# Kinetics of Thermal Gas-Phase Isomerizations and Fragmentations of *cis*- and *trans*-1-(*E*)-Propenyl-2-methylcyclobutanes at 275 °C

John E. Baldwin* and Richard C. Burrell

*Department of Chemistry, Syracuse University, Syracuse, New York 13244*

*jbaldwin@syr.edu*

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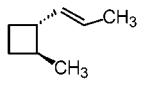
Kinetic studies of the thermal isomerization and fragmentation reactions exhibited by *cis*- and *trans*-1-(*E*)-propenyl-2-methylcyclobutanes at 275 °C in the gas phase have provided first-order rate constants for cis,trans interconversions of the cyclobutanes, 1,3-carbon migrations leading to 3,4- and 3,6-dimethylcyclohexenes, isomerizations providing directly and indirectly four acyclic dienes, and fragmentations to ethylene, propene, and mixtures of pentadienes and hexadienes. Both cis and trans isomers of 1-(*E*)-propenyl-2-methylcyclobutane form *trans*-3,4-dimethylcyclohexene faster than they are converted to *cis*-3,4-dimethylcyclohexene; the trans reactant gives rise to *cis*-3,6-dimethylcyclohexene in preference to its trans isomer, while the cis starting material gives neither at measurable rates; both form the relatively minor product 1,6-(*Z*)-octadiene. The rate constants derived from 35 kinetic runs starting with four distinct 1-(*E*)-propenyl-2-methylcyclobutane samples are consistent to within narrow error limits. The stereomutations, isomerizations, and fragmentations of the 1-(*E*)-propenyl-2-methylcyclobutanes are interpreted in terms of competitive processes involving conformationally flexible short-lived 2-(*E*)-octene-4,7-diyl and 3-methyl-5-(*E*)-heptene-1,4-diyl diradicals.

## Introduction

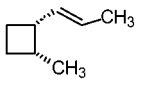
A considerable body of experimental work on the kinetics and stereochemistry of the vinylcyclopropane-to-cyclopentene rearrangements shown by a variety of substituted systems[1] has fostered telling computational efforts toward understanding such reactions.[2] Experimental observations and theoretical approaches both suggest that a vinylcyclopropane reactant affords a transient diradical that may in passage execute conformational changes, leading to stereoisomeric transition structures. The four distinct substituted cyclopentenes derivable from substituted monocyclic vinylcyclopropanes through simple 1,3-carbon shifts are commonly observed to significant though unequal extents.

The formally similar thermal isomerizations of monocyclic vinylcyclobutanes to cyclohexenes have not been subjected to such detailed scrutiny. The reaction type has been well-recognized for nearly 40 years, and several simple hydrocarbon examples of the rearrangement have been studied kinetically.[3] Thermal gas-phase vinylcyclobutane-to-cyclohexene isomerizations in well-seasoned static reactors are uncatalyzed unimolecular processes. This has been rigorously demonstrated through kinetic work over a wide range of pressures and in vessels of widely differing surface-to-volume ratios.[3] Yet full stereochemical characterizations of such reactions have been lacking.

The present work addressed this insufficiency of stereochemical information through studies of the thermal reactions shown by the trans and cis isomers of 1-(*E*)-propenyl-2-methylcyclobutane (**1** and **2**). These reactants augment the minimal vinylcyclobutane system with two methyl groups as stereochemical markers. Prior experience gained through kinetic and stereochemical work with a chiral *trans*-1-(*E*)-propenyl-2-methylcyclopropane[4] provided the first complete profile of the four stereochemical paths available to a vinylcyclopropane rearranging to cyclopentenes. This antecedent no doubt played some role in the selection of 1-(*E*)-propenyl-2-methylcyclobutanes as substrates for the present investigation.




**1**




**2**

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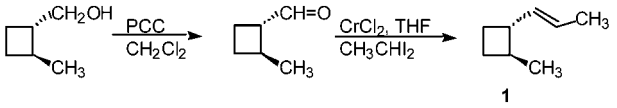
**Scheme 1**




**1**

A second factor contributing to the choice of **1** and **2** was an unpublished study made generally known in summary in a standard secondary source.[5,6] Jordan's 1974 doctoral dissertation included work on the thermal isomerizations shown by racemic **1** and **2**.[5] Most importantly, he found that although the cis isomer **2** decays rapidly through a retro-ene reaction to form 1,5-(*Z*)-octadiene, it also forms trans isomer **1** to a significant extent. Hence these cis and trans substrates present a promising opportunity for securing full stereochemical information on the 1,3-carbon migrations shown by both substrates, an attractive opening not furnished by the related *cis*- and *trans*-1-(*E*)-propenyl-2-methylcyclopropanes.

The present work may be considered an extension of the prior investigations of Andrews[4] and of Jordan.[5] It paved the way for a complete experimental definition of reaction stereochemistry for reactions leading from discrete enantiomers of the *trans*- and *cis*-1-(*E*)-propenyl-2-methylcyclobutanes **1** and **2** to the four stereoisomeric 3,4-dimethylcyclohexenes.[7]

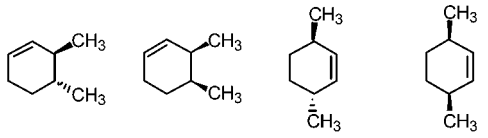
## Results

**Syntheses.** Preparations of racemic samples of **1** and **2** have been reported by Bartlett and Schueller[8] and by Jordan.[5] Our syntheses and characterizations of these hydrocarbons have been recorded.[9] Nonracemic samples of these compounds were prepared from specific stereoisomers of 1-hydroxymethyl-2-methylcyclobutane of high ee and securely established absolute stereochemistry.[9,10]

The last steps in the synthetic sequence in each of the four preparations involved the conversion of a hydroxymethyl function to a 1-(*E*)-propenyl group, as outlined in Scheme 1 for a trans stereoisomer. The Wittig-like coupling reaction employing $CH_3CHI_2$ and $CrCl_2$[11,12] proved superior to the alternative protocols tried. In the case shown, the olefinic product was obtained in 86% yield with ≈14:1 *E*:*Z* stereoselectivity. The *E* isomer was then secured in high purity by preparative GC.

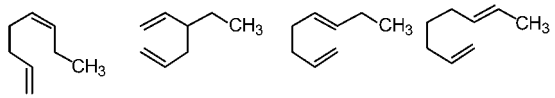
Both racemic samples of the trans and cis substrates (**1** and **2**) and nonracemic samples (**1′** and **2′**) required for subsequent experimental work were used in the present study. Since all reactants and products were monitored by analytical capillary GC, the racemic or nonracemic character of substrates and products played no role. The nonracemic samples were prepared in part through synthetic steps and chromatographic separations of diastereomeric intermediates that were not employed as racemic **1** and **2** were made, and thus the racemic and nonracemic kinetic substrates might possibly have contained very small proportions of different impurities. These subtle differences might have impinged on the kinetic behaviors observed, but that conceivability did not prove to be the case.

Authentic samples of all isomeric thermal reaction products were prepared to secure sure correlations between GC retention times and structural assignments. All of the possible 1,3-carbon shift products, *trans*-3,4-dimethylcyclohexene (**3**), *cis*-3,4-dimethyl-cyclohexene (**4**), *trans*-3,6-dimethylcyclohexene (**5**), and *cis*-3,6-dimethylcyclohexene (**6**), were synthesized and characterized earlier.[13]




**3** **4** **5** **6**

The acyclic diene thermal products 1,5-(*Z*)-octadiene (**7**), 3-ethylhexa-1,5-diene (**8**), 1,5-(*E*)-octadiene (**9**), and 1,6-(*E*)-octadiene (**10**) were secured through Wittig condensations and thermal isomerizations. Oxidation of 4-penten-1-ol with PCC[14] in dry $CH_2Cl_2$ gave 4-penten-1-al; Wittig reactions combining propylidenetriphenylphosphorane and 4-penten-1-al gave 1,5-(*Z*)- and 1,5-(*E*)-octadiene (**7** and **9**). Each isomer was purified through preparative GC and characterized by $^1$H NMR spectroscopy.




**7** **8** **9** **10**

A sample of the 1,5-octadienes (**7**:**9**, 86:14) was diluted with pentane and heated in the gas phase at 275 °C. After 2 h at this temperature the product mixture was transferred to a vacuum line, condensed, and analyzed by capillary GC. It contained 1,5-(*Z*)-octadiene (**7**, 49%); a new component, 3-ethylhexa-1,5-diene (**8**, 7%); and 1,5-(*E*)-octadiene (**9**, 44%). Dienes **7** and **9** were identified through direct comparisons with the authentic compounds prepared as described above; the third component was collected by preparative GC and shown to be 3-ethylhexa-1,5-diene (**8**) by GC/MS and $^1$H NMR.[15] The equilibrations of **7**, **8**, and **9** under the thermal reaction conditions through Cope rearrangements are unexceptional.

5-Hexen-1-ol was oxidized with PCC to the corresponding aldehyde, which was treated with ethylidenetriphenylphosphorane using the Schlosser−Wittig olefination procedure (Scheme 2).[16] A 54:1 mixture of 1,6-(*E*)-octadiene (**10**) and the related 1,6-(*Z*)-diene was obtained; the diene **10** was purifed and characterized spectroscopically.

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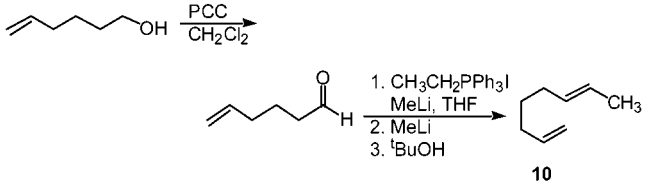
**Scheme 2**




**10**

**Table 1. Mole Percent Data for $C_8H_{14}$ Isomers in Reaction Mixtures Derived from 1 at 275 °C**

| time (s) | 8 | 1 | 9 | 7 | 6 | 10 | 3 | 2 | 4 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.00 | 99.66 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.34 | 0.00 |
| 7 200 | 0.08 | 81.59 | 0.08 | 0.37 | 0.42 | 0.17 | 1.80 | 3.03 | 1.18 |
| 14 400 | | 69.08 | 0.32 | 0.63 | 0.72 | 0.24 | 3.38 | 3.59 | 2.00 |
| 21 600 | 0.20 | 65.05 | 0.64 | 0.96 | 1.08 | 0.42 | 5.23 | 4.10 | 2.95 |
| 28 800 | 0.15 | 51.13 | 0.53 | 0.79 | 1.17 | 0.32 | 6.03 | 3.18 | 3.63 |
| 36 000 | 0.24 | 48.74 | 1.29 | 1.14 | 1.41 | 0.50 | 7.58 | 3.50 | 4.20 |
| 43 200 | 0.21 | 36.97 | 1.50 | 1.28 | 1.59 | 0.52 | 7.33 | 2.48 | 4.39 |
| 57 600 | 0.28 | 25.92 | 1.75 | 1.29 | 1.81 | 0.49 | 8.92 | 2.00 | 4.63 |
| 72 000 | | 18.63 | 2.04 | 1.27 | 1.86 | 0.52 | 9.66 | 1.56 | 4.58 |
| 86 400 | 0.39 | 15.28 | 2.30 | 1.25 | 2.00 | 0.53 | 10.78 | 1.02 | 5.72 |
| 100800 | 0.38 | 12.51 | 3.08 | 1.41 | 2.09 | 0.65 | 11.49 | 1.09 | 6.44 |

Octadiene **10** was subsequently found among the thermal products formed from **1** and **2**.

Trial thermal reaction product mixtures from **1** or **2** and the authentic samples of thermal isomerization products **3**−**10** provided sure identifications of each component in the mixtures. Capillary GC conditions that separated all components with good baseline resolution were developed. Thus, all of the methodology needed for quantitative analyses of thermal reaction mixtures had been secured and tested, and the kinetic work could be addressed.

**Thermal Reactions.** All four kinetic substrates (**1** and **2**, and **1′** and **2′**) were purified through two preparative GC separations, first on a $\beta,\beta'$-oxydipropionitrile (ODPN) column and then on an SE-30 column; these purified samples exhibited kinetic behavior entirely consistent with clean, uncatalyzed first-order unimolecular isomerizations and fragmentations. The trace hydrocarbon impurities that remained after the two preparative GC purifications were negligible and caused no problems in quantifying product mixtures.

Each of the 10 gas-phase thermal rearrangement runs with racemic **1** at 275 °C in the gas phase with pentane as a bath gas and cyclooctane as an internal standard started with about 4 mg of substrate. The reactor was a well-seasoned 300-mL quartz bulb encased in an insulated thermostated aluminum block. When the time period planned for a given thermal reaction was complete, the sample was transferred to a vacuum line, condensed, and analyzed twice by capillary GC. Integrated GC peak intensities, relative to the internal standard cyclooctane, were recorded, tabulated, averaged, and summarized on a mole percent basis (Table 1). The $C_8H_{14}$ isomers included in Table 1 are given left-to-right in the order dictated by relative GC retention times on the analytical column employed.

The GC traces for the thermal reaction product mixtures showed all of the expected components except *trans*-3,6-dimethylcyclohexene (**5**): pentane and retro [2 + 2] products (1.3−4.2 min); 3-ethylhexa-1,5-diene (**8**, 6.0 min), *trans*-1-(*E*)-propenyl-2-methylcyclobutane (**1**, 8.0 min); 1,5-(*E*)-octadiene (**9**, 8.7 min); 1,5-(*Z*)-octadiene (**7**, 8.9 min); *cis*-3,6-dimethylcyclohexene (**6**, 9.1 min); 1,6-(*E*)-octadiene (**10**, 9.3 min), *trans*-3,4-dimethylcyclohexene (**3**, 9.7 min); *cis*-1-(*E*)-propenyl-2-methylcyclobutane (**2**, 10.4 min); *cis*-3,4-dimethylcyclohexene (**4**, 11.7 min); cyclooctane (21.8 min). The mixture also contained a small amount of *trans*-1-(*Z*)-propenyl-2-methylcyclobutane (8.2 min), a contaminant in the substrate that remained even after the two preparative GC purification steps on two different columns.

**Table 2. Mole Percent Data for $C_8H_{14}$ Isomers in Reaction Mixtures Derived from 2 at 275 °C**

| time (s) | 8 | 1 | 9 | 7 | 6 | 10 | 3 | 2 | 4 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.00 | 0.38 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 99.62 | 0.00 |
| 1 800 | 0.18 | 4.52 | 0.31 | 3.25 | 0.00 | 0.41 | 0.95 | 83.20 | 0.25 |
| 3 600 | 0.51 | 9.07 | 1.05 | 6.11 | 0.00 | 0.34 | 2.20 | 80.76 | 0.90 |
| 5 400 | 0.61 | 10.22 | 1.54 | 6.49 | 0.00 | 0.50 | 2.40 | 59.05 | 1.15 |
| 7 200 | 0.76 | 11.99 | 2.52 | 7.11 | 0.00 | 0.63 | 3.17 | 49.35 | 1.38 |
| 9 000 | 0.90 | 13.07 | 3.64 | 7.61 | 0.00 | 0.67 | 3.56 | 40.66 | 1.40 |
| 10 800 | 1.11 | 15.29 | 4.88 | 8.43 | 0.00 | 0.75 | 3.83 | 38.37 | 1.82 |
| 14 400 | 1.21 | 15.44 | 6.59 | 8.13 | 0.00 | 0.85 | 4.96 | 27.11 | 2.03 |
| 16 200 | 1.17 | 15.55 | 7.17 | 7.61 | 0.00 | 0.78 | 4.98 | 23.10 | 1.99 |
| 18 000 | 1.30 | 17.66 | 8.78 | 8.40 | 0.00 | 0.96 | 5.94 | 20.87 | 2.29 |
| 21 600 | 1.49 | 15.57 | 9.23 | 7.11 | 0.20 | 0.82 | 5.78 | 14.77 | 2.40 |
| 25 200 | 1.55 | 15.09 | 10.30 | 6.84 | 0.23 | 0.83 | 5.74 | 12.23 | 2.60 |

**Table 3. Mole Percent Data for $C_8H_{14}$ Isomers in Reaction Mixtures Derived from 1′ at 275 °C**

| time (s) | 8 | 1 | 9 | 7 | 6 | 10 | 3 | 2 | 4 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.00 | 99.78 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.22 | 0.00 |
| 7 200 | 0.00 | 81.94 | 0.00 | 0.16 | 0.35 | 0.11 | 1.76 | 2.59 | 1.07 |
| 14 400 | 0.00 | 74.05 | 0.18 | 0.42 | 0.65 | 0.20 | 3.33 | 3.39 | 2.02 |
| 28 800 | 0.13 | 52.17 | 0.77 | 0.79 | 1.08 | 0.37 | 5.69 | 3.41 | 3.33 |
| 43 200 | 0.17 | 39.25 | 1.22 | 0.95 | 1.33 | 0.42 | 6.77 | 2.47 | 4.05 |
| 57 600 | 0.23 | 31.85 | 1.76 | 1.06 | 1.61 | 0.50 | 8.67 | 2.26 | 5.01 |
| 72 000 | 0.33 | 24.63 | 2.49 | 1.37 | 2.03 | 0.62 | 10.73 | 1.80 | 6.13 |
| 86 400 | 0.32 | 17.60 | 2.59 | 1.29 | 1.94 | 0.55 | 10.62 | 1.31 | 5.99 |

The eleven kinetic runs starting with **2** each started with about 4 mg of substrate; the thermal reactions, product isolations, and quantitative analyses were conducted as described above. The data were tabulated, averaged, and reported as mole percents (Table 2). The GC traces of the thermal reaction mixtures showed the same spectrum of components; again *trans*-3,6-dimethylcyclohexene (**5**) was not detected. The mixture also contained a small amount of *cis*-1-(*Z*)-propenyl-2-methylcyclobutane (10.9 min), an impurity present in the substrate.

Kinetic runs starting with the nonracemic substrates **1′** or **2′** were conducted and processed following the same protocols. Larger samples, about 15 mg, were invested in each run, for the product mixtures were eventually to be subjected to additional chromatographic and chemical steps after the capillary GC analyses reported here were completed, and sufficient material needed to be available. The product distributions as functions of reaction times are summarized in Tables 3 and 4.

Finally, a sample of *cis*-3,4-dimethylcyclohexene (**4**) and cyclooctane in pentane was subjected to the reaction conditions; after 20 h at 275 °C, the recovered material showed no detectable conversion to isomers **1**, **2**, or **3**, or any other rearrangement or fragmentation product.

**Time-Dependent Mole Percent Concentrations of 1 and 2.** The time versus mole percent data for the isomeric vinylcyclobutanes **1** and **2** were consistent with the kinetic situation outlined in Scheme 3. The substrates at 275 °C suffer thermal stereomutations resulting in cis,-

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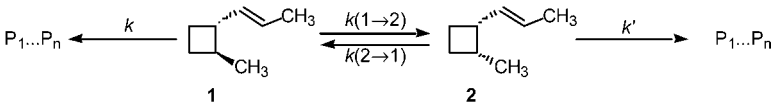
**Scheme 3**




1 2

**Table 4. Mole Percent Data for $C_8H_{14}$ Isomers in Reaction Mixtures Derived from 2′ at 275 °C**

| time (s) | 8 | 1 | 9 | 7 | 6 | 10 | 3 | 2 | 4 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 100.00 | 0.00 |
| 1 800 | 0.13 | 3.89 | 0.17 | 2.90 | 0.00 | 0.00 | 0.98 | 85.08 | 0.42 |
| 3 600 | 0.34 | 7.35 | 0.65 | 4.89 | 0.00 | 0.19 | 1.79 | 70.95 | 0.77 |
| 7 200 | 0.69 | 11.91 | 2.43 | 7.68 | 0.00 | 0.33 | 3.22 | 53.70 | 1.36 |
| 10 800 | 0.89 | 13.86 | 4.30 | 8.11 | 0.00 | 0.30 | 3.98 | 37.07 | 1.70 |
| 14 400 | 1.07 | 14.73 | 6.14 | 8.09 | 0.00 | 0.48 | 4.58 | 28.16 | 1.97 |
| 18 000 | 1.16 | 15.41 | 7.44 | 7.51 | 0.00 | 0.51 | 5.03 | 20.21 | 2.13 |
| 21 600 | 1.20 | 15.96 | 9.05 | 7.35 | 0.05 | 0.57 | 5.71 | 13.88 | 2.42 |

trans equilibrations, and each is converted to various other products, symbolized collectively as $\mathbf{P}_1...\mathbf{P}_n$.

The relevant kinetic expressions are given in eqs 1 and 2; these two simultaneous first-order differential equations have solutions of the forms shown in eqs 3 and 4, where $A_1$, $B_1$, $A_2$, $B_2$, $\lambda_1$, and $\lambda_2$ are constants.[17]

$$-\mathbf{d[1]}/\mathrm{d}t = (k(\mathbf{1}\rightarrow\mathbf{2}) + k)[\mathbf{1}] - k(\mathbf{2}\rightarrow\mathbf{1})[\mathbf{2}] \quad (1)$$

$$-\mathbf{d[2]}/\mathrm{d}t = -k(\mathbf{1}\rightarrow\mathbf{2})[\mathbf{1}] + (k(\mathbf{2}\rightarrow\mathbf{1}) + k')[\mathbf{2}] \quad (2)$$

$$\mathbf{1}(t) = A_1 \exp(-\lambda_1 t) + B_1 \exp(-\lambda_2 t) \quad (3)$$

$$\mathbf{2}(t) = A_2 \exp(-\lambda_1 t) + B_2 \exp(-\lambda_2 t) \quad (4)$$

The same two exponential parameters apply whatever the initial proportions of **1** and **2**; the two coefficients in each equation are subject to boundary conditions dictated by the initial mole percent concentrations and are not independent.

The data sets for the 1-(*E*)-propenyl-2-methylcyclobutanes **1** and **2** presented in Tables 1 to 4 may thus all be fit with eqs 3 and 4 and least-squares-based optimization calculations to match as closely as possible the experimental data with the functional forms required.[18] These calculations provided the exponential parameters $\lambda_1 = 1.84 \times 10^{-5}$ s$^{-1}$ and $\lambda_2 = 9.02 \times 10^{-5}$ s$^{-1}$.

The kinetic plots shown in Figures 1 and 2 present experimental mole percent concentration versus time data from Tables 1 and 2 for isomers **1** and **2**. Similar plots were obtained for the data for isomers **1′** and **2′** provided in Tables 3 and 4. Excellent fits were evident in all of these plots, based on the common $\lambda_1 = 1.84 \times 10^{-5}$ s$^{-1}$ and $\lambda_2 = 9.02 \times 10^{-5}$ s$^{-1}$ parameters and one variable coefficient for each theoretical function. Thus, the time-dependence of **1** and **2** in any series of kinetic runs became available as simple, fully defined mathematical expressions that could be integrated easily and exactly (Table 5).

The slight differences in coefficients for reactions starting with **1** and **1′**, or with **2** and **2′**, reflect slightly different initial concentrations of the two cyclobutanes in the samples (Tables 1−4).

**Isomerizations Through 1,3-Carbon Shifts.** The kinetic situation for the formation of any particular

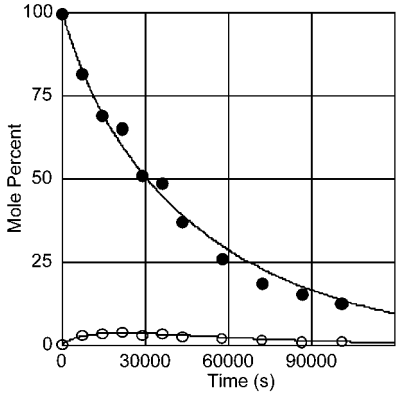



**Figure 1.** Time-dependent evolutions of **1** (closed circles) and **2** (open circles) from heating **1** at 275 °C (data from Table 1).

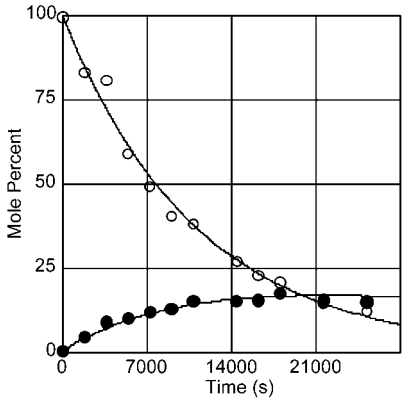
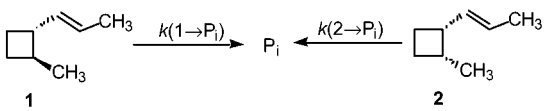



**Figure 2.** Time-dependent evolutions of **2** (open circles) and **1** (closed circles) from heating **2** at 275 °C (data from Table 2).

**Table 5. Time-Dependent Mole Percent Concentrations of 1 and 2: $1(t) = A \exp(-1.84 \times 10^{-5}\ \mathrm{s}^{-1} \times t) + B \exp(-9.02 \times 10^{-5}\ \mathrm{s}^{-1} \times t)$**

| | trans isomer **1** | | cis isomer **2** | |
|---|---|---|---|---|
| reactant | $A_1$ | $B_1$ | $A_2$ | $B_2$ |
| **1** | 85.99 | 13.67 | 6.79 | −6.46 |
| **2** | 31.71 | −31.33 | 0.48 | 99.14 |
| **1′** | 89.39 | 10.40 | 6.55 | −6.33 |
| **2′** | 30.75 | −30.75 | 0.37 | 99.63 |

**Scheme 4**




1 2

isomer $\mathbf{P}_i$ which may be formed directly from **1** and/or **2** at any time $t$ will be governed kinetically by the simple situation presented in Scheme 4.

Hence the time dependence of $\mathbf{P}_i$ is provided by eqs 5 and 6, and one can find optimum values of the rate constants $k(\mathbf{1}\rightarrow\mathbf{P}_i)$ and $k(\mathbf{2}\rightarrow\mathbf{P}_i)$ using a least-squares curve-fitting approach, matching experimental mole percent data with the two-parameter theoretical expression provided by eq 6.

(17) Inter alia, Martin, W. T.; Reissner, E. *Elementary Differential Equations*, 2nd ed.; Addison-Wesley: Reading, MA, 1961; pp 180−185.

(18) The optimizations were secured with computations using DeltaGraph Pro Version 4.0.1; DeltaPoint, Inc.: Monterey, Ca, 1996.

$$-\mathrm{d}[\mathbf{P}_i]/\mathrm{d}t = k(\mathbf{1}\rightarrow\mathbf{P}_i)[\mathbf{1}(t)] + k(\mathbf{2}\rightarrow\mathbf{P}_i)[\mathbf{2}(t)] \quad (5)$$

$$\mathbf{P}_i(t) = k(\mathbf{1}\rightarrow\mathbf{P}_i)\int[\mathbf{1}(t)]\,\mathrm{d}t + k(\mathbf{2}\rightarrow\mathbf{P}_i)\int[\mathbf{2}(t)]\,\mathrm{d}t \quad (6)$$

When **1** is the starting material, the function will depend largely on $k(\mathbf{1}\rightarrow\mathbf{P}_i)$, and when **2** is the substrate, the function will be most sensitive to the value $k(\mathbf{2}\rightarrow\mathbf{P}_i)$. Consistent parameters starting from either **1** or **2** are required and are readily found. The plots of Figures 3 and 4 based on the data gathered in Tables 1 and 2 exemplify the level of agreement between experimental and calculated mole percent values for isomers **3** and **4** starting from **1** or **2**. Similar plots were obtained for the data sets provided in Tables 3 and 4.

The data of Tables 1 and 2 and the data-reduction approach just described provided values for $k(\mathbf{1}\rightarrow\mathbf{3})$, $k(\mathbf{1}\rightarrow\mathbf{4})$, $k(\mathbf{2}\rightarrow\mathbf{3})$, and $k(\mathbf{2}\rightarrow\mathbf{4})$. The data of Tables 3 and 4 provide the same four rate constants independently. A comparison of these values is presented in Table 6. One sees that the individual rate constants agree to within an average difference of some 2.7%, the largest difference being 3.6%. These comparisons provide an important insight into the reliability of the rate constants secured in the present work: they have been obtained reproducibly, to within reasonable error limits. They are not known with infinite precision, but they are reproducible and well-defined.

Neither **1** nor **2** formed *trans*-3,6-dimethylcyclohexene (**5**) at a perceptible rate. The trans substrate formed the *cis*-3,6-dimethylcyclohexene (**6**) slowly, as shown in Figure 5. The rate constants measured were $k(\mathbf{1}\rightarrow\mathbf{6}) = 0.54 \times 10^{-6}$ s$^{-1}$ and $0.51 \times 10^{-6}$ s$^{-1}$ for the two independent determinations. Conversion of the cis isomer **2** to **6** was not observed. The values of $k(\mathbf{1}\rightarrow\mathbf{5})$, $k(\mathbf{2}\rightarrow\mathbf{5})$, and $k(\mathbf{2}\rightarrow\mathbf{6})$ must thus be smaller that about $1 \times 10^{-7}$ s$^{-1}$, the smallest first-order rate constant clearly defined in this work, some 3 orders of magnitude times smaller than the largest rate constant measured (see below).

**Isomerizations to Acyclic Trienes.** For present purposes, the equilibration of **7**, **8**, and **9** through Cope rearrangements was not considered in detail; rather, the time-dependent formations of [**7** + **8** + **9**] starting from **1** or **2** were followed. Not surprisingly, **2** and **2′** gave [**7** + **8** + **9**] rapidly; the rate constants found were $1.97 \times 10^{-5}$ s$^{-1}$ (Figure 6) and $1.88 \times 10^{-5}$ s$^{-1}$ for the two independent determinations. The cis substrate **2** readily accommodates geometrical requirements for a retro-ene reaction to give **7**, while the trans system **1** does not. The [**7** + **8** + **9**] sum of concentrations builds with time in reaction mixtures starting from **1**, but this sum of isomeric products derives to within experimental uncertainties entirely through the sequence **1** → **2** → **7**.

Both starting isomers were found to give 1,6-(*E*)-octadiene (**10**) directly. The rate constant values found for $k(\mathbf{1}\rightarrow\mathbf{10})$ were $0.11 \times 10^{-6}$ s$^{-1}$ and $0.13 \times 10^{-6}$ s$^{-1}$ (Figure 7) for the two independent determinations; the values found for $k(\mathbf{2}\rightarrow\mathbf{10})$ were $0.54 \times 10^{-6}$ s$^{-1}$ and $0.97 \times 10^{-6}$ s$^{-1}$. The difference in these estimates for $k(\mathbf{2}\rightarrow\mathbf{10})$ is quite large absolutely, but quite small, compared with the sum of all rate constants converting **2** to other products, $1.2 \times 10^{-4}$ s$^{-1}$. The imprecision with which $k(\mathbf{2}\rightarrow\mathbf{10})$ was obtained is thus understandable as well as frustrating, but it is not of critical importance. That **10** is formed from both **1** and **2** as a minor product is apparent and consistent with all data, though the relatively small rate constants are not known exactly.

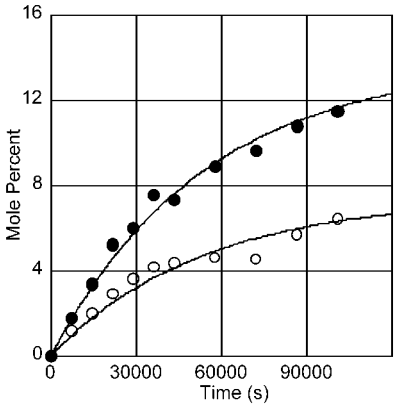



**Figure 3.** Time-dependent evolutions of **3** (closed circles) and **4** (open circles) from heating **1** at 275 °C (data from Table 1).

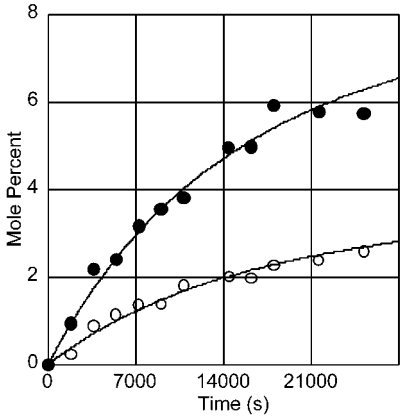



**Figure 4.** Time-dependent evolutions of **3** (closed circles) and **4** (open circles) from heating **2** at 275 °C (data from Table 2).

**Table 6. Rate Constants (s$^{-1}$) for 1,3-Carbon Shifts Converting *cis*- and *trans*-1-(*E*)-Propenyl-2-methylcyclobutanes at 275 °C in the Gas Phase to 3,4-Dimethylcyclohexenes**

| data | $k(\mathbf{1}\rightarrow\mathbf{3})$ | $k(\mathbf{1}\rightarrow\mathbf{4})$ | $k(\mathbf{2}\rightarrow\mathbf{3})$ | $k(\mathbf{2}\rightarrow\mathbf{4})$ |
|---|---|---|---|---|
| Tables 1 and 2 | $2.53 \times 10^{-6}$ | $1.41 \times 10^{-6}$ | $5.48 \times 10^{-6}$ | $2.23 \times 10^{-6}$ |
| Tables 3 and 4 | $2.44 \times 10^{-6}$ | $1.45 \times 10^{-6}$ | $5.34 \times 10^{-6}$ | $2.19 \times 10^{-6}$ |

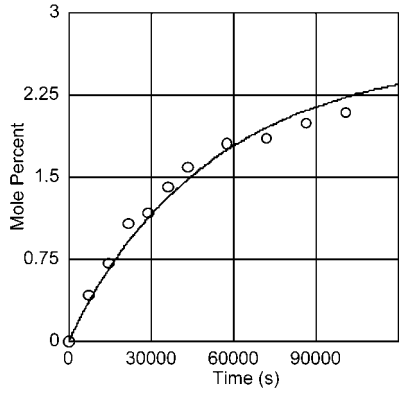



**Figure 5.** Time-dependent evolution of *cis*-3,6-dimethylcyclohexene (**6**) (open circles) from heating **1** at 275 °C (data from Table 1).

**Fragmentations and Stereomutations.** The time-dependence of [**1** + **2**] may be expressed as two-parameter functions, as in eqs 7 and 8. Hence, one may plot [**1** + **2**] against time using data from Tables 1, 2, 3, or 4 and apply a least-squares approach to find the best values of

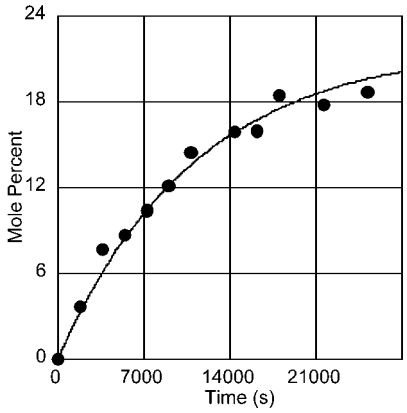



**Figure 6.** Time-dependent evolution of the sums of 1,5-(*Z*)-octadiene (**7**), 3-ethylhexa-1,5-diene (**8**), and 1,5-(*E*)-octadiene (**9**) (closed circles) from heating **2** at 275 °C (data from Table 2).

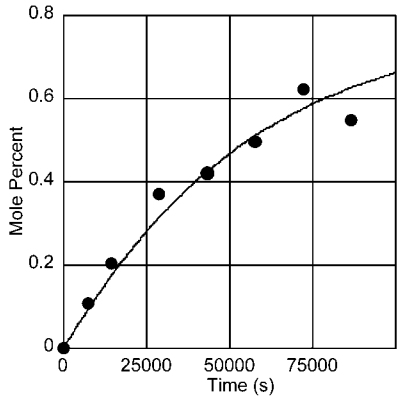



**Figure 7.** Time-dependent evolution of 1,6-(*E*)-octadiene (**10**) (closed circles) from heating **1′** at 275 °C (data from Table 3).

**Table 7. Rate Constants ($s^{-1}$) for cis,trans Interconversions and Decays of 1-(*E*)-Propenyl-2-methylcyclobutanes at 275 °C in the Gas Phase**

| data | $k$(**1**→**2**) | $k$(**2**→**1**) | k | k′ |
|---|---|---|---|---|
| Tables 1 and 2 | $6.46 \times 10^{-6}$ | $2.34 \times 10^{-5}$ | $1.81 \times 10^{-5}$ | $6.72 \times 10^{-5}$ |
| Tables 3 and 4 | $6.55 \times 10^{-6}$ | $2.24 \times 10^{-5}$ | $1.70 \times 10^{-5}$ | $6.81 \times 10^{-5}$ |

the two parameters, $k$ and $k'$. The two functions appropriate to **1** or **2** as starting isomers cover reactions over markedly different time domains, though they of necessity share common values of $k$ and $k'$.

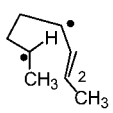
$$-\mathrm{d}[\mathbf{1} + \mathbf{2}]/\mathrm{d}t = k[\mathbf{1}] + k'[\mathbf{2}] \quad (7)$$

$$[\mathbf{1} + \mathbf{2}](t) = k\int[\mathbf{1}(t)]\,\mathrm{d}t + k'\int[\mathbf{2}(t)]\,\mathrm{d}t \quad (8)$$

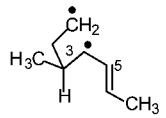
Similarly, one may calculate values for $-\mathrm{d}[\mathbf{1}]/\mathrm{d}t$ and $-\mathrm{d}[\mathbf{2}]/\mathrm{d}t$ as functions of time from the expressions obtained for [**1**]($t$) and [**2**]($t$), and then use eqs 1 and 2 as paired two-parameter functions. The values for $k$, $k'$, $k$(**1**→**2**), and $k$(**2**→**1**) secured through these least-squares fits of data to theoretical functions are summarized in Table 7.

## Discussion and Conclusions

In the gas phase at 275 °C, the 1-(*E*)-propenyl-2-methylcyclobutanes **1** and **2** give rise to an informative mixture of isomers and retro-[2 + 2] fragmentation products. The retro-ene process converting cis reactant **2** to 1,5-(*E*)-octadiene (**7**) and the Cope rearrangements equilibrating **7**, **8**, and **9** may be viewed as standard pericyclic isomerizations; they may well take place through concerted mechanisms.[19] All other thermal reactions of **1** and **2** that were observed may be most readily rationalized as stepwise conversions involving the transient diradicals 2-(*E*)-octene-4,7-diyl (**11**) and 3-methyl-5-(*E*)-heptene-1,4-diyl (**12**).




**11**




**12**

These diradicals formed through cleavage of C1−C2 or C1−C4 in **1** and **2** have short lifetimes, long enough for some conformational explorations before exit channels are encountered but not long enough to permit complete conformational equilibrations and formations of equal product mixtures from **1** and **2**. The diradicals need not be considered intermediates residing in substantial local minima on a potential energy surface. Rather, if conformational isomers of these diradicals are nearly isoenergetic, then dynamic factors rather than $\Delta\Delta H^{\ddagger}$-based preferences may dictate the relative rates of alternative overall reactions.

The geometrical isomerizations governed by $k$(**1**→**2**) and $k$(**2**→**1**) occur by way of diradicals **11** and **12** generated from **1** or **2** reclosing to both **1** and **2**. Such thermal stereomutations in cyclopropanes and cyclobutanes are well-recognized exemplars of nonconcerted, diradical-mediated events.[1b]

The various retro-[2 + 2] fragmentation products stem from cleavage of a C−C bond in **11** and **12**, an eventuality thoroughly probed experimentally and theoretically for the parent 1,4-diradical, tetramethylene.[20] While it has a decay time of some 700 ± 40 fs,[21] diradicals **11** and **12** might well last somewhat longer, thanks to allylic stabilization, a speculation which could be subjected to experimental and theoretical tests.

The stereochemical aspects of the 1,3-carbon migrations leading to dimethylcyclohexene products are striking insofar as the kinetically controlled formation of 3,4-dimethylcyclohexenes favors the trans isomers whatever the stereochemistry of the reactant. The trans isomer **1** gave a 64:36 kinetically controlled **3**:**4** product mixture; the independent kinetic study based on **1′** as starting material found the ratio to be 63:37. The cis isomers **2** and **2′** generated **3**:**4** in a 71:29 ratio. The substrates **1** and **2** give rise to conformationally distinct diradicals **11**, which suffer some (but incomplete) conformational equilibrations before C−C bond-making events provide **3** or **4**.

(19) But compare: Baumann, H.; Voellinger-Borel, A. *Helv. Chim. Acta* **1997**, *80*, 2112−2123.

(20) Cannarsa, M. J. Ph.D. Dissertation, Cornell University, Ithaca, NY, 1984; *Diss. Abst. Int. B* **1984**, *45*, 1468B. (b) Chickos, J.; Annamalia, A.; Keiderling. T. *J. Am. Chem. Soc.* **1986**, *108*, 4398−4402. (c) Goldstein, M. J.; Cannarsa, M. J.; Kinoshita, T.; Koniz, R. F. *Stud. Org. Chem.* (*Amsterdam*) **1987**, *31*, 121−133. (d) Lewis, D. K.; Glenar, D. A.; Kalra, B. L.; Baldwin, J. E.; Cianciosi, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 7225−7227. (e) Doubleday, C. *J. Phys. Chem.* **1996**, *100*, 15083−15086. (f) Marcus, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 4683−4690. (g) Moriarty, N. W.; Lindh, R.; Karlström, G. *Chem. Phys. Lett.* **1998**, *289*, 442−450. (h) De Feyter, S.; Diau, E. W.-G.; Scala, A. A.; Zewail, A. H. *Chem. Phys. Lett.* **1999**, *303*, 249−260.

(21) Pedersen, S.; Herek, J. L.; Zewail, A. H. *Science* **1994**, *266*, 1359−1364.

If one views the same experimental result from the standpoint of orbital symmetry theory and the stereochemical characteristics of "allowed" [1,3]-sigmatropic shifts of carbon, one has **1** giving **3**:**4** through both "allowed" and "forbidden" paths in ≈64:36 proportions, while **2** gives **3**:**4** through "forbidden" and "allowed" paths in a 71:29 ratio. The reactions seem best viewed as diradical-mediated, nonconcerted, stepwise isomerizations. Some products do have stereochemistry consistent with expectations for "allowed" reactions, but such paths enjoy no substantial energy of concert. They are not kinetically dominant. Other reactions of the same sort, stereochemically classed as "forbidden", occur at very similar and sometimes faster rates. That **1** but not **2** gives *cis*-3,6-dimethylcyclohexene (**6**) but not the trans isomer **5** is most suggestive. The trans starting material **1** seems well-positioned for forming the cis product **6** by way of **12** efficiently in a suprafacial fashion. Just why $k$(**1**→**5**), $k$(**2**→**5**), and $k$(**2**→**6**) are too small to be of significance in competitive kinetic circumstances remains unclear.

Both **1** and **2** have access to a conformational isomer of **11** appropriate to a hydrogen transfer from the methyl group to C3 to form 1,6-(*E*)-octadiene (**10**). Similar internal disproportionation processes in 1-vinyl- and 1-alkenyl-2-methylcyclobutanes have been noted previously.[5,22]

Might **11** also lead to 1,5-(*E*)-octadiene (**9**)? Should not **11** prefer a six-centered activated complex to an eight-centered transition structure for a hydrogen transfer leading to an acyclic diene? Perhaps, but no evidence now at hand may serve to answer the question. Substantial amounts of **9** are formed indirectly from **2** or from **1** by way of **2**. A second less-significant reaction path leading from **11** to **9** directly would not have been detected in the present kinetic studies.

The very similar stereochemical balance between trans and cis isomers of 3,4-dimethylcyclopentene formed under kinetic control from *trans*-1-(*E*)-propenyl-2-methylcyclopropane, 73:27,[4] and the stereochemical outcome for 1,3-carbon shifts leading to **3** (63−64%) and **4** (37−36%) starting from trans isomer **1** provides some grounds for hope that the theoretical tactics that have been so illuminating for vinylcyclopropane-to-cyclopentene isomerizations[2] will similarly serve to elucidate in detail just how a conformationally flexible diradical such as **11** or **12** may contort in the brief interval between its genesis from **1** or **2** and its demise as it locates a product-defining transition structure. The allowed−forbidden reversal of 1,3-shifts shown by **1** and **2** provides a strong stimulus for such efforts. Full experimental and theoretically detailed definitions of reaction stereochemistry and mechanism for the parent vinylcyclobutane-to-cyclohexene isomerization remain significant goals.

## Experimental Section

Mass spectra were determined using a GC/MS system and an Ultra 2 (HP, cross-linked 5% phenylmethyl siloxane, 25 m × 0.2 mm × 0.33 μm film thickness) column. Preparative GC purifications employed custom-made 6.35-mm o.d. stainless steel or aluminum packed columns. Analytical GC work was performed with 25 m Ultra 2 and 25 m × 0.2 mm × 0.1 μm film thickness Carbowax 20M columns. For analyses of kinetic data from thermal reactions, a DB-1301 [J & W, 6% (cyanopropylphenyl)methylsiloxane, 30 m × 0.25 mm × 0.50 μm film thickness] column was used.

**4-Penten-1-al.**[23] To a 100-mL flask were added PCC[14] (1.9 g, 8.7 mmol) and dry $CH_2Cl_2$ (25 mL). 4-Penten-1-ol (0.5 g, 5.8 mmol) in $CH_2Cl_2$ (4 mL) was added dropwise to the PCC solution over 5 h. The mixture was stirred for an additional 2 h at room temperature. At that time the black mixture was diluted with ether (35 mL). The brown suspension was then filtered through Florisil. The black tar that remained in the flask was washed with ether (3 × 20 mL), the washings were filtered through Florisil, and the Florisil was washed with ether (35 mL). The ethereal solutions were combined and concentrated by distillation to yield 4-penten-1-al (0.46 g, 94%) as a 17% solution: MS *m*/*z* (rel intensity) 84 (8, $M^+$), 83 (31), 69 (13), 56 (58), 55 (100), 41 (72), 39 (92), 29 (94).

**1,5-(*Z*)-Octadiene (7).**[5,24] To a 50-mL flask were added propyltriphenylphosphonium bromide (0.94 g, 2.5 mmol) and THF (15 mL). The solution was cooled to −78 °C and 1.4 M MeLi (1.8 mL, 2.5 mmol) in ether was added dropwise. The mixture was warmed to 0 °C and stirred for 1 h. At that time, the orange solution was cooled to −78 °C and 4-penten-1-al (0.19 g, 2.3 mmol) was added dropwise in THF (5 mL). The mixture was slowly warmed to room temperature and stirred for 3 h under argon. The yellow reaction mixture was quenched with water (25 mL) and the aqueous layer was extracted with pentane (3 × 20 mL). The organic layers were combined, washed with water (3 × 20 mL), dried ($Na_2SO_4$), filtered, and concentrated to give 0.21 g (85%, 5*Z*:5*E* 6.3:1, Ultra 2) of 1,5-octadienes **7** and **9** as a 3% solution. A sample of **7** was purified by preparative GC (2.3 m, 20% ODPN on Chromosorb P-NAW, 58 °C): $^1$H NMR δ 5.92−5.74 (m, 1 H), 5.47−5.27 (m, 2 H), 5.10−4.92 (m, 2 H), 2.20−1.88 (m, 6 H) 0.96 (t, $J$ = 7.4 Hz, 3 H) (compare ref 5); $^{13}$C NMR δ 138.5, 132.1, 128.3, 114.5, 33.9, 26.6, 20.6, 14.3; MS *m*/*z* (rel intensity) 110 (2, $M^+$), 95 (8), 81 (30), 69 (48), 53 (14), 41 (100), 39 (46).

**3-Ethylhexa-1,5-diene (8).**[15,24] Preparative GC (2.3-m, 20% ODPN on Chromosorb P-NAW, 50 °C) provided a 41-mg sample of dienes **7** and **9** (84:16), which was dissolved in 600 μL of pentane. The sample was injected into the kinetic bulb, heated at 275.1 ± 0.1 °C for 2 h, and removed from the bulb. The GC (DB-1301) trace showed peaks for 1,5-(*Z*)-octadiene (**7**, 8.9 min, 49%), a new component (**8**, 6.0 min, 7%), and 1,5-(*E*)-octadiene (**9**, 8.7 min, 44%). The new component was collected by preparative GC (2.3 m, 20% ODPN on Chromosorb P-NAW, 50 °C) and shown to be 3-ethylhexa-1,5-diene (**8**): $^1$H NMR δ 5.88−5.68 (m, 1 H), 5.65−5.48 (m, 1 H), 5.10−4.88 (m, 4 H), 2.22−1.81 (m, 3 H), 1.52−1.37 (m, 1 H), 1.35−1.17 (m, 1 H), 0.86 (t, $J$ = 7.4 Hz, 3 H) (compare ref 15); $^{13}$C NMR δ 142.5, 137.2, 115.5, 114.3, 45.4, 39.1, 26.9, 11.5 (compare ref 15); MS *m*/*z* (rel intensity) 95 (19), 81 (97), 79 (32), 69 (100), 68 (52), 67 (86), 53 (51), 41 (100), 39 (99), 27 (65).

**1,5-(*E*)-Octadiene (9).**[5,24] To a 50-mL flask were added propyltriphenylphosphonium bromide (1.29 g, 3.4 mmol) and THF (20 mL). The solution was cooled to −78 °C and 1.4 M MeLi (2.4 mL, 3.4 mmol) in ether was added dropwise. The mixture was warmed to 0 °C and stirred for 1 h. At that time the orange solution was cooled to −78 °C and 4-penten-1-al (0.27 g, 3.2 mmol) was added dropwise in THF (3 mL). The reaction mixture was stirred for 15 min at −78 °C and 1.4 M MeLi (2.4 mL, 3.4 mmol) in ether was then added dropwise.[16] The dark red solution was stirred for 40 min at −78 °C. At that time *tert*-butyl alcohol (0.47 g, 6.3 mmol) was added and the mixture was slowly warmed to room temperature. After 2 h at room temperature the mixture was quenched with 1 M HCl (20 mL) and the aqueous layer was extracted with pentane (3 × 20 mL). The organic layers were combined, dried ($Na_2SO_4$), filtered, and concentrated to give 0.28 g (80%) of 1,5-

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(*E*)-octadiene (**9**) and less than 5% of **7** as a 2% solution. A sample of the diene **9** was purified by preparative GC (2.3 m, 20% ODPN on Chromosorb P-NAW, 57 °C): $^1$H NMR $\delta$ 5.92−5.74 (m, 1 H), 5.56−5.33 (m, 2 H), 5.08−4.91 (m, 2 H), 2.21−1.94 (m, 6 H), 0.96 (t, $J$ = 7.4 Hz, 3 H) (compare ref 5); $^{13}$C NMR $\delta$ 138.6, 132.5, 128.4, 114.4, 33.9, 32.0, 25.6, 14.0; MS *m*/*z* (rel intensity) 110 (2, $M^+$), 95 (9), 81 (34), 69 (49), 53 (14), 41 (100), 39 (37).

**1,6-(*E*)-Octadiene (10).**[5,25,26] To a 100-mL flask were added PCC[14] (1.61 g, 7.5 mmol) and dry $CH_2Cl_2$ (25 mL). The 5-hexen-1-ol (0.5 g, 5.0 mmol) in $CH_2Cl_2$ (5 mL) was added dropwise to the PCC solution over 5 h. The oxidation and workup were conducted as detailed above for the preparation of 4-penten-1-al. The 5-hexen-1-al[27] obtained (0.46 g, 92%) as a 22% solution had MS *m*/*z* (rel intensity) 98 (1, $M^+$), 97 (4), 80 (60), 69 (23), 55 (51), 54 (100), 41 (79), 39 (93), 29 (45).

To a 100-mL flask were added ethyltriphenylphosphonium iodide (2.08 g, 5.0 mmol) and THF (20 mL). The solution was cooled to −78 °C and 1.4 M MeLi (3.6 mL, 5.0 mmol) was added dropwise. The reaction and workup were done as detailed above for the preparation of 1,5-(*E*)-octadiene. The diene **10** obtained amounted to 0.39 g (75%, *E*:*Z* 54:1, Ultra 2). A sample of **10** was purified by preparative GC (2.3 m, 20% ODPN on Chromosorb P-NAW, 50 °C): $^1$H NMR $\delta$ 5.90−5.72 (m, 1 H), 5.51−5.33 (m, 2 H), 5.06−4.88 (m, 2 H), 2.11−1.93 (m, 4 H), 1.72−1.58 (m, 3 H), 1.51−1.37 (m, 2 H) (compare ref 5 and 26); $^{13}$C NMR $\delta$ 138.9, 131.2, 125.0, 114.3, 33.2, 32.0, 28.8, 17.9; MS *m*/*z* (rel intensity) 110 (2, $M^+$), 95 (19), 81 (55), 68 (100), 67 (76), 55 (66), 41 (100), 39 (74).

**Thermal Reactions.** Racemic samples of trans and cis isomers **1** and **2** and nonracemic samples of (1*S*,2*S*)-*trans*-1-(*E*)-propenyl-2-methylcyclobutane (**1′**) and (1*S*,2*R*)-*cis*-1-(*E*)-propenyl-2-methylcyclobutane (**2′**)[9,10] were purified through two preparative GC separations, first on a ODPN column and then on an SE-30 column. Kinetic runs were carried out at 275.1 ± 0.1 °C in a 300-mL quartz bulb encased in a thermostated aluminum block.[1d] A Bailey Instruments Model 253 precision temperature controller, a calibrated HP Model 2802A digital thermometer, and a platinum resistance temperature probe (Omega Engineering, OSK5045 PR-11-3-100-1/8-6-E) were employed. The bulb was conditioned before use with a 100-$\mu$L sample of cyclohexene at 275.1 °C for 24 h.

Prior to each thermal reaction, the bulb was evacuated to less than $2.5 \times 10^{-2}$ Torr. The solution of substrate, pentane, and cyclooctane was injected into the bulb through a septum with a 2-mL Pressure-Loc gastight syringe (Precision Sampling Corporation) fitted with a 9-in. needle. When the time period planned for a kinetic run was over, the contents of the kinetic bulb were transferred to a vacuum line and condensed into a liquid nitrogen cooled U-tube. The product mixture was analyzed twice by GC (DB-1301, 40 °C for 20 min, increased 15 °C/min to 150 °C). The data for two analyses for each run were tabulated and averaged (Tables 1−4).

**Thermal Stability of *cis*-3,4-Dimethylcyclohexene (4).** A 8.1-mg sample of *cis*-3,4-dimethylcyclohexene (**4**) was purified by preparative GC (2.3 m, 20% ODPN on Chromosorb P-NAW, 55 °C). The sample of **4** was dissolved in pentane (1.6 mL) and cyclooctane (4 mg) was added as an internal standard. A 500-$\mu$L sample of this solution was injected into the bulb and heated at 275.3 ±0.1 °C for 20 h. The thermal reaction mixture showed no evidence of decomposition or isomerization when analyzed by GC (DB-1301).

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**Supporting Information Available:** Proton and carbon-13 NMR spectra for $C_8H_{14}$ isomers **7**, **8**, **9**, and **10**, and two analytical gas chromatograms of thermal reaction mixtures derived from **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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