2-ol.** *endo*-5-(Tri-*n*-butylstannyl)bicyclo[2.1.1]hexan-2-one (8.4 g, 22.0 mmol) was dissolved in absolute ethanol (50 mL) and added dropwise to a slurry of sodium borohydride (0.84 g, 22.0 mmol) in absolute ethanol (50 mL) while cooling at 0 °C. The flask was allowed to warm to room temperature over 2 h, at which time the reaction mixture was cooled to 0 °C and 4 N aqueous sodium hydroxide (42 mL) was added. The hydrolyzed solution was extracted with hexane (4 × 50 mL), and the combined organic extracts were washed with water (1 × 50 mL), dried, filtered, and concentrated. The remaining oil was purified by flash chromatography (hexane, then 7% ethyl acetate/hexane) and yielded 6.8 g (81%) of material: ^{1}H NMR (CCl_4) δ 1.15 (m, 28 H), 1.80 (m, 5 H), 2.55 (b s, 2 H), 4.40 (d, J = 6.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 10.7 (t), 13.8 (q), 27.6 (t), 29.4 (t), 37.5 (d), 38.0 (t), 44.6 (d), 45.4 (t), 51.1 (d), 72.9 (d).

***syn*-Bicyclo[2.1.1]hexan-2-ol-*endo*-*5*-*d*.** *syn*,*endo*-5-(Tri-*n*-butylstannyl)bicyclo[2.1.1]hexan-2-ol (3.4 g, 8.8 mmol) was dissolved in ether (30 mL) and cooled to 0 °C. *n*-Butyllithium (27.0 mmol, 13.3 mL of a 2.0 M solution in hexane) was added, and the resulting solution was heated to reflux for 7 h. After this, the solution was cooled to 0 °C and deuterium oxide (5 mL) was slowly added, followed by just enough water to dissolve all the salts. The layers were separated, and the aqueous phase was extracted with ether (2 × 25 mL). The combined organic phases were washed with brine (1 × 25 mL), dried, and filtered. Most of the solvent was removed by careful distillation through a 20-cm Vigreux column. When 1–2 mL were left in the pot flask, the residue was bulb-to-bulb distilled, which afforded 4.5 g of a solution of the desired deuterio alcohol in hexane. ^{1}H NMR indicated the solution was approximately 15% alcohol, corresponding to 0.68 g (78%) of compound: ^{1}H NMR (CCl_4) δ 0.95 (m, 1 H), 1.20 (m, 2 H), 1.60 (m, 2 H), 1.95 (m, 1 H), 2.40 (m, 2 H), 4.25 (m, 1 H); ^{13}C NMR ($CDCl_3$) 33.5, 34.7, 35.9 (the three preceding peaks constitute the triplet arising from the CHD moiety), 34.8, 38.4, 38.7, 39.3, 46.2, 72.3.

Bicyclo[2.1.1]hexan-2-one-*endo*-*5*-*d*. To a slurry of pyridinium dichromate (5.2 g, 14.0 mmol) and methylene chloride (50 mL) was added *syn*-bicyclo[2.1.1]hexan-2-ol-*endo*-*5*-*d* (0.68 g, 7.0 mmol) in methylene chloride (10 mL), and the resulting mixture was stirred for 14 h. Ether (30 mL) was added, the slurry was

forced through a 10 × 2 cm column of florisil, and the column was washed with more ether (50 mL). The majority of the solvent was removed from the effluent by careful distillation until 1–2 mL of material remained in the pot flask. The residue left over was bulb-to-bulb distilled, which afforded 0.5 g (75%) of material as a 20% solution in methylene chloride/ether: ^{1}H NMR (CCl_4) δ 1.55 (d, 1.2 H), 2.05 (m, 2 H), 2.15 (m, 2 H), 2.75 (m, 2 H); ^{2}H NMR ($CHCl_3$) δ 1.55.

Bicyclo[2.1.1]hexan-2-one-*endo*-5-*d* (*p*-Tolylsulfonyl)-hydrazone. Bicyclo[2.1.1]hexan-2-one-*endo*-5-*d* (0.55 g, 5.6 mmol) and (*p*-tolylsulfonyl)hydrazine (1.05 g, 5.6 mmol) were dissolved in methanol (50 mL) and refluxed for 10 h. The flask was then placed in a freezer for a few hours, which caused precipitation of a white solid. The solid was collected by vacuum filtration, washing well with ice-cold methanol. The last traces of solvent were removed in vacuo, yielding 0.75 g (60%) of tosylhydrazone. A quantitative yield was obtained by concentrating the mother liquor to a white mass, adding a small amount of methanol, and collecting the solid in the same manner as the first crop. This resulted in 0.50 g more tosylhydrazone: ^{1}H NMR (acetone-d_6) δ 1.25 (d, 1.2 H), 2.25 (m, 2 H), 2.35 (s, 3 H), 2.65 (m, 1 H), 2.80 (m, 2 H), 7.30 (d, J = 7.5 Hz, 2 H), 7.70 (d, J = 7.5 Hz, 2 H), 8.65 (b s, 1 H). As with the unlabeled compound, one proton appears to be hidden under the signal due to solvent (acetone-d_5).

Bicyclo[2.1.1]hex-2-ene-*endo*-5-*d*. Via the same procedure described for the unlabeled compound, bicyclo[2.1.1]hexan-2-one-*endo*-5-*d* (*p*-tolylsulfonyl)hydrazone (0.75 g, 2.8 mmol) was treated with methyllithium (6.5 mL of a 1.3 M solution in ether, 8.5 mmol) and afforded 112 mg (40%) of deuterated hydrocarbon, after preparative gas chromatography: ^{1}H NMR (CCl_4) δ 2.25 (m, 2 H), 2.50 (s, 3.2 H)8, 6.70 (m, 2 H); ^{2}H NMR (isooctane) δ 2.50.

2-Phenyl-*endo*-5-(tri-*n*-butylstannyl)bicyclo[2.1.1]hexan-2-ol. The procedure described for the preparation of 2-phenylbicyclo[2.1.1]hexan-2-ol was used; 2.4 g (70%) of material was obtained after flash chromatography (3% ethyl acetate/hexane): ^{1}H NMR (CCl_4) δ 1.10 (m, 28 H), 1.90 (m, 3 H), 2.20 (d, 1 H), 2.65 (m, 1 H), 2.90 (m, 1 H), 7.25 (m, 5 H); ^{13}C NMR ($CDCl_3$) 11.0 (t), 13.8 (q), 27.6 (t), 29.4 (t), 40.2 (d), 43.5 (t), 44.0 (d), 46.6 (t), 53.9 (d), 81.9 (s), 126.5 (d), 127.1 (d), 128.4 (d), 147.0 (s); IR (film) 3560 cm^{-1}.

2-Phenylbicyclo[2.1.1]hexan-2-ol-*endo*-5-*d*. To a solution of 2-phenyl-*endo*-5-(tri-*n*-butylstannyl)bicyclo[2.1.1]hexan-2-ol (1.2 g, 2.3 mmol) in tetrahydrofuran (50 mL) was added *n*-butyllithium (3.5 mL of a 2.2 M solution in hexane, 7.8 mmol) while cooling at −78 °C. When addition was complete the solution was warmed to 0 °C and held there for 1 h, after which time deuterium oxide (1 mL) was added. The reaction mixture was then poured onto ether–water, and the layers were separated. The organic layer was washed with water (1 × 50 mL) and brine (1 × 25 mL), dried, filtered, and concentrated. Flash chromatography (25% ethyl acetate/hexane) of the remaining residue afforded 0.32 g (80%) of a colorless oil: ^{1}H NMR (CCl_4) δ 1.10 (d, 1 H), 1.60 (s, 1 H), 1.65 (m, 2 H), 1.90 (m, 1 H), 2.25 (d, 2 H) 2.45 (m, 1 H), 2.75 (m, 1 H), 7.20 (m, 5 H); ^{13}C NMR ($CDCl_3$) 35.7, 36.9, 38.1 (triplet due to CHD), 37.5, 38.2, 40.3, 43.8, 49.8, 81.1, 126.5, 127.1, 128.3, 146.8.

2-Phenylbicyclo[2.1.1]hex-2-ene-*endo*-5-*d*. Via the procedure described for the preparation of the unlabeled compound, 2-phenylbicyclo[2.1.1]hexan-2-ol-*endo*-5-*d* (0.29 g, 1.6 mmol) yielded 127 mg (55%) of deuterated hydrocarbon: ^{1}H NMR (CCl_4) δ 2.45 (m, 2 H), 2.70 (m, 2 H), 3.15 (m, 1 H), 7.15 (m, 6 H); ^{2}H NMR (isooctane) δ 2.70.

2-Phenyl-3-(trimethylsiloxy)-1-hexen-5-yne. This compound was prepared as described for methyl 2-phenyl-3-(trimethylsiloxy)-4-pentenoate. 2-Phenyl-1-hexen-5-yn-3-ol (2.5 g, 14.5 mmol) afforded 3.1 g (86%) of material, after flash chromatography (5% ethyl acetate/hexane): ^{1}H NMR (CCl_4) δ 0.00 (s, 9 H), 1.60 (m, 1 H), 2.10 (m, 2 H), 4.45 (t, 1 H), 5.00 (s, 1 H), 5.15 (s, 1 H), 7.05 (s, 5 H); IR (film) 3400 cm^{-1}.

2-Phenyl-6-(tri-*n*-butylstannyl)-3-(trimethylsiloxy)-1,5-hexadiene. Via the procedure described for the preparation of the parent compound, 2-phenyl-3-(trimethylsiloxy)-1-hexen-5-yne (11.0 g, 45.1 mmol) yielded 15.0 g (60%) of material after flash chromatography (1.5% ethyl acetate/hexane): ^{1}H NMR (CCl_4) δ −0.10 (s, 9 H), 1.00 (m, 27 H), 1.95 (dd, J = 7.5, 6.0 Hz, 2 H), 4.40 (t, J = 6.0 Hz, 1 H), 5.00 (d, J = 1.5 Hz, 1 H), 5.10 (d, J = 1.5 Hz, 1 H), 5.60 (d, J = 12.0 Hz, 1 H), 6.25 (dt, J = 12.0, 7.5 Hz, 1 H), 7.10 (s, 5 H).

2-Phenyl-6-(tri-*n*-butylstannyl)-1,5-hexadien-3-ol. Method 1. The procedure used for the preparation of analogous, parent vinyl stannane was followed. 2-Phenyl-3-(trimethylsiloxy)-1-hexen-5-yne (15.0 g, 28.0 mmol) afforded 8.5 g (66%) of material after flash chromatography (7% ethyl acetate/hexane). Spectral data appear with the description of the alternative procedure immediately below.

Method 2. 2-Phenyl-1-hexen-5-yn-3-ol (8.0 g, 46.5 mmol) and tri-*n*-butyltin hydride (13.5 g, 46.5 mmol) were vigorously stirred and irradiated with a sunlamp for 48 h. The vinylstannane was purified by flash chromatography (7% ethyl acetate/hexane) and yielded 10.3 g (48%) of material: ^{1}H NMR (CCl_4) δ 1.15 (m, 28 H), 2.20 (m, 2 H), 4.45 (m, 1 H), 5.15 (d, J = 1.5 Hz, 1 H), 5.30 (d, J = 1.5 Hz, 1 H), 5.85 (d, J = 12.0 Hz, 1 H), 6.40 (dt, J = 12.0, 7.5 Hz, 1 H), 7.20 (s, 5 H); ^{13}C NMR ($CDCl_3$) 10.3, 13.7, 27.3, 29.1, 43.4, 72.7, 112.7, 127.0, 127.7, 128.3, 133.2, 144.1.

2-Phenyl-6-(tri-*n*-butylstannyl)-1,5-hexadien-3-ol Pyruvate Ester. The procedure described for the synthesis of 2-phenyl-1,5-hexadien-3-ol pyruvate ester was used. 2-Phenyl-6-(tri-*n*-butylstannyl)-1,5-hexadien-3-ol (8.3 g, 17.9 mmol) afforded 9.5 g (quantitative) of pyruvate ester: ^{1}H NMR (CCl_4) δ 1.10 (m, 27 H), 2.40 (m, 5 H), 5.25 (s, 1 H), 5.35 (s, 1 H), 5.75 (m, 2 H), 6.35 (m, 1 H, 7.20 (s, 5 H). Spectral data and the results of subsequent reactions were identical whether the pyruvate ester was used crude or purified by flash chromatography (15% ethyl acetate/hexane).

1-Phenyl-*endo*-5-(tri-*n*-butylstannyl)bicyclo[2.1.1]hexan-2-one. Via the procedure used for the preparation of 1-phenylbicyclo[2.1.1]hexan-2-one, 2-phenyl-6-(tri-*n*-butylstannyl)-1,5-hexadien-3-ol (9.0 g, 17.0 mmol) afforded 4.6 g (58%) of material after flash chromatography (7% ethyl acetate/hexane): ^{1}H NMR (CCl_4) δ 1.15 (m, 27 H), 2.25 (m, 3 H), 2.50 (m, 2 H), 2.80 (m, 1 H), 7.15 (s, 5 H); ^{13}C NMR ($CDCl_3$) 9.2 (t), 13.5 (q), 27.3 (t), 29.1 (t), 35.0 (d), 43.6 (t), 48.0 (d), 50.8 (t), 71.4 (s), 126.7 (d), 126.8 (d), 128.1 (d), 137.1 (s), 211.8 (s). This compound was the major product and was assigned a structure with the tri-*n*-butylstannyl group endo; 1.8 g (22%) of a compound having a lower R_f was also obtained. This material was the exo isomer: ^{1}H NMR (CCl_4) δ 1.10 (m, 28 H), 2.35 (m, 4 H), 2.75 (m, 1 H), 7.20 (s, 5 H).

***syn*,*endo*-1-Phenyl-5-(tri-*n*-butylstannyl)bicyclo[2.1.1]-hexan-2-ol.** Via the procedure used for the preparation of the parent bicyclic alcohol, the 1-phenyl derivative (1.6 g, 3.6 mmol) afforded 1.2 g (73%) of compound after flash chromatography (7% ethyl acetate/hexane): ^{1}H NMR (CCl_4) δ 1.10 (m, 28 H), 1.80 (m, 3 H), 2.20 (m, 2 H), 2.50 (m, 1 H), 4.45 (d, 1 H), 7.05 (s, 5 H); ^{13}C NMR ($CDCl_3$) 10.9 (t), 13.8 (q), 27.6 (t), 29.3 (t), 39.3 (t), 39.6 (d), 40.0 (d), 51.1 (t), 63.3 (s), 75.5 (d), 126.4 (d), 126.5 (d), 128.3 (d), 141.7 (s).

1-Phenyl-*exo*-5-(tri-*n*-butylstannyl)bicyclo[2.1.1]hexan-2-ol. The procedure described for the reduction of the parent and 1-phenyl-*endo*-5-(tri-*n*-butylstannyl) ketones with sodium borohydride was followed; 0.46 g (0.80 mmol) of 1-phenyl-*exo*-5-(tri-*n*-butylstannyl)bicyclo[2.1.1]hexan-2-one afforded 0.36 g (78%) of a colorless syrup, after flash chromatography (10% ethyl acetate/hexane): ^{1}H NMR (CCl_4) δ 1.00 (m, 29 H), 2.10 (m, 4 H), 2.45 (b s, 1 H), 4.05 (m, 0.6 H), 4.25 (m, 0.4 H), 7.10 (s, 5 H).

***syn*-1-Phenylbicyclo[2.1.1]hexan-2-ol-*endo*-5-*d*.** The procedure described for the preparation of the analogous 2-phenyl derivative was used. Thus, *syn*,*endo*-1-phenyl-5-(tri-*n*-butylstannyl)bicyclo[2.1.1]hexan-2-ol (0.82 g, 1.8 mmol) yielded 0.30 g (94%) of deuteriated alcohol after flash chromatography (20% ethyl acetate/hexane): ^{1}H NM ($CDCl_3$) δ 1.60 (m, 5 H), 2.10 (m, 1 H), 2.35 (m, 1 H), 4.00 (d, 1 H), 7.05 (s, 5 H).

1-Phenylbicyclo[2.1.1]hexan-2-one-*endo*-5-*d*. To a slurry of pyridinium dichromate (1.6 g, 4.3 mmol) in methylene chloride (15 mL) was added *syn*-1-phenylbicyclo[2.1.1]hexan-2-ol-*endo*-5-*d* (0.25 g, 1.4 mmol) in methylene chloride (10 mL), and the mixture was vigorously stirred for 48 h. Ether (25 mL) was added, the reaction mixture was passed through a short column (3 × 4 cm) of Florisil, and the column was washed well with ether. The effluent was concentrated, and yielded, after flash chromatography (25% ethyl acetate/hexane), 0.20 g (79%) of deuteriated ketone:

^{1}H NMR (CCl_4) δ 2.00 (m, 1.2 H), 2.30 (m, 4 H), 2.75 (m, 1 H), 7.05 (m, 5 H); ^{13}C NMR ($CDCl_3$) 30.9 (d), 42.4 (t), 43.4, 44.4, 45.4 (triplet due to CHD), 44.8 (t), 68.0 (s), 126.6 (d), 127.0 (d), 128.2 (d), 136.8 (s), 211.6 (s); ^{2}H NMR ($CHCl_3$) δ 2.00. In the ^{2}H NMR there were peaks of much lower intensity in the vicinity of δ 7.05. This was due to a minor amount of deuteriation in the phenyl ring.

1-Phenylbicyclo[2.1.1]hexan-2-one-*endo*-5-*d* (*p*-Tolylsulfonyl)hydrazone. Via the procedure described for the unlabeled compound, a quantitative yield (0.39 g) of deuteriated tosylhydrazone was obtained. No spectral data were recorded.

1-Phenylbicyclo[2.1.1]hex-2-ene-*endo*-5-*d*. As described for the all protio compound, 71 mg (43%) of deuteriated olefin were obtained after flash chromatography (pentane): ^{1}H NMR (CCl_4) δ 2.60 (m, 1 H), 2.70 (m, 3.2 H), 6.60 (m, 1 H), 6.80 (m, 1 H), 7.10 (s, 5 H); ^{13}C NMR ($CDCl_3$) 39.3, 58.1, 69.6–70.6–71.6 (triplet due to CHD), 71.0, 126.0, 126.2, 128.2, 143.8, 145.2 (the ipso carbon in the phenyl ring was not observed); ^{2}H NMR (isooctane) δ 2.70.

1-Phenylbicyclo[2.1.1]hex-2-ene-*exo*-5-*d*. This compound was synthesized in the same manner as the *endo*-5-deuterio material except for these important modifications: 2-phenyl-1-hexen-5-yn-3-ol-6-*d* was used in the hydrostannylation reaction with tri-*n*-butyltin hydride instead of 2-phenyl-1-hexen-5-yn-3-ol; the destannylation of *syn,endo*-1-phenyl-5-(tri-n-butylstannyl)-bicyclo[2.1.1]hexan-2-ol-*exo*-5-*d* with *n*-butyllithium was quenched with water instead of deuterium oxide (which was used to quench the destannylation of *syn,endo*-1-phenyl-5-(tri-*n*-butylstannyl)-bicyclo[2.1.1]hexan-2-ol). All other reactions leading to 1-phenylbicyclo[2.1.1]hex-2-ene-*exo*-5-*d* were performed exactly as described for the endo isomer. The ^{2}H NMR contained the major peak at δ 2.60, instead of at δ 2.70. There was no peak observable at δ 2.70 (0.5% could have been detected). Analogous procedures afforded the exo isomers of the other 5-deuteriated bicyclo-[2.1.1]hexenes.

Pyrolysis of Bicyclo[2.1.1]hex-2-ene. Bicyclo[2.1.1]hex-2-ene (100 mg, 1.25 mmol) was dissolved in carbon tetrachloride (300 mL) and placed in an NMR tube, and the tube was degassed and sealed under vacuum. The tube was pyrolyzed for 70 min at 175 °C. At this point ^{1}H NMR indicated the absence of signals due to starting material and the clean formation of bicyclo[3.1.0]-hex-2-ene: ^{1}H NMR (CCl_4) δ –0.20 (m, 1 H), 0.80 (m, 1 H), 1.10 (m, 1 H), 1.25 (m, 1 H), 2.25 (m, 1 H), 2.75 (m, 1 H), 5.20 (m, 1 H), 5.75 (m, 1 H).

Pyrolysis of 1-Phenylbicyclo[2.1.1]hex-2-ene. 1-Phenylbicyclo[2.1.1]hex-2-ene (50 mg, 0.32 mmol) was dissolved in carbon tetrachloride (300 mL), and the solution was placed in an NMR tube and degassed and sealed under vacuum. The tube was pyrolyzed for 1 h at 115 °C. ^{1}H NMR indicated the loss of starting material and clean formation of 3-phenylbicyclo[3.1.0]hex-2-ene: ^{1}H NMR ($CDCl_3$) δ 0.05 (ddd, J = 4.0, 2.0, 2.0 Hz, 1 H), 0.90 (ddd, J = 10.0, 4.0, 4.0 Hz, 1 H), 1.70 (m, 1 H), 1.85 (m, 1 H), 2.60 (d, J = 19.0 Hz, 1 H), 3.00 (dd, J = 19.0, 6.0 Hz, 1 H), 6.25 (m, 1 H), 7.25 (m, 5 H); ^{13}C NMR ($CDCl_3$) 15.5 (t), 17.6 (d), 24.1 (t), 36.3 (d), 125.1 (d), 126.7 (d), 128.2 (d), 129.7 (d), 133.5 (s), 136.6 (s). The material could be purified by flash chromatography (pentane) or preparative gas chromatography, either of which resulted in an approximately 95% recovery. A control experiment was performed in which a purified sample of 3-phenylbicyclo-[3.1.0]hex-2-ene was heated at 125 °C for 700 min, and this pyrolysate showed no change in its ^{1}H or ^{13}C NMR, or its analytical capillary gas chromatograph.

Pyrolysis of 2-Phenylbicyclo[2.1.1]hex-2-ene. 2-Phenylbicyclo[2.1.1]hex-2-ene (1.1 g, 11.0 mmol) was dissolved in isooctane (10 mL), placed in a large tube, then degassed and sealed under vacuum. The tube was pyrolyzed for 180 min at 171.5 °C, at which time capillary gas chromatography indicated the complete loss of starting material and the formation of three products. These three products could be isolated from one another by preparative gas chromatography. They were identified as 1-phenylbicyclo[3.1.0]hex-2-ene: ^{1}H NMR ($CDCl_3$) δ 0.50 (m, 1 H), 1.45 (m, 1 H), 1.75 (m, 1 H), 2.35 (d, J = 18 Hz, 1 H), 2.75 (d of multiplets, J = 18.0 Hz, 1 H), 5.40 (m, 1 H), 6.05 (m, 1 H), 7.05 (s, 5 H); ^{13}C NMR ($CDCl_3$) 24.3, 26.5, 36.5, 38.7, 125.5, 126.2, 127.8, 128.2, 136.3, 142.7; mass spectrum, m/z 156 ($M^{\bullet+}$). The second compound was found to be identical in all respects with 2-phenylbicyclo[3.1.0]hex-2-ene. An authentic sample was prepared from the xanthate ester pyrolysis of 2-phenylbicyclo[3.1.0]hexan-2-ol. The spectral data appear with the experimental description of this reaction. The last compound was found to be identical in all respects with 3-phenylbicyclo[3.1.0]hex-2-ene. This compound was the exclusive product from the pyrolysis of 1-phenylbicyclo[2.1.1]hex-2-ene. Spectral data appear with the experimental particulars of that pyrolysis.

Pyrolysis of 1-Phenylbicyclo[3.1.0]hex-2-ene. 1-Phenylbicyclo[3.1.0]hex-2-ene (50 mg, 0.32 mmol) was dissolved in isooctane (300 mL), placed in an NMR tube, degassed, and sealed. The tube was heated for 11 h at 181.3 °C at which time capillary gas chromatography indicated the presence of starting material and 3-phenylbicyclo[3.1.0]hex-2-ene, by co-injection with an authentic sample and ^{1}H NMR analysis.

Bicyclo[3.1.0]hexan-2-one. Sodium hydride (25.3 mmol, 1.1 g of a 55% dispersion in oil) was placed in a dry flask, and anhydrous hexane was added. The flask was swirled a few times, and the hexane was carefully decanted off. After repeating this procedure twice more, the last bit of hexane was removed in vacuo and, after filling the flask with argon (atmospheric pressure), trimethylsulfoxonium iodide (5.6 g, 25.3 mmol) was added, followed by dimethyl sulfoxide (50 mL). As the salt dissolved, gas was evolved, and after stirring for 20 min, 2-cyclopentenone (2.1 g, 25.3 mmol) was dissolved in dimethyl sulfoxide (20 mL) and added dropwise. After the reaction mixture was stirred for an additional 1.5 h, it was poured onto water and extracted with ether (3 × 50 mL). The combined organic extracts were washed with water (2 × 25 mL), dried, and filtered, and the solvent was removed by careful distillation until 1–2 mL remained in the pot flask. The residue was purified by vacuum distillation, which afforded 0.20 g (17%) of material: bp 65–70 °C (15 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.95 (m, 1 H), 1.25 (m, 1 H), 1.85 (m, 2 H), 2.10 (m, 4 H).

2-Phenylbicyclo[3.1.0]hexan-2-ol. The procedure employed for the preparation of 2-phenylbicyclo[2.1.1]hexan-2-ol was used. Bicyclo[3.1.0]hexan-2-one (0.20 g, 2.1 mmol), bromobenzene (0.65 g, 4.2 mmol), and magnesium (0.11 g, 4.6 mmol) in tetrahydrofuran (50 mL) afforded 0.23 g (63%) of a viscous oil: ^{1}H NMR ($CDCl_3$) δ 0.65 (m, 2 H), 1.20 (m, 1 H), 1.65 (m, 4 H), 1.95 (m, 2 H), 7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$) 6.0, 18.5, 25.8, 27.9, 36.8, 82.9, 124.8, 126.7, 128.2, 148.4.

2-Phenylbicyclo[3.1.0]hex-2-ene. The procedure followed was that described for the synthesis of 2-phenylbicyclo[2.1.1]-hex-2-ene via the xanthate ester of the analogous alcohol. 2-Phenylbicyclo[3.1.0]hexan-2-ol (0.14 g, 0.80 mmol), treated with sodium hydride (80 mg, 1.6 mmol), carbon disulfide (0.13 g, 1.8 mmol), and methyl iodide (0.25 g, 1.8 mmol) in ether (20 mL) afforded 80 mg (64%) of hydrocarbon after flash chromatography (hexane): ^{1}H NMR ($CDCl_3$) δ 0.25 (m, 1 H), 1.15 (m, 1 H), 1.90 (m, 1 H), 2.35 (m, 1 H), 2.65 (d, J = 18.0 Hz, 1 H), 3.00 (dd, J = 18.0, 6.0 Hz, 1 H), 5.85 (m, 1 H), 7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) 14.9 (d), 15.3 (t), 23.5 (d), 35.6 (t), 121.9 (d), 125.8 (d), 127.1 (d), 128.3 (d), 136.1 (s), 147.0 (s). This compound was identical in all respects (spectrally and by co-injection on a capillary gas chromatograph) with one of the minor components formed during the pyrolysis of 2-phenylbicyclo[2.1.1]hex-2-ene.

Kinetics of the Thermal Rearrangement of Bicyclo-[2.1.1]hex-2-enes. Kinetic studies on the bicyclo[2.1.1]hex-2-ene derivatives were performed in dilute (approximately 5×10^{-3} M) isooctane solutions. Between 50 and 200 mL of a solution was syringed into 10 × 0.6 cm annealed, Pyrex tubes that had been soaked in ammonium hydroxide solution for 1–3 h and then baked in an oven for at least 24 h. The tubes were connected to a vacuum line equipped with a mercury diffusion pump and degassed by the "freeze–pump–thaw" cycle method. Tubes were heated using a Tamson Neslabs TX-9 constant temperature oil bath equipped with a MTC-250 thermoregulator. Temperatures were measured with NBS-standardized thermometers, with the appropriate emergent stem correction. Time intervals were measured with a Tektimer quartz SP digital timer. Tubes were removed from the oil bath and immediately plunged into liquid nitrogen. The following parameters were used for the capillary GC analysis.

Bicyclo[2.1.1]hex-2-ene: gas chromatograph, injector 100 °C, oven 40 °C, internal standard toluene. Due to the volatility of the compounds involved in this analysis the tubes were cooled

Table III. Rate Constants for Rearrangement of Bicyclo[2.1.1]hexene to Bicyclo[3.1.0]hex-2-ene

temp, °C	rate constant, s^{-1}
130.10 ± 0.05	(8.21 ± 0.12) × 10^{-6}
139.80 ± 0.05	(2.21 ± 0.05) × 10^{-5}
144.60 ± 0.05	(3.80 ± 0.05) × 10^{-5}
165.83 ± 0.05	(2.89 ± 0.04) × 10^{-4}
170.40 ± 0.05	(4.74 ± 0.06) × 10^{-4}
175.27 ± 0.05	(7.17 ± 0.08) × 10^{-4}

in an ice bath prior to opening and throughout the time it took to make five injections from the tube.

2-Phenylbicyclo[2.1.1]hex-2-ene: gas chromatograph, injector 160 °C, oven 130 °C, internal standard dodecane.

1-Phenylbicyclo[2.1.1]hex-2-ene: gas chromatograph, injector 150 °C, oven 120 °C, internal standard undecane. Due to the relatively low energy of activation for the rearrangement of this compound, it was necessary to check, and was satisfactorily shown, that the material did not rearrange on the gas chromatograph under these conditions.

Pyrolysis of Bicyclo[2.1.1]hex-2-ene-*5-d*. In all pyrolyses 50–250 mg of substrate was dissolved in isooctane (approximately 300 mL), one drop of $CDCl_3$ from a 9-in. Pastuer pipet was added, and the solution was placed in an NMR tube and degassed. The tube was then pyrolyzed at a given temperature until peaks due to starting material were no longer apparent in a ^2H NMR spectrum. From ^2H NMR data at intermediate reaction times it was determined that no scrambling of deuterium in starting material was occurring for any of the three substrates. The relative amounts of exo and endo deuterium at the 6-position as well as deuterium at the 4-position (from migration of the unlabeled bridge) in the bicyclo[3.1.0]hex-2-ene products were determined from ^2H NMR analyses (when starting material was no longer present) by the "cut and weigh" method. Control experiments were run by heating samples of each compound after starting material was gone to determine if scrambling of deuterium was occurring in the product bicyclo[3.1.0]hex-2-enes. No scrambling was observed for the parent or 3-phenyl derivative, but scrambling was observed for 1-phenyl compound. The ratio of exo and endo deuterium in the 1-phenyl compound was corrected by observing the ratio at the 6-position approach a 1:1 ratio at several temperatures.

The parent deuteriated bicyclo[2.1.1]hex-2-ene was contaminated with 1.8–2.6% of the opposite label/epimer at C5, and the ratios in the product were corrected for this. The phenyl-*5-d* compounds showed no detectable amount of the "wrong" isomer. As little as 0.5% could have been detected.

Europium Shift Experiments on Bicyclo[2.1.1]hexan-2-one-*endo-5-d*. A 0.23 M solution of $Eu(fod)_3$ was prepared by dissolving 0.24 g (0.23 mmol) in chloroform such that the total volume of the solution was 1 mL; 20 mg of bicyclic ketones that had been prepared as a 1:1 mixture of *endo*- and *exo*-5-deuterio epimers was dissolved in chloroform and placed in an NMR tube, and chloroform-*d* (5 mL) was added. A 25-mL portion of the 0.23M $Eu(fod)_3$ was added at a time. After each addition a ^2H NMR spectrum was recorded, and the two chemical shifts corresponding to the 5-deuterium at the endo and exo position were noted.

Determination of Response Factors for Phenyl-Substituted Bicyclo[3.1.0]hex-2-enes. The three phenylbicyclo[3.1.0]hex-2-enes (the 1-, 2-, and 3-phenyl derivatives, obtained from the pyrolysis of 2-phenylbicyclo[2.1.1]hex-2-ene) were purified to greater than 99% purity by preparative gas chromatography. A 0.032 M solution of dodecane was prepared by diluting 0.135 g of dodecane to 25 mL with isooctane. A 0.026 M solution of 1-phenylbicyclo[3.1.0]hex-2-ene was prepared by diluting 40 mg to 10 mL with isooctane, a 0.042 M solution of 2-phenylbicyclo[3.1.0]hex-2-ene by diluting 6.6 mg to 1 mL with isooctane, and a 0.035 M solution of 3-phenylbicyclo[3.1.0]hex-2-ene by diluting 11.0 mg to 2 mL with isooctane; 2 mL of each solution was injected on the capillary gas chromatograph five times, and the relative response of each bicyclic hydrocarbon per response of dodecane (per millimole) could be calculated. They are 1-phenylbicyclo[3.1.0]hex-2-ene, 0.924; 2-phenylbicyclo[3.1.0]hex-2-ene, 1.112; 3-phenylbicyclo[3.1.0]hex-2-ene, 1.080. A summary of rate constants for thermal rearrangements is found in Tables III–V.

Table IV. Rate Constants for Rearrangement of 1-Phenylbicyclo[2.1.1]hexene to 3-Phenylbicyclo[3.1.0]hex-2-ene

temp, °C	rate constant, s^{-1}
82.60 ± 0.05	(1.31 ± 0.01) × 10^{-5}
92.15 ± 0.05	(4.34 ± 0.03) × 10^{-5}
101.40 ± 0.05	(1.17 ± 0.01) × 10^{-4}
109.70 ± 0.05	(2.68 ± 0.01) × 10^{-4}
119.95 ± 0.05	(7.43 ± 0.03) × 10^{-4}
125.15 ± 0.05	(1.18 ± 0.01) × 10^{-3}
133.50 ± 0.05	(2.59 ± 0.03) × 10^{-3}

Table V. Rate Constants for Disappearance and Partitioning of 2-Phenylbicyclo[2.1.1]hexene

temp, °C	rate constant for disappearance, s^{-1}	product ratio[a]
130.10 ± 0.05	(1.80 ± 0.04) × 10^{-5}	0.055
139.80 ± 0.05	(4.48 ± 0.03) × 10^{-5}	0.059
152.00 ± 0.05	(1.47 ± 0.01) × 10^{-4}	0.065
160.20 ± 0.05	(3.16 ± 0.01) × 10^{-4}	0.071
169.40 ± 0.05	(7.37 ± 0.05) × 10^{-4}	0.076
175.40 ± 0.05	(1.18 ± 0.01) × 10^{-3}	0.080
181.35 ± 0.05	(2.04 ± 0.02) × 10^{-3}	0.084

[a] The product ratio is defined as the fraction 2-phenylbicyclo[3.1.0]hexene/(1-phenylbicyclo[3.1.0]hexene + 3-phenylbicyclo[3.1.0]hexene). The 3-phenyl isomer is a secondary isomerization product from the 1-phenyl isomer (see text).

***trans*-2-Methylcyclopropanemethanol.** A solution of *trans*-2-methylcyclopropanecarboxylic acid (10.1 g, 0.1 mol) in dry ether (50 mL) was added dropwise to a slurry of lithium aluminum hydride (3.8 g, 0.1 mol) in dry ether (300 mL) at 0 °C. After stirring for 2 h, a standard LAH workup was performed. Distillation gave 7.4 g (86% yield) of a colorless liquid.[34]

***trans*-2-Methylcyclopropanecarboxaldehyde.** *trans*-2-Methylcyclopropanemethanol was oxidized according to the Corey procedure.[35] Pyridinium chlorochromate (21.3 g, 0.1 mol) was suspended in methylene chloride (125 mL) in a 500-mL round-bottom flask fitted with a condenser. The alcohol (5.43 g, 0.063 mol) was added all at once. The solution became black and started to reflux after 10 min. After stirring at room temperature for 2 h, ether (125 mL) was added and the solution was decanted. The tarry black residue was washed with ether. The combined organic material was passed through a 3-in. plug of Florisil. The solvent was removed by distillation through a Vigreux column. Final yield of product was 3.5 g (66% yield): 300 MHz ^1H NMR ($CDCl_3$) δ 0.88 (m, 1 H), 1.17 (2 d, J = 5.9, 3 H), 1.26 (m, 1 H), 1.48 (m, 1 H), 1.57 (m, 1 H), 8.98 (d, J = 5.5, 0.88 H), 9.36 (d, J = 5.5, 0.12 H).

***trans*-2-Methyl-(*trans*-2-phenylethenyl)cyclopropane.** *n*-Butyllithium (35 mL of 1.5 M solution) was added to a suspension of benzyltriphenylphosphonium bromide (21.12 g, 49 mmol) in a 2:1 mixture of THF and ether (300 mL) at 0 °C. The deep red solution was stirred for 1 h at room temperature and then cooled to −78 °C. Additional ether had to be added to keep the solution homogeneous. A THF solution of *trans*-2-methylcyclopropanecarboxaldehyde (3.47 g, 41 mmol) was added over 1 h, and the mixture was stirred overnight. After addition of *tert*-butyl alcohol, the solution was poured into ice water. The water was extracted three times with ether. The combined organic extracts were dried ($MgSO_4$) and concentrated to a white precipitate, which was washed well with hexanes. Concentration gave a yellow liquid. After chromatography, (hexanes) 5.24 g (86%) of a mixture of four isomeric vinylcyclopropane was obtained. The GC retention times were 4.2, 4.9, 6.2, and 6.5 min at 115 °C, in a ratio of 12.6:1:24:1.1. Analytically pure material was obtained by preparative GC on column B at 185 °C. In the following

(34) Andrews, G. D.; Ph.D. Dissertation, The University of Oregon, 1975.

(35) Corey, E. J. *Tetrahedron Lett.* **1975**, 2647.

spectroscopic data trans–cis refers to a trans cyclopropane with a cis double bond, etc.

Trans–trans (t_R = 6.2 min): 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.55 (m, 1 H), 0.65 (m, 1 H), 0.85 (m, 1 H), 1.08 (d, J = 5.9, 3 H), 1.33 (m, 1 H), 5.73 (dd, J = 8.9, 15.8, 1 H), 6.38 (d, J = 15.8, 1 H), 7.13 (m, 1 H), 7.25 (m, 4 H); ^{13}C NMR 137.90, 134.58, 128.44, 126.93, 126.39, 125.51, 23.42, 18.54, 15.77.

Trans–cis (t_R = 4.2 min): 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.6 (m, 2 H), 0.85 (m, 1 h), 1.11 (d, J = 5.9, 3 H), 1.55 (m, 1 H), 5.08 (dd, J = 9.5, 11.5, 1 H), 6.30 (d, J = 11.5, 1 H), 7.30 (m, 5 H); ^{13}C NMR 138.00, 136.39, 128.63, 128.10, 126.83, 126.24, 20.00, 18.30, 16.49, 16.35.

Cis–cis (t_R = 4.9 min): partial 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.22 (d), 5.40 (dd, J = 9.5, 11.5), 6.45 (d, J = 11.5); ^{13}C NMR 132.34, 129.41, 128.73, 128.05, 126.34, 16.49, 16.20, 14.16, 13.72.

Cis–trans (t_R = 6.5 min): partial 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.28 (d), 5.95 (dd, J = 9.0, 15.7), 6.48 (d, J = 15.7).

Preparative Pyrolysis of 2-Methyl(2-phenylethenyl)-cyclopropanes. A 12 in. × 1 in. Pyrex tube was packed with short pieces of Pyrex tubing. A septum capped the upper end, and a pear-shaped flask equipped with a gas outlet capped the bottom. The column was preheated to approximately 450 °C with external heating tape under nitrogen flow. The temperature was measured using an iron-constantan thermocouple held snugly to the column by the heating tape. The thermocouple was connected to an Omega Model 199 digital temperature indicator. The temperature was uncorrected. A stream of nitrogen was passed through the vertical column while a solution of vinylcyclopropanes (0.5 g in 9 mL hexanes) was dripped onto the top of the column at a rate of 2 mL/h. The effluent was collected at the bottom, which was immersed in a −78 °C slush bath. When all the solution had been applied, the column was allowed to cool down and the trapped liquid warmed up. The yellow solution was chromatographed (hexanes) to remove the yellow residue. GC analysis (115 °C) showed the appearance of two new peaks, t_R 3.3 and 3.4 min. These were purified by preparative gas chromatography at 145 °C with retention times 30 and 32 min, respectively. The faster moving component was identified as *trans*-4-methyl-3-phenylcyclopentene and the slower component as *cis*-4-methyl-3-phenylcyclopentene. When the experiment was repeated using a lower column temperature (300 °C), the cyclopentenes represented minor products. The major product had a retention time of 3.8 min at 115 °C and was identified as *cis*-1-phenyl-2,5-hexadiene, **11**.

***trans*-4-Methyl-3-phenylcyclopentene**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.11 (d, J = 7.0, 3 H), 2.02 (app d sept, 1 H), 2.10 (app sept, 1 H), 2.61 (ddddd, 1 H), 3.35 (m, 1 H), 5.67 (m, 1 H), 5.83 (m, 1 H).

***cis*-4-Methyl-3-phenylcyclopentene**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.58 (d, J = 7.0, 3 H), 2.05 (ddddd, J = 2.5, 2.5, 2.5, 6.8, 16.8, 1 H), 2.55 (ddddd, J = 1.7, 1.7, 1.7, 8.0, 16.0, 1 H), 2.65 (app sept d, J = 6.8, 7.0, 8.0, 8.4, 1 H), 3.85 (dm, J = 1.7, 2.5, 2.5, 2.5, 8.4, 1 H), 5.80 (dddd, J = 1.7, 2.5, 2.5, 8.0, 1 H), 5.95 (dddd, J = 1.7, 2.5, 2.5, 8.0, 1 H), 7.15 (m, 5 H).

***cis*-6-Phenyl-1,4-hexadiene**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 2.92 (t, J = 5.9, 2 H), 3.41 (d, J = 7.1, 2 H), 5.01 (ddd, J = 1.6, 3.2, 10.0, 1 H), 5.09 (ddd, J = 1.8, 3.6, 17.0, 1 H), 5.55 (m, 1 H), 5.65 (m, 1 H), 5.85 (m, 1 H), 7.25 (m, 5 H); ^{13}C NMR 31.5, 33.4, 114.9, 125.9, 127.6, 128.3, 129.3, 136.6, 140.8.

1-Phenylpropyne. Potassium *tert*-butoxide (33.7 g, 0.3 mol) was added to a solution of phenylacetylene (11 mL, 0.1 mol) in dry DMSO (350 mL) at 15 °C under nitrogen. The resulting black-brown solution was stirred for 5 min. Methyl iodide (25 mL, 0.4 mol) was added, and after the exothermic reaction subsided, the orange-yellow solution was stirred for 3 h. Water (100 mL) was added, and the mixture was extracted with petroleum ether. The organic material was washed with dilute HCl and brine. The solvent was dried ($MgSO_4$) and evaporated leaving a yellow oil, which was vacuum distilled to give 7.5 g (64% yield) of product: 60-MHz ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3 H), 7.05–7.45 (m, 5 H).

3-Phenylpropyne.[36] 1-Phenylpropyne (7.5 g, 0.065 mol), 1.9 M butyllithium (80 mL, 0.152 mol), and ether (80 mL) were used. Vacuum transfer gave 6.67 g (89% yield) of a clear colorless liquid. 90-MHz ^{1}H NMR ($CDCl_3$) δ 2.05 (t, 1 H), 3.45 (d, 2 H), 7.15 (br s, 5 H).

1-Phenylhex-5-en-1-yne. The procedure was inspired by that of Catellani et al.[37] A 100-mL three-neck flask was charged with bis(cyclooctadiene)nickel (0.3 g, 1.09 mmol) in an inert atmosphere. Dry THF (50 mL) was added, followed by trisisopropylphosphite (0.91 g, 4.37 mmol), **30** (1.0 g, 8.61 mmol), and allyl acetate (860 mg, 8.6 mmol). The yellowish solution was heated to 75 °C for 10 h. After the solution was cooled to room temperature, ether (50 mL) was added. The organic material was washed with dilute HCl, water, $NaHCO_3$, and water again, then dried ($MgSO_4$) and concentrated to a slightly yellow liquid. TLC (5% ethyl acetate in hexanes) revealed one UV active spot, R_f = 0.6. The product was purified by preparative TLC using 2% ethyl acetate in hexanes as eluent, giving 900 mg, 67% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 3.02 (m, 2 H), 3.63 (t, 2 H), 5.19 and 5.42 (2 dm, 2 H), 5.85 (m, 1 H), 7.32 (br s, 5 H); ^{13}C NMR 23.17, 25.17, 78.95, 80.12, 115.8, 126.4, 127.8, 128.4, 133.1, 137.3.

***cis*-6-Phenyl-1,4-hexadiene.** Benzene (40 mL), Lindlar's catalyst (35 mg), and a drop of quinoline were placed in a 100-mL round-bottom flask, attached to an hydrogenator and equilibrated under hydrogen at 0 °C. The ice bath was removed, and 1-phenylhex-5-en-1-yne (150 mg, 0.98 mmol) was added. The reaction was monitored by GC. At 115 °C, the retention times (min) were as follows: starting material 5.1, product 3.8, overreduction product, 4.0. The reaction was stopped when product formation was optimized relative to the other processes. The diene was obtained in greater than 98% purity by preparative gas chromatography. The final yield was 100 mg (65%). The material was identical in every respect to that obtained on pyrolysis of **2**.

(*S*)-(+)-Propane-1,2-diol. The method of Golding was used without modification.[38] (*S*)-(−)-Ethyl lactate (33.0 g, 0.28 mol), lithium aluminum hydride (10.7 g, 0.282 mol), and ether (500 mL) were used. Ice cooling was needed to avoid an overly exothermic reaction. After distillation, 12.3 g (59% yield) of product were obtained.

Acetoxy Bromides of (*S*)-(+)-Propane-1,2-diol. This material was prepared according to the procedure of Golding.[38] Propanediol (12.3 g, 0.16 mol) and HBr in acetic acid (100 mL, 0.47 mol) were used. The yield was 25.3 g (88%) after distillation.

(*S*)-γ-Methyl-(*R*/*S*)-α-carbethoxy-γ-butyrolactone. Sodium hydride (50% dispersion in oil, 5.7 g, 119 mmol) was cautiously dissolved in absolute ethanol (100 mL) with cooling. This was transferred to an addition funnel and added to a solution of the above acetoxy bromides (20.2 g, 0.12 mol) in ethanol (100 mL) over 20 min. The thick solution was distilled through a Vigreux column into a −30 °C bath until approximately 2/3 of the ethanol had distilled. NMR of the distillate showed only ethanol and propylene oxide. In another flask equipped with an overhead stirrer, sodium hydride (5.92 g, 0.12 mol) was dissolved in ethanol (100 mL). Diethyl malonate (19 mL, 0.125 mol) was added followed by the above ethanolic solution of propylene oxide over 10 min. This was stirred at room temperature for 3 h and refluxed for an additional 2 h. Upon cooling, the solution was made acidic with dilute HCl. CH_2Cl_2 and water were added until two layers were obvious. The aqueous layer was extracted well with CH_2Cl_2, and the organic material was washed with water. Drying (Na_2SO_4) and concentration gave 3.05 g of crude product, which was used without further purification. The ^{1}H NMR showed two doublets at 1.35 and 1.40 ppm, plus two multiplets at 4.55 and 4.75 ppm, each pair in a ratio of approximately 1:1.

(*S*)-(−)-γ-Methyl-γ-butyrolactone. γ-Methyl-α-carbethoxy-γ-butyrolactone (3.05 g) from above was dissolved in DMF (50 mL + 1 mL of water) and heated to reflux. When the reaction was completed as judged by TLC (usually 6–10 h), water (20 mL) was added, and the mixture was exhaustively extracted with ether. The ether was carefully washed once with a small amount of water. The ether was dried (Na_2SO_4) and concentrated, and the residue was chromatographed (25% ethyl acetate in hexanes) to yield 2.54 g (24% from 2-acetoxy-1-bromopropane): 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.37 (d, J = 6.2, 3 H), 1.79 (m, 1 H), 2.33 (m, 1 H), 2.51

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(m, 2 H), 4.51 (m, 1 H); ^{13}C NMR 20.62, 28.66, 29.26, 76.81, 176.81.

(*S*)-γ-Methyl-(*R*/*S*)-γ-butyrolactol. A solution of DIBAL in hexane (35 mL, 35 mmol) was added dropwise to a cooled (−60 °C) solution of the lactone from the preceding section (1.17 g, 12 mmol) in dry THF (50 mL). After the mixture was stirred for 15 min, saturated ammonium chloride (5 mL) was carefully added. A standard DIBAL workup was performed, and the organic material was dried (Na_2SO_4) and concentrated. TLC showed only one spot, R_f = 0.3 (50% ethyl acetate in hexanes). This was used without further purification. The ^1H NMR showed two new multiplets at 5.43 and 5.53 ppm, assigned to CHOH.

(*S*)-*cis*- and -*trans*-6-Phenyl-5-hexen-2-ol. Sodium hydride (50% dispersion in oil, 1.68 g, 35 mmol) was added to dry DMSO (50 mL) and heated to 80 °C for 1 h. Benzyltriphenylphosphonium bromide (15.5 g, 36 mmol) was added, and the solution became orange and thick. (S)-γ-Methyl-(*R*/*S*)-γ-butyrolactol was added in ether, and the solution was stirred overnight. Water (20 mL) was added, and the solution was extracted with ether. The ether was washed with water, 1 N HCl, and water again. After drying (Na_2SO_4) and concentration, the solid was slurried and chromatographed (25% ethyl acetate in hexanes). Care had to be taken as most of the material was triphenylphosphine oxide, which was insoluble in the eluting solvent. Product was collected (1.06 g, 52% from the lactone) which had a slight smell of a sulfur impurity that did not affect future reactions: 300-MHz ^1H NMR ($CDCl_3$) δ 1.15–1.25 (2 3 H), 1.59 (m, 2 H), 2.2–2.46 (2 m, 2 H), 3.85 (app sept, 1 H), 5.65 (dt, 0.4 H), 6.20 (dt, 0.6 H), 6.4 and 6.45 (2 d, 1 H), 7.24 (m, 5 H).

(*R*)-*trans*-5-Chloro-1-phenyl-1-hexene. Triphenylphosphine (1.60 g, 6.10 mmol) was added to a solution of (*S*)-*cis*- and -*trans*-6-phenyl-5-hexen-2-ol (1.06 g, 6 mmol) in carbon tetrachloride and heated to reflux under a nitrogen atmosphere. After 5 h, starting material was still present, and more triphenylphosphine (0.5 g) was added. Heating was continued for an additional 10 h. After cooling, methanol (5 mL) was added, and the solution was stirred for 30 min and then concentrated to a solid, which was mostly triphenylphosphine oxide. Steam distillation was performed giving 0.89 g (76%) of an oil. The ^1H NMR data was consistent with two olefinic stereoisomers. The chloride was dissolved in dry benzene (20 mL), a catalytic amount of sublimed iodine was added, and the solution brought to reflux. Periodically an aliquot was removed, concentrated, and an NMR taken to determine the isomeric ratio. When isomerization to the trans isomer was complete, the solution was washed with $Na_2S_2O_3$, dried (Na_2SO_4), and concentrated. Kugelrohr distillation gave 600 mg (51% overall) of pure product: 300-MHz ^1H NMR ($CDCl_3$) δ 1.52 (d, *J* = 6.5, 3 H), 1.86 (dt, *J* = 2.6, 7.9, 2 H), 2.39 (m, 2 H), 4.06 (m, 1 H), 6.16 (dt, *J* = 6.9, 15.8, 1 H), 6.42 (d, *J* = 15.8, 1 H), 7.27 (m, 5 H).

(1*S*,2*S*)-2-Methyl-(*trans*-2-phenylethenyl)cyclopropane. Treatment of (*R*)-*trans*-5-chloro-1-phenyl-1-hexene with 1.5 equiv of NaH ind DMSO at room temperature afforded a 75% yield of (1*S*,2*S*)-2-methyl-(*trans*-2-phenylethenyl)cyclopropane and (1*R*,2*S*)-2-methyl-(*trans*-2-phenylethenyl)cyclopropane in a 0.36:1 ratio (spectral data below).

Crotonaldehyde Diethyl Acetal. Ammonium nitrate (3 g) was dissolved in hot ethanol (50 mL) and added to a solution of distilled anhydrous crotonaldehyde (52.5 g, 0.75 mol) and triethyl orthoformate (120 mL). After stirring at room temperature for 12 h, the red solution was filtered. Solid Na_2CO_3 (4 g) was added to the filtrate, which was then distilled through a Vigreux column. Product was distilled to give 49.5 g (47% yield): bp 146–150 °C; 300-MHz ^1H NMR ($CDCl_3$) δ 1.19 (t, *J* = 7.1, 6 H), 1.70 (dd, *J* = 1.0, 6.5, 3 H), 3.48 (qd, 2 H), 3.61 (qd, 2 H), 4.79 (d, *J* = 5.7, 1 H), 5.50 (ddd, *J* = 1.5, 5.5, 15.4, 1 H), 5.81 (m, 1 H).

Crotonaldehyde Diisopropyl-L-tartrate Acetal.[3] A solution of crotonaldehyde diethyl acetal (15.0 g, 0.11 mol), diisopropyl-L-tartrate (20.57 g, 88 mmol), pyridinium tosylate (cat.), and benzene (200 mL) was heated to reflux for 3 h under Dean–Stark conditions. When cooled, ether (100 mL) was added to the yellow solution, which was washed with water and saturated aqueous Na_2CO_3. This was distilled through a Vigreux column to give 14.45 g (58%) of a yellow liquid: bp (0.1 mm) 95–105 °C; 300-MHz ^1H NMR ($CDCl_3$) δ 1.27 (d, *J* = 6.3, 12 H), 1.74 (dd, *J* = 1.5, 7.4, 3 H), 4.60 (d, *J* = 3.9, 1 H), 4.68 (d, *J* = 3.9, 1 H), 5.10 (quint d, *J* = 1.6, 6.3, 2 H), 5.58 (m, 2 H), 6.00 (m, 1 H).

(1*R*,2*R*)-2-Methylcyclopropanecarboxaldehyde Diisopropyl-L-tartrate Acetal.[3] Diethylzinc (150 mL of a 1.6 M solution in toluene, 240 mmol) was added to a solution of crotonaldehyde diisopropyl-L-tartrate acetal (14.45 g, 51 mmol) in dry hexanes (200 mL), and the resulting solution cooled to −20 °C, with stirring provided by an overhead stirrer. Diiodomethane (42 mL, 520 mmol) was added dropwise to this well-stirred solution. Stirring was continued for 1 h at −20 °C and 5 h at 0 °C. The solution was poured into stirring cold aqueous ammonium chloride, and the reaction flask was rinsed with ammonium chloride and ether. The organic layer was separated, and the aqueous material was extracted with ether. The combined organic extracts were washed with aqueous sodium thiosulfate, water, and dried (Na_2SO_4). After concentration and chromatography (10% ethyl acetate in hexanes), 10.63 g (69%) were collected: 300-MHz ^1H NMR ($CDCl_3$) δ 0.37 (m, 1 H), 0.64 (m, 1 H), 0.92 (m, 2 H), 1.06 (d, *J* = 14.5, 3 H), 1.26 (d, *J* = 5.7), and 1.28 (d, *J* = 6.1, 12 H), 4.54 (d, *J* = 4.2, 1 H), 4.64 (d, *J* = 4.1, 1 H), 4.76 (d, *J* = 6.2, 1 H), 5.09 (m, 2 H).

(1*R*,2*R*)-2-Methyl-(*trans*-2-phenylethenyl)cyclopropane. A solution of (1*R*,2*R*)-2-methylcyclopropanecarboxaldehyde diisopropyl-L-tartrate acetal (10.63 g, 35 mmol) and *p*-toluenesulfonic acid monohydrate (8.1 g, 43 mmol) in THF (200 mL with 10 mL of water added) was heated to reflux for 7 h. When cooled, ether (100 mL) was added, and the solution was washed with water, saturated aqueous Na_2CO_3, and water and dried (Na_2SO_4). The solution was distilled through a Vigreux column until approximately $^1/_2$ of the solvent was removed. In another flask, benzyltriphenylphosphonium bromide (16.0 g, mmol) was suspended in 1:1 THF–ether (250 mL) and cooled to 0 °C under nitrogen. A solution of *n*-butyllithium (1.5 M in hexanes) was added until the mixture became red and homogeneous. The aldehyde solution from above was added dropwise until the red color had dissappeared. Additional *n*-butyllithium was added to regain the red color, and the aldehyde was again added. This was repeated until all the aldehyde solution was used up. After stirring for 1 h, water (5 mL) and hexanes were added. The white precipitate (triphenylphosphine oxide) was filtered through a fritted filter (size C) and washed well with hexanes. The organic material was washed twice with water, dried (Na_2SO_4), and concentrated to an orange viscous oil. This was chromatographed (hexanes) to give 2.64 g (48% from acetal) of a clear colorless liquid. GC analysis (115 °C) showed a 2:1 ratio of the desired trans–trans isomer to the trans–cis isomer. The enantiomeric excess was 80–86%, as determined from the shifts in the ^1H NMR with $Pr(hfc)_3$ and Ag(fod) in $CDCl_3$.

***trans*-2-Methylcyclopentanecarboxylic Acid** (prepared as a mixture with *cis*- and *trans*-3-methylcyclopentanecarboxylic acid). This material was prepared by the procedure of Hill.[39] A solution of selenium dioxide (0.50 g, 4.5 mmol) and hydrogen peroxide (15 mL of a 30% solution) was refluxed on a steam bath for 2.5 h. When cooled, hydrogen peroxide (15 mL) was added, followed by pyridine (0.5 mL) and a solution of 3-methylcyclohexanone (7.4 g, 66 mmol) in *tert*-butyl alcohol (10 mL). This solution was refluxed overnight. The cooled solution was made basic with saturated $NaHCO_3$ and extracted with ether, and the extracts were discarded. The aqueous solution was made acidic with 6 N HCl, saturated with NH_4Cl, and extracted with ether. The ether was dried ($MgSO_4$) and concentrated to give ca. 10 g of a mixture of the acids. Attempts at separating the 1,2 product from the 1,3 products failed, and the mixture was generally used without further purification. The material could be chromatographed (30% ethyl acetate in hexanes) to give a clear colorless oil, which was a mixture of the three isomers of product. The *R* enantiomer was prepared in a similar manner from the corresponding (*R*)-3-methylcyclohexanone.

Methyl *trans*-2-Methylcyclopentanecarboxylate. Diazomethane was used for small-scale esterifications. On a larger scale, the crude acid mixture from above (10 g) was dissolved in methanol (40 mL), sulfuric acid (0.5 mL) was added, and the mixture was heated to reflux for 10 h. After standard workup, the ester was distilled to yield 3.41 g of product, representing a 36% yield from 3-methylcyclohexanone. GC analysis (75 °C) showed two major peaks with retention times of 3.3 and 3.7 min in a ratio of 1:3, respectively. Analytically pure material was collected by preparative gas chromatography. The first component

(retention time of 29 min) was identified as methyl *trans*-2-methylcyclopentanecarboxylate and the second component (retention time of 36 min) tentatively identified as a mixture of *cis*- and *trans*-3-methylcyclopentanecarboxylic acid methyl esters. This is in agreement with the published analysis given by Hill:[39] 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.03 (d, J = 6.5, 3 H), 1.15 (m, 1 H), 1.63 (m, 2 H), 1.78–1.95 (2 overlapping m, 3 H), 2.10 (m, 1 H), 2.23 (m, 1 H), 3.65 (s, 3 H).

Reaction of *cis*-4-Methyl-3-phenylcyclopentene with MCPBA. To a solution of purified *cis*-4-methyl-3-phenylcyclopentene (ca. 25 mg obtained from prep GC) in 1 mL of CH_2Cl_2 was added excess *m*-chloroperoxybenzoic acid (MCPBA). Stirring was continued until TLC showed complete conversion to product. GC analysis showed the appearance of one new major peak, retention time of 7.8 min at 115 °C. The solution was washed with 1 M NaOH and water and dried over Na_2SO_4. Analytically pure material was obtained by chromatography (1:50:50 CH_3CN–hexanes–CH_2Cl_2). Chiral GC analysis showed only one peak at 115 °C, run time 28.4 min: 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.55 (d, J = 6.8, 3 H), 1.43 (m, 1 H), 2.17 (m, 1 H), 2.25 (m, 1 H), 3.30 (d, J = 7.5, 1 H), 3.54 (d, J = 2.6, 1 H), 3.70 (d, J = 2.2, 1 H), 7.05 (d, 2 H), 7.30 (m, 3 H).

Reaction of *trans*-4-Methyl-3-phenylcyclopentene with MCPBA. The procedure was identical with that used to prepare the epoxide from the *cis*-cyclopentene. From *trans*-4-methyl-3-phenylcyclopentene, two new peaks were observed in the GC at 115 °C: retention times of 7.1 and 7.4 min in a ratio of 3:1. Chiral GC analysis at 115 °C gave three peaks, run times of 24.7, 25.0, and 25.5 min. The first two peaks were due to the enantiomers of the major epoxide. Underloaded column chromatography (1:50:50 CH_3CN–hexanes–CH_2Cl_2) gave separation of the two regioisomers for identification purposes: 300-MHz ^{1}H-NMR of the major product ($CDCl_3$) δ 0.93 (d, J = 6.7, 3 H), 1.36 (ddd, J = 1.1, 9.8, 14.1, 1 H), 1.75 (m, 1 H), 2.31 (dd, J = 7.0, 13.9, 1 H), 2.46 (d, J = 9.7, 1 H), 3.40 (br s, 1 H), 3.52 (br s, 1 H), 7.34 (m, 5 H).

Reaction of *trans*-4-Methyl-3-phenylcyclopentene with NBS followed by NaOH. *N*-Bromosuccinimide (NBS, 40 mg) was added to an ice-cooled solution of purified **25** (33 mg, 0.2 mmol) in 0.5 mL of water. This was warmed gently with a heat gun and then stirred at room temperature for 2 h at which time tLC indicated consumption of starting material. The aqueous solution was extracted with ether; the extracts were washed with brine and concentrated. The residue was then stirred with 30% aqueous NaOH (1 mL) for 1 day. The aqueous solution was extracted with pentane, the extracts were washed with 1 M HCl and brine, dried, and concentrated. GC analysis (115 °C) showed only one peak with retention time of 7.4 min. ^{1}H NMR analysis showed this to be identical with the minor isomer from the epoxidation of the same substrate with MCPBA: 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.12 (d, J = 7.4, 3 H), 1.70 (m, 1 H), 2.14 (m, 2 H), 2.94 (br s, 1 H), 3.42 (br s, 1 H), 3.64 (br s, 1 H), 7.25 (m, 5 H).

General Techniques for Kinetic Determinations. Pyrolysis of the vinylcyclopropane **2** and 1-phenyl-2,5-hexadiene, **11**, were carried out in sealed tubes. Aliquots (10–20 mL) of a solution of the substrate and internal standard (tetralin or phenylcyclohexane) were injected into a thick-walled kinetics tube. This was subjected to three freeze–pump–thaw cycles at 10^{-6} Torr and sealed at the constriction. The tube was placed in a holder and immersed in a constant temperature bath.

Constant Temperature Bath. The inside medium was sodium nitrite/potassium nitrate (50:50 w/w) fused salt. The temperature was maintained to ±0.1 °C by a precision temperature controller (Bayley Instrument Co., Model 124). The salt was heated by an MIS Chromalox heating cable (Niagara Electric Sales Co.) wound spirally against the inside wall of the stainless steel container. The stirrer assembly consisted of a three-blade, 2-in. diameter propeller attached to an 18 in. × $^5/_{16}$ in. stainless steel shaft. A ceramic coupling insulated the shaft in the bath from the shaft of the stirrer motor (Lightnin', Model L). The motor was supported by two 3.75 in. × 4.5 in. column clamps attached to a stainless steel frame constructed above the bath. Temperatures were measured with an uncalibrated single junction iron-constantan thermocouple connected to a millivolt potentiometer (Leeds and Northrup Co.) using an external ice water bath for reference.

Vapor Pressure Measurements. A 25-mL three-neck flask was charged with vinylcyclopropane **2** (70.2 mg, 0.44 mmol) and tetralin (6.321 g, 47.8 mmol). The flask was warmed to the appropriate temperature in an oil bath. When the flask had equilibrated, N_2 was blown over the solution with the effluent gas trapped in an acetone/CO_2 cooled bath. This was analyzed by GC for mole ratio of VCP:tetralin using cyclododecane for reference. Retention times, min (115 °C): tetralin, 2.5; cyclododecane, 5.6; vinylcyclopropane, 6.0. The calculated mole ratios are shown below.

temp, °C	mol **2**/mol tetralin
153 (3)	2.67 (2) × 10^{-3}
172 (3)	2.99 (3) × 10^{-3}
184 (4)	3.44 (2) × 10^{-3}

Calculations. All activation parameters were evaluated by direct nonlinear least-squares fit to the raw data on concentration vs time and temperature. These data are included in the supplementary material.

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Supplementary Material Available: Kinetic data for pyrolysis of compounds **2** and **11** (7 pages). Ordering information is given on any current masthead page.

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Effect of High Pressure on the [2 + 2] Cycloaddition of Difluoroallene and (*Z*)-β-Deuteriostyrene

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1,1-Difluoroallene and (*Z*)-β-deuteriostyrene undergo a [2 + 2] cycloaddition to form two regioisomeric products, (*Z*)- and (*E*)-4-deuterio-2,2-difluoro-3-phenyl-1-methylenecyclobutane, **1** (major), and (*Z*)- and (*E*)-2-deuterio-3-phenyl-1-(difluoromethylene)cyclobutane, **2** (minor), each with different degrees of stereochemical retention. The imposition of high pressure (2–13 kbar) on the reaction alters both the regioselectivity and the stereoselectivity of the reaction significantly, decreasing the former and increasing the latter. A mechanism involving two kinetically distinct diradical intermediates is proposed to rationalize the results.

The mechanism of the typical thermal [2 + 2] cycloaddition reaction is considered to be pretty well understood. No one disputes that such reactions are nonconcerted and involve diradical intermediates. Bartlett and

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