in acetonitrile resulted in a poorly defined, broad wave from which no useful oxidation potential data could be obtained. However, in dichloromethane, the oxidation process was well-defined. It was therefore necessary to use the dichloromethane data, and these have been converted to acetonitrile solution values by making the assumption that the oxidation potential difference between $(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$ and $(\eta^5\text{-}C_5Me_5)Mo(CO)_3^-$ is identical in the two solvents.

Acknowledgment. We gratefully acknowledge support from Statoil under the VISTA program, administered by the Norwegian Academy of Science and Letters. We thank Professors J. Halpern and J. R. Norton for many helpful comments and suggestions.

Evidence for Concert in the Vinylcyclopropane Rearrangement. A Reinvestigation of the Pyrolysis of *trans*-1-Methyl-2-(1-*tert*-butylethenyl)cyclopropane

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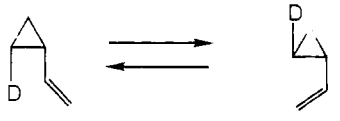
Abstract: Pyrolysis at 280 °C isomerizes *trans*-1-methyl-2-(1-*tert*-butylethenyl)cyclopropane to 1-*tert*-butyl-4-methylcyclopentene and 5,6,6-trimethyl-1,4-heptadiene in a 1:2 ratio. Monodeuteration of the exo methylene and optical activity studies of the rearrangement indicate that the cyclopentene is formed primarily (greater than 72%) through a suprafacial inversion pathway. Deuterium substitution on the trans-methyl group resulted in $k^H/k^{D_3} = 1.11$ with no change in the ratio of cyclopentene to diene, indicating no hydrogen transfer in the rate-determining step for formation of the diene. Dideuteration of the terminal methylene gave $k^H/k^{D_2} = 1.13$ for formation of cyclopentene and 1.03 for formation of diene. The equivalent isotope effects with *trans*-1-methyl-2-vinylcyclopropane are 1.17 and 1.05, respectively, all with an average deviation of 0.03. The isotope effect at the terminal methylene suggests substantial twisting of the methylene in the rate-determining transition state, suggesting that the 1,3-shift of carbon in the vinylcyclopropane rearrangement is concerted.

Since the thermal rearrangement of 2,2-dichlorovinylcyclopropane to 4,4-dichlorocyclopentene was first discovered in 1959,[1] many attempts have been made to elucidate the mechanism of this first-order and presumably unimolecular 1,3-sigmatropic shift. Wellington found that cyclopentene, **2**, comprised 96% of the pyrolysate from vinylcyclopropane, **1**, and was formed with log $k(1/s) = 13.5 - 49700/2.3RT$.[2] The rest of the product mixture consisted of dienes.

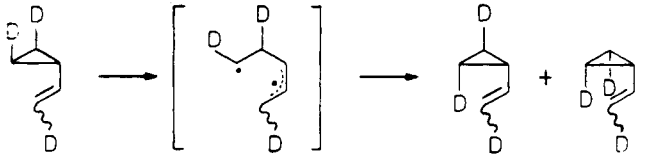
1 2

Geometric isomerization of *cis*-2-deuterio-1-vinylcyclopropane, **3**, occurs with log $k(1/s) = 14.5 - 48200/2.3RT$.[3] Further, if



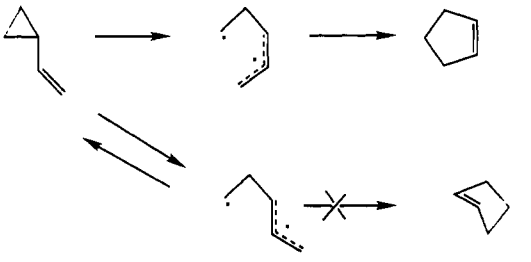
3

only cleavage to C1 occurs, as is expected because of formation of an allylic species, the geometric isomerization of 1-(*trans*-2-deuteriovinyl)-*trans*,*trans*-2,3-dideuteriocyclopropane, **4**, which gives a near statistical ratio of the *trans*- and *cis*-dideuterio isomers, appears to proceed via a randomized biradical intermediate.[4]

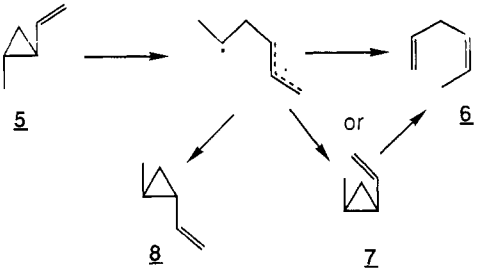


4 2 : 1

Scheme I



Scheme II



Substituents that are cis on the double bond of vinylcyclopropane have been found to decrease the rate of cyclopentene formation.[5] This suggests that for the 1,3 shift, the vinyl group is cisoid in the activated complex and that the cis methyl destabilizes this complex. This conclusion is not unreasonable because a transoid complex would give a *trans*-cyclopentene! (See Scheme I.)

A hydrogen shift to *cis*-hexa-1,4-diene, **6** (Scheme II), is responsible for ca. 93% of the product from pyrolysis of *trans*-2-methyl-1-vinylcyclopropane, **5**, and this diene is the exclusive product at lower temperatures when the corresponding cis isomer,

(1) Neureiter, N. P. *J. Org. Chem.* **1959**, *24*, 2044.
(2) Wellington, C. A. *J. Phys. Chem.* **1962**, *66*, 1671.
(3) Willcott III, M. R.; Cargle, V. H. *J. Am. Chem. Soc.* **1967**, *89*, 723.
(4) Willcott III, M. R.; Cargle, V. H. *J. Am. Chem. Soc.* **1969**, *91*, 4310.
(5) Elliot, C. S.; Frey, H. M. *J. Chem. Soc.* **1965**, 345.

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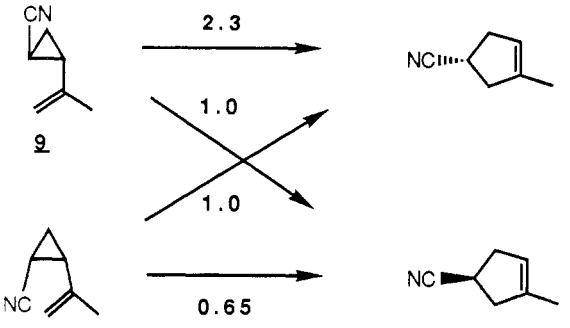
7, is pyrolyzed.[6] It is most likely that trans-2-methyl material opens to a diradical intermediate that either undergoes a hydrogen shift to give diene or recloses to the cis-2-methyl isomer, which undergoes the hydrogen shift.

To gauge the extent of diene formation relative to ring opening, optically active (−)-*trans*-2-methyl-1-vinylcyclopropane, **5**, was pyrolyzed and gave a 1.8:1 ratio of diene **6** to enantiomeric starting material, **8**.[7] If the extent of diene formation represents the extent of *cis*-2-methyl-1-vinylcyclopropane formation, hence geometric isomerization, the product ratio is close to the value expected for a randomly rotating biradical intermediate with random closure back to the vinylcyclopropanes.

If the 1,3-shift of carbon in the vinylcyclopropane rearrangement is concerted, it should occur stereospecifically. There are four possible stereochemical pathways for the 1,3-shift: the Woodward–Hoffmann "allowed" pathways suprafacial inversion and antarafacial retention, and the "forbidden" pathways suprafacial retention and antarafacial inversion. Berson and Salem have noted that the latter two pathways may be more favorable than a random biradical pathway.[8]

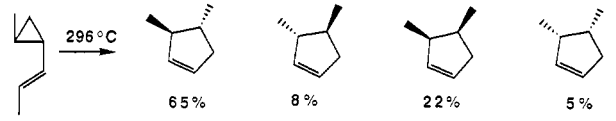
Doering and Sachdev[9] explored the thermal isomerization of *cis*- and *trans*-1-cyano-2-isopropenylcyclopropanes, **9** and **10**,



9 **10**

respectively, to 4-cyano-1-methylcyclopentene and found that ratio of inversion to retention at the migrating carbon is 2.3 for **9** and 0.65 for **10**. Any indication as to the percentage of Woodward–Hoffmann allowed products remains unanswered due to the lack of a stereochemical label at the β vinyl position.

Roth and Schmidt[10] pyrolyzed racemic *trans,trans*-2-methyl-1-propenylcyclopropane, **11**, and found a 2.4 to 1 mixture of *trans*- to *cis*-3,4-dimethylcyclopentene, **12** and **13**, respectively. This



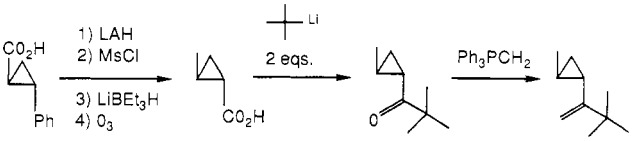
(1s,2s)-11 12-si 12-ar 13-sr 13-ai

ratio represents the extent of Woodward–Hoffmann "allowed" versus "forbidden" stereochemistry, respectively, in the cyclopentene product. In a more detailed study Baldwin[11] found from the pyrolysis of optically active (+)-(1*S*,2*S*)-*trans,trans*-2-methyl-1-propenylcyclopropane that the ratio of the four possible pathways is si(65):ar(8):sr(22):ai(5); thus, the ratio of "allowed" to "forbidden" pathways is 73:27. In this experiment, however, there is the possibility that the methyl groups create a steric bias for *trans*-dimethylcyclopentenes, those that are the "allowed" products.

To elucidate the mechanism of the vinyl cyclopropane 1,3-shift, kinetic isotope effects and stereochemical labeling studies were carried out with *trans*-1-methyl-2-(1-*tert*-butylethenyl)cyclopropane, **14**. This material was chosen with the expectation that transoid biradicals or transition states would be sterically disfavored relative to cisoid species. This then should provide a better opportunity to examine the stereochemistry and deuterium kinetic isotope effects in the vinylcyclopropane rearrangement. A preliminary communication that reported that this material gave a small amount of retention at the migrating carbon and exhibited a small kinetic isotope effect upon deuteration at the exo-vinyl position, which suggested intervention of a biradical,[12] has been found to be in error, and the conclusions are opposite to those drawn here. In addition, the secondary deuterium kinetic isotope effects at the terminal vinyl position of *trans*-1-methyl-2-vinylcyclopropane, **15**, were also examined for comparison with those from **14**.

Results

Synthesis of Vinylcyclopropanes. The synthesis of *trans*-1-methyl-2-(1-*tert*-butylethenyl)cyclopropane, **14**, was accomplished by first converting *trans*-2-phenyl-1-cyclopropanecarboxylic acid, **16**, to *trans*-2-methylcyclopropanecarboxylic acid, **17**, via the route



16 **17** **18** **14**

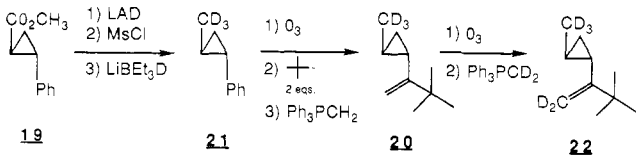
well established by Sugita and Inouye[13] and Baldwin.[14] The acid **17** was then treated with 2 mol of *tert*-butyllithium followed by an aqueous workup to give ketone **18**, which was treated with a Wittig reagent made from methyltriphenylphosphonium iodide and *n*-butyllithium to give **14**.

To examine the stereochemistry at the migrating carbon in the pyrolysis of **14**, (+)-(1*S*,2*S*)-*trans*-2-phenyl-1-cyclopropanecarboxylic acid was obtained by recrystallization of its quinine salt by using 50/50 hexane–ethanol.[15] The acid had 97% enantiomeric excess ($[\alpha]_D^{26}$ = 305°, c = 1.12 (ethanol), lit.[15] $[\alpha]_D^{12}$ = 314°, c = 1.776 (ethanol)). Analysis by ^{1}H NMR of the methyl ester derivative **19**, from (1*S*,2*S*)-**16**, with added tris[3-(heptafluoropropyl)hydroxymethylene-*d*-camphorato]europium, Eu(hfc), showed only one methoxy signal under conditions known to give two signals for the racemic ester. The optically active acid (1*S*,2*S*)-**16** was converted by the reaction sequence described above to (1*S*,2*S*)-**17**. Analysis by ^{1}H NMR of the methyl ester derivative of (1*S*,2*S*)-**17** with added Eu(hfc) showed only one methoxy signal under conditions known to give two signals for the racemic ester. Subjection of optically pure (1*S*,2*S*)-**17** to *tert*-butyllithium, the Wittig reaction sequence described above, and final purification by preparative glc gave (+)-(1*S*,2*S*)-*trans*-1-methyl-2-(1-*tert*-butylethenyl)cyclopropane ($[\alpha]^{26}_{365}$ 91.5 ± 1°, c = 0.337 (cyclohexane)). Analysis by ^{1}H NMR of the ketone **18** obtained from the ozonolysis of (1*S*,2*S*)-**14** showed only one *tert*-butyl signal under conditions known to give two signals for racemic ketone **18**. In previous studies the absolute configuration of (+)-*trans*-2-phenylcyclopropanecarboxylic acid was established to be 1*S*,2*S* by unambiguous correlation with L-isoleucine.[15,16]

To examine the possibility of hydrogen transfer in the rate- or product-determining step of the pyrolysis of **14**, racemic *trans*-1-(trideuteriomethyl)-2-(1-*tert*-butylethenyl)cyclopropane, **20**, was prepared. Lithium aluminum deuteride was used for the reduction of **19** and lithium triethylborodeuteride was used to reduce the mesylate to give hydrocarbon **21**. Ozonolysis, reaction with *tert*-butyllithium, and Wittig reaction as described above gave **20**. The ^{1}H NMR spectrum of **20** revealed the absence of the

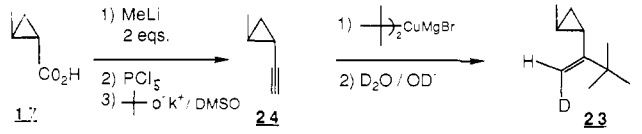
(6) Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 5578.
(7) Work cited in von E. Doering, W.; Sachdev, K. *J. Am. Chem. Soc.* **1975**, *97*, 5512.
(8) Berson, J. A. *Acc. Chem. Res.* **1972**, *5*, 406.
(9) Doering, W. E.; Sachdev, K. *J. Am. Chem. Soc.* **1975**, *97*, 5512.
(10) Schmidt, T. Ph.D. Dissertation, University of the Ruhr, Bochum, 1972.
(11) Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6705.
(12) Gajewski, J. J.; Warner, J. M. *J. Am. Chem. Soc.* **1970**, *106*, 802.
(13) Sugita, T.; Inouye, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1075. See also: Kadaba, P. K. *Synthesis* **1971**, 316.
(14) Baldwin, J. E.; Löliger, J.; Rastetter, W.; Neuss, N.; Huckstep, L. L.; De La Higuera, N. *J. Am. Chem. Soc.* **1973**, *95*, 3796.
(15) Inouye, Y.; Sugita, T.; Walborsky, H. M. *Tetrahedron* **1964**, *20*, 1695.
(16) Doering, W. E.; Kirmse, W. *Tetrahedron* **1960**, *11*, 272.

methyl doublet found in the spectrum of **14**.



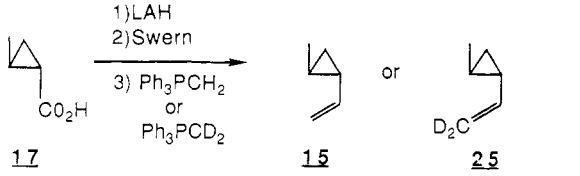
To examine the secondary deuterium kinetic isotope effect at the terminal methylene of **14**, *trans*-(trideuteriomethyl)-2-(1-*tert*-butyl-2,2-dideuterioethenyl)cyclopropane, **22**, was prepared. Ozonolysis of the trideuteriomethyl material, **20**, followed by treatment with a Wittig reagent prepared from (trideuteriomethyl)triphenylphosphonium iodide and *n*-butyllithium gave **22**. The olefin was purified by preparative glc. The ^{1}H NMR spectrum of **22** had a singlet at 4.377 ppm (0.15 H) and a doublet at 4.613 (0.15 H), which correspond to the presence of tetradeuterio-**22**. Two smaller peaks at 4.396 (0.05 H) and 4.624 (0.05 H) correspond to a 5% presence of **20**. The mass spectrum (EI, 50 eV) of olefins **22**, after correction for the $m + 1$ peak contributions to the relative intensity of the molecular ion peaks, revealed that 74% of the mixture consists of pentadeuterio-**22**, 24% of the mixture consists of tetradeuterio-**22**, and 2% trideuterio-**22**.

To examine the stereochemistry of the allylic moiety in the pyrolysis of **14**, *trans*-1-methyl-2-(1-*tert*-butyl-*Z*-2-deuterioethenyl)cyclopropane, **23**, was prepared. Racemic acid **17** was treated with 2 mol of methyllithium followed by conversion to the acetylene, **24**, by reaction with phosphorus pentachloride, and



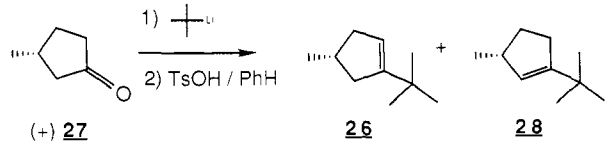
elimination with potassium *tert*-butoxide in DMSO and gc purification.[17] Reaction of the acetylene with the homocuprate $(t\text{-Bu})_2$CuMgBr[18,30] followed by a basic deuterium oxide quench gave **23**, which was purified by gc. ^{1}H NMR revealed that it was 81% deuterated and exclusively cis to the *tert*-butyl group.

To examine the secondary deuterium kinetic isotope effect at the terminal methylene position on the geometric isomerization of a simple vinylcyclopropane, *trans*-2-methyl-1-vinylcyclopropane, **15**, was prepared. Acid **17** was reduced with lithium aluminum



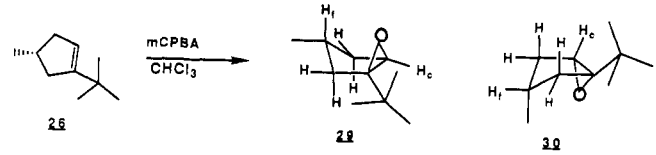
hydride, converted to the aldehyde via a Swern oxidation,[19] and then subjected to a Wittig reaction.[20] *trans*-1-Methyl-2-(2,2-dideuterioethenyl)cyclopropane, **25**, was prepared by using the same sequence except that (trideuteriomethyl)triphenylphosphonium bromide was used in the Wittig reaction. The ^{1}H NMR spectrum (300 MHz) revealed that sample was 86.5% dideuterated. Examination of the residual geminal vinyl proton resonances revealed that monodeuterated olefins comprise the remainder of the sample.

To establish the stereochemistry of the migrating carbon in the pyrolysis of optically active **14**, optically pure vinylcyclopropane rearrangement product from the pyrolysis of **14**, namely, (−)-(*R*)-*tert*-butyl-4-methylcyclopentene, **26**, was synthesized from commercially available (*R*)-(+)-3-methylcyclopentanone, **27**, $[\alpha]_D^{24} = +147°$ $c = 1.16$ (CH_3OH). Thus reaction with 1 equiv

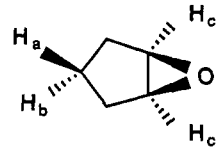


of *tert*-butyllithium followed by an aqueous workup[21] then dehydration with a catalytic amount of *p*-toluenesulfonic acid in benzene gave a 50/50 mixture of **26** and its double-bond isomer, **28**, along with unreacted starting ketone **27**. The product olefins were separated by gc. Cyclopentene **26** has a ^{1}H NMR spectrum identical with the nondiene product recovered from the pyrolysis of **14** and had $[\alpha]^{25}_{365} = -2.4 \pm 0.4$, $c = 1.51$ (cyclohexane). In our preliminary communication[12] we reported that the cyclopentene **26** had $[\alpha]^{25}_{365} = 150.4$; subsequent gc analysis revealed that this sample was the unseparated mixture of **26** and **28**. The absolute stereochemistry of **26** is based on the dextrorotatory enantiomer, (+)-**27**, being obtained from (+)-pulegone, the configuration of which has been assigned from its degradation to (−)-α-methylglutaric acid.[23] (+)-**27** has also been converted to (*R*)-(+)-methylsuccinic acid, whose chemical interrelationship with (*R*)-(+)-2-methylbutan-1-ol has been established.[7,22]

For deuterium analysis in the pyrolysis of **23**, cyclopentene **26** was epoxidized with 3-chloroperbenzoic acid in chloroform.[23] The epoxides were separated with HPLC (silica column, 97% hexane/3% ethyl ether). The ratio of *trans*- to *cis*-epoxides, **29** and **30**, respectively, was 85/15. The assignment of the epoxide



stereochemistry rests on literature precedence and ^{1}H NMR shift reagent studies. Thus the epoxidation of substituted cyclopentenes by peracids such as peroxylauric acid or peroxybenzoic acid have been found to occur predominantly from the less hindered side.[24] The reaction of 4-methylcyclopentene with perlauric acid gives a mixture of *trans*- and *cis*-epoxides in a ratio of 76/24, respectively.[25] ^{1}H NMR shift reagent studies were used to further confirm the assigned stereochemistry of the epoxides. Tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium, Eu(fod)$_3$, 0.063 M in $CDCl_3$, was added in 10–20-μL portions to a 0.2 M sample of the epoxide while successive ^{1}H NMR (300 MHz) spectra were taken. The slopes obtained from the linear plots of shift reagent added versus Δδ (ppm, relative to an internal standard) were calculated for each proton resonance. The value of the slope calculated for the methine proton, H_f of **29**, divided by the slope value of the oxirane ring proton H_c, gives



a value of 0.45 (0.002). A value of 0.30 (0.01) was found for similar calculations with **30**. The difference between these values is similar to that determined for 6-oxabicyclo[3.1.0]hexane. The slope of H_a divided by the slope for the oxirane protons H_c gives a value of 0.68 (0.04). Similar calculations for H_b gives a value of 0.36 (0.02). The slope calculated for the methyl group of **29** divided by the slope for the *tert*-butyl group gives a value of 0.34 (0.01) as compared with a value of 0.44 (0.02) found for **30**.

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(18) Westmijze, H.; Meijer, J.; Bos, M. J. T.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 304.
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(20) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128.
(21) Buhler, J. D. *J. Org. Chem.* **1973**, *38*, 904.
(22) Eisenbraun, E. J.; McElvain, S. M. *J. Am. Chem. Soc.* **1955**, *77*, 1599, 3383.
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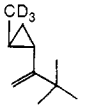
(24) Hanselaer, R.; Samson, M.; Vandewalle, M. *Tetrahedron* **1978**, *34*, 2393.
(25) Henbest, H. B.; McCullough, J. J. *Proc. Chem. Soc.* **1962**, 74.

Table I. Rate Constants for the Disappearance of **14** and **20** and the Appearance of Cyclopentene and 1,4-Heptadiene Products[a]

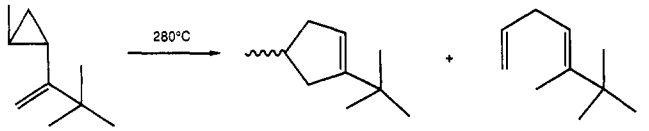
compd		k(enant)[b]	k(tot)[c]	k(1,5-H)[d]	k(1,3-C)[e]
14		0.660 (0.023)	1.51 (0.006)	1.05 (0.004)	0.463 (0.002)
20			1.36 (0.015)	0.936 (0.011)	0.428 (0.007)

[a] All figures in units of 10^{-5}/s. Pyrolysis temperature was 280.0 ± 0.1 °C. Values in parentheses represent standard deviations. [b] One-way rate constant for racemization of starting material. [c] Rate constant for disappearance of starting material. [d] Rate constant for formation of [1,5]-hydrogen shift diene product. [e] Rate constant for formation of [1,3]-carbon cyclopentene shift.

Table II. Kinetic Isotope Effects for the Pyrolysis of **14** and **20**.

rate ratio	value (std dev)
k(tot)**14**/k(tot)**20**-d_3	1.11 (0.013)
k(1,3)**14**/k(1,3)**20**-d_3	1.08 (0.02)
k(1,5)**14**/k(1,5)**20**-d_3	1.12 (0.03)

Kinetics. All pyrolysis experiments were performed in a thermostated (280 ± 0.1 °C), previously evacuated (10^{-3} Torr), 300-mL vessel. For the kinetic studies sample sizes of 0.8 μL were pyrolyzed in the gas phase for times ranging from 5 to 28 h. Recovered samples were analyzed by using capillary gas chromatography as described in the Experimental Section. The two major products (>99%) are the 1,3-carbon shift product, 4-methyl-1-*tert*-butylcyclopentene, **26**, and the 1,5-hydrogen shift product, 5,6,6-trimethyl-1,4-heptadiene, **31**, presumably as the *E* isomer. The results of the kinetic experiments for the pyrolysis of compounds **14** and 1-trideuterio-**14**, namely, **20**, are presented in Tables I and II.



14 26 31

Results from the kinetic experiments for the pyrolysis of compounds **20** and 2′,2′-dideuterio-**20**, namely, **22**, are recorded in Tables III and IV. The kinetic isotope effects reported in Table IV are the corrected values (eq 1) for incomplete deuteration of

$$\left(\frac{k_H}{k_D}\right)_{obsd} = \frac{k_{H_2}}{Ak_{D_2} + Bk_{HD} + Ck_{H_2}} \quad (1)$$

A = mole fraction of dideuteriomethylene–trideuteriomethyl **22** relative to trideuteriomethyl-**20**

B = mole fraction of monodeuterated methylene–trideuteriomethyl **22** relative to trideuterio methyl-**20**

C = mole fraction of trideuteriomethyl-**20**

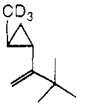
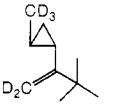
22 at the exo-methylene position. The isotope effects in Table IV are for replacement with deuterium at the exo-methylene position only since any isotope effect from the trideuterio methyl group of **20** and **22** is expected to cancel out.

^{1}H NMR analysis of **22** reveals that relative to trideuterio-**20**, this compound is 65% dideuterated, 30% monodeuterated, and 5% protio. Correction for the incomplete deuteration was made by substituting these values into eq 1:

$$\left(\frac{k_H}{k_D}\right)_{obsd} = \frac{k_{H_2}}{0.65k_{D_2} + 0.30k_{HD} + 0.05k_{H_2}}$$

$$\frac{1}{(k_H/k_D)_{obsd}} = 0.65\left(\frac{k_{D_2}}{k_{H_2}}\right) + 0.30\left(\frac{k_{D_2}}{k_{H_2}}\right)^{1/2} + 0.05$$

Table III. Rate Constants for the Disappearance of **20** and **22** and for the Appearance of Cyclopentene and 1,4-Heptadiene Products[a]

compd		k(tot)[b]	k(1,5)[c]	k(1,3)[d]
20		1.37 (0.01)	0.942 (0.008)	0.428 (0.004)
22		1.31 (0.01)	0.919 (0.007)	0.388 (0.002)

[a] All figures in units of 10^{-5}/s. Pyrolysis temperature was 280.0 ± 0.1 °C. Values in parentheses represent standard deviations. [b] Rate constant for disappearance of starting material. [c] Rate constant for the formation of [1,5]-hydrogen shift diene. [d] Rate constant for formation [1,3]-carbon shift cyclopentene.

Table IV. Kinetic Isotope Effects on the Pyrolysis of **20** and **22**

rate ratio	value (std dev)
k(tot)**20**-d_3/k(tot)**22**-d_5	1.06 (0.012)
k(1,3)**20**-d_3/k(1,3)**22**-d_5	1.13 (0.014)
k(1,5)**20**-d_3/k(1,5)**22**-d_5	1.03 (0.02)

Table V. Rate Constants for the Disappearance of **15** and **25** and for the Appearance of Cyclopentene and 1,4-Heptadiene Products[a]

compd		k(tot)[b]	k(1,5)[c]	k(1,3)[d]
15		3.95	3.70	0.246
25		3.75	3.54	0.210

[a] All figures in units of 10^{-5}/s. Pyrolysis temperature was 280.0 ± 0.1 °C. Values in parentheses represent standard deviations. [b] Rate constant for disappearance of starting material. [c] Rate constant for the formation of [1,5]-hydrogen shift diene. [d] Rate constant for the formation of [1,3]-carbon shift.

Using the observed isotope effect, the corrected isotope effect was found by solving for k_{D_2}/k_{H_2} and inverting this value.

Results from the kinetic experiments for the pyrolysis of compounds **15** and 2′,2′-dideuterio-**15**, namely, **25**, are recorded in Tables V and VI. The kinetic isotope effects reported in Table VI are corrected values for incomplete deuteration. ^{1}H NMR analysis of **25** reveals that this compound is 86.5% dideuterated and 13.5% monodeuterated. The isotope effect reported here for the 1,3-shift is nearly the same as that reported previously,[12] but that for the 1,5-hydrogen shift is substantially higher (now normal) than that reported previously (1/1.11). We attribute the difference to the current use of a high efficiency DB-5 capillary gc column as opposed to the previous use of a silver nitrate in triethyleneglycol on Chromosorb packed column even though the previous separation appeared to be adequate.

The unimolecular rate constant for the disappearance of starting material is represented by k(tot). The unimolecular rate constant

Table VI. Kinetic Isotope Effects on the Pyrolysis of **15** and **25**

rate ratio	value (std dev)
k(tot)**15**/k(tot)**25**-d_2	1.06 (0.01)
k(1,3)**15**/k(1,3)**25**-d_2	1.17 (0.03)
k(1,5)**15**/k(1,5)**25**-d_2	1.05 (0.01)

for the formation of the diene from the above vinylcyclopropane rearrangements was determined by

$$k(1,5) = k(\text{tot})f(1,5)$$

The rate constant for the formation of the diene is $k(1,5)$. The fraction of diene formed is $f(1,5)$. $f(1,5)$ is calculated from the relative concentration of diene divided by the sum of the relative concentrations of the diene and cyclopentene products.

The unimolecular rate constant for the formation of the cyclopentene product was determined by

$$k(1,3) = k(\text{tot})f(1,3)$$

$k(1,3)$ is the rate constant for the formation of cyclopentene product. $f(1,3)$ is the relative concentration of cyclopentene formed divided by the sum of the relative concentrations of diene and cyclopentene products.

Stereochemistry. The optical rotation of (+)-(1*S*,2*S*)-*trans*-1-methyl-2-(1-*tert*-butylethenyl)cyclopropane was found to be $[\alpha]^{26}_{365}$ = 91.5 (1)°, c = 0.337 (cyclohexane). After a 12-h pyrolysis period at 280 ± 1 °C, the optical rotation of the recovered vinylcyclopropane was found to be $[\alpha]^{26}_{365}$ = 51.7 (1), c = 1.01 (cyclohexane). From these two values the two-way rate constant (k_{rac}) for the loss of optical activity in the recovered vinylcyclopropane was calculated to be 1.32 (0.05) × 10^{-5}/s. The one-way rate constant (k_{enant}) is therefore 0.660 (0.023) × 10^{-5}/s.

In an attempt to determine the stereochemistry of the migrating carbon, the optical rotation of the recovered 1-*tert*-butyl-4-methylcyclopentene from the 12-h pyrolysis at 280 ± 1 °C of the optically active vinylcyclopropane was examined and found to be $[\alpha]^{25}_{365}$ = −2 (1), c = 0.2 (cyclohexane). For more accurate enantiomer analysis a Schurig capillary column (25 m × 0.25 mm) coated with 10% nickel(II) bis[(1*R*)-3-(heptafluorobutyryl)] camphorate in OV101 was used for separation of the derived epoxides. The composition of 3*R*- and 3*S*-1-*tert*-butyl-*trans*-3-methyl-6-oxabicyclo[3.1.0]heptane, **29**, is 77.3 (1)% and 22.7 (1)%, respectively (average of three pyrolysis runs).

To determine stereochemistry of the three carbon moiety, *trans*-1-methyl-2-(1-*tert*-butyl-*Z*-2-deuterioethenyl)cyclopropane, **23**, was pyrolyzed for 47.33 h at 280 ± 0.1 °C. The diene was then separated from the vinylcyclopropane and cyclopentene by preparative gc. The NMR (300 MHz) spectrum of the vinylcyclopropane/cyclopentene mixture reveals that 75 (7)% of the deuterium is trans to the C-4 methyl group and 25 (7)% of the deuterium is cis. Deuterium NMR spectroscopy of the monodeuterated cyclopentene gives the more precise values of 83.7 (1)% for trans deuterium and 16.3 (1)% for cis deuterium. The stereochemical assignment is discussed below.

Discussion

trans-1-Methyl-2-(1-*tert*-butylethenyl)cyclopropane, **14**, was chosen for study in anticipation that its geometric isomerization would be slower than that in simple vinylcyclopropanes since the transoid biradical or activated complex would be less stable due to steric interactions. The data of Table VII, which compares rate constants for various vinylcyclopropanes at a common temperature, 280 °C, verifies that expectation. Thus k(enant) for **14** is a factor of 3 smaller than that for *trans,trans*-1-methyl-2-propenylcyclopropane, **11**. Further, $k(1,5)$ for **14** is a factor of 3.5–4.5 smaller than $k(1,5)$ for **11** and for *trans*-1-methyl-2-vinylcyclopropane, **15**. However, $k(1,3)$ for all three compounds is nearly the same.

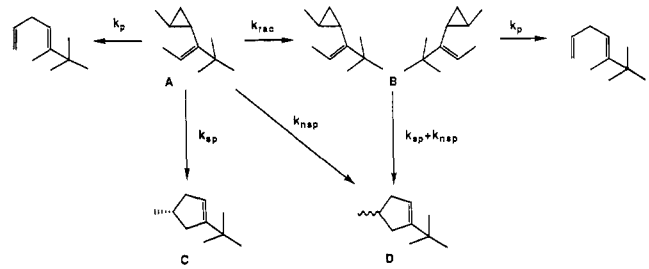
These results are consistent with a predominance of C_1–C_2 bond cleavage in **14** to give a cisoid biradical or activated complex, but the dominant reaction of vinylcyclopropanes **11** and **15** is stereoisomerization via the sterically accessible transoid biradical or activated complex. Thus the addition of the α-*tert*-butyl group in **15** allows the stereochemistry of the 1,3-shift to be studied without the problem of racemization and diene formation competing strongly with the 1,3-shift of carbon to give the cyclopentene.

Table VII. Rate Constants for the Reactions of Various 1-Methyl-2-vinylcyclopropanes[a]

compd		k(enant)	k(1,5-H)	k(1,3-C)	ref
15			3.70	0.246	this work
11		2.12	4.79	0.37	11
14		0.66	1.05	0.463	this work

[a] All values are corrected to 280 °C and in units of 10^{-5} s^{-1}. Standard deviations are in parentheses.

Scheme III



Stereochemistry. Pyrolysis of optically active (1*S*,2*S*)-**14** led to 77.3 (1)% inversion and 22.7 (1)% retention in the cyclopentene product at approximately 1 half-life of the reaction. Compensation for the extent of racemization of starting material to determine the fraction of stereospecificity for the cyclopentene formation was accomplished by assuming the phenomenological scheme of Scheme III.

The fraction of stereospecificity is represented by $(k_{SP})/(k_{SP} + k_{NSP})$, where k_{SP} is the rate constant for the stereospecific path and k_{NSP} is the rate constant for the nonstereospecific, stereorandom, path. This ratio can be determined from the following equation derived from Scheme III:

$$\frac{k_{SP}}{k_{SP} + k_{NSP}} = \left(\frac{C_T}{C_T + D_T}\right)\left(\frac{A_0 - A_T - B_T}{A_0 - A_T}\right)\left(1 + \frac{k_{rac}}{k_P + k_{SP} + k_{NSP}}\right)$$

where A_T = mole fraction of enantiomerically pure A at time T, C_T = mole fraction of enantiomerically pure C at time T, B_T = mole fraction of B (racemic A) at time T, D_T = mole fraction of D (racemic C) at time T, and A_0 = mole fraction of enantiomerically pure A at time zero.

For the 12-h pyrolysis of 1*S*,2*S*-**14** at 280.0 °C

$$k_{rac} = 1.32\ (0.05) \times 10^{-5}/\text{s} = 2k(\text{enant})$$

$$k_P = 1.05\ (0.004) \times 10^{-5}/\text{s}$$

$$k_{SP} + k_{NSP} = 0.463\ (0.002) \times 10^{-5}/\text{s}$$

$$A_0 = 0.97$$

$$A_T = \frac{51.7 \pm 1}{91.5 \pm 1}\ (0.526) = 0.297\ (0.01)$$

$$C_T = 0.079\ (0.001)$$

$$B_T = 0.23\ (0.007)$$

$$D_T = 0.066\ (0.001)$$

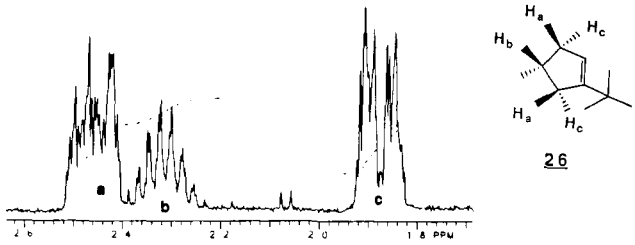


Figure 1. Partial ^1H NMR ($CDCl_3$ solution, 300 MHz) spectrum of the aliphatic region of cyclopentene **26**.

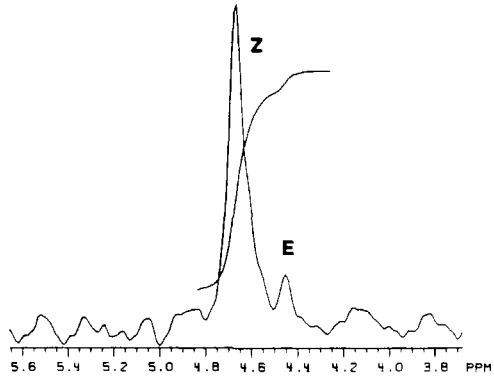
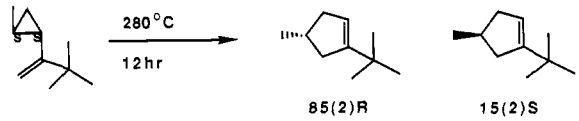


Figure 2. Partial ^2H NMR ($CDCl_3$ solution, 55.4 MHz; insert indicates assignment of deuterium stereochemistry) spectrum of the vinyl region of recovered vinylcyclopropane **23**.

Therefore $k_{SP}/(k_{SP} + k_{NSP}) = 0.69$ (0.02) corresponds to 85 (2)% *R* and 15 (2)% *S* configuration in the recovered cyclopentene:



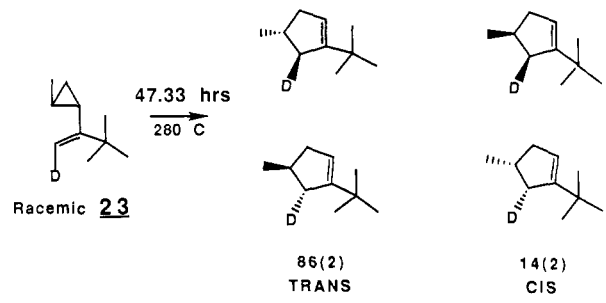
The 85 (2)% *R* configuration in the recovered cyclopentene indicates the majority of the vinylcyclopropane rearrangement occurs with extensive inversion at the migrating methyl group. The extent of antarafacial and suprafacial bond formation on the terminal vinyl carbon was examined with the pyrolysis of racemic, (*Z*)-deuterio-labeled **23**. Determination of the stereochemical location of the deuterium by ^2H NMR revealed the extent of antarafacial and suprafacial components of the rearrangement. The aliphatic ring ^1H NMR (300 MHz) spectrum of the rearrangement product, **26**, is shown in Figure 1 along with the proton assignment, which is discussed later in this section.

The deuterium NMR spectrum of the recovered cyclopentene **26** from the pyrolysis of **23** revealed a peak at 2.45 ppm (D trans to methyl) and a peak at 1.88 ppm (D cis to methyl) with the relative areas of 83.7 (1) and 16.3 (1), respectively. Analysis of the ^2H NMR spectrum of the vinyl region (Figure 2) of the recovered starting material, **23**, revealed that approximately 10% had isomerized from the *Z*-deuterio to the *E*-deuterio position.

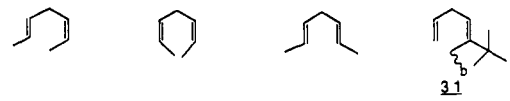
The amount of trans and cis deuterated cyclopentenes must therefore be corrected for deuterium label isomerization. A scheme similar to Scheme III to correct for the extent of racemization of starting material was used (Scheme IV). Here the correction results in the relative amounts of deuterium trans to methyl vs cis to methyl is 86 (2)% to 14 (2)%.

The isomerization of deuterium of the starting material **23** from *Z* to *E* is most likely due to a small amount of reversion of the diene back to starting material. Roth and Konig found from the gas-phase pyrolysis at 350 °C of *cis*-6,6,6-trideuterio-1,4-hexadiene substantial protio incorporation at the methyl group.[27] Berson

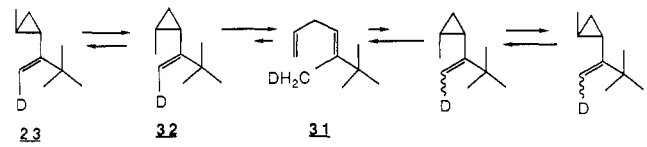
Scheme IV



and Bauer pyrolyzed the *cis,trans*-2,5-heptadiene at 310 °C for 5 h and found 6% of *cis,cis*-diene as the only product formed.[28] Pyrolysis of the *trans,trans*-2,5-heptadiene under similar conditions gave back only the starting diene. The isomerization of *cis,trans*-diene is believed to occur by 1,5-hydrogen shifts via a *cis*-2-methylvinylcyclopropane intermediate. This cyclopropane intermediate is sterically inaccessible from the *trans,trans*-diene and therefore no isomerization is observed for this diene:



Pyrolysis of the 1,4-diene **31** (recovered from pyrolysis of **23**) for 47.3 h at 280 °C revealed formation of 0.4% cyclopentene and approximately 0.05% of the *trans*-2-methylvinylcyclopropane. The deuterium NMR spectrum of the recovered starting material from the pyrolysis of **23** does not reveal any deuterium incorporation at the methyl position, but this could be due to the concentration of the deuterated 2-methylvinylcyclopropane being below the limits of detectability of the ^2H NMR. Thus it is possible for the isomerization of (*Z*)-**23** to (*E*)-**23** to occur, at least to some extent, through a 1,5-shift of hydrogen (not deuterium) in diene **31** to give the *cis*-2-methylvinylcyclopropane, **32**, which undergoes slow geometric isomerization.



The proton assignment for **26** was made on the following basis: Protons H_c, cis to the methyl group, should be the upfield peaks at δ 1.85 ppm because of the expected shielding by the anisotropic field of the $CH-CH_3$ bond.[29] Indeed, the ^1H NOESY spectrum of **26** reveals cross peaks between the methyl signal at 1.01 ppm and the signal at 1.85 ppm. Further, irradiation of the downfield multiplet at 2.45 ppm causes the doubletlike signal at 1.8 ppm to collapse to a singlet. Thus the doublet appearance of the signal at 1.8 ppm is due to geminal coupling of approximately 16 Hz. The cross ring coupling between the cis or trans allylic ring protons of **26**, 2.5 Hz, is too small to allow the possibility that the signal at 1.8 ppm corresponds to two methylene protons on the same side of the ring. Further confirmation of the stereochemical assignment and the deuterium distribution followed from analysis of the epoxides **29** and **30** derived from the cyclopentene product from pyrolysis of **23**.[26a] Finally, the NMR spectrum reveals no detectable deuterium at positions other than at C-5, so there is no

(26) (a) For an extensive analysis see: Squicciarini, M. P. Ph.D. Thesis, Indiana University, 1988. (b) This equation was derived by Prof. C. J. Samuel (University of Warwick) from the integrated rate expressions for the phenomenological scheme depicted. It reduces to those used previously (ref 11 and Gajewski, J. J.; Salazar, J. Del C. *J. Am. Chem. Soc.* **1981**, *103*, 4145) if $k_P = 0$.

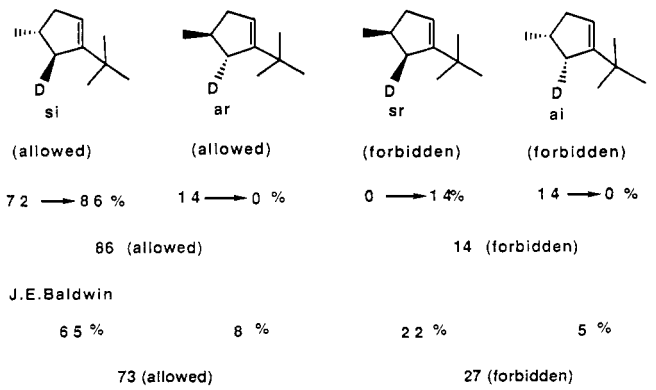
(27) Roth, W. R.; Konig, J. *Justus Liebigs Ann. Chem.* **1965**, *688*, 28.

(28) Berson, J. A.; Bauer, W.; Campbell, M. M. *J. Am. Chem. Soc.* **1970**, *92*, 7515.

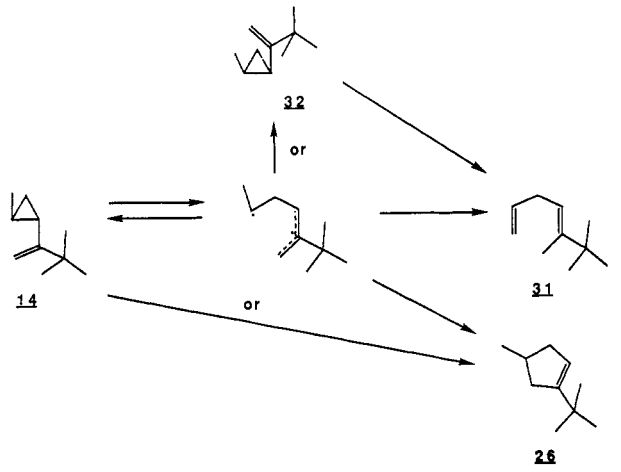
(29) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York; 1969; pp 77–79. Jackman, L. M. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: New York, 1969; pp 115–119.

(30) Westmijze, H.; Kleijn, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 98.

Chart I



Scheme V



random scrambling of deuterium in the cyclopentene from the pyrolysis of **23**.

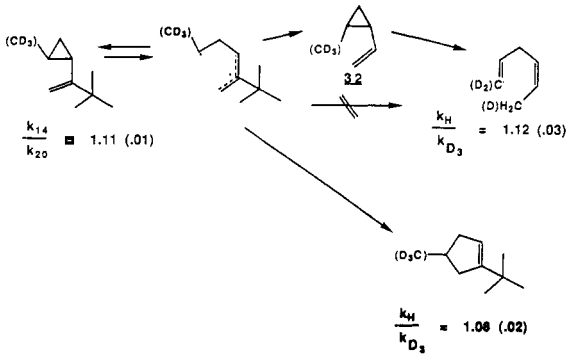
Combining the results of 85 (2)% inversion and 15 (2)% retention of the methyl-bearing carbon configuration with the result that 86 (2)% of the cyclopentene has deuterium trans to methyl and 14 (2)% has deuterium cis to the methyl, the ranges in the product distributions shown in Chart I are possible.

Thus the rearrangement has a total of 86% Woodward–Hoffmann "allowed" and 14% "forbidden" products. By comparison, Baldwin[11] found from the pyrolysis of optically active **11** that the recovered cyclopentene had approximately 73% of the "allowed" stereochemistry. The 13% decrease in "allowed" products for the pyrolysis of **11**, relative to this work, might be due to the allylic stabilizing effect of a β-methyl substitution on a biradical intermediate. This stabilization could promote more of the biradical pathway to cyclopentene formation and therefore account for the larger amount of "forbidden" products relative to this work. The β-methyl group of **11** could also promote a steric bias toward bond formation. In any case there seems to be an increase in the stereospecificity of the rearrangement in going from a methyl to a deuterium label in the β-vinyl position. It may be that the stereospecificity of the rearrangement might increase even further by replacing the methyl group of **14** with a deuterium.

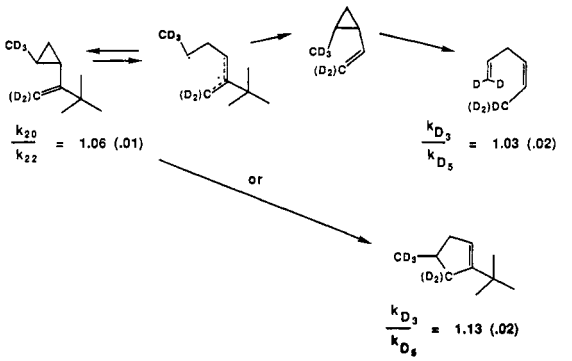
Deuterium Isotope Effects. One likely mechanism for the formation of cyclopentene is by ring opening at the C_1–C_2 position of **14** in the rate-determining step to form a biradical intermediate. This intermediate can then partition to form cyclopentene and diene or reclose to **14** (Scheme V). It is also possible that the cyclopentene is formed by a direct, concerted pathway from **14**. It is also possible that diene **31** is formed via closure of the biradical to the cis-isomer of **14**, namely, **32**, which most likely undergoes a rapid homo 1,5-hydrogen shift.[6]

Mechanism of Diene Formation. To distinguish between the two possibilities for hydrogen shift, vinylcyclopropanes **14** and **20** were pyrolyzed, and a normal isotope effect of 1.11 (0.01) for the disappearance of starting material was found. This isotope effect

Scheme VI



Scheme VII



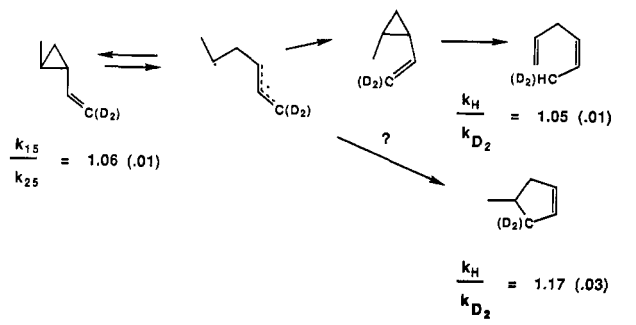
is most likely due to hyperconjugation by β-deuterium substitution and is similar to that observed in the pyrolysis of α-pinene.[31] The observed isotope effects for the formation of the diene and cyclopentene are 1.12 (0.03) and 1.08 (0.02), respectively. Since both isotope effects are normal and within experimental error of each other, a mechanism involving a common biradical intermediate that directly forms the diene does not appear likely. If there is a common intermediate that undergoes hydrogen shift to the diene, a substantial primary isotope effect might have been anticipated for this step. This reduction in rate should have been evident by a reduction of diene product and either no effect on the amount of cyclopentene or, if the ring opening were rate determining, an increase in the amount of cyclopentene. Therefore it is likely that the biradical intermediate first closes to the *cis*-2-methylvinylcyclopropane, **32**, before undergoing a rapid (1,5)-hydrogen shift to form the diene (Scheme VI).

Mechanism of Cyclopentene Formation. The pyrolyses of **20** and **22** reveal a normal isotope effect of 1.06 (0.01) at the exo methylene for the disappearance of starting material and isotope effects at the exo methylene of 1.03 (0.02) for formation of diene and 1.13 (0.014) for the appearance of cyclopentene (Scheme VII). A normal isotope effect for the formation of the cyclopentene is not unexpected since Chickos[32] found a normal isotope effect of 1.17 (0.02) at 338 °C for the rearrangement of (2,2-dideuteriovinyl)cyclopropane to 3,3-dideuteriocyclopentene. This isotope effect probably results from twisting of the methylene group in the rate-determining step for cyclopentene formation, in which case it is a primary kinetic isotope effect where the H–D zero-point energy difference in the reactant is reduced in the transition state because that vibration is part of the reaction coordinate.

The rotational isotope effect reported in this work, 1.13 (0.01), represents a minimum value since superimposed over this effect is the inverse isotope effect normally found when going from sp^2 hybridization to sp^3. For the Cope rearrangement it has been found that the maximum KIE for sp^2 to sp^3 transformation is 1/1.1 for two deuteriums at 250 °C.[33] The rotational isotope effect reported here could have been lowered by as much as 10%.

(31) Gajewski, J. J.; Hawkins, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 838.
(32) Chickos, J. ABS, PAP, ACS, 187 (APR): 228, 84 NOR.
(33) Conrad, N. D. Dissertation, Indiana University, 1978.

Scheme VIII



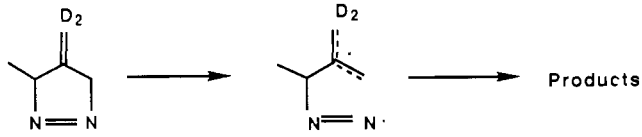
The isotope effects for the formation of diene and cyclopentene are both normal, and therefore a mechanism consisting of a rate-determining step to a common biradical intermediate followed by a product-determining isotope effect is not likely. If this mechanism were operative, the expected normal isotope effect for the formation of the cyclopentene would increase the amount of diradical that would be able to partition to diene or recyclize to starting material. This would cause an estimated inverse isotope effect of 0.98 on the formation of the diene. The experimental fact is that the isotope effect for the formation of the diene is 1.03 (0.02).

The above interpretation is based on the assumption that there would be little or no isotope effect for the formation of the biradical intermediate. The change in hybridization of the terminal vinyl carbon is negligible in going from sp^2 olefin to sp^2 radical, therefore little or no isotope effect might be expected.

To test this assumption compounds **15** and **25** were pyrolyzed. A normal isotope effect of 1.06 (0.01) was found for the disappearance of starting material. Normal isotope effects of 1.05 (0.01) and 1.17 (0.03) were found for the appearance of diene and cyclopentene, respectively (Scheme VIII).

The diene and cyclopentene are formed in a ratio of approximately 16 to 1, respectively, as compared with the ratio of approximately 2.2 to 1 for the above *α-tert*-butyl-substituted vinylcyclopropanes. If the products were formed from a common intermediate, any increase in diene from the rotational isotope effect on the formation of the cyclopentene is expected to be minimal. Therefore no product-determining isotope effect would be expected to be seen. The isotope effects observed for the disappearance of 2-methylvinylcyclopropane and the appearance of diene are essentially a measure of the isotope effect for the formation of a biradical intermediate (most likely transoid) from *trans*-2-methylvinylcyclopropane.

Small normal isotope effects have been reported for a few systems involving a carbon atom changing from olefinic to radical character.[34] Crawford and LeFevre[35] reported a normal isotope effect of 1.05 (0.02) for the formation of a biradical intermediate from the pyrolysis of 3-methyl-4-dideuteriomethylene-1-pyrazoline:



The normal isotope effect can also be rationalized by considering the change in bond vibrational frequencies in going from sp^2 olefin to sp^2 radical. The out-of-plane C–H bending frequencies for the methyl radical have been assigned a value of 730 cm^{-1}.[36] The out-of-plane C–H bending frequencies for an olefin have been assigned a value of 940 cm^{-1}.[37] With the Streitwieser approach the isotope effect was calculated to be approximately 1.07 at 280 °C.

(34) Henderson, R. W.; Pryor, W. A. *Int. J. Chem. Kinet.* **1972**, *4*, 325–330.
(35) LeFevre, G. N.; Crawford, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 1019.
(36) Andrews, L.; Pimentel, G. C. *J. Chem. Phys.* **1967**, *47*, 3637.

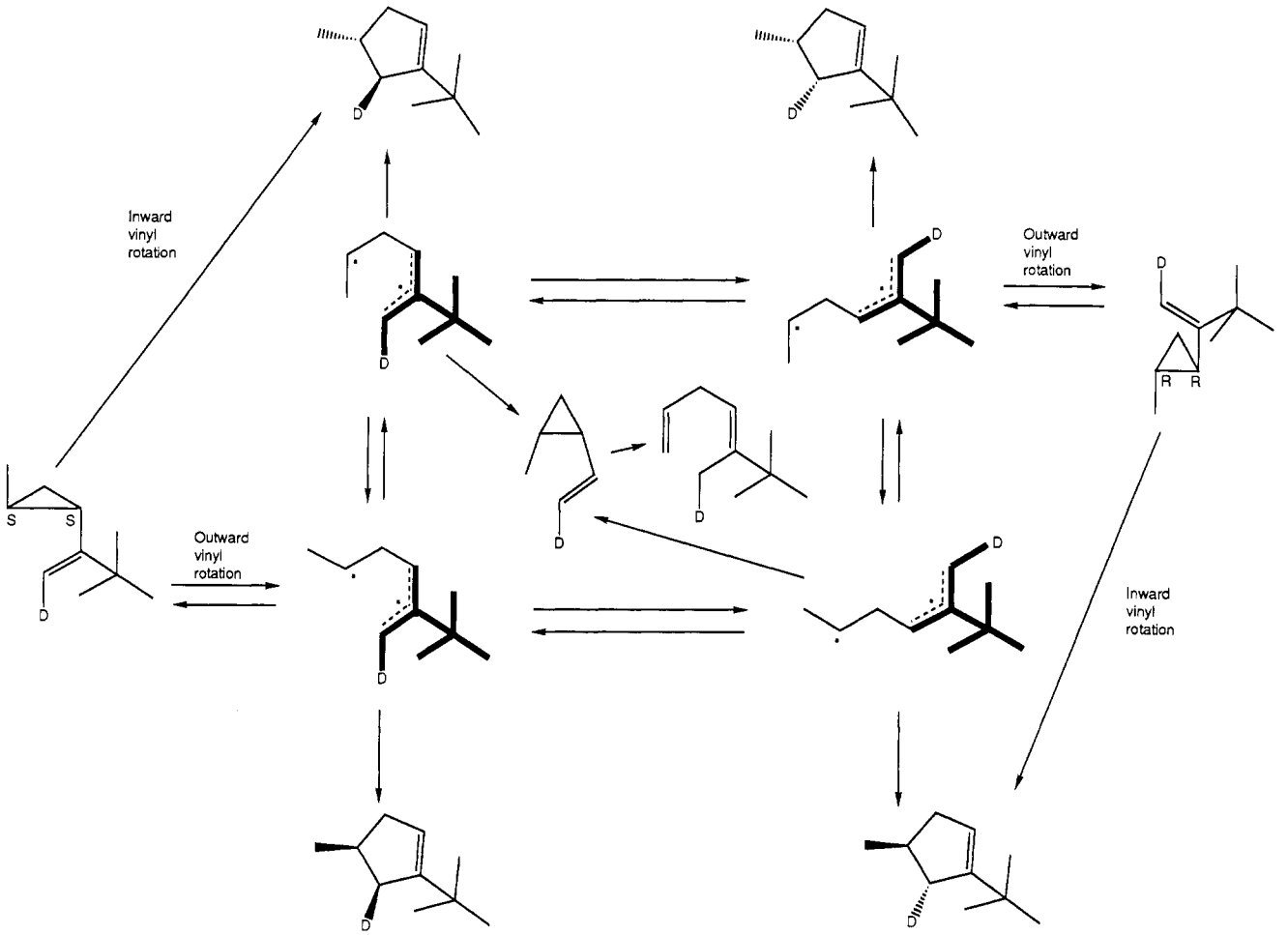
It is therefore apparent that the isotope effects observed from the pyrolysis of **20** and **22** should be examined in light of a 6% isotope effect on the disappearance of starting material. To decide between a common biradical intermediate or a separate pathway for the formation of cyclopentene is difficult when comparing the isotope effects at the exo methylene from the pyrolysis of **20** and **22** with those from the pyrolysis of **15** and **25**. If the error limits of the isotope effect for the diene formation are ignored, it would appear that the lower value of 1.03 (0.02) for the pyrolysis of **20** and **22** relative to the value of 1.05 (0.01) for the pyrolysis of **15** and **25** is due to an expected larger product-determining isotope effect. Therefore it might appear that the cyclopentene is formed from a common biradical intermediate. The fact that both of the isotope effects for diene formation are within experimental error of each other leaves open the possibility of a separate pathway for the formation of the cyclopentene. If the isotope effects for the formation of diene from **20** and from **22** are essentially the same as the isotope effect for the diene formed from **15** and from **25**, a rearrangement where a product-determining isotope effect would not be expected to be observed because of reversible formation of the intermediate, then it is unlikely that the cyclopentene is formed from a common biradical intermediate.

Summary. The relatively large isotope effects at the exo-methylene carbon for the 1,3-shift of vinylcyclopropanes to cyclopentenes are consistent with the twisting of the methylene group in the rate-determining step and suggest a concerted process for cyclopentene formation. If the cyclopentene is formed by a concerted mechanism, the stereochemistry of the rearrangement should be that predicted by the Woodward–Hoffmann rules. It is interesting that the stereochemistry of the cyclopentene product from the pyrolysis of (1*S*,2*S*)-**14** and monodeuterium-substituted **23** show 86% of the rearrangement occurs by the "allowed" suprafacial-inversion and antarafacial-retention pathways. The observation of substantial stereospecificity in the 1,3-shift product stands in contrast to the near-random amounts of geometric isomers formed from starting material, i.e., the ratio of *k*(enant) to *k*(diene) = 0.5. No simple mechanistic scheme can account for this disparate behavior. Parsimony suggests that the nonstereospecific components of the 1,3-shift result from the same intermediates that give rise to the geometric isomerization, and the stereospecific component(s) to be a separate pathway. We suggest that the formation of the suprafacial-inversion product is a concerted reaction accounting for 72% of the reaction and 7% each of the si, ar, sr, and ai products result from the same biradicals responsible for the geometric isomerization. The concerted component of the reaction is by far the most sterically demanding. The vinyl group must rotate inward to interact with the orbital(s) of the migrating methyl group, and the rest of the products can result from outward rotation of the vinyl group. This latter motion effectively uncouples the methyl-bearing carbon and terminal methylene radical centers (Scheme IX).[43]

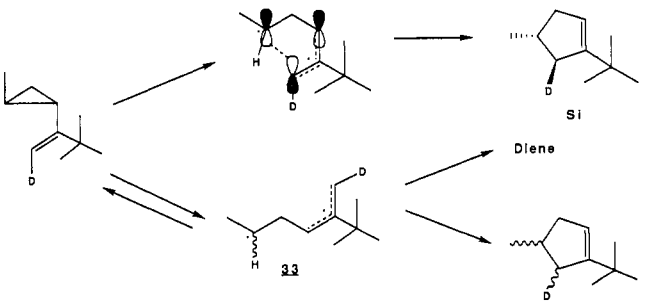
There is a second mechanistic possibility that focuses not on concert but on steric preferences and least-motion closure. The majority of cyclopentene could be formed from a chiral biradical intermediate generated with outward rotation of the methyl group and no rotation of the allylic group. Least-motion closure will give the suprafacial-inversion product. If the vinyl group were also to rotate to give an achiral biradical like **33** (Scheme X), then closure to cyclopentenes would give the stereorandom portion of the 1,3-shift product as well as enantiomerization and formation of the cis isomer of reactant which gives the hydrogen-shifted diene.

The possibility that outward methyl rotation in the formation of a biradical is the cause of the preferred si stereospecificity in the 1,3-shifts of *trans*-2-methylvinylcyclopropanes has some support in the work of Doering and Sachdev,[9] who found that pyrolysis of (+)-*cis*-1-cyano-2-isopropenylcyclopropane gives the cyclopentene with 1.54 to 1 preference for retention over inversion. In this case the concerted pathway requires inward rotation of the methyl at C-2, and the energy cost may be prohibitive in favor of a near-random nonconcerted event. The fact that substantial normal isotope effects have been found at the terminal vinyl

Scheme IX



Scheme X



position argues for involvement of this center as a rotational mode in the rate-determining step of the vinylcyclopropane rearrangement in the form of a weakly concerted reaction and not to the diradical pathway with steric influences. An obvious test between the concerted and nonconcerted hypotheses involves rearrangement of a vinylcyclopropane with a deuterium label at C-2.

Experimental Section

Instrumentation. ^{1}H NMR spectra were obtained with a Varian XL-300 (300 MHz) or a Varian T-60 (60 MHz). ^{13}C NMR spectra were obtained on a Varian XL-300 (75 MHz). ^{2}H NMR spectra were obtained with a Nicolet NT-360 (55.4 MHz) with proton decoupling. The ^{1}H NOESY experiments were performed with a Nicolet NT-360 (360 MHz) with T_m varied between 0.2 and 1 s. The spectrum was obtained by using 512 data points with a 256 × 256 matrix, 8 scans per increment, and zero filling to 512. The ^{1}H NOESY sample, cyclopentene **26**, was a 0.2 M solution in $CDCl_3$. IR spectra were obtained with a Perkin-Elmer 298 infrared spectrophotometer. Mass spectra were obtained on a Kratos MS-80 instrument. ^{1}H NMR shift reagent studies were carried out by adding 10–30-μL aliquots of 63 mM solutions of $Eu(fod)_3$ or $Eu(hfc)_3$ in $CDCl_3$ to approximately 0.2 M samples in $CDCl_3$. Internal standards for epoxide studies were tetramethylsilane or pentane.

***trans*-1-(Hydroxydideuteriomethyl)-2-phenylcyclopropane.**[12,13] A flask flushed with nitrogen containing 6.75 g (0.16 mol) of lithium aluminum deuteride and 250 mL of anhydrous ethyl ether was cooled to 0 °C. Methyl *trans*-phenylcyclopropanecarboxylate (21 g, 120 mmol) was slowly added dropwise. After the addition the mixture was stirred for 30 min, after which 8 mL of water was slowly added dropwise followed by 8 mL of a 15% NaOH aqueous solution. An additional 24 mL of water was added to the mixture, and the white precipitate was then filtered. The organic layer was dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator. The residue was distilled to give 17.5 g (98% yield) of alcohol: bp 145 °C/10 Torr; NMR (60 MHz, CCl_4) δ 0.6–0.9 (m, 2 H), 1–1.4 (m, 1 H), 1.5–1.8 (m, 1 H), 2.5 (br s, 1 H), 6.9 (m, 5 H).

***trans*-1-(Trideuteriomethyl)-2-phenylcyclopropane (21).**[12,38] The mesylate was prepared in the same fashion as for the protio compound starting with 17.5 g (117 mmol) of *trans*-1-(hydroxydideuteriomethyl)-2-phenylcyclopropane, 20 g (13.5 mL, 175 mmol) of methanesulfonyl chloride, and 25 mL (18 g, 178 mmol) of triethylamine. The crude mesylate was placed along with 117 mL of dry tetrahydrofuran in a flask flushed with nitrogen. The flask was cooled to 0 °C, and 256 mL of a 1 M lithium triethylborodeuteride solution in THF was added dropwise with stirring. The solution was then stirred for 4 h, after which the excess hydride was quenched at 0 °C by a slow dropwise addition of water. Workup of the product was carried out in the same fashion as for the protio compound using 82 mL of 3 N NaOH and 85.4 mL of 30% H_2O_2. Distillation gave 13.2 g (84% yield) of *trans*-1-(trideuteriomethyl)-2-phenylcyclopropane: bp 100 °C/25 Torr; NMR (60 MHz, CCl_4) δ 0.49–1.02 (m, 3 H), 1.17–1.62 (m, 1 H), 6.92 (m, 5 H).

***trans*-1-(Trideuteriomethyl)-2-cyclopropanecarboxylic Acid.** The deuterated carboxylic acid was prepared in the same fashion as for the protiocarboxylic acid[12,13] by using 13.2 g (93 mmol) of *trans*-1-(trideuteriomethyl)-2-phenylcyclopropane. Distillation gave 4.0 g (40% yield) of *trans*-1-(trideuteriomethyl)-2-cyclopropanecarboxylic acid: bp

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(38) Holder, R. W.; Matturo, M. G. *J. Org. Chem.* **1977**, *42*, 2166.

115–120 °C/20 Torr; NMR (60 MHz, CCl_4) δ 0.68–1.0 (m, 1 H), 1.03–1.73 (m, 3 H, prominent peaks at 1.33 and 1.43), 13.0 (s, 1 H).

***tert*-Butyl *trans*-2-Methylcyclopropyl Ketone (18).**[39] *trans*-2-Methyl-1-cyclopropanecarboxylic acid (3.5 g, 35 mmol) and 150 mL of anhydrous ethyl ether were placed in a flask flushed with nitrogen. To the flask was slowly added 50 mL (70 mmol) of 1.4 M *tert*-butyllithium with stirring. After addition, the reaction mixture was stirred for an additional 30 min and quenched slowly with 35 mL of water. The organic and aqueous layers were separated, and the aqueous layer was washed 2× with 25 mL of ether. The ether solutions were combined and dried over anhydrous magnesium sulfate. The ether was removed through a 40-cm Vigreux column. The residue was vacuum distilled to give 2.45 g (50% yield) to the ketone: bp 82 °C/20 Torr; NMR (90 MHz, CCl_4) δ 0.35–0.73 (m, 2 H), 0.8–0.9 (m, 1 H), 1.15 (s, 12 H), 1.6–1.85 (m, 1 H); IR neat 2925 (s), 2840 (m), 1680 (s), 1450 (m), 1385 (m), 1350 (m), 1065 (s), 1000 (m), 780 cm^{-1} (m).

***tert*-Butyl *trans*-2-(Trideuteriomethyl)cyclopropyl Ketone.**[39] The deuterated ketone was prepared in the same fashion as for the protio ketone by using 4.0 g (38.8 mmol) of *trans*-1-(trideuteriomethyl)-2-cyclopropanecarboxylic acid and 57 mL (80 mmol) of 1.4 M *tert*-butyllithium. Distillation gave 2.4 g (16.8 mmol, 43% yield) of *tert*-butyl *trans*-2-(trideuteriomethyl)cyclopropyl ketone: bp 80 °C/20 Torr; NMR (60 MHz, CCl_4) δ 0.32–0.6 (m, 2 H), 0.73–0.88 (m, 1 H), 1.07 (s, 9 H), 1.45–1.8 (m, 1 H).

***trans*-1-Methyl-2-(1-*tert*-butylethenyl)cyclopropane (±14).**[12,40] Triphenylmethylphosphonium iodide (13.7 g, 33.6 mmol) with 150 mL of dry THF was placed in a flask flushed with nitrogen. To the flask was added slowly and dropwise 21 mL of 1.6 M *n*-butyllithium. The dark red solution was stirred for 2 h. *tert*-Butyl *trans*-2-methylcyclopropyl ketone (2.45 g, 17.5 mmol) was slowly added to the solution, and the mixture was stirred for an additional 1 h. The reaction mixture was slowly quenched with 25 mL of water, poured into 1 L of water, and extracted 3× with 150 mL of pentane. The pentane solution was washed 2× with 150 mL of water and dried with anhydrous magnesium sulfate, and the pentane removed through a 40-cm Vigreux column. The residue was vacuum transferred to separate it from triphenylphosphine oxide. The olefin was isolated by preparative glc (20% DBTCP on Chromosorb P): NMR (300 MHz, $CDCl_3$) δ 0.35–0.41 (m, 1 H), 0.60–0.73 (m, 2 H), 0.99–1.1 (m, 1 H), 1.12 (s and d, J = 6 Hz, 12 H), 4.391 (s, 1 H), 4.620 (d, 1 H, J = 2.1 Hz); IR (neat) 3100 (m), 3080 (m), 2965 (s), 2740 (w), 2715 (w), 1635 (s), 1460 (s), 1383 (m), 1205 (m), 1155 (m), 1178 (m), 1030 (m), 883 (s), 785 cm^{-1} (m); MS (EI) *m/e* (relative intensity) 138 (24), 123 (56), 109 (30), 95 (29), 91 (12), 81 (100), 69 (15); exact mass, *m/e* 138.141, calcd for $C_{10}H_{18}$ 138.1409.

***trans*-1-(Trideuteriomethyl)-2-(1-*tert*-butylethenyl)cyclopropane (20).**[12,40] Olefin **20** was prepared in the same fashion as the protio compound by using 2.4 g (16.8 mmol) of *tert*-butyl *trans*-2-(trideuteriomethyl)cyclopropyl ketone, 13.4 g of triphenylmethylphosphonium iodide (33 mmol), and 20 mL of 1.6 M *n*-butyllithium (32 mmol). The product was purified by preparative glc (20% DBTCP on Chromosorb P); NMR (300 MHz, $CDCl_3$) δ 0.35–0.42 (m, 1 H), 0.57–0.73 (m, 2 H), 0.98–1.07 (m, 1 H), 1.12 (s, 9 H), 4.390 (s, 1 H), 4.625 (d, 1 H, J = 1.2 Hz).

(1*S*,2*S*)-*tert*-Butyl *trans*-2-Methylcyclopropyl Ketone (18).[39] The optically active ketone (1*S*,2*S*)-**18** was prepared in the same fashion as the racemic ketone **18** by using 1.89 g (19.1 mmol) of the optically active acid (1*S*,2*S*)-**17**[11-14] and 22.4 mL of 2.1 M *tert*-butyllithium. The yield of ketone was 1.45 (52%): NMR (300 MHz, $CDCl_3$) δ 0.63–0.72 (m, 1 H), 1.12 (d, 3 H, J = 6 Hz), 1.2 (s, 9 H), 1.2–1.35 (m, 2 H), 1.8–1.9 (m, 1 H); IR (neat) 2960 (s), 2930 (m), 2860 (m), 1690 (s), 1475 (m), 1400 (s), 1080 cm^{-1} (s).

(+)-(1*S*,2*S*)-*trans*-Methyl-2-(1-*tert*-butylethenyl)cyclopropane (14).[12,40] The olefin was prepared in the same fashion as the racemic compound by using 1.4 g (10 mmol) of the optically active ketone, 11.2 g (28 mmol) of triphenylmethylphosphonium iodide, and 11 mL of 2.5 M *n*-butyllithium. The olefin (1*S*,2*S*)-**14** was isolated by preparative glc (20% OV 101 on Chromosorb P): NMR (300 MHz, $CDCl_3$) δ 0.35–0.41 (m, 1 H), 0.60–0.73 (m, 2 H), 0.99–1.1 (m, 1 H), 1.12 (s and d, J = 6 Hz, 12 H), 4.393 (s, 1 H), 4.625 (d, 1 H, J = 2.1 Hz); IR (neat) 3100 (m), 3090 (m), 2960 (s), 1635 (s), 1460 (s), 1380 (m), 1150 (m), 1075 (m), 880 (s), 780 (m), 630 cm^{-1} (m); $[\alpha]_{365}^{28}$ = +91.5° (1), c = 0.337 (cyclohexane).

Addition of $Eu(hfc)_3$ to an NMR sample of the ketone (1*S*,2*S*)-**18** obtained from the ozonolysis of olefin (1*S*,2*S*)-**14** showed only one *tert*-butyl signal under conditions known to give two signals for the racemic ketone.

***trans*-1-(Trideuteriomethyl)-2-(1-*tert*-butyl-2,2-dideuterioethenyl)cyclopropane (22).**[40,41] *trans*-1-(Trideuteriomethyl)-2-(1-*tert*-butylethenyl)cyclopropane, **20** (0.320 g, 2.27 mmol) and 2 mL of methanol were placed in a flask. The flask was then cooled to −78 °C, and a stream of ozone was bubbled through the solution for 10 min. Dimethyl sulfide (0.251 mL, 3.4 mmol) was added, and the mixture was allowed to warm from −10 °C to room temperature over a period of 3 h. The solution was diluted with water and extracted with pentane. The pentane was washed with water, dried with anhydrous magnesium sulfate, and removed by distilling through a 10-cm Vigreux column until 0.5 mL of liquid remained in the pot. NMR spectroscopy of the crude product revealed no olefinic protons. (The ozonolysis was assumed to be complete for the following Wittig reaction.)

Triphenyl(trideuteriomethyl)phosphonium iodide (4.37 mmol) and 25 mL of anhydrous tetrahydrofuran were placed in a dry flask flushed with nitrogen. With stirring, 2.7 mL (4.37 mmol) of 1.6 M *n*-butyllithium was added dropwise to the flask. The dark red solution was stirred for an additional 2 h, after which 0.5 mL of the crude ozonolysis product was added dropwise. The solution was stirred for an additional 30 min and quenched with 5 mL of water. The contents of the flask were poured into 25 mL of water and extracted with pentane. The solvent was then removed through a 10-cm Vigreux column, and the olefin was isolated by preparative glc (20% DBTCP on Chromosorb P): NMR (300 MHz) δ 0.35–0.41 (m, 1 H), 0.60–0.72 (m, 2 H), 0.99–1.07 (m, 1 H), 1.13 (s, 9 H), 4.377 (s, 0.15 H), 4.396 (0.052 H), 4.613 (d, 0.15 H, J = 2.7 Hz), 4.624 (0.052 H).

***trans*-1-Methyl-2-(1-*tert*-butyl-2,2-dideuterioethenyl)cyclopropane (25).**[20] The deuterated olefin was prepared in the same fashion as the protio **15** by using 0.558 g (60% in a mineral oil dispersion) of sodium hydride, 6 g (0.015 mol) of triphenyl(trideuteriomethyl)phosphonium iodide, and 1.23 g (0.015 mol) of 2-methyl-1-formylcyclopropane.[19,20] The olefin was isolated by preparative glc (20% DBTCP on Chromosorb P followed by 20% OV101 on Chromosorb P): NMR (300 MHz, $CDCl_3$) δ 0.42–0.52 (m, 1 H), 0.54–0.62 (m, 1 H), 0.70–0.84 (m, 1 H), 1.065 (d, 3 H, J = 5.7 Hz), 1.07–1.15 (m, 1 H), 4.8 (d, 0.068 H, J = 10.2 Hz), 5.00 (d, 0.076 H, J = 17.1), 5.32–5.38 (m, 1 H); IR (neat) 2045 (m), 3000 (s), 2945 (s), 2860 (m), 1600 (s), 1450 (m), 1070 (m), 1010 (m), 935 (m), 860 (m), 715 cm^{-1} (s); exact mass, *m/e* 84.091, calcd for $C_6H_8D_2$ 84.0908.

(−)-(*R*)-1-*tert*-Butyl-4-methylcyclopentene (26).[21] In a flame-dried flask cooled to −78 °C was added 36 mL of 1.4 M *tert*-butyllithium. (+)-(*R*)-3-Methylcyclopentanone, **27**, was added dropwise to the stirring solution. The reaction mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with 100 mL of aqueous 15% K_2CO_3, and the layers were separated. The organic layer was dried with anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator to give 0.5 g of a yellow liquid whose NMR (60 MHz, CCl_4) spectrum reveals unresolved multiplets at 0.65–2.4 ppm and a singlet at 0.85 ppm; IR (neat) 3500 (s), 2960 (s), 2860 (m), 1740 (s), 1635 (m), 1450 (m), 1150 (m), 925 (w), 880 cm^{-1} (w).

p-Toluenesulfonic acid monohydrate 0.1 g (0.5 mmol), 200 mL of benzene, and 1 g of the crude alcohol mixture were added to a flask equipped with a Dean–Stark trap. The solution was heated to reflux for 1 h while solvent was occasionally removed from the trap. After reflux the mixture was cooled to room temperature, washed with water, and dried with anhydrous magnesium sulfate. The solvent was removed by using a rotary evaporator, and the remaining residue was vacuum transferred giving 0.5 g of a clear colorless liquid. Capillary GC analysis of the liquid revealed three compounds in 40, 38, and 20% composition which were separated by preparative glc (DBTCP on Chromosorb P) and identified as (−)-(*R*)-*tert*-butyl-4-methylcyclopentene, (+)-(*R*)-*tert*-butyl-4-methylcyclopentene, and (+)-(*R*)-3-methylcyclopentanone, respectively.

(−)-(*R*)-*tert*-Butyl-4-methylcyclopentene showed the following: NMR (300 MHz, $CDCl_3$) δ 1.01 (d, J = 6.6 Hz) and 1.03 (s, 12 H), 1.82–1.92 (m, 2 H), 2.24–2.39 (m, 1 H), 2.41–2.51 (m, 2 H), 5.21 (t, 1 H, J = 3.84 Hz). ^1H NMR decoupling gave the following results: irradiation at 1.01 gave a change in the multiplet at 2.24–2.39, irradiation at 1.87 gave a change in the multiplet at 2.24–2.39 and at 2.41–2.51, irradiation at 2.32 gave a singlet at 1.01, a change in the multiplet at 1.82–1.9, and a change in the multiplet at 2.41–2.51, irradiation at 1.87 or 2.46 collapsed the triplet at 5.21 to a broad singlet, irradiation at 2.46 gave a change in the multiplet at 1.82–1.90 and a change in the multiplet at 2.24–2.39, irradiation at 5.22 gave no pronounced change in the spectrum. ^{13}C NMR (75 MHz, $CDCl_3$) δ (multiplicity) 152.96 (s), 119.24 (d), 40.68 (t), 39.87 (t), 32.64 (s), 32.49 (d), 29.10 (q), 21.69 (q); IR (neat) 3060 (m), 2960 (s), 1635 (m), 1450 (s), 1360 (s), 1250 (m), 1070 (w), 990 (m), 920 (m),

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805 (s) cm^{-1}. MS (EI) *m/e* (relative intensity) 138 (22), 123 (100), 95 (18), 81 (40); exact mass, *m/e* 138.143, calcd for $C_{10}H_{18}$ 138.1409. $[\alpha]_{365}^{25} = -2.4 \pm 0.4°$, $c = 1.51$ (cyclohexane).

(+)-(*R*)-*tert*-Butyl-3-methylcyclopentene showed NMR (300 MHz, $CDCl_3$) δ 0.98 (d, 3 H, $J = 6.3$ Hz), 1.04 (s, 9 H), 2.01–2.12 (m, 1 H), 2.17–2.80 (m, 2 H), 2.64–2.74 (m, 1 H), 5.21 (q, 1 H). ^1H NMR decoupling gave the following results: irradiation at 0.98 gave a change in the multiplet at 2.64–2.74, irradiation at 2.7 gave a singlet at 0.98. IR (neat) 3180 (w), 3040 (m), 2900 (s), 1670 (w), 1635 (m), 1445 (s), 1345 (s), 1260 (m), 1195 (m), 1070 (m), 885 (m), 830 (s) cm^{-1}. MS (EI) *m/e* (relative intensity) 138 (12), 123 (68), 95 (16), 81 (100); exact mass, *m/e* 138.141, calcd for $C_{10}H_{18}$ 138.1409. $[\alpha]_{365}^{25} = 308 \pm 4°$, $c = 0.939$ (cyclohexane).

(+)-*R*-3-Methylcyclopentenone showed the following: NMR (300 MHz, $CDCl_3$) δ 1.13 (d, 3 H, $J = 5.7$), 1.41–1.57 (m, 1 H), 1.0 (t, 1 H), 2.12–2.42 (m, 5 H); IR neat 3480 (m, H_2O contamination), 2960 (s), 2880 (s), 1745 (s), 1640 (w), 1460 (m), 1410 (m), 1240 (m), 1155 (m), 1060 (w), 990 (w), 880 (w) cm^{-1}.

Methyl *trans*-2-Methylcyclopropyl Ketone.[39] 2-Methyl-1-cyclopropanecarboxylic acid (10 g, 0.1 mol) and 400 mL of anhydrous ethyl ether were mixed together in a flask cooled to 0 °C. Then 143 mL (0.2 mol) of 1.4 M methyllithium was slowly added to the solution with stirring. The white slurry was stirred for an additional 20 min followed by a slow dropwise addition of water at 0 °C. The two layers were separated, and the aqueous layer was extracted with ether. The combined ether solutions were dried over anhydrous magnesium sulfate, and the ether was removed by distillation through a 40-cm Vigreux column. The remaining liquid was vacuum distilled (75–80 °C/75 Torr), and 5 g (51% yield) of a clear colorless liquid was obtained. The infrared and NMR spectra of the product revealed some alcohol had formed along with the ketone: IR (neat 3500 (m), 2960 (s), 2870 (m), 1685 (s), 1430 (s), 1400 (s), 1355 (s), 1325 (m), 1255 (w), 1170 (s), 1080 (m), 1020 (w), 950 (m), 850 (m), 795 (w) cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 0.67–0.75 (1 H), 1.0–1.27 (m), and 1.10 (d, $J = 6$ Hz, 6 H, integration is two protons higher due to alcohol impurity), 1.34–1.45 (m, 1 H), 1.64–1.70 (m, 1 H), 2.21 (s, 3 H).

1,1-Dichloro-1-(*trans*-2-methylcyclopropyl)ethane.[17] Phosphorus pentachloride (104.1 g, 0.5 mol) and 120 mL of carbon tetrachloride were placed in a dry flask and cooled to 5 °C. The slurry was stirred while 10.8 g of the methyl *trans*-2-methylcyclopropyl ketone/alcohol mixture was slowly added. The mixture was heated at reflux for 1 h, cooled to room temperature, and poured slowly into 200 mL of ice–water. The organic layer was dried with anhydrous magnesium sulfate, and the solvent was removed on a rotary evaporator. The residue was vacuum distilled to give 2.85 g (18.6 mmol) of the dichloro compound (50 °C/15 Torr): NMR (300 MHz, $CDCl_3$) δ 0.468–0.52 (m, 1 H), 0.90–0.96 (m, 1 H), 1.08 (d, $J = 7.5$ Hz) and 1.10–0.18 (m, 4 H), 1.34–1.40 (m, 1 H), 2.13 (s, 3 H); IR (neat) 3080 (w), 2960 (s), 2940 (m), 2880 (m), 1670 (w), 1450 (s), 1305 (m), 1180 (m), 1070 (s), 900 (m), 870 (m), 790 (m), 690 cm^{-1} (s).

***trans*-(2-Methylcyclopropyl)acetylene (24).**[17] 1,1-Dichloro-1-(*trans*-2-methylcyclopropyl)ethane (2.85 g, 18.8 mmol) was added to a room-temperature suspension of potassium *tert*-butoxide (4.3 g, 38.7 mmol) in absolute dimethyl sulfoxide (34 mL, dried by distilling from calcium hydride). The mixture was vacuum transferred into a receiver cooled to −78 °C. The *tert*-butyl alcohol was removed by washing with cold water, and the acetylene was isolated by preparative glc (20% carbowax on Chromosorb P): NMR (300 MHz, $CDCl_3$) δ 0.51–0.56 (m, 1 H), 0.84–0.93 (m, 2 H), 1.01 (d, $J = 4.5$ Hz) and 1.04–1.10 (m, 4 H), 1.78 (d, 1 H, $J = 2.1$ Hz); IR (neat) 3300 (s), 3080 (m), 2960 (s), 2155 (m), 1445 (m), 1305 (m), 1200 (m), 1070 (m), 1035 (m), 945 (w), 865 (m), 770 cm^{-1} (m). The above spectral data agree with the literature.[42]

***trans*-1-Methyl-2-(1-*tert*-butyl-(*Z*)-2-deuterioethenyl)cyclopropane (23).**[18,30] Cuprous bromide (0.297 mg, 2.07 mmol) was added to a flame-dried flask and placed under vacuum (2 Torr) for 1 h. The flask was flushed with nitrogen. With stirring, 8 mL of anhydrous tetrahydrofuran was syringed into the flask. The flask was cooled to −60 °C, and 2.07 mL (4.14 mmol) of *tert*-butylmagnesium chloride (2.0 M in tetrahydrofuran) was slowly added dropwise so that the temperature of the mixture did not rise above −55 °C. The mixture was stirred for 1 h, after which 140 mg (1.8 mmol) of *trans*-2-methylcyclopropylacetylene was slowly added dropwise. The mixture was warmed to 0 °C and stirred for 30 min, after which it was quenched with a slow dropwise addition of 1.8 mL of D_2O/NaOD. Care was taken during the addition so that the temperature of the mixture did not rise above 5 °C. The contents of the flask were poured into an aqueous solution of 41 mL of saturated ammonium chloride and 0.414 g of sodium cyanide. The solution was stirred for 15 min followed by extraction with pentane. The pentane was washed with water to remove any residual THF. The pentane was removed by distillation through a 40-cm Vigreux column. Capillary glc analysis of the reaction mixture revealed the formation of three products in a 66:5:29 ratio. The mixture was separated by using preparative glc (20% DBTCP on Chromosorb P). The 66 and 29% composition products were identified as *trans*-1-methyl-2-(1-*tert*-butyl-(*Z*)-2-deuterioethenyl)cyclopropane and *trans*-1-methyl-2-(1-deuterio-(*Z*)-2-*tert*-butylethenyl)cyclopropane, respectively. The compound contributing to 5% of the product mixture was not isolated or identified.

trans-1-Methyl-2-(1-deuterio-(*Z*)-2-*tert*-butylethenyl)cyclopropane showed the following: NMR (300 MHz, $CDCl_3$) δ 0.37–0.41 (m, 1 H), 0.60–0.73 (m, 2 H), 0.99–1.05 (m, 1 H), 1.09 (d, 3 H, $J = 6.3$ Hz), 1.12 (s, 12 H), 4.376 (s, 1 H), 4.389 (s, 0.24 H), 4.623 (d, 0.24 H, $J = 1.8$ Hz); IR (neat) 3078 (m), 3085 (m), 2960 (s), 2740 (w), 2280 (w), 1635 (m), 1610 (m), 1465 (s), 1360 (m), 1300 (m), 1205 (m), 1075 (m), 895 (m), 840 (m), 650 cm^{-1} (m); MS (EI) *m/e* (relative intensity) 139 (49.2), 138 (10.72), 124 (100), 110 (39), 96 (21), 82 (48); exact mass, *m/e* 139.148, calcd for $C_{10}H_{17}D$ 139.1471.

trans-1-Methyl-2-(1-*tert*-butyl-(*Z*)-2-deuterioethenyl)cyclopropane showed the following: NMR (300 MHz, $CDCl_3$) δ 0.36–0.50 (m, 2 H), 0.64–0.72 (m, 1 H), 0.971 (s) and 0.91–1.02 (m, 10 H), 1.05 (d, 3 H, $J = 6$ Hz), 4.85 (0.3 H, dd, 15.6, 8.1 Hz), 5.45–5.48 (m, 1 H); IR (neat) 3060 (m), 2950 (s), 2730 (w), 2230 (m), 1643 (m), 1445 (s), 1360 (s), 1200 (m), 1065 (m), 1020 (m), 995 (m), 870 (s), 775 cm^{-1} (m); MS (EI) *m/e* (relative intensity) 139 (61.64), 138 (17.08), 124 (100), 110 (25), 96 (57), 82 (94); exact mass, *m/e* 139.144, calcd for $C_{10}H_{17}D$ 139.1471.

(3*R*)-1-*tert*-Butyl-*cis*- and *trans*-3-Methyl-6-oxabicyclo[3.1.0]hexane (29, 30).[23] In a flame-dried flask was added 154 mg (1.12 mmol) of (−)-(*R*)-1-*tert*-butyl-4-methylcyclopentene along with 25 mL of chloroform. Over a period of 15 min was added 223 mg (1.29 mmol) of 3-chloroperbenzoic acid in 15 mL of chloroform with stirring. After addition the solution was refluxed for 2 h. The organic layer was then washed with 25 mL of aqueous 20% sodium bisulfite solution and 3× with 25-mL portions of aqueous 10% sodium bicarbonate solution. The organic layer was washed with 50 mL of a saturated solution of NaCl, dried with anhydrous magnesium sulfate, and concentrated on a rotary evaporator leaving 0.140 g (82%) of a 85/15 mixture of *trans*- and *cis*-(3*R*)-1-*tert*-butyl-3-methyl-6-oxabicyclo[3.1.0]hexane: IR (neat) 3000 (m), 2940 (s), 1255 (m), 940 (m), 840 (m), 750 cm^{-1} (s). Separation of the trans and cis compounds was accomplished with HPLC (12 in silica column, 97% hexane:3% ethyl ether).

(3*R*)-1-*tert*-Butyl-*trans*-3-methyl-6-oxabicyclo[3.1.0]hexane (**29**) showed the following: NMR (300 MHz, $CDCl_3$) δ 1.0 (s, superimposed on a doublet, 12 H), 1.15 (d of d of d, 1 H, $J = 13.8$, 9.3, 1 Hz), 1.30 (d of d, 1 H, $J = 12.8$, 9.45), 1.79–1.92 (m, 1 H), 1.99 (d of d, 1 H, $J = 13.34$, 7.4 Hz), 2.10 (d of d, 1 H, $J = 13.4$, 6.8 Hz), 3.29 (s, 1 H). ^1H NMR decoupling gave the following results: irradiation at 1.0 gave a change in the multiplet at 1.79–1.92; irradiation at 1.15 gave a change in the multiplet at 2.10; irradiation at 1.30 gave a change in the multiplet at 1.99; irradiation at 1.79–1.92 gave a change in the multiplets at 1.15, 1.30, 1.99, and 2.10 and collapsed the doublet at 1.0 to a singlet; irradiation at 1.99 gave a change in the multiplet at 1.30; irradiation at 2.10 gave a change in the multiplet at 1.15; irradiation at 3.29 collapsed the signal at 1.15 to a doublet of doublets. ^{13}C NMR (75 MHz, $CDCl_3$) δ (multiplicity) 73.52 (s), 60.68 (d), 36.49 (t), 34.79 (t), 31.43 (s), 28.08 (d), 26.58 (q), 19.42 (q); MS (EI), *m/e* (relative intensity) 154 (4), 134 (32), 121 (63), 119 (100), 98.0714 (40); exact mass, *m/e* 154.135, calcd for $C_{10}H_{18}O$ 154.1358.

(3*R*)-1-*tert*-Butyl-*cis*-3-methyl-6-oxabicyclo[3.1.0]hexane (**30**) showed the following: NMR (300 MHz, $CDCl_3$) δ 0.95 (s, 9 H), 0.98 (d, 3 H, $J = 6.9$ Hz), 1.46 (d of d, 1 H, $J = 13.8$, 1.8 Hz), 1.591 (d of d, 1 H, $J = 14.4$, 1.8 Hz), 1.89 (d of d of d, 1 H, $J = 14.3$, 9.3, 1.5 Hz), 2.08 (d of d, 1 H, $J = 14.3$, 9.3, 1.5 Hz), 2.08 (d of d, 1 H, $J = 13.8$, 9.9 Hz), 2.11–2.2 (m, 1 H), 3.33 (s, 1 H). ^1H NMR decoupling gave the following results: irradiation at 0.98 gave a change in the multiplet at 2.1–2.2; irradiation at 1.46 collapsed the signal at 2.08 into a doublet with $J = 9.5$ Hz; irradiation at 1.59 gave a change in the signal at 1.89; irradiation at 1.89 gave a change in the signal at 1.59; irradiation at 2.08 gave a change in the multiplet at 1.46; irradiation at 2.1–2.2 collapsed the signal at 1.46, 1.59, 1.89, and 2.08 into doublets with $J = 14$ Hz, and the doublet at 0.98 collapsed to a singlet, irradiation at 3.33 collapsed the signal at 1.89 to a doublet of doublets with $J = 14$ and 9 Hz. ^{13}C NMR (75 MHz, $CDCl_3$) δ 76.08, 62.62, 35.68, 33.93, 31.68, 29.95, 26.60, 25.18; MS (EI), *m/e* (relative intensity) 110 (37), 98.0717 (43), 83 (49), 69 (100), no molecular ion was observed.

Identification of Pyrolysate Products. Product identification was made of the pyrolysate from the 47.33-h pyrolysis of **23**. Preparative glc (20% DBTCP Chromosorb P) eluted two peaks. The first peak eluted had a ^1H NMR (300 MHz) spectrum similar to that for a mixture of the

(42) Dalacker, V.; Henning, H. *Tetrahedron Lett.* **1974**, 15.
(43) We thank Dr. Kevin E. Gilbert for this suggestion.

Table VIII. Kinetic Data for the Pyrolysis of **14** and **20** at 280 ± 0.1 °C[a]

	time, h				
compd	0	5	7	10	14.5
14	1.00	0.7588	0.6815	0.5807	0.4532
cyclopentene	0.00	0.0735	0.0975	0.1284	0.1666
diene	0.00	0.1664	0.2214	0.2909	0.3799
20	0.9965	0.7793	0.7089	0.6043	0.4907
cyclopentene-d_3	0.00	0.0686	0.0908	0.1238	0.1601
diene	0.00	0.1521	0.2015	0.2673	0.3444

[a] Figures in fractional percent.

Table IX. Kinetic Data for the Pyrolysis of **20** and **22** at 280 ± 0.1 °C[a]

	time, h					
compd	0	5	9	12	18	28
20	0.9990	0.7832	0.6428	0.5533	0.4115	0.2508
cyclopentene-d_3	0.00	0.0678	0.1108	0.1396	0.1842	0.2341
diene-d_3	0.00	0.1490	0.2464	0.3071	0.4042	0.5150
22	0.9964	0.7872	0.6525	0.5648	0.4275	0.2666
cyclopentene-d_5	0.00	0.0633	0.1035	0.1290	0.1695	0.2167
diene-d_5	0.00	0.1495	0.2433	0.3062	0.4029	0.5167

starting material and independently synthesized **26** from 3-methylcyclopentanone.

Capillary glc analysis shows the retention times of these two pyrolysate products are similar to those of **23** and cyclopentene **26**.

The second peak eluted from the preparative glc had the following spectral data: NMR (300 MHz, $CDCl_3$) δ 1.041 (s, 9 H), 1.588–1.614 (m, 2.25 H, partially monodeuterated), 2.752 (t, 2 H, J = 6.3 Hz), 4.929–5.045 (m, 2 H), 5.227 (t, 1 H, J = 6.3 Hz), 5.77–5.90 (m, 1 H). MS (EI) m/e (relative intensity) 139 (19.19), 138 (3.86), 124 (39), 98 (29), 82 (100), 32 (30); exact mass, m/e 139.146, calcd for $C_{10}H_{17}D_1$. The assigned structure of the compound is 5-(monodeuteriomethyl)-6,6-dimethyl-*cis*-1,4-heptadiene.

In all vinylcyclopropane pyrolyses 1-*tert*-butyl-4-methylcyclopentene (**26**) was formed along with a third product in a ratio of 25/1, respectively. The glc retention time of this third product was identical with the retention time found for 1-*tert*-butyl-3-methylcyclopentene (**28**).

That (−)-(*R*)-*tert*-butyl-4-methylcyclopentene (**26**) is stable to pyrolysis conditions was demonstrated by the pyrolysis of (*R*)-(−)-1,4-dimethylcyclopentene under similar conditions.[12] Recovered material had the same optical rotation as starting material ($[\alpha]_{365}^{27}$ −8.26° (0.2) (cyclohexane)). No other products other than recovered (*R*)-(−)-1,4-dimethylcyclopentene were found by glc and ^{1}H NMR analysis to have been formed.

Pyrolysis. Pyrolysis was carried out in a 300-mL Pyrex bulb submerged in a bath of molten salt. The molten salt was composed of a 10:7 mixture of potassium nitrate and sodium nitrite, respectively. The temperature of the bath was maintained by two heaters. A 500-W Vycor immersion resistance heater attached to a variable transformer was used to supply the majority of heat. A 250-W knife blade immersion resistance heater attached to an electronic temperature controller accurate to ±0.10 °C was used for fine temperature control. The temperature of the bath was monitored with an electronic digital thermometer equipped with a platinum resistance probe. The thermometer precision was ±0.1 °C. The molten salt was stirred mechanically.

Table X. Kinetic Data for the Pyrolysis of **15** and **25** at 280 ± 0.1 °C[a]

	time, h			
compd	0	7	9	12
15	1.00	0.3703	0.2812	0.1786
cyclopentene	0	0.0395	0.0452	0.0503
diene	0	0.5904	0.6738	0.7712
25	1.00	0.3922	0.2972	0.1946
cyclopentene-d_2	0	0.0348	0.0387	0.0449
diene	0	0.5728	0.6634	0.7605

[a] Figures in fractional percent.

The pryolysis bulb was attached to a vacuum line that kept the pressure at 10^{-3} Torr. The vacuum line was capable of vacuum transferring samples in and out of the bulb with high efficiency.

The bulb was conditioned by transferring in 2.5 mL of dichlorodimethylsilane. The silane was kept in the bulb for 10 min and then transferred out. Diisopropylamine (1.5 mL) was then transferred into the bulb and was kept there for 15 min. The bulb was then kept open to the vacuum line at 10^{-3} Torr overnight. The bulb was further conditioned by addition of 8 μL of vinylcyclopropane **14**. The vinylcyclopropane was kept in the bulb for 12 h and then evacuated.

All samples pyrolyzed for kinetic analysis, and optical rotation determinations were more than 99% pure as determined by capillary glc. All samples were degassed before they were transferred into the bulb and were pyrolyzed at 280 ± 0.1 °C.

For kinetic studies, 0.8-μL aliquots of sample were loaded into the bulb. After recovery from the bulb the pyrolysate was diluted with 50 μL of $CDCl_3$. Capillary gc analysis was then performed using a Varian 3700 gas chromatograph equipped with flame-ionization detection. Products were separated with a 50-m DB-5 column. Peak area ratios were determined by using a 3390 A Hewlett-Packard integrator. Pyrolysis time and relative concentrations are reported in the Appendix.

For optical rotation determinations, 30–70-μL sample sizes of (+)-(1*S*,2*S*)-*trans*-1-methyl-2-(1-*tert*-butylethenyl)cyclopropane were loaded into the bulb and pyrolyzed for 12 h. The recovered sample was then diluted with 60 μL of $CDCl_3$. The unrearranged vinylcyclopropane was separated from the cyclopentene and diene by preparative glc (20% OV101 Chromosorb P). The mass of the products collected was determined by using decane as an internal standard. The equation used for the mass determination is

$$(\%\text{ area isomer}/\%\text{ area decane})(\text{response correction for decane})(\text{g of decane/mL}) = \text{g of isomer/mL}$$

The percent area ratio was determined by capillary glc analysis of a mixture consisting of the isomer, a weighed amount of decane, and cyclohexane as a solvent (isomer and decane diluted to 1 mL). Optical rotations were determined by using a Perkin-Elmer 241 polarimeter with a wavelength of 365 nm and cyclohexane as the sample solvent.

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Appendix

Kinetic data for the pyrolysis of **14** and **20**, **20** and **22**, and **15** and **25** are given in Tables VIII–X, respectively.