THE EFFECT OF FLUORINE AND TRIFLUOROMETHYL AS
SUBSTITUENTS IN THE ELECTROCYCLIC RING OPENING
OF CYCLOBUTENES AND THE REARRANGEMENT OF
CYCLOPROPYL CARBENES

By

THOMAS ANTHONY GRAY

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE
UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE
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1989
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by

Thomas Anthony Gray
TO MY LOVING WIFE AND FAMILY
ACKNOWLEDGEMENTS

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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August 1989

Fluorine and trifluoromethyl substituents are useful probes for the study of the thermal electrocyclic ring opening of cyclobutenes. Fluorine is expected to serve as a strong donor substituent with little steric effect on the transition state, and is predicted to rotate outward. The trifluoromethyl substituent is a sterically large electron acceptor, and should exhibit substantial steric and electronic effects.
3-Fluorocyclobutene and 3-trifluoromethylcyclobutene are prepared and the kinetics of their electrocyclic ring opening studied. It is found that the ring opening of 3-fluorocyclobutene yields only 1-fluoro-1,3-butadiene, in accordance with prediction. 3-Trifluoromethylcyclobutene ring opens with an activation energy higher than that of cyclobutene, and gives a mixture of Z- and E-5,5,5-trifluoro-1,3-pentadiene. It is believed that this is the result of competition between the unfavorable electrostatic effects of outward rotation and the unfavorable steric effects of inward rotation.

Interest in the ring expansion reaction of cyclopropyl carbenes to cyclobutenes led to the use of fluorine and trifluoromethyl substituents as probes for the reaction. It is predicted that fluorine will make the cyclopropyl ring more nucleophilic. Trifluoromethyl will withdraw electrons from the ring, decreasing its nucleophilicity, and should have a steric effect on the reaction.

The cis and trans isomers of both 2-fluorocyclopropyl-diazomethane and 2-trifluoromethyldiacylopropyldiazomethane
are prepared and decomposed thermally and photolytically. It is found that electrostatic repulsions between fluorine and the diazo substituent increase the amount of fragmentation in the reaction. Trifluoromethyl decreases both ring expansion and fragmentation, principally giving intermolecular products. It is believed that the trifluoromethyl substituent decreases the energy of the carbene.
CHAPTER 1

INTRODUCTION

The electrocyclic ring opening of cyclobutene to butadiene is predicted to be a concerted process. If a substituent is introduced onto the ring at the 3-position, an element of stereochemistry is added, in that two possible products can result from either inward or outward rotation of the substituent.

![Diagram](image)

Figure 1: 3-substituted cyclobutene.
Woodward-Hoffman symmetry rules predict that for the thermal electrocyclic ring opening of a cyclobutene, substituents on the 3- and 4-positions of the ring should move in a conrotatory fashion.¹ Symmetry rules do not state whether inward or outward rotation is preferred by a particular substituent.

Frey and coworkers studied the effects of methyl substituents on the activation energy of the thermal electrocyclic ring opening of cyclobutene.² It was generally observed that alkyl groups lowered the energy of activation for the ring opening, and that C₃ and C₄ alkyl substituent effects on the energy of activation were additive. It was also observed that the alkyl substituents preferred to rotate outward to give trans-alkenes. This preference was attributed to the steric bulk of the alkyl groups which would come into proximity with the C-4 hydrogen during the transition state of inward rotation.

This explanation was commonly accepted until experiments by Curry and Stevens were conducted on the ring opening of 3,3-disubstituted cyclobutenes.³ It was found
that substituents that had more steric bulk than methyl preferred inward rotation over methyl when both groups were on the 3-position of cyclobutene. Even though an extremely bulky substituent like t-butyl prefers outward rotation, its preference is relatively low considering that there is no Z-penta-1,3-diene observed in the ring opening of 3-methylcyclobutene.²

\[ \text{Figure 2: Ring opening of 3,3-disubstituted cyclobutenes.} \]

Such product distributions were explained in terms of the electron donating ability of the substituents at the 3-position and the frontier molecular orbitals (FMOs) involved in the ring opening. FMO analysis of the system shows that acceptor substituents will depress the LUMO of the system, which will increase the stabilizing LUMO-HOMO interaction in
the transition state. Donor substituents will raise the HOMO of the system to similar effect, so donor or acceptor substituents should decrease the energy of activation for ring opening.

Table 1: Ring opening of 3-R,3-methylcyclobutenes.³

<table>
<thead>
<tr>
<th>R</th>
<th>Z-isomer</th>
<th>E-isomer</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Bu</td>
<td>32</td>
<td>68</td>
<td>180</td>
</tr>
<tr>
<td>Isopropyl</td>
<td>65.5</td>
<td>34.5</td>
<td>180</td>
</tr>
<tr>
<td>n-Propyl</td>
<td>62</td>
<td>38</td>
<td>180</td>
</tr>
<tr>
<td>Cyclopropyl</td>
<td>43</td>
<td>57</td>
<td>180</td>
</tr>
</tbody>
</table>

Ab initio molecular orbital calculations of σ-electron flow of substituents on benzene show that methyl and ethyl are more negative than hydrogen, and that methyl is negative relative to ethyl. This would be consistent with ethyl's experimentally observed preference for inward rotation relative to methyl.

Rondan and Houk⁴ studied the effects of substituents on the stereochemistry of the electrocyclic ring opening using
data from Frey, Kirmse and other sources. They calculated the substituent effects on outward rotation from the difference between the energies of activation for the parent cyclobutene and the 3-substituted cyclobutene. Substituent effects on inward rotation were determined by comparison of the energies of activation of the 3-substituted system and the cis-3,4-disubstituted system, where one of the groups must rotate inward.

Figure 3: Ring opening of 3-substituted and cis-3,4-disubstituted cyclobutenes.

The values obtained from these estimations predict the activation energies for the ring opening of cyclobutenes within 1 kcal/mol. It was found that substituents at C₃ and C₄ lower the activation energies for outward rotation, but
increase the activation energies for inward rotation. For trans-3,4-dichlorocyclobutene and trans-3,4-dialkoxydicyclobutenes, it is predicted that inward rotation is respectively 18 and 28 kcal/mol less favorable than outward rotation. Such large differences in the energies of activation for the two possible transition states cannot be due solely to steric effects. Also, the A values and Taft E, values for the systems studied indicate that Cl and OR are relatively close in size, and both are smaller than CH₃.

Table 2: Substituent effects on inward and outward rotation.

<table>
<thead>
<tr>
<th>substituent</th>
<th>outward rotation (kcal/mol)</th>
<th>inward rotation (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>-1</td>
<td>+3</td>
</tr>
<tr>
<td>Cl</td>
<td>-3</td>
<td>+6</td>
</tr>
<tr>
<td>OR</td>
<td>-9</td>
<td>+5</td>
</tr>
</tbody>
</table>

An additional case reported by Dolbier and coworkers cannot be explained by steric arguments. It was found that trans-perfluoro-3,4-dimethylcyclobutene opened
preferentially to the Z,Z-isomer, with both trifluoromethyl groups rotating inward. The transition state leading to the E,E-product is 19.2 kcal/mol higher in energy. If steric factors determined the product, one would expect the E,E-isomer to predominate, since CF₃ is near in steric bulk to t-butyl (Eₐ for CF₃ = -2.4, Eₐ for t-Butyl = -2.78⁷), while F is not much larger than H.

![Figure 4: Ring opening of perfluoro-trans-3,4-dimethylcyclobutene.](image)

Equilibrium studies indicate that the two possible products are nearly equal in energy, so the large difference in activation energy must be purely due to a substituent effect on the relative transition state stabilities. These results were rationalized in terms of the different
directions of pyramidalization of the olefinic carbon atoms of the cyclobutene. The fluorine substituents on the ring make the olefinic carbons pyramidalize in a direction opposite what would be expected if the substituent were methyl. Assuming that pyramidalization dictates the direction of rotation of the substituents at C₃ and C₄, one would expect the opposite stereochemistry for the product.

Figure 5: Pyramidalization of 1,2,3,4-tetramethylcyclobutene and perfluoro-3,4-dimethylcyclobutene.

Relatively recent theoretical and experimental studies by Rondan and Houk have done much to clarify the stereochemical observations. Their results indicate that the HOMO of the transition structures for both inward and outward rotation is the C₃C₄ σ orbital, mixed in a bonding
fashion with the C$_2$C$_2$ π* orbital. Given a donor substituent with nonbonding lone pair electrons, inward rotation brings the electrons on the substituent closer to the HOMO than outward rotation. This proximity generates an unfavorable four electron repulsion. The LUMO of both transition states is the C$_3$C$_4$ σ* orbital mixed with the C$_1$C$_2$ π orbital in an antibonding fashion. Outward rotation of the donor substituent results in overlap of the donor lone pair orbitals with the low lying vacant σ* orbital through the attached carbon atom, giving a two electron interaction which stabilizes the occupied lower orbitals. Inward rotation brings the lone pairs into a node of the σ* orbital, thereby decreasing the interaction and stabilization.

Model calculations were carried out on several trans-3,4-disubstituted cyclobutenes. For heterosubstituted cyclobutenes it was found that all heterosubstituents prefer to rotate outward, but the energy differences between inward and outward rotation increase along the order Cl < F < OH < NH$_2$, a trend paralleling the increase in electron donor
ability. The use of ionization potentials (IPs) to assess electron donating ability is suggested. As the IP decreases, the electron donating ability of the substituent increases. The one exception is Cl, whose ionization occurs from a 3p orbital. Overlap of the nonbonded electrons of Cl with the σ and σ' orbitals is poorer than that of the second row elements. In general, increased donor ability correlates well with increased preference for outward rotation.

Figure 6: Donor orbital interaction with the HOMO and LUMO of cyclobutene. 4
It was also found that the substituent effects on the energy difference between the two transition structures should be very nearly additive. In going from 3-fluorocyclobutene to cis-3,4-difluorocyclobutene, the energy difference in the transition structures is predicted to increase from 20.8 kcal to 40.7 kcal. This indicates that the activation energies are unlikely to be affected by direct interactions between the substituents.

Figure 7: Predicted ring opening of 3-borylcyclobutene.  

An extreme example of an acceptor group was also modeled using the BH₂ group as a substituent. In the case of trans-3,4-diborylcyclobutene inward rotation is favored over outward by 17.8 kcal/mol. In this case the vacant p-orbital on B overlaps in a stabilizing fashion with the σ
orbital of the ring. This overlap is better on inward rotation than on outward. This results in greater stabilization for the inward HOMO and LUMO than the outward HOMO and LUMO.

Figure 8: Ring opening of 3-cyano- and 3-formylcyclobutene.

Recently, 3-cyanocyclobutene and 3-formylcyclobutene were theoretically studied and 3-formylcyclobutene was prepared. Ab initio calculations were used to determine the transition structures for inward and outward rotation of the two substituents in the ring opening of the 3-substituted cyclobutenes. It was found that the CN inward transition structure is 4.3 kcal/mol higher in energy than
the outward transition structure, and that the activation energy of the outward transition structure is 2.3 kcal/mol lower than that for nonsubstituted cyclobutene. This behavior is expected for a very weak donor. Evidently the filled π-orbitals of the cyano group have a greater influence on the transition structure than the vacant π* orbitals. In contrast, CHO in 3-formylcyclobutene prefers inward rotation by 4.5 kcal/mol, and the activation energy for the system is expected to be 6.9 kcal/mol below that of cyclobutene. The preference for inward rotation is not due to product stability, since the Z-2,4-pentadienal is predicted to be 3.1 kcal/mol less stable than the E isomer. The rotational preference is purely due to stabilizing interaction between the vacant π* orbitals of the formyl CO bond and the HOMO of the transition state.

The 3-formylcyclobutene was prepared from methyl 3-chlorocyclobutane carboxylate by reduction of the ester to the alcohol, followed by elimination of HCl from the ring and oxidation of the alcohol to the aldehyde with pyridinium chlorochromate (PCC). The product was observed to ring
open to the pentadienal at 25°C with a half life of approximately 50 hours. In following the reaction by 500 MHz NMR spectroscopy it was found that only the Z-pentadienal was formed. A minimum of 2% of the E isomer could be observed, so inward rotation is favored by at least 2.7 kcal/mol. Kinetics experiments in the temperature range on 50-70°C gave a log A = 14.2 ± 1.2 and E<sub>act</sub> = 27.2 ± 1.8 kcal/mol, in good agreement with the predictions. On equilibrating with acid or base, the Z-2,4-pentadienal completely converts to the more stable E isomer.

In summary, it has been found that single substituents on the 3-position of cyclobutene decrease the energy of activation relative to unsubstituted cyclobutene whether they are electron donating or withdrawing. It has also been found that the ring opening of 3-monosubstituted cyclobutenes is stereospecific, with electron donating substituents rotating outward and electron acceptor groups rotating inward. This stereospecificity is attributed to orbital interactions which serve to stabilize the transition state for outward rotation in the case of donor
substituents, and inward rotation for acceptor substituents. These interactions overwhelm any steric effects in all cases. The orbital interaction theory advanced by Rondan and Houk does not address the stereoselectivity observed in systems where the substituents do not possess orbitals which can interact with the transition state HOMO and LUMO, such as 3-alkyl substituted cyclobutenes.

In order to obtain a more complete picture of the substituent effects on the thermal ring opening of cyclobutene, two new 3-substituted systems were synthesized and the kinetics of their ring opening studied. 3-Fluorocyclobutene is predicted to prefer outward rotation over inward rotation by 20.8 kcal/mol. The fluorine substituent is an excellent example of a nearly pure electronic effect, since fluorine bonded to carbon is not much larger than hydrogen bonded to carbon. The interaction between the fluorine and the inward rotating hydrogen in the transition structure should not be much larger than the interactions in cyclobutene itself. Any stereospecificity in the rotation of the fluorine should be due to the
interaction of its nonbonded electrons with the LUMO of the cyclobutenyl system.

No theoretical studies have been made on how the trifluoromethyl substituent affects the ring opening of cyclobutene, so it is difficult to predict how 3-trifluoromethyl-cyclobutene will behave on ring opening. Though the trifluoromethyl substituent is a strong inductive electron withdrawing group,¹⁰ there are no vacant orbitals to interact with the HOMO of the transition state, as in the case of 3-formylcyclobutene. In addition, the substituent is considered by some measurements to be as large as a tert-butyl group, and should have a large unfavorable steric interaction with hydrogen on inward rotation. If any Z-diene product is observed, it will indicate that electronic effects can be significant even as the absence of nonbonding orbitals, as was shown for the alkyl substituents previously studied.² In this case however, the effect will not be due to relative electron donor ability, but rather to acceptor ability.
The third system to be studied, 3-fluoro,3-trifluoromethylcyclobutene should give a closer approximation of the relative effect of the two substituents than the perfluorosystem previously studied. Based on the results from perfluoro-trans-3,4-dimethylcyclobutene, it is expected that the fluorine will rotate outward.

Figure 9: Ring opening of 3-fluoro-, 3-trifluoromethyl-, and 3-fluoro-3-trifluoromethylcyclobutenes.

Our interest in cyclobutenes bearing a fluorine or trifluoromethyl substituent led to an investigation of cyclopropylcarbene rearrangements. It has been found that
in cycloalkylcarbenes of ring size n, the case in which n = 3 predominantly undergoes rearrangement to cyclobutene and fragmentation to ethylene and acetylene.\textsuperscript{11} Friedman and Shechter reacted the tosylhydrazone of cyclopropylcarbox-aldehyde (6) with sodium methoxide in diethyl carbitol (DEC) or N-methylpyrrolidine (NMP) at 180°C.\textsuperscript{12} They obtained different product yields for each solvent.

The principal products were cyclobutene (7), ethylene (8) and acetylene (9) and 1,3-butadiene (10). No products were observed from α-H or β-H insertion (i.e., methylenecyclopropane (11) or bicyclo[1.1.0]butane (12)).
Table 3: Decomposition of cyclopropylcarboxaldehyde tosyl-hydrazone in the presence of strong base.\textsuperscript{12}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>DEC</td>
<td>60</td>
<td>13</td>
<td>nm</td>
<td>4.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>NMP</td>
<td>67</td>
<td>10</td>
<td>nm</td>
<td>7</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Frey and Stevens repeated the cyclopropylcarboxaldehyde tosylhydrazone work using "essentially the same conditions" while obtaining substantially different results.\textsuperscript{13} In response, a thorough study of the reaction conditions was made, varying solvent, temperature, the amount of base used, and the starting material.\textsuperscript{14} As a result it was found that reaction conditions strongly affect the product ratios. The results show that decomposition of the tosylhydrazone with an equivalent or excess amount of sodium methoxide in an aprotic or poor proton donor solvent leads to cyclobutene and 1,3-butadiene as the major products. With less than one equivalent of sodium methoxide or in the presence of a good proton donor solvent such as ethylene glycol (EG), bicyclo[1.1.0]butane is the major product.
Figure 11: Decomposition of tosylhydrazone under varying conditions.¹⁴

Table 4: Products of decomposition of tosylhydrazone under varying conditions.¹⁴

<table>
<thead>
<tr>
<th>S.M.</th>
<th>NaOCH₃</th>
<th>Solvent</th>
<th>Yield</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1.8</td>
<td>DEC</td>
<td>89</td>
<td>41</td>
<td>9</td>
<td>8</td>
<td>39</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>DEC</td>
<td>85</td>
<td>83</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>DEC</td>
<td>80</td>
<td>85</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>DEC</td>
<td>95</td>
<td>82</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>0.8</td>
<td>DEC</td>
<td>55</td>
<td>26</td>
<td>4</td>
<td>7</td>
<td>4</td>
<td>6</td>
<td>57</td>
</tr>
<tr>
<td>1.1</td>
<td>Et₃COH</td>
<td>82</td>
<td>95</td>
<td>nm</td>
<td>nm</td>
<td>tr</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

The results indicate that bicyclo[1.1.0]butane (12) forms only in environments where acidic protons are present. This would indicate that 12 forms through a cationic mechanism rather than through carbene rearrangement. The
most likely mechanism is through a cyclopropyl carbonium or cyclopropyl diazonium intermediate. Other researchers have also found evidence that bicyclobutane does not arise from cyclopropyl carbene.\textsuperscript{15}

Cyclopropyl diazomethane has been prepared and photolyzed in the gas phase over a pressure range of 1.38 torr to 708.7 torr.\textsuperscript{16} Varying the pressure had little affect on the product distribution and under these condition very little cyclobutene was isolated, the major products observed being butadiene, ethylene and acetylene. The amount of ethylene and acetylene observed indicated that 50% of the starting material had decomposed through the fragmentation pathway. The greater amount of fragmentation products under more energetic conditions would indicate that fragmentation is a higher energy pathway than ring expansion. That the reaction conditions lead to more energetic intermediates is consistent with the large amount of ring opening undergone by cyclobutene to give butadiene ($E_{\text{act}} = 32.5$ kcal/mol).\textsuperscript{2} By treating cyclopropylcarboxaldehyde with carbon vapor in a frozen
matrix, other workers found that the fragmentation reaction was quite rapid, on the same time scale as energy transfer into the frozen matrix. It was suggested that fragmentation could occur concertedly with formation of the carbene. Sasaki and coworkers found that the decomposition of the tosylhydrazones of cis- and trans-2,2-dimethyl-3-isobutenylcyclopropylcaboxaldehyde (chrysanthemylaldehyde) led to a large amount of fragmentation. They stated that the isobutenyl group probably lowered the activation energy for fragmentation by leading to the formation of a conjugated diene in one of the fragmentation products.

![Diagram](image)

**Figure 12: Fragmentation of chrysanthemylaldehyde tosylhydrazones.**

The stereoselectivity of the intramolecular reactions of cyclopropyl carbenes has been studied by several research
groups. Trans-2,3-dimethylcyclopropyl diazomethane was photolytically decomposed and the products were trapped and identified by their IR spectra. The products were acetylene (9), trans-2-butene (13), cis-2-butene (14), E,E-2,4-hexadiene (15), and E,Z-2,4-hexadiene (16).

![Figure 13: Decomposition of trans-2,3-dimethylcyclopropyl-diazomethane.](image)

At lower pressures the reaction appears to be stereospecific, giving 13 and 15 as the major products. The hexadiene probably results from the decomposition of excited trans-3,4-dimethylcyclobutene. The cyclobutene was not identified, but a single unidentified product occurred in high yield in the reactions. The stereospecificity at low pressures indicates that the reaction proceeds through a
singlet carbene which undergoes spin controlled decomposition.

<table>
<thead>
<tr>
<th>P(torr)</th>
<th>9</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>11</td>
<td>41</td>
<td>43</td>
<td>&lt;2</td>
<td>20</td>
</tr>
<tr>
<td>23</td>
<td>23</td>
<td>40</td>
<td>41</td>
<td>&lt;2</td>
<td>25</td>
</tr>
<tr>
<td>21</td>
<td>21</td>
<td>11</td>
<td>10</td>
<td>9</td>
<td>8-15</td>
</tr>
<tr>
<td>(+739 torr)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At higher pressure, collisional deactivation brings some of the carbene to the lower lying triplet state, which can undergo ring cleavage to form a biradical which posseses a long enough lifetime to undergo rotation. Under these conditions, it would be possible for the equilibrating biradical to produce a mixture of cis and trans-2-butene (14) via a fragmentation pathway, and cis and trans-3,4-dimethylcyclobutene, which could then undergo ring opening to give hexadienes 15 and 16.
Bird and coworkers decomposed the tosylhydrazones of 2,2-dimethylcyclopropane, cis-2-methylcyclopropane and trans-2-methylcyclopropane methyl ketones with 3 or 4 equivalents of sodium methoxide. The ketone methyl group could be at the 1- or 2-position of the product cyclobutene ring. Products were analyzed by \textsuperscript{1}H NMR.

In all three cases the major product results from migration of the less substituted cyclopropyl bond, giving the 1-methylcyclobutenes. For the 2,2-dimethyl and the cis-2-methyl specie the selectivity is very large. This selectivity is attributed to steric inhibition caused by the methyl groups on the more substituted double bond.
Figure 15: Methylcyclopropyl methyl carbene rearrangement.\textsuperscript{20}

Table 6: Product cyclobutene distribution in methylcyclopropyl methyl carbene.\textsuperscript{20}

<table>
<thead>
<tr>
<th>Starting methyl ketone tosylhydrazone</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2-dimethyl</td>
<td>97.5</td>
<td>2.5</td>
</tr>
<tr>
<td>cis-2-methyl</td>
<td>95.9</td>
<td>4.2</td>
</tr>
</tbody>
</table>

In decomposing the tosylhydrazones of cis- and trans-chrysanthemyl methyl ketones, Sasaki and coworkers found that the principal ring expansion product for both isomers resulted from the migration of the bond bearing the isobutenyl substituent.\textsuperscript{18} They felt that this result could not be explained by simple steric arguments.
The stereospecificity of the decomposition reaction of cyclopropylcarbenes was addressed by Jones and Galluci, who believed that in forming the triplet carbene they could observe nonstereospecific rearrangement and fragmentation.\textsuperscript{21} Separately irradiating cis- and trans-2,3-dimethylcyclopropylidiazoketoesters in benzene gave distinct stereospecific products mixtures for each isomer. Irradiation using an excess of fluorenone as a triplet sensitizing agent gave no significant change in the product distribution or stereochemistry. That the triplet carbene was formed was confirmed by the increased reactivity of the species with isobutylene on irradiation with fluorenone, indicating an increase in intermolecular over intramolecular
reaction. It was suggested that in this case the singlet and triplet states of the carbene are in equilibrium, and that the singlet decomposition is faster.

Both the preference for ring expansion over fragmentation and the stereospecificity of the cyclopropyl methylene carbene reaction were addressed in a recent paper by Shevlin and McKee. Earlier theoretical studies had indicated that there is an important interaction between the vacant $p$-atomic orbital of the carbene carbon and the occupied antisymmetric Walsh orbital of the cyclopropane ring, resulting in two energy minima for the conformation of the carbene carbon relative to the ring. Shevlin and McKee’s calculations on the two conformers of cyclopropyl carbene indicated that the conformation with the carbene hydrogen eclipsing the $\alpha$-hydrogen on the ring, the syn conformation, was stabilized by 1.8 kcal/mol relative to the anti conformation, with a barrier to interconversion of the two conformers of 14.9 kcal/mol. The high barrier is due to the loss of the stabilizing interaction between the vacant $p$-AO of the carbene and the antisymmetric Walsh orbital of
the ring during rotation; a similar stabilizing interaction exists in the cyclopropylcarbinyl cation.

![Diagram of cyclopropylcarbinyl cation with energies]

\[ \Delta H^* = 14.9 \text{ kcal/mol} \]
\[ \Delta H = 1.9 \text{ kcal/mol} \]

Figure 17: Energies of two conformers of cyclopropylcarbene.\(^2\)

By studying the two conformers separately, it was found that the activation barrier for the rearrangement of the anti conformer to cyclobutene is 15.4 kcal/mol higher in energy than that for the syn conformer, since at some point along the reaction coordinate there must be rotation about the bond between the carbene carbon and the attached ring carbon to prevent formation of a trans double bond. On the
other hand, for fragmentation the activation barrier for the anti conformer is 6.4 kcal/mol lower in energy than the barrier for the syn conformer, and that the lowest energy pathway for the syn conformer to undergo fragmentation is to rotate to the anti conformer first. This is attributed to greater repulsions between the carbene electrons and the developing ethylene π-system in the transition state of the syn conformer.

Based on these calculations, one would expect the anti conformer of cyclopropylcarbene to rotate to the syn conformer and then rearrange to cyclobutene, since the barrier to rotation and the activation barrier for rearrangement of the syn isomer are both lower than the activation barrier for fragmentation of the anti conformer. No fragmentation should be observed, which is not in accord with experimental evidence. Shevlin and McKee suggest that both ring expansion and fragmentation proceed via a singlet pathway, and that fragmentation proceeds via a short lived singlet biradical which fragments before rotation and loss of stereochemistry can occur. Assuming that the singlet and
triplet biradical have similar energies and the ring opening for singlet and triplet state have nearly equal barriers, it is possible that opening to the biradical could occur in the singlet state and be competitive with ring expansion. Calculations based on these assumptions indicate that fragmentation becomes more important at higher temperatures for the syn conformer and is the principal pathway for the anti conformer.

Both the barrier for ring expansion of the syn conformer (5.0 kcal/mol) and the barriers to formation of the 1,4-biradical for the syn and anti conformers (9.0 and 8.0 kcal/mol, respectively) are substantially lower in energy than the barrier to rotation between the two conformers, so the reaction path of the carbene should be dependent on the conformation in which it is formed. It is expected that for most carbene precursors the two conformations should be nearly equal in energy, so in most cases both conformers should be present.

In summary, the two principal pathways for intramolecular reaction of cyclopropyl carbenes are ring
expansion to a cyclobutene, possibly followed by ring opening to a conjugated diene, and fragmentation to an alkene and an acetylene. Experimental evidence indicates that ring expansion is the lower energy pathway, while fragmentation quite possibly occurs in concert with the formation of the carbene. When there are substituents on the cyclopropyl ring an element of stereochemistry is introduced to the reaction, with the strongest bond of the ring migrating to the carbene center. Whether steric hindrance of substituents on the ring or electrostatic interactions between the substituents and the carbene carbon are more important in determining the stereochemistry of the reaction is unclear. A stabilizing interaction between the vacant p-atomic orbital on the carbene and the ring results in two conformers in the system being energy minima with a large barrier to interconversion. Theoretical studies indicate that these two conformers are important in determining the course of the reaction of the carbene, and that both conformers should be present under most circumstances where the cyclopropyl carbene is generated.
By synthesizing cyclopropylcarboxaldehydes bearing trifluoromethyl and fluorine it would be possible to observe how these two substituents could affect the intramolecular reaction. As a probe, fluorine should have a large electrostatic effect and a small steric effect on the carbene's attack on the ring. Also, fluorine should affect the hybridization of the orbitals of the cyclopropyl ring, altering their nucleophilicity. The trifluoromethyl substituent should serve as a probe for the effect of steric bulk in the reaction. Its electron withdrawing nature should also perturb the framework of the ring, and it should serve to 'cool' the reaction by providing additional vibrational and rotational modes to dissipate energy in the system. In both cases, all products should be observable by $^{19}$F NMR.

It is expected that 2-fluorocyclopropyldiazomethane (19) will decompose to give 3-fluorocyclobutene (20), 1-fluoro-1,3-butadiene (21) and vinyl fluoride (22). 2-Trifluoromethylcyclopropyldiazomethane (23) should give 3-trifluoromethylcyclobutene (24), 5,5,5-trifluoro-1,3-
pentadiene (25), and 3,3,3-trifluoropropene (26). The $^{19}\text{F}$ chemical shifts of all products are known or readily obtainable.

\[ \text{CF}_3 \quad \text{CHN}_2 \quad \text{hv or } \Delta \quad \rightarrow \quad \text{CF}_3 \quad + \quad \text{CF}_3 \quad + \quad \text{CF}_3 \quad + \quad \text{HC} \equiv \text{CH} \]

Figure 18: Decomposition of cyclopropyl diazomethanes.

In summary, the effects of fluorine and trifluoromethyl substituents on two mechanistically interesting systems, cyclobutene and cyclopropylcarbene, are to be studied. It is believed that in both systems the substituents will perturb both the reactivities and the product distributions. Also, the fluorine and trifluoromethyl substituents should effect the two systems in substantially different manners,
due to the differences in electronic and steric effects for the two substituents.
CHAPTER 2

SYNTHESES AND EXPERIMENTAL PROCEDURES

All IR spectra were taken on a Perkin-Elmer 983 infrared spectrometer. All $^1$H, $^{13}$C and $^{19}$F NMR spectra were taken on either a Jeol FX-100, a Nicolet 360, a Nicolet QE-300, a Varian XL-200 or a Varian VXR-300 spectrometer.

1-Bromo-3-chloro-2-fluoropropane: $^{25}$ N-Bromosuccinimide (102.2 g, 0.574 mol) was placed with 150 ml THF in a 500 ml polyethylene bottle equipped with a teflon coated stirring bar, a dry ice-isopropanol cooled polyethylene reflux line, a dry ice- isopropanol cooled teflon line from an HF cylinder and a dry ice-isopropanol cooling bath. Hydrogen fluoride (147.5g, 7.372mol) 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 (43.91 g, 0.574 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 NBS 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 one hour. 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, the organic extracts 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 35.12 g (0.200 mol, 34.9%) of material (b.p. 65°-66°C, 33mm Hg) which was shown by $^1$H 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.

$^1$H 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,
$J = 10.2 \text{ Hz, } 5.0 \text{ Hz}$; 4.82 (m, $J = 46.4 \text{ Hz, } 5.4 \text{ Hz, } 5.0 \text{ Hz, } 4.4 \text{ Hz}$).

$^{13}$C-NMR (CDCl$_3$); mixture of two isomers: $\delta = 29.7$ (d, $J = 25.6 \text{ Hz}$); 43.2 (d, $J = 25.8 \text{ Hz}$); 43.8 (d, $J = 4.3 \text{ Hz}$); 47.3 (d, $J = 20.6 \text{ Hz}$); 82.0 (d, $J = 177.2 \text{ Hz}$); 89.7 (d, $J = 181.5 \text{ Hz}$).

$^{19}$F-NMR (CDCl$_3$/CFCI$_3$); mixture of two isomers: $\psi = 178.3$ (81.41%, dtt, $J = 45.9 \text{ Hz, } 17.8 \text{ Hz, } 16.6 \text{ Hz}$); 220.2 (18.59%, dt, $J = 46.6 \text{ Hz, } 18.5 \text{ Hz}$).

**Diethyl 3-fluorocyclobutane-1,1-dicarboxylate:** Sodium metal (6.25 g, 0.272 mol) was added to 500 ml of very dry diglyme in a 1000 ml 3 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, 0.337 mol) was added to the mixture through the funnel and the solution was stirred and heated to $115^\circ\text{C-120}^\circ\text{C}$ 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 (60.41g, 80/20 ratio respectively, 0.2771 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 hours and then another equivalent of sodium was added. A $^{19}$F NMR spectrum of the crude reaction mixture after 2 more hours showed that the starting trihalopropane had been attacked by the nucleophile but had failed to cyclize. Only after the consecutive addition of 2 more equivalents of sodium (12.50 g) at two hour intervals did the uncyclized adduct disappear. The reaction mixture was then cooled to room temperature and 200 ml of water 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 mm Hg). 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 ^13C NMR.

MS(70eV) calculated for C_{10}H_{15}FO_{4}, 218.0954, found 218.0945.

IR: 2980 cm^{-1}(s); 2355 cm^{-1}(m); 1730 cm^{-1}(s,b); 1025 cm^{-1}(s).

^1H-NMR (CDCl₃/TMS): δ = 1.27 (3H, t, 7.12 Hz); 2.75 (2H, m); 2.91 (2H, m); 4.22 (2H, q, J = 7.14 Hz); 4.23 (2H, q, J = 7.12 Hz); 5.10 (1H, dm, J_{H,F}=55.7 Hz, J = 13.55 Hz, 6.63 Hz, 6.83 Hz).

^13C-NMR (CDCl₃): δ = 13.9 (s); 14.0 (s); 38.16 (d, 23.7 Hz); 45.0 (d, J = 15.3 Hz); 61.4 (s); 61.9 (s); 82.18 (d, 210.7 Hz); 170.4 (d, J = 1.6 Hz); 171.2 (d, J = 2.4 Hz).

^19F-NMR (CDCl₃/CFCI₃): ϕ = 171.0 (dm, J = 55.7 Hz, 8.8 Hz, 22.1 Hz).

3-Fluorocyclobutene: Diethyl 3-fluorocyclobutane-1,1-dicarboxylate (8.30 g, 0.0380 mol) was hydrolyzed using
hydrochloric acid, giving the diacid (5.04 g, 81.8% yield).
The diacid was thermally decarboxylated by heating to 190°-200°C at a pressure of 5 mm Hg. 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) and was found to be >95% pure by $^1$H and $^{13}$C NMR.

3-Fluorocyclobutanedicarboxylic acid:

MS (70eV) calculated for C$_6$H$_5$FO$_4$, 144.0222, found 144.0221.

$^1$H-NMR (CDCl$_3$/TMS): $\delta$ = 2.80 (4H, m); 5.10 (1H, dm, J = 55.4 Hz, 6.84 Hz, 4.34 Hz); 8.2 (bs).

$^{13}$C-NMR (CDCl$_3$): $\delta$ = 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).

$^{19}$F-NMR (CDCl$_3$/CFCl$_3$) $\phi$ = 166.3 (dm, J = 55.4 Hz).

3-Fluorocyclobutanecarboxylic acid:

MS (70 eV) calculated for C$_5$H$_7$FO$_2$, 118.0430, found 118.0432.

IR: 3000 cm$^{-1}$ (b, s); 1700 cm$^{-1}$ (b, s); 1420 cm$^{-1}$ (b, s); 1080 cm$^{-1}$ (s, b).

$^1$H-NMR (CDCl$_3$/TMS): $\delta$ = 2.65 (8H, m); 3.16 (2H, m), 4.93 (1H, dm, J = 55.3 Hz); 5.24 (1H, dm, J = 55.7 Hz); 10.25 (bs).
$^{13}$C-NMR (CDCl$_3$): $\delta = 27.5$ (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$_3$/CFCI$_3$): $\varphi = 163.6$ (50%, dm, $J = 55.6$ Hz); 166.2 (50%, dm, $J = 55.5$ Hz).

3-Fluorocyclobutanecarboxylic acid (3.00 g, 0.0254 mol) as a 1:1 mixture of the cis and trans isomers, was dissolved with Cu(OAc)$_2$ H$_2$O (0.0528 g, 0.290 mmol) and pyridine (67 µl) in 10 ml of very dry benzene in a sealed 100 ml round bottomed flask in a dry box. Then a mixture of Pb(OAc)$_4$ (2.56 g, 0.00578 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 minutes in the dry box. The solution of Pb(OAc)$_4$, was then added to the 100 ml flask with the acid and 20 ml of benzene used to wash any undissolved Pb(OAc)$_4$, into the flask. The flask was removed from the dry box while sealed, equipped with a reflux column, a distilling head, a receiver cooled in ice water, a dry ice/isopropanol cooled trap in series, and a nitrogen
inlet. The flask was stirred in the dark for 1.5 hours to insure metathesis of 3-fluorocyclobutane carboxylic acid with the Pb(OAc)$_4$. The solution was then gradually heated over 45 minutes to reflux, then heated at reflux for 2.5 hours. 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 $T_c=60^\circ$C, Flow = 60 ml/min, retention time 2 minutes for 3-fluorocyclobutene). 3-Fluorocyclobutene (0.2676 g, 64.7%) was analyzed by analytical GPLC (10 ft 20% Triton-X, $T_c=25^\circ$) and found to contain a small amount of E-l-fluoro-1,3-butadiene (3.44%). 3-Fluorocyclobutene: MS (70 eV) calculated for C$_4$H$_5$F 72.0375, found 72.0383.
IR: 3140 cm\(^{-1}\) (w); 3122 cm\(^{-1}\) (w); 3060 cm\(^{-1}\) (s); 2940 cm\(^{-1}\) (b, s); 2850 cm\(^{-1}\) (m); 2345 cm\(^{-1}\) (w); 1725 cm\(^{-1}\) (w); 820 cm\(^{-1}\) (s).

\(^1\)H-NMR (CDCl\(_3\)/TMS): \(\delta = 2.71\) (1H, m); 2.87 (1H, m); 5.39 (1H, dd, J = 57.0 Hz, 2.38 Hz); 6.37 (1H, d, J = 0.46 Hz); 6.14 (1H, s).

\(^13\)C-NMR (CDCl\(_3\)): \(\delta = 39.7\) (d, J = 19.9 Hz); 87.9 (d, J = 211.4 Hz); 137.3 (d, J = 19.3 Hz); 139.6 (d, J = 16.9 Hz).

\(^19\)F-NMR (CDCl\(_3\)/CFCI\(_3\)): \(\phi = 171.0\) (d, J = 57.5 Hz).

1-Chloro-3-trifluoromethylcyclobutane: 3-Chlorocyclobutane carboxylic acid was prepared by literature procedures, and 10.00 g (MW 134.57 g, 0.0743 mol) of the acid were placed in an autoclave which was cooled to \(-197^\circ\)C and depressurized. Then 24.09 g (MW 108.06 g, 0.223 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 hours. The autoclave was then cooled to \(-197^\circ\)C and the excess sulfur tetrafluoride 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 pentane. Distillation gave 7.95 g (MW 158.56 g, 0.0501 mol, 67.4%) of pure product. Attempts to eliminate HCl directly to give 3-trifluoromethylcyclobutene were unsuccessful.

$^1$H-NMR (CDCl$_3$/TMS): $\delta = 2.50$ (2H, m); 2.68 (2H, m); 3.17 (1H, m); 4.20 (1H, bm).

$^{13}$C-NMR (CDCl$_3$): $\delta = 31.5$ (s); 34.2 (q, $J = 3.66$ Hz); 46.5 (s); 50.1 (s); CF$_3$ carbon not seen in 25 MHz spectrum.

$^{19}$F-(NMR) (CDCl$_3$/CFC$_3$): $\phi = 73.8$ (32%, d, $J = 5.6$ Hz); 73.37 (68%, d, $J = 5.6$ Hz).

**3-Trifluoromethylcyclobutene:**$^{28,30}$ Magnesium metal (2.50 g, 0.103 g-atoms) and 50 ml of dry THF were placed in a 100 ml round bottomed flask equipped with 2 pressure equalizing dropping funnels, a magnetic stirrer, and reflux condenser attached to a nitrogen line. The 1-Chloro-3-trifluoromethylcyclobutane (8.00 g, 0.0504 mol) was placed in one of the funnels and 4.3 g of 1,2-dibromoethane 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, then the reflux was continued for 6 more hours. As the Grignard tended to crystalize from THF at room temperature, the hot solution was poured directly onto CO₂(s) (22.1 g, 0.5045 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 5.83g (0.0347 mol, 68.8%) of 3-trifluoromethylcyclobutanecarboxylic acid, which distilled over as 2 isomers. The oxidative decarboxylation of the acid was carried out in the same fashion as for the preparation of 3-fluorocyclobutene above to give 3-trifluoromethylcyclobutene in 15.5% yield.
3-Trifluoromethylcyclobutanecarboxylic acid: $^1$H-NMR

$(\text{CDCl}_3/\text{TMS})$: $\delta = 2.50$ (4H, m, $J = 8.98$ Hz, 7.98 Hz); 3.05
(1H, m, $J = 8.89$ Hz, 8.68 Hz); 3.25 (1H, m); 10.05 (1H, bs).

$^{19}$F-NMR $(\text{CDCl}_3/$CFCI$_3$): $\phi = 74.6$ (32%, d, $J = 8.5$ Hz); 75.1
(69%, d, $J = 9.3$ Hz).

3-Trifluoromethylcyclobutene: MS (70 eV): calculated for
C$_5$H$_5$F$_3$ 122.0343, found 122.0344.

IR: 3148 cm$^{-1}$ (w); 3089 cm$^{-1}$ (m); 2980 cm$^{-1}$ (m); 2942 cm$^{-1}$ (s);
1365 cm$^{-1}$ (s); 1150 cm$^{-1}$ (s); 1130 cm$^{-1}$ (s); 720 cm$^{-1}$ (s).

$^1$H-NMR $(\text{CDCl}_3/\text{TMS})$: $\delta = 2.66$ (2H, m); 3.46 (1H, m); 5.93
(1H, dd, $J = 2.81$ Hz, 0.98 Hz); 6.26 (1H, m).

$^{13}$C-NMR $(\text{CDCl}_3)$: $\delta = 31.1$ (q, $J = 3.63$ Hz); 44.6 (q, $J =$
31.49 Hz); 126.4 (q, $J = 276.29$ Hz); 128.4 (s); 131.6 (q, $J$
= 3.95 Hz). INEPT pulse sequence shows peaks at 126.4 and
31.1 are down.

$^{19}$F-NMR $(\text{CDCl}_3/$CFCI$_3$) $\phi = 73.5$ (d, $J = 0.43$ Hz).

1,1,1,2-Tetrafluoro-1,3-pentadiene: 1,1,2-Trifluoro-1,4-
pentadien-3-ol was prepared by reaction of
trifluorovinylolithium with acrylaldehyde according to
literature procedures.$^{31}$ The unsaturated alcohol was not
purified due to its instability. A 60 ml polypropylene bottle with a teflon coated stirring bar is charged with THF (6.0 ml, 5.32 g, 74.0 mmol) and cooled in a dry ice/isopropanol bath. Anhydrous HF is transferred into the bottle using a teflon inlet, and 10 mmol of the unsaturated alcohol was added over 5 minutes. The reaction was then allowed to warm to room temperature with stirring over 4 hours. The mixture is poured onto ice water, extracted with CHCl₃ (3 X 20 ml), washed with water and dried over MgSO₄. The product was isolated using preparative scale GPLC (10' SE-30 column).

MS (70 eV): calculated for C₅H₄F₄ 140.0249, found 140.0258.

Z-Isomer: ¹H-NMR (CDCl₃/TMS): δ = 5.43 (1H, d, J = 10.8 Hz); 5.77 (1H, d, J = 17 Hz); 6.13 (1H, dd, J = 11.3 Hz, 32.1 Hz); 6.60 (1H, ddd, J = 17 Hz, 11.3 Hz, 10.8 Hz).

¹F-NMR (CDCl₃/CFCl₃): ϕ = 72.8 (3F, d, J = 10 Hz); 134.2 (1F, dq, J = 10 Hz, 32.1 Hz).

E-Isomer: ¹F-NMR (CDCl₃/CFCl₃): ϕ = 67.8 (3F, d, J = 12 Hz); 129.7 (1F, dq, J = 12 Hz, 20 Hz).
Attempts to photochemically cyclize 1,1,1,2-tetrafluoro-1,3-pentadiene to the cyclobutene resulted in isomerization of the substituted double bond. No 3-fluoro-3-trifluoromethyl-cyclobutene was isolated from the reaction.

3-Fluoro- and 3-trifluoromethylcyclobutene were thermolyzed in the same fashion. A small pressure of the cyclobutene to be studied (7-10 mm Hg) was condensed with 5 mm Hg pentane as an internal standard into an evacuated bulb which had been equilibrated to the desired temperature in an oil bath. Timing of the reaction was started, and aliquots of the reaction mixture were periodically transferred to an evacuated sample tube to which argon as a spacer gas was then added. The contents of the bulb were analyzed by GPLC using a Hewlett Packard 1095 Gas Chromatograph with a flame ionization detector. A 20’, 10% OV-210 column was used to analyze the ring opening of 3-fluorocyclobutene. The column temperature was maintained at 50°C, while the column flow rate was 60 ml/min. A 20’, 10% OV-210 column coupled with a 10’, 10% TCP column was used for the ring opening of 5,5,5-
trifluoro-1,3-pentadiene. The column temperature was maintained at 70°C, and the column flow at 60 ml/min. Rate constants were calculated from the peak integrals. In each case the total values of the peak integrals for starting material and product remained the same relative to the internal standard, indicating no side reactions were occurring, and all products were accounted for. In both systems the products were equilibrated in CDCl₃, with CFCl₃, as an internal standard by adding a catalytic amount of iodine and heating in a sealed NMR tube until no further changes in the ¹⁹F NMR spectra were observed for each temperature.

**E-1-Fluoro-1,3-butadiene:**

**¹H-NMR (CDCl₃/TMS):**  δ= 5.06 (1H, dm, J = 11.1 Hz, 1.7 Hz, 1.4 Hz); 5.19 (1H, dm, J = 16.0 Hz, 1.5 Hz, 0.8 Hz); 6.08 (2H, m, J = 16.0 Hz, 1.5 Hz, 0.8 Hz); 6.80 (1H, ddm, J = 82.4 Hz, 10.9 Hz, 1.8 Hz, 1.1 Hz).

**¹³C-NMR (CDCl₃):**  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).

**¹⁹F-NMR (CDCl₃/C₆F₆):**  ϕ= 128.3 (dd, J = 82.7 Hz, 16.5 Hz).
E-5,5,5-Trifluoro-1,3-pentadiene: $^1$H-NMR (CDCl$_3$/TMS): $\delta =$

$5.46$ (1H, d, $J = 10.0$ Hz); $5.54$ (1H, d, $J = 16.9$ Hz); $5.73$
(1H, m, $J = 15.6$ Hz, 7.4 Hz); $6.42$ (1H, dddd, $J = 17.0$ Hz, $10.0$ Hz, 0.7 Hz); $6.74$ (1H, dq, $J = 15.6$ Hz, 6.6 Hz).

$^{19}$F-NMR (CDCl$_3$/CFCI$_3$): $\phi = 64.2$ (d, $J = 7.0$ Hz)

Z-5,5,5-Trifluoro-1,3-pentadiene: $^{19}$F-NMR (CDCl$_3$/CFCI$_3$): $\phi =$

$58.3$ (d, $J = 8.2$ Hz).

Table 7: Relative GPLC integrals of starting material and product in the ring opening of 3-fluorocyclobutene at temperature = 67.7°

<table>
<thead>
<tr>
<th>Time (secs)</th>
<th>3-fluorocyclobutene</th>
<th>E-diene</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>93.1</td>
<td>6.9</td>
</tr>
<tr>
<td>4200</td>
<td>94.4</td>
<td>5.7</td>
</tr>
<tr>
<td>13620</td>
<td>91.5</td>
<td>8.5</td>
</tr>
<tr>
<td>28440</td>
<td>86.4</td>
<td>13.6</td>
</tr>
<tr>
<td>48660</td>
<td>80.6</td>
<td>19.4</td>
</tr>
<tr>
<td>87000</td>
<td>70.4</td>
<td>29.6</td>
</tr>
<tr>
<td>95160</td>
<td>66.7</td>
<td>33.3</td>
</tr>
</tbody>
</table>
Table 8: Relative GPLC integrals of starting material and product in the ring opening of 3-fluorocyclobutene at temperature = 78.1°

<table>
<thead>
<tr>
<th>Time (secs)</th>
<th>3-fluorocyclobutene</th>
<th>E-diene</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>94.9</td>
<td>5.2</td>
</tr>
<tr>
<td>6060</td>
<td>85.9</td>
<td>14.2</td>
</tr>
<tr>
<td>15000</td>
<td>79.4</td>
<td>20.6</td>
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<tr>
<td>19200</td>
<td>73.2</td>
<td>26.8</td>
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<tr>
<td>25200</td>
<td>69.7</td>
<td>30.3</td>
</tr>
<tr>
<td>31200</td>
<td>62.6</td>
<td>37.4</td>
</tr>
<tr>
<td>37140</td>
<td>62.0</td>
<td>39.0</td>
</tr>
</tbody>
</table>

Table 9: Relative GPLC integrals of starting material and product in the ring opening of 3-fluorocyclobutene at temperature = 84.2°

<table>
<thead>
<tr>
<th>Time (secs)</th>
<th>3-fluorocyclobutene</th>
<th>E-diene</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>94.4</td>
<td>5.6</td>
</tr>
<tr>
<td>3600</td>
<td>84.2</td>
<td>15.8</td>
</tr>
<tr>
<td>6720</td>
<td>79.5</td>
<td>20.5</td>
</tr>
<tr>
<td>11160</td>
<td>71.4</td>
<td>28.7</td>
</tr>
<tr>
<td>14280</td>
<td>65.1</td>
<td>34.9</td>
</tr>
<tr>
<td>19380</td>
<td>59.5</td>
<td>40.6</td>
</tr>
<tr>
<td>21900</td>
<td>57.4</td>
<td>42.6</td>
</tr>
</tbody>
</table>
Table 10: Relative GPLC integrals of starting material and product in the ring opening of 3-fluorocyclobutene at temperature $= 92.6^\circ$.

<table>
<thead>
<tr>
<th>Time (secs)</th>
<th>3-fluorocyclobutene</th>
<th>E-diene</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>97.0</td>
<td>3.1</td>
</tr>
<tr>
<td>5520</td>
<td>69.9</td>
<td>30.1</td>
</tr>
<tr>
<td>6360</td>
<td>66.9</td>
<td>33.1</td>
</tr>
<tr>
<td>8160</td>
<td>58.9</td>
<td>41.2</td>
</tr>
<tr>
<td>8760</td>
<td>59.6</td>
<td>40.4</td>
</tr>
</tbody>
</table>

Table 11: Relative GPLC integrals of starting material and product in the ring opening of 3-fluorocyclobutene at temperature $= 97.0^\circ$.

<table>
<thead>
<tr>
<th>Time (secs)</th>
<th>3-fluorocyclobutene</th>
<th>E-diene</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>97.0</td>
<td>4.4</td>
</tr>
<tr>
<td>1500</td>
<td>81.1</td>
<td>19.0</td>
</tr>
<tr>
<td>2100</td>
<td>77.4</td>
<td>22.6</td>
</tr>
<tr>
<td>2700</td>
<td>70.5</td>
<td>29.5</td>
</tr>
<tr>
<td>3300</td>
<td>69.1</td>
<td>30.9</td>
</tr>
<tr>
<td>3960</td>
<td>64.4</td>
<td>35.6</td>
</tr>
<tr>
<td>4500</td>
<td>64.5</td>
<td>35.5</td>
</tr>
</tbody>
</table>
Table 12: Relative GPLC integrals of starting material and product in the ring opening of 3-fluorocyclobutene at temperature = 103.1°

<table>
<thead>
<tr>
<th>Time (secs)</th>
<th>3-fluorocyclobutene</th>
<th>E-diene</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>96.2</td>
<td>3.9</td>
</tr>
<tr>
<td>720</td>
<td>82.6</td>
<td>17.4</td>
</tr>
<tr>
<td>1080</td>
<td>76.4</td>
<td>23.6</td>
</tr>
<tr>
<td>1560</td>
<td>70.6</td>
<td>29.5</td>
</tr>
<tr>
<td>2280</td>
<td>63.1</td>
<td>36.9</td>
</tr>
<tr>
<td>2640</td>
<td>59.4</td>
<td>40.6</td>
</tr>
</tbody>
</table>

Table 13: Relative GPLC integrals of starting material and product in the ring opening of 3-trifluoromethyl-cyclobutene at temperature = 146.5°C

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>CF₃-cyclobutene</th>
<th>Z and E dienes</th>
</tr>
</thead>
<tbody>
<tr>
<td>3660</td>
<td>90.7</td>
<td>9.4</td>
</tr>
<tr>
<td>7200</td>
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<tr>
<td>9000</td>
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<td>19.8</td>
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<tr>
<td>14400</td>
<td>71.3</td>
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<tr>
<td>19860</td>
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<td>37.7</td>
</tr>
<tr>
<td>25200</td>
<td>55.4</td>
<td>44.6</td>
</tr>
<tr>
<td>30660</td>
<td>48.6</td>
<td>51.4</td>
</tr>
</tbody>
</table>
Table 14: Relative GPLC integrals of starting material and product in the ring opening of 3-trifluoromethylcyclobutene at temperature = 154.7°C

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>CF₃-cyclobutene</th>
<th>Z and E dienes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>95.4</td>
<td>4.6</td>
</tr>
<tr>
<td>2460</td>
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<tr>
<td>3600</td>
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<td>14.9</td>
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<tr>
<td>4800</td>
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<tr>
<td>6000</td>
<td>75.9</td>
<td>24.1</td>
</tr>
<tr>
<td>9000</td>
<td>66.0</td>
<td>34.0</td>
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<tr>
<td>12000</td>
<td>56.6</td>
<td>43.4</td>
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</table>

Table 15: Relative GPLC integrals of starting material and product in the ring opening of 3-trifluoromethylcyclobutene at temperature = 162.2°C

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>CF₃-cyclobutene</th>
<th>Z and E dienes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1080</td>
<td>89.1</td>
<td>10.9</td>
</tr>
<tr>
<td>2160</td>
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<tr>
<td>3240</td>
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<td>28.0</td>
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<tr>
<td>4320</td>
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<td>36.0</td>
</tr>
<tr>
<td>5400</td>
<td>58.1</td>
<td>41.9</td>
</tr>
<tr>
<td>7800</td>
<td>45.7</td>
<td>54.4</td>
</tr>
<tr>
<td>10800</td>
<td>33.1</td>
<td>66.9</td>
</tr>
</tbody>
</table>
Table 16: Relative GPLC integrals of starting material and product in the ring opening of 3-trifluoromethylcyclobutene at temperature = 169.8°C

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>CF₃-cyclobutene</th>
<th>Z and E dienes</th>
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</thead>
<tbody>
<tr>
<td>900</td>
<td>81.6</td>
<td>18.4</td>
</tr>
<tr>
<td>1800</td>
<td>67.6</td>
<td>32.4</td>
</tr>
<tr>
<td>2760</td>
<td>55.3</td>
<td>44.7</td>
</tr>
<tr>
<td>3600</td>
<td>45.1</td>
<td>54.9</td>
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<tr>
<td>4500</td>
<td>37.5</td>
<td>62.5</td>
</tr>
<tr>
<td>5400</td>
<td>30.4</td>
<td>69.6</td>
</tr>
<tr>
<td>6300</td>
<td>24.7</td>
<td>75.3</td>
</tr>
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</table>

Table 17: Relative GPLC integrals of starting material and product in the ring opening of 3-trifluoromethylcyclobutene at temperature = 177.2°C

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>CF₃-cyclobutene</th>
<th>Z and E dienes</th>
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</thead>
<tbody>
<tr>
<td>600</td>
<td>77.1</td>
<td>22.9</td>
</tr>
<tr>
<td>1200</td>
<td>60.0</td>
<td>40.0</td>
</tr>
<tr>
<td>1800</td>
<td>45.8</td>
<td>54.2</td>
</tr>
<tr>
<td>2400</td>
<td>35.9</td>
<td>64.1</td>
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<tr>
<td>3000</td>
<td>27.7</td>
<td>72.3</td>
</tr>
<tr>
<td>3900</td>
<td>18.7</td>
<td>81.3</td>
</tr>
<tr>
<td>4500</td>
<td>14.7</td>
<td>85.3</td>
</tr>
</tbody>
</table>
Table 18: Relative GPLC integrals of starting material and product in the ring opening of 3-trifluoromethylcyclobutene at temperature = 186.3°C

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>CF₃-cyclobutene</th>
<th>E- and Z-diene</th>
</tr>
</thead>
<tbody>
<tr>
<td>480</td>
<td>63.4</td>
<td>36.6</td>
</tr>
<tr>
<td>1320</td>
<td>28.0</td>
<td>72.0</td>
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<tr>
<td>1680</td>
<td>19.9</td>
<td>80.1</td>
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<tr>
<td>2040</td>
<td>14.3</td>
<td>85.7</td>
</tr>
<tr>
<td>2400</td>
<td>10.1</td>
<td>89.9</td>
</tr>
<tr>
<td>2760</td>
<td>7.0</td>
<td>93.0</td>
</tr>
</tbody>
</table>

1-Fluoro-2-vinylcyclopropane: Fluorodiiodomethane (20.00 g, 69.9 mmol) was placed in an equal volume of toluene and placed in a glass tube. The tube was attached via a rubber hose to a vacuum line, cooled to -197°C, evacuated and degassed. 1,3-Butadiene (8.90 g, 164 mmol) was then condensed into the tube. A 1.6 M solution of diethylzinc in toluene (14 ml) was then added to the tube using a double ended syringe. The tube was then flame sealed and spun while warming to room temperature. The tube was then placed in an oil bath and spun rapidly while the oil bath temperature was increased to 94°C. The tube was heated for
8.5 hrs. During heating a white solid was observed to form inside the tube. The tube was then cooled to -197°C, opened, connected to a nitrogen line and allowed to vent with warming. A saturated aqueous solution of ammonium chloride was then slowly added until no more reaction was observed and almost all the white solid had dissolved. The mixture was then removed from the tube, washed once with saturated ammonium chloride solution (50 ml), and dried over anhydrous magnesium sulfate. The solution was then distilled and the fraction collected at 50°-70°C was observed by $^{19}$F NMR to contain the cis and trans product isomers in a ratio of 45.8:54.2, respectively. Analytical GPLC showed a product ratio of 45.8:54.2 (10' 20% carbowax column, $T_c = 70°C$, flow = 70 ml/min; retention time 4.19 minutes for trans, 6.26 minutes for cis). The products were collected and purified by preparative scale GPLC using a 10' 20% DIDP column to give 0.5848 g of the cis product and 0.4455 g of the trans product (17.11% yield).

MS (70 eV): calculated for $C_5H_7F$ 86.032; found 86.053.
cis-1-Fluoro-2-vinylcyclopropane: IR (neat): 3090 cm\(^{-1}\) (w);
3050 cm\(^{-1}\) (w); 3020 cm\(^{-1}\) (w); 2955 cm\(^{-1}\) (m); 1640 cm\(^{-1}\) (m);
1440 cm\(^{-1}\) (m); 1352 cm\(^{-1}\) (w); 1257 cm\(^{-1}\) (s); 1010 cm\(^{-1}\) (s);
799 cm\(^{-1}\) (s).

\(^1\)H-NMR (CDCl\(_3\)/TMS): \(\delta = 0.98\) (2H, m, \(J = 13.3\) Hz, 12.8 Hz,
7.14 Hz, 0.7 Hz); 1.58 (1H, m, \(J = 13.1\) Hz, 6.6 Hz, 6.2 Hz,
1.2 Hz); 4.69 (1H, dm, \(J = 64.8\) Hz, 6.1 Hz, 6.6 Hz, 0.7 Hz);
5.11 (1H, dd, \(J = 10.3\) Hz, 1.8 Hz); 5.25 (1H, dd, \(J = 17.3,
1.9 Hz); 5.62 (1H, m, \(J = 17.2\) Hz, 9.5 Hz, 0.3 Hz).

\(^{13}\)C-NMR (CDCl\(_3\)): \(\delta = 12.6\) (d, \(J = 10.8\) Hz); 20.81 (d, \(J =
10.3\) Hz); 72.9 (d, \(J = 221.1\) Hz); 115.50 (s); 134.2 (d, \(J =
8.1\) Hz).

\(^{19}\)F-NMR (CDCl\(_3\)/CFC\(_3\)): \(\phi = 223.1\) (dddd, \(J = 64.8\) Hz, 22.5 Hz,
13.2 Hz, 12.7 Hz).

trans-1-Fluoro-2-vinylcyclopropane: IR (neat): 3090 cm\(^{-1}\)
(w); 2960 cm\(^{-1}\) (m); 1635 cm\(^{-1}\) (m); 1259 cm\(^{-1}\) (s); 800 cm\(^{-1}\) (s).

\(^1\)H-NMR (CDCl\(_3\)/TMS): \(\delta = 0.81\) (1H, m, \(J = 10.7\) Hz, 6.2 Hz,
3.8 Hz, 2.4 Hz); 1.25 (1H, m, \(J = 22.0\) Hz, 11.0 Hz); 1.87
(1H, m, \(J = 20.5\) Hz, 10.8 Hz, 2.0 Hz); 4.42 (1H, dm, \(J =
64.1\) Hz, 6.1 Hz, 2.8 Hz, 2.0 Hz); 4.98 (1H, dm, \(J = 7.6\) Hz,
0.9 Hz); 5.05 (1H, dd, J = 1.8 Hz, 0.9 Hz); 5.54 (1H, dm, J = 7.6 Hz, 1.8 Hz).

$^{13}$C-NMR (CDCl$_3$) $\delta$ = 13.1 (d, J = 9.8 Hz); 21.1 (d, J = 11.1 Hz); 74.9 (d, J = 225.8 Hz); 114.1 (d, J = 1.9 Hz); 135.9 (s).

$^{19}$F-NMR (CDCl$_3$/CFCl$_3$): $\phi$ = 205.6 (ddddd, J = 64.1 Hz, 22.0 Hz, 20.2 Hz, 10.7 Hz).

1-Trifluoromethyl-2-vinylcyclopropane:

2,2,2-Trifluoroethylamine hydrochloride (10.00 g, 73.7 mmol) in 10.00 ml of water was slowly added via a pressure equalizing dropping funnel to a stirred solution of sodium nitrite (5.52 g, 79.9 mmol) in 10.00 ml of water at 15°C and 50 mm Hg in a distillation apparatus with a receiver cooled to -78°C. The 2,2,2-trifluorodiazooethane was evolved from the solution as a gas which condenses as a yellow liquid in the receiver. The reaction was complete when all the hydrochloride had been added and all yellow color had left the reaction vessel. The diazo compound was quickly transferred to a cold glass tube which was then attached to a vacuum line, cooled with liquid nitrogen and evacuated.
1,3-Butadiene (17.7 g, 0.327 mol) was then condensed into the tube, which was sealed and placed in an autoclave with 5 g of dry ice to increase the external pressure and heated at 110°C for 8 hours. The tube was removed from the autoclave, cooled to -78°C, opened and the excess butadiene vented on warming. Distillation gave 2.45 g (17.9 mmol, 33.1%) of a mixture of the cis and trans isomers, b.p. 53°-56°C.

Analytical GPLC showed two major products in a ratio of 47.2:52.8 (10' 20% Carbowax column, T_e = 70°C, flow = 70 ml/min; retention time 3.31 minutes for trans, 5.88 minutes for cis). The products were collected and purified by preparative scale GPLC using a 10' 20% DIDP column. Collected were 1.05 g of cis-product and 1.01 g trans-product (yield 21.0%, purity >98% by GPLC). MS (70 eV):
calculated for C_6H_7F_3 136.050; found 136.050.

**cis-1-Trifluoromethyl-2-vinylcyclopropane**: IR (neat):
3098 cm^{-1} (s); 3020 cm^{-1} (s); 3000 cm^{-1} (m); 2960 cm^{-1} (m); 1830 cm^{-1} (m); 1645 cm^{-1} (s); 1470 cm^{-1} (s); 1410 cm^{-1} (s); 799 cm^{-1} (s).
$^1$H-NMR (CDCl$_3$/TMS): $\delta = 1.02$ (1H, q, $J = 6.1$ Hz); 1.16 (1H, m, $J = 8.6$ Hz, 7.5 Hz, 1.5 Hz); 1.72 (2H, m, $J = 12.3$ Hz, 8.4 Hz, 8.0 Hz, 1.7 Hz); 5.12 (1H, ddd, $J = 10.0$ Hz, 1.8 Hz, 0.5 Hz); 5.29 (1H, dd, $J = 16.9$ Hz, 1.8 Hz); 5.59 (1H, m, $J = 17.0$ Hz, 10.1 Hz, 6.7 Hz, 1.7 Hz).

$^{13}$C-NMR (CDCl$_3$): $\delta = 117.3$ (s); 134.1 (s); CF$_3$ carbon not seen.

$^{19}$F-NMR (CDCl$_3$/CFCl$_3$): $\phi = 60.5$ (d, $J = 8.0$ Hz).

trans-1-Trifluoromethyl-2-vinylcyclopropane: IR (neat):
3100 cm$^{-1}$ (w); 2960 cm$^{-1}$ (w); 1645 cm$^{-1}$ (w); 1475 cm$^{-1}$ (m);
1410 cm$^{-1}$ (s); 1270 cm$^{-1}$ (s); 799 cm$^{-1}$ (s).

$^1$H-NMR (CDCl$_3$/TMS): $\delta = 0.86$ (1H, m, $J = 8.8$ Hz, 5.9 Hz, 5.6 Hz, 0.9 Hz); 1.14 (1H, m, $J = 9.1$ Hz, 5.5 Hz, 5.5 Hz, 0.5 Hz); 1.55 (1H, m, $J = 8.9$ Hz, 6.7 Hz, 5.5 Hz, 1.07 Hz); 1.80 (1H, m, $J = 9.0$ Hz, 5.9 Hz); 5.03 (1H, ddd, $J = 9.9$ Hz, 1.7 Hz, 0.7 Hz); 5.18 (1H, ddd, $J = 17.0$ Hz, 1.7 Hz, 0.6 Hz);
5.44 (1H, m, $J = 17.1$ Hz, 10.0 Hz, 7.6 Hz).

$^{13}$C-NMR (CDCl$_3$) $\delta = 9.4$ (q, $J = 2.7$ Hz); 18.6 (q, $J = 2.4$ Hz); 21.2 (q, $J = 36.7$ Hz); 115.3 (s); 125.9 (q, $J = 270.5$ Hz); 137.0 (s).
\[ ^{19}\text{F}-\text{NMR (CDCl}_3/\text{CFCl}_3) : \quad \delta = 66.5 \text{ (d, } J = 6.6 \text{ Hz).} \]

The aldehydes, tosylhydrazones, and sodium salts of the tosylhydrazones for all four isolated vinylcyclopropanes were prepared in an identical manner, and the pyrolyses were conducted in an identical manner. The typical procedure for preparation of the aldehydes is as follows: the cyclopropyl alkene (0.0110 mol) was placed with 30 ml CH\textsubscript{2}Cl\textsubscript{2} in a 100 ml 3-necked round bottomed flask equipped with a magnetic stirring bar, a gas inlet, a cold finger cooled to \(-78^\circ\text{C}\) and a water tower containing 200 ml of a saturated aqueous solution of potassium iodide. The flask was cooled to \(-78^\circ\text{C}\) with stirring and ozone passed through the solution until a blue color persisted. Oxygen was then passed through the solution until all blue color disappeared, then nitrogen for ten minutes. Then dimethyl sulfide (0.692 g, 0.0111 mol) was quickly added and the solution allowed to warm with stirring to room temperature over three hours. Most of the solvent was removed and the crude material passed down a column with 70:30 CH\textsubscript{2}Cl\textsubscript{2}/diethyl ether to remove dimethyl sulfoxide. Evaporation of solvent and GPLC
(10' OV-210, Tc=40°C, F= 40 ml/min) gave 0.88 g (6.37 mmol, 57.9%) of the pure aldehyde.

**cis-2-Fluorocyclopropanecarboxaldehyde (57.0% yield):**

\[^{1}H\text{-NMR (CDCl}_3/TMS): \delta = 1.40 \text{ (1H, m, } J = 12.6 \text{ Hz, 5.6 Hz); 1.93 (2H, m, } J = 12.0 \text{ Hz, 9.9 Hz); 4.97 (dm, } J = \text{ 63.2 Hz, 9.8 Hz, 5.6 Hz, 3.8 Hz); 9.56 (dm, } J = \text{ 5.8 Hz, 2.6 Hz).}

\[^{13}\text{C-NMR (CDCl}_3): \delta = 13.1 \text{ (d, } J = 11.1 \text{ Hz); 28.8 (d, } J = 10.7 \text{ Hz); 73.3 (d, } J = 227.3 \text{ Hz); 196.8 (d, } J = 7.9 \text{ Hz).}

\[^{19}\text{F-NMR (CDCl}_3/CFCI}_3): \phi = 219.1 \text{ (dm, } J = \text{ 63.3 Hz, 19.2 Hz, 12.7 Hz, 12.0 Hz).}

**trans-2-Fluorocyclopropanecarboxaldehyde (56.0% yield):**

\[^{1}H\text{-NMR (CDCl}_3/TMS): \delta = 1.59 \text{ (2H, m, } J = 18.4 \text{ Hz, 5.8 Hz, 3.6 Hz, 1.3 Hz); 2.49 (1H, m, } J = 17.4 \text{ Hz, 5.9 Hz, 1.5 Hz, 0.8 Hz); 4.83 (1H, ddddd, } J = \text{ 64.1 Hz, 6.1 Hz, 3.6 Hz, 1.5 Hz); 9.70 (1H, dd, } J = 2.5 \text{ Hz, 0.8 Hz).}

\[^{13}\text{C-NMR (CDCl}_3) \delta = 15.8 \text{ (d, } J = \text{ 8.1 Hz); 28.6 (d, } J = \text{ 11.2 Hz); 74.8 (d, } J = 231.3 \text{ Hz); 198.3 (s).}
$^1$H-NMR (CDCl$_3$/TMS): $\delta = 1.43$ (2H, m, $J = 5.0, 2.7$); $2.22$ (1H, m, $J = 3.2$ Hz, $2.7$ Hz, $2.2$ Hz); $2.35$ (1H, m, $J = 5.7$ Hz, $3.2$ Hz, $2.0$ Hz, $2.1$ Hz); $9.49$ (1H, dd, $J = 3.2$ Hz, $2.7$ Hz).

$^1$C-NMR (CDCl$_3$): $\delta = 10.7$ (q, $J = 2.7$ Hz); $22.4$ (q, $J = 38.3$ Hz); $24.5$ (q, $J = 1.9$ Hz); $124.5$ (q, $J = 271.2$ Hz); $197.5$ (s).

$^{19}$F-NMR (CDCl$_3$/CFCI$_3$): $\phi = 61.2$ (d, $J = 5.7$ Hz).

trans-2-Trifluoromethylcyclopropylcarboxaldehyde (50.46% yield): IR (neat): $3010$ cm$^{-1}$ (w); $2960$ cm$^{-1}$ (w); $2940$ cm$^{-1}$ (w); $2325$ cm$^{-1}$ (m); $1730$ cm$^{-1}$ (vs); $1160$ cm$^{-1}$ (vs).

$^1$H-NMR (CDCl$_3$/TMS): $\delta = 1.52$ (1H, m, $J = 2.6$ Hz, $1.6$ Hz); $1.75$ (1H, m, $J = 4.4$ Hz, $1.7$ Hz); $2.12$ (2H, m, $J = 5.7$ Hz, $4.3$ Hz, $3.0$ Hz); $9.16$ (1H, dd, $J = 3.4$ Hz, $2.4$ Hz).

$^{13}$C-NMR (CDCl$_3$): $\delta = 9.0$ (q, $J = 2.6$ Hz); $22.5$ (q, $J = 38.7$ Hz); $27.3$ (s); $125.28$ (q, $J = 272.5$ Hz); $196.8$ (s).
\(^{19}\)F-NMR (CDCl\(_3\)/CFCl\(_3\)): \(\phi = 67.6\) (d, \(J = 5.7\) Hz).

The tosylhydrazones were prepared in an identical manner:\(^5\)

Tosylhydrazine (1.12 g, 6.01 mmol) is dissolved in a mixture of 8.80 ml methanol, 1.90 ml water, 1.50 ml acetic acid and 2 drops of concentrated hydrochloric acid. The cyclopropylcarboxaldehyde (4.57 mmol) is then added and the mixture allowed to stir for 3 hours. A white solid should precipitate. The solution is filtered and the white solid recrystallized from methanol with a few drops of water to give the tosylhydrazone.

cis-2-fluorocyclopropylcarboxaldehyde tosylhydrazone: 66.0%;

MS (70 eV): M + H found at 257, corresponding to C\(_{11}\)H\(_{14}\)FN\(_2\)O\(_2\)S.

trans-2-fluorocyclopropylcarboxaldehyde tosylhydrazone:

79.0%

cis-2-trifluoromethylcyclopropylcarboxaldehyde
tosylhydrazone: 84.3%; MS (70 eV): M + H found at 307,
corresponding to C\(_{12}\)H\(_{14}\)F\(_3\)N\(_2\)O\(_2\)S.

trans-2-trifluoromethylcyclopropylcarboxaldehyde
tosylhydrazone: 60.02%
The sodium salt of the tosylhydrazone was prepared by reacting the tosylhydrazone (1.6 mmol) with sodium hydride (47.1 mg, 1.96 mmol) in 40 ml of very dry THF in a dry box. There was a gradual evolution of gas followed by the precipitation of a white solid. The solid salt was filtered, washed with 30 ml of very dry diethyl ether and dried under vacuum.

**Pyrolysis of the Tosylhydrazone Salt:** The salt was pyrolyzed using a sublimator whose cold finger was cooled to -78°C. A small amount (~100 mg) of the salt was placed in the bottom of the sublimator, which was then attached to a trap cooled to -197°C. The apparatus was then evacuated to a pressure of 0.01 mm Hg and the bottom part of the sublimator heated to 110°C (70°C for the fluoro specie) in an oil bath. Over the course of 2 hours a yellow liquid was observed to condense on the cold finger. The cold finger was then allowed to warm to room temperature, and the cyclopropyldiazomethane trapped on the cold finger condensed in the trap. The diazo compound was identified by its $^{19}$F NMR spectrum.
CHAPTER 3
RESULTS AND DISCUSSION

The synthesis of 3-fluorocyclobutene began with the addition of 'BrF' to 3-chloropropene to give 1-bromo-3-chloro-2-fluoropropane.\(^2\) It is believed that the reaction proceeds by formation of the bromonium ion across the double bond, which is then displaced by fluorine. The internal carbon of the three carbon chain should be more able to support a partial positive charge, so attack by the fluorine should be preferred there.

\[ \text{Figure 19: Addition of 'BrF' to 3-chloropropene.} \]
Figure 20: Synthesis of 3-fluorocyclobutene.

Though the product could not be separated from 2-bromo-1-chloro-3-fluoropropane, condensation with diethylmalonate left the undesired isomer unreacted. Several solvent/base combinations were tried for the condensation, and diglyme/sodium with careful monitoring by $^{19}$F NMR was found to give the least amount of elimination. In fact, the principal impurity in the formation of diethyl 3-fluorocyclobutylidicarboxylate was allyl malonate, which could not be separated from the desired product by
distillation. Fortunately, it was found that careful addition of bromine to the mixture resulted in the destruction of allyl malonate, leaving the cyclobutyldicarboxylate ester untouched. Acid hydrolysis of the diester and decarboxylation gave a 50:50 mixture of cis and trans-3-fluorocyclobutanecarboxylic acids, which were oxidatively decarboxylated with lead tetraacetate to give 3-fluorocyclobutene in good yield.

The ring opening of the cyclobutene was conducted in the gas phase at pressures low enough to insure good unimolecular rate data. Pentane was added as an internal standard to insure that no side reactions were occurring, but the kinetics of the reaction were monitored by measuring the GPLC integral of the starting material against the sum of the integrals of starting material and product. The $^1$H NMR spectrum of the product gave a signal at $\delta = 6.80$ which had coupling constants of 82.4 Hz and 10.9 Hz, corresponding to a geminal H-F coupling and a vicinal trans H-H coupling, establishing the product as E-1-fluoro-1,3-butadiene. None of the Z-1-fluoro-1,3-butadiene was observed by GPLC or $^{19}$F
NMR. The rate constants were calculated for each temperature and the activation parameters calculated.

Figure 21: Ring opening of 3-fluorocyclobutene.

Table 19: Rate constants and activation parameters for ring opening of 3-fluorocyclobutene.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(k x 10^-6)/secs</th>
</tr>
</thead>
<tbody>
<tr>
<td>67.7</td>
<td>3.58 ± .14</td>
</tr>
<tr>
<td>78.1</td>
<td>11.9 ± .1</td>
</tr>
<tr>
<td>84.2</td>
<td>22.9 ± .1</td>
</tr>
<tr>
<td>92.6</td>
<td>58.0 ± 2.8</td>
</tr>
<tr>
<td>97.0</td>
<td>91.2 ± 7.0</td>
</tr>
<tr>
<td>103.1</td>
<td>180. ± 7.</td>
</tr>
</tbody>
</table>

E_{act} = 28.1 ± .3 kcal/mol
log A = 12.544 ± .175
ΔH° = 27.4 ± .3 kcal/mol
ΔS° = -3.48 ± .79 e.u.
ΔG° = 28.6 kcal/mol
The ring opening of 3-fluorocyclobutene has been theoretically studied by Rondan and Houk, and is expected to have an activation energy substantially lower than that of unsubstituted cyclobutene, due to the favorable interaction between the nonbonding filled p-orbitals of the fluorine substituent and the LUMO of the transition structure. The energy of activation for the reaction is 28.1 ± 0.3 kcal/mol, as compared to 32.5 kcal/mol for the activation energy of cyclobutene. The energy of activation for 3-fluorocyclobutene is also lower than the value of 29.4 kcal/mol determined for 3-chlorocyclobutene. This is to be expected, due to the better overlap between the 2p orbitals of fluorine with the LUMO of the cyclobutenyl transition structure. The energy of activation is quite near the value of 27.8 kcal/mol predicted for 3-acetoxycyclobutene. Oxygen is a better electron donor than fluorine, but the electron withdrawing effect of the adjacent carbonyl should inhibit its donor ability. In contrast, 3-ethoxycyclobutene is predicted to have an energy of activation of 23.5 kcal/mol.
It is also predicted that the transition structure incorporating inward rotation of the fluorine substituent should be some 20.8 kcal/mol higher in energy than the structure with outward rotation. Though no Z-1-fluoro-1,3-butadiene was observed by GPLC, it is possible that a small amount could not be well resolved on the column that was used, as authentic samples of the E and Z isomers elute quite closely. However, no Z-diene was observed in the $^{19}$F NMR spectra of any of the sample over the entire temperature range that was studied, which places the upper limit of Z-diene at < 2%.

Figure 22: Fluorine interaction with HOMO, LUMO
If inward rotation of the fluorine substituent destabilizes the transition state, it would be expected that there would be little of the Z-diene observed. Since none of the Z-1-fluoro-1,3-butadiene was observed is the ring opening of 3-fluorocyclobutene, it is difficult to see how the relative experimental energies for inward and outward rotation compare with the theoretically determined values. However, Dolbier and coworkers have recently studied the kinetics of ring opening of 3,3-difluorocyclobutene. The energy of activation for ring opening of 3,3-difluorocyclobutene is 16.9 kcal/mol higher in energy than 3-fluorocyclobutene. Because fluorine is a small substituent, it is unlikely that a significant part of the increase in activation energy is due to steric interaction between the fluorine and the inward rotating hydrogen in the transition state. Part of the increase in energy is due to a strengthening of the C₃-C₄ bond due to geminal fluorine substitution. A recent study by Dolbier and coworkers of the rearrangement of 1,1-difluoro-3-(dideuteriomethylene)cyclobutane to 1,1-difluoro-2,2-
dideuterio-3-methylene cyclobutane yielded information on the effect of vicinal fluorine substitution on the homolytic cleavage of a σ bond.\textsuperscript{36}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\linewidth]{figure23}
\caption{Ring opening of 3,3-difluorocyclobutene.\textsuperscript{18}}
\end{figure}

The parent dideuteriomethylene cyclobutane was studied by Doering and Gilbert and found to have $\Delta H^\ddagger = +48.8 \pm 1$ kcal/mol and $\Delta S^\ddagger = 5.3$ e.u.\textsuperscript{37} This indicates that the cyclobutyl bond which is cleaved in the rearrangement is stabilized by approximately 5 kcal/mol by the geminal fluorines in 1,1-difluoro-3-(dideuteriomethylene)cyclobutane relative to the nonfluorinated hydrocarbon. Based on this information it is expected that the σ-bond which is cleaved in the ring opening of 3,3-difluorocyclobutene should be
stabilized by 5 kcal more than the σ-bond in 3-fluorocyclobutene. Adjusting the activation enthalpy of 3,3-difluorocyclobutene for this difference, it is found that there is still a difference of 12.6 kcal/mol in the activation enthalpies of 3,3-difluorocyclobutene and 3-fluorocyclobutene. Since the transition states of both systems are stabilized by outward rotation of one fluorine, this energy difference should serve as a reasonably accurate measure of the effect of inward rotation of a fluorine substituent in the ring opening of cyclobutene.

\[ \Delta H^\ddagger = 53.66 \pm 0.68 \text{kcal/mol} \]
\[ \Delta S^\ddagger = 3.30 \pm 1.00 \text{e.u.} \]

Figure 24: Rearrangement of 1,1-difluoro-3-(dideuteriomethylene)-cyclobutene

The E-1-fluoro-1,3-butadiene was equilibrated by the addition of a catalytic amount of iodine to an NMR tube
containing the diene, which was then sealed. On equilibration it was found that a new peak appeared in the $^{19}$F NMR spectrum at $\varphi = 126.4$, which was assigned to the Z-diene. Heating the tube above 70°C resulted in decomposition of the sample, so the equilibration was studied in the temperature range of 24-60°C.

Figure 25: Equilibration of 1-fluoro-1,3-butadiene.

Over the temperature range it is observed that there is almost no change in the equilibrium constants. The Z-diene is found to be favored at equilibrium by 0.35 kcal/mol. The $^1$H NMR of the equilibrium mixture shows a signal at $\delta = 7.15$ with coupling constants of 69.2 Hz and 6.3 Hz, corresponding to a geminal H-F coupling and a vicinal cis H-H coupling.
Table 20: Equilibration of 1-fluoro-1,3-butadiene.

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature (°C)</th>
<th>K(Z/E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Fluoro-1,3-butadiene</td>
<td>24.0</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>40.0</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>1.76</td>
</tr>
</tbody>
</table>

The synthesis of 3-trifluoromethylcyclobutene was slightly more involved. 3-Chlorocyclobutanecarboxylic acid was prepared according to a standard literature procedure. Treatment of the acid with sulfur tetrafluoride yielded 1-chloro-3-trifluoromethylcyclobutane in good yield, and it was hoped that elimination of HCl from the ring would afford the cyclobutene. It was found instead that the proton geminal to the trifluoromethyl group was eliminated to give 3-chloro(difluoromethylene)cyclobutane and decomposition products. Instead the halocyclobutane was reacted with magnesium to give the 3-trifluoromethylcyclobutyl Grignard. This material had a tendency to precipitate out of THF as an off-white paste if allowed to cool to room temperature, and so was added warm in solution to powdered
dry ice to give 3-trifluoromethylcyclobutanecarboxylic acid. Oxidative decarboxylation of the acid with lead tetraacetate gave the desired trifluoromethylcyclobutene, which was isolated by preparative GPLC using a 10' SE-30 column.

![Chemical Reaction Diagram]

Figure 26: Synthesis of 3-trifluoromethylcyclobutene.

The kinetics of ring opening of 3-trifluoromethyl-cyclobutene was studied using the same procedure as for 3-fluorocyclobutene. GPLC was incapable of separating the E and Z-5,5,5-trifluoro-1,3-pentadienes, but $^{19}$F NMR showed
that both isomers were present, and \textsuperscript{1}H NMR exhibited a doublet of quartets at $\delta = 6.74$ with coupling constants of 15.6 Hz and 6.6 Hz, corresponding to trans H-H and vicinal H-F couplings, respectively for the major isomer. On this basis the major product was assigned as the E-diene.

Table 21: Ring opening products of 3-trifluoromethyl-cyclobutene at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>E-diene</th>
<th>Z-diene</th>
</tr>
</thead>
<tbody>
<tr>
<td>128.1</td>
<td>98.0</td>
<td>2.0</td>
</tr>
<tr>
<td>150.3</td>
<td>97.9</td>
<td>2.1</td>
</tr>
<tr>
<td>162.7</td>
<td>98.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

In order to more accurately determine the product ratios, sealed NMR tubes containing 3-trifluoromethyl-cyclobutene in CDCl\textsubscript{3} with CFCl\textsubscript{3} as an internal standard were heated over the temperature range of the kinetics study and the products measured by their \textsuperscript{19}F NMR signals. There was no measurable decomposition of the starting material or products over the temperature range, and it was found that the relative amounts of the Z and E products changed very
little. The rate constants and activation parameters which were calculated should be most influenced by the reaction which leads to the E-diene, since reaction to the Z-diene proceeds only to a small extent over the time period when the reaction is studied.

Figure 27: Ring opening of 3-trifluoromethylcyclobutene.

Table 22: Rate constants and activation parameters for ring opening of 3-trifluoromethylcyclobutene.

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>(k X 10^{-5})/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>146.5</td>
<td>2.31 ± .01</td>
</tr>
<tr>
<td>154.7</td>
<td>4.83 ± .03</td>
</tr>
<tr>
<td>162.2</td>
<td>10.1 ± .1</td>
</tr>
<tr>
<td>169.8</td>
<td>22.2 ± .2</td>
</tr>
<tr>
<td>177.2</td>
<td>42.6 ± .2</td>
</tr>
<tr>
<td>186.3</td>
<td>96.2 ± .6</td>
</tr>
</tbody>
</table>

\[ E_{act} = 36.3 \pm .5 \text{ kcal/mol} \]
\[ \log A = 14.254 \pm .227 \]
\[ \Delta H^o = 35.5 \pm .5 \text{ kcal/mol} \]
\[ \Delta S^o = 3.94 \pm 1.03 \text{ e.u.} \]
\[ \Delta G^o = 33.7 \text{ kcal/mol} \]
3-Trifluoromethylcyclobutene is unique in comparison with 3-monosubstituted cyclobutenes which have been previously studied. It is the only known example where a single substituent on the 3-position of the ring raises the activation energy ($E_{act}$ for cyclobutene is 32.5 kcal/mol$^2$), and the only example where both product isomers are observed. It is believed that this unique behavior is the result of two characteristics of the trifluoromethyl substituent: its ability as a strong electron withdrawing group, and its large size. The work by Curry and Stevens$^3$ demonstrated that when there is a choice between two donor substituents for outward rotation, the strongest donor will rotate outward unless there are very large steric repulsions for the weaker donor, as in the case of 3-methyl-3-t-butylcyclobutene.$^3$ This argument could be extended to say that electron accepting substituents on the cyclobutene ring would prefer to rotate inward, by virtue of being weaker 'donors' than hydrogen. What is observed in the ring opening of 3-trifluoromethylcyclobutene is the result of two opposing effects. As an acceptor group, the trifluoromethyl
substituent would prefer inward rotation. However, a strong steric interaction with the inward rotating hydrogen at the 4-position destabilizes the transition state for inward rotation. This results in the system opening in the outward mode, which is electronically destabilized by 3.8 kcal relative to cyclobutene. The steric and electronic effects must be relatively close in energy however, because a small amount of the 3-trifluoromethylcyclobutene still rotates inward in the sterically destabilized, but electronically favored transition state.

Figure 28: Inward and outward rotation of 3-trifluoromethyl-cyclobutene.

The Z and E isomers of 5,5,5-trifluoro-1,3-pentadiene were equilibrated using the same procedure as for 1-fluoro-
1,3-butadiene. No decomposition of the two dienes was observed over the temperature range of the study, and it was possible to obtain standard parameters for the equilibrium. Analysis of the data gives a standard enthalpy of $2.49 \pm 0.41$ kcal/mol, and a standard entropy of $0.349 \pm 0.233$ entropy units.

Table 23: Equilibration of 5,5,5-trifluoromethyl-1,3-butadiene.

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature (°C)</th>
<th>K(Z/E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,5,5-Trifluoro-1,3-pentadiene</td>
<td>56.5</td>
<td>0.0230</td>
</tr>
<tr>
<td></td>
<td>88.5</td>
<td>0.0434</td>
</tr>
<tr>
<td></td>
<td>110.6</td>
<td>0.0495</td>
</tr>
<tr>
<td></td>
<td>151.0</td>
<td>0.0578</td>
</tr>
</tbody>
</table>

Though the synthesis of 3-fluoro-3-trifluoromethyl-cyclobutene could not be completed, the synthesis of the diene precursor proved to have wide applications. It was found that alcohols formed by the reaction of alkyl, vinyl and aryl aldehydes with trifluorovinyl lithium reacted with HF/THF to give 1,1,1,2-tetrafluoro,2-alkenes in good yields.
Figure 29: Synthesis of 1,1,1,2-tetrafluoro-2-alkenes.

Careful study of the reaction established that an HF/THF ratio of 5:1 gave the best results. The reaction was found to be stereospecific, giving 95-100% yields of the Z-product isomer depending on the aldehyde starting material. The reaction was also found to convert the alcohols formed from the reactions of acetone and acetophenone with trifluorovinyllithium into the corresponding 1,1,1,2-tetrafluoro-2-alkene, though the yield was somewhat lower and the stereospecificity of the reaction was lost in the case of acetophenone. This synthetic technique has advantages over the similar procedure using diethylamine sulfur trifluoride (DAST) published by Fujita and Hiyama.38
in that HF/THF is cheaper and safer on workup than DAST.

This synthetic method was published in 1987.39

Table 24: Reactions of HF/THF with 1,1,2-trifluoro-1-alken-3-ols.

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Product Yield(%)</th>
<th>Z/E ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>acrylaldehyde</td>
<td>72</td>
<td>95/5</td>
</tr>
<tr>
<td>propionaldehyde</td>
<td>68</td>
<td>100/0</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>72</td>
<td>100/0</td>
</tr>
<tr>
<td>acetone</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>acetophenone</td>
<td>58</td>
<td>50/50</td>
</tr>
</tbody>
</table>

Known literature procedures were used to prepare the cyclopropylidiazomethanes. The reaction of halodiiodomethanes with diethylzinc provides an excellent source of halocarbene.32 By reacting fluorodiiodomethane with diethylzinc in the presence of 1,3-butadiene, it was possible to trap the monofluoromethylene carbene to give 1-fluoro-2-vinylcyclopropane (Scheme I). Analytical GPLC showed three major peaks after distillation of the reaction mixture. The peaks were resolved and collected by preparative GPLC and identified by their \(^1\)H NMR spectra in
order as the two isomers of 1-fluoro-2-vinylcyclopropane and ethyl iodide.

In examining the $^{19}$F NMR spectra of the resolved isomers, it was found that the isomer which eluted first from the column had a chemical shift of $\delta = 205.59$ and coupling constants of $J = 64.1$ Hz, 22.0 Hz, 20.2 Hz, and 10.7 Hz, which are consistent with one geminal, two cis vicinal and one trans vicinal proton fluorine couplings on a cyclopropyl ring. The second isomer had an $^{19}$F chemical shift of $\delta = 223.08$ and coupling constants of $J = 64.8$ Hz, 22.5 Hz, 13.2 Hz and 12.7 Hz, which are consistent with one geminal, one cis vicinal and two trans vicinal proton fluorine couplings on a cyclopropane ring. Also, it is expected that an alkyl group cis to a fluorine on a cyclopropyl ring will shift the fluorine upfield in frequency. On these basis, the first isomer to elute was designated as trans-1-fluoro-2-vinylcyclopropane and the second isomer designated as cis-1-fluoro-2-vinylcyclopropane.
The cis- and trans-1-fluoro-2-vinylcyclopropanes were separately converted to the corresponding aldehydes by ozonolysis of the double bond using a literature procedure. GPLC conditions allowed purification of the aldehydes, but resulted in some loss due to decomposition on the column, particularly in the case of the trans-isomer. It was found that the aldehydes could be purified with less loss of material by passing the crude reaction mixture down a silica gel flash column using a 1:1 mixture of CH₂Cl₂/Et₂O as the eluant. The aldehydes were converted to the tosylhydrazones by acid catalyzed reaction with tosylhydrazine in MeOH/H₂O.

The cis-carboxaldehyde tosylhydrazone readily precipitated out of the reaction mixture and was obtained in 50-70% yield. The trans isomer was much more difficult to isolate from the reaction mixture. Dissolving the tosylhydrazones in very dry THF in a dry box and adding an excess of sodium hydride led to the formation of the sodium salts of the tosylhydrazones. Again in this case, the cis species precipitated out of solution and could be readily
isolated in near quantitative yield, while the trans species formed a suspension in THF which slowly decomposed. By removing the solvent after reaction with the sodium hydride had subsided it was possible to obtain the tosylhydrazone salt of the trans isomer.

Scheme I: Synthesis of 2-fluorocyclopropylcarboxaldehyde tosylhydrazone.

The sodium salts of the tosylhydrazones were decomposed in a modified sublimator that allowed the diazo compounds to condense on a cold finger cooled to $-78^\circ$C approximately 1 cm above the decomposition reaction. Slowly allowing the cold
finger to warm after all the salt had decomposed allowed the diazo compound to condense into a receiver cooled in liquid N₂. By allowing the diazo compounds to become just liquid it was possible to transfer them into NMR tubes for study.

Table 25: ¹⁹F chemical shifts of products of decomposition of cis- and trans-2-fluorocyclopropyldiazomethanes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>¹⁹F chemical shift (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-2-fluorocyclopropyl diazomethane (cis-19)</td>
<td>221.6</td>
</tr>
<tr>
<td>trans-2-fluorocyclopropyl diazomethane (trans-19)</td>
<td>203.4</td>
</tr>
<tr>
<td>3-fluorocyclobutene (20)</td>
<td>170.8</td>
</tr>
<tr>
<td>1-fluoro-1,3-butadiene (21) Z-isomer</td>
<td>126.4</td>
</tr>
<tr>
<td></td>
<td>127.5</td>
</tr>
</tbody>
</table>

Two tubes were prepared for each isomer. The ¹⁹F NMR spectrum of each tube was taken at -55°C, and all peaks integrated. For each isomer, one tube was then heated at 55°C for 30 minutes, and one tube was photolyzed using a Hanovia lamp at -40°C for 30 minutes. The ¹⁹F NMR spectra
and integrations of each tube was then retaken at -55°C and the t₀ integrals subtracted. Taking an NMR spectrum of each tube at room temperature showed little change in the peak distribution, indicating that all the products are stable specie. Several peaks in the region of \( \phi = 210 - 230 \) were found to be nonvolatile, and GC/MS confirmed that they were all products of intermolecular reaction.

The cis- and trans-1-trifluoromethyl-2-vinylcyclopropanes were prepared by the reaction of 1,1,1-trifluoro-2-diazoethane with butadiene (Scheme II). Analytical GPLC showed two major peaks in the material isolated after distillation, which could be separated by preparative scale GPLC. Analysis of the \(^1\)H and \(^{19}\)F NMR spectra of the two materials confirmed that they were the two isomers of 1-trifluoromethyl-2-vinylcyclopropane. Researchers who had reacted 1,1,1-trifluoro-2-diazoethane with propene to give 1-trifluoro-methyl-2-vinylcyclopropane were able to distinguish the two product isomers by fine splitting in the \(^{19}\)F NMR spectrum of the cis isomer. In the case of 1-trifluoromethyl-2-vinylcyclopropane both \(^{19}\)F spectra showed
simple doublets without any noticeable fine splitting. Careful analysis of the $^1$H NMR spectra showed that the isomer which eluted from the column first had coupling constants of 8.8 Hz and 5.9 Hz for the multiplet at 0.86 ppm, and 9.1 Hz and 5.5 Hz for the multiplet at 1.14 ppm. The second isomer appears to have a quartet with a coupling constant of 6.1 Hz for the multiplet at 1.02 ppm, and coupling constants of 8.5 Hz and 7.1 Hz for the multiplet at 1.16 ppm. It is expected that cis H-H coupling on a cyclopropane ring will always be larger than trans coupling on the ring.42 It is also likely that the pair of multiplets in each isomer's spectrum can be assigned to the geminal CH$_2$ protons on the cyclopropane ring, since these proton should be the furthest upfield. This being the case, the first isomer would appear to have a cis and a trans H-H coupling for each of the geminal protons, consistent with the trans isomer. The quartet at 1.02 ppm in the second eluting isomer could be the result of couplings of nearly equal intensity to three protons. One of these would be the geminal proton, but for the other two coupling to be nearly
equal they must be both cis or both trans. Since the other
geminal proton had larger coupling constants, the value of
6.1 Hz must be a trans coupling.

The two isomers were separately converted to the
aldehydes in a manner identical to the procedure used for
the conversion of cis- and trans-1-fluoro-2-
vinylcyclopropanes. Purification of the aldehydes was
accomplished by preparative GPLC using a 10’ OV-210 column
($T_c = 40^\circ$C, flow = 40 ml/min). The tosylhydrazones were
prepared as above, both cis- and trans-2-trifluoromethyl-
cyclopropylcarboxaldehyde tosylhydrazones being obtained in
fair to good yields. On reaction with sodium hydride the
two isomers acted much as the fluorocyclopropyl specie did,
with the cis tosylhydrazone salt readily precipitating from
the solvent while the trans remained suspended in solution.
The decomposition of the salts of the two tosylhydrazones
and the preparation of the samples for NMR study were
identical to the procedure used for the fluorocyclopropyl
compounds. cis-2-Trifluoromethylcyclopropylidiazomethane
proved to be quite stable, decomposing over the period of an
hour at room temperature. An FTIR spectrum of the compound showed a strong band at 2100 cm\(^{-1}\) which decreased in intensity over time, indicating the presence of a diazo group.

\[
\begin{align*}
\text{CF}_3\text{CHN}_2 + & \xrightarrow{\Delta} \text{CHO} + \text{CF}_3 \\
\text{CHO} + \text{TsNHNH}_2 & \xrightarrow{\text{H}^+} \text{MeOH/H}_2\text{O} \rightarrow \text{CHNNHTs}
\end{align*}
\]

Scheme II: Synthesis of 2-trifluoromethylcyclopropylcarboxaldehyde tosylhydrazone.

The decomposition of the cyclopropyldiazomethanes in the sealed NMR tubes was accomplished in a similar manner to that used for the fluorocyclopropyldiazomethanes. One tube for each isomer was heated at 70°C for 30 minutes, and one tube irradiated at a temperature of -40°C using a Hanovia
lamp. Taking a spectrum of the tube after reaction at -55°C and at room temperature showed little change in the $^{19}$F spectra, indicating that all products were stable. Materials having chemical shifts in the range of $\phi = 60 - 62$ were nonvolatile and determined to be the products of intermolecular reaction by GC/MS.

<table>
<thead>
<tr>
<th>Table 26: $^{19}$F chemical shifts of products of cis- and trans-2-trifluoromethylcyclopropyl diazomethane.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>cis-2-trifluoromethylcyclopropyl diazomethane (cis-23)</td>
</tr>
<tr>
<td>trans-2-trifluoromethylcyclopropyl diazomethane (trans-23)</td>
</tr>
<tr>
<td>3-trifluoromethylcyclobutene (24)</td>
</tr>
<tr>
<td>5,5,5-trifluoro-1,3-pentadiene (25)</td>
</tr>
<tr>
<td>Z-isomer</td>
</tr>
<tr>
<td>E-isomer</td>
</tr>
</tbody>
</table>

The results of the decompositions of the cyclopropyl diazomethanes are as follows: cis-2-fluorocyclopropyl diazomethane (cis-19) gives a very low
yield of intramolecular reaction in the thermal reaction. This is due to the appearance of a peak in the $^{19}$F NMR spectrum at $\phi = 114.7$ ppm. This material was observed on repeated runs under identical conditions and its $^{19}$F chemical shift was inconsistent with the possible products of intramolecular reaction. It proved to be less volatile than the isolated products, but did not appear to possess a fluorine on a cyclopropane ring, excluding it from being the product of a simple coupling reaction.

![Diagram of Decomposition of Cyclopropyldiazomethanes](image)

Figure 30: Decomposition of cyclopropyldiazomethanes.

For the products of intramolecular reaction, fragmentation to give vinyl fluoride (22) appears to
predominate to a small degree. There is a small amount of fragmentation of 3-fluorocyclobutene (20) to give 1-fluoro-1,3-butadiene (21) in a Z/E ratio of 0.11. Photolysis of cis-2-fluorocyclopropylidiazomethane gives vinyl fluoride as the major product, and no fluorocyclobutene is observed.

Table 27: Results of pyrolyses of 2-trifluoromethyl- and 2-fluorocyclopropylcarboxaldehyde tosylhydrazone salts.

<table>
<thead>
<tr>
<th>Diazo compound</th>
<th>Cond</th>
<th>Yield(%)</th>
<th>20</th>
<th>22</th>
<th>21(Z/E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-19</td>
<td>55°, 30 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>hv, -40°, 30 min</td>
<td></td>
<td></td>
<td></td>
<td>9.3(0)</td>
</tr>
<tr>
<td>trans-19</td>
<td>55°, 30 min</td>
<td></td>
<td></td>
<td></td>
<td>35(0)</td>
</tr>
<tr>
<td></td>
<td>hv, -40°, 30 min</td>
<td></td>
<td></td>
<td></td>
<td>9.8(1.5)</td>
</tr>
<tr>
<td>cis-23</td>
<td>70°, 30 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>hv, -40°, 30 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-23</td>
<td>70°, 30 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>hv, -40°, 30 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The reactions of trans-2-fluorocyclopropyldiazomethane (trans-19) give much higher yields of intramolecular reaction products. The thermal reaction gives less vinyl fluoride than 3-fluorocyclobutene, but more 1-fluoro-1,3-butadiene is observed than in the reaction of the cis-isomer. In photolysis the yield of intramolecular reaction was almost quantitative. The amount of vinyl fluoride from fragmentation has increased, but is still less than the products from ring expansion.

For cis-2-trifluoromethylcyclopropyldiazomethane (cis-23) the yield of intramolecular products is much lower than for the fluorocyclopropyl systems. Thermal decomposition gives 3-trifluoromethylcyclobutene (24) from ring expansion, with 3,3,3-trifluoropropene (26) from fragmentation also present. No 5,5,5-trifluoro-1,3-pentadiene (21) from ring opening of the cyclobutene was observed. Photolysis gave a slightly increased yield of intramolecular reaction and a larger amount of fragmentation product, though the cyclobutene still dominates the reaction and no products from ring opening are observed.
Finally, for trans-2-trifluoromethylcyclopropyldiazo-
methane (trans-23) there is a greater amount of intramole-
cular reaction compared to the cis isomer. Thermal
decomposition gives nearly the same amount of ring expansion
and fragmentation products as the cis isomer, with no ring
opening products being observed. Photolysis gives a slight
increase in trifluoropropene, as in the case of the cis
isomer, while there is still no ring opening products.

In considering each of the cyclopropyldiazomethanes
separately, two trends are noticed: that the photochemical
reaction leads to a higher amount of intramolecular
reaction, and to a higher amount of fragmentation products.
This is consistent with the observation that fragmentation
is a higher energy process for the carbene than ring
expansion.\textsuperscript{29,30} Intermolecular reaction for the carbene most
likely consists of attack by the carbene on an undecomposed
molecule of the cyclopropyldiazomethane to give a 1,2-
dicycloprenylethylene. In order for this to occur, the
carbene must have a relatively long lifetime, and should
thus be fairly low in energy. A cyclopropyldiazomethane
that has been photolytically decomposed should generate a
higher energy carbene than one that has been thermally
decomposed, and so should lead to less intermolecular
reaction. In the same vein, the higher energy carbene
should react intramolecularly along a higher energy pathway,
and so should exhibit more fragmentation.

\[
\begin{array}{ccc}
\text{X} & + & \text{X} \\
\text{H} & \text{CHN}_2 & \rightarrow \text{N}_2 \\
\end{array}
\]

Figure 31: Intermolecular reaction of cyclopropylcarbene.

The two most obvious differences in between the 2-
fluorocyclopropyldiazomethanes and the 2-trifluoromethyl-
diazomethanes are the amount of intermolecular versus
intramolecular reaction and the amount of ring expansion
versus fragmentation. Fluorine is commonly acknowledged to
be a donor substituent, contributing electron density
through its p-atomic orbitals.\textsuperscript{11} It is possible that
fluorine could be interacting with the unoccupied Walsh orbital of the ring, donating electron density to render the ring more nucleophilic. At the same time the fluorine substituent in cis-2-fluorocyclopropyldiazomethane could be generating an unfavorable electrostatic repulsion with the diazo substituent. If this is the case, the conformation of the cis-diazo compound with the diazo group rotated away from the ring would be preferred, leading to the anti conformer of the carbene. Shevlin’s theoretical work has indicated that fragmentation is the preferred pathway for this conformation.35 This is consistent with the observation that the cis-isomer gives more fragmentation than the trans-isomer.

Figure 32: Conformers of cis-2-fluorocyclopropyldiazomethane.
In the cis- and trans-2-trifluoromethylcyclopropyl-

diazomethanes the trifluoromethyl group increases the amount
of intermolecular reaction and decreases the amount of
fragmentation. The trifluoromethyl substituent is
inductively electron withdrawing, and should reduce the
nucleophilicity of the cyclopropyl bonds. The substituent
is also large ($E_s = -2.4$, compared with $E_s = -2.7$ for t-
butyl) and should have both a large steric effect and a
large electrostatic repulsion to the diazo substituent.
However, the trifluoromethyl group also provides more means
for the carbene to lose energy through rotational and
vibrational modes. This would especially inhibit the higher
energy pathway of fragmentation, as is observed, but would
also allow the carbene to survive long enough to undergo
intermolecular reaction with cyclopropyldiazomethane.
Though intramolecular reaction is inhibited in both the cis-
and the trans-2-trifluoromethylcyclopropyldiazomethanes due
to deactivation of the ring to electrophilic attack by the
carbene carbon, the cis-isomer is further deactivated by
unfavorable steric and electrostatic interactions between
the trifluoromethyl group and the diazo substituent, as is
the case in cis-2-fluoro-cyclopropyldiazomethane. In the
case of the trifluoromethyl system however, fragmentation is
inhibited by loss of energy in the carbene, allowing
intermolecular reactions to occur. The fragmentation
pathway for the trans isomer is also inhibited, but ring
expansion, a lower energy process, is less affected by the
trifluoromethyl group.

\[
\begin{align*}
\text{F} & \quad \text{H} \\
\text{\textbullet} & \quad \text{\textbullet} \\
\text{C} & \quad \text{\textbullet} \\
\end{align*}
\xrightarrow{\text{F}}
\begin{align*}
\text{F} & \quad \text{H} \\
\text{\textbullet} & \quad \text{\textbullet} \\
\text{C} & \quad \text{\textbullet} \\
\end{align*}
\xrightarrow{\text{F}}
\begin{align*}
\text{\textbullet} & \quad \text{\textbullet} \\
\text{\textbullet} & \quad \text{\textbullet} \\
\text{\textbullet} & \quad \text{\textbullet} \\
\end{align*}
\]

Figure 33: Formation of Z-1-fluoro-1,3-butadiene.

The energy of activation for the ring opening of 3-
trifluoromethylcyclobutene (24) is 36.5 kcal/mol, the
highest value observed for a single substituent at the three
position of a cyclobutene ring. This and the decreased
energy of the carbene render it unlikely that 3-trifluoro-
methylcyclobutene generated from the carbene will have enough residual energy to ring open, as is observed. 3-
Fluorocyclobutene (20) has an activation energy for ring opening of 28.1 kcal/mol, and some ring opening products are observed in the 2-fluorocyclopropyl-diazomethane decomposition. There is a surprisingly large amount of the Z-1-fluoro-1,3-butadiene observed in these reactions. It would be difficult to reconcile the Z-diene arising from the cyclobutene with theoretical studies indicating that inward rotation of the fluorine on ring opening of 3-fluorocyclobutene is expected to be about 20 kcal/mol higher in energy than outward rotation.\(^5\) It is more likely that the Z-diene arises from a side reaction of the carbene. One possibility is cleavage of the ring to give the singlet biradical, which could undergo rotation about the C-C bond bearing the fluorine substituent. A 1,3 shift of a hydrogen could generate a mixture of the Z- and E-dienes. It has been found that on equilibration of E- and Z-1-fluoro-1,3-butadiene that the Z-diene predominates.
In conclusion, it has been found that 3-fluorocyclobutene stereospecifically ring opens to give E-1-fluoro-1,3-butadiene, in accordance with theoretical predictions. Calculations of the activation parameters give an energy of activation of 28.1 kcal/mol, indicating that the fluorine substituent stabilizes the cyclobutenyl transition state. Though none of the Z diene was observed, comparing the activation enthalpy of the system with the activation enthalpy for ring opening of 3,3-difluorocyclobutene indicates that inward rotation of the fluorine group raises the energy of the transition state by over 15 kcal/mol. Equilibration of the product shows that the Z diene is energetically preferred over the E-diene. The ring opening of 3-trifluoromethylcyclobutene proceeds to give both E- and Z-5,5,5-trifluoro-1,3-pentadiene, with the E isomer as the major product. The trifluoromethyl substituent raises the energy of the transition state relative to cyclobutene, a unique case for monosubstituted cyclobutenes. The results can be explained as a competition between electronic destabilization of the transition state
on outward rotation and steric destabilization on inward rotation. Equilibration of the product allowed the calculation of the standard enthalpy and entropy for the system. 3-Fluoro-3-trifluoromethylcyclobutene was not synthesized, but the attempted synthesis yielded a new and versatile synthetic methodology for the preparation of partially fluorinated alkenes.

It has also been found that fluorine and trifluoromethyl have differing effects on the decomposition of cyclopropyldiazomethane. Fluorine appears to increase the electron density of the cyclopropyl ring, making it more susceptible to electrophilic attack by the carbene carbon. At the same time fluorine cis to the diazo group causes outward rotation of the diazo group due to electrostatic repulsions. This results in the generation of the anti conformer of the carbene, which leads to a greater degree of fragmentation. The trifluoromethyl substituent appears to decrease the electron density of the ring, making it less susceptible to attack by the carbene, and a trifluoromethyl group cis to the diazo group in the parent molecule further
inhibits attack on the ring. However, the additional modes of energy loss available to the carbene through the trifluoromethyl group inhibit the high energy pathway of fragmentation. The carbene is kinetically stabilized to a degree sufficient to undergo an increased amount of intermolecular reaction.
APPENDIX

NMR Spectra
Spectrum 2: $^1$H NMR of diethyl 3-fluorocyclobutanedicarboxylate.
Spectrum 3: $^1$H NMR of 3-fluorocyclobutanedicarboxylic acid.
Spectrum 4: $^1H$ NMR of 3-fluorocyclobutanecarboxylic acid (cis and trans).
Spectrum 5: $^{13}$C NMR of 3-fluorocyclobutanecarboxylic acid (cis and trans).
Spectrum 6: $^1$H NMR of 3-fluorocyclobutene.
Spectrum 7: 13C NMR of 3-fluorocyclobutene.
Spectrum 8: $^1$H NMR of 1-chloro-3,3-trifluoromethylcyclobutane.
Spectrum 9: $^1$H NMR of 3-trifluoromethylcyclobutanecarboxylic acid.
Spectrum 10: H NMR of 3-trifluoromethylcyclobutene.
Spectrum 11: $^{13}$C NMR of 3-trifluoromethylcyclobutene.
Spectrum 12: $^{13}\text{C}$ NMR of 3-trifluoromethylcyclobutene (INEPT pulse sequence).
Spectrum 13: $^1$H NMR of E-1-fluoro-1,3-butadiene.
Spectrum 14: $^{19}\text{F}$ NMR of E-1-fluoro-1,3-butadiene ($\text{C}_6\text{F}_6$ used as an internal standard).
Spectrum 15: $^{19}$F NMR of equilibration of E- and Z-1-fluoro-1,3-butadienes.
Spectrum 16: H NMR of E-5,5,5-trifluoro-1,3-pentadiene.
Spectrum 17: $^{19}$F NMR of Z- and E-5,5,5-trifluoro-1,3-pentadiene.
NMR of cis-1-fluoro-2-vinylcyclopropane.

Spectrum 18: $^1\text{H}$ NMR of cis-1-fluoro-2-vinylcyclopropane.
Spectrum 19: $^{19}$F NMR of cis-1-fluoro-2-vinylcyclopropane.
Spectrum 20: $^1$H NMR of trans-1-fluoro-2-vinylcyclopropane.
Spectrum 22: $^1$H NMR of cis-2-fluorocyclopropylcarboxaldehyde.
Spectrum 23: $^1\text{H}$ NMR of trans-2-fluorocyclopropylcarboxaldehyde.
Spectrum 24: $^1$H NMR of cis-1-trifluoromethyl-2-vinylcyclopropane.
Spectrum 25: $^1$H NMR of trans-1-trifluoromethyl-2-vinylcyclopropane.
Spectrum 26: $^1$H NMR of cis-2-trifluoromethylcyclopropylcarboxaldehyde.
Spectrum 27: $^1$H NMR of trans-2-trifluoromethylcyclopropylcarboxaldehyde.
REFERENCES


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Thomas Anthony Gray was born in Coral Gables, Florida, on October 15, 1961. He has one brother who is two years older. His family had to move from Leisure City in South Florida to Key Largo when a hurricane destroyed their house. Tom attended school in Key Largo and Islamorada, and helped his father, a commercial fisherman. He received a scholarship to Emory University in Atlanta and obtained a Bachelor of Science in chemistry and a Master of Science in organic chemistry while there. He came to the University of Florida in 1983.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

William R. Dolbier, Jr., Chair
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

William M. Jones
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

Merle A. Battiste
Professor of Chemistry
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

John G. Dorsey
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

Hendrik J. Monkhorst
Professor of Physics

This thesis was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1989

Dean, Graduate School