Symmetry allowed reactions proceed smoothly on heating.
Symmetry forbidden reactions proceed usually on photolysis. Three
families of Pericyclic reactions are - electrocyclic reaction, Cycloa
reaction and Sigmatropic reactions. These reactions are very importan
because -

(1) They create new C-C σ bonds and hence are used for Carbon skeleton construction.

(2) Reactions are independent of external influences such as effect
solvent, change of concentration, Catalysts and side reactions.

(3) Stereospecificity of these reactions is very high.

(3) Orbital Symmetry or HOMO Theory or Frontal Orbital Approach.

Let us examine Thermal Cyclisation of 1,3 Butadiene.

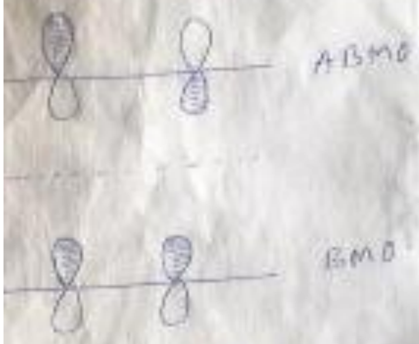
The above electrocyclic reaction involving conversion of 2π bonds into
1σ and 1π bond. The reaction is completely stereospecific. Both σ
σ bond which breaks in cyclobutene must rotate to come in
perpendicular plane of butadiene molecule. There are two po
ways in which this change can occur -

(1) Conrotatory motion when bonds rotate in the same direct

(2) Disrotatory motion when bonds rotate in opposite direction

(I)

(II)



Similarly four molecular orbitals arising from four 'p' orbitals in Butadiene in cis-oid conformation can be represented as -

...tals of same phase will overlap resulting into BMO, while ...ping of orbitals of different phase will lead to repulsive anti-... situation. Essential feature of pericyclic reaction is ...taneous overlapping of bond orbitals of participating in the ... so that they may pass smoothly into the bond orbitals ... products. This transmission passes through a tran... of merging orbitals, which will be of relatively very low ... and the reaction is favoured so long as symmetry ...tals is conserved or retained. When the symmetry of the ...tant and product orbitals is the same, i.e. orbital ...metry is conserved in the reaction, it is said to be ...mmetry allowed or energetically favoured reaction.

Stereochemical effects can be seen clearly as 2,4,6 trans-octa...
cyclic on heating to give cis-1,2 dimethyl 3,5 cyclohexa diene ...
while on photochemical irradiation trans-1,2 dimethyl 3,5 cyclo...
hexadiene is obtained.

trans-1,2 dimethyl 2,4,6 Trans-octa... cis, 1,2 dimethyl 3,5 cyclohexa...
3,5 cyclo hexa diene -triene

The above reaction is Electrocyclic reaction.

Phase and Symmetry of Orbitals

by Wave function,

Individual electrons of an atom can be symbolized as Ψ (Psi).
Analogy can be drawn between the behaviour of such a wave like electron and standing waves that can be generated in a string fastened at both the ends, with the difference that vibrational energy can be in more than one direction only.

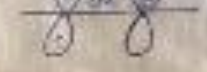
First three possible modes of vibration can be shown as -

On Ψ_1 – Amplitude of wave increases from zero to max and then decreases to zero again.

On Ψ_2 – Amplitude increases to maximum and then decreases to zero (Single node)

On Ψ_3 – Two such nodes are present

The lobes of a 2p atomic orbital which has one nodal plane differ in phase, conventionally designated as + and −
or shading or no shading



Pericyclic Reactions — M.Sc. II Sem. (1)

H-2008

Dr. P.K. Sharma

Orbitally Controlled Reactions (Mechanism and Rxn. ... Pericyclic / ...)

Organic reactions proceed via reaction intermediates, are revealed in reaction mechanisms, yet there are a no. of reactions which proceed neither by polar nor by a radical pathway and are also not influenced by changes in solvent polarity, presence of radical initiators or inhibitors and other catalysts and all the attempts to trap or detect reaction intermediates in such reactions have failed. Examples are – Diels-Alder Reactions and Pyrolytic elimination of carboxylic ester (1) and xanthates (2) to yield alkenes.

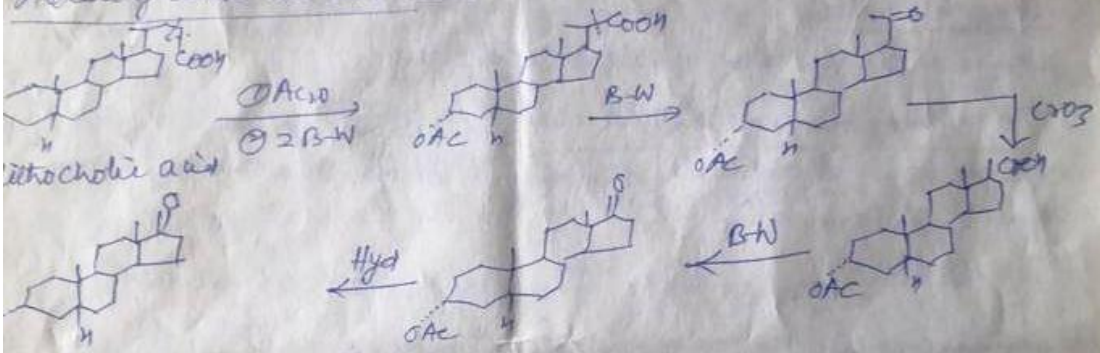
Reactions are concerted i.e. bond making and bond breaking take place simultaneously in one step process. The transition state are cyclic and reactions are stereo selective. Many of these reactions are reversible eg. Diels-Alder Reaction. Thus Pericyclic or Electrocyclic reactions are the concerted reactions which proceed via cyclic transition state.

These reactions can be carried out either thermally or photochemically. Both the factors give different results. Diels-Alder reaction which is a pericyclic reaction can be induced thermally not photochemically while concerted cycloaddition of two molecules of cycloalkene to form cyclo~~butane~~ alkane can be induced photochemically and not thermally.

stanol can be converted into two iso. di carbo acids which on
tion oxidn with CrO_3 form a mixture of two tri carboxylic
e, Lithobilianic and Iso Lithobilianic acids. The same tri-
rboxylic acids are obtained by oxidn of Lithocholic acid, prov
ntical position of OH group of Lithocholic acid and Coprostanol
o OH group is present at C-3 in Lithocholic acid.

Configuration of OH group:

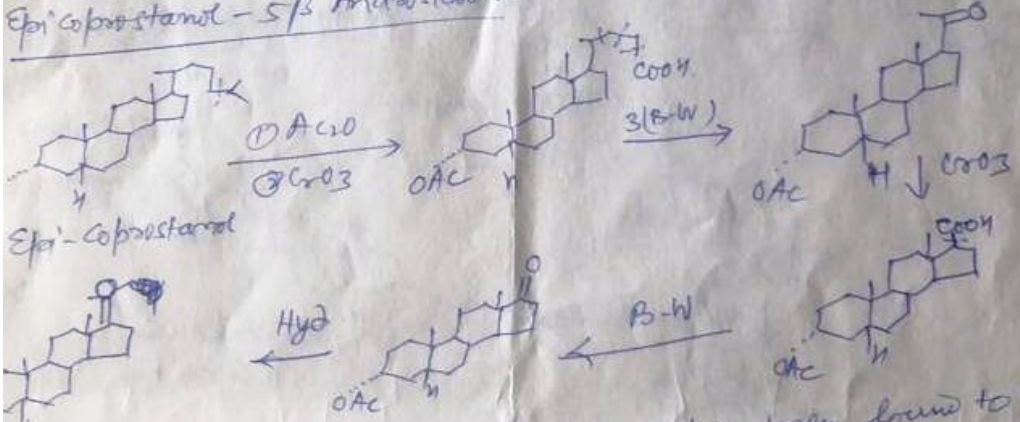
Epi-Coprostanol → 5β androsterone (OH as α)
(3α-hydroxy 5β cholestane)
Acetate of Lithocholic acid



Lithocholic acid

β Androsterone

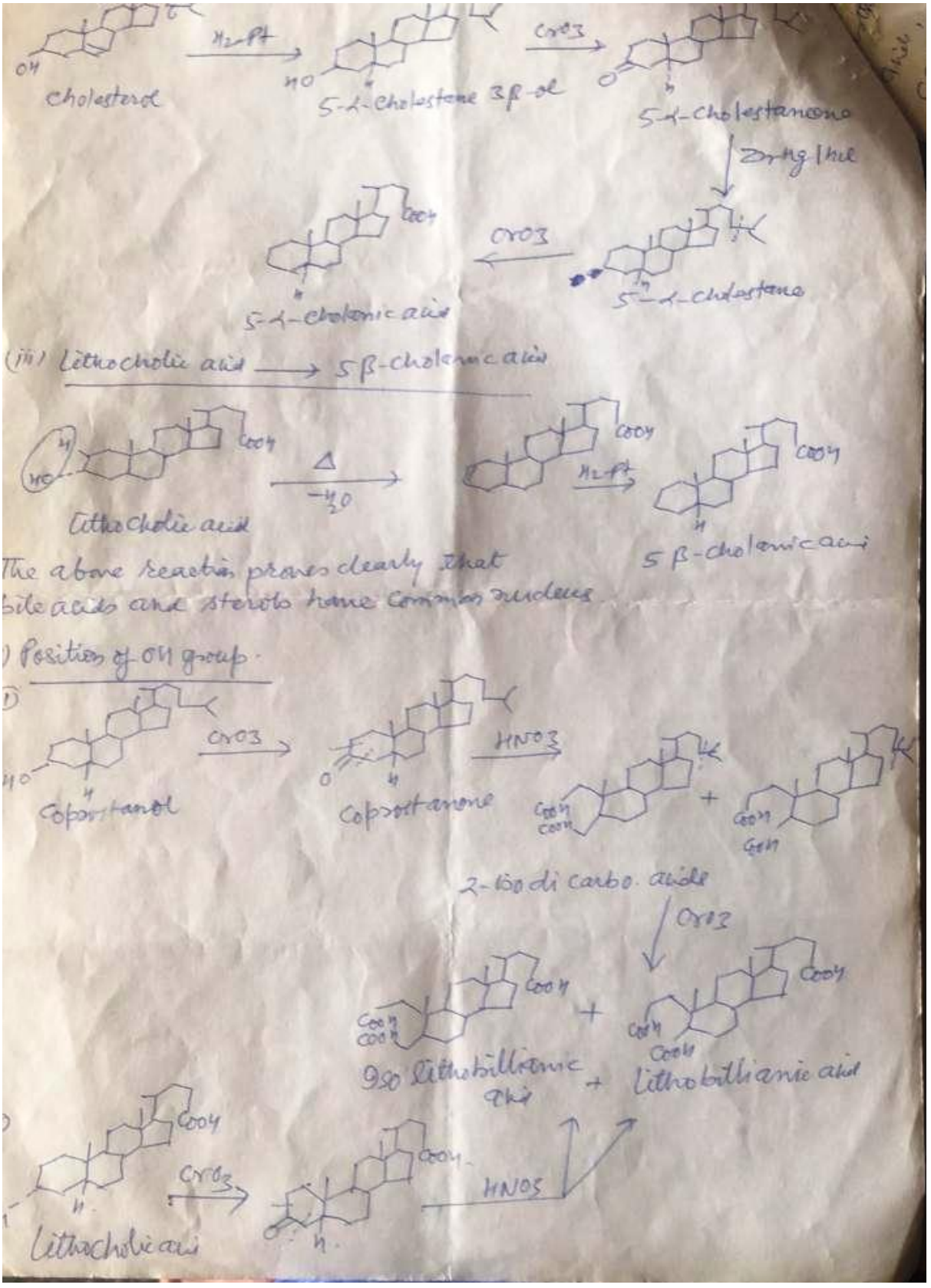
Epi Coprostanol - 5β Androsterone



Epi-Coprostanol

β-Androsterone

Since Epi-Coprostanol has been found to occur in α-configuration, therefore, Lithocholic acid, too, will show α-configuration of OH group.



(iii) Lithocholic acid ⟶ 5β-cholenic acid

The above reaction proves clearly that bile acids and sterols have common nucleus.

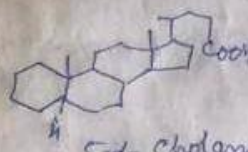
) Position of OH group.

Final M.Sc. IV Sem. : Swami Vivekanand Natural Products H-4016.

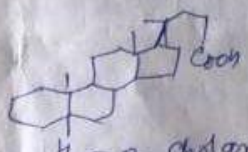
Dr. P.K. Sharma.

BILE ACIDS

Secrets a golden viscous blue fluid, which is known as bile. ntains organic substances as well as inorganic ions, dissolved in it. occurs as sodium salt of glycine or Taurine. Bile acids are hory derivatives of cholanic or allo cholanic acid. Based on the number OH groups present in a molecule, these are divided as mono, di tri hydroxy derivatives.



5-α- cholanic acid
I (allo cholanic acid)



5-β- cholanic acid
II

l the bile acids are found to contain above basic substances, The figuration of OH group is α.

Monohydroxy cholanic acid — lithocholic acid

Dihydroxy cholanic acid — Chenodeoxy cholic acid (30–50%)
Deoxy cholic acid (5–25%)

Trihydroxy cholanic acid — Cholic acid – (25-60%)

emistry of Bile Acids

Prove that Sterols and Bile Acids have common nucleus.

(i) cholesterol ⟶ 5β- cholanic acid

(ii) cholesterol ⟶ 5α- cholanic acid

(iii) Lithocholic acid ⟶ 5β-cholanic acid

, cholesterol ⟶ 5β-cholanic acid