Thermal Rearrangements of 9,10-Bis(trifluorovinyl)phenanthrene

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Received July 9, 1993●

Results from a study of the thermal unimolecular rearrangement of 9,10-bis(trifluorovinyl)-phenanthrene are reported. Kinetic and product studies indicate that it is unexpectedly resistant to rearrangement, that its expected 6π electrocyclic rearrangement plays but a minor role, and that the major rearrangement process was a virtually unprecedented thermal reaction for 1,3,5-trienes, that of conversion to a bicyclo[3.1.0]hex-2-ene system (7). Activation parameters are provided for the minor electrocyclic process ($\Delta H^{\ddagger} = 29.9$ kcal/mol; $\Delta S^{\ddagger} = -19.6$ eu) and for the conversion to 7 ($\Delta H^{\ddagger} = 34.4$ kcal/mol; $\Delta S^{\ddagger} = -6.6$ eu) as well as for the secondary conversions of 7 to 4-(difluoromethylidene)-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)cyclopent-1-ene (8) ($\Delta H^{\ddagger} = 31.3$ kcal/mol; $\Delta S^{\ddagger} = -12.7$ eu) and to 1,2-(9,10-phenanthro)-3,5,5-trifluoro-4-(trifluoromethyl)-1,3-cyclopentadiene (9) ($\Delta H^{\ddagger} = 31.4$ kcal/mol; $\Delta S^{\ddagger} = -13.4$ eu). A rarely encountered fluorine steric effect deriving from the stringent steric demands of the reaction's boat-like transition state is invoked to explain the inhibition of 1's electrocyclic process, while equally rare thermal 1,2-fluorine atom shifts are proposed to explain the rearrangement of 7.

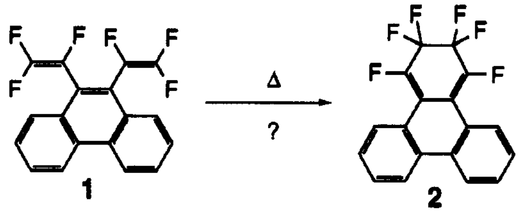
Electronic effects which promote transition-state twisting in a predictable fashion comprise a new aspect of stereoselectivity.[1] This phenomenon is best exemplified by substituent effects which have been observed for the thermal ring-opening, electrocyclic reactions of 3-substituted cyclobutenes.[2,3]

Numerous experimental[2,4,5] and theoretical studies[3,5] have demonstrated that such reactions are highly stereoselective and that such stereoselectivities are strongly influenced by the electronic properties of the substituents. Our present insight into these stereoelectronic effects is largely the result of efforts by Houk and his co-workers, who coined the term *torquoselectivity* to describe these unique effects,[1] which, for example, show fluorine substituents exhibiting a 17.3 kcal/mol preference for outward rotation.

Torquoelectronics are potentially of kinetic significance in *any* reaction which, like cyclobutene in its ring opening, involves transition-state twisting of a substituted methylene group which is undergoing either bond making or bond breaking.

Although disrotatory electrocyclic processes are expected to exhibit rotational preferences to a smaller degree than those observed for conrotatory cases,[6] it remained an important test of the generality of the theory to obtain data on the 6π disrotatory electrocyclic 1,3,5-hexatriene → 1,3-cyclohexadiene system.

In an attempt to probe this electrocyclic reaction, a strategy was devised which would utilize the thermolysis of 9,10-bis(trifluorovinyl)phenanthrene (1).



Divinyl aromatics have been reported to undergo electrocyclic reactions in a manner similar to that of their acyclic analogues in spite of the disadvantageous loss of aromaticity which would derive from such cyclizations.[7] In a directly-related example, 9,10-divinylphenanthrene (3) was found to rearrange at 210 °C to triphenylene in 35% yield, the product apparently arising from electrocyclic ring closure followed by oxidative loss of hydrogen.[8]

From a thermodynamic point of view, the six vinylic fluorine substituents of 1 should give rise to a sizable enthalpic advantage for its cyclization relative to that of hydrocarbon 3. While one can estimate the cyclization of 3 to be exothermic by ~12 kcal/mol,[9] the exothermicity of the cyclization of 1 should be substantially greater (ΔH° = ca. -31 kcal/mol).[10]

One might have expected such an increase in exothermicity to have led to a kinetic enhancement for the cyclization of 1. Indeed, such was the result for the Cope rearrangement of 1,1-difluoro-1,5-hexadiene.[12] However, this proved not to be the case for 1. In this paper, we

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● Abstract published in *Advance ACS Abstracts*, October 15, 1993.

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[4] (a) Dolbier, W. R., Jr.; Koroniak, H.; Burton, d. J.; Heinze, P. *Tetrahedron Lett.* 1986, *27*, 4387. (b) Dolbier, W. R., Jr.; Koroniak, H.; Burton, D. J.; Heinze, P. L.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *J. Am. Chem. Soc.* 1987, *109*, 219. (c) Dolbier, W. R., Jr.; Gray, T. A.; Keaffaber, J. J.; Celewicz, L.; Koroniak, H. *J. Am. Chem. Soc.* 1990, *112*, 363.

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[6] Thomas, B. E., IV; Evanseck, J. D.; Houk, K. N. *J. Am. Chem. Soc.* 1993, *115*, 4165.

[7] . Heimgartner, H.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* 1972, *55*, 1385.

[8] Sukumaran, K. B.; Harvey, R. G. *J. Org. Chem.* 1981, *46*, 2740.

[9] Using the "group equivalent" method as described in Benson, S. W. *Thermochemical Kinetics*, 2nd ed; John Wiley & Sons: New York, 1976.

[10] Using a thermodynamic comparison of cyclobutene and perfluorocyclobutene as a measure.[11]

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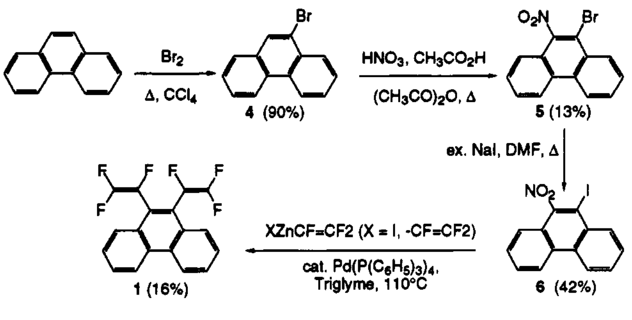
Scheme I



present detailed kinetic results from the thermolysis of 1 which indicate that (a) it is unexpectedly resistant to rearrangement, requiring temperatures >180 °C, (b) the expected electrocyclic reaction plays only a minor role, such that a quantitative probe of torquoselectivity proved infeasible, and (c) its observed major rearrangement pathway proved to be a virtually unprecedented thermal process for 1,3,5-trienes, that of conversion to a bicyclo[3.1.0]hexene species, a type of rearrangement which is commonly observed in the *photochemistry* of such trienes.[13,14]

Results

Synthesis. 9,10-Bis(trifluorovinyl)phenanthrene (1) was synthesized in four steps and isolated in a 1% overall yield, as shown in Scheme I. The first two steps involved literature procedures: bromination of phenanthrene to yield 9-bromophenanthrene (4, 90%)[15] and then nitration to yield 9-bromo-10-nitrophenanthrene (5, 13%).[16] Nucleophilic attack by iodide on 5 led to 9-iodo-10-nitrophenanthrene (6, 42%). This three-step synthesis of 6 in a 5% overall isolated yield was an improvement over the previously reported synthesis of 6 (five steps, 1%).

Finally, the desired 1 was prepared in a single step (14% yield) by treatment of 6 with an excess of (trifluorovinyl)zinc iodide under catalysis by $Pd(P(C_6H_5)_3)_4$.[17] Although these conditions are typical for coupling of fluorinated vinylzinc reagents with aryl iodides, to our knowledge, this is the first reported replacement of a *nitro* functionality under such conditions.

Interestingly, 1 was found to exist as a 1.94:1 mixture of atropisomers (torsional diastereomers), one with the trifluorovinyl groups syn to the plane of the phenanthrene and the other with them anti.[18] Apparently, interaction of the trifluorovinyl groups with the C_1 and C_8 hydrogen substituents of the phenanthrene ring gives rise to a substantial barrier ($\Delta G^{\ddagger}$ = ca. 15 kcal/mol) to interconversion of the two diastereoisomeric forms of 1.

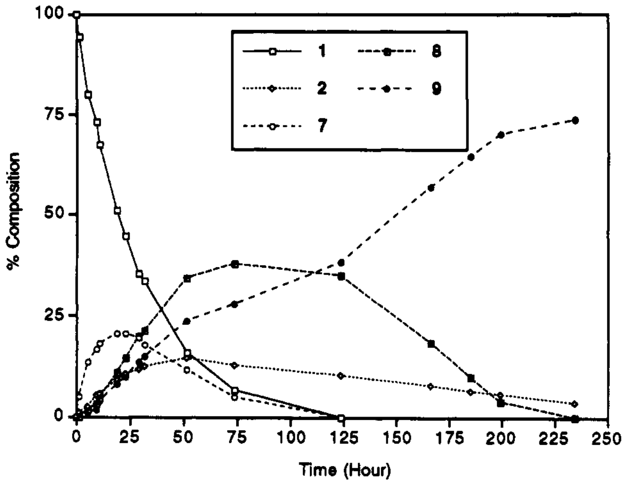
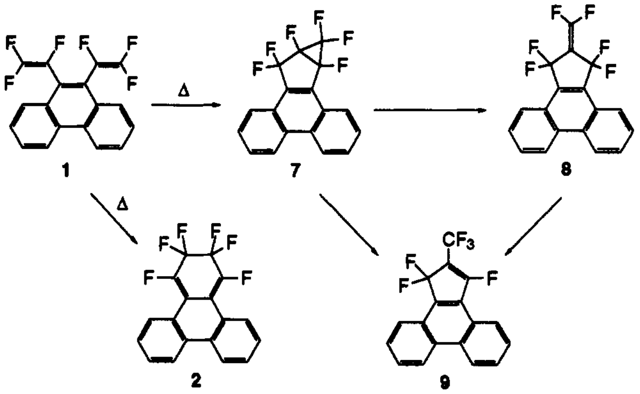


Figure 1. Thermolysis of 9,10-bis(trifluorovinyl)phenanthrene (1) at 180.0 °C as a solution in benzene-d_6.

Scheme II



Thermolysis. The thermolysis of 1 was followed by ^{19}F NMR and by GLPC at temperatures from 140 to 193 °C using 0.1 M solutions in benzene-d_6 (Scheme II). Two primary products 1,2,2,3,3,4-hexafluoro-2,3-dihydrotriphenylene (2, ~12% at 180 °C) and 1,4,4,5,6,6-hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (7, ~88%) are formed upon the thermolysis of 1, with 7 being found to undergo further rearrangement to 4-(difluoromethylidene)-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)cyclopent-1-ene (8) and 1,2-(9,10-phenanthro)-3,5,5-trifluoro-4-(trifluoromethyl)-1,3-cyclopentadiene (9) (8:9 = 1.35).

Figure 1 illustrates the percent composition of all reaction components observed *versus* time for the thermolysis of 1 at 180.0 °C. The reaction is quantitative with regard to the formation of $C_{18}H_8F_6$ structural isomers through 50% reaction of 1, and after 235 h, a 78% yield of $C_{18}H_8F_6$ isomers is obtained as a 21:1 mixture of 9:8.

In order to verify the overall scheme of product interconversion which is depicted in Figure 1, it was necessary to isolate and independently subject each of the intermediate products, 2, 7, and 8, to the conditions which had been used for 1. The thermolysis of 2 at 180.0 °C as

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(11) Smart, B. E. in *Molecular Structure and Energetics;* Liebman, J. F., Greenburg, A., Eds.; VCH Publishers, Inc.: Deerfield Beach, FL, 1986; Vol. 3, p 141.

(12) Dolbier, W. R., Jr.; Alty, A. C.; Phanstiel, O., IV. *J. Am. Chem. Soc.* **1987**, *109*, 3046.

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(15) Dornfeld, C. A.; Callen, J. E.; Coleman, G. H. In *Organic Syntheses Collective Volume 3;* Horning, E. C., Ed. John Wiley and Sons: New York, 1967; p 134.

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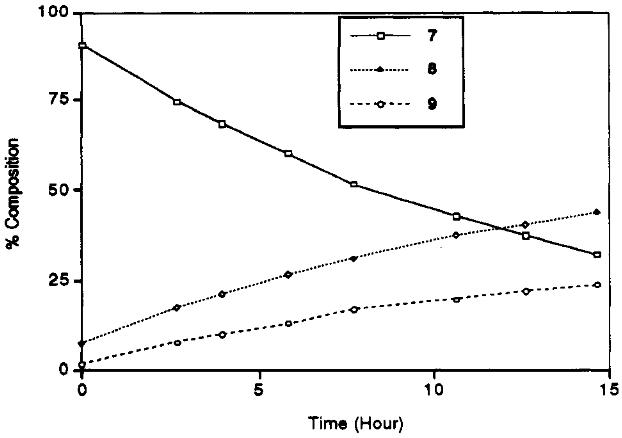


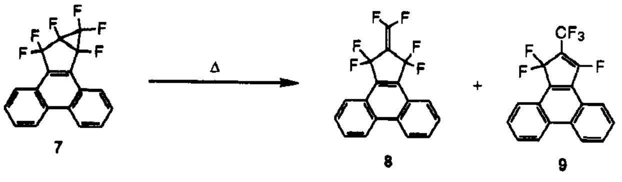
Figure 2. Thermolysis of 1,4,4,5,6,6-hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (7) at 180.0 °C as a solution in benzene-d_6.

Table I. First-Order Rate Constants for the System 1 → 2 + 7

T, °C	10^5k_1, s^{-1}	10^5k_2, s^{-1}	10^5k_7, s^{-1}
180.0	0.991 ± 0.12	0.183	0.808
184.5	1.55 ± 0.01	0.257	1.29
193.0	2.93 ± 0.06	0.476	2.45

a 6:1 mixture of **2**:**9** led only to nonproductive decomposition of **2** with no reaction of **9** being observed. Thus, **1** was not reversibly formed from the electrocyclic product **2** at this temperature nor was **2** seen to convert to **7**, **8**, or **9**.

The thermolysis of key intermediate **7** was examined at three temperatures (180, 185.0, and 192.5 °C), and it was found to rearrange cleanly to **8** and **9**. Figure 2 illustrates the percent composition of all reaction components observed *versus* time for the thermolysis of **7** at 180.0 °C. The conversion of **7** to **8** and **9** is quantitative over this temperature range and through 69% conversion.



As can be seen in Figure 1, from the results at longer reaction times, **8** eventually converts to **9** in a near quantitative process. (This process and this process alone we attribute to a fluoride-catalyzed reaction.)

The thermal conversions of both **1** and **7** were found to follow good first-order kinetics. For the thermolysis of **1** (through 85% conversion), a ratio of (**7** + **8** + **9**)/**2** was maintained at 4.42 ± 0.19 at 180.0 °C, 5.03 ± 0.11 at 184.5 °C, and 5.15 ± 0.16 at 193.0 °C. For the thermolysis of **7** (through 69% conversion), the ratio of **8**/**9** (1.62 ± 0.12) varied little over the temperature range examined.

The reactions of **1** and **7** were found to be irreversible in forming their respective products. Thus, the individual rate constants for formation of **2** and **7** from **1**, and **8** and **9** from **7** could be calculated using the observed overall rate constants for *loss* of **1** and **7** combined with the experimental product ratios. Both the overall observed and calculated individual rate constants for these systems are given in Tables I and II.

Table II. First-Order Rate Constants for the System 7 → 8 + 9

T, °C	10^5k_7, s^{-1}	10^5k_8, s^{-1}	10^5k_9, s^{-1}
180.0	1.96 ± 0.02	1.21	0.751
185.0	2.92 ± 0.01	1.81	1.11
192.5	5.14 ± 0.08	3.17	1.97

Table III. Activation Parameters for the Rearrangements of 1 and 7

system	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
1 to 2	29.9 ± 0.1	−19.6 ± 0.3
1 to 7	34.4 ± 2.8	−6.6 ± 6.0
7 to 8	31.3 ± 0.4	−12.7 ± 0.9
7 to 9	31.4 ± 0.1	−13.4 ± 0.1

Activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$, Table III) for the individual processes were obtained from the Eyring expression[19],

$$k = \frac{kT}{h}e^{\left(-\frac{\Delta G^\ddagger}{RT}\right)}$$

expressed in the form.

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} + \ln\left(\frac{k}{h}\right)$$

Linear least-squares regression plots of $\ln(k/T)$ *versus* T^{-1} yielded $\Delta H^\ddagger$ and $\Delta S^\ddagger$ from the slope and the intercept, respectively, of the fitted line for each system.

The possibility that fluoride catalysis was involved in the observed rearrangements was probed. As expected, rapid conversion of **8** to **9** at 80 °C in the presence of added trace amounts of CsF was observed. On the other hand, it was determined that fluoride catalysis could not have led to the rearrangements observed for **1**. A sample of **1** was warmed to 115 °C in DMF containing CsF, and after 3.5 h, 70% of **1** had been converted to at least three unknown products, none of which were in common with those from the simple thermolysis of **1**.

Discussion

Thus, it was observed that 9,10-bis(trifluorovinyl)-phenanthrene (**1**) could be converted thermally to the desired electrocyclic product 1,2,2,3,3,4-hexafluoro-2,3-dihydrotriphenylene (**2**) but only as a minor component of a much more complicated overall reaction process, the major component of which was the unexpected formation of a bicyclo[3.1.0]hex-2-ene species.[20]

Bicyclo[3.1.0]hexene Formation. The probable mechanism for the rearrangement of **1** to **7** is presented in Scheme III. Although the thermal closure of a 1,3(*Z*),5-triene system to a bicyclo[3.1.0]hex-2-ene product is formally a Woodward–Hoffmann-allowed $4\pi_a + 2\pi_a$ or $4\pi_s + 2\pi_s$ process, it is likely that the conversion of **1** to **7** involves a 1,5-cyclization of the anti atropisomer of **1** to form diradical **10** which then cyclizes to form **11**. **11** then can undergo a rapid aromatizing vinylcyclopropane rearrangement to **7**. The activation parameters ($\Delta H^\ddagger$ = 34.4 kcal/mol; $\Delta S^\ddagger$ = −6.6 eu) which were observed for the conversion of **1** to **7** are more consistent with the diradical mechanism than with the highly ordered transition state which would be required for the pericyclic process.

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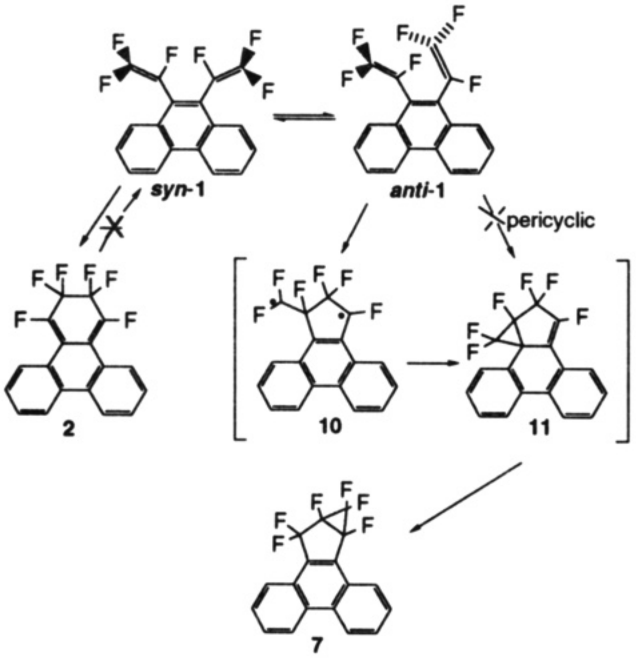
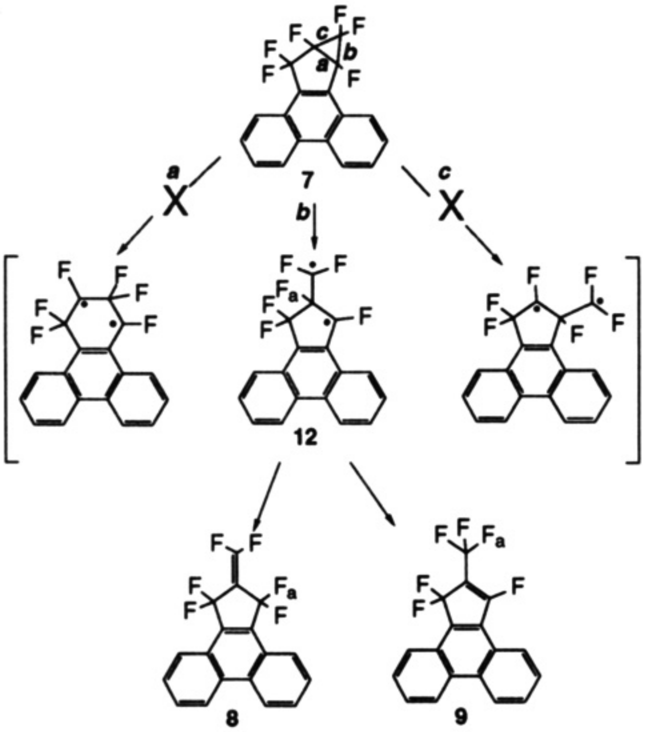
[19] Frost, A. A; Pearson, R. G. *Kinetics and Mechanism*; John Wiley and Sons, Inc.: New York, 1961; p 99.

[20] Only one example of this type of thermal process has been reported, in the thermolysis of 1-(*tert*-butylamino)-1,3(*Z*),5-hexatriene.[21]

Scheme III

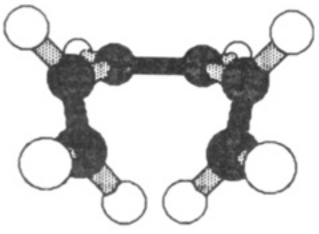


Scheme IV



The Electrocyclic Process. Although exhibiting a much higher $\Delta H^{\ddagger}$ than expected, the activation parameters for the minor, competing electrocyclic conversion of **1** to **2** ($\Delta H^{\ddagger} = 29.9$ kcal/mol; $\Delta S^{\ddagger} = -19.6$ eu) are more or less consistent with expectations for it being a concerted process.[22]

Lack of steric impact is perhaps the most significant and widely recognized characteristic of fluorine as a substituent. Nevertheless, in order to rationalize why the diradical process leading to **7** predominates over the electrocyclic process leading to **2** (which was expected to be so facile because of thermodynamic considerations), we were forced to conclude that the requisite 6π electrocyclic, disrotatory, boat-like transition state **13**, which leads to electrocyclic product **2**, suffers from substantial repulsive steric and electrostatic interactions between the *cis* fluorine substituents of the vinyl CF_2 groups. (Although modeling indicates that overlap of the van der Waals radii of the *cis* fluorines occurs, there will also no doubt be an electrostatic component to the inhibition of the electrocyclic transition state, the relative importance of which is yet unknown.)



13

It has long been known that terminal *cis* substituents, such as methyl, would inhibit the cyclization of 1,3,5-trienes,[23] but in designing our study, we naively thought that steric interference by fluorine substituents might be insignificant. Such obviously was not the case. In fact, the influence of the fluorine substituents caused such a substantial increase in the activation energy for this electrocyclic process that a normally-unfavored process, that of 1,5-closure to form diradical **10**, was able to intervene mechanistically.

Just as it is justifiably understood that fluorine steric effects intervene only in the most demanding of transition states, so **13** would seem to qualify as such a sterically-demanding transition state. Because of such sensitivity of the 6π electrocyclic transition state to steric effects, a quantitative evaluation of torquoelectronic effects utilizing studies of this cyclization reaction was deemed infeasible.

Rearrangement of Bicyclo[3.1.0]hex-2-ene Intermediate 7. The product *versus* time profile for the pyrolysis of **1** combined with our separate study of the thermolysis of intermediate **7** demonstrated unambiguously that **7** is the precursor of ultimate reaction products **8** and **9**.[24] The homolytic mechanism illustrated in Scheme IV is proposed as the probable pathway for the rearrangement of **7**. Homolytic cleavage of only one of the three cyclopropane bonds in **7** can readily lead to the observed products. Cleavage of bonds *a* or *b* would in each case lead to biradicals which would have one benzylic center. The more easily-attained overlap with the C_9–C_{10} phenanthrene π system in cleavage of bond *b* should favor such cleavage over that of *a*.

The observed products **8** and **9** apparently derive from competitive *1,2-fluorine atom shifts* from intermediate biradical **12**. The virtually-identical activation parameters observed for these two competitive processes are consistent with their deriving from a common intermediate.

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[21] Bellas, M.; Bryce-Smith, B.; Clarke, M. T.; Gilbert, A.; Klunkin, G.; Krestonosich, S.; Manning, C.; Wilson, S. *J. Chem. Soc., Perkin Trans. I* **1977**, 2571.

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[24] Results from the thermolysis of perfluorobenzobicyclo[3.1.0]hex-2-ene provide precedent for such rearrangements.[25]

Fluorine atom shifts lack unambiguous precedent in the literature. Thermal 1,3 and 1,5-fluorine atom shifts have been invoked in studies involving thermal isomerizations of dihydrohexafluorocyclohexa-1,3-dienes[26] and perfluoroisoindenes.[27] Nevertheless, it appears certain that homolytic fluorine atom shifts are involved in the rearrangement of **7** to **8** and **9**. The good unimolecular kinetic behavior which was observed for the rearrangment allows one to effectively rule out possible fluoride ion catalysis.

Conclusions

The lack of observation of a dominant electrocyclic pathway for the rearrangement of **1** is rationalized in terms of a rarely-encountered fluorine steric effect which apparently gives rise to significant repulsive interactions in the requisite boat-like 6π electrocyclic transition state, such that a diradical process leading to the formation of a bicyclo[3.1.0]hex-2-ene product becomes the predominant rearrangement process.

Experimental Section

Nuclear magnetic resonance (NMR) chemical shifts are reported in parts per million (ppm) downfield (δ) from internal reference TMS for ^{1}H and ^{13}C NMR spectra and from internal reference $CFCl_3$ for ^{19}F NMR spectra. All NMR spectra were obtained on a Varian VXR-300 instrument. Gas chromatographic separations were performed on packed columns. Quantitative GLPC was performed on a Hewlett-Packard 5890 Series II gas chromatograph with a flame ionization detector and a Hewlett-Packard 3396A reporting integrator. Preparative GLPC was performed on a Varian Aerograph A-90-P3 gas chromatograph equipped with a thermal conductivity detector. The conditions and columns used are discussed where pertinent. Thin-layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} glass plates in the solvent systems indicated. High-resolution (HRMS) and low-resolution (LRMS) mass spectra and exact masses were determined on a Kraytos/AEI-30 spectrometer at 70 eV. UV spectra were obtained on an Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer.

9-Bromo-10-nitrophenanthrene (5). 9-Bromo-10-nitrophenanthrene (**5**) was prepared by adaptation of a procedure as described by Callow and Gulland.[16] 9-Bromophenanthrene (**4**)[15] (26.33 g, 1.025×10^{-1} mol) was dissolved in 60 mL of glacial acetic acid. Acetic anhydride (30 mL) was added, and the mixture was warmed to 90 °C. Concentrated (70%, 10 mL) nitric acid was added dropwise with vigorous stirring over 30 min. Upon completion of addition, the mixture was heated at a gentle reflux for 1 h. After the reflux period, the reaction mixture was allowed to cool to room temperature and an amorphous, deep brick-red solid fell out of a solution of the same color. This material was recrystallized from acetone and CCl_4 and then twice from methyl ethyl ketone. Crystalline **5** was obtained pure from the last recrystallization in methyl ethyl ketone as 8.01 g (25.9%) of light yellow needles, mp 202–204 °C (lit.[16] mp 195 °C). **5**: ^{1}H NMR δ 7.60–7.82 (m, 5H), 8.41 (d with fine splitting, 1H, $^3J_{HH} = 8.0$ Hz, $J_{HH} = 1.74$ Hz), 8.65 (d, 1H, $^3J_{HH} = 7.80$ Hz), 8.66 (d, 1H, $^3J_{HH} = 8.02$ Hz); ^{13}C NMR δ 113.1, 122.2, 122.9, 123.1, 123.5, 128.5, 128.7, 128.7, 129.3, 129.3, 130.1, 130.6; LRMS *m/z* (rel. intensity) 303 (27), 301 (28), 245 (28), 243 (29), 222 (16), 178 (18), 177 (18), 176 (100), 164 (21), 163 (18), 150 (18).

9-Iodo-10-nitrophenanthrene (6). 9-Bromo-10-nitrophenanthrene (**5**, 1.0 g, 3.3×10^{-3} mol), dry NaI (5.64 g, 3.76×10^{-2} mol), and 40 mL of DMF were combined. The mixture was brought to a gentle reflux for 16 h while we followed the reaction by TLC in hexanes/CH_2Cl_2 (2.5:1). The reaction mixture was cooled and added to a separatory funnel containing 250 mL of water. The aqueous mixture was extracted with 4 × 150 mL of diethyl ether. The ether extracts were combined and washed with 3 × 250 mL of water. The ether solution was dried over anhydrous $MgSO_4$, and then, the solvent was removed by rotary evaporation to yield 0.49 g (42%) of burnt-orange crystals of **6**, mp 196–198 °C (lit.[28] mp 198–200 °C). **6**: ^{1}H NMR δ 7.58–7.78 (m, 5H), 8.31 (d with fine splitting, 1H, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.5$ Hz), 8.59 (d, 1H, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.5$ Hz), 8.66 (d, 1H, $^3J_{HH} = 7.8$ Hz); ^{13}C NMR δ 122.3, 122.5, 122.9, 123.1, 123.7, 128.6, 128.7, 128.9, 129.1, 129.3, 130.0, 130.7, 130.8, 134.9; LRMS *m/z* (rel. intensity) 350 (12), 349 (75), 291 (16), 192 (12), 178 (11), 177 (17), 176 (100), 164 (30), 163 (15), 150 (16), 88 (14). Anal. Calcd for $C_{14}H_8INO_2$: C, 48.17; H, 2.31; N, 4.01. Found: C, 48.47; H, 2.21; N, 3.86.

$ZnIFC{=}CF_2$ and $Zn(CF{=}CF_2)_2$. $ZnIFC{=}CF_2$ and $Zn(CF{=}CF_2)_2$ solutions were prepared by the method of Heinze and Burton.[17]

9,10-Bis(trifluorovinyl)phenanthrene (1). 9,10-Bis(trifluorovinyl)phenanthrene (**1**) was prepared by adaptation of a procedure described by Heinze and Burton.[17] The following apparatus was flame-dried under nitrogen purge: a 100-mL, three-necked, round-bottom flask fitted with two septa, a glass stopper, a nitrogen purge tee, and a magnetic stirrer. Dry triglyme (15 mL) was added by syringe followed by 0.400 g (1.14×10^{-3} mol) of 9-iodo-10-nitrophenanthrene (**6**), 0.070 g (5.7×10^{-5} mol) of $Pd(P(C_6H_5)_3)_4$ (weighed in a drybox and transferred by a solid-addition tube), and 6.0 mL of a perfluoroethenyl zinc reagent solution by syringe ($-CF{=}CF_2$ concentration was 0.65 M by internal standard ^{19}F NMR, 6.0 mL is 3.9×10^{-3} mol). The mixture was stirred and heated to 110–112 °C. After 7.5 h, 9-iodo-10-nitrophenanthrene was consumed as indicated by TLC in hexane/THF (2.7:1). Seven compounds were evident with $R_f = 0.57$ (s), 0.44 (w), 0.42 (w), 0.32 (w), 0.26 (w), 0.23 (s), and 0.14 (m). The reaction mixture was decanted from a small amount of black solid into a separatory funnel and diluted with 300 mL of water and then extracted with 5 × 100 mL of diethyl ether. The ether extracts were then combined and washed with 5 × 100 mL of water. The ether solution was dried over anhydrous $MgSO_4$ and then the solvent removed by rotary evaporation to yield 0.20 g of a brownish-yellow solid. This solid was dissolved in ether, 5 g of silica gel was added, and then, the ether was evaporated under a stream of nitrogen. The dry reaction mixture deposited on silica gel was taken up in hexanes and added to a 2- × 30-cm silica gel column packed in hexanes. The column was eluted under flash conditions with hexanes, hexanes/THF (9:1), and, last, acetone. 9,10-Bis(trifluorovinyl)phenanthrene (**1**, 0.063 g, 16%) was obtained as white flakes, mp 133–134 °C with $R_f = 0.57$ in the above solvent system. Further purification by GLPC ($^1/_4$-in. × 5-ft., 20% QF-1 column) provided >99% pure **1**: ^{1}H NMR δ 7.67 (t, 2H, $^3J_{HH} = 8.0$ Hz), 7.75 (t, 2H, $^3J_{HH} = 8.0$ Hz), 8.07 (d, 2H, $^3J_{HH} = 8.1$ Hz), 8.68 (d, 2H, $^3J_{HH} = 8.1$ Hz); ^{19}F NMR syn diastereomer δ (low field ($\approx$100 ppm) signal overlapped with anti diastereomer) −115.7 (dd, 2F, $^3J_{transFF} = 117$ Hz, $^2J_{FF} = 75$ Hz), −159.3 (dd, 2F, $^2J_{FF} = 75$ Hz, $^3J_{cisFF} = 20$ Hz), anti diasteromer: −100.2 (dd, 2F, $^2J_{FF} = 70.9$ Hz, $^3J_{cisFF} = 27.1$ Hz), −115.0 (dd, 2F, $^3J_{transFF} = 119.1$ Hz, $^2J_{FF} = 70.9$ Hz), −160.6 (dd, 2F, $^2J_{FF} = 70.9$ Hz, $^3J_{cisFF} = 27.1$ Hz); ^{13}C NMR δ 123.0, 126.6 (b m), 127.9, 129.1, 131.6; UV spectrum in *n*-pentane, λ (nm) ($E_{(L/cm \times mol)}$), 209 (23742.6), 224 (25146.7), 257 (49706.5), 295 (10428.9), 306 (11760.7); LRMS *m/z* (rel. intensity) 339 (17), 338 (100), 288 (80), 287 (19), 269 (89), 267 (17), 238 (15), 134 (17); HRMS calcd for $C_{18}H_8F_6$ 338.0530, found 338.0539.

Thermolysis of 9,10-Bis(trifluorovinyl)phenanthrene (1). A solution of **1** (0.076 g, 2.2×10^{-4} mol) in 1.9 g of C_6H_6 was prepared and flame-sealed in a thick-walled Pyrex tube under nitrogen. The sample was then placed in a Statim thermostated oil bath at 180 °C and heated for 54 h. The tube was opened and GLPC analysis ($^1/_8$-in. × 20-ft., 20% QF-1 column) showed some remaining starting material and four new products. The percentages of total mass balance were 20% **1**, 7% **2**, 6% **8**, 10% **7**, and 57% **9**. The solvent was evaporated under a stream of

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nitrogen, and then the sample was subjected to vacuum (0.1 mmHg for 1 h) to yield 0.066 g of a yellowish-tan powder, corresponding to an 86% yield of $C_{18}H_8F_6$ isomers. This mixture was taken up in 0.5 mL of diethyl ether and separated into five fractions by preparative GLPC ($^1/_4$-in. × 5-ft., 20% QF-1 column) for a 54% yield of $C_{18}H_8F_6$ isomers isolated. Retention times compound (minutes): **1** (11.0), **7** (16.5), **8** (18.3), **2** (22.5), and **9** (30.5).

Fraction 1. By comparison of the ^{1}H and ^{19}F NMR spectra and the melting point with an earlier obtained sample, the material was found to be **1**. White flakes (6 mg, 9% isolated) were obtained, mp 132–134 °C, ~100% pure by analytical GLPC.

Fraction 2. 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)-bicyclo[3.1.0]-hex-2-ene (7). A white powder (2 mg, 3%) was obtained, actually a 2:1 mixture of **7**:**8**. A second careful separation of such a mixture by the aforementioned preparative GLPC conditions would yield ratios of 24:1, respectively. **7**: ^{1}H NMR δ 7.72–7.86 (m, 4H), 8.25–8.30 (m, 2H), 8.74 (d, 1H, $^{3}J_{HH}$ = 8.4 Hz), 8.76 (d, 1H, $^{3}J_{HH}$ = 8.4 Hz); ^{19}F NMR δ −87.8 (dddm, 1F, $^{2}J_{FF}$ = 267.3 Hz, $^{3}J_{FF}$ = 13.7 Hz, $^{4}J_{FF}$ = 3.4 Hz), −112.4 (dm, 1F, $^{2}J_{FF}$ = 268.0 Hz), −137.7 (dddm, 1F, $^{2}J_{FF}$ = 173.2 Hz, $^{3}J_{FF}$ = 13.7 Hz, $^{4}J_{FF}$ = 5.7 Hz), −147.7 (dtd, 1F, $^{2}J_{FF}$ = 173.2 Hz, $^{3}J_{FF}$ = 15.3 Hz, $^{4}J_{FF}$ = 7.6 Hz), −216.1 to −216.4 (m, 1F), −230.2 (ddddd, 1F, $^{3}J_{FF}$ = 28.3 Hz, $^{3}J_{FF}$ = 15.1 Hz, $^{3}J_{FF}$ = 8.2 Hz, $^{4}J_{FF}$ = 4.2 Hz, $^{4}J_{FF}$ = 1.0 Hz); LRMS *m/z* (rel. intensity) 339 (16), 338 (97), 288 (71), 287 (16), 269 (97), 238 (17),134 (29), 119 (49); HRMS calcd for $C_{18}H_8F_6$ 338.0530, found: 338.0547.

Fraction 3. 4-(Difluoromethylidene)-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)cyclopent-1-ene (8). A light yellow powder (4 mg, 5%) being a 32.3:1 mixture of **8**:**9** was obtained. **8**: ^{1}H NMR δ 7.77 (t with fine splitting, 2H, $^{3}J_{HH}$ = 7.2 Hz, $^{4}J_{HH}$ = 1.4 Hz), 7.68 (t with fine splitting, 2H, $^{3}J_{HH}$ = 7.1 Hz, $^{4}J_{HH}$ = 1.4 Hz), 8.39 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz), 8.78 (d with fine splitting, 2H, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.4 Hz); ^{19}F NMR δ −70.56 to −70.65 (m, 2F), −89.6 (ddm, 4F, $^{4}J_{FF}$ = 3.9 Hz, $^{4}J_{FF}$ = 3.3 Hz); LRMS *m/z* (rel. intensity) 339 (18), 338 (100), 319 (36), 269 (39), 159 (18), 134 (22); HRMS calcd for $C_{18}H_8F_6$ 338.0530, found 338.0552.

Fraction 4. 1,2,2,3,3,4-Hexafluoro-2,3-dihydrotriphenylene (2). A light yellow solid was obtained (4 mg, 5%), being 85% pure with contamination by 3% **8** and 12% **9**. **2**: ^{1}H NMR δ 7.38 (t, 2H, $^{3}J_{HH}$ = 8.7 Hz), 7.47 (t, 2H, $^{3}J_{HH}$ = 8.7 Hz), 7.93 (d, 2H, $^{3}J_{HH}$ = 8.4 Hz), 8.06 (d, 2H, $^{3}J_{HH}$ = 8.4 Hz); ^{19}F NMR δ −132.6 (dm, 4F, $^{3}J_{FF}$ = 12.4 Hz), −135.9 (tm, 2F, $^{3}J_{FF}$ = 12.4 Hz); LRMS *m/z* (rel. intensity) 339 (14), 338 (90), 288 (45), 287 (72), 238 (12), 134 (27), 124 (13), 119 (24); HRMS calcd for $C_{18}H_8F_6$ 338.0530, found 338.0540.

Fraction 5. 1,2-(9,10-Phenanthro)-3,5,5-trifluoro-4-(trifluoromethyl)-1,3-cyclopentadiene (9.) Light yellow needles (24 mg, 32%) were obtained. A second separation of such material by the previous preparative GLPC conditions could yield material ~100% pure by analytical GLPC, mp 125–126 °C. **9**: ^{1}H NMR δ 7.76 (t, 2H, $^{3}J_{HH}$ = 8.4 Hz), 7.81 (t, 2H, $^{3}J_{HH}$ = 8.4 Hz), 8.30 (d, 1H, $^{3}J_{HH}$ = 8.0 Hz), 8.40 (d, 1H, $^{3}J_{HH}$ = 8.1 Hz), 8.76 (d, 1H, $^{3}J_{HH}$ = 8.3 Hz), 8.78 (d, 1H, $^{3}J_{HH}$ = 8.4 Hz); ^{19}F NMR δ −59.3 (dt, 3F, $^{4}J_{FF}$ = 14.1 Hz, $^{4}J_{FF}$ = 2.3 Hz), −103.7 (m,1F), −121.6 (dm, 2F, $^{4}J_{FF}$ = 8.7 Hz); LRMS *m/z* (rel. intensity) 339 (17), 338 (100), 319 (12), 270 (9), 269 (64), 249 (10); HRMS calcd for $C_{18}H_8F_6$ 338.0530, found 338.0518.

Solution-Phase Thermolysis of 9,10-Bis(trifluorovinyl)-phenanthrene (1): A Quantitative Study Followed by ^{19}F NMR. A stock solution of **1** in C_6D_6 was prepared as follows: 0.048 g (1.4×10^{-4} mol) of preparative GLPC-purified **1** (GLPC conditions as in previous discussion) was dissolved in 1.1 mL of C_6D_6, and 7 mg of C_6H_5F was added as an ^{19}F NMR internal standard. An aliquot of the solution was syringed into each of three thick-walled NMR tubes (base-rinsed, deionized-water-rinsed, acetone-rinsed, flame-dried under nitrogen), and then, the tubes were flame-sealed under nitrogen. Thermolysis was carried out by submerging the sample in a Statim thermostated oil bath for a time period and then rapidly removing and cooling the sample in an ice bath. The sample was then observed by ^{19}F NMR using a T_1 delay of 10 s and collecting a minimum of 128 transients before Fourier transforming the spectrum. The relative concentrations of all fluorinated products were arrived at by integration of the sample signals and comparison *versus* the internal standard C_6H_5F. Figure 1 represents the data graphically. Raw data can be found in the supplementary material.

Solution-Phase Thermolysis of 1,4,4,5,6,6-Hexafluoro-2,3-(9,10- phenanthro)bicyclo[3.1.0]hex-2-ene (7): A Quantitative Study Followed by ^{19}F NMR. A stock solution of **7** in C_6D_6 was prepared as follows: 0.0078 g (2.3×10^{-5} mol) preparative GLPC-purified **7** (preparative GLPC as in synthetic discussion section, containing traces of **8** and **9**) was dissolved in 0.52 g of C_6D_6, and 10 mg of C_6F_6 was added as an ^{19}F NMR internal standard. An aliquot of the solution was syringed into each of three thick-walled NMR tubes (base-rinsed, deionized-water-rinsed, acetone-rinsed, flame-dried under nitrogen), and then, the tubes were flame-sealed under nitrogen. The method of observation for this system was the same as that used in the quantitative study of **1** discussed previously. The data which was obtained is represented graphically in Figure 2. Raw data can be found in the supplementary material.

Reaction of 9,10-Bis(trifluorovinyl)phenanthrene (1) with CsF. 9,10-Bis(trifluorovinyl)phenanthrene (**1**, 0.0103 g, 3.05×10^{-5} mol) was dissolved in 2.0 mL of dry DMF to which was added 0.0113 g (7.43×10^{-5} mol) of dry CsF. The reaction mixture was stirred rapidly for 2.5 h at room temperature, and a small aliquot of the reaction mixture was taken, diluted with water, extracted with diethyl ether, concentrated under a stream of nitrogen, and then analyzed by analytical GLPC which revealed that no reaction had occurred. The sample was then heated at 115 °C. After 3.5 h, an aliquot was taken as described earlier and GLPC analysis showed three products with **1** approximately 70% consumed. Comparison with a **1** thermolysis reaction mixture sample (containing materials **1**, **2**, **7**, **8**, and **9**) showed that the CsF reaction had no products in common with the thermal reaction. No further characterization or separation was performed on the CsF reaction mixture.

Reaction of 4-(Difluoromethylidene)-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)cyclopent-1-ene (8) with Catalytic CsF. To an NMR sample in C_6D_6 with a C_6F_6 internal standard containing 30.0% **7**, 44.6% **8**, and 25.4% **9** was added 20 µL of C_6D_6 containing traces of CsF. This fluoride-spiked C_6D_6 solution was prepared by adding 2 mL of dry C_6D_6 to 10 mg of dry CsF and then heating at reflux for 10 min. Visually, no CsF dissolved. The NMR sample was then flame-sealed under nitrogen and placed in a Statim thermostated oil bath at 81 °C for 57 min. After this time, the sample was cooled and found to contain 30.7% **7**, 19.7% **8**, and 49.5% **9** by integration of the ^{19}F NMR signals *versus* the C_6F_6 internal standard. The overall mass balance of **7**, **8**, and **9** *versus* the starting mixture was 95%.

Acknowledgment. Support of this research in part by the National Science Foundation and by the Division of Sponsored Research of the University of Florida is gratefully acknowledged.

Supplementary Material Available: Copies of the ^{19}F NMR spectra of **1**, **2**, **7**, **8**, and **9** and tables of raw concentration data for the kinetic studies of compounds **1** and **7** (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.