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Diane Elizabeth Bradway for the M.S. in Chemistry
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Title THERMAL DECOMPOSITION OF DI-P-TOLUENESULFONYL-
HYDRAZONES

Abstract approved
(Major professor)

Thermal decomposition of several di-p-toluenesulfonylhydrazones was studied. It was found that the carbene decomposition of tetramethyl-1,3-cyclobutanedione, di-p-toluenesulfonylhydrazone gave two products resulting from rearrangement. One was identified as 2,5-dimethyl-1,3,4-hexatriene. A tentative structure for the second was proposed. During the course of the study, a more convenient procedure for thermal decompositions was developed, involving the use of sodium hydride to prepare the salt and vacuum to aid in isolation of the products. The use of an alcohol to protonate the intermediate diazo compound was also studied. Two other di-p-toluenesulfonylhydrazones were decomposed under carbene conditions to give products derived entirely from hydrogen migration via a stepwise mechanism.
DECOMPOSITION OF
DI-P-TOLUENESULFONYLHYDRAZONES

by

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DECOMPOSITION OF DI-P-TOLUENESULFONYLHYDRAZONES

I. INTRODUCTION

The recent development of carbene chemistry has opened a whole new synthetic approach to the field of organic chemistry. The existence of this intermediate had been suspected for many years but only in the last decade has intensive work proved its actual role. From this work has emerged a simple pathway to compounds heretofore either difficult or impossible to synthesize, and the scope of this approach is only just being realized.

Review articles covering the literature on carbones have been published by W. Kirmse in 1961 (26), P. Miginiac in 1962 (29), E. Chinoporos in 1963 (6) and H. Kloosterziel in 1963 (28). In addition, J. Hine has published a textbook, Divalent Carbon (22), which emphasizes reactions and mechanisms.

Carbene Formation

A study of the methods of carbene formation shows that a variety of different reactions occur which lead to this intermediate. Three reactions are considerably more important than the rest and should be examined in detail.

The first is a reaction involving loss of a group with its bonding electron pair from a carbanion. This is the
reaction usually used in the formation of dihalocarbenes.

\[
\text{CX}_3 \rightarrow :\text{CX}_2 + \text{X}^-
\]

The advantage of this reaction is that the trihalomethyl carbanion may be formed in several different ways.

A second reaction is the \(\alpha\)-elimination of a group such as a hydrogen halide.

\[
\text{HCClF}_2 \rightarrow :\text{CF}_2 + \text{HCl}
\]

This reaction has been shown to be a concerted elimination with no \(\text{CClF}_2^-\) intermediate.

The third reaction is one of the most widely used, especially for the formation of alkyl substituted carbenes. It involves homolysis of a double bond and occurs largely due to the stability of the leaving group.

\[
\text{R}_2\text{C}^\circ\text{X} \rightarrow \text{R}_2\text{C} + \text{X}
\]

The compounds which lend themselves most favorably to this mechanism are ketenes, with carbon monoxide as the leaving group, and diazo compounds, with nitrogen as the leaving group. Included in this latter is perhaps the most important single method for the formation of substituted carbenes, a reaction discovered by Bamford and Stevens (3) and further developed by Friedman and Shechter (17), which depends upon the decomposition of the sodium salt of
p-toluenesulfonylhydrazones. The reaction proceeds with loss of p-toluenesulfinic acid to give the diazo compound which can then react by either of two pathways. In an aprotic medium the diazo compound loses nitrogen to give a carbene. In a protic solvent protonation leads to the formation of a diazonium ion followed by loss of nitrogen to give a carbonium ion.

\[
R_2C\equiv N\equiv N\equiv SO_2C_7H_7 \quad \rightarrow \quad R_2C\equiv N\equiv N: + SO_2C_7H_7
\]

\[
R_2C\equiv N\equiv N:\quad \rightarrow \quad R_2C: + N_2
\]

\[
ROH \quad \rightarrow \quad R_2CH\equiv N\equiv N: \quad \rightarrow \quad R_2CH + N_2
\]

This is the reaction with which this thesis will concern itself.

Reactions of Carbenes

Carbenes are extremely reactive intermediates which may decompose by several different pathways. These include insertion into a carbon-hydrogen bond, addition to multiple bonds, and rearrangement. An additional reaction, which is much less common but still of interest, is reaction to form a dimer. Because an understanding of these competing reactions is necessary to an understanding of the results of this work, they must be looked at more closely.
Insertion

It is not unusual to find among the products of carbene reactions compounds arising from insertion of the carbene into a carbon-hydrogen bond. The general reaction may be expressed:

$$\text{R}_3\text{C-H} + :\text{CH}_2 \rightarrow \text{R}_3\text{C-CH}_2\text{-H}$$

It is not surprising, considering the reactivity of the carbene intermediate, to find that intramolecular insertion occurs more rapidly than intermolecular insertion, and generally accounts for a majority of the products. Cyclic compounds, arising from just such a case, are commonly found among the products. Powell and Whiting (31) found that diazocamphor decomposed thermally to give an insertion product, tricyclene, 1.

Bicyclic compounds were found by Friedman and Shechter (19) to be common products of decompositions of $p$-toluenesulfonylhydrazones of cyclic ketones, greater than cyclohexanone.
Although less commonly noted, intermolecular insertion has been observed as in the case reported by Doering and Knox (14). Here it was shown that carboethoxycarbene inserted into the carbon-hydrogen bond of cyclohexane to give the ester, 2.

\[
N_2CHCO_2Et + \text{cyclohexane} \xrightarrow{h\nu} CH_2CO_2Et
\]

**Addition**

An interesting product found in cases where carbenes are generated in the presence of olefins is a cyclopropyl derivative. The explanation for this is that in the presence of a multiple bond direct carbene addition can occur. Intermolecular addition is common in the case of methylene and dihalomethyl carbene but few cases have been reported which involve substituted carbenes. Closs and Closs (10), however, have reported addition of diphenylcarbene to a double bond to give a cyclopropane product.
Similar findings have also been reported by Etter and co-workers (15).

Of greater interest is intramolecular addition such as reported by Stork and Ficini (36). It was found that internal addition produced the bicyclo (4,1,0) heptane derivative, 3.

![Chemical structure 3]

The distance of the double bond from the carbene is apparently no factor, for Closs and Closs (9) have reported an example of carbene addition to a conjugated double bond to give the cyclopropenyl derivative, 4.

![Chemical structure 4]

**Rearrangement**

Reaction pathways involving rearrangements are common for carbenes. The fact that migration of a $\beta$-hydrogen is preferable to migration of a $\beta$-alkyl group was shown by Friedman and Shechter (17). When the p-toluenesulfonyl-hydrazone of methyl ethyl ketone was decomposed, for instance, there was obtained 92% of the cis- and trans-isomers of 2-butenes, 5% of 1-butenes, and 0.5% of the
insertion product, methylcyclopropane. There was no isobutylene, the product of methyl migration. In the absence of a $\beta$-hydrogen, a little rearrangement occurred, but the major product was a cyclopropane derivative arising from insertion.

Much more extensive carbon-skeleton rearrangement occurs in the decomposition of small-ring diazo compounds. Diphenyldiazocyclopropane (25) decomposed thermally to give the allene, 5.

\[
\begin{align*}
\phi & \quad \rightarrow \quad \phi \\
\phi & \quad \rightarrow \quad \phi_2 C=\overset{\sigma}{\sigma}=CH_2
\end{align*}
\]

Cyclopropyldiazomethane (19) decomposed to cyclobutene through ring expansion,

\[
\begin{align*}
\phi \quad \rightarrow \quad \phi \\
\phi & \quad \rightarrow \quad \phi
\end{align*}
\]

whereas diazocyclobutane reacted to give methylenecyclopropane from ring contraction.

\[
\begin{align*}
\phi & \quad \rightarrow \quad \phi \\
\phi & \quad \rightarrow \quad \phi
\end{align*}
\]

It is interesting that no methylenecyclopropane was formed from the decomposition of cyclopropyldiazomethane whereas
it was the chief product from the decomposition of diazo-
cyclobutane. In both cases, rearrangement took place in
preference to hydrogen-shift. In contrast, the cyclo-
alkene was formed in 100% yield from the decomposition of
diazocyclopentane and diazocyclohexane. Hydrogen-shift
accounted for all of the product.

Dimerization

Several cases have been reported in which it appears
that carbenes have reacted together to form a dimer. How-
ever, since this would require that a carbene serve as both
an electrophile and a nucleophile, it appears most likely
that a dimeric product arises from reaction of a carbene
with a carbene precursor. Good evidence exists that this is
the case. Frey (16) found that diazoethane upon photolysis
gave several products, including the dimer, 2-butene. He
showed that kinetic evidence was best satisfied by a
mechanism involving attack of ethyl carbene on diazo-
ethane,

\[ \text{CH}_3\text{CH} + \text{CH}_3\text{CH} = N = N : \rightarrow \text{CH}_3\text{CH} = \text{CHCH}_3 + N_2 \]

rather than by requiring direct dimerization.

\[ 2 \text{CH}_3\text{CH} \rightarrow \text{CH}_3\text{CH} = \text{CHCH}_3 \]

The decomposition of p-nitrobenzylsulfonium ion was found
by Swain and Thornton (37) to give a dimeric product, 6.
It was found that the sulfur isotope effect was too low for
a mechanism which called for formation of the carbene
followed by rapid dimerization. The data were, however,
consistent with formation of the carbene followed by rapid
attack of the carbene on the carbanion.

\[
\begin{align*}
\text{RCHS(CH}_3\text{)}_2 & \xrightarrow{\text{slow}} \text{R-\text{C-H} + :S(CH}_3\text{)}_2 \\
\text{R-\text{C-H} + RCHS(CH}_3\text{)}_2 & \xrightarrow{\text{fast}} \text{R-CH-CHS(CH}_3\text{)}_2 \\
\text{R-CH=CH-R} & \xrightarrow{\text{fast}} :S(CH}_3\text{)}_2
\end{align*}
\]

Kinetic data showed that the initial step was rate-determin-
ing. Finally, Holroyd and Blacet (23) examined the photoly-
sis of ketene vapors and found kinetic evidence that the
dimers observed in the product resulted from attack of the
carbene on the ketene rather than from direct dimerization.

Evidence for a case of dimerization of carbenes was
presented by Chambers and co-workers (5). It was shown that
the thermal decomposition of potassium trifluoromethyl-
fluoroborate resulted in tetrafluoroethylene, perfluoro-
cyclopropane and perfluorocyclobutane. These products were
explained as arising from transfer of fluorine from carbon
to boron in the trifluoromethylfluoroborate ion accompanied
by the elimination of difluoromethylene. The carbene then dimerized to tetrafluoroethylene. Addition of difluoromethylene to tetrafluoroethylene led to perfluorocyclopropane. Dimerization of tetrafluoroethylene gave perfluorocyclobutane. Evidence that tetrafluoroethylene arose from dimerization of difluoromethylene rather than from attack of difluoromethylene on trifluoromethylfluoroborate ion was presented in the form of a separate experiment involving perfluorocyclopropane. At high temperatures this compound was not stable, decomposing to perfluorocyclobutane, perfluoropropylene, and other perfluoroolefins. Perfluorocyclobutane presumably arose from the decomposition of the three-membered ring to tetrafluoroethylene and difluoromethylene.

\[ \text{CF}_2 + \text{F}_2\text{C} = \text{CF}_2 \]

At high temperatures this reaction leads to the formation of perfluorocyclobutane, perfluoropropylene, and other perfluoroolefins. Perfluorocyclobutane presumably arises from the decomposition of the three-membered ring to tetrafluoroethylene and difluoromethylene.

\[ 4 \text{CF}_2 \rightarrow 2 \text{F}_2\text{C} = \text{CF}_2 \]

In this case direct dimerization may occur.

**Dicarbenes**

An interesting hypothesis is the possible existence of
a dicarbene species, a molecule which contains two electron-deficient carbons. Some of the most convincing work on this subject has been done by Skell and co-workers (35) who examined the species :C=C=C:. This intermediate was said to be a major constituent of carbon vapor, and, when reacted with olefins, gave the expected product, 7.

\[ \text{:C=C=C:} + \text{C=C:C:} \rightarrow \text{C=C:C:} \]

7

The first physical evidence for the existence of a species containing two electron-deficient atoms was presented by Trozzolo and co-workers (39) who found that the photolysis of 1,4-bis-(\(\alpha\)-diazobenzyl)-benzene, 8, proceeded with simultaneous or near simultaneous loss of two molecules of nitrogen to give the intermediate, 9.

\[ \text{N}_2 \text{C} \text{C} \text{N}_2 \rightarrow \text{C}=\text{C}=\text{C} \]

8

9

E.p.r. data was most satisfactorily explained by the electronic state, 8, rather than by the other three possible states.
A possibility exists of a dicarbene intermediate in other cases. Kirmse (27) photolysed a 1,3-bisdiazocyclohexanone, 10, to obtain 1-cyclopentenylformic acid, 11. A stepwise mechanism was offered, but a carbene mechanism could explain this product equally well.

Another possibility arises from work done by E. R. H. Jones (24) who developed a method for forming polyacetylenic compounds. Here again a carbene mechanism may be invoked.
Object of Present Work

The present work was undertaken to study the decompositions of several di-p-toluenesulfonylhydrazones under carbene conditions. There were several goals to be considered. First, it was desired to study the competition between various reaction pathways. Insertion, rearrangement, and reaction of the carbene with a diazo group in the same molecule were considered likely. Second, the possibility of intramolecular dicarbene reactions was to be examined, and third, it was hoped that a synthesis of strained ring systems could be realized.

Beginning with tetramethyl-1,3-cyclobutanedione, di-p-toluenesulfonylhydrazone, the following pathways were considered as possible.

1. Insertion into the carbon-hydrogen bond of a methyl group.
2. Ring contraction.

This latter path might then lead further via ring opening to an allene, \( \text{L}_2 \), as was observed by Jones (25).

3. Methyl migration.

The cyclobutane carbene might then undergo ring contraction.
4. Intramolecular bond formation.

The possible formation of the bicyclo-(1,1,0)-butene compound, 13, was an especially attractive goal of such a study. It should be noted that the intermolecular equivalent of pathway four has been examined by Reimlinger (34) and, except for the bond angle strain in 13, the depicted steps are reasonable. It should be noted that 13 would probably be very thermally unstable, decomposing as

indicated to the cumulene, 14, and perhaps further.
In this aspect, it is interesting that cyclopropene systems have been examined by Closs and co-workers (11) who found that compounds of the type, 15, were stable when the β-carbon was fully substituted.

Closs and Boll (8) found that bicyclic systems, containing cyclopropene rings, 16, were stable only when the other ring contained seven or more carbons.

The case of 1,4-cyclohexanedione, di-p-tolunesulfonyl-hydrazone is somewhat simpler. There are really only two pathways open. Hydrogen migration would produce the cyclohexadienes.

Reaction of the carbene with the diazo group would result in ring formation.
If such a system as 17 were unstable, one might isolate further rearrangement products.

It was hoped that the antraquinone, di-p-toluene-sulfonylhydrazone decomposition could be studied. Here decomposition would virtually be forced to follow the intramolecular ring closure pathway leading to the very intriguing benzyclobutadiene, 18, or its decomposition products.

Finally, it was also of interest to study the decomposition of an open chain di-p-toluenesulfonylhydrazone such as 19. Simple carbene formation and hydrogen shift
would lead to the various hexadienes, whereas reaction of the initially formed carbene with the second diazo group would give 1,2-dimethylcyclobutene. The latter pathway would be of synthetic interest, the former might help elucidate the discriminating features in carbene hydrogen shifts.
II. RESULTS AND DISCUSSION

The first di-\(p\)-toluenesulfonylhydrazone to be investigated was that derived from tetramethyl-1,3-cyclobutanedione. In initial studies decomposition was carried out under conditions developed by Friedman and Shechter (17), involving formation of the sodium salt by reaction with sodium methoxide, followed by thermal decomposition of the suspension in diglyme. It was soon found that use of commercially available sodium methoxide resulted in recovery of starting material, so freshly prepared methoxide was used in all decompositions. During the pyrolytic decomposition \(160^\circ\), the product partially distilled into two dry ice/acetone cold traps. The major portion, however, was extracted from the reaction mixture after heating for one hour. Gas-liquid chromatography showed one major product, \(21\), present in both the cold-trap and the ether extract of the reaction mixture.

\[
\text{Na}^+ \quad \xrightarrow{1) \text{NaOMe}} \quad \text{N}^\cdot\text{N}^\cdot\text{TS} \quad \xrightarrow{2) \triangle} \quad \text{N}_2^\cdot\text{N}^\cdot\text{TS} \quad \xrightarrow{\text{Na}^+} \quad \text{N}_2^\cdot\text{N}_2
\]
Carbon-hydrogen analysis established the empirical formula of \(21\) as \(C_8H_{12}\). The infrared spectrum shows the presence of a band at 1941 cm\(^{-1}\) characteristic of allenes, and a band at 875 cm\(^{-1}\) characteristic of a terminal methylene group. The ultraviolet spectrum exhibited a maximum at 218 m\(\mu\), \(\varepsilon = 27,400\) (EtOH). N.M.R. spectral data are shown in Table I.

TABLE I. N.M.R. OF 21.

<table>
<thead>
<tr>
<th>(\delta) (p.p.m.)</th>
<th>rel. area</th>
<th>shape</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.70</td>
<td>6</td>
<td>singlet</td>
<td>2 vinyl methyls</td>
</tr>
<tr>
<td>1.75</td>
<td>3</td>
<td>singlet</td>
<td>vinyl methyl</td>
</tr>
<tr>
<td>4.75</td>
<td>2</td>
<td>multiplet</td>
<td>terminal methylene</td>
</tr>
<tr>
<td>5.67</td>
<td>1</td>
<td>multiplet</td>
<td>vinyl hydrogen</td>
</tr>
</tbody>
</table>

Based on these data, the compound was assigned structure 21, 2,5-dimethyl-1,3,4-hexatriene. Thompson (38), has
previously reported synthesis of a compound to which he assigned the structure $21$. His report gave only density and refractive index, and a comparison of refractive indices with our product showed only fair agreement. Thompson's method of preparation involved a reduction which probably gave $21$ as the major product, although in the absence of g.l.c. data, the compound was probably not pure.

Structure $21$, is entirely consistent with the data presented. Both an allene and terminal methylene group are present as indicated by the infrared spectrum. The ultraviolet spectrum, $\lambda_{\text{max}}$ (EtOH) = 218 m$\mu$, compares favorably with the spectrum of vinyl allene, $\lambda_{\text{max}}$ (EtOH) = 216.5 m$\mu$, $\epsilon = 15,600$. N.m.r. assignments are consistent with structure $21$. The three vinyl methyls, the terminal methylene, and the vinyl hydrogen all show expected chemical shifts. The coupling patterns are also in agreement with the structural assignment. Additional confirmation of the assigned structure was obtained by the hydrogenation of $21$ to 2,5-dimethylhexane.

A reasonable mechanism may be written for the formation of $21$.

\[
\begin{array}{c}
\begin{array}{c}
20 \\
\end{array}
\end{array}
\rightarrow
\begin{array}{c}
\begin{array}{c}
N_2 \\
\end{array}
\end{array}
\rightarrow
\begin{array}{c}
\begin{array}{c}
\end{array}
\end{array}
\]
The attractive feature of this mechanism is that there are analogies among other small ring carbene reactions for both major steps. Ring contraction of cyclobutane carbene has already been observed by Friedman and Shechter (19), and ring-opening of a cyclopropyl carbene has been reported by Jones (25). The last step in the proposed mechanism is a 1,3-hydride shift, possibly a thermal process. While it is surprising that a second shift does not occur at this point to give 2,5-dimethyl-1,3,5-hexatriene, this process may
occur at a higher temperature. Although this mechanism quite satisfactorily explains the observed product, it should be noted that several other mechanisms will also lead to the same vinyl allene. One other mechanism is attractive due to evidence obtained in a later study, *vide infra*.

During the course of this study more convenient reaction conditions were sought. A method was developed in which sodium hydride replaced sodium methoxide in the preparation of the salt. Using this modification, the salt could be prepared directly in the solvent to be used in decomposition, eliminating the risk of introducing methanol into the system. To facilitate isolation of the products, the reaction was run at reduced pressure, removing the products from the reaction as they were formed. A higher boiling solvent was required to prevent co-distillation of the solvent with the reaction products, and triglyme (triethyleneglycol diethyl ether, b.p. 115-117⁰/35 mm.) proved to be well adapted to these conditions.

Using this method, 20 was decomposed and virtually all of the product distilled into the cold traps. At this point it was found that solvent cleavage produced a lower boiling compound, 2-methoxyethyl vinyl ether, which distilled with the products. This compound was not obtained when diglyme was used as the solvent. Since the retention time
of this vinyl ether was appreciably greater than that of the products, no interference in subsequent isolation and purification was incurred.

Examination of the cold trap contents disclosed, in addition to this cleavage product, two other major products. The first was quickly identified as the vinyl allene, 21. The second compound, 22, was a new product of thermal decomposition of 20.

Since two major changes, namely use of a different solvent and reduced pressure, had been made in this run, the original sodium methoxide study was re-examined, with the exception that the products were removed under vacuum. Using these conditions, both 21 and 22 were obtained. The relative amounts of these two products from the various reaction conditions are shown in Table II. Conditions two and three compared with four show that the two reaction conditions give similar results. It was later shown that 22 was thermally labile, being converted to 21 on heating, so the slight fluctuation in yields under conditions two, three, and four was probably due to slightly different efficiencies in removing the products from the reaction mixture. Condition five was run to check on the possibility of a carbonium ion side reaction and will be discussed later.
TABLE II. COMPARISON OF PRODUCTS AND RATIOS FROM THE DECOMPOSITION OF 20.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Product 21</th>
<th>Ratios 22</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>42</td>
<td>58</td>
</tr>
<tr>
<td>5</td>
<td>98</td>
<td>2</td>
</tr>
</tbody>
</table>

1. Sodium methoxide/diglyme.
2. Sodium hydride/triglyme; vacuum.
3. Repeat of 2.
4. Sodium methoxide/diglyme; vacuum.
5. Sodium hydride/triglyme; vacuum; two moles cyclohexanol added.

The compound, 22, proved to be very difficult to handle, and only a tentative structural assignment could be made. The material was volatile and thus difficult to purify and to analyze. Carbon-hydrogen determinations were not satisfactory but seemed to suggest the same formula as 21, i.e. C₈H₁₂. The n.m.r. spectrum was consistent with this formula showing 4 peaks with relative areas of 1:1:1:9. Three unsaturations were also suggested by hydrogenation of 22, and the fact that the product of this reaction appeared to be identical with 2,5-dimethylhexane indicated that 22 was
similar in structure to 21. The infrared spectrum of 22 is quite different, however, from that of 21. There is no indication of either an allene linkage or of a terminal methylene, although a vinyl hydrogen is clearly present.

The ultraviolet spectrum, \( \lambda_{\text{max}} = 233 \text{ m}\mu \), \( \epsilon = 9670 \), confirms the unsaturation and suggests a conjugated diene system. Table III shows the n.m.r. spectral data. As

<table>
<thead>
<tr>
<th>( \delta ) (p.p.m.)</th>
<th>Rel. Area</th>
<th>Shape</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.30</td>
<td>9</td>
<td>singlet</td>
<td>3 vinyl methyls</td>
</tr>
<tr>
<td>4.71</td>
<td>1</td>
<td>multiplet</td>
<td>?</td>
</tr>
<tr>
<td>4.90</td>
<td>1</td>
<td>multiplet</td>
<td>?</td>
</tr>
<tr>
<td>5.60</td>
<td>1</td>
<td>multiplet</td>
<td>vinyl hydrogen</td>
</tr>
</tbody>
</table>

indicated, three magnetically identical vinyl methyl groups are present as is a typical vinyl hydrogen. The two-hydrogen doublet at 4.71 and 4.90 \( \delta \) is the confusing feature as this is normally in the region of a terminal methylene.

The combination of the relatively simple n.m.r. spectrum and the hydrogenation of 22 to 2,5-dimethylhexane suggested a structure containing this skeleton with three vinyl methyls, a vinyl hydrogen, and a terminal methylene. No structure of this type can be written, however, without
postulating an allene or conjugated triene, both of which are inconsistent with other data. It should be mentioned that a simple methyl migration in the carbenoid decompo-
sition would have led to a 2,4-dimethylhexane system and the infrared spectrum of this compound is quite similar to its 2,5-isomer. Nevertheless, no completely consistent struc-
ture can be written even with this rearranged skeleton. Ig-
noring temporarily the evidence in favor of a terminal meth-
ylene group, one structure, 22, is attractive in other regards.

```
\begin{center}
\includegraphics[width=0.3\textwidth]{structure22.png}
\end{center}
```

The ultraviolet spectrum is in very good agreement with this structure. The model compound, methylenecyclobutene shows $\lambda_{\text{max}} = 221 \text{ m}\mu$, $\varepsilon = 11,400$ (isooctane). Compound 22 contains the same chromophore with three additional methyl substitu-
ents. Using the usual value of $+5 \text{ m}\mu$ per substituent, one would predict a $\lambda_{\text{max}}$ of $236 \text{ m}\mu$ for 22, a value which is in close agreement with the observed value of $233 \text{ m}\mu$. The infrared spectrum is not inconsistent with structure 22, nor is the n.m.r. spectrum, except for the doublet at 4.71
and 4.90 ppm which must now be assigned to the doubly allylic hydrogens at C-4. One would generally not predict this large a chemical shift for this type of hydrogen. The results of hydrogenation of 22 are also difficult to explain unless one concedes hydrogenolysis of the cyclobutene ring, an unusual occurrence.

A study of the thermal stability of 22 showed that heating at 160° in diglyme, conditions similar to those of the decomposition, led to gradual conversion of 22 to 21. This is consistent with structure 22, for it is known that cyclobutenes rearrange thermally to butadienes.
The possibility now arises that 21 was formed not by the previously proposed mechanism (p. 21), but entirely from thermal rearrangement of 22, a process which would explain the fact that in the original sodium methoxide study only 21 was observed.

An interesting mechanism may be written for the formation of 22, proceeding via insertion into the methyl group rather than through rearrangement.

\[ \begin{align*}
21 & \xrightarrow{\text{insertion}} 22 \\
21 & \xrightarrow{\text{rearrangement}} 23
\end{align*} \]

It is hard to explain, however, why cross-ring insertion to give 23, would be favored over a second methyl group insertion. An interesting aspect of this mechanism is that a direct route from 23 to 21 is also possible. It must be remembered,
however, that the assignment of structure 22, is tentative so that mechanistic arguments are somewhat dangerous.

An alternative method of decomposing p-toluenesulfonylhydrazones has been developed by Dauben and Wiley (13). This method depends on photochemical rather than thermal energy to initiate decomposition. Since 22 seemed to re-arrange thermally to 21, an attempt was made to effect decomposition under photochemical conditions. Unfortunately, the ultraviolet lamp which was available did not have sufficient energy output in the region of p-toluenesulfonylhydrazone absorption to effect decomposition.

As previously mentioned, the thermal decomposition of diazo compounds may proceed by two different pathways, one leading via loss of nitrogen to a carbene, the other involving protonation to form a diazonium ion followed by loss of nitrogen to give a carbonium ion. It was of interest to see if the alternate pathway via a carbonium
ion could be induced by the addition of a proton source. In accordance with this, the di-p-toluenesulfonylhydrazone, \( \text{20} \), was decomposed at reduced pressure in triglyme in the presence of two moles of cyclohexanol. Although the reaction was run \textit{in vacuo} the only product isolated was \( \text{21} \). It thus appears that \( \text{22} \) is a product only of carbene reaction and \( \text{21} \) is formed by either 1) a carbene mechanism, 2) thermal rearrangement of \( \text{22} \), or 3) a carbonium ion process, or perhaps by a combination of these three processes. A reasonable mechanism for the formation of \( \text{21} \) by a carbonium ion pathway may be written.

The similarity between this carbonium ion route and the
carbene mechanism discussed on p. 21 illustrates the fact that carbenes and carbonium ions, being electrophilic species, might be expected to react in a similar manner.

The original study of p-toluenesulfonylhydrazone decompositions as developed by Bamford and Stevens involved use of a protonic solvent and was shown to proceed via a carbonium ion mechanism. There is a considerable difference between this procedure and the one just discussed. Our method involved addition of an equimolar amount of some proton source to an aprotic solvent. The Bamford-Stevens reaction uses the solvent as the proton source. It was therefore desirable to decompose 20 under conditions similar to those employed by Bamford and Stevens. The product of this reaction, obtained in 62% yield, was shown to be the ethylene ketal of 2,2,4-trimethyl-3-pentenal, 24. The infrared spectrum shows the presence of an ether function at 1108 cm\(^{-1}\). N.m.r. data are summarized in Table IV. Structure 24 is uniquely consistent with this data and

\[
\begin{align*}
\text{H}_3\text{C} & \text{H} \text{CH}_3 \text{H} \text{O--CH}_2 \\
\text{H}_3\text{C} & \text{CH}_3 \text{O--CH}_2 \\
\end{align*}
\]
TABLE IV. N.M.R. OF 24.

<table>
<thead>
<tr>
<th>(p.p.m.)</th>
<th>Rel. Area</th>
<th>Shape</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>6</td>
<td>singlet</td>
<td>2 methyls</td>
</tr>
<tr>
<td>1.66</td>
<td>6</td>
<td>singlet</td>
<td>2 vinyl methyls</td>
</tr>
<tr>
<td>3.79</td>
<td>4</td>
<td>multiplet</td>
<td>H adjacent to ether</td>
</tr>
<tr>
<td>4.47</td>
<td>1</td>
<td>singlet</td>
<td>H adjacent to two ethers</td>
</tr>
<tr>
<td>5.08</td>
<td>1</td>
<td>multiplet</td>
<td>vinyl hydrogen</td>
</tr>
</tbody>
</table>

Confirmation was obtained by conversion of 24, into a known derivative of the parent aldehyde.

Modification of the usual Bamford-Stevens mechanism to involve trapping of the carbonium ion by the solvent, followed by participation in the loss of the second molecule of nitrogen leads to this structure.

\[
\begin{align*}
\text{N}_2 & \quad 1) H^+ \\
\text{N}_2 & \quad 2) \text{-N}_2 \quad \text{N}_2 \\
\text{N}_2 & \quad \text{ethylene} \\
\text{glycol} & \quad \text{glycol}
\end{align*}
\]
Only one other case in which the solvent has trapped the carbonium ion has been reported (30).

A comparison of the two pathways to carbonium ion generation shows certain differences. In an aprotic solvent, the protonating agent did not participate in subsequent reactions of the carbonium ion, and one could thus study the reactions of a non-solvated carbonium ion. When the solvent itself was the proton source, however,
solvation of the carbonium occurred which resulted in trapping the carbonium ion with the solvent.

Previously mentioned investigations by Friedman and Shechter (17) indicated that more straightforward results could be expected from the decomposition of medium-ring di-p-toluenesulfonylhydrazones. Accordingly, decomposition of 1,4-cyclohexanedione, di-p-toluenesulfonylhydrazone, 25, under sodium hydride/vacuum conditions was effected which gave the products indicated in Table V. These products were readily identified by comparison with authentic samples.

**TABLE V. COMPARISON OF PRODUCTS AND RATIOS FROM THE DECOMPOSITION OF 25.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexene</td>
<td>1.5</td>
</tr>
<tr>
<td>1,3-cyclohexadiene</td>
<td>77.0</td>
</tr>
<tr>
<td>1,4-cyclohexadiene</td>
<td>8.5</td>
</tr>
<tr>
<td>benzene</td>
<td>13.0</td>
</tr>
</tbody>
</table>

Two pathways for this decomposition are possible. The first would involve simultaneous loss of two moles of nitrogen to give a dicarbene intermediate, 26. This species should be of such high energy that, although hydrogen migrations are the likely pathway, one would expect virtually equal amounts of the two isomeric cyclohexadienes.
Alternatively, if the reaction proceeds in a stepwise manner, hydrogen shift in the diazocarbene, $27$, would give $28$, which can only give the cyclohexenyl carbene $29$.

At this point a second hydrogen migration must take place and there is now a possibility for discrimination between hydrogens. Since the allylic hydrogen bond is somewhat weaker than the normal carbon-hydrogen bond, it is conceivable that this hydrogen might migrate preferentially.
That this is the case is shown by the data in Table V. The evidence implies, therefore, a stepwise mechanism and essentially eliminates the possibility of a dicarbene intermediate. The surprising aspect of this study is the apparently high degree of discrimination exhibited by a species as energetic as carbene, 27.

The presence of benzene cannot be completely explained. One might expect a small amount of disproportionation of cyclohexadiene to benzene and cyclohexene, in which case the two should be present in equimolar amounts.

It was desirable to include in this study the decomposition of a non-cyclic system such as 2,5-hexanediol, di-p-toluenesulfonylhydrazone, 30. Under the conditions previously employed, namely sodium hydride/vacuum, 30 was decomposed to give results analogous to the cyclohexadiene case in that the product consisted of isomeric hexadienes, Table VI. Only the three major products were identified. Using comparative infrared, ultraviolet and n.m.r. spectroscopy, the product was shown to consist chiefly of 2,4-hexadiene and a small amount of 1,5-hexadiene. Presumably the other isomer, 1,4-hexadiene, was also present as one of three minor components indicated by g.l.c. The non-statistical manner in which hydrogen-migration occurred indicated that the reaction proceeded by a stepwise pathway with loss of one molecule of nitrogen to give the hexenyl
TABLE VI. COMPARISON OF PRODUCTS AND RATIOS FROM THE DECOMPOSITION OF 30.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,5-Hexadiene</td>
<td>15%</td>
</tr>
<tr>
<td>trans,cis-2,4-Hexadiene</td>
<td>62%</td>
</tr>
<tr>
<td>isomeric 2,4-Hexadiene</td>
<td>23%</td>
</tr>
</tbody>
</table>

carbene, 31, followed by hydrogen migration to yield isomeric diazohexenes. Loss of the second molecule of nitrogen and hydrogen-migration would give three isomeric hexadienes.
Intramolecular reaction of carbene \[ \text{31} \] with the diazo group to produce dimethylcyclobutene was not observed.
III. CONCLUSION

It has been shown that di-p-toluenesulfonylhydrazone decompositions follow interesting and rational pathways. The decomposition of tetramethyl-1,3-cyclobutanedione, di-p-toluenesulfonylhydrazone was of special interest in that ring opening was clearly established and cross ring insertion was suggested. From this work a convenient synthesis of 2,5-dimethyl-1,3,4-hexatriene was developed. In addition, a more convenient method for preparing the sodium salt of the di-p-toluenesulfonylhydrazone was discovered, which employed sodium hydride and eliminated the possibility of carbonium ion side reactions due to alcohol impurities. The interesting possibility of studying carbonium ion reactions in an aprotic solvent was cursorily investigated as an outgrowth of the carbene studies.

In no case was there a reaction between the carbene and the diazo group to give a small ring system. Instead, hydrogen-migration was observed and the non-statistical nature of the diene products thus obtained suggests some discriminatory ability for intramolecular reactions of a secondary carbene.
IV. EXPERIMENTAL

Microanalyses were performed by Galbraith Laboratories, Inc. Proton n.m.r. spectra were taken at 60 Mc/sec. on a Varian Model A-60 instrument. Infrared absorption spectra were determined using a Beckman IR-8 spectrometer. Ultraviolet absorption spectra were obtained with a Beckman-DB spectrometer. Gas-liquid chromatograms (g.l.c.) were obtained with an Aerograph Model A-90-P vapor fractometer. Melting points and boiling points are uncorrected.

Di-p-Toluenesulfonylhydrazones

A. Tetramethyl-1,3-cyclobutanedione, di-p-toluenesulfonylehydrazone, 20--A solution of 10 g. (0.0715 mole) of tetramethyl-1,3-cyclobutanedione and 32.9 g. (0.178 mole) of p-toluenesulfonylhydrazide in 250 ml. of 95% ethanol was heated under reflux for one hour. The white crystals which slowly formed during this time were filtered, washed with hot ethanol and dried in vacuo to yield 33.0 g. (97%) of fine crystals, d. 275°. An analytical sample was prepared by dissolving a portion of the crystals in aqueous 5% sodium hydroxide, filtering, reprecipitating by slowly adding 10% hydrochloric acid, filtering through a sintered glass funnel, washing the precipitate with absolute ethanol and drying in an Abderhalden drying pistol.
Anal. Calcd. for C_{22}H_{28}N_{4}O_{4}S_{2}: C, 55.45; H, 5.92; N, 11.76. Found: C, 55.34; H, 5.77; N, 11.50.

The infrared spectrum (nujol mull) showed a weak band at 3230 cm\(^{-1}\) (N-H stretch); a weak band at 1590 cm\(^{-1}\) (aromatic skeletal vibration); and strong bands at 1344 cm\(^{-1}\) and 1166 cm\(^{-1}\) (characteristic of -SO\(_{2}\)-).

B. 1,4-Cyclohexanedione, di-p-toluenesulfonylhydrazone, 25--In a similar manner, the di-p-toluenesulfonylhydrazone of 1,4-cyclohexanedione was prepared from 5 g. (0.044 mole) of cyclohexanedione and 20.6 g. (0.111 mole) of p-toluenesulfonylhydrazide. The p-toluenesulfonylhydrazone precipitated immediately upon heating, and after heating under reflux for one-half hour, was filtered with suction, washed, and dried in vacuo to yield 19.2 g. (98.5%), m.p. 225-227\(^{\circ}\), with decomposition and bubbling. A sample for analysis was prepared as before, m.p. 227-228\(^{\circ}\) (dec.).

Anal. Calcd. for C_{20}H_{24}N_{4}O_{4}S_{2}: C, 54.05; H, 4.54; N, 12.61. Found: C, 53.85; H, 4.48; N, 12.66.

The infrared spectrum (nujol mull) showed a weak band at 3230 cm\(^{-1}\) (N-H stretch); a weak band at 1590 cm\(^{-1}\) (aromatic skeletal vibration); and strong bands at 1330 cm\(^{-1}\) and 1162 cm\(^{-1}\) (characteristic of -SO\(_{2}\)-).

1,4-Cyclohexanediol--Fifty grams (0.45 mole) of hydroquinone and 7.5 g. of Raney nickel catalyst in 250 ml. of methanol were hydrogenated at 1000 psi and 150\(^{\circ}\) for
48 hours. The colorless solution was filtered to remove Raney nickel, and the methanol was removed in vacuo to yield 48.5 g. (94%) of white, crystalline 1,4-cyclohexanediol, m.p. 94-96° after drying in vacuo. (Authentic sample m.p. 100-104°, mixed m.p. 96-101°.)

1,4-Cyclohexanediol--Jones' Reagent was prepared by adding 26.72 g. (0.267 mole) of CrO₃ to 23 ml. of conc. sulfuric acid and pouring into sufficient water to make 100 ml. of solution. To 23.2 g. (0.8 eq.; 0.20 mole) of cyclohexanediol in 500 ml. of acetone (distilled from potassium permanganate) at 0° was added with rapid stirring 100 ml. of Jones' Reagent (8.0 N.). The temperature of the solution was maintained at 10-15°. After addition was complete, the dark green mixture was poured into saturated sodium chloride solution and extracted eight times with chloroform. The combined chloroform extracts were washed well with water, dried over anhydrous magnesium sulfate and the chloroform was removed in vacuo to yield 7.5 g. (33.3%) of yellow crystals, m.p. 72-74°. No attempt was made to further purify the 1,4-cyclohexanediol as the di-p-toluenesulfonylhydrazone could be made from the crude material. The di-p-toluenesulfonylhydrazone was identical in all respects to that prepared from an authentic sample of 1,4-cyclohexanediol.
C. 2,5-Hexanedione, di-p-toluenesulfonfylhydrazone,

As before, the di-p-toluenesulfonfylhydrazone of 2,5-hexanedione was prepared from 5 g. (0.0438 mole) of 2,5-hexanedione and 24.4 g. (0.1314 mole) of p-tolunesulfonfylhydrazide in 250 ml. of 95% ethanol. The white crystals which immediately formed were filtered hot, washed, and dried in vacuo to yield 19.5 g. (98.7%), m.p. 160-160.5°, with bubbling. An analytical sample was prepared by recrystallization from absolute ethanol, m.p. 160.5-161.0° (dec.).

Anal. Calcd. for C_{20}H_{26}N_{4}O_{4}S_{2}:  C, 53.31; H, 5.82; N, 12.44. Found:  C, 53.55; H, 6.09; N, 12.08.

The infrared spectrum showed the same characteristic peaks present in the infrared spectra of 20 and 24.

D. Attempted Preparation of Anthraquinone, di-p-toluenesulfonfylhydrazone—An attempt was made to form the di-p-toluenesulfonfylhydrazone of anthraquinone under forcing conditions by heating under reflux 5.0 g. (0.024 mole) of anthraquinone and 8.93 g. (0.048 mole) of p-toluenesulfonfylhydrazide with 60 ml. of diethylene glycol and 1.0 ml. of conc. hydrochloric acid. The solution was concentrated in an attempt to remove any water which might be formed. Solution was achieved, and nitrogen evolution occurred, presumably from the decomposition of
the \( p \)-toluenesulfonylhydrazide. Anthraquinone was recovered quantitatively from the reaction.

One gram of anthraquinone and 1.8 g. of \( p \)-toluenesulfonylhydrazide were then heated under reflux for 24 hours in 50 ml. of absolute ethanol to which had been added 0.1 g. of \( p \)-toluenesulfonic acid as a catalyst. Water was removed by azeotropic distillation. Again, anthraquinone was recovered quantitatively.

An attempt was made to form the dihydrazone of anthraquinone by heating under reflux 1 g. (0.005 mole) of anthraquinone, 1.5 g. (0.080 mole) of 95% hydrazine, and 0.30 ml. (0.020 mole) of glacial acetic acid in 200 ml. of absolute ethanol. Anthraquinone was recovered quantitatively.

Finally, 1 g. of anthraquinone, 1.5 g. of 95% hydrazine, and 0.30 ml. of glacial acetic acid were heated together in diethyleneglycol. The solution darkened and gas was evolved. Anthraquinone was recovered in almost 100% yield.

**Thermal Decompositions of Tetramethyl-\( 1,3 \)-cyclobutanedione-di-\( p \)-toluenesulfonylhydrazone.**

The decompositions were attempted under a variety of conditions: 1) forming the sodium salt from sodium methoxide and decomposing in diglyme at atmospheric pressure;
2) forming the sodium salt from sodium hydride and decomposing in triglyme under vacuum; 3) forming the sodium salt from sodium methoxide and taking special precautions to remove methanol by azeotroping any remaining methanol with benzene and decomposing in diglyme under vacuum; 4) forming the sodium salt from sodium hydride and decomposing in triglyme under vacuum in the presence of two moles of cyclohexanol; and 5) decomposing the sodium salt in ethylene glycol at atmospheric pressure. Table II in the text shows the products and their relative ratios for the first four methods.

A. Salt Formed from Sodium Methoxide--In a flame-dried 250 ml. three-necked flask containing 75 ml. of dry methanol was dissolved 2.90 g. (0.126 mole) of clean sodium. The methanol was removed in vacuo and the residue was dried overnight at 0.01 mm. About 75 ml. of diglyme (distilled from sodium, then from lithium aluminum hydride) was distilled into the flask. A further 100 ml. of diglyme was distilled into a separate receiver and to this was added 15 g. (0.0315 mole) of tetramethyl-1,3-cyclobutanedione, di-p-toluenesulfonylhydrazone. The flask containing the sodium methoxide/diglyme suspension was fitted with a nitrogen inlet tube and an outlet to two dry-ice/acetone cold traps, and was heated to 150° in an oil bath while stirring. To this hot suspension was slowly added
over a period of one hour the p-toluenesulfonylhydrazone suspension while maintaining a flow of nitrogen through the reaction flask. After addition was complete, heating and stirring was continued for another fifteen minutes. The cold traps were removed and the contents taken up in pentane, washed well with water to remove diglyme and dried over anhydrous magnesium sulfate. The pentane was removed by careful distillation through a Vigreaux column to give 0.59 g. of liquid residue. The reaction mixture remaining in the flask was poured over ice and extracted three times with pentane. The combined pentane extracts were washed 10-12 times with water, dried over anhydrous magnesium sulfate and concentrated by careful removal of pentane through a Vigreaux column. Analysis by g.l.c., using a diethylene glycol succinate column at 100°, showed that the material extracted from the reaction mixture was essentially the same as that taken from the cold traps, so the two were combined to give 2.76 g. of yellow liquid (approximately 20% pentane by g.l.c. analysis; yield 61%). G.l.c. showed one major peak which was collected by preparative g.l.c. for analysis, n\textsuperscript{24.5} = 1.4618 (lit (38) n\textsuperscript{25} = 1.4705).

Examination of the infrared and n.m.r. spectra led to assignment of structure 21 to this compound.

Anal. Calcd. for C\textsubscript{8}H\textsubscript{12}: C, 88.82; H, 11.18. Found: C, 88.68; H, 11.20.
The infrared spectrum showed a weak band at 1941 cm\(^{-1}\) (allene stretch); a medium band at 1613 cm\(^{-1}\) (vinyl hydrogen); and 875 cm\(^{-1}\) (terminal methylene). The n.m.r. spectral data appears in Table I. The ultraviolet spectrum of \(21\) shows a maximum at 218 m\(\mu\), \(\varepsilon = 27,400\) (ethanol).

**Hydrogenation of \(21\)**—A mixture of 0.3473 g. (3.22 mole) of \(21\), 0.01 g. of 5% Pd/C catalyst, and 5 ml. of ethanol was hydrogenated for 2 hours. The uptake of hydrogen was 85% of that calculated for three double bonds. The solution was filtered, taken up in pentane, washed 6-8 times to remove ethanol and dried over anhydrous magnesium sulfate. The pentane was slowly removed by distillation through a Vigreaux column. Analysis by g.l.c. using a 10-foot diethylene glycol succinate column at 65\(^\circ\) showed only one product. A sample was collected by preparative g.l.c. and examined by infrared and n.m.r. spectroscopy. The spectra were virtually identical to those of 2,5-dimethylhexane.

The infrared spectrum showed bands at 3.49, 6.84, 7.25, 7.35, and 8.59 \(\mu\). The reported values (2) were 3.47, 6.84, 7.23, 7.31, and 8.50 \(\mu\).

**B. Salt Formed from Sodium Hydride**—Into a flame-dried 1-l. three-necked flask was distilled about 400 ml. of dry triglyme. To this was added 43.1 g. (0.097 mole) of dry tetramethyl-1,3-cyclobutanedione, di-p-toluenesulfonylhydrazone (dispersion in oil, 52.6% by weight). The flask
was fitted with a nitrogen inlet capillary and an outlet to two dry-ice/acetone cold traps and an aspirator. The flask was evacuated to 150-160 mm. with a nitrogen bleed and heated to 160° in an oil bath for about 1 hour. Nitrogen evolution appeared to take place and the reaction mixture turned deep red-brown. When the reaction was complete, the apparatus was cooled and the cold trap contents taken up in pentane, washed with small portions of water and dried over anhydrous magnesium sulfate. The pentane was carefully removed to yield 4.96 g. of a clear, colorless liquid. Analysis by g.l.c. showed three major peaks. Samples of each of the three peaks were collected by preparative g.l.c. and examined by infrared and n.m.r. spectroscopy. On this basis, peak #1 was assigned structure 22. Peak #2 was identical to the allene, 21, and was shown by co-injection with 21 to be the same. Peak #3 was assigned the structure 2-methoxyethyl vinyl ether, a product of solvent cleavage. Twenty-one and 22 accounted for approximately 80% of the crude liquid, giving a yield of about 3.97 g. (45%). An analytical sample of 22 was collected by preparative g.l.c., n^25° = 1.4345.

**Anal. Calcd. for C₆H₁₂:** C, 88.82; H, 11.18. **Found:** C, 88.02; H, 10.67.

The infrared spectrum showed a weak band at 3080 cm⁻¹ (vinyl hydrogen stretch); a medium peak at 1630 cm⁻¹ (vinyl
hydrogen); and a strong peak at 887 cm\(^{-1}\) (C\(=\)C). The ultraviolet spectrum of 22 showed a maximum at 233 m\(\mu\), \(\epsilon = 9670\) (ethanol).

**Hydrogenation of 22**--A mixture of 0.125 g. of 22, 0.01 g. of 5% Pd/C catalyst and 5 ml. of absolute ethanol were hydrogenated for 2 hours. The uptake of hydrogen was 92% of that calculated for three double bonds. The solution was filtered, taken up in pentane, washed with water and dried over anhydrous magnesium sulfate. The pentane was removed by distillation through a Vigreaux column. The residue was examined by g.l.c. and showed one product, which was collected by preparative g.l.c. The infrared spectrum of this material was identical to that of the hydrogenation product of 21, namely 2,5-dimethylhexane.

**Second Decomposition under the Same Conditions**--Using the same conditions, 10 g. (0.027 mole) of tetramethyl-1,3-cyclobutanedione, di-p-toluenesulfonylhydrazone and 2.1 g. (0.046 mole) of sodium hydride suspension were heated in triglyme. The g.l.c. of the cold trap contents showed the same peaks previously observed and in similar ratios, as shown in Table II.

**Thermal Study**--About 0.15 ml. of the crude mixture from the cold trap was heated in one ml. of diglyme at 160°. At intervals, samples were removed and injected into the g.l.c. At 50 minutes it was noted that the percentage of 22 was
decreasing in favor of an increasing percentage of 21.

<table>
<thead>
<tr>
<th>Time</th>
<th>21</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>33%</td>
<td>67%</td>
</tr>
<tr>
<td>10 min</td>
<td>33%</td>
<td>67%</td>
</tr>
<tr>
<td>25 min</td>
<td>33%</td>
<td>67%</td>
</tr>
<tr>
<td>50 min</td>
<td>40%</td>
<td>60%</td>
</tr>
<tr>
<td>80 min</td>
<td>50%</td>
<td>50%</td>
</tr>
</tbody>
</table>

C. Salt Prepared with Sodium Methoxide--Special Care

Taken in Drying--One gram of clean sodium (0.044 mole) was dissolved in 30 ml. of dry, freshly distilled methanol in a 500 ml. three-necked flask. Five grams (0.0113 mole) of tetramethyl-1,3-cyclobutanedione, di-p-toluenesulfonyl-hydrazone was added and the methanol was removed in vacuo. Benzene (25 ml.) was added and removed in vacuo to azeotrope over any remaining methanol. The solid mass of salt was broken up and pumped overnight at 0.01 mm. About 100 ml. of dry diglyme was distilled into the flask. The flask was fitted with a nitrogen inlet and an outlet to two cold traps and was lowered into an oil bath maintained at 160°. After 1 hour of heating at this temperature and stirring, the flask was evacuated to 150-160 mm. for 10 minutes to further distill any product. The flask was then cooled and the contents of the cold traps taken up in pentane, washed well to remove diglyme, and dried. The pentane was removed by
distillation through a Vigreaux column. The remaining liquid was examined by g.l.c. and compared with the products from previous decompositions.

The product ratios are shown in Table II.

D. Decomposition in the Presence of a Proton Source--
Ten grams (0.027 mole) of tetramethyl-1,3-cyclobutanedione, di-p-toluenesulfonylhydrazone and 2.6 g. (0.056 mole, oil dispersion, 52.6% by weight) of sodium hydride were added to 200 ml. of dry triglyme (distilled from sodium, then from lithium aluminum hydride into a flame-dried 500 ml. three-necked flask, b.p. 115-117°/25 mm.). When evolution of hydrogen was complete (about one-half hour), 5.4 g. (0.055 mole) of dry cyclohexanol was added. A small amount of gas evolution was observed. The flask was fitted with a capillary nitrogen inlet tube and an outlet that led through two dry-ice/acetone cold traps, a drying tube, another trap, and an aspirator equipped with a manometer. The flask was evacuated to about 150 mm. and nitrogen was bled in. The flask was lowered with stirring into an oil bath maintained at 160°. Evolution of gas began and liquid was seen to distill into the cold traps. The flask was heated and stirred for 1½ hours at 140-160°. The suspension in the reaction flask slowly turned to a deep tan color. At the end of 1½ hours, the flask was raised from the oil bath
and the contents of the cold traps, containing 1.95 g. of liquid, were examined by g.l.c., using a 10-foot diethylene-glycol succinate column at 85°, flow rate 50 ml./min. The g.l.c. showed two major peaks, which were collected by preparative g.l.c. The first, relative area 15%, was shown by injection of a sample of cyclohexanol and by co-injection to be cyclohexanol. The second, relative area 60% (yield ca 51%) was shown by examination of the infrared spectrum and by co-injection with 21 to be identical in all respects to the allene, 21.

E. Bamford-Stevens Conditions. A solution of 4.5 g. (0.195 mole) of sodium in 50 ml. of dry ethylene glycol was prepared. To this was added 15 g. (0.0315 mole) of tetra-methyl-1,3-cyclobutanedione, di-p-toluenesulfonylhydrazone and the solution was stirred for eight hours in an oil bath at 110-125°. Slow nitrogen evolution occurred and was essentially complete after four hours. The solution was cooled, poured over ice, and extracted with four portions of ether. The combined ether extracts were washed 10-12 times with water, twice with aqueous sodium bicarbonate solution, once more with water, and dried over anhydrous magnesium sulfate. After removing the drying agent, the ether was removed in vacuo to give 3.04 g. (62%) of yellow liquid. This was shown by g.l.c. on a 5-foot Ucon polar column at
150° to contain one major component, identified by its n.m.r. and infrared spectra as the ethylene ketal of 2,2,4-trimethyl-3-pentenal, 24. From the g.l.c., the crude product consisted of: ethylene glycol, 10% by area; ketal, 85%; minor impurities, 5%. A sample of the ketal was collected by preparative g.l.c., b.p. 203°.

The infrared spectrum (neat) showed a weak band at 1640 cm⁻¹ (C≡C stretch); a very strong band at 1108 cm⁻¹ (characteristic ether C-O stretch); and a weak band at 818 cm⁻¹ (trisubstituted alkene C-H out of plane bending).

The n.m.r. spectrum showed a multiplet centered at 5.08 ppm, relative area 1, assignable to vinyl hydrogen; a singlet at 4.47 ppm, relative area 1, assigned to the hydrogen on the carbon with two ether functions; a multiplet centered at 3.79 ppm, relative area 4, assigned to the ketal ring hydrogens; singlets at 1.66 and 1.01 ppm, with relative areas of 6 each, assigned to the allylic C-methyl hydrogens and the normal C-methyl hydrogens, respectively.

A 0.5 g. sample of the crude product was dissolved in 95% ethanol. To the solution was added 6 drops of conc. hydrochloric acid and the solution was heated under reflux for 20 minutes to hydrolyse the ketal to the aldehyde. The solution was cooled and a mixture of 0.4 g. of 2,4-dinitrophenylhydrazine and 2 ml. of conc. sulfuric acid in 10 ml. of ethanol was added. A yellow precipitate formed
immediately, was filtered and recrystallized from ethanol to give yellow needles, m.p. 139-140.5° (lit. value for the DNP of 2,2,4-trimethyl-3-pentenal, m.p. 142-3°).

**Thermal Decomposition of 1,4-cyclohexanedione, di-p-toluenesulfonylhydrazone**—In a manner similar to part B of the preceding section, 25 g. (0.056 mole) of cyclohexanedione, di-p-toluenesulfonylhydrazone and 5.62 g. (0.123 mole) of sodium hydride were heated under vacuum in about 200 ml. of dry triglyme for about 1 hour. The reaction mixture turned deep red-brown. The cold trap contents weighed 4.11 g. Examination by g.l.c. on a 15% diethylene glycol succinate column at 80°, showed five peaks. Retention times were compared with obtainable compounds and co-injections were made. Samples were collected by preparative g.l.c. and the infrared spectra were compared with obtainable compounds.

Examination of the data showed the presence of cyclohexene (1.5% by area); 1,3-cyclohexadiene (77%); 1,4-cyclohexadiene (8.5%); and benzene (13%). In all cases, infrared spectra were superimposable with spectra of known compounds. Considering the product to be approximately 60% olefins, the yield was about 2.47 g. (55%).

**Thermal Decomposition of 2,5-hexanediene, di-p-toluenesulfonylhydrazone**—In the same manner, 20 g. (0.0445
mole) of 2,5-hexanedione, di-p-toluenesulfonylhydrazone and 4.47 g. (0.098 mole) of sodium hydride oil dispersion were heated under vacuum in 250 ml. of dry triglyme for 1 hour at 120-160°. At about 130° vigorous evolution of gas occurred with much foaming, and the suspension rapidly turned red-brown. This vigorous reaction was complete in about 5 minutes after which the mixture was heated and stirred for another half hour. The cold trap contents weighed 5.57 g. and showed 3 main peaks on g.l.c. using the 15% Carbowax column at 30°. Samples were collected by preparative g.l.c. and examined by infrared and n.m.r. spectroscopy. The first peak was assigned the structure, 1,5-hexadiene. The third peak was assigned to trans-cis-2,4-hexadiene. The second peak appeared to be an isomeric 2,4-hexadiene. Table VI shows the products and their ratios. The yield, figuring the crude liquid to be about 60% olefins, was 3.3 g. (90%).

The infrared spectra of 1,5-hexadiene and trans-cis-2,4-hexadiene were virtually identical to spectra of authentic samples. The ultraviolet spectrum of the crude liquid showed a maximum at 228 mμ, ε = ca. 15,000 (EtOH). The ultraviolet spectrum of trans-cis-2,4-hexadiene showed a maximum at 229 mμ. The isomeric 2,4-hexadiene showed a maximum at 226 mμ.
BIBLIOGRAPHY


