A. General Discussion:

α-Amino-N-cyclohexyl nitrone was prepared directly from formamide and N-cyclohexyl hydroxylamine. The nitrone was isolated as colourless solid, recrystallised from hexane (60°–80° C), mp. 81°C. The nitrone was found to be hygroscopic and slowly decomposed in presence of traces of moisture to the corresponding N-cyclohexyl hydroxylamine.

Structure of the nitrone was confirmed by spectroscopic data (reproduced in Experimental Section). In IR spectra, a broad peak (3500–3300 cm⁻¹) due to intramolecular H-bonding was observed which was unaffected even by changing the dilution, indicating a trans structure of the nitrone. The nitrone was stable at 5°C up to 4 days. While keeping, it was changed gradually to (3+3→6) dimer after 8 days, to a colourless crystalline solid. The structure of the dimer was confirmed by IR, NMR and Mass spectra.
Cycloreversion (6→3→3) of the dimer to monomer and finally to the corresponding cycloadduct was also observed while keeping the dimer in contact with electron deficient dipolarophiles.

The nitrone on refluxing with triphenyl phosphine in dry benzene remained unchanged. Which indicates that the negative charge is not so localised on the oxygen atom like aromatic N-oxides.

1,3-Dipolar cycloaddition reaction of α-amino NN-cyclohexyl nitrone with different dipolarophiles were studied. The nitrone reacted with most of the olefins, even with cyclohexene adduct, smoothly at room temperature. In the case of cyclohexene, no appreciable change of yield was observed at water bath temperature. In the Table-XI, the reaction condition, major products, nature etc., are summarised. The addition of acrylonitrile, chloro acrylonitrile, 3,4-dihydro-2H-pyran and 2,3-dihydro furan with the nitrone were found to be regiospecific. Only 5-substituted adducts were obtained. A red viscous liquid was obtained during the chromatographic purification of acrylonitrile adduct. The same product was also obtained after hydrolysis of the acrylonitrile adduct by aqueous HCl and was characterised by IR, NMR and Mass spectra. With highly electron deficient dipolarophile, viz., N-phenyl maleimide, N-cyclohexyl maleimide and p-benzoquinone, cycloadducts were obtained spontaneously at room temperature.

Reactions with normal or moderately electron rich olefins, viz., 3,4-dihydro-2H-pyran, 2,3-dihydro furan and acenaphthylene were not facile even at water bath temperature.
### TABLE XI.

<table>
<thead>
<tr>
<th>Dipolarophiles</th>
<th>Solvent, Reaction</th>
<th>Nature of Condition</th>
<th>Nature of Products</th>
<th>Structures of Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene</td>
<td>Formamide, R.T.</td>
<td>White 40 Hrs.</td>
<td>Crystalline Solid.</td>
<td>![Structure A]</td>
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<tr>
<td>3,4-Dihydro-2H-pyran</td>
<td>Formamide, Reflux</td>
<td>on Water Bath, 24 Hrs.</td>
<td>Colourless Liquid</td>
<td>![Structure B]</td>
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<tr>
<td>2,3-Dihydro Furan</td>
<td>Formamide, Reflux</td>
<td>on Water Bath, 72 Hrs.</td>
<td>Light Red Liquid</td>
<td>![Structure C]</td>
</tr>
</tbody>
</table>

Cont.
N-phenyl maleimide  Formamide, R.T., White Solid 24 Hrs.

N-cyclohexyl maleimide  Formamide, R.T., Gray Solid 24 Hrs.

P-benzoquinone  Formamide, R.T., 24 Hrs., Stirring in Dark Yellowish Solid

Methylacrylate  Formamide, R.T., Grayish Liquid 24 Hrs. Redish Gum

(G): R¹=H, R²=COOMe.
(H): R¹=COOMe, R²=H.
Cont.
Ethylacrylate
Formamide, R.T., Yellow Gummy
24 Hrs. Liquid

Acrylonitrile
Formamide, R.T., Red Liquid
24 Hrs.

2-Chloroacrylonitrile
Formamide, 50°C, Viscous
12 Hrs. Liquid

Trichloroethylene
Formamide, R.T., Red Crystal
48 Hrs.
Tetrachloroethylene Formamide, R.T., White Crystal 48 Hrs.

Acenaphthalene Formamide, Reflux on Water Bath, White Crystal 72 Hrs.

Dimethylacetylene Formamide, R.T., Yellowish White Solid 24 Hrs.

dicarboxylic acid

PhenylmethylpropioFormamide, R.T., Red Crystal 24 Hrs.

-late Cont.
<table>
<thead>
<tr>
<th>Alkyl Halide</th>
<th>Solvent, Reaction Condition</th>
<th>Nature of Products</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl Chloride</td>
<td>Dry Benzene, R.T., 18 Hrs.</td>
<td>Redish White Crystal</td>
<td>(R)</td>
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<tr>
<td>2-Propyl bromide</td>
<td>Dry Benzene, R.T., 24 Hrs.</td>
<td>Yellow Viscous Liquid</td>
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</table>
In the case of methyl and ethyl acrylate, both the regioselective products were obtained. The Table-XII shows the ratio of the separated 4- and 5-substituted products.

<table>
<thead>
<tr>
<th>Dipolarophiles</th>
<th>Adducts(4-:5-substituted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Methylacrylate</td>
<td>2.9 : 1</td>
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<tr>
<td>(b) Ethylacrylate</td>
<td>1 : 6.6</td>
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</table>

Table-XII

When 4-substituted adduct of ethylacrylate was kept at room temperature for a few weeks, the product was partially converted to 5-substituted adduct. The cycloconversion was studied by refluxing 4-substituted adduct in dry benzene for 8 hrs where complete conversion to 5-substituted adduct was observed. But such type of conversion was not found in the case of methylacrylate adducts. These interesting observations remind once again of Ali's\textsuperscript{133} work.

Another aspect of the cycloaddition reactions is their preference for the endo-addition over the exo-addition. To examine the fact whether endo- or exo-addition occurred, 2D NMR (COSY) of some of the adducts were studied. In the case of ethylacrylate adducts (I and J), a strong interaction between methylene protons of ester group and protons of cyclohexyl group was observed. Therefore, endo-addition was expected in this case.
But in the cases of methylacrylate and N-phenyl maleimide adducts, no such interactions between protons were observed. Therefore, additions in these cases were expected via exo transition state.

![Chemical structure](attachment:chemical_structure.png)

Alkynes, viz., methyl phenyl propiolate and dimethyl acetylene ducarboxylate were studied as dipolarophiles for 1,3-dipolar cycloaddition with α-amino-N-cyclohexyl nitrone. Cycloadducts (P and Q) were obtained at room temperature in satisfactory yields upon purification. The formation of adduct Q is due to secondary orbital effect between the carbon of the nitrone (HOMO) and the adjacent atom of the electron withdrawing group of the dipolarophile (LUMO). Here the transition state was further stabilised by secondary orbital interaction. Both the cycloadducts were thermally stable, but, while studying the mass-fragmentation pattern, base peak (m/e) at 105 (cf. PhCO) for methyl phenyl propiolate adduct was found. Thus during mass-fragmentation, the adduct underwent rearrangement to Aziridine ring.
In order to find out the synthetic potentiality of $\alpha$-amino-N-cyclohexyl nitrone, $\text{SN}_2$ reactions were studied with benzyl chloride and 2-propyl bromide. Purified nitrone was directly used for this purpose and was mixed with equimolar amount of alkyl halide in dry benzene at room temperature. Both the products were isolated (yield: 93.2% and 89.57% respectively) and characterised by NMR and IR. The reaction indicates that $\alpha$-amino-N-cyclohexyl nitrone behaved as a powerful nucleophile in $\text{SN}_2$ reaction. Other nitrones are not known to act as a nucleophile in this fashion.

B. Interpretation Of Mass Spectra:

All the compounds possess 2-cyclohexyl-3-amino-1,2-isoxazolidine moiety in common. Therefore, it was very usual to expect some rationalization in the mass fragmentation patterns of the compounds. On electron impact mass fragmentation of a molecule would generate, generally, a radical ion and expectedly one of the non-bonding electrons of nitrogen atom of 1,2-isoxazolidine ring would be removed as this nitrogen was tertiary in nature. Thus taking cyclohexene adduct as example, a general scheme was formulated (Scheme-V). The fragmentation pattern of all the adducts were discussed on the light of this fission pattern. In the case of cyclic amine, the major fission pattern of such a molecular ion would be due to $\alpha$-cleavage. Among the probable modes of $\alpha$-cleavage, viz., $C_3-C_4$ and $C_6-C_7$, the $C_6-C_7$ cleavage was most probable as this leads to highly substituted bond cleavage. $C_3-C_4$ bond was also cleaved and further transformation led to a number of fragments with $m/e$, $M-142$ (Type-B); 125; 82; 70; 57; 56; 55 were explained. Another process of concerted homolytic fission of cyclohexyl ring might lead to a fragment with $m/e$ $M-56$ (Type-C).

Another type of $\alpha$-cleavage in which at first the $C_3-O$ bond cleaved to lead the ion with $m/e$ $M-141$ (Type-F).

The process of $\beta$-hydrogen rearrangement with C-N bond cleavage might occur in two ways leading to the Type-G with $m/e$ $M-82$ and Type-H with $m/e$ $M-114$. The ion produced in this process may further be fragmented (not shown).
Other major fragmentation might occur with the ionisation of free amino group on C₃ and subsequent α-cleavage leading to m/e 113 and 111 (Type-I).

Occurrence of this common fragments are shown in Table-XIII. The other peaks were dependent on the nature of substituent on 4- and 5-position of the 1,2-isoaxazolidines.

In the fragmentation pattern of the N-phenyl maleimide adduct, in addition to the common expected fragments, other prominent peaks at m/e 156; 96; 60; and 77 were found (Type-J).

For tri- and tetra-chloro ethylene adducts, some of the expected ion fragments were absent. But the other peaks were prominent e.g., m/e 113; 98; 82; 60; 57; 55 (100% for both the adducts). Following peaks were prominent (Type-K₁) m/e 225 and 93 and (Type-K₂) m/e 225; 112; 83, for trichloro ethylene and tetra chloro ethylene adducts respectively.

The fragmentation pattern of 3,4-dihydro-2H-pyran adduct followed the general pattern with some special peaks at m/e 127; 99 and 85 (Type-L₁).

2,3-Dihydro furan adduct also followed the same fragmentation pattern like cyclohexene adduct with some special peaks at m/e 127; 71 (100%) and 85 (Type-L₂).

P-Benzoquinone adduct fragmented following the same pattern with some typical peaks at m/e 112; 96 and 82 (Type-M).

The fragmentation patterns of both the methyl and ethyl acrylate adducts followed the general pattern with some typical peaks for methyl and ethyl ester, e.g., CH₃O (31); CH₃OCO (59); C₂H₅O (45); C₂H₅OCO (73) and a prominent peak for both the cases at m/e 198 probably due to the ion M-31 for methyl and M-45 for ethyl acrylate adducts respectively (Type-N).

Fragmentation pattern ofacenaphthene adduct was similar to the general pattern. Some weak peaks at m/e 126 and 168 were found (Type-O).

Fragmentation pattern of 2-chloro acrylonitrile adduct was also in accordance with the general pattern. The molecular ion peak was associated with M+1 and M-1 peaks. Very weak peaks at m/e 212 (M-CN) and 194 (M-Cl) were also found.
SCHEME I

General patterns of mass fragmentation

Type-A

\[ \text{CH}_3\text{CH}_2\text{CH}_2^+ + \text{R}^+ \rightarrow \text{Products} \]

Type-B

\[ \text{A} \xrightarrow{\text{cleavage}} \text{Products} \]

(142)

(126)
Type-C

\[ \text{Sigmatropic rearrangement} \]

\[ \text{Type-F} \]

\[ \text{Type-G} \]

\[ \beta-\text{H rearrangement with } C_6-\text{N bond cleavage} \]

\[ \text{Type-H} \]

\[ \beta-\text{H rearrangement with } C_3-\text{N bond cleavage} \]

\[ \text{Equation (60)} \]

\[ \text{Equation (113)} \]

\[ \text{蝶} \]

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Table-XII

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+ and - sign indicates presence and absence of the ion fragments.
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Type $L_1$

\[
\text{Type } L_1 \quad \text{H} \quad \rightarrow \quad \text{NH}_2
\]

\[
\text{C}_6 \quad -\text{O}
\]

\[
\text{NH}_2
\]

\[
\text{O} \quad \text{(127)}
\]

\[
\text{(141)} \quad \text{NH}_2
\]

\[
\text{(99)}
\]

\[
\text{Type } L_2 \quad \text{(same as Type } L_1)\]

Type $N$

\[
\text{NH}_2
\]

\[
\text{CO}_2\text{R} \quad \rightarrow \quad \text{CO}_2\text{R}
\]

\[
\text{M-OR}
\]

\[
\text{M-COOR}
\]
Type M

\[
\begin{align*}
+ & \quad -CO \\
\text{NH}_2 & \quad \text{NH}_2 \\
\text{NH}_2 & \quad \text{NH}_2 \\
(96) & \quad (112)
\end{align*}
\]

Type O

\[
\begin{align*}
+ & \quad \text{NH}_2 \\
\text{NH}_2 & \quad \text{NH}_2 \\
\text{NH}_2 & \quad \text{NH}_2 \\
(168) & \quad (126)
\end{align*}
\]

Type P

\[
\begin{align*}
+ & \quad -CN \\
\text{NH}_2 & \quad \text{NH}_2 \\
\text{NH}_2 & \quad \text{NH}_2 \\
(169) & \quad (M-1)
\end{align*}
\]
Type-O

\[
\text{PhCO} + \text{Cyclohexane-N-N-CO}_2\text{CH}_3 \rightarrow \text{Cyclohexane-N-N-CO}_2\text{CH}_3
\]

\[
\text{CH}_3\text{CO} + \text{Cyclohexane-N-C=O} \rightarrow \text{Cyclohexane-N-C=O}
\]
Acrylonitrile adduct similarly followed the general pattern. Some peaks at m/e 169; 127; 68; 54 and M-1 were explained in type-P.

The fragmentation pattern of acetylene adducts were different and explained in type-Q.

C. Interpretation Of NMR Spectra:

On interpreting the NMR spectra of the nitrone adducts, the chemical shifts and coupling constant for the C₅ protons, wherever possible, were studied, as well as the dihedral angle between C₄-C₅ protons. In addition to that, the band width i.e., the distance between the first and the last line of the multiplet of the signals, of the C₅ protons in Hz was also measured. Bauman et al. 188 used this method to elucidate the conformations of the cis- and trans-cyclopentane-1-carbomethoxy-2-ol and found that for trans isomer the band width was 18 C/S and for cis isomer 11 C/S for C₁ proton. Similarly, 13.5-15 C/S for cis compound and 20-22.5 C/S for trans compound were found in the case of α-amino-N-cyclohexyl nitrone adducts (Table-XIV).

<table>
<thead>
<tr>
<th>Adducts</th>
<th>C₅-Protons (δ in ppm)</th>
<th>Band Width (Hz)</th>
<th>Coupling Constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>4.3(q)</td>
<td>15</td>
<td>—</td>
</tr>
<tr>
<td>(B)</td>
<td>4.4(b)</td>
<td>14</td>
<td>—</td>
</tr>
<tr>
<td>(C)</td>
<td>5.4(b)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(D)</td>
<td>5.5(b)</td>
<td>14</td>
<td>—</td>
</tr>
<tr>
<td>(E)</td>
<td>6.2(b)</td>
<td>13.5</td>
<td>—</td>
</tr>
<tr>
<td>(F)</td>
<td>5(b)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(G)</td>
<td>3.48-3.69(b)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(H)</td>
<td>3.81-3.86(d)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(I)</td>
<td>3.82-3.86(t)</td>
<td>22.5</td>
<td>6.17 and 3.85</td>
</tr>
<tr>
<td>(J)</td>
<td>3.90-3.98(b)</td>
<td>21.6</td>
<td>6.30 and 3.70</td>
</tr>
<tr>
<td>(K)</td>
<td>3.42(t)</td>
<td>20.25</td>
<td>7.20 and 5.40</td>
</tr>
<tr>
<td>(O)</td>
<td>4.9(b)</td>
<td>13.5</td>
<td>—</td>
</tr>
</tbody>
</table>

Table-XIV
It may be concluded from these band width values that the dipolarophiles with cis configuration about the double bond gave rise to cis-adducts and therefore, the nitrone additions were stereospecifically cis.

From the coupling constant values of $C_5$-protons of the nitrone adducts with ethyl acrylate (I and J), acrylonitrile (K) and hydrolised product of acrylonitrile adduct, the dihedral angles between $C_5$ and $C_4$ protons were calculated from standard graph. From these calculated values and with general assumption that at normal condition 2-cyclohexyl-1,2-isoxazolidine preferred the "envelope" (Fig-XV), the $C_5$-$C_4$ projections with the corresponding dihedral angles (Fig-XVI) were constructed for I, J, K and the hydrolised product of acrylonitrile.
As the C₅-proton in the other cycloadducts were either absent or the splitting of the signal were not prominent so the dihedral angle between C₄–C₅ protons and the coupling constant could not be calculated. Therefore, nothing could be inferred about their conformational structures.

For most of the cases cyclohexyl protons along with the amine protons were appeared at 1-2.2 8. C₅-Proton in all adducts appeared in the region 2.7-3.6 (8). N-CH proton of cyclohexyl group gave signal in region 2.6-3 (8). C₄ and C₅ proton signals depended on the substituent at C₄ and C₅ positions.

To compare the proton signals, cycloadducts were divided into a number of groups having similar type of structures.

**Cycloadducts (A), (B) and (C):**

Signals for C₄-proton were found at 2.5(b); 2.4(m) and 2.4(m) for (A), (B) and (C) respectively and that of C₅-protons were at 4.3(b), 4.4(b) and 5.4(b). C₅-Proton signal for (C) was slightly in lower field probably due to two fused five membered rings.

**Cycloadducts (D), (E) and (F):**

C₄-Proton signals were found at 4.36-4.41(m), 4.1(b) and 3.8(b) for the adducts (D), (E) and (F) and that of C₅-protons were at 5.35(b), 6.2(b) and 5(m) respectively. In p-benzoquinone adduct (F), signals due to C₄ and C₅ protons and two olefinic protons were merged together at 4.5-5, to give a broad peak.

**Cycloadducts (G) and (I):**

Signals for C₄-protons found at 2.27-2.5(m) and 3.82-3.86(t) and for C₅-protons at 3.48-3.69(b) and 3.9-4(t) for (G) and (I) respectively.

**Cycloadducts (H) and (J):**

C₄-Proton signals for both the adducts were merged with the signals due to cyclohexyl methylene protons at 1-2.2(m). Signals for the C₅-protons were found at 3.8(t) and 3.9-3.98(t) respectively for (H) and (J).
Cycloadducts (K) and (L):

C₄-Proton signals for (L) were found at 2.3-2.5(m) and that of (K) were merged with the signals due to the protons of the cyclohexyl methylene group protons. C₅-Proton signals for (K) found at slightly lower than expected, probably due to the anisotropic effect of the cyano group at C₅-posision.

Cycloadducts (P) and (Q):

In the case of acetylenic adducts C₄ and C₅ protons were absent. The C₃-proton signals were found at lower field between 4-5.5(S) due to the presence of a double bond between C₄ and C₅ posision.

Products (R) and (S):

A singlet of two protons for each case were found at 8.1 and 8 (S) for NH₂ respectively for (R) and (S). The olefinic protons were found at 6.4(b) and 6.6(b) respectively.

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