# Orbital Overlap Constraints in the Thermal Rearrangement of 3,7-Dimethylenetricyclo[4.1.0.0$^{2,4}$]heptane Derivatives

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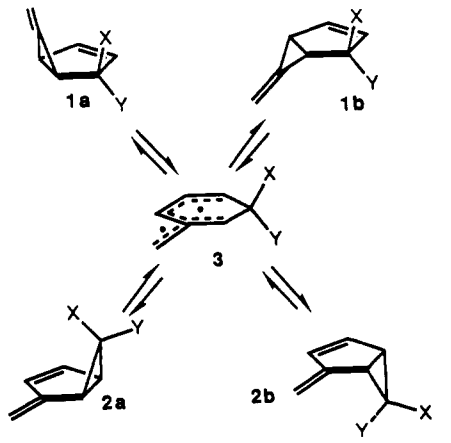
**Abstract:** The thermal rearrangements of the 1-ethyl- and 1-phenyl-3,7-dimethylenetricyclo[4.1.0.0$^{2,4}$]heptanes **4-Et** and **4-Ph** to the corresponding 3-substituted 2,5-dimethylenebicyclo[4.1.0]hept-3-enes **5-Et** and **5-Ph** have been examined. Pyrolysis of **4-Et** over the temperature range 132.0–180.0 °C affords **5-Et** as the only product in a first-order, gas-phase reaction with $E_a$ = 35.9 ± 0.8 kcal/mol and log $A$ = 13.9 ± 0.4. Pyrolysis of **4-Ph** in solution over the range 92.0–140.0 °C likewise gives only **5-Ph** with the activation parameters $E_a$ = 30.2 ± 0.6 kcal/mol and log $A$ = 12.6 ± 0.4. Thermolysis of optically active **4-Et**, analyzed by chiral capillary gas chromatography, results in formation of partially racemized **5-Et** as well as slight racemization of starting material. In contrast, optically enriched **4-Ph** provides **5-Ph** with only a small decrease in optical activity, with recovered **4-Ph** also showing a slight loss of ee. Independent racemization of the product **5-Et** was shown not to intrude on the analysis. The predominant mechanism in the **4-Et** case is taken to result from competitive initial openings of the two reactant methylenecyclopropane (MCP) rings. Separate reaction pathways proceed from these two initial events stereospecifically toward the two product enantiomers, largely avoiding the planar, fully opened vinylogous tetramethylethylene (TME) biradical **6**. Study over the temperature range 115.0–208.0 °C provides the value of $\Delta\Delta H^{\ddagger}$ = 970 ± 130 cal/mol for these two pathways. For compound **5-Ph** derived from **4-Ph**, racemization is relatively temperature-independent over the range 75.0–165.0 °C, with the measured $\Delta\Delta H^{\ddagger}$ = −2.4 ± 3.0 cal/mol and $\Delta\Delta S^{\ddagger}$ = 13 ± 7.8 eu, indicating that a different mechanism is in operation. The competition between initial ring homolyses results in a complete shunting of the reaction onto the lower energy pathway, due to the strong biradical-stabilizing effect of the phenyl group. From this pathway, a few percent of the overall reaction leaks over to the stereorandomizing TME biradical **6-Ph**, resulting in a slight loss of ee in the product.

Thermal rearrangements of 6-methylenebicyclo[3.1.0]hex-2-ene derivatives (**1**) to 2-methylenebicyclo[3.1.0]hex-3-enes (**2**, Scheme I) provide rare examples of reaction pathways in which the symmetry of a metastable intermediate (e.g., **3**), free of conformational memory or dynamical constraints, completely determines the stereochemical outcome.[1] Species **3** is either truly symmetrical (achiral if X = Y) or quasisymmetrical (if X ≠ Y), and the product is, respectively, either an exactly equimolar mixture of enantiomers from enantiomerically enriched reactant or an identical common mixture of diastereomers from either diastereomeric reactant. Such complete reaction symmetrization had not been detected in previous thermal reactions putatively involving biradical intermediates. Hypothetically,[1] it is the increased stability of the vinyltrimethylenemethane (VTMM) biradical **3** that facilitates the detection of the intermediate by depositing it in a deeper energy well than those of the prior cases.

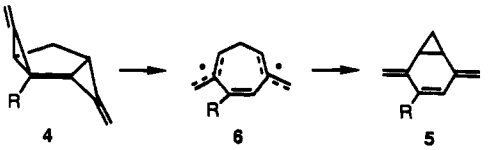
These observations raise several new issues, one of which we examine here: Is stability of the biradical intermediate a sufficient property to ensure reaction symmetrization? Or can other factors, such as orbital overlap constraints, permit the reacting molecules to skirt even a deep energy minimum and thereby escape symmetrization?

**Experimental Design.** To test these questions, we have used the title tricyclic system **4** bearing either an ethyl[2] or a phenyl group at $C_1$ (Scheme II). These substituents serve two purposes: to break the symmetry of the unsubstituted product **5**, thereby rendering it chiral, and to provide a test of the effect of benzylic conjugation by a comparison of the rates and products in the two cases. We reasoned that pyrolysis of the tricycle **4** would cleave both of the 2,2′-linked linked methylenecyclopropane rings at the bridge bond sites, thus potentially generating the hypothetical biradical intermediate **6**, a vinylogous tetramethyleneethane (TME). Hypothetically, ring-closure by bond formation at two

**Scheme I**




**Scheme II**




**Et:** R = Et
**Ph:** R = Ph

of the radical sites of **6** would give the rearrangement product **5** (Scheme II).

The **4** → **6** reaction differs from the reaction **1** → **3** both in the energetic relationships of the points on its potential surface and in the geometric relationships of the breaking bond orbitals. In particular, the energy drop from the transition state to intermediate **6** (**Et** or **Ph**) is even deeper than that to intermediate **3** (see the Discussion section), but the overlap of the orbitals of the two cyclopropane rings of reactant **4**, the potential precursor of **6**, is not as well suited to conjugative interaction during bond-breaking as is that of the cyclopropane ring orbital and the en-

(1) (a) Pikulin, S.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 8274; **1988**, *110*, 8500. (b) Berson, J. A. *Chemtracts: Org. Chem.* **1989**, *2*, 213. (c) Pikulin, S. Ph.D. Dissertation, Yale University, 1986.

(2) (a) Reasons for the choice of the ethyl group instead of simpler substituents such as deuterium or methyl are given in ref 2b, which also lists unsuccessful attempts to synthesize a 1-methyl derivative of **4** by coupling chemistry. (b) Wendt, M. D. Ph.D. Dissertation, Yale University, 1992, pp 55ff.

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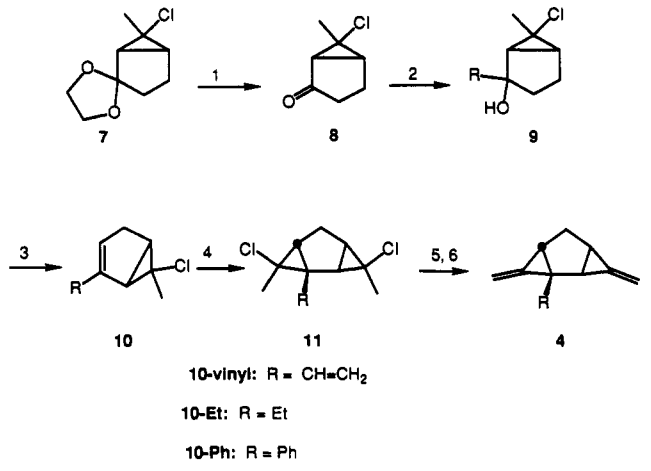
**Scheme III**[a]




[a] Methods: (1) aqueous $H_2SO_4$, THF; (2) RMgBr; (3) $Et_3NSO_2NCO_2Me$; (4) $CH_3CHCl_2$, BuLi; (5) when R = Ph; KOH, DMSO, 18-crown-6; (6) when R = CH=$CH_2$: $H_2$, Pd/C, then KOH, DMSO, 18-crown-6.

docyclic double bond of **1**, the precursor of **3**. The first phase of this study[3] develops the synthesis of the reactants **4-Et** and **4-Ph** and demonstrates the occurrence and kinetics of their thermal rearrangements to **5-Et** and **5-Ph**, respectively. The second phase makes use of the achiral nature of the hypothetical intermediates **6-Et** and **6-Ph** to test for their intervention in the rearrangements of the chiral and enantiomerically enriched reactants **4-Et** and **4-Ph**.

## Results

**Synthesis of 4-Et and 4-Ph.** Scheme III shows the methods by which the common starting material, the known[1c,4] bicyclic chloroketal **7** (a 9:1 mixture of $C_6$ epimers), was hydrolyzed[4c] to the ketone **8** and thence converted to the desired test compounds **4-Et** and **4-Ph**. The synthesis of the ethyl compound **4-Et** used a slightly indirect approach because there was reason[2] to expect that attempts to follow exactly the sequence of steps worked out in the synthesis of the phenyl compound **4-Ph** (see below) would lead to difficulty in the dehydration step. Accordingly, we first prepared the allylic alcohol **9-vinyl** by addition of vinylmagnesium bromide to the chloroketone **8**. Dehydration of **9-vinyl** with Burgess's reagent, $Et_3NSO_2NCO_2Me$,[5] gave the diene **10-vinyl** in yields of about 30%, along with some 3-vinyltoluene and 3-acetyl-1-vinylcyclopent-1-ene. The subsequent carbenic 1-methyl-1-chlorocyclopropanation of **10-vinyl** by 1,1-dichloroethane and BuLi proved highly regioselective for the ring double bond, even though seven equivalents of carbene precursor were used to complete the conversion. The reaction produced a mixture (~1:1) of exo and endo $C_2$ isomeric tricyclic dichlorides. Hydrogenation gave the ethyl compound **11-Et**, and dehydrochlorination and purification steps completed the synthesis of **4-Et**. The cyclopropane rings must be fused anti, since a syn fused structure does not have enough space to accommodate any pairing (Cl + Me, Cl + Cl, or Me + Me) of the two endo substituents of **11-Et** (or **11-Ph**).

The tertiary benzylic alcohol **9-Ph**, obtained upon treatment of **8** with phenyllithium or phenylmagnesium bromide, did not respond satisfactorily to typical methods ($SOCl_2$/pyridine, $CH_3SO_2Cl$/diazabicycloundecane, alkane- or arenesulfonic acids, etc.) of dehydration. The best yields in this series of experiments (~20%) were obtained with $SOCl_2$/pyridine. Finally Burgess's reagent proved effective, giving the phenyl-substituted chlorocycloalkene **10-Ph** in about 60% yield. Cyclopropanation by methyl chlorocarbene addition in ether solution gave an approximately 1:1 mixture of $C_7$ epimers of the tricyclic dichloride **11-Ph**. The double dehydrochlorination step (**11-Ph** → **4-Ph**) again was troublesome. After testing several combinations of strong bases in polar solvents, we obtained the desired hydrocarbon **4-Ph**, although only in yields of 10–30%, with KOH/dimethyl sulfoxide/18-crown-6. The dominant side products were 3-phenyltoluene and small amounts of 4-ethyl-3-phenyltoluene. Although **4-Ph** was too unstable to be purified by preparative gas chromatography and did not separate from the side products upon conventional column chromatography, we were able to purify it by column chromatography on 10% silver nitrate on silica gel.

**Products and Kinetics of Pyrolyses of 4-Et and 4-Ph.** Flash vacuum pyrolysis of the ethyl-substituted tricyclic compound **4-Et** at 400 °C and $10^{-4}$ Torr gave the rearranged triene 2,5-dimethylene-3-ethylbicyclo[4.1.0]hept-3-ene, **5-Et**, characterized by $^1H$ NMR, $^{13}C$ NMR, and high-resolution mass spectroscopy, as the only product (Scheme II). Similarly, the phenyl derivative **4-Ph** at 475 °C and $5 \times 10^{-5}$ Torr gave **5-Ph** as the only product. In static pyrolyses, both rearranged triene products gradually polymerized upon prolonged heating.

In sealed, carefully degassed Pyrex ampules, the ethyl compound **4-Et** rearranged in the gas phase to **5-Et** with high material balance and clean first-order kinetics. From the linear dependence ($r$ = 1.00) of the rate constants on reciprocal temperature (seven temperatures over the range 405–453 K, 132–180 °C), we derived the activation parameters $E_a$ = 35.9 ± 0.8 kcal/mol, log ($A$ in $s^{-1}$) = 13.9 ± 0.4, $\Delta S^{\ddagger}$ = 2.4 ± 1.8 eu. The activation energy is slightly lower than the normal range of values for methylenecyclopropane rearrangements (40–42 kcal/mol),[6] as might be expected from the extra strain energy of **4-Et**. The increment of strain energy in bicyclo[3.1.0]hexane over that of cyclopropane (32.7 vs 27.6 kcal/mol)[7] provides an estimate of the magnitude of this effect. As the entropy of activation is small, its positive sign is plausibly attributed to the loosening of some vibrations in the transition state.

The rate of rearrangement of the ethyl compound **4-Et** in nonane solution at 140 and 170 °C was only slightly faster than that in the gas phase, by factors of 2.2 and 1.8, respectively.

To obtain comparable kinetic data for **4-Ph**, we first attempted static pyrolyses in the gas phase, but in both base-washed silanized Pyrex and lead glass ampules, the derived Arrhenius parameters both were anomalously low: $E_a$ = 21.6 kcal/mol, log ($A$ in $s^{-1}$) = 7.6. These results suggested the incursion of a surface-catalyzed reaction. In undecane solution, however, more plausible results were obtained: $E_a$ = 30.2 ± 0.6 kcal/mol, log ($A$ in $s^{-1}$) = 12.6 ($\Delta S^{\ddagger}$ = −3.3 ± 1.7 eu). The solution-phase pyrolyses also gave triene **5-Ph** as the only product.

The kinetic studies show that the enthalpy and entropy of activation in the phenyl series **4-Ph** are, respectively, 5.7 ± 1.0 kcal/mol and 5.7 ± 2.5 eu lower than those in the ethyl series **4-Et**. Benzylic stabilization of the transition state from **4-Ph**, and the associated restriction of internal rotation about the carbon-phenyl bond to achieve it, plausibly account for these decrements.

**Preparation and Analysis of Enantiomerically Enriched Reactants 4-Et and 4-Ph.** Enantiomerically enriched samples of the bicyclic chloro ketone **8**, prepared by the methods previously described,[1] were carried through the synthetic steps of Scheme III. (+)-Ketone **8** led, in the phenyl series, to the hydrocarbon **4-Ph**, which was analyzed with a 2,3,6-tri-*O*-methyl-β-cyclodextrin (10% in OV-1701) fused silica capillary gas chromatography (GC)

(3) (a) Preliminary communication: Wendt, M. D.; Berson, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 4675. (b) Correction: *J. Am. Chem. Soc.* **1991**, *113*, 7827. (c) Another example of rearrangement of a 2,2'-linked bis(methylenecyclopropane) has since been reported: Snellings, K. J.; Lewis, E. S. *J. Org. Chem.* **1992**, *57*, 4315.

(4) (a) Rule, M.; Matlin, A. R.; Dougherty, D. A.; Hilinski, E. F.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098. (b) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787. (c) Matlin, A. R., Ph.D. Thesis, Yale University, 1982.

(5) Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A. *J. Org. Chem.* **1973**, *38*, 26. We thank Professor S. L. Schreiber for calling our attention to this reagent.

(6) (a) Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Essay 5. (b) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981.

(7) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978; pp 66, 72.

**Table I.** Rearrangement of Enantiomerically Enriched **4-Et** to **5-Et**

| temp (°C) | %ee ret in **5-Et** | $k_1/k_2$ | ln $k_1/k_2$ |
|---|---|---|---|
| 115.0 | 54.89 ± 0.76 | 3.434 ± 0.074 | 1.234 ± 0.021 |
| 140.3 | 53.46 ± 1.34 | 3.297 ± 0.124 | 1.193 ± 0.038 |
| 159.7 | 51.32 ± 2.16 | 3.109 ± 0.184 | 1.134 ± 0.058 |
| 177.0 | 49.46 ± 0.77 | 2.957 ± 0.060 | 1.084 ± 0.020 |
| 195.6 | 47.59 ± 0.67 | 2.816 ± 0.049 | 1.035 ± 0.018 |
| 208.0 | 45.96 ± 1.39 | 2.701 ± 0.095 | 0.994 ± 0.034 |

$y = -0.0096 + 490x$ $R = 0.976$

$\Delta\Delta H^{\ddagger} = 970 \pm 130$ cal/mol $\Delta\Delta S^{\ddagger} = -0.02 \pm 0.29$ eu

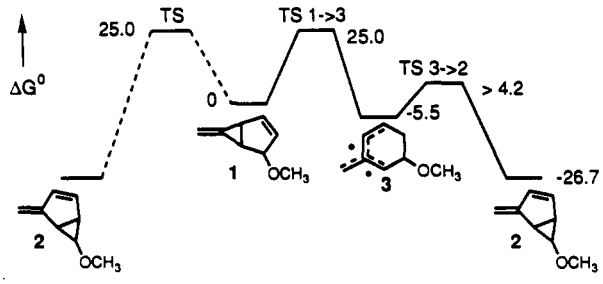



**Figure 1.** Free energy vs reaction coordinate diagram for the thermal rearrangement at 353 K of 2-methoxy-6-methylenebicyclo[3.1.0]hex-3-ene (**1**) to 2-methylene-6-methoxybicyclo[3.1.0]hex-3-ene (**2**). The full line represents the mechanism passing through the metastable intermediate **3**, consistent with the experimental findings.[1] The dashed line represents a hypothetical pathway not involving **3**. The $\Delta G^0$ values are in kcal/mol.

column.[8] The phenyl derivative **4-Ph** was enriched in the later-emergent enantiomer to the extent of 70% enantiomeric excess (ee). Similarly, enriched samples of (+)-**8** and (−)-**8** were converted, respectively, to **4-Et**, ee = 85.6%, enriched in the later-emergent enantiomer, and **4-Et**, ee = 79.2%, enriched in the earlier-emergent enantiomer. The absolute configurations of the reactants **4-Et** and **4-Ph** and the products **5-Et** and **5-Ph** are not known, but they are not necessary for the conclusions of this paper.

**Stereochemistry of the Thermal Rearrangement of the Ethyl Compound 4-Et.** Gas-phase pyrolyses of either enantiomer of **4-Et** gave nonracemic samples of the rearrangement product **5-Et**, whose composition was determined with the same enantiospecific chiral capillary GC column. Experiments at six temperatures over the range 115.0–208.0 °C showed that the preservation of the initial ee of **4-Et** in the product **5-Et** varied monotonically from 46.8 to 35.3%. A small but definite amount of the loss of ee in the rearrangement was caused by a competing racemization (rate constant $k_{rac}$) of the reactant **4-Et**, which became most noticeable at higher temperatures. At 195.6 °C, for example, **4-Et** had lost about 17% of its original ee after 4.3 half-lives of conversion to **5-Et**. By application of the method of Winstein and Trifan (see the supplementary material),[9] we calculated the effective ee of the reactant during each run and obtained thereby ee values of the product **5-Et** formed from unracemized reactant. These are most easily discussed in the form of a set of ratios, $k_1/k_2$, the ratio of rate constants for rearrangement through the pathways leading to the, respectively, more and less favored product enantiomers. Table I shows these values ($k_1/k_2$, is about 3:1 at the midpoint of the temperature range) and their temperature-dependence, from which the differences in activation parameters can be determined: $\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_1 = \Delta\Delta H^{\ddagger} = 970 \pm 130$ cal/mol, $\Delta\Delta S^{\ddagger} = \Delta S^{\ddagger}_1 - \Delta S^{\ddagger}_2 = -0.02 \pm 0.29$ eu.[10]

In the ethyl series **4-Et**, the ratio, $(k_1 + k_2)/k_{rac}$, of rearrangement to reactant racemization rate constants was about 20:1 and did not vary much with temperature.

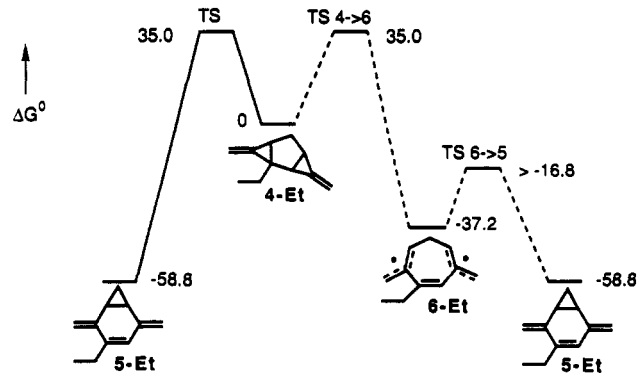



**Figure 2.** Free energy vs reaction coordinate diagram for the thermal rearrangement at 473 K of 1-ethyl-3,7-dimethylenetricyclo[4.1.0.0$^{2,4}$]-heptane (**4-Et**) to 2-ethyl-1,4-dimethylenebicyclo[4.1.0]hept-2-ene (**5-Et**). The full line represents a mechanism that does not pass through the metastable intermediate **6-Et**, consistent with the experimental findings of the present work. The dashed line represents a hypothetical pathway involving **6-Et** as an intermediate. The $\Delta G^0$ values are in kcal/mol.

**Table II.** Rearrangement of Enantiomerically Enriched **4-Ph** to **5-Ph**

| temp (°C) | %ee ret in **5-Ph** | $k_1/k_2$ | ln $(k_1/k_2)$ |
|---|---|---|---|
| 75.0 | 89.06 ± 1.48 | 17.3 ± 2.5 | 2.85 ± 0.15 |
| 95.0 | 93.35 ± 1.30 | 29.1 ± 6.1 | 3.37 ± 0.21 |
| 145.0 | 95.51 ± 1.13 | 43.5 ± 12.0 | 3.77 ± 0.28 |
| 165.0 | 94.59 ± 1.12 | 36.0 ± 8.0 | 3.53 ± 0.23 |

$y = 6.5 - 1207x$ $R = 0.727$

$\Delta\Delta H^{\ddagger} = -2.4 \pm 3.0$ kcal/mol $\Delta\Delta S^{\ddagger} = 13.0 \pm 7.8$ eu

Although product **5-Et** is stereochemically stable under the conditions used to determine the results of Table I, it did slowly racemize upon longer heating or at higher temperatures, plausibly by passage through achiral biradical **6-Et**. Attempts to place the energy of **6-Et** on the reaction coordinate diagram by determination of the Arrhenius parameters of this racemization were unsuccessful because the incursion of surface effects made the kinetic measurements of uncertain significance. The data do permit the conclusion that the activation energy for racemization of **5-Et** is at least 42 kcal/mol (See Figure 2).

In anticipation of further discussion, we briefly indicate here that the results in the ethyl series **4-Et** → **5-Et** show that the hypothetical equilibrated achiral biradical intermediate **6-Et**, with both bridge bonds open, cannot be on the dominant pathway of rearrangement. One of the simplest interpretations of the $k_1/k_2$ ratio is as a measure of the competition between reactions initiated by the opening of one or the other of the two nonequivalent bridge bonds. Comparison with numerous cases in the literature[6,11,12] suggests that the activation energy for reaction at the ethyl-substituted bridge bond might be lower than that at the unsubstituted bond by roughly as much as 3 kcal/mol.

With the more strongly conjugating phenyl group (as in **4-Ph**) in place of ethyl, we already have shown that the overall activation energy is lowered relative to the ethyl case **4-Et** by 5.7 kcal/mol. Consequently, the competition ratio $k_1/k_2$ should increase, since the preference for reaction at the substituted bond should be greater. If the entire 5.7 kcal/mol energy effect were to appear in the $\Delta\Delta G^{\ddagger}$ for the competitive pathways, the $k_1/k_2$ ratio should increase from about 3:1 for **4-Et** → **5-Et** to about 6300:1 for **4-Ph** → **5-Ph**. Given the experimental error of about 1% in the GC analyses, this should manifest itself in a retention of enantiomeric purity indetectably different from 100% in the latter case.

In an experimental test of this prediction, we pyrolyzed undecane solutions of the enantiomerically enriched phenyl derivative

(8) (a) Schurig, V.; Nowotny, H.-P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 939. (b) Nowotny, H.-P.; Schmalzing, D.; Wistuba, D.; Schurig, V. *J. High Res. Chrom.* **1989**, *12*, 383.

(9) Winstein, S.; Trifan, D. *J. Am. Chem. Soc.* **1952**, *74*, 1154.

(10) The slightly different value $\Delta\Delta H^{\ddagger} = 1120 \pm 230$ cal/mol given in our preliminary communication[3a] was derived from ee data uncorrected for prior racemization of reactant **4-Et**.

(11) (a) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976. (b) Benson, S. W.; O'Neal, H. E. *Kinetic Data on Gas Phase Unimolecular Reactions*; NSRDS-NBS 21. U.S. Department of Commerce, Washington, D.C., 1970. (c) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 125.

(12) LeFevre, G. N.; Crawford, R. J. *J. Org. Chem.* **1986**, *51*, 747.

**4-Ph**. Again, some racemization of the reactant **4-Ph** was observed, although it was less than that in the case of **4-Et**. The ratio of rearrangement to reactant racemization rates for **4-Ph**, $(k_1 + k_2)/k_{rac}$, was 45:1. As predicted, the degree of preservation of the original reactant **4-Ph** ee in the product **5-Ph** *was* much higher than in the **4-Et** case. Corrected for the competing racemization of the reactant **4-Ph** by the same procedure used for **4-Et**, rearrangement gave product **5-Ph** with ee values that were essentially independent of pyrolysis time or extent of conversion. Because of the difficulty of analysis for the small amount of the minor product enantiomer, the temperature-dependence of the ee value was difficult to determine accurately (see Table II). The ee retained in product **5-Ph** ranged between 89.1 and 95.5%. Whether the values are meaningfully lower than 100% may be judged from the average of these measurements, 93.2 ± 2.1%, which differs from that hypothetical value by $3.24\sigma$. If the errors of measurement are random, the statistical probability that the average ee value is really different from 100% is 0.997. We are not aware of any obvious systematic error, and therefore we interpret the ee values as indicative of a small but real, nearly temperature-independent loss of ee in the **4-Ph** → **5-Ph** rearrangement. We note that the $k_1/k_2$ value of about 14:1 is far lower than the value of 6300 predicted on the above simple basis.

The data of the phenyl series suffer from more scatter than those in the ethyl series. Nevertheless, there appear to be real qualitative differences. In contrast to the ethyl series, where the stereospecificity of the **4-Et** → **5-Et** rearrangement increases with decreasing temperature (positive $\Delta\Delta H^{\ddagger}$, near-zero $\Delta\Delta S^{\ddagger}$), the stereospecificity in the phenyl series, to the extent that there is any variation at all, actually *decreases* with decreasing temperature (zero or slightly negative $\Delta\Delta H^{\ddagger}$, positive $\Delta\Delta S^{\ddagger}$). This behavior again is inconsistent with the simple prediction of an enthalpy-determined change in the competition between reactions at the substituted and unsubstituted bridge bonds of the tricyclic reactants.

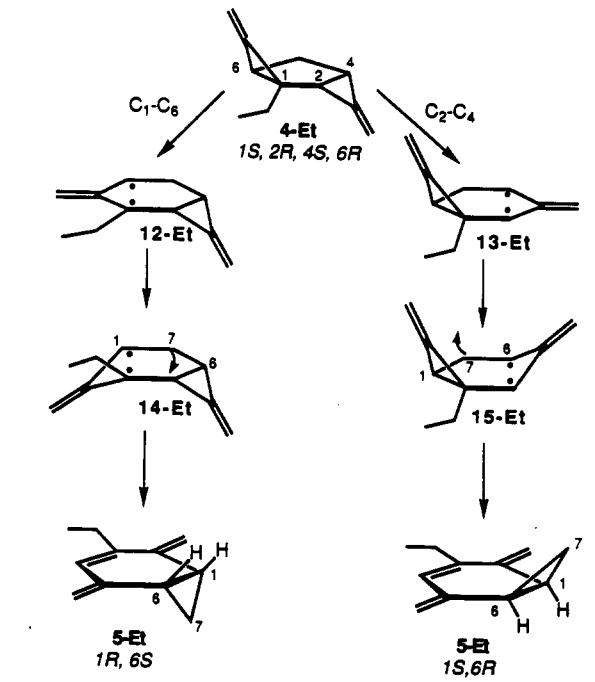
Thus, although the change of an ethyl to a phenyl group increases the rate and the stereospecificity, as predicted, the detailed data require a more subtle mechanistic rationalization than that given so far.

## Discussion

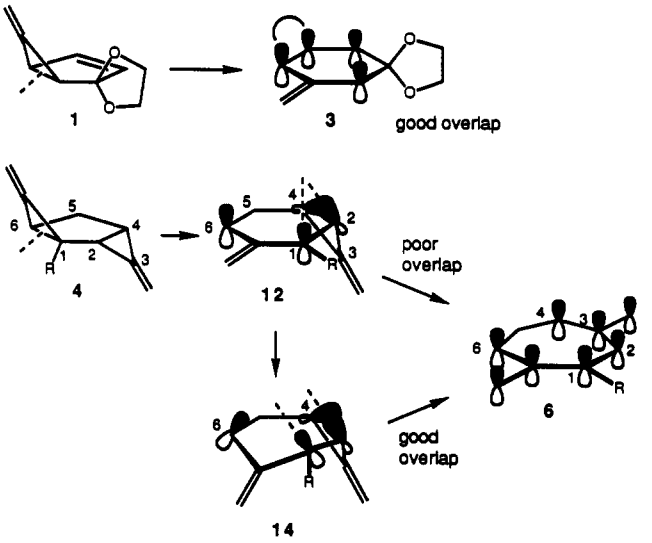
Figures 1 and 2 show the rationale of the experimental design. Free energies of the reactant **4-Et**, hypothetical intermediate **6-Et**, and product **5-Et** were calculated from Benson group equivalents (supplementary material, Table S-24). The entropy contributions are substantial. For example, the $\Delta G°$ of −37.1 kcal/mol for **4-Et** → **6-Et** consists of $\Delta H°$ and $-T\Delta S°$ terms of −13.7 and −23.4 kcal/mol, respectively. Free energies of transition states were calculated by the addition of activation energies, determined by kinetic measurements as already described in the text, to the free energy of the relevant reactant. The figures show that intermediate **3-OCH$_3$** (Figure 1) is flanked by energy barriers of 9.7 and 30.5 kcal/mol, whereas intermediate **6-Et** (Figure 2) lies in a deeper well whose sides are 20.4 and 72.2 kcal/mol. In the present work, the preservation of a substantial portion of the ee of the tricyclic reactants **4-Et** and **4-Ph** in the rearrangement products **5-Et** and **5-Ph** is in clear contrast to the complete reaction symmetrization observed[1] in the thermal rearrangements of the system **1**. Thus, to a significant degree, the deeper energy well constructed for the hypothetical achiral intermediate **6-Et** has failed to ensnare reactant molecules on their pathways to rearrangement product **5-Et**. Obviously, the question of whether stability of the biradical intermediate is a sufficient property to ensure reaction symmetrization now must be answered in the negative.

**Mechanism of the 4-Et → 5-Et Rearrangement.** The most economical representation of the rearrangement in the ethyl series is shown in Scheme IV. Homolysis of either of the bridge bonds $C_1$–$C_6$ or $C_2$–$C_4$ is imagined to lead to a biradical **12** or **13**, respectively. In the biradicals, the orbitals of the remaining intact bridge bonds $C_2$–$C_4$ or $C_1$–$C_6$ are not in good position to overlap with the trimethylenemethane (TMM) $\pi$-orbitals (see Scheme V). Continuation of the atomic motion that led to **12** or **13** will pyramidalize the endocyclic radical sites and generate **14** and **15**,

Scheme IV




Scheme V



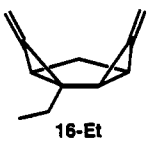

respectively. In the latter species, the necessary orbital overlap is much better than in **12** and **13**. Structures **12**–**15** are not necessarily true intermediates occupying local energy minima. In particular, the acts of pyramidalization symbolized by **12** → **14** and **13** → **15** are necessary for and may occur at the same time as the ultimate $C_1$–$C_6$ bond formation in the product. To maximize orbital overlap during product formation, ring-closure at $C_1$–$C_6$ (bicyclo[4.1.0]heptane numbering) requires that $C_7$ move downward in **14** and upward in **15**. In the mechanism of Scheme IV, it is the competition between the two initial bond-cleavage steps that determines the relative amounts of the enantiomeric forms of the rearrangement product **5-Et**. If we are correct in our conjecture that the substituted bridge bond will be the more reactive one, the pathway initiated by $C_1$–$C_6$ ring-cleavage should be preferred. This would predict a predominance of (1*R*,6*S*)-**5-Et** product from the pyrolysis of (1*S*,2*R*,4*S*,6*R*)-**4-Et** (Scheme IV).

Superficially, cleavage of the weak methylenecyclopropane bridge bond of **12** or **13** to generate the achiral biradical **6** would seem to be an easy reaction, but the experimental results make clear that this pathway is not favored. This reluctance makes a striking contrast to the stereochemistry of the **1** → **2** rearrangement (Scheme I), in which the formation of the achiral biradical

3 dominates the mechanism.[1] Why does achiral biradical 6 not dominate the rearrangement of 4? Scheme V rationalizes the difference. Opening of the bridge bond of 1 leads directly to the achiral intermediate 3 because the endocyclic double bond orbitals come into accurate conjugative alignment with those of the developing TMM unit as soon as the two bridgehead carbons achieve planar configurations. However, the corresponding cleavage of the $C_1$–$C_6$ bridge bond of 4 leads to 12, in which the basis orbitals of the surviving $C_2$–$C_4$ bridge bond overlap poorly with those of the TMM unit. Only after pyramidalization has converted 12 to 14 would the orbitals fated to form the endocyclic $\pi$-bond of 6 achieve the necessary overlap, at which point opening of $C_2$–$C_4$ to form 6 would find itself in competition with the faster closure at $C_4$–$C_6$ to form the cyclopropane ring of product 5.

Of course, the experimental data do not permit us to exclude 6 entirely as a participant in the rearrangement. The overall stereochemical result in the ethyl series, partial racemization of product 5-Et, which we have interpreted in the minimally complex mechanism of Scheme IV as a competition between two stereospecific pathways, also could be achieved by a competition between one (or two) stereospecific pathway(s) and a stereorandomizing pathway through achiral biradical 6. To the extent that such a stereorandomizing pathway contributes, the $\Delta\Delta H^{\ddagger}$ between the competing stereospecific pathways will be higher than that measured by the temperature-dependence studies.

Similarly, we are unable to specify the extent to which compound 16-Et, the (unknown) syn tricyclic isomer of 4-Et, may be involved. Because of its substantial additional strain energy and better orbital overlap, 16-Et should rearrange much faster[13] than 4-Et and therefore should not accumulate during the rearrangement of the latter. Therefore, no mechanistic significance can be attributed to the absence of 16-Et from the pyrolysis products of 4-Et. Compound 16-Et probably would undergo rearrangement to product 5-Et through intermediates similar to those from 4-Et and therefore would serve only as a temporary mechanistic shunt.

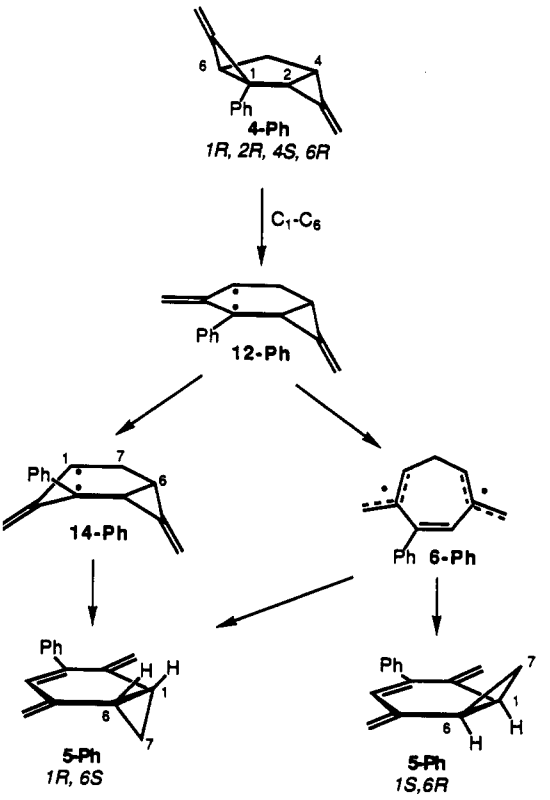


16-Et

A subtle ambiguity about the rearrangements of Scheme IV remains: Are these concerted reactions? Although both pathways from 4-Et to the enantiomers of 5-Et are orbital symmetry forbidden ($_{\sigma}2_s + {}_{\sigma}2_s$) processes,[14] it is possible that the biradical species 12–15 are not true intermediates but rather only points on a flat energy surface in the transition region. Whether the reaction then deserves the name "concerted" becomes almost a matter of definition. On the other hand, if, for example, 14-Et and 15-Et are considered to lie in local energy minima, their cyclization reactions to 5-Et would be properly viewed as additions of a biradical to a formal $\sigma$ bond.

**Mechanism of the 4-Ph → 5-Ph Rearrangement.** For reasons already given, a direct application of the competitive ring-cleavage model outlined in Scheme IV for the ethyl analog would predict essentially complete preservation of ee in the rearrangement of 4-Ph to 5-Ph. It seems likely that this accounts for about 93% of the reaction but that about 7% comes from a different pathway. In Scheme VI, we suggest that in the initial act of cleavage, the phenyl-substituted bond $C_1$–$C_6$ participates to the virtual exclusion of the $C_2$–$C_4$ bond, as expected, but bifurcation of the reaction path occurs *after* the rate-determining step. Part of the reaction continues as in the 4-Et case via pyramidalization of the initial biradical 12-Ph to biradical 14-Ph, followed by ring-closure of 14-Ph to give the predominant isomer of the rearrangement

Scheme VI




product 5-Ph. In the minor part of the reaction, we imagine that some of the initial biradicals 12-Ph are diverted by cleavage of the second bridge bond (at $C_2$–$C_4$) to the achiral monocyclic biradical 6-Ph, which cyclizes to give equal amounts of the two enantiomers of 5-Ph.

In this interpretation, the major visible difference in behavior between the 4-Et and 4-Ph systems is the leakage of the 12-Ph biradical to the achiral vinylogous TME biradical 6-Ph. As we already have indicated, the stereochemical data alone cannot exclude the analogous process as part of the mechanism of the rearrangement of 4-Et. However, the temperature-dependence of the 5-Et enantiomeric product ratios suggests that an ordinary enthalpic competition between the bond-breaking sites largely determines the stereospecificity. A small contribution from the leakage mechanism would not perceptibly affect the observed temperature-dependence. On the other hand, in the 4-Ph case, the preference in the bond-cleavage competition is so overwhelming that any changes with temperature still leave the competition ratio "off-scale" and hence experimentally invariant. All of the observed temperature-dependence arises from the small portion of the reaction that leaks into the achiral channel through 6-Ph.

There remains the question of whether the 12-Ph → 6-Ph reaction should compete against 12-Ph → 14-Ph (Scheme VI) more effectively than the 12-Et → 6-Et reaction does against 12-Et → 14-Et. Among several (presently untestable) hypotheses that come to mind, we mention one which is related to some of Carpenter's ideas[15] on dynamic factors in thermal reaction mechanisms. Consider the sequence of "reactions" shown in Schemes IV and VI as 4 → 12 → 14 and imagine that 12 resides in an energy well. Because of the conjugative effect of the phenyl group, this well should be deeper for 12-Ph than for 12-Et. Dynamical motion would tend to carry the C=$CH_2$ group through the planar configuration of the TMM unit in 12 toward the pyramidalized configuration of 14 in both the ethyl and phenyl cases, but the deeper well at 12-Ph would act as a more efficient trap and thereby

(13) Compare the reaction temperatures of 290 and 380 °C, respectively, for the rearrangements of *syn*- and *anti*-tricyclo[4.1.0.0$^{2,4}$]heptanes to bicyclo[4.1.0]hept-3-ene: Grimme, W., unpublished work. Cited by: Doering, W. v. E.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 115.

(14) Our earlier reference to these as allowed ($_{\sigma}2_s + {}_{\sigma}2_s$) reactions[3a] was incorrect.[3b] We thank Professor R. S. Sheridan for calling this to our attention.

(15) (a) Newman-Evans, R. H.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 7994. (b) Newman-Evans, R. H.; Simon, R. J.; Carpenter, B. K. *J. Org. Chem.* **1990**, *55*, 695.

diminish the relative importance of the momentum-favored **14-Ph**-forming process. This would offer a better opportunity for the diversion to an achiral species **6-Ph**. If this analysis is correct, little of any of the reaction passes through the achiral intermediate **6-Et** in the ethyl system.

## Conclusions

Pyrolysis reactions of 1-substituted-3,7-dimethylenetricyclo-[4.1.0.0$^{2,4}$]heptanes **4-Et** and **4-Ph** lead cleanly to the 3-substituted-2,5-dimethylenebicyclo[4.1.0]hept-3-enes. The activation parameters determined from the kinetics of these rearrangements are in accord with the formation of TMM-type biradical intermediates by cleavage of one of the two 2,2'-linked di(methylenecyclopropyls). Despite the deep energy wells in which achiral biradicals **6-Et** and **6-Ph** reside, orbital overlap constraints restrict the rearrangement mechanism largely to chiral pathways which bypass these intermediates.

## Experimental Section

Proton nuclear magnetic resonance (NMR) spectra and carbon NMR spectra (62.5 MHz) were obtained on a 250 MHz Bruker WM-250. All samples were run in $CDCl_3$ ($\delta$ 7.24, 77.0), and, where specified, benzene-$d_6$ ($\delta$ 7.27, 128.5), and residual $^1$H-containing solvent was used as internal standard in all cases. GC/mass spectral (GC/MS) data are reported in the following order: initial column temperature (°C), time at initial temperature (min), temperature program rate (°C/min), final temperature, and retention time. Mass spectral data are reported as follows: *m/e* fragment (relative abundance). For high-resolution mass spectra, both electron impact (EI) and chemical ionization (CI) using $CH_4$ were used and are specified. Calculated and experimentally determined values for $M^+$ and $(M + 1)^+$ are given, and other data are reported as for low-resolution GC/MS. All infrared spectra are solution-phase using $CDCl_3$ as solvent. Details of GC analyses and kinetic procedures are given in the supplementary material.

**6-Chloro-6-methyl-2-vinylbicyclo[3.1.0]hexan-2-ol (9-Vinyl).** To a mixture of 120 mL of 1.0 M vinylmagnesium bromide (120 mmol) in 100 mL of dry ether was added via dropping funnel a solution of 6-chloro-6-methylbicyclo[3.1.0]hexan-2-one **8**[4b,c] (14.4 g, 100 mmol) at 0 °C, over 30 min. After being stirred for 10 min, the solution was quenched with saturated $NH_4Cl$ solution and then separated. The aqueous layer was washed twice with ether, and the ether layers were combined, washed with water, dried over $MgSO_4$, and concentrated with a rotary evaporator. The orange liquid was chromatographed on Kieselgel, first with pentane and then with 25% ether in pentane ($R_f$ = 0.55), to give 10.9 g (63.2%) of a clear oil: $^1$H NMR 6.05 (dd, 1 H, *J* = 17.5, 11, C-7), 5.22 (dd, 1 H, *J* = 17.5, 1, C-8), 5.04 (dd, 1 H, *J* = 11, 1, C-8), 2.45 (br s, 1 H, hydroxyl), 1.95–2.10 (m, 4 H, C-3,4), 1.62 (s, 3 H, C-9), 1.49–1.59 (m, 2 H, C-1,5); $^{13}$C NMR 144.0, 110.0, 83.5, 52.2, 40.3, 38.0, 32.6, 29.1, 24.6; GC-MS 137 (73.4), 109 (79.9), 102 (70.0), 91 (50.1), 67 (81.4), 55 (100); IR 3576, 3087, 3013, 2968, 2928, 1701, 1633, 1456, 1093.

**6-Chloro-6-methyl-2-vinylbicyclo[3.1.0]hex-2-ene (10-Vinyl).** A solution of **9-vinyl** (6.9 g, 40.0 mmol) and Burgess's reagent[5] (10.4 g, $Et_3NSO_2NCO_2Me$, 44.0 mmol, 1.1 equiv) in 100 mL of THF was stirred for 3 h at 35 °C and then stirred overnight. The solution was poured into water and separated, and the aqueous layer was washed twice with ether. The organic layers were dried over $MgSO_4$ and concentrated with a rotary evaporator to an orange liquid and a small amount of water-soluble sticky brown solid. The liquid was taken up in pentane and chromatographed on Kieselgel ($R_f$ 0.4) to yield 1.82 g (29.4%) of a yellow liquid: $^1$H NMR 6.57 (dd, 1 H, *J* = 17.5, 10.5, C-7), 5.66 (br s, 1 H, C-3), 5.26 (br d, 1 H, *J* = 17.5, C-8), 5.16 (br d, 1 H, *J* = 10.5, C-8), 2.75 (dd, 1 H, *J* = 19.7, C-4), 2.50 (br d, 1 H, *J* = 19, C-4), 2.27 (dd, 1 H, *J* = 7.3, C-1), 1.76 (dd, 1 H, *J* = 7, 7, C-5), 1.75 (s, 3 H); $^{13}$C NMR ($C_6D_6$) 142.9, 133.9, 131.7, 114.9, 50.5, 38.1, 34.4, 31.4, 28.1; MS (CI) calcd (M + 1) 155.0628, found 155.0644.

**3,7-Dichloro-3,7-dimethyl-1-vinyltricyclo[4.1.0.0$^{2,4}$]heptane (11-Vinyl).** To a solution of **10-vinyl** (10.1 g, 65.4 mmol) and 1,1-dichloroethane (35.9 mL, 427 mmol, 6.5 equiv) in 150 mL of ether, cooled with a $CO_2/(HOCH_2)_2$ bath, was added a 2.5 M solution of BuLi (168 mL, 6.5 equiv). The solution was mechanically stirred, and addition was over 80 min, keeping the temperature near −10 °C. The reaction was stirred for 30 min and quenched at −10 °C with water. The layers were separated, and the aqueous layer was washed twice with ether. The organic layers were combined, dried over $MgSO_4$, and concentrated with a rotary evaporator. Chromatography of the resulting yellow liquid was performed on Kieselgel, with pentane. The exo- and endo epimers of the product separated on the column ($R_f$ 0.45, 0.35) and were characterized separately. Total yield was 7.5 g (52.9%): epimer no. 1 $^1$H NMR ($C_6D_6$) 5.62 (dd, 1 H, *J* = 17, 10, C-8), 5.38 (dd, 1 H, *J* = 17, 1, C-9), 5.29 (dd, 1 H, *J* = 10, 1, C-9), 2.40 (dd, 1 H, *J* = 14, 5, C-5 endo), 2.30 (dd, 1 H, *J* = 14, 6, C-5 exo), 1.62 (d, 1 H, *J* = 7, C-2), 1.51 (s, 3 H), 1.41 (s, 3 H), 1.00–1.05 (m, 2 H, C-4,6); $^{13}$C NMR ($C_6D_6$) 135.6, 117.6, 57.0, 53.0, 46.6, 39.4, 37.4, 31.4, 30.0, 28.3, 25.6; MS (CI) calcd (M + 1) 217.0552, found 217.0553. Epimer no. 2 $^1$H NMR ($C_6D_6$) 6.02 (dd, 1 H, *J* = 17, 10, C-8), 5.30 (dd, 1 H, *J* = 17, 1, C-9), 5.23 (dd, 1 H, *J* = 10, 1, C-9), 2.31 (dd, 1 H, *J* = 14, 5.5, C-5 endo), 2.17 (dd, 1 H, *J* = 14, 6, C-5 exo), 1.77 (d, 1 H, *J* = 6, C-2), 1.74 (s, 3 H), 1.64 (s, 3 H), 1.57 (d, 1 H, *J* = 6, C-6), 1.17 (dd, 1 H, *J* = 6.4, 6.2, C-4); $^{13}$C NMR ($C_6D_6$) 136.8, 115.3, 52.4, 51.7, 44.8, 37.8, 35.9, 30.0, 28.2, 28.0, 19.8; MS (CI) calcd (M + 1) 217.0552, found 217.0547.

**3,7-Dichloro-3,7-dimethyl-1-ethyltricyclo[4.1.0.0$^{2,4}$]heptane (11-Et).** This reaction was carried out on either epimer of **11-vinyl** separately or on a mixture of both epimers. A sample of 3 g (13.8 mmol) of **11-vinyl** was stirred with 20 mg of Pd on C catalyst in 100 mL of MeOH, for 8 h, under a $H_2$ atmosphere. The reaction was filtered through a plug of Kieselgel and concentrated with a rotary evaporator to give 3 g (100%) of a clear liquid: epimer no. 1 $^1$H NMR ($C_6D_6$) 2.30 (dd, 1 H), 2.22 (dd, 1 H), 1.58 (d, 1 H), 1.57 (s, 3 H), 1.44 (s, 3 H), 0.95–1.20 (m, 3 H), 1.08 (t, 3 H), 0.75 (d, 1 H); $^{13}$C NMR ($C_6D_6$) 55.5 (s), 54.0 (s), 44.9 (s), 39.0 (d), 35.8 (d), 31.5 (d), 30.2 (t), 28.5 (q), 24.6 (q), 22.8 (t), 12.7 (q); MS (CI) calcd 219.0710, found 219.0703. Epimer no. 2 $^1$H NMR 2.23 (dd, 1 H, *J* = 14, 5.5, C-5 endo), 2.10 (dd, 1 H, *J* = 14, 6, C-5 exo), 1.70 (s, 3 H), 1.65 (m, 1 H, C-8), 1.58 (s, 3 H), 1.51 (d, 1 H, C-2), 1.18 (d, 1 H, *J* = 6, C-6), 1.08 (t, 3 H, *J* = 7.4, C-9), 1.03 (t, 1 H, C-4), 0.91 (1d, 1 H, C-8); $^{13}$C NMR ($C_6D_6$) 54.0, 50.7, 43.9, 36.8, 36.7, 30.7, 29.1, 28.6, 23.7, 20.6, 12.7; MS (CI) calcd 219.0710, found 219.0720.

**3,7-Dimethylene-1-ethyltricyclo[4.1.0.0$^{2,4}$]heptane (4-Et).** A solution of **11-Et** (2.44 g, 11.1 mmol) and KOtBu (6.25 g, 55.7 mmol) in 100 mL of DMSO (freshly distilled over $CaH_2$) was heated to 110 °C for 3 h. The reaction was cooled to room temperature, poured into 100 mL of water, and extracted with 7 × 150 mL of pentane. The extracts were washed with water, dried over $MgSO_4$, and concentrated with a rotary evaporator. The resulting black mixture was run through a plug of Kieselgel with pentane and concentrated. The somewhat lighter-colored mixture was then submitted to gas chromatography. A 1/4″ × 10′ 10% OV-101 on Chromosorb PAW column was used (conditions: injector temperature 120 °C, detector temperature 120 °C, column temp 80 °C, retention time 10.5 min), followed by a 1/4″ × 10′ 5% Carbowax 20M on Anakrom C22AS column (conditions: injector temperature 120 °C, detector temperature 130 °C, column temperature 90 °C, retention time 18 min). Yield was 0.65 g (40.1%) of a clear liquid: $^1$H NMR ($C_6D_6$) 5.63 (s, 2 H), 5.56 (s, 1 H), 5.52 (s, 1 H), 2.33 (m, 2 H, C-5), 2.18 (d, 1 H, *J* = 7, C-2), 1.94 (m, 1 H, C-8), 1.49 (m, 2 H, C-4,8), 1.26 (m, 1 H, C-6), 1.08 (t, 3 H, C-9); $^{13}$C NMR ($C_6D_6$) 148.4 (s, C-3 or 7), 143.2 (s, C-3 or 7), 103.9 (t, exo $CH_2$), 102.2 (t, exo $CH_2$), 42.0 (s, C-1), 38.4 (t, C-5), 31.5 (d), 26.3 (t), 25.7 (d), 21.0 (d), 12.7 (q); MS (EI) calcd 146.1096, found 146.1103 (14.5), 145.1025 (17.2), 131.0859 (100), 117.0697 (94.5), 116.0621 (31.1), 115.0552 (52.1), 91.0544 (74.6), 77.0389 (17.5).

**2,5-Dimethylene-3-ethylbicyclo[4.1.0]hept-3-ene (5-Et).** A 5-mg sample of **4-Et** was placed into a 50-mL flask at the end of a typical flash vacuum system and pyrolyzed at 400 °C and $10^{-4}$ Torr through a quartz tube filled with glass fragments. The pyrolysate was collected on a $N_2$-cooled coldfinger by washing with ether, concentrated with a rotary evaporator, and submitted to gas chromatography on a 1/4″ × 5′ OV-101 on Chromosorb PAW column (conditions: injector temperature 130 °C, detector temperature 150 °C, column temperature 80 °C, retention time 9.5 min): $^1$H NMR 5.89 (s, 1 H, C-4), 5.11 (s, 1 H), 5.06 (s, 1 H), 5.02 (s, 1 H), 4.90 (s, 1 H), 2.26 (m, 2 H, C-9), 1.97 (m, 2 H, C-1,6), 1.10 (m, 1 H, C-t exo), 1.08 (t, 3 H), 0.52 (q, 1 H, C-7 endo); $^{13}$C NMR 143.3 (s, C-2 or 5), 142.3 (s, C-2 or 5), 137.1 (s, C-3), 124.1 (d, C-4), 110.0 (d, exo $CH_2$), 108.3 (d, exo $CH_2$), 25.5 (t, C-7), 20.8 (d), 19.0 (d), 13.3 (t), 13.1 (q); MS (EI) calcd 146.1096, found 146.1099 (63.8), 131.0854 (55.6), 117.0711 (100), 116.0676 (24.2), 115.0553 (39.8), 91.0558 (42.3), 77.0399 (12.7).

**6-Chloro-6-methyl-2-phenylbicyclo[3.1.0]hexan-2-ol (9-Ph).** To a solution of **8** (5.0 g, 34.6 mmol) in 120 mL of anhydrous ether at −78 °C was added a 1.6 M solution of PhLi in cyclohexane/ether (26 mL, 41.5 mmol) over 30 min. The reaction was stirred an additional 30 min, quenched with saturated $NH_4Cl$ solution, and the layers were separated. The aqueous layer was extracted twice with ether and the combined extracts were dried over $MgSO_4$, and concentrated with a rotary evaporator. The yellow liquid was subjected to flash chromatography on Kieselgel with pentane, and then 10% ether as solvent ($R_f$ 0.7), yielding 4.63 g (60.1%) of a yellow oil: $^1$H NMR 7.25–7.55 (m, 5 H), 2.83 (s, 1 H, -OH), 2.15–2.30 (m, 4 H, C-3,4), 1.783 (t, 1 H, C-5), 1.67 (s, 3 H), 1.62 (d, 1 H, C-1); $^{13}$C NMR 149.0 (s), 128.2 (d), 126.6 (d), 123.8 (d), 85.2 (s, C-2), 53.1 (s, C-6), 43.2 (d, C-1 or 5), 41.9 (t, C-3 or 4),

34.2 (d, C-1 or 5), 29.2 (q, C-7), 26.0 (t, C-3 or 4); IR 3580, 3070, 3062, 3027, 2976, 2932, 2871, 1602, 1493, 1446, 1189; GC-MS (60, 1, 20, 200, 6.73) 204 (34.5), 169 (100), 168 (15.6), 143 (69.4), 128 (74.2), 91 (77.7), 77 (28.9).

**6-Chloro-6-methyl-2-phenylbicyclo[3.1.0]hex-2-ene (10-Ph).** A solution of **9-Ph** (2.0 g, 9.0 mmol) and Burgess's reagent (2.57 g, 10.8 mmol) in 150 mL of THF was heated to 48 °C for 5 h. The reaction was cooled to room temperature, poured into water, and thrice extracted with ether. The extracts were dried over $MgSO_4$ and concentrated with a rotary evaporator to yield a thick black oil, which was chromatographed on Kieselgel with pentane ($R_f$ 0.4) to yield 1.18 g (64.1%) of an orange liquid, which upon addition of a small amount of ether and freezer storage produced large, clear crystals: mp 61–63 °C; $^1$H NMR 7.24–7.45 (m, 5 H), 5.94 (br s, 1 H, C-3), 2.79 (dd, 1 H, $J$ = 19, 7, C-4 exo), 2.58 (br d, 1 H, $J$ = 19, 2, C-4 endo), 2.38 (dd, 1 H, $J$ = 7, 2, C-1), 1.82 (t, 1 H, $J$ = 7, 7, C-5), 1.77 (s, 3 H); $^{13}$C NMR 142.2 (s), 136.4 (s), 128.4 (s), 127.2 (d), 126.9 (d), 125.9 (d), 49.6 (s, C-6), 39.8 (d, C-1 or 5), 34.2 (t, C-4), 30.8 (d, C-1 or 5), 27.5 (q, C-7); GC-MS (60, 1, 10, 200, 8.60) 168 (100), 167 (51), 152 (30), 115 (11); MS (CI) calcd (M + 1) 205.0785, found 205.0778.

**3,7-Dichloro-3,7-dimethyl-1-phenyltricyclo[4.1.0.0$^{2,4}$]heptane (11-Ph).** To a solution of **10-Ph** (2.19 g, 1.07 mmol) and 1,1-dichloroethane (9.05 mL, 10.7 mmol, 10 equiv) in 70 mL of dry ether, cooled with a $CO_2$/$(HOCH_2)_2$ bath, was added a 2.5 M solution of BuLi (43.0 mL, 10.7 mmol, 10 equiv). The solution was mechanically stirred, and addition was over 120 min, keeping the temperature below −10 °C. The reaction was stirred for 30 min and quenched at −10 °C with water. The layers were separated, and the aqueous layer was washed twice with ether. The organic layers were combined, dried over $MgSO_4$, and concentrated with a rotary evaporator. Chromatography of the resulting yellow liquid was performed on Kieselgel, with pentane. The exo and endo epimers of the product separated on the column ($R_f$ 0.45, 0.35) and were characterized separately. The later epimer was a white solid, mp 134 °C. Total yield was 2.49 g (86.9%): epimer no. 1 $^1$H NMR 7.27–7.38 (m, 5 H), 2.57 (dd, 1 H, J = 13.5, 5, C-5 endo), 2.44 (dd, 1 H, $J$ = 13.5, 6, C-5 exo), 2.07 (d, 1 H, $J$ = 7, C-2), 1.74 (d, 1 H, $J$ = 5, C-6), 1.56 (s, 3 H), 1.31 (s, 3 H), 1.27 (dd, 1 H, $J$ = 6, 7, C-4); $^{13}$C NMR 137.5, 128.9, 127.8, 126.5, 56.3, 53.1, 47.5, 40.5, 33.4, 30.7, 29.4, 27.8, 24.9; GC-MS (80, 1, 20, 200, 6.40) 231 (48), 195 (100), 180 (40), 169 (65), 167 (67), 165 (94), 152 (58), 141 (42), 128 (46), 115 (62), 91 (53), 89 (51), 77 (65). Epimer no. 2 $^1$H NMR 7.27–7.35 (m, 5 H), 2.44 (dd, 1 H, $J$ = 14, 5.5, C-5 endo), 2.29 (dd, 1 H, $J$ = 14, 6, C-5 exo), 2.00 (d, 1 H, $J$ = 3, C-2), 1.86 (s, 3 H), 1.54 (s, 4 H, one $CH_3$ and C-6), 1.23 (dd, 1 H, $J$ = 6, 6, C-4); $^{13}$C NMR 138.2 (s), 129.2 (d), 127.3 (d), 126.3 (d), 53.0 (s), 51.3 (s), 46.9 (s), 38.2 (d), 34.7 (d), 30.2 (d), 28.2 (t), 27.8 (q), 19.6 (q); GC-MS (80, 1, 15, 200, 7.50) 231 (45), 195 (90), 169 (70), 167 (75), 165 (100), 152 (70), 141 (45), 128 (50), 115 (75), 91 (70), 89 (75), 77 (85); MS (Cl) calcd (M + 1) 267.0709, found 267.0690.

**3,7-Dimethylene-1-phenyltricyclo[4.1.0.0$^{2,4}$]heptane (4-Ph).** A solution of **11-Ph** (2.30 g, 8.6 mmol), KOH (3.2 g, ~50 mmol, 87%), and 18-crown-6 (15 g, ~57 mmol) in 150 mL of DMSO was heated to 110 °C for 2 h and allowed to cool. The reaction was poured into 100 mL of cold water and extracted with 7 × 250 mL pentane. The extracts were washed three times with water, dried over $MgSO_4$, and concentrated with a rotary evaporator. The brown liquid was chromatographed on Kieselgel with pentane to remove tar and any remaining 18-crown-6. The resulting orange liquid was then chromatographed using 10% $AgNO_3$ on silica gel. Elution with pentane removed trace biphenyl and 3-phenyltoluene, the major product of the reaction. Further elution with 1:1 pentane/ether collected 155 mg (9.3%) of pale yellow liquid **4-Ph**: $^1$H NMR 7.12–7.59 (m, 5 H), 5.59–5.61 (m, 2 H), 5.54 (br s, 1 H), 5.50 (br s, 1 H), 2.34–2.49 (m, 3 H, C-2, 5), 1.69–1.72 (m, 2 H, C-4, 6); $^{13}$C NMR 147.4 (s, C-ipso), 142.0 (s, C-3 or 7), 141.7 (s, C-3 or 7), 128.0 (d), 126.4 (d), 125.7 (d), 104.3 (t, exo-$CH_2$), 102.9 (t, exo-$CH_2$), 43.2 (s, C-1), 38.1 (t, C-5), 30.9 (d), 30.8 (d), 19.9 (d); GC-MS (5890 series II, 120, 2, 20, 200, 5.95) 194 (8), 193 (24), 179 (89), 178 (100), 165 (68), 152 (29), 128 (14), 115 (29); MS (EI) calcd 194.1096, found 194.1094.

**2,5-Dimethylene-3-phenylbicyclo[4.1.0]hept-3-ene (5-Ph).** A sample of 20 mg of **4-Ph** was placed into a flask and pyrolyzed under flash vacuum conditions at 470 °C and 5 × $10^{-5}$ Torr through a quartz tube filled with glass fragments. The pyrolysate was collected on a $N_2$-cooled coldfinger by washing with ether, concentrated with a rotary evaporator, and submitted directly for spectroscopic identification: $^1$H NMR 7.21–7.35 (m, 5 H), 6.00 (s, 1 H, C-4), 5.21 (br s, 1 H), 5.13 (br s, 1 H), 5.00 (br s, 1 H), 4.81 (br s, 1 H), 2.00–2.12 (m, 2 H, C-1, 6), 0.71–0.89 (m, 2 H, C-7); $^{13}$C NMR 143.1 (s, C-2 or 5), 142.9 (s, C-2 or 5), 140.6 (s, C-3), 137.7 (s, C-ipso), 128.7 (d), 127.7 (d), 126.9 (d, C-4 or C-para), 126.7 (d, C-4 or C-para), 112.9 (t, exo-$CH_2$), 111.6 (t, exo-$CH_2$), 21.0 (d, C-1 or 6), 19.3 (d, C-1 or 6), 12.7 (t, C-7); GC-MS (5890 series II, 120, 2, 20, 200, 6.74) 194 (44), 193 (26), 179 (100), 178 (99), 165 (81), 152 (30), 115 (24); MS (EI) calcd 194.1096, found 194.1103.

**General Procedures for Pyrolyses of 4-Et and 4-Ph.** Normal kinetic pyrolyses were run on a mixture of substrate and internal standard, while pyrolyses of optically active material were performed on **4-Et** or **4-Ph** alone. Pyrolyses of **4-Et** were performed in the gas phase and in solution, while all pyrolyses reported here of **4-Ph** were done in solution. Standards were chosen which had capillary GC retention times near, but not on top of, those of the compounds in question, and which had the same or nearly the same molecular formula. For **4-Et**, undecane was used as internal standard, and nonane was used as solvent for the solution-phase experiments. For **4-Ph**, tridecane was used as internal standard, with undecane as solvent. Roughly 1 μL of sample was delivered to each pyrolysis tube, which was then sealed with a septum. Solutions were formulated so that 220 μL of solution contained 1 μL of sample. Tubes were individually subjected to three freeze–pump–thaw cycles and sealed at ≤$10^{-5}$ Torr. All pyrolyses were performed in one of two high-temperature baths (see supplementary material). The tubes were removed and run under cold water, and liquid nitrogen was used to collect the sample at the bottom of the tubes. Tubes were then broken, and in the case of gas-phase pyrolyses, ~500 μL pentane was quickly rinsed down the sides of the tubes. Solutions were mixed with a syringe, sealed with rubber septa, and analyzed by capillary GC. Each sample was analyzed until close agreement existed among most of the runs; typically four to six runs were required.

The data of Tables I and II were analyzed by linear least squares. Somewhat different values are obtained for the data of Table II by a direct exponential fit with the program Kaleidagraph: $\Delta\Delta H^{\ddagger}$ = −2.8 kcal/mol; $\Delta\Delta S^{\ddagger}$ = 14.1 eu; $R$ = 0.827. The differences are small with respect to the experimental error.

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**Supplementary Material Available:** Details of determination of rate constants, activation parameters, and analyses of ee of reactants and products and calculations for Figures 1 and 2 (44 pages). Ordering information is given on any current masthead page.