matograph. We are indebted to Dr. David Schubert of UCLA for his assistance with NMR analysis.

Registry No. CH_2Cl_2, 75-09-2; $TiCl_4$, 7550-45-0; $AlCl_3$, 7446-70-0; Ph_2CH_2, 101-81-5; *p*-$PhCH_2C_6H_4CH_3$, 620-83-7; *p*-$PhCH_2C_6H_4NO_2$, 1817-77-2; *o*-$PhCH_2C_6H_4OMe$, 883-90-9; *p*-$MeC_6H_4CH_2$-*o*-C_6H_4OMe, 57076-34-3; *p*-$NO_2C_6H_4$-*o*-C_6H_4OMe, 92199-93-4; $PhCH_2$-*m*-C_6H_4OMe, 23450-27-3; *p*-$MeC_6H_4CH_2$-*m*-C_6H_4OMe, 123594-82-1; *p*-$NO_2C_6H_4CH_2$-*m*-C_6H_4OMe, 123594-83-2; *p*-$PhCH_2C_6H_4OMe$, 834-14-0; *p*-$MeC_6H_4CH_2$-*p*-C_6H_4OMe, 22865-60-7; *p*-$NO_2C_6H_4CH_2$-*p*-C_6H_4OMe, 22865-59-4; 2,4-dichloro-3,5,6-trimethylanisole, 123594-81-0; benzene, 71-43-2; anisole, 100-66-3; benzyl chloride, 100-44-7; *p*-xylyl chloride, 104-82-5; *p*-nitrobenzyl chloride, 100-14-1; 2,4-dichloro-3,5,6-trimethylphenol, 6965-74-8.

Kinetic and Thermodynamic Effects in the Thermal Electrocyclic Ring-Openings of 3-Fluorocyclobutene, 3,3-Difluorocyclobutene, and 3-(Trifluoromethyl)cyclobutene

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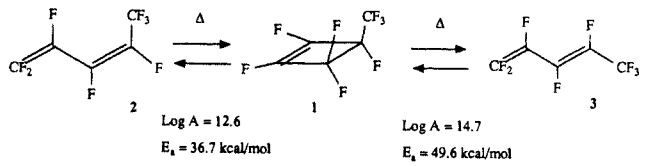
Contribution from the Department of Chemistry University of Florida, Gainesville, Florida 32611. *Received June 1, 1989*

Abstract: The synthesis and thermal electrocyclic ring-opening of 3-fluorocyclobutane, **4**, 3,3-difluorocyclobutane, **5**, and 3-(trifluoromethyl)cyclobutane, **6**, are reported. Activation energies for their ring-openings were found to be 28.1, 45.0, and 36.3 kcal/mol, respectively. **6** was found to form both the (*E*)- and the (*Z*)-5,5,5-trifluoro-1,3-butadienes, in a 95:5 ratio. Thermal equilibrations of the diene products from **4** and **6** were also carried out. The results demonstrate that a CF_3 group exhibits only a slight preference for outward rotation (ΔE_a = 1.2 kcal/mol), while a fluorine substituent gives rise to a much more dramatic outward rotational preference (ΔE_a = 13.8 kcal/mol). These results were consistent with those previously reported for perfluorinated systems and with theoretical expectations.

Recently we have published a number of papers on the thermal electrocyclic interconversion of a series of perfluorinated dienes and their cyclobutene isomers.[1-3] The kinetic and thermodynamic behavior of these systems along with related experimental work of Stevens,[4] Houk, and Kirmse[5] and theoretical work of Rondan and Houk[5,6] have led to a better understanding of the dramatic kinetic effects of substituents in the 3-position of cyclobutene on the *stereochemistry* of cyclobutene ring-opening.

In effect it has been found that single substituents at the 3-position of cyclobutene *decrease* the energy of the transition state for ring-opening and that electron-donating substituents prefer to undergo that conrotatory process which will rotate the substituent outward, while electron acceptors prefer the contrary conrotatory process which leads to inward rotation of the substituent. For the most part these potent electronic effects are found to overwhelm potential steric effects.

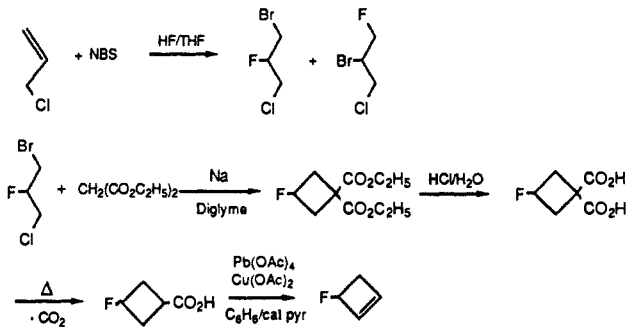
In our earlier studies, for example, we found that in perfluoro systems, such as the perfluoro-3-methylcyclobutene (**1**) system,[2,3] there was a dramatic kinetic preference (ΔE_a = 12.9 kcal/mol)



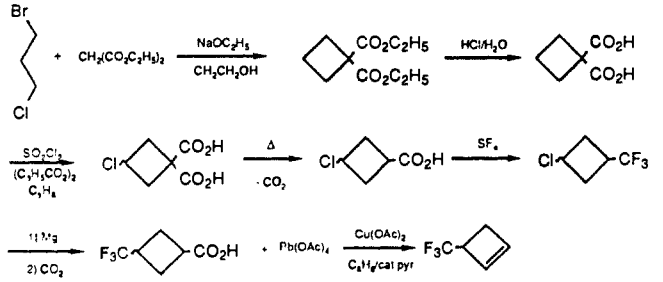
for that conrotatory ring-opening of **1** which led to inward rotation of the very bulky trifluoromethyl substituent, the prime kinetic motivation for such a seemingly sterically unfavorable process being the dominant, very energetically favorable *outward* rotation of the fluorine substituent which was also at the 3-position.

In such a perfluoro system, while an overall accurate picture of the net kinetic effect of a fluorine substituent and a trifluoromethyl substituent can be reasonably surmised, it is not possible to determine unambiguously and quantitatively the effect of a *lone* fluoro or trifluoromethyl substituent from these results.

Scheme I. The Synthesis of 3-Fluorocyclobutanecarboxylic Acid



Scheme II. The Synthesis of 3-(Trifluoromethyl)cyclobutanecarboxylic Acid



† Permanent address: Instytut Chemii, Uniwersytet im. Adama Mickiewicza, Poznan, Poland.

(1) Dolbier, W. R., Jr.; Koroniak, H.; Burton, D. J.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 1871.
(2) Dolbier, W. R., Jr.; Koroniak, H.; Burton, D. J.; Heinze, P. *Tetrahedron Lett.* **1986**, *27*, 4387.
(3) 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.

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Table I. Rate Constants for Ring-Opening of 3-Fluorocyclobutene[a]

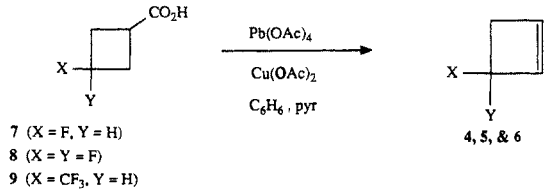
temp, °C	10^6k, s^{-1}	temp, °C	10^6k, s^{-1}
67.7	3.58 ± 0.14	92.6	58.0 ± 2.8
78.1	11.9 ± 0.1	97.0	91.2 ± 7.0
84.2	22.9 ± 0.1	103.1	180. ± 7.0

[a] Log A = 12.5 ± 0.2; E_a = 28.1 ± 0.3 kcal/mol; $\Delta H^{\ddagger}$ = 27.4 kcal/mol; $\Delta S^{\ddagger}$ = −3.5 cal/deg; $\Delta G^{\ddagger}$ = 28.6 kcal/mol.

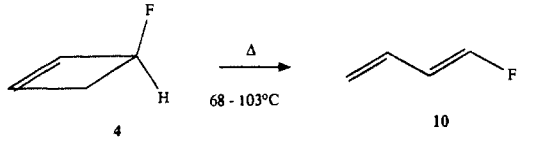
It was thus important to synthesize and examine thermally the appropriate less highly substituted cyclobutenes in order to more clearly quantify and understand these significant kinetic effects. In this paper the syntheses and studies of the thermal ring-openings of three cyclobutenes will be presented: 3-fluorocyclobutene, **4**, 3,3-difluorocyclobutene, **5**,[7] and 3-(trifluoromethyl)cyclobutene, **6**.

Results

Syntheses. Each of these cyclobutenes was synthesized by the oxidative decarboxylation of the respective 3-fluoro-, 3,3-difluoro-, and 3-(trifluoromethyl)cyclobutanecarboxylic acids, **7**–**9**.[7] While the synthesis of **8** has already been published,[7] the syntheses of **7** and **9** are depicted in Schemes I and II.

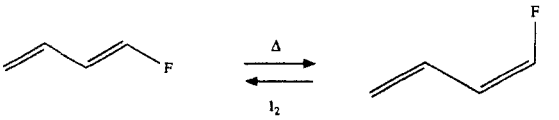


Thermal Isomerizations. 3-Fluorocyclobutene. The thermal ring-openings of the cyclobutenes **4**–**6** were carried out in the gas phase. They were all found to be irreversible, unimolecular reactions, and the kinetics of their rearrangements were followed by GLPC. As expected, the ring-opening of 3-fluorocyclobutene occurred at a relatively low temperature (68–103 °C as compared to 130–176 °C for cyclobutene itself[8]). A single product was formed, and examination of both ^1H and ^{19}F NMR spectra indicated that the product was (*E*)-1-fluoro-1,3-butadiene, **10**, which



was characterized by its cis H/F coupling constant of 16.5 Hz. (The *Z* isomer has a trans H/F coupling of 41 Hz.) Rate constants were obtained at six temperatures (Table I), and an Arrhenius plot of the rate data provided activation parameters for the reaction. It can be seen that the ring-opening of **4** is enhanced substantially (ΔE_a = −4.8 kcal/mol) over that of unsubstituted cyclobutene, which has an E_a for ring-opening of 32.9 kcal/mol.[8]

In order to formally exclude thermodynamic factors as contributing to the observed kinetic stereospecificity observed, a study of the *E*-to-*Z* equilibration of 1-fluoro-1,3-butadiene was carried out. The results are given in Table II, and one can see that, in



actuality, the *Z diene* is actually more stable than the *E* diene

Table II. Equilibration of 1-Fluoro-1,3-butadiene

temp, °C	K (*Z*/*E*)	temp, °C	K (*Z*/*E*)
24.0	1.76	50.0	1.76
40.0	1.76	60.0	1.77

Table III. Rate Constants for Ring-Opening of 3,3-Difluorocyclobutene[a]

temp, °C	10^5k, s^{-1}	temp, °C	10^5k, s^{-1}
228.5	4.46 ± 0.07	247.5	22.7 ± 0.4
237.5	10.0 ± 0.1	257.0	51.3 ± 1.0
239.0	11.5 ± 0.1		

[a] Log A = 15.2 ± 0.2; E_a = 45.0 ± 0.5 kcal/mol; $\Delta H^{\ddagger}$ = 43.9 kcal/mol; $\Delta S^{\ddagger}$ = 8.1 cal/deg; $\Delta G^{\ddagger}$ = 39.8 kcal/mol.

Table IV. Rate Constants for Ring-Opening of 3-(Trifluoromethyl)cyclobutene[a]

temp, °C	10^5k, s^{-1}	temp, °C	10^5k, s^{-1}
146.5	2.31 ± 0.01	169.8	22.2 ± 0.2
154.7	4.83 ± 0.03	177.2	42.6 ± 0.2
162.2	10.1 ± 0.1	186.3	96.2 ± 0.6

[a] Log A = 14.3 ± 0.2; E_a = 36.3 ± 0.5 kcal/mol; $\Delta H^{\ddagger}$ = 35.5 kcal/mol; $\Delta S^{\ddagger}$ = 3.9 cal/deg; $\Delta G^{\ddagger}$ = 33.7 kcal/mol.

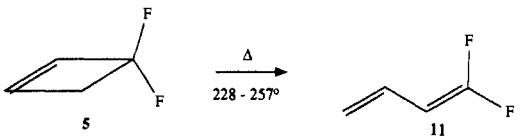
Table V. Kinetic Ratios of Products for the Ring-Opening of **6**[b]

temp, °C	% **13**[a]	% **12**[a]	*E*/*Z* ratio
138.3	2.2	97.8	44.0
144.5	2.3	97.7	42.7
161.5	2.4	97.6	40.8
166.0	2.4	97.6	40.2
175.0	2.5	97.5	38.9

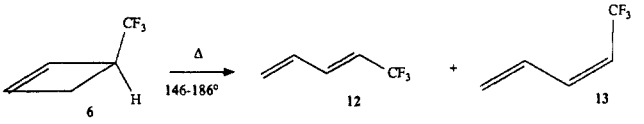
[a] Maximum standard deviations are ±0.1%. [b] For *E* isomer (**12**): log A = 14.2 ± 0.3, E_a = 36.2 ± 0.5 kcal/mol. For *Z* isomer (**13**): log A = 13.2 ± 0.3, E_a = 37.4 ± 0.5 kcal/mol.

($\Delta G°$ = 0.35 kcal/mol), a result consistent with previous findings for other 1-fluoroalkenes.[9]

3,3-Difluorocyclobutene. In contrast, both **5** and **6** were found to be more reluctant to undergo ring-opening than cyclobutene. Rate constants for the rearrangement of 3,3-difluorocyclobutene, **5**,[7] were obtained at five temperatures between 228 and 257 °C (Table III), and an Arrhenius plot yielded activation parameters for the reaction. Note that the activation energy for ring-opening of **5** is *16.9 kcal/mol greater* than that of the monofluoro analogue **4**.



3-(Trifluoromethyl)cyclobutene. The rearrangement of 3-(trifluoromethyl)cyclobutene, **6**, led somewhat surprisingly to a mixture of two products, (*E*)- and (*Z*)-5,5,5-trifluoro-1,3-pentadienes, **12** and **13**, which were distinguished by the characteristic



vicinal proton–proton coupling constants between their C_3 and C_4 protons. **12**, for example, exhibited a typical 15.6 Hz trans vicinal proton coupling. This constitutes the *first* example of a ring-opening of a monosubstituted cyclobutene that did not yield a single product.[10] As one can see from the activation parameters which were derived from the six rate constants (Table IV), the ring opening had an activation energy significantly *greater* than

(4) Curry, M. J.; Stevens, J. D. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1391.
(5) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989.
(6) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099.
(7) Dolbier, W. R., Jr.; Al-Fekri, D. M. *J. Org. Chem.* **1987**, *52*, 1872.
(8) Carr, R. W., Jr.; Walters, W. D. *J. Phys. Chem.* **1965**, *69*, 1073.
(9) Dolbier, W. R., Jr.; Medinger, K. S. *Tetrahedron* **1982**, *38*, 2415.

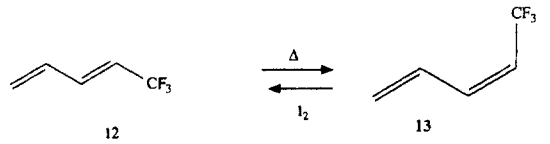
Table VI. Equilibration of Products **12** and **13**

temp, °C	K (E/Z)	temp, °C	K (E/Z)
56.5	43.5	151.0	17.3
88.5	23.0	188.5	13.2
110.6	20.2		

that for cyclobutene. This is the first example of a monosubstituted cyclobutene which did not exhibit an activation energy lowering due to the presence of the substituent.[10]

In this system, it was considered important to determine the precise temperature dependence of the kinetic product ratios, in order to see if any unusual disparity existed in the activation parameters for the competitive conrotatory processes. As one can see from Table V, there is indeed a temperature dependence on the ratio. However, the calculated activation parameters based upon the partial rates for formation of **12** and **13** show no significant unusual kinetic factors to be involved.

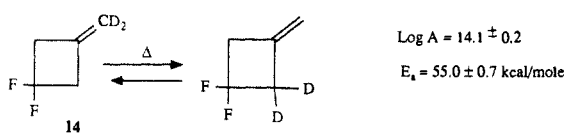
As in the 1-fluoro-1,3-butadiene system, a study of the equilibrium of products **12** and **13** was carried out in order to demonstrate that no special thermodynamic effects are involved in this system. The results of this study are given in Table VI, and it is seen that, as expected, the E diene, **12**, is more stable, with the difference in standard enthalpies observed to be 2.5 ± 0.4 kcal/mol ($\Delta S°$ = 0.3 ± 0.2 cal/deg, not an unexpected value). It is interesting to note that in the case of the perfluorodienes, **2** and **3**, the Z diene is more stable![1-3]



Discussion

As expected, a single fluorine substituent at the 3-position of cyclobutene was observed to enhance the process of ring-opening substantially. The E_a for **5**'s ring-opening was 4.8 kcal/mol lower than that of the parent cyclobutene. Rondan and Houk had predicted such a rate enhancement as well as the observed *strong* preference for outward rotation of the fluorine substituent.[5,6] This, combined with our observation of an E_a of 45.0 kcal/mol for the ring-opening of 3,3-difluorocyclobutene, **5**, wherein one of the fluorine substituents *must* rotate inward, clearly indicates that inward rotation of a fluorine substituent is detrimental to the transition state.

However, in order to determine quantitatively the kinetic impact of inward rotation, one must first know what the intrinsic effect of *gem*-difluoro substitution is on the bond strengths within a cyclobutane ring. This we have accomplished through a study of the degenerate rearrangement of 3,3-difluoro-1-(dideuteriomethylene)cyclobutane, **14**,[11] wherein a *strengthening* of the CF_2–CH_2 bond in **14**, as reflected by the ΔE_a for rearrangement of **14** versus the parent species,[12] was observed in the amount of 5.5 kcal/mol. Assuming that this same inherent bond strengthening of 5.5 kcal/mol holds for the C_3–C_4 bond of 3,3-difluorocyclobutene[13] leads to the conclusion that a substantial part (5.5 kcal/mol) of the 12.1 kcal/mol increase in activation energy for ring-opening of 3,3-difluorocyclobutene versus unsubstituted cyclobutene must be due to an increase in the intrinsic bond strength of the C_3–C_4 bond of **5**. This leaves an increase of 6.6 kcal/mol as due to the kinetic effects of the rotation of the fluorine substituents in the ring-opening of **5**.



For similar reasons, one should also correct for any intrinsic bond strengthening/weakening effect of the *single* fluorine substituent of **4**. A weakening effect of ~1.2 kcal/mol was in fact observed in our study of the methylenecyclobutane-type rearrangement of *exo*-7-fluoro-6-methylenebicyclo[3.2.0]hept-2-ene.[14] Applying such a correction to the ΔE_a of −4.8 kcal/mol observed for the ring-opening of **4** leads to a net effect of outward rotation of −3.6 kcal/mol.

Putting everything together, it would appear that inward rotation of a fluorine substituent raises the activation energy by 10.2 kcal/mol, while outward rotation of a fluorine substituent lowers it by 3.6 kcal, with the difference in activation energy between the two processes being about 13.8 kcal/mol. This compares reasonably with the value calculated by Rondan and Houk of 13 kcal/mol.[6]

The ring-opening of the 3-(trifluoromethyl)cyclobutene, with its modest observed kinetic effect, nevertheless proved to be unique thus far in the anals of 3-monosubstituted cyclobutenes.[10] Upon ring-opening it was observed to form *both* the Z and the E diene products. While the Z isomer comprised only a small fraction of the product, it is nevertheless very significant that any was observed at all. In the case of 3-methylcyclobutene, for example, none of the (*Z*)-1,3-pentadiene could be observed upon thermal ring-opening,[15] this in spite of the fact that a methyl substituent is much smaller than a trifluoromethyl substituent, which has E_s and A values larger than those of the isopropyl group.[16,17] Just as importantly, the activation energy for ring-opening of **7** was 36.3 kcal/mol, which is 3.4 kcal/mol higher than that of the parent cyclobutene. Until this case, *all* single substituents at the 3-position of cyclobutene had enhanced ring-opening.[10] Trifluoromethyl is the first substituent observed to slow it down. While one can attribute 1–2 kcal of this elevation of activation energy to a probable C_3–C_4 intrinsic bond strengthening due to the three β-fluorine substituents,[18] it is not possible to reasonably attribute *all* of the activation energy increase to this factor. Some of the increase must be due to a detrimental effect on transition-state stability resulting from outward rotation of the CF_3 substituent. Such a reluctance to rotate outward can also explain the partial formation of the sterically unfavorable Z product **13**.

The observed kinetic results can actually be nicely explained in terms of a combination of a small electronic effect due to the CF_3 substituent which favors inward rotation, along with a slightly more important steric effect due to the CF_3 substituent which favors outward rotation, the net effect of these two effects being a modest preference for outword rotation, but at the expense of a higher activation energy.

Something should also be said about the *thermodynamics* observed in the equilibrations of the monosubstituted diene systems. In the case of 1-fluoro-1,3-butadiene, **10**, our observation that the cis isomer is more stable, by 0.35 kcal/mol, than the trans isomer is consistent with our earlier observation that *cis*-1-fluoropropene is more stable than the trans isomer, in that case by 1.2 kcal/mol.[11]

An interesting conclusion can be drawn from the thermodynamic results of the 5,5,5-trifluoro-1,3-pentadiene system, wherein the E isomer, **12**, is found to be 2.5 kcal/mol more stable than the Z isomer, **13**. In contrast, as mentioned earlier, in the per-

(10) For a review of the subject, see: Dolbier, W. R., Jr.; Koroniak, H. *Fluorine-Containing Molecules*; Liebman, Greenberg, and Dolbier, Eds.; VCH Publishers: New York, 1988; Chapter 4.

(11) Dolbier, W. R., Jr.; Cooke, L. *Tetrahedron Lett.* **1989**, *30*, 4055.

(12) Doering, W. von E.; Gilbert, J. C. *Tetrahedron Suppl.* **1976**, *7*, 397.

(13) Certainly it is recognized that the *effect* of the intrinsic bond strengthening on the E_a of the nonpericyclic rearrangement of **14** may not indeed be identical with its effect on the E_a for the pericyclic ring-opening of **5**. The present analysis, however, provides us with the best available estimate for the general intrinsic effect of a CF_2 group.

(14) Dolbier, W. R., Jr.; Phanstiel, O., IV. *J. Am. Chem. Soc.* **1989**, *111*, 4907.

(15) Frey, H. M.; Marshall, D. C. *Trans. Faraday Soc.* **1965**, *61*, 1715.

(16) Hansch, C.; Leo, A. *Substituent Constants* for *Correlation Analysis in Chemistry and Biology*; Wiley: New York, 1979.

(17) (a) Hirsch, J. A. *Top. Stereochem.* **1967**, 1, 199. (b) Kitching, W. *J. Org. Chem.* **1982**, *47*, 5153. (c) Della, E. W. *J. Am. Chem. Soc.* **1967**, *89*, 5221.

(18) This can be estimated from the known E_a values for the thermal rearrangement of trifluoromethycyclopropane[19] as compared to the parent species.

fluoropentadiene system, **2** ⇌ **3**, the *Z* isomer, **2**, has been found to be 1.2 kcal/mol more stable than the *E* isomer, **3**.[2,3] Thus, while in an otherwise hydrocarbon system, there is apparently a significant thermodynamic preference for a CF_3 substituent to be trans to alkyl or alkenyl substituents, as one might have expected on the basis of steric effects, in a perfluoro system, a CF_3 substituent seems to prefer to be cis to an alkenyl group rather than to a fluorine substituent. This apparently is not an isolated observation, since we have recently observed that a CF_3 group prefers to be cis to an α-naphthyl group rather than to a fluorine substituent.[20]

Conclusions

The results presented in this paper have demonstrated that while a CF_3 group at the 3-position of cyclobutene exhibits a slight preference (ΔE_a = 1.2 kcal/mol) for outward rotation, a single fluorine substituent gives rise to a much more dramatic outward rotational preference (ΔE_a = 13.8 kcal/mol). Therefore, in the situation where *both* would be simultaneously substituted at the 3-position, one would expect a net strong preference (ΔE_a = 12.6 kcal/mol) for fluorine outward and trifluoromethyl inward rotation. This compares reasonably with our earlier observed results for the perfluoro-3-methylcyclobutene system, **1**, wherein the *combined* effects of a 3-fluoro substituent and a 3-(trifluoromethyl) group were observed to lead to a ΔE_a of 12.9 kcal/mol for the two competitive conrotatory ring-opening processes.

Experimental Section

General Methods. NMRs were generally obtained on a Varian VXR 300 spectrometer with chemical shifts reported for 1 H in ppm downfield from TMS and for ^{19}F in ppm upfield from $CFCl_3$.

1-Bromo-3-chloro-2-fluoropropane.[19] *N*-Bromosuccinimide (102.2 g, 0.57 mol) was placed with 150 mL of THF in a 500-mL polyethylene bottle equipped with a Teflon coated stirring bar, a dry ice–isopropyl alcohol cooled polyethylene reflux line, a dry ice–isopropyl alcohol cooled Teflon line from an HF cylinder and a dry ice–isopropyl-alcohol cooling bath. Hydrogen fluoride (147.5 g, 7.37 mol) was condensed into the bottle. At this time, the contents of the vessel were observed to turn dark red. The condensing line for the HF was then replaced with a Teflon addition funnel containing 3-chloropropene (43.9 g, 0.57 mol), which was slowly added to the solution with stirring. Upon addition, the dark color rapidly faded, and manual agitation was necessary to keep the solids from caking at the bottom of the vessel. Thirty minutes after addition was complete, the temperature of the bath was raised to −10 °C, and the reaction continued for 1 h. The reaction was quenched by cooling the vessel to −78 °C and pouring the contents onto 100 g of ice. The mixture was extracted with 3–100-mL portions of methylene chloride, and the organic extracts were washed with 50 mL of water and dried over anhydrous magnesium sulfate and a small amount of sodium fluoride. Evaporation of solvent and distillation gave 35.1 g (0.200 mol, 34.9%) of material (bp 65–66 °C, mmHg) which was shown by ^1H and ^{19}F NMR to be a mixture of the desired product and 2-bromo-1-chloro-3-fluoropropane in a ratio of 4:1, respectively. The mixture could be used in the subsequent step without further purification: ^1H NMR ($CDCl_3$/TMS) mixture of two isomers δ = 3.79 (dd, *J* = 4.9 Hz, 1.7 Hz), 3.87 (d, *J* = 4.9 Hz), 3.91 (dd, *J* = 5.7 Hz, 0.8 Hz), 4.27 (m, *J* = 5.0 Hz, 1.5 Hz, 0.8 Hz), 4.61 (dd, *J* = 10.2 Hz, 5.0 Hz), 4.82 (m, *J* = 46.4 Hz, 5.4 Hz, 5.0 Hz, 4.4 Hz); ^{13}C NMR ($CDCl_3$) mixture of two isomers δ = 29.7 (d, *J* = 25.6 Hz), 43.2 (d, *J* = 25.8 Hz), 43.8 (d, *J* = 4.3 Hz), 47.3 (d, *J* = 20.6 Hz), 82.0 (d, *J* = 177.2 Hz), 89.7 (d, *J* = 181.5 Hz); ^{19}F NMR ($CDCl_3$/$CFCl_3$) mixture of two isomers φ = 178.3 (81.4%, dtt, *J* = 45.9 Hz, 17.8 Hz, 16.6 Hz), 220.2 (18.6%, dt, *J* = 46.6 Hz, 18.5 Hz).

Diethyl 3-Fluorocyclobutane-1,1-dicarboxylate.[20] Sodium metal (6.25 g, 0.27 mol) was added to 500 mL of very dry diglyme in a 1000-mL, three-necked, round-bottomed flask equipped with a pressure equalizing dropping funnel, a magnetic stirring bar, and a reflux condenser with a nitrogen inlet. Diethyl malonate (53.9 g, 0.34 mol) was added to the mixture through the funnel, and the solution was stirred and heated to 115–120 °C so that the sodium was molten. The mixture was then stirred until all the sodium was dissolved, adding a small amount of diethyl malonate if needed. The flask was observed to contain a white or yellowish-white suspension of the diethyl malonate salt. The mixture of 1-bromo-3-chloro-2-fluoropropane and 2-bromo-1-chloro-3-fluoropropane (60.4 g, 80/20 ratio, respectively, 0.28 mol of the desired 1-bromo-3-chloro-2-fluoropropane) was then added through the funnel to the mixture. The solution was stirred for 2 h, and then another equivalent of sodium was added. A ^{19}F NMR spectrum of the crude reaction mixture after 2 more h showed that the starting trihalopropane had only undergone a single displacement and had failed to cyclize. Only after the consecutive addition of 2 more equiv of sodium (12.50 g) at 2-h intervals did the uncyclized adduct disappear. The reaction mixture was then cooled to room temperature, and 200 mL of water was added to dissolve the sodium salts. No metallic sodium was observed at this time. The resulting mixture had two phases. The upper organic phase was retained, while the lower aqueous phase was extracted three times with 200 mL of methylene chloride. The extracts were combined with the organic layer, washed with 100 mL of water, and dried over anhydrous magnesium sulfate. Removal of methylene chloride and diglyme and subsequent distillation under reduced pressure gave an impure mixture of the desired diester and allyl malonate (bp 60–65 °C, 0.05 mmHg). The allyl malonate decomposed on careful addition of bromine/carbon tetrachloride (1:2), and a second distillation gave 7.50 g (12.4%) of diethyl 3-fluorocyclobutane-1,1-dicarboxylate which was >95% pure by ^1H and ^{13}C NMR: MS (70 eV) calcd for $C_{10}H_{15}FO_4$ 218.0954, found 218.0945; IR 2980, 2355, 1730, 1025 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ = 1.27 (3 H, t, 7.1 Hz), 2.75 (2 H, m), 2.91 (2 H, m), 4.22 (2 H, q, *J* = 7.1 Hz), 4.23 (2 H, q, *J* = 7.1 Hz), 5.10 (1 H, dm, J^2_{HF} = 55.7 Hz, *J* = 13.5 Hz, 6.6 Hz, 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 13.9 (s), 14.0 (s), 38.2 (d, 23.7 Hz), 45.0 (d, *J* = 15.3 Hz), 61.4 (s), 61.9 (s), 82.2 (d, 210.7 Hz), 170.4 (d, *J* = 1.6 Hz), 171.2 (d, *J* = 2.4 Hz); ^{19}F NMR ($CDCl_3$/$CFCl_3$) φ = 171.0 (dm, *J* = 55.7 Hz, 8.8 Hz, 22.1 Hz).

3-Fluorocyclobutanedicarboxylic Acid.[21,22] Diethyl 3-fluorocyclobutane-1,1-dicarboxylate (8.30 g, 0.038 mol) was hydrolyzed with hydrochloric acid, giving the diacid (5.0 g, 81.8% yield): MS (70 eV) calcd for $C_6H_5FO_4$ 144.0222, found 144.0221; ^1H NMR ($CDCl_3$/TMS) δ = 2.80 (4 H, m), 5.10 (1 H, dm, *J* = 55.4 Hz, 6.8 Hz, 4.3 Hz), 8.2 (brs); ^{13}C NMR ($CDCl_3$) δ = 38.7 (d, *J* = 23.4 Hz), 45.2 (d, *J* = 14.8 Hz), 83.1 (d, *J* = 208.8 Hz), 172.5 (s), 172.5 (s), 172.5 (s); ^{19}F NMR ($CDCl_3$/$CFCl_3$) φ = 166.3 (dm, *J* = 55.4 Hz).

3-Fluorocyclobutanecarboxylic Acid. The diacid was thermally decarboxylated by heating to 190–200 °C at a pressure of 5 mmHg. 3-Fluorocyclobutanecarboxylic acid (3.00 g, 81.7%) distilled over at 90–95 °C as a mixture of the two isomers (ratio approximately 1:1) was found to be >95% pure by ^1H and ^{13}C NMR: MS (70 eV) calcd for $C_5H_7FO_2$ 118.0430, found 118.0432; IR 3000, 1700, 1420, 1080 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ = 2.65 (8 H, m), 3.16 (2 H, m), 4.93 (1 H, dm, *J* = 55.3 Hz), 5.24 (1 H, dm, *J* = 55.7 Hz), 10.25 (brs); ^{13}C NMR ($CDCl_3$) δ = 27.5 (d, *J* = 18.9 Hz), 30.8 (d, *J* = 13.3 Hz), 34.0 (d, *J* = 23.1 Hz), 34.3 (d, *J* = 22.4 Hz), 82.3 (d, *J* = 215.0 Hz), 86.0 (d, *J* = 207.6 Hz), 180.15 (d, *J* = 3.8 Hz), 181.9 (d, *J* = 2.6 Hz); ^{19}F ($CDCl_3$/$CFCl_3$) φ = 163.6 (50%, dm, *J* = 55.6 Hz), 166.2 (50%, dm, *J* = 55.5 Hz).

3-Fluorocyclobutene. 3-Fluorocyclobutanecarboxylic acid (3.0 g, 0.025 mol), as a 1:1 ratio of the cis and trans isomers, was dissolved with $Cu(OAc)_2 \cdot H_2O$ (0.053 g, 0.29 mmol) and pyridine (67 μL) in 10 mL of very dry benzene in a sealed 100-mL, found-bottomed flask in a dry box. Then a mixture of $Pb(OAc)_4$ (26 g, 0.0058 mol) in 40 mL of very dry benzene was allowed to stir in a 50-mL, round-bottomed flask with a rubber septum in the dark for 45 min in the drybox. The solution of $Pb(Oac)_4$ was then added to the 100-mL flask with the acid, and 20 mL of benzene was used to wash any undissolved $Pb(OAc)_4$ into the flask. The flask was removed from the drybox while sealed, equipped with a reflux column, a distilling head, a receiver cooled in ice water, a dry ice/isopropyl alcohol cooled trap in series, and a nitrogen inlet. The flask was stirred in the dark for 1.5 h to insure exchange of 3-fluorocyclobutanecarboxylic acid with the $Pb(OAc)_4$. The solution was then gradually heated over 45 min to reflux and then heated at reflux for 2.5 h. Over the initial heating to reflux a solid was observed to first form and then dissolve into the solution. Near the end of the refluxing period, a large amount of solid precipitated out of the solution, which changed color from green to blue-green. A small amount of liquid was observed in the receiver at this time. The solution was then distilled up to the boiling point of benzene, resulting in the collection of approximately 8 mL of liquid. This mixture of benzene and 3-fluorocyclobutene was separated by GPLC (10 ft 10% SE-30 column, T_c = 60 °C, flow = 60 mL/min, retention time 2 min for 3-fluorocyclobutene). 3-Fluorocyclobutene (0.267 g, 64.7%) was analyzed by analytical GPLC (10 ft 20% Triton-X, T_c = 25 °C) and found to contain a small amount of (*E*)-1-fluoro-1,3-butadiene (3.44%): MS (70 eV) calcd for C_4H_5F

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72.0375, found 72.0383; IR 3140, 3122, 3060, 2940, 2850, 2345, 1725, 820 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ = 2.71 (1 H, m), 2.87 (1 H, m), 5.39 (1 H, dd, J = 57.0 Hz, 2.38 Hz), 6.37 (1 H, d, J = 0.46 Hz), 6.14 (1 H, s); ^{13}C NMR ($CDCl_3$) δ = 39.7 (d, J = 19.9 Hz), 87.9 (d, J = 211.4 Hz), 137.3 (d, J = 19.2 Hz), 139.6 (d, J = 16.9 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) ϕ = 171.0 (d, J = 57.5 Hz).

1-Chloro-3-(trifluoromethyl)cyclobutane. 3-Chlorocyclobutanecarboxylic acid was prepared by literature procedures,[23] and 10.0 g (0.74 mol) of the acid was placed in an autoclave which was cooled to −197 °C and evacuated. Then 24.1 g (0.22 mol) of sulfur tetrafluoride were then condensed into the autoclave, which was then sealed, allowed to warm to room temperature, and then heated in a rocker at 145 °C for 14 h. The autoclave was then cooled to −197 °C, and the excess sulfur tetrafluoride was allowed to vent with warming through a bubbling tower charged with aqueous ammonium hydroxide. The fuming liquid was decanted from the autoclave onto 4.0 g of sodium fluoride suspended in 10.0 mL of pentane. Distillation gave 7.95 g (0.050 mol, 67.4%) of pure product. Attempts to eliminate HCl directly to give 3-(trifluoromethyl)cyclobutene were unsuccessful:[24] ^1H NMR ($CDCl_3$/TMS) δ = 2.50 (2 H, m), 2.68 (2 H, m), 3.17 (1 H, m), 4.20 (1 H, bm); ^{13}C NMR ($CDCl_3$) δ = 31.5 (s), 34.2 (q, J = 3.7 Hz), 46.5 (s), 50.1 (s); CF_3 carbon not seen in 25 mHz spectrum; ^{19}F (NMR) ($CDCl_3/CFCl_3$) ϕ = 73.8 (32%, d, J = 5.6 Hz), 73.4 (68%, d, J = 5.6 Hz).

3-(Trifluoromethyl)cyclobutanecarboxylic Acid.[21] Magnesium metal (2.50 g, 0.10 g-atoms) and 50 mL of dry THF were placed in a 100-mL, round-bottomed flask equipped with two pressure-equilizing dropping funnels, a magnetic stirrer, and a reflux condenser attached to a nitrogen line. 1-Chloro-3-(trifluoromethyl)cyclobutane (8.00 g, 0.050 mol) was placed in one of the funnels, and 4.3 g of 1,2-dibromoethane was placed in the second. The flask was heated to reflux, and approximately 1 g of the cyclobutane was added, followed by 3–4 drops of the dibromide. Alternate addition was continued until all the cyclobutane was added, and then the reflux was continued for 6 more h. As the Grignard tended to crystallize from THF at room temperature, the hot solution was poured directly onto CO_2 (s) (22.1 g, 0.50 mol) and vigorously stirred until the excess cardice had evaporated. The reaction was worked up by addition of 20% hydrochloric acid until just acidic, followed by extraction with 3–100-mL portions of diethyl ether. The ethereal extracts were combined and extracted with 3–50-mL portions of 10% aqueous sodium hydroxide. The aqueous extracts were acidified with concentrated hydrochloric acid, extracted with ether, and dried over anhydrous magnesium sulfate. Removal of solvent and subsequent distillation gave 5.8 g (0.035 mol, 68.8%) of 3-(trifluoromethyl)cyclobutanecarboxylic acid, which distilled over as two isomers: ^1H NMR ($CDCl_3$/TMS) δ = 2.50 (4 H, m, J = 9.0 Hz, 8.0 Hz), 3.05 (1 H, m, J = 8.9 Hz, 8.7 Hz), 3.25 (1 H, m), 10.05 (1 H, brs); ^{19}F NMR ($CDCl_3/CFCl_3$) ϕ = 74.6 (32%, d, J = 8.5 Hz), 75.1 (69%, d, J = 9.3 Hz).

3-(Trifluoromethyl)cyclobutene. The oxidative decarboxylation of the acid was carried out in the same fashion as for the preparation of 3-fluorocyclobutene above to give 3-(trifluoromethyl)cyclobutene in 15.5% yield: MS (70 eV) calcd for $C_5H_5F_3$ 122.0343, found 122.0344; IR 3148, 3089, 2980, 2942, 1365, 1150, 1130, 720 cm^{-1}; ^1H NMR ($CDCl_3$/TMS) δ = 2.66 (2 H, m), 3.46 (1 H, m), 5.93 (1 H, dd, J = 2.8 Hz, 1.0 Hz), 6.26 (1 H, m); ^{13}C NMR ($CDCl_3$) δ = 31.1 (q, J = 3.6 Hz), 44.6 (q, J = 31.5 Hz), 126.4 (q, J = 276.3 Hz), 128.4 (s), 131.6 (q, J = 4.0 Hz); INEPT pulse sequence shows peaks at 126.4 and 31.1 are down; ^{19}F NMR ($CDCl_3/CFCl_3$) ϕ = 73.5 (d, J = 0.43 Hz).

Thermal Isomerizations of 4, 5, and 6. The kinetics of the thermal ring openings of **4**, **5**, and **6** were carried out in the gas phase, under static conditions by methods described earlier.[3] In each case the total values of the GLPC peak integrals for starting material and product(s) remained initially the same relative to internal standard (pentane), indicating that no side reactions were occurring. See Tables II, III, and IV for the results.

(*E*)-1-Fluoro-1,3-butadiene: ^1H NMR ($CDCl_3$/TMS) v = 5.06 (1 H, dm, J = 11.1 Hz, 1.7 Hz, 1.4 Hz), 5.19 (1 H, dm, J = 16.0 Hz, 1.5 Hz, 0.8 Hz), 6.08 (2 H, m, J = 16.0 Hz, 1.5 Hz, 0.8 Hz), 6.80 (1 H, ddm, J = 82.4 Hz, 10.9 Hz, 1.8 Hz, 1.1 Hz); ^{13}C NMR ($CDCl_3$) δ = 114.6 (d, J = 14.4 Hz), 117.3 (d, J = 11.6 Hz), 129.2 (s), 152.3 (d, J = 261.8 Hz); ^{19}F NMR ($CDCl_3/C_6F_6$) ϕ = 127.3 (dd, J = 83 Hz, 17 Hz).

(*Z*)-1-Fluoro-1,3-butadiene: ^{19}F NMR ($CDCl_3/C_6F_6$) ϕ = 126.2 (dd, J = 83 Hz, 41 Hz).

(*E*)-5,5,5-Trifluoro-1,3-pentadiene: ^1H NMR ($CDCl_3$/TMS) δ = 5.46 (1 H, d, J = 10.0 Hz), 5.54 (1 H, d, J = 16.9 Hz), 5.73 (1 H, m, J = 15.6 Hz, 7.4 Hz), 6.42 (1 H, dddm, J = 17.0 Hz, 10.0 Hz, 0.7 Hz), 6.74 (1 H, dq, J = 15.6 Hz, 6.6 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$), ϕ = 64.2 (d, J = 7.0 Hz).

(*Z*)-5,5,5-Trifluoro-1,3-pentadiene: ^{19}F NMR ($CDCl_3/CFCl_3$) ϕ = 58.3 (d, J = 8.2 Hz).

Equilibrations of 4 and 6. The diene products were equilibrated in $CDCl_3$ with $CFCl_3$ as an internal standard by adding a catalytic amount of iodine and heating in a sealed NMR tube until no further changes in the ^{19}F NMR spectra were observed for each temperature. See Tables II and VI for results.

Kinetic Ratios of 12:13. The kinetic runs of ring-opening of 3-(trifluoromethyl)cyclobutene (**6**), yielding *Z* and *E* dienes, **12** and **13**, were carried out according to the procedure described earlier. The loss of starting material and the formation of **12** and **13** were followed by GLPC. The GLPC method, however, did not give satisfactory base line separation of **12** and **13**. Therefore, these ratios were determined independently from ^{19}F NMR integrations of their CF_3 group absorptions.

3-(Trifluoromethyl)cyclobutene (**6**) was transferred to the kinetic apparatus (~3–4 mm pressure) and kept for at least 5 half-lives of the ring-opening reaction. The sample was then vacuum transferred to an NMR tube along with $CDCl_3$ (solvent) and $CFCl_3$ (reference) and sealed, and the ^{19}F NMR spectrum was then obtained on a Varian FT 300 MHz spectrometer. Only the narrow region of the spectrum (ϕ between 57 and 67 ppm) was scanned so as to observe both signals of interest (ϕ of **12** and **13** are 64.2 and 58.3 ppm, respectively). At least 160 accumulations were collected for each sample, and the region of interest was then recorded, and the peaks were integrated. This procedure was repeated at least 6 times, and the average data for the amounts of **12** and **13** are reported in Table V. The calculated deviation at each temperature did not exceed ±0.1% of the measured amounts of **12** and **13**.

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Registry No. 4, 123812-80-6; **5**, 29507-09-3; **6**, 123812-84-0; *cis*-**7**, 123812-78-2; *trans*-**7**, 123812-79-3; *cis*-**9**, 123812-82-8; *trans*-**9**, 123812-83-9; **10**, 692-44-4; **11**, 590-91-0; **12**, 123812-85-1; **13**, 123812-86-2; **14**, 123812-87-3; 3-chloropropene, 107-05-1; 1-bromo-3-chloro-2-fluoropropane, 32753-90-5; 2-bromo-1-chloro-3-fluoropropane, 32753-89-2; diethyl 3-fluorocyclobutane-1,1-dicarboxylate, 123812-76-0; 3-chlorocyclobutanecarboxylic acid, 35207-71-7; 1-chloro-3-(trifluoromethyl)cyclobutane, 123812-81-7; 3-fluorocyclobutanedicarboxylic acid, 123812-77-1.

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