

Swami Birkkanand

STEROIDS

IV Sem

DNsc final

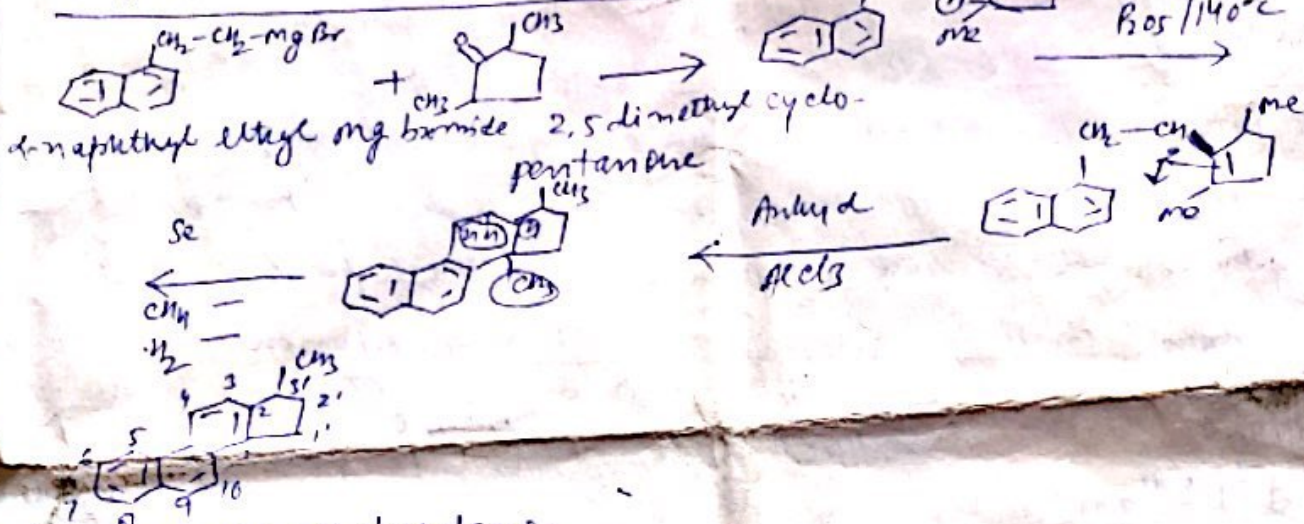
Natural Products

H-4016 ①

Dr. P.K. Sharma Steroids

Steroids are widely distributed compounds of animal and plant origin. They contain 1,2 cyclopentanophenanthrene nucleus. Steroids include bit acids, sex hormones, adrenal corticosteroid hormones, cardiac cardiac and toxic poisons. One of the important features of all the steroids is that upon Se -dehydrogenation they give Diels hydro. (3'-methyl 1,2 cyclopentanophenanthrene) The structure of which is proved from its synthesis.

Harper, Kohn and Kusicka 1934



3'-methyl 1,2 cyclopentano-phenanthrene (Diels hydrocarbon)

Sterols. Sterols are found in animal and plant fats and oils. These are solid alcohols. These are divided into three classes -

- ① Zoosterols - cholesterol, cholestanol and coprostanol
- ② Phytosterols - stigmasterol
- ③ Mycosterols - Ergosterol and vit-D

cholesterol. Main sources are brain, spinal cord, Gall stones, and fish liver oils, it was mainly isolated from human-gall stones, deposited in bile duct; and hence the name cholesterol. (chole - bile)

Swami Birkkanand.

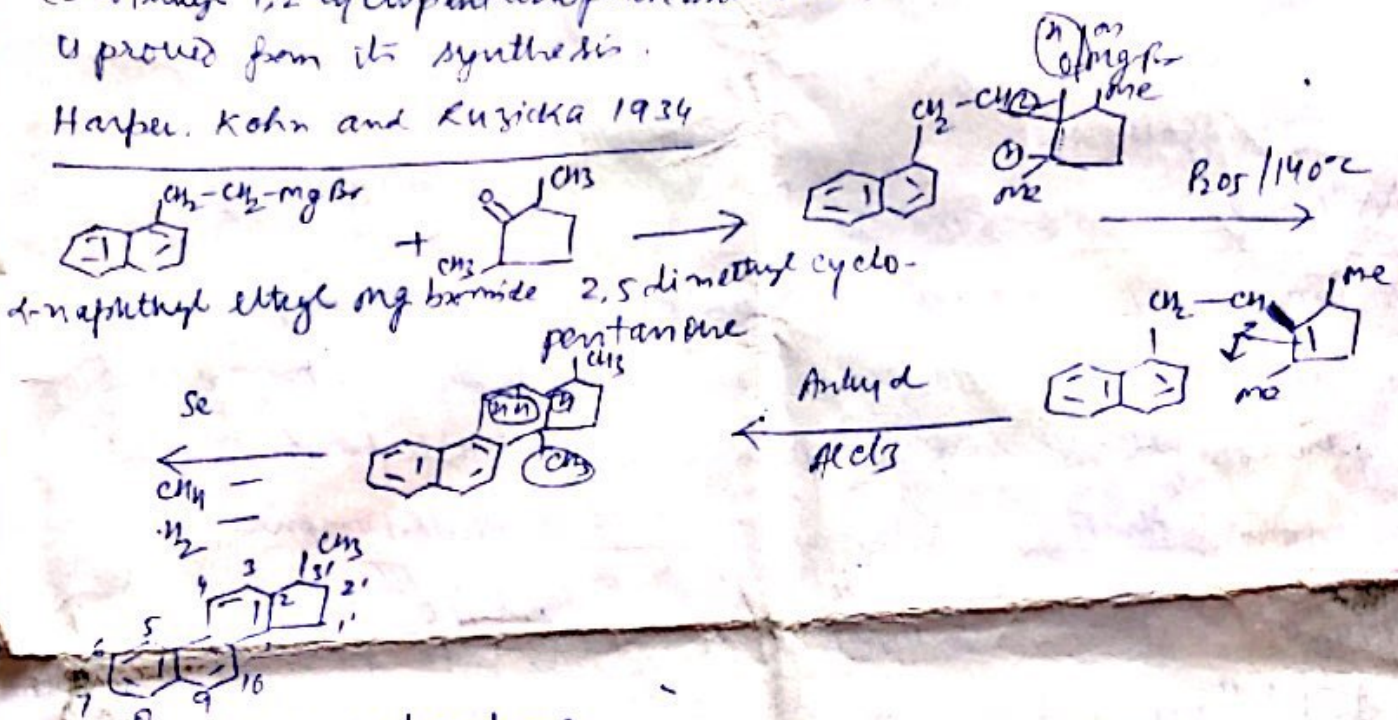
STEROIDS

IV Sem Natural Products H-4016 (1) 018c final

Dr. P.K. Sharma (steroids)

Steroids are widely distributed compounds of animal and plant origin. They contain 1,2 cyclopentanophenanthrene nucleus. Steroids include bile acids, sex hormones, adrenocortical hormones, cardiac and toxic poisons. One of the important features of all the steroids is that upon Se dehydrogenation they give Diels hydrocarbon (3'-methyl 1,2 cyclopentanophenanthrene) the structure of which is proved from its synthesis.

Harper, Kohn and Kuzicka 1934

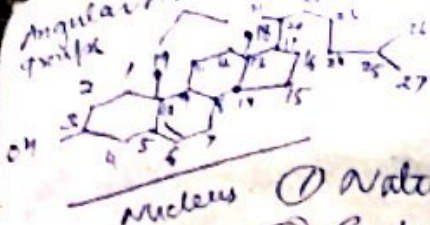


3'-methyl 1,2 cyclopentanophenanthrene (Diels hydrocarbon)

Sterols. Sterols are found in animal and plant fats and oils. These are solid alcohols, These are divided into three classes -

- ① Zoosterols - cholesterol, cholestanol and coprostanol
- ② Phytosterols - Stigmasterol
- ③ Mycosterols - Ergosterol and Vit D

cholesterol. Main sources are brain, spinal cord, Gall stones, and fish liver oils, it was mainly isolated from human gall stones, deposited in bile duct; and hence the name cholesterol. (chole - bile)



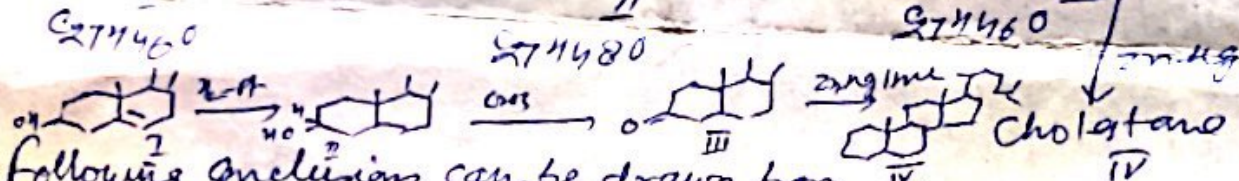
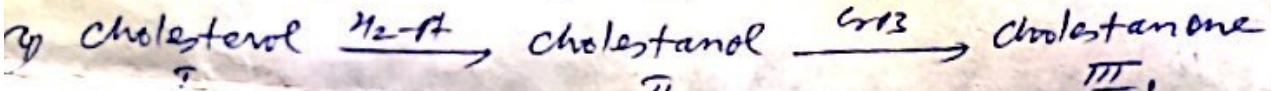
Constitution can be discussed in following points

174460
 I

- ① Nature of nucleus
- ② Position of OH groups
- ③ Position of double bonds
- ④ Nature and position of side chain
- ⑤ Point of attachment of side chain to the nucleus
- ⑥ Position of angular methyl groups
- ⑦ Synthesis.

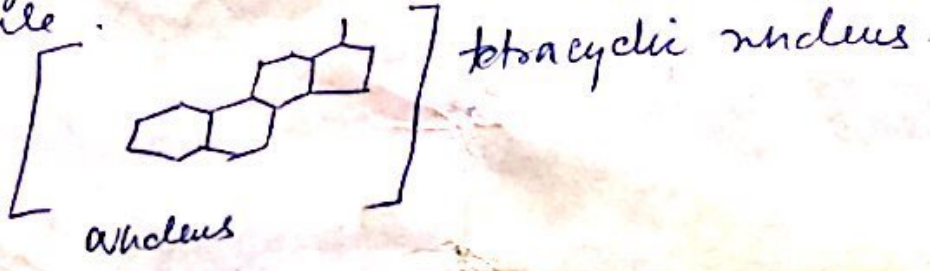
① Nature of nucleus - ① mole. formula $C_{27}H_{46}O$

- ② It forms mono acetate showing the presence of 1-OH group.
- ③ It takes up one molecule of Br_2 or H_2 to form di bromo or dihydro compound showing the presence of 1-double bond.

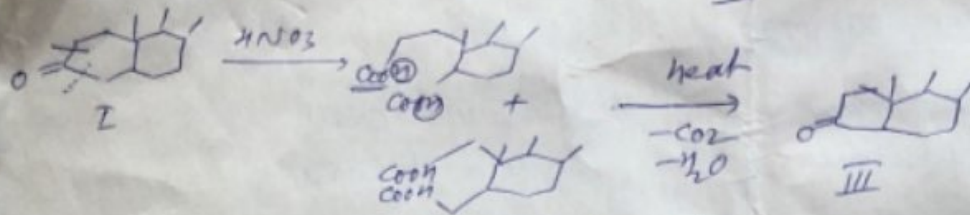
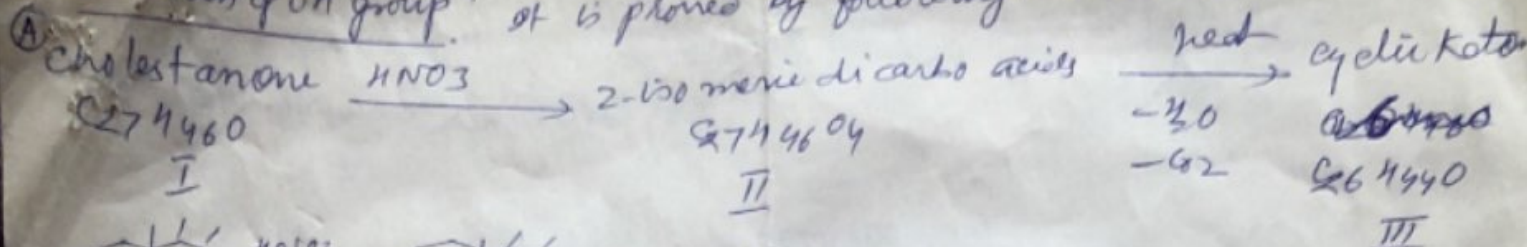


Following conclusions can be drawn from above series of reactions -

- ① Conversion of I \rightarrow II indicates that double bond has been hydrogenated
- ② Conversion of II \rightarrow III suggests that secondary OH group has been oxidised to ketonic group.
- ③ mole. formula of cholestanone ($C_{27}H_{48}O$) corresponds to C_nH_{2n-6} showing tetracyclic nature of the nucleus.
- ④ Upon Δ dehydrogenation at $360^\circ C$ it gives Diels hydrocarbon, showing the presence of following steroidal nucleus in the molecule.



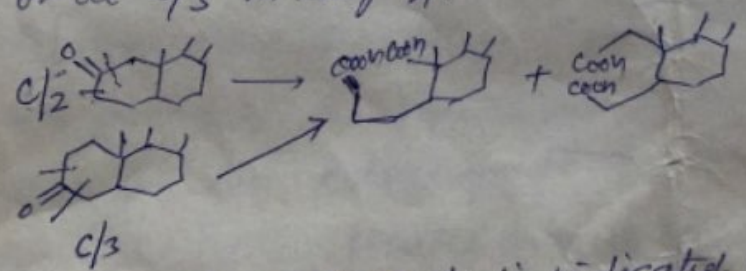
Position of OH group: It is proved by following reactions -



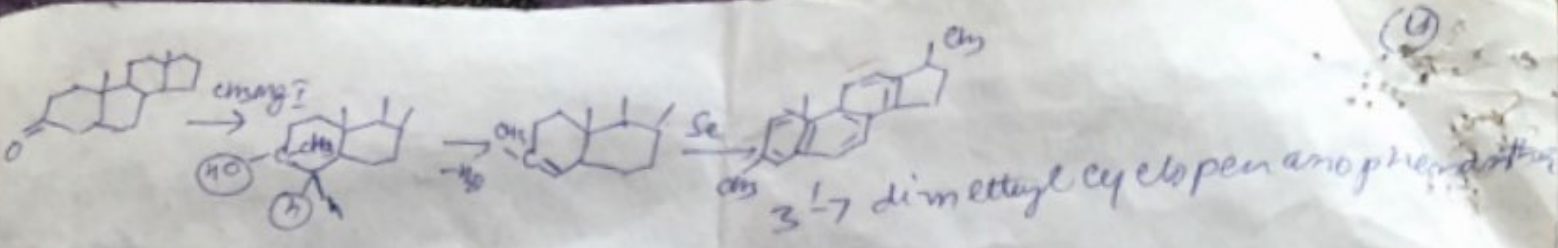
2 iso dicarbo. acids

Following conclusions can be drawn from above set of reactions -

- ① Conversion of I \rightarrow II with the same number of carbon atoms, indicate that ketonic group must be present inside the ring.
- ② Formation of cyclic ketone from di carbo acids suggest that it should be 1,6 or 1,7 di carbo. acids. According to Blanc's rule (Di carbo. acids ^{upto 1,5} give cyclic anhydride on heating where as 1,6 or 1,7 give cyclic ketone) Therefore COOH group can not be present in five membered ring D. It should be either in rings A B or C.
- ③ Formation of two iso meric di carbo. acids indicate that ketonic group should be flanked on both the sides by two methylene groups that is it should have $[-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-]$ type of grouping and it is possible only if ketonic group is present either at C/2 or at C/3 in ring A.



Definite position of OH group is indicated by another reaction. Cholestanone on treatment with CH_3MgI , followed by I_2 dehydrogenation gives 3'-7 dimethyl 1,2 cyclo penta phenanthrene. Position of Diel's hydrocarbon, equals position 3 of cholesterol. Thus OH group must be present in ring A at C/3.



Terminology

5- α -cholestane	cholestane	(dotted H at C-5)
5- β -cholestane	coprostan	(dashed H at C-5)

Prefix

Meaning

3-desero	-	Lacking a 3-keto group
3-desoxy	-	Lacking a 3 OH group
Homo-(acid)	-	COOH extended to -CH ₂ COOH
p-homo	-	Five member ring D has been extended to six member ring
Nor-(acid)	-	CH ₂ CH ₂ COOH has been shortened to -CH ₂ COOH (1C. less)
Bis-nor-(acid)	-	CH ₂ CH ₂ COOH " " " -COOH (2C. less)