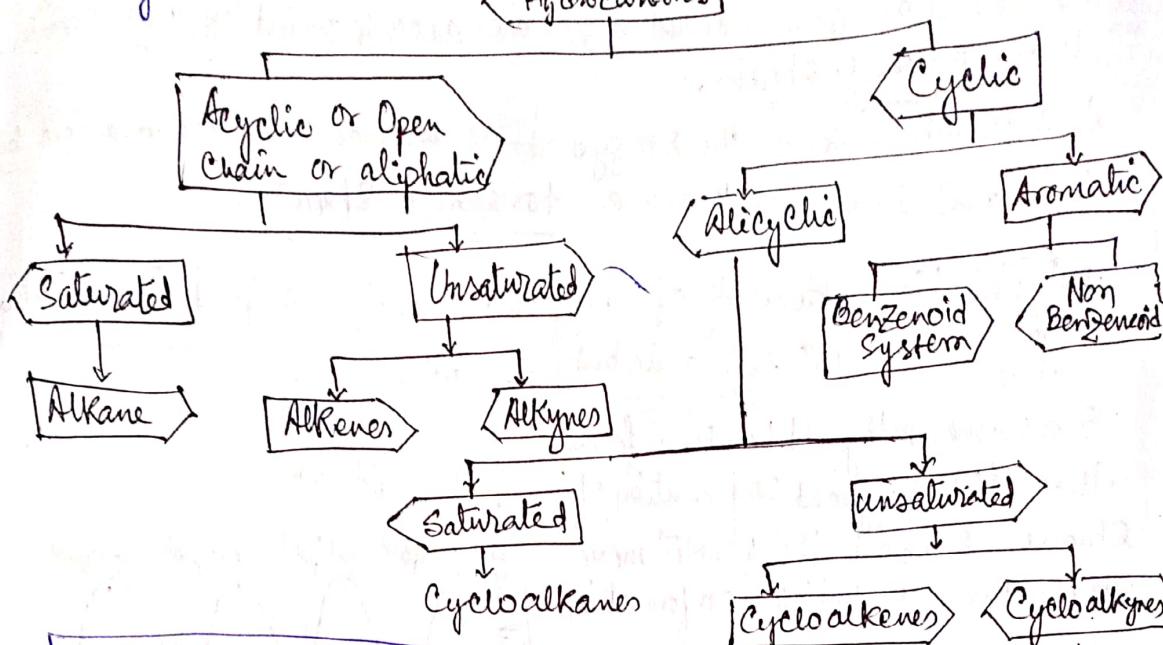


11/12/18

Hydrocarbons

Organic compounds composed of only C and H are called hydrocarbons.



Conformational isomers

Infinite no. of stereoisomers may be present in alkane due to free rotation along C-C single covalent bond by 360° . The different arrangements of atoms in space that results from the free rotation of groups about C-C bond axis are called conformational (or rotational) isomers & this phenomenon is known as Conformational (or rotational) isomerism.

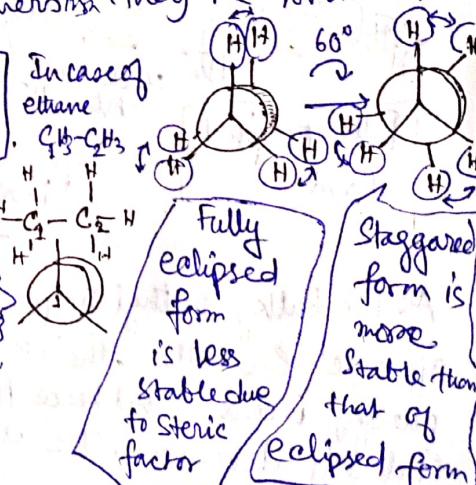
With the help of 2 projectional formulas we can understand these conformational or rotational isomerisms. They're known as

— a) Newman projectional formula

— b) Sawhorse projectional formula

These are obtained by viewing the molecule along the bond joining the 2 carbon atoms.

The carbon near the eye is represented by a point & the 3 atoms or groups attached to it by 3 equally spaced (bond angle 120°) radii. The atom which is far from the eye is designated by a circle, (◎) & the 3 atoms/groups are attached to it by 3 equally spaced radial extensions.



Three kinds of strains are important in understanding the behaviour of conformations. These are — Angle Strain, Torsional Strain

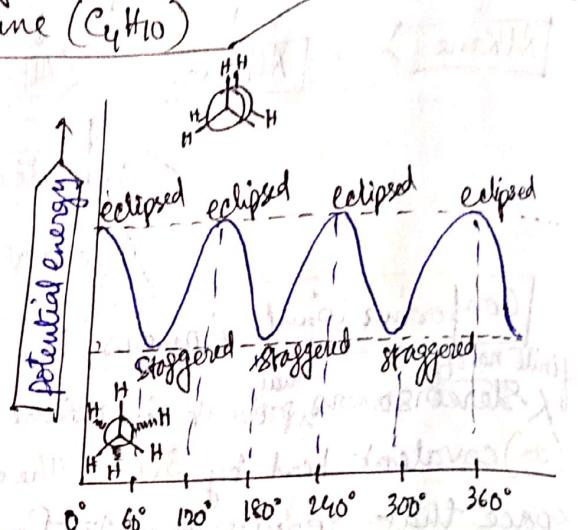
• Vander Waal's or Steric Strain non bonded groups when brought closer together than the sum of their Vander Waal's radii causes steric strain.

Any deviation from normal angles are accompanied by angle strain. Known as Angle strain.

Any deviation from the staggered arrangement are accompanied by torsional strain is known as torsional strain.

• Relative stability of staggered and eclipsed Conformation of ethane (C_2H_6) and n-butane (C_4H_{10})

Experimentally it has been found that the staggered conformation of ethane is about 12.5 kJ mol^{-1} more stable than the eclipsed conformation.

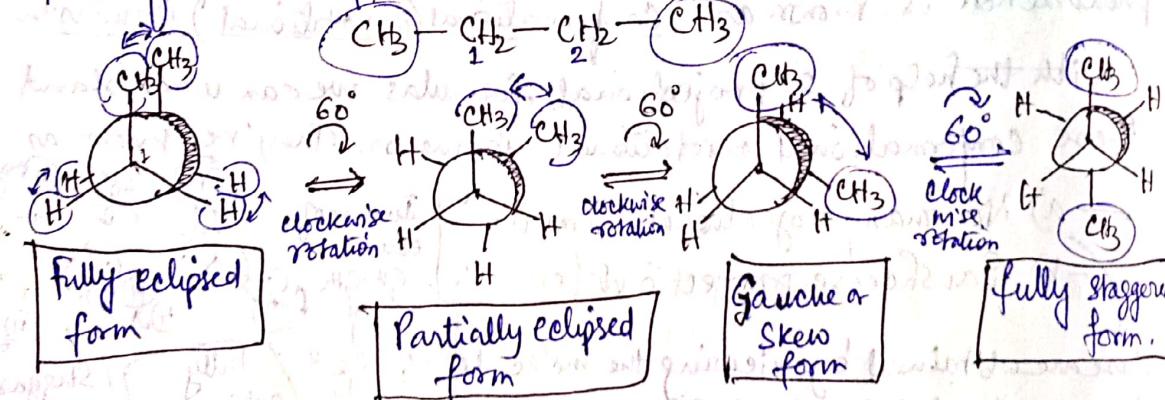


Now if we'll draw the

Newman projection's of

n-butane then we'll get total

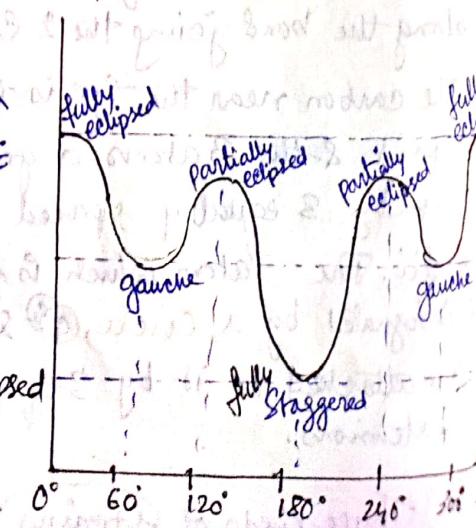
4 conformers as follows :-



As the bulky methyl groups ($-CH_3$) approach each other, their relative energy increases and hence their stability decreases. The stability decreases in the order given as follows

Staggered $>$ Gauche $>$ partially eclipsed $>$ fully eclipsed

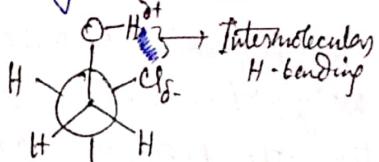
Stability increases.



Angle of rotation

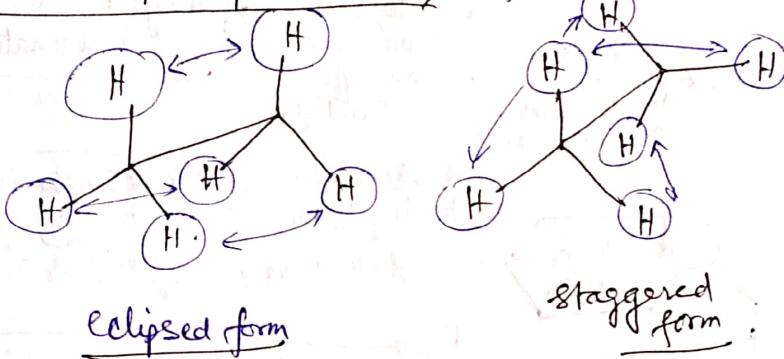
Intramolecular hydrogen bonding and stability of conformations

Usually the staggered form is more stable than the gauche or skew form but in molecules of the type $\text{CH}_2\text{Y}-\text{CH}_2\text{Z}$ (where Y and Z are Cl, Br, I, OH etc.) intramolecular H-bonding is possible in the skew form but not in the staggered form.



This stabilisation is great enough to make the skew form (or gauche form) more & more stable than the staggered form.

In sawhorse representation for ethane :-

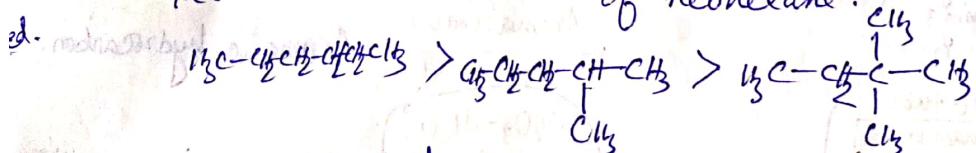


General properties of alkanes

- The normal alkanes are colourless gases (C_1 to C_4), colourless liquids (C_5 to C_{17}) and from C_{18} onwards colourless waxy solids.
- Boiling point \propto number of C atoms in the straight chain,

and
$$\text{B.pt} \propto \frac{1}{\text{Branching for same number of C-atoms}}$$

i.e. $\text{B.pt of n-Hexane} > \text{B.pt of Isohexane} > \text{B.pt of neohexane}$



i.e. As branching increases melting & boiling point decrease. The boiling point increases steadily with increase in molecular mass.

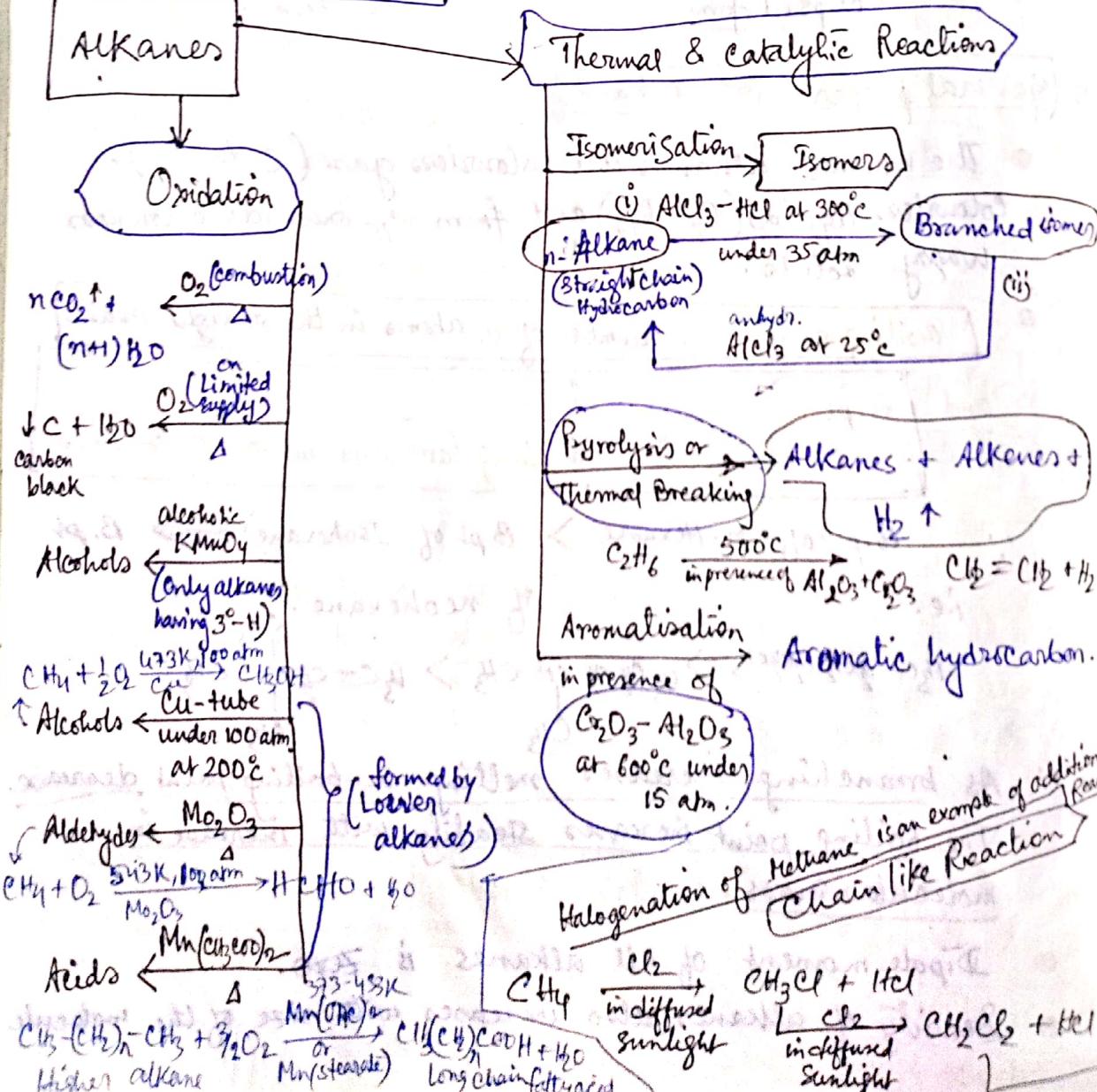
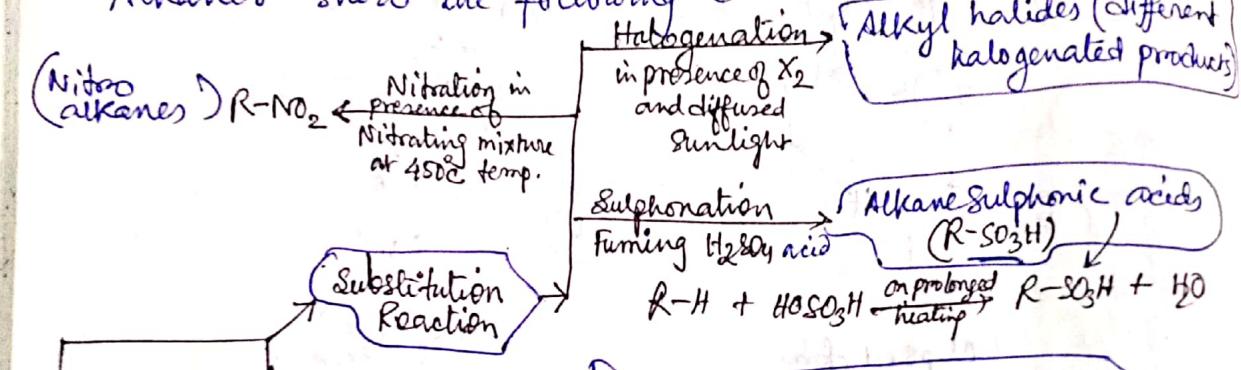
- Dipole moment of all alkanes is zero.
- Density of alkanes also increases with size of the molecule.

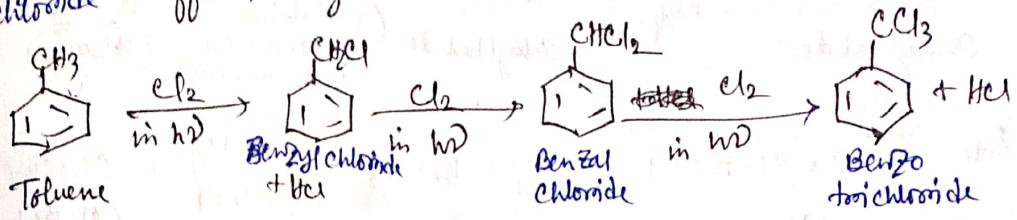
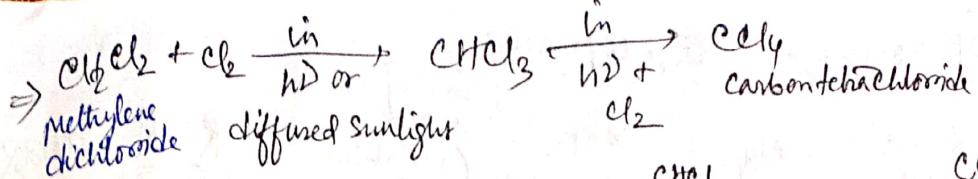
They're generally insoluble in polar solvents like H_2O , ethanol etc. but soluble in nonpolar solvent (or organic solvents) like ether, chloroform etc. (This is due to "like dissolves like" forces of interactions)

Melting point of alkanes increases with increase in molecular weight but alkanes with even no. of C-atoms have higher m.pt. than the preceding and succeeding members.

Chemical properties of Alkanes

Alkanes show the following chemical properties :-

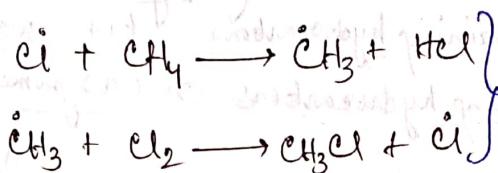




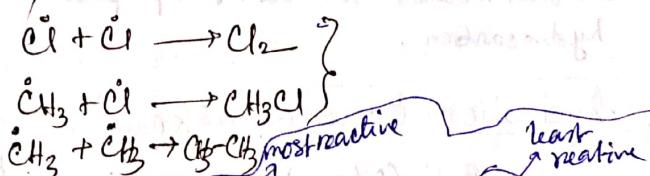
The mechanism of halogenation rxn is believed to be preceded with the formation of free radicals.

Initiation step $\text{Cl}_2 \rightarrow \cdot\text{Cl} + \cdot\text{Cl}$

Step of propagation

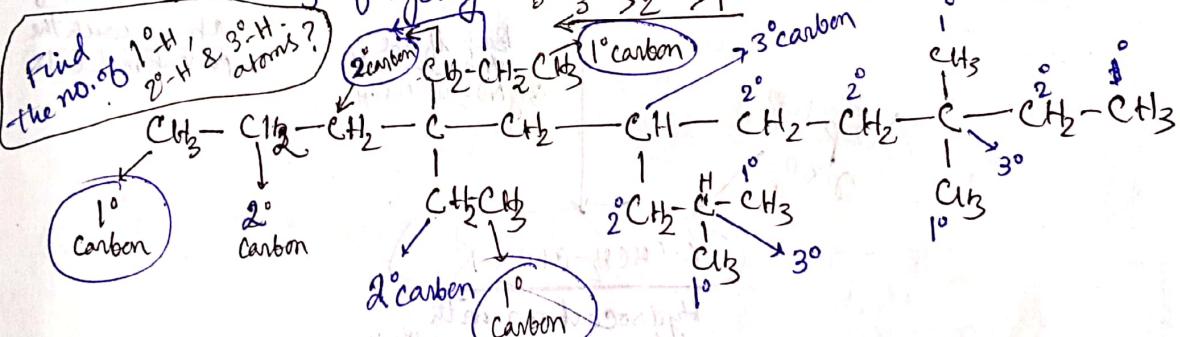


Termination step



■ The reactivity order of halogens : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

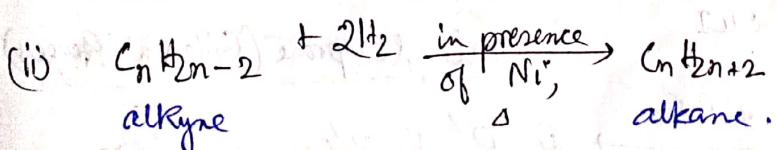
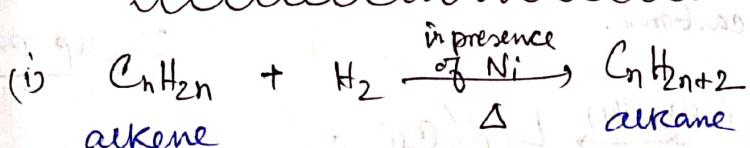
■ The reactivity of Hydrogen :



Methods of Preparation of Alkanes

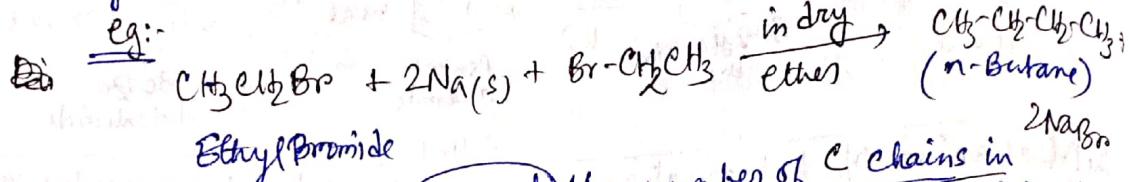
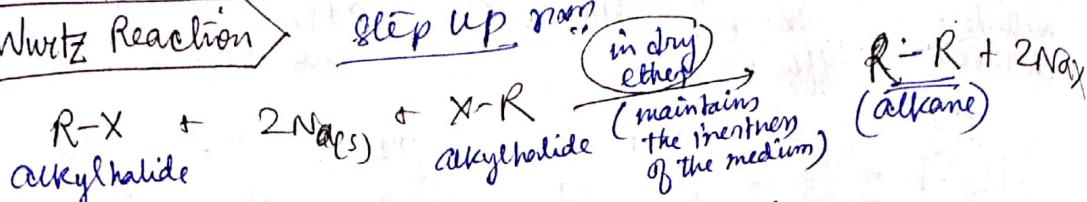
① By hydrogenation of unsaturated hydrocarbons

* Sabatier & Senderen's Reaction :-



Next page →

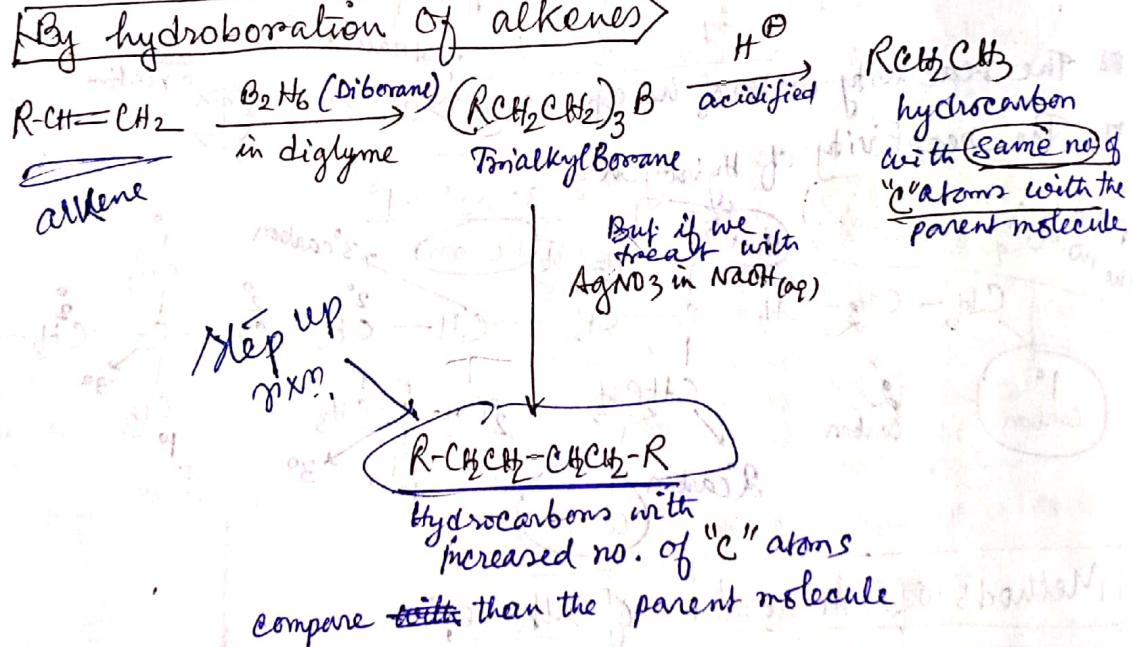
② Wurtz Reaction



In this method we can expand the number of C chains in the hydrocarbon but ~~in this rxn~~ 2 limitations are present they're :-

- (i) We can prepare only symmetrical hydrocarbon i.e. even no. "C" containing hydrocarbons but we can't prepare odd no. "C" containing hydrocarbons or asymmetrical hydrocarbons.
- (ii) In this method we can't prepare "methane" — The simplest hydrocarbon.

③ By hydroboration of alkenes

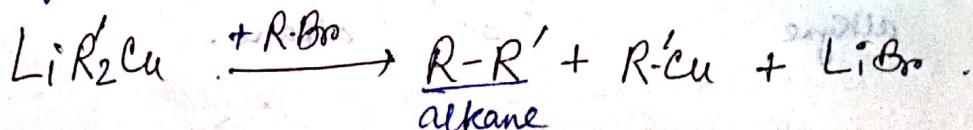
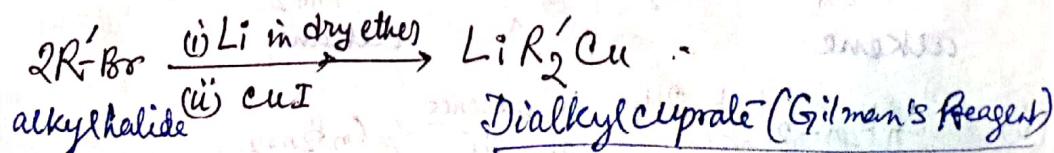


④ Corey House Synthesis

C - containing hydrocarbons.

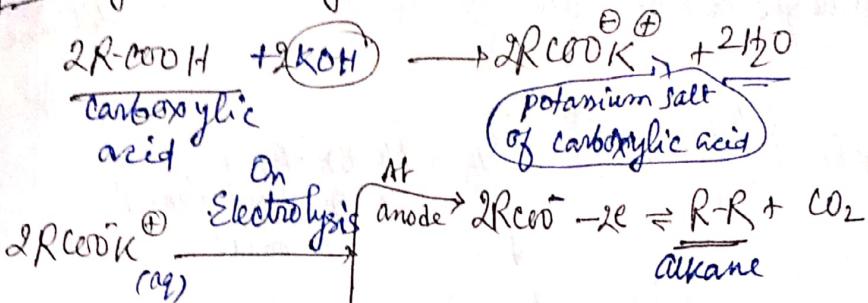
In this method we are able to prepare both odd and even no.

Step up rxn



18/1/18

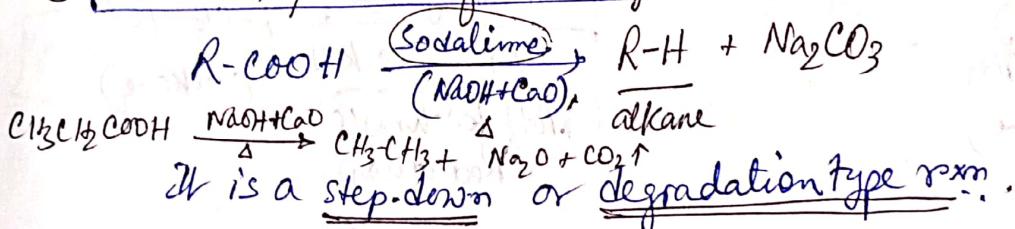
⑤ Kolbe's Electrolysis

Step up rxn.

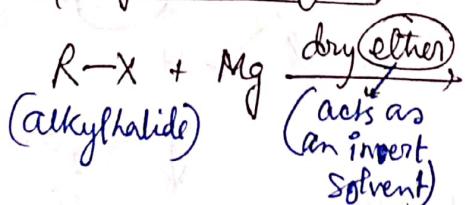
The mechanism of such type of rxn is believed to proceed via carbon free radical ($\cdot\text{C}$) formation. It is another method of C-nr. increasing in hydrocarbon. but it has some few limitations such as-

- (i) We can't prepare methane in this method.
- (ii) Only symmetrical hydrocarbons (alkanes) can be prepared not asymmetrical hydrocarbon in this method.

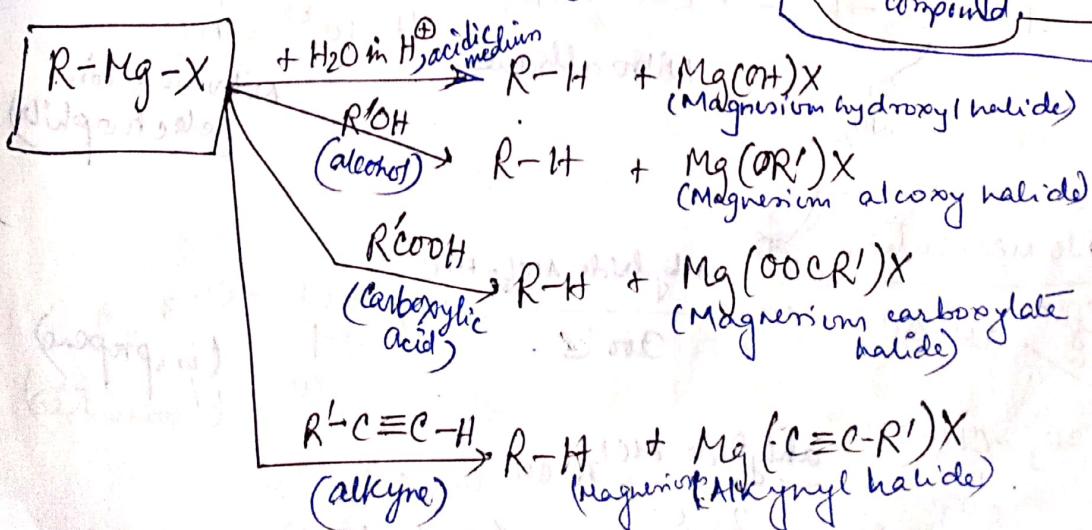
⑥ Decarboxylation of carboxylic acid

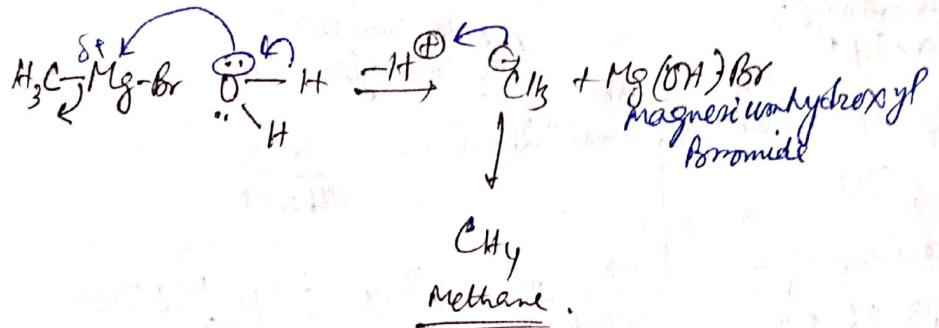
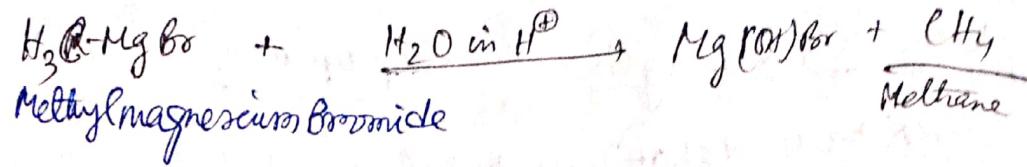


⑦ For Grignard's Reagent

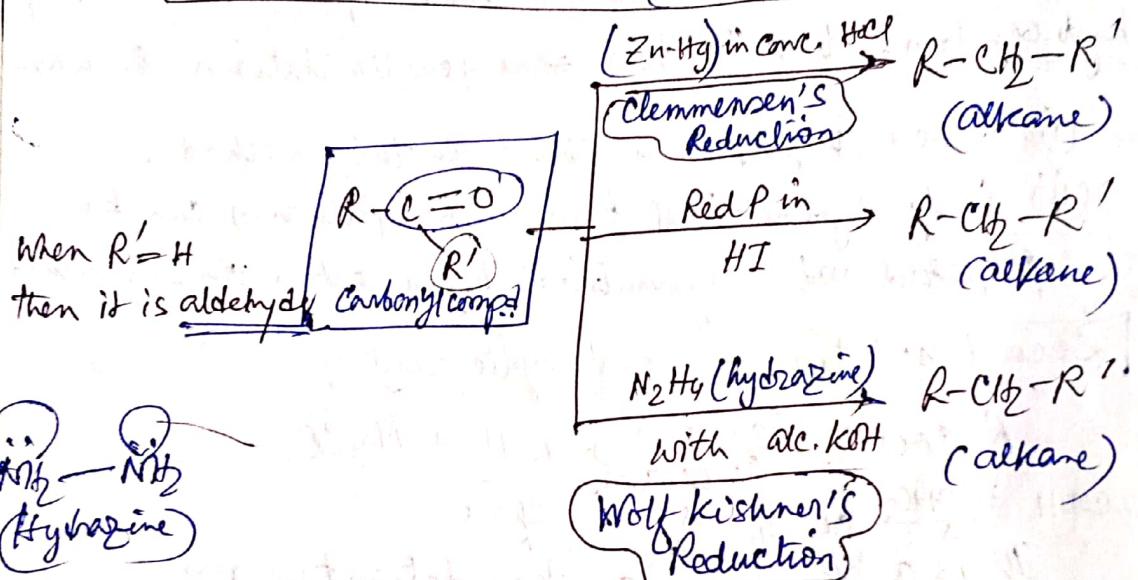


Grignard's Reagent
(Alkyl Magnesium halide)
It is an Organometallic compound

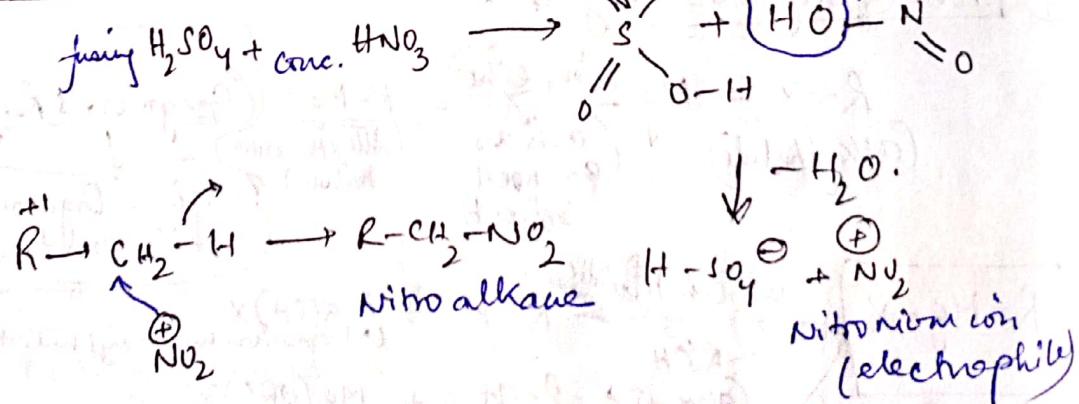
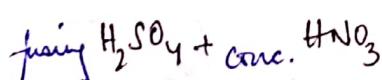




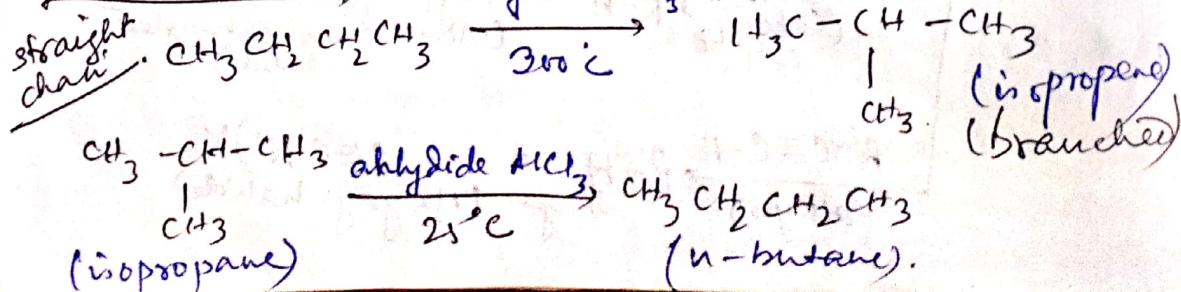
(8) By the reduction of Carbonyl Compounds
 $\text{C-CHO} + \text{Xe=O}$

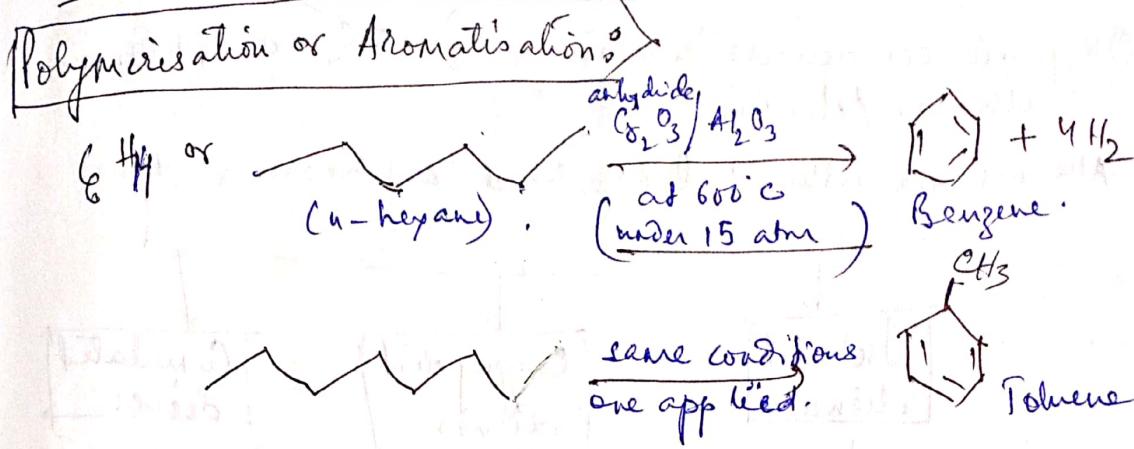


Nitration

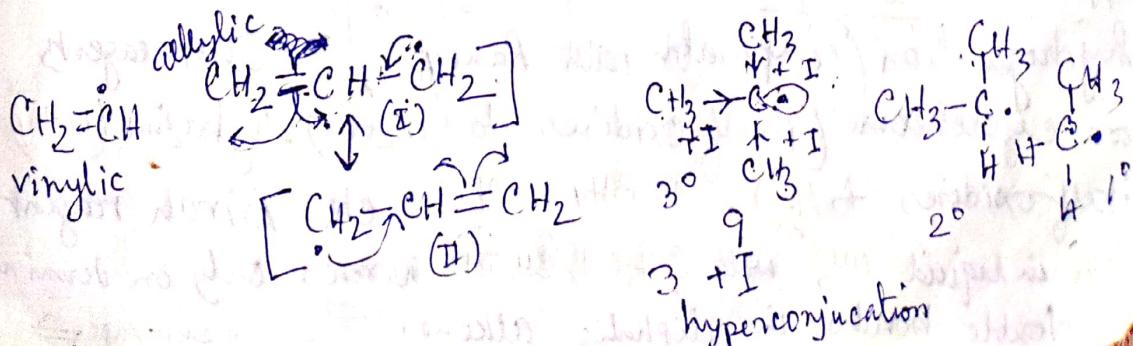
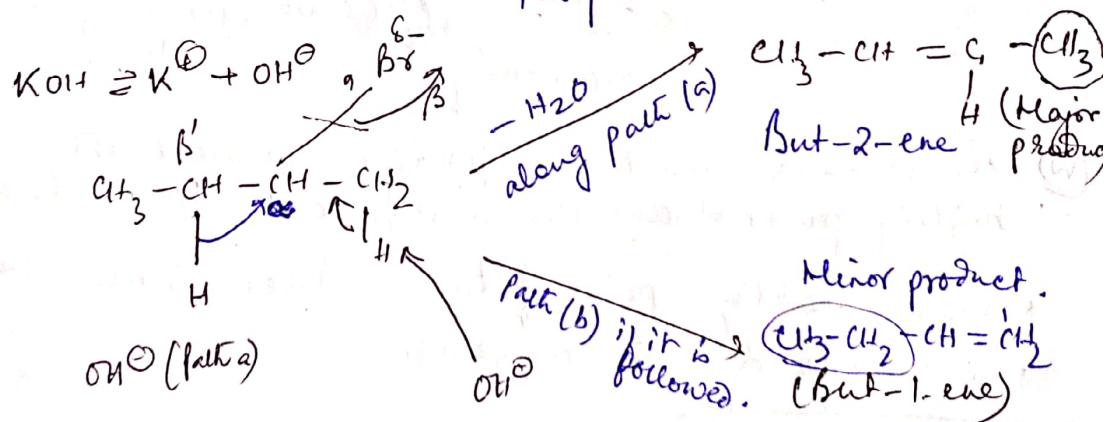
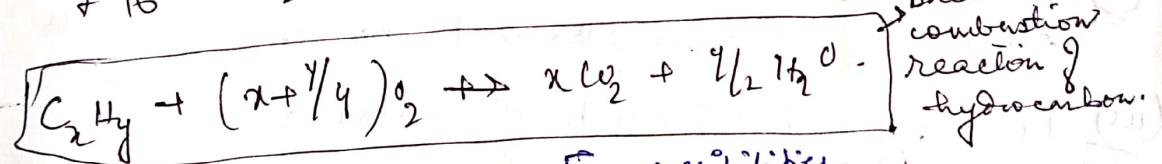
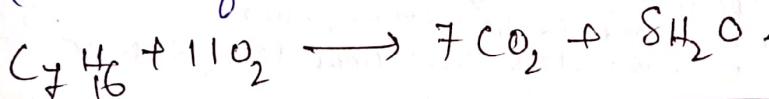
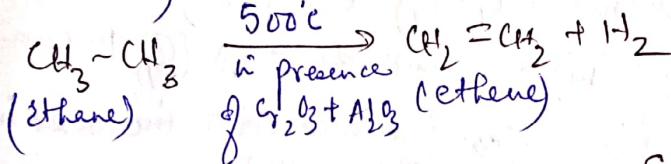
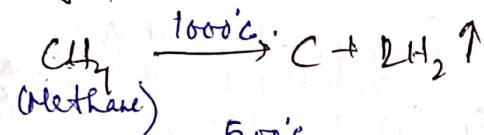


Ionomerisation

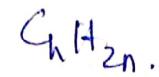




Pyrolysis or Cracking:



Alkenes



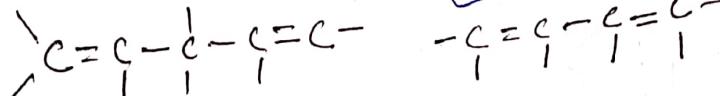
Organic compounds containing $\text{C}=\text{C}$ are known as Alkenes (olefins).

Alkenes with 2 double bonds are known as dienes.

Isolated dienes

Conjugated dienes

Cumulated dienes



Physical Properties of Alkenes — All alkenes are colourless and except Ethene all are odourless. Ethene has pleasant odour.

(i) The first three alkenes (C_2H_4) are gases, next (C_3H_6) are liquids and (C_4H_8) to max.

(ii) 14 alkenes (C_5H_{10}) are liquids. rest are solids. Bpt, m.pt and specific densities increase with increase in molecular mass in homologous series.

(iii) All alkenes are colourless and odourless, except ethene which has pleasant odour.

(iv) Boiling point \propto number of C-atoms.

$$\propto \frac{1}{\text{Branching}} \quad (\text{for some number of C-atoms})$$

(v) cis-Alkene has more (μ) dipole moment and boiling point than the corresponding trans-alkene.

However, melting point of trans-alkene is more than the corresponding cis-alkene.

Chemical Properties

Alkenes show the following chemical properties :-

Wilkinson's catalyst $\Rightarrow \text{RhCl}\left[\left(\text{C}_6\text{H}_5\right)_3\text{P}\right]_3$ is a good catalyst for hydrogenation (comparable with Raney Ni).

Other reagents are cyclohexane (itself oxidises to benzene), hydrazine (N_2H_4) (itself oxidises to N_2), NaBH_4 , PtCl_2 etc. Birch reagent

(Na in liquid NH_3 with $\text{CH}_3\text{OH}/\text{CH}_2\text{OH}$) works only on terminal double bonds in aliphatic alkenes.

next page \rightarrow

2/1/9
 ■ for Alkane, Total no. of isomers (T) = $2^{n-4} + 1$
 where n = number of C atoms (Valid upto C no. = 7)

① if $n=1$, then $T = 2^{1-4} + 1$
 $= 2^{-3} + 1 = 1$ only one isomer
 for methane
 This can be neglected & considering it as equal to zero.

② If $n=2$ (Ethane) then $T = 2^{2-4} + 1$
 $= 2^{-2} + 1 = 1$ only one isomer
 for ethane.

③ $n=5$ (Pentane) then $T = 2^{5-4} + 1$
 $= 2^1 + 1 = 3$ isomers are possible

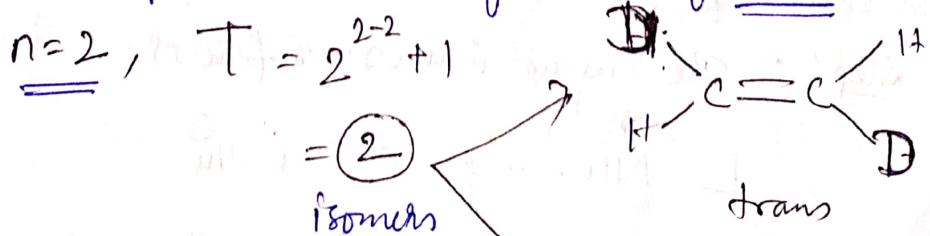
■ For Alkenes, with even no. of C atoms :-

① The total no. of isomers (T) = $2^{n-2} + 1$

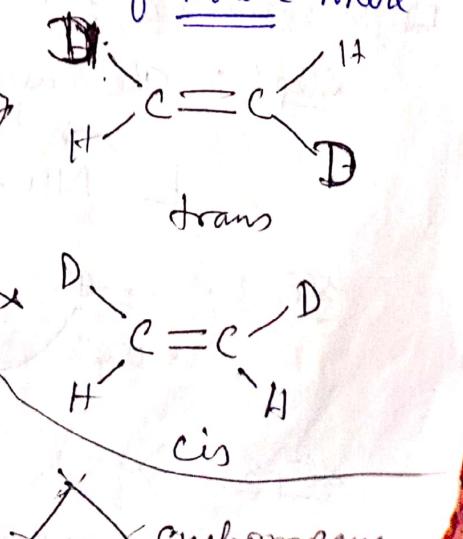
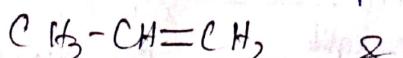
② For those alkenes having odd no. of C atoms :-
 The total no. of isomers (T) = 2^{n-2}

③ Total no. of ring isomers, The total no. of isomers (T) = $n-1$

As an example, the total no. of isomers of Ethene where



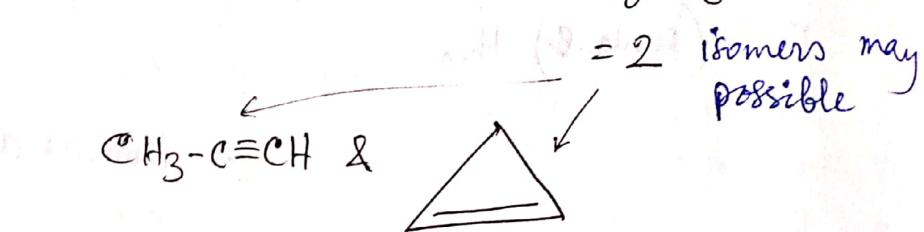
But for propene where $n=3$,
 $T = 2^{3-2} = 2$ isomers are possible



* For Alkyne

- 1) For odd number of C-atoms, total no. of isomers = $2^n - 2n$.
- 2) For even number of C-atoms, total no. of isomers = $2^n - (2n-1)$.
- 3) Total number of Open chain, total no. of isomers = $n(n-2)$.

for $n=3$ (i.e. propyne), $T = 2^3 - 2 \times 3$
 $= 8 - 6$



if $n=2$ (i.e. ethyne), $T = 2^2 - (2 \times 2 - 1)$
 $= 4 - 3$

only $\equiv 1$ isomer is possible

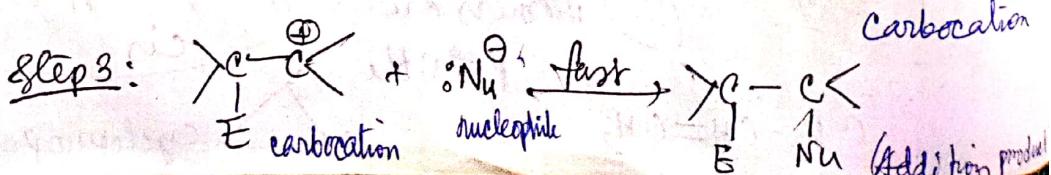
if $n=4$ (i.e. Butyne), $T = 2^4 - (2 \times 4 - 1)$
 $= 16 - 7$

$= 9$ isomers are possible

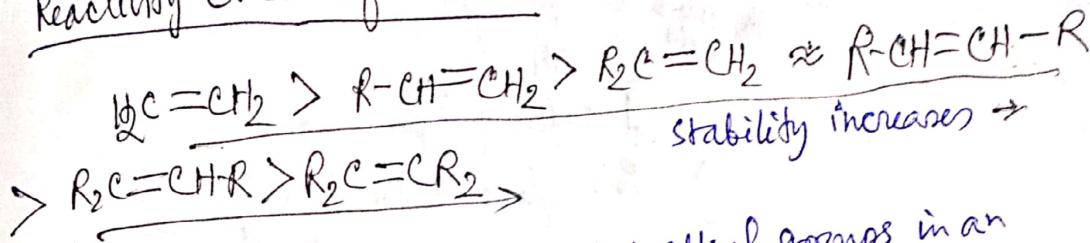
Chemical properties of alkenes

■ Mechanism of electrophilic addition rxn of alkenes

Step 1: The reagent ionises as follows:



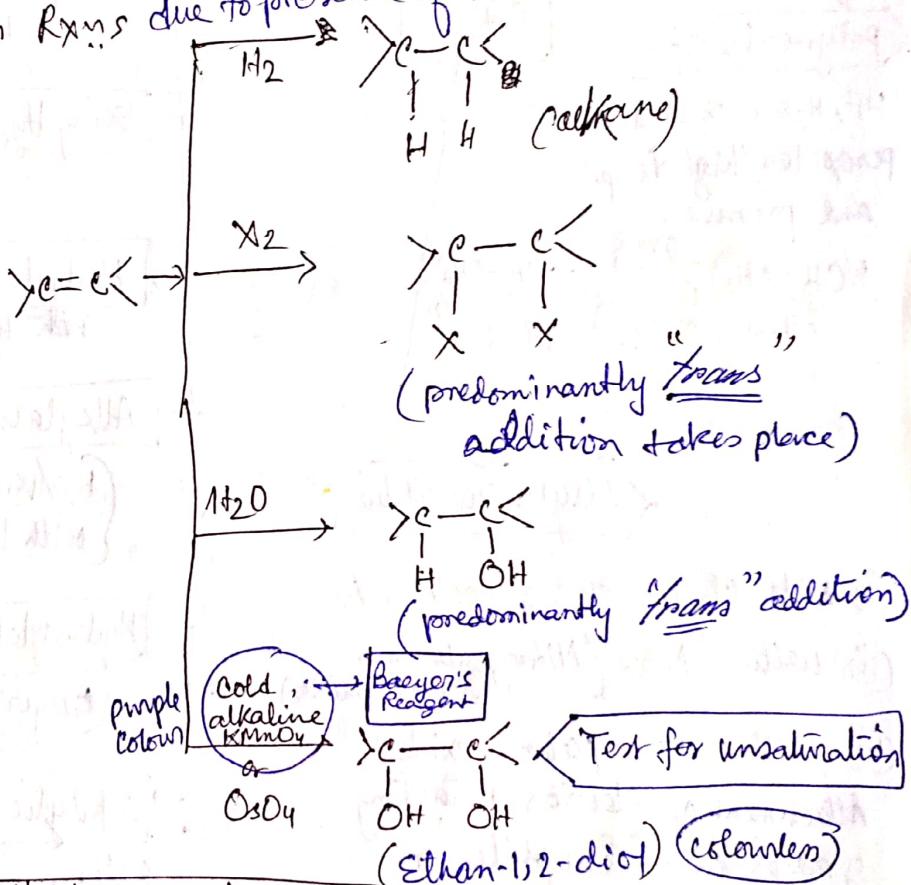
Reactivity Order of Alkenes



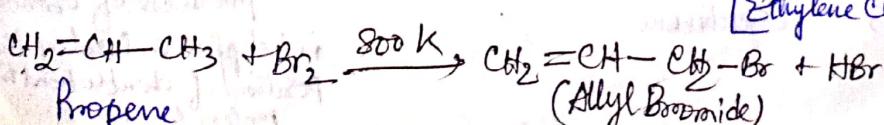
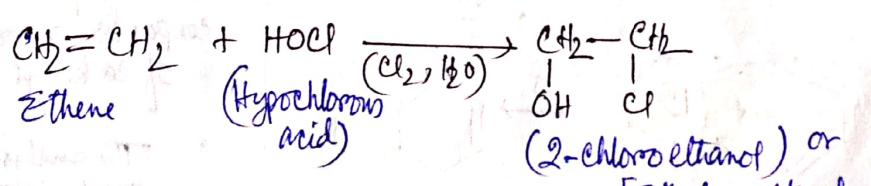
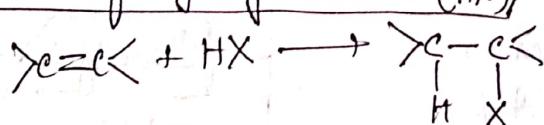
Conclusion: More the number of substituted alkyl groups in an unsaturated hydrocarbon (i.e. alkenes) more will be its stability.
 than that of less substituted alkenes.

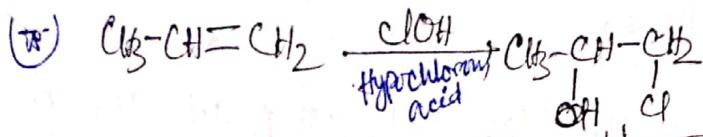
② The values of "Heat of hydrogenation" \approx "Stability of alkenes"

□ Addition Rxns due to presence of π bond between $\text{C}=\text{C}$

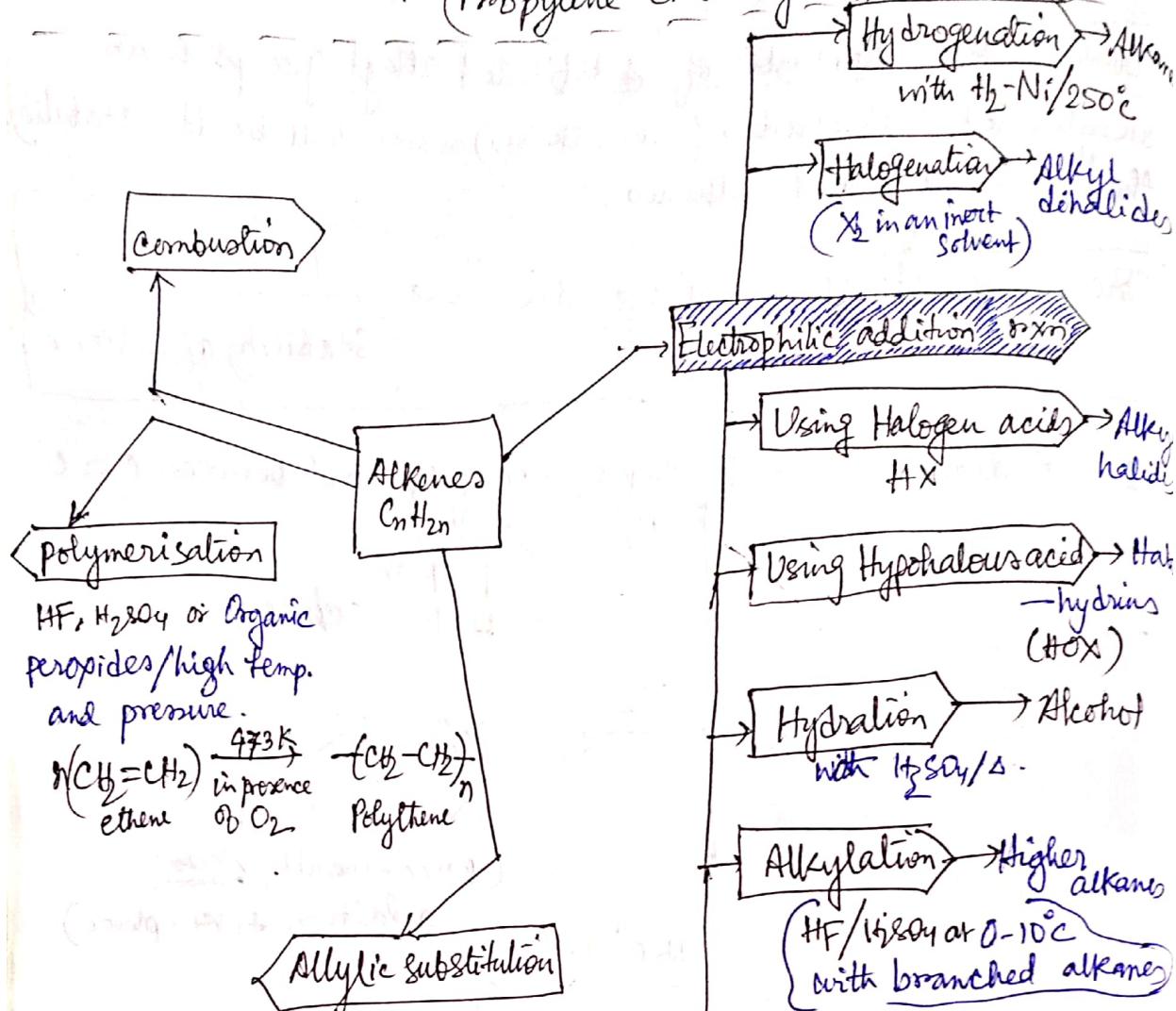


□ Addition of Hydrogen halides (HX)

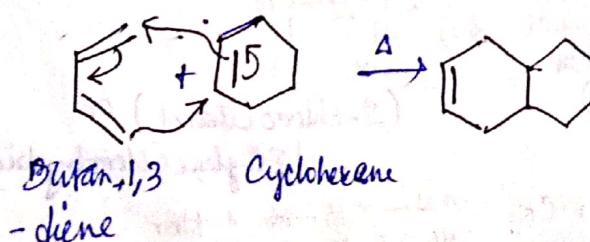




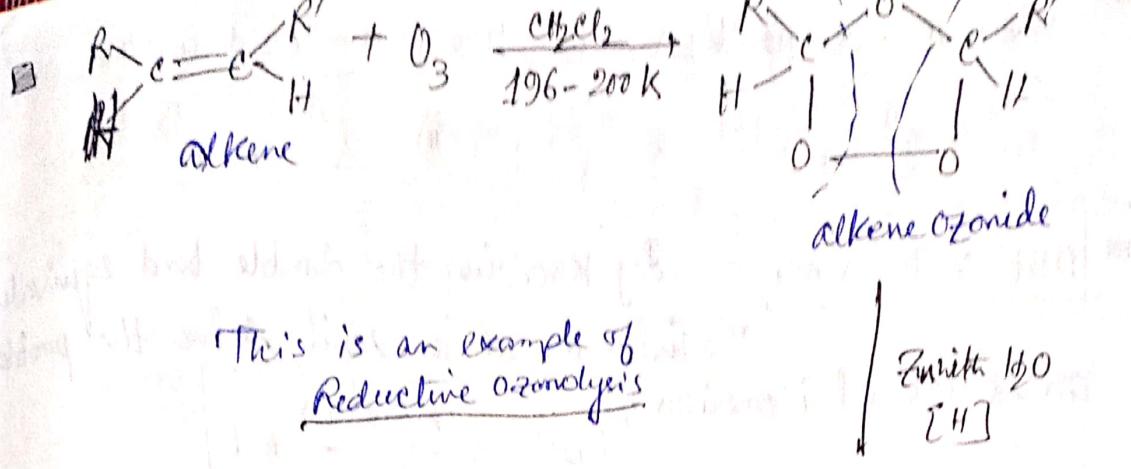
1-Chloropropan-2-ol
or (Propylene chlorohydrin)



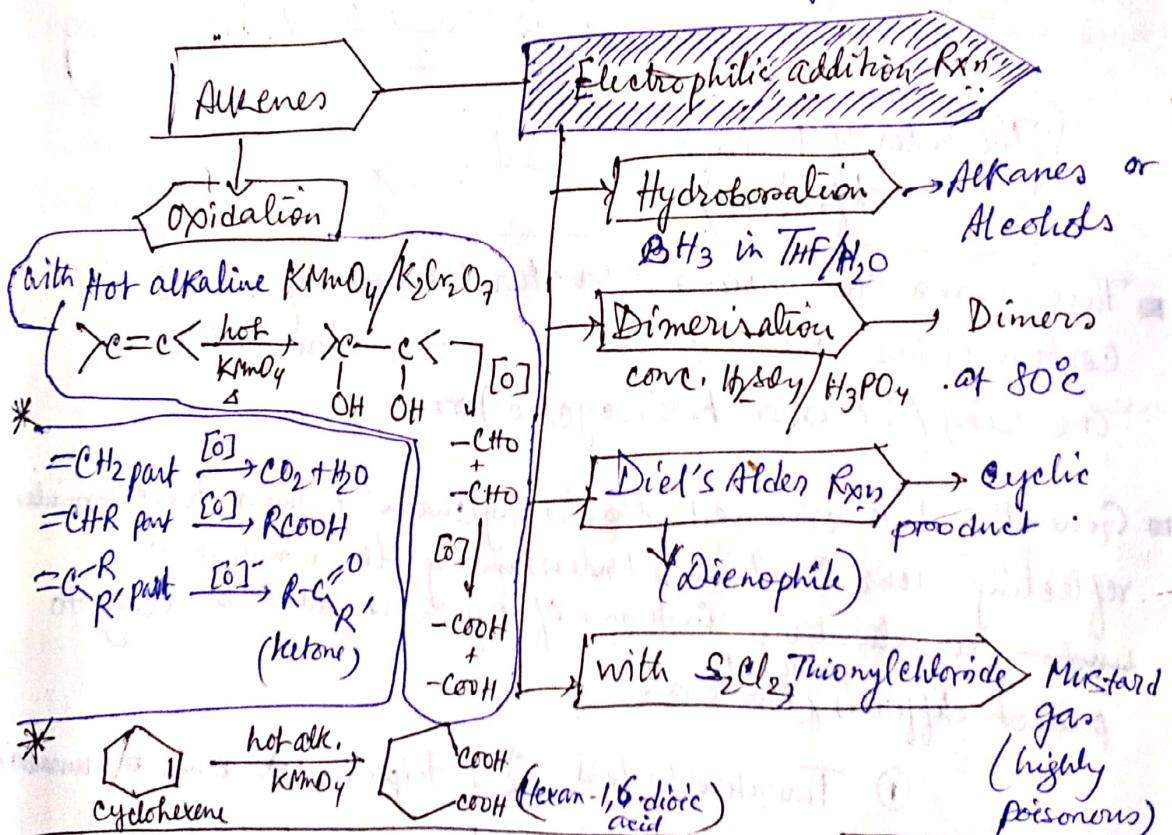
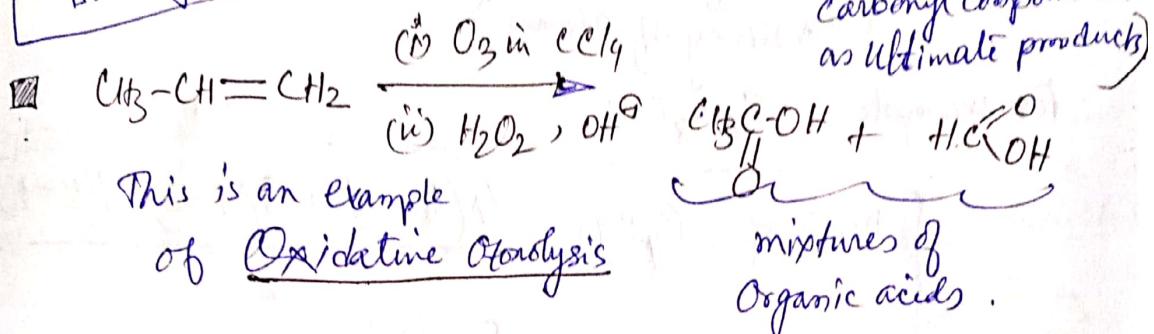
- (i) with Cl_2/Br_2 at $500-600^\circ\text{C}$ or Δ
(ii) with NBS (NitrogenBromo succinimide)
(iii) with SeO_2 (Seleniumoxide)
Attachment of electron attracting groups in dienophile or electron releasing groups in conjugated diene increases the rate of Diel's Alder rxn.



- The analysis of the products of ozonolysis is helpful in locating the position of double bond in alken molecule.



THF
 = Tetrahydrofuran
 is an organic solvent



Q: How to find the number of geometrical isomers?

- If a compound has two double bonds in which the two ends are different (e.g. $\text{A}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{B}$) then number of geometrical isomers is 2^n where $n = \text{no. of double bonds}$
- If however the two ends are identical (i.e. $\text{A}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{A}$) then the number of geometrical isomers is →

$$\begin{array}{l|l} \text{When } n = \text{even no. then} & \text{When } n = \text{odd no. then} \\ \text{(i)} \quad 2^{\frac{n-1}{2}} + 2^{\frac{n-1}{2}-1} & \text{(ii)} \quad 2^{\frac{n-1}{2}} + 2^{\frac{n-1}{2}-\frac{1}{2}} \end{array}$$

■ DBE or Index no. \rightarrow By knowing the double bond equivalents or index no. we can easily solve the problem on structural isomerism.

$$\text{DBE} = \frac{\sum n(v-2)}{2} + 1$$

(where $n = \text{no. of atoms}$
 $v = \text{valency of atoms}$)

For example, C_4H_8O :

$$\text{DBE of } C_4H_8O = \frac{4(4-2) + 8(1-2) + 1(2-2)}{2} + 1$$

$$= \frac{8 - 8 + 0}{2} + 1$$

The index of hydrogen deficiency = 1

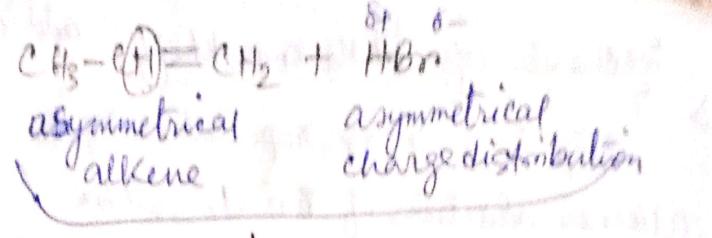
- This means the various structural isomers of C_4H_8O will contain either one $C=O$ or $C=C$ double bond or one ring (homo or heterocyclic).
- Generally it is observed that ring chain isomers have formulae reflecting unsaturation, understanding the amount of unsaturation in terms of equivalents it'll be easy to predict different isomers.

- ① Two double bonds $\not\equiv$ 1 triple bond $\not\equiv$ 2 rings \approx 1 unsat.
- ② 1 double bond = 1 ring.

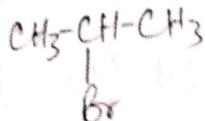
3/01/19

Alkene

Nucleophilic addition rxn of alkene



According to Markovnikoff's addition rule



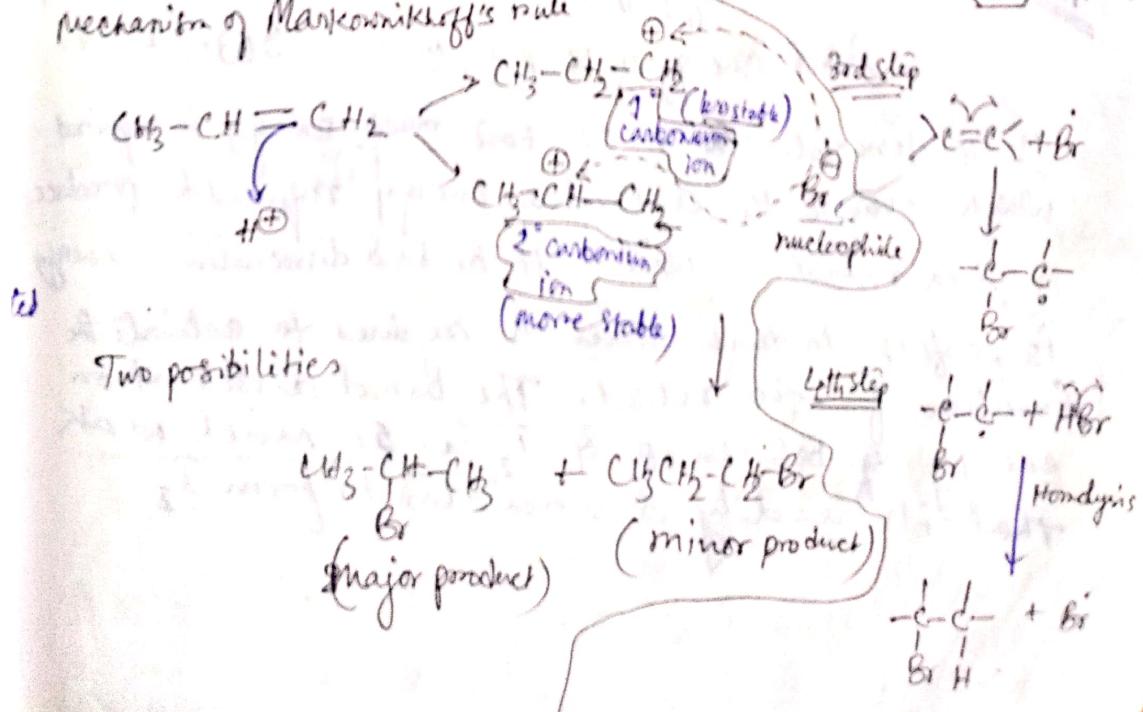
2-Bromopropane

This rxn proceeds via the formation of carbocation i.e. it follows ionic mechanism.

According to Markovnikoff's rule:

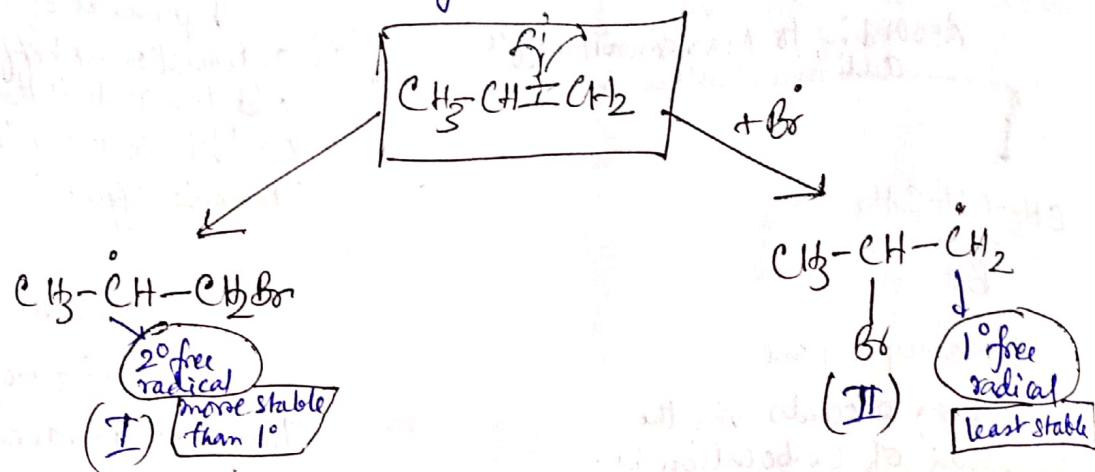
When an asymmetrical alkene is made to react with an asymmetrical reagent (in this case HBr, as the charge distribution isn't symmetric) the negative part of the reagent goes to that double bonded C atom which bears the least no. of H-atom.

Mechanism of Markovnikoff's rule

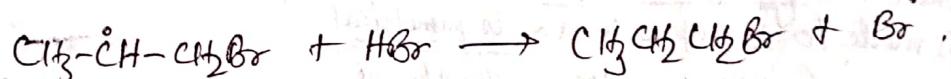


Mechanism of Anti-Markownikoff's addition Rxn.

Step 3 & 4 are repeated again & again. In case of unsymmetrical alkenes addition of Br^{\cdot} to alkene (step 3) may take place through 2 possible ways



Since free radical (I) is more stable than that of (II) so it more easily formed & hence the rxn proceeds via (I) resulting in the formation of Anti-Markownikoff's product.



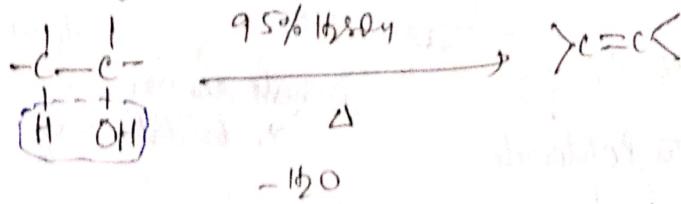
Q. Only HBr can take part in Anti-Markownikoff's addition Rxn. not HCl, nor HI etc. Explain why?

Ans Bond energy of H-Cl bond is 430 kJ mol^{-1}
Bond energy of H-Br " " $363.7 \text{ kJ mol}^{-1}$

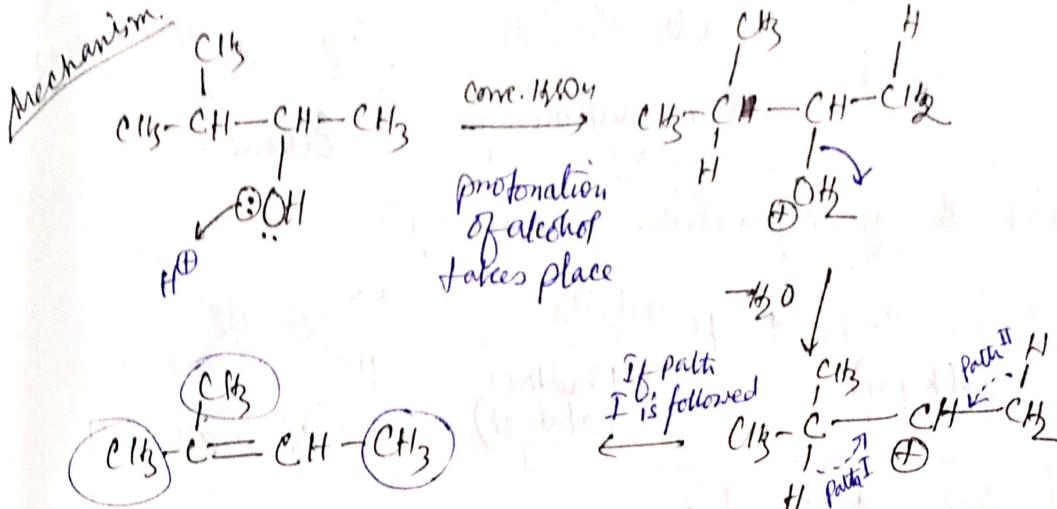
To dissociate the H-Cl bond much energy is required which overcomes the activation energy (E_a) required to produce free radical. While H-Br bond dissociation energy is perfect to that which is required to activate the formation of free radical. The bond dissociation energy between H₂ & I₂ is so much weak that it readily dissociates to form I₂.

Methods of Preparation

By Dehydration of alcohols



Mechanism:



2. Methyl but-2-ene

Major product

According to Saytzeff's

rule — More the number of substituted alkyl groups in an unsaturated compd more will be the stability of that compd.

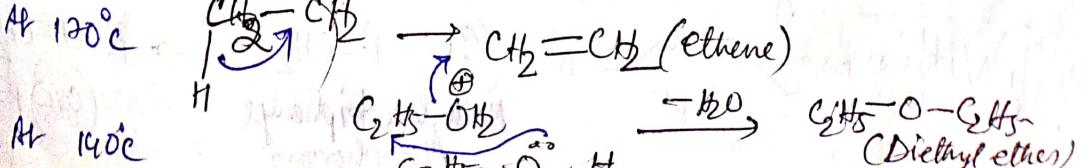
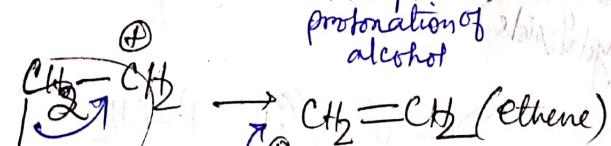
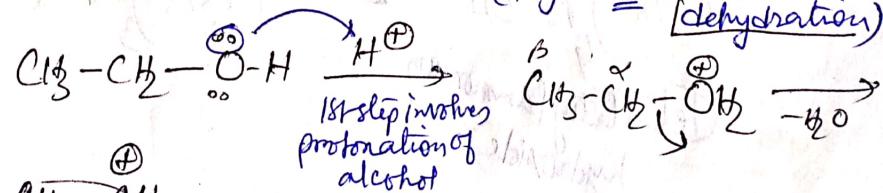
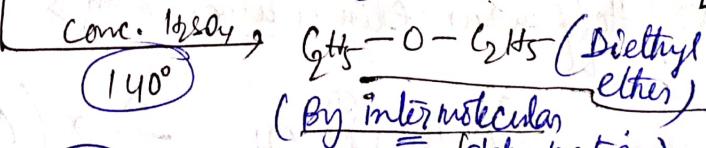
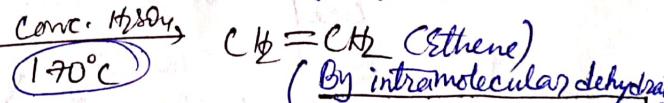
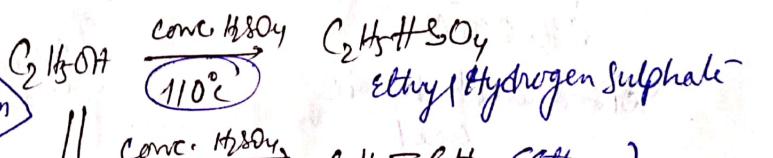
2. Methyl butene

Minor product

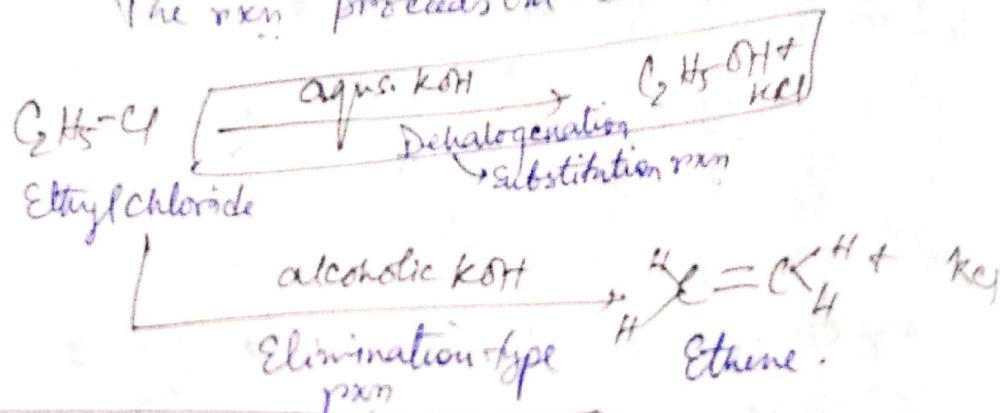
Preparation of Alkenes

Dehydration of ethanol

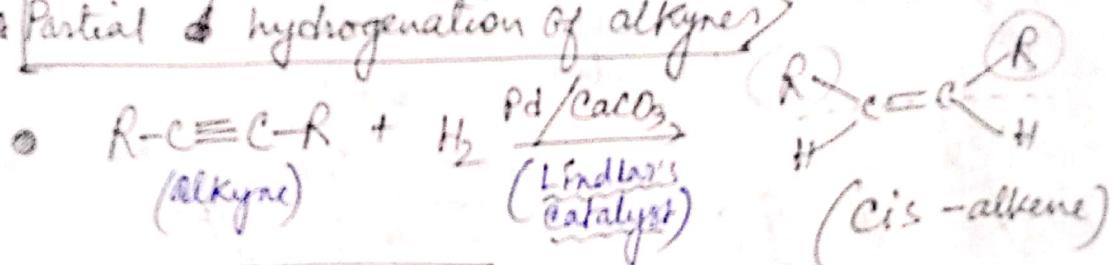
Intramolecular Dehydration Mechanism



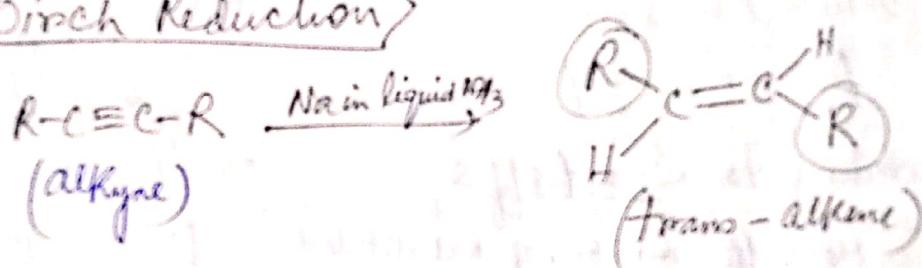
By dehydrohalogenation of alkyl halides
The rxn: proceeds via elimination ROX



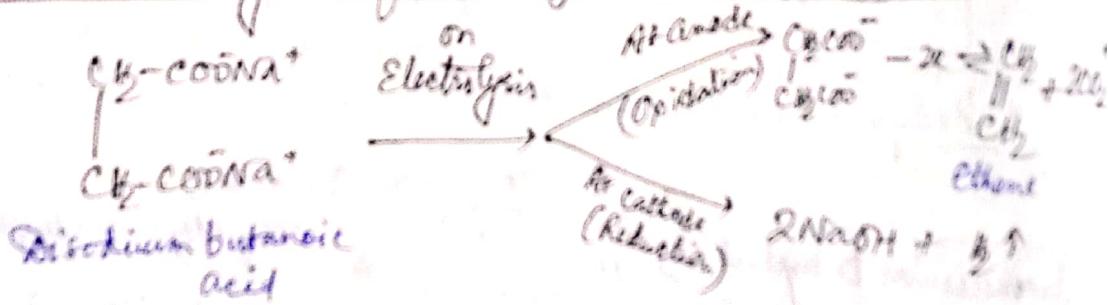
■ Partial & hydrogenation of alkynes



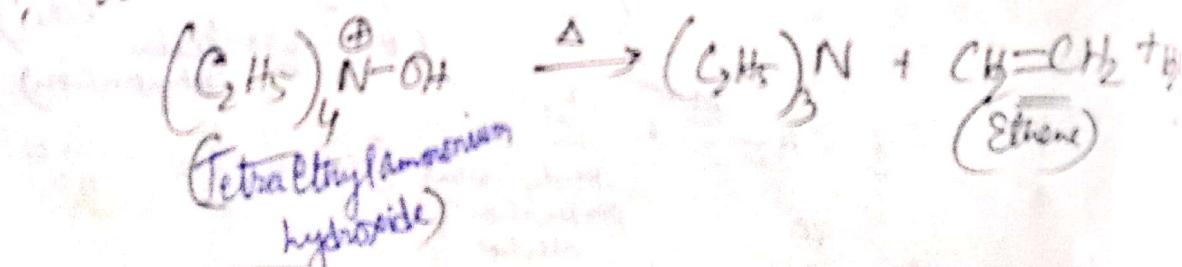
o Birch Reduction



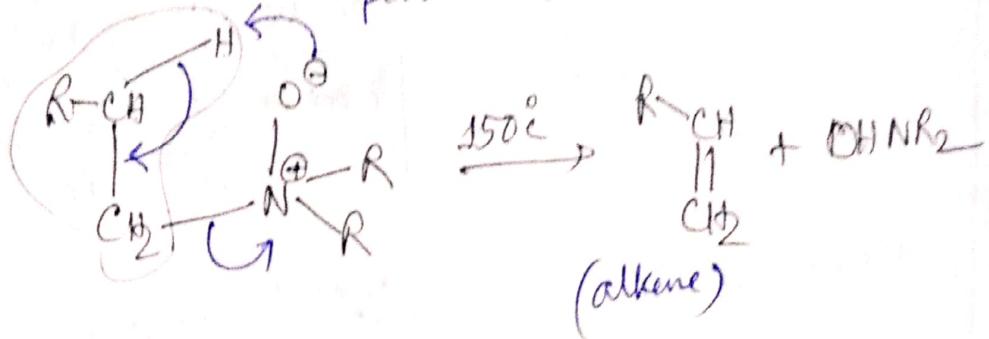
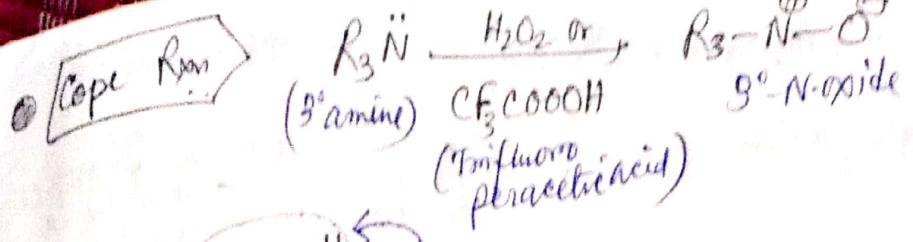
• By electrolysis of salt of chloroacrylic acids:



Hoffmann elimination Rxn



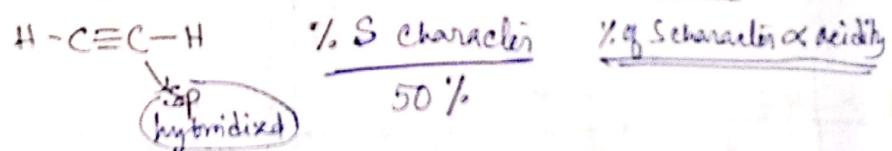
Witting Rxn: $\text{R}_2\text{C}=\text{O} + \text{H}(\text{C}_6\text{H}_5)_3\text{P}=\text{CH}_2 \xrightarrow{\Delta} \text{R}-\text{CH}(\text{CH}_2)\text{C}_6\text{H}_5$
 Methylene-triphenyl
 phosphorane $(\text{C}_6\text{H}_5)_3\text{P}=\text{CH}_2$



19/01/19
 Alkyne \rightarrow General formula C_nH_{2n-2} \rightarrow Hydrocarbons
 with $-C\equiv C-$ are known as alkynes and have general
 formula -

Physical Properties

- (i) First 3 members of alkynes are colorless gases, next 8 are liquids and higher alkynes are solids.
- (ii) All alkynes are colorless except acetylene or ethyne (Garlic odour).
- (iii) Melting point and boiling point and densities of alkynes are (higher) than the corresponding alkanes and alkenes.
- (iv) Acetylene and terminal alkynes are acidic in nature.



(v) Order of acidity for different alkynes is



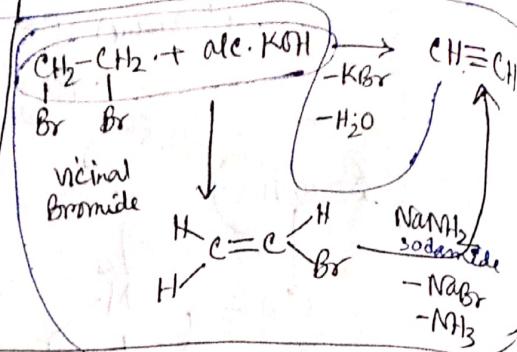
Methods of preparation \rightarrow Acidity increases

Methods	Rxns. involved
① Hydrolysis of metal carbides	$MC_2 + 2H_2O \rightarrow HC\equiv CH + M(OH)_2$; $Mg_2C_3 + H_2O \rightarrow C_2H_2-C\equiv CH + Mg(OH)_2$ (where M = Mg, Ca, Sr, Ba)
② Dehalogenation (by heating iodoform with Ag ₂ O)	$ \begin{array}{c} \text{---C---I} \\ \\ \text{---C---I} \end{array} \xrightarrow{\text{Zn dust}} -C\equiv C- + 2ZX_2, 2CHX_3 + 6Ag \xrightleftharpoons[\text{Halogen}]{} H\equiv C\text{H} + 6AgI $ <p style="text-align: center;"><small>yellow crystals</small></p>

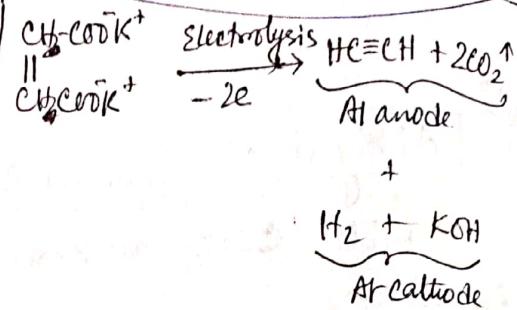
Method of Preparation of Alkynes

Risks involved

③ Dehydrohalogenation



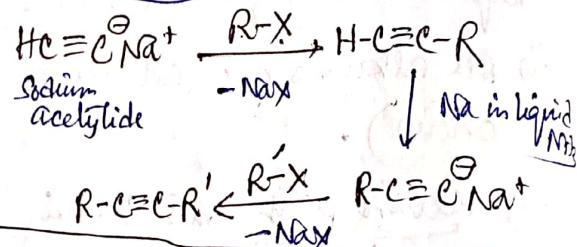
(4) Kolbe's Electrolysis



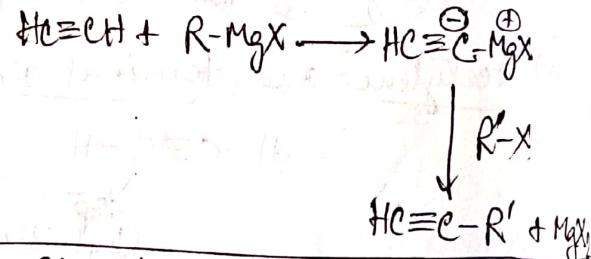
(5) From Sodium acetylide



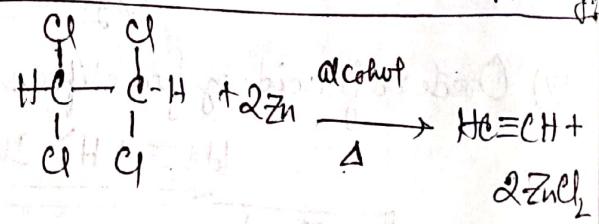
in liquid NH_3



⑥ From Grignard's reagent

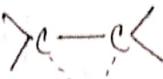


(7) By heating 1,1,2,2-tetrachloro-
-ethane with Zn



Chemical Properties of Alkynes → Alkynes shows electrophilic addition rxn due to availability of π -bonded electrons but they're less reactive than alkenes due to strain in cyclic intermediate as shown below :-

Additional π -bond creating more strain.



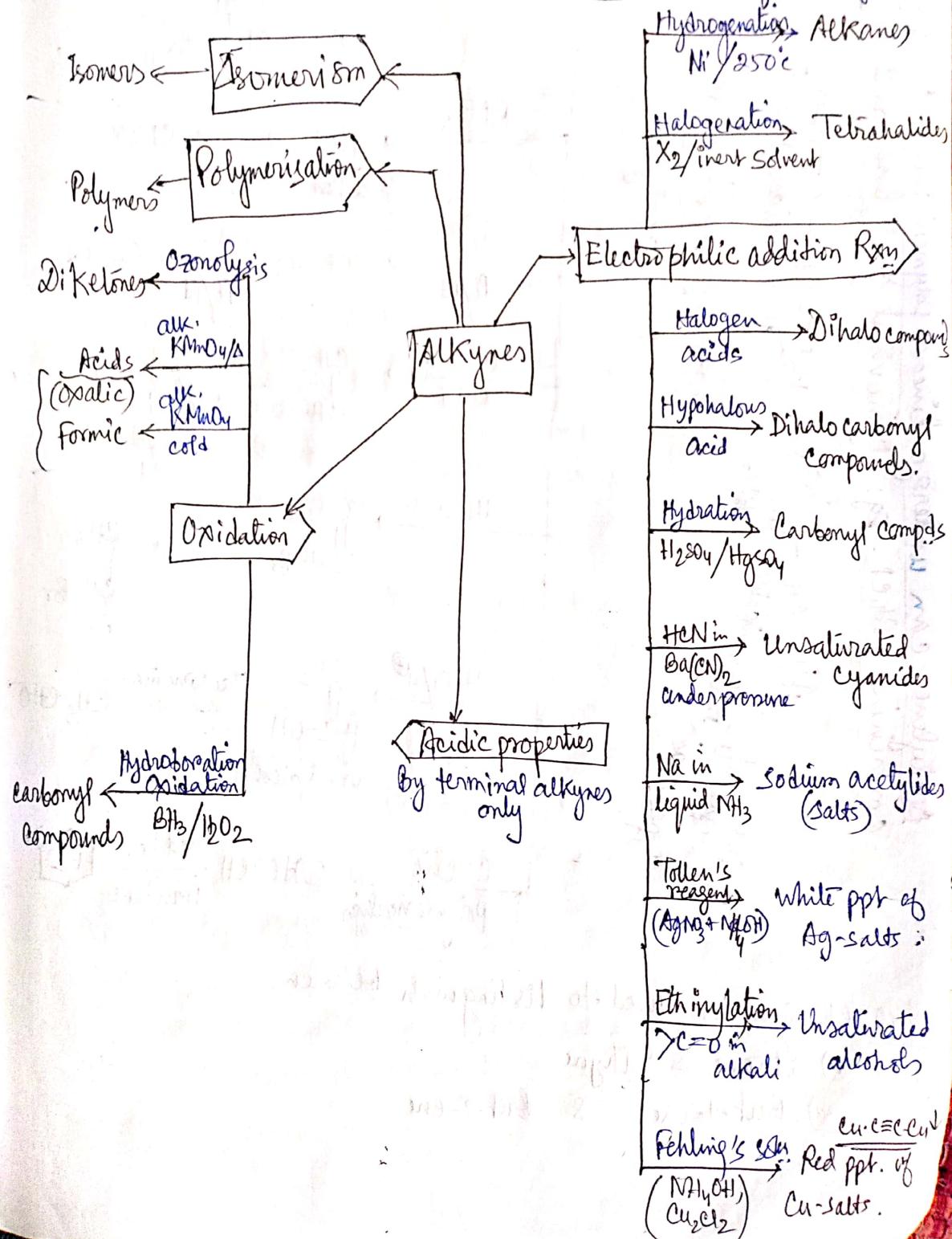
E^{\oplus}

Less strained
more stable cyclic
intermediate of alkenes

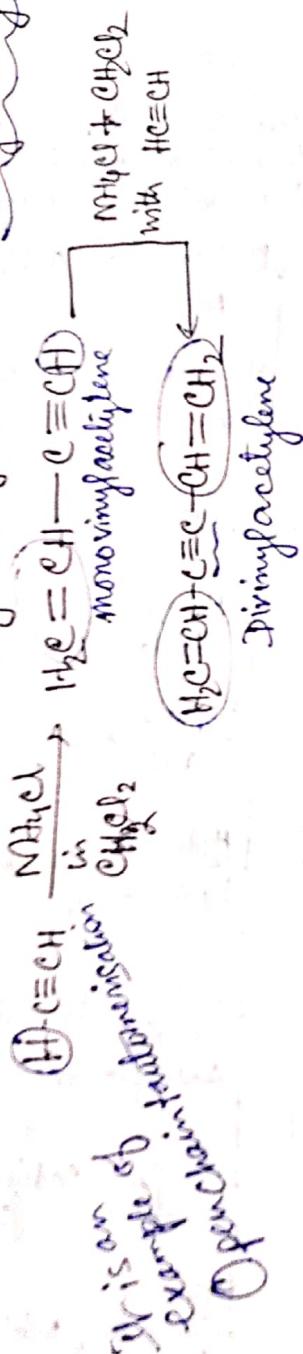


E^{\oplus}

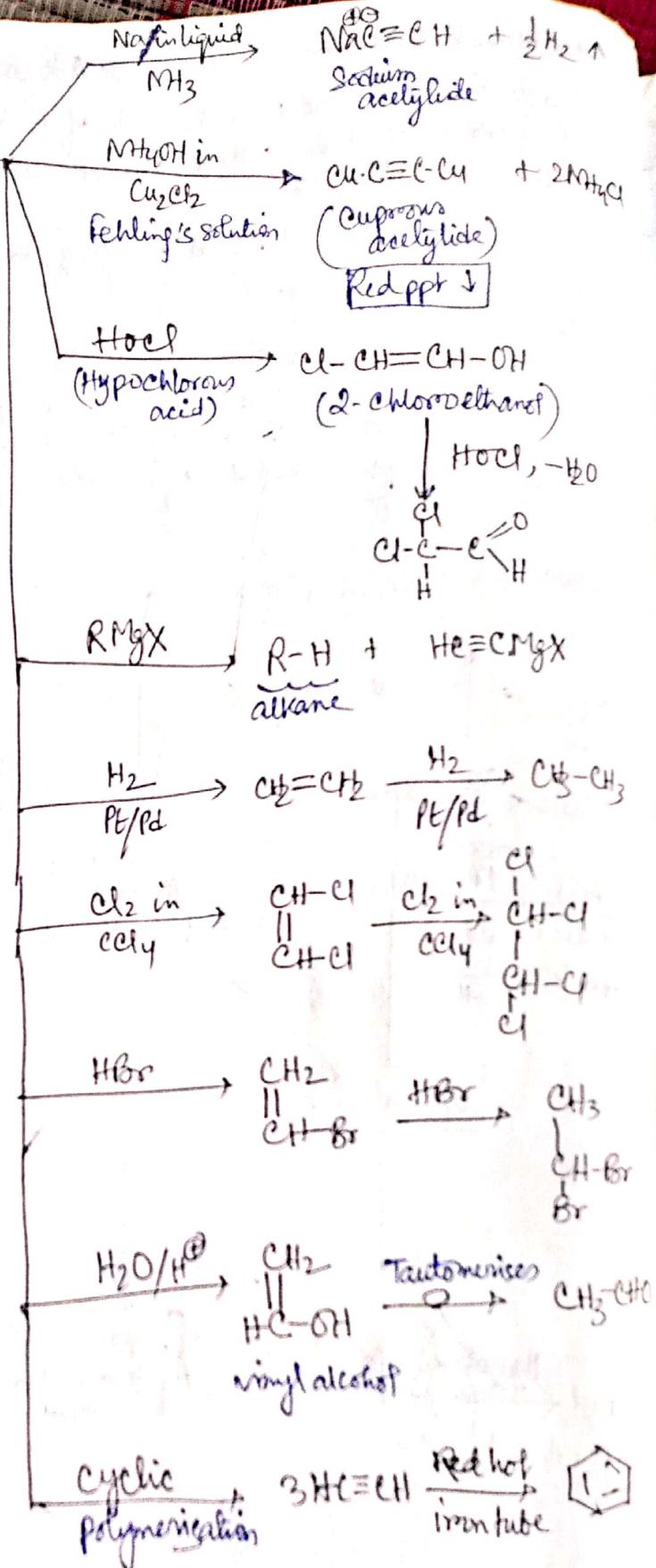
More strained,
less stable cyclic
intermediate of alkynes.



Ethyne can undergo linear polymerization by containing NH_3 . e.g.: Monovinyl acetylene and divinyl acetylene are formed.



Alkynes

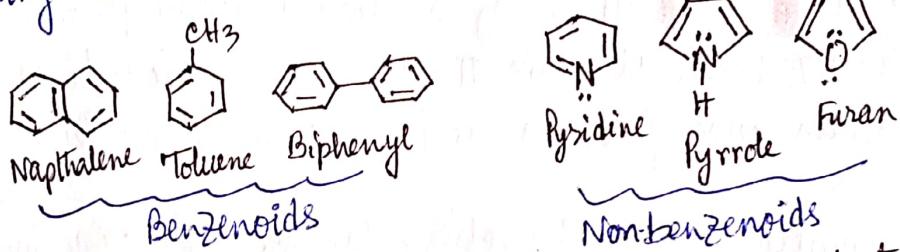


Q. Chemical test used to distinguish between

- Ethene & Ethyne
- But-1-ene & But-2-ene

Aromatic Hydrocarbons

Benzene (C_6H_6), Toluene (C_7H_8), Naphthalene ($C_{10}H_8$) etc. are unsaturated hydrocarbons containing conjugated double bonds within the rings. Inspite of this unsaturation these don't undergo addition rxns easily instead of undergoing easy electrophilic substitution of ring H-atoms. These have also unusual thermodynamic stability compared to corresponding hypothetical cyclic unsaturated system. These hydrocarbons are called aromatic hydrocarbons or arenes. Most of the aromatic compounds contain benzene ring called benzenoids and those not containing Benzene ring are called non-benzenoids.

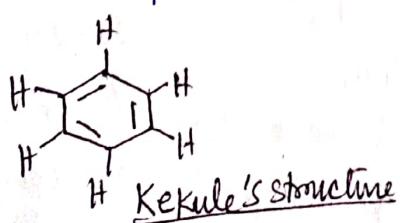


Aromatic compds are cyclic, planar, conjugated π -electron system containing $(4n+2)\pi$ electrons as per Hückel's rule of aromaticity.

Coal & petroleum are the two important sources of aromatic hydrocarbons and other aromatic compounds.

General Introduction to Structure of Benzene

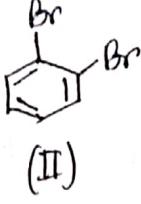
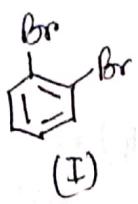
The simplest hydrocarbon is benzene, its structure :-



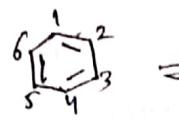
In benzene all the Hs are equivalent as it forms only a single monosubstitution product but three disubstituted products

(1,2), (1,3) and (1,4).

From Kekulé structure two (1,2) disubstitution products are possible (i) and (ii). However benzene forms only one (1,2) disubstituted product.

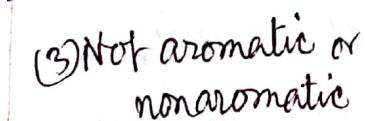
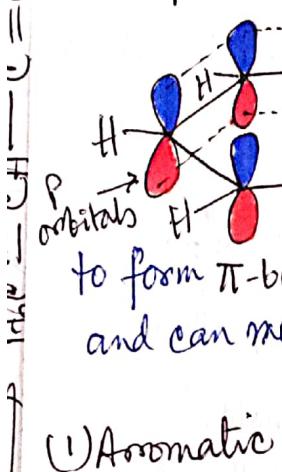


This was overcome by Kekulé.
He suggested the delocalisation of double bonds in the ring.



In benzene all C-C bond lengths are equal (139 pm) which is intermediate between C-C single bond (154 pm) and C=C double bond (133 pm). This indicates that double bonds are not fixed, they're delocalised.

In benzene each C-atom is sp^2 hybridised leaving one p-orbital unhybridised, \perp to plane of the ring.



So each p-orbital has equal probability to overlap with any one of the two adjacent p-orbitals to form π -bond. Thus six π -electrons are delocalised and can move freely about the six carbon nuclei.

- A cyclic, planar, completely conjugated compound with $(4n+2)\pi$ electrons
 $5\pi e^\ominus, 6\pi e^\ominus, 10\pi e^\ominus$

- A cyclic, planar, completely conjugated with $4\pi e$ electrons.
 $4, 8, 12 \pi e^\ominus$

- A compound that lacks one (or more) of the four requirements to be aromatic or antiaromatic.

Nonaromatic



Aromatic

Cyclopentadienyl anion

- $6\pi e^\ominus$
- contains $(4n+2)\pi e^\ominus$



Antiaromatic

Cyclopentadienyl cation

- $4\pi e^\ominus$
- contains $4\pi e^\ominus$



pyridine N+ pyrrole

Tropyl cation



cyclopentadienyl radical

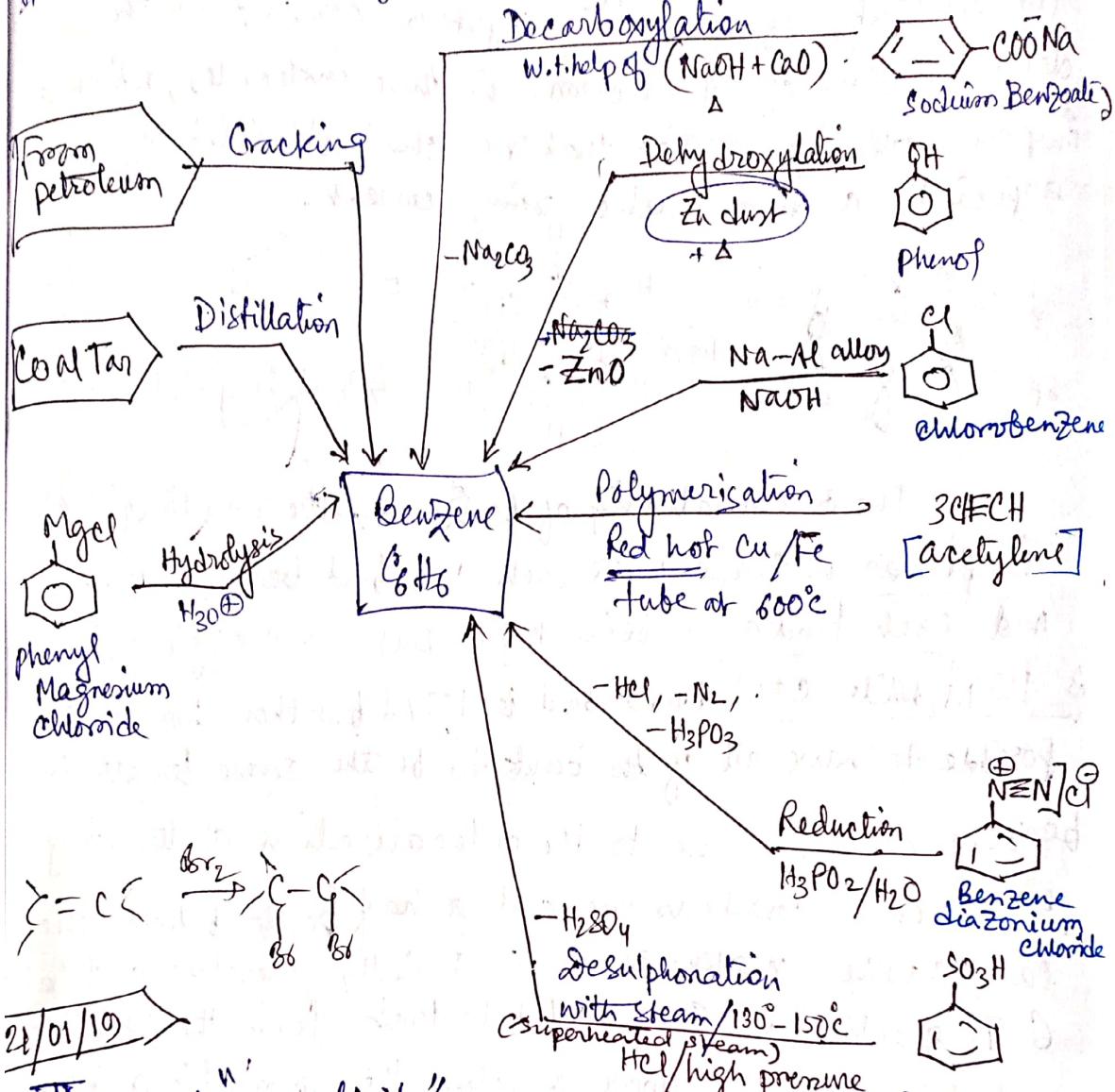
- $5\pi e^\ominus$

- doesn't contain $4\pi/4n+2\pi e^\ominus$

Benzene

Method of Preparation

Can be prepared through the following methods :-



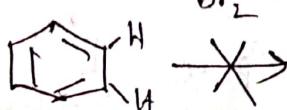
The word "aromaticity" has evolved

as understanding of the special properties

of benzene and other aromatic molecules has deepened.

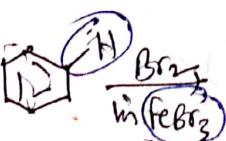
Originally aromaticity was associated with a specific chemical reactivity. The aromatic hydrocarbons undergo substitution rxns in preference to addition. Later the idea of special stability became more important.

Addition doesn't occur



Addition product would no longer contain a benzene ring.

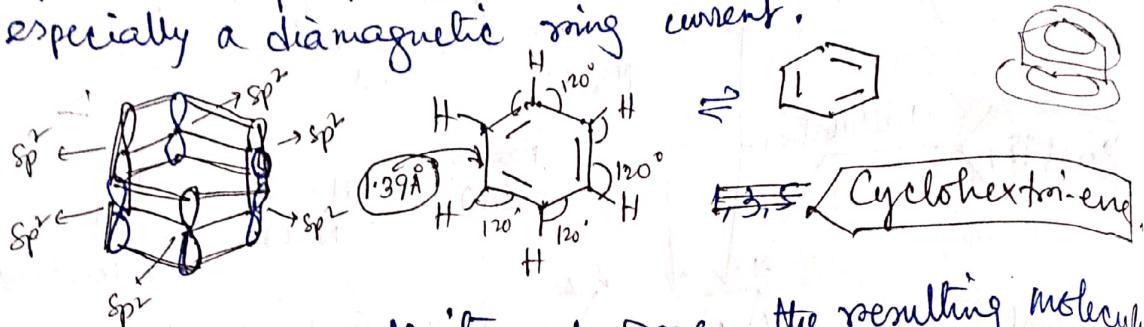
Substitution occurs



A substitution product still contains a benzene ring.

**Basic structure
of Benzene**

Aromaticity is now generally associated with the property of special ~~esp~~ stability of certain completely conjugated cyclic molecules. A major contribution, the stability of aromatic system comes from the delocalisation of π electrons in these molecules, which also imparts other properties that're characteristic of aromaticity, especially a diamagnetic ring current.



Due to aromaticity of benzene, the resulting molecule is planar in shape with each C-C bond being 1.39\AA in length and each bond angle being 120° . But C-C single bond length is 1.54\AA , while C=C double bond is 1.34\AA then how it's possible to have all of the bonds to be the same length in benzene ring? Due to the delocalisation of the ring makes each count as one and a half bonds between the carbons which makes sense. Finally there're a total of 6 π electrons in 6 p-orbitals that form the stabilising electron clouds above & below the aromatic ring.

Evidence of Aromaticity : Heats of Hydrogenation

If we compare cyclohexane, 1,3-cyclohexadiene, and benzene we would expect that their heats of hydrogenation will ↑ since the number of double bonds increases ~~rapidly~~ respectively.

		ΔH° observed in kJ/mol°	ΔH° predicted in (kJ/mol°)
(1)	Cyclohexane $\xrightarrow[\text{Pd-C}]{\text{H}_2}$ Cyclohexane	-120	-
(2)	1,3 Cyclohexadiene $\xrightarrow[\text{Pd-C}]{\text{H}_2}$ Cyclohexane	-232	$2 \times (-120) = -240$ (Small difference)
(3)	Benzene $\xrightarrow[\text{Pd-C}]{\text{H}_2}$ Cyclohexane	-208	$3 \times (-120) = -360$ Large difference

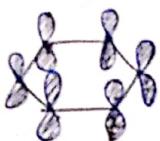
The low heat of hydrogenation of benzene rings means that benzene is especially stable even more so than the conjugated compounds. This unusual stability is characteristic of aromatic compounds.

The Criteria for Aromaticity — Hückel's Rule

Where $n = 0, 1, 2, 3, \dots$ any $\frac{(n+2)\pi}{2}$ electron

A molecule must be — cyclic, planar, completely conjugated and contain a particular number of π electrons.

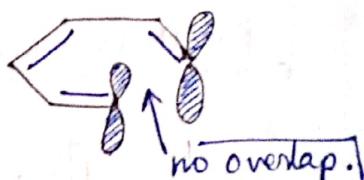
Cyclic Compound



Benzene

Every p-orbital overlaps with 2 neighbouring p-orbitals

Acyclic Compound



1,3,5-hexatriene

There can be no overlap between the p-orbitals on the 2 terminal C atoms

aromatic

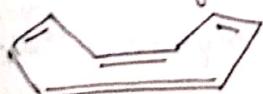
$$(n+2)\pi$$

$$n = \frac{6}{2}$$

Example 1



CycloOctatetraene



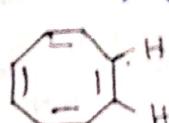
Tub shaped

A molecule must be planar

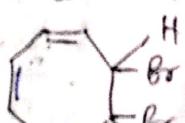
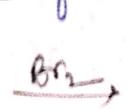
(1) All adjacent p-orbitals must be aligned so that the πe^- density can be delocalised

(2) Cyclooctatetraene resembles benzene ring in that it is a cyclic molecule with alternating double bonds. but Cyclooctatetraene is tub shaped, not planar, so overlapping between adjacent π bonds is impossible.

Since Cyclooctatetraene isn't aromatic so it can undergo addition rens like those of other alkenes.



CycloOctatetraene



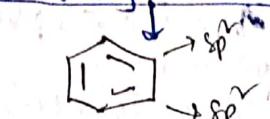
addition product

more stable than isolated double bonds

more stable than isolated double bonds

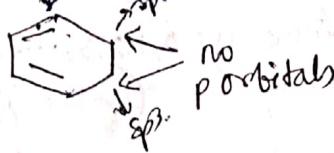
(B) A molecule must be completely Conjugated

A completely conjugated ring



a 'p' orbital on every c (aromatic)

These rings aren't completely conjugated

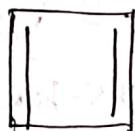


1,3-Cyclohexadiene
(not aromatic)



1,3,5-Cycloheptatriene
(not aromatic)

(C) A molecule must satisfy Hückel's rule & contain a particular number of π electrons



Cyclobutadiene

a planar, cyclic, completely conjugated molecule that's not aromatic

- It turns out that in addition to being cyclic, planar, and completely conjugated, a molecule that's not aromatic

compound needs a particular no. of π electrons to be aromatic.

Erich Hückel first recognised in 1931 that the following criterion, expressed in two parts and now known as Hückel's rule, had to be satisfied as well:

Cyclic, planar, and completely conjugated compounds that contain $4n\pi$ electrons are especially unstable, and are said to be antiaromatic.

Thus compounds that contain 2, 6, 10, 14, 18 and so forth π -electrons are aromatic, as shown in Table.

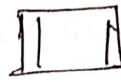
The no. of π -electrons that satisfy Hückel's Rule

n	$4n+2$
0	2
1	6
2	10
3	14
4 etc.	18

- Benzene is aromatic and especially stable because it contains 6π electrons. Cyclobutadiene is antiaromatic and especially unstable because it contains 4π electrons.

Benzene
An aromatic compound

Cyclobutadiene
An antiaromatic compd



$$4n+2 = 4(1) + 2 \\ = 6\pi \text{ electrons}$$

$$4n = 4(1) = 4\pi \\ \text{electrons}$$

Aromatic

Antiaromatic

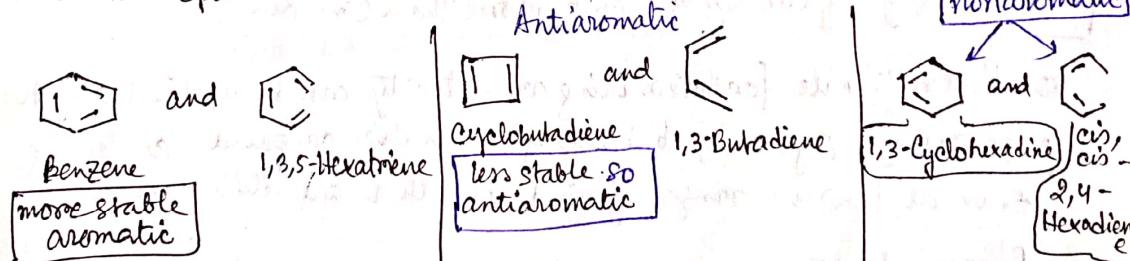
9/2/19

Considering aromaticity, all compounds can be classified in one of three ways :-

- (i) **Aromatic** : A cyclic, planar, completely conjugated compound with $(4n+2)\pi$ electrons.
- (ii) **Antiaromatic** : A cyclic, planar, completely conjugated compound with $4n\pi$ electrons.

- (iii) **Nonaromatic** : A compound that lacks one (or more) of the four requirements to be aromatic or antiaromatic.

Note : too, the relationship between each compound type and a similar open-chained molecule having the same number of π -electron

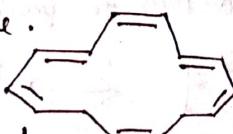


Aromaticity of Compounds with a Single Ring

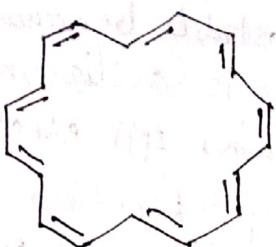
- Benzene is the most common aromatic compound having a single ring. Completely conjugated rings larger than benzene are also aromatic if they are planar & have $(4n+2)\pi$ electrons
- Hydrocarbons containing a single ring with alternating double and single bonds are called Annulenes.
- To name an annulene, indicate the number of atoms in the ring in brackets and add the word annulene. Thus benzene is [6]-annulene.

$$4n+2 = 4(3)+2 \\ = 14\pi \text{ electrons}$$

aromatic [14] annulenes



cyclic, planar.



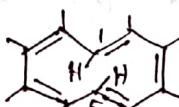
[18]-annulene $\pi_{\text{eff}} = 4(4) + 2 = 18\pi$

Electrons aromatic Cyclic and planar.

- [10]-Annulene that has only cis double bonds can't have the planar conformation because of angle strain.
- [10]-Annulene that has 2-trans double bonds adopt a planar conformation either, because two H-atoms interfere with each other.
- [10]-Annulene fits Hückel's rule, but it's not planar.

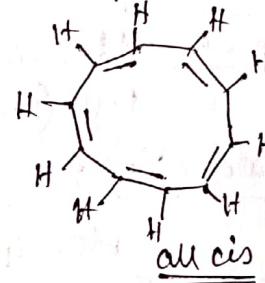


[10]-annulene
10 π electrons not
aromatic



1,5-trans

[10]-annulenes



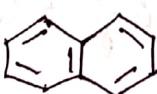
Unstable Planar configurations

transannular crowding in trans-isomer
angle strain (240° total) in cis-isomer.

Aromaticity of Compounds with More than One Ring

- Hückel's rule for determining aromaticity can be applied only to monocyclic systems, but many aromatic compounds containing several benzene rings joined together are also known.

For example -



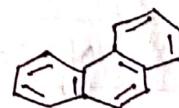
Naphthalene

10 π electrons



Anthracene

14 π electrons



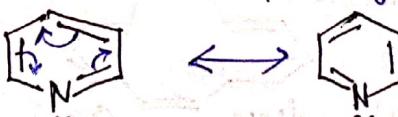
phenanthrene

14 π electrons

Aromaticity of Heterocyclic Compounds

- Heterocycles containing oxygen, nitrogen or sulphur atoms that also have at least one lone pair of electrons can also be aromatic.
- With heteroatoms, we must always determine whether the lone pair is localised on the heteroatom or part of the delocalised π system.

- Pyridine



Two resonating structures
for pyridine π electrons

Pyridine is cyclic, planar & completely conjugated & satisfy $(4n+2)\pi$ i.e. 6π electrons, so it an aromatic compound. The nitrogen atom of pyridine also has a nonbonded electron pair i.e. lonepair which is localised on the N atom so it's not a part of the delocalised π -electron system of the aromatic ring.

• Pyrrole

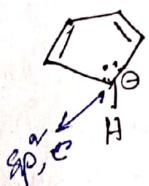


It is a five membered ring with 2 π bonds and one nitrogen atom with one lone pair of electrons.

Pyrrole is cyclic and planar with a total of 4π electrons from 2 π bonds.

Aromaticity of charged Aromatic Compounds

The cyclopentadienyl Anion



cyclic and planar anion with 2 double bonds & a non-bonded electron pair. In this way it resembles Pyrrole.

By Hückel's rule having 6π electrons (2 π bonds contribute $4e^-$'s + the lone pair contributes two) confers aromaticity.

Aromaticity of Cyclopentadienyl anion, Cyclopentadienyl Cation, Cyclopentadienyl radical :-



Cyclopentadienyl anion

- 6π electrons
- contains $(4n+2)\pi$ electrons



Cyclopentadienyl cation

- 4π electrons
- contains $4n\pi$ electrons



Cyclopentadienyl radical

- 5π electrons
- does not contain either $4n$ or $(4n+2)\pi$ electrons

Tropylium cation

It is a planar carbocation charge contained in a carbocation is

the +ve charged hybridised C



with 3 double bonds and a +ve 7 membered ring. This

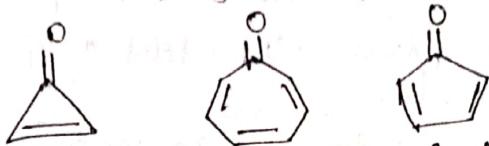
completely conjugated, because

carbon is sp^2 hybridised and has a vacant p-orbital that overlaps with the 6 p-orbitals from the carbons of the three double bonds.

It is aromatic because it is cyclic, planar, completely conjugated & has 6π electrons delocalised over the 7 atoms of the ring.

Aromaticity of Cyclic Ketones We know that the double bond in carbonyl ($C=O$) group is polarised to give partial +ve (or δ^+) charge on the carbon & the partial negative (-ve or δ^-) charge on the oxygen atom. So cyclopropanone and cyclohepta trienone are considered to be aromatic as it obeys $(4n+2)\pi$ rule.

But the same reason makes cyclopentadienone to be antiaromatic & it is unstable, rapidly undergoes a Diels-Alder dimerisation.



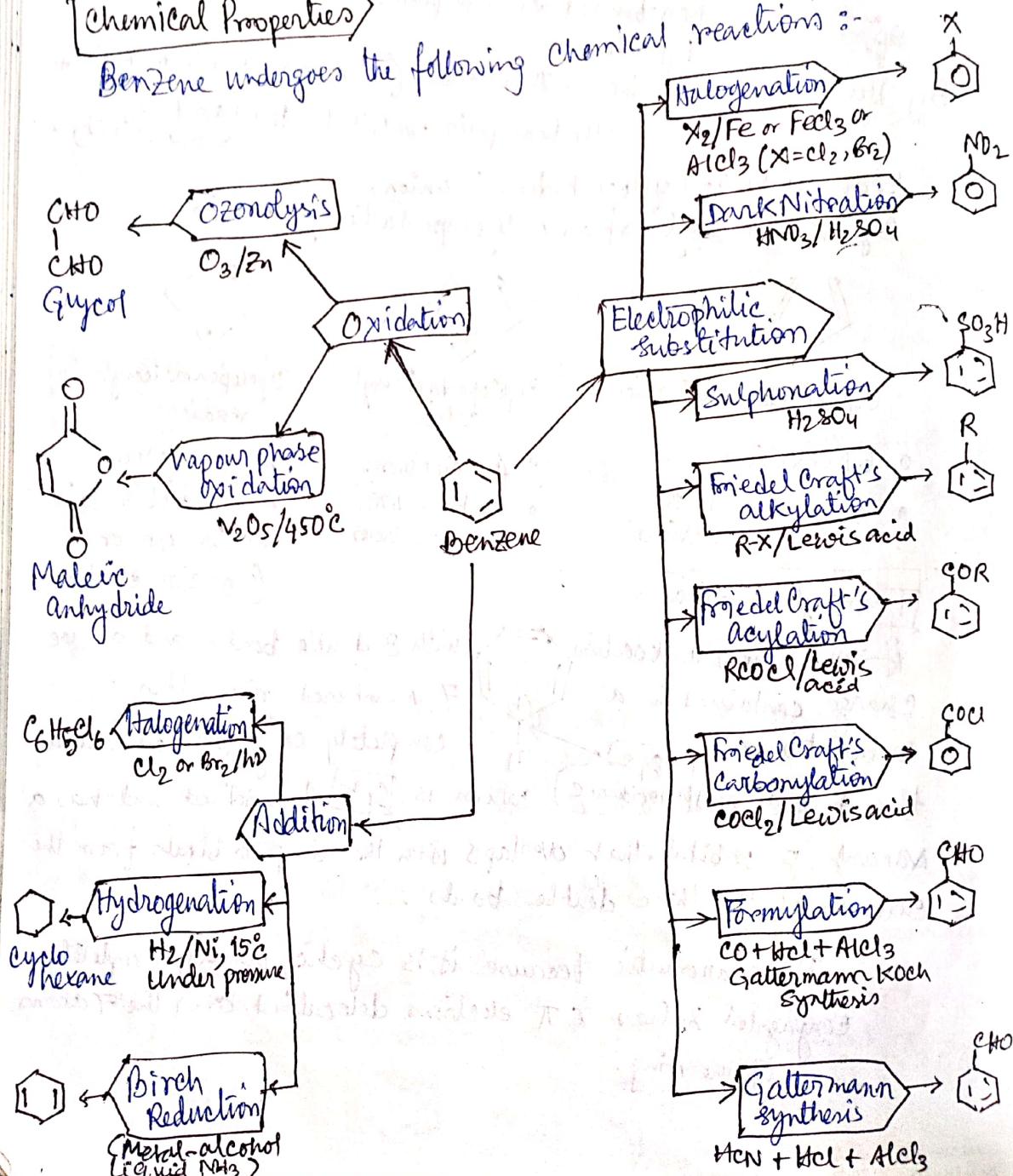
Cyclopropanone
(aromatic)

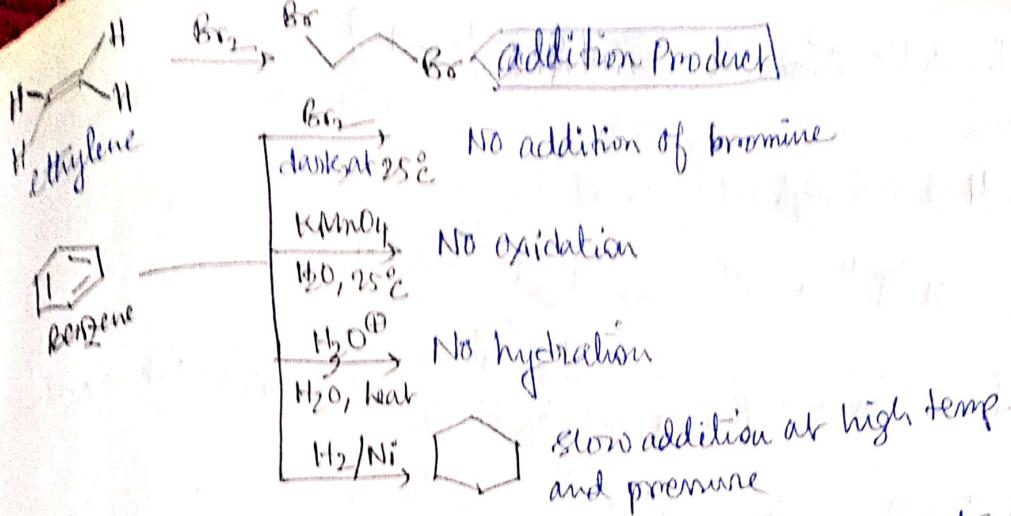
Cyclohepta-
-1,3-diene
(aromatic)

Cyclopentadienone
(Antiaromatic)

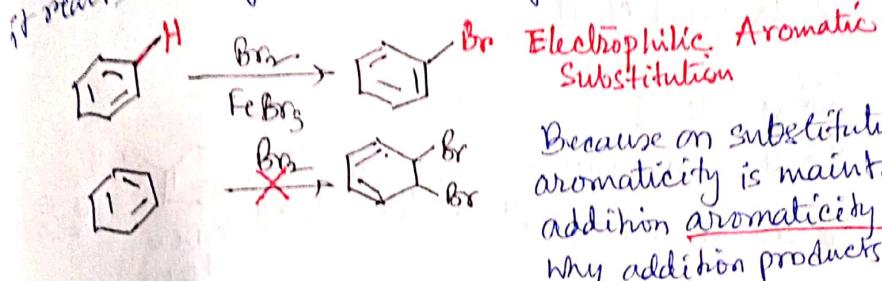
Chemical Properties

Benzene undergoes the following chemical reactions :-



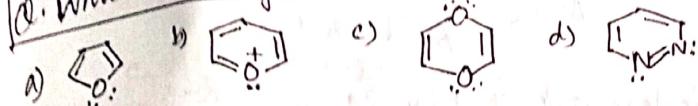


Benzene doesn't react with bromine but only in the presence of a Lewis acid catalyst such as - Ferva bromide. Most surprisingly, however it reacts not by addition but by substitution - benzene substitution



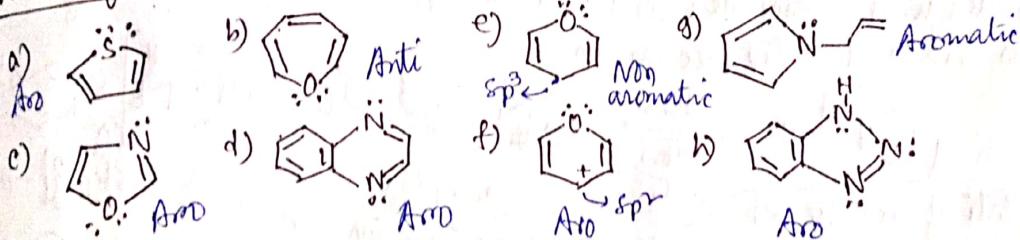
Because in substitution rxn of C_6H_6 aromaticity is maintained but on addition aromaticity is lost that's why addition products are unstable.

Q. Which heterocycles are aromatic?



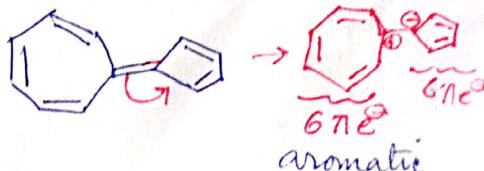
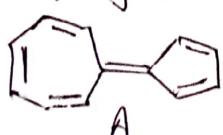
- a) $6\pi\text{e}^\ominus$ (Aromatic)
 b) aromatic due to δTe
 c) $8\pi\text{e}^\ominus$ (Anti-aromatic)
 d) $8\pi\text{e}^\ominus$ (Aromatic)

Q. Which of the following heterocycles are aromatic?



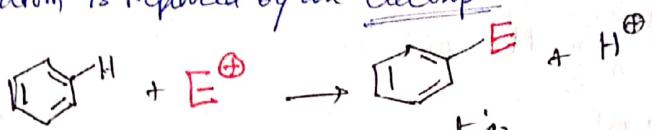
- Ans: (a) aromatic (b) $8\pi\text{e}^\ominus$, Antiaromatic (c) NO continuous conjugation present here since it's Nonaromatic
 (d) aromatic ($6\pi\text{e}^\ominus$) (e) $6\pi\text{e}^\ominus$ (aromatic) (f) aromatic
 (g) aromatic h) Aromatic

Q. Hydrocarbon A possesses a significant dipole, even though it is composed of only C-C and C-H bonds. Explain why the dipole arises and which ring is more electron rich?

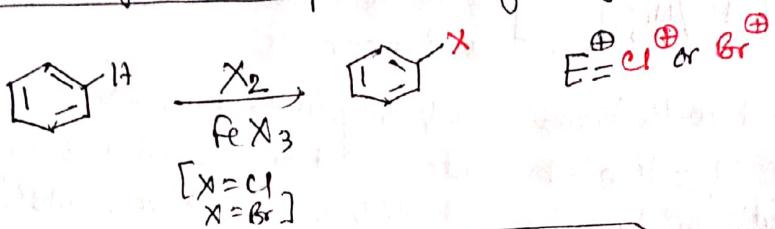


Electrophilic Aromatic Substitution $S_E A r$

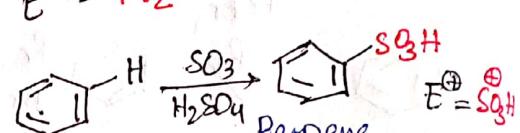
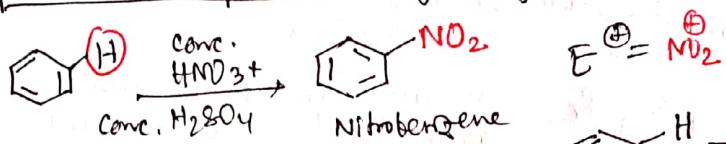
The characteristic rxn of benzene is electrophilic aromatic substitution
— an H-atom is replaced by an electrophile.



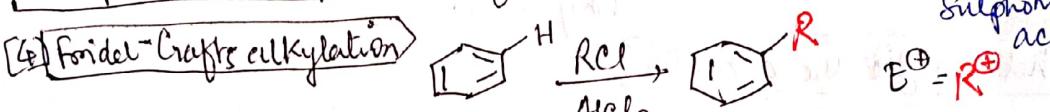
[1] Halogenation - Replacement of H by X (Cl or Br) \rightarrow In halogenation



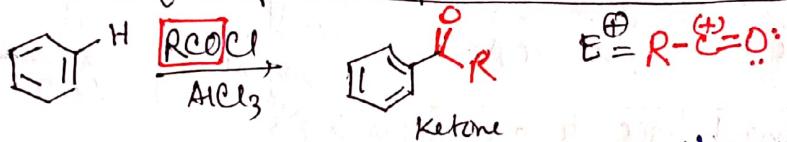
[2] Nitration - Replacement of H by NO_2



[3] Sulphonation - Replacement of H by SO_3^\oplus

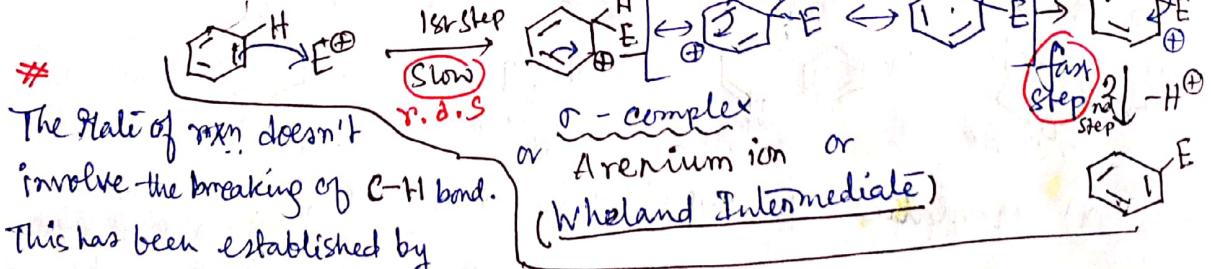


[4] Friedel-Crafts alkylation - Replacement of H by RCO



$\text{R}-\text{C}\ddot{\text{O}}$
acyl group.

No matter what electrophile is used / all electrophilic aromatic substitution rxns occur via a two step mechanism



EXERCISES

SECTION A: TOPICWISE QUESTIONS

Physical Properties of Alkanes and Method of Preparation

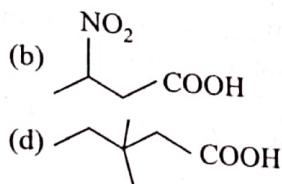
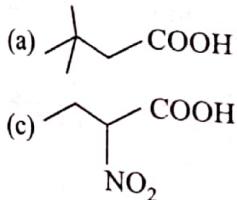
1. The number of isomeric sodium salt that will be required to obtain neopentane is

- (a) 3
- (b) 1
- (c) 4
- (d) 6

2. Which of the following compounds will form a hydrocarbon on reaction with a Grignard reagent?

- (a) $\text{CH}_3\text{CH}_2\text{OH}$
- (b) CH_3CHO
- (c) CH_3COCH_3
- (d) $\text{CH}_3\text{CO}_2\text{CH}_3$

3. Which of the following carboxylic acid can undergo decarboxylation on simple heating even in the absence of soda lime?



- (c)
- (d)

4. The reagent used for catalytic hydrogenation of an alkene as well as bring about homogeneous catalysis is

- (a) Raney nickel
- (b) $(\text{Ph}_3\text{P})_3\text{RhCl}$ "Wilkinson's reagent"
- (c) Pd/C
- (d) PtO_2

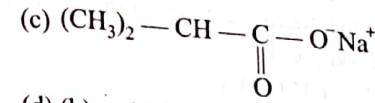
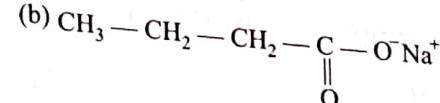
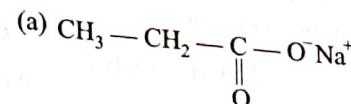
5. Successive alkanes differ by

- (a) CH_2
- (b) CH
- (c) CH_3
- (d) C_2H_4

6. Methane is formed when

- (a) Sodium acetate is heated with soda-lime
- (b) Iodomethane is reduced
- (c) Aluminium carbide reacts with water
- (d) All of these

7. Which sodium salt will be heated with sodalime to obtain propane?



- (d) (b) and (c) both

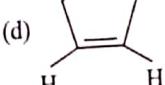
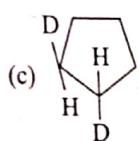
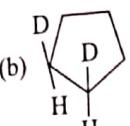
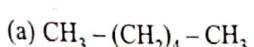
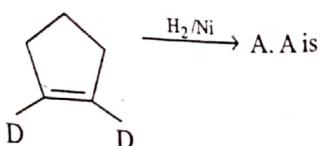
8. Sodium propionate on decarboxylation with sodalime gives

- (a) Propane
- (b) Ethane
- (c) Butane
- (d) Pentane

9. An optically active hydrocarbon X has molecular formula C_6H_{12} . X on catalytic hydrogenation gives optically inactive C_6H_{14} . X could be

- (a) 3-methyl-1-pentene
- (b) 3-methyl-2-pentene
- (c) 4-methyl-2-pentene
- (d) 2-ethyl-1-butene

10.



11. Which of the following reactions can be used to prepare an alkane from an alkyl halide?

- (a) Wurtz reaction (b) Kolbe electrolysis
 (c) Hoffmann reaction (d) Fittig reaction

12. Which of the following gives CH_4 when treated with water?

- (a) Aluminium carbide (b) Calcium carbide
 (c) Silicon carbide (d) Iron carbide

13. A reaction between methyl magnesium bromide and ethyl alcohol gives

- (a) Butane (b) Ethane
 (c) Propane (d) Methane

14. Which one of the following cannot be prepared by Wurtz reaction?

- (a) CH_4 (b) C_2H_6
 (c) C_3H_8 (d) C_4H_{10}

15. During electrolysis which anion migrates towards anode so as to produce 2,3-dimethyl butane

- (a) $\text{CH}_3 - \text{CH}_2 - \text{COO}^-$ (b) $\text{CH}_3 - \text{CH} \begin{cases} \text{COO}^- \\ \text{COO}^- \end{cases}$
 (c) $\text{CH}_3 - \text{CH} \begin{cases} \text{COO}^- \\ | \\ \text{CH}_3 \end{cases}$ (d) CH_3COO^-

16. Which of the following alkanes can be synthesized by the Wurtz reaction in good yield?

- (a) $(\text{CH}_3)_2\text{CH} - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$
 (b) $(\text{CH}_3)_2\text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$
 (c) $\text{CH}_3 - \text{CH}_2 - \text{C}(\text{CH}_3)_2\text{CH}_2 - \text{CH}_3$
 (d) $(\text{CH}_3)_3\text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$

17. $(\text{CH}_3)_3\text{CMgCl}$ on reaction with D_2O produces

- (a) $(\text{CH}_3)_3\text{CD}$ (b) $(\text{CH}_3)_3\text{COD}$
 (c) $(\text{CD}_3)_3\text{CD}$ (d) $(\text{CD}_3)_3\text{COD}$

18. Which of the following alkanes cannot be produced by Kolbe's electrolysis of sodium or potassium salts of carboxylic acids?

- (a) Methane (b) Ethane
 (c) Butane (d) Hexane

19. During the preparation of ethane by Kolbe's electrolytic method using inert electrode the pH of the electrolyte

- (a) Increases progressively as the reaction proceeds
 (b) Decreases progressively as the reaction proceeds
 (c) Remains constant throughout the reaction
 (d) May decrease as the concentration of the electrolyte is not very high

20. Which of the following reaction can be employed for getting unsymmetrical alkanes in good yield?

- (a) Wurtz reaction (b) Corey-House reaction
 (c) Both (d) None

21. $(\text{CH}_3)_3\text{COH} + \text{CH}_3\text{MgBr} \rightarrow \text{Hydrocarbon (A)}$; (A) is

- (a) $(\text{CH}_3)_3\text{CCH}_3$ (b) $(\text{CH}_3)_3\text{CH}$
 (c) CH_4 (d) none of these

22. When water vapours are passed over aluminium carbide, we get:

- (a) acetaldehyde (b) ethylene
 (c) methane (d) methyl alcohol

23. In catalytic reduction of hydrocarbons which catalyst is mostly used

- (a) Pd (b) Pt / Ni
 (c) SiO_2 (d) Misch Metal

24. Which among the following reagents convert alkyl halide into alkane?

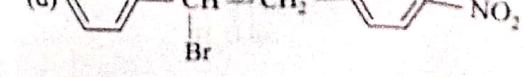
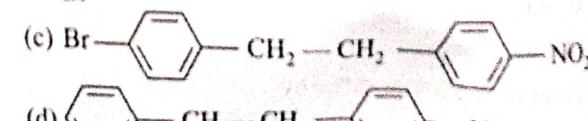
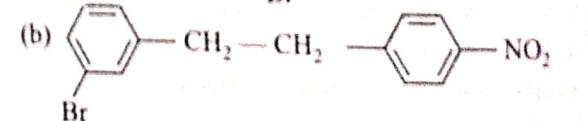
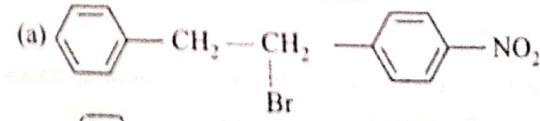
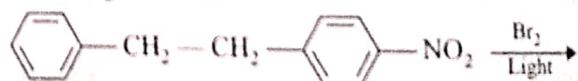
- (a) Bu_3SnH (b) Na/dry ether
 (c) R_2CuLi (d) All of these

25. C_6H_{12} (P) has only two types of alkenes that can be reduced to only one type of alkane C_6H_{14} (Q). Q is:

- (a) (b)
 (c) (d)

Chemical Properties of Alkanes

26. What is the major monobromination product in the following reaction?

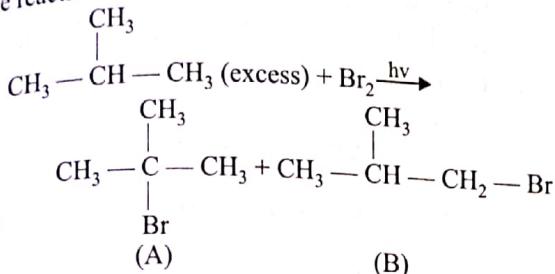


27. The homolytic fission of hydrocarbon results in the formation of

- (a) Free radicals (b) Carbocations
- (c) Carbanions (d) Carbenes

28. The relative reactivity of 1°H , 2°H and 3°H in bromination reaction has been found to be 1 : 82 : 1600 respectively.

In the reaction



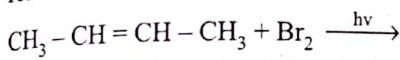
The percentage yields of the products (A) and (B) respectively are expected to be

- (a) 99.4 %, 0.6 % (b) 50 %, 50 %
- (c) 0.6 %, 99.4 % (d) 80 %, 20 %

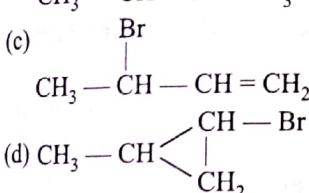
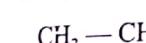
29. Halogenation of alkanes is an example of

- (a) Free radical addition reaction
- (b) Free radical substitution reaction
- (c) Nucleophilic substitution reaction
- (d) Nucleophilic addition reaction

30. What is the major bromination product in the following reaction?



- (a) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 + \text{Br}$



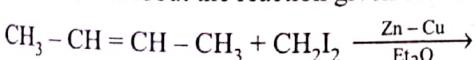
31. Chlorination of an alkane involves the attack of

- (a) An electrophile (b) A nucleophile
- (c) A base (d) A free radical

32. When n-butane is heated in the presence of AlCl_3/HCl it will be converted into

- (a) Ethane (b) Propane
- (c) Butene (d) Isobutane

33. What is true about the reaction given below?



- (a) Reaction involves a carbocation intermediate
- (b) Reaction involves a carbanion intermediate
- (c) Meso or racemic products are formed depending on configuration at double bond
- (d) Product is an acyclic alkane

34. The reactivity of hydrogen atoms attached to carbon atom in the halogenation of an alkane has the order:

- (a) tertiary > primary > secondary
- (b) secondary > primary > tertiary
- (c) tertiary > secondary > primary
- (d) primary > secondary > tertiary

35. Which of the following is oxidised by KMnO_4 ?

- (a) Methane (b) Isobutane
- (c) Pentane (d) Neopentane

36. In which of the following pairs, the bromination of first member is easier than the second member?

- (a) Isobutane, n-butane (b) n-Butane, isobutane
- (c) Methane, ethane (d) None of these

37. The addition of tetraethyl lead to petrol

- (a) Lowers its octane number
- (b) Has no effect on octane number
- (c) May raise or lower the octane number
- (d) Raises its octane number

38. Which of the following cannot be considered as a step of mechanism in chain reaction of methane with Cl_2 ?

- (a) $\text{Cl}_2 \longrightarrow \text{Cl}^\bullet$
- (b) $\text{CH}_4 + \text{Cl}^\bullet \longrightarrow \text{CH}_3\text{Cl} + \text{H}^\bullet$
- (c) $\text{Cl}^\bullet + \text{CH}_4 \longrightarrow \text{CH}_3^\bullet + \text{HCl}$
- (d) $\text{Cl}^\bullet + \text{CH}_3^\bullet \longrightarrow \text{CH}_3\text{Cl}$

39. Which of the following has maximum boiling point?

- (a) n-octane
- (b) iso-octane
- (c) 2, 2, 3, 3-tetramethyl butane
- (d) n-butane

40. During chlorination of methane to methyl chloride, the propagation step is represented by

- (a) $\text{Cl} - \text{Cl} \xrightarrow{h\nu} \cdot \text{Cl} + \cdot \text{Cl}$
- (b) $\cdot \text{CH}_3 + \cdot \text{Cl} \longrightarrow \text{CH}_3\text{Cl}$
- (c) $\text{CH}_4 + \cdot \text{Cl} \longrightarrow \cdot \text{CH}_3 + \text{HCl}$
- (d) $\cdot \text{Cl} + \cdot \text{Cl} \longrightarrow \text{Cl} - \text{Cl}$

41. $\text{BrCH}_2 - \text{CH}_2 - \text{CH}_2\text{Br}$ reacts with Na in the presence of ether at 100°C to produce

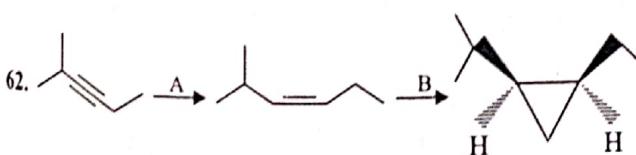
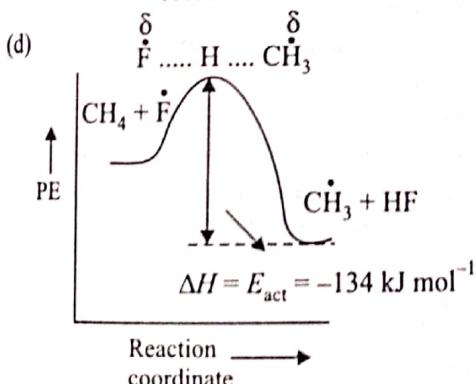
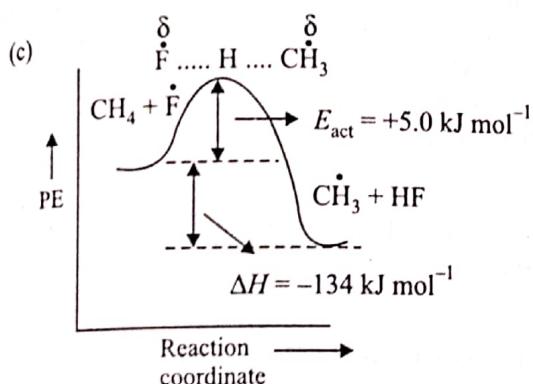
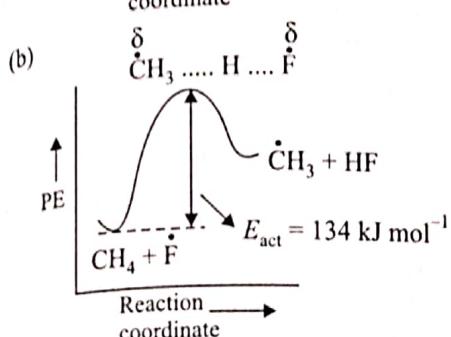
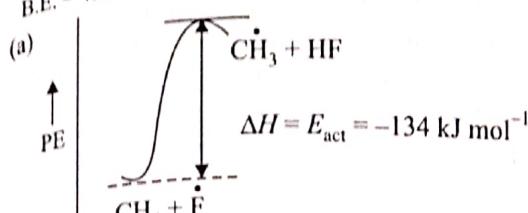
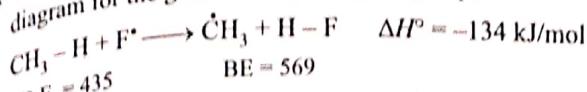
- (a) $\text{BrCH}_2 - \text{CH} = \text{CH}_2$ (b) $\text{CH}_2 = \text{C} = \text{CH}_2$
- (c) $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$ (d) All of these

42. Which of the following is not an endothermic reaction?

- (a) Combustion of propane
- (b) Ethane to ethene
- (c) Dehydrogenation
- (d) Change of chlorine molecule into chlorine atoms.

43. Methane reacts with excess of chlorine in diffused sunlight to give the final product as
 (a) Chloroform (b) Carbon tetrachloride
 (c) Methylene chloride (d) Methyl chloride
44. A mixture of propene and methane is obtained by the cracking of
 (a) 1-butene (b) n-butane
 (c) 2-butene (d) Isobutane
45. A gaseous hydrocarbon 'X' on reaction with bromine in light forms a mixture of two monobromo alkanes and HBr. The hydrocarbon 'X' is:
 (a) $\text{CH}_3\text{-CH}_3$ (b)
 (c)
 (d)
46. The final product of complete oxidation of hydrocarbons is
 (a) $\text{H}_2\text{O} + \text{CO}_2$ (b) Aldehyde
 (c) Acid (d) Dihydric alcohol
47. The appropriate reagent for the transformation
 is
 (a) $\text{Zn}(\text{Hg})/\text{conc. HCl}$ (b) $\text{NH}_2\text{NH}_2, \text{OH}^-$
 (c) H_2/Ni (d) NaBH_4
48. The number of monochloro derivatives of isohexane is
 (Only structural isomers)
 (a) 3 (b) 4
 (c) 5 (d) 6
49. Which of the following represents the most oxidized form of hydrocarbon?
 (a) RCHO (b) CO_2
 (c) RCOOH (d) RCOOOH
50. Iodination of an alkane is carried out in presence of
 (a) Alcohol (b) $\text{P} + \text{I}_2$
 (c) HNO_3 or HIO_3 (d) A reducing agent
51. What is the chief product obtained when n-butane is treated with Br_2 in the presence of light at 130°C ?
 (a) $\text{CH}_3 - \text{CH}_2 - \text{CHBr} - \text{CH}_3$
 (b) $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$
 (c) $(\text{CH}_3)_3\text{CBr}$
 (d) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Br}$
52. A sample of petrol is a mixture of 30% n-heptane and 70% iso-octane. The sample has octane number
 (a) 70 (b) 30
 (c) 15 (d) 35
53. The maximum ease of abstraction of a hydrogen atom by a chlorine atom is shown by
 (a) $(\text{CH}_3)_3\text{C} - \text{CH}_3$ (b) $(\text{CH}_3)_2\text{CH}_2$
 (c) $\text{C}_6\text{H}_5\text{CH}_3$ (d) $\text{CH}_2 = \text{CHCH}_3$
54. Propene on reaction with methylene iodide in presence of Zn-Cu couple gives:
 (a) Cyclopropane (b) Cyclopentene
 (c) Methyl cyclopropane (d) Cyclobutene
55. For the given reaction how many products are optically active (all isomers):
 (b) 2
 (c) 3 (d) 4
56. Gasoline has composition
 (a) $\text{C}_8 - \text{C}_{12}$ (b) $\text{C}_6 - \text{C}_{11}$
 (c) $\text{C}_2 - \text{C}_5$ (d) None of these
57. Which of the following statement is correct in relation to the halogenation of alkane?
 (a) The reactivity of chlorine is less than bromine towards alkanes.
 (b) Photochemical chlorination of methane is formed in slowest step.
 (c) Free radicals are pyramidal intermediate, stabilised by hyperconjugation and resonance.
 (d) Bromine has much higher regioselectivity than chlorine in abstracting 3° hydrogen.
58. Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is
 (a) n-hexane (b) 2, 2-dimethylbutane
 (c) 2, 3-dimethylbutane (d) 2-methylpentane
59. The number of possible enantiomer pairs that can be produced during monochlorination of 2-methylbutane is:
 (a) 2 (b) 3
 (c) 4 (d) 1
60. Which statement is incorrect about free radical halogenation of alkanes?
 (a) The number of product molecules formed by one photon is very high.
 (b) If O_2 is added, initially the rate of reaction decreases, then increases.
 (c) Inhibitors combine with free radical and terminate the chain reaction.
 (d) presence of $\text{C}_6\text{H}_5 - \text{CO} - \text{OC} - \text{C}_6\text{H}_5$ inhibits the free radical reaction.

61. Which of the following is correct potential energy diagram for the given chain propagating step?



A and B are

- (a) A - Na/Liq. NH₃, B - CH₂N₂, hν
- (b) A - Ni/H₂, B - CH₂ = C = O, hν

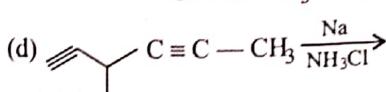
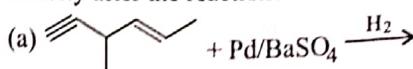
- (c) A - Lindlar's catalyst, B - CH₂I₂/Zn
- (d) All of the above

63. Number of isomers which can be theoretically obtained on monochlorination of 2-methylbutane is:

- (a) 1
- (b) 2
- (c) 3
- (d) 4

Methods of Preparation of Alkenes

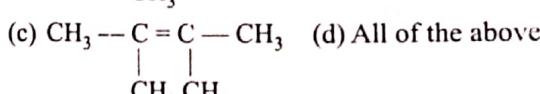
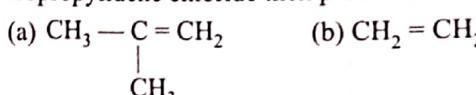
64. Which of the following compounds will lose optical activity after the reaction?



65. sec-Butyl chloride on boiling with alc. KOH givesas the main product.

- (a) 1-Butene
- (b) 2-Butene
- (c) 1-Butanol
- (d) 2-Butanol

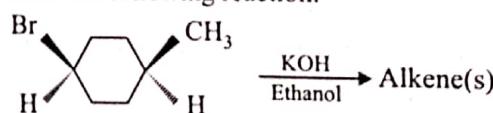
66. In the above reaction if we take methylene chloride and isopropylidene chloride then products are



67. An alkene is formed from a carbocation by

- (a) Elimination of a H⁺ ion
- (b) Elimination of H⁻ ion
- (c) Addition of a H⁺ ion
- (d) Addition of a H⁻ ion

68. Consider the following reaction.



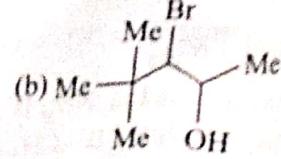
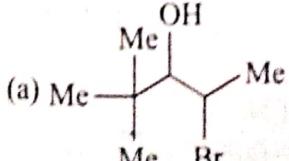
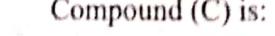
The correct statement concerning product of the above reaction is

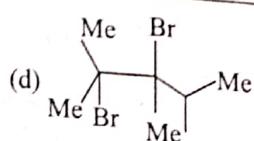
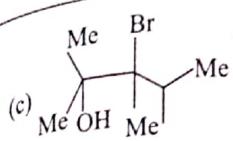
- (a) only a single alkene is formed
- (b) a pair of geometrical isomers are formed
- (c) a pair of enantiomers in equal amount is formed
- (d) a pair of diastereomers in equal amount is formed

69. Ethylene may be obtained by dehydration of which of the following with concentrated H₂SO₄ at 160–170°C

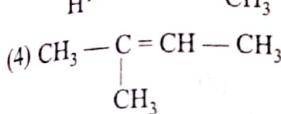
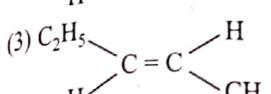
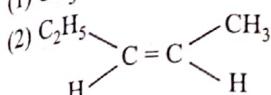
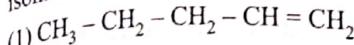
- (a) C₂H₅OH
- (b) CH₃OH
- (c) CH₃CH₂CH₂OH
- (d) (CH₃)₂CHCH₂OH

15.38 Chemistry





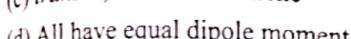
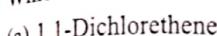
85. Which is the correct increasing order of the stability of isomers of pentene?



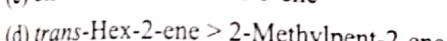
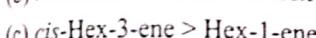
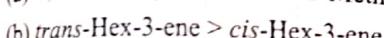
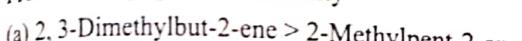
- (a) $1 < 2 < 3 < 4$ (b) $1 < 3 < 2 < 4$

- (c) $4 > 3 > 2 > 1$ (d) $4 < 2 < 3 < 1$

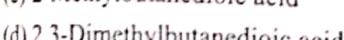
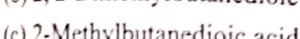
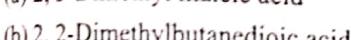
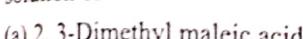
86. Which of the following will have zero dipole moment?



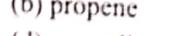
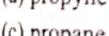
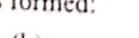
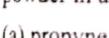
87. Predict wrong option for stability



88. But-2-ene can be obtained by electrolysis of an aqueous solution of

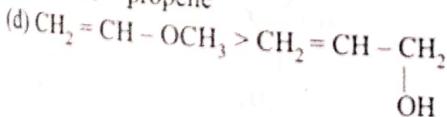
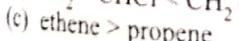
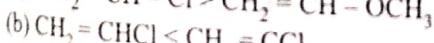
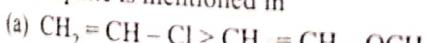


89. When 1,1,2,2-tetrabromopropane is heated with zinc powder in alcohol, which is formed:

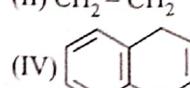
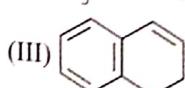
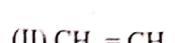
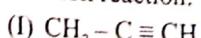


Chemical Properties of Alkenes

90. The correct order of alkene reactivity towards an electrophile is mentioned in



91. The correct order of reactivity towards electrophilic addition reaction:

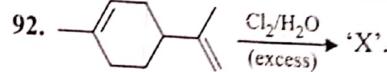


- (a) II > I > IV > III

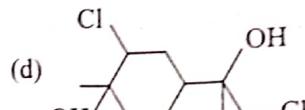
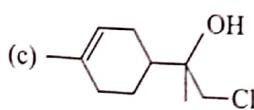
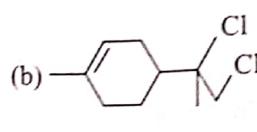
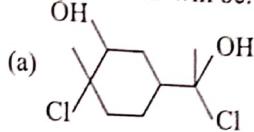
- (b) III > I > IV > II

- (c) I > III > IV > II

- (d) III > IV > II > I



Compound 'X' will be:



93. Which of the following statements is correct?

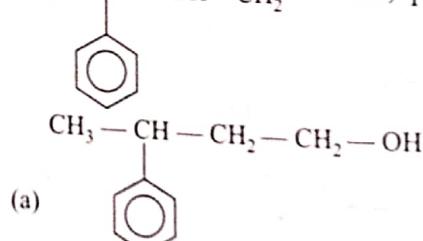
- (a) Alkynes are more reactive than alkenes towards halogen addition.

- (b) Alkenes are more reactive than alkynes towards halogen addition

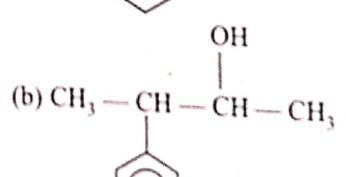
- (c) Both alkynes and alkenes are equally reactive towards halogen addition

- (d) Primary vinylic cation $\text{RCH} = \text{CH}_2^+$ is less reactive than secondary vinylic cation $\text{RC} = \text{CH}_2^+$

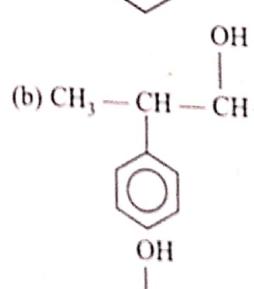
94. $\text{CH}_3 - \text{CH} - \text{CH} = \text{CH}_2 \xrightarrow{\text{H}_3\text{O}^+} \text{P} \text{ (major), P is:}$



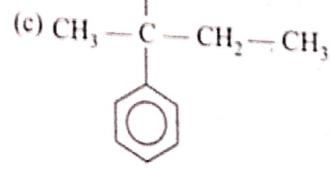
(a)



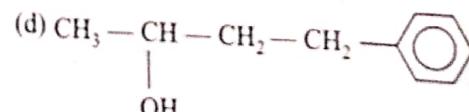
(b)



(c)



(d)

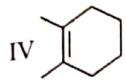
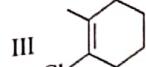
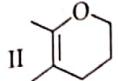
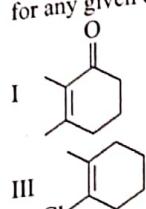


15.40 Chemistry

95. $\text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{CH}_3 \xrightarrow{\text{H}_2\text{O}/\text{H}^+}$ P (major), P is:

- (a)
- (b)
- (c)
- (d)

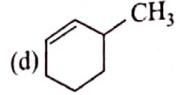
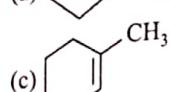
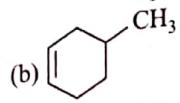
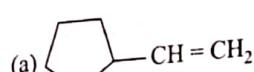
96. The correct relative rate of reaction of the given alkenes for any given electrophiles is



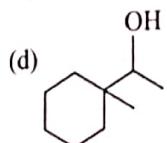
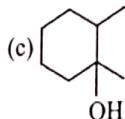
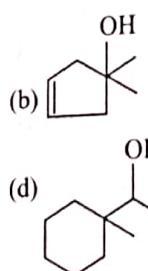
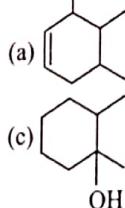
- (a) I > II > IV > III
(c) II > III > IV > I

- (b) II > IV > I > III
(d) IV > I > III > II

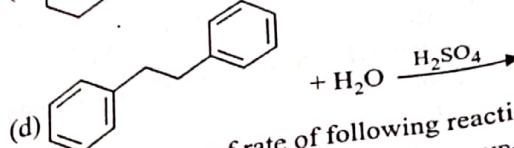
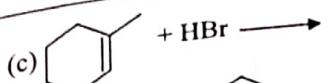
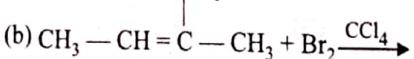
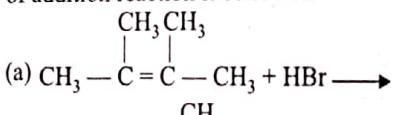
97. Which of the following alkene will give P on oxymercuration reduction reaction, $P = \text{C}_6\text{H}_{11}\text{OH}$



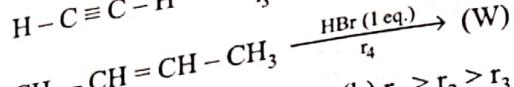
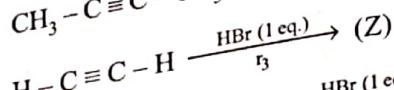
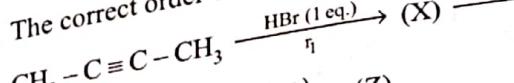
98. $\xrightarrow{\text{H}_3\text{O}^+}$ P. Identify major product 'P' is:



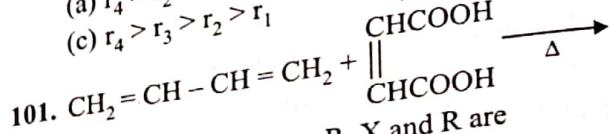
99. In which of the following reactions Markownikoff's rule of addition reaction is followed



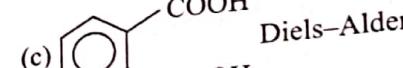
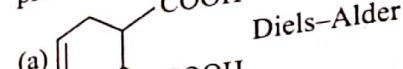
100. The correct order of rate of following reactions is



- (a) $r_4 > r_2 > r_1 > r_3$
(c) $r_4 > r_3 > r_2 > r_1$
- (b) $r_1 > r_2 > r_3 > r_4$
(d) $r_3 > r_4 > r_2 > r_1$

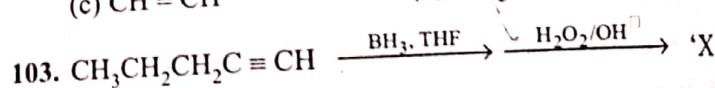


product X by reaction R. X and R are

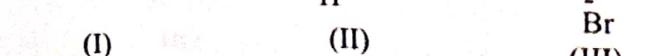
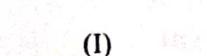
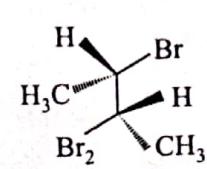
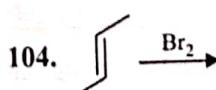
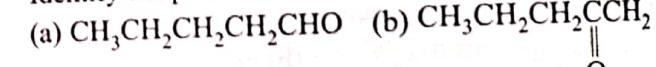


102. Which of the following shows least reactivity towards bromination?

- (a) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$ (b) $\text{CH}_2=\text{CH}_2$
(c) $\text{CH}\equiv\text{CH}$ (d) $\text{CH}_3-\text{CH}=\text{CH}_2$



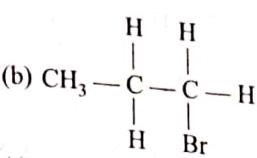
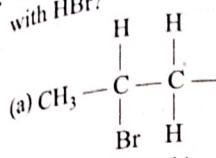
Identify the product 'X':



- (a) I and III
(c) I only

- (b) II and III
(d) II only

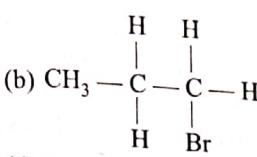
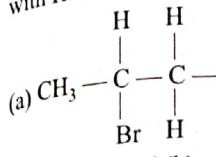
105. What would be the main product when propene reacts with HBr?



- (c) Both (a) and (b)

- (d) $\text{Br} - \text{CH}_2 - \text{CH} = \text{CH}_2$

106. What would be the main product when propene reacts with HBr in presence of benzoyl peroxide?



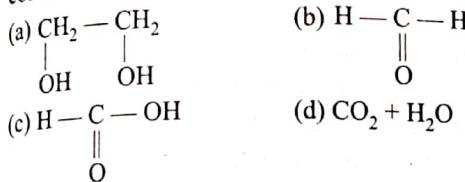
- (c) Both (a) and (b)

- (d) $\text{Br} - \text{CH}_2 - \text{CH} = \text{CH}_2$

107. Ethene reacts with HOCl to form

- (a) Hydroxyethene (b) Chloroethene
(c) Ethylene chlorohydrin (d) None of these

108. What would be the product when ethene is oxidised with cold dil. KMnO_4 solution?



109. Propene reacts with Cl_2 at 500°C the product is formed

- (a) 1-chloro propene-1 (b) 2-chloro propene-1
(c) 1,2-dichloro propane (d) 3-chloro propene-1

110. Anti-Markownikoff's addition of HBr is not observed in

- (a) Propene (b) But-2-ene
(c) Butene (d) Pent-2-ene

111. At low temperatures, the slow addition of molecular bromine to $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{C} \equiv \text{CH}$ gives

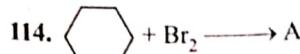
- (a) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CBr}_3$
(b) $\text{BrCH}_2 - \text{CHBr} - \text{CH}_2 - \text{C} \equiv \text{CH}$
(c) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CBr} = \text{CHBr}$
(d) $\text{CH}_3 - \text{CBr}_2 - \text{CH}_2 - \text{C} \equiv \text{CH}$

112. Reactivity of alkenes towards HX decreases in the order

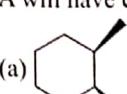
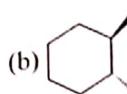
- (a) Butene > Propene > Ethene
(b) Butene > Ethene > Propene
(c) Ethene > Propene > Butene
(d) None of these

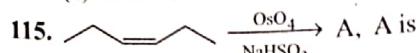
113. $\text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow[\text{H}_2\text{O}_2/\text{OH}^-]{\text{BD}_3}$ product X
X is

- (a) $\text{CH}_3 - \underset{\substack{| \\ \text{OH}}}{\text{CH}} - \text{CH}_2\text{D}$ (b) $\text{CH}_3 - \underset{\substack{| \\ \text{D}}}{\text{CH}} - \text{CH}_2\text{OH}$
(c) $\text{CH}_3 - \underset{\substack{| \\ \text{OD}}}{\text{CH}} - \text{CH}_3$ (d) None of these

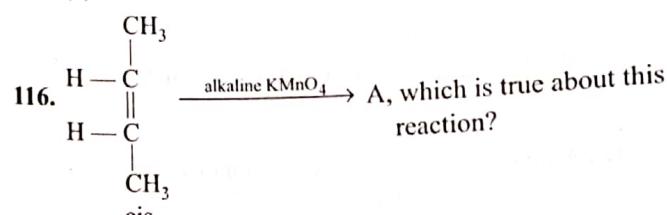


A will have configuration

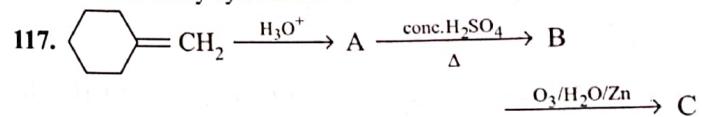
- (a)  (b) 
(c) both are true (d) None of these



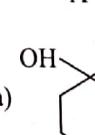
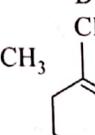
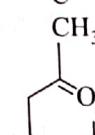
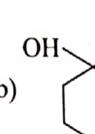
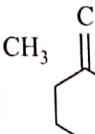
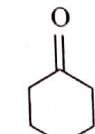
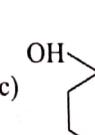
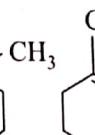
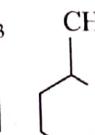
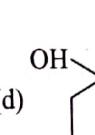
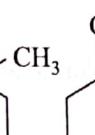
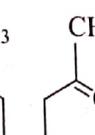
- (a) meso diol (b) racemic diol
(c) both are correct (d) none of these

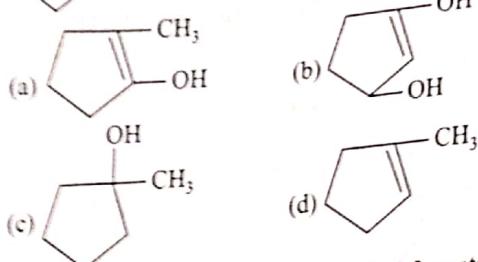
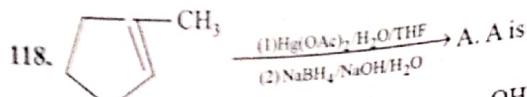


- (a) A is meso 2, 3-butan-di-ol formed by syn addition
(b) A is meso 2, 3-butan-di-ol formed by anti addition
(c) A is a racemic mixture of d and l, 2, 3-butan-di-ol formed by anti addition
(d) A is a racemic mixture of d and l, 2, 3-butan-di-ol formed by syn addition

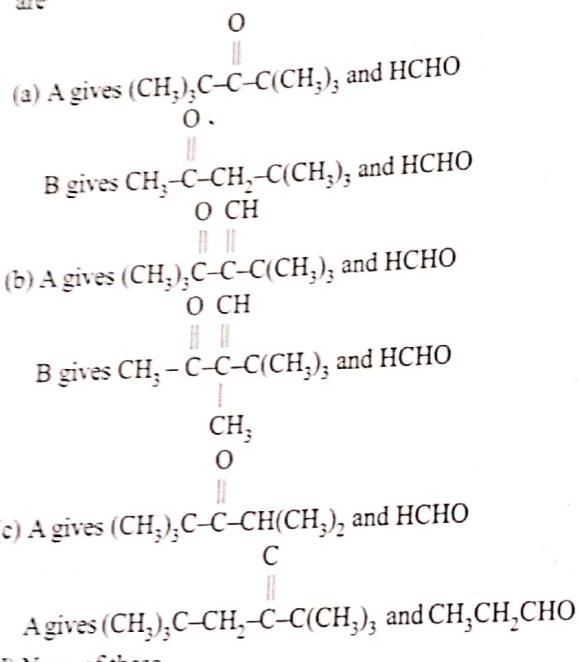


A, B and C are

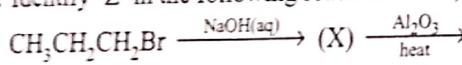
- | A | B | C |
|---|--|---|
|  |  |  |
| (a) | (b) | (c) |
|  |  |  |
| (d) | | HCHO |
|  |  |  |
| (c) | (b) | (a) |
|  |  |  |
| (d) | | HCHO |



119. Dehydration of 2, 2, 3, 4, 4-pentamethyl-3-pentanol gave two alkenes A and B. The ozonolysis products of A and B are



120. Identify 'Z' in the following reaction series,



- (a) Mixture of $\text{CH}_3-\overset{|}{\text{CH}}-\text{CH}_2$ and $\text{CH}_3-\overset{|}{\text{CH}}-\overset{|}{\text{CH}}_2$
 (b) $\text{CH}_3-\overset{|}{\text{CH}}-\overset{|}{\text{CH}}_2$
 (c) $\text{CH}_3-\overset{|}{\text{CH}}-\overset{|}{\text{CH}}_2$
 (d) $\text{CH}_3-\overset{|}{\text{CH}}-\overset{|}{\text{CH}}_2$

121. Propene on treatment with chlorine at 500–600°C gives the following product(s):

- (a) $\text{CH}_3-\text{CH}=\text{CH}-\text{Cl}$ (b) $\text{CH}_3-\overset{\text{Cl}}{\underset{|}{\text{C}}}-\text{CH}=\text{CH}_2$
 (c) $\text{Cl}-\text{CH}_2-\text{CH}=\text{CH}_2$ (d) All the above

122. When HCl gas is passed through propene in the presence of benzoyl peroxide, it gives:
 (a) n-Propyl chloride (b) 2-Chloropropene
 (c) Allyl chloride (d) No reaction

123. The addition of OsO_4 on an alkene followed by hydrolysis produces the following product
 (a) H_4OsO_4 (b) H_3OsO_4
 (c) Os_2O_3 (d) H_2OsO_4

124. In hydroboration it is evident that in the overall reaction a molecule of water has been added to propene and the addition is:
 (a) According to Markownikoff's rule
 (b) Contrary to Markownikoff's rule
 (c) Not concerned with Markownikoff's rule
 (d) None of above

125. The C = C bond is reduced to an alkane without making use of hydrogen and metal catalyst, by the following process:

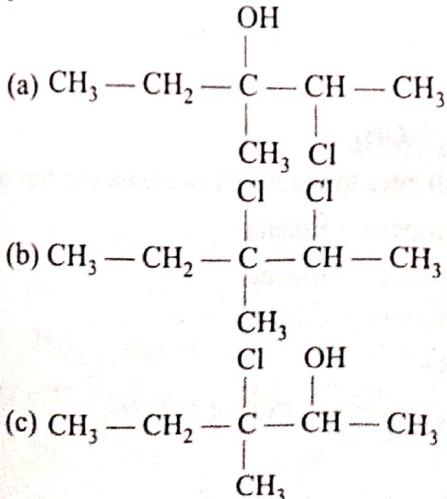
- (a) Sulphonation
 (b) Nitration
 (c) Hydrohalogenation
 (d) Boronation or hydroboronation

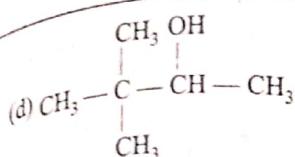
126. Cyclopentene on treatment with alkaline KMnO_4 gives
 (a) cis 1, 2-cyclopentanediol
 (b) trans 1, 2-cyclopentanediol
 (c) Cyclopentanol
 (d) 1 : 1 mixture of cis and trans 1, 2-cyclopentanediol

127. Which reactions are most common in alkenes?

- (a) Electrophilic addition reactions
 (b) Nucleophilic substitution reactions
 (c) Electrophilic substitution reactions
 (d) Nucleophilic addition reactions

128. The predominant product formed when 3-methyl-2-pentene reacts with HOCl is





129. How many grams of bromine will react with 21 g of C_5H_6 ?

- (a) 320 (b) 160
(c) 240 (d) 80

130. Which one of the following reactions would be the best for the formation of 2-bromobutane?

- (1) $\text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_2 \xrightarrow{\text{HBr}}$
(2) $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 \xrightarrow{\text{HBr}}$
(3) $\text{CH}_3\text{CH} = \text{CHCH}_3 \xrightarrow{\text{Br}_2}$
(4) $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 \xrightarrow[\text{Peroxide}]{\text{HBr}}$
(a) 1 (b) 3
(c) 2 (d) 4

131. What is the product of the reaction of 1, 3-butadiene with Br_2 ?

- (a) 2,3-dibromo-2-butene (b) 1,2-dibromobutene
(c) 3,4-dibromobutene (d) 1,4-dibromobutene

132. Addition of HI on the double bond of propene yields isopropyl iodide and not n-propyl iodide as the major product. This is because the addition proceeds through

- (a) A more stable free radical
(b) A more stable carbanion
(c) A more stable carbonium ion
(d) None of the above being a concerted reaction

133. An alkene, on ozonolysis gives formaldehyde and acetaldehyde. The alkene is:

- (a) Ethene (b) Butene-2
(c) Butene-1 (d) Propene

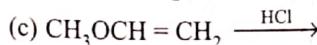
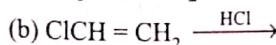
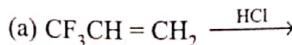
134. The only alcohol that can be prepared by the indirect hydration of alkene is

- (a) Isobutyl alcohol (b) Propyl alcohol
(c) Ethyl alcohol (d) Methyl alcohol

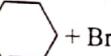
135. Which of the following is wrong statement about oxymercuration-demercuration?

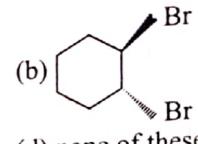
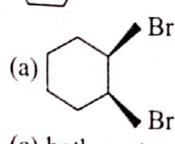
- (a) In the first step oxymercuration occurs, i.e., water and Hg(OAc)_2 add to double bond
(b) In the second step demercuration occurs, i.e., NaBH_4 reduces $-\text{HgOAc}$ group to hydrogen
(c) The net reaction is addition of water according to Markownikoff's rule
(d) Rearrangement takes place

136. In which reaction the product following anti-Markownikoff's rule is observed:



(d) None of these

137.  + $\text{Br}_2 \rightarrow$ P, P will have configuration:

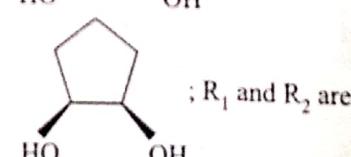
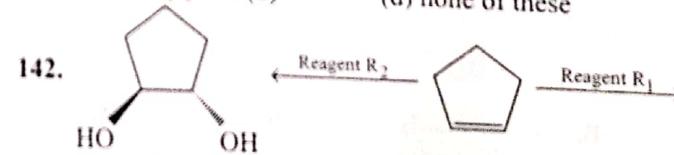
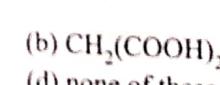
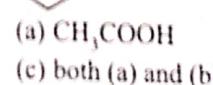
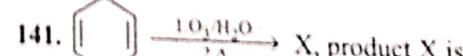
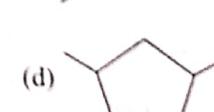
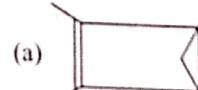
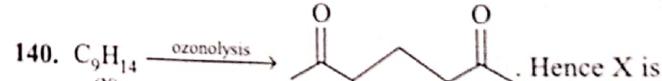
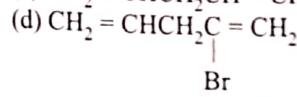
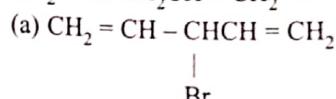
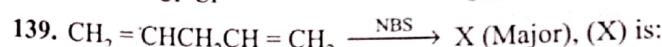
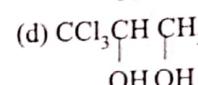
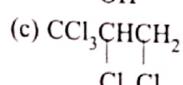
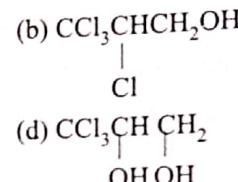
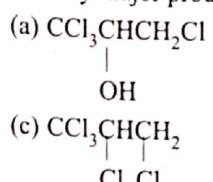


(c) both are true

(d) none of these



Identify major product P.



- (a) Cold alkaline KMnO_4 , $\text{OsO}_4 \cdot \text{H}_2\text{O}_2$
- (b) Cold alkaline KMnO_4 , HCO_3H and H_3O^+
- (c) Cold alkaline KMnO_4 , $\text{C}_6\text{H}_5\text{CO}_3\text{H}$
- (d) $\text{C}_6\text{H}_5\text{CO}_3\text{H}$, HCO_3H

143. The relative rates of hydrogenation is in the order of

- (a) $\text{CH}_2 = \text{CH}_2 > \text{RCH} = \text{CH}_2 > \text{RCH} = \text{CHR} > \text{R}_2\text{C} = \text{CHR}$
- (b) $\text{R}_2\text{C} = \text{CHR} > \text{RCH} = \text{CH}_2 > \text{RCH} = \text{CH}_2 > \text{CH}_2 = \text{CH}_2$
- (c) $\text{RCH} = \text{CHR} > \text{R}_2\text{C} = \text{CHR} > \text{RCH} = \text{CH}_2 > \text{CH}_2 = \text{CH}_2$
- (d) $\text{R}_2\text{C} = \text{CHR} > \text{CH}_2 = \text{CH}_2 > \text{RCH} = \text{CH}_2 > \text{RCH} = \text{CHR}$

144. $\text{Ph} - \text{CH}_2 - \text{CH} = \text{CH}_2 \xrightarrow{\text{dil H}_2\text{SO}_4} \text{X}$,

Identify product 'X' is:

- (a) $\text{Ph} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$

$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{C} - \text{C} - \text{CH}_3 \end{array}$$
- (b) $\text{Ph} - \text{C} \left(\begin{array}{c} \text{H} \\ | \\ \text{OH} \end{array} \right) - \text{C} \left(\begin{array}{c} \text{H} \\ | \\ \text{H} \end{array} \right) - \text{CH}_3$
- (c) $\text{Ph} - \text{C} \left(\begin{array}{c} \text{OH} \\ | \\ \text{H} \end{array} \right) - \text{C} \left(\begin{array}{c} \text{H} \\ | \\ \text{H} \end{array} \right) - \text{CH}_3$
- (d) $\text{Ph} - \text{CH}_2 - \text{OH}$

145. $\text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow[\text{H}_2\text{O}_2/\text{OH}^-]{\text{BD}_3/\text{THF}} \text{X}$,

- (a) $\text{CH}_3\text{CHCH}_2\text{D}$

$$\begin{array}{c} | \\ \text{OH} \end{array}$$
- (b) $\text{CH}_3\text{CHCH}_2\text{OH}$

$$\begin{array}{c} | \\ \text{D} \end{array}$$
- (c) CH_3CHCH_3

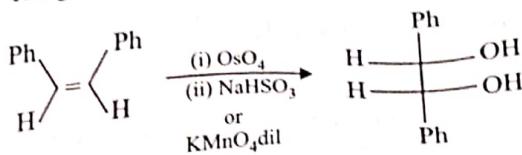
$$\begin{array}{c} | \\ \text{OD} \end{array}$$
- (d) $\text{CH}_2\text{D}-\text{CH}-\text{CH}_3$

$$\begin{array}{c} | \\ \text{OH} \end{array}$$

146. $\text{H}_3\text{C} \begin{array}{c} \diagdown \\ \text{C} = \text{C} \\ \diagup \end{array} \text{CH}_3 + \text{Br}_2 \xrightarrow{\text{CCl}_4} ?$ Product is:

- (a) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H} - \text{C} - \text{Br} \\ | \\ \text{H} - \text{C} - \text{Br} \\ | \\ \text{CH}_3 \end{array}$
- (b) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H} - \text{C} - \text{Br} \\ | \\ \text{Br} - \text{C} - \text{H} \\ | \\ \text{CH}_3 \end{array}$
- (c) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{Br} - \text{C} - \text{Br} \\ | \\ \text{H} - \text{C} - \text{H} \\ | \\ \text{CH}_3 \end{array}$
- (d) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{Br} - \text{C} - \text{H} \\ | \\ \text{H} - \text{C} - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$

147. The given reaction,



is an example of:

- (a) Stereospecific reaction
- (b) Stereo selective reaction
- (c) (a) and (b) Both
- (d) Ordinary reaction

148. $\begin{array}{c} \text{C}_6\text{H}_5\text{CO}_2\text{H}, \text{CHCl}_3 \\ \text{at } 25^\circ\text{C} \end{array} \rightarrow \text{X}$, product X is

- (a) $\begin{array}{c} \text{OH} \\ | \\ \text{C}_6\text{H}_5-\text{C} \\ | \\ \text{OH} \end{array}$
- (b) $\begin{array}{c} \text{OH} \\ | \\ \text{C}_6\text{H}_5-\text{C} \\ | \\ \text{OH} \end{array}$
- (c) $\begin{array}{c} \text{O} \\ | \\ \text{C}_6\text{H}_5-\text{C} \\ | \\ \text{OH} \end{array}$
- (d) $\begin{array}{c} \text{OH} \\ | \\ \text{C}_6\text{H}_5-\text{C} \\ | \\ \text{OH} \end{array}$

Method of Preparation of Alkynes

149. An organic compound X ($\text{C}_6\text{H}_{13}\text{Br}$) is optically active. X on treatment with $(\text{CH}_3)_3\text{COK}$ in $(\text{CH}_3)_3\text{COH}$ gives Y (C_6H_{12}), a major product. Y on treatment with $\text{Br}_2 - \text{CCl}_4$ in the presence of FeBr_3 gives a dibromide which on further treatment with NaNH_2 gives C_6H_{10} which is still optically active. Hence, X and Y respectively are

- (a) $\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$ and $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{CH}-\text{CH}_3 \end{array}$
- (b) $\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$ and $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$
- (c) $\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$ and $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$
- (d) $\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$ and $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$

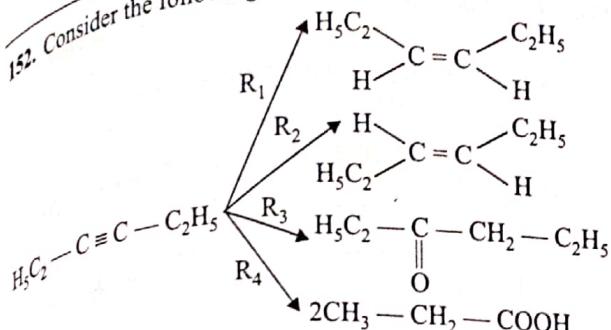
150. When 1-alkyne is treated with $\text{Na} + \text{Liq. NH}_3$ and product is reacted with methyl chloride, the end product of the reaction will be

- (a) Lower alkyne having two carbons less than 1-alkyne
- (b) Lower alkyne having one carbon less than 1-alkyne
- (c) Higher alkyne having one carbon more than 1-alkyne
- (d) Higher alkyne having two carbons more than 1-alkyne

151. Which of the following will not react with an ammoniacal silver nitrate solution?

- (a) $\text{CH}_3\text{C} \equiv \text{CH}$
- (b) $(\text{CH}_3)_2\text{CH} - \text{C} \equiv \text{CH}$
- (c) $\text{CH}_3\text{C} \equiv \text{CCH}_3$
- (d) $\text{HC} \equiv \text{CH}$

152. Consider the following reactions

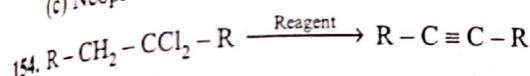


The correct set of reagents for these reactions is

	R_1	R_2	R_3	R_4
(a)	$\text{H}_2/\text{Lindlar}$ catalyst	$\text{Na}/\text{liq. NH}_3$	(i) O_3 , (ii) H_2O	$\text{H}_2\text{O}, \text{H}_2\text{SO}_4,$ HgSO_4
(b)	$\text{H}_2/\text{Lindlar}$ catalyst	$\text{Na}/\text{liq. NH}_3$	$\text{H}_2\text{O}, \text{H}_2\text{SO}_4,$ HgSO_4	(i) O_3 , (ii) H_2O
(c)	(i) O_3 , (ii) H_2O	$\text{H}_2\text{O}, \text{H}_2\text{SO}_4,$ HgSO_4	$\text{Na}/\text{liq. NH}_3$	$\text{H}_2/\text{Lindlar}$ catalyst
(d)	$\text{H}_2\text{O}, \text{H}_2\text{SO}_4,$ HgSO_4	$\text{H}_2/\text{Lindlar}$ catalyst	(i) O_3 , (ii) H_2O	$\text{Na}/\text{liq. NH}_3$

153. The product formed when acetylene is passed through red hot tube is

- (a) Benzene (b) Cyclohexane
(c) Neoprene (d) Ethane



The reagent is

- (a) Na (b) HCl and H_2O
(c) KOH in $\text{C}_2\text{H}_5\text{OH}$ (d) Zn

155. Acetylene can be prepared from

- (a) Potassium fumarate (b) Calcium carbide
(c) Ethylene bromide (d) All of these

156. Ethylene dibromide on treating with alcoholic KOH gives

- (a) C_2H_6 (b) CH_4
(c) C_2H_4 (d) C_2H_2

157. Carbide which react with water to give propyne is

- (a) CaC_2 (b) Mg_2C_3
(c) SiC (d) Al_4C_3

158. To prepare But-2-yne from 2, 2, 3, 3-tetrachlorobutane, reagent used is:

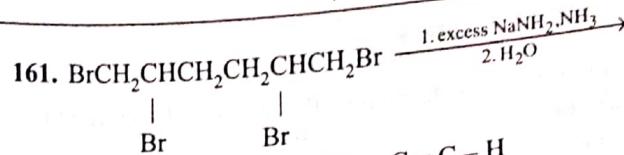
- (a) Zinc dust/ Δ (b) Sodaamide
(c) Alc. KOH (d) aq. KOH

159. Which of the following compounds on hydrolysis gives acetylene?

- (a) CaC_2 (b) Mg_2C_3
(c) Al_4C_3 (d) Cu_2Cl_2

160. Acetylene may be prepared by electrolysis of

- (a) potassium oxalate (b) potassium acetate
(c) potassium maleate (d) potassium succinate



- (a) $\text{H}-\text{C} \equiv \text{C}-\text{CH}_2-\text{CH}_2-\text{C} \equiv \text{C}-\text{H}$
(b) $\text{H}-\text{C} \equiv \text{C}-\text{C} \equiv \text{C}-\text{H}$
(c) $\text{H}-\text{C} \equiv \text{C}-\text{CH}_2-\text{C} \equiv \text{C}-\text{H}$
(d) $\text{H}-\text{C} \equiv \text{C}-\text{H}$

162. Acetylene is obtained by the electrolysis of

- (a) Sodium succinate (b) Potassium fumarate
(c) Both (a) and (b) (d) None of these

163. Which of the C - C bond is strongest

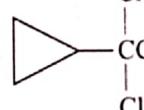
- (a) Formed by sp^3-sp^3 hybridised carbon atoms (as in alkanes)
(b) Formed by sp^2-sp^2 hybridised carbon atoms (as in alkenes)
(c) Formed by $sp-sp$ hybridised carbon atoms (as in alkynes)
(d) All are equal

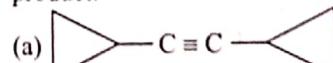
164. 1, 2-dibromoethane when heated with alcoholic potash gives

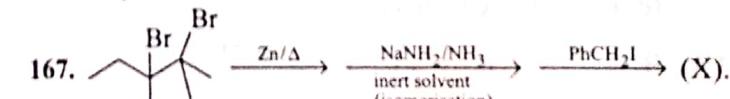
- (a) Ethane (b) Acetylene
(c) Ethylene (d) Methane

165. Acetylene can be obtained by the reaction

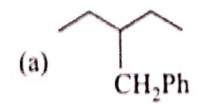
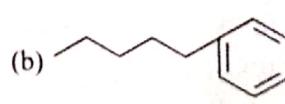
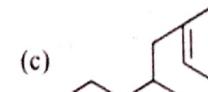
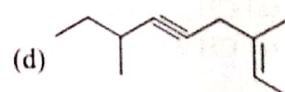
- (a) $\text{HCOOK} \xrightarrow{\text{electrolysis}}$
(b) $\text{CHI}_3 + 6\text{Ag} + \text{CHI}_3 \xrightarrow{\Delta}$
(c) $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{443 } ^\circ\text{C}]{\text{Conc. H}_2\text{SO}_4}$
(d) $\text{Be}_2\text{C} + \text{H}_2\text{O} \rightarrow$

166.  $\xrightarrow[\text{Heat}]{\text{KOC(CH}_3)_3, \text{DMSO}}$. Identify the product.

- (a) 
(b) $\text{H}-\text{C} \equiv \text{C}-\text{H}$
(c) 
(d) 



The end product (X) is

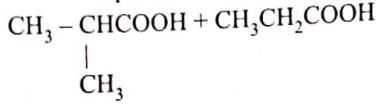
- (a) 
(b) 
(c) 
(d) 

Properties of Alkynes

168. Gem dihalide is formed by the reaction of alkyne and

- (a) HX
- (b) X₂
- (c) H₂
- (d) O₂

169. An alkyne C₇H₁₂ on reaction with hot alkaline KMnO₄ and subsequent acidification with HCl yields a mixture of



The alkyne is

- (a) 3-Hexyne
- (b) 2-Methyl-3-hexyne
- (c) 2-Methyl-2-hexene
- (d) 2-Methyl-2-hexene

170. Which of the following reagents cannot be used to locate the position of triple bond in CH₃—C≡C—CH₃?

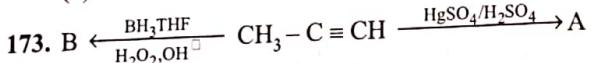
- (a) Br₂
- (b) O₃
- (c) Cu²⁺
- (d) KMnO₄

171. The product of reaction between one mole of acetylene and two mole of HCHO in the presence of Cu₂Cl₂

- (a) HOCH₂—C≡C—CH₂OH
- (b) H₂C=CH—C≡C—CH₂OH
- (c) HC=C—CH₂OH
- (d) None of these

172. In the presence of strong bases, triple bonds will migrate within carbon skeletons by the

- (a) removal of protons
- (b) addition of protons
- (c) removal and re-addition of protons
- (d) addition and removal of protons



A and B are

- O
||
(a) CH₃CH₂CHO, CH₂—C—CH₃
- O
||
(b) CH₃—C—CH₃, CH₃CH₂CHO
- O
||
(c) CH₃CH₂CHO (both)
- O
||
(d) CH₃—C—CH₃ (both)



A and B are geometrical isomers (R—CH=CH—R)

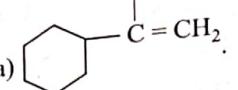
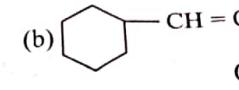
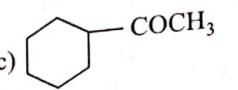
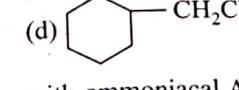
- (a) A is trans, B is cis
- (b) A and B both are cis
- (c) A and B both are trans
- (d) A is cis, B is trans

175. Which is expected to react most readily with bromine

- (a) CH₃CH₂CH₃
- (b) CH₂=CH₂
- (c) CH≡CH
- (d) CH₃—CH=CH₂

176. Hydration of  C≡CH in presence of

H₂SO₄/HgSO₄ gives (as a major product)

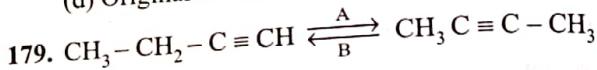
- (a) 
- (b) 
- (c) 
- (d) 

177. A compound (C₅H₈) reacts with ammoniacal AgNO₃ to give a white precipitate and reacts with excess of KMnO₄ solution to give (CH₃)₂CH—COOH. The compound is

- (a) CH₂=CH—CH=CH—CH₃
- (b) (CH₃)₂CH—C≡CH
- (c) CH₃(CH₂)₂C≡CH
- (d) (CH₃)₂C=C=CH₂

178. A mixture of CH₄, C₂H₄ and C₂H₂ gases are passed through a Wolf bottle containing ammoniacal cuprous chloride. The gas coming out is

- (a) Methane
- (b) Acetylene
- (c) Mixture of methane and ethylene
- (d) Original mixture



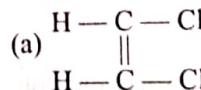
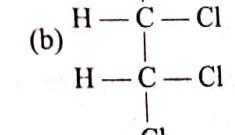
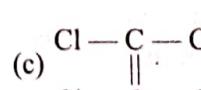
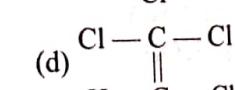
A and B are

- (a) alcoholic KOH and NaNH₂
- (b) NaNH₂ and alcoholic KOH
- (c) NaNH₂ and Lindlar
- (d) Lindlar and NaNH₂

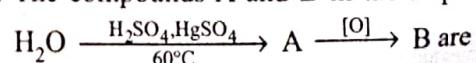
180. Alkynes can be reduced to alkenes by hydrogenation in presence of

- (a) Raney Ni
- (b) Anhy. AlCl₃
- (c) Pd
- (d) Lindlar's catalyst

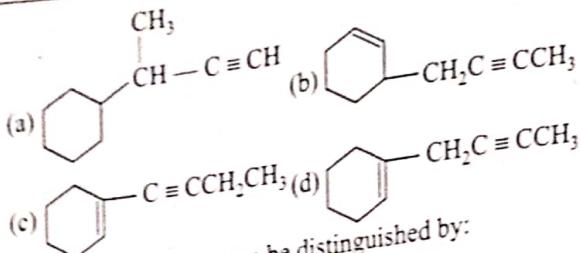
181. Westrosol has the following formula

- (a) 
- (b) 
- (c) 
- (d) 

182. The compounds A and B in the sequence CH≡CH+



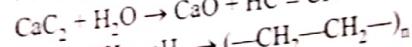
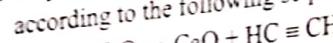
- (a) Acetone and acetic acid respectively
- (b) Acetaldehyde and acetic acid respectively
- (c) Acetaldehyde and ethyl alcohol respectively
- (d) Acetone and acetaldehyde respectively



200. Propyne and propene can be distinguished by:

- (a) Conc. H_2SO_4 (b) Br_2 in CCl_4
 (c) Dil. KMnO_4 (d) AgNO_3 in ammonia

201. Polyethylene can be produced from calcium carbide



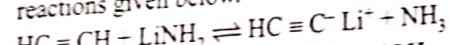
The mass of polyethylene which can be produced from 40.0 kg of CaC_2 is

- (a) 6.75 kg (b) 17.5 kg
 (c) 8.75 kg (d) 9.75 kg

202. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne.

- (a) bromine, CCl_4
 (b) H_2 , Lindlar catalyst
 (c) dilute H_2SO_4 , HgSO_4
 (d) ammoniacal Cu_2Cl_2 solution

203. Predict the order of base strength of anions from the reactions given below.

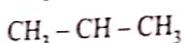
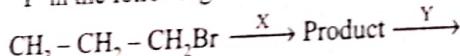


- (a) $\text{OH}^- < \text{HC} \equiv \text{C}^- < \text{NH}_3^-$
 (b) $\text{HC} \equiv \text{C}^- < \text{OH}^- < \text{NH}_3^-$
 (c) $\text{OH}^- < \text{NH}_3^- < \text{HC} \equiv \text{C}^-$
 (d) $\text{NH}_3^- < \text{OH}^- < \text{HC} \equiv \text{C}^-$

204. Structural formula for lewisite is

- (a) $\begin{array}{c} \text{CHCl} \\ || \\ \text{CHAsCl}_3 \end{array}$ (b) $\begin{array}{c} \text{CHCl} \\ || \\ \text{CHAsCl}_2 \end{array}$
 (c) $\begin{array}{c} \text{CHCl}_2 \\ | \\ \text{CHAsCl}_3 \end{array}$ (d) None of these

205. Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformations.



- (a) X = concentrated alcoholic NaOH , 80°C ; Y = HBr / acetic acid, 20°C

- (b) X = dil. aq. NaOH , 20°C , Y = HBr / acetic acid, 20°C

- (c) X = dil. aq. NaOH , 20°C , Y = Br_2 / CHCl_3 , 0°C

- (d) X = conc. alc. NaOH , 80°C , Y = Br_2 / CHCl_3 , 0°C

206. Which of the following will be the final product when C_2H_2 reacts with HCl ?

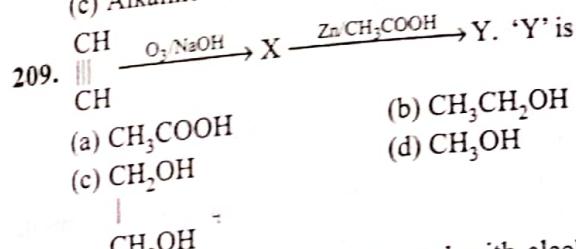
- (a) $\begin{array}{c} \text{CH} \\ || \\ \text{CHCl} \end{array}$ (b) $\begin{array}{c} \text{CHCl} \\ || \\ \text{CHCl} \end{array}$
 (c) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CHCl}_2 \end{array}$ (d) None of these

207. When propyne reacts with aqueous H_2SO_4 in the presence of HgSO_4 , the major product is

- (a) Propanal
 (b) Acetone
 (c) Propyl hydrogen sulphate
 (d) Propanol

208. The distinguishing test for triple bond containing acidic hydrogen is

- (a) AlCl_3 (b) Br_2 in CCl_4
 (c) Alkaline KMnO_4 (d) $\text{Ag}(\text{NH}_3)_2^+$



210. 1, 2-dibromoethane when heated with alcoholic potash gives

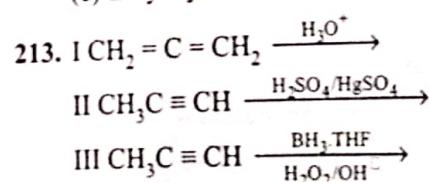
- (a) Ethane (b) Ethylene
 (c) Acetylene (d) Methane

211. In its reaction with silver nitrate acetylene shows

- (a) Acidic property (b) Reducing property
 (c) Basic property (d) Oxidising property

212. Addition of HCN to ethyne in presence of $\text{Ba}(\text{CN})_2$ as catalyst gives

- (a) 1, 1-dicyano ethane (b) Vinyl cyanide
 (c) Ethyl cyanide (d) Divinyl cyanide



Acetone is the major product in:

- (a) I, II (b) I, III
 (c) II, III (d) I, II, III

Benzene

214. The electrophile involved in chlorination of benzene is

- (a) chloride ion (b) Chloronium ion
 (c) Nitronium ion (d) None of the above

215. Benzene reacts with CH_3Cl in the presence of anhydrous AlCl_3 to form
 (a) Toluene (b) Chlorobenzene
 (c) Benzyl chloride (d) Xylene

216. Benzene reacts with fuming sulphuric acid to give
 (a) Sodium benzene sulphonate
 (b) Benzene sulphonic acid
 (c) Sodium benzoate
 (d) All the above

217. $\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \xrightarrow[\text{anhydrous } \text{AlCl}_3]{\quad} \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl}$ is an example of:

- (a) Friedel-Crafts reaction (b) Kolbe's synthesis
 (c) Wurtz reaction (d) Grignard reaction

218. Benzene reacts with benzoyl chloride to form
 (a) benzophenone (b) Acetophenone
 (c) Benzylchloride (d) Maleic anhydride

219. Which of the following reactions takes place when a mixture of concentrated HNO_3 and H_2SO_4 reacts on benzene at 350 K?
 (a) Sulphonation (b) Nitration
 (c) Hydrogenation (d) Dehydration

220. Toluene may be prepared by
 (a) Friedel-Crafts' reaction (b) Wurtz-Fitting reaction
 (c) Methyl lithium (d) All of the above

221. Attacking or reactive or electrophilic species in nitration of benzene is or In the nitration of benzene with concentrated HNO_3 and H_2SO_4 , the attack on ring is made by:

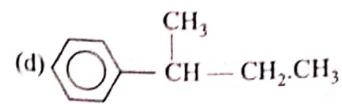
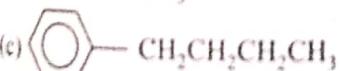
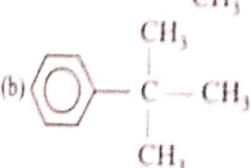
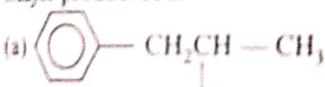
- (a) NO_2^- (b) NO_2^+
 (c) NO_3^- (d) NO_2

222. Which among the following is deactivating group?

- (a) $-\text{Cl}$ (b) $-\text{OR}$
 (c) $-\text{NH}_2$ (d) $-\text{NHR}$

223. $\text{C}_6\text{H}_5\text{CH}_3 + \text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{AlCl}_3} (\text{X}) \text{ hydrocarbon (X)}$.

Major product X is

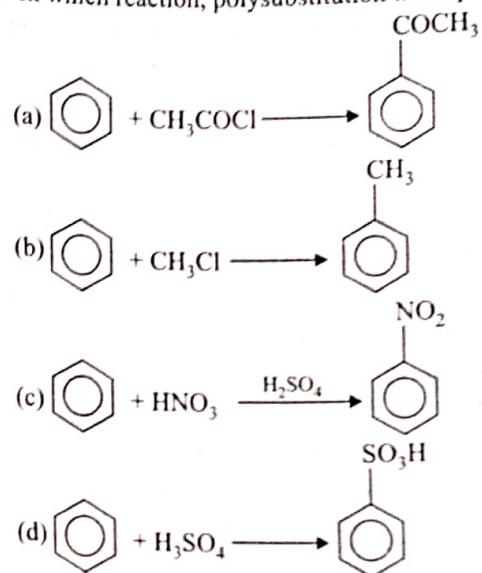


224. Nitration of toluene takes place at

- (a) o-position (b) m-position
 (c) p-position (d) Both o- and p-positions

225. Chlorobenzene is o, p-directing in electrophilic substitution reaction. The directing influence is explained by
 (a) +M of Ph (b) +I of Cl
 (c) +M of Cl (d) +I of Ph

226. In which reaction, polysubstitution takes place:



227. Presence of a nitro group in a benzene ring.

- (a) Activates the ring towards electrophilic substitution
 (b) Renders the ring basic
 (c) Deactivates the ring towards nucleophilic substitution
 (d) Deactivates the ring towards electrophilic substitution

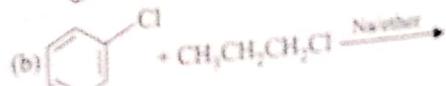
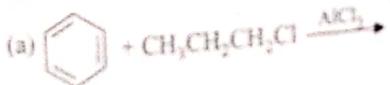
228. During nitration of benzene with nitrating mixture, HNO_3 acts as

- (a) an acid (b) a base
 (c) catalyst (d) reducing agent

229. n-Propyl benzene can be obtained in quantitative yield by following method:

- By treating benzene with n-propyl chloride in presence of AlCl_3
 - By treating excess of benzene with n-propyl chloride in presence of AlCl_3 ,
 - By treating benzene with allyl chloride in presence of AlCl_3 followed by reduction
 - By treating benzene with propionyl chloride in the presence of AlCl_3 followed by Clemmensen reduction.
- (a) By (ii), (iii) and (iv) (b) By (i), (iii) and (iv)

- (c) By (iii) and (iv) (d) By (ii) only
 230. Which method is preferred for the preparation of n-propyl chloride from benzene?



- (c) Both are undesirable
 (d) Both give similar result

231. When nitrobenzene is treated with Br⁺ in presence of FeBr₃, the major product formed is m-bromo-nitrobenzene. Statement which is related to obtain the m-isomer is

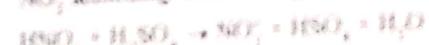
- (a) the electron density on meta carbon is increased than that on ortho- and para positions
 (b) the intermediate carbonium ion formed after initial attack of Br⁺ at the meta position is least destabilised
 (c) loss of aromaticity when Br⁺ attacks at the ortho and para positions and not at meta position
 (d) easier loss of H⁺ to regain aromaticity from the meta position than from ortho and para positions.

232. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds:



- (a) A > B > C > D (b) D > C > B > A
 (c) B > A > C > D (d) B > C > A > D

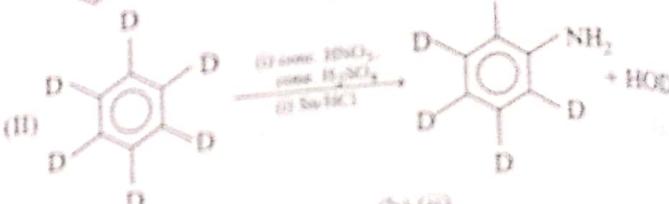
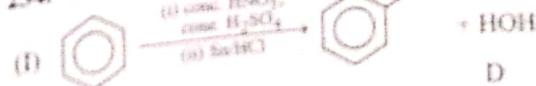
233. During nitration of benzene using a mixture of conc. HNO₃ and conc. H₂SO₄, function of conc. H₂SO₄ is to increase the rate of reaction by increasing the concentration of NO₂ according to following reaction:



Here nitric acid acts as

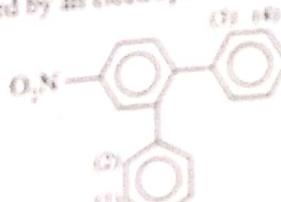
- (a) a stronger acid (b) a weaker acid
 (c) a base (d) none of the these

234. Which of the two reactions proceed faster?



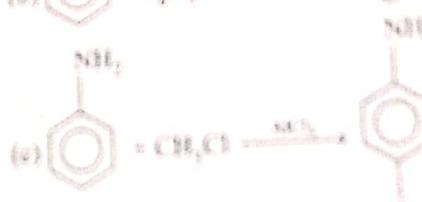
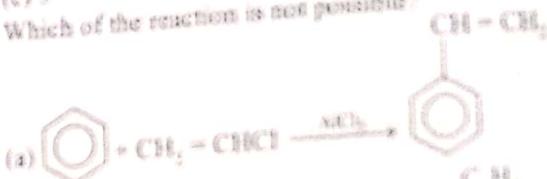
- (a) (i) (b) (ii)
 (c) (i) = (ii) (d) Not definite

235. Which of the positions in the following compound is liable to be attacked by an electrophile?



- (a) 1 (b) 2
 (c) 3 (d) 4

236. Which of the reaction is not possible?



SECTION B: ASSERTION-REASONING QUESTIONS

These questions consist of two statements each, printed as Assertion and Reason. While answering these questions you are required to choose any one of the following four responses:

- (a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
 (c) If assertion is true but reason is false.
 (d) If assertion is false but reason is true.

1. Assertion: (i) Iodoform does not react with Cl₂ in dark.

Reason: Chlorination of ICl takes place in sunlight.

2. Assertion: I. 1,3-Butadiene is the monomer for natural rubber.

Reason: Natural rubber is formed through anionic addition polymerization.

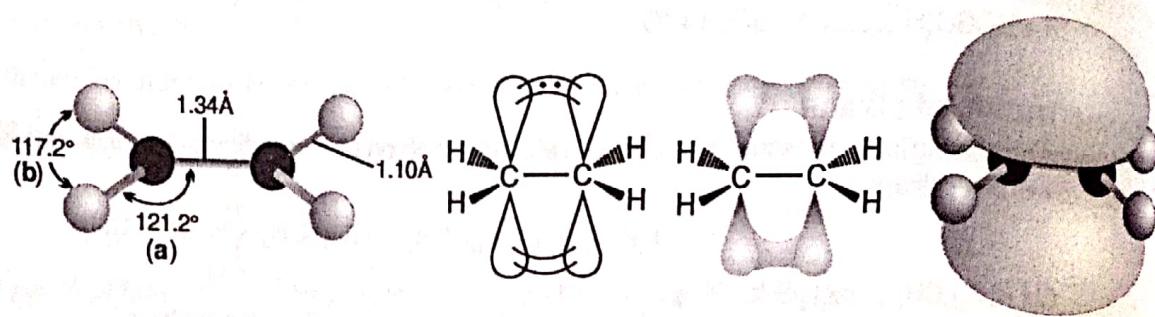
3. Assertion: Acetylene on reacting with sodium's sodium acetylide and ammonia.

Reason: sp-hybridised carbon atoms of acetylene are considerably electronegative.

ALKENE

1. Structure and bonding

- (A) Alkenes are unsaturated hydrocarbons having at least one double bond.
- (B) These are represented by general Formula (G.F.) C_nH_{2n} (one double bond)
- (C) In Ethene $C = C$ bond length is 1.34 \AA
- (D) Its bond energy is $146 \text{ kcal.mol}^{-1}$
- (E) The hybridization of ($C = C$) carbon is sp^2
- (F) The πe^- cloud is present above and below the plane of σ - bonded skeleton.
- (G) These are also known as olefins since ethene, the first member of the homologous series forms only liquid substance when treated with halogens.
- (H) Compounds may exist as conjugated polyenes or as cumulated polyenes or as isolated polyenes



Note : That angle $a > b$ since repulsion due to π electrons (double bond - single bond repulsion $>$ single bond - single bond repulsion according to VSEPR theory).

2. Comparative study of alkane, alkene & alkyne :

Hydrocarbon	Alkane	Alkene	Alkyne
(A)	$\begin{array}{cc} H & H \\ & \\ H-C & -C-H \\ & \\ H & H \end{array}$	$\begin{array}{cc} H & H \\ & \diagdown \\ & C=C \\ & \diagup \\ H & H \end{array}$	$H-C\equiv C-H$
(i) C—C Bond distance	1.54 \AA	1.34 \AA	1.20 \AA
(ii) C—H Bond distance	1.09 \AA	1.08 \AA	1.05 \AA
(iii) Hybridisation state	sp^3	sp^2	sp
(iv) Structure	Tetrahedral	Planner	Linear
(v) Electronegativity $sp^3 < sp^2 < sp$	less than sp^2/sp	less than sp more than sp^3	more than sp^2/sp^3
(vi) C—C bond energy	415 kJ	615 kJ	835 kJ
(vii) density	0.5 g/cm^3	0.52 g/cm^3	0.67 g/cm^3
(viii) % s-character	25%	33.33 %	50 %

Lab test

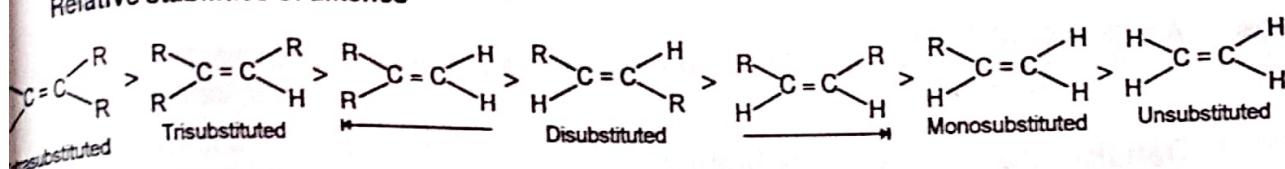
Hydrocarbon	Alkane	Alkene	Alkyne (Terminal)
(i) $\text{Br}_2/\text{H}_2\text{O}$ solution	No effect	Decolorise	Decolorise
(ii) Cold dil. alkaline + KMnO_4 Solution	No effect	Brown colour	Brown colour
(iii) Tollen's Reagent	No effect	No effect	White ppt. of silver acetenilied
(iv) Ammonical cuprous chloride solution	No effect	No effect	Red ppt. of cuprous acetenilied

Stability of alkenes

Overall relative stabilities of Alkenes

Studies of numerous alkenes reveal pattern of stabilities that related to the number of alkyl groups attached to the carbon atoms of the double bond. The greater the number of attached alkyl groups (i.e., the highly substituted the carbon atoms of the double bond), the greater is the alkene's stability. This order of stabilities can be given in general terms as follows.

Relative stabilities of alkenes



- More and More alkylated double bonded alkene will be more stable.
- The way of measuring stability of alkene is the determination of heat of hydrogenation. It is applicable only those isomeric alkene which gives same product after hydrogenation.

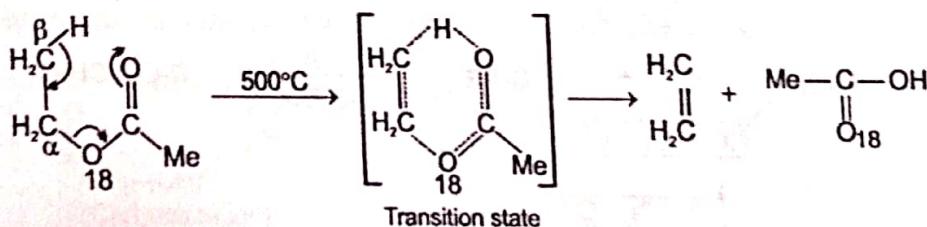
$$\text{Stability} \propto \frac{1}{\text{Heat of Hydrogenation}}$$

i.e. more stable the alkene \rightarrow less will be heat of hydrogenation.

Preparation of alkene :

Pyrolysis of ester :

It is the preparation of alkene along with carboxylic acid via formation of six membered cyclic transition state. It is syn elimination and alkene is formed corresponding to alkyl part of alcohol from ester. This addition is also said to be Hoffman elimination

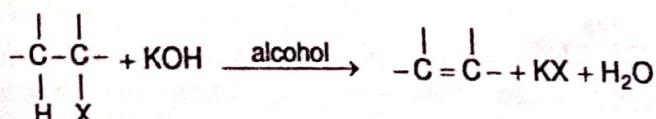


Note : As a direct consequence of cyclic transition state, both the leaving groups namely proton and carboxylate ion are eliminated from the syn position. This is an example of **syn elimination**.

Dehydro-halogenation of alkyl halide :

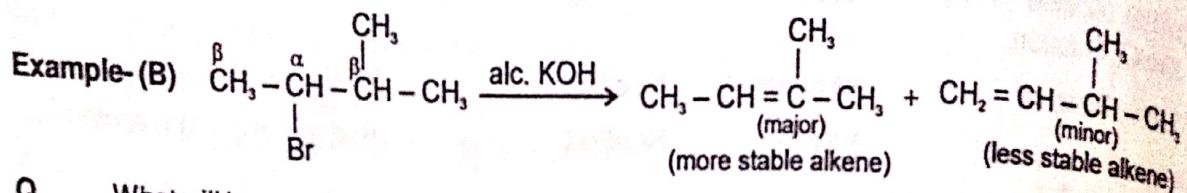
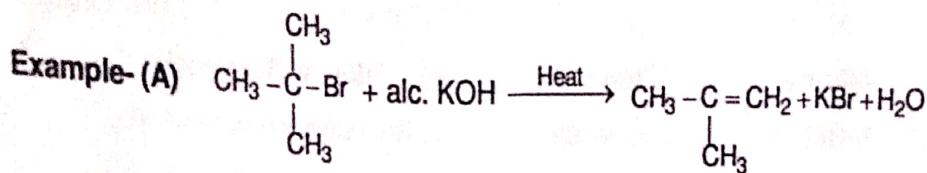
It is removal of H-X from alkyl halide where this reaction is said to be β -elimination reaction.

Reagent : alcoholic KOH or NaNH_2

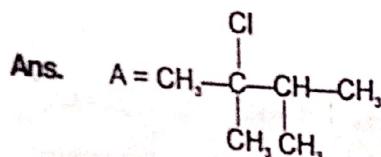
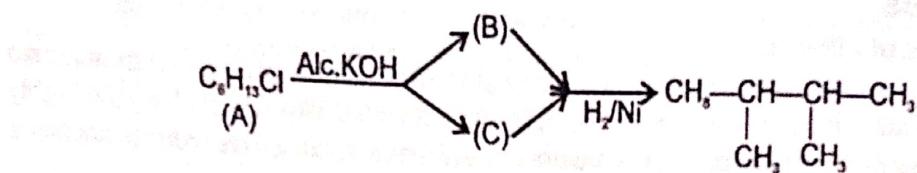


Here $\beta - \text{H}$ is eliminated by base hence called β elimination (follows Saytzeff rule).

i.e. (Highly substituted alkene is major product). It also involves an anti elimination of HX .



Q. What will be the structure of A in given question?

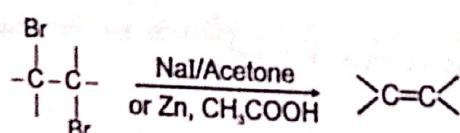


Dehalogenation of dihalo-alkane :

It is removal of X_2 from dihalo alkane.

Reagent: NaI in acetone or zinc in presence of acetic acid or ethanol or Zn/Δ
Dihalides are of two types :

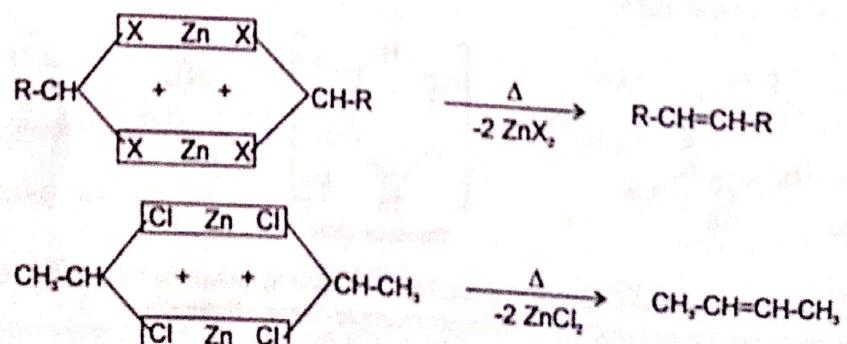
(A) Vicinal dihalide or Alkylene halides
General Reaction



(B) Gem-dihalide or Alkylidene halides

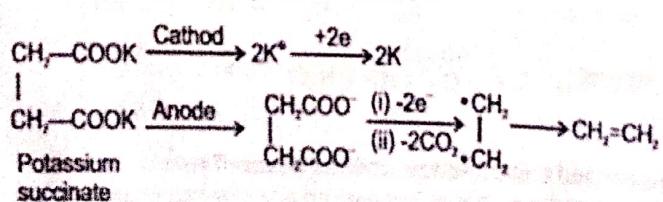
e.g.: $\text{CH}_3 - \text{CHCl}_2$ (ethylidene chloride)

When gem dihalide is heated with Zinc dust at 300°C then higher alkenes are formed, which is based on free radical mechanism.

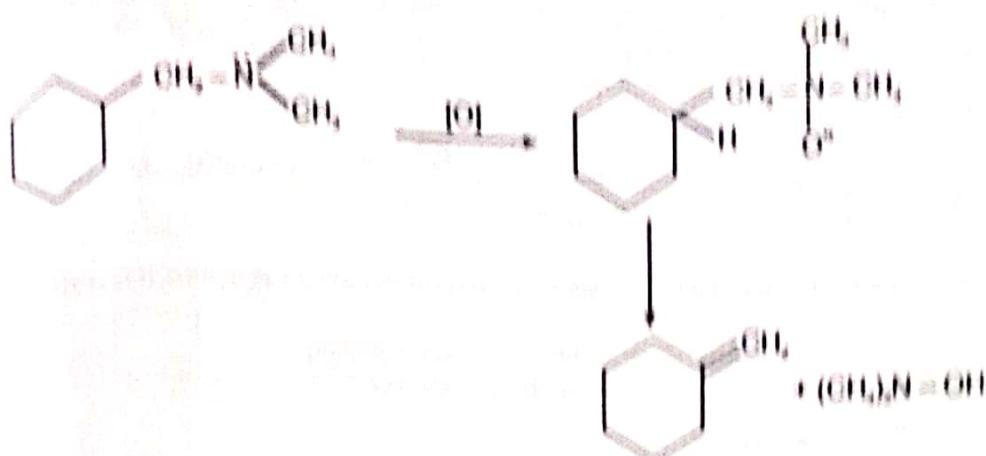


Electrolysis of potassium succinate :

This reaction gives ethylene as follows



Cope reaction: Tertiary amine oxides on heating forms alkene if there is β -hydrogen atom in it.



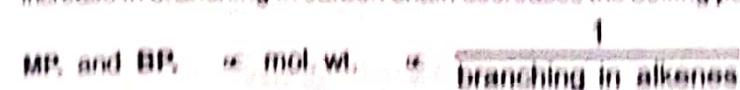
Physical properties of alkene

From $\text{C}_2 = \text{O}_2$ they are colourless, odourless gases; from $\text{C}_6 = \text{O}_6$, they are colourless liquids; C_{10} onwards alkenes are solids.

Alkenes are practically insoluble in water because they can not form hydrogen bonds with H_2O molecules. They dissolve freely in organic solvents like benzene, chloroform, CCl_4 , petroleum ether, etc.

The boiling and melting points of alkenes are slightly higher than the corresponding alkanes because the intermolecular forces of attraction are stronger due to the presence of easily polarizable a bond. Alkenes are therefore, less volatile than the corresponding alkanes.

Their boiling points, melting points and specific gravities rise with the increase of molecular weight. The increase in branching in carbon chain decreases the boiling point among isomeric alkenes.

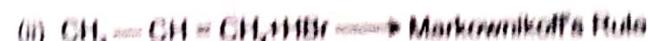
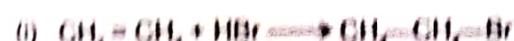


Chemical reactions of alkene

Electrophilic addition reaction :

This addition is initiated by electrophile and produces via carbonium ion intermediate.

Addition of Hydrogen-Halide(HX) over alkene



(Unsymmetrical
alkene)

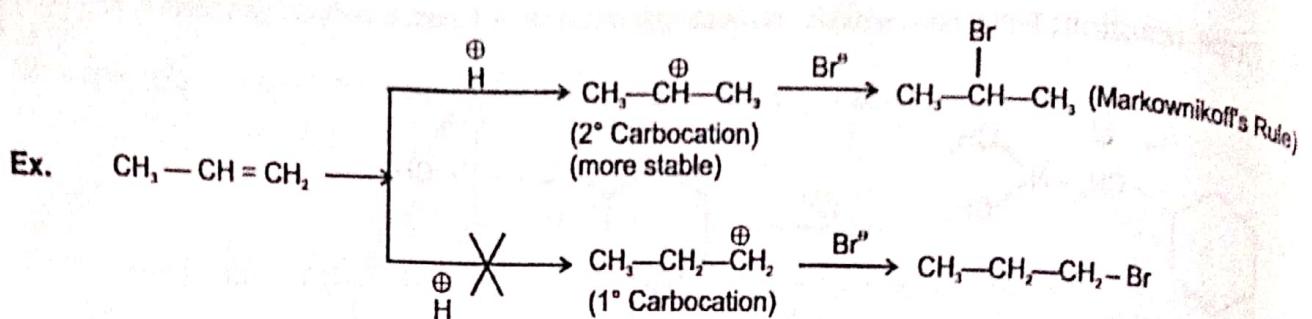
Markownikoff's rule :

Negative part of alkene and acid reagent will go to that carbon atom of $\text{C}=\text{C}$ which has less number of H-atoms.

Since in above (ii) reaction it is electrophilic addition reaction hence it is electrophile that will go to that carbon atom of $\text{C}=\text{C}$ which has more no of H-atoms to give two type carbonium ions.

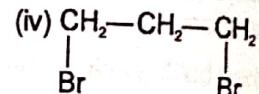
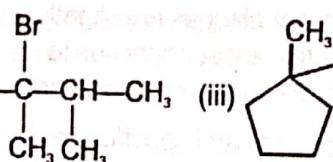
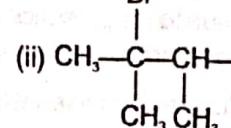
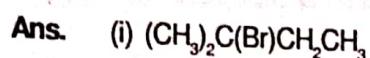
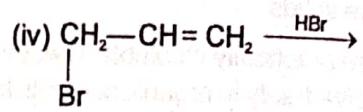
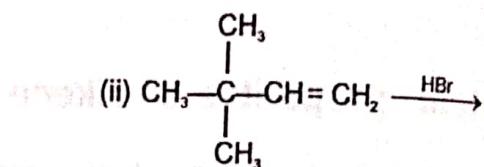
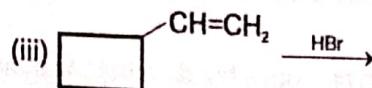
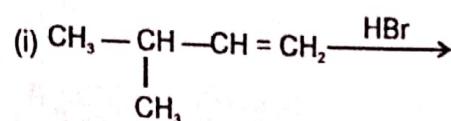
(i) Primary carbocation (ii) Secondary carbocation

Since 2° carbocation is more stable hence major product is 2-bromopropane. This can be represented as :

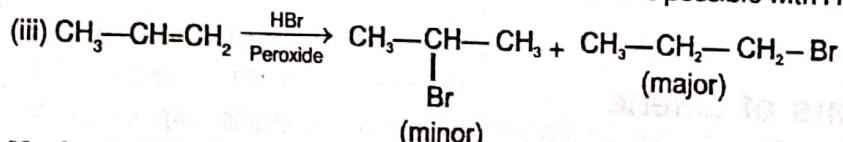


Note : Product will be corresponding to more stable carbonium ion formed with in structure, this carbonium ion is obtained either by
 (i) H-atom shifting (ii) —CH₃ group shifting
 (iii) Phenyl group shifting (iv) Bond migration

Que. Predict the product for the followings



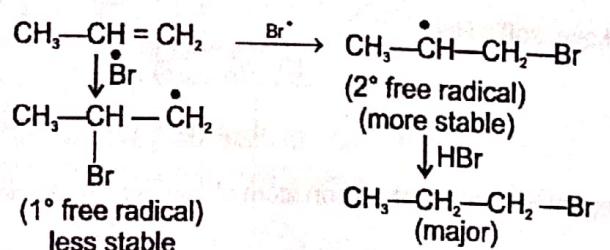
Note : (i) If above addition reaction is carried out in the presence of peroxide then it is said to be anti markownikoff's reaction.
 (ii) This addition is free-radical addition reaction which is possible with HBr only.



Mechanism : This reaction is free radical addition reaction in this reaction peroxide undergoes homolytic cleavage to give a free radical from HBr to give Br[•]. This Br[•] will go to either carbon of carbon-carbon double bond of propene to give two type of free radicals.

(i) 1° free radical (ii) 2° free radical

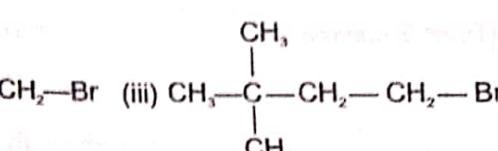
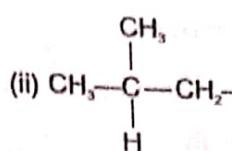
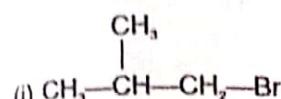
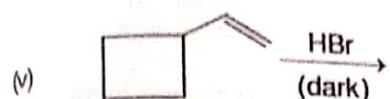
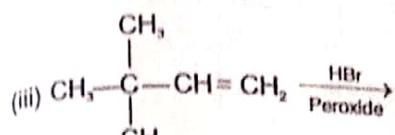
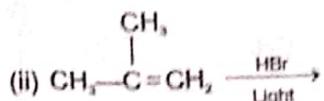
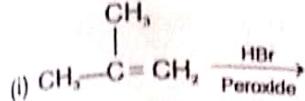
Since 2° free radical is more stable then 1° free radical has major product is 1-bromopropane this can be represented as.



Among the HX addition is possible with HBr only, not with HF, HCl, HI.

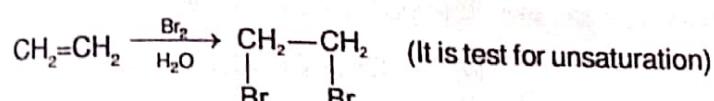
Because HF and HCl are held together by strong electrostatic force. So they can never be broken into free radical. HI will give I[•] but being larger in size I[•] (inspite of going to C = C) will combine with another I[•] to give I₂ molecule. Thus because of comparable size addition is possible in HBr only.

Predict the product for the following.

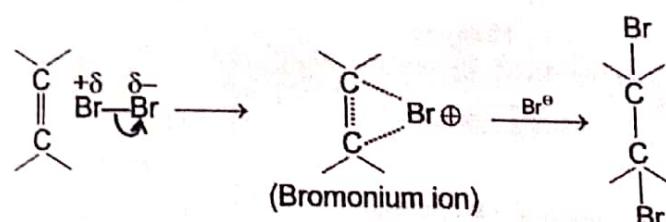


Addition of bromine water solution over alkene :

It is a test for unsaturation where Bromine water solution is decolourized. It is also electrophilic addition reaction.



It was assumed that during addition of Br_2 molecular over $\text{C}=\text{C}$, Br atom which is nearer to π electron acquire slight +ve charge under its influence to give bromonium ion (A) over with Br^- is going to give dibromo alkane.



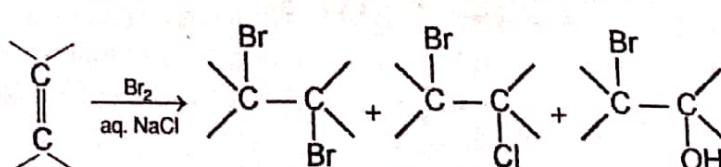
Evidence to support above reaction :

When addition of Br_2 was carried out in the presence of aq. NaCl we get 3-products.

(i) 1,2-dibromoethane

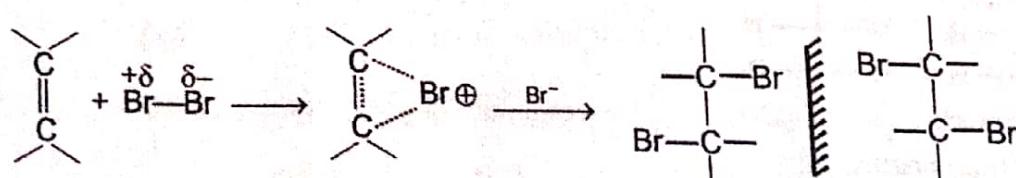
(ii) 1-Bromo-2-chloroethane

(iii) 2-Bromoethanol

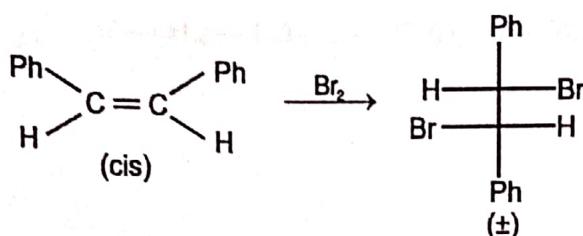
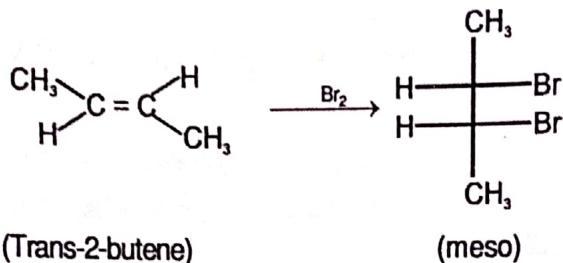
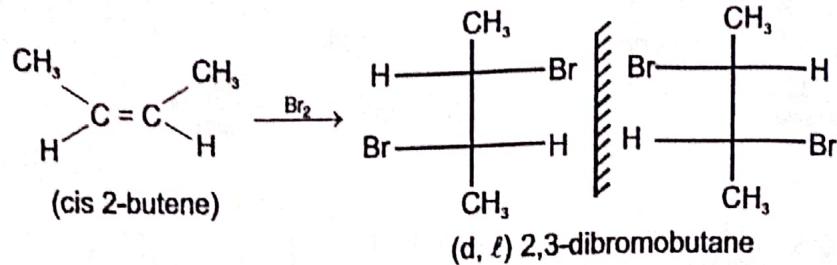


Formation of these three products clearly indicates about intermediate (A) thus addition of bromine water over alkene is electrophilic addition reaction.

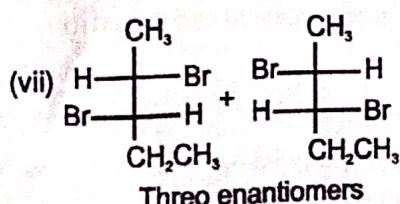
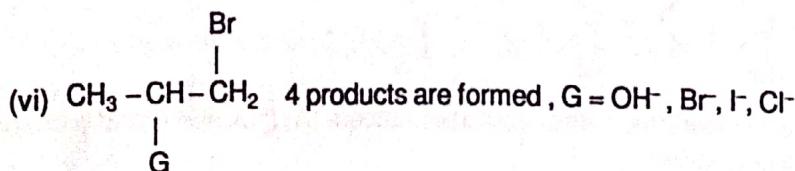
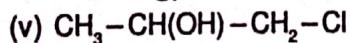
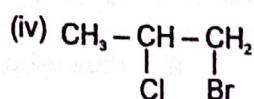
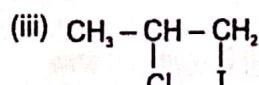
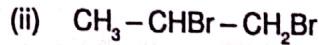
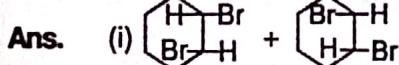
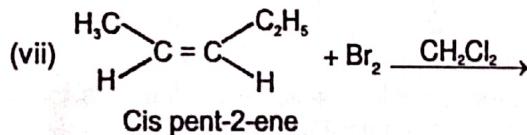
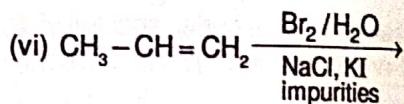
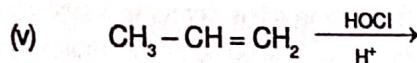
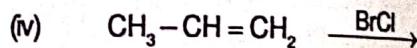
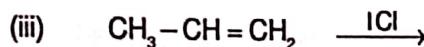
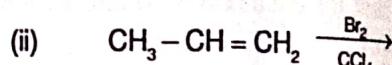
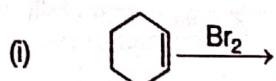
This addition always takes place in trans manner because of bulky nature of bromine atom in bromonium, which is a cyclic bridge intermediate. Cyclic bridge intermediate is not classical carbonium ion.



Ex.

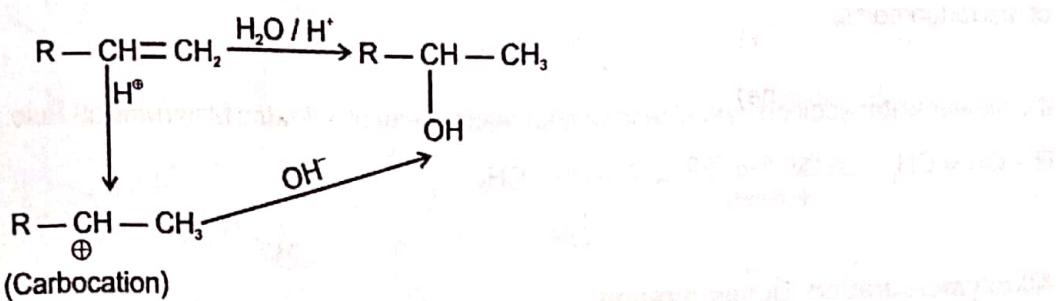


Que. Predict the product for the following :-

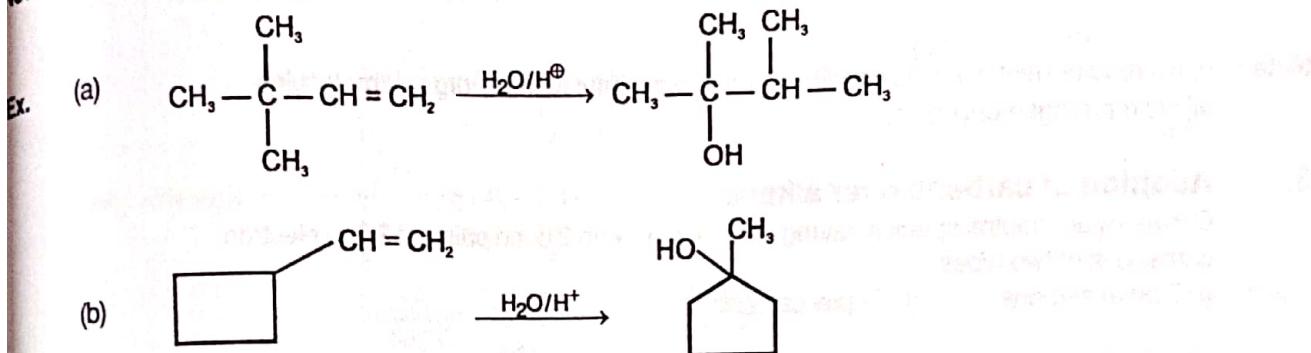


Hydration of alkene :

It is electrophilic addition reaction and proceeds via carbocation.



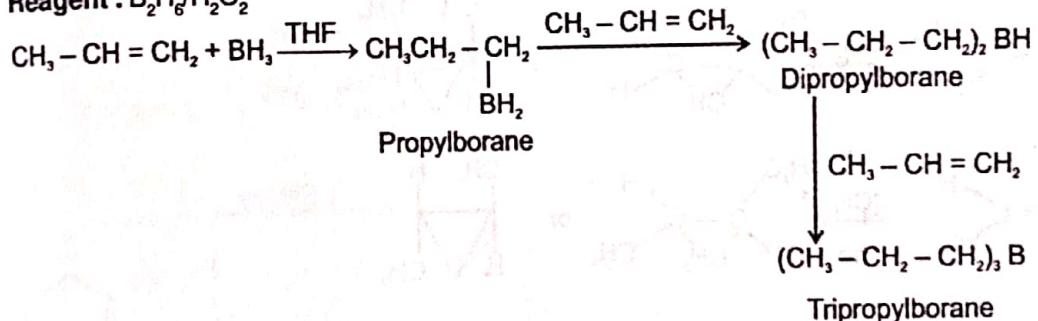
Note : Since this reaction proceeds via carbocation hence we get rearranged product.



4. Hydroboration of alkene :

It is used to get primary alcohol from alkene. Addition of borane on alkenes. In this reaction, the addition of electrophilic Borane & the nucleophilic H^- take place in one steps i.e. it is concerted reaction. No intermediate is formed.

Reagent : B_2H_6 / H_2O_2

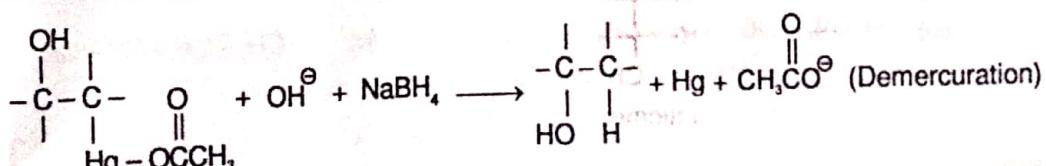
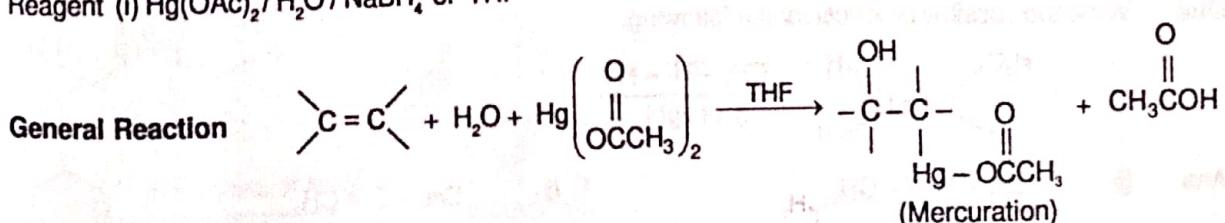


Note : (i) During process of addition H-comes from BH_3 and OH comes from H_2O_2 .
(ii) This addition looks like anti-markownikoff's addition of water over alkene.

5. Oxymercuration demercuation of alkene

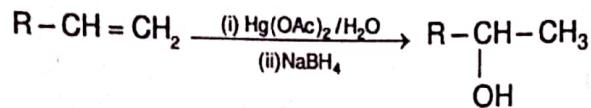
Alkenes react with mercuric acetate in a mixture of water and tetrahydrofuran (THF) to produce (hydroxyalkyl) mercury compounds. These can be reduced to alcohols with sodium borohydride and water.

Reagent (i) $Hg(OAc)_2 / H_2O / NaBH_4$ or THF

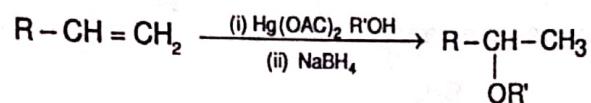


In the oxymercuration step, water and mercuric acetate add to the double bond; in the demercuration step, sodium borohydride reduces the acetoxymercury group and replaces it with hydrogen. The net addition of H and -OH takes place with Markovnikoff regioselectivity and generally takes place without the complication of rearrangements.

It is similar water addition over alkene without rearrangement following Markownikoff Rule.



Alkoxymercuration-Demercuration :



Note : (i) No requirement of acidic condition, which is harmful to many organic molecules.
(ii) No rearrangement occurs.

6. Addition of carbene over alkene :

Carbenes are neutral species having carbon atom with 2 bond pair and 2 free electron carbene is of two types.

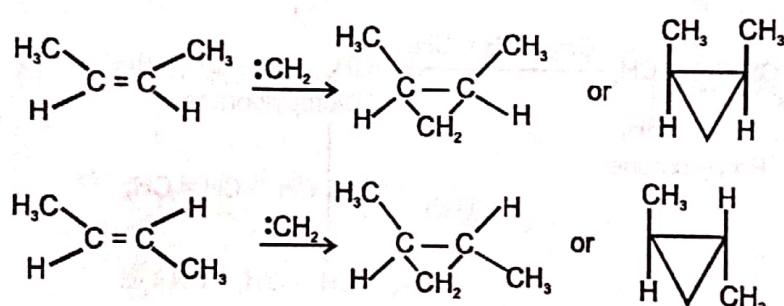
- (i) Singlet carbene (ii) Triplet carbene

Singlet Carbene : Here two electrons are present with opposite spin.

Triplet Carbene : It is bivalent free radical and two electrons have same spin.

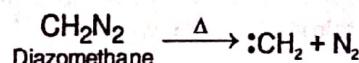
Note : Addition of singlet carbene over double bond is stereospecific.

Example : cis-alkene gives cis-product and trans-alkene gives trans product.

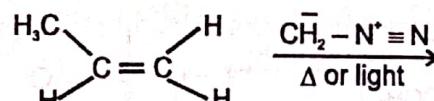


Note :

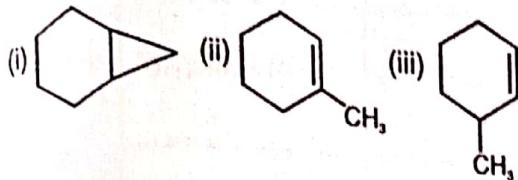
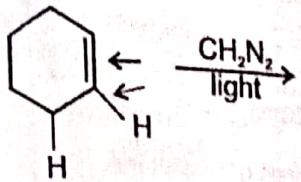
1. Methylene is simplest carbene uncharged reactive intermediate, where carbon atom has two bonded and two non-bonded electrons.
2. It is electrophile and added to electron rich π-bond of alkene.
3. It is obtained by heating diazomethane



Que. Write the possible products for the following.

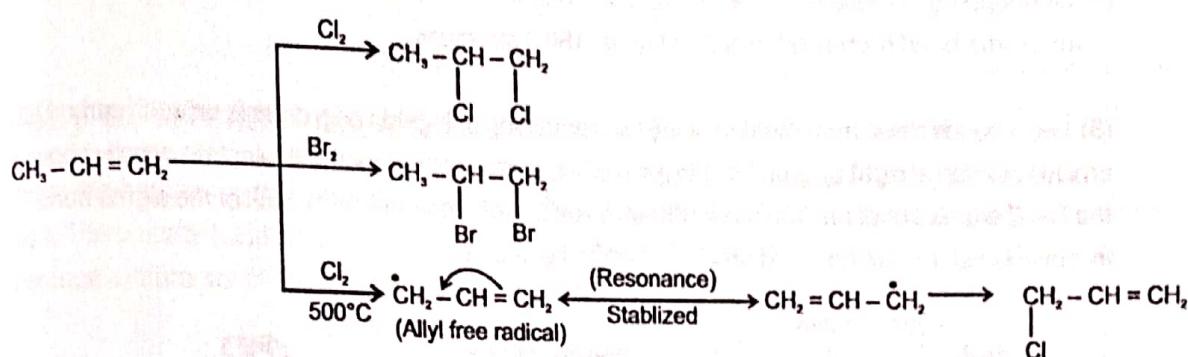


Write any three products obtained during carbene insertion over cyclo hexene

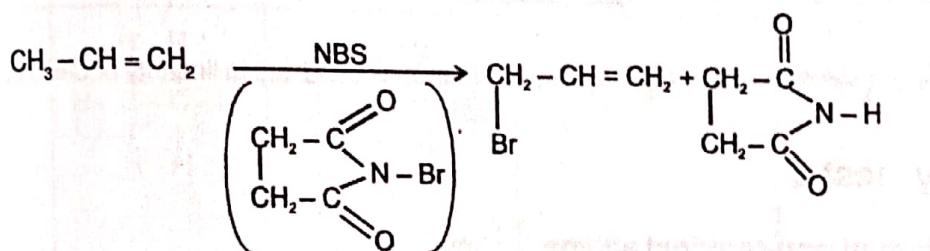


Allylic substitution over alkene :-

It takes place at high temperature by reaction of Cl_2/Br_2 over alkene.



Note: Allylic substitution at low temperature is carried out with NBS.



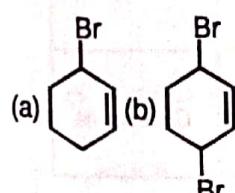
Que.



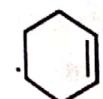
(a) NBS

(b) NBS (2eq.)

Ans.



Que.



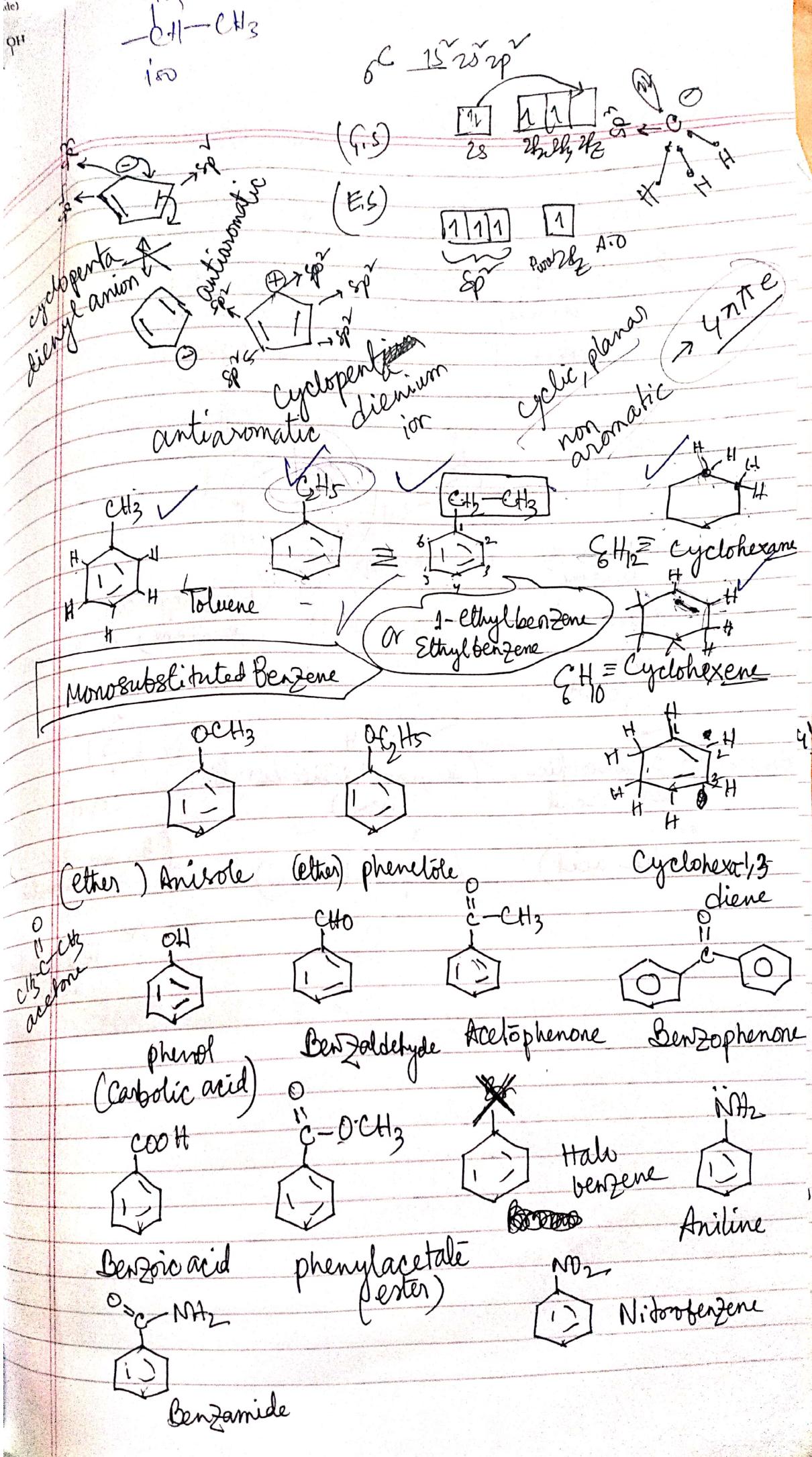
(i) 2 moles of NBS

(ii) 2 moles of al. KOH

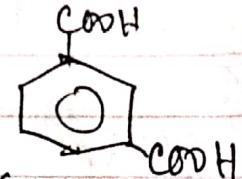
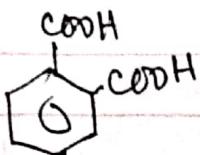
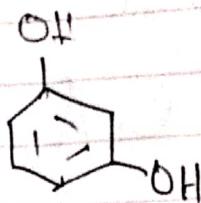
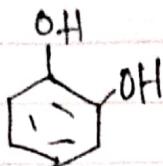
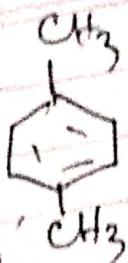
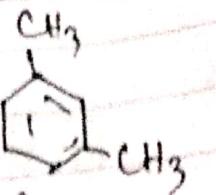
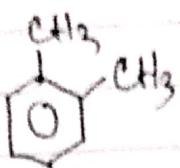
Product

Ans.





Disubstituted Derivative



or
Phthalic acid)

or
(Isophthalic acid)

(Benzene-1,4-Dicarboxylic
acid)
or
Terephthalic
acid.