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## Theoretical Study of the Isomeric Cyclopropylidenemethyl and 1-Cyclobutenyl Cations, Unusually Stable Vinyl Cations

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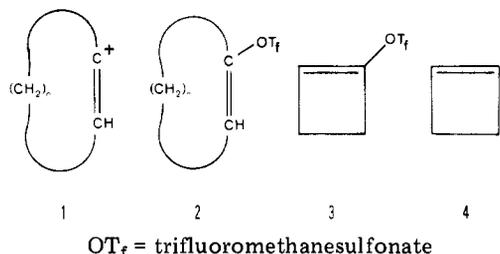
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Ab initio and MINDO/3 calculations were employed to explore the geometries and energies of unusual vinyl cations. In agreement with experiment, both the cyclopropylidenemethyl (8) and the cyclobutenyl (4) cations were found to be highly stabilized species. The former benefits from effective hyperconjugation involving the cyclopropyl ring while the latter is indicated to be a nonclassical ion with C<sub>3</sub> bridging almost equidistantly between C<sub>1</sub> and C<sub>2</sub>. This 1-cyclobutenyl cation (4) is found to be significantly more stable than 8. This difference is very much reduced in the methyl-substituted isomers 10 and 11. The homopropargyl ion (9), not a minimum on the potential energy surface, should rearrange directly to the much more stable 4.

Extensive studies of vinyl cations over the last decade have established their intermediacy in solvolytic reactions.<sup>2</sup> The relative stabilities of vinyl cations are usually deduced from solvolysis rates, but ground-state and solvation effects may complicate the interpretations.<sup>2</sup> Related experimental data in the gas phase are limited,<sup>3a-c</sup> although some new measurements were reported recently by Aue and Bowers.<sup>3d</sup> A more detailed understanding of the stabilities and the structures of this relatively new class of carbenium ions can be obtained computationally; a large number of substituted vinyl cations have already been investigated.<sup>4</sup>

Cyclic vinyl cations (1) are of special interest.  $\alpha$ -Substituted vinyl cations,<sup>2,4</sup> as well as the C<sub>2v</sub> classical form of the parent vinyl cation, H<sub>2</sub>C=CH<sup>+</sup>,<sup>5</sup> are indicated to



prefer linear over bent structures. As the ring size of cyclic vinyl cations (1) is reduced, increased bending away from linearity at the carbocation site should result in decreasing stability. MINDO/3 calculations of cyclic vinyl cations (1) confirm these qualitative expectations.<sup>6</sup>

Indeed, Hanack, Schleyer, Stang, and their co-workers have found the ease of formation of cyclic vinyl cations (1) to decrease with decreasing ring size.<sup>7a</sup> Thus, the relative solvolysis rates (in 50% ethanol) of cyclononyl (2, n = 7), cyclooctenyl (2, n = 6), cycloheptenyl (2, n = 5), and cyclohexenyl (2, n = 4) triflates are 1.9 × 10<sup>6</sup>:3.7 × 10<sup>4</sup>:3.5 × 10<sup>3</sup>:1.<sup>7</sup> The solvolysis rates of larger cyclic systems such as cyclododecenyl (2, n = 10), cycloundecenyl (2, n = 9), and cyclodecenyl (2, n = 8) triflates are all similar and are 2-7 times slower than that of cyclononyl triflate (2, n = 7).<sup>7a</sup> Cyclopentenyl triflate (2, n = 3) solvolyzes even

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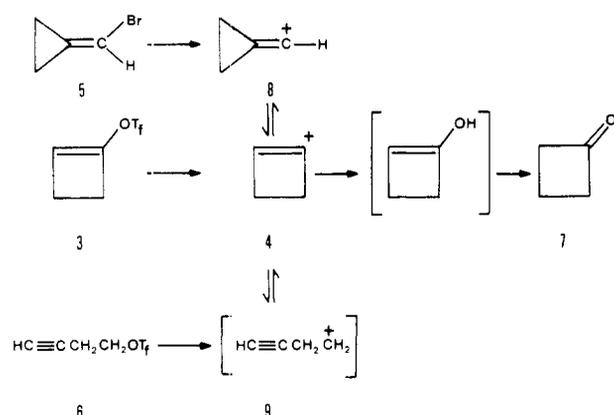
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Table I. Optimized Geometries of 4 and 9-11 (STO-3G and MINDO/3)<sup>a</sup>

geometrical parameter <sup>a</sup>	4 <sup>b</sup>		8 <sup>c</sup>		10 <sup>c</sup>		11 <sup>i</sup>	
	STO-3G	MINDO/3	STO-3G	MINDO/3	STO-3G	MINDO/3	STO-3G	MINDO/3
r(C <sub>1</sub> -C <sub>2</sub> )	1.250	1.285	1.220	1.229	1.256	1.292	1.228	1.249
r(C <sub>2</sub> -C <sub>3</sub> )	1.733	1.606	1.577	1.558	1.722	1.662	1.556	1.544
r(C <sub>3</sub> -C <sub>4</sub> )	1.587	1.563	1.466	1.432	1.577	1.551	1.473	1.440
r(C <sub>1</sub> -C <sub>4</sub> )	1.479	1.446	-	-	1.478	1.445	-	-
r(C <sub>1</sub> -C <sub>3</sub> )	1.787	1.683	-	-	1.769	1.662	-	-
r(C <sub>1</sub> -H <sub>1</sub> )	-	-	1.091	1.078	-	-	-	-
r(C <sub>2</sub> -H <sub>1</sub> )	1.085	1.085	-	-	-	-	-	-
r(C <sub>3</sub> -H <sub>2</sub> )	1.092	1.108	1.093	1.051	1.092	1.107	1.092	1.103
r(C <sub>4</sub> -H <sub>3</sub> )	1.092	1.105	1.093	1.051	1.091	1.105	1.092	1.103
r(C <sub>2</sub> -C <sub>5</sub> )	-	-	-	-	1.502	1.458	1.458	1.429 <sup>h</sup>
r(C <sub>5</sub> -H <sub>5</sub> )	-	-	-	-	1.091	1.108	1.091	1.109 <sup>h</sup>
C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	71.5	70.2	152.3	152.6	70.9	67.1	151.8	152.2
C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	124.2	123.2	-	-	-	-	-	-
C <sub>1</sub> C <sub>2</sub> H <sub>1</sub>	156.8	153.0	180.0	180.0	157.5 <sup>f</sup>	155.7 <sup>f</sup>	180.0 <sup>g</sup>	180.0 <sup>g</sup>
C <sub>2</sub> C <sub>3</sub> b <sub>1</sub> <sup>d</sup>	124.1	126.2	136.1	133.5	124.3	123.7	138.6	135.9
H <sub>2</sub> C <sub>3</sub> H <sub>2</sub>	117.5	110.4	116.9	111.0	117.2	109.7	116.5	110.6
C <sub>3</sub> C <sub>4</sub> b <sub>2</sub> <sup>e</sup>	143.2	145.0	136.1	133.5	143.7	146.8	159.6	135.9
H <sub>3</sub> C <sub>4</sub> H <sub>3</sub>	115.3	109.3	116.9	111.0	114.8	108.9	116.5	110.6
H <sub>2</sub> C <sub>5</sub> C <sub>2</sub>	-	-	-	-	109.3 <sup>j</sup>	110.5	110.0 <sup>j</sup>	111.8 <sup>h</sup>
H <sub>3</sub> C <sub>5</sub> C <sub>2</sub>	-	-	-	-	-	111.5	-	109.6 <sup>h</sup>

<sup>a</sup> Atom numberings are given in Figure 1. Bond lengths in angstroms, angles in degrees. <sup>b</sup> Keeping C<sub>s</sub> symmetry (ab initio); no symmetry was assumed for the MINDO/3 calculations, but the carbon skeleton turns out to be essentially planar. <sup>c</sup> Keeping C<sub>2v</sub> symmetry (ab initio); no symmetry was assumed (MINDO/3), but an essentially planar carbon skeleton resulted. <sup>d</sup> b<sub>1</sub> is the bisector of the H<sub>2</sub>C<sub>3</sub>H<sub>2</sub> angle. <sup>e</sup> b<sub>2</sub> is the bisector of the H<sub>3</sub>C<sub>4</sub>H<sub>3</sub> angle. <sup>f</sup> The C<sub>1</sub>C<sub>2</sub>C<sub>3</sub> bond angle. <sup>g</sup> The C<sub>2</sub>C<sub>3</sub>C<sub>4</sub> bond angle. <sup>h</sup> Assuming local C<sub>s</sub> symmetry for the methyl group. <sup>i</sup> Assuming C<sub>2v</sub> symmetry and local C<sub>s</sub> symmetry at the methyl groups. <sup>j</sup> Assuming local C<sub>3v</sub> symmetry at the methyl group.

Scheme I. Solvolysis of 3, 5, and 6 in 50% EtOH<sup>a</sup>

<sup>a</sup> The main product is 7.

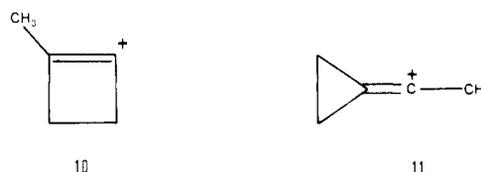
more slowly than cyclohexenyl triflate but not via a vinyl cation mechanism.<sup>7b</sup> On this basis, it might be expected that the lower cyclic homologue, the cyclobutenyl triflate (3), should also solvolyze by a mechanism bypassing the highly strained cation 4.

Surprisingly, Hanack and co-workers found that 3 solvolyzes 3700 times faster than cyclohexenyl triflate (2, *n* = 4).<sup>8</sup> Alternative mechanisms were considered, but it has been now established that 3 reacts by an S<sub>N</sub>1 mechanism via the 1-cyclobutenyl cation 4.<sup>8</sup> Furthermore, 4 was also proposed to be an intermediate in the solvolysis of cyclopropylidenemethyl bromide (5) and of the corresponding homopropargyl derivative 3-butyn-1-yl triflate (6). The main solvolysis product (in 50% EtOH) from all three starting materials is cyclobutanone (7). Hanack postulated that cation 4 is a common intermediate in the solvolysis of 3, 5, and 6 (Scheme I).<sup>2c,d,9</sup>

The cyclopropylidenemethyl cation (8) also exhibits unusual stability;<sup>10</sup> 5 solvolyzes much faster than secondary

vinyl bromides such as (CH<sub>3</sub>)<sub>2</sub>C=C(Br)CH<sub>3</sub>.<sup>2c,d,11</sup> The proposed intermediate 8 is so far the only primary vinyl cation that can be generated solvolytically.

In this paper we report ab initio and MINDO/3 calculations on 4, 8, 9, and their methylated derivatives 10 and 11. In contrast to the numerous theoretical studies de-



voted to the analogous cyclopropylcarbinyl and cyclobutyl cations,<sup>12</sup> only one previous CNDO/2 study of 4 and 8 is available.<sup>13</sup>

**Quantum Mechanical Methods.** We have employed both the semiempirical MINDO/3<sup>14</sup> and standard single determinant ab initio molecular orbital methods.<sup>15</sup> Com-

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(11) (CH<sub>3</sub>)<sub>2</sub>C=C(Br)CH<sub>3</sub> and other simple alkyl-substituted vinyl bromides do not react at temperatures as high as 200 °C.<sup>10</sup> The solvolysis rate of (CH<sub>3</sub>)<sub>2</sub>C=C(Br)CH<sub>3</sub> is estimated from the reaction rate of the corresponding tosylate or triflate.<sup>10</sup>

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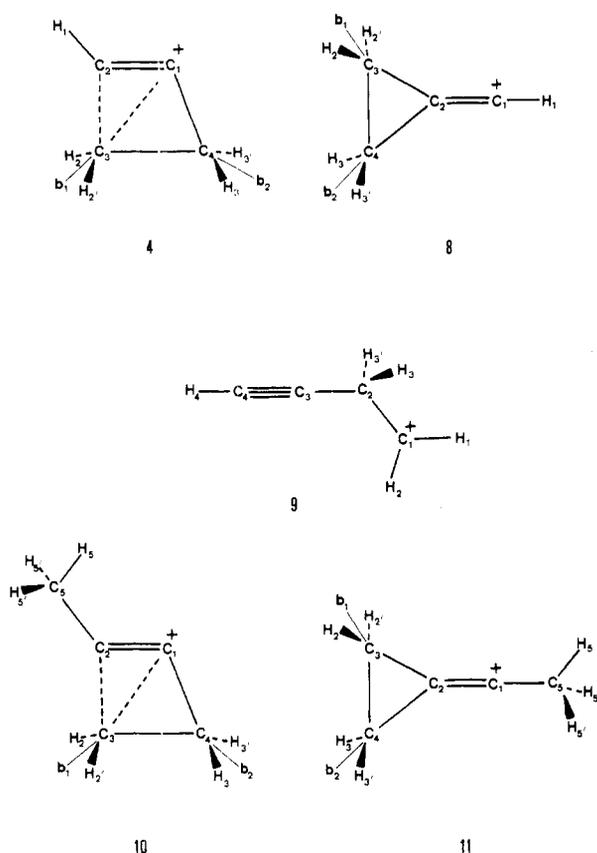


Figure 1. Numbering scheme in 4 and 8–11.

plete geometry optimizations within each assumed symmetry were carried out for 4 and 8–11, using the minimal STO-3G basis set<sup>16a</sup> and the Fletcher–Powell gradient-optimization method.<sup>16b</sup> Single-point calculations on optimized STO-3G geometries were performed with the split-valence 4-31G<sup>16c</sup> and two augmented basis sets: one with d functions on nonhydrogen atoms (6-31G\*)<sup>16d</sup> and other with an additional set of p functions on each hydrogen (6-31G\*\*).<sup>16d</sup> These calculations are designated 4-31G//STO-3G, 6-31G\*\*//STO-3G, and 6-31G\*\*//STO-3G, respectively. The corrections due to electron correlation were estimated at the 4-31G level by using the second-order perturbation procedure suggested by Møller and Plesset (MP2/4-31G//STO-3G).<sup>17</sup>

## Results and Discussion

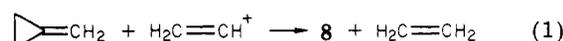
The optimized geometries of 4, 8, 10, and 11 (both STO-3G and MINDO/3) are given in Table I (also see Figure 1); Table II provides similar details for 9. The calculated total energies (ab initio) and the calculated heats of formation (MINDO/3) are summarized in Table III.

**A. The Cyclopropylidenemethyl Cation (8).** The rapid solvolysis of cyclopropylidenemethyl bromide (5) was attributed by Hanack to the high stability of the intermediate cation 8.<sup>2c,d,10</sup> Our calculations support this conclusion. The hydride-transfer isodesmic reaction 1, which compares the stability of 8 to that of the parent vinyl cation, is calculated to be highly exothermic (Table IV); 8 is found to be 31.8 kcal/mol (6-31G\*); 34.2 kcal/mol,

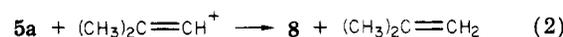
Table II. Optimized Geometry of 9 (STO-3G and MINDO/3)<sup>a</sup>

geometrical parameter	STO-3G	MINDO/3
$r(C_1-C_2)$	1.500	1.418
$r(C_2-C_3)$	1.475	1.444
$r(C_3-C_4)$	1.173	1.205
$r(C_1-H_1)$	1.115	1.103
$r(C_1-H_2)$	1.115	1.104
$r(C_2-H_3)$	1.106	1.129
$r(C_4-H_4)$	1.073	1.073
$C_1C_2C_3$	115.1	124.7
$C_1C_3C_4$	179.9	177.9
$H_1C_1C_2$	120.2	123.2
$H_2C_1C_2$	122.6	126.1
$C_3C_2b_1^b$	129.8	127.0
$H_3C_2H_3'$	104.1	98.8
$H_4C_4C_3$	180.4	180.0

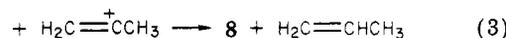
<sup>a</sup> Atom numbering is given in Figure 1. Bond lengths in angstroms, angles in degrees. The  $CH_2^+$  and CCC units were held in one plane. <sup>b</sup>  $b_1$  is the bisector of the  $H_3C_2H_3'$  angle.



5a



12



13

MINDO/3) more stable than  $\text{H}_2\text{C}=\text{CH}^+$ . It must be stressed that such calculations apply to the gas phase where polarization (size) stabilization effects are important. Size effects are, however, of only minor importance in solution so that a more pertinent comparison with solvolysis studies is given by reaction 2, where 8 and 12 are both  $C_4$  cations.

Reaction 2, calculated to be exothermic by 14 kcal/mol (STO-3G),<sup>18</sup> demonstrates the large stabilization afforded by the cyclopropane ring compared with the two  $\beta$ -methyl groups. It is not surprising that 8 is the only primary cation which can be generated in solution. Furthermore, 8 is considerably more stable (7.9 kcal/mol, 6-31G\*; 5.9 kcal/mol, MINDO/3) than the secondary 2-propenyl cation 13 (reaction 3, Table IV). This result is consistent with the observation that 5 solvolyzes  $10^4$ – $10^5$  times faster than 2-propenyl derivatives.<sup>2,19–21</sup>

The stabilizing effect of the  $\beta$ -cyclopropane ring in 8 may

(18) The optimized STO-3G energy for 12 is  $-153.36836$  hartrees (Mayr, H.; Wilhelm, D., unpublished results); the MINDO/3 value is 224.9 kcal/mol when  $C_{2v}$  symmetry is imposed. Although higher level calculations for 12 are not yet available, the data in Table IV show that the energies of isodesmic reactions such as reaction 1 are not very sensitive to the basis set. 12 is not a local minimum at MINDO/3 and collapses to a bridged structure upon optimization ( $\text{CH}_2\text{CH}=\text{CH}^+$  behaves similarly, see also ref 25).

(19) Comparisons between solvolysis rates and the stabilities of the intermediate cations in the gas phase may be misleading. In the gas phase 8 is calculated to be 0.5 kcal/mol less stable than  $\text{CH}_3\text{CH}=\text{CCH}_3^+$ . In solution, however, 2-butenyl bromide solvolyzes  $10^4$ – $10^5$  times slower than cyclopropylidenemethyl bromide.<sup>2,11</sup> This apparent discrepancy results from the much greater importance of polarization (size) effects in the gas phase.  $\text{CH}_3\text{CH}=\text{CCH}_3^+$  is 9.7 kcal/mol (STO-3G); 7.9 kcal/mol, experimental<sup>20</sup>) more stable than  $\text{H}_2\text{C}=\text{CCH}_3^+$  (evaluated by a hydride-transfer reaction), but the solvolysis rates of their derivatives are similar.<sup>2</sup> Better solvation of  $\text{H}_2\text{C}=\text{CCH}_3^+$  relative to  $\text{CH}_3\text{CH}=\text{CCH}_3^+$  probably is responsible for the small effect of the  $\beta$ -methyl group in solution. Hydrogen bonding is important in determining solvation energies;<sup>21</sup>  $\text{H}_2\text{C}=\text{CCH}_3^+$ , which possesses two relatively acidic  $sp^2$  hydrogens, may therefore be solvated better than  $\text{H}_3\text{CCH}=\text{CCH}_3^+$  which has only one vinylic hydrogen.

(20) Experimentally,  $\Delta H_f^\circ(\text{H}_2\text{C}=\text{CCH}_3^+) = 233$  kcal/mol;  $\Delta H_f^\circ(\text{CH}_3\text{CH}=\text{CCH}_3^+) = 218$  kcal/mol, see ref 3d.

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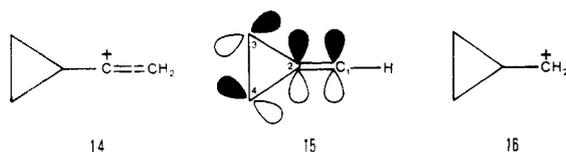
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Table III. Total Energies, Relative Energies, and Heats of Formation of 4, 8, 10 and 11<sup>a</sup>

computational method	total energies <sup>b</sup>			relative energies <sup>c</sup>		
	4	8	9 <sup>f</sup>	4	8	9
MINDO/3 <sup>e</sup>	236.3	235.0	257.3	1.4	0.0	22.5
STO-3G	-152.15581	-152.15863	-152.12566	1.8	0.0	20.7
4-31G	-153.74556	-153.76809	-153.74924	14.1	0.0	11.8
6-31G*	-153.99211	-153.99277	-153.96916	0.4	0.0	14.8
6-31G**	-154.00113	-154.00207	-	0.6	0.0	-
MP2/4-31G	-154.11282	-154.12167	-154.08939	5.5	0.0	20.3
MP2/6031G**est <sup>d</sup>	-	-	-	0.0 <sup>d</sup>	8.0 <sup>d</sup>	23.3 <sup>d</sup>
	10	11		10	11	
MINDO/3	213.9 <sup>e</sup>	203.5 <sup>e</sup>		10.4	0.0	
STO-3G	-190.76201	-190.77352		7.2	0.0	

<sup>a</sup> At the optimized STO-3G or MINDO/3 geometries specified in Table I. <sup>b</sup> In hartrees. <sup>c</sup> In kcal/mol. <sup>d</sup> Estimated by combining the MP2/4-31G and the 6-31G\*\* results (see text). <sup>e</sup> Heats of formation in kcal/mol. <sup>f</sup> Form with  $C_s$  symmetry, with the  $H_2C^+$  and CCC units in one plane (9). The conformer of 9 with the  $H_2C^+$  and CCC units perpendicular collapses upon optimization to one of the bridged structures 4 or 8. See text.

be compared with that of the  $\alpha$ -cyclopropane substituent in 14.<sup>4a</sup> The high stability of the primary cation 8 is due

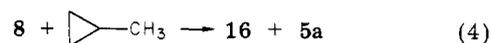


to its special geometry which maximizes the hyperconjugative interaction between the empty cationic 2p orbital and the antisymmetric Walsh orbital of the  $\beta$ -cyclopropyl ring (see 15). A massive charge transfer (0.413 and 0.404 e at STO-3G and at 6-31G\*, respectively) from the cyclopropyl ring to the 2p ( $C^+$ ) orbital results. This hyperconjugative charge transfer is even larger than in the  $\alpha$ -cyclopropyl vinyl cation 14 where the 2p ( $C^+$ ) population is 0.334 (STO-3G).<sup>4a</sup> The smaller distance between the formally vacant orbital and the cyclopropane rings in 8 than in 14 contributes to this difference.

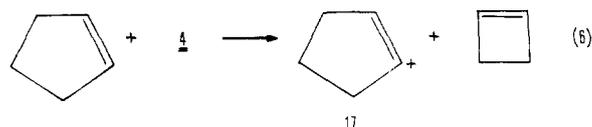
Structural changes also take place. As the occupied antisymmetric Walsh orbital of the cyclopropane ring has  $C_2-C_3$  and  $C_2-C_4$  bonding character, these bonds in 8 (1.577 Å, STO-3G) are substantially longer than the corresponding bonds in methylenecyclopropane (1.474 Å).<sup>22</sup> The  $C_1-C_2$  (1.220 Å) and  $C_3-C_4$  (1.466 Å) bonds, on the other hand, are shorter in 8 (vs. 1.298 and 1.522 Å, respectively, in methylenecyclopropane<sup>22</sup>).

Similar stabilization energies and structural changes have been found in 14<sup>4a</sup> and in the saturated alkyl analogue of 8, the bisected cyclopropylmethyl cation 16.<sup>12</sup> Vinyl cations are generally less stable than the corresponding alkyl cations (with the same number of carbons) by 12–17 kcal/mol (4-31G).<sup>4</sup> This tendency is less clearly born out in the case of 8 vs. 16. Reaction 4 is nearly thermoneutral in STO-3G and even exothermic in MINDO/3. This is not unexpected in view of the strongly enhanced  $C^+$ -cyclopropyl interaction in 8 vs. 16, which will certainly compensate for part of the normal 12–17 kcal/mol vinyl  $\rightarrow$  alkyl cation destabilization. The 4-31G and 6-31G\* results indicate, however, that MINDO/3 presumably overestimates this effect.

**B. 1-Cyclobutenyl Cation (4).** As mentioned in the introduction, the energy of the highly bent 1-cyclobutenyl



cation (4) might well be very high. However, comparison of the stability of 4 with that of the linear 2-propenyl cation (13) (reaction 5, Table IV) reveals the two cations to have



comparable stabilities (at 6-31G\*; the basis-set dependency is discussed below). This result is consistent with the similar solvolysis rates of cyclobutenyl and 2-propenyl derivatives.<sup>8</sup> The high stability of 4 is even more pronounced when compared with the 1-cyclopentenyl cation (17). 4 is calculated (reaction 6, MINDO/3) to be 11.3 kcal/mol more stable, even though 17 is expected to possess less angle strain. Indeed, 1-cyclopentenyl triflate (2,  $n = 3$ ) does not give 17 but solvolyzes by sulfur-oxygen cleavage.<sup>7b</sup> The remarkable stability of 4 is due to the strong interaction between the vacant 2p ( $C^+$ ) orbital and the  $\beta$ - $C_2-C_3$  bond, resulting in a bridged "nonclassical" structure. The bridging carbon  $C_3$  is nearly equidistant to  $C_2$  (1.733 Å) and to  $C_1$  (1.787 Å). These bridging distances are shorter than in other monocyclic bridged cations (i.e., 1.834 Å in corner-protonated cyclopropene,<sup>4c</sup> 1.803 Å in corner-protonated cyclopropane<sup>23</sup>) but similar to the 1.756-Å bridging distance in the puckered cyclobutyl cation (all values at STO-3G).<sup>12c</sup> The MINDO/3  $C_1-C_3$  and  $C_2-C_3$  bond lengths are indicated to be considerably shorter (1.606 and 1.683 Å, respectively), but the main structural feature, i.e., the bridging of  $C_3$ , prevails. The MINDO/3 structure of 4 is very similar to previous CNDO/2 calculations by Fischer, Hummel, and Hanack.<sup>13</sup> The formation of a bridged cation also results in the release of some of the unfavorable angle strain around the cationic center ( $C_1$ ). The  $C_2C_1C_4$  angle widens to 124.2° (STO-3G; 123.2° with MINDO/3); compare with the 94.7° value in cyclobutene.<sup>22</sup>

**C. Homopropargyl Cation (9).** Like many other primary cations,<sup>12</sup> the homopropargyl (3-buten-1-yl) cation (9) is indicated computationally not to be a minimum on the  $C_4H_5^+$  potential-energy surface. At both STO-3G and MINDO/3 levels,  $C_s$  symmetry with all four carbon atoms

(21) The solvation of carbenium ions has been studied recently theoretically: (a) Jorgensen, W. L. *Chem. Phys. Lett.* 1978, 53, 525. (b) Jorgensen, W. L.; Cournoyer, M. E. *J. Am. Chem. Soc.* 1978, 100, 5278, and references therein. (c) Jorgensen, W. L. *Ibid.* 1978, 100, 1049, 1057; 1977, 99, 4274, 3840. (d) Köhler, H.-J.; Lischka, H. *Theor. Chim. Acta*, in press. Also see: (e) Mayr, H.; Förner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1979, 101, 6032.

(22) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* 1975, 97, 6941.

(23) Radom, L.; Pople, J. A.; Buss, V.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1972, 94, 311.

Table IV. Calculated Energies for Reactions 1-5 (kcal/mol)<sup>a,b</sup>

computational method	reaction				
	1 <sup>c</sup>	2	3 <sup>d</sup>	4 <sup>e</sup>	5
MINDO/3 <sup>f</sup>	-34.2	-21.0	-5.9	4.0 <sup>g</sup>	-3.8
STO-3G//STO-3G	-35.0	-14.0	-9.2	0.6	10.8
4-31G//STO-3G	-33.7		-8.5	-12.7	11.1
6-31G*//STO-3G	-31.8		-7.9	-17.6 <sup>h</sup>	0.3

<sup>a</sup> Using optimized geometries for all molecules. <sup>b</sup> A minus sign indicates that the reaction is exothermic as written. <sup>c</sup> Ab initio energies for C<sub>4</sub> hydrocarbons from ref 22. <sup>d</sup> Ab initio energies for 13 from ref 4c and 24. <sup>e</sup> Ab initio energies for 16 from ref 12. <sup>f</sup> Energies of hydrocarbons from ref 14b, except  $\Delta H_f^\circ$  of methylcyclopropane = 1.2 kcal/mol. <sup>g</sup>  $\Delta H_f^\circ$  of 16 = 206.6 kcal/mol. <sup>h</sup> The 6-31G\*//4-31G energy of 16 from ref 12e was used.

and the C<sup>+</sup>H<sub>2</sub> hydrogens in the same plane had to be imposed in order to retain this form on optimization. Optimization of the conformation of 9 with the C<sup>+</sup>H<sub>2</sub> groups perpendicular resulted in 4 or 8 (depending on the initial geometry of 9 assumed).<sup>6</sup>

In the *n*-propyl cation<sup>23,25</sup> (also not an energy minimum), the empty carbocation lobe prefers to interact with the C<sub>2</sub>-C<sub>3</sub> bond rather than with the C<sub>2</sub>-H bonds; the C<sub>s</sub> conformation with the C<sup>+</sup>H<sub>2</sub> group perpendicular to the CCC plane is preferred. In 9, the situation is different, apparently because its C<sub>sp</sub>-C<sub>sp<sup>3</sup></sub> bond is lower in energy than the C<sub>sp<sup>3</sup></sub>-C<sub>sp<sup>3</sup></sub> bond in the *n*-propyl cation. Thus, if the C<sub>s</sub> optimized geometry of 9 with the C<sup>+</sup>H<sub>2</sub> group in the carbon plane was taken as reference and the C<sup>+</sup>H<sub>2</sub> group rotated 90° (keeping all other parameters constant), the MINDO/3 MINDOS/3 energy was raised by 6.0 kcal/mol. A standard geometry STO-3G study gave a similar result.

It is thus unlikely that solvolysis of homopropargyl derivatives (e.g., 6) will lead to discrete 3-butyne-1-yl cations (9). Instead, neighboring-group participation by the triple bond during ionization should lead to 4 or 8 directly.<sup>2c,d,9</sup> S<sub>N</sub>2 reactions may compete.

**Relative Stabilities of 4 and 8.** Which isomer is more stable, 4 or 8? The cyclobutenyl cation 4 is a bent secondary vinyl cation stabilized by bridging, while the cyclopropyldenemethyl cation 8, although primary, is stabilized by unusually effective hyperconjugation with the cyclopropyl ring. The calculated relative energies of 4 and 8, given in Table III, vary significantly with the basis set. This is expected since the relative energies of methylenecyclopropane (vs. cyclobutene) show a similar dependence on the basis (kcal/mol), 18.3 (STO-3G), 5.4 (4-31G), and 7.8 (6-31G\*), compared to the experimental value of 10.5 kcal/mol.<sup>22</sup> Furthermore, bridged cations are stabilized to different extents relative to their open isomers when polarization functions (d orbitals) are included in the basis set (e.g., 6-31G\*) or when electron correlation (EC) is taken into account; e.g., by 23.1 (d + EC),<sup>5c-e</sup> 13.6 (d + EC),<sup>5c-e</sup> and 10.1 (d functions)<sup>4c,24</sup> kcal/mol for the vinyl, ethyl, and bridged propenyl cations, respectively.<sup>25</sup> Similar changes occur in the relative energies of 4 and 8 (Table III). On going from STO-3G to 4-31G, 8 is stabilized relative to 4. Polarization functions (6-31G\*) on the other hand stabilize the bridged cation 4 more and  $\Delta E$  (4 - 8) is reduced by 13.7 kcal/mol. Electron correlation (MP2/4-31G) also stabilizes 4 relative to 8 by 8.6 kcal/

mol.<sup>24</sup> At 6-31G\*\*, which is the largest basis set where direct comparison is available, 8 is calculated to be 0.6 kcal/mol more stable than 4.

Although MP2/6-31G\*\* or MP2/6-31G\* calculations on 4 and 8 are beyond our present calculational capability, we predict that 4 should be *more stable* than 8.<sup>25</sup> 4 is estimated to be 8 kcal/mol more stable than 8 (Table III), assuming that the MP2 correction of 8.6 kcal/mol correlation energy difference found at the 4-31G level holds with the 6-31G\*\* basis.

Experience with other systems shows, however, that the MP2 procedure may exaggerate the effect of correlation energy.<sup>27</sup> This error may be compensated by optimization at higher basis-set levels,<sup>26</sup> so that our best estimate is that 4 should be more stable than 8 by about 8 kcal/mol. Surprisingly, this is almost identical with the 6.4-kcal/mol energy difference (4 more stable) obtained previously by CNDO/2 calculations,<sup>13</sup> but this agreement is only fortuitous. The minimal STO-3G basis set gives similar energy orderings for 4, 8, and 9 (Table III) as that at 6-31G\*//STO-3G; this also results from cancellation of errors. Thus, the overestimation of the strain associated with the cyclopropane ring in 8 is roughly counterbalanced by the underestimation of the stabilizing effect associated with the bridging in 4. MINDO/3 and STO-3G calculations give similar relative-energy orderings of 4, 8, and 9. Further comparisons among the various theoretical levels are provided in Table III. The reasonable success of MINDO/3 suggests that this method can be used for investigating homologous vinyl cations which are too large for study with ab initio methods, employing larger basis sets, although corrections may be needed. Our conclusion that 4 should be more stable than 8 in the gas phase is consistent with Hanack's solvolysis results: cyclobutanone (7) is the main product from the solvolysis of 3, 5, and 6 (Scheme I).<sup>2c,d,9</sup> Rearrangement of 8, probably the first intermediate formed in the solvolysis of 5, to the more stable 4 could be expected to be rapid under the solvolysis conditions. The open 3-butyne-1-yl cation (9) is calculated to be considerably less stable (e.g., 14.8 kcal/mol relative to 8, 6-31G\*, Table III)<sup>28</sup> than either 4 or 8; as discussed above, triple-bond participation to give 4 or 8 is expected and indeed is found.<sup>2c,d,9b</sup> The reader will recognize that solvation has not been taken into account in the calculations, so that agreement with experiment, although gratifying, may to some extent be fortuitous.

**2-Methylcyclobutenyl (10) and 1-Methylcyclopropyldenemethyl (11) Cations.** The effect of methyl substitution (i.e., cations 10 and 11) on the relative stabilities of 4 and 8 was investigated by STO-3G and MINDO/3 calculations. The structures of 10 and 11 are similar to those of the corresponding parent cations 4 and 8 (Table I). In 11 the  $\alpha$ -methyl substituent reduces the need for charge dispersal and the interaction of the 2p (C<sup>+</sup>) orbital with the antisymmetric Walsh orbital of the cyclopropyl ring should be smaller than in 8. Indeed, in 11 the C<sub>1</sub>-C<sub>2</sub> and C<sub>3</sub>-C<sub>4</sub> bonds are longer and the C<sub>2</sub>-C<sub>3</sub> and C<sub>2</sub>-C<sub>4</sub> bonds are shorter than those in 8 (Table I). The methyl

(24) Köhler, H.-J.; Lischka, H. *J. Am. Chem. Soc.* **1979**, *101*, 3479, have found recently that the electron-correlation correction stabilizes the bridged propenyl cation preferentially relative to the 1-propenyl cation by 9.9 kcal/mol. The change that these authors found on the addition of d functions (1.3 kcal/mol) is, however, much smaller than that reported in ref 23.

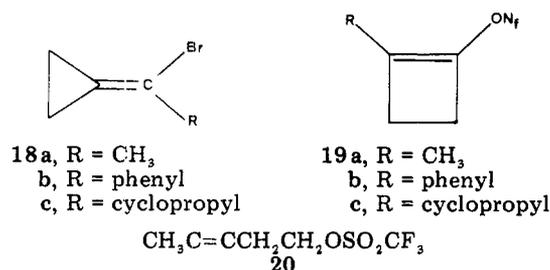
(25) A smaller stabilization (2-4 kcal/mol) of the bridged relative to the open structure upon additions of d functions was found for C<sub>3</sub>H<sub>5</sub><sup>+</sup> cations; see: Hariharan, P. C.; Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 599. However, d functions and correlation energy are generally more important for bridged vinyl cations than for the corresponding bridged alkyl cations (ref 4c, 5c-e, 24, and unpublished results of Krishnan, R.; Pople, J. A.).

(26) Geometry optimization at 6-31G\* is also expected to be more important for the nonclassical ion 4 than for 8.

(27) Krishnan, R.; Pople, J. A., unpublished results.

(28) This energy difference corresponds to the C<sub>2</sub> 3-butyne-1-yl cation 9 with the CH<sub>2</sub><sup>+</sup> and CCH groups in the same plane. See text.

substituent stabilizes 8 significantly more than it stabilizes 4 (Table III): compare the 8 – 11 with the 4 – 10 energy differences (31.5 vs. 22.4 kcal/mol (MINDO/3), respectively). This is expected; in 11 the methyl is attached directly to the carbenium center while in 10 it is  $\beta$  to  $C^+$ . With MINDO/3, 11 is calculated to be 10.4 kcal/mol more stable than in 10, compared with a difference of 1.4 kcal/mol for the parent cations 8 and 4 (Table III). The corresponding STO-3G energy differences are 7.2 and 1.8 kcal/mol, respectively. The calculated energy differences between the methyl derivatives should be corrected by about 10 kcal/mol, assuming that 4 is actually about 8 kcal/mol more stable than 8 (Table III and discussion above). Therefore, 10 and 11 should be comparably stable. Solvolysis of 18a,<sup>29</sup> 19a,<sup>8a</sup> or 2-pentynyl triflate (20)<sup>9,29</sup> yields, however, products which are derived from solvent

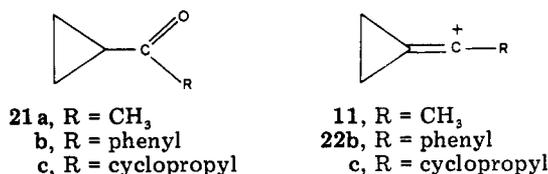


capture of 10 (i.e., 2-methylcyclobutanone) with at most traces of products from 11 (i.e., methyl cyclopropyl ketone 21a)). Apparently, even the corrected MINDO value overestimates somewhat the stability of 11 relative to 10.<sup>30</sup> The corrected STO-3G value is in better agreement. Solvolysis studies confirm the basic conclusion, i.e., that the cyclopropylidenemethyl cation is stabilized more than the 1-cyclobutenyl cation by such substitution. With better stabilizing substituents than methyl e.g., phenyl (18b or 19b) or cyclopropyl (18c or 19c), the major solvolysis products (21b and 21c, respectively) are indeed derived

(29) Hanack, M.; Bässler, T.; Eyman, W.; Heyd, W. E.; Kopp, R. *J. Am. Chem. Soc.* 1974, 96, 6686. Kopp, R. Hanack, M. *Chem. Ber.* 1979, 112, 2453.

(30) This is probably due to an overestimation of the  $\alpha$ -methyl stabilization effect. Thus the 2-propenyl cation is calculated by MINDO/3 to be more stable than the parent vinyl cation by 40.7 kcal/mol compared to only 33 kcal/mol experimentally.<sup>3d</sup>

from the corresponding substituted cyclopropylidenemethyl cations 22b and 22c.<sup>8a,29</sup>



**Note Added In Proof.** After submission of this paper we learned of the independent experimental investigation of  $C_4H_5^+$  ions by Schwarz et al. in the gas phase.<sup>31</sup> The conclusions of our two studies agree remarkably well. Schwarz finds that the 1-cyclobutenyl (4) and the cyclopropylidenemethyl (8) cations exist in potential-energy wells, but there was no evidence for the independent existence of the homopropargyl ion (9). 4 is more stable than 8, just as our calculations indicate. We thank Professor Schwarz for communicating this information.

Further Fletcher-Powell<sup>16b</sup> optimizations (STO-3G) of 4 and 8 resulted in slight (ca. 0.1 kcal/mol) but significant energy lowerings. Tables I and II give the final STO-3G energies and geometries, even though the latter were not used for the single point calculations at higher levels.

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(31) Franke, E.; Schwarz, H.; Stahl, D. *J. Org. Chem.*, preceding paper in this issue.