Tetrahedron Vol. 48, No. 44, pp. 9649-9660, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

THE THERMAL CONVERSIONS OF 6,6-DIFLUOROBICYCLO[3.1.0]HEX-2-ENES TO FLUOROBENZENES. AN INTERESTING DICHOTOMY OF MECHANISMS[1]

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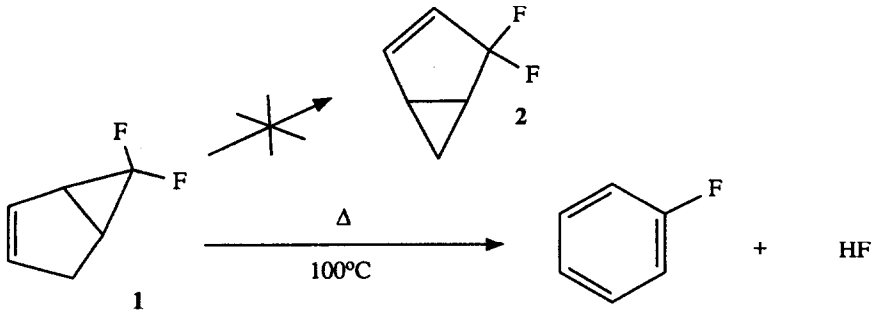
(*Received in USA* 18 *August* 1992)

Abstract: A kinetic study of the thermal, dehydrofluorinative aromatization reactions of two ostensibly-similar 6,6-difluorobicyclo[3.1.0]hex-2-ene systems led to the conclusion that drastically different mechanisms operate for the two reactions. Activation parameters, solvent effects, kinetic isotope effects, isotope labelling experiments and observation of reactive intermediates all contributed to the conclusion that the reaction of 6,6-difluorobicyclo[3.1.0]hex-2-ene, **1**, proceeds via a homolytic hydrogen-shift rearrangemet, while the reaction of 2,3-benzo-6,6-difluorobicyclo[3.1.0]hex-2-ene, **6**, proceeds via a solvolytic mechanism involving rate-determining carbocation formation.

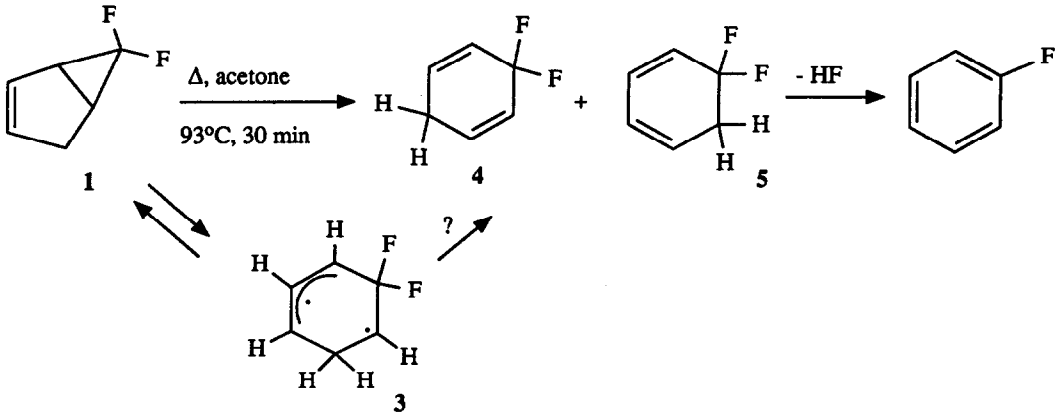
A number of years ago, in studying the thermal rearrangements of a series of bicyclo[n.1.0] gem-difluorocyclopropane systems,[2] we observed the curious gas phase dehydrofluorinative aromatization reaction of 6,6-difluorobicyclo[3.1.0]hex-2-ene, **1**.



On the basis of precedent from the hydrocarbon literature[3-7] and the known effect of gem-difluoro substituents on the kinetic behavior of cyclopropanes,[8] we had expected to observe in this reaction the facile vinylcyclopropane rearrangement of **1** to **2**. No such rearrangement could be detected.

The reaction which was observed had the gas-phase kinetic behavior of a first-order, unimolecular reaction and yielded Arrhenius parameters which were consistent with such: Log A = 11.6 ± 0.5, E_a = 27.4 ± 0.8 kcal/mole. Such unexpected results raised a number of questions. First and foremost, *what is the mechanism* of this first-order reaction?

The 6,6-Difluorobicyclo[3.1.0]hex-2-ene System - The question of mechanism was at least partially answered when unstable intermediates **4** and **5** were detected in the early stages of the reaction when it was carried out in acetone or DMF solution. For example, after 20 minutes at 93 °C, 69% of **1** had converted to a 5.5:1 ratio of **4**:**5**. The 3,3-difluoro-1,4-cyclohexadiene, **4**, was characterized largely by its in-situ ^{19}F nmr



spectrum (ϕ = -70.0 ppm, t of t, J = 16.9 and 5.1 Hz). 5,5-Difluoro-1,3-cyclohexadiene, **5**, was similarly characterized (ϕ = -77.3 ppm, t of d, J = 22.4 and 6.0 Hz). Table 1 shows the product distribution as a function of time. As one can see, little fluorobenzene is formed in the initial stages of the reaction, but its

Table 1. Product Ratios for the Thermolysis of **1** in Acetone at 93 °C.

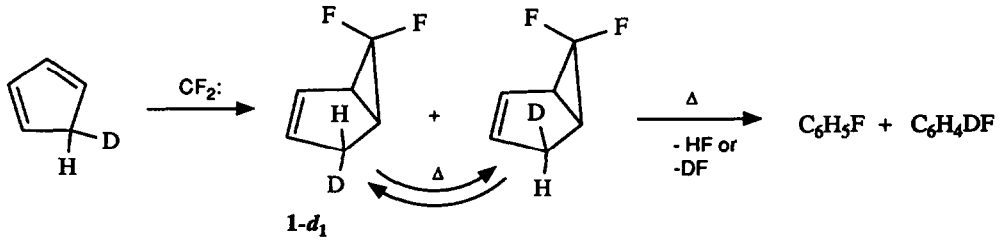
t, min	1	fluorobenzene	4	5	ratio 4:5
0	91.2	8.8	0	0	-
10	55.4	9.5	29.6	5.5	5.4
20	37.8	9.7	44.4	8.1	5.5
30	23.1	11.3	54.8	10.7	5.1
60	4.9	74.6	9.2	11.4	0.81

formation would seem to be autocatalytic. In all likelihood, the coproduct from the formation of fluorobenzene, HF, catalyzes the loss of HF from **4** and **5**. The reason that **4** and **5** are observed in acetone and DMF solutions, but not in the gas phase or hexane reactions of **1**, also likely derives from this reactivity of HF. DMF and acetone are known to somewhat "tame" the reactivity of HF, while in hexane and the gas phase HF's ability to assist in F^- loss from **4** and **5** would be unabated. The good first-order behavior of **1** in all of the solvents indicates that HF does not effectively catalyze its thermal reaction. Addition of KF, a notorious HF sponge, to reaction mixtures also did not affect the rates of reaction of **1**.

The mechanism thus clearly appears to involve a 1,2-hydrogen shift as the mechanistically-significant step. Whether this H-shift reaction is pericyclic or whether it involves a preequilibrium homolytic cleavage to form diradical intermediate **3** is not totally clear, but a kinetic study of 4-deuterio- and perdeuterio-substituted substrate provided values of k_H/k_D = 1.73 (93 °C in acetone), for the intramolecular, and k_H/k_D = 2.29 (84 °C in acetone), for the intermolecular kinetic deuterium isotope effects, respectively. The former effect clearly represents the primary deuterium isotope effect for the *product-determining* hydrogen-shift process. The latter is some combination of secondary and perhaps primary isotope effects for the *rate-determining* process, which could be C_1-C_5 homolysis, the H-shift, or

some combination thereof.

It was also observed that the ratio of exo to endo hydrogens at the 5-position remained *constant* during the course of the pyrolysis of **1-d_1**. This indicates, primarily, that **1** cannot be converting *directly* to **4** and **5** via a pericyclic process, unless a mechanistically-independent equilibration of the exo and endo species is competing with the H-shift. (It would be very unlikely that the exo and endo hydrogens would shift with identical kinetic propensity in a pericyclic process.) More likely is the mechanistic path whereby



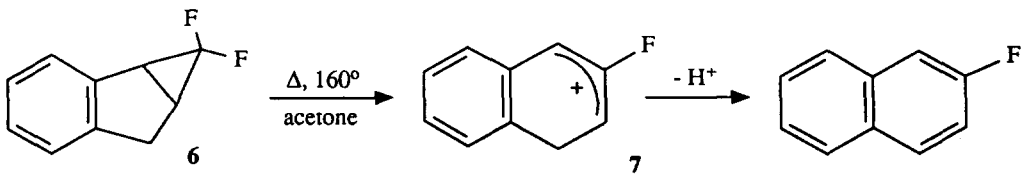
1-d_1

1 undergoes homolysis of the C_1-C_6 bond to form planar (or easily planarized) diradical **3**, which undergoes competitive hydrogen-shift processes to form products **4** and **5**. Another finding which unambiguously implicated the H-shift mechanism was the observance, by deuterium nmr, of deuterium at the ortho and para position of the fluorobenzene product formed from **1-d_1**. The observed ratio of *o*:*m*:*p* was 5.2:80.6:14.2. Possible spurious deuterium incorporation at the ortho and para positions by a deuterium-exchange process involving electrophilic deuteration of fluorobenzene by DF was ruled out by the lack of ms detection of any *di*deuterated fluorobenzene in the product mixture.

Because of the lack of observation of the expected product **2** one must invoke, within this mechanistic scheme, the caveat that diradical **3** either is inhibited from cyclizing to **2** or simply preferentially undergoes the observed hydrogen shifts to form products **4** and **5**. Since in analogous hydrocarbon systems the hydrogen-shift processes are much higher activation-energy-processes than the respective vinylcyclopropane rearrangement processes ($\Delta\Delta G^{\neq}$ = 7 kcal/mole), one must conclude that somehow the fluorine substituents in diradical **3** perturb the reactivity of the intermediate in such a way as to divert its thermal chemistry towards the hydrogen-shift process.

Thus there is a curious aspect of this problem which requires further attention, namely the question of how and why the fluorine substituents in **1** give rise to such an enhanced rate of hydrogen-shift relative to its vinylcyclopropane rearrangement. Studies dedicated to the understanding of this unusual behavior are currently in progress.

Benzo System - Because of the relative thermal instability of **1** and the resultant difficulties in its handling, it was decided early on to try to use the more-stable and more-easily prepared benzannelated analogue **6** for carrying out the mechanistic investigations of the aromatization process.

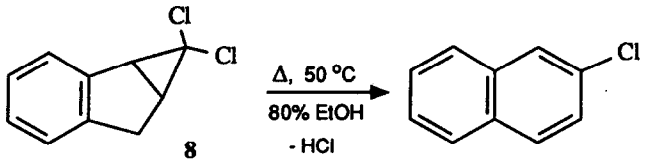


6 **7**

Not unexpectedly **6** proved to be considerably less reactive, requiring temperatures >140 °C for its

dehydrofluorinative aromatization reaction to occur. This reaction, however, exhibited very different kinetic character from **1**, characteristics which were more consistent with the reaction proceeding via an *ionization* mechanism rather than a homolytic H-shift process!

It is well known that halo and dihalo cyclopropanes undergo solvolyses via a mechanism which involves synchronous ionization and disrotatory electrocyclic ring-opening of the incipient cyclopropyl cation to an allyl cation.[9,10] The kinetic and stereochemical aspects of such reactions have been studied at length.[10,11] Among the systems studied was **8**, the dichlorocarbene adduct of indene, which was found by Parham to aromatize with loss of HCl at 50 °C in 80% EtOH.[12] The mechanisms of this and related



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reactions have been demonstrated to involve rate-determining, ring-opening ionization of chloride ion to form intermediates analogous to **7**, followed by rapid proton loss to form 2-chloronaphthalene.

The aromatization of **6** gave every indication of proceeding via an analogous mechanism. The activation parameters for its reaction in acetone [Log A = 8.0, E_a = 24.2 kcal/mole] reflect a large negative entropy of activation [$\Delta S^{\neq}$ = -25 cal/deg.](Table 2), a result which is characteristic of the unusually high

Table 2. Arrhenius Parameters for Bicyclo[3.1.0]hex-2-ene Systems

Substrate	Solvent	Log A	E_a[a]	$\Delta H^{\neq}$[a]	$\Delta S^{\neq}$[b]
1	gas	12.0 ± 0.5	28.0 ± 0.8	27.3 ± 0.8	-6.0 ± 2
6	acetone	8.0 ± 0.1	24.2 ± 0.3	23.3	-24.6
6	HOAc	12.0 ± 0.3	27.0 ± 0.5	26.2	-5.9
9	acetone	13.8 ± 0.2	26.3 ± 0.3	25.7	+2.3
10	acetone	10.0 ± 0.3	25.6 ± 0.5	24.7	-15.6

[a]kcal/mole; [b]cal/deg.

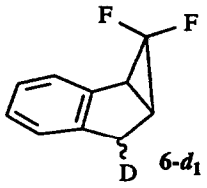
solvation demands for F^- formation in the transition state. As expected, this entropy effect is considerably diminished when the reaction is carried out in acetic acid [Log A = 12.0, E_a = 27.0 kcal/mole, $\Delta S^{\neq}$ = -6 cal/deg.]. Also, as would be expected for an ionization process, there was a significant solvent effect exhibited for the reaction: $k_{DMF}/k_{acetone}$ = 468 at 70 °C. This can be contrasted with the value of 3.8 (at 93 °C) observed for the non-ionizing rearrangement of **1**.

As in the case of **1**, the monodeuterio derivative of **6** was prepared as a 50:50 mixture of endo and exo isomers, and its aromatization process examined. As was observed for **1-d_1**, the exo/endo ration of **6-d_1** did not change during the course of the reaction, thus indicating that the proton(deuteron) loss occurred *after* the rate-determining step. A *product-forming* isotope effect of k_H/k_D = 1.31 (at 50 °C) was observed, and we consider this consistent with expectations for a primary isotope effect for an aromatization process involving proton-loss. Isotope effects in the range of 1.4 - 2.0 have been observed previously for *non*-aromatization E_1 processes.[13-15]

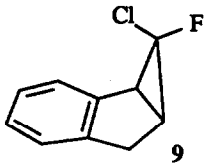
No deuterium was detected at the 3-position of the 2-fluoronaphthalene product, where some would have inevitably been had **6** undergone a 1,2-hydrogen shift mechanism analogous to that of **1**.

Therefore, the evidence is overwhelmingly in favor of a mechanism for this reaction which involves rate-determining loss of endo-fluoride concomitant with a disrotatory electrocyclic ring-opening of the

incipient cyclopropyl cation to form the carbocation intermediate **7**, which rapidly loses a proton to form the 2-fluoronaphthalene.



6-d_1



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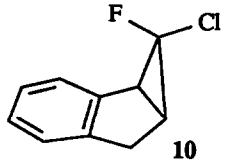

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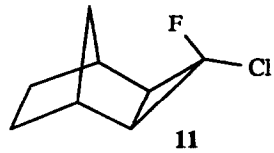

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The Chloro, Fluoro System - An interesting and pertinent related study involved the dehydrohalogenative aromatization reactions of the epimeric adducts of chlorofluorocarbene to indene.

The endo-chloro compound, **9**, was found to easily lose Cl^- at >40 °C in acetone to form 2-fluoronaphthalene, while the endo-fluoro epimer, **10**, was totally unreactive under analogous conditions, requiring temperatures >140 °C to undergo loss of F^- to form 2-chloronaphthalene as the only product. A determination of activation parameters reflected similar enthalpies of activation for the two reactions (25.7 and 24.7 kcal/mole, respectively). Indeed the main cause for the two epimers' observed difference in reactivities was found to be their respective entropies of reactions, with the chloride loss having a slightly positive $\Delta S^{\neq}$ (+2.3 cal/deg), while the fluoride loss gave rise to a *large* negative $\Delta S^{\neq}$ (-15.6 cal/deg).

The studies of **9** and **10** clearly indicated that these epimers were *not* interconverting under the solvolysis conditions, a result which lent further credibility to the proposed ionizing mechanism for aromatization of **6**.

There have been reported three interesting, related studies of bicyclic chlorofluorocyclopropanes. First, in 1972, Jefford reported that in the addition of chlorofluorocarbene to norbornene, only the endo-fluoro adduct, **11**, could be isolated, the other epimer apparently undergoing loss of Cl^- during isolation.[16] **11**, was found to specifically lose F^- upon solvolysis, a result consistent with our observations.

In contrast, Wakselman claimed that *both* chlorofluorocarbene adducts of 1,4-dioxene, obtained in a 58:42 ratio, undergo exclusive Cl^- loss.[17] Particularly in the ethanolic medium, this is a suspicious report, because we found that the prohibitive entropic requirements for F^- vs Cl^- loss (which we observed in acetone solvent for **6**) become considerably reduced in a protic solvent (as we observed for **6** in HOAc).

In a third report, Volchkov reported a study of our very system, i.e. epimers **9** and **10**.[18] In their report they certainly observed a difference in reactivities for the two epimers, but they claim that *both* epimers specifically lose chloride ion. This clearly cannot be correct. In our hands, *only* 2-chloronaphthalene was obtained in the pyrolysis of **10** in acetone, while *only* 2-fluoronaphthalene was obtained from the pyrolysis of **9**.

Conclusions - Although a homolytic hydrogen-shift mechanism appears to be operative in the thermal dehydrofluorinative aromatization of 6,6-difluorobicyclo[3.1.0]hex-2-ene, **1**, the ostensibly similar reaction of the benzannelated system **6** appears unambiguously to proceed via a solvolytic mechanism involving rate-determining carbocation formation.

In acetone, at 100 °C, the rate data indicate a $\Delta\Delta G^{\neq}$ of ~5 kcal/mole for the homolytic process of **1** versus the solvolytic process of **6**. However, the E_a's for the two processes show that the solvolysis of **6** actually has a *lower* activation energy than the homolytic process of **1** (24.2 vs 25.5 kcal/mole). Thus it is obviously the more favorable activation entropy for the homolytic H-shift process which allows such

mechanism to compete favorably with the potential solvolytic pathway in the case of **1**. Indeed, in more polar solvents, particularly protic solvents where negative entropies of activation for F^- loss are not prohibitively high, the solvolytic pathway for aromatization of **1** may well compete. Appropriate experiments to test this possibility were not carried out, but it can be clearly seen that the homolytic and the solvolytic pathways for thermal reaction of **1** are *very* close in free energy requirement.

In all likelihood, *only* geminal fluorine substituents at the 6-position of **1** will give rise to the hydrogen-shift mechanism in the pyrolysis of bicyclo[3.1.0]hex-2-enes. They appear both to inhibit the solvolytic mechanism, largely due to entropy effects, and to enhance the H-shift process in some way not yet completely understood. Any other 6,6-dihalogenobicyclo[3.1.0]hex-2-ene would almost surely undergo aromatization by a preferential solvolytic mechanism.

EXPERIMENTAL SECTION

6,6-Difluorobicyclo[3.1.0]hex-2-ene (1). The procedure used in this synthesis is that of Wojtowicz & Dolbier.[19]

A 100 mL 3-necked round bottom flask was equipped with a magnetic stirrer, thermometer, rubber septum with N_2 inlet needle and a pressure-equalizing addition funnel. The system was flushed with N_2 and 10 mL of dry THF, 1.49g (22.8mmol) activated zinc and 0.50g (7.6mmol) of freshly cracked cyclopentadiene was added. In addition, a small crystal of iodine was added. The addition funnel was charged with 4.79g (22.8mmol) of CF_2Br_2 in 10 mL THF. The CF_2Br_2 was added over a 1.5-2 hour period slowly with the reaction temperature not exceeding 30 °C. After addition, the mixture was allowed to stir for one hour at room temperature as the zinc was slowly consumed. The reaction mixture was then washed twice with water and the organic layer was separated. The yield as determined by ^{19}F NMR was 21% using hexafluorobenzene as the internal standard. The product **1** was separated and purified by preparative gc using a Triton X-305 column at 50 °C/60 psi. A total of 425mg was obtained:

^1H NMR (300 MHz), δ 5.72 (complex m, 1H, olefinic), 5.63 (m, 1H, olefinic), 2.82-2.58 (complex m, 3H, $-CH_2-$, cyclopropyl H), 2.20 (m, 1H, cyclopropyl H); ^{19}F NMR, ϕ = -155.7 (d, $^2J_{FF}$ = 146.8 Hz); -129.4 (ddd, $^2J_{FF}$ = 146.5 Hz, $^3J_{cisHF}$ = 11.1 Hz); mass spectrum, m/z (% relative intensity) 116 (M^+, 1.93), 96 (9.72), 64 (22.76), 46 (100.00).

Thermal Rearrangement of 6,6-difluorobicyclo[3.1.0]hex-2-ene(1). 6,6-Difluorobicyclo[3.1.0]hex-2-ene (60.0mm) was expanded into a well-conditioned pyrolysis bulb and pyrolyzed at six temperatures between 74.0 and 131.25 °C.[2] An internal standard (benzene) was added (15.0mm). The reaction was followed by gc using a 2 ft. x 1/8 in., CARBOPACK C column at 50 °C. The rate constants are given in Table 3. The pyrolysis afforded fluorobenzene as the sole product, easily characterized by its ^{19}F NMR: ^{19}F NMR, ϕ= -113.6 (dd, $^3J_{HF}$ = 7.5 Hz).

Solution Kinetics Procedure for the Thermolysis of 1. The kinetic vessels were sealed 507 NMR tubes. In each tube was placed approximately 10mg of **1**, along with 0.5mL acetone-d_6, n-hexane or DMF plus **2ul** of an internal standard hexafluorobenzene. A statim-type isothermal heater was used to pyrolyze the tubes in the temperature range 75.0-104.0 °C depending on the solvent. At designated time intervals, the tubes were cooled to -50 °C and the relative concentrations data of **1** fluorobenzene and hexafluorobenzene determined by quantitative

^{19}F NMR integration. Rate constants are reported in Table 3.

Table 3. Rate Constants for Thermolysis of **1**.

Solvent	Temp., °C	k x 10^5
gas	74.0	0.213 ±0.02
	96.0	2.57 ± 0.2
	105.5	8.08 ± 0.5
	114.8	15.9 ± 0.9
	123.3	29.8 ± 0.9
	131.3	74.7 ± 8
acetone	93.0	56.1 ± 2
hexane	93.0	4.3 ± 0.3
DMF	93.0	213 ± 6

Detection of 4 & 5 in Thermolysis of 1 in Acetone. An NMR tube containing approximately 30mg 6,6-difluorobicyclo[3.1.0]hex-2-ene,**1**, and 2uL hexafluorobenzene (as internal standard) dissolved in approximately 1mL acetone-d_6, was sealed at ambient pressure. The tube was heated in a thermostated oil bath at 93.0°C for 10-minute intervals. The ^1H and ^{19}F NMR spectra were taken after each interval. The ratios of product, intermediates, and starting material were determined by integration of the ^{19}F NMR spectra, and are given in Table 1. The mass balance for the reaction was calculated using the integration of the internal standard in the ^{19}F NMR spectra.

The two intermediates in the reaction were clearly visible in the ^{19}F NMR spectra of the reaction mixture. In addition, the major intermediate could also be detected in the ^1H NMR spectra.

3,3-difluorohexa-1,4-diene,**4**: ^{19}F NMR (282 MHz, acetone-d_6) ϕ-70.04 (t,t, J_{HF}=17.1 and 5.1 Hz); ^1H NMR (300 MHz, acetone-d_6) δ 6.47 (m,2H), 6.03 (m,2H), 2.90 (m, 2H).

5,5-difluorohexa-1,3-diene,**5**: ^{19}F NMR (282 MHz, acetone-d_6) ϕ-77.26 (tdt, J_t=22.4, J_6=6.3, and J_t=1.5 Hz).

1,2,3,4,5,5-hexadeuteriocyclopentadiene. At 0 °C a NaOD/D_2O solution was prepared by adding 8.4g of Na to D_2O slowly. Into a 100mL round bottom flask equipped with a stir bar, rubber septa and cooled to 0 °C was added 18mL of freshly cracked cyclopentadiene and 20mL of DMSO. To this organic mixture, 20mL of the NaOD/D_2O solution was added. The mixture was stirred vigorously for one hour, and an intense pink color was observed during the exchange. The top, cyclopentadiene layer was separated and syringed into another 100mL flask containing 20mL each of fresh DMSO and NaOD/D_2O solution at 0 °C. This procedure was repeated 6 times (6 exchanges) and ^1H NMR confirmed deuteration to >95%. Approximately 7mL (39%) of the product was isolated and utilized immediately.

1,2,3,4,4,5-hexadeuterio-6,6-difluorobicyclo[3.1.0]hex-2-ene. The procedure for the preparation of **1-d**^{6} is analogous to that which was described for the parent **1**. Into the standard apparatus was placed 1.0g (13.9mmol) of the freshly prepared cyclopentadiene-d_6 and 2.73g (41.7mmol) activated Zn dust in 10mL dry THF. To this stirred mixture, 8.8g (41.7mmol) CF_2Br_2 in 15mL THF was slowly added over a two hour period. The yield by

^{19}F NMR was 24%: NMR, Φ = -129.2 (d, $^2J_{FF}$ = 148.2 Hz); -155.4 (d, $^2J_{FF}$ = 148.0 Hz); mass spectrum, m/z (relative intensity) 122 (M^+, 8.02), 120 (M -2, 100.00), 101 (6.35), 72 (19.96).

Thermal Rearrangement of 1-d_6. 1,2,3,4,4,5-Hexadeuterio-6,6-difluorobicyclo[3.1.0]hex-2-ene (80.0mm) was expanded into the same well-conditioned pyrolysis bulb and pyrolyzed at three temperatures between 92.80 and 125.75°C. Benzene was used (15mm) as an internal standard. The parent (H_6) system **1** (80.00mm) was pyrolyzed in the same vessel and temperature immediately following the pyrolysis of **1-d_6**. The gc analysis of starting material and internal standard gave the kinetic data which resulted in the rate constants and kinetic isotope effect data listed in Table 4. The acetone solution kinetic runs were monitored at 84.0 °C in the same way as the earlier described runs with the parent system **1**. The rate constants and the solution isotope effect is reported in Table 4.

Table 4. Kinetic Isotope Effects for **1-d_6**

Substrate	Solvent	Temp., °C	k x 10^5	k_H/k_D
1	gas	92.8	4.07 ± 0.11	
1-d_6	gas	92.8	1.59 ± 0.11	2.55
1	acetone	84.0	9.34 ± 0.22	
1-d_6	acetone	84.0	4.07 ± 0.05	2.29

5-Deuteriocyclopentadiene. In a 125mL Erlenmyer flask with a stir bar, 6.0g (0.091mol) freshly cracked cyclopentadiene, 30mL 4N NaOH and 10.08g (0.020mol) Tl_2SO_4 were allowed to react for a short time. The crude product cyclopentadienyl thallium (10.5g: 80.0%) was collected by filtration. The crude cyclopentdienyl thallium was sublimed pure (0.6atm, 105°C) to give fine yellow needle-like crystals. The hydrolysis went smoothly using a standard 3-necked round bottom flask equipped with a magnetic stir bar and a pressure-equalizing addition funnel. The apparatus, under nitrogen flow was kept at room temperature. Three traps (ice, dry ice/iPrOH and liquid nitrogen) were placed in series. Into the reaction flask, 3.09g (11.5mmol) cyclopentadienyl thallium was added, and the addition funnel was charged with 2mL 10% D_2SO_4. The product, 5-deuteriocyclopentadiene, was collected (0.5g, 40%) in the dry ice trap. The material was kept at -78°C and used directly for the carbene addition. Purity was checked by ^1H NMR and integration of the material verified the structure (4:1, vinylic:methylene).

exo and endo-4-Deuterio-6,6-difluorobicyclo[3.1.0]hex-2-ene 1-d_1. As described earlier, 1.00g (8.5mmol) of 5-deuteriocyclopentadiene in 10mL THF was added to 1.67g (25.5mmol) zinc in the reaction flask. To this mixture, 5.35g (25.5mmol) CF_2Br_2 in 15mL THF was slowly introduced. The ^{19}F NMR yield was 19%. Approximately 100mg was isolated by preparative GC at 50 °C with the detecter and injector temperature at 50 °C to guard against rearrangement. A Triton X-305 column was used, and both epimers were collected together: ^1H NMR δ 5.71 (m, 1H, olefinic), 5.62 (m, 1H, olefinic), 2.66 (complex m, 2H, - CHD + cyclopropyl), 2.19 (complex m, 1H, cyclopropyl); ^2H NMR δ 2.75 (s, 1D), 2.53 (s, 1D), each δ represents <u>one</u> epimer; ^{19}F NMR ϕ = -129.3 (ddd?, $^2J_{FF}$ = 147.0 Hz, $^3J_{cisHF}$ = 11.6 Hz), -155.7 (d, $^2J_{FF}$ = 147.0 Hz).

Thermolysis of exo and endo 1-d_1. The pyrolysis in acetone solution of the 50:50 mixture of the exo and

endo epimers was followed in a sealed 507 NMR tube by ^2H NMR. The tube was heated in a Statim-type oil heater at 93.0 °C, cooled to -50 °C and analyzed by NMR with acetone-d_6 as an internal standard. The reaction was allowed to proceed for approximately 6 half-lives and the aromatic product mixture was isolated by preparative gc from the NMR tube. All three (m, p and o) monodeuteriofluorobenzene isomers could be detected by ^2H NMR in a ratio of 80.6:14.2:5.2, respectively. The purified aromatic mixture was analyzed by mass spectrometry (17eV). A pure sample of fluorobenzene provided the reference spectrum. The MS absolute intensities and ^2H NMR ratios were used to calculate the mole fractions of the four products.

Fluorobenzene: mass spectrum, m/z (absolute intensity) 97 (M + 1, 2624), 96 (M^+, 41472).

Product Mixture: mass spectrum, m/z (absolute intensity) 98 (4456), 97 (63232), 96 (16112).

2,3-Benzo-6,6-difluorobicyclo[3.1.0]hex-2-ene (6).[23] Into a 100mL round bottom flask with reflux condenser and magnetic stir bar under argon was placed 4.65g (13.4mmol) of $PhHgCF_3$ and 5.72g (38.2mmol) NaI. Each solid was dried overnight on a vacuum line. The NaI was heated at 150°C while drying. Before adding the solids to the flask, they were ground together. In addition, 5.50g (47.4mmol) of freshly distilled dry (CaH_2) indene and 5mL of dry benzene was added to the solid mixture. The reaction mixture was vigorously stirred and heated at reflux (oil bath at 95 °C) for 20 hours. Following the reaction, the mixture was filtered and vacuum transferred. The ^{19}F NMR yield was 41% using hexafluorobenzene as an internal standard. The compound **6** was separated and gc purified utilizing a 20ft Triton X-305 column at 100°C. The desired compound **6** was characterized as a low melting solid (mp 35-38 °C) and 525mg was isolated: ^1H NMR δ 7.35 (m, 1H, aromatic), 7.18 (m, 3H, aromatic), 3.10-3.40 (m, 2H, $-CH_2-$; m, 1H, cyclopropyl), 2.45 (p, 1H, cyclopropyl); ^{19}F NMR, ϕ = -128.2 (ddd, $^2J_{FF}$ = 151.5 Hz, $^3J_{cisHF}$ = 10.3 Hz, $^3J_{cisHF}$ = 12.2 Hz), -153.8 (dd, $^2J_{FF}$ = 151.4 Hz, $^3J_{transHF}$ = 1.5 Hz); ^{13}C NMR, δ 143.2 (d, aromatic quaternary, $^3J_{CF}$ = 5.5 Hz), 137.0 (s, aromatic quaternary), 127.0 (s, aromatic), 126.7 (s, aromatic), 124.9 (s, aromatic), 124.5 (s, aromatic), 113.0 (dd, $^1J_{CF}$ = 280.5 Hz, $^1J_{CF}$ = 280.7 Hz), 35.4 (dd, cyclopropyl, $^2J_{CF}$ = 12.9 Hz), 31.9 (d, $-CH_2$, $^3J_{CF}$ = 2.2 Hz), 27.1 (dd, cyclopropyl, $^2J_{CF}$ = 10.2 Hz, $^2J_{CF}$ = 10.1 Hz); mass spectrum: m/z (% relative intensity) 166 (M+, 14.74), 146 (100.00), 85 (17.78), 71 (25.30), 57 (51.39), 43 (80.26).

Thermolysis of 2,3-Benzo-6,6-difluorobicyclo[3.1.0]hex-2-ene (6). The kinetic vessels were sealed melting point capillaries. A "mother" solution was prepared by adding approximately 5mg of starting material **6** to 0.5mL of the appropriate solution media. Runs were carried out using acetone (n-decane internal standard), buffered acetic acid, n-heptane (n-decane) and DMF as solvents. The buffered acetic acid was prepared by combining freshly distilled acetic acid (5mL sodium acetate 0.265g: 2.50mmol) and freshly distilled acetic anhydride (-0.306g: 3.0mmol). The capillaries were pyrolyzed in a Statim-type isothermal heater at 140.0, 150.0, 160.0, 170.0 and 180.0°C for acetone; 81.0, 100.0 and 119.0°C for acetic acid; 186.0 and 70.0°C for n-heptane and DMF respectively. The reactions were followed by gc with a J & W Scientific MEGABORE™ column at lower temperatures (50-100°C) to avoid rearrangements on the column. In each case, one product, fluoronaphthalene, was observed by gc and the rate constants are reported in Table 5: ^{19}F NMR ϕ = -115.4 (dd, $^2J_{HF}$ = 8.7 Hz, $^2J_{HF}$ = 8.6 Hz).

Table 5. Rate Constants for Pyrolysis of **6**

Solvent	Temp., °C	k x 10^5
acetone	140.0	1.71 ± 0.08
	150.0	3.32 ± 0.14
	160.0	6.42 ± 0.05
	170.0	12.1 ± 0.5
	180.0	23.1 ± 0.5
HOAc	81.0	2.49 ± 0.05
	100.0	16.5 ± 0.4
	119.0	102 ± 2
n-Heptane	186.0	5.82 ± 0.16
DMF	70.0	0.87 ± 0.01

Indene-d_1. Into a 250mL round bottom flask charged with a 50mL pressure-equalizing addition funnel, reflux condenser, stopper and magnetic stir bar under nitrogen was placed 40mL of dry THF and 45mL (2.5M in hexane: 110.0mmol) n-butyllithium. The flask was cooled to 5-10 °C. Freshly distilled dry (CaH_2) indene (11.6g: 100.0mmol) was introduced to the addition funnel and added slowly while maintaining the temperature. Following the addition a reddish-orange homogeneous solution of indenyllithium resulted. The reaction mixture was warmed to room temperature and then heated at 50 °C for 45 minutes. After heating, the indenyllithium was cooled to 0-5 °C and transferred via cannula to a 250mL pressure-equalizing addition funnel under nitrogen,. The funnel was fitted to another 250mL round bottom flask with a mixture of 10g D_2O and 15g 20% DCI stirring at 0-5°C. The indenyllithium was added slowly, then the flask was allowed to warm to room temperature. The organic layer was separated and 7.7g of deuterated product was isolated after distillation (80°C, 20mm). A mass spectral analysis of the deuterated indene (17 eV) showed the desired compound indene-d_1, (mw 117) was 81% of the product mixture. Undeuterated material (mw 116) was present in 8% while dideuterated compounds (mw 118) were observed in 11%. A mass spectrum of pure indene (17 eV) was used to make the appropriate quantitative corrections (e. g. ^{13}C content). The total yield of the desired compound (indene-d_1) was 66.0%.

endo and exo-2,3-Benzo-4-deuterio-6,6-difluorobicyclo[3.1.0]hex-2-ene, 6-d_1. The procedure for the carbene addition previously described for the undeuterated case was used. Into the apparatus was placed the ground dry solids $PhHgCF_3$ (7.24g: 20.9mmol) and NaI (9.41g: 62.8mmol). Also, 7.36g (62.8mmol) deuterated indene and 10mL benzene were added and stirred at 80 °C for 15 hours. The ^{19}F NMR yield was 31.8% and 547mg was isolated pure by preparative gc.

endo and exo-2,3-Benzo-4-deuterio-6,6-difluorobicylo[3.1.0]hex-3-ene: ^1H NMR δ 7.05-7.41 (m, 4H, aromatic), 3.04-3.43 (m, 2H, CHD + cyclopropyl), 2.45 (m, 1H, cyclopropyl); ^{19}F NMR ϕ = -127.9 (dm, $^2J_{FF}$ = 154.0 Hz), -153.7 (d, $^2J_{FF}$ = 153.7 Hz.)

Thermolysis of a 50:50 Mixture. The controlled pyrolysis of the mixture was carried out in a sealed 507 NMR tube in acetone-d_6 solution at 150.0 °C. A total of 10mg of starting materials was pyrolyzed. At 20% conversion, a ^1H NMR spectrum confirmed that the ratio of starting materials was unchanged (essentially 1:1).

The integration at δ 3.33 was 0.4547. At time zero, this integration was 0.4541. This chemical shift represents one of the methylene protons and integrates to one in the undeuterated system. The 20% pyrolysis products were separated using preparative gc at 50 °C. Also, this injector and detector were each set at 50 °C to insure no rearrangement. The product peak contained both the deuterated and the undeuterated 2-fluoronaphthalene. This solid sample was submitted along with pure 2-fluoronaphthalene for quantitative low voltage (17eV) mass spectrometry. Corrections were made for un- and dideuterated material which existed in the indene starting material. The corrected ratio of 4-deuterio-2-fluoronaphthalene to 2-fluoronaphthalene was determined to be 1.31:1.00.

2-Fluoronaphthalene: mass spectrum, m/z (absolute intensity) 147 (M + 1, 1407), 146 (M^+, 13595), 145 (M - 1, 1273).

Product Mixture: mass spectrum, m/z (absolute intensity) 148 (4144), 147 (25387), 146 (20980), 145 (2591).

endo and exo-2,3-Benzo-6-chloro-6-fluorobicyclo[3.1.0]hex-2-ene (10 & 11). The procedure used in this synthesis was that of Burkholder and Dolbier.[23]

A 100mL, three-necked, round bottom flask was equipped with a magnetic stirrer, thermometer, rubber septum with nitrogen inlet needle and a pressure-equalizing addition funnel with nitrogen outlet. The flask with 30mL THF was cooled in a salt-ice bath and then 4.33g (22.8mmol) $TiCl_4$ was added at such a rate to keep the temperature below 5 °C. A yellow precipitate was formed. Another addition funnel was introduced containing a solution of 0.91g (22.8mmol) $LiAlH_4$ in 20mL THF. This solution was carefully added with the temperature remaining below 15°C. The reaction mixture turned a dark brown color and was allowed to stir without cooling following the addition for one hour.

The flask was cooled again in a salt-ice bath. At 0 °C, 0.88g (7.6mmol) of freshly distilled indene was added. Then a solution of 3.13g (22.8mmol) $CFCl_3$ in 10mL THF was added at such a rate that the temperature remained at 0°C. The mixture was allow ed to stir for an additional 20 minutes. The reaction mixture was hydrolyzed and the light brown organic layer was dried over magnesium sulfate and then vacuum transferred. The THF present was rotary evaporated, and a viscous, high-boiling, yellow oil was obtained. NMR analysis confirmed the presence of the chlorofluorocyclopropanes in a 2.3:1.0 endo/exo ratio with indene and 2-fluoronaphthalene present as impurities. The ^{19}F NMR yield was 73%:

endo-2,3-Benzo-6chloro-6-fluorobicyclo[3.1.0]hex-2-ene (10): ^{19}F NMR ϕ = -128.4 (dd, $^3J_{cisHF}$ = 16.3 Hz, $^3J_{cisHF}$ = 18.8 Hz)[18]; mass spectrum: m/z (% relative intensity) 183 (M^+, 0.05), 146 (100.00).

exo-2,3-Benzo-6-chloro-6-fluorobicyclo[3.1.0]hex-2-ene (11): ^{19}F NMR ϕ = -162.6 (s, $^3J_{transHF}$: v. small)[18]; mass spectrum: m/z (% relative intensity) 183 (M^+, 0.37), 182 (M - 1, 0.87), 181 (M -2, 1.16), 148 (10.97), 147 (100.00), 146 (44.05).

Thermolysis of the endo and exo systems 10 and 11. The pyrolysis of both isomers was carried out in acetone-d_6 solution in sealed 507 NMR tubes without separating and purifying each isomer. Approximately 5mg of the isomeric mixture was added to each tube. The endo- isomer remained stable and did not react over this

temperature range. The reaction was followed by ^{19}F NMR and a first-order conversion to 2-fluoronaphthalene via HCl elimination was observed.

The pyrolysis of the exo- isomer required higher temperatures and was observed at 140.0, 150.0 and 160.0°C used hexafluorobenzene as an internal standard. The sole pyrolysis product was 2-chloronaphthalene . No increase in 2-fluoronaphthalene was observed. Rate constants for both thermolysis processes are found in Table 6.

2-Chloronaphthalene: mass spectrum: m/z (% relative intensity) 164 (M + 2, 32.89), 163 (M + 1, 11.26), 162 (M^+, 100.00), 127 (40.56).

Table 6. Rate Constants for Pyrolysis of **9** and **10** in Acetone

Substrate	Temp., °C	k x 10^4
9	140.0	2.81 ±0.09
	150.0	6.15 ± 0.13
	160.0	11.8 ± 0.38
10	39.0	0.234 ±0.005
	51.0	1.08 ± 0.02
	64.0	5.42 ± 0.19

Acknowledgements. Support of this research, in part, by the National Science Foundation is gratefully acknowledged.

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