CHAPTER - II.1

GENERAL INTRODUCTION

The chemistry of nitryl iodide additions to unsaturated compounds has only recently experienced a surge of interest owing to its synthetic and mechanistic applications. The work on nitryl iodide additions\(^1,2\) has been done mainly as an extension of pseudohalogen chemistry\(^3\) and to and to correlate and compare the reactivity of nitryl iodide with other known pseudohalogens in different organic synthesis. Several features of nitryl iodide additions to olefinic compounds such as reaction pathways, regiochemistry and stereochemistry have also been reported, to some extent, in order to assess the versatility and applicability of the reagent in synthetic organic chemistry.

The reaction of nitryl iodide with cyclohexene was reported for the first time by Birchenbach et al.\(^4\) in 1932 to give dinitro and iodo-nitro adducts (nitryl iodide was generated by reaction of silver nitrile with iodine). However in 1964, its synthetic utility and mild reaction conditions were initially described at the symposium on electrophilic additions to olefins by Hassner et al.\(^1,5,6\). Later the reaction of nitryl iodide was proved to be a useful tool in the nitration of sugars\(^7\).
Nitryl iodide like carbenes, is a transient species which owing to its high reactivity and instability cannot be isolated in free state and hence its reactions are carried out 'in situ', subsequent to its generation in solution. The existence of nitryl iodide in solution is evidenced by its capability to form nitro-iodo adducts with olefinic compounds.

The generation of nitryl iodide can be achieved by stirring a mixture of silver nitrite and iodine (in 1:1 ratio) in dry ether. In analogy with other pseudohalogens, the reaction of silver nitrite with iodine is expected to lead to \( \text{INO}_2 \). This reagent is theoretically capable of dual heterolysis to \( \text{NO}_2^+ \) and \( \text{I}^- \); and \( \text{I}^+ \) and \( \text{NO}_2^- \) as well as to homolysis into free radicals, hence it can function both as nitryl iodide or as iodine nitrite and it can add to the double bond either ionically or free radically.

An alternate method to generate nitryl iodide via the strong oxidising agents such as dinitrogen tetroxide, has also been described by Stevens and Emmons who showed that slow addition of dinitrogen tetroxide in a stream of dry nitrogen to solvent ether containing excess of iodine gave the reagent.

Reactions, regiochemistry and stereochemistry

Interest in the chemistry of nitryl iodide stems from its ambivalent capability to act as nitryl iodide (\( \text{NO}_2\text{I} \)) or iodonium nitrite (\( \text{INO}_2 \)) in its reaction with olefinic
compounds. This has led to different theoretical assumptions along with the interesting studies in this direction, which has resulted in many significant findings on its dual behaviour towards various types of olefins. In fact it has been observed that in most of the cases reported so far, it acts as nitryl iodide \((\text{NO}_2\text{I})^1\), however, in few cases the resulting product(s) of the reaction seems to be formed via iodonium nitrite \((\text{INO}_2)^2\). Another fascinating problem involved in the regiochemistry of such additions is whether nitryl iodide or its counterpart attacks on the double bond through the ionic mechanism or through free radical path. This aspect has also been worked out to some extent. However, evidences available so far, are limited to a few particular reactions and cannot be generalized unless they are strongly founded on the basis of extensive investigations on the regiochemistry and related aspects of nitryl iodide additions. Similar problems are involved with an alternate source of nitro-iodides formed from dinitrogen tetroxide and iodine.

With a view to find out the solution to above mentioned problems and to ascertain the pathways, regio- and stereochemistry of nitryl iodide additions, Harsner, Kropp and Kent\(^1\) have reported an outstanding work on the subject. They observed that when 2-cholestene (1) was allowed to react with silver nitrile and iodine in presence of solvent ether, \(2\beta\)-iodo-\(3\alpha\)-nitro-cholestane (2) was obtained as the
major product in 51 percent yield together with 3α-iodo-2β-cholestanyl nitrate (3) in 5 percent yield and 26 percent unreacted 2-cholestene (scheme -1). The presence of nitro group at C3 in structure (2) was confirmed by its dehydroiodination, using base, to 3-nitrocholest-2-ene (4) which on subsequent reduction gave the known 3-cholestanone (5). Similarly the vinyl nitro compound (4) was subjected to sodium borohydride reduction to afford known 3β-nitrocholestane(6). Further the position of the nitro group at C3 and the iodo group at C2 as trans diaxially oriented functions is fully supported by NMR studies of the product (2).

The fact that the nitro group in the product (2) occupied the 3α-position suggested that the reagent formed by silver nitrite and iodine, was not reacting as iodonium nitrite (INO2) through a three membered iodonium ion intermediate, but instead behaved as nitryl iodide (NO2I).

The nitro-iodo product (2) was also synthesized by slow addition of dinitrogen tetroxide to an ethereal solution of 2-cholestene (1) in presence of iodine. The mechanism of the reaction has been shown to proceed through the attack of NO2 on the double bond followed by quenching of the radical with iodine1.

The trans stereochemistry of the adduct (2), as evidenced by NMR spectroscopy, suggests that either a stable pyramidal radical is produced or the quenching reaction is
more rapid than inversion of the radical formed. Since Brand and Stevens\textsuperscript{9} have shown that 2-nitrocyclohexyl radical leads to a great deal of epimerization, the \textit{trans}-dixial NO\textsubscript{2}I addition to 2-cholestenone needs an explanation. Approach from the \(\alpha\)-side of the steroids occurs for steric reasons. In the \textit{trans} fused decalin system stereoelectronic factors are responsible for the preferred axial attack by the NO\textsubscript{2} radical with simultaneous development of an axial radical. The resulting adduct radical will prefer to have a chair rather than a twist-boat conformation thus giving rise to conformational structure (2a). As reported by Brand and Stevens\textsuperscript{9} radical structure (2a) must be short lived and does not allow for the epimerization that takes place in the case of nitryl chloride, dinitrogen tetroxide or dinitrogen pentoxide additions to cyclohexene. Instead the intermediate nitroalkyl radical (2a) is apparently trapped very rapidly and efficiently by iodine before it can invert to structure (2b) (scheme -2). In this fashion the product is kinetically controlled giving rise to the sterically unfavoured 1,3-diaxial arrangement of iodine and C\textsubscript{19}-methyl.

Further, stereochemistry of the nitryl iodide additions to \textit{cis} and \textit{trans} stilbene (7a,b) has also been reported\textsuperscript{1}. When \textit{cis} and \textit{trans} stilbenes were separately treated with nitryl iodide, the resulting products appeared to be a diastereomeric mixture (8), as confirmed by NMR
spectral studies. The diastereomeric mixture (8) on dehydroiodination in presence of pyridine gave the same cis-1,2-diphenyl-1-nitroethylene (9) (scheme-3). Similar findings have also been reported by Steven and Emmons\(^2\) using an alternative procedure, which consists of addition of dinitrogen tetroxide to an ethereal solution of stilbene in the presence of an excess of iodine.

When an excess of cis-stilbene was reacted with nitryl iodide, the resulting crude product, obtained was shown to be solely cis isomer of stilbene by NMR spectrum, suggesting that the formation of the nitro radical is non-reversible. Since no cis-trans stilbene isomerization had occurred yet a diastereomeric mixture of products was obtained, a long lived pyramidal structure (10) must not be formed. Instead, the phenyl stabilized radical is interconverted to structure (11) before it is quenched by iodine (scheme -4).

Further, regiochemical studies\(^1\) have been done to verify the mode of addition of the reagent, formed from silver nitrite and iodine. This reagent on reaction with styrene (12) afforded an unstable product (13) which on treatment with pyridine furnished the known \(\beta\)-nitrostyrene (14)(scheme -5), indicating that the adduct is formed through the addition of nitryl iodide and not through the iodonium nitrite.
SCHEME 2

(1) \[ \text{NO}_2^+ \text{I} \rightarrow \]

(2a) \[ \leftrightarrow \]

(2b) 

SCHEME 3

(7a) \[ \text{NO}_2^+ \text{I} \rightarrow \]

(8) \[ \text{Pyridine} \rightarrow \]

(9)
The regioselectivity of nitryl iodide additions has been further demonstrated by the formation of 3-iodo-3-(nitromethyl) cholestan e (16) by the addition of NO2I to 3-methylene cholestan e (15) (scheme -6). The structure of the product (16) was proved by elimination of HI from (16) with sodium acetate when 3-(nitromethylene)-cholestan e (17) was obtained.

Although, the above results give an indication regarding the mode of addition of the reagent as nitryl iodide (NO2I), they however, do not differentiate between the attack of NO2I as either through heterolysis by NO2+ or through homolysis by the free radical, NO2, on the terminal carbon of the olefin (14). Substantiation for the free radical pathway was obtained by studying the nitryl iodide addition to an unsaturated ester substrate, methyl acrylate (18), because the creation of positive charge, but not of a free radical, next to a carbonyl group is very unfavourable10,11. The product (19), formed from the reaction of methyl acrylate (18) with nitryl iodide, on subsequent elimination of HI by treatment with sodium acetate gave methyl-3-nitroacrylate(20) (scheme -7). The product (20) was found to be identical with that obtained by Shechter et.al12 through the free radical addition of nitryl chloride (NO2Cl) to methyl acrylate. A free radical addition is also consistent with the fact that the formation of nitro-iodo- adducts from nitryl iodide is
greatly inhibited in the presence of $\rho$-oxygen and hence the reactions are carried out in an inert atmosphere.

In an analogous reaction Stevens and Emmons\textsuperscript{2} have also reported the formation of methyl-3-nitro-2-iodopropionate (19) and its HI elimination product, methyl-3-nitro acrylate (20) by the addition of dinitrogen tetroxide to a solution of methyl acrylate (18) and iodine in nonpolar solvent. In both the cases formation of only 3-nitroacrylate was observed through $\text{NO}_2\text{I}$ addition, and not the corresponding nitrate ester, as expected from an alternative pathway through iodonium nitrite ($\text{INO}_2$).

However, in few cases the formation of small amounts of nitrate esters has also been reported\textsuperscript{13}, although as minor products. This gives an indication regarding the probable existence of an alternate reagent, iodonium nitrite formed in the reaction of silver nitrile with iodine; and also in dinitrogen tetroxide iodine solution, which undergoes oxidation in protic solvents to give iodonium nitrate.

Thus in the reaction of propylene and 1-butene with dinitrogen tetroxide-iodine mixture, formation of both nitro iodo products and iodonitrites has been reported\textsuperscript{2}. However, isolation and purification of the latter contaminants, in both the reactions, was not possible because of the lower yields and instability of the products. The formation
of these nitrates has been suggested to probably proceed by the ionic addition process, as reported by Bachmann and Logan\textsuperscript{13} for an analogous reaction, and not by free radical addition pathway.

Since the formation of nitro-iodo adduct by nitryl iodide, following free radical addition pathway, is differentiated in a clear cut manner with that of the formation of nitrate esters, which follow ionic addition\textsuperscript{2} pathway, it gives an indication that an alternate species, other than NO\textsubscript{2}I is involved in the nitrate ester formation, suggesting the probable role of iodinium nitrite (INO\textsubscript{2}) in the reaction.

Similarly, in the reaction of cyclohexene with dinitrogen tetroxide in presence of iodine a mixture of nitrate ester and nitro iodo compound was formed whose IR spectrum indicated the latter as major product\textsuperscript{2}. The products of reaction were too unstable to be purified due to considerable liberation of iodine. However, some 1-nitrocyclohexane was obtained on subsequent distillation.

In addition to above, reactions of phenyl acetylene and tolane with dinitrogen tetroxide in presence of iodine have also been reported by the same authors\textsuperscript{2} to afford α-iodo β-nitro styrene, having phenyl group \textit{trans} with respect to nitro group and a mixture of \textit{cis} and \textit{trans} α-nitro-2'-iodostilbenes, respectively. These reactions also failed to give any nitrate ester.
The only information available so far, regarding the studies towards examining the effect of bulky groups upon the addition of nitryl iodide is illustrated by its reaction with tert-butylethylene (21). When (21) was treated with silver nitrite and iodine, the crude nitro iodo adduct (22) was obtained which on elimination of HI with pyridine furnished vinyl nitro compound (23). The NMR spectrum of the product (23) showed it to be a trans olefin and ruled out the possibility of a terminal C=CH₂. Reduction of the compound (23) by sodium borohydride gave the saturated nitro compound (24) (scheme -3) that showed a classical A₂X₂ absorption in the NMR spectrum.

Since the nitro group is the attacking species and it becomes bonded to the terminal carbon, the intermediate radical or ion was not bridged; otherwise opening by INO₂ should have led to opposite regioisomer.

As apparent from the above discussion it is quite obvious that the nitryl iodide addition reactions provide a convenient method for the selective synthesis of β-ido-nitro, vinyl nitro, and nitroalkanes under mild reaction conditions in addition to their interesting stereochemical and regiochemical aspects. However, there is much scope for more work in the field for a better understanding of the chemistry of nitryl iodide addition to olefins.
REFERENCES


4. L. Birchenbach, J. Goubeau and E. Berniger; Ber., 1932, 65, 1339.


CHAPTER II.2

ADDITION OF NITRILY IODIDE TO TERPENOIDAL OLEFINS

ABSTRACT

The reaction of nitryl iodide with several terpenoidal olefinic compounds such as longifolene, camphene, isolongifolene, terpinolene, γ-terpinene, limonene, α-pinene, β-pinene and Δ3-carene were carried out. Longifolene, camphene and β-pinene furnished nitroiodo adducts which on treatment with base gave vinyl nitro compounds and the corresponding aldehydes on subsequent reduction with zinc and acetic acid. Isolongifolene, γ-terpinene, and limonene gave nitroiodo adducts which on treatment with base furnished vinyl nitro compounds. Terpinolene gave nitroiodo adduct which on reaction with base furnished 2-nitro-Δ3-p-menth-1,4(8)-diene. Subsequent reduction of the nitro compounds gave the ketone, p-menth-4(8)-en-2-one. α-Pinene and Δ3-carene did not undergo the reaction under similar conditions and no identifiable product(s) could be isolated. The results indicate that the addition of nitryl iodide takes place by a free radical pathway through the attack of NO2 radical on the carbon-carbon double bond followed by quenching of the radical by iodine to give nitroiodo adduct. The position of attachment of the nitro group to the carbon-carbon double bond has been proved by treatment of the
nitrioiodo adduct(s) with base followed by reduction of the vinyl nitro compound(s) with zinc in acetic acid to the corresponding carbonyl compound(s). The results with terpinolene and γ-terpinene reveal that the attack of nitryl iodide takes place preferentially on the C$_{1}$-C$_{2}$ double bond whereas in the case of limonene, the exocyclic double bond at C$_{8}$-C$_{9}$ is attacked in preference to the C$_{1}$-C$_{2}$ double bond.
INTRODUCTION

Addition reactions of pseudohalogen compounds to the terpenoidal olefinic compounds have been extensively studied in the past few decades. The reaction of nitrosyl chloride has been used for the nitrosation of terpenoidal hydrocarbons and their structural and conformational elucidation. However little work has been done on the reaction of nitryl iodide with the terpenoidal unsaturated systems. The only work on the addition of nitryl iodide to terpenoidal olefins was reported by Stevens and Emmons in 1958, who showed that the reaction of dinitrogen tetroxide and iodine with camphene gave a nitrioiodo adduct namely 3-iodo-3-nitromethyl camphenilane, which was formed as a result of addition of nitryl iodide to the carbon-carbon double bond. On treatment with ethanolic sodium hydroxide, the nitrioiodo adduct underwent dehydroiodination to furnish w-nitro-camphene. There is no other reference available on the addition of the nitryl iodide to terpenoidal substrates.
The work on the addition reaction of nitryl iodide to terpenoidal olefinic compounds viz., longifolene (1), camphene (6), isolongifolene (10), terpinolene (13), γ-terpinene (17), limonene (20), α-pinene (27), β-pinene (23) and Δ³-carene (28) was undertaken keeping in view the usefulness of this emerging reagent in the synthesis of nitro-iodo, vinylnitro, nitroalkanes and corresponding carbonyl compounds.

RESULTS AND DISCUSSION

(i) Addition of nitryl iodide to longifolene (1)

The reaction of longifolene (1) with nitryl iodide, generated 'in situ' by the action of silver nitrite in ether gave 53 percent 7-iodo-7-nitromethyl longibornylane (2), 6.6 percent nitrate ester of longifolene (3) and 10 percent unreacted longifolene (1).

The nitroiodo adduct (2) was found to be unstable on standing at room temperature for few hours and liberates iodine. On treatment with silver oxide in methanol, the nitroiodo adduct (2) underwent dehydroiodination to give w-nitrolongifolene (4) in 30.2 percent yield. The structure of compound (4) was established by comparison of IR and NMR spectra with that of an authentic sample of w-nitrolongifolene and determination of mixed melting point (no depression).
Further confirmation of the structure of w-nitro-longifolene (4) was made by its reduction with zinc dust-acetic acid in protic media when the known longifolaldehyde (5) was obtained in an yield of 17 percent.

The formation of longifolaldehyde (5) clearly shows the position of nitro group at terminal carbon atom and indicates that nitryl iodide adds free radically through attack of NO₂ radical on the double bond of longifolene (1) followed by quenching of the radical with iodine, to give nitroiodo adduct. The results are in agreement with those obtained by Hassner and coworkers² in the case of addition of nitryl iodide to 2-cholestene and 3-methylene cholestane, who showed that the addition proceeds by a free radical pathway. The possibility of the reaction proceeding through a carbonium ion intermediate has already been discarded by Hassner et al² in their work on addition of nitryl iodide to unsaturated ester substrates viz., methyl acrylate.

The instability of the nitroiodo adduct can possibly be explained on the assumption that the product formed i.e., 7-iodo-7-nitromethyl longibornylane due to sterie hindrance by the large bridge (C₂-C₅) liberates iodine and eliminates HI on treatment with base, to give w-nitrolongifolene (4) (scheme -1).
The formation of w-nitrolongifolene establishes the position of nitro group at terminal carbon atom and hence it is apparent that the attack of NO\textsubscript{2}I takes place from the back side of longifolene giving rise to 7-iodo-7-nitromethyl longibornylane (2).

The structure of the corresponding nitrate ester (3) is based on chemical and spectroscopic analysis. Its IR spectrum showed bands at 1635 cm\textsuperscript{-1} characteristic of N=O stretching vibrations, 860 cm\textsuperscript{-1} for O-N stretching vibrations and at 760 and 700 cm\textsuperscript{-1} for NO\textsubscript{2} bending vibrations. Band at 515 cm\textsuperscript{-1} indicated the presence of C-I bond.

Thus, the reaction of nitryl iodide with longifolene (1) provides a convenient route for the synthesis of w-nitrolongifolene (4) and longifolaldehyde (5) under mild reaction conditions.

(ii) Addition of nitryl iodide to camphene (6)

The reaction of camphene (6) with nitryl iodide furnished 51 percent of 3-iodo-3-nitromethyl camphenilane(7) which was very unstable. It was subjected to dehydroiodination by treatment with base to obtain the known w-nitrocamphene (8) in an yield of 37 percent. The identity of w-nitrocamphene was established by the comparison of IR spectra with that of an authentic sample and determination of mixed melting point (no depression)(scheme -2).
SCHEME 1

1. \( \text{AgNO}_2 - I_2 \rightarrow \) 

2. \( \text{CH}_2\text{NO}_2 \)

3. Nitrate ester

SCHEME 2

6. \( \text{AgNO}_2 - I_2 \rightarrow \) 

7. \( \text{CH}_2\text{NO}_2 \)

8. \( \text{NO}_2 \)

9. \( \text{CHO} \)
Further conclusive evidence for the structure of \( w \)-nitrocamphene was gained by its subsequent reduction with zinc dust-acetic acid to obtain an epimeric mixture camphenilanaldehyde (9) in 22 percent yield.

The formation of camphenilanaldehyde (9) proves the position of nitro group at terminal carbon atom. It also indicates that the reaction of nitryl iodide with camphene(6) gave a nitroiodo adduct formulated as 3-iodo-3-nitro-methylcamphenilane (7) which owing to its unstable character liberates iodine and is transformed into \( w \)-nitrocamphene (8) on treatment with base.

Further, the formation of an epimeric mixture of camphenilanaldehyde (9) establishes the fact that a diastereomeric mixture of nitroiodo adduct was originally formed by the attack of \( NO_2 \) radical onto the double bond of camphene(6) from both sides followed by the quenching of the radical formed with iodine (scheme -2).

(iii) Addition of nitryl iodide to isolongifolene (10)

The reaction of nitryl iodide with isolongifolene(10) furnished 65 percent of nitroiodo adduct (11) (scheme -3) which was characterised by spectroscopic methods. Its infra-red spectrum (fig. 1) showed bands at 1505 and 1375 cm\(^{-1}\) characteristic of \( N=O \) stretching vibrations and at 855 cm\(^{-1}\) indicative of \( N-O \) stretching vibrations of \( NO_2 \) group. An absorption band at 515 cm\(^{-1}\) is due to stretching vibrations
of C-I linkage. The saturated character of the compound (11) is proved by the disappearance of absorption band in the olefinic range.

The NMR spectrum of (11) (Fig. 2) indicated secondary protons at \( \delta 1.95 \) germinal to nitro function showing a shift of 0.70 ppm from the signal in isolongifolene (10). A signal at \( \delta 4.7 \) was assigned to the proton attached to \( C-NO_2 \).

Further evidence for the structure of (11) was obtained by dehydroiodination of the nitroiodo adduct which on treatment with base furnished 44 percent of 8-nitroisolongifolene (12). The IR spectrum of (12) (Fig. 3) exhibited characteristic bands for \( NO_2 \) stretching vibrations at 1500 and 1330 cm\(^{-1}\) and for \( C=C \) stretching vibrations at 1640 cm\(^{-1}\) (weak). NMR spectrum (Fig. 4) showed no absorption signal for unsaturated proton.

Attempts to reduce the compound (12) by zinc dust-acetic acid did not succeed and an oily material was obtained which could not be characterised.

(iv) Addition of nitryl iodide to terpinolene (13)

The reaction of nitryl iodide with terpinolene (13) gave 64 percent of crude adduct (14) which on elimination of HI with silver oxide in methanol furnished 2-nitro-p-menth-1,4(8)-diene (15) 54 percent yield (scheme -4).

The structure of 2-nitro-p-menth-1,4(8)-diene (15) is based on spectroscopic analysis. The infrared spectrum
SCHEME 3

(10) \[ \xrightarrow{\text{AgNO}_2 - I_2} \] \[ \xrightarrow{\text{O}_2 N} \] (11) \[ \xrightarrow{\text{Base}} \] \[ \xrightarrow{\text{O}_2 N} \] (12)

SCHEME 4

(13) \[ \xrightarrow{\text{AgNO}_2 - I_2} \] (14) \[ \xrightarrow{\text{Base}} \] (15)

(16) \[ \xrightarrow{\text{Zn - HOAc}} \]
(Fig. 5) showed characteristic stretching vibrations of NO₂ function at 1510 and 1340 cm⁻¹ and a weak band at 1650 cm⁻¹ indicative of C=C stretching vibrations. The NMR spectrum of (15) shows no signal for unsaturated proton indicating tetrasubstituted double bonds. A shift of 0.3 ppm is observed for the methyl protons germinal to the double bond and appears at δ 1.65.

The formation of vinyl nitro compound (15) proves the fact that addition of nitryl iodide is stereospecific and the attack of NO₂ radical occurs onto the endocyclic double bond of terpinolene (13), to furnish 1-iodo-2-nitro-p-menth-4(8)-ene (14).

2-Nitro-p-menth-1,4(8)-diene (15) on reduction with zinc dust-acetic acid in protic media furnished 30 percent of p-menth-4(8)-en-2-one(16) which was characterised by IR and NMR spectra.

The infrared spectrum (Fig. 6) of p-menth-4(8)-en-2-one(16) showed bands at 1740 cm⁻¹ characteristic of C=O stretching vibration and shoulder 1630 cm⁻¹ characteristic of tetrasubstituted C=C stretching vibrations, along with other absorption bands. The NMR spectrum (Fig. 7) showed a chemical shift of 1.35 ppm for secondary protons germinal to the C=O function and appears at δ 2.6.
(v) **Addition of nitryl iodide to γ-terpinene (17)**

γ-Terpinene (17) on reaction with nitryl iodide, generated 'in situ' by the action of silver nitrite and iodine in ether, furnished the crude adduct (18) which on elimination of HI by treatment with silver oxide in methanol gave 2-nitro-p-menth-1,4-diene (19) in an yield of 53 percent (scheme -5).

The compound 2-nitro-p-menth-1,4-diene (19) was characterised by IR and NMR spectroscopy. Its infrared spectrum showed strong absorption bands at 1500 and 1320 cm\(^{-1}\) characteristic of NO\(_2\) group and at 1635 and 790 cm\(^{-1}\) indicative of C=C function. The NMR spectrum (Fig.8) showed signal at δ 5.35 (triplet) which was assigned to the unsaturated proton attached to C\(_5\).

The formation of 2-nitro-p-menth-1,4-diene (19) shows that the crude adduct (18) is 1-iodo-2-nitro-p-menth-4-ene.

From the results obtained by the reaction of nitryl iodide with γ-terpinene (17), it may be observed that, although, both the double bonds in γ-terpinene are endocyclic but the attack of NO\(_2\)I species occurs stereospecifically on the C\(_1\)-C\(_2\) double bond and it does not attack the other double bond, which however is equivalent environmentally.

Attempts to obtain a reduction product of 2-nitro-p-menth-1,4-diene (19) with zinc dust-acetic acid did not
succeed and no characterisable product could be isolated.

(vi) **Addition of nitryl iodide to limonene (20)**

The reaction of nitryl iodide with limonene (20) furnished 42 percent of crude adduct (21) which on subsequent dehydroiodination by treatment with silver oxide in methanol gave 36 percent of 9-nitro-p-menth-1,8(9)-diene (22) (scheme-6).

The structural elucidation of 9-nitro-p-menth-1,8(9) diene was made by IR and NMR spectral analysis. The infrared spectrum showed characteristic absorption bands at 1505 and 1335 cm
-1 showing the stretching vibrations of NO₂ group at 1640, 890 and 800 cm
-1 indicating the presence of exo-and endocyclic double bond. The NMR spectrum (Fig. 9) depicted signal at δ 5.35 assigned to the unsaturated proton at C₂ and at δ 6.7 indicating a shift of 2.03 ppm for the unsaturated proton at C₉ from the signal in limonene.

The formation of 9-nitro-p-menth-1,8(9)-diene (22) established the structure of crude adduct (21) to be 8-iodo-9-nitro-p-menth-1-ene, which is obtained as a result of attack of NO₂I to the exocyclic double bond of limonene (20) by a free radical pathway. It is also apparent from the mode of addition of nitryl iodide that the attack of the NO₂ radical preferentially takes place on the exocyclic double bond which is sterically less hindered than the trisubstituted double bond (C₁-C₂).
(vii) Addition of nitryl iodide to β-pinene (23)

The reaction of nitryl iodide with β-pinene furnished nitroiodo adduct (24) in an yield of 54 percent. Subsequent dehydroiodination of (24) with silver oxide and methanol furnished 32 percent of vinyl nitro compound (25)(fig.10) which on reduction with zinc dust-acetic acid gave the known dihydromyrtenal (26) in 22 percent yield (scheme -7).

The formation of dihydromyrtenal (26) proves the structure of (25) to be 10-nitro-2(10)-pinene and establishes the position of nitro group in (24) at terminal carbon atom. Thus the addition of nitryl iodide occurs through free radical pathway.

(viii) Addition of nitryl iodide to α-pinene (27) and \( \Delta^3 \)-carene (28)

The reaction of α-pinene (27) and \( \Delta^3 \)-carene (28) with nitryl iodide generated 'in situ' in the usual manner, gave the crude reaction product(s), which in each case was found to contain unreacted starting material as identified by the comparison of IR spectra with that of authentic samples.

The reaction product(s) was highly viscous and became dark on standing at room temperature for a few hours, and no identifiable component could be isolated.
### TABLE - 1

**Overall yields of products obtained**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Nitriodo adduct (percent)</th>
<th>Vinylnitrro compound (percent)</th>
<th>Carbonyl compound (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Longifolene (1)</td>
<td>53</td>
<td>30.2(57)</td>
<td>17.1(57)</td>
</tr>
<tr>
<td>2. Camphene (6)</td>
<td>51</td>
<td>37.2(73)</td>
<td>22.3(60)</td>
</tr>
<tr>
<td>3. Isolongifolene(10)</td>
<td>65</td>
<td>44.2(68)</td>
<td>-</td>
</tr>
<tr>
<td>4. Terpinolene(13)</td>
<td>64</td>
<td>54.4(85)</td>
<td>29.99(55)</td>
</tr>
<tr>
<td>5. γ-Terpinene (17)</td>
<td>62</td>
<td>52.8(85.3)</td>
<td>-</td>
</tr>
<tr>
<td>6. Limonene (20)</td>
<td>42</td>
<td>35.7(85)</td>
<td>-</td>
</tr>
<tr>
<td>7. β-Pinene (23)</td>
<td>54</td>
<td>31.5(58.4)</td>
<td>22.3(71)</td>
</tr>
</tbody>
</table>

* Yield on the basis of olefin recovered.

** Yield on the weight of nitriodo adduct.

*** Yield on the weight of vinylnitrro compound.
Fig. 1: IR spectrum of nitroethene adduct of 3-methyl-3-butenone (II).
Fig. 2: NMR spectrum of nitroiodo adduct of isolingifolene (II).
Fig. 3: IR spectrum of 8-nitroisolongifolene (12)
Fig. 4: NMR spectrum of 8-alloisoolongifolene (12).
Fig. 5: In region of 2-nitro-p-phenylen-diamine (8)-diamine (12)

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Fig. 7: NMR spectrum of p-naphth-4(8)-one-2-one (16).
**Fig. 8**: NMR spectrum of 2-nitro-p-menth-1,4-diene (19).
Fig. 9: NMR spectrum of 9-nitro-p-menth-1,8(9)-diene (22).
Fig. 10: NMR spectrum of 10-nitro-2(10)-pipene (25).
The yields of the nitroiodo adducts, vinyl nitro compounds and the corresponding carbonyl compounds obtained are summarised in Table -1.

**EXPERIMENTAL**

All the melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer infrared instrument. NMR spectra (CDCl₃/CCl₄) were recorded on a varian A-60 spectrometer using TMS as an internal standard. Gas chromatography was carried on a C.I.C. (Baroda) model gas chromatograph having dual column using nitrogen as a carrier gas and a column of 10 percent DEGA on 30/60 chromosorb-P-NAW at 110⁰/160⁰. The reaction of nitryl iodide with all the terpenoidal olefins was carried out in an atmosphere of nitrogen.

**Starting Materials**

All the reagents except silver nitrite and solvents were obtained from commercial sources (BDH, E.Merck, S.M. Polyphorm). The purity of substrates longifolene, camphene, isolongifolene, terpinolene, γ-terpinene, α-pinene, β-pinene and Δ₃-carene was checked by TLC and gas chromatography and wherever necessary, they were purified by chromatography.

**Preparation of Silver nitrite**

A solution of 5 g potassium nitrite was added to a solution of 8 g silver nitrate in distilled water. The resulting yellow precipitate was filtered on a sintered glass
funnel and washed with distilled water several times and dried. Repeated crystallization with hot water gave silver nitrite which was dried under vacuum.

(i) **Addition of Nitryl iodide to longifolene (1)**

In a 250 ml round bottom flask was taken silver nitrite (3.83 g; 25 mmol) and iodine (12.7 g; 50 mmol) in dry ether (300 ml) and stirred for 30 min. Longifolene (1) (5.1 g; 25 mmol) was added to the reaction mixture and stirring was continued for 8 hr. The reaction mixture was filtered, washed with 5 percent solution of sodium thiosulphate (100 ml), saturated solution of sodium chloride (100 ml) and water and dried over anhydrous sodium sulphate. The solvent was evaporated to furnish the crude reaction product (6.7 g) which was chromatographed over silica-gel. Elution with petroleum ether gave 0.5 g (10 percent) of an oily product which was identified to be unreacted longifolene (1) by comparison of TLC and IR spectrum with an authentic sample of (1).

Further elution with petroleum-ether-benzene (1:1) and benzene-ethyl-acetate (1:1) gave 4.5 g (53 percent) of another fraction (2) which was found to contain iodine and nitrogen. This fraction (4 g) was refluxed with silver oxide (4.62 g, 20 mmol)(dried in a vacuum oven) in methanol (300 ml) for 5 hr, and filtered through a sintered glass funnel. Removal of the solvent gave the crude reaction product which on repeated crystallization from chloroform-methanol gave
w-nitrolongifolene (3), mp and mixed mp 74-5° (Lit^3 mp 75-7°); yield : 1.5 g (30.2 percent).

**Anal. data**

found : C, 72.05 ; H, 9.6 ; N, 5.31 percent
C_15H_23NO_2 requires : C, 72.25 ; H, 9.23; N, 5.62 percent

Its identity was established by comparison of IR and NMR spectra with that of an authentic sample of w-nitrolongifolene(3). The compound (3) decolourised bromine in carbon tetrachloride and gave positive test for nitrogen.

Further elution with benzene-ethyl acetate (1:1) gave the third fraction which on crystallization from chloroform-methanol furnished the nitrate ester (3) mp 54-5°;
yield : 0.4 g (6.6 percent).

**IR spectrum** (KBr) : 1635, 860, 760, 700 and 515 cm\(^{-1}\).

Reduction of w-nitrolongifolene (4)

A warm suspension (40°) of w-nitrolongifolene (4) (1 g) in acetic acid (50 ml) and water (2 ml) was stirred and zinc dust (3.2 g) was added in small portions during 1 hr. The reaction mixture was refluxed for 4 hr, filtered hot and zinc was washed with hot acetic acid. Water was added to the reaction mixture and the organic phase was extracted with ether. Evaporation of the solvent furnished a crude reaction product which on chromatography over silica-gel furnished longifolaldehyde (5) bp 118°/2 mm (Lit^4 bp 115°/1.5 mm); yield : 0.5 g (17 percent).
The identity of compound (5) was established by comparison of IR and NMR spectra with an authentic sample of longifolaldehyde (5). The compound gave a semicarbazone derivative mp 216° (Lit5 mp 217-8°) and 2,4-DNP derivative mp 171° (Lit5 mp 172-3°).

(ii) Addition of nitryl iodide to camphene (6)

The procedure as described above was followed. From camphene (6) (6.8 g, 50 mmol) silver nitrite (7.7 g, 50 mmol) and iodine (25.4 g, 100 mmol) there was obtained a crude reaction product (6.5 g, 51 percent) which was treated with silver oxide (9.8 g, 42 mmol) in methanol (300 ml) and refluxed for 5 hr. Usual work up of the reaction mixture followed by crystallization from chloroform-methanol gave w-nitrocamphene (8) mp and mixed mp 63-4° (Lit3 mp 64.5°) yield: 2.8 g (37.2 percent)

Anal. data found: C, 66.71; H, 8.02; N, 7.47 percent

C10H15NO2 requires: C, 66.29; H, 8.28; N, 7.73 percent.

The identity of compound (8) was established by the comparison of IR and NMR spectra with that of an authentic sample of w-nitrocamphene (8).

The mother liquor was found to contain the unreacted starting material (1.2 g, 18 percent) as identified by comparison of IR spectra and gas chromatographic retention times with an authentic sample of camphene (6).
Reduction of w-nitrocamphene (8)

The procedure as described before was followed. From zinc dust (3.2 g), acetic acid (50 ml) and w-nitrocamphene (8) (1 g), there was obtained a solid compound which on repeated crystallization from chloroform-methanol gave camphenilanaldehyde (9) mp and mixed mp 63-4° (Lit mp 65-7°); yield: 0.5 g (22.3 percent).

The identity of compound (9) was established by comparison of IR spectra with an authentic sample of (9).

(iii) Addition of nitryl iodide to isolongifolene (10)

The procedure as described above was followed. From isolongifolene (10)(5.1 g, 25 mmol), silver nitrite (3.83 g, 25 mmol) and iodine (12.7 g, 50 mmol), there was obtained a crude reaction product (6 g) which was chromatographed over silica-gel. Elution with petroleum ether (40°-60°) gave the unreacted olefin (0.5 g, 10 percent). Further elution with petroleum ether-benzene (1:1) and benzene-ethyl acetate (1:1) gave pure nitriiodo adduct (11) yield: 5.5 g (65 percent).

The compound showed one spot on TLC.

Analytical data. found: C, 47.47; H, 6.87; N, 3.23 percent

C_{15}H_{24}NO_2I requires: C, 47.74; H, 6.36; N, 3.71 percent

IR spectrum (neat): 1505, 1375, 855 and 515 cm⁻¹.

NMR spectrum (CDCL₃): δ 1.95 (1H) and δ 4.7 (1H).

The compound (11) gave positive test for iodine and nitrogen and was saturated towards bromine in carbon tetra-chloride.
Dehydroiodination of nitriodo adduct (11):

The compound (11) (1 g, 2.6 mmol) and silver oxide (1.2 g, 5.2 mmol) in methanol (100 ml) was refluxed for 5 hr. The reaction mixture was cooled to room temperature, filtered through a sintered glass funnel. Evaporation of the solvent gave a solid compound which on crystallization from chloroform-methanol furnished (12) mp 60-62\(^\circ\); yield 0.45 g (44.2 percent).

Anal. data found: C, 72.63; H, 8.89; N, 6.03 percent

C\(_{15}\)H\(_{23}\)N\(_2\)O\(_2\) requires: C, 72.25; H, 9.23; N, 5.82 percent.

IR spectrum (KBr): 1500, 1330 and 1640 cm\(^{-1}\).

(iv) Addition of Nitryl Iodide to terpinolene (13)

The procedure as described above was followed. From terpinolene (13) (3.4 g, 25 mmol), silver nitrite (3.83 g, 25 mmol) and iodine (12.7 g, 50 mmol), there was obtained a crude reaction product which was chromatographed over silica-gel. Elution with petroleum ether gave the first fraction (0.5 g), which was identified to be the unreacted olefin by comparison of IR spectra and gas chromatographic retention times with an authentic sample of (13).

Further elution with benzene-ethyl acetate (1:1) gave the second fraction (4.2 g, 64 percent) which was found to contain nitrogen and iodine and did not decolourise bromine in carbon tetrachloride.

The crude adduct (14) (3 g) was refluxed with silver oxide (4.5 g, 19.4 mmol) in methanol (500 ml) for 5 hr. The
reaction mixture was worked up in the usual manner to obtain a solid material which on recrystallization from chloroform-
methanol gave 2-nitro-p-menth-1,4(8)-diene (15) mp 95-7°; yield 1.5 g (54.4 percent).

**Anal. data**

found: C, 65.95; H, 8.89; N, 8.03 percent.

C\textsubscript{10}H\textsubscript{15}NO\textsubscript{2} requires: C, 66.29; H, 8.28; N, 7.73 percent.

**IR spectrum (KBr)**: 1510, 1340 and 1650 (w) cm\textsuperscript{-1}.

**NMR spectrum (CDCl\textsubscript{4})**: δ 1.65 (3H, CH\textsubscript{3}).

The compound gave a positive test for nitrogen and decolourised bromine in carbon tetrachloride.

**Reduction of 2-nitro-p-menth-1,4(8)-diene (15)**

A warm suspension (40°) of 2-nitro-p-menth-1,4(8)-diene (15) (1 g) in acetic acid (60 ml) and water (2 ml) was stirred and zinc dust (3.2 g) was added in small portions during 30 min. The reaction mixture was refluxed for 4 hr and worked up in the usual manner to obtain the crude product, which was chromatographed over silica-gel. Elution with benzene-ethyl acetate (9:1) gave p-menth-4(8)-ene-2-one (16) bp 106°/10 mm; yield 0.46 g (29.99 percent). TLC showed one spot and gas chromatography indicated it to be a uniform product.

**Anal. data**

found: C, 78.43; H, 11.09 percent.

C\textsubscript{10}H\textsubscript{16}O requires: C, 78.94; H, 10.53 percent.

**IR spectrum (neat)**: 1740 cm\textsuperscript{-1} (>C = 0)

**NMR spectrum (CDCl\textsubscript{4})**: δ 2.6 (2H, CH\textsubscript{2}- C = 0)
The compound (16) decolourised bromine in carbon tetrachloride and gave 2,4-dinitrophenyl-hydrazone derivative mp 149°.

(v) Addition of nitryl iodide to γ-terpinene (17)

The reaction of γ-terpinene (17) (3.4 g, 25 mmol) with silver nitrite (3.83 g, 25 mmol) and iodine (12.7 g, 50 mmol) in ether (200 ml) furnished a crude product which was chromatographed over silica-gel. Elution with petroleum ether gave the first fraction (0.2 g) identified to be the unreacted starting material by comparison of its IR spectra with an authentic sample of (17).

Elution with benzene-ethyl acetate (1:1) gave the second fraction (4.5 g, 62 percent) of 1-iodo-2-nitro-p-menth-4-ene (18) which was found to contain iodine and nitrogen and decolourised bromine in carbon tetrachloride.

The compound (18)(4 g) on treatment with silver oxide (5.8 g, 25 mmol) in methanol (500 ml) furnished a solid material which on crystallization from chloroform-methanol gave 2-nitro-p-menth-1,4-diene (19) mp 106-7°; yield: 2 g (52.87 percent).

**Anal. data.** found: C, 66.43; H, 8.5; N, 7.3 percent

\[ \text{C}_{10}\text{H}_{15}\text{NO}_2 \]

requires: C, 66.29; H, 8.28; N, 7.73 percent

**IR spectrum** (KBr): 1500, 1320, 1635 and 790 cm\(^{-1}\).

**NMR spectrum** (CCl\(_4\)): δ 5.35 \(\text{(1H, -CH)}\)
(vi) Addition of nitryl iodide to limonene (20)

The reaction of silver nitrite (7.7 g, 50 mmol), iodine (25.4 g, 100 mmol) and limonene (20) (6.8 g, 50 mmol) furnished a crude reaction product which was chromatographed over silica-gel. The first fraction (0.5 g) was eluted with petroleum ether which was identified to be the unreacted olefin by comparison of IR spectra and gas chromatographic retention times with an authentic sample of limonene (20). Elution with benzene-ethyl acetate (1:1) gave the second fraction (6 g, 42 percent) of 8-ido-9-nitro-p-menth-l-ene (21). The compound gave one spot on TLC and showed the presence of nitrogen and iodine.

The compound (21) (5 g) on reaction with silver oxide (7.5 g, 32 mmol) in methanol (500 ml) furnished a solid material which on recrystallization from chloroform-methanol furnished 9-nitro-p-menth-1,8(9)-diene (22) mp 85-86°; yield: 2.5 g (35.7 percent).

Anal. data found: C, 66.92; H, 7.9; N, 7.6 percent.

C₁₀H₁₅NO₂ requires: C, 66.29; H, 8.28; N, 7.73 percent.

IR spectrum (KBr): 1505, 1335, 1640, 890 and 800 cm⁻¹.

NMR spectrum (CCl₄): δ 5.3 (1H, C₂-CH); δ 6.7 (1H, C₉-CH).

(vii) Addition of nitryl iodide to β-pinene (23)

The reaction of β-pinene (23) (3.4 g, 25 mmol), silver nitrite (3.83 g, 25 mmol) and iodine (12.7 g, 50 mmol) in ether (100 ml) furnished a crude addition product which was
chromatographed over silica-gel. Elution with petroleum ether gave the unreacted olefin (0.3 g) identified by comparison of IR spectra and gas chromatographic retention times with an authentic sample of (23).

Further elution with benzene-ethyl acetate (1:1) gave the nitroiodo adduct (24) (3.8 g, 54 percent) which gave a positive test for iodine and nitrogen and was inert towards bromine in carbon tetrachloride.

The compound (24) (3.5 g) on reaction with silver oxide (5.1 g, 22 mmol) in methanol (300 ml) furnished a solid compound which on crystallization from chloroform-methanol gave the vinyl-nitro compound (25) mp 68-9°, yield: 1.2 g (31.5 percent).

Anal. data found: C, 66.71; H, 8.02; N, 7.47 percent.
C_{10}H_{15}NO_2 requires: C, 66.29; H, 8.28; N, 7.73 percent.
IR spectrum (KBr): 1510, 1340 and 1630 cm\(^{-1}\).
NMR spectrum (CCl\(_4\)): \(\delta\) 6.68 (1H, CH NO\(_2\)).

Reduction of vinylnitro compound (25)

The treatment of vinylnitro compound (25) (1 g) with zinc dust (3.2 g), acetic acid (50 ml) and water (2 ml) furnished a crude product which on elution with benzene-ethyl acetate (1:1) on a column of silica-gel furnished dihydromyrtrenal (26) bp 77-8°/2.5 mm (Lit\(^7\) bp 75-6°/2.5 mm) yield: 0.6 g (22.3 percent).
Anal. data found: C, 78.34; H, 10.89 percent.
C\textsubscript{10}H\textsubscript{16}O requires: C, 78.94; H, 10.52 percent.

Its IR spectrum was found to be identical with that of an authentic sample of dihydromyrtenal (26). The compound gave semicarbazone derivative mp 151\textdegree (Lit\textsuperscript{8} mp 152-153\textdegree).