J. Am. Chem. Soc. **1992**, *114*, 1244–1248

Vinylcyclopropyl Anion: Structure, Reactivity, Thermodynamic Properties, and an Unusual Rearrangement

Hangzhou Guo[†] **and Steven R. Kass***

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received July 19, 1991*

Abstract: Vinylcyclopropane (**1**) is deprotonated in the gas phase by NH_2^- or Me_2N^- to afford its conjugate base (**1a**). Vinylcyclopropyl anion is quite basic ($\Delta H_{acid}(\mathbf{1}) = 394 \pm 3$ kcal mol^{-1}), has a relatively small electron binding energy (12 ± 5 kcal mol^{-1}), and reacts with a variety of reagents including N_2O, CS_2, COS, O_2, and SO_2. The reaction of **1** with OH^- ($\Delta H_{acid}(H_2O) = 390.7$ kcal mol^{-1}) leads to a surprising rearrangement and the formation of the conjugate base of methylenecyclobutane (**2a**). A mechanism is proposed to account for this unusual reaction and it is in accord with ab initio molecular orbital calculations. In particular, the orbital symmetry allowed ($\sigma_{2s} + \pi_{4s}$) transition state leading to **2a** is slightly preferred over the conrotatory ring opening of **1a** (1.2 kcal mol^{-1} (MP2/6-31+G*//6-31+G*)).

Introduction

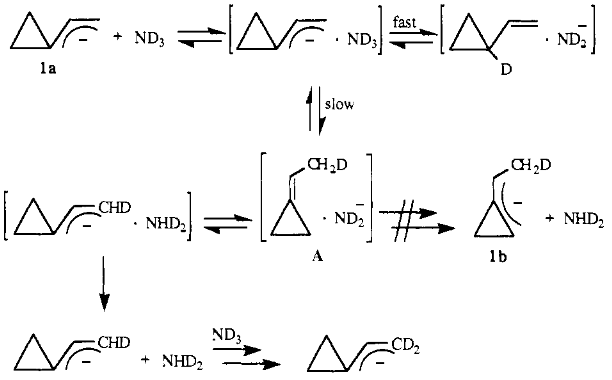
Substituent effects have been the subject of countless investigations and have been studied by a myriad of different techniques.[1] In recent years, intrinsic effects have been probed by gas-phase experiments, and the results have provided new insights into liquid-phase behavior.[2] Relatively little data, however, have been obtained on carbanions which possess a substituent at the negatively charged site, despite their synthetic importance.[3] One reason for this is that linear free energy relationships are unlikely to be generally applicable to this class of compounds, and thus, classical analyses cannot be applied. Interesting perturbations should result nevertheless, and consequently, we have begun a systematic investigation of vinyl, cyclopropyl, and allyl anions bearing α-substituents.[4] Vinylcyclopropane (**1**) is of interest in this regard. Moreover, we were intrigued about the structural stability of its conjugate base (**1a**) since vinylcyclopropanes and cyclopropyl anions are known to undergo unimolecular rearrangements.[5] In this paper we report on a novel isomerization as well as the thermodynamic properties and chemical reactivity of vinylcyclopropyl anion.

Experimental Section

Vinylcyclopropane and methylenecyclobutane (**2**) were prepared as previously described and were purified by distillation and/or preparative gas–liquid chromatography (15′, 25% β,β-oxydipropionitrile).[6] All other compounds were obtained from commercial sources, and other than removing the noncondensible impurities from the liquid samples via several freeze–pump–thaw cycles, they were used as supplied. The gas-phase experiments were conducted with our variable-temperature flowing afterglow apparatus, which has already been described.[7] In brief, this device consists of an ion source separated from a quadrupole mass analyzer by a one meter long reaction region (flow tube). Ions are generated by electron ionization and are carried toward the detector by a constant flow of rapidly moving helium. The thermalized ions react in transit with reagents, which may be added to the flow tube at various locations. In this way, multistep transformations can be carried out and reaction rates measured. The ionic products are continuously monitored in this experiment, but the neutral materials are not detected. Typical operating pressures in the reaction region are 0.35–0.40 Torr, and consequently, everything comes into rapid thermal equilibrium with the walls of the apparatus. Heaters and cooling coils are attached to the flow tube, and this enables us to probe reactions over a wide temperature range (ca. −190 to 400 °C).

Ab initio molecular orbital calculations were carried out on a Cray X-MP at the Minnesota Supercomputer Institute using Gaussian 90.[8] Geometry optimizations were performed with the 6-31+G* basis set and several conformers for each structure were explored in order to try and locate the lowest energy configuration.[9] Vibrational frequencies were computed analytically to ensure that each species corresponds to a true minimum (no negative eigenvalues) or a transition state (one imaginary frequency) on the potential energy surface, and to provide the zero-point energies (ZPEs). Electron correlation was accounted for by carrying out single-point calculations using second-order Møller–Plesset theory (MP2/6-31+G*//6-31+G*).[10] Acidities were obtained by taking the

Scheme I



[†] Visiting scholar from the Institute of Pharmacology and Toxicology, Beijing, People's Republic of China.

(1) For example, see: (a) Isaacs, N. S. *Physical Organic Chemistry*; John Wiley and Sons: New York, 1987. (b) March, J. *Advanced Organic Chemistry Reactions, Mechanisms, and Structure*, 3rd ed.; John Wiley and Sons: New York, 1985. (c) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory In Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; and references therein.

(2) (a) Taft, R. W. *Prog. Phys. Org. Chem.* **1987**, *16*, 1. (b) Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 247. (c) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463. (d) Taft, R. W.; Koppel, I. A.; Topsom, R. D.; Anvia, F. *J. Am. Chem. Soc.* **1990**, *112*, 2047, and references therein.

(3) (a) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277. (b) Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 932. (c) Wierstuk, N. H. *Tetrahedron* **1983**, *39*, 205. (d) Biellmann, J. F.; Ducep, J. P. *Org. React.* **1982**, *27*, 1. (e) Krief, A. *Tetrahedron* **1980**, *36*, 2531, and references therein.

(4) (a) Dahlke, G. D.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 5566. (b) Rabasco, J. J.; Kass, S. R. *J. Am. Soc. Mass Spectrom.*, in press. β-Substituents are also of interest and work on these systems is in progress.

(5) Vinylcyclopropane: (a) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; pp 85–87. Cyclopropyl anion: (b) Chou, P. K.; Kass, S. R. *Org. Mass Spectrom.* **1991**, *26*, 1039. (c) Staley, S. W. In *Organic Chemistry. Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 1, pp 199–264. (d) le Noble, W. J. In *Reactive Intermediates*; Jones, M., Jr., Moss, R., Eds.; John Wiley and Sons: New York, 1978; Vol. 1, pp 27–67. (e) Dewar, M. J. S.; Nelson, D. J. *J. Org. Chem.* **1982**, *47*, 2614, and references therein.

(6) Vinylcyclopropane: (a) Bertz, S. H.; Dabbagh, G. *J. Org. Chem.* **1983**, *48*, 116. (b) Kirmse, W.; Bulow, B.-G.; Schepp, H. *Justus Liebigs Ann. Chem.* **1966**, *691*, 41. (c) Herzog, H. L. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 753. Methylenecyclobutane: (d) Roberts, J. D.; Sauer, C. W. *J. Am. Chem. Soc.* **1949**, *71*, 3925.

(7) Kass, S. R.; Guo, H.; Dahlke, G. D. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 366.

(8) Gaussian 90, Revision F. Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1990.

(9) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Spitznegel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363. (c) Clark, T.; Chandrasekhar, J.; Spitznegel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

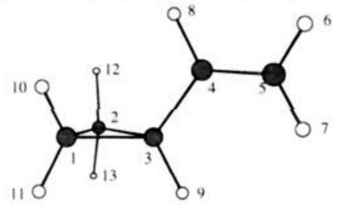
0002-7863/92/1514-1244$03.00/0

Table I. Calculated Energies (Hartrees) for a Variety of C_5H_8 and $C_5H_7^-$ Compounds

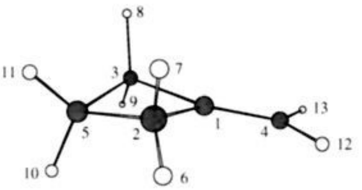
compd	6-31+G*[a]	MP2/6-31+G*[a]	ZPE[b]	ΔH_{acid}[c]	E_a[d]
1	−193.945 565	−194.591 890	68.5	392.3 (394 ± 3)	
1a	−193.284 133	−193.951 622	59.0		
2	−193.947 144	−194.591 419	68.8	385.2 (386 ± 5)	
2a	−193.297 920	−193.961 300	58.6		
3a	−193.312 040	−193.970 645	57.9		
$TS_{1a\to 3a}$	−193.226 038	−193.910 646			25.7 (26 ± 4)
$TS_{1a\to 2a}$	−193.228 394	−193.912 557			24.5

[a] Geometries were optimized with the 6-31+G* basis set. [b] Vibrational frequencies (6-31+G*) were scaled by the usual factor of 0.89 and are in kilocalories per mole. [c] The calculated acidities (MP2/6-31+G*) and the experimental values (in parentheses) are in kilocalories per mole. [d] The computed activation energies (MP2/6-31+G*) and the experimental value for the ring opening of phenylcyclopropyl anion (in parentheses, P. Chou, unpublished results) are in kilocalories per mole.

Table II. Calculated 6-31+G* Geometries of Vinylcyclopropane and Methylenecyclobutane[a]



C_1C_2	1.494	C_4H_8	1.080	$C_1C_2C_3$	60.2	$C_1C_2C_3C_4$	-109.1
C_2C_3	1.505	C_5H_6	1.075	$C_2C_3C_1$	59.5	$C_2C_3C_4C_5$	-145.1
C_3C_4	1.483	C_5H_7	1.077	$C_2C_3C_4$	119.7	$C_1C_2C_3H_9$	106.4
C_4C_5	1.324	$C_3C_4C_5$	125.2	$C_4C_5H_6$	121.4	$C_3C_2C_1H_{10}$	107.6
C_2H_{12}	1.076	$C_1C_3H_9$	116.2	$C_4C_5H_7$	121.8	$C_3C_2C_1H_{11}$	-107.5
C_2H_{13}	1.076	$C_1C_2H_{12}$	118.2	$C_5C_4H_8$	119.0	$H_8C_4C_3H_1$	-34.9
C_3H_9	1.077	$C_1C_2H_{13}$	118.4	$H_{10}C_1H_{11}$	114.2	$H_8C_4C_5H_6$	0.0
						$H_8C_4C_5H_7$	180.0



C_1C_2	1.519	$C_1C_2C_5$	88.1	$H_{10}C_5H_{11}$	108.8	$C_3C_1C_2H_7$	-100.3
C_1C_4	1.318	$C_2C_1C_3$	91.7	$H_{12}C_4H_{13}$	117.0	$H_8C_3C_5H_{10}$	145.9
C_2C_5	1.552	$C_2C_1C_4$	134.0	$C_3C_1C_2C_5$	13.2	$H_8C_3C_5H_{11}$	19.4
C_2H_6	1.084	$C_1C_2H_6$	116.9	$C_4C_1C_2C_5$	-160.9		
C_2H_7	1.086	$C_1C_2H_7$	112.3	$C_1C_2C_5H_{10}$	100.8		
C_4H_{12}	1.077	$C_1C_4H_{12}$	121.5	$C_1C_2C_5H_{11}$	-132.7		
C_4H_{13}	1.077	$C_2C_5H_{10}$	112.2	$C_2C_1C_4H_{12}$	-4.0		
C_5H_{10}	1.084	$C_2C_5H_{11}$	116.7	$C_2C_1C_4H_{13}$	-175.8		
C_5H_{11}	1.083	$H_6C_2H_7$	108.6	$C_3C_1C_2H_6$	133.1		

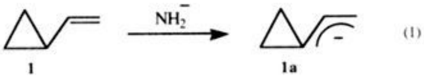
[a] All bond lengths are in angstroms and angles in degrees.

difference in energy, including ZPEs, between the neutral acid and its conjugate base. The results are summarized in Tables I–IV.

Results and Discussion

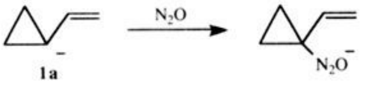
The deprotonation enthalpy of vinylcyclopropane can be estimated by equating the difference in acidity between **1** and propene (ΔH_{acid} = 390.8 kcal mol^{-1})[11] to the difference between phenylcyclopropane and toluene (ΔH_{acid} = 390 ± 3 and 381 kcal mol^{-1}, respectively). This leads to a predicted value of 400 kcal mol^{-1}, and thus we were somewhat surprised to find that OH^- ($\Delta H_{\mathrm{acid}}(H_2O)$ = 390.7 kcal mol^{-1}) deprotonates **1**. The resulting M − 1 ion (m/z 67) does not have to have the same structure as when stronger bases are used, and therefore, we decided to generate it with several different bases and examine their corresponding reactivities.

Amide. Vinylcyclopropane reacts readily with NH_2^- to afford an M − 1 ion the structure of which is assigned to **1a** (eq 1). This

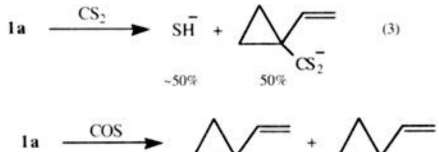


(1)

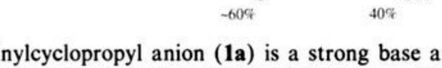
species slowly undergoes two hydrogen–deuterium (H/D) exchanges with ND_3 which is consistent with the proposed structure (Scheme I). The exchange process is inefficient in this instance, presumably because deuteronation at the cyclopropyl end of the allylic ion is thermodynamically favored by ca. 10 kcal mol^{-1},[12] whereas attack must occur at the methylene carbon in order for deuterium to be incorporated into the ion. Isomerization of **1a** to **1b** does not take place during H/D exchange or the deprotonation of vinylcyclopropane for essentially the same reason that the reaction with ND_3 is inefficient; i.e., the methyl hydrogens in A are more acidic than those on the ring.[13,14] Electrophiles also tend to add to the cyclopropyl end of the allylic system, and this leads to adduct formation with N_2O, CS_2, and COS (eqs 2–4). Additional products are formed in the latter two reactions, SH^- and sulfur atom transfer, respectively, both of which can be rationalized by initial attack at the tertiary position in **1a**.[15]



(2)



(3)



(4)

Vinylcyclopropyl anion (**1a**) is a strong base and is rapidly deuteronated with acids such as MeOD (ΔH_{acid} = 381.4) and D_2O (ΔH_{acid} = 392.0) to cleanly afford their corresponding conjugate bases (MeO^- and OD^-, respectively). Dimethylamine (ΔH_{acid} = 396.2) slowly protonates **1a**, thereby suggesting that the acidity of **1** lies between 392.0 and 396.2 kcal mol^{-1}. Consistent with

---

(10) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1. In this paper we abbreviate MP2/6-31+G*//6-31+G* simply as MP2/6-31+G*.

(11) All cited acidities, unless otherwise noted, come from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

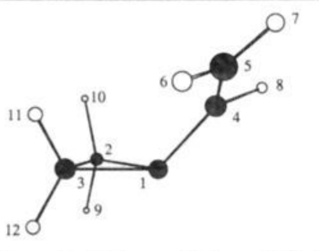
(12) The heats of formation of **1** (31.1 kcal mol^{-1}) and ethylidenecyclopropane (40.2 kcal mol^{-1}) were derived using Benson's group equivalents: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley and Sons: New York, 1976.

(13) The difference between the heat of formation of **1a** (394 − 365.7 + 31.1 = 59 kcal mol^{-1}) and **1b** (390 − 365.7 + 40.2 = 65 kcal mol^{-1}) is approximately 6 kcal mol^{-1}, with the former being more stable.

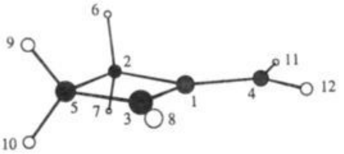
(14) The conjugate base of methylenecyclopropane has previously been reported. It undergoes 5 H/D exchanges and displays very different reactivity. For further details see: Reference 15a.

(15) For mechanistic details of the reactions of N_2O, CS_2, and COS, see: (a) Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 2849. (b) Schmitt, R. J.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1979**, *101*, 6443. (c) DePuy, C. H. *Org. Mass Spectrom.* **1985**, *20*, 556, and references therein.

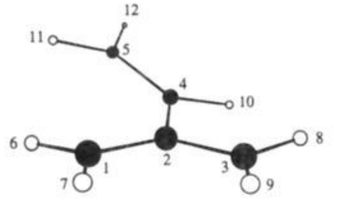
Table III. Calculated 6-31+G* Geometries of the Conjugate Bases of Vinylcyclopropane, Methylenecyclobutane, and 2-Vinylpropene[a]



C_1C_2	1.488	$C_2C_1C_3$	61.8	$C_4C_5H_7$	121.2
C_1C_3	1.482	$C_2C_1C_5$	123.6	$H_6C_5H_7$	117.0
C_1C_4	1.420	$C_1C_2C_3$	58.9	$C_3C_1C_2H_9$	-107.6
C_2C_3	1.525	$C_1C_2H_9$	120.7	$C_3C_1C_2H_{10}$	102.6
C_2H_9	1.085	$C_1C_2H_{10}$	120.9	$C_4C_1C_2C_3$	-114.0
C_2H_{10}	1.089	$H_9C_2H_{10}$	112.0	$C_2C_1C_3H_{11}$	-103.8
C_3H_{11}	1.089	$C_1C_3H_{11}$	120.1	$C_2C_1C_3H_{12}$	107.5
C_3H_{12}	1.084	$C_1C_3H_{12}$	120.7	$C_2C_1C_4C_5$	120.7
C_4C_5	1.361	$H_{11}C_3H_{12}$	112.3	$C_2C_1C_4H_8$	-62.1
C_4H_8	1.086	$C_1C_4H_8$	114.3	$C_1C_4C_5H_6$	-1.5
C_5H_6	1.079	$C_5C_4H_8$	115.5	$C_1C_4C_5H_7$	173.8
C_5H_7	1.079	$C_4C_5H_6$	121.6	$H_8C_4C_5H_6$	-178.6
				$H_8C_4C_5H_7$	-3.4



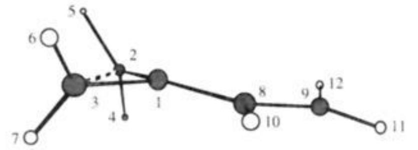
C_1C_2	1.529	$C_3C_1C_4$	141.1	$H_9C_5H_{10}$	106.4
C_1C_3	1.388	$C_1C_2C_5$	88.2	$C_3C_1C_2C_5$	0.0
C_1C_4	1.384	$C_1C_2H_6$	114.8	$C_3C_1C_2H_6$	116.7
C_2C_5	1.557	$H_6C_2H_7$	108.3	$C_4C_1C_2C_5$	180.0
C_2H_6	1.090	$C_1C_3C_5$	95.5	$C_2C_1C_3H_8$	180.0
C_3C_5	1.511	$C_1C_3H_8$	133.0	$C_2C_1C_4H_{11}$	0.0
C_3H_8	1.079	$C_5C_3H_8$	131.5	$C_2C_1C_4H_{12}$	180.0
C_4H_{11}	1.079	$C_1C_4H_{11}$	120.6	$C_1C_2C_5H_9$	118.9
C_4H_{12}	1.079	$C_1C_4H_{12}$	121.9		
C_5H_9	1.098	$H_{11}C_4H_{12}$	117.5		
$C_2C_1C_3$	90.9	$C_2C_5C_3$	85.4		
$C_2C_1C_4$	128.0	$C_2C_5H_9$	113.9		



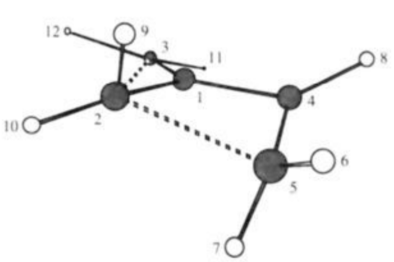
C_1C_2	1.389	$C_1C_2C_4$	118.8	$C_4C_5H_{12}$	120.8
C_2C_3	1.393	$C_2C_4C_5$	128.3	$H_{11}C_5H_{12}$	116.9
C_2C_4	1.500	$C_3C_2C_4$	113.0	$H_6C_1C_2C_3$	-173.2
C_4C_5	1.329	$C_2C_1H_6$	121.9	$H_6C_1C_2C_4$	7.2
C_1H_6	1.076	$C_2C_1H_7$	120.6	$H_7C_1C_2C_3$	0.6
C_1H_7	1.078	$H_6C_1H_7$	117.2	$C_1C_2C_3H_8$	-176.6
C_3H_8	1.077	$C_2C_3H_8$	121.3	$C_1C_2C_3H_9$	-2.0
C_3H_9	1.078	$C_2C_3H_9$	121.3	$C_1C_2C_4C_5$	20.1
C_4H_{10}	1.079	$H_8C_3H_9$	117.2	$C_1C_2C_4H_{10}$	-161.3
C_5H_{11}	1.075	$C_2C_4H_{10}$	114.3	$C_2C_4C_5H_{11}$	0.0
C_5H_{12}	1.079	$C_5C_4H_{10}$	117.4	$C_2C_4C_5H_{12}$	179.3
$C_1C_2C_3$	128.2	$C_4C_5H_{11}$	123.3		

[a] All bond lengths are in angstroms and angles in degrees.

Table IV. Calculated 6-31+G* Transition State Geometries for the Ring Opening and Ring Expansion of Vinylcyclopropyl Anion[a]



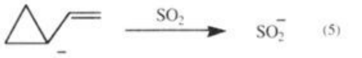
C_1C_2	1.407	$C_1C_2C_3$	45.0	$C_2C_3H_6$	131.0	$C_2C_1C_3H_6$	-115.7
C_1C_3	1.433	$C_1C_3C_2$	44.0	$C_2C_3H_7$	97.4	$C_2C_1C_3H_7$	65.1
C_1C_8	1.411	$C_2C_1C_3$	91.0	$H_6C_3H_7$	113.8	$C_2C_1C_8C_9$	15.1
C_2C_3	2.025	$C_2C_1C_8$	132.5	$C_1C_8C_9$	129.0	$C_2C_1C_8H_{10}$	-164.2
C_8C_9	1.362	$C_3C_1C_8$	133.8	$C_1C_8H_{10}$	114.4	$H_4C_2C_3H_6$	-159.0
C_2H_4	1.097	$C_1C_2H_4$	123.4	$C_9C_8H_{10}$	116.7	$H_4C_2C_3H_7$	-28.4
C_2H_5	1.077	$C_1C_2H_5$	122.3	$C_8C_9H_{11}$	121.0	$H_5C_2C_3H_6$	-26.5
C_3H_6	1.092	$C_3C_2H_4$	129.8	$C_8C_9H_{12}$	121.7	$H_5C_2C_3H_7$	104.1
C_3H_7	1.080	$C_3C_2H_5$	99.3	$H_{11}C_9H_{12}$	117.3	$C_1C_8C_9H_{11}$	-177.5
C_8H_{10}	1.083	$H_4C_2H_5$	114.1	$C_3C_1C_2H_4$	-115.1	$C_1C_8C_9H_{12}$	3.6
C_9H_{11}	1.078	$C_1C_3H_6$	124.6	$C_3C_1C_2H_5$	68.8		
C_9H_{12}	1.077	$C_1C_3H_7$	121.6	$C_8C_1C_2C_3$	162.6		

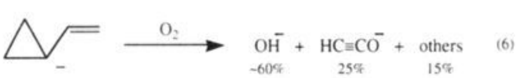


C_1C_2	1.470	C_5H_7	1.076	$C_1C_3H_{11}$	121.3	$C_1C_4C_5H_6$	-148.6
C_1C_3	1.383	$C_1C_2C_3$	25.3	$C_1C_3H_{12}$	121.3	$C_1C_4C_5H_7$	60.8
C_1C_4	1.423	$C_1C_2C_5$	74.7	$C_1C_4H_8$	128.5	$C_2C_1C_3H_8$	-146.5
C_2C_3	2.562	$C_1C_3C_2$	27.0	$C_2C_5H_6$	132.8	$C_4C_1C_2H_9$	69.0
C_2C_5	2.132	$C_1C_4C_5$	105.0	$C_2C_5H_7$	89.2	$C_4C_1C_2H_{10}$	-152.0
C_4C_5	1.408	$C_2C_1C_3$	127.7	$C_5C_4H_8$	126.0	$C_4C_1C_3H_{11}$	10.6
C_2H_9	1.079	$C_2C_1C_4$	99.7	$H_6C_2H_{10}$	112.6	$C_4C_1C_3H_{12}$	-168.4
C_2H_{10}	1.096	$C_2C_5C_4$	74.2	$H_6C_5H_7$	111.0	$H_8C_4C_5H_6$	23.8
C_3H_{11}	1.079	$C_4C_1C_3$	132.4	$H_{11}C_3H_{12}$	117.4	$H_8C_4C_5H_7$	-126.8
C_3H_{12}	1.078	$C_5C_2C_3$	98.3	$C_2C_1C_4C_5$	25.6	$H_9C_2C_3H_{11}$	104.9
C_4H_8	1.079	$C_1C_2H_9$	115.7	$C_3C_1C_4C_5$	-149.6	$H_9C_2C_3H_{12}$	-86.4
C_5H_6	1.095	$C_1C_2H_{10}$	119.0	$C_4C_1C_2C_3$	-175.5	$H_{10}C_2C_3H_{11}$	-133.1

[a] All bond lengths are in angstroms and angles in degrees.

this notion, ethyl amide ($\Delta H_{acid}(EtNH_2) = 399.0$) and dimethyl amide deprotonate vinylcyclopropane to afford **1a** whereas hydroxide does not (vide infra).[16] Therefore, we assign ΔH_{acid}(**1**) = 394 ± 3 kcal mol^{-1}, which is in good accord with a calculated value of 392.2 kcal mol^{-1} (MP2/6-31+G* + ZPEs). Agreement of this sort has become fairly routine with ab initio molecular orbital computations when electron correlation, diffuse orbitals, polarization functions, and zero-point energies are accounted for. The electron binding energy of **1a** was also obtained by examining several electron-transfer reactions. Vinylcyclopropyl anion reacts readily with sulfur dioxide ($EA(SO_2) = 1.10$ eV) to afford SO_2^-, whereas only a trace of O_2^-($EA(O_2) = 0.45$ eV) is observed in the reaction with molecular oxygen (eqs 5 and 6).[17] Upon heating,





1a undergoes electron detachment just like other weakly bound anions, e.g., $O_2^{\bullet -}$ and allyl anion.[18] Therefore, the electron affinity of the vinylcyclopropyl radical (**1r**) is probably less than 1.10 eV and just slightly greater than 0.45 eV. We propose EA(**1r**) = 0.50 eV (12 kcal mol^{-1}), which leads to a homolytic bond energy of 92 kcal mol^{-1} for the allylic C–H bond in vinylcyclopropane. There is a relatively large uncertainty (±5 kcal mol^{-1}), however,

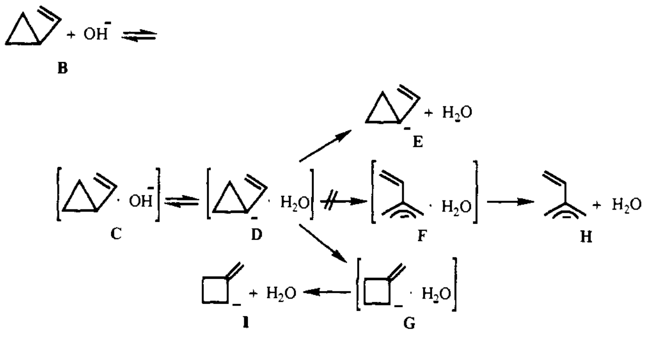
---

(16) The reactivity of the M − 1 ion when $EtNH^-$ and Me_2N^- were used as the base was explored. The reactions with N_2O and D_2O indicate that the former base leads exclusively to **1a**, whereas Me_2N^- affords an approximately 9:1 mixture of **1a** and **2a**.

(17) References for the EAs are as follows: (SO_2) (a) Celotta, R. J.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740. (b) Nimlos, M. R.; Ellison, G. B. *J. Phys. Chem.* **1986**, *90*, 2574. (O_2) (c) Travers, M. J.; Cowles, D. C.; Ellison, G. B. *Chem. Phys. Lett.* **1989**, *164*, 449.

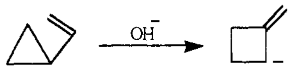
(18) Ion **1a** was found to be structurally stable up to the point where it becomes difficult to generate (~200 °C). This conclusion was reached by examining the reactivity of **1a** and comparing it to the behavior of **2a** and **3a**.

Scheme II

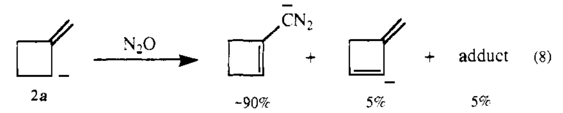


associated with the latter two quantities.

Hydroxide. Vinylcyclopropane reacts with hydroxide to afford an M − 1 ion which is clearly distinct from **1a**. This new ion arises from an unusual rearrangement (vide infra) and is formulated as the conjugate base of methylenecyclobutane (**2a**, eq 7). It is much less reactive than vinylcyclopropyl anion and gives entirely different products with a number of neutral reagents. For example, **2a** undergoes up to five hydrogen–deuterium exchanges with D_2O and affords no OD^-, whereas **1a** reacts exclusively via deuteron transfer. The reactions with N_2O, O_2, and CS_2 are also characteristic, but those with COS and SO_2 are not (eqs 8–12).[19] The

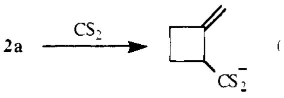


2a (7)

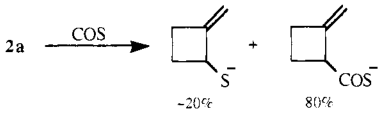


$$2a \xrightarrow{O_2} OH^- + O_2^- + HO_2^- + HC{\equiv}CO^- + {}^-CH_2CHO + HCO_2^- \quad (9)$$

~20% 10% 25% 15% 10% 20%



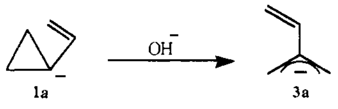
(10)



(11)

$$2a \xrightarrow{SO_2} SO_2^- \quad (12)$$

products of the first group of reactions are consistent with the proposed structure, **2a**, and are independent of the method by which it is generated; i.e., *the formation of* ***2a*** *from vinylcyclopropane or methylenecyclobutane (****2****) leads to identical results.* Alternative structures were considered, nevertheless, but it appears that they can all be excluded. This includes the 2-vinylallyl anion (**3a**), which can arise, in principle, from an energetically favorable orbital symmetry allowed process (eq 13).[20] It is worth noting that we did prepare **3a** independently by deprotonating isoprene, and that it can readily be distinguished from **1a** and **2a**. For example, **3a** undergoes 7 H/D exchanges with D_2O and gives characteristic products or different product distributions with O_2, COS, and N_2O (eqs 14–16).[21] The last reagent, however, is the least useful since **2a** and **3a** differ only in the formation of a minor dehydrogenation product (eq 8 vs 16).



1a **3a** (13)

$\Delta H = -21 \pm 6$ (expt); -17.5 (6-31+G*) and -11.9 (MP2) kcal mol^{-1}

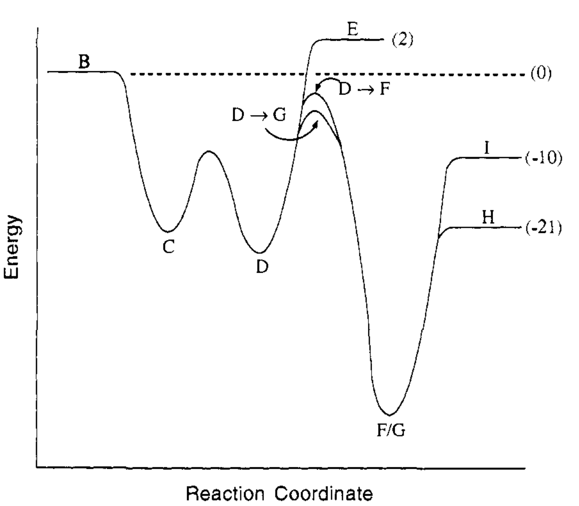
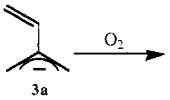
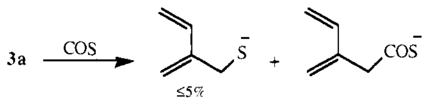


Figure 1. A qualitative potential energy diagram for the reaction between vinylcyclopropane and hydroxide ion. Parenthetical values are in kilocalories per mole.

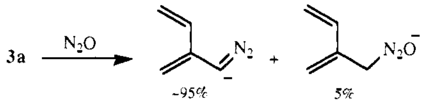


$$OH^- + CH_3C{\equiv}C^- + HC{\equiv}CO^- + CH_2{=}CHC{\equiv}C^- + CH_2{=}C(CH{=}CH_2)O^- \quad (14)$$

~8% 39% 20% 6% 27%



(15)



(16)

The formation of the conjugate base of methylenecyclobutane (**2a**) from the reaction between vinylcyclopropane and OH^- is surprising. There do not appear to be any reports of such an isomerization in solution, and there are relatively few examples of rearrangements in the gas phase which do not simply involve the shuttling of a proton back and forth.[22] From a thermodynamic perspective, however, this rearrangement is exothermic, whereas the competing proton-transfer channel leading to **1a** is not. A mechanism which can account for this unusual transformation is given in Scheme II, and the corresponding reaction coordinate is illustrated in Figure 1. The first step along the isomerization pathway, undoubtedly, involves the formation of an energized ion–neutral complex, C. This species has approximately 15–20 kcal mol^{-1} available to it, which can be used to drive an endothermic proton transfer. The resulting ion, D, does not have enough energy to separate into its two components (E). Therefore, it may revert back to B or isomerize to the observed product (I). Both channels appear to be taking place since OD^- is isotopically scrambled in the reaction with **1**; i.e., OH^- is produced.[23] Our

---

[19] The reaction of **2a** with N_2O has previously been reported. See: Reference 15a.

[20] The heat of formation of **2a** (386 (±5) − 365.7 + 29.0 = 49 ± 5 kcal mol^{-1}) and **3a** (386 (±5) − 365.7 + 18.1 = 38 ± 5 kcal mol^{-1}) were derived from data obtained from: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall, New York, 1986.

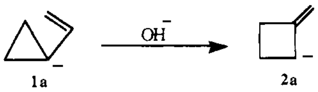
[21] The reactions of **2a** and **3a** with CS_2 and SO_2 lead to exactly the same products (eqs 10 and 12), and therefore these two reagents are not diagnostic for the structure of the ion.

[22] (a) Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 1025. (b) Bowie, J. H. *Mass Spectrom. Rev.* **1990**, *9*, 349, and references therein.

[23] The $C_5H_7^-$ ion, as one would predict, does not incorporate any deuterium.

results also suggest that the ring opening barrier (D → F) is larger than the one for ring expansion (D → G) since the former pathway does not take place. The difference between the two transition states (D → F and D → G), however, probably is not very large since we have found that other substituted cyclopropyl anions open to their allylic anions.[5b,24] Finally, if one employs stronger bases such as NH_2^-, $EtNH^-$, or Me_2N^-, then the proton-transfer pathway leading to **1a** becomes thermodynamically accessible and the isomerization channel becomes less competitive.[16]

Ab initio molecular orbital calculations have been carried out in order to further explore the mechanism by which **2a** is formed. The calculated energies appear to be reliable in that the acidities of vinylcyclopropane (**1**) and methylenecyclobutane (**2**) are accurately reproduced ($\Delta H_{acid}(\mathbf{1}) = 394 \pm 3$ (expt) and 392.3 kcal mol^{-1} (calc), $\Delta H_{acid}(\mathbf{2}) = 386 \pm 5$ (expt)[25] and 385.2 kcal mol^{-1} (calc)), as are the isomerization energies given in eqs 13 and 17.[20]

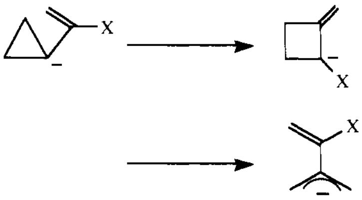


(17)

1a **2a**

$\Delta H = -10 \pm 6$ (expt); -8.7 (6-31+G*) and -6.1 (MP2) kcal mol^{-1}

The calculated geometries of **1** and **2** are also in accord with experiment,[26] and the results for the ions (**1a**, **2a**, and **3a**) seem quite reasonable. Vinylcyclopropyl anion is computed to be pyramidal, as are many other cyclopropyl anions,[27] but the inversion barrier is small (4.4(6-31+G*) and 4.8 (MP2) kcal mol^{-1}). Methylenecyclobutane flattens out and becomes planar upon deprotonation, presumably, to accommodate the introduction of another sp^2 center into the ring and to enhance charge delocalization. Ion **3a** is relatively flat, as one would expect, but there is some bending in order to minimize the nonbonded interactions. Transition states for the ring-opening and ring-expansion pathways ($TS_{1a\to3a}$ and $TS_{1a\to2a}$, respectively) were also located with the 6-31+G* basis set (Table IV). Their energies are very similar (Table I), but the latter process is favored both at the Hartree–Fock and electron-correlated (MP2) levels. This is consistent with our experimental observations and indicates that the orbital symmetry allowed $\sigma_{2s} + \pi_{4s}$ ring expansion (**1a** → **2a**) can favorably compete with the conrotatory ring opening (**1a** → **3a**). The addition of an electron-withdrawing or resonance-stabilizing group at the nodal position in **1a** should further facilitate the ring expansion (eq 18a) relative to the ring opening (eq 18b) and suggests that it should be possible to induce this rearrangement in solution as well.



(18a)

(18b)

Conclusions

Vinylcyclopropane (**1**) reacts with very strong bases to afford its conjugate base (**1a**). The reactivity and thermodynamic properties of this ion have been presented. When OH^- is allowed to react with **1** a novel rearrangement takes place, and the conjugate base of methylenecyclobutane (**2a**) is produced. A reasonable mechanism is proposed which is found to be consistent with ab initio molecular orbital calculations. Transition states for the isomerization of **1a** into **2a** and **3a** have been located, and although they are very similar in energy, the former pathway is preferred. These results strongly suggest that it should be possible to induce a similar rearrangement in solution.

Acknowledgment. The transition state for the conrotatory ring opening of cyclopropyl anion was made available to us by Dr. Adam Kallel and Professor Ken Houk. Their generosity made it much easier for us to locate the ring-opening transition state for vinylcyclopropyl anion. Support from the Minnesota Supercomputer Institute, University of Minnesota McKnight Land Grant Professorship program, National Science Foundation (CHE-8907198), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged.

Registry No. 1, 693-86-7; **1a**, 84064-88-0; **2**, 1120-56-5; **2a**, 100812-23-5; **3a**, 60835-78-1; NH_2^-, 17655-31-1; Me_2N^-, 34285-60-4; N_2O, 10024-97-2; CS_2, 75-15-0; COS, 463-58-1; O_2, 7782-44-7; SO_2, 7446-09-5; OH^-, 14280-30-9; $HC{\equiv}CO^-$, 64066-01-9; $^-CH_2CHO$, 64723-93-9; $CH_3C{\equiv}C^-$, 36147-87-2; $CH_2{=}CHC{\equiv}C^-$, 58870-47-6; $CH_2{=}C(CH{=}CH_2)O^-$, 125251-12-9; isoprene, 78-79-5; hydroxy(1-vinylcyclopropyl)diazene anion, 138154-11-7; 1-vinylcyclopropane(dithioic) acid anion, 138154-12-8; 1-vinylcyclopropanethiol anion, 138154-13-9; 1-vinylcyclopropanethioic acid anion, 138154-14-0; (1-cyclobutenyl)diazomethane anion, 138154-15-1; methylenecyclobutene anion, 127697-05-6; 2-methylenecyclobutane(dithioic) acid anion, 138154-16-2; 2-methylenecyclobutanethiol anion, 138154-17-3; 2-methylenecyclobutanethioic acid anion, 138154-18-4; 2-methylene-3-butenethiol anion, 138154-19-5; 3-methylene-4-pentenethioic acid anion, 138154-20-8; 1-diazo-2-methylene-3-butene anion, 101233-40-3; hydroxy(2-methylene-3-butenyl)diazene anion, 138154-21-9.

---

(24) P. Chou, unpublished data.

(25) The acidity of methylenecyclobutane was bracketed in the forward and reverse directions, and in both cases it was found to lie in between MeOH and H_2O.

(26) Vinylcyclopropane: (a) Nijveldt, D.; Vos, A. *Acta Crystallogr.* **1988**, *B44*, 296. (b) Traetteberg, M.; Bakken, P.; Almenningen, A.; Luttke, W. *J. Mol. Struct.* **1988**, *189*, 357. Methylenecyclobutane: (c) Allinger, N. L.; Mastryukov, V. S. *J. Struct. Chem.* **1983**, *24*, 484.

(27) (a) Tyrrell, J.; Kolb, V. M.; Meyers, C. Y. *J. Am. Chem. Soc.* **1979**, *101*, 3497. (b) Hopkinson, A. C.; McKinney, M. A.; Lien, M. H. *J. Comput. Chem.* **1983**, *4*, 513. (c) Tupitsyn, I. F.; Shibaev, A. Y. *Theor. Exp. Chem.* **1985**, *21*, 563. (d) Kroeker, R. L.; Bachrach, S. M.; Kass, S. R. *J. Org. Chem.* **1991**, *56*, 4062. (e) G. Dahlke, unpublished data.