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An Experimental and Computational Investigation of the Electrocyclic Ring Opening of α-Fluorocyclopropyl Radicals†

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Abstract: A series of α-fluorobicyclopropyl radicals were generated by the reaction of CF with the corresponding cycloalkene. The tendency of these radicals to undergo electrocyclic ring opening to the corresponding cyclic allyl radicals was evaluated computationally and experimentally. The symmetry forbidden ring openings will occur if there is significant thermodynamic driving force. AM1 calculations and product analysis indicate that those radicals with calculated ring opening exothermicities of 50 kcal/mol or more give ring opened products © 1997 Elsevier Science Ltd.

Introduction

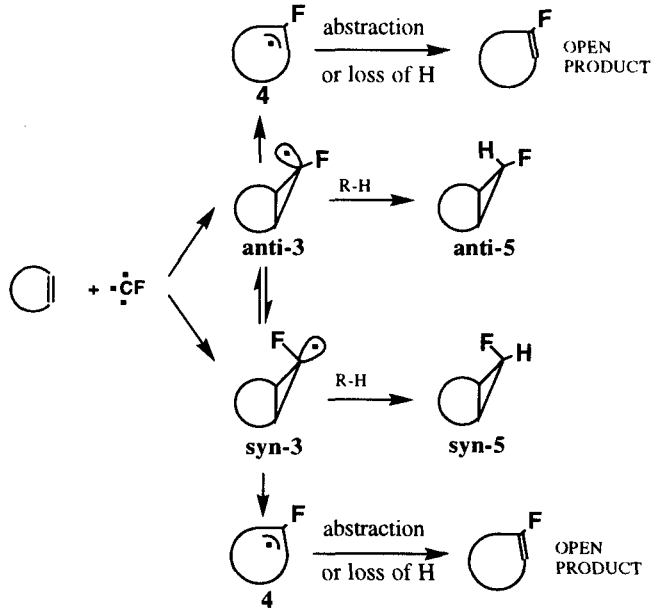
The electrocyclic ring opening of the cyclopropyl radical, **1**, to the allyl radical, **2**, has been the

1 **2**

subject of intense scrutiny over many years.[1] Longuet-Higgins and Abrahamson were the first to point out that a consideration of state symmetry correlation diagrams indicates that the reaction is forbidden in both conrotatory and disrotatory modes.[2] Nevertheless, the opening of **1** has been reported to occur in the gas phase with a barrier of 22±2 kcal/mol in a reaction estimated to be exothermic by 27.8 kcal/mol.[3,4] Of course, the reaction is not required to follow a strict conrotatory or disrotatory pathway and may proceed without a C_2 axis or a plane of symmetry. In fact, Dewar and Kirschner,[5] using the results of MINDO/3 calculations, have proposed that methylene rotation during ring opening is nonsynchronous with one methylene rotating by 50° and the other having rotated not at all in the transition state. Olivella, Sole, and Bofill[6] have confirmed this nonsynchronicity in a calculation of transition state geometry at the CASSCF/3-21G level in which they find rotations of 33° and 6° for the methylene groups. These workers calculate a barrier of 24.5 kcal/mol with AM1 and 21.9 kcal/mol at their highest level of calculation (CASSCF/6-31G*//CASSCF/3-21G+ZPC). Thus, both semiempirical and ab initio calculations reproduce the experimental barrier quite well and are in agreement that the transition state is nonsynchronous. This latter point appears to render the question of conrotatory or disrotatory opening moot. However, systems in which the cyclopropyl radical is fused to another ring are constrained to open in a

disrotatory manner and may be more synchronous. In order to examine the factors effecting the electrocyclic ring opening of such species, we now report an experimental and computational investigation of a series of fluorobicyclo[n.1.0]alkyl radicals, **3** (scheme 1).

Scheme I. The reaction of CF with cyclic alkenes



The reaction of arc generated carbon atoms with CF_4 yields the monovalent carbon species CF which can be trapped by alkenes to give α-fluorocyclopropyl radicals.[7] In the current study, we have used this convenient methodology to generate a number of radicals with general structure **3** which have been examined for their potential to undergo electrocyclic ring opening to monocyclic allyl radicals, **4** (scheme 1). We have also evaluated the energetics of these fluorocyclopropyl radical openings computationally.

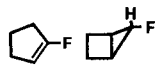
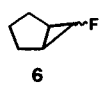
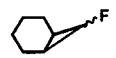
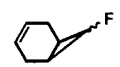
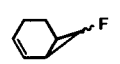
Experimental Section

Analysis. Fluorine NMR spectra were recorded with a Bruker AC 250 spectrometer operating at 235 MHz. The NMR solvent was $CDCl_3$ in all cases and α,α,α-trifluorotoluene was added as an internal standard. All ^{19}F chemical shifts are relative to the shift for $CFCl_3$ at zero ppm. The GC/MS analysis were carried out on a Fisons VG Trio-2000 Mass Spectrometer with a Hewlett Packard 5890 Series II Gas Chromatograph equipped with a J&W 30m x 0.25mm DB5 column.

Generation of CF and its Reaction With Alkenes. The reactions were carried out by cocondensing CF_4 and alkene substrate with arc generated carbon at 77K in an evacuated reactor.[8] The alkene substrate (15 mmol) was allowed to mix with an equimolar amount of CF_4 in the vapor phase for one hour before beginning the reaction. The substrates were bled into the reactor at an approximate rate of 1 mmol/min and condensed on a 77K surface while an arc was struck intermittently between two high purity graphite rods. At the conclusion of the reaction, the reactor was allowed to warm to room temperature while the volatile

products were removed under vacuum and collected in 195K and 77K traps. The contents of the traps were analyzed by ^{19}F NMR and GC/MS. In a typical reaction 75 mmoles of carbon are lost from the graphite rods producing $1x10^{-6}$ mmoles of fluorocyclopropane. Table 1 lists the ^{19}F nmr spectra of products along with their

Table 1. The products of CF reactions and their ^{19}F NMR spectral data

SUBSTRATE	PRODUCT	PRODUCT YIELD (nmol)		^{19}F NMR DATA δ (ppm)[a]	$^2J_{H-F}$ (Hz)	$^3J_{H-F}$ (Hz)	anti/syn	REFERENCE
□	 12 anti-11	12	$5x10^{-3}$	12 -123	—	—		15
		anti-11	$3x10^{-2}$	anti -216	67.3	14.1		
⬠	 6	anti	3.2	anti -214	64.7	20.9	2.2	13
		syn	1.5	syn -235	66.7	3.8		
⬡	 7	anti	0.5	anti -205	64.5	23.1	2.5	13
		syn	0.2	syn -235	67.3	—		
⬠	 8		1.0	-114	—	8.7		7b
⬡	 9	anti	1.4	anti -213	64.7	21.2	3.6	
		syn	0.4	syn -239	67.5	8.3		
⬡	 10	anti	1.6	anti -204	63.8	21.2	2.2	
		syn	0.7	syn -227	65.7	—		
⬡	 8		1.4	-114	—	8.7		7b

[a] Chemical shifts are realtive to $CFCl_3$

yields. Since much carbon is physically removed from the rods in large chunks and it is impossible to determine the quantities of reactive C_1 produced, percentage yields are not meaningful and absolute yields of products, as determined by GC with naphthalene as internal standard, are listed in table 1. All of the products listed in table 1 showed molecular ion peaks in the mass spectra and the appropriate ^{19}F nmr spectra. Additional carbon atom reactions were carried out with $CFCl_3$ and CF_3Cl as fluorine sources employing the same methodology described above. An alternate procedure in which small portions of substrate are repeatedly cocondensed at 77K followed by reaction with arc generated carbon gives the same products (although in lower yield) as in cocondensation of C with substrate.

Reaction of Chlorofluorocarbene with Cyclobutene. This reaction was carried out using a

procedure reported by Dolbier and Burkholder[9] with their apparatus modified by the addition of a dry ice condenser. Under an argon atmosphere, 2.5 ml of $TiCl_4$ (22.8 mmol) was added dropwise to 30 ml of distilled dried THF at -10°C. $LiAlH_4$ (0.911 g, 24 mmol) suspended in 20 ml of THF was then added dropwise. The resulting brown mixture was allowed to warm to room temperature for 30 minutes, cooled back to -10°C, and cyclobutene (0.4 g, 7.6 mmol) condensed into the chilled mixture. A solution of 2 ml $CFCl_3$ (21.8 mmol) in 10 ml of THF was added dropwise to the mixture, which then continued to stir at -10°C for 30 minutes. The cold mixture was hydrolyzed with 100 ml of 10% HCl in ice and extracted with methylene chloride (3 x 25 ml). Analysis of the crude organic layer showed the presence of 5-chloro-1-fluorocyclopentene, **23**. ^{19}F NMR ($CDCl_3$) δ -130.5.[10] MS *m/z* 122 (M+2, 2.4), 120 (M, 7.2), 102 (2.5), 85 (100), 84 (19.3), 65 (19.1), 59 (12.6). Reduction of that crude mixture by refluxing with $(Bu)_3SnH$ and AIBN gave 1-fluorocyclopentene, **12**.^{19}F NMR ($CDCl_3$) δ -122.9.[15] MS *m/z* 86 (M, 19.2), 84 (23.5), 68 (23.9), 67 (24.1), 62 (100), 61 (38).

Computational Methods.

The activation energies and exothermicities for the ring opening of the bicyclic radical intermediates as well as for cyclopropyl and fluorocyclopropyl radicals were calculated by semi-empirical methods using the AM1 Hamiltonian and UHF formalism.[11] The structures were fully optimized with no symmetry constraints. Gradients were minimized by the NLLSQ procedure and all transitions states were characterized by one negative eigen vector which was followed on to products and back to reactants in order to insure that the proper transition state had been identified. The results of these calculations are listed in Table 2. Table 2 also includes AM1

Table 2. Activation enthalpies and (enthalpies of reaction) in kcal/mol calculated by AM1 for ring opening of various reactive intermediates.

Substrate	Radical[a]	Cation	Anion
Cyclopropyl, **1**	24.53 (-28.98)	5.80 (-34.38)	
1-Fluorocycloprop-1-yl, **3**	24.28 (-24.39)	13.48 (-14.27)	
anti-**20**	6.90 (-60.39)	[b]	24.14 (-62.52)
syn-**20**	8.57 (-60.12)	[b]	24.13 (-58.87)
anti-**13**	16.66 (-38.10)	3.81 (-38.26)	30.84 (-42.39)
anti-**15**	11.39 (-52.00)	1.57 (-58.03)	24.45 (-59.60)
syn-**15**	12.91 (-51.64)		
anti-**14**	19.21 (-29.53)	11.82 (-31.94)	28.76 (-34.31)
syn-**14**	18.56 (-29.16)		
anti-**16**	20.11 (-29.92)	14.03 (-30.03)	29.91 (-35.59)
anti-**17**	18.44 (-37.03)	14.00 (-38.97)	24.26 (-47.61)
anti-**18**	8.45 (-41.19)	5.22 (-66.93)	11.28 (-37.71)
Bicyclo[4.1.0]heptadien-7-yl	7.90 (-43.84)	[b]	
Average	16.60 (-40.05)	8.72 (-35.13)	26.27 (-43.88)

[a]Calculated using the UHF formalism. [b]Geometry optimization of these cations led to the open species suggesting that there is little or no barrier to ring opening in these allowed reactions.

calculated heats of reaction and activation enthalpies for the carbocations and carbanions corresponding to the fluorocyclopropyl radicals we have studied. The barriers to ring opening and inversion for the 5-fluorobicyclo[2.1.0]pentan-5-yl radical, **20**, were also evaluated at the UHF/3-21G level using the Gaussian 92 programs.[12]

Results

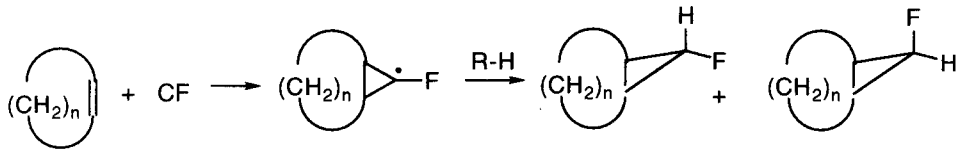
Characterization of Products. We have established that CF is formed in the reaction of atomic carbon with CF_4 and that it adds to a carbon-carbon double bond in a concerted fashion to yield a fluorocyclopropyl radical, **3**.[7] When the addition is to an endocyclic double bond, there is the possibility of forming both syn and anti-**3** which may subsequently abstract hydrogen to give the corresponding cyclopropyl fluorides, **5**, (Scheme 1). Since the same products are formed when substrates are cocondensed with carbon or condensed on the 77K walls of the reactor prior to carbon evaporation, we feel that these reactions occur in the condensed phase on the cold reactor walls.

The possibility that the fluorocyclopropanes in these reactions arise from addition of fluoromethylene to alkenes has been previously considered and rejected.[7] The fact that syn:anti ratios in fluorocyclopropane products are dependant upon H donor concentration indicates that products result from initial addition of CF to the alkene followed by hydrogen abstraction. An alternate sequence in which initial hydrogen abstraction to give fluoromethylene is followed by double bond addition would give products whose stereochemistry was independent of H donor concentration.

Although most cyclopropyl radicals are rapidly inverting σ radicals, the α-fluorocyclopropyl radical is a σ radical in which the rate of inversion is comparable to or slower than that of intermolecular abstraction.[1, 13] Since we have observed that syn:anti ratios in **5** to go to zero with increasing H donor concentration, we have postulated that CF adds initially to give anti-**3** which may either invert to syn-**3** or abstract hydrogen.[7] If the rate of electrocyclic ring opening in **3** is faster than that for hydrogen abstraction, we expect some products of ring opening to monocyclic allyl radical **4** will be observed.

Since abstraction of fluorine by any of these radicals is precluded on energetic grounds, the products are all expected to be monofluoro compounds which can be characterized by their ^{19}F NMR spectra. The fluorocyclopropane products are generally present as syn and anti isomers (scheme 1) in which the ^{19}F chemical shift is more than 200 ppm upfield of $CFCl_3$ with the syn isomer typically 20-30 ppm upfield of the anti isomer.[13] Fluorocyclopropanes are characterized by a strong geminal F-H coupling on the order of 65 Hz. The stereochemistry of the two isomers is confirmed by the vicinal F-H coupling. Typically the syn isomer has $^3J_{H\text{-}F}$= 3-12 Hz while the anti isomer has $^3J_{H\text{-}F}$= 18-23 Hz.[14] The product of ring opening will be a monocyclic allyl radical which, if it abstracts hydrogen, will yield a 1-fluorocycloalkene. Fluorines in such compounds have ^{19}F chemical shifts 90-110 ppm upfield of $CFCl_3$. The signals are split into a doublet by coupling to the vinyl hydrogen and may be further split by vicinal coupling to the adjacent CH_2 group. Such coupling is not a factor in the case of 1-fluorocyclopentene, but becomes increasingly more important as the rings get larger.[15] Table 1 lists the products of the CF reactions along with their ^{19}F NMR spectral data. Syn and anti **6** and **7**[13] as well as **8**[7b] and **12**[15] are known compounds and their presence has been confirmed by comparison of their ^{19}F NMR spectral data with that of authentic samples. Syn and anti **9** and **10** and anti-**11** have not previously been reported. Their presence has been deduced by the fact that their ^{19}F NMR spectral data matches the pattern established by the known species.

Observed Reactivity of Fluorocyclopropyl Radicals. Addition of CF to cyclopentene and cyclohexene generates the bicyclic radicals **13** and **14** respectively which do not ring open.

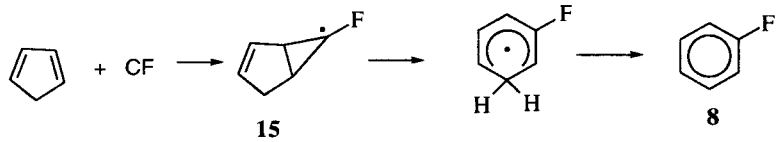


13; n=3
14; n=4

anti-**6**; n=3
anti-**7**; n=4

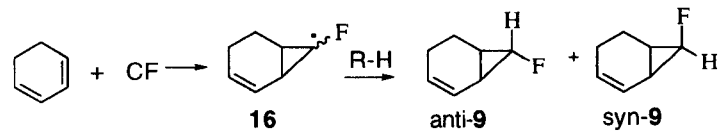
syn-**6**; n=3
syn-**7**; n=4

However, reaction of CF with cyclopentadiene yields fluorobenzene, **8**, in a reaction we postulate to involve initial formation of the 6-fluorobicyclo[3.1.0]pent-2-en-6-yl radical, **15**, which opens to the 2-fluorocyclohexadienyl radical and subsequently looses hydrogen to form fluorobenzene. There is no

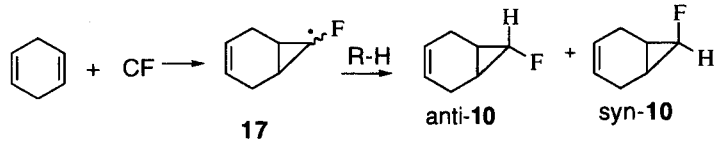


15 **8**

evidence for the formation of products corresponding to hydrogen abstraction by **15**. CF reacts with 1,3- and 1,4-cyclohexadiene to give, after hydrogen abstraction, only the 7-fluorobicycloheptenes **9** and **10**. This is particularly interesting in the case of the reaction with 1,3-cyclohexadiene in which the intermediate radical, **16**, should have the same electronic driving force for ring opening as **15**. It appears that the increased ring strain in **15** as compared to **16** is responsible for the ring opening of the former.

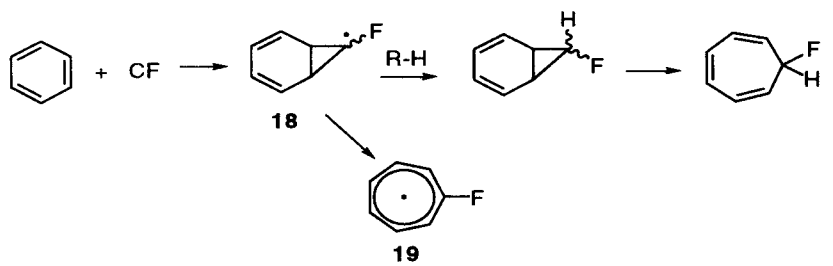


16 anti-**9** syn-**9**



17 anti-**10** syn-**10**

We have previously reported that reaction of CF with benzene generates the 7-fluorobicyclo[4.1.0]hepta-2,4-dien-7-yl radical, **18**, which can be trapped by the addition of hydrogen donors and also undergoes ring opening to the fluorotropyl radical, **19**.[7h] Radical **18** is unique among the



18 **19**

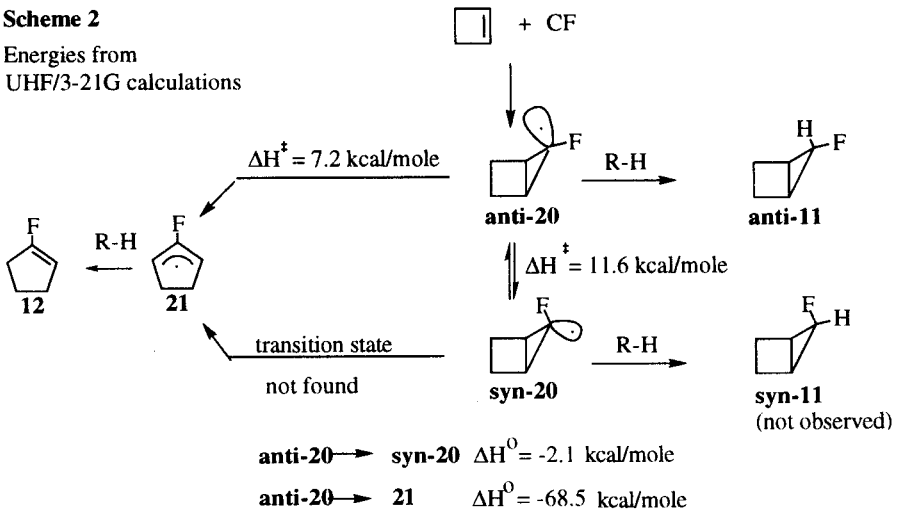
radicals generated here in that the degeneracy of the orbitals in **19** provides a choice of orbitals with which to correlate the SOMO of **18** allowing the ring opening to become symmetry allowed.

The reaction of CF with cyclobutene is expected to generate the rather strained 5-fluorobicyclo-

[2.1.0]pent-5-yl radical, **20** (scheme 2). In this case, an examination of the ^{19}F nmr spectrum revealed

Scheme 2

Energies from
UHF/3-21G calculations



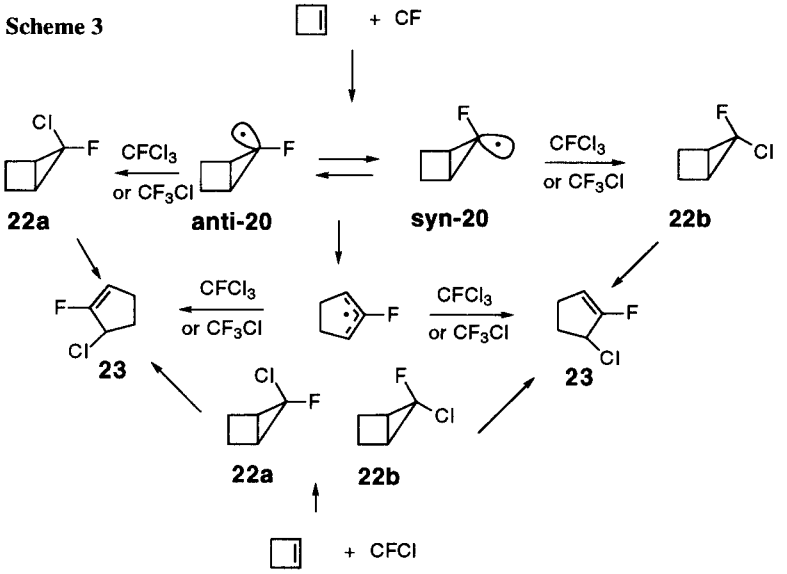
anti-20 → **syn-20** ΔH^{O} = -2.1 kcal/mole

anti-20 → **21** ΔH^{O} = -68.5 kcal/mole

only one signal that could be assigned to a fluorine on a cyclopropyl ring. On the basis of the chemical shift (δ=-216 ppm) and the $^{3}J_{H\text{-}F}$ coupling of 14.1 Hz, we assign this peak to **anti-11**. It is interesting that the other product of hydrogen abstraction by **20**, **syn-11**, is not observed. The ^{19}F nmr spectrum also shows the presence of the known 1-fluorocyclopentene, **12**, which could arise by ring opening of **20** to radical **21** followed by hydrogen abstraction. Attempts to change the ratio of **11:12** or to observe **syn-11** by increasing the concentration of H donor were unsuccessful. When propene was used as a hydrogen donor, only products of the reaction of CF with propene were observed leading us to conclude that propene reacts more rapidly with CF than the strained cyclobutene. Addition of isobutane actually decreased the ratio of **11:12** indicating that isobutane is a less efficient H donor than cyclobutene itself and simply acts to dilute the cyclobutene.

We have previously reported that reaction of C with chlorofluoromethanes gives both CF and CCl with the chlorofluorocarbon substrate also functioning as a source of abstractable chlorine. Accoringly, we have reacted $CFCl_3$ and CF_3Cl with carbon and cyclobutene in hopes of trapping **20** as the 5-chloro-5-fluorobicyclo[2.1.0]pentanes, **22a** and **22b** (Scheme 3). However the ^{19}F nmr spectra of products showed no evidence for either **22a** or **22b** which would be expected as triplets at δ≈-120 to -130 and δ≈-150 to -160 ppm respectively.[9,15] Instead the product of ring opening followed by chlorine abstraction, 5-chloro-1-fluorocyclopentene, **23**, was detected in the ^{19}F spectra (δ=-130.6 ppm).[10] This result indicates that **20** ring opens faster than it can abstract chlorine and/or **22a** and **22b** are unstable under the reaction conditions. That the latter is true is indicated by the fact that attempts to prepare these compounds by the addition of chlorofluoromethylene to cyclobutene give only **23** (Scheme 3).

Scheme 3



Discussion

Correlation of Experimental and Computational Results. We have been able to use the results of AM1 calculations to provide a qualitative rationalization of our experimental results. Table 2, which lists the calculated enthalpies of and barriers to the ring openings investigated here, demonstrates that those radicals with a calculated barrier to ring opening of 16.7 kcal/mol or more give no ring opened products. In contrast those radicals with calculated barriers of 11.4 kcal/mol or less all show ring opening to some extent. That these semiempirical calculations adequetly describe the energetics of these systems is indicated by a reasonable correspondance between experimental and calculated barriers and exothermicities for the opening of the parent cyclopropyl radical ($\Delta H^{\ddagger}_{exp}$ = 22 kcal/mol, $\Delta H^{\ddagger}_{calc}$ = 24.5 kcal/mol; ΔH_{exp} = 27 kcal/mol, ΔH_{calc} = 29 kcal/mol). An examination of the results in table 2 demonstrates that this computational method adequetly distinguishes between allowed and forbidden pathways. Thus, the allowed ring openings of the cations have an average barrier of 8.7 kcal/mol while the forbidden openings of the radicals and anions average 16.0 and 26.3 kcal/mol respectively

Ring Opening of the 5-Fluorobicyclo[2.1.0]pent-5-yl Radical, 20. The results from the reaction of CF with cyclobutene are interesting in that both ring opened and closed products are observed but the only product of hydrogen abstraction by fluorocyclopropyl radicals is anti-5-fluorobicyclo[2.1.0]pentane, anti-**11**. This result is not predicted by the calculations if one assumes that both syn and anti-**20** are generated initally. As shown in table 2, syn-**20** is calculated to open slower than anti-**20** leading to the expectation that more syn-**20** will remain to be trapped. Several of the other radicals investigated here are calculated to show a similar, although less pronounced preference for opening of the anti isomer over the syn (table 2).

In scheme 2, we have rationalized the results of the reaction of CF with cyclobutene by assuming that, in analogy with the addition of CF to other cycloalkenes, only the anti-5-fluorobicyclo-[2.1.0]pent-5-yl radical, anti-**20**, is generated initially. If the barrier to inversion in anti-**20** is greater than that for ring

opening and hydrogen abstraction, we expect no syn-**20** and consequently no products of its hydrogen abstraction. However, this expectation cannot be confirmed using the AM1 method which gives an unreasonably low barrier of ~1 kcal/mole for the inversion of anti-**20**. The barrier to inversion of the α-fluorocyclopropyl radical has been calculated to be 10.5 (CNDO/2)[1] and 13.7 ([UMP2/6-31G*][7] kcal/mol. It has been established that the fluorocyclopropyl radical generally abstracts hydrogen faster than it inverts.[1,13] Accordingly, we have investigated the energetics of the CF + cyclobutene system at the ab initio UHF/3-21G level which has been shown to adequetly describe the energetics of the parent cyclopropyl radical.[6] In this case, the calculated barriers to inversion (11.6 kcal/mol) and ring opening (7.2 kcal/mol) in anti-**20** bear out the assumption that ring opening is faster than inversion. Since the barrier to hydrogen abstraction is estimated to be appoximately 7 kcal/mol,[16] we expect ring opening and hydrogen abstraction by anti-**20** but no inversion to syn-**20**. Thus if CF adds to endocyclic double bonds to give initially only the anti radicals, as indicated by our previous results,[7] we expect no products from syn-**20** radicals in the CF + cyclobutene system. Of course, in the less strained larger ring systems, the barrier to ring opening is larger than that of inversion and syn:anti product ratios are dependent on the concentration of H donor.[7]

In the reactions of CF with chlorofluorocarbons and cyclobutene and in the reaction of CFCl with cyclobutene, neither **22a** nor **22b** was observed (scheme 3). Since **23** was produced in both reactions, it seems reasonable to conclude that **22** is unstable under the reaction conditions and rearranges to **23** by the cationic cyclopropyl-allyl rearrangement.[17] However, this rearrangement would not explain the absence of syn-**11** in the reaction of CF with cyclobutene, as the cyclopropyl-allyl rearrangement product of **11** would be 3-fluorocyclopentene rather than the observed 1-fluorocyclopentene, **12**. Although 3-fluorocyclopentene is unknown, its ^{19}F chemical shift is expected to be similar to that of the known 3-fluorocyclohexene (δ=-166 ppm)[18] and peaks in this region are not observed.

Evaluation of these Forbidden Reactions. If the disrotatory electrocyclic ring openings studied here are examples of forbidden reactions driven to occur by their exothermicities, we should be able to correlate the calculated barriers with the calculated exothermicities. That this can be done is illustrated in figure 1 by a plot of calculated $\Delta H^{\ddagger}$ vs calculated heat of reaction for the fluorocyclopropyl radicals studied here. It is interesting that the one point which fails to correlate is that for the ring opening of **18**, the only symmetry allowed reaction. When this point is not included, a correlation coefficeint of 0.98 is obtained for the remaining points.

The geometry of the transition state for these forbidden reactions indicates considerable bond breaking in the transition state but little rotation, a result expected if rotation provides little benefit in terms of symmetry allowed interaction of the breaking bond with the SOMO of the radical. If Δr_{ts} is the increase in the distance between the bridgehead carbons in going from reactant to the transition state for ring opening and Δr_{prod} is the corresponding increase in going from reactant to product, we find that $\Delta r_{ts}/\Delta r_{prod} = 0.42$ in the forbidden opening of anti-**13** while it is 0.29 in the allowed opening of anti-**18**. Figure 2 shows the transition states for these two reactions. If the distance between the bridgehead carbons reflects the extent of reaction (reaction coordinate), these forbidden electrocyclic ring openings have late transition states whose energies should correlate with reaction exothermicities providing a rational for figure 1.

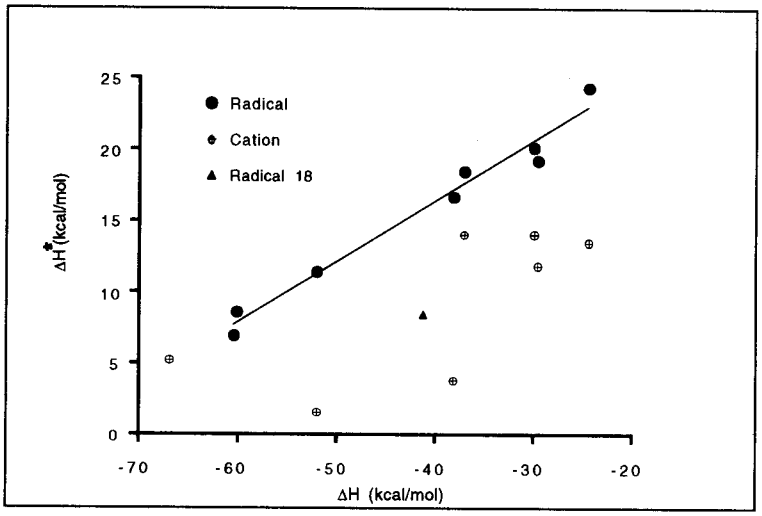


Figure 1. Calculated (AM1) activation enthalpies as a function of calculated exothermicities

It is interesting to compare these forbidden disrotatory radical openings with the corresponding allowed openings of the cyclopropyl cations. Figure 1 shows this data in the form of a plot of $\Delta H^{\ddagger}$ vs ΔH^{o}

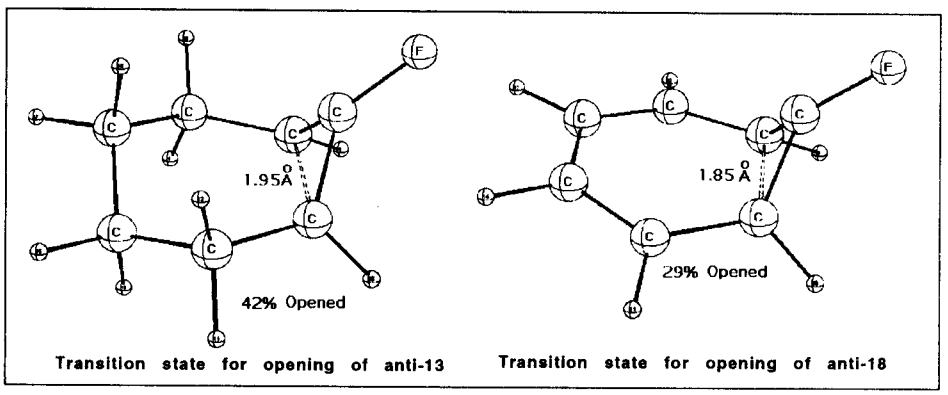


Figure 2. Geometries of the transition states for the forbidden ring opening of anti-**13** and for the allowed opening of anti-**18**.

calculated for the ring openings of the cyclopropyl cations corresponding to the radicals we have studied. In this case, the lack of correlation (R=0.72) between $\Delta H^{\ddagger}$ and ΔH^{o} suggest that the transition state, which now benefits from favorable orbital interactions, is earlier.

An interesting aspect of this work is the computational evidence that syn-**20** in which the fluorine and carbocyclic ring are syn is predicted to open with a higher barriers than anti-**20** with the F and ring anti (table 2). A consideration of the orbital crossings characteristic of forbidden reactions provides a simple rational for this behavior. In these cases this orbital crossing is a SOMO-LUMO crossing initiated by a developing overlap between the orbital containing the unpaired electron and the bonding orbital of the

breaking C-C bond which correlates with an excited orbital of the allyl radical as shown in figure 3a. When the breaking C-C bond is a ring fusion, the sterically permissible disrotatory mode forces this unfavorable overlap early in the reaction for syn-**20** in figure 3b. However, anti-**20** in figure 3c does not feel this unfavorable overlap as early in the reaction and this pathway is calculated to be more favorable.

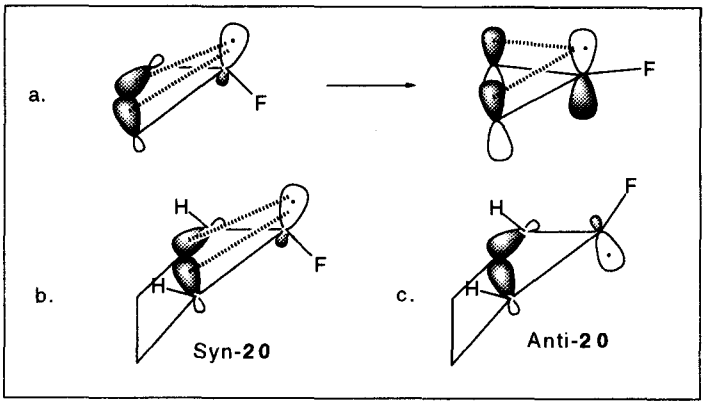


Figure 3. (a) SOMO-LUMO crossing induced by unfavorable overlap between the breaking C-C bond and the orbital containing the unpaired electron. (b) Unfavorble overlap in the disrotatory opening of syn-**20**. (c) Avoidance of initial unfavorable overlap in the disrotatory opening of anti-**20.**

Conclusions

This work provides an example of the use of the high energy associated with carbon atom reactions to produce interesting reactive intermediates, in this case α-fluorocyclopropyl radicals, whose chemistry may then be investigated. These studies demonstrate that reaction of CF with cycloalkenes is a convenient way of generating and studying the reactions of α-fluorobicyclopropyl radicals. An examination of the electrocyclic ring opening of these α-fluorobicyclopropyl radicals demonstrates that this reaction, like many others which are formally symmetry forbidden, requires considerable thermodynamic driving force.[19] The fact that there is a correlation between calculated exothermicities and activation energies indicates late transition states for these forbidden reactions. These transition states appear to be characterized by considerable bond breaking but little rotation. This geometry minimizes the unfavorable overlap which develops between the breaking C-C bond and the orbital containing the unpaired electron in the sterically required disrotatory opening.

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