

Triphenylcyclopropenide Anion in the Gas Phase

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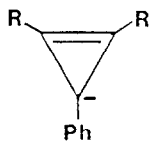
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**Abstract:** The triphenylcyclopropenide anion has been generated in the gas phase, and the approximate gas phase acidity of triphenylcyclopropene is reported. The dimethylphenylcyclopropenide anion has also been formed, but it appears to undergo a rearrangement that is induced by the acids used to probe its base strength.

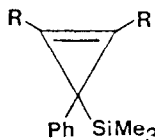
The nominally anti-aromatic cyclopropenide anion  $C_3H_3^-$  has not been observed in the gas phase, although other isomers of this formula have been.<sup>2</sup> It has been argued, based on molecular orbital calculations, that this anion is unstable with respect to loss of an electron in the gas phase.<sup>3</sup> In solution, the anion and derivatives have been formed by electrochemical reduction;<sup>4</sup> and, more recently, triphenylcyclopropenide anion **1a** has been generated by fluorodesilylation.<sup>5</sup> In this communication we report the generation of the triphenylcyclopropenide anion in the gas phase. We find it to be stable with respect to electron loss, and we have measured its basicity using ion cyclotron resonance techniques.<sup>6</sup>



**1**

**1a:** R = Ph

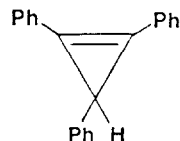
**1b:** R = CH<sub>3</sub>



**2**

**2a:** R = Ph

**2b:** R = CH<sub>3</sub>



**3**

We originally had intended to form anion **1a** by fluorodesilylation of **2a**, as was done in solution, since this has been shown to be an efficient way of producing carbanions regiospecifically in the gas phase.<sup>7</sup> We found, however, that when **2a** is desorbed off a solid probe at room temperature into the ICR spectrometer (pressure ca.  $2 \times 10^{-6}$  torr in the cell by

the transient relaxation technique), thermal electron impact produces both the parent radical anion and the desilylated species  $\text{Ph}_3\text{C}_3^-$ . The two anions are formed in approximately equal amounts. The stability of the parent radical anion is consistent with fact that stilbene has an electron affinity of 9 kcal/mole.<sup>8</sup>

The putative anion **1a** is stable for the 1-2 sec timescale of the experiment. The anion is not protonated by water, but reacts with methanol and stronger gas phase acids.<sup>9</sup> No deuterium exchange with  $\text{D}_2\text{O}$  or  $\text{CH}_3\text{OD}$  is observed. Although the anion falls in a poorly developed region of the gas phase acidity scale, the bracketing of the acidity between that of methanol and water establishes the  $\Delta\text{H}_{\text{acid}}^\circ$  of the conjugate acid **3** as  $385 \pm 5$  kcal/mole. The observed basicity of the anion argues against it being a rearranged form, such as triphenylallenide or diphenylindenide, both of which should be considerably less basic. Although we cannot rule out a rearrangement to some other structure, both the mode of generation and the basicity are consistent with the observed anion being **1a**.

From the measured gas phase acidity, the ring C-H bond dissociation energy of **3** may be obtained from the equation  $\Delta\text{H}_{\text{acid}}^\circ(\text{AH}) = \text{DH}^\circ(\text{A-H}) \pm \text{IP}(\text{H}\cdot) - \text{EA}(\text{A}\cdot)$ . Unfortunately, the electron affinity of the triphenylcyclopropenyl radical is as yet unknown; however, its reduction potential has been measured in solution and found to be 0.05 V more negative than that of cycloheptatrienyl radical.<sup>4</sup> If the solvation effects on the reduction potentials of these two delocalized species are taken to be the same, from the known EA of cycloheptatrienyl<sup>9b</sup> we derive the triphenylcyclopropenyl EA to be ca. 15 kcal/mole. Thus an approximate value of  $\text{DH}^\circ = 86$  kcal/mole is obtained for the C-H bond dissociation energy in **3**. Although this is only a very crude estimate, it is not unreasonable in terms of the expected effect of phenyl substitution on decreasing the cyclopropene C-H bond strength from  $91 \pm 4$  kcal/mole.<sup>10</sup>

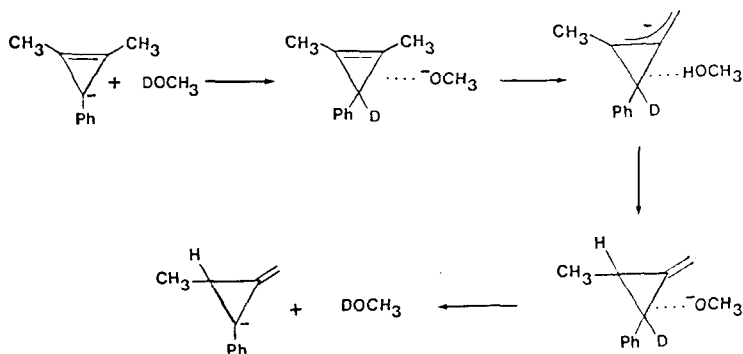
The gas phase acidity of  $\Delta\text{H}_{\text{acid}}^\circ = 385 \pm 5$  kcal/mole for **3** can be compared with the  $\Delta\text{H}_{\text{acid}}^\circ$  of  $379.0 \pm 2.3$  kcal/mole for toluene.<sup>9</sup> Based on polarizability arguments, the former should be more acidic than the latter, but this is not the case. Although it is tempting to ascribe the greater acidity of toluene to the antiaromaticity of the cyclopropenyl anion,<sup>4</sup> increased ring strain attending phenyl conjugation in the cyclopropenyl anion also plays a role. In fact, phenylcyclopropane with  $\Delta\text{H}_{\text{acid}}^\circ > 391$  kcal/mole is even less acidic than triphenylcyclopropene. The conjugate base of phenylcyclopropane deprotonates  $\text{D}_2\text{O}$ ,<sup>11</sup> whereas **1a** does not.

The greater stability of **1a** relative to 1-phenylcyclopropanide in the gas phase probably comes from delocalization of the negative charge by more than one phenyl group. In solution, **3** is a stronger acid than dipropylphenylcyclopropene by more than 8  $\text{pK}_a$  units,<sup>4</sup> and **2a** undergoes fluorodesilylation at least several orders of magnitude faster than does

1,2-dimethyl-3-phenyl-3-trimethylsilylcyclopropene **2b**.<sup>5</sup> We therefore expected that anion **1b** would prove to be even more basic in the gas phase than **1a**.

In order to test this prediction, **2b** was subjected to thermal electron impact in the ICR spectrometer under conditions similar to those used for **2a**. No parent radical anion is observed, but there is an appreciable peak at 143 amu, corresponding to **1b**. Surprisingly, this ion does not undergo protonation by water, methanol, or tert-butyl alcohol. It is sufficiently basic to react with benzyl alcohol, however. No deuterium exchange is observed with MeOD or D<sub>2</sub>O.

We believe that the unexpectedly low basicity of **1b** is due to a rearrangement of this ion, induced by the probe acid in the collision complex. This rearrangement is illustrated in the Scheme, and is driven by the conversion of **1b** into increasingly stable allylic carbanions. The observed gas phase basicity is consistent with that expected for a 1-phenylallyl carbanion.<sup>9</sup> The proposed rearrangement in the Scheme also predicts the lack of observed deuterium exchange with CH<sub>3</sub>OD: the deuterium originally donated to the ring is the one that must be removed to generate the carbanion that is the final product. The lack of deuterium exchange with D<sub>2</sub>O is more problematic, in that the deuterium left on the D<sup>-</sup> in the complex should be able to exchange with the exo-allyl anion in the complex. The lack of exchange either indicates that the complex is too short-lived for this process to occur, or that the strain associated with the cyclopropyl ring makes this allylic exchange less likely than for the unstrained propene.<sup>7</sup>



The gas phase chemistry of other substituted cyclopropenide anions is currently being studied.

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#### References

1. a. Current address: Department of Chemistry, Univ. of Tennessee, Knoxville TN 37996-1600; b. Indiana Univ.; d. Univ. of Washington.
2. Oakes, J.M.; Ellison, B.G. J. Amer. Chem. Soc. **1983** 105, 2696.
3. Davidson, E.R.; Borden, W.T. J. Chem. Phys. **1977** 67, 191; Winkelhofer, G.; Janoschek, R.; Frater, F. Spitznagel, G.W.; Chandrasekhar, J.; Schleyer, P. von R. J. Am. Chem. Soc. **1985** 107, 332.
4. Wasielewski, M.R.; Breslow, R. J. Am. Chem. Soc. **1976** 98, 4222.
5. Köser, H.G.; Renzoni, G.E.; Borden, W.T. J. Amer. Chem. Soc. **1983** 105, 6359.
6. McIver, R.T., Jr. Rev. Sci. Instrum. **1970** 41, 555; McIver, R.T., Jr. Ibid. **1978** 49, 111; McIver, R.T., Jr.; Hunter, R.L.; Ledford, E.B., Jr.; Locke, M.J.; Francl, T. J. Int. J. Mass Spectrom. Ion Phys. **1981** 39, 65; Bartmess, J.E.; Caldwell, G. Ibid. **1981** 41, 125.
7. DePuy, C.H.; Bierbaum, V.M.; Flippin, L.A.; Grabowski, J.J.; King, G.K.; Schmitt, R.J.; Sullivan, S.A. J. Am. Chem. Soc. **1980**, 102, 5012.
8. Wojnarovits, L.; Foldiak, G. J. Chromatog. **1981** 206, 511.
9. (a) Cumming, J.B.; Kebarle, P. Can. J. Chem. **1978** 78, 1; (b) Bartmess, J.E.; Scott, J.A.; McIver, R.T., Jr. J. Am. Chem. Soc. **1979**, 101, 6046; (c) Bartmess, J.E.; Scott, J.A.; McIver, R.T., Jr. J. Am. Chem. Soc. **1979**, 101, 6056; (d) Bartmess, J.E.; McIver, R.T., Jr. "The Gas Phase Acidity Scale", in "Gas Phase Ion Chemistry", vol. 2, M.T. Bowers, Ed., Academic Press, 1979, Ch.11.
10. McMillen, D.F.; Golden, D.M. Ann. Rev. Phys. Chem. **1982** 33, 493; DeFrees, D.D.; McIver, R.T., Jr.; Hehre, W.J. J. Am. Chem. Soc. **1980** 102, 3334.
11. Andrist, A.H.; DePuy, C.H.; Squires, R.H. J. Am. Chem. Soc. **106** 1984, 845.

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