CHAPTER III
EXPERIMENTAL

IR spectra were recorded as film or in solution or in nujol by Perkin - Elmer 1800 (FR - IR) and Perkin - Elmer 881 or Perkin - Elmer 557 machine. Absorption maxima stated were in cm^{-1} ; abbreviations used were ;

S = Strong, m = medium, w = week, b = broad .

Proton NMR spectra were recorded by Bruker WM 400 (400 MHZ, FT NMR),varian EM-360 L (60 MHZ) and EM 390 (90 MHZ) instruments. TMS as internal standard. Solvents were specified in each case. Abbreviations used were :

S = singlet, d = boublet, t = triplet, q = quartred ,
b = broad, m = multiplet .

Mass spectra were recorded by Jeol D - 300 (CI) spectrometer. All melting points are uncorrected. TLC of the reaction mixture and that of pure compounds were compared. Hand drawn silica gel(E.Merck) plates of 0.5-0.7 mm thickness were used for TLC studies. Silica gel (Loba;60-200 mesh) alumina (BDH) were used for column chromatography. All the solvents and most of the reagents were purified before use.

(A) Preparation of the N- cyclohexyl hydroxyl amine (246):

Pyridine hydrochloride was prepared by passing dry hydrogen chloride through a solution of dry and distilled pyridine, in dry ether, till white precipitation of pyridine hydrochloride was completed. The precipitate was quickly filtered, washed with dry ether and dried under vaccum.

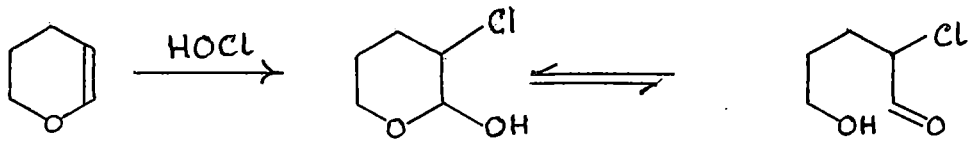
To a solution of pyridine hydrochloride (65.9g, 0.57mole) suspended in dry pyridine (150 ml), a solution of soddium - borohydride (22.24g , 0.58 mole) in dry pyridine (575 ml) was added dropwise under nitrogen atmosphere. The reaction mixture was filtered quickly under suction and the filtrate concentrated at 50° c / 5mm , when pyridine borane remained in the flask as a pale yellow liquid (49g , 93 %). The reagent was used in the next step without further purification.

A solution of cyclohexanone oxime (5.6g , 0.05 mole) and pyridine borane (25ml ,0.25mole) in ethanol (25ml) was stirred at 5° c for 30 minutes, rendered alkaline with ether saturated aquous sodium bicarbonate and extracted with ether (25 X 3)ml. The combined ether layer was washed with H_2O (25 X 3)ml and anhydrous $MgSO_4$. Upon removal of ether, N- cyclohexyl hydroxyl amine was obtained as a white solid (5.2g 91 %), which was recrystallized from ethanol as white needles.

M.P - 140° c

IR (Nujol) : 3220 (s); 3120 (s,b); 1515 (s); 1345 (m); 1310 (m); 1270 (w); 1245 (w); 1210 (s); 1150 (s); 1120 (m); 1075 (s); 1065 (s); 1030 (s); 970 (s); 930 (s); 920 (s); 900 (s); 840 (s); 830 (s); 810 (s); 790 (s) .

(B) Preparation of "Chloro - hydrin" (Communicated):



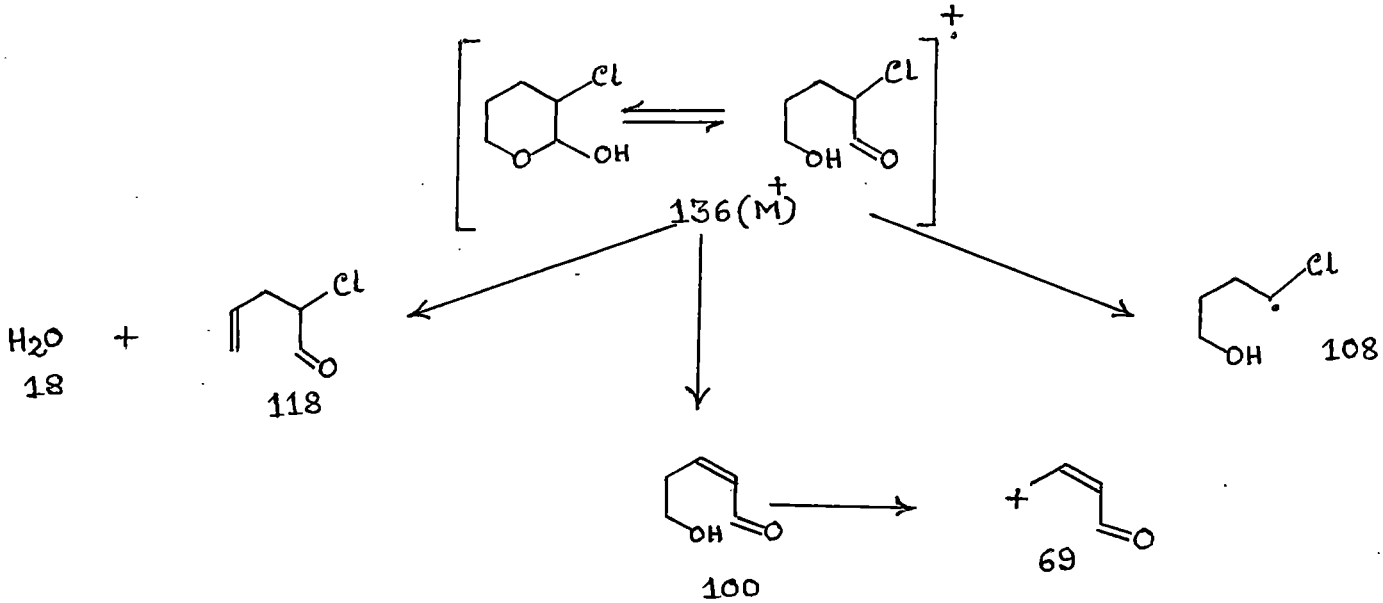
Dihydropyran (1 equivalent) was taken with water (2 - equivalent) at 10° c . With stirring hypochlorous acid (HOCl), (produced by passing dry Cl_2 in a saturated $NaHCO_3$ solution) was added in one portion and the reaction mixture was cooled to 0-5° c. It was followed by-quenching the reaction mixture into water and finally the product was isolated with ether extraction (25ml X 3).

IR : 3300 - 3480 (b); 2940 - 2960 (s); 1640 (m); 1450 (w); 1360 (w); 1280 (w) .

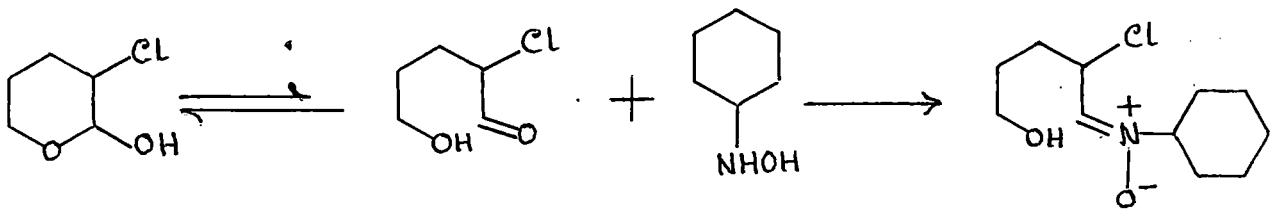
PMR : ($CDCl_3$) : δ (5.2 - 5.1; b, 1H; -OH) δ 9.1 (1H, $\overset{O}{\overset{\|}{C}}-\underline{H}$)
5 - 4.9 (C-1, $\underset{H}{\overset{}{>}}C$ - O) ; d, J = 6Hz; 1H)
4.1 - 3.9 (C-2, $\underset{H}{\overset{}{>}}C$ - Cl) ; m, 1H, - $\underset{|}{C}H$ - Cl).
3.8 - 3.4 (m, 2H, - O - CH_2 -).
2.4 - 0.7 (m, 4H, - CH_2 -).

Mass(m/z) : 136(M^+); 118; 108; 102; 85; 78; 69; 52; 49; 35; 32; 18.

The major mass fragmentation patterns of "chloro hydrin" was explained as follows :



(C) Preparation of N-cyclohexyl chloro- nitrone (Communicated):



N - cyclohexyl hydroxyl amine, 0.500g (4.34 m. mole) was added to a solution of 0.6167g (4.52 m.mole) chlorohydrin in dry ether (150 ml) and anhydrous $MgSO_4$, under nitrogen atmosphere and was kept at R.T. for 24 hrs, while the formation of nitrone was monitored by TLC(Silica gel ; ethyl acetate / Benzene = 1:10). The nitrone was isolated as colourless crystal by column chromatography using 10g Al_2O_3 (5 % deactivated) and ether as eluent. Nitrone was highly hygroscopic and showed characteristic IR bands at 1610 (s) cm^{-1}.

M.P. - 58° c

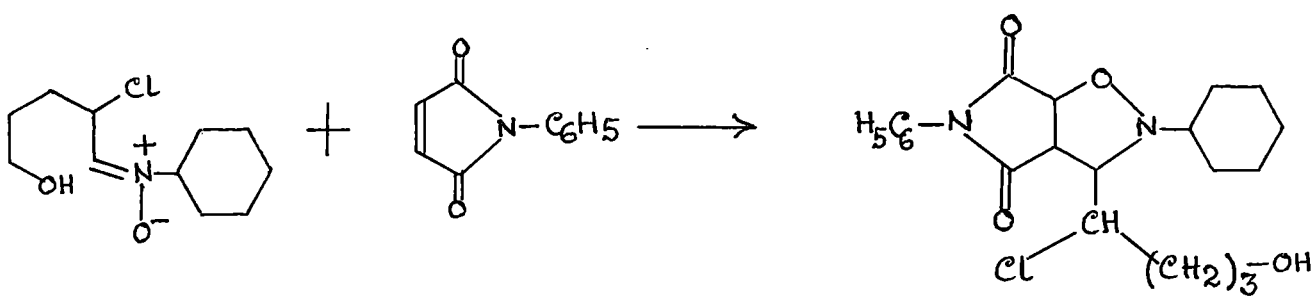
IR : 3200 - 3400 (b); 2930 (s); 2880 (w); 1660 (m); 1610 (s);
(Neat) 1450 (s); 1390 (m); 1340 ; 1300 ; 1230 ;1150 ;
1100 ; 1080 ; 1020 ; 1000 ; 940 ; 900 ; 870;

PMR ($CDCl_3$);
90 MHZ :

δ 7.0-6.8 (d, 1H; $\overset{H}{\diagdown}C = \overset{+}{N}\diagup$; J = 7.5 HZ)
4.3 - 4.1 (m, 1H; $-\underset{|}{C}H - Cl$; J = 4.5 HZ)
3.7 - 3.6 (m, $\underset{H}{\diagdown\diagup}C - \overset{+}{N} =$)
2.2 - 1.0 (m, 16H)

The nitrone was generated by the above method and used in-situ for the following reactions.

1. Reaction of Nitrone With N- Phenyl maleimide :



N- cyclohexyl hydroxyl amine 0.250g (2.17 m. mole) was added to a solution of 0.298g (2.17 m. mole) chlohydrin in dry ether(100 ml) with anhydrous $MgSO_4$, under nitrogen atmosphere and was kept at R.T. for 24 hrs, while the reaction was monitored by TLC (Silica gel ; ethyl acetate / Benzene = 1 : 10).

N- phenyl maleimide, 0.375g (2.17 m. mole) was added at this stage and the reaction mixture was again kept at R.T. for further 48 hrs. The solvent was evaporated off to afford the cyclo adduct as gray white solid (o.398g).. The product was purified by column chromatography using 20g. Silica gel and Benzene : ether = 5 : 1 eluent.

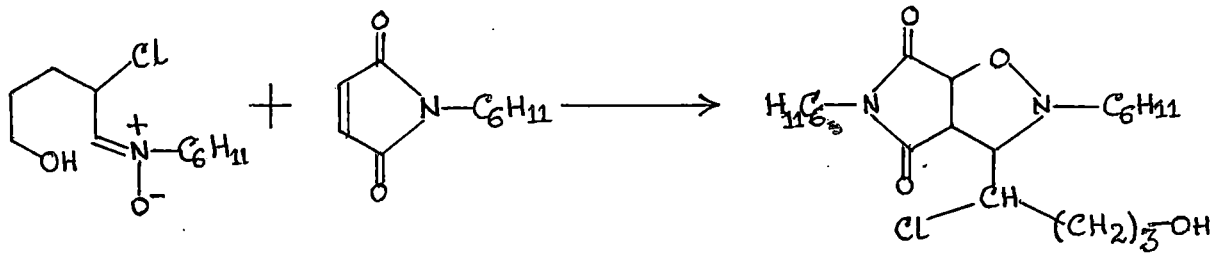
Yield: 45.14 %
M.P. : 150° c
Rf : 0.20 (Benzenel/ethyl acetate = 10 : 1)

IR (KBr) : 3520(s); 3360(s); 2840(s); 1700(s); 1690(s); 1600(s); 1500(s); 1395; 1190.

Mass : (m/z) : 407(M^+); 391; 366; 323; 306; 299; 289; 273; 245; 191; 172; 133; 117; 98; 69; 52; 35; 18.

PMR ($CDCl_3$) : δ 7.7 - 7.3 (m, 5H, C_6H_5) .
5.7 - 5.4 (b, 1H, C(5)H, D_2O exchanged).
5 - 4.43 (d, 1H, J = 5.25 Hzs. C(4)H).
4.39 - 4.33 (d, 1H, J = 5.25 Hzs, H - C(H) - Cl)
3.39 - 3.1 (dd, 1H, J = 5.25 Hzs, C(3)H) .
3 - 2.65 (m, 1H, >N - CH<).
2.3 - 1 (m, - CH_2 -) .

2. Reaction of Nitrone With N- Cyclohexyl maleimide :



N- cyclohexyl hydroxyl amine , 0.2639g (2.29 m. mole) was added to a solution of 0.312g(2.29 m. mole) chlorohydrin in dry ether (100 ml) with anhydrous $MgSO_4$, under nitrogen atmosphere and was kept at R.T. for 24 hrs, while the reaction was monitored by TLC (Silica gel; ethyl acetate / Benzene = 1 : 10).

N- cyclohexyl maleimide (0.428g), 2.39 m. mole was added at this stage and the reaction mixture was again kept at R.T. for further 48 hrs. The solvent was evaporated off to afford yellowish white solid (o.6487g) as product. The product was purified by column-chromatography using 20g. Silica gel and Benzene : ether = 2 : 1 as eluent .

Yield: 67.55 %
M.P. : 77°c
Rf : 0.60 (Benzene / ethyl acetate = 10 : 1)

IR : ($CHCl_3$) : 3580(b); 2920(S); 2840(m); 1760; 1700(b); 1440; 1380.

Mass : (m/z) : 412(M^+); 408; 399; 366; 344; 321; 283; 260; 220; 208; 178; 171; 142; 126; 110; 102; 96; 79; 52; 35; 18.

PMR ($CDCl_3$):

δ 4.63 - 4.57 (d, J = 6.06 Hzs, 1H, C(5)H),

4.05 - 3.93 (m, 1H, - CHCl)

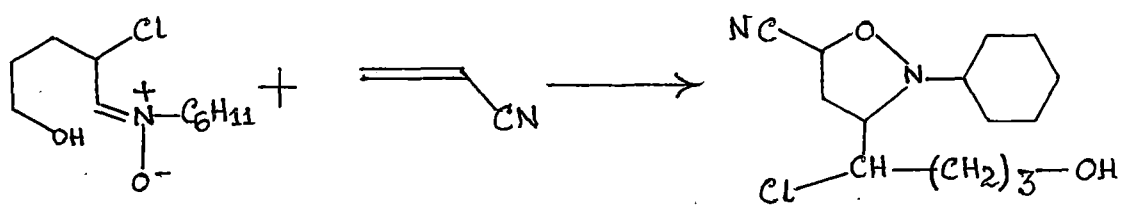
3.38 - 3.77 (q, J = 6.06 Hzs, 1H, C(4)H]

3.19 - 3.11 (d, J = 6.06 to 7.75, 1H, C(3)H)

2.7 - 2.59 (b, 2H, >N - CH<)

2.2 - 1.1 (m, 26H, $-[CH_2]_{13}-$].

3. Reaction of Nitrone With Acrylonitrile :



N- cyclohexyl hydroxyl amine 0.274g (2.38 m. mole) was added to a solution of 0.3103g (2.28 m. mole) chlorohydrin in dry ether (100 ml) with anhydrous $MgSO_4$, under nitrogen atmosphere and was kept at R.T. for 24 hrs, while the reaction was monitored by TLC (Silica gel; ethyl acetate / Benzene = 1 : 10) .

Acrylonitrile, 0.248g (4.679 m. mole) was added at this stage and the reaction mixture was again kept at R.T. for further 48 hrs. The solvent was evaporated off to afford the cycloadduct as dark yellow gummy liquid (0.4713g). The product was purified by column chromatography using 20g Silica gel and Pet ether :

Benzene = 1:1 as eluent.

Yield : 71.52 %

Rf : 0.65 (Benzene / ethyl acetate = 10 : 1)

IR : 3450-3400 (b); 2880 (s); 2840 (s); 1620 (br); 1440 (s); 1360 ;

Mass (m/z) : 286(M^+); 195; 168; 151; 142; 124; 98; 85; 82; 60; 41 .

PMR : ($CDCl_3$) :

δ 5.49 (dd, J = 2.7 & J = 4.05 Hzs, X part of ABX spectrum, 1H, C(5)H).

4.7-4.6 (dd, J = 4.05 & J = 8.1 Hzs, X part of ABX spectrum, 1H, C(3)H).

3.9-3.8 (m, J = 4.05, 5.4, 2.7, X part of ABMX spectrum, 1H, - CHCl)

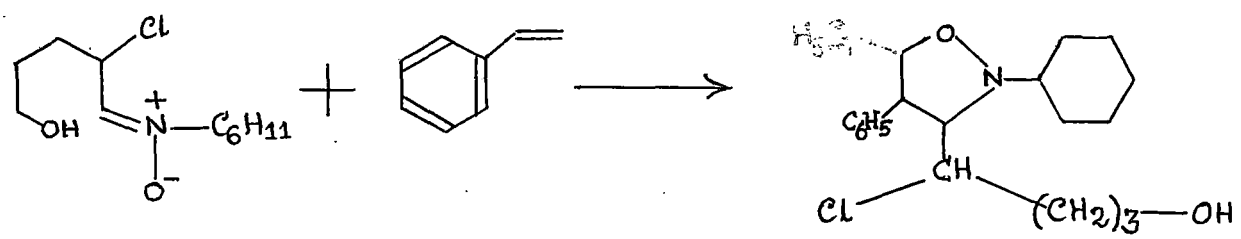
3.55-3.3 (m, AB part of MABX, 2H, C(3)H, $C(4)H_2$, C(5)H)

2.85-2.7 (m, 1H, >N - CH<)

2.3 - 1.1 (m, 16H, $-(CH_2)_8-$)

Configuration of the compound is Syn C(5) with respect to C(3) via exo Transition State.

4. Reaction of Nitrone With Styrene :



N- cyclohexyl hydroxyl amine 0.2492g(2.16m.mole) was added to a solution of 0.3123g (2.29 m. mole) chlorohydrin in dry ether (100 ml) with anhydrous $MgSO_4$, under nitrogen atmosphere and was kept at R.T for 24 hrs, while the reaction was monitored by TLC (Silica gel; ethyl acetate / Benzene = 1 : 10) .

Styrene (2.63 m. mole), 0.274g was added at this stage and the reaction mixture was again kept at R.T for further 48 hrs.

The solvent was evaporated off to afford the cycloadduct as white crystalline solid (0.320g). The product was purified by column chromatography using 20g. Silica gel and Benzene / pet ether = 1:1 as eluent .

Yield : 43.89 %

M.P. : 97°c.

Rf : 0.23 (Benzene / ethyl acetate = 1 : 10)

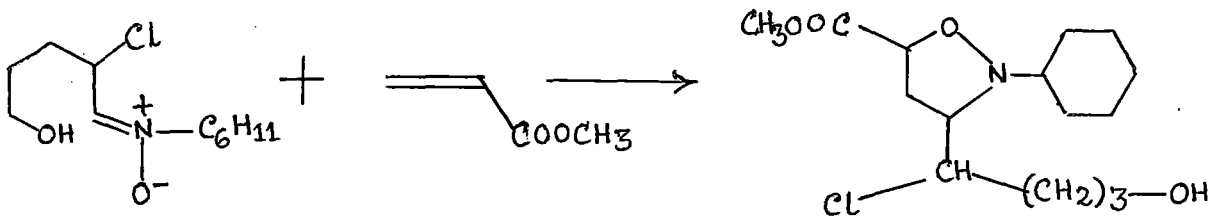
IR : 3580(s); 3320-3180(br); 2960-2840(b); 2400(m); 1700(m); 1650(m); 1435(m); 1310; 1230-1210(b) .

Mass (m/z) : 338(M^+); 219; 142; 114; 96 .

PMR ($CDCl_3$) :

δ 7.6 - 7.35 (m, 5H, C_6H_5) ,
3.55 - 3.43 (q, J = 7.57, 7.57, 13.63, X part of ABX Spectrum, 1H, C(4)H ,)
2.58 - 2.44 (t, J = 6.06, AB part of ABX Spectrum 2H, $C(5)H_2$)
2.4 - 2.33 (m, 1H, >N - CH<)
2.285 - 2.145 (t, J = 6.06 Hz, 1H C(3)H)
2.9 - 0.75 (m, 16H, $-(CH_2)_8-$) .

5. Reaction of Nitrone With Methyl Acrylate



N - Cyclohexyl hydroxyl amine 0.276g (2.40 m. mole) was added to a solution of 0.327g (2.40 m. mole) chlorohydrin in dry ether (100 ml) with anhydrous $MgSO_4$, under nitrogen atmosphere and was kept at R.T for 24 hrs, while the reaction was monitored by TLC (Silica gel ; ethyl acetate / Benzene = 1 : 10) .

Methyl acrylate, 0.206g (2.39 m. mole) was added at this stage and the reaction mixture was again kept at R.T for further 48 hrs. The solvent was evaporated off to afford the cyclo

adducts as dark red gummy liquid (0.422g) . The product was purified by column chromatography using 20g Silicagel and Benzene : ether = 2 : 1 as eluent.

Yield : 55.264 %

Rf : 0.09 (Benzene / ethyl acetate = 10 : 1)

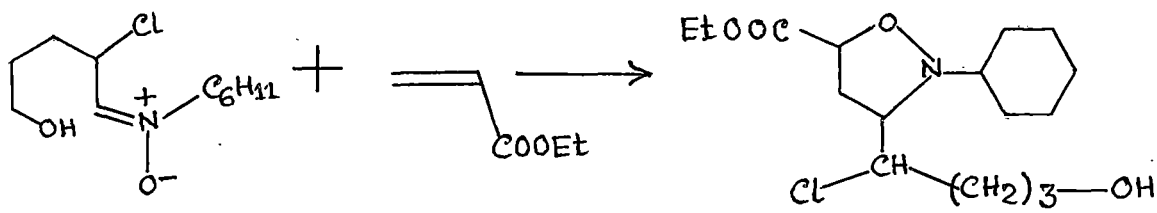
IR ($CHCl_3$) : 3360-3340 (b); 2930(s); 2850(m); 1625(b); 1440; 1100 .

Mass (m/z) : 319(M^+); 309; 294; 288; 278; 262; 253; 226; 216; 212; 207; 200; 194; 186; 184; 170; 152; 112; 98; 90; 73; 55; 44 .

PMR ($CDCl_3$) :

δ 4.0-3.9 (m, 1H, —CH(Cl)—);
3.87-3.6 (b, X part of ABX spectrum, 1H, C(5)H)
3.53- (s, 3H, $-CH_3$).
3.05-2.9 (dd, J = 6.06 Hz; M part of MABX spectrum, 1H, C(3)H).
2.80-2.63 (b, 1H, >N - CH<)
2.60-2.30 (m, AB part of MABX spectrum, $C(4)H_2$
2.2 - 1 (m, 16H, $-(CH_2)_8-$)

6. Reaction of Nitrone With ethyl Acrylate



N- cyclohexyl hydroxyl amine, 0.264g (2.29 m. mole) was added to a solution of 0.313g (2.30 m. mole) chlorohydrin in dry ether (100 ml) with anhydrous $MgSO_4$, under nitrogen atmosphere and was kept at R.T for 24 hrs, while the reaction was monitored by TLC (Silica gel ; ethyl acetate / Benzene = 1 : 10) .

Ethyl acrylate 0.230g (2.30 m. mole) was added at this stage and the reaction mixture was again kept at R.T for further 48 hrs. The solvent was evaporated off to afford the cycloadduct as yellow gummy liquid (0.407 g). The product was purified by column

chromatography using 20g silica gel and Benzene as eluent.

Yield : 61.541 %

Rf : 0.11 (Benzene / ethyl acetate = 10 : 1)

IR ($CHCl_3$) : 3340-3360(b); 2930(s); 2850(m); 1720(s); 1440 .

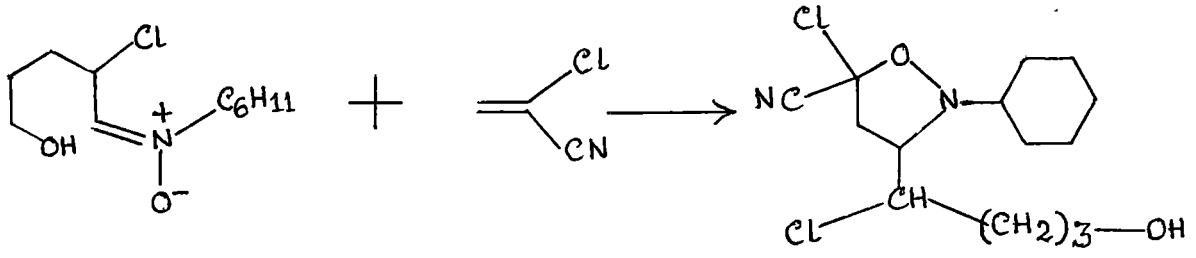
Mass (m/z) : 333(M^+); 323; 322; 316; 312; 296; 284; 276; 270; 269; 260; 242; 231; 226; 216; 214; 200 (B.P); 187; 180; 170; 161; 145; 131; 114; 102; 100; 52; 35; 18 ;

PMR ($CDCl_3$) :

δ 4.25-4.12 (q, 2H, $-COCH_2.CH_3$)
3.95-3.87 (t, J = 6.06 Hz, 1H, $>CH-Cl$)
3.6-3.5 (b, X part of ABX Spectrum, 1H, C(5)H).
3.18-3.0 (m, M part of MABX Spectrum, 1H, C(3)H)
2.67-2.43 (m, 1H, $>N-CH<$)
2.37-2.13 (m, AB part of MABX Spectrum, 2H, $C(4)H_2$)
1.93-0.8 (m, 19H, $-(CH_2)_8-$ & $-CH_3$).

Sturcture is syn with respect to. $>CH-Cl$ via exo Transition State .

7. Reaction of Nitrone With Chloro Acrylo-nitrile



N- cyclohexyl hydroxyl amine 0.237g (2.06 m. mole) was added to a solution of 0.281g (2.06 m. mole) chloro hydrin in dry ether (100 ml) with anhydrous $MgSO_4$, under nitrogen atmosphere and was kept at R.T for 24 hrs, while the reaction was monitored by TLC (Silica gel ; ethyl acetate/ Benzene = 1 : 10) .

Chloro acrylonitrile, 0.180g (2.06 m. mole) was added at this stage and the reaction mixture was again kept at R.T for further 48 hrs. The solvent was evaporated off to afford the cycloadduct as yellow gummy liquid (0.326g). The product was purified by column chromatography, using 20g. Silica gel and

Benzene : Pet ether = 1 : 1 as eluent.

Yield : 49.29 %

Rf : 0.83 (Benzene / ethyl acetate = 10 : 1)

IR ($CHCl_3$): 3384(b); 2932(s); 2856(s); 2337(m); 1603(b); 1451; 1383; 1153;

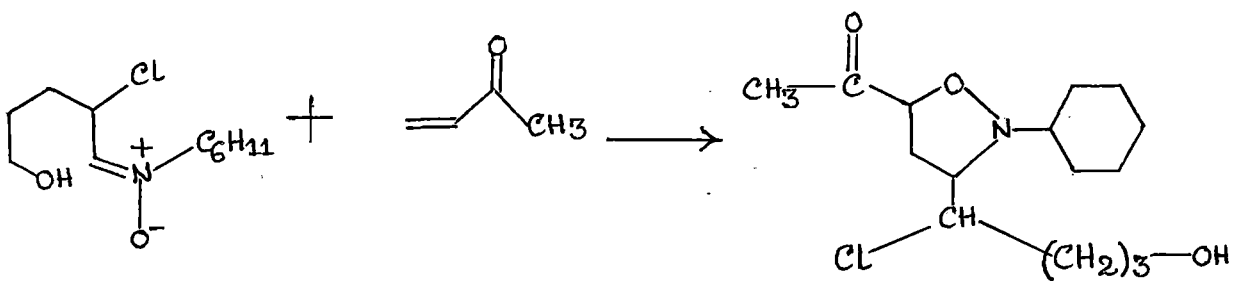
Mass (m/z) : 321(M^+); 308(B.P); 297; 288; 260; 248; 241; 231; 227; 210; 202; 193; 186; 184; 145; 131; 119; 117; 114; 102; 52; 35; 18 .

PMR ($CDCl_3$) :

δ 5.9-5.8 (b, 1H, -OH);
4.1-3.9 (m, 1H, -CH-Cl) ;
3.45-3.36 (q, J = 6.06, X part of ABX spectrum, 1H, C(3)H)
3.0-2.86 (dd, J = 6.06 Hzs & J = 15.15 Hzs, AB part of ABX spectrum, 2H, $C(4)H_2$)
2.78-2.68 (m, 1H, >N - CH<)
2.3-0.8 (m, 16H, $-(CH_2)_8-$)

Structure is expected to be Syn with respect to - CH - Cl .
|

8. Reaction of Nitrone With Methyl Vinyl Ketone:



N- cyclohexyl hydroxyl amine, 0.253g (2.20 m. mole) was added to a solution of 0.300g (2.20 m. mole) of chlorohydrin in dry ether (100 ml) with anhydrous $MgSO_4$, under nitrogen atmosphere and was kept at R.T for 24 hrs, while the reaction was monitored by TLC (Silica gel; ethyl acetate / Benzene = 1:10).

Methyl Vinyl Ketone, 0.154g (2.20 m. mole) was added at this stage and the reaction mixture was again kept at R.T for further 48 hrs. The solvent was evaporated off to afford the cycloadduct as oily greenish liquid (0.586g). The product was purified by column chromatography, using 20g Silica gel, and Benzene as eluent.

Yield : 87.76%

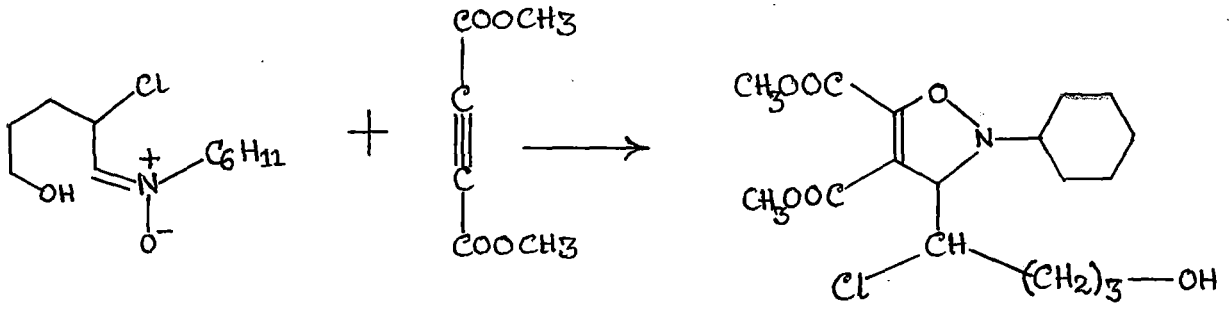
Rf : 0.24 (Benzene / ethyl acetate = 10 : 1)

IR (Neat) : 3440(br); 2920(s); 2840(s); 1710(s); 1440; 1320.

Mass (m/z): 303(M^+); 298; 281; 274; 260; 246; 236; 228; 211; 206; 186; 176; 169; 158; 148; 141; 119; 102; 85; 52; 35(B.P); 18.

PMR ($CDCl_3$): δ 4.9-4.8 [t, J = 6.06 Hzs, X part of ABX spectrum, 1H, C(5)H]
4.15-4.07 (b, 1H, >CH-Cl)
4.07-3.9 [m, 1H, J = 6.06, J = 9 Hzs, X part of MABX spectrum C(3)H]
3.6-3.5 [q, J = 6.06 Hzs, 1H, AB part of MABX spectrum, C(4)H]
2.54-2.48 [b, 1H, >N-CH<]
2.1 [s, 3H, CH_3-]
2-0.8 (m, 16H)

9. Reaction of Nitrone With Dimethyl Acetylene di carboxylate:



N- cyclohexyl hydroxyl amine 0.263g (2.28 m. mole) was added to a solution of 0.312g (2.29 m. mole) chlorohydrin in dry ether (100 ml) with anhydrous $MgSO_4$, under nitrogen atmosphere and was kept at R.T. for 24 hrs, while the reaction was monitored by TLC (Silica gel; ethyl acetate / Benzene = 1:10) .

Dimethyl acetylene dicarboxylate 0.325g (2.28 m. mole) was added at this stage and the reaction mixture was again kept at R.T. for further 48 hrs. The solvent was evaporated off to afford the cycloadduct as oily yellow liquid (0.698g). The product was purified by column chromatography using 20 g Silica gel and Benzene : ether = 5:1 as eluent.

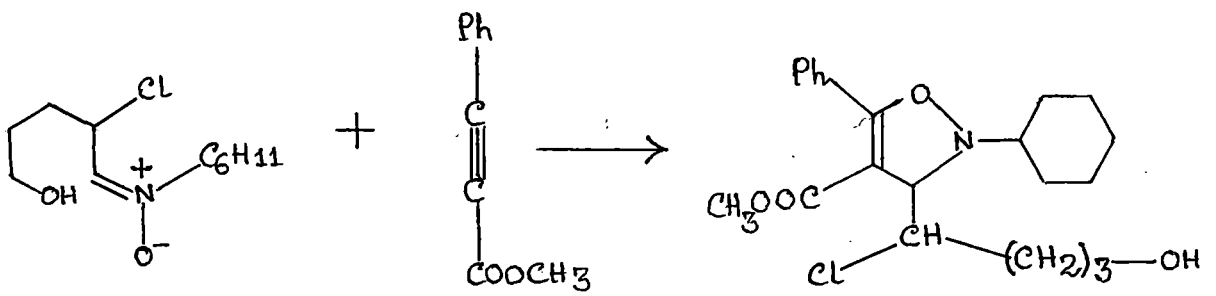
Yield : 81.09 %

Rf : 0.56 (Benzene/Ethyl acetate = 10 : 1)
IR : 3600-3316(b); 2960(s); 2940(s); 1740(s); 1720(s); 1520(s); 1440(m); 1320; 1080;

Mass (m/z) : 375(M^+); 369; 367; 351; 345; 331; 328; 312; 306(B.P); 298; 284; 275; 270; 258; 242; 236; 234; 219; 203; 189; 172; 158; 139; 131; 122; 117; 100; 69;.

PMR ($CDCl_3$) : δ 5-4.9 (d, J = 4.5Hz, 1H, C(3)H)
3.8-3.7 (d, J = 2Hz 1H, -CHCl)
3.63 (S, 3H, $-CO_2Me$)
3.59 (S, 3H, $-CO_2Me$)
2.7-2.5 (b, 1H, - N - CH<)
2.3-0.9 (m, 16H, $-(CH_2)_8-$).

10. Reaction of Nitrone With Phenyl - methyl propiolate



N - cyclohexyl hydroxyl amine 0.251g (2.18 m. mole) was added to a solution of 0.298g (2.19 m. mole) chlorohydrin in dry ether (100 ml) with dry $MgSO_4$, under nitrogen atmosphere and was kept at R.T for 24 hrs, while the reaction was monitored by TLC (Silica gel; ethyl acetate/Benzene = 1:10).

Phenyl - methyl - propiolate, 0.348g (2.18 m. mole) was added at this stage and the reaction mixture was again kept at R.T for further 48 hrs. The solvent was evaporated off to afford the cycloadduct as Red liquid (0.573g) . The product was purified by column chromatography using 20g Silicagel and Benzene : ether = 4 : 1 as eluent .

Yield : 66.79 %

Rf : 0.42 (Benzene / ethyl acetate = 10 : 1)

IR : 3620-3540(b); 2940(s); 2920(s); 1760(s); 1440; 1360; 1240; 1120; 1080; 960 ;.

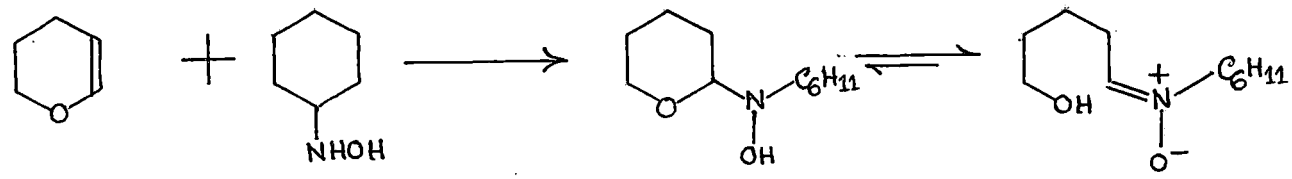
Mass (m/z) : 393(M^+); 385; 378; 372; 354; 336; 344; 336; 324; 319; 316; 302; 299; 288; 275; 361; 260; 253; 234; 217; 204; 195; 186; 178; 119; 102; 69 ;.

PMR ($CDCl_3$):

δ 7.85-7.35 (m, 5H, $-C_6H_5$)
4.55-4.45 (q, J = 6.06 Hzs, 1H, C(3)H)
3.9 -3.8 (b, 1H, - CHCl)
3.7 (S, 3H, $-CO_2CH_3$)
2.8-2.75 (m, 1H, >N - CH<)
2.3-0.8 (m, 16H, $-(CH_2)_8$ -)

Preparation of N- cyclohexyl 5 - hydroxy Nitrone (245)

N- cyclohexyl hydroxyl amine 0.250g(2.17 m. mole) was added to a solution of 2,3 dihydro -4H- pyran 0.2 ml [0.182g; 2.17 m. mole] in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 12 hrs, while the reaction was monitored by TLC (Silica gel , Ethyl acetate / Benzene = 1:10). The solvent was evaporated off and the soild nitrone was isolated by column chromatography, (Benzene / Pet - ether (60° - 80°).



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

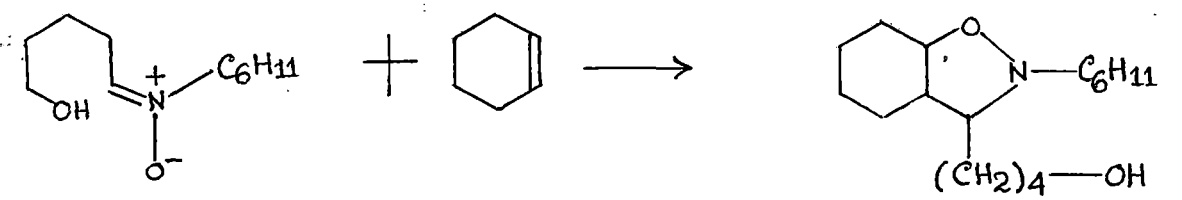
PMR ($CDCl_3$) : δ **6.0-5.8 (b, m,**  **- CH)**

2.5-2.3 (m, $(CH_2)_4$ -OH),

1.9-1.2 (m, 10H).

The nitrone was generated from dihydropyran by the above method and used in-situ for the following reactions.

1. Reaction of Nitrone With Cyclohexene :



N- cyclohexyl hydroxyl amine, 0.252g (2.19 m. mole) was added to a solution of 2,3 dihydro -4H- Pyran (0.1846g = 2.21 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 24 hrs, while the reaction was monitored by TLC (Silica gel, ethyl acetate / Benzene = 1:10) .

Cyclohexene 0.177g (2.15 m. mole) was added at this stage and the reaction mixture was further refluxed for 24 hrs. The solvent was evaporated off to afford the cycloadduct as gray solid (0.207g). The product was purified by column chromatography using 20g Silica gel and Benzene as eluent.

Yield : 34.26 %

M.P. : 106° c

Rf : 0.30 (Benzene : ethyl acetate = 10 : 1)

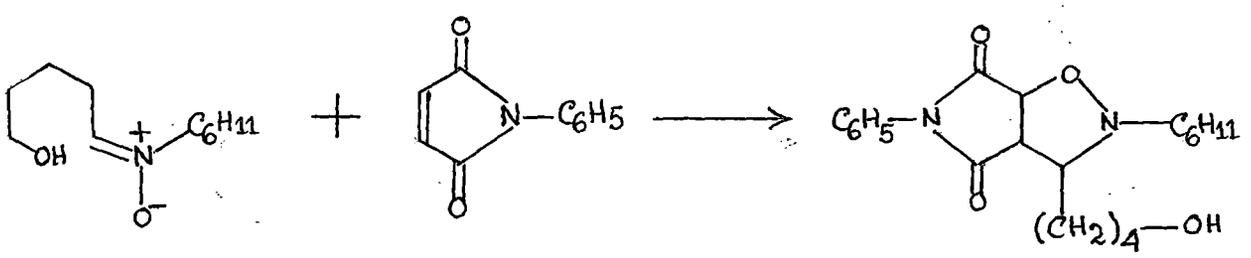
IR ($CHCl_3$) : 3264(br), 2924, 2851, 1540, 1443, 1248 .

Mass (m/z) : 281(M^+); 113(b.p); 98; 42; 18;.

PMR ($CDCl_3$): δ

3.80-3.7 (d, 1H, J = 4.5Hz, C(5)H)
3.10-3.06 (b, 1H, >CH - N<)
2.63-2.46 (q, 1H, J = 7.5Hz, C(3)H)
2.36-2.16 (dd, 1H, J = 4.5, J = 7.5Hz, C(4)H)
2.00-0.50 (m, 26H)

2. Reaction of Nitrone With N- phenyl maleimide :



N- cyclohexyl hydroxyl amine, 0.250g (2.17 m. mole) was added to a solution of 2,3 -dihydro -4H- pyran, 0.1822g (2.17 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 124hrs, while the reaction was monitored by TLC (Silica gel, ethyl acetate / Benzene = 1:10) .

0.3514g (2.13 m. mole) N- phenyl maleimide was added at this stage and the reaction mixture was further refluxed for 24 hrs. The solvent was evaporated off to afford the cyclo adduct as yellowish white solid (0.210g). The product was purified by column chromatography using 20g Silica gel and Benzene as eluent.

Yield : 30.4 %

M.P. : 132° c

Rf : 0.34 (Benzene : ethyl acetate = 10 : 1)

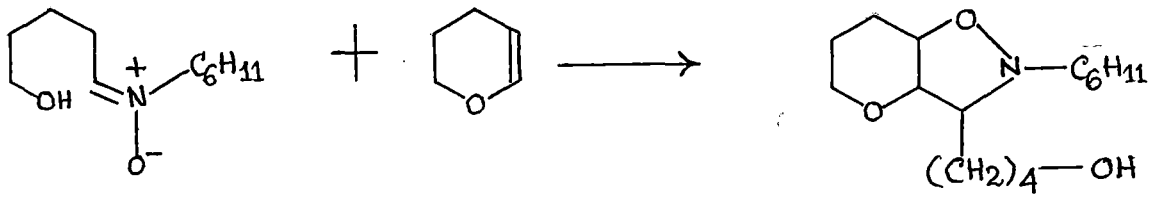
IR ($CHCl_3$): 3460(br), 2940; 2840; 1700; 1690; 1480; 1395; 1190 ;.

Mass (m/z): 372(M^+), 299, 289, 242, 173, 117, 113, 78.

PMR: ($CDCl_3$): δ

7.8-7.3 (m, 5H, C_6H_5).
5.7-5.46 (b, 1H, C(5)H, exchanged in D_2O shake).
4.5-4.26 (dd, 1H, J = 6Hz, C(4)H)
3.38-3.1 (dd, 1H, J = 6.0Hz, C(3)H).
3.0-2.83 (m, 1H, >CH - N<)
2.16-0.43 (m, 18H).

3. Reaction of Nitrone With Dihydropyran :



N- cyclohexyl hydroxyl amine, 0.261g (2.36 m. mole) was added to a solution of 2,3 - dihydro - 4H - pyran 0.3964g (4.72 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 48 hrs, while the reaction was monitored by TLC (Silica gel, Ethylacetate / Benzene = 1:10). The solvent was evaporated off to afford the cycloadduct as brown solid, (0.212g). The product was purified by column chromatography, using 15g Silica gel and Benzene as eluent.

Yield : 31.74 %

M.P. : 103° c

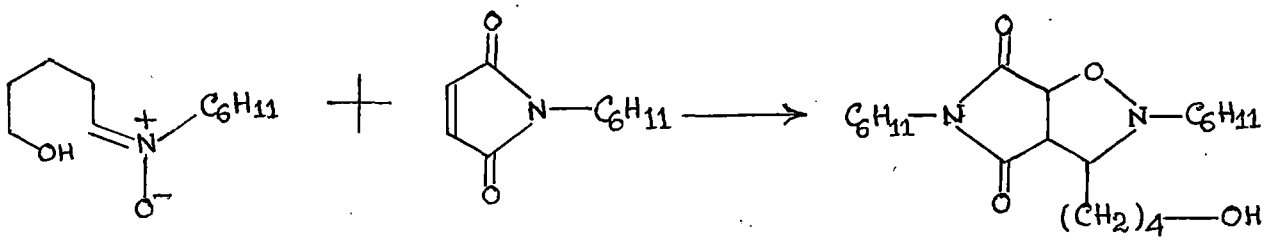
Rf : 0.42 (Benzene : ethyl acetate = 10 : 1)

IR ($CHCl_3$): 3580(s); 3300-3160(b); 2880(s); 2740(m); 1660(s); 1440(b); 1360(m); 1310; 1240-1190(b); 1130; 1100(s); 980;.

Mass (m/Z) : 283(M^+); 227; 209; 193; 182; 168; 152; 142; 114; 98;.

PMR ($CDCl_3$): δ 2.5-2.4 (C-5, 1H, t,)
2.3-2.2 (C-4, 1H, d,)
2.2-2.1 (>N - CH, m,)
1.7-1.6 (C3 - 1H, m,)
1.6- 1.5 (m, 24H).

4. Reaction of Nitrone With N- cyclohexyl maleimide :



N- cyclohexyl hydroxyl amine, 0.251g (2.17 m. mole) was added to a solution of 2,3 dihydro -4H- pyran, 0.182g (2.17 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 24 hrs, while the reaction was monitored by TLC (Silica gel, ethyl acetate Benzene = 1:10) .

N- cyclohexyl maliemide, 0.3884g (2.16 m. mole) was added at this stage and the reaction mixture was further refluxed for 24 hrs. The solvent was evaporated off to afford the cycloadduct as yellow solid (o.242g). The product was purified by column chromatography using 20g Silica gel and Benzene as eluent.

Yield : 29.50 %

M.P. : 114° c

Rf : 0.38 (Benzene : ethyl acetate = 10 : 1)

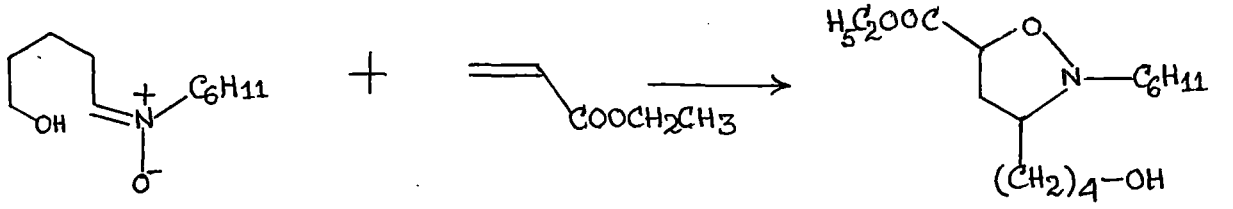
IR ($CHCl_3$): 3580, 2920(br), 1775, 1690, 1440, 1390, 1140, 890.

Mass (m/z): 378(M^+), 323, 305, 295, 277, 267, 251, 208, 196, 170, 114, 83 .

PMR ($CDCl_3$) : δ

5.75-5.0 (b, 1H, C(5)H, exchanged in D_2O shake).
4.15-3.93 (dd, 1H, J = 6.06 Hz, J = 6.06, C(4)H).
3.20-3.10 (m, 1H, >CH - N<)
3.06-2.94 (dd, 1H, J = 6.06Hz, C(3)H)
2.93-2.84 (m, 1H, >CH - N<^{O})
2.20-1.03 (m, 28H)

5. Reaction of Nitrone With Ethyl acrylate :



N- cyclohexyl hydroxyl amine 0.255g (2.20 m. mole) was added to a solution of 2,3 dihydro 4H - Pyran, 0.182g (2.17 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 24 hrs, while the reaction was monitored by TLC (Silica gel, ethyl acetate / Benzene = 1:10) .

Ethyl acrylate, 0.217g (2.17 m. mole) was added at this stage and the reaction mixture was further refluxed for 24 hrs. The solvent was evaporated off to afford the cyclo adduct as dark red liquid (0.363g). The product was purified by column chromatography using 25g Silica gel and Benzene : Pet ether = 1:2 as eluent.

Yield : 55.94 %

Rf : 0.46 (Benzene : ethyl acetate : 1:10).

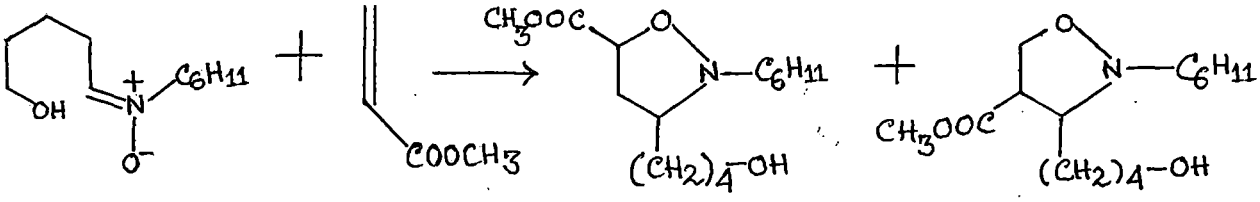
IR ($CHCl_3$) : 3340(br), 2930, 2850, 1725, 1440.

Mass (m/z) : 299(M^+); 296; 242; 226; 204; 187; 142; 131(b.p).

PMR ($CDCl_3$) : δ

4.77-4.64 (b, 1H, C(5)H, exchanged in D_2O shake).
4.20 (q, 2H, - O CH_2CH_3).
3.10-2.98 (t, 1H, J = 8.1Hz, C(3)H).
2.98-2.80 (b, 1H, >CH - N<).
2.80-2.60 (q, 2H, J = 8.1Hz, $C(4)H_2$).
2.35-0.60 (m, - CH_3 and remaining protons).

6. Reaction of Nitrone With Methyl Acrylate :



N- cyclohexyl hydroxyl amine, 0.254g (2.18 m. mole) was added to a solution of 2,3 dihydro -4H- pyran, 0.182g (2.17 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 24hrs, while the reaction was monitored by TLC (Silica gel, ethyl acetate/Benzene = 1:10) .

Methyl acrylate, o.1866g (2.16 m. mole) was added at this stage and the reaction mixture was further refluxed for 24 hrs. The solvent was evaporated off to afford two cycloadducts as yellow liquids (0.400 g) identified by TLC. The products were purified and separated by column chromatography using 20g silica gel.

Benzene : Pet ether = 1 : 2 (eluent for product A)
Benzene : Pet ether = 1 : 1 (eluent for product B)

Yield : 64.67 % (total)

Physical Data for Product A :

Rf : 0.47 (Benzene : ethyl acetate = 10:1)

IR (Neat) : 3360(b); 2960(s); 2940(m); 1760(s); 1440; 1400; 1320; 1300; 1160; 1120; 880;.

Mass (m/z) : 285(M^+); 278; 267; 262; 252; 236; 221; 211; 196; 180; 169; 151; 154; 128; 126; 113; 98; 83; 55;.

PMR ($CDCl_3$) : δ 3.7 (C-5, 1H, b)
3.1-2.9 (C-4, 2H, b, m,)
2.7 (- C(=O) - OCH_3 , 3H,)
2.2-2.1 (>N - CH< , m)
1.8-1.6 (C-3, 1H, m,)

1.4-1.2 (m, 14H) ;

Physical Data for Product B

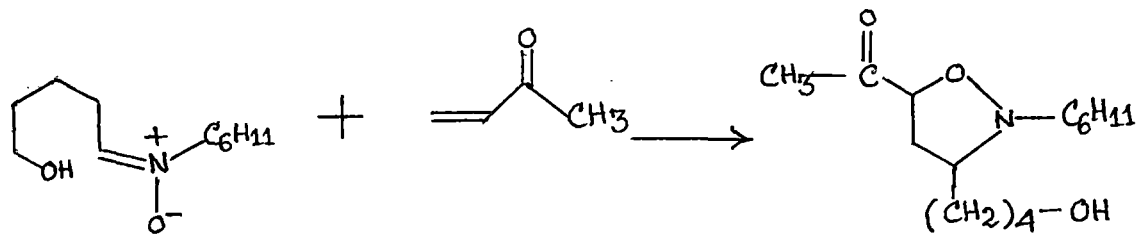
Rf = 0.38

IR (Neat) : 3360(b); 2940(s); 2920(m); 1740(s); 1435; 1400; 1250; 1130; 860;

Mass (m/z) : 287 (M+2); 285(M^+); 267; 242; 229; 211; 209; 183; 178; 165; 102.

PMR ($CDCl_3$) : δ 3.75-3.6 [s, 3H, $-OCH_3$]
3.1-2.8 [m, 2H, $C(5)H_2$ AB part of ABX spectrum, J = 12.3 Hzs]
2.8-2.6 [m, X part of ABX spectrum, 1H, C(4)H & 1H of >CH - N<]
2.4-2.3 [q, 1H, J = 6.06 Hzs, C(3)H]
1.9-1.1 [m, 18H,]

7. Reaction of Nitrone With Methyl Vinyl Ketone :



N- cyclohexyl hydroxyl amine, 0.250g (2.17 m. mole) was added to a solution of 2,3 dihydro -4H- Pyran, 0.182g (2.17 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 124hrs, while the reaction was monitored by TLC (Silica gel, ethyl acetate / Benzene = 1:10).

Methyl Vinyl Ketone, 0.151g (2.17 m. mole) was added at this stage and the reaction mixture was further refluxed for 24 hrs. The solvent was evaporated off to afford the cycloadduct as crystalline white solid (0.453g). The product was purified by column chromatography using 25g Silicagel and Benzene : Pet ether = 2:1 as eluent.

Yield : 77.60 %

M.P. : 140° c

Rf : 0.30 (Benzene : ethyl acetate = 10:1)

IR : 3200(b); 2960(s); 2940(s); 1700; 1650; 1480; 1440; 1240; 1120; 1000; 960; 920;.

Mass (m/z) : 269(M^+); 254; 242; 225; 206; 183; 168; 156; 142; 114; 96; 41;.

PMR ($CDCl_3$): δ

2.6-2.5 (C-5, 1H, m,)

2.4 (- C(=O) -CH_3 , 3H, S)

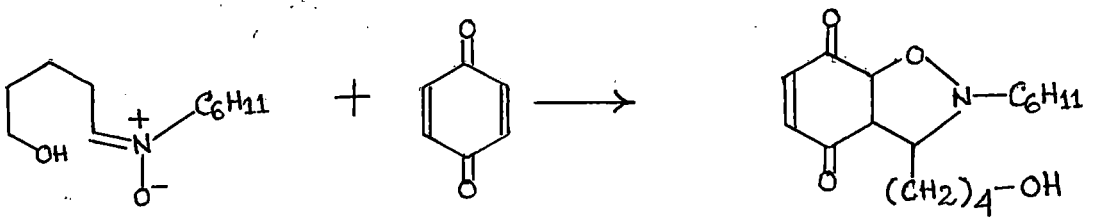
2.3 (C-4, 2H, m)

2.2 (>CH - N< , m)

1.7 (C-3, 1H, m,)

1.5 (m, 18H),

8. Reaction of Nitrone With P-benzoquinone :



N- cyclohexyl hydroxyl amine, 0.250g (2.17 m. mole) was added to a solution of 2,3 dihydro -4H- Pyran, 0.182g (2.17 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 24hrs, while the reaction was monitored by TLC (Silica gel, ethyl acetate / Benzene = 1:10) .

P-benzoquinone, 0.234g (2.16 m. mole) was added at this stage and the reaction mixture was further refluxed for 24 hrs. The solvent was evaporated off to afford the cyclo adduct as brown solid (0.417g). The product was purified by column chromatography using 20g Silicagel and Benzene : Pet-ether = 4:1 as eluent.

Yield : 62.65 %

M.P. : 143° c.

Rf : 0.45 (Benzene / ethyl acetate = 10:1)

IR : 3200(b); 2960(s); 2940(m); 1660; 1480; 1440; 1240; 1120; 960; 920 ;.

Mass (m/z) : 307(M^+); 302; 285; 251; 224; 202; 169; 126; 113; 110; 98; 72;.

PMR ($CDCl_3$) :

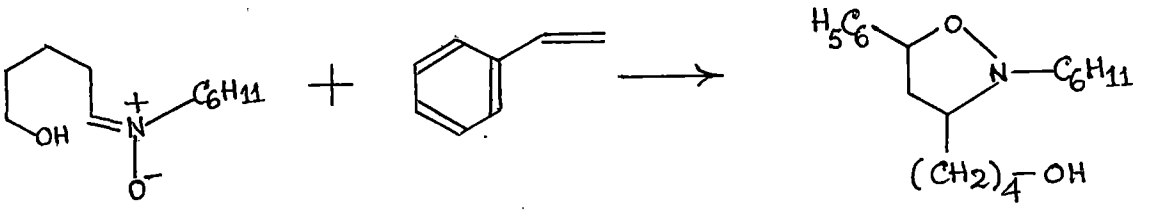
δ 6.7 (O =C(H)–C(H)= O, 2H, S,)

2.5 (C-5, m, 1H,)
2.3 (C-4, m, 1H,)

2.2 (>N – CH , 1H, m)

1.7 (C-3, 1H, m)
1.6 (m, 18H)

9. Reaction of Nitrone With Styrene :



N- cyclohexyl hydroxyl amine, 0.255g (2.18 m. mole) was added to a solution of 2,3 dihydro -4H- Pyran, 0.182g (2.17 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 124hrs, while the reaction was monitored by TLC (Silica gel, ethyl acetate / Benzene = 1:10).

Styrene, 0.2256g (2.44 m. mole) was added at this stage and the reaction mixture was further refluxed for 24 hrs. the solvent was evaporated off of afford the cyclo adduct as Brown solid (0.3027g). The product was purified by column chromatography using 20g Silicagel and Benzene : ether = 5:1 as eluent.

Yield : 46.03 %
M.P. : 137° c

Rf : 0.52 (Benzene / ethyl acetate = 10:1)

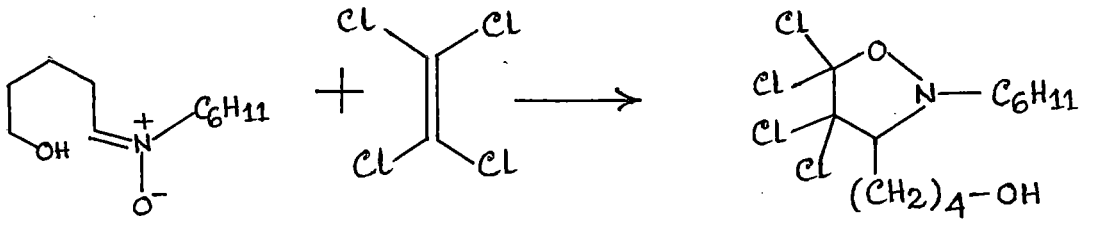
IR : 3580(s); 3200-3180(b); 2920(s); 2840(s); 1650(m); 1440(b); 1350(s); 1310; 1230-1180(b); 1130; 1100; 990(s); 930(s); 880(s);.

Mass (m/z) : 303(M^+); 299; 260; 232; 204; 154; 142; 114; 96;.

PMR : δ
($CDCl_3$)

7.5-7.00	(5H, m, C_6H_5)
2.6-2.5	(1H, m, C_5H , J = 6.06 Hz)
2.3-2.2	(2H, dd, C_4H)
2.1-2.0	(1H, m, C_3H)
1.8-1.7	(- N - CH , m)
1.6-1.4	(m, 18H).

10. Reaction of Nitrone With Tetra-Chloro-ethylene



N- cyclohexyl hydroxyl amine, 0.249g (2.16 m. mole) was added to a solution of 2,3 dihydro -4H- Pyran, 0.182g (2.17 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 24hrs, while the reaction was monitored by TLC (Silica gel, ethyl / Benzene = 1:10) .

Tetra-chloro-ethylene was added, 0.36g (2.17 m. mole) at this stage and the reaction mixture was further refluxed for 24 hrs. The solvent was evaporated off to afford cycloadduct as brown solid (0.276g). The product was purified by column chromatography using 20g Silicagel and Benzene:ether = 5:1 as eluent.

Yield : 34.84 %

M.P. : $99^{\circ} - 102^{\circ}$ c

Rf : 0.34 (Benzene : ethyl acetate = 10:1)

IR : 3580(s); 3320-3140(b); 2900(s); 2840(m); 1660(s); 1440-1400; 1360; 1310(s); 1220-1190(b); 1130; 1100; 980; 930; 880;.

Mass (m/z) : 365(M^+); 227; 211; 194; 168; 152; 142; 114; 98;.

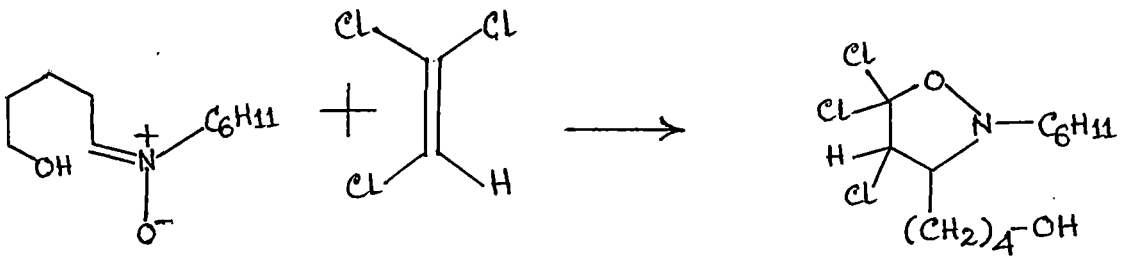
PMR ($CDCl_3$)

δ 2.6-2.5 (m, >N - CH< ;)

2.3-2.2 (m, C-3, 1H)

1.7-1.5 (m, 18H);

11. Reaction of Nitrone With Trichloro ethylene :



N- cyclohexyl hydroxyl amine, 0.253g (2.18 m. mole) was added to a solution of 2,3 dihydro -4H- Pyran, 0.182g (2.17 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 24hrs, while the reaction was monitored by TLC (Silica gel, ethyl acetate / Benzene = 1:10).

Trichloro ethylene, 0.287g (2.19 m. mole) was added at this stage at the reaction mixture was further refluxed for 24 hrs. The solvent was evaporated off to afford the cyclo adduct as yellowish white solid (0.2713g). The product was purified by column chromatography using 20g. Silicagel and Benzene : Pet-ether = 1:1 as eluent.

Yield : 37.82 %

M.P. : 98° c

Rf : 0.31 (Benzene : ethyl acetate = 10:1)

IR : 3580(s); 3300-3200(b); 2920(s); 2840(m); 1660(m); 1440(m); 1360; 1310; 1250-1190(b); 1130(s); 1100(s); 980(s); 930; 880;.

Mass (m/z) : 330(M^+); 283; 233; 207; 190; 163; 147; 114; 96; 69; 61;.

PMR ($CDCl_3$):

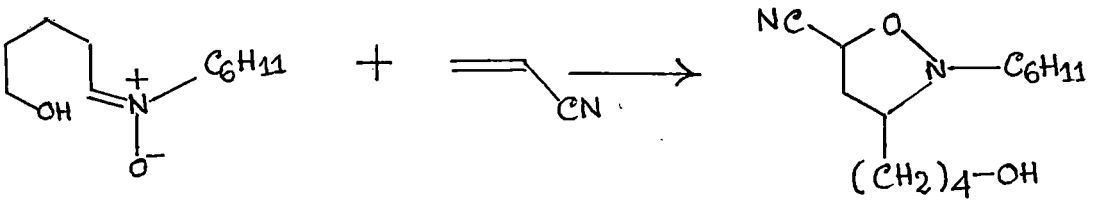
δ 2.5 (m, C-4, 1H,)

2.3 (m, >N - CH<;)

2.2 (m, C-3, 1H ;)

1.6 (m, 18H);.

12. Reaction of Nitrone With Acrylonitrile :



N- cyclohexyl hydroxyl amine,0.260g (2.26 m. mole) was added to a solution of 2,3 dihydro -4H- Pyran, 0.1997g (2.36 m. mole) in dry benzene (20 ml) under nitrogen atmosphere and was refluxed for 24hrs, while the reaction was monitored by TLC (Silica gel, ethyl acetate / Benzene = 1:10). Acrylonitrile, 0.134g (2.46 m. mole) was added at this stage and the reaction mixture was further refluxed for 24 hrs. The solvent was evaporated off to afford the cyclo adduct as dark yellow gummy liquid (0.443g). The product was purified by column chromatography using 20g Silicagel and Benzene : Pet-ether = 5:1 as eluent.

Yield : 77.78 %

Rf : 0.25 (Benzene : ethyl acetate = 10:1)

IR : 3222(b); 2934(s); 2857(m); 1664(m); 1449; 1437; 1385; 1350; 1225; 1138; 1073; 993; 899;.

Mass (m/z) : 252 (M^+); 227; 187; 170; 142; 131(B.P); 114; 52;.

PMR ($CDCl_3$) :

δ 3.7-3.5 (C-5- 1H, m;)

3.1-2.9 (C-4, -2H, m;)

2.5 (m, >N - CH<;)

2.2 (m, C-3, 1H ;)

1.7-1.5 (m, 18H);