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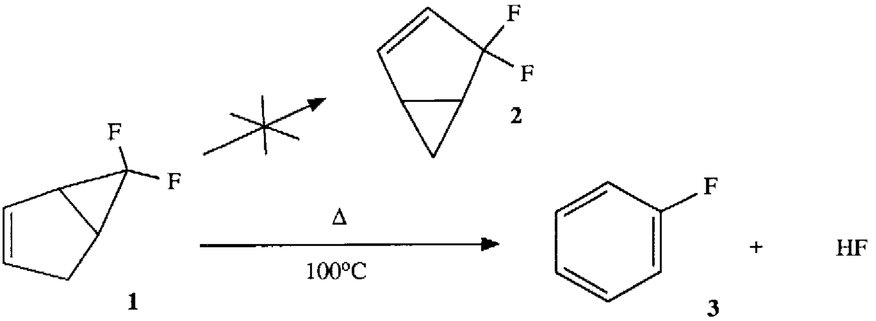
The Thermal Conversion of 6,6-Difluorobicyclo[3.1.0]hex-2-ene to Fluorobenzene. A Novel Mechanism

William R. Dolbier, Jr.*, Jeffrey J. Keaffaber[1a], Conrad R. Burkholder,
Simon F. Sellers, Henryk Koroniak[1b] and Jyotsna Pradhan[1c]

Department of Chemistry, University of Florida, Gainesville, FL 32611

Abstract. The dehydrofluorinative aromatization reaction of 6,6-difluorobicyclo[3.1.0]hex-2-ene (**1**) has been found to proceed via a two-step mechanism, the first being a novel, rate-determining homolytic H-shift process.

Numerous investigations have shown that vinylcyclopropane rearrangements are to be expected when bicyclo[3.1.0]hex-2-enes undergo thermal isomerization.[2-6] In this respect, the thermal conversion of 6,6-difluorobicyclo[3.1.0]hex-2-ene (**1**) to 4,4-difluorobicyclo[3.1.0]hex-2-ene (**2**) should have the additional advantage of both a kinetic and a thermodynamic impetus.[7] It was thus a surprise when only a dehydrofluorinative, aromatization process to form fluorobenzene was observed in the pyrolysis of **1**[8] at temperatures as low as 70°C, even in the gas phase. Adding to the puzzlement were rate studies of the reaction in the gas phase which indicated that the observed HF extrusion was a well-behaved first-order process, an unexpected result considering that analogous losses of HCl from 6,6-dichlorobicyclo[3.1.0]hex-2-enes[10] are reported to be solvolytic processes involving rate-determining loss of Cl^- to form carbocation intermediates, hardly the type of process one would expect to occur in the gas phase.



We wish to report, at this time, the results of a preliminary study of the HF extrusion process of **1** which indicate that a novel, non-solvolytic thermal rearrangement process is operative in this system.

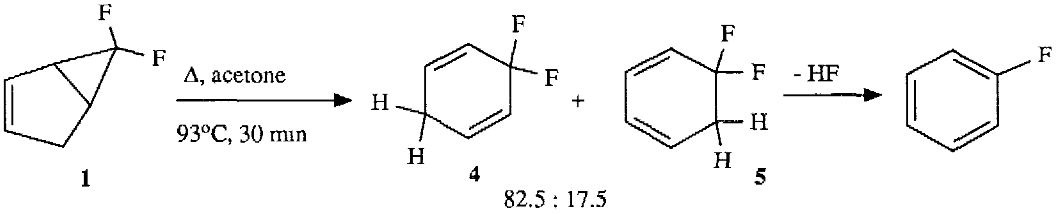
The thermal dehydrofluorinative aromatization of **1** exhibits kinetic behavior characteristic of a non-polar, unimolecular process. As can be seen from the rate data (Table), little solvent dependency is observed ($k_{DMF}/k_{acetone}$= 3.8 at 93°C). Indeed, a plot of the gas phase rate data gives activation parameters characteristic of a normal unimolecular rearrangement process:

Table. Rate Constants for the Thermal Aromatization of **1**

Solvent	Temp.,°C	k(x10^5),sec^{-1}	Solvent	Temp.,°C	k(x10^5),sec^{-1}
gas phase	74.0	0.213±0.02	gas phase	131.3	74.7±3
"	96.0	2.57±0.2	acetone	93.0	56.1±2
"	105.5	8 08±0.5	n-hexane	93.0	4.25±0.3
"	114.8	15.9±0.9	DMF	93.0	214±6
"	123.3	29.8±0.9			

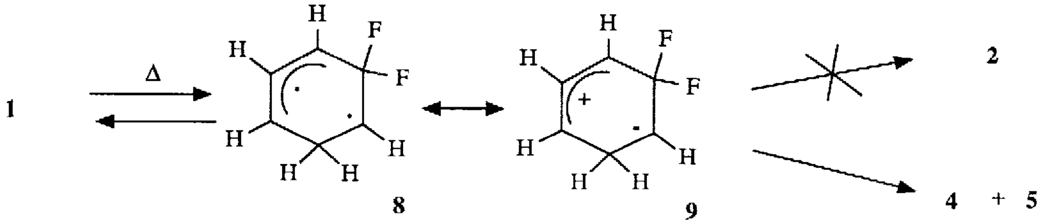
$$\log A = 11.6 \pm 0.5, \ E_a = 27.4 \pm 0.8 \text{ kcal/mol}$$

The definitive proof that a rearrangement, not an ionization, process is involved in this reaction came from a detailed examination of the reaction in solution. In acetone it was found that after 30 min of reaction at 93° practically no fluorobenzene had been formed, while **1** had been converted almost completely to two intermediate products. These products were stable enough at RT in acetone to be characterized by ^{1}H and ^{19}F nmr, but they converted slowly to fluorobenzene The two intermediates, formed in a 4 7:1 ratio were identified to be 3,3-difluoro-1,4-cyclohexadiene (**4**) and 5,5-difluoro-1,3-cyclohexadiene (**5**).[11,12]



Therefore it is apparent that the mechanism for aromatization of **1** involves rate-determining hydrogen shift processes.[13] However, an important question remains as to whether the observed reaction is pericyclic in nature, or whether it involves a preequilibrium bond-homolysis which is followed by the hydrogen shift. In attempting to gain insight into this question, a primary kinetic deuterium isotope effect (k_H/k_D = 2.55 at 93°C) was observed by comparing the gas-phase rates of rearrangement of **1** to its 1,2,3,4,4,5-hexadeuterio analog, **6**.[16] Also, in a preliminary study of the 4-deuterio species, **7** (a 50:50 mixture of endo/exo epimers)[16], it was found that the epimeric ratio in recovered **7** remained constant throughout the reaction.

The observation of a primary kinetic isotope effect (indicating a rate-determining H-shift), coupled with the constancy of the endo/exo ratio during the course of the thermolysis (indicating either a planar intermediate or interconversion of endo and exo isomers much faster than rearrangement), and the observed nonregiospecificity of the H-shift (almost inconceivable if the process were to be a direct pericyclic conversion from **1**), virtually rule out a pericyclic H-shift mechanism for formation of intermediates **4** and **5**. A mechanism involving diradical intermediate **8** is consistent with the observed facts, but that being the case, there remains still another significant question, namely why the mechanistically-accessible vinylcyclopropane rearrangement to **2** is not observed to occur. *All* other thermal isomerizations of bicyclo[3.1.0]hex-2-ene systems, including those of the kinetically and thermodynamically closely-related 6-methylenebicyclo[3.1.0]hex-2-enes,[6] proceed via such rearrangements, with hydrogen-shift processes not being kinetically competitive. Indeed for the parent hydrocarbon system there is an observed ΔE_a of ~7 kcal/mole between the vinylcyclopropane and the H-shift processes.[18]



Why should such a diradical as **8** undergo an exclusive H-shift in preference to simple cyclization to its more stable isomer **2**? The answer to this question may derive from our understanding of the special effect of fluorine substituents on the electron distribution of molecules. If "diradical" **8** were to have an electron distribution resembling dipolar resonance form **9**, then the H-shift step might be expected to be enhanced significantly. Regardless of the rationale for this unexpected observation, the conclusion that the aromatization of **1** occurs via a rate-determaining, non-pericyclic H-shift mechanism, similar to that observed in the homolytic cyclopropane to propene conversion,[19] would appear to be inescapable.

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References and Footnotes

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8. Substrate **1** was synthesized by addition of CF_2: to cyclopentadiene,[9] and it was characterized by ^1H, ^{19}F and ^{13}C nmr spectroscopy as well as by high and low resolution mass spectrometry.
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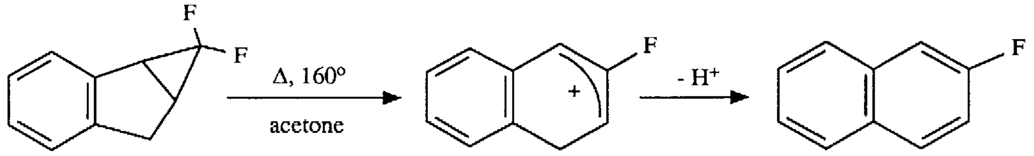
11. Intermediates **4** and **5** were identified largely on the basis of their characteristic ^{19}F nmrs (**4**: ϕ70.0 ppm, t of t, J = 16.9 and 5.1 Hz; **5**: ϕ77.3 ppm, t of d, J = 22.4 and 6.0 Hz), and by the fact that they convert (**4** considerably more rapidly than **5**) quantitatively to fluorobenzene.
12. These intermediates could also be observed when the reaction was carried out in DMF (ratio = 2.5 at 93°) but not at all in hexane or in the gas phase.
13 In interesting contrast, it was demonstrated[1a] that benzannelated analog **10** undergoes dehydrofluorinative aromatization via the ordinary solvolytic pathway which is characteristic of 1,1-dihalocyclopropanes.[14,15]



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