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STUDIES ON VINYL CATIONS AND UNSATURATED CARBENES

DISSERTATION

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

By

Wei Chuan Liang, B.A., M.S.

The Ohio State University

1972

Approved by

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Adviser
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DEDICATION

To my parents
ACKNOWLEDGMENT

The author wishes to express his sincere gratitude to Professor Melvin S. Newman for his constructive criticism, guidance, and encouragement throughout the course of this research, and for his generous assistance in the preparation of this manuscript.

And a special thanks is due to the author's wife, Yu-Lan, for her untiring patience and support.
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INTRODUCTION

The intermediacy of either a vinyl cation\(^1-4\) or an unsaturated car-


\(^2\)\(^3\)\(^5\)\(^8\)\ has been postulated to explain the products obtained from


the base induced decomposition of 5,5-disubstituted-N-nitroso-2-oxazolidones.

\[\begin{align*}
R & \quad \text{(1)} \quad R \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\text{N} & \quad \text{N} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}\]
In a similar study N-nitrosoacetylaminooalcohols were decomposed in base to give products which were also explained by the intermediacy of an unsaturated carbene.

Typical reaction products are shown in Scheme I.

The objective of this work was to study the stereochemistry of products resulting from an unsymmetrical vinyl cation or an unsymmetrical unsaturated carbene; to study the reactions of a nitroso compound which could not conceivably proceed through an unsaturated carbene intermediate; and finally to explore new chemistry on the alkaline decomposition of N-nitrosoacetylaminooalcohols.
HISTORICAL

Since the isolation of a high yield of cyclohexanecarboxaldehyde from the alkaline decomposition of 3-nitroso-1-oxa-3-azaspiro[4,5]decan-2-one, further work on this reaction has been done in these laboratories.


Newman and Kutner showed that the alkaline decomposition of 3-nitroso-2-oxazolidones (1) gave a variety of products on changing the substituents and the base.

\[
\begin{align*}
\text{R}_1 & \quad \text{C} - \text{O} & \quad \text{C} - \text{O} \\
\text{R}_2 & \quad \text{CH}_2 - \text{N} - \text{NO}
\end{align*}
\]

(1)

If the \(\text{R}_1\) and \(\text{R}_2\) groups were aliphatic, aldehydes \(\text{R}_1\text{R}_2\text{CHCHO}\) were formed. If the \(\text{R}_1\) and \(\text{R}_2\) groups were phenyl, a quantitative yield of diphenylacetylene was obtained. If the reaction was carried out in absolute alcohols using sodium ethoxide as base, vinyl ethers were obtained in good yields. A mechanism (see Scheme II) which involved the vinyl cation as a key intermediate was postulated to account for the products. Thus, the nucleophilic attack by water or alcohols on the
Scheme II

(1)

(2)
vinyl cation yielded aldehydes or vinyl ethers and the migration of R₁ or R₂ gave acetylenes.

When 5,5-dialkyl-3-nitroso-2-oxazolidones (1) were decomposed with a base in the presence of a large excess of halide salts, good yields of vinyl halides were obtained (see Table 1). The authors assumed

Table 1

Alkaline decomposition of 5,5-dialkyl-3-nitroso-2-oxazolidones (1) in the presence of halide ions

<table>
<thead>
<tr>
<th>R₁</th>
<th>R₂</th>
<th>Products²</th>
<th>% Yield</th>
</tr>
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<tr>
<td>-(CH₂)₅-</td>
<td></td>
<td><img src="image1" alt="Product 1" /></td>
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<tr>
<td></td>
<td></td>
<td><img src="image2" alt="Product 2" /></td>
<td>73</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="image3" alt="Product 3" /></td>
<td>78</td>
</tr>
<tr>
<td>-(CH₂)₄-</td>
<td></td>
<td><img src="image4" alt="Product 4" /></td>
<td>81</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td><img src="image5" alt="Product 5" /></td>
<td>80</td>
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². Lithium 2-methoxyethoxide was used as the base. A saturated solution of halide of sodium or lithium in 2-methoxyethanol was employed.
that the vinyl cation 2 was involved, although they did not rule out the possibility of an unsaturated carbene intermediate.

In order to test the stereoselectivity in the reactions of an unsymmetrical vinyl cation, the alkaline decomposition of 5-methyl-5-t-butyl-3-nitroso-2-oxazolidone (3) under similar conditions was examined. The ratios of isomeric products are shown below.

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{C} & \quad \text{C} \quad \text{O} \quad \text{C} = \text{O} \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{N} \quad \text{N} \quad \text{O} \\
+ \quad \text{NaX} \quad \text{IIOCCH}_2\text{CH}_2\text{OCH}_3 & \rightarrow \quad \text{(CH}_3\text{)}_3\text{C} \quad \text{C} = \text{C} \quad \text{H} \\
& \quad \text{CH}_3 \quad \text{X} \\
\text{(3)} & \quad \text{X = I} \\
& \quad \text{X = Br} \\
& \quad 94 \quad 93
\end{align*}
\]

These results were interpreted as the consequence of the preferred halide ions attack from the unhindered side of the unsymmetrical vinyl cation.

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{C} & \quad \text{C} \quad \text{C} \quad \text{H} \\
\text{CH}_3 & \quad \text{X} \\
\text{X} & \quad \text{X} \\
\end{align*}
\]

Treatment of 5,5-dimethyl-3-nitroso-2-oxazolidone (4) in glyme with sodium phenoxide in the presence of phenol offered new proof for the
existence of a vinyl cation intermediate. Instead of obtaining the expected high yield of 2-methyl-1-propanoyl phenyl ether (5) there were obtained high yields of anisole (6) and 2-methoxyethyl 2-methyl-1-propenyl ether (7). To account for the unexpected cleavage of the solvent in this reaction the authors postulated that the vinyl cation 8 was formed from 4 and complexed with the oxygen atom of glyme to give the oxonium salt 9, which was then attacked by the phenoxide ion to yield the products as shown in Scheme III. As cleavage of ethers by carbenes only take place under pyrolytic conditions, the experimental results strongly supported that a vinyl cation was involved and not the unsaturated carbene.


(11) See Scheme II for the mechanism leading to 8.


In 1964 Hine suggested in his book a different mechanism which involved an unsaturated carbene to account for the products from the alkaline decomposition of 5-substituted-3-nitroso-2-oxazolidones (1).
Scheme III

\[ \text{CH}_3\text{C} - \text{O} - \text{C} = \text{O} \quad \text{several steps}^{\text{II}} \quad \text{CH}_3\text{C} = \text{O} \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{O} - \text{CH}_2\text{CH}_2\text{OCCH}_3 \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \quad \text{minor product} \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

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\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

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\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

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\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]

\[ \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{CH}_3\text{C} = \text{C} - \text{H} \quad \text{C}_6\text{H}_5\text{O}^- \]
Curtin and coworkers also postulated the unsaturated carbene as a possible intermediate for the formation of diphenylacetylene from the deamination of the vinyl amine.

The addition of carbenes to olefins has been used as a criterion to establish the formation of these intermediates. In 1963 Tanabe and


\[ \text{(15) M. Tanabe and R. A. Walsh, ibid., 85, 3522 (1963).} \]

Walsh reported the formation of methylenecyclopropanes by the reaction of vinyl halides with potassium t-butoxide in olefins. By using methyl lithium as base Hartzler reported the same kind of products. Both groups assumed the unsaturated carbenes \( 10 \) to be the intermediates.

\[ \text{When 5,5-dialkyl-3-nitroso-2-oxazolidones (1) were treated with alkoxides in the presence of olefins methylenecyclopropanes were obtained (Table 2). The authors proposed a mechanism which involved the unsaturated carbenes \( 10 \) to explain the products (Scheme IV).} \]

\[ \text{The formation of 9-\text{(methoxymethylene)-fluorene from the decomposition of 3-nitrosospiro[fluorene-9',5-oxazolidin]-2-one with 50\% potassium}\}}\]

\[ \text{(10)} \]
<table>
<thead>
<tr>
<th>R₁</th>
<th>R₂</th>
<th>Olefin</th>
<th>Product</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>- (CH₂)₅-</td>
<td></td>
<td>cyclohexene</td>
<td></td>
<td>65</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>(CH₃)₂C=CH(CH₃)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₂=CH-Ph</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cyclohexene</td>
<td></td>
<td>43</td>
</tr>
</tbody>
</table>
**Scheme IV**

\[
\begin{align*}
R_1 & \quad \text{O} \quad \text{C} = \text{O} \\
& \quad \text{CH}_2 - \text{N} - \text{NO} \\
\xrightarrow{\text{LiOEt}} & \quad \text{R}_1 \quad \text{O} - \text{C} - \text{OEt} \\
& \quad \text{CH}_2 - \text{N} = \text{N} = \text{O} \\
& \quad \text{R}_2 \\
\end{align*}
\]

\[(1)\]

\[
\begin{align*}
& \quad \text{R}_1 \quad \text{C} = \text{C} : \\
& \quad \text{R}_2 \\
& \quad \text{N}_2 \\
& \quad \text{R}_3 \quad \text{C} = \text{C} \quad \text{R}_5 \\
& \quad \text{R}_4 \quad \text{C} = \text{C} \quad \text{R}_6 \\
\end{align*}
\]

\[(10)\]
hydroxide in methanol was explained in terms of a vinyl cation inter-


mediate. However, when 3-nitroso-1-oxa-3-azaspiro[4,5]decan-2-one (12) was treated with lithium ethoxide in a mixture of ethanol and cyclo-

hexene, both vinyl ether and methylenecyclopropane were obtained. The unsaturated carbene was suggested as the common intermediate to account

\[
\begin{align*}
\text{cyclohexene} & \xrightarrow{\text{LiOEt}} \text{HOC}_2\text{Et} + \text{cyclohexene} \\
(12) &
\end{align*}
\]

for the products. The vinyl ether could be formed by the insertion of the unsaturated carbene into the O-H bond of ethanol. Treatment of

(18) The formation of ethers by reaction of carbenes with alcohols has been reported by R. M. G. Nair, E. Meyer, and G. W. Graffin, Angew. Chem. Intern. Ed., 7, 463 (1968) and references therein.

\[
\begin{align*}
\text{CH}_3OD & \quad \text{CH}_3OD \\
(13) & \quad (14)
\end{align*}
\]

12 with dry sodium methoxide in CH$_3$OD gave vinyl ether 13 with the methylene hydrogen being mainly deuterium. No incorporation of deuterium
was detected at the methylene position when 11 was treated with sodium methoxide in CH$_3$OD. Furthermore, when 12 was treated with insufficient sodium methoxide in CH$_3$OD, the 12 isolated after partial reaction did not show any incorporation of deuterium. Although these experimental results strongly suggested that the unsaturated carbene was the intermediate, there remained a possibility that deuterium exchange of some intermediate prior to the formation of the unsaturated carbene or vinyl cation might have occurred.

Carbonium ions abstract hydride ion from trialkylsilanes, while carbenes insert between the silicon-hydrogen bond of trialkylsilanes.


The formation of vinyl silane 15 from the alkaline decomposition of 4 in the presence of an excess of triethylsilane was therefore assumed to go through an unsaturated carbene intermediate.
The alkaline decomposition of 3 in triethylsilane yielded predominantly (10:1) the cis isomer 16. This result was explained by

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{C} & \xrightleftharpoons{\text{Et}_3\text{SiH}} \text{(CH}_3\text{)}_3\text{C} & \xrightarrow{\text{Si(Et)}_3} \text{(CH}_3\text{)}_3\text{C} \\
\text{C} & \text{C} & \text{H} & \text{C} & \text{C} & \text{H} \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{(17)} & \text{(16)} & \text{(19)}
\end{align*}
\]

assuming that the unsymmetrical unsaturated carbene 17 abstracted a hydride ion from the less hindered side to form an ion pair 18 as the initial step. The collapse of the ion pair 18 yielded the major product 16. Thus the insertion of the unsaturated carbene to the silicon-hydrogen bond appeared to be stereoselective.

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{C} & \xrightarrow{\text{HSiEt}_3} \text{(CH}_3\text{)}_3\text{C} & \xrightarrow{\text{Si(Et)}_3} \text{(CH}_3\text{)}_3\text{C} \\
\text{C} & \text{C} & \text{Si(Et)}_3 & \text{C} & \text{C} & \text{Si(Et)}_3 \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{(17)} & \text{(18)} & \text{(16)}
\end{align*}
\]

When 4 was decomposed with sodium alkoxides in the presence of ethoxyacetylenes allenic acetals were isolated instead of the expected substituted methylenecyclopropenes. A mechanism (Scheme V) was postulated to account for the observed products. Methylenecyclopropene 25 was assumed to be a labile species. The attack of the alkoxide ion on

25 yielded 26 which was then protonated to give 20, 21, and 22. Alternatively 24 could rehybridize to give 27 which then reacted with alcohols to give the products.

Recently an improved method of generating unsaturated carbenes which involved the treatment of N-nitroso acetylaminoalcohols with base by means of Phase-Transfer Catalysis was reported. 22 An example is


(24) Aliquat 336 is methyl tricaprylylammonium chloride obtained from General Mills Chemicals, Kankakee, Ill.

high yields of the products and the relatively low temperature (-10°) at which one could carry out the reactions.

In the present work 1-(N-nitrosoacetylaminomethyl)cyclohexanol was decomposed with base in ketones, aldehydes, sodium azide, potassium thiocyanate, and trialkyl phosphites respectively. Some of the related reactions as well as preparative methods for products similar to those obtained from the present study but done in other laboratories are reviewed in the following section.

Reactions of Carbenes with Carbonyl Compounds.

Photolysis of diazomethane in acetone with light of wavelength > 3200 Å yielded four major products: 25

2-butanone, 2,2-dimethyloxirane,

2-methoxypropene, and 2,2,4,4-tetramethyl-1,3-dioxolane. With the exception of 2-butanone which was explained by a direct carbene insertion.

into a C-H bond, the remaining products were thought to be derived from
the dipolar intermediate 28.

\[
\begin{align*}
\text{hv} & \quad > 3200 \text{ Å} \\
\text{CH}_3 - \text{C} - \text{CH}_3 + \text{CH}_2\text{N}_2 & \rightarrow \text{CH}_3\text{CH}_2\text{C} - \text{CH}_3 + (\text{CH}_3)_2\text{C} - \text{O} - \text{CH}_2
\end{align*}
\]

\[(28)\]

Copper-catalyzed decomposition of diazoacetate in the presence of
benzaldehyde gave predominantly 1,3-dioxolane. Again, the 1,3-dipolar


species \((29)\) was postulated as the intermediate.
Ethyl diazoacetate has been reported to react with acetone to yield a variety of products. The formation of these products was explained by the carboethoxycarbene attack of the carbonyl oxygen to give the 1,3-dipolar intermediate. By a proton shift gave enol ester, from which was derived by further addition of acetone. The reaction of with another molecule of acetone yielded (Scheme VI).

An enol ether was obtained as the major product when benzosuberone was treated with ethyl diazoacetate and copper powder.

\[
\text{CH}_3\text{C} - \text{CH}_3 + \text{N}_2\text{CHCO}_2\text{Et} \xrightarrow{\text{Cu} \ 90^\circ} \text{CH}_2=\text{C} - \text{O} - \text{CH}_2\text{CO}_2\text{Et} \\
\text{CH}_3
\]

\[
\begin{array}{c}
\text{CH}_3 \\
+ \text{CH}_2=\text{C} - \text{O} - \text{CH}_2\text{CO}_2\text{Et} \\
\text{H} \text{O} - \text{C(CH}_3\text{)}_2
\end{array} \quad + \quad \begin{array}{c}
\text{(CH}_3\text{)}_2\text{C} - \text{O} - \text{CH}_2\text{CO}_2\text{Et} \\
\text{O} --- \text{C(CH}_3\text{)}_2
\end{array}
\]

\[
\left(31\right) \quad \left(32\right)
\]

\[
\text{CH}_3 \\
+ \text{CH}_2\text{C} - \text{O} - \text{CH}_2\text{CO}_2\text{Et} \\
\text{H} \text{C}_2\text{CO}_2\text{Et}
\]

\[
\left(33\right)
\]

**Scheme VI**

\[
\begin{array}{c}
\text{CH}_3 \\
+ \text{CH}_2\text{C} - \text{O} - \text{CH}_2\text{CO}_2\text{Et}
\end{array} \xrightarrow{\text{H}^+ \text{ shift}} \text{CH}_2=\text{C} - \text{CH}_3 \\
\text{CH}_3\text{COCH}_3
\]

\[
\left(35\right) \quad \left(30\right) \quad \left(33\right)
\]
Interestingly, oxiranes were not among the products of ethoxycarbonyl carbenoid reactions. However, the addition of bis(trifluoromethyl)-carbene to difluoro ketone gave perfluoroisobutylene oxide in 40% yield.

Highly fluorinated ketones also formed oxiranes with dichlorocarbene generated by heating PhHgCCl₂Br.

$$\text{PhHgCCl}_2\text{Br} + (\text{CF}_2\text{X})_2\text{CO} \rightarrow \text{ClF}_2\text{C} - \text{C} - \text{Cl}$$
$$\text{ClF}_2\text{C} - \text{O} - \text{C} - \text{Cl}$$

$$X = \text{Cl}, \text{F}$$
Dihalocarbenes generated from haloforms and base have a tendency to attack the enolate ions of carbonyl compounds, followed by dehalogenation whenever possible. Some of these results are illustrated by the following equations:

\[
RCH(CO_2R')_2 + CHX_3 + NaOR' \rightarrow X_2CH \xrightarrow{R} C(CO_2R)_2 \quad X = F, Cl, Br
\]

Ethoxycarbonylcarbene and difluorocarbene are known to react with α-methoxymethylene ketones by 1,4-addition. Elimination of methanol (whenever possible) yielded furans.
Vinyl Azides

Vinyl azides have been prepared in a number of ways. The simplest one, azidoethylene, was prepared as early as 1910. Triazaethanol was used as the starting material. After treatment with phosphorous tribromide halogen exchange was affected with sodium iodide and the resulting 2-iodo-1-azidoethane was dehalogenated in the presence of alcoholic potassium hydroxide to give vinyl azide.

\[
\begin{align*}
\text{HOCH}_2\text{CH}_2\text{N}_3 & \xrightarrow{\text{PBr}_3} \text{BrCH}_2\text{CH}_2\text{N}_3 \\
& \xrightarrow{\text{NaI}} \text{ICH}_2\text{CH}_2\text{N}_3 \xrightarrow{\text{alc. KOH}} \text{CH}_2=\text{CH-N}_3
\end{align*}
\]

α-Azidostyrene was prepared in 1961 by the reaction of styrene dibromide with sodium azide in dimethylformamide, followed by treatment of the bromoazide formed with potassium t-butoxide. In the subsequent year


a more general method for the preparation of vinyl azides was developed.  


Some of the results are shown below:

Vinyl azides have also been prepared from β-iodo azides generated by the addition of iodoazide to olefins.  

olefins was highly stereospecific. Terminal olefins formed adducts where the azido function was at the 2-position. This is by far the most general method in preparing vinyl azides to date. However, terminal vinyl azides cannot be prepared by this route. The only exception is the following case.

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{C}_-\text{C}=-\text{CH}_2 & \xrightarrow{\text{IN}_3} \text{(CH}_3\text{)}_3\text{C}_-\text{CH}-2\text{CH}_2\text{N}_3 & \xrightarrow{\text{t-ButO}_4\text{K}} \text{(CH}_3\text{)}_3\text{C}_-\text{C}=-\text{CH}-\text{H} \\
\text{H} & & \text{H} \\
\end{align*}
\]

Other reported preparations of terminal vinyl azides are illustrated by the equations below.


\[
\begin{align*}
a. & \quad \text{Ph} - \text{C} - \text{CH}_2\text{N}_3 \xrightarrow{\frac{1}{2}\text{NaBH}_4} \text{PhCHOH} \xrightarrow{-25^\circ} \text{PhCH} - \text{Cl} \\
& \quad \downarrow \text{t-ButO}_4\text{K} \\
& \quad \text{Cl} \\
& \quad 17\% \text{ PhC} = \text{Cl}_2 + \text{PhCH} = \text{CHN}_3 \quad 44\%
\end{align*}
\]
b. 
\[
\begin{align*}
\text{Br} & \quad \xrightarrow{\text{NaN}_3, \text{DMF}} \\
\text{H} & \quad \xrightarrow{} \\
\text{C} & \quad \text{N}_3
\end{align*}
\]
Yield not reported

\[
\begin{align*}
\text{C} & \quad \text{OH} \\
\text{O} & \quad \text{CH}_2 \\
\text{R}_1 & \quad \text{CH}_2 \\
\text{R}_2 & \quad \text{CH}_2 \\
\text{N}_3 & \quad \text{C} = \text{CH-N}_3
\end{align*}
\]

\[
\begin{align*}
\text{R}_1 & = \text{Ph}, \quad \text{R}_2 = \text{CH}_3 \\
\text{R}_1 & = \text{Ph}, \quad \text{R}_2 = \text{Ph}
\end{align*}
\]

Vinyl Thiocyanates

Vinyl thiocyanate was prepared by the dehalogenation of the β-bromo or β-chloro ethyl thiocyanates with tertiary amines.


\[
\begin{align*}
\text{XCH}_2\text{CH}_2\text{SCN} + \text{B} & \rightarrow \text{CH}_2=\text{C}-\text{SCN} + \text{B-HX} \\
\text{X} = \text{Br}, \quad \text{B} = \text{Et}_3\text{N} & \rightarrow 80\% \\
\text{X} = \text{Cl}, \quad \text{B} = \text{PhCH}_2\text{N(CH}_3)_2 & \rightarrow 50\%
\end{align*}
\]
Tobler and Foster reported that vinylmercuric acetate reacted with sodium thiocyanate to yield vinylmercuric thiocyanate. Thermal decomposition of vinylmercuric thiocyanate at 100-120° and 100 mm gave a mixture which consisted of 30% of vinyl isothiocyanate and 66% of vinyl thiocyanate by vapor phase chromatographic analysis. The actual yields of these two vinyl compounds were not reported.

\[
\text{CH}_2=\text{CH}-\text{HgOAc} + \text{NaSCN} \quad \xrightarrow{\text{decomposition}} \quad \text{CH}_2=\text{CH}-\text{HgSCN}
\]

\[
\text{decomposition} \quad 100-120°/100 \text{ mm}
\]

\[
30\% \quad \text{CH}_2=\text{CH}-\text{N} = \text{C} = \text{S} + \text{CH}_2=\text{CH}-\text{S} - \text{C} = \text{N} \quad 66\%
\]

Dialkyl Vinylphosphonates

The preparation of dialkyl vinylphosphonates is illustrated by the following methods.

1. Vinylphosphonic dichlorides with alcohols.

One of the main methods of preparing the starting acid chlorides was to add phosphorous pentachloride to olefins, followed by the treatment of the adducts with sulfur dioxide or phosphorous pentoxide.

\[
\text{RCH} = \text{CHCl}_2 + 2 \text{PCl}_5 \rightarrow \text{RCHClCH}_2\text{PCl}_4 \cdot \text{PCl}_5
\]

\[
3 \text{ RCH} = \text{CHPOCl}_2 + 3 \text{POCl}_3 + 6 \text{SO}_2 + 6 \text{SOCl}_2 + 3 \text{HCl}
\]

\[
3 \text{RCHClCH}_2\text{PCl}_4 \cdot \text{PCl}_5 + 2 \text{P}_2\text{O}_5 \rightarrow 3 \text{RCH} = \text{CHPOCl}_2 + 7 \text{POCl}_3 + 3 \text{HCl}
\]

2. Alkenyltetrachlorophosphoranes with alcohols.

\[
\text{R'}\text{PCl}_4 + 3 \text{ROH} \rightarrow \text{R'}\text{PO(OR)}_2 + \text{RCl} + 3 \text{HCl}
\]

where \(\text{R'}\) is an unsaturated radical
3. Dehydrohalogenation of esters of β-halogenoalkylphosphonic acids, dehalogenation of esters of dihalogenoalkylphosphonic acids, and dehy-
dration of esters of α-hydroxyalkylphosphonic acids according to the following general scheme:

$$R'\text{CHX--}CF''\text{R''PO(OR)}_2 \xrightarrow{-HX(R''X \text{ or } H_2O)} R'\text{CH} = CR''\text{PO(OR)}_2$$

where $X = \text{halogen or hydrogen}$

$R'' = \text{halogen, hydroxyl or hydrogen}$

4. Base-catalyzed condensations of methylenebisphosphonate with alde-
hydes or ketones.


5. Arbusov type rearrangement.

DISCUSSION OF RESULTS

The first part of the present work is concerned with the study of the stereoselectivity of an unsymmetrical carbene or unsaturated vinyl cation derived from the alkaline decomposition of 5-methyl-5-t-butyl-3-nitroso-2-oxazolidone. The second part deals with the reactions of N-nitroso-4,5,5-trimethyl-2-oxazolidone, a compound which cannot give an unsaturated carbene intermediate during the course of its alkaline decomposition. In the third part decomposition of l-(N-nitrosoacetylaminomethyl)cyclohexanol, was conducted in the presence of carbonyl compounds, nucleophiles, phosphorous compounds, and amines respectively. The miscellaneous section includes the attempted nitrosations of 2-acetylamino-3-methyl-2-butanol and ethyl N-(2-chloro-2-methylpentyl) carbamate; alkaline decomposition of 3-nitroso-spiro[fluoren-9',5-oxazolidin]-2-one in the presence of cyclohexone; alkaline decomposition of methyl N-butyl-N-chlorocarbamate, etc.

1. Preparation of 5-methyl-5-t-butyl-N-nitroso-2-oxazolidone (2).

Compound (2) was prepared as described. The product of the Reformatsky reaction between 3,3-dimethyl-2-butanone, ethyl bromoacetate, and activated zinc was treated with anhydrous hydrazine to give the acid hydrazide. The acid azide obtained from the nitrous acid treatment of the acid hydrazide was subjected to a Curtius rearrangement in refluxing
benzene to give 2-oxazolidone. N-Nitrosooxazolidone 3 was obtained from the nitrous acid treatment of 2-oxazolidone.

2. Decomposition of 5-methyl-5-t-butyl-N-nitroso-2-oxazolidone (3).

a. with sodium methoxide in methanol

A solution of sodium methoxide in absolute methanol was added drop-wise to a stirred solution of the nitroso compound in absolute methanol. The evolved nitrogen was collected, measured over water, and corrected to standard conditions. After the usual work-up, products were iso-

(47) See Generalization in the Experimental section.

lated by distillation. The trans and cis isomers were separated by preparative vapor phase chromatography.

The decomposition of (3) gave a mixture of methyl trans-2,3,3-tri-
methyl-1-butenyl ether (36) and methyl cis-2,3,3-trimethyl-1-butenyl ether (37) in 82% overall yield. By vpc analysis the trans and cis isomeric vinyl ethers were found to be in a ratio of 97:3.

![Chemical Structures]

(3) (36) trans (major) (37) cis (minor)
The following nmr signals were observed for \(36\) and \(37\). The structures of \(36\) and \(37\) were assigned according to the observation in nmr made by Meyers and Sataty\(^\text{48}\) that the signals of the protons trans to the heteroatom (O and S) across a carbon-carbon double bond are shifted upfield more than are those from the cis protons.

The decomposition of other 3-nitroso-2-oxazolidones with sodium methoxide in the presence of absolute methanol has been reported.\(^\text{5}\) The formation of vinyl ethers could be explained by the unsaturated carbene insertions into the O-H bond or by the reaction of a vinyl cation with alcohols. In the present experiment if an unsaturated carbene intermediate is assumed, its insertion into the O-H bond will favor the formation of \(36\) over \(37\) by virtue of the attack on the alcohol from the less hindered side of the carbene.
According to the calculations by Gleiter and Hoffman singlet


carbenes at an unsaturated carbon are preferred to triplet. If \(17\) is assumed to be a singlet carbene, it will approach methanol with its vacant orbital in the plane of the paper. Clearly, the side with the \(t\)-butyl group is more hindered. The formation of \(36\) is therefore favored.

\[
\begin{array}{c}
\text{(CH}_3\text{)}_3\text{C} \quad \bigodot \\
\text{CH}_3 \\
\end{array}
\rightarrow
\begin{array}{c}
\text{(CH}_3\text{)}_3\text{C} \quad \bigodot \\
\text{CH}_3 \\
\end{array}
\rightarrow
\begin{array}{c}
\text{(CH}_3\text{)}_3\text{C} \quad \bigodot \\
\text{CH}_3 \\
\end{array}
\]

\(17\)

\(36\)

If a vinyl cation is assumed to be the intermediate, isomer \(36\) would still be predicted to be the major product.

A priori a vinyl cation can have two structures: a linear structure \(38\) with a sp-hybridized carbon and an empty p-orbital, or a trigonal structure \(39\) with a sp\(^2\)-hybridized carbon and an empty sp\(^2\)-orbital.
Based on the analyses of the relationship of the substituents in the reactants and the products in the recent solvolytic studies of vinyl cations, the linear sp-hybridized geometry $3\delta$ is the preferred one.

(50) For a complete review of the structure of vinyl cations see the chapter of vinyl and allenyl cations by Peter J. Stang in "Progress in Physical Organic Chemistry," 10 (1972), in press.

Thus, by assuming that the geometry of vinyl cation $4\Omega$ is linear with its vacant p-orbital in the plane of the paper the approach of the methanol molecule will be mainly from the less hindered side to give $3\delta$ as the major product.

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

(36)

In summary, the decomposition of $2$ in methanol gave $3\delta$ as the major product and $2\Gamma$ the minor product. This stereoselectivity can be explained in terms of an unsaturated carbene $1\gamma$ or a vinyl cation $4\Omega$ intermediate.

In the case where the size of the substituents at the β carbon of the unsaturated carbene or vinyl cation does not vary as greatly as in the present case, a more even distribution of the trans and cis products has been reported.
b. with sodium phenoxide in phenol-glyme

A solution of 5-methyl-5-t-butyl-3-nitroso-2-oxazolidone (2) in glyme was added dropwise to a stirred solution of sodium phenoxide and phenol in glyme. The theoretical amount of nitrogen was evolved in 18 hr. After the usual work-up, the mixture was distilled and the isolation of the products was carried out by preparative vpc.

The products obtained from the decomposition of 2 with sodium phenoxide in phenol-glyme are shown in Table 3.

The structure of 2-methoxyethyl trans-2,2,3-trimethyl-1-buteny ether (41) was established by the elemental analysis, ir, nmr, and mass spectral data. The assignment of the trans stereochemistry was based on the comparison of nmr τ values of the t-butyl and the methyl groups with methyl trans-2,3,3-trimethyl-1-buteny ether (36). The former has proton signals at τ 8.97 for the t-butyl group and τ 8.45 for the methyl group, while the latter has signals at τ 8.98 for the t-butyl group and τ 8.45 for the methyl group.
Table 3

Alkaline decomposition of 5-methyl-5-t-butyl-3-nitroso-2-oxazolidone (3)

with sodium phenoxide in phenol-glyme

\[
\begin{align*}
(\text{CH}_3)_3\text{C} & \quad \begin{array}{c}
\text{C} \quad \text{O} \\
\text{CH}_3 \quad \text{C} = \text{O}
\end{array} \\
\text{CH}_2 & \quad \text{N} \quad \text{NO}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Products</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>(43) ((\text{CH}_3)_3\text{C} \equiv \text{CCH}_3)</td>
<td>7.7</td>
</tr>
<tr>
<td>PhOCH(3)</td>
<td>52.7(^a)</td>
</tr>
</tbody>
</table>
| (41) \((\text{CH}_3)_3\text{C} \quad \begin{array}{c}
\text{O} = \text{C} \quad \text{H} \\
\text{CH}_3 \quad \text{OCH}_2\text{CH}_2\text{OCH}_3
\end{array}\) | 45.7 |
| (42) \((\text{CH}_3)_3\text{C} \quad \begin{array}{c}
\text{C} = \text{CH(O} \text{Ph}) \\
\text{CH}_3
\end{array}\) | 2.2 |
| (45) \((\text{CH}_3)_3\text{C} \quad \begin{array}{c}
\text{C} \quad \text{CH}_2\text{OPh} \\
\text{CH}_2
\end{array}\) | 11.3 |
| \((\text{CH}_3)_3\text{C} \quad \begin{array}{c}
\text{C} \quad \text{O} \\
\text{CH}_3 \quad \text{NH}
\end{array}\) | 4.8 |

\(^a\) based on one mole of anisole per mole of 3-nitroso-2-oxazolidone used.
The stereochemistry of the very small amount (2.2%) of phenyl 2,3,3-trimethyl-1-butenyl ether (42) was difficult to determine. Due to the phenyl group adjacent to the oxygen atom the t-butyl and the methyl proton signals have been deshielded too far downfield for any meaningful comparison with either 36 or 37.

2,2-Dimethyl-3-pentyne (43) could conceivably come from a carbon skeleton rearrangement.

\[
\begin{align*}
(CH_3)_3C & \quad \overset{\Theta}{C=\text{C}} \quad -\text{H} \quad \longrightarrow \quad CH_3C & \quad \overset{\Theta}{C=\text{C}} \quad -\text{H} \\
& \quad \overset{\Theta}{\text{C}} \quad \overset{\text{H}}{\text{O}} \quad (\text{ClI}_3)_3 \quad \longrightarrow \quad CH_3C & \quad \overset{\Theta}{\text{C}} \quad \overset{\text{H}}{\text{O}} \quad (\text{ClI}_3)_3
\end{align*}
\]

\((40)\) \hspace{1cm} \((43)\)

In a similar study the cleavage of glyme was reported in the decomposition of 5,5-dimethyl-3-nitroso-2-oxazolidone (4). Thus, the complexation of the vinyl cation \((40)\) with glyme takes place from the less hindered side to form an oxonium salt \((44)\). Displacement of \((44)\) by the phenoxide ion gives anisole and the vinyl ether \((41)\).

\[
\begin{align*}
(CH_3)_3C & \quad \overset{\Theta}{C=\text{C}} \quad -\text{H} \quad \longrightarrow \quad (CH_3)_3C & \quad \overset{\Theta}{C=\text{C}} \quad -\text{H} \\
& \quad \overset{\Theta}{\text{C}} \quad \overset{\text{H}}{\text{O}} \quad CH_3 & \quad \overset{\Theta}{\text{C}} \quad \overset{\text{H}}{\text{O}} \quad CH_2CH_2OCH_3 \\
& \quad \overset{\Theta}{\text{C}} \quad \overset{\text{H}}{\text{O}} \quad CH_2CH_2OCH_3 & \quad \overset{\Theta}{\text{C}} \quad \overset{\text{H}}{\text{O}} \quad CH_2CH_2OCH_3 \\
& \quad \overset{\Theta}{\text{C}} & \quad \overset{\text{H}}{\text{O}} \quad CH_2CH_2OCH_3 & \quad \overset{\Theta}{\text{C}} \quad \overset{\text{H}}{\text{O}} \quad CH_2CH_2OCH_3
\end{align*}
\]

\((40)\) \hspace{1cm} \((44)\) \hspace{1cm} \((41)\)
An intermediate other than \( 40 \) must be invoked in order to explain the formation of 2-phenoxymethyl 3,3-dimethyl-1-butene (45). In their attempt to prepare pure 2-methyl-1-propenyl phenyl ether (46) Newman and Beard reported the presence of another product, 2-methylallyl phenyl ether (47). Mechanisms which involve 1,3-hydride shifts were discussed. Based on the results from the deuterium experiments one or more than one of the following mechanisms were believed to be involved in the formation of 47.

**Mechanism (1)**

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

**Mechanism (2)**

\[
\begin{align*}
\text{CH}_3\text{C} = \text{C} \quad \text{N}_2^+ & \quad \rightarrow \quad \text{CH}_3\text{C} - \text{CH}_2 - \text{N}_2^+ \\
\text{CH}_3\text{C} = \text{C} \quad \text{H} & \quad \rightarrow \quad \text{CH}_3\text{C} - \text{CH}_2 - \text{N}_2^+ \\
\text{CH}_3\text{C} = \text{C} \quad \text{H} & \quad \rightarrow \quad \text{CH}_3\text{C} - \text{CH}_2 - \text{N}_2^+
\end{align*}
\]
Similarly the above mechanistic pathways can also be applied to account for the formation of \( \text{45} \) in the present experiment.

3. Preparation of N-nitroso-4,5,5-trimethyl-2-oxazolidone (48).

Compound \( \text{48} \) was prepared by the reactions outlined in Scheme VII. A Reformatsky reaction was carried out on acetone, ethyl \( \alpha \)-bromopropionate and zinc to give the hydroxy ester \( \text{49} \). Treatment of the hydroxy ester with anhydrous hydrazine led to the acid hydrazide \( \text{50} \). The azide obtained from the nitrous acid treatment of the acid hydrazide was converted to the 2-oxazolidone \( \text{51} \) by a Curtius rearrangement. Nitrosation of the 2-oxazolidone with nitrous acid yielded N-nitroso-2-oxazolidone \( \text{48} \).

Compound \( \text{48} \) was chosen for study because in accordance with the suggested mechanism (see Scheme IV) its decomposition could not conceivably proceed via an unsaturated carbene intermediate. An alternative mechanism would be through a vinyl cation intermediate.
Scheme VII

\[ \text{CH}_3\text{C} = \text{CH} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{NH}_2\text{NH}_2 \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

\[ \text{CH}_3\text{C} = \text{C} + \text{CH}_3\text{C} = \text{C} - \text{OEt} \xrightarrow{1. \text{Zn}} \xrightarrow{2. \text{HCl}} \text{CH}_3\text{C} - \text{C} = \text{OEt} \]

a. in 2-methoxyethanol containing sodium iodide.

A 20% solution of sodium 2-methoxyethoxide in 2-methoxyethanol was added to a solution of N-nitroso-2-oxazolidone 48 in 2-methoxyethanol saturated with sodium iodide. After the evolution of the theoretical amount of nitrogen, the mixture was worked up as usual and distilled. By vpc analysis of the products 8.2% 3-methyl-2-butanone (52), 7.1% 2-methoxyethyl 3-methyl-2-butyl ether (53), and 22.4% 2-methoxyethyl 3-methyl-1-buten-3-yl carbonate (54) (see Table 4) were shown to be present. Many other minor components which were not identified were also noted. Surprisingly, the expected 2-iodo-3-methyl-2-butene (55) was not among the major components.

By postulating that a vinyl cation is involved, the formation of 52 and 53 can be rationalized (Scheme VIII). Vinyl cation 56 can react either with the 2-methoxyethoxide ion to form 53 or with the hydroxide ion to form 52. In view of the absence of the vinyl iodide 55 vinyl cation 56 appears to show a preference for the reactions with the 2-methoxyethoxide ion or the hydroxide ion rather than the iodide ion, a fact contrary to that observed by Newman and Beard.
### Table 4

Alkaline decompositions of N-nitroso-4,5,5-trimethyl-2-oxazolidone (48)

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Products</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. from</strong> CH₃OCH₂CH₂ONa + NaI + CH₃CCH₂CH₂OH</td>
<td><strong>B. from</strong> PhONa + PhOH + CH₃OCH₂CH₂OH</td>
</tr>
<tr>
<td>CH₃</td>
<td>O</td>
</tr>
<tr>
<td>(52)</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>C = C</td>
</tr>
<tr>
<td>(53)</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>C</td>
</tr>
<tr>
<td>(54)</td>
<td></td>
</tr>
<tr>
<td>PhOCH₃</td>
<td>---</td>
</tr>
<tr>
<td>CH₃</td>
<td>C = C</td>
</tr>
<tr>
<td>(60)</td>
<td></td>
</tr>
</tbody>
</table>
Assuming 57 loses nitrogen to give the carbonium ion 58 instead of proceeding to give vinyl cation 56, the subsequent loss of a proton from 58 leads to the carbonate 54.

\[
\begin{align*}
&\text{CH}_3\text{O} - \text{C} - \text{OCH}_2\text{CH}_2\text{OCH}_3 \\
\text{CH}_3\text{H} - \text{C} - \text{CH}_3 \\
\text{(57)}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{O} - \text{C} - \text{OCH}_2\text{CH}_2\text{OCH}_3 \\
\text{CH}_3\text{C} - \text{C} - \text{H} - \text{H} \\
\text{(58)}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{O} - \text{C} - \text{OCH}_2\text{CH}_2\text{OCH}_3 \\
\text{CH}_3\text{CH} = \text{CH}_2 \\
\text{(54)}
\end{align*}
\]

Compound 54 was the major product in this reaction. If the above assumption was correct, it might imply that the loss of nitrogen from 57 to 58 was more facile than the elimination reaction from 57 to 59 as shown in Scheme VIII. One can perhaps rationalize that the methyl group next to the carbonium site of 58 may have a stabilizing effect on the ion, thus providing a driving force for the loss of nitrogen.

b. in phenol-glyme.

A solution of 3-nitroso-2-oxazolidone 48 in glyme was added to a solution of sodium phenoxide and phenol in glyme. The total phenol to glyme ratio was (1:1)\text{m}. The theoretical amount of nitrogen was collected
in 2 hr. After the usual work-up and distillation vpc analysis of the products showed many components, but only three were identified, 2.6% 2-methoxyethyl 3-methyl-2-butenyl ether (53), 3.9% anisole, and 10.6% phenyl 3-methyl-2-butenyl ether (60) (see Table 4).

In comparison with the decomposition of 5,5-dimethyl-3-nitroso-2-oxazolidone (4) under similar conditions the degree of the cleavage of glyme was much less in this experiment, and compound 60, a product presumably derived from the reaction of vinyl cation 56 with the phenoxide ion, became the major product of those isolated.

c. in 2-methoxyethanol.

A 20% solution of sodium 2-methoxyethoxide in 2-methoxyethanol was added to a solution of 3-nitroso-2-oxazolidone (4) in 2-methoxyethanol. The theoretical amount of nitrogen was evolved in 0.5 hr. By suitable work-up and preparative vpc 9.6% of 2-methoxyethyl 3-methyl-2-butenyl ether (53) and 19.8% of 2-methoxyethyl 3-methyl-1-buten-3-yl carbonate (54) were isolated (see Table 4).

The yield of the vinyl ether 53 was lower than that of the carbonate 54. This may imply that the formation of cation 58 is preferred rather than the vinyl cation 56. On the other hand, the total yield of the products in this reaction was quite low and not all of the components shown in vpc were isolated and identified. The possibility remains that there might be other products which could be derived from the vinyl cation but were in such small amount or so volatile that their isolation became very difficult. For example, 1,1-dimethyl allene, a product which
could presumably be formed by the loss of a proton from the vinyl cation 56, might have been present but eluded detection because of its high volatility.

5. Preparation of 1-(N-nitrosoacetylamino)methyl)cyclohexanol (61).

Compound 61 was prepared according to the method previously reported. A modification was made in the nitrosation step in which methylene chloride was used as a co-solvent (15 ml per 50 ml of acetic acid used). The use of methylene chloride kept the acetic acid solution of the amide from freezing at ice temperature during the reaction without sacrificing the yield of the product.

Compound 61 was chosen for study because the alkaline decomposition of this compound in the presence of a phase transfer agent was considered to be a superior method of generating the unsaturated carbene.

6. Decomposition of 1-(N-nitrosoacetylamino)methyl)cyclohexanol (61) in the presence of ketones.

The sodium hydroxide solution was added dropwise to a stirred solution of nitrosoamide 61, Aliquat 336, and the corresponding ketone in pentane held at -10 to 10°C. The evolved gas was collected and measured over water. After the usual work-up the mixture was distilled and the isolation of the pure products was carried out by preparative vpc.

The yield of the divinyl ethers from the corresponding ketones are shown in Table 5. The divinyl ethers were identified by their elemental analyses, nmr, ir, and mass spectra. Where accurate elemental analysis (within 0.3%) could not be obtained due to the instability of the com-
Table 5

Alkaline decomposition of 1-(N-nitrosoacetylaminomethyl)cyclohexanol (61) in the presence of ketones and aldehydes

\[
\begin{align*}
\text{Products} & \rightarrow \text{Products} \\
\text{Products} & \rightarrow \text{Products} \\
\text{Products} & \rightarrow \text{Products} \\
\text{Products} & \rightarrow \text{Products} \\
\text{Products} & \rightarrow \text{Products}
\end{align*}
\]

<table>
<thead>
<tr>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>Products (^a)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et</td>
<td>Et</td>
<td>![Product Image]</td>
<td>22</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{CH})</td>
<td>((\text{CH}_3)_2\text{CH})</td>
<td>![Product Image]</td>
<td>4.4</td>
</tr>
<tr>
<td>(-(\text{CH}_2)_5)</td>
<td>![Product Image]</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>((\text{CH}_3)_3\text{C})</td>
<td>H</td>
<td>![Product Image]</td>
<td>4.5</td>
</tr>
<tr>
<td>((\text{CH}_3)_2\text{CH})</td>
<td>H</td>
<td>![Product Image]</td>
<td>35.7</td>
</tr>
</tbody>
</table>

\(^a\) The products listed here were not the only products isolated in these reactions.

\(^b\) Nmr showed a mixture of \textit{cis} and \textit{trans} isomers.
pound or the contamination by impurities, the exact mass measurement was also used. Divinyl ethers were also treated with dilute hydrochloric acid and the resultant mixtures of cyclohexanecarboxaldehyde and the corresponding ketones were compared with the authentic samples in nmr, vpc retention times, and the molecular weight (by mass spec) of their 2,4-dinitrophenylhydrazine derivatives.

Products other than the divinyl ethers isolated from these reactions were acetoxymethylenecyclohexane \((62)\) (10-15%), cyclohexanone (approx. 5% from the reaction of diethyl ketone or diisopropyl ketone), cyclohexanecarboxaldehyde (approx. 5%), and cycloheptanone (approx. 5%).

By assuming a mechanism similar to those proposed for the decomposition of N-nitroso-2-oxazolidones \(^{1,5}\) which involves either a vinyl cation or an unsaturated carbene intermediate the formation of the products from the decomposition of \(61\) can be accounted for (see Scheme IX).

The base promoted elimination of water from the diazonium ion \(63\) gives \(64\), which loses nitrogen to form the vinyl cation \(65\) or loses a proton first, followed by the loss of nitrogen to form the unsaturated carbene \(66\).

An alternative mechanism which can lead to the vinyl cation \(65\) or the unsaturated carbene \(66\) is shown in Scheme X. The hydroxyl proton is removed by the base in the first step. The attack of the anion at the carbonyl function gives a cyclic intermediate which eventually leads to the diazonium ion \(64\). The subsequent conversion of \(64\) to \(65\) or \(66\) is the same as in Scheme IX.
Scheme IX

\[
\text{(61)} \xrightarrow{\Theta_{OH}} \text{(62)} \xrightarrow{\Theta_{OH}} \text{(63)} \xrightarrow{-\text{H}_2\text{O}} \text{H}_2\text{O} \rightarrow \text{(64)} \xrightarrow{-\text{N}_2} \text{(65)} \xrightarrow{-\text{H}} \text{(66)}
\]
Scheme X

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
S & \quad S
\end{align*}
\]
If the unsaturated carbene $66$ reacts with the oxygen atom of a ketone to give a 1,3-dipolar intermediate as hypothesized in the cases of the copper catalyzed decomposition of ethyl diazoacetate in various ketones reported in the literature, a proton shift of an $\alpha$-hydrogen or protonation of the dipolar species $67$, followed by the formation of a double bond leads to the divinyl ethers.

Another possible mechanism is by going through an allene oxide intermediate as shown below. However, there has been no precedent for such allene oxide rearrangements reported in the literature.

Since the enolization of ketones is base catalyzed, the unsaturated carbene $66$ can presumably insert into the O-H bond of the enol forms
or react with the enolate ions, followed by protonation to give the divinyl ethers 68.
Alternatively, the vinyl cation 65 can also lead to divinyl ethers by reaction with an enolate ion or with the enol form of the ketones, followed by deprotonation.

The formation of acetoxymethylenecyclohexane (62) can be visualized by the reaction of either the vinyl cation 65 or the unsaturated carbene 66 with the acetate ion derived from the cleavage of the carbonyl-nitrogen bond of 61 (see Scheme IX and X).

\[
\begin{align*}
\text{(65)} &: \quad \text{C} &\text{H} + \Theta &\text{O} \quad &\text{CH}_3 \\
\text{(62)} &: \quad \text{C} &\text{H} &\text{O} \quad &\text{CH}_3
\end{align*}
\]

The reaction of 65 with water gives cyclohexanecarboxaldehyde, one of the product isolated.

The diazonium ion 63 can lead to cycloheptanone by the following pathway.

\[
\begin{align*}
\text{(63)} &: \quad \text{C} &\text{H} &\text{O} \quad &\text{N}_2^+ \quad \text{OH} \\
\text{C} &\text{H} &\text{O} \quad &\text{N}_2^+ \quad \text{OH} &\text{N}_2^+ \quad \text{OH} \\
\text{C} &\text{H} &\text{O} \quad &\text{N}_2^+ \quad \text{OH} &\text{N}_2^+ \quad \text{OH} &\text{N}_2^+ \quad \text{OH}
\end{align*}
\]
7. Decomposition of l-(N-nitrosoacetyleaminomethyl)cyclohexanol (61) in the presence of aldehydes.

A 50% sodium hydroxide solution was added dropwise to a solution of the nitrosoamide 61, Aliquat 336 and the corresponding aldehyde in pentane, held at -5 to -15°C. The evolution of nitrogen was quantitative in 0.25 to 0.5 hr. After the usual work-up the mixture was distilled and the isolation of the products was carried out by preparative vpc.

The yields of the α,β-unsaturated ketones are shown in Table 5. The conjugated ketones were identified by their elemental analyses, nmr, ir, uv, and mass spectra. The 2,4-dinitrophenylhydrazine derivatives were also prepared. Furthermore, cyclohexyldienemethyl t-butyl ketone (69) was prepared by an independent route for comparison (see Scheme XI).

Triethyl phosphonoacetate was prepared from the reaction between triethyl phosphite and ethyl bromoacetate. The sodium salt of triethyl phosphonoacetate obtained from the reaction with sodium hydride was treated with cyclohexanone to yield ethyl cyclohexyldieneacetate,


which was then saponified to give cyclohexyldieneacetic acid. Treatment of the conjugated acid with t-butyllithium gave cyclohexyldienemethyl t-butyl ketone (69).
Scheme XI

\[
\text{(EtO)}_3P + \text{BrCH}_2\text{CO}_2\text{Et} \xrightarrow{165-170^\circ} \text{EtPO} - \text{CH}_2\text{CO}_2\text{Et} \quad (73\%)
\]

\[
\xrightarrow{\text{NaH}} \quad \text{EtPO} - \text{CH}_2\text{CO}_2\text{Et} \quad \text{Na}^+
\]

\[
\xrightarrow{1. \text{NaOH} \quad 2. \text{HCl}} \quad \text{EtPO} - \text{CH}_2\text{CO}_2\text{Et} \quad \text{Na}^+
\]

\[
\xrightarrow{\text{CH}_3\text{-O} \quad \text{Li}^+} \quad \text{EtPO} - \text{CH}_2\text{CO}_2\text{Et} \quad \text{Na}^+
\]

\[
\xrightarrow{2^\circ} \quad \text{EtPO} - \text{CH}_2\text{CO}_2\text{Et} \quad \text{Na}^+
\]

(67%)

(86%)

(69) (47%)
The formation of the α,β-unsaturated ketones can be explained by a direct unsaturated carbene insertion into the carbonyl-hydrogen bond of the corresponding aldehydes. In support of this hypothesis an experiment using a deuterated aldehyde should be run in the future. If the insertion does take place one should be able to find the incorporation of deuterium at the carbon next to the carbonyl function.

\[
\begin{align*}
\text{O} & \quad | \quad \text{C} & \quad | \quad \text{R} \\
\text{C} & \quad | \quad \text{D} & \quad | \quad \text{C} & \quad | \quad \text{R}
\end{align*}
\]

Interestingly, in the alkaline decomposition of 61 in the presence of isobutyraldehyde no divinyl ether was isolated although the molecule possesses an enolizable hydrogen.

The yield of the α,β-unsaturated ketone was very low when 2,2-dimethyl propanal was used. This might be due to the steric hindrance of the t-butyl group which inhibited the unsaturated carbene insertion.

In a separate experiment in which the nitrosoamide 61 was decomposed in isobutyraldehyde with triethylamine as base, there were isolated 15% of acetoxy methylenecyclohexane (62) and only 12.6% of cyclohexylidenemethyl isopropyl ketone. Thus, the choice of an organic base (triethylamine) did not improve the yield of the α,β-unsaturated ketone.
8. Decomposition of 1-(N-nitrosoacetylaminoethyl)cyclohexanol (61) in the presence of nucleophiles.

a. sodium azide.

A solution of the nitrosoamide 61 in pentane was added dropwise to a stirred mixture of sodium azide, sodium hydroxide, Aliquat 336, and water at 3°. The evolution of nitrogen was quantitative in 15 min. After the usual work-up the crude vinyl azide was purified by passing through neutral Woelm alumina oxide activity grade I with hexane. The yield of the azido-methylene cyclohexane was 56% (see Table 6). The vinyl azide was identified by its elemental analysis, nmr, and ir spectra.

b. potassium thiocyanate.

A solution of the nitrosoamide 61 in pentane was added dropwise to a stirred mixture of potassium thiocyanate, sodium hydroxide, Aliquat 336, and water, held at 5-7°. After the theoretical amount of nitrogen had been collected (in 15 min), the aqueous layer of the mixture was extracted with ether and the combined organic phase was worked up as usual. After distillation cyclohexylidenemethyl thiocyanate was obtained in 39% yield (see Table 6). The vinyl thiocyanate was identified by elemental analysis, nmr, and ir spectra.

c. sodium iodide.

A solution of the nitrosoamide 61 in pentane was added dropwise to a stirred mixture of sodium iodide, sodium hydroxide, Aliquat 336, and water, held at 3-5°. The theoretical amount of nitrogen was evolved in
Table 6
Alkaline decomposition of 1-(N-nitrosoacetylaminomethyl)cyclohexanol (61) in the presence of nucleophiles

![Chemical structure of 1-(N-nitrosoacetylaminomethyl)cyclohexanol](61)

<table>
<thead>
<tr>
<th>Nucleophiles</th>
<th>Products</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaN₃</td>
<td><img src="NaN%E2%82%83_product" alt="Chemical structure of NaN₃ reaction product" /></td>
<td>56</td>
</tr>
<tr>
<td>KSCN</td>
<td><img src="KSCN_product" alt="Chemical structure of KSCN reaction product" /></td>
<td>39</td>
</tr>
<tr>
<td>NaI</td>
<td><img src="NaI_product" alt="Chemical structure of NaI reaction product" /></td>
<td>72</td>
</tr>
</tbody>
</table>
25 min. After the usual work-up distillation gave 72% of iodomethyl-
enecyclohexane (see Table 6). The vinyl iodide was identified by com-
parison of its ir and nmr spectra with those of an authentic sample.

The products listed in Table 6 can be explained by either the
reaction of the vinyl cation $^6$ with the nucleophiles or the reaction
of the unsaturated carbene $^6$ with the nucleophiles, followed by pro-
tonation of the ions derived therefrom.

Most of the methods available for the preparation of vinyl azides
(see Historical section) give only products with the azido function at
the more substituted carbon of the double bond. The present route pro-
vides a general method for the preparation of terminal vinyl azides.

Very few methods for the preparation of vinyl thiocyanates have
been reported in the literature $^{40,41}$ (see Historical section). In view
of the potential application of this class of compounds as monomers for
polymerization, the present route offers a valuable new synthetic method
for substituted vinyl thiocyanates.

9. Decomposition of 1-(N-nitrosoacetylaminomethyl)cyclohexanol (61) in
the presence of triethyl phosphite and acetone.

Carbenes are known to react with triphenyl phosphine to form
ylides. The study of the present reaction was undertaken to see if

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(54) G. Wittig and M. Schlosser, Angew. Chem., 72, 324 (1960); D. Sey-
(1960); ibid., 83, 1617 (1961); D. Seyferth, J. K. Heeren, G.
Singh, S. O. Grim, and W. B. Hughes, J. Organometal. Chem., 5,
Chem. Soc., 82, 1260 (1960); A. J. Speziale and K. W. Ratts, J.
the unsaturated carbene 66 would yield an ylide with triethyl phosphite. If such were the case, further reaction of the ylide with ketones could lead to allenes.

A solution of nitrosoamide 61 and 1.1 eq of triethyl phosphite in pentane at -10° was treated with sodium methoxide in portions. After the evaluation of nitrogen ceased (72% in 1 hr) the solid in the mixture was filtered and the filtrate was concentrated. Acetone was added to the residue. After stirring for one hour distillation gave two fractions which were analyzed by vpc. The products obtained are shown below.

The expected allene was not detected.

Mechanisms which involve either the vinyl cation 65 or the unsaturated carbene 66 can be postulated to explain the formation of cyclohexyldenemethyl diethyl phosphonate (70).
10. Decomposition of 1-(N-nitrosoacetilaminomethyl)cyclohexanol (61) in the presence of trialkyl phosphites.

Since the vinyl phosphonate 70 obtained from the previous experiment is a compound of interest, attention was directed to the improvement of the yields of this kind of products.

a. Cyclohexylidenemethyl dimethyl phosphonate.

A solution of equimolar amount of nitrosoamide 61 and trimethyl phosphite in pentane was treated at 5-7°C with sodium methoxide in portions.
After the nitrogen evolution (72% in 15 min) and the usual work-up distillation of the residue afforded 10.8% of cyclohexyldenemethyl dimethyl phosphonate.

b. cyclohexyldenemethyl diethyl phosphonate (70).

A solution of 1 eq. of nitrosoamide 61 in pentane was added dropwise to a stirred ice cold mixture of 5 eq. of triethyl phosphite, sodium hydroxide, Aliquat 336, and water. After the nitrogen evolution (72% in 15 min) and the usual work-up distillation of the residue yielded products which by vpc showed 3.6% cycloheptanone, 4.2% triethyl phosphate, and 42% cyclohexyldenemethyl diethyl phosphonate (70).

When a 50% solution of sodium hydroxide was added to a mixture of the nitrosoamide, triethyl phosphite, pentane, and Aliquat 336, followed by the same work-up as above, the vinyl phosphonate 70 was obtained in 44.2% yield.

11. Decomposition of 1-(N-nitrosoacetylaninomethyl)cyclohexanol (61) with pyrrolidine.

A stirred solution of a ten fold excess of pyrrolidine in hexane at 0° was treated dropwise with a solution of the nitrosoamide 61 in hexane. After the nitrogen evolution ceased (89% in 0.5 hr) excess pyrrolidine and the solvent were removed on a rotary evaporator. The residue was distilled and the isolation of the products was carried out by preparative vpc. The products obtained are shown below.

N-acetyl pyrrolidine (71) was identified by an independent synthesis from the reaction of pyrrolidine and acetic anhydride. N-(1-Hydroxy-...
cyclohexylmethyl)pyrrolidine (72) was identified by the elemental analysis, nmr, ir, and mass spectra.

In order to account for the products a mechanism is proposed (see Scheme XII). Assuming the attack of the pyrrolidine on 61 takes place at the carbonyl function cleavage of the C-N bond leads to the formation of N-acetyl pyrrolidine (71). Another molecule of pyrrolidine attacks the diazonium ion to give 72.

As pyrrolidine is not as strong a base as sodium hydroxide, the base promoted dehydration of the diazonium ion becomes more difficult. This might be the reason why products derived from the vinyl cation 65 or the unsaturated carbene 66 were not detected in this reaction.

12. Miscellaneous.


(1) in diethylamine.

Freshly distilled diethylamine in large excess amount was treated with 12 in portions. After the gas evolution ceased (in 9 min), distillation on a spinning-band column yielded 56.6% cyclohexanecarboxaldehyde and a residue (22% w of the starting nitroso compound). The product was identified by the comparison of its ir and nmr with those of an authentic sample.
Scheme XII

\[
\begin{align*}
\text{OH} & \text{N} = \text{N} - \text{OH} & \xrightarrow{\text{H}^+} & \text{OH} & \text{N} = \text{N} - \text{O}^- & + & \text{CH}_3 - \text{C} - \text{N}^+ \\
\text{OH} & \text{N}_2 & \xrightarrow{-\text{N}_2} & \text{OH} & \text{N} & \xrightarrow{-\text{H}^+} & \text{OH}
\end{align*}
\]
The amount of gas evolved during the reaction was 1.4 eq. However, no attempt was made to analyze the effluent gas.

(2) in the presence of cyclohexene and a phase transfer agent.

A 25% solution of sodium hydroxide was added dropwise to a well stirred solution of 12, cyclohexene, benzene, and Aliquat 336. The theoretical amount of nitrogen was collected in 4 hr. After the usual work-up, distillation yielded 43% of bicyclo[4.1.0]hept-7-ylidene cyclohexane (73).

(73)

b. Decomposition of 3-nitroso-spiro[fluorene-9',5-oxazolidin]-2-one (74) in the presence of cyclohexene.

A stirred solution of 74 and cyclohexene in benzene was treated with solid sodium ethoxide. The mixture was heated at 60-70° for 2 hr. After the evolution of the theoretical amount of gas (in 2 hr) and the usual work-up the residue was chromatographed on silica gel. There were obtained 12.7% of 9-(bicyclo[4.1.0]hept-7-ylidene)fluorene (75) and 40.7% of fluorenone.

(74)  
(75)  12.7%  
(40.7%)
c. Attempted nitrosation of 3-acetylamino-2-methyl-2-butanol (76).

Compound 76 was prepared according to the sequence of reactions as shown below.

All attempts to nitrosate 76 failed to give a high conversion to the desired N-nitroso product. The N-nitroso compound was desired as a vinyl cation precursor.

d. Attempted nitrosation of ethyl (N-2-chloro-2-methylpenty1)carbamate (77).

Compound 77 was prepared as shown below.

All attempts to nitrosate 77 failed.

e. Alkaline decomposition of methyl n-butyl-N-chlorocarbamate (78) in the presence of cyclohexene.

Compound 78 was needed to see if a nitrene intermediate would be formed on treatment with base. Cyclohexene was used as a trapping agent for the possible nitrene intermediate.

Preparation of 78 - A measured amount of chlorine was evaporated into a mixture of methyl n-butylcarbamate and water held at 15°C. The lower yellow layer was separated and the aqueous layer was extracted with ether. The combined organic phase was dried over anhydrous potassium
carbonate. After the removal of the solvent the residue was distilled
to give 78% of 78.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{-} N - C - \text{OCH}_3 \xrightarrow{\text{Cl}_2} \text{CH}_3\text{CH}_2\text{CH}_2\text{-} N - C - \text{OCH}_3
\]

(78)

Decomposition of 78 - A solution of 78 and cyclohexene in benzene
was treated under nitrogen with sodium methoxide in portions. The mix­
ture was filtered and the filtrate was distilled to yield 50% of methyl
n-butylcarbamate. An aziridine type product was not detected.

f. Alkaline decomposition of methyl n-butyl-N-chlorocarbamate (78).

Sodium methoxide was added to a solution of N-chlorocarbamate in
anhydrous ether. After the exothermic reaction cooled down to room
temperature, the solid was filtered. Distillation of the filtrate gave
51.3% methyl n-butylcarbamate. The distillate collected in the dry ice
trap showed two products by vpc analysis: 15% of dimethylcarbamate and
40% of n-butyl cyanide.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{-} N - C - \text{OCH}_3 \xrightarrow{\text{NaOCH}_3} \text{CH}_3\text{CH}_2\text{CH}_2\text{-} N - C - \text{OCH}_3
\]

(78)

+ \text{CH}_3\text{CH}_2\text{CH}_2\text{C} = \text{N} \quad 40%

+ \text{CH}_3\text{O}-C-\text{OCH}_3 \quad 15%
The above reaction was repeated several times under slightly different reaction conditions. In each run the yield of methyl n-butyl-carbamate was always between 50-60%.

Further investigation of this reaction should be directed towards the decomposition of compounds like methyl 4-chlorophenyl-N-chlorocarbamate whose structure is such that its decomposition cannot possibly lead to a cyanide.

Conclusions

The alkaline decomposition of 5-methyl-5-t-butyl-N-nitroso-2-oxazolidone (3) in methanol gave methyl trans-2,3,3-trimethyl-1-butenyl ether (36) and methyl cis-2,3,3-trimethyl-1-butenyl ether (37) in 82% overall yield. The ratio of 36 to 37 was (97:3). This stereoselectivity can be explained by the reaction of either an unsaturated carbene or a vinyl cation with methanol from the less hindered side of either intermediate.

Decomposition of 3 in phenol-glyme afforded 52.7% of anisole and 45.7% of 2-methoxyethyl trans-2,3,3-trimethyl-1-butenyl ether (41) as the major products and none of the corresponding cis-isomer. A vinyl cation intermediate seems required to explain this result.

The formation in high yields of vinyl iodides and vinyl ethers from the decomposition of 5,5-disubstituted-N-nitroso-2-oxazolidones can be explained by either a vinyl cation or an unsaturated carbene intermediate. However, when the 4-position of the 5,5-disubstituted-N-nitroso-2-oxazolidone is substituted with a methyl group as in the pre-
sent work, the yields of similar products decreased significantly. For example, decomposition of N-nitroso-4,5,5-trimethyl-2-oxazolidone (48) in 2-methoxyethanol saturated with sodium iodide afforded 8.2% of 3-methyl-2-butanone (52), 7.1% of 2-methoxyethyl 3-methyl-2-butenyl ether (53), 22.4% of 2-methoxyethyl 3-methyl-1-buten-3-yl carbonate (54), and none of the expected 2-iodo-3-methyl-2-butene (55). When 48 was decomposed in 2-methoxyethanol, only 9.6% of the vinyl ether 53 and 19.8% of the carbonate 54 were obtained. Since a vinyl carbene cannot be formed from 48, the vinyl ether 53 produced must have arisen from a vinyl cation. Judging from the low yields of products isolated a trimethyl vinyl cation is much less favored than the corresponding dimethyl vinyl cation in the reactions in question.

When 48 was decomposed in phenol-glyme, there were isolated 2.6% of the vinyl ether 53, 3.9% of anisole and 10.6% of phenyl 3-methyl-2-butenyl ether (60). Though the yields of the products resulted from the cleavage of glyme were low, these products indicate the intermediacy of a vinyl cation.

Decomposition of 1-(N-nitrosoacetylaminomethyl)cyclohexanol (61) in diethyl ketone produced 22% of cyclohexyldenemethyl 3-pentenyl ether. Decomposition of 61 in diisopropyl ketone gave 4.4% of cyclohexyldenemethyl 2,4-dimethyl-3-pentenyl ether. Decomposition of 61 in cyclohexanone gave 32% of cyclohexyldenemethyl 1-cyclohexenyl ether. Thus, in the presence of enolizable ketones decomposition of 61 generated divinyl ethers. The formation of divinyl ethers can be explained by the intermediacy of either an unsaturated carbene or a vinyl cation.
Decomposition of 61 in 2,2-dimethylpropanal yielded 4.5% of cyclohexyldenemethyl t-butyl ketone (69). Decomposition of 61 in isobutyraldehyde gave cyclohexyldenemethyl isopropyl ketone in 35.7% yield. The formation of these α,β-unsaturated ketones can be best explained by direct insertion of the unsaturated carbene 66 into the aldehydic hydrogen-carbon bond of the aldehydes. Although isobutyraldehyde is enolizable, a conjugated ketone was obtained as the product in preference to the divinyl ether.

Treatment of 61 with base in sodium azide and a phase transfer agent gave azidomethylenecyclohexane in 56% yield. The azido function of this vinyl azide is at the terminal carbon of the double bond. Most of the known general methods of preparing vinyl azides give only those with the azido function at the more substituted carbon of the double bond. The present route provides a general route to terminal vinyl azides.

Decomposition of 61 in potassium thiocyanate yielded 39% of cyclohexyldenemethyl thiocyanate. Thus, a new synthetic route to substituted vinyl thiocyanates has been developed.

Decomposition of 61 in triethyl phosphate gave 44.2% of cyclohexyldenemethyl diethyl phosphonate (70). This provides a new method for the preparation of substituted vinyl phosphonates.
EXPERIMENTAL

Generalizations

1. All melting and boiling points are uncorrected. Melting points were taken with a Thomas-Hoover capillary melting point apparatus. The thermometers for boiling point determination were not standardized.

2. Microanalyses were performed by the M-H-W Laboratories, Garden City, Michigan, and Chemalytics, Tempe, Arizona.

3. Infrared absorption spectra were recorded on a Perkin-Elmer Infrared Spectrophotometer.

4. Nuclear magnetic resonance spectra were recorded on A-60 and A-60A nmr spectrophotometers, Varian Associates, Palo Alto, California.

5. Vapor phase chromatographic analyses were recorded on a Varian Aerograph, Model 1200, flame ionization gas chromatograph, and a Varian Aerograph, Model A-90P-3 gas chromatograph. A Varian Aerograph Autoprep, Model A-700, was used for preparative vapor phase chromatography. Column A represents 10' x 3/8" column of 10% Carbowax 20M on Chromosorb W, Column B represents 5' x 1/4" column of 10% SE30 on Chromosorb W.

All vpc yields were based on the number of mole of the nitroso compounds used before decomposition.

6. Ultraviolet spectra were recorded on a Perkin-Elmer Model 202 UV spectrophotometer.
7. Mass spectra were recorded on an AEI Model MS-9 instrument by Mr. Richard Weisenberger.

8. The phrase "worked up as usual" means that the reaction mixture was diluted with ice water and the products extracted into ether. The ethereal extracts were washed with a saturated salt solution, dried by filtration through a cone of anhydrous magnesium sulfate or by the addition of anhydrous magnesium sulfate followed by filtration through a pad of Celite. The solvents were removed by distillation or on a rotary evaporator.

9. Unless otherwise specified, the nitrogen evolution usually finished as soon as all of the base had been added.

Alkaline Decompositions of 5-Methyl-5-t-butyl-N-nitroso-2-oxazolidone (3)

a. Decomposition with sodium methoxide in methanol

A slurry of 5.59 g (0.03 m) of N-nitrosooxazolidone 3 in 30 ml of absolute methanol (freshly distilled over magnesium) was treated dropwise at 40° during 0.5 hr. with a solution of 1.78 g (0.033 m) of sodium methoxide in 10 ml of absolute methanol. After the theoretical amount of nitrogen had been evolved the mixture was worked up as usual. The residue was distilled to give 3.15 g (82%) of colorless materials at 63-65°/50 mm, which by vpc (column A, 40°, helium flow 100 cc/min) consisted of 97% of methyl trans-2,3,3-trimethyl-1-butyl ether (36) and 3% of methyl cis-2,3,3-trimethyl-1-butyl ether (37).
Methyl trans-2,3,3-trimethyl-1-butenyl ether (36): ir (neat), bands at 5.95 μ (C=O), 8.90 μ (C=C-OCH₃); nmr (CCl₄), τ 8.98 (s, 9, t-Bu), τ 8.45 (d, J = 1 Hz, 3, CH₃), τ 6.49 (s, 3, -OCH₃), τ 4.27 (m, J = 1 Hz, 1, =CH); mass spectrum, mol. wt. 128, exact mass measurement: 128.1202 (calcd value = 128.1201).


Found: C, 74.9; H, 12.6.

For further characterization, a 2,4-dinitrophenylhydrazone, mp 125-126°C, was prepared; mass spectrum, mol. wt. 294.

Methyl cis-2,3,3-trimethyl-1-butenyl ether (37) showed nmr (CCl₄), τ 8.89 (s, 9, t-Bu), τ 8.52 (d, J = 1.5 Hz, 3, CH₃), τ 6.54 (s, 3, -OCH₃), τ 4.42 (m, J = 1.5 Hz, 1, =CH).

b. Decomposition with sodium phenoxide in phenol-glyme.

To a stirred solution of 5.1 g (0.044 m) of sodium phenoxide and 33.6 g (0.4 m) of phenol in 20 g of glyme was added dropwise at room temperature during 5 min a solution of 7.45 g (0.04 m) of 5-methyl-5-t-butyl-N-nitroso-2-oxazolidone (3) in 16 g of glyme. The evolution of nitrogen was very slow. The theoretical amount was obtained only after 18 hr. After the usual work-up which included four washes with 10% KOH, distillation gave three fractions. Preparative vpc (column A, helium flow 150 cc/min) gave pure materials from each of the fractions described below.

Fraction 1 (78-103°C): column temp. 50°C, 1.4 min, 0.297 g (7.7%) of 2,2-dimethyl-3-pentyne (43).
Figure 1 - Nmr spectrum, 60 MHz, of \( \text{CCH}_3 \) in CCl\(_4\)
Fraction 2 (48-108°/20 mm): column temp. 110°, A, 3.5 min, 2.28 g (52.7%) of anisole; B, 4.7 min, 3.15 g (45.7%) of 2-methoxyethyl trans-2,3,3-trimethyl-1-butene-1-ether (41).

Fraction 3 (96°/0.4 mm): column temp. 150°, A, 7 min, 0.179 g (2.2%) of phenyl 2,3,3-trimethyl-1-butene-1-ether (42); B, 10 min, 0.921 g (11.3%) of 2-phenoxyethyl 3,3-dimethyl-1-butene (45).

In addition to the above fractions, 0.3 g (4.8%) of the 5-methyl-5-t-butyl-2-oxazolidone was recovered from the residue by recrystallization from benzene-Skellysolve B.

2,2-Dimethyl-3-pentyn (43): same vpc retention time and nmr as authentic sample, nmr (glyme), τ 8.85 (s, 9, t-Bu), τ 8.32 (s, 3, =C=CH3), τ 6.71 (s, CH3O-), τ 6.55 (s, CH3OCH2CH2OCH3).

2-Methoxyethyl trans-2,3,3-trimethyl-1-butene-1-ether (41): ir (neat), bands at 6.00 μ (C=C), 8.58 μ, 8.92 μ; nmr (CCl4), τ 8.97 (s, 9, t-Bu), τ 8.45 (d, J = 1.5 Hz, 3, CH3C=), τ 6.67 (s, 3, -OCH3), τ 6.10-6.63 (two groups of broad peaks, -OCH2CH2-OCH3), τ 4.13 (m, 1, =CH); mass spectrum, mol. wt. 172.


Found: C, 70.1; H, 11.8.

Phenyl-2,3,3-trimethyl-1-butene-1-ether (42): ir (neat), bands at 6.05 μ (C=C), 6.30 μ (aromatic C=C), 8.15 μ, 9.20 μ, 13.35 μ, 14.58 μ; nmr (CCl4), τ 8.82 (s, 9, t-Bu), τ 8.26 (d, J = 1.5 Hz, 3, CH3C=), τ 3.69 (m, 1, =CH), τ 2.50-3.20 (m, 5, aromatic); mass spectrum, mol. wt. 190.

2-Phenoxyethyl 3,3-dimethyl-1-butene (45): ir (neat), 6.10 μ (C=C), 6.25 μ (aromatic C=C), 8.12 μ, 13.35 μ, 14.58 μ; nmr (CCl4), τ 8.86 (s, 9,
Preparation of N-Nitroso-4,5,5-trimethyl-2-oxazolidone (48).

Ethyl 2,3-dimethyl-3-hydroxybutanoate (49).

A mixture of 130 g (2.0 m) of activated zinc and 300 ml of benzene was brought to reflux. After 50 ml of benzene had been distilled, a solution of 105 g (1.8 m) of acetone in 250 ml of ether was added. To the refluxed well-stirred mixture was added dropwise 362 g (2.0 m) of ethyl α-bromopropionate during 3 hr. After one additional hour of reflux the mixture was cooled to room temperature, and then hydrolyzed in 1.5 l of 10% hydrochloric acid. The mixture was worked up as usual and the residue was distilled to give 214 g (74%) of 49, bp 77-78° (10 mm); ir (neat), bands at 2.8 μ (-OH), 5.80 μ, 5.85 μ (C=O).

Anal. Calcd for C_{6}H_{16}O_{3}: C, 60.0; H, 10.0.

Found: C, 59.9; H, 10.1.

2,3-Dimethyl-3-hydroxybutanoic Acid Hydrazide (50).

To 194 g (1.21 m) of the hydroxy ester 49 cooled in an ice bath was added 57.5 g (1.8 m) of anhydrous hydrazine. The mixture solidified at
Figure 2 - Infrared spectrum of 41
Figure 3 - Nmr spectrum, 60 MHz, of 41 in CCl₄
Figure 4 - Infrared spectrum of 45
Figure 5 - Nmr spectrum, 60 MHz, of $\text{H}_2$ in CCl$_4$
room temperature after 24 hr and the excess hydrazine was removed in a vacuum desiccator over concentrated sulfuric acid. Recrystallization from 95% ethanol-chloroform afforded 112 g (63%) of 50 as a white crystalline solid, mp 124-125°C.

**Anal.** Calcd for C₆H₁₄N₂O₂: C, 49.3; H, 9.6.

**Found:** C, 49.5; H, 9.6.

4,5,5-Trimethyl-2-oxazolidone (51).

A solution of 41.4 g (0.6 m) of sodium nitrite in 120 ml of water was added dropwise at 5°C during 3 hr to a stirred solution of 73.1 g (0.5 m) of the hydrazine 50 in 250 ml of 2N hydrochloric acid. The mixture was extracted with benzene-chloroform (3:1). The extract (kept cold at all times) was washed with a saturated sodium chloride solution and then added into 100 ml of refluxing benzene during 2 hr. After the removal of the solvents on a rotary evaporator the residue was distilled at 105°C/0.15 mm. Recrystallization from benzene-Skellysolve B afforded 54 g (83%) of oxazolidone 51, mp 61.0-61.5°C; ir (KBr), 3.03 μ (-NH), 5.77 μ (C=O); nmr (CDCl₃), τ 8.80 (d, J = 7 Hz, 3, -CHCH₃), τ 8.64 (s, 3, -CH₃), τ 8.52 (s, 3, -CH₃), τ 6.30 (q, J = 7 Hz, 1, CHCH₃), τ 3.52 (m, 1, NH).

**Anal.** Calcd for C₆H₁₁NO₂: C, 55.8; H, 8.5.

**Found:** C, 56.0; H, 8.7.

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(57) The extract decomposed very readily at room temperature.
N-Nitroso-4,5,5-trimethyl-2-oxazolidone (48).

To a stirred solution of 42 g (0.325 m) of oxazolidone 51 in 150 ml of 6N hydrochloric acid was added dropwise at 5° a solution of 26.8 g (0.390 m) of sodium nitrite in 100 ml of water. The yellow precipitate was collected, washed thoroughly with cold water, and then dried in vacuo over phosphorous pentoxide. Recrystallization from ether-pentane afforded 47.7 g (93%) of yellow N-nitroso-4,5,5-trimethyl-2-oxazolidone (48), mp 88-89°, IR (KBr), 5.57 μ (C=O).

Alkaline Decomposition of N-Nitroso-4,5,5-trimethyl-2-oxazolidone (48).

a. in 2-methoxyethanol containing sodium iodide.

A 20% solution of sodium 2-methoxyethanolate in 2-methoxyethanol (20 g) was added dropwise during 10 min to a well-stirred solution of 2.37 g (0.015 m) of nitrosooxazolidone 48 in 50 ml of 2-methoxyethanol saturated with sodium iodide (18 g/50 ml). The theoretical amount of nitrogen was evolved in 10 min. The temperature was maintained below 30° by cooling with an ice-water bath. The mixture was worked up as usual. Two fractions were collected by distillation. Pure samples were obtained by preparative vpc (column A).

Fraction 1 (35-70°/35 mm): column temp. 100°, helium flow 100 cc/min, < 1 min, 0.091 g (8.2%) of 3-methyl-2-butanone (52).

Fraction 2 (85-122°/35 mm): column temp. 132°, helium flow 100 cc/min, A, 1 min, 0.153 g (7.1%) of 2-methoxyethyl 3-methyl-2-butenyl ether (53); B, 3.5 min, 0.631 g (22.4%) of 2-methoxyethyl 3-methyl-1-buten-3-yl carbonate (54).
3-Methyl-2-butanone (52) was identified by comparison with the infrared spectrum and the 2,4-dinitrophenylhydrazine derivative of the authentic sample.

2-Methoxyethyl 3-methyl-2-butenyl ether (53): ir (neat), 5.93 μ (C=O), 8.52 μ (C=C-0-), 8.85 μ; nmr (CCl₄) τ 8.43 (broad singlet, 6, (CH₃)₂C=), τ 8.26 (broad singlet, 3, =-(CH₃)O-C), τ 6.69 (6, 3, -OCH₃), τ 6.30-6.57 (complex multiplet, 4, -OCH₂CH₂-OCH₃); mass spectrum, mol. wt. 144, exact mass measurement 144.1152 (calcd. 144.1150).

For further characterization, a 2,4-dinitrophenylhydrazone, mp 119-120°, was prepared: mass spectrum (mol. wt. 294) identical to that prepared from 3-methyl-2-butanone.

2-Methoxyethyl 3-methyl-1-buten-3-yl carbonate (54): ir (neat), 5.73 μ (C=O), 6.10 μ (C=C, weak band), 7.90 μ, 8.80 μ; nmr (CCl₄), τ 8.48 (s, 6, (CH₃)₂C), τ 6.68 (s, 3, -OCH₃), τ 5.74-6.60 (complex multiplet, 4, -OCH₂CH₂OCH₃), τ 3.65-5.10 (multiple peaks, -CH=CH₂); mass spectrum, mol. wt. 188.

Anal. Calcd for C₉H₁₆O₄: C, 57.4; H, 8.6.

Found: C, 57.4; H, 8.6.

b. with sodium phenoxide in phenol-glyme.

To a stirred solution of 5.57 g (0.048 m) of sodium phenoxide and 33.6 g (0.4 m) of phenol in 16 g of glyme was added dropwise a solution of 6.33 g (0.04 m) of nitrosooxazolidone 48 in 20 g of glyme. The theoretical amount of nitrogen was obtained in 2 hr. The temperature was maintained below 50°. After the usual workup (2 washes with 30% sodium hydroxide) distillation at 70-117°/35 mm afforded 2.61 g of colorless
Figure 6 - Infrared spectrum of 53
Figure 7 - Infrared spectrum of 54
Figure 8 - Nmr spectrum, 60 MHz, of 54 in CCl₄
products which by vpc (10' x 3/8" column of 5% Carbowax on Chromosorb W, 140°, helium flow 100 cc/min) showed many components but only three were identified: A, 1.2 min, 0.15 g (2.6%), 2-methoxyethyl 3-methyl-2-butenyl ether (53); B, 1.3 min, 0.168 g (3.9%) anisole; C, 1.7 min, 0.687 g (10.6%) phenyl 3-methyl-2-butenyl ether (60).

Phenyl 3-methyl-2-butenyl ether (60): ir (neat), 5.92 μ (C=O), 6.25 μ (aromatic C=C), 8.20 μ, 8.69 μ, 13.25 μ, 14.48 μ; nmr (CCL₄), τ 8.42 (s, 3, trans CH₃-C=C-OPh), τ 8.28 (broad singlet, 6, cis CH₃-C=C-OPh and =C(CH₃)OPh), τ 2.68-3.40 (m, 5, aromatic); mass spectrum, exact mass measurement m/e 162.1046 (calcd. m/e 162.1045).

Anal. Calcd for C₁₁H₁₄O: C, 81.4; H, 8.7.

Found: C, 81.2; H, 8.9.

c. with 2-methoxyethoxide.

A 20% solution of sodium 2-methoxyethoxide (0.036 m) in 2-methoxyethanol was added dropwise to a solution of 4.73 g (0.03 m) of nitros oxazolidone 48 in 45 ml of 2-methoxyethanol. After the theoretical amount of nitrogen was collected (in 0.5 hr) the mixture was worked up as usual. Distillation at 31-120° (10 mm) yielded 2.46 g of products which by vpc (column A, 140°, helium flow 100 cc/min) showed many components besides the solvent peak, but only two were isolated and identified: A, 3 min, 0.416 g (9.6%) of 2-methoxyethyl 3-methyl-2-butenyl ether (53) and B, 4 min, 1.12 g (19.8%) of 2-methoxyethyl 3-methyl-1-buten-3-yl carbonate (54).
Figure 9 - Infrared spectrum of 60
Alkaline Decomposition of 1-(N-Nitrosoacetylaminomethyl)cyclohexanol (61) in the Presence of Ketones.

Decomposition in diethyl ketone.

To a stirred solution of 4.9 g (0.0245 mol) of nitrosoamide 61 in 25 ml of pentane containing 0.6 g of Aliquat 336 and 21 ml of diethyl ketone was added dropwise at -10°C during 10 min a 50% solution of sodium hydroxide in water. After the nitrogen evolution had stopped (90% of the theoretical amount), the mixture was poured into 100 ml of a saturated sodium chloride solution and worked up as usual. Distillation at 40-87°C/0.05 mm furnished 1.7 g of colorless products which by vpc (column B, helium flow 75 cc/min) showed five components: A, 1.5 min, 0.13 g (5.4%) cyclohexanone; B, 2 min, 0.15 g (5.4%) cyclohexanecarboxaldehyde; C, 2.5 min, 0.16 g (5.6%) cycloheptanone; D, 6 min, 0.38 g (10%) acetoxymethylene-cyclohexane (62); E, 11 min, 0.99 g (22%) cyclohexylidenemethyl 3-pentenyl ether (79). Pure materials were obtained by preparative vpc on the above column.

Cyclohexanone, cyclohexanecarboxaldehyde, and cycloheptanone were identified by comparison of ir and vpc retention time with the authentic samples.

Acetoxymethylene-cyclohexane (62): ir (neat), bands at 5.70 μ (C=O), 5.90 μ (C=C); nmr (CCl₄), τ 8.40 (s, 3, CH₃), τ 7.93 (s, 6, -CH₂-), τ 3.13 (s, 1, =CH).
A 2,4-dinitrophenylhydrazone, mp 166-167°, was prepared which showed identical mass spectrum to that prepared from cyclohexanecarboxaldehyde (m/e 292).

Cyclohexylidenemethyl 3-pentenyl ether (72): vapor phase chromatographic analysis in a different column (10' x 1/8" 5% SE 30 on 60/80 Chromosorb W, 138°, F and M Model 609 Flame Ionization Gas Chromatograph) showed two components with very close retention time in the ratio of 53:47, possibly a mixture of cis and trans isomers. Infrared spectrum (neat), 5.95 μ (C=C), 8.40 μ (C=O); nmr (CCl₄), τ 8.97, τ 8.92 (2 triplets, J = 7 Hz, 3, CH₂CH₃), τ 8.42 (m, 9, -CH₂- and CH₃C=), τ 7.90 (m, 6, CH₂C=), τ 5.50, τ 5.35 (2 quartets, J = 7 Hz, 1, CH₃CH=), τ 4.14 (m, 1, =CH); mass spectrum, mol. wt. 180, exact mass measurement 180.1515 (calc'd. 180.1514).

For further characterization, a drop of 1% hydrochloric acid was added to the divinyl ethers and the resultant mixture was subjected to vpc analysis. The retention time of the major peaks and the nmr spectrum of the mixture indicated a mixture of cyclohexanecarboxaldehyde and diethyl ketone. Mass spectrum of the 2,4-dinitrophenylhydrazone derivatives showed peaks at m/e 266 and m/e 292, corresponding to those derived from diethyl ketone and cyclohexanecarboxaldehyde.

Decomposition in diisopropyl ketone.

To a stirred solution of 2.5 g (0.0125 m) of nitrosoamide 61 and 14.3 g (0.125 m) of diisopropyl ketone in 20 ml of pentane containing 0.5 g of
Aliquat 336 was added dropwise during 0.5 hr a 50% solution of sodium hydroxide in water. The temperature was maintained below 10°. After the theoretical amount of nitrogen had been evolved (in 0.5 hr) the mixture was poured into 50 ml of a saturated sodium chloride solution and worked up as usual. The residue was distilled at 29-125°/0.01 mm to afford 1 g of colorless liquid which by vpc (column B, 165°, helium flow 75 cc/min) showed several components, but only two were isolated: A, 2.5 min, 0.30 g (15.5%) acetoxymethylene cyclohexane (62); B, 8 min, 0.12 g (4.4%) cyclohexylidenemethyl 2,4-dimethyl-3-pentenyl ether (80).

The divinyl ether 80 has ir (neat), bands at 6.00 μ (C=O), 8.45 μ, 8.70 μ, 8.95 μ; nmr (CCl₄), τ 9.00 (d, J = 7 Hz, 6, -CH(CH₃)₂), τ 8.38 (m, 12, -CH₂- and =C(CH₃)₂), τ 8.02 (m, 2, trans -CH₂-C=CH₂-), τ 7.78 (m, 2, cis -CH₂-C=CH₂-), τ 7.18 (m, 1, -CH(CH₃)₂), τ 4.34 (m, 1, =CH), mol. wt. 208 (mass spectrum).

Found: C, 80.4; H, 11.6.

**Decomposition in cyclohexanone.**

A 50% solution of sodium hydroxide in water was added dropwise at 3° in 25 min to a well-stirred solution of 5.0 g (0.025 m) of nitrosoamide 61 and 19.6 g (0.2 m) of cyclohexanone in 30 ml of pentane containing 1 g of Aliquat 336. The temperature was maintained below 10°. After the evolution of the nitrogen gas (95% of the theoretical amount) the mixture was poured into 100 ml of saturated sodium chloride solution and worked up as usual. Distillation at 60-94°/0.05 mm afforded 2.1 g of
Figure 10 - Infrared spectrum of 80
colorless products. Vapor phase chromatograph (column B, 158°, helium
flow 120 cc/min) showed two main components: A, 1.7 min, 0.19 g (5%)
acetoxydymethylenecyclohexane (62); B, 7 min, 1.6 g (32%) cyclohexylidene-
methyl 1-cyclohexenyl ether (81). Pure materials were obtained by pre-
parative vpc on the above column.

The infrared spectrum of cyclohexylideneemethyl cyclohexenyl ether
showed bands at 6.00 μ (C≡C) and 8.50 μ; nmr (CCl₄), τ 8.44 (m, 10, -CH₂-),
τ 7.92 (m, 8, CH₂C=), τ 5.28 (m, 1, =CH-C), τ 4.10 (m, 1, =CH-0); mass
spectrum, exact mass measurement 192.1514 (calcd. value: 192.1516).

Anal. Calcd for C₁₃H₂₀O: C, 81.3; H, 10.5.

Found: C, 81.3; H, 10.3.

Alkaline Decomposition of 1-(N-Nitrosoacetylaminomethyl)cyclohexanol
(61) in the Presence of Aldehydes.

Decomposition in 2,2-dimethylpropanal.

A 50% solution of sodium hydroxide in water was added dropwise at
-15° during 0.5 hr to a well-stirred solution of 2.5 g (0.0125 m) of
nitrosoamide 61 and 4.4 g (0.051 m) of 2,2-dimethylpropanal in 15 ml of
pentane containing 0.75 g of Aliquat 336. The theoretical amount of
nitrogen was evolved. The temperature was maintained below -5°. The mix-
ture was then poured into 75 ml of a saturated sodium chloride solution
and worked up as usual. Distillation at 57-100°/0.04 mm afforded 0.7 g
of colorless products which by vpc (column B, 135°, helium flow 130 cc/
min) showed several components, but only two were isolated and charac-
terized: A, 0.5 min, 0.385 g (27.5%) cyclohexanecarboxaldehyde; B, 4 min,
Figure 11 - Infrared spectrum of 81
Figure 12 - Nmr spectrum, 60 MHz, of 81 in CCl₄
0.1 g (4.5%) cyclohexylidenemethyl t-butyl ketone (70).

The infrared spectrum of the conjugated ketone 70 showed bands at 5.87 μ, 5.98 μ, and 6.20 μ (C=O); nmr (CCl₄), τ 8.87 (s, 9, t-Bu), τ 8.36 (m, 6, -CH₂-), τ 7.80 (m, 2, CH₂C=), τ 7.25 (m, 2, CH₂C=), τ 3.79 (m, 1, =CH); mass spectrum, mol. wt. 180, exact mass measurement, 180.1517 (calcd. value: 180.1519); UV (abs. EtOH), 241 μm (ε 12,700).


Found: C, 80.25; H, 11.09.

For further characterization, a 2,4-dinitrophenylhydrazone, mp 125.5-127.0°, was prepared: mass spectrum, mol. wt. 360.

Decomposition in isobutyr aldehyde.

To a stirred solution of 2.5 g (0.0125 m) of nitrosoamide 61 and 9 g (0.125 m) of isobutyraldehyde in 15 ml of pentane containing 1 g of Aliquat 336 was added dropwise at -10° a 50% solution of sodium hydroxide in water. The theoretical amount of nitrogen was collected in 15 min. The mixture was then poured into 75 ml of a saturated sodium chloride solution and worked up as usual. Distillation at 60-137°/0.2 mm yielded 2.18 g of colorless product. From the preparative vpc (column B, 125°, helium flow 120 cc/min, retention time 5.5 min) there was isolated 0.74 g (35.7%) of cyclohexylidenemethyl isopropyl ketone (82), ir (neat), 5.94 μ (C=C), 6.15 μ (C=O), and 6.90 μ (doublet (CH₃)₂CH-); nmr (CCl₄), τ 8.97 (d, J = 7 Hz, 6, -CH(CH₃)₂), τ 8.38 (m, 6, -CH₂-), τ 7.94 (m, 2, CH₃C=), τ 7.36 (m, J = 7 Hz, 1, -CH(CH₃)₂), τ 7.26 (m, 2, CH₂C=), τ 4.10 (m, 1, =CH); UV (abs. EtOH), 241 μm (ε 11,200); mass spectrum, m/e at 166, 123, 95.
Anal. Calcd for C_{11}H_{18}O: C, 79.5; H, 10.9.

Found: C, 79.2; H, 11.1.

For further characterization a 2,4-dinitrophenyl hydrazone, mp 127.5-128.0°, mass spectrum, mol. wt. 346, was prepared.

Preparation of Cyclohexyldieneemethyl t-Butyl Ketone (69).

Triethyl phosphonoacetate.

To 70 g (0.42 m) of triethyl phosphite was added dropwise 70 g (0.42 m) of ethyl bromoacetate in 1.5 hr. The mixture was heated to 90° and ethyl bromide was distilled. The mixture was then heated at 165-170° for 9 hr. The residue was distilled to give 69 g (73%) of triethyl phosphonoacetate, bp 164°/25 mm (reported bp 109-109.5°/0.80 mm), ir (neat), 5.78 μ (C=O), 9.80 μ (P-O-C); nmr (CCl₄), τ 8.71 (t, J = 7 Hz, 3, -COOCH₂CH₃), τ 8.66 (t, J = 7 Hz, 6, (CH₃CH₂O)₂P(0)-), τ 7.15 (d, J = 22 Hz, 2, -P(0)CH₂C(0)-), τ 5.89 (m, J = 7 Hz, 6, -CH₂CH₃).

Ethyl Cyclohexyldieneacetate.

A 2.9 g (0.07 m) sample of a suspension of 56.2% sodium hydride in mineral oil was washed repeatedly with hexane and the remaining sodium hydride was suspended in 25 ml of benzene which had been dried by filtering through sodium hydride. To this suspension was added dropwise during 0.5 hr 17.9 g (0.08 m) of triethyl phosphonoacetate under a nitrogen atmosphere. The mixture became milky then changed to a clear light yellow solution. The resulting solution was stirred for 0.5 hr and then 6.85 g (0.07 m) of cyclohexanone was added dropwise in 15 min. The temperature was maintained at 30-35° with an ice-water bath. A gel-
Figure 13 - Infrared spectrum of 82
Figure 14 - Nmr spectrum, 60 MHz, of 82 in CCl₄
like material precipitated. The mixture was heated at 60-65° for 15
min, cooled to room temperature and the gel-like precipitate was separa-
ted and washed with three portions of 25 ml of hot benzene. The combined
benzene solution was concentrated on a rotary evaporator and the residue
was distilled to yield 7.8 g (67%) of ethyl cyclohexylideneacetate, bp
115°/15 mm (reported bp 48-49°/0.02 mm). The product was of > 95%
purity by vpc analysis (column B, 135°) and had infrared absorption bands
at 5.85 μ (conjugated ester C=O) and 6.10 μ (conjugated C=C); nmr (CCl₄)
τ 8.75 (t, J = 7 Hz, 3, -CH₂CH₃), τ 8.36 (m, 6, -CH₂-), τ 7.80 (m, 2,
-CH₂C=), τ 7.16 (m, 2, -CH₂C=), τ 5.91 (q, J = 7 Hz, 2, -CH₂-CH₃), τ 4.47
(m, 1, =CH).

Cyclohexylideneacetic acid.

To a solution of 1.84 g (0.0458 m) of sodium hydroxide in 10 ml of
ethanol containing a small amount of water (enough to make the solution
homogeneous) was treated with 7 g (0.0416 m) of ethyl cyclohexylidene-
acetate. The mixture was heated at 70° for 3 hr. After the mixture had
been cooled to room temperature 10 ml of water was added. Ethanol was
removed on the rotary evaporator and the resulting solution was acidified
with 10% hydrochloric acid. The white solid was collected and dissolved
in ether. After the usual work-up there was obtained 5 g (86%) of white
product, mp 87.0-88.5° (reported mp 89°), ir (neat), 3.0 μ (associated

(59) O. Wallach, Ann., 314, 151 (1900).
\( \text{OH}, 6.0 \mu \) (conjugated \( \text{C}=\text{O} \)) and \( 6.15 \mu \) (conjugated \( \text{C}=-\text{C} \)); nmr \( (\text{CCl}_4) \),
\[ \begin{align*}
\tau 8.34 & \text{ (m, 6, -CH}_2_-), \tau 7.75 \text{ (m, 2, -CH}_2_-\text{C}=-), \tau 7.12 \text{ (m, 2, -CH}_2_-\text{C}=-), \\
\tau 4.38 & \text{ (m, 1, =CH)}, \tau -2.30 \text{ (s, 1, -COOH).}
\end{align*} \]

Cyclohexylidenemethyl t-Butyl ketone (69).

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To a well-stirred solution of 1.4 g (0.01 m) of cyclohexylideneacetate in 20 ml of dry ether was added under a nitrogen atmosphere with a syringe 20 ml of 1.29 N (0.0248 m) solution of t-butyllithium in hexane at 2° over a period of 1.5 hr. The mixture was stirred for an additional 11 hr with the temperature maintained below 10°, then poured into an ice cold ammonium chloride solution followed by ether extraction. The ethereal extract was worked up as usual. From the preparative vpc (column B, 132°, helium flow, 136 cc/min, retention time 2 min) there was isolated 0.85 g (47%) of cyclohexylidenemethyl t-butyl ketone (69) with ir, nmr, and uv identical with that obtained from the decomposition of the nitroso amide 61 in 2,2-dimethyl propanal.

Decomposition of 1-(N-Nitrosoacetylaminomethyl)cyclohexanol (61) with Triethylamine in the Presence of Isobutyraldehyde.

A solution of 2.5 g (0.0125 m) of nitrosoamide 61 and 9 g (0.125 m) of isobutyraldehyde in 20 ml of pentane was treated dropwise at 0° with 1.68 g (0.0166 m) of triethylamine during 15 min. The mixture was stirred
at 10-12° for 1.5 hr. After the evolution of nitrogen was complete the mixture was poured into a saturated sodium chloride solution and worked up in the usual manner. Distillation at 34-69° (0.05 mm) yielded 0.8 g of products which by vpc (column B, 135°, helium flow 136 cc/min) showed two main components: A, 2 min, 0.288 g (15%) of acetoxymethyleneacyclohexane (62) and B, 4 min, 0.260 g (12.6%) of cyclohexylidenemethyl isopropyl ketone (82).

Alkaline Decompositions of 1-(N-Nitrosoacetylaminomethyl)cyclohexanol (61) in the Presence of Nucleophiles.

a. sodium azide.

To a stirred mixture of 10 g (0.154 m) of sodium azide in 25 ml of water containing 1 g (0.025 m) of sodium hydroxide and 0.5 g of Aliquat 336 was added dropwise at 3° a solution of 2.5 g (0.0125 m) of nitrosamide 61 in 20 ml of pentane. After the evolution of nitrogen (quantitative in 15 min) the mixture was worked up as usual. The crude unsaturated azide (2.2 g) was purified by passing through 30 g of neutral Woelm alumina oxide activity grade I with hexane. After the removal of the solvents in vacuo 0.95 g (56%) of azidomethyleneacyclohexane was produced as a yellow liquid, ir (neat), 4.75 μ (=C-N3), 6.00 μ (C=C); nmr (CCl4), τ 8.48 (m, 6, -CH2-), τ 7.92 (m, 4, CH2C=), τ 4.16 (m, 1, -CH).

Anal. Calcd for C7H11N3: C, 61.3; H, 8.1; N, 30.6.

Found: C, 61.4; H, 8.2; N, 30.8.

The analytical sample was obtained by bulb to bulb distillation at room temperature and 0.1 mm.
Figure 15 - Infrared spectrum of azidomethylene cyclohexane
Figure 16 - NMR spectrum, 60 MHz, of azidomethylenecyclohexane in CCl₄
b. potassium thiocyanate.

To a stirred mixture of 12.1 g (0.125 m) of potassium thiocyanate, 0.75 g (0.0185 m) of sodium hydroxide, 8 g of water, and 0.5 g of Aliquat 336 was added dropwise at 5-7° a solution of 2.5 g (0.0125 m) of nitrosoamide 61 in 25 ml of pentane. After the quantitative amount of nitrogen had been collected (in 15 min), the aqueous layer was extracted with ether and the combined organic phase was worked up as usual. Distillation of the residue (2.25 g) at 68-80°/0.15 mm yielded 0.78 g (41%) of colorless cyclohexylidenemethyl thiocyanate (> 95% pure by vpc). The analytical sample was obtained by preparative vpc (column A, 140°, helium flow 100 cc/min, retention time 5 min). Infrared spectrum (neat), bands at 4.65 μ (=C-SCN, sharp band), 6.20 μ (C=C, weak band); nmr (CCl₄),


All the organic thiocyanates show a sharp strong peak due to the nitrile stretching around 4.67 μ, 2140 cm⁻¹ as compared to a broad and very strong band centered around 4.78 μ, 2100 cm⁻¹ for organic isothiocyanates.

ν 8.39 (m, 6, -CH₂-), ν 7.70 (m, 4, CH₂-C=), ν 4.28 (m, 1, =CH); mol. wt. 153 (mass spectrum).

Anal. Calcd for C₆H₁₁N₃S: C, 62.7; H, 7.2; N, 9.1; S, 20.9.

Found: C, 62.6; H, 7.1; N, 9.3; S, 20.9.

c. sodium iodide.

A solution of 2.5 g (0.0125 m) of nitrosoamide in 15 ml of pentane was added dropwise during 25 min to a stirred mixture of 20 g (0.138 m)
Figure 17 - Infrared spectrum of cyclohexylidemethyl thiocyanate
Figure 18 - NMR spectrum, 60 MHz of cyclohexylidenemethyl thiocyanate in CCl₄
of sodium iodide, 1 g (0.025 m) of sodium hydroxide, 0.75 g of Aliquat 336, and 10 g of water at 3-5°. After the quantitative amount of nitrogen had been evolved the mixture was worked up as usual. Distillation afforded 2.0 g (72%) of iodomethylenecyclohexane, bp 30-30.5°/0.15 mm, nmr (CCl4), τ 8.46 (m, 6, -CH2-), τ 7.72 (m, 4, CH2C=), τ 4.27 (m, 1, =CH); mol. wt. 222 (mass spectrum); ir identical with an authentic sample.

Alkaline Decomposition of 1-(N-Nitrosoacetylaminomethyl)cyclohexanol (61) in the Presence of Triethyl Phosphate and Acetone.

A solution of 2.5 g (0.0125 m) of nitrosoamide 61 and 2.08 g (0.0138 m) of triethyl phosphate in 25 ml of pentane at -10° was treated with 2 g (0.037 m) of sodium methoxide in portions during 8 min. After the evolution of nitrogen (72% of the theoretical amount in 1 hr) the solid in the mixture was filtered and the filtrate was concentrated on the rotary evaporator. When 1.5 g (0.026 m) of acetone was added an exothermic reaction took place. After stirring for 1 hr distillation gave two fractions which were analyzed by vpc (column B, helium flow 75 cc/min).

Fraction 1 (30-140°/40 mm): column temp. 115°, A, 2 min, triethyl phosphate; B, 4 min, 0.208 g (14.8%) of cycloheptanone; C, 7 min, 0.278 g (12.2%) of triethyl phosphate.

Fraction 2 (110-130°/0.15 mm): column temp. 190°, 7 min, 0.77 g (26.6%) of cyclohexyldenemethyl diethyl phosphonate (70).

The pure products were isolated by preparative vpc on the above column.
Cycloheptanone and triethyl phosphate were identified by comparison of ir and vpc retention times with the authentic samples.

Vinyl phosphonate 70: ir (neat), bands at 6.14 μ (C=O), 8.07 μ (P=O), 9.50 μ, 9.75 μ, 10.45 μ (P-O-C); nmr (CCl₄), τ 8.68 (t, J = 7 Hz, 6, -CH₃), τ 8.34 (m, 6, -CH₂-), τ 7.76 (m, 2, trans -CH₂C=O-P), τ 7.30 (m, 2, cis -CH₂C=C-P), τ 5.97 (m, J = 7 Hz, 4, -CH₂-CH₃), τ 4.78 (d, J = 17 Hz, 1, -CH-P); mass spectrum, exact mass measurement 232.1226 (calcd. value: 232.1228).

Anal. Calcd for C₁₁H₂₁O₃P: C, 56.9; H, 9.1; P, 13.3.
Found: C, 56.8; H, 9.5; P, 13.5.

Alkaline Decomposition of 1-(N-Nitrosoacetylaminomethyl)cyclohexanol (61) in the Presence of Trialkyl Phosphites.

Decomposition in trimethyl phosphite.

A solution of 2.5 g (0.0125 m) of nitrosoamide 61 and 1.55 g (0.0125 m) of trimethyl phosphite in 30 ml of pentane at 5° was treated with 1.0 g (0.0185 m) of sodium methoxide in portions during 15 min. The temperature was maintained below 7°. After the nitrogen evolution (72% of the theoretical amount in 15 min) the solid was filtered and washed repeatedly with ether. Distillation of the residue at 40-97°/0.1 mm after the usual work-up afforded 0.4 g of a colorless liquid which by vapor phase chromatograph (column B, 190°, helium flow 66 cc/min) showed only one major component: 6 min, 0.28 g (10.8%) of cyclohexylenemethyl dimethyl phosphonate (83), ir (neat), 6.14 μ (C=O), 8.07 μ (P=O), 9.50 μ, 9.75 μ; nmr (CCl₄), τ 8.34 (m, 6, -CH₂-), τ 7.77 (m, 2, trans -CH₂C=O-P), τ 7.37 (m, 2, cis -CH₂C=C-P), τ 6.36 (d, J = 11 Hz, 6, CH₃OP-), τ 4.82 (d, J =
Figure 19 - Nmr spectrum, 60 MHz, of 70, in CCl₄
17 Hz, 1, =CH-P); mol. wt. 204 (mass spectrum).

**Anal. Calcd for C₉H₁₇O₃P: C, 53.3; H, 8.4; P, 15.2.**

**Found: C, 53.0; H, 8.5; P, 14.9.**

**Decomposition in triethyl phosphite.**

A solution of 2.5 g (0.0125 m) of nitrosoamide in 25 ml of pentane was added dropwise to a stirred ice cold mixture of 10.4 g (0.0625 m) of triethyl phosphite, 1 g (0.025 m) of sodium hydroxide, 1.5 g of water, and 1 g of Aliquat 336 during 25 min. After the evolution of nitrogen (72% of the theoretical amount in 15 min) the mixture was worked up as usual. Distillation of the residue at 55-120°/0.1 mm yielded 1.75 g of products which by vpc (column B) showed three components at column temperature of 115° (helium flow 87 cc/min): A, 1.8 min, triethyl phosphite; B, 3 min, 0.05 g (3.6%) cycloheptanone; C, 6 min, 0.096 g (4.2%) triethyl phosphate and one main component at column temperature of 190° (helium flow 75 cc/min); D, 6 min, 1.22 g (42%) cyclohexylidenemethyl diethyl phosphonate (70).

When a 50% solution of sodium hydroxide was added dropwise to a mixture of nitrosoamide, triethyl phosphite, pentane, and Aliquat 336, followed by the same work-up as above, vinyl phosphonate 70 was obtained in 44.2% yield.

**Decomposition of 1-(N-Nitrosoacetylaminomethyl)cyclohexanol (61) with Pyrrolidine.**

A stirred solution of 8.9 g (0.125 m) of pyrrolidine in 15 ml of hexane at 0° was treated dropwise with a solution of 2.5 g (0.0125 m) of
nitrosoamide in 15 ml of hexane during 0.5 hr. The mixture was stirred for two more hours at 10-17°. After the nitrogen evolution stopped (89% of the theoretical amount) solvents and excess pyrrolidine were removed on the rotary evaporator. The residue was distilled at 62°/0.03 mm to give 1.95 g of liquid which by vpc (column B, l45°, helium flow 136 cc/min) showed two major components: A, 3.5 min, 1.19 g (84%) N-acetyl pyrrolidine (71); B, 8.5 min, 0.51 g (22%) N-(1-hydroxycyclohexylmethyl)pyrrolidine (72). Pure materials were obtained by preparative vpc on the above column.

N-Acetyl pyrrolidine (71) was identified by the independent synthesis from the reaction of pyrrolidine and acetic anhydride. Infrared spectrum (neat), bands at 6.15 μ (C=O); nmr (CCl4), τ 8.10 (m, 7, -CH3 and -CH2-), τ 6.64 (m, 4, -CH2-N-); mass spectrum, m/e 113, 98, 85, and 70.

N-(1-Hydroxycyclohexylmethyl)pyrrolidine (72): ir (neat), 2.90 μ (C-OH); nmr (CCl4), τ 8.50 (m, 6), τ 8.25 (m, 8), τ 7.51 (s, 2, -C(OH)-CH2-N-), τ 7.30 (m, 4, -CH2-N), τ 6.65 (s, 1, OH, this peak exchanged with one drop of D2O); mol. wt. 183 (mass spectrum).


Found: C, 72.7; H, 12.0; N, 7.8.

Decomposition of 3-Nitroso-1-oxa-3-azaspiro[4,5]decan-2-one (12) in Diethylamine.

A 50 ml of freshly distilled diethylamine was treated with 5.52 g (0.03 m) of nitrosooxazolidone. The reaction was very exothermic (54°)
and 950 ml of gas was collected in 7 min. Distillation on a spinning-band column yielded 1.90 g (56.6%) of cyclohexanecarboxaldehyde, bp 59°/12 mm, and 1.21 g residue. The infrared spectrum and nmr of the product was identical with an authentic sample.


A 25% solution of sodium hydroxide in water was added dropwise to a stirred solution of 11.0 g (0.06 m) of nitrosooxazolidone 12 in 49.2 g (0.6 m) of freshly distilled cyclohexene and 74 g of benzene containing 1.52 g of Aliquat 336. The theoretical amount of nitrogen was collected in 4 hr. The mixture was worked up as usual. Distillation yielded 4.55 g (43%) of bicyclo[4.1.0]hept-7-ylidenecyclohexane (73), bp 59° at 0.45 mm (reported bp 68-70°/0.3 mm).

Alkaline Decomposition of 3-Nitroso-spiro[fluorene-9',5-oxazolidin]-2-one (74) in the Presence of Cyclohexene.

A stirred solution of 2.66 g (0.01 m) of nitrosooxazolidone and 8.2 g (0.1 m) of cyclohexene in 32 ml of benzene was treated with 0.68 g (0.01 m) of sodium ethoxide. The mixture was heated at 60-70° for 2 hr. The evolution of gas did not take place until the temperature reached 40°. The yellow color of the mixture turned into purple and the quantitative amount of nitrogen was collected. The mixture was worked up as usual after it had been cooled to room temperature. The residue (2.06 g) was chromatographed in 200 g of activated 60-200 mesh Silica Gel. The first fraction collected from Skellysolve B-benzene (3:1) gave white
fluorescent crystal. Recrystallization from Skellysolve B yielded 0.20 g (12.7%) pure 9-(bicyclo[4.1.0]hept-7-ylidene)fluorene (75): mp 126.0-126.5° (reported mp 126-127°); ir (KBr), 3.10 μ, 6.20 μ, 8.90 μ, 12.90 μ, 13.34 μ, 13.70 μ; nmr (d6-acetone), τ 9.21 (m, 2, cyclopropyl), τ 8.39 (m, 8, -CH2-), τ 2.37-3.16 (m, 8, aromatic); mass spectrum, mol. wt. 258.

**Anal. Calculated for C20H18: C, 93.0; H, 7.0.**

**Found: C, 93.1; H, 7.0.**

The fraction collected from chloroform-benzene (1:4) gave 0.470 g (40.7%) of fluorenone after recrystallization from Skellysolve B. The infrared spectrum and the melting point of the 2,4-dinitrophenylhydrazine derivative (298°) were identical with an authentic sample.

**Preparation of 3-Acetylamino-2-methyl-2-butanol (76).**

To a solution of 56 g (1 m) of potassium hydroxide in 80 ml of water was added 31.8 g (0.246 m) of 4,5,5-trimethyl-2-oxazolidone under a nitrogen atmosphere. After refluxing for 3 hr the upper organic layer was separated from the cooled mixture and dissolved in 80 ml of methanol. The methanol solution was treated dropwise with 25 g (0.246 m) of acetic anhydride during 0.5 hr. After 2 hr at reflux the mixture was concentrated on a rotary evaporator. The crude product containing acetic anhydride was dissolved in 200 ml of methylene chloride, washed with a saturated sodium bicarbonate solution. After a saturated sodium chloride solution wash and the usual work-up only 2.2 g of brown oil was obtained. The aqueous portion was continuously extracted with ether for two days. After work up 32.1 g of oil was distilled at 115-117°/0.1 mm. Recry-
stallization from benzene yielded 25.9 g (73%) of white crystalline 76,
mp 83.5-84.5°, ir (KBr), 3.0 μ (-CH, -NH), 6.1 μ (C=O); nmr (CDCl₃), τ
8.90 (d, J = 7 Hz, 3, -CH₂-CH₃), τ 8.78 (s, 6, (CH₃)₂O), τ 5.83-6.33 (m, 2, -CH₂CH₃ and OH), τ 3.00 (m, 1, NH).

Anal. Calcd for C₇H₁₅N O₂: C, 57.9; H, 10.4.
Found: C, 58.1; H, 10.3.

Preparation of Methyl n-Butyl-N-chlorocarbamate (78).

(62) This is the procedure of V. A. Shokol, N. K. Mikhailyuchenko, and

To a stirred mixture of 13.1 g (0.1 m) of methyl n-butylcarbamate
and 40 ml of water was added at 10° 15 ml (0.33 m) of chlorine by eva-
poration through a dispenser partially submerged in a dry ice-acetone
bath. The reaction was exothermic and the temperature of the reaction
mixture was maintained below 15°. The lower yellow layer was separated

(63) If the reaction temperature is allowed to go above 80° by a rapid
rate of chlorine addition, one obtains a poor yield of the product.

and the aqueous layer was extracted with ether. The combined organic
phase was dried over anhydrous potassium carbonate. Ether was removed
on a rotary evaporator and the residue was distilled to give 12.9 g (78%)
of methyl n-butyl-N-chlorocarbamate (78) as a colorless liquid, bp 36-
38°/0.4 mm, ir (neat), 5.80 μ (C=O), 13.30 μ; nmr (CCl₄), τ 9.03 (m, 3,
-CH₃), τ 8.14-8.86 (m, 4, -CH₂-), τ 6.41 (t, J = 7 Hz, 3, -CH₂-N-Cl, one of the peaks superimposed on the singlet from -OCH₃), τ 6.27 (s, 3, -OCH₃).

Anal. Calcd for C₇H₁₅ClNO₂: C, 43.5; H, 7.3; Cl, 21.4.
Found: C, 43.6; H, 7.2; Cl, 20.2.

Alkaline Decomposition of Methyl n-Butyl-N-chlorocarbamate (78) in the Presence of Cyclohexene.

To a stirred solution of 4.14 g (0.025 m) of chlorocarbamate in 8.2 g (0.1 m) of cyclohexene and 12 g of benzene was treated under nitrogen atmosphere with 1.62 g (0.03 m) of sodium methoxide in portions during 5 min. The reaction became very exothermic (temperature rose to 64°). The mixture was filtered after it had been cooled to room temperature. Distillation of the filtrate afforded 1.70 g (50%) of methyl n-butylcarbamate, bp 50° (0.3 mm).

Alkaline Decomposition of Methyl n-Butyl-N-chlorocarbamate (78).

To a solution of 4.14 g (0.025 m) of chlorocarbamate in 20 ml of anhydrous ether was added sodium methoxide. The reaction was very exothermic and the mixture began to reflux. After the mixture cooled down to room temperature the solid was removed by filtering through a pad of Celite under reduced pressure. The Celite pad was thoroughly rinsed
with more ether. The solvent was removed by distillation at atmospheric pressure, and the residue was distilled at 44°/0.1 mm to give 1.68 g (51.3%) of methyl n-butylcarbamate. The distillate (1.0 g) collected in the dry ice trap showed two peaks by vpc analysis (8' x 3/8" column of Carbowax 20M on Chromosorb W, 100°, helium flow 30 cc/min): A, 1.5 min, 0.33 g (15%) of dimethyl carbonate; B, 4.0 min, 0.67 g (40%) of butyl cyanide.

Dimethyl carbonate showed identical infrared spectrum and nmr as the authentic sample.

Butyl cyanide showed ir (neat) band at 4.5 μ; nmr (CCl₄), τ 8.92 (t, J = 6.5 Hz, 3, -CH₃), τ 8.33 (m, J = 6.5 Hz, 2, -CH₂-), τ 7.70 (t, J = 6.5 Hz, 2, -CH₂CN).

In a separate experiment where the reaction was run at 5°, with the rest of the condition identical with that employed above, the distribution of products varied as follows: 57.5% of methyl n-butylcarbamate, 6.7% of dimethyl carbonate, and 13.3% of butyl cyanide.