PART - V

RESULTS AND DISCUSSIONS
In this chapter, at first the genesis of the problem will be described. In connection with another project, reductive removal of the hydroxyl group in compound (3a) was required. It was reported by Whalley et al. that allylic trimethylsiloxy group can be reductively removed with lithium aluminium hydride and aluminium chloride under mild reaction conditions, e.g., 3β-trimethylsiloxy-cholest-4-ene (1) when treated with LAH-AlCl₃ furnished 4α-cholestene (2) in ~90% yield.

However, reaction of compound (3a) with LAH-AlCl₃ furnished only calamenene (4).
It was, therefore, decided to search out milder reaction conditions for the reductive removal of allylic trimethylsiloxy group in compound (3b). Reaction of compound (3b) with sodium borohydride in methanol did not furnish any product and the starting material was recovered quantitatively. Since sodium borohydride in dimethyl sulfoxide and diethylene glycol dimethyl ether (diglyme) was reported to be more effective in the reductive removal of tosylates and halides, the reaction of compound (3b) was attempted with sodium borohydride in diglyme, but no reaction was observed (t.l.c.). At this stage it was decided to try the reaction of compound (3b) with nickel boride which has been earlier exploited for the cleavage of carbon-sulfur bonds. Therefore, nickel chloride was added to the above reaction mixture which resulted in the immediate formation of black precipitate of nickel boride. Reaction mixture was stirred at room temperature for 20 min when t.l.c. indicated that all the starting material was converted into a new product which was identified as (4a).
Similarly, reaction of the alcohol (5a) and (7a) with hexamethyldisilazane and chlorotrimethylsilane furnished the corresponding trimethylsilyl ethers (5b) and (7b) respectively in quantitative yield which on treatment with nickel boride (generated in situ) furnished the desired products (6) and (8) respectively in excellent yields.

\[(5)\quad a, \; R = H\]
\[b, \; R = -\text{SiMe}_3\]

\[(6)\]

\[(7)\quad a, \; R = H\]
\[b, \; R = -\text{SiMe}_3\]

\[(8)\]
Reduction of parthenin (9) with sodium borohydride in methanol at 0°C furnished the diol (10a) which on treatment with hexamethyldisilazane and chlorotrimethylsilane gave the silyl ether (10b) in quantitative yield. The reduction of (10b) with nickel boride in diglyme furnished a product in 60% yield which was identified as (11a) on the basis of NMR spectrum. In the NMR spectrum H-2 appeared as a multiplet at 5.30 ppm, the proton under the trimethylsiloxy group and H-6 appeared as overlapping signals at 4.00 to 4.20 ppm, H-7 appeared as a multiplet at 2.62 ppm, H-13, H-14 and H-15 appeared as overlapping signals at 1.30 ppm and the presence of a broad singlet at 0.20 ppm integrating to nine protons confirmed the presence of trimethylsiloxy group in it. The low resolution mass spectrum of (11a) recorded the molecular ion peak at m/z 322. Obviously, elimination of the tert-trimethylsiloxy group is attended with the migration of 2-3 double bond resulting in the formation of (11a). As the trimethylsiloxy group at C-4 is not allylic, it is not affected under the reaction conditions.

\[
\begin{align*}
(9) & \quad (10) & \quad (11) \\
 a, R_1 = R_2 = H & \quad b, R_1 = H, R_2 = \text{SiMe}_3 & a, R_2 = \text{SiMe}_3
\end{align*}
\]
Reaction of the diol (12a) with hexamethyldimethylsilazane and chlorotrimethylsilane furnished the trimethylsilyl ether (12b) in quantitative yield. Reaction of the trimethylsilyl ether (12b) with in situ generated nickel boride furnished a product in whose NMR spectrum, the presence of the methyl on double bond at 1.85 ppm suggested that the reductive elimination of the trimethylsiloxy group at C-3 is attended with the migration of the exomethylene group to furnish compound (13b). The NMR spectrum of (13b) further revealed the presence of the C-14 exomethylene protons at 4.90 ppm, H-3 appeared as a multiplet at 5.50 ppm, H-6, H-7 & H-8 appeared as overlapping signals at 3.50 to 4.20 ppm, H-13 - as a doublet with $J=7$ Hz at 1.40 ppm. A broad singlet at 0.25 ppm suggested the presence of one trimethylsiloxy group in it.

Further confirmation for the structure of compound (13b) was obtained by converting it into the acetate (13c) which on epoxidation with m-chloroperbenzoic acid in dichloromethane furnished the epoxide (14). In the NMR spectrum of epoxide (14), H-14 appeared as a multiplet at 5.20 ppm, H-8 - as a multiplet at 4.80 ppm, H-6 & H-7 - as overlapping signals at 3.60 to 4.20 ppm, H-13 as a doublet with $J=7.5$ Hz at 1.25 ppm, H-15 as a
singlet at 1.50 ppm and a singlet at 2.00 ppm suggested the presence of acetate.

\[(12) \quad a, \ R_1 = R_2 = H \]
\[(13) \quad a, \ R_2 = H \]
\[b, \ R_1 = R_2 = -\text{SiMe}_3 \]
\[c, \ R_2 = -\text{COCH}_3 \]

It is pertinent to know that nickel boride has been reported to act as a selective hydrogenation catalyst and some hydrogenation also takes place under the above reaction conditions\(^5\). However, no hydrogenation of the products (13b) and (11a) was observed.
Reaction of the trimethylsilyl ethers of cholest-4-en-3\(\beta\)-ol (1d) and cholest-5-en-4\(\beta\)-ol (15b) with nickel boride furnished cholest-4-ene and cholest-5-ene in 80 and 50% yield respectively.

Since the reductive removal of an allylic hydroxy group is normally difficult because of its propensity to undergo dehydration under mild reaction conditions, the single pot procedure described above for the reductive removal of trimethylsilyl ether group will make an attractive alternative to the existing methods\(^6\).

At this stage it was decided to examine the scope of this reaction on various other allylic functions. For this purpose various derivatives of cholest-4-en-3\(\beta\)-ol (1c) were prepared and their reactions with nickel boride were studied (Table 1).
\[ C, R = H g, R \sim -\text{COC}_6\text{H}_5 \]
\[ d( R \sim -\text{SiMe}_3 h, R * -\text{COC}_6\text{H}_4\text{Br}(p) \]

Table 1

Reductive removal of allylic functional groups with nickel boride and Raney nickel

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Reagent used</th>
<th>Time/r.t.</th>
<th>% Yield of(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>Nickel boride 8 hr</td>
<td>No reaction</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Raney nickel 8 hr</td>
<td>No reaction</td>
<td></td>
</tr>
<tr>
<td>lb</td>
<td>Nickel boride 8 hr</td>
<td>No reaction</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Raney nickel 6 hr</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>lc</td>
<td>Nickel boride 6 hr</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>ld</td>
<td>Nickel boride 6 hr</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Raney nickel 8 hr</td>
<td>No reaction</td>
<td></td>
</tr>
<tr>
<td>le</td>
<td>Nickel boride 10 min</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Raney nickel 7 hr</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>lf</td>
<td>Nickel boride 5 min</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>lg</td>
<td>Nickel boride 10 min</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Raney nickel 4 hr</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>lh</td>
<td>Nickel boride 5 min</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Raney nickel 5 min</td>
<td>60*</td>
<td></td>
</tr>
</tbody>
</table>

*30% of (1g) was also obtained.
It was observed that the reductive removal of an allylic functional group proceeds most easily and efficiently with nickel boride as the bond being cleaved becomes a better leaving group (e.g. OCH$_3$ (OH) (OSiMe$_3$

Although trifluoroacetate (1e) and p-bromobenzoate (1h) are most easily cleaved but preparation of the former from the allylic alcohol (1c) is attended with poor yield. Since acetates from primary or secondary allylic alcohols and trimethylsilyl ethers from tert-allylic alcohols can be obtained in almost quantitative yield and the subsequent reductive removal with nickel boride is carried out under extremely mild reaction conditions, it appears that this would prove to be a very useful procedure for achieving the transformation of an $\alpha,\beta$-unsaturated ketone to an olefin.

Although no reduction of the double bond was observed in the case of cholest-4-en-3$\beta$-ol (1c) and its derivatives, but in two other cases, the reduction of the double bond was observed.

Acetylation of the diol (10a) with acetic anhydride and pyridine furnished the acetate (10c). The reaction of compound (10c) with in situ generated nickel boride furnished a mixture of three products in equal amounts (A, B & C) which were identified as follows.
Compound (A), m.p. 105°C, exhibited the NMR signals at 5.30 ppm — a multiplet, 5.10 ppm — a doublet with \( J = 8 \) Hz, 4.16 ppm — a doublet with \( J = 6 \) Hz, an overlapping signals of three methyls were present at 1.20 ppm and a sharp singlet integrating to three protons was present at 2.10 ppm. Its IR spectrum displayed absorption band at 1765 and 1740 cm\(^{-1}\). The low resolution mass spectrum gave the molecular ion peak at m/z 292. On the basis of above data the structure (IIb) was assigned to (A).

The NMR spectrum of compound (B) was devoid of any signal due to olefinic protons. The only low field signal was that of proton under the lactone at 4.80 ppm — a doublet with \( J = 8 \) Hz. The IR spectrum showed an absorption band at 3500 cm\(^{-1}\) suggesting the presence of a hydroxyl group in it. In the IR spectrum, the lactone band appeared at 1765 cm\(^{-1}\) and it was devoid of any absorption due to acetoxy group. On the basis of above data, structure (17) was assigned to compound (B) which was fully corroborated by its mass spectrum where the molecular ion peak was observed at m/z 252.
Compound (C), m.p. 108-110°C (EtOAc), displayed the NMR signals at 5.60 ppm - a triplet with J=8 Hz, 4.80 ppm - a doublet with J=6.5 Hz, 2.80 ppm - a multiplet integrating to one proton and a sharp singlet - integrating to three protons at 2.00 ppm besides the presence of overlapping signals due to methyl groups at 1.00 - 1.40 ppm. The IR spectrum exhibited the absorption bands at 3500, 1770 and 1740 cm⁻¹ indicating the presence of hydroxyl, lactone and acetate functionalities. On the basis of above data structure (16) was assigned to compound (C) which was in full accord with its low resolution mass spectrum where the molecular ion peak was observed at m/z 310.
\[ \text{(10)} \]
\[ R_1 = H, \quad R_2 = -COCH_3 \]

\[ \text{(11)} \]
\[ R_2 = -COCH_3 \]

\[ \text{(16)} \]
\[ R_1 = H, \quad R_2 = -COCH_3 \]

\[ \text{(17)} \]
Reaction of the geranyl acetate (18) with nickel boride in diglyme furnished a mixture of two products (19) and (20). Similarly, the reaction of the epoxide (21) with nickel boride in diglyme furnished compound (22). Surprisingly no reductive removal of the allylic acetate was observed in these two cases. Obviously, reduction of the double bond is taking place at a faster rate as compared to the reductive removal of the allylic group.
Citral (a and b) was epoxidized with MCPBA in dichloromethane to furnish compound (23) which was reduced with sodium borohydride in methanol followed by acetylation of the crude mixture which was separated on t.l.c. to obtain compound (21) and (24). Reaction of (24) with nickel boride in diglyme furnished only compound (25).

Reductive removal of the allylic functions was also studied with Raney nickel and the results are discussed in table 1. Comparative study of the two catalysts, nickel boride and Raney nickel\(^7\) (table 1) reveals that the former is indeed a superior reagent for the reductive removal of an allylic acetate and the latter is superior for reductive removal of an allylic benzyl ether group\(^8\). The above observation could be made use of when selectivity is required.
It may be important to mention here that diglyme is the solvent of choice in the nickel boride reductive elimination reactions. Reactions were slow in methanol, ethanol, ether, tetrahydrofuran, dioxane and benzene.

Conversion of an $\alpha,\beta$-unsaturated ketone to an olefin is generally achieved through thioketal formation followed by Raney nickel desulphurization or Wolff-Kishner reduction. Another procedure is through allylic alcohol which on reduction with metal hydrides furnished the required olefin. The procedure described (Ni$_2$B) above would be a useful alternative to these methods.

Formation of nickel boride from sodium borohydride and nickel chloride is accompanied by a sufficient amount of hydrogen evolution which may be partly adsorbed on the catalyst surface and would be responsible for hydrogenation as well as the reductive removal of allylic functional groups.

\[
2\text{NiCl}_2 + 4\text{NaBH}_4 + 9\text{H}_2\text{O} \longrightarrow \text{Ni}_2\text{B} + 3\text{B(OH)}_3 + 4\text{NaCl} + 12.5\text{H}_2 \quad \text{(eq. 8a)}
\]
PART - V

EXPERIMENTAL

General procedure for the preparation of TMS ether of allylic alcohol:

To a solution of 0.25 m mol of the substrate in 2 ml of hexamethyldisilazane (a drop of pyridine was also added when the substrate was not soluble in the reagent) added 0.3 ml of CTMS and the reaction mixture was kept at room temperature for 1 h. The excess reagents were removed under vacuum and allylic TMS ether was obtained in quantitative yield which needed no purification.

General procedure for the preparation of allylic acetate:

To a solution of 0.25 m mol of the allylic alcohol in 2 ml of acetic anhydride added 1 ml of pyridine and the reaction mixture was kept for 12 hr at room temperature monitoring by t.l.c. The reaction mixture was diluted with water and extracted with chloroform (3 x 50 ml). Evaporation of the washed and dried extract at reduced pressure left pure allylic acetate in quantitative yield.
General procedure for reductive cleavage of allylic functions with nickel boride:

A solution of 0.25 m mol of the substrate (allylic functions) in 4 ml of dry diglyme was treated with 2 m mol of nickel chloride and 4 m mol of NaBH₄ and the reaction mixture was stirred at room temperature for 5 min to 8 hr monitoring by t.l.c. The reaction mixture was then quenched with water and extracted with chloroform (3 x 100 ml). The chloroform extract was washed well with water and dried over anhydrous sodium sulfate which was then evaporated under reduced pressure. The trace of diglyme present in the reaction mixture was then removed under high vacuum. The crude residue so obtained was then purified on preparative t.l.c. to get the pure products.
Preparation of methyl ether (1a):

A solution of 100 mg of the alcohol (1c) in 4 ml of dry N,N-dimethylacetamide was stirred at room temperature with 200 mg of NaH (50% dispersion in oil, washed with hexane). After half an hour 0.5 ml of methyl iodide was added and stirring was continued for 8 hr monitoring the reaction by t.l.c. The reaction mixture was quenched with cold water and extracted with chloroform (3 x 100 ml). The washed and dried extract was evaporated under reduced pressure and the trace of N,N-dimethylacetamide was removed using high vacuum. The crude residue on purification by preparative t.l.c. (EtOAc:Bz, 1:2) yielded 90 mg of (1a) as a crystalline solid m.p. 75°C (MeOH), reported m.p. 75 - 75.5°C.

Preparation of (1b):

To a solution of 100 mg of (1c) in 4 ml of dry N,N-dimethylacetamide added 200 mg of NaH (50% dispersion in oil, washed with hexane) and stirred at room temperature. After half an hour 0.5 ml of benzyl chloride was added and the stirring was continued for 12 hr. The reaction mixture was worked up as described in the preparation of methyl ether (1a). The crude residue after purification...
through preparative t.l.c. (EtOAc:Bz, 1:20) furnished 90 mg of (1b) as a crystalline solid m.p. 105°C (MeOH). It displayed IR bands at 3000, 1750, 1275 and 750 cm\(^{-1}\); NMR: 7.30 s br (aromatic protons), 5.35 m (H-4), 5.40 s br (O-CH\(_2\)-Ph), 5.30 s br (H-3); MS m/z 476 (M\(^{+}\)), 385, 369 and 71.

**Preparation of allylic alcohol (1c):**

A solution of 100 mg of cholestan-4-en-3-one in 4 ml methanol was stirred with 200 mg of NaBH\(_4\) at 0°C for 10 min. Usual work up followed by purification on preparative t.l.c. (EtOAc:Bz, 1:9) furnished 90 mg of (1c) as a crystalline solid m.p. 132°C (EtOAc), reported\(^{10}\) m.p. 131-132°C.

**Preparation of (1d):**

The reaction of 100 mg of the allylic alcohol (1c) with HMDS-CTMS as described in the general procedure furnished (1d) in quantitative yield as a crystalline solid m.p. 83°C, reported\(^{11}\) m.p. 83-86°C.
Preparation of (le) :

Acetylation of 100 mg of (lc) with $\text{Ac}_2\text{O}$-Pyridine as described earlier gave (le) in quantitative yield as a crystalline solid m.p. 85°C (MeOH), reported $^{12}$ m.p. 85°C.

Preparation of trifluoroacetate (if) :

To a solution of 100 mg of the allylic alcohol (lc) in 2 ml of pyridine added 0.5 ml of trifluoroacetic anhydride and was kept at 0°C for 15 min monitoring the reaction on t.l.c. Usual work up followed by preparative t.l.c. (EtOAc:Bz, 1:9) yielded 60 mg of (if) which was crystallized from acetone, m.p. 87°C, reported $^{13}$ m.p. 88°C.

Preparation of benzoate (lg) :

A solution of 100 mg of the alcohol (lc) in 1 ml of pyridine was treated with 2 ml of benzoyl chloride and the reaction mixture was kept at room temperature for 12 hr. Usual work up followed by preparative t.l.c. (EtOAc:Bz, 1:20) furnished 90 mg of crystalline (lg) m.p. 126°C (MeOH-acetone), reported $^{14}$ m.p. 125-128°C.
Preparation of (1h):

To a solution of 100 mg of the alcohol (1c) in 1 ml of pyridine was added 100 mg of p-bromobenzoyl chloride and the reaction mixture was kept at room temperature for 12 hr. Usual work up followed by preparative t.l.c. (EtOAc:Bz, 1:20) furnished 90 mg of (1h) as a gum. It showed IR bands at 3000, 1725, 1225 and 750 cm$^{-1}$; NMR signals at 7.90 d (J=8 Hz, H-2' & H-6'), 7.50 d (J=8 Hz, H-3' & H-5'), 5.40 s br (H-3); 5.50 m (H-4); MS m/z 569 (M$^+$), 489, 385, & 71.

Reaction of 1(a-h) with nickel boride:

Reductive cleavage of 100 mg of each of the substrates 1(a-h) with nickel boride in diglyme as described in the general procedure furnished (2) as a crystalline solid, m.p. 80°C, reported $^{15}$ m.p. 80-81°C, in yields as reported in the table 1. In case of (1a) and (1b) there was no reaction at all. The compound (2) was found to be identical with its authentic sample (t.l.c., mixed m.p.).
Reaction of (1e) with Raney nickel:

A solution of 100 mg of (1a) in 4 ml of absolute alcohol was treated with 200 mg of Raney nickel (in methanol) and stirred at room temperature monitoring the reaction on t.l.c. The reaction mixture was then diluted with water and extracted with chloroform. The extract after drying over anhydrous Na$_2$SO$_4$ was evaporated under reduced pressure. The crude residue on purification by preparative t.l.c. (EtOAc:Bz, 1:20) yielded 70 mg of (2) which was found to be identical with its authentic sample (t.l.c., mixed m.p.).

Following the above procedure the reactions of the substrates 1 (a, b, d, g and h) with Raney nickel were studied and the results are described in table 1 (see discussion).

Preparation of (3a):

Compound (3a) was prepared from the natural product available in our laboratory.$^{16}$

Reaction of (3a):

The reaction of (3a) with LAH-AlCl$_3$ as described in the ref. 1 furnished Calamenene (4).$^{16}$
Preparation of (3b):

The reaction of 50 mg of (3a) with HMDS-CTMS as described earlier furnished the ether (3b) as a gum in quantitative yield which was then treated with nickel boride as follows.

Reaction of (3b) with nickel boride:

The nickel boride reduction of 50 mg of (3b) in diglyme (for 20 min) as described earlier furnished after usual work up and purification by preparative t.l.c. (pet-ether) 38 mg of (4a) as an oil; \( \int_{25}^{\infty} D + 8^\circ \) (C, 0.35, CHCl\(_3\); reported\(^17\) \( \int_{D}^{\infty} + 175^\circ \); UV \( \max 243 \text{ nm} \) (\( \epsilon \) 12200); IR 1650, 1610 and 860 cm\(^{-1}\); NMR: 6.18 br (H-5), 3.10 m (H-1), 1.80 br (H-11), 1.00 d (J=7 Hz, H-13, H-14 & H-15); m/z m/z 204 (M\(^+\)), 189 and 161 (base peak).

Preparation of (5a):

Compound (5a) was prepared as discussed in the literature\(^16\).

Preparation of (5b):

The reaction of 100 mg of (5a) with HMDS-CTMS as described in the general procedure furnished (5b) in
quantitative yield as a gum. It showed IR bands at 3600 - 3700 (br), 1565, 1490, 1430, 1355, 1060, 1010 and 870 cm\(^{-1}\); NMR: 7.20 s br (H-16), 7.10 s br (H-17), 6.12 s br (H-15), 5.05 m (3H), 3.98 s br (H-19), 1.60 s (3H), 1.55 s (6H), 0.2 (SiMe\(_3\)); MS m/z 374 (M\(^+\)), 302, 286, 269, 252, 241, 231, 189, 95 and 81.

**Reaction of (5b) with nickel boride:**

The reaction of 100 mg of each of (5b) with nickel boride (for 1 hr) as described above furnished after preparative t.l.c. (EtOAc:Hexane, 1:20) 80 mg of ambiofuran (6). The t.l.c., NMR, IR and Mass spectral data (6) was identical with the authentic ambiofuran\(^{13}\).

**Preparation of (7a):**

Compound (7a) was prepared from the natural product available in the laboratory\(^{18}\).

**Preparation of (7b):**

The reaction of 100 mg of (7a) with HMDS-CTMS as described earlier furnished (7b) as a gum in quantitative yield. IR bands at 3600 - 3200 (br), 1420, 1405,
1370, 1240, 1170, 1110, 1060, 1075 and 875 cm⁻¹; NMR
7.27 s br (H-16), 7.10 s br (H-17), 6.15 s br (H-15),
5.00 – 5.40 (overlapping signals of H-7 and H-11),
4.00 s br (H-19), 1.55 s br (H-18), 1.25 s br (H-18 &
H-20), 0.20 (SiMe₃); MS m/z 390 (M⁺), 300, 259, 201, 168,
95 and 81.

Reaction of (7b) with nickel boride:

The reaction of 100 mg of (7b) with nickel boride
for 1.5 hr as described earlier furnished after preparative
t.l.c. (Bz:Hexane, 1:20) 75 mg of (8) as a gum. 60 mg of
(8) was then deoxygenated with toluene-p-sulphonic acid
and sodium iodide in acetonitrile in the usual way. Customary
work up and purification by preparative t.l.c. (EtOAc:Hexane,
1:1) furnished 52 mg of (6) as a gum which was identical
with authentic amblyofuran¹⁸ (t.l.c., NMR, IR and MS).

Sodium borohydride reduction of (9):

A solution of 100 mg of parthenin (9) isolated
from Parthenium hysterophorous, in 4 ml of methanol was
treated with 200 mg of NaBH₄ and stirred at 0°C for 15 min.
Usual work up followed by preparative t.l.c. (EtOAc:Bz,
1:1) furnished 70 mg of (10a) as a gum. IR bands at 3500,
1770 and 1225 cm\(^{-1}\); NMR: 5.80 br (H-2 & H-3), 5.00 d (J=6.5 Hz, H-6), 4.40 m (H-4), 3.30 m (H-7), 0.80 - 1.40 (overlapping signals of H-13, H-14 & H-15); MS m/z 266 (M\(^+\)), 249 & 232; Anal. calcd. for C\(_{15}\)H\(_{22}\)O\(_4\): C, 67.65; H, 8.33; Found: C, 66.95; H, 8.21.

**Preparation of (10b):**

Silylation of 100 mg of (10a) with HMDS-CTMS as described earlier furnished (10b) in quantitative yield as a gum. IR bands at 3500, 1770, 1225, 765 cm\(^{-1}\); NMR: 5.80 s (H-2 & H-3), 4.90 d (J=7 Hz, H-6), 2.90 m (H-7), 1.00 - 1.40 (overlapping signals of H-13, H-14 & H-15), 0.20 double intensity (2SiMe\(_3\)); Mass spectrum peaks were at m/z 410 (M\(^+\)), 264 and 71 (as base peak).

**Reaction of (10b) with nickel boride:**

The reductive cleavage of 100 mg of the TMS ether (10b) in diglyme for 1 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:3) 60 mg of (11a) as the least polar product which was crystallized from EtOAc, m.p. 67-68°C. It showed IR bands at 3500, 1770 and 1225 cm\(^{-1}\); NMR: 5.30 m (H-2), 4.00 - 4.20 (overlapping signals of H-4 & H-6), 2.62 m (H-7), 1.15 - 1.30
Preparation of (12a):

Compound (12a) was prepared from the natural product available in our laboratory.

Preparation of (12b):

The silylation of 100 mg of (12a) with HMDS-CTMS as described in the general procedure furnished (12b) in quantitative yield as a gum. IR bands at 3500, 1700 and 1600 cm⁻¹; NMR: 4.80 - 5.30 (overlapping signals of H-14 & H-15), 4.40 m (H-6), 3.40 - 4.00 (overlapping signals of H-3, H-7 and H-8), 1.40 d (J=7 Hz, H-13) and 0.20 (2SiMe₂). 

Reaction of (12b) with nickel boride:

The reaction of 50 mg of (12b) with nickel boride in diglyme for 1 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:12) 30 mg of (13b) as a gum. It showed IR bands at 3500, 1700, 1600 and 1350 cm⁻¹; NMR: 5.50 m (H-3), 4.90 m (H-14), 3.50 - 4.20 (overlapping signals of H-6, H-7 & H-8), 1.40 d (J=7 Hz).
H-13), 1.35 s (H-15), 0.25 s br (SiMe₃); MS m/z 320 (M⁺), 248 and 222.

**Acetylation of (13b):**

A solution of 80 mg of (13b) in 1 ml of pyridine was treated with 2 ml of acetic anhydride and heated on water bath for 3 hr. The reaction mixture was then quenched with cold water and extracted with chloroform (3 x 50 ml). The extract was then evaporated under reduced pressure and the residue was purified on preparative t.l.c. (EtOAc:Bz, 1:9) which furnished 36 mg of (13c) as a gum; IR bands at 1775, 1740, 1225, and 750 cm⁻¹; NMR: 5.40 m (H-3), 4.90 - 4.98 (overlapping signals of H-8 & H-11), 3.65 - 4.10 (overlapping signals of H-5 & H-7), 1.35 d (J=7 Hz, H-13), 1.85 s (H-15) and 2.00 (OAc); MS m/z 290, 247, 232 and 215.

**Epoxidation of (13c):**

A solution of 50 mg of (13c) in 4 ml of dichloromethane was treated with 50 mg of MCPBA and the reaction mixture was stirred at room temperature for 3 hr monitoring by t.l.c. Usual work up followed by preparative t.l.c. (EtOAc:Bz, 1:6) yielded 42 mg of (14) as a gum. IR bands at 1775, 1740, 1455, 1375, 1250, 1185, 1165, 1025 and 750 cm⁻¹.
NMR: 5.20 s (H-14), 4.00 m (H-8), 3.60 - 4.20 (overlapping signals of H-6 & H-7), 2.00 (acetate), 1.50 s (H-15), 1.25 d (J=7.5 Hz, H-13); MS m/z 306 (M+), 263, 247 and 231; Anal. calcd. for C_{17}H_{22}O_{3}: C, 66.65; H, 7.24; Found: C, 66.95; H, 7.01.

Preparation of (15a):

A solution of 120 mg of cholest-5-ene in 2 ml of dioxane and 0.20 ml of pyridine was treated with 120 mg of selenium dioxide and refluxed for 2 hr monitoring on t.l.c. The reaction mixture was quenched with water and extracted with dichloromethane. The washed and dried extract was evaporated under reduced pressure and the crude residue on purification by preparative t.l.c. (Bz:Hexane, 1:4) furnished 50 mg of 4β-hydroxycholest-5-ene (15a) identical with the authentic compound.

Preparation of (15b):

A solution of 100 mg of cholest-5-en-4β-ol (15a) in MeOH was treated with CSA as described in the general procedure of making the ether. After usual work up the residue (15b) was treated with nickel boride as follows.
Reaction of (15b) with nickel boride:

The reaction of 100 mg of (15b) with nickel boride for 6 hr as described earlier furnished after preparative t.l.c. (Bz:Hexane, 1:9) 50 mg of a compound which was found to be identical with authentic cholest-5-ene (t.l.c., mixed m.p.).

Preparation of (10c):

Acetylation of 100 mg of (10a) with acetic anhydride and pyridine furnished the monoacetate (10c) in quantitative yield as a gum. It displayed IR bands at 3500, 1770, 1735, 1245 cm⁻¹; NMR: 5.75 - 6.10 (overlapping signals of H-2, H-3 & H-4), 4.80 d (J=6 Hz, H-6), 2.70 m (H-7), 2.00 (OAc), 0.80 - 1.20 (overlapping signals of H-13, H-14 & H-15); m/z m/z 308 (M⁺), 291, 265 and 248.

Reaction of (10c) with nickel boride:

A solution of 100 mg of (10c) in 4 ml of diglyme was treated with nickel boride as described earlier. The reaction was continued for 3 hr monitoring by t.l.c. Usual work up followed by preparative t.l.c. (EtOAc:Bz, 1:3) furnished 30 mg of each of (11b), (16) and (17).
The least polar product was (11b) which was crystallized from EtOAc, m.p. 105°C. It exhibited IR bands at 1785, 1740, 1240, 785 and 770 cm\(^{-1}\); NMR: 5.30 m (H-2), 5.10 d (J=8 Hz, H-4), 4.16 d (J=6 Hz, H-6), 2.70 m (H-7), 2.10 (OAc), 1.20 - 1.15 (overlapping signals of H-13, H-14 & H-15); MS m/z 292 (M\(^+\)), 249, 234 and 71 (as base peak); Anal. calcd. for C\(_{17}\)H\(_{24}\)O\(_4\): C, 69.84; H, 8.27; Found: C, 70.12; H, 8.01.

The next in polarity was (17) as a gum; IR bands at 3500, 1765, 1225 and 765 cm\(^{-1}\); NMR: 4.80 d (J=8 Hz, H-6), 2.90 m (H-7), 1.00 - 1.40 (overlapping signals of H-13, H-14 & H-15); MS m/z 252 (M\(^+\)), 235 and 71; Anal. calcd. for C\(_{15}\)H\(_{24}\)O\(_3\): C, 71.93; H, 9.59; Found: C, 71.11, H, 9.32.

The most polar product was (16) as a crystalline, m.p. 108-110°C (EtOAc); IR bands at 3500, 1770, 1740, 1225, 765 cm\(^{-1}\); NMR: 5.60 t (J=8 Hz, H-4), 4.80 d (J=6.5 Hz, H-6), 3.60 br (OH), 2.60 m (H-7), 2.00 (OAc), 1.00 - 1.40 (overlapping signals of H-13, H-14 & H-15); MS m/z 310 (M\(^+\)), 292, 250, 232 and 71; Anal. calcd. for C\(_{17}\)H\(_{26}\)O\(_5\): C, 65.78; H, 8.44; Found: C, 65.34; H, 8.15.
Reaction of geranyl acetate (18) with nickel boride:

The reaction of 100 mg of (18) with nickel boride in diglyme for 1 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:20) 15 mg of (19) and 75 mg of (20) as an oil. Compound (19) exhibited IR bands at 2950, 1750, 1465, 1375, 1240 and 1025 cm⁻¹; NMR: 5.05 br (H-6), 4.00 t (J=6 Hz, H-1), 2.00 (OAc), 1.62 s (H-5), 1.55 s (H-10), 0.60 - 1.40 (overlapping signals of H-2, H-3, H-4 & H-9); MS m/z 198 (M⁺), 155 and 140.

Compound (20) displayed IR bands at 3485, 1750, 1470, 1380, 1250, and 1050 cm⁻¹; NMR: 4.10 t (J=6 Hz, H-1), 2.05 (OAc), 1.10 - 1.70 (overlapping signals of H-2, H-3, H-4, H-5 & H-6), 0.70 - 1.00 (overlapping signals of H-8, H-9 & H-10); MS m/z 200 (M⁺), 157 and 142.

Epoxidation of (19):

A solution of 50 mg of (19) in 4 ml of chloroform was treated with 1 ml of perbenzoic acid solution (8%) in chloroform and kept at room temperature for 12 hr monitoring on t.l.c. The reaction mixture was diluted with chloroform and washed successively with dilute KI.
solution, sodium thiosulfate solution and water.
Evaporation of the dried (anhydrous Na$_2$SO$_4$) extract
gave an oily residue which on purification by preparative t.l.c. (EtOAc:Bz, 1:20) furnished 40 mg of (22)
as an oil; IR bands at 2900, 1750, 1725, 1470, 1385,
1250, 1125 and 1055 cm$^{-1}$; NMR: 4.00 t (J=6 Hz, H-1),
2.60 m (H-6), 2.00 (OAc), 1.20 - 1.70 (overlapping
signals of H-2, H-3, H-4 & H-5), 1.20 br (H-8 & H-10),
0.90 d (J=7 Hz, H-9); MS m/z 214 (M$^+$), 171 and 156.

**Preparation of (21):**

See the experimental section of **PART-IV** (Page No. 146).

**Reaction of (21) with nickel boride:**

The reaction of 100 mg of (21) with nickel boride
in diglyme for 1 hr as described earlier furnished after
purification by preparative t.l.c. (EtOAc:Hexane, 1:20)
80 mg of (22) as an oil which was found to be identical
with its authentic sample (t.l.c., IR, NMR & MS).

**Preparation of (24):**

A solution of 200 mg of citral (which was a mixture
of cis and trans isomers) in 5 ml of dichloromethane was
epoxidized by 200 mg of MCPBA keeping the reaction mixture
at room temperature for overnight. After usual work up and purification on preparative t.l.c. (EtOAc:Bz, 1:20), 160 mg of epoxide (23) was obtained as an oil which on reduction with NaBH₄ in methanol and subsequent acetylation with Ac₂O-Pyridine furnished 150 mg of a residue as an oil. This residue was then purified by preparative t.l.c. (EtOAc:Hexane, 1:15), 120 mg of (24) and 30 mg of (21) were obtained. The compound (24) exhibited IR bands at 3000, 1740, 1395, 1225 and 750 cm⁻¹; NMR: 5.30 m (H-2), 4.50 d (J=7 Hz, H-1), 2.60 t (J=6 Hz, H-6), 2.00 (OAc), 1.65 br (H-9), 1.20 s br (H-8 & H-9); MS m/z 212 (M⁺), 169, 152 and 71.

**Reaction of (24) with nickel boride**

The reaction of 100 mg of (24) with nickel boride in diglyme for 1 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:20) 70 mg of (25) as an oil; IR bands at 3500, 1710, 1385, 1225, 1125 and 750 cm⁻¹; NMR: 5.20 m (H-2), 2.60 t (J=6 Hz, H-6), 1.70 s (H-1), 1.75 s (H-9), 1.35 m (H-8 & H-10); MS m/z 154 (M⁺) and 71 (base peak).
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