NEW ADDITION REACTIONS OF NITRO COMPOUNDS WITH OLEFINIC SYSTEMS

Dissertation

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By

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SECTION I

ADDITIONS OF DINITROGEN TETROXIDE AND NITRYL CHLORIDE TO OLEFINIC SYSTEMS

PART I

ADDITION OF DINITROGEN TETROXIDE TO METHYL ACRYLATE

PART II

ADDITION OF NITRYL CHLORIDE TO METHYL ACRYLATE, ACRYLIC ACID, AND ACRYLONITRILE
PART I

ADDITION OF DINITROGEN TETROXIDE TO METHYL ACRYLATE

A. BACKGROUND AND PURPOSE

In order to obtain more information concerning the orientation and actual mode of addition of dinitrogen tetroxide to unsymmetrical electronegatively-substituted olefins, the direction of addition of dinitrogen tetroxide to acrylic systems has now been reinvestigated.

The addition of dinitrogen tetroxide to olefins has been the subject of many previous investigations. In 1869, Kolbe treated tetrachloroethylene with dinitrogen tetroxide and obtained a product described as \( \text{C}_2\text{Cl}_4(\text{NO}_2)_2 \). Since that time, the results of the numerous investigations have been both confusing and conflicting. The confusion results from (1) the fact that nitrous fumes instead of pure dinitrogen tetroxide were often used, (2) reaction conditions were often not clearly defined, (3) the possible products are numerous and often unstable and difficult to isolate, and (4) structure was often inferred from an elementary analysis, the methods for which were not always reliable.

In general, it may be stated that reaction of olefins
and oxides of nitrogen yields a mixture of addition products which contains nitroso, nitro, nitrite, and nitrate groups. The nitroso adducts probably arise from addition of dinitrogen trioxide; the nitrates are probably derived from oxidation of the nitrites initially formed.

Recently, it has been found that addition of dinitrogen tetroxide to alkenes may be controlled at -10° to 25° in the presence of oxygen and basic solvents of the ether-ester type (ethyl ether, benzyl methyl ether, dioxane, ethyl formate, ethyl acetate) to yield vicinal dinitroalkanes and nitro-nitrites. The total yield of nitrated derivatives is usually between 65-85% but the ratio of dinitro to nitro-nitrite varies according to the particular alkene and experimental conditions. Oxidation of the nitro-nitrites by dinitrogen tetroxide or oxygen also yields nitro-nitrates. The reaction mixtures are usually separated after the solvent and excess dinitrogen tetroxide have been removed under vacuum on a falling film evaporator and the nitro-nitrites are converted to the nitroalcohols by reaction with methanol or water.

The mode of addition of dinitrogen tetroxide to unsymmetrical alkenes has been found to be specific, resulting in an orientation such that the nitro group is always attached to the carbon atom containing the larger number of hydrogen atoms. For instance, propene yields 1,2-dinitro-
propane (18-20%), 1-nitro-2-propyl nitrite (33-41%, isolated as 1-nitro-2-propanol), and 1-nitro-2-propyl nitrate (3-4%) (Equations 1).

It has been proposed\(^3\) on the basis of the directive influence exerted by unsymmetrical olefins, the specific solvent effect of certain ethers and esters, and the function of oxygen, that dinitrogen tetroxide adds as an electrophilic reagent. The initial step is attachment of the electronegative nitrogen atom of \(\text{NO}_2^+\) to the activated olefinic system; the second group, as \(\text{NO}_2^-\), is attached through \(\text{C}-\text{N}\) to yield a dinitroalkane or through \(\text{C}-\text{O}\) to yield nitro-nitrite.

A number of structures have been proposed for dinitrogen tetroxide.

\[
\begin{align*}
\text{I} & : \quad \cdot\text{O}^+ + \cdot\text{O}^- \\
\text{II} & : \quad \cdot\text{O}^+ = \text{O-N=O} \\
\text{III} & : \quad \cdot\text{O}=\text{N-O}=\text{O}^+ \\
\text{IV} & : \quad \cdot\text{O}=\text{N-O}=\text{O}^-
\end{align*}
\]

At present, on the basis of entropy measurements\(^5\), X-ray diffraction studies\(^6,7,8\), and spectroscopic data\(^9\), it is
believed that dinitrogen tetroxide has the symmetrical Structure I. In this structure, nitrogen is attached to nitrogen by a weak covalent bond; the nitrogen-nitrogen bond distance is $1.64 \pm 0.03 \text{Å}$, compared to a normal N-N bond distance of $1.47 \text{Å}$.

Structure II has been suggested on the basis of chemical reactions which dinitrogen tetroxide undergoes to yield both nitronium and nitrite ions; this structure also has the advantage of not violating the adjacent charge rule. Ingold and Ingold\textsuperscript{4} discount this aspect by suggesting that Structure I will also yield the nitronium and nitrite ions readily by the following polarization:

\[
\text{NO}_2^+ + \text{NO}_2^-
\]

There has been little evidence for Structure III; Structure IV has been recently proposed because it satisfies the physical requirements of symmetry and it can possibly be cleaved to give nitrogen dioxide, nitroso, nitronium, nitrite, and nitrate ions. Structure I will be used in the interpretation of the results of this dissertation.

The principle electronic structures of the linear nitronium ion and the triangular nitrite ion are $\overset{+}{\text{O}}=\overset{+}{\text{N}}:\overset{-}{\text{O}}$.
and \( \text{N}::\text{O} \): respectively. The nitronium ion usually gives C-N attachment upon reaction with a carbanionic center; the nitrite ion in reactions with alkylation agents (sources of positive centers) usually results in attack on either oxygen or nitrogen of the nitrite ion to give both alkyl nitrites and nitroalkanes\(^{10,11,12,13}\). Thus, reaction of silver or potassium nitrite with alkyl halides yields various amounts of both nitro and nitrite derivative; the ratio depends on the structure of the particular alkyl halide and the dielectric nature of the solvent medium (Equation 2).

\[
\text{R-} + \text{M}^+\text{NO}_2^- \rightarrow \text{R-ONO} + \text{R-NO}_2 + \text{M}
\]

The solvent is very important in moderating the oxidizing effect of the dinitrogen tetroxide in addition reactions to olefins. For example, propylene or isobutylene, in the absence of a solvent, are extensively oxidized and give no dinitroalkanes\(^3\). The moderating effect of the ether-ester type solvents is undoubtably related to their ability to form molecular addition compounds with dinitrogen tetroxide. For example, ethyl ether, tetrahydrofuran, tetrahydropyran, and dioxane\(^\text{14}\) form the following molecular complexes with dinitrogen tetroxide: \( \text{N}_2\text{O}_4\cdot2(\text{C}_2\text{H}_5)_2\text{O} \) (m.p. -78.4\(^\circ\)), \( \text{N}_2\text{O}_4\cdot\text{C}_4\text{H}_8\text{O} \) (m.p. -20.5\(^\circ\)), \( \text{N}_2\text{O}_4\cdot2\text{C}_5\text{H}_{10}\text{O} \) (m.p. -65.5\(^\circ\)), and \( \text{N}_2\text{O}_4\cdot0(\text{CH}_2\text{CH}_2)_2\text{O} \) (m.p. -45.2\(^\circ\)). It is also known\(^3\) that ethers with reduced electron density on oxygen, i.e. less tendency to form these...
molecular addition compounds, are poor solvents. Thus extensive oxidation takes place with 2,2'-dichloroethyl ether as a solvent; this ether shows no tendency to form a molecular addition compound with dinitrogen tetroxide\textsuperscript{14}. Formic esters, such as ethyl formate, are intermediate solvents, in that both oxidation and formation of dinitroalkanes occur. The ratio of solvent to dinitrogen tetroxide is also important; if the concentration of dinitrogen tetroxide is high, extensive oxidation occurs.

In addition to reducing the oxidizing effect of dinitrogen tetroxide, it has been suggested\textsuperscript{3a} that the formation of molecular addition compounds with solvents will act to further weaken the elongated nitrogen-nitrogen bond (1.64 ±0.03Å\textsuperscript{0} compared to 1.47Å\textsuperscript{0} for a typical N-N covalent linkage\textsuperscript{9}) in dinitrogen tetroxide and thus aid in forming nitronium and nitrite ions.

The role of oxygen\textsuperscript{3a} is probably that of minimizing the effective concentration of dinitrogen trioxide formed when the tetroxide acts as an oxidizing agent. In many instances, the presence of oxygen also apparently increases the yield of nitro-nitrate at the expense of nitro-nitrite.

Addition of dinitrogen tetroxide to unsymmetrical, electronegatively-substituted olefins was first investigated by Egoroff\textsuperscript{15}. It was reported that acrylic acid, methyl acrylate, crotonic acid, ethyl crotonate, and methacrylic acid all added dinitrogen tetroxide to give mixtures of
dinitro and mononitro adducts. Since the reaction products could not be separated, their compositions were inferred from their quantitative analysis, and their structures were deduced from the hydroxyamino acids isolated after reducing the mixtures. Crotonic acid and ethyl crotonate yielded \( \alpha \)-amino-\( \beta \)-hydroxybutyric acid (Equations 3), whereas methyl acrylate and methacrylic acid gave isoserine and \( \beta \)-amino-\( \alpha \)-hydroxy-\( \alpha \)-methylpropionic acid respectively (Equations 4).

(3)  
\[ \text{CH}_3\text{-CH} = \text{CH}\text{-CO}_2\text{H} + \text{N}_2\text{O}_4 \xrightarrow{1. \text{Pet. Ether}} \xrightarrow{2. \text{H}_2\text{O}} \text{H} \quad \text{CH}_3\text{-C} - \text{C} - \text{CO}_2\text{H} \xrightarrow{\text{Sn}} \text{H} \quad \text{H} \quad \text{NO}_2 \quad \text{OH} \]

(4)  
\[ \text{CH}_2\text{-CH}\text{-CO}_2\text{CH}_3 + \text{N}_2\text{O}_4 \xrightarrow{\text{EtOH}} \xrightarrow{\text{HCl}} \text{CH}_2\text{-CH}\text{-CO}_2\text{CH}_3 \quad \text{Sn} \quad \text{H} \quad \text{H} \quad \text{NO}_2 \quad \text{OH} \]

Aberhalden and Heyns\(^{16}\) report that crotonic acid and dimethylacrylic acid give a mixture of dinitro adducts and the 2-hydroxy-3-nitro and 3-hydroxy-2-nitro acids.

If addition of dinitrogen tetroxide does occur by an electrophilic ionic process, reaction of dinitrogen tetroxide and all acrylic homologs would be expected to yield
the dinitro derivatives and the nitrite and nitrate ester of substituted 3-hydroxy-2-nitropropionates (Equations 5).

\[
\begin{align*}
\text{R}^1\text{C}^+\text{H}^+ - \text{CH-}\text{CO}_2\text{R} + \text{O}_2\text{N}-\text{NO}_2 & \rightarrow \text{R}^1\text{C}^+\text{H}^+ - \text{CH-}\text{CO}_2\text{R} + \text{ON}_2\text{NO}_2 \\
\text{R}^1\text{C}^+\text{H}^+ - \text{CH-}\text{CO}_2\text{R} + \text{O}_2\text{N}-\text{NO}_2 & \rightarrow \text{R}^1\text{C}^+\text{H}^+ - \text{CH-}\text{CO}_2\text{R} + \text{ON}_2\text{NO}_2
\end{align*}
\]

The formation of methyl 2-hydroxy-3-nitropropionates reported for methyl acrylate\textsuperscript{15,16}, methacrylic acid\textsuperscript{15}, and dimethylacrylic acid\textsuperscript{16} cannot be reconciled with the proposed electrophilic ionic mechanism.

Olefins which are substituted with electronegative groups such as the cyano, nitro, sulfone or carboxyl are known to undergo nucleophilic ionic additions with amines and mercaptans\textsuperscript{40}. The acrylate homologs are included in this class of olefins and on this basis, the addition of dinitrogen tetroxide could be postulated to proceed by an initial nucleophilic ionic attack. However, little is gained by postulating this mechanism since it leads to the same orientations already outlined for the electrophilic ionic mechanism.
B. RESULTS OF PRESENT RESEARCH

Reaction of methyl acrylate and dinitrogen tetroxide occurred rapidly in ethyl ether at 0° in the presence of oxygen to yield, after hydrolysis, neutralization, and distillation of the products, methyl 3-nitroacrylate (13%), methyl 2-hydroxy-3-nitropropionate (27%), oxalic acid, and high boiling, ether-insoluble residues assumed to be polymers of methyl acrylate or methyl 2-nitroacrylate (Equations 6).

\[ \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 + \text{N}_2\text{O}_4 \xrightarrow{0^\circ} \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 + \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 + \text{H}_2\text{O} \]

1. H\textsubscript{2}O
2. CO(N\textsubscript{2})\textsubscript{2}
3. Dist. → CH=CH-CO\textsubscript{2}CH\textsubscript{3} + CH=CH-CO\textsubscript{2}CH\textsubscript{3}

There was no evidence for the formation of the isomeric products, methyl 2-nitroacrylate or methyl 3-hydroxy-2-nitropropionate. In solvents such as methanol extensive oxidation of the reaction mixture and solvent occurred, and the reactions could not be controlled. Treatment of the aqueous
solutions with urea (Equations 6, 2) was found to greatly increase the stability of the reaction mixtures. Treatment with urea prevents appreciable amounts of oxides of nitrogen from being carried into the ethereal extracts. The products are then more stable to distillation and oxidation of the products to oxalic acid (up to 80%) is prevented. No dinitro or nitro-nitrate derivatives could be isolated; however, it is believed that the methyl 3-nitroacrylate, isolated directly from the reaction mixture, resulted from loss of nitrous or nitric acids from methyl 2-nitrito-3-nitro-propionate and methyl 2-nitrato-3-nitropropionate.

Methyl 2-hydroxy-3-nitropropionate was identified, after hydrolysis with dilute sulfuric acid, as 2-hydroxy-3-nitro-propionic acid (94%, Equation 7), previously prepared by

\[
\begin{align*}
\text{(7)} & \quad \frac{\text{CH}_2\text{CH}-\text{CO}_2\text{CH}_3}{\text{NO}_2\text{OH}} \xrightarrow{\text{H}_2\text{O}} \quad \frac{\text{CH}_2\text{CH}-\text{CO}_2\text{H}}{\text{NO}_2\text{OH}} \\
\end{align*}
\]

Hill and Black\(^{17}\) by decarboylation of 2-hydroxy-3-nitro-succinic acid. 2-Hydroxy-3-nitropropionic acid was also prepared independently by the base catalyzed condensation of glyoxylic acid and nitromethane (72%, Equation 8).

\[
\begin{align*}
\text{(8)} & \quad \frac{\text{CH}_3\text{NO}_2}{\text{H}} \quad \frac{\text{O}=\text{C}-\text{CO}_2\text{H}}{\text{NaOH}} \quad \frac{\text{CH}_2\text{CH}-\text{CO}_2\text{H}}{\text{NO}_2\text{OH}} \\
\end{align*}
\]
Exhaustive hydrolysis of methyl 2-hydroxy-3-nitropropionate gave oxalic acid; the oxalic acid was presumably formed by oxidation of glyoxylic acid.

Methyl 3-nitroacrylate, identical with that obtained directly from methyl acrylate and dinitrogen tetroxide, was obtained by acetylation of methyl 2-hydroxy-3-nitropropionate with acetyl chloride and subsequent thermal decomposition of the ester (Equation 9).

\[
\begin{align*}
1. & \quad \text{CH}_2\text{COCl} \\
& \quad \text{CH}_2=\text{CHCO}_2\text{CH}_3 \\
& \quad \text{CH}=\text{CH}_2\text{CO}_2\text{CH}_3
\end{align*}
\]

Methyl 3-nitroacrylate may exist in cis and trans modifications; however, the stereochemistry of the product in this research has not been established (it is assumed to be trans).

The research was extended to include the addition of dinitrogen tetroxide to acrylic acid and acrylonitrile. However, the reaction mixtures were never sufficiently stable under the experimental conditions to permit isolation of any products. Frequent violent decompositions occurred, often while the reaction mixture was still in the ethereal solutions.
C. DISCUSSION OF RESULTS

On the basis of this investigation, it can be concluded that, under conditions identical with those used in the addition of dinitrogen tetroxides to alkenes, orientation in the addition of dinitrogen tetroxide to methyl acrylate is opposite from that which would be predicted on the basis of the electrophilic ionic mechanism proposed for the simple alkenes. Since this ionic mechanism cannot be extended to explain the results found for methyl acrylate, it seems advisable to reopen the question of the mechanism of the addition of dinitrogen tetroxide to olefinic systems in solvents of low dielectric constant.

Initial dissociation or bond rupture in bimolecular additions of dinitrogen tetroxide to unsaturated systems may be represented by at least three processes (Equations 10, 11, 12).

(10) \[ \text{N}_2\text{O}_4 \rightleftharpoons \text{NO}^+ + \text{NO}_3^- \]

(11) \[ \text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2^+ + \text{NO}_2^- \]

(12) \[ \text{N}_2\text{O}_4 \rightleftharpoons \cdot\text{NO}_2 + \cdot\text{NO}_2 \]

Addison and Thompson review many reactions of dinitrogen tetroxide which appear to involve NO\(^+\) and NO\(_3^-\) ions, (Equation 10); however, the evidence is derived chiefly from ionic
reactions with inorganic salts or measurements in strongly acidic and polar solvents such as nitric acid. The specific conductivity of liquid dinitrogen tetroxide is reported to be $1.3 \times 10^{-3}$ ohm$^{-1}$ cm$^{-1}$ at $17^\circ$; it may be concluded that dissociation into ionic species is negligible at this temperature. Dissociation of liquid dinitrogen tetroxide into nitrogen dioxide (Equation 12) is reported to be 0.15% at $0^\circ$; dissociation in carbon tetrachloride at $8.2^\circ$ is approximately 0.2-0.4%.

Rubin has made rather thorough thermal, magnetic, and spectroscopic studies of the molecular addition compounds of the general type $N_2O_4 \cdot 2R_2O$, which dinitrogen tetroxide forms with various ethers. The following thermal results were reported; ethyl ether, $N_2O_4 \cdot 2(C_2H_5)_2O$ (m.p. $-74.8^\circ$); tetrahydrofuran, $N_2O_4 \cdot C_4H_8O$ (m.p. $-20.5^\circ$) and $N_2O_4 \cdot 2C_4H_8O$ (incongruent melting); tetrahydropyran, $N_2O_4 \cdot 2C_5H_10O$ (m.p. $-65.5^\circ$); and dioxane, $N_2O_4 \cdot 0(CH_2CH_2)_2O$ (m.p. $-45.2^\circ$). The shape of the freezing point curves also indicate that these compounds exist to some extent in the liquid state. The compounds are assumed to form by an acid-base reaction with the ether oxygens acting as the base center. The low basicity of 2,2'-dichloroethyl ether, probably the result of the inductive effect of the chlorine atoms and possible steric interference of the beta chlorine atoms, prevents this ether from forming a molecular addition compound.
Magnetic studies were made to determine if the compounds involved nitrogen dioxide or dinitrogen tetroxide as an entity. All the compounds were found to be diamagnetic even at temperatures well above their melting points. However, \( \text{N}_2\text{O}_4 \cdot 2(\text{C}_2\text{H}_5)_2\text{O} \) becomes paramagnetic (formation of nitrogen dioxide) at \(-7.1^\circ\), \( \text{N}_2\text{O}_4 \cdot \text{C}_4\text{H}_8\text{O} \) at \(-6.8^\circ\), and \( \text{N}_2\text{O}_4 \cdot 2\text{C}_5\text{H}_{10}\text{O} \) at \(-4.4^\circ\). The dioxane adduct is still diamagnetic at room temperature, but becomes dark brown a few degrees below its melting point. Since dinitrogen tetroxide becomes paramagnetic at \(-2.4^\circ\), it appears that coordination with ethers has no great effect on the dissociation of dinitrogen tetroxide into nitrogen dioxide.

Infrared and Raman spectra of the addition compounds were taken to determine if any of the ionic species derived from dinitrogen tetroxide (Equations 10, 11) are present in the addition compounds. Lines corresponding to characteristic dinitrogen tetroxide and ether frequencies were identified but no evidence for \( \text{NO}_2^+ \), \( \text{NO}_2^- \), \( \text{NO}^+ \), or \( \text{NO}_3^- \) was found.

On the basis of the orientation found, the properties of dinitrogen tetroxide in ethyl ether, and the apparent extensive polymerization during reaction, it is suggested that the reaction of methyl acrylate and dinitrogen tetroxide in ethyl ether may occur not by an electrophilic ionic process but rather by a free radical attack by nitrogen.
dioxide or dinitrogen tetroxide. The initial attack occurs on the terminal carbon exclusively by C-N attachment; the resulting radical may then undergo reaction with dinitrogen tetroxide or nitrogen dioxide by either C-O or C-N attachment to yield vicinal nitro-nitrite or dinitro adducts and nitrogen dioxide (Equations 13).

\[
(13) \quad \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 + \cdot\text{NO}_2 \rightarrow \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 \quad \frac{\text{N}_2\text{O}_4}{\text{NO}_2} \quad \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 + \cdot\text{NO}_2 \\
\text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 + \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 + \cdot\text{NO}_2
\]

Nitrogen dioxide, a relatively stable free radical, may be assigned the resonating structures\textsuperscript{21} in which the odd electron may be assigned to nitrogen or oxygen, possibly as a three electron bond. Electron pairing reactions of nitrogen dioxide with triphenylmethylyl and ethyl radicals are known to result in both oxygen and nitrogen alkylation\textsuperscript{22,23}.

The apparent specificity with which the nitrogen dioxide radical initially attacks the terminal position must be attributed to the greater stability of the intermediate radical. Thus, four resonating forms may be written for the
methyl 3-nitro-2-propionyl radical, whereas the methyl

\[
\begin{align*}
\text{H} & \quad \text{H}^- \quad \text{H} \\
\text{NO}_2 - \text{C} - \text{C} - \text{CO}_2 \text{H} & \quad \text{NO}_2 - \text{CH} = \text{C} - \text{CO}_2 \text{CH}_3 & \quad \text{NO}_2 - \text{C} = \text{CH} - \text{CO}_2 \text{CH}_3 \\
\text{H} & \quad \text{H} & \quad \text{H} \\
(1) & (2) & (3)
\end{align*}
\]

2-nitro-3-propionyl radical only has two important forms.

\[
\begin{align*}
\text{H} & \quad \text{H}^- \\
\text{CH}_2 - \text{C} - \text{CO}_2 \text{CH}_3 & \quad \text{CH}_2 - \text{C} - \text{CO}_2 \text{CH}_3 \\
\text{NO}_2 & \quad \text{NO}_2 \\
(1) & (2)
\end{align*}
\]

The apparent specificity of the initial attack of nitrogen dioxide by C-N rather than C-O attachment may be explained on the same basis. For example, with C-N attachment, radical hyperconjugation produces a completely conjugated system,

\[
\begin{align*}
\text{H}^- \\
\text{O} = \text{N} - \text{C} = \text{C} - \text{C} = \text{O} \\
\text{C} & \quad \text{OR} \\
\text{H} & \quad \text{H}
\end{align*}
\]

whereas, this conjugation or similar stabilizing forces are partially destroyed by C-O attachment.
The added enhancement of resonance stabilization as a result of C-N attachment must also be a contributing factor in determining the point of initial attack as well as the type attachment. Thus, attack at the terminal position produces a radical which is capable of a high degree of conjugation with the nitro group,

\[ H^* \]
\[ O=\overset{\text{N-0-C}}{\text{N}} = C-C^=O \]
\[ / I \quad I \quad \text{OR} \]
\[ \text{H} \quad \text{H} \]

but attack on the alpha carbon yields a radical of lesser conjugate ability.

\[ H^* \]
\[ \overset{\text{N-C}}{\text{N}} = C-C^=O \]
\[ / I \quad I \quad \text{OR} \]
\[ \text{H} \quad \text{H} \]

Methacrylic acid follows the same pattern described for methyl acrylate.

Extending these same arguments to crotonic and \( \rho,\rho \)-dimethylacrylic acids show that if the initial attack by nitrogen dioxide is on the alpha carbon of crotonic acid, an intermediate radical results which is capable of radical hyperconjugation with four hydrogen atoms, (\( \rho,\rho \)-dimethylacrylic acid would have 7 hydrogen atoms).
Initial attack at the beta position however results in an intermediate radical capable of radical hyperconjugation with only one hydrogen (\(\beta,\beta\)-dimethylacrylic acid has none).

Here then are plausible reasons for the fact that initial attack occurs exclusively by C-N attachment at the beta carbon atom in methyl acrylate and methacrylic acid\(^1\) but on the alpha carbon atom in crotonic acid\(^1\) and dimethylacrylic acid\(^1\).

On the basis of a radical mechanism, it is now apparent that the initial attack of dinitrogen tetroxide on an unsymmetrical olefin is not necessarily on the carbon atom containing the greater number of hydrogen atoms\(^3\) but may occur at the carbon atom which yields an intermediate radical capable of the highest degree of radical hyperconjugation.

The radical mechanism can be applied equally well to unsymmetrical terminal alkenes\(^3\). For example, if nitrogen dioxide or dinitrogen tetroxide attacks propylene at the
terminal position, it yields an intermediate radical with three important resonating radicals (hyperconjugation is also possible with the methyl group):

\[
\begin{align*}
\text{H} & \quad \text{H}^+ \\
\text{CH}_3\text{-}\text{C}-\text{CH} & \quad \text{CH}_3\text{-C}=\text{CH} \quad \text{CH}_3\text{-C}=\text{C} \quad \text{H}^+ \\
\text{H NO}_2 & \quad \text{H NO}_2 \quad \text{H NO}_2
\end{align*}
\]

(1) (2) (3)

the 2-nitropropyl radical has only two.

\[
\begin{align*}
\text{H} & \quad \text{H}^+ \\
\text{CH}_3\text{-C} - \text{CH}_2 & \quad \text{CH}_3\text{-C}=\text{CH} \\
\text{NO}_2 & \quad \text{NO}_2
\end{align*}
\]

(1) (2)

Wheland\textsuperscript{24} gives an excellent discussion of similar resonance structures which determine orientation in the peroxide catalyzed addition of hydrobromic acid to propene, vinyl bromide, and methyl acrylate. Orientation in the addition of benzenediazonium chloride to acrylonitrile\textsuperscript{25} and crotonic acid\textsuperscript{26} can be explained in a similar manner.

D. CONCLUSIONS

It now appears that the orientation observed in the reaction of dinitrogen tetroxide and unsymmetrical alkenes cannot be used as definitive evidence that addition occurs by an electrophilic ionic process. If initial radical attack
on the terminal position of an olefin by nitrogen dioxide occurs by C-N attachment, it is apparent that the end result will be the same as that predicted by an ionic process. There is very good evidence to support the supposition that in ethereal solvents, the initial attacking species is nitrogen dioxide rather than the nitronium ion.

E. EXPERIMENTAL

(1) Reaction of Dinitrogen Tetroxide and Methyl Acrylate.

Dinitrogen tetroxide (106 g., 1.15 moles, Matheson Co., dried over phosphoric anhydride) and ethyl ether (296 g., 4 moles, dried over sodium) was cooled to 0° in a flask equipped with a sealed stirrer, a gas inlet tube, and a dropping funnel. A stream of oxygen was bubbled through the mixture until it became light amber in color. Methyl acrylate (108 g., 1.25 moles, freshly distilled) was added dropwise over a one hour period. While stirring was continued, a stream of oxygen was passed into the reaction mixture for five hours at 0°.

The mixture was dropped slowly through a falling film evaporator, operating at 40° and a pressure of 100 mm., to remove the ether and excess dinitrogen tetroxide; the product was collected as an oil in distilled water at 0°. Urea (28 g., 0.5 mole) was added to neutralize any nitrous
acid present. The mixture was extracted with ethyl ether (7 x 200 ml. portions) and the aqueous layer was then continuously extracted with ethyl ether. The combined ether extracts were dried and then evaporated at reduced pressure. Yield of crude adduct: 152 g., 74%.

The crude product was distilled rapidly in nitrogen at pressures of 2-6 mm. to yield: (1) gaseous product (42.0 g., oxides of nitrogen, methyl acrylate, and water), (2) nitrated product (69.8 g.), b.p. 40-130° and (3) residue (40.2 g., decomposition and polymerization products, unidentified).

In order to prevent excessive decomposition or violent explosion during distillation, the distillation was stopped and the pot residue was extracted with ethyl ether to remove the insoluble polymer. Distillation of the ether extract was then resumed. Distillation of the nitrated product (Fraction 2, 69.8 g.) yielded: (1) methyl 3-nitroacrylate (19.8 g., 13% conversion), b.p. 45-50° (0.8-1.5 mm.), m.p. 34-35°, (2) methyl 2-hydroxy-3-nitropropionate (40.7 g., 27% conversion), b.p. 95-110° (0.8-1.5 mm.), m.p. 44-46° and (3) residue (3.2 g.). Methyl 3-nitroacrylate was crystallized as a yellow solid from methanol-water, m.p. 34-35°.

**Anal. Calcd for C₄H₅NO₄:** C, 36.57; H, 3.82; N, 10.69.

**Found:** C, 36.45; H, 3.80; N, 10.51.
Methyl 2-hydroxy-3-nitropropionate was recrystallized from chloroform-carbon tetrachloride as white needles, m.p. 46.5-47.5°.

Anal. Caled for C₄H₇NO₅: C, 32.31; H, 4.70; N, 9.40.  
Found: C, 32.28; H, 4.44; N, 9.38.

Methyl acrylate containing hydroquinone can be used; however, results obtained with this reagent are erratic. Reactions in which dinitrogen tetroxide was added to methyl acrylate in ether did not result in improved yield and the products have greater instability. Vigorous oxidation of the reaction mixture occurred when methanol was used as a solvent. Oxalic acid dihydrate (m.p. 100°, lit.¹ 100-101°; converted to oxanilide, m.p. 253-255°, lit.² 255-259°) was obtained in 80% yields when the excess dinitrogen tetroxide was not removed from the ether extracts; this is extremely important if the results are to be duplicated. Stronger bases than urea, such as sodium bicarbonate, caused a marked deterioration of the product. Distillations should be conducted behind a barricade with special care to prevent overheating during the first phases of the distillation. Once isolated from the reaction mixture, the products can be redistilled without danger.
Reactor of Methyl 2-Hydroxy-3-nitropropionate with Acetyl Chloride; Methyl 3-Nitroacrylate. A mixture of methyl 2-hydroxy-3-nitropropionate (6.8 g., 0.046 mole) and acetyl chloride (15.7 g., 0.2 mole) was refluxed for 30 minutes; hydrogen chloride was evolved continually. After acetyl chloride and acetic acid has been removed, a viscous, colorless oil was obtained, which, upon distillation under nitrogen, yielded: (1) nitrated product (6.5 g.), 40-90\(^\circ\) (5 mm.) and (2) residue (negligible). Redistillation of the nitrated product under nitrogen gave, after removal of acetic acid, methyl 3-nitroacrylate (2.6 g., 43% conversion, 65% yield), 57-60\(^\circ\) (4 mm.) and a crude mixture of methyl 2-acetoxy-3-nitropropionate and methyl 2-hydroxy-3-nitropropionate, (2.2 g.). Methyl 3-nitroacrylate crystallized on standing to form a green yellow solid, m.p. 34-35\(^\circ\). The melting point of the nitroacrylate was undepressed by addition of methyl 3-nitroacrylate obtained directly from methyl acrylate and dinitrogen tetroxide.

Hydrolysis of Methyl 2-Hydroxy-3-nitropropionate;

a. 2-Hydroxy-3-nitropropionic Acid.

A mixture of methyl 2-hydroxy-3-nitropropionate (5.0 g., 0.033 mole), distilled water (75 ml.) and concentrated sulfuric acid (3 drops) was distilled slowly over a 5 hour period; as distillate was removed, water (200 ml.) was added
to the mixture to maintain its volume of 75 ml. The solution was extracted continuously with ethyl ether; the ether extract was dried over sodium sulfate. After ether was removed by vacuum distillation, 2-hydroxy-3-nitropropionic acid was obtained as a white solid (4.3 g., 94% yield). The acid, after recrystallization from a mixture of ethyl ether and chloroform, melted at 77-78°, lit.17 76-77°; neut. equiv. (calcd.) 135, neut. equiv. (found) 134.6. The melting point of the product was not depressed by addition of 2-hydroxy-3-nitropropionic acid prepared from nitromethane and glyoxylic acid.

b. Oxalic Acid.

Hydrolysis of methyl 2-hydroxy-3-nitropropionic acid over a 3 hour period, while using the same procedure and proportions of reagents as previously described but without repenishing the water removed, yielded crude oxalic acid dihydrate, identified as anhydrous oxalic acid (1.54 g., 85% yield); m.p. 183-185° (sublimation over 150°), lit.29 186-187°; neut. equiv. of monosodium oxalate (calcd.) 130, neut. equiv. (found) 129.

(4) Condensation of Glyoxylic Acid and Nitromethane; 2-Hydroxy-3-nitropropionic Acid. An aqueous solution of glyoxylic acid30 (3.3 g., 0.0455 mole in 50 ml. of water)
was neutralized with 10% sodium hydroxide (phenolphthalein indicator) and then excess base (one ml.) was added. Nitromethane (16.5 g., 0.27 mole) was added and the mixture was stirred at 25-30° for 19 hours and then at 60-80° for one hour. Sulfuric acid (100 ml., 6N) was added, and the solution was continuously extracted with ethyl ether. The ether extract was decolorized with charcoal, filtered, and dried over anhydrous sodium sulfate. After evaporation of the ether at reduced pressure, a yellow solid (5.3 g.) remained; recrystallization of the solid from ethyl ether-benzene gave a white crystalline solid (4.35 g.) and red oil (0.86 g.). The white solid was identified as 2-hydroxy-3-nitropropionic acid (72% yield); m.p. 75-76°, lit.17 76-77°; neut. equiv. (calcd.) 135, neut. equiv. (found) 134.6. The red oil was characterized as glyoxylic acid by reaction with 2,4-dinitrophenylhydrazine.
PART II

ADDITION OF NITRYL CHLORIDE TO METHYL ACRYLATE, ACRYLIC ACID, AND ACRYLONITRILE

A. BACKGROUND AND PURPOSE

The present studies were made in order to obtain more information concerning the mode of addition and mechanism in the additions of nitryl chloride to unsymmetrical olefins in solvents of low dielectric strength. Methyl acrylate, acrylic acid, and acrylonitrile were chosen for this study.

Previous to this research, Steinkopf and Kuhnel\textsuperscript{31} reported the following additions of nitryl chloride to olefinic systems. Ethylene yields ethylene dichloride; sym-dichloroethylene yields 1,1,2-trichloro-2-nitroethane; trichloroethylene gives 1,1,1,2-tetrachloro-2-nitroethane; tetrachloroethylene yields 1,1,1,2,2-pentachloro-2-nitroethane; and vinyl bromide in carbon tetrachloride gives 1-bromo-1-chloro-2-nitroethane. Cyclohexene yields 1-chloro-2-nitrocyclohexane; styrene in ether gives styrene pseudo-nitrosite but in benzene yields 1-chloro-2-nitro-2-phenylethane; stilbene in ether gives stilbene dichloride but in benzene gives 1-chloro-1-phenyl-2-phenylethane; and cinnamic acid yields 2-chloro-3-nitro-3-phenylpropanoic acid. No
evidence of isomeric compounds was found in these additions.

In a more recent study, Sears\textsuperscript{32} reports that cyclohexene not only gives 1-chloro-2-nitrocyclohexane but also 1,2-dichlorocyclohexane and a pseudonitrosite; 2-butene gives 2-chloro-3-nitrobutane; propylene gives 2-chloro-1-nitropropane; and isobutylene gives a pseudonitrosite, 2-chloro-1-nitroisobutane, and the nitrite ester of 1-nitro-2-methyl-2-propanol. Again no evidence for isomeric compounds was found.

During the course of this research, it was reported\textsuperscript{33} by Brentzinger and Pfannstiel that reaction of nitryl chloride with methyl acrylate and acrylonitrile in the absence of a solvent yields methyl 2-chloro-3-nitropropionate and 2-chloro-3-nitropropionitrile, respectively. No physical or chemical evidence was given for the structures of these products; the structures were inferred from an elementary analysis. Much of the work of Brentzinger and Pfannstiel differs from that of the present investigation.

\textbf{B. THE PRESENT RESEARCH}\textsuperscript{a}

(1) Preparation of Nitryl Chloride. Nitryl chloride

\textsuperscript{a} Parts of this work were carried out by A.L. Daulton. It is presented here to provide continuity and give the details necessary to support the conclusions drawn. The work done by Mr. Daulton will be so marked in the experimental section.
was prepared from anhydrous nitric and chlorosulfonic acids (Equation 14).

\[
HNO_3 + ClSO_3H \rightarrow NO_2Cl + H_2SO_4
\]

(2) Reactions of Nitryl Chloride and Methyl Acrylate.

Nitryl chloride and methyl acrylate react at 0° to give methyl 2,3-dichloropropionate (7%), methyl 2-chloro-3-nitropropionate (75%), and dimethyl 2-chloro-4-nitromethylpentanedioate (5-10%). An impure solid was also obtained which is believed to be a mixture of methyl 2-nitrito-3-nitropropionate and methyl 2,3-dinitropropionate; these products could not be separated completely because of the difficulties involved in their purification (Equations 15).

\[
\begin{align*}
\text{O}_2\text{N-CH}_2\text{-CH}_2\text{-CO}_2\text{CH}_3 + NO_2\text{Cl} & \rightarrow \text{CH}_2\text{-CH-CO}_2\text{CH}_3 + \text{CH}_2\text{-CH-CO}_2\text{CH}_3 + \\
\text{Cl} & \quad \text{Cl} \\
\text{NO}_2\text{C1} &
\end{align*}
\]

\[
\text{O}_2\text{N-CH}_2\text{-C} - \text{CH}_2\text{-CH-CO}_2\text{CH}_3 + \left[ \text{NO}_2\text{ON0} \right] \quad \left[ \text{CH}_2\text{-CH-CO}_2\text{CH}_3 \right] \quad \left[ \text{CH}_2\text{-CH-CO}_2\text{CH}_3 \right]
\]

Reaction of nitryl chloride and methyl acrylate also occurred readily in anhydrous ether and the direction of addition was identical with that obtained in the absence of a solvent; however, reaction in the absence of a solvent, gave products
which were more readily distillable.

Methyl 2-chloro-3-nitropropionate was identified by conversion into methyl 3-nitroacrylate, identical with that obtained from dinitrogen tetroxide and methyl acrylate (Section I, Part I). The dehydrochlorination was effected with either pyridine, N,N-dimethylaniline (65%), or anhydrous sodium acetate (92%) (Equation 16).

\[
\begin{align*}
\text{(16)} & \quad \text{CH}_2-\text{CH}-\text{CO}_2\text{CH}_3 + \text{NaC}_2\text{H}_3\text{O}_2 + \text{HCl} \rightarrow \text{CH}=\text{CH}-\text{CO}_2\text{CH}_3 + \text{NO}_2^2
\end{align*}
\]

The methyl 3-nitroacrylate is presumed to be trans.

The structure of dimethyl 2-chloro-4-nitromethylpentanedioate was established as follows: Conversion into glutaric acid by hydrolysis and decarboxylation with 70% sulfuric acid at 110-115° and subsequent reduction with 57% hydriodic acid (Equations 17).

\[
\begin{align*}
\text{(17)} & \quad \text{O}_2\text{N}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CO}_2\text{CH}_3 + \text{H}_2\text{SO}_4(70\%) \rightarrow (\text{HO}_2\text{C})_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CO}_2\text{H} + \text{Cl} \\
& \quad \text{H}_2\text{CO}_2\text{C} \quad \text{Cl} \\
& \quad \text{Cl} \\
& \quad \text{Cl}
\end{align*}
\]

Glutaric acid was characterized as its di-p-bromophenacyl
ester. Similar treatment of the probable isomeric adducts, dimethyl 2-chloromethyl-4-nitropentanedioate and dimethyl 2-chloromethyl-3-nitromethylsuccinate would be expected to yield 2-methylsuccinic acid.

3) Reaction of Nitryl Chloride and Glacial Acrylic Acid. Nitryl chloride and glacial acrylic acid react at 0° to yield principally 2-chloro-3-nitropropionic acid (65-71%); the orientation is identical in direction with that of addition of nitryl chloride to methyl acrylate (Equation 18).

\[
\text{CH}_2\text{=CH-CO}_2\text{H} + \text{NO}_2\text{Cl} \rightarrow \text{CH}_2\text{=CH-CO}_2\text{H} \\
\mid \mid \mid \text{NO}_2\text{Cl}
\]

The structure of 2-chloro-3-nitropropionic acid was established, after thermal dehydrochlorination (65-70%) or reaction with anhydrous sodium acetate (98%) to give 3-nitroacrylic acid, by conversion to 2-hydroxy-3-nitropropionic acid\(^\text{17}\) (83%) with 70% formic acid (Equations 19).

\[
\text{CH}_2\text{=CH-CO}_2\text{H} \rightarrow \text{CH}=\text{CH-CO}_2\text{H} \\
\mid \mid \mid \text{NO}_2\text{Cl} \rightarrow \text{NO}_2\text{Cl} \\
1. \text{Heat} \\
2. \text{NaC}_2\text{H}_3\text{O}_2
\]

\[
\text{HCO}_2\text{H}(70\%), \text{H}_2\text{O} \rightarrow \text{CH}_2\text{-CH-CO}_2\text{H} \\
\mid \mid \mid \text{NO}_2\text{OH} \\
85-100^\circ
\]
Reactions of Nitryl Chloride and Acrylonitrile.

Reaction of acrylonitrile and nitryl chloride at 0° in the absence of a solvent gave 2,3-dichloropropionitrile (13.5%) and 2-chloro-3-nitropropionitrile (76%, Equation 20); when ethyl ether was used as a solvent, 3-nitroacrylonitrile (48.2%) and ammonium chloride were also produced.

The identity of 2-chloro-3-nitropropionitrile was established by (a) dehydrochlorination to 3-nitroacrylonitrile with anhydrous sodium acetate (79%), (b) hydrolysis of the unsaturated nitronitrile with sulfuric acid to 3-nitroacrylamide (54%), and acid hydrolysis of 3-nitroacrylonitrile and subsequent reaction with nitrous acid to yield 3-nitroacrylic acid (68%), (Equations 21). The 3-nitroacrylic acid, presumably trans, is identical with that obtained by dehydrochlorination of 2-chloro-3-nitropropionic acid derived from nitryl chloride and glacial acrylic acid.

(21) $\text{CH}_2=\text{CH-CN} \xrightarrow{\text{NaC}_2\text{H}_3\text{O}} \text{CH}=\text{CH-CN} \xrightarrow{\text{H}_2\text{SO}_4(85\%)} \text{CH}=\text{CH-COH}_2 \\
\text{NO}_2\text{Cl} \quad \text{NO}_2 \quad \text{NO}_2 \quad \text{NO}_2 \\
\xrightarrow{\text{HNO}_2} \text{CH}=\text{CH-CO}_2\text{H} \\
\text{NO}_2 \quad \text{NO}_2
C. DISCUSSION OF RESULTS.

The results of this and previous investigations\textsuperscript{31,32} illustrate that the orientation in addition of nitryl chloride to vinyl bromide, terminal olefins, and acrylic systems is identical in that a nitro group is attached to the terminal carbon. Thus, vinyl bromide yields 1-chloro-1-bromo-2-nitroethane, propene gives 2-chloro-1-nitropropane, and methyl acrylate gives methyl 2-chloro-3-nitropropionate (Equations 22, 23, 24); no evidence for isomeric compounds appears to have been obtained.

\begin{align*}
\text{(22)} \quad \text{NO}_2\text{Cl} + \text{CH}_2\text{=CHBr} & \rightarrow \frac{\text{CH}_2\text{=CH-Br}}{\text{NO}_2\text{Cl}} \\
\text{(23)} \quad \text{NO}_2\text{Cl} + \text{CH}_2\text{=CH-CH}_3 & \rightarrow \frac{\text{CH}_2\text{=CH-CH}_3}{\text{NO}_2\text{Cl}} \\
\text{(24)} \quad \text{NO}_2\text{Cl} + \text{CH}_2\text{=CH-CO}_2\text{CH}_3 & \rightarrow \frac{\text{CH}_2\text{=CH-CO}_2\text{CH}_3}{\text{NO}_2\text{Cl}}
\end{align*}

If it is assumed that addition of nitryl chloride to vinyl bromide, terminal olefins, and acrylic systems occurs by the same mechanism, it may be concluded that neither the inductive nor the resonance demands of the group attached to the olefin determines the specificity of orientation of addition. Upon considering the inductive effect of the constituent groups, it would be predicted that in the activated state in alkenes the terminal position would be
relatively negative; whereas in vinyl bromide and the various acrylates, the relative polarities are reversed and the terminal positions are relatively positive.

\[
\begin{align*}
\text{CH}_3\rightarrow&\text{CH}^\text{\#}\text{CH}_2 \\
\text{Br}\rightarrow&\text{CH}^\text{\#}\text{CH}_2 \\
\text{CH}_2\rightarrow&\text{CH}^\text{\#}\text{CO}_2\text{CH}_3
\end{align*}
\]

Upon considering the usual resonance effects of the substituent groups, it would be predicted in alkenes that the terminal position is relatively negative; in vinyl bromide the terminal position also becomes relatively negative; with the acrylates the resonance effects enhance the inductive effects and thus the terminal position is relatively positive.

\[
\begin{align*}
\text{H}^+\rightarrow&\text{CH}^\text{\#}\text{CH}^\text{\#}\text{CH}_2 \\
\text{Br}\rightarrow&\text{CH}^\text{\#}\text{CH}_2 \\
\text{CH}_2\rightarrow&\text{CH}^\text{\#}\text{C}^\text{\#}\text{O}
\end{align*}
\]

Upon comparing the combined inductive and resonance effects in terminal alkenes and in acrylic systems, it seems certain that polarization of the unsaturated centers are of the opposite type.

The three possible modes of heterolytic and homolytic cleavage of nitryl chloride which might account for the addition products are as follows: (Equations 25, 26, 27).

(25) \[ \text{NO}_2\text{Cl} \rightleftharpoons \text{NO}_2^+ + \text{Cl}^- \]
Reaction of benzene with nitryl chloride results in the formation of appreciable percentages of both nitrobenzene and chlorobenzene. In the presence of the Lewis acid, aluminum chloride, the relative yield of nitrobenzene from benzene and nitryl chloride is greatly increased. Since it has been generally accepted that the active species in the nitration of aromatic hydrocarbons is the nitronium ion \( \text{NO}_2^+ \), Sears has postulated ionization of nitryl chloride in aluminum chloride as \( \text{NO}_2\text{Cl} + \text{AlCl}_3 \leftrightarrow \text{NO}_2^+ + \text{AlCl}_4^- \). If it is assumed that reaction of \( \text{NO}_2\text{Cl} \) involves initial heterolytic dissociation into nitronium and chloride ions or bimolecular heterolytic attack of a similar type, it would be predicted that reaction with propylene and vinyl bromide would yield the observed products (Equations 22, 23) but that reaction with acrylic derivatives will result in orientation (Equation 28) which is opposite to that which has been found in this investigation (Equations 15, 18, 20).

\[
\text{NO}_2\text{Cl} \leftrightarrow \text{NO}_2^+ + \text{Cl}^-
\]

(22) \hspace{1cm} \text{BrCH}=\text{CH}_2 + \text{NO}_2^+ \cdots \text{Cl}^- \rightarrow \text{BrCH}-\text{CH}_2 \hspace{1cm} \text{Cl} \hspace{1cm} \text{NO}_2
(23) \[ \text{CH}_3-\text{CH}==\text{CH}_2 + \text{NO}_2^+ \cdots \text{Cl}^- \rightarrow \text{CH}_3-\text{CH}-\text{CH}_2 \]
\[ \text{Cl} \text{ NO}_2 \]

(28) \[ \text{CH}_2=\text{CH-CO}_2\text{R} + \text{NO}_2^+ \cdots \text{Cl}^- \rightarrow \text{CH}_2\text{CH-CO}_2\text{R} \]
\[ \text{Cl} \text{ NO}_2 \]

The "positive" character of chlorine in nitryl chloride (Equation 26) has also been well established. Although as yet no conclusive evidence has been obtained for dissociation of nitryl chloride into chloronium (Cl\(^+\)) and nitrite (NO\(_2^-\)) ions, certain of the characteristics of chlorine in nitryl chloride resembles those of the halogen in hypochlorous acid and in N-chlorinated sulfonamides. Schmeisser\(^{34}\) has shown that hydrolysis of nitryl chloride yields hypochlorous acid, and reaction with ammonia gives monochloroamine and ammonium nitrate. Batey\(^{35}\) has made further studies of the positive character of chlorine in nitryl chloride. If initial heterolytic dissociation of NO\(_2\)Cl into NO\(_2^-\) and Cl\(^+\) ions occurs, or if addition involves bimolecular heterolytic attack of nitryl chloride as NO\(_2^-\cdots\text{Cl}^+\), it would lead to the prediction that reaction with olefins will result in formation of 1-chloro-2-nitroalkanes and 1-chloro-2-alkyl nitrites (Equation 29).

\[ \text{NO}_2\text{Cl} \leftrightarrow \text{NO}_2^- + \text{Cl}^+ \]

(29) \[ \text{CH}_3-\text{CH}=\text{CH}_2 + \text{NO}_2^- \cdots \text{Cl}^+ \rightarrow \text{CH}_3-\text{CH}=\text{CH}_2 + \text{CH}_3-\text{CH} - \text{CH}_2 \]
\[ \text{NO}_2 \text{ Cl} \text{ ONO} \text{ Cl} \]
With vinyl bromide, 1-nitro-1-bromo-2-chloroethane and chloroacetaldehyde would be the products expected (Equations 30).

\[
\text{Br-CH=CH}_2 + \text{NO}_2\cdots\text{Cl}^+ \rightarrow \text{BrCH - CH}_2 + \text{Br-CH - CH}_2 \\
\text{NO}_2 \quad \text{Cl} \quad \text{ONO} \quad \text{Cl}
\]

\[\rightarrow \text{O=CH-CH}_2\text{Cl} + \text{NOBr}\]

Heterolytic attack of the \(\text{NO}_2\cdots\text{Cl}^+\) type would account for the observed orientation with acrylic systems; however, 2-chloro-3-nitritopropionic acid derivatives should also be expected (Equation 31).

\[
\frac{\delta^+}{\delta^-} \frac{\text{CH}_2\text{CH}=\text{CHCO}_2\text{R}}{} + \frac{\text{NO}_2\cdots\text{Cl}^+}{\text{NO}_2\cdots\text{Cl}^+} \rightarrow \frac{\text{CH}_2\text{CH}-\text{CHCO}_2\text{R}}{\text{NO}_2 \quad \text{Cl}} + \frac{\text{CH}_2\text{CH}=\text{CHCO}_2\text{R}}{\text{ONO} \quad \text{Cl}}
\]

Nitryl chloride has been reported to decompose in the gas phase into nitrogen dioxide and chlorine by a first order process in the following manner (Equations 32, 33).

\[
\text{NO}_2\text{Cl} \rightarrow \cdot\text{NO}_2 + \text{Cl}^+ \quad \text{(slow)}
\]

\[
\text{NO}_2\text{Cl} + \text{Cl}^+ \rightarrow \cdot\text{NO}_2 - \text{Cl}_2 \quad \text{(fast)}
\]

The kinetics are quasi-monomolecular changing to second order. All contaminants increase the rate equally except nitrogen
dioxide which is 20% more efficient. Although some doubt has been cast on this work, it is agreed that nitryl chloride does decompose to give both nitrogen dioxide and chlorine. At present very little is known concerning the decompositions of nitryl chloride in the liquid phase. It has been observed in this investigation that decomposition of the acid chloride into nitrogen dioxide and chlorine occurs slowly at -5 to +5°. Nitryl chloride (light amber colored) on storage for two weeks becomes dark red in color; rectification of the deteriorated product indicates the increased concentration of nitrogen dioxide and chlorine. It may be concluded that nitryl chloride is relatively unstable with respect to nitrogen dioxide and chlorine since many attempts to prepare nitryl chloride from nitrogen dioxide and chlorine have failed.

From consideration of (a) the evidence for the possible modes of cleavage of nitryl chloride, (b) the specific direction of addition in reactions of nitryl chloride and acrylic systems, (c) the formation of dimethyl 2-chloro-4-nitromethylpentandioate from methyl acrylate and nitryl chloride, (d) the identical addition of nitryl chloride to electronegatively or electropositively substituted olefins, and (e) the similarity in the specificity of orientation of addition of nitryl chloride as with dinitrogen tetroxide, it appears that reaction of nitryl chloride and acrylate
systems in solvents of low dielectric constant does not involve heterolytic polarization or heterolytic initial dissociation during addition. It is suggested that addition of nitryl chloride to acrylic systems involved essentially a homolytic process in which nitrogen dioxide or nitryl chloride attacks the terminal carbon of the double bond resulting exclusively in C-N attachment. The reaction is completed by exchange of the intermediate radical with nitryl chloride to yield chloronitro compound and nitrogen dioxide (Equation 34).

\[
\begin{align*}
\text{CH}_2=\text{CH-} & \text{CO}_2\text{CH}_3 & \text{CH}_2=\text{CH-} & \text{CO}_2\text{CH}_3 \\
\cdot\text{NO}_2 & \xrightarrow{\text{NO}_2\text{Cl}} & \text{CH}_2=\text{CH-} & \text{CO}_2\text{CH}_3 + \cdot\text{NO}_2 \\
\text{NO}_2 & \text{Cl} & \text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl} \end{align*}
\]

The similarity of the mechanism of this reaction to that proposed for the addition of dinitrogen tetroxide to methyl acrylate is apparent. The initial attack of nitrogen dioxide may occur exclusively at the terminal carbon because the resulting methyl 3-nitro-2-propionyl radical is more stable than its methyl 2-nitro-3-propionyl isomer (see Part I). The same arguments hold for both acrylic acid and acrylonitrile. Although the arguments are not as definite (because as yet reaction as \text{NO}_2^+\cdot\cdot\cdot\text{Cl}^- cannot be ruled out) a mechanism of this type can be extended to other unsymmetrical olefins such as propylene and vinyl bromide (Equations 35, 36).
Formation of dimethyl 2-chloro-4-nitromethylpentane-dioate from nitryl chloride and methyl acrylate may result from reaction of the intermediate methyl 3-nitro-2-propionyl radical (Equation 37) with another molecule of methyl acrylate.

\[
\ce{CH_2=CH-CH_3 + CH_2=CH-CH_3 -> CH_2=CH-CH_2-CH-CO_2CH_3}
\]

The formation of this "dimer" is certainly suggestive of a radical mechanism; that similar "dimeric" products were not isolated for acrylic acid or acrylonitrile may be due to inability to isolate them or due to their absence.
for both reactions, initial attack involves formation of the terminal nitro derivative and subsequent final exchange to yield chloronitro adduct. Reaction involving dimerization of the radicals produced by competitive terminal attack of nitryl chloride (or nitrogen dioxide and chlorine) to yield secondary methyl 3-chloropropionyl and methyl 3-nitropropionyl radicals would result in the formation of dimethyl 2-nitromethyl-3-chloromethylsuccinate (Equations 38, 39, 40).

\[
\text{(38)} \quad \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 + \text{NO}_2\text{Cl} \rightarrow \text{CH}_2-\ddot{\text{CH}}-\text{CO}_2\text{CH}_3 + \text{NO}_2. \\
\text{(39)} \quad \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 + \text{NO}_2\text{Cl} \rightarrow \text{CH}_2-\ddot{\text{CH}}-\text{CO}_2\text{CH}_3 + \text{Cl}. \\
\text{(40)} \quad \text{CH}_2-\ddot{\text{CH}}-\text{CO}_2\text{CH}_3 + \text{CH}_2-\ddot{\text{CH}}-\text{CO}_2\text{CH}_3 \rightarrow \text{ClCH}_2-\text{CH}-\text{CO}_2\text{CH}_3
\]

Reaction involving initiation by halogen attack at the terminal position followed by addition of a second molecule of methyl acrylate and subsequent exchange with nitryl chloride would yield dimethyl 2-chloromethyl-4-nitropentanedioate (Equations 41, 42, 43).

\[
\text{(41)} \quad \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 + \text{NO}_2\text{Cl} \rightarrow \text{CH}_2-\ddot{\text{CH}}-\text{CO}_2\text{CH}_3 \\
\text{(42)} \quad \text{CH}_2-\ddot{\text{CH}}-\text{CO}_2\text{CH}_3 + \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 \rightarrow \text{ClCH}_2-\text{CH}-\text{CH}_2-\ddot{\text{CH}}-\text{CO}_2\text{CH}_3
\]
The proof of structure of the dimer adduct isolated militates against these mechanisms since 2-chloromethyl or 2-hydroxy-methylsuccinic acid (expected to be isolated as 2-methyl-succinic acid after reduction) would be expected if these alternate paths had been followed. The proof of structure does not rule out the possibility that the "dimer" adduct is dimethyl 2-chloro-4-nitroadipate, obtained by dimerization of primary methyl 2-chloropropionyl and methyl 2-nitropropionyl radicals (Equations 44, 45, 46);

\[
(44) \quad \text{CH}_2=\text{CH-CO}_2\text{CH}_3 + \text{NO}_2\text{Cl} \rightarrow \text{CH}_2=\text{CH-CO}_2\text{CH}_3 + \text{Cl} \cdot \text{NO}_2
\]

\[
(45) \quad \text{CH}_2=\text{CH-CO}_2\text{CH}_3 + \text{NO}_2\text{Cl} \rightarrow \text{CH}_2=\text{CH-CO}_2\text{CH}_3 + \text{NO}_2 \cdot \text{Cl}
\]

\[
(46) \quad \text{CH}_2=\text{CH-CO}_2\text{CH}_3 + \text{CH}_2=\text{CH-CO}_2\text{CH}_3 \rightarrow \text{CH}_3\text{O}_2\text{C-CH-CH}_2-\text{CH}_2-\text{CH-CO}_2\text{CH}_3
\]

Hydrolysis and reduction of this adduct is also expected to yield glutaric acid. It is believed however that the "dimer" adduct is not dimethyl 2-chloro-4-nitroadipate because (1) it fails to give a pseudonitrole and (2) exclusive head to
head addition and subsequent tail to tail dimerization for monomer systems is very rare.

The 2,3-dichloro adduct from methyl acrylate (up to 16%) may arise from an analogous radical-exchange process in which addition of a chlorine atom occurs at the terminal position followed by reaction with nitryl chloride. No final conclusions can be drawn at present concerning the importance of this mechanism since decomposition of nitryl chloride also yields chlorine and nitrogen dioxide.

It might be expected that dinitro or nitro-nitrite derivatives would be formed by reaction of the intermediate radical with nitrogen dioxide or nitryl chloride in a chain terminating reaction resulting in either C-N or C-O alkylation (Equation 47).

\[
(47) \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 + \cdot\text{NO}_2 \rightarrow \text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 \text{ or CH}_2=\text{CH}-\text{CO}_2\text{CH}_3
\]

It is strongly suspected that mixtures of methyl 2,3-dinitropropionate and methyl 2-nitrito-3-nitropropionate were also obtained. However, because of difficulties in their separation, the solids could not be purified or characterized. At present, it cannot be concluded from this study that they were not formed.
D. CONCLUSIONS

It is now felt that the reaction of nitryl chloride with unsymmetrical olefins, and the acrylic system in particular, proceeds by a radical process. In the initial step, nitrogen dioxide adds exclusively at the terminal carbon resulting exclusively in C-N attachment, the reaction is completed by exchange of the intermediate radical with nitryl chloride to yield chloronitro compound and nitrogen dioxide (Equation 34). The intermediate radical may also terminate the chain process by adding nitrogen dioxide by C-N or C-O attachment to form dinitro or nitro-nitrite derivatives (Equation 47). Although the fact that the direction of addition of nitryl chloride to terminal olefins, vinyl bromide, and acrylic systems is identical, it cannot be used as conclusive evidence as yet that all three reactions proceed by the same mechanism; it is of interest that the reaction of the same olefins with hydrogen bromide in the presence of peroxides gives identical addition in which the bromine atom adds exclusively at the terminal position (Equations 48, 49, 50).²⁴

(48) \[ \text{CH}_3\text{-CH=CH}_2 + \text{HBr} \xrightarrow{\text{H}_2\text{O}_2} \text{CH}_3\text{-CH}_2\text{-CH}_2\text{Br} \]

(49) \[ \text{BrCH=CH}_2 + \text{HBr} \xrightarrow{\text{H}_2\text{O}_2} \text{BrCH}_2\text{-CH}_2\text{Br} \]

(50) \[ \text{CH}_2\text{-CH-CO}_2\text{H} + \text{HBr} \xrightarrow{\text{H}_2\text{O}_2} \text{BrCH}_2\text{-CH}_2\text{-CO}_2\text{H} \]
E. **EXPERIMENTAL**

(1) **Preparation of Nitryl Chloride.**

Nitryl chloride was prepared from nitric acid (100%) and chlorosulfonic acid (100%) at 0°; the procedure is a modification of the method of Dachlauer.

a. **Reagents.** Technical chlorosulfonic acid (Eastman Kodak Co.) was distilled at atmospheric pressure in a glass apparatus protected by drying tubes containing anhydrous calcium chloride: b.p. 149-151°. Nitric acid (100%), prepared by distillation of a mixture of concentrated nitric acid (70% HNO₃, C.p.) and excess sulfuric acid (96%, C.p.) at a pressure of 22mm. in a glass apparatus, was used efficiently; however, it was more convenient to use fuming nitric acid (91.6%) to which was added sufficient fuming sulfuric acid to combine with the water present. Anhydrous nitric acid (100%) is now commercially available from The General Chemical Division, Allied Chemical and Dye Corporation, and may be used directly in this preparation.

b. **Procedure.** All operations were performed in a hood. All connections in the apparatus were of ground glass; openings in the system were fitted with drying tubes containing calcium chloride.

Fuming sulfuric acid (123 g., 30% sulfur trioxide) was added dropwise to fuming nitric acid (100 g., 1.47 moles,

b. The portions of the experimental carried out by Mr. Daulton are marked by an asterisk.
sp. gr. 1.50, 91.6% acid content) at 0° in a 500 ml. three-necked, round bottom flask equipped with an equi-pressure dropping funnel, and efficient motor-driven glass stirrer sealed with sulfuric acid, and a condenser cooled by Dry Ice-acetone. A receiver (a test tube of 125-150 ml. capacity) was connected to the condenser and then immersed in a cooling mixture of Dry Ice-acetone. The mixed acids were stirred vigorously at 0° while chlorosulfonic acid (170.5 g., 97.5 ml., 147 moles) was added slowly in 3-4 hours, or at a rate such that brown "nitrous fumes" did not appear above the reaction mixture. With the addition of each drop of chlorosulfonic acid, almost colorless gaseous nitryl chloride was evolved. After chlorosulfonic acid had been added, the cooling bath was removed and the mixture was stirred for one-half hour.

The product was a dense pale-yellow liquid freezing at -145 - 2°, lit. 36 -145° and boiling from -17 to -15°, lit. 36 -15°. Yield: 95-108 g. (80-90%). On the basis of analysis, the nitryl chloride is 98-99% pure° (98% based on Cl content, 99% on acidity).

Anal. Calcd. for NO₂Cl: Acidity in water, 24.55 m. eq. gm. per cent.

Found: 24.72.

Calcd. for NO₂Cl: Cl, 43.6.

Found: Cl, 44.9.

c. These analytical data were supplied by Castarina and Tomlinson, Chemical Research Section, Picatinny Arsenal, Dover, New Jersey.
(2) Reaction of Nitryl Chloride and Methyl Acrylate.

Nitryl chloride (195.6 g., 2.4 moles, 20% excess) was distilled through a gas delivery tube in 2 hours into methyl acrylate (172 g., 2 moles, anhydrous, b.p. 43.5° (200 mm.)) at 0° in a three-necked flask equipped with a liquid sealed stirrer and a series of drying tubes. The mixture, orange-red in color, was stirred for one hour at room temperature. Excess nitryl chloride (now containing chlorine and nitrogen dioxide) was removed by distillation at reduced pressure; the color of the mixture became light yellow-orange. The product was distilled under nitrogen at reduced pressure to yield:

Fraction 1 (22.2 g., 71%), b.p. 43-82° (18-22 mm.); Fraction 2 (251 g., 75.1%), b.p. 68-110° (2-4 mm.), and residue (43 g., 12.1%). Rectification of Fractions 1 and 2 at reduced pressure under nitrogen in a helix-packed column (24 x 2 cm.) yielded Fraction 1a (18.5 g., 5.9%), b.p. 72.5° (21 mm.), Fraction 2a (207.1 g., 62.1%), b.p. 88° (4 mm.), and higher boiling products.

Fraction 1a, after rerectification, was identified as methyl 2,3-dichloropropionate, a yellow liquid; b.p. 72.5° (21 mm.), lit.41 72-75° (21 mm.); d_4^{20} 1.329, lit.42 d_4^{20} 1.3283, n_D^{20} 1.4543, lit.41 n_D^{20} 1.4482 (this fraction contained traces of methyl 3-nitroacrylate).


Found: C, 31.44; H, 4.02.
Rectification of Fraction 2a yielded methyl 2-chloro-3-nitropropionate, a yellow liquid, b.p. 88° (4 mm.), lit. 91° (4 mm.), n\textsubscript{D}^20 1.4573, d\textsubscript{4}^20 1.389, lit. 91° d 1.43.

Anal. Calcd. for C\textsubscript{4}H\textsubscript{6}O\textsubscript{4}NC\textsubscript{l}: C, 28.66; H, 3.58; N, 8.36; Cl, 21.2.

Found: C, 28.87; H, 3.19; N, 8.69; Cl, 21.3.

Distillation of the residue, upon removal of the dinitro and the nitro-nitrite adducts, yielded dimethyl 2-chloro-4-nitromethylpentanedioate (5-10%), a yellow liquid, b.p. 131° (0.8 mm.), n\textsubscript{D}^20 1.4715, d\textsubscript{4}^20 1.3423, MR\textsubscript{D} (calcd.) 52.94, MR\textsubscript{D} (found) 52.84.

Anal. Calcd. for C\textsubscript{8}H\textsubscript{12}O\textsubscript{6}NC\textsubscript{l}: C, 37.87; H, 4.73; N, 5.52; Cl, 14.00.

Found: C, 38.31; H, 4.31; N, 5.59; Cl, 14.88.

Reaction of methyl acrylate and nitryl chloride in anhydrous ethyl ether at 0° yielded methyl 2,3-dichloropropionate (7.6%), methyl 2-chloro-3-nitropropionate (69.7%) and unidentified higher boiling products (methyl 2,3-dinitropropionate, dimethyl 2-chloro-4-nitromethylpentanedioate, etc.); in general, reaction in the absence of a solvent gave products which were more readily distillable. Methyl 2-chloro-3-nitropropionate dissolves in alkaline media to form deep red solutions. The pure chloronitro ester may be kept for months without appreciable decomposition.
Dehydrochlorination of Methyl 2-Chloro-3-nitropropionate; Methyl 3-Nitroacrylate.* Methyl 2-chloro-3-nitropropionate (167 g., 1 mole) was added dropwise to a stirred suspension of anhydrous sodium acetate (90 g., 1.1 mole) in ethyl ether (200 ml., anhydrous) at 5°. After addition was completed, stirring was stopped and the sodium chloride and sodium acetate were filtered. The solution was concentrated at reduced pressure until ether and most of the acetic acid had been removed. The dark red concentrate was distilled in nitrogen at reduced pressure to yield, after removal of acetic acid: (1) volatile product (116.9 g.), b.p. 72-76° (9-10 mm.), and (2) residue (15.8 g.). Redistillation of the volatile product under nitrogen gave methyl 3-nitroacrylate (115.6 g.), b.p. 72° (11 mm.), a yellow solid, m.p. 38°, no depression by a sample obtained from methyl acrylate and dinitrogen tetroxide. The residue from the initial distillation was washed with water and extracted with ethyl ether. The ether extract was dried over calcium sulfate and then distilled to give, after removal of ether, methyl 3-nitroacrylate (4.8 g.), b.p. 73° (10 mm.), m.p. 36-38°, and methyl 2-chloro-3-nitropropionate (7.2 g.), b.p. 80-90° (1-2 mm.). The combined methyl 3-nitroacrylate totaled 120.4 g. (91.9% yield).

Anal. Calcd. for C₄H₅NO₄: C, 36.64; H, 3.82; N, 10.69.

Found: C, 36.48; H, 3.82; N, 10.56.
The yield of methyl 3-nitroacrylate, a lachrymatory solid, is lowered when hydrated sodium acetate is used. The quality and yield of product are greatly improved if the reaction mixture is worked up immediately and is not exposed to air. Methyl 3-nitroacrylate may be recrystallized from methanol-water; however, a purer product is obtained by vacuum distillation. Dehydrohalogenation of methyl 2-chloro-3-nitropropionate with N,N-dimethylaniline in anhydrous ethyl ether at 25° gave methyl 3-nitroacrylate in 64.7% yield. Similar results were obtained by reaction of anhydrous pyridine with the chloronitro ester; however, the product was much more difficult to purify. Methyl 3-nitroacrylate is insoluble in water but dissolves readily in aqueous acids or bases, and organic solvents. The nitroacrylate is rapidly oxidized by dilute potassium permanganate, but does not add bromine readily in carbon tetrachloride.

(4) Proof of Structure of 2-Chloro-4-nitromethylpentanedioate; Glutaric Acid. A mixture of dimethyl 2-chloro-4-nitromethylpentanedioate (2.4 g., 0.0094 mole) and 70% sulfuric acid (20 ml.) was heated at 110-115° for 6 hours and then cooled. After the mixture had been diluted with water and then continuously extracted with ethyl ether, its ether extract was concentrated at reduced pressure to give a clear yellow acidic oil (1.15 g.).
The hydrolysate (1.0 g. aliquot) was dissolved in 57% hydriodic acid (20 ml.) and refluxed for 48 hours. The cooled mixture was diluted with water and continuously extracted with ethyl ether. After removal of ether, crude glutaric acid remained. The dibasic acid, after neutralization with sodium carbonate and reaction with p-bromophenacyl bromide, was converted into di-p-bromophenacyl glutarate; m.p. 133-134° after recrystallization from ethanol-water; m.p. of authentic sample, 137-138°; lit. 136.8°; mixed m.p. 136-137°, X-ray diffraction patterns of the derivative and authentic di-p-bromophenacyl glutarate were identical. (See Appendix 2).

(5) Reaction of Nitryl Chloride and Acrylic Acid.*
Nitryl chloride (85 g., 1.05 mole, 20% excess) was distilled into glacial acrylic acid (64 g., 0.89 mole) at 0°. After the orange-red mixture was stirred at room temperature for one hour, excess nitryl chloride was removed at reduced pressure. The syrupy product crystallized slowly at 0-5° into a white solid (109.3 g., 71.2% yield).

(a) The white solid (20 g. aliquot, 18.3%) was dissolved in benzene (a gummy product (1.5 g.) remained which was not identified; the residue decomposed when left exposed to the atmosphere); the solution was concentrated at reduced pressure until precipitation occurred. Filtration of the
mixture yielded a white solid (11.4 g., 40.5%) m.p. 72-74°,
which when recrystallized from benzene gave 2-chloro-3-nitro-
propionic acid; m.p. 78-80°, neut. equiv. (calcd.) 153.5,
equiv. (found) 157.4. The acid is soluble in ethyl
ether, acetone, hot benzene, alkaline media, and mineral acids.

Anal. Calcd. for C₃H₄NO₂Cl: C, 23.45; H, 2.61; Cl, 23.13;
and N, 9.12.
Found: C, 23.66; H, 2.70; Cl, 22.55;
and N, 9.03.

The benzene solutions were concentrated at reduced
pressures, but no further crystallization occurred. Distill-
ation of the liquid residue at 6 mm. gave a yellow solid
(m.p. 134°); recrystallization of the product from hot benzene
gave 3-nitroacrylic acid; m.p. 136°, no depression by an
authentic sample (see following Experimental).

(b) Distillation of the crude reaction product at
reduced pressures (0.7 mm.) resulted in dehydrochlorination
of 2-chloro-3-nitropropionic acid into 3-nitroacrylic acid
(65-70% yield), a yellow needle-like solid, m.p. 136°, neut.
equiv. (calcd.) 117, equiv. (found) 118. The product
is identical with that isolated in procedure (a). 3-Nitro-
acrylic acid is soluble in ethyl ether, hot benzene, mineral
acids, and aqueous alkali.

Anal. Calcd. for C₃H₅NO₂: C, 30.77; H, 2.56; N, 11.96.
Found: C, 30.70; H, 2.73; N, 12.04.
(6) Reaction of 2-Chloro-3-Nitropropionic Acid and Sodium Acetate; 3-Nitroacrylic Acid. Anhydrous sodium acetate (0.43 g., 0.005 mole) was added slowly to a stirred solution of 2-chloro-3-nitropropionic acid (0.7 g., 0.046 mole) in anhydrous ethyl ether (50 ml.). The yellow-orange mixture was refluxed for one hour and then filtered. The filtrate was concentrated under reduced pressure until yellow crystals began to form; the semi-liquid was allowed to stand for one hour. Upon filtration, 3-nitroacrylic acid (0.53 g., 98.1% yield) was obtained; m.p. 136°; neut. equiv. (calcd.) 117, neut. equiv. (found) 118.

Found: C, 30.54; H, 2.44; N, 11.86.

(7) Hydration of 3-Nitroacrylic Acid; 2-Hydroxy-3-nitropropionic Acid. 3-Nitroacrylic acid (0.25 g., 0.0017 mole) dissolved in 70% formic acid (10 ml.) was heated for 3 hours at 85-100°. The mixture was diluted with distilled water (20 ml.) and then concentrated at reduced pressures until a yellow oil remained. The product was dissolved in ethyl ether, decolorized with charcoal, and filtered. Benzene was added to the filtrate and the mixture was evaporated until a white crystalline solid precipitated. The solid was identified as 2-hydroxy-3-nitropropionic acid (0.24 g., 83% yield); m.p. 76-77°, lit.¹⁷ 76-77°, no
depression by an authentic sample.

(8) Reaction of Nitryl Chloride and Acrylonitrile:

2-Chloro-3-nitropropionitrile.* Nitryl chloride (91.8 g., 1.2 moles, 20% excess) was distilled through a gas delivery tube in 2 hours into acrylonitrile (53 g., 1 mole, freshly distilled) at 0° in a flask equipped with a sealed stirrer, a condenser, and a drying tube. The dark red mixture was stirred at room temperature for one hour. Excess nitryl chloride (now containing dinitrogen tetroxide) was distilled from the mixture at reduced pressure; precaution was taken to prevent warming up of the product during the operation. The green-yellow product was distilled under nitrogen to yield: (1) 2,3-dichloropropionitrile (16.7 g., 13.5%), b.p. 61°-67° (14-15 mm.), (2) nitrated product (103 g., 0.76 moles, 76.1%), b.p. 88°-91° (1-1.5 mm.), and (3) residue (16.7 g., unidentified). Rectification of the nitrated product at reduced pressure in a helix-packed column (24 x 2 cm.) gave 2-chloro-3-nitropropionitrile, a yellow liquid, b.p. 83° (1 mm.), lit. 33 b.p. 82° (1.5 mm.), \( \rho_D^20 \) 1.4743, \( \rho_4^25 \) 1.417, lit. 33 d 1.421.

Anal. Calcd. for \( C_3H_5N_2O_2Cl \): C, 27.76; H, 2.23; Cl, 26.40.

Found: C, 27.16; H, 2.27; Cl, 26.84.

Reaction of nitryl chloride and acrylonitrile in ethyl
ether at 0° yields ammonium chloride, 2,3-dichloropropionitrile, and 3-nitroacrylonitrile (48.2%) as well as 2-chloro-3-nitropropionitrile. The products from reaction in ethyl ether are very unstable and violent decomposition may occur when they are distilled. 2-Chloro-3-nitropropionitrile prepared from nitryl chloride and acrylonitrile must be distilled carefully several times at reduced pressure before it reaches maximum stability. The chloronitronitrile is very corrosive and blisters skin rapidly. It forms dark red solutions rapidly in dilute alkaline media.

(9) Reaction of 2-Chloro-3-nitropropionitrile and Sodium Acetate; 3-Nitroacrylonitrile.* 2-Chloro-3-nitropropionitrile (402 g., 3 moles) was added dropwise in one hour to a stirred suspension of anhydrous sodium acetate (297 g., 3.3 moles) in absolute ethyl ether (500 ml.) at 0°. Immediately after addition was completed, the red suspension was filtered free of sodium acetate and sodium chloride. Ethyl ether and acetic acid were removed at reduced pressure; the residue was distilled under nitrogen to yield: (1) volatile product (265.5 g., 93%), b.p. 59-87° (3-4 mm.) and (2) residue (31.9 g.). Refractionation of the volatile product under nitrogen in a glass-packed column (24 x 2 cm.) gave: 3-nitroacrylonitrile, a yellow oil (231 g., 2.35 moles, 78.3%), b.p. 53-54° (3.3-3.4 mm.), $n_D^{20} 1.4929$, $d_4^{20} 1.268$, and
residue (26 g). The residue is composed principally of unreacted 2-chloro-3-nitropropionitrile.

**Anal.** Calcd. for $C_2H_2N_2O_2$: C, 36.73; H, 2.04; N, 28.57

Found: C, 36.43; H, 2.04; N, 28.12.

3-Nitroacrylonitrile is a powerful vesicant and lachrymator. It is oxidized by permanganates but absorbs bromine slowly. The nitronitrile can be stored for long periods at 0-5°C without serious decomposition.

(10) **Reaction of 3-Nitroacrylonitrile and Sulfuric Acid; 3-Nitroacrylamide.** A mixture of 3-nitroacrylonitrile (3.0 g., 0.030 mole) and 85% sulfuric acid (25 ml.) was heated at 50-55°C for 7 hours and then poured on ice. A yellow solid precipitated (1.23 g.), m.p. 165°C (dec.); continuous extraction of the aqueous filtrate yielded additional solid (0.64 g.), m.p. 155-160°C, m.p. 165°C after recrystallization from benzene, and an oil (1.1 g., unidendified) that did not crystallize. An infrared spectrogram of the solid (See Appendix I) contained definite absorption bands for $\alpha$-nitro unsaturation (6.45-6.50 microns), carbonyl (5.85-5.90 microns), amide (2.85-3.05 microns), and olefinic groups (6.0-6.05 microns); no bands characteristic of hydroxyl or nitrile groups were present. (A possible product of this reaction is 2-hydroxy-3-nitropropionitrile). On the
basis of the spectrographic and analytical data, the product is assigned the structure, 3-nitroacrylamide (54% yield).

    Found: C, 31.25; H, 3.46; N, 24.53.

(11) Conversion of 3-Nitroacrylonitrile to 3-Nitroacrylic Acid by Hydrolysis and Deamination. A mixture of 3-nitroacrylonitrile (2.5 g., 0.025 mole) and 85% sulfuric acid (20 ml.) was heated at 70-80° for 2.5 hours. The mixture was cooled, and a concentrated solution of sodium nitrite (3.5 g., 0.05 mole) in water was added slowly. After the mixture stopped foaming, it was heated to 80° for 10 minutes. The solution was cooled, diluted with water, and continuously extracted with ethyl ether. After the ether had been evaporated, a yellow solid remained which, after recrystallization from chloroform, was identified as 3-nitroacrylic acid (2.0 g., 0.0171 mole, 69.4%); m.p. 134.5°, no depression by an authentic sample; neut. equiv. (calcd.) 117, neut. equiv. (found) 116.7.
SECTION I
APPENDIX I - INFRARED ABSORPTION SPECTRA

I. 3-NITROACRYLAMIDE
   (0.10 mm. cell; 5% in tetrahydrofuran)
SECTION I

APPENDIX II - ULTRAVIOLET SPECTRUM

Di-p-bromophenacyl Glutarate

Di-p-bromophenacyl Glutarate (authentic sample)
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SECTION II

NEW REACTIONS OF NITROALLYL HALIDES AND SALTS OF NITROALKANES
A. INTRODUCTION: STATEMENT OF THE PROBLEM

The purpose of this investigation was to study the possible use of aliphatic nitroallyl halides of the general type:

\[
\begin{align*}
\text{R-C} &= \text{CH-CH}_2 \text{X} \\
\text{R} &= \text{H or Alkyl}
\end{align*}
\]

as alkylation agents for the salts of primary or secondary nitroalkanes. 1-Chloro-3-nitro-2-butene was chosen as representative of this class of compound and sodium 2-nitropropane was chosen as the nitroalkane salt.

Hass and Bender\textsuperscript{1} have found in general that benzyl halides which are substituted in the ortho or para positions with electronegative or electropositive groups react with salts of nitroalkanes to result in oxygen alkylation. Oxygen alkylated products undergo thermal cleavage\textsuperscript{2} to substituted benzaldehydes and the oximes derived from the nitroalkanes (Equations 1).

\[
\begin{align*}
\text{G-C}_6\text{H}_4-\text{CH}_2\text{X} + \text{NaO}_2\text{N=C(CH}_3\text{)_2} & \rightarrow \text{NaX} + \text{G-C}_6\text{H}_4-\text{CH}_2-\text{O-N=C(CH}_3\text{)_2} \\
\rightarrow & \text{G-C}_6\text{H}_4-\text{CHO} + \text{HON=C(CH}_3\text{)_2}
\end{align*}
\]
Ortho or para-nitrobenzyl halides, however, are exceptions and result primarily in carbon alkylation (Equation 2).

\[
\text{NO}_2
\]

Equation 2

Ortho or para-nitrobenzyl halides, however, are exceptions and result primarily in carbon alkylation (Equation 2).

The analogy expected between aliphatic nitroallyl halides and \(0\) and \(\Phi\)-nitrobenzyl halides is thus apparent. The analogy is not complete however, since nitroallyl halides are capable of undergoing addition reactions of the Michael type, whereas the aromatic analog is restricted to displacement reactions involving the benzyl halogen atom.

B. HISTORICAL

The possible use of alkyl halides as carbon alkylating agents for the salts of nitroalkanes has been widely investigated since it may afford an extremely useful synthetic tool for the direct synthesis of mono and polynitro compounds. The results have been discouraging, resulting mainly in products derived from oxygen alkylation.

Mono and polynitroalkanes containing an acidic hydrogen are pseudo-acids and are neutralized by bases to yield nitronate ions. The nitronate ion may be capable of existing in two forms:
Structure II has been concluded to predominate from considerations of the strong electronegative character of oxygen, from the fact that salts of optically active nitroalkanes are completely racemized, and the fact that the Raman spectra of salts of nitroalkanes show a C=N frequency accompanied by complete disappearance of the frequency for C-N deformation found in nitroalkanes.

Nitroalkanes are weak acids (Ka nitroethane = 2.67 x 10^{-9} at 23°C) but the corresponding nitronic acid is a relatively strong acid (Ka aci-nitroethane = 3.39 x 10^{-5} at 23°C). The neutralization of a nitroalkane is slow, and first involves the removal of a proton from the alpha carbon atom followed by an electronic shift within the resulting anion to produce the aci-form of the nitronate ion (Equation 3).

Although it has been generally assumed that the relationship between the carbanion (I) and nitronate ion (II) is one
of resonance, it has been pointed out\textsuperscript{13} that a change from
the carbanion (I) to the nitronate ion (II) involves a
spacial rearrangement of the atoms within the anion from a
tetrahedral to a planar configuration. In so doing, resonance
within the nitro group of the carbanion (I) is also destroyed.
The energy increment of such a change may be relatively high
and thus result in an "oscillating" system rather than
resonance. Such an "oscillating" system contains both the
carbanion (I) and the aci-nitronate ion (II) as separate
entities and attack by either carbon or oxygen may occur
to yield either carbon or oxygen alkylation.

Hantzsch\textsuperscript{14} found that silver trinitromethane and methyl
iodide react to form 1,1,1-trinitroethane. At -75°, the two
reagents form a stable complex\textsuperscript{15} which can be isolated but
explodes when heated. All attempts to prepare 1,1,1-trinitro-
propane from silver trinitromethane and ethyl iodide have
failed. Nef\textsuperscript{16} made a study of reactions of silver 1,1-di-
nitroethane with methyl and ethyl iodides. Reactions of
methyl iodide and silver 1,1-dinitroethane gave formalde-
hyde, ethyl nitrolic acid, 1,1-dinitroethane, 2,2-dinitro-
propane, and possibly methyl ethyl nitrolate. Nef proposed
the following mechanism for these reactions: (1) A direct
displacement on the salt to form the nitronic ester which
decomposes to formaldehyde and ethyl nitrolic acid; (Equations
4).
ethyl nitrolic acid then reacts with excess silver 1,1-dinitroethane to yield 1,1-dinitroethane and silver ethyl nitrate; silver ethynitrate reacts with excess methyl iodide to form methyl ethynitrate (Equation 5).

\[
\begin{align*}
\text{CH}_2\text{C} = \text{NO}_2 + \text{CH}_3\text{I} &\rightarrow \text{AgI} + \text{CH}_2\text{C} - \text{NO}_2 \\
\text{CH}_2\text{C} - \text{NO}_2 &\rightarrow \text{CH}_2\text{O} + \text{CH}_3\text{C} - \text{NO}_2
\end{align*}
\]

(2) Formation of 2,2-dinitropropane occurs by a direct displacement reaction of methyl iodide and silver 1,1-dinitroethane (Equations 6).

\[
\begin{align*}
\text{CH}_3\text{C} - \text{CH}_2\text{C} - \text{NO}_2 &\rightarrow \text{AgI} + \text{CH}_2\text{C} - \text{CH}_3 - \text{NO}_2
\end{align*}
\]

It is apparent that Nef recognized that attack on a nitronate ion can occur on either oxygen or carbon.

Thurston and Shriner\textsuperscript{3} and Weisler\textsuperscript{17} have unsuccessfully attempted to devise a system of predicting the type alkylation reactions which a nitronate ion and an alkyl halide
under go from a consideration of their structures.

Hass and Bender found that, with the exception of ortho and para-nitrobenzyl halides, substituted benzyl halides and salts of nitroalkanes gave exclusively a substituted benzaldehyde and an oxime derived from the nitroalkane. In contrast, p-nitrobenzyl chloride and sodium 2-nitropropane gave 83% carbon alkylation and 1% oxygen alkylation; o-nitrobenzyl chloride gave 46% carbon alkylation and 30% oxygen alkylation. Both carbon and oxygen alkylation were found to proceed by second order kinetics and at the same relative rates as reaction of the same benzyl halides with potassium iodide in acetone. A correlation was also found between the benzyl halides giving carbon alkylation and those exhibiting stilbene formation in the Williamson reaction. The mechanism of stilbene formation postulates the ready removal of a benzylic hydrogen as facilitated by an ortho or para-nitro group. On the basis of these facts, they propose that the first step in both carbon and oxygen alkylation reactions of nitroalkanes is the formation of a nitronic ester (Equation 7).

\[
O_2N\text{C}(CH_3)_2 - C\text{H}_2\text{Cl} + O_2N=\text{C(CH}_3)_2 \rightarrow\]

The products of oxygen alkylation result from thermal cleavage of the nitronic ester (Equation 8).
However, if the benzylic hydrogens are sufficiently acidic, ionization may occur to produce a resonance stabilized carbanion (Equation 9).

After ionization has occurred, the carbon alkylation product may be formed by an internal nucleophilic displacement reaction (Equation 10).

The position of the atoms in the carbanion are such that the internal cyclization step is sterically favored. The relative amounts of carbon and oxygen alkylation products would depend
chiefly on the relative rates of the cleavage and ionization steps. A solvent effect was noted; yields of oxygen alkylation are higher as the acid strength of the solvent is increased, thereby making the ionization step more difficult.

In conclusion, the following factors are apparently instrumental in determining whether carbon or oxygen alkylation products are produced in displacement reactions between alkyl or benzyl halides and salts of nitroalkanes. (1) Initial attack by a nitronate ion may occur at both carbon and oxygen. (2) Formation of a carbon-carbon bond is irreversible; formation of a carbon-oxygen bond may be reversible; however, thermal cleavage of the nitronic ester to an aldehyde and oxine may occur. (3) The charge distribution of the nitronate ion, as deduced from its structure, should not be construed as determining relative stabilities in an "activated complex" during reaction.

It might well be argued that the heavy negative charge about the oxygens and the spacial arrangement of the atoms in a nitronate ion are such that an initial attack should occur almost wholly at oxygen. This consideration is not disturbing if one considers that such an attack may actually produce an orientating effect which places carbon in a more favorable spacial position for bond formation, although actual formal bonding has not occurred. The choice of bond formation as this point would be determined by factors
operative in the "activated complex" during reaction.

C. THE PRESENT RESEARCH

(1) Synthesis of l-Chloro-3-nitro-2-butene. l-Chloro-3-nitro-2-butene was synthesized by (1) condensation of chloroacetaldehyde and nitroethane in the presence of triethylamine to yield l-chloro-3-nitro-2-butanol (56%), (2) reaction of l-chloro-3-nitro-2-butanol with acetic anhydride to give l-chloro-3-nitro-2-butyl acetate (89%), and (3) deacetylation of the acetate with anhydrous sodium carbonate to yield l-chloro-3-nitro-2-butene (72%). The reaction scheme may be pictured by the following sequence (Equations 11).

(11)

$$\begin{align*}
\text{CH}_3\text{-CH}_2\text{NO}_2 + \text{OCH-CH}_2\text{Cl} & \xrightarrow{\text{(C}_2\text{H}_5)_3\text{N}} \text{CH}_3\text{-CH-CH}_2\text{Cl} \quad \text{(III)} \\
\text{CH}_3\text{-CH-CH}_2\text{Cl} & \xrightarrow{\text{Na}_2\text{CO}_3} \text{CH}_3\text{-C=CH-CH}_2\text{Cl} \quad \text{(IV)} \\
\text{CH}_3\text{-CH_2\text{NO}_2 + OCH-CH}_2\text{Cl} & \xrightarrow{\text{(C}_2\text{H}_5)_3\text{N}} \text{CH}_3\text{-CH-CH}_2\text{Cl} \quad \text{(II)} \\
\text{CH}_3\text{-CH_2\text{NO}_2 + OCH-CH}_2\text{Cl} & \xrightarrow{\text{(C}_2\text{H}_5)_3\text{N}} \text{CH}_3\text{-CH-CH}_2\text{Cl} \quad \text{(III)} \\
\text{CH}_3\text{-CH-CH}_2\text{Cl} & \xrightarrow{\text{Na}_2\text{CO}_3} \text{CH}_3\text{-C=CH-CH}_2\text{Cl} \quad \text{(IV)}
\end{align*}$$

This series of compounds (III, IV, V) has not been previously reported. The possibility exists that the l-chloro-3-nitro-2-butene may also contain its isomer, l-chloro-3-nitro-1-butene. l-Chloro-3-nitro-1-butene may possibly be
formed by rearrangement of its isomer or by dehydration of the following type (Equations 12):

\[
\text{CH}_3\text{-CH-CH}-\text{CH}_2\text{Cl} \xrightarrow{\text{-H}_2\text{O}} \text{CH}_3\text{-CH-CH}=\text{CHCl}
\]

Dehydration of alpha nitroalcohols has been found in certain cases to yield the unexpected non-conjugate nitro olefin; i.e. reactions of cyclopentanone and cyclohexanone with nitromethane and piperidine give 1-nitromethylcyclopentene and 1-nitromethylcyclohexene; dehydration of 2-methyl-1-nitro-2-propanol yields a mixture of 2-methyl-1-nitro-1-propene and 2-methyl-3-nitro-1-propene. Similarly, reaction of methallyl chloride with nitrous anhydride (N\(_2\)O\(_3\)) and subsequent reaction of the adduct with hydroxides yields 2-methyl-3-nitro-1-chloro-1-propene (Equations 13):

\[
\text{CH}_3\text{-C}=\text{CH}_2 + \text{N}_2\text{O}_3 \rightarrow \text{CH}_3\text{-C}-\text{CH}_2\text{NO}_2 \xrightarrow{\text{OH}^-} \text{CH}_3\text{-C}=\text{CHCl}
\]

Formation of these non-conjugated nitro olefins would usually not be expected unless there were present other structural influences which are more important than nitro-conjugation.

Shepherd has found that either 2-methyl-3-nitro-1-propene or 2-methyl-1-nitro-1-propene may be isomerized in
the presence of alkaline agents into an equilibrium mixture containing approximately 85% of the conjugate nitro olefin (Equation 14).

\[
\begin{align*}
\text{CH}_2=\text{C}-\text{CH}_2\text{NO}_2 & \quad \text{CH}_3-\text{C}=\text{CHNO}_2 \\
15\% & \quad 85\%
\end{align*}
\]

It was also found that infrared analysis could be used to determine the composition of a mixture of the two isomers in an inert solvent; the nitro group of the non-conjugate isomer absorbs at 6.4 microns, the conjugated nitro group at 6.6 microns. Mixtures of the two isomers in solution gave sharply defined, split peaks at 6.4 and 6.6 microns and the relative intensities of each of these peaks may be related quantitatively to the concentrations of each of the two isomers.

The infrared spectrum of the 1-chloro-3-nitro-2-butene prepared contains a single absorption band at 6.5 microns (Appendix I, II); in solution, this peak is narrow, sharp, and well-defined at 6.5 microns. Since there was no evidence for the presence of a split peak at 6.4 microns characteristic of non-conjugate nitro olefins, it was concluded that the 1-chloro-3-nitro-2-butene prepared in this research contains, at worst, only traces of its isomer 1-chloro-3-nitro-1-butene. The chemical reactivity of the 1-chloro-3-nitro-2-butene also bears out this conclusion. The possibility that
another isomer, 3-chloro-3-nitro-1-butene is present was eliminated on the basis of infrared spectrum and chemical reactivity.

(2) Reactions of 1-Chloro-3-nitro-2-butene and Sodium 2-Nitropropane.

a. General Properties of 1-Chloro-3-nitro-2-butene.

The present investigation consists primarily of a study of the reactions of 1-chloro-3-nitro-2-butene with salts of 2-nitropropane. From the standpoints of structure and reactivity, 1-chloro-3-nitro-2-butene is a halide of the allyl type. Its properties however are markedly influenced by the conjugate nitro group. 1-Chloro-3-nitro-2-butene gives a typical rapid chloride ion reaction with silver nitrate; with sodium iodide in acetone, however, iodine is liberated (its homolog, 3-chloro-1-nitro-1-propene does not give a positive reaction with silver nitrate unless heated; it gives, however, an instantaneous oxidation reaction with iodide ion to yield iodine). It appears therefore, that the chlorine atom in 1-chloro-3-nitro-2-butene has certain "positive" as well as "negative" characteristics.

\[
\begin{align*}
\text{NO}_2 & \quad \text{(1)} \\
\text{CH}_3\text{-C}=\text{CH}-\text{CH}_2\text{Cl} & \quad \longleftrightarrow \\
\text{CH}_3\text{-CH}=\text{CH}_2\text{··Cl}^+ & \quad \text{(2)}
\end{align*}
\]

All attempts to esterify 1-chloro-3-nitro-2-butene by dis-
placement reaction with salts of para-nitrobenzoic acid were unsuccessful. Similarly, efforts to hydrolyze 1-chloro-3-nitro-2-butene in acid or alkaline media into nitroethane and chloroacetaldehyde or their derivatives were also unsuccessful.

b. Hypothetical Reactions of 1-Chloro-3-nitro-2-butene and Sodium 2-Nitropropane.

Although the information concerning the chemical properties of nitroallyl halides is quite limited, it has been proposed that 1-chloro-3-nitro-2-butene may undergo at least three types of reactions in the presence of a base such as the 2-propanenitronate ion: (1) displacement of chloride ion (presumably of the SN₂ type) by the 2-nitropropane anion to result in either carbon or oxygen alkylation, (2) addition of the Michael type of 2-nitropropane to the conjugate nitro olefin resulting in carbon or oxygen alkylation and the subsequent internal displacement of halogen involving carbon or oxygen alkylation, and (3) rearrangement of 1-chloro-3-nitro-2-butene into 3-chloro-3-nitro-1-butene with subsequent displacement of chloride ion by the 2-nitropropane anion to result in either oxygen or carbon alkylation.

Reaction of 1-chloro-3-nitro-2-butene with the 2-propanenitronate ion resulting in displacement of chloride ion (as Cl⁻) may be expected to result in carbon or oxygen alky-
lation. If carbon alkylation occurs as in the analogous ortho or para-nitrobenzyl halide systems, 5-methyl-2,5-dinitro-2-hexene would be expected as a principal product (Equation 15); if oxygen alkylation occurs, as in most alkylation reactions

\[
\text{(15) } \underset{\text{NO}_2}{\text{CH}_3-\text{C}=\text{CH}-\text{CH}_2\text{Cl}} + \text{Na}^+_{\text{NO}_2}\text{N}=\text{C-(CH}_3)_2 \rightarrow \text{CH}_3-\text{C}=\text{CH}-\text{CH}_2\text{Cl} + \text{NO}_2^- + \text{NO}_2
\]

of salts of nitroalkanes both acetoneoxime and 3-nitro-2-butenal would be predicted as reaction products (Equation 16).

\[
\text{(16) } \underset{\text{NO}_2}{\text{CH}_3-\text{C}=\text{CH}-\text{CH}_2\text{Cl}} + \text{Na}^+_{\text{NO}_2}\text{N}=\text{C-(CH}_3)_2 \rightarrow \text{CH}_3-\text{C}=\text{CH}-\text{CH}_2\text{Cl} + \text{NO}_2^- + \text{NO}_2
\]

Michael condensation of sodium 2-nitropropane with 1-chloro-3-nitro-2-butene, resulting in carbon alkylation, may lead to an intermediate anion of structure (G) (Equation 17). This anion may then undergo internal nucleophilic displacement of chlorine: (1) to result in oxygen-alkylation with the resulting formation of an isoxazoline oxide (Equation
18) or (2) to result in carbon-alkylation and formation of substituted nitrocyclopropane (Equation 19).

\[
\begin{array}{c}
\text{CH}_3\text{C} - \text{CH} - \text{C} (\text{CH}_3)_2 \\
\text{N} \quad \text{O} \quad \text{CH}_2 \quad \text{NO}_2
\end{array} \rightarrow \begin{array}{c}
\text{CH}_3\text{C} - \text{CH} - \text{C} (\text{CH}_3)_2 \\
\text{N} \quad \text{O} \quad \text{CH}_2 \quad \text{NO}_2
\end{array}
\]

Kohler and his associates\(^{22}\) in a long series of studies have found a similar ring closure of alpha-bromo, gamma-nitro-ketones in the presence of bases to yield both isoxazoline oxides and substituted nitrocyclopropyl ketones. Recently Smith and Engelhardt\(^{23}\) have studied the preparation of nitrocyclopropyl ketones by an extension of the methods of the Kohler group; the formation of isoxazoline oxides was not reported in this work, however.

Michael addition of 1-chloro-3-nitro-2-butene with the 2-propanenitronate anion, resulting in initial oxygen alkylation would yield the following nitronic ester intermediate (Equation 20).
Ring closure and displacement of halogen resulting in oxygen alkylation followed by decomposition of the nitronic ester could then give an oxoisoxazoline oxide and acetone oxime (Equation 21).

\[
\begin{align*}
\text{CH}_3-C=CH-CH_2Cl + O_2N\equiv C(CH_3)_2 & \rightarrow \text{CH}_3-C=CH-CH_2Cl + O-N\equiv C(CH_3)_2 \\
\end{align*}
\]

Similarly ring closure and displacement of halogen resulting in carbon alkylation may give the corresponding nitronate ester of the substituted nitrocyclopropane, decomposition of which could give acetone oxime and a substituted nitrocyclopropanone (and/or its degradation products) (Equation 22).

\[
\begin{align*}
\text{O}_2N\equiv C(CH_3)_2 & \rightarrow \text{CH}_3-C=O + (CH_3)_2C\equiv NOH \\
\end{align*}
\]

Allylic rearrangement of 1-chloro-3-nitro-2-butene may occur to yield 3-chloro-3-nitro-1-butene (Equation 23).

\[
\begin{align*}
\text{CH}_3-C=CH-CH_2Cl & \rightarrow \text{CH}_3-C\equiv CHCH_2Cl \\
\end{align*}
\]
Displacement reaction with sodium 2-nitropropane resulting in carbon alkylation would then yield 3,4-dinitro-3,4-dimethyl-1-pentene (Equation 24); oxygen alkylation would result in formation of a nitronitronic ester, hydrolysis of which might yield methyl vinyl ketone, 2-nitropropane, and nitrous acid (Equation 25).

\[
\begin{align*}
\text{(24) } & \quad \text{NO}_2 \\
\text{CH}_3\text{-C-CH=CH}_2 + \text{NaO}_2\text{N}=\text{C(CH}_3)_2 \rightarrow \text{H}_3\text{C-C-CH=CH}_2 + \text{NaCl} \\
\text{Cl} & \quad \text{CH}_3\text{ NO}_2 \\
\text{(25) } & \quad \text{NO}_2 \\
\text{CH}_3\text{-C-CH=CH}_2 + \text{NaO}_2\text{N}=\text{C(CH}_3)_2 \rightarrow \text{CH}_3\text{-C-CH=CH}_2+\text{HNO}_2+\text{(CH}_3)_2\text{CH-NO}_2 \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

c. Experimental results from reactions of 1-Chloro-3-nitro-2-butene and sodium 2-nitropropane.

Reaction of equimolar amounts of 1-chloro-3-nitro-2-butene and sodium 2-nitropropane in absolute ethanol at -20 to -15° yields 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide (I) (35-40%), 2,3-dimethyl-2,3-dinitrobutane (II) (10-12%), 5-methyl-2-nitro-2,4-hexadiene (III) (3.5%), and a complex tarry residue (20%). A complex low-boiling liquid fraction was also obtained which could not be separated and identified.
d. Proof of Structure of 3-Methyl-4-(2-nitro-2-propyl)-isoxazoline Oxide. (I)

1. Physical properties. - 3-Methyl-4-(2-nitro-2-propyl)-isoxazole is a white solid which crystallizes from acetone; m.p. 77-78°. It is soluble in acetone, fairly soluble in ethanol, relatively insoluble in ethyl ether, and insoluble in water and carbon tetrachloride. The insolubility of this compound in ether and similar organic solvents is suggestive of a polar compound. The solubility characteristics of this compound are similar to those reported by Kohler\textsuperscript{22} for isoxazoline oxides. In contrast, nitrocyclopropanes\textsuperscript{22,23} nitro olefins, and dinitroalkanes of comparable molecular weight and structure are soluble in the usual organic solvents.

2. Chemical Properties. - 3-Methyl-4-(2-nitro-2-propyl)-isoxazoline oxide is oxidized readily by neutral permanganates. It dissolves readily in dilute aqueous alkali; however, it gives no reaction for a primary or secondary nitroalkane upon acidification in the presence of nitrite ion. The isoxazoline oxide is relatively unaffected by dilute acids. It dissolves in concentrated sulfuric acid with evolution of heat; on dilution, mixtures of this type evolve oxides of nitrogen.

3. Infrared Spectrum (Appendix I,9). - A nitro group
attached to a saturated carbon atom may be identified by absorption bands at 6.4 microns (asymmetric stretching), 7.4 microns (symmetrical stretching) and 11.75 microns (deformation of C-N bond; this band may be unreliable).

3-Methyl-4-(2-nitro-2-propyl)-isoxazoline oxide exhibits a sharp, intense absorption band at 6.05 microns; the band is believed to indicate the presence of a C=N linkage. Daasch\(^2\) has found that the C=N bond in Schiff bases absorb at 6.1 microns; Barnes\(^2\) reports that the C=N linkage absorbs at 6.0 to 6.3 microns. Kohlrausch and Seka\(^2\) have studied the Raman spectrum of the C=N linkage in many imides, oximes, their esters and salts, and benzalanilides and found its absorption frequency to range from 6.0 to 6.5 microns.

Since an isoxazoline oxide is a cyclic nitronic ester, it was felt that comparison with the infrared spectrum of a nitronic ester would be more conclusive. Dimethyl(methyl-nitronato) malonate - the methyl ester of dimethyl nitro-malonate - was synthesized by the method of Arndt and Rose\(^2\) and its infrared spectra was determined and compared with that of dimethyl nitromalonate. The nitro group in dimethyl nitromalonate (Appendix I, 6) absorbs at 6.4 microns; the carboxyl carbonyl group absorbs at 5.7 microns. In dimethyl (methylnitronato) malonate (Appendix I, 7), the band (N\(_O\)) at 6.35 microns has been replaced by a C=N absorption band at 6.2 microns; the carbonyl group, now enhanced by
conjugation, has been shifted to 5.8 microns. The spectra of acetone oxime (C=N at 5.95 microns) and trimethyl isoxazole (C=N at 6.1 microns) were also determined (Appendix I, 5, 8); the data obtained are in agreement with the spectrum of the isoxazoline oxide.

The Raman spectra of 1-nitropropane and its sodium salt have been determined by Mathiew and Massignon. The spectrum of the nitroalkane contains two bands at 11.45 and 11.1 microns arising from C-N deformation. The sodium salt of 1-nitropropane does not show these absorption bands; the salt absorbs instead intensely at 6.3 microns (C=N bond). It is of interest to note that Mathiew and Massignon conclude that the Raman spectrum observed for the 2-nitropropane anion definitely proves that the aci structure proposed for nitronate ions is correct.

4. **Ultraviolet Spectrum** (Appendix II, I). - Little or no absorption should be expected for 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide in the ultraviolet region above 220 m\(\lambda\). Primary and secondary nitro groups show weak absorption at 225-235 m\(\lambda\). An isolated C=N group absorbs below 220 m\(\lambda\). The absorption of tertiary nitro groups has not been determined; however, it is quite probable that compounds of this type will exhibit absorption characteristics which are similar to those of primary and secondary nitroalkanes.
3-Methyl-4-(2-nitro-2-propyl)-isoxazoline oxide absorbs weakly (possibly the tertiary nitro group) at about 220 μm; there is little absorption over the range of 220 to 400 μm. It can be concluded that the ultraviolet spectrum of the product being identified is consistent with the structure proposed.

(3) Reactions of 3-Methyl-4-(2-nitro-2-propyl)-isoxazoline Oxide with Bases; Formation of Isoxazoles. Nitronic esters are very sensitive to heat and usually decompose into oximes and aldehydes. Since decompositions of this type are accelerated by bases, it appears that reaction may proceed by the following mechanism (Equations 26).

\[
\begin{align*}
R-\text{CH}=\text{N}-0-\text{CH}_3 + \text{OH}^- & \rightarrow R-\text{CH}=\text{N}^\text{O} :\text{CH}_2 + \text{H}_2\text{O} \\
R-\text{CH}=\text{N}^\text{O} :\text{CH}_2 & \rightarrow R-\text{CH}=\text{N} + \text{CH}_2\text{O} \\
R-\text{CH}=\text{N}-0^- + \text{H}_2\text{O} & \rightleftharpoons R-\text{CH}=\text{NOH} + \text{OH}^-
\end{align*}
\]

It would also appear that nitronic esters would undergo hydrolysis (or saponification) into nitro compounds and alcohols (Equations 27); however, strangely enough, reactions (27) would also appear that nitronic esters would undergo hydrolysis (or saponification) into nitro compounds and alcohols (Equations 27); however, strangely enough, reactions
of this type have never been observed.

Kohler et al have reported that 3,5-disubstituted isoxazoline oxides and 3,4,5-triphenylisoxazoline oxides are converted into their corresponding isoxazoles by bases. In the conversion of 5-benzoyl-3,4-diphenylisoxazoline oxide into its isoxazole, it was possible to isolate a keto-oxime intermediate (Equations 28).

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{CO-}\phi \\
\phi-C = N & \quad \longrightarrow \\
\text{OH} & \quad \phi-C=\text{CO-}\phi \\
\phi-C = \text{NOH} & \quad \longrightarrow \\
\phi-C = \text{N} & \quad \longrightarrow \\
\end{align*}
\]

In the conversion of 3,4,5-triphenylisoxazoline oxide into 3,4,5-triphenylisoxazole, the keto-oximino intermediate could not be isolated. It can be concluded therefore that action of bases on isoxazoline oxides is analogous to their action on nitronic esters; however, under alkaline conditions, the intermediate keto-oximes may be converted rapidly into their corresponding isoxazoles with elimination of water.

In an attempt to develop a chemical proof of structure for 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide, its reactions with dilute aqueous sodium hydroxide (1-2%) at 55° was investigated. Decomposition of the isoxazoline oxide occurred readily to give 3-methyl-4-(2-isopropenyl)-isoxazole and impure 3-methyl-4-(2-nitro-2-propyl)-isoxazole (Equations 29).
All attempts to obtain a sample of 3-methyl-4-(2-nitro-2-propyl)-isoxazole of analytical purity were unsuccessful; the compound is quite unstable and decomposes rapidly on storage. Proof of structure of the impure compound was attempted on the basis of its reaction with strong bases. 3,5-Disubstituted and 3,4,5-trisubstituted isoxazoles are insensitive to alkali. Isoxazoles with an unsubstituted 3-position are converted into beta-ketonitriles\(^2\) by cold alcoholic bases (Equation 30); isoxazoles having a free 5-position but substituted in the 3-position are converted into carboxylic acids and nitriles\(^2\) by the action of bases (Equation 31).

\begin{equation}
\begin{split}
\text{H-C} & \quad \overset{\text{R}}{\smile} \\
\text{H-C} & \quad \overset{\text{C}}{\smile} \\
\text{H-C} & \quad \overset{\text{N}}{\smile} \\
\text{H-C} & \quad \overset{\text{O}}{\smile}
\end{split}
\end{equation}

\begin{equation}
\begin{split}
\text{H-C} & \quad \overset{\text{CH}}{\smile} \\
\text{R-C} & \quad \overset{\text{N}}{\smile} \\
\text{R-C} & \quad \overset{\text{O}}{\smile}
\end{split}
\end{equation}

The isoxazoles derived from 3-methyl-4-(2-nitro-2-propyl)-
-isoxazoline oxide are members of the latter class and would be expected to yield acetonitrile and 3-methyl-3-nitrobutanoic acid or 3-methyl-2-butenoic acid (dimethyl-acrylic acid) (Equations 32).

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \quad \text{N} \quad \text{C} \quad \text{C} \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{O} \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{O} \quad \text{C} \quad \text{CH}_3
\end{align*}
\]

\[
\text{OH}^- \quad \text{CH}_3 \text{-CN} + (\text{CH}_3)_2\text{C(NO}_2)\text{-CH}_2\text{-CO}_2\text{H}
\]

\[
\text{OH}^- \quad (\text{CH}_3)_2\text{C=CH-CO}_2\text{H}
\]

Reaction mixtures derived from 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide and aqueous alkali after isolation of the insoluble isoxazoles, contain large quantities of nitrite ion; however, neither 3-methyl-3-nitrobutanoic acid or 3-methyl-2-butenoic acid could be isolated upon acidification of the reaction mixture (the products derived from this reaction are acidic however).

a. Proof of structure of 3-methyl-4-(2-isopropenyl)-isoxazole.

3-Methyl-4-(2-isopropenyl)-isoxazole is a liquid of fragrant odor which is insoluble in water and has a density less than one. The isoxazole was identified by quantitative analysis, its ability to form a sol. i complex with mercuric chloride (this reaction is characteristic of isoxazoles),
and by the similarity of its infrared spectrum (Appendix I, 14) and ultra-violet spectrum (Appendix II, V) with those of 3,4,5-trimethylisoxazole (Appendix I, 8; Appendix II, IV).

b. **Properties of 3-methyl-4-(2-nitro-2-propyl)-isoxazole.**

Freshly distilled 3-methyl-4-(2-nitro-2-propyl)-isoxazole (b.p. 50° (0.02 mm.)) is a light yellow liquid having a pleasant subdued odor; on standing the compound quickly turns dark red and assumes the more powerful and fragrant odor of 3-methyl-4-(2-isopropenyl)-isoxazole. The refractive index of the isoxazole is high ($n^2_0 1.5330$). This is indicative of its conjugate nature. The infrared spectrum of the freshly distilled isoxazole has a marked resemblance to those of 3-methyl-4-(2-isopropenyl)-isoxazole and 3,4,5-trimethylisoxazole; the principal difference is that due to the nitro group (6.4 and 7.3 microns) as expected.

c. **Proof of structure of 2,3-dimethyl-2,3-dinitrobutane.**

2,3-Dimethyl-2,3-dinitrobutene was identified by its chemical properties, melting point, and mixes melting point with an authentic sample.

d. **Proof of structure of 5-methyl-2-nitro-2,4-hexadiene.**

5-Methyl-2-nitro-2,4-hexadiene was formed in very low yield (3.5%) from reaction of 1-chloro-3-nitro-2-butene and...
sodium 2-nitropropane. Its structure was determined by its quantitative analysis, solubilities, chemical properties, infrared spectrum, and ultraviolet spectrum.

Difficulty was experienced in purifying 5-methyl-2-nitro-2,4-hexadiene because its boiling point is similar to that of 2,3-dimethyl-2,3-dinitrobutane. It could only be crystallized from organic solvents at -80°. Its quantitative analysis is just out of the range usually desired for new compounds; however, its analysis excludes other predicted structures.

Its infrared spectrum (Appendix I, 10) contains well defined bands at 6.15 microns (conjugated diene system), 6.65 microns (nitro group conjugated with diene system), and 7.65 microns (nitro group). A very small band occurs at 6.45 microns; this absorption, characteristic of a non-conjugated nitro group, may arise from the slight impurity.

The ultraviolet spectra of conjugate nitro olefins contain from one to three bands of almost equal intensities, ranging from 6-10 millimicrons apart, in the region of 225-260 mμ; \( \varepsilon_{\text{max}} \) values range from 3300 to 9700. 1-Nitro-1,3-pentadiene, a conjugated nitrodiene, has a weaker band at 225 mμ and an intense band at 298 mμ; the \( \varepsilon_{\text{max}} \) values are 5500 and 12,000, respectively. Omega-nitrostyrene absorbs at 227 and 309 mμ; its \( \varepsilon_{\text{max}} \) values are 9,500 and 16,500, respectively. 5-Methyl-2-nitro-2,4-hexadiene (Appendix II,
III) shows a weak peak at 230 m$\bar{e}$ and an intense peak at 335 m$\bar{e}$; the $\epsilon_{\text{max.}}$ values are 7700 and 11,700 respectively.

D. DISCUSSION OF RESULTS

The formation of 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide from 1-chloro-3-nitro-2-butene and sodium 2-nitropropane may be explained by the following sequence: (1) addition of the Michael type of the 2-propanenitronate anion by carbon-alkylation to 1-chloro-3-nitro-2-butene (Equation 33);

\[
\text{CH}_3\text{C}=\text{CH}-\text{CH}_2\text{Cl} + \text{NO}_2^- \rightarrow \text{CH}_3\text{C}-\text{CH}-\text{CH}_2\text{Cl} + \text{Cl}^-
\]

(33)

(2) internal nucleophilic displacement of chlorine by the intermediate ion involving oxygen alkylation to yield the isoxazoline oxide (Equation 34).

\[
\text{CH}_3\text{C}=\text{CH}-\text{CH}_2\text{Cl} + \text{NO}_2^- \rightarrow \text{CH}_3\text{C}-\text{CH}-\text{CH}_2\text{Cl} + \text{Cl}^-
\]

(34)

Addition of the Michael type of acidic nitroalkanes to conjugate nitro olefins to yield 1,3-dinitroalkanes is a general reaction; Kohler et al., have reported similar internal cyclization reactions of alpha-bromo gamma-nitroktones to yield
isoxazoline oxides. Both, Kohler et al., and Smith et al., report however, that carbon-carbon alkylation occurs to give nitrocyclopropanes; Smith and Engelhardt report only the formation of nitrocyclopropanes. The principal difference in this investigation from those of Kohler et al., and Smith et al., is that their compounds all contained a halogen atom which was alpha to a carbonyl group. This investigation may indicate that oxygen alkylation resulting in formation of an isoxazoline oxide (a five membered ring) is preferred over formation of nitrocyclopropanes in ring-closure of 3-halo-l-nitroalkanes. It is also suggested that in base-catalyzed ring closure of -halo-Y-nitroketones a carbonyl group may exert a shielding effect on the negatively charged oxygen atoms of the nitronate group; the result, therefore, may be to drive the electron pair on carbon and thus favor formation of the nitrocyclopropane (Equation 34).

Two systems are suggested for further study. (1) Reactions of simple 1-halo-3-nitroalkanes and bases; on the basis of this and previous investigations it is predicted that the principal reaction is formation of isoxazoline oxides and not cyclopropanes. (2) Bimolecular reactions of alpha-halo
carbonyl compounds and salts of nitroparaffins; on the basis of the proposed shielding effect of a carbonyl group, it is suggested that reactions of this type may lead to new carbon-alkylation products.

The formation of 2,3-dimethyl-2,3-dinitrobutane in sizable amounts (10-12%) is to be expected if one considers that the "positive" nature of chlorine may lead to an exchange reaction between sodium 2-nitropropane and 1-chloro-3-nitro-2-butene (Equations 35) to yield some 2-chloro-2-nitropropane.

\[ \text{CH}_3\text{C}-\text{CH}-\text{CH}_2\text{Cl} + \text{CH}_3\text{C}-\text{CH}-\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{C}-\text{CH}-\text{CH}_2\text{Br} + \text{CH}_3\text{C}-\text{CH}-\text{CH}_2\text{Cl} \]

Hass and Seigle\(^2\) have shown that salts of nitroalkanes (particularly secondary nitroalkanes) and the corresponding gem-halonitroalkanes react to give good yields of 1,2-dinitroalkanes. VanTamelen and Zyl\(^3\) have demonstrated that an analogous exchange of a "positive" halogen occurs in reactions of esters of sodium malonate and gem-halonitroalkanes. For example, 2-bromo-2-nitropropane and the sodium salt of diethyl ethylmalonate yield sodium bromide, sodium 2-nitropropane, diethyl bromoethylmalonate and 2,3-dimethyl-2,3-dinitrobutane. The authors propose that the influence of the nitro group is to render bromine susceptible to a
nucleophilic attack by the base (Equation 36).

\[
\text{(36) } \begin{align*}
\text{CH}_3\text{C}\text{CH}_3 & \xleftrightarrow{\text{Br}} \text{CH}_3\text{C}\text{CH}_3 \\
\text{Br} & \quad \text{Br}^+ \quad \text{Br} & \quad \text{Br}^+ \quad \text{Br}^+ \\
\text{NO}_2^- & \quad \text{NO}_2^- & \quad \text{CO}_2\text{Et} & \quad \text{CO}_2\text{Et} & \quad \text{CO}_2\text{Et} & \quad \text{NO}_2^- \\
\end{align*}
\]

Formation of 2,3-dimethyl-2,3-dinitrobutane then results from reaction of excess 2-bromo-2-nitrobutane with the 2-propanenitronate ion formed in the exchange reaction. In general any halogen on a carbon atom containing two or more nitrogroups is a good oxidizing agent\textsuperscript{31}; for example, bromodinitromethane or bromotrinitromethane will quantitatively oxidize iodide to iodine.

On the basis of the positive character of chlorine in 1-chloro-3-nitro-2-butene and the many analogous results that have been reported, the following mechanism is proposed to account for the formation of 2,3-dimethyl-2,3-dinitrobutane. (1) Reaction of 1-chloro-3-nitro-2-butene with sodium 2-nitropropane and exchange to yield 2-chloro-2-nitropropane and 3-nitronato-1-butene (reaction may involve initial ionization of the halide and subsequent chlorination of the 2-nitropropane ion or direct displacement of halide by the 2-nitropropane anion) (Equations 37).

\[
\text{(37) } \begin{align*}
\text{CH}_3\text{C}\text{CH}_2\text{Cl} + \overset{\text{NO}_2^-}{\text{O}_2\text{N}\text{C}(\text{CH}_3)_2} & \leftrightarrow \overset{\text{Cl}}{\text{CH}_3\text{C}\text{CH}_2} + \overset{\text{NO}_2^-}{\text{CH}_3\text{C}\text{CH}_3}
\end{align*}
\]
(2) Displacement of 2-chloro-2-nitropropane with sodium 2-nitropropane to give 2,3-dimethyl-2,3-dinitrobutane and chloride ion (Equation 38).

\[
\text{CH}_3\text{C}=\text{CHCH}_2\text{Cl} + (\text{CH}_3)_2\text{C}=\text{NO}_2^- \rightarrow \text{H}_3\text{C}-\text{C}=\text{C}-\text{CH}_3 + \text{Cl}^- \nonumber
\]

If the scheme proposed is correct, then 3-nitro-2-butene and 2-chloro-2-nitropropane should be found as reaction products. Similarly rearrangement of 1-chloro-3-nitro-2-butene (Equation 39) or reaction of the 1-butene-3-nitronate anion with 2-chloro-2-nitropropane would be expected to give 3-chloro-3-nitro-1-butene (Equation 40).

\[
\text{CH}_3\text{C}=\text{CHCH}_2\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}=\text{C}-\text{CH}_3 + \text{Cl}^+ \nonumber
\]

A liquid product was obtained which had the physical and chemical properties (Appendix I) of a mixture of the compounds; however, this product could not be separated readily into its constituents and therefore was not investigated exhaustively.

The formation of 5-methyl-2-nitro-2,4-hexadiene is
attributed to a normal metathetical displacement of chloride ion from 1-chloro-3-nitro-2-butene by the 2-nitropropane anion (Equations 41). This reaction is analogous to that reported by Hass and Bender for salts of nitroalkanes and ortho and para-nitrobenzyl halides. Elimination of nitrous acid from 5-methyl-2,5-dinitro-2-hexene in the presence of bases would be expected to give 5-methyl-2-nitro-2,4-hexadiene (Equations 41).

\[
\begin{align*}
\text{CH}_3\text{C}=\text{CH}-\text{CH}_2\text{Cl} + (\text{CH}_3)_2\text{C}-\text{NO}_2 & \rightarrow \text{CH}_3\text{C}=\text{CH}-\text{CH}_2\text{C}-\text{CH}_3 \\
\text{CH}_3\text{C}=\text{CH}-\text{CH}_2\text{NO}_2 & \rightarrow \text{CH}_3\text{C}=\text{CH}-\text{CH}_2\text{C}-\text{NO}_2
\end{align*}
\]

E. EXPERIMENTAL

(1) Preparation of 1-Chloro-3-nitro-2-butanol. A stirred solution of nitroethane (75 g., 1.0 mole), chloroacetaldehyde (98 g., 0.5 mole of 40% aqueous solution) and 95% ethanol (75 ml.) was heated to 65-70°C. Triethylamine (3 ml.) was then added; additional portions (1 ml.) were added at hourly intervals. After 4 hours, water (300 ml.) and concentrated hydrochloric acid (5 ml.) were added to the reaction mixture; the solution then separated into two layers. The aqueous layer was extracted with ether (3x150 ml. portions); the ethereal extract was then concentrated under vacuum.
The high boiling residue was distilled to yield 1-chloro-3-nitro-2-butanol, b.p. 80-86° (1.2 mm.), 42.9 g., 56% yield. The physical constants of an analytical sample are: b.p. 74-76° (0.8 mm.); nD²⁰ 1.4778; d²⁰/²⁰ 1.3424; M.R. (calcd.) 32.58, M.R. (found) 32.39.

   Found: C, 31.29; H, 4.71; N, 9.38.

Commercial grade nitroethane which had been thoroughly washed with aqueous sodium bicarbonate and dried by extraction with saturated sodium chloride is sufficiently pure for this synthesis. If the chloroacetalddehyde is very acidic, it should be neutralized in order to obtain best results. Large runs (2-3 moles) were not as successful; yields were erratic and usually in the vicinity of 40-45%. Ethanol was added to effect complete solution of the starting materials; it may be omitted, however, without serious effect.

The experimental conditions described are believed nearly optimum. Use of benzyltrimethylammonium hydroxide (Triton B) yielded a lower boiling product which was not characterized. The possibility that stronger bases may yield an epoxide should be studied.

(2) The Preparation of 1-Chloro-3-nitro-2-butyl Acetate.

Acetic anhydride (53 g., 0.575 mole) was slowly added to a stirred solution of 1-chloro-3-nitro-2-butanol (76.8 g.,
0.5 mole) and conc. sulfuric acid (1 ml.). The rate of addition was controlled such that the temperature of the reaction did not rise above 45°. After addition was completed, the reaction mixture was distilled at reduced pressure to yield acetic acid, excess acetic anhydride, and 1-chloro-3-nitro-2-butyl acetate, 86.8 g., 89% yield, b.p. 84-92° (1.2 mm.). Physical constants of an analytical sample are: b.p. 76-77° (0.8 mm.); \( n_D^{20} \) 1.4553; \( d^{20}/20 \) 1.2702; M.R. (calcd.) 42.05, M.R. (found) 41.53.

Anal. Calcd. for \( C_6H_10O_4Cl \): C, 36.83; H, 5.16; N, 7.16.

Found: C, 37.05; H, 4.97; N, 6.88.

Attempts to prepare the acetate from crude 1-chloro-3-nitro-2-butyl alcohol (i.e. reaction mixture from which the solvents and excess reagents had been removed but not distilled) always resulted in considerably lower yields.

(3) **Preparation**\(^{32}\) of 1-Chloro-3-nitro-2-butene. A stirred mixture of 1-chloro-3-nitro-2-butyl acetate (78.4 g., 0.4 mole), anhydrous sodium carbonate (21.2 g., 0.2 mole), and C.P. benzene (200 ml., dried over calcium hydride) was refluxed from 5 to 6 hours and then cooled. The solid was filtered and washed with benzene (200 ml.) and ether (200 ml.); the filtrates were combined and concentrated under vacuum. The residue was distilled at reduced pressure to yield 1-chloro-
-3-nitro-2-butene, 39.4 g., 72% yield, b.p. 75-90° (3.0-4.0 mm.). Physical constants for an analytical sample are:
b.p. 64-65° (2.5 mm.); \( \rho_D^{20} \) 1.4997; \( d_2^{20}/20 \) 1.2719; M.R.(calcd.) 31.37, M.R. (found) 31.55.

Anal. Calcd. for \( C_4H_6O_2NC1 \): C, 35.16; H, 4.40; N, 10.25.

Found: C, 35.10; H, 4.17; N, 10.25.

It is essential that C.P. benzene be dried and that the sodium carbonate be anhydrous to obtain consistently good yields. Substitution of potassium carbonate for sodium carbonate is not recommended; the products are often degraded to unidentified lower boiling liquids. The time factor should be increased several hours for larger runs.

Deacetylation of 1-chloro-3-nitro-2-butyl acetate by heating with anhydrous sodium acetate at reduced pressures was not as successful. The product obtained was of much lower refractive index (1.461 to 1.485) and boiling point (58-66° at 2.5 mm.). It is suspected that 1-acetoxy-3-nitro-2-butene, formed by reaction of 1-chloro-3-nitro-2-butene and acetic acid or sodium acetate, is a contaminant. Purification of this product could not be made readily by redistillations.

(4) Reactions of 1-Chloro-3-nitro-2-butene and Sodium 2-Nitropropane. Reaction was conducted in a three neck flask
equipped with a sealed stirrer, a dropping funnel, and a plug. 2-Nitropropane (62 g., 0.70 mole) was slowly added to a cooled solution of sodium (15.0 g., 0.65 mole) in absolute ethanol (700 ml.). The mixture was cooled to -20° and 1-chloro-3-nitro-2-butene was rapidly added; the mixture was then stirred for 24 hours.

The cold reaction mixture, which now contained a white solid, was filtered; the precipitate was washed with ether (100 ml.); the ether washings and the alcoholic filtrate (I) were combined. The white solid, a mixture of sodium chloride, organic salts, and insoluble organic products was triturated with water (100 ml.) and refiltered. Titration of the aqueous filtrate with silver nitrate (Mohr method) showed that 95-98% of the theoretical chloride ion had formed. The white solid was recrystallized from C.P. acetone to yield 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide, 37.3 g., m.p. 77-78°.

Anal. Calcd. for C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: C, 44.67; H, 6.43; N, 14.89.

Found: C, 44.71; H, 6.24; N, 14.28.

The alcoholic filtrate (I) was evaporated under vacuum until the solution had a volume of about 150 ml. Ether (100 ml.) was added and the mixture was placed in a refrigerator for 24 hours. The yellow solid which formed was filtered; the filtrate (II) was saved. The yellow solid was washed with water (100 ml.) and filtered to yield additional
3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide, 4.4 g. The total yield of isoxazoline oxide was 42.2 g., 36% of theoretical. The aqueous filtrate, after acidification, gave a test for a carbonyl grouping with 2,4-dinitrophenylhydrazine. The trituration procedure therefore removed unreacted sodium 2-nitropropane or other nitronate salts which undergo the Nef reaction on acidification to yield a carbonyl function.

The solvents were removed from the filtrate(II) at reduced pressure; the resulting thick syrup was cooled for 2 days in a refrigerator. A solid (5.2 g.) precipitated and was filtered; the filtrate (III) was saved. The solid, after recrystallization from ether, gave white crystals of 2,3-dimethyl-2,3-dinitrobutane, m.p. 205-207°; no depression with an authentic sample (m.p. 208-210°).

The filtrate (III) was distilled to yield a yellow liquid, b.p. 50-75° at 2 mm. Ether (10 ml.) was added and the solution was cooled to -78°. A yellow solid precipitated which was then filtered; the filtrate (IV) was saved. The yellow solid, impure 5-methyl-2-nitro-2,4-hexadiene (3.2 g., 3.5% of theoretical) melted at 25-28° after several recrystallizations from cold ether.

**Anal. Calcd. for C₇H₁₁N₂O₂:** C, 59.57; H, 7.30; N, 9.93.

**Found:** C, 58.11; H, 7.06; N, 9.15

The filtrate (IV) was again distilled to yield a yellow liquid (33 g.) b.p. 50-58.5° at 0.8 mm., in five fractions;
the refractive indexes ranged progressively from 1.4812 to 1.5042. Repeated distillations failed to result in further purification of this mixture.

The combined residues from all distillations, 20.3 g., were steam distilled to yield additional 2,3-dimethyl-2,3-dinitrobutane (1.2 g.); the total yield of 2,3-dimethyl-2,3-dinitrobutane was 6.4 grams, 11% of theoretical based on starting sodium 2-nitropropane.

Reaction temperatures were varied from room temperature to -20°; the yields of the isoxazoline oxide were much lower (10-15%) and the amount of tarry residue much greater at the higher temperatures. The reactions are exothermic as evidenced by warming of the reaction mixture for runs made at room temperature. The extent to which 1-chloro-3-nitro-2-butane had reacted was followed by titrating the sodium chloride precipitated during the reaction; at -20°, the reaction is only about 80% complete at the end of 8 hours but 95-98% complete after 16 hours. On the basis of these figures it may be concluded that the tarry residue is not polymerized 1-chloro-3-nitro-2-butene since the residues run as high as 20%.

(5) Reactions of 3-Methyl-4-(2-nitro-2-propyl)-isoxazoline Oxide and Aqueous Alkali. 3-Methyl-4-(2-nitro-2-propyl)-isoxazoline oxide (25 g., 0.14 mole) was shaken vigorously with 2% aqueous sodium hydroxide (200 ml.) at 55-60°.
Within several minutes the isoxazoline oxide had dissolved to give a clear yellow solution. After 5 minutes, cloudiness developed and an oil settled at the bottom of the reaction mixture. The mixture was allowed to remain for 0.5 to one hour at 55-60°. After cooling, the oil was extracted with ether (2x100 ml. portions); the extract was dried over anhydrous sodium sulfate and then concentrated. The residue was then heated to 60° at 1 mm.; the volatile material was collected in a Dry-Ice trap.

Distillation of the volatile material gave 1.4 g., of 3-methyl-4-(2-isopropenyl)-isoxazole, b.p. 70-71° (17 mm.), nD 1.4863, 8.1% yield. The isoxazole has a density less than water and a powerful, pleasingly fragrant odor.

**Anal. Calcd. for C7H9N0:** C, 68.29; H, 7.32; N, 11.38.

**Found:** C, 68.27; H, 7.17; N, 11.31.

When shaken with saturated mercuric chloride, this isoxazole gives a white solid which softens at 124-126° but does not entirely melt; the isoxazole appears to distil from mercuric chloride at this temperature.

The high boiling residue (12.4 g.) was distilled in a Hickman type still at 0.08 mm. to yield a highly viscous yellow oil, (3.2 g.). Redistillation of this product at 0.02 mm. (b.p. approximately 50°) gave an oily product (2.9 g.), nD 1.5335. On standing, this product quickly turns dark red and assumes the odor of 3-methyl-4-(2-isopropenyl)-
isoxazole. It also slowly dissolves when heated with dilute alkali and the odor of 3-methyl-4-(2-isopropenyl)-isoxazole becomes noticeable. A consistant analysis could not be obtained for this product; apparently decomposition during the time required for analysis was responsible. The product is believed to consist primarily of unstable 3-methyl-4-(2-nitro-2-propyl)-isoxazole.
SECTION II
APPENDIX I - INFRARED ABSORPTION SPECTRA

1. Sandwich cell.
2. 0.10 mm. cell; 0.4 M in Cl₂CH - CHCl₂
3. Sandwich cell.
4. 0.10 mm. cell; 0.4 M in Cl₂CH - CHCl₂
SECTION II
APPENDIX I - INFRARED ABSORPTION SPECTRA

100
80
60
40
20
0

100
80
60
40
20
0

100
80
60
40
20
0

100
80
60
40
20
0

ACETOXIME
DIMETHYL NITROMALONATE
DIMETHYL-2-(METHYL NITRONATO) MALONATE
3,4,5-TRIMETHYLISOXAZOLE

WAVE LENGTH IN MICRONS

5. 0.10 mm. cell, 0.4 M in C2H5OH - CHCl3
6. 0.10 mm. cell, 0.4 M in C2H5OH - CHCl3
7. 0.10 mm. cell, 0.4 M in C2H5OH - CHCl3
8. Sandwich cell, pure compound
SECTION II
APPENDIX I - INFRARED ABSORPTION SPECTRA

3-METHYL-4-(2-NITRO-2-PROPYL)-ISOXAZOLINE OXIDE

SOLID - from 1-CHLORO-3-NITRO-2-BUTENE and SODIUM 2-NITROPROPANE

LIQUID - from 1-CHLORO-3-NITRO-2-BUTENE and SODIUM 2-NITROPROPANE

4-(CHLORONITROPROPENYL)-ISOXAZOLINE OXIDE from 3-CHLORO-1-NITRO-1-PROPENE and SODIUM 2-NITROPROPANE

9. 0.10 mm. cell, 10% in C\(_2\)H\(_4\)-CHCl\(_2\)
10. 0.10 mm. cell, 0.4 M in C\(_2\)H\(_4\)-CHCl\(_2\)
11. 0.10 mm. cell, 0.4 M in tetrahydrofuran
12. 0.10 mm. cell, 0.4 M in C\(_2\)H\(_4\)-CHCl\(_2\)
APPENDIX I - INFRARED ABSORPTION SPECTRA

3-METHYL-4-(2-NITRO-2-PROPYL) ISOXAZOLE
(0.10mm. cell; 0.8M in C\textsubscript{6}CH\textsubscript{2}CHCl\textsubscript{2})

3-METHYL-4-(2-ISOPROPENYL) ISOXAZOLE
Sandwich cell
SECTION II
APPENDIX II - ULTRAVIOLET ABSORPTION SPECTRA

I 3-METHYL-4-(2-NITRO-2-PROPYL)-ISOXAZOLINE OXIDE
Conc \( c \) = \( 1 \times 10^{-4} \) M
Cell \( d \) = 1 cm.
Solvent = 50\% Ethanol

II ISOXAZOLINE OXIDE - from 3-CHLORO-1-NITRO-1-PROPENE
Conc \( c \) = \( 5 \times 10^{-5} \) M.
Cell \( d \) = 1 cm.
Solvent = 50\% Ethanol
SECTION II
APPENDIX II - ULTRAVIOLET ABSORPTION SPECTRA

III Solid – from 1-CHLORO-3-NITRO-2-BUTENE SODIUM 2-NITRO PROPANE

Conc (c) = 1 x 10^-4 M.
Cell (d) = 1 cm.
Solvent = 95% Ethanol
SECTION II
APPENDIX II ULTRAVIOLET ABSORPTION SPECTRA

IV  3,4,5-TRIMETHYL ISOXAZOLE
Conc (c) 1 x 10^{-4} M
Cell (d) 1 cm.
Solvent 50% Ethanol

V  3-Methyl-4-(2-ISOPROPENYL) ISOXAZOLE
Conc (c) 1 x 10^{-4} M.
Cell (d) 1 cm.
Solvent 50% Ethanol

VI  3-METHYL-4-(2-NITRO-2-PROPYL) ISOXAZOLE
Conc (c) 5 x 10^{-5} M
Cell (d) 1 cm.
Solvent 50% Ethanol

Wave Length in m\(\mu\)
APPENDIX III

REACTIONS OF 3-CHLORO-1-NITRO-1-PROPENE AND SODIUM 2-NITROPROPANE

A. INTRODUCTION

Reactions of 3-chloro-1-nitro-1-propene with salts of nitroalkanes would be expected to closely parallel those of its homolog, 1-chloro-3-nitro-2-butene. Some difference might be expected in the "positive" character of chlorine however. For example, in 1-chloro-3-nitro-2-butene, resonance between the nitro group and chlorine (a) may be somewhat dampened by the opposing inductive effect of the methyl group (b). In 3-chloro-1-nitro-1-propene, the effect of the nitro group on chlorine is not opposed by an inductive effect (c).

\[
\begin{align*}
\text{(a)} & \quad CH_3-C=CH-CH_2Cl \leftrightarrow CH_3-C-CH=CH_2 Cl^+ \\
\text{(b)} & \quad H_2C-C=CH-CH_2Cl \leftrightarrow CH_2=CH=CH_2 Cl^-
\end{align*}
\]

Although studies with 3-chloro-1-nitro-1-propene are at present incomplete, it is apparent that the increased "positive"
character of chlorine is an important consideration in its reactivity with bases.

B. THE PRESENT RESEARCH

1-Chloro-3-nitro-2-propanol and 1-chloro-3-nitro-2-propyl acetate were synthesized in a manner analogous to that described for the butane analogs; (1) nitromethane and chloroacetaldehyde condense in the presence of triethylamine to form 1-chloro-3-nitro-2-propanol (52%); (2) acetic anhydride and 1-chloro-3-nitro-2-propanol react to yield 1-chloro-3-nitro-2-propyl acetate (96%).

Treatment of 1-chloro-3-nitro-2-propyl acetate with anhydrous sodium carbonate does not yield the expected 3-chloro-1-nitro-1-propene; instead, a white crystalline solid, believed to be 4-(3-chloro-3-nitro-3-propenyl)-isoxazoline oxide was the only product isolated (60%).

3-Chloro-1-nitro-1-propene (52.5%) was obtained directly from 1-chloro-3-nitro-2-propanol by heating with 3-nitrophthalic anhydride. The infrared spectrum of 3-chloro-1-nitro-1-propene (Appendix I, 4) in solution shows a single, sharp peak at 6.5 microns (conjugated nitro olefin); no split peaks resulting from mixtures of conjugated and nonconjugated nitro olefins are present. On this basis, it was concluded that the 3-chloro-1-nitro-1-propene synthesized contains no
more than traces of position isomers such as 3-chloro-3-nitro-1-propene and 3-nitro-1-chloro-1-propene.

The only product isolated from reaction of 3-chloro-1-nitro-1-propene and sodium 2-nitropropane was a solid believed to be 4-(3-chloro-3-nitro-3-propenyl)-isoxazoline oxide (18.5%); this product is identical with that obtained from reaction of 1-chloro-3-nitro-2-propyl acetate and sodium carbonate.

The solid was tentatively assigned the structure 4-(3-chloro-3-nitro-3-propenyl)-isoxazoline oxide for the following reasons. (1) Its solubility characteristics are very similar to those observed by Kohler for substituted isoxazoline oxides. (2) The following groupings were identified from its infrared spectrum (Appendix I, 12): C=N at 6.2 to 6.25 microns and the unconjugated nitro grouping at 6.4 microns (asymmetric stretching) and 7.25 microns (symmetrical stretching). (3) The halogen is vinylic in character as evidenced by its failure to give a precipitate with warm alcoholic silver nitrate or sodium iodide in acetone (the vinylic character of chlorine may be due to an actual vinyl structure or a gem-chloronitro grouping).

C. DISCUSSION

The "positive" character of chlorine in 1-chloro-3-nitro-2-butene was discussed in Part I. Chemical evidence
shows that the positive character of chlorine in 3-chloro-1-nitro-1-propene is greatly enhanced; heat is required to bring about reaction with alcoholic silver nitrate, and copious evolution of iodine occurs immediately with sodium iodide in acetone.

Since the same product (an isoxazoline oxide, $C_6H_7N_2O_4Cl$) is formed by reaction of sodium carbonate on 1-chloro-3-nitro-2-propyl acetate or sodium 2-nitropropane with 3-chloro-1-nitro-1-propene, the reactions which actually yield this isoxazoline oxide may be summarized as the action of a base on 3-chloro-1-nitro-1-propene (Equation 1).

$$\text{(1) } \begin{align*}
\text{NO}_2^- \\
2 \text{HC}=\text{CH}-\text{CH}_2\text{Cl} + \text{B}^- & \rightarrow C_6H_7N_2O_4\text{Cl} + \text{HCl}
\end{align*}$$

The following mechanism is proposed to account for formation of 4-(3-chloro-3-nitro-3-propenyl)-isoxazoline oxide. (1) Isomerization of 3-chloro-1-nitro-1-propene occurs in the presence of bases (Equations 2).

$$\text{(2) } \begin{align*}
\text{NO}_2^- \\
\text{HC}=\text{CH}-\text{CH}_2-\text{Cl} + \text{B}^- & \leftrightarrow \left[ \text{NO}_2^- \begin{array}{c} \text{HC}=\text{CH}-\text{CH}_2^- \\
\text{CH}=\text{CH}=\text{CH}_2 \end{array} \right] + \text{B}^-\text{Cl}^+ \\
& \rightarrow \text{NO}_2^- \\
\text{CH}=\text{CH}=\text{CH}_2 + \text{B}^- \left[ \text{Cl} \\
\text{CH}=\text{CH}=\text{CH}_2 \right]
\end{align*}$$

(2) Addition of the Michael type of 3-chloro-3-nitro-1-propene to 3-chloro-1-nitro-1-propene followed by internal cyclization
to form 4-(3-chloro-3-nitro-3-propenyl)-isoxazoline oxide, (Equations 3).

\[
\begin{align*}
\text{NO}_2^- + \text{CH}=\text{CH}-\text{CH}_2\text{Cl} & \quad \xrightarrow{E^-} \quad \text{HC} = \text{CH}-\text{CH}_2\text{Cl} + \text{BH}^+ \\
\text{Cl}-\text{C}-\text{NO}_2^- & \quad \xrightarrow{\text{CH}} \quad \text{CH} - \text{C} - \text{CH}=\text{CH}_2 + \text{Cl}^- \\
\end{align*}
\]

It is suggested that the proposed structure of 4-(3-chloro-3-nitro-3-propenyl)-isoxazoline oxide would be most easily checked by an independent synthesis using a base catalyzed cond. of 3-chloro-1-nitro-1-propene and 3-chloro-3-nitro-1-propene.

E. EXPERIMENTAL

(1) Preparation of 1-Chloro-3-nitro-2-propanol. A stirred mixture of nitromethane (1150 ml., 20 moles) and chloroacetaldehyde (393 g., 2 moles of 40% aqueous solution) was heated to 65°. Triethylamine was then added (5 ml.); an additional portion (3 ml.) was added after 4 hours. After 7 hours, saturated sodium chloride solution (400 ml.) and
concentrated hydrochloric acid (10 ml.) was added to the reaction mixture and the aqueous layer was extracted with ether (3 x 150 ml. portions). The ethereal extract was concentrated under vacuum and the residue was distilled at reduced pressure to yield 1-chloro-3-nitro-2-propanol, b.p. 82-90° (1.5 mm.), 145 g., 52% yield. The physical constants of an analytical sample are: b.p. 84-85° (1.5 mm.); n_D^20 1.4833; d_20/20^20 1.4167; M.R. (calcd.) 28.03, M.R. (found) 28.14.

Commercial nitromethane which has been thoroughly washed with aqueous sodium bicarbonate and dried by extraction with several portions of saturated sodium chloride is sufficiently pure. The precautions listed for the preparation of 1-chloro-3-nitro-2-butanol are equally applicable in this case.

(2) Preparation of 1-Chloro-3-nitro-2-propyl Acetate.
Acetic anhydride (28 g., 0.275 mole) was slowly added to a stirred solution of 1-chloro-3-nitro-2-propanol (34 g., 0.25 mole) and concentrated sulfuric acid (10 drops). The rate of addition was controlled such that the temperature of the reaction mixture did not rise above 45°. After addition was completed, acetic acid and excess acetic anhydride were removed under vacuum and the residue was distilled to give 1-chloro-3-nitro-2-propyl acetate, b.p. 94-100° (2-3 mm.), 43.8 g., 96% yield. Physical constants of an analytical
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sample are: b.p. 84-85° (1.2 mm.); n_D \textsuperscript{20} 1.4578; d_{20/20} 1.3213; M.R. (calcd.) 37.43, M.R. (found) 37.48.

Anal. Calcd. for C\textsubscript{5}H\textsubscript{8}O\textsubscript{4}NC\textsubscript{1}: C, 33.07; H, 4.41; N, 7.72.  
Found: C, 33.73; H, 4.06; N, 7.65.

(3) Dehydration of 1-Chloro-3-nitro-2-propanol with 3-Nitrophthalic Anhydride; 3-Chloro-1-nitro-1-propene.

1-Chloro-3-nitro-2-propanol (77 g., 0.55 mole) and 3-nitrophthalic anhydride were mixed in a round bottom flask attached to an unimpacted column (45x2 cm.) attached to a vacuum distillation takeoff. At a pressure of 8-10 mm. the pot temperature was raised to 165-180°. Distillate was collected until solid began to form in the condenser. The distillate, diluted with ether (100 ml.), was washed with water and with 2% sodium bicarbonate solution until it was no longer acidic. After the extract had been dried, ether was removed under vacuum and the residue was distilled to yield 3-chloro-1-nitro-1-propene, b.p. 72-75° (4-5 mm.), 35.0 g., 52.5% yield. Physical constants of an analytical sample are: b.p. 62-64° (3.5 mm.); n_D \textsuperscript{20} 1.5020; d_{20/20} 1.3525; M.R. (calcd.) 26.07, M.R. (found) 26.51.

Anal. Calcd. for C\textsubscript{3}H\textsubscript{4}O\textsubscript{2}NCl: C, 29.63; H, 3.29; N, 11.52; Cl, 29.21.  
Found: C, 29.08; H, 3.13; N, 10.78; Cl, 28.22.
Considerable difficulty was experienced in obtaining an analytically pure sample.

(4) **Attempted Deacetylation of 1-Chloro-3-nitro-2-propyl Acetate; Formation of a Substituted Isoxazoline Oxide**

\( \text{C}_6\text{H}_7\text{N}_2\text{O}_4\text{Cl} \). A stirred mixture of 1-chloro-3-nitro-2-propyl acetate (25.0 g., 0.138 mole), anhydrous sodium carbonate (14.6 g., 0.138 mole) and C.P. benzene (100 ml.) was refluxed for 5 hours and then cooled. The solid material was filtered and washed twice with hot benzene (2x50 ml. portions). The combined filtrates were evaporated under vacuum to leave a brown solid (9.5 g.). The solid was dissolved in acetone, treated with charcoal, filtered, and the filtrate concentrated. On cooling in an ice bath, a white solid crystallized in long needles, 8.6 g., m.p. 114.5-115\(^\circ\)

**Anal.** Calcd. for \( \text{C}_6\text{H}_7\text{O}_4\text{N}_2\text{Cl} \): C, 35.04; H, 3.41; N, 13.63; Cl, 17.27.

**Found:** C, 34.84; H, 3.43; N, 12.81; Cl, 17.29.

The yield is 60% of theoretical.

(5) **Reaction of 3-Chloro-1-nitro-1-propene and Sodium 2-Nitropropane.** 2-Nitropropane (9.3 g., 0.105 mole) was slowly added to a cold, stirred solution of sodium (2.3 g., 0.1 mole) dissolved in absolute ethanol (250 ml.). The solution was cooled to -20\(^\circ\) and 3-chloro-1-nitro-1-propene
(12.2 g., 0.1 mole) was rapidly added. After 18 hours, the white solid which had formed was filtered and washed with ether (100 ml.); the filtrates (I) were combined. The solid was sodium chloride and titrated (Mohr method) for 44.5% of the theoretical chloride ion (based on 3-chloro-1-nitro-1-propene).

The filtrates (I) were evaporated under reduced pressure to leave a viscous red oil which was extracted with hot chloroform (50 ml.); a viscous red tarry material was left. The chloroform extract was treated with charcoal, filtered, and evaporated under vacuum to leave a white solid (1.9 g.). Recrystallization from acetone gave long crystalline needles, m.p. 112-114°; there was no depression in melting point when this product was mixed with the solid obtained from 1-chloro-3-nitro-2-propyl acetate and sodium carbonate. The yield of substituted isoxazoline oxide (C₆H₇N₂O₄Cl), based on 3-chloro-1-nitro-1-propene is 18.5% of theoretical.
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