J. Am. Chem. Soc. **2000,** *122,* 8490−8494

Kinetics and Mechanism of the Thermal Rearrangement of [1.1.1]Propellane

Oliver Jarosch,[†] Robin Walsh,*,[‡] and Günter Szeimies*,[†]

Contribution from the Institut für Chemie, Humboldt Universität zu Berlin, Hessische Strasse 1-2, D-10115 Berlin, Germany, and Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading RG6 6AD, UK

Received November 17, 1999. Revised Manuscript Received June 20, 2000

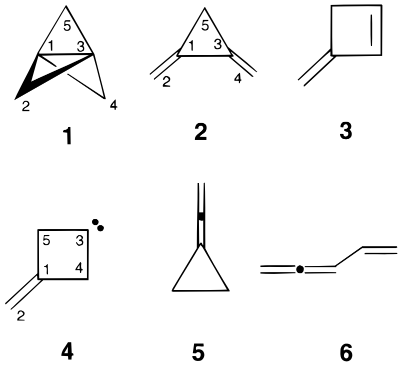
Abstract: The kinetics of the thermal rearrangement of [1.1.1]propellane (**1**) have been investigated by gas-phase pyrolysis in a stationary system. The unimolecular reaction leads to dimethylenecyclopropane (**2**) and its thermal isomerization product ethenylidenecyclopropane (**5**) with the following Arrhenius parameters: $\log(A/\mathrm{s}^{-1}) = 14.02 \pm 0.23$; $E_\mathrm{A}/\mathrm{kcal\ mol}^{-1} = 39.66 \pm 0.52$. Furthermore, it was shown that the minor product methylenecyclobutene (**3**) and its thermal isomerization product 1,2,4-pentatriene (**6**) result from a heterogeneous side reaction catalyzed by the reaction vessel surface. Ab initio and DFT calculations of the potential energy surface indicate that the isomerization follows an asynchronous reaction path in which two side bonds of the [1.1.1]propellane (**1**) are involved. The activation barrier at the CCSD(T)/6-311G(2d,p)//MP2/6-311G(2d,p) level of theory was calculated as 40.0 kcal/mol.

Introduction

[1.1.1]Propellane, **1**, is one of the most remarkable organic compounds known. It has a central bond weakened by the combined strain of three fused cyclopropane rings and yet it is thermally stable to well over 100 °C. It is somewhat surprising, therefore, that no detailed gas-phase kinetic study of its thermal isomerization has yet been carried out. A product investigation of the thermolysis of **1**, carried out several years ago in a flow system at 430 °C by Belzner and Szeimies,[1] gave dimethylenecyclopropane (**2**) as the major product. Wiberg and Walker[2] had earlier observed that **1** in the gas phase at 114 °C was converted into 3-methylenecyclobutene (**3**), almost certainly in a catalyzed process. In 1986 Pierini and co-workers[3] investigated the thermal isomerization of **1** by ab initio calculations using the PRDDO-RHF method. According to their findings, **1** was converted into **2** via methylenecyclobutylidene (**4**) as an intermediate. The reaction barrier was computed to be 46.3 kcal/mol. In this paper we report a new kinetic study of the thermal isomerization of [1.1.1]propellane (**1**) in a static reactor. In addition, we have tried to obtain some deeper insight into the isomerization process by DFT and ab initio calculations.

Results and Discussion

Rate Measurements. Our kinetic studies were carried out using the internal standard method in which the reactant **1** was co-pyrolyzed together with *n*-pentane as a stable, nonreacting substance in a fixed ratio. Gaseous mixtures containing reactant and internal standard highly diluted in N_2 were prepared and used for the kinetic runs. Checks of the mass balance at various conversions indicated no undetected side reactions (the maximum mass loss observed was 1.2%). The reaction was studied at five temperatures in the range 204−244 °C.



1 **2** **3**

4 **5** **6**

(Numbering of **2** as in **TS2**, and of **4** as in **7**)

The products of the decomposition of **1**, identified by NMR analysis, were dimethylenecyclopropane (**2**) and ethenylidenecyclopropane (**5**) in a ratio of ca. 20:1. In addition, small amounts of methylenecyclobutene (**3**) and 1,2,4-pentatriene (**6**) could be detected in yields each of about 2%.

A set of 5 or 6 runs was carried out for each temperature for times giving between 20% and 80% decomposition of **1**. The initial pressure of the reactant mixture was kept constant at 48 ± 2 Torr. Good linear first-order plots [log(% reactant) versus time] were obtained at all temperatures. Rate constants were calculated by least-mean-squares fitting. The first-order rate constants are shown in Table 1. The data were fitted to the Arrhenius equation to give the following parameters: $\log(A/\mathrm{s}^{-1}) = 14.02 \pm 0.23$; $E_\mathrm{a} = 39.66 \pm 0.52\ \mathrm{kcal\ mol}^{-1}$. The quality of the data may be judged by the relatively small uncertainties in these parameters.

Further Kinetic Tests. Unimolecular rate processes can show characteristic pressure dependencies.[4] In addition, at high temperature, the isomerization of **1** could be affected by free

---

[†] Humboldt University.

[‡] University of Reading.

(1) Belzner, J.; Szeimies, G. *Tetrahedron Lett.* **1986**, 5839−5842.

(2) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239−5240.

(3) Pierini, A. B.; Reale, H. F.; Medrano, J. A. *J. Mol. Struct. (THEOCHEM)* **1986**, *148*, 109−118.

10.1021/ja994043v CCC: $19.00

Table 1. Rate Constants k and Correlation Factors $|r|$

T [°C (K)]	$10^4 k$ [s^{-1}]	$\|r\|$
204.45 (477.6)	0.703 ± 0.005	0.99989
214.45 (487.6)	1.718 ± 0.024	0.99961
224.65 (497.8)	3.99 ± 0.10	0.99882
234.75 (507.9)	8.28 ± 0.04	0.99996
244.75 (517.9)	18.82 ± 0.12	0.99994

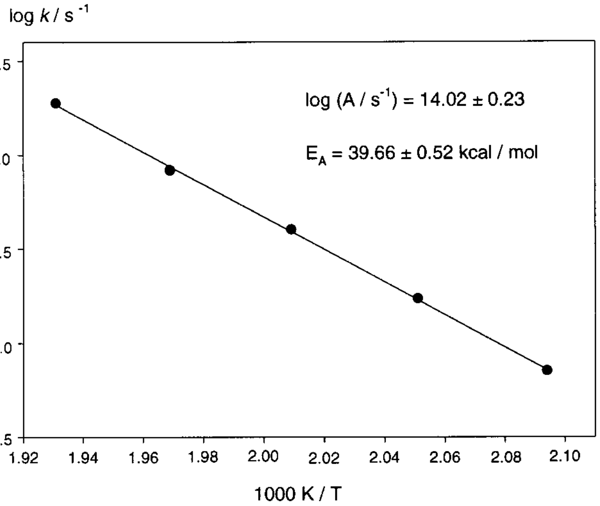
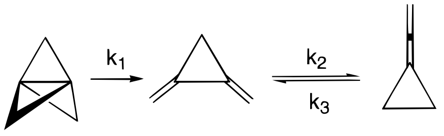


Figure 1. Arrhenius plot of the kinetic data.

radical chain contributions and heterogeneous catalysis. Checks were carried out in this investigation to test whether any of these effects were occurring. For instance, at 224.65 °C in a 30 min run at a total pressure of 48 Torr the conversion of **1** was 52.0%, while the conversion of **1** at a total pressure of 16 Torr was 48.3%. The isomerization of **1** in the presence of a 20-fold excess of propene (used as a radical inhibitor) in 60 min runs at 214.45 °C was 52.1% (49.1% without the inhibitor). Within experimental error, these variations indicate that the isomerization of **1** has only a marginal pressure dependence within the pressures range of study. Furthermore, the lack of inhibition by propene suggests little or no contribution of a free radical process.

Tests for heterogeneity were carried out in a cylindrical vessel, packed with glass tubes (with flame-polished ends). This vessel had a surface-to-volume ratio, S/V, of ca. 11.5 cm^{-1} compared with a value of about 0.7 cm^{-1} in the normal (unpacked) vessel. The packed vessel was conditioned with hexamethyldisilazane prior to use. The reaction of **1** was significantly affected in the packed vessel. The pyrolysis for 60 min at 215.7 °C gave complete conversion of **1**, while in the unpacked vessel under these conditions the conversion was only about 50%. Analysis of the products of the pyrolysis of **1** from a 45 min run in the packed vessel gave the ratio **2**:**5**:**3**:**6** of 26.3:1.6:32.6:39.5. There is thus a dramatic increase of the minor products **3** and **6** which were identified by ^{1}H NMR.[5] Since this finding indicated a considerable heterogeneous contribution, its effect was further investigated, under more controlled conditions, by reducing the vessel packing to about 50% ("half-packed" vessel with a surface-to-volume ratio of ca. 1.5 cm^{-1}). The overall rate constant for the conversion of **1** in the "half-packed" vessel was 3.70×10^{-4} s^{-1} for a 25 min run at 215.7 °C and the yields of **3** and **6** were significantly less.

Scheme 1



1 **2** **5**

Assuming a parallel reaction path for the heterogeneous formation of the products **3** and **6**, the rate constant for the formation of **2** and **5** was calculated as 1.80×10^{-4} s^{-1}. Since the rate constant for the conversion of **1** in the unpacked vessel at 214.75 °C was 1.718×10^{-4} s^{-1}, this suggests that within the experimental error, in the half-packed vessel the formation of **2** and **5** is mainly homogeneous. While we cannot rule out a small surface contribution to the rate, we believe the effect to be minimal in the unpacked vessel.

As far as product formation is concerned, the interesting question arises as to the mode of formation of **2** and **5**: whether they are formed in parallel or sequentially and whether they are in equilibrium as shown in Scheme 1. From the product-time evolution from **1**, the ratio [**2**]/[**5**] stays virtually independent of time, although varying slightly with temperature (see Experimental Section). There is a tendency to higher values of the ratio at the lowest conversion, but since in those runs the yields of **5** were <1% this is probably accidental since the uncertainties are ca. ±0.3% under these conditions. This points to *either* parallel formation *or* sequential formation in which the products are in rapid equilibrium. It is known that **2** can be formed from **5** since it was first synthesized by this route by Conia and co-workers.[6] To test whether **5** is formed from **2** a pyrolysis of **1** was carried out to completion in a flow system at 430 °C, giving a ratio **2**:**5** of 88:12.

The products **2** and **5** were then separated by preparative gas chromatography. Pure **2** was then re-pyrolyzed under the same conditions to yield the same ratio of **2** to **5** of 88:12 (by ^{1}H NMR analysis). This certainly confirms the equilibrium hypothesis at 430 °C and gives $K_{eq} = [\mathbf{5}]/[\mathbf{2}] = 0.136$ which corresponds to $\Delta G^{\theta} = +2.78$ kcal mol^{-1}. The values for the ratio [**5**]/[**2**] formed from **1** in the kinetic experiments lie in the range 0.040−0.056 which would imply $\Delta G^{\theta} = +\ 2.94 \pm 0.10$ kcal mol^{-1} if it represented equilibrium. Since the ΔS^{θ} difference between **2** and **5** is expected to be very small the similarity of these two ΔG^{θ} numbers implies that the ratios at the temperature range 478−518 K must be very close to the true equilibrium value. The only unresolved question is whether the kinetics of $\mathbf{5} \leftrightarrow \mathbf{2}$ is fast enough to satisfy this. There are no secure published rate studies and an independent investigation was beyond the scope of this work; however, Aue and Meshishnek[7] have estimated Arrhenius parameters for step (3) ($\mathbf{5} \rightarrow \mathbf{2}$) from a single temperature rate study which, if correct, would imply that the equilibration of steps (2) ($\mathbf{2} \rightarrow \mathbf{5}$) and (3) should be too slow. This is obviously a reaction system ripe for further study. There remains one further intriguing possibility, viz. that the release of strain energy from **1** results in the initial formation of **2** with enough excess internal (vibrational) energy for direct conversion of **2** to **5** prior to collisional deactivation. In that case the formation of **5** should be quenched at high pressure. There is some indication that yields of **5** decrease with pressure (see Experimental Section) but a systematic investigation was not attempted. This phenomenon has been observed in the thermal rearrangements of other highly strained hydrocarbons

---

(4) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions;* Wiley: New York, 1972. Holbrook, K. A.; Pilling, M. J.; Robertson, S. H. *Unimolecular Reactions*, 2nd ed.; Wiley: Chichester, 1996.

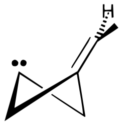
(5) Pasto, D. J.; Kong, W. *J. Org. Chem.* **1989**, *54*, 4028−4033.

(6) (a) Bloch, R.; Le Perchec, P.; Conia, J.-M. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 798. (b) LePerchec, P.; Conia, J.-M. *Tetrahedron Lett.* **1970**, 1587−1590.

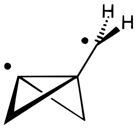
such as cubane[8] and cuneane.[9] Thus, although not completely conclusive, the evidence suggests that the mechanism of product formation in Scheme 1 is probably correct.

Ab Initio and DFT Calculations

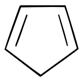
Computational methods were used to learn more about the details of the thermal isomerization of [1.1.1propellane (**1**). Does the thermal conversion of propellane **1** into **2** proceed in one step, or are one or more intermediates involved in the isomerization process? Carbene **4**, as already suggested,[3] the puckered carbene **7a** or biradical **7b** could be possible candidates as intermediates.



7a



7b



8

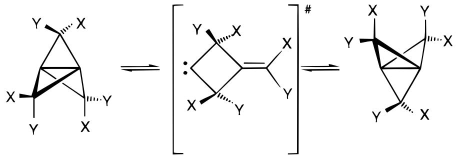
Computational Methodology. Throughout, the Gaussian 94 and Gaussian 98[10] program packages have been used. Specifically, DFT methods with the three-parameter hybrid functionals of Becke[11] and the correlation functional of Lee, Yang, and Parr[12] (B3LYP) and the correlation functional of Perdew and Wang[13] (B3PW91) have been applied with the basis sets 6-311G(d,p) and D95(d,p).[14] In addition to the DFT calculations, geometry optimization was carried out at the MP2 and QCISD level of theory with the basis sets 6-311G(2d,p) and 6-31G(d). Finally, the energies of the MP2 stationary points were calculated by the CCD(T)/6-311G(2d,p) method and the energies of the QCISD stationary points by the QCISD(T)/6-311G(d,p) procedure. The stationary points were characterized by frequency calculations as either local minima or first-order saddle points. The electronic energies were corrected for zero-point energies. The calculated zero-point energies were not scaled.

The DFT calculations of the stationary points connecting **1** and **2** were carried out in the spin restricted and spin unrestricted mode. Starting at $\langle S^2 \rangle = 1.00$, the latter converged to $\langle S^2 \rangle = 0.0$, leading to the same result as the restricted formalism. This would indicate that the diradical character of the stationary points, specifically of **7**, should be marginal. To provide greater flexibility for the wave functions of the stationary points, CASSCF(6,6)/6-311G(d,p) calculations were also performed. For **1**, the orbitals of the central CC bond and of the two breaking CC side bonds and their antibonding counterparts were chosen as the active space. The active space of **TS1**, **7**, and **TS2** was constructed from the orbitals related to the those of the active space of **1**.

Results and Discussion

Apart from the reactant **1** and the product **2**, three further stationary points were found on the potential energy surface by the DFT methods. These stationary points correspond to one local minimum of structure **7** and to two transition states **TS1**, **TS2**. IRC calculations at the B3PW91/95D level of theory showed that **7** is linked to the reactant **1** with **TS1** and to the product **2** with **TS2**. The search for stationary points with the QCISD/6-31G(d) formalism did not lead to **7** as an intermediate; **1** and **2** were directly connected with **TS2**. Planar carbene **4** is not a local energy minimum. At the B3LYP/6-311G(d,p)// B3LYP/6-311G(d,p) and B3PW91/D95(d,p)// B3PW91/D95-(d,p) and also on the QCISD/6-31G(d)//QCISD-6-31G(d) level of theory planar **4** is a transition state, not related to product **2**. **4** could be regarded as the transition state for a thermal stereomutation process converting propellane of type **1a** into its stereoisomer **1b** as indicated in Scheme 2.

Scheme 2



1a **1b**

At the B3PW91/6-311G(d,p)//B3PW91/6-311G(d,p) and MP2/6-311G(2d,p)//MP2/6-311G(2d,p) level of theory **4** was characterized as a second-order saddle point. Relative energies (kcal/mol) of the stationary points with respect to **1** are given in Table 2.

The CAS(6,6)/6-311G(d,p) calculations led to similar results as the DFT calculations. Again, a local minimum **7** was located between **1** and **2**, and the second transition state **TS2** was higher in energy than **TS1**.

Structures. The structure of [1.1.1]propellane (**1)** has been determined experimentally[15] and has been calculated at several levels of theory.[16] The most interesting structural feature, the length of the C1−C3 bond of **1**, is computed slightly too short by the DFT methods and CAS(6,6), but is satisfactory at the MP2/311-G(2d,p) and QCISD/6-31G(d) level of theory. Selected structural data of **1** and of **2**, for which experimental values are not available, are given in the Supporting Information.

The structure (B3PW91/D95(d,p)) of intermediate **7** is depicted in Figure 2, which also shows some structural parameters. The calculations were carried out without symmetry restriction; **7** shows C_s symmetry.

Although structure **7** is reminiscent of the bicyclo[1.1.0]butane framework, some structural features deserve attention. At 1.339−1.350 Å, the C1−C2 bond is very short and close to the length of a CC double bond. The dihedral angle C4−C1−C3−C5 is similar to the one in bicyclo[1.1.0]butane (122.7°[17]), but the angle C2−C1−C3 is much greater (about 170° for **7)** than H−Cl−C3 for bicyclo[1.1.0]butane[14] (128.4°). A better model for the structure of **7** is probably an internal complex of carbene **4** with the CC double bond. A NBO analysis[18] of **7** showed two nonbonding orbitals at C3, one orbital empty and

---

[7] Aue, D. H.; Meshishnek, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 223−231.

[8] Martin, H.-D.; Urbanek, T.; Pföhler, P.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1985**, 964.

[9] Hassenrück, K.; Martin, H.-D.; Walsh, R. *Chem. Ber* **1988**, *121*, 369.

[10] Gaussian 98, Revision A.3, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1998.

[11] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

[12] Lee, C. L.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

[13] Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B45*, 13244.

[14] Huzinaga, S. J. *J. Chem. Phys.* **1965**, *42*, 1293−1302. Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823−2833. Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716−723.

[15] Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 7257−7260.

[16] Adcock, W.; Brunger, M. J.; Clark, C. I.; McCarthy, I. E.; Michalewicz, M. T.; von Niessen, W.; Weigold, E.; Winkler, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 2896−2904, and references therein. See also: Zerbetto, F. *Chem. Phys. Lett.* **1995**, *241*, 445−449. Lammertsma, K.; Guner, O. F.; Sudakar, P. V. *J. Chem. Phys.* **1991**, *94*, 8105−8111.

[17] Harmony, M. D.; Cox, K. W. *J. Am. Chem. Soc.* **1966**, *88*, 5049. Cox, K. W.; Harmony, M. D.; Nelson, G.; Wiberg, K. B. *J. Chem. Phys.* **1969**, *50*, 1976.

[18] Glending, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO Version 3.1*, implemented in Gaussian 98. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

Table 2. E_{rel} (kcal/mol) with Respect to **1** of **2**, **7**, **TS1**, **TS2**, **4**, and **8**, Corrected for ZPE's[a]

	B3LYP/ 6-311G(d,p)	B3PW91/ 6-311G(d,p)	B3PW91/ D95(d,p)	MP2/ 6-311G(2d,p)	QCISD/ 6-31G(d)	QCISD(T)/ 6-311G(d,p)[b]	CCSD(T)/ 6-311G(2d,p)[c]	CAS(6,6) 6-311G(d,p)
2	−21.58	−14.62	−11.01	−4.32	−12.20	−9.15	−11.99	
7	31.41	35.65	37.86	43.64			38.39	27.96
TS1	31.94	36.99	38.73	45.53			36.85	40.26
TS2	32.69	37.89	40.60	45.73	44.45	42.44	39.96	42.14
4	32.39	39.57	39.77	51.42	38.30	41.25	37.34	
8	−61.05	−55.3	−53.3	−51.4	−56.2	−53.1	−57.9	

[a] See Supporting Information for total energies and ZPE's. [b] Energies corrected for ZPE (QCISD/6-31G*). [c] Energies corrected for ZPE (MP2/6-311G(2d,p)).

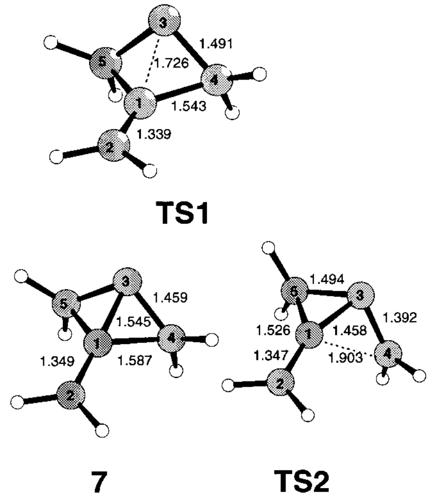


Figure 2. B3PW91/D95(d,p) Structures of **TS1**, **7**, and **TS2** (bond length in Å).

one doubly occupied. The empty orbital overlaps with the π orbitals of the C1−C2 double bond and the short C1−C3 distance is the result of this strong orbital interaction. In addition, a second interaction of the empty p orbital with the C1−C4 bond and the C1−C5 bond can be seen in the NBO analysis, which leads to the elongation of these bonds. This analysis is strongly in favor of carbene structure **7a** over the diradical structure **7b**. A related interaction has been found when the rearrangement of cyclobutylidene to methylenecyclopropane was analyzed by computational methods.[19,20]

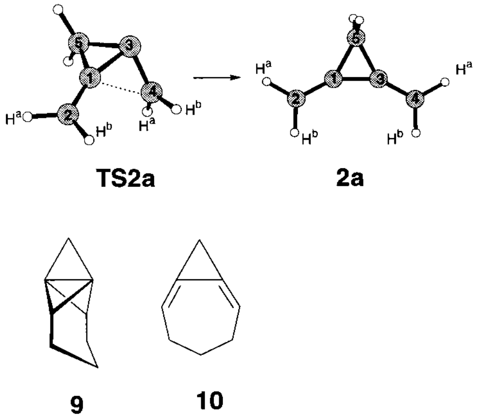
The CAS(6,6)/6-311G(d,p) structure of **7** differs substantially from the DFT structures of **7**. Specifically, the distance C1−C3 is much larger and the four-membered ring is less puckered. Therefore, the CAS structure of **7** clearly shows the carbene nature of this intermediate and is further evidence of **7a** versus **7b** (for details see Supporting Information).

The search for a transition structure between **1** and **7** led to **TS1**, which is also depicted in Figure 2. **TS1** also shows C_s symmetry. The C1−C3 distance is longer and the C1−C2 bond slightly shorter than in **7**. Also, the angle C2−C1−C3 is smaller than that in **7**.

Again, the CAS(6,6)/6-311G(d,p) structure of **TS1** differs from the DFT structures, specifically the angle C2−C1−C3 is much smaller within the CAS structure, indicating an earlier transition state (see Supporting Information).

The transition structure **TS2** is nonsymmetric. Some structural parameters are given in Figure 2. C1−C2 and C3−C4 are considerably shortened and C1−C4 is going to be completely broken. It should be noticed that at the QCISD/6-31G(d) level of theory **TS2** is the only stationary point we could find between **1** and **2**. For **TS2**, the CAS(6,6) structure differs only slightly from the DFT structures.

Scheme 3



An interesting feature, not yet tested experimentally, is the motion of C4 of **TS2**. According to the IRC calculation, **TS2a** leads to **2a** as depicted in Scheme 3. This mode of ring-opening is consistent with the observation by Belzner and Szeimies[1] that bridged propellane **9** on thermolysis gives diene **10**.

Energies. The E_{rel} values of Table 2 reveal that the thermal isomerization of **1** into **2** proceeds, according to the applied DFT methods and at the MP2/6-311(2d,p) level of theory, via the intermediate **7a**. Our results at these levels show that **7a** is in a shallow local energy minimum. The barrier of **7a** back to **1** ranges from 0.5 to 1.9 kcal/mol, the barrier of **7a** to **2** ranges from 1.3 to 2.7 kcal/mol. However, we cannot be sure if these barriers are real, because at the QSISD/6-31G(d) level of theory, **7a** is not a local minimum and the reaction **1** → **2** could be regarded as concerted but strongly asynchronous, passing through **TS2** as the transition state. This view is further supported by the results of the single-point CCSD(T)/6-311G-(2d,p) calculations, carried out for the stationary points of MP2/6-311G(2d,p) structures. At this level of theory the barrier of **7a** → **1** vanishes. The thermal isomerization of **1** → **2** seems to be related to the thermal isomerization of bicyclo[1.1.0]butane giving 1,3-butadiene, which has been analyzed thoroughly by Nguyen and Gordon,[21] and shown also to proceed concertedly, but strongly asynchronously.

The CAS(6,6) results place **7a** only 28 kcal/mol above **1** (see Table 2). At 42.1 kcal/mol, the total barrier of the isomerization of **1** → **2** is comparable to the DFT results.

The experimental value of $E_{\mathrm{A}} = 39.6$ kcal/mol for the thermal isomerization of **1** → **2** is, for the most part, well reproduced by our calculated barriers (see Table 2). The highest level ab initio methods, QCISD(T)/6-311 g(d,p)//QCISD/6-31G(d) and CCSD(T)/6-311G(2d,p)//MP2/6-311G(2d,p), give barriers of

---

(19) Schoeller, W. W. *J. Am. Chem. Soc.* **1979**, *101*, 4811−4815.

(20) Sulzbach, H. M.; Platz, M. S.; Schaefer, H. F., III; Hadad, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 5682−5689.

(21) Nguyen, K. A.; Gordon, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 3835−3847. See also: Shevlin, P. B.; McKee, L. *J. Am. Chem. Soc.* **1988**, *110*, 1666−1671.

42.4 and 40.0 kcal/mol. The DFT methods B3PW91/D95(d,p)//B3PW91/D95(d,p) and B3PW91/6-311G(d,p)//B3PW91/6-311G-(d,p) show barriers of 40.6 and 37.9 kcal/mol and deviate only marginally from the experimental barrier. The CAS(6,6) calculations gave a barrier of 42.1 kcal/mol. At 32.7 kcal/mol, the B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p) barrier shows the least agreement with the experimental value. To trace the cause for this unexpected deficiency, we have calculated the relative energies of cyclopentadiene (**8**), a further isomer of **1**. In the last line of Table 2, the energy difference $\Delta E(\mathbf{1}-\mathbf{8})$ (kcal/mol) is given. The experimental value is (-52.0 ± 1) kcal/mol.[22,23] Again, the B3LYP/6-311G(d,p) value gives the poorest agreement. This demonstrates that the B3LYP/6-311G(d,p) procedure leads to a poor estimate of the total energy of [1.1.1]propellane (**1**) relative to the results of the other procedures used in this study.

Comparing the E_{rel} values of Table 2 of **TS2** and of the planar 3-methylenecyclobutylidene (**4**), it is seen that the higher level ab initio methods show a slightly higher barrier for the isomerization of **1** → **2** than for the stereomutation **1a** → **1b** (see Scheme 2). This finding should encourage experimental efforts toward the detection of this process.

Conclusion

The thermal isomerization of [1.1.1]propellane (**1**) with an activation energy of 39.6 kcal/mol leads to dimethylenecyclopropane (**2**), which in the temperature range of 205−245 °C appears to be in equilibrium with ethenylidenecyclopropane (**5**). Investigation of the thermal isomerization **1** → **2** by ab initio methods suggests a mechanism in which two side-bonds of **1** are broken strongly asynchronously. DFT methods locate a species **7** as an intermediate, formed by the breaking of one exocyclic C−C bond and therefore notionally a biradical **7b**. The calculations, however, suggest that **7** is better regarded as **7a**, an internal complex of a carbenic center with the exocyclic C═C double bond at the opposite carbon of the four-membered ring. Most of the computational methods showed that planar 3-methylencyclobutylidene (**3**) is a transition state for a degenerate rearrangement of [1.1.1]propellane (**1**), which could possibly be observed experimentally with a properly substituted model compound.

Experimental Section

Kinetic Measurements. Apparatus: The apparatus, procedures, data acquisition, and analysis methods have been described earlier.[24−26] Gases were handled in conventional grease-free vacuum systems made from Pyrex with Youngs stopcocks. The reaction vessel used for most experiments was spherical (volume ca. 170 mL); it was placed in a stirred salt ($NaNO_2/KNO_3$ eutectic) thermostat controlled by an AEI (GEC) RT5 controller. Temperatures were measured with a Pt/Pt−13% Rh thermocouple calibrated against a precalibrated Pt resistance thermometer (Tinsley, Type 5187 SA). Pressures were measured with a conventional Hg manometer. The reaction vessel was conditioned with hexamethyldisilazane (HMDS) every five runs.

Analysis: Product identities (**2**,[1,6a] **4**,[6b] **5**, and **6**[5]) were confirmed by ^{1}H and ^{13}C NMR spectra on isolated samples after pyrolysis. Quantitative product analyses were made by gas chromatography (Perkin-Elmer 8310) with FID detection and electronic peak integration (Hewlett-Packard HP 3380 A). A Silicon Oil MS550 column on Chromosorb W operated at 35 °C was used to separate the products.

Experimental procedure: Solvent free [1.1.1]propellane (**1**) was prepared by reaction of 1,3-diiodobicyclo[1.1.1]pentane with sodium cyanide in dimethyl sulfoxide.[27] The reaction of **1** was studied using an internal standard chosen for stability and analytical convenience. The reactant master mixture consisted of about 1.9% of **1** and 1.9% of *n*-pentane diluted to about 600 Torr with N_2. Runs were carried out by admitting a known pressure of the master mixture into the reaction vessel for a certain time (2.5 to 320 min). The reaction was quenched by sharing the reaction vessel contents with a preevacuated sample bulb, from which samples could be injected into the gas chromatograph. After every run a blank analysis was made of the unused master mixture to check the mass balance of the reaction. Blank analyses showed no deterioration or loss of GC signal of **1** during the course of this study. The analytical results at each temperature are shown in the Supporting Information.

Acknowledgment. This investigation was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

Supporting Information Available: Energies and ZPE's of **1**, **2**, **7**, **TS1**, **TS2**, **4**, and **8** (au); selected structural data of **1**, **2**, **7**, **TS1**, **TS2**, and **4**; product distributions of the kinetic runs as a function of time at five temperatures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA994043V

---

[22] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970. Pedley, J. B.; Naylor, R. B.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London 1986. See also: Roth, W. R.; Adamczak, O.; Breuchmann, R.; Lennartz, H.-W.; Böse, R. *Chem. Ber.* **1991**, *124*, 2499−2521.

[23] Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *J. Am. Chem. Soc.* **1985**, *107*, 7247−7257.

[24] Hopf, H.; Wachholz, G.; Walsh, R. *Chem. Ber.* **1985**, *118*, 3579−3587.

[25] Hopf, H.; Wachholz, G.; Walsh, R. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1103−1106.

[26] Hopf, H.; Plagens, A.; Walsh, R. *Liebigs Ann.* **1996**, 825.

[27] Alber, F.; Szeimies, G. *Chem. Ber.* **1992**, *125*, 757−758.