(2.7, M + 2 - EtOH), 192 (7.9, M - EtOH), 167 (22, M + 2 - COOEt), 165 (68, M - COOEt), 140 (10), 138 (29), 103 (100), 77 (60), 76 (44).

Acknowledgment. We are grateful to the National Science Foundation and to the Robert A. Welch Foundation for their support of this research. Partial funding for the mass spectrometer system was provided by the National Science Foundation.

The Chemistry of the *trans*-Trimethylenenorbornene Ring System. 4. A Kinetic and Molecular Mechanics Study of the Thermal Rearrangement of 9-Carbomethoxy-*trans*-5,6-trimethylene-2-norbornene[1]

George B. Clemans* and Jean K. Blaho[2]

Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403

Received September 5, 1986

Thermal rearrangements of bicyclo[3.2.0]heptenes to norbornenes (e.g., 1 → 2) have been known[3] for some time and have been used by Berson[4] to establish the steric course of such 1,3-sigmatropic carbon migrations generally. In most reported cases,[4,5] however, these reactions occur at higher temperatures (>300 °C) and yield a number of products of which some are unstable under the reaction conditions.

1a, X=OAc, Y=D
1b, X=Y=H

2a, X=OAc, Y=D
2b, X=Y=H

We have described[6] the facile rearrangement of the *trans*-trimethylenenorbornene 3 to the tricyclodecene 4, a process that is analogous to those above, but that occurs in the opposite direction. This rearrangement, however, is observed at temperatures well below 200 °C and yields 4 as the sole product. Since it is the first such rearrangement of a norbornene derivative to be reported, we have undertaken a combined kinetic and molecular mechanics investigation to elucidate the energetics of this remarkable process and to reexamine under more favorable experimental circumstances earlier conclusions concerning the mechanism of 1,3-sigmatropic migrations in such systems.

3

4

Table I. Average Rate Constants for the Rearrangement of 3

temp,[a] °C	rate constant[b]
178	$(8.79 \pm 0.15) \times 10^{-6}$
188	$(2.11 \pm 0.02) \times 10^{-5}$
199	$(6.46 \pm 0.06) \times 10^{-5}$
210.5	$(1.61 \pm 0.01) \times 10^{-4}$

[a] Maintained at ±0.5 °C. [b] Average of duplicate determinations. Reported error range is the deviation from the average.

Table II. Comparison of Kinetic Parameters

reactant	E_a[a]	log A
3	39.4	13.6
1a	46.8[b]	13.7[b]
1b	48.6[c]	14.8[c]

[a] In kilocalories/mole. [b] Reference 4b. [c] Reference 5, for total disappearance of starting material.

Table III. Calculated Heats of Formation

compound	ΔH°_f[a]	compound	ΔH°_f[a]
1b	28.1	**5**	37.4
2b	19.3	**6**	16.8[c]
3	-48.1[b]	**7**	-68.2[b]
4	-60.4[b]		

[a] In kilocalories/mole. [b] Average of syn and anti epimers. [c] Average for syn and anti conformations.

Results and Discussion

The kinetics of the rearrangement of 3 in decalin were conveniently followed by ^{1}H NMR by periodic integration of the vinyl region (see Experimental Section). Duplicate determinations were made at each of four different temperatures over a range of 35 °C, and the reactions were followed to over 70% completion. Rate constants were then calculated from kinetic plots and averaged at each temperature. Table I summarizes the results.

An Arrhenius plot made by using these rate constants was found to be linear, and the activation energy for the rearrangement was thus determined. Table II compares the kinetic parameters of this reaction with those of related processes reported earlier.

In order to gain further insight into the nature of energy changes in these rearrangements, enthalpies of reaction were determined from heats of formation calculated by using Allinger's MM2 molecular mechanics program.[7] The results are summarized in Table III. It was thus found that the rearrangement of **1b** was exothermic by 8.8 kcal/mol, while the rearrangement of 3 was exothermic by 12.4 kcal/mol. For purposes of comparison, all of the energies determined for these rearrangements are combined in Figure 1.

Berson has pointed out[4] that the anticipated difference in activation energies betweeen concerted and diradical pathways for the rearrangement of **1a** is quite small and that the distinction between the two on this basis is not straightforward. The high stereospecificity of the rearrangement of 3 as in the case of **1a** argues strongly for a concerted mechanism in both cases, however. Molecular mechanics calculations for the rearrangement of 3 provide additional support for this conclusion. A diradical intermediate formed by homolytic cleavage of the 4,5 bond in 3 could close either to 4 or to 7, the endo,cis isomer of 3. The calculated heats of formation of the isomeric systems

---

(1) (a) Presented at the 18th Central Regional Meeting of the American Chemical Society, Bowling Green, Ohio, June, 1986. (b) Part 3 of this series: Clemans, G. B.; Samaritoni, J. G.; Holloway, R. J.; Edinger, W. *J. Org. Chem.* **1984**, *49*, 3457.

(2) Dreyfus Undergraduate Research Student, Summer 1985.

(3) For a review, see: Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187.

(4) (a) Berson, J. A. *Acc. Chem. Res.* **1968**, *1*, 152. (b) Berson, J. A. *Acc. Chem. Res.* **1972**, *5*, 406.

(5) Cocks, A. T.; Frey, H. M. *J. Chem. Soc. A* **1971**, 2564.

(6) Clemans, G. B. *J. Org. Chem.* **1973**, *38*, 3459.

(7) (a) Program no. 395 available from QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47450. (b) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.

0022-3263/87/1952-1621$01.50/0

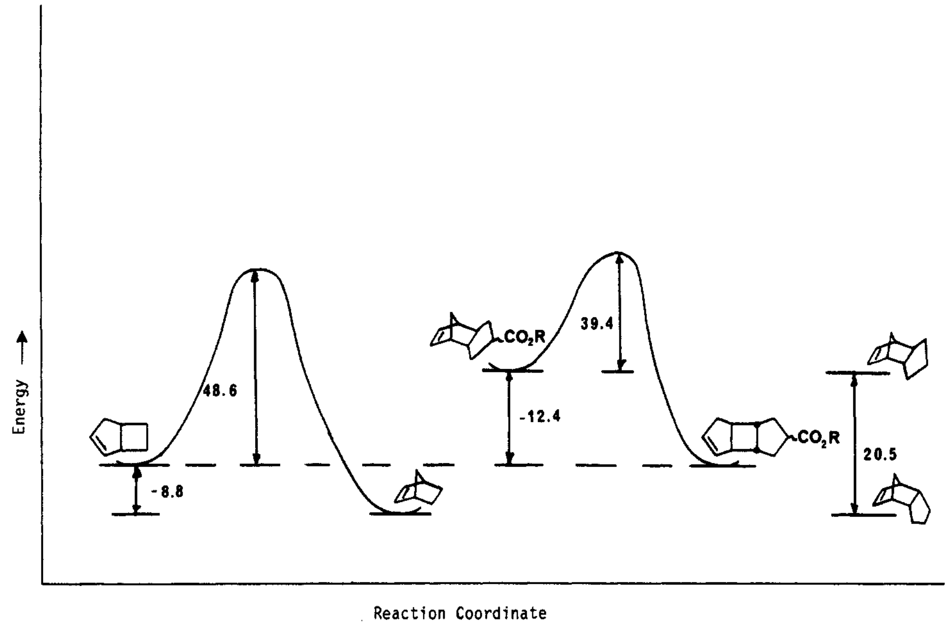
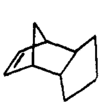
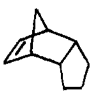


Figure 1. Comparison of the energy changes during the rearrangement of **1b** and **4**. (Values are in kilocalories/mole.)

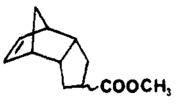
(Table III) indicate that **4** is ca. 8 kcal/mol less stable than **7**. Thus, any hypothetical diradical intermediate derived from **3** would not be expected to produce **4** as the exclusive product. This conclusion is supported by the observation that in those cases[4b] in which diradical intermediates would be most likely, multiple products are formed as expected.



5



6



7

That the reversal of the direction of the **3** → **4** rearrangement compared to that of **1** is indeed due to the high degree of internal strain associated with the trans bridge in **3** as previously suggested[6] is evident from Figure 1. The sum of the enthalpies of reaction calculated for these two processes (−21.2 kcal) is essentially identical with the calculated difference in the heats of formation of the *trans*- and *endo-cis*-trimethylenenorbornenes **5** and **6** (−20.5 kcal). The strain of the cyclobutane ring in **4** is thus more than compensated by the strain of the trans bridge in **3**, and **4** therefore becomes the thermodynamically favored product.

The geometry of the trans ester **3** calculated with the MM2 program provides insight into the probable nature of the transition state in a concerted **3** → **4** rearrangement. The C8–C5–C6–C10 dihedral angle is greatly reduced from its normal value near 120° in undistorted norbornenes to about 60° in **3**. This distortion greatly facilitates the inversion of the configuration of carbon 5 required by orbital-symmetry considerations.[8] Further, the torque applied about the 5,6 bond twists the norbornene ring so that the distance between carbons 5 and 2 is decreased from a normal value of about 3.0 Å to about 2.7 Å, thereby reducing the distance across which the developing 2,5 bond must bridge. Geometric changes thus combine to favor a concerted migration with inversion of configuration.

From Figure 1 it is also evident that strain of the trans bridge in **3** is largely relieved in the transition state leading to **4**. As C5 inverts in traversing the reaction coordinate, internal strain is relieved as the trans geometry of the cyclopentane ring in **3** approaches the cis geometry of **4**. The sum of the activation energy and the absolute value of the enthalpy of reaction for the rearrangement of **3** (39.4 + 12.4 = 51.8 kcal/mol) is close to the measured activation energy for the rearrangement of **1a** (46.8 kcal/mol). Most, but not all, of the strain of the trans bridge therefore is relieved when the transition state for **3** is reached. Thus, the concerted mechanism predicted by orbital-symmetry rules would seem to be the simplest explanation of the present data.

Experimental Section

Materials and Equipment. 9-Carbomethoxy-*trans*-5,6-trimethylene-2-norbornene (**3**)[9] was evaporatively distilled at reduced pressure before use. Its spectroscopic properties were identical with those reported earlier. Reagent grade decalin was washed with concentrated sulfuric acid and distilled before use. ^{1}H NMR spectra were obtained with a Varian Model EM-360 spectrometer. Kinetic plots and linear least-squares analysis were done by using the Curve Fitter program of Interactive Microware, Inc., with an Apple II+ computer.

Kinetic Determinations. Approximately 0.75 M solutions of **3** in decalin were sealed under nitrogen in 5-mm NMR tubes and were heated at the desired temperature (±0.5 °C) in a thermostatically controlled oil bath. The tubes were periodically removed and quickly cooled to room temperature. The vinyl proton absorptions of both **3** and **4** were clearly visible[9] and were measured by averaging six integrations for each set of protons. From these measurements the amount of unreacted starting material was calculated. For each run, the reaction was followed to over 70% completion. Kinetic plots utilizing a minimum of eight points were then made of −ln [**3**] vs. time in seconds. Linear least-squares fit of the curve yielded the rate constants. In all cases, correlation coefficients were in excess of 0.990. Standard deviations about the regression (S_r) ranged from 0.02 to 0.08, and the deviation of any individual rate constant from the average was less than 2%. The results are given in Table I.

The activation parameters were obtained from an Arrhenius plot of −ln (k) vs. $1/T$. Linear least-squares fit of the curve gave a correlation coefficient of 0.999 and a standard deviation about the regression (S_r) of 0.07. The results are given in Table II.

---

[8] Woodward, R. B.; Hoffman, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1971.

[9] For a description of the ^{1}H NMR spectrum of **3**, see: Clemans, G. B.; Essiet, M. N.; Tyson, R. L. *J. Org. Chem.* **1972**, *37*, 2312. The ^{1}H NMR spectrum of **4** is given in ref 6.