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REARRANGEMENTS OF CYCLOPROPYL AND RELATED CARBENES

DISSERTATION

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

By

Leon I. Cherney, A.B., M.S.

The Ohio State University
1971

Approved by

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VITA

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</tbody>
</table>
# 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>viii</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>HISTORICAL</td>
<td>4</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>24</td>
</tr>
<tr>
<td>Synthesis of Cyclopropanecarboxaldehydes, Cyclopropyl Methyl Ketones, Their Sulfonylhydrazones, Their Respective Carbenic Decomposition Products, and Other Intermediates</td>
<td>24</td>
</tr>
<tr>
<td>Alkaline Decomposition of Substituted Cyclopropyl Methyl Ketone and Cyclopropylcarboxaldehyde Arylsulfonyl-hydrazone</td>
<td>36</td>
</tr>
<tr>
<td>Decomposition of Salts of 2,2-Dimethylbutanal Tosylhydrazone</td>
<td>62</td>
</tr>
<tr>
<td>Decomposition of Salts of 2-Phenylpropanal Tosylhydrazone</td>
<td>74</td>
</tr>
<tr>
<td>EXPERIMENTERS</td>
<td>86</td>
</tr>
<tr>
<td>General Procedures and Techniques</td>
<td>86</td>
</tr>
<tr>
<td>Melting points</td>
<td>86</td>
</tr>
<tr>
<td>Boiling points</td>
<td>86</td>
</tr>
<tr>
<td>Elemental analyses</td>
<td>86</td>
</tr>
<tr>
<td>Infrared spectra</td>
<td>86</td>
</tr>
</tbody>
</table>

iv
Nuclear magnetic resonance spectra ................ 86
Gas-liquid chromatography ........................ 87
Preparative gas-liquid chromatography ............. 88
Product identification ............................. 88
Product composition ................................ 89
Intermediates ....................................... 89

Synthesis of: 1,1-Dichloro-cis-2,3-dimethyl-2-
  vinylcyclopropane .............................. 89
  cis-1,2-Dimethyl-1-vinylcyclopropane .......... 92
  cis-1,2-Dimethylcyclopropanecarboxaldehyde .... 93
  1,1-Dichloro-trans-2,3-dimethyl-2-
  vinylcyclopropane ................................ 95
  trans-1,2-Dimethyl-1-vinylcyclopropane ......... 96
  trans-1,2-Dimethylcyclopropanecarboxaldehyde ... 96
  (2',2'-Dichloro-trans-3'-methylcyclo-
    propyl)-trans-1-propene ....................... 97
  (trans-2'-Methylcyclopropyl)-trans-1-
    propene ....................................... 98
  trans-2-Methylcyclopropanecarboxaldehyde ...... 98
  2-(trans-2'-Methylcyclopropyl)-1,3-
    dithiane ..................................... 99
  2-(trans-2'-Methylcyclopropyl)-1,3-
    dithiane-2-d ................................ 100
  trans-2-Methylcyclopropanecarboxaldehyde-\alpha-d . 101
  2,2-Dimethylcyclopropyl methyl ketone ......... 102
  trans-\alpha,2-Dimethylcycloproplmethanol ...... 103
<table>
<thead>
<tr>
<th>Compound</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl trans-2-methylcyclopropyl ketone</td>
<td>104</td>
</tr>
<tr>
<td>3-Pentene-2-ol-2-d</td>
<td>105</td>
</tr>
<tr>
<td>1,3-Pentadiene-2-d and 4-d</td>
<td>106</td>
</tr>
<tr>
<td>Product Standards</td>
<td>107</td>
</tr>
<tr>
<td>Preparation of cyclobutenes by photolysis of dienes</td>
<td>107</td>
</tr>
<tr>
<td>1,3-Dimethylcyclobutene</td>
<td>108</td>
</tr>
<tr>
<td>1,4-Dimethylcyclobutene</td>
<td>109</td>
</tr>
<tr>
<td>1,3,3-Trimethylcyclobutene</td>
<td>109</td>
</tr>
<tr>
<td>3-Methylcyclobutene</td>
<td>109</td>
</tr>
<tr>
<td>3-Methylcyclobutene-1-d and 4-d</td>
<td>110</td>
</tr>
<tr>
<td>Synthesis of 1-methyl-1-ethylcyclopropane</td>
<td>112</td>
</tr>
<tr>
<td>Arylsulfonylhydrazones</td>
<td>113</td>
</tr>
<tr>
<td>trans-2-Methylcyclopropanecarboxaldehyde 2,4,5-trichlorobenzene-sulfonylhydrazone</td>
<td>113</td>
</tr>
<tr>
<td>trans-2-Methylcyclopropanecarboxaldehyde-a-d 2,4,5-trichlorobenzene-sulfonylhydrazone</td>
<td>114</td>
</tr>
<tr>
<td>Methyl trans-2-methylcyclopropyl ketone 2,4,5-trichlorobenzene-sulfonylhydrazone</td>
<td>114</td>
</tr>
<tr>
<td>2,2-Dimethylcyclopropyl methyl ketone tosylhydrazone</td>
<td>115</td>
</tr>
<tr>
<td>2,2-Dimethylcyclopropyl methyl ketone 2,4,5-trichlorobenzensesulfonylhydrazone</td>
<td>115</td>
</tr>
<tr>
<td>Reaction</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td><strong>cis-1,2-Dimethylcyclopropanecarboxaldehyde 2,4,6-triisopropylbenzene-</strong></td>
<td>115</td>
</tr>
<tr>
<td>sulfonylhydrazone</td>
<td></td>
</tr>
<tr>
<td><strong>trans-1,2-Dimethylcyclopropanecarboxaldehyde 2,4,5-trichlorobenzene-</strong></td>
<td>116</td>
</tr>
<tr>
<td>sulfonylhydrazone</td>
<td></td>
</tr>
<tr>
<td><strong>cis-1,2-Dimethylcyclopropanecarboxaldehyde 2,4,5-trichlorobenzenesul</strong></td>
<td>117</td>
</tr>
<tr>
<td>fonylsulfonylhydrazone</td>
<td></td>
</tr>
<tr>
<td>2,2-Dimethylbutanal tosylhydrazone</td>
<td>117</td>
</tr>
<tr>
<td>2-Phenylpropanal tosylhydrazone</td>
<td>118</td>
</tr>
<tr>
<td>Thermal decomposition of Salts of arylsulfonylhydrazones</td>
<td>118</td>
</tr>
<tr>
<td>Preparative scale pyrolysis of the sodium salt of trans-2-methylcyclo-</td>
<td>119</td>
</tr>
<tr>
<td>propanecarboxaldehyde 2,4,5-trichlorobenzenesulfonylhydrazide</td>
<td></td>
</tr>
<tr>
<td>Preparative scale pyrolysis of the sodium salt of trans-2-methylcyclo-</td>
<td>120</td>
</tr>
<tr>
<td>propanecarboxaldehyde-α-d 2,4,5-trichlorobenzenesulfonylhydrazide</td>
<td></td>
</tr>
</tbody>
</table>

**APPENDIX** .................................................................................................................. 121

Infrared and Nuclear Magnetic Resonance Spectra ............................................. 122
# TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cyclobutenes Prepared Photochemically from 1,3-Dienes</td>
<td>34</td>
</tr>
<tr>
<td>2.</td>
<td>Base-Catalyzed Decomposition of 2,2-Dimethylcyclopropyl Methyl Ketone Tosylhydrazone at 140° in Diglyme</td>
<td>37</td>
</tr>
<tr>
<td>3.</td>
<td>Base-Catalyzed Aprotic Decomposition of Methyl trans-2-Methylcyclopropyl Ketone 2,4,5-Trichlorobenzenesulfonylhydrazone</td>
<td>42</td>
</tr>
<tr>
<td>4.</td>
<td>Decomposition of Salts of trans-1,2-Dimethylcyclopropane-carboxaldehyde 2,4,5-Trichlorobenzenesulfonylhydrazone</td>
<td>48</td>
</tr>
<tr>
<td>5.</td>
<td>Decomposition of Salts of cis-1,2-Dimethylcyclopropane-carboxaldehyde 2,4,5-Trichlorobenzenesulfonylhydrazone in Diglyme</td>
<td>53</td>
</tr>
<tr>
<td>6.</td>
<td>Rearrangements of Substituted Cyclopropyl Carbenes</td>
<td>62</td>
</tr>
<tr>
<td>7.</td>
<td>Competition Constants for Intramolecular Insertion of Alkylcarbenes as Generated by Thermolysis of Tosylhydrazone Salts</td>
<td>64</td>
</tr>
<tr>
<td>8.</td>
<td>Competition Constants for Intramolecular Insertion of Substituted Neopentylcarbenes</td>
<td>65</td>
</tr>
<tr>
<td>9.</td>
<td>Products of Intramolecular Reactions of Neohexylcarbene</td>
<td>65</td>
</tr>
<tr>
<td>10.</td>
<td>Aprotic Decomposition of Salts of 2,2-Dimethylbutanal Tosylhydrazone</td>
<td>69</td>
</tr>
<tr>
<td>11.</td>
<td>Decomposition of Salts of 2-Phenylpropanal Tosylhydrazone</td>
<td>78</td>
</tr>
</tbody>
</table>
INTRODUCTION

The most common intramolecular reactions of carbenes are rearrangement of alpha-hydrogen to give olefins, insertion into carbon-hydrogen bonds to yield cycloalkanes, and addition to unsaturated centers; carbon skeleton rearrangement in usual systems is rare. The cyclopropylcarbene differs, however, in that its major isomerization reaction results in ring expansion, that is carbon skeleton rearrangement, to give cyclobutene accompanied by some fragmentation to ethylene and acetylene (Equation 1) (1).

\[
\begin{align*}
\text{CH:} & \rightarrow [\phantom{\text{H}}] + \text{H}_{2}\text{C=CH}_{2} + \text{HC≡CH} \quad (1) \\
60-67\% & \quad 10-13\% \quad 10-13\%
\end{align*}
\]


The purpose of the present research was to investigate electronic and steric effects of substituents, on the cyclopropyl ring, on the various rearrangement reactions of cyclopropylcarbenes. Previous and somewhat tentative studies of (2,2-dimethylcyclopropyl)methylcarbene (I) and methyl(trans-2-methylcyclopropyl)carbene (II) showed that the lesser substituted beta carbon atom of the cyclopropyl group preferred
to migrate in formation of cyclobutenes (Equation 2, path b) (2). In

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

\[ \text{R} = \text{CH}_3 \text{ (I)} \]
\[ \text{R} = \text{H} \text{ (II)} \]

(2) J. Smith, Ph.D. Dissertation, The Ohio State University, 1964.

the present research, the two systems I and II were investigated in detail along with other substituted cyclopropylcarbenes in an effort to determine if electronic effects, as is the case with carbenic systems free of steric complications, are of significance in isomerization of the carbenes to cyclobutenes. As a consequence of this study, a new reaction sequence for synthesis of stereochemically pure substituted cyclopropanecarboxaldehydes was developed. It was also necessary to develop advantageous syntheses of various cyclobutenes for proof of
structure of the products of rearrangement of the cyclopropylcarbenes.  
As a corollary of the cyclopropylcarbene study, an investigation of rearrangement and insertion of 2,2-dimethylbutylidene (neohexylcarbene) (III) and 2-phenylpropylidene (IV) was conducted in order to determine if these systems were electronically or sterically controlled.
Intramolecular reactions of carbenes are subjects of intense interest (3). A major purpose of these previous researches (3) has been to determine the roles of steric and electronic factors on the various isomerization reactions of divalent carbon intermediates. Considerable information has been accumulated with respect to reorganization reactions of carbenes via singlet processes; very little is known however concerning intramolecular processes involving triplet carbenes.

Important information has been obtained by thermolysis of relatively simple diazo compounds. Thus decomposition of 1-diazo-2-methylpropane (4) at 140° yields isobutene (63%) and methylcyclopropane (37%); similarly 1-diazo-2,2-dimethylpropane (4) decomposes to 2-methyl-2-butene (5%) and 1,1-dimethylcyclopropane (95%). 3-Diazo-2,2-dimethyl-
butane (4) thermolyzes to 1,1,2-trimethylcyclopropane (47%) and 3,3-
dimethylbutene (52%) (Equation 3); conversion to 2,3-dimethyl-2-butene
(1%) is a very minor process. It is thus apparent that the principal
reactions of the carbenic intermediates of the above systems involve

\[
\begin{align*}
\text{CH}_3 & \quad \text{N}_2 \\
\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} - \underset{\text{CH}_3}{\text{C}} - \text{CH}_3 & \longrightarrow \text{CH}_3 \cap \text{CH}_3 + \underset{\text{CH}_3}{\text{CH}} - \underset{\text{CH}_3}{\text{C}} - \text{CH} = \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

rearrangement of α-hydrogen to give olefins and β-hydrogen insertion
to yield cyclopropanes. Carbon skeleton rearrangement of methyl groups
in these aliphatic carbenic systems is unimportant. The prevalence of
insertion rather than carbon skeleton rearrangement of carbenes is
further illustrated by conversions of camphor tosylhydrazone (5) by


excess sodium methoxide to tricyclene (100%) and of bicyclo[2.2.1]-
heptan-2-one tosylhydrazone (5) by sodium methoxide (Equation 4) to
nortricyclene (99.5%) and bicyclo[2.2.1]hept-2-ene (0.5%).
Aryl groups migrate to divalent carbon. Thus 2-diazo-1,1,1-triphenylethanes (Equation 5) loses nitrogen to yield 1,1,2-triphenyl-

\[
\begin{align*}
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 - \text{CH}=\text{N}_2 \\
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 - \text{CH}=\text{N}_2 \\
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 - \text{CH}=\text{N}_2 \\
\end{align*}
\]

ethylene (6). The carbenic intermediates generated in such processes


are electrophilic since in decomposition of 2-diazo-1,1,1-triphenylethanes (7a-c) and 1-diazo-2,2-diphenylpropanes (7d), phenyl groups
which are substituted by electron-donating groups rearrange more rapidly
than those containing electron-withdrawing substituents (Equation 6).
In these systems the electrical effects are small; however linear free energy correlations (7a-d) have been found for $\sigma$ or $\sigma^+$ substituent constants and the logarithms of the relative migration aptitudes of the migrating substituted phenyl groups. Decomposition of 1-diazo-2-methyl-2-phenylpropane (8) reveals that $\beta$-C-H insertion and phenyl migration occur more readily than does methyl migration (Equation 7) in the neophyl carbene.

\[
\begin{align*}
\text{CH}_3 \\
\text{C}_6\text{H}_5 - \text{C} - \text{CH}=\text{N}_2 & \xrightarrow{\text{N}_2} \text{C}_6\text{H}_5\text{CH}=\text{C(\text{CH}_3)2} + \text{CH}_3 & \text{C}_6\text{H}_5 \\
\text{CH}_3 & & \text{CH}_3 \\
\end{align*}
\]

50% 41% 9%

Rearrangement of $\beta$-mercapto groups (9) is the principal reaction of $\beta$-mercaptoalkylcarbenes (Equation 8). Carbenic migration of $\beta$-alkoxy groups (Equations 9 and 10) has been observed (10); however the abilities of such groups to rearrange (9,10) are considerably less than that of
sulfur analogs. The abilities of such groups to rearrange have been related to the participative contributions of the non-bonding electrons of β-hetero atoms to electrophilic carbenic sites (9).

\[
\begin{align*}
\text{N}_2 & \quad \text{C}_6\text{H}_5 - \text{C} - \text{CH}_2 - \text{SR} \quad \xrightarrow{\text{Na}} \quad \text{C}_6\text{H}_5\text{C} = \text{CH}_2 + \text{C}_6\text{H}_5\text{CH} = \text{CH} - \text{SR} \\
\text{R} = \text{C}_2\text{H}_5 & \quad \text{85-91%} \\
\text{R} = \text{C}_6\text{H}_5 & \quad \text{92-100%}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 - \text{C} - \text{CH} = \text{N}_2 \quad \xrightarrow{\text{Na}} \quad \text{OCH}_3 + \text{CH}_3\text{C} = \text{OCH}_3 + \text{CH}_3\text{C} = \text{OCH}_3 + \text{ CH}_3\text{OCH}_3 \\
& \quad \text{14%} \\
& \quad \text{29%}
\end{align*}
\]


The cyclopropylcarbene has been of extreme interest (1,2,11)


because it isomerizes to cyclobutene and 1,3-butadiene and fragments to ethylene and acetylene (Equation 11). Ring expansion to cyclobutene and conversion to 1,3-butadiene are prime examples of carbon-skeleton rearrangement of carbenes. The rearrangement and fragmentation pattern of cyclopropylcarbenes is general in that (1-diazoethyl)cyclopropane thermolyzes to 1-methylcyclobutene, 2-methyl-1,3-butadiene and vinyl-cyclopropane along with ethylene and methylacetylene (1,2) (Equation 12). The marked ability of the cyclopropylcarbene to rearrange is indicated further by decomposition of the following diazo compounds (2) to the
indicated hydrocarbons: \textit{dicyclopentyldiazomethane}: 1-dicyclopentyl-
cyclobutene and 2-cyclopentyl-1,3-butadiene; \textit{cyclopropyldiazophenyl-
methane}: 1-phenylcyclobutene; \textit{diazo-(1-phenylcyclopropyl)methane}:
1-phenylcyclobutene, 2-phenyl-1,3-butadiene and phenylacetylene; and
\textit{diazophenyl(1-phenylcyclopropyl)methane}: 1,2-diphenylcyclobutene.

Vacuum pyrolysis of the sodium salt of 1-phenylcyclopropanecarboxalde-
hyde-d tosylhydrazone gives principally 1-phenylcyclobutene-2-d, and
the lithium salt of cyclopropanecarboxaldehyde-d tosylhydrazone yields
cyclobutene-1-d and 1,3-butadiene-2-d (2,11). These data reveal that
rearrangements of the intermediate carbenes do not involve intermediate
bicyclobutanes.

Low pressure gas phase photolysis of \textit{trans}-2,3-dimethylcyclo-
propyldiazomethane gives acetylene, 2-butene (primarily \textit{trans}) by
fragmentation, and \textit{trans,trans}-2,4-hexadiene and traces of \textit{cis,trans}-
2,4-hexadiene (12) by rearrangement via \textit{trans}-3,4-dimethylcyclobutene
(Equation 13). The predominance of the \textit{trans}-2-butene and \textit{trans,trans}-
2,4-hexadiene was interpreted as evidence for decomposition of the diazo compound by a singlet process. Dilution of the diazo compound with nitrogen led to substantial formation of cis-2-butene and cis, trans-2,4-hexadiene. This has been attributed to triplet processes (Equation 14).
Thermal decomposition of trans-2,3-dimethylcyclopropanecarboxaldehyde tosylhydrazone by sodium methoxide in diglyme gives trans-2,3-dimethylcyclobutene, trans,trans-2,4-hexadiene, and trans-2-butene (13).


These results are similar to the singlet photochemical decomposition of trans-2,3-dimethylcyclopropyl diazomethane (Equation 13).

Decomposition of cyclopropylcarbenes has been extended to bicyclic systems. Bicyclo[\textit{n.1.0}]alkyldiazomethanes (14) decompose to bicyclo-


[bicyclo[\textit{n.2.0}]alkenes and to cycloalkenes and acetylene (Equation 15); bicyclo[\textit{n.2.0}]alkenes are produced by carbenic collapse of spirodiazo intermediates (2,15) such as in Equation 16. The complex products

\[
\begin{align*}
\text{(CH}_2\text{n)}_n & \quad \xrightarrow{-N_2} \quad \text{(CH}_2\text{n)}_n \\
n = 3, 4
\end{align*}
\]

derived from the bicyclo[5.1.0]octa-2,4-dien-8-yl carbene (16) (Equation 16)


17) and bicyclo[6.1.0]nona-2,4,6-trien-9-yl carbenes (17) (Equation 18)

are interpretable via usual isomerization reactions of cyclopropyl-carbene intermediates. Collapse to $\Delta^3$-cyclopentenylacetylene is the principal carbenic reaction of nortricyclonone tosylhydrazone (18) with excess sodium methoxide (Equation 19); presumably the strain in this carbenic system prevents isolation of the quadricyclene insertion product (Equation 19). Analogously 2-diazobicyclo[4.1.0]heptane (2,19)


(19) P. K. Freeman and D. G. Keeper, ibid., 30, 1047 (1965).
converts carbenically to bicyclo[4.1.0]-2-heptene and to 1-hepten-6-yne and its isomeric allene (Equation 20). Interesting rational cyclopropylcarbene processes occur in conversion of V (20) to mixtures of o, m, and p-terphenyl (Equation 21) and in collapse of VI (21) to benzene and atomic carbon (Equation 22).

\[
\begin{align*}
\text{Na} & \\
\text{NaN} & \\
\text{H}_5\text{C}_6 & \quad \text{hv} \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{H}_5\text{C}_6 & \quad \text{hv} \\
\end{align*}
\]


Ring expansion is not limited to cyclopropylcarbene systems. Cyclobutylidiazomethane decomposes carbenically to cyclopentene (41%), methylenecyclobutane (34%), and bicyclo[2.1.0]pentane (25%), products derived from carbon-skeleton rearrangement, rearrangement of α-H, and insertion into β-H of the intermediate carbene (22) (Equation 23).


Cyclopentylcarbene however gives only methylenecyclopentane (27.5%) and bicyclo[3.1.0]hexane (72.5%) (Equation 24); no ring expansion occurs (23). Similarly, cyclohexylcarbene yields only methylenecyclohexane.
Although only strained unsubstituted cycloalkylcarbenes undergo carbon-skeleton rearrangement, alkaline decomposition of a series of 1-phenylcycloalkanecarboxaldehyde tosylhydrazones (VII) is reported to give products derived from expansion of rings containing from 3 to 7 atoms (24) (Equation 26). These results are perplexing since phenyl...
groups migrate to carbenic centers much more readily than do alkyl groups (8) and unstrained cycloalkylcarbenes do not ring expand (23).

The decompositions of VI were carried out in N-methyl-2-pyrrolidone using only 1.2 equivalents of base. Since base-catalyzed decomposition of tosylhydrazones in the presence of a slight excess of base frequently leads to cationic rather than carbenic processes (11,25) and since N-

methyl-2-pyrrolidone facilitates cationic decomposition of tosylhydrazones, decomposition of VI may in actuality have involved cationic reactions of the intermediate cycloalkyl diazonium ions.

The sensitivity of diazo compounds to environment is illustrated dramatically by cyclopropydiazomethane. When cyclopropydiazomethane is generated in aprotic solvents or from the dry tosylhydrazone salt of cyclopropanecarboxaldehyde, it decomposes to cyclobutene, 1,3-butadiene, acetylene, and ethylene (Equation 27). Small amounts of proton donors such as alcohols, water, or unneutralized tosylhydrazone lead to formation of bicyclo[1.1.0]butane, and methylenecyclopropane along with cyclobutene, 1,3-butadiene, acetylene, and ethylene. Solvents such as ethylene glycol and glycerol result in production of

\[
\begin{align*}
\text{CH=N=N} & & \overset{\text{H}^+}{\longrightarrow} & & \text{CH}^{-} \cdots \text{N}_2 \\
\text{CH} : & & \overset{\text{H}^+}{\longrightarrow} & & \text{CH}_2^+ \\
\text{HC} = \text{CH} & + & \text{H}_2 \text{C} = \text{CH}_2 \\
\end{align*}
\]
bicyclo[1.1.0]butane (11) in up to 79% yield. Camphor tosylhydrazone which gives only tricyclene when decomposed carbenically in excess base (5) yields large amounts of camphene when decomposed in less than 1 equivalent of base. The sensitivity of diazo compounds and carbenic intermediates to proton sources must be respected in attempting to effect carbenic decomposition of sulfonylhydrazones. Generally, carbonium ion processes are avoided in aprotic solvents by using large (8-10 equiv) excesses of bases such as methoxides, or by using strong bases whose conjugate acids cannot protonate the reactive intermediates; n-butyllithium and sodium hydride are particularly useful.

The carbenic reactions that have been summarized thus far are believed to provide appropriate background for the present research. Among other carbenic rearrangements to have been observed are those which lead to ring shrinkage of cycloalkyldene systems: thus diazo-cyclobutane decomposes to methylenecyclopropane along with cyclobutene and 1,3-butadiene (25) (Equation 28); pentamethylenecarbene gives trace amounts of methylenecyclopentane along with cyclohexene and bicyclo[3.1.0]hexane (26) (Equation 29); diazocyclopropane and trans-

2,3-diphenyldiazocyclopropane collapse with rearrangement to allene and to 1,3-diphenyllallene (27) (Equation 39). Processes of the type


Illustrated in Equations 28 and 30 are both seen in carbenic decomposition of the disodium salt of 2,2,4,4-tetramethylcyclobutane-1,3-dione bis-tosylhydrazone in which shrinkage to the alkylidencyclopropyl intermediate (VIII) is followed by further collapse to 1,1,4,4-tetramethyl-1,2,3-butatriene (28) (Equation 31).

2,3-Diphenylcyclopropenylcarbene unfortunately collapses to tolane and acetylene; products derived from carbene-olefin insertion to give intermediates which are derivatives of tetrahedrane, were not observed (29) (Equation 32). Other examples of interesting carbene rearrangements are included in the bibliographies of references 3 and 30.


RESULTS AND DISCUSSION

Synthesis of Cyclopropanecarboxaldehydes, Cyclopropyl Methyl Ketones, Their Sulfonylhydrazones, and Their Respective Carbenic Decomposition Products.

The present research involves study of base-catalyzed decomposition of arylsulfonylhydrazones of 2,2-dimethylcyclopropyl methyl ketone (IX), methyl trans-2-methylcyclopropyl ketone (X), cis and trans-1,2-dimethylcyclopropanecarboxaldehydes (XI and XII), trans-2-methyl-cyclopropanecarboxaldehyde (XIII), and α-deuterio-trans-2-methylcyclopropanecarboxaldehyde (XIV). It was thus necessary to develop adequate syntheses of the cyclopropyl ketones and aldehydes, their corresponding

![Chemical Structures](image-url)
sulfonylhydrazones, and their subsequent base-catalyzed decomposition products.

2,2-Dimethylcyclopropyl methyl ketone (IX) and methyl trans-2-methylcyclopropyl ketone (X) were prepared from mesityl oxide and from trans-3-penten-2-ol by the sequences (Equations 33 and 34) indicated. The procedures developed involve minor modification of those described previously by Smith (2). The synthesis of methyl trans-2-methylcyclopropyl ketone (X) depends on the stereo-specific addition of zinc-copper-methylene iodide to trans-2-penten-2-ol.

\[
\text{CH}_3\text{C}==\text{C}^{\text{H}}\text{CH}_3 \xrightarrow{\text{(CH}_3\text{)}_2\text{SOCH}_2} \text{CH}_3\text{C}==\text{C}^{\text{H}}\text{CH}_3 \quad \text{(33)}
\]
cis and trans-1,2-Dimethylcyclopropanecarboxaldehydes (XI and XII) have been prepared previously (31) as components of isomeric mixtures.


(Equations 35 and 36) as obtained by epoxidation of 1,4-dimethylcyclobutene and 1,3-dimethylcyclobutene, and acid-catalyzed rearrangement of the resulting epoxides. The sequences were found presently to be:

\[
\text{cis} \quad 50\% \quad \text{trans} \quad 30\%
\]

\[
\text{trans} \quad 20\% \quad \text{cis} \quad 35\%
\]
impractical because of the difficulties in preparing the cyclobutenes in large quantities (to be discussed later) and the tedious gas-liquid chromatographic separations of the rearrangement products.

\( \text{cis-1,2-Dimethylcyclopropanecarboxaldehyde (XI)} \) was then synthesized in preparative quantities by a new reaction sequence (Equation 37) involving selective and stereospecific addition of dichlorocarbene to 3-methyl-1,\text{-}trans-3-pentadiene, reduction of 1,1-dichloro-2,3-dimethyl-2-vinylcyclopropane with sodium in liquid ammonia, and oxidation of the resulting \( \text{cis-1,2-dimethyl-1-vinylcyclopropane} \). Addition

\[
\begin{align*}
\text{cis-1,2-Dimethylcyclopropanecarboxaldehyde (XI)} & \quad \text{Cl Cl} \\
& \quad \text{Na} \quad \text{NH}_3 \\
& \quad \text{O=C} \\
\end{align*}
\]

\[ (37) \]

of dichlorocarbene to olefins was known previously to occur with retention of stereochemistry (32). Furthermore, addition of dihalocarbenes to substituted 1,3-dienes occurs selectively at the more substituted double bonds (33) and halocyclopropanes are reduced by

\[ (32) \text{P. S. Skell and A. Y. Garner, J. Amer. Chem. Soc., 78, 3409 (1956).} \]

\[ (33) \text{L. Skattebøl, J. Org. Chem., 29, 2951 (1964) and references therein.} \]
metals in ammonia to cyclopropanes having the same stereochemistry as their parents (34) (35). What was not known previously was whether 


reduction of the chlorines of 1,1-dichloro-2,3-dimethyl-2-vinylcyclopropane could be accomplished by sodium-ammonia without alteration of the cyclopropyl ring (possibly as in Equation 38).

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

\[
\xrightarrow{\text{Na}, \text{NH}_3} \quad \xrightarrow{-\text{NaCl}} \\
\begin{align*}
&\text{CH}_3 \quad \text{C} = \text{C} \\
&\text{H} \quad \text{C} \quad \text{Cl} \\
&\quad \text{C} \quad \text{CH} = \text{CH}_2 \\
&\quad \text{CH}_3
\end{align*}
\]

\(\text{etc.}\)

(38)

Reaction of dichlorocarbene with 3-methyl-1, trans-3-pentadiene was found to be totally selective at the 3,4-double bond in that no 1,2-adduct (or its subsequent reduction product) was observable by gas-liquid chromatography. Reduction of 1,1-dichloro-2,3-dimethyl-2-vinylcyclopropane with sodium in ammonia did not lead to rearrangement, and cis-1,2-dimethyl-1-vinylcyclopropane was isolated in high purity and reasonable yield (~ 50%). Oxidative cleavage of the vinyl group of cis-1,2-dimethyl-1-vinylcyclopropane to give cis-1,2-dimethylcyclopropanecarboxaldehyde (XI) was carried out with osmium tetroxide-sodium
meta-periodate (36) or ozone in methanol (37).


Ozonolysis proved to be superior, although neither oxidation method was found to attack the cyclopropyl ring. Final proof of the structure and stereochemistry of cis-1,2-dimethylcyclopropanecarboxaldehyde was obtained by comparison of its ir and nmr spectra with that previously reported (31) and from the melting point of the 2,4-dinitrophenylhydrazone (31).

trans-1,2-Dimethylcyclopropanecarboxaldehyde (XII) was prepared satisfactorily from 3-methyl-1,cis-3-pentadiene (Equation 39) by the same method used for cis-1,2-dimethylcyclopropanecarboxaldehyde (XI). The structure of XII was confirmed from its spectral properties (31) and from the melting point of its 2,4-dinitrophenylhydrazone (31).

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{CH}_3 & \quad \text{H} \\
\text{CH}_3 & \quad \text{H} \\
\text{Cl} & \quad \text{Cl} \\
\text{CH}_3 & \quad \text{H} \\
\end{align*}
\]

Equation 39
Analogously dichlorocarbene was added to 2,4-trans,trans-hexadiene to yield (2',2'-dichloro-trans-3'-methylcyclopropyl)-trans-1-propene. Oxidative cleavage of the trans-1-propene in methanol resulted in trans-2-methylcyclopropanecarboxaldehyde (XIII, Equation 40). Use of the hexadiene instead of less expensive trans-1,3-pentadiene made it unnecessary to rely on the selectivity of the carbene in addition to the relatively electron-rich double bond of the 1,3-pentadiene. The hexadiene was of further synthetic advantage in that attack at either of the olefinic centers leads to an adduct of the same structure of trans stereochemistry.

Although XIII would appear to be more readily accessible by methylene transfer to crottyl alcohol followed by oxidation to the aldehyde, attempts to prepare the methylene adduct of crottyl alcohol led only to impure trans-2-methylcyclopropylcarbinol contaminated both by cis-2-methylcyclopropylcarbinol and crottyl alcohol. Thus geometric purity, a critical factor in this work, could not be assured.

The three step synthesis as summarized in Equations 37, 39, and 40 is believed to be adaptable to preparation of a wide variety of cyclo-
propene carboxaldehydes and cyclopropyl ketones in reasonable preparative yields, if appropriate 1,3-dienes are available. In all of the transformations, starting materials never contaminated the products, the hydrocarbon from the reduction can be fractionated readily at atmospheric pressure, and the ozonolysis reaction products are quite clean.

Conversion of trans-2-methylcyclopropanecarboxaldehyde (XIII) to α-deuterio-trans-2-methylcyclopropanecarboxaldehyde (XIV) was accomplished through the 1,3-dithiane (XV) (Equation 4) via reaction with t-butyllithium at -50°C, hydrolysis with deuterium oxide and then mercuric chloride-cadmium carbonate (38). Methyllithium and n-butyllithium were unsatisfactory bases. Loss of initial stereochemistry of the cyclopropane does not occur (39) since the chemical shifts of all the peaks in the nmr spectra of α-deuterio-trans-2-methylcyclopropanecarboxaldehyde (XIV) are identical to those of the non-deuterated analog XIII and the aldehyde proton signal at 9.08 δ in XIII is absent in XIV. Deuterium incorporation in XIV appears to be greater than 98% since aldehydic protium is barely detectable in XIV by nmr methods (Figure 1).
The aldehydes and ketones IX-XIV were in general converted to their sulfonylhydrazones (Equation 42) by addition to a sulfonylhydrazide in an alcohol, removing the solvent, freezing the residue or adding water or combining the two methods. The usual derivatives were toluenesulfonylhydrazones (tosylhydrazones). In certain cases, the tosylhydrazones did not crystallize. Greater crystallinity was achieved by using 2,4,6-triisopropylbenzenesulfonylhydrazide (monstro-sylhydrazide) (40) in particular systems. The most crystalline hydra-
zones were obtained from 2,4,5-trichlorobenzenesulfonylhydrazide. It was subsequently demonstrated that the course of base-catalyzed decomposition of the arylsulfonylhydrazones was not affected by differences in structure of the arylsulfinate leaving group.

Independent synthesis of the cyclobutenes resulting from rearrangement of various cyclopropylcarbenes was accomplished by photochemical cyclization of appropriate conjugated dienes in solution as summarized in Table 1 (Equation 43) (41,42,43). The cyclobutenes were used to

![Diagram](image)


identify the products of rearrangement of cyclopropylcarbenes by comparing glc retention times. The photochemical conversion of the dienes to preparative quantities of cyclobutenes was an unsatisfactory method.
### TABLE 1

<table>
<thead>
<tr>
<th>Diene</th>
<th>Cyclobutene</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Methyl-1, trans-3-pentadiene</td>
<td>2,3-Dimethylcyclobutene</td>
</tr>
<tr>
<td>2-Methyl-1, trans-3-pentadiene</td>
<td>1,3-Dimethylcyclobutene</td>
</tr>
<tr>
<td>trans-1,3-Pentadiene</td>
<td>3-Methylcyclobutene</td>
</tr>
<tr>
<td>2,4-Dimethyl-1,3-pentadiene</td>
<td>1,3,3-Trimethylcyclobutene</td>
</tr>
<tr>
<td>1,3-Pentadiene-2-d</td>
<td>3-Methylcyclobutene-1-d</td>
</tr>
<tr>
<td>+ 1,3-pentadiene-4-d</td>
<td>+ 3-methylcyclobutene-3-d</td>
</tr>
</tbody>
</table>

1,3-Pentadiene-2-d whose conversion to 3-methylcyclobutene-1-d has been discussed previously (Table 1) was prepared along with 1,3-pentadiene-4-d from 3-pentene-2-one by reduction with lithium aluminum deuteride to give 3-pentene-2-ol-2-d which was subsequently dehydrated with sulfuric acid (Equation 44).

\[
\begin{align*}
\text{CH}_3\text{=CH=CH-CD-CH}_3 & \overset{\text{LiAlD}_4}{\longrightarrow} \text{CH}_3\text{=CH=CH-C-CH}_3 \\
\text{CH}_3\text{=CH=CH-CD-CH}_3 + \text{CH}_3\text{=CH-CD=CH}_2 & \overset{-\text{H}^+}{\longrightarrow} \left[\text{CH}_3\text{CH}_2=\text{CH-C-CH}_3\right] \\
\end{align*}
\]
The 3-penten-2-one (tech grade, Aldrich Chemical Co.) was of undetermined geometry, but the 3-pentene-2-ol-2-d obtained by reduction of the crude 3-pentene-2-one had the same glc retention time as authentic trans-3-pentene-2-ol (Chemical Samples Co.). The 1,3-pentadienes-2-d and 4-d obtained by dehydration of the deuterio alcohol were assigned trans configurations by comparison of glc retention times to that of trans-1,3-pentadiene (Chemical Samples Co.). The mixture of 1,3-pentadiene-2-d and 4-d was purified by preparative glc and photolyzed at 2537 Å as a diglyme (~1.5%) solution (Equation 45) to give 3-methylcyclobutene-1-d and 3-d respectively. The 3-methyl-

\[
\begin{align*}
\text{CH}_3 &- 
\text{CH} &- 
\text{CH} &- 
\text{CD} &- 
\text{CD} &- 
\text{CH} &- 
\text{CH} &- 
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 &- 
\text{CH} &- 
\text{CD} &- 
\text{CD} &- 
\text{CH} &- 
\text{CH} &- 
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 &- 
\text{CH} &- 
\text{CD} &- 
\text{CD} &- 
\text{CH} &- 
\text{CH} &- 
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 &- 
\text{CH} &- 
\text{CD} &- 
\text{CD} &- 
\text{CH} &- 
\text{CH} &- 
\end{align*}
\]

cyclobutenes were isolated by preparative glc in which the effluent carrier gas was passed through tetrachloroethylene at -5° in order to scrub out the cyclobutenes. A solution of the cyclobutenes in tetrachloroethylene, sufficiently concentrated for nmr study, was thus obtained.
Alkaline Decomposition of Substituted Cyclopropyl Methyl Ketone and Cyclopropylcarboxaldehyde Arylsulfonylhydrazones

(2,2-Dimethylcyclopropyl)methylcarbene (I), presumably as derived by pyrolysis of the dry sodium salt of 2,2-dimethylcyclopropyl methyl ketone tosylhydrazone, has been previously reported (2) to rearrange to 1,3,3-trimethylcyclobutene (XVI) and 2,4-dimethyl-1,3-pentadiene (XVII) via initial ring expansion of the 1,3-bond of the cyclopropyl ring (Equation 46, path b) and subsequent isomerization. 1,4,4-Trimethylcyclobutene (XVIII), the product of rearrangement of the 1,2-bond

\[ \overset{\text{a}}{\text{CH}_3} \quad \overset{-\text{N}_2}{\text{N}_2} \quad \overset{\text{a}}{\text{2}} \quad \overset{\text{b}}{\text{1}} \quad \overset{\text{b}}{\text{3}} \quad \overset{\text{a}}{\text{1}} \quad \overset{\text{4}}{\text{4}} \]

Equation 46
of the cyclopropyl group (Equation 46, path a) was not observed. Since carbenes are electrophilic, the absence of XVIII was unexpected because XVIII would have resulted from migration of the electron-rich 1,2-cyclopropyl ring bond; the observed rearrangement of I to XVI means that the relatively electron-deficient bond rearranges preferentially to the carbenic center.

In order to rule out the possibility that cationic processes were responsible for these unexpected results, 2,2-dimethylcyclopropyl methyl ketone tosylhydrazone was decomposed with sodium methoxide and with lithium methoxide under various conditions summarized in Table 2 (44).

(44) The previous study of this system (2) involved vacuum pyrolysis of the dry sodium salt of 2,2-dimethylcyclopropyl methyl ketone tosylhydrazone at 175-180°.

<table>
<thead>
<tr>
<th>No.</th>
<th>Base</th>
<th>Equiv. of Base</th>
<th>(XV)</th>
<th>(XIV) (45)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>NaOCH₃</td>
<td>0.8</td>
<td>99% *</td>
<td>1% *</td>
</tr>
<tr>
<td>6</td>
<td>NaOCH₃</td>
<td>11</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>LiOCH₃</td>
<td>10</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>LiOCH₃</td>
<td>0.8</td>
<td>98</td>
<td>2</td>
</tr>
</tbody>
</table>

*Yields are expressed as % of total measured hydrocarbon products.
Chromatographic analysis of the reaction products shows the presence of a compound of slightly greater retention time than 1,3,3-trimethylcyclobutene. Though the quantity of this material was insufficient to permit its unambiguous identification, the longer retention time is consistent for 1,4,4-trimethylcyclobutene (XVIII).

The results obtained are essentially identical to those reported previously (2); namely, virtually exclusive ring opening via path b (Equation 46). One major difference is that no 2,4-dimethyl-1,3-pentadiene (XVII) is formed under the reaction conditions of the present work (140° in diglyme); decomposition of the salt of the tosylhydrazone in solution at 140° avoids thermal isomerization of XVI to XVII (2).

The fact that XVI is almost the exclusive product of decomposition of 2,2-dimethylcyclopropyl methyl ketone tosylhydrazone using either insufficient base (protic conditions which lead in part to cationic decomposition) or a large excess of base (aprotic conditions which result in carbenic decompositions) suggests that the 1-(2,2-dimethylcyclopropyl)ethyl cation possibly generated undergoes rearrangements similar to that of its carbene analog (I). Similarly, excess lithium ion from excess lithium methoxide gives only XVI as the hydrocarbon product. There is thus no observable lithium ion effect. Lithium ions can alter the course of decomposition of diazo compounds in a manner similar to that discussed earlier for carbonium ions (46); if the

rearrangement path for the carbonium ion in the present system is the same as for the carbene, no lithium ion effect will be observed.

The fact that rearrangement of I occurs by expansion of the 1-3 side of the cyclopropyl ring is explainable by steric effects. The carbene center may possibly attack either C2 or C3 of the cyclopropyl ring. However, attack (or insertion) at C2 (a, Equation 47) is blocked by the C2-methyl group which is cis- to the carbene center. On the other hand, C3 is less hindered than C2 and thus is more readily attacked (b, Equation 47) to give XVI.

The possibility that differences in the bicyclic transition states XIX and XX (resulting from carbene attack at C2 and C3 respectively) lead to selective rearrangement of (2,2-dimethylcyclopropyl)methylcarbene
(I) to XVI is consistent with steric control of the rearrangement process. Intermediate XIX has 2 methyl groups at the bridging carbon atom ($C_2$) and 1 methyl group on neighboring $C_4$. Steric interaction between vicinal $C_4$- and $C_2$-methyl groups is undoubtedly substantial. The pseudo-equatorial methyl group at $C_2$ may also interact sterically with the edges of the bent bicyclobutyl ring system. Intermediate XX has no methyl groups at the bridging position to crowd the ring edges as does XIX. Also the $C_4$ and $C_2$-methyl groups in XX are not vicinal. Thus, less steric crowding in XX compared to XIX may control rearrangement of I. It should also be noticed that path b (Equation 47) leads to 1,3,3-trimethylcyclobutene (XVI) which is less crowded than 2,3,3-trimethylcyclobutene (XVIII), the product of path a. It is not likely, however, that the rearrangement processes are controlled by thermodynamic factors.

An alternate explanation of rearrangement of I is that the hyper-conjugative ability of the migrating group determines which side of the cyclopropyl ring expands; if hyperconjugation of type XXI is greater than XXII, then the course of rearrangement can be rationalized electronically.
To study the rearrangements of substituted cyclopropylcarbenes further, the decomposition of methyl trans-2-methylcyclopropyl ketone (X) 2,4,5-trichlorobenzenesulfonylhydride was investigated. A previous study (2) of the pyrolytic decomposition of the dry sodium salt of the tosylhydrazone of X showed that methyl(trans-2-methylcyclopropyl)-carbene (II) rearranges to 1,4- and 1,3-dimethylcyclobutenes (XXIII and XXIV) by ring expansion, and 3-methyl- and 2-methyl-1,trans-3-pentadienes (XXV and XXVI) by thermal isomerization of XXIII and XXIV respectively (Equation 48).
Products of path a (XXIII and XXV) accounted for ~ 35% of the isolated hydrocarbons while XXIV and XXVI (derived via path b) made up the remaining 65%. The preference for II to rearrange via path b was ~ 2/1 over path a.

The results of the current investigation of this system (II) are summarized in Table 3. Alkaline decomposition of the 2,4,5-trichloro-

**TABLE 3**

**Base-Catalyzed Aprotic Decomposition of Methyl trans-2-Methyl-cyclopropyl Ketone 2,4,5-Trichlorobenzenesulfonylhydrazone**

<table>
<thead>
<tr>
<th>No.</th>
<th>T°</th>
<th>Base</th>
<th>Equiv. of Base</th>
<th>b(XXIII)</th>
<th>b(XXIV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>125°</td>
<td>NaH</td>
<td>3.7</td>
<td>26%c</td>
<td>74%c</td>
</tr>
<tr>
<td>55</td>
<td>135°</td>
<td>LiOCH₃</td>
<td>15</td>
<td>23</td>
<td>77</td>
</tr>
<tr>
<td>167</td>
<td>140°</td>
<td>NaH</td>
<td>1.1</td>
<td>21</td>
<td>79</td>
</tr>
<tr>
<td>57</td>
<td>140°</td>
<td>NaH</td>
<td>11</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>168</td>
<td>150°</td>
<td>NaH</td>
<td>1.0</td>
<td>22</td>
<td>78</td>
</tr>
<tr>
<td>50</td>
<td>200°</td>
<td>NaH</td>
<td>1.9</td>
<td>24</td>
<td>76</td>
</tr>
<tr>
<td>52</td>
<td>200°</td>
<td>NaH</td>
<td>1.1</td>
<td>25</td>
<td>75</td>
</tr>
</tbody>
</table>

a The solvent was diglyme except in no. 54 where decalin was used.
b Measured as open-chain dienes except for no. 167 and 168 (see text).
c Yields are expressed as % of total measured hydrocarbon products.
benzenesulfonylhydrazone of X at temperatures less than 140° gave cyclobutenes XXIII and XXIV sole rearrangement products. Decompositions at 200° with lithium or sodium bases led to isolation of 3-methyl and 2-methyl-1,trans-3-pentadienes (XXV and XXVI) presumably derived from further rearrangement of XXIII and XXIV respectively (Equation 48). At all reaction temperatures, trace quantities of propene and propyne, fragmentation products, were observed (Equation 49). The ring opening processes to the methylpentadienes were used to advantage in analysis of dimethylcyclobutenes XXIII and XXIV. Because gc separation of XXIII and XXIV was inadequate for accurate analysis, the products of decomposition of the sulfonylhydrazone at 125-140° were heated to 200° to isomerize cyclobutenes XXIII and XXIV to dienes XXV and XXVI which are easily separated by gc. The accuracy of determining the ratios of cyclobutenes XXIII and XXIV from the gas chromatograms of butadienes XXV and XXVI was confirmed by pyrolyzing a 1/1 mixture of XXIII and XXIV in diglyme at 200° to give a 1/1 mixture of dienes XXV and XXVI. All hydrocarbon products were identified by comparing their gc retention times to those of authentic samples (47).
Syntheses of 1,4- and 1,3-dimethylcyclobutenes (XXIII and XXIV) were described earlier. 2- and 3-Methyl-1,trans-3-pentadienes were obtained from Chemical Samples Co., Columbus, Ohio.

The product distribution of rearrangement of II (Table 3) remains constant over the temperature range (125-200°) studied. Also, there was no detectable lithium ion effect on the distribution of the products of reaction.

Study of methyl(trans-2-methylcyclopropyl)carbene (II) was initiated on the basis that with the C2-methyl group trans to the carbenic center, steric interference of the type in (trans-2,2-dimethylcyclopropyl)methylcarbene (I) would be eliminated. It might be expected that migration to C2 (path a, Equation 48) might be preferred since C2 is the more highly substituted electron-rich center.

The results of the present study show however that 1,5-dimethylcyclobutene (XXIV), formed via path b (Equation 48) is the major product of rearrangement of II. The ratio of XVI/XXIII is ~ 5/1; the value obtained previously for pyrolysis of the dry sodium salt of the tosylhydrazone is 2/1 (2). It was previously reported (2) that glc separation of 1,3- and 1,4-dimethylcyclobutene is difficult; this experimental difficulty in the prior work could account for the slight difference in product ratios from the present results.

Despite the reduced steric factors in II as compared to I, carbenic rearrangement of II occurs preferentially to the lesser substituted side of the cyclopropyl ring. However, the degree of preference in rearrangement has been reduced sharply in II. One explanation, involving
steric effects, for preference of path b (Equation 48) over path a, is that transition state XXVII formed by attack of the carbenic center (C₄) on C₂, is more strained than XXVIII, which results from C₄ attack at C₃ (2). Transition state XXVII has a methyl group at the bridging position (C₂) which appears less favorable than for XXVIII in which the methyl groups are as far apart as possible and removed from the bicyclic ring edges.

Although steric control in rearrangement of methyl(trans-2-methylcyclopropyl)carbene (Equation 48) is reasonable, the hyperconju-
gation hypothesis proposed earlier for I is applicable: if hyperconjugative stabilization of XXIX is greater than of XXX, then preferential migration of the less substituted group may occur. The combined

\[ \text{XXXIX} \]

\[ \text{XXX} \]

results of studies of I and II indicate that the migration aptitude of the carbon atom located \( \beta \)- to the carbenic center, in cyclopropyl carbene rearrangement, is quaternary > tertiary > secondary. This is best explained, at the moment, in terms of the hyperconjugation arguments.

In order to examine further the steric and electronic factors influencing rearrangements of cyclopropylcarbenes, a series of carbenes (XXXI, XXXII, XXXIII) derived from cyclopropanecarboxaldehydes were studied. The aldocarbenes, XXXI, XXXII, and XXXIII, have hydrogen

\[ \text{XXXI} \]

\[ \text{XXXII} \]

\[ \text{XXXIII} \]
rather than methyls at their carbenic centers and thus are expected to show different steric effects.

**trans-1,2-Dimethylcyclopropylcarbene (XXXI)** as derived from pyrolysis of salts of **trans-1,2-dimethylcyclopropanecarboxaldehyde (XII)** 2,4,5-trichlorobenzencesulfonylhydrazone was expected to rearrange to 1,3-dimethylcyclobutene (XXIV) via path a and 1,4-dimethylcyclobutene (XXIII) via path b (Equation 50). Fragmentation to propene and propyne (path c) was also expected. The results observed for decomposition and rearrangement of XXXI are summarized in Table 4. Fragmentation to propene and propyne amounts to about 50% of the observed hydrocarbon products. Also, virtually no 1,3-dimethylcyclobutene (XXIX) is observed. The rearrangement process is selective for ring expansion of the unsubstituted side of the cyclopropyl ring (path b, Equation 50) to give 1,4-dimethylcyclobutene.
### TABLE 4

**Decomposition of Salts of trans-1,2-Dimethylcyclopropanecarboxaldehyde 2,4,5-Trichlorobenzencesulfonylhydrazone**

<table>
<thead>
<tr>
<th>No.</th>
<th>T°</th>
<th>Base</th>
<th>Equiv of Base</th>
<th>(XXIV)</th>
<th>(XXIII)</th>
<th>(\text{CH}_3\text{CH}==\text{CH}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>100°</td>
<td>(\text{NaOCH}_3)</td>
<td>10</td>
<td>0%</td>
<td>53%</td>
<td>47%</td>
</tr>
<tr>
<td>36</td>
<td>100°</td>
<td>(\text{NaH})</td>
<td>2</td>
<td>0</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>41</td>
<td>100°</td>
<td>(\text{NaH})</td>
<td>1.2</td>
<td>0</td>
<td>52</td>
<td>48</td>
</tr>
<tr>
<td>42a</td>
<td>100°</td>
<td>(\text{NaH})</td>
<td>1.3</td>
<td>0</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>47</td>
<td>100°</td>
<td>(\text{LiOCH}_3)</td>
<td>14</td>
<td>t(^b)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>38</td>
<td>105°</td>
<td>(\text{NaOCH}_3)</td>
<td>25</td>
<td>0</td>
<td>56</td>
<td>44</td>
</tr>
<tr>
<td>24</td>
<td>140°</td>
<td>(\text{NaOCH}_3)</td>
<td>11</td>
<td>0</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>161</td>
<td>150°</td>
<td>(\text{NaH})</td>
<td>1.0</td>
<td>&lt; 1%</td>
<td>&gt; 99%</td>
<td>c</td>
</tr>
<tr>
<td>46</td>
<td>200°</td>
<td>(\text{NaH})</td>
<td>1.3</td>
<td>0</td>
<td>(\sim 51%^d)</td>
<td>(\sim 49%)</td>
</tr>
</tbody>
</table>

\(^a\)trans-1,2-Dimethylcyclopropanecarboxaldehyde monstrosylhydrazone was decomposed in this experiment.

\(^b\)\(t = \) Trace

\(^c\)Substantial fragmentation was observed but was not measured.

\(^d\)Determined as 3-methyl-1,3-pentadiene.
As in the previous studies of cyclopropylmethylcarbenes (I and II), the relative paths of decomposition of trans-1,2-dimethylcyclopropylcarbene (XXXI) are insensitive to pyrolysis temperatures over the 100-200° range studied, in that the product distribution is unchanged.

The decomposition of the 2,4,5-trichlorobenzenesulfonylhydrazone of XII was also insensitive to the type of base used. Excess sodium methoxide (10-25 equiv) gave essentially the same results as did sodium hydride (1-2 equiv). Excess lithium methoxide (14 equiv) yielded product mixtures identical to those obtained from sodium bases and thus this system shows no lithium ion effect (46) under the conditions studied.

Use of the 2,4,6-triisopropylbenzenesulfonylhydrazone (40) of trans-1,2-dimethylcyclopropane carboxaldehyde gave the same product distribution observed for the 2,4,5-trichlorobenzenesulfonylhydrazone (Table 4, no. 42).

A likely explanation of the great selectivity in rearrangement of XXXI involves steric effects. Rearrangement via path a to give 1,3-dimethylcyclobutene requires that carbenic attack occur at relatively hindered C2, the ring carbon bearing the methyl substituent. Such a bicyclic transition state (XXXIV) has methyl groups at the bridging and bridged positions and furthermore has one methyl group between the 'V' of the rings. On the other hand, path b to give 1,4-dimethylcyclobutene, involves attack of the carbenic center on a relatively unhindered side (C3 is substituted only by hydrogen) of the cyclopropyl ring and the resulting transition state (XXXV) carries only one methyl
at a bridging position and it is not within the "V" of the rings.
Thus, on the basis of the geometry of the transition state or of the 
ground state, steric factors appear largely responsible for the fact 
that XXXI does not rearrange by carbenic attack at C2 (path a) and thus 
1,3-dimethylcyclobutene (XXIV) is not formed. Hyperconjugative effects, 
as discussed for ketone-derived carbenes I and II, would also favor
rearrangement of XXXI by path b, but the extremely high order selectivity observed is probably primarily a steric function.

The extensive fragmentation observed may also be a result of steric interaction between the carbenic center at C₁ and the C₂-methyl group. In cyclopropylcarbenes, derived from cyclopropanecarboxaldehydes, in which the carbenic center has no substituents of cis geometry, fragmentation usually accounts for 20-26% of the total hydrocarbon products (48). The 50% observed for XXXI is unusually high. Crowding in the reactant (XXXI) could lead to weakening of the C₁-C₂ bond of the cyclopropane ring which in turn could result in fragmentation (Equation 51). Since the carbenic center cannot readily attack at ring C₂ from the topside, reaction at that site might result in fragmentation above that inherent to the system.

The controlling factor for the selective rearrangement and high-order fragmentation of XXXI appears to be cis-C₁-C₂ substituent crowding. The tendency in this system for the carbene to move toward the

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

XXXI
the unsubstituted side of the cyclopropyl ring was also observed in rearrangement of (trans-2,2-dimethylcyclopropyl)methylcarbene (I) which features a similar cis-steric crowding of the carbenic center.

Rearrangement of cis-1,2-dimethylcyclopropylcarbene (XXXII) was investigated because steric effects were expected to be less than in the cyclopropylcarbenes previously studied. As was possible for the trans-1,2-dimethyl isomer (XXXI), XXXII could rearrange to 1,3-dimethylcyclobutene (XXIV) via path a and to 1,4-dimethylcyclobutene (XXIII) via path b (Equation 52). The results of pyrolyses of salts of cis-

\[
\begin{align*}
\text{XXXII} & \xrightarrow{\Delta} \text{XXIV} \quad \text{and} \quad \text{XXIII} \\
\text{XXXII} & \xrightarrow{\Delta} \text{XXV} \quad \text{and} \quad \text{XXVI}
\end{align*}
\]

1,2-dimethylcyclopropane carboxaldehyde 2,4,5-trichlorobenzensulfonylehydrazone in diglyme are shown in Table 5.

Fragmentation of XXXII to propene and propyne accounts, on an average, for 25% of the volatile hydrocarbon products. 1,3- and 1,4-Dimethylcyclobutenes (XXIV and XXIII) are obtained in a ratio of approximately 1.5/1 upon isomerization of XXXII; rearrangement of XXXII thus
TABLE 5
Decomposition of Salts of cis-1,2-Dimethylcyclopropanecarboxaldehyde
2,4,5-Trichlorobenzenesulfonylhydrazone in Diglyme

<table>
<thead>
<tr>
<th>No.</th>
<th>T°</th>
<th>Base</th>
<th>Equiv of Base</th>
<th>CH₃-CH=CH₂ + CH₃=CH²</th>
<th>XXIV</th>
<th>XXIII</th>
<th>XXIV/XXIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>100°</td>
<td>NaOCH₃</td>
<td>8</td>
<td>22%</td>
<td>47₄</td>
<td>31₄</td>
<td>1.5</td>
</tr>
<tr>
<td>37</td>
<td>100°</td>
<td>NaH</td>
<td>1.0</td>
<td>35</td>
<td>39₄</td>
<td>26₄</td>
<td>1.5</td>
</tr>
<tr>
<td>66</td>
<td>100°</td>
<td>NaH</td>
<td>1.3</td>
<td>n.m.</td>
<td>60₄</td>
<td>40₄</td>
<td>1.5</td>
</tr>
<tr>
<td>49</td>
<td>105°</td>
<td>NaH</td>
<td>1.1</td>
<td>n.m.</td>
<td>59₅</td>
<td>41₅</td>
<td>1.4</td>
</tr>
<tr>
<td>56</td>
<td>105°</td>
<td>NaH</td>
<td>1.1</td>
<td>n.m.</td>
<td>62₅</td>
<td>38₅</td>
<td>1.6</td>
</tr>
<tr>
<td>170</td>
<td>150°</td>
<td>NaH</td>
<td>1.0</td>
<td>2%</td>
<td>4₆</td>
<td>27₆</td>
<td>1.6</td>
</tr>
<tr>
<td>162</td>
<td>150°</td>
<td>NaH</td>
<td>1.0</td>
<td>10%</td>
<td>4₆</td>
<td>3₆</td>
<td>1.4</td>
</tr>
<tr>
<td>48</td>
<td>200°</td>
<td>LiOCH₃</td>
<td>16</td>
<td>n.m.</td>
<td>58₇</td>
<td>42₇</td>
<td>1.4</td>
</tr>
<tr>
<td>53</td>
<td>200°</td>
<td>NaH</td>
<td>13</td>
<td>n.m.</td>
<td>58₈</td>
<td>42₈</td>
<td>1.4</td>
</tr>
</tbody>
</table>

aThe product distributions are reported as percentages of the measured products, not as percent overall yields; bThe cyclobutenes were measured as their open-chain dienes (XXVI and XXV) as obtained by heating the pyrolysis mixtures at 200° for 15-20 min (Equation 52); cN.m. = not measured; danalyzed on a 200 ft squalane/hexadecane capillary gc column; eestimated from poorly-resolved gc peaks; fanalyzed on a 300 ft squalane/hexadecane capillary gc column.
occurs preferentially via path a (Equation 52). The ratio of rearrangement of XXXII to XXIV and XXIII is insensitive to reaction temperatures from 100° to 200°, as well as to excess base and to excess lithium ion. Decomposition of XXXII at 200° yields 2- and 3-methyl-1,3-pentadienes (XXVI and XXV) rather than their isomeric cyclobutenes (XXIV and XXIII).

The preference for cis-1,2-dimethylcyclopropylcarbene (XXXII) to rearrange via path a (expansion via the C₁-C₂ bond of the cyclopropyl group) represents a startling departure from the trend established previously for carbenes I, II, and XXXI. In I, II, and XXXI, rearrangement involving migration of the lesser substituted β-cyclopropyl bond occurred preferentially. In XXXII, however, migration of the more substituted β-cyclopropyl bond is favored over the lesser substituted one by a factor of 1.5. Transition states XXXVI and XXXVII for rearrangement of XXXII via paths a and b respectively, seem to be nearly equivalent with respect to steric crowding. Therefore, it is tempting to conclude that the observed selectivity of the carbenic center in XXXII for reaction at C₂ over C₃ arises from methyl substitution making C₂ relatively electron rich compared to C₃. Such a hypothesis, however, is opposite to the hyperconjugation postulate, as discussed
for I and II, which requires that the lesser substituted cyclopropyl carbon atom undergo favored rearrangement.

An alternate explanation for preference of path a for rearrangement of XXXII arises if the C₁-C₂ bond is weakened by cis C₁-methyl-C₂-methyl steric interaction. For trans-1,2-dimethylcyclopropylcarbene (XXXI), it was suggested that the C₁-C₂ bond is weakened by cis-steric interaction of the carbenic center and the C₂-methyl group. Because attack of the carbenic carbon at C₂ of the cyclopropyl ring was blocked by the methyl group, the weakened C₁-C₂ bond led to enhanced fragmenta-
tion. In XXXII, the C₁-C₂ cyclopropyl bond may also be weakened; however, carbenic attack at C₂ is sterically as facile as at C₃, and thus the cis-dimethyl weakening of the C₁-C₂ cyclopropyl bond could facilitate preferential attack at C₂. Thus, the results of rearrange-

![XXXII]

ment of XXXII may be rationalized on the basis of steric or electronic effects. With respect to all of the cyclopropylcarbene systems studied up to this point, steric factors appear to be more significant in affecting the rearrangement pathway.

In an effort to reduce steric effects to a minimum, rearrangement of trans-2-methylcyclopropylcarbene-α-d (XXXIII) was studied. The products expected from XXXIII were 3-methylcyclobutene-2-d (XXXVIII) and 3-methylcyclobutene-1-d (XXXIX) via paths a and b respectively, and propene and acetylene-d by fragmentation (path c) (Equation 55).

Fragmentation, where measured, amounted to 26-30% of the volatile products. The labelled cyclobutenes, XXXVIII and XXXIX, obtained are impossible to separate. Thus relatively large-scale (1g) decompositions of trans-2-methylcyclopropanecarboxaldehyde-α-d 2,4,5-trichlorobenzenesulfonylhydrazone were conducted so that sufficient quantities of XXXVIII and XXXIX could be obtained for analysis by nmr techniques.
The nmr analysis was initiated by first assigning the appropriate signals to $H_1$ and $H_2$ of 3-methylcyclobutene (XL) (49). The vinyl protons ($H_1$ and $H_2$) in XL appear as an AB quartet in the $6\delta$ region with signal A ($J=3.0$ Hz) at 5.94 $\delta$ and B ($J=3.0$ Hz) at 6.00 $\delta$. Each line of the A doublet is further split into triplets ($J < 1$ Hz) while each line of the B doublet is split into a doublet ($J = 1$ Hz) (Figure 2). Thus, the A signal is assigned to $H_1$ and the triplets arise from

---

(49) Assistance in obtaining 100 mHz spectra was given by Dr. Joseph Wander, Louisiana State University, Baton Rouge, Louisiana.
vicinal coupling to the two similar protons on C₄. The B signal is assigned to H₂ and the doublets result from vicinal coupling to the methine proton on C₃.

These assignments are further supported by comparing chemical shifts of the vinylic protons in 1,3- and 1,4-dimethylcyclobutenes (XXIV and XXIII). In the 60 MHz nmr spectrum of XXIII, H₁ appears at 5.55 δ; the shift for H₂ in XXIV is 5.75 δ. The relative shifts of H₁ and H₂ (H₁ being upfield from H₂) are the same as those for H₁ and H₂ as assigned previously for 3-methylcyclobutene (XL).

Final evidence supporting the assignment of low and high field vinyl nmr shifts in XL to H₂ and H₁ respectively, was obtained by the independent synthesis of 3-methylcyclobutene-1-d (XXXIX). The vinyl proton shift (H₂) of this independently obtained compound matches the shift of the major product from rearrangement of XXIII. This is discussed in detail in the Experimental chapter of this dissertation.

Nmr analysis of the mixture of 1-d and 2-d 3-methylcyclobutenes (XXXVIII and XXXIX) obtained from XXXIII (Equation 55) gave a spectrum having a broad peak at 5.99 δ (rel area = 3 ± 0.5) and a broad peak at 5.93 δ (rel area = 1) (Figure 3). Since XXXIX has only the H₂ vinyl proton and XXXVIII only H₁, the ratio of XXXIX/XXXVIII formed from
XXXIII is $3 \pm 0.5/1$.

Formation of XXXIX and XXXVIII in a ratio of $3 \pm 0.5/1$ means that XXXIII opens preferentially via path b (Equation 53) by attack at the lesser-substituted position ($C_2$) for expansion of the cyclopropane ring. In this system, there do not appear to be steric factors which can account for the observed selectivity of rearrangement. Transition states XLI and XLII [produced by carbenic attack at $C_2$ (path a) and $C_3$ (path b) respectively] appear to be nearly equally crowded, and $C_2$ looks as vulnerable as $C_3$ for frontside attack by the carbenic center.

Inductive effects do not account for preferential formation of XXXIX over XXXVIII. This leaves the possibility that hyperconjugative effects (as discussed earlier) may be operative. Hyperconjugative analysis of transition states XLIII and XLIV predicts that XLIV is stabilized more by the extra proton on $C_3$ than is XLIII by methyl on $C_2$. 
The hyperconjugation explanation is also consistent with the results of isomerization of methyl trans-2-methylcyclopropylcarbene (II), a second system in which steric effects are expected to be small. It is also noted that the reaction path preferences are essentially the same (~3:1 for migration of the less/more-substituted cyclopropyl ring carbon) for XXXIII and II.

The results obtained for rearrangement of XXXIII lead possibly to reappraisal of the factors leading to isomerization of (2,2-dimethylcyclopropyl)methylcarbene (I) and trans-1,2-dimethylcyclopropylcarbene (XXXI) which give exclusively products derived from expansion of the unsubstituted side of their cyclopropyl groups. Although these exclusive rearrangements probably result primarily because of cis steric interference in carbenic attack at the C2 positions of cyclopropyl groups, the paths of rearrangement might be augmented by hyperconjugative effects. cis-1,2-Dimethylcyclopropylcarbene (XXXII) is anomalous in that it prefers to undergo rearrangement of the more substituted side
of its cyclopropyl group. The preference however is slight (1.5/1) and may indicate only that hyperconjugative effects are not as significant as severe steric interaction in determining the course of intramolecular rearrangement of cyclopropylcarbenes.

During the course of this work, Stevens and coworkers (50) communicated the results of their research on rearrangements of cyclopropylcarbenes. Their studies are summarized in Table 6. Their data for (2,2-dimethylcyclopropyl)methylcarbene (I) and methyl (trans-2-methylcyclopropyl)carbene (II) are nearly identical to that of this dissertation. Methyl(cis-2-methylcyclopropyl)carbene, a system not studied here, rearranges almost exclusively to 1,4-dimethylcyclobutene (XXIV), the product of ring expansion of the cyclopropyl group from the unhindered side. This result is consistent with examples I and XXXI in which the carbenic center is cis to the cyclopropyl methyl group, and thus emphasizes steric control created by cis 1,2-interaction. The results of Stevens et al for rearrangement of cis-1,2-dimethylcyclopropylcarbene (XXXII) do not agree with that of the present dissertation. The author of this dissertation can not offer an explanation for the difference in results, but the data obtained in these laboratories has been reproduced repeatedly (Table 5) under a variety of conditions and using several different analytical techniques, and thus, is submitted as correct.

TABLE 6
Rearrangement of Substituted Cyclopropyl Carbenes

<table>
<thead>
<tr>
<th>Carbene</th>
<th>R^1</th>
<th>R^2</th>
<th>R^3</th>
<th>R^4</th>
<th>A(%)</th>
<th>B(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (I)</td>
<td>CH₃</td>
<td>CH₃</td>
<td>H</td>
<td>CH₃</td>
<td>97.5</td>
<td>2.5</td>
</tr>
<tr>
<td>b</td>
<td>H</td>
<td>CH₃</td>
<td>H</td>
<td>CH₃</td>
<td>95.6</td>
<td>4.4</td>
</tr>
<tr>
<td>c (II)</td>
<td>CH₃</td>
<td>H</td>
<td>H</td>
<td>CH₃</td>
<td>72.1</td>
<td>27.9</td>
</tr>
<tr>
<td>d (XXXII)</td>
<td>CH₃</td>
<td>H</td>
<td>CH₃</td>
<td>H</td>
<td>49.3</td>
<td>50.7</td>
</tr>
</tbody>
</table>

Decomposition of Salts of 2,2-Dimethylbutanal Tosylhydrazone

The discovery that steric rather than electronic control occurs in rearrangement of various 2-substituted cyclopropylcarbenes suggested that carbenic rearrangements of non-cyclic systems be investigated. Kirmse and Wächtershäuser (23,51) had previously noted several cases in
which branched alkylcarbenes undergo preferential intramolecular insertion into primary > secondary > tertiary carbon-hydrogen bonds (Tables 7 and 8). Carbenes of the neopentyl type (III) in particular display preference for insertion at the lesser substituted carbon atom. Products of carbon-skeleton rearrangement were not reported, however. Friedman and Berger (52) have summarized possible carbenoid reactions of 2,2-dimethyl-1-butylidene (neohexylcarbene) (III) as derived from

\[
\text{CH}_3 \\
\text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_2 \\
\text{CH}_3 \\
\text{III}
\]

neohexyl chloride and either sodium or sodamide. The results (Table 9) give an insertion ratio into secondary hydrogen and primary hydrogen of 1.6 (statistically corrected) which is quite different than the value of 0.78 by Kirmse and Wächtershäuser (25). In another paper, Kirmse and Wächtershäuser (53) report a sec.C-H/prim.C-H insertion
TABLE 7

Competition Constants for Intramolecular Insertion of Alkylcarbenes as Generated by Thermolysis of Tosylhydrazone Salts (23)

![Diagram of reaction pathways]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>H</td>
<td>H</td>
<td>1.60</td>
<td>0.49 (cis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂</td>
<td>H</td>
<td>H</td>
<td>2.54 (trans)</td>
<td>0.47 (cis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>H</td>
<td>CH₃</td>
<td>0.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂</td>
<td>H</td>
<td>CH₃</td>
<td>0.85</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(CH₃)₂CH</td>
<td>H</td>
<td>CH₃</td>
<td>0.95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>H</td>
<td>0.83</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
<td>0.38</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 8

Competition Constants for Intramolecular Insertion of Substituted Neopentylcarbenes (51)

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

<table>
<thead>
<tr>
<th>X</th>
<th>-CH₃</th>
<th>-CH=CH₂</th>
<th>-C₆H₅</th>
<th>-N(CH₃)₂</th>
<th>-OCH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>sec. C-H</td>
<td>0.78</td>
<td>0.43</td>
<td>0.50</td>
<td>0.21</td>
<td>0.06</td>
</tr>
<tr>
<td>prim. C-H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 9

Products of Intramolecular Reactions of Neohexylcarbene (III)(52)

<table>
<thead>
<tr>
<th>Product</th>
<th>% of Total</th>
<th>Run A</th>
<th>Run B</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Ethyl-1-methylcyclopropane</td>
<td>61</td>
<td>67</td>
<td></td>
<td>prim. C-H insertion</td>
</tr>
<tr>
<td>1,1,2-Trimethylcyclopropane</td>
<td>32</td>
<td>34</td>
<td></td>
<td>sec. C-H insertion</td>
</tr>
<tr>
<td>2-Methyl-2-pentene</td>
<td>0.7</td>
<td>1.3</td>
<td></td>
<td>ethyl migration</td>
</tr>
<tr>
<td>cis-3-Methyl-2-pentene</td>
<td>1.4</td>
<td>3.1</td>
<td></td>
<td>methyl migration</td>
</tr>
<tr>
<td>trans-3-Methyl-2-pentene</td>
<td>3.4</td>
<td>4.2</td>
<td></td>
<td>methyl migration</td>
</tr>
</tbody>
</table>
ratio of 1.59 for the neohexyl chloride/sodium amide system. 1,1-
Diiodo-2,2-dimethylbutane with sodium, lithium, and magnesium gave
insertion ratios into secondary and primary hydrogen of 1.44, 1.70,
and 2.18 respectively (53). Since decomposition of 1-diazo-2,2-
dimethylbutane in 2-phenylethanol and in benzyl alcohol (protic media)
resulted in sec./prim. insertion ratios of 2.4 and 1.95 respectively
(54), it appears that the "carbenes" generated from neohexyl halides
and metals or strong bases show behavior similar to the "hot"
carbonium ions generated by protic decomposition of 1-diazo-2,2-
dimethylbutane. The product distributions from neohexyl halides and
metals or strong bases thus can not be used as evidence that discrete
carbenes are involved in the reaction system.

Friedman and Berger (52) also report that "thermal decomposition
of 2,2-dimethylbutanal tosylhydrazone in aprotic media yields the same
products [as for decomposition of neohexyl chloride with sodium or
sodium amide] in similar amounts" (Table 9). This summary of their
results is at odds with those of Kirmse and Wächtershäuser (23) for
carbenic decomposition of 2,2-dimethylbutanal tosylhydrazone and thus
makes investigation of 2,2-dimethyl-1-butylidene (III) necessary in
order to determine the migration aptitudes of methyl versus ethyl in
this important non-cyclic alkylcarbene system.

2,2-Dimethyl-1-butylidene (III), as presently generated by thermo-
lysis of 2,2-dimethylbutanal tosylhydrazone in the presence of bases,

yields 3-methyl-\textit{trans}-2-pentene (XLV), 3-methyl-\textit{cis}-2-pentene (XLVI), 2-methyl-2-pentene (XLVII), 2-ethyl-1-butene (XLVIII), 2-methyl-1-pentene (XLIX), 1-ethyl-1-methylcyclopropane (L), and 1,1,2-trimethylcyclopropane (LI) (Equation 54). These products were identified by
comparison of glc retention times, on a squalane/hexadecane capillary column (300 ft), to those of authentic samples.

The results of decomposition of 2,2-dimethylbutanal tosylhydrazone are summarized in Table 10. The distribution of products formed from reaction of the tosylhydrazone are influenced by temperature, large excesses of sodium hydride, and even the amount of rubber exposed to the reactants. It is of note that the rearrangement products from the system decrease from 59% at 100° to 7% at 200°, and the methyl/ethyl insertion ratio is raised from 0.39 to 1.6 as the reaction temperature is increased from 100 to 200°. The relative migration of methyl and ethyl groups is only slightly affected however by temperature since the ratio is only lowered from 2.3 at 100° to 1.9 at 200°. Excess hydride (6 equiv) does not affect the methyl/ethyl rearrangement ratio, but does lead to increased rearrangement. Also, the methyl/ethyl insertion ratio, which is ~1.4 at 150°, is lowered to 1.0 by excess hydride (6 equiv).

Use of small rather than large rubber septa in the reaction vials reduces total rearrangement from ~27% to 13% at 150°. Isolating the reaction components from rubber completely by either covering the septa with Teflon tape or using sealed ampules as reaction vessels lowers total rearrangement to 9%. Furthermore, formation of 2-ethyl-1-butene (XLVIII) and 2-methyl-1-pentene (XLIX) is eliminated by removal of rubber surfaces. Elimination of rubber surfaces does not change the insertion ratio for reaction at 150°, but the methyl/ethyl rearrangement ratio decreases slightly when rubber is absent (2.2 to 1.9).
Aprotic Decomposition of Salts of 2,2-Dimethylbutanal Tosylhydrazone

| No. | $T^\circ$ | Base | Base | XLV | XLVI | XLVII | XLVIII | XLIX | LX | Rearrange- | Insert- | % | % |
|-----|----------|------|------|-----|------|-------|--------|------|----|ment: Methyl | tion: Ethyl | Ethyl | Rearrange- | Insertion |
| 92  | 105° | MeOH | 1.2  | 23  | 16  | <7   | <7    | <3   | <5 | 21 | 18 | 2.3           | 0.57  | 59 | 41 |
| 93  | 125° | n-But | 1.4  | 19  | 15  | 7    | 5     | <3   | <5 | 36 | 15 | 2.5           | 0.60  | 51 | 49 |
| 94  | 160° | n-But | 1.1  | 8   | 6   | 3    | 1     | <1   | <1 | 64 | 16 | 2.2           | 1.5   | 20 | 20 |
| 95  | 200° | n-But | 1.0  | 5   | 2   | 1    | <1   | <1 | 78 | 16 | 1.9 | 1.6   | 7   | 95 |

| 100 | 150° | Ethyl | 6.0  | 18  | 12  | 6    | 4     | 2    | 14 | 44 | 14 | 2.3           | 1.0   | 14 | 58 |
| 101 | 150° | Ethyl | 1.5  | 10  | 8   | 4    | <2   | 1   | 60 | 16 | 2.3 | 1.3   | 14 | 24 | 76 |
| 102 | 150° | Ethyl | 5.6  | 11  | 8   | 4    | 2    | 1   | 59 | 14 | 2.2 | 1.4   | 27 | 73 |
| 103 | 150° | Ethyl | 1.1  | 11  | 8   | 5    | 2    | 1   | 59 | 14 | 2.1 | 1.4   | 27 | 73 |
| 104 | 150° | Ethyl | 1.2  | 12  | 9   | 5    | <2   | 1   | 58 | 14 | 2.1 | 1.4   | 27 | 73 |
| 105 | 150° | Ethyl | 6.2  | 16  | 13  | 7    | 3    | 3   | 43 | 14 | 2.2 | 1.0   | 14 | 56 |

| 109  | 105° | n-ButLi | 1    | 19  | 16  | 7    | 7     | 5    | 21 | 25 | 2.5 | 0.28  | 54 | 45 |
| 110  | 150° | n-ButLi | 1    | 7   | 5   | 3    | 3     | 1   | 66 | 15 | 2.3 | 1.5   | 19 | 82 |
| 113  | 200° | n-ButLi | 1/2  | 5   | 4   | <2   | <2   | <1  | 71 | 17 | >2.3 | 1.4   | 12 | 88 |

| 113c | 150° | MeOH | 1.4  | 3   | 2   | trace | trace | 74  | 17 | 1.9 | 1.4   | 9   | 91 |
| 114c | 150° | MeOH | 1.2  | 6   | 4   | 2.5   | <1   | trace | 68 | 18 | 2.1 | 1.3   | 15.5 | 66 |
| 115c | 150° | MeOH | 1.2  | 6   | 4   | 2    | <1   | trace | 70 | 18 | 2.1 | 1.3   | 15 | 66 |
| 116c | 160° | MeOH | 1.2  | 5   | 4   | <1   | <1   | 70  | 17 | 2.1 | 1.4   | 13 | 67 |
| 117c | 160° | MeOH | 1.2  | 5   | 4   | <1   | <1   | 71  | 17 | 2.3 | 1.4   | 13 | 67 |
| 118c | 160° | MeOH | 1.6  | 5   | 3   | <0-   | <0-   | 72  | 18.5 | 2.0 | 1.3   | 9 | 92.5 |
| 119  | 160° | MeOH | 1.1  | 4   | 3   | <0-   | 73.5 | 17 | 1.9 | 1.4   | 9 | 90.5 |

---

*No. 92--113: Decomposition was effected in 5 ml vials with large rubber septa. *Decomposition was effected in a 5 ml vial equipped with a Teflon-covered septum. *Decomposition was effected in 5 ml vials provided with small rubber septa. *Decomposition was effected in sealed glass ampules. 

The ratios were calculated prior to rounding the percent values. The figures are rounded to the nearest 1% except where the value is < .5.

*These decompositions were effected using decalin as solvent. All others were done in dilauryl.
The paths of decomposition of 1-diazo-2,2-dimethylbutane have thus been found to be extremely sensitive to environment. Relatively low reaction temperatures or exposure to red rubber surfaces apparently lead to carbonium ion processes (Equation 55).
Olefins XLVIII and XLIX are clearly formed by carbonium ion processes; the other olefins, XLV, XLVI, and XLVII may result from either carbenic or cationic processes. Thus, in decompositions in which XLVIII and XLIX are not formed, the observed rearrangement products are interpreted to be derived wholly by carbenic processes. It should also be noted that at relatively high reaction temperatures (200°, no. 95, Table 10), carbonium ion processes are virtually eliminated even though a large red rubber septum was present in the system. Presumably, at 200°, 1-diazo-2,2-dimethylbutane loses nitrogen and converts to products before reacting with the rubber surface or other acidic sites in the reaction medium.

The methyl/ethyl insertion ratio of 1.3-1.4 for carbenic decomposition of 1-diazo-2,2-dimethylbutane at 150° is equivalent to a sec.C-H/prim.C-H insertion ratio of $\sim 0.74 \pm 0.03$. The latter ratio is in agreement with the value of 0.78 reported by Kirmse and Wächtershäuser (23).

2,2-Dimethyl-1-butylidene (III) is more discriminating undergoing rearrangement than insertion since the methyl/ethyl rearrangement ratio is $\sim 1.9$. The greater ability of the lesser-substituted alkyl group to migrate in isomerization of III parallels the behavior of the 2-substituted cyclopropylcarbenes described earlier. A similar circumstance (55) has been found in isomerization of 2,2,3-trimethylbutylidene

---

In that the ratio of methyl/isopropyl migration is 3/1. The apparent migration aptitudes of alkyl groups of tertiary alkylcarbenes are thus methyl > ethyl > isopropyl.

There are two principal explanations which may account for the greater migration of methyl than of ethyl groups in decomposition of 1-diazo-2,2-dimethylbutane. Steric effects, in which eclipsing interactions in the transition state favor methyl alignment with the vacant p-orbital of the carbene, could be controlling if the transition state is close to reactant (LIII is thus more favorable than is LIV). Another possibility is that hyperconjugative stabilization of the transition state, as previously discussed for cyclopropylcarbenes and as shown below (LV and LVI), is the major factor (transition state LV is thus better stabilized than is LVI).
It has thus been found that the patterns of intramolecular rearrangement of alkyl-substituted carbenes cannot be predicted or rationalized on the bases used to explain intermolecular processes. In the latter, carbenes react preferentially at the more highly substituted of two given centers. In the intramolecular processes presently reported, carbenic attack is favored at the lesser or least substituted carbon atoms and conformational and/or hyperconjugative effects appear to play important roles.

One effect not yet discussed nor previously observed in decomposition of sulfonylhydrazones is the marked increase in rearrangement when 6 equiv of sodium hydride were used (Table 10, no. 100 and 106). In order to rule out the possibility that 1-ethyl-1-methyl cyclopropane (L) and 1,1,2-trimethylcyclopropane (LI), the insertion products, were being isomerized to olefins by sodium hydride, a mixture of L and LI in diglyme was heated with sodium hydride under the conditions used for decomposition of the parent sulfonylhydrazone and found to give no olefins. A mixture of all seven products (XLV-LI) observed from
reorganization of III was similarly treated and did not undergo change. Thus the increased rearrangement when 2,2-dimethylbutanal tosylhydrazone is decomposed in six equiv of sodium hydride is not the result of base catalyzed rearrangement of the products but rather of based-induced alteration of the decomposition pathway. Such an effect has not been reported previously, and is in need of further investigation.

Decomposition of Salts of 2-Phenylpropanal Tosylhydrazone

Since the work presently described resulted in unexpected migration aptitudes for rearrangement of carbenes along with recognition of certain literature errors, rearrangement of 2-phenylpropylidene (IV) was restudied. Rearrangement of 2-phenylpropylidene (IV) is of interest in that in principal, measurement of hydrogen, methyl and phenyl migratory aptitudes can be made in one system. Previous investigation of decomposition of 2-phenylpropanal tosylhydrazone in the presence of sodium methoxide (46) as summarized in Table 11 indicated that IV rearranges to 3-phenyl-1-propene (LVII), 2-phenyl-1-propene (LVIII), cis-1-phenyl-1-propene (LIX), phenylcyclopropane (LX), and trans-1-phenyl-1-propene (LXI) (Equation 56). Allylbenzene (LVII) is of note in that if derived from a carbenic process, double rearrangement is involved. It has also been reported (56) that isopropylcarbene

(2-methylpropylidene), as generated by decomposition of 2-methylpropanal tosylhydrazone, yields only 2-methylpropene and methylcyclopropane,
products of α-hydrogen migration and β-C-H insertion respectively. Since methyl migration was not observed, migration of hydrogen occurs much more readily. Similarly it has been found (57) that 2-methyl-


propene (53.6%), methylcyclopropane (45.5%), trans-2-butene (0.5%) and cis-2-butene (0.3%) are obtained from thermal decomposition of isopropylidiazirene. These data for rearrangement of isopropylcarbene give a migration ratio for hydrogen/methyl of ~ 135/1. Thus, in 2-phenyl-propylidene (IV), rearrangement involving methyl migration is expected to be quite insignificant.

A phenyl/methyl migration aptitude of ~ 10/1 was obtained for thermal decomposition of 1-diazo-2-methyl-2-phenylpropane (8b) to 1-methyl-2-phenyl-2-propene (phenyl rearrangement), 1-methyl-1-phenyl-cyclopropane (β-H insertion), and 2-phenyl-2-butene (methyl rearrangement). 2,2-Diphenylethylidene rearranges only to 1,1-diphenylethylene,

\[
\begin{align*}
\text{CH}_3 & \quad \text{C}_6\text{H}_5-C-\text{CH}_3 \quad 60^\circ \quad (\text{CH}_3)_2\text{C} &= \text{CH}-\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5-\begin{array}{c}\text{CH=CH-CH}_3 \\
\text{C}_6\text{H}_5\end{array} \\
\text{CH}_3 & \quad 50\% \quad 41\% \quad 9\%
\end{align*}
\]

the product of hydrogen migration (46). Similarly, 2-diazo-1-phenyl-propane decomposes to cis (17%) and trans (69%)-1-phenyl-1-propenes and
3-phenyl-1-propene (14\%) (46), all products of hydrogen migration. Thus, migration aptitudes in these systems for the following groups are in the order: hydrogen > phenyl > methyl.

Decomposition of 2-phenylpropanal tosylhydrazone by sodium hydride, sodium methoxide, and lithium methoxide, respectively, was presently investigated in tetraethylene glycol dimethyl ether (tetraglyme, Ansul Ether 181). Contrary to the findings of the earlier study, no-3-phenyl-1-propene (LVII) was found (Table 11) under the conditions studied. The major product is 2-phenylpropene (LVIII) which arises from α-hydrogen migration. Phenylcyclopropane (LIX), the product of β-H insertion, is the next most abundant product. 1-Phenylpropene (cis and trans, LIX and LXI), arising from phenyl migration, accounts for less than 30\% of the total hydrocarbon products. The migration ratio for hydrogen/phenyl is thus ~ 1.5/1 (LVIII/LIX+LXI).

In order to assure that the product ratios measured arose from isomerization of IV and not from product re-isomerization under the reaction conditions, a standard mixture of the five hydrocarbon products (LVII-LXI) in tetraglyme was heated with sodium hydride to simulate average reaction conditions. The ratios of the five hydrocarbons remained unchanged after heating, within experimental error.

An additional study, in which 2,2-dimethylcyclopropyl methyl ketone tosylhydrazone was decomposed carbenically in the presence of 3-phenyl-1-propene (LVII), 2-phenylpropene (LVIII), cis-1-phenyl-1-propene (LIX), phenylcyclopropane (LX), and trans-1-phenyl-1-propene (LXI) (products of rearrangement of IV), showed that ~ 31\% of the 3-phenyl-1-propene (LVII) present was converted to trans-1-phenyl-1-propene.
TABLE 11

Decomposition of Salts of 2-Phenylpropanal Tosylhydrazone

<table>
<thead>
<tr>
<th>No.</th>
<th>T°</th>
<th>Base</th>
<th>Equiv of Base</th>
<th>( \text{C}_6\text{H}_5\text{CH}_2\text{CH} = \text{CH}_2 )</th>
<th>( \text{C}_6\text{H}_5\text{C} = \text{CH}_2 )</th>
<th>( \text{C}_6\text{H}_5\text{C} = \text{C} - \text{CH}_3 )</th>
<th>( \text{C}_6\text{H}_5\text{C} )</th>
<th>( \text{C}_6\text{H}_5\text{C} = \text{C} - \text{H} )</th>
<th>( \text{H} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>LVII</td>
<td>LVIII</td>
<td>LIX</td>
<td>LX</td>
<td>LXI</td>
<td>( \text{C}_6\text{H}_5 )</td>
</tr>
<tr>
<td>153</td>
<td>160</td>
<td>NaH</td>
<td>1.0</td>
<td>0%</td>
<td>38%</td>
<td>18%</td>
<td>33%</td>
<td>11%</td>
<td>1.3</td>
</tr>
<tr>
<td>154</td>
<td>160</td>
<td>NaH</td>
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<td>0</td>
<td>40</td>
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<td>31</td>
<td>11</td>
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<tr>
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<td>115</td>
<td>NaH</td>
<td>1.1</td>
<td>0</td>
<td>48</td>
<td>18</td>
<td>24</td>
<td>10</td>
<td>1.7</td>
</tr>
<tr>
<td>178</td>
<td>150</td>
<td>NaOCH₃</td>
<td>12</td>
<td>0</td>
<td>41</td>
<td>13</td>
<td>31</td>
<td>12</td>
<td>1.6</td>
</tr>
<tr>
<td>179</td>
<td>150</td>
<td>LiOCH₃</td>
<td>18</td>
<td>0</td>
<td>44</td>
<td>18</td>
<td>29</td>
<td>10</td>
<td>1.6</td>
</tr>
<tr>
<td>180</td>
<td>155</td>
<td>NaH</td>
<td>2.8</td>
<td>0</td>
<td>41</td>
<td>15</td>
<td>33</td>
<td>11</td>
<td>1.6</td>
</tr>
<tr>
<td>a</td>
<td>110-125</td>
<td>NaOCH₃</td>
<td>1.1</td>
<td>13</td>
<td>45</td>
<td>13</td>
<td>10</td>
<td>19</td>
<td>1.4</td>
</tr>
<tr>
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<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>a</td>
<td></td>
<td>n-BuLi</td>
<td>1.0</td>
<td>4</td>
<td>38</td>
<td>23</td>
<td>21</td>
<td>14</td>
<td>1.0</td>
</tr>
</tbody>
</table>

\( ^a \) Results reported by Kauffman (46) using diethyl carbitol as solvent.

\( ^b \) The solvent was tetraglyme for experiments no. 153-180.

\( ^c \) Not reported (46).
(LXI) under these conditions. Thus, if LVII were formed during rear-
grangement of 2-phenylpropylidene (IV), at least some of it would be
expected to be isomerized to trans-1-phenyl-1-propene. The total
absence of 3-phenyl-1-propene (LVII) from the product mixture obtained
by decomposition of 2-phenylpropanal tosylhydrazone suggests that LVII
was never formed. No other changes in hydrocarbon product ratios were
observed in these experiments.

The temperature dependence of the relative amounts of insertion
versus rearrangement is not as dramatic as that reported earlier for
reorganization of 2,2-dimethylbutylidene (III). The previously noted
trend, however, for greater rearrangement at lower temperatures, is
maintained in reaction of IV.

The most likely source of the 3-phenyl-1-propene (LVII) reported
by Keuffman (46) is from cationic decomposition of 1-diazo-2-phenyl-
propane (Equation 57). cis and trans-1-Phenyl-1-propenes (LIX and

\[
\begin{align*}
  \text{CH}_3 & \quad \text{CH}_3 \quad \text{CH}_3 \\
  \text{C}_6\text{H}_5 - \text{CH} - \text{CH}=\text{N}_2 & \quad \text{H} & \quad \text{C}_6\text{H}_5 - \text{CH} - \text{CH}_2 - \text{N}_2 & \quad \text{C}_6\text{H}_5 - \text{CH} - \text{CH}_2 & \\

\end{align*}
\]

LIX and LXI

\[
\begin{align*}
  \text{CH}_2=\text{CH} - \text{CH}_2 - \text{C}_6\text{H}_5 \quad \text{LVII} \quad \text{CH}_3 \quad \text{CH}_2-\text{C}_6\text{H}_5 - \text{CH} - \text{CH}_2

\end{align*}
\]
are also formed in this process. In the present work, the complete absence of LVII suggests that cationic processes have been successfully suppressed and the observed rearrangement products are derived carbenically. Use of only a slight excess of methoxide bases usually leads in part to carbonium ion processes in decomposition of arylsulfonylhydrazones due to the equivalent of methanol formed during neutralization of the sulfonylhydrazone. Cationic decomposition can be avoided by use of large excesses of base or of bases whose conjugate acid is effectively aprotic (hydrides).

Thus, the migration aptitudes observed in the study of rearrangement of 2-phenylpropylidene (IV) are hydrogen $>$ phenyl by a factor of $\sim 1.5$. This is unexpectedly low considering that 2,2-diphenylethyli-dene and 2-diazo-1-phenylpropane, as discussed earlier, give only products of hydrogen migration. 1-Phenylpropene (LIX and LXI) can be derived from methyl as well as phenyl migration in rearrangement of IV. Though unlikely, it is possible that methyl migration in this system is more significant than expected. The source of LIX and LXI in this work has been assumed to be from phenyl migration, but could be determined with greater certainty by studying the decomposition of 2-phenylpropanal-1-d tosylhydrazone (Equation 58). Phenyl migration (path a) will give 1-phenylpropene-1-d whereas methyl migration results in 1-phenylpropene-2-d; thus formation of 1-phenylpropene-2-d would mean that methyl does migrate, and is the cause of the low H/phenyl rearrangement ratio observed for 2-phenylpropylidene.
Preferred formation of cis-1-phenylpropene (LIX) rather than trans-1-phenylpropene (LXI) (Table 11) indicates that the geometry of the products of phenyl migration is not thermodynamically controlled. This phenomenon had been observed previously in rearrangement of 2,2-diarylpropylidenes (Equation 59) (7d). Bridged structures LXII and LXIII collapsing concertedly would lead to cis- and trans-2-phenylpropenes (LIX and LXI) respectively. If the filled orbital on C₁ aligns itself with the vacant one forming on C₂ as the phenyl group leaves, LXII will lead only to cis-1-phenylpropene (LIX) and LXIII...
exclusively to the trans isomer (LXI). The predominance of LXIX suggests that LXII is favored over LXIII and thus conformer LXIV, from which LXII is derived, is favored over conformer LXV, from which LXIII originates. Sterically then, the filled orbital on C₁ must have less effective volume than the proton on C₁ if it prefers to be near the 2-methyl group.

These arguments also apply to 2,2-diarylpropyliidenes which rearrange preferentially to cis rather than trans-stilbenes (7d). The phenyl group which does not migrate prefers to eclipse with the lone pair on C₁ rather than the proton on C₁.

 Totally aliphatic carbenes such as 2,2-dimethylbutyliidene (III) and 2,2,3-trimethylbutyliidene (LII) preferentially give the thermodynamically more stable trans-olefins on rearrangement. These results can be explained by conformational effects similar to those proposed for 2-phenylpropyliidene (IV) and 2,2-diarylpropyliidenes. However, for aliphatic carbenes, it is suggested that the transition state leading
to rearrangement reflects the structure of the parent diazo compound rather than a bridged intermediate involving steric effects of an electron pair. Thus conformer LXVII is favored over conformer LXVI because the larger alkyl group on C₂ prefers to be near hydrogen rather than departing nitrogen. It is presumed that conformer XLVI collapses to cis-olefins and conformer LXVII gives trans-olefins. It is thus proposed that the differences in migration pathways for phenyl versus methyl groups is a function of the nearness of the structure of the rearrangement process to that of initial reactant. Methyl migration is influenced by departing nitrogen whereas phenyl migration appears controlled by bridging processes after nitrogen has been expelled.
EXPERIMENTAL

General Procedures and Techniques

Melting Points

Melting points were determined in a Thomas-Hoover capillary melting-point apparatus. All melting points are uncorrected.

Boiling Points

Boiling points were recorded as the compounds distilled. Thermometer corrections were not made.

Elemental Analyses

Elemental analyses were performed by Micro-Analysis, Inc., Marshalltown, Wilmington, Delaware and by Chemalytics, Inc., Phoenix, Arizona.

Infrared Spectra

The infrared spectra of the compounds used and prepared in this research were obtained with a Perkin-Elmer Infracord recording infrared spectrophotometer. Spectra of solid compounds were recorded from pressed potassium bromide wafers while spectra of liquid compounds were obtained from liquid films between sodium chloride plates.

Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance spectra were obtained on Varian Associates spectrometers, Model A-60, Model A-60A, or Model HA-100.
Spectra were obtained from either neat compounds or solutions in carbon tetrachloride unless otherwise noted. Internal standards of either tetramethyldisilane or chloroform were used.

Gas Chromatography

Gas chromatography was used for product identification, determination of product composition, following the progress of a reaction, and separation and purification of products. The instruments employed include a Perkin-Elmer Gas Fractometer, Model 154C, equipped with a thermistor detector and connected to a 2.5 millivolt full-scale deflection Brown Electronik recorder; an Aerograph chromatograph, Model A-90-C, equipped with a hot-wire detector, connected to a 2.5 millivolt full-scale deflection Brown Electronik recorder; an Aerograph chromatograph, Model A-90-P, equipped with a hot-wire detector, connected to a 2.5 millivolt full-scale deflection Brown Electronik recorder; a Barber-Colman chromatograph, Series 5000, equipped with a hot-wire detector, connected to a one millivolt full-scale deflection Sargent, Model SR, recorder and equipped also with a hydrogen-flame ionization detector connected to either Sargent, Model SR, 1 millivolt or Brown Electronik, 2.5 millivolt, full-scale deflection recorders.

Unless noted, all gas chromatography was performed on the following packed columns: (A) 23% β,β'-oxydipropionitrile on 42/60 mesh firebrick, ½in x 5ft; (B) 35% propylene carbonate on 60/80 mesh firebrick, ½in x 5ft; (C) 20% SE-30 on 40/60 mesh Chromosorb P, ½in x 6ft.

The Barber-Colman, Model 5000, flame ionization detector unit was equipped with a capillary column. This column consisted of a 200 ft
x 0.03 in (I.D.) stainless steel tube coupled to a 100 ft x 0.02 in (I.D.) tube, both of which were coated by blowing a solution of squalane/hexdecane (2/1) in methylene chloride through it.

The carrier gas was helium except for the flame detector unit where nitrogen was employed.

Preparative Gas Chromatography

Preparative gas chromatography was sometimes used for separation and purification of liquid compounds prior to chemical and physical identification. Samples of up to 2 ml were separated and purified on either 1/4" or 3/8" outside diameter columns by injections of quantities varying from 10 to 250 microliters, depending on column size and peak separation. Samples were collected by manually attaching receivers to the detector exit while the respective peak was being recorded. For collecting low boiling materials, the receivers were cooled in a Dry Ice/isopropyl alcohol bath. For high boiling (> 140°) compounds, the receivers were cooled with ice water. Two types of receivers were used: (1) a coiled-tube collector (~ 2 ml) with a pear-shaped bottom, and (2) a U-tube (7 mm O.D.) with one end drawn to a taper to fit the detector exit.

Product Identification

Hydrocarbon products from the pyrolytic decompositions of salts of sulfonylhydrazones were generally identified by comparison of their gas chromatographic retention times to those of authentic samples. Usually, two different columns were used to verify the results. Furthermore, where practical, identification was confirmed by infrared
and nuclear magnetic resonance spectroscopic examination of collected samples.

**Product Composition**

Product compositions were determined using gas chromatographic peak areas (58). Where standards were available, calibration checks were made. In most cases, differences in thermal conductivity for the compounds involved were found to be within experimental error. Therefore, except as noted, corrections for variations in thermal conductivity were not made (59).


**Intermediates**

1,1-Dichloro-cis-2,3-dimethyl-2-vinylcyclopropane

**Method A:** A 250 ml flask equipped with a mechanical stirrer, thermometer, gas inlet, and rubber septum was flamed dry and purged with argon. Anhydrous tetrahydrofuran (60) (100 ml) and carbon tetrachloride

(60) Distilled from sodium immediately prior to use.
(13.5 g, 0.08 mole, Fisher Certified Reagent) were added to the flask and the mixture was cooled to -105° (61). n-Butyllithium in hexane

(61) The cooling bath was either a Genetron 11 (mp -110°) or methyl-cyclohexane (mp -126°) slush cooled by liquid nitrogen.

(54 ml, 0.09 mole, Foote Mineral Co.) was syringed in 30 min into the stirred reaction mixture maintained at -100°. The solution was then stirred for 3 hr at -100°, after which 3-methyl-1,trans-3-pentadiene (15 g, 0.09 mole, Chemical Samples Co.) was added slowly, and the mixture stirred for 1.5 hr at -100°. Upon removal of the cold bath, the temperature of the reaction mixture rose slowly; at -65°, an exotherm was observed and the solution turned from its milky color to black. When the mixture warmed to 0°, it was poured into iced water. The layers were separated and the aqueous phase was extracted thoroughly with diethyl ether. The combined ethereal layers were dried over anhydrous sodium sulfate and the solvent was partially removed by distillation at atmospheric pressure through a helix-packed column (10 x 1cm). Vacuum distillation of the remaining material gave about 10 ml (70%) of 1,1-dichloro-cis-2,3-dimethyl-2-vinylcyclopropane (bp 34°/3mm), whose nmr and ir spectra (62) and elemental analysis were consistent

(62) Nmr spectrum: vinyl proton (-CH=CH₂), 5.55-6.1 8 (quart), rel area 1 (centered at 5.78); vinyl protons (-CH=CH₂), 4.9-5.5 (m) rel area 2; methyl and cyclopropyl protons [-CH(CH₃)-O(CH₃) (-CH=CH₂)-], 1.1-1.75 (m), rel area ~ 7. Ir spectrum: terminal olefin bands, 1620 cm⁻¹ (d) and 920.
with the assigned structure. Subsequent attempts to repeat this reaction gave erratic yields (0-54%) of product.

**Anal.** Calcd for C$_7$H$_{10}$Cl$_2$: C, 50.93; H, 6.11

Found: C, 50.64; H, 5.87.

**Method B:** 3-Methyl-1,trans-3-pentadiene (1 equiv) and sodium trichloroacetate (63) (1 equiv, Dow Chemical Co.) in dry 1,2-dimethoxyethane (64) (diene/glyme = 1/10 by volume) was heated slowly to reflux.

(63) Dow 95% Sodium TCA was dried overnight in an oven at 94°C. Higher temperatures lead to scorching.

(64) Dimethoxyethane (glyme) was distilled from lithium aluminum hydride just prior to use.

After evolution of carbon dioxide ceased, additional sodium trichloroacetate (0.15 equiv) was added and refluxing was continued until gas evolution again ceased (65). Cold water was added to dissolve the precipitated sodium chloride and the mixture was extracted thoroughly with pentane. The organic portion was dried overnight over anhydrous sodium sulfate. Pentane and residual 1,2-dimethoxyethane were removed.

(65) Although some initial diene was still present at this point (glc on columns A and C), additional sodium trichloroacetate led to loss of product and an increase in the amount of a high-boiling product which appears to result from addition of dichlorocarbene to both double bonds of the diene.
either by distillation through a glass helix-packed column (10 cm) or on a rotary evaporator at 25-35° and reduced pressure. Fractional distillation of the remaining material at reduced pressure through a vacuum-jacketed helix-packed column (13 cm) gave 1,1-dichloro-cis-2,3-dimethyl-2-vinylcyclopropane (bp 80°/40 mm) in 44-66% yields. The ir (Figure 4) and nmr spectra are identical to that of the material prepared by Method A.

Method B is the more satisfactory route for this synthesis since it is less costly, less trouble, more reproducible and yields a product of greater purity than does Method A.

cis-1,2-Dimethyl-1-vinylcyclopropane

Ammonia (500-800 ml) was condensed into a 2-liter 3-neck flask equipped with a mechanical stirrer, thermometer, gas inlet, and a Dry Ice condenser. The system was kept under argon and cooled by a Dry Ice-isopropyl alcohol bath. Sodium (4.2 equiv) was then dissolved in the liquid ammonia. A 25% solution of 1,1-dichloro-cis-2,3-dimethyl-2-vinylcyclopropane (1 equiv) in diethyl ether was dropped into the well-stirred mixture of sodium in liquid ammonia. Immediately after addition was complete, solid ammonium chloride (4.5 equiv) was added slowly through Gooch tubing. Water was then added slowly to the mixture until its temperature reached 0°. The mixture was extracted thoroughly with pentane or with diethyl ether. The combined organic layers were dried over anhydrous sodium sulfate; solvents were removed by distillation through a Widmer column (15 in) and the residue was fractionated through a vacuum jacketed glass helix-packed column (13 cm).
The yields of pure cis-1,2-dimethyl-1-vinylcyclopropane (bp 87.5\(^\circ\)C/atm) ranged from 36-50%. The nmr spectrum (66) and elemental analysis are in agreement with the assigned structure. The ir spectrum (Figure 5) has bands at 1625 and 1445 cm\(^{-1}\) which are characteristic of terminal olefins.

**Anal. Calcd for C\(_7\)H\(_{12}\): C, 87.61; H, 12.48.**

**Found: C, 87.43; H, 12.58.**

**cis-1,2-Dimethylcyclopropanecarboxaldehyde**

**Method A:** In a typical run, cis-1,2-dimethyl-1-vinylcyclopropane (12.0 g, 0.12 mole) was dissolved in a solution of tetrahydrofuran (240 ml) and water (80 ml) containing osmium tetroxide (approximately 0.15 g, Mallinkrodt Reagent, 0.25-0.5 mole \%). Sodium meta-periodate (56 g, 0.25 mole, G. F. Smith Co.) was then added in 30 min. The mixture was stirred (3-6 hr) until the olefin could not be detected by glc (column A). A small amount of Celite was stirred into the mixture and the solution was vacuum filtered. The filter cake was washed thoroughly with ether. Aqueous sodium chloride was then added to the filtrate, and the layers were separated. The aqueous layer was extracted with diethyl ether; the organic portions were combined and then dried over anhydrous sodium sulfate. Distillation was accom-
plished in two stages. First, the volatile materials were distilled at increasingly lowered pressure into a receiver cooled by Dry Ice-isopropyl alcohol. Next, the solvents were removed at atmospheric pressure through a glass helix-packed column (10 cm) and the residue fractionated through a vacuum jacketed helix-packed column (13 cm). 

\textit{cis}-1,2-Dimethylcyclopropanecarboxaldehyde (bp $40^\circ/20$ mm; $132^\circ$/atm) was obtained in low yield. Its structure was confirmed by its ir and nmr spectra (67) and by the melting point and elemental analysis of its

(67) Ripoll and Conia (31) provide the following nmr and infrared data as well as the melting point of the 2,4-dinitrophenylhydrazone of \textit{cis}-1,2-dimethylcyclopropanecarboxaldehyde: nmr: aldehydic proton, 8.61 $\delta$ (s); other protons, two broad masses at 1.66 to 0.94 (centered at 1.19) and at 0.67 to 0.40 (centered at 0.53); ir: 3070 cm$^{-1}$ (w), 2965 (s), 2932 (s), 2876 (m), 2822 (m), 2720 (m), 1700 (vs), 1450 (s), 1390 (m), 1322 (m), 1275 (m), 1238 (m), 1171 (m), 1110 (m), 1078 (w), 1025 (m), 995 (w), 970 (s), 920 (w), 887 (s), 855 (s), 790 (w), 645 (w), 605 (w); mp (2,4-dinitrophenylhydrazone) 180-181$^\circ$.

\textbf{Anal.} Calcd. for C$_{12}$H$_{14}$O$_{4}$N$_{4}$: C, 51.75; H, 5.07; N, 20.18.

Found: C, 52.05; H, 5.04; N, 20.46.

**Method B:** Ozone from a Wellsbach ozone Generator was bubbled through a solution of \textit{cis}-1,2-dimethyl-1-vinylcyclopropane (18 g, 0.19 mole) and methanol (150 ml) in a gas washing bottle equipped with a coarse glass frit and cooled to $-78^\circ$ by a Dry Ice/actone bath. After 90 min, the solution turned blue and the ozone flow was discontinued. The bottle was flushed with oxygen until the blue color was discharged. The cold mixture was poured into a stirred solution of sodium iodide
(75 g) in glacial acetic acid (100 ml). Sodium thiosulfate was added until the brown solution cleared. Addition of water (75-100 ml) accelerated this step. The mixture was poured into 3-4 volumes of water and extracted many times with pentane. After drying the pentane solution over anhydrous sodium sulfate, the solvents were distilled off through a Widner column (15 in) and the residue was fractionated through a vacuum jacketed helix-packed column (13 cm) at atmospheric pressure to give cis-1,2-dimethylcyclopropanecarboxaldehyde (bp 67°/80 mm, 132°/atm) (11 g, 0.11 mole, 57%). This material was identical to that prepared by Method A.

Method B is vastly superior to A because the use of costly and highly toxic osmium tetroxide is avoided. Furthermore, Method B is faster, easier, and affords a purer product in higher yields.

1,1-Dichloro-trans-2,3-dimethyl-2-vinylcyclopropane

Dichlorocarbene was added to 3-methyl-1-trans-3-pentadiene (Chemical Samples Co.) by methods A and B (as previously described for preparation of the cis-dimethyl isomer) to give 1,1-dichloro-trans-2,3-dimethyl-2-vinylcyclopropane (bp 70°/25mm). The yield from method A was poor while that from method B ranged from 73-75%. The nmr spectrum of the vinylcyclopropane is in agreement with the assigned structure (68). The ir spectrum (Figure 6) has characteristic terminal

(68) Nmr spectrum: vinyl proton (-CH=CH2), 5.4-6.0 δ (quart), rel area 1 (centered at 5.67); vinyl protons (-CH=CH2), 4.9-6.0 (m), rel area 2 (centered at 5.23); methyl and cyclopropyl protons, [-CH(CH3)-C(CH3)(-CH=CH2)-], 1.0-1.8 (m), rel area 7.
olefin bands at 1625, 1440, and 915 cm\(^{-1}\).

**Anal.** Calcd for C\(_7\)H\(_{10}\)Cl\(_2\):  C, 50.93; H, 6.11.

**Found:** C, 50.90; H, 6.11.

**trans-1,2-Dimethyl-1-vinylcyclopropane**

1,1-Dichloro-trans-2,3-dimethyl-2-vinylcyclopropane was reduced by sodium in liquid ammonia by the procedure described for the cis-isomer, to give trans-1,2-dimethyl-1-vinylcyclopropane (bp 84°/atm) in 58-88% yield. The structure of trans-1,2-dimethyl-1-vinylcyclopropane was confirmed by its nmr spectrum (69) and by elemental analysis.

(69) Nmr spectrum: \(\alpha\)-vinyl proton (\(-\text{CH}=\)), 5.3-5.85 \(\delta\) (quart), rel area 1 (centered at 5.56); terminal vinyl protons (\(=\text{CH}_2\)), 4.7-5.1 (m), rel area 2 (centered at 4.98); methyl and ring protons \([-\text{CH}(\text{CH}_3)-\text{C}(\text{CH}_3)(\text{CH}=\text{CH}_2)-\text{CH}_2-\]), complex series of bands at 0.28-1.3, rel area 9.

**Anal.** Calcd for C\(_7\)H\(_{12}\):  C, 87.62; H, 12.38.

**Found:** C, 87.43; H, 12.58.

**trans-1,2-Dimethylcyclopropanecarboxaldehyde**

**trans-1,2-Dimethyl-1-vinylcyclopropane** was oxidized with sodium meta-periodate/osmium tetroxide, by the same procedure previously described for the cis-isomer (method A), to give trans-1,2-dimethylcyclopropanecarboxaldehyde (bp 112°/atm) in yields of 28-50%. The nmr and ir spectrum of the product match those reported in the literature (70) as does the mp of its 2,4-dinitrophenylhydrazone (mp 150-151°, lit. (31) 150-151°).
(70) Ripoll and Conia (31) give the following spectral data for trans-1,2-dimethylcyclopropanecarboxaldehyde; nmr: aldehydic proton; 9.21 δ (s); methyl and ring protons; 1.45 to 0.87 (complex mass) centered at 0.53; ir: 3075 (w), 3000 (m), 2963 (s), 2933 (s), 2880 (m), 2835 (w), 2730 (w), 2625 (w), 1682 (C=O)(vs), 1455 (s), 1380 (m), 1313 (s), 1250 (w), 1208 (s), 1166 (m), 1105 (w), 1075 (m), 1033 (w), 961 (m), 915 (w), 870 (s), 860 (s), 725 (w).

Anal. Calcd for C_{12}H_{14}O_{4}N_{4}:  C, 51.75; H, 5.07; N, 20.18.

Found: C, 51.60; H, 5.28; N, 19.87.

(2',2'-Dichloro-trans-3'-methylcyclopropyl)-trans-1-propene

Dichlorocarbene was added to trans,trans-2,4-hexadiene (Chemical Samples Co.) using the procedure described for synthesis of 1,1-dichloro-cis-2,3-dimethyl-2-vinylcyclopropane (Method B). (2',2'-Dichloro-trans-3'-methylcyclopropyl)-trans-1-propene (bp 65°/15mm) was obtained in 50-58% yield. The nmr spectrum of this material has a vinyl multiplet at 5.0-6.0 δ (rel area 1) and a complex series of bands for ring and methyl protons at 1.2-1.9 (rel area 4). Within these bands is a doublet (1.72 δ) which appears to be the 3-methyl (=CH-CH_{3}) protons. The ir spectrum (Figure 7) has characteristic absorptions at 1650 (C=O) and 969 (trans-C=C-) cm\(^{-1}\). These spectra and the elemental analysis are consistent with the structural assignment as (2',2'-dichloro-trans-3'-methylcyclopropyl)-trans-1-propene.

Anal. Calcd for C_{7}H_{10}Cl_{2}:  C, 50.93; H, 6.11

Found: C, 50.87; H, 6.11.
(trans-2'-Methylcyclopropyl)-trans-1-propene

Reduction of (2',2'-dichloro-trans-3'-methylcyclopropyl)-trans-1-propene with sodium in liquid ammonia (as described previously for the synthesis of 1,2-cis-dimethyl-1-vinylcyclopropane) gave (trans-2'-methylcyclopropyl)-trans-1-propene (bp 97°/atm) in 75-77% yield. Spectral data (71) and elemental analysis are in agreement with the proposed structure.

(71) For (trans-2'-methylcyclopropyl)-trans-1-propene: nmr; vinyl protons, 4.8-5.7 δ (m), rel area 2; 1-methyl protons (=CH-CH₃), 1.5-1.7 (d) centered at 1.68, rel area 3; ring and ring-methyl protons, 0.2-1.3 (m), rel area 7; ir; 1680 cm⁻¹ (C=C), 962 (trans-C=C-) (Figure 8).

Found: C, 87.43; H, 12.58.

trans-2-Methylcyclopropanecarboxaldehyde

(trans-2'-Methylcyclopropyl)-trans-1-propene was ozonized by the general method described for synthesis of cis-1,2-dimethylcyclopropane-carboxaldehyde. Use of chloroform instead of pentane facilitated extraction of the aldehyde from the alcohol-water-acetic acid mixture. The chloroform solution was dried over anhydrous sodium sulfate. Solvents were removed through a vacuum-jacketed helix-packed column (13 cm) at atmospheric pressure and the residue was fractionated.

trans-2-Methylcyclopropanecarboxaldehyde (bp 114°/atm) was obtained in 42-62% yield and its structure was confirmed by spectral data (72).
(72) Nmr: aldehyde proton, 9.10 δ (d); methyl and ring protons, 0.66-1.76 (m) centered at 1.22. Ir: aldehyde bands, 2860, 2730 cm⁻¹; carbonyl band, 1710.

(Figures 1 and 9) and by elemental analysis of its 2,4-dinitrophenylhydrazone (mp 163-164°) and 2,4,5-trichlorobenzenesulfonylhydrazone derivatives (mp 97.5-98°).

     Found: N, 21.69.

     Found: C, 38.43; H, 3.22; N, 8.16.

2-(trans-2'-(Methylcyclopropyl)-1,3-dithiane

trans-2-Methylcyclopropanecarboxaldehyde (12 g, 0.14 mole) was dissolved in chloroform (150 ml) along with one equiv of 1,3-propane-dithiol (15.6 g, 0.14 mole, Aldrich Chemical Co.). Dry hydrogen chloride was bubbled into the mixture through a fritted gas-dispersion tube until the solution was saturated (~ 5 min) (38). The mixture was magnetically stirred for 30 min after which the system was purged with argon to remove excess hydrogen chloride. The solution was then washed with water (2 x 50 ml), 10% aqueous potassium hydroxide (2 x 70 ml), and water (50 ml). After the mixture had been filtered through anhydrous sodium sulfate, the solvents were removed on a rotary evaporator until the flask weight remained constant. The yellow oil (24.3 g) represents a 98% conversion to 2-(trans-2'-methylcyclopropyl)-1,3-dithiane (73). This compound was used for preparation of 2-(trans-2'-
The nmr spectrum of the product (Figure 10) has bands at 3.63 δ (d) (S-CH-S), rel area 1; 2.90 (m) (-S-CH2-CH2-CH2-S), rel area 4; 2.07 (m) (-CH2-CH2-CH2), rel area ~ 2; 1.05 (d), rel area ~ 3; 0.67 (m), rel area ~ 4; which is consistent for 2-(trans-2'-methylcyclopropyl)-1,3-dithiane. The ir spectrum exhibited a characteristic band at 912 cm\(^{-1}\) (dithiane) (38) (Figure 11).

methylicyclopropyl)-1,3-dithiane-2-d without further purification.

2-(trans-2'-Methylcyclopropyl)-1,3-dithiane-2-d

A hexane (170 ml) -ether (30 ml) solution containing crude 2-(trans-2'-methylcyclopropyl)-1,3-dithiane (22 g, 0.125 mole) was cooled to -55°. t-Butyllithium in hexane (150 ml, 0.15 mole) was added in 20 min at below -45°. Stirring was continued for 8.5 hr at -60 to -70°; the temperature was then raised to -35°. Deuterium oxide (17 g, 0.95 mole) was added and the temperature permitted to rise. At -10°, the milky yellow solution cleared as a mild exotherm was observed. After having been washed with dilute hydrochloric acid, aqueous sodium bicarbonate (5%), and saturated sodium chloride solution, the organic material was dried over anhydrous sodium sulfate, filtered, and the solvents evaporated until the flask weight remained constant. The nmr spectrum of the residual oil (Figure 10) shows no peak in the 3.5-3.7 δ area (the region where H\(_2\) appears in the non-deuterated compound), indicating essentially complete deuterium incorporation. The signals at 2.90, 2.07, and 1.05 δ are identical in shift, splitting, and relative area to those of the non-deuterated dithiane, while the multiplet at 0.67 δ, in the deuterated material, is less complex than in the non-deuterated dithiane presumably because the H\(_1\)' is no longer split.
by H₂. The fact that the deuterated and non-deuterated dithianes have identical spectra, save those differences expected by the introduction of deuterium at C₂, indicates that the cyclopropyl ring remained intact during the deuterium replacement reaction. Unlike other 1,3-dithianes (38,74), n-butyllithium was not strong enough to remove the proton.

\[\text{(H₂) on C₂ of the present system at } -50°. \text{ The ir spectrum of the deuterated compound (Figure 12) was similar to that of the non-deuterated dithiane (Figure 11) except that new bands occur at 2140 (weak; C-D stretch) and 938 cm}^{-1}, \text{ and the 912 (dithiane) band was shifted to 908 cm}^{-1}.\]

**trans-2-Methylcyclopropanecarboxaldehyde-α-d**

2-(trans-2'-Methylcyclopropyl)-1,3-dithiane-2-d (20 g, 0.15 mole), dissolved in acetone (200 ml) and benzene (100 ml), was added to a stirred slurry of mercuric chloride (140 g, approx 5 equiv) and cadmium carbonate (50 g, 4.5 equiv) in acetone (150 ml) and water (13 ml). After stirring for 2 hr at room temperature, the mixture was heated to 40° for 15 min (75). The mixture was vacuum filtered and the solids

\[(75) \text{ This step proved unnecessary as the yield, as followed by glc (Column C), was not observed to increase.}\]
washed with acetone. The volatile components of the filtrate were
crudely distilled (50-2 mm) into Dry Ice traps. The solvents were then
removed by distillation through a vacuum-jacketed column (13 cm) packed
with Helipak (76). trans-2-Methylcyclopropanecarboxaldehyde-a-d

(76) Podbielniak Inc., Box 42, 203 Gateway Rd., Bensonville, Ill.

(~ 5 g, 0.059 mole; bp 114°/atm) was recovered in 39% yield. The nmr
spectrum (Figure 1) was identical to that of the non-deuterated alde­
hyde except for the disappearance of the aldehyde proton peak (Hα) at
9.10 δ. The infrared spectrum (Figure 13) is similar to that of the
undeuterated aldehyde (Figure 9) but shows a new band at 2070 cm⁻¹
(Strong, C-D) while the characteristic aldehyde doublet in the 2700-
2900 region is absent. The carbonyl band has been shifted from 1710
to 1695 cm⁻¹ by introduction of the deuterium. Elemental analysis of
the 2,4-dinitrophenylhydrazone of trans-2-methylcyclopropanecarbox­
aldehyde-a-d was slightly off, due to insufficient sample. However
analysis of the 2,4,6-trichlorobenzensulfonylhydrazone, described
later, was correct.


Found: C, 49.30; H (D), 4.59; N, 21.27.

2,2-Dimethylcyclopropyl Methyl Ketone

2,2-Dimethylcyclopropyl methyl ketone (bp 132°/atm) was prepared
in 74% yield essentially as described previously (2) from mesityl oxide
and dimethyloxosulfonium methyld. An important modification of the
previous procedure involves stirring the reaction mixture first for 1.5 hr at room temperature, and then heating to 60°, and allowing the solution to cool. The reaction time is shortened by 3 hr, and the yield is increased by 50%.

trans-α,2-Dimethylcyclopropylmethanol

trans-α,2-Dimethylcyclopropylmethanol was prepared by a modified version of the literature method (2). Methylene iodide (1 g) was added to a stirred slurry of anhydrous ether (100 ml) and zinc-copper couple (2). The mixture was then heated until refluxing initiated.

(77) The preparation of zinc-copper couple described by E. Legoff, J. Org. Chem., 29, 2048 (1964) has been modified as follows: 3 to 4 equivalents of zinc (30 mesh granular) per mole of methylene iodide and 1.5-2 g of cuprous acetate monhydrate per mole of zinc are used.

Heating was discontinued, and the remaining methylene iodide (33 ml, 113 g, 0.42 mole total), along with trans-3-pentene-2-ol (17.2 g, 0.2 mole; Chemical Samples Co.) in anhydrous diethyl ether (25 ml) was added dropwise in 0.5 hour during which vigorous, self-sustaining reflux was observed. The mixture was heated for 2 hr and filtered through glass wool into an ice-filled separatory funnel. The ether solution was washed with 20% hydrochloric acid, saturated sodium bicarbonate solution and saturated sodium chloride solution, then dried over anhydrous sodium sulfate and potassium carbonate. Ether was removed by distillation through a helix-packed column (11 cm) and the residue fractionated through a vacuum-jacketed helix-packed column
trans-α,2-dimethylcyclopropanemethanol (bp 73-74°/68mm; lit. (2) 75-80°/80mm) (12.5 g, 0.125 mole, 60%). This material was used without further purification to prepare methyl trans-2-methylcyclopropyl ketone. The nmr spectrum of this cyclopropyl alcohol differed slightly from that reported by Smith (78): the

(78) Smith (2) reports the following spectral data for α,2-dimethylcyclopropylmethanol: nmr; hydroxylic proton, 3.60 δ (s); 0.1-1.3 (complex series of bands); ir; 3.00 μ (-OH), 9.70 μ (cyclopropane), and 11.54 μ (cyclopropane).

hydroxyl proton (s, rel area 1) appeared at 4.4 δ; the α-methyl protons (d, rel area ~ 3) centered at 1.18, the 2-methyl protons (d, rel area ~ 3) centered at 1.0; and the ring protons (2 m, rel area 4) fell between 1.0 and 0.68. The difference in shift for the hydroxyl proton is probably due to solvent or concentration effects. The ir spectra were essentially the same.

Methyl trans-2-Methylcyclopropyl Ketone

A modified version of the literature method (2) was used to prepare methyl trans-2-methylcyclopropyl ketone. Crude trans-α,2-dimethylcyclopropylmethanol (12.5 g, ~ 0.12 mole) in acetone (60 ml) was placed in a 250 ml flask, equipped with a mechanical stirrer, thermometer and addition funnel, and cooled to 0°. Cold (0-5°) chromium trioxide solution [prepared by slowly adding sulfuric acid (7.3 ml, 0.13 mole, 96%) to a solution of chromium trioxide (8.4 g, 0.84 mole) in water (12 ml at 0°), and diluting with additional water (24 ml)] was added dropwise, with rapid stirring, to the mixture maintained at 20°. Stirring was
continued for 3 additional hr, keeping the temperature at 20°. Sodium bisulfate was added until the top layer of the reaction mixture lost its brown-green color. The layers were separated and the aqueous (lower) layer extracted with diethyl ether. Upon combining the ether extracts with the organic phase separated earlier, additional water separated. The aqueous portions were combined and again extracted with ether. The ether was then added to the other organic layers and the combined solution washed with saturated sodium chloride (2 x 50 ml), saturated aqueous sodium bisulfate (2 x 50 ml), and again with saturated sodium chloride. After drying the solution over anhydrous magnesium sulfate, the solvents were removed by distillation at atmospheric pressure. Fractionation of the remaining material gave pure methyl trans-2-methylcyclopropyl ketone [bp 58-60°/63mm; lit. (2) 66-80°/78mm] (6.5 g, ~ 60%), along with additional impure material. The nmr and ir spectra of the product are identical to those reported previously (79).

(79) Smith (2) reports the following spectral data for methyl trans-2-methylcyclopropyl ketone: nmr; methyl ketone, 2.13 δ (s); tert-cyclopropyl hydrogen, 0.58 (m); other ring and methyl protons, 1.0-2.1 (series of complex bands); ir; 5.91 μ (C=O); 9.65 (cyclopropyl ring); and 11.68 μ (cyclopropyl ring).

3-Pentene-2-ol-2-d

3-Pentene-2-one of unspecified geometry (7.7 g, 0.094 mole, tech grade, Aldrich Chemical Co.) [presently distilled prior to use (bp 120-122°/atm) and found to be 85-90% pure by glc] in diethyl ether (10 ml) was added slowly to a stirred slurry of lithium aluminum deuteride (0.93 g, 0.022 mole, Ventron Corp) in diethyl ether (40 ml)
cooled by a Dry Ice/isopropyl alcohol bath. The solution was subse­quent­ly refluxed for 30 min after which water was added. The result­ing gelatinous precipitate was dissolved by addition of hydrochloric acid (3N). The mixture was extracted thoroughly with diethyl ether and the ethereal solution was dried over a mixture of anhydrous magnesium sulfate and potassium carbonate. Distillation of the ether solution gave impure 3-pentene-2-ol-2-d (~ 6 ml). The deuterio alcohol was identified by comparison of its nmr spectrum (Figure 14) with that of non-deuterated 3-pentene-2-ol (Chemical Samples Co.). The deuterated alcohol lacks a signal at 4.17 δ, the assignment for H2 in 3-pentene-2-ol and the methyl doublet at 1.18 δ, observed in the spectrum of 3-pentene-2-ol, appears as a singlet in the deuterated alcohol. The deuterated alcohol was used without further purification.

1,3-Pentadiene-2-d and 4-d

Crude 3-pentene-2-ol-2-d (2.5 ml) was placed in a flask equipped with a Vigreaux Column (6 in) and a gas inlet tube. The Vigreaux column was connected to a trap cooled by Dry Ice/isopropyl alcohol. The 3-pentene-2-ol-2-d was cooled and 6 microdrops of concentrated sulfuric acid was added. While argon was being bubbled slowly (~ 6 ml/min) through the system, the flask was immersed into an oil bath at 50°. The temperature of the bath was raised to 90° over a 4 hr period and approximately 0.5 ml of a mixture of 1,3-pentadiene-2-d and 4-d was collected in the trap. Preparative gas chromatography of 0.1 ml of impure 1,3-pentadiene-2-d and 4-d mixture (6 ft x ¼ in column of 45% propylene carbonate on firebrick) in which the diene was trapped
in cold tetrachloroethylene gave a suitable nmr sample. The glc retention time of the deuterated 1,3-pentadienes was identical to that of authentic trans-1,3-pentadiene (Chemical Samples Co.), and therefore the deuterated dienes are assigned a trans-configuration.

The nmr spectrum (Figure 15) of the products shows it to be a mixture of 1,3-pentadiene-2-d and 1,3-pentadiene-4-d. This conclusion is drawn from the fact that the C-5 methyl group in trans-1,3-pentadiene (Figure 15) appears as a doublet (1.72 δ) in the nmr spectrum and would be expected to be a doublet in the 2-d isomer. However, the

\[
\begin{align*}
\text{CH}_3 - CH = CH - CD - CH_2 \\
\text{nmr: CH}_3 = \text{doublet}
\end{align*}
\]

4-d isomer is expected to give a singlet for the C-5 methyl group.

The observed spectrum for the product of dehydration of 3-pentene-2-ol-2-d has a triplet at \(\sim 1.72 \delta\) (the C-5 methyl shift in 1,3-pentadiene) which is believed to be a combination of the C-5 methyl doublet from 1,3-pentadiene-2-d and the C-5 methyl singlet from 1,3-pentadiene-4-d. A mixture of both isomers is thus concluded to have been formed.

**Product Standards**

**Preparation of Cyclobutenes by Photolysis of Dienes**

Dienes were photolyzed in a quartz tube (1 in x 18 in) fitted with a ground glass stopper which held a rubber septum. The joint was sealed
with a Teflon sleeve and clamped together to withstand the buildup of internal pressure. The dienes were photolyzed for 3-10 days as magnetically stirred 3-5% ethereal or diglyme solutions. The reactions were monitored by glc (Columbus A or B) and then discontinued when there was no initial material left.

The light source was a bank of 16 low pressure mercury lamps (General Electric G25T8, 25 watts) mounted parallel inside an aluminum drum (13 in) (80). These lamps provide most of their ultraviolet output at 2537 Å.

1,3-Dimethylcyclobutene

A solution of 2-methyl-1,3-pentadiene (5 g, Chemical Samples Co.) in ether (150 ml), on photolysis by the above procedure, gave 1,3-dimethylcyclobutene (27). Preparative glc on a column (3/8 in x 8 ft) packed with 23% ODPN on firebrick gave a sample whose nmr spectrum is consistent with that reported for 1,3-dimethylcyclobutene (81).

(81) Ripoll and Conia (31) report the nmr spectra of both 1,3- and 1,4-dimethylcyclobutene. 1,4-Dimethylcyclobutene; methyl protons: (-CH-CH3) 1.10 δ (d)(J:7cps); (=C-CH3) 1.62 (m); ring protons: (-CH2-CH-) (2m) centered at 2.60 and 1.90; vinylic proton: 5.59 (m). Nmr for 1,3-dimethylcyclobutene: protons for CH3: (-CH-CH3) 1.09 δ (d)(J:7cps); (=C-CH3) 1.66 (m); ring protons: (-CH2-CH-) (2m) centered at 2.69 and 1.93; vinylic proton: 5.71 (m).
1,4-Dimethylcyclobutene

3-Methyl-1,1-trans-3-pentadiene (Chemical Samples Co.) was photolyzed by the previous procedure. The product, isolated by glc, had a nmr spectrum identical to the reported spectrum for 1,4-dimethylcyclobutene (81).

1,3,3-Trimethylcyclobutene

Photolysis of 2,4-dimethyl-1,3-pentadiene (Chemical Samples Co.) gave one major product which was assumed to be 1,3,3-trimethylcyclobutene. This assumption is supported by the fact that its glc retention time was identical to that of the major product of the rearrangement of 2,2-dimethylcyclopropylmethylycarbene, which has already been identified (2).

3-Methylcyclobutene

A solution of 1,3-pentadiene (4 ml) in diglyme (90 ml) was photolyzed for 4 days. Two product peaks were observed upon glc on column B. By using more photolysis solution, that is, filling the quartz tube further, conversion to one of the products was reduced significantly; the major component isolated and identified was 3-methylcyclobutene as reported (42). Use of diglyme as a photolysis solvent allowed easy distillation of the highly volatile products. No nmr data for 3-methylcyclobutene has been reported (42) but the nmr spectrum obtained here is consistent with the assigned structure (82). The extra product

(82) Nmr: (60 MHz) Methyl protons, 1.15 (d); methine and methylene protons [-CH(CH₃)-CH₂-], 2.0-2.9 (complex m); vinylic protons (-CH=CH-), 5.96 (broad s); Figure 16.
observed when the quartz tube was unfilled probably is the result of gas phase photolysis in the space above the solutions. Photochemical cyclization of dienes is generally confined to condensed stages and is rarely observed in the gas phase (42). The 3-methylcyclobutene produced photochemically was shown, by nmr spectroscopy, to be identical to the major product of the carbenic decomposition of trans-2-methylcyclopropanecarboxaldehyde 2,4,5-trichlorobenzenesulfonylhydrazone.

3-Methylcyclobutene-1-d and 3-d

A mixture of 1,3-pentadiene-2-d and 4-d (~0.35 ml) was preparatively gas chromatographed directly into cold diglyme (12 ml) (~ -60°) and photolyzed in a quartz tube (83) for 39 hr in the apparatus described earlier. The photolysis solution was preparatively gas chromatographed (12 ft x ½ in column of 20% tris-(cyanethoxy)propane on firebrick) and the cyclobutenes scrubbed from the effluent gas by cold tetrachloroethylene. A dilute nmr sample of the 3-methylcyclobutene-1-d and 3-d in tetrachloroethylene was thus obtained. The 60 MHz nmr spectrum of the cyclobutene mixture was quite similar to that reported earlier for 3-methylcyclobutene (84). Examination of the

Nmr spectrum (60 MHz) of the mixture of 3-methylcyclobutene-1-d and 3-d revealed the following: methyl protons (CH₃), ~1.178 (t); allylic protons (-CH₂-CH<), 1.7-2.1 (m series); vinyl protons [-CH=CH(D)=], 6.02 δ s.
vinylic proton signal of the cyclobutene mixture by 100 MHz nmr (Figure 17) gave a spectrum which results from superimposition of the $H_2$ singlet ($\sim 6.03 \delta$) of 3-methylcyclobutene-1-d on top of the A3 quartet from $H_1$ and $H_2$ of 3-methylcyclobutene-3-d. The fact that the $H_2$ signal

\[
\begin{align*}
&\text{CH}_3 &\text{H}_2 \\
&\text{D} & \\
\text{major} & \\
\text{XXXIX} \\
&\text{CH}_3 &\text{D} \\
&\text{H}_1 & \\
\text{XXIV} & \\
\end{align*}
\]

\[
\begin{align*}
&\text{CH}_3 &\text{H}_2 \\
&\text{H}_1 & \\
\text{XL} &
\end{align*}
\]

\[
\begin{align*}
&\text{CH}_3 &\text{H}_2 \\
&\text{D} & \\
\text{XXXIX} & \\
&\text{CH}_3 &\text{H}_2 \\
&\text{D} & \\
\end{align*}
\]

\[
\begin{align*}
\text{e.00} & 5.94 \delta \text{ (in CCl}_4) \\
\text{(see Figure 3)}
\end{align*}
\]

\[
\begin{align*}
\text{e.0} & 5.94 \delta \text{ (in CCl}_4) \\
\text{(see Figure 2)}
\end{align*}
\]

\[
\begin{align*}
\text{e.03} & 5.97 \delta \text{ (in Cl}_2\text{C=CCl}_2} \\
\text{(see Figure 17)}
\end{align*}
\]

from 3-methylcyclobutene is at the lower field position of the two vinylic protons confirms that the major product of decomposition of trans-2-methylcyclopropanecarboxaldehyde 2,4,5-trichlorobenzenesulfonylhydrazone is 3-methylcyclobutene-1-d.
1-Methyl-1-ethylcyclopropane (85)


Methylene iodide (1 ml) was added to a slurry of zinc-copper (72 g, 1.1 mole) (77) in anhydrous ether (50 ml) and the mixture was gently heated and stirred. Additional methylene iodide (93 g, 28.3 ml, 0.35 mole total) was mixed with 2-methyl-1-butene (20 g, 0.285 mole, Chemical Samples Co.) and anhydrous diethyl ether (75 ml), and the solution was added in 45 min to the zinc-copper-methylene iodide system. After the mixture had been refluxed for 3 hr, additional methylene iodide (4 ml, 13 g) was added and refluxing was continued for another 3 hr. At this point, glc (column A) of the reaction mixture showed that only traces of 2-methyl-1-butene remained. The ether solution was poured into a dilute mixture of hydrochloric acid in ice. The ether layer was washed with dilute sodium hydroxide solution and with saturated sodium chloride solution, and then dried over anhydrous sodium sulfate. The ethereal solution was distilled through a jacketed column (30 cm) packed with Helipak (76) to give 1-methyl-ethylcyclopropane [bp 56-57°, lit. (86), 56.8°; n_D^20 1.3896, lit. 1.3888 (86)].

Arylsulfonylhydrazones

trans-2-Methylcyclopropanecarboxaldehyde 2,4,5-Trichlorobenzenesulfonylhydrazone

trans-2-Methylcyclopropanecarboxaldehyde (1.0 g, 0.012 mole) was added dropwise to a stirred suspension of 2,4,5-trichlorobenzenesulfonylhydrazide (3.25 g, 0.012 mole, Aldrich Chemical Co.) in absolute ethanol (15-25 ml). After 15 min of additional stirring a white crystalline solid (~0.5 g) was filtered from the solution (87). The combined filtrate and washings (~75 ml) was stirred while water (~50 ml) was added slowly. Clouding occurred and the solution was stripped slowly on a rotary evaporatory at room temperature to a volume of ~25 ml. The concentrate was filtered and the crystals (2.5 g) washed with ethanol. Further stripping of the filtrate gave additional product (~0.5 g). trans-2-Methylcyclopropanecarboxaldehyde 2,4,5-trichlorobenzenesulfonylhydrazone (mp 95.5-96° with decomposition) (3.0 g, 0.0086 mole, 72%) was identified by its infrared spectrum [bands at 1170 cm\(^{-1}\) (-SO\(_2\)-), 1320 (-SO\(_2\)-NH-) and 3250 (N-H)] and elemental analysis.

Anal. Calcd for C\(_{11}\)H\(_{11}\)N\(_2\)O\(_2\)Cl\(_3\): C, 38.65; H, 3.22; N, 8.20.

Found: C, 38.43; H, 3.22; N, 8.16.
trans-2-Methylcyclopropanecarboxaldehyde-α-d 2,4,5-Trichlorobenzene-
sulfonylhydrazone

trans-2-Methylcyclopropanecarboxaldehyde-α-d 2,4,5-trichloro-
benzenesulfonylhydrazone was prepared from trans-2-methylcyclopropane-
carboxaldehyde-α-d by the method described for the non-deuterated
compound. Two crops of crystalline hydrazone were recovered (crop 1,
4.5 g, mp 95-95.5°; crop 2, 1.2 g, mp 92-93.5°; total yield, 0.0164
mole, 68%). trans-2-Methylcyclopropanecarboxaldehyde 2,4,5-trichloro-
benzenesulfonylhydrazone has ir bands at 5270 (-\text{C-H}), 1345 (-\text{SO}_2\text{NH}-),
and 1165 cm\(^{-1}\) (-\text{SO}_2\text{-}) and its elemental analysis is consistent with
its structure.

Anal. Calcd for C\(_{11}\)H\(_{10}\)Cl\(_3\)N\(_2\)O\(_2\)S\(_2\): C, 38.55; H (D), 3.24; N, 8.18.
Found: C, 38.51; H (D), 3.16; N, 8.28.

Methyl trans-2-Methylcyclopropyl Ketone 2,4,5-Trichlorobenzenesulfonyl-
hydrazone

Because methyl trans-2-methylcyclopropyl ketone tosylhydrazone is
difficult to crystallize (2), the 2,4,5-trichlorobenzenesulfonylhydrada-
zone was prepared instead. 2,4,5-Trichlorobenzenesulfonylhydrazide
(5.3 g, 0.019 mole) was added to a stirred solution of methyl trans-2-
methylcyclopropyl ketone (2.0 g, 0.020 mole) in methanol (30 ml).
After stirring for 0.5 hr, the solution was filtered and methanol was
slowly removed on a rotary evaporator. Two crops of crystals were ob-
tained; the first was discolored and was recrystallized from ethanol;
the second was used without further purification. Methyl trans-2-
methylcyclopropyl ketone 2,4,5-trichlorobenzenesulfonylhydrazone (mp
131.5-133°) was obtained (4.3 g, 0.012 mole) in 63% yield.

**Anal.** Calcd for C_{12}H_{13}N_{2}S_{2}O_{3}Cl\_3:  C, 40.51; H, 3.66; N, 7.88.

Found:  C, 40.04; H, 3.50; N, 8.13.

2,2-Dimethylcyclopropyl Methyl Ketone Tosylhydrazone

Tosylhydrazide (9.5 g, 0.05 mole) was dissolved in warm absolute methanol (20 ml). 2,2-Dimethylcyclopropyl methyl ketone (5.8 g, 0.051 mole) was added and the mixture was stirred without further heating for 15 min. Refrigeration overnight gave 2,2-dimethylcyclopropyl methyl ketone tosylhydrazone as flocculant white crystals [mp 125-126°, lit. (2), 129-131°] (12.0 g, 85%).

2,2-Dimethylcyclopropyl Methyl Ketone 2,4,5-Trichlorobenzenesulfonylhydrazone

2,4,5-Trichlorobenzenesulfonylhydrazide (2.4 g, 0.088 mole) was added to a solution of 2,2-dimethylcyclopropyl methyl ketone (1.0 g, 0.09 mole) in absolute methanol (30 ml). After stirring for several hours, the solution was filtered, the solvent volume reduced, and crystalline 2,2-dimethylcyclopropyl methyl ketone 2,4,5-trichlorobenzenesulfonylhydrazone (1.45 g, 42%, mp 163-166°) was obtained. The ir bands (3190 cm\(^{-1}\), N-H; 1130, -SO\(_2\)-NH-; 1170, -SO\(_2\)-) confirm the structure.

**cis-1,2-Dimethylcyclopropanecarboxaldehyde 2,4,6-Triisopropylbenzenesulfonylhydrazone (88)**

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(88) The 2,4,6-triisopropylbenzenesulfonyl group has been named "monostroysyl" for convenience (40).
cis-1,2-Dimethylcyclopropanecarboxaldehyde (0.18 g, 0.0018 mole) was added to a stirred solution of monstrosyl hydrazide (0.5 g, 0.019 mole) [prepared by the literature method (40)] in methanol. Refrigeration overnight resulted in the formation of white needles. After 2 hr in a freezer, the solution was filtered. The crystals were washed with cold petroleum ether and dried in a vacuum desiccator. The solvents on removal by rotary evaporation, left a white solid residue (mp 145-145.5°). The ir spectrum [3300 (NH); 1320 (-SO₂-NH-); 1170 cm⁻¹ (-SO₂)] of this material is consistent with cis-1,2-dimethylcyclopropanecarboxaldehyde monstrosylhydrazone.

trans-1,2-Dimethylcyclopropanecarboxaldehyde 2,4,5-Trichlorobenzene-sulfonylhydrazone

trans-1,2-Dimethylcyclopropanecarboxaldehyde (3.7 g, 0.037 mole) methanol (10 ml) was added dropwise to a stirred solution of 2,4,5-trichlorobenzenesulfonylhydrazide (9.8 g, 0.036 mole) in methanol/ethyl acetate (50/50, 200 ml). The mixture became cloudy and was refrigerated overnight. Filtration gave the unknown material (0.65 g) invariably recovered from 2,4,5-trichlorobenzenesulfonylhydrazone preparations (87). The filtrate was concentrated on a rotary evaporator at room temperature to give white crystals (6.41 g, mp 148.5-149.5°) which were filtered and dried in a vacuum desiccator. Further concentration gave an additional 1.4 g of trans-1,2-dimethylcyclopropanecarboxaldehyde 2,4,5-trichlorobenzenesulfonylhydrazone. The total yield of derivative was 61%.

Anal. Calcd for C₁₂H₁₃N₂O₂Cl₃S: C, 40.51; H, 3.66; N, 7.88.

Found: C, 40.61; H, 4.01; N, 8.28.
cis-1,2-Dimethylcyclopropanecarboxaldehyde 2,4,5-Trichlorobenzene-sulfonylhydrazone

A solution of cis-1,2-dimethylcyclopropanecarboxaldehyde (1 g, 0.01 mole) in methanol (5 ml) was added dropwise to 2,4,5-trichlorobenzenesulfonylhydrazide (2.5 g, 0.9 mole) and was stirred at room temperature for 1 hr. Magnesium sulfate (~0.5 g) was added and the mixture stirred for 15 min. This slurry was filtered and the solvent removed by rotary evaporation until a white paste remained. This paste, on refrigeration overnight, crystallized. The moist cis-1,2-dimethylcyclopropanecarboxaldehyde 2,4,5-trichlorobenzenesulfonylhydrazone crystals were then placed overnight in a freezer, pressed dry on filter paper, and dried under vacuum (2 mm Hg) at room temperature for 18 hr. This hydrazone (mp 91-95°) was used without further purification. An analytical sample was obtained by recrystallization of a small quantity of the sulfonylhydrazone from methanol-water.

Anal. Calcd for C_{12}H_{13}N_2O_2Cl_3S: C, 40.51; H, 3.66; N, 7.88.
Found: C, 40.39; H, 3.57; N, 7.74.

2,2-Dimethylbutanal Tosylhydrazone

2,2-Dimethylbutanal (Chemical Samples Co., 2 g, 0.02 mole) in absolute ethanol (10 ml) was added to a solution of tosylhydrazide (3.7 g, 0.02 mole) in absolute ethanol (25 ml). The slurry cleared and was stirred for 1 hr at room temperature. The solvent was removed by rotary evaporation leaving a colorless oil which was redissolved in anhydrous ether. Addition of hexane drove out white crystals believed to be 1,2-bis-tosylhydrazide, an impurity in the starting tosylhydrazide;
additional hexane caused separation of 2,2-dimethylbutanal tosylhydrazone as an oil. Overnight freezing led to crystallization of the tosylhydrazone (4.0 g, mp 56.5-57.5°C). Concentration of the solvents resulted in isolation of additional product (0.8 g) for a total yield of 89%.

**Anal.** Calcd for C₁₃H₂₀N₂O₂S: C, 58.17; H, 7.51; N, 10.44.

**Found:** C, 58.28; H, 7.33; N, 10.62.

2-Phenylpropanal Tosylhydrazone

2-Phenylpropanal (Chemical Samples Co., 13.4 g, 0.10 mole) was added to a solution of tosylhydrazide (18.6 g, 0.10 mole) in ethanol (80 ml) and the mixture was stirred for 1 hr. The volume was reduced on a rotary evaporator, water was added just short of the cloud-point, and the mixture was refrigerated. The crystalline precipitate of 2-phenylpropanal tosylhydrazone was washed with cold ethanol-water and dried in a vacuum desiccator for 48 hr. A second crop (6 g) of product was isolated from the mother-liquor and washings. Crude 2-phenylpropanal tosylhydrazone (mp 92-93°C, lit. (46) 97-98°C) was thus prepared in 93% (28.1 g) yield.

**Decompositions of Arylsulfonylhydrazones**

**Thermal Decomposition of Salts of Arylsulfonylhydrazones**

Pyrolytic decompositions of salts of arylsulfonylhydrazones were conducted in serum vials (5 ml), (89) which had been washed with

(89) Kimble Glass Co., Catalog No. 15095 or No. 15085.
ethanolic potassium hydroxide and distilled water, and stored in a desiccator. Between 0.06 and 0.08 grams (approximately $2.5 \times 10^{-4}$ mole) of dry arylsulfonylhydrazone was placed in a vial. The required amount of base was added and the vial was stoppered and immediately evacuated. Solvent was then syringed into the vial and the solution allowed to stand for a period of 2-24 hr. In some cases, the vials were rotated to facilitate mixing.

An alternate method for preparing these solutions was first to weigh the base into the vial. After evacuating the stoppered vial, a solution of the arylsulfonylhydrazone was added by syringe. This procedure resulted in faster neutralization and less discoloration of the solution.

In all cases, the vials were re-evacuated after the salt was formed and placed in a stirred oil bath at the desired temperature. The time for pyrolysis ranged from 4 to 20 min, depending on the compound and the temperature involved. Temperature variation was $\pm 2^\circ$ in most cases over the pyrolysis period. The pyrolytic time was generally shorter at high temperatures and/or upon the use of salts of aldehyde tosylhydrazones. Lithium salts of tosylhydrazones also required less time. The faster decomposition of lithium than of sodium salts and of aldehyde versus ketone sulfonylhydrazones has been observed before (46).

Preparative Scale Pyrolysis of the Sodium Salt of trans-2-Methylcyclopropanecarboxaldehyde 2,4,5-Trichlorobenzene sulfonylhydrazone

trans-2-Methylcyclopropanecarboxaldehyde 2,4,5-trichlorobenzene-sulfonylhydrazone (1 g, $2.8 \times 10^{-3}$ moles) was stirred with sodium
hydride (0.125 g of 57% sodium hydride-mineral oil dispersion, \( \sim 2.8 \times 10^{-3} \) moles) in tetraethylene glycol dimethyl ether (tetraglyme, Ansul Ether 181) until hydrogen evolution ceased. The flask was evacuated and placed in an oil bath at 120° for 10 min. The products were distilled under vacuum into a trap cooled with liquid nitrogen where they were diluted with carbon tetrachloride or benzene-d₆. The yields were not measured, but generally, sufficient 3-methylcyclobutene was obtained for nmr analysis.

Preparative Scale Pyrolysis of the Sodium Salt of trans-2-Methylcyclopropanecarboxaldehyde-α-d 2,4,5-trichlorobenzenesulfonylhydrazone

A mixture of 3-methylcyclobutene-1-d and 2-d was obtained by pyrolysis of the sodium salt of trans-2-methylcyclopropanecarboxaldehyde-α-d 2,4,5-trichlorobenzenesulfonylhydrazone by the procedure previously described for the salt of the non-deuterated 2,4,5-trichlorobenzenesulfonylhydrazone.
APPENDIX

Infrared and Nuclear Magnetic Resonance Spectra
Figure 1
Figure 3
Figure 4
Figure 7
Figure 9
Figure 10
Figure 11
Figure 12
Figure 13
Figure 14
Figure 15
Figure 16
Figure 17