INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing, or chart, etc., was part of the material being photographed the photographer followed a definite method in “sectioning” the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a slight overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from “photographs” if essential to the understanding of the dissertation. Silver prints of “photographs” may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms
300 North Zeck Road
Ann Arbor, Michigan 48106
MERRILL, Dwight Edward, 1945-
A STUDY OF THE CYCLOPROPYLCARBINYL CATION
BEARING ELECTRON WITHDRAWING SUBSTITUENTS ON
THE CYCLOPROPANE RING.

The Ohio State University, Ph.D., 1975
Chemistry, organic

Xerox University Microfilms, Ann Arbor, Michigan 48106

© 1975

Dwight Edward Merrill

All Rights Reserved

This dissertation has been microfilmed exactly as received.
A STUDY OF THE CYCLOPROPYLCARBINYL CATION BEARING ELECTRON WITHDRAWING SUBSTITUENTS ON THE CYCLOPROPANE RING

Dissertation

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Dwight Merrill, B.A.

The Ohio State University

1975

Reading Committee:

Dr. Derek Horton
Dr. Melvin S. Newman
Dr. Harold Shechter

Approved by

Dr. Harold Shechter
Adviser
Department of Chemistry
ACKNOWLEDGMENTS

The author wishes to extend his appreciation to his preceptor, Dr. Harold Shechter. Financial support from both The Ohio State University and The National Science Foundation is also gratefully acknowledged.
VITA

January 14, 1945 ....................... Born - Berkeley, California

1966 ........................................ B.A., University of California, 
                                           Berkeley, California

1968-1970 ................................. Teaching Assistant, Department of 
                                           Chemistry, The Ohio State Uni- 
                                           versity, Columbus, Ohio

1970-1973 ................................. Research Associate, Department of 
                                           Chemistry, The Ohio State Uni- 
                                           versity, Columbus, Ohio
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>ii</td>
</tr>
<tr>
<td>VITA</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>HISTORICAL</td>
<td>6</td>
</tr>
<tr>
<td>I. Introduction</td>
<td>7</td>
</tr>
<tr>
<td>II. Reviews</td>
<td>14</td>
</tr>
<tr>
<td>III. Reactions of the Cyclopropylcarbinyl Cation</td>
<td>15</td>
</tr>
<tr>
<td>A. Ring Expansion; Effect of Substituent Groups on Ring Expansion</td>
<td>15</td>
</tr>
<tr>
<td>B. Ring Opening</td>
<td>19</td>
</tr>
<tr>
<td>1. Effect of Substituents</td>
<td>19</td>
</tr>
<tr>
<td>2. Mechanism</td>
<td>21</td>
</tr>
<tr>
<td>3. Stereochemistry</td>
<td>24</td>
</tr>
<tr>
<td>C. Degenerate Rearrangements and Stereochemistry Thereof</td>
<td>27</td>
</tr>
<tr>
<td>IV. Nmr Studies of Cyclopropylcarbinyl Cations</td>
<td>31</td>
</tr>
<tr>
<td>V. Solvolysis Rate Studies</td>
<td>32</td>
</tr>
<tr>
<td>VI. Implications of Theoretical Calculations</td>
<td>42</td>
</tr>
<tr>
<td>VII. Structures Proposed for the Cyclopropylcarbinyl Cation</td>
<td>45</td>
</tr>
<tr>
<td>VIII. Previous Investigation of the 2,2-Dichlorocyclopropyl carbinyl Cation</td>
<td>54</td>
</tr>
</tbody>
</table>
# RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Product Studies</td>
<td>56</td>
</tr>
<tr>
<td>A. 2,2-Dichlorocyclopropylcarbinyl Systems</td>
<td>56</td>
</tr>
<tr>
<td>1. Introduction and Survey of Solvent and Leaving Group Effects</td>
<td>56</td>
</tr>
<tr>
<td>2. Acetolysis</td>
<td>56</td>
</tr>
<tr>
<td>3. Silver Ion Assisted Acetolysis</td>
<td>63</td>
</tr>
<tr>
<td>4. Deuterium Labeled Probe for Degenerate Rearrangement</td>
<td>70</td>
</tr>
<tr>
<td>5. Deamination</td>
<td>74</td>
</tr>
<tr>
<td>6. Friedel-Crafts Reactions</td>
<td>79</td>
</tr>
<tr>
<td>a. Antimony Pentachloride in Benzene</td>
<td>79</td>
</tr>
<tr>
<td>b. Aluminum Chloride in Benzene</td>
<td>92</td>
</tr>
<tr>
<td>c. Aluminum Chloride in Nitromethane</td>
<td>98</td>
</tr>
<tr>
<td>7. Summary</td>
<td>102</td>
</tr>
<tr>
<td>B. Monobromo Substrates</td>
<td>102</td>
</tr>
<tr>
<td>II. Kinetics</td>
<td>118</td>
</tr>
<tr>
<td>A. Introduction</td>
<td>118</td>
</tr>
<tr>
<td>B. Results</td>
<td>118</td>
</tr>
<tr>
<td>C. Discussion</td>
<td>120</td>
</tr>
<tr>
<td>III. Acid Dissociation Constants Determination</td>
<td>136</td>
</tr>
<tr>
<td>A. Introduction</td>
<td>136</td>
</tr>
<tr>
<td>B. Results</td>
<td>137</td>
</tr>
<tr>
<td>C. Discussion</td>
<td>139</td>
</tr>
</tbody>
</table>

## EXPERIMENTAL

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>General Information--Product Studies</td>
<td>144</td>
</tr>
<tr>
<td>Preparation of Methyl 2,2-Dichlorocyclopropanecarboxylate</td>
<td>146</td>
</tr>
<tr>
<td>2,2-Dichlorocyclopropylmethanol-(\text{\textalpha,\textalpha-d}_2)</td>
<td>147</td>
</tr>
<tr>
<td>2,2-Dichlorocyclopropylmethyl-(\text{\textalpha,\textalpha-d}_2) p-Toluenesulfonate</td>
<td>148</td>
</tr>
<tr>
<td>Topic</td>
<td>Page</td>
</tr>
<tr>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Acetolysis of 2,2-Dichlorocyclopropylmethyl-α,α-d₂ p-Toluenesulfonate</td>
<td>148</td>
</tr>
<tr>
<td>2,2-Dichlorocyclopropylmethyl-α,α-d₂ Bromide</td>
<td>149</td>
</tr>
<tr>
<td>Silver Ion Assisted Acetolysis of 2,2-Dichlorocyclopropylmethyl-α,α-d₂ Bromide</td>
<td>149</td>
</tr>
<tr>
<td>Preparation of 2,2-Dichlorocyclopropylmethyl Bromide via Phenyl(trichloromethyl)mercury</td>
<td>150</td>
</tr>
<tr>
<td>Preparation of 2,2-Dichlorocyclopropylmethylamine</td>
<td>150</td>
</tr>
<tr>
<td>Deamination of 2,2-Dichlorocyclopropylmethylamine</td>
<td>151</td>
</tr>
<tr>
<td>2,2-Dichlorocyclopropylmethanol via Acid Catalyzed Transesterification of 2,2-Dichlorocyclopropylmethyl Acetate</td>
<td>152</td>
</tr>
<tr>
<td>Phase Transfer Reactions: General Procedures</td>
<td>153</td>
</tr>
<tr>
<td>1. 2,2-Dichlorocyclopropylmethyl Bromide</td>
<td>155</td>
</tr>
<tr>
<td>2. 2,2-Dichlorocyclopropylmethyl Acetate</td>
<td>156</td>
</tr>
<tr>
<td>3. 2,2-Dichloro-1-methylcyclopropylmethyl Acetate</td>
<td>157</td>
</tr>
<tr>
<td>4. 2,2-Dichloro-1-methylcyclopropylmethyl Chloride</td>
<td>157</td>
</tr>
<tr>
<td>5. 1,2,2-Trichlorocyclopropylmethyl Chloride</td>
<td>158</td>
</tr>
<tr>
<td>6. 2,2-Dichlorocyclopropylmethyl Chloride</td>
<td>159</td>
</tr>
<tr>
<td>7. 2,2-Dichloro-3-phenylcyclopropylmethyl Chloride</td>
<td>159</td>
</tr>
<tr>
<td>8. 2,7,7-Trichlorobicyclo[4.1.0]heptane</td>
<td>160</td>
</tr>
<tr>
<td>9. Attempted Reaction of Acrylonitrile with Dichlorocarbene</td>
<td>160</td>
</tr>
<tr>
<td>10. Reaction of Cyclopentadiene with Dichlorocarbene</td>
<td>161</td>
</tr>
<tr>
<td>11. Preparation of 2,2-Dichloro-1-vinylcyclopropane</td>
<td>161</td>
</tr>
<tr>
<td>12. Preparation of 2,2-Dichlorocyclopropane-carboxylic acid</td>
<td>163</td>
</tr>
</tbody>
</table>
3. With 1-Chloro-1-(2,2-dichlorocyclopropyl)ethane .... 176

Friedel-Crafts Reactions of Cyclopropylcarbiny1 Halides with Aluminum Chloride in Benzene: General Procedure .... 177

1. With 2,2-Dichlorocyclopropylmethyl Bromide .......... 178
2. With 2,2-Dichloro-1-methylcyclopropylmethyl Chloride ......................................................... 179
3. With 1,1-Dichloro-3-phenyl-1-butene ................. 180

Friedel-Crafts Reactions of 2,2-Dichlorocyclopropylmethyl Halides with Aluminum Chloride in Nitromethane:
General Procedure ......................................................... 181
1,1,4-Trichloro-1-butene ........................................ 181
Preparation of Diethyl 1,1-Cyclopropanedicarboxylate .... 182
Preparation of Ethyl Hydrogen 1,1-Cyclopropanedicar-
boxylate ............................................................................. 183
Ethyl 1-Bromocyclopropanecarboxylate ...................... 183
1-Bromocyclopropanecarboxylic Acid ......................... 184
1-Bromocyclopropylmethanol via Reduction ..................... 185
1-Bromocyclopropylmethyl Acetate ......................... 186
Preparation of 1-Bromocyclopropylmethyl p-Toluenesulfonate .. 186
Solvolysis of 1-Bromocyclopropylmethyl p-Toluenesulfonate .. 187
Preparation of 3-Bromo-3-buten-1-yl Acetate .............. 188
Isolation of Standard trans-4-Bromo-3-buten-1-yl Acetate .... 189
Isolation of Standard cis-4-Bromo-3-buten-1-yl Acetate ...... 189
trans-2-Bromocyclopropylmethanol .............................. 190
trans-2-Bromocyclopropylmethyl Acetate ..................... 191
trans-2-Bromocyclopropylmethyl p-Toluenesulfonate .. 191
<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvolysis of trans-2-Bromocyclopropylmethyl p-Toluene-sulfonate</td>
<td>192</td>
</tr>
<tr>
<td>cis-2-Bromocyclopropylmethanol</td>
<td>193</td>
</tr>
<tr>
<td>cis-2-Bromocyclopropylmethyl Acetate</td>
<td>193</td>
</tr>
<tr>
<td>cis-2-Bromocyclopropylmethyl p-Toluenesulfonate</td>
<td>193</td>
</tr>
<tr>
<td>Solvolysis of cis-2-Bromocyclopropylmethyl p-Toluenesulfonate</td>
<td>194</td>
</tr>
<tr>
<td>Preparation of trans-2-Bromocyclopropanecarboxylic Acid</td>
<td>194</td>
</tr>
<tr>
<td>Preparation of cis-2-Bromocyclopropanecarboxylic Acid</td>
<td>195</td>
</tr>
<tr>
<td>KINETICS</td>
<td>196</td>
</tr>
<tr>
<td>Materials</td>
<td>196</td>
</tr>
<tr>
<td>Sealed Tube Techniques</td>
<td>197</td>
</tr>
<tr>
<td>Titrations</td>
<td>198</td>
</tr>
<tr>
<td>pKa DETERMINATIONS</td>
<td>201</td>
</tr>
<tr>
<td>Materials</td>
<td>201</td>
</tr>
<tr>
<td>Preparation of 1-Methylcyclopropanecarboxylic Acid</td>
<td>202</td>
</tr>
<tr>
<td>trans-2-Methylcyclopropanecarboxylic Acid via a Simmons-Smith Reaction</td>
<td>202</td>
</tr>
<tr>
<td>Equipment</td>
<td>204</td>
</tr>
<tr>
<td>Procedure</td>
<td>204</td>
</tr>
<tr>
<td>Calculations</td>
<td>205</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>210</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Taft's Substituent Parameters</td>
<td>39</td>
</tr>
<tr>
<td>2</td>
<td>Solvolysis Rates of Substituted Cyclopropylcarbinyl Chlorides (50% Aqueous Ethanol, 100°)</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>Reaction of SbCl₅ in Benzene with 2,2-Dichlorocyclopropylmethyl Chlorides</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>Summary of the Fate of Several Substituted 2,2-Dichlorocyclopropylmethyl Cations Generated Under Various Conditions</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>Acetolysis of 1-Bromocyclopropyl p-Toluene sulfonate</td>
<td>106</td>
</tr>
<tr>
<td>6</td>
<td>First-order Rate Constants for Solvolysis of Halo Substituted Cyclopropylmethyl p-Toluene sulfonates (80% Aqueous Ethanol, 80°)</td>
<td>119</td>
</tr>
<tr>
<td>7</td>
<td>Relative First-order Rate Constants for Solvolysis of Methyl Substituted Cyclopropylmethyl 3,5-Dinitrobenzoates in 60% Aqueous Acetone at 100°</td>
<td>122</td>
</tr>
<tr>
<td>8</td>
<td>Relative First-order Rate Constants for Solvolysis of Phenyl Substituted Cyclopropylmethyl β-Naphthalene-sulfonates in 90% Aqueous Dioxane at 25°</td>
<td>122</td>
</tr>
<tr>
<td>9</td>
<td>pKa's of Various Cyclopropanecarboxylic Acids in Water at 35°</td>
<td>138</td>
</tr>
<tr>
<td>10</td>
<td>Typical Titration Data, 1-Bromocyclopropylmethyl p-Toluene sulfonate (80% Aqueous Ethanol, 70°)</td>
<td>200</td>
</tr>
<tr>
<td>11</td>
<td>Typical Titration Data, Titration of 1-Bromocyclopropanecarboxylic Acid</td>
<td>206</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Scheme 1</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>Scheme 2</td>
<td>105</td>
</tr>
<tr>
<td>3</td>
<td>Scheme 3</td>
<td>107</td>
</tr>
<tr>
<td>4</td>
<td>Scheme 4</td>
<td>112</td>
</tr>
<tr>
<td>5</td>
<td>Suggested Transition State for Solvolysis of Mono-bromocyclopropylcarbinyl p-Toluenesulfonates</td>
<td>124</td>
</tr>
<tr>
<td>6</td>
<td>Conformers in Displacement of Optically Active Cyclopropylcarbinyl Methanesulfonates</td>
<td>125</td>
</tr>
<tr>
<td>7</td>
<td>Scheme 5</td>
<td>128</td>
</tr>
<tr>
<td>8</td>
<td>Plot of pH vs Added Sodium Hydroxide, 1-Bromocyclopropanecarboxylic Acid</td>
<td>132</td>
</tr>
</tbody>
</table>
INTRODUCTION AND STATEMENT OF PROBLEM.

Solvolyis of most cyclopropylcarbinyl derivatives proceeds unusually rapidly and yields rearranged products; "non classical" carbonium ions have been suggested as intermediates in these reactions \(^1\) (Eq 1). Cyclopropylcarbinyl cations have been studied intensively over the last 25 years. By contrast, the cyclopropylcarbinyl cation bearing electron withdrawing substituents on the cyclopropane ring has received almost no attention.

Acetolyses of 2,2-dichlorocyclopropylmethyl bromide and of 2,2-dichlorocyclopropylmethyl p-toluenesulfonate yield only unrearranged products. \(^2\) Ethanolyses of 2,2-dichlorocyclopropylmethyl chloride and

---

(1) (a) J. D. Roberts and R. H. Mazur, J. Amer. Chem. Soc., 73, 2509 (1951); (b) Idem., ibid., 72, 3542 (1951).
of the 1- and 3-methyl homologs proceed at unusually low rates and give only unrearranged products. These observations contrast strongly with the behavior of the parent cyclopropylcarbinyl analogy and the alkyl, aryl, and fused-ring homologs thereof.

(2) C. Houser, Ph.D. Thesis, The Ohio State University, 1968.

The solvolytic behavior of 2,2-dichlorocyclopropylmethyl compounds warrants further investigation. A primary objective of this research was to study the 2,2-dichlorocyclopropylcarbinyl cation. In order to confirm and generalize the observation that rearrangement did not occur, a series of 2,2-dihalocyclopropylcarbinyl substrates were prepared and solvolyzed. Thus 2,2-dichlorocyclopropylmethyl bromide, 2,2-dichlorocyclopropylmethyl chloride, 2,2-dichlorocyclopropylmethyl p-toluenesulfonate, 2,2-dibromocyclopropylmethyl p-toluenesulfonate, 2,2-dichloro-1-methylcyclopropylmethyl chloride, 2,2-dichloro-3-phenylcyclopropylmethyl chloride, 1-chloro-1-(2,2-dichlorocyclopropyl)ethane, and 2,7,7-trichlorobicyclo[4.1.0]heptane were solvolyzed in buffered acetic acid.

Subsequently, silver ion assisted solvolyzes of 2,2-dichlorocyclopropylmethyl bromide, 2,2-dichlorocyclopropylmethyl chloride, 2,2-dichloro-1-methylcyclopropylmethyl chloride, 2,2-dichloro-3-phenylcyclopropylmethyl chloride, 2-chloro-1-(2,2-dichlorocyclopropyl)-
ethane, and 2,7,7-trichlorobicyclo[4.1.0]heptane were studied in the expectation that there would be greater rearrangement under electrophilic catalytic conditions.

Deamination of 2,2-dichlorocyclopropylmethylamine had been briefly investigated previously.\(^2\) There was some indication that some rearrangement might occur, but no rearranged materials had been identified or isolated. Thus, 2,2-dichlorocyclopropylmethylamine was prepared in the present study, carefully purified, and deaminated under a variety of conditions, and the products were isolated.

In order to determine if an occult methylene equilibration rearrangement were occurring of the type first observed by Roberts et al. in the unsubstituted cyclopropylcarbinyl system,\(^{1b}\) (Eq 2), 2,2-

\[
\begin{align*}
"CH_2-X" & \xrightarrow{-X} "CH_2OS" + "CH_2OS" + \text{other products} \\
& \text{(2)}
\end{align*}
\]

2,2-dichlorocyclopropylmethyl-$\alpha,\alpha$-$d_2$ \(p\)-toluenesulfonate and 2,2-dichlorocyclopropylmethyl-$\alpha,\alpha$-$d_2$ bromide were subjected to acetylation and silver ion assisted acetylation respectively.

Generation of the 2,2-dichlorocyclopropylcarbinyl cation via Friedel-Crafts catalysis might result in a more electron deficient carbinyl cation than by solvolysis. Thus 2,2-dichlorocyclopropylmethyl bromide was treated with a variety of Friedel-Crafts catalysts and the
products studied. On the basis of these observations, the reactions of antimony pentachloride in benzene with 2,2-dichlorocyclopropylmethyl chloride, 2,2-dichloro-1-methylcyclopropylmethyl chloride and 1-chloro-1-(2,2-dichlorocyclopropyl)ethane were investigated in order to elucidate various aspects of the mechanistic pathway of ring opening. In an extension of the study of Friedel-Crafts catalysis, the reactions of aluminum chloride in benzene and aluminum chloride in nitromethane with several 2,2-dichlorocyclopropylmethyl chlorides were investigated.

Since the 2,2-dihalocyclopropylcarbinyl system showed little tendency to rearrange under solvolytic conditions, the effect of one halogen in the ring on the course of solvolysis of cyclopropylcarbinyl derivatives was investigated. It was of interest to determine if one halogen would be sufficient to prevent rearrangement. Thus 1-bromo-, cis-2-bromo-, and trans-2-bromocyclopropylmethyl tosylates were prepared and subjected to acetylalysis and the products studied.

A second objective of this research was to study the transmission of the electronic effects of halogen substituents on a cyclopropane ring through the ring to an adjacent site. Thus the rates of ethanoly- sis of 2,2-dichlorocyclopropylmethyl p-toluenesulfonate, 2,2-dibromo- cyclopropylmethyl p-toluenesulfonate, 1-bromocyclopropylmethyl p-toluenesulfonate, cis-2-bromocyclopropylmethyl p-toluenesulfonate, and trans-2-bromocyclopropylmethyl p-toluenesulfonate were determined. It was also anticipated that this kinetic study might reveal participation of the cyclopropyl ring in the solvolytic displacement.
In order to investigate the transmission of electronic effects in the absence of complicating factors involved in the solvolytic process, acid dissociation constants of several acids, corresponding to the cyclopropylcarbinyl substrates, were determined. In a Taft treatment the electronic effect of a substituent should be directly proportional to the change in pKa of the substituted acid relative to the unsubstituted acid. Thus the pKa's of 2,2-dichlorocyclopropane-carboxylic acid, 2,2-dibromocyclopropanecarboxylic acid, 1-bromocyclopropane-carboxylic acid, cis-2-bromocyclopropanecarboxylic acid, and trans-2-bromocyclopropanecarboxylic acid were determined. In order to elucidate an anomaly in the observed solvolytic rates, the pKa study was extended to 1-methylcyclopropanecarboxylic acid and trans-2-methylcyclopropanecarboxylic acid.
HISTORICAL

Cyclopropylcarbinyl systems undergo ring expansion (Eq 3), ring opening (Eq 4), and degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement (Eq 5). These reactions have attracted intense interest over the last 25 years, and a great amount of information has been accumulated. This historical survey will only briefly summarize significant developments and is organized in the following manner:

I. Introduction
II. Reviews Available
I. Introduction

Numerous and apparently somewhat disparate observations had been made with regard to the chemistry of cyclopropylcarbinyl, cyclobutyl, and homoallylic derivatives. For many years, no satisfactory explanation was available to rationalize the puzzling chemistry. However, after the suggestion was put forth that carbonium ions could delocalize charge via carbon-carbon single bonds in a manner analogous to that observed with carbon-carbon double bonds, a variety of proposals were advanced to explain the apparently anomalous chemistry of the cyclopropylcarbinyl systems.

One of the first reported puzzling observations relative to the chemistry of the cyclopropylcarbinyl system was that treatment of cyclobutylamine or cyclopropylmethyllamine with nitrous acid gives essentially identical mixtures of cyclobutanol and cyclopropylmethanol (Eq 6). Deamination of cyclopentylamine or cyclobutylmethylamine with nitrous acid yields a similar mixture of products.
\[
\text{CH}_2\text{NH}_2 \xrightarrow{\text{HNO}_2} \text{OH} + \text{CH}_2\text{OH}
\]

(6)

\[
\text{NH}_2 + \text{side products}
\]

(4) N. J. Demjanow, Chem. Ber., 40, 4393 (1907); Idem., ibid., 40, 4961 (1907).

(Eq 7); therefore, this rearrangement is not an exclusive feature of

\[
\text{NH}_2 \xrightarrow{\text{HONO}} \text{OH} + \text{C}_3\text{H}_5
\]

(7)

\[
\text{CH}_2\text{OH} + \text{C}_3\text{H}_2
\]
cyclopropylcarbinyl-cyclobutyl systems. However, only in the cyclo-
propylcarbinyl-cyclobutyl case are essentially identical mixtures of
products obtained irrespective of starting amine, suggesting that
desamination of both cyclopropylcarbinyl- and cyclobutylamine proceed
through a common intermediate.

Homoallylic systems also equilibrate with cyclobutyl and cyclo-
propylcarbinyl systems. Thus cyclopropylmethanol and phosphorus
tribromide gives allylcarbinyl bromide, cyclobutyl bromide, and cyclo-
propylmethyl bromide (Eq 8). Acetolysis of cholesterol tosylate

\[
\text{CH}_2\text{OH} \xrightarrow{\text{PBr}_3} \text{Br} + \text{Br} + \text{CH}_2\text{Br}
\]

(8)

yields the epimeric i-cholesteryl acetate (Eq 9). 1-Chloro-4-methyl-
3-pentene apparently hydrolyzed to cyclopropyldimethylcarbinol (Eq 10),
but reaction of this alcohol with aqueous hydrochloric acid gives the open chain compound back again.

No satisfactory explanation for these deep-seated rearrangements was advanced until the concept of the non classical carbonium ion was developed. The non classical carbonium ion concept originated from consideration of a system quite different than cyclopropylcarbinyl derivatives, viz camphene hydrochloride.
Camphene hydrochloride rearranges to isobornyl chloride (Eq 11). To explain this deep-seated reorganization of the carbon skeleton, it was suggested that a bridged ion is formed. Such a formulation implies that a carbon-carbon single bond delocalizes charge in a manner analogous to carbon-carbon double bonds.

Studies of the cholesteryl-i-cholesteryl chloride equilibration likewise led to suggestions that a non classical delocalized ion is involved. The cyclopropylcarbinyl moiety forms an "unsymmetrical homoallylic cation" which spreads charge over several atoms; this
sequence provides an explanation of the reverse reaction, homoallylic to cyclopropylcarbinyl.

The most dramatic observations on and suggestions about delocalized non-classical ions were made by Roberts and coworkers. Pure cyclopropylmethylic chloride was prepared for the first time and observed to solvolyze very rapidly, faster even than methallyl chloride. Kinetic studies also revealed that cyclobutyl chloride solvolyzes more rapidly than expected for a secondary chloride. Products of the solvolysis of cyclopropylmethylic chloride are not only ring opened and ring expanded materials, but also large amounts of cyclobutyl chloride, which must arise from internal return of the chloride to the ring expanded cation. An unusual sort of bonding and interaction is indicated. This led to additional experiments which resulted in the discovery that the methylene carbons equilibrate upon deamination (Eq 12) of cyclopropylmethylicamine. Reagents such as

(13) (a) S. Weinstein and A. H. Schlesinger, J. Amer. Chem. Soc., 70, 3528 (1948); (b) E. M. Kosower and S. Weinstein, ibid., 78, 4347 (1956); (c) E. M. Kosower and S. Weinstein, ibid., 78, 4354 (1956); (d) S. Weinstein and E. M. Kosower, ibid., 81, 4399 (1959) and references therein.

thionyl chloride, with cyclopropylmethanol result in total equilibration (Eq 13). A variety of delocalized ions were proposed to

\[ \text{[Diagram]} \]

(eq 13)
Some workers, notably H. C. Brown, attacked these proposals arguing that delocalized ions were nonsense and a long and acrimonious controversy ensued. The delocalized norbornyl ion is now well established.

For selected papers and commentary, see P. D. Bartlett, 'Non Classical Ions,' W. A. Benjamin, New York, 1965.


II. Reviews

Many excellent reviews encompassing various aspects of the cyclopropylcarbinyl cation have appeared. Reference 18 is a monograph on not only cyclopropylcarbinyl solvolysis, but solvolytic displacement reactions in general. Reference 19 concentrates on cyclopropyl and cyclopropylcarbinyl systems. Generation and observation of the cyclopropylcarbinyl ion in strong acid solutions are the subjects of reference 20. Reference 21 discusses neighboring group participation, and cyclopropyl and homoallylic ions are considered from that standpoint. A general but now slightly out of date review of the cyclopropylcarbinyl cation is found in reference 22. References 23 and 24
well summarize thought and information on the topic into 1971.


III. Reactions

A. Ring Expansion; effect of substituent groups on ring expansion

Ring expansion is often an important reaction of cyclopropylcarbinyl systems. The parent gives similar proportions of ring expanded and unexpanded products, with only a small amount of ring opening (Eq 14). These ratios are the result of kinetic control,

\[
\begin{align*}
\text{CH}_2\text{ONs} & \rightarrow \text{CH}_2\text{OH} + \text{ONs} - \beta \text{naphthalenesulfonate} \\
& \quad 58\% \\
& \quad 42\% \\
& \quad \text{trace}
\end{align*}
\]

(14)
because upon equilibration different proportions of material are obtained. Thus heating cyclopropylmethanol in aqueous hydrochloric acid yields a mixture composed primarily of cyclobutanol \(\text{eq 15}\) (Eq 15). If heating is prolonged, cyclobutanol is also consumed and only ring opened products are observed \(\text{eq 16}\) (Eq 16).

\[
\begin{align*}
\text{CH}_2\text{OH} & \xrightarrow{\text{eq. } \text{HCl} \atop \Delta} \text{Cyclobutanol} + \text{CH}_2\text{OH} \\
36:1
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{Cl} & \xrightarrow{\text{HCl} \atop \text{ZnCl}_2} \text{Cl} + \text{other ring opened isomers} \\
\text{(16)}
\end{align*}
\]

The proportion of ring expanded product is generally increased by substitution in the 1-position on the ring of a cationic stabilizing group such as phenyl or alkyl. Indeed, exclusive formation of cyclobutyl products substituted in the 1-position is usually observed.
(Eqs 17, 18).

\[
\begin{align*}
\text{CH}_3 & \quad \text{HONO} \\
\text{CH}_2\text{NH}_2 & \quad \text{H}_2\text{O} \\
\end{align*}
\]

\[\text{OH} \quad \text{CH}_3\]

(17)

\[
\begin{align*}
\text{Ph} & \quad \text{AcOH} \\
\text{CH}_2\text{OTs} & \quad \text{NaOAc} \\
\end{align*}
\]

\[\text{OAc} \quad \text{Ph}\]

(18)


(27) This reference indicates no ring expansion upon solvolysis of the parent cyclopropylmethyl tosylate, but this was corrected in later publications in the series.

Generally neither ring opening nor ring expansion is observed when a cation stabilizing group is attached to the carbinyl carbon generated via solvolysis. Investigation of the 1-cyclopropylethanol system reveals, however, that a large amount of cyclobutanol can be
formed (Eq 19). Continued treatment with 1 N perchloric acid eventually gives nearly all ring opened materials.

\[ \text{Scheme 19} \]

In another example of the effect of substitution on the carbonyl carbon (Eq 20), ring opened product is eventually formed, but only because the overall equilibrium favors this product. However, it is produced from the intermediate unrearranged material 17.
B. Ring opening

1. Effect of substituents on ring opening.

Ring opening appears to be favored by cationic stabilizing groups in the 2-position of the cyclopropyl ring (Ar-, Alkyl-, Ph0-). The proportion of ring opened products increases and ring expanded material is not usually observed, although recently this latter generalization has been questioned. Treatment of 2-phenylcyclopropylmethanol with bisulfate gives 1-phenyl-1,3-butadiene (Eq 21); warming alcohol 2 with dilute sulfuric acid yields aldehyde 3 (Eq 22). Many other

\[
\begin{align*}
\text{Ph} &\xrightarrow{\text{CH}_2\text{OH}} \quad \text{KHSO}_4 \quad \Delta \\
\text{PhCH} &= \text{CH-CH}=\text{CH}_2 \\
\end{align*}
\]


reports of ring opening of cyclopropylcarbinyl systems appear in the literature; thus the terpine \( \frac{4}{3} \) gives \( \frac{5}{2} \), but no cyclopentene product (Eq 23).  

Finally with regard to the effects of substitution in the 2-position on ring opening, often large amounts of rearranged cyclopropylcarbinyl product are also observed (Eq 24) in addition to ring
opened material. This is actually an example of the cyclopropyl-carbinyl-cyclopropylcarbinyl rearrangement to be discussed later.


2. Mechanism

The above examples all illustrate the usual direction of opening of the cyclopropane ring; the cationic stabilizing group is in the 4-position of the homallylic system. This can be rationalized by ring opening to give the more stable secondary rather than the primary carbonium ion (Eq 25).
In contrast to the many studies of the direction of ring opening, the molecularity of reaction has only been investigated in one case. The rate is first order both in the cyclopropylcarbinyl cation and the nucleophile water (Eq 26). This implies that the rationalization of a carbonium ion intermediate to explain the direction of opening is too simplistic.

Cyclopropane 6, substituted with two carbinyl functions, opens up in one of two directions depending on the nature of the nucleophile. Thus 6 is converted by aqueous hydrobromic acid to 7, but treatment with sulfuric acid in acetic acid gives 8 (Eq 27).

\[ \begin{align*}
\text{CH}_2\text{Br} & \quad \text{HBr} \\
\text{PhCH}=\text{CH}-\text{CCH}_2\text{OH} & \quad \text{H}_2\text{SO}_4, \text{HOAc} \\
\text{OAc} & \\
\text{CH}_3 & \\
\end{align*} \]

(27)

\[ \text{CH}_3 \]


The observation that the homoallylic ion derived from the ring opening does not rearrange to allylic stabilized ions before capture occurs has also been cited as evidence that the ring opening reaction may be bimolecular. Thus deamination of 3-butenylamine yields nearly 40% rearranged open chain material (Eq 28), whereas the cyclopropyl-

\[ \begin{align*}
\text{H}_2\text{N} & \quad \text{HONO} \\
\text{HO} & \quad \text{OH} \\
\text{45%} & \quad \text{21%} \\
\text{7%} & \quad \text{15%} & \quad \text{13%} \\
\end{align*} \]

(28)
methylamine gives none (Eq 29). Likewise, cyclopropylmethanol and

\[
\begin{align*}
\text{CH}_2\text{NH}_2 & \xrightarrow{\text{HONO}} \text{CH}_2\text{OH} + \text{HO} - \\
& \text{56\%} + \text{40\%} + h\% 
\end{align*}
\]

Lucas reagent initially give only 4-chloro-1-butene and no 3-chloro-1-butene or 1-chloro-2-butene (Eq 30). If ring opening proceeds through

\[
\begin{align*}
\text{Cl} & \xrightarrow{\text{aq. HCl}} \xrightarrow{\text{ZnCl}} \text{CH}_2\text{OH} \\
\rightarrow & \text{Cl} + \text{Cl} 
\end{align*}
\]

an intermediate carbonium ion, a hydride shift to give the more stable allylic cation should occur. The fact that capture takes place in the homoallylic position must indicate participation of the nucleophile in the ring opening perhaps via a delocalized ion which undergoes bimolecular attack to yield the homoallylic product.


The stereochemistry of ring opening has been investigated. In general the least sterically hindered product is formed when sub-
Substitution is on the carbinyl carbon. Thus in 2 where R' is larger than R, the trans product is formed preferentially (Eq 31).

\[
\begin{align*}
\text{CRR'}-X & \rightarrow \begin{array}{c}
\text{major} \\
\text{minor}
\end{array} \\
\begin{array}{c}
\text{X} \\
\text{X}
\end{array} & + \begin{array}{c}
\text{R} \\
\text{R'}
\end{array} \\
\begin{array}{c}
\text{R} \\
\text{R'}
\end{array} & \begin{array}{c}
\text{R} \\
\text{R'}
\end{array}
\end{align*}
\]

(R=H, R'=CH₃, ca 65%)

A steric argument has been advanced to explain this stereochemical preference. The large R' will favor conformation 12 of the starting cyclopropylcarbiny1 material, since if R' lies over the ring in cis-bisected geometry, it should suffer steric interaction with the cis-2-hydrogens. Hence more 12 will be formed than 13; since interconversion of 12 and 13 is not expected because theoretical calculations, nmr studies, and labeling experiments (vide infra) indicate this to be unfavorable, ring opening will proceed to give 14 and 15, with 14 formed in the greater proportion (Eq 32).
A better explanation probably has been advanced. Anchimeric assistance or a 'bicyclobutonium' ion could account for the observed products, since conformation 10 would be more subject to attack by the ring than 11, where steric interaction with the cis ring hydrogens would be greater. Optically active 1-cyclopentylethanol, however, racemizes as rapidly as it undergoes 130 exchange. A bicyclobutonium


intermediate would maintain optical activity. In order to reconcile this observation with the anchimeric assistance argument, it was
suggested that at least one other ion, perhaps a 'tricyclobutonium' or puckered cyclobutyl ion which had flipped by some means, is involved in the racemization.

C. Degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement.

Perhaps the most interesting reaction of the cyclopropylcarbinyl cation is the degenerate rearrangement first discovered by Roberts and coworkers (Eq 12). In a similar experiment the carbon scrambling has been confirmed by C-13 nmr and deuterium labeling has also been used to demonstrate methylene scrambling.

\[
\begin{align*}
\text{CH}_2\text{NNi}_2 & \rightarrow \text{CH}_2\text{OH} + \text{CH}_2\text{CH}_2\text{OH} + \text{C}_\text{cyclopropyl} \text{OH} \\
\text{47\%} & \quad \text{53\%} \quad \text{28\%} \quad \text{36\%} \quad \text{66\%} \quad \text{33\%}
\end{align*}
\]

\[(12)\]


The methylene carbons are completely equilibrated in the alkylcarbinol; shuffling is less complete in the cyclopropylmethanol. Approximately one-half of the labeled carbon has gone into the ring in the 2-position, but, within experimental error, none into the 1-
position. The cyclobutanol obtained shows similar scrambling. It is concluded that the cyclopropylcarbiny1 cation is undergoing a degenerate rearrangement (Eq 33).

\[
\begin{align*}
\text{CH}_2^+ & \iff \text{CH}_2^+ \\
\text{CH}_2^+ & \iff \text{CH}_2^+
\end{align*}
\] (33)

The degenerate rearrangement is stereospecific. A very elegant demonstration of this stereospecificity has been reported. \(42\) Hexa-

deutercyclopropylmethanol methanesulfonate containing a single hydrogen in the cis-2-position on the ring was solvolyzed in aqueous acetone and the products examined by nmr. Complete equilibration of the methylene groups had occurred, but the hydrogen appeared only in the cis positions (Eq 34).

The reaction has also been examined in the reverse direction.

Thus acetolysis of cis-\( d \)-3-butene-1-ol p-toluenesulfonate gives cyclopropyl products with all the deuterium (within experimental error) in the cis-positions (Eq 35).

\[ \text{(35)} \]

The generalizations about the effects of substitution on reactivity break down when the cyclopropylcarbinyl system is constrained in bicyclic or polycyclic systems. The products formed are strongly

\[ \text{(43)} \]

influenced by the geometry of the reactant. Much has been learned about the steric demands for cyclopropane interaction with a cation site in these systems. One interesting example is the bicyclo[2.1.0]-pentane system 18. The endo compound gives a mixture of four major products, but the exo-isomer undergoes very little rearrangement (Eq 36). 14 Many other examples have been reported; ref (24) provides a recent review.

\[ \text{solvolysis} \]

\[ \text{18a} \]

\[ \text{solvolysis} \]

\[ \text{18b} \]

\[ (36a) \]

\[ (36b) \]

IV. Nmr Studies of Cyclopropylcarbinyl Cations

Nmr has been one of the most valuable methods to probe the structure of the cyclopropylcarbinyl cation.

Cyclopropylcarbinyl cations have been prepared in concentrated sulfuric acid solutions and studied by nmr. More recently, in a series of over 150 papers the preparation of solutions of cyclo-

---


propylcarbinyl and other carbocations in various eutetic mixtures of SO$_2$-FSO$_3$D-SbF$_5$ or related "super acid" media has been described. The pmr and C-13 nmr of such solutions has yielded much information about the structures of the cyclopropylcarbinyl cation. The parent ion exhibits a simple spectrum consistent with either a "tricyclo-

---


butonium ion" 19, or non classical cations of either the unsymmetrical bicyclobutonium type 20 and a cis bisected ion 21 rapidly equilibrating perhaps via a puckered cyclobutyl cation 22. The lifetime of 20 or 21 would have to be short to allow the methylene protons to become equiva-
lent as is observed. Cyclopropylcarbinyl systems substituted on carbinyl carbon give spectra consistent with cis-bisected geometry.

In all cases the C-13 chemical shift data appear to preclude equilibrating classical ions.

V. Solvolysis Rate Studies

Solvolytic rate studies are another important means of investigating the cyclopropylcarbinyl cation. Unfortunately, the solvolysis process is quite complex, thus rendering interpretation of the observed rates difficult.

The rate of solvolysis is often described in terms of $k_s$ (rate of displacement by solvent) and $k_A$ (rate of displacement by neighboring group). $k_s$ should vary with the nucleophilicity and ionizing power of the solvent, and several treatments of solvent effects on solvolytic displacement have been presented.
Many rates are correlated with Eq 37, where $k$ is the rate in a new solvent, $k_o$ is a standard rate, $N$ is the nucleophilicity of the solvent, $Y$ is the ionizing power of the solvent, and $l$ and $m$ are parameters characteristic of the substrate. $\text{t-Butyl chloride was chosen as a standard, since it might not be sensitive to the nucleophilicity of the solvent ($l = 0$), and from the rates of solvolysis in various solvents, values of $Y$ are determined.}$

Recently proposals have been advanced to evaluate $l$ and $N$ in Eq 37. $^{50}$ A new parameter, $Q$, reflecting the ratio of ionizing to nucleophilic attack was introduced, and evaluated from Eq 38. $Q$ for

$$\log \left( \frac{k}{k_o} \right) = lN + mY$$

$$\log \left( \frac{k}{k_o} \right) = (1-Q) \log \left( \frac{k^A}{k_o^A} \right) + Q \log \left( \frac{k^B}{k_o^B} \right)$$
since methyl is highly susceptible to nucleophilic attack because there is little steric interference; contrariwise, 2-adamantyl should not undergo significant nucleophilic attack. The ratio of the rates in a highly nucleophilic solvent of low ionizing power \((k_A^A/k_O^A)\) versus the ratio of the rates in a poorly nucleophilic solvent of high ionizing power \((k_B^B/k_O^B)\) then permits evaluation of \(l\) and \(N\). \(Q\) and \(N\) values for various reactants and solvents have been tabulated.

When the second order component of the rate law for a reaction is small with respect to the first order rate, the solvolysis is designated as limiting and the rate designated \(k_{lim}^{AB}\). 2,2,2-Trifluoroethanol has been proposed as the solvent most favoring limiting solvolysis.


The actual processes by which displacement reactions occur are matters of vigorous investigation. On the basis of the observation that some reactions exhibit first order kinetics whereas others show first order dependence on both substrate and nucleophile, \(''S_N^1''\) and \(''S_N^2''\) type reactions were proposed. The most consistent interpretation of solvolytic behavior however has been made in terms of a

scheme involving an intimate ion pair, a solvent separated ion pair, and a solvated carbonium ion. Each of these moieties must involve some positive charge on the central carbon atom. \(^{53,54}\)


If this scheme is correct, the second order component in the rate equation could arise from attack on the ion pair by the nucleophile, rather than via a classical \(S^2_N\) transition state. The intimate ion pair would also be expected to maintain its stereointegrity, and react with inversion when attacked by a nucleophile (Walden Inversion).

Attempts have been made to treat \(S^1_N\) and \(S^2_N\) reactions as a merged mechanism. \(^{55}\) Very recently a study has been made of isotope effects of solvolysis in aqueous acetone with added azide ion, and it was concluded that there are two distinct \(S^1_N\) and \(S^2_N\) processes. \(^{56}\)


Changing substituent groups on a molecule often leads to predictable effects. Quantitative evaluation of these effects is often
informative. Replacing hydrogen with an electron withdrawing group on the aromatic ring of a benzoic acid results in increased acidity; an electron donating group reduces the acidity. Hammett was able to quantitatively correlate substituent effects with the acidity of benzoic acids, the basicity of aromatic amines, and many other reactions of substituted benzenes by a simple relationship (Eq 39). $^37$ $k_o$ is the rate (or equilibrium) observed for the unsubstituted substrate, $k$ is

$$\log \frac{k}{k_o} = \rho \sigma$$  \hspace{1cm} (39)


the rate observed for the substituted compound, $\sigma$ is the substituent constant characteristic of the substituent, and $\rho$ is the reaction constant defined as unity for ionization of benzoic acids in water at $25^\circ$. Hence a strongly electron withdrawing group such as nitro will have a positive $\sigma$ value. As expected, groups in the ortho position cannot be correlated well by the equation; somewhat better fits are obtained by using different $\sigma_m$ for meta and $\sigma_p$ for para substituents. Reactions involving sites which interact strongly via resonance with the ring, such as the benzylic cation show large deviations particularly with substituent groups such as dimethylamino which can interact directly by resonance with the substituent group (Eq 40). For such reactions $\sigma^+$ and $\sigma^-$ values have been proposed. Extensive compilations
Many approaches have been taken to separate the substituent constant in the Hammett equation into resonance and inductive parts $\sigma_I$ and $\sigma_R$. A reasonably successful approach to the question has been proposed by Taft. Previously a set of $\sigma^*$ values had been obtained for aliphatic systems (isolated from the reacting center) analogous to $\sigma$ values in aromatic systems. These $\sigma^*$ values should reflect primarily inductive effects and would be proportional to $\sigma_I$. Reactions taking place at some site effectively insulated from the pi
framework of the benzene ring allows a set of $\sigma^o$ values to be obtained which reflect inductive and ordinary resonance effects. Thus Eq 41 defines $\sigma^o_R$; values of $\sigma_I$ and $\sigma_R$ have been tabulated (Table 1)

$$\sigma^o_R = \sigma^o - \sigma^o*$$

(41)

where $\sigma^o* = \sigma_I$

which have good predictive ability for a great variety of reactions and physical properties. To complete the separation of induction and resonance, a series of new $\rho$ can be determined also, so the modified Hammett equation becomes Eq 42 for some property $i$. Notice that this approach utilizes two fewer parameters than the Yakawa-Tsuno equation,

$$\log k^i/k^o = \sigma^i_R + \sigma^i_I$$

(42)

a method often used (Eq 43), since different $\sigma$ values must be utilized for the meta and para positions.

$$\log k/k^o = \rho[\sigma + r(\sigma^+ - \sigma)]$$

(43)


The extension of the Hammett equation to systems such as cyclopropanes has been reviewed.
Table 1

Taft's Substituent Parameters

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\sigma^I$</th>
<th>$\sigma^R$</th>
<th>$\sigma^\circ$</th>
<th>Substituent</th>
<th>$\sigma^I$</th>
<th>$\sigma^R$</th>
<th>$\sigma^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMe$_2$</td>
<td>0.05</td>
<td>-0.52</td>
<td>-0.47</td>
<td>I</td>
<td>0.39</td>
<td>-0.12</td>
<td>0.27</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>0.10</td>
<td>-0.48</td>
<td>-0.38</td>
<td>CH$_3$</td>
<td>-0.05</td>
<td>-0.10</td>
<td>-0.15</td>
</tr>
<tr>
<td>NHAc</td>
<td>0.26</td>
<td>-0.22</td>
<td>0.04</td>
<td>SMe</td>
<td>0.19</td>
<td>-0.17</td>
<td>0.02</td>
</tr>
<tr>
<td>OH</td>
<td>0.27</td>
<td>-0.44</td>
<td>-0.17</td>
<td>CF$_3$</td>
<td>0.41</td>
<td>0.13</td>
<td>0.54</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>0.26</td>
<td>-0.41</td>
<td>-0.15</td>
<td>MeCO</td>
<td>0.28</td>
<td>0.19</td>
<td>0.47</td>
</tr>
<tr>
<td>F</td>
<td>0.51</td>
<td>-0.34</td>
<td>0.17</td>
<td>CO$_2$R</td>
<td>0.31</td>
<td>0.15</td>
<td>0.46</td>
</tr>
<tr>
<td>Cl</td>
<td>0.47</td>
<td>-0.29</td>
<td>0.27</td>
<td>CN</td>
<td>0.52</td>
<td>0.14</td>
<td>0.66</td>
</tr>
<tr>
<td>Br</td>
<td>0.45</td>
<td>-0.16</td>
<td>0.29</td>
<td>NO$_2$</td>
<td>0.64</td>
<td>0.19</td>
<td>0.83</td>
</tr>
</tbody>
</table>

*From ref 62.*
Induction may take place (1) by through space field effects, (D⁻¹r⁻²cosθ for point charges), (2) by *sigma* bond transmission, or (3) by field and/or *sigma* bond transmission from the substituent group to the transmitting unit and from the transmitting unit to the reactive site by field and/or *sigma* bond transmission and/or *pi* transmission but through the transmitting unit *via* *pi* delocalization. The resonance component will be transmitted by (1) direct resonance or (2) by resonance interaction of the substituent group with the transmitting unit, but from the transmitting unit to the reactive site by field and/or *sigma* transmission. Additional mechanisms for the transmission of electronic effects may be visualized but the five listed above are probably the most significant in the absence of steric effects. These effects have had extended discussion.

---


---

Many attempts have been made to calculate through space field effects. One model, generally referred to as the Kirkwood-Westheimer method, has received much attention. In this model the molecule is

---

assumed to have low dielectric constant and be surrounded by a solvent, generally of higher dielectric constant and thus insulating. The effect of the dipole or charge of the substituent group on the reaction center is then evaluated by classical methods. Experimental results generally indicate, however, that through bond inductive effects are equal to or greater than the through space effects. For example, when the rigid bicyclo[2.2.2]octane-1-carboxylic acids were studied and compared with values calculated using reasonable parameters in the Kirkwood-Westheimer method, the calculated effects were only about one-half those actually found (Eq 44).

(66) J. D. Roberts and W. T. Moreland, Jr., J. Amer. Chem. Soc., 75, 2167 (1953); for a different view, however, see ref. 64b.

Large resonance contributions are often present in reactions which are formally insulated from (cannot resonate with) the benzene ring. Phenylacetic acids, for example, have a $\lambda$ factor ($\rho_R/\rho_I$) of 0.6. By some measures even $\sigma^*$ and $\sigma_I$ contain a significant reso-
nance contribution. Since a resonance interaction is apparently operant across systems formally insulated from each other, crossed conjugated groups (groups which cannot formally interact by resonance although the $\pi$ orbitals are on adjacent atoms) might therefore exhibit extensive resonance interaction. Many theoretical calculations do indicate appreciable delocalized interactions between formally cross conjugated units. A related observation is that meta substituents have a significant $p_R$. There may be a resonance interaction of the substituent group with the ring, but from the ring to the reactive site by sigma or field effects. Alternately the simple theory of resonance is insufficient to describe meta interactions.

VI. Theoretical Calculations

Theoretical calculations exploring the $C_4H_7^+$ potential surface have been reported.


Additional studies are listed in references 23 and 24.

An extensive study employing Extended Huckel calculations investigated numerous geometries of the C₄H₇ cation. The bisected structure 2⁴, with the empty carbyl orbital parallel to the plane of the ring was found to be more stable than the perpendicular structure 2⁵ by about 9 kcal/mole, in good agreement with earlier calculations utilizing EH⁷⁰ and CNDO.⁷¹ Small rotations (< 30°) about the cyclopropyl carbyl bond have little effect on the energy. The tricyclobutonium cations 2⁶ and 2⁷ are of comparable energies, but
much higher than that of cyclopropylcarbinyl geometry and thus are probably not involved in cyclopropylcarbinyl rearrangements. The cyclobutyl cation is found to prefer a puckered conformation $28^\circ$ with the hydrogen in the axial position. The alternative conformation $29^\circ$ is unfavored. This result contrasts somewhat with calculations which found a classical 'flat' ion. Bicyclobutonium cations of various geometries were also considered. The potential surface is rather flat for small variations in the angles $\alpha$ and $\beta$. The symmetrical bicyclobutonium ion ($\alpha = \beta$) was not a distinct minimum.

A CNDO study $^{30}$ monitoring charge density indicates that a flat symmetrical homoallylic structure $31^\circ$ is favorable. This result contrasts strongly with most other studies.
Localized molecular orbitals have been utilized in another study. The bisected geometry $2^b$ is the most favorable, and it is predicted that rearrangement to cyclobutyl occurs via a bicyclobuto- 

nium (unsymmetrical homoallylic) ion. An INDO study also favors the bisected geometry.

Interesting results are obtained via ab initio calculations. The homoallylic ion in all geometries examined collapses without barrier to the bisected cyclopropylcarbinyl ion $2^h$. Solvation is suggested as a possible interaction which gives rise to the homoallylic products actually observed upon solvolysis.

VII. Structures Proposed for the Cyclopropylcarbinyl Cation

Several models have been proposed for the bonding in cyclopropyl-

carbinyl ions. The seven models presently considered are the (1) unsymmetrical homoallylic, (2) symmetrical homoallylic, (3) π complex, (4) bicyclobutonium, (5) tricyclobutonium, (6) Coulson-Moffitt cis bisected, and (7) Walsh cis bisected (vertically stabilized) cyclo-

propylcarbinyl cations.

1. The unsymmetrical homoallylic ion has charge placed on the ring via resonance as in $3^d$ or as in the distorted homoallylic ion $3^e$ (Eq 45).

\[ \begin{align*}
\text{32} & \equiv \text{33} \quad \text{34} \equiv \text{35} \\
\end{align*} \]
2. The symmetrical homoallylic ion \((36)\) has C-3 and C-4 simultaneously involved in delocalization (Eq 46).

\[
\begin{align*}
36 & \quad 37 & \quad 38 & \quad 39 & \quad 40 \\
\end{align*}
\]

3. \(n\)-Complexes such as \(41-44\) have been considered, primarily as aids to theoretical calculation. Complex \(42\) is stabilized both by

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\| & \quad \| \\
+\text{CH} & \quad +\text{CH} \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\end{align*}
\]

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

\[
\begin{align*}
41 & \quad 42 \\
\end{align*}
\]
donation of negative charge to the cationic center and by back donation as indicated by the long curved arrow; a twisted geometry $h_4$ is also possible.

4. Bicyclobutonium ion $h_5^{14}$ has, in contrast to the homoallylic ions, some charge at C-2. Ion $h_5$ is assumed to be in rapid equilibrium with closely related isomers in which C-1, C-3, and C-4 have exchanged positions.

\[ h_5 \quad h_6 \quad h_7 \quad h_8 \]

5. Tricyclobutonium ion $h_9^{14}$, mentioned earlier as a possible intermediate, has been rejected because C-1, C-3, and C-4 do not
always completely equilibrate in reactions believed to involve cyclo-
propylcarbinyl cations.

6. The minimum energy of a cyclopropane ring has been calculated
to be reached when the C-C bond orbitals are at an angle of 104° with
sp4 hybridization. The high p-character bonds can overlap with

(75) C. A. Coulson and W. E. Moffitt, Phil. Mag., 40, 1 (1949).

the p orbital of the carbinyl cation to delocalize charge to give ion

50.

7. Walsh, originally considering the bonding in boranes, has
proposed a model generally considered superior to that of Coulson


and Moffitt. The carbon atoms in sp2 hybridized; each ring atom
has one sp2 orbital pointing into the center of the ring to form a
three centered bond (51), and the p orbitals lie in the plane of the
ring and contain four electrons which occupy two degenerate molecular orbitals, \( \psi_1 \) and \( \psi_2 \). \( \psi_3 \) is a high energy empty non-bonding orbital.

For qualitative arguments one should use a basis set as close as possible to the bonding in the molecule. The Walsh model predicts high electron density within the ring, while the Coulson-Moffitt does not. Microwave measurements have shown such high electron density in three membered rings,\(^{77}\) and hence the Walsh model is the better description of the actual molecule.


In this model of the cyclopropylcarbinyl cation the empty p orbital of the cationic center overlaps with \( \psi_1 \); this forces the mole-
cule \( \text{cis} \) to assume a \text{cis} bisected geometry.

Nmr spectroscopy of substituted cyclopropylcarbinyl cations in super acid media at low temperature clearly indicate ions of the geometry in \( \text{cis} \). Much of the work is due to Olah \(^{16}\) and has been reviewed. \(^{20,23,24}\)

The Walsh model for the cyclopropylmethyl cation has recently been extended and elaborated. Quantum mechanical calculations have, based on this model, been employed to investigate the transmission of substituent effects through the cyclopropane ring (\text{vide infra}).

The ability of the cyclopropane ring to transmit substituent effects by resonance is not certain, although most recent work indicates that the ring does not. One early study examines the near ir of a series of substituted cyclopropanes and concludes that significant resonance transmission is occurring. \(^{78}\) Subsequently, however, additional cyclopropanes have been prepared and examined, and the best correlation is obtained using Taft \( \sigma^* \) values, \(^{79}\) thus indicating little resonance transmission. This topic has been reviewed recently. \(^{co}\)

---


---

In addition to near ir studies, spectroscopic examination of charge-transfer complexes has been employed to study the ability of the cyclopropane ring to transmit substituent effects. No shifts
characteristic of resonance interaction are observed, suggesting the absence of pi-electron transmission.


Although the recent near ir and charge-transfer complex spectral studies do not indicate transmission by resonance, the rate of solvolysis of trans-2-methoxycyclopropylcarbonyl p-nitrobenzoate has been reported to be 791 times faster than that of the unsubstituted compound. This could be taken as evidence for resonance interaction, since methoxy withdraws charge via induction, retarding solvolysis.


as in norbornyl systems where the methoxy group generally decelerates reaction; however, it can donate electrons by resonance, and hence accelerates solvolysis if resonance interaction is involved. It was suggested, however, that the acceleration was due to frangomeric (distortional) acceleration. The cyclopropane ring could distort--start to open to give a homoallylic ion or a stabilized non classical ion be formed--and the methoxy group would exert a stabilizing effect in this intermediate ion. It is further argued that the charge transfer complexes are an excellent probe for resonance stabilization (vertical stabilization).
Theoretical calculations utilizing INDO methods\(^{82}\) and CNDO/2\(^{83}\) agree with the conclusion that no large resonance interaction would

\begin{align*}
(82) & \quad \text{L. D. Kispert, C. Engelman, C. Dyas, and C. U. Pittman, Jr., J. Amer. Chem. Soc., 93, 6948 (1971).} \\
(83) & \quad \text{C. F. Wilcox, L. M. Loew, and R. Hoffmann, J. Amer. Chem. Soc., 95, 8192 (1973).}
\end{align*}

be expected. The CNDO/2 calculation is particularly informative, and an attractive model for the cyclopropylcarbinylication and the effect of substituents has been proposed on the weight of these calculations. The orbital of the cationic center is allowed to mix with one of the in-plane \( p \) orbitals in the Walsh model (Eq 49). The resulting molecular orbital \( \psi_2 \) has the bulk of the electron density concentrated on the carbonyl atom \( \alpha \); the wave function coefficients from the CNDO/2

\[
\begin{array}{c}
\text{HOMO} \\
\sqrt{0.05}
\end{array} + \begin{array}{c}
\text{LUMO} \\
\sqrt{0.73}
\end{array} \xrightarrow{\sqrt{0.1}} \psi_2
\]

\[(49)\]
calculation of Wilcox et al. are given in Eq 49. There is little electron density in the 2-position to interact with a substituent placed there. Quantitative results were obtained by Wilcox et al. upon comparing this orbital with model systems and applying simple perturbation arguments. A phenyl group interacting directly with a carbocation (e.g. a benzylic system) is observed to accelerate solvolysis (in the case of tert. derivatives) $250,000,000 = 10^{9.4}$ in a cyclopropylcarbinylcation the effect of phenyl substitution in the 2-position of the ring should be reduced by a factor of the square of the coefficient of the wave function on that atom. Thus it was calculated

(84) The square of the wave function corresponds to electron density; see any introductory text on quantum mechanics such as Born. The above argument assumes that the effect of substitution is a linear free energy relationship, and the principles previously discussed for the Hamnett equation apply. The perturbation argument here explicitly neglects the probable difference in energy levels of the different LUMOs.


that the rate should be $10^{8.4} \times 0.1 = 10^{8.4} = 7$. This is close to the value of 2.2 reported for the trans-2-phenylcyclopropylmethyl-2-naphthalene sulfonate solvolysis. Likewise it can be calculated that methyl, which accelerates solvolysis on adjacent carbon by a factor of $10^{4.7}$, should only accelerate a cyclopropylcarbinyl system when placed in the 2-position by $10^{4.7}/10 = 3$, not far from the value of 11 observed for trans-2-methylcyclopropylcarbinyl. The effect of
substitution in the 1-position, at least via vertical stabilization (resonance) should be even less.


VIII. Studies of the 2,2-Dichlorocyclopropylcarbinyl System

As noted previously, very little investigation of the 2,2-dihalo-cyclopropylcarbinyl system has been carried out, limited to the dichloro system. Shortly after the initiation of this study, solvolysis (50 vol% aqueous ethanol, 100°) of three 2,2-dichlorocyclopropylmethyl chlorides was reported (Table 2). No rearrangement is observed. This agrees with the study in this laboratory.

In a related study, 2,2-dichlorocyclopropane carboxylic acid and 98% H₂SO₄ yields succinic acid, presumably ring opening occurs,


contrasting to the solvolytic reaction (Eq 50).
Table 2

Solvolytic Rates of Substituted Cyclopropylcarbinyl Chlorides (50% Aqueous Ethanol, 100°)

<table>
<thead>
<tr>
<th>RCH₂Cl</th>
<th>k x 10³ sec⁻¹</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopropyl</td>
<td>&gt;&gt; 1.3 x 10²</td>
<td>&gt;&gt; 67</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>9.7ᵇ</td>
<td>5.0</td>
</tr>
<tr>
<td>2,2-Dichlorocyclopropyl</td>
<td>1.94</td>
<td>1</td>
</tr>
<tr>
<td>2,2-Dichloro-1-methylocyclopropyl</td>
<td>1.32</td>
<td>0.68</td>
</tr>
<tr>
<td>trans-2,2-Dichloro-3-methylocyclopropyl</td>
<td>4.0</td>
<td>2.05</td>
</tr>
</tbody>
</table>

ᵃRate at 50°; ref 1. ᵇRate at 101.6°; C. A. Vernon, J. Chem. Soc., 1954, 423. ᶜFrom ref. 3.
RESULTS AND DISCUSSION

I. Product Studies

A. 2,2-Dichlorocyclopropylcarbinyl Substrates

1. Introduction

Only two studies of 2,2-dichlorocyclopropylcarbinyl systems have been reported as outlined in the Historical Section of this work. 2,2-Dichlorocyclopropylmethyl p-toluenesulfonate had been subjected to acelolysis and found not to rearrange; 2,2-dichlorocyclopropylmethyl bromide and silver ion in acetic acid was reported to give rearrangement; this bromide and aluminum chloride in benzene gave extensive reaction but the products were only tentatively (and incorrectly) assigned; 2,2-dichlorocyclopropylmethylamine upon deamination was reported to give besides unarranged product, 4-18% unidentified material, which was not characterized. Aqueous ethanolation of three simple 2,2-dichlorocyclopropylmethyl chlorides had also been studied and no rearrangement noted. The present investigation was undertaken to systematize and extend these observations.

2. Uncatalyzed Solvolyses

In this investigation acelolysis of 2,2-dichlorocyclopropylmethyl p-toluenesulfonate in 96% and in glacial acetic acid has been found to give only 2,2-dichlorocyclopropylmethyl acetate in
high yield (Eq 51), in accord with earlier results. Ester 55 is

\[
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{CH}_2\text{OTs} \\
\end{array} \xrightarrow{\text{AcOH} \quad 120^\circ} 
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{CH}_2\text{OAc} \\
\end{array}
\]

(51)

homogeneous by vpc on several stationary phases and its nmr and ir
are identical to that of authentic 55 prepared via phenyl(trichloro-
methyl)mercury and allyl acetate; by chloroform, aqueous sodium
hydroxide, phase transfer catalyst, and allyl acetate; and from 2,2-
dichlorocyclopropylmethyl bromide by displacement with sodium acetate
in acetic acid.

The failure to observe more than a single product from 54 is
somewhat surprising, for if acetolysis of 54 were to follow the same
pattern as the parent, one would anticipate, in addition to unrearranged
ester 55 (Eq 52): 3,3-dichlorocyclobutan-1-yl acetate (57) and 3-

\[
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{CH}_2\text{OTs} \\
\end{array} \xrightarrow{-\text{Tos}^-} 
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{CH}_2^+ \\
\end{array} \xrightarrow{\text{HOAc}} 
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{CH}_2\text{OAc} \\
\end{array}
\]

(52)

butenoic acid (59) via ring expansion of the 1-2 bond (Eq 53); 2,2-

dichlorocyclobutan-1-yl acetate (61) and 4,4-dichloro-3-buten-1-yl acetate (63) via ring expansion of the 1-3 bond (Eq 54); cyclopropane-
carboxylic acid (67) and 4,4-dichloro-3-buten-1-yl acetate (65) via participation of the 1-3 bond and cleavage of the 2-3 bond (Eq 55);

![Chemical reaction diagram](image)

and 3-butenolic acid (59) and 2,2-dichloro-3-buten-1-yl acetate (68) by direct homoallylic ring opening (Eq 56).

![Chemical reaction diagram](image)
The homogeneity of the ester and adequate mass balance exclude the rearrangement processes outlined in Eq 53-56. As a check, however, the solvolysis mixture has been examined by gas chromatography for cyclopropanecarboxylic acid (67) (Eq 55) and 3-butenolic acid (59) (Eq 53 and 56a). The analysis would detect a 3% yield of cyclopropanecarboxylic acid (67) or a 1% yield of 3-butenolic acid (59). Neither acid is found.

Aqueous ethanolysis of p-toluenesulfonate ester 54 likewise gives unrearranged products, 2,2-dichlorocyclopropylmethylethyl ether (69) and 2,2-dichlorocyclopropylmethanol (70) (Eq 57). The closely related 2,2-dibromocyclopropylmethyl p-toluenesulfonate (71) also is found not to rearrange (Eq 58).
Failure to observe rearrangement may be a consequence of the solvolytic conditions and leaving group selected. Aqueous ethanol generally gives less rearranged material than glacial acetic acid; chloride as a leaving group favors rearrangement with respect to p-toluene sulfonate. Hence acetolysis of 2,2-dichlorocyclopropylmethyl bromide (74a) has been investigated. In refluxing 96% acetic acid-water with sodium acetate 74a gives only unrearranged ester 55 (Eq 59). 2,2-Dichlorocyclopropylmethyl chloride (74b) likewise does not rearrange.

\[
\text{Cl} \quad \text{Cl} \quad \frac{96\% \text{ AcOH}}{\text{NaOAc, } 120^\circ} \quad \text{Cl} \quad \text{Cl} \quad \text{CH}_2\text{OAc}
\]

\(X = \text{Br} \quad 74a\)

\(X = \text{Cl} \quad 74b\)

While this work was in progress it was reported that aqueous ethanolation of 2,2-dichlorocyclopropylmethyl chloride, 2,2-dichloro-1-methylcyclopropylmethyl chloride, and cis/trans-2,2-dichloro-3-methylcyclopropylmethyl chlorides yield only unrearranged products. This is in accord with the present observation that ethanolation of 74a gives unrearranged ether 62 (Eq 60).
Modification of the 2,2-dichlorocyclopropylcarbiny1 structure by alkyl substitution might promote rearrangement. 1-Alkylcyclopropylcarbiny1 systems have been observed to yield a greater proportion of ring expanded products than the ring unsubstituted analogs. Thus in order to determine if rearrangement could be observed in such systems, 2,2-dichloro-1-methylycyclopropylmethyl chloride (75) has been solvolyzed in 96% acetic acid containing excess sodium acetate, but gives only 2,2-dichloro-1-methylycyclopropylmethyl acetate (76) (Eq 61)

\[
\begin{align*}
\text{Cl} & \text{Cl} \quad \text{EtCH} \quad 100^\circ \quad \text{Cl} & \text{Cl} \\
\text{CH}_2\text{Br} & \quad \to \quad \text{CH}_2\text{OEt} \\
74a & \quad \to \quad 62
\end{align*}
\]

in better than 90% yield. Ester 76a is homogeneous by vpc (SE-30) and exhibits the expected nmr. The structure of 76a is further confirmed by alternate preparation of the ester by methallyl acetate and chloroform-aqueous sodium hydroxide-phase transfer catalyst which yields material identical (vpc, nmr, ir) to that from solvolysis. Saponifica-
tion of 76a gives the known 2,2-dichloro-1-methylcyclopropylmethanol (76b), identified as its phenyl urethane.

3. Silver ion assisted solvolyses

Silver ion and alkyl halide sometimes give rearrangement when ordinary solvolysis does not. Thus 2,2-dichlorocyclopropylmethyl bromide (74a) and silver acetate in acetic acid has been studied. These conditions yield only 2,2-dichlorocyclopropylmethyl acetate (55), exactly in accord with the previous report \(^2\) (Eq 62).

\[
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{Cl} \quad \text{CH}_2\text{Br} \\
\end{array} \xrightarrow{\text{AgOAc}, \text{HOAc}, \text{H}_2\text{O}} \quad \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{CH}_2\text{OAc} \\
\end{array}
\]

\(74a\)

\(55\)

By contrast, \(72\) and silver acetate in glacial acetic acid give unrearranged ester 76 and 4,4-dichloro-3-methyl-3-buten-1-yl acetate (77) in a ratio of 89:11 (Eq 63). The spectral and analytical data do not immediately distinguish between 77 and 2,2-dichloro-1-methylcyclo-
butyl acetate, another possible isomer. Therefore, ester II has been independently synthesized via a Wittig reaction from 3-oxo-1-butyl acetate (obtained from the crossed aldol condensation of acetone and formaldehyde followed by esterification with acetyl chloride-pyridine) and dichloromethylenetriphenylphosphorane. Conversion of I to II is the only example of loss of the 2,2-dichlorocyclopropylmethyl structure encountered under solvolytic conditions.

Homoallylic alcohol acetate II may come from collapse of 2,2-dichloro-1-methylcyclobutyl carbonium ion (78) arising from ring expansion upon ionization of 75 (Eq 64). Tertiary cyclobutyl cations

$$
\text{Cl} \quad \text{Cl} \quad \text{Ag}^+ \quad \text{CH}_2\text{Cl} \quad \text{Cl} \quad \delta^+ \quad \text{CH}_2\cdot\cdot\cdot\text{Cl}\cdot\cdot\cdot\text{Ag} \quad \text{Cl} \quad \text{CH}_3
$$

$$
75 \quad 78
$$

$$
\text{Cl} \quad \text{C} \quad \text{CH}_3 \quad \text{AcOH} \quad \text{-H}^+ \quad \text{Cl} \quad \text{C} = \text{O} \quad \text{CH}_3 \quad \text{CH}_2\text{OAc}
$$

II
open up to give homoallylic products when cationic stabilizing groups such as phenyl are in the 3-position, although solvolytically generated 1-methylocyclobutyl cation generally gives unrearranged material. An alternate pathway, outlined in Eq 65, similar to Eq 56, should give 1-methylocyclopropanecarboxylic acid (79) in addition to homoallylic product 77. The base soluble fraction of the solvolate has not been examined for acid 79; however a satisfactory mass balance is obtained, and since no ring reorganization has been observed in reaction of 2,2-dichlorocyclopropylmethyl chloride, it is unlikely that 77 would exhibit appreciably greater ring participation and methylene scrambling (the absence of methylene scrambling is also demonstrated in deuterium labeling experiments described presently).
The appearance of \( J_3 ^{\text{II}} \), derived from ring expansion of \( J_3 ^{\text{II}} \), demonstrates that solvolytic conditions which place appreciable charge on the carbinyl carbon can induce rearrangement in favorably substituted dihalocyclopentyldiaryl systems. Thus the failure to observe rearrangement previously may indicate that the electron deficient species in the solvolytic experiments do not have extensive positive charge on the carbinyl carbon.

Study of silver ion assisted solvolysis of 2,2-dibromocyclopropylcarbinyl systems is not indicated, for it is known that silver ion can attack both gem-dibromo- and gem-dichlorocyclopropanes to give ring opened products, presumably via cyclopropylcarbinium ions (Eq 66).

\[ \text{(66) P. S. Skell and S. R. Sandler, J. Amer. Chem. Soc., 80, 2024 (1958).} \]

66). Attack on chloride is much slower than on bromide and occurs only at elevated temperatures (150°). In this connection, it is noteworthy that no 1,3-dichloro-3-buten-1-yl acetate derivatives are observed in the 2,2-dichlorocyclopropylmethyl chloride solvolyses.
Study of silver ion assisted solvolysis of 2,2-dichlorocyclopropylcarbinyl systems has been extended to several alkyl and aryl substituted systems to delineate the factors controlling rearrangement. Thus trans-2,2-dichloro-3-phenylcyclopropylmethyl chloride, 1-chloro-1-(2,2-dichlorocyclopropyl)ethane, and 2,7,7-trichlorobicyclo-[4.1.0]heptane have been prepared and both the silver ion assisted acetolysis and simple acetolysis of each examined.

trans-2,2-Dichloro-3-phenylcyclopropylmethyl chloride (80) upon acetolysis under the conditions employed for halides 74a, 74b, and 75 above yields only trans-2,2-dichloro-3-phenylcyclopropylmethyl acetate (81) (Eq 67), identified by spectral and analytical data, and by synthesis from cinnamyl acetate and chloroform-aqueous sodium hydroxide-phase transfer catalyst; silver ion assisted acetolysis also only gives unarranged product. Thus cyclopropylcarbinyl cations with cationic stabilizing groups placed in the 3-position of the ring do not rearrange.

The effect of methyl substitution in the alpha position on the course of the solvolysis is illustrated by 1-chloro-1-(2,2-dichloro-
cyclopropyl)ethane (82). The substrate and product ester exist as
diastereomeric pairs, creating experimental complications. Prepara-
tive vpc of 82 yields apparently one diastereomer which upon aceto-
lysis gives a homogeneous ester product, 1-(2,2-dichlorocyclopropyl)-
ethyl acetate (83), identified by spectral and analytical data, and
no ring opened or ring expanded esters (Eq 68). Solvolyses of alpha-
substituted cyclopropylcarbinyl substrates do not usually show
rearrangement.

2,7,7-Trichlorobicyclo[4.1.0]heptane (84) represents an alpha
substituted 2,2-dichlorocyclopropylcarbinyl chloride with the addi-
tional element of strain introduced by the fused six-membered ring.
Acetolysis of this substrate under the general conditions yields the
known 7,7-dichlorobicyclo[4.1.0]heptane-2-yl acetate (85) (Eq 69). Nmr
investigation of the product indicates that the starting chloride has an equatorial: axial ratio of $1:7$; the product has a ratio of $9:1$. The reported assignment, based on nmr, can only be considered tentative; however, the indication is that inversion occurs. The intermediate ion may approach planarity and the predominance of the equatorial isomer may reflect thermodynamic stability; or an "$S_N^2"$ like process may be giving inversion.

The failure in general in the present study to observe products other than unarranged cyclopropylmethyl derivatives does not exclude the possibility that delocalized ions of some sort are being formed which isomerize rapidly through a series of classical or non classical structures. The product data merely require that if the ions have appreciable lifetime to equilibrate, either equilibrium favors the cyclopropylcarbinyl ion (in which case the additional structures would not be adding much stability to the ion unless via an anchimeric assistance mode) (Eq 70), and/or solvolytic capture is

\[ \text{other ions} \quad \xrightarrow{\text{Cl}} \quad \text{Cl} \quad \text{Cl} \quad \xleftarrow{\text{CH}_2^+} \quad \text{Cl} \quad \text{Cl} \quad \xrightarrow{\text{64}} \quad \text{64} \quad \text{(70)} \]

more efficient for the cyclopropylcarbinyl ion than for the alternative ions (Eq 71).
4. Deuterium labeling as a probe for degenerate cyclopropylcarbinyl rearrangement.

In order to test this hypothesis that 2,2-dihalocyclopropylcarbinyl cation, as generated solvolytically, might be in equilibrium with other ions, or exist as a non-classical ion, as the parent cyclopropylcarbinyl cation does, deuterium labeling has been employed as a probe for methylene equilibration (Eq 72).

\[ \text{products} \xrightarrow{k_1} \text{capture} \triangle \quad \overset{K}{\text{\overset{56}{\leftrightarrow}}} \quad \text{other ions} \quad \underset{k_2}{\text{\overset{\downarrow}{\text{capture}}} \quad \text{products}} \]

where \( k_1 \gg k_2 \)

\[ \text{Cl} \quad \text{Cl} \quad \overset{\text{solvolyysis}}{\xrightarrow{\text{SOM, -HX}}} \quad \text{Cl} \quad \text{Cl} \quad + \quad \text{Cl} \quad \text{Cl} \]

\[ \text{CD}_2\text{-X} \quad \text{D}_2 \quad \text{CH}_2\text{OS} \quad \text{CD}_2\text{OS} \]

\[ X = \text{OTs} \quad 88 \]
\[ = \text{Br} \quad 89 \]

Synthesis of the deuterated substrates is straightforward and is outlined in Scheme 1. Reduction of methyl 2,2-dichlorocyclopropyl-
carboxylate (86) (obtained from methyl acrylate and phenyl(trichloromethyl)mercury) with lithium aluminum deuteride in dry tetrahydrofuran gives 2,2-dichlorocyclopropylmethanol-α,α-d₂ (87). Nmr examination of 87 reveals no proton signals from the -CH₂-O group which are prominent in the spectrum of the undeuterated alcohol; the isotopic purity of 87 is > 99%. The deuterated alcohol 87 and tosyl chloride in pyridine at 0° gives the p-toluenesulfonate ester 88. Nmr again reveals no proton
resonances in the \(-\text{CH}_2\text{OSO}_2^-\) grouping.

2,2-Dichlorocyclopropylmethyl-\(\alpha,\alpha-\text{d}_2\) bromide (89) is obtained from the deuterated alcohol 87 and phosphorous tribromide in toluene at 100\(^\circ\). The isotopic purity of the carbinyl position is > 99\%, since the p.m.r. spectrum shows no resonances in the \(-\text{CH}_2\text{-Br}\) region, readily discernable in the undeuterated homolog.

2,2-Dichlorocyclopropylmethyl-\(\alpha,\alpha-\text{d}_2\) p-toluenesulfonate (88) and glacial acetic acid give only 2,2-dichlorocyclopropylmethyl-\(\alpha,\alpha-\text{d}_2\) acetate (90) (Eq 73). P.m.r. examination shows no ester methylene absorp-

\[
\text{Cl} \quad \text{Cl} \quad \frac{\text{AcCH}}{120^\circ} \quad \text{Cl} \quad \text{Cl} \quad \text{No} \quad \text{Cl} \quad \text{Cl} \quad \text{CH}_2\text{OAc}
\]

\[
(73)
\]

\[
\text{CD}_2\text{OTs}
\]

\[
\text{CD}_2\text{OAc}
\]

lications in 90. Integration of the entire spectrum also gives the calculated values (+ 3\%). When the solvolysis is conducted in a sealed n.m.r. tube and monitored by periodic scans, no transient absorption is observed in the \(\delta 4\) region. These observations preclude any methylene equilibration.

Silver acetate and 2,2-dichlorocyclopropylmethyl-\(\alpha,\alpha-\text{d}_2\) bromide (89) in acetic acid at 100\(^\circ\) give similar results; only 2,2-dichlorocyclopropylmethyl-\(\alpha,\alpha-\text{d}_2\) acetate (90) is obtained (Eq 74). When the reaction is carried out at 100\(^\circ\) for 12 hr, bromide 89 is about one-half
consumed. Vpc separation of the product ester 20 and unreacted bromide 89 and pmr examination of each shows no protons in the carbinyl position.

It is concluded, under the specified solvolytic conditions, no methylene equilibration of the type observed by Mazur, Roberts, et al. in cyclopropylcarbinyl systems is taking place. This indicates that either (a) the 2,2-dichlorocyclopropylcarbinyl cation generated solvolytically not only maintains the cyclopropylcarbinyl structure but is not in equilibrium with other carbocations (Eq 70, 71) or (b) the solvolysis process does not yield a strongly electron deficient carbinyl carbon, i.e. the transition state is more 'S_N2' like than in the parent studied by Roberts. As kinetic experiments to be described presently indicate, 2,2-dihalocyclopropylcarbinyl systems are deactivated with respect to the parent cyclopropylcarbinyl system; this may be evidence that the solvolysis process does not yield a strongly electron deficient carbinyl carbon.
5. Deamination

In order to generate more electron deficient carbinyl carbon, deamination of 2,2-dichlorocyclopropylmethylamine \( (91) \) was examined (Eq 75). 2,2-Dichlorocyclopropylmethylamine \( (91) \) in 0.3% aqueous hydrochloric acid solution at 0° and sodium nitrite give 2,2-dichlorocyclopropylmethanol \( (90) \) and 2,2-dichlorocyclopropylmethyl chloride \( (74b) \) \( (6\%) \) (Eq 74, \( S=H, X=\text{Cl}^- \) ) in overall yields of 45-55%; no other significant products are obtained, although high amplification vpc reveals traces of other materials \( (<0.5\% \text{ wt each}) \). This observation also excludes capture by nitrite to yield products containing \(-\text{ONO} \) or \(-\text{NO}_2 \) groups. 2,2-Dichlorocyclopropylmethyl chloride \( (74b) \) is identified by retention time and g.c.-mass spectroscopy; the alcohol \( (90) \) is identical (ir, nmr) with authentic material prepared elsewhere in this work, and is homogeneous on SE-30, Carbowax 20M, and FFAP.

2,2-Dichlorocyclopropylmethylamine \( (91) \) is not stable, as might be expected for a halo primary amine; even in the absence of air the amine rapidly turns black and a red crystalline precipitate forms. It is
convenient to store the amine as its hydrochloride, then free it by treatment with base and subject the free amine to preparative vpc (5% Carbowax 20M/5% KOH) immediately before use; in this fashion pure amine is obtained for deamination studies. The failure to recognize the instability of the amine may have led to the earlier report that an 'unidentified product' was formed in 4-18% yield by weight of the alcohol or acetate in a series of deaminations under equivalent conditions to those employed here.

Additional examination of the deamination reaction of in acetic acid failed to turn up any unexplainable products. Indeed, the amine acetate in acetic acid gives upon diazotization (addition of sodium nitrite) solely the cyclopropylcarbiny1 acetate (Eq 75, S = Ac, X = AcCl^-). The overall yield of in acetic acid, determined by internal standards (toluene and bromobenzene) is 55 ± 1%. Some of the product may be lost through solubility in the aqueous extract, since careful backwashing raises the apparent yield 10%.

Deamination of the parent compound, cyclopropylmethylamine, has been investigated via radioactive carbon labeling. It is informative to compare the results of that study with the present observations. The products in the parent system show extensive scrambling of the methylene carbons (Eq 76), although not so extensive as upon solvolysis of the chloride. It seems reasonable that the intermediate diazonium ion places similar charge demands upon the carbiny1 carbon, whether the
ring is halogenated or not. Since in the present case no rearranged products are observed, it appears that the 2,2-dihalocyclopropyl ring cannot participate in the same fashion as a normal cyclopropyl ring can with an adjacent electron deficient site. The following summary of deamination reactions indicates understanding of such reactions is not complete and further interpretation of the present results is uncertain.

Treatment of amines with nitrosating agents leads to loss of nitrogen and products formally derived from carbonium ions (Eq 77):

\[
\begin{align*}
\text{R-NH}_2 & \xrightarrow{\text{HONO}} [\text{R}^+] & \xrightarrow{\text{SH}} \text{R-S, olefins} \\
\end{align*}
\]

a recent summary (without references) has appeared. Presumably a

carbocation. The products obtained often differ significantly from those resulting from simple solvolysis. Thus n-propyl tosylate

\[ \text{CH}_2\text{NH} + \text{HONO} \rightarrow \text{OAc} \text{CH}_2\text{NH} \quad + \quad \text{OAc} \text{CH}_2\text{NH} \]

\[ \text{30\%} \quad \text{70\%} \]

shows very little rearrangement when solvolyzed in acetic acid, while \(\text{n}-\text{propylamine gives 30\% 2-propyl acetate (Eq 78).}\)

\[ \text{CH}_2\text{OTs} \quad + \quad \text{OAc} \text{CH}_2\text{OTs} \]

\[ \text{2.8\%} \quad \text{97\%} \]

One suggestion offered to explain this difference is that the carbocation formed is "hot," i.e. more energetic (poorly solvated) than the ion resulting from conventional solvolysis. This hypothesis


91 (a) J. D. Roberts and J. A. Yancey, J. Amer. Chem. Soc., 74, 5943 (1952); (b) J. D. Roberts and C. M. Regan, ibid., 75, 2069 (1953); (c) J. D. Roberts and M. Halmann, ibid., 75, 5759 (1953); (d) J. D. Roberts and J. A. Yancey, ibid., 77, 5558 (1955).
fails to explain the stereospecific nature of many deaminations since the carbonium ion center should approach planarity; for example, the cyclohexyl system gives ring contraction, but its geometric isomer yields cyclohexanone (Eq 79). The intermediate diazonium ions and were proposed to account for this stereospecificity. It should be pointed out, however, that many carbonium ions exhibit 'memory effects'.
More recently, an ion pair mechanism has been advanced in an attempt to unify the previous theories. Hence, 1-, 2-, 3-, and 4-octylamines were deaminated and the results interpreted in terms of simultaneous C-N and N-X (X = OH, i.e. RN\(_2\)OH from RNH\(_2\) + HONO via RNHNO\(_2\) X = OCOR from RN(NO)COR via a cyclic intermediate, etc.) bond breaking to give a nitrogen separated ion pair, followed by rather rapid capture of the ion before extensive molecular rotation takes place. It has also been advanced that the stereochemistry of deamination is affected by the orientation of the reacting molecules on a micelle interface.

6. Friedel-Crafts reactions
   a. Antimony pentachloride in benzene

   In order to generate still more electron deficient carbyl carbon adjacent to the 2,2-dihalocyclopropyl moiety and to see if rearrangement occurs, several 2,2-dichlorocyclopropylmethyl halides have been treated with Friedel-Crafts catalysts.
2,2-Dichlorocyclopropylmethyl bromide (74c), or better 2,2-dichlorocyclopropylmethyl chloride (74b) with antimony pentachloride in benzene gives primarily 1,1-dichloro-3-phenyl-1-butene (101) (Table 3); (Eq 80). This could arise via a simple ring opening process to

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{SbCl}_5 & \quad \text{Cl} \\
\text{CH}_2\text{X} & \quad \text{Cl} \\
\text{Cl} & \quad \text{SbCl}_5 \\
\end{align*}
\]

\[X = \text{Br} \quad 74a \quad 99 \quad 58 \]

\[X = \text{Cl} \quad 74b \]

\[
\begin{align*}
\text{Cl} & \quad -\text{Cl} \\
\text{PhH} & \quad \text{Cl} \\
\text{H}^+ & \quad \text{Cl} \\
\end{align*}
\]

\[100 \quad 101 \]

give a homoallylic ion 58 which then rearranges to an allylic ion 101 before capture by benzene (Eq 80).

The initial ionization is the conventional interpretation of attack on halides by Friedel-Crafts reagents. The ring opened ion 58 might, in addition to rearrangement, undergo recapture of Cl\(^-\) to give 4,4,4-trichloro-1-butene (102) (Eq 81); react with benzene to yield 4,4-dichloro-4-phenyl-1-butene (103) (Eq 82); or eliminate a proton to
### Table 3

Reactions of Antimony Pentachloride in Benzene with 2,2-Dichlorocyclopropylmethyl Chlorides

<table>
<thead>
<tr>
<th>cyclopropylcarbinyl halide</th>
<th>equivalents SbCl₅</th>
<th>% reaction</th>
<th>Products (mole ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂Cl₂CH₂Cl</td>
<td>0.2</td>
<td>47</td>
<td>H₃C-CH₂H-C=CCl₂ (63) + Ph₂CHCH₃ (4) + Ph₂C=CH₂ (1)</td>
</tr>
<tr>
<td>Cl₂Cl₂CH₃</td>
<td>0.5</td>
<td>71</td>
<td>H₃C-CH₂H-C=CCl₂ (46) + Ph₂CHCH₃ (43) + Ph₂C=CH₂ (10)</td>
</tr>
<tr>
<td>Cl₂Cl₂CH₂Cl</td>
<td>0.125</td>
<td>53</td>
<td>Cl₂C=C&lt;CH₂CH₂CH₂Cl (51) + Cl₂C=C&lt;CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>+ Ph₂CHCH₃ (15) + Ph₂C=CH₂ (4)</td>
</tr>
<tr>
<td>Cl₂Cl₂CHCl₃</td>
<td>0.125</td>
<td>75</td>
<td>Non Volatile Tars</td>
</tr>
<tr>
<td>Cl₂Cl₂CH₂Cl₂</td>
<td>0.125</td>
<td>88c</td>
<td>Cl₂C=C&lt;CH₂CH₂CH₂CH₃ (65) + Cl₂C=C&lt;CH₂CH₂CH₃ (35)</td>
</tr>
</tbody>
</table>

*aBased on vpc analysis of starting material after 1 hr at room temperature (25°C). bNormalized % calculated from weight ratios determined by vpc. cAt 0°C.
Table 4

Summary of Fate of Substituted 2,2-Dichlorocyclopropylcarbinyl Cations Generated Under Various Conditions

<table>
<thead>
<tr>
<th>Cyclopropylcarbinyl halide</th>
<th>Conditions</th>
<th>AcOH/NaOAc</th>
<th>AcOH/AgOAc</th>
<th>SbCl₅/PhH</th>
<th>AlCl₃/PhH</th>
<th>AlCl₃/CH₃NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₃Cl</td>
<td>no rearrangement</td>
<td>no</td>
<td>ring opening</td>
<td>extensive degradation</td>
<td>no rearrangement</td>
<td></td>
</tr>
<tr>
<td>CH₂Br</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl₂Cl</td>
<td>no rearrangement</td>
<td>no</td>
<td>ring opening</td>
<td>extensive degradation</td>
<td>degradation; no rearrangement</td>
<td></td>
</tr>
<tr>
<td>CH₂Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl₂Cl</td>
<td>no rearrangement</td>
<td>99% expansion</td>
<td>ring opening and ring expansion</td>
<td>ring expansion and degradation</td>
<td>ring opening degradation</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₂Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclopropylcarbinyl halide</td>
<td>AcOH/NaOAc</td>
<td>AcOH/AgOAc</td>
<td>SbCl$_5$/PhH</td>
<td>AlCl$_3$/PhH</td>
<td>AlCl$_3$/CH$_3$NO$_2$</td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>------------</td>
<td>------------</td>
<td>--------------</td>
<td>--------------</td>
<td>---------------------</td>
<td></td>
</tr>
<tr>
<td>Cl $\equiv$ Cl</td>
<td>no rearrangement</td>
<td>no rearrangement</td>
<td>ring opening and ring expansion</td>
<td>ring opening</td>
<td>no expansion degradation</td>
<td></td>
</tr>
<tr>
<td>Cl $\equiv$ Cl</td>
<td>no rearrangement</td>
<td>decomposition</td>
<td>decomposition</td>
<td>decomposition</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Cl $\equiv$ Cl</td>
<td>no rearrangement</td>
<td>no rearrangement</td>
<td>--</td>
<td>--</td>
<td>no rearrangement degradation</td>
<td></td>
</tr>
<tr>
<td>Cl $\equiv$ Cl</td>
<td>no rearrangement</td>
<td>no rearrangement</td>
<td>--</td>
<td>--</td>
<td>no rearrangement degradation</td>
<td></td>
</tr>
</tbody>
</table>
give 1,1-dichloro-1,3-butadiene (104) (Eq 83).

No 102 is observed, which can reasonably be explained on the expectation that the gem-trihalide is considerably more reactive towards the catalyst than is the starting primary halide. Hence, capture may occur, but reionization would be rapid and the back reaction would predominate (Eq 80). The failure to observe 103 (Eq 81) may be due to either the reactivity of this hypothetical product or to the rapidity
of rearrangement of 58 to 100 (Eq 79). Both the terminal primary olefin structure and the α,α-dichlorobenzyl link in 103 are expected to be exceptionally sensitive to the reaction conditions, presumably yielding high molecular weight products. Some non-volatiles are obtained, but certainly the chief pathway is via ion 100.

Diene 104 could be an intermediate in the rearrangement of 58 to 100 (Eq 84). This rearrangement is also formally a 1,3 sigmatropic migration of H to the terminus of the π system. Such rearrangements must take place antarafacially and are therefore not probable. The assistance of the empty p orbital may facilitate the migration, although it would be predicted a priori that such a suprafacial migration would still be forbidden (Eq 85).
By analogy to the well documented cyclopropylcarbiny1-cyclobutyl interconversion, alternative pathways can be visualized for product formation. Ring expansion might take place and the cyclobutyl carbonium ion(s) 60 and 64 resulting collapse and rearrange to ion 100 (Eq 86).

Another pathway is suggested by the known methylene equilibration in unsubstituted cyclopropylcarbiny1 systems. The carbiny1 methylene could dance around the ring in a manner akin to that proposed for the parent system, followed by homoallylic ring opening (Eq 87, where 65 represents the delocalized ion proposed for the parent system by Wiberg).
In order to determine which of these possible routes (Eq 80, 86, or 87) might be operating, the degeneracy of the system was lifted by methyl substitution. Thus 2,2-dichloro-1-methylcyclopropylmethyl chloride (75) was reacted with antimony pentachloride in benzene and the principle products found to be 1,1,4-trichloro-2-methyl-1-butene (105) and 1,1-dichloro-3-methyl-3-phenyl-1-butene (106) (Eq 88).

It is evident that 106 cannot be formed by routes similar to Eq 86b (Eq 89) or 87 (Eq 90), because this would result in 1,1-dichloro-2-methyl-3-phenyl-1-butene (107). The product must arise via routes
similar to Eq 86ad (Eq 91) (expansion then opening), Eq 85ae (Eq 92) (direct opening), or Eq 80 (Eq 93). The 1,1,4-trichloro-2-methyl-1-butene (105), an unexpected rearrangement product, by contrast must come about through the pathways outlined in Eq 89 and 90. The proof of structure of 105 is discussed later (vide infra).
The question immediately arises why does not 105 react to give 1,1-dichloro-2-methyl-3-phenyl-1-butene (110). In a separate experiment, 105 and antimony pentachloride in benzene under the same conditions as 75 in Eq 88 are found to be unreactive (Eq 94). Since it is
postulated that \textsuperscript{105} arises from capture of the homoallylic ion \textsuperscript{108} before rearrangement (Eq 89 and 90), it might be asked why this ion \textsuperscript{108} does not also capture benzene to yield 1,1-dichloro-2-methyl-4-phenyl-1-butene (\textsuperscript{114}). It must be concluded that capture by chloride is much faster than irreversible attack on an aromatic system. Since the 2,2-dichlorocyclopropylmethyl chlorides react with antimony pentachloride under conditions in which the primary homoallylic chloride \textsuperscript{105} does not, it is evident that the 2,2-dichlorocyclopropyl ring is accelerating this reaction, in contrast to the solvolytic reactions where the ring deactivates toward solvolytic attack (vide infra).

The origin of \textsuperscript{105} is best explained on the basis that cyclopropylcarbiny1 systems with cationic stabilizing groups in the 1-position on the ring tend to expand under solvolytic conditions to give almost exclusively cyclobutyl products.\textsuperscript{24} Thus, Eq 90 is the anticipated route for formation of \textsuperscript{105}.

Further evidence has been obtained relative to these possible reaction pathways by employing 1-chloro-1-(2,2-dichlorocyclopropyl)ethane (\textsuperscript{115}) as substrate. Antimony pentachloride and \textsuperscript{115} in benzene
give 1,1-dichloro-3-phenyl-1-pentene (116) and 2-methyl-1,1,3-tri-
chlorocyclobutane (117) (Eq 95).

\[ \text{SbCl}_5/\text{PhH} \]

These observations allow exclusion of the pathway outlined in Eq
86ad. Thus the ring opening to give ions which can be captured by
benzene must occur by one of the two routes below (Eq 96 and 97). No
labeling experiment can distinguish between these two routes, since
the cyclobutyl cation will be puckered and maintain its geometry. In

\[ \text{SbCl}_5/\text{PhH} \]

\[ \text{SbCl}_5/\text{PhH} \]
the parent (unhalogenated) system theoretical calculations have been employed to shed light on this point.

The cyclobutane can be rationalized by capture of the intermediate ion 118. The halide would be reactive under the conditions employed generally, but the greater reactivity of the secondary halide 115 permits reaction with antimony pentachloride under slightly milder conditions than employed for the other substrates.

b. Aluminum chloride in benzene.

It had earlier been reported tentatively² that 2,2-dichlorocyclopropylmethyl bromide (74a) and aluminum chloride yields 3-methyl-2-phenylindene and 2,3-diphenyl-1,3-butadiene. Although aluminum chloride is generally a more powerful Friedel-Crafts catalyst than is antimony pentachloride, it seemed unlikely that the course of reaction of 2,2-dichlorocyclopropylcarbinyll halides should change so drastically with this variation of catalyst. Hence the system has been reexamined.

2,2-Dichlorocyclopropylmethyl bromide (74a) and aluminum chloride (0.4 equivalent) in warm benzene give 1,1-diphenylethane (122) and 1,1-diphenylethene (123) in a ratio of 5:1 in 48-61% yield (Eq 98). The

\[ \text{Cl} \quad \text{Cl} \quad \text{CH}_2\text{Br} \quad \overset{\text{AlCl}_3}{\text{PhH}} \rightarrow \quad \text{Ph} \quad \text{HC} - \text{CH}_3 \quad + \quad \text{Ph} \quad \text{C} = \text{CH}_2 \quad (98) \]
assignments are unequivocal and based on chemical, spectral, and vpc comparison with authentic materials. The non-volatile residue may consist of dimers and telomers.

(97) Examination of the spectral and physical values in the original report for 3-methyl-2-phenylindene and 2,3-diphenylbutadiene shows them to be identical to those of 1,1-diphenylethane and 1,1-diphenylethene. The nmr data cannot be interpreted correctly in terms of the indene and butadiene. Most notably in the indene, the vinyl hydrogen should exhibit a distinct resonance separate from the aromatic absorptions as calculated from "group contribution values." Also CH-CH would not appear as a quartet, but would exhibit additional splitting ca 2 Hz from the allylic hydrogen in the indene system. For the butadiene, the terminal proton olefin resonance should not appear as a singlet, because of the differing environments of the cis and trans hydrogens.


Direct vpc examination of the quenched reaction mixture shows the presence of 1,1-dichloro-3-phenyl-1-butene (101), identical in retention time to that isolated from the antimony pentachloride catalyzed reaction discussed earlier in this work. Dichlorobutene 101 and aluminum chloride (Eq 99) in benzene give 1,1-diphenylethane (122) and 1,1-diphenylethene (123) in good yield under conditions equivalent to those for the 2,2-dichlorocyclopropylcarbiny1 reaction (Eq 98). Thus dichlorobutene 101 may be an intermediate in the conversion of 74 to
$\text{Cl}_2\text{C}^\equiv\text{CH}_2\text{CHCH}_3\begin{array}{c}
\text{AlCl}_3
\end{array}\begin{array}{c}
\text{PhH}
\end{array}\begin{array}{c}
x_2 + x_3
\end{array}$

Equation 99

122 and 123 in benzene as catalyzed by aluminum chloride (Eq 98).

Extension of the reactions with aluminum chloride to additional substrates reveals anticipated trends. 2,2-Dichlorocyclopropylmethyl chloride (74b) is more reactive than the bromide, but the products are the same. 2,2-Dichloro-1-methylcyclopropylmethyl chloride (75) yields: starting material (2.2%); 1,1,4-trichloro-2-methyl-1-butene (105) (20.8%); 1,1-diphenylethane (122) (9.9%); 1,1-diphenylethene (123) (2.3%); and 2,2-diphenylpropane (125) (17.3%) (Eq 100).
Compounds 105, 122, 123, and 124, respectively, exhibit the same vpc retention times and nmr spectra as materials prepared earlier in this work. 2,2-Diphenylethane is identified from its pmr spectrum; the mp and refractive index agree well with reported values (see Experimental Section).

The details of the reaction of 2,2-dichlorocyclopropylmethyl halides with aluminum chloride-benzene are not clear. Since 1,1-dichloro-3-phenyl-1-butene (101) is apparently an intermediate in the conversion of 74 to 122 and 123 (Eq 98), it may be cleaving via a $\beta$-scission process to yield eventually the products. Thus dichloro-

\[ 100 \]

carbenium ion 126 might be generated from 101 under strongly acidic conditions. $\beta$-Cleavage would give ion 127 and vinylidene chloride (128) (Eq 101). Both 127 and 128 are known to form 122 and 123, respectively under the reaction conditions. Hence 128 in benzene with aluminum

\[ 101 \xrightarrow{H^+} \begin{array}{c} \text{H} \\ \text{Cl} \end{array} + \begin{array}{c} \text{CH}_3-\text{C}=\text{CH}_2-\text{C}^+ \\ \text{Ph} \end{array} \rightarrow \begin{array}{c} \text{H} \\ \text{Cl} \end{array} + \begin{array}{c} \text{CH}_3-\text{CPh} \\ + \end{array} \begin{array}{c} \text{H}_2\text{C}=\text{CCl}_2 \end{array} \] (101)

126 127 128
chloride gives $\text{123}$ and its dimer $\text{129}$ (Eq 102). Ion $\text{127}$ is a pre-


sumed intermediate in Friedel-Crafts reaction of o-chloroethylbenzene

$$\text{122}$$

$$\text{123}$$

$$\text{129}$$

with aluminum chloride in benzene to yield 1,1-diphenylethane ($\text{122}$) (Eq 103).


$$\text{127}$$

Alternatively, aluminum chloride might attack the vinylidene chloride moiety in $\text{101}$ to form ion $\text{130}$ which undergoes $\beta$-scission to
protonated styrene \( \text{127} \) and chloroacetylene \( \text{131} \) (Eq 104). Reaction

\[
\begin{align*}
\text{H} & \quad \text{AlCl}_3 \quad \text{H} \\
\text{CH}_3-C-\text{CH}=\text{CCl}_2 & \quad \rightarrow \quad \text{CH}_3-C-\text{CH}+ \\
\text{Ph} & \quad -\text{AlCl}_4^- \\
\text{101} & \quad \rightarrow \\
\text{130} & \quad + \quad \text{CH}_3\text{CHPh} \quad + \quad \text{HC}≡\text{C}-\text{Cl} \\
\end{align*}
\]

(104)

of ion \( \text{127} \) with benzene would give \( \text{122} \) (Eq 103). Acetylene \( \text{131} \) might add hydrogen chloride to form vinylidene dichloride \( \text{128} \), which then yields \( \text{129} \) (Eq 102). This second reaction pathway seems less likely than the first (Eq 100), particularly since the reaction of 1-chloro-1-(2,2-dichlorocyclopropyl)ethane, which has the \(-\text{CH}=\text{CCl}_2\) structure but not the \(\text{CH}_3\text{CHPh}\)- group after ring opening and rearrangement, does not yield any \(\text{1,1-diphenylethane (122)}\) or \(\text{1,1-diphenylethenene (123)}\).

Excess (> 1 equivalent) aluminum chloride in benzene and gem-dihalocyclopropanes substituted with simple alkyl groups do give indenes. \(^{103,104}\) Thus \(\text{1,1-dichloro-1,1,3,3-tetramethylcyclopropane (132)}\)

---


yields 1,2,3,3-tetramethyldiene (133) (Eq 105). In light of this

observation, in the present investigation 2,2-dichlorocyclopropylmethyl bromide (74a) has been treated with 1.5 equivalents of aluminum chloride in benzene. The major products are still 122 and 123. If indanes are formed, they are present only in low yield.

In addition to antimony pentachloride and aluminum chloride several other Friedel-Crafts catalysts have been examined. Fused zinc chloride and cupric chloride fail to give any reaction with 74a in refluxing benzene. Antimony pentafluoride gives a purple solution with 2,2-dichlorocyclopropylmethyl bromide (74a) in benzene, but when employed in 0.1 equivalent quantities, little reaction is observed after prolonged reflux.

c. Aluminum chloride in nitromethane.

Aluminum chloride in nitromethane is a mild Friedel-Crafts catalyst; furthermore, the organic halide can be studied in the absence of capturing solvent. Thus the reactions of several 2,2-dichlorocyclopropylmethyl chlorides in nitromethane-aluminum chloride have been examined.
2,2-Dichloro-1-methylcyclopropylmethyl chloride (T5) is converted by aluminum chloride in nitromethane to an isomer (Eq 106). About 50% material is isolated after work-up, containing some T5 and an isomer thereof. A red-black polymer is also formed. Spectral data (IR, NMR) do not clearly distinguish between two possibilities, 1,2,2-trichloro-1-methyleclobutane and 1,1,4-trichloro-2-methyl-1-butene (105). Other isomers, such as 1,1,3-trichloro-3-methyl-1-butene, can be excluded on the basis of the NMR spectrum, which exhibits no vinyl absorption, has a singlet methyl absorption, and shows a \(-\text{CH}_2-\text{CH}_2-\) link uncoupled with any other hydrogens. The structure of the product is proven to be butene 105 by its conversion to 4,4-dichloro-3-methyl-3-buten-1-y1 acetate (II) (unambiguously prepared elsewhere in this work) by reaction with acetic acid-silver acetate.

Only with 2,2-dichloro-1-methylcyclopropylmethyl chloride (T5) has it been possible to obtain rearranged material. 2,2-Dichlorocyclopropylmethyl chloride (T4a), 2,2-dichloro-3-phenylcyclopropylmethyl chloride (80), 1-chloro-1-(2,2-dichlorocyclopropyl)ethane (82), 1,2,2-trichlorocyclopropylmethyl chloride (119), and 2,7,7-trichloro-
bicyclo[4.1.0]heptane (84) give upon work-up only starting material and black polymer; vpc examination only shows traces of other products. Nmr examination of the recovered starting material confirms no isomerization has taken place.

In order to obtain tractable products from the aluminum chloride-nitrobenzene reaction, alkyl substitution in the 1-position is apparently imperative. As noted, substitution in the 1-position favors ring expansion; the resulting 1-alkyl-2,2-dichlorocyclobutyl cation 134 could then undergo collapse to the homoallylic ion 135 which, upon chloride capture, gives the product 136 (Eq 107). This is equivalent to the mechanism proposed in this study for the silver ion assisted

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{R} & \quad \text{CH}_2\text{Cl} & \quad \text{Cl} & \quad \text{R} \\
\text{Cl} & \quad \text{CH}_2\text{Cl} & \quad \text{Cl} & \quad \text{AlCl}_3
\end{align*}
\]

(107)

\[
\begin{align*}
\text{Cl} & \quad \text{C} \quad \text{Cl} & \quad \text{AlCl}_4 & \quad \text{Cl} & \quad \text{C} \quad \text{R} \\
\text{R} & \quad \text{AlCl}_4 & \quad \text{Cl} & \quad \text{C} \quad \text{CH}_2\text{Cl}
\end{align*}
\]
acetolysis rearrangement (Eq 64). In a control experiment, 1,1,4-
trichloro-2-methyl-1-butene (105) was found to be almost unreactive
under the experimental conditions (Eq 108). Therefore 105 is not in
equilibrium with 75.

\[
\begin{align*}
\text{Cl} & \quad \text{C} = \text{C} \quad \text{CH}_3 \\
\text{Cl} & \quad \text{CH}_2 - \text{CH}_2 \text{Cl}
\end{align*}
\]

\[
\text{AlCl}_3 \quad \text{CH}_3 \text{NO}_2 \quad \text{N.R.} \quad (108)
\]

By contrast, without substitution in the 1-position ring expansion apparently does not occur. In these cases it is suggested that
the major process is direct homoallylic ring opening to give material
which polymerizes under the reaction conditions.

A study of the reaction of cyclopropylmethyl chloride (137) in
nitromethane-aluminum chloride has been reported. The results were

(105) G. A. Olah and Chi-Hsiung Liu, J. Amer. Chem. Soc., 90, 6468
(1968).

interpreted in terms of a bimolecular attack on AlCl$_4^-$ on the halide
which was partially ionized by attack of the catalyst on the halogen.
Products obtained were cyclobutyl chloride, 4-chloro-1-butene (139),
and polymer (Eq 109). These observations can be correlated with the
present results if it is assumed that (consistent with previous
observations in this study) the 2,2-dichlorocyclopropylcarbinyl
cation does not ring expand as readily as the unsubstituted cyclo-
propylcarbinyl ion.

7. Summary

In summary, 2,2-dichloro- and 2,2-dibromocyclopropylcarbinyl
derivatives do not rearrange under normal solvolytic conditions. The
1-alkyl-2,2-dichlorocyclopropylcarbinyl system does undergo significant
ring expansion under sufficiently severe solvolytic conditions. Power-
ful Friedel-Crafts catalysts do result in ring enlargement and ring
opening. The 2,2-dihalocyclopropylcarbinyl cation generated under
these Friedel-Crafts conditions does not, however, exhibit a lifetime
sufficient for capture; only ring opened products are observed, and
in one instance, a ring expanded cyclobutyl derivative.

B. Monobromocyclopropylcarbinyl substrates

At this juncture, it is logically asked what is the effect of a
single bromine or chlorine substituted on the ring on the course of
solvolysis of cyclopropylcarbinyl systems. Would one halide be suffi-
cient to prevent rearrangement in those reactions which can involve
significant positive charge on the carbinyl atom?

Further, separate solvolysis of the cis and trans isomers might yield valuable information about the stereochemistry of possible ring opening. If ring opened product retained stereochemistry, this would provide evidence that the halo-deactivated ring may still participate with an electron deficient site in a manner similar to that of the unsubstituted ring.

1-Halocyclopropylcarbinyl derivatives are also of interest. Despite the deactivating effect, expansion might be favored by the ability of halide to stabilize a positive charge on an alpha carbon atom.

Kinetic studies of the solvolysis of the cis-2-, trans-2-, and 1-halocyclopropylcarbinyl derivatives will be of special interest, since such studies should permit evaluation of the steric effects, and through space and through bond inductive electronic effects of the halo group on a cyclopropane ring. The 1-halo substrates will be of interest in these kinetic studies to evaluate the resonance interaction of the halo group with the cyclopropane ring, particularly since it has been suggested that the resonance interaction of substituent groups in the cyclopropylcarbinyl cation are small and even less in the 1-position than in the 2-position.

Determinations of the pKa's of the corresponding 1- and 2-halo-
cyclopropanecarboxylic acids should yield information confirmative of and in part complementary to the kinetic studies.
In order to undertake such studies, it would be desirable to prepare pure cis and trans isomers of the 2-halocyclopropylcarbinols as well as the 1-halocyclopropylcarbinols and the corresponding cyclopropanecarboxylic acid of each carbinol.

Initial interest was focused on solvolytic displacements of 1-bromocyclopropylcarbinyl systems. 1-Bromocyclopropylmethanol (142) has been previously prepared from methylenecyclopropane and hypobromous acid. Although this route to 142 is attractive because of the recent observation that methylenecyclopropane can be obtained in good yield from methallyl chloride and sodium hydride, 1-bromocyclopropanecarboxylic acid 141 is also needed in this research. Since both 141 and 142 are desired, the Hunsdiecker reaction has been utilized to prepare ethyl 1-bromo-1-cyclopropanecarboxylate. The route is similar to that for synthesis of ethyl cis/trans-2-bromo-1-cyclopropanecarboxylates. Thus partial saponification of diethyl 1,1-cyclopropanedicarboxylate (readily available from diethyl malonate and 1,2-dibromoethane), preparation of mercuric 1-carboxethoxy-1-

cyclopropanecarboxylate, and reaction of the mercuric salt with bromine gives ethyl 1-bromocyclopropanecarboxylate (140). Saponification of 140 and acidification yields 1-bromocyclopropanecarboxylic acid (141); reduction of 140 gives 1-bromocyclopropylmethanol (142), which is converted by tosyl chloride to p-toluenesulfonate 143.

The routes to 141 and 143 are outlined in Scheme 2.

Figure 2: Scheme 2

\[
\begin{align*}
\text{CO}_2\text{Et} & \xrightarrow{\text{1/ saponification}} \text{CO}_2\text{CO}_2\text{Et} \\
& \xrightarrow{\text{H}^+} \text{CO}_2\text{CO}_2\text{Et} \\
& \xrightarrow{1) \text{HgO}} \text{Br} \\
& \xrightarrow{2) \text{Br}_2} \\
\end{align*}
\]

\[
\text{LAH} \xrightarrow{\text{THF}} 1) \text{KOH} \xrightarrow{2) \text{H}^+} \\
\]

\[
\begin{align*}
\text{Br} \xrightarrow{\text{TaCl}} \text{CH}_2\text{OTs} & \xrightarrow{\text{pyridine}} \text{Br} \\
& \xrightarrow{\text{CH}_2\text{OH}} \text{Br} \\
& \xrightarrow{\text{CO}_2\text{H}} \\
\end{align*}
\]
Acetolysis of 1-bromocyclopropylmethyl p-toluenesulfonate (143) gives, upon work up, primarily cyclobutanone (144); in addition 1-bromocyclopropylmethyl bromide (145); 1-bromocyclopropylmethyl acetate (146), and 3-bromo-3-butene acetate (147) are formed. The results are summarized in Table 5.

### Table 5
Acetolysis of 1-Bromocyclopropylmethyl p-Toluene-

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Product 144</th>
<th>Product 145</th>
<th>Product 146</th>
<th>Product 147</th>
</tr>
</thead>
<tbody>
<tr>
<td>96% AcOH</td>
<td>60.1</td>
<td>24.9</td>
<td>13.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Glacial AcOH</td>
<td>62.1</td>
<td>16.1</td>
<td>18.8</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The products of acetolysis of 143 can be understood in terms of the following Scheme 3. Cyclobutanone (144) is believed to arise from the unobserved 1-bromocyclobutyl acetate (151) via hydrolysis and loss of hydrogen bromide. In 96% acetic acid hydrolysis of 151 takes place during the solvolysis, releasing bromide ion which would capture the 1-bromocyclopropylcarbiny1 cation (148) to give 1-bromocyclopropyl-bromide (145). Bromide 145 could also arise from direct displacement on 143 and/or 146 by bromide ion. Anhydrous conditions should suppress
Figure 3: Scheme 3

\[ \text{CH}_2\text{OTs} \]  \( \rightarrow \)  \[ \text{CH}_2^+ \]  \( \text{Br} \]  \( \text{Br} \]  

\[ \text{Br} \]  \( \text{CH}_2\text{Br} \]  \( \text{Br} \]  

\[ \text{AcOH} \]  \( \text{H}^+ \)  \( \text{AcOH} \)  \( \text{OAc}^- \)  \( \text{H}_2\text{O} \)  \( \text{OH} \)  

\[ \text{Br} \]  \( \text{Br} \]  \( \text{OH} \)  \( \text{OAc} \)  

\[ \text{Br} \]  \( \text{CH}_2\text{OAc} \]  \( \text{Br} \]  

\[ \text{Br} \]  \( \text{HBr} \)  

\[ \text{AcOH} \]  \( \text{H}^+ \)  

\[ \text{CH}_2\text{Br} \]  \( \text{Br} \]  

\[ \text{CH}_2\text{OAc} \]  

\[ \text{Br} \]  \( \text{OAc} \)
the formation of bromide ion (preventing the hydrolysis of 151 to 152 which loses hydrogen bromide); under such conditions the yield of 145 should be very low. Acetolysis of 143 in glacial acetic acid, although not under strictly anhydrous conditions, clearly shows this trend (Table 5). The other products, 146 and 147, are expected from capture of the unrearranged ion 148 and homoallylic opening of 148 preceding capture, respectively.

The product ratios from acetolysis of 143 are of considerable interest. Placement of a cationic stabilizing group in the 1-position on the ring of a cyclopropylcarbinyl system usually favors ring expansion; in acetic acid either Ph- or CH3- substituents lead to exclusive formation of cyclobutyl derivatives. The parent cyclo-

---


---

propylcarbinyl cationic system generally shows 50-74% unrearranged products. Hence, the bromo group in 1-bromocyclopropylcarbinyl systems is favoring ring expansion, although not as strongly as a methyl or phenyl. The product derived from homoallylic ring opening is minor, as in the alkyl and aryl substituted cases.

Homoallylic acetate 147 is present only in small amounts, making confirmation of structure difficult (initial assignment was made on the basis of nmr and ir, neither of which have been previously reported)};
hence synthesis of \(147\) was undertaken via the reported route.\(\text{111,112}\)


2,4-Dibromo-1-butene (from potassium hydroxide and 1,2,4-tribromobutane) and potassium acetate in acetic anhydride were reported to give \(147\).\(\text{111}\) Subsequently, it was stated that the reaction could be carried out in one step, heating 1,2,4-tribromobutane with potassium acetate in acetic anhydride; the high boiling by-product was assigned the structure 1,2,4-triacetoxybutane.\(\text{112}\) In this study repetition of this one pot reaction yielded six major products; they were, in order of retention time on SE-30, 3-bromo-3-butyl-1-yl acetate (\(147\)), trans-4-bromo-3-butyl-1-yl acetate (\(148\)), cis-4-bromo-3-butyl-1-yl acetate (\(149\)), 2-butene-1,4-diyl diacetate, dibromobutyl acetate, and butanetriyl triacetate (Eq 110). Only the 3- and 4-bromo acetates (\(147-149\))

\[
\begin{align*}
\text{Br} & \quad \underline{\text{Br}} & \quad \underline{\text{Br}} & \xrightarrow{\text{NaOAc} \quad \text{Ac}_2\text{O}} & \quad \underline{\text{OAc}} & \quad \underline{\text{Br}} & \quad \underline{\text{OAc}} & + & \quad \underline{\text{Br}} & \quad \underline{\text{OAc}} \\
& & & & \quad \underline{\text{Br}} & \quad \underline{\text{OAc}} & \quad \underline{\text{Br}} & \quad \underline{\text{OAc}} & \quad \underline{\text{Br}} & \quad \underline{\text{OAc}}
\end{align*}
\]

were examined in detail. The multiplicity of products is in accord with the observations on elimination reactions in later work on similar
systems. For example, 1,2-dibromopropane upon treatment with sodium ethoxide in ethanol yields a mixture of 1-bromopropane and cis/trans 2-bromopropenes.


The cis- and trans-4-bromo-3-buten-1-yl acetates 148 and 149 are distinguished by nmr. Examination of the chemical shifts of over 1000 olefinic protons has permitted the compilation of "Z values" for calculation of chemical shifts. For -Br, the values (δ) are


\[ Z_{\text{gem}} = 1.04, \ Z_{\text{cis}} = 0.40, \ \text{and} \ Z_{\text{trans}} = 0.55; \ \text{for} -\text{alkyl, 0.44}, -0.26, \ \text{and} -0.29, \ \text{respectively.} \]

Employing the additivity (Eq 111) the olefinic absorptions for 147 calculate to be δ 5.57 and 5.39 (observed 5.63 and 5.45). Since hyperfine geminal splitting is less than 2 Hz in systems of this sort, the absorptions appear as broad singlets.

Similarly, the trans derivative 148 is calculated to have absorptions at § 6.06 and 6.16, with significant hyperfine coupling ($J_{\text{trans}} \approx 10 \text{ Hz}$), which would result in an AB pattern, i.e. a doublet at 6.11.


For 148 there is actually observed a narrow multiplet at § 6.06, an excellent agreement with the calculated spectrum. The cis acetate 148 should have absorptions at § 6.03 and 6.27 with small hyperfine splitting ($J_{\text{cis}} \leq 5 \text{ Hz}$). Actually observed is a multiplet from § 6.36 to 6.00, composed of five sharp peaks, again consistent with the predicted spectrum. Chemical intuition also concurs with the assignments on the basis of the product ratios and vpc retention times observed.

The 1-bromocyclopropylcarbinyl system thus briefly surveyed, attention was then directed to cis- and trans-2-bromocyclopropylcarbinyl systems in order to study further the points previously outlined.

The desired substrates are prepared in a manner similar to that employed for the 1-bromo analogs. A Hunsdiecker reaction on the ethyl half ester of 1,2-cyclopropanedicarboxylic acid (154) yields a cis/trans mixture of ethyl 2-bromocyclopropanecarboxylate (155), which is readily resolved by fractionation or preparative glpc. Reduction then gives the desired alcohols, 156a and 156b, while saponification and acidification yields the acids. These transformations are depicted in Scheme 4.
Figure 4: Scheme 4
Acetolysis of cis-2-bromocyclopropylmethyl p-toluenesulfonate (157a) proceeds with considerable loss of the cyclopropyl structure. Products observed (normalized mole % yield) are: 3-butenal (159) (6.5%); cyclopropanecarboxaldehyde (160) (trace); cis-2-bromocyclopropylmethyl bromide (161a) (4.1); cis-1,4-dibromo-1-butene (162a) (0.9%); cis-2-bromocyclopropylmethyl acetate (163a) (67.6); and cis-4-bromo-3-buten-1-yl acetate (149) (20.9) (Eq 112).

$$\text{CH}_3\text{OTs} \xrightarrow{96\% \text{ AcOH}} \text{CHO} + \text{CHO} + \text{BrCH}_2\text{Br}$$

157a

159, 6%

160, trace

161a, 4%

162a, 1%

163a, 68%

149, 21%

The other isomer, trans-2-bromocyclopropylmethyl p-toluenesulfonate (157b), gives upon acetolysis (normalized mole % yield): 3-butenal (159) (8.6); cyclopropanecarboxaldehyde (160) (trace); trans-
2-bromocyclopropylmethyl bromide (161b) (1.1); trans-1,4-dibromo-1-butene (162b) (4.7); trans-2-bromocyclopropylmethyl acetate (163b) (62.2); and trans-4-bromo-3-buten-1-yl acetate (14b) (14.2) (Eq 113).

These products are believed to arise in a manner similar to the processes proposed for the 1-bromocyclopropylmethyl p-toluenesulfonate. The aldehydes are derived from the corresponding α-bromocarbinols; the dibromides may arise via capture of intermediate carbonium ions by bromide and/or displacement on the corresponding tosylate or acetate; the acetates are formed from the unrearranged initially produced cyclopropylcarbinyl cation and the rearranged homoallylic ion resulting from rearrangement of the cyclopropylcarbinyl ion first formed.
It is especially noteworthy that the ring opening to yield homomallylic products is stereospecific, in that 157b gives 148, and 157a gives 149; also no products derived from ring expansion are observed; there is a considerable amount of ring opening, in contrast to the 2,2-dihalocyclopropylcarbinyl system; and ring opening, by whatever process, appears to favor placing bromine in the vinylic position.

Unsubstituted deuterium labeled cyclopropylcarbinyl systems have been shown to open stereospecifically.42,43 The stereospecific retention of bromine cis or trans suggests that the same process is involved in the halocyclopropylcarbinyl system as in the unsubstituted cyclopropylcarbinyl substrates. The exact nature of that process is a matter of discussion. However, it is proposed here that the transition state which will best explain all the observations is a non-planar unsymmetrical homoallylic ion such as 164a (Eq 114). The carbinyl carbon attacks the backside of the 2-3 bond, or this could be visualized as ring assisted displacement of the leaving group. The major portion of the reacting molecules are captured as the unrearranged product, but a significant proportion undergo 2-3 and 1-3 bond rupture. The breaking of bonds 1-3 and 2-3 is believed to be essentially simultaneous; if 1-3 bond rupture occurs first, yielding cyclobutyl ion 151a, this could collapse to the homoallylic ion 152a from which the bulk of the rearranged products are derived. The aldehydic products could arise from ion 150a, derived from breaking of the 2-3 bond before rupture of the 1-3 bond.
a) simultaneous $2-3 + 1-3$ break

\[ \text{trans} = 164b \]

b) $1-3$ breaks first

c) $2-3$ breaks first

puckered $\alpha$ ion

$150a$
The ion $^{164}$ is essentially the unsymmetrical homoallylic ion $^{13}$ suggested by Winstead and Kosower for the cholesterol system. These product studies do not provide unambiguous evidence to exclude some of the other suggestions in the literature for the structure of the cyclopropylcarbinyl cation (see Historical Section). The subsequent kinetic studies, however, clearly indicate that this formulation is the most satisfactory (*vide infra*).
KINETICS

I. Introduction

Since the types of reaction products from solvolysis of di-halogenated cyclopropylmethyl derivatives are quite different than that from mono-halogenated and non-halogenated analogs, an underlying change of mechanism might be indicated. Thus a study of the kinetics of solvolysis of cyclopropylmethyl p-toluenesulfonates might reveal mechanistic differences in reactions of their mono-halogenated and di-halogenated derivatives. Further, transmission of electronic effects through the cyclopropane rings is a topic of current interest (see Historical Section) and thus quantitative determination of rate constants for solvolysis of cyclopropylmethyl derivatives bearing halogen substituents on the ring will provide additional information on this subject.

II. Results

Kinetics of aqueous ethanolysis of the cyclopropylmethyl p-toluenesulfonates were monitored by titrating the liberated p-toluene-sulfonic acid with sodium hydroxide solution. Reactions were followed to greater than 80% completion and exhibited first order kinetics. The rate constants obtained are summarized in Table 6.

It is found that all halogenated cyclopropylcarbinyl p-toluenesulfonates studied solvolyze much more slowly than does the parent
Table 6

First-order Rate Constants for Solvolysis of Halo-Substituted Cyclopropylmethyl
p-Toluenesulfonates in 80% Aqueous Ethanol at 70°

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Compound Number</th>
<th>Number of runs</th>
<th>Rate constant x 10^5 sec^-1</th>
<th>Rel rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td></td>
<td></td>
<td>1400</td>
<td>1250</td>
</tr>
<tr>
<td>trans-2-bromo</td>
<td>157b</td>
<td>3</td>
<td>32.0 ± 0.1</td>
<td>29.2</td>
</tr>
<tr>
<td>cis-2-bromo</td>
<td>157a</td>
<td>2</td>
<td>11.4 ± 0.6</td>
<td>10.1</td>
</tr>
<tr>
<td>1-bromo</td>
<td>143</td>
<td>3</td>
<td>6.07 ± 0.02</td>
<td>5.4</td>
</tr>
<tr>
<td>2,2-dichloro</td>
<td>88</td>
<td>6</td>
<td>1.13 ± 0.02</td>
<td>1</td>
</tr>
<tr>
<td>2,2-dibromo</td>
<td>168</td>
<td>2</td>
<td>1.08 ± 0.06</td>
<td>0.96</td>
</tr>
<tr>
<td>trans-2-bromo&lt;sup&gt;b&lt;/sup&gt;</td>
<td>157b</td>
<td>2</td>
<td>25.6 ± 0.8</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Extrapolated from 49.9° with the data in ref 117 by the Arrhenius equation \((\Delta \ln k/\Delta T = (E_a/T_2 - E_a/T_1)1/R)\).

<sup>b</sup>90% Ethanol.
cyclopropylcarbiny1 p-toluenesulfonate. Since the rates of solvolysis of 2,2-dichloro- and 2,2-dibromocyclopropylcarbiny1 tosylates (88 and 168) are essentially identical, it appears that the electronic effects of chlorine and bromine substituents in these systems are grossly similar. Bromine in the 1-position retards the solvolysis to a greater extent than does the substituent in either the cis or trans 2-positions. Perhaps the most interesting observations are that the cis-2-bromo ester 157a solvolyzes only approximately twice as fast as the 1-bromo ester 143 and at only one-third the rate of the trans-2-bromo ester 157b.

III. Discussion

The retardation of solvolysis by halogen substituents is reasonable and in accord with the limited previous study on 2,2-dichlorocyclopropylmethyl chlorides (Table 1). Bromine and chlorine are powerful electron withdrawing groups by induction and, in the absence of resonance effects or neighboring group assistance, are predicted to retard aqueous ethanolysis of the cyclopropylcarbiny1 p-toluenesulfonates, since the solvolytic process involves generation of electron deficient carbonyl carbon.

On the basis of simple inductive effects, it is to be expected that 1-bromo ester 143 is less reactive than cis-2-bromo or trans-2-bromo esters 157a and 157b. No anchimeric assistance is expected from the β-halogen in the 1-position in 143 because of the inflexible geometry of the cyclopropane ring. The absence of anchimeric assistance
from alkyl and aryl substituents in the 1-position in cyclopropylcarbinyl solvolyses has been demonstrated previously.


The origin of the three-fold difference in the rates of solvolysis of the cis and trans substrates 157a and 157b is not immediately evident. Previous investigations have indicated small to large solvolysis rate differences in a variety of cis/trans cyclopropylcarbinyl pairs. In one investigation the effect of methyl substitution on the ring on the rate of solvolysis of cyclopropylmethyl 3,5-dinitrobenzoates was studied (Table 7). In that investigation cis substituents result in slightly less solvolysis rate acceleration than do the trans substituents, but only by small amounts. The rate constant for solvolysis of the cis-2-cis-3- derivative is less than for the trans-2-trans-3- isomer by a factor of 1.5, the cis-2-methyl- ester differs from the trans-2-methyl- isomer by a factor of only 1.33, and the rate constant for solvolysis of the cis-2-cis-3-dimethyl compound is essentially the same as that of the cis-2-trans-3-dimethyl- isomer.

Study of the cis/trans effect in phenyl substituted cyclopropylmethyl 8-naphthalenesulfonates has been reported. A somewhat larger cis/trans difference is revealed (Table 8); the cis-phenyl substrate is less reactive than the trans by a factor of 3.6.
Table 7
Relative First-order Rate Constants for Solvolysis of Methyl Substituted Cyclopropylmethyl 3,5-Dinitrobenzoates in 60% Aqueous Acetone at 100°C

<table>
<thead>
<tr>
<th>Cyclopropyl Substituent</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>1</td>
</tr>
<tr>
<td>1-methyl</td>
<td>5.0</td>
</tr>
<tr>
<td>cis-2-methyl</td>
<td>8.2</td>
</tr>
<tr>
<td>trans-2-methyl</td>
<td>11.0</td>
</tr>
<tr>
<td>cis-2-cis-3-dimethyl</td>
<td>82</td>
</tr>
<tr>
<td>cis-2-trans-3-dimethyl</td>
<td>80</td>
</tr>
<tr>
<td>trans-2-trans-3-dimethyl</td>
<td>124</td>
</tr>
<tr>
<td>2,2-dimethyl</td>
<td>92</td>
</tr>
<tr>
<td>trans-2,2,3-trimethyl</td>
<td>490</td>
</tr>
<tr>
<td>2,2,3,3-tetramethyl</td>
<td>1570</td>
</tr>
</tbody>
</table>

*aRef 86.

Table 8
Relative First-order Rate Constants for Solvolysis of Phenyl Substituted Cyclopropylmethyl β-Naphthalenesulfonates in 90% Aqueous Dioxane at 25°C

<table>
<thead>
<tr>
<th>Cyclopropyl Substituent</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>1</td>
</tr>
<tr>
<td>cis-2-phenyl</td>
<td>0.62</td>
</tr>
<tr>
<td>trans-2-phenyl</td>
<td>2.19</td>
</tr>
</tbody>
</table>

*aRef 25.*
In fused ring cyclopropylcarbinyl systems cis vs trans derivatives often show very large differences in their solvolytic reactivities. The relative rate constants for solvolysis of several bicyclo[6.1.0]nonan-2-yl 3,5-dinitrobenzoates (or β-nitrobenzoates) are tabulated (Eq 115). To explain the differences in rates, one group of researchers has emphasized ground state geometry, noting that the leaving group lies over the cyclopropane ring, 'making it difficult to achieve a stabilizing interaction between the developing π orbital and the cyclopropane ring in the activated complex.'
5); another group emphasizes participation of the ring bond by actual movement of one of the sides of the cyclopropane ring toward the developing charge.

![Figure 5](image)

In the present system, that the cis-2-bromo substrate 157a is less reactive than the trans isomer 157b appears to have a steric rather than a through space electronic origin. This question was examined in subsequent pKa studies (vide infra) and the indication is that such electronic effects are minor. It thus appears that the rate difference is a result of steric factors.

The observation that cis-2-bromocyclopropylmethyl p-toluenesulfonate solvolyzes more slowly than the trans isomer suggests that the cyclopropane ring is displacing the leaving sulfonate anion via a transition state which resembles an unsymmetrical homoallylic ion. The back lobe of the developing empty p orbital may interact with the methylene ring bond as in Figure 6. Attack by the ring bond of the carbon bearing the bromine is less likely due to electronic factors. The carbonyl carbon must rotate forcing the leaving group up over the
plane of the ring, where in the cis isomer the leaving group encounters steric interference with the bromine, thus regarding solvolysis because the transition state has an unfavorable steric interaction not present in the trans isomer. As visualized this transition state closely resembles the unsymmetric homoallylic ion proposed by Weinstein and Kosower.

Alternate proposals could be advanced, that the cis bromine offers steric interference to approaching displacing solvent, or that it creates unfavorable steric interactions impeding solvation of the incipient ion. As will be made explicit, however, the geometry in most other formulations of the reaction transition states do not appear to result in appreciable steric interaction.

The case against each of the other suggested transition states will now be summarized. As outlined in the Historical Section, nine formulations of the cyclopropylcarbiny1 cation have been prominently
advanced: 1) tricyclobutonium; 2) rapidly equilibrating classical ions; 3) Coulson-Moffitt \textit{cis} bisected; 4) $\pi$ complex; 5) Walsh; 6) bicyclobutonium; 7) symmetrical homoallylic; 8) planar unsymmetrical homoallylic; and 9) non-planar unsymmetrical homoallylic.

In the following analysis the transition state for solvolytic displacement is assumed to resemble one of the models for the cyclopropylcarbinyl cation.

The first four ions are eliminated from consideration or combined with other structures for the following reasons. The tricyclobutonium ion has previously been rejected on experimental and theoretical grounds, and there is no evidence in the present work to favor resurrection. Likewise, rapidly equilibrating classical ions have fallen into disfavor, and, in order to explain the product ratios, questionable assumptions would have to be made in order to explain why the more stable ions do not give the major products. The Coulson-Moffitt and Walsh vertical stabilization models are equivalent formulations, and are combined in subsequent discussion. The $\pi$-complex, depending on the actual geometry chosen for the array of atoms, is equivalent to either the symmetrical homoallylic, unsymmetrical homoallylic, or non-planar unsymmetrical homoallylic cyclopropylcarbinyl cations, and will not be discussed separately.

Of the remaining five formulations, super acid experiments demonstrate that the Walsh vertical stabilization model almost certainly best represents the free ion. Thus \textit{a priori} a transition state
for ionization of the p-toluenesulfonate would be expected to closely resemble this ion which is believed to be an intermediate. However, the transition state leading most directly to this ion does not adequately explain the cis/trans rate difference. The transition state leading to this ion would best be represented by a bisected structure, in which the incipient empty orbital is parallel to the plane of the ring (Eq 116). Upon development of the transition state the solvent

would approach from the side, and would not be expected to suffer much steric interaction with the bromine, whether the halogen were cis or trans to the carbonyl center. No other effect should result in a significant cis/trans difference: the inductive effect through bonds must be equal for cis and trans substituents; the through space electronic effect would be small (this assumption is confirmed in the subsequent pK\text{a} study); nor should there be significant steric difficulty for the leaving group in the cis case versus the trans.

Very recently a study has appeared suggesting that the cis bisected (Walsh) structure best represents the intermediate cyclo-
propylcarbinyl cation and also the transition state leading to this ion. The optically active methanesulfonate depicted in Figure 7 was prepared. The absolute configuration is known with considerable certainty. The displacement occurs with backside attack, the cyclopropylcarbinyl cation retains its configuration, and stereochemistry is thus known for the products. Since some of the products derived from participation of the 1-2 bond are distinct from those of 1-3 participation solely by virtue of deuterium labeling, it was possible to calculate that 1-2 bond participation was greater than 1-3 bond participation by a factor of 3.1. It was suggested that an unsymmetrical homoallylic ion would exhibit a larger factor for 1-2 as opposed to 1-3 bond participation. The underlying causes of this acceleration of the 1-2 versus the 1-3 bond participation remain unanswered.
The ratios of products derived from 1-2 or 1-3 bond participation were exactly the same (exclusive of the position of deuterium), thus indicating that the intermediate ion, once formed, was symmetric (thus favoring cis bisected geometry over the unsymmetrical homoallylic). The present kinetic study cannot address this point, because the rate is determined by the structure of the transition state leading to the intermediate, not the intermediate itself. Thus the case against the unsymmetrical homoallylic ion type transition state is still undecided.

Turning to the other ions under consideration, the bicyclobutonium ion can be considered as an ion very similar in structure to the non-planar unsymmetrical homoallylic ion, but further along a nearly identical reaction coordinate, the bond distances α-1, 1-2, and 3-α being about the same, with appreciable charge on the number one carbon (Eq 117). Hence the placement of a bromine on the number one carbon

\[
\begin{align*}
\begin{array}{c}
\text{1} \\
\text{2} \\
\text{3} \\
\text{4} \\
\text{5} \\
\end{array}
\end{align*}
\quad \equiv \quad \begin{array}{c}
\oplus \\
\ominus \\
\ominus \\
\ominus \\
\ominus \\
\end{array}
\quad \begin{array}{c}
\oplus \\
\oplus \\
\oplus \\
\oplus \\
\oplus \\
\end{array}
\quad \begin{array}{c}
\oplus \\
\oplus \\
\oplus \\
\oplus \\
\oplus \\
\end{array}
\quad \begin{array}{c}
\oplus \\
\oplus \\
\oplus \\
\oplus \\
\oplus \\
\end{array}
\end{align*}
\]

(117)

might accelerate the rate of solvolysis; however, the reverse is observed. It is also unlikely that such an ion should exhibit a large difference in rate if the bromine were forced up into the axial position (for the cis-2-bromo substrate) as opposed to the equatorial (for the trans-2-bromo compound).
Looking next at the symmetrical homoallylic ion (Eq 118), substitution of bromine in the two-position would perturb the symmetry. As a result homoallylic ion 152 would be expected to become involved more strongly in conversion to products, but the percentage of homoallylic products derived from 152 is not appreciably larger than in unsubstituted systems (Eq 118). Ion 152 has the positive charge alpha to the bromine, which could stabilize the electron deficient atom via resonance and thus be a major contributor to the overall electronic structure.

Planar structures could not exhibit a retardation of rate for the cis substrates relative to the trans isomers. If the transition state did actually approach planarity, the cis isomer would exhibit acceleration due to release of steric strain.

Thus the unsymmetrical homoallylic ion 164 proposed by Winstead and Kosower appears to best represent the transition state for displacement of leaving group in the cyclopropylcarbinyln systems studied, and adequately explains the results as discussed above. Several caveats must be appended, however. Since the factor of three does
not represent a large energy difference, subtle effects in solvation of a cis bisected structure not evident from examination of molecular models could be responsible for the rate difference. Also, the cis bisected model might exhibit some steric problems, especially if the bond order for bonds α-1, 1-2, and 1-3 increased significantly, thus shortening these bond lengths. Additionally, the halogenated cyclopropylcarbinyl systems are strongly deactivated with respect to the unsubstituted and alkyl substituted substrates, thus the displacement process may involve a transition state at a somewhat different stage of development than for the more reactive compounds. The transition between the cis bisected ion and the rearranged cis bisected ion (degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement) is generally held to be of very low energy, and thus the conclusion that the initial displacement process has geometry akin to that low energy rearrangement is reasonable.

It is informative to compare the results of the present solvolyses with the solvolyses of simple alkyl systems. Cyclopropylcarbinyl systems are usually excluded from discussions of the solvolysis of simple alkyl systems because of their special features. The present investigation, however, indicates that the halo substituted cyclopropylcarbinyl systems have solvolysis rates much more comparable to simple alkyl systems than to normal cyclopropylcarbinyl systems.

A generalized scheme for solvolysis is indicated below (Scheme 5). In this scheme NR and SCR (as opposed to RN and ROS) indicate
Figure 8: Scheme 5

\[
\begin{align*}
R-X & \xrightleftharpoons[k_1]{S_{N1}^I} R+X^- \\
& \xrightleftharpoons[k_{-1}]{S_{N1}^I} R+X^- \\
N^- & \xrightleftharpoons[k_4]{S_{N2}^I} N^- \\
& \xrightleftharpoons[k_5]{S_{N2}^II} N^- \\
NR+X & \xrightleftharpoons[k_6]{S_{N2}^III} NR+RN \\
& \xrightleftharpoons[k_7]{S_{N2}^IV} NR+RN + R-O6 \\
& \xrightleftharpoons[k_{-4}]{S_{N1}^I} N^- \\
& \xrightleftharpoons[k_{-5}]{S_{N1}^I} N^- \\
& \xrightleftharpoons[k_{-6}]{S_{N1}^I} N^- \\
& \xrightleftharpoons[k_{-7}]{S_{N1}^I} N^- \\
& \xrightleftharpoons[k_{-1}]{S_{N1}^I} R+X^- \\
& \xrightleftharpoons[k_{-2}]{S_{N1}^I} R+X^- \\
& \xrightleftharpoons[k_{-3}]{S_{N1}^I} R+X^- \\
S_{OR} + ROS &
\end{align*}
\]
that inverted product from capture by added nucleophile \( \text{N}^- \) or solvent \( \text{SOH} \) is obtained. The designation \( S^\text{II}_N \) to a reaction implies that \( k_1/k_{-1} \) is rate controlling. The scheme argues that substrate initially dissociates to a '"tight'" ion pair \( \text{R+X-} \) which can then undergo bimolecular nucleophilic attack to give inverted product \( \text{NR} \) or further dissociate to a '"solvent separated'" ion pair which could collapse to \( \text{ROS} \) or (by nucleophilic attack) \( \text{NR} \) and \( \text{RN} \) or further dissociate to a '"free'" but still solvated cation which would give a racemic mixture of products.

Secondary and tertiary systems which offer the greatest steric resistance to attack by solvent or a neighboring group tend to exhibit first order kinetics, due to the lowering of rate constants \( k_4 \) and \( k_5 \), while primary systems usually demonstrate 2nd order kinetics, since rate constants \( k_4 \) and/or \( k_5 \) can be high.

The present observations can be fit into the first portion of the elaborated Weinstein Scheme 4 by assuming that \( k = k_1/k_{-1} \) is shifted to the left with respect to the parent system by the strong electron withdrawing inductive effect of the halogens. However, then it is argued that the resulting ion pair suffers expulsion of the anion via anchimeric assistance of the 3-1 bond of the cyclopropane. This would account for the \( \text{cis/trans} \) rate difference (vide infra).
The resulting ion is then captured by solvent, or can rearrange via various geometries to give ring opened products.

The steric effect observed would be due to the poorer ability of the ring bond to assist anchimerically to give the activated complex when the bromine is cis to the carbiny1 center. The vertical stabilization arguments of Traynor and of Wilcox would indicate that the ability of the ring bond to displace would be little impaired by the substitution of bromine for hydrogen: bromine cannot interact via resonance with the filled $p$ orbitals of the ring, and the $p$ orbitals of the ring are to a first approximation, orthogonal to the sigma framework, and therefore little electron density will be withdrawn inductively. The rate determining step would be the anchimerically assisted displacement of the leaving group. With respect to cyclopropylcarbiny1 systems without electron withdrawing halogens on the ring, the pre-equilibrium ($k_1/k_{-1}$) has been shifted to the left, so the observed solvolytic rate is lower than in normal cyclopropylcarbiny1 systems. This model would imply a larger steric effect in the study of Schleyer and Van Dine than that observed (Table 7). The apparent lack of a large steric effect is not understood, but it may be that in the methyl substituted system there are no major electronic effects which prevent one of the ring bonds from attacking (in the bromo substituted case, the ring bond on the bromine side appears not to participate due to the electron withdrawing effect of the bromine). Thus either the 1-2 or 1-3 bond may attack with similar facility.
is interesting that in the tetramethyl case (Table 7), the rough additivity of the effect of methyl substitution breaks down; this may be a result of the steric effect which appears to be operant in the mono-bromo system. Thus the single datum in ref. 86 which is not explicable in the present interpretation is the rate of the cis-2-cis-3-dimethyl substrate, which is three times higher than expected.

The rates of solvolysis of the halo-substituted cyclopropyl-carbiny1 derivatives are thus readily explicable in terms of a transition state where the geometry is slightly perturbed from the cis bisected conformation as the carbiny1 carbon moves toward the cyclopropane ring bond.
ACID DISSOCIATION CONSTANT DETERMINATIONS

I. Introduction

In order to learn more about transmission of electronic effects in halocyclopropanes, the acid dissociation constants of a series of cyclopropanecarboxylic acids have been determined. The acid dissociation constants should provide information similar to that of the solvolysis rate studies in this work, but uncomplicated by the complexities of the solvolytic process. Thus, the pKa determinations might place some of the conclusions in the previous section on firmer ground.

As discussed in the historical section of this work, pKa determinations is a classical method of evaluating the transmission of electronic effects through molecules. Halocyclopropanecarboxylic acids have not been studied systematically, however, to measure the transmission of electronic effects. Several related investigations have appeared. In the first the pKas of several para substi-


tuted \textit{trans}-2-phenylcyclopropanecarboxylic acids were measured, and it was concluded that little resonance transmission was occurring. Both the accuracy of those determinations and the conclusions therefrom were questioned subsequently in a study employing similar substrates, \textsuperscript{\textit{124b}} and the opposite position was taken, that significant resonance effect is transmitted through the cyclopropane ring. In a theoretical paper, the field effect was held to be the most significant factor, \textsuperscript{\textit{124c}} but this was questioned on the basis of additional data. \textsuperscript{\textit{124d}} More recently, the effects of bulky groups (alkyl, silyl, germanyl) on the acidities of cyclopropanecarboxylic acids were studied, and an important steric factor was indicated. \textsuperscript{\textit{124e}} The effects of \textit{cis} and \textit{trans} methyls on the acidity of cyclopropanecarboxylic acid has been reported to be essentially identical.  

\section*{II. Results}

Acids were titrated with increments of standardized sodium hydroxide solution and the pH determined after each addition. The measurements were carried out at approximately equal ionic strength (added sodium chloride). Hydrogen ion concentration was calculated from the pH and ionic strength by the Davies equation (see Experimental) and the pKa determined from the titration curve by established methods (see Experimental). The dissociation constants found are summarized in Table 9.

The halogenated acids are all stronger than the parent acid as expected. The \textit{trans-} and \textit{cis}-2-bromo- acids \textsuperscript{\textit{158b}} and \textsuperscript{\textit{158a}} have nearly
Table 9

pKₐ's of Various Cyclopropanecarboxylic Acids in Water at 35°

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Compound Number</th>
<th>Number of Runs</th>
<th>Lit. pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>67</td>
<td>4</td>
<td>4.846 ± .003</td>
</tr>
<tr>
<td>trans-2-bromo</td>
<td>158b</td>
<td>2</td>
<td>4.046 ± .002</td>
</tr>
<tr>
<td>cis-2-bromo</td>
<td>158a</td>
<td>2</td>
<td>4.064 ± .005</td>
</tr>
<tr>
<td>1-bromo</td>
<td>141</td>
<td>2</td>
<td>3.267 ± .017</td>
</tr>
<tr>
<td>2,2-dichloro</td>
<td>120</td>
<td>6</td>
<td>3.321 ± .003</td>
</tr>
<tr>
<td>2,2-dibromo</td>
<td>121</td>
<td>2</td>
<td>3.328 ± .003</td>
</tr>
<tr>
<td>trans-2-methyl</td>
<td>167</td>
<td>2</td>
<td>4.964 ± .004</td>
</tr>
<tr>
<td>1-methyl</td>
<td>165</td>
<td>2</td>
<td>5.078 ± .003</td>
</tr>
<tr>
<td>cis-2-methyl</td>
<td>169</td>
<td></td>
<td>5.02&lt;sup&gt;a,d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>At 25°.  <sup>b</sup>Ref 125.  <sup>c</sup>Ref 140.  <sup>d</sup>Ref 124f.  <sup>e</sup>At 23°.  <sup>f</sup>At 24°.
equivalent acidities. The effect of bromo substituents in the 2,2-
positions (121) is nearly the same as that of corresponding chloro
substituents. (120). The effect of halogen substitution (158a, 158b,
120, 121) appears to be nearly additive. A reasonable fall off factor
(1/2.1) is observed for the change 1-bromo to 2-bromo and there is a
similar fall off factor (1/2) for 1-methyl to 2-methyl.

III. Discussion

The most interesting observation is that the trans- and cis-2-
bromocyclopropanecarboxylic acids (158a and 158b) have very similar
dissociation constants. This contrasts with the solvolytic results,
and suggests that the through space field effect is negligible. The
alternate interpretation that steric factors and through space electron-
ic effects are balancing out can be rejected on the basis of the pre-
viously reported observation 124f that cis-2- and trans-2-methyl acids
159 and 167 have equivalent acidities. Here there cannot be a large
through space electronic effect, and the steric factors must be similar,
because bromine and methyl have equivalent van der Waals radii. 128


1-Bromocyclopropanecarboxylic acid (141) is slightly more acidic
than 2,2-dibromo and 2,2-dichloro acids 121 and 120, and much stronger
than the 2-bromo acids 158a and 158b. In solvolysis, the reactivity
of the 1-bromo tosylate 143 is intermediate between that of the 2,2-dibromo analog 168 and the 2-bromo substrates 157a and 157b. The inversion of order may indicate that appreciable stabilization is occurring in solvolysis of the 1-bromo substrate 143 via ring expansion.

One puzzling point the pKa determinations fail to resolve is why 1-methylcyclopropylmethyl chloride solvolyzes more slowly\(^3\) (Table 2) than the unsubstituted parent halide (Table 2). Methyl, by Taft's measure, is electron donating both by induction and resonance, although the effect is relatively small, and should therefore accelerate reaction. One must conclude that either steric factors cause the deceleration or that methyl is electron withdrawing under the solvolytic conditions. Since a model does not indicate any obvious steric problem (although since the effect is small, only minor interaction with approaching solvent may be indicated), the second possibility, that methyl is withdrawing electron density, must be considered. This question, does methyl donate or withdraw electron density with respect to hydrogen and does it vary, is a topic of past and current interest.\(^{127}\)

\[^{127}\] More than 20 leading references have been listed: L. Libit and R. Hoffmann, J. Amer. Chem. Soc., 96, 1370 (1974).

Convincing evidence has been assembled that alkyl groups stabilize simple anions.\(^{128a}\) Thus gas phase acidities of \(t\)-butyl alcohol, isopropyl alcohol, and ethanol show that \(t\)-butyl alcohol is the most
acidic, followed monotonically by the lesser substituted alcohols. This is apparently an intrinsic property of the alkyl group. It is electron withdrawing by induction; this is consonant with nmr chemical shifts (methine hydrogen is deshielded with respect to methylene, which is deshielded with respect to methyl), and Pauling electronegativities, which show carbon electron deficient compared to hydrogen. Amine gas phase basicities follow the opposite sequence.

Thus a tertiary amine, $R_3N$, is more basic than a secondary amine, $R_2NH$, which is more basic than a primary amine, $RNH_2$. In this series it is argued that the conjugate acid $R_3NH^+$ is stabilized by the polarizable alkyl group. The alkyl group would withdraw electron density from the free amine, making it less basic; this effect is overridden by the donation of electron density in the charged species, where presumably polarizability is more important than in uncharged molecules. This would imply that alkyl groups change their electron donating or withdrawing character depending upon the electronic demands placed upon them.
An alkyl group attached to an sp$^2$ hybridized carbon, such as a carbonium ion or unsaturated carbon, is a different case. The alkyl might well donate electron density with respect to hydrogen since the sp$^2$ bond with greater s character will be more electron demanding than an sp$^3$ bond. No definitive data are available. Of interest, however, is an Extended Hückel calculation which investigates the effect of methyl substitution on the benzene nucleus. Very little net charge is transferred, but the ring is polarized, enhanced electron density appearing in the para and ortho positions, while the meta and ipso positions become electron poor. The cyclopropane carbons are nearly sp$^2$ hybridized and hence the inductive electronic effect should be similar to that in a benzene ring. Thus one would predict, recalling that Wilcox et al. calculated little resonance contribution in the cyclopropane ring, that the effect of 1-methyl substitution should be nearly zero (Hoffmann predicts inductively neutral and Wilcox predicts no resonance interaction) in both cyclopropanecarboxylic acid strength and rate of solvolysis of cyclopropylcarbinyl derivatives. Since solvolysis is slightly slowed and acid strength reduced by methyl substitution in the 1-position, it must be concluded that either methyl changes its donating ability depending on electronic demands or that there is some steric retardation of solvolysis in the system examined.

The acid dissociation constants thus indicate that the cis/trans rate difference in the 2-bromo tosylates $^{157a}$ and $^{157b}$ is almost certainly a result of a transition state where the participating cyclo-
propane ring must move toward the carbinyl center as the leaving group is displaced. The pKa determinations do not, however, shed much light on the cause of the small rate depression in solvolysis of 2,2-dichloro-1-methylcyclopropylmethyl chloride relative to the 2,2-dichloro homolog.
EXPERIMENTAL

General Information - Product Studies

Melting Points - Melting points were determined on a Thomas Hoover apparatus and are uncorrected.

Analyses - Analyses were performed by Micro-Analysis, Inc. of Wilmington, Delaware, and Chem-Analytics of Tempe, Arizona.

Infrared Spectra - All spectra were obtained on a Perkin-Elmer Infracord 137 Spectrophotometer. Potassium bromide pellets were employed for solids, and liquids were scanned neat between sodium chloride plates.

Mass Spectra - Mass spectra were taken on an AEI MS-902 double focusing mass spectrometer at an ionizing voltage of 70 eV, accelerating potential of 8 kV, and a source and inlet temperature of 150° unless otherwise noted.

Nmr - The nmr of various products were determined on Varian A-60 and A-60A, or Jeol Co. MH-100 instruments using dilute solutions in carbon tetrachloride with tetramethylsilane or chloroform (δ = 7.28) as internal standard unless otherwise specified.

Gas Chromatography - Gas chromatography was used for product separation and determination of product composition. Analytical and preparative separations were generally performed on copper columns (1/4"). Loadings of stationary phases are expressed as per cent of total weight, contrary to general custom but consonant with local practice. Product compositions
were determined by comparing peak areas (height times width at half-height). For chromatograms obtained with a thermal conductivity bridge and helium as the carrier gas a response factor of unity was taken. Compound response factors for chromatograms recorded with a flame ionization detector were determined by measurement of standard solutions. Peaks were identified as the compounds indicated both by retention time and by actual isolation by preparative vpc and subsequent spectroscopic examination (ir, nmr), unless noted otherwise.

Chemicals and Solvents - Reagent grade materials were stored over molecular sieves and used without further purification unless specified. Commercial grade solvents were distilled prior to use. All starting materials were checked by vpc and/or nmr before use and subjected to suitable purification if contaminated.

Evaporations - Low boiling solvents were generally removed at water aspirator pressure on a rotary evaporator.

Preparation of Methyl 2,2-Dichlorocyclopropanecarboxylate (86)

Phenyl(trichloromethyl)mercury (191 g, 0.48 mole), dry heptane (1.2 L), and methyl acrylate (95 g, 1.1 mole) were placed in a flask equipped with mechanical stirrer, reflux condenser, and nitrogen inlet. A slow current of nitrogen was passed through the flask and the stirred mixture was refluxed 72 hr. The flask was cooled (ice bath; 1 hr), the liquid was decanted, and the semisolid precipitate was triturated thoroughly with heptane. The combined organic layers were concentrated (ca 400 ml) and fractionated through a spinning band (50 cm) to yield methyl 2,2-dichlorocyclopropanecarboxylate (86) (30.8 g, 38%), bp 68-70° (8 Torr), lit 77-78° (23 Torr). Vpc analysis (6' x 1/4" 20% UC W-98 on Chrom P, 120°) and nmr showed this material to be only 80% pure, containing 20% of three additional components. Preparative vpc was employed to obtain pure samples for subsequent experiments. Long reflux is essential to secure adequate conversion, a point not noted originally.


(132) Org. Syn., 46, 98 (1966); phenylmercuric chloride from Ventron Corporation, Beverly, Mass. was found to give good results, but material from Columbia Organic Chemicals Company, Columbia, S.C. was not satisfactory.
After trial runs on isotopically normal material, the following procedure was adopted. Methyl 2,2-dichlorocyclopropanecarboxylate (B7) (1.4 g, 8.3 mmole) was syringed dropwise into a chilled suspension of lithium aluminum deuteride (0.173 g, 4.2 mmole) in dry tetrahydrofuran (5 ml) in a flask equipped with serum stoppers, condenser protected with a tube of Drierite, and magnetic stirrer. The flask was swept with a slow stream of nitrogen and stirred magnetically. After addition was complete, the mixture was refluxed 1 hr; an aliquot was withdrawn and pipetted into ether/water. The organic layer, after washing and drying (Na$_2$SO$_4$), was examined by vpc. The reaction was about 80% complete; additional lithium aluminum deuteride was added (0.035 g) and the mixture refluxed (1 hr). An aliquot withdrawn at this point showed reduction to be complete. After cautious addition of water, the contents of the flask were poured into 5% hydrochloric acid (70 ml). Extraction with ether (4 x 50 ml), followed by washing with 5% sodium bicarbonate (25 ml), water (25 ml), saturated sodium chloride solution (50 ml), drying (MgSO$_4$), and removal of solvent gave 1.63 g of material which contained 60% product alcohol and 39% tetrahydrofuran. Preparative vpc yielded pure 2,2-dichlorocyclopropylmethanol-$\alpha,\alpha$-d$_2$ (B7) (1.03 g, 85%): nmr $\delta$ 3.8 (s, 1, OH), 2.3-1.4 (m, 3, ring H); isotopically normal material has an additional absorption $\delta$ 3.9-3.6 (m, 2, -CH$_2$-O), and the low field side of ring H's exhibit sharper resonances.
2,2-Dichlorocyclopropylmethyl-α,α-d₂ p-Toluenesulfonate (88)

2,2-Dichlorocyclopropylmethanol-α,α-d₂ (88) (1.0 g, 6.98 mmole) in dry pyridine (25 ml, stored over CaH₂) was chilled in an ice bath, and recrystallized p-toluenesulfonyl chloride (2.6 g, 14 mmole) was added. The mixture was swirled briefly, then stored in a refrigerator overnight. The pyridine solution was poured into crushed ice and water (100 ml), and stirred until the ice had melted (10 min). The solid was filtered and dried at room temperature in a vacuum desiccator to constant weight (2 hr). Recrystallization from 3:1 ether-petroleum ether (250 ml, 30-60°) and Norit (slow cooling and scratching; crystallization was completed at -78°) gave 2,2-dichlorocyclopropylmethyl-α,α-d₂ p-toluenesulfonate (88), mp 82-83.5°, lit² (isotopically normal material) mp 83-84°. The ir spectrum exhibits peaks at 1930 (w, sh) and 775 cm⁻¹ (s, b) not present in isotopically normal material.

Acetolysis of 2,2-Dichlorocyclopropylmethyl-α,α-d₂ p-Toluenesulfonate (88)

Dichlorocyclopropylmethyl-α,α-d₂ p-toluenesulfonate (88) (200 mg) was placed in an nmr tube and glacial acetic acid (800 mg) added. The tube was sealed and the nmr spectrum was run to confirm the absence of absorption around δ 4.0. The tube was then heated to 120° for 24 hr and the nmr spectrum periodically monitored. No absorbance appeared in the
The tube was then opened and the contents examined by vpc. Only a single product corresponding to 2,2-dichlorocyclopropylmethylo,α-α-d₂ acetate (90) was eluted; its retention time is identical to that of isotopically normal material. Preparative vpc (6' x 1/4" 20% SF-96 60 ml He/min, 150⁰, ret. time 4.5 min) of the acetate 90 and nmr examination confirmed the observation. Integration of the spectrum indicated within experimental error (estimated ± 3%) that deuterium in the methylene position had not exchanged with ring protons. Acetate 90 exhibits nmr absorptions at δ 2.1 (s, 3, C(=O)CH₃), and 2.3-1.3 (m, 5, ring H).

2,2-Dichlorocyclopropylmethyl-α,α-d₂ Bromide (89)

2,2-Dichlorocyclopropylmethanol-α,α-d₂ (87) (1.0 g, 6.95 mmole) was dissolved in toluene (3 ml) and phosphorous tribromide (0.33 ml, 0.95 g, 3.7 mmole) was added. The mixture was refluxed (8 hr), cooled, decanted from the orange polymer into a centrifuge cone, diluted with ether, and washed with 5% sodium bicarbonate solution (5 ml), and dried (CaSO₄/K₂CO₃). The bromide was formed cleanly. Preparative vpc yielded 2,2-dichlorocyclopropylmethyl-α,α-d₂ bromide (89): nmr δ 2.4-1.2 (m, ring H); no methylene hydrogen alpha to a bromine could be detected.

Silver Ion Assisted Acetolysis of 2,2-Dichlorocyclopropylmethyl-α,α-d₂ Bromide (89)

2,2-Dichlorocyclopropylmethyl-α,α-d₂ bromide (89) (204 mg, 1 mmole) was dissolved in glacial acetic acid (5 ml) containing silver
acetate (200 mg, 1.2 mmole). The suspension was incubated at 100° for 12 hr. Vpc examination of the material showed reaction to be approximately 50% complete. Nmr analysis revealed no absorption in the δ = 3.5 region. Preparative vpc (SF-96) was utilized to separate acetate 90 and unreacted bromide 89. Nmr examination of these materials confirmed that no deuterium scrambling had taken place. Acetate 90 was identical (vpc (SF-96), ir, nmr) to material obtained previously in the solvolysis of the labeled tosylate 88.

Preparation of 2,2-Dichlorocyclopropylmethy1 Bromide (74a) via Phenyl-(trichloromethyl)mercury

Allyl bromide (250 ml) and phenyl(trichloromethyl)mercury (78 g, 0.197 mole) were placed in a flask outfitted with a reflux condenser and magnetic stirrer. The solution was refluxed with stirring under nitrogen 64 hr during which time phenylmercuric chloride slowly precipitated. The thoroughly cooled solution was filtered; the solid was triturated with pentane and the washings combined with the filtrate. Careful distillation through a small spinning band gave 2,2-dichlorocyclopropylmethy1 bromide (74a) (18.4 g, 46%), bp 68-72° (12-15 Torr), lit 78-80° (15 Torr). Vpc (SE-30, 150°) showed the product to be only 95% 74a; there were two components at slightly longer retention times.

Preparation of 2,2-Dichlorocyclopropylmethy1amine (91)

2,2-Dichlorocyclopropylmethy1 bromide (74a) (18.4 g, 0.09 mole) was added dropwise to methanol (100 ml) and concentrated ammonium
hydroxide (70 ml). The solution was warmed gently on a steam bath (20 hr). The cooled mixture was diluted with water and extracted with ether; the organic layer was dried (saturated sodium chloride solution, then MgSO₄), and concentrated.

The residue (which by vpc contained no starting bromide) was distilled to give 2,2-dichlorocyclopropylmethylamine (91) (2.4 g, 18%), colorless liquid, bp 68-70° (10 Torr), lit bp 73-78° (18 Torr). The large pot residue was attributed to the presence of sec- and tert- amines, and also intra- or inter-molecular displacement of chloride by nitrogen which would give polymeric products. The colorless distilled material turned dark overnight, apparently as a result of displacement of ring chlorine by the amine function.

2,2-Dichlorocyclopropylmethylamine (91) from subsequent runs was stored as its hydrochloride 92. Hydrogen chloride gas was passed into a solution of 91 in dry ether (10 ml/g of amine). After absorption of gas ceased, the crystals were filtered, rinsed with ether, and dried in a vacuum desiccator; 87% yield, mp 151-156° (d). Hydrochloride 92 was stored in a tightly capped container; small amounts of free amine were regenerated by treatment of 92 with sodium hydroxide solution and extraction with ether, followed by preparative vpc (5% KOH/5% Carbowax 20M) immediately before use.

Deamination of 2,2-Dichlorocyclopropylmethylamine (91)

2,2-Dichlorocyclopropylmethylamine hydrochloride (92) (171 mg, 0.96 mmole) and toluene (89 mg, internal standard) were added to acetic
acid (10 ml, 4% water). The mixture was cooled to 0° and sodium nitrite (400 mg, 5.8 mmole) was added in several portions (0.5 hr). The solution was stored in a refrigerator overnight, poured into water (50 ml) and extracted with dichloromethane (3 x 5 ml). The organic layer was washed with 5% sodium bicarbonate solution (2 x 5 ml) (which was backwashed with dichloromethane (2 x 1 ml)), and dried (Na₂SO₄). Vpc analysis (10' x 1/8" 20% Carbowax 20M, 145°, flame ionization, calibrated area response with authentic samples) revealed 2,2-dichlorocyclopropylmethyl acetate (55) (54%) and 2,2-dichlorocyclopropylmethyl chloride (74b) (1%). A pair of similar runs in which the bicarbonate was not backwashed gave 55 and 74b in 45% total yield. A replicate run with bromobenzene as internal standard gave a 54% yield of 55 and 74b.

In a separate experiment amine 21 was collected directly in acetic acid from preparative vpc and the resulting salt nitrosated with sodium nitrite as above; no 2,2-dichlorocyclopropylmethyl chloride (74b) was observed. Nitrosation in very dilute (ca 0.3%) hydrochloric acid at 0° yielded 1,1-dichlorocyclopropylmethanol (70) (94%) and 2,2-dichlorocyclopropylmethyl chloride (74b) (6%) in 52% overall yield. Running the nitrosation at room temperature did not appreciably affect the yield or product ratio.

2,2-Dichlorocyclopropylmethanol (70) via Acid-Catalyzed Transesterification of 2,2-Dichlorocyclopropylmethyl Acetate

2,2-Dichlorocyclopropylmethyl acetate (55) (7.05 g, 38.5 mmole) (prepared from allyl acetate and phenyl(trichloromethyl)mercury),
methanol (20 ml), and sulfuric acid (10 microdrops) were distilled slowly through a short column until all the methyl acetate had distilled and the temperature in the still head had risen to 65°. The pot residue was cooled and stirred with solid sodium bicarbonate (1 g) and filtered through cotton. A small amount of methanol was employed to facilitate transfers. Distillation of this residue gave 2,2-dichlorocyclopentylmethanol (70) (4.44 g, 82%), bp 92-94° (16 Torr), lit 93-94° (15 Torr). Vpc and nmr examination of 70 demonstrated no rearrangement had occurred. Basic catalysis (NaOMe) failed to effect the transesterification and resulted in degradation of the starting material.

Phase Transfer Reactions: General Procedures

Chloroform (3 equivalents), 50% aqueous sodium hydroxide (6 equivalents), olefin (1 equivalent), and phase transfer catalyst (ca 0.5 g/100 g chloroform) were stirred together. When the sodium hydroxide had been consumed, the aqueous phase rose to the top. To achieve reaction adequate stirring was important; in this work magnetic stirring was sufficient for small quantities, but if total volume exceeded 250 ml, mechanical stirring was usually employed.

The reaction was initiated with the flask in an ice bath, since the reaction is mildly exothermic. If total volume was greater than 50 ml, the reaction was watched carefully initially to prevent overheating. If reaction became too vigorous, stirring was discontinued until the reaction mixture had cooled down. After reaction became less vigorous, the ice bath was removed, because reaction was very slow at
0°, and the reaction was allowed to run to completion at 25-40°.

An alternate procedure was examined, where the sodium hydroxide solution was warmed to ca 70° and the chloroform and olefin added dropwise so as to maintain gentle reflux, but the yields were lower than in the above preferred procedure.

At the end of the reaction period, the mixture was carefully diluted with 2-4 volumes of water and stirred slowly. With reactive olefins, this resulted in clean separation of the phases. Less reactive olefins had, however, an emulsified brown polymer and it was necessary to filter the diluted reaction mixture through a heavy aqueous pad of filter aid. This gave a clean two phase mixture. The organic layer was drawn off and the transfer completed with a little dichloromethane or chloroform. The product layer was washed with saturated sodium chloride solution and dried (MgSO₄). In all the cited examples, distillation yielded product.

Reagent preparation was straightforward. Sodium hydroxide solution was made up and chilled in an ice bath; it was not allowed to stand at 0° to avoid freezing. Benzyltriethylammonium chloride was a convenient catalyst and readily prepared by warming on a water bath or steam bath (reflux condenser, protected from atmospheric moisture) overnight equi-molar quantities of benzyl chloride and triethylamine. The solid mass was broken up and triturated thoroughly with ether, collected on a Büchner funnel, rinsed with ether, and dried in vacuo. The quaternary salt will deliquesce and was stored in a tightly capped
bottle. The catalyst was dissolved in the chloroform before addition of hydroxide; addition of the catalyst to the sodium hydroxide layer was inefficient.

1. 2,2-Dichlorocyclopropylmethyl Bromide (74a) via Phase Transfer Catalysis

Chloroform (150 g, 1.25 mole), allyl bromide (50 g, 0.41 mole), sodium hydroxide solution (50 wt %, 200 g, 2.5 mole), and benzytriethylammonium chloride (0.3 g) were vigorously stirred; temperature control (ca 25° was provided by a water bath through which tap water was circulated slowly. After 8 hr the organic phase had dropped to the bottom; the mixture was cooled and water (700 ml) was added slowly with gentle stirring. After several minutes the emulsion had nearly all broken. The mixture was filtered through aqueous Celite and the layers separated. The aqueous phase was washed with dichloromethane (1 x 25 ml); the combined organic layer was washed with saturated sodium chloride (1 x 150 ml), and dried (MgSO₄). Evaporation of solvent and distillation through a spinning band column (50 cm) gave, after a forerun of 2,2-dichlorocyclopropylmethyl chloride (74b) (5.0 g, 7.5%), 2,2-dichlorocyclopropylmethyl bromide (74a) (40.5 g, 48%), bp 70-72° (14-15 Torr), identical to material prepared earlier in this work. A larger run (6x) gave similar yields. The ease of this preparation and the purity of the product are much superior than that via the phenyl(trichloromethyl)mercury route.
2. 2,2-Dichlorocyclopropylmethyl Acetate (55) via Phase Transfer Catalysis

Chloroform (300 g, 2.5 mole), allyl acetate (100 g, 1 mole), aqueous sodium hydroxide solution (50 wt%, 400 g, 5 mole), and benzyltriethylammonium chloride (3 g) were stirred in an ice bath. Aliquots were periodically withdrawn, washed, dried, and examined by vpc (SE-30). After conversion of the allyl acetate to product was about 25% complete, substantial quantities of 2,2-dichlorocyclopropylmethanol (70) began to appear. As the alcohol concentration rose, the rate of dichloromethylene transfer appeared to drop off rapidly, presumably due to interception of dichlorocarbene by 70 to give a dichloroether, which upon hydrolysis regenerates the alcohol 70 plus sodium formate.

After 24 hr no additional conversion to 55 was observed. The mixture was diluted with 3 volumes of ice water, stirred, and the phases separated. The aqueous layer was washed with a small portion of chloroform. The combined organic layers were washed with saturated sodium chloride solution and dried (MgSO4). Removal of solvent and distillation yielded a 1:3 mixture of 2,2-dichlorocyclopropylmethanol (70) and 2,2-dichlorocyclopropylmethyl acetate (55) (64 g, 39%), bp 80-98° (22 Torr). This mixture may be separated by fractionation, or it may all be converted to acetate 55 by acetyl chloride-pyridine, or it all may be converted to alcohol 70 by transesterification with methanol and removal of ethyl acetate. In a run carried out at 40°, the overall yield was lower due to additional saponification.
3. 2,2-Dichloro-1-methylcyclopropylmethyl Acetate Standard

Methallyl acetate (10 g, 85 mmole, prepared from methallyl chloride and sodium acetate in acetic acid at reflux 48 hr, bp \(122-127^\circ\), lit \(124^\circ\), 95% pure by vpc), chloroform (15 g, 125 mmole),


Aqueous sodium hydroxide (20 g, 50 wt%, 250 mmole), and benzyltriethylammonium chloride (0.2 g) were stirred at room temperature 4 hr. Dilution with water, separation of phases, washing (saturated sodium chloride solution), drying (\(\text{MgSO}_4\)), and distillation yielded a mixture of 2,2-dichloro-1-methylcyclopropylmethyl acetate (76a) and 2,2-dichloro-1-methylcyclopropylmethanol (76b). Pure samples of each were collected by preparative vpc. Ester 76a was identical (vpc retention on SE-30 at \(178^\circ\), nmr, and ir) with that prepared previously in the solvolysis of the chloride 75 \(\text{vide infra}\). Treatment of 76a with lithium aluminum hydride in tetrahydrofuran gave alcohol 76b. Phenyl isocyanate converted 76b to its phenyl urethane, recrystallized from carbon tetrachloride; mp 75-77\(^\circ\), lit \(78.5-79.5^\circ\).

4. 2,2-Dichloro-1-methylcyclopropylmethyl Chloride (75) via Phase Transfer Catalysis

Chloroform (150 g), 50% sodium hydroxide (200 g), and methallyl chloride (37 g, 0.41 mole) were stirred in an ice bath with a catalytic quantity of benzyltriethylammonium chloride (0.5 g) for 4 hr, then at
room temperature overnight. Customary work-up and distillation gave
2,2-dichloro-1-methyleyclopropylmethyl chloride \((\text{I}5)\) (50.1 g, 71%), bp 75-77.5\(^\circ\) (25 Torr), lit \(135\) \(89^\circ\) (50 Torr); the nmr (100 MHz, \(\delta\) 3.68 (s,


2, \(\text{CH}_2\text{Cl}\), 1.50 (s, 3, \(\text{CH}_3\)), 1.42 and 1.38 (m, 2, ring H)) is also in agreement with reported values \(^3\) (60 MHz, \(\delta\) 3.85 and 3.72 (m, 2), 1.55 (s, 3), and 1.53 and 1.25 (m, 2)).

5. 1,2,2-Trichlorocyclopropylmethyl Chloride (119) via Phase Transfer Catalysis

A mixture of 2,3-dichloropropene (22 g, 0.2 mole), chloroform (75 g, 0.63 mole), 50% aqueous sodium hydroxide (100 g, 1.25 mole), and benzyltriethylammonium chloride (0.3 g) was stirred at 0\(^\circ\) for 1 hr, allowed to warm to room temperature and then stirred for 8 hr. The reaction mixture, containing considerable emulsified brown polymer, was diluted with water (3 volumes), stirred for 5 min, and then filtered through a heavy aqueous Celite pad. The filter cake was rinsed with a little dichloromethane. The layers were separated and the organic phase was washed with saturated sodium chloride solution, dried, concentrated, and distilled, to yield 1,2,2-trichlorocyclopropylmethyl chloride (119) (6.2 g, 16%), bp 90-92\(^\circ\) (23 Torr), lit \(2\) 90-92\(^\circ\) (15 Torr).

The nmr of 119 is identical to that reported. \(^2\) Surprisingly the ring protons exhibit a sharp resonance at \(\delta\) 1.94 and a smaller, sharp
resonance at $\delta$ 2.08; the chloromethylene absorbance is a singlet at $\delta$
3.96.

6. 2,2-Dichlorocyclopropylmethyl Chloride (74b) via Phase Transfer Catalysis

Allyl chloride (50 g, 0.65 mole), aqueous sodium hydroxide (50%, 266 g), chloroform (200 g), and benzyltriethylammonium chloride (0.5 g) were stirred at 0° for 4 hr. The mixture was then allowed to warm to room temperature and stirred overnight. Vpc examination of an aliquot indicated conversion of allyl chloride was 60% complete. Customary work-up yielded 2,2-dichlorocyclopropylmethyl chloride (74b) (58 g, 92%, corrected for unreacted starting material), bp 59.5-62° (17-18 Torr), lit $^{138}$ 56° (17 Torr).


7. 2,2-Dichloro-3-phenylcyclopropylmethyl Chloride (80) via Phase Transfer Catalysis

Cinnamyl chloride (31 g, 0.20 mole), chloroform (75 g), aqueous sodium hydroxide (50%, 100 g), and benzyltriethylammonium chloride (0.50 g) were stirred at room temperature 24 hr. The mixture was diluted with water (3 volumes), stirred for 15 min, and then filtered through Celite; the flask and pad were rinsed with dichloromethane. The layers were separated and the organic phase washed with saturated sodium
chloride solution. Drying (MgSO₄) and removal of solvent, followed by vacuum distillation, gave 2,2-dichloro-3-phenylcyclopropylmethyl chloride (80) (40.2 g, 84%), bp 93-96⁰ (0.15 Torr); ir cm⁻¹ 1495, 745, and 690; nmr δ 7.3 (s, 5, aromatic H), 3.75 (m, 2, CH₂Cl), 2.65 (d, 1, PhCH), 2.3 (m, 1, ring H). Exact mass calcd for C₁₀H₉Cl₃: 233.2769; observed 233.9773. A satisfactory elemental analysis, despite repeated efforts, was not obtained; the acetate 81, a derivative of 80, did give the proper analysis (vide infra).

8. 2,7,7-Trichlorobicyclo[4.1.0]heptane (84) via Phase Transfer Catalysis

3-Chlorocyclohexene (11.7 g, 0.1 mole), chloroform (25 g), 50% aqueous sodium hydroxide (33 g), and benzytriethylammonium chloride (0.2 g) were stirred at room temperature 16 hr; standard work-up gave 2,7,7-trichlorobicyclo[4.1.0]heptane (84) (15.1 g, 81%), bp 112.5-114.5⁰ (15 Torr): ir cm⁻¹ 1445, 1220, 1050, 800; nmr δ 4.25 (m, 17 Hz wide, 1, CHCl), 1.2-2.2 (m, 9, ring H).

Found: C, 42.26; H, 4.57.

9. Attempted Reaction of Acrylonitrile with Dichlorocarbene via Phase Transfer Catalysis

Acrylonitrile (2.6 g, 0.05 mole), chloroform (13 g), 50% aqueous sodium hydroxide (16 g), and benzytriethylammonium chloride (0.1 g) were stirred at room temperature. The mixture rapidly turned black, due to the sensitivity of the nitrile to the reaction conditions. Vpc
examination of the organic phase after work-up revealed the presence of 2,2-dichlorocyclopropane nitrile in less than 5% yield, retention time identical to authentic material prepared from phenyl(trichloromethyl)mercury and acetonitrile.

10. Reaction of Cyclopentadiene with Dichlorocarbene via Phase Transfer Catalysis

Freshly distilled cyclopentadiene (6.6 g, 0.1 mole), chloroform (25 g), 50% aqueous sodium hydroxide solution (33 g), and benzyltriethylammonium chloride (0.2 g) were stirred in an ice bath. The solution quickly turned a deep red color, doubtless due to the cyclopentadienyl anion. Work-up and distillation gave a complex mixture which was not examined further.

11. Preparation of 2,2-Dichloro-1-vinylcyclopropane via Phase Transfer Catalysis

Butadiene (325 g, 6 mole) was collected in a dry ice trap and added to a flask outfitted with thermometer, dry ice condenser, and mechanical stirrer, and containing chloroform (750 ml, 1100 g, 9.3 mole), 50% aqueous sodium hydroxide (1112 g, 13.9 mole), and benzyltriethylammonium chloride (3 g, 0.013 mole), all chilled in an ice bath to 0°. The mixture was stirred vigorously. When the temperature rose to 10°, stirring was discontinued. The temperature continued to rise to 20-25° despite the ice bath; the butadiene refluxed rapidly. After reaction had subsided and the temperature fallen to 10-15° (ca 1-1.5 hr) stirring was cautiously resumed. The temperature was maintained between
10-15°; after 2-3 hr the flask was allowed to warm slowly to room temperature. Stirring was continued until butadiene no longer refluxed appreciably (ca 3 hr). The flask was cooled and ice water (1 l) was added slowly. The mixture was stirred 10 min then the liquid was decanted and the organic layer was separated. The aqueous layer was extracted with chloroform (50 ml) and discarded. The undissolved salts were stirred with additional water and chloroform until dissolved. The phases were separated. The combined organic layers were washed with saturated sodium chloride solution (2 x 1 l), and dried (MgSO₄). The solution was evacuated at room temperature until the butadiene had been removed. The temperature was then raised and the solvent and product flash distilled. Only a small residue remained. The distillate was stabilized by the addition of a small amount of hydroquinone and fractionated (80 cm Vigreux) to yield 2,2-dichlorovinylcyclopropane (407 g, 49%), bp 122.5-124°, lit 122.5° (730 Torr).


This demonstrates that the phase transfer method can be used to produce the vinylcyclopropane in good yield without appreciable diaduct, contrary to the previous indication. The product is not contaminated

(138) E. V. Dehmlow, Tetrahedron, 28, 175 (1972).
with 1,1-dichloro-2,2-dimethylcyclopropane (which can only be removed by very careful fractionation), a drawback to the potassium t-butoxide-chloroform procedure. The volatility of 1,3-butadiene would require a high pressure apparatus for the trichloroacetate procedure. Hence for purity, convenience, economy, and ease of operation the above method is preferred.

12. Preparation of 2,2-Dichlorocyclopropanecarboxylic acid (120)

2,2-Dichlorocyclopropanecarboxylic acid (120) was prepared from 2,2-dichlorovinylcyclopropane by the reported method modified in that


the potassium permanganate solution was warmed on the steam bath several hr and had mp 74-76°, lit 74-75°. The acid deliquesced in moist air and was stored in a tightly capped bottle. Recrystallization from petroleum ether (ca 3 ml/g) gave on one occasion a lower melting allotropic form which spontaneously was transformed into the more stable modification.

13. 2,2-Dibromocyclopropanecarboxylic Acid (121) via Phase Transfer Catalysis

Bromoform (63.2 g, 0.25 mole), aqueous sodium hydroxide (50 wt%, 13.6 g, 0.33 mole), dichloromethane (100 ml), and benzyltriethylammonium chloride (0.5 g) were placed in a flask equipped with a mechanical
stirrer, Dry Ice condenser, and thermometer. The flask was chilled in an ice bath, butadiene (10.8 g, 0.20 mole) was added, and the mixture was stirred rapidly 4 hr at 0°, then at room temperature overnight. Cautious addition of ice water to the stirred liquid, separation of phases, washing of the organic layer with saturated sodium chloride solution, drying (MgSO₄), and concentration yielded a mixture of bromoform and 1,1-dibromo-2-vinylcyclopropane (3:1 by vpc).

An aliquot of this material (15 ml, 44 g, 11 g of 1,1-dibromo-2-vinylcyclopropane, 0.05 mole) was oxidized with potassium permanganate (16 g, 0.1 mole in 1% aqueous acetone (250 ml) overnight). The resulting basic suspension was diluted with water (500 ml), filtered through Celite (pad rinsed with hot water and dichloromethane), and the filtrate was extracted with dichloromethane (3 x 50 ml). The combined organic layers were extracted with 5% sodium bicarbonate (3 x 50 ml), which was backwashed with dichloromethane. The bicarbonate extract was combined with the aqueous filtrate, acidified (20% H₂SO₄), saturated with sodium chloride, and extracted with dichloromethane (4 x 25 ml). Drying (MgSO₄), treatment with Norit, removal of solvent, and extraction of the residue with hot petroleum ether (30-60°, ca 150 ml) gave, upon cooling, 2,2-dibromocyclopropane carboxylic acid (121) (1.38 g, 11%), mp 92-93°, lit 94°. Oxidation is not complete, thus accounting for the low yield.
1-Chloro-1-(2,2-dichlorocyclopropyl)ethane (82) via Phase Transfer Catalysis

3-Chloro-1-butene (Chemical Samples Co., 98%, ca 60% by vpc, nmr; 37 g, 0.41 mole) was dissolved in chloroform (150 g) containing benzytriethylammonium chloride (0.5 g), and stirred with sodium hydroxide solution (200 g, 50 wt%), initially in an ice bath, then at room temperature overnight. Distillation gave, after work-up, two fractions, bp 71-74.5° (26 Torr) (15.1 g) and bp 75-81° (26 Torr) (20.6 g); total yield 35.7 g, 50.4%. The lower boiling fraction, further purified by vpc, was identified as 1-chloro-1-(2,2-dichlorocyclopropyl)ethane (82): ir cm⁻¹ 3000, 2940, 1580, 1495, 1370, 1220, 1170, 1115, 1040, 965 (s), 880, 800 (s, b), 760 (s, b), 710 (s, b); nmr δ 3.74 (m, 1, CHCl), 2.4-1.4 (m, 6, the -CH₃ appears as a pseudo d, J = 6 Hz at 1.84); mass spectrum Daltons (rel intensity) 176(2), 174(4), 172(5) (Cl₃⁻ molecular ion), 139(5), 137(9), 111(16), 109(25), 78(31), 76(100), 65(26), 55(81). Exact mass calcd for C₅H₇Cl₃: 171.9613; observed 171.9615.

Anal. Calcd for C₅H₇Cl₃: C, 34.62; H, 4.04

Found: C, 34.62; H, 3.93.

The higher boiling fraction was 2,2-dichloro-3-methylcyclopropylmethyl chloride; its nmr and ir correspond with that previously reported.

Acetolysis Experiments: General Procedure

Sodium acetate (0.5 g) dried at 100°, 96% acetic acid (10 ml), and a weighed amount of halide (0.5-1.0 g) were heated at 115-120°
for 12-24 hr in a 25 ml Erlenmeyer flask capped with a serum stopper, and vented with a 22 gauge needle. The mixture was then cooled and poured into water (50 ml). The solution was extracted with dichloromethane (3 x 5 ml), which was washed with 5% sodium bicarbonate solution (2 x 25 ml), saturated sodium chloride solution (25 ml), dried (MgSO₄), and concentrated. The residue was usually examined by vpc (SE-30).

1. Acetolysis of 2,2-Dichlorocyclopropylmethyl Bromide (74a)

Acetolysis under the general conditions gave unarranged 2,2-dichlorocyclopropylmethyl acetate (55). After several days an equilibrium was established, containing 91 mole% acetate 55 and 9% bromide 74a.

2. Acetolysis of 2,2-Dichlorocyclopropylmethyl Chloride (74b)

The results are similar to solvolysis of the bromide 74a. The product, 2,2-dichlorocyclopropylmethyl acetate (55), is identical to material obtained from the bromide 74a, and prepared earlier in this work from phenyl(trichloromethyl)mercury and allyl acetate.

3. Acetolysis of 2,2-Dichloro-1-methycyclopropylmethyl Chloride (75)

Under the general conditions, acetolysis of 2,2-dichloro-1-methycyclopropylmethyl chloride (75) gave, as the sole ester product, 2,2-dichloro-1-methycyclopropylmethyl acetate (76a): ir cm⁻¹ 1740 (s), 1250 (s, b); nmr δ 4.18 (AA' quartet, 2, CHOAc), 2.05 (s, 3, -OAc),
1.40 (s, \(\text{CH}_2\)), and 1.52, 1.20 (m, ring H, total 5); mass spectrum Daltons (rel intensity) 198, 196 (molecular ion), 100(19), 43(100).

Anal. Calcd for \(\text{C}_7\text{H}_10\text{Cl}_2\text{O}_2\): C, 42.67; H, 5.12.

Found: C, 42.97; H, 5.26.

This material was identical to material prepared via phase transfer catalysis; saponification yielded the known alcohol identified as its phenyl urethane (see above).

4. Acetolysis of 1-Chloro-1-(2,2-dichlorocyclopropyl)ethane (82)

1-Chloro-1-(2,2-dichlorocyclopropyl)ethane (82) treated 12 hr and worked up exactly as described above under the general procedure yielded 1-(2,2-dichlorocyclopropyl)ethyl acetate (83), mp 40-41°: ir cm\(^{-1}\) 1725 (s), 1240 (s, br), 765; nmr \(\delta\) 4.52 (m, 1, CHOAc), 2.02 (s, 3, ring \(\text{CH}_3\)), 1.95-1.20 (m, ring H), and 1.38 (d, CH\(\text{CH}_3\), total 5). That crystalline product was obtained must indicate one diasteromeric pair predominates. No other ester products were found.

Anal. Calcd for \(\text{C}_7\text{H}_{10}\text{Cl}_2\text{O}_2\): C, 42.67; H, 5.12.

Found: C, 42.97; H, 5.26.

5. Acetolysis of 2,2-Dichloro-3-phenylcyclopropylmethyl Chloride (80)

Acetolysis of 80 under the standard conditions gave 2,2-dichloro-3-phenylcyclopropylmethyl acetate (81): ir cm\(^{-1}\) 1740 (s), 1245 (s, br); nmr \(\delta\) 7.2 (s, 5, aromatic), 4.3 (m, 2, -CH\(\text{CH}_2\)OAc), 2.65 (d with fine structure, 1, PhCH), 2.36-2.10 (m, 1, ring H), 2.05 (s, 3, OAc);
mass spectrum Daltons (rel intensity) 260, 258 (molecular ion), 163
(-Cl, AcOH, 20), 43(100).

Anal. Calcd for C_{12}H_{12}Cl_{2}O_{2}: C, 55.62; H, 4.67.
Found: C, 55.33; H, 4.68.

Silver Ion Assisted Acetolysis: General Procedure

Silver acetate (reagent grade, ca 0.1 g for ratio studies, 0.5 g
for preparative scale), 96% acetic acid (10 ml), and halide (molar
equivalent to silver acetate) were heated at 115-120° for 12 hr in a
25 ml Erlenmeyer flask capped with a serum stopper, and vented with
a small gauge needle; the hot mixture was swirled to bring a portion
of the silver acetate into solution. At the end of the reaction
period the mixture was cooled, and the solution was decanted from the
precipitated silver halide into water (50 ml). The residue was
washed thoroughly with dichloromethane. The aqueous solution was ex­
tracted with dichloromethane (3 x 5 ml); the combined organic layer
was washed with saturated sodium chloride solution (2 x 25 ml), 5%
sodium bicarbonate solution (10 ml), dried (MgSO₄), and stripped to a
small volume which was examined by vpc.

1. Silver Ion Assisted Acetolysis of 2,2-Dichlorocyclopropyl-
methyl Bromide (74a)

This acetolysis was performed in the first portion of this work
in conjunction with acetolysis of the α,α-δ₂ analog (see above). No
rearranged ester product is obtained; the sole product is ester 5₅.
2. Silver Ion Assisted Acetolysis of 2,2-Dichlorocyclopropyl-methyl Chloride (74b)

Under the standard conditions described above, only unrearranged starting chloride 74b and unrearranged ester 55 were obtained.

3. Silver Ion Assisted Acetolysis of 2,2-Dichloro-1-methylcyclopropylmethyl Chloride (75)

The reaction was carried out under the general conditions described above. Conversion of 75 is approximately 30%. The products were 2,2-dichloro-1-methylcyclopropylmethyl acetate (76a) (88 rel mole %) and 4,4-dichloro-3-methyl-3-buten-1-yl acetate (77) (12%). A small amount of the chloride 75 had also rearranged to 1,1,4-trichloro-2-methyl-1-butenone (105). 2,2-Dichloro-1-methylcyclopropylmethyl acetate (76a) is identical to material described earlier in this work. The properties and proof of structure of 4,4-dichloro-3-methyl-3-buten-1-yl acetate (77) and 1,1,4-trichloro-2-methyl-1-butenone (105) are described in the following section of this work.

4. Silver Ion Assisted Acetolysis of 1,2,2-Trichlorocyclopropyl-methyl Chloride (119)

Reaction under the general conditions resulted in the rapid precipitation of silver chloride and the formation of a silver mirror on the wall of the flask. The precipitated halide was black, either due to colloidal silver or organic polymer. Work-up and vpc examination showed only 25% recovery (internal standard) of starting material, and no volatile products of any sort.
5. Silver Ion Assisted Acetolysis of 1-Chloro-1-(2,2-dichlorocyclopropyl)ethane (82)

Reaction was carried out as described and the ester obtained, 1-(2,2-dichlorocyclopropyl)ethyl acetate (83), was identical to material prepared earlier in this work.

6. Silver Ion Assisted Acetolysis of 2,2-Dichloro-3-phenylcyclopentylmethyl Chloride (80)

Under the general conditions, the only product was unrearranged ester 81, identical to material prepared earlier in this work.

7. Silver Ion Assisted Acetolysis of 2,7,7-Trichlorobicyclo[4.1.0]heptane (84)

Reaction was complete within 12 hr under the general conditions. The product is 7,7-dichlorobicyclo[4.1.0]heptan-2-yl acetate (85); nmr exhibited absorptions for H-C-OAc centered at δ 5.4 (cis, ca 90%) with a shoulder at 5.1 (trans, ca 10%).

8. Silver Acetate Assisted Solvolysis of 1,1,4-Trichloro-2-methyl-1-butene (105)

1,1,4-Trichloro-2-methyl-1-butene (105) (0.87 g, 5 mmole), the preparation of which is described later in this work, silver acetate
(0.84 g, 5 mmole) were mixed with acetic acid (10 ml) and the mixture heated at 115° overnight. The cooled organic phase was decanted and the precipitate washed with water and dichloromethane. The combined solutions were washed with water (3 x 10 ml), saturated sodium chloride solution and 5% sodium bicarbonate. Drying (MgSO₄) and stripping yielded a mixture of starting material (81%) and 4,4-dichloro-3-methyl-3-buten-1-yl acetate (77) (19%). The pure acetate exhibited: \( \text{IR cm}^{-1} \) 1740 (s), 1620 (w), 1210 (s, b), 1045 (s), and 900 (s); \( \text{nmr} \delta 4.10 \) (t, J = 7, 2, CH₂OAc), 2.56 (t, J = 7, 2, CH₂-CH₂), 1.96 and 1.92 (s, total 6, CH₃); mass spectrum Daltons (rel intensity) 200, 198, 196 (molecular ion, < 1), 140(5), 139(1), 138(32), 137(2.5), 136(52, -CH₃COOH), 103(3), 101(10.5), 89(2), 87(4), 73(5), 65(8), 43(100).

\text{Anal. Calcd for C}_5\text{H}_7\text{Cl}_3: \text{C}, 42.66; \text{H}, 5.12.
\text{Found: C}, 42.41; \text{H}, 4.86.

**Preparation of Butan-2-on-4-yl Acetate**

Butan-2-on-4-ol (8.8 g, 0.1 mole), prepared from acetone and para-formaldehyde in dichloromethane (100 ml), was cooled to 0°, stirred magnetically, and treated with acetyl chloride (7.93 g, 0.101 mole) and pyridine (7.9 g, 0.100 mole) added dropwise simultaneously over 10 min. After addition was complete, the mixture was allowed to stand

15 min, then poured into water (100 ml) and shaken thoroughly. The organic phase was washed with additional water (50 ml), 5% aqueous sodium bicarbonate (2 x 25 ml), saturated sodium chloride (50 ml), and dried (MgSO₄). Distillation after removal of solvent gave butan-2-on-4-yl acetate (10.8 g, 83%), bp 82-83° (5.2 Torr), lit 78-84° (15 Torr): nmr δ 4.20 (t, 2, CH₂OAc), 2.68 (t, 2, CH₂CH₂), 2.10 (s, 3, C(=O)CH₃), 1.96 (s, 3, OAc).

Preparation of 4,4-Dichloro-3-methyl-3-buten-1-yl Acetate (77) via the Wittig Reaction

To dichloromethylenetriphenylphosphorane (0.05 mole) in heptane under nitrogen at 0° was added dropwise over 30 min butan-2-on-4-yl acetate (6.5 g, 0.05 mole). The suspension was stirred 2 hr at 0°, then at room temperature overnight. Filtration and concentration of liquors, followed by preparative vpc (SE-30; last of 3 ester peaks) gave 4,4-dichloro-3-methyl-3-buten-1-yl acetate (77), whose spectral properties were identical to those of the material prepared earlier via silver ion assisted solvolysis of 1,1,4-trichloro-2-methyl-1-butenene (105).
Friedel-Crafts Reactions of Cyclopropylcarbinyl Halides with Antimony

Pentachloride in Benzene

Benzene (ca 3 ml), dried by azeotropic distillation, was placed in a 10 ml round bottomed flask equipped with a magnetic stirrer and capped with a serum stopper vented with a fine needle attached to a tube filled with Drierite. After addition of halide, the flask was chilled, and a measured volume of antimony pentachloride (0.125-0.5 mole/mole of organic halide) was syringed in. The syringe was rinsed immediately with concentrated sulfuric acid to prevent plugging. The ice bath was removed and the mixture was stirred at room temperature for the given reaction period. Work-up was carried out by stirring the mixture with saturated sodium chloride (50 ml) and extracting with ether (3 x 5 ml). The ether layer was neutralized with 5% aqueous sodium bicarbonate (2 x 25 ml), dried (saturated NaCl and MgSO₄), and concentrated. The residue was examined by vpc.

1. Reaction of 2,2-Dichlorocyclopropymethyl Chloride (74b) with Antimony Pentachloride in Benzene

2,2-Dichlorocyclopropymethyl chloride (74b) (0.77 g, 5 mmole) and antimony pentachloride (125 mmol, 0.3 g, 1 mmole) reacted (1 hr) under the above conditions gave 47% conversion to 1,1-dichloro-3-phenyl-1-butene (101) (63%), 1,1-diphenylethane (122) (4%), and 1,1-diphenylethene (123) (1%). The reaction was carried out many times with different concentrations of reagents; the product ratio was not greatly affected, although larger amounts of antimony pentachloride gave higher
conversion. Refluxing only marginally increased the yields of 122 and 123. Some chlorobenzene was obtained from chlorination of the benzene.

1,1-Dichloro-3-phenyl-1-butene (101) has the following physical properties: ir cm\(^{-1}\) 3060, 2950, 1610, 1480, 1440, 880, 690; nmr δ

(144) This compound has been reported but no instrumental data given: K. Bott, Chem. Ber., 100, 2791 (1964).

7.2 (s, 5, aromatic H), 5.92 (d, J = 10, 1, vinyl H), 3.84 (m, 1, PhCH), 1.36 (d, J = 7, 3, CH\(_3\)); mass spectrum base and parent 200 Daltons.

Anal. Calcd for C\(_{10}\)H\(_{10}\)Cl\(_2\): C, 59.72; H, 5.01.

Found: C, 59.46; H, 5.08.

The mass spectra of 1,1-diphenylethane and 1,1-diphenylethene correspond peak for peak, both in position and intensity, with authentic spectra. The ir spectra are also identical with authentic values. Oxidation of 1,1-diphenylethene gave benzophenone, identified as its 2,4-dinitrophenylhydrazone, mp 233-235\(^{0}\), lit. 232\(^{0}\). Hydrogenation of the mixture of 1,1-diphenylethane and 1,1-diphenylethene by the method of Brown \(^{148}\) resulted in a single symmetrical peak in the vpc

(145) American Petroleum Institute Research Project 44, 'Catalog of Selected Mass Spectral Data,' Texas A&M University, College Station, Texas, 1968, Nos. 750 and 751.

(146) Idem, 'Catalog of Infrared Spectral Data,' Texas A&M University, College Station, Texas, 1968, Nos. 2260 and 2465.
(SE-30), corresponding to 1,1-diphenylethane. Subsequently a commercial sample of 1,1-diphenylethane was employed as a standard, and by hydrogenation a standard sample of 1,1-diphenylethane obtained. By vpc comparison on SE-30, Carbowax 20M and FFAP the two were identical with the products of the Friedel-Crafts reaction by both retention time and peak enhancement.

2. Reaction of 2,2-Dichloro-1-methylcyclopropylmethyl Chloride (75) with Antimony Pentachloride in Benzene

2,2-Dichloro-1-methylcyclopropylmethyl chloride (75) (1.0 g, 5.75 mmole) was dissolved in benzene (3 ml). Antimony pentachloride (0.3 g, 1.0 mmole) was added and the resulting mixture allowed to react 1 hr. Customary work-up yielded, upon vpc examination, four components, 92 wt % of volatile material: starting chloride (47 mole %); 1,1,4-
trichloro-2-methyl-1-butene (105) (22); 1,1-dichloro-3-phenyl-3-methyl-1-butene (106) (15.5); and 1,1-diphenylethane containing 20% 1,1-
diphenylethane (122 and 123) (8.5).

1,1-Dichloro-3-methyl-3-phenyl-1-butene (106) had the following properties: ir cm\(^{-1}\) 2950, 1600, 1480, 860, 765, 700; nmr & 7.25 (s, 5, aromatic H), 6.18 (s, 1, =CH), 1.50 (s, 6, CH\(_3\)); mass spectrum Daltons (rel intensity) 218(< 1), 216(9), 214(15), 181(30), 180(11), 179(100),
1,1,4-Trichloro-2-methyl-1-butene (105) exhibits predicted instrumental analytical values: ir cm⁻¹ 2970, 1625 (m, s), 1450 (m, b), 1375 (w), 1320 (w), 1290 (m), 1255, 1145, 895 (s, b), 805 (w, b), and 730 (m, b); nmr δ 3.54 (t, J = 7, 2, CH₂), 2.70 (t, J = 7, 2, CH₂C), 1.92 (s, 3, CH₃); mass spectrum Daltons (rel intensity) 138(4), 136(5), 127(10), 125(65), 123(100), 89(13), 87(37), 65(18). Exact mass Calcd for C₅H₇Cl₃: 171.9613; observed 171.9615.

Found: C, 34.91; H, 4.22.

Acetolysis of 105 gave 4,4-dichloro-3-methyl-3-buten-1-yl acetate (77), identical with material prepared earlier in this work.

3. Reaction of 1-Chloro-1-(2,2-dichlorocyclopropyl)ethane (82) with Antimony Pentachloride in Benzene

1-Chloro-1-(2,2-dichlorocyclopropyl)ethane (82) (0.69 g, 3.85 mmole), freed from traces of 2,2-dichloro-3-methylcyclopropylmethyl chloride by preparative vpc, was dissolved in benzene (3 ml). Addition of antimony pentachloride (0.15 g, 0.5 mmole) to the chilled mixture and warming to room temperature resulted in evolution of hydrogen chloride. Quenching and work-up after 1 hr gave three compounds, 93 wt %
of volatile material: starting chloride 82 (13 mole %); 1,1,3-trichloro-2-methylcyclobutane (117) (56%), and 1,1-dichloro-3-phenyl-1-pentene (116) (30%).

1,1-Dichloro-3-phenyl-1-pentene (116) was characterized as follows: ir cm⁻¹ 3070-2880 (5, m, sp), 1620 (m, sp), 1475 (m, sp), 1450 (m, sp), 1370 (w, sp), 910 (m, sh), 895 (s, b), 850 (m, b), 755 (s, b), and 690 (s, b); nmr δ 7.28 (narrow m, 5, aromatic H), 6.05 (d, J = 9, 1, vinyl H), 3.60 (m, 1, benzylic H), 1.78 (pseudo pentuplet, J = 8, 2, CH₂), 0.92 (t, J = 7, 3, CH₃); nD²⁰ = 1.5370, lit 1.5373.

1,1,3-Trichloro-2-methylcyclobutane (117) has: ir cm⁻¹ 3000, 1440 (m, s), 1370 (m, s), 1250 (m), 1130 (m, sh), 1060 (m, b), 1000 (m), 950 (m), 800 (s, sh), 780 (s, b), and 695 (s, b); nmr δ 4.08 (q, 1, CHCl), 3.2-2.6 (m, 2, CH₂), 2.3-2.0 (m, 1.4, CH₃), and 1.6 (d, J = 5, 1.6 CH₃); mass spectrum Daltons (rel intensity) 139(34), 137(53), 78(29), 77(9), 76(100). Exact mass Caled for C₅H₇Cl₃: 171.9613; observed 171.9617.


Found: C, 34.91; H, 4.22.

Friedel-Crafts Reactions of Cyclopropylcarbiny1 Halides with Aluminum Chloride in Benzene: General Procedure

Benzene (5-50 ml, dried by azeotropic distillation) and fresh aluminum chloride were placed in a round bottom flask protected with a drying tube. The mixture was stirred magnetically as the halide was added dropwise. The solution turned red, then dark, became warm, and
evolved hydrogen chloride. After the reaction subsided, the flask was warmed gently on a steam bath (0.25 hr). The reaction mixture was quenched by pouring into a large volume of water and stirring thoroughly. The organic layer was washed with sodium bicarbonate solution until neutral, and then saturated sodium chloride, and dried (MgSO₄). The residue was examined by vpc.

1. Reaction of 2,2-Dichlorocyclopropylmethyl Bromide (74a) with Benzene and Aluminum Chloride

2,2-Dichlorocyclopropylmethyl bromide (74a) (4.0 g, 20 mmole) was added to a slurry of aluminum chloride (1.3 g, 10 mmole) in dry benzene (100 ml). The mixture was stirred magnetically. After the initially vigorous reaction had subsided, the mixture was warmed on a steam bath (1 hr). The cooled solution was poured into water (500 ml) and stirred to destroy the aluminum chloride complex. The benzene layer was washed with water, 5% sodium bicarbonate, saturated sodium chloride, and dried (MgSO₄). The benzene was evaporated (rotary) and the residue taken up on alumina. Chromatography (1" x 6" alumina I, petroleum ether) gave a mixture of 1,1-diphenylethane (122) and 1,1-diphenylethene (123) (80:20), separated by vpc (Carbowax 20M). The indicated yield (3.54 g, 102%) was checked by addition of internal standard (hexadecane for SE-30), and it was found that only ca 55% of the material was volatile.

In subsequent experiments, the column chromatography was discarded in order to examine the entire reaction mixture. Small amounts of 1,1-
dichloro-3-phenyl-1-butene (101), identified by vpc retention time comparison with authentic sample, were detected. When the reaction was monitored, however, no build-up of this apparent intermediate was noted.

Substitution of the more reactive 2,2-dichlorocyclopropylmethyl chloride (74b) for the bromide 74a gave very similar results. The reaction could be carried out at room temperature on the chloride 74b but 24 hr were required for 91% conversion with 0.33 mole aluminum chloride per mole of halide.

2. Reaction of 2,2-Dichloro-1-methylcyclopropylmethyl Chloride (75) with Aluminum Chloride and Benzene

2,2-Dichloro-1-methylcyclopropylmethyl chloride (3.9 g, 22.5 mmole) was added dropwise to benzene (50 ml) and aluminum chloride (1.0 g, 7.5 mmole) in a flask equipped with magnetic stirrer, condenser, and drying tube. The mixture was stirred at room temperature (0.75 hr) and then warmed gently on a steam bath (0.25 hr). Standard work-up and concentration to 17.5 g yielded (vpc examination, hexadecane as an internal standard was added to an aliquot for determination of absolute yield): 2,2-dichloro-1-methylcyclopropylmethyl chloride (75) (87 mg, 2.2%); 1,1,4-trichloro-2-methyl-1-butene (105) (811 mg, 20.8%); 1,1-dichloro-3-methyl-3-phenyl-1-butene (106) (136 mg, 2.8%); 1,1-diphenylethane (122) (404 mg, 9.9%); 1,1-diphenylethene (123) (101 mg, 2.3%), and 2,2-diphenylpropane (125) (765 mg, 17.3%).
Each of the above materials was isolated by preparative vpc and examined by nmr.

The retention times and nmr spectra of the first five compounds were identical to authentic material previously obtained in this work. 2,2-Diphenylpropane (125) was identified by its properties: mp 26-28° (freezing induced by cooling with dry ice and scratching), lit 29°; nD 1.5705, lit 1.570; nmr 6 7.12 (s, 10, aromatic H), 1.67 (s, 6, CH3). The crude mixture, in addition to solvent, contained traces of other materials, and substantial quantities of high boiling tails which were not volatile enough for vpc examination.

A second run, identical save that the heating period was extended to 0.5 hr, gave: 2,2-dichloro-1-methyleclopropylmethyl chloride (75) (57.5 mg, 1.5%); 1,1,4-trichloro-2-methyl-1-butene (105) (658.7 mg, 16.9%); 1,1-dichloro-3-methyl-3-phenyl-1-butene (106) (33 mg, 0.7%); 1,1-diphenylethane (122) (428.9 mg, 10.5%); 1,1-diphenylethane (123) (96.7 mg, 2.4%); and 2,2-diphenylpropane (125) (543.9 mg, 12.3%).

3. Reaction of 1,1-Dichloro-3-phenyl-1-butene (101) with Aluminum Chloride in Benzene

1,1-Dichloro-3-phenyl-1-butene (101) (60 mg) and aluminum chloride (100 mg) in dry benzene (3 ml) were stirred by occasional shaking (1.5 hr, 33°), then poured into water and thoroughly agitated. The water
was drawn off, and the organic phase was washed with 5% aqueous sodium bicarbonate, and dried (Na₂SO₄). Hexadecane (61 mg) was added as an internal standard and the solution analyzed by vpc (20% SE-30 on Chrom W® 195°). The analysis showed 9% starting material and 54 mole % yield of 1,1-diphenylethane (122) - 1,1-diphenylethene (123) (4:1).

Reaction of 2,2-Dichlorocyclopropymethyl Halides with Aluminum Chloride in Nitromethane: General Procedure

Solutions of nitromethane (dried over 3 Å molecular sieves) and aluminum chloride were made up in dried glassware protected from atmospheric moisture. The solutions were chilled in an ice bath and the various halides added dropwise. Several work-up procedures were employed; when nitromethane is extracted with bicarbonate troublesome emulsions are formed. Generally the reaction mixtures were poured into saturated aqueous sodium chloride solution and extracted with ether. The combined ether layers were washed with saturated brine, 5% bicarbonate, and then saturated brine again. The dried (MgSO₄) extract was concentrated and the residue examined.

1,1,4-Trichloro-1-butene (105)

2,2-Dichloro-1-methycyclopropymethyl chloride (75) (150 g, 0.87 mole) was added to ice cold nitromethane (450 ml) and aluminum chloride (40 g, 0.30 mole). The mixture was allowed to stand at 20-25° for 36 hr. The resulting black solution was poured into water (1 l), shaken thoroughly, then diluted with ether. The aqueous phase was discarded;
the ether layer was extracted with additional water (2 x 1 l), then 5% sodium bicarbonate, saturated sodium chloride solution, and dried (Na₂SO₄). The solution was concentrated in vacuo. The liquid was decanted from precipitated salts, and then distilled. The material collected at bp 68-75°C (13 Torr) (81 g, 53%), consisting of a 1:1 mixture of the starting halide 75 and 1,1,4-trichloro-1-butene (105), was stored over sodium carbonate prior to fractionation. A small column packed with a metal spiral was employed to separate the isomers; a large intermediate fraction was collected. The final fraction, bp 73.5-75°C (13 Torr), was 96% pure 105 by vpc. Analytical samples were collected by preparative vpc.

Preparation of Diethyl 1,1-Cyclopropanedicarboxylate

The reported procedure was modified in that volatile material was distilled occasionally to maintain the reflux temperature near 78°C;


apparently vinyl bromide was being formed. The reaction did not go entirely to completion after 12 hr of reflux and additional dibromoethane (10% mole excess) was added and reflux continued for 3 hr whereupon 6 ml of acetic acid were required to make the solution exactly neutral. Aqueous work-up (dichloromethane) and distillation yielded diethyl 1,1-cyclopropanedicarboxylate (81.2 g, 28%), bp 98-110°C (10-11 Torr), 96% pure by nmr, contaminated with a small amount of diethyl malonate.
Preparation of Ethyl Hydrogen 1,1-Cyclopropanedicarboxylate

Diethyl 1,1-cyclopropanedicarboxylate (50 g, 0.269 mole) was dissolved in 95% ethanol (380 ml). Potassium hydroxide (17.6 g, 0.269 mole, contains 15% H₂O) was dissolved in water (135 ml) and chilled. The two solutions were mixed and let stand at room temperature (ca 25°C) until the pH of the solution dropped to 8 (about 3 hr). The solvent volume was reduced in vacuo, the residue was diluted with water (500 ml), and washed with dichloromethane (3 x 25 ml). Acidification with 10% sulfuric acid, extraction with dichloromethane (4 x 50 ml), drying (MgSO₄), and removal of the solvent in vacuo gave ethyl hydrogen 1,1-cyclopropanedicarboxylate (43.6 g, 82%), which was used directly and immediately in the next step.

Ethyl 1-Bromocyclopropanecarboxylate

Ethyl hydrogen 1,1-cyclopropanedicarboxylate (34.6 g, 0.184 mole), yellow mercuric oxide (23.6 g, 0.092 mole), and carbon tetrachloride (325 ml) were placed in a flask equipped with a mechanical stirrer, dropping funnel, and Soxhlet extractor, the thimble of which was charged with calcium chloride. The solution was refluxed and the flask walls heated intermittently with a heat gun to drive the water up into the extractor. After 3 hr, no further azeotropic distillation of water was
observed; a white precipitate remained. Bromine was added dropwise over 1 hr to the warm solution (foaming). Bromine reacted immediately upon addition. An end point was reached after only a portion of an equivalent amount of bromine had been added (12 g, 0.10 mole); the amber color persisted and no further evolution of gas took place upon further addition of bromine. The solution was cooled, filtered, and washed successively with 5% sodium thiosulfate solution, 5% sodium bicarbonate solution, and saturated brine. Drying (MgSO₄), concentration in vacuo, and distillation yielded ethyl 1-bromocyclopropanecarboxylate (I4O) (11.3 g, 78.2% based on bromine consumed), bp 64-67° (10-11 Torr): ir cm⁻¹ 1720 (s, d), 1290 (s); nmr δ 4.14 (q, 2, CH₂O), 1.6 (m, 2, ring H), 1.28 (t, CH₃), and 1.30 (m, ring H) (total 5).

Anal. Calcd for C₆H₇BrO₂: C, 37.33; H, 4.70.

Found: C, 37.33; H, 4.66.

The pot residue contained a substantial amount of the starting diester.

1-bromocyclopropanecarboxylic Acid (I4J)

Ethyl 1-bromocyclopropanecarboxylate (I4O) (1.0 g, 5.16 mmole) in methanol (10 ml) was chilled, and combined with potassium hydroxide solution (0.5 g in 2 ml H₂O). The mixture was stored at room temperature (3 hr), then poured into water (75 ml), and extracted with dichloromethane (2 x 5 ml). Acidification with 20% sulfuric acid and extraction with dichloromethane (4 x 5 ml), drying (MgSO₄), and evaporation of the solvent gave 1-bromocyclopropanecarboxylic acid (I4J) (0.71 g, 84%), mp 76-78°. Recrystallization from hot water (ca 5 ml/g)-Norit or
petroleum ether (ca 10 ml/g)-Norit chilled in Dry Ice-acetone gave material melting at 77.5-78°: ir cm⁻¹ 3000 (O-H), 2550 (m, sp, H bonded OH), 1690 (s, d, C=O); mass spectrum Daltons (rel intensity) 166(18), 164(19), 148(11), 146(11), 18(100); nmr δ 12.15 (s, 1, CO₂H), 1.72 and 1.48 (m, 4, ring H). Exact mass calcd for C₄H₅BrO₂: 163.94734; observed 163.94750.

Anal. Calcd for C₄H₅BrO₂: C, 29.12; H, 3.05.
Found: C, 29.30; H, 2.86.

Preparation of 1-Bromocyclopropylmethanol (142)

Ethyl 1-bromocyclopropanecarboxylate (9.7 g, 0.05 mole) was dissolved in tetrahydrofuran (125 ml) which had been dried by refluxing over sodium hydride and distilling. The flask was then outfitted with a magnetic stirrer and reflux condenser protected with a drying tube. Lithium aluminum hydride was then added portionwise (1 g, 0.025 mole); after addition was complete, the solution was stirred and heated to reflux. A vpc aliquot revealed that reduction was not complete; an additional portion of lithium aluminum hydride was added (1 g, 0.025 mole) and the mixture was refluxed 1 hr. Addition of 20% ammonium tartrate solution destroyed unreacted lithium aluminum hydride; additional tartrate solution (500 ml) dissolved the aluminum salts. This solution was extracted with ether (4 x 60 ml). The organic layer was washed with saturated sodium chloride solution (200 ml), dried (MgSO₄), concentrated and distilled to yield 1-bromocyclopropylmethanol (142) (5.4 g, 72%), bp 83-88° (31 Torr), lit 68° (12 Torr). A middle fraction, bp
85.5-86° (31 Torr) was used for instrumental analysis.

1-Bromocyclopropylmethyl Acetate (146)

1-Bromocyclopropylmethanol (300 mg, 2 mmole) and pyridine (240 mg, 3 mmole) were dissolved in dichloromethane (4 ml) in a centrifuge cone. Dropwise addition of acetyl chloride (200 mg, 2.5 mmole) and shaking precipitated pyridinium hydrochloride. The tube was kept at room temperature a few minutes, then washed with water (5 ml), cold 5% hydrochloric acid (2 x 1 ml), 5% sodium bicarbonate (1 ml), and dried (Na₂SO₄). Removal of solvent gave 1-bromocyclopropylmethyl acetate (146) (383 mg, 99%). Preparative vpc (SE-30, injector, detector 150°) was employed to obtain analytical samples: n²⁴_D = 1.4702; ir cm⁻¹ 1745, 1230, 1040; nmr 4.08 (s, 2, CH₂OAc), 2.04 (s, 3, OAc). 1.14 and 1.00 (m, 4, ring H); mass spectrum Daltons (rel intensity) 134(9), 132(9), 113(14), 53(30), 43(100). Exact mass calcd for C₆H₅BrO₂: 191.9786; observed 191.9789.

Anal. Calcd for C₆H₅BrO₂: C, 37.33; H, 4.70.
Found: C, 37.19; H, 4.83.

Preparation of 1-Bromocyclopropylmethyl p-Toluenesulfonate (143)

The general procedure recommended for preparing p-toluenesulfonates was used. 1-Bromocyclopropylmethanol (3 g) gave crude 143

Recrystallization from petroleum ether (30-60°C, 375 ml/g) yielded pure l-bromocyclopropylmethyl p-toluenesulfonate (143) (5.85 g, 96%), mp 54.5°, lit 57.5-58.0°. A second recrystallization failed to raise the melting point of 143.

Solvolyis of l-Bromocyclopropylmethyl p-Toluenesulfonate (143)

l-Bromocyclopropylmethyl p-toluenesulfonate (143) (1 g, 3.27 mmole) and sodium acetate (0.533 g, 6.54 mmole) were dissolved in 96% acetic acid (10 ml) in a flask sealed with a serum cap. The mixture was heated at 120° for 13 hr; aliquots were periodically examined by vpc. At the end of the reaction period, the solvolate was cooled, poured into water (50 ml), and extracted with dichloromethane (3 x 10 ml). Thorough washing with 5% sodium bicarbonate (2 x 25 ml), drying (MgSO₄), and evaporation of solvent gave 340 mg of material. Preparative vpc on SE-30 yielded (a) cyclobutanone (144), identified by nmr and as


its 2,4-dinitrophenylhydrazone, recrystallized from 50% aqueous ethanol, orange needles, mp 144.5°, lit 146°; (b) l-bromo-l-bromomethylcyclo-


propane (145), nmr δ 3.66 (s, 2, CH₂Br), 1.28 and 1.12 (m, 4, ring H),
lit\(^{107}\) (neat) 3.72 (s, 2), 1.33 and 1.13 (m, 4); (c) 1-bromocyclopropylmethyl acetate (146), identical (ir, nmr) to material prepared earlier in this work; and (d) 3-bromo-3-buten-1-yl acetate (147), identical to an authentic sample (vide infra). An identical series of runs were carried out in glacial acetic acid with similar results. Analysis by nmr (dichloromethane internal standard) and by vpc (temperature programmed, dichloromethane internal standard) indicated overall yields of 95-100% before removal of solvent.

Preparation of 3-Bromo-3-buten-1-yl Acetate (147)

4-Bromo-1-butene (1.35 g, 10 mmole) was dissolved in dichloromethane (10 ml), chilled and titrated with bromine (1.6 g, 10 mmole) in dichloromethane (10 ml). After nearly all the bromine solution had been added, a deep amber color persisted. The solution was washed with 10% sodium thiosulfate solution and 5% sodium bicarbonate solution, then dried (MgSO\(_4\)). Filtration and removal of solvent in vacuo yielded 1,2,4-tribromobutane (2.91 g, 98%), \(n^D_{30} = 1.5702\), lit\(^{156}\) \(n^D_{20} = 1.5680\).


To the crude tribromide were added sodium acetate (2.5 g, 30 mmole) and acetic anhydride (15 ml) and the mixture was heated to 160\(^\circ\) for 8 hr. The dark solution was cooled, poured into water (75 ml), and extracted (dichloromethane). The organic phase was shaken with several portions of 5% sodium bicarbonate solution and make up solvent
until all the anhydride was decomposed and acid extracted. Washing (saturated sodium chloride), drying (MgSO₄), treatment with activated charcoal, and removal of solvent gave a light brown oil (2.41 g). Vpc analysis (SE-30, 98°), showed this to be a mixture of six major components, four at short retention times and two with long retention times. The material at shortest retention time was the major component (about 25 wt %), and was identified at 3-bromo-3-buten-1-yl acetate (147); the vpc retention time, ir, and nmr were identical to those of the material prepared earlier via solvolysis of 143: ir cm⁻¹ 1730, 1630 (C=C), 895 (C=CH₂); nmr δ 5.63 and 5.45 (s, broad, 2, vinyl H), 4.17 (t, J = 7 Hz, 2, CH₂OAc), 2.75 (t with fine structure, J = 7 Hz, 2, allylic H), 1.95 (s, 3, OAc).

trans-4-Bromo-3-buten-1-yl Acetate (148)

The second material which eluted in the above experiment was identified as the previously unreported trans-4-bromo-3-buten-1-yl acetate 148: ir cm⁻¹ 3050, 2950, 1735 (s), 1620 (sh), 1360 (d), 1220 (s, b), 1030, 930, 700; nmr δ 6.04 (s, ca 12 Hz wide, 2, vinyl H), 4.00 (t, 2, CH₂OAc), 2.40 (m, 2, allylic H), 1.96 (s, 3, OAc).

Anal. Calcd for C₅H₆BrO₂:  C, 37.33; H, 4.70.

Found:  C, 37.16; H, 4.46.

cis-4-Bromo-3-buten-1-yl Acetate (149)

The third material which eluted in the above experiment was assigned as cis-4-bromo-3-buten-1-yl acetate (149): ir cm⁻¹ 3050, 2950, 1735, 1625 (m, sh); nmr δ 6.36-6.00 (m, 5 peaks, 2, vinyl H),
4.08 (t, 2, CH₃OAc), 2.52 (q, 2, allylic H), 1.98 (s, 3, OAc).

**Anal.** Calcd for C₆H₅BrO₂: C, 37.33; H, 4.70.

**Found:** C, 37.16; H, 4.78.

The last three compounds to elute in this experiment were possibly 2-buten-1,4-diyldiacetate, 3,4-dibromobuty1acetate, and starting tribromide, but were not examined carefully.

**trans-2-Bromocyclopropylmethanol (156b)**

In a sequence similar to that effected in the present work upon diethyl 1,1-cyclopropanedicarboxylate, diethyl 1,2-cyclopropanedicarboxylate (50 g, Aldrich, stereochemistry unknown) was partially saponified to the half ester (35.2 g, 85%), and the mercuric salt treated with bromine by the reported procedure to give a cis-trans mixture (85:15) of ethyl 2-bromocyclopropanecarboxylate (13.7 g, 37.5%), bp 72-86°C (10-11 Torr). The small quantities of the cis and trans isomers required for this work were conveniently obtained by preparative vpc. A 6' x 4" column packed with 17% SE-30 on Chrom G at 175°C was employed; injection size was 130 µl. Ethyl **trans-2-bromocyclopropanecarboxylate** has shorter retention time than the cis isomer. Reductions were carried out with lithium aluminum hydride on isomerically pure ester in three gram lots exactly as previously described in this work for 142. From reduction of the **trans** ester was obtained **trans-2-bromocyclopropylmethanol (156b)**: ir cm⁻¹ 3350 (s, b), 1245, 1210, 1030 (s, b); nmr δ 3.48 (s) and 3.76-3.20 (m, total 3, CH₂OH and OH), 2.80-2.64 (m, 1, CHBr), 1.64-1.30 (m, 1, ring H), 1.20-.90 (m, 2, ring H);
mass spectrum Daltons (rel intensity) 152(1), 150(1), 71(16), 44(100), 31(14), 27(13).

Found: C, 31.97; H, 4.75.

trans-2-Bromocyclopropylmethyl Acetate (163b)

trans-2-Bromocyclopropylmethanol (156b) (300 mg, 2 mmole) was acetylated with pyridine-acetyl chloride (in exactly the same manner as was 1-bromo alcohol 142) to give trans-2-bromocyclopropylmethyl acetate (163b): n_D^25 = 1.4685; ir cm⁻¹ 1740, 1430, 1370, 1235 (s, b), 1030; nmr δ 3.90-3.76 (m, 2, CH₂OAc), 2.78-2.57 (m, 1, CHBr), 2.00 (s, 3, OAc), 1.6-1.4 (m, 1, ring H), 1.1-0.90 (m, 2, ring H); mass spectrum Daltons (rel intensity) 194(1), 192(1), 152(1), 150(1), 134(4), 132(4), 113(s), 86(12), 53(12), 43(100). Exact mass Calcd for C₇H₇BrO₂: 191.9786; observed 191.9789.

Anal. Calcd for C₇H₆BrO₂: C, 37.33; H, 4.70.
Found: C, 37.44; H, 4.82.

trans-2-Bromocyclopropylmethyl p-Toluenesulfonate (157b)

The general procedure previously described for 143 was employed to esterify alcohol 156b with tosyl chloride to obtain trans-2-bromocyclopropylmethyl p-toluenesulfonate (157b): mp 50-51.5°, ir cm⁻¹ 1355, 1180, 958 (s, sh); nmr (CDCl₃) δ 7.76 and 7.32 (pseudo dd, 4, aromatic H), 3.96 (m, 2, CH₃O), 2.7 (m, 1, CHBr), 2.42 (s, 3, CH₃), 1.6 (m, 1, ring H), 1.0 (m, 2, ring H).
Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{BrO}_{3}\text{S}$: C, 43.29; H, 4.29.

Found: C, 43.59; H, 4.35.

Solvolyis of trans-2-Bromocyclopropylmethyl p-Toluenesulfonate (157b)

Acetolysis of 157b in 96% acetic acid was carried out exactly as previously executed in this study for the 1-bromo isomer 143. Preparative vpc (SE-30) yielded trans-2-bromocyclopropylmethyl acetate (163b) (62.2 mole %), identical to material (ir, nmr) previously prepared in this work; trans-4-buten-1-yl acetate (148) (14.2%), identical to material (ir, nmr) obtained earlier in this work; trans-1,4-dibromo-1-butene (162b) (4.7%); trans-2-bromocyclopropylmethyl bromide (161b) (11.1%); and a mixture of 3-butenal (159) and cyclopropanecarboxaldehyde (160, 8.6%). Confirmation of the presence of the aldehydes 159 and 160 was provided by vpc comparison of authentic samples prepared by the dibutyl aluminum hydride reduction of allyl cyanide and oxidation of cyclopropylmethanol, respectively. Dibromobutene 162b was identified on the basis of spectral data (ir, nmr) and was also obtained (as one of several isomers) from the sodium methoxide promoted elimination of 1,2,4-tribromobutene. trans-2-Bromocyclopropylmethyl bromide (161b) gave the anticipated spectrum: nmr δ 3.44-3.00 (m, 2, $\text{CH}_2\text{Br}$), 2.7 (m, 1, $\text{CHBr}$), 1.7 (m, 1, ring H), 1.04 (m, 2, ring H).

Anal. Calcd for $\text{C}_4\text{H}_6\text{Br}_2$: C, 22.46; H, 2.83.

Found: C, 22.86; H, 2.85.
cis-2-Bromocyclopropylmethanol (156a)

Reduction with lithium aluminum hydride of the cis ester 155a (obtained by preparative VPC) as described above for the trans ester 155b yielded cis-2-bromocyclopropylmethanol (156a): $n_D^{25} = 1.5068; \text{IR cm}^{-1} 3350 (s, b), 2900, 1475-1350 (f), 1250, 1030 (s, b), 820; \text{NMR } \delta 3.90-3.40 (m, 2, CH$_2$O), 3.18-2.92 (m, 1, CHBr), 1.92 (s, 1, CH), 1.82-1.12 (m, 2, ring H), 0.82-0.66 (m, 1, tert ring H); \text{mass spectrum Daltons (rel intensity) 150, 152(< 1), 44(100).}


Found: C, 31.81; H, 4.68.

cis-2-Bromocyclopropylmethyl Acetate (163a)

Acetylation of 156a as described for the trans alcohol 156b above gave cis-2-bromocyclopropylmethyl acetate (163a): $n_D^{25} = 1.4750; \text{IR cm}^{-1} 1740 (s), 1430 (m, sh), 1355 (m, sh), 1210 (s, b), 1025 (m, b); \text{NMR } \delta 4.3-3.9 (m, 2, CH$_2$OAc), 3.1-2.9 (m, 1, CHBr), 2.02 (s, 3, OAc), 1.3 (m, 2, ring H), 0.75 (m, 1, ring H).

Anal. Calcd for C$_6$H$_9$BrO$_2$: C, 37.33; H, 4.70.

Found: C, 36.96; H, 4.73.

cis-2-Bromocyclopropylmethyl p-Toluenesulfonate (157a)

The general procedure described above for the trans ester above (156b to 157b) yielded, with 156a, cis-2-bromocyclopropylmethyl p-toluenesulfonate (157a): leaves, mp 24-26°; \text{IR cm}^{-1} 1590, 1360, 1170, 1090, 940 (b); \text{NMR } \delta 7.60, 7.24 (m, 4), 3.04 (m, 2, CH$_3$O), 2.96 (m, 1, CHBr), 2.40 (s, 3, PhCH$_3$), 1.24 (m, 2, ring H), 0.68 (m, 1, ring H).
Solvolysis of cis-2-Bromocyclopropylmethyl p-Toluenesulfonate (157a)

Reaction of 157a in 96% acetic acid as previously described for the trans ester 157b gave cis-2-bromocyclopropylmethyl acetate (163a) (67.6%), identical to material prepared earlier in this work; cis-4-bromo-3-buten-1-yl acetate (20.9%), exhibiting the same spectral properties (ir, nmr) as material previously prepared in this work; cis-1,4-dibromo-1-butene (162a) (0.9%), identical retention time with material prepared above via elimination; cis-2-bromocyclopropylmethyl bromide (161a) (4.1%); and 3-butenal 152 and cyclopropanecarboxaldehyde 160 (6.5%), identical to authentic samples. cis-2-Bromocyclopropylmethyl bromide 161a gave the following analysis:

Anal. Calcd for C_{11}H_{13}BrO_{2}: C, 43.29; H, 4.29.
Found: C, 43.03; H, 4.10.

Preparation of trans-2-Bromocyclopropanecarboxylic Acid (156b)

Ethyl trans-2-bromocyclopropanecarboxylate (1.0 g, 5.18 mmole), purified by preparative vpc on SE-30 at 175°, was dissolved in ice cold methanol (10 ml) and treated with potassium hydroxide solution (0.5 g, 7.14 mmole in 2 ml water). The solution was clarified by

addition of a few drops of methanol and allowed to warm to ambient temperature. After 3 hr, the reaction mixture was poured into water (75 ml) and extracted with dichloromethane (2 x 5 ml). Acidification (20% H₂SO₄) and saturation (NaCl) followed by extraction (dichloromethane, 2 x 5 ml + 2 x 3 ml), drying (MgSO₄), and evaporation of solvent in vacuo gave trans-2-bromocyclopropanecarboxylic acid (156b) (0.570 g, 67%), mp 65-65.5°, lit 66-67°. For pKa studies this acid was recrystallized twice from low boiling petroleum ether (ca 10 ml) in Dry Ice-acetone; no increase in the mp was observed.

Preparation of cis-2-Bromocyclopropanecarboxylic Acid (156a)

Saponification of ethyl cis-2-bromocyclopropanecarboxylate from preparative vpc in exactly the same manner as described above for the trans isomer yielded cis-2-bromocyclopropanecarboxylic acid (156a): mp 68-69.5°, lit 69.5-71°. Two recrystallizations from petroleum ether (ca 10 ml/g) failed to raise the melting point.
KINETICS

General Information

I. Materials

Absolute Ethanol - Rossville Gold Shield absolute ethanol was distilled from sodium (2 g/500 ml) and stored under nitrogen.

Water - Double distilled water, obtained from the Ohio State University Reagents Laboratory, was degassed by boiling in Pyrex and stored under nitrogen.

0.01 N NaOH - Standardized 0.1 N NaOH solution was obtained from the Ohio State University Reagents Laboratory and diluted 10 times with water. As a crosscheck it was back titrated against potassium acid phthalate (Matheson Coleman and Bell Primary Standard).

Brom cresol Red - Brom cresol red indicator solution was obtained from the Ohio State University Reagents Laboratory.

90% Aqueous Ethanol - 90% Aqueous ethanol was prepared by pipetting 10 ml of water into a 100 ml volumetric flask, adding ethanol to the stem, mixing thoroughly, then making up exactly to 100 ml with ethanol.

80% Aqueous Ethanol - 80% Aqueous ethanol was prepared by pipetting 20 ml of water into a 100 ml volumetric flask, adding ethanol up to the stem, mixing thoroughly, then making up exactly to 100 ml with ethanol.
**p-Toluenesulfonic Esters** - The preparation and properties of the tosylates employed are described earlier in the present work. Solutions (0.015-0.03 N) of these tosylates for sealed tube experiments were prepared by weighing tosylate into a volumetric flask, making up to exact volume, and shaking to dissolve.

**II. Sealed Tube Techniques**

Pyrex test tube (13 x 75 mm) were washed with sodium dichromate cleaning solution, washed thoroughly with water, rinsed with ordinary distilled water (7x) and then double distilled water (3x), and dried in an oven. A glass cane was fused to the lip of the tube, and the top part of the tube heated and drawn out into a thin neck; the cane was removed by gently knocking the tube against the bench top. After flushing with nitrogen, the tubes were filled via a syringe equipped with a 6" long needle; approximately 4 ml of solution was transferred. The needle was wiped dry prior to filling the tube and care was taken not to wet the neck of the tube. The tubes were immediately sealed by heating the neck in a hot flame and pulling.

The sealed tubes were placed in a wire gauze basket and immersed in a stirred, constant temperature bath (± 0-1°C) and the timer started. Only a slight temperature depression was noted when the tubes were immersed.

At intervals a tube was removed, and the reaction quenched by plunging the tube into ice water. The tube was wiped clean, scored all the way around with a small file, and scored heavily on one side.
Then a molten glass cane was placed against the score to crack the tube; if the tube did not crack within 5 sec, the score was deepened and the hot cane reapplied. The top was knocked off with a gentle tap.

A clean 2 ml volumetric pipet was rinsed with a portion of the solution in the tube, then blown out quickly, filled, and exactly 2 ml of the solution was transferred into a 100 ml beaker containing 10 ml of double distilled water and a magnetic stirring bar, each previously washed in a manner similar to that of the tubes. For sequential points in the same kinetic run, the pipet and beaker with stirring bar were washed out with acetone (3x), distilled water (7x), and then double distilled water. The pipet was drained and quickly blown out to remove most of the water; the subsequent rinse with solution removed remaining water.

More rapid reactions were followed by removing aliquots from a single flask.

Similar procedures have been described.


III. Titrations

The aqueous solution to which one drop of indicator solution had been added was titrated against 0.01 N sodium hydroxide solution delivered from a 10 ml buret. The initial endpoint tended to fade;
the final endpoint, 1-3% more sodium hydroxide, was taken when the
pale pink color persisted for at least 30 sec. Titrant was delivered
by air pressure to the buret through capillary Pyrex tubing and was
protected with Ascarite. Evaporative losses were reduced by keeping
the system closed except during the actual titration and filling.

For each run seven to ten points were taken at intervals which
approximately corresponded to eight per cent increase (out of 100 per
cent) in production of acid. All reactions were followed to better
than eighty per cent completion (greater than two half-lives). In-
finity values were taken at twenty half-lives in triplicate; some
reactions were also examined at one hundred half-lives. These in-
finity titers were very close to calculated values in the case of
2,2-dichloro- and 2,2-dibromocyclopropylmethy1 tosylates, but were
high with the mono-bromo substrates due to loss of hydrogen bromide.
First order rate constants were then calculated for each point from
the integrated rate law \( k = \left( \frac{1}{t} \right) \ln \left( \frac{\text{infty titer}}{\text{infty titer} - \text{titer}} \right) \). The best value of the rate constant was determined by the
method of averages. The results are presented in Table 6. A typical
kinetic run is presented in Table 10.
Table 10

Typical Titration Data, 1-Bromocyclopropylmethyl
p-Toluenesulfonate, 80% Aqueous Ethanol, 70°

<table>
<thead>
<tr>
<th>time, min</th>
<th>NaOH, ml</th>
<th>$k \times 10^5$ sec$^{-1}$</th>
<th>deviation $\times 10^5$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.37</td>
<td>0.53</td>
<td>6.03</td>
<td>0.01</td>
</tr>
<tr>
<td>59.49</td>
<td>1.05</td>
<td>6.02</td>
<td>0.00</td>
</tr>
<tr>
<td>81.79</td>
<td>1.38</td>
<td>5.98</td>
<td>0.04</td>
</tr>
<tr>
<td>130.78</td>
<td>2.05</td>
<td>5.97</td>
<td>0.05</td>
</tr>
<tr>
<td>180.59</td>
<td>2.60</td>
<td>6.01</td>
<td>0.01</td>
</tr>
<tr>
<td>222.60</td>
<td>2.99</td>
<td>5.99</td>
<td>0.03</td>
</tr>
<tr>
<td>266.26</td>
<td>3.37</td>
<td>6.07</td>
<td>0.05</td>
</tr>
<tr>
<td>309.01</td>
<td>3.69</td>
<td>6.14</td>
<td>0.12</td>
</tr>
<tr>
<td>556.63</td>
<td>4.69</td>
<td>5.97</td>
<td>0.05</td>
</tr>
<tr>
<td>(46 hr)</td>
<td>5.44, 5.42, 5.43</td>
<td>6.02</td>
<td>$\pm 0.05$</td>
</tr>
</tbody>
</table>
ACID DISSOCIATION CONSTANT DETERMINATIONS

I. Materials

**NaCl** - Crystalline analytical reagent grade (Fisher) sodium chloride was dried overnight at 100⁰ and stored in a tightly capped bottle.

**Water** - Double distilled water, obtained from the Ohio State University Reagents Laboratory, was degassed by boiling in Pyrex and stored under nitrogen.

**Sodium Hydroxide** - Standardized sodium hydroxide solution was obtained from the Ohio State University Reagents Laboratory; any solution not used after 6 months was discarded.

**Acids** - The preparations and properties of 1-bromocyclopropanecarboxylic (141), trans-2-bromocyclopropanecarboxylic (158b), cis-2-bromocyclopropanecarboxylic (158a), 2,2-dibromocyclopropanecarboxylic (121), and 2,2-dichlorocyclopropanecarboxylic (120) acids are described earlier in the present work.

A commercial sample of cyclopropanecarboxylic acid (Chemical Samples Co.) was dissolved in petroleum ether (30-60⁰), treated with Norit (1 g/20 g acid), and chilled in Dry Ice-acetone to precipitate the acid. The recrystallized acid was distilled, and the fraction (nearly all the material) boiling at 102.5-103⁰ (38 Torr) was collected. Frozen samples of 67 melted sharply at 18.3-18.8⁰, lit 159 18-19⁰.
1-Methylcyclopropanecarboxylic acid was prepared from methyl methacrylate, diiodomethane, and activated zinc sand by a reported procedure. After stirring the reaction mixture 48 hr at 30°, the only volatile product was methyl 1-methylcyclopropanecarboxylate (165), which was collected by distillation after aqueous work-up. Saponification as for 140 and work-up gave 1-methylcyclopropanecarboxylic acid (166), purified in the same manner as cyclopropanecarboxylic acid above. Frozen samples of 166 melted at 27°, but when this liquid was incubated at this temperature and scratched, crystallization was induced to give an allotrope, mp 31.5-33°, lit 32°.

trans-2-Methylcyclopropanecarboxylic acid (167) was prepared from ethyl trans-crotonate and diiodomethane by the Conia modification of the Simmons-Smith reaction. A mixture of granular zinc (20 mesh, 32 g) and glacial acetic acid (100 ml) was warmed on a steam bath. Silver nitrate (0.5 g) dissolved in water (5 ml) was poured into the hot acid and the mixture was swirled (2 min). The acetic acid was decanted and the zinc washed with glacial acetic acid (2 x 50 ml, 0.5 min ea), and then with dry ether (3 x 50 ml, 0.5 min ea). The activated
zinc was covered with ether and used immediately after adding additional ether (50 ml).

A mixture of freshly distilled diiodomethane (67 g, 0.25 mole) and ethyl trans-crotonate (28.5 g, 0.25 mole) was added dropwise at a rate which maintained gentle reflux (ca 1 hr). The mixture was then refluxed gently overnight. The reaction mixture was decanted from the zinc, which was rinsed with additional ether and digested in warm water to prevent ignition. The combined ether fractions were made up to 250 ml with ether, chilled in an ice bath, and pyridine (35 g, 0.45 mole) was added dropwise to the stirred solution (caution). The pasty precipitate was filtered and rinsed thoroughly. Additional pyridine was added dropwise to the filtrate until no more precipitate formed. After a second filtration, the organic layer was washed with saturated brine, dried (MgSO₄), concentrated in vacuo, and distilled. The distillate (16.7 g) was a mixture of starting material and ethyl trans-2-methylcyclopropanecarboxylate separable by fractionation, but for the small quantities required better purified by preparative vpc (SE-30). Saponification and work-up as above for the 1-methyl acid 166 yielded acid 167, which was purified by vpc (FFAP) since it could not be induced to crystallize even at -78°. Acid 167 has been characterized as the amide, 161 and a portion of the acid was hence treated with thionyl chloride followed by ammonia. Several recryst-

---

(161) D. E. Applequist and A. H. Peterson, J. Amer. Chem. Soc., 82, 2372 (1960). These authors obtained two isomeric amides from 3-(chloromethyl)butanenitrile and base (ring closure followed
by partial hydrolysis), and consider the lower melting ($112.3^\circ$) the cis and the higher melting ($128^\circ$) the trans isomer. The present results suggest that the opposite assignment is possible.

stallizations from petroleum ether-dichloromethane gave the amide, which melted sharply at $110^\circ$, lit $112.3^\circ$.

II. Equipment

A radiometer pH meter (Model 26) with G 202 B glass and K 401 reference electrodes was employed in conjunction with a Radiometer automatic buret. The solution was mechanically stirred and temperature was indicated by a calibrated thermometer ($\pm 0.05^\circ$). Temperature control was provided by a Haake constant temperature apparatus which circulated water through a constant temperature jacket around the solution. The electrodes were standardized against 1:3.5 diacid phosphate-monoacid phosphate and potassium acid phthalate (NBS operational definition of pH) as recommended.


III. Procedure

Standard volumetric techniques were employed throughout. The organic acid and sodium chloride were weighed ($\pm 0.1 \text{ mg}$) into a volumetric flask and made up with water to exact volume. The solutions were ca 0.1 M in sodium chloride and 0.04-0.1 M in the acid.
An aliquot of this acid solution (10 ml) was pipetted into a beaker. The electrodes were immersed in the solution, which was then manually heated with a hot water bath to near the desired temperature. The jacket was then fitted in place, and the temperature was allowed to stabilize before the titration was begun. The acid was titrated against ca 0.1 N NaOH, with the buret operated in the manual mode. Titrant was added in portions so that the pH rose ca 0.1 unit. After the pH reading had stabilized (ca 15 sec), the stirrer was stopped, and the pH and volume of titrant recorded. Titration was continued to better than 90% neutralization. About 25 data points were collected per run. A typical data set and titration curve are presented in Table 11 and Figure 8. Each acid was titrated at least twice; the number of runs is included in Table 9.

IV. Calculations

Curve fitting was carried out by standard regression analysis in a sophisticated computer program written by Dr. W. Sachs of the Ohio State University Chemistry Department; for the pKa determinations a subroutine prepared by Dr. Carl Fischer was employed. The theory and details of these programs are presented elsewhere.

Table 11  
Titration of 1-Bromocyclopropanecarboxylic Acid (141)  
a Typical Titration$^a,c$

<table>
<thead>
<tr>
<th>pH</th>
<th>Volume of Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.350</td>
<td>0.000$^b$</td>
</tr>
<tr>
<td>2.375</td>
<td>0.128</td>
</tr>
<tr>
<td>2.435</td>
<td>0.264</td>
</tr>
<tr>
<td>2.539</td>
<td>0.496</td>
</tr>
<tr>
<td>2.658</td>
<td>0.717</td>
</tr>
<tr>
<td>2.711</td>
<td>0.891</td>
</tr>
<tr>
<td>2.770</td>
<td>1.031</td>
</tr>
<tr>
<td>2.844</td>
<td>1.210</td>
</tr>
<tr>
<td>2.933</td>
<td>1.433</td>
</tr>
<tr>
<td>3.029</td>
<td>1.653</td>
</tr>
<tr>
<td>3.170</td>
<td>2.000</td>
</tr>
<tr>
<td>3.239</td>
<td>2.173</td>
</tr>
<tr>
<td>3.352</td>
<td>2.442</td>
</tr>
<tr>
<td>3.453</td>
<td>2.660</td>
</tr>
<tr>
<td>3.539</td>
<td>2.834</td>
</tr>
<tr>
<td>3.663</td>
<td>3.061</td>
</tr>
<tr>
<td>3.737</td>
<td>3.213</td>
</tr>
<tr>
<td>3.839</td>
<td>3.330</td>
</tr>
<tr>
<td>3.936</td>
<td>3.452</td>
</tr>
<tr>
<td>4.017</td>
<td>3.532</td>
</tr>
<tr>
<td>4.166</td>
<td>3.663</td>
</tr>
<tr>
<td>4.252</td>
<td>3.726</td>
</tr>
<tr>
<td>4.369</td>
<td>3.793</td>
</tr>
<tr>
<td>4.462</td>
<td>3.839</td>
</tr>
<tr>
<td>4.560</td>
<td>3.877</td>
</tr>
<tr>
<td>4.787</td>
<td>3.941</td>
</tr>
<tr>
<td>4.974</td>
<td>3.976</td>
</tr>
<tr>
<td>5.2</td>
<td>4.002$^b$</td>
</tr>
<tr>
<td>6.18</td>
<td>4.045</td>
</tr>
</tbody>
</table>

$^a$4 ml 0.101336 N (25°) in 5 ml 0.09999 M sodium chloride (35°) titrated against 0.10062 N (35°) sodium hydroxide.

$^b$Not used in calculation

$^c$Calculated pK$_a$ = 3.285 ± 0.002.
Figure 9. Titration Curve of 1-Bromocyclopropanecarboxylic Acid
Hydrogen ion activity coefficients were calculated from the Davies equation; concentrations were corrected from 25° for volume change from standard tables. The best least squares fit of the charge balance equation was obtained by varying the pKa and the initial concentration of acid. The results are presented in Table 9.

The charge balance equation is

\[ 0 = [Na^+] + [H^+] - [OH^-] - [Cl^-] - [A^-] \]

\[ = [Na^+] + [H^+] - \frac{K_w}{[H^+]V_0} - [Cl^-] - \frac{K_a[total \ acid]}{[H]Y_0^2 + K_a} \]

The best least squares fit to this equation was found upon varying \( K_a \); the best fit was also determined upon varying both \([total \ acid]\) and \( K_a \). Including the dilution factors, the charge balance equation is, where \( V_0 \) is the initial volume of solution, \( V \) the amount of titrant, \([Na_o]\) the concentration of sodium in the initial solution, \([Na_{OH}]\) the concentration of the titrant, and \([Cl] \) the concentration of chloride ion in the initial solution:
Typical precision of a given run was ± 0.001 to ± 0.002 pKₐ unit. However, variation between runs was generally larger. This was due to electrode drift, since at the completion of a series of titrations, recalibration of the electrode showed deviations of up to 0.04 pH units. The standard deviations of the pKₐ's determined were calculated from two or more independent titrations of 21-32 points each. The accuracy may be less than the standard deviation, but the relative order of the pKₐ's is very precise, since titration series were carried out on pairs of acids, so any drift could be scaled and corrected for.

\[ 0 = \left\{ \frac{[Na_0]}{V_0 + V} \frac{V}{V + V_0} + \frac{[NaOH]}{V + V_0} + \frac{10^{-PH}}{\gamma_+} - \frac{K_{water}}{\gamma_+ 10^{-PH}} - \frac{[Cl]}{V_0 + V} \right\} (\gamma_+ 10^{-PH} + K_a) - K_a[\text{total acid}] \]
BIBLIOGRAPHY

1. (a) J. D. Roberts and R. H. Mazur, J. Amer. Chem. Soc., 73, 2509 (1951); (b) Idem., ibid., 73, 3542 (1951).


13. (a) S. Winstein and A. H. Schlesinger, J. Amer. Chem. Soc., 70, 3528 (1948); (b) E. M. Kosower and S. Winstein, ibid., 76, 4347 (1954); (c) E. M. Kosower and S. Winstein, ibid., 76, 4354 (1954); (d) S. Winstein and E. M. Kosower, ibid., 81, 4399 (1959) and references therein.


27. This reference indicates no ring expansion upon solvolysis of the parent cyclopropylmethyl tosylate, but this was corrected in later publications in the series.


66. J. D. Roberts and W. T. Moreland, Jr., J. Amer. Chem. Soc., 75, 2167 (1953); for a different view, however, see ref. 64b.


69. Additional studies are listed in references 23 and 24.


84. The square of the wave function corresponds to electron density; see any introductory text on quantum mechanics such as Born. The above argument assumes that the effect of substitution is a linear free energy relationship, and the principles previously discussed for the Hammett equation apply. The perturbation argument here explicitly neglects the probable difference in energy levels of the different LUMOs.
91. (a) J. D. Roberts and J. A. Yancey, J. Amer. Chem. Soc., 74, 5943 (1952); (b) J. D. Roberts and C. M. Regan, ibid., 75, 2069 (1953); (c) J. D. Roberts and M. Halman, ibid., 75, 5759 (1953); (d) J. D. Roberts and J. A. Yancey, ibid., 77, 5558 (1955).
97. Examination of the spectral and physical values in the original report for 3-methyl-2-phenylindene and 2,3-diphenylbutadiene shows them to be identical to those of 1,1-diphenylethane and 1,1-diphenylethene. The nmr data cannot be interpreted correctly in terms of the indene and butadiene. Most notably in the indene, the vinyl hydrogen should exhibit a distinct resonance separate from the aromatic absorptions as calculated from 'group contribution values'. Also CH-CH₂ would not appear as a quartet, but would exhibit additional splitting ca 2 Hz from the allylic hydrogen in the indene system. For the butadiene, the terminal proton olefin resonance should not appear as a singlet, because of the differing environments of the cis and trans hydrogens.


132. Org. Syn., 46, 98 (1966); phenylmercuric chloride from Ventron Corporation, Beverly, Mass. was found to give good results, but material from Columbia Organic Chemicals Company, Columbia, S.C. was not satisfactory.

133. S. W. Pelletier, Chem. Ind., 1953, 1034.


144. This compound has been reported but no instrumental data given: K. Bott, *Chem. Ber.*, 100, 2791 (1964).


146. *Idem., 'Catalog of Infrared Spectral Data,'* Texas A&M University, College Station, Texas, 1968, Nos. 2260 and 2465.


161. D. E. Applequist and A. H. Peterson, J. Amer. Chem. Soc., 82, 2372 (1960). These authors obtained two isomeric amides from 3-(chloromethyl)butanenitrile and base (ring closure followed by partial hydrolysis), and consider the lower melting (112.3°) the cis and the higher melting (128°) the trans isomer. The present results suggest that the opposite assignment is possible.


167. The charge balance equation is

\[ 0 = [Na^+] + [H^+] - [OH^-] - [Cl^-] - [A^-] \]

\[ = [Na^+] + [H^+] - \frac{K_w}{[H^+]Y_+^2} - [Cl^-] - \frac{K_a[total~acid]}{[H^+]Y_+^2 + K_a} \]
The best least squares fit to this equation was found upon varying $K_a$; the best fit was also determined upon varying both $[\text{total acid}]$ and $K_a$. Including the dilution factors, the charge balance equation is, where $V_0$ is the initial volume of solution, $V$ the amount of titrant, $[Na_o]$ the concentration of sodium in the initial solution, $[Na_{OH}]$ the concentration of the titrant, and $[Cl]$ the concentration of chloride ion in the initial solution.

$$
0 = \left\{ \begin{array}{l}
\left[ Na_o \right] \frac{V_0}{V_0 + V} + \left[ Na_{OH} \right] \frac{V}{V + V_0} + \frac{10^{-pH}}{\gamma_+} - \frac{K_{\text{water}}}{\gamma_+ 10^{-pH}} \\
- \left[ Cl \right] \frac{V_0}{V_0 + V} \end{array} \right\} (\gamma_+ 10^{-pH} + K_a) - K_a [\text{total acid}]
$$