dried. Crude product was dissolved in boiling 2-propanol at a concentration of 0.02 g/mL and was allowed to cool slowly. Fine needles precipitated: yield 78%; mp 152-154 °C; IR (tetrachloroethane, cm^{-1}) ν_{NH} 3412 (m), ν_{CH} 2957 (m), 2927 (m), 2859 (m), ν_{OCN} 2279 (s), 2262 (s), 2239 (s), $\nu_{C=O}$ 1725 (br s), ν_{amide} 1678 (s), 1603 (m), 1501 (s).

Anal. Calcd for $C_{34}H_{36}N_4O_7$: C, 66.65; H, 5.92; N, 9.14. Found: C, 66.60; H, 6.00; N, 9.09.

Poly(Z-Tyr-Tyr-Hex-Iminocarbonate) (5). A solution of equimolar quantities of Z-Tyr-Tyr-Hex and Z-Tyr-Tyr-Hex-dicyanate was prepared in THF (0.2 mmol/mL) and placed in a sealed flask under an atmosphere of argon at 50 °C. With stirring, 0.1% (w/w) of potassium *tert*-butoxide (0.5 M in 2-methyl-2-propanol) was injected into the reaction mixture. The solution became viscous, and after 90 min polymer precipitated. After 4 h the polymer was completely precipitated by addition of acetone, collected on a Buchner funnel, washed with acetone, and dried in vacuo; yield 90-95%. The progress of the polymerization reaction was followed by end group analysis employing the pyridine-barbituric acid color reaction for determination of cyanate esters.[15]

Compound **5**: IR (tetrachloroethane, cm^{-1}) ν_{NH} 3412 (m), 3332 (w), ν_{CH} 2958 (m), 2928 (m), 2859 (w), $\nu_{C=O}$ 1726 (br s), ν_{amide} 1676 (br s, shoulder at 1690 (iminocarbonate)), ν(aromatic ring) 1603 (w), 1502 (w), 1310 (br s), 1056 (br m), the regions obscured by solvent absorptions (cm^{-1}) were 3040-2960, 1300-1170, 1040-990, <860; ^{1}H NMR (CDCl$_3$) δ 0.88 (3 H, t, CH$_3$), 1.27 (6 H, m narrow, 3CH$_2$), 1.56 (2 H, br m, CH$_2$), 3.00 (4 H, br m, 2CH$_2$), 4.05 (2H, br m, CH$_2$), 4.42 (1 H, br m, CH), 4.78 (1 H, br m, CH), 5.05 (2 H, s, CH$_2$), 5.55 (2 H, br m, 2 NH$_{amide}$), 6.57 (1 H, br s, NH$_{imino}$), 7.08 (8 H, m, two 1,4-Ph), 7.31 (5 H, m, Ph); molecular weight (GPC and vapor pressure osmometry in chloroform) M_n = 11 500, M_w = 19 500, DP = 19-20.

Anal. Calcd for $C_{33}H_{37}N_3O_7$: C, 67.45; H, 6.35; N, 7.15. Found: C, 66.81; H, 6.57; N, 7.10.

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Thermal Reorganization of Two Pyramidalized Alkenes by Reverse Vinylcyclopropane Rearrangements

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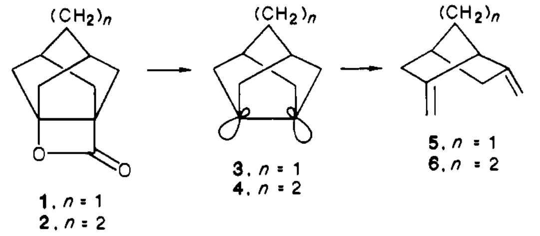
Abstract: 2,6-Dimethylenebicyclo[2.2.*n*]alkanes **5** and **6** are formed, respectively, by flash vacuum pyrolysis of the β-lactone precursors (**1** and **2**) of pyramidalized alkenes **3** and **4** at high temperatures. The mechanism by which **5** and **6** are formed has been elucidated by isolation of an intermediate (**8**) in the transformation of **4** to **6**. The sensitivity of **8** to acid suggests that its rearrangement to **6** may be surface catalyzed. The formation of **8** from **4**, which is the reverse of the usual vinylcyclopropane rearrangement, can also be induced photochemically. From the thermal isomerization of **4** to **8** it is possible to establish a lower limit to the strain energy in **4** that is attributable to the presence of the pyramidalized double bond. This value is compared to the olefin strain energy computed for **4** by MM2 and by MNDO calculations.

We have previously reported[1] that flash vacuum pyrolysis (FVP) of β-lactone **1**[2] at temperatures above 550 °C leads to formation of small amounts of the dimer of pyramidalized alkene **3** but that the major product isolated is 2,6-dimethylenebicyclo[2.2.1]heptane (**5**). Herein, we describe the thermal chemistry of the homologous alkene **4**,[2,3] which bears on the mechanism by which **5** is formed from **3**. We also show that from this data a lower limit can be placed on the strain caused by the presence of the pyramidalized double bond in **4**.



Results

The β-lactone precursor **2** of alkene **4** is 50% decarboxylated on FVP at 410 °C. At this pyrolysis temperature, IR analysis of the pyrolysate, trapped at 10 K, shows the sole products to be **4** and CO$_2$.[3] The only product detected after warm-up is the "2 + 2" dimer of **4**.[2]

However, as the pyrolysis temperature is raised, formation of an isomer of **4** is observed.[3] GLC analysis of the pyrolysate shows that at 440 °C the dimer constitutes about 90% by weight of the product mixture and the new hydrocarbon 10%, but at 530 °C the new hydrocarbon is the major product, and the dimer of **4** comprises only about 10% of the product mixture.

Interestingly, this isomer of **4** is itself thermally labile, undergoing rearrangement to 2,6-dimethylenebicyclo[2.2.2]octane (**6**). When **2** is pyrolyzed, small amounts of **6** can be detected at 480° C, and at 530 °C **6** comprises about 40% of the product mixture. That the isomer formed from **4** can act as the direct precursor of **6** was shown by partial rearrangement of the former to the latter on FVP at 500 °C.

The rearrangement of **4** to the thermally labile isomer was established unequivocally in the following manner. β-Lactone **2** was pyrolyzed under conditions where its conversion to **4** was about 90% complete, and then the pyrolysate was passed through a second hot zone. GLC analysis of the product mixture showed that passage through the second hot zone resulted in a 40% decrease in the amount of the dimer formed from **4** and a corresponding increase in the combined amounts of the thermally labile isomer and its rearrangement product (**6**).

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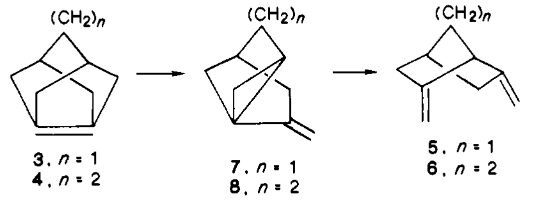


3, $n = 1$
4, $n = 2$
7, $n = 1$
8, $n = 2$
5, $n = 1$
6, $n = 2$

The thermally labile isomer of **4** was identified spectroscopically as 8-methylenetricyclo[4.2.1.$0^{1,3}$]nonane (**8**). Its ^{13}C NMR spectrum showed 10 resonances, consistent with the absence of any element of symmetry in this hydrocarbon. Resonances at δ 93.2 and 153.8 were indicative of the presence of a vinylidene ($C{=}CH_2$) group, as were the observation of sharp singlets, integrating to one proton each, at δ 4.30 and 4.42 in the ^1H NMR spectrum and IR absorptions at 3083, 2997, 1668, 1431, 869, and 861 cm^{-1}. The appearance of a ^1H resonance at δ 0.07 suggested strongly that the hydrocarbon also contains a cyclopropane ring, as did an IR absorption at 3068 cm^{-1}.

All 14 protons of **8** were resolved in its ^1H NMR spectrum at 500 MHz. A complete decoupling study led to the assignment of each proton. The results of the decoupling study are summarized in Table I, which also contains the chemical shift assignments. As shown in Table I, the observed vicinal coupling constants are in good agreement with those predicted[4] from the dihedral angles that were obtained by MM2 optimization[5] of the geometry of **8**.

Alkene **4** is converted to **8** by light as well as by heat. Pyrolytically produced **4**, matrix isolated in argon, was found to have a broad UV absorption with a maximum around 245 nm.[3] Irradiation of the matrix with the 248-nm line of a KrF laser or with a low-pressure mercury lamp caused a gradual, concurrent decrease of both the UV and IR bands[3] attributed to **4**. The product of irradiation did not absorb in the accessible UV region. It was characterized by its IR bands in the matrix, as well as by its mass spectrum and GLC retention time after matrix warm-up. The photoproduct proved identical in all these respects with a sample of **8**, isolated from the pyrolysis of β-lactone **2**.

Discussion

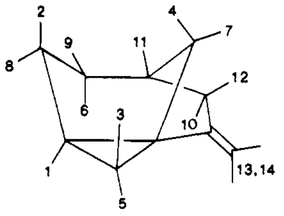
The finding that **8** is an intermediate in the thermal rearrangement of the $n = 2$ alkene (**4**) to 2,6-dimethylenebicyclo[2.2.2]octane (**6**) suggests that the analogous rearrangement of **3** to **5** in the $n = 1$ series proceeds via the intermediacy of **7**. Since **3** is only formed from **1** at high temperatures, where the rearrangement of **7** to **5** is likely to be very rapid, our failure[1] to detect **7** is understandable.

Both **7** and **8** are themselves strained hydrocarbons. They may be viewed, respectively, as derivatives of *trans*-bicyclo[4.1.0]heptane[6] and *trans*-bicyclo[5.1.0]octane.[7] The strain present in **8** is manifested by its sensitivity to acid. For example, stirring a chloroform solution of **8** over molecular sieves results in rapid rearrangement to **6**.[8] Although a plausible diradical mechanism can be written for the rearrangement of **8** to **6** in our FVP apparatus at high temperature,[9] the acid catalysis of this reaction at room temperature leaves open the possibility that some or all of the gas-phase rearrangement may actually be surface catalyzed.

Table I. ^1H NMR Chemical Shifts, Coupling Constants, and Assignments in 8-Methylenetricyclo[4.2.1.$0^{1,3}$]nonane (**8**), Obtained from a Complete Decoupling Study. Coupling Constants Calculated[4] from the MM2[5] Optimized Geometry of **8** Are Also Given

chemical shift	proton	couples with protons	coupling const, Hz	MM2 calcd coupling const, Hz
4.42	14			
4.30	13			
2.60	12	11	7.2	6.9
		10	16.2	
2.25	11	12	7.2	6.9
		9	8.1	8.3
		7	3.6	4.7
		4, 6, 10	≈0	1.5, 1.0, 0.9
2.20	10	12	16.2	
		11	≈0	0.9
		4	2.7	
2.07	9	11	8.1	8.3
		8	≈0	0.3
		6	14.4	
		2	7.2	7.5
1.73	8	9	≈0	0.3
		6	7.2	7.9
		2	13.5	
		1	6.3	4.4
1.52	7[a]	11	3.6	4.7
		4	10.8	
1.41	6[a]	11	≈0	1.0
		9	14.4	
		8	7.2	7.9
		2	12.6	12.8
1.40	5	3	5.4	
		1	8.1	10.3
1.01	4	11	≈0	1.5
		10	2.7	
		7	10.8	
0.97	3	5	5.4	
		1	6.3	9.5
0.89	2	9	7.2	7.5
		8	13.5	
		6	12.6	12.8
		1	10.8	9.8
0.07	1[a]	8	6.3	4.4
		5	8.1	10.3
		3	6.3	9.5
		2	10.8	9.8

[a] There is also some very small, long-range coupling between 7 and both 6 and 1.



The reaction by which **8** is formed from pyramidalized olefin **4** may be viewed as the reverse of the well-known vinylcyclopropane rearrangement.[10] Usually the equilibrium in this reaction lies far on the side of the cyclopentene product, since the heat of formation of cyclopentene is 17.5 kcal/mol less than that of vinylcyclopropane.[11] Therefore, assuming that the entropies of **4** and **8** are comparable, the fact that the equilibrium between these two hydrocarbons favors **8** implies that the strain energy of pyramidalized alkene **4** destabilizes it, relative to cyclopentene, by at least 17.5 kcal/mol more than the strain energy of **8** exceeds that of vinylcyclopropane. A conservative estimate of 9 kcal/mol for the latter strain energy difference, based on the enthalpy of

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(8) Reasonable mechanisms can be written for this rearrangement whether electrophilic attack occurs at the double bond of **8** to form a tertiary carbocation or at the methylene group of the cyclopropane to form, after ring opening, a secondary, homoallylic carbocation.

(9) Cleavage of the same bond of the cyclopropane ring as in the second mechanism for the acid-catalyzed rearrangement, followed by a 1,2-vinylidene shift through the intermediacy of a cyclopropyldicarbinyl diradical, transforms **8** to **6**.

(10) Review: Gajewski, J. J. *Hydrocrabon Thermal Isomerizations*; Academic: New York, 1981; pp 81–87.

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isomerization of a *trans*- to a *cis*-bicyclo[5.1.0]octane,[7h] gives 27 kcal/mol as a lower limit to the amount by which the presence of the double bond in **4** causes its strain energy to exceed that of cyclopentene.

This energy difference can also be calculated from the olefin strain energy (OSE)[12] of **4** and that of cyclopentene. With the MM2 force field[5] the OSE of cyclopentene—the difference between its strain energy and that of cyclopentane—is small and negative, amounting to −3.1 kcal/mol. With the same force field the double bond in **4** is predicted to have a pyramidalization angle[13] of 48.8°, and the OSE of **4** is calculated to be 18.3 kcal/mol.[14] The resulting value of 21.4 kcal/mol for the OSE difference between **4** and cyclopentene is smaller than that indicated by our experimental results.

Although an MM2 calculation gives a geometry in good agreement with the crystal structure for one pyramidalized olefin,[15] for double bonds contained in five-membered rings the standard MM2 parameters apparently give out-of-plane bending force constants that are too small.[16] Therefore, we also performed quantum mechanical calculations, using the semiempirical MNDO method,[17] to optimize the geometry of **4** and to compute the heat of hydrogenation of this alkene.

MNDO predicts a pyramidalization angle of 43.5° for the double bond in **4**, which is somewhat smaller than the value of 48.8° predicted by MM2. In addition, the MNDO difference of 42.0 kcal/mol between the calculated heat of hydrogenation of **4** (72.1 kcal/mol) and that of cyclopentene (30.1 kcal/mol) is nearly twice the MM2 difference of 21.4 kcal/mol between the OSEs of these two alkenes. The MNDO number is more compatible with our experimental results.

For the $n = 1$ alkene (**3**) MNDO again predicts a smaller pyramidalization angle (53.0°) than MM2 (57.4°). The heat of hydrogenation of **3** is computed by MNDO to be 91.8 kcal/mol, which is fully 61.7 kcal/mol greater than the heat of hydrogenation calculated for cyclopentene. In contrast, MM2 finds the OSE of **3** to exceed that of cyclopentene by only 27.6 kcal/mol.

A better reference compound than cyclopentene for estimating the OSEs of pyramidilized alkenes **3** and **4** from their calculated heats of hydrogenation is bicyclo[3.3.0]oct-1(5)-ene. Its heat of hydrogenation is computed by MNDO to be 25.2 kcal/mol. Use of this alkene, instead of cyclopentene, as the reference thus increases by 4.9 kcal/mol the OSEs of **3** and **4** that are obtained from their MNDO heats of hydrogenation.

The MM2 OSE for bicyclo[3.3.0]oct-1(5)-ene is −0.7 kcal/mol. When the MM2 OSEs of **3** and **4** are compared with that of this alkene, the relative MM2 OSEs of the pyramidalized alkenes are, therefore, each 2.4 kcal/mol smaller than when the MM2 OSE of −3.1 kcal/mol for cyclopentene is used as the reference. Thus, the change from cyclopentene to bicyclo[3.3.0]oct-1(5)-ene as the reference alkene increases by 7.3 kcal/mol the disparity between the MM2 and MNDO estimates of the strain energy in **3** and **4** that is attributable to the presence of the pyramidalized double bond in each of these two alkenes.

Ab initio calculations on **3** and **4** are being carried out to help resolve the issue of which of the two semiempirical methods provides a better estimate of the strain caused by the pyramidalized double bond that each of these alkenes contains.

Experimental Section

GLC analyses were performed with a 25-m ultraperformance capillary column of cross-linked 5% phenylmethylsilicone and a flame ionization detector. For preparative GLC a 12-ft × $^3/_8$-in. column of 20% Carbowax 20M on Chromasorb W was used.

Flash Vacuum Pyrolyses (FVP). An FVP apparatus was constructed from a 12- × 0.5-in. quartz tube, which was wrapped with nichrome wire and covered with insulation for about 10 in. of its length. The tube was fitted with a 14/20 joint at each end, and a thermocouple was inserted under the insulation in the center of the hot zone. Thus, the pyrolysis temperatures reported are external, rather than internal, readings. The top of the pyrolysis column was connected by means of a short U-tube, wrapped with aluminum foil, to a flask in which was placed the β-lactone to be pyrolyzed. The bottom of the column was attacked to a trap that was immersed in liquid nitrogen, and the trap was connected to a vacuum system. The apparatus was operated at a pressure of about 10^{-3} torr. In order to achieve reasonable rates of sublimation of the β-lactone into the pyrolysis column at this pressure, it was necessary to heat the flask containing the β-lactone to about 60 °C with an oil bath.

For the pyrolyses of β-lactone **2**[2] in which two different hot zones were used, the pyrolysis column was rewound with two separate strands of heating wire. The first zone was 7 in. long, and the second was 3 in. A thermocouple was inserted in the center of each zone to monitor the temperature. In a typical run the first zone was heated to a temperature of 510 °C andd the second to 220 °C. Under these conditions the pyrolysate was found to consist of 6.8% **6**, 31.9% **8**, 49.6% dimer of 4, and 11.7% unreacted **2**. When the temperature of the second zone was raised to 585 °C, the composition of the pyrolysate changed to 19.5% **6**, 42.1% **8**, 30.8% dimer, and 7.6% unreacted **2**.

The composition of the pyrolysate was determined by analytical GLC. At a GLC column temperature of 100 °C, **6** and **8** had retention times of 1.89 and 2.14 min, respectively. The dimer[2] of the $n = 2$ olefin (4) had a retention time of 11.24 min when, after 3.75 min at 100 °C, the GLC column temperature was programmed to increase by 15°/min, and β-lactone **2** had a retention time of 6.40 min under these conditions.

A preparative-scale pyrolysis of **2** was performed at 530 °C, since at this temperature analytical GLC showed maximal amounts of **6** and **8** to be formed, accompanied by only a small amount of the dimer of 4. The two rearrangement products were separated by preparative GLC. At a column temperature of 95 °C, 6 and 8 had retention times of, respectively, 20 and 28 min.

2,6-Dimethylenebicyclo[2.2.2]octane (6): ^{1}H NMR δ 1.56 (br d of d, 2 H, $J = 7.7, 3.4, <1$ Hz), 1.72 (d of d, 2 H, $J = 7.7, 2.7$ Hz), 1.94 (m, 1 H, $J = 3.4, 2.6, 1.7$ Hz), 2.27 (br d of d, 2 H, $J = 17.2, 1.7, <1$ Hz), 2.37 (m, 2 H, $J = 17.2, 2.6, 1.8$ Hz), 2.77 (d, 1 H, $J = 2.7$ Hz), 4.62 (d, 2 H, $J = 1.8$ Hz), 4.79 (d, 2 H, $J = 1.8$ Hz). Decoupling experiments helped to estblish the coupling constants and led to the assignment of the ^{1}H resonances as belonging, respectively, to the hydrogens on C-8, C-7, C-4, C-3 and C-5 (endo), C-3 and C-5 (exo), C-1, and the methylidene carbons. The ^{13}C NMR spectrum showed δ 25.37, 27.50, 27.60, 35.02, 46.77, 105.63, 150.42. Exact mass calcd for $C_{10}H_{14}$ 134.1096, found 134.1097.

8-Methylenetricyclo[4.2.1.$0^{1,3}$]nonane (8). The ^{1}H NMR chemical shifts and the results of a complete decoupling study are contained in Table I: ^{13}C NMR δ 14.93, 19.06, 25.27, 29.49, 29.69, 32.01, 34.30, 43.03, 93.16, 153.72; exact mass calcd for $C_{10}H_{14}$ 134.1096, found 134.1099.

Matrix Isolation and Irradiation of 4. Argon matrices containing **4**, which was formed by passage of **2** through a quartz tube heated to 480 °C, were deposited on CsI windows that were attached to the cold tip of an Air Products CS-202 Displex closed-cycle helium cryostat with indium gaskets. Irradiation was performed with a low-pressure Hg lamp (254 nm) or with the 248-nm KrF line of a Lambda Pysik EMG 50E excimer laser. Total disappearance of the IR peaks of **4** required about an hour of laser irradiation.

Spectra were recorded on a Nicolet 6000 Series FT IR spectrometer, a Spex Ramalog 4 spectrometer, and a Cary 17D UV-visible spectrometer. The IR spectrum of **4** and the linear dichroism of each IR band, obtained from a sample of **4** that was partially oriented by irradiation with linearly polarized UV light, have been published previously.[3] The Raman spectrum of **4**, excited with an argon laser (5145 A, 100 mW), showed peaks at the same positions as the IR spectrum but with different relative intensities. The C=C stretching band at 1557 cm^{-1}, which was very weak in the IR spectrum of **4**, was the strongest absorption in the Raman spectrum. The IR spectrum of **8** in an argon matrix at 12 K was obtained as the difference between spectra taken before and after photobleaching of **4**. In addition to the characteristic vinylidene and cyclopropane absorptions given in the text, IR bands for **8** were also observed at 1476, 1444, 1331, 1193, 1130, 1050, 1028, 1017, 917, 820, and 580 cm^{-1}.

Acknowledgment. We thank the National Science Foundation for support of this research.

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[13] The double bond pyramidalization angle in **4** is defined as the angle between the plane containing C-2, C-3, and C-4 and the extension of the bond between C-3 and C-7. An angle of 54.7° would correspond to pyramidalization of the olefinic carbons to a tetrahedral geometry.

[14] With MM1 the OSE of **4** is computed to be 24.2 kcal/mol.[12]

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