PART - IV

RESULTS AND DISCUSSIONS
Deoxygenation of epoxides has been carried out with iodotrimethylsilane$^1$ as well as with chlorotrimethylsilane and sodium iodide$^2$. It has been described that the reaction takes place via iodotrimethylsiloxane as shown below in Scheme 1.

\[
\text{Scheme 1} \\
+\text{TMS on CTMS-NaI} \\
\]

It was argued that trifluoroacetic acid (TFA) and sodium iodide combination would generate hydrogen iodide which can react with the epoxides to furnish iodo hydrins. The reaction of iodo hydrins with excess sodium iodide in presence of acid catalyst (TFA or HI) should then provide the corresponding olefins in good yields. This hypothesis was tested on several epoxides given in Table I$^3$ and it
was found that deoxygenation occurs smoothly in the case of substrates (1), (3) & (5).

In the case of substrates (7), (9) and (11), the yield of the corresponding olefins is less and the formation of other products start taking place (t.l.c.) if the reaction time is increased. That the deoxygenation reaction was stereospecific is evident from table I.

Earlier, deoxygenation of epoxides has been affected with toluene-p-sulphonic acid and sodium iodide. Since trifluoroacetic acid is volatile, it offers the necessary advantages during purification of the products as compared to toluene-p-sulphonic acid. Comparison of the two procedures (i.e. TFA/NaI and TsOH/NaI) when applied to all the substrates listed in the table I revealed that both were equally effective for deoxygenation; nevertheless, it may not be true for other multifunctional compounds.

An epoxide function could be a useful protective group for a double bond provided its deprotection could be achieved under mild reaction conditions compatible with sensitive functionalities. As new methodology is always welcome, it is anticipated that this method of deoxygenation will be a useful addendum to other existing procedures.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Reaction time in min/r.t.</th>
<th>Product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) 5,6α(-Epoxy-5α(-cholestane</td>
<td>5</td>
<td>2) Cholest-5-ene</td>
<td>90</td>
</tr>
<tr>
<td>3) 3β-Hydroxy-5, 6α-epoxy-5α(-cholestane</td>
<td>10</td>
<td>4) 3β-Hydroxy-cholest-5-ene</td>
<td>90</td>
</tr>
<tr>
<td>5) Trans-stilbene epoxide</td>
<td>5</td>
<td>6) Trans-stilbene</td>
<td>90</td>
</tr>
<tr>
<td>7) 1-Acetoxy-3,7-dimethyl-6,7-epoxy-oct-2(E)-ene</td>
<td>30</td>
<td>8) 1-Acetoxy-3, 7-dimethyl-2(E), 6-octadiene</td>
<td>50</td>
</tr>
</tbody>
</table>

R = \( \text{ester group} \)
EXPERIMENTAL

General procedure for the preparation of epoxides:

A solution of 0.5 m mol of the alkene in 4 ml of chloroform was treated with 0.5 m mol of MCPBA and kept at room temperature for overnight. The reaction mixture was diluted with chloroform, excess MCPBA was destroyed by treating with a solution of potassium iodide and the liberated iodine was removed by washing with sodium thiosulfate solution. The extract was then washed with a solution of NaHCO₃ followed by water and distilled under reduced pressure. The residue on purification by preparative t.l.c. furnished the pure epoxide.

General procedure for the deoxygenation of epoxides:

To a solution of 0.5 m mol of the substrate in dry acetonitrile (2 ml) a few drops of dry dichloromethane was added when the substrate was sparingly soluble in acetonitrile was added dry sodium iodide (2 m mol) with stirring at room temperature. Then 0.5 ml of trifluoroacetic acid was added dropwise slowly when the colour of the
reaction mixture turns reddish brown. The reaction was continued for 5 to 30 min monitoring by t.l.c. The reaction mixture was then quenched with water (200 ml) followed by extraction with chloroform which was washed with dilute sodium thiosulfate solution and water. The extract was then dried over anhydrous sodium sulfate and distilled under reduced pressure. The crude residue so obtained was purified by preparative t.l.c.

**Preparation of epoxide (1):**

Epoxidation of 100 mg of cholest-5-ene for overnight as described in the general procedure furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:20) 80 mg of (1) as crystalline solid m.p. 80°C (acetone), reported m.p. 80°C.

**Deoxygenation of (1) with TFA-NaI:**

Deoxygenation of 40 mg of (1) with TFA-NaI as described in the general procedure yielded 36 mg of cholest-5-ene m.p. 90°C (acetone), reported m.p. 90°C, which was found to be identical with its authentic sample (t.l.c., mixed m.p.).
**Preparation of epoxide (3):**

Epoxidation of 100 mg of cholesterol for overnight as described earlier furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:7) 70 mg of (3), m.p. 141°C (MeOH), reported, m.p. 141°C.

**Deoxygenation of (3) with TFA-NaI:**

Reaction of 60 mg of (3) with TFA-NaI as described earlier furnished after purification by preparative t.l.c. 54 mg of (4) which was identical with authentic cholesterol (t.l.c. and mixed m.p.).

**Preparation of epoxide (5):**

Epoxidation of 100 mg of trans-stilbene for overnight as described in the general procedure furnished after purification by preparative t.l.c. (Hexane) 90 mg of (5) as solid m.p. 69°C (EtOAc), reported, m.p. 69-70°C.

**Deoxygenation of (5) with TFA-NaI:**

Reaction of 50 mg of (5) with TFA-NaI as described in the general procedure yielded after purification by preparative t.l.c. (Hexane) 45 mg of (6) which was found to be identical with trans-stilbene (t.l.c., mixed m.p.).
Preparation of epoxide (7):

Epoxidation of 100 mg of 1-acetoxy-3,7-dimethyl-2(E), 6-octadiene with MCPBA in dichloromethane for 18 hr as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:20) 65 mg of the epoxide (7) as an oil; IR bands at 1740, 1385, 1225 and 765 cm\(^{-1}\); NMR: 5.25 t (J=7 Hz, H-2), 4.50 d (J=7 Hz, H-1), 2.60 t (J=5 Hz, H-6), 2.00 s (OAc), 1.70 (H-9), 1.25 (H-8 & H-10); MS m/z 212 (M\(^+\)), 169 & 152.

Deoxygenation of (7) with TFA-NaI:

Deoxygenation of 50 mg of epoxide (7) with TFA-NaI in acetonitrile as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:20) 25 mg of alkene (8) which was identical with the authentic sample (t.l.c., NMR, IR and MS).

Preparation of epoxide (9):

See experimental section of PART - II A. (Page No. 109).

Deoxygenation of (9) with TFA-NaI:

Deoxygenation of 50 mg of epoxide (9) with TFA-NaI in acetonitrile as described earlier furnished 30 mg of a
compound which was identical with the authentic sample of (10) (t.l.c., IR, NMR and MS) (See experimental section of PART - II A, Page No.108).

Preparation of alkene (12):

See experimental section of PART - II B (Page No.119).

Preparation of epoxide (11):

Epoxidation of 100 mg of (12) in 4 ml of chloroform with 100 mg of MCPBA as described earlier furnished after purification by preparative t.l.c. (EtOAc:Bz, 1:5) 40 mg of (11) as a gum. It exhibited IR bands at 1765, 1730, 1660, 1130 and 1000 cm⁻¹; NMR: 6.30 d (J=2 Hz, H-13a), 5.78 d (J=2 Hz, H-13b), 5.20 - 5.50 (overlapping signals of H-5, H-6 & H-8), 3.50 m (H-7), 1.25 s (H-14), 1.98 br (H-15), 1.08 d (J=7 Hz, H-3' & H-4') ; MS m/z 348 (M⁺), 278, 260, & 71.

Deoxygenation of (11) with TFA-NaI:

Deoxygenation of 40 mg of (11) with TFA-NaI in acetonitrile as described earlier furnished 12 mg of (12) which was found to be identical with its authentic sample (t.l.c., m.p., IR, NMR and MS).
REFERENCES