

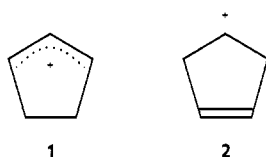
# Structures and Energies of Isomeric Cyclopentenyl Cations. Resolution of the Question of Anchimeric Assistance in Cyclopenten-4-yl Solvolysis

Paul von Ragué Schleyer,<sup>\*†</sup> T. William Bentley,<sup>‡</sup> Wolfram Koch,<sup>§</sup> Alexander J. Kos,<sup>†</sup> and Helmut Schwarz<sup>\*\*§</sup>

Contribution from the Institut für Organische Chemie, Friedrich-Alexander Universität Erlangen-Nürnberg, D-8520 Erlangen, West Germany, Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, Great Britain, and Institut für Organische Chemie der Technischen Universität Berlin, D-1000 Berlin, West Germany. Received November 3, 1986

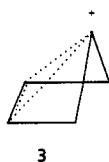
**Abstract:** At high levels of ab initio theory (MP3/6-31G\*\*//6-31G\*) the allylic cyclopenten-3-yl cation (**1**) is the most stable C<sub>5</sub>H<sub>7</sub><sup>+</sup> species. The second most stable isomer, the cyclopenten-4-yl cation, lies about 19 kcal/mol higher in energy and strongly favors the bridged structure **3** over the planar classical alternative, **2**. Due to the inductive effect of the double bond, **2** is destabilized, relative to the cyclopentenyl cation, by about 5–10 kcal/mol. This explains why solvolysis rate enhancements, e.g. for cyclopenten-4-yl tosylate (**5**) vs cyclopentyl tosylate (**6**), are not observed, despite the stereochemical evidence (retention of configuration) for anchimeric assistance in the former. Rate measurements in hexafluoro-2-propanol (HFIP), one of the least nucleophilic solvents, confirm the earlier experimental observations: the **5/6** rate ratio is 0.12. Hence, cyclopentyl is not a suitable basis for comparison, and considerable double-bond participation during reaction of **5** is indicated. The calculated energy difference between **1** and **3** is quite close to the activation energy for hydrogen scrambling in the cyclopentenyl cations but is significantly higher than approximate differences deduced indirectly by gas-phase measurements. In agreement with experimental observations, cyclization of the pentadienyl cation (**4**) to **1** is very exothermic (–20.3 kcal/mol). The cyclopentenyl cation (**1**) is somewhat more stable than acyclic allyl cations with comparable degrees of substitution, e.g. the *trans,trans*-1,3-dimethylallyl cation, but “pseudoaromatic” 6π-electron stabilization, if present at all, is small.

The isomeric cyclopentenyl cations, **1** and **2**, both pose interpretative problems.<sup>1–3</sup> Despite ring strain, **1** is indicated experimentally to be more stable than comparably substituted acyclic allyl and cyclohexenyl cations.<sup>3</sup> This extra stabilization has been



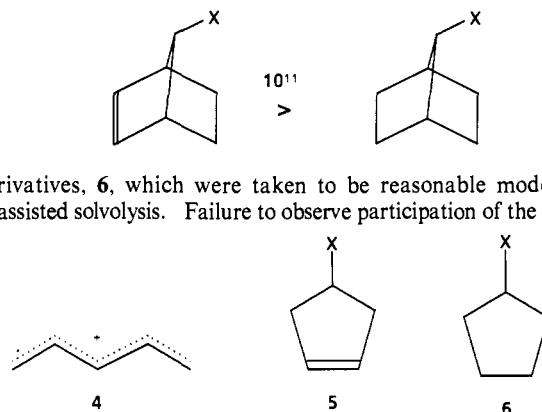
attributed to the “pseudoaromatic” 6π character of **1** involving enhanced hyperconjugative interactions of the allyl cation with the CH<sub>2</sub>CH<sub>2</sub> moiety,<sup>2</sup> but this interesting possibility (considered to be the “preferred explanation”)<sup>3b</sup> has not been analyzed by high-level theoretical calculations. The nature of the homoconjugated species, **2**, has received considerable attention particularly because of the structural analogy with the 7-norbornenyl cation.<sup>1</sup>

The latter affords one of the most spectacular examples of double-bond participation (Chart I); the solvolysis rates of suitable derivatives are enhanced by 10<sup>11</sup> over those of the corresponding saturated 7-norbornyl systems.<sup>1</sup> The 7-norbornenyl cation, directly observable in superacid media, has a bridged structure; 3-center 2-electron bonding is responsible for its stability.<sup>1</sup> However, attempts to clarify the nature of the monocyclic analogue, **2** or **3**, have given conflicting results,<sup>1,2</sup> and this remains an unsolved problem.



Early solvolysis studies attempting to detect double-bond participation gave negative results.<sup>4</sup> The reactions of **5**-OTs and of **5**-Br were slower than those of the corresponding cyclopentyl

Chart I



derivatives, **6**, which were taken to be reasonable models for unassisted solvolysis. Failure to observe participation of the double

bond in **5** was attributed to the excessive angle strain necessary to achieve the bent geometry in the bridged intermediate, **3**. (The five-membered rings in the 7-norbornyl system are strongly bent to begin with.)

However, the solvents employed in these studies (e.g. acetic acid and 50% aqueous acetone) may have been inappropriate.<sup>5</sup> The

(1) Recent reviews: (a) Vogel, P. *Carbocation Chemistry*, Elsevier: Amsterdam, 1985. (b) Barkhash, V. A. *Top. Curr. Chem.* **1984**, *116/117*, 1. (c) Olah, G. A.; Surya Prakash, G. K.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987.

(2) Houriet, R.; Schwarz, H.; Zummack, W.; Andrade, J. G.; Schleyer, P. v. R. *Nouv. J. Chim.* **1981**, *5*, 505.

(3) Solvolysis rates: (a) Kiefer, E. F.; Roberts, J. D. *J. Am. Chem. Soc.* **1962**, *84*, 784. (b) Brown, H. C.; Rao, C. G.; Ravindranathan, M. *J. Org. Chem.* **1978**, *43*, 4939. Stability in strong acids: (c) Deno, N. C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. 2, Chapter 18, p 783. (d) Sorensen, T. S. *J. Am. Chem. Soc.* **1969**, *91*, 6398. Sorensen, T. S. Reference 3c. Chapter 19, p 807. (e) Olah, G. A.; Clifford, P. R.; Halpern, Y.; Johanson, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4219. (f) Gas phase (small or negligible difference in hydride ion affinities): Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: London, 1979; Vol. 2, Chapter 9, p 1.

(4) (a) Bartlett, P. D.; Rice, M. R. *J. Org. Chem.* **1963**, *28*, 3351. (b) Winstein, S.; Sonnenberg, J. *J. Am. Chem. Soc.* **1961**, *83*, 3235.

(5) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

<sup>\*</sup>Friedrich-Alexander Universität Erlangen-Nürnberg.

<sup>†</sup>University College of Swansea.

<sup>§</sup>Universität Berlin.

**Table I.** Total Energies (in Hartrees) of  $C_5H_7^+$  Ions and Some Reference Molecules

species	3-21G//3-21G <sup>a</sup>	6-31G**//6-31G*	6-31G**//6-31G*	MP2/6-31G**//6-31G*	MP3/6-31G**//6-31G*	ZPE <sup>d</sup>
1	-192.06035	-193.14213	-193.15429	-193.80414	-193.84491	63.4 <sup>e</sup>
2	-192.01633	-193.09737	-193.10171	-193.74864	-193.79292	61.6 <sup>e</sup>
3	-192.00318	-193.10121	-193.11353	-193.77878	-193.81489	63.3 <sup>e</sup>
4	-192.03580	-193.11596	-193.12834	-193.77215	-193.81312	62.6 <sup>e</sup>
7, $C_5$ cyclopentadiene	-193.21217 <sup>b</sup> -191.71708 <sup>a</sup>	-194.29283 -192.79172 <sup>a</sup>	-194.30724 <sup>b</sup> -192.80241	-193.47174	<sup>c</sup>	57.4 <sup>f</sup>
cyclopentene	-192.90168 <sup>a</sup>	-193.97717 <sup>a</sup>	-193.98914 <sup>b</sup>			10.7 <sup>f</sup>
cyclopentane	-194.08847 <sup>a</sup>	-195.16358	-195.17822 <sup>b</sup>			85.3 <sup>f</sup>

<sup>a</sup>Data from: Ibrahim, M. R.; Schleyer, P. v. R. *J. Comput. Chem.* **1985**, *6*, 157 and ref cited therein. <sup>b</sup>Raghavachari, K.; Schleyer, P. v. R., to be submitted for publications. 3-21G geometries. <sup>c</sup>Not calculated due to technical problems. <sup>d</sup>Zero-point energies (kcal/mol). <sup>e</sup>ZPE: 3-21G values, scaled by 0.9 (at 3-21G geometries). All structures are minima (zero imaginary frequencies) at this level. <sup>f</sup>Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1985**, *113*, 291.

**Table II.** Relative Energies (kcal/mol) of  $C_5H_7^+$  Ions 1-4 and Proton Affinities<sup>a</sup> of Cyclopentadiene

species	3-21G//3-21G	6-31G**//6-31G*	6-31G**//6-31G*	MP2/6-31G**//6-31G*	MP3/6-31G**//6-31G*	+ZPE <sup>a</sup>
1	0.0	0.0	0.0	0.0	0.0	0.0
2	27.6	28.1	33.0	34.8	32.6	30.8
3	35.8	25.6	25.6	15.9	18.8	17.7
4	15.4	16.4	16.3	20.1	21.1	20.3
cyclopentadiene	215.4	219.9	220.8	208.6	...	202.6 <sup>b</sup>

<sup>a</sup>MP3/6-31G\*\*//6-31G\* values corrected for zero-point energy (ZPE) differences (see Table I). <sup>b</sup>The experimental PA is 200.0 at 25 °C.<sup>3f</sup>

solvolysis of cyclopentyl derivatives are now known to be accelerated by nucleophilically assisted ( $k_s$ ,  $S_N2$ -like) processes.<sup>5</sup> Hence, one aspect of the present study was to reexamine the solvolysis of these compounds in hexafluoro-2-propanol (HFIP), one of the least nucleophilic solvents available for this purpose.

In contrast to the rate measurements, the stereochemistry of the solvolysis products has provided evidence for the intermediacy of the bridged cyclopentenyl intermediate, **3**. Lambert et al.,<sup>6</sup> using deuterated precursors, have shown that homoallylic substitution during solvolysis of **5** occurs with *complete retention of configuration* in formic acid. In contrast, the substitution products obtained from cyclopentyl solvolyses (**6**) generally are *inverted*.<sup>7</sup> The intermediacy of bridged **3** has also been deduced by Kirmse et al.,<sup>8</sup> who generated the cation by protonation of the corresponding isoelectronic carbene (where an electron-deficient center may also interact with the double bond).<sup>9</sup>

Attempts to study **3** directly by NMR in superacid media were foiled by rapid rearrangement to the more stable cycloallyl isomer, **1**.<sup>10</sup> Indeed, interconversion between these two species results in complete scrambling of all the hydrogens. Saunders has determined the energy barrier,  $E_a = 18.0 \pm 0.9$  kcal/mol, for this process,<sup>10a</sup> but the nature of the transition state (**2**, **3**, or some intermediate structure) could not be elucidated. A second experimental estimate of the energy difference between **1** and **3** (or **2**) has been obtained from ion cyclotron measurements by using deuterated samples and double-resonance techniques.<sup>2</sup> Weaker bases, used in bracketing experiments, were able to abstract protons, presumably from the less stable cyclopentenyl cation isomer, **3** (or **2**). On this basis, **1** was indicated to be from 6.9 to 8.6 kcal/mol more stable than **3**. This interpretation was supported by semiempirical MINDO/3 calculations, which indicated a 10.7 kcal/mol energy difference between **1** and **3**.<sup>2,11</sup> There also is evidence from mass spectrometric studies for two

$C_5H_7^+$  cations differing in energy by about 12 kcal/mol.<sup>12</sup>

Through advances in ab initio programs and computer technology,<sup>13</sup> it is now possible to study  $C_5H_7^+$  systems at sufficiently high theoretical levels where reliable results can be expected. While classical carbocations and their relative energies are given quite well with relatively small basis sets, nonclassical species require more sophisticated descriptions via polarized basis sets and corrections for electron correlation. Four  $C_5H_7^+$  isomers have been investigated in this manner, **1-4**. The pentadienyl cation (**4**) has been included since it represents the class of pentadienyl cations that are known experimentally to cyclize to cyclopentenyl cations.<sup>3d</sup> We want to estimate the exothermicity of this reaction. Our discussion also deals with the conjugated cyclopentenyl cation (**1**).

## Methods

**Calculations.** The ab initio calculations<sup>13</sup> were carried out with the GAUSSIAN 82 program<sup>14</sup> on various computers. The initial geometry optimizations employed the split-valence 3-21G basis set.<sup>15</sup> The geometries were reoptimized with the 6-31G\* basis set,<sup>16</sup> which includes d-type polarization functions on carbon. Higher level MP3/6-31G\*\*//6-31G\* single points completed the investigation. The basis set contains additional p-type polarization functions on the hydrogens;<sup>17</sup> Møller-Plesset electron correlation corrections were included through third order (MP3).<sup>18</sup> In the standard designation, the “//” means “at the geometry of”.

The absolute energies of **1-4**, along with those of reference molecules, are given in Table I. The relative energies of **1-4**, summarized in Table II, are an indication of the reliability of the results with three quite different types of carbocations: classical, allylic, and bridged. The relative energies of **1**, **2**, and **4** are relatively insensitive to the theoretical level, although there are 5 kcal/mol variations on going from 3-21G to MP3/6-31G\*\*. This increase appears to be due to the inclusion of hydrogen polarization functions in the case of **2** but to electron correlation corrections in **4**. As expected from previous experience,<sup>13</sup> the energy of the nonclassical isomer, **3**, relative to **1** is reduced significantly both by the inclusion of polarization functions and by electron correlation corrections. Since there is a significant (3 kcal/mol) difference between the

(6) (a) Lambert, J. B.; Finzel, R. B.; Belec, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 3281. (b) Lambert, J. B.; Finzel, R. B. *Ibid.* **1983**, *105*, 1954. (c) Cf.: Lambert, J. B.; Featherman, S. I. *Ibid.* **1977**, *99*, 1542.

(7) (a) Humski, K.; Sendjarević, V.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 7722. (b) Seib, R. C.; Shiner, V. J., Jr.; Sendjarević, V.; Humski, K. *Ibid.* **1978**, *100*, 8133.

(8) Kirmse, W.; Chiem, P. V.; Henning, P. G. *J. Am. Chem. Soc.* **1983**, *105*, 1695.

(9) Schoeller, W. W.; Brinker, U. H. *J. Am. Chem. Soc.* **1978**, *100*, 6012. Baird, M. S.; Jefferies, I. *Tetrahedron Lett.* **1986**, *27*, 2493.

(10) (a) Saunders, M.; Berger, R. *J. Am. Chem. Soc.* **1972**, *94*, 4049. (b) Olah, G. A.; Prakash, G. K. S.; Liang, G. *Ibid.* **1979**, *101*, 3932. Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N.; Whittacker, D.; Rees, J. C. *Ibid.* **1979**, *101*, 3935.

(11) MINDO/3 calculations on **2** and **3** were first carried out by W. L. Jorgensen, private communication (Jorgensen, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 3840) and by J. Chandrasekhar.

(12) Wolkoff, P.; Holmes, J. L.; Lossing, F. P. *Adv. Mass Spectrom.* **1980**, *8A*, 743.

(13) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(14) Binkley, J. S.; Frisch, M. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Revision H; Carnegie-Mellon University: Pittsburgh, PA, 1984.

(15) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(16) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(17) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(18) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 818. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

**Table III.** Solvolytic Rate Constants at 60 °C for Cyclopent-3-enyl (5) and Cyclopentyl (6) Tosylates

solvent <sup>a</sup>	rate constants, 10 <sup>4</sup> k/s <sup>-1</sup>		
	5, X = OTs <sup>b</sup>	6, X = OTs <sup>c</sup>	k <sub>5</sub> /k <sub>6</sub>
97% (CF <sub>3</sub> ) <sub>2</sub> CHOH	8.0 <sup>d</sup>	65 <sup>e</sup>	0.12
97% CF <sub>3</sub> CH <sub>2</sub> OH	1.94	14 <sup>f</sup>	0.14
CH <sub>3</sub> CO <sub>2</sub> H	0.14 <sup>g</sup>	1.2 <sup>h</sup>	0.12 <sup>g</sup>
60% EtOH	5.73	25.0	0.23
80% EtOH	1.80	9.0	0.20
EtOH	0.298	1.4 <sup>h</sup>	0.21

<sup>a</sup>Refers to percent v/v organic solvent/water except for fluorinated alcohol/water mixtures which are percent w/w. <sup>b</sup>Kinetic data from ref 6b, except where noted otherwise. <sup>c</sup>Kinetic data from ref 22, except where noted otherwise. <sup>d</sup>This work. Extrapolated from the following data [*k*, T/°C]: (2.8 ± 0.3) × 10<sup>-5</sup>, duplicate, 25.0; (1.2 ± 0.1) × 10<sup>-4</sup>, 39.8; (3.4 ± 0.2) × 10<sup>-4</sup>, duplicate, 50.0; Δ*H*<sup>‡</sup> = 18.4 kcal/mol; Δ*S*<sup>‡</sup> = -17.6 eu. <sup>e</sup>This work. Extrapolated from the following data [*k*, T/°C]: (3.0 ± 0.1) × 10<sup>-4</sup>, duplicate, 25.0; (1.14 ± 0.01) × 10<sup>-3</sup>, 39.8; (2.95 ± 0.02) × 10<sup>-3</sup>, 50.0; Δ*H*<sup>‡</sup> = 16.8 kcal/mol; Δ*S*<sup>‡</sup> = -18.3 eu. <sup>f</sup>Estimated from data in 100% CF<sub>3</sub>CH<sub>2</sub>OH at 53 °C.<sup>20</sup> <sup>g</sup>Observed rate ratio (k<sub>5</sub>/k<sub>6</sub>) at 50 °C.<sup>4b</sup> assumed to be the same at 60 °C. <sup>h</sup>Extrapolated from data at other temperatures.

MP2 and MP3 relative energies of 3 in Table II, the Møller-Plesset series obviously has not converged; the value will be somewhat different (probably lower) at higher orders. Nevertheless, we follow convention in discussing only the highest level MP3/6-31G\*\*//6-31G\* results in the text unless otherwise indicated.

**Experimental Procedures.** The tosylates 5 and 6 (X = OTs) were prepared from the corresponding alcohols (X = OH); 5-OH<sup>19</sup> was purified by gas chromatography. HFIP was distilled from 4-Å molecular sieves. Kinetic data were obtained conductimetrically as described previously.<sup>20</sup>

## Discussion

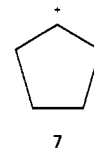
**Solvolysis Results.** The kinetic data (Table III) show a remarkable lack of solvent dependence of relative solvolysis rates for cyclopent-3-enyl (5) and cyclopentyl (6) tosylates over a wide range of solvent nucleophilicity and ionizing power. As cyclopentyl tosylate (6) is known to be sensitive to solvent nucleophilicity,<sup>5,20</sup> solvolyses of cyclopent-3-enyl tosylate (5) also appear to be *k*<sub>s</sub> processes, leading largely to elimination products.<sup>6b</sup> The best estimates of rates leading to cationic intermediates are given from solvolyses in the least nucleophilic solvent examined (HFIP), in which 5 reacts 8 times more slowly than 6.

Substitution products from solvolyses of derivatives of 5 have been reported to be mainly derived by hydride shift to give cyclopent-2-enyl derivatives.<sup>6a,21</sup> Lambert and Finzel<sup>6b</sup> later mentioned only homoallylic substitution products and reported that hydrolysis (70% dioxane/water) and acetolysis of 5, X = OTs, gave inverted homoallylic alcohol and acetate, respectively.<sup>6b</sup> Solvolysis of 6, X = OTs, also gives substitution with inversion of configuration in competition with elimination (up to 80% in fluorinated alcohols).<sup>7</sup> In contrast, formolysis of 5, X = OTs, gave homoallylic substitution with ca. 95% retention of configuration,<sup>6b</sup> although no other products were discussed, the NMR reported for the formate product indicated that hydride shifts must have occurred. Double-bond participation was suggested to account for these results,<sup>6b</sup> but this is probably just the onset of a *k*<sub>Δ</sub> pathway.

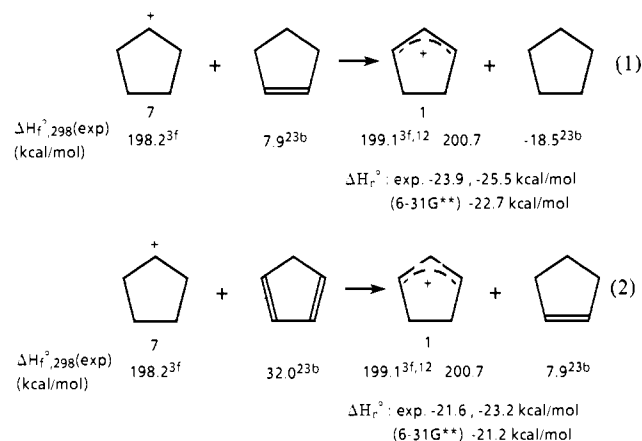
We infer from the above stereochemical data for 5, X = OTs, that solvolysis in HFIP should also occur with double-bond participation, because HFIP has a higher ionizing power and a lower nucleophilicity than formic acid.<sup>5</sup> The high percent of retention in formic acid could correspond to a rate enhancement of about 20 for homoallylic substitution, and even higher values would be expected in HFIP. To reconcile these deductions from product data with the kinetic data (Table III) showing *reduced*

solvolytic reactivity for 5, X = OTs, we have examined the energies of relevant carbocations by means of ab initio molecular orbital theory.

**Theoretical Calculations.** In any theoretical study, it is desirable to establish the reliability of the method being employed. This can be done in two ways: by comparing results with those of the experiment (whenever the latter are available) and by internal consistency of the results as the sophistication of the theoretical level is increased. As discussed above, reasonable, but not perfect, convergence was achieved in the relative energies of Table II. Experimentally, the difference in heats of formation of 1 and 4, 21 kcal/mol,<sup>12</sup> is in nearly exact agreement with our highest level results. The heats of formation of the cyclopentyl (7) and cy-



clopentenyl (1) cations also are known,<sup>23</sup> and their relative energies can be compared by means of isodesmic equations (1 and 2). The



agreement between theory and experiment also is good, although correlated energies are not available for the reference molecules. The calculated proton affinity of cyclopentadiene (202.6 kcal/mol, MP3/6-31G\*\*/6-31G\*\* ZPE; Table II) also agrees well with the experiment (200 kcal/mol).<sup>3f</sup>

In contrast, the calculated energy differences between 1 and 3 do not agree very well with the earlier, albeit indirect, experimental estimates of 6.9–8.5<sup>2</sup> or 12 kcal/mol.<sup>12</sup> Although our estimated "best" difference of 18.8 kcal/mol favoring 1 over 3 (Table II) might become somewhat less at higher levels of theory, we expect a significant difference to remain. Hence, it seems likely that the experimental gas-phase difference between 1 and 3 is underestimated.

The second source of experimental energy information is the activation barrier of 18.0 ± 0.9 kcal/mol for hydrogen scrambling in the c-C<sub>5</sub>H<sub>7</sub><sup>+</sup> system. This agrees remarkably well with the 18.8 kcal/mol calculated energy difference between 1 and 3 (Table II). The classical nonconjugated isomer, 2, is much higher in energy and seems clearly to be ruled out as a participating species in this degenerate rearrangement. This establishes the bridged structure of the cyclopenten-3-yl cation (3) as a likely intermediate.

The question arises as to whether it fair to compare calculated energy differences for 1 and 3 in the isolated state with those measured in superacid media. We believe that this very likely is the case. While Jorgensen has shown convincingly that delocalized (e.g., planar allyl) and more localized (e.g., perpendicular allyl) cations are solvated to different extents,<sup>24</sup> both 1 and 3 (as

(19) Hess, H. M.; Brown, H. C. *J. Org. Chem.* **1967**, *32*, 4138.

(20) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466.

(21) Hanack, M.; Schneider, H.-J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 674.

(22) Roberts, D. D. *J. Org. Chem.* **1968**, *33*, 118.

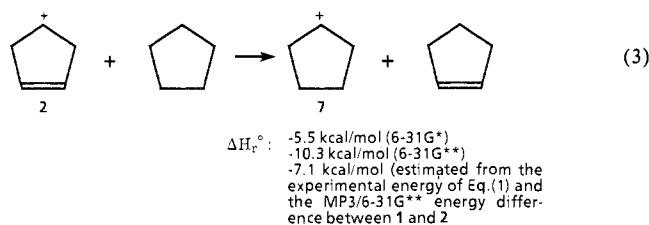
(23) (a) Lossing, F. P.; Traeger, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 1579.

(b) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, No. 1.

(24) Cournoyer, M. E.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 5104.

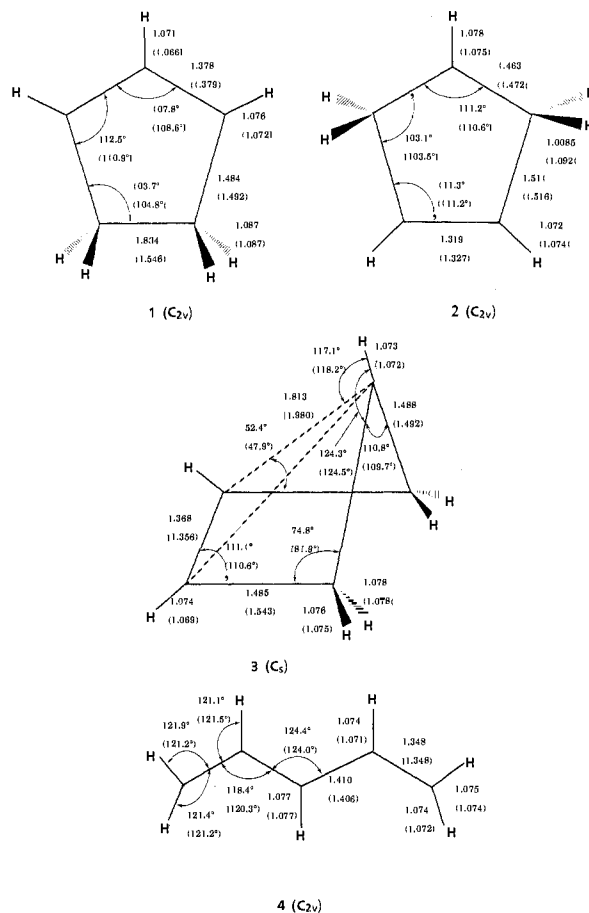
well as the possible transition state between them) fall into the "delocalized" category. There are a number of experimental instances where large changes in solvent types have negligible effects on the equilibria or the rates of interconversion of delocalized species.<sup>25</sup> Thus, we do not expect the relative energies of **1** and **3** to change appreciably on going from gas phase to solution. The same is true of the possible transition state interconnecting these species. We have not sought such a transition structure calculationally but, in general, 1,2-hydride shifts in cyclopentyl and other carbocation systems have very low barriers.<sup>25</sup> Hence, we do not expect the transition structure for rearrangement of **3** to **1** to lie very much above **3** in energy. Solvation may indeed stabilize **2** differentially by as much as 10 kcal/mol (the value indicated by Jorgensen's work).<sup>24</sup> If so, the bridged form, **3**, would still be significantly more stable than **2**; calculations indicate the **3** should be about 14 kcal/mol more stable than **2** in the gas phase.

The relevance of these results for the interpretation of the solvolysis behavior is questioned. Even in HFIP, cyclopentyl tosylate solvolyzes about 10 times faster than cyclopenten-4-yl tosylate (Table III). The relative energies of the classical non-conjugated cyclopentenyl cation, **2**, and the cyclopentyl cation provide an explanation. As shown by eq 3, the unsaturated cation



(**2**) is about 5–10 kcal/mol less stable than the saturated species. Since the planar,  $C_{2v}$  structure was used for **2**, there can be no question of destabilization through extreme angle deformation (two of the CCC angles in **3** are  $74.9^\circ$  at 6-31G\*). Since  $sp^2$ -hybridized carbons are more electronegative than their  $sp^3$  counterparts, the double bond in **2** destabilizes the cation inductively. Hyperconjugative stabilization by the adjacent  $CH_2$  groups also is reduced when a more electronegative substituent (the double bond) is present. In analyses of the extent of neighboring group participation, such corrections for the inductive effects of participating groups have often been made.<sup>26</sup> This means that saturated compounds without double bonds in the vicinity of the leaving groups are not satisfactory standards on which to base estimates of anchimeric assistance. This problem is also present in the 7-norbornenyl system,<sup>1</sup> but the very large anchimeric assistance obscures the need for an inductive correction. However, in more weakly participating cyclopentenyl, cyclohexenyl,<sup>6c</sup> norbornenyl, etc., systems, such corrections are essential. Indeed, the decelerating effect of the double bond is shown experimentally by the 44 times slower solvolysis rate of 2-*endo*-norbornenyl over 2-*endo*-norbornyl tosylate.<sup>27</sup> If we apply this correction factor of 44 to the cyclopent-3-enyl case, anchimeric assistance of about 5 is indicated. An effect of this magnitude is necessary to explain the stereochemical results of Lambert;<sup>6</sup> the degree of product control and the degree of neighboring group participation must be directly related.<sup>26</sup>

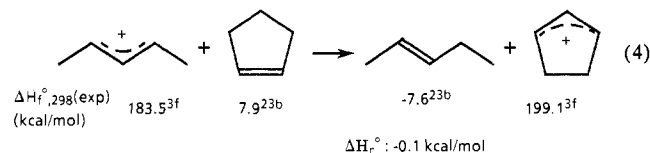
The solvolysis behavior can be interpreted as follows. As Winstein often noted, "bridging lags behind ionization".<sup>28</sup> This is especially likely to be the case in systems where considerable changes in geometry are needed on going from ground to bridged



**Figure 1.** Optimized geometries of **1–4** at 6-31G\* (3-21G values in parentheses). Angles are in degrees and distances in angstroms. Noteworthy features: in **1**, the small allyl cation CCC angle,  $107.6^\circ$  (108.6); in **4**, the different CC bond lengths, end = 1.348 (1.346) and central = 1.410 (1.406), and narrower outer CCC bond angles,  $119.4^\circ$  (120.3) vs  $124.4^\circ$  (124.0); in **3**, the small CCC bond angle at the methylene group,  $74.9^\circ$  (81.9), and the distance between the "cationic" (C4) and the "olefinic" carbons (C1 and C2), 1.813 (1.990). Polarization functions favor the nonclassical structure; not only the C1–C4 but also the C2–C3 bond lengths become significantly shorter (6-31G\* vs 3-21G), and the C1–C2 length becomes somewhat longer in **3**.

transition state. Cyclopentene and its simple derivatives are nearly planar, whereas the bridged intermediate (Figure 1 shows the 6-31G\* geometry) is highly distorted. Overlap between the developing carbocation and the  $\pi$  electron of the double bond cannot become effective unless the distortion is rather large.<sup>4</sup> This, coupled with the unfavorable inductive effect of the double bond, reduces the solvolysis rate constant of cyclopent-3-enyl tosylate below that of cyclopentyl tosylate.

The final point to be discussed concerns the energy of the conjugated cyclopentenyl cation, **1**. The solvolysis rates of cyclopent-2-enyl derivatives are significantly higher than those of both acyclic and cyclic allylic counterparts. Allyl cations in five-membered ring systems in superacid solution have an enhanced stability, and this is reflected in solvolysis rates.<sup>3</sup> Since each of the two methylene groups can contribute two electrons to a cyclic  $6\pi$  array, Sorensen has suggested that **1** might be a "pseudoaromatic" system.<sup>3d</sup> However, more recent gas-phase energy measurements do not indicate any particularly large stability for **1**, e.g. the results of eq 4. This matter will be discussed



in greater length in a separate publication. However, the 21

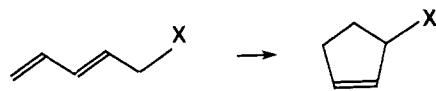
(25) Review: Saunders, M.; Chandrasekar, J.; Schleyer, P. v. R. In *Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, p 1.

(26) For example, for  $\beta$ -phenyl participation, see: Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. 3, Chapter 22, p 1347.

(27) Brown, H. C. (with comments by Schleyer, P. v. R.) *The Nonclassical Ion Problem*; Plenum: New York, 1977; p 110. For a 51-fold rate depression due to a  $\gamma$ -double bond, see: Creary, X. *J. Am. Chem. Soc.* **1976**, *98*, 6608.

(28) See, e.g., ref 27 and: Bartlett, P. D. *Nonclassical Ions*; Benjamin: New York, 1965.

kcal/mol greater stability of **1** over its acyclic isomer, the pentadienyl cation (Table II),<sup>12</sup> is noteworthy. Since the gain in energy on going from 1,3-pentadiene to cyclopentene is only 11 kcal/mol, some favorable electronic features, such as those discussed by Sorensen, must be present in **1**. The pentadienyl radical also is only  $10.6 \pm 3$  kcal/mol less stable than the cyclopent-3-enyl radical.<sup>29</sup>



X=H <sup>23b</sup>	-10.7 kcal/mol (expt)
X=• (radical) <sup>28</sup>	-10.6±3 kcal/mol (expt)
X=+ (cation) <sup>3f</sup>	-21 kcal/mol (expt; also see Table 1)

### Conclusion

The calculated energy difference of 5–10 kcal/mol between the classical cyclopenten-4-yl cation (**2**) and the cyclopentyl cation (**7**) corresponds to a solvolytic rate ratio ( $k_c/k_s$ ) of up to  $10^7$ . As the observed rate ratio is only 5–8 (Table III), a rate enhancement up to  $10^6$  due to anchimeric assistance ( $k_A$  process) may accelerate solvolyses of **5**; this would explain the high proportion (ca. 95%) of retention of stereochemistry in the homoallylic substitution

(29) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

product. Interpretation of the solvent effects on reactivity using the extended Grunwald–Winstein equation<sup>20</sup> leads to the alternative explanation that solvolyses of **5** and **6** may both be predominantly  $k_s$  processes. Stereochemical measurements may be detecting only the onset of the  $k_A$  process because homoallylic substitution occurs in low yield. This explanation implies that the energy difference between solvated ions **2** and **7** is smaller than that calculated for the free ions. Although the bridged cation (**3**) is calculated to be 13 kcal/mol more stable, the classical isomer (**2**) rate enhancements are not observed because bridging lags behind ionization. There also may be a barrier to double-bond participation.

**Acknowledgment.** Financial support of our work by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank the Computer Centers at the Universities of Berlin, Erlangen, and Munich for providing generous computer time. We are grateful to G. Llewellyn (Swansea) and W. Zummack (Berlin) for technical assistance and to K. Raghavachari for some of the energies in Table I. This paper is dedicated to Paul D. Bartlett on the occasion of his retirement from Texas Christian University.

**Registry No.** **1**, 63346-43-0; **2**, 81107-93-9; **3**, 81181-41-1; **4**, 54448-32-7; **5**, 36367-85-8; **6**, 3558-06-3.

**Supplementary Material Available:** Geometries at 6-31G\* of ions of **1–3** (3 pages). Ordering information is given on any current masthead page.

## A Study of Long-Range $\pi^*$ , $\pi^*$ Interactions in Rigid Molecules Using Electron Transmission Spectroscopy

V. Balaji,<sup>†</sup> L. Ng,<sup>†</sup> K. D. Jordan,<sup>\*†</sup> M. N. Paddon-Row,<sup>\*‡</sup> and H. K. Patney<sup>§</sup>

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, University of New South Wales, Kensington, New South Wales, Australia 2033, and New South Wales Institute of Technology, New South Wales, Australia 2007. Received November 17, 1986

**Abstract:** Electron transmission (ET) spectroscopy is used to determine the vertical electron affinities of a series of nonconjugated dienes **2–9** and their benzene analogues **11–17** in which the unsaturated moieties are separated by two to six  $\sigma$  bonds. For the compounds in which the benzene or ethylene groups are separated by three or more  $\sigma$  bonds, through-bond interactions are found to be primarily responsible for the observed splittings in the energies of the anion states. In order to explain satisfactorily the energies of the anion states of these compounds, relative to those of the isolated ethylene and benzene molecules, it is necessary to invoke mixing of the  $\pi^*$  orbitals with both the occupied  $\sigma$  and unoccupied  $\sigma^*$  orbitals comprising the connecting  $\sigma$  chains. The large splittings between the symmetric  $\pi$  ( $\pi_g$ ) MO's in the photoelectron spectra of **8** and **16** and the absence of such splittings between the  $\pi^*$  MO's in the ET spectra of these compounds provide convincing support for the presence of hyperconjugation between the  $\pi_g$  and bridge orbitals in **8** and **16**.

### I. Introduction

This paper is part of a comprehensive program designed to explore orbital interactions through  $n$   $\sigma$  bonds<sup>1,2</sup> (OIT- $n$ -B), involving  $\pi$  and  $\pi^*$  MO's, and how the magnitudes of such interactions depend on the number,  $n$ , and the geometry of the relaying  $\sigma$  framework.<sup>2</sup> The techniques of photoelectron spectroscopy (PES)<sup>1d,3</sup> and electron transmission spectroscopy (ETS)<sup>4,5</sup> have been the principal experimental probes in these investigations. The former technique gives the ionization potentials (IP's) and the latter the electron affinities (EA's). In an orbital picture (i.e., within the context of Koopmans' theorem<sup>6</sup>), the IP's and EA's

may be associated with the negatives of the energies of the filled and unfilled molecular orbitals, respectively. Hence these experimental methods are ideally suited for the study of intramolecular interactions between remote functional groups.

(1) (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (c) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696. (d) Martin, H.-D.; Mayer, B. *Ibid.* **1983**, *22*, 283.

(2) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *14*, 245.

(3) (a) Bock, H.; Ramsey, B. G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 734. (b) Heilbronner, E.; Meier, J. P. In *Electron Spectroscopy: Theory, Techniques, and Applications*; Brundle, C. R., Baker, A. D., Eds.; Academic Press: New York, 1977; Vol. 1.

(4) Sanche, L.; Schulz, G. J. *Phys. Rev. A* **1968**, *5*, 1972.

(5) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

(6) Koopmans, T. *Physica* **1934**, *1*, 104.

<sup>†</sup> University of Pittsburgh.

<sup>‡</sup> University of South Wales.

<sup>§</sup> New South Wales Institute of Technology.