J. Am. Chem. Soc. 1994, 116, 783–784

3-Carbomethoxycyclopropen-3-yl Anion. Formation and Characterization of an Antiaromatic Ion

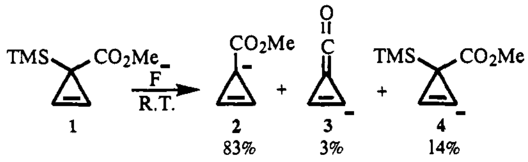
Roseann Kroeker Sachs† and Steven R. Kass*,‡

Department of Chemistry
University of Minnesota
Minneapolis, Minnesota 55455

Received September 24, 1993

For many years it has been known that fully conjugated monocyclic compounds with $4n$ π electrons can be difficult to prepare and highly reactive. It was not until 1965, however, that Breslow first described some of these species as being antiaromatic, i.e., molecules which are destabilized by cyclic conjugation.[1] Cyclobutadiene[2] and cyclopentadienyl cation[3] have been prepared and characterized, but cyclopropenyl anion, the simplest member of this family and the archetypical antiaromatic species, has not been synthesized. Landmark studies by the Breslow group have been carried out on the kinetic and thermodynamic acidities of a number of cyclopropenes,[4] but the reactivity of their conjugate bases is essentially unknown. In this paper we report the formation and characterization of the first cyclopropenyl anion using gas-phase methodology.

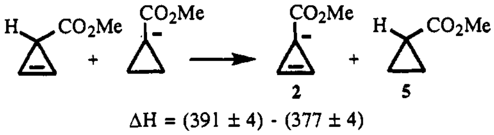
Fluorodesilylation of trialkylsilyl derivatives has been shown to be a powerful method for the regio- and stereospecific preparation of carbanions in the gas phase.[5] 3-Carbomethoxy-3-(trimethylsilyl)cyclopropene (**1**), synthesized in two steps starting from (trimethylsilyl)acetylene and ethyl (trimethylsilyl)diazoacetate,[6] reacts readily with fluoride in our variable temperature flowing afterglow to afford three products (eq 1).[5c]



(1)

The dominant species is the cyclopropenyl anion **2**, but small amounts of the conjugate bases of triafulvenone and **1** are formed as well. If this reaction is carried out with **1**-d_5 (deuterium at the vinyl and methyl ester positions), then **2**-d_5, **3**-d_1, and **4**-d_4 are produced. The conjugate bases of 3-carbomethoxycyclopropene (vinyl anion), carbomethoxyallene ($CH_2{=}C{=}CHCO_2Me$), and 3-carbomethoxypropyne ($HC{\equiv}CCH_2CO_2Me$) were also generated and can readily be distinguished from **2** since they are much less basic and reactive.[7]

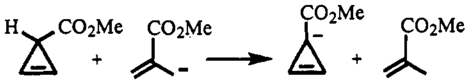
The proton affinity of **2** was measured by "titration" with a series of acids of increasing strength. Ethylamine and dimethylamine (ΔH_{acid} = 399.4 and 396.3 kcal mol^{-1}, respectively) are not acidic enough to protonate the cyclopropenyl anion, whereas fluorobenzene, methanol-*O*-*d*, and *tert*-butyl alcohol-*O*-*d* (ΔH_{acid} = 387.2, 382.5, and 374.6 kcal mol^{-1}, respectively) rapidly transfer a proton or a deuteron.[8] Water and deuterium oxide (ΔH_{acid} = 390.8 and 392.0 kcal mol^{-1}, respectively) produce only a trace of hydroxide or deuteroxide, so the bracketed acidity (ΔH_{acid}) of the conjugate acid of **2** is 391 ± 4 kcal mol^{-1}. This value is in good accord with a calculated result for the formyl derivative, ΔH_{acid} = 386.7 kcal mol^{-1} (MP2/6-31+G(d)//6-31+G(d)), given that esters are less acidic than aldehydes (the difference between methyl acetate and acetaldehyde is 6.0 kcal mol^{-1}).[8] In a similar fashion, the acidity of methyl cyclopropanecarboxylate (**5**) was measured (ΔH_{acid} = 377 ± 4 kcal mol^{-1}) and found to be 14 kcal mol^{-1} more acidic than its unsaturated derivative.[9] Consequently, the reaction shown in eq 2 is endothermic by 14 kcal mol^{-1}. This



(2)

$$\Delta H = (391 \pm 4) - (377 \pm 4)$$
$$= 14 \pm 6 \text{ kcal mol}^{-1}$$

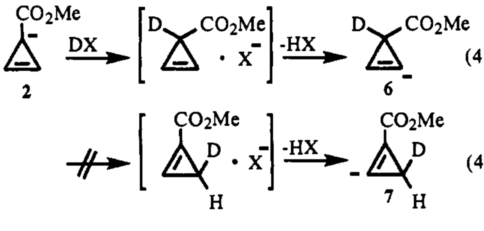
compares quite favorably with an *ab initio* value of 12.1 kcal mol^{-1} (MP2/6-31+G(d)// 6-31+G(d)) for the analogous reaction involving formyl derivatives. The carbomethoxy-substituted cyclopropenyl anion (**2**) is also less stable than its acyclic analog ($CH_2{=}C(CO_2Me)CH_2^-$) by approximately 14 kcal mol^{-1} (eq 3),[10] and thus these classical models indicate that **2** is significantly destabilized, i.e., antiaromatic.



(3)

$$\Delta H \approx 14 \text{ kcal mol}^{-1}$$

3-Carbomethoxycyclopropen-3-yl anion (**2**) undergoes an acid-catalyzed isomerization which only is apparent upon reaction with deuterated reagents. More specifically, D_2O, MeOD, and *t*-BuOD react with **2** to form their conjugate bases (deuteron transfer) and a more stable vinyl anion. Two structures, **6** and **7**, can be envisioned depending upon the site of protonation in **2** (eq 4). The former species is favored since subsequent addition of diethylhydroxylamine-*O*-*d* leads to the incorporation of a second deuterium atom, a result consistent with **6** but not **7**.



(4a)
(4b)

As anticipated, **2** is extremely reactive. One interesting example is its reaction with carbon dioxide (eq 5). Three products are formed but the major species is the conjugate base of triafulvenone

---

† Current address is Colorado College, Colorado Springs, CO 80903.

‡ Alfred P. Sloan Research Fellow.

(1) Breslow, R. *Chem. Eng. News* **1965**, *43*, 90.

(2) (a) Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343. (b) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309 and references therein.

(3) Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffman, J. M.; Perchonock, C.; Wasserman, E. *J. Am. Chem. Soc.* **1973**, *95*, 3017.

(4) (a) Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927. (b) Wasielewski, M. R.; Breslow, R. *J. Am. Chem. Soc.* **1976**, *98*, 4222. (c) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393. (d) Breslow, R.; Brown, J.; Gajewski, J. J. *J. Am. Chem. Soc.* **1967**, *89*, 4383.

(5) (a) Rabasco, J. J.; Kass, S. R. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 91. (b) Chou, P. K.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 4357. (c) Kass, S. R.; Guo, H.; Dahlke, G. D. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 366. (d) Damrauer, R. In *Selective Hydrocarbon Activation: Principles and Progress*, VCH Publishers: New York, 1990. (e) O'Hair, R. A. J.; Gronert, S.; DePuy, C. H.; Bowie, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 3105. (f) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3385. (g) Squires, R. R.; DePuy, C. H. *Org. Mass Spectrom.* **1982**, *17*, 187. (h) 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.

(6) Clauberg, H. Ph.D. Thesis, Harvard University, 1993.

(7) Sachs, R. K. Ph.D. Thesis, University of Minnesota, 1993.

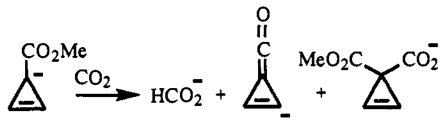
(8) All of the cited acidities come from the following: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(9) Compound **5** is deprotonated by OH^-, MeO^-, EtO^-, and *t*-BuO^-, but not by F^- nor CH_2CN^-. The conjugate base of **5** deprotonates MeOD, EtOD, *t*-BuOD, and CH_3CN, but not D_2O, C_6H_5F, nor C_6H_5CN.

(10) The acidity of the acyclic ester was not measured, but that of the corresponding aldehyde (methacrolein) is known (ΔH_{acid} = 377 kcal mol^{-1})[8] and should be a good model for it.

0002-7863/94/1516-0783$04.50/0

(**3**). This intriguing ion was examined further. It contains one

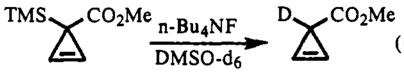


3

≤ 2% ≥ 98% trace (5)

deuterium when **2**-d_5 is used as the substrate and loses this label upon reaction with acetic acid and formic acid, but not 3-chloropropionic acid. We assign ΔH_{acid} = 343 ± 3 kcal mol^{-1} for triafulvenone (**8**), which makes it 21 kcal mol^{-1} more acidic than 3-carbomethoxycyclopropene (vinyl position)[11] and 40 kcal mol^{-1} more acidic than cyclopropene.[12] This somewhat surprising acidity enhancement is in excellent accord with a computed value of ΔH_{acid}(**8**) = 346.8 kcal mol^{-1} (MP2/6-31+G(d)//6-31+G(d)). From a mechanistic standpoint, we favor an addition–fragmentation pathway which can be accompanied by a methyl transfer from one carboxylate to the other over a symmetric cyclic anhydride intermediate because, when $^{13}CO_2$ is used, the product contains only 15–20% of the label.

It seems natural to ask what bearing our gas-phase results have on the prospect of generating a cyclopropenyl anion in solution. The measured acidity difference between the saturated and unsaturated cyclopropyl derivatives is 14 kcal mol^{-1}, which corresponds to 10 pK_a units. If we assume that this difference is the same in solution, then the pK_a of 3-carbomethoxycyclopropene should be approximately 41–44.[13] Consistent with this estimate, a deuteron is abstracted from dimethyl sulfoxide-d_6 (pK_a(DMSO) = 35) upon reacting **1** with "dry" tetrabutylammonium fluoride (eq 6).[14] On a few occasions the deuterium



(6)

content in the product was as high as 80–85%, but it is difficult to consistently achieve this level of incorporation because of variable amounts of water in the tetrabutylammonium fluoride. In any case, the fluorodesilylation of an appropriately substituted cyclopropene may provide a valuable means for preparing cyclopropenyl anions in condensed media. Experiments to test this hypothesis are currently being carried out and will be reported in due course.

Acknowledgment. We wish to thank Dr. H. Clauberg and Professor P. Chen for kindly providing us with a procedure for the synthesis of 3-carbomethoxy-3-(trimethylsilyl)cyclopropene, and Professor A. Pinhas for his mechanistic insight involving the reaction of **2** with CO_2. Support from the Minnesota Supercomputer Institute (including a travel grant for R.K.S.), the National Science Foundation, and the donors of the Petroleum Research Foundation, as administered by the American Chemical Society, are gratefully acknowledged.

---

(11) Carbomethoxycyclopropene is readily deprotonated by OH^-, t-BuO^-, $FCH_2CH_2O^-$, and $C_6H_5NH^-$, but not by $CF_3CH_2O^-$, c-$C_4H_4N^-$, nor t-BuS^-. In the reverse direction deuteron transfer occurs with CF_3CH_2OD and EtSD, but proton transfer does not occur with weaker acids such as $C_6H_5NH_2$ or FCH_2CH_2OH. Therefore, ΔH_{acid} = 364 ± 3 kcal mol^{-1}.

(12) McCarthy, R.; Kass, S. R. Unpublished data.

(13) The acidity of methyl cyclopropanecarboxylate has not been measured but can easily be estimated to have a pK_a of 31–34. This value is derived by taking the known difference between the values for cyclopropyl phenyl ketone and phenyl methyl ketone (3.5 pK_a units) and adding it to the pK_a of ethyl acetate (27.5 or 30.5). For the relevant pK_a data, see: (a) Bordwell, F. G.; Vanier, N. R.; Matthews, W. S.; Hendrickson, J. B.; Skipper, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 7160. (b) Bordwell, F. G.; Fried, H. E. *J. Org. Chem.* **1981**, *46*, 4327. (c) Arnett, E. M.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 809.

(14) An incipient triphenylcyclopropenyl anion has previously been shown to abstract a proton from water using a similar procedure. Köser, H. G.; Renzoni, G. E.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 6359.