

Formation of Transient and Long-Lived Cyclopropenyl Anions

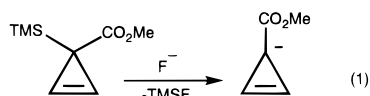
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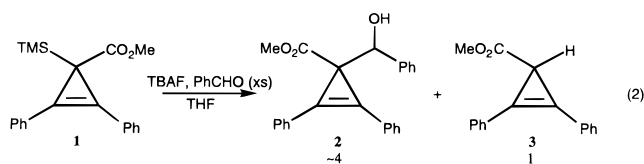
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Cyclobutadiene has been viewed as the Mona Lisa of organic chemistry by Cram et al.¹ This description also applies to cyclopropenyl anion since it too has captured the imagination of chemists, inspires wonder, and has been the subject of considerable effort.^{2–14} However, in contrast to cyclobutadiene, cyclopropenyl anion remains largely unknown. A more apt analogy, therefore, might be to compare it to the pyramids since it is unclear how they were constructed or how a long-lived cyclopropenyl anion can be prepared in condensed media.

In 1994 we reported the first preparation of a stable cyclopropenyl anion by reacting fluoride ion with 3-carbomethoxy-3-trimethylsilylcyclopropene in the gas phase (eq 1).¹⁵ In this work we provide condensed-phase mechanistic evidence that the fluoride-induced desilylation of a 3-trimethylsilylcyclopropene derivative leads to a transient cyclopropenyl anion intermediate. The first preparation of a long-lived cyclopropenyl anion in solution and its corresponding UV–visible spectrum also are presented.

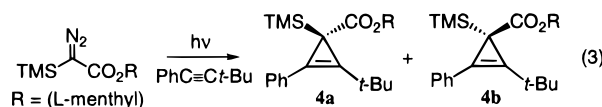


Valuable information regarding the structure and reactivity of cyclopropenyl anions can, in principle, be obtained by studying the fluorodesilylation of 3-trimethylsilylcyclopropenes. In an important experiment, Borden et al. looked at the desilylation of ¹³C-labeled 1,2,3-triphenyl-3-trimethylsilylcyclopropene with tetra-*n*-butylammonium fluoride (TBAF) in tetrahydrofuran.¹⁶ They found that the ¹³C label scrambled around the ring in the proton-trapped product. We have explored the regioselectivity in unsymmetrical substrates and have found that carbon electrophiles can be used to give good yields of the trapped cyclopropene (eq 2).^{17,18} While these results are consistent with the putative formation of

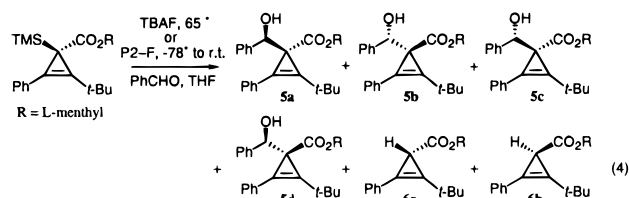


a cyclopropenyl anion intermediate, such a species is not required mechanistically. A hypervalent penta- or hexacoordinate silicon anion cannot be ruled out.

To distinguish between these possibilities a chiral cyclopropene (**4**) was synthesized by photochemical addition of *L*-menthyl (trimethylsilyl)diazoacetate to *tert*-butyl-phenylacetylene (eq 3).



The 2 diastereomers (**4a** and **4b**) were separated by MPLC to give the optically pure ($\geq 98\%$) esters. These substrates were reacted with TBAF and Schwesinger's P2-F phosphazenum fluoride source; the latter reagent is a "naked" and extremely reactive source of fluoride.^{19,20} If a cyclopropenyl anion intermediate is formed, racemization at C-3 is expected although it is not required because of the chiral menthyl group (pathway 1, Scheme 1). However, if a penta- or hexacoordinate silicon intermediate reacts with the electrophile then retention of configuration at C-3 should result (pathway 2, Scheme 1). In both cases when the desilylation reaction was carried out in the presence of benzaldehyde four benzylic alcohols were formed in a 1:1: 0.7:0.7 ratio as indicated by ¹H NMR (eq 4).



Separation of two of the benzylic alcohols and a mixture of the other two was achieved via HPLC, but subsequent chemical transformations were carried out on equimolar **5a/5b** and **5c/5d** mixtures. Oxidation of the trapped alcohols with MnO₂ affords the corresponding phenyl ketones in which a chiral center has been eliminated. Both sets of compounds afforded diastereomeric ketones, which indicates that **5a** and **5b**, as well as **5c** and **5d**, have different configurations at C-3. In a similar manner, reduction of the menthyl esters with DIBAL at -78 °C afforded enantiomers. Again, this shows that racemization occurred at C-3. The protodesilylation products (**6a** and **6b**), which are formed with either fluoride source due to the presence of protic impurities,²¹ also were produced in a 1:1 ratio.²² This indicates that complete racemization at C-3 takes place. Pathway 1 in Scheme 1, consequently, appears to be operating, and a cyclopropenyl anion intermediate is formed in these desilylation reactions. This

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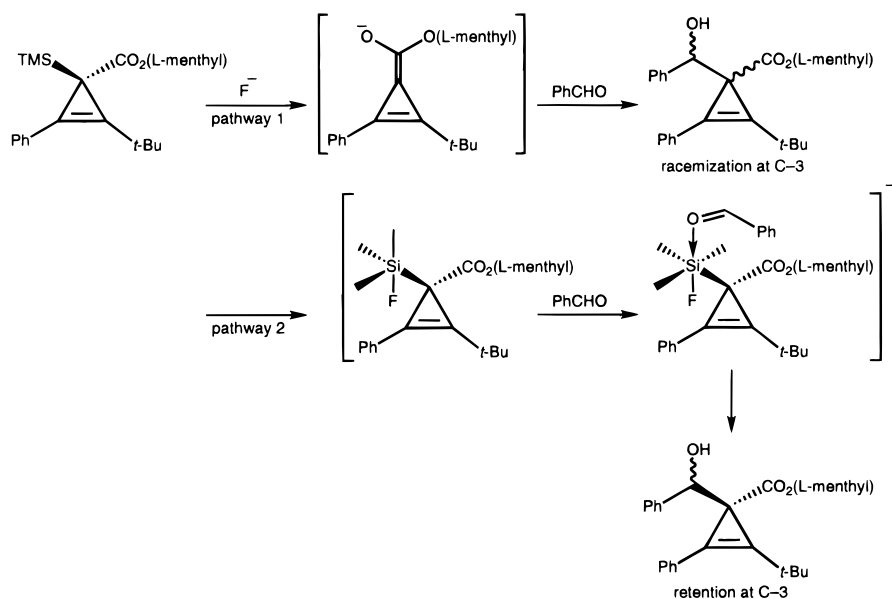
(19) The structures of P2-F and P5-5 are as follows: (Me₂N)₃P=N⁺=P(NMe₂)₂F⁻ and ((Me₂N)₃P=N)₂P⁺F⁻, respectively. Schwesinger, R.; Link, R.; Thiele, G.; Rotter, H.; Honert, D.; Limbach, H.; Männle, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1372–1375.

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(21) When THF-*d*₃ was used as the solvent, no deuterium was incorporated into **6**. This strongly suggests that this product does not arise via a radical pathway.

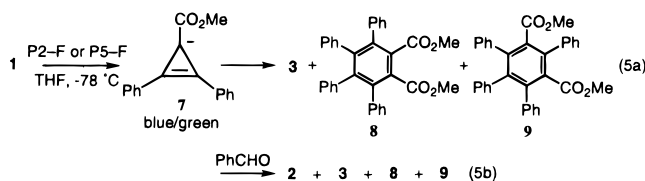
(22) Trapping in DMSO also leads to a 1:1 mixture of proton-trapped products.

Scheme 1



methodology thus may be useful for measuring the inversion barrier of a pyramidal cyclopropenyl anion.

Substitution of a phenyl group for the *tert*-butyl substituent in **4** will lead to a more stable cyclopropenyl anion. We therefore decided to examine the fluorodesilylation of 3-carbomethoxy-1,2-diphenyl-3-trimethylsilylcyclopropene (**1**) in the absence of an added electrophile. TBAF is unsuitable for this purpose because of the residual water in the reagent; protodesilylation takes place in this case.¹⁷ Schwesinger's P2-F and P5-F fluoride sources, however, can be made anhydrous and relatively free of protic (alcohol) contamination.^{19,20} Consequently, P2-F or P5-F was reacted with **1** at $-78\text{ }^\circ\text{C}$ in the absence of an added electrophile. Upon mixing the reagents the solution turns dark blue/green and the color persists for extended periods of time before turning yellow.²³ A water quench of the reaction mixture causes the yellow color to disappear and leads to the recovery of proton-trapped material along with *o*- and *m*-tetraphenylterephthalate (eq 5); the *meta* isomer predominates at low temperature whereas



the *ortho* product and the terephthalates are favored at higher temperature.^{24–27} If benzaldehyde is added to the blue/green

(23) The lifetime of the blue/green color depends on the amount of methanol or 2-propanol present in the fluoride source. We have prepared solutions which persist for up to 1 h, but longer times are possible since all of our fluoride reagents have had some protic impurities.

(24) The *meta* product can be accounted for by a pathway previously suggested by Breslow (refs 25–27) involving the addition of **7** to either **1** or **3**. The *ortho* product requires a different pathway, and we suggest that at elevated temperatures **7** decomposes to its corresponding radical which rapidly dimerizes. The dimer subsequently undergoes a fluoride-induced rearrangement to **8**.

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(28) Additional bands at 336, 353, 387, and 478 nm also are predicted, but the intensities are relatively small, or the absorptions fall in a region where they would be obscured.

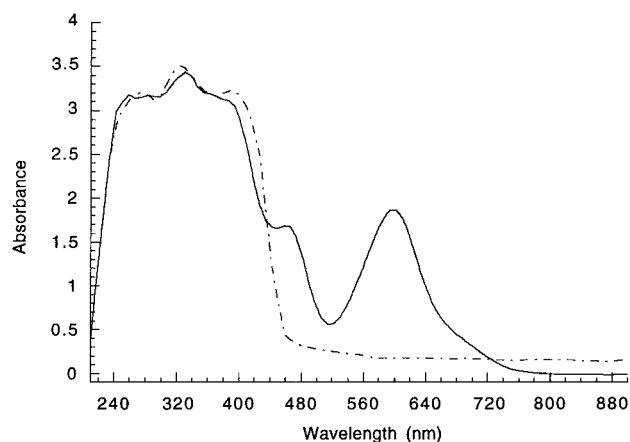


Figure 1. UV/visible spectrum of **7** at $-72\text{ }^\circ\text{C}$ (solid line) and the spectrum after quenching with benzaldehyde (dashed line).

solution, the color rapidly disappears, and a small amount of trapped alcohol (**2**) is obtained along with **3**, **8**, and **9**.

A low temperature ($-72\text{ }^\circ\text{C}$) UV–visible spectrum of the blue/green solution was obtained (Figure 1). Upon addition of the fluoride source to the cyclopropene new bands at 380, 480, and 600 nm were simultaneously observed. Subsequent addition of benzaldehyde led to the rapid disappearance of the 480 and 600 nm absorptions but not the feature at 380 nm. Independent preparation of $(\text{TMSF}_2)^- \text{P5}^+$ via the reaction of TMSF with P5-F revealed that this compound is responsible for the high energy band at 380 nm. As none of the starting materials or products absorb above 350 nm, we attribute the absorbances at 480 and 600 nm to the cyclopropenyl anion **7**. CIS calculations on 3-carbomethoxycyclopropenyl anion (**7** without the two phenyl substituents) are in good accord with this assignment in that absorbances at 426 and 545 nm are predicted and the absence of the phenyl groups should lead to a blue shift.²⁸

Additional experiments and computations on transient and long-lived cyclopropenyl anions will be reported in due course.

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