

Chapter: 16

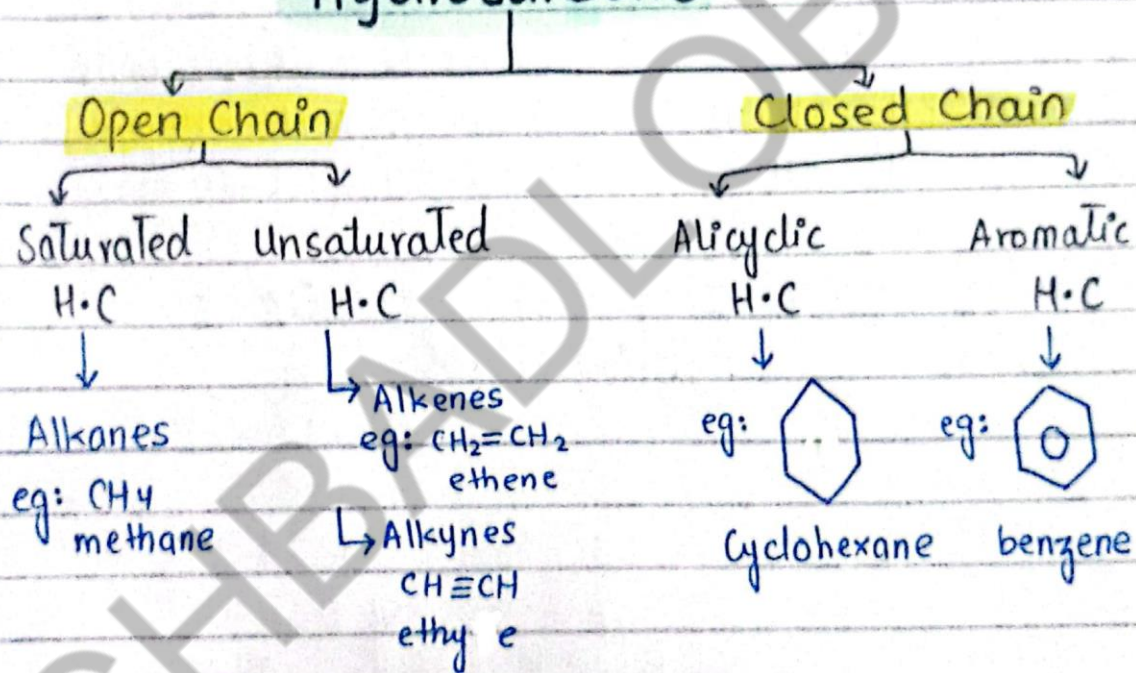
Hydrocarbons

Q1. What are Hydrocarbons? How are they classified?

Hydrocarbons: Compounds containing carbon and Hydrogen only are called Hydrocarbons.

Catenation: Self-linking ability of element to form long chains. eg $C-C-C-C$ unlimited

Hydrocarbons



Open chain H.C

/ Aliphatic / Acyclic

Hydrocarbon in which C-atom are attached to each other in form of open chains.

TYPES:

- Saturated H.C
- Unsaturated H.C

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Scanner

Saturated H.C

Definition

H.C in which there is all single bond b/w C-atom.

Hybridization

All Carbons are sp^3

Type of Reaction

Undergo Substitution rxn

Example

1. CH_4 Methane
2. CH_3-CH_3 Ethane
3. $CH_3-CH_2-CH_3$ propane

Unsaturated H.C

H.C in which there is $C=C$ or $C\equiv C$ bond b/w C-atom.

$C=C$ sp^2 $C\equiv C$ sp

Undergo addition rxn

1. $CH_2=CH_2$ ethene
2. $CH\equiv CH$ ethyne
3. $CH_2=CH-CH_3$ propene

Trick for Hybridization:

Group

Hybridization

1. s
2. sp
3. sp^2
4. sp^3

* $CH_2=CH_2$
= & $\equiv$ counted
as 1 Grp.
* lone pair is
counted as 1 Grp.

Another
trick for sp^3
Hybridization

eg: CH_4

→ Valency of central
atom + attached
atom

→ $4 + 1(4) \Rightarrow 8$

→ Divide by 2 ($2 \div 8$)
= 4 (sp^3)

Closed chain H.C

/cyclic / Ring

Hydrocarbons in which C-atom are attached with each other to form ring.

Types: /non-aromatic

Alicyclic H.C

Close chain H.C without benzene ring

Definition

Close chain H.C containing at least one benzene ring.

Aromatic H.C

Alternative Name

Non-benzoid

Benzoid

Huckel Rule

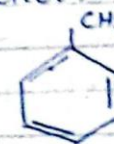
Do not obey

Obey Huckel rule

Example



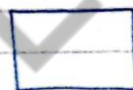
• benzene



• toluene



• cyclopropane



• Cyclobutane



• Cyclo-pentane



• Cyclo-hexane



• Naphthalene



• Anthracene

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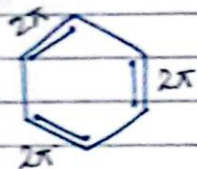
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Huckel Rule:

$$4n + 2 = \pi e^-$$

$n \rightarrow 1, 2, 3 \dots$ (whole digit)

Q. Why benzene is aromatic?



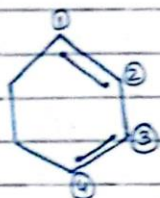
$$4n + 2 = 6\pi$$

$$4n = 6 - 2$$

$$4n = 4$$

$$n = 1$$

Obey huckle rule



1,3 cyclohexadiene

$$4n + 2 = \pi e^-$$

$$4n + 2 = 4$$

$$4n = 4 - 2$$

$$\frac{4n}{4} = \frac{2}{4}$$

$$n = 0.5$$

• does not obey
• Non-aromatic

Q. Why benzene is aromatic Hydrocarbon?

Benzene is an aromatic Hydrocarbon because it obey Huckel Rule. Originally, benzene was considered aromatic because of its smell. It has an aromatic odour. Huckel rule states that, a molecule is aromatic if it is cyclic, conjugated and has $(4n+2)\pi$ electrons.

Calculation:

$$4n + 2 = \pi e^-$$

$$4n + 2 = 6\pi e^-$$

$$4n = 6 - 2$$

$$4n = 4$$

$$n = 1$$

• it obeys Huckel Rule.



$$2+2+2 = 6\pi e^-$$

Alkane

Paraffins (inert)

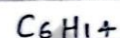
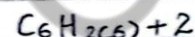


$\hookrightarrow$ Saturated

$\hookrightarrow$ Substitution rxn



$\hookrightarrow$ Hexane



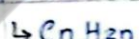
Alkenes

Olefins



$\hookrightarrow$ Unsaturated

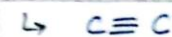
$\hookrightarrow$ Addition rxn



$\hookrightarrow$ Hexene



Alkynes

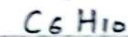


$\hookrightarrow$ Unsaturated

$\hookrightarrow$ Addition rxn



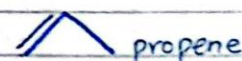
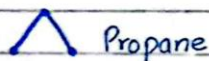
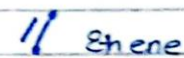
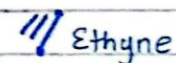
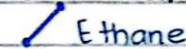
$\hookrightarrow$ hexyne



Homologous Series:-

Series of compound in which each member differ by $-CH_2$ group.

Structure



Cyclo-hexane

Alkyl Group (R):-

When one H is removed from any alkane group form is called alkyl group / alkyl radical. $-R$ $C_n H_{2n+1}$

Rule: Replace ane $\rightarrow$ yl

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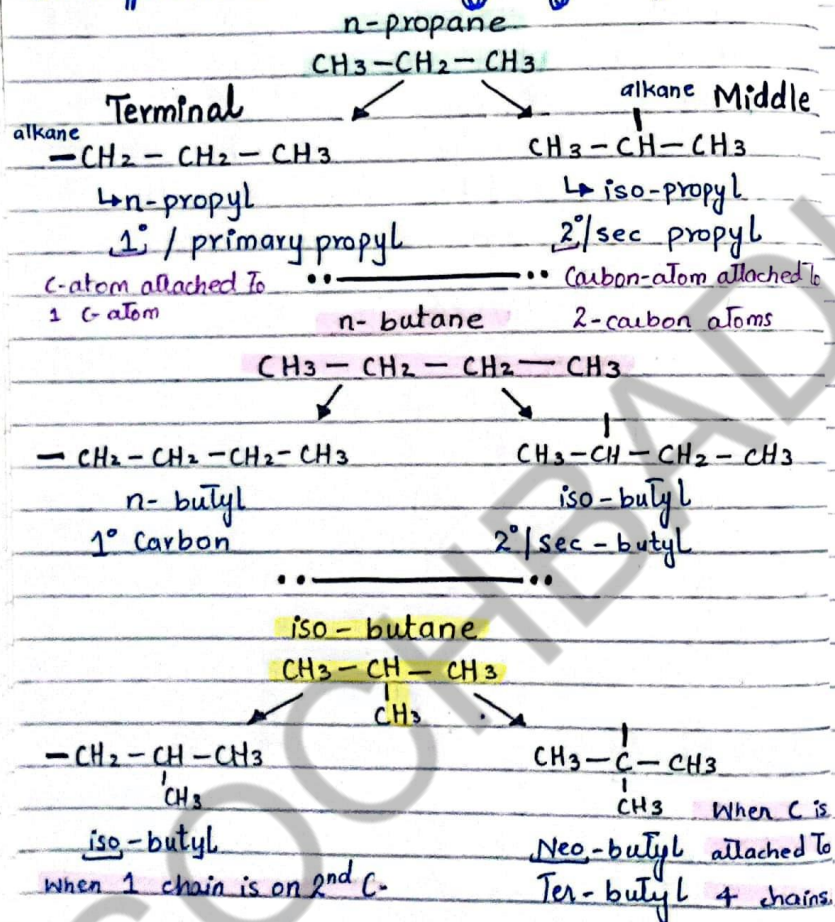
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Homologous Series of alkyl groups

Name	M.F	St. formula	Abbreviation
Methyl	-CH ₃	$\begin{array}{c} \text{H} \\ \\ \text{C}-\text{H} \end{array}$	Me
Ethyl	-C ₂ H ₅	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{C}- & \text{C}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$	Et
n-propyl	-C ₃ H ₇		n-Pr
n-butyl	-C ₄ H ₉		n-bu

Important alkyl groups:-



CH₂=CH-
Vinyl group (CH removed from ethane)

Common Names of alkanes / Paraffins

- ① CH₄ Marsh gas (found in marshes)
- ② CH₃-CH-CH₃ iso-butane
- ③ CH₃-CH-CH₂-CH₃ iso-pentane
- ④ CH₃-C-CH₃ neo-pentane

Quick Rules

- When branch is on 2nd Carbon it is called iso.
- When 2 branch is on 2nd Carbon it is called Neo.
- Primary → Carbon connected to 1 Carbon.
- Sec → Carbon connected to 2 Carbons.
- Tertiary → Carbon connected to 3 C.
- Branch should be from 2nd Carbon.

IUPAC Naming: 197

International union of pure & applied chemistry.

1. CH₃-CH₂-CH₂-CH₂-CH₃
n-pentane

Tips → Only use in alkane when there is no branch & straight chain.

2. CH₃
CH₂-CH₂-CH₂-CH₂-CH₃
n-hexane

Tips → C - which can be written in straight line is a part of long chain.
→ Longest chain containing larger number of C-atoms is selected which can be straight, bend etc.

- The side which has more branches we will start numbering C-atom from there.
- For more than one similar group we use Di, Tri, Tetra.
- group on same C. no will be repeated twice.

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→ Steps to Name:

- Locate the longest Carbon chain.
- Name the parent chain.
- Figure out the ending.
- Number your C-atoms.
- Name the side groups.
- Put in alphabetical order.

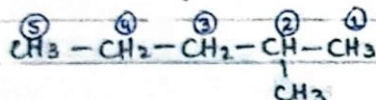
→ Order:

* Remember!

③ Number → group → parent chain → 2, 2

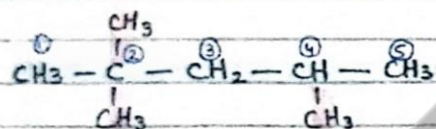
ex: 2-Methyl pentane → 2-Methyl

→ 2-Methyl

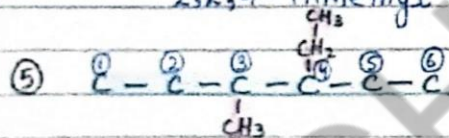


Tip → Start numbering from that side which has more branches.

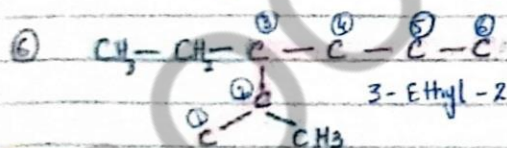
④ More than one same branches



2,2,4-Trimethyl pentane

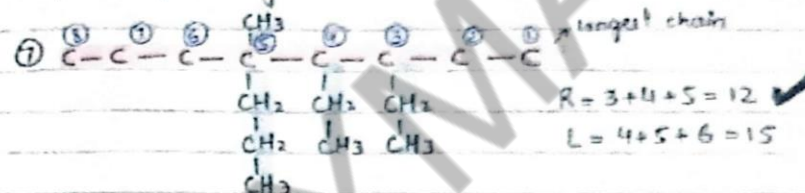


3-Ethyl-4-Methyl hexane



3-Ethyl-2-methyl hexane

Tip → Prefer long chain with more substituents.



3,4-Diethyl-5-methyl-5-n propyl octane

Physical Properties of Alkane

- ① C₁ - C₄ Colourless, odourless gases
C₅ - C₁₇ Colourless, odourless liquid
C₁₈ - ... Solid (waxy solid)

② Alkanes are non-polar due to electronegativity difference.

③ Soluble in non-polar solvents.

④ M.P & B.P increases with increase in no. of Carbon atoms.

⑤ Straight chain has more B.P as compared to branch chain.

⑥ M.P, B.P & density ∝ Carbon
Solubility ∝ $\frac{1}{\text{C-atom}}$ ⑦ B.P increase by adding CH₂ group ⇒ 20-30°C

* n-chain has high boiling point due to strong LDF & surface area whereas iso-chain has weak forces so have low boiling point.

Isomerism in alkane:-

The compounds which have same molecular formula but different structural formula are called isomers. This phenomenon is known as isomerism.

Note: Methane, Ethane, propane has no isomers bcz they have only 1 possible structure.

Isomers of butane: C_4H_{10}

- ① $CH_3 - CH_2 - CH_2 - CH_3$ n-butane
- ② $CH_3 - \underset{\substack{| \\ CH_3}}{CH} - CH_3$ iso-butane (C.N)
2-Methyl propane (IUPAC)

Isomers of Pentane: C_5H_{12}

- ① $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$ n-pentane
- ② $CH_3 - \underset{\substack{| \\ CH_3}}{CH} - CH_2 - CH_3$ iso-pentane (C.N)
2-Methyl butane (IUPAC)
- ③ $CH_3 - \underset{\substack{| \\ CH_3}}{\underset{\substack{| \\ CH_3}}{C}} - CH_3$ Neo pentane (C.N)
2,2-Dimethyl propane (IUP)

Relative stability of alkane

Branch chain alkane are more stable than straight chain.

eg: 2-Methyl propane is more stable than n-butane.

Reactivity of alkane

↓
Paraffin

Parrum (little)

Affin (reactivity/affinity)

Alkane

↳ do not react with

Acid, base, oxidizing agent, reducing agent

but on suitable condition they react and give

(i) Thermal & Catalytic reaction

(ii) Substitution rxn

↳ Why alkanes are less reactive?

Alkanes are paraffins meaning less reactive bcz

- They have sigma bonds which is very strong as electrons are tightly held and it requires large energy to break.

- They are non-polar due to less electronegativity difference between C-H.

- They have equal sharing of e^- making it non-polar.



① Inertness of sigma bond
linear overlap
sigma bond

② Non-polar bond

C-C

$$2.5 - 2.5 = 0$$

C-H

$$2.5 - 2.1 = 0.4$$

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↳ diff of electro-negativity is small but under suitable condition two rxns are possible 3.

(1) Thermal & Catalytic rxn

(2) Substitution rxn

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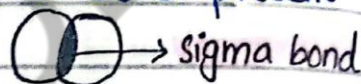
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'SLO-BASED QUESTIONS'

1. Why alkanes are less reactive?

Alkane (paraffins) are less reactive, this is bcz of the inertness of the sigma bond present b/w them.



• Alkanes are non-polar in nature due to less electronegativity diff b/w C-H bond and they have = sharing of electrons as well.

eg: $C = 2.5$, $H = 2.1$ $C-C = 2.5 - 2.5 = 0$

$C-H = 2.5 - 2.1 = 0.4$

2. Why alkanes are called paraffins?

The term paraffin means little affinity. Basically alkanes are stable bcz of their inertness, they are called so bcz bcz they have lesser affinity towards general reagents. It means that they do not react with acid, base, oxidizing & reducing agents but only on suitable condition they react.

nder
le.

3. Why branch chain alkanes are more stable?

Branching reduces the molecular surface area and so leads to a lowering of energy and hence increases stability.

eg: 2-Methyl propane is more stable than n-butane. Also, it's difficult to break the substituent as it contains sigma so we could say that branched chain alkanes are less reactive but more stable.

4. Why branched chain have lower B.P than linear chain?

The boiling point of branched chain alkanes are lower than linear chain. This is bcz of L.D.F (weak) present in the branched chains of alkanes.

The Surface area would be less & therefore they would have lower B.P. Linear chains have higher melting/boiling point due to better stacking and surface area contact.

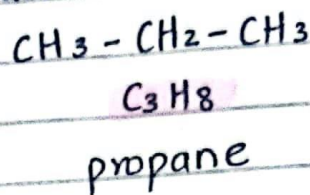
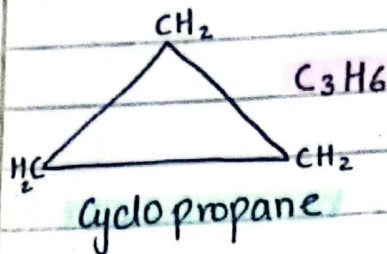
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→ Nomenclature of Cycloalkane:

- We use prefix **cyclo** • General formula C_nH_{2n}
- The rest of the rules are same as that of alkane



In cycloalkane
→ there is always
2H less than
straight chain
alkane.



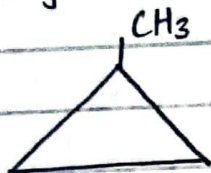
Cyclobutane



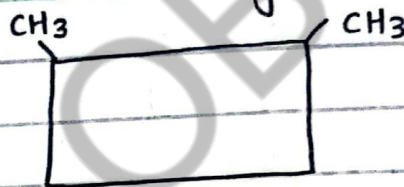
Cyclopentane



Cyclohexane



1-Methyl cyclopropane



1,2-Dimethyl cyclobutane

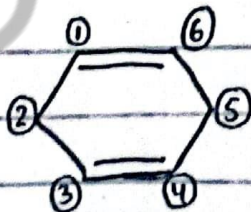
→ Physical Properties:-

- * London Dispersion forces
 - * M.P & B.P = low
- same as
alkane

→ Reactivity:-

Cycloalkane is also **less reactive** due To

- Sigma bond
- Non-Polar bond



Cyclo 1,3-hexadiene

or Cyclohexa-1,3-diene

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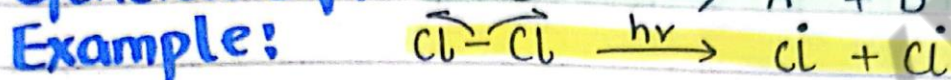
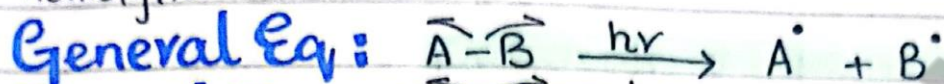
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BOND FISSION:

↳ Homolytic fission

When a chemical bond is broken in such a way that both of bonded atoms acquire equal electrons such fission is called homolytic.



↳ Heterolytic fission

When a chemical bond is broken in such a way that one of the bonded atom acquire both e^- s. such fission is heterolytic.



Q. What is a free radical?

It has

↳ odd no. of e^-

↳ Neutral charge

↳ Highly reactive

↳ Chain rxn

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↳ Radical Substitution Reaction:

Halogenation: (X) (F, Cl, Br, I)

Replacement of Hydrogen atom by Halogen is called Halogenation.

↳ Condition for Halogenation

Halogenation of alkane takes place in presence of

↳ Sunlight

↳ UV radiation

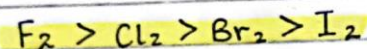
↳ High Temp

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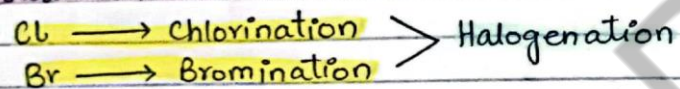
↳ Reactivity of Halogen:



⊙ For Halogenation Cl_2 and Br_2 are used.

⊙ F_2 and I_2 are not used.

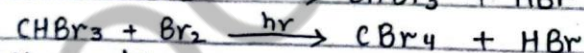
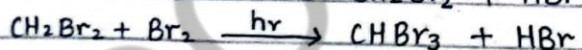
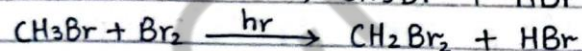
⊙ In case of F_2 reaction take place violently and in case of I_2 reaction is slow and reversible.



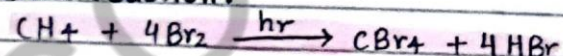
Steps:

1. **Initiation** → formation of free radical
2. **Propagation** → both side radical (R & P)
3. **Termination** → reactant radical

Reaction:

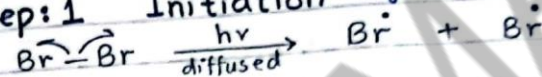


Overall reaction:

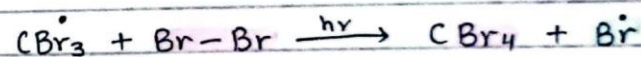
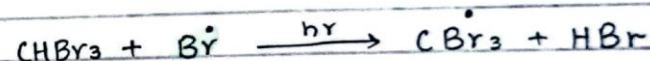
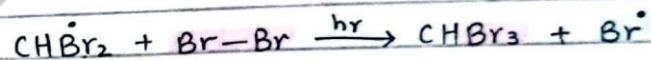
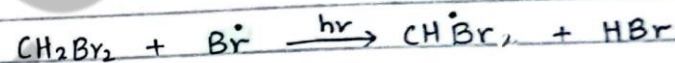
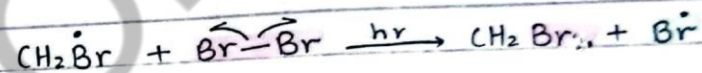
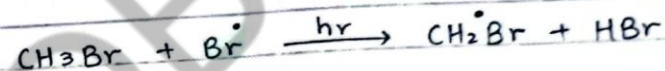
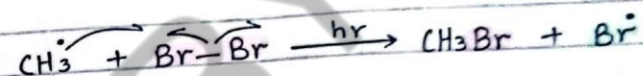
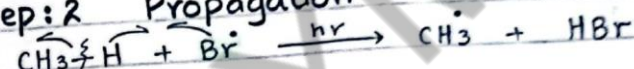


Mechanism:

Step: 1 Initiation (generation of free radical)



Step: 2 Propagation

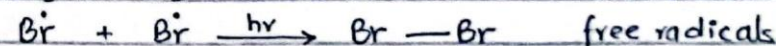
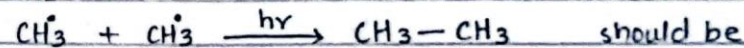
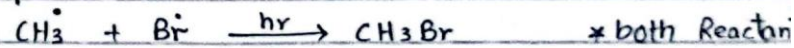


→ Whenever $Br-Br$ reacts, it is added to other.

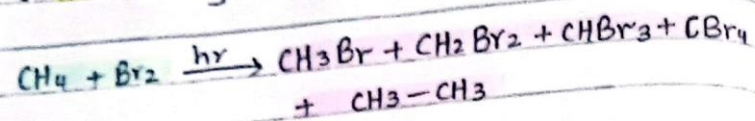
→ Whenever $Br\cdot$ reacts, it takes away H & form HBr making other comp free radical.

→ Use $Br\cdot$ and $Br-Br$ alternatively.

Step: 3 Termination



Q How many products are possible?



Oxidation

- Addition of Oxygen
ie more C-O bond.
- Removal of H
ie less CH
- Loss of electron
- Increase in O.S
 $\text{Cu}^0 \rightarrow \text{Cu}^{+2} + 2\text{e}^-$

Reduction

- Removal of Oxygen
ie less of C-O bond
- Addition of H
ie more CH
- Gain of electron
- Decrease in O.S
 $\text{Zn}^{+2} + 2\text{e}^- \rightarrow \text{Zn}^0$

Isomerism

Definition:

Different compounds having same Molecular formula but different structural formula & Physical properties are called isomers. This phenomenon is known as isomerism.

- Methane, ethane, propane has no isomers.
- Butane has two isomers.
- Pentane has three isomers.
- Hexane has five isomers.

Note:

As No. of C-atom increases, no. of

Types:-

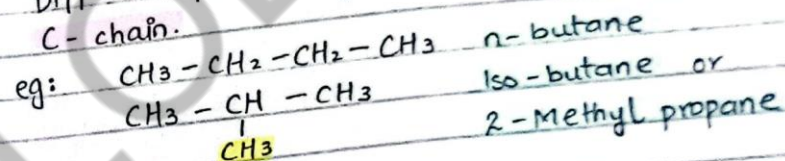
1) STRUCTURAL ISOMERISM:

Different compounds having same M.F but diff structures are called structural isomers & Phenomenon is called structural isomerism.

Sub-types:

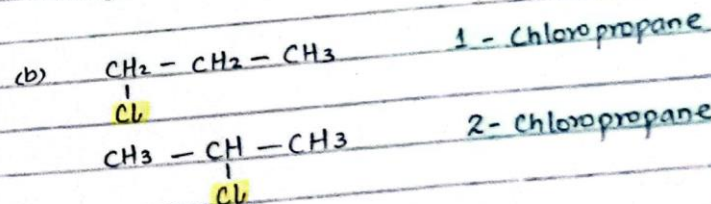
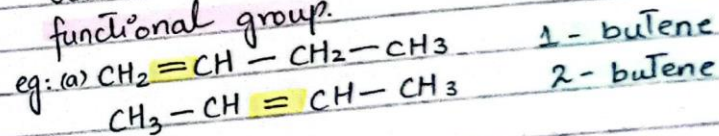
i- Chain isomerism:

Diff comp having same M.F but diff C-chain.



ii- Position isomerism:

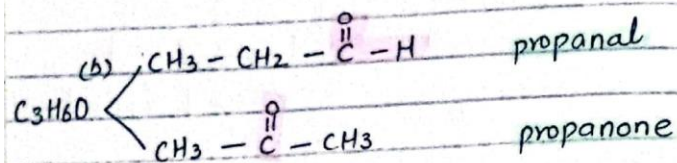
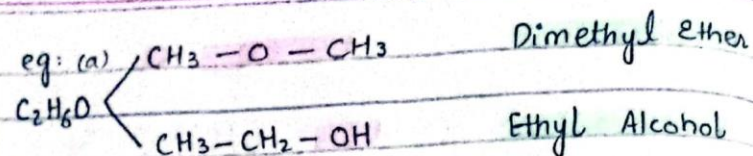
Same M.F but diff position of same functional group.



iii- functional group isomerism:

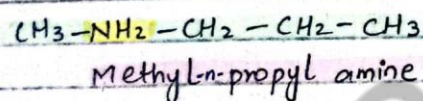
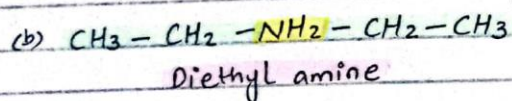
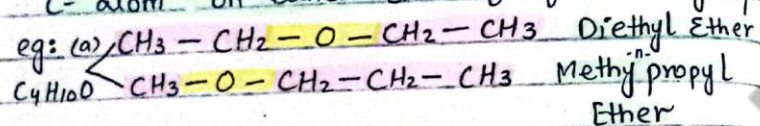
Same M.F but diff functional group.

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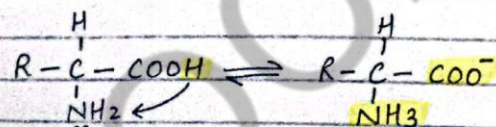
4. Metamerism:

Same M.F but unequal distribution of C-atom on either side of functional group.

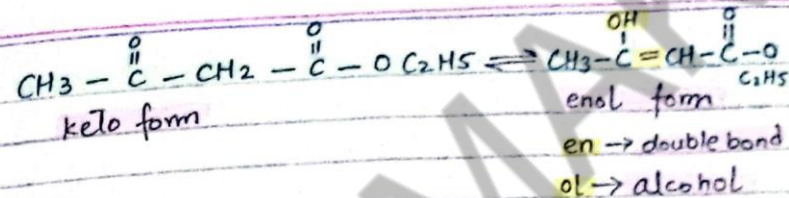


5. Tautomerism:

Type of isomerism in which 1 isomer is converted in other isomer due to migration of H ion are called tautomer & phenomenon is called tautomerism.



zwitter ion (Internal salt)



2) Stereo-Isomerism:

Different compounds having same Molecular formula but diff arrangement or orientation of atoms or groups in the 3D space are called stereo isomers. This phenomenon is known as stereo-isomerism.

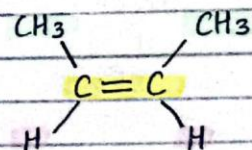
Sub-types:

1. Geometrical Isomerism:

Same M.F but diff position of identical group in space.

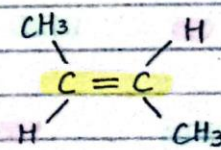
Cis form: When two identical groups lie on same side of = bond.

Trans form: When two identical groups lie on opposite side of = bond.



Cis-2-butene

Unstable $\mu \neq 0$



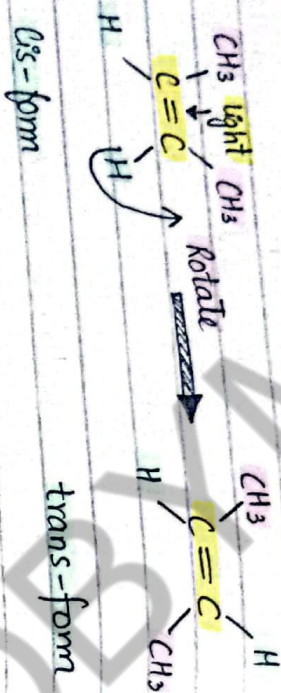
trans-2-butene

Stable - $\mu = 0$

Q. Why dipole moment of trans is zero?

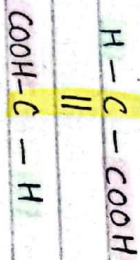
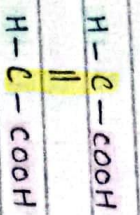
Bcz two bulky grps lie on opposite side of = bond so steric repulsion is less & dipole moment = 0

* They are interconvertible into each other in presence of light / high temp bcz of π bond breaking & C-C will rotate.



Conditions for geometrical isomerism:

- (a) Two groups attach with same carbon must be different.
- (b) C-C bond should be not rotate about its axis.



cis-2-butene-1,4-dioic acid

Trans-2-butene-1,4-dioic acid

Q. Why 1-butene does not form cis and trans isomerism?

In the case of 1-butene, its structure is $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_3$. 1-butene will not have cis-trans isomerism the reason for this is CH_2 & CH_3 are not identical groups.

Reasons:

1. Position of double bond:

In 1-butene, the double bond is located b/w the 1st & 2nd C-atoms in the chain (1-position)

2. Lack of different groups:

For geometric isomerism to occur, each carbon in the double bond must have two diff groups attached. In 1-butene, the first carbon of the double bond has two hydrogen atoms attached ($\text{H}_2\text{C}=\text{}$), and the second carbon is connected to a hydrogen atom & an ethyl group (CH_2CH_3).

Conclusion:

Since the 1st C-atom in the double bond has two identical hydrogen atoms attached to it, it cannot form cis & trans isomers.

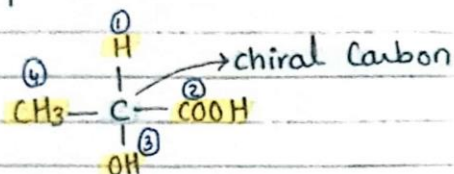
Optical Isomerism:

Condition:

- 1- atom should have chiral Carbon.
- 2- Should not have plane of Symmetry.

1) Chiral center / chiral Carbon Asymmetric

Carbon atom which is bonded with 4 different groups or atom is called chiral carbon.



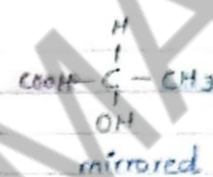
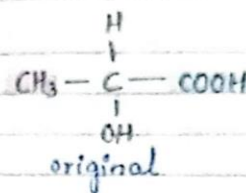
2) Plane of Symmetry:

Plane which divides an object into symmetrical halves is called plane of symmetry.

Example: A person or hat has plane of Sym.
A person hand & gloves lack plane of Sym.

Conditions for chiral molecule:

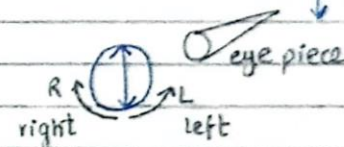
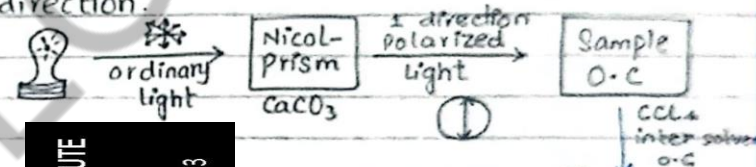
Chiral molecule has at least an asymmetric Carbon and does not have plane of symmetry and are not superimposable on their mirror image.



3) Optical activity:



Solution of some O.C have ability to rotate plane polarized light in opposite direction.



Dextro-rotatory (+) isomer clockwise	Levorotatory (-) isomer anticlockwise
--	---

Optical isomerism:

Optically active compound can exist in 2 isomeric forms which rotate plane polarized light in opposite direction.

→ Dextrorotatory & Levorotatory are called Enantiomer.

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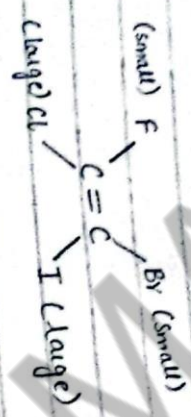
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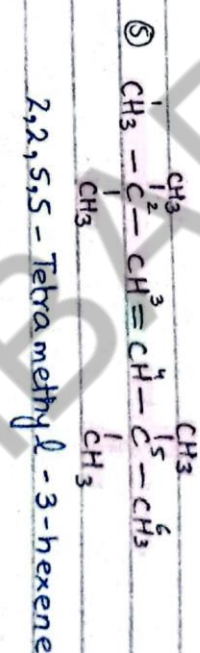
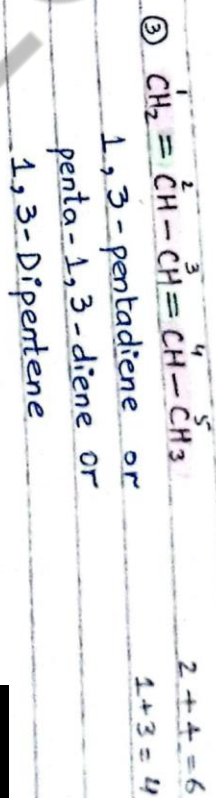
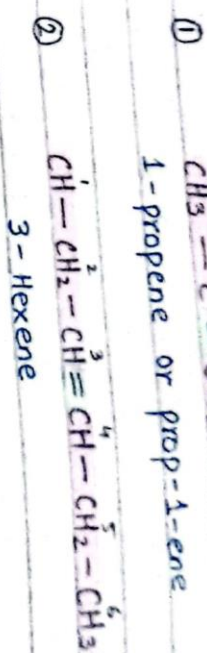
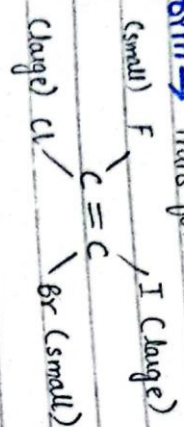
→ Alkene

Nomenclature:-

Z-form → When 4 diff group



E-form → Trans form



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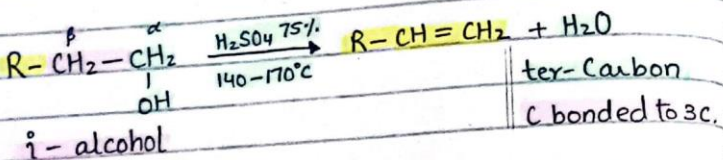
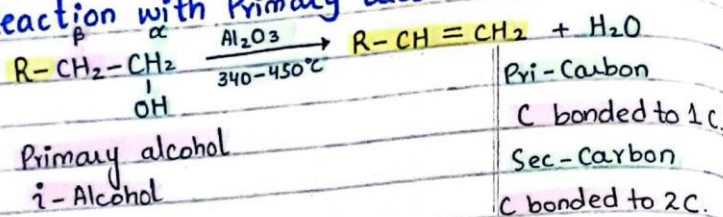
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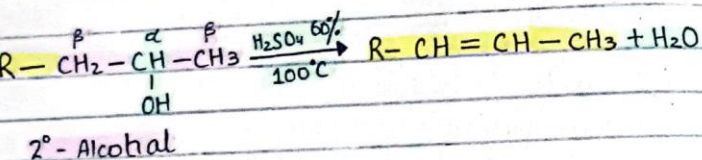
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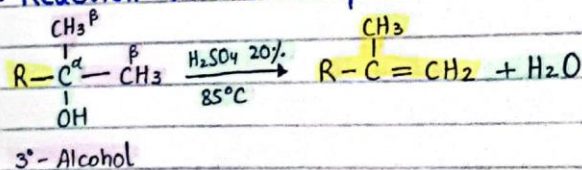
Reaction with Primary alcohol:



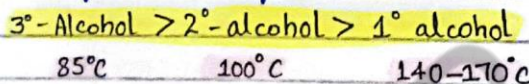
Reaction with Secondary Alcohol:



Reaction with tertiary Alcohol:



Order of Reactivity:



due to stability of Carbo-cation, there are 3 branches to support C therefore tertiary alcohol more reactive.

2. Dehydrohalogenation:

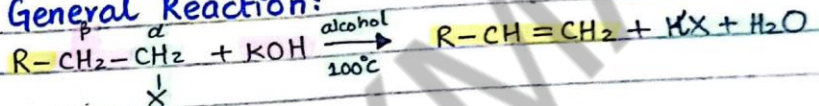
"Removal of H & X from alkyl halide"

Reagent → participate in Rxn

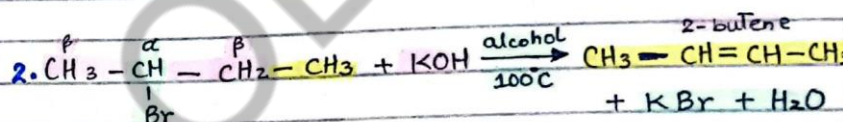
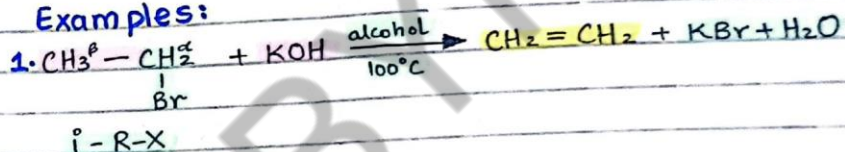
* Md Cat *

Alcoholic KOH → Elimination
Aqueous KOH → Substitution

General Reaction:



Examples:



SLO Question

- How will you prepare alkene from dehydrohalogenation?
- Write 2 methods for preparation of alkene?
- How will you obtain 1-butene from
 - alcohol
 - alkyl Halide

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Relative stability:

1. Degree of Substitution

alkyl group $\propto$ stability

* Highly alkylated

Highly alkylated alkene are more stable e.g.

Tetra > tri > Di > Monosubstituted

* Branch increase B.P increase

Branched structure is more stable bcz its B.P will be high and it will be difficult to break the bond.

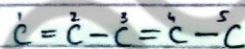
2. Stereochemistry

Trans alkene is more stable than cis alkene due to reduced steric hindrance (bulky groups are in opposite direction)

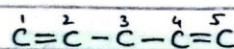
3. Conjugation (alternate C-C=C-C=C) ^{conjugated}
conjugated alkene are more stable than isolated alkene.

(C=C-C-C=C) $\rightarrow$ Isolated

$\rightarrow$ Delocalization of π bond

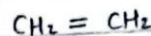


more stable



isolated

Structure of alkene:-



- sp^2 hybridization
- 1 sigma & 1 π -bond
- 1s & 2p orbital overlap

M.C.Q.

Alkane C-C

1.54 Å

Alkene $\text{CH}_2=\text{CH}_2$

1.34 Å

$\text{C}=\text{C} \rightarrow e^- \text{ density } \uparrow$

Preparation of alkene

Saytzeff's Rule: (Elimination)

β Carbon that has less H, H will be removed & = bond will be formed on that carbon.

1. Dehydration of Alcohol:-

"Removal from alcohol of H_2O "

Dehydrating agents:

- Al_2O_3 Alumina
- H_3PO_4 Phosphoric acid
- P_4O_{10}
- P_2O_5

• $\text{H}_2\text{SO}_4 \rightarrow$ best dehydrating agent for alcohol bcz it can tell reactivity order of alcohol.

α -Carbon C-atom with OH

β -Carbon C-atom bonded to α -carbon

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4. Why alkene are more reactive than alkane?

$C=C$ $\frac{1}{\pi}$
More diffused bond
(more e^- density)

π -bond weak

Less amount of Energy is required to break bond.

$C-C$

less diffused bond

σ -bond strong

More amount of Energy is required to break bond.

Electrophilic addition Reaction of alkene:-

Electrophile

Electron loving

$E^+ \rightarrow$ cation

$\rightarrow$ Electron deficient

$\rightarrow BF_3$ B^+

Nucleophile

Nucleus loving

$Nu^- \rightarrow$ Anion

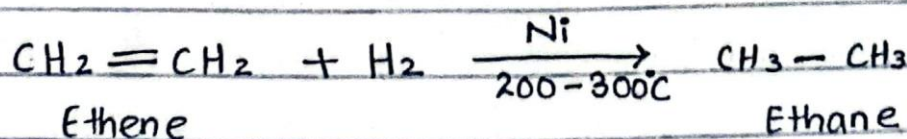
$\rightarrow$ Electron rich

$\rightarrow$ Mostly bases OH^-

$\downarrow$ (preparation of alkane)

1. Hydrogenation:- (Addition of H_2)

"Addition of Hydrogen molecule H_2 in the molecule of alkene"

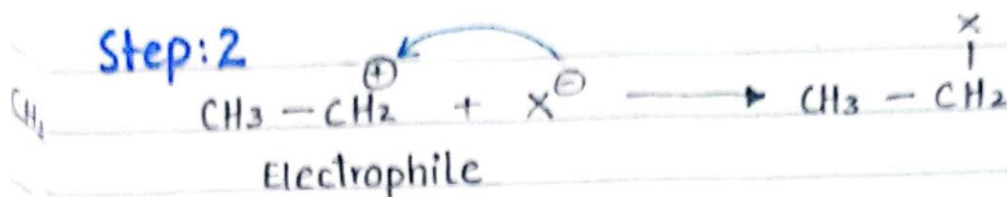


Mdcat

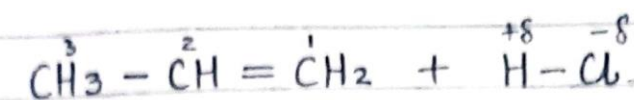
$\rightarrow$ It is always an Endothermic rxn (Bond breaking)

$\rightarrow$ Veg ghee prepared from veg oil $\quad 1 \text{ bond releases } -120 \text{ KJ/mol}$

Step: 2

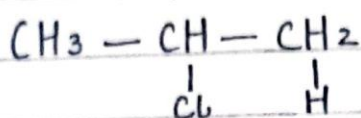


Markownikov's Rule :- (for Addition Rxn)



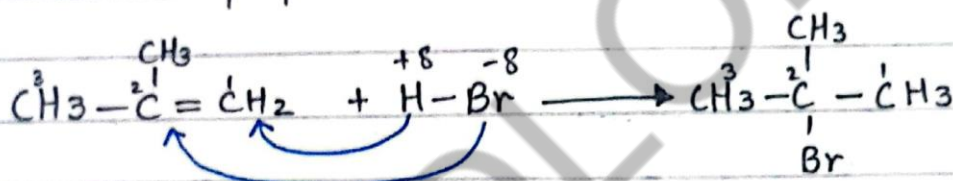
Unsymmetrical alkene

1-propene



2-Chloro propane

- δ will go
towards =
Carbon which
has less H.



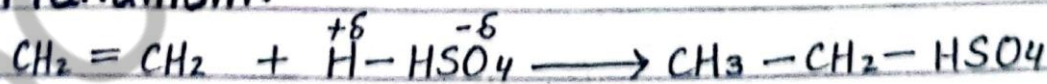
2-methyl-1-propene

2-bromo-2-methyl
propane

3. Hydration:

Addition of H_2O to alkene molecule is called hydration.

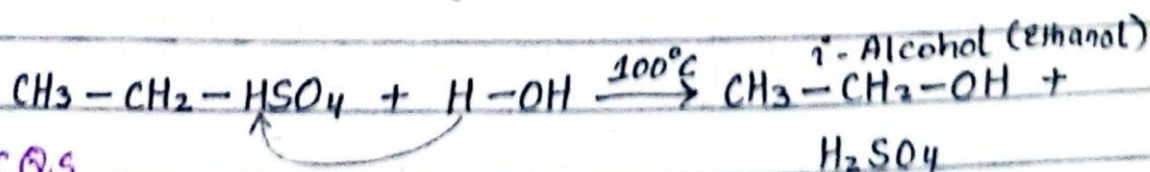
↳ Alkene does not dissolve in water so H_2SO_4 is added to dissolve it

Mechanism:

Ethene

Conc.

Catalyst

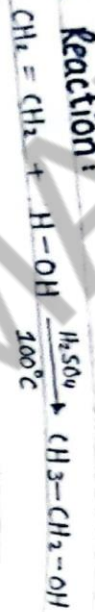
alkyl Hydrogen
Sulphate (intermediate)

1-Alcohol (ethanol)

MCQs

Hydration of alkene produces alcohol.

Overall Reaction:



2-propanol

2-Hydroxypropane

Conversion:

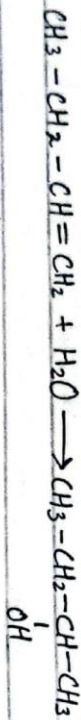


cyclohexane

1,3,5-cyclohexatriene



butene



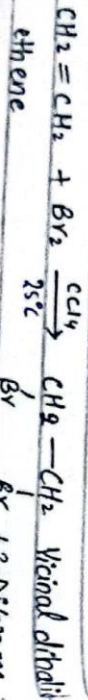
4: Halogenation (Test for unsaturation)

"Addition of halogen in the molecule"

→ Alkene halogenation takes place in the presence of sunlight.

→ Alkene halogenation in solvent CCl_4 .

→ Halogenation of alkene produces vicinal dihalide.



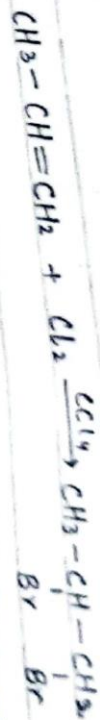
ethene

Br

Br

1,2-Dibromomethane

* $\text{C}-\overset{\text{Br}}{\text{C}}-\text{Br} \longrightarrow$ Geminal (1 C has two Halogens)

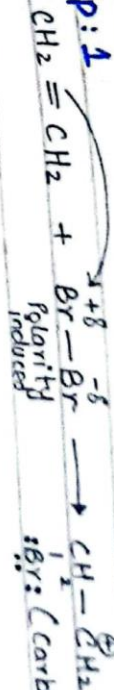


Propene

1,2-Dibromopropane

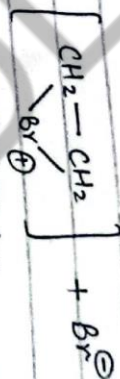
→ Mechanism:

Step: 1



* Br^- Carbo cation

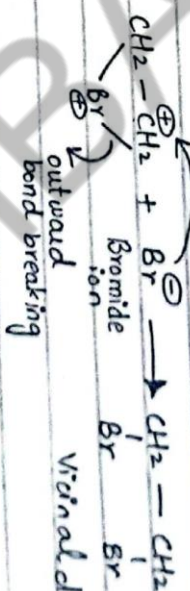
* +8 along on left side Br.



bromonium ion intermediate

* $\text{Br}^- \rightarrow$ Bromide ion

Step: 2



Vicinal dihalide

* If Br colour disappears, it means double bond is present. Start → brown End → colourless

* Saturated (single bond) → No change in colour

Conversion: 2-butene → 2,3-Dibromobutane

* Halogenation



5. Halohydratation:-

"Addition of hypohalous Acid (HOX) is called halohydratation"

⇒ Water as solvent act as a reactant, it can be called as reagent.

generally,

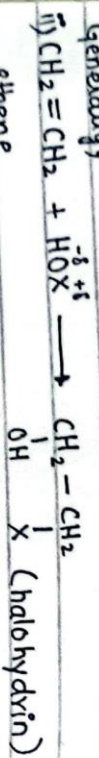


Q. How will you produce Halohydrin by using ethene?

Q. How will you produce chlorohydrine by using ethene?



Generally,

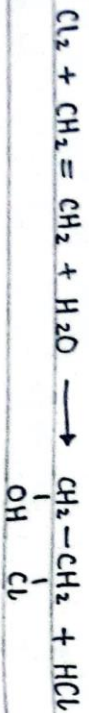


ethene



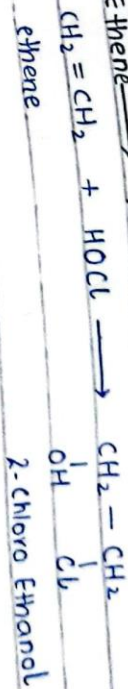
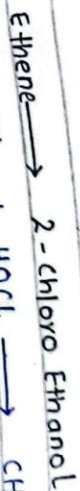
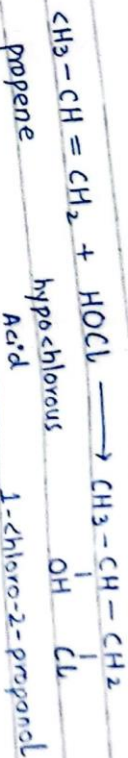
ethene

General overall rxn:



* Similarly bromohydrin, Iodohydrin etc

Conversion:

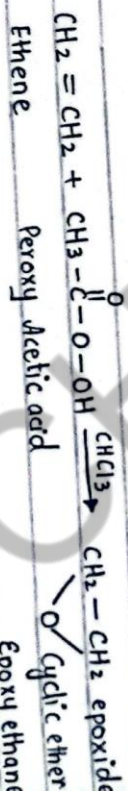


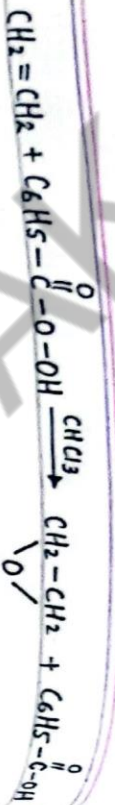
6. Epoxidation:-

↳ Epoxidation of alkene produces epoxy alkane

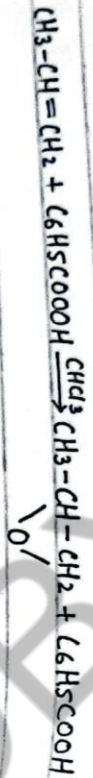
↳ Peroxy Acid → Peroxy Acetic Acid

↳ Peroxy Benzoic Acid





Conversion:

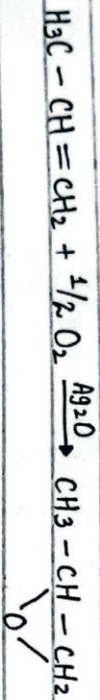


Q. How will you produce ethylene epoxid or ethylene oxide? (3)



\ O / ethylene epoxid

or ethylene oxide



\ O / Propylene epoxid

1. Ozonolysis:-

"Addition of ozone which causes unsaturated compound to break"

↳ Ozonolysis of alkene produces carbonyl comp (aldehyde & ketone)

Test: Used to locate position of = bond in alkene.

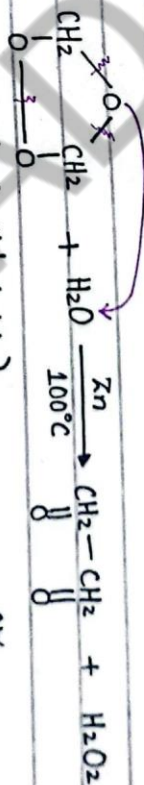
Steps:

① Alkene + O₃ → Molozoneide ^{② rearrangement} → ozonide (unstable) (mild stable)

③ Ozonide + H₂O $\xrightarrow[\text{reduction}]{\text{Zn}}$ Carbonyl comp + H₂O₂ (Aldhyde & ketone) by-product
Boiling water

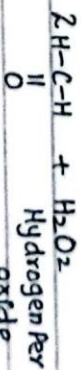


Example: Q. Convert alkene into formaldehyde by ozonolysis:

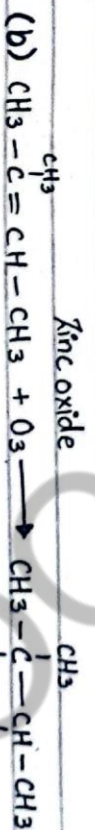


ozonide (mild stable)

OR



formaldehyde (Methanal)

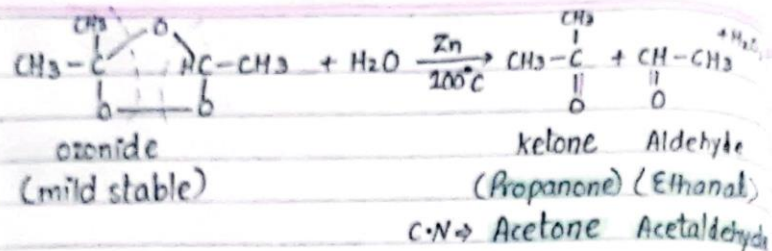


Molozoneide (Unstable)

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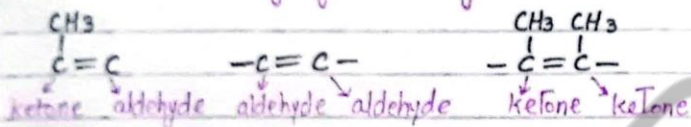
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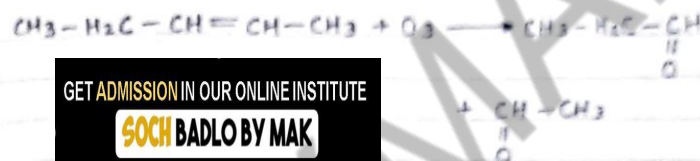
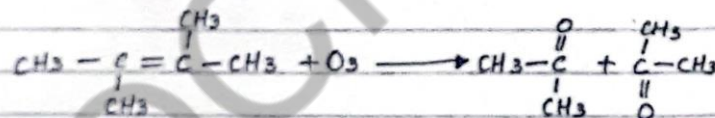
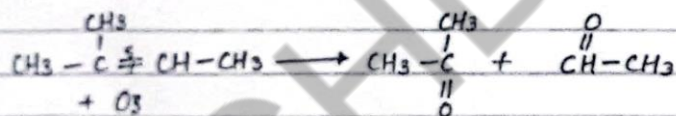
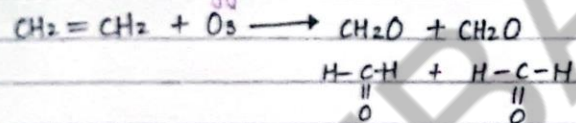
TRICK: Alkene in which (=) Carbon has branch they give ketone.

Alkene in which double bonded carbon has no branch they give aldehyde.



SHORT CUT FOR MCQ:

add one oxygen on = bond.

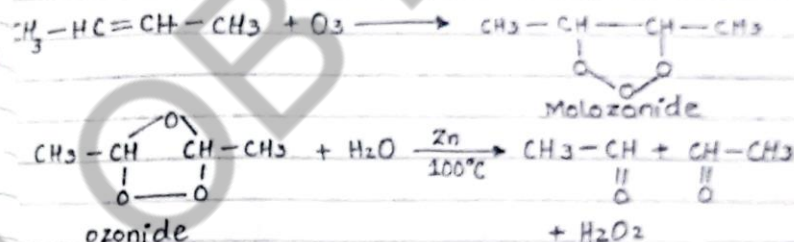


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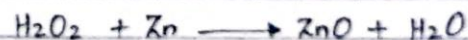
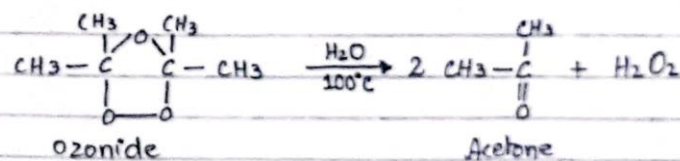
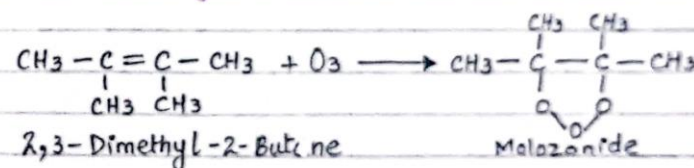
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Q. How will you convert alkene into acetaldehyde?



Q. How will you convert alkene into acetone?

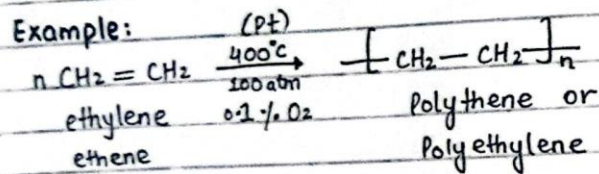


8. Polymerisation:-

"The process in which small molecules combine to give large molecule in the presence of heat and catalyst."

"Process in which small ^{called monomer} combine with each other & form large molecule called polymer is called polymerization"

Small Molecule $\longrightarrow$ Large Molecule
monomer Polymer



* More O_2 will cause combustion.

Other Catalyst:

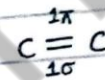
* (Pt, Pd, TiCl_4 , Ni)

* For high quality polyethene $\text{Al}(\text{C}_2\text{H}_5)_3$ aluminium triethyl & TiCl_4 (Titanium tetrachloride) is used as a catalyst.

Alkynes

Relative stability:-

Alkynes are more stable than alkene due to extra π bond therefore alkynes are less reactive than alkenes.



Less reactive
More stable
 $\uparrow e^-$ density

More reactive
Less stable
 $\downarrow e^-$ density

$\rightarrow$ Order of reactivity: (dec order of reactivity)
Alkene > alkyne > alkane

$\rightarrow$ Order of stability: (dec order of stability)
(σ) Alkane > alkyne (2π) > alkene (1π)

1-Hexyne

$\Delta H = 290 \text{ KJ/mol} \rightarrow 2\pi$

1-Hexene

$\Delta H = 126 \text{ KJ/mol} \rightarrow 1\pi$

Physical Properties of alkyne:-

1- They are non-polar insoluble in water but soluble in non-polar organic solvent.

CCl_4 , C_6H_6 , toluene, alcohol, ether, Acetone, hexene etc

2- All alkynes are colourless & odourless except (acetylene) ethyne which has garlic like odour

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- 3- Melting point & Boiling point, density increase with increase in no. of carbon atom.
- 4- Increase in s-character causes increase in E.N. of Carbon. **Macat**
- $$C \equiv C > C = C > C - C$$
- $Sp = 50\%$ polar $Sp^2 = 33.3\%$ $Sp^3 = 25\%$

s-character $\propto$ Polarity

5. Lower alkanes $\rightarrow$ Gases ($C_2 - C_4$)
 higher alkanes $\rightarrow$ Liquids ($C_5 - C_{12}$)
 More higher alkanes $\rightarrow$ Solids ($C_{13} - C_n$)

Preparation of alkynes by Elimination

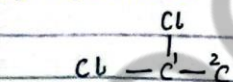
1- Dehydrohalogenation:

"Removal of HX from the molecule"

Reagent = (i) Alcoholic KOH $\rightarrow$ Elimination

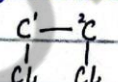
(ii) $NaNH_2 + liq. NH_3$ at $100-200^\circ C$
 (sodaamide) $\rightarrow -33^\circ C$

A) Geminal



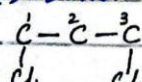
Geminal dihalide

(B) Vicinal



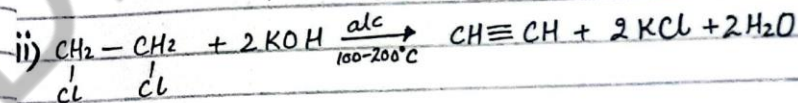
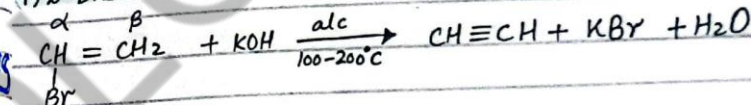
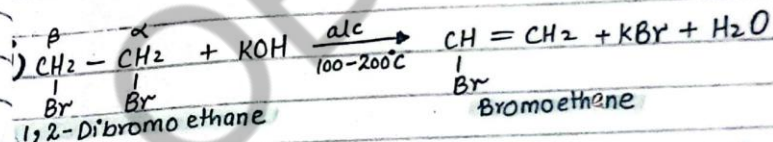
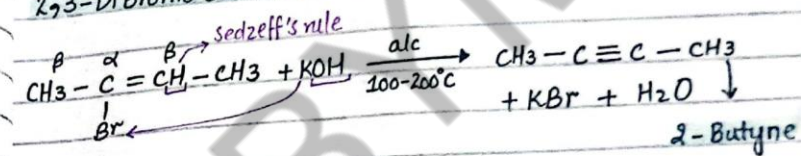
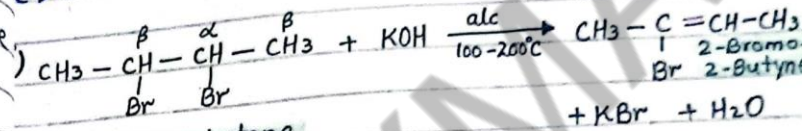
Vicinal dihalide

(C) Dihalide



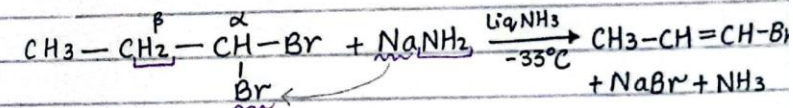
Dihalide

(A) From Vicinal dihalide

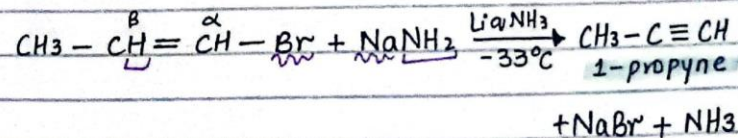


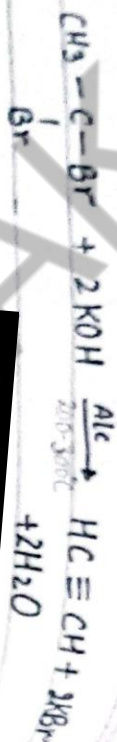
1,2-Dichloroethane

(B) From Geminal dihalide



1,1-Dibromopropane

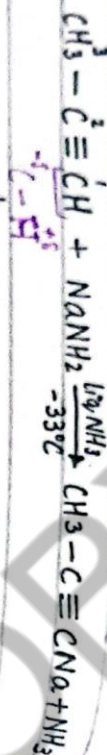




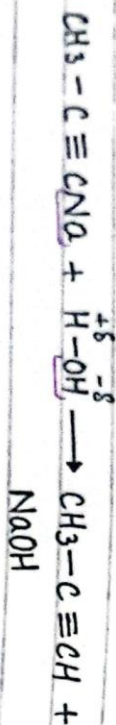
1,1-Dibromoethane
Geminal dihalide

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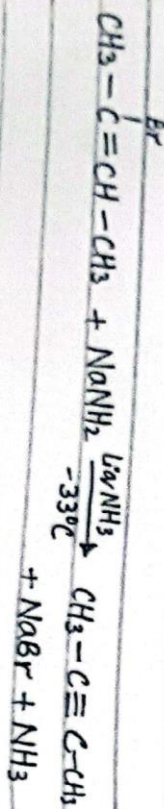
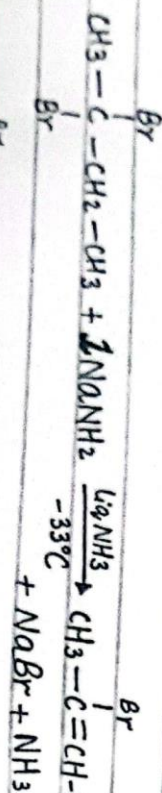
Terminal alkynes → are those in which $\equiv$ bond is offer 1st carbon (CH) is acidic.



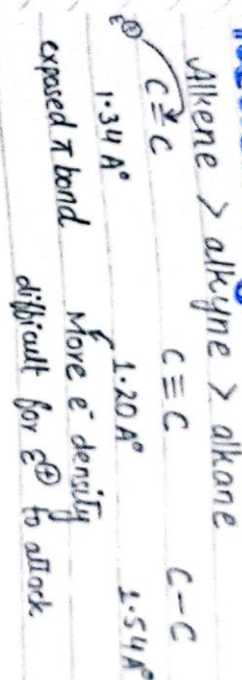
↑
become polarized due to increase in s-character



Home-Work



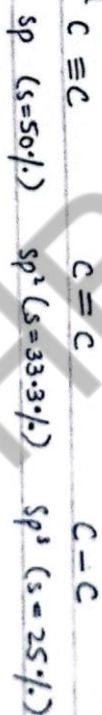
Reactivity:-



Acidity of terminal alkyne

→ Ethyne or 1-balkyne like propyne are acidic in nature bcz in these alkynes triple bond carbon is sp hybridized it contains 50% s-character

s-character α polarity
due to more "s" character as compared to sp² & sp³ hybridized C.

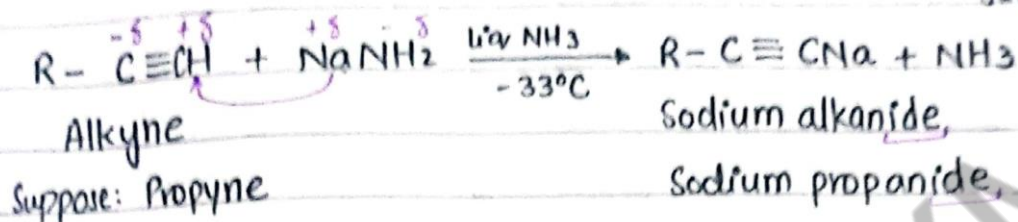


Due to this H-C≡C is more E.N so become polar.
↓
• bond polarity created
→ Easy to remove H & become Acidic

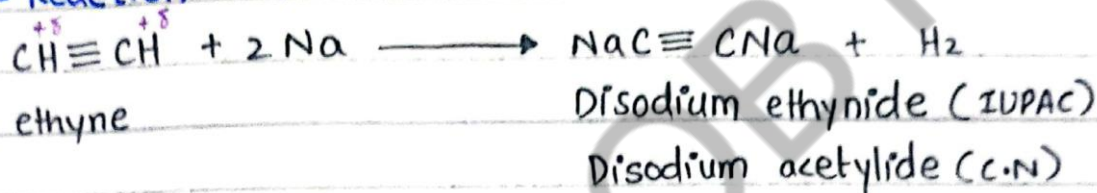
Hydrogen attach with these carbon (terminal) become electron deficient behave as Acidic.

Electrophillic substitution rxn of Terminal Alkynes:

1- Reaction with Sodaamide (NaNH_2)



2- Reaction with Na metal

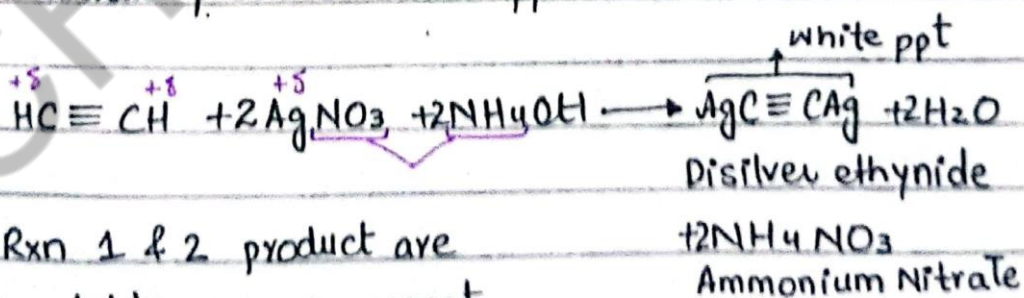


3. Reaction with Ammonical silver nitrate (AgNO_3 NH_4OH)

OR

Identification of test for 1-alkyne

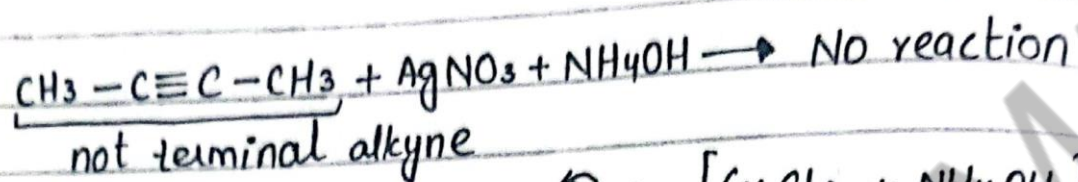
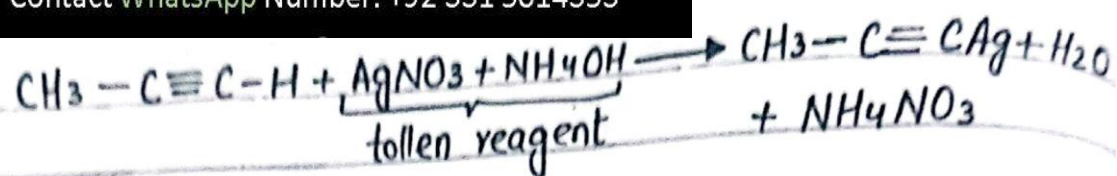
"Ethyne or 1-alkyne react with Ammonical silver nitrate produce white ppt"



Note: Rxn 1 & 2 product are water soluble so we cannot identify 1-alkyne.

⇒ Identification test $\rightarrow$ Insoluble in H_2O

is rxn 3 $\rightarrow$ colour change white ppt

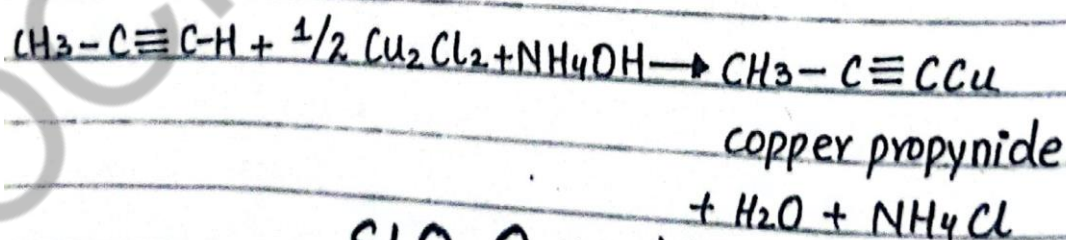
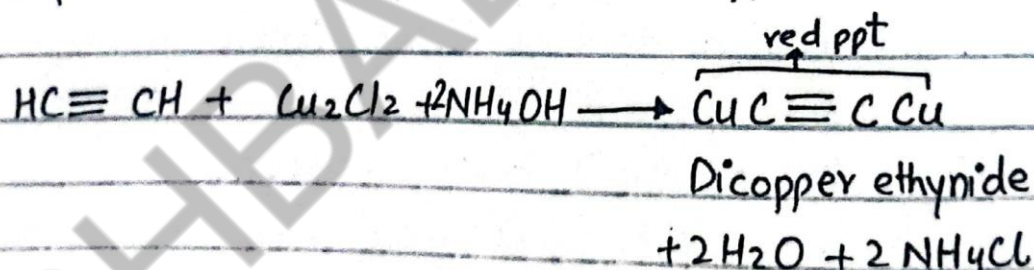


identification Test for 1-alkyne $\leftarrow$ or $[\text{CuCl}_2 + \text{NH}_4\text{OH}]$
4- Rxn with Ammonical Cuprous Chloride:

ous $\rightarrow$ low Oxidation state vic $\rightarrow$ high O.S
 Cuprous $\rightarrow \text{Cu}^+$ Cupric $\rightarrow \text{Cu}^{+2}$
 Ferrous $\rightarrow \text{Fe}^{+2}$ Ferric $\rightarrow \text{Fe}^{+3}$

Identification test:

* Ethyne or 1-alkyne like 1-propyne, 1-butyne etc react with Ammonical cuprous chloride produce Red ppt



SLO Question

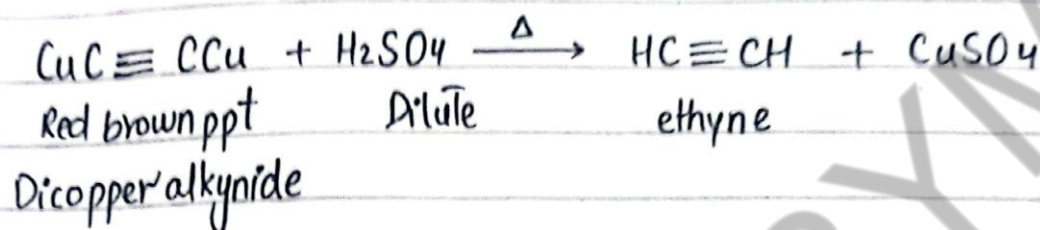
Q. How will you distinguish b/w Test / Reactions

① Ethene & Ethyne

② 1-pentyne & 2-pentyne

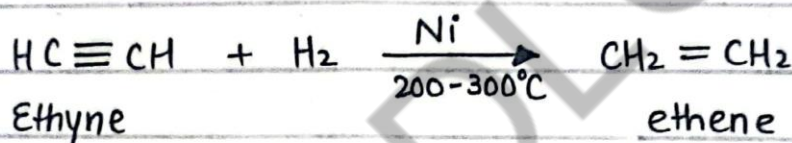
Uses of alkynes:

- 1- Preparation
- 2- Purification $\longrightarrow \text{AgC} \equiv \text{CAg} + 2\text{HCl} \xrightarrow{\Delta} \text{HC} \equiv \text{CH}$
- 3- Separation white ppt Acid + 2AgCl
- 4- Identification purified alkyne

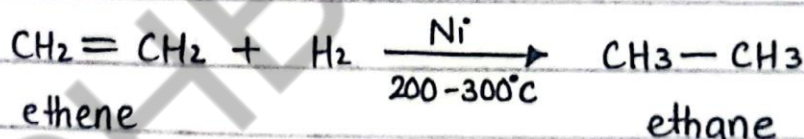


Addition rxns of alkyne :- E^+ add

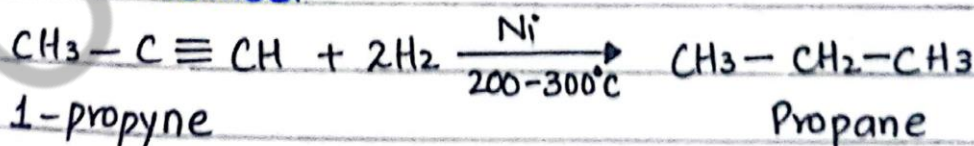
1. Hydrogenation: Addition of H_2 in a molecule



other catalysts: Pt, Pd
at Room Temp



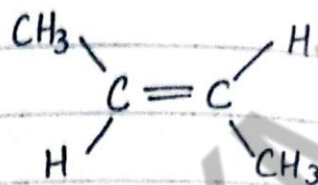
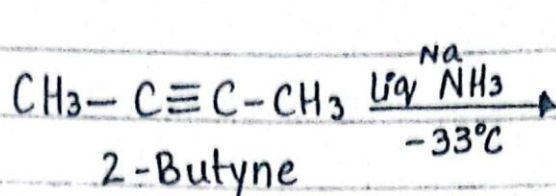
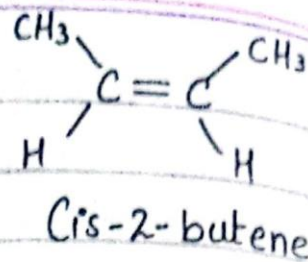
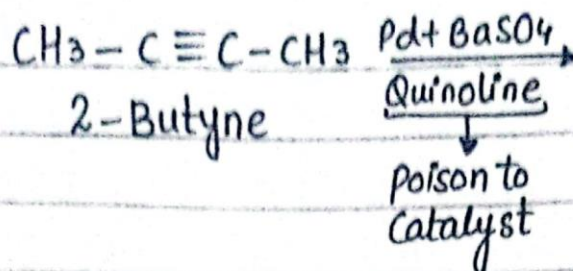
Direct Method:



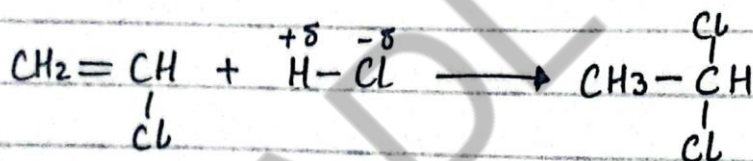
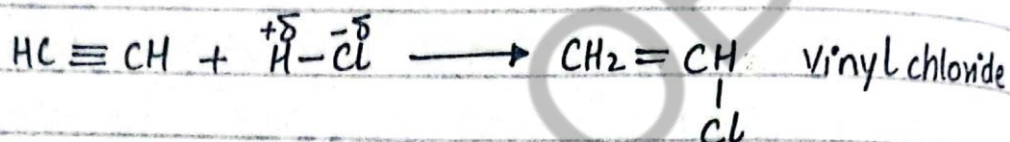
(a) Partial Hydrogenation of alkyne

* To make Cis $\longrightarrow$ we use 2-butene ($\text{Pd}, \text{BaSO}_4 +$
Quinoline) Lindler catalyst

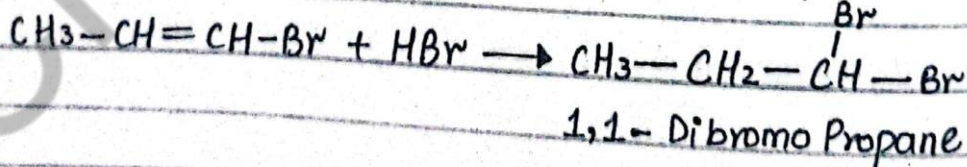
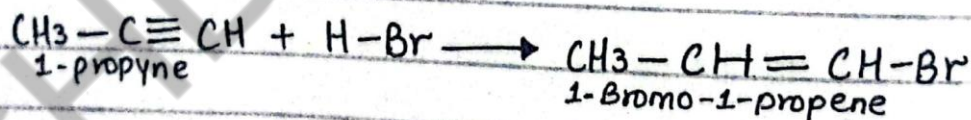
* To make Trans-2-butene ($\text{Na} + \text{liq. NH}_3 - 33^\circ\text{C}$)



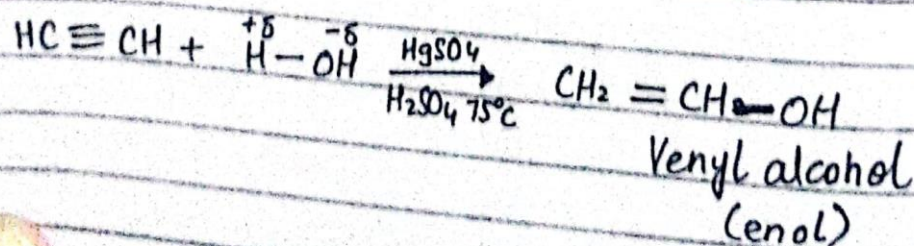
2. Hydrohalogenation: Addition of HX

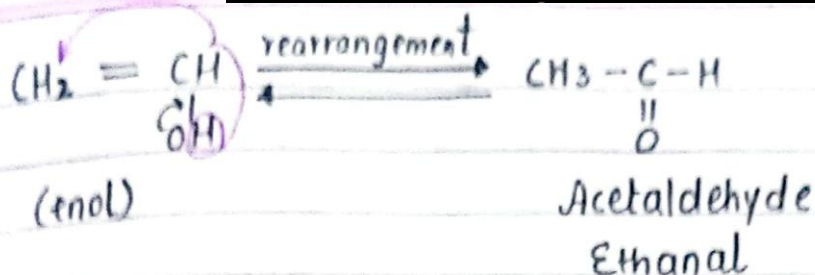


Geminal dihalide
1,1-Dichloroethane

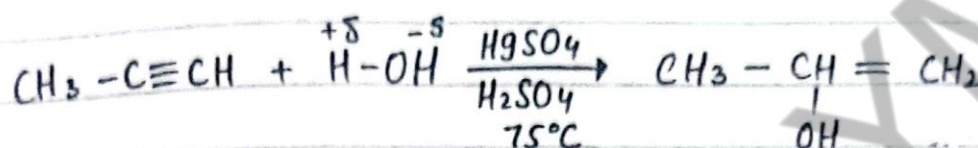


3. Hydration: "Addition of H₂O in molecule"



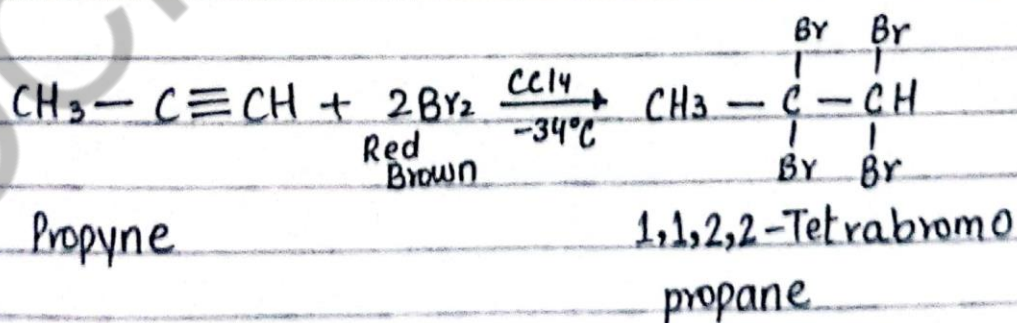
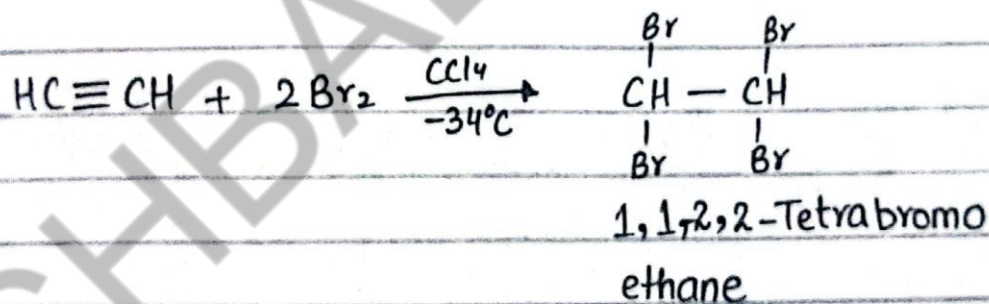


arrow inward $\rightarrow$ bond formation
 arrow outward $\rightarrow$ bond breaking



4. Bromination: / Test for unsaturation / "Addition of Br₂"

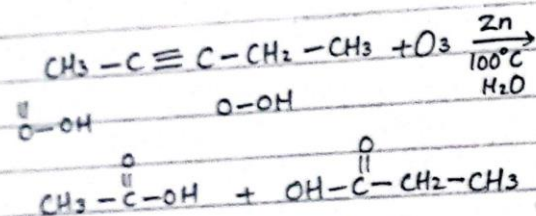
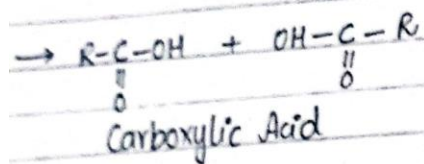
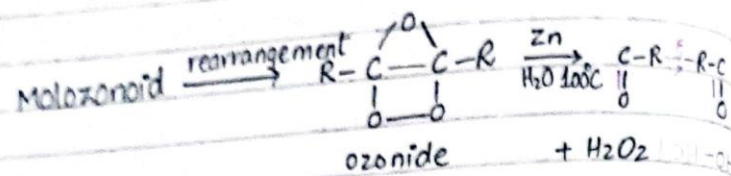
$\rightarrow$ Inert solvent is used (CCl₄)



Disappear



5. Ozonolysis: "Addition of O_3 "
 $R-C \equiv C-R + O_3 \longrightarrow R-C \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} C-R$ molozonoid



Benzene Nomenclature

- ↳ Discovered by Michel Faraday 1825
- ↳ Isolated by Hoffman
- ↳ Molecular weight: 78 amu

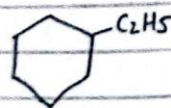
① Substituent is named before benzene.



Chlorobenzene

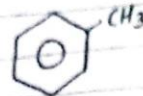


Nitrobenzene



Ethyl benzene

(2) Special names are included in IUPAC



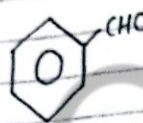
Toluene
Methyl benzene



Aniline
Amino benzene



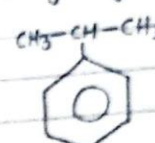
Phenol
Hydroxy benzene



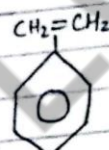
benzaldehyde



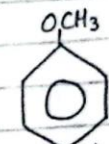
Benzoic Acid



Cumene
Isopropyl benzene

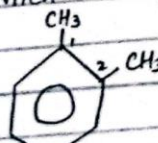


Styrene
Vinyl benzene

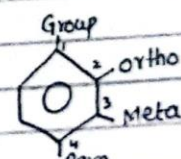


Anisole
Methoxy benzene

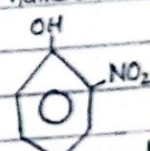
3) When two grps are attached, it will be numbered.



1,2-Dimethyl
benzene
(xylene)



1-2 [ortho]
1-3 [Meta]
1-4 [Para]

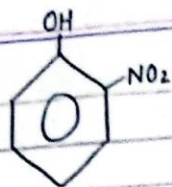


O-nitro phenol

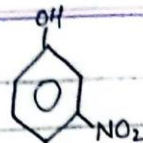
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O-Nitro phenol

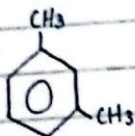


m-nitro phenol

Meta nitrophenol

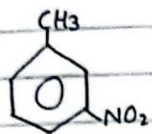


p-nitro phenol



m-xylene

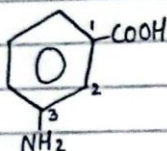
1,3-Dimethyl benzene



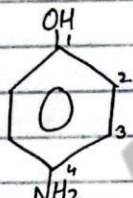
m-nitro toluene

(4) Priority order of different functional groups.

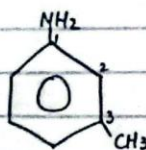
$-\text{COOH}$, $\text{C}\equiv\text{N}$, $\text{C}=\text{O}$, $\text{C}-\text{O}-\text{H}$, $\text{C}-\text{O}-\text{R}$, OH , NH_2 , $-\text{OR}-\text{R}$
methoxy



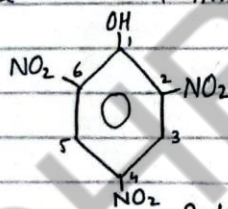
3-Amino Benzoic Acid



4-Amino phenol

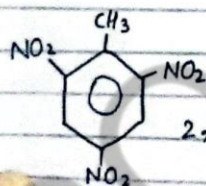


3-methyl Aniline



2,4,6-Trinitro phenol

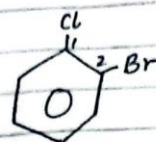
Picric Acid



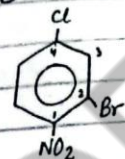
2,4,6-Trinitrotoluene (TNT)

(6) When no group in list then follow alphabetical order

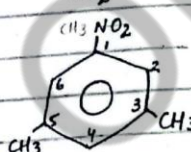
B
C
N



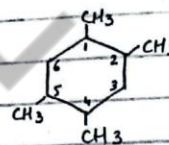
2-Bromochlorobenzene



2-Bromo-4-chloronitrobenzene



1,3,5-Trimethylbenzene
(mesitylene)

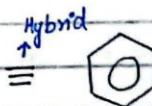


1,2,4,5-Tetramethylbenzene
(Durene)

Molecular structure:



Kekulé structure



Robinson structure

Special Features:

1- Resonance

2- Electrophilic Substitution Rxn

* Benzenes & its derivatives is called Arenes.

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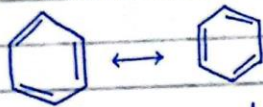
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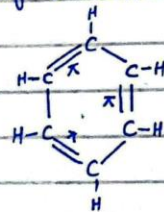
Physical Properties:

- Benzene is non-polar in nature and not dissol in polar solvent.
- low M.P & B.P.
- In the presence of polar substituents benzene act as slightly polar compound.

Q. Explain the structure of benzene proposed by Kekule? (3)



The structure proposed by Kekule is very stable. In which benzene contains conjugated double bonds. The structure of benzene is Planar hexagonal in nature.



Q. Write down the objections in Kekule structure? (3)

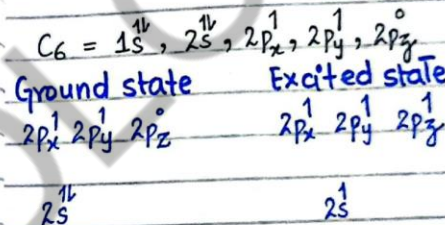
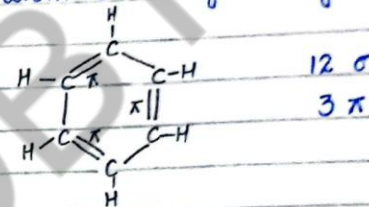
- It fails to explain why (less reactive) benzene is a stable compound.
- It shows dual character i.e. it shows addition rxn & substitution rxn also.
- It goes into substitution reaction readily and addition reaction reluctantly.
- The bond distances in benzene are all same



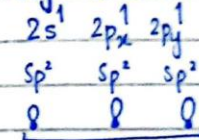
- 5. All bonds in benzene are 120°.
- 6. It has less heat of formation.

Q. Explain Atomic orbital treatment of benzene with the help of diagrams by using hybridization theory. (6)

Each Carbon-atom on benzene ring is 'sp²' hybridized



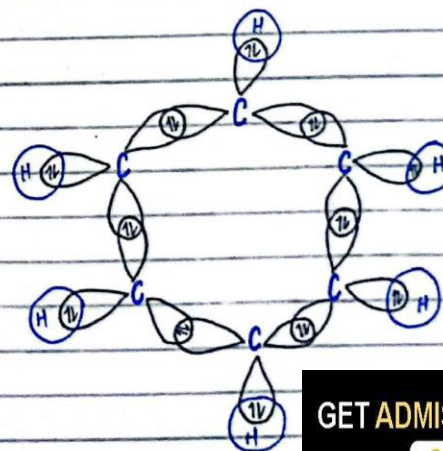
Hybrid State



show 1 loop

UnHybridized
 $2p_z^1$

$H_1 = 1s^1$



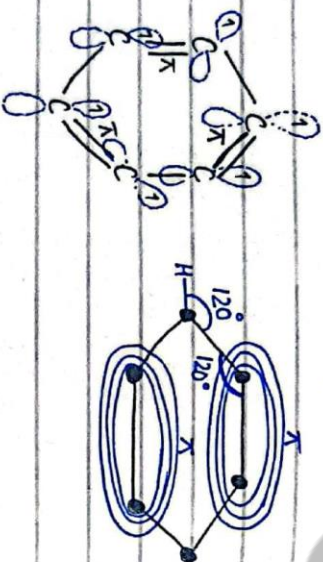
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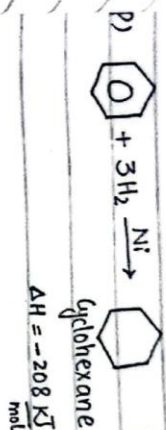
Explanation:

1. Each carbon atom on benzene ring has three sp^2 hybridized orbitals & one sp^2 unhybridized orbital.
2. The three sp^2 hybridized orbitals form three σ bonds with adjacent carbon atoms and one with hydrogen atom.
3. In this way sigma framework of benzene is formed having '12 σ ' bonds.
4. The three sp^2 hybridized orbitals form three π bonds on alternate positions.

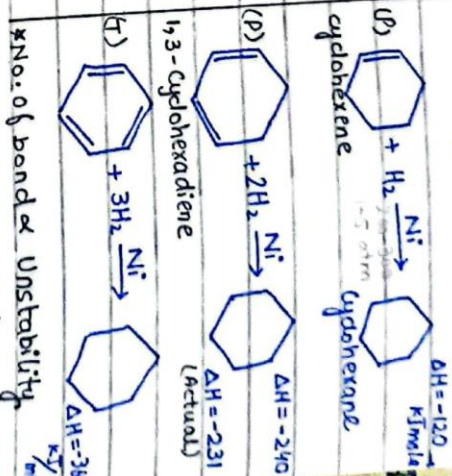


Q. Compare the stability of benzene with a hypothetical compound. (6)
Compound with less energy is more stable than with more energy.

Benzene



Hypothetical Comp.



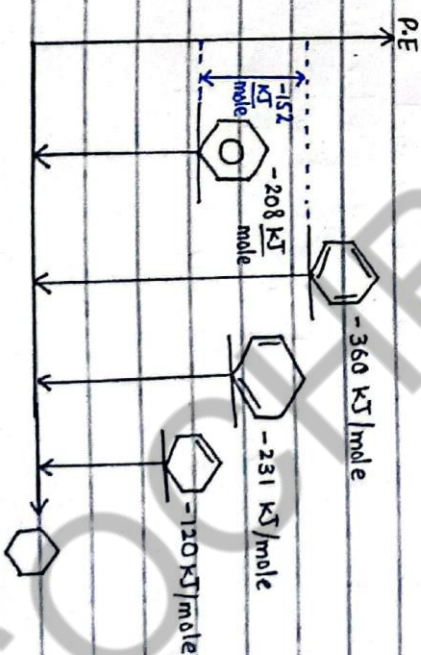
Explanation:

According to heat of hydrogenation data, benzene produces less heat of hydrogenation than hypothetical compound. So, benzene is -152 KJ/mole is more stable than hypothetical compound.

Hypothetical compound = -360 KJ/mole

Benzene = -208 KJ/mole

Resonance Energy = -152 KJ/mole



Q. Draw all the Resonance structures of benzene & explain with the help of diagram.



It will show benzene unstable bcz long bond due to more distance & less attraction can be easily broken & become unstable.

Explanation:-

Benzene can be represented by all five resonance structures proposed by Kekule & Dewar. But in dewar structures the long bonds b/w C_1-C_4 , C_2-C_5 & C_3-C_6 are very weak bond, can be easily attacked by any electrophile which shows that benzene is unstable compound. On the other hand, Kekule has conjugated bond system which is a strong system & represent that benzene is a stable compound. Now we only use Kekule structure to represent benzene molecule.

Q. Discuss stability of benzene on the basis of Resonance energy.

Decrease in energy due to resonance is called resonance energy.

$$\text{Resonance energy} = \Delta H_{\text{cal}} - \Delta H_{\text{obs}}$$

(Theoretical) (Experimental)

OR

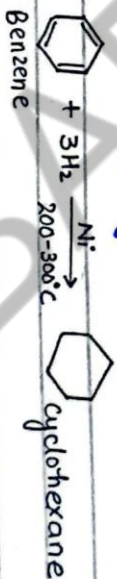
Difference b/w heat of hydration calculated & heat of hydrogenation observed is called resonance.

Resonance energy $\propto$ stability

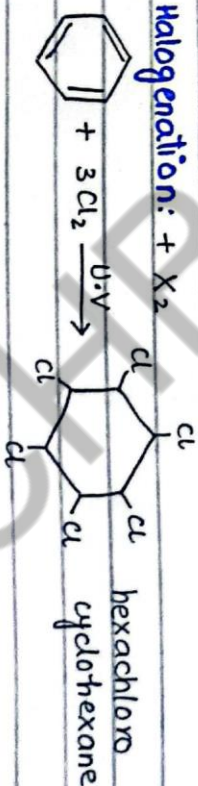
Reaction of Benzene

① Addition Rxns: + H_2

→ Catalytic Hydrogenation:

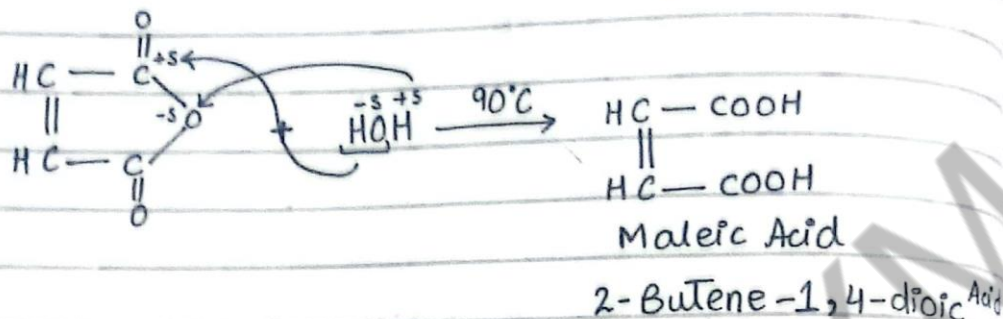
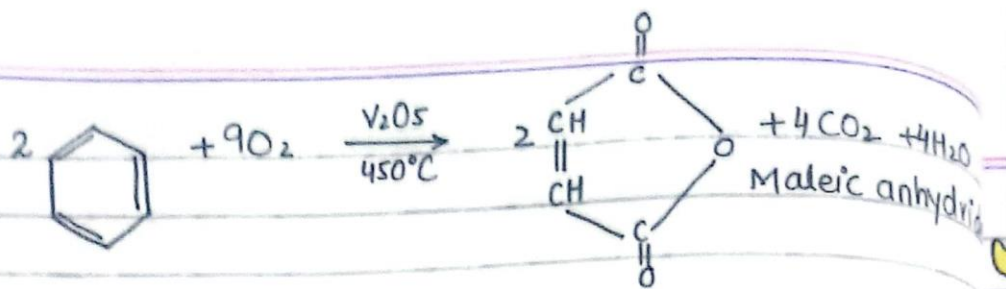


→ Halogenation: + X_2

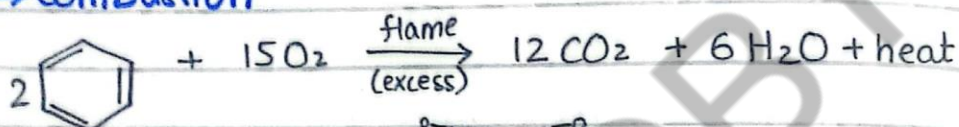


③ OXIDATION Rxns:

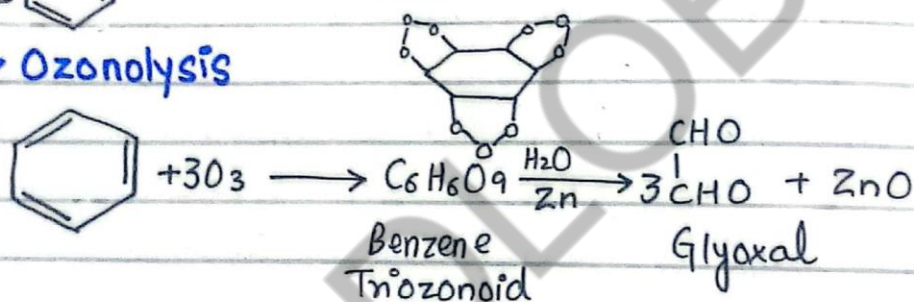
→ Catalytic Oxidation: Benzene cannot be oxidized with $KMnO_4$ & $K_2Cr_2O_7$.
for oxidation of benzene V_2O_5 $450^\circ C$ + O_2



→ Combustion

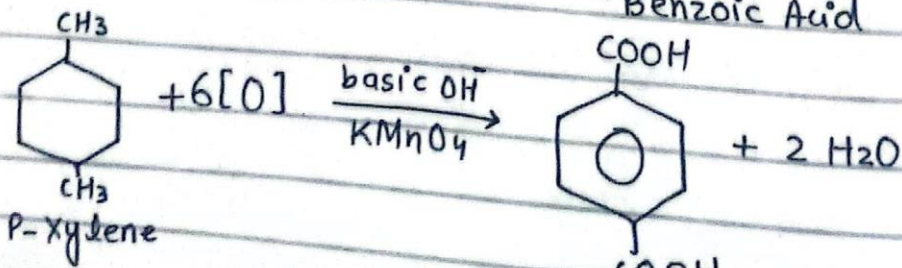
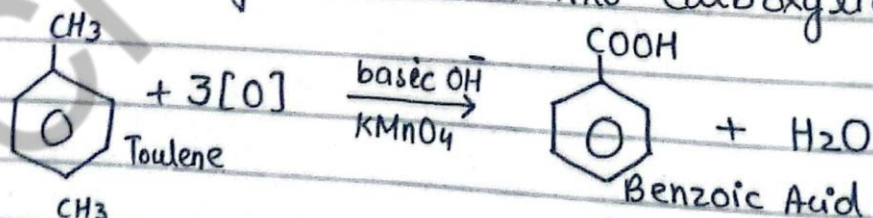


→ Ozonolysis



→ Side Chain Oxidation : Identification Test for alkyl benzene

Benzene does not react with KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ however alkyl group present on benzene ring is oxidized into Carboxylic grp.



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CamScanner

CS

¹H removed
Benzene

Maleic anhydride

This is commercial method for the preparation of maleic anhydride. Benzene is not oxidized by KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$.

(ii) **Combustion**

When benzene is burnt in the presence of air or oxygen, CO_2 and H_2O are produced, just like other aliphatic hydrocarbons

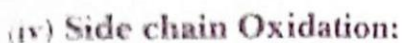


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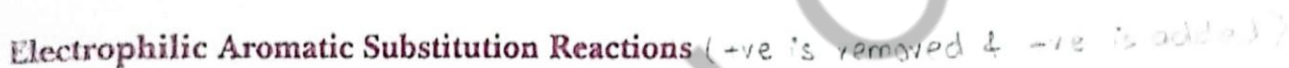
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Benzene reacts with ozone and gives glyoxal, passing through triozonide as an intermediate



When alkaline or acidic solution of KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ is added to alkyl benzene, alkyl groups present in the benzene ring are oxidized into carboxylic groups.

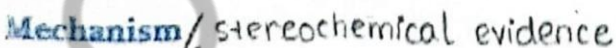


Introduction

The pi-electrons of benzene are highly stabilized due to resonance. They are not readily available for the electrophilic attack like the electros of alkenes. A weak electrophile cannot attack on benzene ring. Hence more powerful electrophiles are required for a successful attack to penetrate and break the continuous sheath of electron cloud in benzene. Substitution is preferred over addition in order to preserve the stable aromatic character

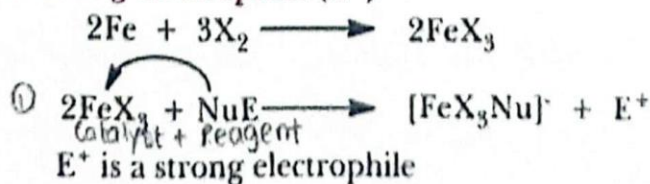
General reaction

Benzene on reaction with an electrophile in the presence of Lewis acid catalyst gives substituted benzene.



It consists of the following three steps.

1. Formation of a strong electrophile (X^+)



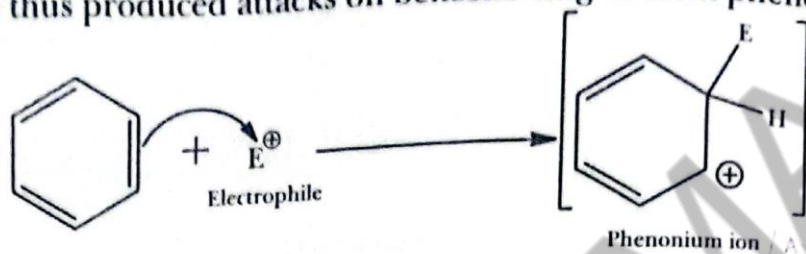
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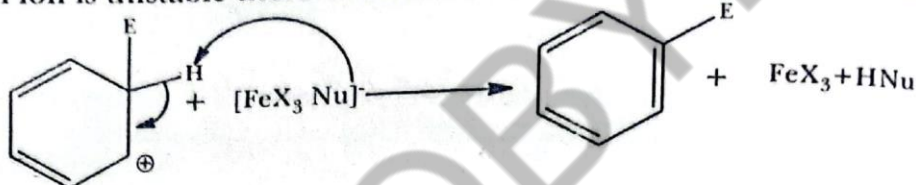
2. Formation of phenonium ion / Attack of electrophile

The electrophile E^+ thus produced attacks on benzene ring to form phenonium ion.



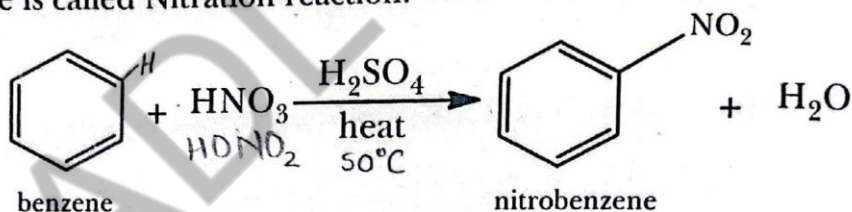
3. Regeneration of catalyst

The phenonium ion is unstable therefore H^+ ion is removed to give substitution product.



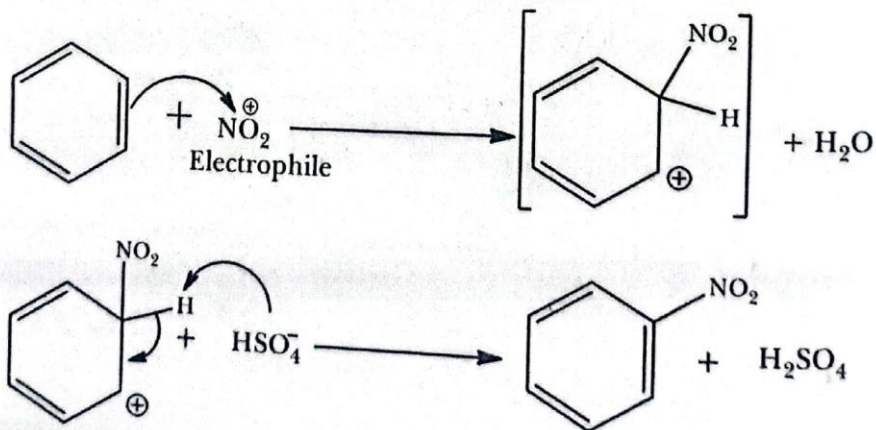
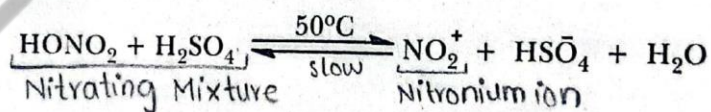
Nitration

The substitution of NO_2 group to a benzene ring in the presence of conc. H_2SO_4 at $50-55^\circ C$ form nitrobenzene is called Nitration reaction.



Mechanism

Sulphuric acid reacts with nitric acid to generate nitronium ion.

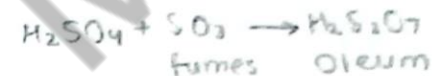
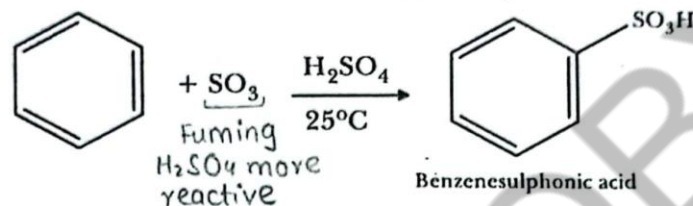
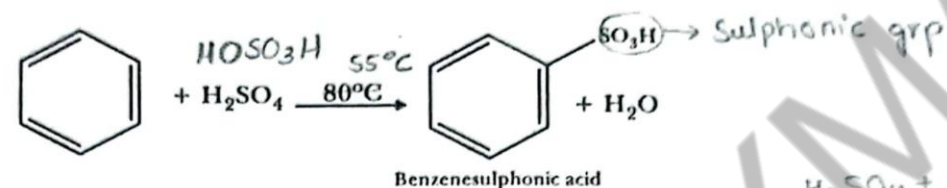


Sulphonation

The substitution of sulphonic acid group to a benzene ring is called Sulphonation. When benzene is heated with fuming H_2SO_4 or concentrated H_2SO_4 it yields benzene sulphonic acid.

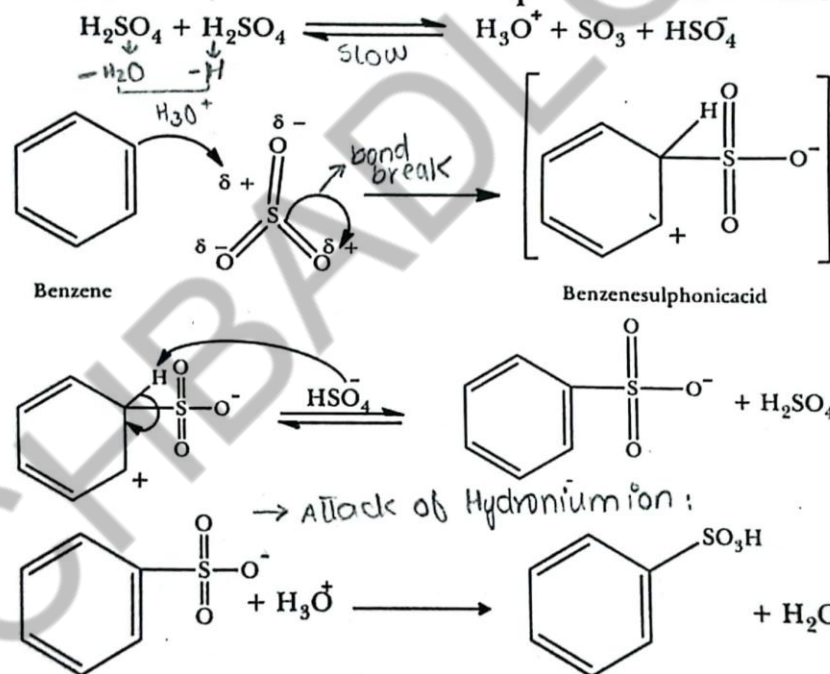


Fuming H_2SO_4 has free sulphur trioxide which is electron deficient (electrophile) and causes substitution.



Mechanism

When sulphuric acid alone is used, the actual electrophile in this reaction is SO_3



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Halogenation

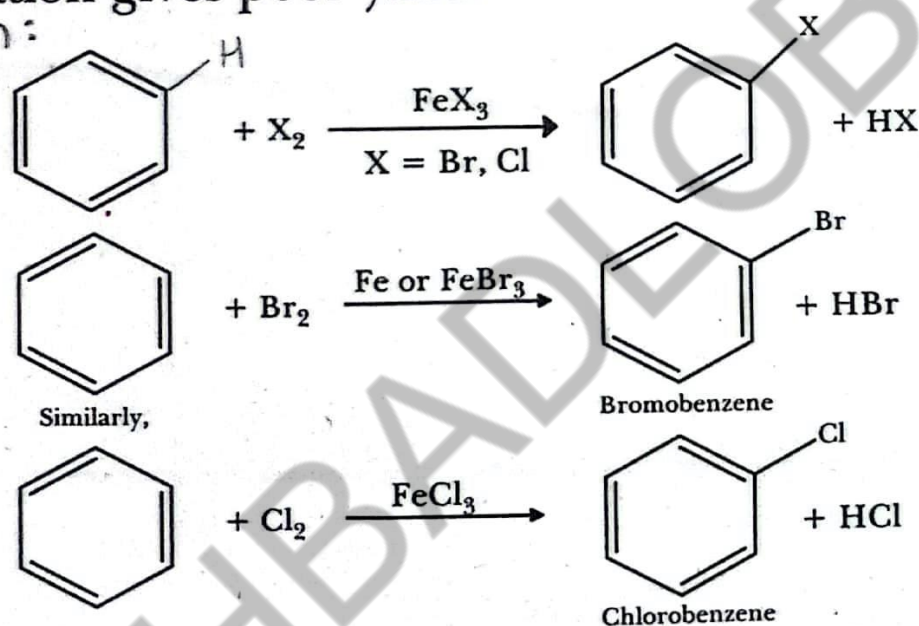
The substitution of halogen to a benzene ring is called halogenation.

Halogenation

The substitution of halogen to a benzene ring in the presence of a Lewis acid catalyst to form halobenzene is called halogenation reaction.

Halogenation of benzene occurs with halogens (X_2) in the presence of a Lewis acid catalyst FeX_3 . Chlorination and bromination are normal reaction but fluorination is too vigorous to control. Iodination gives poor yield.

* Single Step Rxn:



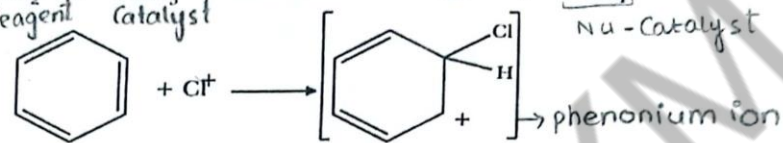
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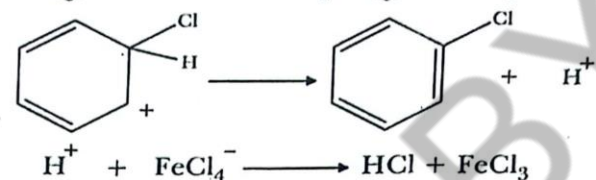
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Mechanism① Formation of E^+ :

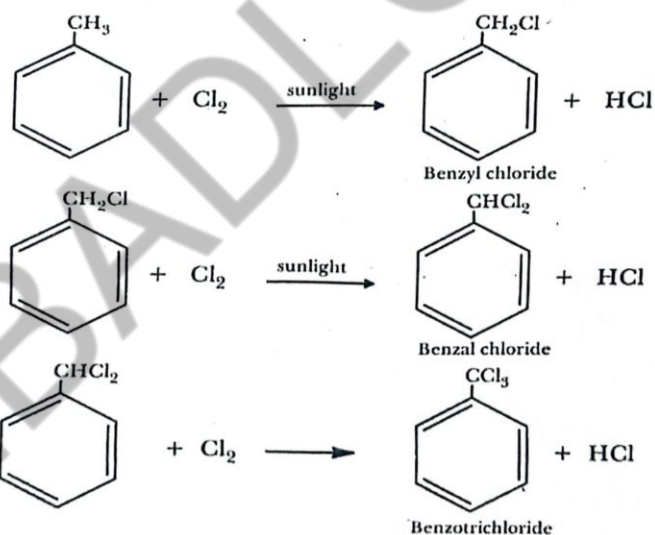
② Attack of electrophile:



③ loss of Proton

**Halogenation of alkyl side chain**

When alkylated benzene is treated with chlorine or bromine in the presence of sunlight, only the alkyl groups are substituted.



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Friedel-Crafts Alkylation Q. Give Friedel craft Alkylation rxn of Benzene?

The substitution of an alkyl group in the benzene ring in the presence of a Lewis acid catalyst $AlCl_3$ to form an alkylated benzene is called Friedel Crafts alkylation reactions.

Q. Convert benzene into toluene?

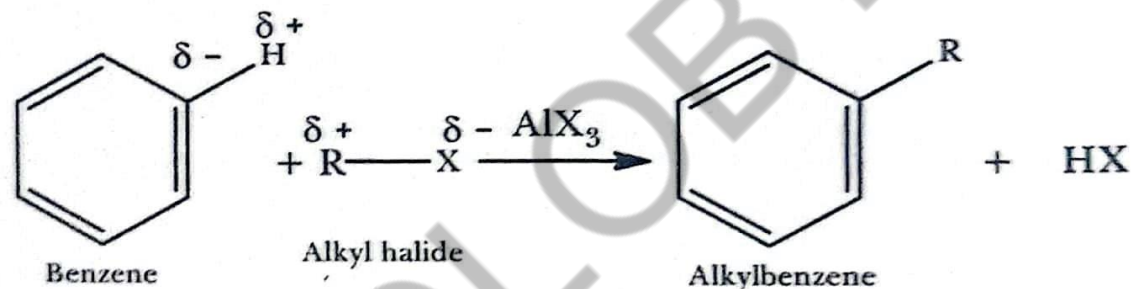
M. Imp

Benzotrichloride

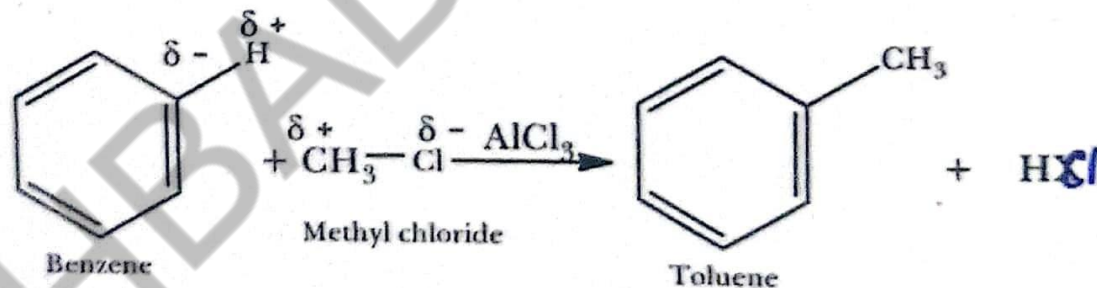
Friedel-Crafts Alkylation Q. Give Friedel craft Alkylation rxn of Benzene?

The substitution of an alkyl group in the benzene ring in the presence of a Lewis acid catalyst AlCl_3 to form an alkylated benzene is called Friedel Crafts alkylation reactions.

General reaction Q. Convert benzene into toluene?



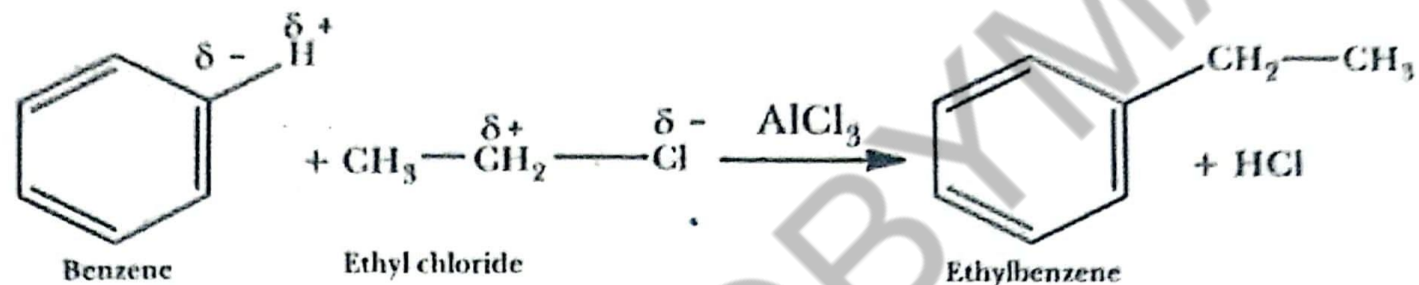
Examples / One-step Rxn:



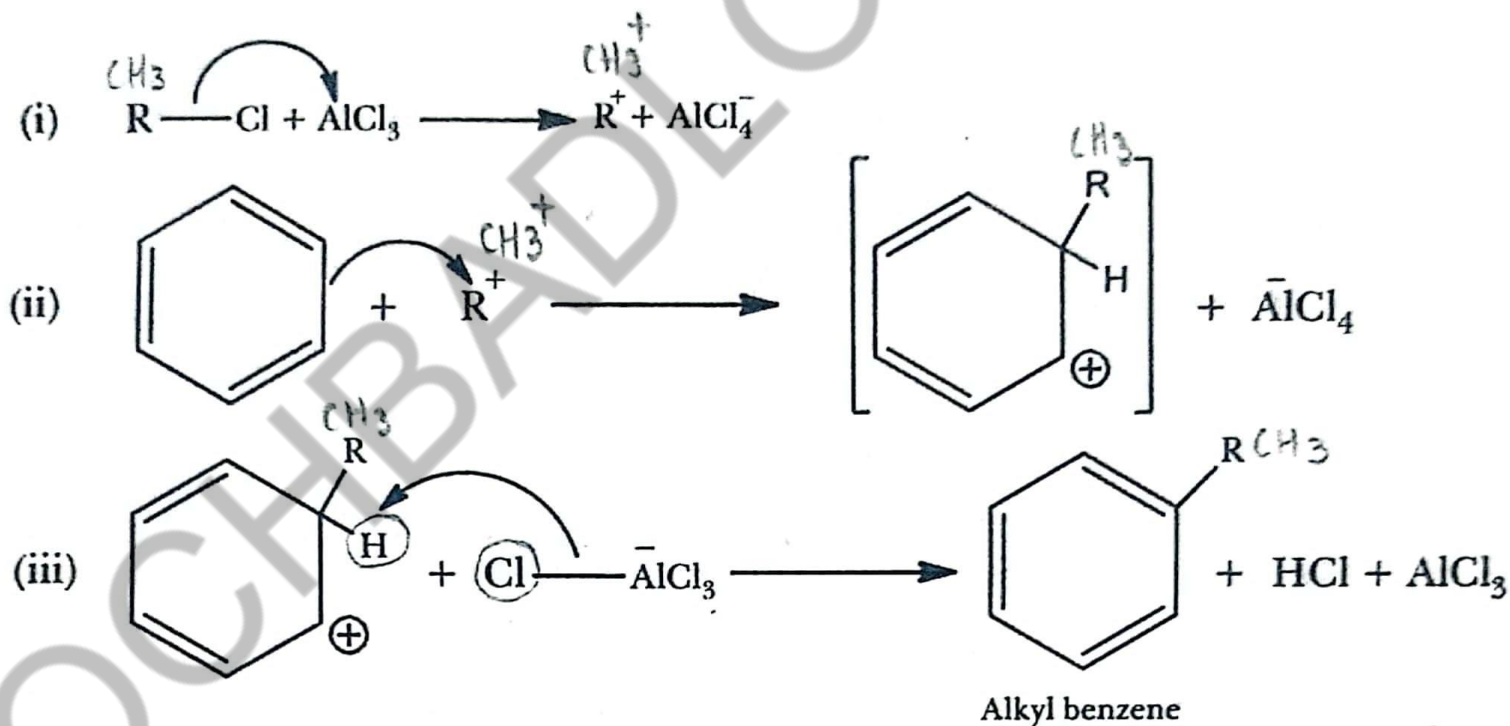
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Mechanism



* u. Imp

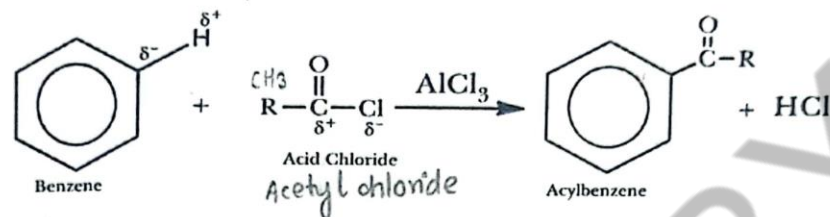
Imp

Friedel-Crafts Acylation

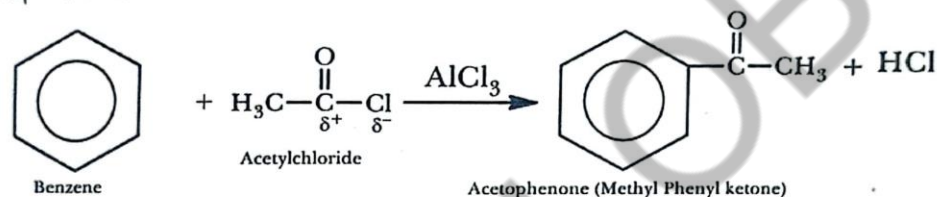
Q. Give Friedel craft acylation Rxn?

The substitution of an acyl group ($\text{RCO}^\ominus$) to a benzene ring in the presence of a Lewis acid catalyst such as AlCl_3 to form an acetylated benzene is called Friedel Crafts Acylation.

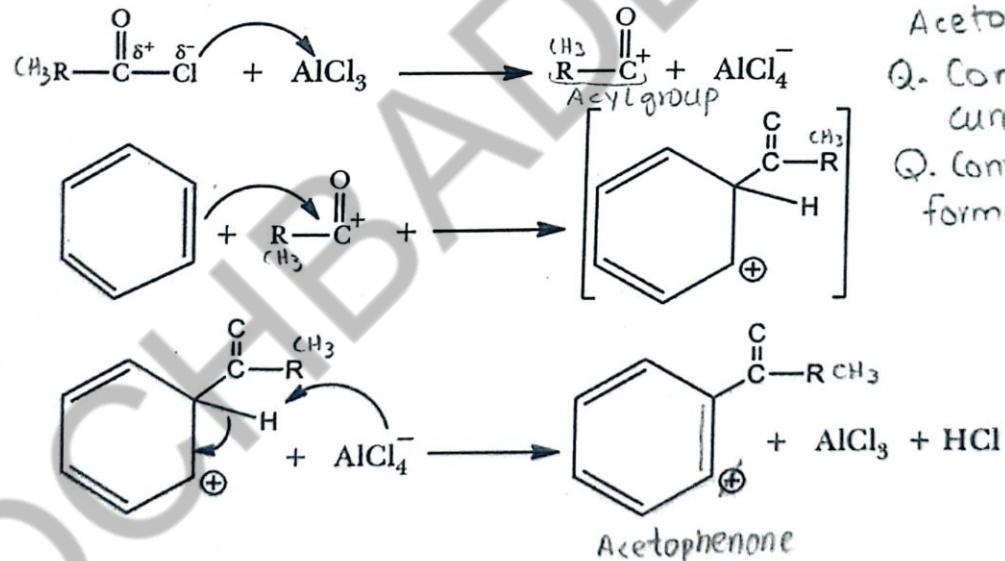
General reaction



Example/One-step Rxn:



Mechanism



Q. Convert benzene into Acetophenone?

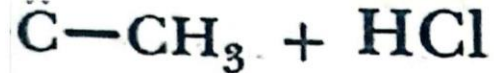
Q. Convert benzene into cumene by alkylation

Q. Convert benzene into formaldehyde?
→ take formyl chloride

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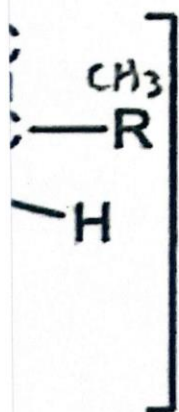
ketone)

Q. Convert benzene into
Acetophenone?

Q. Convert benzene into
cumene by alkylation?

Q. Convert benzene into
formaldehyde?

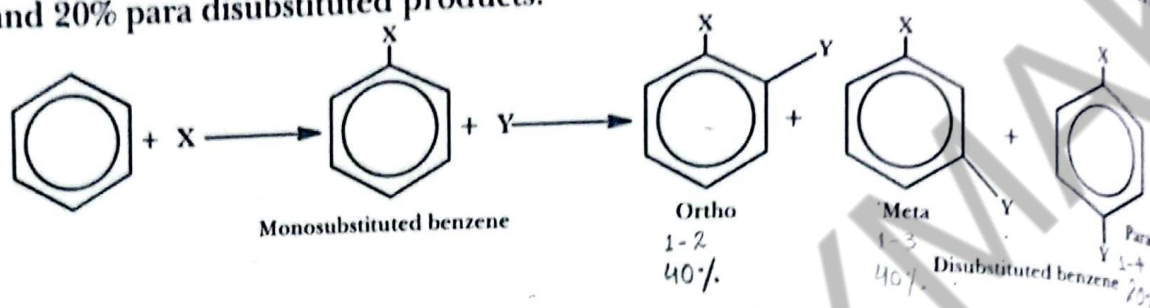
↳ take formyl
chloride



The Effect of Substituents (orienting effect)

When an electrophilic substitution reaction takes place on benzene ring, we get only one monosubstituted benzene because all the six positions in the ring are equivalent. However, the position of a second group into the ring depends on the nature of the first group. The second substituted may enter at ortho, para or meta position.

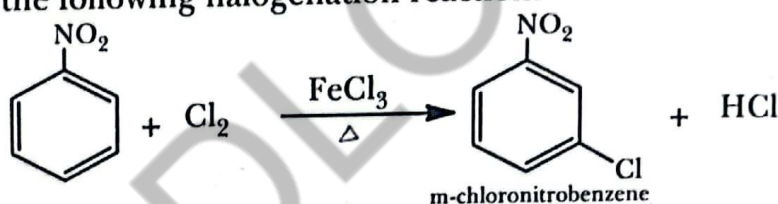
On statistical basis the proportion of disubstituted products would be 40% ortho, 40% meta and 20% para disubstituted products.



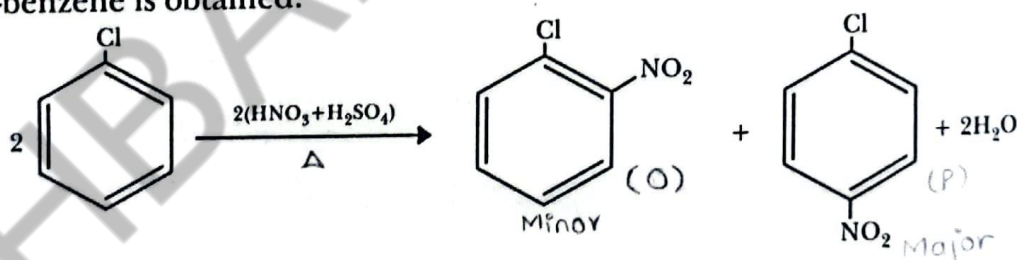
Example

chlorination of nitrobenzene in the presence of Lewis acid catalyst forms 3-nitrochlorobenzene as the main product.

However, the results do not agree with chance substitution ratio, e.g. m-nitro-chlorobenzene the main product of the following halogenation reaction.



However, nitration of chlorobenzene gives a mixture of o-nitrochloro-benzene and nitrochloro-benzene is obtained.



Classification of substituent on benzene ring

There are two types of groups:

- a. Ortho- and para- directing groups
- b. Meta- directing groups

what are

1. Ortho and para directing groups ?

These groups release electrons towards the benzene ring, at ortho and para positions. Because these positions are electron rich, therefore the second group is substituted at ortho and para positions. They also enhance the reactivity of benzene ring.

Example

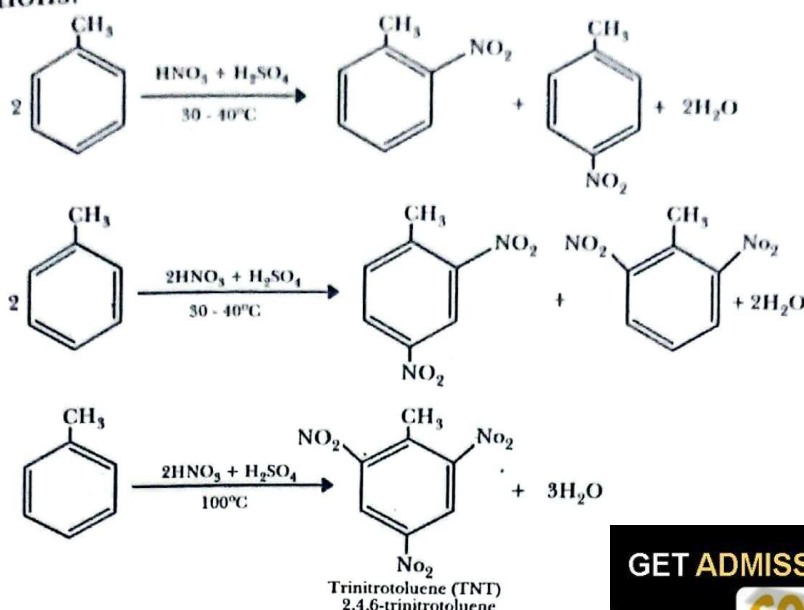
The electron releasing effect of methyl groups is significant and it makes the ring a good nucleophile. Due to this increased reactivity, more nitro groups can enter the ring.

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ortho and para positions.



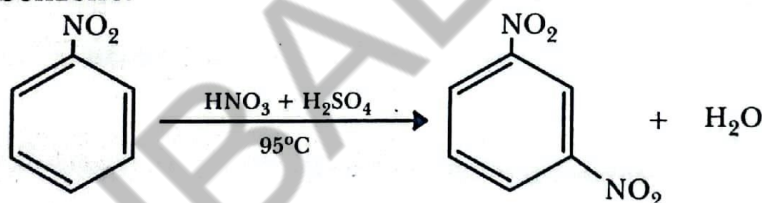
Examples of ortho and para directing groups are

$-\text{N}(\text{CH}_3)_2$, $-\text{NH}_2$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$ and R -

Although $-\text{F}$, $-\text{Cl}$, $-\text{Br}$ and $-\text{I}$ are ortho-para directing groups but they deactivate the ring for further substitution.

2. Meta-Directing Groups

These groups withdraw the electrons of the benzene ring from ortho and para positions. Therefore the ortho and para positions are more electrons deficient than the meta position. Thus, the incoming electrophile will prefer to attack on meta position rather than ortho and para positions. These groups are called meta-directing groups. These groups decrease the chemical reactivity of benzene.

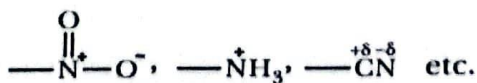


The substitution of third nitro groups is not possible because nitro group has deactivated the ring, other examples of meta directing groups are

$-\text{NO}_2$, $-\text{COOH}$, $-\text{CHO}$, $-\text{SO}_3\text{H}$, $-\text{CN}$, $-\text{COR}$ etc.

Determining the directive, activating and deactivating effects of the substituents

1. All alkyl groups, phenyl group and groups having one or more non bonding electron pairs on the atom adjacent to the ring are ortho-para directing. $-\text{R}$, $-\text{OH}$, $-\text{OR}$, $-\text{NH}_2$, $-\text{X}$.
2. substituent having a positive (or partial positive) charge on the atom adjacent to the ring are meta directing groups.



3. All ortho-para directing groups activate the ring except halogens which are partially deactivators.
4. All meta directing groups are deactivators.

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Groups like CN , -CHO , $^+\text{NH}_3$, $^+\text{NR}_3$, which decrease the reactivity of Benzene nucleus and direct the incoming group at m- position

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Exercise

Select the right answer from the choices given with each question.

- i. The molecule of ethane posses which hybridization;
☒ a. sp^3 b. sp^2 c. sp d. sp^2d
- ii. The sp^2 hybrid orbitals are oriented in space at one angle;
a. 109.5° b. 180° c. 100° ☒ d. 120°
- iii. The geometry of acetylene is,
a. angular b. bent c. trigonal ☒ d. linear
- iv. Which reaction is used as test for the presence of alkene;
☒ a. reaction of cold diluted alkaline KMnO_4 b. Combustion
c. Polymerization d. Catalytic hydrogenation
- v. The general formula of alkane is;
☒ a. $\text{C}_n\text{H}_{2n+2}$ b. C_nH_n c. C_nH_{2n} d. $\text{C}_n\text{H}_{2n-2}$
- vi. Sodalime is;
a. NaOH b. KOH c. Mixture of Na and Ca hydroxide ☒ d. CaO and NaOH
- vii. The marsh gas is
a. Ethane ☒ b. Methane c. Propane d. Butane

- viii. Acidic hydrogen is present in
☒ a. Acetylene b. Ethane c. Benzene d. Ethene
- ix. The electrophile in aromatic sulphonation is;
 a. H_2SO_4 b. HSO_4^- ☒ c. SO_3 d. SO_4^{2-}
- x. Catalyst used for Friedal Craft's reaction is;
 a. HNO_3 b. MgCl_2 c. BeCl_2 ☒ d. FeCl_3
- xi. Benzene can not undergo
☒ a. Elimination b. Substitution c. Oxidation d. Addition
- xii. Shape of benzene molecule is
 a. Pyramidal b. Linear planar c. Trigonal ☒ d. Hexagonal planar
- xiii. The isomers of a substance must have
 (a) same chemical properties ☒ (b) same molecular weight
 (c) same structural formula (d) same functional groups
- xiv. Ethanol and dimethyl ether are best considered:
☒ (a) structural isomers (b) stereoisomers (c) enantiomers (d) diastereomers
- xv. Alkenes show geometrical isomers due to
 (a) asymmetry (b) rotation around a single bond
 (c) resonance ☒ (d) restricted rotation around a double bond
- xvi. Geometrical isomerism is shown by
 (a) lactic acid ☒ (b) maleic acid (c) 1-butene (d) 1,1-dichloroethylene
- xvii. A molecule is said to be chiral
 (a) if it contains plane of symmetry (b) it contains center of symmetry
☒ (c) if it cannot be superimposed on its mirror image
 (d) if it can be superimposed on its mirror image
- xviii. Which of the statements is false regarding chiral compounds
 (a) rotate the plane of polarized light ☒ (b) have cis and trans isomers
 (c) exist as enantiomers (d) can be detected with a polarimeter
- xix. An optically active compound
 (a) must contain at least four carbons
☒ (b) when in solution rotate the plane of polarized light
 (c) must always contain an asymmetric carbon atom
 (d) in solution always give a negative reading in polarimeter
- xx. Plane polarized light is affected by
 (a) identical molecules (b) all polymers
☒ (c) chiral molecules (d) all biomolecules
- xxi. It is possible to distinguish between optical isomers
 (a) by using chemical tests (b) by mass spectrometry
☒ (c) by IR spectroscopy ☒ (d) by polarimetry

2: Answer the following questions briefly.

- What is cis-trans isomerism?
- Why alkenes are relatively chemically inert?
 Alkenes usually undergo addition reactions while alkanes do not why?