CHAPTER IV
RESULTS & DISCUSSION

General Discussion :

Eschenmoser et al (236-238) have shown the synthetic potentiality of α -chloro nitrone in 1,4 dipolar cycloaddition reactions with an unactivated double bonds. We wish to report an application of α - chloro - nitrone in 1,3 dipolar cycloaddition reactions with different dipolarophiles.

N- cyclohexyl chloro nitrone was synthesised from a mixture of chlorohydrin and its toutomer with N- cyclohexyl hydroxyl amine in dry ether and anhydrous $MgSO_4$ with constant stirring for 24 hours, under N_2 - atmosphere at room temperature.

Chlorohydrin (240) and its tautomer were obtained when 2,3 dihydro -4H- pyran was subjected to chloro hydration with HOCl.

The nitrone was a colourless crystalline solid, M.P., 58^{0} c (uncorrected).

IR (Nujol) : 1660 (m); 1610 (s) ; 1155 (m).

PMR (CDCl$_3$):δ 7.05-6.65 (b, 1H); 4.3-4.15 (d, J=4.5Hz, 1H)
    90 Mhz   3.7-3.5 (b, 1H);
               2.6-0.5 (m, 16H)
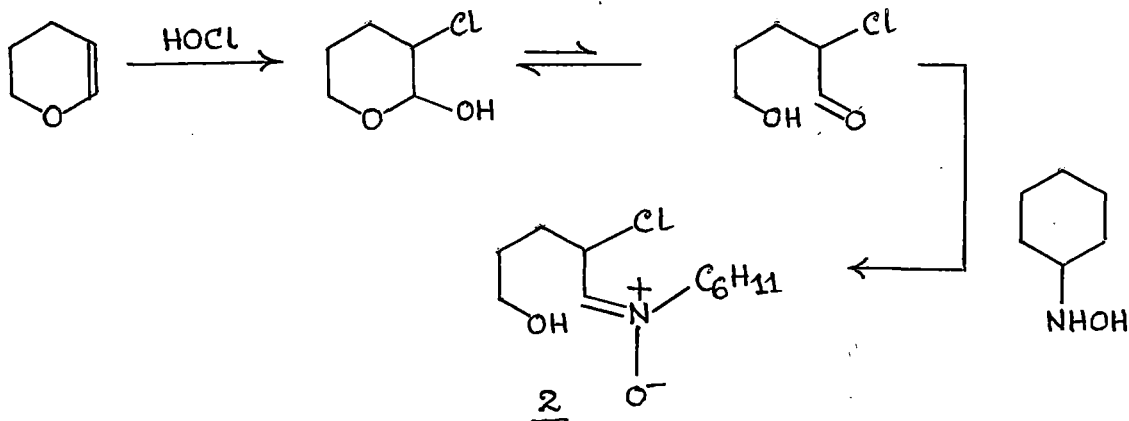
Nitrone 2, was very unstable, therefore it was generated insitu and trapped with different dipolarophiles at room temperature in a 1,3 dipolar cycloaddition reaction to furnish cyclo adducts in satisfactory yields. With methyl vinyl ketone and acrylonitrile, the reaction was found to be highly regio selective to form solely 5-substituted isoxazolidines respectively. The regio selectivity in these reactions were rationalised by use of the frontier-orbital theory. Nitrone 2 has considerably higher ionization potentials than normal nitrones due to the electron with drawal effect of chlorine. So Nitrone (LUMO) - Dipolarophile (HOMO) interactions were so important that it

completely dominates the reaction and leads to the formation of only 5- substituted adducts.

1,3 dipolar cyclo additions of nitrone $\underline{2}$ were not only regio selective but also stereo selective. The relative configurations of C-3; C-4; C-5 protons of the cycloadducts formed in most often cases were syn. Since most of the nitrones were exist exclusively in the Z- configuration, therefore the cycloadducts were formed from Z- nitrone through an exo-transition state.

In table VI, the reaction condition, major products, nature etc. are summarised.
In the case of methyl acrylate adduct both the regio selective products were obtained. When the 4, substituted adduct of methyl acrylate was kept at room temperature for few weeks, the products were partially converted to 5-substituted adducts. These interesting cyclo reversion observations remind once again of Ali's work (178).

With highly electron deficient dipolarophiles viz, N- phenyl maleimide, N- cyclohexyl maleimide and p- benzoquinone cyclo adducts were obtained spontaneously at room temperature.

In the case of 'chloro acrylonitrile', 'methyl vinyl ketone' of N-cyclohexyl chloro nitrone and 'methyl acrylate' of N-cyclohexyl 5-hydroxy nitrone, the cyclo adducts were expected to form via endo Transition State,

$R = (CH_2)_4-OH$

$= -\underset{Cl}{CH}-(CH_2)_3-OH$

$R' = -COCH_3 \cdot$

$= -COOCH_3 \cdot$
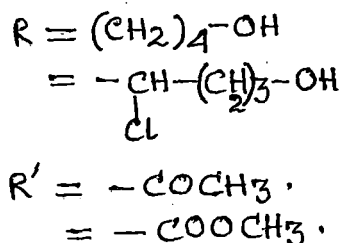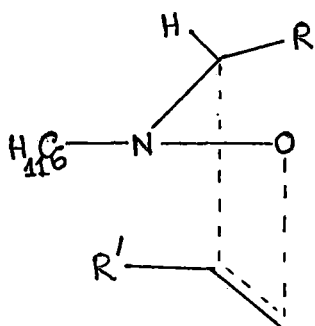
While N-phenyl-maleimide, ethyl acrylate etc. the cycloadducts were expected to form via exo Transition State.

$R = (CH_2)_4-OH$

$= -\underset{Cl}{CH}-(CH_2)_3-OH$

$R' = -COOCH_2CH_3 \cdot$
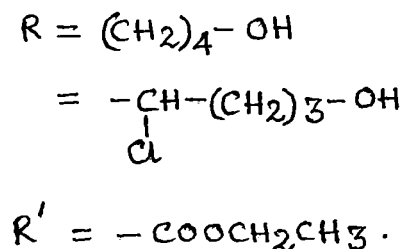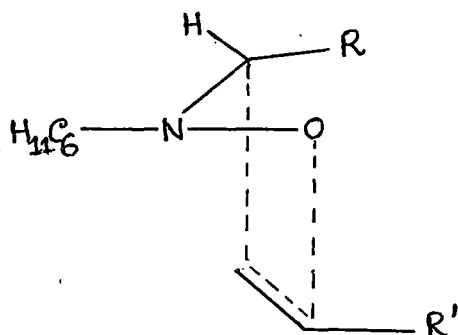
Alkynes, viz, methyl phenyl propiolate and dimethyl acetylene dicarboxylate were studied as dipolarophiles for 1,3 dipolar cyclo addition with N- cyclohexyl chloro-nitrone. Cyclo adducts were obtained at room temperature in satisfactory yields upon purification. Here, the adduct formation can be explained due to secondary orbital effect between the carbon of the nitrone (HOMO) and the adjacent atom of the electron withdrawing group of the dipolaro phile (LUMO).

Both the cycloadducts were thermally stable but while studing the mass fragmentation pattern, base peak (m/e) at 105 (i.e. due to PhCO) for methyl phenyl propiolate adduct was found. Thus during mass fragmentation, the adduct under went the rearrangement to Aziridine ring.
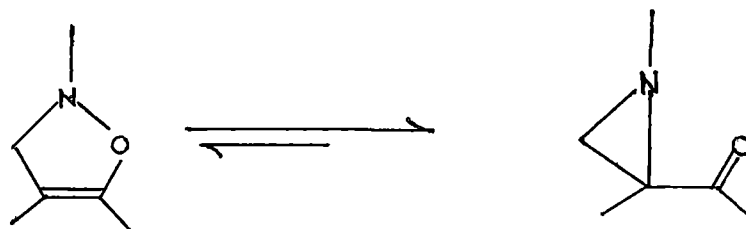
In all the cases number of products formed were explained on the basis of TLC and the major products were isolated in each case. However for the addition of nitrone with some dipolarophiles, the polarity of both the products were so close that the separation was not possible, and both the products were isolated from the reaction mixture and was distinguished from PMR integration curve of the mixture for the respective C-5 protons.

The mode of regio selections in all the cases can be well explained on the basis of qualitative frontier orbital model treatment of nitrone and the dipolaro philes. In qualitative treatment for 1,3 dipolar cyclo additions two major aspects are stressed. One is the energy levels of the dipoles and the dipolarophiles and the other is the HOMO & LUMO coefficients on the concerning atoms of the dipoles and the dipolarophiles. The HOMO – LUMO energy gap of the reactants indicates the fastness of the addition. This gap is low for the additions of the nitrone with moderately electron deficient dipolaro philes and therefore the reactions are comparatively fast.
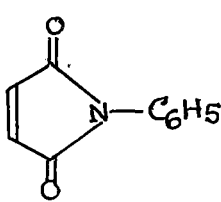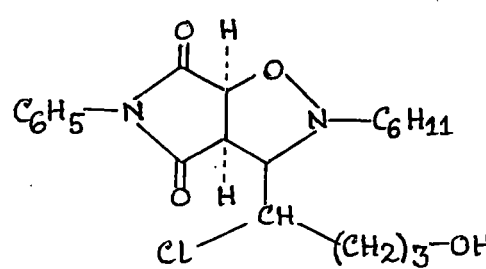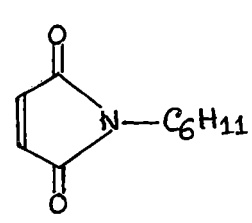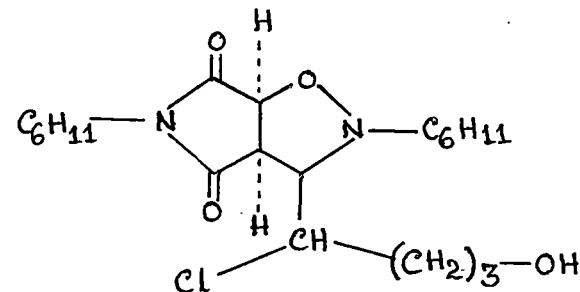
However, the question of regio selection is only applicable for the cases where the kinetically controlled products are considered. The thermodynamic product may be the next product as expected from the regio selection rule (177).
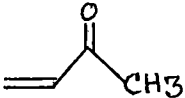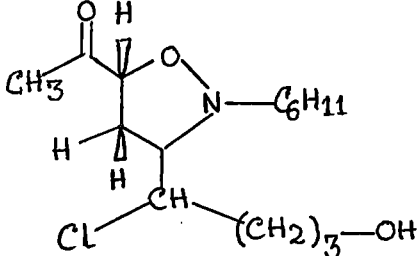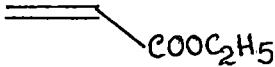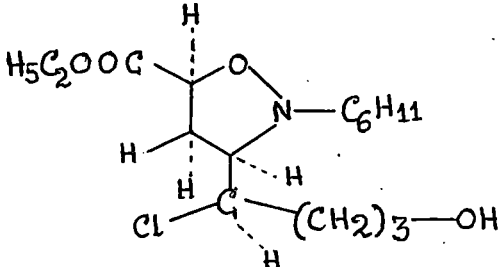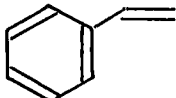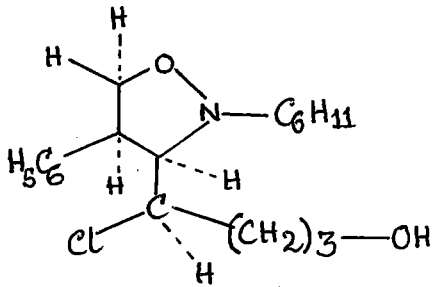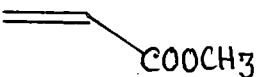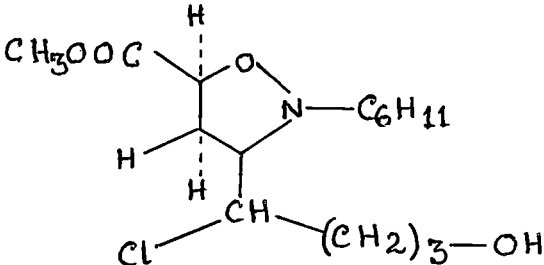
All the olefines considered so far undergo cycloadditions with N- cyclohexyl chloro nitrone at room temperature, but the cycloaddition with styrene which is a electron rich olefin was not facile unless some drastic conditions were applied. For that

purpose, styrene was heated with the nitrone for 24 hours, the 4-substituted adduct was obtained and in accordance with the regio selection rules.

Another aspect of the cycloaddition reactions is their preference for the _endo_ addition over the _exo_ addition. In the present cases of cycloadditions of N- cyclohexyl chloro-nitrone , the question cannot be answered from the inspection of the product structure since in such a case either the _endo_ or _exo_ addition affords the some product. But in as such as these cyclo additions hold all the criteria of other cyclo additions,there is no reason to expect that the secondary orbital interactions will be absent in such cases. Houk et al have proposed that the preference for the endo transition state will only be large in these cycloadditions when the dipole - LUMO and dipolaro phile - HOMO inter action will be important which are also in accordance with P.Deshong et. al (206).
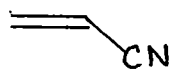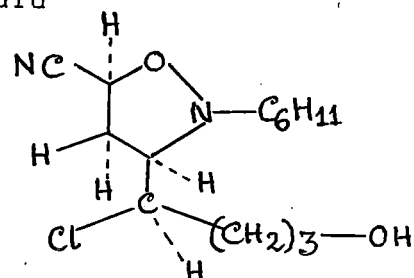
Table-VI

Dipolarophiles	Solvent/Reaction Condition	Nature of Products	Str. of Products
1.	Ether; R.T. 72 hours	Grayish white Solid	
2.	Ether; R.T. 72 hours	Yellowish white Solid	

Dipolarophiles	Solvent/Reaction Condition	Nature of Products	Str. of Products

3.

Ether; R.T.
72 hours

Oily greenish
Liquid

4.

Ether; R.T.
72 hours

Yellow Oily
Liquid

5.

Ether; R.T.
72 hours,

White crystall-
ine Solid

6.

Ether; R.T.
72 hours

Dark Red
Gummy Liquid

Dipolarophiles	Solvent/Reaction Condition	Nature of Products	Str. of Products

3.

Ether; R.T.
72 hours

Oily greenish
Liquid

4.

Ether; R.T.
72 hours

Yellow Oily
Liquid

5.

Ether; R.T.
72 hours,

White crystall-
ine Solid

6.

Ether; R.T.
72 hours

Dark Red
Gummy Liquid

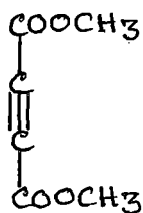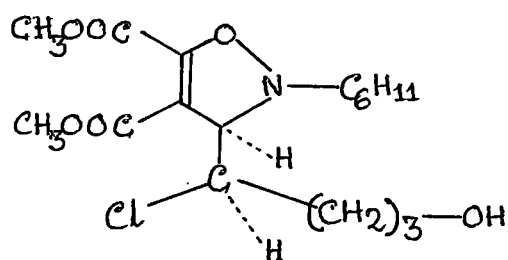|	Dipolarophiles	Solvent/Reaction Condition	Nature of Products	Str. of Products
7.	CH₂=CH–CN	Ether; R.T. 72 hours	Dark Yellow Gummy Liquid	
8.	Cl,CN substituted alkene	Ether; R.T. 72 hours	Yellow Gummy Liquid	
9.	COOCH₃–C≡C–COOCH₃	Ether; R.T. 72 hours	Yellow Oily Gummy Liquid	
10.	C₆H₅–C≡C–COOCH₃	Ether; R.T. 72 hours	Pale Yellow Liquid	
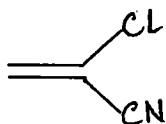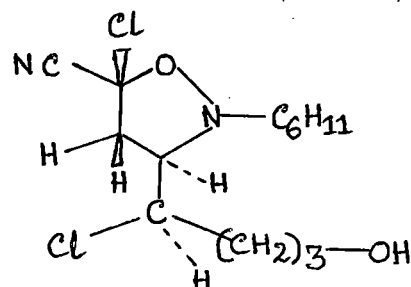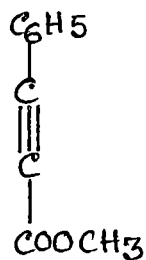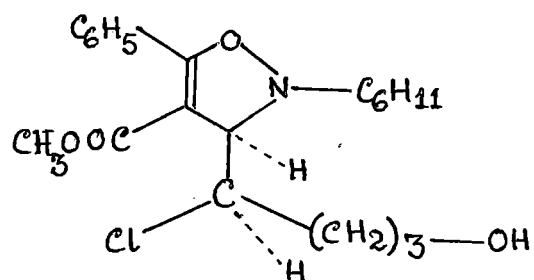
N-cyclohexyl 5-hydroxy nitrone (245) was generated by refluxing N-cyclohexyl hydroxyl amine and 2,3 dihydro-4H pyran in dry benzene for ;24 hours

The nitrone was obtained as crystalline solid, M.P. - 77° c (uncorrected).

(3)
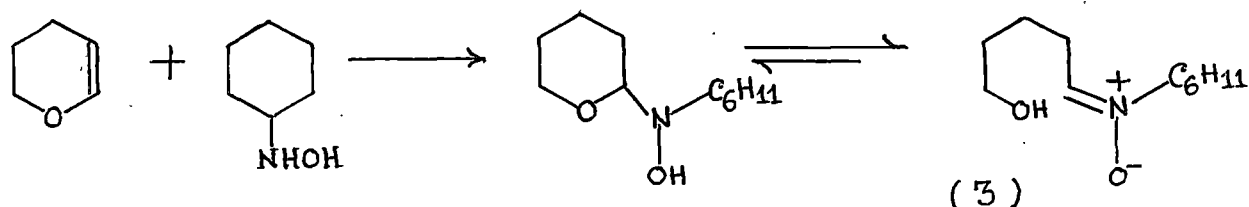
IR (KBr) : 3603(s); 3272(b); 3012(s); 2927(s); 2854(s); 2397(s); 743(m);.

PMR (CDCl$_3$): δ :

6.0-5.8 (b, m, $\overset{+}{N}$ - CH)

2.5-2.3 (m, (CH$_2$)$_4$ - OH)

1.9-1.2 (m, 10H).

Like that of nitrone (2); nitrone (3) was also very unstable, and hygroscopic in nature and therefore it was generated insitu and trapped with different dipolarophiles in 1 , 3 dipolar cycloaddition reaction to furnish cyclo adducts in satisfactory yields. Dimerisation of the nitrone can also be controlled under this condition.

The concerted nature of cycloaddition reactions with nitrone (245)as 1,3 dipole was generally accepted . The regio selectivity in this relations were rationalised by the use of the frontier - orbiral theory. The ethyl acrylate adduct corresponds to this theory.Therefore the 5- substituted adduct for ethyl acrylate is due to LUMO (nitrone) - HOMO (dipolaro phile) interaction.
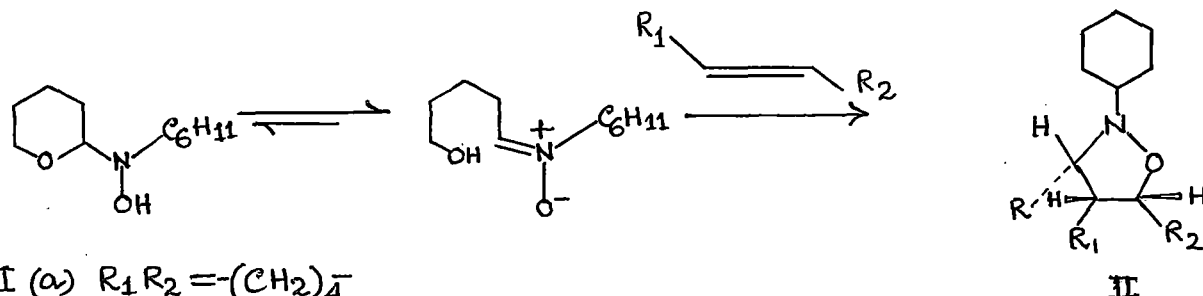
II (a) R$_1$R$_2$ =-(CH$_2$)$_4^-$

(b) R$_1$R$_2$ = -CONPhCO-

(c) R$_1$R$_2$ = -CONC$_6$H$_{11}$CO-
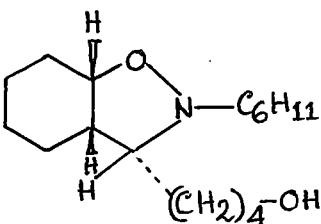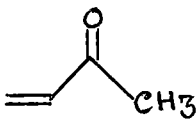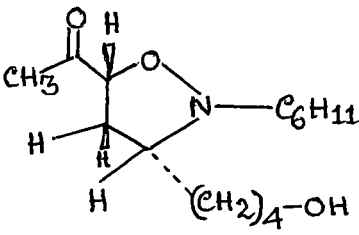
(d) R$_1$ = H , R$_2$ = -CO$_2$CH$_2$CH$_3$

R = -(CH$_2$)$_3$-CH$_2$OH

Cyclo addition of Z- nitrone via an exo - transition state results in the formation of syn isoxazolidines. The relative configuration of C3, C4 and C5 in the adducts were in favour of exo-transition state geometry. The proton at C3 and C4 were syn in II-(b) and II-(c) and their coupling constants (J = 6 Hz) were also indicative of this stereo chemical relationship, whilst a D_2O shake revealed the presence of one rapidly exchangeable proton at C-5. Stereo chemistry of II-(a) and II-(d) at C-3, C-4 and C-5 on the isoxazolidine ring were also determined from PMR spectrum. The coupling constant values viz, J = 7.5-8 Hz, were revealed the formation of syn-isoxazolidine in both the cases vis exo transition state.
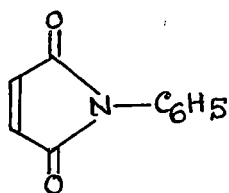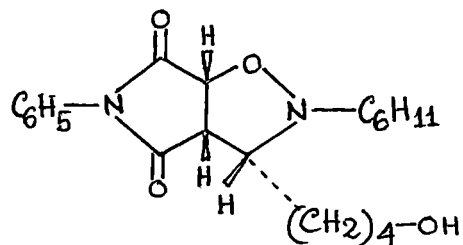
In table VII, the reaction condition, major products and its nature are summarised.
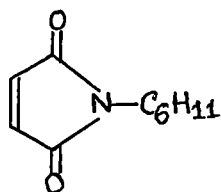
Table-VII

Dipolarophiles	Solvent/Reaction Condition	Nature of Products	Str. of Products
1.	Benzene; reflux 48 hrs	Gray Solid	
2.	Benzene; reflux 48 hrs	Crystalline White Solid	

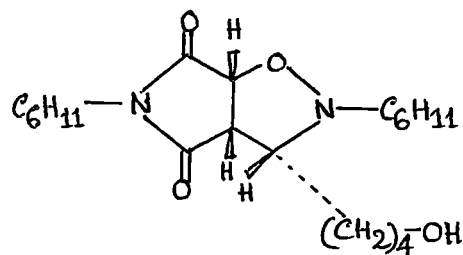| Dipolarophiles	Solvent/Reaction Condition	Nature of Products	Str. of Products
3.	Benzene; reflux 48 hrs	Yellowish White Solid	
4.	Benzene; reflux 48 hrs	Yellow Solid	
5.	Benzene; reflux 48 hrs	Yellowish White Soild	
6.	Benzene; reflux 48 hrs	Brown Solid	
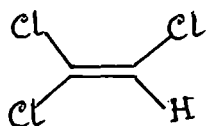
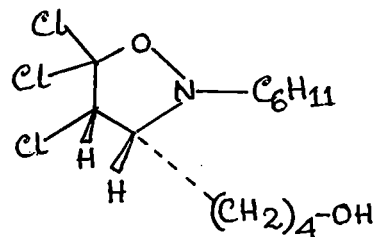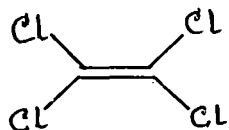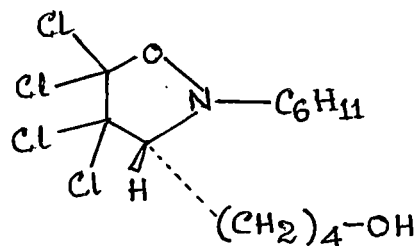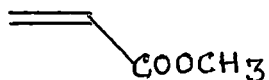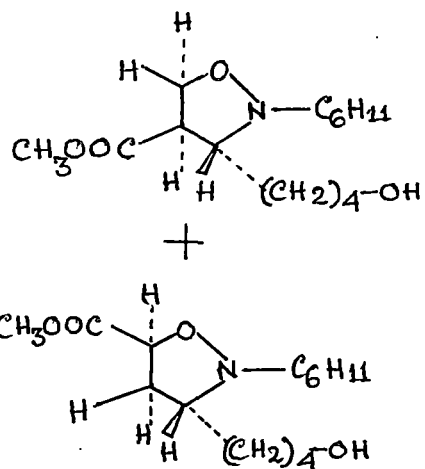| Dipolarophiles	Solvent/Reaction Condition	Nature of Products	Str. of Products
7. $=\!\!\!\!\diagdown$COOCH$_3$	Benzene; reflux 48 hrs	Yellow Liquid	
8. $=\!\!\!\!\diagdown$COOC$_2$H$_5$	Benzene; reflux 48 hrs	Red Liquid Gummy	
9. 	Benzene; reflux 48 hrs	Brown Solid	
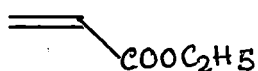
7.

Benzene; reflux 48 hrs

Yellow Liquid

H

H

CH$_3$OOC

H H

N—C$_6$H$_{11}$

(CH$_2$)$_4$–OH

+

H

CH$_3$OOC

H

H H

N—C$_6$H$_{11}$

(CH$_2$)$_4$–OH

8.

Benzene; reflux 48 hrs

Red Liquid Gummy

H

CH$_3$H$_2$C OOC

H

H H

N—C$_6$H$_{11}$

(CH$_2$)$_4$–OH

9.

Benzene; reflux 48 hrs

Brown Solid

H

O

H

H H

N—C$_6$H$_{11}$

(CH$_2$)$_4$–OH
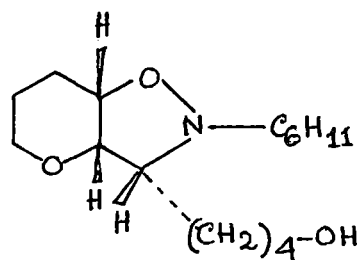
Dipolarophiles	Solvent/Reaction Condition	Nature of Products	Str. of Products

10.

Benzene; reflux 48 hrs

Brown Solid

C_6H_5 ... O—N—C_6H_{11} ... $(CH_2)_4$-OH (with H substituents)
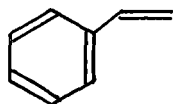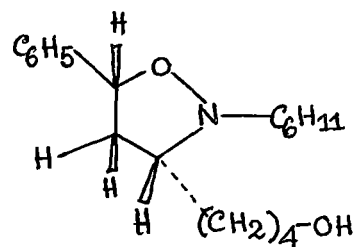
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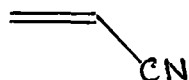
Benzene; reflux 48 hrs

Yellowish White Crystalline Solid

NC ... O—N—C_6H_{11} ... $(CH_2)_4$-OH (with H substituents)
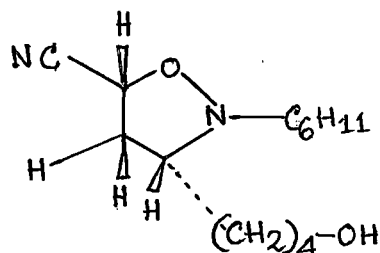
2. Interpretation of Mass Spectra:

For both the N- cyclohexyl chloro nitrone and N- cyclohexyl 5- hydroxy nitrone, all the cyclo adducts formed possess 2-cyclohexyl 3 chloro butanol 1,2 isoxazolidine moiety or 2- cyclohexyl 3- butanol 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 VI) .

The fragmentation pattern of all the adducts were discussed on the light of this fission pattern.

Scheme – VI
General Pattern of mass fragmentation

Type – A:

Type – B:

Type - C:

Sigmatropic rearrangement

(a) 281

(d) M-56 ; 225

(e) M-57 ; 224

Type-F C_5-O bond breaking.

281

(f)   83

198

Type - G:

β_H rearrangement with C_6-N bond cleavage

(a) ; 281

(g) ; 199

82

117

82

199

Type - H:

β_H rearrangement with C_3-N bond cleavage

(a) ; 281

(b) 167

281

114

113
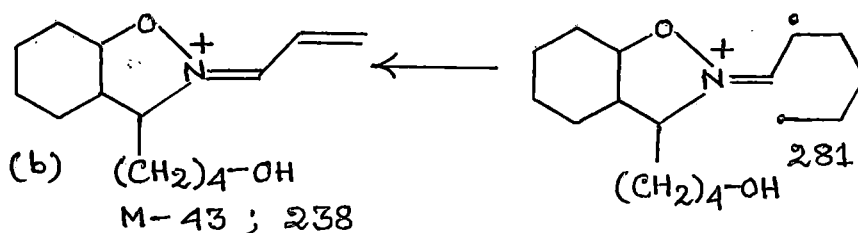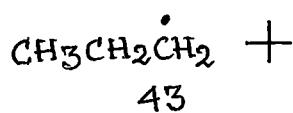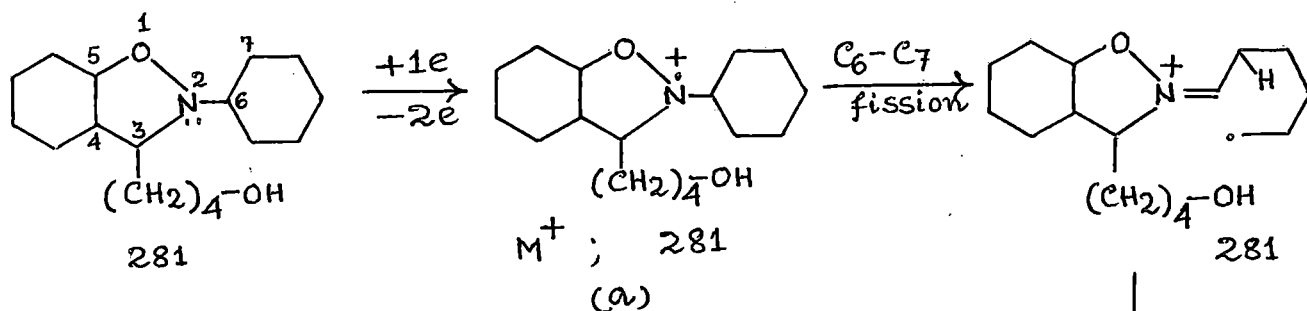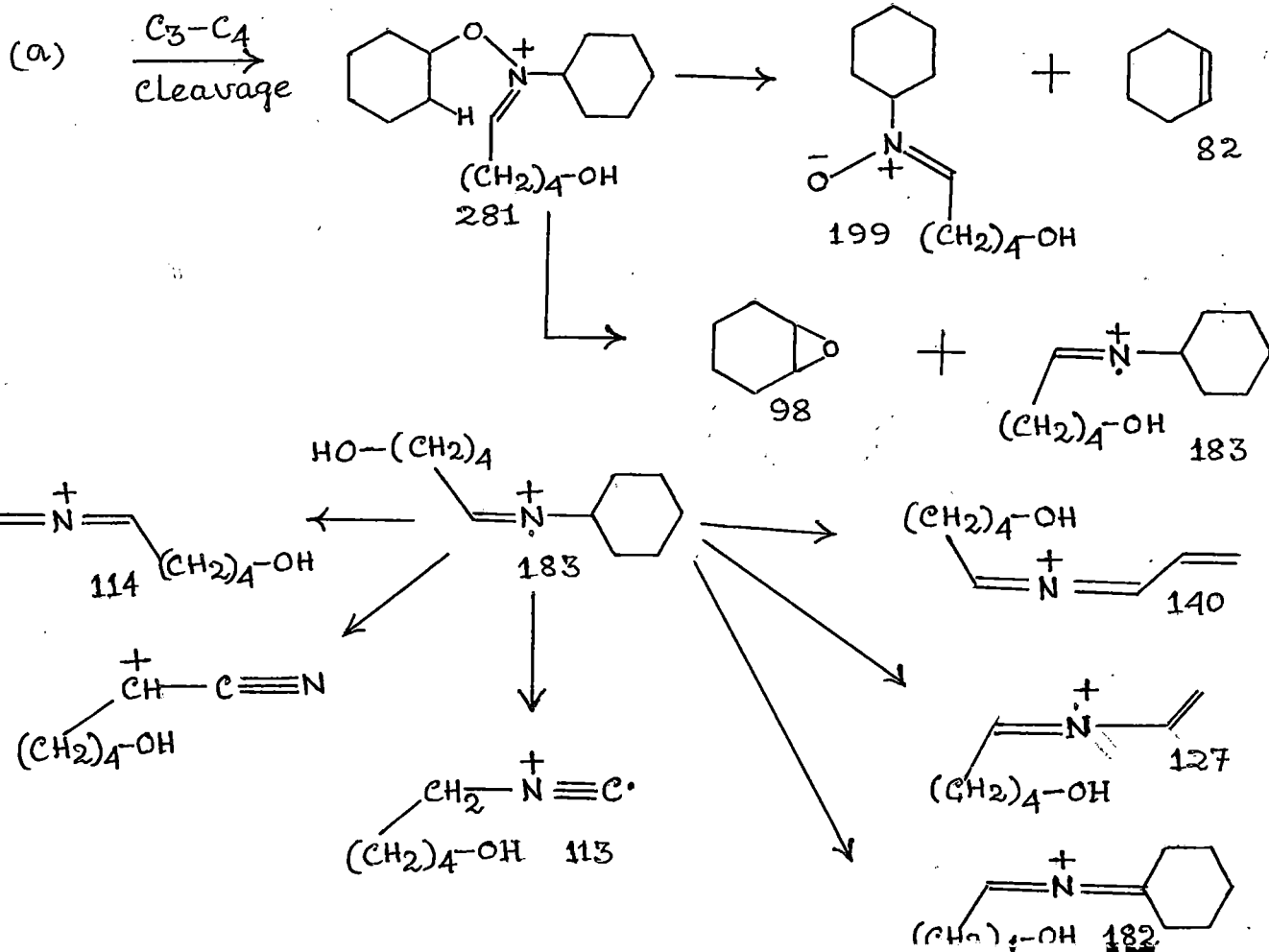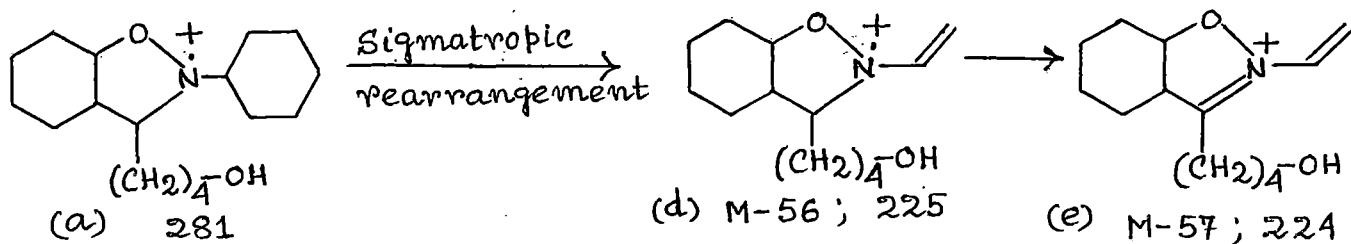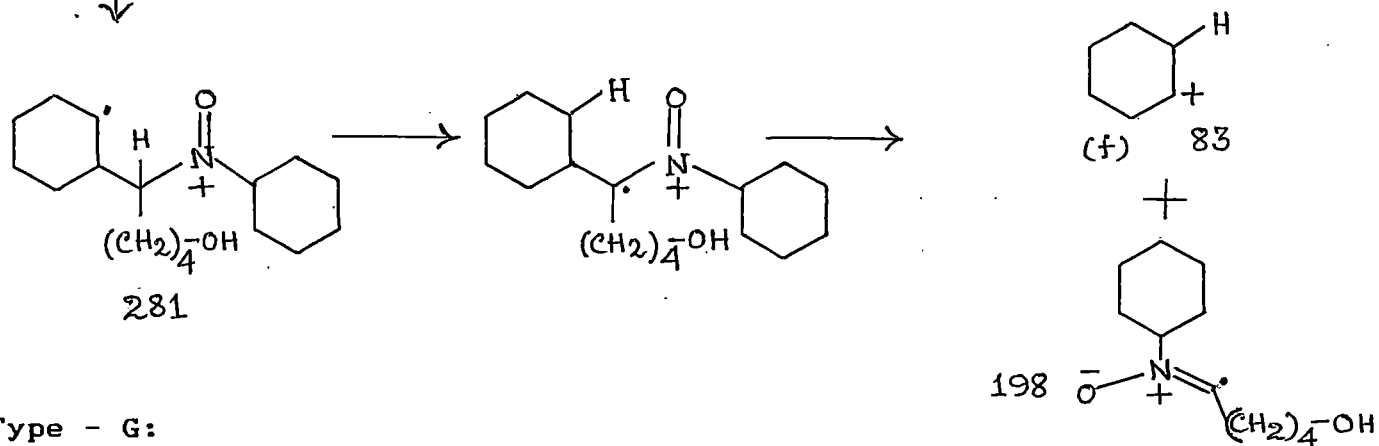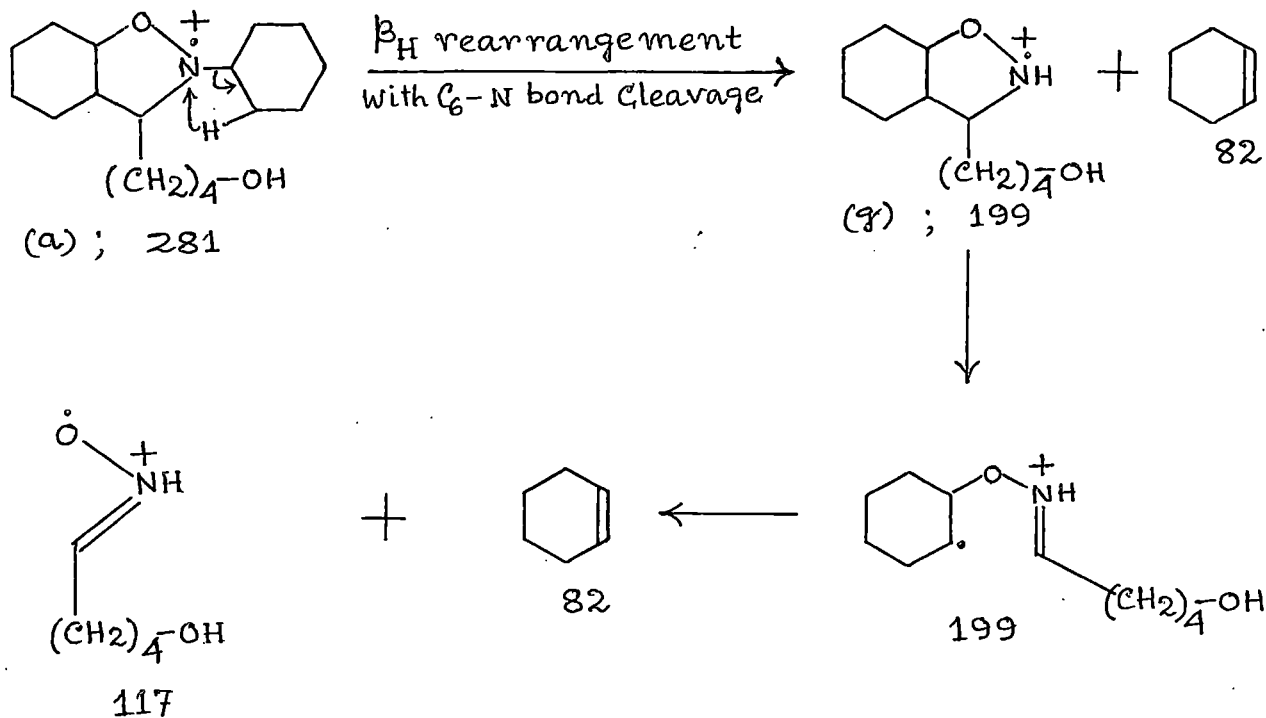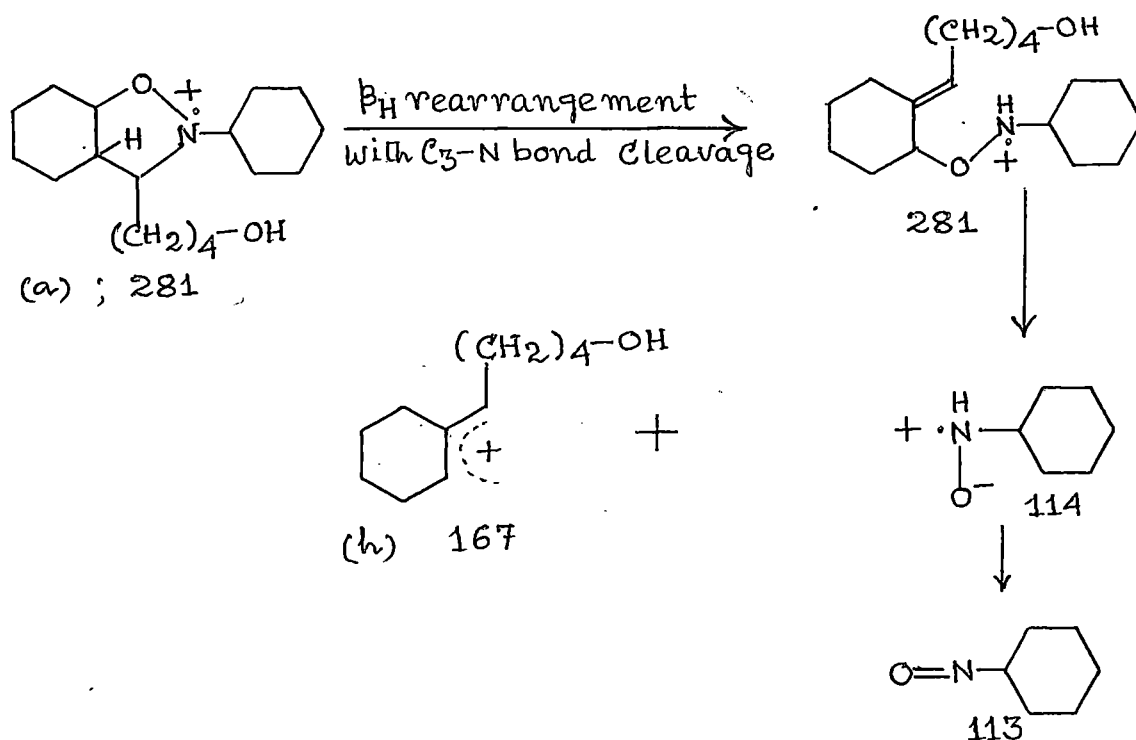
In the case of cyclic amine, the major fission pattern of such a molecular ion would be due to α - cleavage. Among the probable modes of α - cleavage, viz, C3 - C4 and C6 - C7, the C6 - C7 cleavage was most probable as this leads to highly substituted bond cleavage. C3 - C4 bond was also cleaved and further transformation led to a number of fragments with m/e, M - 199; (type - B) 82; 182; 140; 127; 114; 113; 112, 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 α - cleavage in which at first the C5 - 0 bond cleaved to lead the ion with m/e M-198. (type - F).

The process of β - 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 ions produced in this process may further be fragmented (not shown).

Other major fragmentation might occur with the ionization of free butanol or chloro butatol gr at C3 and subsequent α - cleavage leading to m/e 208; 207; 72 in the case of N- cyclohexyl 5- hydroxy nitrone while different m/e, fragmentation values are obtained in the case of cycloadducts with N- cyclohexyl - chloro - nitrone.

Type I for cyclohexene adduct with N- cyclohexyl 5-OH-nitrone:

Type I
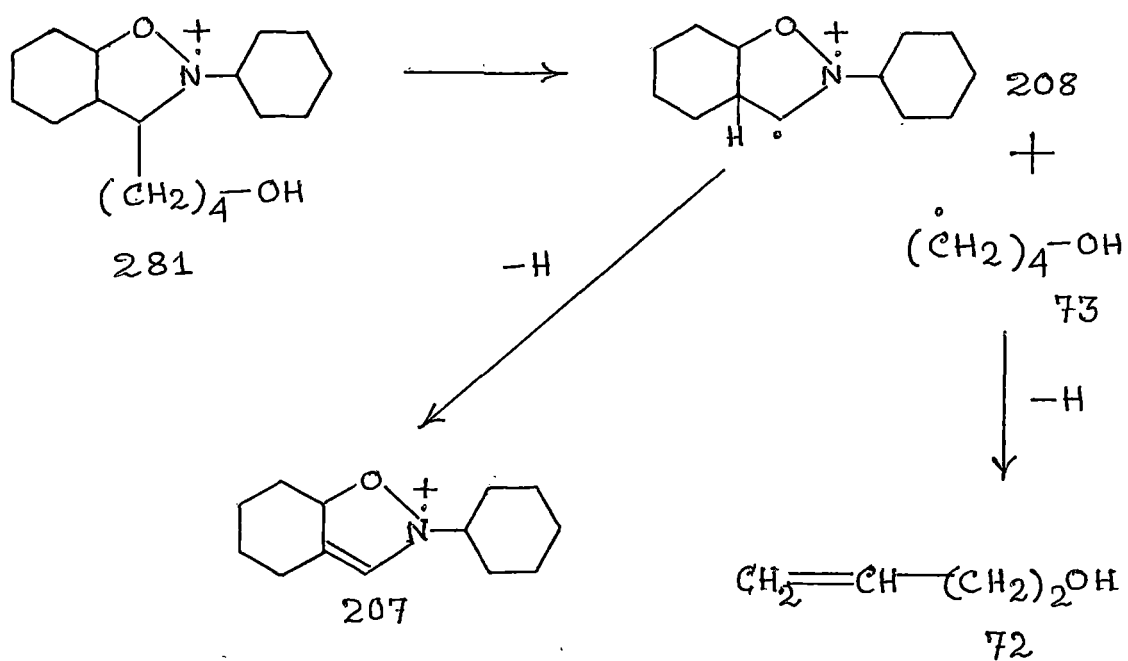
Occurance of common fragments are shown in Table - X & XI.

Table-X
Cycloadducts With N-cyclohexyl 5-OH-nitorne :

Adduct	M	M-1	M-43	M-56	M-57	M-113	M-114	M-199	M-198
1.Cycloh-exene.	+	-	-	-	+	+	+	+	+
2.Ethyl acrylate.	+	-	+	+	+	+	-	+	-
3.Methyl acrylate.	+	-	+	+	+	+	+	+	+
4. Methyl Vinyl Ketone	+	-	+	-	-	+	+	-	-
5.P-benzo-quinone	+	-	-	+	-	+	-	+	-
6. Acrylo-nitrile	+	-	-	-	-	-	-	+	-
7. Dihydro Pyran	+	-	-	+	+	-	+	+	-
8.N-cy-male imide.	+	-	-	+	-	-	-	+	-
9.N-ph-male imide.	+	-	-	+	+	+	+	+	+
10.Styrene.	+	-	+	-	-	-	-	+	-
11.Trichloro ethylene	+	-	-	-	-	+	+	+	-
12.Tetra Chloro ethylene	+	-	-	-	-	-	-	+	-

'(+)' and '(-)' sign indicates the presence and absence of the ion fragments.

Table-X Contd.

Adduct	267	225	168	142	114	113	98	169	227	196	226
1.	+	−	−	−	+	+	+	−	−	−	−
2.	−	−	−	+	−	−	−	−	−	−	+
3.	+	−	−	−	−	+	−	+	−	+	−
4.	−	+	+	+	+	−	+	+	−	−	−
5.	−	−	−	−	−	+	+	+	−	−	−
6.	−	−	−	+	+	−	−	−	−	−	+
7.	−	−	+	+	+	+	+	−	−	−	−
8.	+	−	−	+	+	−	+	−	−	−	−
9.	−	+	−	−	−	−	−	−	−	−	−
10.	−	−	−	+	+	−	−	−	−	−	−
11.	−	−	−	+	+	+	−	−	−	−	−
12.	−	−	+	+	+	+	+	−	−	−	−

The '+' and '−' sign indicates the presence and absence of ions

Table-XI
Cycloadducts With N-cyclohexyl Chloro nitrone

Adduct	M	M-1	M-43	M-56	M-57	M-113	M-114	M-233	M+1
N-Ph-male-imide	+	−	−	−	−	+	+	+	+
N-cy-male-imide	+	−	−	−	−	+	−	+	−
Methyl Vinyl ketone	+	−	+	+	+	+	+	−	−
Styrene	+	−	−	−	−	−	−	+	−
Ethyl Acrylate	+	−	+	+	+	+	−	+	−
Methyl Acrylate	+	−	+	+	+	+	−	+	−
Acrylonitrile	+	−	−	−	−	−	−	+	−
Chloro Acrylonitrile	+	−	−	−	+	−	−	+	+
Phenyl Methyl Propiolate	+	−	−	−	−	−	−	+	−
Dimethyl Acetylene dicarboxylate	+	+	+	+	−	+	+	+	−

The '+' and '-' sign indicates the presence and absence of ion.

Table-XI Contd.

| Adduct	298	288	226	186	187	172	142	114	102	98
1. Methyl Acrylate	−	+	+	+	−	+	−	−	−	+
2. Ethyl Acrylate	+	−	+	−	+	−	−	+	−	−
3. Styrene	−	−	−	−	−	−	+	+	−	−
4. Methyl vinyl Ketone	+	−	−	−	−	−	−	−	−	−
5. N-Cy maleimide	−	−	−	−	−	−	+	−	−	−
6. N-Ph maleimide	−	+	−	−	−	−	−	−	−	+
7. Dimethyl acetylene dicarboxylate	−	−	−	−	−	+	−	−	−	−
8. Phenyl Methyl propiolate	−	−	−	+	−	−	−	−	+	−
9. Acrylo-nitrile	−	−	−	−	−	−	+	−	−	+
10. Chloro-Acrylo-nitrile	−	−	−	−	−	−	+	−	−	+

The '+' and '−' sign indicates the presence and absence of ions.

In the fragmentation pattern of N- phenyl maleimide of both the nitrones in addition to the common expected fragments, other prominent peaks at m/e 77; 329; 323; 288 in N- cyclohexyl chloro nitrone and m/e 77; 295; 212 in N- cyclohexyl 5- OH nitrone were found. (type - J)
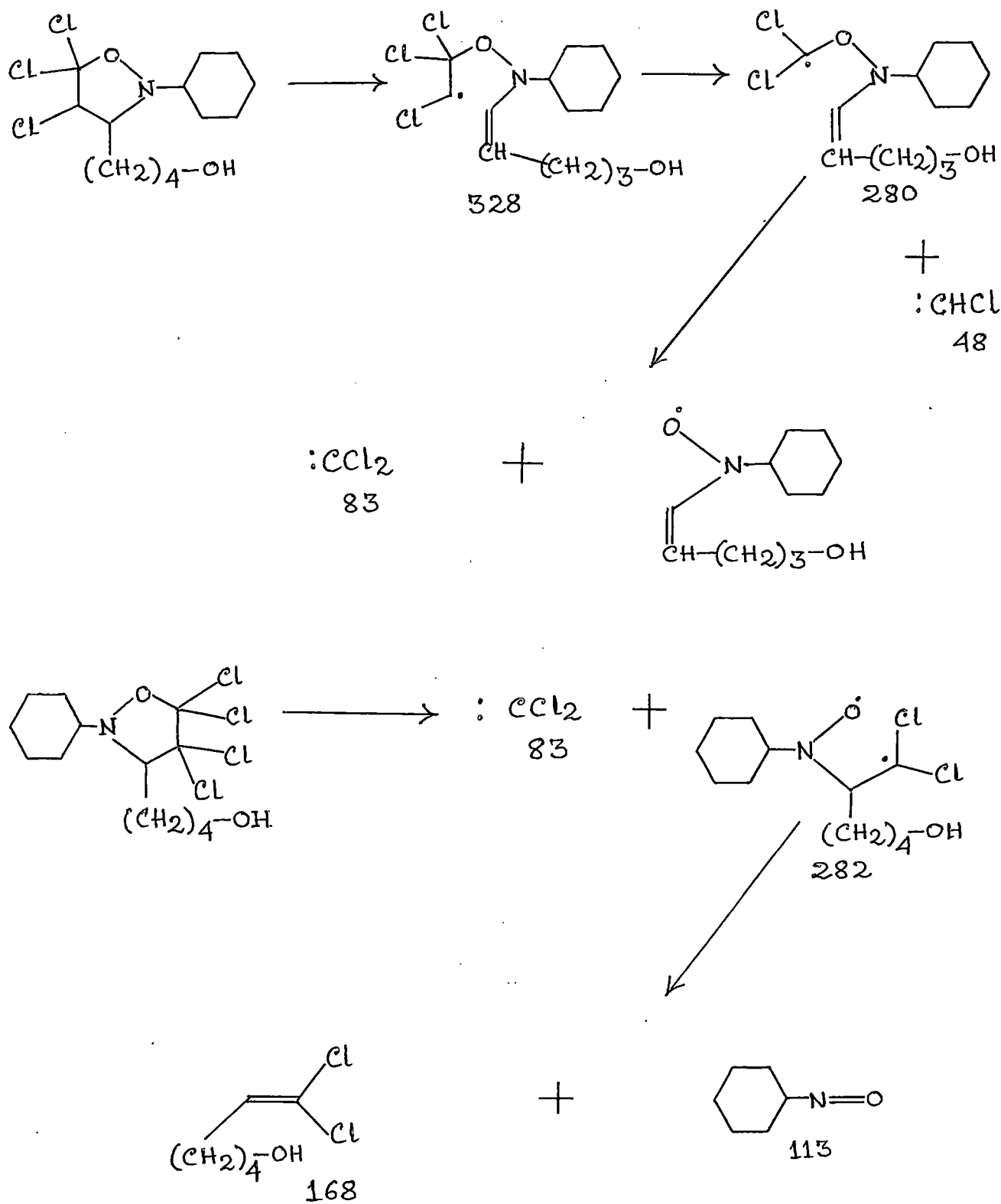
(i)
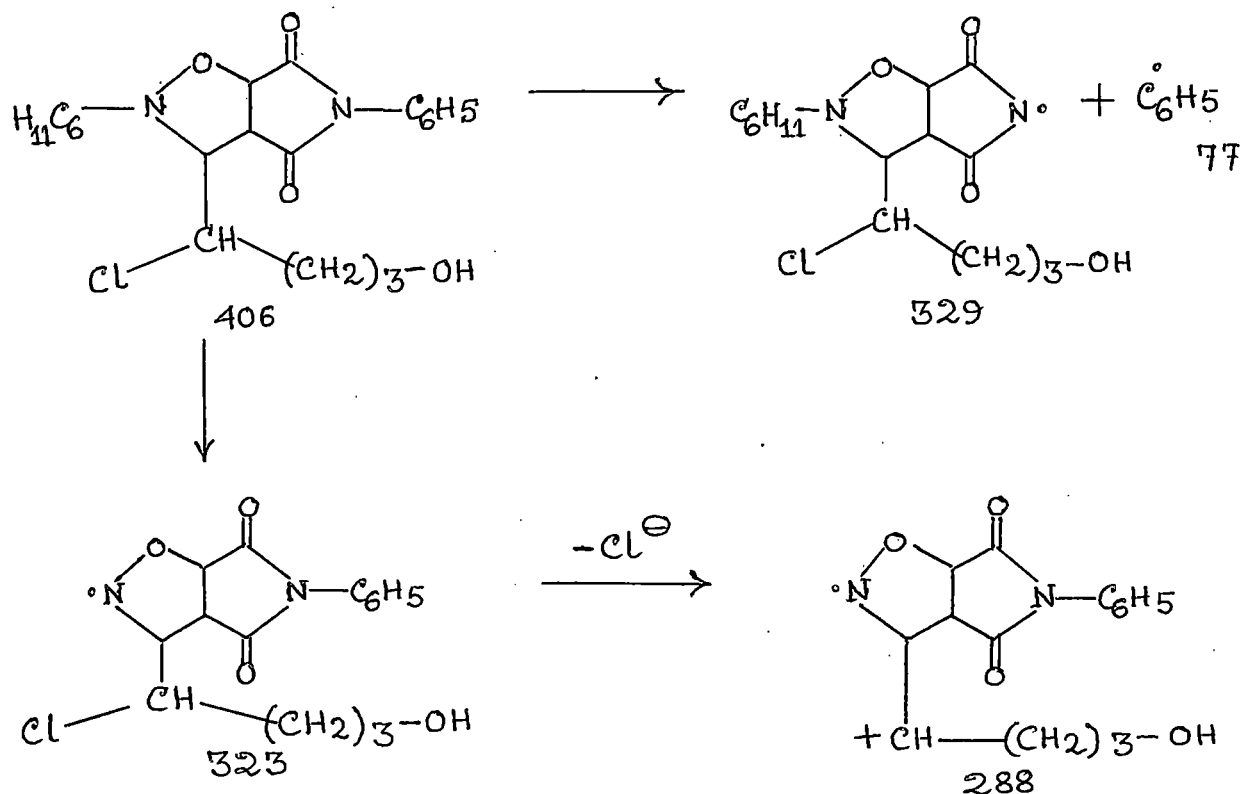
(ii)
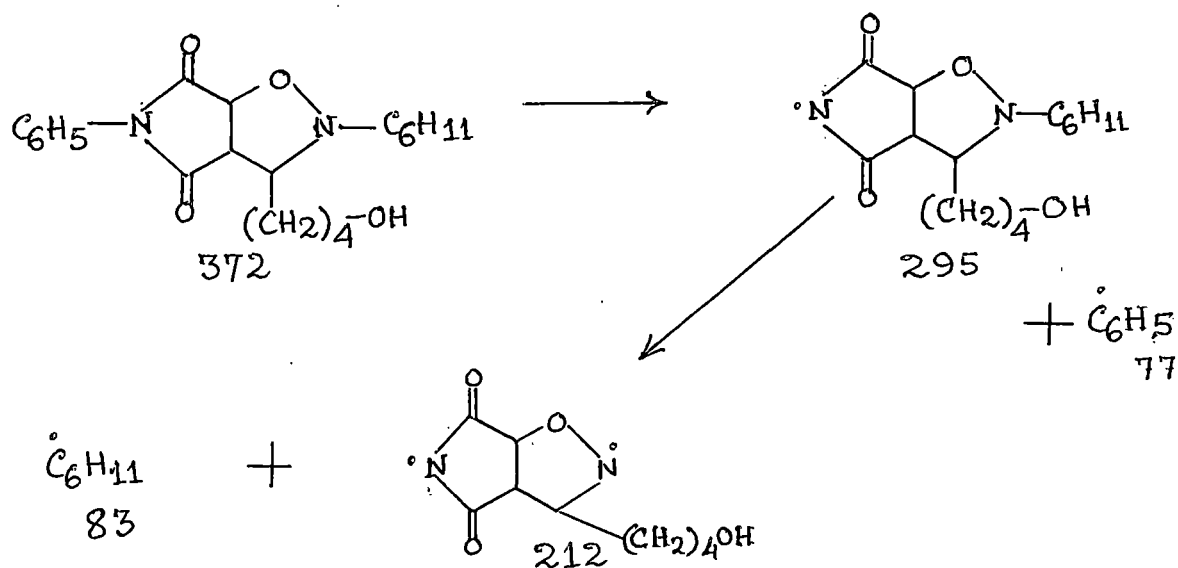
With N- cyclohexyl 5- OH nitrone and trichloro & tetra-
chloro ethylene adducts some of the expected ion fragments were
absent. But the other peaks were prominent. e.g. 280; 48; 83; in
the case trichloro ethylene while 282; 83; 168 in the case of tetra
chloro ethylene (Type K1 and K2):

:CCl₂
83

:CHCl
48

:CCl₂
83

168

113

The fragmentation patterns of both the methyl and ethyl acrylate adducts with both the nitrones followed the general pattern with some typical peaks for methyl and ethyl ester e.g. CH_3O (31); CH_3COO (59); CH_3CH_2O (45); CH_3CH_2COO (73) and prominent peaks for both the cases (at m/e 254,) probably due to the ion M-31 for methyl and M-45 for ethyl acrylate adducts respectively. (type L)

(i)

(ii)
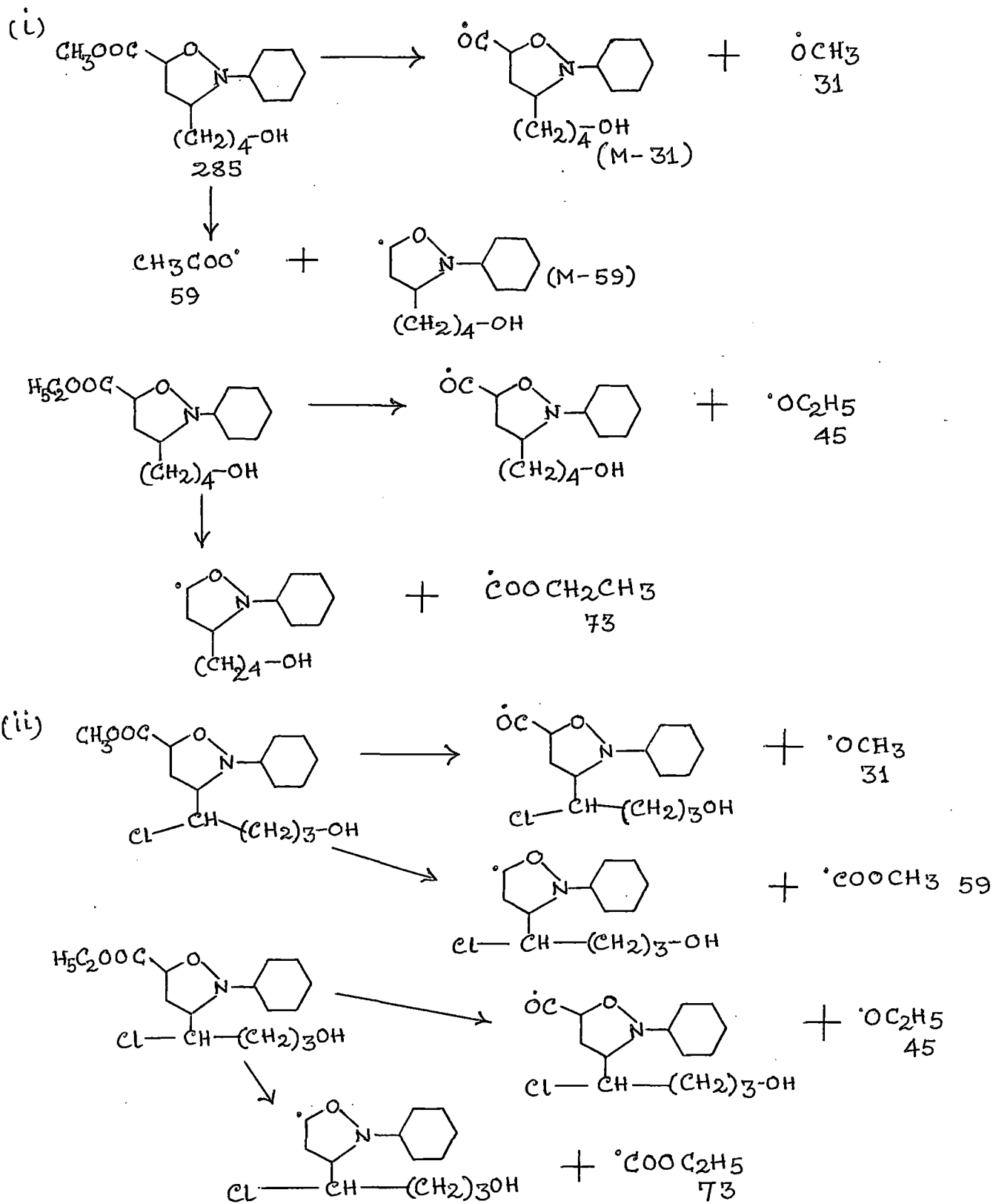
In the case of methyl acrylate adduct with N- cyclohexyl 5-hydroxy nitrone, from mass spectro scopic analysis we can cite strong evidence in favour of 4- substituted cycloadd over that of 5- substituted adduct.
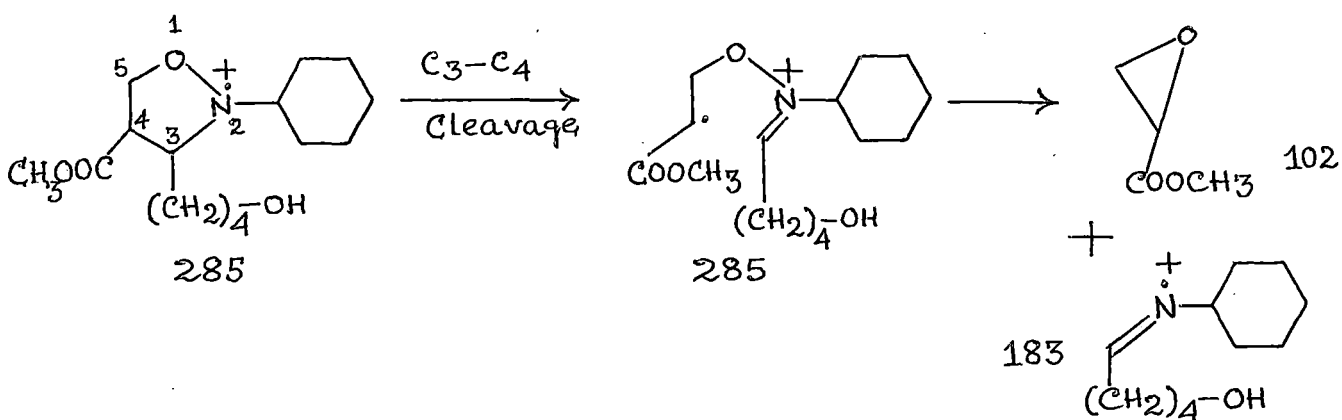

The fragmentation pattern of dihydro pyran with N-cyclohexyl 5 - OH - nitrone followed the general pattern with some special peaks at 184 and 99. (type M)
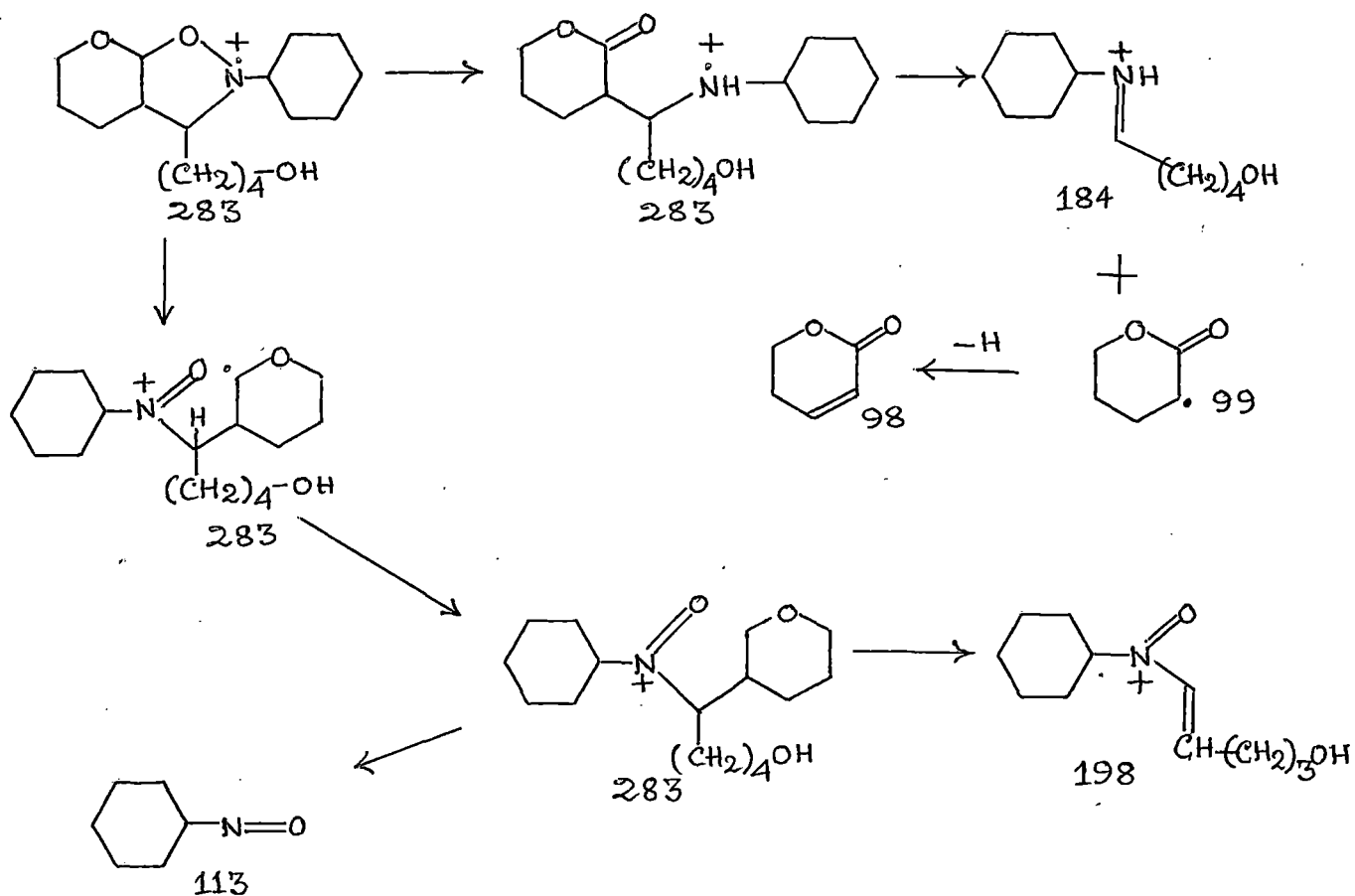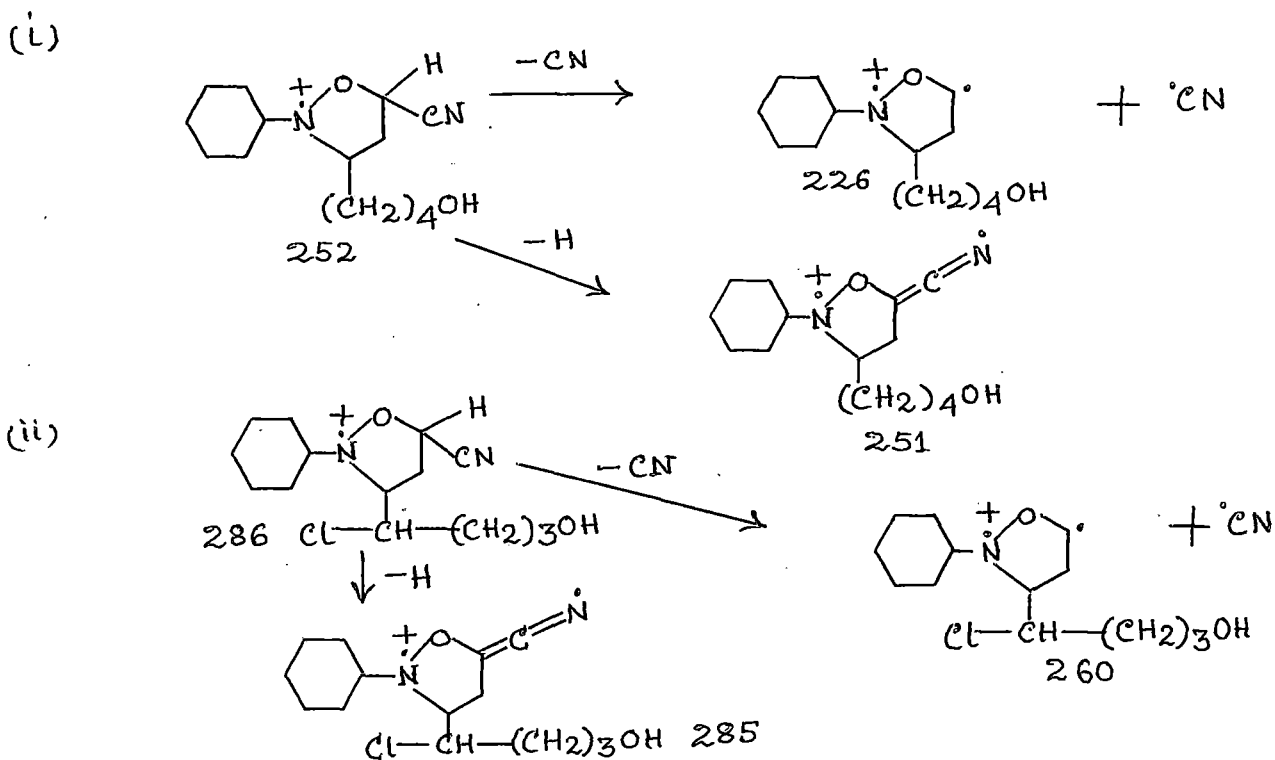
P- benzoquinone adduct formed from N- cyclohexyl 5- hydroxy nitrone fragmented following the same pattern with some typical peaks at 196, 168, 153, 251, 162. (type N).
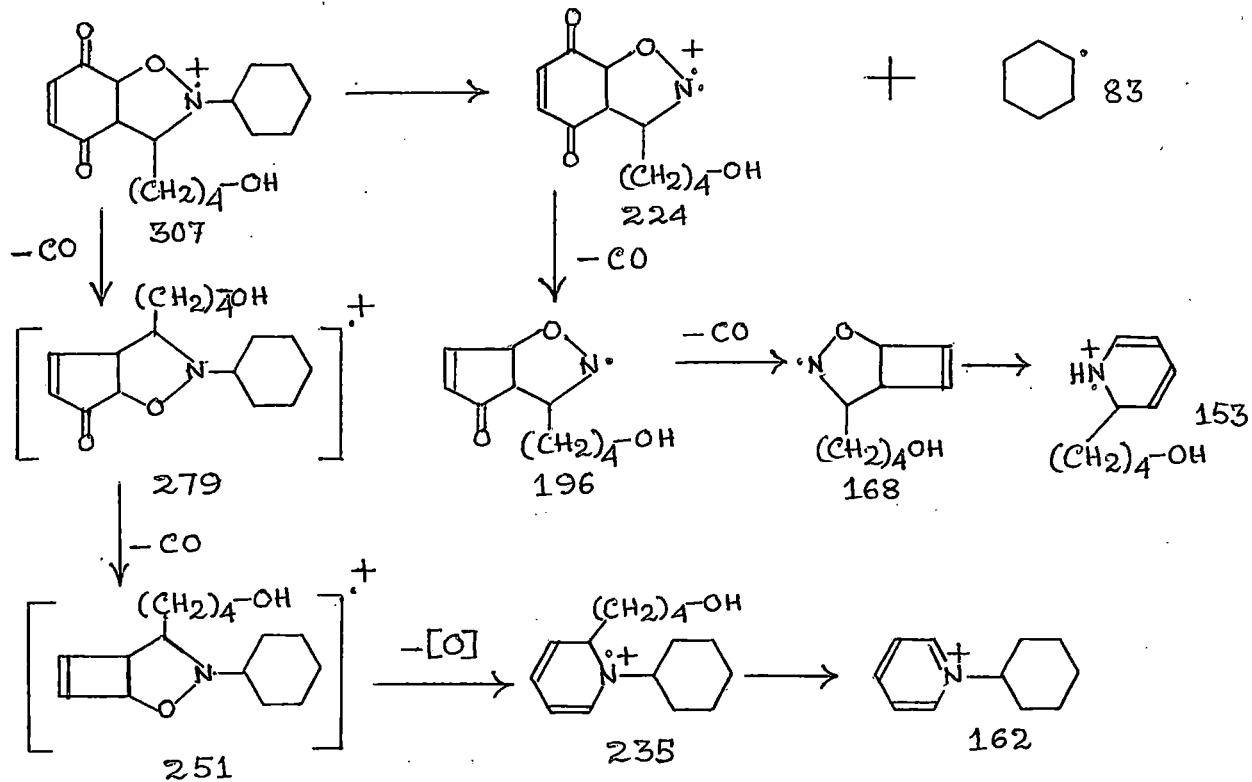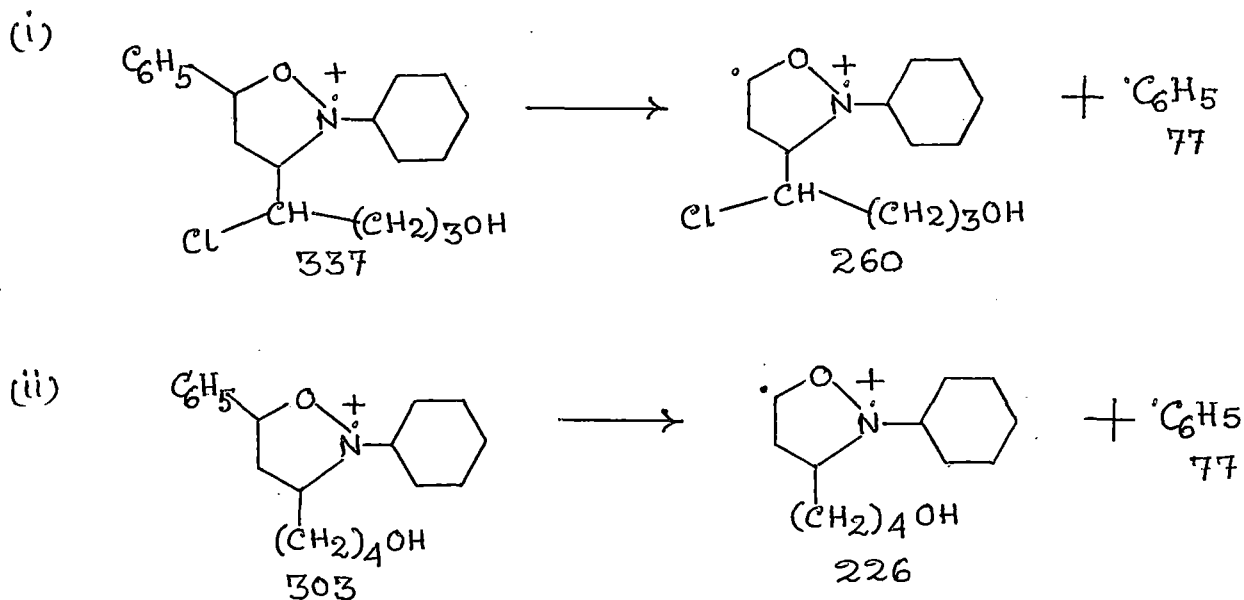

Fragmentation pattern of 2-chloro-acrylonitrile formed from N- cyclohexyl chloro nitrone was also in accordance with the general pattern. The molecular ion peak was associated with M+1 peak. Very weak peaks at 295 (M-26) and 286 (M-35) due to (M-CN) and (M-Cl) were also found. (type O)
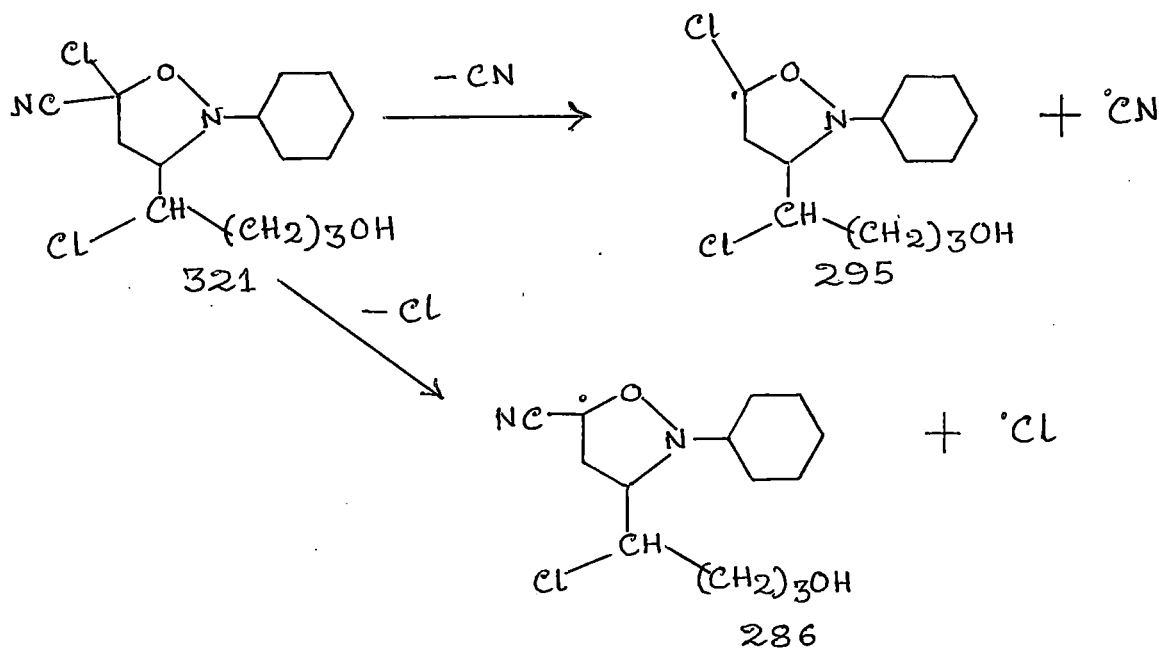
Acrylonitrile adduct for both the N- cyclohexyl chloro-nitrone and N- cyclohexyl 5- hydroxy nitrone follwed the same general pattern with some special peaks at 251, 226 and 260, 285. (type P)

(i)

$-CN$

226

$(CH_2)_4OH$

252

$+ \cdot CN$

$-H$

251

$(CH_2)_4OH$

(ii)

286

$Cl-CH-(CH_2)_3OH$

$-CN$

$+ \cdot CN$

$Cl-CH-(CH_2)_3OH$

260

$-H$

$Cl-CH-(CH_2)_3OH$ 285

The cycloadduct of styrene with both N- cyclohexyl chloro nitrone and N- cyclohexyl 5- hydroxy nitrone also followed the same fragmentation pattern with some weak peaks (M-77) due to the loss of phenyl gr. (type Q)

(i)

C_6H_5

$Cl-CH-(CH_2)_3OH$

337

$+ \cdot C_6H_5$

77

$Cl-CH-(CH_2)_3OH$

260

(ii)

C_6H_5

$(CH_2)_4OH$

303

$+ \cdot C_6H_5$

77

$(CH_2)_4OH$

226

The fragmentation patterns of methyl vinyl ketone adduct with both the nitrones were also in accordance with the general pattern with some special peaks in both the cases. (type R)
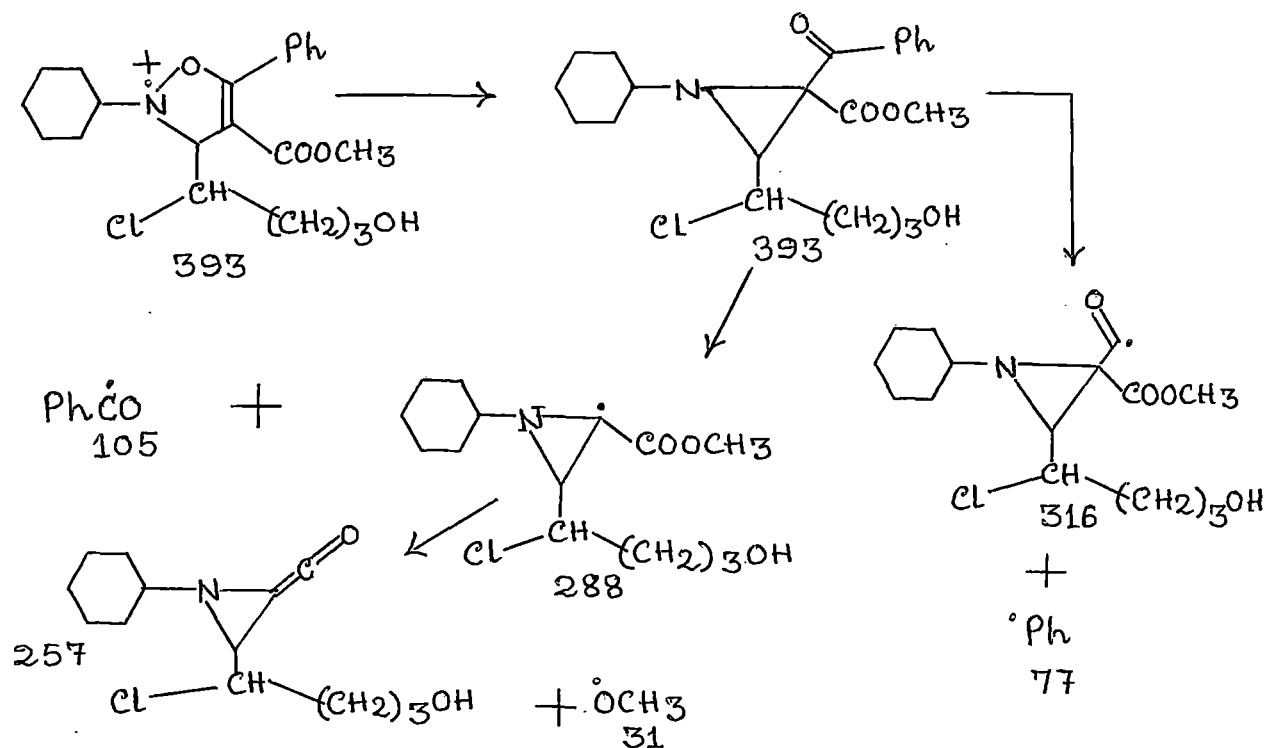
(i)

(ii)
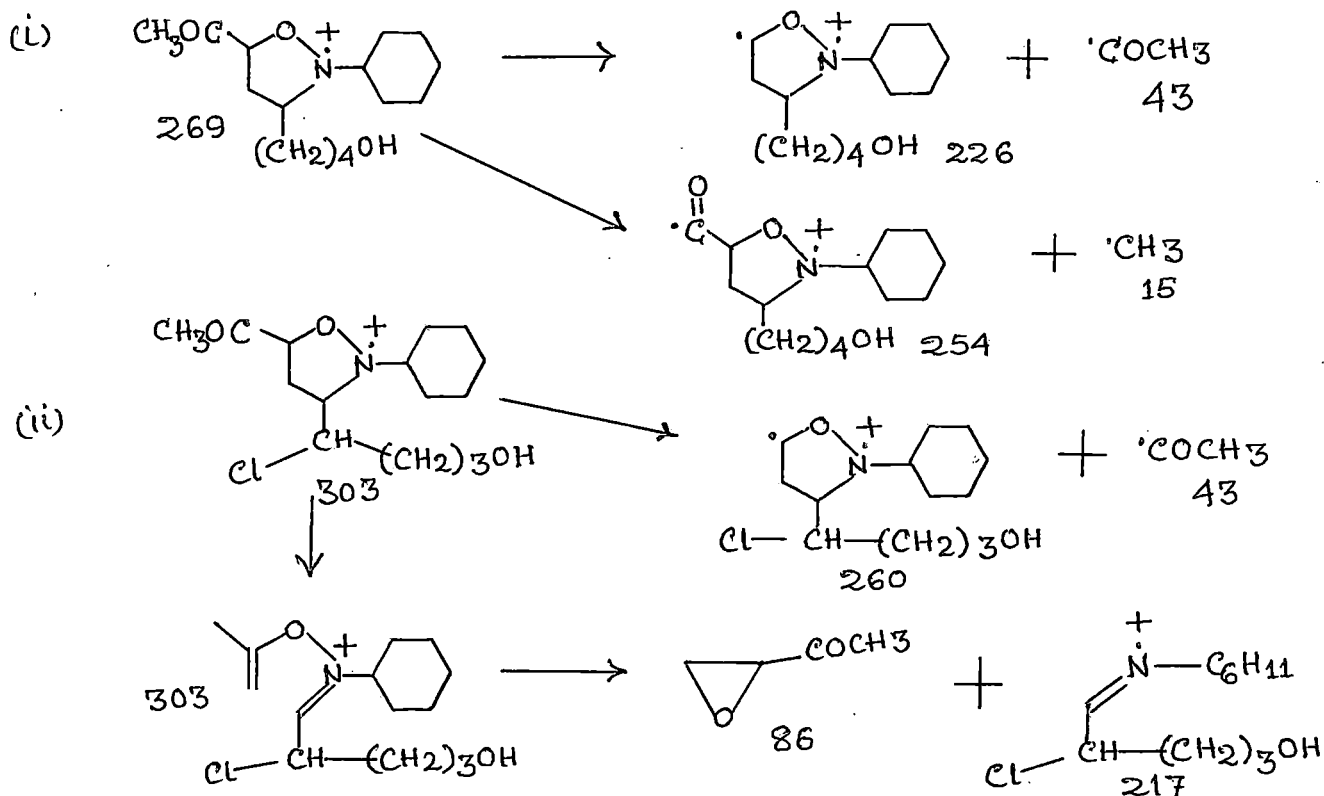
In addition to the general pattern of mass fragmentation, some special peaks of N- cyclohexyl maleimide adduct with both the nitrones were explained (type S).
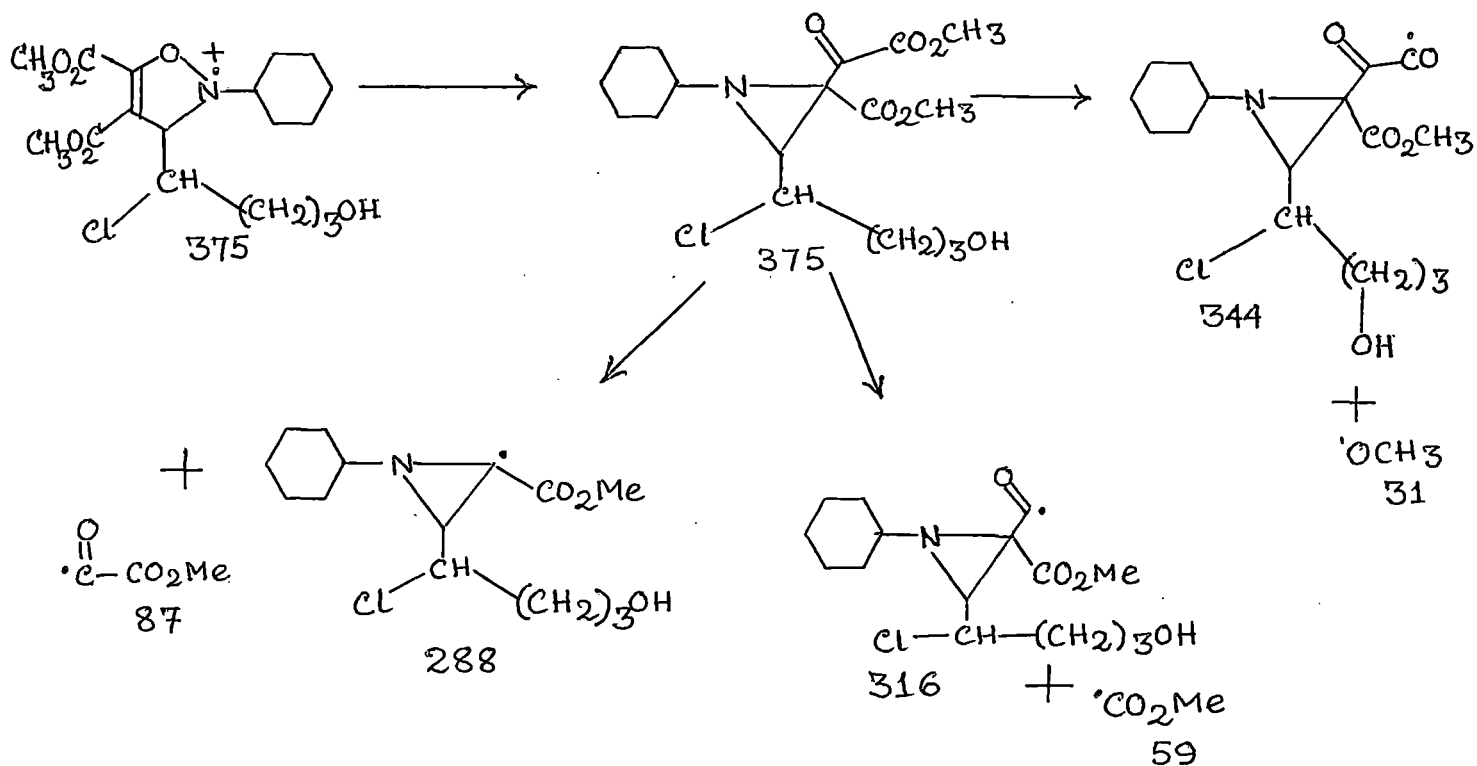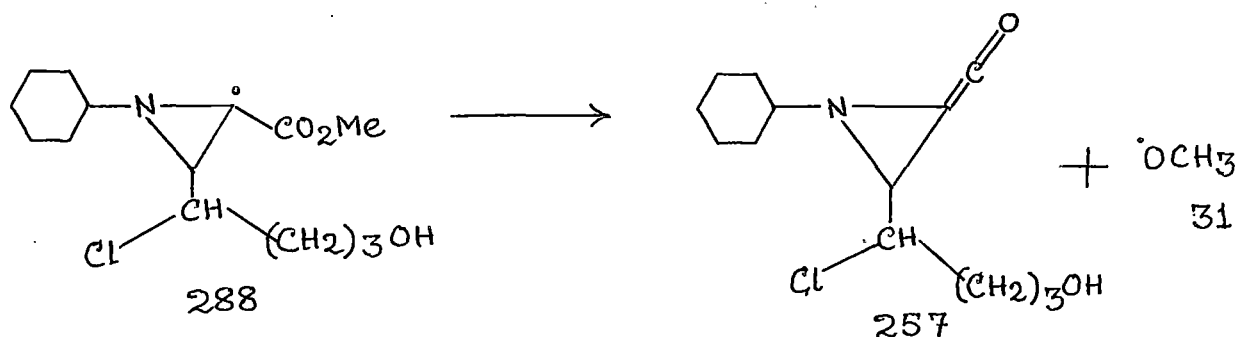
(i)

(ii)
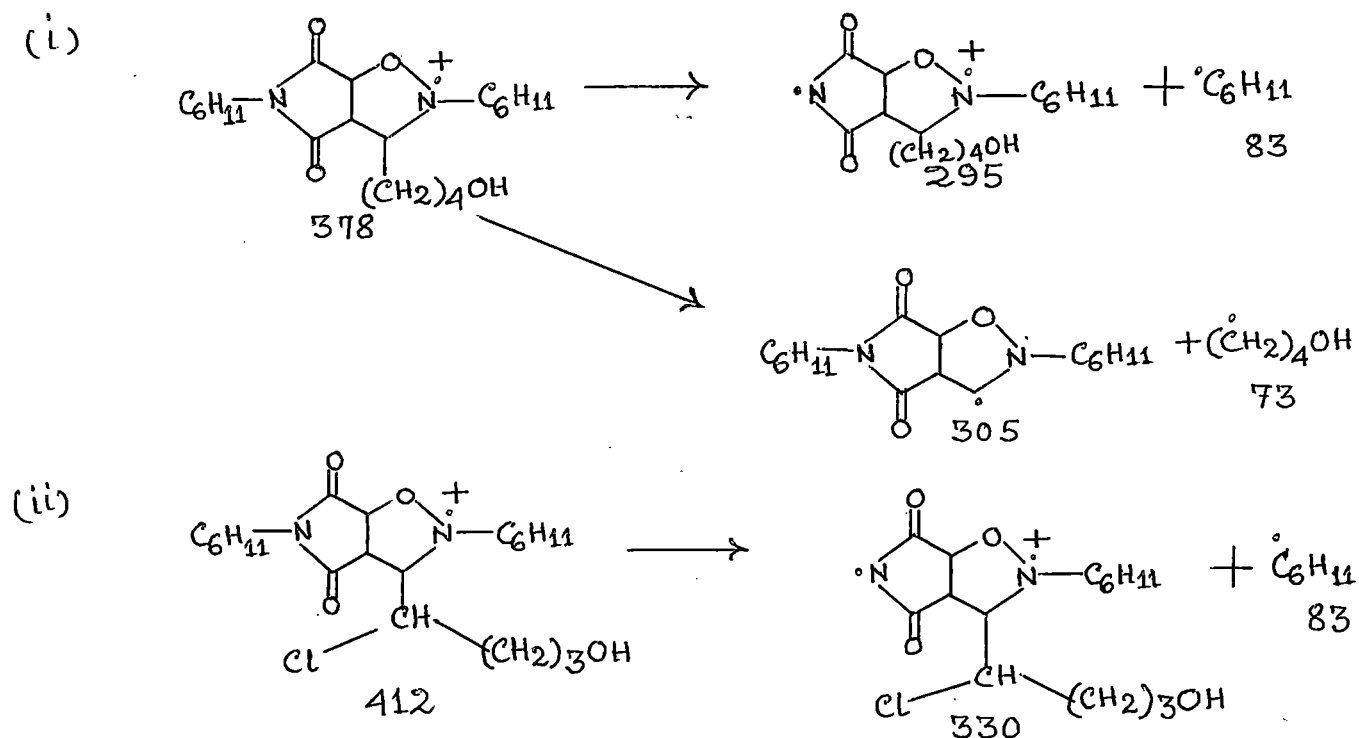
The fragmentation pattern of acetylene adducts were different and explained in type T.

i) Phenyl methyl propiolate adduct :

ii) Dimethyl acetylene dicarboxylate :

3. Interpretation of PMR Spectra

On interpreting the NMR Spectra of the nitrone adducts, the chemical shifts and coupling constant for 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 (241) used this method to elucidate the conformations of the cis and trans cyclopentane 1 - carbo methoxy - 2 - ol and found that for trans. isomer the band width was 18 Hzs and for cis isomer 11 Hzs. (Table XII).

Table-XII
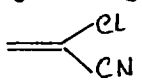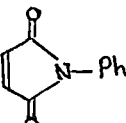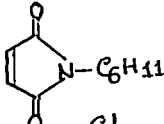### Cyclo adducts with N-cyclohexyl-chloro-nitrone
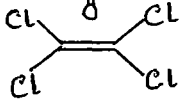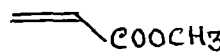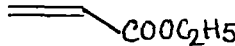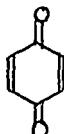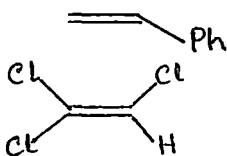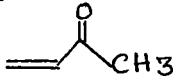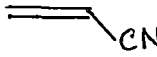
Adduct	C5-H in ppm	Band-Width (Hz)	Coupling Const(J) in(Hz)
N-Cy-maleimide.	4.63-4.57 (d)	9 Hz	6.06 Hz
Styrene.	2.58-2.44 (t)	10 Hz	6.06 Hz
Me-Vinyl Ketone.	4.9-4.8 (t)	8 Hz	6.06 Hz
N-Ph-maleimide.	5.7-5.4 (b)	11 Hz	---
MeO₂C—C≡C—CO₂Me	—	—	—
Acrylonitrile.	5.0-4.9 (dd)	9 Hz	4.05; 2.7
Ethyl Acrylate.	3.6-3.5 (b)	10 Hz	
Methyl Acrylate.	3.87-3.6 (b)	12 Hz	
⊨⟨Cl/CN	—	—	—
Ph-C≡C-CO₂Me	—	—	—

Table-XIII

Cyclo adducts with N-cyclohexyl 5-hydroxy nitrone(245)

Adduct	C5-H (d ppm)	Band-Width (Hz)	Coupling Const(J) in(Hz)
cyclohexene	4.9 (q)	10 Hz	4.5; 4.5
N-Ph maleimide	5.6 (b)	9 Hz	3
N-C$_6$H$_{11}$ maleimide	5.75-5.00 (b)	12 Hz	
Cl$_2$C=CCl(Cl) (tetrachloro)	—	—	—
CH$_2$=CH-COOCH$_3$	3.1-2.8 (m)	12 Hz	12.3
CH$_2$=CH-COOC$_2$H$_5$	4.77-4.64 (b)	10 Hz	
benzoquinone	9-8.65 (b)	12 Hz	
CH$_2$=CH-Ph	2.6-2.5 (m)	9 Hz	6.06 Hz
Cl$_2$C=CCl-H (trichloro)	—	—	—
CH$_2$=CH-CO-CH$_3$	2.6-2.5 (t)	9 Hz	
CH$_2$=CH-CN	3.7-3.5 (t)	10 Hz	4.05; 2.7
dihydropyran	2.5 (m)	12 Hz	

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

From the coupling constant values for C-5 protons of the nitrone adducts with (i) acrylo nitrile;(ii) styrene, in the case of N- cyclohexyl 5- hydroxy nitrone (245) we have calculated the dihedral angles between C5 - C4 protons from standard graph. From these calculated values along with the assumption that 2- cyclohexyl 1,2 isoxazolidine at normal condition will prefer the envelop configuration with N- cyclohexyl group at equatorial position, (Fig V), and the free butanol group will also be in equatorial position at C3 .
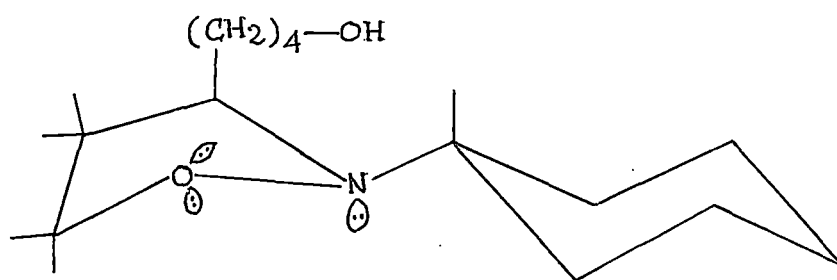
We have constructed the C5-C4 with the corresponding dihedral angles (fig VI) for the compounds acrylonitrile; styrene and ethyl acrylate for N- cyclohexyl 5- hydroxy nitrone (245).
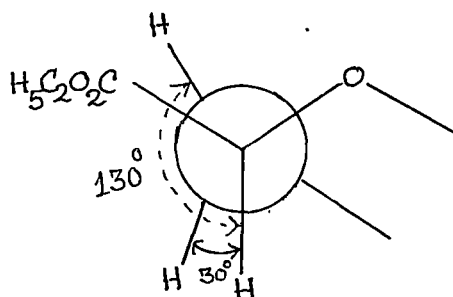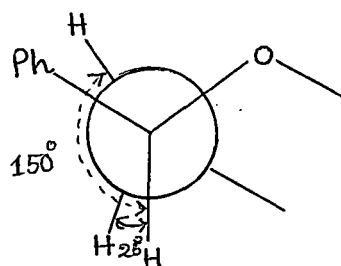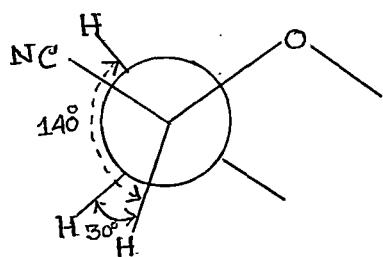
From these figures it is clear that the substituents at the
C-5 position tries to have the equatorial position from the quasi
- equatorial position of the envelop form. As a result, the 1,2
isoxazolidine conformation shifts from envelop to half chair form
- depending on the bulkiness of the C-5 substituents.

The conformation of acrylonitrile has less bulky gr and is
close to the envelop form and that of methyl acrylate and styrene
are close to the half chair form. The pseudo-rotation of the
five-memered ring is restricted by the substituents in all these
compounds.
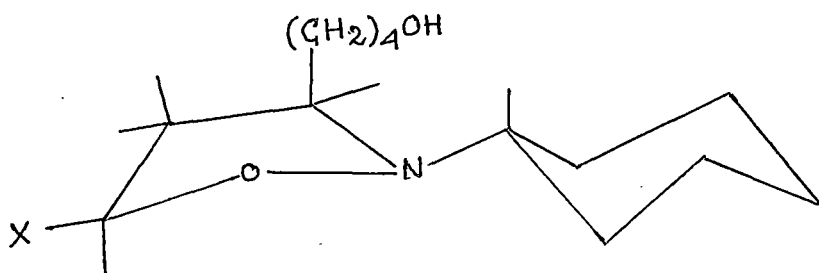
This indicates that in each of the compounds C5 proton and
C4 proton couple in the same way and comparison of the
corresponding dihedral angle suggests that the dihedral angle
of the proton is $50°$. The normal dihedral angles for cyclohexene
in perfect chair form are $60°$ for cis proton and $180°$ for trans
protons. The deviation is due to the strain of the five membered
ring.

As the C5 proton in the other cyclo adducts 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 infered about
their conformational structures.

For most of the cases cyclohexyl protons along with -n-
butanol protons as well as chloro butanol protons were appeared
at 0.75 - 2.3 δ . C3 protons in all adducts appeared in the
region 2.7 - 3.6 δ . N - CH - proton of cyclo hexyl group gave
signal in region 2.6 - 3.3 δ . C4 & C5 proton signals depended on
the substituent at C4 and C5 positions.

'Syn' cyclo adducts were formed via " exo Transition State " in the case of cyclohexene; N- phenyl - maleimide ; N- cyclohexyl maleimide; ethyl acrylate; acrylonitrile etc. with N- cylohexyl 5-hydroxy-nitrones.The "Band-Width" values and J values were also in support of them.

The coupling constant, J values calculated for 'chloro - acrylonitrile', and 'methyl vinyl ketone' of N- cyclohexyl chloro nitrone were found to be 15.15 & 9 Hzs respectively while it was 12.3 Hzs for methyl acrylate of N- cyclohexyl 5- hydroxy nitrone (245) and were in favour of anti-cycloadducts formed via endo transition state (206).

In the case of methyl acrylate adduct of N- cyclo hexyl 5- hydroxy nitrone (245), the major product was confirmed as 4- substituted one and not the 5- substituted one also explained from mass spectral analysis.

'Syn' cycloadducts were formed via exo- transition - state in the case of acrylonitrile; chloro acrylonitrile; ethyl acrylate etc. with N- cyclohexyl chloronitrone. Band-Width values and coupling constant (J) values were also in support of them.

In the case of di-methyl acetylene dicarboxylate & phenyl-methyl propiolate, both the cyclo adducts were 'Syn' considering C_3H and $- \underset{\underset{Cl}{|}}{CH} -$ protons.