

# Thermal Rearrangements of Bicyclopropylidene and Substituted Bicyclopropylidenes – A Gas Phase Kinetic and Product Study<sup>[‡]</sup>

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*Dedicated to Professor Barry M. Trost on the occasion of his 60th birthday*

**Keywords:** Bicyclopropylidene / High-temperature chemistry / Radical reactions / Rearrangements / Small ring systems

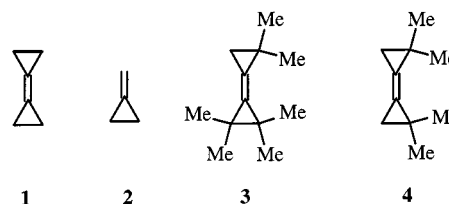
The gas phase thermal rearrangement of bicyclopropylidene (**1**) has been studied, and the pressure-independent Arrhenius parameters determined as  $\log(k/s^{-1}) = (14.02 \pm 0.33) - (39.2 \pm 0.7) \text{ kcal} \cdot \text{mol}^{-1} / RT \cdot \ln 10$ , almost the same as those for methylenecyclopropane (**2**). Thus, the second cyclopropane ring in **1** exerts virtually no influence on the kinetics of the thermal rearrangement of one of its methylenecyclopropane subunits. The rearrangement of **1** to methylenespiropentane (**5**) was found to be reversible, with an equilibrium composition at 230 °C of 1:166. These findings are discussed and accounted for. When heated to 350 °C in a flow system, **1** undergoes a clean rearrangement to **5** [90% yield,  $\geq 95\%$  purity on a preparative scale (17.4 g)]. Allyl- (**7**), ethenyl- (**9**), and (*E*)-(2-methoxycarbonylphenyl)bicyclopropylidene (**10**) were

prepared from **1** in 50, 45, and 69% overall yields, respectively. The thermal rearrangements of **9** and **10** proceeded smoothly at 150–160 °C, resulting in the formation of 4-methylenespiro[2.4]hept-5-ene (**14**) and its derivative **17** in 79 and 50% isolated yields, respectively, as the sole products, while the rearrangement of **7** required higher temperatures (200 °C) and resulted in a complex mixture of isomeric substituted methylenespiropentanes **18**–**20**. Under flash vacuum pyrolysis conditions at 550 °C, the methylenespiroheptene **14**, initially formed from **9** via 1-methylene-2-vinylspiropentane (**13**), underwent a further vinylcyclopropane-to-cyclopentene rearrangement to yield a 1:1 mixture of the isomeric tetrahydropentalenes **15** and **16**. This constitutes a novel and easy access to the tetrahydropentalene skeleton.

## Introduction

Because of its unique reactivity, bicyclopropylidene (**1**),<sup>[1]</sup> has developed into a versatile, multifunctional C<sub>6</sub> building block for organic synthesis, especially since it has become readily available in multigram quantities.<sup>[2]</sup> In planning any synthetic transformation of bicyclopropylidene that would require thermal activation, however, one has to bear in mind that this molecule is a methylenecyclopropane derivative and as such can rather easily undergo a rearrangement that is not degenerate like that of the parent methylenecyclopropane (**2**), but produces the isomer methylenespiropentane (**5**).<sup>[3]</sup> The thermally and photochemically induced rearrangements of **2** and its ordinary derivatives have been investigated in great detail both from mechanistic<sup>[4]</sup> and

from preparative<sup>[5]</sup> points of view. However, mechanistically oriented studies of bicyclopropylidene (**1**) have been performed mainly with substituted derivatives. Crandall et al. were the first to show that the hexamethylbicyclopropylidene **3** rearranges at 400 °C in a flow pyrolysis system to yield a 10:1 mixture of two isomeric hexamethylmethylenespiropentanes<sup>[6]</sup> formed through trimethylenemethane diradical intermediates.



Analogous transformations have been reported for the tetramethylbicyclopropylidene **4**,<sup>[7]</sup> a dichlorotetramethylbicyclopropylidene,<sup>[8]</sup> and 1,1-dideuteriobicyclopropylidene.<sup>[9]</sup> The mechanistic and kinetic aspects of these rearrangements have been reviewed, together with subsequent transformations of the resulting methylenespiropentane into dimethylenecyclobutane derivatives at higher temperatures.<sup>[10]</sup> As a rule,<sup>[1,11]</sup> although with several exceptions,<sup>[12]</sup> the thermal rearrangements of functionally substituted bicyclopropylidenes yield mixtures of compounds. As far as

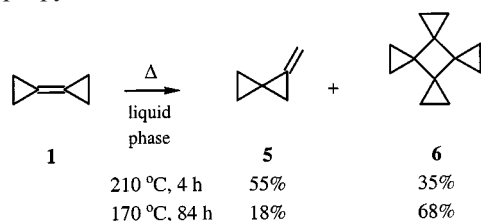
[‡] Cyclopropyl Building Blocks for Organic Synthesis, 71. – Part 70: S. Löhre, A. de Meijere, Synlett 2001, 489–492. – Part 69: K. Miyazawa, D. Demus, A. de Meijere, Mol. Cryst. Liq. Cryst., in press

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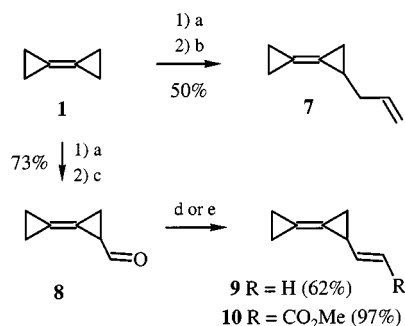
bicyclopopylidene (**1**) itself is concerned, the two thoroughly investigated reactions are the ring-opening of the radical cation generated from **1**, to give the tetramethylenecyclobutane radical cation,<sup>[13]</sup> and the low-temperature, bromine-promoted photolytic isomerization of **1** to 1,2-dimethylenecyclobutane with the intermediate occurrence of the tetramethylenecyclobutane tetraradical.<sup>[14]</sup> Although it is known qualitatively that unsubstituted **1**, when heated either as a pure compound in a closed vessel<sup>[3b]</sup> or in solution (50% in toluene),<sup>[15]</sup> forms not only the expected methylenespiropentane (**5**) (55–18%), but also a substantial proportion of the dimer [4]rotane (**6**) (35–68%, for a possible mechanism of its formation see ref.<sup>[16]</sup>) (Scheme 1), no kinetic studies have been reported. We have therefore analyzed the thermal rearrangement of **1** in the gas phase, both quantitatively and qualitatively, in order to make it more reasonably applicable in the design of new approaches to certain carbon frameworks. With this purpose in mind, we also studied the isomerization reactions of several new monosubstituted bicyclopopylidene derivatives in solution.



Scheme 1. Known thermal transformations of bicyclopopylidene (**1**)

## Results and Discussion

Bicyclopopylidene (**1**) was prepared according to the recently published procedure.<sup>[2b]</sup> Monosubstituted derivatives can easily be obtained from bicyclopopylidene (**1**) by deprotonation with *n*-butyllithium in tetrahydrofuran at 0 °C and electrophilic substitution of the formed lithiobicyclopopylidene with appropriate reagents.<sup>[17]</sup> Using this route, allyl- (**7**) and formylbicyclopopylidene (**8**) were prepared in 50 and 73% yields by trapping with allyl bromide and dimethylformamide, respectively (Scheme 2).



Scheme 2. Preparation of substituted bicyclopopylidenes. a) *n*BuLi, THF, 0 °C, 1 h; b) allyl bromide, −78 → 20 °C; c) DMF, 0 → 20 °C, 1 h; d) NaH, DMSO, 70 °C, 45 min, then  $\text{Ph}_3\text{P}^+\text{CH}_3\text{Br}^-$ , 20 °C, 50 min, then **8**, 20 °C, 50 min; e)  $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Me}$ ,  $\text{CH}_2\text{Cl}_2$ , 20 °C, 24 h

Wittig olefination of the aldehyde **8** with the ylide generated from methyltriphenylphosphonium bromide and dimethylsodium in DMSO or with (methoxycarbonyl)methylene-triphenylphosphorane in  $\text{CH}_2\text{Cl}_2$  furnished the ethenyl-substituted bicyclopopylidenes **9** and **10** in 62 and 97% yields, respectively.

Samples of bicyclopopylidene (**1**) were pyrolyzed in the gas phase as mixtures with 1% of *n*-hexane (as internal standard) and 98% of nitrogen at five different temperatures in the 200–240 °C region. To check that the reaction was really first order and not in the “fall-off” range at the reactor pressure of  $p_i = 30\text{--}40$  Torr, and also to rule out any participation of a radical chain mechanism in the isomerization of **1** to **2**, the rearrangement was also performed under different pressures, with different reactor surface areas, and in the presence of *cis*-butene as a radical inhibitor. The results are shown in Tables 2 and 3 (see Exp. Sect.). For the data listed in Table 2, good linear first order plots [ $\log(\%1)$  versus time] were found at all temperatures, and rate constants  $k$  were obtained by least-mean-squares fitting (Table 1). These data produced the Arrhenius parameters presented in [Equation (1)].

Table 1. Variation of rate coefficients  $k$  with temperature for the thermal rearrangement of bicyclopopylidene (**1**)

$T$ [°C]	200.0	209.5	220.1	230.0	240.0
$10^4 k$ [s <sup>−1</sup> ]	0.792	2.024	4.489	9.581	21.578

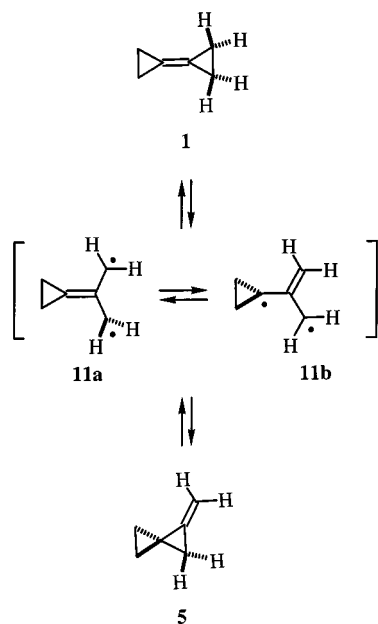
$$\log(k/\text{s}^{-1}) = (14.02 \pm 0.33) - (39.2 \pm 0.7) \text{ kcal} \cdot \text{mol}^{-1} / RT \cdot \ln 10 \quad (1)$$

To check for the reversibility of the rearrangement, a sample of **1** was kept at 230 or 240 °C for 80 and 40 half-life periods, respectively. Subsequent GC analyses (column DE 117) showed that 0.6 and 0.2% of **1** were still present. This rearrangement must therefore genuinely be reversible, albeit with the equilibrium far on the side of methylenespiropentane (**5**). To rule out any mistakes arising from the occasional presence of impurities in the starting material, the GC analyses were repeated with the phase OV 101. Because of the difficulty in determining the small concentrations of **1** in the equilibrium mixture with high precision, it is not possible to calculate the exact equilibrium constants, but the results obtained provided a rough estimate of them as  $K = 166$  at 230 °C or  $K = 499$  at 240 °C.

Taking the 230 °C value to be the more reliable, this corresponds to  $\Delta G^\circ = -5.1 \text{ kcal} \cdot \text{mol}^{-1}$ . With a symmetry factor of 4 (corresponding to  $\Delta S^\circ = 2.75 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) favoring the reaction, this implies  $\Delta H^\circ = -3.7 \text{ kcal} \cdot \text{mol}^{-1}$ . Even with the alternative value for  $K$  (240 °C), this would only change slightly to  $-4.9 \text{ kcal} \cdot \text{mol}^{-1}$ . This indicates a small, but definitive, exothermicity of ca.  $4 \text{ kcal} \cdot \text{mol}^{-1}$  in the rearrangement of **1** to **5**.

The factor  $A$  is reasonable for this type of rearrangement (Scheme 3) and is close to that for 2-methylmethylenecyclopropane isomerization.<sup>[18]</sup> The  $E_a$  value of  $39.2 \text{ kcal} \cdot \text{mol}^{-1}$

is essentially the same as those reported for tetramethylbicyclopropylidene (**4**) ( $38.9 \text{ kcal}\cdot\text{mol}^{-1}$ )<sup>[6]</sup> and for 2-methylmethylenecyclopropane ( $40.4 \text{ kcal}\cdot\text{mol}^{-1}$ ).<sup>[18]</sup> It is also very close to the value of  $39.9 \text{ kcal}\cdot\text{mol}^{-1}$  computed for parent methylenecyclopropane (**2**) at the CASPT2/6-31G level of theory.<sup>[4a]</sup> This indicates that, compared with **2**, there is no effect on the kinetics of rearrangement of **1** exerted by the second cyclopropane ring attached to the double bond in **1**. This might appear surprising, given that the strain energy of **1** is about  $36 \text{ kcal}\cdot\text{mol}^{-1}$  greater in **1** than **2**.<sup>[1b,19]</sup> The essential point, however, would appear to be that the strain energy of the second methylenecyclopropane system in **1** is locked into the reaction both in the initially formed biradical intermediate **11a**, and also in the methylenespiropentane product **5**.



Scheme 3

In addition, and unlike the case of methylenecyclopropane (**2**) itself,<sup>[4]</sup> the orthogonal trimethylenemethane (TMM) diradical intermediate produced from bicyclopropylidene (**1**) first of all (species **11a**) is not identical to the alternative structure (**11b**) formed by  $90^\circ$  rotation of its methylene group; nevertheless the energies are probably close, since **11b** has the high-energy cyclopropyl radical center. In any case, to form methylenespiropentane (**5**), **11b** would have to close to reform the second three-membered ring, which would reestablish the methylenecyclopropane strain.<sup>[20]</sup>

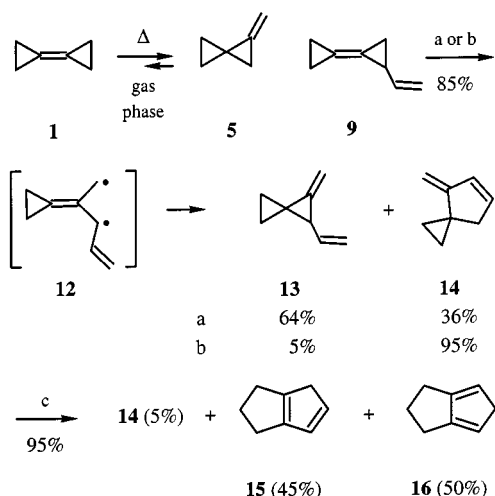
Concerning the overall thermodynamics of the rearrangement **1**  $\rightarrow$  **5**, the exothermicity of ca.  $4 \text{ kcal}\cdot\text{mol}^{-1}$  demonstrates that the spiro linkage in **5** is slightly less strained than the *exo* double bond to the second cyclopropane in **1**. Additivity estimates<sup>[15,19]</sup> give a value for the spiro strain (in spiro-pentane) of  $63.5 - (2 \times 27.6) = 8.3 \text{ kcal}\cdot\text{mol}^{-1}$  and the *exo*-methylene strain [in methylenecyclopropane (**2**)] of  $41.0 - 27.6 = 13.4 \text{ kcal}\cdot\text{mol}^{-1}$ , in very good agreement with the findings of this work. These findings are also reas-

onably well supported by recent experimental values of  $\Delta H_f^\circ(\mathbf{1}) = 77.4 \text{ kcal}\cdot\text{mol}^{-1}$  <sup>[22]</sup> and  $\Delta H_f^\circ(\mathbf{5}) = 75.5 \text{ kcal}\cdot\text{mol}^{-1}$ .<sup>[23]</sup> A theoretically calculated value of  $\Delta H_f^\circ(\mathbf{1}) = 75.5 \text{ kcal}\cdot\text{mol}^{-1}$  <sup>[24]</sup> looks slightly low. These results also help to explain the controversy concerning reversibility in the bicyclopropylidene-to-methylenespiropentane system. Thus, the photoinitiated reorganizations of 2,2-diarylmethylenespiropentanes to 2,2-diarylbicyclopropylidenes<sup>[14b]</sup> appear to imply reversibility, whereas the biradicals implicated in the rearrangement of **5** by cleavage of cyclopropane C–C bonds have been shown to rearrange to tetramethylenethane, which collapses to form a mixture of 1,2- and 1,3-dimethylenecyclobutanes.<sup>[6b][7a,25]</sup> This work shows that the equilibrium concentration of **1** formed from **5** is less than 1%. Hence, in the thermal studies cited above, although **5** would be expected to give rise to **1**, it would almost certainly have passed unnoticed. In the photochemically rearranging systems, thermodynamic limitations can be overcome by the light flux.

As far as the practical application of this rearrangement to production of methylenespiropentane (**5**) as a building block for organic synthetic applications was concerned,<sup>[26]</sup> the conditions for it to occur cleanly and rapidly needed to be optimized. When heated to  $230^\circ\text{C}$  in a flow system, bicyclopropylidene (**1**) did not isomerize, but at  $350^\circ\text{C}$  it underwent a clean rearrangement to methylenespiropentane (**5**), which was obtained in 90% yield and in  $\geq 95\%$  purity on a preparative scale (17.4 g) (see Exp. Sect.). In view of the ready availability of **1**,<sup>[2]</sup> this rearrangement constitutes the most convenient preparative approach to **5**, in comparison to the two known traditional syntheses.<sup>[7a,27]</sup>

The vinyl substituent in ethenylbicyclopropylidene (**9**) dramatically facilitates the thermal methylenecyclopropane rearrangement of the bicyclopropylidene unit in **9**, in comparison with that of the parent hydrocarbon **1** and to those of bicyclopropylidene derivatives with electron-withdrawing substituents.<sup>[11,12]</sup> This is of course a consequence of conjugative stabilization by the vinyl group of the trimethylenemethane intermediate **12** (Scheme 4), in close analogy to what had been observed previously for 2-ethenylmethylenecyclopropane.<sup>[28]</sup>

When heated at  $100^\circ\text{C}$  for 1 h, ethenylbicyclopropylidene (**9**) completely rearranged to give a mixture of 2-ethenyl-1-methylenespiropentane (**13**) and 4-methylenespiro[2.4]hept-5-ene (**14**) in a ratio of 1.75:1. Thus, special precautions must be taken to prevent its isomerization when ethenylbicyclopropylidene (**9**) is isolated on a preparative scale (see Exp. Sect.). The methylenespiroheptene **14** apparently arises from a vinylcyclopropane-to-cyclopentene rearrangement<sup>[29]</sup> in the initially formed **13**; this is also dramatically facilitated thanks to the strained structure of **13**. The first-order rate coefficient calculated from the kinetic curve for the disappearance of **9** measured at  $100^\circ\text{C}$  in  $10^{-1} \text{ mol}\cdot\text{L}^{-1}$  benzene solution (see Exp. Sect.) is  $k_1 = (1.45 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ . Upon prolonged heating (3.5 h) at a temperature of  $150^\circ\text{C}$ , **9** was converted virtually quantitatively (via **13**) into **14**, and these conditions may actually be applied for preparative purposes. At higher temperatures ( $550^\circ\text{C}$  in a flash



Scheme 4. Thermal rearrangement of bicyclopropylidene (**1**) and ethenylbicyclopropylidene (**9**): a)  $\text{C}_6\text{H}_6$ , 100 °C, 1 h; b)  $\text{C}_6\text{H}_6$ , 150 °C, 3.5 h; c) FVP, 550 °C, 0.1 Torr

vacuum pyrolysis set-up), **14** underwent a further vinylcyclopropane-to-cyclopentene rearrangement, ultimately to yield a 1:1 mixture of the two isomeric tetrahydropentalenes **15** and **16**<sup>[30]</sup> (Scheme 3). Since the position of the endocyclic methylene group in **14** could not be established unambiguously on the basis of its NMR spectroscopic data, its structure was determined by X-ray crystal structure analysis (Figure 1).<sup>[31]</sup>

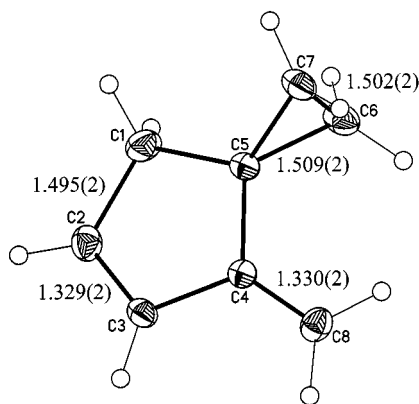
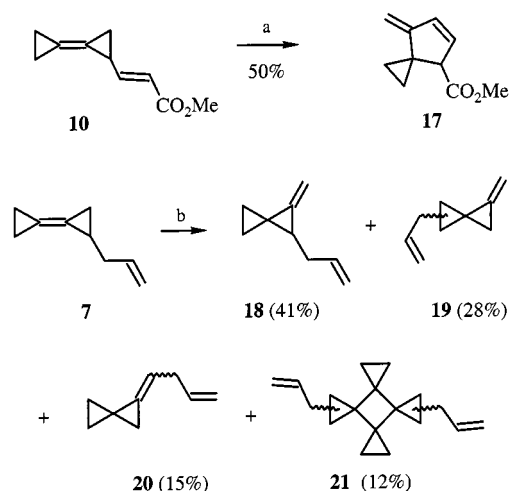


Figure 1. Structure of 4-methylenespiro[2.4]hept-5-ene (**14**) in the crystal;<sup>[31]</sup> the bond lengths and standard deviations are given in Å

The methoxycarbonyl-substituted ethenylbicyclopropylidene **10** behaved in the same way as **9**. After attempted purification of **10** by distillation under reduced pressure at 70 °C, the distillate was found to be contaminated with up to 10% of the rearranged product **17** (the methylenespiropentylacrylate analogous to the primary rearrangement product **14** from **9** was detected only in trace amounts), while heating of **10** at 160 °C for 1 h resulted in complete isomerization to **17** (50% isolated yield) (Scheme 5).

The allylbicyclopropylidene (**7**), in which the allyl group cannot stabilize any initial trimethylenemethane intermediate, undergoes rearrangement only at significantly higher temperatures, just as ethyl bicyclopropylidenecarboxylate does,<sup>[11]</sup> but far less selectively. When heated at 200 °C for



Scheme 5. Thermal rearrangement of (methoxycarbonyl)ethenyl- and allylbicyclopropylidenes **10** and **7**: a)  $(\text{MeOCH}_2\text{CH}_2)_2\text{O}$ , 160 °C, 1 h; b)  $\text{C}_6\text{H}_6$ , 200 °C, 3.5 h

3.5 h, 96% of **7** had reacted. The product mixture, besides starting material (4%), contained five rearrangement products (84% overall) and a mixture of ten diastereomeric [2+2] dimers **21** (12%), of which the four main ones (84% overall) were present in a ratio of 8:15:14:47. The three major fractions in the mixture of rearrangement products were identified as 1-allyl-2-methylenespiropentane (**18**) (41%), two diastereomers of 1-allyl-4-methylenespiropentane (**19**) (28% in total), and two diastereomers of (allylmethylene)spiropentane (**20**) (15%) (Scheme 4, GC proportions). Thus, the selectivity for homolytic ring-opening of a distal bond in the substituted cyclopropyl group versus the unsubstituted one in **7** was 2:1 [**(18 + 20)/19**], lower than that found for the rearrangement of (bicyclopropylidenyl)methanol at the same temperature (2.6:1) and, especially, that found for ethyl bicyclopropylidenecarboxylate (100:0).<sup>[11]</sup> The first-order rate coefficients calculated from the kinetic curves measured at 200 °C in  $10^{-1} \text{ mol}\cdot\text{L}^{-1}$  benzene solution (see Exp. Sect.) for the formation of (**18 + 20**) and **19**  $k_2$  and  $k_3$  were equal to  $(5.2 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$  and  $(3.6 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$ , respectively.

## Conclusion

The thermal rearrangement of bicyclopropylidene (**1**) to methylenespiropentane (**5**) has been shown to occur at similar rates and with similar activation parameters to the rearrangements of simple methylenecyclopropanes. The negligible effect of the second methylenecyclopropane ring is explained by the “locking-in” of its strain energy during the rearrangement. The small exothermicity of this reaction (ca. 4 kcal·mol<sup>-1</sup>) is explained by the extra strain of the *exo*-methylene linkage to the second cyclopropane ring in **1** in comparison to the spiro strain in **5**. The very small concentration of **1** (< 1%) that has now been observed in the equilibrium mixture of **1** and **5** had understandably been overlooked in previous thermal decomposition studies



of **5** yielding 1,2- and 1,3-dimethylenecyclobutanes.<sup>[6b][7a,25]</sup>

The lower stability of ethenylbicyclopropylidene (**9**), and its observed ring-expansion products parallel the rate-enhancing effect of the vinyl group in the vinylcyclopropane-to-cyclopentene isomerization. No special effect is exerted on the latter rearrangement by an added methoxycarbonyl substituent. For allylbicyclopropylidene (**7**), no special enhancing effect from the allyl substituent relative to **1** was found, although from the product distribution it is evident that distal C–C bond breaking is favored 2:1 over remote C–C bond fission.

## Experimental Section

**General:** <sup>1</sup>H and <sup>13</sup>C NMR: Spectra were recorded at 250 (<sup>1</sup>H), and 62.9 [<sup>13</sup>C, additional DEPT (Distortionless Enhancement by Polarization Transfer)] MHz with a Bruker AM 250 instrument in CDCl<sub>3</sub> solution, CHCl<sub>3</sub>/CDCl<sub>3</sub> as internal reference; δ in ppm, *J* in Hz. – MS (EI): Finnigan MAT 95 spectrometer (70 eV). – M.p.: Büchi 510 capillary melting point apparatus, values uncorrected. – GC analyses: Siemens Sicromat 1–4, 25 m capillary column CP-SIL-5-CB, if not otherwise specified. – GC separations: Intersmat 130 instrument, 20% SE-30 on Chromaton W-AW-DMCS, 2000 × 8.2 mm Teflon column. – TLC: Macherey–Nagel precoated sheets, 0.25 mm G/UV<sub>254</sub> silica. – Column chromatography: Merck silica gel, grade 60, 230–400 mesh. – Starting materials: anhydrous diethyl ether and THF were obtained by distillation from sodium benzophenone ketyl, DMSO from CaH<sub>2</sub>, and dichloromethane from P<sub>4</sub>O<sub>10</sub>. Bicyclopropylidene (**1**)<sup>[2b]</sup> was prepared according to the published procedure. All other chemicals were used as commercially available (Merck, Acros, BASF, Bayer, Hoechst, Degussa AG, and Hüls AG). All reactions were performed under argon. Organic extracts were dried with MgSO<sub>4</sub>.

### Preparation of the Starting Materials for Thermal Rearrangements

**Allylbicyclopropylidene (7):** Allyl bromide (11.61 g, 8.1 mL, 96 mmol) was added dropwise at –78 °C over 40 min to a solution of lithiobicyclopropylidene [prepared from bicyclopropylidene (**1**) (7.69 g, 9.0 mL, 95.9 mmol) and *n*BuLi (96 mmol, 62.7 mL of a 1.53 M solution in hexane) in anhydrous THF (150 mL) according to published procedures<sup>[17]</sup>]. The resulting mixture was allowed to warm to ambient temperature, poured into ice-cold water (200 mL), and extracted with Et<sub>2</sub>O (3 × 50 mL). The combined organic solutions were washed with brine (100 mL), dried, and concentrated under reduced pressure at 0 °C. The residue was “bulb-to-bulb” distilled into a cold (–78 °C) trap under vacuum (0.1 Torr), and the contents of the cold trap were distilled under reduced pressure to give the diene **7** (5.77 g, 50%) as a colorless liquid, b. p. 83–85 °C (85 mbar). – <sup>1</sup>H NMR: δ = 0.90 (ddt, *J* = 2.2, 6.7, 10.0 Hz, 1 H), 1.10–1.20 (m, 4 H), 1.37 (tt, *J* = 2.2, 8.1 Hz, 1 H), 1.50–1.65 (m, 1 H), 2.0–2.25 (m, 2 H), 4.96 (dm, *J* = 10.5 Hz, 1 H, =CH<sub>2</sub>), 5.14 (ddd, *J* = 1.8, 3.6, 17.3 Hz, 1 H, =CH<sub>2</sub>), 5.82–5.98 (m, 1 H, =CH). – <sup>13</sup>C NMR: δ = 2.7, 3.0, 9.3, 37.0, 114.8 (CH<sub>2</sub>), 15.0, 137.5 (CH), 110.3, 115.3 (C). – MS (CI): *m/z* (%) = 138 (25) [M + NH<sub>4</sub><sup>+</sup>], 121 (100) [M + H<sup>+</sup>].

**Bicyclopropylidenecarbaldehyde (8):** Anhydrous DMF (16.52 g, 17.5 mL, 226 mmol) was added dropwise at 0 °C over 1 h to a solution of lithiobicyclopropylidene [prepared from bicyclopropylidene (**1**) (8.01 g, 9.4 mL, 100 mmol) and *n*BuLi (100 mmol, 37.6 mL of a 2.66 M solution in hexane) in anhydrous THF (150 mL)]. The

resulting mixture was allowed to warm to ambient temperature, and worked up as described for compound **7** above to give the aldehyde **8** (7.91 g, 73%) as a colorless liquid, b. p. 68–72 °C (20 mbar). – <sup>1</sup>H NMR: δ = 1.21–1.34 (m, 4 H), 1.89–1.95 (m, 2 H), 2.46–2.51 (m, 1 H), 8.64 (d, *J* = 6.5 Hz, 1 H, CHO). – <sup>13</sup>C NMR: δ = 3.6, 4.0, 10.3 (CH<sub>2</sub>), 28.5, 198.5 (CH), 108.0, 116.2 (C).

**Ethenylbicyclopropylidene (9):** A suspension of sodium hydride (64.6 mmol, 2.58 g of a 60% suspension in mineral oil) was heated with stirring in anhydrous DMSO (100 mL) at 70 °C for 45 min, and the mixture was then allowed to cool to ambient temperature. Anhydrous methyltriphenylphosphonium bromide (23.07 g, 64.6 mmol) was added to this mixture in several small portions over 30 min. After further stirring for 20 min, the aldehyde **8** (5.83 g, 53.9 mmol) was added dropwise over 30 min, and the resulting mixture was stirred for 20 min. All the volatile material was “bulb-to-bulb” distilled into a cold (–78 °C) trap under reduced pressure (0.1 Torr) at a maximum flask temperature of 35 °C. According to its <sup>1</sup>H NMR spectrum, the contents of the cold trap (5.26 g) were a 67% solution of almost pure diene **9** in benzene. This corresponds to a yield of 62%. Compound **9** was used without further purification; an analytical sample was obtained by preparative GC at 60 °C. – <sup>1</sup>H NMR: δ = 1.22–1.34 (m, 5 H), 1.68 (tt, *J* = 2.3, 7.8 Hz, 1 H), 2.29–2.35 (m, 1 H), 4.99 (dd, *J* = 1.6, 10.0 Hz, 1 H, =CH<sub>2</sub>), 5.23 (ddd, *J* = 0.7, 1.6, 17.6 Hz, 1 H, =CH<sub>2</sub>), 5.54–5.68 (m, 1 H, =CH). – <sup>13</sup>C NMR: δ = 2.7, 3.0, 12.0, 112.9 (CH<sub>2</sub>), 20.0, 139.6 (CH), 111.6, 114.3 (C). – MS (CI): *m/z* (%) = 124 (10) [M + NH<sub>4</sub><sup>+</sup>], 107 (100) [M + H<sup>+</sup>].

**Methyl (E)-3-(Bicyclopropylidenyl)acrylate (10):** A solution of the aldehyde **8** (3.60 g, 33.2 mmol) and (methoxycarbonyl)methylene-triphenylphosphorane (14.0 g, 41.9 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (300 mL) was stirred at ambient temperature for 24 h. Pentane (300 mL) was added, and the resulting mixture was stirred for 3 h and filtered through “flash” silica gel (100 g as a 2 cm pad). The silica gel was washed with the same mixture of solvents (600 mL). Concentration of the combined extracts under reduced pressure gave **10** (5.28 g, 97%) of ≥ 92% purity; this was used without further purification. – <sup>1</sup>H NMR: δ = 1.16–1.26 (m, 4 H), 1.36–1.46 (m, 1 H), 1.75–1.87 (m, 1 H), 2.27–2.40 (m, 1 H), 3.73 (s, 3 H, OMe), 5.92 (d, *J* = 17.5 Hz, 1 H, CH), 6.56 (dd, *J* = 10.0, 17.5 Hz, 1 H, =CH). – <sup>13</sup>C NMR: 51.3 (CH<sub>3</sub>), 3.2 (2 CH<sub>2</sub>), 13.5 (CH<sub>2</sub>), 19.4, 118.5, 151.4 (CH), 113.1, 113.5, 167.0 (C). – MS (EI): *m/z* (%) = 164 (1) [M<sup>+</sup>], 163 (3) [M<sup>+</sup> – H], 136 (8) [M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>], 133 (10), 132 (15), 124 (20) [M<sup>+</sup> – C<sub>3</sub>H<sub>4</sub>], 105 (100) [M<sup>+</sup> – CO<sub>2</sub>CH<sub>3</sub>], 104 (41), 103 (45), 91 (22) 79 (40), 77 (48) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>]. – MS (HR-EI): 164.0837 (C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>, calcd. 164.0837).

### Preparative Thermal Rearrangements

**1. Of Bicyclopropylidene (1):** The alkene **1** (19.30 g, 22.60 mL, 240.9 mmol) was slowly added by syringe pump over 4.7 h to a pre-heated (80 °C) 50-mL flask under a constant stream of nitrogen (250 mL/min through a capillary which almost reached the bottom of the flask). The flask was connected to a quartz tube (3 × 60 cm) that had been filled with quartz rings and pre-heated to 350 °C. The product was collected in a cold (–196 °C) trap. After the addition was complete, the stream of nitrogen was passed through the apparatus for an additional 20 min, and the cold trap was allowed to warm up to 20 °C. Its contents (17.4 g) were methylenespiropentane (**5**) of ≥ 95% purity, as a colorless or slightly yellow liquid, yield 90%. Its NMR spectroscopic data are identical to those published.<sup>[7a]</sup> – <sup>13</sup>C NMR: δ = 10.1 (3 CH<sub>2</sub>), 98.4 (CH<sub>2</sub>), 10.7, 137.5 (C). – Attempted distillation of **5** at atmospheric pressure did not increase its purity, but only reduced the yield due to partial polymerization.

## 2. Of Ethenylbicyclopropylidene (9)

**a)** A solution of the diene **9** (650 mg, 6.12 mmol) in benzene (2 mL) was heated in a sealed tube at 100 °C for 1 h. After cooling to ambient temperature, the contents of the tube were subjected to preparative GC separation at 90 °C to give 1-ethenyl-2-methylenespiropentane (**13**) (350 mg, 54%) and 4-methylenespiro[2.4]hept-5-ene (**14**) (201 mg, 31%).

**b)** A solution of the diene **9** (1.59 g, 15.0 mmol) in benzene (5 mL) was treated under the conditions of the preceding experiment (150 °C, 3.5 h). Dienes **13** (68 mg, 4%) and **14** (1.26 g, 79%) were obtained after preparative GC separation.

**1-Ethenyl-2-methylenespiropentane (13):** <sup>1</sup>H NMR: δ = 0.90–1.50 (m, 4 H), 2.33 (dm, *J* = 9.0 Hz, 1 H), 4.95 (ddd, *J* = 0.5, 1.9, 10.1 Hz, 1 H, =CH<sub>2</sub>), 5.11 (ddd, *J* = 0.5, 1.9, 17.1 Hz, 1 H, =CH<sub>2</sub>), 5.18 (d, *J* = 2.1 Hz, 1 H, =CH<sub>2</sub>), 5.36 (s, 1 H, =CH<sub>2</sub>), 5.45–5.60 (m, 1 H, =CH). – <sup>13</sup>C NMR: δ = 8.2, 10.2, 99.1, 113.6 (CH<sub>2</sub>), 25.5, 138.5 (CH), 17.7, 140.8 (C). – MS (CI): *m/z* (%) = 141 (60) [M + NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>], 124 (40) [M + NH<sub>4</sub><sup>+</sup>], 107 (100) [M + H<sup>+</sup>].

**4-Methylenespiro[2.4]hept-5-ene (14):** <sup>1</sup>H NMR: δ = 0.75–0.95 (m, AA'BB', 4 H), 2.60 (br. s, 2 H), 4.10 (br. s, 1 H, =CH<sub>2</sub>), 4.60 (br. s, 1 H, =CH<sub>2</sub>), 6.15–6.36 (m, 2 H, HC=CH). – <sup>13</sup>C NMR: δ = 18.3 (2 CH<sub>2</sub>), 43.3, 95.3 (CH<sub>2</sub>), 134.5, 137.3 (CH), 22.7, 159.7 (C). – MS (CI): *m/z* (%) = 107 (100) [M + H<sup>+</sup>].

**c)** The diene **14** (300 mg, 2.83 mmol) was subjected to flash vacuum pyrolysis at 500 °C and 0.1 Torr over a period of 1.5 h in the experimental set-up described previously.<sup>[30b]</sup> According to its <sup>1</sup>H and <sup>13</sup>C NMR spectra, the obtained mixture of hydrocarbons (285 mg, 95%) consisted of the starting diene **14** (26%), 1,2,3,4-tetrahydropentalene (**15**) (36%), and 1,2,3,5-tetrahydropentalene (**16**) (38%) (the spectral signals were assigned according to the published data<sup>[30]</sup>). The resulting mixture obtained from 280 mg (2.64 mmol) of **14** under the same experimental conditions, but at 550 °C (267 mg, 95%), consisted of **14** (5%), **15** (45%), and **16** (50%).

**3. Of Methyl trans-3-(Bicyclopropylidenyl)acrylate (10):** A solution of the acrylate **10** (1.0 g, 6 mmol) in diethylene glycol dimethyl ether (10 mL) was heated under reflux for 1 h. After cooling to room temperature, it was poured into water (100 mL), and the mixture was extracted with pentane (3 × 100 mL). The combined extracts were washed with water (100 mL) and brine (100 mL), dried, and concentrated under reduced pressure. Column chromatography of the residue (0.82 g) (50 g of silica gel; 30 × 3 cm column; hexane/*i*BuOMe, 50:1) gave methyl 7-methylenespiro[2.4]hept-5-ene-4-carboxylate (**17**) (500 mg, 50%) as a colorless oil. – <sup>1</sup>H NMR: δ = 0.79–1.06 (m, 4 H), 3.55 (s, 1 H, CH), 3.65 (s, 3 H, OMe), 4.20–4.21 (m, 1 H, =CH<sub>2</sub>), 4.69 (s, 1 H, =CH<sub>2</sub>), 6.10–6.17 (m, 1 H, =CH), 6.46–6.49 (dd, *J* = 1.8, 5.8 Hz, 1 H, =CH). – <sup>13</sup>C NMR: δ = 51.7 (CH<sub>3</sub>), 14.6, 19.2, 97.6 (CH<sub>2</sub>), 57.3, 134.16, 136.87 (CH), 26.0, 157.2, 172.5 (C). – MS (EI): *m/z* (%) = 164 (25) [M<sup>+</sup>], 136 (10) [M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>], 105 (100) [M<sup>+</sup> – CO<sub>2</sub>CH<sub>3</sub>], 103 (15), 79 (18), 77 (22) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>]. – MS (HR-EI): 164.0837 (C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>, calcd. 164.0837).

**4. Of Allylbicyclopropylidene (7):** A solution of the diene **7** (650 mg, 5.41 mmol) in benzene (2 mL) was heated in a sealed tube at 200 °C for 3.5 h. After cooling to ambient temperature, all the volatile material was “bulb-to-bulb” distilled into a cold (–78 °C) trap under reduced pressure (0.1 Torr), at a maximum flask temperature of 40 °C. The remaining residue in the flask (75 mg), according to its NMR spectra, was most probably a mixture of isomeric disub-

stituted [4]rotane derivatives **21**, arising from [2+2] dimerization of **7**. GC analysis showed all ten of the possible diastereomers, the main four of which amounted to 8, 15, 14, and 47%. According to a gas chromatogram, the contents of the cold trap consisted of the starting material **7** (5%), along with a mixture of five rearrangement products, in the ratio 47:19:12:7:10. Upon attempted GC separation, three main fractions were isolated. According to its <sup>1</sup>H and <sup>13</sup>C NMR spectra, fraction 1 (240 mg, 37%) appeared to be 1-allyl-2-methylenespiropentane (**18**). – <sup>1</sup>H NMR: δ = 0.85–1.30 (m, 4 H), 1.70 (tm, *J* = 6.8 Hz, 1 H), 2.18 (tp, *J* = 0.9, 6.4 Hz, 2 H), 4.97 (dm, *J* = 10.0 Hz, 1 H, =CH<sub>2</sub>), 5.03 (dm, *J* = 17.8 Hz, 1 H, =CH<sub>2</sub>), 5.12 (d, *J* = 2.1 Hz, 1 H, =CH<sub>2</sub>), 5.33 (s, 1 H, =CH<sub>2</sub>), 5.76–5.97 (m, 1 H, =CH). – <sup>13</sup>C NMR: δ = 7.5, 10.2, 35.5, 98.1, 114.4 (CH<sub>2</sub>), 19.3, 137.5 (CH), 16.1, 141.9 (C). – MS (CI): *m/z* (%) = 155 (100) [M + NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>], 138 (75) [M + NH<sub>4</sub><sup>+</sup>], 121 (55) [M + H<sup>+</sup>]. – Fraction 2 (122 mg, 19%) was a mixture of two isomeric 1-allyl-4-methylenespiropentanes (**19**), ratio 1.6:1. – Major isomer: <sup>1</sup>H NMR: δ = 0.78 (t, *J* = 4.5 Hz, 1 H), 1.22–1.45 (m, 3 H), 1.56 (m, 1 H), 2.11 (tm, *J* = 6.6 Hz, 2 H), 4.95–5.07 (m, 2 H, =CH<sub>2</sub>), 5.16 (td, *J* = 0.7, 2.4 Hz, 1 H, =CH<sub>2</sub>), 5.35 (s, 1 H, =CH<sub>2</sub>), 5.76–5.97 (m, 1 H, =CH). – <sup>13</sup>C NMR: δ = 10.5, 16.1, 36.1, 98.7, 114.6 (CH<sub>2</sub>), 21.9, 137.4 (CH), 16.5, 135.9 (C). – Minor isomer: <sup>1</sup>H NMR: δ = 0.92 (t, *J* = 4.6 Hz, 1 H), 1.22–1.45 (m, 4 H), 2.18 (td, *J* = 1.2, 6.4 Hz, 2 H), 4.97 (dm, *J* = 10.0 Hz, 1 H,

Table 2. Rearrangement of bicyclopropylidene (**1**) to methylenespiropentane (**5**): proportions of **1** (%) as a function of time *t* [min] and temperature *T* [°C]

<i>T</i> = 200.0	<i>T</i> = 209.5	<i>T</i> = 220.1	<i>T</i> = 230.0	<i>T</i> = 240.0
<i>t</i> <b>1</b>	<i>t</i> <b>1</b>	<i>t</i> <b>1</b>	<i>t</i> <b>1</b>	<i>t</i> <b>1</b>
30    81.49	14    82.65	5    83.09	5    66.00	5    46.13
60    70.80	30.5    70.50	10    70.25	10    48.92	7.5    34.64
120    54.23	45    60.66	15    63.75	15    35.95	10    22.97
180    39.69	60    46.60	30    40.86	30    14.97	15    12.33
240    30.42	90    34.04	45    26.31	35    11.37	20    6.87
360    16.68	120    23.19	60    19.52	45    7.03	22.5    4.70
508    8.54	152    15.89	90    8.24	50    4.70	

Table 3. Rearrangement of bicyclopropylidene (**1**) to methylenespiropentane (**5**) at 230 °C after 20 min: proportions of **1** (%) as a function of pressure *p*<sub>i</sub> [Torr], abundance of radical chain reaction-inhibiting agents (*cis*-butene), and surface area/volume ratio (*s/v*)

<i>p</i> <sub>i</sub>	3	7	13	31
<b>1</b>	31.7	29.4	29.8	29.8
<b>1</b> (with <i>cis</i> -butene)			28.4	
	Low <i>s/v</i> reactor		High <i>s/v</i> reactor	
<b>1</b> (after 15 min)	36.0		36.0	
<b>1</b> (after 20 min)	29.8		27.6	

Table 4. Rearrangement of ethenylbicyclopropylidene (**9**) at 100 °C: proportions of **9**, **13**, and **14** (%) as functions of time *t* [min]

<i>t</i>	0	6	12	18	24	30	38
<b>9</b>	99.5	62.1±0.5	36.8±0.5	24.6±0.5	14.2±1	8.5±1	4.3±0.5
<b>13</b>	0.5	20.7±0.5	36.6±0.5	46.7±0.5	51.6±1	54.8±0.5	59.3±1.5
<b>14</b>	–	15.0±0.5	24.8±0.5	28.6±0.5	33.0±0.5	35.5±1	36.8±0.5

Table 5. Rearrangement of allylbicyclopropylidene (**7**) at 200 °C: proportions of **7**, **18**, **19**, and **20** (%) as functions of time *t* [min]

<i>t</i>	0	10	20	30	40	50	60
<b>7</b>	99.5	86.6±1	76.6±0.7	66.8±1	58.3±0.5	50.2±1.6	41.7±2
<b>18</b>	—	5.8±0.1	12.0±0.6	17.1±0.6	21.2±0.1	26.5±0.5	30.5±0.7
<b>19</b>	—	3.9±0.5	6.7±1	9.3±1	11.2±0.2	12.7±0.8	15.5±2
<b>20</b>	—	2.2±0.2	3.7±0.3	5.5±0.8	7.4±0.2	8.9±0.8	10.3±1
<b>18 + 20</b>	—	8.0±0.2	15.7±0.6	22.6±0.8	28.6±0.2	35.4±0.8	40.8±1

=CH<sub>2</sub>), 5.02 (dm, *J* = 15.3 Hz, 1 H, =CH<sub>2</sub>), 5.13 (t, *J* = 2.2 Hz, 1 H, =CH<sub>2</sub>), 5.26 (s, 1 H, =CH<sub>2</sub>), 5.78–5.96 (m, 1 H, =CH). – <sup>13</sup>C NMR: δ = 7.8, 16.3, 36.2, 97.9, 114.7 (CH<sub>2</sub>), 20.3, 137.1 (CH), 16.53, 136.8 (C). – MS (CI): *m/z* (%) = 155 (100) [M + NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>], 138 (32) [M + NH<sub>4</sub><sup>+</sup>], 121 (90) [M + H<sup>+</sup>]. – Fraction 3 (85 mg, 13%) was a mixture of two diastereomeric (allylmethylene)spiropentanes (**20**), ratio 3:2. – Major diastereomer: <sup>1</sup>H NMR: δ = 0.95–1.20 (m, AA'BB', 4 H), 1.35 (s, 2 H), 2.79 (tp, *J* = 1.5, 6.4 Hz, 2 H), 4.94–5.12 (m, 2 H, =CH<sub>2</sub>), 5.74 (td, *J* = 1.5, 5.0 Hz, 1 H, =CH), 5.78–5.91 (m, 1 H, =CH). – <sup>13</sup>C NMR: δ = 9.73 (2 CH<sub>2</sub>), 10.2, 35.8, 114.7 (CH<sub>2</sub>), 113.8, 137.2 (CH), 10.7, 128.2 (C). – Minor diastereomer: <sup>1</sup>H NMR: δ = 0.95–1.20 (m, AA'BB', 4 H), 1.38 (s, 2 H), 2.96 (tp, *J* = 1.3, 6.6 Hz, 2 H), 4.94–5.12 (m, 2 H, =CH<sub>2</sub>), 5.51 (tt, *J* = 2.2, 6.7 Hz, 1 H, =CH), 5.81–6.05 (m, 1 H, =CH). – <sup>13</sup>C NMR: δ = 9.67 (2 CH<sub>2</sub>), 9.3, 36.0, 114.6 (CH<sub>2</sub>), 111.1, 137.4 (CH), 10.4, 128.8 (C). – MS (CI): *m/z* (%) = 172 (53) [M + 2 NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>], 155 (93) [M + NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>], 138 (15) [M + NH<sub>4</sub><sup>+</sup>], 121 (100) [M + H<sup>+</sup>].

**Kinetic Measurements of the Rearrangement of Bicyclopropylidene (1) in the Gas Phase:** The apparatus was identical to that used in earlier studies.<sup>[32]</sup> Gases were handled in conventional grease-free vacuum systems made from Pyrex, with Rotafluo (Quickfit) stopcocks. The cylindrical reaction vessel (volume ca. 250 mL) was placed in a stirred salt (NaNO<sub>2</sub>/KNO<sub>3</sub> eutectic) thermostat controlled by an AEI (GEC) RT 5 controller. Temperatures were measured with a Pt/Pt-13% Rh thermocouple calibrated against a precalibrated Pt resistance thermometer (Tinsley, Type 5187 SA). Pressures ≥ 1 Torr were measured with a conventional mercury manometer, pressures < 1 Torr with Pirani G6A and Speedivac B4 instruments. Product analyses were performed by gas chromatography at 60 °C (Perkin–Elmer 8310, 1.5 m × 1/8" column, 5% silicon oil DE 117 on Chromosorb W) with FID detection and electronic peak integration (Hewlett–Packard HP 3380 A). The reaction of **1** was studied using *n*-hexane as an internal standard. The reactant master mixture consisted of about 1% of **1** and 1% of hexane diluted to about 500 Torr with N<sub>2</sub> in a 500 mL reservoir. Runs were carried out by admitting a known pressure of the mixture (30–40 Torr) into the preevacuated (≤ 0.005 Torr) reaction vessel for a certain time. The reaction was quenched by sampling some of the reaction vessel contents with a pre-evacuated sample bulb, from which samples (diluted with 80 Torr of N<sub>2</sub>) could be injected into the gas chromatograph. After five to six runs, a blank analysis of the unused master mixture was performed to check the mass balance of the reaction. To assess the influence of surface area, the reaction vessel was filled with Pyrex tubes, which increased its surface area by a factor of ca. 16. The results are presented in Tables 2 and 3.

**Kinetics of the Rearrangement of Dienes 7 and 9 in Solution:** Glass tubes were filled with 0.1 M solutions of the corresponding diene in benzene, carefully degassed by three freeze-pump-thaw cycles, and then sealed. The tubes were immersed in a well-stirred silicone

oil bath, then extracted one after another after the appropriate length of time, and the reaction quenched by immersing the tube in ice/water. The variation in temperature, monitored by means of a quartz thermometer, was always less than 0.5 °C. The ratio of the products was estimated by gas chromatography (Siemens Si-chromat 1–4, 25 m capillary column CP-SIL-5-CB) with FID detection and electronic peak integration (Hewlett–Packard HP 3394 A). The average values of four integrations were used in the ensuing calculations (Tables 4 and 5).

## Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 357, Project A14) and the Fonds der Chemischen Industrie. The authors are grateful to the companies BASF AG, Bayer AG, Chemetall GmbH, Degussa AG, and Hüls AG for generous gifts of chemicals. S. I. K. is indebted to the Ausländeramt, Stadt Göttingen, for the extension of his German residence permit. We are particularly grateful to Dr. B. Knieriem, Universität Göttingen, for his careful reading of the final manuscript.

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Received April 4, 2001

[O01166]