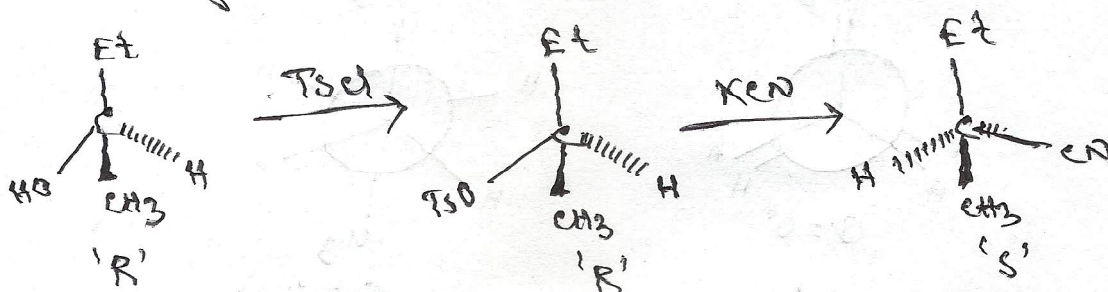


Section-A

Q1) Define absolute configuration and relative configuration.

Ans:- The precise arrangement of substituents around a chiral centre is known as absolute configuration.



The corresponding configuration of the product is known as relative configuration.

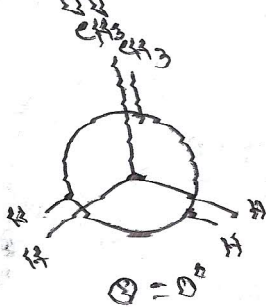
Q2) Arrange the following groups to get (R) configuration according to CIP rule (H, Cl, Me, COOH).

Ans:- To get 'R' configuration the order will be -
 (a) = -Cl, (b) = -COOH, (c) = -Me, (d) = -H
 where $a > b > c > d$

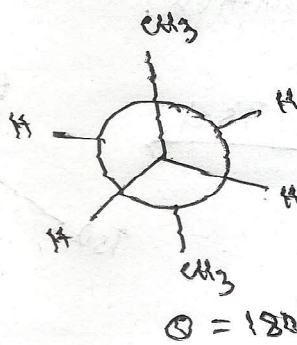
When the lower priority group on atom (d) is in top or bottom in y-axis in fisher projection formula and the order $a \rightarrow b \rightarrow c$ is in clockwise direction, then the configuration will be -R.

(iii) Define eclipsed and staggered conformation.

Ans:— infinite number of momentary arrangement of groups or atoms in a molecule which arise out of rotation around carbon single bond rotation. stable form of these type of arrangement is called conformer. when the bond angle between two carbon centre (front and back) in newmann projection formula is 0° then it is known as eclipsed and when $\theta = 180^\circ$ then it is known as staggered conformation.



Eclipsed form



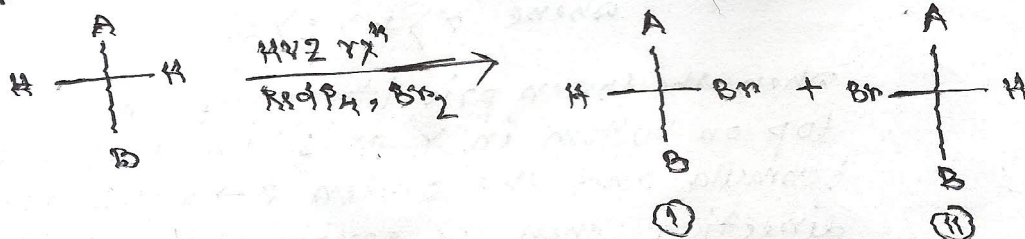
$\theta = 180^\circ$ staggered form.

(iv) Define the topicity of the hydrogen atoms in the following compound.



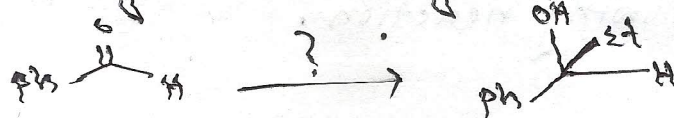
A and B are alkyl groups.

Ans:—



compound 1 and 2 are enantiomers.
Hence the H atoms are enantiotopic.

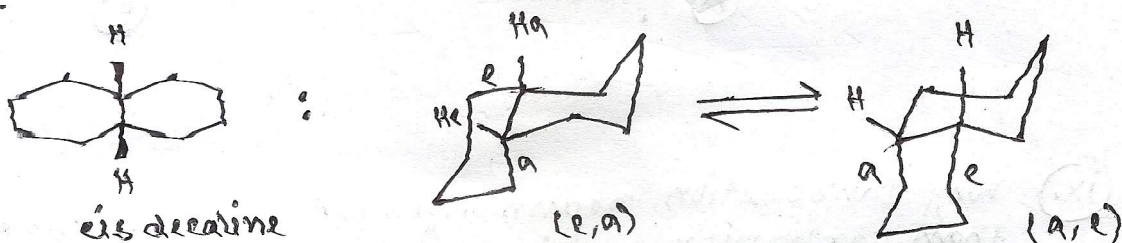
Q. Identify the asymmetric catalyst (?) in the following rxⁿ.



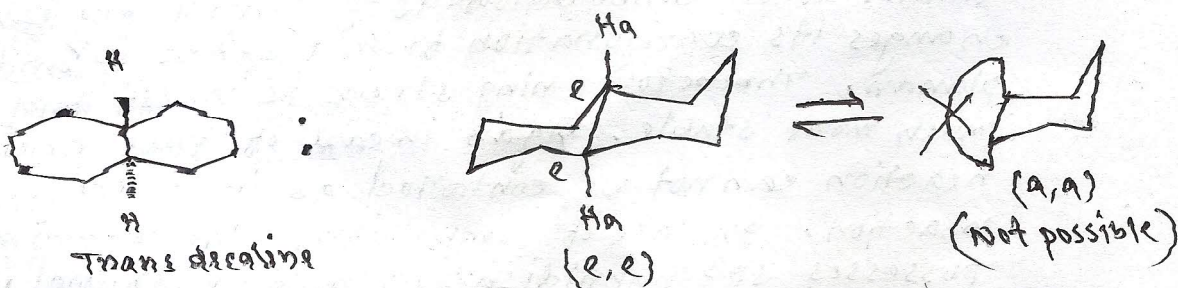
Ans :- The catalyst is - 2 mol% of (-) DAIB and Et₂Zn in presence of toluene at 0°C.

Q. Draw the conformation of cis and trans decaline.

Ans :-



cis decalin presents as equimolar mixture of (e, a) and (a, e) form.

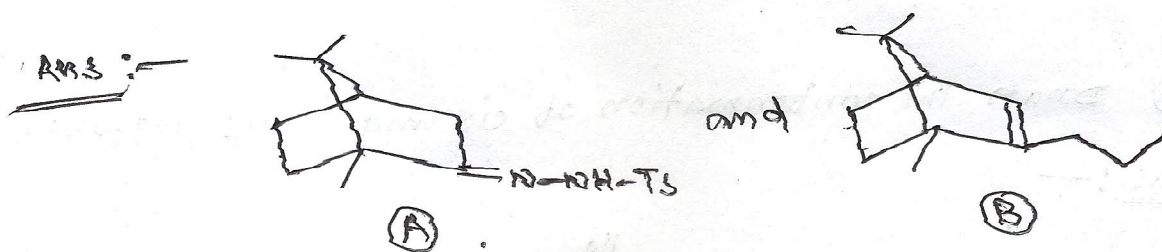
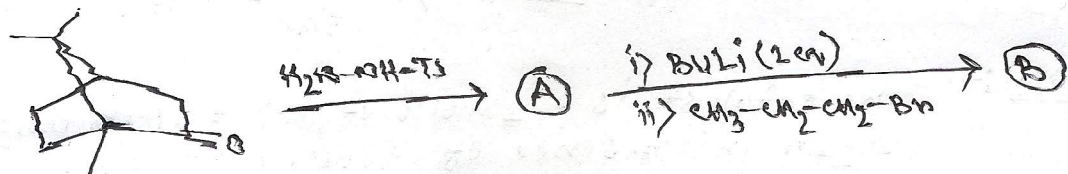


only this form is possible.

Q. Choose correct answer and fill up the blank.

Favorskii rearrangement is an example of a - stereospecific reaction and inversion of configuration takes place at carbon attached to halide.

VIII. Draw only the structure of the products A-B from the following reaction.



IX. Why carbocation rearrangement are more common than carbanion and free radicals counterpart?

Ans: - carbocation rearrangement are more common than other, when carbocation is generated the carbon changes its configuration from sp^3 to sp^2 and becomes planar. therefore ring strain is lowest and it is much more stable. Again in case of free radical the reaction cannot be controlled as it undergoes chain reaction. In case of carbanion, the carbon atom possesses sp^3 hybridisation and tetrahedral configuration, which is also not so much stable.

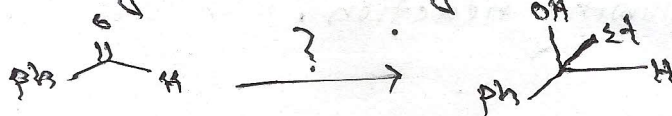
X. What are the major advantages of Sharpless reagent?

Ans: - i) The chiral epoxide can be easily converted to diols, amino alcohols or ethers in enantiomerically pure form. So the formation of chiral epoxide is very important.

ii) The reaction can be done in many primary and secondary allylic alcohols.

iii) The product of the Sharpless epoxidation frequently have enantiomeric excess above 90%.

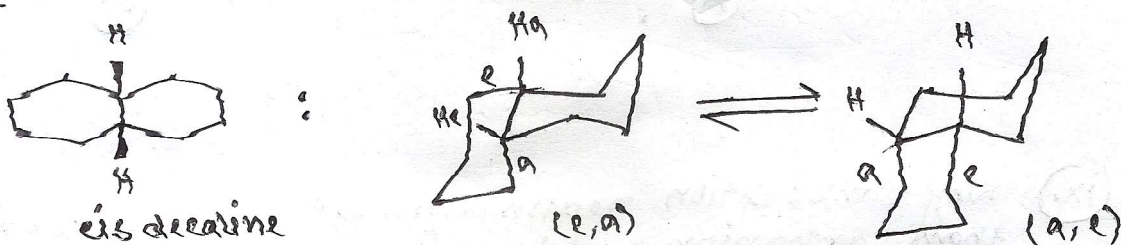
(v) Identify the asymmetric catalyst (?) in the following rxⁿ.



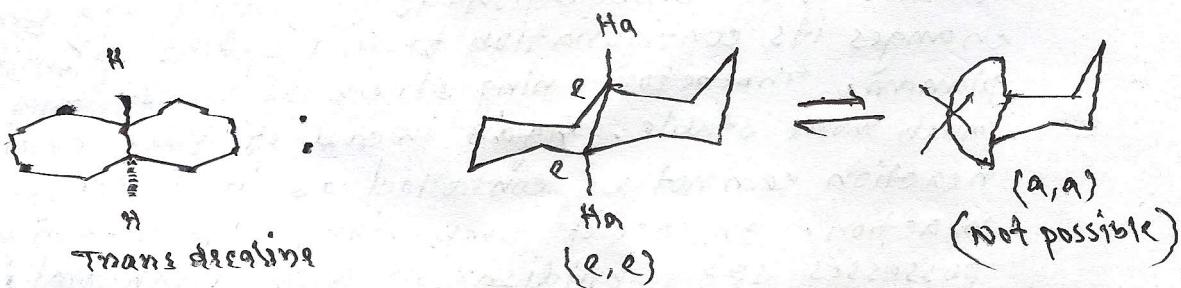
Ans :- The catalyst is - 2 mol% of (-) DAIB and Et₂Zn in presence of toluene at 0°C.

(vi) Draw the conformation of cis and trans decaline.

Ans :-



cis decalin presents as equimolar mixture of (e,a) and (a,e) form.



only this form is possible.

(vii) choose correct answer and fill up the blank.

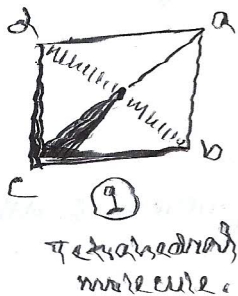
Favorskii rearrangement is an example of a - stereospecific reaction and inversion of configuration takes place at carbon attached to halide.

Section-B

2) (a) (i) Explain the principle of axial chirality.

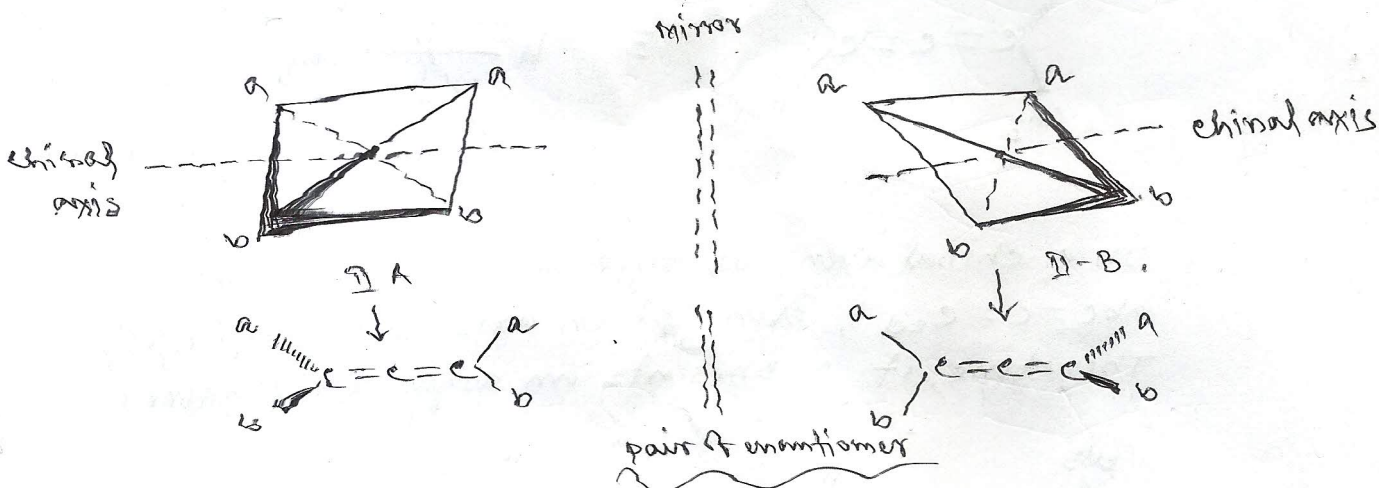
Ans:— Elongated tetrahedron approach can be applied to explain the principle of axial chirality.

A chiral centre can be detected in a molecule when the four different ligands of a central atom are located on the corners of a tetrahedron e.g; c in Cabcd molecule (1) is a chiral centre.



When this centre is replaced by a linear grouping $c=c=c$ the tetrahedron becomes elongated, i.e., extended along the axis of grouping.

Such an elongated tetrahedron has lesser symmetry than a regular tetrahedron and that elongated tetrahedron will be chiral if only the two ligands at each end of the axis are different i.e., the minimum condition for chirality is that of $a \neq b$.



This axis along which the tetrahedron is elongated is called chiral axis and the molecular chirality of this type is termed as axial chirality.

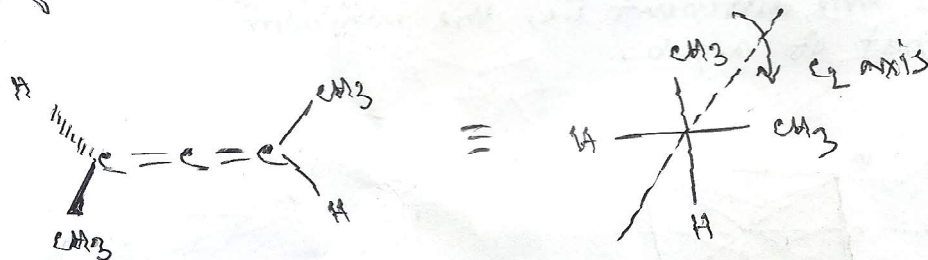
(a) Discuss that the presence of chiral centre is not always essential for a compound to exhibit chirality.

Ans:— There are several molecules which are chiral not due to having one or more chiral centres but due to other element of chirality namely axial chirality and planar chirality.

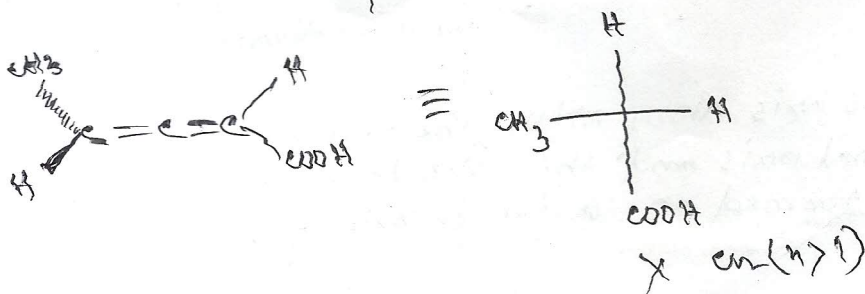
Suitably substituted alkenes, spirans, biphenyls do not contain any formal chiral centre but exhibit enantio-merism due to the presence of a chiral axis.

(b) What are the dissymmetric and asymmetric alkenes? Illustrate with suitable examples.

Ans:— A chiral alkene of the type $abc = c = cab$ has a C_2 simple axis of symmetry. Therefore it represents a dissymmetric molecule.



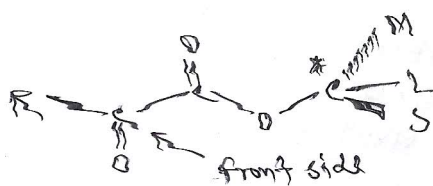
or a chiral alkene of type $abc = c = cab$ or $abc = c = cab$, even the C_n axis is absent ($n > 1$) therefore, it represents an asymmetric alkene.



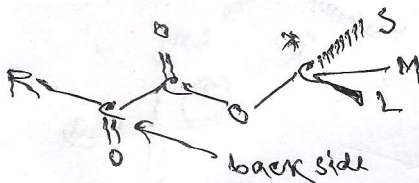
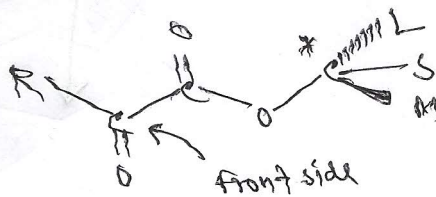
5. (a) Discuss conformations of keto ester ($R-CO-CO-O^*SML$) where S, M, L are small, medium and large groups respectively for nucleophilic addition reaction.

Ans:— Prout's rule predicts the stereochemical outcome of nucleophilic addition reactions with keto-esters of the type $R-CO-CO-O^*SML$ where S, M, L are small, medium and large group respectively on the chiral centre.

There are three energetically favourable conformations—



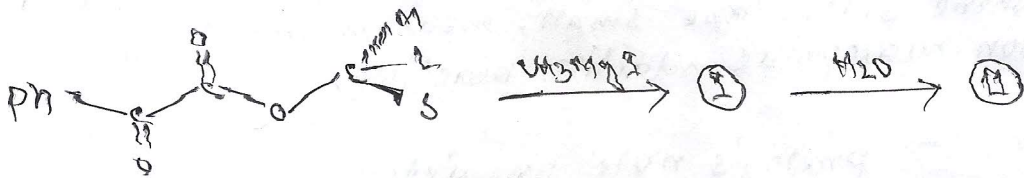
{ most populated conformation }



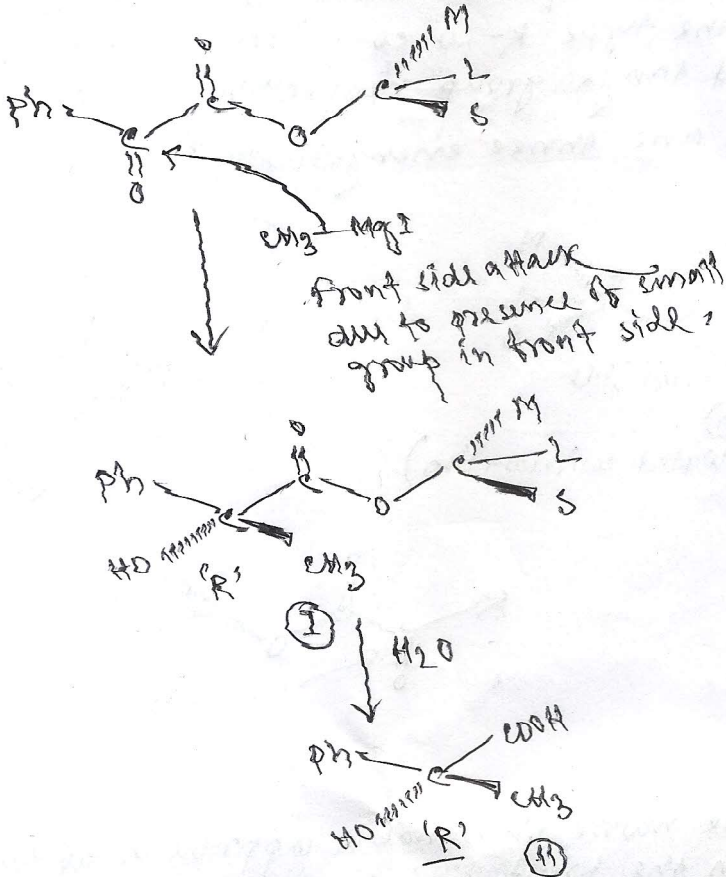
in (a) the more favourable approach of the reagent will be from the front side because between the two groups M and S, S is smaller.

in case of (b) and (c), the direction of approach would be from the front and the rear side respectively.

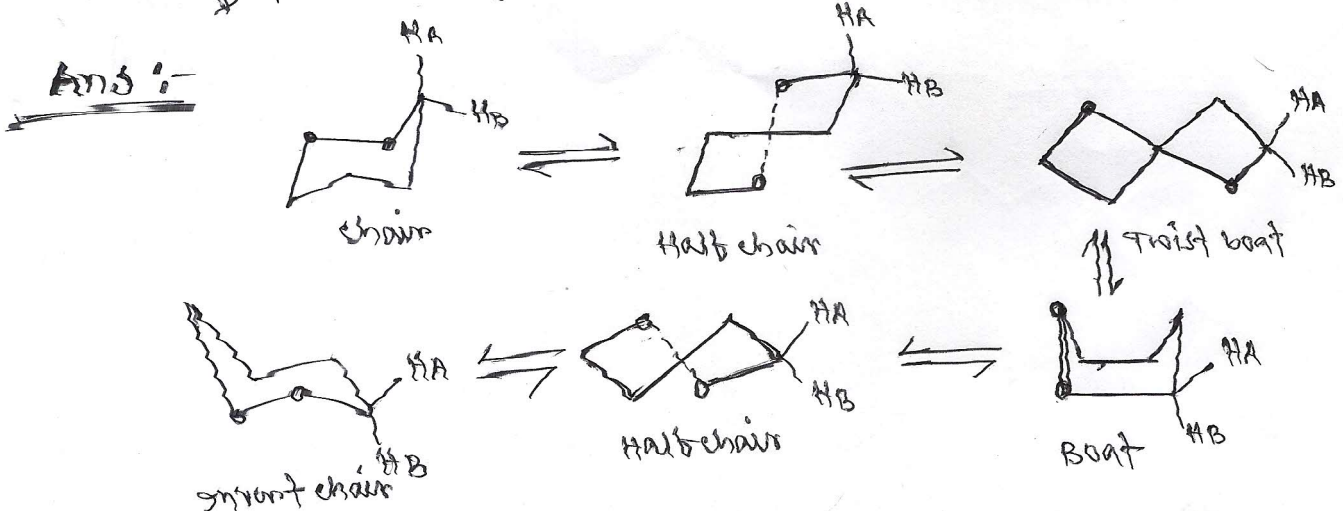
6. Identify the products (I and II) in the following reaction and discuss about the major product.



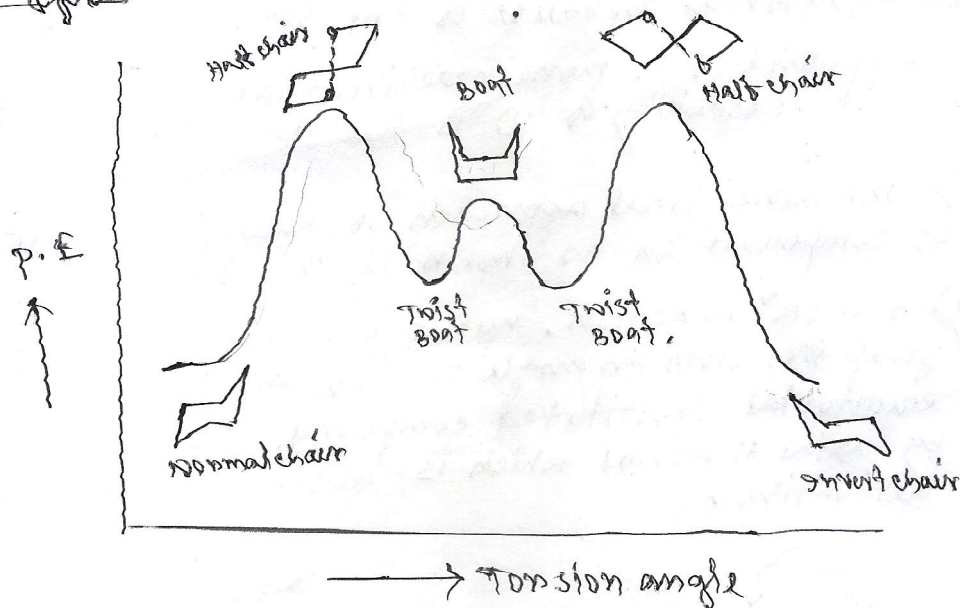
Ans: →



7. Draw all the conformations that involve for the inter-conversion of one chair form to another and also draw the energy profile diagram of this conversion.

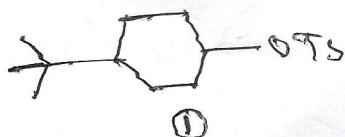


Energy profile diagram :-

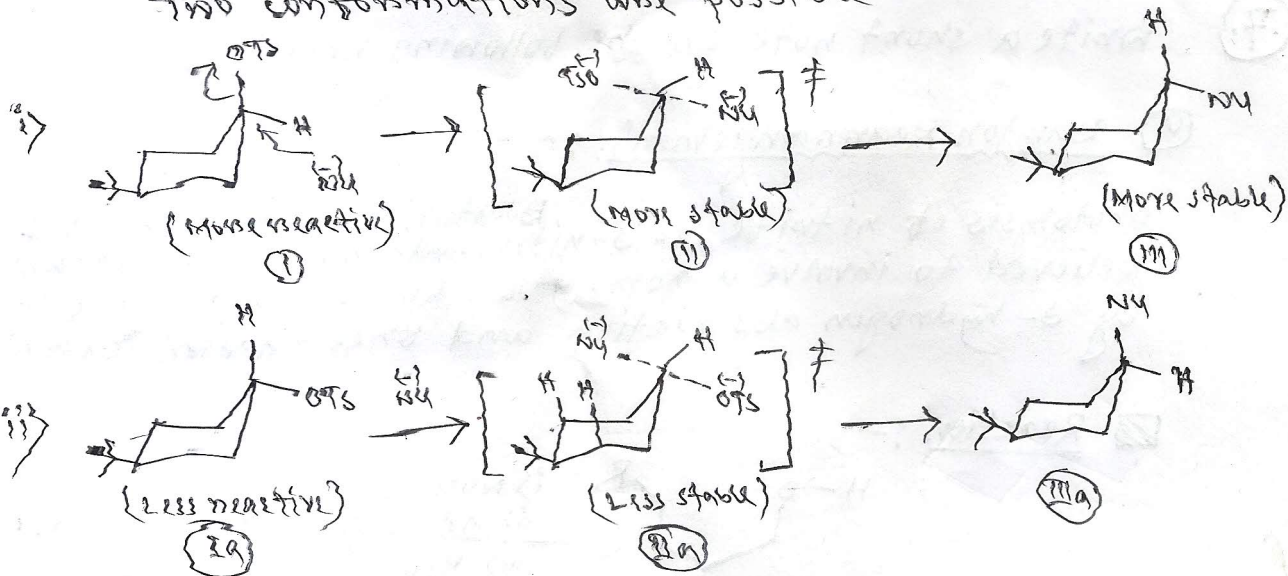


Q. Draw all possible conformations of compound (I) and explain which form will react faster with thiophene (PhSH) and why?

Ans :-



Two conformations are possible -



The substituent at the axial will be more reactive than the equatorial because of the following reason -

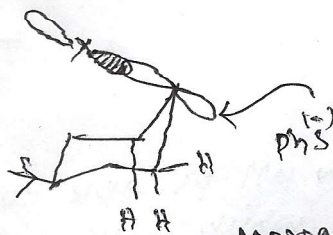
i) compound ① is more reactive than compound ②a.
 {stability of ① is less than 2a}

ii) The diectional approach of nucleophile is hindered in case of compound 2a as shown in T.S 2a.

iii) for S_N2 reaction, nucleophile must attack from the leaving group i.e, from an angle 180° of the $C-X$ bond. In case of equatorial substituted compound this line of attack is hindered by axial H atoms which is absent in case of axial substituted derivative.



Approach is hindered by axial H atoms.



Approach is not hindered by axial H atom.

∴ compound ① reacts faster with $PhSH$.

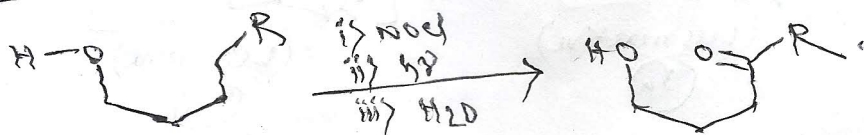
7.

write a short note on the following reactions -

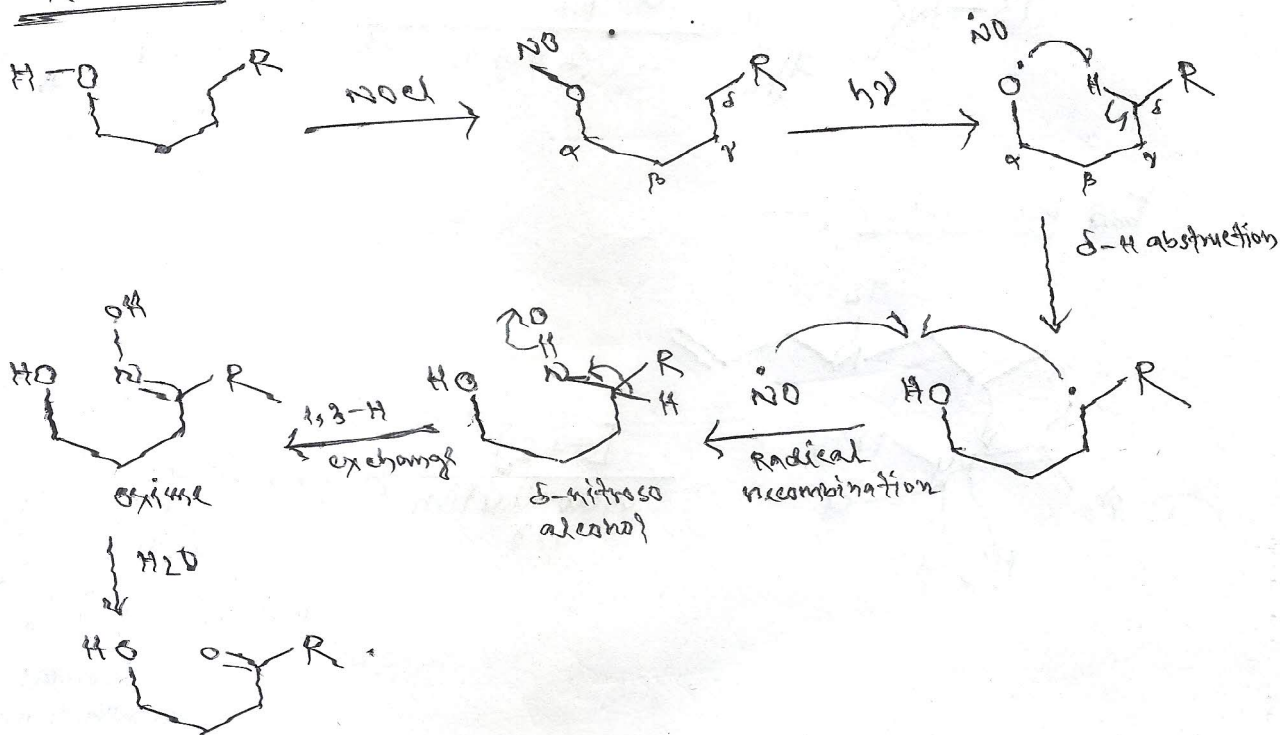
① Barton Rearrangement :-

Barton reaction involves the photolysis of nitrite to δ -nitroso alcohol. The mechanism is believed to involve a homolytic $RO-NO$ cleavage followed by δ -hydrogen abstraction and free radical recombination.

Reaction :-



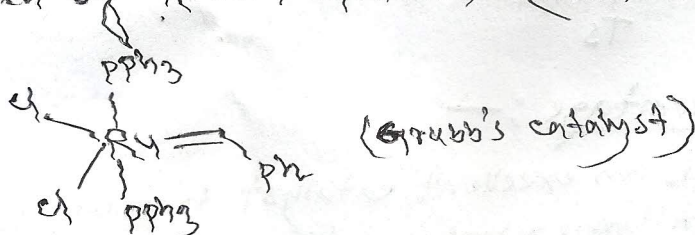
Mechanism:



By Barton reaction we can functionalise an unreactive carbon atom in alkyl group which is at position δ to a hydroxy group. So the Barton reaction is also known as remote functionalisation reaction. This reaction is widely applied in steroid chemistry for the functionalisation of angular methyl group.

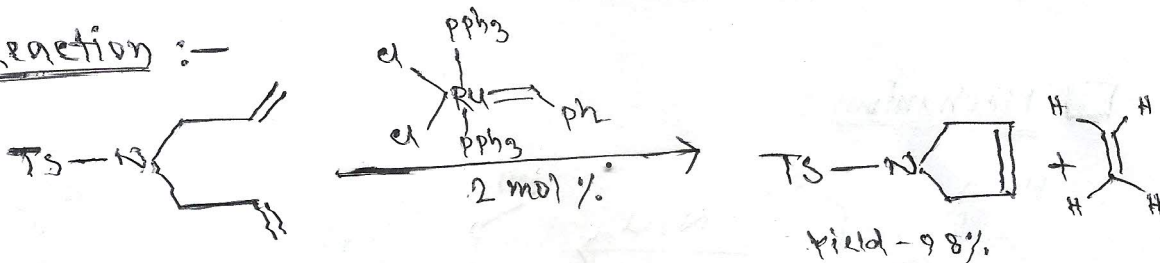
3. Metathesis Reaction:

The metathesis reaction recently has been carried out by using a $Ru(II)$ carbene complex developed by Robert Grubb's, known as Grubb's catalyst.

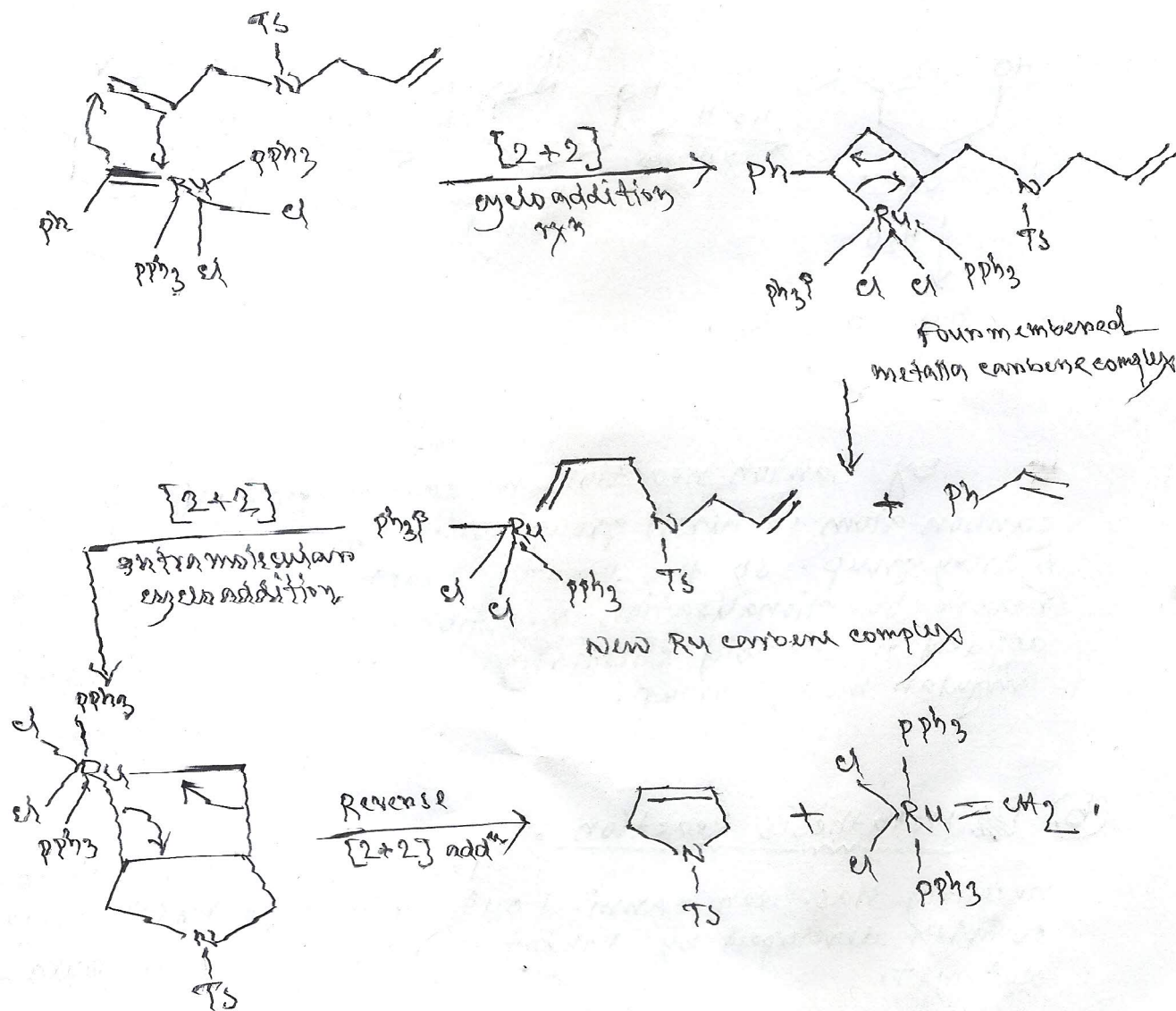


Grubb's catalyst: It is the most important carbene derived reagent, a stable $Ru(II)$ complex which can be stored for a month.

Reaction :-



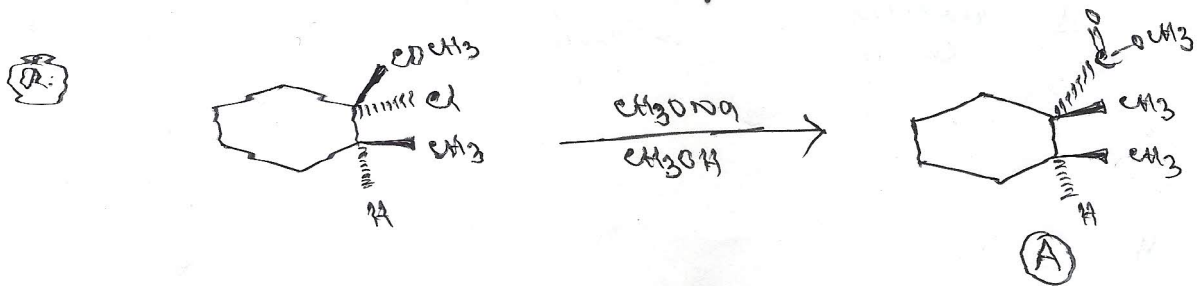
Mechanism :-



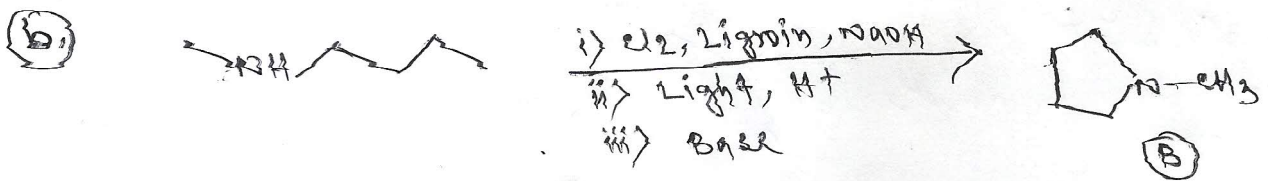
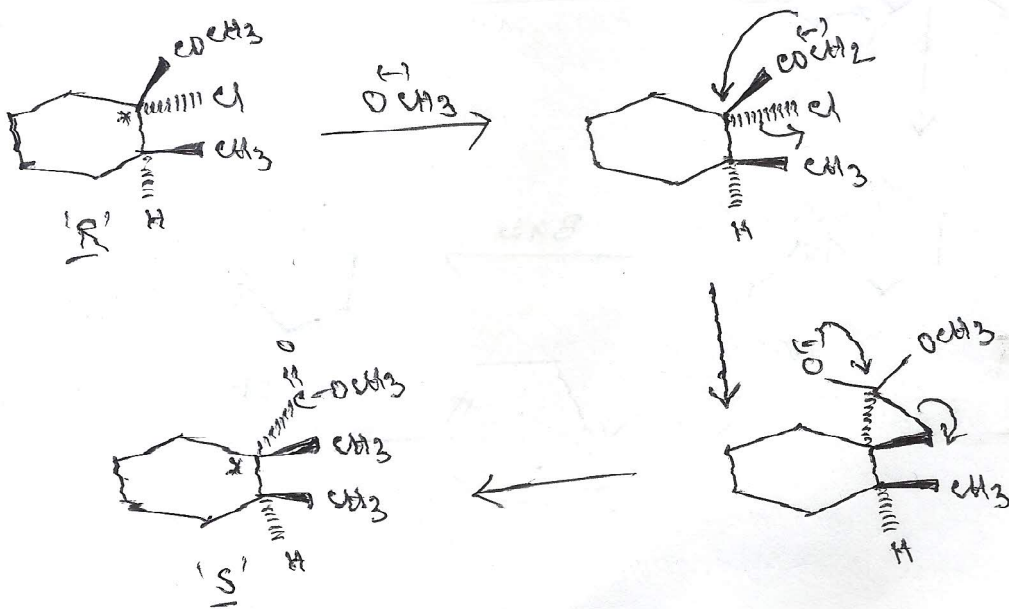
Advantages :-

- i) It is an excellent catalyst to make a difficult ring.
- ii) For large member ring the reaction is E-selective.
- iii) The stereogenic centre are not racemised by this catalyst.
- iv) The catalyst is compatible with many functional groups such as -OH, -OMe, -CO₂Me, ethers etc.

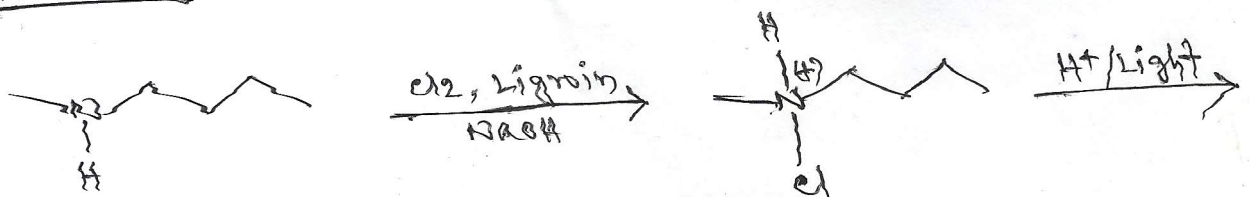
8. complete the reactions with mechanism.

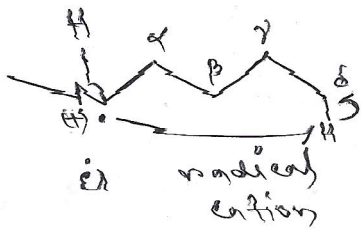


Mechanism :-

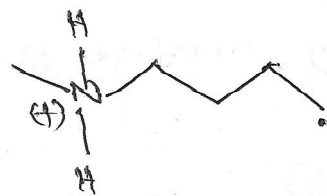


Mechanism :-

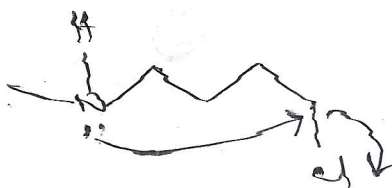




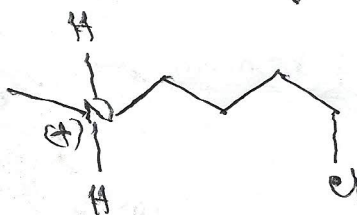
abstraction of
 δ -H by radical cation



Radical recombination



Base



↓



Base



N-methyl pyrrolidine