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Rearrangements of 3-Aryl-Substituted Cyclopropenyl Anions and the Gas-Phase Acidity of 3-(4-Methylphenyl)cyclopropene

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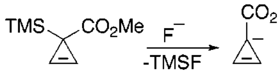
3-(4-Methylphenyl)-3-trimethylsilylcyclopropene and 3-(4-trifluoromethylphenyl)-3-trimethylsilylcyclopropene react with fluoride ion in the gas phase to afford 6-substituted 3-indenyl anions via a spontaneous rearrangement of their corresponding cyclopropenyl anions. These isomerizations led us to reinvestigate the reported gas-phase generation of 1,2,3-triphenylcyclopropenyl anion, and contrary to the previous study, a similar rearrangement to 1,2-diphenyl-1-indenyl anion is observed. Despite the instability of 3-aryl-3-cyclopropenyl anions, we were able to measure the acidity of 3-(4-methylphenyl)cyclopropene at the allylic position ($\Delta H^\circ_{\text{acid}} = 398.6 \pm 1.4$ kcal/mol) by the DePuy kinetic method. Ab initio calculations on the structures and energies of mono- and triaryl-substituted cyclopropenyl anions also are presented.

Introduction

Antiaromatic molecules can be described as fully conjugated 4n ($n = 1, 2, 3..$) π electron monocyclic compounds which are destabilized relative to their acyclic counterparts. They also are characterized by paramagnetic ring currents in their ^{1}H NMR spectra and the potential for unusually small singlet−triplet gaps.[1,2] Cyclopropenyl anion is the smallest such system, and consequently, numerous studies have been carried out over the years on this ion and its derivatives. Breslow and co-workers showed that the allylic position of cyclopropenes is very weakly acidic with some pK_A's in excess of 50 while Borden and co-workers successfully trapped 1,2,3-triphenylcyclopropenyl anion as a transient intermediate.[3−9] In 1994, Sachs and Kass prepared the first stable cyclopropenyl anion, **1**, by reacting fluoride ion with 3-methoxycarbonyl-3-trimethylsilylcyclopropene in the gas phase (eq 1).[10] The proton affinity of this anion was compared to its saturated derivative (eq 2), and the observed difference of 14 ± 6 kcal/mol is consistent with the notion of antiaromatic destabilization. 3-Cyano-3-cyclopropenyl anion also has been generated and shown to be 15 ± 6 kcal/mol less stable than 1-cyanocyclopropyl anion.[11] More recently, we extended these experiments to the condensed phase and observed the first long-lived cyclopropenyl anion, 3-methoxycarbonyl-1,2-diphenylcyclopropenyl anion, by UV spectroscopy.[12]



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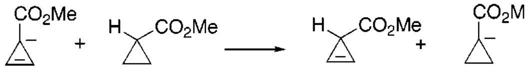

$\Delta H^\circ = -14$ kcal/mol (2)

In addition to generating highly stabilized cyclopropenyl anions in the gas phase, we sought to explore derivatives which are more basic and would better reflect the thermochemistry of the parent. High-level ab initio calculations indicate that cyclopropenyl and 3-methyl-3-cyclopropenyl anions are unstable with regard to electron loss (i.e., the anions are unbound).[13,14] Other simple alkyl derivatives also are apt to be unstable, so we decided to examine aryl-substituted cyclopropenes. Herein, we report the results of this study along with computed structures and energies of the anions. On the basis of our findings, we also reinvestigated the reported gas-phase generation of 1,2,3-triphenylcyclopropenyl anion.[15]

Experimental Section

3-Aryl-3-trimethylsilylcyclopropenes and their corresponding indene isomers were synthesized according to previously reported procedures.[16] These compounds were purified by preparative gas chromatography on a 12 ft × 0.25 in. 10% SE 30 on Chrom W column at 150 °C except for 3-(4-methylphen-

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yl)-3-trimethylsilylcyclopropene. This derivative was initially purified by column chromatography; however, it was necessary to further separate it from traces of coeluting trimethylsilyl impurities which would have affected the ratio in the kinetic acidity measurement. To this end, 3-(4-methylphenyl)-3-trimethylsilylcyclopropene was treated with 1 equiv of tetra-*n*-butylammonium fluoride in THF at room temperature for 1 h and then subsequently purified by medium-pressure liquid chromatography using hexanes as the eluting solvent. 3-Trimethylsilyl-1,2,3-triphenylcyclopropene[9] and 2,3-diphenylindene[17] were prepared as in the literature. Reference silanes for the kinetic acidity measurement were prepared by standard methods and purified by preparative gas chromatography using a 10% SE 30 on Chrom W column. In the case of trimethylsilylcyclopropane, a XF-1150 column was employed.

The gas-phase experiments were carried out in a dual cell model 2001 Finnigan Fourier transform mass spectrometer (FTMS) equipped with a 3.0 T superconducting magnet and controlled by a Sun workstation running the Odyssey version 4.2 software package. Ions were generated by fluoride-induced desilylation of the requisite neutral. Fluoride ion was prepared upon electron ionization (6 eV) of carbon tetrafluoride. The ions of interest were then transferred to the second cell and isolated by applying a SWIFT waveform or chirp broad band excitation.[18,19] Argon was pulsed into the cell at pressures of 10^{-5} Torr in an attempt to thermalize the ions. All neutral reagents were introduced via slow leak valves, and the subsequent reactions were monitored over time. For the kinetic acidity measurements, hydroxide was prepared in the FTMS upon electron ionization of H_2O or $H_2{}^{18}O$ at 6 eV and transferred to the other cell where the requisite silane was present at a constant pressure. After a cooling pulse of argon and an initial reaction period (~500 ms), all product ions were ejected in order to reduce the effects of nonthermalized hydroxide. The ratio of product ions ($Me_3SiO^-/R(Me)_2SiO^-$) was recorded as a function of time (1 to 5 s) and found to be constant. Ion intensities were isotopically corrected and an error analysis which accounted for the uncertainties in the calibration data was carried out.[20,21]

All computations were carried out using Gaussian 94[22] or GAMESS[23] on UNIX-based workstations or Cray supercomputers. Structures were optimized at the Hartree–Fock level of theory using the 6-31G(d) or 6-31+G(d) basis set. In some cases, geometries also were explored with Møller–Plesset second-order perturbation (MP2) theory. Vibrational analyses were carried out to ensure structures correspond to true energy minima. Single point energy determinations were made at the MP2 level of theory, which accounts for electron correlation, and also were investigated with density functional theory using the B3LYP hybrid functional. These two approaches render acidities which agree within 1–2 kcal/mol of each other for most of the compounds in this work. Larger differences (3–5 kcal/mol) are observed for the trifluoromethyl substituted species. Zero-point energies were scaled by 0.9135 (HF) and 0.9646 (MP2), and all energies were adjusted from 0 to 298 K by scaling the harmonic frequencies by 0.8929 (HF) and 0.9427 (MP2).[24] All acidities are reported at 298 K.

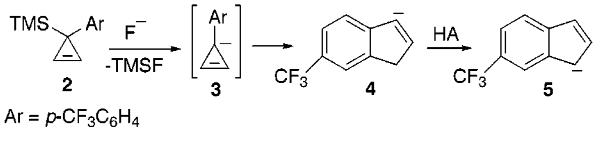
Table 1. Summary of the Reactivity of the [2-TMS]$^-$, [2-TMS]$^-$-d_1 Ions and Independently Prepared 4 with Reference Acids

acid	$\Delta H°_{acid}$ (kcal/mol)[a]	[**2**-TMS]$^-$	[**2**-TMS]$^-$-d_1	**4**
		H/D Exchange[b]		
D_2O	392.9 ± 0.1	2[c]	-	2[c]
CH_3OD	383.5 ± 0.7	1	-	1
$(CH_3)_3COD$	374.6 ± 2.1	1	-	-
CF_3CH_2OD	361.8 ± 2.5	1	0	1
CD_3CO_2D	348.6 ± 2.9	2	−1[d]	2
$(CH_3)_3CO_2D$	344.7 ± 2.1	2	−1[d]	2
		Proton Transfer		
$C_2H_5OCH_2CO_2H$	342.0 ± 2.0	no	no	no
HCl	333.4 ± 0.1	yes	yes	yes

[a] Values taken from ref 33. [b] Deuteron transfer is not observed for any of the deuterated reagents listed. [c] The two sites are nonequivalent, d_1:d_2 = 4:1. [d] A value of −1 indicates the initial deuterium can be exchanged for a hydrogen if protio reagent is used.

Results and Discussion

We were interested in generating a minimally stabilized cyclopropenyl anion in order to explore its thermochemistry and reactivity. An aryl group seemed to be a reasonable substituent since ab initio calculations predict that methyl (G2+) and vinyl (MP2/6-31+G(d) via isogyric reactions with cyclopropyl and allyl radicals) derivatives are unstable with regard to electron loss, and efforts to generate 3-methyl-3-cyclopropenyl anion were unsuccessful.[14,25] The same approach that was used to generate 3-methoxycarbonyl-3-cyclopropenyl anion (**1**) was attempted, and 3-(4-trifluoromethylphenyl)-3-trimethylsilylcyclopropene (**2**) was reacted with fluoride ion in a Fourier transform mass spectrometer (eq 3). A few initial experiments, however, revealed that the ion which corresponds to loss of the trimethylsilyl group, [**2**-TMS]$^-$, is not cyclopropenyl anion **3** as its proton affinity is too low. Specifically, the ion does not react to give the conjugate base of a reference acid until it is reacted with hydrochloric acid. This result along with those given in Table 1 lead to a bracketed proton affinity of 338 ± 5 kcal/mol. This can be contrasted with **1** which is sufficiently basic to deprotonate water ($\Delta H°_{acid}$ (**1H**) = 391 ± 4 kcal/mol). In addition, calculations predict the proton affinity of **3** and its vinyl anion isomer to be 386.8 and 359.8 kcal/mol (MP2/6-31+G(d)//HF/6-31+G(d)), respectively, or 382.1 and 361.3 kcal/mol (B3LYP/6-31+G(d)//HF/6-31+G(d)), respectively (Table 3); these levels of theory will be denoted as MP2//HF and B3LYP//HF, respectively.



(3)

The observed reactivity of the [**2**-TMS]$^-$ ion is consistent with that expected for vinyl anion **4**. In particular, reaction with deuterated acids ranging from methanol-

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Table 2. Data for the Kinetic Acidity Measurement Using 3-(4-Methylphenyl)-3-trimethylsilylcyclopropene (12) and 6-Methyl-3-trimethylsilylindene (13)[a]

R-TMS	$Me_3SiO^-/R(Me)_2SiO^-$ [b]	ln(3*ratio)	$\Delta H°_{acid}$ (RH) kcal/mol
ethyl	0.122 ± 0.01	−1.01 ± 0.13	420.1 ± 2.0
methyl	1.00	0.000	416.7 ± 0.7
cyclopropyl	0.876 ± 0.034	0.966 ± 0.05	411.5 ± 2.0
vinyl	2.32 ± 0.02	1.94 ± 0.01	409.4 ± 0.6
phenyl	8.84 ± 0.27	3.28 ± 0.03	401.7 ± 0.5
12	20.6 ± 1.4	4.12 ± 0.08	398.6 ± 1.4
13	91.8 ± 22.1	5.62 ± 0.23	392.2 ± 2.9

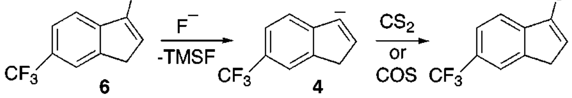
[a] Acidity values for calibrant species are taken from ref 33. [b] Ratios are isotopically corrected.

Table 3. Summary of Experimental and Computed Acidities[a]

cmpd	expt	MP2//HF[b]	B3LYP//HF[c]
3H (C3)		386.8	382.1
(C1)		359.8	361.3
4H (C3)	338 ± 5	383.3	386.1
(C1)		335.2	339.9
15H (C3)	398.6 ± 1.4[d]	398.0 (398.1)[e]	399.0
(C1)		368.6	370.5
16H (C1)	390 ± 3[f]	386.9 (387.0)[e]	386.3
indene (C3)	392.2 ± 2.9[g]	392.0	-
8H (C3)		-	389.5[h]

[a] All values in kcal/mol. [b] MP2/6-31+G(d)//HF/6-31+G(d), 298 K. [c] B3LYP/6-31+G(d)//HF/6-31+G(d), 298 K. [d] Experimental value for 3-(4-methylphenyl)cyclopropene (**14H**). [e] MP2/6-31+G(d)//MP2/6-31+G(d) values given in parentheses. [f] Reference 38. [g] Value for the 3 position of 6-methylindene. [h] Calculated by eq 10, see text.

d_1 to 2,2,2-trifluoroethanol-d_1 induces a single hydrogen−deuterium exchange and an isomerization to the more stable indenyl ion **5** (eq 3, Table 1). The latter species is capable of undergoing a second H/D exchange with stronger acids such as acetic acid-d_4 and trimethylacetic acid-d_1. The significantly faster rate for the first exchange with these acids supports the idea of two nonequivalent sites. Evidence for a rearranged ion also was obtained by observing that the deuterium atoms incorporated in the [**2**-TMS]$^-$ ion upon reaction with D_2O could not be washed out with H_2O. To verify our proposed structure for the [**2**-TMS]$^-$ ion, **4** was independently prepared by fluoride-induced desilylation of 3-trimethylsilyl-6-trifluoromethylindene (**6**, eq 4a). The reactivity of this ion was found to be identical to that observed for the [**2**-TMS]$^-$ ion (Table 1). The bracketed proton affinity of **5** (338 ± 5 kcal/mol) also is in agreement with theory, 335.2 kcal/mol (MP2//HF) and 339.9 kcal/mol (B3LYP//HF). Carbon disulfide and carbonyl sulfide also are effective probe reagents for distinguishing **4** from **5**. In the former case, the ion abstracts a sulfur atom from both reagents while no products are detected in the latter case (eq 4). The ion generated from **2** and its d_1 species display similar reactivity differences with these reagents.



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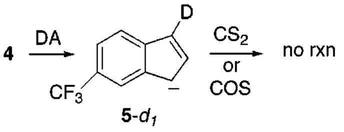
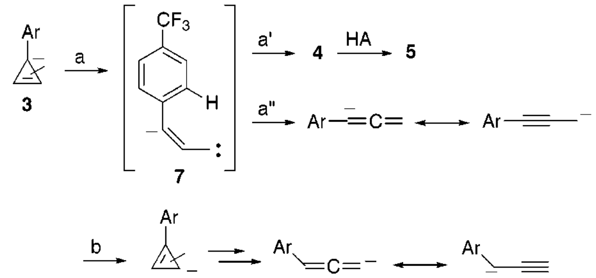


(4b)

Scheme 1. Possible Rearrangements of 3-(4-Trifluoromethylphenyl)cyclopropenyl Anion (3)



The following mechanism is proposed for the formation of **4** from **3** (Scheme 1). The initially generated antiaromatic species ring opens to give vinylcarbene intermediate **7** which then readily reacts by C−H bond insertion to afford vinyl ion **4** (pathway a′). Upon reaction with an acid, this species isomerizes to indenyl anion **5**. The transformation of neutral aryl cyclopropenes to indene derivatives is a known thermal and photochemical process in solution.[16,26] Alternatively, one could envision **7** generating aryl-substituted deprotonated allenes or alkynes (pathway a″). Initial pseudorotation of **3** prior to ring opening also could give rise to a similar product via pathway b. Given our results, these latter two reaction pathways (a″ and b) do not appear to be occurring to a significant extent, if at all, as these product ions are expected to be more basic and/or incorporate two deuteriums when only one is observed with the [**2**-TMS]$^-$ ion.[27] Moreover, in the reaction with carbon disulfide, the known reaction pathways for allenyl and propargylic derivatives are not detected.[28−30]

Given the propensity for rearrangement of 3-aryl-substituted cyclopropenyl anions, we decided to reinvestigate the chemistry of the triphenyl derivative **8**. Bartmess and co-workers reported generation of this ion upon thermal electron impact of **9** in an ICR; no reaction was observed with water, and proton transfer was noted with methanol and stronger acids which suggested a proton affinity for **8** of 385 ± 5 kcal/mol.[15] In our study, **9** was introduced into the FTMS via a heated (45 °C) solid probe inlet and reacted with fluoride ion.[31] The chemistry of the resulting thermalized desilylated ion was explored, and in contrast to the previously reported work, proton transfer was not observed upon reaction with methanol-d_1, 2,2,2-trifluoroethanol-d_1, or acetic acid-d_4, but was with hydrochloric acid. Acetic acid-d_4 induces a single hydrogen−deuterium exchange. Identical behavior is observed if the [**9**-TMS]$^-$ ion is generated by electron

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[27] The proton affinities of the alkynyl and allenyl derivatives are not known, but they are estimated to be larger (more basic) than that for **5** based on the following acidities: $\Delta H°_{acid}$ = 380 (allene), 371 (phenylacetylene), and 368 kcal/mol (3-phenylpropene).

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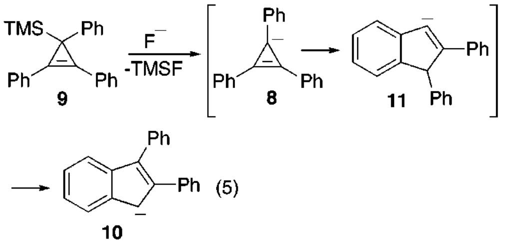
[30] An additional ion that was considered, but which can be ruled out, is the vinyl anion derived from **3**. Acid-induced isomerization of cyclopropenyl anions is known, but this species is inconsistent with the observed H/D exchange behavior (one should not be able to wash out the label); it is predicted to be much more basic (359.8 kcal/mol at the MP2//HF level), and the reactivity of this type of ion (see ref 40) is different from the species we observed.

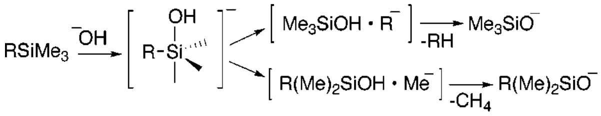
[31] In the experiments with **9** an M-1 ion at *m/z* 339 also is generated. This ion arises from electron ionization not from reaction with F$^-$. The **9**-TMS ion displays the same reactivity when it is not isolated and the entire experiment is done in 1 cell.

ionization and stray electrons are kept out of the cell.[32] Our results lead to a bracketed proton affinity of 341 ± 8 kcal/mol for the [**9**-TMS]$^-$ ion. This value is too low for a cyclopropenyl anion and strongly suggests the initially formed anion rearranges to 1,2-diphenyl-1-indenyl ion (**10**) (eq 5). To support this hypothesis, **10** was independently prepared by deprotonation of its conjugate acid, and its reactivity with the reference acids mentioned above was found to be identical to that of the [**9**-TMS]$^-$ ion. In addition, the thermochemistry is in accord with the reported gas-phase acidities of 1,3-diphenylindene (335.2 ± 2.1 kcal/mol) and 1,2,3-triphenylindene (335.5 ± 2.1 kcal/mol).[33]



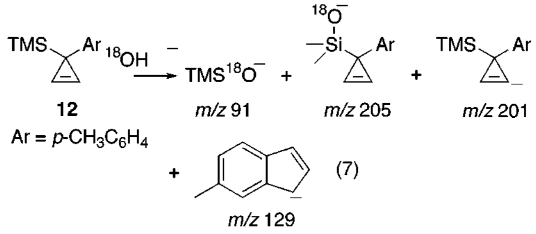
Results for the [**9**-TMS]$^-$ ion indicate that the initially observed species is not vinyl ion **11**. Specifically, the indicative behavior of one hydrogen−deuterium exchange with weaker acids and sulfur-atom abstraction with carbon disulfide is not observed. In the absence of an acid-induced isomerization, as we have proposed for 3-aryl-3-cyclopropenyl anions, two sequential phenyl migrations are postulated to account for the formation of **10** from **11**. Such rearrangements are precedented under photolytic conditions for 1,2,3-triphenylcyclopropene[26] and for 2-phenylethyl anion in the gas phase.[34] Isomerization of **9** while it was heated (45 °C) during the course of the experiments did not occur since **9** is stable in refluxing THF (65 °C) and higher temperatures were required to induce its isomerization (i.e., **9** rearranges at 190−200 °C to an undetermined isomer with a half-life of ~90 h.)

Although 3-aryl-3-cyclopropenyl anions appear to be unstable with respect to rearrangement in the gas phase, their experimental proton affinities (or, equivalently, $\Delta H^\circ_{\text{acid}}$ of their conjugate acids) might be obtained using kinetic methods. DePuy and co-workers have measured such thermochemical data for various alkanes whose conjugate bases are unbound.[35] This approach does not require the anion to be generated as a free species, but rather determines an unknown's acidity relative to that of methane based on the fragmentation of a pentacoordinate siliconate anion (eq 6). Specifically, the intermediate formed upon reaction of a substituted trialkylsilane such as $RSiMe_3$ with hydroxide can dissociate by expulsion of either CH_3^- or R^-. The incipient ion then deprotonates the hydroxysilane to generate $R(Me)_2SiO^-$ or Me_3SiO^-, respectively. While this is the commonly given explanation for this reaction, it is important to recognize that the species in brackets need not be intermediates, but can represent transition state structures. In fact, ab initio calculations indicate that explusion of an alkyl anion is facilitated by the simultaneous deprotonation of the alcohol.[36] In any case, the natural logarithm of the statistically corrected ratio of these products correlates linearly with gas-phase acidities. In this work, various substituted trimethylsilanes were used to construct a calibration curve which yielded the following equation: $\Delta H^\circ_{\text{acid}}(RH) = -4.29 \times \ln(Me_3SiO^-/R(Me)_2SiO^-) + 416.3$, $r^2 = 0.984$. A complete listing of the data is given in Table 2.



(6)

The calculated gas-phase acidity of 3-(4-trifluoromethylphenyl)cyclopropene suggests this compound would not be suitable for the described kinetic measurement as the $\Delta\Delta H^\circ_{\text{acid}}$ relative to methane is larger than that of the calibrant species and is too big to give an accurate $Me_3SiO^-/R(Me)_2SiO^-$ ratio. Therefore, 3-(4-methylphenyl)-3-trimethylsilylcyclopropene (**12**) was used. It should be mentioned that the [M − TMS]$^-$ ion generated upon fluorodesilylation of **12** was briefly explored and found to rearrange, presumably, to the indenyl derivative; the [M − TMS]$^-$ ion undergoes 2 H/D exchanges with D_2O, 1 with MeOD, and 2 with CF_3CH_2OD, and proton transfer is observed with CD_3CO_2D, which is consistent with the acidity of indene ($\Delta H^\circ_{\text{acid}} = 352.0 \pm 2.1$ kcal/mol). The reaction of hydroxide with **12** affords two product ions at *m/z* 201 and *m/z* 129 in addition to the desired $R(Me)_2SiO^-$ and Me_3SiO^- ions (eq 7). The ion at *m/z* 201 corresponds to deprotonation of **12** at the vinyl position ($\Delta H^\circ_{\text{acid}} = 369$ kcal/mol (MP2//HF) for the equivalent site in 3-phenylcyclopropene). The presence of this ion complicates measurement of the $R(Me)_2SiO^-$ intensity due to its significant ^{13}C, ^{29}Si, and ^{30}Si isotope peaks at the same nominal mass. The use of oxygen-18 labeled hydroxide eliminates this interference by shifting the $R(Me)_2SiO^-$ signal from *m/z* 203 to *m/z* 205. Overall, a ratio of 46:1 was observed for the *m/z* 201 and *m/z* 205 ions, and thus it would have been difficult to reliably measure the desired ratio without removing the isotopic overlap (Figure 1).



The other product, *m/z* 129, corresponds to loss of a trimethysilyl group from **12**, and its origin must be accounted for. The structure of this ion was determined to be the conjugate base of 6-methylindene based on observed proton transfer with acetic acid but not weaker acids and the absence of hydrogen−deuterium exchange

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(32) The yield of the [**9**-TMS]$^-$ ion by electron ionization (1.3 eV, 25 s) is low.

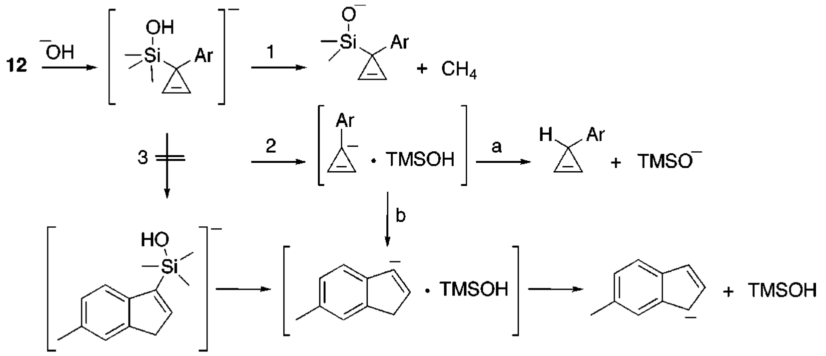
(33) All acidities unless otherwise noted come from the following reference: Bartmess, J. E. NIST Chemistry WebBook, NIST Standard Reference Database Number 69. In *Secondary NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD 20899 (http://webbook.nist.gov).

(34) Maas, W. P. M.; van Veelen, P. A.; Nibbering, N. M. M. *Org. Mass. Spectrom.* **1989**, *24*, 546−558.

(35) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968−1973.

(36) Davis, L. P.; Burggraf, L. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 3056−3062.

Scheme 2. Possible Reaction Pathways in the Kinetic Acidity Measurement with 12



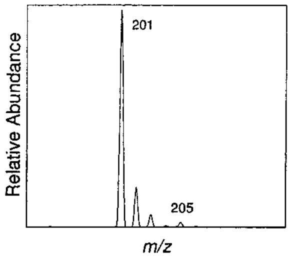


Figure 1. Abundance of the *m*/*z* 201 and *m*/*z* 205 ions generated in the reaction of **12** with oxygen-18 labeled hydroxide.

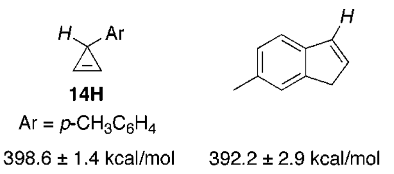
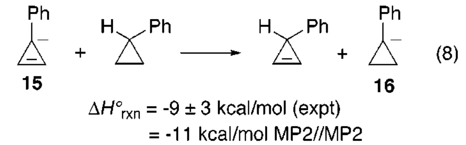


Figure 2. Experimental gas-phase acidites obtained by the Depuy kinetic method.

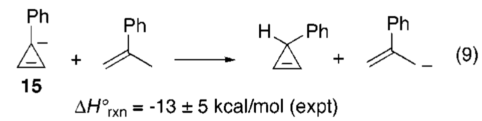
with D_2O; deuterium incorporation is expected if the $C_{10}H_9^-$ ion corresponds to a cyclopropenyl anion or a 3-indenyl anion derivative. Two possible pathways (2 and 3) for the formation of the *m*/*z* 129 ion are shown in Scheme 2. The distinct ratios for the loss of CH_4 and $C_{10}H_{10}$ observed for the siliconates of **12** and 6-methyl-3-trimethylsilylindene (**13**) (Table 2, Figure 2), the good agreement with computed acidities (Table 3), and the fact that pathway 3 does not take place with other 3-trimethylsilyl-substituted cyclopropenes giving rise to stabilized cyclopropenyl anions[10,11] argues against this reaction channel. Therefore, we attribute the formation of the $C_{10}H_9^-$ ion (*m*/*z* 129) to pathway 2b, and consequently its intensity was added to that of trimethylsiloxide for the acidity measurement. Overall, the correction is minor and results in a smaller (more acidic) $\Delta H°_{\text{acid}}$ for 3-(4-methylphenyl)cyclopropene (**14H**) by 2 kcal/mol.[37]

Based on our measurements with **12**, a value of 398.6 ± 1.4 kcal/mol can be assigned for the gas-phase acidity of **14H**. This is in favorable agreement with ab initio and density functional calculations for 3-phenylcyclopropene (**15H**) which predict a deprotonation energy of 398.0 (MP2//HF), 398.1 (MP2//MP2), and 399.0 (B3LYP//HF) kcal/mol. The *p*-methyl group in **14H** should have a negligible impact on the thermochemistry; thus, **14H** and **15H** will be considered equivalent for further discussion. 3-(4-Methylphenyl)cyclopropene represents the simplest cyclopropene whose acidity has been measured experimentally in the gas phase. Cyclopropene, itself, is computed to be 20 kcal/mol less acidic, 418.9 kcal/mol at the CCSD(T)/6-311+G(2df,2pd)//MCSCF(10(9),9)/6-31+G(d,p) level.[13] Comparison of the proton affinity of **15** with that of its saturated analogue **16** (390 ± 3 kcal/mol)[38] indicates that the cyclopropenyl system is destabilized by 9 ± 3 kcal/mol (11 kcal/mol MP2//MP2) (eq 8). This quantity is slightly larger than an equivalent isodesmic reaction for the parent system (i.e., 3-cyclopropenyl anion is destabilized relative to cyclopropyl anion by 5.8 kcal/mol at the CCSD(T)/6-311+G(2df,2pd)//MCSCF(10(9),9)/6-31+G(d,p)) level.[13] The difference (3 kcal/mol) can be attributed, at least partially, to the preferential stabilization (~2 kcal/mol) of the cyclopropyl group by the phenyl substituent as a result of improved resonance delocalization.[39] The energetics of eq 8 are predominantly due to the antiaromatic interaction in **15**; however, subtle differences in strain energy, polarizability, and inductive effects must be considered as well. 3-Phenyl-3-cyclopropenyl anion also can be compared with a linear analogue, 2-phenylallyl anion (eq 9). This model indicates comparable destabilization within experimental error (13 ± 5 kcal/mol) for **15** upon cyclic conjugation. One can compare **15** to 1-phenylallyl anion ($\Delta H°_{\text{acid}}$(3-phenylpropene) = 369 ± 4 kcal/mol)[38] too, in which case the difference (30 ± 4 kcal/mol) is much larger but no different than for the parent system (i.e., $\Delta\Delta H°_{\text{acid}}$(cyclopropene − propene) = 418.9−389.1 = 29.8 kcal/mol).



(8)

$\Delta H°_{\text{rxn}}$ = -9 ± 3 kcal/mol (expt)
= -11 kcal/mol MP2//MP2



(9)

$\Delta H°_{\text{rxn}}$ = -13 ± 5 kcal/mol (expt)

We have used theory to gain insights into the structures of 3-aryl-3-cyclopropenyl anions. The geometries discussed here were optimized at the HF/6-31+G(d) level

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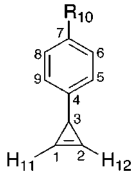
(37) The error limits in our measured acidity come from an error analysis which includes the uncertainty in the measured ion ratios and the reference acids. As in any kinetic determination, unaccounted-for systematic errors can lead to larger uncertainties in the final result. There is no apparent reason there should be a problem in this case and, indeed, experiment and theory are in excellent agreement.

(38) Chou, P. K.; Dahlke, G. D.; Kass, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 315−324.

Table 4. HF/6-31+G(d) Geometries for Phenylcyclopropene (15H), 3-(4-Trifluoromethylphenyl)cyclopropene (3H) and Their C3 Conjugate Bases[a]



	R = H		R = CF$_3$	
parameter	**15H** (C_s)	**15** (C_s)	**3H** (C_1)	**3** (C_s)[b]
C1−C2	1.277 (1.306)	1.291(1.322)	1.276	1.303
C1−C3	1.497 (1.512)	1.511 (1.510)	1.497	1.452
C2−C3	1.497 (1.512)	1.511 (1.510)	1.498	1.452
C3−C4	1.505 (1.494)	1.449 (1.426)	1.503	1.331
C4−C5	1.392 (1.404)	1.416 (1.428)	1.389	1.473
C5−C6	1.388 (1.398)	1.382 (1.394)	1.388	1.355
C6−C7	1.386 (1.400)	1.394 (1.408)	1.383	1.424
C7−C8	1.388 (1.400)	1.394 (1.408)	1.391	1.424
C8−C9	1.386 (1.398)	1.382 (1.394)	1.381	1.355
C4−C9	1.394 (1.403)	1.416 (1.428)	1.396	1.473
C7−R10	1.076 (1.088)	1.077 (1.090)	1.502	1.456
C1−H11	1.069 (1.081)	1.073 (1.085)	1.069	1.070
C2−H12	1.069 (1.081)	1.073 (1.085)	1.069	1.070
C1−C3−C2	50.5 (51.2)	50.6 (52.0)	50.5	53.3
C2−C1−C3	64.7 (64.4)	64.7 (64.0)	64.8	63.4
C3−C1−C2	64.7 (64.4)	64.7 (64.0)	64.8	63.4
α[c]	53.5 (54.8)	64.2 (49.2)	53.7	0.5
β[d]	1.6 (2.3)	9.8 (12.4)	1.0(0.9)	0.0(0.0)
C2−C3−C4−C5	149.6 (149.6)	62.3 (58.8)	149.6	1.0

[a] Bond lengths are in angstroms, and angles are in degrees. Parenthentical values correspond to MP2/6-31+G(d) geometries. [b] **3** was optimized using no symmetry constraints but has C_s symmetry. [c] α is the displacement of the aryl group from the plane of the cyclopropene ring. See Figure 3. [d] β is the deviation of H11 and H12 from the plane of the cyclopropene ring. In **3H** and **15H**, H11 and H12 are on the same side of the three-membered ring as the aryl group whereas the opposite is true for **15**.

of theory unless otherwise noted. Deprotonation of phenylcyclopropene (**15H**) at the 3 position (i.e., formation of **15**) induces several structural changes (Table 4). The phenyl group which is aligned with the Walsh orbitals of **15H** rotates 90° to be conjugated with the newly formed charge. The C3−C4 bond length decreases by 0.056 Å (0.068 Å MP2), indicating delocalization of the charge into the phenyl group. This interaction is slightly counterbalanced by movement of the phenyl group out of the plane of the cyclopropene ring (α increases from 53.5° to 64.2°, Figure 3), but this parameter is sensitive to the computational method (i.e., α decreases by 5.6° at the MP2 level). The vinyl hydrogens in **15** move 11.4° to the opposite side of the cyclopropene plane, and the paraffinic bonds (C1−C3 and C2−C3) lengthen by 0.014 Å. Both distortions serve to disrupt overlap of the C1−C2 π bond with the electron lone pair. Elongation of the C4−C5 and C4−C9 bonds in the phenyl ring by 0.024 and 0.022 Å, respectively, also is noteworthy. Introduction of a *p*-trifluoromethyl substituent on the phenyl ring provokes a markedly different anion structure; **3** is nearly planar, $\alpha = 0.5°$ (Figure 3). The increased delocalization in **3** is also reflected in the considerably shorter C3−C4 bond length relative to **3H** (1.331 vs 1.503 Å). This difference is more than three times that computed for **15** and **15H**. The olefinic bond in **3** lengthens a modest amount (1.276 to 1.303 Å) as is typical for cyclopropenyl anions, and the paraffinic bonds decrease (1.497(8) to 1.452 Å) as also noted for 3-formyl- and 3-methoxycarbonyl-3-cyclopropenyl anions.[11,25,40] This last structural change presumably arises because of the hybridization change at C3.

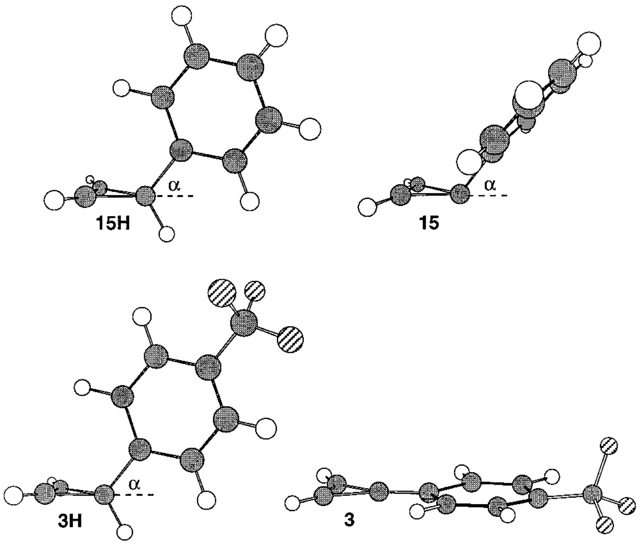


Figure 3. HF/6-31+G(d) structures of phenylcyclopropene, 3-(4-trifluoromethylphenyl)cyclopropene, and their conjugate bases.

To predict the gas-phase acidity of triphenylcyclopropene (**8H**) we turned to theory. A reliable computed number requires an optimized structure for the conjugate base which includes diffuse functions since they are needed to properly describe the electron distribution of anions. We were unable to obtain the energy (or a geometry) of **8H** with the 6-31+G(d) basis set at the HF, B3LYP, and BVWN5 levels of theory, however, which precluded a direct determination of the acidity with this basis set. We, therefore, computed the acidity of **8H** relative to 3-phenylcyclopropene as shown in eq 10 and adjusted this difference using our experimental number for 3-(4-methylphenyl)cyclopropene (see above). This approach yields a value of 389.5 kcal/mol for the acidity of 1,2,3-triphenylcyclopropene and indicates that the additional phenyl groups at the vinyl positions stabilize the anion by 9 kcal/mol or slightly less than half of the effect of the first phenyl group. In contrast, the acidity of **8H** in solution is only 11 pK_A units (or 15 kcal/mol) more acidic than cyclopropene (50 vs 61),[41,42] and although the pK_A of 3-phenylcyclopropene has not been measured, it is clear that the remote phenyl groups have less of an impact in solution (at least in an absolute sense). Nevertheless, based on a variety of trapping experiments, it is apparent that remote phenyl groups facilitate the generation of the corresponding cyclopropenyl anions and that incorporation of *p*-trifluoromethyl

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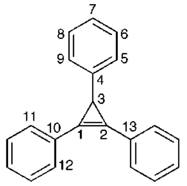
(39) The value of 2 kcal/mol comes from acidity differences: $\Delta\Delta H°_{acid}$ (cyclopropane − phenylcyclopropane) = 22 ± 4 kcal/mol (expt, see refs 33 and 38) and $\Delta\Delta H°_{acid}$ (cyclopropene − phenylcyclopropene) = 20.3 kcal/mol (calc, see refs 13 and this work). Similar preferential stabilizations for the methyl ester (7 kcal/mol, ref 40) and cyano (7 kcal/mol, ref 11) derivatives also have been found.

(40) Kroeker-Sachs, R. Ph.D. Thesis, University of Minnesota, 1993.

(41) Breslow, R.; Balasubramanian, K. *J. Am. Chem. Soc.* **1969**, *91*, 5182−5183.

(42) Breslow, R.; Chu, W. *J. Am. Chem. Soc.* **1973**, *95*, 411−418.

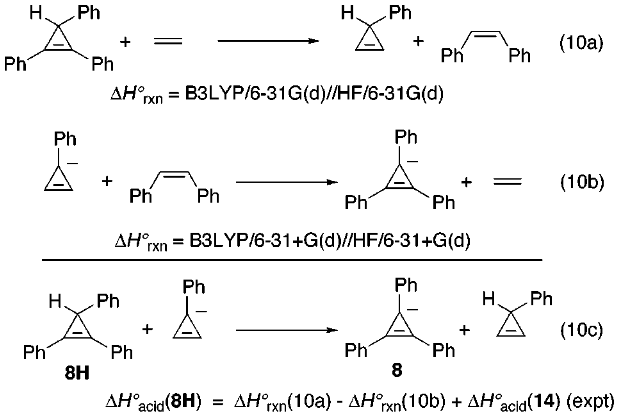
Table 5. Hartree–Fock Geometries for Triphenylcyclopropene (8H, 6-31G(d)) and Its Conjugate Base (8, 6-31+G(d))



parameter	**8H** (C_s)[a]	**8** (C_s)
C1–C2	1.288 (1.293)	1.302
C1–C3	1.495 (1.513)	1.505
C2–C3	1.495 (1.518)	1.505
C3–C4	1.506 (1.470)	1.463
C4–C5	1.390	1.411
C5–C6	1.386	1.384
C6–C7	1.384	1.392
C7–C8	1.387	1.392
C8–C9	1.384	1.384
C3–C9	1.393	1.411
C1–C10	1.454 (1.422)	1.451
C2–C13	1.454 (1.443)	1.451
C1–C3–C2	51.0 (50.5)	51.3
C1–C2–C3	64.5 (65.0)	64.3
C2–C1–C3	64.5 (64.6)	64.3
α[b]	53.2	56.0
β[c]	0.6 (5.4)	14.5
C2–C3–C4–C5	149.2	62.2
C11–C10–C1–C2	176.3	−141.6
C12–C10–C1–C2	−3.9	38.0

[a] X-ray data from ref 43 are given in parentheses. [b] α is the displacement of the 3-phenyl group from the plane of the cyclopropene ring. [c] β is the deviation of the C1 and C2 phenyl groups from the plane of the cyclopropene ring. In **8H**, the C1 and C2 phenyl rings are on the same side of the three-membered ring as the C3 phenyl group whereas the opposite is true for **8**.

substituents increases the reaction rate even further.[9,43]



$$\Delta H^\circ_{acid}(\mathbf{8H}) = \Delta H^\circ_{rxn}(10a) - \Delta H^\circ_{rxn}(10b) + \Delta H^\circ_{acid}(\mathbf{14})\ (expt) = 389.5\ kcal/mol$$

The structural changes upon deprotonation of 1,2,3-triphenylcyclopropene proved to be most intriguing (Table 5, Figure 4). The optimized geometry of **8H** at the HF/6-31G(d) level of theory was found to be in reasonable accord with experimental X-ray crystallography data[44] (Table 5) with minor deviations observed in the C1–C10 and C3–C4 bonds lengths; theory predicts the bonds to be longer than experiment by 0.032 and 0.036 Å, respectively. The 3-phenyl group is orthogonal to the cyclopropene plane while the phenyl rings at C1 and C2 adopt a nearly planar configuration with the cyclopropene ring in order to be optimally conjugated with its double bond. Upon anion formation, the 3-phenyl group moves into conjugation with the electron lone pair and slightly bends away from the plane of the cyclopropene ring ($\alpha = 53.2°$ vs 56.0°). The C3–C4 bond length exhibits the largest alteration, decreasing by 0.043 Å. The vinyl phenyl substituents move out of the plane of the cyclopropene ring by 14.5° as well as undergoing a dramatic rotation about the C1–C10 and C2–C11 bonds (Figure 4). The magnitude of the latter distortion is reflected in the change in the C11–C10–C1–C2 (176.3° vs. −141.6°) and C12–C10–C1–C2 (−3.9° vs 38.0°) dihedral angles between **8H** and **8**. The out-of-plane distortion (the increase in β) is consistent with ab initio calculations for related systems and results so as to minimize the unfavorable cyclic 4π electron interaction.[13] The rotation of the C1 and C2 phenyl groups results in diminished conjugation with the cyclopropene double bond, apparently, because of steric congestion between the *o*-aryl hydrogens in all three phenyl rings. As it is, the hydrogen–hydrogen distances between the C3 and C1 (or C2) and the C1 and C2 rings are 2.72 and 2.36 Å, respectively. If the phenyl groups did not rotate then these two distances would be 2.04 and 1.85 Å, respectively (Figure 4). In 3-methoxycarbonyl-1,2-diphenylcyclopropenyl anion, where this steric interaction is not present, the phenyl rings do not rotate.[25] Finally, it is worth noting that a MNDO semiempirical geometry was previously reported for **8**; the structure is nearly C_{2v} with the C3 phenyl group orthogonal to the three-membered ring and the other two phenyls nearly in the ring plane.[45] This geometry is entirely different from the ab initio one and most likely is the result of MNDO's now known problems in reproducing carbanion geometries.

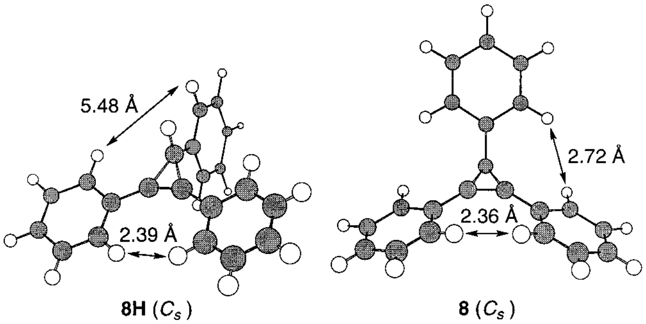


Figure 4. Computed structures for **8H** (HF/6-31G(d)) and **8** (HF/6-31+G(d)).

Conclusion

3-Aryl-substituted cyclopropenyl anions were found to be unstable in the gas phase as they spontaneously rearrange to 6-substituted 3-indenyl anions. 1,2,3-Triphenylcyclopropenyl anion undergoes a similar gas-phase isomerization, contrary to a previous report describing its preparation. Despite the instability of its conjugate base, the acidity of 3-(4-methylphenyl)cyclopropene was

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(43) Han, S. Ph.D. Thesis, Unversity of Minnesota, 1997.

(44) Domnin, I. N.; Kopf, J.; Keyaniyan, S.; DeMeijere, A. *Tetrahedron* **1985**, *41*, 5377–5382.

(45) Winkelhofer, G.; Janoschek, R.; Fratev, F.; Spitznagel, G. W.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 332–337.

determined by the DePuy kinetic method ($\Delta H°_{acid} = 398.6 \pm 1.4$ kcal/mol), and the value is in good agreement with ab initio calculations. This result represents the simplest cyclopropene whose acidity has been measured in the gas phase. The structures and energies of 3-(4-methylphenyl)-cyclopropene, 3-(4-trifluoromethylphenyl)cyclopropene, 1,2,3-triphenylcyclopropene, and their conjugate bases were explored with theory. Formation of 1,2,3-triphenylcyclopropenyl anion is predicted to be accompanied by dramatic changes in the orientation of all three phenyl substituents at the HF/6-31+G(d) level.

Acknowledgment. Support from the National Science Foundation, the donors of the Petroleum Research Foundation, as administered by the American Chemical Society, and the Minnesota Supercomputer Institute are gratefully acknowledged.

Supporting Information Available: Computed energies and structures (*x*,*y*,*z* coordinates). This material is available free of charge via the Internet at http://pubs.acs.org.

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