J. Org. Chem. 1980, 45, 3493-3496 3493

Experimental Evidence for the Existence of Stable 1-Cyclobutenyl and Cyclopropylidenemethyl Cations in the Gas Phase

Wilfried Franke,[1a] Helmut Schwarz,*[1a] and Daniel Stahl[1b]

Institut für Organische Chemie der Technischen Universität Berlin, D 1000 Berlin 12, Federal Republic of Germany, and the Institut de Chimie Physique, École Polytechnique Fédérale de Lausanne, CH 1015 Lausanne, Switzerland

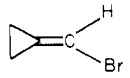
Received January 16, 1980

Experimental evidence is presented that the 1-cyclobutenyl (**5**) and cyclopropylidenemethyl cations (**6**) are stable species in the gas phase, whereas the isomeric homopropargyl ion (**7**) does not exist in a potential-energy well. The small kinetic energy release associated with Br· loss from ionized C_4H_5Br precursors indicates that simple bond cleavages of the C–Br bonds in the cation radicals from both 1-bromocyclobutene (**1**) and cyclopropylidenemethyl bromide (**2**) take place. The dissociation of ionized **2**, however, is partially accompanied by an exothermic isomerization leading to the more stable isomer **5**. Br· loss from ionized homopropargyl bromide **3** is assisted by neighboring-group participation of the triple bond; exothermic isomerization of the incipient homopropargyl ion **7** to **5** occurs. In addition to the direct isomerization, **7** → **5**, evidence is presented for the existence of an alternative pathway, **7** → **6** → **5**.

Introduction

Many intrinsic properties of ions can be examined advantageously in the absence of solvent, i.e., in the gas phase. For example, collisional-activation (CA) mass spectrometry can reveal the number of isomeric structures of an ion capable of existing in significant minima on the potential-energy surface.[3] Complementary information may be obtained from the kinetic-energy release, *T*, observed to accompany unimolecular dissociation of a metastable ion of interest.[2,3d,4] The shape of these metastable peaks affords a "direct picture" of what happens when dissociation take place. As has been shown for several systems, when a $(R-X)^+$ ion loses X (X = Br, CO, CH_2O, or H_2O) to form a carbocation R^+, exothermic isomerization of the incipient cation is indicated by an increase in the kinetic-energy release which accompanies dissociation.[4,5] This increase in kinetic-energy release, which can be conveniently measured for metastable ion decompositions occurring in one of the field-free regions of a double-focusing mass spectrometer, arises because part of the potential energy, liberated upon exothermic isomerization of the incipient cation, is partitioned into the bond which is finally broken in the dissociation step. Such data are not accessible from solution experiments because collisions between reactant, product, and solvent molecules lead to rapid absorption of any kinetic energy released upon unimolecular dissociation into the various vibrational modes of the system. In this paper we report results of gas-phase experiments on dissociative ionization of isomeric C_4H_5Br compounds, i.e., 1-bromocyclobutene (**1**), cyclopropylidenemethyl bromide (**2**), and the corresponding homopropargyl derivative (**3**).

1

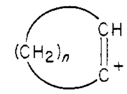


2

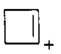
$HC\equiv CCH_2CH_2Br$

3

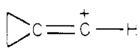
Whereas the existence of vinyl cations as intermediates in solvolytic reactions is now established,[6] related experimental data on gaseous vinyl cations are much more limited.[4b,7] An understanding of the stabilities and properties of this class of carbenium ions can also be obtained by means of molecular-orbital theory, and a large number of substituted vinyl cations have already been investigated computationally.[8] Among the cyclic vinyl cations (**4**), the



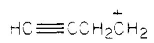
4



5



6



$HC\equiv CCH_2\overset{+}{C}H_2$

7

highly strained 1-cyclobutenyl cation (**5**) is of particular interest. Hanack demonstrated that **5** was a common intermediate in the solvolysis of the trifluoromethanesulfonate derivatives of **1** and **3** (SO_3CF_3 substituted for Br) and also of **2**.[6b,e,9a–c] The surprisingly high solvolysis

---

(1) (a) Technische Universität Berlin. (b) École Polytechnique Fédérale de Lausanne.

(2) (a) Williams, D. H. *Acc. Chem. Res.* **1977**, *10* 280. (b) Bowen, R. D.; Williams, D. H.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 451.

(3) For reviews see: (a) Levsen, K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 509; (b) McLafferty, F. W. "Chemical Applications of High Performance Mass Spectrometry"; American Chemical Society: Washington, D.C., 1978; (c) Cooks, R. G., Ed. "Collision Spectroscopy"; Plenum Press: New York, 1978; (d) Levsen, K. "Fundamental Aspects of Organic Mass Spectrometry"; Verlag Chemie: Weinheim/Bergstr., Germany, 1978.

(4) (a) Williams, D. H.; Stapleton, B. J.; Bowen, R. D. *Tetrahedron Lett.* **1978**, 2919. (b) Bowen, R. D.; Williams, D. H.; Schwarz, H.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1979**, *101*, 4681. (c) Bowen, R. D.; Williams, D. H.; Schwarz, H.; Wesdemiotis, C. *J. Chem. Soc., Chem. Commun.* **1979**, 261. (d) Stapleton, B. J.; Bowen, R. D.; Williams, D. H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1219. (e) Schwarz, H.; Stahl, D. *Int. J. Mass Spectrom. Ion Phys.*, in press.

(5) (a) Mead, T. J.; Williams, D. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 876. (b) Bowen, R. D.; Williams, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 6822. (c) Bowen, R. D.; Stapleton, B. J.; Williams, D. H. *J. Chem. Soc., Chem. Commun.* **1978**, 24. (d) Bowen, R. D.; Williams, D. H. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *29*, 47. (e) Wesdemiotis, C.; Wolfschütz, R.; Schwarz, H. *Tetrahedron*, **1980**, *36*, 275.

(6) For reviews see: (a) Modena, G.; Tonellato, V. *Adv. Phys. Org. Chem.* **1971**, *9*, 185; (b) Hanack, M. *Acc. Chem. Res.* **1970**, *3*, 209; **1976**, *9*, 364; (c) Rappoport, Z. *Acc. Chem. Res.* **1976**, *9*, 265. (d) Stang, P. J. *Prog. Phys. Org. Chem.* **1976**, *10*, 205; (e) Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 333; (f) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, R. "Vinyl Cations"; Academic Press: San Francisco, 1979.

(7) (a) Lossing, F. P. *Can. J. Chem.* **1971**, *49*, 357; **1972**, *50*, 3973. (b) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5920. (c) Aue, D. H.; Davidson, W. R.; Bowers, M. T. *Ibid.* **1976**, *98*, 6700. (d) Schwarz, H.; Wesdemiotis, C.; Levsen, K.; Bowen, R. D.; Williams, D. H. *Z. Naturforsch.* **1979**, *34b*, 488. (e) Wesdemiotis, C.; Wolfschütz, R.; Höhne, G.; Schwarz, H.; *Org. Mass Spectrom.* **1979**, *14*, 231. (f) For recent discussion of some new experimental approaches see: Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979.

(8) (a) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Org. Chem.* **1977**, *42*, 3004. (b) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291. (c) Radom, L.; Hariharan, P. L.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1973**, *95*, 6531.

0022-3263/80/1945-3493$01.00/0

rate of **1**, SO_3CF_3 substituted for Br or $SO_3C_4F_9$ (in comparison with that of cyclopentenyl or of cyclohexenyl triflate), was accounted for by an unusual stability of **5**,[9d] attributed to a bridged, nonclassical structure. The observation that **2** solvolyzes much faster than secondary vinyl bromides, such as $(CH_3)_2C{=}C(Br)CH_3$, was attributed to an extraordinary cyclopropylcarbinyl-type stability of the resulting cation **6**.[6b,e,10] In a recent theoretical study, Schleyer and co-workers[11] found that **5** and **6** are indeed both unusually stabilized nonclassical vinyl cations; the former was indicated to be approximately 8 kcal mol^{-1} more stable than the latter. For the homopropargyl ion **7** no minimum could be detected on the potential-energy surface. The calculations suggest that **7** should rearrange spontaneously to either **5** (more likely) or **6**. Both **5** and **6** were indicated to be minima on the potential-energy surface.

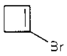
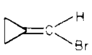
To our knowledge no gas-phase experiments on these isomeric $C_4H_5^+$ ions have been described in literature.[12] In this paper we present experimental evidence for the existence of the 1-cyclobutenyl (**5**) and the cyclopropylidenemethyl (**6**) cations as stable species in the gas phase. In addition, it is shown that Br· loss from ionized **3** is accompanied by spontaneous rearrangements: **7** → **5** and **7** → **6** → **5**. We could find no evidence for the existence of a stable homopropargyl ion (**7**) in the gas phase.

The very close agreement between our experimentally derived conclusions and those obtained computationally[11] is even more noteworthy since both studies were carried out completely independently and without any knowledge of the final results.

Experimental Section

1-Bromocyclobutane (**1**) was synthesized by a literature procedure; i.e., Br_2 addition to cyclobutene[13] was followed by HBr elimination.[14] Cyclopropylidenemethyl bromide (**2**) was obtained by HBr elimination from 1-bromo-1-(bromomethyl)cyclopropane,[15] and the homopropargyl bromide (**3**) by the convenient two-step procedure: 3-butyn-1-ol → 3-butyn-1-yl tosylate → **3**.[16] All compounds were purified by preparative gas chromatography and characterized by NMR spectroscopy. The collisional-activation (CA)[3] spectra were obtained by using a ZAB-2F double-focusing mass spectrometer, in which ions pass through the magnetic field before entering the electric field. The collision cell was differentially pumped and situated in front of the energy-resolving slit. Samples were introduced via the heated gas inlet system and subjected to an accelerating voltage of 8 kV, with a nominal electron-beam energy of 70 eV and a source temperature of approximately 180 °C. The magnetic and electric fields were adjusted to transmit $C_4H_5^+$ ions (m/z 53); helium was then introduced into the collision cell via a variable leak until the precursor-ion abundance decreased to one-third of its original value due to scattering and decomposition. CA spectra were then obtained by scanning the electrostatic sector potential, recorded on an XY recorder, and normalized to the sum of the fragments. Only peak heights were measured and the abundances were not corrected for reduced multiplier response. The CA spectra (Table II) are mean values from at least five independent measurements. The reproducibility was ±3 to ±10%, depending on the abundance of the precursors. The unimolecular decomposition of metastable ions was recorded, using the same technique (MIKES) without adding collision gas.[17] The kinetic energy release measurements for ^{79}Br loss from ionized **1**, **2**, and **3** were obtained by using the same instrument and the same technique (unimolecular decomposition of $M^{+}\cdot$ occurring in the field-free region between the magnetic and electric fields). The kinetic energy release data (Table I) are mean values from at least three scans. The energy resolution ($E/\Delta E$) of the instrument was approximately 2500; corrections were applied for the widths of the main beams.

Table I. Kinetic-Energy Release, *T*, for Br· Loss from Ionized 1, 2, and 3[a]

precursor	T, kcal mol^{-1}
 **1**	0.08
 **2**	0.06 (3.48)[b]
$HC\equiv CCH_2CH_2Br$ **3**	0.77 (1.75)[b]

[a] The kinetic energy release data were derived from the metastable peak width at half-height by using Beynon's equation.[17d] [b] Composite peak; the estimated values in parentheses refer to the broader component of the peak.

Results and Discussion

Values, *T*, of the kinetic-energy release that accompanies Br· loss from each of the three isomers of $C_4H_5Br^+$ (**1**–**3**) are given in Table I.

Loss of Br· from ionized 1-bromocyclobutene (**1**) and from cyclopropylidenemethyl bromide (**2**) is characterized by extremely small kinetic-energy release (0.08 and 0.06 kcal mol^{-1}, respectively). In accordance with theory and the current interpretation of *T* values,[2,3d,4,5] this is clear evidence that the gaseous $[M - Br]^+$ ions formed from $1^{+}\cdot$ and from $2^{+}\cdot$ undergo simple C–Br bond cleavage, occurring without rearrangement of the incipient $C_4H_5^+$ cations. The ions derived from **1** and **2** thus may be represented by structures **5** and **6**. On the other hand, the kinetic-energy release associated with Br· loss from ionized homopropargyl bromide (**3**) is substantially larger (0.77 kcal mol^{-1}). This clearly indicates that the dissociative ionization of **3** is accompanied by exothermic isomerization of the incipient homopropargyl ion (**7**) to a more stable carbocation. The fact that Br· elimination from ionized **3** (and also from **2**) gives rise to composite metastable peaks (Figure 1) can be taken as experimental evidence that the isomerization of **7** occurs via at least two different reaction pathways.[18] Furthermore, the broader component of the composite metastable peak for Br· loss from ionized

---

(9) (a) Hanack, M.; Häffner, J.; Herterich, I. *Tetrahedron Lett.* **1965**, 875. (b) Hanack, M.; Bocher, S.; Herterich, I.; Hummel, K.; Vött, V. *Justus Liebigs Ann. Chem.* **1970**, 733. (c) Collins, C. J.; Benjamin, B. M.; Hanack, M.; Stutz, H. *J. Am. Chem. Soc.* **1977**, *99*, 1669. (d) Hanack, M.; Carnahan, E. J.; Krowczynski, A.; Schobert, W.; Subramanian, L. R.; Subramanian, K. *J. Am. Chem. Soc.* **1979**, *101*, 100.

(10) (a) Bässler, T.; Hanack, M. *Tetrahedron Lett.* **1971**, 2171. (b) Hammen, G.; Bässler, T.; Hanack, M. *Chem. Ber.* **1974**, *107*, 1676. (c) Hanack, M.; Bässler, T.; Eymann, E.; Heyd, W. E.; Kopp, R. *J. Am. Chem. Soc.* **1974**, *96*, 6686.

(11) Apeloig, Y.; Collins, J. B.; Cremer, D.; Bally, T.; Haselbach, E.; Pople, J. A.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.*, following paper in this issue.

(12) For data on $C_4H_5^+$ ions of unestablished structure, see: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Supplement 1.

(13) Bacha, J. D.; Kochi, J. K. *Tetrahedron* **1968**, *24*, 2215.

(14) Abell, P. I.; Chia, Ch. *J. Am. Chem. Soc.* **1960**, *82*, 3610.

(15) Köster, R.; Arora, S.; Binger, P. *Synthesis* **1971**, 322.

(16) Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: Amsterdam, 1971.

(17) For pertinent literature concerning the MIKES technique (*M*ass *A*nalyzed *I*on *K*inetic *E*nergy *S*pectroscopy) see: (a) Beynon, J. H.; Cooks, R. G.; Amy, J. W.; Baitinger, W. E.; Ridley, T. Y. *Anal. Chem.* **1973**, 45, 1023A; (b) Schlunegger, U. P. *Angew. Chem., Int. Ed. Engl.* **1975**, 14, 679; (c) Beynon, J. H.; Cooks, R. G. "Mass Spectrometry, International Review of Science"; Maccoll, A., Ed.; Butterworths: London, 1975; p 159; (d) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. "Metastable Ions"; Elsevier: Amsterdam, 1973.

(18) For further examples of composite metastable peaks and the interpretation of such singals see, for instance: (a) Cooks, R. G.; Bertrand, M.; Beynon, J. H.; Rennekamp, M. E.; Sester, D. *J. Am. Chem. Soc.* **1973**,

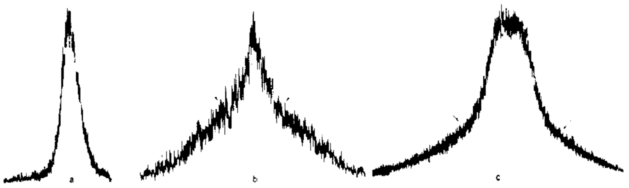
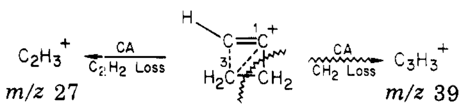


Figure 1. Metastable peaks (ZAB-2F mass spectrometer, second field-free region) for ^{79}Br loss from the molecular ions of (a) 1-bromocyclobutene (1), (b) cyclopropylidenemethyl bromide (2), and (c) homopropargyl bromide (3). The peaks were recorded by using the MIKES technique described in the experimental section and in ref 17. The composite nature of the metastable peaks for loss of ^{79}Br from ionized 2 and 3 is indicated by arrows.

2 indicates that the incipient cyclopropylidenemethyl cation (**6**) undergoes an exothermic isomerization to a more stable $C_4H_5^+$ cation. The ion so formed is likely be the 1-cyclobutenyl cation, because Br· elimination from **1** is not associated with any line broadening. Although the kinetic energy release data reveal that the incipient $C_4H_5^+$ cations from homopropargyl bromide (**3**) (and, in part, those from **2**) isomerize, these experiments do not give direct information regarding the structure of the $C_4H_5^+$ isomer formed after rearrangement. This problem, however, may be resolved by using collisional-activation (CA) spectroscopy.[3] Relevant CA data of $C_4H_5^+$ ions formed from **1**–**3** are given in Table II.

The CA data for the $C_4H_5^+$ ions are essentially identical for **1** and **3** and are broadly similar for **2**. Due to excess energies, partial interconversion of the isomeric $C_4H_5^+$ ions probably occurs before and/or after collision. Nevertheless, some significant differences are observed, especially in the relative abundances of the fragments *m/z* 39 and 27. *m/z* 39 is produced formally from $C_4H_5^+$ by CH_2 loss, and *m/z* 27 via C_2H_2 elimination. The relative abundances of both signals are enhanced for those $C_4H_5^+$ isomers derived from **1** (and **3**), indicating that these ions do not interconvert completely with the isomeric $C_4H_5^+$ cations from **2**. Thus, we conclude that at least two distinct $C_4H_5^+$ structures can exist as stable species in the gas phase. Despite the lack of detailed energetic data, collision-induced loss of CH_2 as well as $C_2H_3^+$ formation from **5** may occur as indicated in **5a**. In particular, the enhanced loss of CH_2 may be a consequence of the proposed bridged structure[6e,9,11] of the 1-cyclobutenyl cation (**5a**).



5a

Conclusions

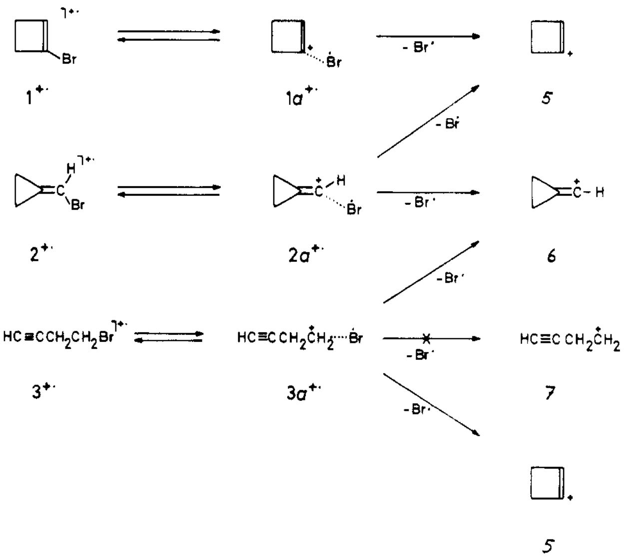
The combination of the *T* value and the CA data allows the following conclusions (summarized in Scheme I) to be made. (1) Br· loss from ionized 1-cyclobutenyl bromide (**1**) is a simple C–Br bond cleavage process, leading to the 1-cyclobutenyl cation **5**. This interpretation is substantiated by the extremely small kinetic-energy release associated with Br· loss and the distinct CA spectrum. The latter exhibits some diagnostically useful fragmentation processes. There is no experimental evidence for an exothermic isomerization of **5** to a more stable cation. (2) Br· loss from ionized cyclopropylidenemethyl bromide (**2**) is also indicated to be a direct cleavage reaction leading to a different stable $C_4H_5^+$ isomer, i.e., the cyclopropylidenemethyl cation (**6**). However, the composite metastable peak associated with Br· elimination from $2^{+\cdot}$ suggests that at least part of the incipient $C_4H_5^+$ ions from $2^{+\cdot}$ must undergo exothermic isomerization to a more stable product. This cation is indicated to be **5**. Thus, the computationally predicted stability order[11] (**5** more stable than **6**) is experimentally verified. The solvolysis results lead to the same conclusions.[6e] (3) The large kinetic-energy release associated with Br· loss from $3^{+\cdot}$ provides clear evidence that the incipient homopropargyl ion **7** is not a stable species in the gas phase. The shape of the metastable peak (composite peak) points to two separate isomerization pathways; these likely lead to **5** and to **6**. The nearly identical CA data of the $[M - Br]^+$ ions derived from $1^{+\cdot}$ and from $3^{+\cdot}$, however, suggest that the ions have structure **5** exclusively under these conditions. Thus, the excess energy of the $[M - Br]^+$ ion from $3^{+\cdot}$ either is sufficient to overcome the barrier **6** → **5**, or isomerization of **6** occurs after collisional activation.

Table II. Collisional Activation Spectra of $C_4H_5^+$ Ions Formed from Isomeric C_4H_5Br Precursors 1, 2, and 3

fragment ions, *m/z*[a]	$C_4H_5^+$ from precursor $1^{+\cdot}$	$2^{+\cdot}$	$3^{+\cdot}$
52	20	24	21
51	26	31	27
50	18	22	17
49	3.4	3.9	3.8
39	3.1	1.5	3.0
38	2.4	2.5	2.6
37	1.9	2.0	2.0
36	0.6	0.7	0.8
27	22	10	20
26	2.5	2.4	2.7

[a] The relative abundances are normalized to a total of 100 units over the *m/z* range 26–52.

Scheme I. Br· Loss from Ionized 1, 2, and 3[a]



[a] For experimental evidence for the isomerization of the incipient cations 2a (which isomerizes partially) and 3a (complete isomerization), see text.

Acknowledgment. Financial support of this work by the Fonds der Chemischen Industrie and the Schweizer Nationalfonds zur Förderung der wissenschaftlichen

---

95, 1732; (b) Beynon, J. H.; Bertrand, M.; Cooks, R. G. *Ibid.* **1973**, *95*, 1739; (c) Holmes, J. L.; Benoit, F. M. In "Mass Spectrometry, MTP International Review of Science"; Maccoll, A., Ed.; Butterworths: London, 1973; (d) Holmes. J. L.; Yinen, D.; Rye, R. T. B. *Org. Mass Spectrom.* **1977**, *12*, 254; (e) Vijfhuizen, P. C.; Terlouw, J. L. *Ibid.* **1976**, *11*, 888; (f) see also ref 7d and 17d.

Forschung is greatfully acknowledged. H.S. thanks the EPF Lausanne for a visiting professorship (1979) and Professor T. Gäumann, Lausanne, for his kind hospitality. We thank Professor E. Haselbach, Basel, and Professor P. v. R. Schleyer, Erlangen, for exchanges of information after completion of both the experimental and the theoretical work. Professor Schleyer's assistance in preparing the English version of this manuscript is also gratefully acknowledged.

Registry No. 1, 33954-15-3; 2, 33745-37-8; 3, 18668-72-9; 5, 12316-90-4; 6, 24448-93-9.

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

Yitzhak Apeloig,[1a] John B. Collins,[1b] Dieter Cremer,[1c] Thomas Bally,[1d] Edwin Haselbach,[1d] John A. Pople,[1e] Jayaraman Chandrasekhar,[1f] and Paul v. R. Schleyer*[1f]

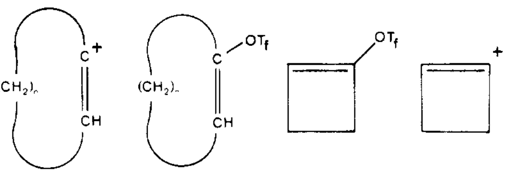
Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, 8520 Erlangen, Federal Republic of Germany; the Departments of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel; Princeton University, Princeton, New Jersey 08540; Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213; the Physikalisch-Chemisches Institut der Universität, 4056 Basel, Switzerland; and the Lehrstuhl für Theoretische Chemie der Universität zu Köln, D-5000 Köln 41, Federal Republic of Germany

Received November 26, 1979

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_3 bridging almost equidistantly between C_1 and C_2. 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.[2] The relative stabilities of vinyl cations are usually deduced from solvolysis rates, but ground-state and solvation effects may complicate the interpretations.[2] Related experimental data in the gas phase are limited,[3a–c] although some new measurements were reported recently by Aue and Bowers.[3d] 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.[4]

Cyclic vinyl cations (**1**) are of special interest. α-Substituted vinyl cations,[2,4] as well as the C_{2v} classical form of the parent vinyl cation, $H_2C{=}CH^+$,[5] 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.[6]



1 2 3 4

OT_f = trifluoromethanesulfonate

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.[7a] Thus, the relative solvolysis rates (in 50% ethanol) of cyclononenyl (**2**, n = 7), cyclooctenyl (**2**, n = 6), cycloheptenyl (**2**, n = 5), and cyclohexenyl (**2**, n = 4) triflates are $1.9 \times 10^6{:}3.7 \times 10^4{:}3.5 \times 10^3{:}1$.[7] 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 cyclononenyl triflate (**2**, n = 7).[7a] Cyclopentenyl triflate (**2**, n = 3) solvolyzes even

---

(1) (a) Technion; (b) Princeton; (c) Köln; (d) Basel; (e) Carnegie-Mellon; (f) Erlangen-Nürnberg.

(2) For reviews see: (a) Stang, P. J. *Prog. Phys. Org. Chem.* **1976**, *10*, 205. (b) Rappoport, Z. *Acc. Chem. Res.* **1976**, *9*, 265. (c) Hanack, M. *Ibid.* **1976**, *9*, 364; **1970**, *3*, 209. (d) Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 333. (e) Modena, G.; Tonellato, V. *Adv. Phys. Org. Chem.* **1971**, *9*, 185. (f) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, R. "Vinyl Cations"; Academic Press: San Francisco, 1979.

(3) (a) Lossing, F. P. *Can. J. Chem.* **1971**, *49*, 357; **1972**, *50*, 3973. (b) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5920. (c) Aue, D. H.; Davidson, W. R.; Bowers, M. T. *Ibid.* **1976**, *98*, 6700. (d) Aue, D. H.; Bowers, M. T. In "Gas-Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979.

(4) (a) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Org. Chem.* **1977**, *42*, 3004. (b) Apoloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291. (c) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1973**, *95*, 6531.

(5) (a) Weber, J.; McLean, A. D. *J. Am. Chem. Soc.* **1976**, *98*, 875; *J. Chem. Phys.* **1976**, *64*, 4159. (b) Zarawski, B.; Ahlrichs, R.; Kutzelnigg, W. *Chem. Phys. Lett.* **1973**, *21*, 302. (c) Hariharan, P. C.; Lathan, W. A.; Pople, J. A. *Ibid.* **1972**, *14*, 385. (d) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808. (e) Pople, J. A. *Int. J. Mass. Spectrosc. Ion Phys.* **1975**, *19*, 89.

(6) (a) Chandrasekhar, J.; Schleyer, P. v. R., to be published. (b) Mayr, H.; Schneider, R.; Fackler, H., to be published.

(7) (a) Pfeifer, W. D.; Bahn, C. A.; Schleyer, P. v. R.; Bocher, S.; Harding, C. E.; Hummel, K.; Hanack, M.; Stang, P. J. *J. Am. Chem. Soc.* **1971**, *93*, 1513. Lamparter, E.; Hanack, M. *Chem. Ber.* **1972**, *105*, 3789. Hargrove, R. J.; Stang, P. *Tetrahedron* **1976**, *32*, 37. (b) Hanack, M.; Bentz, H.; Märkel, R.; Subramanian, L. R. *Justus Liebigs Ann. Chem.* **1978**, 1894.

0022-3263/80/1945-3496$01.00/0