PREPARATION OF NITROCYCLOPROPANES USING YLIDES

DISSERTATION

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

By

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To my parents who had faith and patience.
ACKNOWLEDGMENTS

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INTRODUCTION

The purpose of this investigation was two-fold: (1) a convenient synthesis of conjugated nitro olefins under mild conditions and (2) an efficient general method for preparing substituted nitrocyclopropanes.

Present syntheses of conjugated nitro olefins are inefficient and time consuming. One aspect of the present study thus involves the possible use of nitromethylenetriphenylphosphorane (I) as a precursor for the conversion of aldehydes and ketones to terminal nitromethylene derivatives (Equation 1).

\[
\phi_3P=CH-NO_2 + R-C-R' \rightarrow R'\underset{\text{H}}{C=C}{\phi_3P=O} \quad (1)
\]

Existing methods and procedures for preparing nitrocyclopropanes are inadequate and ineffective. This study involves the reactions of substituted triphenylphosphoranes (II, Equation 2) and dimethylsulfoxonium methyldene (III, Equation 3) with conjugated nitro olefins to give nitro ylides (IV) and nitrocyclopropanes (V), respectively.

\[
\phi_3P=CH-R + R'\underset{\text{NO}_2}{C=C} \rightarrow \phi_3P=C-\text{CH-NO}_2 \quad \text{II} \\
\text{R} = -\text{CO}_2\text{CH}_3 \quad \text{IV} \quad \text{R} = \text{H} \quad \text{V}
\]
The structures of the products of the various reactions were established from their infrared, ultraviolet and nuclear magnetic resonance absorptions. Subsequent reactions of the products with various organic reagents were also studied.
HISTORICAL

A. Structures, Synthesis and Reactions of Ylide Reagents.

A new synthesis of olefins has been developed by Wittig and coworkers which consists of reaction of an aldehyde or ketone with an alkylidenetriphenylphosphorane (II, Equation 4). This reaction, known as the Wittig Reaction, proceeds smoothly with aldehydes but exhibits difficulties with hindered ketones.

\[
\begin{align*}
\text{R-C-H (R')} & + \text{P=CH-R''} \\
\text{II} & \rightarrow \text{R} = \text{C=O} = \text{H (R')} \\
\end{align*}
\]

\((\text{4})\)

(2) G. Wittig, Angew. Chem., 68, 505 (1956).

(7) S. Trippett, Chem. and Ind., 990 (1961).
The substituents on a Wittig triphenylphosphorane can be either electron-withdrawing (VI), electron-donating (VII) or both (VIII). The phosphoranes are prepared by reaction of base with

\[
\text{Ph}_3\text{P} = \begin{array}{c}
\text{R}_1 \\
\text{R}_2
\end{array}
\]

\[\begin{array}{cc}
\text{O} & \text{O} \\
\text{H} & \text{H}
\end{array}\]

VI \quad \text{R}_1 = \text{H}, \phi \\
\text{R}_2 = -\text{CN}, -\text{CO}_2\text{R}, -\text{C-R}, -\text{C-N-R}, \phi

VII \quad \text{R}_1 = \text{H}, \text{alkyl} \\
\text{R}_2 = \text{H}, \text{alkyl}

VIII \quad \text{R}_1 = \text{alkyl} \\
\text{R}_2 = -\text{CO}_2\text{R}

the corresponding phosphonium salts (IX) which in turn are prepared by reaction of triphenylphosphine with an alkyl halide (Equation 5).

\[
\text{Ph}_3\text{P} + \text{X-CH}_2-\text{R} \rightarrow \text{Ph}_3\text{P-CH}_2-\text{R}\leftarrow \text{Base} \rightarrow \text{Ph}_3\text{P-CH-R}
\]

\[
\text{Br} \quad \text{X}
\]

IX

While the investigation of nitromethylenetriphenylphosphorane was in progress in the present study (1959-1960), the reaction of triphenylphosphine with bromonitromethane (Equation 6) was reported.

\[
\text{Ph}_3\text{P} + \text{Br-CH}_2-\text{NO}_2 \rightarrow \text{Ph}_3\text{P-CH}_2-\text{NO}_2
\]

\[
\text{Br} \quad \text{X}
\]

Treatment of the phosphonium salt (X) with aqueous sodium hydroxide was stated to result in formation of fulminate ion and quantitative

---

recovery of triphenylphosphine oxide. 1-Nitroethyltriphenylphosphonium bromide was reported from triphenylphosphine and 1-


bromo-1-nitroethane but its chemistry was not investigated. Trippett further found that if longer chain 1-bromo-1-nitroalkanes were used, the only products isolable were aliphatic nitriles and not the expected phosphonium salts (Equation 7).

While the present dissertation study was in progress, reactions of Wittig reagents with activated double bonds became of interest. Reaction of fluorenone and n-butylidenetriphenylphosphorane gave spiro (2,3-di-n-propylcyclopropane-1,9'-fluorene)


(XI, Equation 8); the product being formed by addition of a second equivalent of the phosphorane to the expected 9-alkyldenefluorene.
\[
\text{CH-(CH}_2\text{)}_2\text{CH}_3 + \text{CH=CH-(CH}_2\text{)}_2\text{CH} = \text{CH-CH} = \text{CH}_{3}
\]
The course of reaction between Wittig reagents and activated double bonds was then found to be dependent upon the substituents of the phosphorane (Equation 9). The polar addition product (XII) could stabilize itself in two ways: 1) by formation of a cyclo-

\[
\text{II} \xrightarrow{a} \text{III} + \text{PhP} + \\
\text{II} \xrightarrow{b} \text{IV} + \text{PhP}
\]

propane with loss of triphenylphosphine (path a) or 2) through proton transfer, giving rise to a new ylide (path b). When R = alkyl or groups exhibiting a + I effect, path a was preferred. Resonance stabilized groups which introduce a - I effect allowed the reaction to proceed extensively by path b.
Treatment of styrene oxide, 1-octene oxide and cyclohexene oxide, respectively, with carboethoxymethylenetriphenylphosphorane (Equation 10) results in the corresponding cyclopropane derivatives: ethyl trans-2-phenylcyclopropanecarboxylate (21%), ethyl trans-2-hexylcyclopropanecarboxylate (46%) and ethyl norcaranecarboxylate (56%). $\alpha$-Carboethoxyethylidenetriphenylphosphorane (XIII) and benzoylmethylenetriphenylphosphorane (XIV) do not give cyclopropanes upon reaction with 1-octene oxide.

$$\text{CH}_3$$

$$\text{CH}_3$$

$$\text{C}_3\text{P}=\text{CH}-\text{C}=\text{O}$$

$$\text{C}_3\text{P}=\text{CH}-\text{C}=\text{O}$$

XIII

XIV

A similar synthesis of cyclopropanes has been reported from phosphonate carbanions (XV) and epoxides (Equation 11).

(13) D. Denney, J. Vill and M. Boskin, ibid., 84, 3944 (1962).

Dimethylsulfoxonium methylide (III), a sulfur ylide analog of a phosphorane has been prepared by treatment of trimethylsulfoxonium iodide with sodium hydride. The reagent, however, reacts with aldehydes and ketones to give epoxides (yields greater than $70\%$) and not olefins. In systems (activated double bonds) susceptible to Michael addition, a different mode of reaction results, formation of cyclopropanes (Equation 12).

$$\begin{align*}
\text{III} & \\
\text{(CH}_3\text{)}_2\text{S}=\text{CH}_2 & + \phi-\text{CH}=\text{CH-C-}\phi & \rightarrow & \text{C-}\phi
\end{align*}$$

The utility of III has been extended to functions other than $\alpha,\beta$-unsaturated ketones. Cyclopropanedicarboximides are formed readily from maleimides and III (Equation 13).


The scope of reaction of III was further expanded to include addition to activated carbon-nitrogen double bonds. Benzal-

\[(CH_3)_2S=CH_2 + \phi CH=N-N=CH\phi \rightarrow \phi CH=N-N-CH_2 \phi \]  

(13)


Diazine on reaction with III affords N-[2-phenylethlenimino-(1)]-benzaldimine (Equation 14).

\[(CH_3)_2S=CH_2 + \phi CH=N-N=CH\phi \rightarrow \phi CH=N-N-CH_2 \phi \]  

(14)


The reaction between III and amides of \(\alpha,\beta\)-unsaturated acids gave either pyrrolidones or cyclopropanecarboxylic acid amides as products (Equation 15). The best yields of pyrrolidone derivatives

\[III + R-CH=CH-C-N-R' \rightarrow \text{products} \]  

(15)
were obtained from acrylic acid arylamides. Cinnamic acid anilide
gave a mixture of pyrroldione and cyclopropanecarboxylic acid amide
in the ratio 3.5 to 1. Cinnamic amide yielded only the cyclopro-
pane derivative.

It has further been shown that III upon addition to cis or
trans conjugated sulfones gave only the trans isomer as product


(Equation 16). This, however, did not answer the question of

\[
\text{III} + \text{R'}-\text{CH}=\text{CH}-\text{SO}_2\text{R} \rightarrow \text{R} \downarrow \text{SO}_2\text{R}
\]

stereochemistry of addition conclusively for the authors also
found that the cis cyclopropylsulfone derivative isomerized com-
pletely to the trans isomer under the conditions of the reaction.

Other sulfur ylides have also been prepared. Dimethylsulfo-
nium methylide (XVI) \[(21)\] has been prepared and has been found to be

(1962).

an excellent and highly reactive reagent for selective synthesis of
oxiranes (Equation 17). Reaction of XVI with benzalaniline yields

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{S} = \text{CH}_2 + \phi-\text{CH} = \text{CH}-\phi & \rightarrow \phi-\text{CH} = \text{CH}-\text{C} = \text{CH}_2 \\
\text{XVI} & \downarrow
\end{align*}
\]
1,2-diphenylazirane (91%), whereas, III reacts more slowly and gives a mixture of products (Equation 18). Ylide XVI reacts

\[(\text{CH}_3)_2S=\text{CH}_2 + \phi\text{CH}=\text{N} - \phi \rightarrow \phi\text{CH} \rightarrow \text{N} - \phi + \phi\text{C}=\text{N} - \phi + \phi\text{CH}\text{N} - \phi\]  

III

\[(\text{CH}_3)_2S=0\]

with 1,1-diphenylethylene to give 1,1-diphenylcyclopropane (60%), whereas III does not react at all.

An additional sulfur ylide (XVII) has been prepared by treatment of benzylidiphenylsulfonylum tetrafluoroborate with n-


butyl lithium. Treatment of the ylide with acenaphthylene affords 7-phenyl-7H-6b,7a-dihydrocycloprop[a]acenaphthylene (Equation 19).

\[\phi_2S=\text{CH} - \phi + \text{acenaphthylene} \rightarrow \text{7-phenyl-7H-6b,7a-dihydrocycloprop[a]acenaphthylene}\]  

(19)
B. Synthesis of Conjugated Nitro Olefins and Nitrocyclopropanes.

Modern methods of preparing conjugated nitro olefins are not only inefficient and time consuming but also give rise to unconjugated nitro-olefins. The common methods of synthesizing

\[ \text{OH NO}_2 + \text{C} \xrightarrow{\Delta \text{Reduced Pressure}} \text{C} = \text{C NO}_2 \]  

(20)

conjugated nitro olefins are: (1) elimination of water from vicinal nitro alcohols (Equation 20), (2) base-catalyzed thermolysis of vicinal nitro acetates (Equation 21),

\[ \text{O-Ac NO}_2 + \text{NaOAc} \xrightarrow{\Delta \text{Reduced Pressure}} \text{C} = \text{C NO}_2 \]  

(21)


(25) D. Ley, Ph.D. Thesis, 1954, The Ohio State University, Columbus, Ohio.


(3) condensation of aromatic aldehydes with primary nitroalkanes in the presence of base (Equation 22) and (4) addition of

(28) L. Bouveault and A. Wohl, Compt. rend., 134, 1145 (1902).


\[
\phi\text{-C-H} + R\text{-CH}_2\text{-NO}_2 \xrightarrow{\text{NaOH}} \phi\text{CH} = \text{CR-NO}_2
\]  

(22)

dinitrogen tetraoxide to olefins followed by treatment of the reaction products with base (Equation 23).


\[
\text{C=O} + \text{N}_2\text{O}_4 \rightarrow \text{C-C} \xrightarrow{\text{Base}} \text{C=O} \text{NO}_2
\]  

(23)

or

The first nitrocyclopropane, 1-benzoyl-2-nitro-3-phenylcyclopropane (XVIII), was prepared as shown in the following scheme.
The nitrocyclopropane prepared (XVIII) was different in its behavior towards base than are ordinary nitroparaffins. Rather than form the expected nitronate anion (XVIII a), XVIII decomposed...
to phenylacetylacetophenone (XXI, Equation 25).

\[
\text{XVIII} + \text{NaOMe} \rightarrow \phi-\text{CH}_2-\text{C-CH}_2-\text{C-}\phi \quad (25)
\]

In order to study the action of bases on nitrocyclopropanes further, the following series of compounds were prepared: XXII, XXIII, XXIV, XXV and XXVI. The synthetic method for the compounds was the same as that used in the preparation of XVIII.


(b) E. P. Kohler and M. Srinivasa Rao, ibid., 41, 1697 (1919); E. P. Kohler and L. I. Smith, ibid., 44, 624 (1922).

(c) E. P. Kohler and P. Allen, ibid., 50, 884 (1928).

(d) E. P. Kohler and S. F. Darling, ibid., 52, 424 (1930).

(e) E. P. Kohler and S. F. Darling, ibid., 52, 1174 (1930).
Another study of the mechanism of the decomposition and rearrangement of nitrocyclopropanes with base resulted in the synthesis of a new series of nitrocyclopropanes, again prepared according to the method of Kohler: compounds XXXI, XXXII, XXXIII, XXXIV, XXXV, XXXVI, XXXVII, XXVIII, XXVII, XXVIII, and XXXIX.

(b) L. I. Smith and V. A. Engelhardt, ibid., 71, 2676 (1949).

(c) L. I. Smith and E. R. Rozier, ibid., 73, 3851 (1951).


(f) L. I. Smith and R. M. Sribmer, ibid., 78, 3412 (1956).

In a like manner, treatment of 1-halo-3-nitropropane with an alkali metal amide in liquid ammonia or with an alkali metal hydroxide, carbonate or bicarbonate in an inert solvent at 100-150° (Equation 27) results in the formation of nitrocyclopropane.
trans-1,2-Dinitro-3,3-dimethylcyclopropane (XL) \textsuperscript{37} was also synthesized by a procedure similar to that of Kohler (Equation 28).

\begin{equation}
\text{X-CH}_2\text{-CH}_2\text{-CH}_2\text{-NO}_2 + \text{LiNH}_2/\text{NH}_3 \rightarrow \text{NO}_2 \tag{27}
\end{equation}

or

\begin{equation}
\text{K}_2\text{CO}_3/\text{CH}_3; \Delta
\end{equation}

A different procedure for preparing other nitrocyclopropanes \textsuperscript{38} was not reported until it was found that vapor phase nitration of cyclopropane with nitric acid or nitrogen dioxide afforded the parent nitrocyclopropane (XLI). Its identity was confirmed by its
reduction with iron and hydrochloric acid to cyclopropylamine. Compound XLI was also found to lack reactivity with base.

Another approach to the synthesis of nitrocyclopropanes involves addition of diazomethane to conjugated nitro olefins.

\[ R'CH=CR'NO_2 + CH_2N_2 \rightarrow R-CH=CR'NO_2 + CH_2NNR' \xrightarrow{\text{Reaction 29}} R-CH=CR'NO_2 + CH_2N-NR' \]


The products of the reaction, however, were nitropyrazolines (XLII) and not nitrocyclopropanes (Equation 29).

Addition of 9-diazofluorene to β-nitrostyrene produced 2-nitro-3-phenylspiro-(cyclopropane-1,9'-fluorene)(XLIII) in 73% yield (Equation 30).

(40) S. Ranganathan, Ph.D. Thesis, 1962, The Ohio State University, Columbus, Ohio.
Addition of diazomethane to trisubstituted nitrobenzenes gave products which contained nitrocyclopropanes (Equation 31).

\[ \Phi CH=CH-NO_2 + \text{Product} \rightarrow \text{Product} \]  


Compound XLIV, trismethylene trinitrobenzene, was found to undergo oxidative decarboxylation with sodium dichromate to yield cis and trans nitrocyclopropanecarboxylic acid (XLV, Equation 32).

\[ \text{XLIII} \rightarrow \text{XLVa} \quad \text{XLVb} \]  

Compound XLVa was found to isomerize to XLVb by heating in sodium hydroxide solution at 100° for two hours.
RESULTS AND DISCUSSION

Part I. Attempted Preparation of Nitromethylenetriphenylphosphorane and Its Subsequent Reactions with Aldehydes and Ketones.

A study has been made of synthesis of nitromethylenetriphenylphosphorane (I) as a possible precursor for the conversion of aldehydes and ketones to terminal nitromethylene derivatives (Equation 33). The selected synthetic scheme involved reaction

\[
\begin{align*}
\text{I} & \quad \text{P} = \text{CH-NO}_2 + \text{R-C-H} (R') \rightarrow \text{R-CH-C=CH-NO}_2 + \text{P}=\text{O} \\
& \quad \text{I} \quad \text{X} 
\end{align*}
\]

of triphenylphosphine with bromonitromethane (Equation 34) to produce nitromethyltriphenylphosphonium bromide (X) and its subsequent reaction with base (Equation 35).

\[
\begin{align*}
\text{I} & \quad \text{P} + \text{Br-CH}_2\text{-NO}_2 \rightarrow \text{P} = \text{CH}_2\text{-NO}_2 \\
& \quad \text{I} \quad \text{X} 
\end{align*}
\]

The reaction of triphenylphosphine and bromonitromethane gave a white solid whose infrared spectrum showed it to have a
major absorption at 6.2 μ. Attempted recrystallization of the
product gave a highly explosive material from which only triphenyl-
phosphine oxide could be isolated. While this investigation was
in progress, the preparation of X was reported. Attempts to
duplicate this work were unsuccessful; only the forementioned pro-
duct could be isolated.

Since there was a possibility that the phosphonium salt X was
oxygen sensitive, reaction of triphenylphosphine with bromonitro-
methane was carried out under a nitrogen atmosphere and isolation
of the product was not attempted. The reaction product was treated
with potassium t-butoxide and then with benzaldehyde. Again, no
product save triphenylphosphine oxide was isolated.

Further expansion of this investigation to include reaction of
triphenylphosphine with 1-bromo-1-nitroethane was also without suc-
cess. α-Nitroethyltriphenylphosphonium bromide (XLVI, Equation 36)
could not be prepared and only triphenylphosphine oxide was iso-
lated from the reaction product.

\[
\text{C}_6\text{H}_5\text{P} + \text{CH}_3\text{-CHBr-NO}_2 \xrightarrow{\text{H}} \text{C}_6\text{H}_5\text{P}\text{-CH-CH}_3
\]

(36)

XLVI

It became evident from these findings that attack of the tri-
phenylphosphine was not on the carbon atom but on the oxygen of the
nitro group. It is also of interest to note that after our inves-
tigation was terminated, Trippett has since repudiated his initial
work and has found that the reaction of triphenylphosphine with bromonitromethane does not give the expected phosphonium salt X but hydroxyiminomethyltriphenylphosphonium bromide (XLVII, Equation 37).

\[
2\phi_3P + Br-CH_2-NO_2 \rightarrow \phi_3P=O + \phi_3P-CH=NOH \quad (37)
\]

XLVII
Part II. Reactions of Conjugated Nitro Olefins with Phosphoranes and with Dimethylsulfoxonium Methyldide to Give Ylides and Nitrocyclopropanes, Respectively.

A. Reactions of Conjugated Nitro Olefins with Carbethoxymethyl-enetriphenylphosphorane.

A study has been made of reactions of various conjugated nitro olefins with carbethoxymethyl-enetriphenylphosphorane (XLVIII). The initial objective of this investigation was to determine if addition of the phosphorane (XLVIII) and nitro olefins occurs (Equation 38) with expulsion of triphenylphosphine to yield substituted nitrocyclopropanes (path c) and/or the isomeric isoxazoline oxides (path d).

\[
\begin{align*}
R_1\text{C}=\text{C(NO}_2\text{)}R_2R_3 + \Phi_3\text{P}=\text{CH-CO}_2\text{CH}_3 & \rightarrow \Phi_3\text{P}-\text{CH-}R_1R_2C\text{-NO}_2 \\
\text{XLVIII} & \quad \text{XLIX} \\
\end{align*}
\]

(38)
The first system investigated was 2-nitro-1-phenylpropene and XLVIII in toluene at 90°. Addition of the phosphorane to the conjugated nitro olefin occurs readily with subsequent proton-transfer (Equation 39) to give methyl β-(1-nitroethyl)-α-(triphenylphosphoranylidenec)hydrocinnamate (L) in 49% yield. The structure (L) of

\[
\begin{align*}
\phi_3P=CH-CO_2CH_3 & \quad \phi_3P=CH-CH-C=NO_2 & \quad \phi_3P=C-CH-CH-NO_2 \\
\phi_3P=CH-CH-C=NO_2 & \quad \phi_3P=CH-CH-C=NO_2
\end{align*}
\]

(39)

the product is assigned on the basis of analytical and spectral data which will be discussed subsequently.

To determine possible electrical effects of β-substituents in conjugated nitro olefins in reaction with XLVIII and to see if ring closure to give cyclopropanes might occur before proton-transfer, reaction of XLVIII and 1-nitropropene was investigated. Addition and proton-transfer take place, however, to give methyl β-methyl-4-nitro-2-(triphenylphosphorylidenel)butyrate (LI, Equation 40).

\[
\begin{align*}
\phi_3P=CH-CO_2CH_3 & \quad CO_2CH_3 & \quad CH_3 \\
\phi_3P=CH-CH-C-NO_2 & \quad \phi_3P=CH-CH-C-NO_2 & \quad \phi_3P=C-CH-CH-NO_2 \\
\phi_3P=CH-CH-C-NO_2 & \quad \phi_3P=CH-CH-C-NO_2
\end{align*}
\]

(40)

Subsequent reactions of XLVIII with β-nitrostyrene, 2-nitropropene, 2-nitro-2-butene, α-nitrostilbene and 2-(2-nitrovinyl)furan occur similarly (Equation 41) by Michael-addition and proton-transfer to
\[
\Phi_3\text{P}=\text{CH-}\text{CO}_2\text{CH}_3 + R_1\text{CH}=\text{CR}_2\text{-NO}_2 \rightarrow \Phi_3\text{P}-\text{CH-CH-}\overset{\Theta}{\text{O}}\text{O}_2
\]

\[R_1=\text{CH}_3, \phi, \overset{0}{\text{O}}; R_2=\text{H} \]
\[R_1=\text{H}, \text{CH}_3; R_2=\text{CH}_3 \]
\[R_1=\phi; R_2=\phi, \text{CH}_3 \]

(41)

\[\Phi_3\text{P}=\text{CH-CH-NO}_2 \rightarrow \Phi_3\text{P}-\text{C-CH-CH-NO}_2 \leftrightarrow \Phi_3\text{P}=\text{C-CH-CH-NO}_2 \]

\[R_1=\text{CH}_3, \phi, \overset{0}{\text{O}}; R_2=\text{H} \]
\[R_1=\text{H}, \text{CH}_3; R_2=\text{CH}_3 \]
\[R_1=\phi; R_2=\phi, \text{CH}_3 \]

LIII

generate new phosphorous ylides (LIII). The products, their structures and the yields obtained in this study are summarized in Table I. Attempts to isolate possible isomers were not made. The phosphorous ylides (LIII) prepared by this method are stable green-white solids which can be recrystallized conveniently from hydrocarbons and from ethyl acetate. The structures of the various products are assigned on the basis of their infrared (Tables II and III) and ultraviolet (Tables IV and V) absorptions.

The infrared absorption of the phosphoranes indicate that the nitro groups are present as such (LIII) and not as their nitronate anions as indicated in structures LII. The products exhibit absorption for nitro groups at 6.48-6.51 \(\mu\); if their structures are
Table I

Phosphoranes Derived from Reaction of Carbomethoxymethyleneetriphenylphosphorane and Various Conjugated Nitro Olefins.

<table>
<thead>
<tr>
<th>Starting Nitro Olefin</th>
<th>Product</th>
<th>M.P.</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>CO₂CH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \phi-\text{CH}=\text{C-NO}_2 )</td>
<td>( \phi_3\text{P=C-CH-CH-NO}_2 ) L</td>
<td>204-207° (dec.)</td>
<td>49</td>
</tr>
<tr>
<td>CH₃-CH=CH-NO₂</td>
<td>CO₂CH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \phi-\text{CH}=\text{C-NO}_2 )</td>
<td>( \phi_3\text{P=C-CH-CH}_2\text{-NO}_2 ) LI</td>
<td>164-166° (dec.)</td>
<td>33</td>
</tr>
<tr>
<td>( \phi-\text{CH}=\text{C-NO}_2 )</td>
<td>( \phi_3\text{P=C-CH}-\text{CH}_2\text{-NO}_2 ) LIV</td>
<td>180-181° (dec.)</td>
<td>23</td>
</tr>
<tr>
<td>( \phi-\text{CH}=\text{C-NO}_2 )</td>
<td>( \phi_3\text{P=C-CH-CH}_2\text{-NO}_2 ) LV</td>
<td>173-174° (dec.)</td>
<td>28</td>
</tr>
<tr>
<td>( \phi-\text{CH}=\text{C-NO}_2 )</td>
<td>( \phi_3\text{P=C-CH-CH}_2\text{-NO}_2 ) LVI</td>
<td>162-164° (dec.)</td>
<td>57</td>
</tr>
<tr>
<td>Starting Nitro Olefin</td>
<td>Product</td>
<td>M.P.</td>
<td>% Yield</td>
</tr>
<tr>
<td>----------------------</td>
<td>---------</td>
<td>---------------</td>
<td>---------</td>
</tr>
<tr>
<td>CH$_3$-CH=C-NO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO$_2$CH$_3$</td>
<td>193.5-195.5$^\circ$ (dec.)</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>$\phi_3$P=O-CH—CH-CH-NO$_2$ LVII</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$CH-CH=CH-NO$_2$</td>
<td>CO$_2$CH$_3$</td>
<td>184.5-185.5$^\circ$ (dec.)</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>$\phi_3$P=O-CH-CH$_2$-NO$_2$ LVIII</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table II

Infrared Absorption of Phosphoranes Derived from Reaction of XLVIII and Conjugated Nitro Olefins.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbonyl</td>
</tr>
<tr>
<td>L</td>
<td>6.17</td>
</tr>
<tr>
<td>LI</td>
<td>6.14</td>
</tr>
<tr>
<td>LIV</td>
<td>6.17</td>
</tr>
<tr>
<td>LV</td>
<td>6.14</td>
</tr>
<tr>
<td>LVI</td>
<td>6.13</td>
</tr>
<tr>
<td>LVII</td>
<td>6.13</td>
</tr>
<tr>
<td>LVIII</td>
<td>6.23</td>
</tr>
</tbody>
</table>
Table III

Infrared Absorption of Related Phosphoranes and Phosphonium Salts.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbonyl Absorption (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi_3 P=CH-CO_2CH_3 )</td>
<td>XLVIII</td>
</tr>
<tr>
<td>( CH_3 )</td>
<td></td>
</tr>
<tr>
<td>( \phi_3 P=C-CO_2CH_3 )</td>
<td>LIX</td>
</tr>
<tr>
<td>( \phi_3 P=CH-C-CH_3 ) ( \phi )</td>
<td>LX</td>
</tr>
<tr>
<td>( \phi_3 P=CH-C-\phi ) ( \phi )</td>
<td>LXI</td>
</tr>
<tr>
<td>( \phi_3 P-CH_2-CO_2CH_3 ) ( \theta )</td>
<td>LXII</td>
</tr>
<tr>
<td>( Br )</td>
<td></td>
</tr>
<tr>
<td>( CH_3 )</td>
<td></td>
</tr>
<tr>
<td>( \phi_3 P-CH-CO_2CH_3 ) ( \theta )</td>
<td>LXIII</td>
</tr>
<tr>
<td>( Br )</td>
<td></td>
</tr>
<tr>
<td>( \phi_3 P-CH_2-C-CH_3 ) ( \phi ) ( \theta )</td>
<td>LXIV</td>
</tr>
<tr>
<td>( X ) (X=Cl, I)</td>
<td></td>
</tr>
<tr>
<td>( \phi_3 P-CH_2-C-\phi ) ( \phi ) ( \theta )</td>
<td>LXV</td>
</tr>
<tr>
<td>( X ) (X=Br, I)</td>
<td></td>
</tr>
</tbody>
</table>

Table IV
Ultraviolet Absorption of the Phosphoranes Derived from Reaction of XLVIII and Conjugated Nitro Olefins.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength (95% Ethanol)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>223-224</td>
<td>42,600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>262</td>
<td>5,600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>267</td>
<td>6,600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>274</td>
<td>6,900</td>
<td></td>
</tr>
<tr>
<td></td>
<td>309-312</td>
<td>10,300</td>
<td></td>
</tr>
<tr>
<td>LI</td>
<td>224.5</td>
<td>37,600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>261</td>
<td>5,700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>5,600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>273</td>
<td>4,800</td>
<td></td>
</tr>
<tr>
<td>LIV</td>
<td>225</td>
<td>39,100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>261</td>
<td>5,700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>6,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>273</td>
<td>5,500</td>
<td></td>
</tr>
<tr>
<td></td>
<td>304-311</td>
<td>5,400</td>
<td></td>
</tr>
<tr>
<td>LV</td>
<td>223</td>
<td>38,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>261</td>
<td>6,200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>267</td>
<td>5,800</td>
<td></td>
</tr>
<tr>
<td></td>
<td>273</td>
<td>4,800</td>
<td></td>
</tr>
<tr>
<td>LVI</td>
<td>225</td>
<td>38,700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>261</td>
<td>5,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>266.5</td>
<td>5,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>273.5</td>
<td>4,400</td>
<td></td>
</tr>
<tr>
<td>LVII</td>
<td>225</td>
<td>32,200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>260.5</td>
<td>5,100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>267</td>
<td>5,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>273.5</td>
<td>4,200</td>
<td></td>
</tr>
<tr>
<td>LVIII</td>
<td>225</td>
<td>28,400</td>
<td></td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>4,500</td>
<td></td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>4,300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>273</td>
<td>3,700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>347</td>
<td>6,800</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Wavelength (95% Ethanol)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\varepsilon_{\text{max}}$</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------</td>
<td>-----------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>XLVIII</td>
<td>223-225</td>
<td>225</td>
<td>21,200</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>260</td>
<td>1,300</td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>266</td>
<td>1,700</td>
</tr>
<tr>
<td></td>
<td>272.5</td>
<td>272.5</td>
<td>1,400</td>
</tr>
<tr>
<td>LIX</td>
<td>224</td>
<td>224</td>
<td>32,100</td>
</tr>
<tr>
<td></td>
<td>260.5</td>
<td>260.5</td>
<td>1,800</td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>266</td>
<td>2,300</td>
</tr>
<tr>
<td></td>
<td>273</td>
<td>273</td>
<td>1,900</td>
</tr>
<tr>
<td>LIX$^4$</td>
<td>268</td>
<td>268</td>
<td>6,600</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>275</td>
<td>6,500</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>288</td>
<td>5,700</td>
</tr>
<tr>
<td>LXI</td>
<td>225</td>
<td>225</td>
<td>33,000</td>
</tr>
<tr>
<td></td>
<td>268.5</td>
<td>268.5</td>
<td>5,600</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>275</td>
<td>5,800</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>320</td>
<td>11,800</td>
</tr>
</tbody>
</table>
LII, nitronate ion absorption is expected at lower wave lengths


(6.2 μ). The present phosphoranes also exhibit carbonyl absorption at 6.13-6.25 μ. These absorptions are anticipated for conjugated carbonyl groups and are similar to those found (Table III) in carboxomethoxymethylene triphenylphosphorane (6.17 μ, XLVIII) and α-carboxomethoxymethylene triphenylphosphorane (6.23 μ, LIX). The carbonyl absorptions also resemble more closely those reported for phosphoranes than for phosphonium salts (Table III).

A lowering in absorption of the carbonyl frequency is reported when the phosphonium salts, LXIV and LXV (Table III),


are converted to the corresponding ylides, LX and LXI. The lower carbonyl frequencies stem from the resonance in the conjugate ylides.

\[
\begin{align*}
\text{P} & \equiv \text{CH-C-R} \
\text{P-GH-C-R} & \equiv \text{O} \
\text{P} & \equiv \text{CH=C-R} \
\end{align*}
\]

A shift in absorption to longer wave length for the cyano group (4.42 μ to 4.60 μ) also occurs when the cyanomethyltriphenylphosphonium chloride (LXVI) is converted to cyanomethylenetriphenylphosphorane (LXVII) (Equation 42).

\[
\begin{align*}
\text{P}\equiv\text{CH}=\text{CN} & \xrightarrow{\text{Base}} \text{P}\equiv\text{CH-CN} \\
\text{LXVI} & \xrightarrow{\text{Cl}} \text{LXVII}
\end{align*}
\]

The ultraviolet absorption of the phosphoranes of the present study (Tables IV and V) also indicate that the nitro groups are present as assigned (III) and not as nitronate anions. The products exhibit absorption in 95% ethanol at λ max 223-225 μ, ε max 28,400-42,600; 260-262, 1300-6200; 266-267, 1700-6600; and 273, 1400-6900. If the products were the dipolar adducts III, there

\[\text{(49)(a) Aliphatic nitro compounds exhibit a principal absorption banded at 270-280 μ; the absorption is of low intensity (ε ca. 15-30). (b) H. E. Ungnade and R. A. Smiley, J. Org. Chem., 21, 995 (1956).}\]

should be strong ultraviolet absorption for alkanenitronate groups at ~223-234 μ (9,000-11,000) or for arylmethanenitronate ion at

\[ \sim 291 \text{m} \mu (12,000) \]. The present phosphoranes also exhibit similar ultraviolet absorption to those found in related compounds (Table V).

To demonstrate chemically that the products isolated are ylides (LIII) rather than polar (Michael) adducts (LII), the product (LVI) of 2-nitropropene with XLVIII was brominated (Equation 43). The bromination product exhibits carbonyl and nitro absorptions at 5.81 \( \mu \) and 6.48 \( \mu \) respectively; there is no shift in the initial nitro absorption. If LIIa is the correct structure, then LXIX would be expected to be the reaction product. This product,
however, does not explain the spectral properties observed. No shift in the wave length of the carbonyl absorption would be expected in LXIX since the carbonyl group in the reactant and the product should have similar stretching vibrations. A shift in the nitro absorption to a lower wave length (≈ 6.37 μ) is also expected because of the electron-withdrawing ability of bromine in α-bromo-α-nitro structures.


Structure LXVIII is assigned therefore to the product of bromination of LVI since it fulfills the demands of the spectral data. Furthermore, when the bromination product is treated with base, only the phosphorane (LVI) (Equation 44) is isolated from the reaction mixture. If LXIX were the correct structure of the bromination product, a phosphorane (LXX) containing bromine would have been formed (Equation 45).

\[
\begin{align*}
\text{LXVIII} & \quad \text{LVI} \\
\phi_3P-\text{C}-\text{CH}_2-\text{CH}-\text{NO}_2 + \text{Na}_2\text{CO}_3 & \quad \phi_3P=\text{C}-\text{CH}_2-\text{CH}-\text{NO}_2 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{LXIX} & \quad \text{LXX} \\
\phi_3P-\text{CH}-\text{CH}_2-\text{C}-\text{NO}_2 + \text{Na}_2\text{CO}_3 & \quad \phi_3P=\text{C}-\text{CH}_2-\text{C}-\text{NO}_2 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]
The new phosphoranes (L-LVIII) are of limited value with respect to the interests of the present dissertation. Attempts were made to effect thermal decomposition of L and LI to nitrocyclopropanes via reverse proton-transfer and elimination of triphenylphosphine (Equation 46). However, adducts L and LI are stable in refluxing xylene for 5 days. Small amounts of triphenylphosphine oxide and decomposition products which do not contain nitro groups are formed in these experiments; however, the principal products are the initial phosphoranes. It is thus apparent that the equilibrium reaction indicated in Equation 46 is overwhelmingly in favor of the initial ylide (L or LI).

A study was made of the possible utility of LI and LIV as ylide reagents for reactions with activated aldehydes (Equations 47 and 48). Reaction of m-nitrobenzaldehyde with LI and LIV,
however, were found to yield the same product, methyl m-nitro-cinnamate (Equation 49). It is apparent that normal ylide reactions of LI and LIV do not occur and that the phosphoranes undergo proton-transfer reversal and reverse Michael addition to generate carbomethoxymethylene triphenylphosphorane and the conjugated nitro olefins (Equation 50). Reaction of m-nitrobenzaldehyde and

$$\text{LI or LIV} + \text{CH}=\text{CH}-\text{CO}_2\text{CH}_3 \rightarrow \text{CH}=\text{CH}-\text{CO}_2\text{CH}_3$$  (49)
carbomethoxymethylenetriphenylphosphorane then yields methyl m-
nitrocinamnate (LXXI). The lack of direct reactivity of LI and
LIV as ylide reagents with aldehydes probably stems from steric
factors.

Reversal reactions for other phosphoranes containing strong
electron withdrawing groups in the $\alpha$-position to the phosphorous-
carbon double bond (Equation 51) have been reported.\(^5\)

$$
\begin{align*}
\phi_3P=CH-CN & \quad + \quad \text{EtO-CH=C(CO}_2\text{Et)}_2 \quad \rightarrow \quad \phi_3P-\text{CH-CH-C(CO}_2\text{Et)}_2 \\
\phi_3P-\text{CH-CH-C(CO}_2\text{Et)}_2 & \quad \text{-EtOH} \quad \rightarrow \quad \phi_3P=C-\text{CH=C(CO}_2\text{Et)}_2
\end{align*}
$$

(Equation 51)


It has also been reported\(^4,5\) that phosphoranes hydrolyze
to triphenylphosphine oxide and the corresponding alkyl derivatives


$$
\begin{align*}
\phi_3P=\text{C} & \quad + \quad \text{H}_2\text{O} \quad \rightarrow \quad \phi_3P-O \\
\phi_3P-O & \quad + \quad \text{H}_2\text{C} & \quad \text{C} & \quad \text{X} & \quad \text{Y} \\
\end{align*}
$$

(Equation 52). Hydrolysis of methyl $\beta$-(nitromethyl)-$\alpha$-triphenyl-
phosphoranyliden)-hydrocinanmate (LIV) was attempted with trace
amounts of aqueous base in order to prepare methyl 4-nitro-3-
phenylbutyrate (Equation 53). Triphenylphosphine oxide is formed

\[
\phi_3\text{P}=\text{C}-\text{CH}-\text{CH}_2-\text{NO}_2 + \text{H}_2\text{O} \rightarrow \phi_3\text{P}=\text{O} + \text{CH}_3\text{O}_2\text{C}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{NO}_2 \quad (53)
\]

but the organic product did not contain a nitro group and underwent extensive decomposition.


54. Oxidation of LIV with peracetic acid was studied (Equation 55) in an effort to prepare methyl 2-keto-4-nitro-3-phenylbutyrate.

\[
\phi_3\text{P}=\text{C}-\phi + \text{CH}_3-\text{C}=\text{O}-\text{O}-\text{H} \rightarrow \phi_3\text{P}=\text{O} + \phi-\text{C}-\text{C}-\phi \quad (54)
\]

\[
\phi_3\text{P}=\text{C}-\text{CH}-\text{CH}_2-\text{NO}_2 + \text{CH}_3\text{CO}_2\text{H} \rightarrow \phi_3\text{P}=\text{O} + \text{CH}_3\text{O}_2\text{C}-\text{C}-\text{CH}-\text{CH}_2-\text{NO}_2 \quad (55)
\]

Reaction of LIV occurred with peracetic acid to give triphenylphosphine oxide; however, the desired product was not obtained. The products isolated did not contain nitro groups and the initial oxidation products apparently had undergone loss of nitrous acid.
Reactions of α-carbomethoxyethylidenetriphenylphosphorane (LIX), acetonylidenetriphenylphosphorane (LX), phenacylidenetriphenylphosphorane (LXI) and cyanomethylenetriphenylphosphorane (LXVII) with conjugated nitro olefins were also studied in this investigation. Reaction of LIX with omega-nitrostyrene (Equation 56) was carried out in an attempt to prepare a polar adduct (LXXII)

\[
\begin{align*}
\text{CH}_3 \\
\Phi_3\text{P} &\text{C-CO}_2\text{CH}_3 \\
+ & \phi\text{CH=CH-NO}_2 \\
\rightarrow & \Phi_3\text{P} \text{C-CH-CH-NO}_2 \\
\text{LIX} & \text{LXXII}
\end{align*}
\]

which was not capable of proton-transfer to a new ylide and which might undergo loss of triphenylphosphine to form a nitrocyclopropane (LXXIII). Triphenylphosphine oxide was isolated from the reaction; however, the desired product was not obtained. Omega-Nitrostyrene polymer, produced in high yield, was the only organic product identified from the reaction mixture. Phosphonium nitronates (LXXII) which do not self-neutralize to nitroalkyl phosphoranes (LIII) thus continue Michael addition to conjugated nitro olefins (Equation 57) to give multiple adducts (LXXIV).
Reaction of acetonylidinetriphenylphosphorane (LX) with omega-nitrostyrene was also carried out (Equation 58) in an effort to prepare a new class of nitro substituted phosphoranes (LXXVI). No product save triphenylphosphine oxide and omega-nitrostyrene polymer were isolated from the reaction material. Subsequent studies of reactions of phenacylidenetriphenylphosphorane (LXI) and cyano-methyleneetriphenylphosphorane (LXVII) with conjugated nitro olefins led only to decomposition of the starting phosphoranes and polymerization of the nitro olefins.

Denney has reported that LIX and LX do not react with epoxides whereas XLVIII does (Equation 59). He postulated that the difference was in the nucleophilicity of the attacking agent. Compounds LIX and LX have groups present which destabilize the
ionic character of the phosphorane in such a manner that no nucleophilic attack could take place on the epoxide.

B. Reactions of Conjugated Nitro Olefins with Methylene-diphenyl-phosphorane.

A study has been made of reactions of various conjugated nitro olefins with methylenetripheny1phosphorane (LXXVII). The initial objective of this investigation was to determine if addition of the phosphorane (LXXVII) to nitro olefins occurs (Equation 61) with expulsion of triphenylphosphine to yield substituted nitrocyclopropanes (LXXIX, path e) or with proton transfer to form a new ylide (LXXX, path f).

\[
\begin{align*}
\Phi_3P=CH-CO_2CH_3 + R-CHCH_2 & \rightarrow \Phi_3PCH_2-CH_2-CH\equivNO_2 \\
\text{LXXVII} & \\
\Phi_3P=CH_2 + R-CH=CH\equivNO_2 & \rightarrow \Phi_3PCH_2-CH-CH\equivNO_2 \\
\text{LXXXVII} & \\
\end{align*}
\]

\[
\begin{align*}
\Phi_3P=CH-CH\equivNO_2 + \Phi_3P \rightarrow \Phi_3P=CH-CH-CH_2NO_2 \\
\text{LXXIX} & \\
\Phi_3P=CH-CH\equivCH-NO_2 \rightarrow \Phi_3P=CH_2-CH-CH\equivNO_2 \\
\text{LXXX} & \\
\end{align*}
\]
The first system investigated was 1-nitropropene and LXXVII in anhydrous dimethyl sulfoxide at 10°. Addition of LXXVII to the conjugated nitro olefin occurs with expulsion of triphenylphosphine to give 2-methyl-1-nitrocyclopropane (LXXXI, Equation 61) in poor yield (5%); however, there is extensive Michael polymerization (LXXXII) of the nitro olefin under these conditions along with conversion of the phosphorus-containing materials to triphenylphosphine oxide. The structure of the product is assigned on the basis of analytical and spectral data. The stereochemistry of the products will be discussed in the succeeding section.

Reaction of LXXVII with 2-nitro-2-buten gives 1,2-dimethyl-1-nitrocyclopropane (LXXXIII, Equation 62) also in poor yield (7%).

The poor yields of product may be attributed to the extensive Michael polymerization of the conjugated nitro olefins under the conditions of the reaction. It is apparent that the rate of ring
closure and expulsion of triphenylphosphine is slower than that of poly-Michael addition. A cyclopropane is not obtained when 2-nitropropene reacts with LXXVII; polymerization of the nitro olefin under these conditions is essentially quantitative.

Ethylidenetriphenylphosphorane (LXXXIV) fails to react with β-nitrostyrene, 1-nitropropene and 2-nitro-1-butene to give cyclopropanes. Extensive polymerization and decomposition of the conjugated nitro olefins results under the experimental conditions. The conditions for formation of nitrocyclopropanes from either methylenetriphenylphosphorane (LXXVII) or ethylidenetriphenylphosphorane (LXXXIV) were not optimized because of the greater promise of dimethylsulfoxonium methylide (III) as a reagent.

C. Reaction of Conjugated Nitro Olefins with Dimethylsulfoxonium Methylide.

A study was then made of reactions of various conjugated nitro olefins with dimethylsulfoxonium methylide (III). Reaction of III with conjugated nitro olefins in anhydrous dimethylsulfoxide at 0-10° (Equation 63) gives nitrocyclopropanes (LXXIX) in good yields (40-50%). The products are usually isolable and purifiable without complication.
The first system investigated was reaction of 1-nitropropene with 10% excess III (Equation 64) at 0-10° to give 2-methyl-1-

\[
\text{(CH}_3\text{)}_2\text{S}=\text{CH}_2 + \text{R-CH}=\text{CH-NO}_2 \rightarrow \text{(CH}_3\text{)}_2\text{S}-\text{CH}_2-\text{CH-CH-NO}_2
\]

Equation 65

\[
\text{III} \ \rightarrow \ \text{LXXXV} \rightarrow \ \text{LXXXIX} \ + \ \text{(CH}_3\text{)}_2\text{S}=\text{O}
\]

The first system investigated was reaction of 1-nitropropene with 10% excess III (Equation 64) at 0-10° to give 2-methyl-1-
nitrocyclopropane (LXXXI) in 31% yield. Attempts to isolate other products were not made. Subsequent reactions of III with 2-nitro-2-butene, 2-nitrostyrene, 1-nitro-1-butene and 1-nitro-1-pentene occur similarly to give the corresponding nitrocyclopropanes (Equation 65). The nitrocyclopropanes (Table VI) are colorless, pleasant liquids stable to storage, insoluble in aqueous bases and readily separable from their parent nitro olefins by distillation methods.
Table VI
Nitrocyclopropanes Derived from Reaction of Dimethylsulfoxonium Methyldie with Various Conjugated Nitro Olefins.

<table>
<thead>
<tr>
<th>Starting Nitro Olefin</th>
<th>Product</th>
<th>B.P.</th>
<th>% Yield*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃-CH=CH-NO₂</td>
<td><img src="" alt="LXXXI" /></td>
<td>69°/30 mm</td>
<td>31</td>
</tr>
<tr>
<td>CH₃-CH=C(CH₃):NO₂</td>
<td><img src="" alt="LXXXII" /></td>
<td>70°/20 mm</td>
<td>37</td>
</tr>
<tr>
<td>CH₂=C(CH₃):NO₂</td>
<td><img src="" alt="LXXXVI" /></td>
<td>80°/22 mm</td>
<td>8 (Impure Sample)</td>
</tr>
</tbody>
</table>

*The actual yields are much higher; the values reported are those for multiply distilled analytical samples.
Table VI (continued)

<table>
<thead>
<tr>
<th>Starting Nitro Olefin</th>
<th>Product</th>
<th>B.P.</th>
<th>% Yield*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃-CH₂-CH=CH-NO₂</td>
<td>LXXXVII</td>
<td>62°/10 mm</td>
<td>40</td>
</tr>
<tr>
<td>CH₃-CH₂-CH₂-CH=CH-NO₂</td>
<td>LXXXVIII</td>
<td>76°/11 mm</td>
<td>43</td>
</tr>
<tr>
<td>φCH=CH-NO₂</td>
<td>LXXXIX</td>
<td>85-87°/1 mm</td>
<td>44</td>
</tr>
</tbody>
</table>

*The actual yields are much higher; the values reported are those for multiply distilled analytical samples.
(55)(a) The resistance of conversion of 2-methyl-1-nitrocyclopropane to its corresponding nitronate ion is also indicated by the observation that the ultraviolet absorption of the nitrocyclopropane is unchanged in homogeneous solution upon addition of excess base. (b) C. Kaiser, B. M. Trout, J. Beeson and J. Weinstock, J. Org. Chem., 30, 3972 (1965).

Conversion of 2-nitropropene into 1-methyl-1-nitrocyclopropane (LXXXVI, Equation 66) with III at 0-10° was inefficient, however, because of extensive polymerization of the nitro olefin

\[
\begin{align*}
\text{CH}_2=\text{O}-\text{CH}_3 + (\text{CH}_3)_2\text{S}=\text{CH}_2 & \rightarrow \\
\text{III} & \rightarrow \\
\text{LXXXVI}
\end{align*}
\]

by III. This was not too surprising in that 2-nitropropene is known to polymerize in the presence of anions.

The spectral properties (Table VII) of the nitrocyclopropanes are of some note. The nitrocyclopropanes in which the nitro groups are at secondary carbon (LXXXI, LXXXVII, LXXXVIII and LXXXIX) exhibit absorption at 6.48-6.49 μ and 7.33-7.34 μ; their absorptions thus occur in general at longer wave lengths than do secondary aliphatic nitro compounds (6.38-6.47 μ and 7.22-7.35 μ).  

Table VII

Infrared and Ultraviolet Absorption of the Nitrocyclopropanes

Derived from Reaction of Dimethylsulfoxonium Methyldide

with Various Conjugated Nitro Olefins.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR Absorption, μm</th>
<th>UV Absorption, nm (ε max) (in 95% Ethanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LXXXI</td>
<td>6.48, 7.34</td>
<td>219 (6650)</td>
</tr>
<tr>
<td>LXXXIII</td>
<td>6.51, 7.39</td>
<td>216 (6236)</td>
</tr>
<tr>
<td>LXXXVI</td>
<td>6.52, 7.41</td>
<td>215 (--) (Impure)</td>
</tr>
<tr>
<td>LXXXVII</td>
<td>6.48, 7.33</td>
<td>219 (6950)</td>
</tr>
<tr>
<td>LXXXVIII</td>
<td>6.49, 7.33</td>
<td>219 (6445)</td>
</tr>
<tr>
<td>LXXXIX</td>
<td>6.49, 7.34</td>
<td>213 (11,230) 252 (8,230)</td>
</tr>
</tbody>
</table>
Ultraviolet absorption of the nitrocyclopropanes (Table VII) occurs with intensity ($\epsilon$ max $\sim 6,000$) in the 213-219 m$\mu$ in 95% ethanol. Since nitroalkanes and conjugated nitroalkenes exhibit $\pi \rightarrow \pi^*$ bands at $\sim 210$ m$\mu$ and at 220-250 m$\mu$ ($\epsilon$ max 3,300-12,400).

respectively, it is thus apparent that there is an appreciable conjugative effect in nitrocyclopropanes.

The $\alpha$-nitro-$\beta$-substituted cyclopropanes presently prepared are apparently of trans-stereochemistry. It has been shown that ethyl trans-cinnamate (Equation 67) and trans-N,N-dimethylcinnamide (Equation 68) react with III to give ethyl trans-2-phenylcyclopropanecarboxylate (XC, 98.9% stereoselective) and trans-N,N-dimethyl-2-phenylcyclopropanecarboxamide (XCI, 100% stereoselective). Ethyl cis and trans-2-phenylcyclopropanecarboxylate are not epimerized by the above reaction environment.

\[
\begin{align*}
\phi &\quad C=CH_2 \quad CO_2CH_2CH_3 \\
&\quad H \quad \rightarrow \quad \phi \\
&\quad \left(\text{CH}_3\right)_2C=CH_2
\end{align*}
\]

(67)
The reaction of trans-cinnamonic nitrile with III, however, is not as stereoselective and gives a mixture of trans (73%) and cis (28%) 2-phenylcyclopropanecarbonitriles (Equation 69). The size of the cyano group is small enough to allow an appreciable amount of cis-cyclopropane derivative to form.

\[ \Phi\text{C} = \text{C} \quad \text{H} \quad \Phi - \text{N(CH}_3\text{)}_2 \quad + \quad (\text{CH}_3\text{)}_2\text{S} = \text{CH}_2 \quad \rightarrow \quad \Phi \quad \text{C} = \text{N}\text{(CH}_3\text{)}_2 \]

(68) (XCl)

It has also been shown that trans-phenyl \( \omega \)-styryl sulfone and III yield only trans-1-phenyl-2-phenylsulfonylcyclopropane (XCII, Equation 70); cis-1-phenyl-2-phenylsulfonylcyclopropane is isomerized nearly quantitatively, however, to its trans isomer under the conditions for addition of III to the trans-sulfone.

\[ \Phi\text{C} = \text{C} \quad \text{H} \quad \Phi - \text{SO}_2\text{Ph} \quad + \quad (\text{CH}_3\text{)}_2\text{S} = \text{CH}_2 \quad \rightarrow \quad \Phi \quad \text{C} = \text{N}\text{(CH}_3\text{)}_2 \]

(70) (XCII)

The structure of the product of reaction of III and 1-nitro-1-propene (principally the trans isomer) is assigned as trans-2-methyl-1-nitrocyclopropane (LXXXI) on the basis of its n.m.r. for two deshielded cyclopropyl hydrogens between \( \tau 8.0 \) and \( 8.35 \) (H \(_3\)).
and $H_γ$, multiplet, area 1.95), a methyl group which is not deshielded and which integrates with cyclopropyl hydrogen ($H_δ$, not deshielded) between $\tau$ 8.70 and 9.06 (multiplet, area 4.25), and, cyclopropyl hydrogen at $\tau$ 5.95 ($H_ε$, quintet, area 1.0) on carbon bearing the nitro group.

![Diagram](image)

LXXXI

(59)(a) Hydrogen cis to a nitro group in a nitrocyclopropane is expected to be highly deshielded. S. Ranganathan, Ph.D. Dissertation, Ohio State University, Columbus, Ohio, 1962, observed that in 2-nitrosopropylcyclopropane-1,9'-fluorene, the $\tau$ values of the $\beta$ and $\beta'$-hydrogens relative to the nitro groups of the cyclopropane ring are 8.25 and 8.85, respectively. It is presumed that the $\beta$ and $\beta'$-hydrogens are cis and trans, respectively, relative to the nitro group.

(b) The n.m.r. of shielded and unshielded methyl groups in the following cyclopropanes are: 1-methyl ($\tau$ 8.87)-trans-2-phenylcyclopropane, 1-methyl ($\tau$ 9.20)-cis-2-phenylcyclopropane, 1,cis-2-dimethyl ($\tau$ 8.87)-trans-3-phenylcyclopropane, 1,cis-2-dimethyl ($\tau$ 9.05)-cis-3-phenylcyclopropane, and 1,trans-2-dimethyl ($\tau$ 8.85 and 9.22)-trans-3-phenylcyclopropane; J. P. Freeman, J. Org. Chem., 29, 1379 (1964) and G. L. Closs and R. A. Moss, J. Am. Chem. Soc., 86, 4042 (1964).

(c) Hydrogen on carbon attached to nitro groups in the present nitrocyclopropanes have $\tau$ values of 5.94-5.96. Protons on carbon bearing nitro groups in 2-nitropropane and 2-nitrobutane exhibit resonance at $\tau$ 5.33 and 5.48, respectively; Varian Associates NMR Spectra Catalog, Palo Alto, California, Spectrum No. 41 and 42.
Chemical evidence for the stereochemical assignment was obtained in that the product (LXXXI) of 1-nitropropene and III is not separated into geometric isomers by gas chromatography on GF-1 (Dow Corning Co.)-Chromosorb, and reduction by iron and hydrochloric acid gives 2-methyl-1-cyclopropylamine (Equation 71) whose

\[
\text{CH}_3\text{CH} = \text{C} - \text{H} \quad \text{Fe} \quad \text{HCl} \quad \text{NO}_2 \quad \text{H}_3\text{C} \quad \text{Zn, Cu, CH}_2\text{I}_2 \quad 1) \text{Zn, Cu, CH}_2\text{I}_2 \quad 2) \text{CrO}_3 \quad 3) \text{SOCl}_2; \text{NaN}_3 \quad 4) \Delta \text{H}_3\text{O}^+ \quad \text{CH}_3 \quad \text{H}_3\text{C} \quad \text{C} = \text{C} \quad \text{CH}_2\text{OH} \quad 1) \text{Zn, Cu, CH}_2\text{I}_2 \quad 2) \text{CrO}_3 \quad 3) \text{SOCl}_2; \text{NaN}_3 \quad 4) \Delta \text{H}_3\text{O}^+ \quad \text{CH}_3 \quad \text{NH}_2 \quad \text{NH}_2
\]

(60) Such columns are effective for separating cis and trans-alkynitrocycloalkanes, G. E. Booth, Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1967.

(61) Iron and hydrochloric acid reduce various exo and endo-nitro-bicycloalkanes to their corresponding amines without alteration of the initial stereochemistry; P. W. K. Flanagan, Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1957.

gas chromatographic properties are essentially identical with that of trans-2-methyl-1-cyclopropylamine (XCIII) prepared as indicated in Equation 72 and obtained as an authentic sample. The preparation of LXXXI from III and 1-nitropropene thus is stereospecific to give only the trans product.

The products, LXXXVII, LXXXVIII and LXXXIX, from reaction of III with 1-nitro-1-butene, 1-nitro-1-pentene and trans-β-nitro-styrene, respectively, could not be separated effectively by gas chromatographic methods. The chromatographic traces were symmetrical upon passing each nitrocyclopropane through a variety of columns. Upon attempting to separate the products through long, highly polar, heated columns, there was distortion in the chromatographic responses. It could not be established, however, whether small amounts of initial geometrical isomers were present, whether there was some cis-trans isomerization during chromatography or whether thermal decomposition of initial products led to unsymmetrical broadening of the gas chromatographic peaks.

\[
\text{CH}_3-\text{CH}_2 \quad \text{H}_\alpha \quad \text{CH}_3-\text{CH}_2-\text{CH}_2 \quad \text{H}_\alpha \quad \phi
\]

LXXXVII LXXXVIII LXXXIX

The structure of LXXXVII is indicated as trans-2-ethyl-1-nitrocyclopropane from its n.m.r. absorption for two deshielded ring protons ($H_\beta$ and $H_\gamma$) multiplet, $\tau$ 8.28-8.40, area 2.10), methyl and ring protons ($\text{CH}_3$ and $H_5$, multiplet, $\tau$ 8.85-9.20, area 4.1) which are not deshielded, alkylmethylene hydrogen ($\text{CH}_2$, sextuplet, $\tau$ 8.47-8.55, area 2.10) and hydrogen ($H_\alpha$, quintet, $\tau$ 5.95, area 1.0) on carbon substituted by a nitro group. Similarly LXXXVIII and LXXXIX are assigned trans stereochemistries from their n.m.r. properties.
(a) The n.m.r. of LXXXVIII indicates $H_\alpha$ (quintet, area 1.0) at $\tau$ 5.95, $H_\beta$ and $H_\gamma$ (multiplet, area 2.09) between $\tau$ 8.10 and 8.33, alkylmethylene hydrogens (-CH$_2$-CH$_2$-, multiplet, area 4.20) at $\tau$ 8.35-8.86 and $H_6$ along with methyl protons (multiplet, area 4.14) at $\tau$ 8.86-9.24.

(b) LXXXIX exhibits resonance for $H_\alpha$ (quintet, area 1.0) at $\tau$ 5.96, $H_\beta$ (deshielded, multiplet, area 1.06) at $\tau$ 7.07-7.52, $H_\gamma$ (deshielded, multiplet, area 1.05) at $\tau$ 8.04-8.44, $H_6$ (quartet, area 1.06) at $\tau$ 8.60-9.02 and H on phenyl (area 4.86) at $\tau$ 2.80-3.24.

Although no attempts were made to separate the adduct obtained from 2-nitro-2-butene and III by precision g.l.c. techniques, it is clear from the n.m.r. properties of the product that 1,cis-2-dimethyl-1-nitrocyclopropane (LXXXIII) must be at least the principal component. The n.m.r. of LXXXIII reveals methyl protons at $\tau$ 8.34 (singlet, area 2.80) on carbon bonded to the nitro group, $H_\beta$ and $H_\gamma$ (multiplet, area 1.80) at $\tau$ 8.00-8.33, methyl protons (multiplet, area 3.10) between $\tau$ 8.76-8.96 and $H_6$ (multiplet, area 1.0) at $\tau$ 9.14-9.33.

![LXXXIII]

LXXXIII
EXPERIMENTAL

General Information

Melting points. — Melting points were determined with a stirred bath of Dow Corning 550 silicone oil and on a melting point block manufactured by the Fisher Scientific Company. All melting points are uncorrected.

Elemental analyses. — Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee and Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Infrared spectra. — Infrared spectra were obtained with a Perkin-Elmer Infracord Spectrophotometer. The spectra of solid samples were obtained from potassium bromide wafers.

Ultraviolet spectra. — Ultraviolet spectra were determined on a Perkin-Elmer No. 202 recording spectrophotometer. The solvent used was 95% ethanol.

Nuclear magnetic resonance spectra. — Nuclear magnetic resonance spectra were measured on an A-60 instrument manufactured by Varian Associates. All samples were calibrated with tetramethylsilane.
Molecular weights. -- Molecular weights were obtained by using a vapor pressure osmometer, model 301A, manufactured by Mechrolab, Incorporated. The solvent used was chloroform.

Solvents. -- Dimethyl sulfoxide was dried over calcium hydride pellets and used without further purification. Tetrahydrofuran was distilled from sodium and dried over calcium hydride pellets. Reagent grade xylene and toluene (Mallinckrodt) were used as is.
Preparation of Intermediates

1-Nitro-1-propene. — 1-Nitro-1-propene, b.p. 54°/28 mm., was prepared by dehydration of 1-nitro-2-propanol with phthalic anhydride under reduced pressure.

2-Nitropropene. — 2-Nitropropene, b.p. 58°/90 mm., was obtained by dehydration of 2-nitro-1-propanol with phthalic anhydride under reduced pressure.

2-Nitro-2-butene. — Pyrolysis of 2-acetoxy-3-nitrobutane with anhydrous sodium acetate under reduced pressure gave 2-nitro-2-butene, b.p. 70°/30 mm.

1-Nitro-1-butene. — 1-Nitro-1-butene, b.p. 55°/12 mm., was synthesized by pyrolysis of 2-acetoxy-1-nitrobutane in the presence of anhydrous sodium acetate under reduced pressure.

1-Nitro-1-pentene. — 1-Nitro-1-pentene, b.p. 69-70°/12 mm., was prepared by pyrolysis of 2-acetoxy-1-nitropentane with anhydrous sodium acetate under reduced pressure.

β-Nitrostyrene. — Condensation of benzaldehyde with nitromethane in the presence of sodium hydroxide yielded β-nitrostyrene, m.p. 57-58°.

α-Nitrostilbene. — α-Nitrostilbene, m.p. 73°, was prepared by treatment with piperidine the product from reaction of stilbene
with dinitrogen tetroxide.

\[ \text{2-Nitro-1-phenylpropene} \] -- 2-Nitro-1-phenylpropene, m.p. 65\(^\circ\), was obtained by reaction of benzaldehyde with nitroethane in the presence of sodium hydroxide.

\[ \text{2-(2-Nitrovinyl)furan} \] -- 2-(2-Nitrovinyl)furan, m.p. 74\(^\circ\), was derived by condensation of furfural with nitromethane in the presence of sodium hydroxide.

\[ \text{2-Acetoxy-3-nitrobutane} \] -- 2-Acetoxy-3-nitrobutane, b.p. 103\(^\circ\)/10 mm., was prepared by reaction of 3-nitro-2-butanol with acetic anhydride in the presence of trace amounts of conc. sulfuric acid.


\[ \text{2-Acetoxy-1-nitrobutane} \] -- Reaction of 1-nitro-2-butanol with acetic anhydride in the presence of trace amounts of conc. sulfuric acid yielded 2-acetoxy-1-nitrobutane, b.p. 105-106\(^\circ\)/11 mm.

\[ \text{2-Acetoxy-1-nitropentane} \] -- 1-Nitro-2-pentanol and acetic anhydride in the presence of catalytic amounts of conc. sulfuric acid yielded 2-acetoxy-1-nitropentane, b.p. 111-113\(^\circ\)/10 mm.
3-Nitro-2-butanol. — 3-Nitro-2-butanol, b.p. 92°/10 mm.,
was obtained from acetaldehyde and nitroethane in the presence of
sodium hydroxide.

2-Nitro-1-propanol. — 2-Nitro-1-propanol, b.p. 99°/10 mm.,
resulted from the condensation of nitroethane and formaldehyde in
the presence of sodium hydroxide.

1-Nitro-2-propanol. — 1-Nitro-2-propanol, b.p. 112°/30 mm.,
was obtained from condensation of acetaldehyde with nitromethane
in the presence of sodium hydroxide.


1-Nitro-2-butanol. — 1-Nitro-2-butanol, b.p. 123-125°/55 mm.,
was prepared by condensation of propanol with nitromethane cata-
lyzed by sodium hydroxide.


1-Nitro-2-pentanol. — Condensation of butyraldehyde and nitro-
methane in the presence of sodium hydroxide resulted in 1-nitro-2-
pentanol, b.p. 87-88°/3 mm.

Triphenylmethylphosphonium bromide.-- Triphenylmethylphosphonium bromide, m.p. 227-229°, was prepared from triphenylphosphine and excess methyl bromide in a bomb at 100°.

Triphenylethylphosphonium bromide.-- Triphenylethylphosphonium bromide, m.p. 203-205°, was synthesized from triphenylphosphine and excess ethyl bromide in a bomb at 120°.


Carbomethoxymethylenetriphenylphosphorane.-- Carbomethoxymethylenetriphenylphosphorane, m.p. 162-163°, was prepared from carbomethoxymethyltriphenylphosphonium bromide and aqueous sodium hydroxide.


Carbomethoxymethyltriphenylphosphonium bromide.-- Treatment of triphenylphosphine with methyl α-bromoacetate in refluxing benzene gave carbomethoxymethyltriphenylphosphonium bromide, m.p. 163°.

α-Carbomethoxyethylidenetriphenylphosphorane.-- α-Carbomethoxyethylidenetriphenylphosphorane, m.p. 152-153°, was
prepared from α-carbomethoxyethyltriphenylphosphonium bromide and aqueous sodium hydroxide.

α-Carbomethoxyethyltriphenylphosphonium bromide. — α-Carbomethoxyethyltriphenylphosphonium bromide, m.p. 173-180°, was prepared from triphenylphosphine and methyl α-bromopropionate in refluxing benzene.

Acetonylidenedetriphenylphosphorane. — Acetonylidenedetriphenylphosphorane, m.p. 205-206°, was prepared from acetonyltriphenylphosphonium chloride and aqueous sodium carbonate.

Acetonyltriphenylphosphonium chloride. — Acetonyltriphenylphosphonium chloride, m.p. 234-237°, was prepared from triphenylphosphine and chloroacetone.

Phenacylidenedetriphenylphosphorane. — Phenacylidenedetriphenylphosphorane, m.p. 173-180°, was prepared from phenacyltriphenylphosphonium bromide and aqueous sodium carbonate.

Phenacyltriphenylphosphonium bromide. — Phenacyltriphenylphosphonium bromide, m.p. 267-269°, was prepared from triphenylphosphine and α-bromoacetophenone.

Cyanomethylenetriphenylphosphorane. — Cyanomethylenetriphenylphosphorane, m.p. 195-196°, was prepared from cyanomethyltriphenylphosphonium chloride and aqueous sodium carbonate.
Cyanomethyltriphenylphosphonium chloride. -- Cyanomethyltriphenylphosphonium chloride, m.p. 278-279°, was prepared from triphenylphosphine and chloroacetonitrile.

Trimethylsulfoxonium iodide. Trimethylsulfoxonium iodide, m.p. 218-220°, was prepared from methyl iodide and excess dimethyl sulfoxide.

Preparation of Methyl $\beta$-(1-Nitroethyl)-$\alpha$-(triphenylphosphoranylidene)hydrocinnamate (L).

2-Nitro-1-phenylpropene (8.2 g, 0.05 mole) and carboxmethoxy-methylenetriphenylphosphorane (16.7 g, 0.05 mole) were heated at 90-100° in dry toluene (150 ml.) for 24 hours in a 3-necked 250 ml. round bottom flask equipped with a stirrer and a condenser fitted with a drying tube. The reaction mixture was then cooled and the toluene evaporated to give a brown solid. Dry ether (200 ml.) was added and the resulting mixture filtered to give a yellow solid (9.5 g., 58% yield). Additional yellow solid (2.8 g., 49% total yield) was obtained when the ether solution was concentrated to ~50 ml. The product was recrystallized twice from ethyl acetate to yield methyl $\beta$-(1-nitroethyl)-$\alpha$-(triphenylphosphoranylidene)hydrocinnamate, m.p. 204-207° (dec.).

Anal. Calcd for C$_{30}$H$_{26}$NO$_4$P: C, 72.43; H, 5.65; N, 2.82.

Found: C, 72.15; H, 6.05; N, 2.67.

The infrared spectrum (Fig. 1) of the product (KBr pellet) contains strong bands for a carbonyl group (6.17 $\mu$) and an aliphatic nitro group (6.50 $\mu$). Its ultraviolet absorption (Fig. 13) is:

$\lambda_{\text{EtOH}}^{\text{max}}$ 223 m$\mu$ (c 42,600); 262 (5,600); 267 (6,600); 274 (6,900); 309-312 (10,300).
Preparation of Methyl 3-Methyl-4-nitro-2-(triphenylphosphoranylidene)butyrate (II).

1-Nitropropene (3.27 g., 0.037 mole) and carboxethoxymethyl-ethenetriphenylphosphorane (12.6 g., 0.037 mole) were heated at 90-100 in dry toluene (150 ml.) for 48 hours in a 3-necked 250 ml. round bottom flask equipped with a stirrer and a condenser fitted with a drying tube. The reaction mixture was then cooled and the toluene evaporated to yield a brown oily-solid. Dry ether (200 ml.) was added and the resulting mixture filtered to give a brown solid (4.0 g., 26% yield). Additional brown solid (1.2 g., 33% total yield) was obtained when the ether solution was concentrated to 50 ml. The product was recrystallized twice from ethyl acetate to afford methyl 3-methyl-4-nitro-2-(triphenylphosphoranylidene)butyrate, m.p. 164-166° (dec.).

Anal. Calcd for C_{24}H_{24}NO_{4}P: C, 68.50; H, 5.70; N, 3.32.
Found: C, 68.26; H, 5.55; N, 3.38.

The infrared spectrum (Fig. 2) of the product (KBr pellet) contains strong bands for a carbonyl group (6.14 µ) and an aliphatic nitro group (6.49 µ). Its ultraviolet absorption (Fig. 14) is:

\[ \lambda_{	ext{EtOH}}^{	ext{max}} \begin{align*} &225 \text{ m} \mu \ (c 37,600); \ 261 (5,700); \ 266 (5,600); \ 273 (4,800). \end{align*} \]

Preparation of Methyl Ω-(Nitromethyl)-g-(triphenylphosphoranylidene)hydrocinnamate (LIV).

ω-Nitrostyrene (7.5 g., 0.05 mole) and carboxethoxymethylenetriphenylphosphorane (16.7 g., 0.05 mole) were heated at
90-100° in dry toluene (150 ml.) for 24 hours in a 3-necked 250 ml. round bottom flask equipped with a stirrer and a condenser fitted with a drying tube. The reaction mixture was then cooled and the toluene evaporated to yield a yellow-brown solid. Dry ether (200 ml.) was added and the resulting mixture filtered to give a brown solid (18.2 g., 75% yield). The product was recrystallized twice from ethyl acetate to afford methyl α-(nitromethyl)-
β-(triphenylphosphoranylidene)hydrocinnamate (5.5 g., 23% yield), m.p. 180-181° (dec.).

Anal. Calcd for C_{28}H_{28}NO_{4}P: C, 72.01; H, 5.38; N, 2.90.

Found: C, 71.95; H, 5.48; N, 2.85.

The infrared spectrum (Fig. 3) of the adduct (KBr pellet) contains strong bands for a carbonyl group (6.17 µ) and an aliphatic nitro group (6.48 µ). Its ultraviolet absorption (Fig. 15) is:

λ_{max}^{EtOH} 225 mµ (ε 39,100); 261 (5,700); 266 (6,000); 273 (5,500); 304-311 (5,400).

Preparation of Methyl 4-Nitro-3,4-diphenyl-2-(triphenylphosphoranylidene)butyrate (LV).

α-Nitrostilbene (0.75 g., 0.0053 mole) and carbomethoxy-methylenetriphenylphosphorane (1.1 g., 0.0033 mole) were heated at 90-100° in dry toluene (75 ml.) for 18 hours in a 3-necked 250 ml. round bottom flask equipped with a stirrer and a condenser fitted with a drying tube. The reaction mixture was then cooled and the toluene evaporated. Dry ether (50 ml.) was added to the orange
residue and the resulting mixture filtered to furnish a tan solid (0.53 g., 26% yield). No further product could be isolated on concentration of the ether solution. The product was recrystallized twice from ethyl acetate to yield methyl 4-nitro-3,4-diphenyl-2-(triphenylphosphoranylidene)butyrate, m.p. 173-174° (dec.).

Anal. Calcd for C₃₅H₃₀N₂O₄P: C, 75.13; H, 5.37; N, 2.50.

Found: C, 75.16; H, 5.56; N, 2.66.

The infrared spectrum (Fig. 4) of the butyrate (KBr pellet) contains strong bands for a carbonyl group (6.14 μ) and an aliphatic nitro group (6.48 μ). Its ultraviolet absorption (Fig. 16) is: λmax EtOH 223 mμ (ε 38,000); 261 (6,200); 267 (5,800); 273 (4,800).

Preparation of Methyl 4-Nitro-2-(triphenylphosphoranylidene)valerate (LVI).

2-Nitropropene (3.5 g., 0.04 mole) and carbomethoxymethylene-triphenylphosphorane (13.4 g., 0.04 mole) were heated at 90-100° in dry toluene (100 ml.) for 40 hours in a 3-necked 250 ml. round bottom flask equipped with a stirrer and a condenser fitted with a drying tube. The reaction mixture was then cooled and the toluene evaporated to give a dark brown solid. Dry ether (200 ml.) was added and the resulting mixture filtered to yield a light brown solid (9.7 g., 57% yield). Concentration of the ether afforded no additional product. The material was recrystallized twice from ethyl acetate to afford methyl-4-nitro-2-(triphenylphosphoranylidene)valerate, m.p. 162-164° (dec.).
A nal. Calcd for C_{24}H_{24}NO_{4}P: C, 68.50; H, 5.70; N, 3.32.

Found: C, 68.21; H, 5.71; N, 3.44.

The infrared spectrum (Fig. 5) of the green adduct (KBr pellet) contains strong bands for a carbonyl group (6.13 \mu) and an aliphatic nitro group (6.51 \mu). Its ultraviolet absorption (Fig. 17) is: \( \lambda_{\text{EtOH}}^{\text{max}} \) 225 m\u (e 38,700); 261 (5,000); 266.5 (5,000); 275.5 (4,400).

Preparation of Methyl 3-Methyl-4-nitro-2-(triphenylphosphoranyliden)valerate (LVII).

2-Nitro-2-butene (2.02 g., 0.02 mole) and carbomethoxymethylenetriphenylphosphorane (6.7 g., 0.02 mole) were heated at 90-100\(^{\circ}\) in dry toluene (80 ml.) for 40 hours in a 3-necked 250 ml. round bottom flask equipped with a stirrer and a condenser fitted with a drying tube. The reaction mixture was then cooled and the toluene evaporated to give a dark brown solid. Dry ether (200 ml.) was added and the resulting mixture filtered to afford a light brown solid (2.9 g, 33\% yield). Concentration of the ether afforded no additional product. The light brown solid was recrystallized twice from ethyl acetate to furnish methyl 3-methyl-4-nitro-2-(triphenylphosphoranyliden)valerate, m.p. 193.5-195.5\(^{\circ}\) (dec.).

A nal. Calcd for C_{30}H_{28}O_{4}P: C, 68.96; H, 6.00; N, 3.22.

Found: C, 68.81; H, 6.12; N, 3.30.

The infrared spectrum (Fig. 6) of the analytical product (KBr pellet) contains strong bands for a carbonyl group (6.13 \mu) and an
aliphatic nitro group (6.51 μ). The ultraviolet absorption (Fig. 18) of the adduct is: \( \lambda_{\text{EtOH}}^{\text{max}} \) 225 μ (ε 32,200); 260.5 (5,100); 267 (5,000); 273.5 (4,200).

Preparation of Methyl 4-Nitro-2-(triphenylphosphoranylidene)-3-furanbutyrate (LVIII).

2-(2-Nitrovinyl)furan (4.88 g., 0.035 mole) and carbomethoxy-methylenetriphenylphosphorane (11.4 g., 0.035 mole) was heated at 90-100° in dry toluene (80 ml.) for 24 hours in a 3-necked 250 ml. round bottom flask equipped with a stirrer and a condenser fitted with a drying tube. The reaction mixture was then cooled and the toluene evaporated to result in a black solid. Dry ether (200 ml.) was added and the resulting mixture filtered to afford a green solid (7.7 g., 47% yield). No further product could be isolated on concentration of the ether solution. The green solid was re-crystallized twice from ethyl acetate to give methyl 4-nitro-2-(triphenylphosphoranylidene)-3-furanbutyrate, m.p. 184.5-185.5° (dec.).

Anal. Calcd for C_{27}H_{24}NO_{4}P: C, 68.50; H, 5.08; N, 2.96.

Found: C, 68.76; H, 5.24; N, 3.24.

The infrared spectrum (Fig. 7) of the solid (KBr pellet) contains strong bands for a carbonyl group (6.23 μ) and an aliphatic nitro group (6.48 μ). Its ultraviolet absorption (Fig. 19) is: \( \lambda_{\text{EtOH}}^{\text{max}} \) 225 μ (ε 28,400); 260 (4,500); 266 (4,300); 273 (3,700); 347 (6,800).
Attempted Reaction of omega-Nitrostyrene with \( \alpha \)-Carbomethoxy-ethylidene-triphenylphosphorane.

omega-Nitrostyrene (2.98 g., 0.02 mole) and \( \alpha \)-carbomethoxy-ethylidene-triphenylphosphorane (6.96 g., 0.02 mole) were heated at 90-100\(^\circ\) in dry toluene (100 ml.) for 24 hours in a 3-necked, 250 ml. round bottom flask equipped with a stirrer and a condenser fitted with a drying tube. The reaction mixture was then cooled and the toluene evaporated. Dry ether (200 ml.) was added to the dark residue and the resulting mixture filtered. The infrared spectrum of the brown solid (2.70 g.) identified it as omega-nitrostyrene polymer.

Evaporation of the ether filtrate yielded a brown oil. Addition of 95\% ethanol-ether (1:1, 200 ml.) afforded, upon cooling, a brown solid (1.87 g.) which was identified as triphenylphosphine oxide by its infrared spectrum. Evaporation of the filtrate yielded an oil (4.1 g.) from which no further solid could be isolated. The infrared spectrum of the residue showed only that a carbonyl group was present. Further comparison of its infrared spectrum with known compounds indicated that the material isolated was a mixture of triphenylphosphine oxide and starting material, \( \alpha \)-carbomethoxyethylidene-triphenylphosphorane.
Attempted Reaction of \textit{omega}-Nitrostyrene with Acetonylidene-triphenylphosphorane.

\textit{omega}-Nitrostyrene (4.47 g., 0.03 mole) and acetonylidene-triphenylphosphorane (9.54 g., 0.03 mole) were heated at 90-100\(^\circ\)C in dry toluene (100 ml.) for 14 hours in a 3-necked 250 ml. round bottom flask equipped with a stirrer and a condenser fitted with a drying tube. The reaction mixture was then cooled and the toluene evaporated. Dry ether (200 ml.) was added to the black oil and the resulting mixture was filtered. The brown solid (2.0 g) isolated was identified as \textit{omega}-nitrostyrene polymer by its infrared spectrum. Concentration of the filtrate and cooling gave a tan solid (1.6 g.) identified as triphenylphosphine oxide by its infrared spectrum. Complete evaporation of the filtrate and storage in a refrigerator for one week gave a brown semi-solid. Addition of dry ether (50 ml.) yielded a tan solid (4.7 g.) identified as a mixture of triphenylphosphine oxide and \textit{omega}-nitrostyrene by its infrared spectrum. Evaporation of the filtrate afforded a black oil from which no further solid product could be isolated. The infrared spectrum of the oil indicated that it consisted of triphenylphosphine oxide and decomposition products which showed very faint absorption for a nitro group.
Reaction of Methyl $\beta$-(Nitromethyl)-$\alpha$-(triphenylphosphoranylidene)hydrocinnamate (LIV) with m-Nitrobenzaldehyde.

Adduct LIV (3.19 g., 0.0066 mole) and m-nitrobenzaldehyde (1.00 g., 0.0066 mole) were heated at 100° in dry xylene (65 ml.) for 40 hours in a 3-necked 100 ml. round bottom flask equipped with a stirrer and a condenser fitted with a drying tube. The mixture was then cooled and the xylene evaporated. Dry ether (100 ml.) was added to the orange residue and the resulting mixture was filtered. The yellow solid (1.94 g.) isolated was identified as starting material, LIV, by its infrared spectrum. The filtrate on concentration in vacuo gave an orange oil which was dissolved in hot 95% ethanol. A yellow-brown solid (0.34 g.) crystallized upon cooling the solution overnight. The product was recrystallized from 95% ethanol to afford methyl m-nitrocinnamate (LXXI), m.p. 120-122°, identified by a comparison of its infrared spectrum and by a mixed melting point with an authentic sample.

Reaction of Methyl $3$-Methyl-$4$-nitro-$2$-(triphenylphosphoranylidene)butyrate (LI) with m-Nitrobenzaldehyde.

Adduct LI (0.63 g., 0.0015 mole) and m-nitrobenzaldehyde (0.23 g., 0.0015 mole) were heated at 110-120° in dry xylene (30 ml.) for 96 hours in a 3-necked 100 ml. round bottom flask equipped with a stirrer and a condenser fitted with a drying tube. On cooling the mixture and evaporating the xylene, an orange-yellow solid was obtained. Dry ether (200 ml.) was added and the
resulting mixture was filtered. The brownish-white solid (0.15 g.) isolated was identified as methyl \(m\)-nitrocinnamate (LXXI) by its infrared spectrum. Concentrating the ether solution to \(\sim 50\) ml. afforded triphenylphosphine oxide (0.10 g.), a white solid, identified by its infrared spectrum. Removal of the filtrate in vacuo gave an orange oil which was dissolved in hot 95\% ethanol (10 ml.). The only product (0.10 g.) that crystallized upon cooling the solution was methyl \(m\)-nitrocinnamate, identified by its infrared spectrum. Evaporation of the solvent yielded an orange oil whose infrared spectrum indicated it to be a mixture of triphenylphosphine oxide and LXXI.

**Preparation of Methyl \(m\)-Nitrocinnamate (LXXI).**

Carbomethoxymethylene triphenylphosphorane (6.68 g., 0.02 mole) and \(m\)-nitrobenzaldehyde (3.02 g., 0.02 mole) were refluxed in benzene for 12 hours. The reaction mixture was cooled and the benzene removed in vacuo. The white solid isolated was identified, upon recrystallization from 95\% ethanol, as methyl \(m\)-nitrocinnamate, (3.5 g., 84\% yield), m.p. 119-121°.

**Anal. Calcd for C\(_{10}\)H\(_9\)NO\(_4\):**  C, 57.97; H, 4.30; N, 6.76.

**Found:**  C, 58.06; H, 4.36; N, 6.63.

**Attempted Cyclization of Methyl \(\beta\)-(1-Nitroethyl)-\(g\)-(triphenylphosphoranylidene)hydrocinnamate (L).**

Adduct L (7.5 g., 0.015 mole) was refluxed in dry oxylene (150 ml.) for 5 days in a 3-necked 250 ml. round bottom flask
equipped with a stirrer and a condenser fitted with a drying tube. The mixture was cooled overnight in a refrigerator and filtered. The yellow residue (1.5 g.) was identified as starting material by infrared analysis. The filtrate was then concentrated in vacuo.

Dry ether (150 ml.) was added to the orange residue; filtration of the resulting mixture yielded additional starting material. Concentrating and cooling the ether solution afforded no further product. Complete evaporation of the solvent and cooling the residue in a refrigerator gave a tan solid (1.3 g.) identified as triphenylphosphine oxide by infrared analysis. An attempt to distill a portion of the orange oil resulted in its destruction. The infrared spectrum of the remaining oil indicated that it was a mixture of triphenylphosphine oxide and decomposition products which showed very faint absorption for a nitro group.

**Attempted Hydrolysis of Methyl β-(Nitromethyl)-α-(triphenylphosphoranylidenemethyl)hydrocinnamate (LIV).**

A mixture of compound LIV (4.83 g., 0.01 mole) and 12 ml. of a methanol-water solution (2:1) was made basic (pH ~ 8) with a 2M NaOH solution, placed in a bomb and heated at 150° for 3 hours and then at 105° for 16 hours. The reaction mixture was then cooled and water (100 ml.) added. The orange-brown solution was neutralized with dilute HCl solution and extracted thrice with ether (200 ml.). Drying and removal of the solvent in vacuo gave an oily solid as residue. Addition of ether (100 ml.) and filtering
yielded a brown solid (0.51 g.) identified as triphenylphosphine oxide by infrared analysis. Additional solid (0.56 g.) was obtained when the ether solution was concentrated to 10 ml. Complete evaporation of the solvent gave an oil from which no further solid could be obtained upon cooling. Its infrared spectrum showed no absorption for a nitro group and indicated that the starting material was completely decomposed.

**Attempted Peracid Oxidation of Methyl β-(Nitromethyl)-α-(triphenyl-phosphoranylidene)hydrocinnamate (LIV).**

Adduct LIV (2.42 g., 0.005 mole) and a 4% solution of per-acetic acid in acetic acid (1.0 g., 0.0055 mole) were stirred in dry benzene (150 ml.) for 20 hours at room temperature in a 250 ml. Erlenmeyer flask. The reaction mixture was then washed twice with water (100 ml.) and twice with 10% sodium carbonate solution (100 ml.). Drying and removal of the solvent in vacuo gave an orange oil. Addition of pet. ether (100 ml.) and filtering afforded a white solid (0.64 g.) identified as triphenylphosphine oxide by infrared analysis. The solvent was again removed in vacuo and the resulting oil dissolved in 95% ethanol (20 ml.). Addition of 2,4-dinitrophenylhydrazine reagent yielded no solid derivative upon cooling. The infrared spectrum of the original oil showed no absorption for a nitro group and indicated that the product was primarily triphenylphosphine oxide.
Reaction of Methyl 4-Nitro-2-(triphenylphosphoranylidene)valerate (LVI) with Bromine.

Adduct LVI (1.17 g., 0.0028 mole) was dissolved in dry carbon tetrachloride (60 ml.) at room temperature in a 3-necked 100 ml. round bottom flask equipped with a stirrer, a dropping funnel and a condenser fitted with a drying tube. Bromine (0.48 g., 0.003 mole) in dry carbon tetrachloride (10 ml.) was added dropwise and the resulting mixture stirred for 18 hours. The mixture was then filtered to afford a yellow solid (1.46 g., 91% yield), m.p. 116-120° (dec.). The infrared spectrum of the brominated product, 2-bromo-4-nitro-2-(triphenylphosphonium bromide)valerate (LXVIII), contained strong bands for a carbonyl group (5.81 μ) and an aliphatic nitro group (6.48 μ). Attempts to recrystallize the material from hot absolute ethanol, benzene, carbon tetrachloride, chloroform or pentane led only to triphenylphosphine oxide.

Compound LXVIII (1.28 g., 0.0022 mole) was dissolved in distilled water (150 ml.) at room temperature, filtered and treated with 10% sodium carbonate solution until the water solution was basic. The mixture was filtered to yield a green solid (0.51 g., 55% yield), identified as compound LVI by a comparison of its infrared spectrum and by a mixed melting point with an authentic sample.
Preparation of trans-2-Methyl-1-nitrocyclopropane (LXXXI).

a) Trimethylsulfoxonium iodide. — Trimethylsulfoxonium iodide (24.2 g., 0.11 mole) was added through Gooch tubing from an Erlenmeyer flask to a stirred suspension of sodium hydride (2.64 g., 0.11 mole) in dimethyl sulfoxide (150 ml.) in a 3-necked 500 ml. round bottom flask equipped with a stirrer, a dropping funnel and a condenser connected to a nitrogen train over a period of 30 minutes. After stirring at room temperature for 2 hours, the mixture was cooled to 10° and 1-nitro-1-propane (8.7 g., 0.1 mole) in dimethyl sulfoxide (25 ml.) was added dropwise over a period of 30 minutes. The mixture was stirred at 50° for 4 hours and then at room temperature for 12 hours, poured onto ice and extracted thrice with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulfate and then concentrated at reduced pressure. The orange oil (3.1 g., 31½ yield) was vacuum distilled by means of a short-path still to yield a light yellow oil (1.9 g., 19½ yield) which upon further vacuum distillation gave a colorless product, trans 2-methyl-1-nitrocyclopropane (1.6 g., 16½ yield), b.p. 69°/30 mm.
Anal. Calcd for C₄H₇NO₂: C, 47.52; H, 6.93; N, 13.87.
Found: C, 47.67; H, 6.71; N, 14.00.

The infrared spectrum (Fig. 8) of LXXXI contains a strong band for an aliphatic nitro group (6.48 and 7.34 μ). Its ultraviolet absorption maxima (Fig. 20) occurs at 219 μ (ε 6,650). The nuclear magnetic resonance spectrum (Fig. 25) is consistent with the assigned structure: two cyclopropyl hydrogens between τ 8.0 and 8.35 (multiplet, area 1.95), a methyl group which integrates with a cyclopropyl hydrogen between τ 8.70 and 9.06 (multiplet, area 4.25) and cyclopropyl hydrogen at τ 5.95 (quintet, area 1.0) on carbon bearing the nitro group.

b) Triphenylmethylphosphonium bromide. -- A mixture of sodium hydride (1.20 g., 0.05 mole) and dry dimethyl sulfoxide (75 ml.) was heated at 65° under a nitrogen atmosphere until no further hydrogen was evolved (~ 90 minutes). The pale yellow solution was cooled to 15° and triphenylmethylphosphonium bromide (17.85 g., 0.05 mole) was added through Gooch tubing from an Erlenmeyer flask over a period of 10 minutes. After additional stirring at room temperature for 30 minutes, the mixture was cooled to 10° and 1-nitro-1-propene (4.35 g., 0.05 mole) in dimethyl sulfoxide (25 ml.) was added over a period of 30 minutes. The mixture was stirred at 75° for 6 hours and then at room temperature for 12 hours. Afterwards, the reaction mixture was poured onto ice and extracted thrice with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulfate and then concentrated at reduced pressure.
The orange-black residue was vacuum distilled by means of a short-path still to yield an orange oil which upon redistillation afforded a pale yellow product (0.23 g., 5% yield) identified as 2-methyl-1-nitrocyclopropane by a comparison of its infrared spectrum with an authentic sample.

Preparation of 1,2-Dimethyl-1-nitrocyclopropane (LXXXIII).

a) Trimethylsulfoxonium iodide. — Trimethylsulfoxonium iodide (24.2 g., 0.11 mole) was added through Gooch tubing from an Erlenmeyer flask to a stirred suspension of sodium hydride (2.64 g., 0.11 mole) and dimethyl sulfoxide (150 ml.) in a 3-necked round bottom flask equipped with a stirrer, a dropping funnel and a condenser connected to a nitrogen train over a period of 30 minutes. After stirring at room temperature for 2 hours, the mixture was cooled to 10° and 2-nitro-2-butene (10.1 g., 0.10 mole) in dimethyl sulfoxide (25 ml.) was added dropwise over a period of 30 minutes. The mixture was stirred at 55° for 4 hours and then at room temperature for 8 hours. Afterwards, the reaction mixture was poured onto ice and extracted thrice with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulfate and then concentrated under reduced pressure. The orange oil (4.2 g., 37% yield) was vacuum distilled through a short-path still to give a light yellow oil which upon further vacuum distillation yielded a colorless product, 1,2-dimethyl-1-nitrocyclopropane (2.8 g., 24% yield), b.p. 70°/20 mm.
The infrared spectrum (Fig. 9) of LXXXIII contains a strong band for an aliphatic nitro group (6.51 and 7.39 μ). Its ultraviolet absorption maxima (Fig. 21) occurs at 216 μ (ε 6236).

The nuclear magnetic resonance spectrum (Fig. 26) was consistent with the assigned structure: methyl protons at τ 8.34 (singlet, area 2.80) on carbon bonded to the nitro groups, two cyclopropyl hydrogens between τ 8.00 and 8.33 (multiplet, area 1.80), methyl protons between τ 8.76-8.96 (multiplet, area 3.10) and cyclopropyl hydrogen at τ 9.14-9.33 (multiplet, area 1.0).

b) Triphenylmethylphosphonium bromide.-- A mixture of sodium hydride (1.20 g., 0.05 mole) and dry dimethyl sulfoxide (75 ml.) were heated at 65° in a 3-necked 500 ml. round bottom flask equipped with a stirrer and a condenser connected to a nitrogen train until no further hydrogen was evolved (~ 90 minutes). The pale yellow solution was cooled to 15° and triphenylmethylphosphonium bromide (17.85 g., 0.05 mole) was added through Gooch tubing from an Erlenmeyer flask over a period of 10 minutes. After additional stirring at room temperature for 30 minutes, the mixture was cooled to 10° and 2-nitro-2-butene (5.05 g., 0.05 mole) in dimethyl sulfoxide (25 ml.) was added during a 30 minute period. The mixture was stirred at 75° for 6 hours and then at room temperature for 12 hours. Afterwards, the reaction mixture was poured onto ice and extracted thrice with ether. The ether extracts were washed with water,
dried over anhydrous magnesium sulfate and then concentrated at reduced pressure. The orange-black residue was vacuum distilled through a short-path still to give an orange oil which upon re-distillation afforded a pale yellow product (0.40 g., 7% yield) identified as 1,2-dimethyl-1-nitrocyclopropane by a comparison of its infrared spectrum with an authentic sample.

**Preparation of 1-Methyl-1-nitrocyclopropane (LXXXVI).**

Trimethylsulfoxonium iodide (24.2 g., 0.11 mole) was added through Gooch tubing from an Erlenmeyer flask to a stirred solution of sodium hydride (2.64 g., 0.11 mole) and dimethyl sulfoxide (150 ml.) in a 3-necked 500 ml. round bottom flask equipped with a stirrer, a dropping funnel and a condenser connected to a nitrogen train over a period of 30 minutes. After stirring at room temperature for 4 hours, the mixture was cooled to 10° and 2-nitropropene (8.7 g., 0.10 mole) in dimethyl sulfoxide (25 ml.) was added drop-wise in 30 minutes. The mixture was stirred at 50° for 4 hours and then at room temperature for 8 hours. Afterwards, the reaction mixture was poured onto ice and extracted three times with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulfate and then concentrated at reduced pressure. The orange oil (0.80 g., 8% yield) was vacuum distilled in a short-path still to give a light yellow oil which upon further distillation yielded a pale yellow product, 1-methyl-1-nitrocyclopropane, b.p. 80°/22 mm.
The infrared spectrum of LXXXVI contains a strong band for an aliphatic nitro group (6.52 and 7.41 μ). Its ultraviolet absorption maxima occurs at 215 μm.

Preparation of trans-2-Ethyl-1-nitrocyclopropane (LXXXVII).

Trimethylsulfoxonium iodide (103.4 g., 0.47 mole) was added through Gooch tubing from an Erlenmeyer flask to a stirred suspension of sodium hydride (11.28 g., 0.47 mole) and dimethyl sulfoxide (250 ml.) in a 3-necked 500 ml. round bottom flask equipped with a stirrer, a dropping funnel and a condenser connected to a nitrogen train for 30 minutes. After stirring at room temperature for 4 hours, the mixture was cooled to 10° and 1-nitro-1-butene (40.0 g., 0.40 mole) in dimethyl sulfoxide (50 ml.) was added dropwise over a period of 45 minutes. The mixture was stirred at 50° for 4 hours and then at room temperature for 12 hours. Afterwards, the reaction mixture was poured onto ice and extracted thrice with ether.

The ether extracts were washed with water, dried over anhydrous magnesium sulfate and then concentrated at reduced pressure. The orange-red oil (18.4 g., 40% yield) was vacuum distilled to give a colorless product, 2-ethyl-1-nitrocyclopropane (8.3 g., 18% yield), b.p. 62°/10 mm.

Anal. Calcd for C₅H₇NO₂: C, 52.27; H, 7.82; N, 12.17.

Found: C, 52.65; H, 7.79; N, 12.35.
The infrared spectrum (Fig. 10) of LXXXVII contains a strong band for an aliphatic nitro group (6.48 and 7.33 μ). Its ultraviolet absorption maxima (Fig. 22) occurs at 219 μ (ε 6950).

The nuclear magnetic resonance spectrum (Fig. 27) of the product is consistent with the assigned structure: two cyclopropyl hydrogens between τ 8.28 and 8.40 (multiplet, area 2.10), a methyl group which integrates with a cyclopropyl hydrogen between τ 8.85 and 9.20 (multiplet, area 4.1), alkylmethylene hydrogen between τ 8.47 and 8.85 (sextuplet, area 2.10) and cyclopropyl hydrogen at τ 5.95 (quintet, area 1.0) on carbon bearing the nitro group.

Preparation of trans-2-Propyl-1-nitrocyclopropane (LXXXVIII).

Trimethylsulfoxonium iodide (96.8 g., 0.44 mole) was added through Gooch tubing from an Erlenmeyer flask to a stirred suspension of sodium hydride (10.56 g., 0.44 mole) and dimethyl sulfoxide (250 ml.) in a 3-necked 500 ml. round bottom flask equipped with a stirrer, a dropping funnel and a condenser connected to a nitrogen train over a period of 30 minutes. After stirring at room temperature for 4 hours, the mixture was cooled to 10° and 1-nitro-1-pentene (46.0 g., 0.40 mole) in dimethyl sulfoxide (50 ml.) was added dropwise in 45 minutes. The mixture was stirred at 50° for 4 hours and then at room temperature for 12 hours. Afterwards, the reaction mixture was poured onto ice and extracted thrice with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulfate and then concentrated at reduced pressure.
The orange-red oil (22.2 g., 43% yield) on distillation yielded a colorless product, 2-(n-propyl)-1-nitrocyclopropane (11.9 g., 23% yield), b.p. 76°/11 mm.

Anal. Calcd for C₆H₁₁NO₂: C, 55.81; H, 8.52; N, 10.85.

Found: C, 55.81; H, 8.62; N, 11.01.

The infrared spectrum of LXXXVIII (Fig. 11) contains a strong band for an aliphatic nitro group (6.49 and 7.35 μ). Its ultraviolet absorption maxima (Fig. 23) occurs at 219 μg (ε 6,445).

The nuclear magnetic resonance spectrum (Fig. 28) of the product is consistent with the assigned structure: two cyclopropyl hydrogens between τ 8.10 and 8.35 (multiplet, area 2.09), alkylmethylene hydrogens between τ 8.33 and 8.86 (multiplet, area 4.20), methyl protons which integrates with a cyclopropyl hydrogen between τ 8.86-9.24 (multiplet, area 4.14) and cyclopropyl hydrogen at τ 5.95 (quintet, area 1.0) on carbon bearing the nitro group.

Preparation of trans-2-Phenyl-1-nitrocyclopropane (LXXXIX).

Trimethylsulfoxonium iodide (6.6 g., 0.03 mole) was added through Gooch tubing from an Erlenmeyer flask to a stirred suspension of sodium hydride (0.75 g., 0.03 mole) and dimethyl sulfoxide (110 ml.) in a 3-necked 500 ml. round bottom flask equipped with a stirrer, a dropping funnel and a condenser connected to a nitrogen train over a period of 30 minutes. After stirring at room temperature for 6 hours, the mixture was cooled to 10° and omega-nitrostyrene (4.2 g., 0.028 mole) in dimethyl sulfoxide (60 ml.) was
added dropwise in 30 minutes. The mixture was stirred at 50° for
4 hours and then at room temperature for 12 hours. Afterwards,
the reaction mixture was poured onto ice and extracted thrice with
ether. The ether extracts were washed with water, dried over mag-
nesium sulfate and then concentrated at reduced pressure. The
orange oil (2.01 g., 44% yield) was vacuum distilled in a short
column to yield a light yellow oil which upon further distillation
gave a colorless product, 2-phenyl-1-nitrocyclopropane (1.28 g.,
28% yield), b.p. 85-87°/1 mm.

Anal. Calcd for CsHgNO2: C, 66.26; H, 5.52; N, 8.58.

Found: C, 65.93; H, 5.70; N, 8.65.

The infrared spectrum (Fig. 12) of LXXXIX contains a strong
band for an aliphatic nitro group (6.49 and 7.34 μ). Its ultra-
violet absorption maxima (Fig. 24) occur at 213 μ (ε 11,230) and
252 μ (ε 8,230). The nuclear magnetic resonance (Fig. 29) of the
product is consistent with the assigned structure: a cyclopropyl
hydrogen between τ 7.07 and 7.52 (deshielded, multiplet, area 1.0),
a cyclopropyl hydrogen between τ 8.04 and 8.44 (deshielded, multi-
plet, area 1.06), a cyclopropyl hydrogen between τ 8.60 and 9.02
(shielded, quartet, area 1.06), a cyclopropyl hydrogen at τ 5.96
(quintet, area 1.0) on carbon bearing the nitro group and hydrogen
on phenyl between τ 2.80 and 3.24 (area 4.86).
Preparation of 2-Methylcyclopropylcarbinol.

A mixture of crotyl alcohol (~80% trans-20% cis, 18.0 g., 0.25 mole) and methylene iodide (83.8 g.) was added in 2 hours to a stirred suspension prepared by dropwise addition of methylene iodide (10 g., total CH₂I₂, 0.35 mole) to zinc-copper couple (32.7 g., 0.5 mole), in ethyl ether (100 ml.). After the stirred mixture had refluxed for 25 hours, the ether solution was slowly decanted into a mixture of ice and hydrochloric acid. The ether solution was separated, washed with ice-hydrochloric acid and then water, dried over potassium carbonate and then concentrated. Distillation of the resulting oil gave 2-methylcyclopropylcarbinol (8.2 g., 38% yield), b.p. 128-159°, lit. 155°. Vapor phase chromatography showed the reaction product to be a 80:20 mixture of trans and cis-2-methylcyclopropylcarbinols.

Preparation of 2-Methylcyclopropanecarboxylic Acid.

2-Methylcyclopropylcarbinol (3.3 g., 0.04 mole) was added dropwise to a stirred solution of chromic trioxide (15.5 g., 0.15 mole), sulfuric acid (13.6 ml.) and water (45 ml.) at 0-5°. The mixture
was then stirred for 3 hours. The acid solution was extracted with ethyl ether; the ether extracts were dried over magnesium sulfate, concentrated, and vacuum distilled to yield 2-methylcyclopropanecarboxylic acid (2.4 g., 60% yield), b.p. 101-102°/22 mm., lit. b.p. 97-98°/17.6 mm. Vapor phase chromatography showed the reaction product to be a 80:20 mixture of trans and cis-2-methylcyclopropanecarboxylic acids.

**Preparation of 2-Methylcyclopropylamine (XClI).**

2-Methylcyclopropanecarboxylic acid (2.2 g., 0.02 mole) and thionyl chloride (10 ml.) was stored for 24 hours at 25-30°. The excess thionyl chloride was then removed in vacuo to give 2-methylcyclopropanecarbonyl chloride (1.7 g.). The acid chloride was dissolved in acetone (40 ml.), cooled to 10°, and then treated dropwise with a solution of sodium azide (2.6 g., 0.04 mole) in water (8 ml.). The mixture was stirred for 30 minutes and then poured into ice water (250 ml.). The aqueous solution was extracted with ether; the ether washings were dried over anhydrous magnesium sulfate and concentrated. The residual azide was added to dry toluene (30 ml.), heated on a steam bath for 2 hours, and concentrated to give 2-methylcyclopropyl isocyanate. The isocyanate was hydrolyzed in refluxing hydrochloric acid (50 ml.) for 12 hours and vacuum-concentrated to yield crude 2-methylcyclopropylamine hydrochloride. The hydrochloride was dissolved in water (50 ml.), made alkaline with 10% sodium hydroxide solution.
and extracted with ether. The ether extracts were dried and concentrated to afford 2-methylcyclopropylamine whose infrared spectrum is essentially identical with that obtained for the product of reduction of trans-2-methyl-1-nitrocyclopropane (LXXXI).

Reduction of trans-2-Methyl-1-nitrocyclopropane (LXXXI).

Concentrated hydrochloric acid (8 ml.) was added in 3 hours to a refluxing mixture of trans-2-methyl-1-nitrocyclopropane (1.15 g., 0.011 mole) and iron dust (2.0 g., 0.056 mole) in water (20 ml.). The mixture was then refluxed for 6 hours, cooled, made alkaline with aqueous sodium hydroxide (10%) and then filtered. The filtrate was extracted with ether; the combined ether extracts were dried over anhydrous magnesium sulfate and concentrated at reduced pressure. The infrared spectrum of the product (XCII) was identical with that of authentic trans-2-methyl-1-cyclopropylamine. Its gas phase chromatographic properties revealed that the principal component is identical with that from the Curtius reaction of trans-2-methylcyclopropanecarboxylic acid.
APPENDIX A

Infrared Spectra
Figure 1. Methyl β-(1-Nitroethyl)-α-(triphenylphosphoranylidene) hydrocinnamate.

Figure 2. Methyl 3-Methyl-4-nitro-2-(triphenylphosphoranylidene) butyrate.

Figure 3. Methyl β-(Nitromethyl)-α-(triphenylphosphoranylidene) hydrocinnamate.
Figure 4. Methyl 4-Nitro-3,4-diphenyl-2-(triphenylphosphoranylidene)butyrate.

Figure 5. Methyl 4-Nitro-2-(triphenylphosphoranylidene)valerate.

Figure 6. Methyl 3-Methyl-4-nitro-2-(triphenylphosphoranylidene)valerate.
Figure 7. Methyl 4-Nitro-2-(triphenylphosphoranylidene)-3-furanbutyrate.

Figure 8. trans-2-Methyl-1-nitrocyclopropane.

Figure 9. 1,2-Dimethyl-1-nitrocyclopropane.
Figure 10. trans-2-Ethyl-1-nitrocyclopropane.

Figure 11. trans-2-Propyl-1-nitrocyclopropane.

Figure 12. trans-2-Phenyl-1-nitrocyclopropane.
APPENDIX B

Ultraviolet Spectra
APPENDIX C

NMR Spectra
trans-2-Methyl-1-nitrocyclopropane

Figure 25
Figure 26

1,2-Dimethyl-1-nitrocyclopropane
trans-2-Ethyl-1-nitrocyclopropane
trans-2-Propyl-1-nitrocyclopropane

Figure 28
trans-2-Phenyl-1-nitrocyclopropane