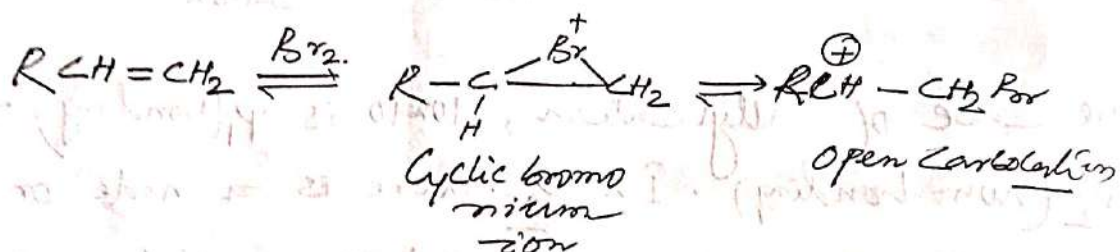# Alkene and alkyne

Addition of Halogen:

Chlorinations and brominations of alkenes are widely studied reactions. These are electrophilic additions and proceed through a discrete positively charged intermediate which may be bridged or a carbo cation. This discrete positively charged intermediate is formed after the addition of Br^+ to the alkene.

$$RCH=CH_2 \xrightleftharpoons{Br_2} R-\overset{\overset{+}{Br}}{\underset{H}{C}}-CH_2 \rightleftharpoons \overset{\oplus}{RCH}-CH_2 \text{ Por}$$

Cyclic bromonium ion   Open Carbocation

The anti addition of bromine is observed for alkenes which do not have substituent groups that would strongly stabilize carbocation intermediate.

* Thus addition of bromine to cis and trans-2-butene is stereospecific. The first step is the formation of a bridged cation and in the second step the nucleophile Br^- adds to the face away from the bridging group to give the overall anti addition.

cis-2-butene

(A)

rac-2,3-dibromobutane
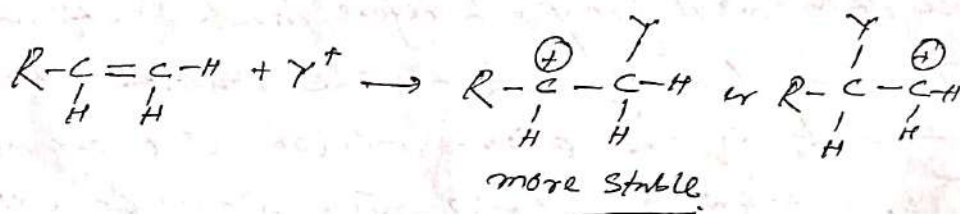
meso-2,3-dibromobutane.
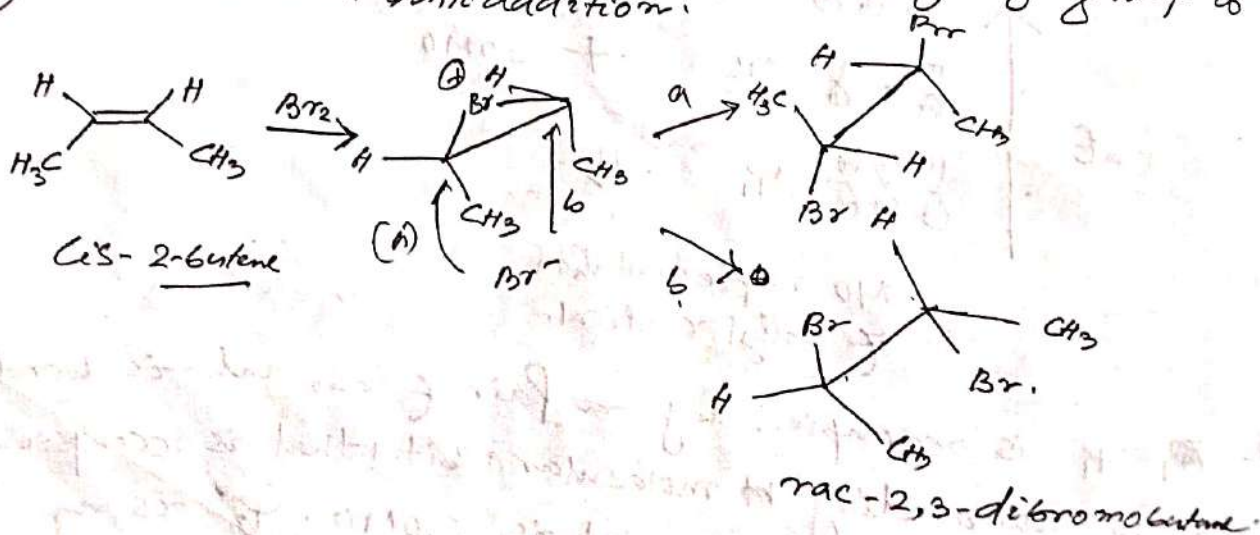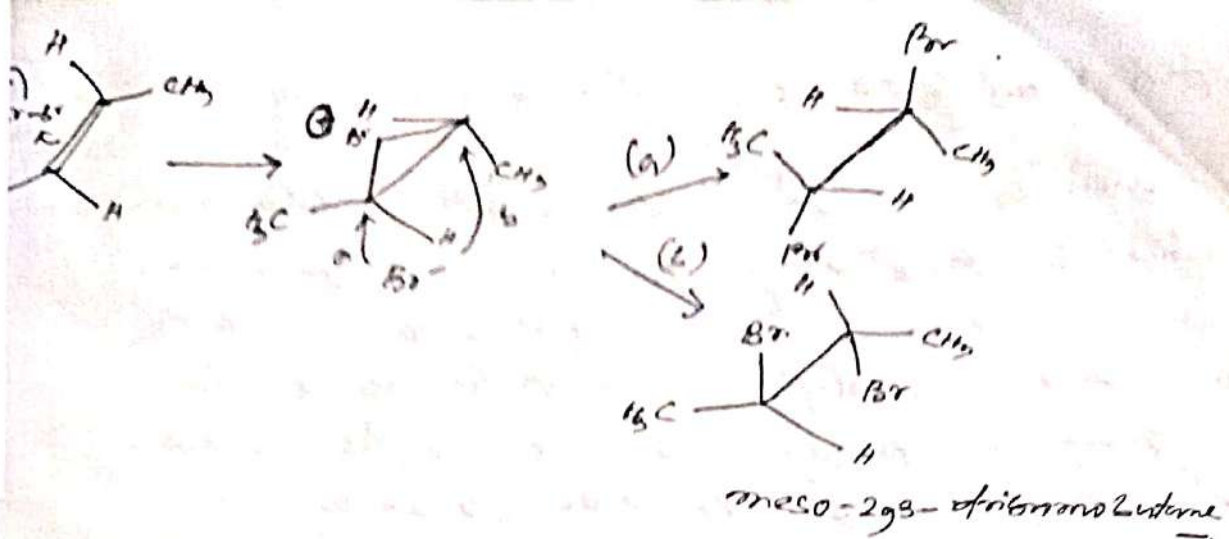
‡ When the alkene has an aryl group attached to the doubled bond, the selectivity becomes less and both syn and anti adducts are formed. This is so, because now the positive charge on the intermediate is delocalized on the aromatic ring. The presence of a phenyl group, therefore provides sufficient stabilization to allow carbocation formation. The situation reduces the effectiveness of bridging and allows rotation to occur as shown below. The freely rotating open carbocation would be expected to yield both the syn as well as anti addition product.
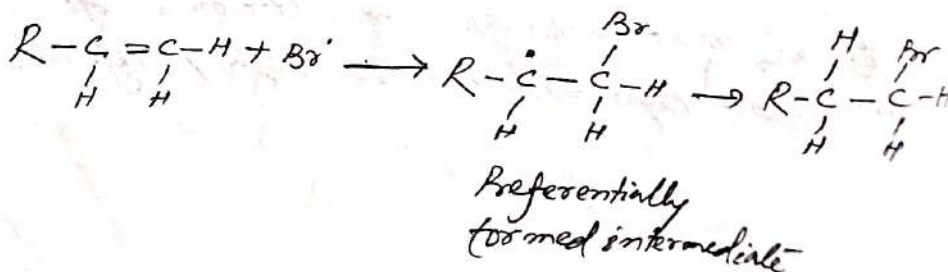

The syn and anti addition product
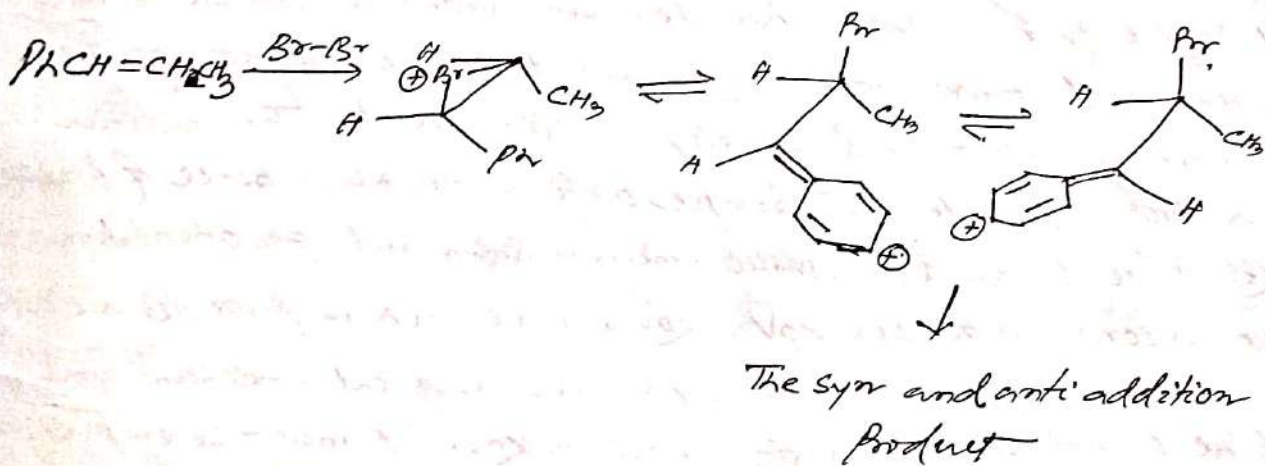
Chlorine being a weaker bridging group (it is less polarizable and more reluctant to become positively charged), it is thus found that although anti addition is dominant during bromination syn addition is slightly preferred for chlorination.

Addition of halo acid to olefins:

When an unsymmetrical reagent is added to an unsymmetrical substrate, the question arises; ~~the question arises~~ which side of the reagent goes to which side of the double or triple bond? For electrophilic attack, the answer is given by Markonikov's rule: the positive portion of the reagent goes to the side of the double or triple bond that has more hydrogens. A number of explanations have been suggested for this regioselectivity, but the most ~~pr~~ probable is that 'y+' adds to that side that will give more stable carbocation. Thus when an alkyl group is present, secondary are more stable than primary.

$$R-\underset{H}{\overset{|}{C}}=\underset{H}{\overset{|}{C}}-H + Y^+ \longrightarrow R-\underset{H}{\overset{\oplus}{\underset{|}{C}}}-\underset{H}{\overset{\overset{\displaystyle Y}{|}}{\underset{|}{C}}}-H \quad \text{or} \quad R-\underset{H}{\overset{\overset{\displaystyle Y}{|}}{\underset{|}{C}}}-\underset{H}{\overset{\oplus}{\underset{|}{C}}}-H$$

<u>more stable</u>

Any of the four hydrogen halides can added to double bonds; HI, HBr, and HF add at room temperature. The addition of HCl is more difficult and usually requires heat. The addition of hydrogen halides to simple olefins, in the absence of peroxide takes place by an electrophilic mechanism, and the orientation is in accord with Markovnikov's rule. When peroxides are ad the addition of HBr occurs by a free radical mechanism and the orientation is anti-Markovnikov. It must be emphasize that this is true only for HBr, free-radical addition of HF and HCl only rarely.

$$R-\underset{H}{\overset{|}{C}}=\underset{H}{\overset{|}{C}}-H + Br^{\cdot} \longrightarrow R-\underset{H}{\overset{\cdot}{\underset{|}{C}}}-\underset{H}{\overset{\overset{\displaystyle Br}{|}}{\underset{|}{C}}}-H \longrightarrow R-\underset{H}{\overset{\overset{\displaystyle H}{|}}{\underset{|}{C}}}-\underset{H}{\overset{\overset{\displaystyle Br}{|}}{\underset{|}{C}}}-H$$

Preferentially
formed intermediate

Justify the observation that addition of Br_2 to maleic acid gives racemic mixture whereas the same reaction with fumaric acid yields meso-product.

Ans

Maleic acid

Rac-mixture.

fumaric acid

Meso-form.
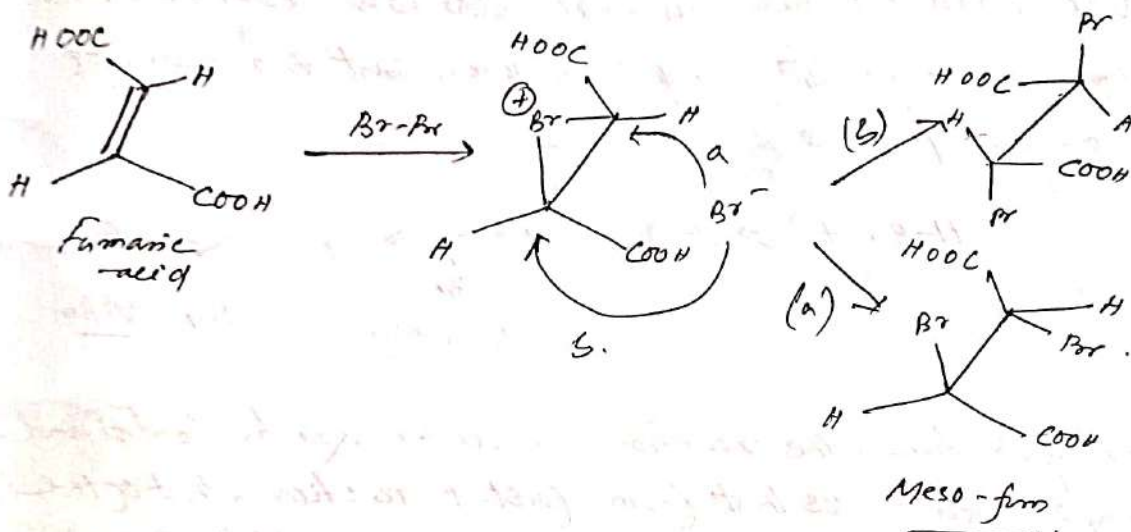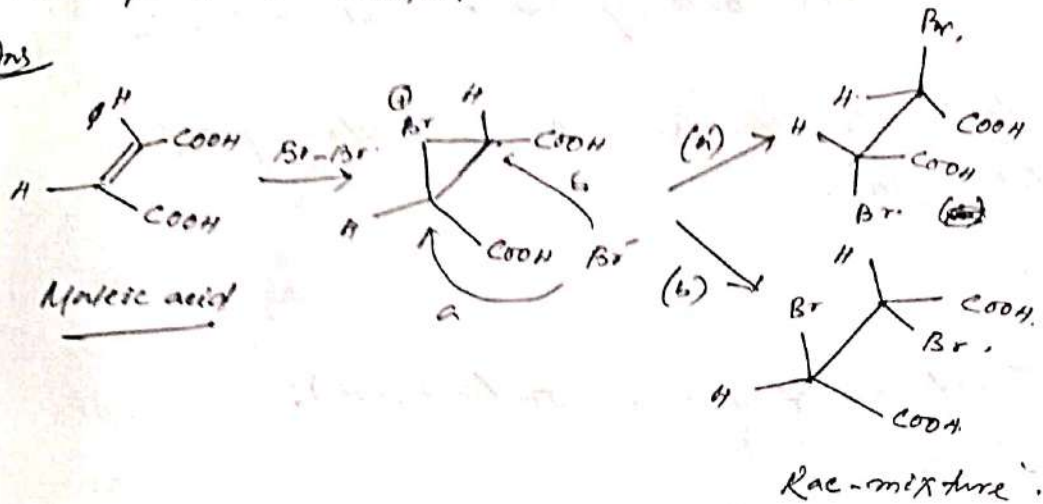
Addition of bromine to maleic acid and fumaric acid is stereospecific. The first step is the formation of a bridged cation and in the second step the nucleophilic Br^- adds to the face away from the bridging group to give the overall anti addition.

* Why does only HBr give anti-Markownikov's product in presence of peroxide among all the haloacids?

Ans:

In the presence of peroxide and light, addition of HBr to unsymmetrical alkenes occour contrary to Markovnikov's rule. But HCl and HI do not show peroxide effect. Radical chain reactions are successful when propagation steps are exothermic. An endothermic propagation step is reversible and would break the chain. With HI, the first propagation step is endothermic, because C-I bond is weak. Moreover, HI is oxidized by peroxide to I_2 under reaction conditions. With HCl the second propagation

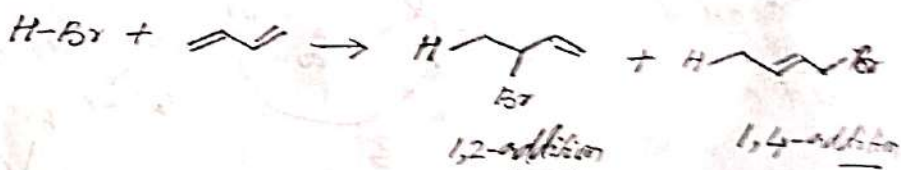Step is exothermic, because the HCl bond is strong. with HBr both the propagation steps are exothermic and HBr adds to the double bond by free radical mechanism.

* Addition of Br_2 to $Ph\,CH=CH-CH_3$ is less stereospecific than $CH_3\,CH=CHCH_3$.

Ans
See in notes

* Conjugate addition of HBr to butadiene (e.q):

Ans:
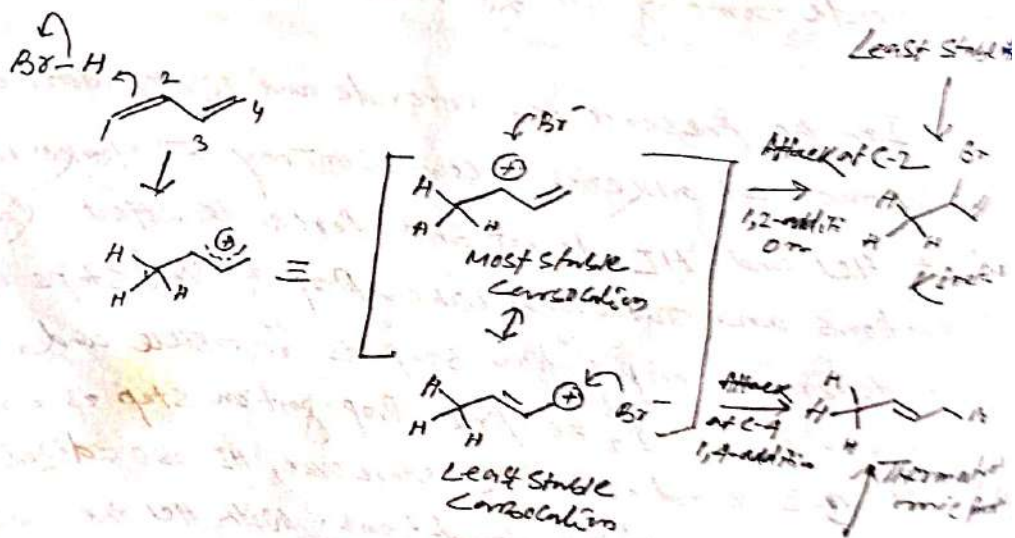
Conjugated dienes undergo addition reactions in similar manner to simple alkenes, but two modes of addition are possible

$$H-Br + \diagup\!\!\!\diagdown\!\!\!\diagup \longrightarrow H\diagdown\!\!\!\diagup\!\!\!\diagdown + H\diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown Br$$

1,2-addition   1,4-addition

At low temperature, the reaction is under Kinetic Control and the major product is that from fastest reaction, that of the bromide with the secondary cation (1,2-addition product)
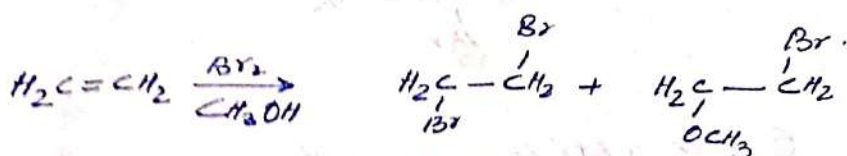
At higher temperature, the reaction is under thermodynamic control and the major product is the more stable system (more highly substituted alkene)
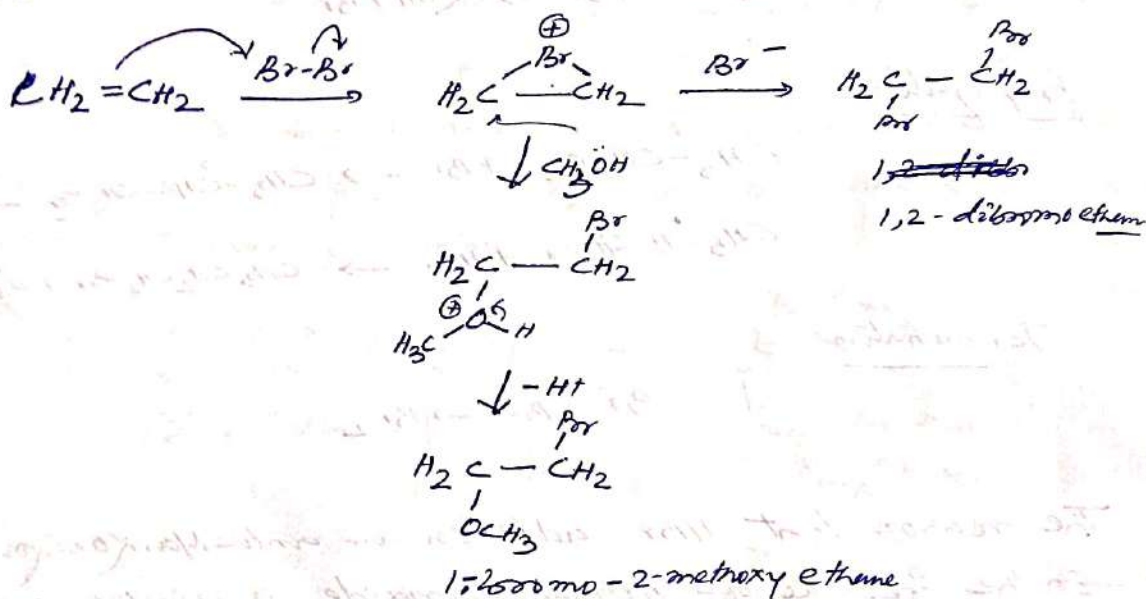
Mechanism

Least Stable

Attack at C-2
1,2-addition or Kinetic

Most stable carbocation

Attack at C-4
1,4-addition Thermodynamic product

Least stable carbocation

* In methanol solution, bromine adds to ethene to yield ~~~
only 1,2-dibromoethane but also 1-bromo-2-methoxy ethane?
Explain

Ans:

$$H_2C=CH_2 \xrightarrow{Br_2 \; CH_3OH} \quad H_2\overset{|}{C}-CH_2 \;+\; H_2C-\overset{\overset{Br}{|}}{C}H_2$$
$$\underset{Br}{} \qquad \qquad \underset{OCH_3}{}$$

The first part of the mechanism is same as halogenation,
a bromonium ion is formed. Then both Br^- or CH_3OH
acting can acts as a nucleophile to give mixture of
products.

$$eH_2=CH_2 \xrightarrow{Br-Br} H_2C\overset{\overset{\oplus}{Br}}{\underset{}{\cdots}}CH_2 \xrightarrow{Br^-} H_2\overset{|}{C}-\overset{\overset{Br}{|}}{C}H_2$$
$$\underset{Br}{}$$

$$\downarrow CH_3 \overset{..}{O}H$$

$$H_2\overset{|}{C}-\overset{\overset{Br}{|}}{C}H_2$$
$$H_3C\overset{\oplus}{\underset{}{O}}\overset{\ominus}{H}$$

$$\downarrow \begin{array}{c}-H^+ \\ for\end{array}$$

$$H_2\overset{|}{C}-CH_2$$
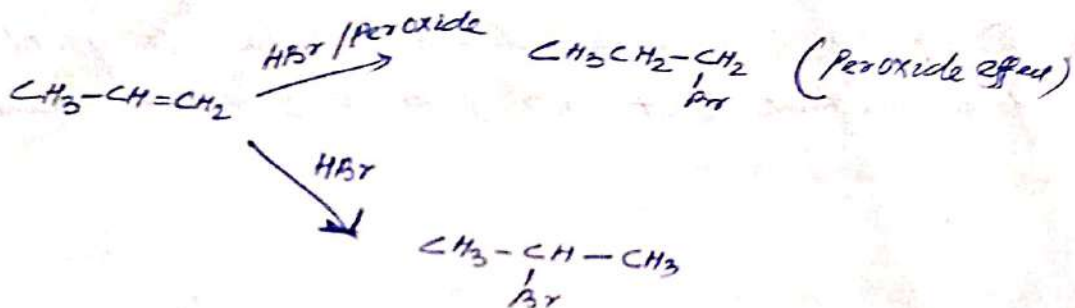$$\underset{OCH_3}{}$$

1-bromo-2-methoxy ethane

1,2-dibromo ethane

* What happens when trans-2-butene is allowed to react with Br₂
Predict the Products with possible stereochemistry?
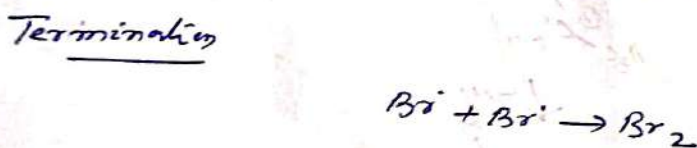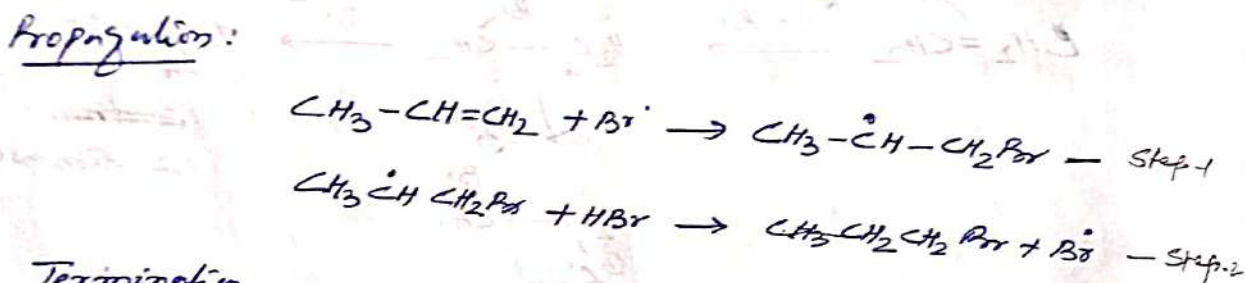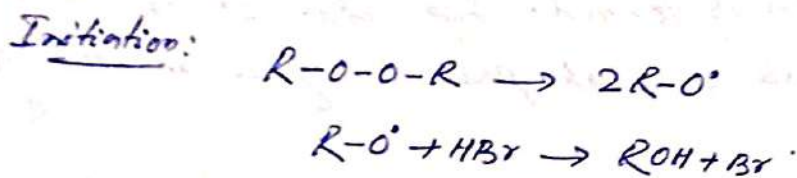
Ans: See in notes.

* Peroxide effect of HBr addition to alkene (short note):

Ans:
Normally, when a molecule HBr adds to a carbon-
carbon double bond, the hydrogen becomes attached to the
carbon with the more hydrogen on already. ~~Because~~ This is
known as Markovnikov's rule. Because the HBr adds to the
wrong way around in the presence of organic peroxides, this is
often known as the peroxide effect or anti-Markovnikov addition.

$$CH_3-CH=CH_2 \xrightarrow{\text{HBr/Peroxide}} CH_3CH_2-\underset{\underset{Br}{|}}{CH_2} \quad (\text{Peroxide effect})$$

$$CH_3-CH=CH_2 \xrightarrow{\text{HBr}} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

Mechanism of HBr addition in the presence of Peroxide is supposed to proceed via a radical mechanism.

Initiation:

$$R-O-O-R \longrightarrow 2R-O^\circ$$

$$R-O^\circ + HBr \longrightarrow ROH + Br^\circ$$

Propagation:

$$CH_3-CH=CH_2 + Br^\circ \longrightarrow CH_3-\overset{\circ}{C}H-CH_2Br \quad - Step_1$$

$$CH_3\overset{\circ}{C}H CH_2Br + HBr \longrightarrow CH_3CH_2CH_2Br + Br^\circ \quad - Step_2$$

Termination

$$Br^\circ + Br^\circ \longrightarrow Br_2$$

The reason that HBr adds in an anti-Markonikov fashion in the Presence of organic peroxide is simply a question of reaction rates. The free radical is much faster than the alternative electrophilic addition mechanism.

* The addition of fluorine to ethylenic double bond is non-stereospecific whereas addition of ~~double bond~~ bromine to double bond is trans.

Ans:

Fluorin reacts very vizorously to form not only fluorinated but also several oxidation Products. rest Explain yourself:

Stereospecific and Stereoselective reaction:-

Stereoselective reaction is one in which stereochemically different isomers react to stereochemically different products.
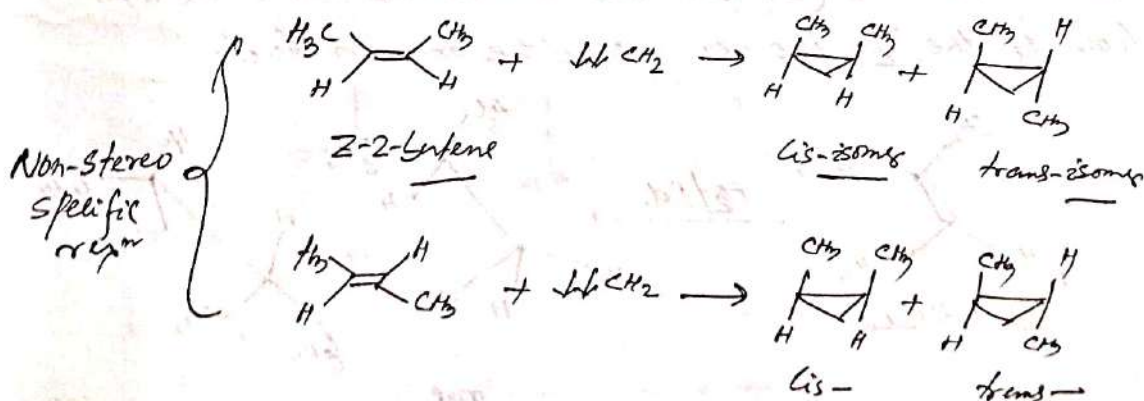
A stereoselective reaction is one which produces one diastereoisomer in excess over the other. A stereospecific reaction is one in which stereochemically different isomers lead to stereochemically different products.

A good example of stereospecific reaction is addition of singlet and triplet carbenes with an alkene having E and Z isomers.

Singlet carbene having two spin-paired electron in sp^2 hybrid orbital reacts stereospecifically to form cis-1,2-dimethyl cyclopropane from cis-2-butene and trans 1,2-dimethyl cyclopropane from trans-2-butene. Cis-2-butene cannot form trans-product and trans-2-butene does not give cis product.

Stereospecific
reaction

(Z)-2-Butene + $\uparrow\downarrow CH_2$ → cis-1,2-dimethyl cyclopropane

(E)-2-Butene + $\uparrow\downarrow CH_2$ → trans-1,2-dimethy cyclopropane.
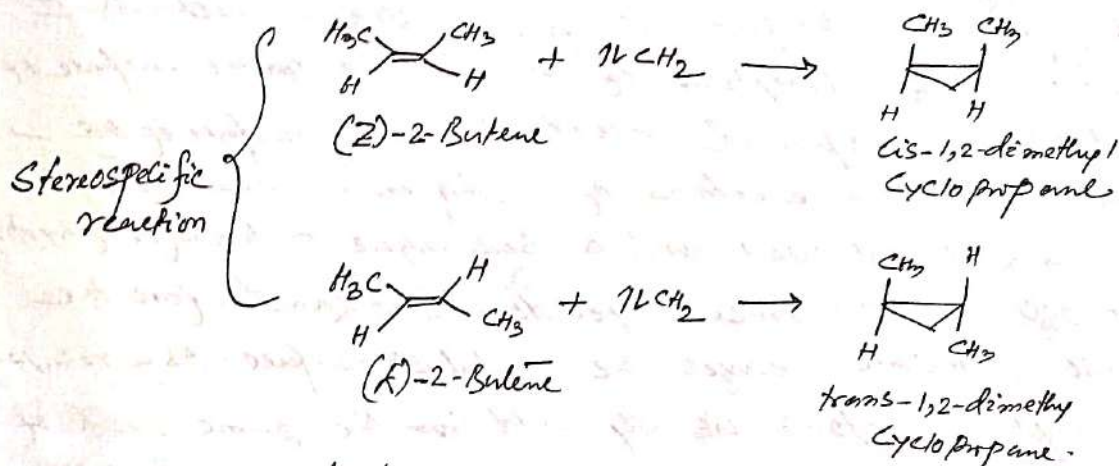
On the other hand, triplet carbene has two electrons in two 'P'-orbitals with parallel spins on a sp^2 hybridised carbons. It reacts stereo selectively either with cis-2-butene or with trans-2-butene to form a mixture of cis-and trans- 1,2-dimethyl cyclopropane. Single product is never obtained.

Non-stereo
specific
reᵗⁿ

Z-2-butene + $\downarrow\downarrow CH_2$ → cis-isomer + trans-isomer

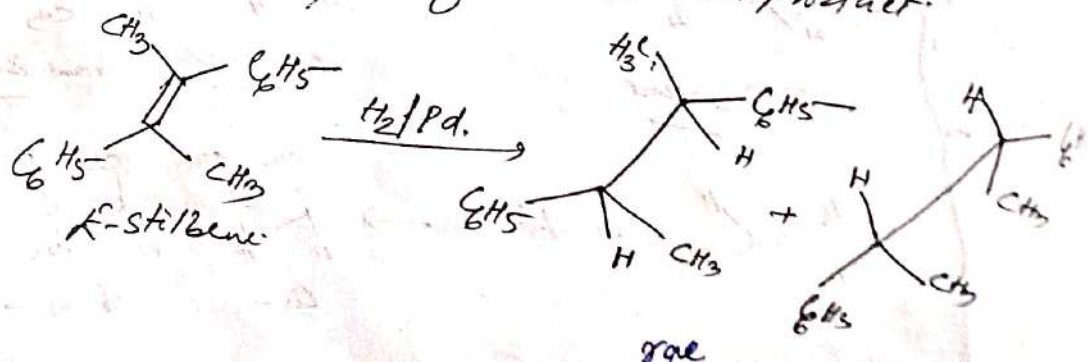+ $\downarrow\downarrow CH_2$ → cis- + trans-

The preferential formation of a equatorial trans-alcohol along with smaller amount of cis-isomer by LiAlH₄ reduction of 4-2-butylcyclohexanone is a stereoselective reaction.

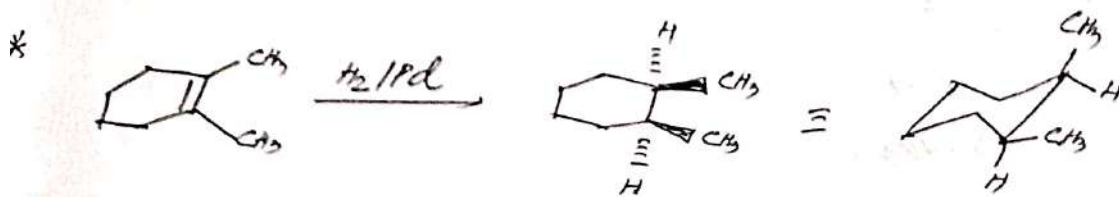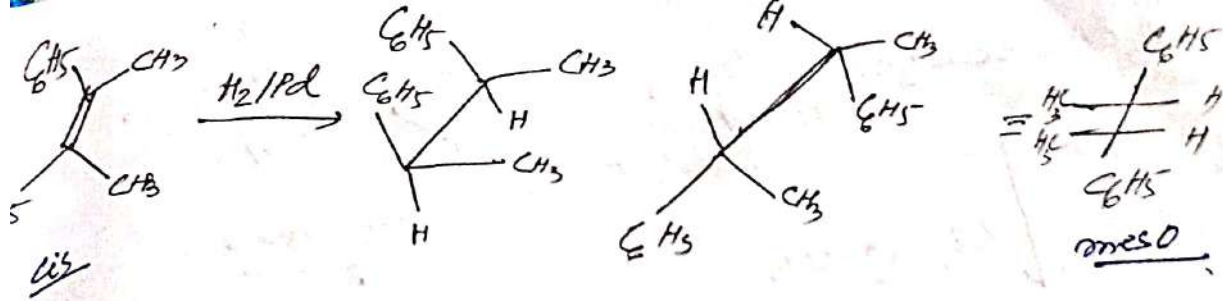

trans (90%)   cis (10%)
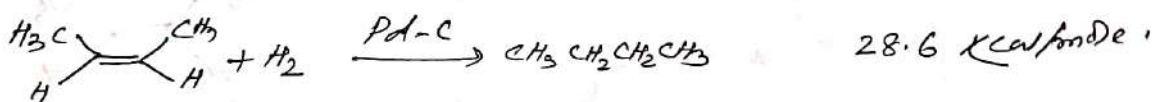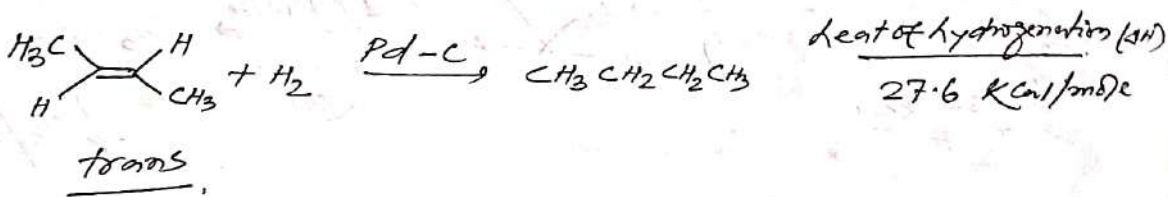
Stereoselective isomers
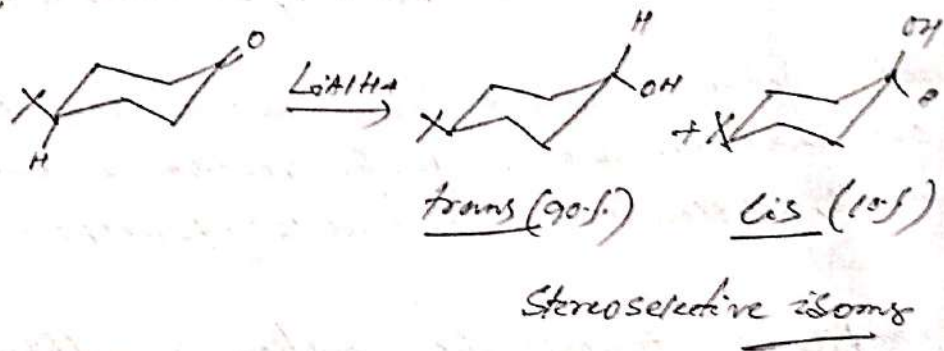
Hydrogenation of alkene:

Alkanes, which are strained can be reduced catalytically by rupturing C-C bonds. The C-C cleavage relieve the strain. Normally all olefins can be reduced by treating with hydrogen in the presence of catalyst. The process of hydrogenation is thought to proceed via a mechanism involving the adsorption of 'H₂' molecule on the surface of catalyst. The unpaired electrons on the surface of the metal, pair with electrons of hydrogen causes adsorption of the alkene as well and a subsequent transfer of hydrogen atom occours. The process yields an alkane before the organic molecule leaves the catalyst surface. As a result both hydrogen atoms usually add from the same side of the molecule, a process termed syn addition.

Stereochemically, the hydrogenation of an olefin occours in a syn-fashion. Thus, when one considers the hydrogenation of the E-stilbene derivative, the syn addition gives the (±) dihydro-derivative while the syn addition to the 'Z-isomer gives the meso product.

H_2/Pd.

E-stilbene

rac

C_6H_5 ―CH₃ / C_6H_5 / CH₃ → H₂/Pd → (products with stereochemistry: C_6H_5, CH₃, H, CH₃, H / H, CH₃, C_6H_5, CH₃, C_6H_5 / C_6H_5, H, H, C_6H_5 **meso**)

cis

*

(cyclohexene with CH₃, CH₃) → H₂/Pd → (cis product with CH₃, CH₃) ≡ (chair form with CH₃, H, CH₃, H)
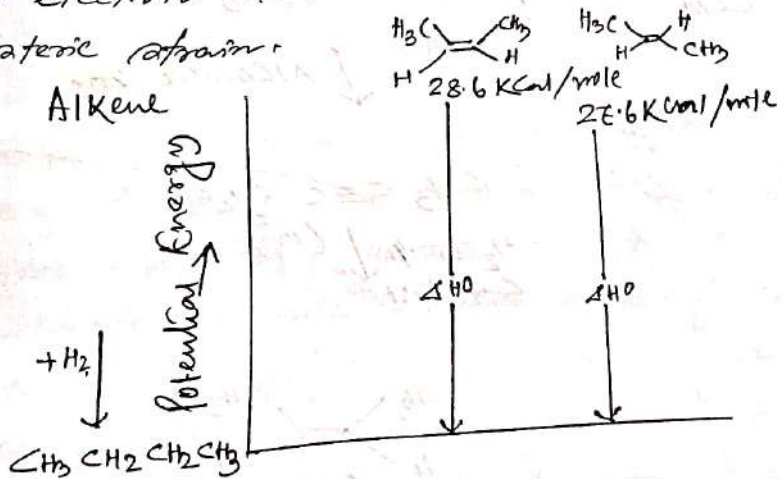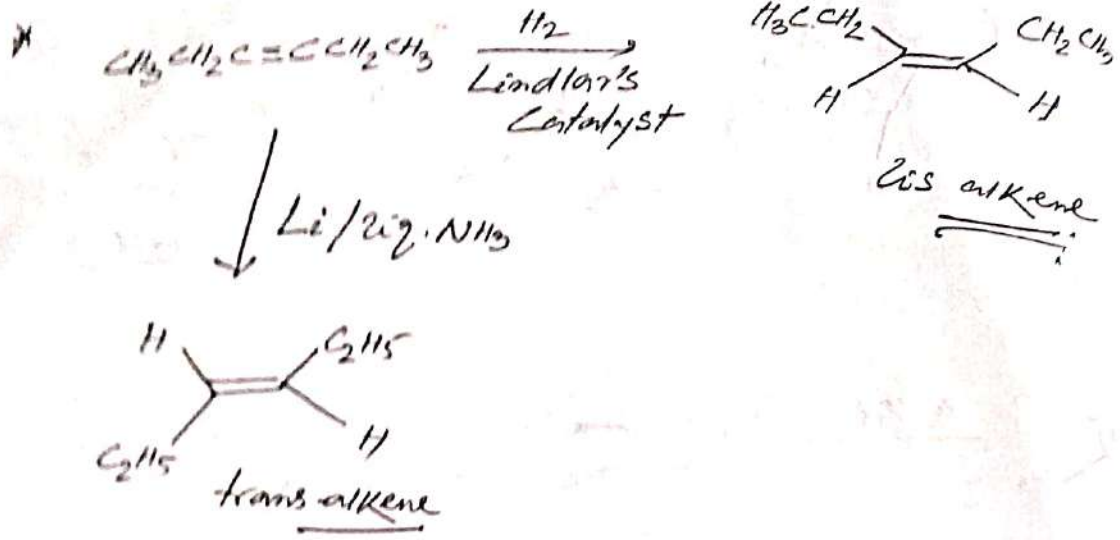
cis-2-butene evolves 1 Kcal/mole more energy than trans isomer during the addition of 1 mole of hydrogen - Explain -

Both trans-2-butene and cis-2-butene have two alkyl groups bonded to their sp² carbons, but trans-2-butene has a smaller [ext] of hydrogenation. This means that the trans isomer, in which large substituents are farther apart, is more stable than the cis isomer, in which the large substituent are closer together.
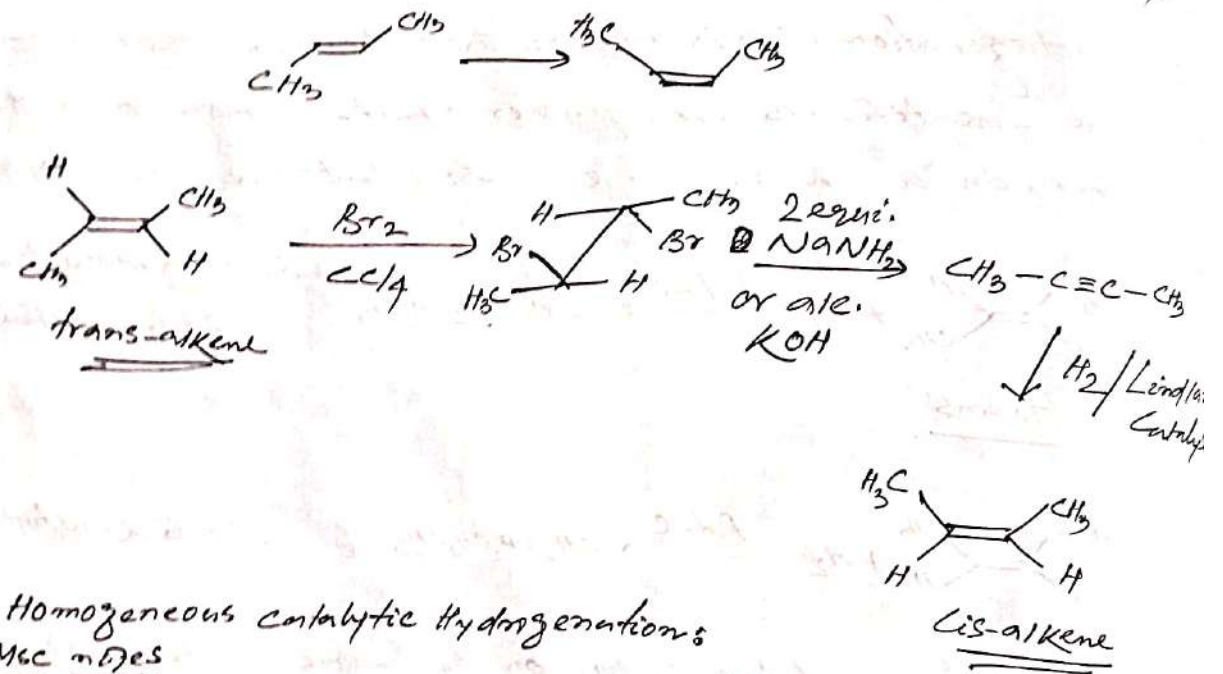

H_3C , H / H , CH₃ + H_2 → Pd-C → $CH_3 CH_2 CH_2 CH_3$

trans

Heat of hydrogenation (ΔH)
27.6 Kcal/mole

H_3C , CH₃ / H , H + H_2 → Pd-C → $CH_3 CH_2 CH_2 CH_3$

28.6 Kcal/mole·

When the large substituents are on the same side of the mole-cule, their [reaction] electron clouds can interfere with each other, causing strain in the molecule and making it less stable. When the large substituents are on opposite side of the molecule their electron clouds cannot interact and the molecule has less steric strain.

H_3C , CH₃ / H , H 28.6 Kcal/mole
H_3C , H / H , CH₃ 27.6 Kcal/mole

Alkene

Potential Energy →

+H₂ ↓

ΔH^0 ΔH^0

$CH_3 CH_2 CH_2 CH_3$

Energy Profile diagram of the catalytic hydrogenation of cis- and trans-2-butene.

*

$CH_3CH_2C \equiv CCH_2CH_3$ $\xrightarrow[\text{Lindlar's Catalyst}]{H_2}$

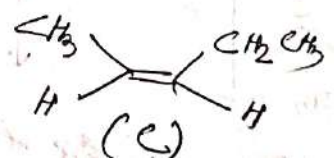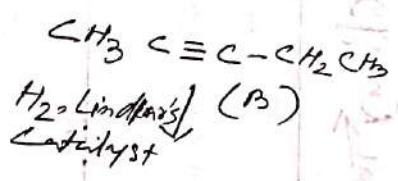cis alkene

$\downarrow$ $Li / liq. NH_3$

trans alkene

*

How would you carryout the following transformation. Give the plausible mechanism:

trans-alkene

$\xrightarrow[CCl_4]{Br_2}$

$\xrightarrow[\substack{or\ ale.\\ KOH}]{\substack{2\ equi.\\ NaNH_2}}$ $CH_3 - C \equiv C - CH_3$

$\downarrow$ $H_2 / Lindlar$ Catalyst

cis-alkene

* Homogeneous catalytic Hydrogenations are Mcc models.

* Identify A, B and C:

$CH_3 CH = CH - CH_2 CH_3$ $\xrightarrow[CCl_4]{Br_2}$ $CH_3 CH - \underset{Br}{\overset{Br}{CH}} - CH_2 CH_3$ (A)

$\downarrow$ Alcoholic KOH

$CH_3 C \equiv C - CH_2 CH_3$ (B)

H_2, Lindlar's Catalyst

(C)
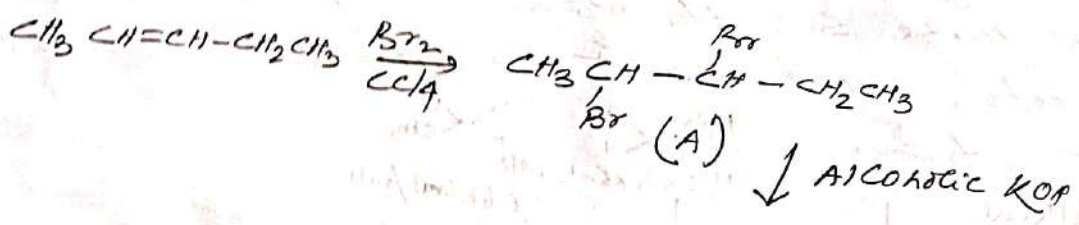
Birch reduction:

Partial reduction of aromatic rings can be achieved by dissolving metal systems and the reaction is called Birch reduction. The reduction medium usually consist of lithium or sodium in liquid ammonia.

$$NH_3 + Na \longrightarrow (NH_3)\cdots e^-(NH_3) \text{ (deep blue soln}^n) + Na^+$$
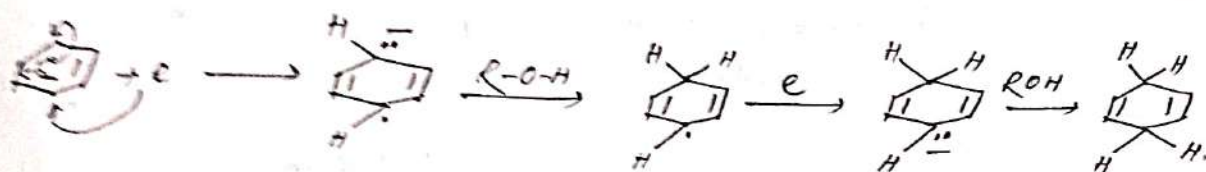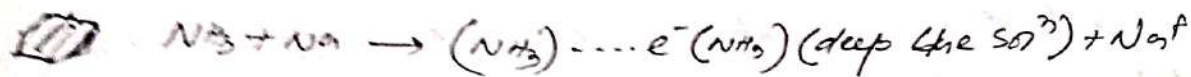
The rate of reduction is also affected in a predictable way by substituent groups. Electron-releasing groups retard electron transfer, electron-withdrawing group facilitate reduction. Alkyl and alkoxy aromatics, phenols and benzoate anion are the most useful substrate for Birch reduction. Several functional group e.g. ketone and nitro, are reduced in preference to aromatic ring. The Substituents also govern the position of protonation. Alkyl and alkoxy aromatics normally give the 2,5-dihydro derivative. Benzoate anion give 1,4-dihydro derivatives.
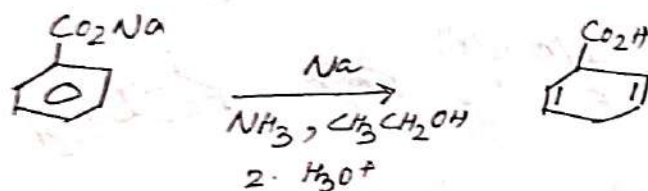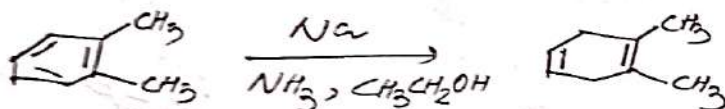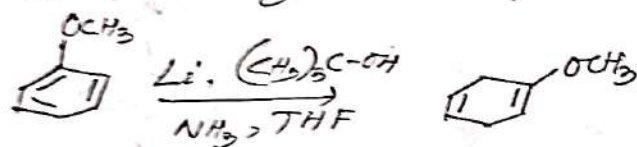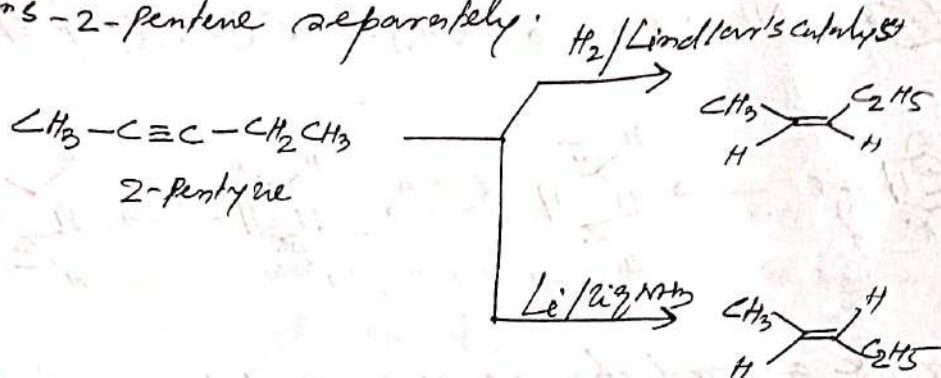

This is due to the fact that the two carbon atoms which are reduced on the aromatic ring go through carbanionic intermediates. Electron withdrawing group stabilize the carbanions, while electron-donating substituents destabilize them. Thus reduction occurs on a carbon bearing an electron withdrawing substituents and not on a carbon bearing electron releasing substituent.
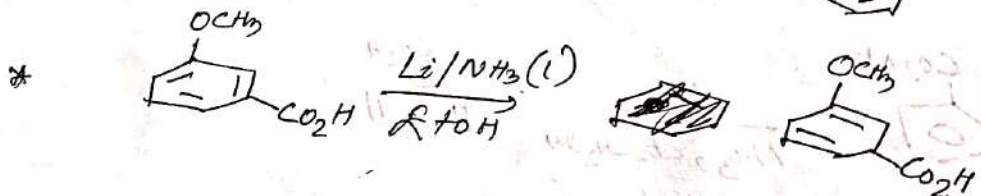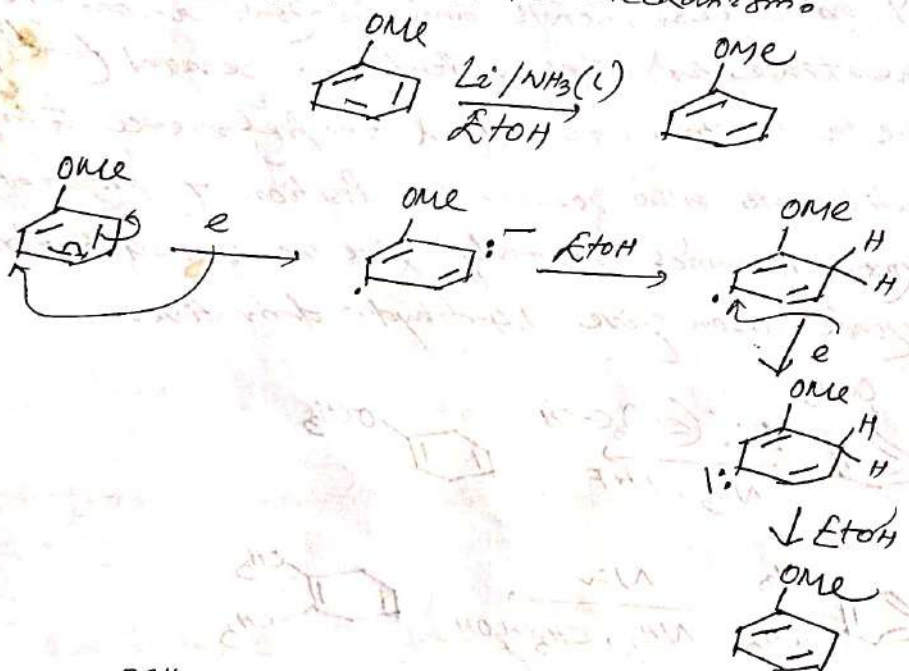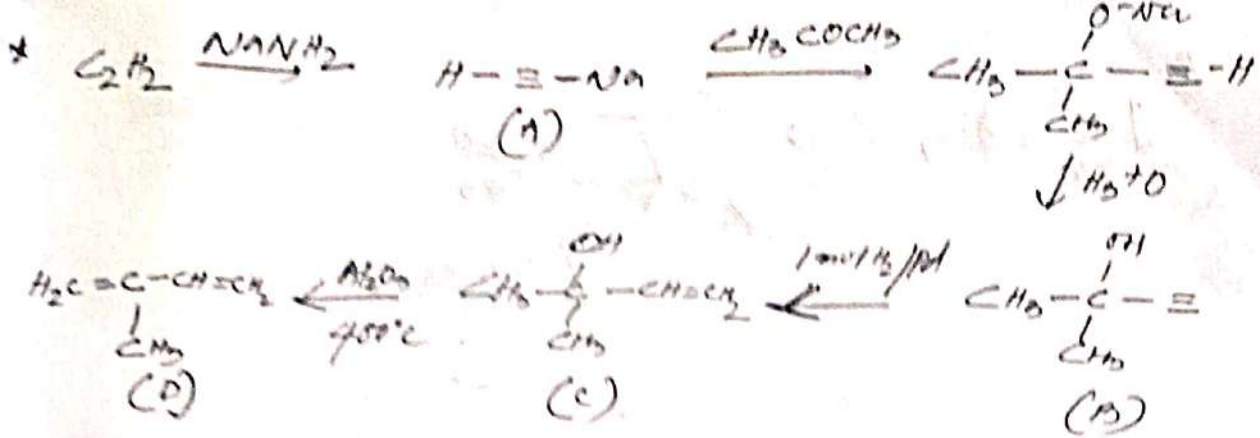
2-cyclohexanone

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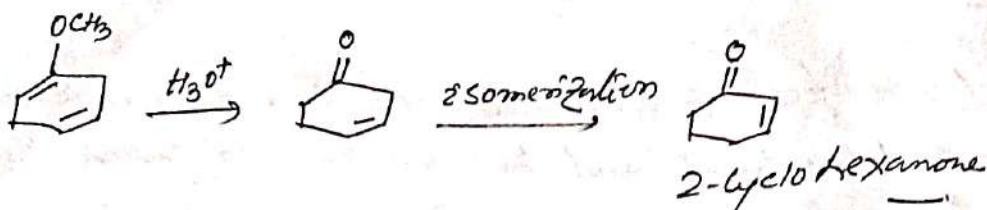
* Show how you convert 2-Pentyne to cis-2-Pentene and trans-2-Pentene separately.

Ans
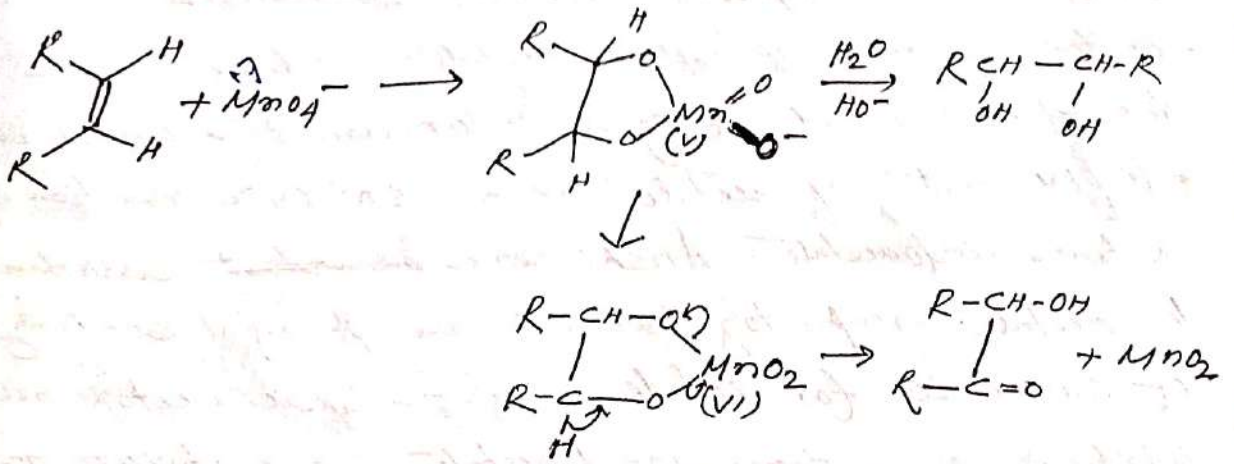
$$CH_3 - C \equiv C - CH_2CH_3$$

2-Pentyne

$H_2/Lindlar's catalyst$

$Li/liq\ NH_3$

---

* Predict the Products with mechanism.

$\xrightarrow[\text{EtOH}]{Li/NH_3(l)}$

$\xrightarrow{e}$

$\xrightarrow{EtOH}$

$\downarrow e$

$\downarrow EtOH$

---

*

$\xrightarrow[\text{EtOH}]{Li/NH_3(l)}$

$* \quad C_2H_2 \xrightarrow{NaNH_2} \quad H-\equiv-Na \quad \xrightarrow{CH_3COCH_3} \quad CH_3-\overset{\overset{O^-Na}{|}}{\underset{\underset{CH_3}{|}}{C}}-\equiv-H$
$\qquad\qquad\qquad\qquad (A) \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow H_3^+O$

$H_2C=\overset{\overset{}{}}{\underset{\underset{CH_3}{|}}{C}}-CH\equiv CH_2 \xleftarrow[450°C]{Al_2O_3} \quad CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH\equiv CH_2 \xleftarrow{1 mol \ H_2/Pd} \quad CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-\equiv$
$\qquad\qquad (D) \qquad\qquad\qquad\qquad\qquad\qquad (C) \qquad\qquad\qquad\qquad\qquad\qquad\qquad (B)$
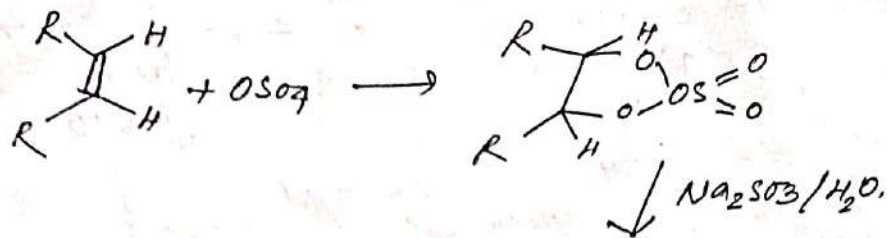
Diol formation:

Alkenes on reaction with $KMnO_4$, under milder conditions convert alkenes to glyclols, this oxidation pro- ceeds through the intermediate formation of cyclic mang- anese ester, and as a result Glycols are formed via Syn addition. Depending on the P_H of the medium, the Permanganate oxidation of alkenes also gives ketols. A ketol is formed ~~by the formed~~ by the oxidation of cyclic intermediate Glycols can also be formed by stereospecific syn addition with OSO_4 Which is highly selective oxidant. OSO_4 is used Catalytically, often in combination with t-BuOOH (tertiary butyl hydroperoxide) which acts as the oxidant. The reaction takes place via a cyclic osmate ester. Due to large steric requirements of the reagent, it attacks rigid cyclic systems from the less hindered side.

$$\underset{R}{\overset{R}{>}}\!\!\!\underset{H}{\overset{H}{<}} + \overset{\curvearrowright}{MnO_4^-} \longrightarrow \quad \underset{R}{\overset{R}{>}}\!\!\!\underset{H}{\overset{H}{<}}\!\!\!\underset{O}{\overset{O}{}}\!\!Mn\overset{O}{\underset{O^-}{(V)}} \xrightarrow[HO^-]{H_2O} \quad R\,\underset{OH}{\overset{}{CH}}-\underset{OH}{\overset{}{CH}}-R$$

$$\downarrow$$

$$R-CH-O \atop R-C-O-Mn(VI) \atop \overset{}{\underset{H}{}} \quad MnO_2 \longrightarrow \quad R-CH-OH \atop R-C=O \quad + MnO_2$$

$$R \overset{R}{\underset{R}{\diagup}}\!\!=\!\!\overset{H}{\underset{H}{\diagdown}} + OSO_4 \longrightarrow$$

$$R\text{CH} - \text{CHR}$$
$$\quad |\qquad |$$
$$\quad OH\quad OH$$

cis-hydroxylation

$$\underset{R^2}{\overset{R^1}{\diagup}}\!\!=\!\!\underset{R^4}{\overset{R^3}{\diagdown}} \xrightarrow{OSO_4} \quad \xrightarrow{Na_2SO_3 / H_2O}$$

cis-hydroxylation
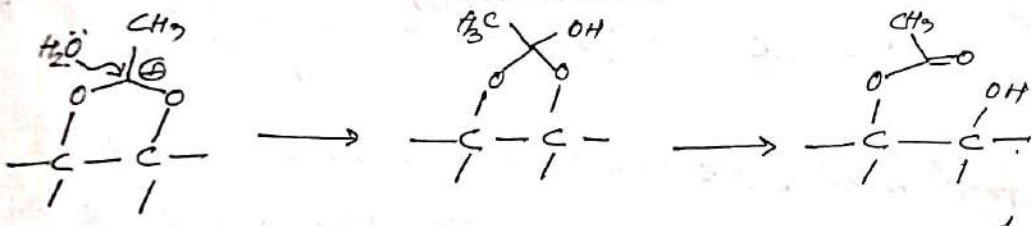

$$\xrightarrow{OSO_4} \qquad \xrightarrow{H_2O}$$

*
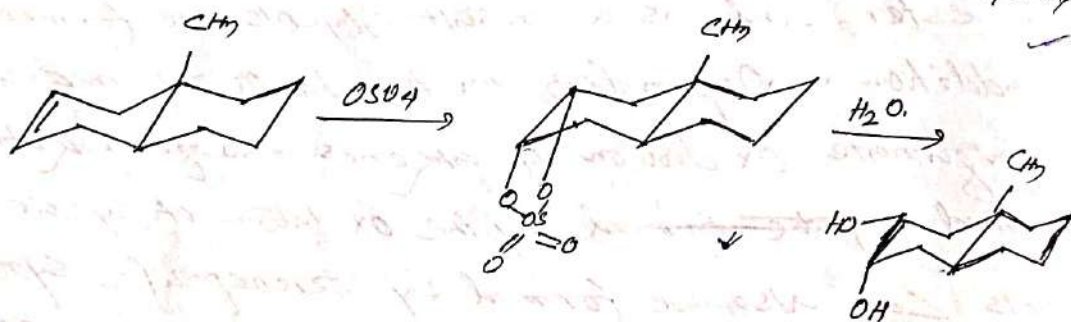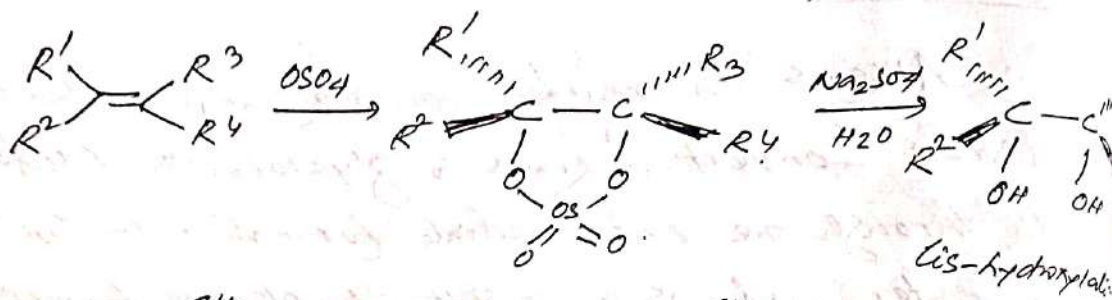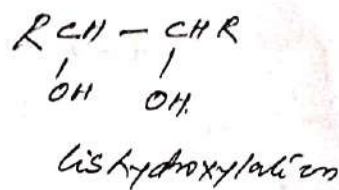
Prevost method involves the reaction of an olefin with iodine and silver acetate. Under dry condition (absence of water) the method leads to trans-1,2-diacetate from which the trans- -diol is obtained by hydrolysis. Woodward reaction is carried out in the presence of water to yield the mono ester of the cis-diol, and the final hydrolysis gives the cis-diol. The olefin is reacted ~~is reacted~~ with iodine in the presence of silver acetate. Iodine reacts with the double bond to give iodonium ion which undergo displacement by acetate in the SN2 type reaction, giving a trans-iodoacetate. Anchimeric ~~assistant~~ assistance by the acetate group, together with the powerful bonding capab. of silver ion for iodide gives a cyclic acetoxonium ion, which gives a trans-1,2-diacetate. The acetoxonium ion under wet conditions traps water and reacts to yield cis-hydroxy acetate.
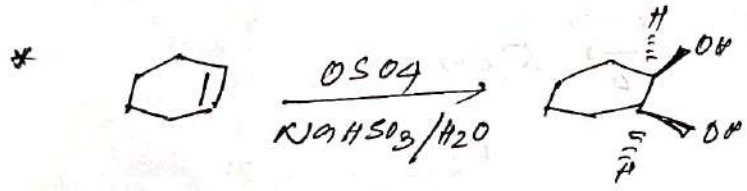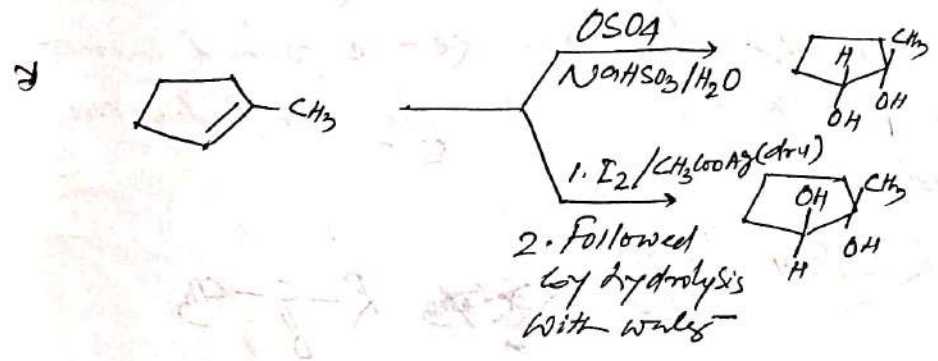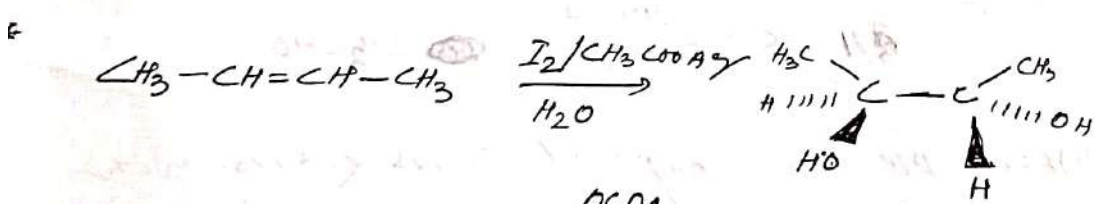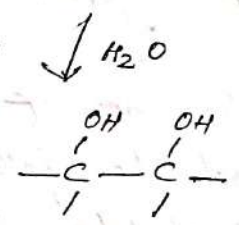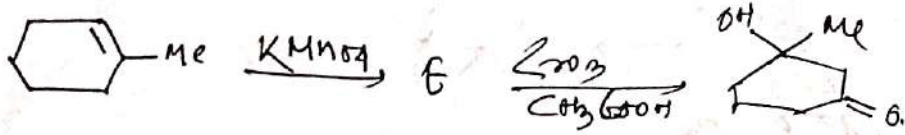
The absence of water

Trans-diol
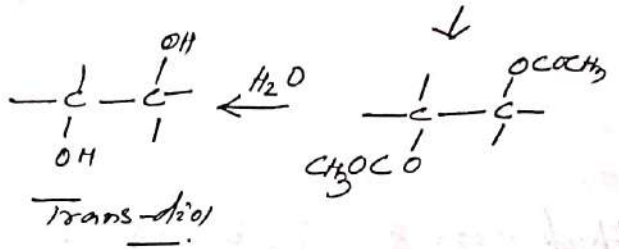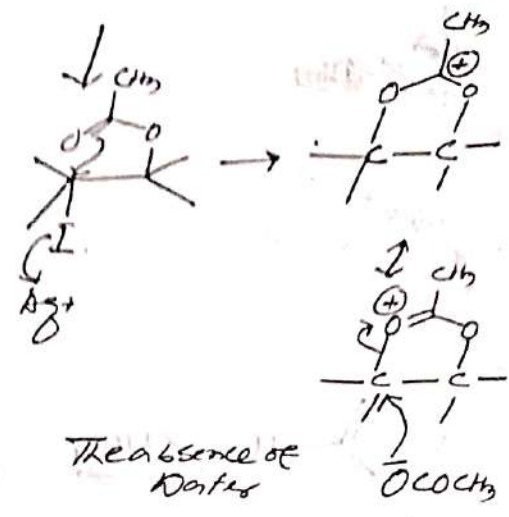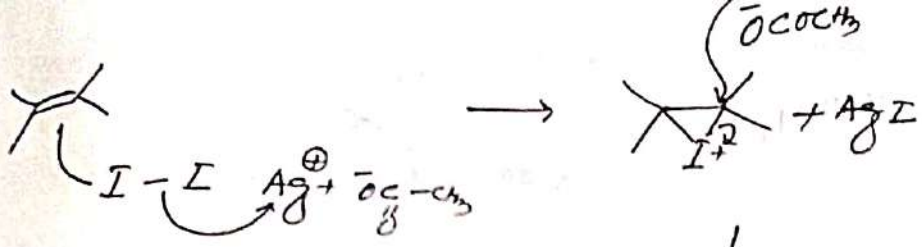
Provost reaction

the Presence of Water

Iodine – Silver acetate (Wet). The Woodward method

$CH_3 - CH = CH - CH_3 \xrightarrow[H_2O]{I_2/CH_3COOAg}$
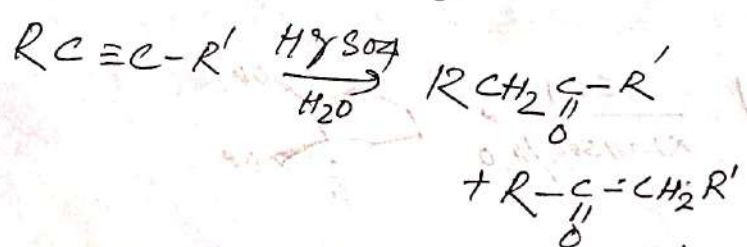
OSO$_4$ / NaHSO$_3$/H$_2$O

1. I_2/CH$_3$COOAg (dry)
2. Followed by hydrolysis with water

OSO$_4$ / NaHSO$_3$/H$_2$O

*

(cyclohexene)—Me $\xrightarrow{\text{KMnO}_4}$ E $\xrightarrow[CH_3COOH]{CrO_3}$ (product with OH, Me, =O)

__Ans.__

(cyclohexene)—Me $\xrightarrow{\text{KMnO}_4}$ (diol with OH, H, OH, Me) E $\xrightarrow[CH_3COOH]{CrO_3}$ (product HO, Me, =O)

Hydration of Triple bonds:

$$-C\equiv C- \ + H_2O \ \xrightarrow{HgSO_4} \ \underset{H}{\overset{H}{-}}\overset{|}{C}-\overset{\|}{\underset{O}{C}}-$$
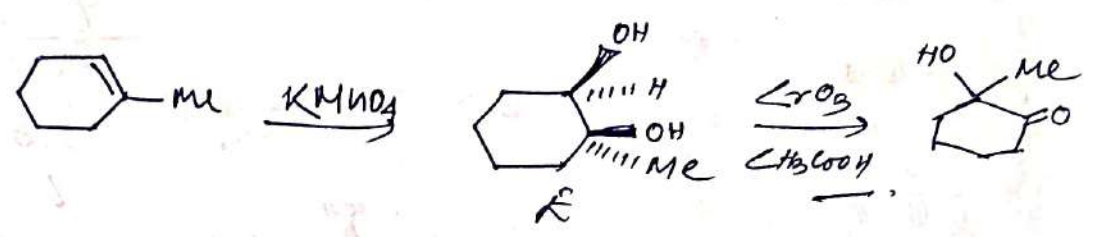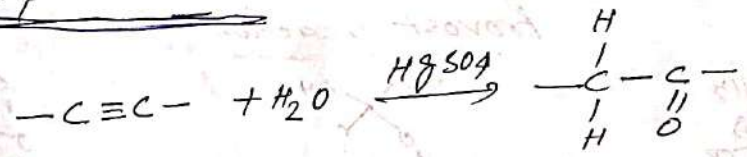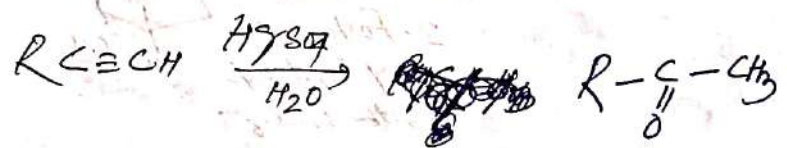
The hydration of triple bonds is generally carried out with mercuric ion salts as catalysts. Mercuric oxide in the presence of an acid is also a common reagent. Since the addition follows Markonikov's rule, only acetylene gives acetaldehyde.

$$HC\equiv CH \ \xrightarrow[H_2O]{HgSO_4} \ CH_3CHO$$
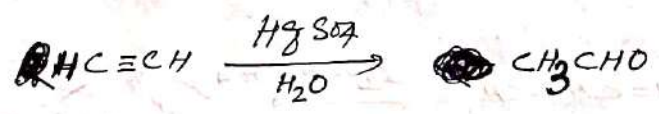
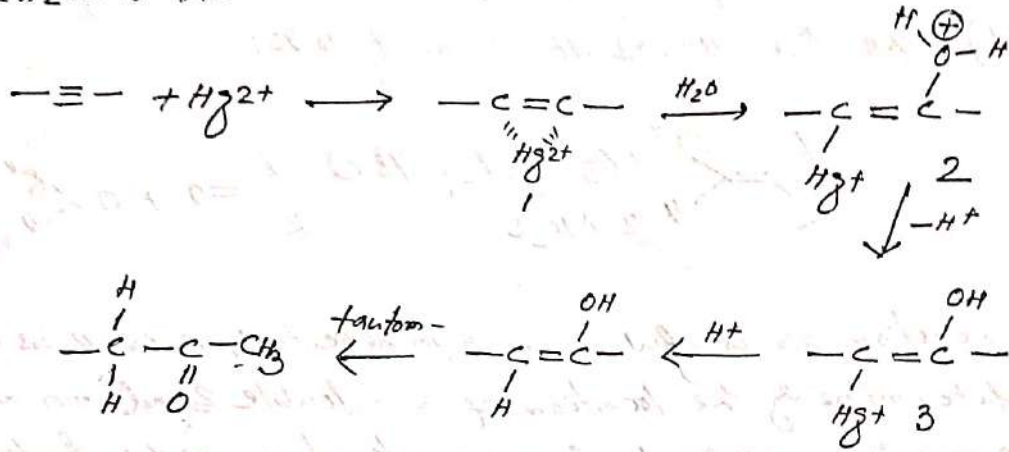All the other triple-bond compounds gives ketones. With alkynes of the form $RC\equiv CH$, methyl ketone formed almost exclusively, but with $RC\equiv CR'$ both possible products are usually obtained.

$$RC\equiv CH \ \xrightarrow[H_2O]{HgSO_4} \ R-\overset{\|}{\underset{O}{C}}-CH_3$$

$$RC\equiv C-R' \ \xrightarrow[H_2O]{HgSO_4} \ RCH_2\overset{\|}{\underset{O}{C}}-R'$$

$$+ \ R-\overset{\|}{\underset{O}{C}}-CH_2R'$$
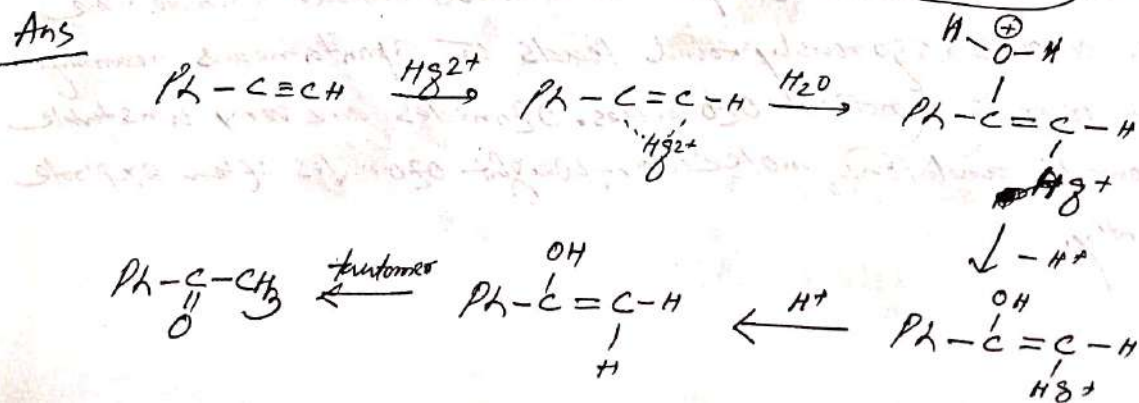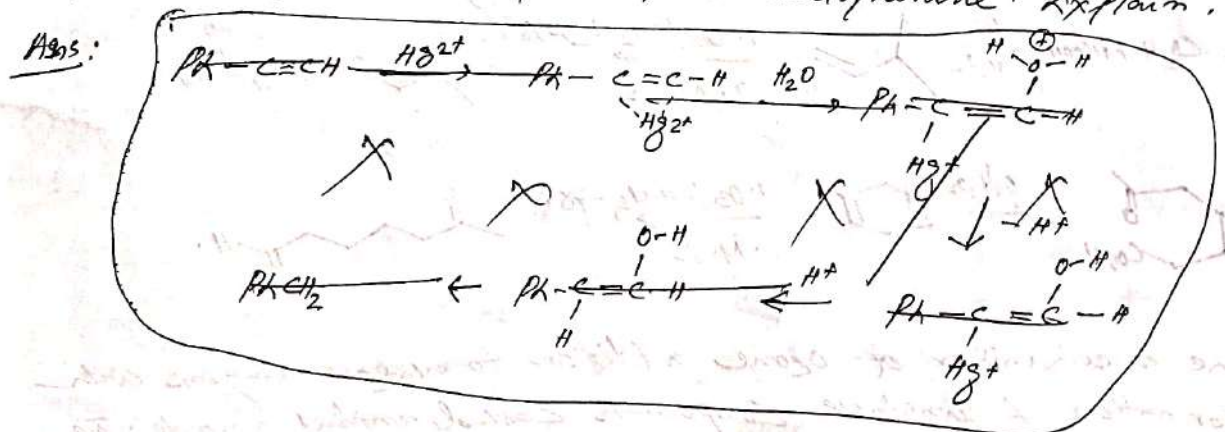
The reaction can be conveniently carried out ...

* The first step of the mechanism is (formation of a complex (ions like Hg^{2+} form complex with alkyne). Water then attacks —in an SN^2 type process to give the intermediate 2, which loses a proton to give 3. Hydrolysis of 3 gives — (in the end), which tautomerizes to the product.

$$-\equiv- + Hg^{2+} \longrightarrow -\overset{\overset{\displaystyle \|}{Hg^{2+}}}{\underset{|}{C}}=C- \xrightarrow{H_2O} -\overset{|}{\underset{Hg^+}{C}}=\overset{\overset{\displaystyle H\searrow \overset{\oplus}{O}-H}{|}}{C}- \quad \mathbf{2}$$

$$\Big\downarrow -H^+$$

$$-\overset{\overset{\displaystyle H}{|}}{\underset{|}{C}}-\overset{\overset{\displaystyle \|}{O}}{C}-CH_3 \quad \xleftarrow{tautom-} \quad -\overset{|}{\underset{H}{C}}=\overset{\overset{\displaystyle OH}{|}}{C}- \quad \xleftarrow{H^+} \quad -\overset{|}{\underset{Hg^+}{C}}=\overset{\overset{\displaystyle OH}{|}}{C}- \quad \mathbf{3}$$

Carboxylic esters, thiol esters and amides can be made, respectively, by acid-catalyzed hydration of acetylenic ethers, thioethers and ynamines, without a mercuric catalyst.
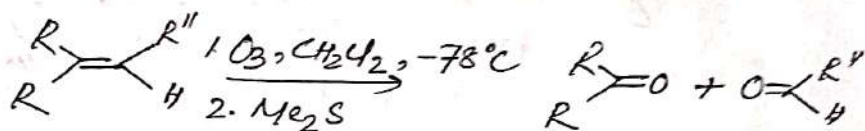
$$-C\equiv C-A \xrightarrow[H^+]{H_2O} -CH_2-\overset{\overset{\displaystyle \|}{O}}{C}-A \qquad A=OR, SR, NR_2$$
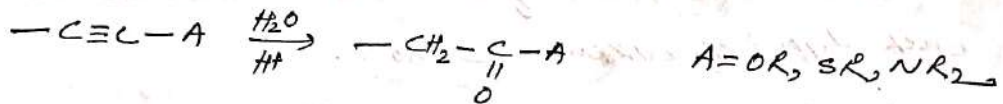
* Hydration of Phenyl acetylene gives acetophenone. Explain.

Ans:

Ans

$$Ph-C\equiv CH \xrightarrow{Hg^{2+}} Ph-\overset{\overset{\displaystyle \|}{Hg^{2+}}}{\underset{}{C}}=C-H \xrightarrow{H_2O} Ph-\overset{|}{\underset{Hg^+}{C}}=\overset{\overset{\displaystyle H\searrow\overset{\oplus}{O}-H}{|}}{C}-H$$

$$\Big\downarrow -H^+$$

$$Ph-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xleftarrow{tautomer} Ph-\overset{|}{\underset{H}{C}}=\overset{\overset{\displaystyle OH}{|}}{C}-H \xleftarrow{H^+} Ph-\overset{|}{\underset{Hg^+}{C}}=\overset{\overset{\displaystyle OH}{|}}{C}-H$$
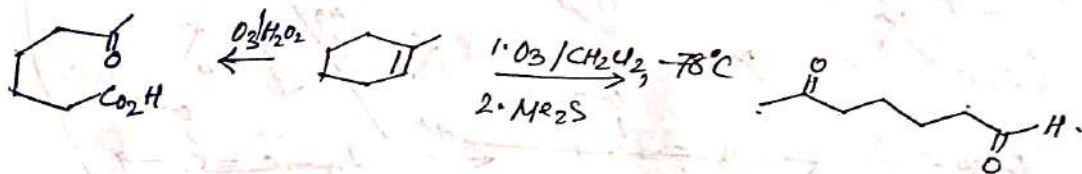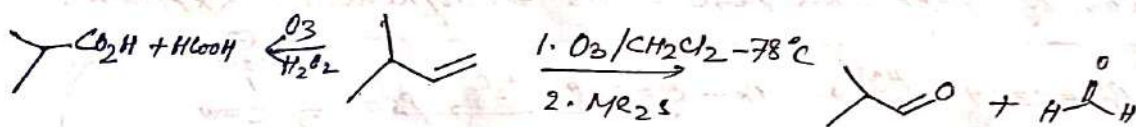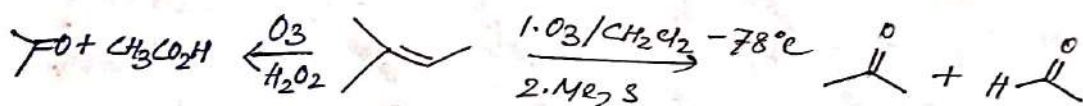
* Write the mechanism portion from above.

Ozonolysis:

Ozonolysis consists of bubbling ozone into very cold (-78°C) solution of the alkene in CH_2Cl_2, followed by testing of the solution with dimethyl sulfide (or Zinc and acetic acid). The overall result is as follows:

$$R \overset{R}{\underset{R}{\rightleftharpoons}} \overset{R''}{\underset{H}{\leftharpoons}} \xrightarrow[\text{2. } Me_2S]{\text{1. } O_3, CH_2Cl_2, -78°C} \quad R \overset{R}{\underset{R}{\rightleftharpoons}} O + O \overset{R''}{\underset{H}{\leftharpoons}}$$

The reaction is useful as a synthetic tool, as well as a me for determining the location of a double bond in an al by reasoning backward from the structures of the products.

The overall process results in alkene cleavage at the double With each carbon of the double bond becoming doubly bon to an oxygen atom.

The following examples illustrate the results f each type of alkene carbon.

$$\overset{}{\rightleftharpoons} O + CH_3CO_2H \xleftarrow[H_2O_2]{O_3} \quad \rightleftharpoons \quad \xrightarrow[\text{2. } Me_2S]{\text{1. } O_3/CH_2Cl_2 \, -78°C} \quad \overset{O}{\underset{}{\Vert}} + H \overset{O}{\underset{}{\Vert}}$$

$$\overset{}{\rightleftharpoons} CO_2H + HCOOH \xleftarrow[H_2O_2]{O_3} \quad \rightleftharpoons \quad \xrightarrow[\text{2. } Me_2S]{\text{1. } O_3/CH_2Cl_2 \, -78°C} \quad \overset{}{\rightleftharpoons} O + H \overset{O}{\underset{H}{\Vert}}$$

$$\text{[cyclohexane with } CO_2H \text{]} \xleftarrow[]{O_3/H_2O_2} \quad \text{[benzene/cyclohexene]} \xrightarrow[\text{2. } Me_2S]{\text{1. } O_3/CH_2Cl_2 \, -78°C} \quad \text{[dialdehyde structure with } H \text{ and } O\text{]}$$
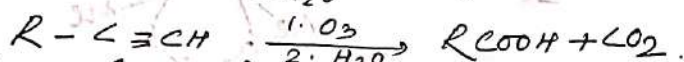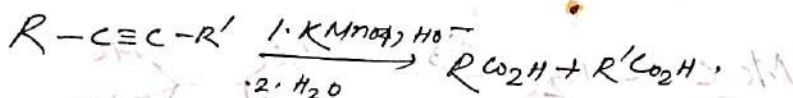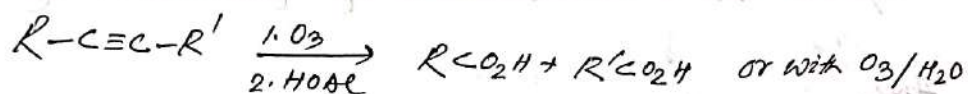
The mechanism of ozone addition to alkenes begins with formation of unstable compounds called initial ozonide. The process occurs vigorously and leads to spontaneous rearrang to compounds known as ozonides. Ozonides are very unstable compounds and low molecular-weight ozonides often explode violently.

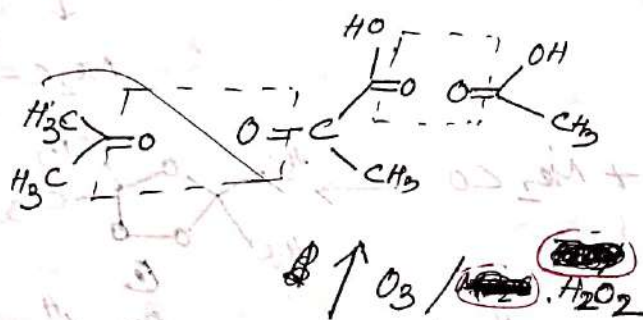Initial ozonide

$\xrightarrow{Me_2S}$ $>=O + O=C< + Me_2SO$
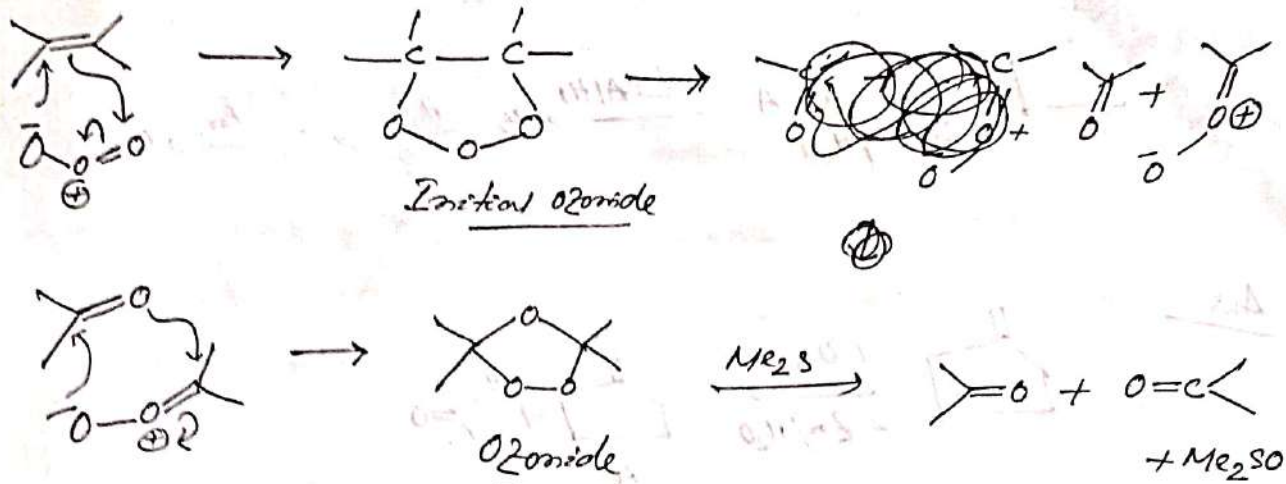
The fragments recombine to form the ozonide

Ozonide

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* Treating alkynes with ozone followed by acetic acid or with basic $KMnO_4$ followed by acids, leads to cleavage at the carbon–carbon triple bond. The products are carboxylic acids.
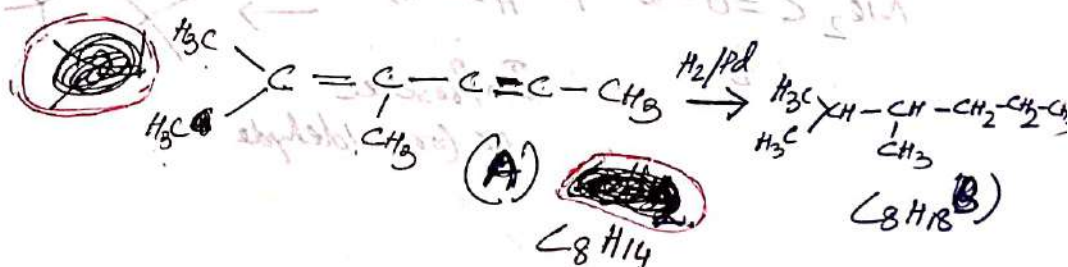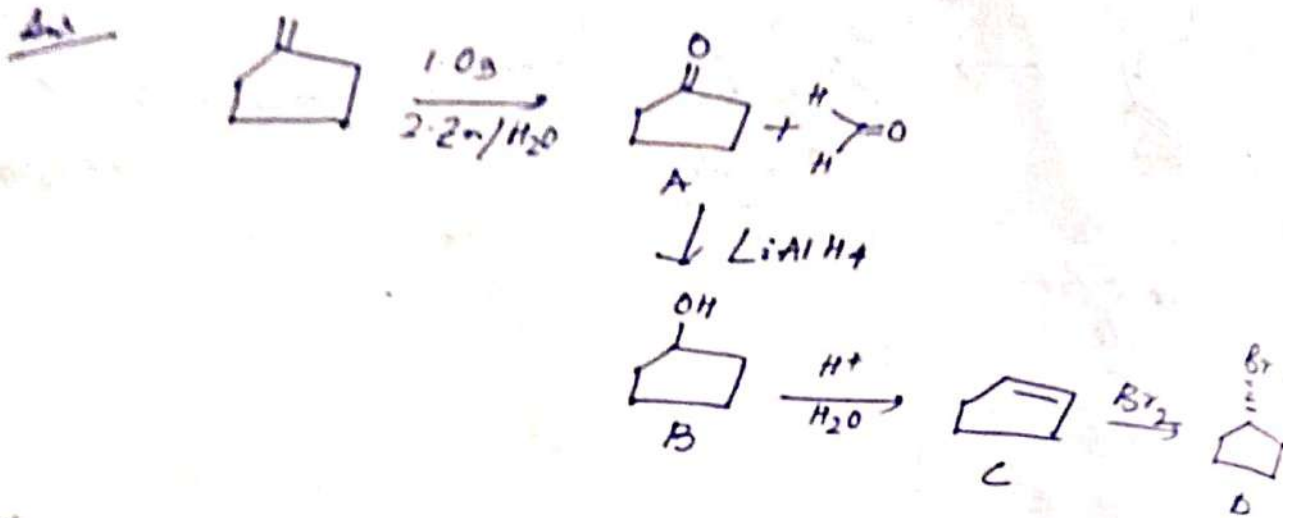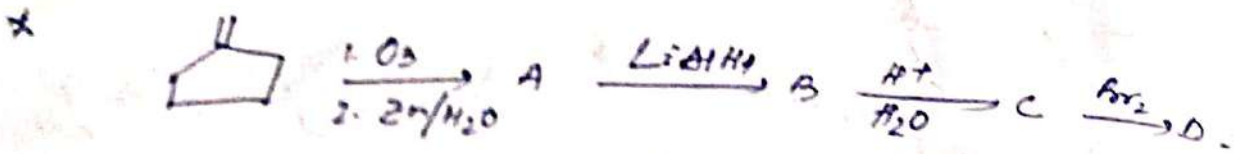
$$R-C\equiv C-R' \xrightarrow[\text{2. HOAc}]{\text{1. } O_3} RCO_2H + R'CO_2H \quad \text{or with } O_3/H_2O$$

$$R-C\equiv C-R' \xrightarrow[\text{2. } H_2O]{\text{1. } KMnO_4, HO^-} RCO_2H + R'CO_2H$$

$$R-C\equiv CH \xrightarrow[\text{2. } H_2O]{\text{1. } O_3} RCOOH + CO_2$$

* Compound A (C_8H_{12}) on catalytic reduction gives B (C_8H_{18}). Ozonolysis of A gives acetic acid, acetone and pyruvic acid (CH_3COCO_2H). What are A and B?
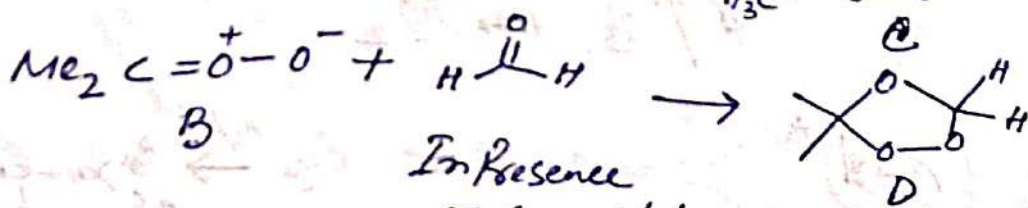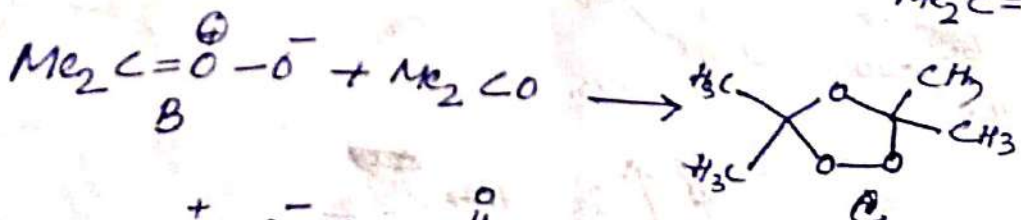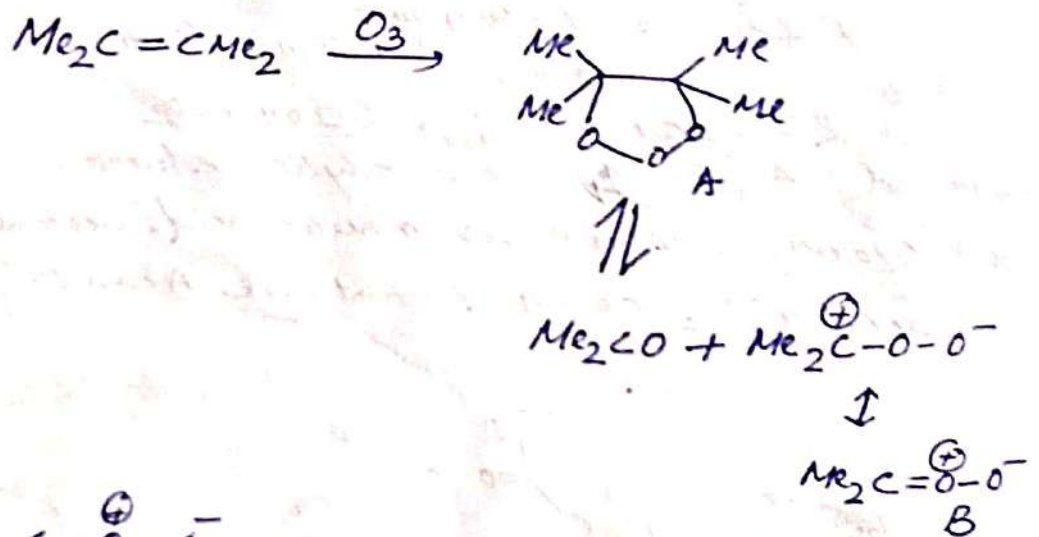
Ans:

$$H_3C > C=C-C\equiv C-CH_3 \xrightarrow{H_2/Pd} H_3C > CH-CH-CH_2-CH_2-C$$

(A) C_8H_{14}

(B) C_8H_{18}

* tetra substituted double bond always gives ketone.

*

$$\text{(cyclopentene-like structure)} \xrightarrow[2.\ Zn/H_2O]{1.\ O_3} A \xrightarrow{LiAlH_4} B \xrightarrow[H_2O]{H^+} C \xrightarrow{Br_2} D.$$

Ans

$$\text{(structure)} \xrightarrow[2.\ Zn/H_2O]{1.\ O_3} \underset{A}{\text{(dialdehyde/keto structure)}} + \overset{H}{\underset{H}{}}C=O$$

$$\downarrow LiAlH_4$$

$$\underset{B}{\text{(diol structure, OH)}} \xrightarrow[H_2O]{H^+} \underset{C}{\text{(cyclopentene)}} \xrightarrow{Br_2} \underset{D}{\text{(dibromo, Br)}}$$

*

Two ozonides are formed when $Me_2C=CMe_2$ is treated with ozone in the presence of formaldehyde. Give the mechanism of formation of two ozonide

Ans

$$Me_2C=CMe_2 \xrightarrow{O_3} \underset{A}{\text{(1,2,3-trioxolane intermediate)}}$$

$$\Updownarrow$$

$$Me_2C=O + Me_2\overset{\oplus}{C}-O-O^-$$

$$\updownarrow$$

$$\underset{B}{Me_2C=\overset{\oplus}{O}-O^-}$$

$$\underset{B}{Me_2C=\overset{\oplus}{O}-O^-} + Me_2C=O \longrightarrow \underset{C}{\text{(ozonide structure)}}$$

$$\underset{B}{Me_2C=\overset{+}{O}-O^-} + H\overset{O}{\underset{}{C}}H \xrightarrow[\text{of formaldehyde}]{\text{In presence}} \underset{D}{\text{(ozonide structure)}}$$
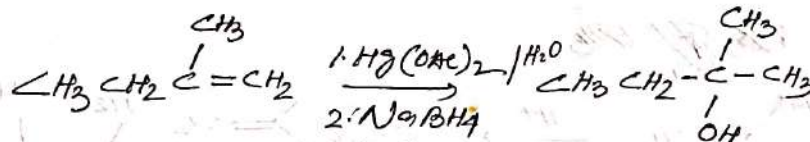
Reaction of ozone to tetramethylene~~o~~ forms first an unstable compound called initial ozonide (A) which decomposes to give a zwitterion(B) and a ~~carbonyl compound~~ acetone. The Zwitterion then combine with ~~carbonyl compound~~ acetone to give (C). But in presence of formaldehyde the highly reactive Zwitterion may combine with ~~it to~~ formaldehyde to give ozonide (D) also.

Hydration of double bond:

$$-\underset{|}{C}=\underset{|}{C}- \xrightarrow[\text{2. NaBH}_4]{\text{1. Hg(OAc)}_2/H_2O} -\underset{|}{\overset{H}{C}}-\underset{|}{\overset{OH}{C}}-$$
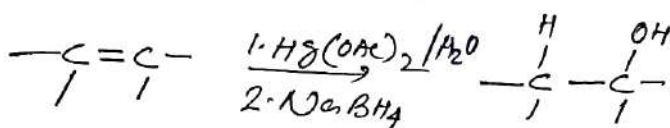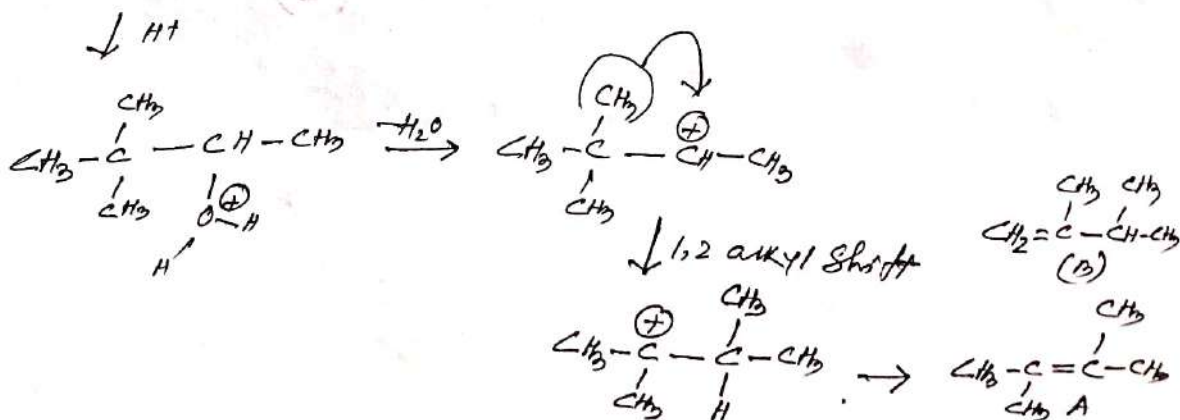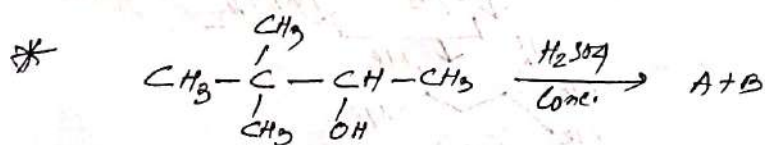
Olefins can be hydrated quickly under mild conditions in high yields without rearrangement products by the use of oxymercuration followed 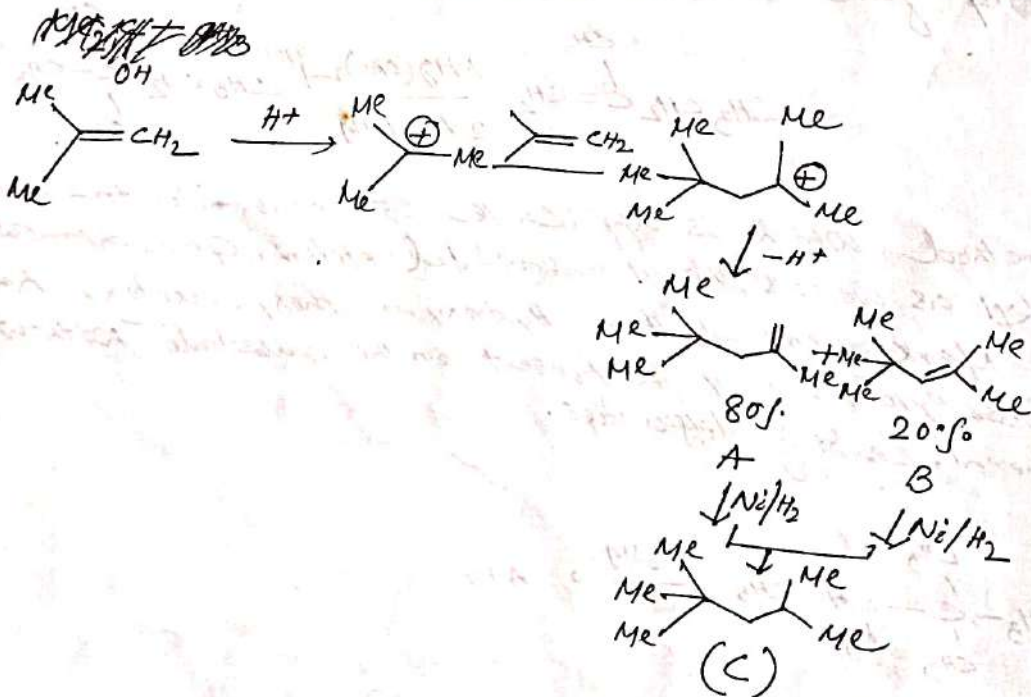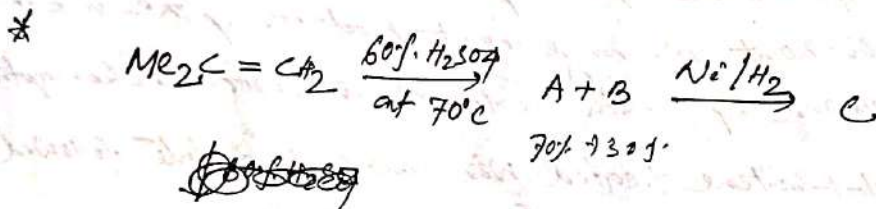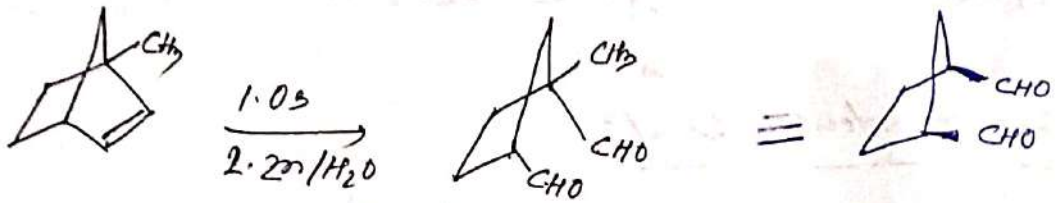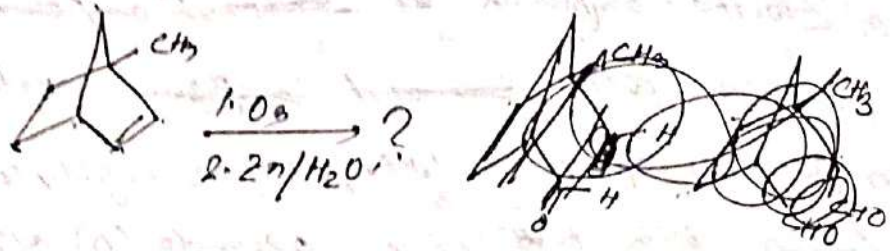by insitu treatment with sodium borohydride. For example, 2-methyl-1-butene treated with mercuric acetate, followed by NaBH₄ gave 2-methyl-2-butanol):

$$CH_3 CH_2 \overset{CH_3}{\underset{|}{C}}=CH_2 \xrightarrow[\text{2. NaBH}_4]{\text{1. Hg(OAc)}_2/H_2O} CH_3 CH_2-\overset{CH_3}{\underset{\underset{OH}{|}}{C}}-CH_3$$

This method, which is applicable to mono-, di-, tri- and tetraalkyl as well as phenyl substituted olefins, Gives almost complete Markonikov addition. Hydroxy, methoxy, acetoxy, halo and other groups may be present in the substrate without, in general, causing difficulties.
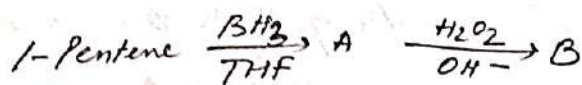
$$* \quad CH_3-\overset{CH_3}{\underset{\underset{CH_3}{|}}{\underset{|}{C}}}-\overset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{conc.}]{H_2SO_4} A+B$$

$$\downarrow H^+$$

$$CH_3-\overset{CH_3}{\underset{\underset{\overset{|}{O}-H}{\underset{H}{\oplus}}}{\underset{|}{C}}}-CH-CH_3 \xrightarrow{H_2O} CH_3-\overset{CH_3}{\underset{\underset{CH_3}{|}}{C}}-\overset{\oplus}{CH}-CH_3$$

$$\downarrow \text{1,2 alkyl shift}$$

$$CH_3-\overset{\oplus}{\underset{\underset{CH_3}{|}}{C}}-\overset{CH_3}{\underset{\underset{H}{|}}{C}}-CH_3 \rightarrow CH_3-\overset{CH_3}{\underset{\underset{CH_3}{|}}{C}}=\overset{}{C}-CH_3 \quad A$$

$$\overset{CH_3}{\underset{\underset{}{}}{CH_2}}=\overset{CH_3}{\underset{\underset{}{}}{C}}-CH-CH_3 \quad (B)$$

* Predict the product with R/S notations of the following reaction:

$$\text{compound} \xrightarrow[\text{2. } Zn/H_2O]{\text{1. } O_3} \text{?}$$

$$\xrightarrow[\text{2. } Zn/H_2O]{\text{1. } O_3} \equiv$$

*

$$Me_2C = CH_2 \xrightarrow[\text{at } 70°c]{60\% \ H_2SO_4} A + B \xrightarrow{Ni/H_2} C$$

$$70\% \quad 30\%$$

$$Me_2C = CH_2 \xrightarrow{H^+} \quad \text{(cation)} \quad Me \quad + \quad Me$$

80% A   20% B

$$\downarrow Ni/H_2 \qquad \downarrow Ni/H_2$$

(C)

* Predict the Product A and Product B in the following Synthetic sequence and explain mechanistically: 3

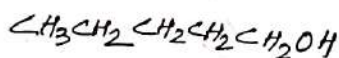$$1\text{-Pentene} \xrightarrow[THF]{BH_3} A \xrightarrow[OH-]{H_2O_2} B$$

Ans

$$CH_3 CH_2 CH_2 CH=CH_2 \xrightarrow{BH_3} CH_3 CH_2 CH_2 CH_2 CH_2 BH_2$$

$\downarrow @ 1\text{-Pentene}$

$$\left(CH_3 CH_2 CH_2 CH_2 CH_2 \right)_2 BH$$

$\downarrow 1\text{-Pentene}$

$$\left(CH_3 CH_2 CH_2 CH_2 CH_2 \right)_3 B$$

$\downarrow H_2O_2 / OH^-$

$R = CH_3 CH_2 CH_2 CH_2 CH_2 -$

$$CH_3 CH_2 CH_2 CH_2 CH_2 OH$$

$$R_3B + \bar{O}-O-H \longrightarrow R_3\overset{\ominus}{B}-O-\overset{A}{O}H \xrightarrow{HO^-} R-\overset{R}{\underset{\underset{R}{|}}{B}}-OR$$

$\downarrow$ Repeat of Previous step

$\downarrow$

$$3ROH + B(OH)_3 \xleftarrow{H_2O/OH^-} RO-\overset{OR}{\underset{\underset{OR}{|}}{B}}$$

*

$$\xrightarrow[2. H_2O_2/NaOH \, (aq)]{1. B_2H_6/THF} \left(\right)_3 B$$
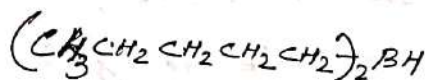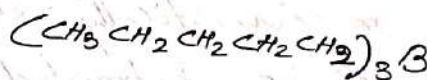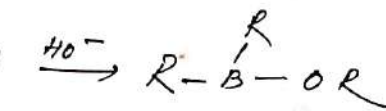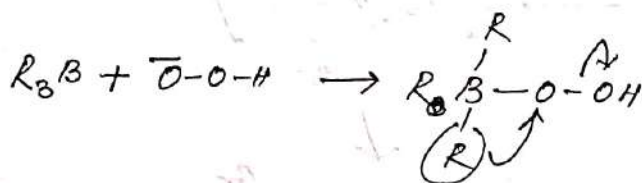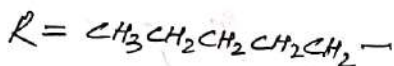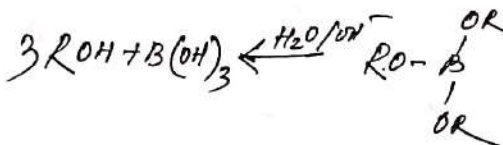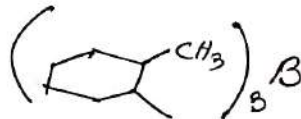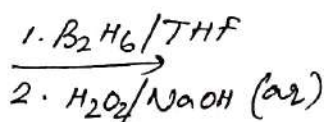
$\downarrow H_2O_2 / NaOH$
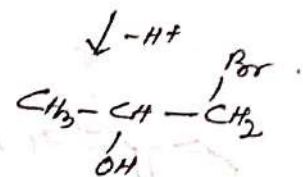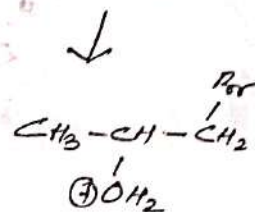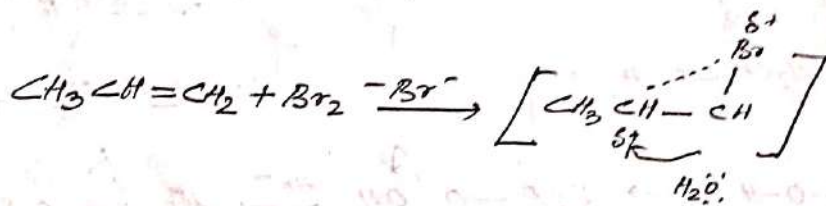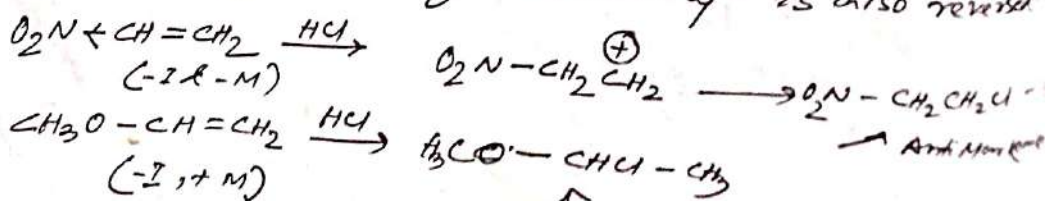
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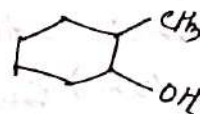
Strong bridging ensures that the anti product will be major product of addition. However, as far as regio-selectivity is concerned the intermediate ion behaves as the more stable of two possible cations. The addition of bromine to propylene in water follows the course. The halonium ion opening is regioselective: the more highly substituted carbon is attacked preferentially by the added nucleophile. In the halonium ion the nucleophile attacks the more highly substituted carbon of the ring; this carbon is more positively polarized than the other. In summary the bridged halonium ions are subject to stereospecific and regioselective ring opening in a fashion mechanistically very similar to the nucleophilic opening of the protonated epoxide.

$$CH_3-CH=CH_2 + Br_2 \xrightarrow{-Br^-} \left[CH_3-\overset{\delta+}{CH}-\underset{\delta+}{CH} \overset{\overset{\delta+}{Br}}{\vert} \right] \xrightarrow{H_2\overset{..}{O}:}$$

$$\downarrow$$

$$CH_3-CH-\overset{\overset{Br}{\vert}}{CH_2}$$
$$\underset{\oplus OH_2}{\vert}$$

$$\downarrow -H^+$$

$$CH_3-CH-\overset{\overset{Br}{\vert}}{CH_2}$$
$$\underset{OH}{\vert}$$

*

When the alkene contains substituents of electron attracting type i.e. of −I and/or −M not only the rate of electrophilic addition is retarded (these groups destabilize carbocations) but the regioselectivity is also reversed.
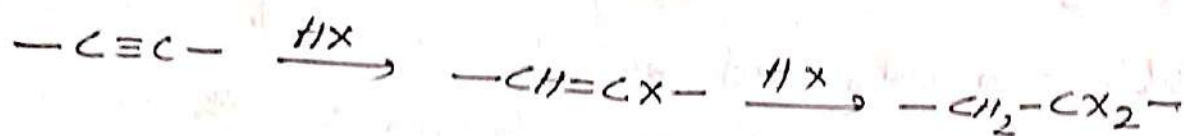
$$O_2N-CH=CH_2 \xrightarrow{HCl} O_2N-CH_2-\overset{\oplus}{C}H_2 \longrightarrow O_2N-CH_2CH_2Cl$$
$$(-I,-M) \qquad\qquad\qquad\qquad\qquad\qquad \nearrow Anti Markov$$

$$CH_3O-CH=CH_2 \xrightarrow{HCl} H_3CO-CHCl-CH_3$$
$$(-I,+M) \qquad\qquad\qquad\qquad \nwarrow$$
$$\qquad\qquad\qquad\qquad\qquad Markovnikov$$
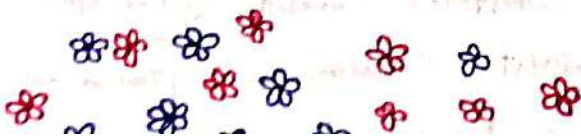
+M effect is of greater consequence than the −I effect.

Addition of hydrogen halide to alkynes:

It is possible to add one or two moles of any of the four hydrogen halides to triple bonds.

$$-C \equiv C- \xrightarrow{HX} -CH=CX- \xrightarrow{HX} -CH_2-CX_2-$$

Markonkov's rule ensures that gem-dihalides and not vic-halides are the products of the addition of two moles.
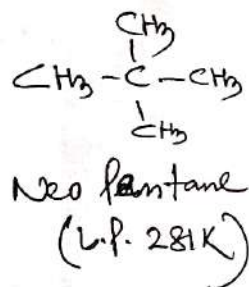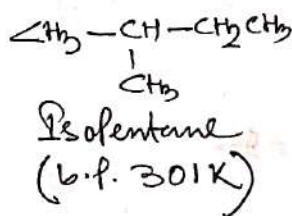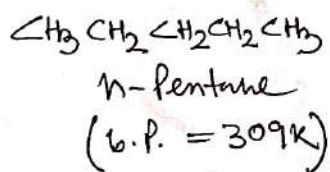
Physical Properties of alkanes:

Solubility: Alkanes being non-Polar in nature are insoluble in Water but soluble in non-Polar solvents like ether, benzene etc. Solubility decreases with increase in molecular size.

Boiling Points:

As alkanes are non-Polar molecules, they have only weak Vander Waals' forces operating between them. Vander Waal's forces of attraction depend upon the molecular size and increase with increase in molecular size. Among the chain isomers of a compound, the branched chain isomer has lower boiling point compared to straight-chain isomer. For example, the boiling points of three isomeric pentanes are given below:

$CH_3 CH_2 CH_2 CH_2 CH_3$
n-Pentane
(b.P. = 309K)

$CH_3 - CH - CH_2 CH_3$
            |
           CH_3
Isopentane
(b.P. 301K)

$CH_3 - \overset{\overset{CH_3}{|}}{C} - CH_3$
          |
         CH_3
Neo Pentane
(b.P. 281K)

Why boiling Point decreases with branching?

The boiling Point of a substance depends upon the force of attraction between the molecules. Force of attraction between the molecules depends upon the of contact between them. Area of contact and force attraction will be maximum for straight chain compound. As branching increases, the area of contact decreases. Consequently, the force of attraction and boiling point will decreases.

Melting Point:

Alkanes show lower melting points because of absence of charge. Melting point is expected to increase with increase in molecular size. This is found to be true but the increase is not uniform.

Alkane	Melting Point (K)
C_3H_8	85.9
$n-C_4H_{10}$	138
$n-C_5H_{12}$	143.3
$n-C_6H_{14}$	179

* Increase in melting point is relatively more in going from odd-carbon to even carbon alkane compared to when we move from even-carbon to odd-carbon alkane. Explain

Ans: It may be realised that in even-carbon alkanes (e.g. C_6H_{14}) the packing of molecules can take place to a greater extent, resulting in greater attraction forces and hence greater melting points. This is not so with odd carbon alkanes.

Representation
of two chain of $n-C_6H_{14}$
(Greater attractive forces)

n-heptane

* Write the structural formula of n-Pentane, isopentane and neopentane. Which of these has highest boiling point and why?

Ans:

$CH_3CH_2CH_2CH_2CH_3$
n-Pentane

$CH_3-CH_2-CH-CH_3$
                    |
                   CH_3
Isopentane

         CH_3
          |
CH_3-C-CH_3
          |
         CH_3
Neopentane

Of the three pentanes, n-pentane has the highest boiling point.

All the three pentanes are non-polar compounds having only weak intermolecular forces of attraction. The molecular weights of the three isomers are naturally the same but they have different surface areas. As the surface area of n-pentane is larger than those of the other two, it has strongest intermolecular force of attraction. Therefore it has highest boiling point followed by ~~other two~~ iso-and neopentanes.

* As we move up from n-pentane to n-hexane, there is an increase of about 35° in the melting point but on moving from n-hexane to n-heptane the increase is only about 4°. How can you account for these observation?

Ans

Disproportionate variation in melting points of three alkanes can be explained on the basis of their molecular weights and their ability to fit in the crystal structure.

In alkanes, the carbon atoms from zig-zag chains depicted below for n-pentane, n-hexane and n-heptane.

n-Pentane
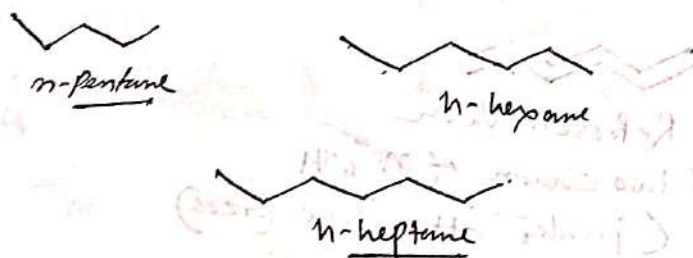
n-hexane

n-heptane

It is apparent that in n-hexane, the two terminal methyl lie on opposite sides of the zig-zag chain which enables this chain to fit in closely in the crystal structure. But in n-pen and n-heptane, the two terminal groups lie on the same so that the crystal structure is not so closely packed.

As we move from n-pentane to n-hexane the M increases, also the packing arrangement become more closed these factors require greater energy to melt the solid. As

here is a large increase

On the other hand, as we move from n-hexane to n-heptane, the m.p. increases but the packing arrangement does not remain so close. While the melting point would tend to increases due to increase in molecular weight, the decrease in close packing would tend to have the opposite effect. The net result is that there is only small increase in melting point in this case.

* n-butyl alcohol has much higher boiling point than its isomers iso butyl alcohol as well as diethyl ether. Explain

Ans:
Boiling point of isomeric alcohols depends on the extent to which the individual molecule can attract each other. With n-alkyl groups, the molecules pack well and can interact/bind with each other. Here, the alkyl chain interact through hydrophobic interactions and the OH groups interact through H-bonding. iso-butanol have branching, and this lowers their boiling points because the branch points decrease the intermolecular interactions.
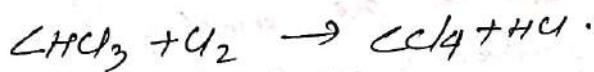
Diethyl ether has no —OH portion, therefore, the ether group cannot form hydrogen bond with another ether molecules. Since ether molecules are not held together by H-bond it is more volatile than n-butyl alcohol).

Halogenation of alkane:

Methane on treatment with chlorine in the presence of diffused sunlight or by heating the reaction mixture to 523-673 K gives chloromethane.
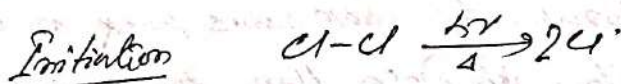
$$CH_4 + Cl_2 \xrightarrow{Sunlight} CH_3Cl + HCl.$$

The reaction does not stop here. Chloromethane is further chlorinated to dichloromethane, and further chlorination stops until tetrachloromethane form.
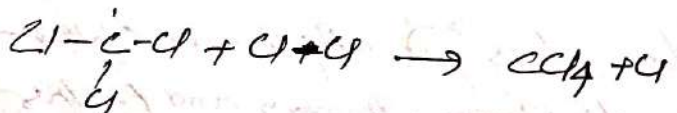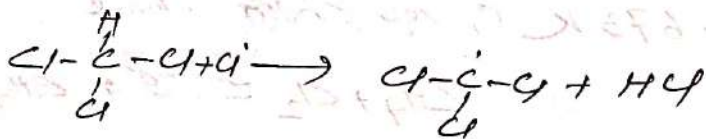
$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl.$$

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$
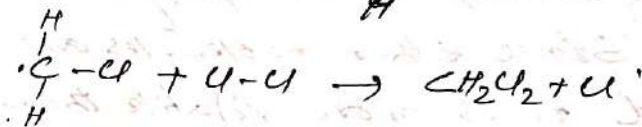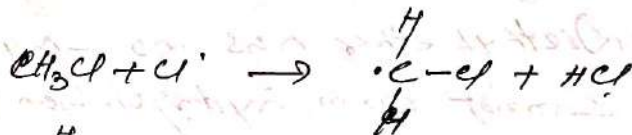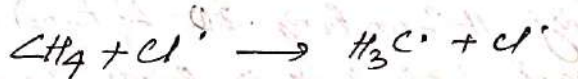
$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl.$$

Bromination of alkanes take place in similar way but less readily. Direct iodination of alkanes is not possible as the reaction is reversible

$$R-H + I_2 \rightleftharpoons R-I + HI$$

Mechanism of chlorination:

Initiation

$$Cl-Cl \xrightarrow[\Delta]{h\nu} 2Cl\cdot$$

Propagation

$$CH_4 + Cl\cdot \longrightarrow H_3C\cdot + Cl'$$

$$\cdot CH_3 + Cl-Cl \longrightarrow H_3C-Cl + Cl\cdot$$

$$CH_3Cl + Cl\cdot \longrightarrow \overset{H}{\underset{Cl}{\cdot C}}-Cl + HCl$$

$$\overset{H}{\underset{\cdot H}{\cdot C}}-Cl + Cl-Cl \longrightarrow CH_2Cl_2 + Cl\cdot$$

$$Cl-\overset{H}{\underset{Cl}{C}}-H + Cl\cdot \longrightarrow Cl-\overset{H}{\underset{Cl}{C}}\cdot + HCl$$

$$Cl-\overset{H}{\underset{Cl}{C}}\cdot + Cl-Cl \longrightarrow Cl-\overset{H}{\underset{Cl}{C}}-Cl-Cl$$

$$Cl-\overset{H}{\underset{Cl}{C}}-Cl + Cl\cdot \longrightarrow Cl-\overset{\cdot}{\underset{Cl}{C}}-Cl + HCl$$

$$Cl-\overset{\cdot}{\underset{Cl}{C}}-Cl + Cl-Cl \longrightarrow CCl_4 + Cl\cdot$$

Termination

$$Cl\cdot + Cl\cdot \longrightarrow Cl_2$$

$$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3CH_3 -$$
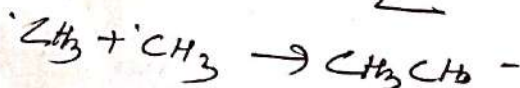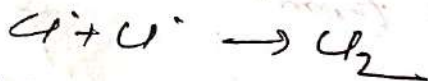
Evidence in Support of mechanism:

1. Reaction does not take place in dark at room temperature but requires energy in the form of heat or light. This is due to the fact that the chain initiation step is endothermic and hence needs a large amount of energy to break Cl-Cl bond into radicals.

II. Oxygen acts as an inhibitor. This is due to the fact oxygen combines with alkyl free radical to form peroxy alkyl radical. ($R-O-O^{\cdot}$). This radical is much less reactive than alkyl free radical to continue the chain. As a result, the halogenation of alkyl in the presence of oxygen is slowed down or stopped. Thus the role of inhibitors like oxygen in this reaction gives support to the above mechanism.

* ## Ozonalysis of alkyne:

$$\angle H \equiv \angle H \xrightarrow[\text{II. } Zn/H_2O]{\text{1. } O_3} H-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H$$

$$\angle H_3-C\equiv C-CH_3 \xrightarrow[\text{2. } Zn/H_2O]{\text{1. } O_3} \angle H_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$$