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Computational Discovery of a Novel Automerization Process for 1-Fluorocyclopropene

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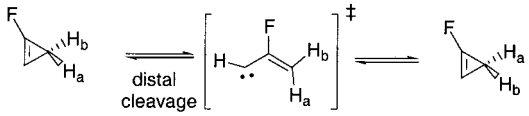
ABSTRACT



Both DFT and CCSD and CCSD(T) computational methods indicate that 1-fluorocyclopropene can undergo an unprecedented "electrocyclic" automerization process involving a full 180° rotation of its methylene group, without the formation of an intermediate carbene or diradical.

Numerous computational and experimental studies of fluorinated cyclopropanes have clearly demonstrated the unique influence of fluorine substituents on cyclopropane structure and reactivity.[1−3] In particular, the presence of geminal fluorine substituents gives rise to a significant increase in strain and an elongation of the C_2-C_3 bond, which is accompanied by a significant, specific weakening of this bond, a fact reflected by the relative E_a's for the thermal interconversion of *cis*- and *trans*-1,1-difluoro-2,3-dimethylcyclopropane and its nonfluorinated analogue.[2]

In keeping with our interest in the influence of fluorine substituents on the structure and reactivity of small-ring compounds, a study of the effect of fluorine on cyclopropene has been initiated, and our preliminary computational results related to 1-fluorocyclopropene are hereby presented in this Letter.

The structures of all and energies of most of the fluorine-substituted cyclopropenes have been previously examined computationally,[4−6] most importantly in a recent paper by Wiberg,[7] who however did not look at the 1-fluorocyclopropene system. Our DFT calculations,[8−13] consistent with recent ab initio calculations by Panchencko,[5] revealed that a *single* fluorine substituent at the 1-position of cyclopropene exerts an influence on its structure that is very similar to that of geminal fluorines on the structure of cyclopropane. That is, the distal (C_2-C_3) bond is lengthened to 1.559 Å

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(8) All structures were optimized using density functional theory calculations within the Gaussian98w program package.[9] The level of theory was set to Becke's hybrid three-parameter functional (B3LYP),[10] and using the 6-31G(d) basis set,[11] frequency calculations were performed on all stationary points to identify transition structures and to determine thermochemical information. Transition structures were characterized by a single imaginary frequency. Thermal energies and entropy terms were obtained using frequencies scaled by 0.9807 at 298.15 K and 1 atm.[12] An intrinsic reaction coordinate (IRC) calculation was performed for each transition structure to follow the entire reaction pathway for each transition structure. Single-point energies were calculated using B3LYP level of theory and the 6-311+G(2df,2p) basis set.[13] Calculated rate constants were derived from transition-state theory.

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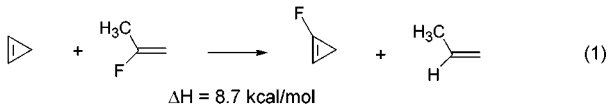
and the proximal (C_1-C_3) bond is shortened to 1.472 Å (from the normal 1.509 Å of cyclopropene).

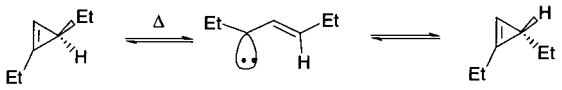
DFT energy calculations,[8] as reflected by isodesmic eq 1,



(1)

indicate that the 1-fluoro substituent also gives rise to a significant increase in strain in the system. Since the *single* fluorine substituent of 1-fluorocyclopropene increased the molecule's strain, shortened its proximal, C_1-C_3 bond, and lengthened its distal, C_2-C_3 bond, much as two fluorine substituents did to cyclopropane, we wondered if, as for the cyclopropane systems, 1-fluorocyclopropene would also exhibit an enhanced *reactivity* of its distal bond.

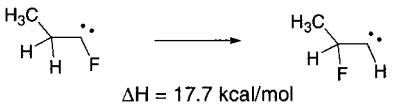
Cyclopropene itself undergoes a number of characteristic thermal unimolecular processes, including irreversible isomerization to allene and propyne.[14−16] However, it also undergoes a thermal automerization process via C_1-C_3 homolysis to form an intermediate vinylmethylene, which can revert to the cyclopropene. The thermal racemization of chiral cyclopropenes has been proposed to proceed via such a two-step mechanism.[17] The details of this mechanism of ring-opening and recyclization of the vinylmethylene, as well as of the other unimolecular processes of cyclopropene, have been elucidated by a number of computational studies, the most



important of which were the series of papers by Yoshimine, Pacansky, and Honjou.[18,19] Although these papers, and the experimental studies that followed,[20,21] indicate that the structural isomerizations of cyclopropene proceed largely via a vinylidene intermediate (E_a = 41.5 kcal/mol), their calculations also confirm that a lower energy, automerization process (E_a = 36.5 kcal/mol) can proceed via the vinylmethylene intermediate originally proposed by Bergman.[17]

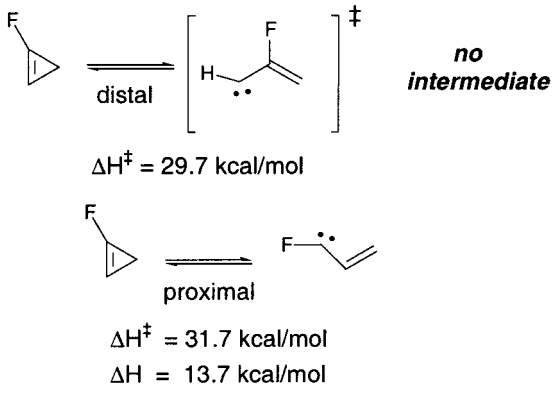
In our initial examination of the reactivity of 1-fluorocyclopropene, the homolyses of the proximal, C_1-C_3 and distal, C_2-C_3 bonds were examined computationally using DFT [B3LYP/6-311+G(2df,2p)//B3LYP/6-31G(d)] methodology.[8]

It is interesting that although the geometrical distortions of 1-fluorocyclopropene's ground-state structure deriving from the fluorine substituent point toward favored C_2-C_3 homolysis, the carbene potentially formed by such homolysis will be considerably less stable than that formed by the C_1-C_3 homolysis (because of fluorine's ability to stabilize carbenes). Isodesmic eq 2 below gives an estimate of the relative effects of α- versus β-fluorine substitution on the stability of a carbene structure.



(2)

What our calculations[8] revealed was that, despite the large difference in probable stability of the two vinylmethylene intermediates that could be potentially formed by the two competing homolyses, the distal bond has a slightly lower barrier to cleavage than the proximal bond. More surprisingly, upon distal cleavage *no vinylmethylene intermediate is formed*. Instead, the homolysis is accompanied by a 180° rotation of the C_3 methylene group to re-form the cyclopropene, with such rotation occurring *via a single transition state*. Therefore it appears that the potential vinylmethylene structure is not an intermediate in this rotational process but is rather a transition state.



An energetic comparison of distal versus proximal bond cleavage is depicted in Figure 1. The computed barrier for breaking the proximal bond, to form the fluorine-stabilized

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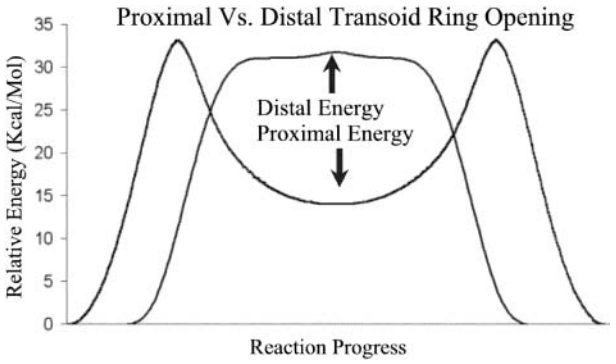

Figure 1. Comparison of energy surfaces for distal versus proximal ring-opening for 1-fluorocyclopropene.

vinyl, fluoromethylene intermediate, is only slightly greater (1.9 kcal/mol) than that for breaking the distal bond. In this case the expected carbene intermediate is formed, and the energy of this intermediate is actually much lower than that of the transition state for the distal automerization process.[22]

Realizing that the DFT method might have limitations that would limit its ability to detect a small energy minimum for the carbene, CCSD and CCSD(T) methods,[23−28] which should provide an unambiguous perspective, were applied to this system, with effectively the same result being obtained. That the carbene is indeed a transition state is indicated by the calculated CCSD(T) energies, which indicate no difference between the transition state and the carbene energies (−215.455 and −215.455 Hartrees, respectively, which equates to 29.44 kcal/mol each). Calculating the vibrational frequencies using CCSD(T) confirmed this, since one of the frequencies was imaginary.

Therefore, 1-fluorocyclopropene appears to undergo an unprecedented "electrocyclic" automerization process involving a 180° rotation of its methylene group, without the formation of an intermediate carbene or diradical. Experimental substantiation for this novel, predicted transformation is currently being sought, although the small difference in activation barriers between distal and proximal cleavage, combined with the significant stability of the fluorovinylmethylene intermediate obtained from proximal cleavage, may lead to reactions being derived from this intermediate.

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Supporting Information Available: Molecular geometries, energies, thermal energies, and entropies for 1-fluorocyclopropene and vinylmethylene intermediates and transition states derived therefrom (including CCSD and CCSD(T) energies), and of molecules used in isodesmic equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Note that the 17.7 kcal/mol difference between an α-fluoro- and a *β*-fluorocarbene that was estimated in eq 2 provides a value for the energy of the putative carbene intermediate from distal bond cleavage (31.4 kcal/mol) that is quite close, but higher than the computed $\Delta E^{\ddagger}$ value of 29.7 kcal/mol.

(23) **Computational Methods**. The carbene was shown to be a transition state at the CCSD(T) level of theory[24] using a basis set of triple-*ζ* plus double polarization[25] quality. The harmonic frequencies needed to show that the structure is a transition state[26,27] were obtained analytically.[28]

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