

Model Answer, B. Sc. III Semester

Paper Code: As-2807

SECTION - A  
(Short Answer Type Questions)

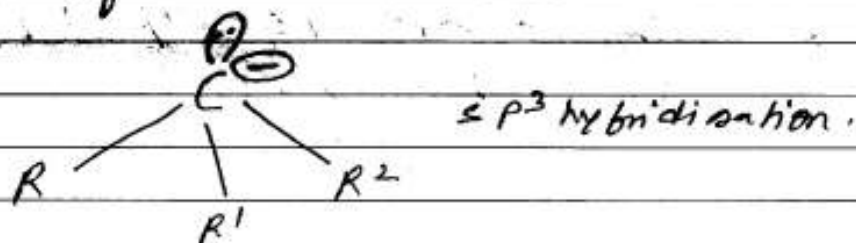
Answer 1 (i):

Ans: Phenol is acidic because the -ve charge in the conjugate base called phenoxide ion is stabilized by delocalisation while the ethoxide ion from alcohol has no such stability.

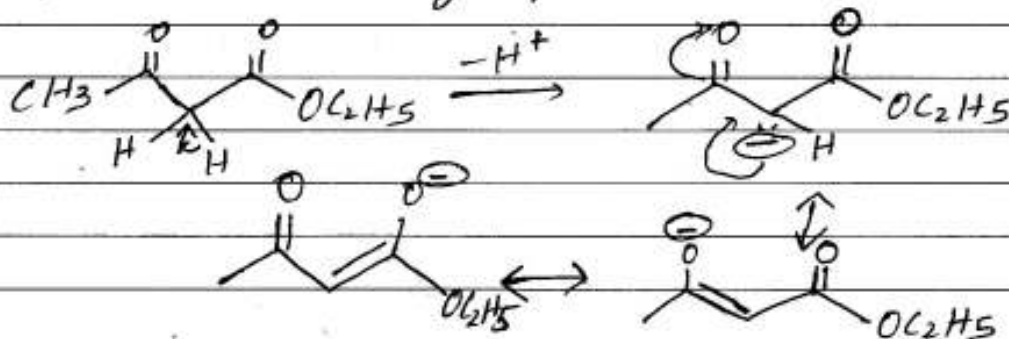
Answer 1 (ii):

Ans: → All anions in which -ve charge is carried by carbon are called carbanions.

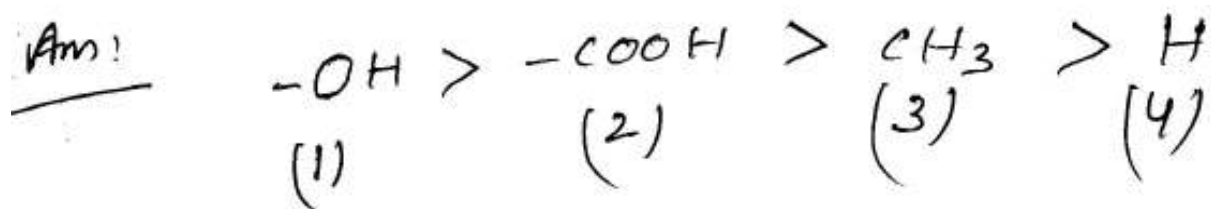
→ Carbanion has pyramidal type of geometry & one corner of the carbanion is occupied by a lone pair of  $e^-$



→ Due to the presence of two  $e^-$  withdrawing gps, active methylene group is acidic in nature & easily produces carbanion as follows:



Answer 1 (iii):



Answer 1 (iv):

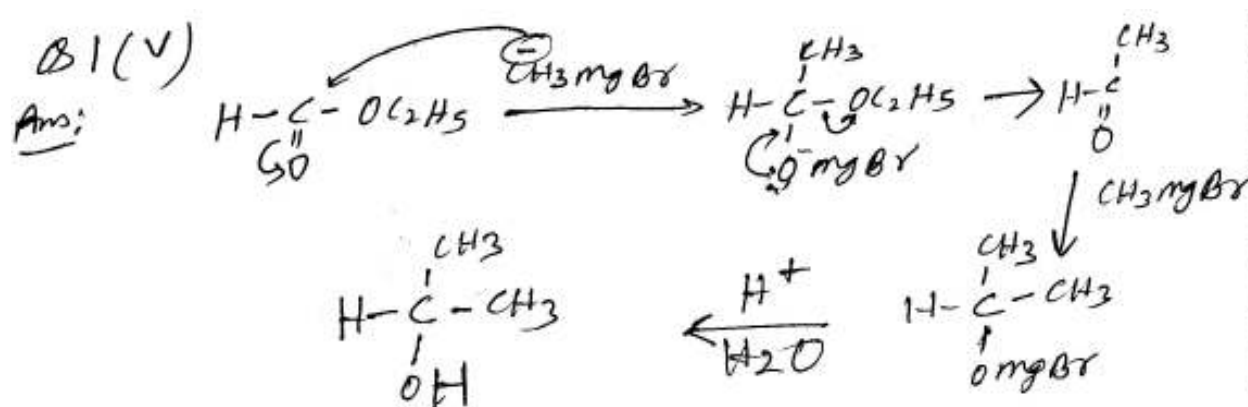
Diastereomer.

- Isomers that are not mirror image.
- They may be chiral or achiral
- They have different physical properties.

Enantiomer.

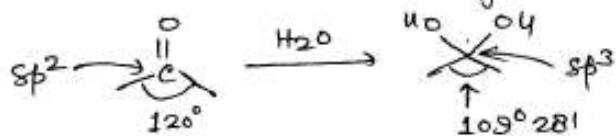
- Enantiomers are non-superimposable mirror image isomers.
- They are chiral.
- They have identical physical properties except the direction of rotation of plane polarised light.

Answer 1 (v):



Answer 1 (vi):

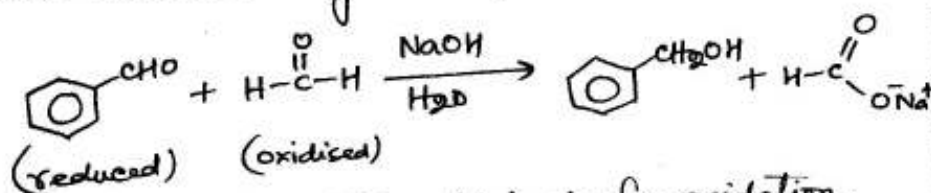
Solubility of  $>C=O$  group in water depends on both the steric as well as electronic effect. In water, a  $>C=O$  group converted into a hydrate i.e. from  $sp^2$  to  $sp^3$  of carbonyl carbon takes place as shown in figure. So, in forming the hydrate, groups are moved closer to each other.



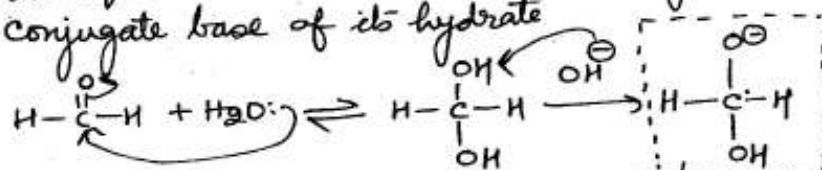
Therefore, formaldehyde leads to more stable hydrate while other higher aldehyde e.g. hexanal leads to unstable hydrate and hence formaldehyde is soluble in water while hexanal is not. Increasing alkyl group on carbonyl carbon decreases polarity of  $>C=O$  group and hence decreases solubility in water also.

Answer 1 (vii):

In case, when formaldehyde is one of the substrate in crossed cannizzaro reaction, the formaldehyde always undergoes oxidation and in such situation only two products are formed.



- HCHO is most reactive aldehyde for oxidation.
- In aq. basic solution it exists mainly as the conjugate base of its hydrate



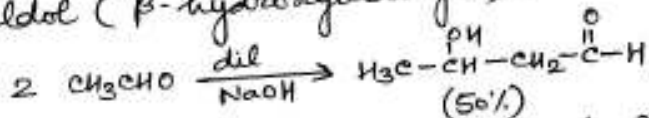
This is one of the intermediate of the reaction.

- The other aldehyde hydrate anion has only one H while formaldehyde hydrate anion has two Hs for

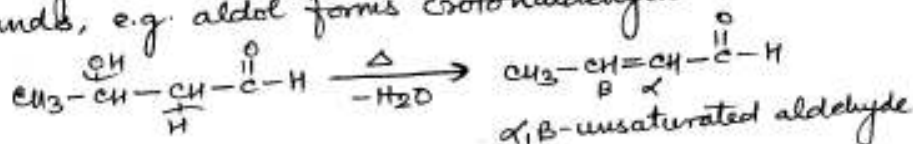
Answer 1 (viii):

Answer Q.1 (viii)

When acetaldehyde is treated with dil. NaOH solution, it undergoes condensation to form a syrupy liquid known as aldol ( $\beta$ -hydroxyaldehyde).

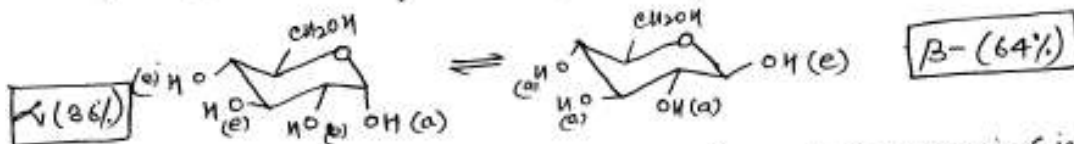


On heating, aldols eliminate water to form unsaturated compounds, e.g. aldol forms crotonaldehyde



Answer 1 (ix):

Glucose exists in equilibrium between  $\alpha$  and  $\beta$ -glucopyranose form (six memb) given as following —



all OH groups are equatorial except one at anomeric.

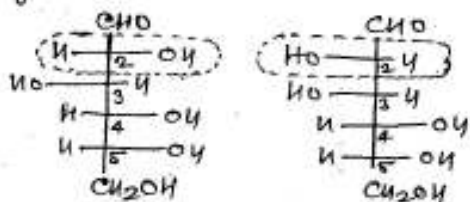
When OH at anomeric C is axial it is  $\alpha$ -form but when it is equatorial it is  $\beta$ -form.

Answer 1 (x):

Diastereomers that differ in configuration at only one chiral centre are called epimers.

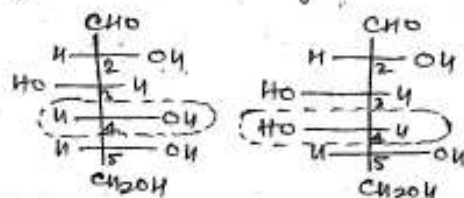
Examples

D-glucose and D-mannose are C<sub>2</sub> epimers



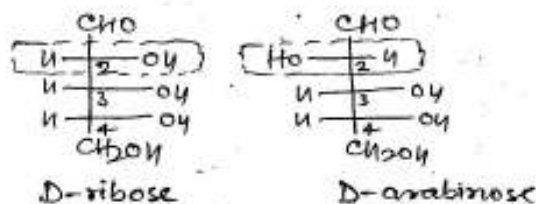
only differ at C-2 centre

D-glucose and D-galactose are C<sub>4</sub> epimer



D-glucose and D-galactose only differ at C-4 centre.

D-arabinose and D-Ribose are C<sub>2</sub> Epimer

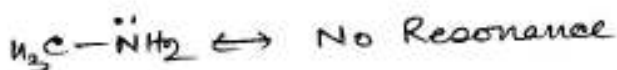
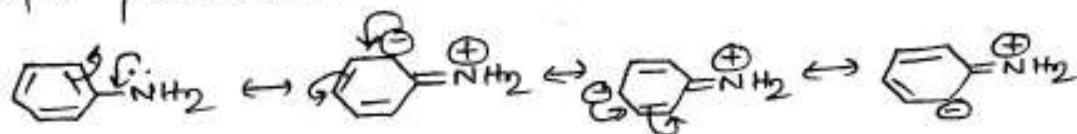


## SECTION - B

### (Long Answer Type Questions)

Answer 2 (a):

Availability of lone pair on N-atom in amine is the reason for basicity. In aniline lone pair of N-atom is delocalised and hence not available, while that in methylamine is localised and is available for protonation.



Therefore, based on above discussion it may be explained that methylamine is more basic than aniline.

Answer 2 (b):

∴ The strength of an acid is generally indicated by its pKa value. Smaller the pKa the stronger is the acid.

$$\text{pKa} = -\log K_a$$

$\text{CH}_3\text{CO}_2\text{H}$	$\text{ClCH}_2\text{CO}_2\text{H}$	$\text{Cl}_2\text{CHCO}_2\text{H}$	$\text{Cl}_3\text{CCO}_2\text{H}$	Acids
4.76	2.86	1.25	0.65	pKa value
————— Increasing Acidity —————>				Acidity

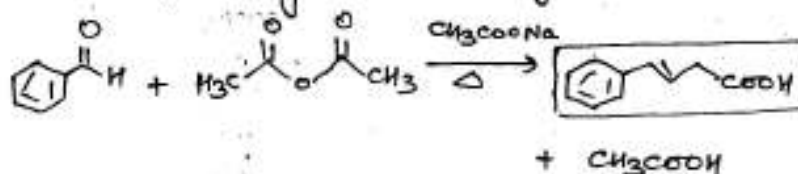
The pKa value shows that in the given order, acidity increases on ~~decreasing~~ as the pKa value decreases. It may also be explained that chlorine group is -I group and -I group increases acidity. Therefore, from left to right in the above series of acids, acidity increases due to increase in number of -I groups and decrease in their pKa value.

Answer 3:

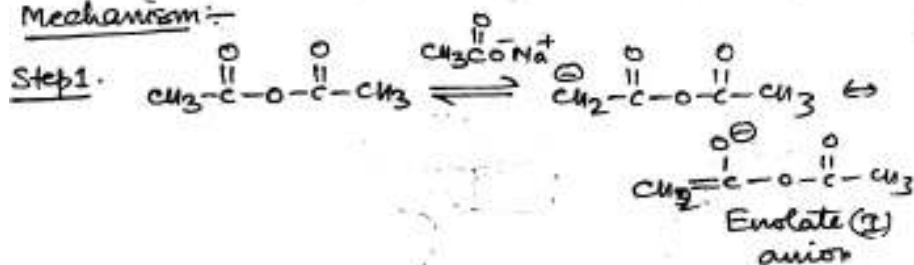
**PERKIN CONDENSATION:** This reaction may be explained by two different mechanisms –

**First Mechanism:**

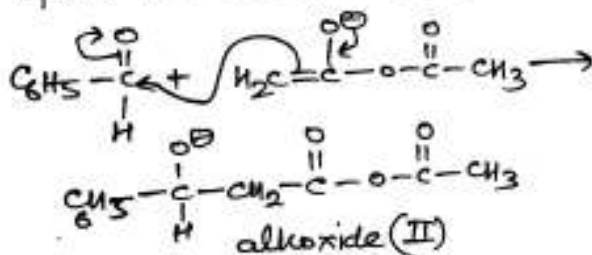
Reaction of an aromatic aldehyde with aliphatic acid anhydride having atleast 2  $\alpha$ -H's in the presence of a base i.e. sodium salt of the acid corresponding to the anhydride.



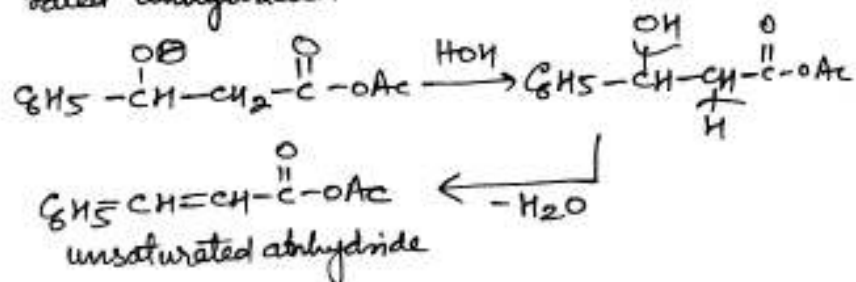
Mechanism:-



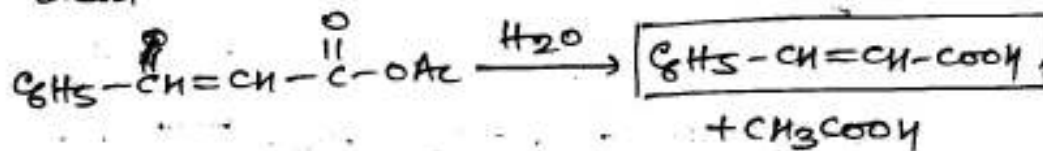
Step 2. The enolate anion gives nucleophilic addition reaction with aromatic aldehyde to form an alkoxide (II)



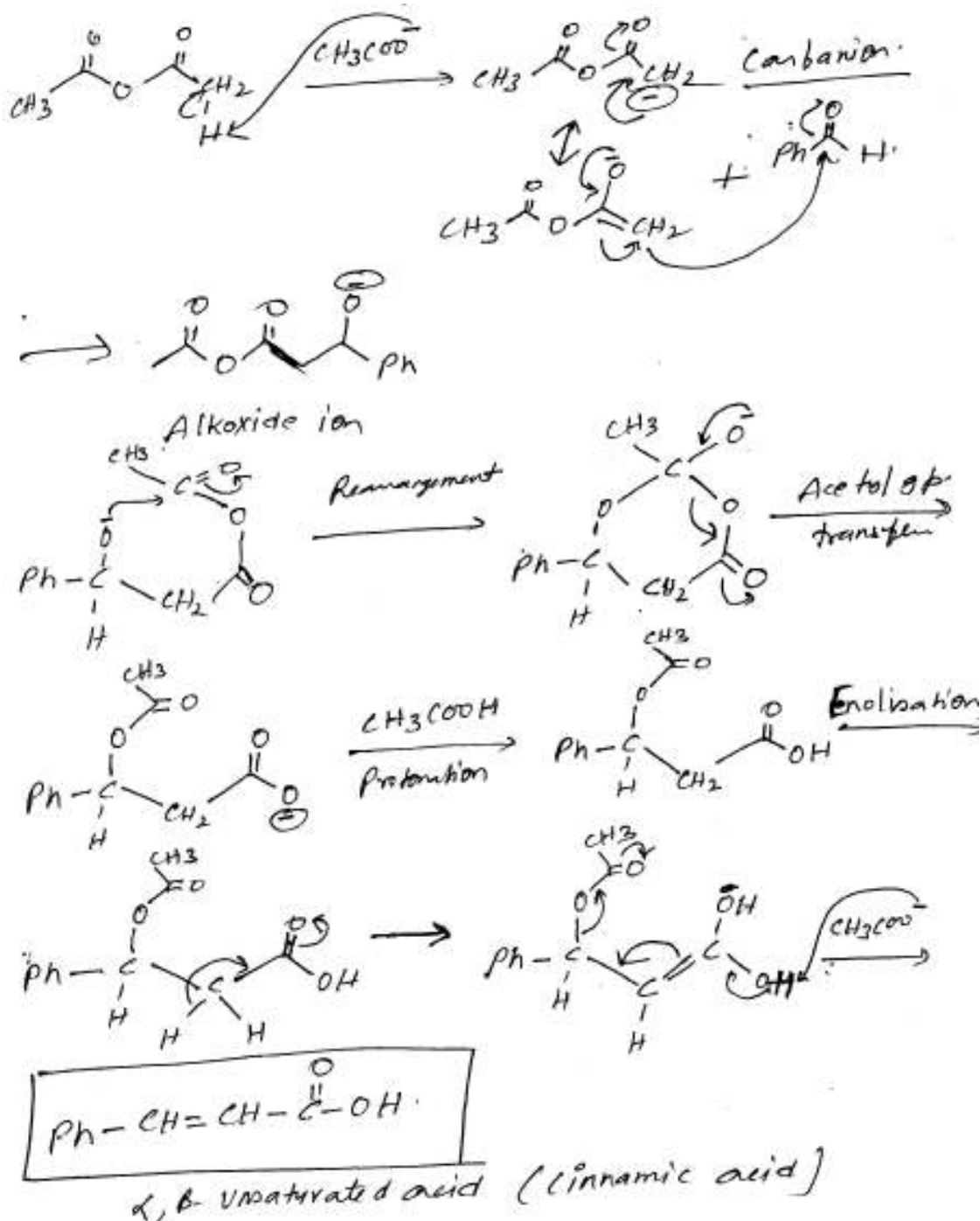
Step 3. The alkoxide ion gets protonated by  $\text{H}_2\text{O}$  and subsequent removal of  $\text{H}_2\text{O}$  produces unsaturated anhydride.



Step 4. Unsaturated anhydride is finally hydrolyzed to form the unsaturated acid.

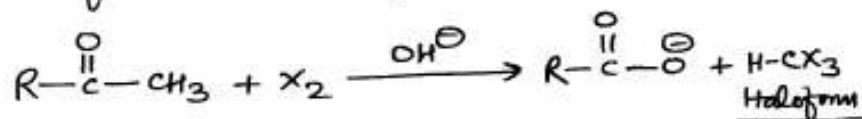


**Second Mechanism:**



## HALOFORM REACTION:

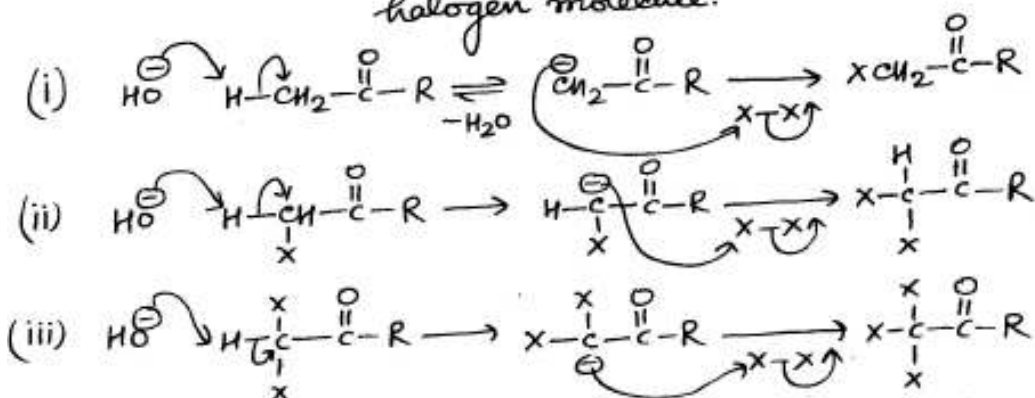
Aldehydes and ketones having  $\text{CH}_3$  group at  $\alpha$ -position (eg. Acetaldehyde and methyl ketones) react rapidly with halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ) in the presence of alkali to form haloform.



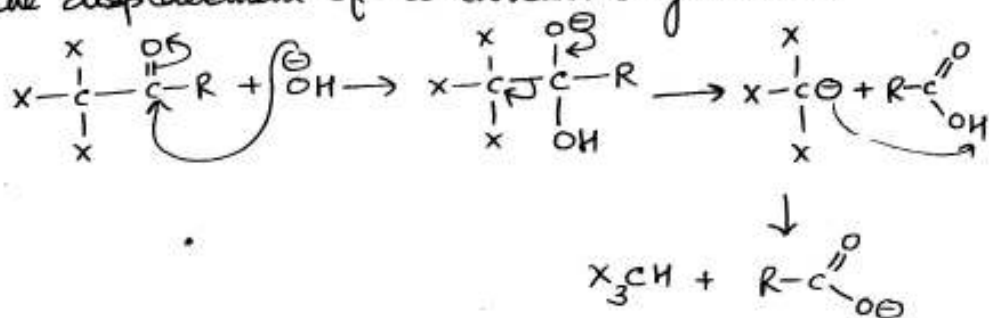
### Mechanism:-

In the haloform reaction, the  $\alpha$ -H of aldehyde or ketone replaced by halogens one by one. Each substitution of  $\alpha$ -H by halogen involves two steps — formation of carbanion.

Carbanion displaces a halide from halogen molecule.

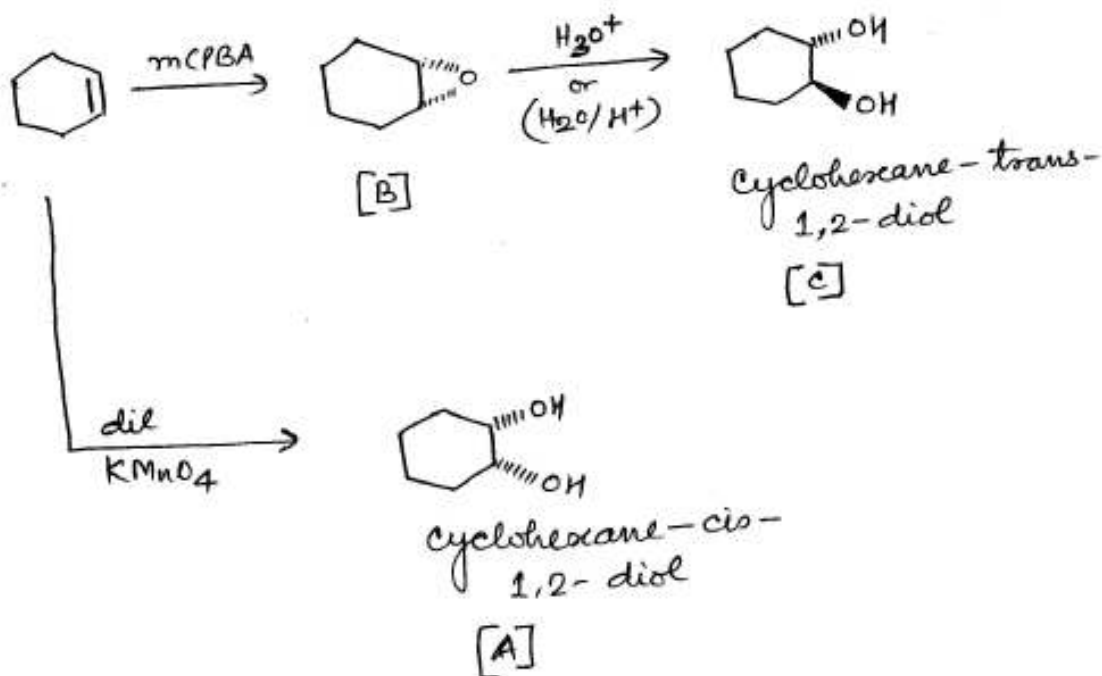


The trihalogenated aldehydes/ketones are unstable to base and are attacked at carbonyl carbon, with the displacement of a trihalomethyl anion.

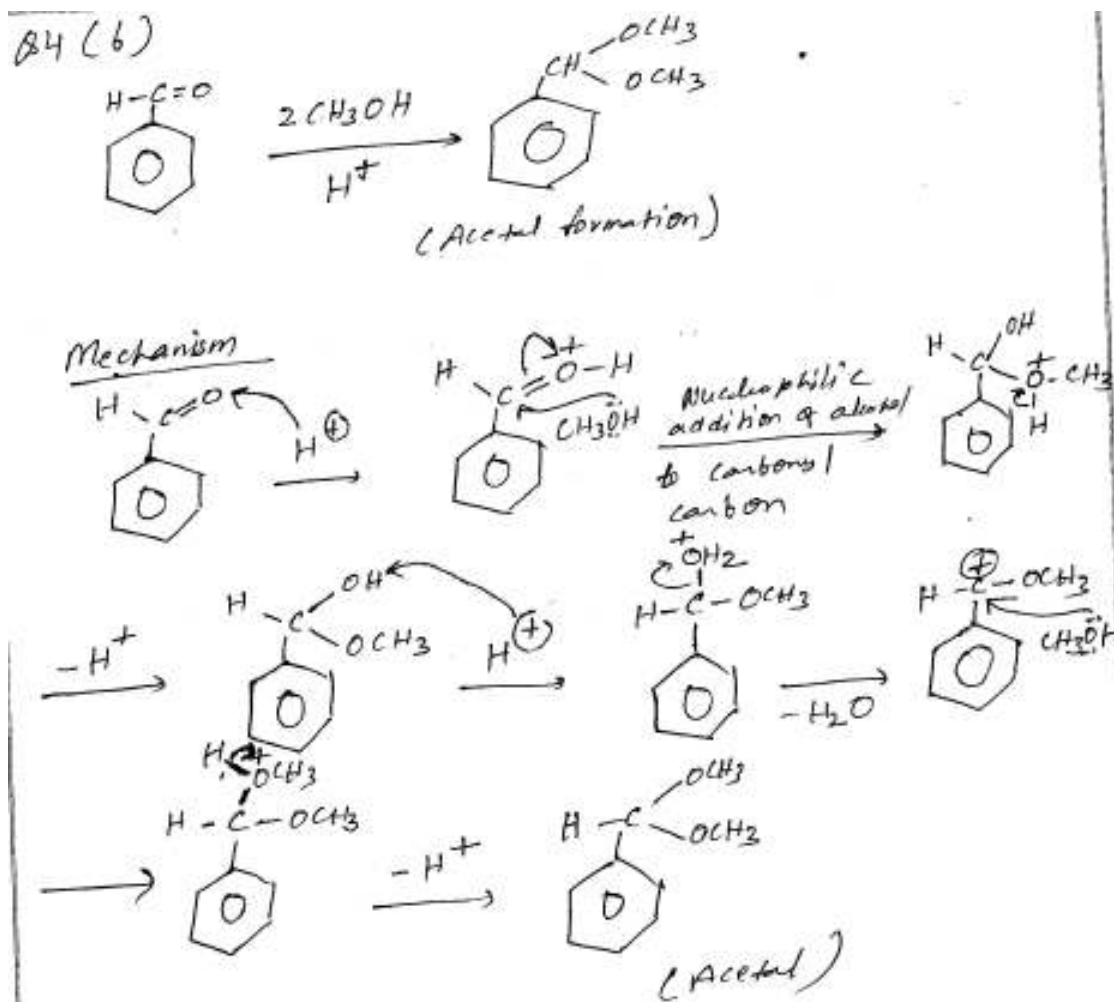




Answer 4 (a):



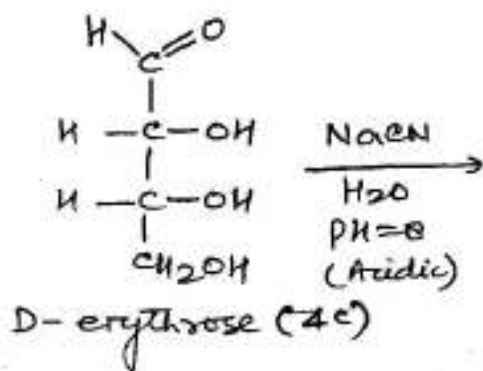
Answer 4 (b):



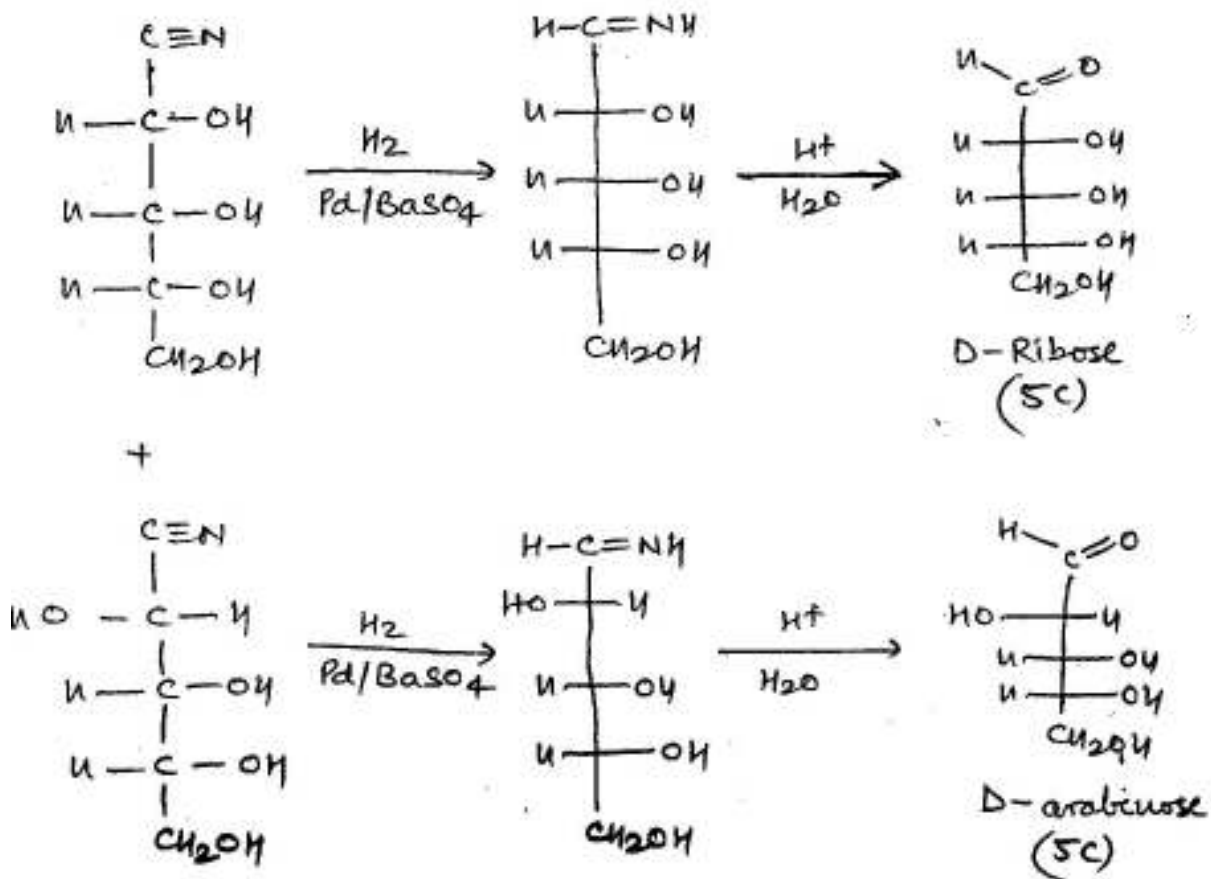
Answer 5:

**Kiliani F. Synthesis:**

The carbon chain of an aldose can be increased by one carbon by Kiliani-Fischer synthesis.



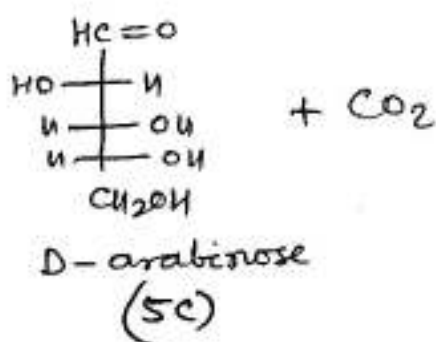
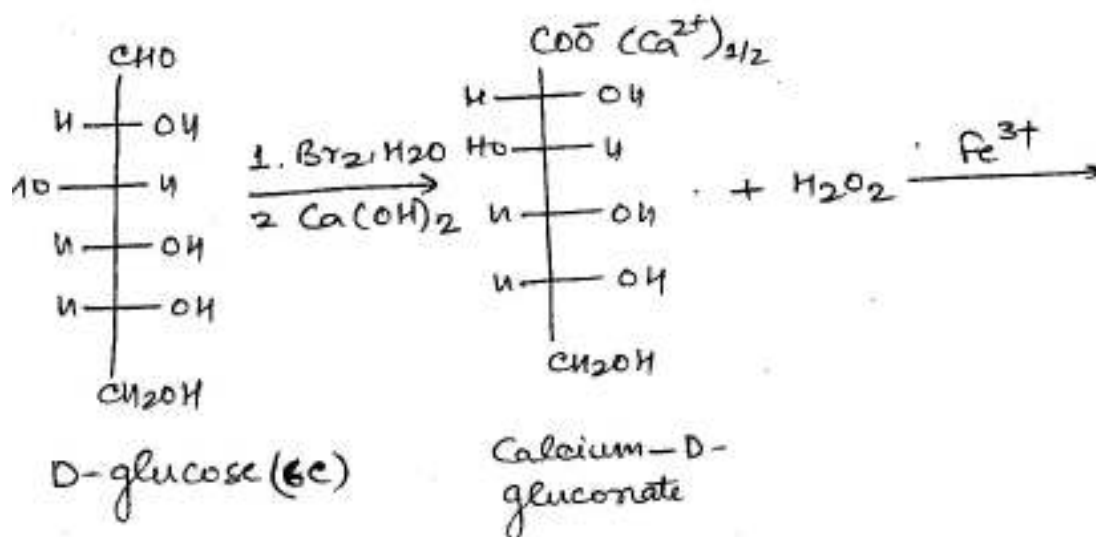
Addition of  $\text{CN}^-$  to carbonyl group creates a new chiral centre. Consequently, two cyanohydrins that differ at C-2 are formed and these form epimers at C-2.



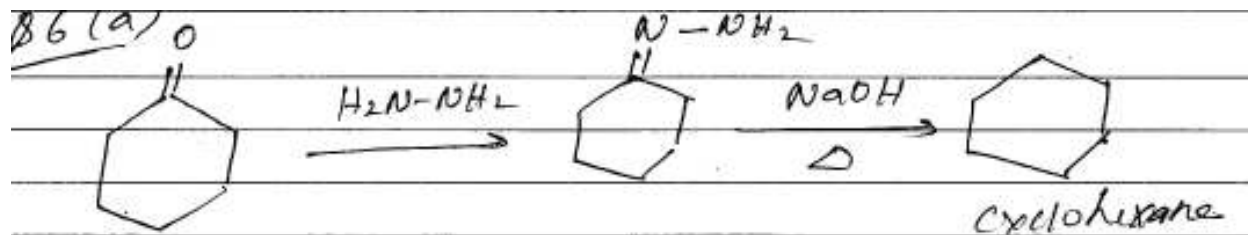
## Ruff degradation:

The higher aldoses are converted to a next lower aldoses by Ruff degradation.

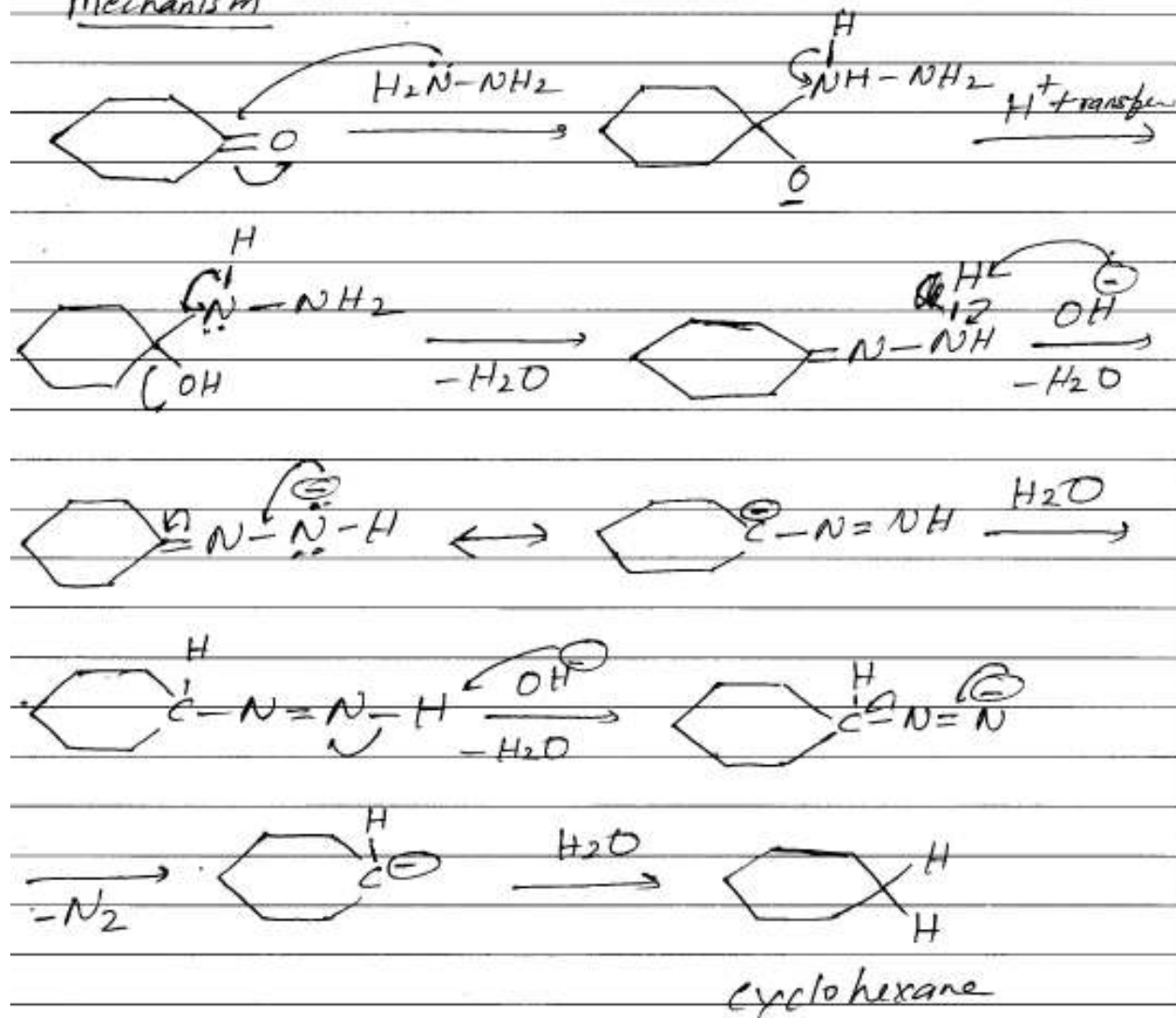
In this reaction, aldose is oxidised to corresponding aldonic acid. The aldonic acid is then converted into its calcium salt. The calcium salt is then oxidised with  $H_2O_2$  catalysed by  $Fe^{3+}$  ion. The oxidation cleaves the bond between C-1 and C-2 forming  $CO_2$  and an aldehyde. Mechanism of this reaction is not well understood.



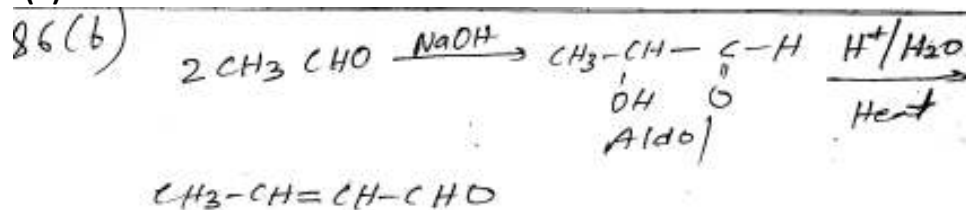
Answer 6 (a):



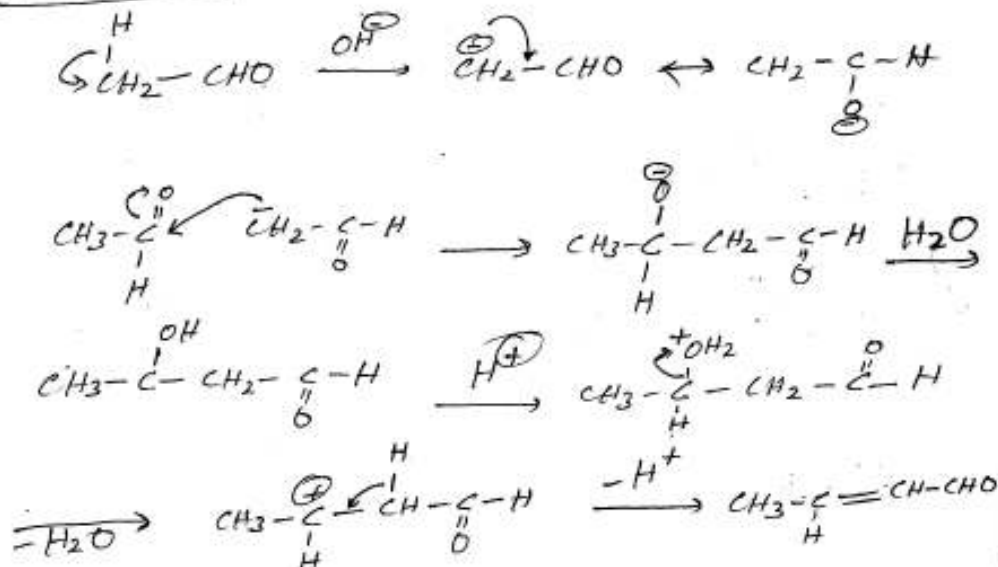
Mechanism



Answer 6 (b):



Mechanism:



Answer 7 (a):

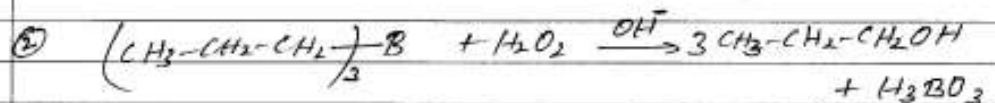
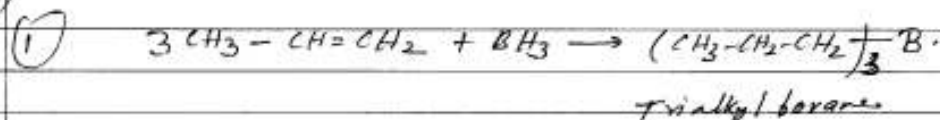
### Hydroboration-Oxidation of Alkenes

→ Alkenes react with diborane, B<sub>2</sub>H<sub>6</sub> to form trialkylboranes.

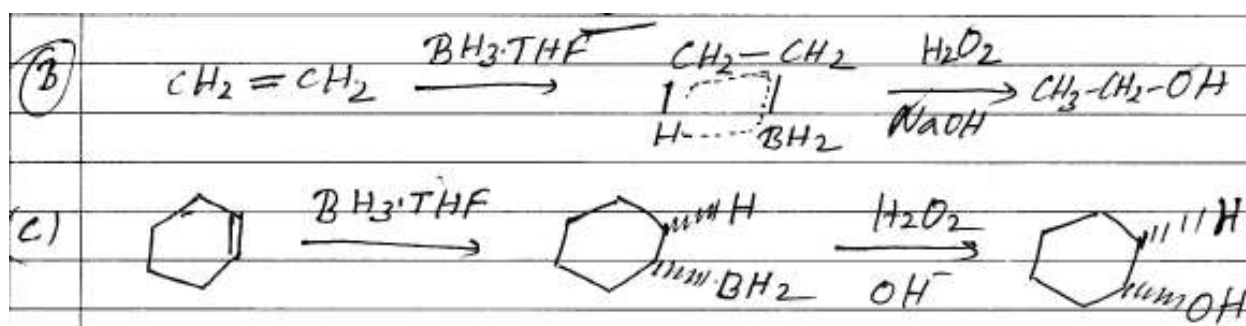
→ Diborane adds as borane, BH<sub>3</sub>.

→ Trialkylboranes are used for making primary alcohols by reaction with alkaline aqueous soln of H<sub>2</sub>O<sub>2</sub>.

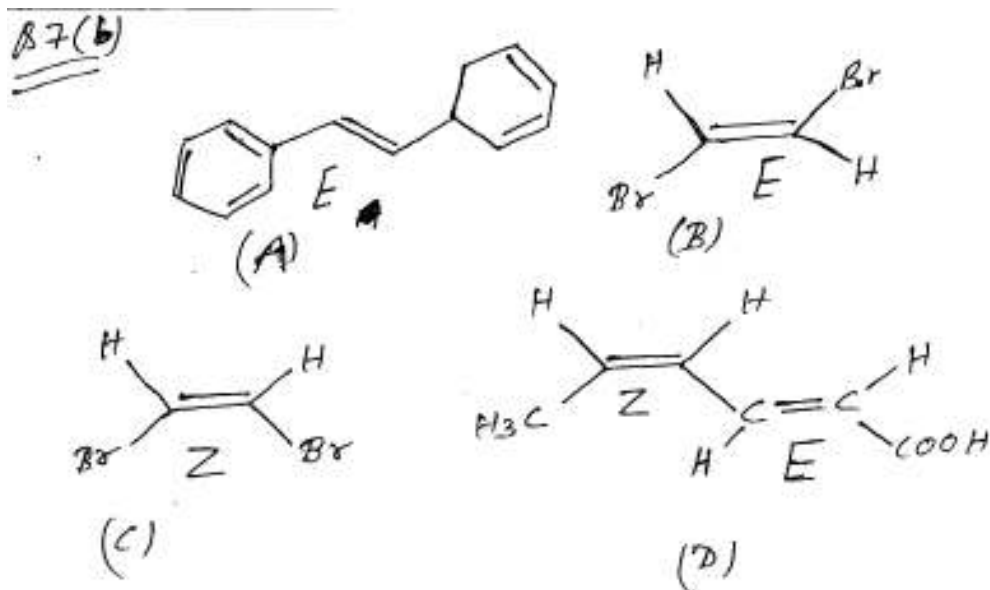
(A)



→ The above reaction appears to be Anti-Markovnikov addition



Answer 7 (b):



Answer 8 (a):

**Enantiomers:**

- Optical isomers that are mirror images are called enantiomers. These always exist as discrete pairs.
- Enantiomers have identical properties in all respects except in their interaction with plane of polarized light. They have same melting point, density, solubility, color, and reactivity.
- Both rotate the the plane of polarized light to exactly the same extent (same angle) but one rotates the plane to the right (clockwise: called dextrorotatory), while the other rotates the plane to the left (anticlockwise: called laevorotatory).
- Enantiomers are stable, isolable, compounds that differ from each other in 3-D spatial arrangement. They cannot be interconverted under ordinary conditions

Example: Two optical isomers of lactic acid.

