Unimolecular Rearrangements of Carbanions in the Gas Phase. 2. Cyclopropyl Anions†

Phillip K. Chou, Gregg D. Dahlke, and Steven R. Kass*

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received August 13, 1992*

Abstract: We have examined the gas-phase unimolecular rearrangements of a series of substituted cyclopropyl anions ($\overline{CHXCH_2CY}^-$; X = H, Y = Ph, CHO, and CN; X = Y = CO_2CH_3) with a variable temperature flowing afterglow device. The ring-opening barriers range from 19 to ≥36 kcal mol^{-1} and are well reproduced by ab initio molecular orbital calculations. An analysis of eight monosubstituted cyclopropyl anions reveals that the flexibility (ease of inversion) and thermodynamic stability of these ions account for their tendency to isomerize.

Introduction

A tremendous number of unimolecular rearrangements have been studied, and they have proven to be fascinating mechanistically, useful synthetically, and a challenge for theoretical methods.[1] In addition, a wealth of information on energetics, bonding, and the relationship between structure and reactivity has been obtained from these investigations. Nonnucleophilic solvents have been used to examine relatively free carbonium ions, but equivalent conditions for probing carbanions do not exist.[2] As a result, aggregation, counterion, and solvation effects are always a complicating issue when dealing with the latter species. These obscuring influences, however, can be eliminated by carrying out gas-phase investigations. The results from such studies are often quite similar to those obtained in solution, and they have the advantage of being directly comparable to molecular orbital calculations.

A major obstacle impeding the exploration of ionic rearrangements in the gas phase is that the products cannot be differentiated simply on the basis of their mass to charge ratio. Moreover, it is necessary to have thermally equilibrated ions in order to measure rearrangement rates and obtain activation energies, but this condition is not met with most mass spectrometers. Recent developments in mass spectrometry (MS), such as collision-induced dissociation[3] and neutralization–reionization,[4] can be used to differentiate isomeric species and have enabled Bowie and co-workers to observe several unimolecular processes.[5] The first studies involving thermalized ions and reporting activation energies were carried out using a radiolytic technique[6] and a variable temperature flowing afterglow (VTFA) device.[7] The latter experiment is particularly well suited for studying unimolecular isomerizations since both positively and negatively charged isomeric ions can be distinguished on the basis of their reactivity, thermodynamic properties, and kinetic behavior. In addition, a wide range of activation energies (4–41 kcal mol^{-1}) can be measured since temperatures from ca. −190 to 400 °C can be accessed.

We have recently reported on the thermolysis of bicyclobutyl and phenylcyclopropyl anions in our VTFA apparatus.[7] The former species is remarkably stable and is unaffected by heat, at least to 300 °C ($E_a \geq 32$ kcal mol^{-1}). The latter ion is much more labile and starts to isomerize to 2-phenylallyl anion at temperatures as low as 200 °C ($E_a = 26$ kcal mol^{-1}). This difference is startling and clearly reflects an interesting relationship between structure and reactivity. We have continued to explore this relationship and describe some of our work on the structural stability of mono- and disubstituted cyclopropyl anions in this paper.

Experimental Section

Phenylcyclopropane, 2-phenylpropene, allylbenzene, cyclopropanecarboxaldehyde, methacrolein, crotonaldehyde, cyanocyclopropane, methacrylonitrile, crotononitrile, and dimethyl itaconate were obtained from commercial sources and were subjected to several freeze–pump–thaw cycles immediately before their use in order to remove noncondensible impurities. A mixture of *cis*- and *trans*-dimethyl 1,2-cyclopropanedicarboxylate was prepared as previously reported.[8]

All of the gas-phase experiments described in this paper were carried out with a variable temperature flowing afterglow device which has previously been described.[9] Precursor ions were generated by electron ionization of the appropriate neutral reagents and were swept down a 120-cm × 7.6-cm flow tube by a constant flow (ca. 160 STP cm^3 s^{-1}) of helium. System pressures of 0.35–0.45 Torr were maintained with a large Kinney Roots pumping system (547 L s^{-1} for air at 0.4 Torr), and under these multicollision conditions the ions rapidly become thermally equilibrated with the walls of the apparatus. Multistep reactions were conveniently carried out by adding neutral reagents through any number of fixed inlets along the reaction region. A fraction of the resulting ions was sampled through a 0.5-mm orifice and detected with a quadrupole mass spectrometer. The temperature was varied from 20 to 375 °C by using two resistive tubular heaters and an Omega CN5001 temperature controller. It was monitored with several type E thermocouples. Rate constants were measured by adding a neutral reagent through a movable inlet and varying either its location (distance) or the flow of the neutral material. In this standard way, pseudo-first-order rate coefficients were

† Dedicated to Professors Kenneth B. Wiberg and Charles H. DePuy on the occasion of their 65th birthdays.

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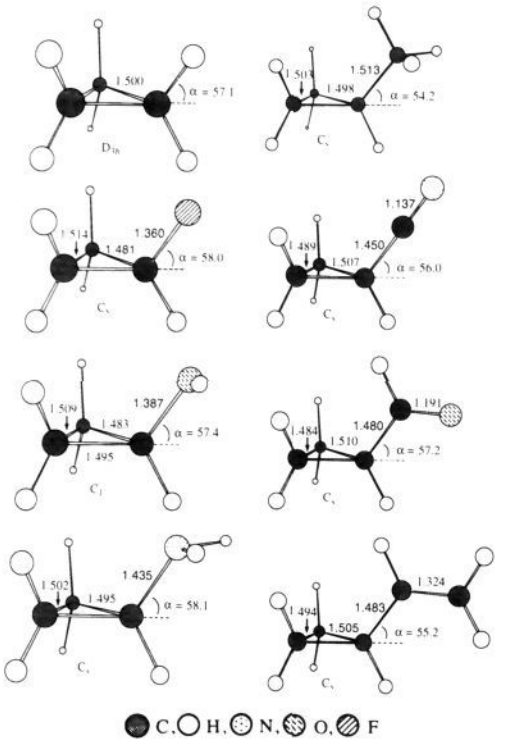

Figure 1. Calculated structures (6-31+G(d)) for a series of monosubstituted cyclopropanes. All bond lengths are in angstroms, and angles are in degrees.

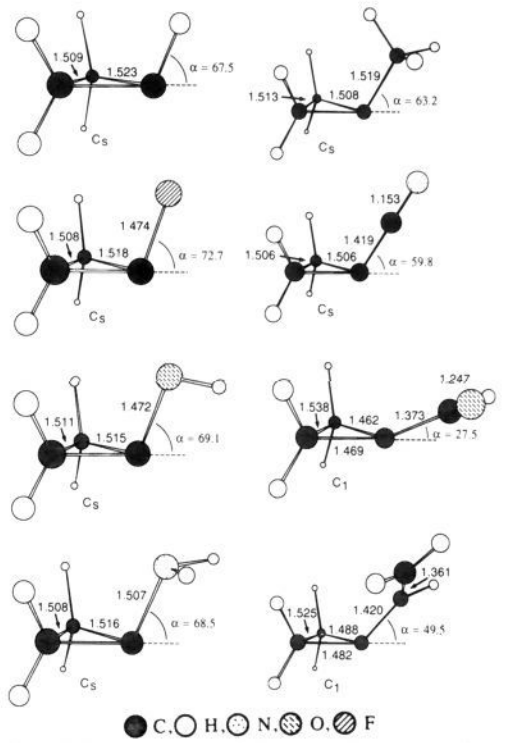

Figure 2. Calculated structures (6-31+G(d)) for a series of monosubstituted cyclopropyl anions. All bond distances are in angstroms, and angles are in degrees.

obtained. Their reliability was ascertained by examining the reaction between He^+ and N_2, since its rate is very well established.[10] Over a period of 2 years, 12 independent measurements were made by three different workers, and the average of their results ($(1.18 \pm 0.12) \times 10^{-9}$ cm^3 s^{-1}) is in excellent accord with the literature value of 1.2×10^{-9} cm^3 s^{-1}.

Accessible Activation Energies. The energy barriers for unimolecular rearrangements which can be measured in our experiment can be calculated using the Arrhenius equation (eq 1). In order to apply it, information is needed about the rate constants, which can be obtained from the integrated form of the rate equation (eq 2). The sensitivity of our

$$k = Ae^{(-E_a/RT)} \tag{1}$$

$$\ln \frac{[A^-]}{[A^-]_0} = -kt \tag{2}$$

instrument is such that for a typical ion a 5% difference (i.e., $[A^-]/[A^-]_0 = 0.95$ or 0.05) can readily be detected. The maximum reaction time is just 7 ms; this is calculated from the average velocity of the helium buffer gas ($\bar{v}_{He} \approx 9000$ cm s^{-1} at 0.4 Torr), the average velocity of the ions ($\bar{v}_{ions} = 1.6(\bar{v}_{He})$),[11] and the length of the reaction region (100 cm). The minimum reaction time that can reliably be probed is ca. 1 ms. Therefore, unimolecular rearrangements with rate constants from 7 to 3000 s^{-1} can be observed in our flow tube. Rates which fall outside of this range correspond to reactions in which only the reactants or products will be detected. Typical values for an A factor in a unimolecular rearrangement are 10^{13}–10^{14} s^{-1}.[12] Substituting for A and k in the Arrhenius equation leads to activation energies of 13–41 kcal mol^{-1}, which can be probed over the temperature range of 20–400 °C.

Calculations. Ab initio molecular orbital calculations were carried out on a Cray X-MP at the Minnesota Supercomputer Center using Gaussian 90.[13] Geometry optimizations of a series of eight monosubstituted cyclopropanes ($c\text{-}C_3H_5X$, X = H, F, OH, NH_2, CH_3, CN, CHO, and C_2H_3) and their corresponding 1-substituted cyclopropyl anions were done at the Hartree–Fock level of theory with the 6-31+G(d) basis set.[14]

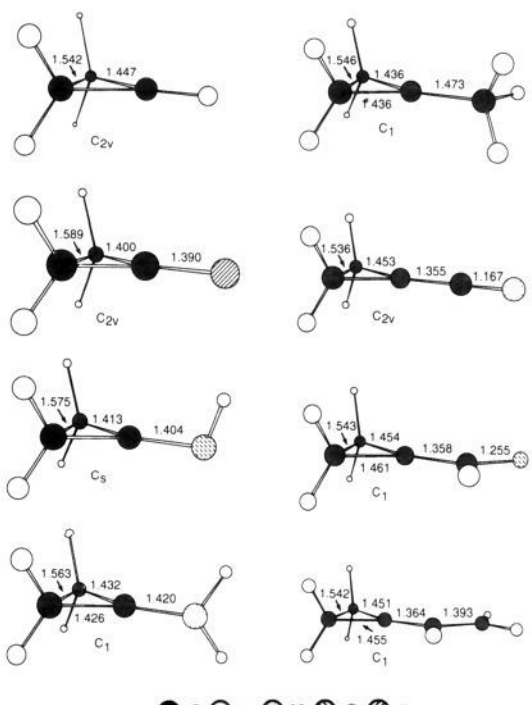

Figure 3. Calculated inversion transition-state structures (6-31+G(d)) for a series of monosubstituted cyclopropyl anions. All bond lengths are in angstroms.

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Table I. Calculated Energies (in hartrees) for a Series of Monosubstituted Cyclopropanes and Their Corresponding 1-Substituted Cyclopropyl Anions[a]

substituent (X)	theory	neutral[b]	anion[b,c]
H	RHF	−117.060 917 (49.1)	−116.372 790 (39.4)
	MP2	−117.454 674	−116.781 352
NH_2	RHF	−172.087 817 (60.0)	−171.401 304 (50.4)
	MP2	−172.647 414	−171.981 256
OH	RHF	−191.913 579 (52.2)	−191.237 750 (42.3)
	MP2	−192.487 182	−191.831 030
F	RHF	−215.914 456 (44.7)	−215.251 442 (35.1)
	MP2	−216.479 245	−215.834 473
CN	RHF	−208.799 686 (48.9)	−208.172 608 (40.1)
	MP2	−209.467 756	−208.856 040
CHO	RHF	−229.793 936 (55.3)	−229.161 951 (46.3)
	MP2	−230.487 785	−229.876 699
C_2H_3	RHF	−193.945 565 (69.3)	−193.284 133 (59.7)
	MP2	−194.591 890	−193.951 622
CH_3	RHF	−156.098 198 (66.1)	−155.412 500 (56.2)
	MP2	−156.624 924	−155.958 380

[a] Energies were calculated using optimized RHF/6-31+G(d) geometries. [b] Zero-point energies (scaled by 0.90) are in parentheses.

Table II. Calculated Energies (in hartrees) for a Series of 1-Substituted Cyclopropyl Anion Inversion and Ring-Opening Transition States[a]

substituent (X)	theory	inversion T.S.[b]	ring-opening T.S.[b]
H	RHF	−116.340 682	−116.308 882
	MP2	−116.755 436	−116.735 654
NH_2	RHF	−171.349 940	−171.336 791
	MP2	−171.933 222	−171.933 775
OH	RHF	−191.167 014	−191.168 404
	MP2	−191.766 751	−191.778 786
F	RHF	−215.166 438	−215.179 678
	MP2	−215.758 772	−215.781 373
CN	RHF	−208.157 144	−208.103 592
	MP2	−208.842 380	−208.806 019
CHO	RHF	−229.161 491	−229.099 751
	MP2	−229.875 325	−229.831 548
C_2H_3	RHF	−193.277 195	−193.226 038
	MP2	−193.943 967	−193.910 646
CH_3	RHF	−155.370 299	−155.348 011
	MP2	−155.919 051	−155.910 949

[a] Energies were calculated using optimized RHF/6-31+G(d) geometries. [b] Each transition state (T.S.) was characterized by one and only one imaginary frequency in the vibrational analysis.

Cyclopropane was optimized under the constraint of D_{3h} symmetry, and a mirror plane was enforced for all of the other species (neutrals and anions). In many cases (X = OH, NH_2, CH_3, CHO, and C_2H_3) there are two different C_s conformations, and in these instances both structures were fully optimized. The difference in their Hartree–Fock energies was ≤3 kcal mol^{-1} for the neutral cyclopropanes and somewhat larger (≤6.1 kcal mol^{-1}) for the cyclopropyl anions. Vibrational frequencies were computed analytically with the 6-31+G(d) basis set for the lower energy structures in order to ensure that they correspond to true minima on the potential energy surface (no negative eigenvalues) and to provide their zero-point energies (ZPEs). In three cases the symmetry constraints led to species with one imaginary frequency (c-C_3H_5OH, c-$C_3H_4CHO^-$, and c-$C_3H_4C_2H_3^-$), and these compounds were reoptimized without any restrictions. The results for the lowest-energy structures of the cyclopropanes and cyclopropyl anions are summarized in Figures 1 and 2, respectively.[15] Inversion and conrotatory ring-opening transition states for the latter species were also located with the 6-31+G(d) basis set (Figures 3 and 4, respectively). In this case, three of the transition states for inversion (X = H, F, and CN) were constrained to C_{2v} symmetry, and all of the other structures were optimized under the C_1 point group. Each first-order saddle point was characterized by its vibrational frequencies, and, as required, they all had one and only one negative eigenvalue. Second-order Møller–Plesset perturbation theory (MP2)[16] was used to account for electron correlation and provide more reliable energies for each computed structure (Tables I and II). The resulting acidities, inversion barriers, and ring-opening barriers are summarized in Table III.

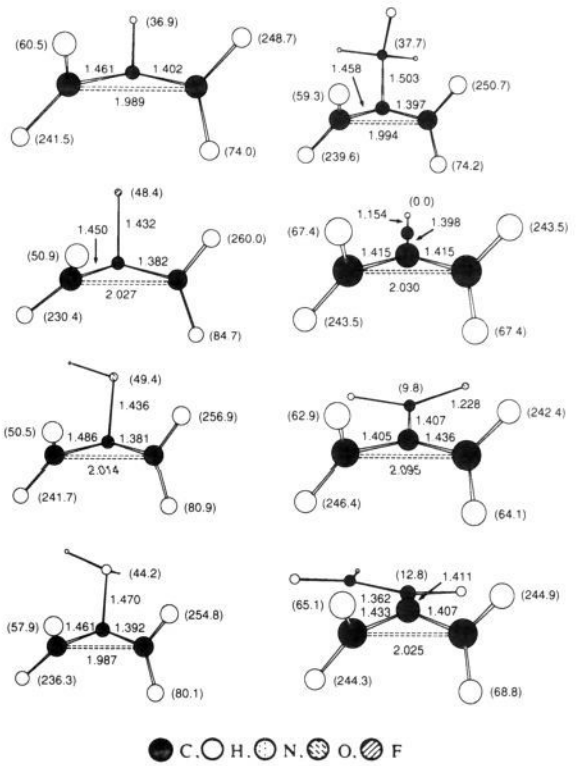

Figure 4. Calculated ring-opening transition-state structures (6-31+G(d)) for a series of monosubstituted cyclopropyl anions. All distances are in angstroms, and angles are in degrees. Parenthetical values correspond to a H–C–C_1–C torsion angle or the degree to which the central substituent is bent out of the C–C–C plane.

Table III. Calculated and Experimental Proton Affinities, Inversion Barriers, Ring-Opening Barriers, and Isomerization Enthalpies for a Series of 1-Substituted Cyclopropyl Anions[a]

substituent (X)	proton affinity[b]	inversion barrier[c]	ring-opening barrier[c]	ΔH_{isom}[d]
H	412.8 (412 ± 3)[e]	16.3	28.7	−29
NH_2	408.4	30.1	29.8	
OH	401.8	40.3	32.8	
F	395.0	47.5	33.3	−27[f]
CN	375.0 (376 ± 3)[e]	8.6	31.4 (≥36)[g]	−11
CHO	374.5 (374.7 ± 2)[g]	0.9	28.3 (29 ± 4)[g]	−10
C_2H_3	392.2 (394 ± 3)[h]	4.8	25.7 (26 ± 4)[g,i]	−11[i]
CH_3	408.4 (409 ± 3)[e]	24.7	29.8	−34

[a] All values are in kcal mol^{-1}. [b] MP2/6-31+G(d)//6-31+G(d) with zero-point energy corrections (frequencies were scaled by a factor of 0.90). Experimental values are in parentheses. [c] MP2/6-31+G(d)//6-31+G(d) energies. [d] Data from refs 12, 17, and 18 were used to obtain experimental isomerization energies. [e] Reference 17. [f] The calculated acidity was used in deriving the heat of formation of 1-fluorocyclopropyl anion (−2.0 kcal mol^{-1}). [g] This work. [h] Reference 19. [i] The experimental value corresponds to phenylcyclopropyl anion.

Results

Phenylcyclopropyl Anion (1a). The conjugate bases of phenylcyclopropane (**1a**), 2-phenylpropene (**1b**), and 3-phenylpropene (**1c**) have previously been generated by proton abstraction.[20] Each

(15) The energies of the two C_s conformations for cyclopropanecarboxaldehyde are within 0.2 kcal mol^{-1} at the Hartree–Fock level and differ by only 0.3 kcal mol^{-1} when electron correlation is accounted for (MP2).

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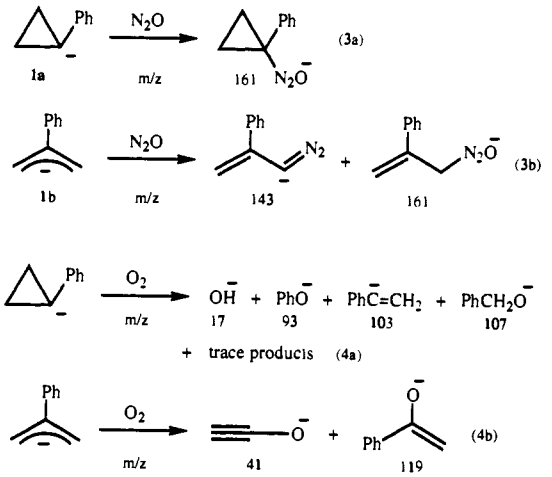
Table IV. Reaction Products of **1a**, **1b**, and **1c** with a Variety of Neutral Reagents

	products		
reagent	**1a**	**1b**	**1c**
O_2	OH^- + PhO^- + $PhC^-{=}CH_2$ + $PhCH_2O^-$ + trace products	$HC{\equiv}CO^-$ + $PhC(O^-){=}CH_2$	no reaction
N_2O	adduct	adduct + $CH_2{=}C(Ph)C^-{=}N_2$	no reaction
CS_2	adduct	adduct	adduct
COS	adduct (~80%) + c-$C_3H_4(Ph)S^-$ (20%)	adduct (~98%) + $CH_2{=}C(Ph)CH_2S^-$ (2%)	adduct
SO_2	adduct (~55%) + SO_2^- (30%) + HSO_2^- (15%)	adduct (~70%) + SO_2^- (30%)	adduct (~70%) + SO_2^- (30%)
MeSSMe	MeS^-	MeS^-	MeS^-
$MeCO_2Me$	M - 1 (~95%) + c-$C_3H_4(Ph)COCH_2^-$ (5%)	M - 1 (~80%) + $CH_2{=}C(Ph)CH^-COCH_3$ (20%)	no reaction
$MeCO_2CH_2CF_3$	M - 1 (~60%) + $CF_3CH_2O^-$ (40%)	M - 1 (~55%) + $CF_3CH_2O^-$ (10%) + $CH_2{=}C(Ph)CH^-COCH_3$ (35%)	M - 1 + $CF_3CH_2O^-$ (major) + $Ph(H)C{=}CHCH^-COCH_3$
D_2O	OD^- + 7 H/D exchanges	8 H/D exchanges (4 fast/4 slow)	no reaction
EtOD	EtO^-	EtO^-	3 H/D exchanges (3rd is slow)
t-BuOD	*t*-BuO^-	*t*-BuO^-	3 H/D exchanges

of these isomers can be distinguished, as described by Andrist, DePuy, and Squires, on the basis of its reactivity with D_2O, N_2O, and O_2. For example, D_2O reacts slowly with **1a** ($k \approx 5.0 \times 10^{-13}$ cm^3 s^{-1}) to afford OD^- and up to seven hydrogen–deuterium (H/D) exchanges,[21] it induces four rapid H/D exchanges and four slower ones in **1b**, and it does not react with **1c**. The reactions with N_2O and O_2, however, are more useful for our purposes. Phenylcyclopropyl anion reacts with the former reagent to afford an adduct (*m/z* 161, eq 3a) and with the latter compound ($k \approx 10^{-11}$ cm^3 s^{-1}) to give a complex mixture of products (eq 4a). 2-Phenylallyl anion, on the other hand, produces a ca. 3:1 mixture of a diazo anion (*m/z* 143) and an adduct with N_2O (eq 3b) and cleanly forms the enolates of ketene (*m/z* 41) and acetophenone (*m/z* 119, eq 4b) upon interaction with O_2 ($k = 2.0 \times 10^{-10}$ cm^3 s^{-1}). The fully conjugated isomer **1c** is less reactive, as one might expect, and it does not react with either reagent.



Additional methods for distinguishing between **1a**, **1b**, and **1c** were explored by examining their reactions with a number of reagents, including CS_2, COS, SO_2, CH_3SSCH_3, $CH_3CO_2CH_3$, and $CH_3CO_2CH_2CF_3$. The results are consistent with previous investigations using these structural probes and are summarized in Table IV.[22] A variety of Brønsted acids can also be used to differentiate **1c** (PA = 369 ± 4 kcal mol^{-1})[23] from its more basic isomers, but acid–base chemistry is less effective for distinguishing between **1a** and **1b**. Nevertheless, we have found that water, fluorobenzene, and furan slowly protonate **1a** (PA = 390 ± 3 kcal mol^{-1}), whereas they do not protonate **1b** (PA = 386 ± 5 kcal mol^{-1}, Table V).[17] The 1-phenylallyl anion can also be identified by hydrogen–deuterium exchange; it undergoes up to three ex-

Table V. Acidities Used and Measured in This Work[a]

compound	acidity	compound	acidity
NH_3	403.7	$(CH_3CH_2)_2NOH$	370.7
H_2O	390.8	$(CH_3)_2CO$	369.0
c-$C_3H_5(Ph)$	390 ± 3[b]	$CH_2{=}CHCH_2(Ph)$	369 ± 4[b]
C_4H_4O	388	$(CH_3)_2C{=}NOH$	366.2
C_6H_5F	387.2	CH_3CHO	365.9
$CH_2{=}C(Ph)CH_3$	386	CF_3CH_2OH	361.9
CH_3OH	380.6	NH_2CHO	359.9
CH_3CH_2OH	377.4	$CH_2{=}CHCH_2CN$	359 ± 3[b]
$CH_2{=}C(CHO)CH_3$	377.2	c-C_4H_5N	358.7
c-C_3H_5CN	375.5	CH_3SH	356.8
c-C_3H_5CHO	374.7 ± 2[b]	CH_3CH_2SH	355.2
$(CH_3)_3COH$	374.5	$CH_2{=}C(CO_2CH_3)$-$CH_2CO_2CH_3$	355 ± 3[b]
CH_3CN	372.8		
1,2-c-$C_3H_4(CO_2CH_3)_2$	372 ± 3[b]	$CH_2{=}CHCH_2CHO$	354.7
HF	371.4	$(CH_3)_3CSH$	352.5
$CH_2{=}C(CN)CH_3$	370.7	CH_3CO_2H	348.7

[a] All values, unless otherwise noted, come from ref 17 and are in kcal mol^{-1}. [b] This work.

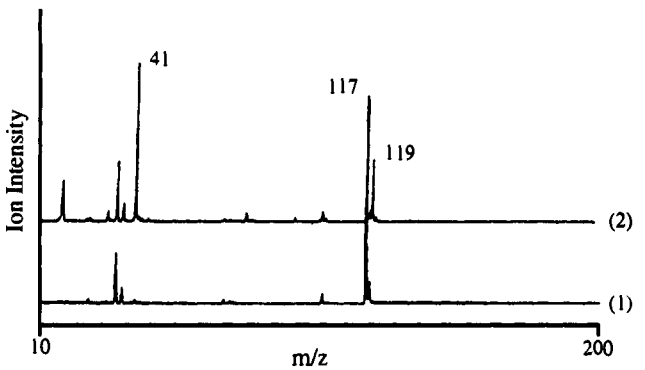


Figure 5. Mass spectra of the reaction of phenylcyclopropane with hydroxide (1) and phenylcyclopropyl anion with molecular oxygen (2) at ca. 250 °C.

(20) Andrist, A. H.; DePuy, C. H.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 845.

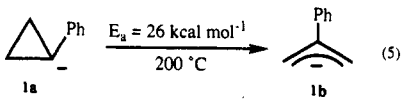
(21) Similar behavior is observed in solution. Treatment of phenylcyclopropane with Lochmann's base, *n*-butyllithium/potassium *tert*-butoxide in hexane, followed by a deuterium oxide quench, leads to deuterium incorporation in the benzylic, β-cyclopropyl, and phenyl ring. See: Ogle, C. A.; Black, K. C.; Sims, P. F. *J. Org. Chem.* **1992**, *57*, 3499.

(22) (a) DePuy, C. H. *Org. Mass Spectrom.* **1985**, *20*, 556. (b) Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Phys. Chem.* **1984**, *88*, 1389. (c) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 901. (d) Bartmess, J. E.; Hays, R. L.; Caldwell, G. *J. Am. Chem. Soc.* **1981**, *103*, 1338.

(23) The acidity of 3-phenylpropene was assigned on the basis of the following observations: fluoride (PA = 371.4 kcal mol^{-1}) deprotonates 3-phenylpropene, whereas $Me_2C{=}NO^-$ (PA = 366.2 kcal mol^{-1}) does not. On the other hand, $Me_2C{=}NOH$ protonates 1-phenylallyl anion (**1c**), but Et_2NOH (ΔH_{acid} = 370.6 kcal mol^{-1}) does not.

changes with EtOD and *t*-BuOD, whereas **1a** and **1b** undergo deuteron transfer.

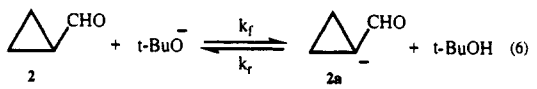
The reactivities of **1a**, **1b**, and **1c** were explored at a variety of elevated temperatures. Some reactions appear to become faster and others slower, but from a qualitative standpoint the reactions do not change significantly. Likewise, the product distributions are not affected dramatically except for phenylcyclopropyl anion. This ion, regardless of whether it is generated in a thermoneutral reaction (deprotonation of **1** by OH^-) or a 15 kcal mol^{-1} exothermic process (deprotonation of **1** by NH_2^-), begins to show different behavior at ca. 200 °C. In particular, the reaction with N_2O affords a diazo anion (eq 3b), and the one with O_2 yields deprotonated ketene and acetophenone (eq 4b, Figure 5). These products are indicative of 2-phenylallyl anion, and this strongly suggests that a unimolecular rearrangement is beginning to occur at ca. 200 °C. The relative contribution of **1b** increases with temperature, and at ca. 300 °C the m/z 117 ions generated from phenylcyclopropane and 2-phenylpropene are indistinguishable. This enables us to estimate an activation barrier for this process of 26 kcal mol^{-1}, assuming an A factor of 10^{13} s^{-1} (eq 5). Since activation energies are relatively insensitive to temperature (a 25 °C change only affects E_a by 1–2 kcal mol^{-1}), our estimate should be reasonably reliable (±4 kcal mol^{-1}) as long as the A factor is not too unusual.[24]



(5)

Alternative explanations for the conversion of **1a** to **1b** have been considered. Pyrolysis of phenylcyclopropane leads to ring-opened products but requires higher temperatures and longer contact times ($t_{1/2} \approx 130$ h at 350 °C).[25] Rearrangement of the starting cyclopropane, therefore, is not a factor. A bimolecular elimination is another possibility. However, this route might be expected to afford 1-phenylallyl anion (**1c**) since it is thermodynamically favored. A more compelling argument is the fact that a bimolecular pathway will depend critically on the nature of the reactant ion, whereas a unimolecular process should be independent of the method by which the ion is generated. Since identical results were obtained with two different bases (OH^- and NH_2^-), we conclude that the isomerization of **1a** to **1b** is a unimolecular reaction.[26]

Formylcyclopropyl Anion (2a). Cyclopropanecarboxaldehyde (**2**) is deprotonated by a variety of bases, including NH_2^-, OH^-, MeO^-, EtO^-, and *t*-BuO^-, but not by F^- or $^-CH_2CN$. The resulting cyclopropyl anion **2a** is readily protonated by CH_3CN and *t*-BuOH but not by weaker acids such as EtOD, MeOD, and D_2O. These results imply that $\Delta H_{acid}(\mathbf{2}) = 375 \pm 3$ kcal mol^{-1}. In order to confirm this assignment, we measured the rate constants for the forward ($k_f = (3.61 \pm .72) \times 10^{-10}$ cm^3 s^{-1}) and reverse ($k_r = (1.18 \pm .24) \times 10^{-9}$ cm^3 s^{-1}) directions of the reaction shown in eq 6.[27] From the equilibrium constant, $K = k_f/k_r = 0.31 \pm 0.09$,



(6)

$K = k_f/k_r = 0.31 \pm 0.09$

a free energy difference of 0.7 ± 0.2 kcal mol^{-1} at 298 K is obtained. The change in entropy ($T\Delta S = 0.6$ kcal mol^{-1}) can be reliably estimated as the sum of the translational and rotational contributions as given by standard statistical formulae.[28] Consequently, the reaction enthalpy is 0.1 kcal mol^{-1}, and when it is combined with the known acidity of *t*-BuOH, one obtains $\Delta H_{acid}(\mathbf{2}) = 374.7 \pm 2$ kcal mol^{-1}.

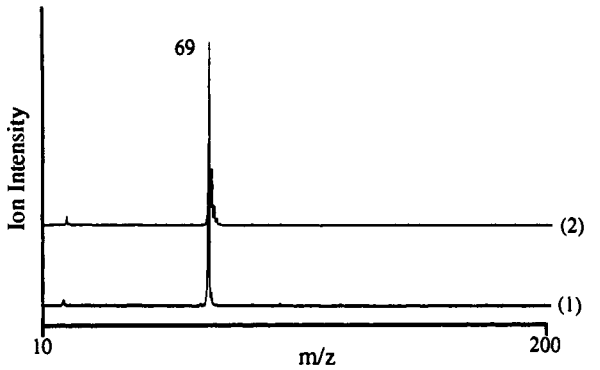
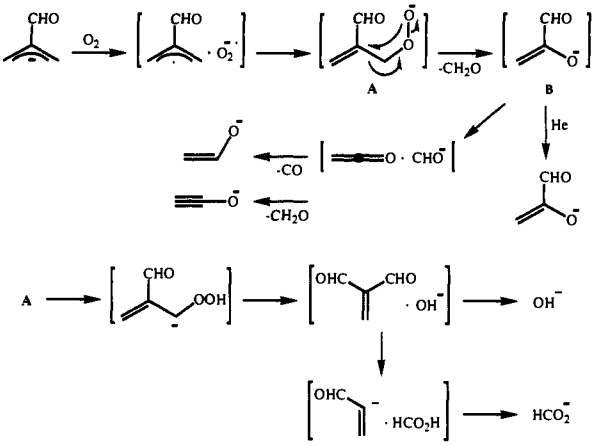


Figure 6. Mass spectra of the reaction of cyclopropanecarboxaldehyde with hydroxide (1) and 1-formylcyclopropyl anion (**2a**) with deuterium oxide (2) at ca. 275 °C.

Scheme I



2-Formylpropene is slightly less acidic ($\Delta H_{acid} = 377.2$ kcal mol^{-1}) and 3-formylpropene is considerably more acidic ($\Delta H_{acid} = 354.7$ kcal mol^{-1}) than cyclopropanecarboxaldehyde.[17] As a result, it is a relatively simple matter to distinguish 1-formylallyl anion (**2c**) from 2-formylallyl anion (**2b**) and **2a**. A variety of compounds will protonate the latter two ions without affecting the former species. In addition, **2c** undergoes up to a total of three H/D exchanges (two are facile) with CF_3CD_2OD, whereas **2a** and **2b** are simply deuteronated. As for differentiating between the conjugate bases of cyclopropanecarboxaldehyde and 2-formylpropene, the latter ion undergoes four H/D exchanges with D_2O, MeOD, and EtOD, while the former species does not react.

Several standard reagents were allowed to react with **2a**, **2b**, and **2c** in order to probe their reactivities. The results are summarized in Table VI and indicate that O_2 can be used to differentiate between 2-formylallyl anion (**2b**, $k \approx 10^{-12}$ cm^3 s^{-1}) and its isomers. A mechanism which can account for the observed ions at m/z 17, 41, 43, 45, and 71 is given in Scheme I. It is similar to the pathway suggested by Andrist, DePuy, and Squires for the reaction of O_2 with phenylcyclopropyl anion.[20] Electron transfer and a subsequent spin flip presumably occur first so that the peroxy anion **A** can be formed. Fragmentation of this ion into formaldehyde and the conjugate base of methylglyoxal ($CH_2{=}C(O^-)CHO$, **B**, m/z 71) is a very exothermic process overall (ca. 60 kcal mol^{-1})[29] and will afford the latter species in a highly excited state. Collisional stabilization of **B** would lead to its observation, whereas its dissociation should produce an ion–neutral complex

(24) If the A factor is 100 times less than a typical value of 10^{13}, then our estimate of the activation energy will be 4 kcal mol^{-1} too large. If the onset temperature is 25 °C too high (if it is too low, then the errors will cancel), then our estimate of the activation energy will also be in error by 1–2 kcal mol^{-1}. Taken together, it is unlikely that the activation energies are more reliable than ±4 kcal mol^{-1}.

(25) Leermaker, P. A.; Ross, M. E. *J. Org. Chem.* **1966**, *31*, 301.

(26) Elimination reactions involving cyclopropanes are disfavored by the poor orbital overlap between the C–H and C–C bonds.

(27) The reported uncertainty in the rate constants is estimated to be ±20%.

(28) Bartmess, J. E.; McIver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, Chapter 11.

(29) All of the necessary thermochemical information comes from refs 12, 17, and 18 except for the acidity of methylglyoxal. This value (ΔH_{acid}) was estimated to be 360 kcal mol^{-1}.

Table VI. Reaction Products of **2a**, **2b**, and **2c** with a Variety of Neutral Reagents

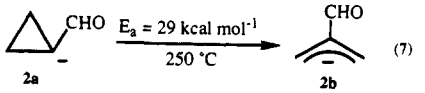
	products		
reagent	**2a**	**2b**	**2c**
O_2	no reaction	OH^- (16%) + $HC{\equiv}CO^-$ (19%) + $^-CH_2CHO$ (22%) + HCO_2^- (14%) + $CH_2{=}C(CHO)O^-$ (30%)	no reaction
N_2O	no reaction	no reaction	no reaction
CS_2	adduct	adduct (40%) + $CH_2{=}C(CHO)CH_2S^-$ (60%)	adduct (85%) + $^-SCH_2CH{=}CH(CHO)$ (15%)
COS	adduct	adduct (~85%) + $CH_2{=}C(CHO)CH_2S^-$ (15%)	adduct
SO_2	adduct	adduct (~45%) + $CH_2{=}C(CHO)CH_2O^-$ (30%) + SO_2^- (25%)	adduct
$CH_3CO_2CH_3$	M − 1 (~75%) + $c\text{-}C_3H_4(CHO)COCH_2^-$ (25%)	adduct (trace) + M − 1	no reaction
D_2O	no reaction	4 H/D exchanges	no reaction
MeOD	no reaction	4 H/D exchanges	no reaction
EtOD	no reaction	4 H/D exchanges	no reaction
CF_3CD_2OD	$CF_3CD_2O^-$	$CF_3CD_2O^-$	3 H/D exchanges (3rd is slow)

Table VII. Reaction Products of **3a**, **3b**, and **3c** with a Variety of Neutral Reagents

	products		
reagent	**3a**	**3b**	**3c**
O_2	NCO^- (very slow)	CN^- (8%) + NCO^- (69%) + $NCC{\equiv}C^-$ (10%) + $CH_2{=}C(CN)O^-$ (13%)	no reaction
N_2O	no reaction	no reaction	no reaction
CS_2	adduct (~85%) + $NCC{\equiv}CS^-$ (15%)	adduct (83%) + $CH_2{=}C(CN)CH_2S^-$ (17%)	adduct
COS	adduct (~90%) + $c\text{-}C_3H_4(CN)S^-$ (10%)	adduct (~90%) + $CH_2{=}C(CN)CH_2S^-$ (10%)	adduct
SO_2	adduct	adduct (~90%) + $CH_2{=}C(CN)CH_2O^-$ (10%)	adduct
MeSSMe	MeS^-	MeS^-	MeS^- (~5%) + $CH_2{=}CHC(SMe)CN^-$ (95%)
D_2O	no reaction	no reaction	no reaction
MeOD	no reaction	4 H/D exchanges	2 H/D exchanges (slow)
t-BuOD	*t*-BuO^-	4 H/D exchanges	3 H/D exchanges (3rd is slow)

between ketene and formyl anion. The latter species is a strong base and a potent source of hydride.[30] Therefore, the reaction between formyl anion and ketene can account for the formation of ketene enolate ($HC{\equiv}CO^-$, *m/z* 41) and acetaldehyde enolate ($^-CH_2CHO$, *m/z* 43). Hydroxide and formate can arise from an alternative pathway starting with **A**.

All three aldehyde anions (**2a**, **2b**, and **2c**) were allowed to react with deuterium oxide, molecular oxygen, trifluoroethanol-d_3, acetonitrile, and pyrrole at elevated temperatures. The reactivities of **2b** and **2c** are relatively insensitive to temperature, but the same cannot be said for **2a**. Its behavior starts to change at ca. 250 °C when it is generated *in* a thermoneutral or an endothermic process (i.e., deprotonation of cyclopropanecarboxaldehyde by *t*-BuO^- and F^-, respectively).[31] In particular, D_2O induces four H/D exchanges (Figure 6), O_2 leads to the formation of ions at *m/z* 17, 41, 43, 45, and 71, and the other reagents simply protonate/deuteronate the anion. These results suggest that the conjugate base of cyclopropanecarboxaldehyde starts to rearrange to **2b** at 250 °C. The activation energy for this ring-opening is estimated to be 29 kcal mol^{-1}, assuming that the *A* factor in the Arrhenius equation is 10^{13} s^{-1} (eq 7). It is worth adding that



2a 2b (7)

when hydroxide is used to deprotonate **2** (ΔH_{rxn} = −16 kcal mol^{-1}), there is evidence for the formation of **2b** at lower temperatures (ca. 200 °C). This is a situation we have encountered before, in which the heat of reaction, if it is sufficiently large, can induce isomerization. However, for less exothermic reactions (ca. ≤15 kcal mol^{-1}) the rearrangement onset temperatures are independent of the method of generation.

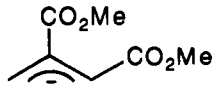
Cyanocyclopropyl Anion (3a). The deprotonation enthalpies for cyanocyclopropane (**3**) and 2-cyanopropene (**3d**) have been reported previously (ΔH_{acid} = 375.5 and 370.7 kcal mol^{-1}, respectively),[17] and therefore we only measured the acidity of 3-cyanopropene (**3e**). A variety of bases including acetaldehyde and formamide enolates (PA = 365.8 and 359.9 kcal mol^{-1}, respectively) were found to deprotonate **3e**, whereas *tert*-butylmercaptide (PA = 352.5 kcal mol^{-1}) and methanethiolate (PA = 356.8 kcal mol^{-1}) did not. On the other hand, 1-cyanoallyl anion (**3c**) is protonated by *tert*-butylmercaptan and methanethiol but not by weaker acids such as trifluoroethanol (ΔH_{acid} = 361.9 kcal mol^{-1}), formamide, and acetaldehyde. Taken together, these results enable us to assign ΔH_{acid}(**3e**) = 359 ± 3 kcal mol^{-1}. In accord with this value, **3c** was found to undergo two slow H/D exchanges with MeOD and up to three (the third was very slow) with *t*-BuOD. This behavior contrasts with that of the cyanocyclopropyl and 2-cyanoallyl anions (**3a** and **3b**, respectively); the former does not undergo any H/D exchange with D_2O, MeOD, or *t*-BuOD (the last reagent does deuteronate **3a**), and the latter exchanges four times with MeOD and *t*-BuOD.

In order to increase the number of ways by which **3a**, **3b**, and **3c** can be distinguished, reactions with N_2O, O_2, CS_2, COS, SO_2, and MeSSMe were explored. The suggested products are given *in* Table VII, and *in* a few cases they are useful for differentiating

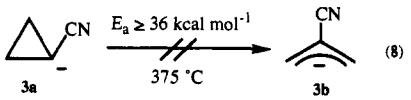
(30) (a) Karpas, Z.; Klein, F. S. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *18*, 65. (b) Kleingeld, J. C.; Ingemann, S.; Jalonen, J. E.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1983**, *105*, 2474.

(31) Fluoride does not deprotonate cyclopropanecarboxaldehyde at 25 °C, but it will at higher temperatures. This is simply due to the fact that endothermic reactions become more facile at higher temperatures.

Table VIII. Reaction Products of **4a** and **4b** with Several Standard Neutral Reagents

	products	
		
reagent	**4a**	**4b**
O_2	no reaction	no reaction
N_2O	no reaction	no reaction
CS_2	adduct	adduct
COS	adduct	adduct
SO_2	adduct	adduct
MeSSMe	MeS^-	no reaction
MeOD	1 H/D exchange	no reaction
EtOD	1 H/D exchange	no reaction
t-BuOD	1 H/D exchange	no reaction
CF_3CD_2OD	$CF_3CD_2O^-$	2 H/D exchanges
EtSD	EtS^-	EtS^- + 2 H/D exchanges (2nd is slow)

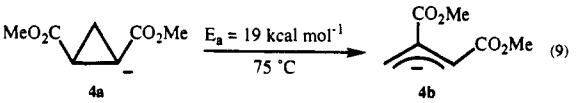
between the three isomers. As a result, each ion was allowed to react with MeOD, *t*-BuOD, O_2, CS_2, and MeSSMe at a variety of temperatures up to a maximum of ca. 375 °C. The reactivities of these ions do not change markedly with temperature, they still can be readily distinguished, and there is no indication of **3a** undergoing any isomerization. Consequently, a lower limit of 36 kcal mol^{-1} can be assigned to the ring-opening barrier of cyanocyclopropyl anion (eq 8).



(8)

***cis*- and *trans*-Dimethyl 1,2-Cyclopropyldicarboxylate Anion (4a).** The vapor pressure of dimethyl 1,2-cyclopropanedicarboxylate (**4**) at 0.4 Torr is insufficient to carry out experiments in a flowing afterglow device. This limitation can readily be overcome by entraining the sample with a stream of gaseous helium. In this way, a variety of bases, such as NH_2^-, OH^-, EtO^-, and *t*-BuO^- but not fluoride, acetone enolate, and trifluoroethoxide, were found to deprotonate **4**. In the reverse direction, **4a** is protonated by 2-methyl-2-propanethiol, ethanethiol, trifluoroethanol, acetone oxime, and acetone. It also undergoes one hydrogen–deuterium exchange, without any accompanying deuteron transfer, upon reaction with *t*-BuOD, EtOD, and MeOD. These results enable us to assign $\Delta H_{acid}(\mathbf{4}) = 372 \pm 3$ kcal mol^{-1}. The acyclic diester dimethyl itaconate ($CH_2{=}C(CO_2CH_3)$-$CH_2CO_2CH_3$, **4c**), is considerably more acidic and can be deprotonated by fluoride, trifluoroethoxide, pyrrolide, and methanethiolate. Weaker bases such as *tert*-butylmercaptide and acetate do not abstract a proton from **4c**, but their conjugate acids readily protonate the conjugate base of dimethyl itaconate (**4b**). These data, along with the observation that CF_3CD_2OD and EtSD both induce two H/D exchanges in **4b** (in the latter case the second exchange is extremely slow and is accompanied by deuteron transfer), enable us to assign $\Delta H_{acid}(\mathbf{4c}) = 355 \pm 3$ kcal mol^{-1}.

Both diester anions (**4a** and **4b**) are stabilized by resonance, and as a result neither of them is very reactive. A number of standard reagents (O_2, N_2O, CS_2, COS, SO_2, and MeSSMe) were explored, nevertheless, and the results are summarized in Table VIII. None of the reactions are useful for distinguishing between these two ions, but the isomers can be differentiated on the basis of their proton affinities and H/D exchange behavior. For example, pyrrole protonates **4a** but not **4b**, *t*-BuOD induces one exchange in **4a** but not in **4b**, and EtSD and CF_3CD_2OD react via hydrogen–deuterium exchange with **4b** but not **4a**. The reactivity of **4b** does not change as the temperature is increased, whereas **4a** appears to undergo a unimolecular ring-opening reaction starting at ca. 75 °C (eq 9). In other words, proton transfer to **4a** is no longer complete at 75 °C, and some H/D exchange occurs upon reaction with EtSD.[32] This leads to an estimated

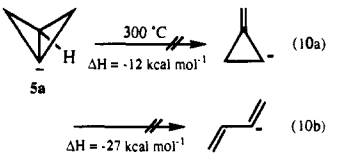


(9)

activation energy of 19 kcal mol^{-1}, assuming an Arrhenius *A* factor of 10^{13} s^{-1} for the isomerization process.

Discussion

We recently reported that bicyclobutyl anion (**5a**) is surprisingly robust and does not isomerize, even when heated to 300 °C (eq 10).[7] The conjugate bases of phenylcyclopropane, cyclo-

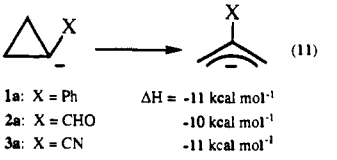


(10a)

(10b)

propanecarboxaldehyde, and *cis*- and *trans*-dimethyl 1,2-cyclopropanedicarboxylate (**1a**, **2a**, and **4a**, respectively), on the other hand, start to rearrange to their corresponding allylic isomers anywhere from 75 to 250 °C. These monocyclic derivatives clearly are more reactive than **5a** and reveal an interesting structure–reactivity relationship. Similar results have been found in the liquid phase; mono- and bicyclic cyclopropyl anions are structurally stable and isomerize only when there are two stabilizing substituents on the ring.[33] One might anticipate that under the appropriate reaction conditions it should be possible to induce the ring-opening of monosubstituted cyclopropyl anions in solution, and indeed one example involving a polymetalated ion has recently been reported.[21,34]

Two intriguing questions arise from our gas-phase data: (1) Why do the monocyclic cyclopropyl anions **1a**, **2a**, and **4a** rearrange more readily than bicyclobutyl anion? and (2) How can one explain the different structural stabilities of the various cyclopropyl anions? An obvious answer to both questions is that the isomerization rate reflects the driving force for rearrangement. In other words, the more exothermic the ring-opening, the faster it takes place. The reaction energetics, calculated from experimentally derived heats of formation, do not bear this out.[12,17,18] All three monosubstituted cyclopropyl anions (**1a**, **2a**, and **3a**) are



(11)

less stable than their allylic counterparts by the same amount (ca. 11 kcal mol^{-1}, eq 11), whereas the rearrangement of **5a** is exothermic by 12 or 27 kcal mol^{-1}, depending upon the pathway (eq 10). The thermodynamic driving force, consequently, cannot

(32) The cyclopropyl anion was generated by proton abstraction in almost a thermoneutral reaction by using *tert*-butoxide as the base. When hydroxide ion was used, the deprotonation was quite exothermic (~20 kcal mol^{-1}), and the reactant appeared to start isomerizing at lower temperatures.

(33) Only one of the substituents needs to end up at the terminal position of the allyl anion. For further details, see: (a) *The Chemistry of the Cyclopropyl Group*; Rapport, Z., Ed.; John Wiley and Sons: New York, 1987; Parts 1 and 2. (b) Boche, G. *Top. Curr. Chem.* **1988**, *146*, 1. (c) Boche, G.; Marsch, M. *Tetrahedron Lett.* **1983**, *24*, 3225. (d) Coates, R. M.; Last, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 7322. (e) Mulvaney, J. E.; Londrigan, M. E.; Savage, D. J. *J. Org. Chem.* **1981**, *46*, 4592. (f) 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. (g) 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. (h) Newcomb, M.; Ford, W. T. *J. Am. Chem. Soc.* **1974**, *96*, 2968.

(34) (1-Phenylcyclopropyl)potassium fails to ring-open even in refluxing hexane, but polymetalated phenylcyclopropane at the benzylic and aryl positions rearranges quite readily to the cross-conjugated allyl anion. The driving force for this isomerization has been attributed to the reduction of electron–electron repulsion. See: Ogle, C. A.; Riley, P. A.; Dorchak, J. J.; Hubbard, J. L. *J. Org. Chem.* **1988**, *53*, 4409.

Figure 7. Conrotatory ring-openings of a bent and a planar monosubstituted cyclopropyl anion.

account for differences in reactivities between **1a**, **2a**, **3a**, and **5a**. It is worth adding that the disubstituted cyclopropyl anion **4a** has a greater thermodynamic impetus for ring-opening than the monosubstituted derivatives (eq 12). This difference probably is responsible for the relative ease in which **4a** isomerizes.

(12)

4a: X = CO_2Me ΔH = -23 kcal mol^{-1}
5a: X = CHO -26 kcal mol^{-1}

Cyclopropyl anions are pyramidal and have significant inversion barriers in solution.[33,35] Molecular orbital calculations reproduce these observations and indicate that the lowest energy ring-opening pathway is a conrotatory process.[36] This latter result is consistent with orbital symmetry arguments (Woodward–Hoffmann rules) and a considerable body of experimental work.[33,37] In a conrotatory process, the orbital overlap between the breaking carbon–carbon σ-bond and the negative charge is greater in a planar ion than in a bent one (Figure 7). This suggests that the flexibility (i.e., inversion barrier) of a cyclopropyl anion and its tendency to form an allyl anion may be directly related. Moreover, this idea would account for the thermal stability of bicyclobutyl anion (**5a**), since its ring structure prevents it from readily inverting. In order to further explore the relationship between ring-opening barriers and inversion barriers, a variety of electronic structure calculations were carried out.

Geometries of eight cyclopropanes (C_3H_5X, X = H, F, OH, NH_2, CH_3, CN, CHO, and C_2H_3) and their conjugate bases were fully optimized (Figures 1 and 2). All of the resulting structures were characterized by their vibrational frequencies and were found to be true minima on the potential energy surface (i.e., no negative eigenvalues). The geometries of all of the neutral cyclopropanes are in accord with previous calculations and experimental observations.[38] The pyramidalization angle α does not vary greatly (54.2°–58.1°), and resonance-stabilizing substituents (CN, CHO, and C_2H_3) are conjugated to the three-membered ring. As a result, the C_1C_2 bonds are longer than the C_2C_3 bonds, whereas the opposite is true (i.e., $C_2C_3 > C_1C_2$) for the other derivatives. All of the anions are pyramidal, but the extent to which they are bent varies from 27.5° (CHO) to 72.7° (F). The pyramidalization angle is smallest for resonance-stabilizing substituents, which are oriented so that they are conjugated to the negative charge rather than the cyclopropane ring, and largest for those atoms or groups in which repulsive lone pair–lone pair interactions can take place (F, OH, NH_2). In fact, the more lone pairs on the substituent, the greater the pyramidalization angle (F > O > N).

Second-order Møller–Plesset perturbation theory (MP2/6-31+G(d)//6-31+G(d)) was used to calculate the acidity of each cyclopropane.[16] This fundamental thermodynamic quantity corresponds to the heterolytic bond dissociation energy of a compound HA, as defined in eq 13. It is calculated simply by

$$HA \rightarrow H^+ + A^- \qquad \Delta H_{rxn} = \Delta H_{acid}(HA) \qquad (13)$$

taking the difference between the computed electronic energies of HA and A^-. The resulting deprotonation energy must be corrected for changes in the zero-point energies (this typically lowers the acidity by ca. 8–10 kcal mol^{-1}) in order to obtain reliable absolute values.[39] Our results are summarized in Table III and are within the experimental uncertainty (±2–3 kcal mol^{-1}) in every case in which the experimental value is known. This kind of agreement between theory and experiment has become fairly routine for small molecules and encouraged us to calculate the inversion and ring-opening barriers for all of the cyclopropyl anions.

Relatively little theoretical work has gone into computing barriers for unimolecular rearrangements of carbanions. Most likely this is because of the dearth of experimental data available in the gas phase. As a result, the requirements (basis set, extent of electron correlation, etc.) for calculating accurate activation energies are less certain than those for computing deprotonation energies. The transition-state energy for the conrotatory ring-opening of cyclopropyl anion was, therefore, calculated using second-order Møller–Plesset theory and 6-31+G(d) and MP2/6-31+G(d) optimized geometries.[40] The results from these two calculations are identical (28.7 kcal mol^{-1}), so Hartree–Fock geometries (6-31+G(d)) were used instead of correlated structures (the differences between the two are relatively small). The computed inversion barriers seem to be intuitively reasonable, and the ring-opening transition-state energies are in good agreement with our experimental estimates (Table III).

Inversion barriers ranging from less than 1 to more than 45 kcal mol^{-1} were calculated for the different cyclopropyl anions. The derivatives with resonance-stabilizing substituents (CHO, C_2H_3, and CN) have the smallest barriers, and those with a lone pair of electrons adjacent to the negative charge (F, OH, and NH_2) have the largest activation energies. The latter result is due to electron–electron repulsion, which increases with the number of nonbonded electrons on the substituent (F > OH > NH_2). Resonance-stabilizing groups can invert readily, because conjugation increases as the cyclopropyl anion flattens out and becomes planar. As a result, the predicted configurational stability order CHO < C_2H_3 < CN can be accounted for by each substituent's resonance-stabilizing ability, as given by Taft's σ_R parameter (0.19, 0.15, and 0.10, respectively).[41] These trends are also reflected in the geometries of the cyclopropyl anions and the transition states. For example, the smaller the pyramidalization angle α in the former and the closer the C_1C_2 and C_2C_3 bond lengths are to the corresponding values in the transition state, the smaller the inversion barrier (Figure 8).[42]

The geometries of the ring-opening transition states (Figure 4) are not related to the activation barriers in any simple way. However, it is interesting to note that the cyclopropyl anions with resonance-stabilizing substituents have nearly symmetric transition states, whereas the others are asymmetric (i.e., rotation of one

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(39) Zero-point energies are obtained from the vibrational frequencies. A temperature correction, strictly speaking, is also needed to convert the calculated acidities from 0 to 298 K, but in practice this term is usually small and, therefore, neglected.

(40) The transition state of the ring-opening of cyclopropyl anion was made available to us by Drs. A. Kallel and K. Houk.

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(42) Additional trends could also be pointed out. For example, the larger the difference between the C_1C_2 and C_2C_3 bond lengths in the transition state, the bigger the inversion barrier.

Table IX. Parameters Used in the Multivariate Analysis of the Ring-Opening Barriers[a]

substituent (X)	inversion barrier	$-E_{HOMO}$	EA(CH_2X)[b]	PA(c-$C_3H_4X^-$)	σ_F[c]	σ_R[c]	$\sigma_{R'}$[d]
H	16.3	27.7	1.8	412.8	0.00	0.00	0.00
NH_2	30.1	22.1	-12.4[e]	408.4	0.14	-0.52	0.00
OH	40.3	37.3	-0.5	401.8	0.30	-0.38	-0.22
F	47.5	48.7	4.7[e]	395.0	0.44	-0.25	-0.22
CN	8.6	58.7	35.6	375.0	0.60	0.10	0.10
CHO	0.9	50.7	41.9	374.5	0.31	0.19	0.19
C_2H_3	4.8	26.1	8.3	392.2	0.06	0.15	0.15
CH_3	24.7	27.2	-6.0	408.4	0.00	-0.08	-0.08

[a] All parameters are in kcal mol^{-1} and come from HF/6-31+G(d) optimized structures and MP2/6-31+G(d)//6-31+G(d) energies unless indicated otherwise. [b] Reference 17. [c] Linear free energy parameters come from ref 41. [d] Reference 44. [e] The electron affinity was obtained by using the following relationship: EA(X) = BDE(HX) + IP(H) - ΔH_{acid}(HX), where $\Delta H_{acid}(CH_3F)$ = 409 ± 4 (ref 45), $\Delta H_{acid}(Me_3N)$ = 410 (estimated), BDE(H-CH_2F) = 100 ± 2 (ref 46), and BDE (Me_2NCH_2-H) = 84.0 ± 2.0 (ref 46).

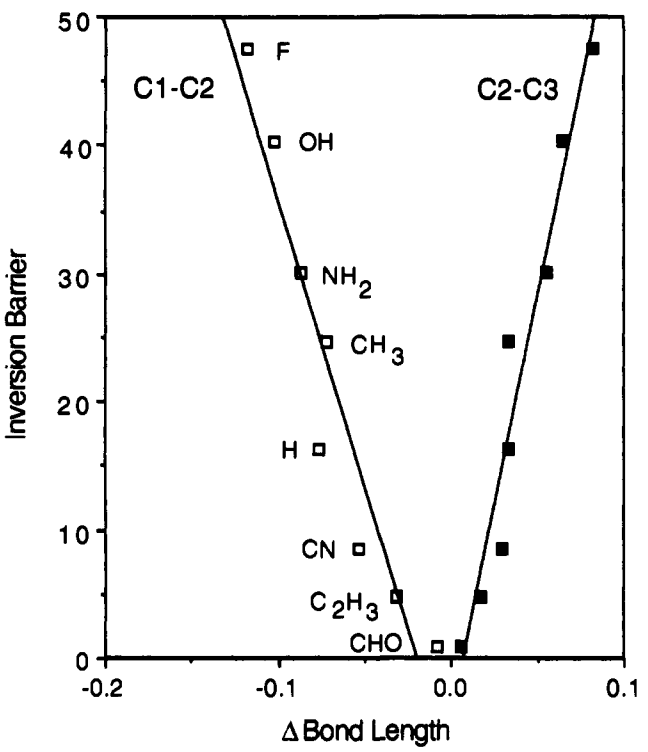

Figure 8. Inversion barriers (MP2/6-31+G(d)//6-31+G(d)) versus the change in bond lengths (6-31+G(d)) among a series of monosubstituted cyclopropyl anions and their transition states (y = -445.3(Δ length) - 8.85, r = 0.953; y = 652.9(Δ length) - 4.30, r = 0.970). Distances are in angstroms, and energies are in kcal mol^{-1}.

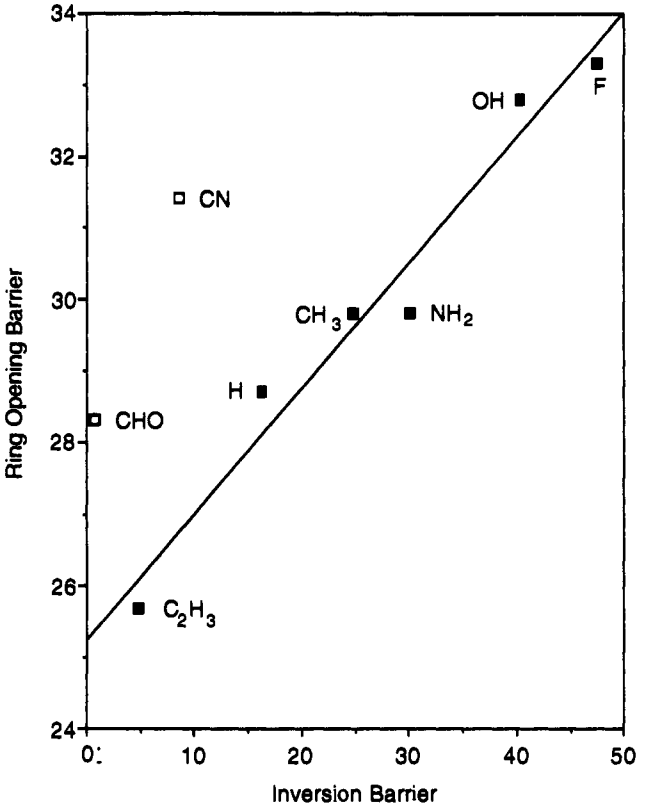

Figure 9. Calculated ring-opening barriers versus inversion barriers in kcal mol^{-1} (MP2/6-31+G(d)//6-31+G(d)). The solid line is a least-squares fit of the data, omitting the two deviant points (y = 0.176(inversion barrier) + 25.2, r = 0.982).

methylene group is much farther ahead of the other). A plot of the ring-opening activation energies versus the inversion barriers is reasonably linear if one ignores the formyl and cyanocyclopropyl anions (Figure 9).[43] This strongly suggests that the flexibility of these ions is an important parameter affecting the ring-opening barrier and probably accounts for the remarkable stability of bicyclobutyl anion. The failure of this correlation to account for the formyl and cyano derivatives indicates that the inversion barrier is not the only important factor controlling the isomerization process. Therefore, we examined a number of two-parameter fits to the data. The results should be treated with extra caution since only eight points were used in the analysis. Nevertheless, the ring-opening barrier is reasonably correlated to the inversion barrier and the anion's electron-binding energy (the electron affinity of the corresponding radical as it is reflected by the anion's highest occupied molecular orbital energy) (Figure 10). Reasonable fits to the data were also found by using the inversion barrier and the electron affinity of the corresponding methyl radical (y = 0.180(inversion barrier) + 0.0870(EA(CH_2X)) + 25.3, r = 0.934), the inversion barrier and the proton affinity of the cyclopropyl anions (y = 0.154(inversion barrier) - 0.0859(PA) + 60.6, r = 0.893), and Taft's σ_F and $\sigma_{R'}$ parameters ($y = 6.47\sigma_F - 12.0\sigma_{R'} + 28.4$, r = 0.969, Table IX).[41,44] It thus appears that the cyclopropyl-to-allyl anion conversion is influenced by the former ion's configurational stability and some measure of its thermodynamic stability. Whether one uses σ_F or the ion's stability relative to its radical (electron affinity) or its conjugate acid

(43) Other single-parameter fits were examined, but none of them was found to be as good.

(44) We have empirically corrected σ_R for those groups (NH_2, OH, and F) which have at least one lone pair of electrons at the attachment site. Substituents on nitrogen, oxygen, and fluorine were placed as far apart as possible (120°), and the electron pairs were oriented so as to minimize the overlap with an adjacent p orbital (i.e., the sum of the cosines of the angles between the lone pairs and the p orbital was minimized). This interaction was also maximized, and Taft's σ_R parameter was reduced by the resulting fraction to afford $\sigma_{R'}$. This scheme is a simple way to account for the fact that substituents such as NH_2, OH, and F can orient themselves so as to minimize the interaction with an adjacent negative charge and thus diminish the destabilizing resonance effect. For an example of such an interaction, see: Dahlke, G. D.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 5566. It is worth adding that the inversion barrier correlates quite well with $\sigma_{R'}$ ($y = -104.2\sigma_{R'} + 20.6$, r = 0.961).

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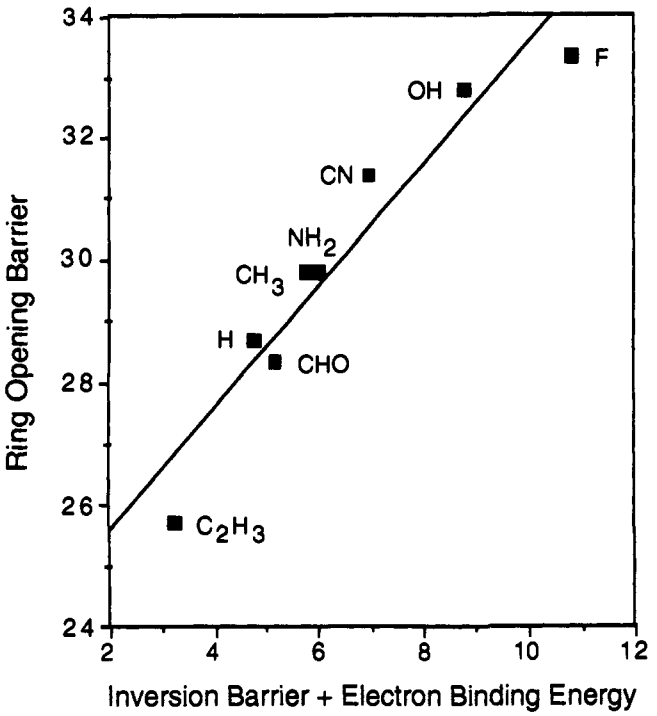


Figure 10. Calculated ring-opening barriers versus inversion barriers and electron binding energies, as reflected by the HOMO energies of the anions. The solid line is a least-squares fit of the data (y = 0.124(inversion barrier) - 0.101(HOMO energy) + 23.5, r = 0.955), where all of the values are at the MP2/6-31+G(d)//6-31+G(d) level and are in kcal mol^{-1}.

(proton affinity) makes relatively little difference. These results do account for the differences between the cyclopropyl anions and clearly indicate that there is a delicate balance of factors affecting the rearrangement rates. The plot shown in Figure 10 also indicates that those ions with low electron-binding energies (high HOMOs) and small inversion barriers will isomerize most readily. These two requirements are at odds with each other in that ions with small inversion barriers usually have large electron-binding energies and those with small binding energies typically have large epimerization barriers. These conflicting tendencies are well balanced in vinylcyclopropyl anion and, presumably, phenylcyclopropyl anion. In accord with expectations, the latter ion rearranges to 2-phenylallyl anion at 200 °C while the former isomerizes upon its formation.[47] The product, however, is not the expected 2-vinylallyl anion but rather the conjugate base of methylenecyclobutane. This ion arises from a competitive pathway which also is allowed by orbital symmetry.

We have shown that a variable temperature flowing afterglow device is a powerful instrument for studying unimolecular rearrangements. The structure of the substrate is an important factor influencing the activation energy and so is the presence of substituents. Cyclopropyl anions with small inversion barriers and small electron-binding energies rearrange most readily. Consequently, the bicyclobutyl anion, which is fairly rigid, is remarkably robust thermally. The conjugate bases of dimethyl 1,2-cyclopropanedicarboxylate, phenylcyclopropane, and cyclopropanecarboxaldehyde (**4a**, **1a**, and **2a**, respectively), on the other hand, rearrange anywhere from 75 to 250 °C. A wide variety of unimolecular rearrangements can be explored both qualitatively and quantitatively, and the results from such work will be reported in due course.

Acknowledgment. Support from the Minnesota Supercomputer Institute, the National Science Foundation (CHE-8907198), and the donors of the Petroleum Research Fund, as administered by the American Chemical Society, is all gratefully acknowledged.

(47) Vinylcyclopropane reacts with OH^- to give a rearranged product ion, whereas NH_2^- reacts to afford vinylcyclopropyl anion. For further details, see ref 19.

The Photoelectron Spectrum of Thioformyl Cyanide

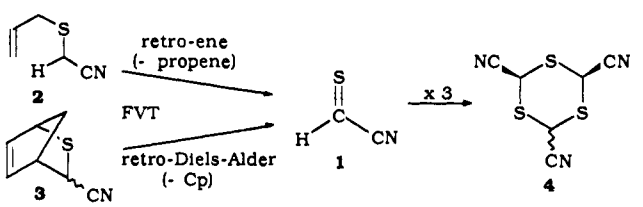
Geneviève Pfister-Guillouzo,*,† Françoise Gracian,† Anna Senio,† François Bourdon,‡ Yannick Vallée,‡ and Jean-Louis Ripoll‡

Contribution from the Laboratoire de Physicochimie Moléculaire (associé au CNRS), Université de Pau, 64000 Pau, France, and the Laboratoire des Composés Thioorganiques (associé au CNRS), ISMRA, 14050 Caen, France. *Received June 16, 1992*

Abstract: Thioformyl cyanide, HCSCN, was generated, under flash vacuum thermolysis conditions, by retro-ene and retro-Diels–Alder cleavages of allylcyanomethyl sulfide and 3-cyano-2-thiabicyclo[2.2.1]hept-5-ene, respectively, and unambiguously characterized in the gas phase by photoelectron spectroscopy. Its unimolecular decomposition into carbon monosulfide and hydrogen cyanide was found to be strongly disfavored.

The formation of the reactive thioaldehyde thioformyl cyanide (**1**) has been demonstrated, in several reactions performed in the presence of 1,3-dienes, by the observation of the corresponding Diels–Alder adducts.[1] A kinetic investigation of the thermal retro-ene decomposition of allylcyanomethyl sulfide (**2**), leading to propene and 2,4,6-tricyano-*s*-trithiane, also involved the transient formation of **1**.[2] More recently, the flash vacuum thermolysis (FVT) of the same precursor **2** as well as the dehydrochlorination of cyanomethanesulfenyl chloride under vacuum gas solid reaction

Scheme I



conditions allowed the first direct observation of compound **1** by millimeter wave spectroscopy.[3] The moments of inertia of **1**,

†Université de Pau.
‡ISMRA.

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