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OF TOSYLHYDRAZONES.

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STUDIES OF BASE-CATALYZED DECOMPOSITIONS
OF TOSYLHYDRAZONES

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

By
Gary Martin Kaufman, B.A.

*****

The Ohio State University
1967

Approved by

[Signature]
Adviser
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Dedicated to my family,
especially my wife, Sonya Louise
I wish to express my appreciation to Dr. Harold Shechter for his suggestion of this research problem, for his guidance and encouragement in the course of this work, and for his tireless help in preparing this manuscript.

I am grateful to the National Science Foundation and the Department of Chemistry of The Ohio State University for financial assistance.
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INTRODUCTION

The present study is concerned with preparation and decomposition of tosylhydrazones, benzenesulfonylhydrazones, and methanesulfonylhydrazones of aliphatic, alicyclic, and aromatic aldehydes and ketones. The primary areas of interest that developed as this investigation progressed are:

1. Determination of the relative migratory aptitudes of substituents (H, methyl and phenyl) in carbenic decompositions of appropriate tosylhydrazones with n-butyllithium, sodium amide and sodium methoxide in diethyl Carbitol.

2. Development of efficient techniques for preparing pure diazoalkanes and aryldiazomethanes by vacuum pyrolysis of lithium salts of tosylhydrazones of aliphatic aldehydes, suitably substituted aliphatic ketones, and aromatic ketones.

3. Decomposition of selected tosylhydrazones with incremental amounts (0.5 to 10 equivalents) of sodium and lithium bases in aprotic solvents to ascertain the influence of the nature and concentration of a base upon carbenic processes.

4. Decomposition of salts of benzenesulfonylhydrazones and methanesulfonylhydrazones to evaluate the merits of benzenesulfinate and methanesulfinate anions as leaving-groups relative to p-toluenesulfinate anion.
5. Thermolytic and catalytic reactions of diazoalkanes, to determine the susceptibility of carbenic processes to temperature, solvents, reactor surfaces, acids (Lewis and protonic), bases, and metal salt catalysts.
Tosylhydrazones of aldehydes and ketones undergo base-catalyzed thermal decomposition with loss of $p$-toluenesulfinate anion to give intermediate diazo compounds (eq. 1). The fate of

$$R-C=\text{N}-\text{NH}-SO_2C_7H_7 + B \rightarrow R-C=\text{N}_2 + BH^+ + O_2SC_7H_7$$

(1)

the diazo compounds is dependent upon their structures and their interactions with their environment. Environmental influences affecting the decomposition processes include: temperature, light, solvent polarity and proticity, and protonic, cationic, or metallic catalysis. The decomposition processes may be generally categorized as carbenic, in which nitrogen is expelled to give a bivalent intermediate, or as cationic in which there is coordination with an electron-deficient reagent to give diazonium and/or carbonium ion intermediates. The decomposition processes are complicated by the fact that they may be occurring simultaneously; the carbenic processes may also involve singlet and triplet spin-state factors.

The decomposition of $p$-tosylhydrazones has been actively investigated since it was realized that there are methods for controlling the reaction mechanisms (1).

Progress in this field has been recently reviewed by P. B. Sargeant, G. G. Vander Stouw, J. A. Smith, F. B. Cook, and C. G. Moseley (2-6).

(2) P. B. Sargeant, Ph.D. dissertation, The Ohio State University, 1962.

(3) G. G. Vander Stouw, ibid., 1964.

(4) J. A. Smith, ibid., 1965.

(5) F. B. Cook, ibid., 1967.


Important references in this area are summarized (7-25).


Preparation of Tosylhydrazones, Benzenesulfonylhydrazones, Methanesulfonylhydrazones, and Their Sodium and Lithium Salts

The several facets of the present research all involve the decomposition reactions of 1) tosylhydrazones, benzenesulfonylhydrazones, or methanesulfonylhydrazones of representative aldehydes and ketones, 2) the various salts of these hydrazones, or 3) the diazo compounds derived from these hydrazone intermediates. Therefore, in this section the techniques and results of the preparation of these various hydrazones and their sodium and lithium salts are discussed and tabulated.

A series of tosylhydrazones of aliphatic, alicyclic, and aromatic aldehydes and ketones were prepared (Table 1) in order to study their decompositions with bases under various conditions. In general, the tosylhydrazones were obtained by addition of carbonyl compounds to tosylhydrazide in methanol. Because of the thermal instability of certain of the derivatives, it was occasionally necessary to modify the procedure [see Experimental]. Benzenesulfonylhydrazones (Table 2) and methanesulfonylhydrazones (Table 3) were obtained by methods analogous to those used for synthesis of the tosylhydrazones.

Sodium salts of tosylhydrazones were prepared by 1) addition of sodium methoxide to a tosylhydrazone in dry tetrahydrofuran under
### TABLE 1

**Preparation of Tosylhydrazones**

<table>
<thead>
<tr>
<th>Tosylhydrazone</th>
<th>Melting point °</th>
<th>Yield</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanal tosylhydrazone</td>
<td>68°</td>
<td>50%</td>
<td>methanol</td>
</tr>
<tr>
<td>Propanal tosylhydrazone</td>
<td>69</td>
<td>77</td>
<td>&quot;</td>
</tr>
<tr>
<td>Propanone tosylhydrazone</td>
<td>151</td>
<td>85</td>
<td>&quot;</td>
</tr>
<tr>
<td>Butanal tosylhydrazone</td>
<td>64</td>
<td>90</td>
<td>petroleum ether</td>
</tr>
<tr>
<td>2-Methylpropanal tosylhydrazone</td>
<td>106</td>
<td>83</td>
<td>methanol</td>
</tr>
<tr>
<td>2-Butanone tosylhydrazone</td>
<td>127</td>
<td>87</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cyclopropanecarboxaldehyde tosylhydrazone</td>
<td>100</td>
<td>65</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pentanal tosylhydrazone</td>
<td>50</td>
<td>79</td>
<td>&quot;</td>
</tr>
<tr>
<td>2-Methylbutanal tosylhydrazone</td>
<td>72</td>
<td>60</td>
<td>methylene chloride</td>
</tr>
<tr>
<td>3-Methylbutanal tosylhydrazone</td>
<td>79</td>
<td>79</td>
<td>methanol</td>
</tr>
<tr>
<td>2,2-Dimethylpropanal tosylhydrazone</td>
<td>113</td>
<td>90</td>
<td>&quot;</td>
</tr>
<tr>
<td>Furfural tosylhydrazone</td>
<td>122</td>
<td>85</td>
<td>&quot;</td>
</tr>
<tr>
<td>3-Pentanone tosylhydrazone</td>
<td>102</td>
<td>65</td>
<td>&quot;</td>
</tr>
<tr>
<td>3-Methyl-2-butane tosylhydrazone</td>
<td>120</td>
<td>81</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cyclopentanone tosylhydrazone</td>
<td>183</td>
<td>95</td>
<td>&quot;</td>
</tr>
<tr>
<td>3,3-Dimethyl-2-butanone tosylhydrazone</td>
<td>155</td>
<td>95</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cyclohexanone tosylhydrazone</td>
<td>159</td>
<td>89</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cycloheptanone tosylhydrazone</td>
<td>148</td>
<td>95</td>
<td>&quot;</td>
</tr>
<tr>
<td>Phenylacetaldehyde tosylhydrazone</td>
<td>114</td>
<td>62</td>
<td>&quot;</td>
</tr>
<tr>
<td>Acetophenone tosylhydrazone</td>
<td>147</td>
<td>92</td>
<td>&quot;</td>
</tr>
<tr>
<td>Tosylhydrazone</td>
<td>Melting point</td>
<td>Yield</td>
<td>Solvent</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>---------------</td>
<td>-------</td>
<td>---------</td>
</tr>
<tr>
<td>2,2,5,5-Tetramethyltetrahydrofuran-3-one tosylhydrazone</td>
<td>171°</td>
<td>76%</td>
<td>methanol</td>
</tr>
<tr>
<td>2-Phenylpropanal tosylhydrazone</td>
<td>98</td>
<td>85</td>
<td>Skelly</td>
</tr>
<tr>
<td>3-Phenylpropanal tosylhydrazone</td>
<td>106</td>
<td>84</td>
<td>ether</td>
</tr>
<tr>
<td>3-Phenylpropenal tosylhydrazone</td>
<td>163</td>
<td>70</td>
<td>methanol</td>
</tr>
<tr>
<td>1-Phenyl-2-propanone tosylhydrazone</td>
<td>136</td>
<td>83</td>
<td>&quot;</td>
</tr>
<tr>
<td>4-Phenylbutanal tosylhydrazone</td>
<td>86</td>
<td>75</td>
<td>&quot;</td>
</tr>
<tr>
<td>4-Phenyl-3-buten-2-one tosylhydrazone</td>
<td>183</td>
<td>86</td>
<td>&quot;</td>
</tr>
<tr>
<td>Benzophenone tosylhydrazone</td>
<td>180</td>
<td>86</td>
<td>&quot;</td>
</tr>
<tr>
<td>Phenyl cyclohexyl ketone tosylhydrazone</td>
<td>93</td>
<td>50</td>
<td>&quot;</td>
</tr>
<tr>
<td>9-Fluorenone tosylhydrazone</td>
<td>162</td>
<td>80</td>
<td>&quot;</td>
</tr>
<tr>
<td>Perinaphthenone tosylhydrazone</td>
<td>183</td>
<td>85</td>
<td>&quot;</td>
</tr>
<tr>
<td>Diphenylacetaldehyde tosylhydrazone</td>
<td>145</td>
<td>88</td>
<td>&quot;</td>
</tr>
<tr>
<td>Dibenzyl ketone tosylhydrazone</td>
<td>185</td>
<td>75</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

* Melting points (uncorrected) are given for unrecrystallized tosylhydrazones.  
  Yields of the tosylhydrazones are based upon amount of initial tosylhydrazide.
### TABLE 2
Preparation of Benzenesulfonylhydrazones

<table>
<thead>
<tr>
<th>Benzenesulfonylhydrazones</th>
<th>Melting point</th>
<th>Yield</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propanone benzenesulfonylhydrazone</td>
<td>140°</td>
<td>95%</td>
<td>propanone</td>
</tr>
<tr>
<td>2-Butanone benzenesulfonylhydrazone</td>
<td>98</td>
<td>92</td>
<td>methanol</td>
</tr>
<tr>
<td>2,2-Dimethylpropanal benzene-sulfonylhydrazone</td>
<td>102</td>
<td>89</td>
<td>&quot;</td>
</tr>
<tr>
<td>3-Methyl-2-butanone benzenesulfonylhydrazone</td>
<td>109</td>
<td>68%</td>
<td>&quot;</td>
</tr>
<tr>
<td>3-Pentanone benzenesulfonylhydrazone</td>
<td>100</td>
<td>95</td>
<td>isopropanol</td>
</tr>
<tr>
<td>3,3-Dimethyl-2-butanone benzenesulfonylhydrazone</td>
<td>111</td>
<td>97</td>
<td>methanol</td>
</tr>
</tbody>
</table>

*The melting points (uncorrected) are given for unrecrystallized benzenesulfonylhydrazones. The yields of the benzenesulfonylhydrazones are based upon amount of initial benzenesulfonylhydrazide.*

*The low yield of 3-methyl-2-butanone benzenesulfonylhydrazone is due primarily to its great solubility in methanol.*

### TABLE 3
Preparation of Methanesulfonylhydrazones

<table>
<thead>
<tr>
<th>Methanesulfonylhydrazones</th>
<th>Melting point</th>
<th>Yield</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propanone methanesulfonylhydrazone</td>
<td>112°</td>
<td>98%</td>
<td>propanone</td>
</tr>
<tr>
<td>2-Butanone methanesulfonylhydrazone</td>
<td>57</td>
<td>54%</td>
<td>methanol</td>
</tr>
<tr>
<td>2,2-Dimethylpropanal methanesulfonylhydrazone</td>
<td>135</td>
<td>84</td>
<td>&quot;</td>
</tr>
<tr>
<td>3,3-Dimethyl-2-butanone methanesulfonylhydrazone</td>
<td>108</td>
<td>83</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

*The melting points (uncorrected) are given for the unrecrystallized methanesulfonylhydrazones. Yields of the methanesulfonylhydrazones are based upon amount of initial methanesulfonylhydrazide.*

*The low yield of 2-butanone methanesulfonylhydrazone is due primarily to formation of an oil which is difficult to crystallize.*
nitrogen; 2) by injection of a solution of a tosylhydrazone in dry
tetrahydrofuran into a suspension of sodium methoxide in dry pentane
under nitrogen; or 3) by addition of a carbonyl compound to a sus-
pension of the sodium salt of tosylhydrazide in dry tetrahydrofuran
under nitrogen.

A study was made of the utility of decomposition of lithium
salts of tosylhydrzones. The initial method for preparing the
salts involved adding n-butyllithium to a tosylhydrazone dissolved
in tetrahydrofuran and subsequent removal of the solvent to leave
the product caked on the flask wall. Although this method afforded
large surface areas for even heat distribution during pyrolysis, it
was very difficult to remove residual solvents, especially tetra-
hydrofuran, from the salt before thermolysis. Concurrently, a
procedure was devised to obviate isolation of unstable tosylhydrzones,
especially those from low-molecular weight aldehydes (C₂-C₅). In this
procedure n-butyllithium was added to a tosylhydrzone formed in situ
from tosylhydrazide and an aldehyde in tetrahydrofuran. Vacuum
evaporation again gave products which were difficult to free of sol-
vents and impurities.

A major procedural improvement is accomplished by precipitating
the lithium salt from tetrahydrofuran with pentane, washing the fil-
tered product with pentane, and vacuum drying. The higher quality
salts provide increased yields of diazo compounds, but residual tetra-
hydrofuran still contaminates the pyrolysis products unless special
precautions are taken to separate solvent expelled during pyrolysis.

To eliminate the problem of residual solvents in the salts,
tosylhydrzones suspended in purified pentane are treated with
n-butyllithium in pentane [see Experimental]. After filtration, washing and drying, salts of high purity are obtained which give diazo compounds of 95-98% purity in excellent yield (92-100%).

Lithium salts of tosylhydrazones prepared with n-butyllithium offer at least three advantages over sodium salts prepared from sodium methoxide for the preparation of diazo compounds by vacuum pyrolysis. Most significantly lithium salts decompose at appreciably lower temperatures (15-30° lower) than do sodium salts. Secondly, formation of methanol, a potential proton source which is difficult to remove from a salt by drying, is avoided. Finally, anhydrous transfers of standardized n-butyllithium by syringe are possible under humid conditions. Handling of sodium methoxide under similar conditions is difficult.

The sodium and lithium salts of benzenesulfonylhydrazones and methanesulfonylhydrazones can be prepared by the methods just described for tosylhydrazone salt formation.
CHAPTER 2

Base-Catalyzed Thermal Decomposition of Tosylhydrazones

Thermal decomposition of salts of tosylhydrazones in aprotic media leads to intermediate diazo compounds which subsequently decompose by carbenic processes. In carbenic rearrangements a neighboring substituent group can migrate to the carbenic center. In order to study relative migratory aptitudes of hydrogen, aryl (phenyl) and alkyl (methyl) groups, base-catalyzed decompositions of appropriate tosylhydrazones were examined. Qualitative migratory aptitudes are based upon product distributions determined by gas chromatography. The aspect of intramolecular cyclization by insertion into a phenyl carbon-hydrogen bond was also studied.

Phenylacetaldehyde tosylhydrazone and sodium methoxide in diethyl Carbitol, upon being heated to 125°, initially form the sodium salt of the tosylhydrazone which then decomposes heterogeneously to 1-diaz0-2-phenylethane as a transient pink intermediate. Thermolysis of the intermediate then occurs with loss of nitrogen and hydrogen migration to give styrene as the sole product of carbenic rearrangement (Eq. 2). Styrene is also the only hydrocarbon formed in base-

\[
\begin{align*}
\phi-\text{CH}_2-\text{CH}=\text{N}-\text{NH}-\text{SO}_2\text{C}_7\text{H}_7 & \xrightarrow{\text{NaOH}_3} \phi-\text{CH}_2-\text{CH}=\text{N}-\text{N}-\text{SO}_2\text{C}_7\text{H}_7 \\
\text{Na}^+ & \\
-\text{NaSO}_2\text{C}_7\text{H}_7 & \xrightarrow{110-125^\circ} \xrightarrow{\text{[\phi-\text{CH}_2-\text{CH}=\text{N}_2]}} \xrightarrow{\text{[\phi-\text{CH}=\text{CH}_2]}} \text{N}_2 \xrightarrow{\phi-\text{CH}=\text{CH}_2} & \text{100%}
\end{align*}
\]

catalyzed decomposition of phenylacetaldehyde tosylhydrazone with n-butyllithium in diethyl Carbitol under the above conditions.

Benzocyclobutene was not found in either experiment, a fact which indicates that insertion into a carbon-hydrogen bond of the
phenyl ring is not competitive with hydrogen migration in this system (Eq. 3).

\[
\begin{array}{c}
\text{\textbullet} \quad \text{CH}_2 \\
\text{\textbullet} \\
\end{array} 
\xrightarrow{\text{H}} 
\begin{array}{c}
\text{\textbullet} \\
\text{\textbullet} \\
\text{CH}_2 \\
\text{\textbullet} \\
\end{array}
\] (3)

3-Phenylpropanal tosylhydrazone in diethyl Carbitol is converted immediately to its lithium salt upon addition of an equivalent of n-butyllithium at 25°. Thermal decomposition of the lithium salt in diethyl Carbitol at 110-130° gives 3-phenyl-1-propene (Eq. 4) as the only hydrocarbon product. Similar results are obtained from

\[
\phi\text{-CH}_2\text{-CH}_2\text{-CH=N-NH-SO}_2\text{C}_7\text{H}_7 + \text{n-C}_4\text{H}_9\text{Li} \xrightarrow{\text{DEG}, 25°} \phi\text{-CH}_2\text{-CH}_2\text{-CH=N-N-SO}_2\text{C}_7\text{H}_7
\]

\[
\xrightarrow{-\text{LiSO}_2\text{C}_7\text{H}_7, 110-130°} [\phi\text{-CH}_2\text{-CH}_2\text{-CH=N}_2] -\text{N}_2 \xrightarrow{\text{H}} [\phi\text{-CH}_2\text{-CH-CH}:] \xrightarrow{\phi\text{-CH}_2\text{-CH}=\text{CH}_2} \sim 100% (4)
\]

decomposition of 3-phenylpropanal tosylhydrazone with a 10% excess of sodium methoxide in diethyl Carbitol at 110-130° (Eq. 5).

\[
\phi\text{-CH}_2\text{-CH}_2\text{-CH=N-NH-SO}_2\text{C}_7\text{H}_7 + \text{NaOCH}_3 (1.1 \text{ equiv.}) \xrightarrow{-\text{NaSO}_2\text{C}_7\text{H}_7, -\text{N}_2} \phi\text{-CH}_2\text{-CH}=\text{CH}_2 \sim 100% (5)
\]

Phenylocyclopropane and indane are not formed (Eq. 6). This result indicates that insertion into \(\beta\)-carbon-hydrogen or phenyl carbon-hydrogen bonds does not occur competitively with hydrogen migration in this system.
Decomposition of 1-phenylpropanone tosylhydrazone with an equivalent of sodium methoxide in diethyl Carbitol at 115-140° gives 3-phenyl-1-propene (14%), cis-1-phenyl-1-propene (17%) and trans-1-phenyl-1-propene (69%) (eq.7). In the carbenic rearrangement,

\[
\begin{align*}
\text{Decomposition} & \quad \xrightarrow{\text{NaOCH}_3, \text{HOC}_2} \quad \text{Decomposition} \\
\end{align*}
\]

migration of primary hydrogen (14%) gives 3-phenyl-1-propenes (eq.8);

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

migration of secondary hydrogen occurs more readily (86%) to produce both cis- and (major) trans-1-phenyl-1-propene (eq.9). Since 2-phenyl-

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

1-propene is not formed (eq.10), in this system secondary hydrogen must migrate far more readily than does the phenyl group.
In order to investigate a system in which a hydrogen, a phenyl, or a methyl group may migrate competitively to a carbenic site, base-catalyzed thermal decompositions of 2-phenylpropanal tosylhydrazone in diethyl Carbitol were examined.

2-Phenylpropanal tosylhydrazone with sodium methoxide (10% excess) decomposes at 110-120° in diethyl Carbitol to give 3-phenyl-1-propene (13%), 2-phenyl-1-propene (45%), cis-1-phenyl-1-propene (13%), phenylcyclopropane (10%) and trans-1-phenyl-1-propene (19%) (eq.11).

\[
\text{Ph-S}=\text{CH}=\text{N}-\text{NH-SO}_2\text{C}_7\text{H}_5 \xrightarrow{\text{NaOCH}_3} \text{Ph-S}=\text{CH}=\text{N}-\text{SO}_2\text{C}_6\text{H}_4 \xrightarrow{\text{HOC}_2\text{H}_3} \text{Ph-S}=\text{CH}=\text{N}-\text{SO}_2\text{C}_6\text{H}_4 \xrightarrow{\text{Na}^+}\text{C}_7\text{H}_7
\]

\[
\text{Ph-S}=\text{CH}=\text{N}-\text{NH-SO}_2\text{C}_7\text{H}_5 \xrightarrow{\text{NaOCH}_3} \text{Ph-S}=\text{CH}=\text{N}-\text{SO}_2\text{C}_6\text{H}_4 \xrightarrow{\text{HOC}_2\text{H}_3} \text{Ph-S}=\text{CH}=\text{N}-\text{SO}_2\text{C}_6\text{H}_4 \xrightarrow{\text{Na}^+}\text{C}_7\text{H}_7
\]

The identity of each component is confirmed by its retention time; 3-phenyl-1-propene was also identified by its infrared spectrum.

The major component, 2-phenyl-1-propene (45%), is formed by migration of the tertiary hydrogen to the carbenic center (Eq.12).
Formation of cis- and trans-1-phenyl-1-propenes can be formally accomplished by migration of either the phenyl or the methyl group in the carbenic rearrangement. However, only a small amount of methyl migration (9%) is reported from 2-methyl-2-phenylpropylidene (Eq.13) (26), and even less methyl migration (trace -3%) is obtained from 

\[
\begin{align*}
\ce{\phi - C - CH3 &\rightarrow \phi - C = CH - CH3 + CH3 - C = CH - \phi + CH3 - C = CH2} \\
&\quad \quad 9\% \quad 50\% \quad 41\% (13)
\end{align*}
\]


2,2-diphenylpropylidene (Eq.14) (6). Therefore, it is also very

\[
\begin{align*}
\ce{\phi - C - CH3 &\rightarrow \phi - C = CH - CH3 + \phi - C(CH3) = CH\phi + \phi - C = CH2} \\
&\quad \quad \text{trace - 3\%} \quad 65-75\% \quad 16-20\% (14)
\end{align*}
\]

likely that in the present system, migration of the phenyl group predominates over migration of the methyl group (Eq.15). Carbenic insertion into a carbon-hydrogen bond of the neighboring methyl group gives phenylcyclopropane (10%) (Eq.16).
The origin of 3-phenyl-1-propene is less obvious, and it was necessary to determine whether 3-phenyl-1-propene is produced by isomerization of one or more of the other hydrocarbon products under the decomposition conditions, or if, indeed, it is a product of carbenic rearrangement. The possibility that formation of 3-phenyl-1-propene is related to the presence of methanol from the methoxide base was explored.

With sodium amide (10% excess) as base, decomposition of 2-phenylpropanal tosylhydrazone in diethyl Carbitol provides the same five hydrocarbons identified previously, and in nearly the same distribution (Eq.17). 3-Phenyl-1-propene (10-12%) is again obtained.

\[
\begin{align*}
\phi-\text{CH-CH=NH-SO}_2\text{C}_7\text{H}_7 & \xrightarrow{\text{NaNH}_2/\text{-NH}_3} \phi-\text{CH-CH=N-}\bar{\text{N}}-\text{SO}_2\text{C}_7\text{H}_7 \\
\text{CH}_3 & \\
\text{-NaSO}_2\text{C}_7\text{H}_7 & \xrightarrow{-\text{N}_2} \phi-\text{CH}_2-\text{CH}=\text{CH}_2 + \phi-\text{C}=\text{CH}_2 + \phi-\text{C}=\text{C-CH}_3 \\
+ \phi-\text{C-CH}_2 + \phi-\text{C}=\text{C-CH}_3 & (17)
\end{align*}
\]
Significantly, the amount of 3-phenyl-1-propene formed is not appreciably altered by the absence of methanol during decomposition of the tosylhydrazone.

To determine further the effects of different bases upon formation of 3-phenyl-1-propene, n-butyllithium was utilized. Decomposition of 2-phenylpropanal tosylhydrazone with one equivalent of n-butyllithium (in hexane) at 110-125°C in diethyl Carbitol gives 3-phenyl-1-propene (4%), 2-phenyl-1-propene (38%), cis-1-phenyl-1-propene (23%), phenylcyclopropane (21%), and trans-1-phenyl-1-propene (14%) (Eq.18).

\[
\text{\begin{align*}
\phi-\text{CH-CH}=\text{N-NH-SO}_2\text{C}_7\text{H}_7 & \xrightarrow{\text{n-C}_4\text{H}_9\text{Li}} \phi-\text{CH}_2-\text{CH=CH}_2 \\
\text{CH}_3 & \quad \text{C}_4\text{H}_{10}, \quad \text{-LiSO}_2\text{C}_7\text{H}_7 \\
& \quad \text{-N}_2 \\
+ \phi-\text{C}=\text{CH}_2 & + \phi-\text{C}=\text{C-CH}_3 \\
\text{CH}_3 & 38\% \quad 23\% \quad 21\% \quad 21\% \quad 14\% \\
\end{align*}}
\]

With n-butyllithium as the base, 3-phenyl-1-propene is produced, although in smaller amount than with sodium methoxide or sodium amide. The ability of n-butyllithium to substantially alter product distribution in base-catalyzed decompositions of tosylhydrazones will be discussed in a later section.

To determine if 3-phenyl-1-propene is produced by isomerization of one or more of the other hydrocarbon products under the experimental conditions for their formation, 2-phenyl-1-propene, cis- and trans-1-phenyl-1-propenes and phenylcyclopropane were individually subjected to the conditions for decomposition of the tosylhydrazone. 3-Phenyl-1-propene was also tested under these conditions to see if it isomerized.
3-Phenyl-1-propene, 2-phenyl-1-propene, cis- and trans-1-phenyl-1-propenes and phenylcyclopropane were separately exposed to the conditions for decomposition of cyclohexanone tosylhydrazone in diethyl Carbitol at 125-150° using excess (10-30%) sodium methoxide, sodium amide and n-butyllithium as bases in individual reactions. Phenylcyclopropane was also treated with each base in diethyl Carbitol at 150°. There was no evidence, however, for isomerization of any hydrocarbons. It is concluded, therefore, that 3-phenyl-1-propene is indeed a primary product from base-catalyzed decomposition of 2-phenylpropanal tosylhydrazone in diethyl Carbitol.

If decomposition of 2-phenylpropanal tosylhydrazone occurs by a carbenic process, 3-phenyl-1-propene can be formed by a double rearrangement involving 1) transfer of hydrogen from the methyl group to the divalent center, and 2) migration of the phenyl group (Eq. 19);

\[
\begin{align*}
H_2C-H & \rightarrow H_2C^+ \\
\phi - \overset{\ddagger}{C} - \overset{\ddagger}{CH} & \rightarrow \phi - \overset{\ddagger}{C} - \overset{\ddagger}{CH}_2 & \rightarrow \phi - \overset{\ddagger}{CH}_2=CH=CH_2
\end{align*}
\]  

(19)

the rearrangement may involve singlet or triplet processes. With the use of one equivalent (or a very slight excess) of base in the reaction, carbonium-ion processes may operate competitively with carbenic processes. 3-Phenyl-1-propene thus can also be formed by a classical carbonium-ion process (Eq. 20) involving phenyl rearrangement and loss of hydrogen ion.
This study of rearrangements of the 2-phenylpropylidene system shows that migration of tertiary hydrogen (38-45%) slightly exceeds that of a phenyl group (32-37%). It has not been possible to determine precisely the amount of methyl migration, but it is likely a minor process. Insertion (10-21%) is also a relatively minor reaction. The processes leading to formation of 3-phenyl-1-propene (4-13%) are not fully understood and require additional study.

A system in which two phenyl groups compete with a single hydrogen in a carbenic rearrangement provides a statistically favorable opportunity to study the migratory aptitude of an aryl group relative to hydrogen. Such a system is diphenylacetaldehyde tosylhydrazone, which forms a sodium salt with sodium methoxide in diethyl Carbitol. Thermal decomposition of this sodium salt in diethyl Carbitol occurs at 110-130°. A single hydrocarbon product was produced which was shown by gas chromatography and infrared analysis to be 1,1-diphenylethylene (Eq. 21). It is apparent from this result that in carbenic rearrangement of this system tertiary hydrogen migrates...
much more readily than does a phenyl group, statistical probability notwithstanding.

Qualitative conclusions concerning relative migratory aptitudes of selected substituent groups in carbenic processes can be drawn from the preceding experiments: 1) the order of migration is hydrogen > phenyl > methyl; 2) migratory aptitude of secondary hydrogen > primary hydrogen. It can also be concluded: 1) that with a single β-methyl group present, insertion into a carbon-hydrogen bond of that methyl group is a minor process compared to migration of a hydrogen or a phenyl group; 2) intramolecular insertion into a phenyl carbon-hydrogen bond to give a cyclization product is not a competitive process.
CHAPTER 3

Vacuum Pyrolysis of Lithium Salts of Tosylhydrazones

Decomposition of tosylhydrazones by bases on a preparative scale in aprotic solvents such as diethyl Carbitol, hexadecane, and tributylamine suffers several shortcomings. In particular, collection of gases and isolation of high-boiling products are inefficient, laborious, and time-consuming. In an effort to simplify the techniques for carbenic decomposition of tosylhydrazones, vacuum pyrolysis of their dry salts was studied. An important objective of this study was to isolate the intermediate diazo compounds in reasonable purity for further investigation.

Bamford and Stevens showed (7) that aryl diazomethanes are intermediates in decomposition of aromatic aldehyde and ketone tosylhydrazone by sodium in ethylene glycol, but only olefinic products were isolated from aliphatic ketone tosylhydrazones. Farnum (27) modified the Bamford and Stevens (7) method and obtained fairly good yields of moderately pure aryl diazoalkanes using sodium methoxides in pyridine, but also failed to prepare aliphatic diazoalkanes from the appropriate tosylhydrazones.

Smith (4) utilized vacuum pyrolysis (1-80 mm., 100-200°) of dry sodium salts of aliphatic and aromatic aldehyde and ketone
tosylhydrazones to obtain hydrocarbons (major) and occasionally intermediate diazo compounds (minor). In aromatic systems, and with 2,2,4,4-tetramethylcyclobutanone tosylhydrazone (28), diazo compounds were actually isolated. Fox (29) reported a small amount of an orange liquid product, presumably the diazo compound, from vacuum pyrolysis (0.3 mm., 140-186°) of the dry sodium salt of 1-norbornanecarboxaldehyde tosylhydrazone.

Diazoalkanes are usually prepared by nitrosation methods (30a), oxidation of hydrazones (30b), reaction of chloroform with hydrazine and potassium hydroxide (30c), and reaction of carbanionic reagents with chloramine (30d), hydroxylamine-2-sulfonic acid (30d), and p-tosylazide respectively (30e). These methods have limitations in


(29) A. S. Fox, Post-doctoral research, The Ohio State University, 1963.

(30a) These methods are summarized by T. J. deBoer and H. J. Backer, Rec. trav. chim., 72, 229(1954); (b) H. Staudinger and A. Gaule, Ber., 42, 1897 (1916); (c) H. Staudinger and O. Kuffer, Ber., 45, 301 (1912); (d) J. Meinwald, P. G. Gassman, and E. G. Miller, J. Am. Chem. Soc., 81, 4751 (1959); (e) W. von E. Doering and C. H. Depuy, J. Am. Chem. Soc., 75, 5955 (1953).
preparation of pure diazo compounds in that the reactions are often inefficient, inconvenient, and hazardous, and separation of the diazo compounds from solvents is usually necessary.

After reviewing existing methods for syntheses of diazoalkanes it was realized that a need existed for a simple, reliably efficient method for preparing pure diazoalkanes in good yields. It seemed that vacuum pyrolysis of pure, dry salts of tosylhydrazones could fulfill this need.

Preliminary investigations in the present research indicated that n-butyllithium was superior to sodium methoxide as a base for preparing dry salts of tosylhydrazones. With n-butyllithium as base, methanol, a proton donor, is not generated and cannot affect the salt or the diazo compound. Also, lithium salts of tosylhydrazones decompose at advantageously lower temperatures than do sodium salts.

Several series of pure, dry lithium salts of representative aldehyde and ketone tosylhydrazones were prepared and vacuum pyrolyzed in the present study to evaluate the scope and generality of the decomposition method for preparing diazo compounds. An arbitrary goal of a 50% yield of diazo compound (based on initial tosylhydrazone) was set as a criterion to evaluate the method for specific cases. If this minimum yield was achieved, further attempts to improve this yield usually were not made, although progressively improved techniques developed later in the research would now permit this.

In general, the procedure [see Experimental] involves reaction of a tosylhydrazone in anhydrous tetrahydrofuran or dry pentane (preferred) with a slight excess (2-5%) of n-butyllithium in pentane under nitrogen (eq.22).
The lithium salt is filtered under nitrogen, washed with pentane and vacuum dried.

The pure, dry lithium salt of a tosylhydrazone is vacuum pyrolyzed (0.1-1.5 mm., 100-130°) [see Experimental] to give the diazo compound (Eq.23) which distills from the pyrolysis flask and

\[
\text{R}-\text{C}=\text{N}-\text{NH-SO}_2\text{C}_7\text{H}_7 \xrightarrow{\text{n-C}_4\text{H}_9\text{Li}} \text{R}^1\text{Li}^+ \xrightarrow{\text{n-C}_4\text{H}_10} \text{R}^1\text{C}=\text{N} - \text{N} - \text{SO}_2\text{C}_7\text{H}_7 \quad (22)
\]

is collected at -80°. The lithium p-toluenesulfinate remains in the pyrolysis flask. If hydrocarbons from thermolysis of the diazo compound are desired, rather than the intermediate diazo compound, higher pressures (80-760 mm.) are used during pyrolysis. The hydrocarbons are obtained in good yield, free from solvents and impurities.

The yield of a diazo compound is determined by the weight loss of the lithium salt of tosylhydrazone. Purity is based upon corrected volumes of nitrogen evolved when neat or dilute (hexane) aliquots of the diazo compound are injected [see Experimental] into a benzoic acid-benzene solution (Eq.24).

\[
\text{R}^1\text{C}=\text{N}_2 + \text{C}_8\text{H}_8\text{CO}_2\text{H} \xrightarrow{0.1 \text{ mm., } 120-130°} \text{R}^1\text{CH-0-C-} + \text{N}_2 \quad (23)
\]

Lithium salts of tosylhydrazones of aliphatic aldehydes in the C\textsubscript{2}-C\textsubscript{9} range were studied (Table 4). Primary diazoalkanes were obtained in 53-98% yields. Cyclopropyl diazomethane was obtained
TABLE 4
Primary Diazooalkanes from Aliphatic Aldehyde Tosylhydrazones

<table>
<thead>
<tr>
<th>Primary diazoalkane</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diazomethane</td>
<td>80</td>
</tr>
<tr>
<td>1-Diazopropane</td>
<td>56</td>
</tr>
<tr>
<td>Cyclopropylidiazomethane</td>
<td>~10</td>
</tr>
<tr>
<td>1-Diazobutane</td>
<td>80</td>
</tr>
<tr>
<td>1-Diazo-2-methylpropane</td>
<td>75</td>
</tr>
<tr>
<td>1-Diazo-3-methylbutane</td>
<td>65</td>
</tr>
<tr>
<td>1-Diazo-4-methylbutane</td>
<td>65</td>
</tr>
<tr>
<td>1-Diazo-2,2-dimethylpropane</td>
<td>98</td>
</tr>
<tr>
<td>1-Diazo-2-phenylethane</td>
<td>~50%</td>
</tr>
<tr>
<td>1-Diazo-2-phenylpropane</td>
<td>80</td>
</tr>
<tr>
<td>1-Diazo-3-phenylpropane</td>
<td>~50%</td>
</tr>
</tbody>
</table>

a Vacuum pyrolyses were effected on pure, dry lithium salts of tosylhydrazones at 0.1-1.5 mm., 100-130°. b Yields are based on the weight of initial tosylhydrazone or the weight loss of the lithium salt; the purity was determined from the corrected volume of nitrogen from titration of the diazo compound with benzoic acid-benzene solution. c l-Diazo-2-phenylethane and l-diazo-3-phenylpropane were prepared in good yields, but mechanical circumstances prevented their isolation.

only in very low yields (less than 10%) in several attempts. The diazo compound apparently is quite unstable; however, improved techniques developed later in this study might allow its efficient synthesis.
The wide range of yields of primary diazoalkanes obtained reflects: 1) the purity of a starting tosylhydrazone or its lithium salt; 2) technical and procedural improvements; and 3) structural effects of neighboring alkyl groups in stabilizing the diazo compound. The stabilizing effect is exerted primarily by sterically shielding the diazo function from attack by protons or metal cations or from bimolecular reaction yielding azines and nitrogen. As expected, the tert-butyl group shows a large stabilizing effect. Thermal stability of the diazo compound also seems to increase with increased alkyl substitution on α-carbon.

Lithium salts of tosylhydrazones of representative aliphatic and alicyclic ketones in the molecular weight range of C₃-C₁₅ were vacuum pyrolyzed. Yields of secondary diazoalkanes prepared show wide variance (Table 5).

Lithium salts of tosylhydrazones of propanone, 2-butanone, cyclopentanone, and cyclohexanone decompose at temperatures (170-200°) much higher than do lithium salts of tosylhydrazones of aliphatic aldehydes (100-125°) of comparable molecular weights. When the secondary diazoalkanes are generated at 170-200°, thermolysis into nitrogen and hydrocarbon products occurs before the diazo compounds can be swept from the pyrolysis flask into a cold collection trap. Only small yields (less than 10%) of 2-diazopropane, 2-diazobutane, diazocyclopentane and diazocyclohexane were obtained by vacuum pyrolysis.

Lithium salts of tosylhydrazones of 3-methyl-2-butanone (125-135°), 3,3-dimethyl-2-butanone (115-125°), 1-phenyl-2-propanone
**TABLE 5**

Secondary Diazoalkanes from Aliphatic and Alicyclic Ketone Tosylhydrazones

<table>
<thead>
<tr>
<th>Secondary diazoalkanes</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Diazopropane</td>
<td>~10b</td>
</tr>
<tr>
<td>2-Diazobutane</td>
<td>~10b</td>
</tr>
<tr>
<td>Diazocyclopentane</td>
<td>~10b</td>
</tr>
<tr>
<td>Diazocyclohexane</td>
<td>~10b</td>
</tr>
<tr>
<td>2-Diazo-3-methylbutane</td>
<td>90a</td>
</tr>
<tr>
<td>2-Diazo-3,3-dimethylbutane</td>
<td>95</td>
</tr>
<tr>
<td>2-Diazo-1-phenylpropane</td>
<td>50</td>
</tr>
<tr>
<td>2-Diazo-1,3-diphenylpropane</td>
<td>~50d</td>
</tr>
</tbody>
</table>

* a Vacuum pyrolyses (0.1-1.5 mm.) were effected on dry lithium salt of tosylhydrazone. 
  b Lithium salts decompose at 170-200°. 
  c 2-Diazo-3-methylbutane was prepared by vacuum pyrolysis (0.15-0.5 mm., 125-135°) after Experimental Section was typed. 
  d Part of the 2-diazo-1,3-diphenylpropane decomposed upon generation when the optimum temperature was exceeded during the final phase of vacuum pyrolysis.

(110-120°) and 1,3-diphenyl-2-propanone (130-135°) decompose at more favorable temperatures. Excellent yields of 2-diazo-3-methylbutane (90%) and 2-diazo-3,3-dimethylbutane (95%) are obtained by vacuum pyrolysis of dry lithium salts of their respective tosylhydrazones. Moderate yields (31) of 2-diazo-1-phenylpropane (31) The lower yields of 2-diazo-1-phenylpropane and 2-diazo-1,3-diphenylpropane resulted primarily from technical difficulties. 

(31) The lower yields of 2-diazo-1-phenylpropane and 2-diazo-1,3-diphenylpropane resulted primarily from technical difficulties. 

~50% were obtained by vacuum pyrolysis.
It is of interest that lithium salts of aldehyde tosylhydrazones decompose at lower temperatures than do those of ketone tosylhydrazones. A possible rationalization for the relatively high decomposition temperatures of lithium salts of unsubstituted aliphatic ketone tosylhydrazones involves electrical and steric effects. For explanation of these effects, the possible structures of lithium salts of unsubstituted aliphatic ketone tosylhydrazone are used as illustrative examples. Possible structures of the lithium salt of propanal tosylhydrazone include Ia and Ib. On the assumption that it is more difficult for the p-toluenesulfinate ion to leave with its electron pair in Ia than in Ib, structural factors in salts of tosylhydrazone which tend to position the lithium ion on nitrogen as in Ia and IIa should increase the decomposition temperatures of the salts. Sterically in propanal tosylhydrazone anion there is little hindrance to partial placement of the lithium cation on carbon as in Ib and the p-toluenesulfinate group may leave easily as its anion. For propanone tosylhydrazone anion there is greater hindrance to positioning of the lithium cation.
on carbon of IIb; thus structure IIa may more nearly resemble that of salt and then the p-toluenesulfinate anion cannot leave as easily. The close packing that might occur in a crystalline lattice for relatively rigid and symmetrical tosylhydrazone anions as possibly derived from alicyclic ketones could make it relatively difficult for the p-toluenesulfinate anion to leave.

It is also of interest that lithium salts of tosylhydrazones of aliphatic ketones possessing bulky substituents (isopropyl, tert-butyl or phenyl groups) on a-carbon decompose at lower temperatures (115-140°) than do those of aliphatic ketones with only hydrogens or a single methyl group on an a-carbon (170-200°). Using structures IIIa and IIIb, a possible explanation, when there is a tert-butyl substituent on a-carbon, involves steric crowding in IIIa which is relieved by loss of lithium cation and p-toluene-
sulfinate anion to form IIIb in which the diazo function is linear. Another important aspect of bulky substituents on a-carbon is the steric protection from external attack these groups give to the diazo function.

The generally higher decomposition temperature for dry sodium
salts of tosylhydrazones may reflect the stronger ionic forces in a crystal lattice of sodium cations and tosylhydrazone anions. In general sodium salts are higher melting than lithium salts. Higher temperatures would be required to break these lattices and allow formation of the diazo compound and sodium p-toluenesulfinate.

Vacuum pyrolysis of lithium salts of tosylhydrazones from alkyl aromatic and diaryl ketones gave moderate yields of diazo compounds (Table 6). These relatively high molecular weight \( \text{C}_8-\text{C}_{13} \)

### TABLE 6

<table>
<thead>
<tr>
<th>Diazo compound</th>
<th>Yield, ( % )_b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Diazo-1-phenylethane</td>
<td>65</td>
</tr>
<tr>
<td>Phenylcyclohexyl diazomethane</td>
<td>65</td>
</tr>
<tr>
<td>Diphenyl diazomethane</td>
<td>50</td>
</tr>
</tbody>
</table>

_a_ Vacuum pyrolyses (0.1-1.5 mm.) were effected on dry lithium salts of tosylhydrazones. 
_b_ The yields are lowered by competitive azine formation.

diazo compounds distill readily from their precursor tosylhydrazone salts. Lithium salts of acetophenone tosylhydrazone and phenyl cyclohexyl ketone tosylhydrazone decompose rapidly at 120-130°; the lithium salt of benzophenone tosylhydrazone is more stable, decomposing rapidly at 150°. The yields of these diazo compounds are lowered by competitive formation of azines; diphenyl diazomethane is readily converted to benzophenone azine (Eq. 25)

\[
2 \phi_2\text{C}=\text{N}_2 \xrightarrow{-\text{N}_2} \phi_2\text{C}=\text{N}=\text{N}=\phi_2 \quad (25)
\]
The preparation of α,β-unsaturated diazo compounds was attempted from 3-phenylpropenal tosylhydrazone and from 4-phenyl-3-butene-2-one tosylhydrazone. However, the products from the tosylhydrazones and n-butyllithium failed to give diazo compounds upon vacuum pyrolysis. The products may be substituted pyrazoles formed by cyclization (Eq. 26).

\[
\begin{array}{c}
\text{SO}_2\text{C}_7\text{H}_7 \\
\text{H--N--N--C--R} \\
\text{H--C--C--H} \\
\phi \\
\end{array}
\xrightarrow{n-\text{C}_4\text{H}_q\text{Li}}
\begin{array}{c}
\text{Li}^+\text{SO}_2\text{C}_7\text{H}_7 \\
\text{H--N--N--C--R} \\
\text{H--C--C--H} \\
\phi \\
\end{array}
\xrightarrow{-\text{LiSO}_2\text{C}_7\text{H}_7}
\begin{array}{c}
\text{H--N--N--C--R} \\
\phi \\
\end{array}
\]

\[R = \text{H, CH}_3\]  

The present study thus shows that vacuum pyrolysis of lithium salts of tosylhydrazones is indeed an excellent and reliably general method for preparing diazoalkanes. It is superior in its simplicity and productivity to previously existing routes. The method is particularly effective for synthesis of primary diazoalkanes and of suitably substituted secondary diazoalkanes. For preparing aryl-diazoalkanes, vacuum pyrolysis of lithium salts of aromatic ketone tosylhydrazones is comparable to previous methods.

Advantages of the present method include: 1) readily available starting materials; 2) easily synthesized and stable precursors; 3) simple and efficient procedures; and 4) good preparative yields of diazo compounds that are free from solvents and contaminants.

A principal value of the vacuum pyrolysis method is that it conveniently provides diazoalkanes for direct study of their thermal,
photolytic, and catalytic decompositions. These results can then be compared with similar decompositions of tosylhydrazone salts in which the diazoalkanes are formed as transient intermediates in solution. With pure, neat diazoalkanes, intramolecular carbenic rearrangements can be effected in controllable environments.

The chemical aspects involved in preparation of diazoalkanes from tosylhydrazones are quite simple. However, successful generation of the diazo compounds by vacuum pyrolysis does involve certain technical prerequisites: 1) the lithium salt must be pure and dry or the diazo compound will be contaminated with solvents; 2) agitation or stirring of a dry salt during pyrolysis facilitates escape of the diazo compound and promotes even heat distribution; 3) care must be exerted to find a satisfactory temperature for rapid generation, but not thermolysis, of the diazo compound; and 4) the diazo compound collected must be adequately protected from heat, light, and contamination by the environment.

Diazoalkanes prepared in the present study have not presented any explosive hazards in preparation, handling or storage. There may be danger, however, from the toxicity of low molecular weight diazoalkanes (32). If a diazo compound begins to decompose upon

(32) Diazomethane is very toxic.

generation (when optimum pyrolysis temperature is exceeded), large volumes of nitrogen and hydrocarbons are produced. Vacuum pumps with adequate free air capacity (140 l. per minute) and rubber serum caps on all traps should be used.
Diazooalkanes can be safely stored for various periods of time at $-78^\circ$C, protected from light. Dilution with a hydrocarbon increases their storage lives and retards formation of azines. Provisions should be made to accommodate or release nitrogen evolved if storage temperatures should rise to that for decomposition of the diazo compound.

Diazomethane will decompose on contact with ground glass or sharp edges. No difficulty of this type was encountered with the diazoalkanes prepared in this study. Ground glass surfaces of joints and syringe plungers were coated with silicon grease as a general precaution.
CHAPTER 4

Reactions of Tosylhydrazones with Various Bases in Selected Solvents

It became of interest to determine the effects of various bases and solvents on base-catalyzed decompositions of tosylhydrazones. A study was thus made of reaction of 3,3-dimethyl-2-butanone tosylhydrazone with incremental amounts (0.5, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, and 10.0 equiv.) of sodium methoxide, lithium methoxide and n-butyllithium in decalin and in diethyl Carbitol. A less extensive study was made of reaction of 2,2-dimethylpropanal tosylhydrazone with sodium methoxide, lithium methoxide, potassium tert-butoxide and n-butyllithium in diethyl Carbitol.

In diethyl Carbitol (Table 7) with insufficient sodium methoxide (0.5 and 0.8 equiv.) 3,3-dimethyl-2-butanone tosylhydrazone decomposes to give major amounts (55-59%) of carbon-skeleton rearranged products. 2,3-Dimethyl-1-butene (41-37%) and 2,3-dimethyl-2-butene (18%) are produced along with 3,3-dimethyl-1-butene (30%) and 1,1,2-trimethylcyclopropane (10-14%). A very minor reduction product, 2,2-dimethylbutane (1%), is also formed.

When 1 to 1.6 equivalents of sodium methoxide are used (Table 7), formation of 3,3-dimethyl-1-butene (44-52%) and 1,1,2-trimethylcyclopropane (34-46%) show increases. There are correspondingly lesser amounts of 2,3-dimethyl-1-butene (14-2%) and 2,3-dimethyl-2-butene (8-0%) obtained.
Decomposition of 3,3-Dimethyl-2-butanone Tosylhydrazone with Sodium Methoxide in Diethyl Carbitol

<table>
<thead>
<tr>
<th>Equiv. base</th>
<th>CH$_3$-C=CH$_2$CH$_3$</th>
<th>H$_2$C=CH-CH$_3$</th>
<th>CH$_3$-C = C-CH$_3$</th>
<th>CH$_3$-C=CH$_2$-CH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>30</td>
<td>10</td>
<td>41</td>
<td>18</td>
</tr>
<tr>
<td>0.8</td>
<td>30</td>
<td>14</td>
<td>37</td>
<td>18</td>
</tr>
<tr>
<td>1.0</td>
<td>44</td>
<td>34</td>
<td>14</td>
<td>8</td>
</tr>
<tr>
<td>1.2</td>
<td>51</td>
<td>45</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>1.4</td>
<td>51</td>
<td>46</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>1.6</td>
<td>52</td>
<td>46</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>1.8</td>
<td>53</td>
<td>47</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.0</td>
<td>53</td>
<td>47</td>
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<td>0</td>
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<tr>
<td>2.5</td>
<td>53</td>
<td>47</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.0</td>
<td>53</td>
<td>47</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4.0</td>
<td>53</td>
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<td>5.0</td>
<td>53</td>
<td>47</td>
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</tr>
<tr>
<td>10.0</td>
<td>53</td>
<td>47</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

3,3-Dimethyl-2-butanone tosylhydrazone (0.1000 g., 0.373 millimole) and the appropriate amount of sodium methoxide are reacted in diethyl Carbitol (1 ml.) at 25-40° in a sealed serum vial (10 ml.). The resulting sodium salt of the tosylhydrazone is decomposed at 150° in preheated pyrolysis block. □ Hot (150°) gas-phase product samples are analyzed by gas chromatography [15% propylene carbonate, 20' x 1/4", Chromosorb G (reg.), 60/80 mesh, 10-15°]. □ The amounts of sodium methoxide are corrected for their 97.5% purity.
When larger excesses of sodium methoxide (1.8, 2.0, 2.5, 3.0, 4.0, 4.0, and 10.0 equiv.) are employed (Table 7), no carbon-skeleton rearrangement products are formed. 3,3-Dimethyl-1-butene (53%) and 1,1,2-trimethylcyclopropane (47%) are the only products produced. These latter results are in general agreement with those obtained by Friedman who reported (1b) 3,3-dimethyl-1-butene (52%), 1,1,2-trimethylcyclopropane (46%) and 2,3-dimethyl-1-butene (2%) as the products from decomposition of 3,3-dimethyl-2-butanone tosylhydrazone with 1.2 equivalents of sodium methoxide in diethyl Carbitol at 180°.

In the 3,3-dimethyl-2-butyldene system carbenic rearrangement can lead to four products. Two of these products can be formed without rearrangement of the carbon skeleton: 1) 3,3-dimethyl-1-butene is produced by migration of a primary hydrogen from the α-methyl group (eq.27); 2) 1,1,2-trimethylcyclopropane is derived by insertion

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

(eq.27)

into a carbon-hydrogen bond of a β-methyl group (eq.28). Formation

\[
\begin{align*}
\text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \quad \rightarrow \quad \text{CH}_3 - \text{C} \quad \text{CH} \quad \text{CH} - \text{CH}_3
\end{align*}
\]

(eq.28)

of the other two products by carbenic processes involves carbon-skeletal rearrangement: 3) 2,3-dimethyl-1-butene may arise by abstraction of
a hydrogen from a β-methyl group by the carbenic center, and subsequent
migration of a β-methyl group (Eq. 29); and 4) 2,3-dimethyl-2-butene

\[
\begin{align*}
    & H_2C^+ - H \\
    & H_3C - C - C - CH - CH_3 \rightarrow H_3C - C - CH - CH_3 \quad (29)
\end{align*}
\]

results from migration of a β-methyl group to the carbenic site (Eq. 30).

\[
\begin{align*}
    & CH_3 \\
    & H_3C - C - C - CH - CH_3 \rightarrow H_3C - C = C - CH_3 \quad (30)
\end{align*}
\]

Carbonium-ion processes, resulting from protonation of 2-diazo-
3,3-dimethylbutane or 3,3-dimethyl-2-butyldiene by the environment
(Eq. 31), can also give the three olefinic products: 1) 3,3-dimethyl-

\[
\begin{align*}
    & N_2^+ \\
    & (CH_3)_3C-C-CH_3 \rightarrow (CH_3)_3C-CH-CH_3 \rightarrow (CH_3)_3C-CH_2 \rightarrow (CH_3)_3C-CH_2 \quad (31)
\end{align*}
\]

1-butene is formed by loss of a proton from the α-methyl group (Eq. 32);

\[
\begin{align*}
    & CH_3 + \quad H^+ \\
    & CH_3 - C - C - CH_2 \rightarrow CH_3 - C - CH = CH_2 \quad (32)
\end{align*}
\]

2) 2,3-dimethyl-1-butene results from rearrangement of a β-methyl
group to give the 2,3-dimethyl-2-butyl cation, a tertiary carbonium
ion, with subsequent loss of a proton from a methyl group adjacent to
the new positive center (Eq. 33); and 3) 2,3-dimethyl-2-butene

\[
\begin{align*}
    & CH_3 + \quad H_2C-H \\
    & CH_3 - C - CH - CH_3 \rightarrow CH_3 - C - CH - CH_3 \rightarrow CH_3 - C - CH - CH_3 \rightarrow CH_3 - C - CH - CH_3 \quad (33)
\end{align*}
\]
arises from rearrangement of a \( \beta \)-methyl group followed by loss of the adjacent tertiary proton (Eq. 34). 1,1,2-TrimeThyLCyclopropane

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & - \quad \text{C} - \quad \text{CH} - \quad \text{CH}_3 & \rightarrow & \text{CH}_3 & - \quad \text{C} - \quad \text{CH} - \quad \text{CH}_3 & \rightarrow & \text{H}^+ & \quad \text{CH}_3 & - \quad \text{C} = \quad \text{C} - \quad \text{CH}_3 \\
\end{align*}
\]

(Eq. 34)

may also be produced by a carbonium-ion insertion process (Eq. 35).

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & - \quad \text{C} - \quad \text{CH} - \quad \text{CH}_3 \rightarrow & \text{H}^+ & \quad \text{CH}_3 & - \quad \text{C} - \quad \text{CH} - \quad \text{CH}_3 & \rightarrow & \text{CH}_2 & \quad \text{CH} - \quad \text{CH}_3 \\
\end{align*}
\]

(Eq. 35)

Formation of methylcyclopropane has been reported (33, 34) in aprotic
diazotization of isobutylamine.

Apparently, when insufficient sodium methoxide is used (Table 7), unneutralized tosylhydrazone or methanol can protonate either 2-diazo-3,3-dimethylbutane or 3,3-dimethyl-2-butyldiene (see Eq. 31). As a result the products obtained are probably formed by competitive carbonium-ion and carbenic processes.

The significant decrease in the 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene produced when an equivalent or more of sodium methoxide is used (Table 7) indicates that these two products arise by carbonium-ion processes (see Eq. 33 and 34). Although 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene can be formally derived from
3,3-dimethyl-2-butyldiene by carbenic processes (see Eq. 29 and 30) it appears that such carbon-skeletal rearrangements do not occur competitively with insertion or hydrogen migration at 120-150° under the experimental conditions.

The amount of 2,3-dimethyl-1-butene formed is always greater than that of 2,3-dimethyl-2-butene (Table 7). This result indicates that in the energetic carbenium-ion processes statistically favored (6:1) loss of a primary hydrogen from the 2,3-dimethyl-2-butyl cation occurs more frequently than that of tertiary hydrogen (Eq. 36).

\[
\begin{align*}
\text{N}_{2}^{+} & \rightarrow \text{CH}_{3}\text{CH} = \text{CH} - \text{CH}_{3} \rightarrow \text{CH}_{3} - \text{CH} - \text{CH}_{3} \rightarrow \text{CH}_{3} \text{CH}_{3} - \text{H}^{+} \\
\text{(CH}_{3}\text{)}_{3}\text{C} - \text{CH} - \text{CH}_{3} & \rightarrow \text{CH}_{2} - \text{CH} - \text{CH}_{3} \rightarrow \text{CH}_{3} \text{CH}_{3} - \text{H}^{+} \\
\text{2}^\circ & \rightarrow \text{H}^{+} \rightarrow \text{(CH}_{3}\text{)}_{2}\text{C} = \text{C(CH}_{3}\text{)}_{2} \text{ minor (36)}
\end{align*}
\]

When larger excesses (1.8-10 equiv.) of sodium methoxide are used (Table 7) all of the tosylhydrazone is neutralized, the proton-donating ability of the methanol generated is sufficiently suppressed, and the products are derived entirely from carbenic processes.

In decalin (Table 8) with insufficient sodium methoxide (0.5 and 0.8 equiv.) 3,3-dimethyl-2-butanone tosylhydrazone decomposes (120-150°) to 3,3-dimethyl-1-butene (41-42%), 1,1,2-trimethylcyclopropane (15-17%), 2,3-dimethyl-1-butene (30-32%) and 2,3-dimethyl-2-butene (6-10%) by competitive carbenic and carbenium-ion processes. 2,2-Dimethylbutane is formed in low yield (2-3%) by a reduction process, possibly of the Wolff-Kishner type.

With the use of increasing amounts (1.0, 1.2, 1.4, 1.6 and 1.8
### Table 8

Decomposition of 3,3-Dimethyl-2-butanone Tosylhydrazone with Sodium Methoxide in Decalin

<table>
<thead>
<tr>
<th>Equiv. base</th>
<th>CH$_3$-C=CH=CH$_2$</th>
<th>H$_2$C=C=CH-CH$_3$</th>
<th>CH$_3$-C=CH$_3$</th>
<th>CH$_3$-C=CH$_2$-CH$_3$</th>
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<td>10</td>
</tr>
<tr>
<td>1.2</td>
<td>45</td>
<td>27</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>1.4</td>
<td>46</td>
<td>34</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>1.6</td>
<td>52</td>
<td>44</td>
<td>4</td>
<td>0</td>
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</tr>
<tr>
<td>10.0</td>
<td>52</td>
<td>48</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*The sodium salt of 3,3-dimethyl-2-butanone tosylhydrazone (0.1000 g., 0.373 millimole) is prepared in situ with the appropriate amount of sodium methoxide in decalin at 25-40°C, then decomposed at 150°C. b Vapor-phase sample taken at 150°C are analyzed by gas chromatography [15% propylene carbonate, 20°C x 1/4", 60/80 Chromosorb G (reg.), 10-15°C]. c The amounts of sodium methoxide are corrected for their 97.5% purity.*
equiv.) of sodium methoxide formation of the two rearranged products, 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene, is gradually reduced from 34% to 1%. The tosylhydrazone and sodium methoxide are less soluble in decalin than in diethyl Carbitol, and it is difficult to accomplish complete neutralization of the tosylhydrazone heterogeneously. Incomplete neutralization of the tosylhydrazone can lead to carbonium-ion processes. Decreased solubility of the reactants in decalin and the resulting carbonium-ion processes may explain the larger amounts of rearranged products formed in decalin than in diethyl Carbitol when 1.0, 1.2, and 1.4 equivalents of sodium methoxide are used.

When more sodium methoxide (2.0, 10.0 equiv.) is employed 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene are not formed, and the ratio of 3,3-dimethyl-1-butene (52%) and 1,1,2-trimethylcyclopropane (48%) remains constant.

Aside from reactant solubility factors there are no significant differences between diethyl Carbitol and decalin as solvents for decomposition of 3,3-dimethyl-2-butanone tosylhydrazone with excess sodium methoxide.

The effects of lithium methoxide on decomposition of 3,3-dimethyl-2-butanone tosylhydrazone in diethyl Carbitol were then investigated (Table 9). The lithium salt of 3,3-dimethyl-2-butanone tosylhydrazone as formed in situ using 0.5 and 0.8 equivalents of lithium methoxide decomposes at 120-150° in diethyl Carbitol (Table 9) to 3,3-dimethyl-1-butene (28-31%), 1,1,2-trimethylcyclopropane (9-14%), 2,3-dimethyl-1-butene (44-38%), 2,3-dimethyl-2-butene (16-15%), and 2,2-dimethylbutane (4-1%). As the quantity of lithium methoxide is
### TABLE 9

Decomposition\(^a\) of 3,3-Dimethyl-2-butanone Tosylhydrazone with Lithium Methoxide in Diethyl Carbitol

<table>
<thead>
<tr>
<th>Equiv. base</th>
<th>CH(_3)C—CH=CH(_2)</th>
<th>CH(_3)C—CH=CH(_3)</th>
<th>H(_2)C=C—CH—CH(_3)</th>
<th>CH(_3)—C=CH—CH(_3)</th>
<th>CH(_3)—C—CH(_2)—CH(_3)</th>
</tr>
</thead>
<tbody>
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<td>15</td>
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</tr>
<tr>
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<td>1</td>
</tr>
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<td>0</td>
</tr>
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<td>40</td>
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<td>25</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>1.4</td>
<td>43</td>
<td>30</td>
<td>19</td>
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<td>8</td>
</tr>
<tr>
<td>1.6</td>
<td>43</td>
<td>31</td>
<td>17</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>1.8</td>
<td>42</td>
<td>31</td>
<td>19</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>2.0</td>
<td>44</td>
<td>33</td>
<td>16</td>
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<td>7</td>
</tr>
<tr>
<td>2.5</td>
<td>44</td>
<td>34</td>
<td>15</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>3.0</td>
<td>45</td>
<td>36</td>
<td>13</td>
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<td>6</td>
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<tr>
<td>4.0</td>
<td>46</td>
<td>37</td>
<td>12</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>5.0</td>
<td>47</td>
<td>37</td>
<td>11</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>10.0</td>
<td>46</td>
<td>36</td>
<td>12</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

\(^a\) The lithium salt of 3,3-dimethyl-2-butane tosylhydrazone (0.100 g., 0.373 millimole) is prepared in situ with the appropriate amount of lithium methoxide in diethyl carbitol at 25-40°, then decomposed at 150° in preheated block. \(^b\) Vapor-phase samples taken at 150° are analyzed by gas chromatography [15% propylene carbonate, 20° x 1/4", 60/80 Chromosorb G (reg.), 10-15°]. \(^c\) The amounts of lithium methoxide are corrected for their 98.4% purity.
increased incrementally from 1 to 3 equivalents (Table 9), the distribution of hydrocarbon products exhibits predicted trends:

1) formation of the reduced product, 2,2-dimethylbutane, ceases;
2) the percentages of 3,3-dimethyl-1-butene (37-45%) and 1,1,2-trimethylcyclopropane (24-36%) both increase; and 3) the percentages of 2,3-dimethyl-1-butene (26-13%) and 2,3-dimethyl-2-butene (13-6%) both show corresponding decreases. Significantly however, even with larger excesses of lithium methoxide (4.0, 5.0, and 10.0 equiv.) there is still 11-12% of 2,3-dimethyl-1-butene and 5-6% of 2,3-dimethyl-2-butene formed by rearrangement in diethyl Carbitol (Table 9). This is in sharp contrast to the results obtained using excesses of sodium methoxide in diethyl Carbitol (Table 7).

To expand the study of the effects of lithium methoxide on the decomposition of 3,3-dimethyl-2-butanone tosylhydrazone, a sequence of experiments was conducted in decalin (Table 10). The product distribution as obtained by increasing the equivalents of lithium methoxide (0.5-10.0 equiv. by selected increments) show these expected features: 1) formation of the unrearranged product, 3,3-dimethyl-1-butene (36-48%) and 1,1,2-trimethylcyclopropane (13-44%), is progressively increased; 2) production of the rearranged products, 2,3-dimethyl-1-butene (38-6%) and 2,3-dimethyl-2-butene (9-2%) is decreased; and 3) the reduction product, 2,2-dimethylbutane (5-2%), is formed only when insufficient (0.5-0.8 equiv.) lithium methoxide is used.
### TABLE 10

Decomposition\(^{a}\) of 3,3-Dimethyl-2-butanone Tosylhydrazone with Lithium Methoxide in Decalin

<table>
<thead>
<tr>
<th>Equiv.(^{a}) base</th>
<th>Hydrocarbon Product Distribution(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH(_3) - C-CH=CH(_2)</td>
</tr>
<tr>
<td>0.5</td>
<td>36</td>
</tr>
<tr>
<td>0.8</td>
<td>39</td>
</tr>
<tr>
<td>1.0</td>
<td>41</td>
</tr>
<tr>
<td>1.2</td>
<td>45</td>
</tr>
<tr>
<td>1.4</td>
<td>46</td>
</tr>
<tr>
<td>1.6</td>
<td>46</td>
</tr>
<tr>
<td>1.8</td>
<td>47</td>
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<tr>
<td>5.0</td>
<td>49</td>
</tr>
<tr>
<td>10.0</td>
<td>48</td>
</tr>
</tbody>
</table>

\(^{a}\) The lithium salt of 3,3-dimethyl-2-butanone tosylhydrazone (0.1000 g., 0.373 millimole) is prepared in situ with the appropriate amount of lithium methoxide in decalin at 25-40\(^{\circ}\), then decomposed at 150\(^{\circ}\). \(^{b}\) Vapor-phase samples of pyrolysis products at 150\(^{\circ}\) are analyzed by gas chromatography [15% propylene carbonate, 20\(^{\prime}\) x 1/4\(^{\prime}\); 60/80 Chromosorb G (reg.), 10-15\(^{\circ}\)]. \(^{c}\) The amounts of lithium methoxide are corrected for their 98.4\% purity.
The carbon-skeleton rearranged products are produced even when using large excesses of lithium methoxide in decalin, but in smaller percentages than in diethyl Carbitol. There thus appears to be a larger solvent effect upon use of lithium methoxide than with sodium methoxide. Lithium methoxide and the lithium salt of 3,3-dimethyl-2-butenone tosylhydrazone are both quite soluble in diethyl Carbitol, but much less soluble in decalin.

It is apparent from the product distributions from the previous four sets of experiments (See Tables 7-10). that lithium methoxide and sodium methoxide exert different effects; increasing concentrations of both bases produce similar trends, however, in product distributions. Since factors such as temperature, methanol formation, solvents and base concentration ranges were constant it is concluded that the lithium cation is responsible for formation of the rearranged products when excess lithium methoxide is used in either diethyl Carbitol or decalin.

The lithium cation (ionic radius 0.60\(\text{Å}\)) is considerably smaller than a sodium cation (ionic radius 0.95\(\text{Å}\)). As a result of its greater charge density a lithium cation should exhibit a greater tendency than a sodium cation to complex with an electron pair of 2-diazo-3,3-dimethylbutane or of 3,3-dimethyl-2-butylidene (Eq. 37).

\[
\begin{align*}
\text{CH}_3 & \text{N}_2^+ \\
\text{CH}_3 & \text{Li}^+ \\
\text{CH}_3 & \text{Li}^+ \\
\end{align*}
\]
At high concentrations (1.8-10.0 equiv.) of lithium methoxide, where the usual protonating agents, unneutralized tosylhydrazone and methanol, are eliminated or suppressed, this metalloid carbonium ion can rearrange to give 2,3-dimethyl-1-butene (Eq. 38) and 2,3-dimethyl-2-butene (Eq. 39). 3,3-Dimethyl-1-butene and 1,1,2-trimethylcyclopropane may also be produced via the metalloid carbonium ion. The fact that more of the rearranged products are formed in the more polar diethyl Carbitol supports the concept of a metalloid carbonium-ion process.

To test the concept that a lithium cation–carbenoid complex may lead to metalloid carbonium-ion processes 3,3-dimethyl-2-butanone tosylhydrazone was treated with sodium methoxide (1.2 equiv.) and purified (35) lithium p-toluenesulfinate (2.4 equiv.) in diethyl (35) Lithium p-toluenesulfinate, prepared from vacuum pyrolysis of the lithium salt of 3,3-dimethyl-2-butanone tosylhydrazone, was treated with n-butyllithium to remove or neutralize any protons impurities, washed with anhydrous pentane, and dried in vacuo.

Carbitol. A second sample of 3,3-dimethyl-2-butanone tosylhydrazone was treated with lithium methoxide (1.2 equiv.) and sodium
p-toluenesulfinate (36) (2.4 equiv.) in diethyl Carbitol. The salts

(36) Anhydrous sodium p-toluenesulfinate, prepared by vacuum pyrolysis of the sodium salt of 3,3-dimethyl-2-butanone tosylhydrazone, was washed with pentane and dried in vacuo.

of the tosylhydrazone, formed in situ, were thermolyzed at 150° and
the products analyzed by gas chromatography. The results are shown
in Table 11.

When 3,3-dimethyl-2-butanone tosylhydrazone is decomposed with
sodium methoxide in the presence of lithium p-toluenesulfinate (Eq. 40),

\[
\begin{align*}
\text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 & \quad \text{NaOCH}_3 (1.2 \text{ equiv.}) \\
\text{CH}_3 & \quad \text{LiSO}_2\text{C}_7\text{H}_6 (2.4 \text{ equiv.}) \\
& \xrightarrow{\text{DEC, 150°}} \text{CH}_3 - \text{C} - \text{CH} = \text{CH}_2 + \\
& \quad \text{CH}_3 \quad 38\% \\
\end{align*}
\]

the product distribution is nearly identical with that obtained with
lithium methoxide (1.2 equiv.) (see Table 11). The much larger
total (37%) of rearranged products is in marked contrast to that (4%)
from use of sodium methoxide (1.2 equiv.) without lithium p-toluene-
sulfinate (see Table 11).

When 3,3-dimethyl-2-butanone tosylhydrazone is decomposed with
lithium methoxide in the presence of sodium p-toluenesulfinate (Eq. 41)
the total amount (14%) of rearranged products is considerably less
than that obtained (35%) from reaction of lithium methoxide (1.2
equiv.) without sodium p-toluenesulfinate (see Table 11).
<table>
<thead>
<tr>
<th>Base</th>
<th>Equiv. base</th>
<th>Reagent</th>
<th>Equiv. reagent</th>
<th>Product Distribution</th>
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</table>

⁻ Decompositions effected upon the tosylhydrazone salt, prepared in situ, in diethyl carbital at 150°.  
⁻ Purified lithium p-toluenesulfonate or sodium p-toluenesulfinate.  
⁻ Equivalents of base or reagent compared to 0.373 millimoles (0.100 g.) of tosylhydrazone.  
⁻ Corrected for 97.5% purity of sodium methoxide.  
⁻ Corrected for 98.4% purity of lithium methoxide.
\[
\begin{align*}
\text{CH}_3 \text{N-NH-SO}_2\text{C}_7\text{H}_7 & \quad \text{LiOCH}_3 \text{(1.2 equiv.)} \\
\text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 & \quad \text{NaSO}_2\text{C}_7\text{H}_7 \text{(2.4 equiv.)} \\
& \quad \text{DEC, 150°} \\
\text{CH}_3 - & \quad \text{C} - \text{CH = CH}_2 + \\
\text{CH}_3 & \quad 46\% \\
\text{H}_3\text{C} - & \quad \text{CH}_2 = \text{C} - \text{C} - \text{CH}_3 + \text{CH}_3 - \text{C} = \text{C} - \text{CH}_3 \\
\text{CH}_2 - & \quad \text{CH-CH}_3 \\
& \quad 40\% \quad 11\% \quad 3\%
\end{align*}
\]

It can be concluded that there is a lithium cation effect which may well operate through formation of a metalloid carbonium-ion complex to produce rearranged products (Eq. 38 and 39).

The use of n-butyllithium provides an opportunity to study further the action of a lithium base and to compare its effects with that of lithium methoxide. Experiments in which 3,3-dimethyl-2-butane tosylhydrazone reacts with increasing amounts (0.5-10.0 equiv.) of n-butyllithium in diethyl Carbitol and then thermolyses at 150° reveal (Table 12) that: 1) with insufficient base (0.5 and 0.8 equiv.) large amounts (65-47\%) of rearrangement products (2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene) are formed, indicating that carbonium-ion processes are prevalent; 2) upon increasing the relative quantities of n-butyllithium (1.0-1.6 equiv.) the percentages of rearranged olefins rapidly diminish to zero and the ratio of 3,3-dimethyl-1-butene (59\%) to 1,1,2-trimethylcyclopropane (39\%) is unusually high; 3) at still higher ratios of base (1.8-10.0 equiv.) to tosylhydrazone, the percentage of 1,1,2-trimethylcyclopropane decreases from a maximum of 39\% to zero and 3,3-dimethyl-1-butene becomes the only product.
**TABLE 12**

Decomposition\(^a\) of 3,3-Dimethyl-2-butenone Tosylhydrazone with n-Butyllithium in Diethyl Carbitol

<table>
<thead>
<tr>
<th>Equiv. base</th>
<th>CH(_3)-CH-CH=CH(_2)</th>
<th>H(_3)C-CH (_3)</th>
<th>CH(_2)-CH-CH(_3)</th>
<th>H(_2)C=C-CH-CH(_3)</th>
<th>CH(_3)-C=CH-CH(_3)</th>
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<tr>
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<td>42</td>
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<tr>
<td>0.8</td>
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<td>13</td>
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<tr>
<td>1.4</td>
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<td>7</td>
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<tr>
<td>1.6</td>
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<tr>
<td>1.8</td>
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<tr>
<td>10.0</td>
<td>100</td>
<td>0</td>
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</tr>
</tbody>
</table>

\(^a\) The lithium salt of 3,3-dimethyl-2-butenone tosylhydrazone (0.1000 g., 0.373 millimole) was prepared in situ in pentane with appropriate amount of n-butyllithium, then decomposed at 150° in diethyl Carbitol. \(^b\) Vapor-phase samples taken at 150° are analyzed by gas chromatography [15% propylene carbonate, 20' x 1/4", 60/80 Chromosorb G (reg.), 10-15°]. \(^c\) The reduced product, 2,2-dimethylbutane, is not produced when n-butyllithium is used as base. \(^d\) The appropriate volumes of 1.53 M solution of n-butyllithium in pentane are used.
When these experiments are repeated in decalin (Table 13), use of insufficient n-butyllithium (0.5-0.8 equiv.) causes formation of 2,3-dimethyl-1-butene (38-28%) and 2,3-dimethyl-2-butene (15-13%), probably by carbonium-ion rearrangements. With one equivalent of n-butyllithium in decalin, 3,3-dimethyl-1-butene (57%), 1,1,2-trimethylcyclopropane (40%) and only 3% of 2,3-dimethyl-1-butene are formed. Excess n-butyllithium (1.2-1.8 equiv.) in decalin causes a very rapid increase in the percentage (57-100%) of 3,3-dimethyl-1-butene with corresponding exclusion of 1,1,2-trimethylcyclopropane. n-Butyllithium in diethyl Carbitol or in decalin at 150° does not isomerize 1,1,2-trimethylcyclopropane to any olefinic products.

From the experiments with 3,3-dimethyl-2-butanone tosylhydrazone and n-butyllithium in diethyl Carbitol and in decalin it can be concluded: 1) with insufficient n-butyllithium, proton-initiated carbonium-ion processes probably account for formation of the carbon-skeleton rearranged products; 2) with moderate excesses of n-butyllithium a new non-carbenic process begins to function, causing exclusive formation of 3,3-dimethyl-1-butene and preventing formation of 1,1,2-trimethylcyclopropane; 3) the apparent influence of the lithium cation is much less pronounced, especially in decalin, when n-butyllithium is utilized than when lithium methoxide is used; and 4) the nature of the solvent has a definite effect upon product distribution.

It is possible that the great base strength of excess n-butyllithium results in the abstraction of a proton from the α-methyl
**TABLE 13**

Decomposition of 3,3-Dimethyl-2-butanone Tosylhydrazone with n-Butyllithium in Decalin

<table>
<thead>
<tr>
<th>Equiv. base</th>
<th>Hydrocarbon Product Distribution</th>
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</thead>
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<tr>
<td></td>
<td>CH₃-C-CH=CH₂</td>
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<td>36</td>
</tr>
<tr>
<td>0.8</td>
<td>41</td>
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<tr>
<td>1.0</td>
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<td>1.4</td>
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</tr>
<tr>
<td>1.8</td>
<td>100</td>
</tr>
<tr>
<td>2.0</td>
<td>100</td>
</tr>
</tbody>
</table>

*The lithium salt of 3,3-dimethyl-2-butanone tosylhydrazone (0.1000 g., 0.373 millimole) was prepared in situ in pentane with an appropriate amount of n-butyllithium, then decomposed at 150° in decalin. vapor-phase samples taken at 150° are analyzed by gas chromatography [15% propylene carbonate, 20¹ x 1/4", 60/80 Chromosorb G (reg.), 10-15°]. The reduced product, 2,2-dimethylbutane, is not produced when n-butyllithium is used as base. The appropriate volumes of 1.53 M solution of n-butyllithium in pentane are used.*
group of the lithium salt of 3,3-dimethyl-2-butanone tosylhydrazone (eq. 42). This sequence could explain the exclusive formation of

\[ \begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{Li}^+ \\
\text{CH}_3 & \quad -\text{C} \quad \text{Li}^+ \\
\end{align*} \]

\[ \begin{align*}
\text{CH}_3 & \quad -\text{C} \quad \text{Li}^+ \\
\text{CH}_3 & \quad -\text{C} \quad \text{Li}^+ \\
\end{align*} \]

The need for further study of such a process involving dianionic species is indicated (37).

(37) While the present study was in progress W. Kirmse, B. G. von Bulow, and H. Schepp, Ann., 691, 41 (1966), reported the exclusive production of 3,3-dimethyl-1-butene from decomposition of 3,3-dimethyl-2-butanone tosylhydrazone with 7 equivalents of sodium amide in decalin at 180°. However, the mechanism proposed in this report is different than the dianionic process suggested in the present study.

The fact that larger excesses of n-butyllithium are required in diethyl Carbitol (1.8 equiv.) than in decalin (1.2 equiv.) to eliminate formation of the 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene may indicate: 1) that the lithium cation can function more effectively in the more polar solvent (diethyl Carbitol) to produce the rearranged
products via metalloid carbonium-ion processes (eq. 38 and 39) and/or
2) that n-butyllithium is consumed by attack upon diethyl Carbitol
and thus is less available to neutralize the tosylhydrazone. Require-
ment of larger amounts of n-butyllithium in diethyl Carbitol (4.0
equiv.) than in decalin (1.8 equiv.) to eliminate formation of 1,1,2-
trimethylcyclopropane may also be explained by loss of n-butyllithium
by cleavage of the solvent.

In summary, reference to Table 14 (a composite table showing
results of all experiments with 3,3-dimethyl-2-butane tosylhydrazone)
provides these conclusions concerning base-catalyzed thermal decompo-
sition of 3,3-dimethyl-2-butane tosylhydrazone: 1) optimum conditions
for carbenic processes are provided by use of at least 1.8 equivalents
of sodium methoxide in diethyl Carbitol; decalin is judged slightly
less desirable because of the insolubility of the reactants in the non-
polar solvent; 2) lithium methoxide is somewhat inferior because the
lithium cation apparently causes metalloid carbonium-ion processes
that compete with normal carbenic processes, especially in diethyl
Carbitol; 3) large excesses of n-butyllithium result in non-carbenic
processes possibly via dianionic intermediates which compete with
normal carbenic and metalloid carbonium-ion processes; 4) carbonium-
ion processes operate competitively when insufficient base is used;
and 5) solvent effects are minor with sodium methoxide; more pro-
nounced with lithium methoxide, and very significant with n-butyll-
lithium.

Base-catalyzed decompositions of 2,2-dimethylpropanal tosyl-
hydrazone, a system closely analogous to 3,3-dimethyl-2-butane
TABLE 14
Summary of Decompositions of 3,3-Dimethyl-2-butanone Tosylhydrazone with Various Bases in Selected Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Base</th>
<th>Equiv.</th>
<th>CH₃C-CH=CH₂</th>
<th>H₂C-C-CH₂-CH₃</th>
<th>H₂C=CH-CH₃</th>
<th>CH₃-C = C-CH₃</th>
<th>CH₃-C-CH₂-CH₃</th>
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<td>10</td>
<td>41</td>
<td>18</td>
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<tr>
<td>Decalin</td>
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<tr>
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<td>44</td>
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<td>5</td>
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<td>( \text{CH}_2\text{-CH-CH}_3 )</td>
<td>( \text{H}_2\text{C=C-CH-CH}_3 )</td>
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</tr>
<tr>
<td>DEC</td>
<td>BuLi</td>
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<td>87</td>
</tr>
<tr>
<td>DEC</td>
<td>NaOCH₃</td>
<td>4.0</td>
<td>53</td>
</tr>
<tr>
<td>Decalin</td>
<td></td>
<td>52</td>
<td>48</td>
</tr>
<tr>
<td>DEC</td>
<td>LiOCH₃</td>
<td>4.0</td>
<td>46</td>
</tr>
<tr>
<td>Decalin</td>
<td></td>
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<td>42</td>
</tr>
<tr>
<td>DEC</td>
<td>BuLi</td>
<td>4.0</td>
<td>100</td>
</tr>
<tr>
<td>Solvent</td>
<td>Base</td>
<td>Equiv.</td>
<td>CH₃-C-CH₂-CH₂</td>
</tr>
<tr>
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<td>----------------</td>
</tr>
<tr>
<td>DEC</td>
<td>NaOCH₃</td>
<td>5.0</td>
<td>53</td>
</tr>
<tr>
<td>Decalin</td>
<td></td>
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<tr>
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<td>LiOCH₃</td>
<td>5.0</td>
<td>47</td>
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<tr>
<td>Decalin</td>
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<td>49</td>
</tr>
<tr>
<td>DEC</td>
<td>BuLi</td>
<td>5.0</td>
<td>100</td>
</tr>
<tr>
<td>DEC</td>
<td>NaOCH₃</td>
<td>10.0</td>
<td>53</td>
</tr>
<tr>
<td>Decalin</td>
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</tr>
<tr>
<td>DEC</td>
<td>LiOCH₃</td>
<td>10.0</td>
<td>46</td>
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<tr>
<td>DEC</td>
<td>BuLi</td>
<td>10.0</td>
<td>100</td>
</tr>
</tbody>
</table>

* This table is a composite summary of data from Tables 7-10, 12, and 13.
* DEC is an abbreviation for diethyl carbitol. (CH₃-CH₂-O-CH₂-CH₂-O-CH₂-CH₂-O-CH₂-CH₃).
* BuLi is an acronym for n-butyllithium
tosylhydrazone, were studied to determine if the effects of bases and concentration previously observed are general.

Thermal decompositions of the sodium salt of 2,2-dimethylpropanal tosylhydrazone prepared in situ in diethyl Carbitol give 1-diazo-2,2-dimethylpropane as a transient intermediate (Eq. 43). Subsequent thermolysis of the diazo compound proceeds with loss of nitrogen to yield 2,2-dimethylpropylidene which inserts into a $\beta$-methyl group to give 1,1-dimethylcyclopropane or undergoes carbon-skeletal rearrangement to form 2-methyl-2-butene via methyl migration (Eq. 43).

\[
\begin{align*}
\text{CH}_3 &\text{CH}_3\text{-C-CH=N-NH-SO}_2\text{C}_7\text{H}_7 \xrightarrow{\text{NaOCH}_3, \text{DCE}} \text{CH}_3\text{-C-CH=N-N-SO}_2\text{C}_7\text{H}_7 \\
\text{CH}_3 &\text{CH}_3
\end{align*}
\]

- \text{NaSO}_2\text{C}_7\text{H}_7 \xrightarrow{120-150^\circ} \left[ \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array} \right] \xrightarrow{-\text{N}_2} \left[ \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array} \right] \\
\text{H}_3\text{C} &\text{CH}_3 + \text{CH}_3\text{-C=CH-CH}_3
\]

The results of experiments in which 2,2-dimethylpropanal tosylhydrazone is decomposed at 150° after treatment with 0.8, 1.2, 1.6, and 3.0 equivalents of sodium methoxide in diethyl Carbitol are summarized in Table 15.

With insufficient sodium methoxide (0.8 equiv.) 2-methyl-1-butene (56%) and 2-methyl-2-butene (39%) are formed probably via
TABLE 15

Base-catalyzed Decompositions$^a$ of 2,2-Dimethylpropanal Tosylhydrazone in Diethyl Carbitol

<table>
<thead>
<tr>
<th>Base</th>
<th>Equiv. base</th>
<th>CH$_3$</th>
<th>CH$_3$-C=CH-CH$_3$</th>
<th>CH$_3$-C=CH-CH$_3$</th>
<th>CH$_3$-C=CH-CH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOCH$_3$$^b$</td>
<td>0.8</td>
<td>5</td>
<td>56</td>
<td>39</td>
<td>0</td>
</tr>
<tr>
<td>NaOCH$_3$</td>
<td>1.2</td>
<td>96</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>NaOCH$_3$</td>
<td>1.6</td>
<td>95</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>NaOCH$_3$</td>
<td>3.0</td>
<td>95</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>LiOCH$_3$$^c$</td>
<td>1.2</td>
<td>7</td>
<td>53</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>LiOCH$_3$</td>
<td>1.6</td>
<td>67</td>
<td>16</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>LiOCH$_3$</td>
<td>3.0</td>
<td>68</td>
<td>15</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>KOC(CH$_3$)$_3$$^d$</td>
<td>3.0</td>
<td>79</td>
<td>0</td>
<td>5</td>
<td>16</td>
</tr>
<tr>
<td>KOC(CH$_3$)$_3$$^d$</td>
<td>3.0</td>
<td>83$^e$</td>
<td>0</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td>n-C$_4$H$_9$Li$^f$</td>
<td>3.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$ Salts of 2,2-dimethylpropanal tosylhydrazone were prepared in situ at 25-45°, then decomposed at 150°. $^b$ The amounts of sodium methoxide are corrected for their 97.5% purity.
$^c$ The amounts of lithium methoxide are corrected for their 98.4% purity. $^d$ The amounts of potassium tert-butoxide were corrected for their 95% purity. $^e$ Product distribution for 2,2-dimethylpropanal benzenesulfonylhydrazone. $^f$ n-Butyllithium (1.53 M in pentane).
carbonium-ion processes initiated by protonation of the intermediate diazo compounds or of 2,2-dimethylpropylidene by unneutralized tosylhydrazone or methanol (eq. 44). 1,1-Dimethylocyclopropane (5%) may

\[
\begin{align*}
\text{CH}_3 & - \text{C} - \text{CH} - \text{N}_2^+ \xrightarrow{H^+} \text{CH}_3 - \text{C} - \text{CH}_2 - \text{N}_2^+ \xrightarrow{-N_2} \text{CH}_3 - \text{C} - \text{CH}_2^+ \\
& \text{CH}_3 - \text{C} - \text{CH} \\
& \text{CH}_3 \\
& \text{CH}_3 \\
\end{align*}
\]

result from carbenic or carbonium-ion processes.

When excess sodium methoxide (1.2, 1.6, and 3.0 equiv.) is used, 1,1-dimethylocyclopropane (95-96%) and 2-methyl-2-butene (4-5%) are formed. Friedman (1b) reported 1,1-dimethylocyclopropane (92%), 2-methyl-1-butene (1%), and 2-methyl-2-butene from decomposition of 2,2-dimethylpropanal tosylhydrazone with a 20% excess of sodium methoxide in diethyl Carbitol at 180°. 2-Methyl-2-butene probably arises by a carbenic process involving methyl migration; therefore, in this system with excess sodium methoxide it is likely that the processes involved are totally carbenic. It is of interest to note, then, under these conditions (base type and concentration, solvent and temperature) the very high order of insertion (95%) compared to methyl migration (5%) from 2,2-dimethylpropylidene.
2,2-Dimethylpropanal tosylhydrazone was also subjected to base-catalyzed thermal decompositions in diethyl Carbitol with lithium methoxide. The lithium salts, formed in situ, were thermolyzed in the presence of incremental excesses of lithium methoxide in diethyl Carbitol at 150°. The results of these experiments are indicated in Table 15.

With 1.2 equivalents of lithium methoxide 1,1-dimethylcyclopropane (7%), 2-methyl-1-butene (53%), and 2-methyl-2-butene (40%) are formed. When larger excesses of lithium methoxide (1.6 and 3.0 equiv.) are used, the product distribution of 1,1-dimethylcyclopropane (67-68%), 2-methyl-1-butene (15-16%), and 2-methyl-2-butene (17%) remains constant.

It is proposed that when lithium methoxide is employed, lithium ions can complex with 1-diazo-2,2-dimethylpropane or 2,2-dimethylpropylidene to give a metalloid carbonium ion which rearranges to 2-methyl-1-butene and 2-methyl-2-butene (Eq.45). 1,1-Dimethylcyclopropane might also be formed by a metalloid carbonium-ion.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3-\overset{\scriptstyle \text{Li}^+}{\text{CH}} - \overset{\scriptstyle \text{N}_2}{\text{CH}} & \quad \text{CH}_3 \\
\text{CH}_3-\overset{\scriptstyle \text{Li}^+}{\text{CH}} - \overset{\scriptstyle \text{N}_2}{\text{CH}} & \quad \text{CH}_3 - \overset{\scriptstyle \text{Li}^+}{\text{CH}} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 - \overset{\scriptstyle \text{Li}^+}{\text{CH}} & \quad \text{CH}_3 \\
\text{CH}_3 - \overset{\scriptstyle \text{Li}^+}{\text{CH}} & \quad \text{CH}_3 \\
\text{CH}_3 - \overset{\scriptstyle \text{Li}^+}{\text{CH}} & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_3 \\
\end{align*}
\]

(45)
This metalloid carbonium-ion process (~30%) occurs competitively with the carbenic process (~70%). Metalloid carbonium-ion rearrangement is apparently more extensive in the 2,2-dimethylpropyldene system (~30%) than in the 3,3-dimethyl-2-butylidene system (~18%). These results may reflect the lesser hindrance for reaction of a lithium ion with 1-diazo-2,2-dimethylpropane or 2,2-dimethylpropylidene.

Carbenic (minor) (Eq. 43), metalloid carbonium-ion (major) (Eq. 45), and carbonium-ion (major) (Eq. 44) processes probably all contribute to the product distribution obtained with 1.2 equivalents of lithium methoxide.

Closs (38) found 1,1-dimethylcyclopropane (69%), 2-methyl-1-


butene (18%) and 2-methyl-1-butene (13%) to be the products from addition of methylene chloride to tert-butyllithium (Eq. 46). The close

\[
\begin{align*}
CH_3 & \quad C - Li + CH_2Cl_2 \longrightarrow :CHCl + CH_3 - C - H + LiCl \\
CH_3 & \quad C - Li + :CHCl \longrightarrow CH_3 - C - CH + LiCl \\
H_3C & \quad \bigg\downarrow \quad \bigg\downarrow \\
CH_2CH_2 & \quad + CH_2 \quad \quad + CH_3 - C = CH - CH_3 \\
\end{align*}
\]

69% 18% 13% (46)
similarity of the product distributions from the work of Closs and the present study with lithium methoxide may well indicate that similar lithium-complexed carbenes are involved in both systems.

2,2-Dimethylpropanal tosylhydrazone and 2,2-dimethylpropanal benzenesulfonylhydrazone decompose in the presence of potassium tert-butoxide (3.0 equiv.) in diethyl Celbitol at 150° (Table to give 1,1-dimethylcyclopropane (79-83%), 2-methyl-2-butene (3-5%), and 2,2-dimethylpropane (14-16%). 1,1-Dimethylcyclopropane and 2-methyl-2-butene are formed by carbenic processes and in same ratio as with excess sodium methoxide (~20:1). 2,2-Dimethylpropane may result from a process analogous to Wolff-Kishner reduction, initiated in this case by competitive attack of tert-butoxide anion upon sulfonyl group (Eq. 47).

\[
\begin{align*}
&\text{CH}_3 \quad \text{C} - \text{CH}=\text{N}-\text{NH-SO}_2\text{C}_7\text{H}_7 + \text{O-C(CH}_3)_3 \rightarrow (\text{CH}_3)_3\text{-C-O-SO}_2\text{C}_7\text{H}_7 \\
+ &\text{CH}_3 \quad \text{C}-\text{CH-N}=\text{N-H} \rightarrow \text{CH}_3 \quad \text{C}-\text{CH}_2 \quad \text{N}=\text{N} \xrightarrow{N_2} \\
&\text{CH}_3 \quad \text{C} - \text{CH}_2 \quad \text{HOC(CH}_3)_3 \rightarrow \text{CH}_3 \quad \text{C}-\text{CH}_3 + \text{HOC(CH}_3)_3
\end{align*}
\]

(47)

2,2-Dimethylpropanal tosylhydrazone in pentane was treated with n-butyllithium (3.0 equiv.) at room temperature, then heated
at 150° in diethyl Carbitol (Table 15). None of the usual hydrocarbon products could be detected by gas chromatography. Apparently non-carbenoid reactions produced by the excess n-butyllithium occur, but these processes are not understood. A sequence analogous to that proposed by Moseley (6) for 2,2-diphenylpropanal tosylhydrazone, may illustrate the function of excess n-butyllithium in preventing the usual products from being formed (eq. 48). Kirmse (37) decomposed

\[ \text{CH}_3 \quad \text{Li}^+ \quad \text{CH}_3 \quad \text{Li}^+ \]

\[ \text{CH}_3 - \text{C} - \text{CH} = \text{N} - \text{N} - \text{SO}_2 \text{C}_7\text{H}_7 \quad \rightarrow \quad \text{CH}_3 - \text{C} - \text{CH} = \text{N} - \text{N} - \text{SO}_2 \text{C}_7\text{H}_7 \quad \rightarrow \quad \text{CH}_3 \quad \text{Li}^+ \]

\[ \text{CH}_3 \quad \text{Li}^+ \quad \text{CH}_3 \quad \text{Li}^+ \]

\[ \text{CH}_3 - \text{C} - \text{CH} - \text{N} - \text{N} - \text{SO}_2 \text{C}_7\text{H}_7 \quad \rightarrow \quad \text{CH}_3 - \text{C} - \text{CH} - \text{N} - \text{N} - \text{SO}_2 \text{C}_7\text{H}_7 \quad \rightarrow \quad \text{Li}^+ \text{SO}_2 \text{C}_7\text{H}_7 \]

\[ \text{CH}_3 \quad \text{Li}^+ \quad \text{CH}_3 \quad \text{Li}^+ \]

\[ \text{CH}_3 - \text{C} - \text{CH} - \text{N} - \text{N} - \text{SO}_2 \text{C}_7\text{H}_7 \quad \rightarrow \quad \text{CH}_3 - \text{C} - \text{CH} - \text{N} - \text{N} - \text{SO}_2 \text{C}_7\text{H}_7 \quad \rightarrow \quad \text{Li}^+ \text{SO}_2 \text{C}_7\text{H}_7 \]

2,2-dimethylpropanal tosylhydrazone with large excesses (7-8 equiv.) of sodium amide and sodium hydride, but none of the usual hydrocarbon products were found.

From the experimental results for 2,2-dimethylpropanal tosylhydrazone system it can be concluded: 1) the use of at least 1.2 equivalents of sodium methoxide in diethyl Carbitol provides suitable conditions for carbenic processes during thermal decompositions; 2) the use of even larger excesses (3.0 equiv.) of lithium
methoxide results in formation of rearranged products (~30%), probably via lithium carbonium-ion processes; 3) potassium tert-butoxide causes formation of 2,2-dimethylbutane, by a process of the Wolff-Kishner type; and 4) excess amounts of n-butyllithium (3.0 equiv.) are suitable in this system.

During the work on decomposition of tosylhydrazones with various bases, a simple and efficient method was developed to provide comparative data from pyrolyses of prepared salts of these tosylhydrazones. The technique [see Experimental-Gas Chromatography] involves: 1) preparation and isolation of salts of tosylhydrazones with varying equivalents of base; 2) sealing a few milligrams of tosylhydrazone salt (with or without a solvent) in a short (20-25 mm.) section of capillary tubing (1 mm. i.d.); 3) injection of the sealed tube intact into a preheated (150-200°) injector of a gas chromatograph; 4) allowing time for pyrolysis of the sample, then breaking the tip of the tube by external manipulation of a push rod; and 5) analysis of hydrocarbon products of the pyrolysis as they are swept into chromatography column by the carrier gas. This procedure allowed many varied experiments to be performed quickly and simply with small quantities of material. The results of these experiments are reproducible and in good agreement with results obtained from comparable investigations using more elaborate techniques.
CHAPTER 5

Decompositions of Benzenesulfonylhydrazones and Methanesulfonylhydrazones

A comparative study of base-catalyzed decompositions of selected benzenesulfonylhydrazones and methanesulfonylhydrazones was made. The objective of this effort was to evaluate the relative merits of benzenesulfinate and methanesulfinate anions compared to p-toluenesulfinate anion as leaving-groups in thermal decomposition of salts of hydrazones.

The reactions of benzenesulfonylhydrazones of 2,2-dimethylpropanal and 3,3-dimethyl-2-butanone were examined for preparation of 1-diazo-2,2-dimethylpropane and 2-diazo-3,3-dimethylbutane.

Vacuum pyrolysis of pure lithium salt of 3,3-dimethyl-2-butanone benzenesulfonylhydrazone provides 2-diazo-3,3-dimethylbutane (Eq. 49) in 90% yield. The decomposition range (110-125°) and the general decomposition characteristics of the lithium benzenesulfonylhydrazone are substantially identical with those of the lithium tosylhydrazone which (using improved pyrolysis technique) gives 2-diazo-3,3-dimethylbutane in 95% yield.
Pyrolysis of dry lithium salt of 3,3-dimethyl-2-butanone benzenesulfonylhydrazone in capillary tubes within a preheated injector of a gas chromatograph yields four hydrocarbons: 3,3-dimethyl-1-butene (32%), 1,1,2-trimethylcyclopropane (28%), 2,3-dimethyl-1-butene (23%) and 2,3-dimethyl-2-butene (17%). The product distribution agrees favorably with that from a similar pyrolysis of the lithium salt of the tosylhydrazone.

2,2-Dimethylpropanal benzenesulfonylhydrazone is decomposed by potassium tert-butoxide (3.0 equiv.) in diethyl Carbitol at 150° to (Table 16) 1,1-dimethylcyclopropane (83%), 2-methyl-2-butene (3%) and 2,2-dimethyl propane (14%) (Eq. 50).

\[
\begin{align*}
&\text{CH}_3-	ext{C}-\text{CH} = \text{N}-\text{NH-SO}_2\text{C}_6\text{H}_5 \xrightarrow{\text{KOC(CH}_3)_2, 150°} \quad \text{H}_3\text{C}=\text{C}=\text{CH} - \text{CH}_3 \\
&\quad + \quad \text{CH}_3-\text{C}=\text{CH}-\text{CH}_3 \\
&\quad \quad \quad \text{83%} \quad \text{3%}
\end{align*}
\]

This result is almost identical with that for 2,2-dimethylpropanal tosylhydrazone, which under the same conditions yields, 1,1-dimethylcyclopropane (79%), 2-methyl-2-butene (5%), and 2,2-dimethyl propane (16%) (Table 16).

Since there are no appreciable differences in the behavior of tosylhydrazones and benzenesulfonylhydrazones during decomposition, it became of interest to investigate the pyrolytic properties of salts of typical methanesulfonylhydrazones.
TABLE 16

Decomposition* of the Benzenesulfonylhydrazone and the Tosylhydrazone of 2,2-Dimethylpropanal with Potassium tert-
Butoxide in Diethyl Carbitol

| Hydrocarbon Product Distribution$ | 2,2-Dimethylpropanal hydrazone | Benzenesulfonyl-
<table>
<thead>
<tr>
<th></th>
<th>Equiv.(^b) base</th>
<th>hydrazone</th>
<th>Tosylhydrazone</th>
</tr>
</thead>
</table>
| Hydrocarbon Product Distribution$ | 2,2-Dimethylpropanal hydrazone | Benzenesulfonyl-
|                                 | Equiv.\(^b\) base | hydrazone | Tosylhydrazone |
| Hydrocarbon Product Distribution$ | 2,2-Dimethylpropanal hydrazone | Benzenesulfonyl-
|                                 | Equiv.\(^b\) base | hydrazone | Tosylhydrazone |
| Hydrocarbon Product Distribution$ | 2,2-Dimethylpropanal hydrazone | Benzenesulfonyl-
|                                 | Equiv.\(^b\) base | hydrazone | Tosylhydrazone |

* The potassium salts of the hydrazones are formed in situ at 25-40\(^\circ\) in diethyl Carbitol in sealed serum vials, then decomposed at 150\(^\circ\). \(^b\) The amounts of potassium tert-butoxide are corrected for their 95\% purity. \(^$\) Samples of the vapor phase (150\(^\circ\)) are analyzed by gas chromatography [15\% propylene carbonate, 20' x 1/4", 60/80 Chromosorb G(reg.), 10-15\(^\circ\)].
In vacuum pyrolysis of the lithium salt of 2-butanone tosylhydrazone, decomposition occurs rapidly at 170-180° to give hydrocarbons; 2-diazobutane is not obtained. A study was made of the methanesulfonylhydrazone of 2-butanone to determine if its decomposition temperature is significantly lower than that of 2-butanone tosylhydrazone. Vacuum pyrolysis of the lithium salt of 2-butanone methanesulfonylhydrazone occurs at 80-100°; however, the diazo compound was not isolated. Decomposition reactions of lithium salts of methanesulfonylhydrazones are apparently complex, and they are not understood at this time.

Addition of n-butyllithium to tosylhydrazones or to benzenesulfonylhydrazones results in transient, intense, yellow-red solutions. Such coloration is absent during addition of n-butyllithium to all of the methanesulfonylhydrazones of the present study.

Higher temperatures (148-162°) are necessary to vacuum pyrolyze the lithium salt of 2,2-dimethylpropanal methanesulfonylhydrazone. 1-Diazo-2,2-dimethylpropane is obtained in poor yield (23%), and the volatile products and the residue are extremely malodorous. Pyrolysis of the lithium salt of 3,3-dimethyl-2-butanone methanesulfonylhydrazone, in sealed capillary tubes in a preheated gas chromatographic injector, also occurs inefficiently to give complex, malodorous products.

A study was then made of decomposition of methanesulfonylhydrazones by sodium methoxide in suspension in aprotic solvents. Decomposition of 2,2-dimethylpropanal methanesulfonylhydrazone was effected in diethyl Carbitol in sealed serum vials [see Experimental]
with 1.2 and 3.0 equivalents and compared with that for the tosylhydrazone under the same conditions (Table 17). With 1.2 equivalents of sodium methoxide, the methanesulfonylhydrazone gives rearrangement products almost completely (Eq. 51), whereas the tosylhydrazone

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3-C-\text{CH}=\text{N}-\text{NH-SO}_2\text{CH}_3 & \xrightarrow{\text{NaOCH}_3(1.2\ \text{equiv.)}} & \quad \text{H}_3\text{C} \quad \text{CH}_3 \\
\text{DEC, 150°} & & & \quad \text{CH}_2 \quad \text{CH}_3 \\
\text{CH}_3 & + \ H_2\text{C} = \text{C} - \text{CH}_2 - \text{CH}_3 & + & \text{CH}_3 - \text{C} = \text{CH} - \text{CH}_3 \\
\text{60%} & & & \text{38%} \quad \text{(51)}
\end{align*}
\]

yields primarily the insertion product. Use of 3 equivalents of sodium methoxide results (Table 17) in a much more similar mixture of products from the methanesulfonylhydrazone and the tosylhydrazone. It is apparent from the results that the methanesulfonylhydrazone follows a more cationic decomposition route than does the tosylhydrazone, even in the presence of a large excess of sodium methoxide.

3,3-Dimethyl-2-butanone methanesulfonylhydrazone and tosylhydrazone were decomposed by sodium methoxide at 150° in diethyl Carbitol in sealed serum vials [see Experimental]. The percentage distribution of hydrocarbon products varies with the amount of the initial base (Table 18). In this system when 1.2 equivalents of sodium methoxide are used, carbon-skeletal rearrangement is greater with the methanesulfonylhydrazone than with the tosylhydrazone; however, with 3 equivalents of base, the carbenic response of
TABLE 17
Decompositions$^a$ of the Methanesulfonylhydrazone and the Tosylhydrazone of 2,2-Dimethylpropanal with Sodium Methoxide in Diethyl Carbitol

<table>
<thead>
<tr>
<th>Hydrocarbon Product Distribution$^b$</th>
<th>2,2-Dimethyl-propanal hydrazone</th>
<th>2,2-Dimethyl-propanal hydrzone base</th>
<th>Methanesulfonyl-hydrazone</th>
<th>Methanesulfonyl-hydrazone base</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methanesulfonyl-hydrazone</td>
<td>1.2</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Tosylhydrazone</td>
<td>1.2</td>
<td>96</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Methanesulfonyl-hydrazone</td>
<td>3.0</td>
<td>81</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Tosylhydrazone</td>
<td>3.0</td>
<td>95</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ The sodium salts of the hydrazones are formed in situ at 25-40° in diethyl Carbitol in sealed vials, then decomposed at 150°.
$^b$ The amounts of sodium methoxide are corrected for their 97.5% purity. $^c$ Samples of the vapor phase (150°) are analyzed by gas chromatography [15% propylene carbonate, 20' x 1/4", 60/80 Chromosorb G (reg.), 10-15°].
TABLE 18

Decompositions\(^{a}\) of the Methanesulfonylhydrazone and the Tosylhydrazone of 3,3-Dimethyl-2-butane with Sodium Methoxide in Diethyl Carbitol

<table>
<thead>
<tr>
<th>3,3-Dimethyl-2-butane hydrazone</th>
<th>Hydrocarbon Product Distribution(^{c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equiv. base</td>
<td>CH(_3)-C-CH=CH(_2)</td>
</tr>
<tr>
<td>Methanesulfonylhydrazone</td>
<td>1.2</td>
</tr>
<tr>
<td>Tosylhydrazone</td>
<td>1.2</td>
</tr>
<tr>
<td>Methanesulfonylhydrazone</td>
<td>3.0</td>
</tr>
<tr>
<td>Tosylhydrazone</td>
<td>3.0</td>
</tr>
</tbody>
</table>

\(^{a}\) The sodium salts are prepared in situ at 25-40° in diethyl Carbitol in sealed serum vials, then decomposed at 150°. \(^{b}\) The amounts of sodium methoxide are corrected for their 97.5% purity. \(^{c}\) Samples of the vapor phase (150°) are analyzed by gas chromatography [15% propylene carbonate, 20' x 1/4", 60/80 Chromosorb G. (reg.), 10-15°].
the methanesulfonylhydrazone is essentially identical with that of the tosylhydrazone (Table 18).

The results of this portion of the present study thus show that behavior of tosylhydrazones and benzenesulfonylhydrazones are essentially identical, whereas methanesulfonylhydrazones are generally of disadvantage in that they give diazo compounds inefficiently and they undergo effective carbenic decomposition only in the presence of large excesses of sodium methoxide.
An investigation of thermolysis of 2-diazo-3,3-dimethylbutane and 1-diazo-2,2-dimethylpropane was initiated. The main objective of this study was to determine the effects of selected variables upon the processes responsible for the various products of thermolysis. The variables investigated include temperature, solvent effects, acid and base catalysis, selected reactants, and reactor composition. 2-Diazo-3,3-dimethylbutane and 1-diazo-2,2-dimethylpropane were studied because they can be prepared in excellent yields and purity by vacuum pyrolysis of lithium salts of their respective tosylhydrazones and information concerning reactions, in which the diazo compounds are generated as intermediates, is available from the previous study.

2-Diazo-3,3-dimethylbutane (92% yield, 95% purity) was prepared from the lithium salt of 3,3-dimethyl-2-butanone tosylhydrazone [see Experimental], analyzed for yield and purity, then stored under nitrogen in a sealed serum vial at -78° and protected from light. Small samples (0.05 ml., 0.58 millimole) of the diazo compound were transferred with chilled, dry syringes and injected into dry, nitrogen-flushed, sealed serum vials (specially treated) for the thermolyses [see Experimental]. "Fast thermolyses" were accomplished by placing the sealed vials in a preheated aluminum block (Fig. 10) at 150°;
"slow thermolyses" were effected by heating a sample vial from room temperature to 100-130° in 60-120 minutes, or by allowing a sample (protected from light) to warm from -78° to room temperature overnight. In all cases samples were taken in the gas phase from the vials at 150° and analyzed by gas chromatography [15% propylene carbonate, 20" x 1/4", 60/80 Chromosorb G (reg.), 10-15°]. The results of these experiments are shown in Table 19.

2-Diazo-3,3-dimethylbutane (neat) thermolyses rapidly at 150° in a glass vial to give 3,3-dimethyl-1-butene (49%), 1,1,2-trimethyl-cyclopropane (40%), 2,3-dimethyl-1-butene (9%), and 2,3-dimethyl-2-butene (2%). As expected, the products formed by carbenic processes not involving carbon-skeletal rearrangements greatly predominate (89%). By contrast, a neat sample of the diazoalkane in a glass vial thermolyses slowly (25-150°, 30 minutes) to yield a greatly different product mixture (Table 19): 3,3-dimethyl-1-butene (24%), 1,1,2-trimethylcyclopropane (22%), 2,3-dimethyl-1-butene (33%), and 2,3-dimethyl-2-butene (21%). 2-Diazo-3,3-dimethylbutane (neat) slowly thermolyses at room temperature overnight in dry Teflon and in dry stainless steel vials to give products nearly identical in composition to that obtained from the slow thermolysis in glass vials (see Table 19). It would appear that the thermolytic processes are virtually independent of surface characteristics (or less likely, similarly dependent on the surface characteristics) of the containers.

In the presence of lithium methoxide (10.0 equiv.), the diazo compound in diethyl Carbitol in a glass vial decomposes upon slow heating (25-100°, 30 minutes) to 3,3-dimethyl-1-butene (34%);
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Reactant</th>
<th>Reaction mode</th>
<th>Reaction temp.</th>
<th>Hydrocarbon product distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat</td>
<td>none</td>
<td>fast</td>
<td>150°C</td>
<td>CH₃-C-CH=CH₂: CH₃-C=CH₃: CH₃ = C-CH₃</td>
</tr>
<tr>
<td>neat</td>
<td>none</td>
<td>slow</td>
<td>25-150°C</td>
<td>49: 24: 21</td>
</tr>
<tr>
<td>neat</td>
<td>Teflon</td>
<td>slow</td>
<td>25°C</td>
<td>29: 24: 17</td>
</tr>
<tr>
<td>neat</td>
<td>stainless steel</td>
<td>slow</td>
<td>25°C</td>
<td>25: 23: 21</td>
</tr>
<tr>
<td>neat</td>
<td>DEC</td>
<td>slow</td>
<td>25-100°C</td>
<td>34: 26: 16</td>
</tr>
<tr>
<td>neat</td>
<td>NaOCH₂</td>
<td>slow</td>
<td>25-150°C</td>
<td>37: 26: 18</td>
</tr>
<tr>
<td>neat</td>
<td>DEC</td>
<td>slow</td>
<td>-78 to 25°C</td>
<td>27: 24: 19</td>
</tr>
<tr>
<td>decalin</td>
<td>none</td>
<td>slow</td>
<td>-78 to 25°C</td>
<td>29: 22: 15</td>
</tr>
<tr>
<td>pentane</td>
<td>none</td>
<td>slow</td>
<td>25°C</td>
<td>21: 20: 31</td>
</tr>
<tr>
<td>pentane</td>
<td>iodobenzene</td>
<td>none</td>
<td>-78 to 25°C</td>
<td>30: 24: 31</td>
</tr>
<tr>
<td>pentane</td>
<td>TBA</td>
<td>slow</td>
<td>25-150°C</td>
<td>32: 28: 16</td>
</tr>
<tr>
<td>pentane</td>
<td>LiSO₂C₇H₁₇</td>
<td>fast</td>
<td>150°C</td>
<td>47: 37: 10</td>
</tr>
<tr>
<td>neat</td>
<td>PINTHZLk</td>
<td>fast</td>
<td>150°C</td>
<td>46: 38: 10</td>
</tr>
<tr>
<td>neat</td>
<td>DEC</td>
<td>&quot;fast&quot;</td>
<td>25°C</td>
<td>53: 16: 21</td>
</tr>
<tr>
<td>neat</td>
<td>copper</td>
<td>slow</td>
<td>25°C</td>
<td>31: 22: 30</td>
</tr>
<tr>
<td>DEC</td>
<td>AgNO₃</td>
<td>&quot;fast&quot;</td>
<td>25°C</td>
<td>36: 20: 25</td>
</tr>
</tbody>
</table>
**TABLE 19 (Cont.)**

<table>
<thead>
<tr>
<th>Solvent (1-ml.)</th>
<th>Reactant</th>
<th>Reaction mode</th>
<th>Reaction temp.</th>
<th>Hydrocarbon product distribution b</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME</td>
<td>Fe(DPM)</td>
<td>slow</td>
<td>25-100°</td>
<td>CH₃-H-C=CH=CH₂ H₂C=CH₂ H₂C=CH₃ CH₃ \ CH₃-CH=CH₃</td>
</tr>
<tr>
<td>DME</td>
<td>FeCl₃</td>
<td>&quot;fast&quot;</td>
<td>25</td>
<td>28  21  33  18</td>
</tr>
<tr>
<td>octane</td>
<td>AlCl₃</td>
<td>&quot;fast&quot;</td>
<td>0</td>
<td>18  7   20  55</td>
</tr>
<tr>
<td>EG</td>
<td>EG</td>
<td>slow</td>
<td>25-150°</td>
<td>40  30  19  11</td>
</tr>
<tr>
<td>EG/DEC</td>
<td>SO₂CO₂H</td>
<td>&quot;fast&quot;</td>
<td>25</td>
<td>25  15  42  18</td>
</tr>
</tbody>
</table>

a The reactions were conducted upon the diazo compound (0.05 ml., 0.58 millimole) sealed in glass serum vials. b In all cases samples were taken in the gas phase from the vials at 150° and analyzed by gas chromatography [15% propylene carbonate, 20' x 1/4", 60/80 Chromosorb G (reg.), 10-15%]. £ Fast thermolytic reactions were effected by placing the sealed vials in a preheated block at 150°; slow thermolytic reactions were accomplished by heating the sealed vials from 25-150° in 60-120 minutes, or by allowing a sample (protected from light) to warm from -78° to 25° overnight. A A Teflon vial was used. £ A stainless steel vial was used. f DME is an abbreviation for diethyl carbonate. e Ten equivalents (based on amount of diazo compound) of LiOCH₃ were used. ™ Ten equivalents of NaOCH₃ were used. TBA is an abbreviation for tri-n-butylamine. Three equivalents of LiSO₂C₆H₅ were used. P PINTHZLi is an acronym for the lithium salt of 3,3-dimethyl-2-butanone (pinacolone) tosyldiazonane. l Three equivalents of powdered, anhydrous cupric sulfate were used. "fast" catalytic reactions of the diazoalkane were completed within seconds at 25°. A Powdered copper (10 equiv.) was used. Fe(DPM)₃ is ferric dipivaloylmethide (0.05 equiv.). Anhydrous, powdered ferric chloride (1 equiv.) was used. Anhydrous, powdered aluminum chloride (0.1 equiv.) was used, then quenched with aqueous sodium hydroxide. EG is purified, anhydrous ethylene glycol.
1,1,2-trimethylcyclopropane (26%), 2,3-dimethyl-1-butene (24%), and 2,3-dimethyl-2-butene (16%). Similarly, neat 2-diazo-3,3-dimethylbutane containing sodium methoxide (10.0 equiv.) thermolyzes slowly (25-150°, 120 minutes) to 3,3-dimethyl-1-butene (27%), 1,1,2-trimethylcyclopropane (26%), 2,3-dimethyl-1-butene (29%), and 2,3-dimethyl-2-butene (18%). The apparent effect of these bases upon product distribution in these two experiments is minimal. These results indicate: 1) that protonic contamination by container surfaces is either absent or ineffectual and/or 2) that the diazo compound itself is not contaminated by protonic impurities.

In experiments to evaluate solvent effects upon processes involved in slow thermolyses of 2-diazo-3,3-dimethylbutane, samples of the diazoalkane in diethyl Carbitol, decalin, pentane, iodobenzene, and tri-n-butylamine were decomposed in sealed glass vials in darkness at room temperature overnight. The results (Table 19) of these experiments are in good agreement with those from slow thermolyses of neat samples of the diazo compound. Although there are minor deviations in the product distribution when different solvents are used, there are no distinct trends. Table 20 illustrates the nearly identical average product distributions for a series of "slow thermolyses" of 2-diazo-3,3-dimethylbutane in aprotic solvents (diethyl Carbitol, decalin, pentane, iodobenzene, and tri-n-butylamine). It is apparent that processes operating during thermolysis of 2-diazo-3,3-dimethylbutane are highly temperature dependent, but nearly independent of inert surface characteristics and solvent effects (polarity, not proticity). Also, the processes occurring in a "slow
TABLE 20

Summary of "Slow Thermolyses" of 2-Diazo-3,3-dimethylbutane

<table>
<thead>
<tr>
<th>Hydrocarbon Products - Average Distribution&lt;sup&gt;b&lt;/sup&gt;</th>
<th>CH₃</th>
<th>H₂C - C - CH - CH₃</th>
<th>H₂C = C - CH - CH₃</th>
<th>CH₃ - C = C - CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction mode</td>
<td>CH₃</td>
<td>CH₂-CH-CH₃</td>
<td>CH₃ CH₃</td>
<td>CH₃ CH₃</td>
</tr>
<tr>
<td>neat&lt;sup&gt;a&lt;/sup&gt;</td>
<td>26</td>
<td>23</td>
<td>31</td>
<td>20</td>
</tr>
<tr>
<td>solution&lt;sup&gt;d&lt;/sup&gt;</td>
<td>28</td>
<td>23</td>
<td>30</td>
<td>19</td>
</tr>
</tbody>
</table>

<sup>a</sup> "Slow thermolyses" are accomplished by heating the diazo compound (neat or with solvent and/or reagent) from 25-130° in 60-120 minutes or by allowing the mixture to warm from -78 to 25° overnight.

<sup>b</sup> Samples of the vapor phase (150°) in the sealed vial are analyzed by gas chromatography [15% propylene carbonate, 20′ x 1/4", 60/80 Chromosorb G (reg.), 10-15°].

<sup>c</sup> "Slow thermolyses" of neat diazo compound were conducted in glass, Teflon, and stainless steel vials (Table 19).

<sup>d</sup> "Slow thermolyses" of samples of 2-diazo-3,3-dimethylbutane were effected in diethyl Carbitol, decalin, pentane, iodobenzene, and tri-n-butylamine (Table 19). 1 ml. of each solvent was used.
thermolysis" of the diazoalkane are not appreciably altered by the presence of strong bases (lithium methoxide and sodium methoxide). This apparent lack of effect of strong bases tends to minimize the probability that the significant increase (30-40%, absolute) of rearrangement products is caused by carbonium-ion processes during "slow thermolysis" of the diazo compound.

To explain the profound variance in the product apportionments that result from "slow and fast thermolyses" of 2-diazo-3,3-dimethylbutane, it is possible that different spin states of the carbene are responsible. At 150°, the diazo compound decomposes to nitrogen and singlet 3,3-dimethyl-2-butyldiene (Eq. 52).

\[
\begin{align*}
\text{CH}_3\text{N}_2^+ + \text{CH}_3 & \rightarrow \text{N}_2 + \text{CH}_3\text{C} = \text{CH}_2 \\
\text{CH}_3 & \rightarrow \text{CH}_3\text{C} = \text{CH}_2 
\end{align*}
\] (52)

At this relatively high temperature the singlet carbene undergoes hydrogen rearrangement or inserts (cyclopropane formation) before spin inversion can occur (Eq. 53 and 54). At much lower temperatures

\[
\begin{align*}
\text{CH}_3\text{C} = \text{CH}_2 & \rightarrow \text{CH}_3\text{C} - \text{CH} = \text{CH}_2 \\
\text{H}_2\text{C} - \text{C} & \rightarrow \text{CH}_3\text{C} - \text{CH} = \text{CH}_2
\end{align*}
\] major (53)

\[
\begin{align*}
\text{CH}_3\text{C} - \text{C} & \rightarrow \text{CH}_3\text{C} - \text{CH} = \text{CH}_2 \\
\text{CH}_3 & \rightarrow \text{CH}_3\text{C} - \text{CH} = \text{CH}_2
\end{align*}
\] major (54)
(25° or lower) the diazo compound decomposes to singlet carbene which may undergo spin inversion to triplet carbene. The triplet carbene is of lower energy and should undergo different rearrangement processes. Possible routes by which the observed "slow thermolysis" products may arise are shown (Eq. 55).

\[
\begin{align*}
\text{singlet} & : \quad \text{CH}_3 - C - C - \text{CH}_3 \rightleftharpoons \text{CH}_3 - C - C - \text{CH}_3 \rightarrow \text{CH}_3 - C - C - \text{CH}_3 \\
\text{triplet} & : \quad \text{CH}_3 - C - C - \text{CH}_3 \rightarrow \text{CH}_3 - C - C - \text{CH}_3 \rightarrow \text{CH}_3 - C - \text{CH} = \text{CH}_2 \\
& \quad \quad \downarrow \quad \quad \downarrow \\
& \quad \quad \text{H}_2\text{C}^* \quad \quad \text{H}_2\text{C}^* \\
& \quad \quad \text{CH}_3 - C - \text{CH} = \text{CH}_3 \rightarrow \text{H}_3\text{C} - C - \text{CH}_3 \\
& \quad \quad \quad \downarrow \\
& \quad \quad \text{H}_2\text{C}^* \\
& \quad \quad \text{CH}_3 - C - \text{CH}_3 \\
\end{align*}
\]

(55)

A study of thermolytic and catalytic reactions of 2-diazo-3,3-dimethylbutane with solid reagents was initiated (Table 19). Thermolysis of the neat diazoalkane ("fast," 150°) in the presence
of lithium p-toluenesulfinate (3.0 equiv.) yields (Table 19) 3,3-dimethyl-1-butene (47%), 1,1,2-trimethylcyclopropane (37%), 2,3-dimethyl-1-butene (10%), and 2,3-dimethyl-2-butene (6%). Previously it was found that pyrolysis of pure, dry lithium salt of 3,3-dimethyl-2-butanone tosylhydrazone at atmospheric pressure and 150° gives (Table 19) an identical product distribution (46:38:10:6), and rapid thermolysis of neat 2-diazo-3,3-dimethylbutane results in 3,3-dimethyl-1-butene (49%), 1,1,2-trimethylcyclopropane (40%), 2,2-dimethyl-1-butene (9%), and 2,3-dimethyl-2-butene (2%). The slight increase (5%, absolute) in the amount of carbon skeleton rearranged products found when lithium p-toluenesulfinate is present may be due to a slight lithium cation effect, similar to that discussed previously, but greatly diminished in effect because there is no real solvent to dissolve the lithium salts.

Cold 2-diazo-3,3-dimethylbutane decolorizes immediately (39)

(39) When cold 2-diazo-3,3-dimethylbutane is injected into diethyl Carbitol at 25° the orange color of the solution persists for a finite time (30-120 minutes).

upon injection into a suspension of finely powdered, anhydrous copper sulfate (3.0 equiv.) in diethyl Carbitol at room temperature. Analyses of hot (150°), gas-phase samples reveal an unusual product distribution (Table 19): 3,3-dimethyl-1-butene (53%), 1,1,2-trimethylcyclopropane (16%), 2,3-dimethyl-1-butene (21%), and 2,3-dimethyl-2-butene (10%). This product distribution is significantly different from that (27:24:30:19) for slow thermolysis of the diazoalkane in diethyl Carbitol at room temperature.
By contrast, a neat, cold sample of 2-diazo-3,3-dimethylbutane injected into a glass vial at room temperature containing powdered copper (10 equiv.) and allowed to decompose at room temperature gives 3,3-dimethyl-1-butene (31%), 1,1,2-trimethylcyclopropane (22%), 2,3-dimethyl-1-butene (30%), and 2,3-dimethyl-2-butene (17%). This product distribution (Table 19) is closer to that for slow, neat thermolysis of the diazoalkane (26:23:31:20), and it is difficult to assess the effect or contribution of the copper powder apart from slow thermal processes.

Copper sulfate, however, apparently exerts a definite influence in that an unusually large amount of 3,3-dimethyl-1-butene is formed. This increase is compensated by equally divided losses of the other three products. A small amount of reddish-brown residue, possibly reduced copper, appears upon heating the mixture to 150° for sampling, but black, colloidal copper is not observed.

One possible interpretation of the catalytic decomposition of 2-diazo-3,3-dimethylbutane by cupric sulfate involves reduction of cupric ion to colloidal copper. Upon loss of nitrogen, the singlet 3,3-dimethyl-2-butylidene may undergo instantaneous spin inversion in the presence of a heavy metal atom to form a triplet carbene complexed on the copper metal surface (Eq. 56).

\[ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 + \text{Cu} \rightarrow \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \]  
\[ \rightarrow \text{CH}_3 - \text{N}_2^* \]  
\[ \rightarrow \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \]  
\[ \rightarrow \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \]  
\[ \rightarrow \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \]  
(56)
Such a copper-complexed triplet carbene might rearrange by the following scheme to form the observed products (Eq. 57).

(57)

A second possible explanation for the catalytic effect of cupric sulfate upon the decomposition of 2-diazo-3,3-dimethylbutane in diethyl carbonate at 25° concerns the formation of a metalloid carbonium-ion with either cupric or cuprous ions (Eq. 58). Such a
metalloid carbonium ion may rearrange to yield the observed products (Eq. 59).

\[
\begin{align*}
\text{CH}_3 - &\stackrel{+}{C} - \text{CH}_2 \xrightarrow{-\text{H}^+} \text{CH}_3 - &\stackrel{+}{C} - \text{CH}_3 \quad \text{CH}_3 - &\stackrel{+}{C} - \text{CH} = \text{CH}_2 \\
\text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+
\end{align*}
\]

major (53%) 

\[
\begin{align*}
\text{CH}_3 - &\stackrel{+}{C} - \text{CH}_3 \xrightarrow{-\text{H}^+} \text{CH}_3 - &\stackrel{+}{C} - \text{CH}_3 \xrightarrow{-\text{Cu}^{++}} \text{CH}_3 - &\stackrel{+}{C} - \text{CH} - \text{CH}_3 \\
\text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+
\end{align*}
\]

minor (16%) 

\[
\begin{align*}
\text{CH}_3 - &\stackrel{+}{C} - \text{CH}_3 \xrightarrow{-\text{H}^+} \text{CH}_3 - &\stackrel{+}{C} - \text{CH}_3 \xrightarrow{-\text{Cu}^{++}} \text{CH}_2 = &\stackrel{+}{C} - \text{CH} - \text{CH}_3 \\
\text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+
\end{align*}
\]

minor (21%) 

\[
\begin{align*}
\text{CH}_3 - &\stackrel{+}{C} - \text{CH}_3 \xrightarrow{-\text{H}^+} \text{CH}_3 - &\stackrel{+}{C} - \text{CH}_3 \xrightarrow{-\text{Cu}^{++}} \text{CH}_3 - &\stackrel{+}{C} = \text{CH} - \text{CH}_3 \\
\text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+ &\quad \text{CH}_3 \text{Cu}^+
\end{align*}
\]

minor (10%) 

(59)

A third possible process to describe the catalytic decomposition of 2-diazo-3,3-dimethylbutane by cupric sulfate in diethyl Cerbitol at 25° involves the abstraction of an electron from 2-diazo-3,3-dimethylbutane or 3,3-dimethyl-2-butylidene by cupric or cuprous ion (Eq. 60). Cupric ion would be reduced to cuprous ion, which
in turn could be reduced to metallic copper. If such a process is operative, loss of a proton from the α-methyl group (Eq. 61) and abstraction of a hydrogen atom from the solvent (SH), to give 3,3-dimethyl-1-butene (53%), must occur. The other products can arise by seemingly less favorable rearrangements (Eq. 62). Hydrogen-atom abstraction from the environment by an intermediate radical specie may be a necessary step in this radical-cationic process. Analysis for deuterium incorporation into the products following cupric sulfate-catalyzed decomposition of the diazo compound in a deuterated, aprotic solvent could provide information concerning such a process.
Injection of cold, neat 2-diazo-3,3-dimethylbutane into a saturated solution of silver nitrate (1 equiv.) in diethyl Carbitol at room temperature causes immediate formation of black colloidal silver which gradually forms a mirror. During formation of the silver precipitate, heat is evolved and 3,3-dimethyl-1-butene (35%), 1,1,2-trimethylcyclopropane (20%), 2,3-dimethyl-1-butene (25%), and 2,3-dimethyl-2-butene (19%) are formed (Table 19). Silver ion may be functioning in a manner similar to copper ion, possibly by abstraction of an electron from the diazo compound or the carbene to give a radical-cation (Eq. 63). The proposed rearrangement route for
the radical-cation has been shown previously (Eq. 61). The product distribution for decomposition of 2-diazo-3,3-dimethylbutane in the presence of silver nitrate (36:20:25:19) shows less product discrimination than with copper sulfate (53:16:21:19). Perhaps the bulkier (ionic radius 1.26Å) silver ion is less effective for generating a radical-cation than is a cupric ion (ionic radius 0.70Å) or cuprous ion (ionic radius 0.96Å) and the product composition reflects larger contributions from triplet carbenic rearrangements. Alternatively, perhaps the silver ion is more easily reduced to metallic silver which may less effectively influence rearrangement processes than copper metal.

Slow decomposition of 2-diazo-3,3-dimethylbutane (25°, 15 minutes; 25-100°, 45 minutes) in diethyl Carbitol containing ferric dipivaloylmethide (40) (0.05 equiv.) (Table 19) results in 3,3-dimethyl-1-butene
This material was graciously provided by Dr. J. S. Swen-
ton.

(28%), 1,1,2-trimethylcyclopropane (21%), 2,3-dimethyl-1-butene (33%), and 2,3-dimethyl-2-butene (18%). This product distribution is very similar to that obtained from the diazo compound in diethyl Carbitol alone (27:24:30:19); the chelate ferric reagent $[\text{Fe(DPM)}_3]$ has very little apparent effect upon rearrangement processes in this system (41).

(41) K. R. Kopecky, G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc., 84, 1015 (1962), report the addition product, norcarane, as the sole product when diazomethane is decomposed by $[\text{Fe(DPM)}_3]$ in cyclohexene in the dark at 25°. They attribute this result to formation of "a charge-transfer complex of triplet methylene with some metallic species." Thermolysis (265°) of diazomethane in cyclohexene (without $[\text{Fe(DPM)}_3]$) gave a mixture of addition and insertion products.

2-Diazo-3,3-dimethylbutane reacts vigorously with an equivalent of ferric chloride in diethyl Carbitol at 25° (Table 19) to form 3,3-dimethyl-1-butene (18%), 1,1,2-trimethylcyclopropane (7%), 2,3-dimethyl-1-butene (20%), and 2,3-dimethyl-2-butene (55%). In a similar experiment, the diazo compound reacts immediately with anhydrous aluminum chloride (0.1 equiv.) in octane at 0°. After five minutes at 0°, the mixture was quenched with aqueous sodium hydroxide and heated to 150° for sampling. The products obtained are 3,3-dimethyl-1-butene (27%), 1,1,2-trimethylcyclopropane (20%), 2,3-dimethyl-1-butene (16%), and 2,3-dimethyl-2-butene (37%). This experiment, in which the aluminum chloride is quenched, may give a
product distribution that more closely corresponds to that of the primary process.

Diethyl Carbitol and decalin both are unsuitable solvents with the strong Lewis acid catalysts. Each solvent (diethyl Carbitol or decalin) reacts with ferric chloride or aluminum chloride at room temperature and this situation becomes worse when the reaction products are heated to 150°, for sampling.

The reaction scheme shown below illustrates a possible course for the action of a Lewis acid upon 2-diazo-3,3-dimethylbutane (Eq. 64 and Eq. 65).
In the experiment in which ferric chloride was used, but not quenched, isomerization of 3,3-dimethyl-1-butene, 1,1,2-trimethylcyclopropane, and 2,3-dimethyl-1-butene by the strong Lewis acid may account for the high percentage of 2,3-dimethyl-2-butene found in vapor-phase samples taken at 150° (Eq. 66, Eq. 67 and Eq. 68).

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

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

\[
\begin{align*}
\text{CH}_3 \quad \text{FeCl}_3 \\
\text{CH}_3 - \text{C} - \text{CH} = \text{CH}_2 & \quad \rightarrow \quad \text{CH}_3 - \text{C} - \text{CH} = \text{CH}_2 - \text{FeCl}_3 \\
\text{CH}_3 & \quad \rightarrow \quad \text{CH}_3 - \text{C} - \text{CH} = \text{CH}_2 - \text{FeCl}_3 \\
\end{align*}
\]
It is difficult to assess the effect of Lewis acid catalysis upon 2-diazo-3,3-dimethylbutane because of several complicating factors: 1) the Lewis acids vigorously attack diethyl Carbitol (acetaldehyde odor is very noticeable) and decalin, especially when the mixtures are heated to 150° for sampling; 2) the hydrocarbon products can be isomerized (secondary processes) by the Lewis acid catalyst; and 3) competitive carbenic and classical carbonium-ion processes may contribute to any and/or all products formed. It is probable that the main function of the Lewis acid catalyst is to complex with a pair of electrons of the 2-diazo-3,3-dimethylbutane or 3,3-dimethyl-2-butylidene and promote carbonium-ion type rearrangements.

Decomposition of 2-diazo-3,3-dimethylbutane in protic solvents and reactants was investigated. Cold 2-diazo-3,3-dimethylbutane was injected into ethylene glycol at room temperature. The diazoalkane is insoluble in ethylene glycol; after 10 minutes the mixture was rapidly heated to 150° for gas chromatographic sampling. The products (Table 19), 3,3-dimethyl-1-butene (40%), 1,1,2-trimethylcyclopropane (30%), 2,3-dimethyl-1-butene (19%), and 2,3-dimethyl-2-butene (11%), are probably derived from composite low and high temperature thermolytic, and carbonium-ion processes initiated by proton-donating ethylene glycol. The proton-donating function of ethylene glycol is greatly
diminished by the insolubility of the diazo compound in the solvent. Part of the diazo compound apparently decomposes at room temperature, possibly by singlet and triplet processes. The undecomposed diazo compound thermolyzes when heated to 150°C; at this higher temperature, the singlet process (hydrogen migration or insertion) apparently becomes of increased importance.

When cold 2-diazo-3,3-dimethylbutane is injected into benzoic acid (3.0 equiv.) in diethyl Carbitol—ethylene glycol at room temperature, the orange-red color of the diazo compound immediately disappears. The product distribution (Table 19), 3,3-dimethyl-1-butene (25%), 1,1,2-trimethylcyclopropane (15%), 2,3-dimethyl-1-butene (42%), and 2,3-dimethyl-2-butene (18%), reveals that large amounts (60%) of carbon-skeleton rearranged products are produced. The preponderance of 2,3-dimethyl-1-butene is expected from carbonium-ion processes initiated by benzoic acid (Eq. 69). Evidently, acid catalysis by a relatively weak acid like benzoic acid is not as effective in causing isomerization (secondary processes) of hydrocarbon products as are the Lewis acids.
To extend the study of thermolytic and catalytic reactions of diazoalkanes, an investigation of 1-diazo-2,2-dimethylpropane was conducted.

1-Diazo-2,2-dimethylpropane was prepared (100% yield, 98% purity) by vacuum pyrolysis of pure, dry lithium salt of 2,2-dimethylpropanal tosylhydrazone [see Experimental], and stored neat and dark at -80° under nitrogen in a sealed, glass serum vial. Small samples (0.05 ml., ~0.58 millimole) were transferred with chilled, dry syringes and injected into cold (-40 to -80°) nitrogen-flushed vials [see Experimental]. If solvents (purified) were used, the sealed vial and solvent were evacuated and flushed with nitrogen, chilled, then inverted so that cold (-80°) diazo compound could be injected upwards through the rubber serum stopper into cold solvent. For solid reactants in solvents, the same procedure was used [see Experimental].

"Fast thermolyzes" were effected by placing the sealed vials in a preheated aluminum block (Fig. 10) at 150°; "slow thermolyzes" were accomplished by allowing a sample in a sealed vial (protected from light) to warm from -78 to 25° overnight. In all cases samples were taken in the gas phase from the vials at 150° (except where specifically noted) and analyzed by gas chromatography [15% propylene carbonate, 20' x 1/4", 60/80 Chromosorb G (reg.), 10-15°]. The results of these experiments are summarized in Table 21.

Neat 1-diazo-2,2-dimethylpropane in a glass vial decomposes thermally (45-60 sec.) at 150° (Table 21) to 1,1-dimethylcyclopropane (80%), 2-methyl-1-butene (1%), and 2-methyl-2-butene (19%). As
<table>
<thead>
<tr>
<th>Solvent (1 ml.)</th>
<th>Reactant</th>
<th>Reaction mode</th>
<th>Reaction temp.</th>
<th>Hydrocarbon product distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat</td>
<td>none</td>
<td>fast</td>
<td>150°</td>
<td>( \begin{align*} \text{H}_3\text{C} &amp; \text{CH}_3 \ \text{CH}_2 &amp; \text{CH}_2 \end{align*} )</td>
</tr>
<tr>
<td>neat</td>
<td>none</td>
<td>slow</td>
<td>25</td>
<td>( \begin{align*} 80 &amp; 1 \ 4 &amp; 43 \end{align*} )</td>
</tr>
<tr>
<td>neat</td>
<td>stainless steel</td>
<td>slow</td>
<td>25</td>
<td>( \begin{align*} 9 &amp; 9 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>neat</td>
<td>Teflon®</td>
<td>slow</td>
<td>25</td>
<td>( \begin{align*} 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>decalin</td>
<td>none</td>
<td>fast</td>
<td>150°</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>decalin</td>
<td>none</td>
<td>fast</td>
<td>150°</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>octane</td>
<td>none</td>
<td>fast</td>
<td>150°</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>piperidine</td>
<td>none</td>
<td>fast</td>
<td>150°</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>TBA®</td>
<td>none</td>
<td>fast</td>
<td>150°</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>DEC</td>
<td>none</td>
<td>fast</td>
<td>150°</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>water</td>
<td>none</td>
<td>fast</td>
<td>150°</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>DEC</td>
<td>none</td>
<td>slow</td>
<td>25</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>decalin</td>
<td>none</td>
<td>slow</td>
<td>25</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>octane</td>
<td>none</td>
<td>slow</td>
<td>25</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>&quot;fast&quot;</td>
<td>150°</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>TBA®</td>
<td>none</td>
<td>slow</td>
<td>25</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>piperidine</td>
<td>none</td>
<td>slow</td>
<td>25</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>&quot;fast&quot;</td>
<td>150°</td>
<td>( \begin{align*} 93 &amp; 0 \ 4 &amp; 53 \end{align*} )</td>
</tr>
<tr>
<td>Solvent</td>
<td>Reactant</td>
<td>Reaction</td>
<td>Reaction mode</td>
<td>Reaction temp.</td>
</tr>
<tr>
<td>------------</td>
<td>----------</td>
<td>----------</td>
<td>---------------</td>
<td>----------------</td>
</tr>
<tr>
<td>decalin</td>
<td>CaO</td>
<td>slow</td>
<td>25°</td>
<td>21 9 70</td>
</tr>
<tr>
<td>DEC</td>
<td>NaOCH₂</td>
<td>slow</td>
<td>25</td>
<td>27 15 58</td>
</tr>
<tr>
<td>DEC</td>
<td>CuSO₄</td>
<td>slow</td>
<td>25</td>
<td>20 37 43</td>
</tr>
<tr>
<td>vacuum</td>
<td>glass</td>
<td>preheat</td>
<td>160</td>
<td>ten products</td>
</tr>
<tr>
<td>vacuum</td>
<td>stainless</td>
<td>preheat</td>
<td>160</td>
<td>ten products</td>
</tr>
</tbody>
</table>

---

**Notes:**
- High purity (98-99%) samples of 1-diazo-2,2-dimethylpropane (0.05 ml., ~0.58 millimole) were used.
- Samples were taken of the gas phase from the vials at 150° (except where specifically noted) and analyzed by gas chromatography [15% propylene carbonate, 20' x 1/4", 60/80 Chromosorb G (reg.), 10-15°].
- Fast thermolyses were effected by placing the vials in a preheated block at 150°; slow thermolyses were accomplished by allowing the vials (protected from light) to warm from -78 to 25° overnight.
- This reaction was run in a stainless steel vial.
- A Teflon vial was used.
- TBA is tri-n-butylamine.
- DEC is diethylcarbitol.
- In amine solvents, some diazoalkane remained undecomposed after 3 days at 25°; vapor-phase samples of the gas phase at 25°, then solutions were heated to 150° and gas-phase samples again taken.
- Powdered, anhydrous CaO (20 equiv., based on amount of diazo compound) was used.
- Fresh sodium methoxide (97.5%, 10 equiv.) was used.
- Powdered, anhydrous cupric sulfate (3 equiv.) in chilled DEF was used.
- l-Diazo-2,2-dimethylpropane (neat, 0.05 ml.) was injected into evacuated, preheated (160°) glass and stainless steel vials.
- The complex mixtures of products were not completely identified.
anticipated, the product formed by a carbenic process not involving
carbon-skeletal rearrangement greatly predominates (80%).

Three experiments were conducted to examine the "slow thermolysis" (at room temperature) of the neat diazo compounds in glass, stainless steel, and Teflon vials. The results of these experiments are shown in Table 21. In a glass vial, neat 1-diazo-2,2-dimethylpropane (protected from light) thermolyzes (25°) to 1,1-dimethylcyclopropane (9%), 2-methyl-1-butene (9%), and 2-methyl-2-butene (82%). The diazoalkane is thermolyzed (25°) in stainless steel and in Teflon vials to give 1,1-dimethylcyclopropane (4%), 2-methyl-1-butene (43-53%), and 2-methyl-2-butene (43-53%). The amount of the insertion product (1,1-dimethylcyclopropane) produced is drastically reduced by allowing the primary diazoalkane to slowly thermolyze; the magnitude of change is greater even than that observed with 2-diazo-3,3-dimethylbutane. It appears that the "slow thermolysis" processes of the primary diazo compound, 1-diazo-2,2-dimethylpropane, are strongly influenced by the surface characteristics of the reactor wall. The ratio of 2-methyl-1-butene to 2-methyl-2-butene produced seems particularly dependent upon features of the container surfaces. This is in marked contrast to observations made in experiments with the secondary diazo compound; the thermolytic processes of 2-diazo-3,3-dimethylbutane exhibit virtual independence of the container surface composition.

In a series of experiments to survey solvent effects, samples of 1-diazo-2,2-dimethylpropane were rapidly (30-60 seconds) decomposed at 150° in various purified aprotic solvents; results of these "fast thermolyses" in solvents are compiled in Table 21. The diazo
compound decomposes at 150° in decalin, octane, piperidine or tri-n-butylamine to yield 1,1-dimethylcyclopropane (93-99%) and 2-methyl-2-butene (1-7%). No 2-methyl-1-butene is formed. Results of these experiments indicate that a higher percentage (93-99%) of 1,1-dimethylcyclopropane, the insertion product, is formed by a fast thermolysis of the diazo compound in these solvents than arises (80%) from rapidly thermolyzing a neat sample of the diazo compound (Table 21).

In dry diethyl Carbitol or in water, rapid thermolysis (150°) of 1-diazo-2,2-dimethylpropane provides 1,1-dimethylcyclopropane (76-77%), 2-methyl-1-butene (5-8%) and 2-methyl-2-butene (16-18%) (Table 21). In diethyl Carbitol and in water more carbon-skeleton rearranged products are found than in the four solvents previously discussed. A possible reason is that diethyl Carbitol or water might allow partial ionization of the diazo compound (α-hydrogen), thereby permitting autocatalytic decomposition via carbonium-ion processes that would compete with carbenic processes.

1-Diazo-2,2-dimethylpropane was also thermolyzed slowly (25°) in a variety of solvents (Table 21). Slow thermolysis of the diazo compound (protected from light) in diethyl Carbitol and in decalin in sealed glass vials give similar product distributions: 1,1-dimethylcyclopropane (13-18%), 2-methyl-1-butene (23-25%), and 2-methyl-2-butene (59-62%). 1-Diazo-2,2-dimethylpropane thermolyzes slowly in octane (25°) forming 1,1-dimethylcyclopropane (9%), 2-methyl-1-butene (16%), and 2-methyl-2-butene (75%). The primary diazoalkane seems to show a greater solvent effect, especially in the ratio of 2-methyl-1-butene to 2-methyl-2-butene formed, during slow thermolyses than does the secondary diazo compound previously studied.
Samples of 1-diazo-2,2-dimethylpropane in piperidine and in tri-n-butylamine form deep orange-colored solutions. Even after three days at 25° these retain a light yellow coloration. The vapor phase above each basic solution was sampled at 25°, and again after each had been heated to 150°. The solutions are completely decolorized upon heating. The results of these analyses are listed in Table 21.

For 1-diazo-2,2-dimethylpropane in tri-n-butylamine at 25° the gas phase consists of 1,1-dimethylcyclopropane (10%), 2-methyl-1-butene (33%), and 2-methyl-2-butene (57%); samples taken at 150° (vapor phase) contain 1,1-dimethylcyclopropane (41%), 2-methyl-1-butene (16%), and 2-methyl-2-butene (43%). With 1-diazo-2,2-dimethylpropane in piperidine similar results are found. A gas-phase sample above the yellow solution at 25° yields 1,1-dimethylcyclopropane (8%), 2-methyl-1-butene (65%), and 2-methyl-2-butene (26%); after the solution is heated to 150°, analysis of the vapor phase indicates 1,1-dimethylcyclopropane (37%), 2-methyl-1-butene (43%), and 2-methyl-2-butene (20%).

Apparently, in basic solutions the diazo compound has increased thermal stability. Perhaps the amine solvents scavenge protonic contaminants. The yellow coloration of the solutions probably represented undecomposed diazoalkane. The change between analyses of vapor-phase samples taken at 25° and again at 150° shows an increase in the percentage of the insertion product and a decrease in the percentages of rearrangement products. This fact tends to substantiate previous observations that in this system formation of the insertion product (1,1-dimethylcyclopropane) is favored at higher temperature (150°).
It has been demonstrated: 1) that 1-diazo-2,2-dimethylpropane thermolyzes rapidly at 150°, neat or in aprotic solvents, to 1,1-dimethylcyclopropane (major, 80-99%) by insertion, and to 2-methyl-1-butene and 2-methyl-2-butene (both minor) by carbon-skeletal rearrangements; and 2) that the diazoalkane decomposes slowly at 25°, neat or in aprotic solvents, to give major amounts (82-94%) of carbon-skeleton rearranged products (2-methyl-1-butene and 2-methyl-2-butene), and only minor quantities of 1,1-dimethylcyclopropane by an insertion process.

As a possible explanation for this great temperature dependence of the decomposition processes, it is suggested that at 150° 1-diazo-2,2-dimethylpropane decomposes with loss of nitrogen to singlet 2,2-dimethylpropylidene which predominately undergoes a carbenic insertion process to form the cyclopropane preferentially (Eq. 70). 2-Methyl-2-butene (minor) and 2-methyl-1-butene (very minor) may possibly be formed by singlet carbenic rearrangements (Eq. 71 and Eq. 72).

\[
\begin{align*}
\text{CH}_3 &- \text{C} - \text{CH} = N_2 \xrightarrow{-N_2} \text{CH}_3 &- \text{C} - \text{CH} &\xrightarrow{150\degree} \text{CH}_3 &- \text{C} - \text{CH}_2 &\xrightarrow{\text{singlet}} &\text{CH}_3 &- \text{C} - \text{CH}_3 \\
\end{align*}
\]

(singlet major (80-99%))

\[
\begin{align*}
\text{CH}_3 &- \text{C} - \text{CH} &\xrightarrow{\text{singlet}} &\text{CH}_3 &- \text{C} = \text{CH} - \text{CH}_3 \\
\end{align*}
\]

(minor (1-19%))

\[
\begin{align*}
\text{CH}_3 &- \text{C} - \text{CH} &\xrightarrow{\text{singlet}} &\text{CH}_2 &- \text{C} - \text{CH}_2 - \text{CH}_3 \\
\end{align*}
\]

(very minor (1-8%))
At lower temperatures (25°) it is possible that 1-diazo-2,2-dimethylpropane decomposes with loss of nitrogen to singlet 2,2-dimethylpropylidene, a major portion of which may undergo spin inversion to triplet 2,2-dimethylpropylidene (eq. 73) before insertion or carbon-skeletal rearrangement can occur. Triplet 2,2-dimethylpropylidene should be of lower energy, and may rearrange by different processes than does singlet 2,2-dimethylpropylidene. Preferentially, the triplet carbene may undergo carbon-skeletal rearrangements to 2-methyl-1-butene and 2-methyl-2-butene (major) (eq. 74 and 75). It is possible, also, that 1,1-dimethylcyclopropane

\[
\begin{align*}
\text{H}_2\text{C}_2-\text{H} & \rightarrow \text{CH}_3 - \text{C} = \text{CH}_2 \\
\text{CH}_3 & \text{triplet}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{C}_2-\text{H} & \rightarrow \text{CH}_3 - \text{C} = \text{CH}_2 \\
\text{CH}_3 & \text{triplet}
\end{align*}
\]

(minor) may be formed by a triplet carbenic process (Eq. 76).

\[
\begin{align*}
\text{CH}_3 - \text{C} & \rightarrow \text{CH}_3 - \text{C} = \text{CH}_2 \\
\text{CH}_3 & \text{triplet}
\end{align*}
\]
The possibility that carbonium-ion processes are causing the rearrangements to give 2-methyl-1-butene and 2-methyl-2-butene, especially at lower temperatures where the diazo or the carbene are exposed to the environment for longer periods of time, does exist. However, the fact that slow thermolysis of 1-diazo-2,2-dimethylpropane in basic solvents (piperidine and tri-n-butyramine), which gave homogeneous mixtures, produces mainly rearranged products tends to diminish the probability that carbonium-ion processes are the predominant cause of rearrangements.

1-Diazo-2,2-dimethylpropane was allowed to thermolyze \(25^\circ\) slowly (18-24 hours) in mixtures of solid reactants (Table 21). In a slurry of powdered, anhydrous calcium oxide (20 equiv.) and decalin, the diazo compound gives 1,1-dimethylocyclopropane (21%), 2-methyl-1-butene (9%), and 2-methyl-2-butene (70%); with sodium methoxide (10 equiv.) in diethyl Carbitol, the diazoalkane forms 1,1-dimethylocyclopropane (27%), 2-methyl-1-butene (15%), and 2-methyl-2-butene (58%). It is of significance to note that even in the presence of anhydrous calcium oxide or sodium methoxide (both powerful scavengers of protonsic contaminants) the diazoalkane thermolyzes \(25^\circ\) predominantly to rearranged products (73-79% total). This observation substantiates previous contentions that 2-methyl-1-butene and 2-methyl-2-butene do not result primarily from carbonium-ion processes. When cold 1-diazo-2,2-dimethylpropane is injected into a slurry of powdered, anhydrous cupric sulfate (3 equiv.) in cold diethyl Carbitol, and allowed to remain overnight at room temperature there is produced (Table 21) 1,1-dimethylocyclopropane (20%), 2-methyl-1-butene (37%) and
2-methyl-2-butene (43%). The apparent effect of copper sulfate upon decomposition processes of 1-diazo-2,2-dimethylpropane is much less pronounced than with 2-diazo-3,3-dimethylbutane (see proposed mechanism, p. 86). A mechanism of a similar type has been proposed by Müller (42). Compared to results of slow thermolysis (25°) of 1-diazo-2,2-dimethylpropane in diethyl Carbitol (18:23:59) (Table 21) the main effect of addition of copper sulfate seems to be the alteration of the ratio of 2-methyl-1-butene and 2-methyl-2-butene formed (20:37:43).

Small samples (0.05 ml.) of cold 1-diazo-2,2-dimethylpropane were injected into glass and stainless steel vials which had been evacuated (0.1 mm.) and preheated to 160°. The three expected products, 1,1-dimethylcyclopropane, 2-methyl-1-butene, and 2-methyl-2-butene are formed (Table 21) along with seven other products. Not all of the products are identified, but some have shorter retention times than 1,1-dimethylcyclopropane and some have longer retention times than 2-methyl-2-butene. This may indicate fragmentation of the 2,2-dimethyl-1-propyldiene; in fact some C₂ and C₃ products were tentatively identified. Possible recombinations of these fragments with parent might account for higher boiling products. The product distribution patterns are only slightly different for glass and stainless steel vials.
The conclusions concerning thermolytic and catalytic decomposition of 2-diazo-3,3-dimethylbutane and 1-diazo-2,2-dimethylpropane, are as follows:

1. There is a pronounced temperature (and/or time) effect on the pyrolysis reactions. Rapid thermolysis (150°) promotes carbenic processes leading to products that arise by hydrogen (β) migration or by insertion (cyclopropane formation); carbenic processes involving carbon-skeletal rearrangements are very minor. Conversely, thermolysis at 25° (or lower) results in major amounts of products resulting from carbon-skeletal rearrangements. It is possible that different spin states of the carbenic intermediates (high temperature - singlet; low temperature - triplet) are responsible for the different processes involved.

2. The diazoalkanes are relatively indifferent to inert or aprotic environments, either at high (150°) or low (25°) temperatures. Thus, aprotic solvents and inert surfaces have only minor effects on the decomposition processes. The primary diazoalkane exhibits a slightly greater response to aprotic and inert surface influences (aprotic or inert) than does the secondary diazo compound.

3. The diazoalkanes undergo a wide range of reactions with various catalysts. Strong bases (sodium or lithium methoxide) or basic solvents (amines) have virtually no effect upon the decomposition processes; yield mostly rearrangement products, perhaps via complexed carbonium ions. Protonic reagents give rise to rearrangements via diazonium/carbonium-ion intermediates. Copper and silver salts
cause immediate decolorization of the diazo compounds, reduction of the metal ions, and product distributions that show various degrees of discrimination. This area is of great interest and merits further study.
EXPERIMENTAL

General Procedures and Techniques

Melting points. Melting points were determined in a stirred silicone oil (DC550) bath. All melting points are uncorrected.

Boiling points. Boiling points were obtained as the compounds distilled at the pressures indicated, unless otherwise noted. Thermometer corrections were not made.

Elemental analyses. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, and by Micro-Analysis, Inc., Wilmington, Delaware.

Infrared spectra. The infrared spectra of the compounds prepared in this research were obtained on a Perkin-Elmer Infracord recording infrared spectrophotometer. The spectra of solid compounds were determined from potassium bromide wafers, and the spectra of liquid compounds from liquid films, unless otherwise noted.

Gas chromatography. Gas chromatography was frequently employed for product identification and distribution. The gas chromatographs employed were an Aerograph, Model A90-C, an Aerograph, Model A90-P, and an Aerograph, Model A90-P3, each equipped with a thermal conductivity detector and each connected to a 2.5 millivolt full-scale deflection Brown Electronik recorder; and a Barber-Coleman, Model 20, equipped with a hydrogen flame detector, connected to a 1.25 millivolt full-scale deflection Sargent recorder, Model MR (S-72150).
A technique was developed for pyrolysis of solids within the preheated injector of a gas chromatograph and subsequent analysis of gaseous pyrolysis products. Salts of tosylhyrazones, benzenesulfonylhyrazones and methanesulfonylhyrazones were prepared with various amounts (0.8-1.2 equivalents) of n-butyllithium, lithium methoxide and sodium methoxide, and pyrolyzed dry or in purified solvents (diethyl Carbitol or decalin).

Glass melting point capillary tubes (1 mm. i.d. x 50 mm.) were treated with alcoholic potassium hydroxide, rinsed with distilled water and dried. The tubes were then sealed at one end and redried in vacuo (0.1 mm., 50°, 24 hours). A few milligrams of a salt were placed in a tube (3-8 mm. deep when compacted) and, if desired, solvent was introduced by syringe to saturate and cover the salt. The upper end of the tube was sealed using a small, hot flame to produce a short-tapered, sharp tip. The overall length of sealed tube was 20-25 mm.

The sealed sample tube was coated with silicon grease and placed in an insertion guide tube [a metal rod, 1/4" x 2", with a hole (1/16" dia) bored to its length] fastened to the external end of chromatograph injector. A metal push rod (1/16" dia. x 8") was used to insert the sample tube through a silicon rubber septum into the liner (thin-walled stainless steel tubing, 3/32" i.d. x 5", closed at inner end with carrier gas inlet and outlet hole near each end) of the preheated (150-190°) injector. The sharp tip of the sample tube easily penetrated the septum and remained intact during insertion. (Fig. 1).
Figure 1.-- Capillary Tube Pyrolysis Apparatus and Sequence.
Time was allowed for the sample to pyrolyze (2-5 minutes) before the tube was pushed against the closed end of the injector liner to break the tip of the sample tube. Carrier gas swept the gaseous pyrolysis products into the chromatography column. Solid residue remained in the tube. Product peak sizes were controlled by the amount of sample placed in the tube and by instrument attenuation.

Successive sample tubes were inserted in identical manner and tips broken against end of previous tube. An injector liner and a septum had a capacity for five sample tubes before replacement.

Product peak sizes and per cent distribution were consistently reproducible and this method permitted many varied experiments to be effected on small amounts of material.

Gas chromatography column temperatures below ambient were needed occasionally to effect adequate separation of low-boiling, isomeric olefins. To achieve these temperatures the chromatography column was wound tightly around the outside of a cylindrical copper sleeve (4" long x 4-1/2" dia. x 18 ga.). Coolant was circulated through copper tubing (1/4" x 20') which was tightly coiled against the inner surface of the copper sleeve. The complete unit fitted easily into the column chamber of a gas chromatograph. Cold tap water gave column temperatures of 10-15°. Lower temperatures can be achieved by recirculating a coolant through an external heat exchanger.
Intermediates

p-Toluenesulfonyl hydrazide. Tosylhydrazide, m.p. 110-112°, was prepared as previously described (43).


Benzenesulfonylhydrazide. The general procedure followed was that for the preparation of tosylhydrazide (43). Anhydrous hydrazine (95%, 100 g., 3.0 moles) and water (80 g.) were chilled (10°) and carefully mixed. The resulting hydrazine hydrate (85%) solution was added in 65 minutes to a stirred solution of benzenesulfonyl chloride (250 g., 1.42 moles) in tetrahydrofuran (350 ml.). The mixture was maintained at 10-15° during the addition. Benzenesulfonylhydrazide, 208 g., (85%), m.p. 101-103° dec., was obtained as a finely granulated white solid.

Methanesulfonylhydrazide. The material was supplied by W. W. Sullivan (44).

(44) H. Kloes, Ger. 1,069,637, Nov. 26, 1959.

4-Phenylbutyronitrile. l-Bromo-3-phenylpropane (200 g., 1.0 mole, Columbia Organic Chemicals Co.) was added in 30 minutes to a stirred mixture of sodium cyanide (60 g., 1.2 moles) in dimethyl sulfoxide (270 ml.) at 60-65° (45). When the addition was completed, the mixture was heated to 90° for 15 minutes, then cooled and diluted with water (400 ml.). The brown, oily layer
which separated was extracted with ether (3 x 150 ml.). The combined ether extracts were washed with 6N hydrochloric acid (2 x 200 ml.) and with water (2 x 200 ml.), then dried over calcium chloride overnight. The ether was removed on a rotary evaporator and the residual liquid distilled from phosphorus pentoxide (b.p. 120-125°, 6-10 mm.) to give 116.6 g. (80%) of 4-phenylbutyronitrile.


4-Phenylbutanal. Ethyl acetate (45.1 g., 0.51 mole, dried over anhydrous potassium carbonate) was added in 120 minutes to a suspension of lithium aluminum hydride (13.65 g., 0.34 mole) in dry diethyl ether under nitrogen at 4-7°. Stirring was continued one hour at 4-7° to complete the formation of lithium triethoxylalumino-hydride (46). 4-Phenylbutyronitrile (49.5 g., 0.34 mole) was added in five minutes and the resulting viscous mixture stirred one hour at 0-3°. Sulfuric acid (5N, 340 ml.) was added to hydrolyze the mixture. The ether layer was separated and the aqueous layer extracted with ether (3 x 100 ml.). The combined ether extracts were washed with saturated sodium bicarbonate solution and water (8 x 50 ml.), then dried over anhydrous sodium sulfate. After removal of the ether on a rotary evaporator, the residue was distilled (81-84°, 0.3 mm.) to give 4-phenylbutanal, 30.2 g. (60%). The 2,4-dinitrophenyl-hydrazone was prepared, m.p. 111.5-112.5° (lit. (46) m.p. 112-113°).

Tosylhydrazones - General Techniques. Tosylhydrazide (0.05-0.2 mole) was added to refluxing absolute methanol (50-100 ml.). The mixture was stirred magnetically until the tosylhydrazide completely dissolved. An aldehyde or ketone (freshly distilled or new sample, 1-2% excess) was added to the warm solution. Stirring was continued as the mixture cooled to room temperature. If precipitation of the product occurred during this time rapid stirring gave a fine crystalline material. Frequently, overnight storage in a refrigerator or in Dry Ice was needed to cause precipitation. The tosylhydrazone was filtered, washed with a low-boiling hydrocarbon solvent and dried in vacuo (10-20 mm., 25°C, 24 hours). Recrystallization, if necessary, was effected from hot aqueous methanol or a methylene chloride—hexane mixture. In a few cases when the product could be obtained only as an oil from methanol, addition of the aldehyde to a cold suspension of tosylhydrazide in petroleum ether (b.p. 30-60°C) gave a solid product which could be recrystallized from the usual solvents.

Benzencesulfonylhydrazones and methanesulfonylhydrazones were also prepared in absolute methanol by this general method. The stability of the hydrazones at room temperature varied over a wide range and as a general precaution all samples were stored in a refrigerator.

Ethanal Tosylhydrazone. To a cold (0°C) solution of tosylhydrazide (37.25 g., 0.20 mole) in absolute methanol (100 ml.) was slowly added a solution of ethanal (9.69 g., 0.22 mole) in absolute methanol (38 ml.). The reaction was exothermic. The reaction
solution was maintained at 0° under nitrogen and stirred one hour, then sealed and stored in Dry Ice until crystallization of the product had occurred. Ethanal tosylhydrazone, 21.0 g. (50%), m.p. 67-68° (dec.) was obtained. The product was unstable and decomposed at room temperature in 15 minutes. Elemental analysis of the product was not attempted.

Propanal Tosylhydrazone. Tosylhydrazide (18.62 g., 0.10 mole) was dissolved in refluxing absolute methanol (75 ml.). This solution was cooled until the tosylhydrazide began to precipitate. To this stirred mixture was added freshly distilled propanal (5.81 g., 0.10 mole, b.p. 49°). The reaction flask was transferred to an ice bath and stirring continued until all of the tosylhydrazide had dissolved. The clear, colorless solution was stored in Dry Ice overnight. The white solid mass which formed was pulverized, filtered, washed with cold petroleum ether and dried in vacuo to give 17.40 g. (77%) of propanal tosylhydrazone, m.p. 68-69° with decomposition, lit. (47) 68-69°. This tosylhydrazone was not very stable and decomposed in a few days, even when stored in a freezer. Recrystallization was not attempted.

(47) L. Friedman, Ph.D. dissertation, The Ohio State University, 1959.

Propanone Tosylhydrazone. Propanone (6.4 g., 0.11 mole) was added to a warm (40°) magnetically stirred solution of tosylhydrazide (18.62 g., 0.10 mole) in absolute methanol (90 ml.). An exothermic
reaction occurred that caused the resulting clear solution to reflux. The product crystallized as fine white platelets as the stirred solution cooled to room temperature. Propanone tosylhydrazone was filtered, washed with cold Skelly Solve F (0°) and dried in vacuo. A yield of 19.3 g. (85%) of the hydrazone, m.p. 150-151°, lit. (7) 153°, was obtained.

Butanal Tosylhydrazone. Tosylhydrazide (18.62 g., 0.10 mole) was ground to a fine powder and suspended by vigorous agitation with a Vibrostirrer in petroleum ether (200 ml., b.p. 30-60°) at 0°. Butyraldehyde (8.00 g., 0.11 mole, b.p. 75°) in petroleum ether (10 ml.) was added, drop by drop, to this suspension over a period of one hour. Vigorous agitation was maintained during the addition and then was continued three hours as the reaction mixture became very thick. The product was filtered, washed thoroughly with large volumes of petroleum ether and dried in vacuo. A yield of 21.6 g. (90%) of butanal tosylhydrazone, m.p. 63-64° (dec.), lit. (47) 62-63° (dec.), was obtained by this method.

2-Methylpropanal Tosylhydrazone. 2-Methylpropanal tosylhydrazone, m.p. 105-106° was prepared as previously described in 83% yield (47).

2-Butanone Tosylhydrazone. The tosylhydrazone of 2-butanone, m.p. 125-127° was prepared as previously described (47).

Cyclopropanecarboxaldehyde Tosylhydrazone. Cyclopropanecarboxaldehyde tosylhydrazone, m.p. 89-100° with decomposition was prepared according to the published procedure (5).
**Pentanal Tosylhydrazone.** The tosylhydrazone of pentanal, m.p. 49-50° (dec.) was prepared as described (47) in 79% yield. The hydrazone was pulverized and washed with cold petroleum ether (200 ml.). A small amount of yellow oil was removed; however, the tendency of pentanal hydrazone to decompose rapidly at room temperature was not altered. The product was stored in a freezer.

**2-Methylbutanal Tosylhydrazone.** Freshly distilled 2-methylbutanal (8.6 g., 0.1 mole) was slowly added (15 minutes) to a cool (20°), stirred solution of tosylhydrazide (18.6 g., 0.1 mole) in methylene chloride (150 ml.). The resulting exothermic reaction caused the solvent to reflux. The clear solution was stirred one hour at room temperature and then stored in Dry Ice overnight. The crystalline hydrazone was filtered, washed with cold pentane (0°) and dried in vacuo. A yield of 15 g. (60%) of 2-methylbutanal tosylhydrazone, m.p. 71-72° with decomposition, was obtained.

**3-Methylbutanal Tosylhydrazone.** Tosylhydrazide (18.62 g., 0.10 mole, m.p. 109-111°) was dissolved in refluxing absolute methanol (60 ml.). When this stirred solution had cooled to room temperature freshly distilled 3-methylbutanal (8.61 g., 0.10 mole, b.p. 92°) was added. After the exothermic reaction subsided (5-10 minutes), the reaction flask was placed in a cold bath (-70°) and stirring was continued one hour. The clear, colorless solution was stored in Dry Ice overnight. The white solid which precipitated was filtered, washed with cold petroleum ether, and dried in vacuo. A yield of 20 g. (79%) of 3-methylbutanal tosylhydrazone, m.p. 78-79° with decomposition, lit. (47) 50-60°, was obtained.
2,2-Dimethylpropanal Tosylhydrazone. 2,2-Dimethylpropanal (18.09 g., 0.21 mole) produced an exothermic reaction when added to a warm, stirred solution of tosylhydrazide (37.25 g., 0.20 mole) in absolute methanol (50 ml.). Stirring was continued for one hour at room temperature, then at 0° until a precipitate formed. The crystalline hydrazone was filtered, washed with pentane and dried in vacuo to give 27.50 g. (54%) of product, m.p. 112-113.5°, lit. ( ) 110-112°. Water was added to the refluxing, concentrated filtrate until the mixture became turbid. A second crop of crystals, 18.25 g. (36%), m.p. 112-113° was collected and dried in vacuo. The combined yield of 2,2-dimethylpropanal tosylhydrazone was 90%.

Furfural Tosylhydrazone. Furfural (9.61 g., 0.10 mole) was added to a refluxing solution of tosylhydrazide (18.62 g., 0.10 mole) in absolute methanol (50 ml.). The reaction was exothermic. The clear, brown solution was stored overnight in a refrigerator. The tan, crystalline precipitate was collected by suction filtration, washed with Skelly Solve F and dried in vacuo (10 mm.) at room temperature. A first crop, 21 g. (85%) of furfural tosylhydrazone, m.p. 120-122°, was obtained.

3-Pentanone Tosylhydrazone. 3-Pentanone tosylhydrazone, m.p. 100-102°, was prepared according to the previously reported method (47).

3-Methyl-2-butanone Tosylhydrazone. 3-Methyl-2-butanone tosylhydrazone, m.p. 118-120°, was prepared as previously described (47).
Cyclopentanone Tosylhydrazone. Cyclopentanone tosylhydrazone was prepared in 95% yield, m.p. 181.5-182.5°C, according to a described method (5).

3,3-Dimethyl-2-butanone Tosylhydrazone. 3,3-Dimethyl-2-butanone (27.8 g., 0.28 mole) was added to a hot (50°C), stirred solution of tosylhydrazide (46.6 g., 0.25 mole) in absolute methanol (85 ml.). The hydrazone started to crystallize from the warm solution. The reaction mixture was cooled to 0°C and stirred vigorously for one hour. The product was filtered, washed with pentane and dried in vacuo. A yield of 63.8 g. (95%) of 3,3-dimethyl-2-butanone tosylhydrazone, m.p. 153-155°C, lit. (7) 155°C, was realized. (Fig. 2).

Cyclohexanone Tosylhydrazone. Previously described procedures (5) were slightly modified for preparation of cyclohexanone tosylhydrazone by employing vigorous stirring as the cooled reaction mixture crystallized. An 89% yield of the hydrazone, m.p. 158-159°C, lit. (7) 156°C, was obtained.

Cycloheptanone Tosylhydrazone. The tosylhydrazone of cycloheptanone, m.p. 146-148°C, was prepared as described previously (47).

Phenylacetaldehyde Tosylhydrazone. A solution of phenylacetaldehyde (12.60 g., 0.105 mole) in absolute methanol (10 ml.) was slowly added (15 minutes) to a cool (20°C), stirred solution of tosylhydrazide (18.62 g., 0.10 mole) in absolute methanol (70 ml.). The resulting clear, colorless solution was stirred (two hours) at room temperature until precipitation of the hydrazone began. The product was cooled (0°C), filtered, washed with Skelly Solve F and
Figure 2.—Infrared Spectrum of 3,3-Dimethyl-2-butanone Tosylhydrazone
cold ether and dried in vacuo. Phenylacetaldehyde tosylhydrazone, 17.5 g. (62%) as white needle crystals, m.p. 113-114°C with decomposition, was obtained.

**Anal.** Calcd. for C₁₅H₁₆O₂N₂S: C, 62.50; H, 5.55; N, 9.72

Found: C, 62.60; H, 5.54; N, 9.61.

**Acetophenone Tosylhydrazone.** The tosylhydrazone of acetophenone, m.p. 146-147°C with decomposition, was prepared as previously indicated (5).

2,2,5,5-Tetramethyltetrahydrofuran-3-one-tosylhydrazone. To a hot, stirred solution of tosylhydrazide (18.62 g., 0.10 mole) in absolute methanol (75 ml.) was added 2,2,5,5-tetramethyltetrahydrofuran-3-one (14.63 g., 0.105 mole). An exothermic reaction occurred which caused the solvent to reflux. The product began to crystallize as the solution cooled to room temperature. Stirring was continued while the mixture was stored at 0°C to complete the crystallization. The hydrazone was filtered, washed with petroleum ether and dried in vacuo. A first crop yield of 23.7 g. (76%) of 2,2,5,5-tetramethyltetrahydrofuran-3-one tosylhydrazone, m.p. 170-171°C, was obtained.

**2-Phenylpropanal Tosylhydrazone.** 2-Phenylpropanal (13.42 g., 0.10 mole) in Skelly Solve F (30 ml.) was slowly added over a period of one and one-half hours to a vigorously stirred suspension of powdered tosylhydrazide (18.62 g., 0.10 mole) in Skelly Solve F (750 ml.). Additional Skelly Solve F (1000 ml.) was added to the thick, fluffy precipitate and stirring was continued at 0°C for six hours. The 2-phenylpropanal tosylhydrazone, 26.0 g. (85%), was collected by suction filtration, washed with Skelly Solve F and dried in vacuo.
(10 mm. Hg.), m.p. 95-96°. A sample recrystallized from aqueous methanol, m.p. 97-98°, was analyzed.

Anal. Calcd. for C₁₆H₁₈O₂N₂S: C, 63.55; H, 5.99; N, 9.26
   Found: C, 63.58; H, 6.01; N, 9.27.

3-Phenylpropanal Tosylhydrazone. 3-Phenylpropanal (14.80 g., 0.11 mole) was slowly added (60 minutes) to a vigorously agitated suspension of finely ground tosylhydrazide (18.62 g., 0.10 mole) in ether (200 ml.) at room temperature. The suspension became very thick as the hydrazone formed (three hours). The product was filtered, washed with ether and dried in vacuo to give 25.2 g. (84%) of 3-phenylpropanal tosylhydrazone, m.p. 102-104° (dec.). The entire sample was recrystallized from hot aqueous methanol to give 24 g. (95% recovery) of white needles, m.p. 105.5-106° (dec.).

Anal. Calcd. for C₁₆H₁₈O₂N₂S: C, 63.57; H, 5.96; N, 9.27

3-Phenylpropenal Tosylhydrazone. 3-Phenylpropenal (13.22 g., 0.10 mole) in absolute methanol (10 ml.) was added to a refluxing solution of tosylhydrazide (18.62 g., 0.10 mole) in absolute methanol (50 ml.). The reaction mixture immediately formed a completely solid mass which was recrystallized from hot methanol (270 ml.) to give 21.0 g. (70%) of light yellow 3-phenylpropenal tosylhydrazone, m.p. 161-163° with decomposition (red).

Anal. Calcd. for C₁₆H₁₈O₂N₂S: C, 63.57; H, 5.96; N, 9.27

1-Phenyl-2-propanone Tosylhydrazone. Tosylhydrazide (18.6 g., 0.1 mole), 1-phenyl-2-propanone (13.4 g., 0.1 mole) and absolute methanol (50 ml.) were refluxed briefly (15 minutes). After overnight storage in a freezer the white crystalline hydrazone was
collected, washed with Skelly Solve F and dried in vacuo to give 25 g. (83%) of 1-phenyl-2-propanone tosylhydrazone, m.p. 134-136°, lit. (7) 134-135°.

4-Phenylbutanal Tosylhydrazone. 4-Phenylbutanal (7.48 g., 0.051 mole, b.p. 81-84°/0.3 mm.) was added drop by drop to a stirred warm (35°) solution of tosylhydrazide (9.31 g., 0.051 mole, m.p. 109-111°) in absolute methanol (30 ml.). An exothermic reaction occurred. The clear, colorless solution was stirred one hour at room temperature, then stored in Dry Ice until crystallization of the product occurred (three days). The white crystalline tosylhydrazone was filtered, washed with cold hexane and dried in vacuo to give material with m.p. 74-76°. Recrystallization from glacial acetic acid gave 11.9 g. (75%) of 4-phenylbutonal tosylhydrazone, m.p. 85.5-86.5° (dec.).

4-Phenyl-3-buten-2-one Tosylhydrazone. 4-Phenyl-3-buten-2-one (14.62 g., 0.10 mole) was added to a refluxing solution of tosylhydrazide (18.62 g., 0.10 mole) in absolute methanol (75 ml.). The exothermic reaction was followed immediately by precipitation of the bright yellow product which was filtered, washed with ether and dried in vacuo to give 26.8 g. (86%) of 4-phenyl-3-buten-2-one tosylhydrazone, m.p. 181-183°.

Benzophenone Tosylhydrazone. Tosylhydrazide (18.62 g., 0.10 mole) and benzophenone (18.22 g., 0.10 mole) were added to refluxing absolute methanol (60 ml.). White crystalline benzophenone tosylhydrazone formed in the stirred solution as it cooled. After overnight
storage at room temperature the product was filtered, washed with Skelly Solve F and dried \textit{in vacuo}. A combined yield of 30 g. (86%), m.p. 179-180°, lit. (7) 180°, with decomposition, was obtained.

**Phenyl cyclohexyl ketone Tosylhydrazone.** Phenyl cyclohexyl ketone (18.83 g., 0.10 mole) was added to a warm, stirred solution of tosylhydrazide (18.62 g., 0.10 mole) in absolute methanol (75 ml.). The dark amber solution failed to crystallize even after two days at room temperature. A solid which separated at -80° melted when collection was attempted. Addition of water (30 ml.) to the heated amber solution caused an oil to separate. This oil was stirred in Skelly Solve F (250 ml.) at room temperature. After four days the white microcrystalline solid which had formed was collected, washed with pentane and dried \textit{in vacuo} to give 17.9 g. (50%) of phenyl cyclohexyl ketone tosylhydrazone, m.p. 92-93°. The volume of the filtrate was reduced to 100 ml. and cooled to 0°. A second crop of the hydrazone, 10.2 g. (28%), m.p. 91-92°, was obtained. The combined yield of phenyl cyclohexyl ketone tosylhydrazone was 28.1 g. (78%).

**9-Fluorenone Tosylhydrazone.** Solid 9-fluorenone (18.02 g., 0.10 mole, m.p. 83-84°) was added to a refluxing solution of tosylhydrazide (18.62 g., 0.10 mole) in absolute methanol (60 ml.). The light yellow solution was stirred and refluxed for ten minutes, then allowed to cool to room temperature. Stirring was continued as precipitation of the yellow tosylhydrazone occurred. Skelly Solve F (150 ml.) was added to make the heavy precipitate more fluid. The
product was filtered, washed with ether and pentane, and dried in vacuum to give 28 g. (80%) of 9-fluorenone tosylhydrazone, m.p. 161.5-162.5° (dec.), lit. (7) 159-160°. A small second crop (2 g.) was collected from chilled filtrate, m.p. 165.5-166° (dec.).

Perinaphthenone Tosylhydrazone. Tosylhydrazide (9.31 g., 0.05 mole), perinaphthenone (9.01 g., 0.05 mole) and absolute methanol (50 ml.) were refluxed six hours. Perinaphthenone tosylhydrazone crystallized from the red solution. The yellow-brown product, 14.8 g. (85%), was collected and dried in vacuum, m.p. 182-183°.

Diphenylacetaldehyde Tosylhydrazone. Diphenylacetaldehyde (4.9 g., 0.025 mole) (48) was added to a refluxing solution of tosylhydrazide (4.65 g., 0.025 mole) in absolute methanol (50 ml.). The resulting solution was stirred as it cooled to room temperature. Long, white needle crystals of diphenylacetaldehyde tosylhydrazone, precipitated overnight. A yield of 7.9 g. (88%), m.p. 143-144°, was obtained. Recrystallization of the product from aqueous methanol gave material of m.p. 144.5-145°.

Dibenzyl ketone Tosylhydrazone. Dibenzyl ketone (21.0 g., 0.1 mole) was added to a hot, magnetically stirred solution of tosylhydrazide (18.6 g., 0.1 mole) in absolute methanol (60 ml.). The reaction is noticeably exothermic. Stirring was continued at room temperature for one hour, then the solution was stored overnight at 0°. The crystalline product which formed was collected by suction
filtration, washed with cold petroleum ether and dried in vacuo. Dibenzyl ketone tosylhydrazone, 28 g. (75%), m.p. 184-185°, lit. (7) 186°, was obtained as a white microcrystalline powder.

Propanone Benzenesulfonylhydrazone. Benzenesulfonylhydrazide (3.44 g., 0.020 mole) was dissolved in propanone (50 ml.) at room temperature. The clear, colorless solution was heated to reflux for five minutes, then allowed to cool to room temperature. The excess propanone was removed on a rotary evaporator to give 4.0 g. (95%) of propanone benzenesulfonylhydrazone, m.p. 138-140°.

2-Butanone Benzenesulfonylhydrazone. 2-Butanone (9.00 g., 0.125 mole) reacted with a warm, stirred solution of benzenesulfonylhydrazide (21.55 g., 0.125 mole) in absolute methanol (45 ml.) to give a clear, colorless solution. The product precipitated as fine, white platelets upon standing overnight in a refrigerator. The crystalline hydrazone was filtered, washed with cold petroleum ether and dried in vacuo. 2-Butanone benzenesulfonylhydrazone, 26 g., m.p. 96-98°, was obtained in 92% yield.

2,2-Dimethylpropanal Benzenesulfonylhydrazone. 2,2-Dimethylpropanal (10.77 g., 0.125 mole) was quickly added to a warm (50°) stirred solution of benzenesulfonylhydrazide (21.55 g., 0.125 mole) in absolute methanol (60 ml.). Overnight storage of the reaction solution provided a white crystalline solid. The hydrazone was filtered, washed with Skelly Solve F and dried in vacuo. A second crop of crystals obtained from the concentrated and chilled filtrate was combined with the first crop to provide 26.55 g. (88.5%) of 2,2-dimethylpropanal benzenesulfonylhydrazone, m.p. 101-102°, in the form of tiny white platelets.
3-Methyl-2-butanone Benzenesulfonylhydrazone. 3-Methyl-2-butanone (10.77 g., 0.125 mole) gave an exothermic reaction when added to a warm, magnetically stirred solution of benzenesulfonylhydrazide (21.55 g., 0.125 mole) in absolute methanol (45 ml.). The resulting clear solution was stirred 30 minutes as it cooled to room temperature. The white, solid mass, which formed upon standing overnight in a refrigerator, was pulverized, filtered, washed with Skelly Solve F and dried in vacuo. 3-Methyl-2-butanone benzenesulfonylhydrazone, 20 g., (68%) was obtained as a pure white powder, m.p. 108-109°.

3-Pentanone Benzenesulfonylhydrazone. 3-Pentanone (13.35 g., 0.16 mole) and benzenesulfonylhydrazide (26.72 g., 0.15 mole) were added to refluxing absolute isopropanol (30 ml.). The cloudiness of the resulting solution was dispelled by addition of absolute methanol (5 ml.). Water was added to the refluxing solution until it became turbid. Rapid stirring of the cooling mixture gave a very fine, white precipitate. The product was filtered, washed with water and pentane, and dried in vacuo to give 34 g. (95%) of 3-pentanone benzenesulfonylhydrazone, m.p. 98-100°.

3,3-Dimethyl-2-butanone Benzenesulfonylhydrazone. 3,3-Dimethyl-2-butanone (13.95 g., 0.139 mole) was slowly added to a warm, stirred solution of benzenesulfonylhydrazide (21.55 g., 0.125 mole) in absolute methanol (45 ml.). The reaction was exothermic. The clear, colorless solution was stirred until cool, then stored in a refrigerator until the product had crystallized. The white solid was pulverized,
filtered, washed with pentane and dried in vacuo. 3,3-Dimethyl-2-
butanone benzenesulfonylhydrazone, 28.55 g. (97%), m.p. 110-111°,
was obtained as a white crystalline powder.

Propanone Methanesulfonylhydrazone. Methanesulfonylhydrazide
(5.50 g., 0.050 mole) was dissolved in propanone (50 ml.) at room
temperature. The clear, colorless solution was heated to reflux
temperature for five minutes, then was allowed to cool to room
temperature. The excess propanone was removed on a rotary evaporator
to give 7.0 g. (98%) of propanone methanesulfonylhydrazone, m.p.
106-108°. The product was recrystallized from a hot methylene
chloride—hexane solution to give long, white needles, m.p. 110-112°
without decomposition.

2-Butanone Methanesulfonylhydrazone. 2-Butanone (7.21 g.,
0.10 mole) in absolute methanol (10 ml.) was added to a warm,
stirred solution of methanesulfonylhydrazide (11.00 g., 0.10 mole)
in absolute methanol (50 ml.). The reaction was exothermic. The
clear, colorless solution was stirred one hour as it cooled to room
temperature, then stored overnight in Dry Ice. The amorphous solid
was collected and recrystallized from ether to give 8.8 g. (54%) of
2-butanone methanesulfonylhydrazone as white needles, m.p. 55-57°.

2,2-Dimethylpropanal Methanesulfonylhydrazone. 2,2-Dimethyl-
propanal (8.61 g., 0.10 mole) was added to a warm, stirred solution
of methanesulfonylhydrazide (11.01 g., 0.10 mole) in absolute methanol
(30 ml.). A heavy precipitate of white platelets formed as the
stirred reaction mixture stood at room temperature for one hour. The
crystalline hydrazone was chilled to 0°, collected, washed with cold
pentane and dried in vacuo. A yield of 14.93 g. (83.7%) of 2,2-
dimethylpropanal methanesulfonylhydrazone, m.p. 134-135 was obtained.

3,3-Dimethyl-2-butane Methanesulfonylhydrazone. 3,3-
Dimethyl-2-butane (7.25 g., 0.073 mole) reacted with evolution
of heat when added to a warm, stirred solution of methanesulfonyl-
hydrazone (7.16 g., 0.065 mole) in absolute methanol (25 ml.).
Stirring was continued as the solution cooled to room temperature.
The crystalline hydrazone which precipitated as tiny, white plate-
lets was cooled to 0°, then collected, washed with cold pentane and
dried in vacuo. Two crops of crystals yielded 10.3 g. (83%) of
3,3-dimethyl-2-butane methanesulfonylhydrazone, m.p. 106-108°.

2-Butanone β-Naphthalenesulfonylhydrazone. Freshly distilled
2-butane (1.44 g., 0.02 mole) reacted with β-naphthalenesulfonyl-
hydrazone (49) (4.45 g., 0.02 mole) in refluxing absolute methanol

(49) This hydrazide was supplied by C. Walker.

(40 ml.) to give a clear, light yellow solution. After brief stir-
ring (15 minutes) at room temperature the solution was stored overnight
in a refrigerator. The white precipitate was filtered, washed with
pentane and dried in vacuo to yield 5.11 g., (98%) of 2-butane
β-naphthalenesulfonylhydrazone, m.p. 135-137°.

Lithium Salts of Tosylhydrazones, Benzenesulfonylhydrazones
and Methanesulfonylhydrazones. General Techniques — Lithium Salts
flask (250 ml.) containing a magnetic stirring bar was fitted with
a 3-necked adapter (candelabra style). The first neck of the
adapter was fitted with a nitrogen inlet tube. Two small holes in the end of this inlet tube divided the flow of nitrogen. A length of polyethylene tubing (0.05" o.d.) inserted into one hole in the end of the inlet tube carried nitrogen below the surface of the solvent. Nitrogen flowing from the other hole swept across the surface of the solvent and flushed the upper regions of the flask and the adapter. The center neck of the adapter was fitted with a rubber serum stopper and served as inlet for the hypodermic syringe used to transfer the n-butyllithium. The third neck of the adapter was equipped with a short (6"), water-cooled condenser. A Drierite filled drying tube was mounted in the top of the condenser. (Fig.3).

Reagents. Whenever feasible and convenient the hydrazones were recrystallized from an appropriate solvent and dried in vacuo overnight at room temperature. Reagent grade tetrahydrofuran was treated with potassium hydroxide pellets, distilled from calcium hydride and stored under nitrogen. Reagent grade pentane was chromatographed through basic, then neutral alumina directly into a reaction vessel. n-Butyllithium (Foote Mineral Company, 1.5-1.6M in hexane or pentane) and lithium methoxide, (Alfa Inorganics, Inc., 98.4-100%) were titrated with standardized hydrochloric acid solution with phenolphthalein indicator. A carefully measured volume (5.0 ml.) of n-butyllithium solution or weight (0.3-0.7 g.) of lithium methoxide was added to rapidly stirred water (100 ml.) and the resulting basic solution titrated.
Figure 3.-- Equipment for Preparing Lithium Salts of Tosylhydrazones.
Procedure. Method A. A tosylhydrazone was dissolved in dry tetra-
hydrofuran. The stirred solution was flushed with dry nitrogen and cooled
to 0° or -78°. Standardized n-butyllithium was transferred by syringe to
the solution. After the mixture had been stirred for an hour the sol-
vents were removed at room temperature on a rotary evaporator. The
lithium salt was left as a white solid or light yellow glass on the
wall of the flask. This material was left intact and dried in vacuo
(3-24 hours), then the flask was attached to the vacuum pyrolysis equipment.

The advantages of this method include the large area of the salt
exposed for even heating during pyrolysis. The disadvantages included
the difficulty in removal of residual solvent and the inability to re-
mov impurities from the salt before pyrolysis. The disadvantages
necessitated attempted separation of the diazo compound from the
residual solvents and impurities during the vacuum pyrolysis.

One method of separation utilized a trap cooled to 0° placed
between the pyrolysis flask and the first cold (-78°) trap (used to
collect the diazo compound) to remove high-boiling components from the
diazo compound during vacuum pyrolysis of a salt. A more elaborate
method employed the cool trap (0°) and an additional cold (-78°) trap and
valves so that the forerun of solvents expelled from the salt as it was
heated to the decomposition temperature could be diverted into one trap
and the diazo compound then collected in a separate cold (-78°) trap.

These methods worked well for effecting separations, but
both required the diazo compound to travel an increased distance in
areas of relatively warm temperatures. This is a serious factor with
thermally unstable diazo compounds.

The presence of impurities or the possible thermal
decomposition of the diazo compound incurred during the separation of these impurities may partially explain the relatively low yields (purity) of some of the diazoalkanes prepared from lithium salts obtained by this method.

**Method B.** Tosylhydrazones of low molecular weight aldehydes (C$_2$ to C$_5$) are very unstable at room temperature and difficult to isolate in reasonable purity. Consequently this alternative method was devised.

Equivalent amounts of tosylhydrazide and the aldehydes were dissolved in tetrahydrofuran, stirred at room temperature (1-3 hours) and stored overnight in a refrigerator. The clear, colorless solution was then thoroughly flushed with dry nitrogen and cooled to 0° or -78°. n-Butyllithium (~1.6M in hexane, equivalent amount) was slowly added. After a brief period of stirring, the solvents were removed on a rotary evaporator leaving the lithium salt of the tosylhydrazone coated on the inner wall of the flask. This flask was connected to the vacuum system and the salt thoroughly dried before pyrolysis.

The main advantage of this method is that handling of the unstable tosylhydrazones could be avoided. Also, in each case the diazoalkane generated from the lithium salts obtained by Method B were of higher purity than from the corresponding salt obtained by Method A.

**Method C.** In order to improve the quality of the lithium salt before the pyrolysis, a method was devised whereby the salt is precipitated, filtered and washed.
n-Butyllithium (~1.6M in hexane) in slight excess (1-10%) was added to a stirred solution of the sulfonylhydrazone in dry tetrahydrofuran at 0° under nitrogen. The resulting mixture is stirred (30-60 minutes); then pentane (50-150 ml.) is added to cause complete precipitation of the lithium salt. This precipitate is filtered under nitrogen, washed with pentane and dried in vacuo. The salt was pulverized, transferred to the pyrolysis equipment and dried under vacuum (0.1 mm., 40-50°, 30-60 minutes) before vacuum pyrolysis. The powdery salt was internally stirred by a magnetic bar during pyrolysis to provide agitation and heat distribution. Residual traces of solvent, especially tetrahydrofuran, were found as impurities in the diazo compounds generated from salts prepared by this method. The following method eliminates this final disadvantage.

**Method D.** n-Butyllithium (1.53M in pentane) in slight excess (5-10%) was added to a vigorously stirred suspension of the tosylhydrazone in pentane at 0° to 25° under nitrogen. The suspension was stirred overnight at 25° under nitrogen. The lithium salt was filtered under nitrogen, thoroughly washed with dry pentane and dried in vacuo. The salt cake was transferred to a flask and carefully redried in vacuo (0.1 mm., 40-45°, one hour). A magnetic stirring bar pulverized and agitated the salt during this final drying phase. The lithium salts were fine, white powders, stable to the atmosphere and free from impurities and residual solvents. These salts were obtained in quantitative yields and gave excellent yields (92-95%) of diazoalkanes of high purity (95-98%).
Lithium Salts via Lithium Methoxide. Equipment. The equipment used for the preparation of lithium salt using lithium methoxide was the same as described previously (p. 130).

Procedure. Standardized lithium methoxide was added to a cold (0°), stirred solution of tosylhydrazone in dry tetrahydrofuran under nitrogen. After the lithium salt began to precipitate, pentane was added and the product filtered, washed with pentane and dried in vacuo. In an alternate procedure a solution of the tosylhydrazone in tetrahydrofuran was added to a suspension of lithium methoxide in pentane. The slurry was stirred three hours and the product filtered and treated as above. No coloration was observed at any phase of the reaction in contrast to reactions with n-butyl-lithium.

Lithium Salt of Ethanal Tosylhydrazone. Method B. A solution of tosylhydrazone (18.62 g., 0.10 mole) in tetrahydrofuran (80 ml.) was added slowly (90 minutes) to a stirred solution of ethanal (4.41 g., 0.10 mole) in tetrahydrofuran (20 ml.) at 0°. The resulting clear, colorless solution was stirred one hour at 0° and stored overnight in Dry Ice. A white precipitate formed, but was not collected. The mixture was warmed to 0° and n-butyl-lithium (1.62M in hexane, 0.10 mole, 61.5 ml.) was added in one hour under nitrogen. As the addition neared completion, a white viscous material separated from solution. The solvents were removed and the lithium salt of ethanal tosylhydrazone remained coated on the inner wall of the flask. This product was thoroughly dried in vacuo before vacuum pyrolysis.
Lithium Salt of Propanal Tosylhydrazone. Method A. Propanal
tosylhydrazone (4.52 g., 0.020 mole, m.p. 68-70° dec.) was dissolved
in tetrahydrofuran (50 ml.) at room temperature. The clear, color-
less solution was cooled to -78° under nitrogen. n-Butyllithium
(1.60M in hexane, 0.020 mole, 12.4 ml.) was quickly added (three
minutes). An exothermic reaction occurred and a clear amber-colored
solution resulted. The mixture was stirred at -78° for 35 minutes,
then allowed to warm to room temperature. The solvent was removed
on a rotary evaporator leaving the heavy, white precipitate of the
lithium salt of propanal tosylhydrazone uniformly coated on the inner
wall of the flask. A quantitative yield (4.62 g.) was obtained after
drying the salt in vacuo (20 mm., one hour, 25°).

Method B. For the purpose of generating 1-diazopropane it
was not necessary to isolate the unstable propanal tosylhydrazone.
Therefore, a second method of preparation was utilized. Freshly
distilled propanal (2.90 g., 0.050 mole, b.p. 49°) was added to a
stirred solution of tosylhydrazone (9.31 g., 0.050 mole, m.p. 109-111°)
in dry tetrahydrofuran (100 ml.) at room temperature. The resulting
clear, colorless solution was stirred one hour under nitrogen at
room temperature, then sealed and stored in a refrigerator overnight.
n-Butyllithium (1.60M in hexane, 0.060 mole, 37.5 ml.) was added
in ten minutes to the stirred solution of propanal tosylhydrazone
under nitrogen at 0°. The white salt began precipitating immediately
when the n-butyllithium was added and there was a very thick sus-
pension when the addition was completed. The suspension was stirred
at 0° for 30 minutes under nitrogen. Then the solvents were removed
on a rotary evaporator, leaving the white lithium salt of propanal tosylhydrazone coated on the inner wall of the flask. The salt was dried in vacuo (0.3 mm., 25°) for five hours before vacuum pyrolysis.

**Lithium Salt of Propanone Tosylhydrazone. Method C.** n-Butyllithium (1.62M in hexane, 0.030 mole, 18.5 ml.) was added in 15 minutes to a stirred mixture of propanone tosylhydrazone (6.789 g., 0.030 mole, m.p. 145-147 dec.) in tetrahydrofuran (35 ml.) under nitrogen at 0°. After three ml. of the n-butyllithium had been added, the tosylhydrazone had completely dissolved; after 12 ml. of the n-butyllithium had been added, precipitation of the lithium salt of propanone tosylhydrazone began. A transient yellow-orange color produced upon contact of the n-butyllithium solution with the tosylhydrazone solution was observed. When the addition was completed a moderately heavy, white precipitate had formed. Stirring of the suspension was continued at 0° for 30 minutes under nitrogen, then pentane (100 ml.) was added to complete the precipitation of the salt. After overnight storage in a refrigerator, the salt was filtered under nitrogen, washed with pentane and dried in vacuo to give 6.97 g. (100%) of the lithium salt of propanone tosylhydrazone.

**Lithium Salt of Butanal Tosylhydrazone. Method A.** Butanal tosylhydrazone (2.40 g., 0.010 mole, m.p. 65° dec.) was dissolved in tetrahydrofuran (50 ml.) and the solution was cooled to 0°. n-Butyllithium (1.60M in hexane, 0.010 mole, 6.2 ml.) was added via a syringe. When the lithium salt began to precipitate the mixture was cooled to -78°. After the addition was completed stirring was continued two hours at -78°. The solvents were removed on a rotary evaporator leaving the white residue coated on the inside of the flask. The lithium salt of butanal tosylhydrazone was dried in vacuo prior to vacuum pyrolysis.
Method B. Tosylhydrazide (9.31 g., 0.050 mole, m.p. 109-111°) and freshly distilled butanal (3.60 g., 0.050 mole, b.p. 74.5°/741 mm.) were dissolved in dry tetrahydrofuran (100 ml.) at 25°. A slightly exothermic reaction occurred. The clear, colorless solution was stirred one hour, then stored overnight in a refrigerator. n-Butyllithium (1.60M in hexane, 0.050 mole) was added in 15 minutes to the stirred solution at 0° under nitrogen. During an additional 30-minute stirring period at 0°, a very heavy, white precipitate formed. The solvents were removed on a rotary evaporator leaving the lithium salt of butanal tosylhydrazone caked on the inner wall of the flask.

Lithium Salt of 2-Methylpropanal Tosylhydrazone. Method A. n-Butyllithium (1.60M in hexane, 0.050 mole, 31.2 ml.) was added over a 10-minute period to a stirred solution of 2-methylpropanal tosylhydrazone (12.02 g., 0.050 mole, m.p. 107.5-108°) in freshly distilled tetrahydrofuran (90 ml.) under nitrogen at 0°. The lithium salt began to precipitate before the addition was completed. Additional tetrahydrofuran (50 ml.) was added to the mixture to facilitate stirring. The solvents were removed and the lithium salt of 2-methylpropanal tosylhydrazone remained caked on the wall of the flask. A quantitative yield (12.30 g.) of the salt was obtained after drying in vacuo.

Lithium Salt of 2-Butanone Tosylhydrazone. Method C. n-Butyllithium (1.62M in hexane, 0.050 mole, 30.7 ml.) was added in 10 minutes to a cold (0°), stirred solution of 2-butanone tosylhydrazone (12.02 g., 0.050 mole, m.p. 125-127°) in tetrahydrofuran (50 ml.) under nitrogen. A white precipitate began to form in the clear, light yellow solution after stirring had been continued for one hour at 0°. Complete precipitation of the salt was promoted by addition of pentane (100 ml.).
lithium salt of 2-butanone tosylhydrazone was filtered under nitrogen, washed with pentane and dried *in vacuo*. A yield of 12.3 g. (100%) of the lithium salt was obtained.

**Lithium Salt of 2-Butanone Methanesulfonylhydrazone.** *n*-Butyllithium (1.62M in hexane, 0.020 mole, 12.3 ml.) was added to a cool (0°) stirred solution of 2-butanone methanesulfonylhydrazone (3.28 g., 0.020 mole, m.p. 55-57° dec.) in tetrahydrofuran (25 ml.) under nitrogen. The slightly cloudy solution was stirred 15 minutes, then pentane (20 ml.) was added. The viscous material which separated did not crystallize and was dried to a glassy residue on the inner wall of the flask.

**Lithium Salt of Cyclopropanecarboxaldehyde Tosylhydrazone.**

**Method A.** *n*-Butyllithium (1.60M in hexane, 0.033 mole, 21 ml.) was slowly added to a stirred solution of cyclopropanecarboxaldehyde tosylhydrazone (7.15 g., 0.030 mole, m.p. 95-98° dec.) in dry tetrahydrofuran (60 ml.) at 0° under nitrogen. The heavy, white residue that remained after removal of the solvents on a rotary evaporator was pulverized and dried overnight *in vacuo* (10 mm.) at room temperature. The lithium salt of cyclopropanecarboxaldehyde tosylhydrazone was obtained as a fine white powder.

**Method B.** Cyclopropanecarboxaldehyde (4.13 g., 0.050 mole, b.p. 97-99°/750 mm.) and tosylhydrazide (9.31 g., 0.050 mole, m.p. 109-111°) were dissolved in dry tetrahydrofuran (100 ml.) at room temperature. The clear, colorless solution was stirred one hour, then stored overnight in a freezer. *n*-Butyllithium (1.60M in hexane, 0.055 mole, 34 ml.) was added to the stirred solution at 0° under nitrogen. The lithium salt of the tosylhydrazone began to precipitate before the addition of the *n*-butyllithium was completed. Stirring was continued one hour at 0°.
The solvents were removed from the white precipitate which was then pulverized and dried in vacuo to give the lithium salt of cyclopropane-carboxyaldehyde tosylhydrazone in quantitative yield as a fine, white powder.

**Lithium Salt of Pentanal Tosylhydrazone. Method A.** n-Butyllithium (1.60M in hexane, 0.030 mole, 18.7 ml.) was added to a stirred solution of pentanal tosylhydrazone (7.62 g., 0.030 mole, m.p. 49-50° dec.) in tetrahydrofuran (50 ml.) at -78° under nitrogen. Neither stirring (30 minutes, -78°) nor addition of ether (50 ml.) caused precipitation of the salt. Lithium salt of pentanal tosylhydrazone was obtained as a clear, light yellow glass after removal of the solvents on a rotary evaporator. Removal of residual solvents by drying in vacuo (0.1 mm.) left the salt as a dried froth coated on the inner wall of the flask.

**Method B.** Pentanal (4.31 g., 0.050 mole) was slowly added to a stirred solution of tosylhydrazide (9.31 g., 0.050 mole) in freshly distilled tetrahydrofuran (100 ml.) at 0° under nitrogen. Stirring was continued one hour at 0°, then the clear, colorless solution was stored overnight in a refrigerator. n-Butyllithium (1.60M in hexane, 0.050 mole, 31.0 ml.) was added in 15 minutes to the cold (0°), stirred solution. The lithium salt of pentanal tosylhydrazone was obtained, after removal of solvents, in quantitative yield as a clear glass which was dried in vacuo to a white, pumiceous solid.

**Lithium Salt of 2-Methylbutanal Tosylhydrazone. Method B.** Tosylhydrazide (9.31 g., 0.050 mole, m.p. 109-111°) and freshly distilled 2-methylbutanal (4.31 g., 0.050 mole, b.p. 91.5°/750 mm.)
were added to dry tetrahydrofuran (100 ml.) at room temperature. n-Butyllithium (1.60M in hexane, 0.050 mole, 31.2 ml.) was slowly added to the clear, colorless solution of 2-methylbutanal tosylhydrazone (formed in situ) in tetrahydrofuran at 0°. No precipitate formed. The lithium salt of 2-methylbutanal was obtained as a clear, spongy glass after removal of solvents. This material was pulverized and dried in vacuo. This salt was unstable to the atmosphere.

Method C. n-Butyllithium (1.60M in hexane, 0.02 mole, 12.4 ml.) was added to a stirred solution of 2-methylbutanal tosylhydrazone (5.08 g., 0.02 mole, m.p. 71-72° dec.) in tetrahydrofuran at -78°. After overnight storage at -78°, a white precipitate had formed which redissolved when warmed to room temperature. The salt was reprecipitated by addition of ether (50 ml.) to the stirred solution. The lithium salt of 2-methylbutanal tosylhydrazone was collected by filtration under nitrogen, washed with cold ether and dried in vacuo.

Lithium Salt of 3-Methylbutanal Tosylhydrazone. Method A.

n-Butyllithium (1.6M in hexane, 0.076 mole, 47 ml.) was added to a cold (-78°), stirred solution of 3-methylbutanal tosylhydrazone (19.27 g., 0.076 mole, m.p. 74-75° dec.) in tetrahydrofuran (100 ml.) to give a clear, light yellow solution which was stirred for 30 minutes at -78°. The solvents were slowly removed to leave a light yellow, soupy residue. This residue was dried in vacuo (0.3 mm.) overnight at room temperature to give the lithium salt of 3-methylbutanal tosylhydrazone coated on the inner wall of the flask for the subsequent vacuum pyrolysis.
Method B. Freshly distilled 3-methylbutanal (4.31 g., 0.050 mole, b.p. 93°/749 mm.) and tosylhydrazide (9.31 g., 0.050 mole) were dissolved in tetrahydrofuran (100 ml.) at room temperature and stored overnight in a refrigerator. n-Butyllithium (1.60M in hexane, 0.050 mole, 31.2 ml.) was added in 15 minutes to the clear, colorless solution at 0° and stirring was continued for 30 minutes. Solvent removal on a rotary evaporator and drying in vacuo gave a quantitative yield (13 g.) of the lithium salt of 3-methylbutanal tosylhydrazone as a white solid caked on the wall of the flask.

Lithium Salt of 2,2-Dimethylpropanal Tosylhydrazone. Method C. n-Butyllithium (1.58M in hexane, 0.10 mole, 63.5 ml.) was added in one hour to a stirred solution of 2,2-dimethylpropanal tosylhydrazone (25.44 g., 0.10 mole) in dry tetrahydrofuran (100 ml.) at 0° under nitrogen. A very dense, white precipitate formed during the addition. Pentane (100 ml.) was added and stirring was continued one hour at 0° under nitrogen. The product was filtered under nitrogen, washed with pentane and dried in vacuo. The lithium salt of 2,2-dimethylpropanal tosylhydrazone was obtained as a fine, white powder that appeared stable to the atmosphere. However, all lithium salts were stored in a desiccator. It was difficult to remove all traces of the tetrahydrofuran and for that reason preparation of the lithium salt as a suspension in pentane (as described below) is a superior method.

Method D. 2,2-Dimethylpropanal tosylhydrazone (12.717 g., 0.050 mole, m.p. 112-113°) was suspended in pentane (100 ml.) at
room temperature under nitrogen. n-Butyllithium (1.53M in pentane, 34.5 ml., 0.053 mole) was slowly added (30 minutes) to the vigorously stirred suspension. The reaction was exothermic. When the solvent began refluxing, a cold water bath (15-20°C) was used to moderate the reaction. Characteristically the yellow-orange color, produced upon contact of the n-butyllithium solution with the tosylhydrazone, was quickly dispelled by the rapid stirring until nearly an equivalent amount of the base had been added. After that time the light yellow suspension retained its color. The suspension was stirred overnight at room temperature. The salt was filtered under nitrogen, washed with pentane and dried in vacuo (10 mm., 2 hours, 25°C). Final drying (0.1 mm., 30 minutes, 45°C) gave a quantitative yield (13.02 g.) of the lithium salt of 2,2-dimethylpropanal tosylhydrazone as a fine, white powder. Although this salt appeared to be stable to the atmosphere the transfer to the vacuum pyrolysis equipment was effected in a dry box.

**Lithium Salt of 2,2-Dimethylpropanal Tosylhydrazone via Lithium Methoxide.** A solution of 2,2-dimethylpropanal tosylhydrazone (1.00 g., 3.93 millimoles, m.p. 112.5-113.5°C) in dry tetrahydrofuran (4.5 ml.) was added to a vigorously stirred slurry of lithium methoxide (0.168 g., 4.32 millimoles) in pentane (20 ml.) at 0°C under nitrogen. A heavy, white precipitate began to form immediately. Pentane (100 ml.) was added and stirring at 0°C under nitrogen was continued one hour. The lithium salt of 2,2-dimethylpropanal tosylhydrazone was filtered under nitrogen, washed with pentane and dried in vacuo. The product contained a quantitative yield of the lithium salt and the excess lithium methoxide.
Lithium Salt of 2,2-Dimethylpropanal Methanesulfonylhydrazone.

2,2-Dimethylpropanal methanesulfonylhydrazone (8.91 g., 0.050 mole, m.p. 134-135°) was dissolved in dry tetrahydrofuran (70 ml.) The solution was thoroughly flushed with nitrogen and cooled to 0°. n-Butyllithium (1.62M in hexane, 0.050 mole, 31 ml.) was added to the stirred solution in 20 minutes. During the addition a precipitate began to form and became so heavy that it was necessary to add tetrahydrofuran (45 ml.). In contrast to observations made during the reaction of n-butyllithium with tosylhydrazones and besylhydrazones, no coloration was produced in this reaction. The slurry was stirred at 0° for 30 minutes, then pentane (60 ml.) was added and stirring was continued an additional 30 minutes. The product was filtered under nitrogen, washed with pentane and dried in vacuo. The thick, white paste dried to hard chunks which were pulverized and redried. A yield of 9.15 g. (99.5%) of the lithium salt of 2,2-dimethylpropanal methanesulfonylhydrazone was obtained. This salt appeared to be quite stable to the atmosphere.

Lithium Salt of 3-Methyl-2-butanone Tosylhydrazone. Method C.
n-Butyllithium (1.62M in hexane, 0.050 mole, 31 ml.) was added in 10 minutes to a magnetically stirred solution of 3-methyl-2-butanone tosylhydrazone (12.72 g., 0.050 mole, m.p. 118-120°) in dry tetrahydrofuran (50 ml.) at 0° under nitrogen. A bright yellow coloration was observed in the solution during addition of the n-butyllithium. No precipitate formed in the clear, colorless solution, even with the addition of pentane (100 ml.), until after the solution had been stored several days in a refrigerator. The white product was
filtered under nitrogen, washed with pentane and dried in vacuo. A quantitative yield of 13 g. of the lithium salt of 3-methyl-2-butanone tosylhydrazone was obtained.

**Lithium Salt of Cyclopentanone Tosylhydrazone.** N-Butyllithium (1.6M in hexane, 0.019 mole, 11.8 ml.) was added to a stirred solution of cyclopentanone tosylhydrazone (5.04 g., 0.020 mole, m.p. 179-180°) in tetrahydrofuran (50 ml.) under nitrogen at -78°. The solvents were removed, the residue dried in vacuo, then pulverized and redried. The lithium salt of cyclopentanone tosylhydrazone was obtained as a white powder.

**Lithium Salt of 3,3-Dimethyl-2-butanone Tosylhydrazone.** Method C. n-Butyllithium (1.62M in hexane, 0.050 mole, 31 ml.) was added in 30 minutes to a stirred solution of 3,3-dimethyl-2-butanone tosylhydrazone (13.42 g., 0.050 mole) in tetrahydrofuran (60 ml.) at 0° under nitrogen. A transient yellow-orange color, produced upon contact of the two reactants, was observed in this reaction. This color is easily dispelled by the stirring action until one equivalent of base has been added, then the color persists. Pentane (150 ml.) was added and stirring was continued one hour at 0°. The white lithium salt of 3,3-dimethyl-2-butanone tosylhydrazone was collected by filtration under nitrogen, washed with pentane and dried in vacuo. A yield of 16.25 g. (118%) was obtained after initial drying. The lithium salt was pulverized and redried, but the excess weight was not appreciably reduced. This abnormal weight increase was not observed when the lithium salt was prepared using pentane as the only solvent. The absence of residual solvent is particularly
importance for the generation of pure diazo compounds via the vacuum pyrolysis of the salts of hydrazones.

**Method D.** 3,3-Dimethyl-2-butanone tosylhydrazone (13.419 g., 0.050 mole, m.p. 153-155°) was suspended by vigorous stirring with a magnetic stirring bar in pentane (125 ml., dried over neutral alumina) at 0° under nitrogen. n-Butyllithium (1.53M in pentane, 36.5 ml., 0.055 mole) was slowly added to the stirred suspension over a 30 minute period. The reaction was exothermic and produced the typical yellow-orange color that is quickly dispelled by the stirring. The excess n-butyllithium caused the final suspension to be a light yellow color. Stirring was continued under nitrogen overnight. The lithium salt of 3,3-dimethyl-2-butanone tosylhydrazone was collected by vacuum filtration under nitrogen, washed with pentane and dried in vacuo. A quantitative yield (13.71 g.) of the white, powdery salt was obtained after drying. This salt was stable at room temperature if protected from moisture. (Fig. 4).

**Lithium Salt of 3,3-Dimethyl-2-butanone Tosylhydrazone via Lithium Methoxide.** Lithium methoxide (0.76 g., 0.020 mole) was quickly added to a stirred solution of 3,3-dimethyl-2-butanone tosylhydrazone (5.37 g., 0.020 mole) in tetrahydrofuran (25 ml.) at 0° under nitrogen. The small amount of lithium methoxide that did not dissolve formed a finely divided suspension. After 15 minutes of stirring at 0° a dense, white precipitate formed. Pentane (50 ml.) was added and stirring was continued 30 minutes, then the slurry was stored overnight at 0°. The product was filtered under nitrogen, washed with pentane and dried in vacuo. The first crop yielded
Figure 4.--Infrared Spectrum of the Lithium Salt of 3,3-Dimethyl-2-butanone Tosylhydrazone
5.07 g. (93%) of the lithium salt of 3,3-dimethyl-2-butanone tosyl-
hydrazone as a fine, white powder.

**Lithium Salt of 3,3-Dimethyl-2-butanone Benzenesulfonyl-
hydrazone.** n-Butyllithium (1.62 M in hexane, 0.055 mole, 34 ml.) was
added to a stirred solution of 3,3-dimethyl-2-butanone benzene-
sulfonylhydrazone (13.99 g., 0.055 mole, m.p. 110-111°) in dry
tetrahydrofuran (70 ml.) under nitrogen. The solution was cooled
to 0° to moderate the exothermic reaction. The addition was com-
pleted in 20 minutes. A yellow-orange color was observed upon
contact of the two reactants. This transient coloration was
quickly dispelled by the stirring action. The lithium salt began
to precipitate before addition of the base was completed. This
mixture was stirred 40 minutes, pentane (125 ml.) was added and
stirring continued one hour. The salt was filtered under nitrogen,
washed with pentane and dried in vacuo.

**Lithium Salt of 3,3-Dimethyl-2-butanone Methanesulfonyl-
hydrazone.** 3,3-Dimethyl-2-butanone methanesulfonylhydrazone (5.77 g.,
0.030 mole, m.p. 107-108°) was dissolved in dry tetrahydrofuran
(50 ml.) at room temperature. This stirred solution was thoroughly
flushed with dry nitrogen and cooled to 0° before n-butyllithium
(1.62 M in hexane, 0.030 mole, 18.5 ml.) was injected over a 10-minute
period. No coloration was observed at any time during the addition.
Precipitation of the lithium salt began during the addition. Pentane
(100 ml.) was added. The mixture was allowed to stir 30 minutes,
then the thick, white precipitate was collected under nitrogen and
washed with pentane. The lithium salt of 3,3-dimethyl-2-butanone
methanesulfonylhydrazone (6 g., quantitative yield) was pulverized and dried in vacuo.

**Lithium Salt of Cyclohexanone Tosylhydrazone.** n-Butyl-lithium (1.45M in hexane, 0.020 mole, 13.8 ml.) was added to a stirred solution of cyclohexanone tosylhydrazone (5.32 g., 0.020 mole) in tetrahydrofuran (50 ml.) at 0° under nitrogen. After the solution had been stirred for 30 minutes ether (50 ml.) was added to precipitate the salt. The solvents were removed from the heavy, white precipitate which was then pulverized and dried in vacuo.

**Lithium Salt of Phenylacetaldehyde Tosylhydrazone. Method A.** Phenylacetaldehyde tosylhydrazone (2.88 g., 0.010 mole) was dissolved in tetrahydrofuran (30 ml.) at 0° under nitrogen. n-Butyl-lithium (1.58M in hexane, 0.010 mole, 6.4 ml.) was added to the stirred solution. The mixture was stirred 30 minutes, then the solvents were removed to give the lithium salt of phenylacetaldehyde tosylhydrazone coated on the wall of the flask. This material was dried in vacuo at room temperature prior to vacuum pyrolysis.

**Lithium Salt of Acetophenone Tosylhydrazone. Method C.** Acetophenone tosylhydrazone (14.42 g., 0.050 mole) was dissolved in dry tetrahydrofuran and the resulting clear, colorless solution was cooled to 0° and thoroughly flushed with nitrogen. The addition of n-butyllithium (1.62M in hexane, 0.050 mole, 31 ml.) produced a distinct yellow-orange color that was quickly dispelled by stirring. Ether (75 ml.) was added to the solution after it had been stirred for 30 minutes. A white precipitate immediately began to form which became very thick during the two-hour period of stirring at 0°. The
lithium salt of acetophenone tosylhydrazone collected by filtration under nitrogen was washed with dry ether and dried overnight in vacuo (10 mm.) at room temperature. The lithium salt developed a pink color from its decomposition to 1-diazo-1-phenyl ethane under these conditions.

**Lithium Salt of 2-Phenylpropanal Tosylhydrazone. Method A.**

2-Phenylpropanal tosylhydrazone (3.02 g., 0.010 mole) was dissolved in tetrahydrofuran (50 ml.). n-Butyllithium (1.60M in hexane, 0.010 mole, 6.3 ml.) was added in 15 minutes to the stirred solution at -78°. Stirring was continued for 30 minutes at -78°. The solvents were removed on a rotary evaporator to give the lithium salt of 2-phenylpropanal tosylhydrazone as a colorless glass coated on the inner wall of the flask. This residue was dried in vacuo to remove residual solvents prior to vacuum pyrolysis.

**Lithium Salt of 3-Phenylpropanal Tosylhydrazone.**

3-Phenylpropanal tosylhydrazone (3.02 g., 0.010 mole) was dissolved in tetrahydrofuran (50 ml.) at 0°. n-Butyllithium (1.59M in hexane, 0.010 mole, 6.3 ml.) was added in 20 minutes to the solution under nitrogen. After the addition was completed the white slurry was stirred at room temperature for one hour. The lithium salt of 3-phenylpropanal tosylhydrazone was filtered and dried in vacuo.

**Lithium Salt of 3-Phenylpropenal Tosylhydrazone. Method C.**

n-Butyllithium (1.62M in hexane, 0.022 mole, 13.6 ml.) was added to a stirred solution of 3-phenylpropenal tosylhydrazone (6.65 g., 0.022 mole, m.p. 161-163° dec.) in tetrahydrofuran (100 ml.) under nitrogen at 0°. A very deep red coloration, which occurred upon
addition of the n-butyllithium, was quickly dispelled by the stirring action. The addition of pentane (100 ml.) caused a very heavy, white precipitate of the product to form. This slurry was stirred 30 minutes at 0° under nitrogen then the product was filtered under nitrogen, washed with pentane and dried in vacuo. A quantitative yield (6.7 g.) of this salt was obtained.

**Lithium Salt of 1-Phenyl-2-propanone Tosylhydrazone.**

**Method C.** n-Butyllithium (1.59M in hexane, 0.052 mole, 32.5 ml.) was added to a stirred solution of 1-phenyl-2-propanone tosylhydrazone (15.10 g., 0.050 mole, m.p. 134-135°) in dry tetrahydrofuran (100 ml.) under nitrogen at 0°. No precipitate formed in the clear, light yellow solution even after 30 minutes of stirring. The addition of dry ether (50 ml.) produced an immediate fine, white precipitate which became very heavy after being stirred at 0° for 30 minutes. The lithium salt of 1-phenyl-2-propanone tosylhydrazone was filtered under nitrogen, washed with cold ether and dried in vacuo. This salt did not appear to be hygroscopic and was stable at room temperature.

**Lithium Salt of 4-Phenyl-3-buten-2-one Tosylhydrazone.**

**Method C.** n-Butyllithium (1.6M in hexane, 0.050 mole, 31 ml.) was added to a stirred mixture of 4-phenyl-3-buten-2-one (15.72 g., 0.050 mole, m.p. 181-183° dec.) in tetrahydrofuran (200 ml.) at room temperature under nitrogen. All of the tosylhydrazone had dissolved after 10 ml. of n-butyllithium had been added. The clear, yellow solution was cooled to 0° and the remainder of the
n-butyllithium added in 15 minutes. Pentane (200 ml.) was added and gradually a white precipitate formed. This product was collected under nitrogen, washed with pentane and dried \textit{in vacuo}. A quantity of yellow tar isolated from the filtrate explained the relatively low yield of 14.95 g. (93\%) of the lithium salt of 4-phenyl-2-buten-2-one tosylhydrazone obtained in this experiment.

\textbf{Lithium Salt of Benzophenone Tosylhydrazone.} n-Butyllumtium (1.62M in hexane, 0.050 mole, 31 ml.) was added to a stirred solution of benzophenone tosylhydrazone (17.52 g., 0.050 mole, m.p. 179-180° in dry tetrahydrofuran (50 ml.) at room temperature under nitrogen. The heavy, white precipitate was filtered, washed with pentane and dried \textit{in vacuo}. A quantitative yield of 17.8 g. of the lithium salt of benzophenone tosylhydrazone was obtained.

\textbf{Lithium Salt of Phenyl cyclohexyl ketone Tosylhydrazone.} Phenyl cyclohexyl ketone (8.91 g., 0.025 mole, m.p. 92°) was dissolved in tetrahydrofuran (50 ml.) at 0°. The clear, light tan solution was stirred and thoroughly flushed with dry nitrogen. n-Butyllithium (1.62M in hexane, 0.025 mole, 15.4 ml.) was added in 10 minutes. Stirring for 30 minutes and the addition of pentane (100 ml.) both failed to initiate precipitation of the lithium salt. The solution was concentrated on a rotary evaporator to a viscous, amber oil. Treatment of this oil with pentane (100 ml.) and Skelly Solve F failed to promote crystallization. All solvents were then removed to give the lithium salt of phenyl cyclohexyl ketone tosylhydrazone as a light yellow, glassy residue. This product was dried, pulverized and redried \textit{in vacuo}. 
Lithium Salt of Dibenzyl Ketone Tosylhydrazone. n-Butyl-lithium (1.62M in hexane, 0.050 mole, 31 ml.) was quickly added (five minutes) to a magnetically stirred solution of dibenzyl ketone tosylhydrazone (17.72 g., 0.05 mole, m.p. 183-184°) in tetrahydrofuran (100 ml.) under nitrogen at 0°. An oil soon separated which gradually crystallized after the addition of pentane (75 ml.). After overnight storage at -78° the product was filtered under nitrogen, washed with pentane and dried in vacuo. The lithium salt of dibenzyl ketone tosylhydrazone was obtained as a white powder in quantitative yield (18 g.).

Sodium Salt of 2,2-Dimethylpropanal Tosylhydrazone. Sodium methoxide (97.5%, 5.82 g., 0.105 mole) was added to a stirred solution of 2,2-dimethylpropanal tosylhydrazone (25.44 g., 0.10 mole, m.p. 112-113°) in dry tetrahydrofuran (50 ml.) under nitrogen at room temperature. The mixture was stirred three hours before dry pentane (100 ml.) was added to precipitate the product. The thick, white precipitate was filtered under nitrogen, washed with dry pentane (3 x 50 ml.) and dried in vacuo (0.1 mm., 25°) for 24 hours. A quantitative yield (27.6 g.) of the sodium salt of 2,2-dimethylpropanal tosylhydrazone was obtained. Although the finely powdered, white salt appeared to be stable to the atmosphere, it was stored in a desiccator over Drierite granules.

Sodium Salt of 3,3-Dimethyl-2-butanone Tosylhydrazone. 3,3-Dimethyl-2-butanone tosylhydrazone (26.04 g., 0.10 mole, m.p. 155-156°) dissolved in dry tetrahydrofuran (25 ml.) was injected into a
stirred suspension of sodium methoxide (97.5%, 5.82 g., 0.105 mole) in dry pentane (25 ml.) under nitrogen at 25°. The mixture soon became very cloudy and a heavy white precipitate formed during three hours of stirring. Dry pentane (100 ml.) was added and the product filtered under nitrogen, washed with dry pentane (3 x 50 ml.) then dried in vacuo (0.1 mm., 25°) 18 hours to give 27.8 g. (99%) of the sodium salt of 3,3-dimethyl-2-butanone tosylhydrazone. The very fine, white powder was stored in a desiccator.

The sodium salt was also prepared by mixing the sodium salt of tosylhydrazide (1.04 g., 0.005 mole) and 3,3-dimethyl-2-butanone (0.50 g., 0.005 mole) in dry tetrahydrofuran (15 ml.) and stirring the suspension five hours at room temperature. Dry hexane (15 ml.) was added to precipitate the product which was filtered, washed with hexane and dried under vacuum overnight. During the time that the suspension was stirred, its appearance changed from granular to very fine microcrystalline. A small sample (0.05 g.) of the salt was pyrolyzed in diethyl Carbitol at 150° in a sealed serum vial. Gas chromatographic analysis of the pyrolysis products (150° gas-phase sample) showed the presence of 3,3-dimethyl-1-butene, 1,1,2-trimethylcyclopropane, 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene.

Sodium Salt of Tosylhydrazide. A solution of tosylhydrazide (18.625 g., 0.100 mole) in dry tetrahydrofuran (25 ml.) was injected into a stirred suspension of sodium methoxide (97.5%, 5.600 g., 0.101 mole) in dry tetrahydrofuran (35 ml.) under nitrogen at room
temperature. After the mixture had stirred three hours, dry hexane (60 ml.) was added to precipitate the salt. The thick, white product was filtered, washed with dry hexane (3 x 60 ml.) and dried in vacuo 24 hours (0.1 mm., 25-30\(^\circ\)). A yield of 20.61 g. (99%) of the sodium salt of tosylhydrazide was obtained. The fine, white powder was freely water-soluble, but not noticeably hygroscopic.
Decomposition of Tosylhydrazones with Bases in Diethyl Carbitol

**General Techniques.** The tosylhydrazones of phenylacetaldehyde, 1-phenylpropanone, 2-phenylpropanal, 3-phenylpropanal, and diphenylacetaldehyde and various bases (sodium methoxide, sodium amide and n-butyllithium) were added to diethyl Carbitol at -78° to 25°. The resulting slurries were slowly heated to 120-140° to decompose the salts of tosylhydrazones formed in situ. The decomposition products were extracted with pentane, isolated and analyzed by gas chromatography.

**Equipment.** A 2-necked (§ 14/35), round-bottomed flask (100-250 ml.) was equipped with a magnetic stirring bar and a water-jacketed reflux condenser (8", Liebig type). The second neck of the flask, which was used for the addition of reactants and solvents, was sealed with a rubber serum stopper. An adapter (90°) in the top of the condenser was connected by Tygon tubing to an efficient cold trap (6" base with numerous Vigreaux indentations). The outlet of the cold trap was connected by Tygon tubing to the glass inlet tubing of the gas collector, which consisted of an inverted, water-filled graduated cylinder (500-2000 ml.) standing in a crystallizing dish (6-1/2") partially filled with water. The glass inlet tubing was positioned under the pouring lip of the inverted cylinder. (Fig. 5).

A rubber serum stopper in the base of the inverted cylinder permitted sampling of the collected gas for analysis and facilitated refilling of the cylinder with water by removal of the gas collected.
Figure 5. -- Apparatus for Decomposition of Tosylhydrazones and for Analysis of Diazo Compounds
Each unit of the system could be isolated by tightening a screw clamp upon the sections of Tygon tubing. All ground glass joints were secured by tightly stretched rubber bands attached to wire hooks on both sections of the joint and all Tygon tubing connections were secured with wire to prevent gas leakage.

The cold trap was immersed in a Dry Ice—isopropanol bath (-78°C). An internally heated, thermostatically controlled oil bath was mounted on a magnetic stirring motor which propelled the magnetic stirring bars in the oil bath and in the round-bottomed flask. The bath and motor were raised to immerse the flask by a laboratory jack.

Reagents. The tosylhydrazones were recrystallized and dried in vacuo overnight at room temperature. n-Butyllithium (1.59M in hexane, Foote Mineral Company) was titrated with standardized acid solution (0.500 N HCl). Two different samples of sodium methoxide (Matheson, Coleman and Bell) were each titrated (72% and 78%) against standardized acid solution. Sodium amide (sample supplied by Dr. Greenlee) was not standardized and was assumed to be of 95% purity. Generally excess base (10-30%) was used in the decomposition of a tosylhydrazone. Diethyl Carbitol was treated with potassium hydroxide pellets, distilled from calcium hydride and stored under nitrogen. Reagent grade pentane was used for the extractions.

Procedure. A tosylhydrazone (0.005-0.020 mole) and freshly distilled diethyl Carbitol (25-50 ml.) were transferred to a 2-necked (⌀ 14/35), round-bottomed flask (100-250 ml.) which was
fitted with a magnetic stirring bar and water-cooled condenser. The mixture was briefly warmed to complete solution and allowed to cool to room temperature before an appropriate amount of a solid base was added through a powder funnel placed in the second neck of the flask. The second neck was quickly sealed with a serum stopper. When n-butyllithium was used as base, the appropriate volume of a standardized solution of n-butyllithium in hexane was injected by syringe through the serum stopper into the flask.

The screw clamps on the Tygon tubing connecting the cold trap to the adapter in the top of the condenser and to the gas collector were opened. As the cold trap was chilled to -78°C nitrogen was injected into the system to prevent back flow of water from the gas collector into the cold trap. The oil bath was raised into position and stirring of the slurry in the flask was begun. The flask was slowly heated (60-120 minutes) from room temperature to 120-140°C. During this heating period the slurry became very thick and viscous as the tosylhydrazone salt formed, then very fluid as this salt decomposed. The rate and progress of this decomposition was monitored by observing the volume of gas evolved.

When the reaction was completed each unit of the system was isolated by closing the screw clamps on the Tygon tubing. The net volume of evolved gas was measured and corrected to S.T.P. and for expansion of solvent and gas in the heated flask as determined from control experiments. This corrected volume of gas was compared to theoretical volume to determine per cent reaction and used as a guide to estimate reaction efficiency.
The oil bath was removed and the flask contents allowed to cool before water and pentane were added. The solid residue in the flask quickly dissolved and the two-phase liquid system was transferred to a separatory funnel where the lower (aqueous) layer was drawn off and discarded. The upper (pentane) layer containing the hydrocarbon products of the reaction was repeatedly washed with water to remove diethyl Carbitol, then dried over powdered anhydrous magnesium sulfate (3-24 hours). After most of the pentane had been removed under vacuum at room temperature, the residue was analyzed by gas chromatography.

The products were identified by comparison of retention times with authentic standards. Occasionally these identifications were confirmed by comparison of the infrared spectrum of material collected from the effluent gas stream of the gas chromatograph with the infrared spectrum of authentic standard. Per cent product distributions were determined by calculation of peak areas on the chromatograms.

**Decomposition of Phenylacetaldehyde Tosylhydrazone with n-Butyl-lithium.** (12.8 ml., 1.59M in hexane, 0.021 mole) was slowly added (25 minutes) to a stirred solution of phenylacetaldehyde tosylhydrazone (5.76 g., 0.020 mole, m.p. 110-110.5°) in diethyl Carbitol (50 ml.) at room temperature. A dense, cream-colored precipitate formed in the mixture during the addition. When the addition was completed the mixture was slowly heated (110 minutes) to 125°. The decomposition of the lithium salt became regular and rapid as the temperature reached 110° and attained its peak rate at 118°. The decomposition was judged
complete when gas evolution ceased and then the reacted mixture was cooled to 25°.

After the addition of pentane (25 ml.) and water (25 ml.) the contents of the flask were transferred to a separatory funnel where the lower (aqueous) layer was drawn off and discarded. The pentane layer was washed with water (3 x 100 ml.), dried over anhydrous magnesium sulfate and concentrated by removal of pentane under reduced pressure at room temperature. The light, orange-colored liquid residue was analyzed by gas chromatography.

Analyses of the decomposition products from phenylacetaldehyde tosylhydrazone with n-butyllithium and sodium methoxide were effected on 30% SE30 on 42/60 firebrick 5' x 1/4" and squalane 100' capillary columns. Styrene was shown to be the only hydrocarbon product from each reaction. Benzocyclobutene, ethylbenzene and o-xylene were not present.

Decomposition of Phenylacetaldehyde Tosylhydrazone with Sodium Methoxide. Phenylacetaldehyde tosylhydrazone (1.44 g., 0.005 mole) and sodium methoxide (72%, 0.41 g., 0.0055 mole) were added to diethyl Carbitol (30 ml.). The stirred mixture was slowly (60 minutes) heated to 145°. A nearly quantitative corrected volume of nitrogen was evolved.

The reacted mixture was cooled before water (25 ml.) and pentane (50 ml.) were added to dissolve the solid residue and extract the decomposition products. The aqueous layer was discarded. The pentane layer was repeatedly washed with water to remove diethyl Carbitol and dried over anhydrous magnesium sulfate.
After removal of the pentane under reduced pressure at room temperature the residue was analyzed by gas chromatography. Styrene was the only hydrocarbon product from the decomposition.

Decomposition of 1-Phenylpropanone Tosylhydrazone with Sodium Methoxide. Sodium methoxide (78%, 3.5 g., 0.05 mole) was added to a stirred solution of 1-phenylpropanone tosylhydrazone (15.1 g., 0.05 mole) in diethyl Carbitol (50 ml.) at 25°. The stirred mixture was slowly (60 minutes) heated to 140°. Rapid decomposition commenced as the temperature reached 115°. When gas evolution ceased, a nearly quantitative (95%) volume (corrected) had been collected.

The cooled reaction mixture was extracted with water (50 ml.) and pentane (100 ml.) and the aqueous layer discarded. The pentane layer was washed with water (6 x 50 ml.), dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator at 25-30°.

Gas chromatographic analysis of the residual decomposition products on 30% DC550 (15' x 1/4") and squalane 100' capillary columns showed the presence of 3-phenyl-l-propene (14%), cis-l-phenyl-l-propene (17%) and trans-l-phenyl-l-propene (69%). It was also shown that 2-phenyl-l-propene was not present. All identifications were made by the use of authentic samples of these products.

Decomposition of 2-Phenylpropanal Tosylhydrazone with n-Butyllithium. n-Butyllithium (1.59M in hexane, 12.6 ml., 0.020 mole) was injected in 10 minutes into a stirred solution of 2-phenylpropanal (6.04 g., 0.020 mole, m.p. 95-96°) in diethyl Carbitol (50 ml., freshly chromatographed through neutral alumina) at 0° in a closed system protected from the atmosphere. The stirred mixture
was allowed to warm to room temperature, then slowly (one hour) heated to 125°. A white precipitate began to form at 70°, and at 105° the precipitated salt of the tosylhydrazone was so thick that all stirring action stopped. At 110° decomposition of the salt began and became very rapid at 120°. During the decomposition 422 ml. (corrected, 94%) of gas was evolved.

The final mixture of solvent, hydrocarbon products and lithium p-toluenesulfinate was cooled to 0°. Pentane (25 ml.) and water (25 ml.) were added to the stirred mixture. All solid material dissolved to give a two-phase liquid system which was transferred to a separatory funnel. The lower layer was removed and discarded. The pentane layer was washed with water (4 x 250 ml.) to extract diethyl Carbitol, stirred three hours with powdered anhydrous magnesium sulfate, filtered and concentrated by removal of pentane under reduced pressure to give three ml. of light yellow liquid.

3-Phenyl-1-propene (4%), 2-phenyl-1-propene (38%), cis-1-phenyl-1-propene (23%), phenylcyclopropane (21%), and trans-1-propene (14%) were identified as the decomposition products by gas chromatography on a 100' squalane capillary column with the aid of authentic samples. The percentages are only approximate because incomplete separation by gas chromatography of 2-phenyl-1-propene and cis-1-phenyl-1-propene made precise measurements of respective peak areas impossible.

Decomposition of 2-Phenylpropanal Tosylhydrazone with Sodium Amide. Sodium amide (0.86 g., 0.022 mole) was added from an enclosed side arm into a flask containing 2-phenylpropanal tosylhydrazone
(6.02 g., 0.02 mole) dissolved in diethyl Carbitol at -78°. The mixture was stirred vigorously and allowed to warm to room temperature, then slowly (65 minutes) heated to 125°. The gas evolved during the decomposition was passed through dilute acid (HCl) solution and collected over water. The corrected volume was 88% of the amount expected.

Water (200 ml.) and pentane (100 ml.) were used to transfer the decomposition mixture to a separatory funnel where the lower layer was drawn off and discarded. The pentane was washed with water, dried over anhydrous magnesium sulfate and concentrated under reduced pressure at 25-30° to give 3 g. of light yellow liquid.

Gas chromatographic analysis effected on a 100' squalane capillary column identified the five decomposition products as 3-phenyl-1-propene, 2-phenyl-1-propene, cis-1-phenyl-2-propene, phenylcyclopropane and trans-1-phenyl-2-propene, in order of increasing retention times. All products were identified by comparison of retention times with authentic standards and the identity of 3-phenyl-1-propene was confirmed by comparison of the infrared spectrum of a sample trapped from the gas chromatograph with the spectrum of an authentic standard.

Decomposition of 2-Phenylpropanal Tosylhydrazone with Sodium Methoxide. Sodium methoxide (standardized 78%, 1.19 g., 0.022 mole) was added to a flask containing a cold (0°), stirred solution of 2-phenylpropanal tosylhydrazone (6.04 g., 0.020 mole, m.p. 95-96°) in diethyl Carbitol (50 ml., treated with neutral alumina) and the system quickly resealed. The mixture was briskly stirred and gradually heated to 120°. A heavy precipitate (sodium salt of
2-phenylpropanal tosylhydrazone), which had formed by the time the temperature reached 100°, began to decompose rapidly at 105-110° with vigorous gas evolution.

Work-up of the reaction products was effected by dissolution of the solid material and solvent with water (100 ml.) and extraction of the hydrocarbon products with pentane (100 ml.). The lower, aqueous, layer was discarded and the light yellow pentane layer was extracted with water (4 x 250 ml.) to remove residual diethyl Carbitol, dried over powdered anhydrous magnesium sulfate (three hours) and concentrated by removal of pentane on a rotary evaporator at 25-30°.

Gas chromatographic separation and identification of the five hydrocarbon products of the decomposition was accomplished on a 100' squalane capillary column. The products (in order of their retention time), 3-phenyl-1-propene (13%), 2-phenyl-1-propene (45%), cis-1-phenyl-1-propene (13%), phenylcyclopropane (10%), and trans-1-phenyl-1-propene (19%), were identified by comparison of their retention time with those of authentic samples. The percentages are approximate because incomplete gas chromatographic separation of 2-phenyl-1-propene and cis-1-phenyl-1-propene made precise measurement of their respective peak areas impossible.

Decomposition of 3-Phenylpropanal Tosylhydrazone with n-Butyl-lithium. 3-Phenylpropanal tosylhydrazone (6.04 g., 0.020 mole, m.p. 106°) was dissolved in diethyl Carbitol (50 ml., alumina treated) at room temperature. n-Butyllithium (1.59M in hexane, 12.6 ml., 0.020 mole) was added to the clear, stirred solution in 10 minutes.
Precipitation of the lithium salt of 3-phenylpropanal tosylhydrazone commenced immediately. When the addition was completed, the viscous, white slurry was heated from 30° to 122° in 95 minutes. Decomposition of the tosylhydrazone salt began at 85°, became regular at 110° and reached a maximum rate at 116°. Total gas evolution (uncorrected) was 470 ml.

Pentane (75 ml.) was used to transfer the decomposition slurry to a separatory funnel (250 ml.). Water (100 ml.) was added to dissolve the solid material. The aqueous layer of the two-phase system was drawn off and discarded. The pentane layer was washed with four 100-ml. portions of water to remove residual diethyl Carbitol, then dried 24 hours over anhydrous magnesium sulfate.

The pentane was removed at room temperature under reduced pressure to give five ml. of light yellow residue. This residue was analyzed by gas chromatography on a 23% DC550, 10' x 1/4", 42/60 firebrick column at 170-200°. By the use of authentic samples it was shown that 3-phenyl-1-propene was the sole hydrocarbon product of the decomposition. Indane, phenylcyclopropane, cis-1-phenyl-1-propene or trans-1-phenyl-1-propene were not present. An infrared spectrum of a sample collected from the effluent gas from the gas chromatograph for a peak identified as 3-phenyl-1-propene by retention time corresponded perfectly to the spectrum of an authentic sample of 3-phenyl-1-propene.

Decomposition of 3-Phenylpropanal Tosylhydrazone with Sodium Methoxide. A white, fluffy precipitate formed immediately upon the addition of sodium methoxide (72% purity, 0.41 g., 0.0055 mole) to
a stirred solution of 3-phenylpropanal tosylhydrazone (1.51 g., 0.005 mole) in diethyl Carbitol (50 ml.) at room temperature. The rapidly stirred suspension was gradually heated to 130°. The corrected volume of gas evolved during the decomposition indicated 90% reaction.

The decomposition products were treated in the usual manner to yield one to two ml. of a light yellow residue. The gas chromatographic analysis of this residue showed 3-phenyl-1-propene to be the only hydrocarbon product from the decomposition of the sodium salt of 3-phenylpropanal tosylhydrazone under these conditions. A 23\% DC550 101 x 1/4" (42/60 firebrick) column at 180-200° was used for the analysis.

Decomposition of Diphenylacetaldehyde Tosylhydrazone with Sodium Methoxide. Sodium methoxide (72\%, 1.65 g., 0.022 mole) was added to a stirred solution of diphenylacetaldehyde tosylhydrazone (7.28 g., 0.020 mole) in diethyl Carbitol (50 ml.). The mixture was slowly heated to a maximum temperature of 140° with precipitation of the sodium salt occurring at 85-90° and decomposition of the salt beginning at 110°. The theoretical volume (corrected) of gas was evolved.

Water (25 ml.) was added to the cooled mixture to dissolve the solid residue (sodium p-toluenesulfinate). Pentane (50 ml.) was added and the two-phase liquid system transferred to a separatory funnel. The aqueous layer was discarded. The pentane layer was washed repeatedly with water to remove diethyl Carbitol, dried over anhydrous sodium sulfate and concentrated by removal of pentane under reduced pressure.
Gas chromatographic analysis on a 15' Carbowax 1500 column at 173° and on a 100' polar capillary column at 120° showed one product peak which corresponded to the retention time of both 1,1-diphenylethylene and cis-stilbene. *Trans*-stilbene was shown not to be present by the use of an authentic sample. A mixture of authentic samples of 1,1-diphenylethylene (b.p. 277°) and *cis*-stilbene (b.p. 278°) could not be separated under these conditions. An infrared spectrum of the decomposition concentrate was in good agreement with the absorption pattern for 1,1-diphenylethylene.

Preparation of Diazooalkanes by Vacuum Pyrolyses of Lithium Salts of Tosylhydrazones

**General Techniques. Equipment.** The equipment in its most effective modified form (Fig. 6) consisted of a round-bottomed, 1-necked flask (100 ml., # 24/40) connected by an adapter (90°) to a series of three traps. The first two traps were designed (Fig. 6) for efficient collection and facile removal of diazo compounds. The third trap was of the vacuum pump type and was used to collect residual solvent during final drying of the lithium salts. The temperature and sequence of cooling for each trap was controlled by individual Dewar flasks.

The connections between each unit of the vacuum system were made with short sections of Tygon tubing (3/16" i.d.) secured with wire. A screw clamp was tightened on each of these sections of Tygon tubing to isolate the units of the vacuum system at the completion of a pyrolysis.

The pyrolysis flask and each trap was suspended from special
Figure 6.—Vacuum Pyrolysis Equipment.
vertical type clamps (Fig. 7) which permitted deep immersions. A
glass wool plug was fitted into the neck of the adapter to prevent
passage of particles into the traps. A small metal tray was fitted
beneath the side arm of the adapter to hold small pieces of Dry Ice
which cooled the diazo compound enroute from the pyrolysis flask
to the first cold trap. A magnetic stirring bar in the pyrolysis
flask pulverized the salt during the final drying phase and agi-
tated it to facilitate heat transmission during pyrolysis.

Heating was provided by a thermostatically controlled oil
bath mounted on a laboratory jack. A hollow Teflon cylinder with
a large magnetic stirring bar mounted across the top and bottom was
rotated by a magnetic stirring motor below the oil bath. This
fluted cylinder stirred the oil bath and the upper magnetic bar in
the cylinder propelled the magnetic bar in the pyrolysis flask.

All glassware was treated in alcoholic potassium hydroxide,
rinsed in distilled water and dried at 98° before assembly.

Procedure. Vacuum Pyrolysis. The lithium salts of tosyl-
hydrzones which had been filtered in a sintered glass funnel under
nitrogen were dried preliminarily in a vacuum desiccator, then
transferred under nitrogen to the round-bottomed pyrolysis flask.
After the net weight of the salt was determined, the flask was con-
ected to the vacuum line and very cautiously evacuated.

The action of a magnetic stirring bar pulverized the salt
to a fine, dry powder and agitated the salt as it was heated (40-50°)
under vacuum (0.1 mm.) for 30-60 minutes to remove residual solvent.
During this drying phase the adapter and the first two traps were
Figure 7.—Cold Trap and Clamp.
maintained at room temperature. The vacuum pump trap was chilled to -78° to collect the residual solvent.

When drying of the salt was completed, the adapter section and the first two traps were heated with a hot air gun to remove traces of moisture or solvent. During this period the oil bath was lowered from the pyrolysis flask and preheated to 85-90°.

When the adapter section had been cooled with small pieces of Dry Ice and the first two traps chilled to -78° in Dry Ice— isopropanol baths, the preheated oil bath was again raised to immerse the pyrolysis flask. After allowing sufficient time for the temperature of the salt to equilibrate (3-6 minutes), the temperature of the oil bath was slowly and cautiously raised by adjusting the thermostat until the peak rate of decomposition of the salt was attained.

Considerable care was exerted to obtain optimum salt decomposition without thermolyzing the diazo compound being generated before it distilled out of the heated area. The progress and condition of the pyrolysis was monitored visually and by pressure readings on a McLeod gauge. If only slight thermolysis of the diazo compound occurred the pressure in the system generally did not exceed 1.0-1.5 mm. at the peak rate of salt decomposition.

After the pyrolysis was completed the oil bath was lowered when each unit of the vacuum system had been isolated by closing the screw clamp upon each Tygon connector. After the color and volume of the diazo product had been noted, nitrogen was syringed into the cold trap containing the diazo compound to equalize the pressure.
If no reactions other than titrations were to be run on the diazo compound, cold (-78°) hexane was syringed into the trap to dilute the diazo compound to 25 ml. If other reactions were to be run upon the diazo compound neat samples were analyzed.

The net weight of the contents of the pyrolysis flask was determined. From this weight the weight loss of the salt and the yield of the diazo compound were determined.

Analysis of the Diazo Compound. The purity of a diazo compound was determined gasometrically by injection of aliquots (neat or dissolved in hexane) into a chilled (0°), stirred solution of benzoic acid in benzene or toluene. The aliquots were removed from the cold trap with a chilled syringe and long needle.

The nitrogen evolved from reaction of the diazo compound with benzoic acid passed through a water-cooled condenser and an efficient cold trap (-78°) and was collected over water. The volume was corrected to S.T.P. and compared to theoretical volume of gas to determine purity of the diazo compound. (See Fig. 5).

In a few cases titrimetric analysis was performed by back titration of the excess benzoic acid solution with standardized base. The results from gasometric and titrimetric analyses always compared very favorably.

Diazoethane. The lithium salt of ethanal tosylhydrazone had been prepared from the tosylhydrazone formed in situ in tetrahydrofuran and was coated on the inner wall of the flask. The lithium salt of ethanal tosylhydrazone (21.8 g., 0.1 mole) was pyrolyzed at 90-110° and 0.5-1.7 mm. pressure in 35 minutes to give
a light orange-colored liquid (4.5 ml.) trapped at -78°.

The diazoethane was diluted with cold hexane and aliquots were titrated. Based on the theoretical weight of lithium salt used, a yield of 80% of diazoethane was obtained.

Gas chromatographic analysis of neat samples of diazoethane showed ethylene to be the sole product of thermolysis (25°). Diazoethane is very unstable thermally and decomposes well below 0°.

1-Diazopropane. The lithium salt of propanal tosylhydrazone (11.6 g., 0.05 mole) which had been prepared from propanal tosylhydrazone formed in situ in tetrahydrofuran was pyrolyzed at 90° to 120° under 0.3-0.6 mm. pressure in 30 minutes. Decomposition of the salt to 1-diazopropane began at 95° and reached a peak rate of decomposition at 105-110°. The volume of the deep orange pyrolysis product trapped at -78° was 3.0 ml. Gasometric analysis with a standardized solution of benzoic acid in toluene indicated a 56% yield of 1-diazopropane.

Propylene was the only product of thermolysis of 1-diazopropane as shown by gas chromatography. 1-Diazopropane decomposes below 0°, but is stable for several hours at -78°.

1-Diazobutane. 1-Diazobutane was prepared in 81% yield by vacuum pyrolysis (0.3 mm., 100-120°) of the lithium salt of butanal tosylhydrazone (12.3 g., 0.05 mole). The 1-diazobutane passed through a trap at 0° and was collected at -78°. The orange liquid showed strong infrared absorption at 4.85μ.

Gasometric analyses were made on aliquots of a hexane solution of the 1-diazobutane using benzoic acid in toluene. Gas chromatographic analysis of a neat sample of the 1-diazobutane showed the
a light orange-colored liquid (4.5 ml.) trapped at -78°.

The diazoethane was diluted with cold hexane and aliquots were titrated. Based on the theoretical weight of lithium salt used, a yield of 80% of diazoethane was obtained.

Gas chromatographic analysis of neat samples of diazoethane showed ethylene to be the sole product of thermolysis (25°). Diazoethane is very unstable thermally and decomposes well below 0°.

1-Diazopropene. The lithium salt of propanal tosylhydrazone (11.6 g., 0.05 mole) which had been prepared from propanal tosylhydrazone formed in situ in tetrahydrofuran was pyrolyzed at 90° to 120° under 0.3-0.6 mm. pressure in 30 minutes. Decomposition of the salt to 1-diazopropene began at 95° and reached a peak rate of decomposition at 105-110°. The volume of the deep orange pyrolysis product trapped at -78° was 3.0 ml. Gasometric analysis with a standardized solution of benzoic acid in toluene indicated a 56% yield of 1-diazopropene.

Propylene was the only product of thermolysis of 1-diazopropene as shown by gas chromatography. 1-Diazopropene decomposes below 0°, but is stable for several hours at -78°.

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Gasometric analyses were made on aliquots of a hexane solution of the 1-diazobutane with benzoic acid in toluene. Gas chromatographic analysis of a neat sample of the 1-diazobutane showed the
presence of only nitrogen and 1-butene. 1-Diazobutane decomposes slowly (half-life about two to three days) at -78° and very rapidly (5-10 minutes) when warmed to room temperature.

**Attempted Preparation of Cyclopropyldiazomethane.** Several attempts to prepare cyclopropyldiazomethane by vacuum pyrolysis of the lithium salt of cyclopropanecarboxaldehyde tosylhydrazone were unsuccessful. This was the only primary carbonyl compound attempted which was not successfully converted to the diazo compound. The lithium salt did decompose and gas chromatographic analysis showed the presence of hydrocarbons in the material collected in the cold traps. Infrared analysis confirmed the absence of the diazo compound.

Application of improved technique developed later in this research for preparation and purification of the lithium salt and for rapid cooling of the diazo compound to prevent its decomposition could well transform this method into a successful preparation for cyclopropyldiazomethane.

**1-Diazo-2-methylpropane.** 1-Diazo-2-methylpropane was prepared by the vacuum pyrolysis of the lithium salt of 2-methylpropane tosylhydrazone (0.05 mole, 12.3 g.) at 0.3 mm. pressure at 100-120°. The deep orange liquid product, 97% yield based upon weight loss of lithium salt, showed strong infrared absorption at 4.87μ.

Gas chromatography of a neat sample of 1-diazo-2-methylpropane indicated 2-methylpropene to be the major product (>95%) of thermolysis. Gasometric analysis of aliquots of the 1-diazo-2-methylpropane diluted to 25 ml. with cold (-78°) hexane indicated purity to be 85%.
1-Diazopentane. Vacuum pyrolysis of the lithium salt of pentanal tosylhydrazone (13.0 g., 0.05 mole) at 0.3-1.3 mm. pressure at 95-105° in 15 minutes gave 1-diazopentane as an orange liquid (5 ml.) trapped at -78°. Gasometric analysis of aliquots of a hexane solution of the diazo compound indicated a yield of 53%. 1-Diazopentane appeared to be unstable even at -78° and additional analyses were not attempted.

A shorter path between the pyrolysis flask and the cold trap (-78°), eliminating a 0° trap, would very likely improve the yield and purity of this diazo compound.

1-Diazo-2-methylbutane. The lithium salt of 2-methylbutanal tosylhydrazone (13.0 g., 0.05 mole) was pyrolyzed under 0.3-1.0 mm. pressure at 90-100° to give 1-diazo-2-methylbutane. The orange liquid (4 ml.) trapped at -78° was diluted to 25 ml. with cold (-78°) hexane. Gasometric analysis with a solution of benzoic acid in toluene indicated a 65% yield of 1-diazo-2-methylbutane.

1-Diazo-3-methylbutane. 1-Diazo-3-methylbutane was generated by vacuum pyrolysis of the dry lithium salt of 3-methylbutanal tosylhydrazone (13.0 g., 0.05 mole) at 0.3-1.2 mm. pressure at 100-110°. The dark orange diazo compound (2 ml.) was trapped at -78°.

Gasometric analysis of aliquots of this product diluted to 25 ml. with cold hexane showed a yield of 57% based on the amount of lithium salt used. A neat sample of 1-diazo-3-methylbutane was thermolyzed in a preheated injector (50°) and the products were analyzed by gas chromatography; 3-methyl-1-butene was the major product (90%).
The purity of a sample of 1-diazo-3-methylbutane from a previous vacuum pyrolysis was raised from 47% to 59% by distillation (0°/0.27 mm.) into a receiver at -78°.

**1-Diazo-2,2-dimethylpropane.** The lithium salt of 2,2-dimethylpropanal tosylhydrazone (13.0 g., 0.05 mole) was pyrolyzed at 90-110° at 0.1-0.25 mm. in 20 minutes to give 1-diazo-2,2-dimethylpropane (4.3 ml.) as a deep orange liquid with strong infrared absorption at 4.88μ. The weight loss of the lithium salt during pyrolysis was quantitative (100% yield). The purity of the diazo compound, determined by gasometric analysis, was nearly quantitative (98%).

The results of gas chromatographic analysis of the thermolysis products from the 1-diazo-2,2-dimethylpropane under various conditions is discussed in a separate section.

This diazo compound decomposes in a few minutes (10-15 minutes) at room temperature, but was successfully stored at -78° for more than six weeks.

**2-Diazo-3,3-dimethylbutane.** 2-Diazo-3,3-dimethylbutane was prepared by vacuum pyrolysis of the dry lithium salt of 3,3-dimethyl-2-butanol tosylhydrazone (12.76 g., 0.0465 mole) at 0.1-1.2 mm. at 125-130° in 15 minutes. The dark red 2-diazo-3,3-dimethylbutane (4.0 ml.) collected at -78° represented a 92% yield, based upon the weight loss (4.78 g.) of the lithium salt during vacuum pyrolysis. The purity of the diazo compound (95%) was determined by gasometric methods. An infrared spectrum shows strong absorption at 4.85μ (Fig. 8).

Gas chromatographic analyses were effected on the products
Figure 8.---Infrared Spectrum of 2-Diaz0-3,3-dimethylbutane
from decomposition of the diazo compound under various conditions and are discussed in a separate section.

A sample of 2-diazo-3,3-dimethylbutane which had been stored two weeks at -78° still standardized at 95%.

2-Diazo-3,3-dimethylbutane was also prepared in excellent yield (90%) by vacuum pyrolysis of the lithium salt of 3,3-dimethyl-2-butane benzenesulfonylhydrazone (14.32 g., 0.055 mole) at 0.07-0.4 mm. at 115-125° in 20 minutes.

1-Diazo-l-phenylethane. The lithium salt of acetophenone tosylhydrazone (14.7 g., 0.05 mole) was pyrolyzed at 0.08-0.5 mm. at 105-135° in 30 minutes to give 1-diazo-l-phenylethane as a very deep red to purple-colored liquid (4.3 ml.) which was collected at -20° and showed strong infrared absorption at 4.90μ. The yield of the diazo compound, based on the volume of material collected, was estimated to be 65% although exact determination was not made.

Gas chromatographic analysis of the 1-diazo-l-phenylethane was made upon injection of neat samples into a gas chromatograph. Thermolysis of the diazo compound was accomplished in the heated injector (125°) of the instrument. Analysis on a 3% SF96 (10' x 1/4") column showed styrene and nitrogen to be the only products of thermolysis.

A solution of 1-diazo-l-phenylethane in hexane retained its deep red color overnight at room temperature. The neat diazo compound in cold storage (-78°) slowly transformed (-7 days) into a light yellow solid, acetophenone azine, m.p. 121-123°, lit. m.p. 124° (7).
Because the lithium salt of acetophenone tosylhydrazone turned pink on drying overnight (10 mm., 25°), final drying (0.1 mm., 40-50°) normally used prior to vacuum pyrolysis was omitted. Residual solvents in the diazo compound may account in part for its relatively low purity (65%). Also, formation of acetophenone azine could be a contributing factor.

### 1-Diazo-2-phenylpropane
Vacuum pyrolysis of the lithium salt of 2-phenylpropanal tosylhydrazone (2.7 g., 0.009 mole) under 0.5-1.0 mm. pressure at 125° in a preheated oil bath afforded orange-red 1-diazo-2-phenylpropane (1 ml.). Although neither gasometric nor titrimetric analyses were made, the yield of the diazo compound (strong infrared absorption at 4.89μ) was estimated to be 70-80% based upon volume and color intensity of the product. The 1-diazo-2-phenylpropane, which was collected at -78°, exhibited surprising thermal stability at room temperature and even at 90°.

### 2-Diazo-1-phenylpropane
2-Diazo-1-phenylpropane was prepared in 50% yield by vacuum pyrolysis of the lithium salt of 1-phenyl-2-propanone tosylhydrazone (15.4 g., 0.05 mole) under 0.08-0.15 mm. pressure at 100-115°. The pyrolysis, in which the dark red diazo compound (3 ml.) was collected in the first cold trap (0°), was completed in 15 minutes.

Gas chromatographic analysis indicated large amounts of hydrocarbons in an ether extract of the pyrolysis residue and in the second cold trap (-78°). This result indicated that the low yield (48%) of 2-diazo-1-phenylpropane was due primarily to decomposition of the diazo compound during vacuum pyrolysis of the lithium salt.

Procedural improvements such as stirring the powdered salt
during the pyrolysis, more thorough drying of the lithium salt, a colder collecting trap (-20 to -80°) and more adequate cooling of the diazo compound in an area near its point of generation would certainly improve the yield and purity of the diazo compound.

Gas chromatographic analysis of neat samples of 2-diazo-1-phenylpropane showed the presence of allylbenzene (4%), cis-propenylbenzene (19%) and trans-propenylbenzene (77%).

Phenylcyclohexyl diazomethane. Vacuum pyrolysis (0.1-0.4 mm.) of the lithium salt of phenyl cyclohexyl ketone tosylhydrazone (9.0 g., 0.025 mole) at 100-130° afforded phenylcyclohexyl diazomethane (3.5 ml., 65% yield by gasometric analysis) as a deep red-colored liquid (strong infrared absorption at 4.85μ) collected at 0°. Residual solvent (1 ml.) from the lithium salt passed through this trap was collected in the second cold trap (-78°).

A neat sample of the diazo compound was thermolyzed by injection into the hot injector (180°) of a gas chromatograph. Analysis showed one major product which showed infrared absorption for olefinic double bond. The phenylcyclohexyl diazomethane was quite stable at room temperature as shown by the strong diazo band (4.8μ) in a sample that had been stored at room temperature for 45 minutes and a hexane solution of the diazo compound was stored one year in a refrigerator without appreciable diminution of the intensity of the red color.

Diphenyldiazomethane. The lithium salt of benzophenone tosylhydrazone was pyrolyzed at 0.08-1.5 mm. and at 110-150° to give diphenyldiazomethane and benzophenone azine. The first trap (0°) contained dark purple diphenyldiazomethane (1 ml.); the second trap (-80°) also contained the diazo compound (3.5 ml.). The
estimated yield of diphenyldiazomethane (very strong infrared absorption at 4.88μ) from this pyrolysis was 40-50%. Competitive formation of benzophenone azine accounted for the low yield of the diazo compound. An ether extract of the residue from the pyrolysis flask yielded light yellow benzophenone azine, m.p. 159.5-160°, lit. (7) 164°.

2-Diazo-1,3-diphenylpropane. The lithium salt of dibenzyl ketone tosylhydrazone (17.7 g., 0.046 mole) was pyrolyzed at 0.15 mm. pressure. The diazo compound began to distill slowly when the temperature of the pyrolysis bath reached 130°. The bath temperature was gradually raised to accelerate the rate of generation of the diazo compound. At 152° very rapid decomposition of the diazo compound occurred as it was produced and only the thermolysis products from the diazo compound distilled into the cold trap.

When the pyrolysis was completed, the first cold trap (-25°) contained a light orange-colored liquid (5 ml.); the second cold trap (-78°) contained a colorless liquid (2.5 ml.). A sample of the orange liquid decolorized immediately upon warming to room temperature and infrared analysis failed to show the characteristic absorption for a diazo compound. Gasometric analysis of the orange liquid was not attempted. The yield of 2-diazo-1,3-diphenylpropane by this method could certainly be greatly improved by more careful execution of the vacuum pyrolysis.

Samples of the orange liquid, which decolorized very rapidly even in a chilled syringe, were analyzed by gas chromatography. Trans-1,3-diphenylpropene (90%) and cis-1,3-diphenylpropene (10%) were the thermolysis products.
1-Diazo-2-phenylethane and 1-Diazo-3-phenylpropane. 1-Diazo-2-phenylethane and 1-diazo-3-phenylpropane were prepared by vacuum pyrolysis of lithium salts of their respective tosylhydrazones. Very small amounts of the lithium salts (1-2 g.) were used and consequently only a few drops of orange liquid were collected in each case. These samples were allowed to warm to room temperature to thermolyze the diazo compounds (indicated by loss of orange color) for gas chromatographic analysis of the hydrocarbon products.

2-Diazo propane, 2-Diazo butane, Diazocyclopentane and Diazocyclohexane. Vacuum pyrolysis of the lithium salts of propanone tosylhydrazone, 2-butanone tosylhydrazone, 2-butanone mesylhydrazone (50), cyclopentanone tosylhydrazone and cyclohexanone tosylhydrazone afforded by corresponding diazo compounds in very low yields (less than 10%). One common factor which probably contributed to these failures was the fact that the decomposition temperatures for these lithium salts were much higher (170-200°) than for the lithium salts of aldehyde tosylhydrazones of similar molecular weights (90-125°).

The application of better procedural techniques, which were developed much later, and variation of the leaving group could possibly lead to successful preparation of secondary diazo compounds by this method.

Attempted Preparation of 1-Diazo-3-phenyl-2-propene and 2-Diazo-4-phenyl-3-butene. Vacuum pyrolyses of the lithium salts of
3-phenylpropenal tosylhydrazone and 4-phenyl-3-buten-2-one tosylhydrazone failed completely to give either of the corresponding diazo compounds. In each instance as the pyrolysis temperature exceeded 100-105° the lithium salt seemed to melt and a large amount of material sublimed upward and condensed or solidified on the inner wall of the cooler upper half of the pyrolysis flask. These materials were probably the corresponding pyrazoles formed by cyclization. Identification of these materials was not undertaken. No material of any type was collected in the cold traps. Constant pressure readings during the pyrolysis indicated that nitrogen was not evolved.

Pyrolysis of Salts of Tosylhydrazones Under Various Conditions

General Techniques. Salts of 3,3-dimethyl-2-butanone tosylhydrazone, 2,2-dimethylpropanal tosylhydrazone and 3-methyl-2-butanone tosylhydrazone were prepared in situ from various bases (n-butyllithium, sodium methoxide, lithium methoxide or potassium tert-butoxide) in diethyl Carbitol or decalin. The concentration of the bases was varied over a wide range (0.5-10.0 equivalents). These salts were pyrolyzed in a solvent at 150° and the decomposition products analyzed gas chromatographically.

Equipment. The 10-ml. serum vials, rubber serum stoppers, hypodermic syringe and needles were treated overnight in an alcoholic potassium hydroxide bath, thoroughly rinsed with distilled water, dried at 100° for 24 hours and stored in a desiccator over Drierite.

A device (Fig. 9) for rotating, heating and evacuating the serum vials was constructed from a small variable speed
Figure 9.—A Device for Rotating, Evacuating, Flushing, and Heating Serum Vials
(20-500 r.p.m.) electric motor with a special chuck to hold the vials, a small (1" x 1/2") cartridge-type heating unit (100 watt) and a three-way stopcock. The entire unit was mounted upon a rectangular metal plate (6" x 20") and could be pivoted in a vertical plane about its support rod.

The heating unit was mounted in a small metal block which was positioned underneath the chuck and vial. The three-way stopcock was fitted with a hypodermic needle, vacuum and nitrogen lines and mounted upon a sliding plate so that the needle could be inserted or withdrawn from the serum stopper in the vial. The sliding plate was also slotted in such a fashion that the unit could be slid aside to facilitate injection of solvents into the serum vial. By manipulation of the stopcock, the vial could be alternately evacuated and flushed with nitrogen.

The heater block (Fig. 10) used for the pyrolysis was constructed from a cylindrical block of aluminum (2" dia. x 4" high). The serum vial fitted into a hole (2-3/8" x 25/32") in the top of the block. The block was heated by three cartridge-type heating units (3-1/4" x 3/8" x 100 watt) imbedded in the block. A thermometer fitted into a hole in the top of block beside the vial.

The solvents, diethyl Carbitol and decalin, were treated with potassium hydroxide, distilled from calcium hydride and stored in serum bottles (25 ml.) under nitrogen.

The bases, n-butyllithium (Foote Mineral Co., 1.53M in pentane), sodium methoxide (Matheson, Coleman and Bell, 97.5%),
Figure 10.--Heater Block and Vials
and lithium methoxide (Alfa Inorganics, Inc., 98.4%), were standardized against 0.5007N HCl. Potassium tert-butoxide (51)

(51) Material supplied by C. Moseley.

was twice sublimed and used without standardization (assumed 95%).

Procedure. A tosylhydrazone (0.1000 g.) and the appropriate amount of a solid base were weighed into a serum vial (10 ml.) which was immediately sealed with a serum stopper. The amount of base used varied from 0.50 to 10.0 equivalents (0.5, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0 and 10.0).

The vial was fitted into the chuck of the vial rotator and the hypodermic needle of the vacuum and nitrogen valve was inserted through the serum stopper. The tumbling action mixed the dry reactants while the vial was alternately evacuated and flushed with nitrogen three times. Then the needle was removed, the valve assembly was slid aside and solvent (1 ml.) was injected into the rapidly rotating evacuated vial with a syringe.

To promote formation of the tosylhydrazone salt the vial was heated to 40-50° by the small heating unit beneath the vial and rotated 30-60 minutes to allow complete neutralization of the tosylhydrazone. During this reaction period the granular appearance of the tosylhydrazone and base gradually changed to the tiny, colorless platelets characteristic of salts of tosylhydrazones. When diethyl Carbitol was used as solvent the salt precipitate was very thick and often formed a gel.
When n-butyllithium was used as the base the procedure was slightly modified. The tosylhydrazone was weighed into a serum vial (10 ml.) which was immediately sealed with a serum stopper, rotated briskly while being evacuated and flushed with nitrogen three times, and finally evacuated. Dry pentane (2 ml.) was injected into the vial to suspend the tosylhydrazone and as the vial was rapidly spun, the appropriate volume of a standardized solution of n-butyllithium in pentane was transferred by syringe and injected into this suspension. An immediate exothermic reaction was observed. Agitation of the suspension by mechanical rotation and by the bubbling action of evolved butane facilitated complete neutralization of the tosylhydrazone.

If an equivalent amount, or less, of n-butyllithium was used, the suspension changed from yellow to colorless and a colorless salt was produced. If more than equivalent amount of n-butyllithium was used the suspension remained a clear, light yellow color even after the reaction was completed.

The vial was rotated and heated (40-50°) for 30-60 minutes before the solvents were removed under vacuum. The salt was dried (50°, 0.1 mm., 30-60 minutes), suspended in a high-boiling, aprotic solvent (decalin or diethyl Carbitol, 1 ml.) and pyrolyzed at 150° in the preheated pyrolysis block.

The thick, heavy tosylhydrazone salts became very fluid during the pyrolyses which were completed very quickly (3-5 minutes) at 150°. A transient pink coloration probably due to formation of diazo compounds was often observed in the suspension during the
pyrolyses. Samples of the gaseous phase were taken at 150° and analyzed by gas chromatography (20' x 1/4", 15% propylene carbonate on 60/80 Chromosorb G regular, at 10-15°).

Reactions of Diazo Compounds

General Techniques. Two diazo compounds, 1-diazo-2,2-dimethylpropane and 2-diazo-3,3-dimethylbutane, were generated by vacuum pyrolysis of pure lithium salts of their respective tosylhydrazones. Small samples (0.05 ml.) of these diazo compounds were thermolyzed at various temperatures in glass, Teflon and stainless steel vials in the presence of several different solvents and reactants. The identities and per cent distribution of the thermolysis products were determined by gas chromatography.

Equipment. Glass serum vials (10 ml.) were used with rubber serum stoppers. Stainless steel and Teflon vials (3" x 3/4" dia. o.d.) were machined with screw caps. A small hole in these caps permitted insertion of hypodermic needles, and Teflon and neoprene seals provided gas tight operations. All vials, stoppers, caps and seals were treated in an alcoholic potassium hydroxide bath, rinsed with distilled water and dried 24 hours at 100°.

A circular aluminum block (4-1/2" dia. x 2") was drilled with six vertical holes (25/32" dia. x 1-3/4" deep). This block (cold sink) was placed in a Dewar flask on Dry Ice and provided stable cold storage for serum vials containing diazo compounds.

The heater block used to thermolyze the diazo samples was previously described (p. 187).
The solvents diethyl Carbitol, decalin and octane were treated with potassium hydroxide pellets, distilled from calcium hydride and stored under nitrogen in serum bottles (60 ml.).

Tri-n-butylamine and piperidine were treated with potassium hydroxide pellets, distilled from anhydrous calcium oxide and stored in serum bottles (60 ml.) under nitrogen.

All reactants were dried in vacuo (0.1 mm.) at 40-80° prior to use (1-24 hours).

Procedure. The diazo compounds were generated by vacuum pyrolysis of the lithium salt of tosylhydrazones and were collected in a cold trap at -78°. A sample of diazo compound (2 ml.) was removed from the cold trap and transferred to a chilled (-78°) glass serum vial (10 ml.) using a cold syringe (5 ml.) and long needle (12", 18 ga.). The serum vial served as supply vial and was stored at -78° in the aluminum block on Dry Ice. Small samples (0.05 ml.) of the diazo compound were transferred by chilled syringe (0.25 ml.) and needle (27 ga., 5/8") to the various reaction vials. All vials, glass, Teflon and stainless steel, were sealed, alternately evacuated and flushed with nitrogen and finally evacuated (0.1 mm.).

For a fast, neat thermolysis a sample of the diazo compound was transferred to a chilled vial which was immediately inserted into the preheated (150°) thermolysis block. For a fast, solution thermolysis, solvent (1 ml.) was injected into a vial. The vial and solvent were chilled, then suspended in an inverted position. The diazo compound was injected upwards through the serum stopper into the solvent. The vial was immediately placed in the preheated (150°)
thermolysis block. When solid reactants were used, the material was weighed into the vial which was then sealed, evacuated and flushed with nitrogen and again evacuated. A solvent (1 ml.) was injected and the mixture chilled, then supported in an inverted position. As soon as the diazo compound was injected into the chilled mixture the vial was immediately heated to 150°.

For slow thermolyses the chilled vials containing the diazo compounds (and solvents and reactants, if used) were placed in the cool (25°) thermolysis block and slowly heated (60-120 minutes) to 150°. Alternately, the cold vials were placed in a precooled Dewar flask with a small piece of Dry Ice and allowed to warm to room temperature overnight. In some cases it was necessary to allow the diazo compound in solvent to stand at room temperature two to three days before the orange color of the diazo compound completely disappeared. Room temperature, gas phase samples were analyzed gas chromatographically from these slow thermolyses, then the vials heated to 150° for hot gas phase sampling, also.

In all cases gas phase samples at 150° were taken and analyzed by gas chromatography (15% propylene carbonate on 60/80 Chromosorb G, regular, 20' x 1/4", 15°) to identify the products and to determine the percent distribution.

**Gas Chromatography Standards.** Analytical samples (98-99.9%) of 1,1-dimethylcyclopropane, 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene, 1,1,2-trimethylcyclopropane, 3,3-dimethyl-1-butene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene,
2,2-dimethylbutane, 3-phenyl-1-propene, cis-1-phenyl-1-propene, 
trans-1-phenyl-1-propene and 2-phenyl-1-propene were obtained from 
Chemical Samples Company, Columbus, Ohio.

Phenylcyclopropane. Phenylcyclopropane was prepared from 
the cyclization of 1,3-dibromo-1-phenylpropane with zinc—copper 
couple according to the literature method (52).

(52) T. F. Corbin, R. C. Hahn and H. Shechter, Org. Syn., 
44, 30 (1964).

Anal. Calcd. for C₉H₁₀: C, 91.47; H, 8.53
Found: C, 90.95; H, 8.51.

1,1-Diphenylethylene. 1,1-Diphenylethylene was prepared 
by the dehydration of methyldiphenylcarbinol as described previously 
(53).

p. 226.
ADDENDUM

Reactions of Sulfonarylhydrazones with Alkylamines

Preliminary investigations of reactions which involve the use of primary and secondary alkylamines as solvent and basic catalyst for the decomposition of various sulfonarylhydrazones were performed. From these studies evolved an improved general method of preparing diazo compounds from sulfonarylhydrazones of aromatic aldehydes and ketones. Particular advantages of the method include low temperatures (25-75°) and short time periods (15-30 minutes) required for the conversion. A rapidly developing orange-red color indicates formation of the diazo compound in the homogeneous solution.

Isolation of the diazo compound is effected by removal of solvent from a purified pentane extract of the reaction mixture. Solid diazo products can be recrystallized from ether. Results of the qualitative explorations indicate a wide generality of application, and good yield of high purity diazo compounds.

A second phase of studies in this area encompassed the formation of sulfonarylhydrazones of selected aromatic aldehydes and ketones in situ by dissolving appropriate amounts of a carbonyl compound and a sulfonarylhydrazide in pyridine, a weak base ($k_b=1.7\times10^{-9}$). After a requisite period of time, an alkylamine, a stronger base ($k_b \sim 10^{-5}$ to $10^{-3}$), was added to decompose the sulfonarylhydrazone.
In essence, this procedure affords a rapid and direct conversion of an aromatic carbonyl compound to a diazo compound.

Alternatively, an alkylamine salt of a sulfonhydrazide was reacted with an aromatic carbonyl compound in pyridine. The resulting sulfonhydrazone salt was converted to the diazo compound by thermal decomposition.

In general, diazoalkanes do not possess sufficient thermal stability to be isolated by this method; only hydrocarbon products from thermolysis of the diazo compound are obtained. However, the utility of basic solvents which can scavenge protonic contaminants in carbenic decompositions should be considered.