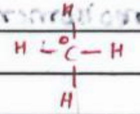
CHAPTER :-

HYDROCARBONS

→ Classification of HC (FTB)

→ Types of Carbon Atoms :

1. zero carbon /(methyl) :- directly bonded to no other carbon atoms

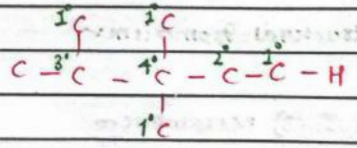


2. Primary carbon (1°) :- directly bonded to one other carbon atoms.

3. Secondary Carbon (2°): directly bonded to two other carbon atoms.

4. Tertiary Carbon (3°): directly bonded to 3 other carbon atoms.

5. Quarternary Carbon (4°): directly bonded to 4 other carbon atoms.



1. Primary Hydrogen (1°) :- bonded to 1° carbon.

2. Secondary H (2°) :- bonded to 2° carbon

4. Tertiary H (3°) :- bonded to 3° carbon

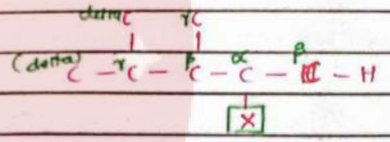
5. Quanternary H (4°) :- bonded to 4° carbon.

1. α - carbon :- the carbon to which functional group is attached is called α - carbon.

→ α - carbon can be 1°, 2°, 3° or 4° etc.

2. β - carbon :- the carbon adjacent to the α - carbon is called β - carbon.

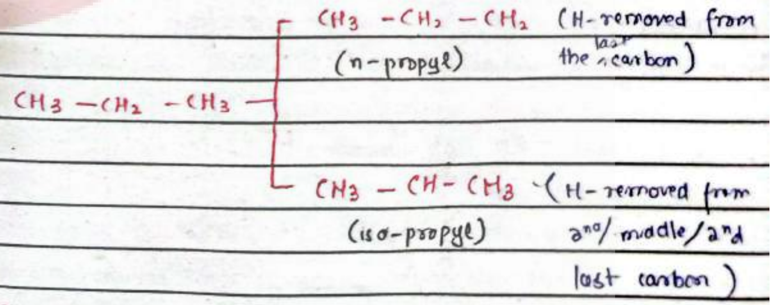
3. γ - carbon :- the carbon adjacent to the β - carbon.



4. Alkyl Group (-R) :-

→ formed after the removal of H from alkane

→ C_nH_{2n+1} (general formula).


$CH_3 - CH_2 - CH_3$

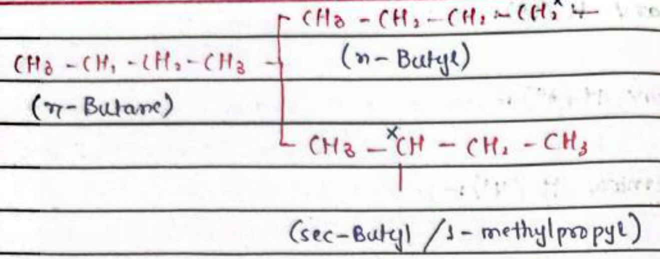
$CH_3 - CH_2 - CH_2$ (H - removed from the last carbon)

(n-propyl)

$CH_3 - CH - CH_3$ (H - removed from 2nd / middle / 2nd last carbon)

(iso-propyl)

①



$CH_3-CH_2-CH_2-CH_3$

(n-Butane)

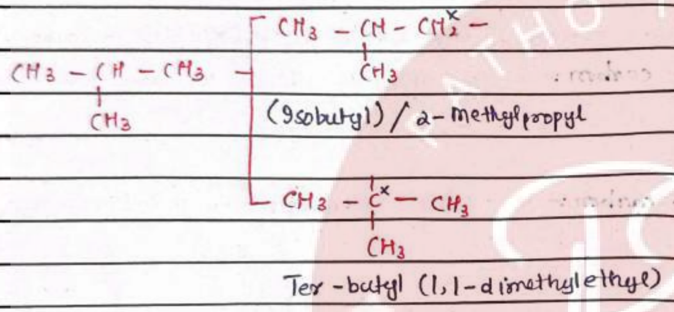
$CH_3-CH_2-CH_2-CH_2-$

(n-Butyl)

$CH_3-\overset{\times}{C}H-CH_2-CH_3$

(sec-Butyl / 1-methylpropyl)

②



$CH_3-CH(CH_3)-CH_3$

$CH_3-CH(CH_3)-\overset{\times}{C}H_2-$

(Isobutyl) / 2-methylpropyl

$CH_3-\overset{\times}{C}(CH_3)_2-$

Ter-butyl (1,1-dimethylethyl)

5. Vinyl Group :-

when a hydrogen is removed from ethene, vinyl group is obtained.

$H_2C=CH_2 \xrightarrow{-H} H_2C=CH-$

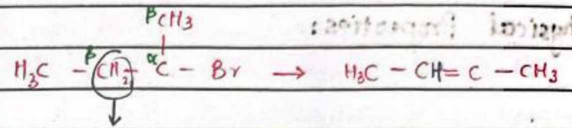
6. Allyl Group :-

Similarly, when a hydrogen is removed from propene, allyl group is obtained.

$CH_3-CH=CH_2 \xrightarrow{-H} -CH_2-HC=CH_2$

* In the β-elimination rxns, if two β-carbon are attached to one α-carbon then from which one the hydrogen will be removed?

Acc. to Zeitzev's rule, the H will be removed from that carbon which leads to the formation of more substituted alkene.



$H_3C-\overset{\beta}{CH_2}-\overset{\alpha}{C}(\overset{\beta}{CH_3})-Br \rightarrow H_3C-CH=C-CH_3$

→ H will be removed from this carbon.

(poor gets poorer.) جس carbon کے پاس H کم ہوں گے اسی سے 'H' remove ہوں گے

Saturated HC

↙ ↘

Alkanes (C_nH_{2n+2})

⇓

paraffins (less reactive)

↓

Latin word "parum affinis (means little affinity)

Cycloalkanes (C_nH_{2n})

ALKANES

1. Less Reactivity :-

Reason :-

i, having non-polar bond $\boxed{\text{polarity} \propto \text{reactivity}}$

ii, due to strong sigma bond ($C\overset{\sigma}{-}H$ and $C\overset{\sigma}{-}C$)

→ alkanes and ethers are the least reactive organic compounds.

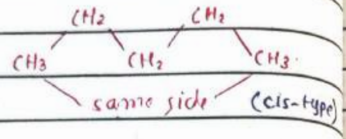
CH_3 CH_2 type.

(diff. side)

2. Structure

'C' is sp^3 hybridized so having a tetrahedral structure.

odd. No



3. Physical Properties:

1) non-polar

2) having LDF due to non-polar nature

3) MP inc↑ down the group in a zig-zag manner.

MP is irregular due to even and odd no. of carbon atoms.

- even no. of C-atoms (best packing in solid state)
- odd no. of C-atoms (poor packing " " ")

MP of odd no. < MP of even no. of C-atoms.

4) BP :- BP ∝ no. of C-atoms (molecular mass)

BP inc↑ with the inc↑ in m-mass.

BP of straight chain alkanes > branched chain alkanes

e.g

n-pentane (36°C) iso-pentane (28°C)

5) Density :- Density ∝ no. of C-atoms

6) But alkanes generally have low BP and MP.

7) highly volatile (highly inflammable).

Reactions :

1) thermal / catalytic reactions 2) combustion reactions
3) Substitution rxns.

Types of Substitution Rxns
- 1. Free Radical Substitution (alkanes)
- 2. Electrophilic Substitution (Benzene)
- 3. SN (alkyl-halides)

→ Where there is Saturation, there is substitution.

→ Alkanes are saturated compounds, so they undergo substitution rxns.

→ Characteristics Rxns :- Free-radical substitution rxns (normal condition).

2) Combustion ↔ doesn't occur at normal condition
↳ occurs at drastic conditions.

→ Alkanes are neither electrophilic nor nucleophilic.

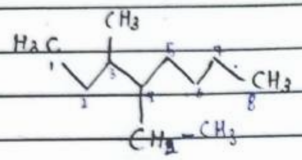
Nomenclature of Alkanes:

MCQ :- the compound that has one isopropyl group is;

Ⓐ 2- Methylpentane Ⓑ 2, 2, 3, 3 - tetramethylpentane

Ⓒ 2, 2-Dimethylpentane Ⓓ 2, 2, 3-Trimethylpentane

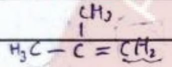
MCQ :- Name the compound given Below;



(A) 5-ethyl-6-methyloctane (B) 4-Ethyl-3-methyloctane

(C) 3-Methyl-4-ethyloctane (D) 2,3-Diethylheptane

MCQ :- the compound having only primary hydrogen atom.



$$H_3C-\overset{CH_3}{\overset{|}{C}}=CH_2$$

(A) Butane (B) Isobutylene (C) cyclohexane

(D) 2,2-Dimethylbutane

Free Radical Substitution Rxn:

1) also called chain rxn. (auto-catalyzed)- free radical acts as catalyst
2) 3-step rxn
3) an oxidation rxn bcz the oxi. state of C inc↑.
4) 1st step → endothermic rxn. $[Cl_2 \xrightleftharpoons{UV} 2\dot{Cl}]$
(Kc = least)
5) 2nd step → propogation. (rate determining step/ slowest step)
6) 3rd step → exothermic rxn (fastest step)
$[\dot{Cl} + \dot{Cl} \longrightarrow Cl_2]$ (Kc = greater)

7) Halogenation of alkane

BOND FISSION / CLEAVAGE

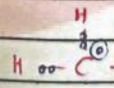
Homolysis | Heterolysis

$A-B \longrightarrow A^{\circ} + B^{\circ}$ | $A-B \longrightarrow A^{+} + B^{-}$

Homolysis	Heterolysis
→ Non-polar	→ Polar bond
→ Light / High temp/ catalyst. (condition needed for homolysis).	→ add the molecule to polar solvent for lysis. e.g (H_2O, R-OH, acetone)
→ Free radicals are produced as a result of homolysis.	→ Charged radicals are produced as a result of heterolysis.

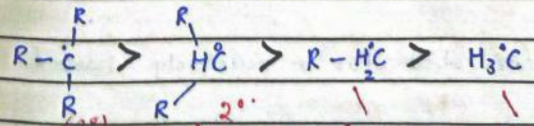
Free radicals :-

1) having unpaired ēs (odd no. of ē).
2) due to unpaired ēs paramagnetic in nature.
3) neutral in nature.
4) highly reactive (highly unstable) $\boxed{\text{stability} \propto \frac{1}{\text{reactivity}}}$
5) Examples :- H°, $\dot{Cl}$, $\dot{Br}$, $\dot{C}H_3$, $\dot{C}H_3-CH_2$ etc.



$$H-\overset{H}{\dot{C}}-H \rightarrow C \begin{cases} 7\bar{e}s \\ sp^2\text{-hybridized (planar structure)} \end{cases}$$

→ Order of stability of Free Radical :-



$$R-\overset{R}{\underset{R}{\dot{C}}} > R_2H\dot{C} > R-H_2\dot{C} > H_3\dot{C}$$

(3°) 2° (free-radical) (1° free radical) (methyl free radical)

* $(C_6H_5)_3\dot{C}$ > $(C_6H_5)_2\dot{C}H$ > $(C_6H_5)\dot{C}H_2$ >

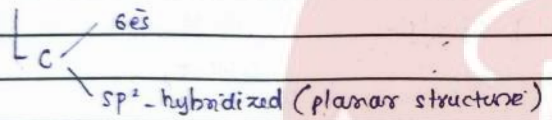
$CH_2=CH-\dot{C}H_2$ > $(CH_3)_3\dot{C}$ > $(CH_3)_2\dot{C}H$ >

$CH_3\dot{C}H_2$ > $\dot{C}H_3$ > $CH_2=\dot{C}H$ > $HC\equiv\dot{C}$

* Carbocation :- (Carbonium Ion)

1) A carbocation is an ion in which a carbon atom has a +ive charge and 3 bonds

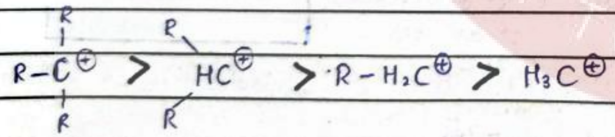
e.g $H_3\overset{\oplus}{C}$, $CH_3-\overset{\oplus}{C}H_2$. etc.



2) have even no. of ēs so diamagnetic

3) Electrophile

→ Order of Stability of Carbocation :-



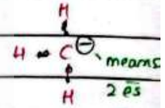
(3°) (2°) (1°) (methyl)

* Carbanion :-

1) an organic anion which has a negatively charged carbon.

2) It is -ively charged carbon having 8ēs in valence shell.

3) sp³ - hybridized 'C'. (Pyramidal shape)

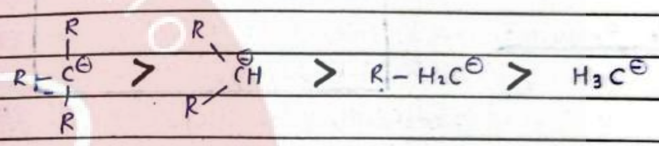


4) conjugate base of carbon acid;

$$\boxed{R_3CH + B^- \longrightarrow R_3C^- + B^-}$$

5) Nucleophile 6) Diamagnetic (even no. of ēs).

→ Carbanion stability Order :-

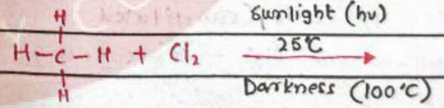


→ The Stability of the Carbocation is Affected By :-

1) Resonance 2) Hyperconjugation 3) No. of R- groups

4) Positive inductive effect.

→ Halogenation of Alkanes : (CH_4 , C_2H_6)



$$\boxed{\text{conditions}}$$

catalyst (R-O-O-R) - mostly di-benzyl peroxide.

Step 1 :- $Cl_2 \xrightarrow{UV} 2C\dot{l}$ (Initiation) — endothermic

Step 2 :- $\dot{C}H_4 + \dot{C}l \longrightarrow \dot{C}H_3 + HCl$. (Propagation) - RDS

$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \dot{C}l$

free radical is not initial but an intermediate specie.

3rd Step (Termination) :- (exothermic)

$\dot{C}l + \dot{C}H_3 \rightarrow CH_3-Cl$

$\dot{C}l + \dot{C}l \rightarrow Cl-Cl$

$\dot{C}H_3 + \dot{C}H_3 \rightarrow CH_3-CH_3$

→ 3rd step is exothermic bcz the product is formed from highly reactive reactants.

→ **Rxn Kinetics :-**

Rate $= k[CH_4]^1[Cl_2]^{1/2}$

O.R. $= 1 + 1/2 = 1.5$ or $3/2$

Possible Products :-

1) Cl_2 2) CH_3Cl 3) CH_2Cl_2 4) $CHCl_3$
5) CCl_4 6) CH_3-CH_3 7) HCl (by product)

→ Substituted Products :-

1) CH_3Cl 2) CH_2Cl_2 3) $CHCl_3$ 4) CCl_4.

→ Products for Chlorination of Ethane

1) C_2ClH_5 2) $C_2H_4Cl_2$ 3) $C_2H_3Cl_3$ 4) $C_2H_2Cl_4$
5) C_2HCl_4 6) C_2HCl_5 7) C_2Cl_6 (substituted products) 8) HCl 9) n-butane ($H_3C-CH_2-CH_2-CH_3$)

→ Order of Reactivity of Halogens :-

$$\boxed{F_2 > Cl_2 > Br_2 > I_2}$$

F_2 :- ① no substituted products are formed
② breaks the C–C bond and forms flourinated

alkanes instead of replacing H-atoms.
③ explosive rxn
④ can occur in dark $CH_4 + F_2 \xrightarrow[\text{can't follow}]{\text{in dark}}$ (x).

→ Br_2 / Cl_2 :- $CH_4 + Br_2/Cl_2 \xrightarrow{UV}$ (✓)
→ (only chlorination and bromination are useful in Lab)
→ moderate speed rxn.

→ I_2 :-
→ very slow rxn, needs catalyst (oxidants HNO_3, H_2SO_4)
→ reversible rxn

$$CH_4 + I_2 \rightleftharpoons CH_3-I + HI$$ (strong Reducing agent).

when the rxn reaches the equilibrium the product conc. is approx. zero and reactants are in high conc.

Rate of radical substitution rxn / rate of H-abstraction ∝ stability of free radical.

→ Stability and Reactivity Order of free radical :-

$$\boxed{\underset{3^\circ}{(CH_3)_3\dot{C}} > \underset{2^\circ}{(CH_3)_2\dot{C}H} > \underset{1^\circ}{CH_3\dot{C}H_2} > \underset{\text{methyl}}{\dot{C}H_3}}$$

Initial species :- more stable → less reactive
less stable → more reactive

Intermediate species :- more stable → more reactive
less stable → less stable

→ Order of Reactivity of Alkanes:

Tertiary alkane > sec. alkane > Pri-alkanes

3° free radical is the most stable that's why 3°-alkanes react faster

MCQ:- WOF is least reactive towards Cl_2/UV?

[✓ (A) CH_4] (B) CH_3-CH_3 (C) $(CH_3)_2CH_2$ (D) $(CH_3)_3CH$

less reactive CH_3 radical

→ Extent of Halogenation:-

⇓

depends upon the amount of halogen used;

$$\underset{\text{(Limited)}}{CH_4} + \underset{\text{(excess)}}{Cl_2} \longrightarrow \underset{\text{(major product)}}{CCl_4} + HCl + \underset{\text{(minor product)}}{CH_3Cl}$$

↓

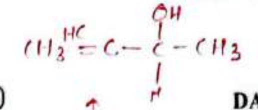
(more halogenated / tetrahalogenated compound)

$$\underset{\text{(excess)}}{CH_4} + \underset{\text{(limited)}}{Cl_2} \longrightarrow \underset{\text{(major)}}{CH_3Cl} + \underset{\text{(minor)}}{CCl_4}$$

$$\underset{\text{(same)}}{CH_4} + \underset{\text{(same)}}{Cl_2} \longrightarrow \text{mixture form}$$

MCQ:- $CH_3-CH_3 + Cl_2 \xrightarrow{UV}$. How many chiral molecules are possible if Cl_2 is continuously reacted with CH_3-CH_3

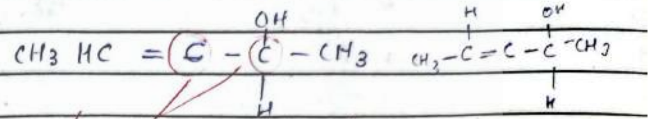
(A) 1 (B) 2 (C) 3 [✓ (D) 0]



$CH_3HC=C-\overset{OH}{\underset{H}{C}}-CH_3$

MCQ:- How many stereoisomers are possible for;

(A) 1 (B) 2 (C) 3 [✓ (D) 4]



$CH_3HC=C-\overset{OH}{\underset{H}{C}}-CH_3$ $CH_3-\overset{H}{C}=C-\overset{OH}{\underset{H}{C}}-CH_3$

(2 steriogenic centres)

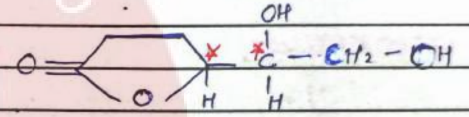
$2^n = 2^2 = 4.$

MCQ:- Vitamin 'C' has how many optical centres?/

[✓ (A) 2] (B) 3 (C) 1 (D) None

ascorbic acid.

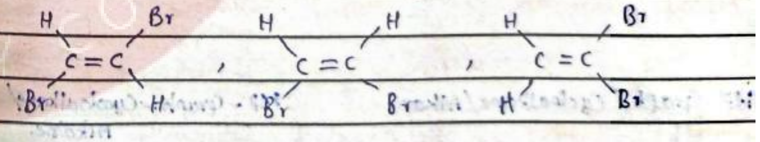
chiral centre ↓ (asymmetric carbon)



MCQ:- $(C_2H_2Br_2)$. WOF isomerism is possible? How many isomers are possible

(A) structural isomerism
(B) cis-trans
(C) optical
[✓ (D) both A and B]

(A) 2
[✓ (B) 3]
(C) 4
(D) 1

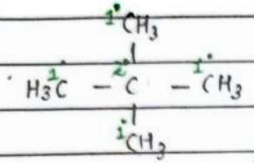


MCQ:- WOF is a HC?

(A) urea (B) Phenol (C) Acetonitrile [✓ (D) Anthracene]

MCQ:- No. of primary-H in neopentane is;

(A) 2 (B) 6 (C) 10 [✓ (D) 12]



4 1° C = 3 1°H

4 x 3 = 12 1°H

common name (neopentane)

IUPAC (2,2-dimethylpropane)

MCQ :- Reactivity of chlorine and bromine towards methane is differ by a factor nearly;

(A) 10^3 (B) 10^4 (C) 10^2 [✓ D] $>10^5$

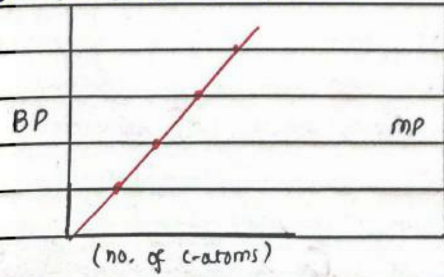
$\boxed{>10^5 \text{ (375000 times)}}$

MCQ :- Which product is not obtained during the chlorination of CH_4 ?

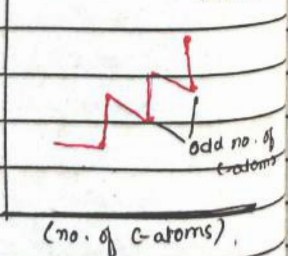
(A) C_2H_6 (B) $CHCl_3$ [✓ C] C_3H_8 (D) CCl_4

CYCLOALKANES

BP Graph/ cycloalkane/Alkane



MP – Graph:- Cycloalkane Alkane.



$\boxed{\text{BP of cycloalkane} > \text{BP of open chain alkane}}$

(for corresponding)

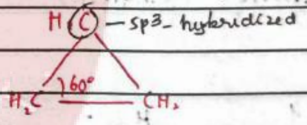
e.g cyclopentane > n-Pentane

mP, BP, density > mP, BP, density of n-pentane.

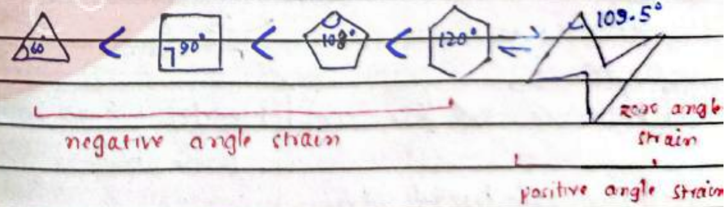
→ Heat of combustion of cycloalkane :-

$$\boxed{(CH_2)_n + n\frac{3}{2}O_2 \longrightarrow nH_2O + nCO_2}$$

→ Structure of Cyclopropane :



→ Angle Strains in Cycloalkanes :-



$$\boxed{\text{stability} \propto \frac{1}{\text{angle strain}}}$$

Reactivity ∝ angle strain

Ring opening rxn ∝ angle strain

⇓

(followed only by cyclobutane and cyclopropane)

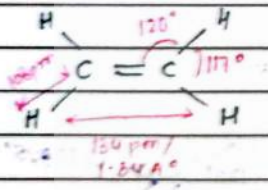
⇓

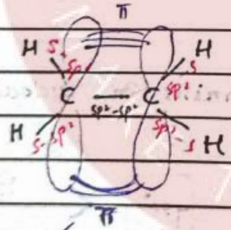
other b/c they are more reactive due to the ring opening rxns.

→ All other follow free radical substitution rxns like open chain alkanes.

ALKENES

Structure of Ethene :- (ethylene)





[2py - 2py and (2pz - 2pz)] → overlap → form π bond

(2px + py → sp² - hybridized)

→ Due to π electronic system, alkene is considered as a nucleophile

• the sigma bonds are coplanar whereas π bond of unhybridized p-orbital is perp to the plane of hybridized orbital.

→ the C−C double bond represents:-

i, structural unit ii, functional group
iii, reaction site iv, influence the geometry of the molecule.

→ Type of Isomerism shown by Alkenes:-

1) Chain Isomerism 2) Position. I 3) Geometric I

→ Types of Isomerism shown by Alkanes:

1) Chain. I 2) Confirmational. I

→ Types of Alkenes (On the basis of No. of C=C).

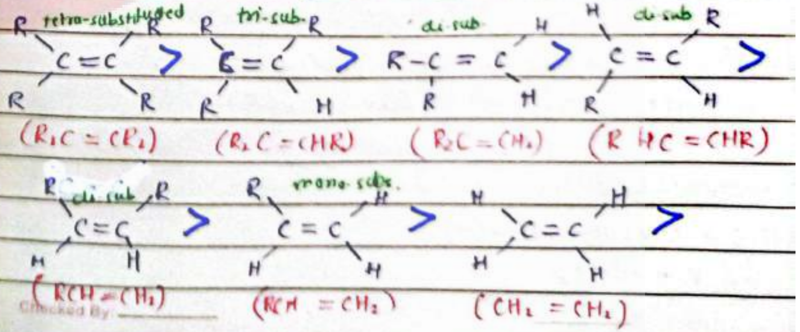
1) monoene $\boxed{C_nH_{2n}}$
2) diene $\boxed{C_nH_{2n-2}}$

→ **Relative Stability of Alkenes/ Reactivity of Alkenes:**

→ depends upon the following factors:-

① Degree of substitution :-

Stability ∝ no. of substituents.



- more 'R', more stable and vice versa.
- more H, more reactive and vice versa.

② Position of the double bond :-

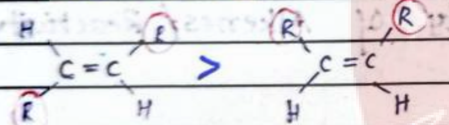
terminal < non-terminal
(—C = CH₂)   (R—C = C—R)

③ Nature of the "R" groups :- (more bigger 'R', more stable)

stability ∝ no. of α-hydrogen

④ Stereochemistry :-
(the relative position of substituents in space)

Trans > cis



(less steric repulsion b/w R-R)

⑤ Conjugation :-

Conjugated alkene > Isolated alkene >

$H_2C = CH - HC = CH - CH_3$ $H_2C = CH - CH_2 - CH = CH_2$
(1,3 - pentadiene)   (1,4-pentadiene)

cummulated alkene

$H_2C = C = CH - CH_2 - CH_3$
(1,2 - Pentadiene)

conjugated > isolated > cummulated

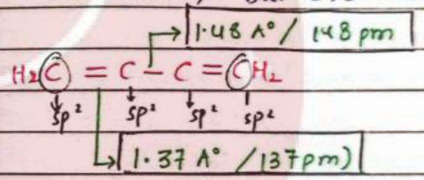
→ relative stability/reactivity Order for alkenes, free radicals, carbocations (same).

Alkene Stability ∝ $\frac{1}{\text{Heat of hydrogenation/ oxidation/ combustion}}$

Alkene Reactivity ∝ H.O.H / oxidation / combustion

→ Conjugation In Alkenes:-

1,3- Butadiene / But-1,3-diene.



→ all sigma bonds lie in one plane. (coplanar)

→ C=C (double bond) normal = 134 pm
in conjugated alkene = 137 pm (longer than expected)

→ C-C (single bond) normal = 154 pm
in conjugated alkene = 148 pm (shorter than expected)

→ Applications :-

1) due to conjugation ;

i, extra stability (resonance energy) → energy is less than the expected.

ii, Analmous bond length → bond length are less/ greater than the expected.

→ Ethene Vs Ethyne Reactivity :-

1) single π bond in ethene is more exposed and easily accessable. $H-C\equiv C-H$

(less denser electronic cloud / low density) → less reactive

2) bond dissociation energy : < BD energy of ethyne & ethene

{ more charge density / more denser electronic cloud / more reactivity }

3) ethene (unsymmetrical pi-bond)

ethyne (symmetrical pi-bond) / cylindrical pi-cloud

↓ ↓

(more symmetry so more stable)

→ more % s-character → more EN → more attraction on π es.

→ Order of Reactivity of Hydrocarbons (for Electrophilic Rxn)

Alkenes > Alkynes > Benzene > Alkanes

→ Order of Reactivity of Hydrocarbons (for the Nucleophilic Reaction)

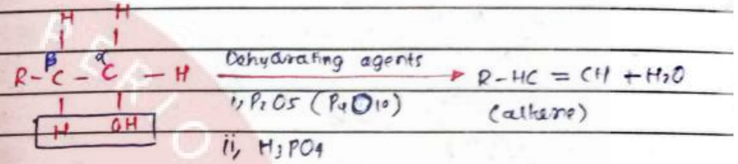
Alkynes > Alkenes > Benzene > Alkanes

• Preparation of Ethene :-

1· Dehydration of Alcohols :-

→ De (remove) hydra (H_2O) and tion (process).

→ (alcohol $\xrightarrow{-H_2O}$ alkene)



$R-\overset{\beta}{C}H(H)-\overset{\alpha}{C}H(OH)-H \xrightarrow{\text{Dehydrating agents}} R-HC=CH + H_2O$ (alkene)

i, P_2O_5 (P_4O_{10})

ii, H_3PO_4

iii, ~~conc~~ H_2SO_4

Intra - E_2

Inter - SN_2

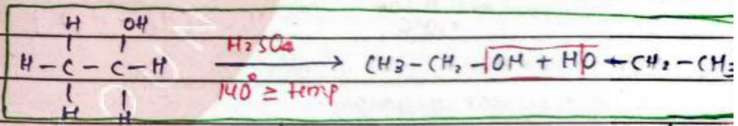
i, conc H_2SO_4 (170° ≤ temp)

ii, E_2-mechanism is followed.

iii, Intramolecular dehydration (within the molecule)

iv, alcohol ⟶ carbocation ⟶ alkene

(reactant) (rxn intermediate) (product).

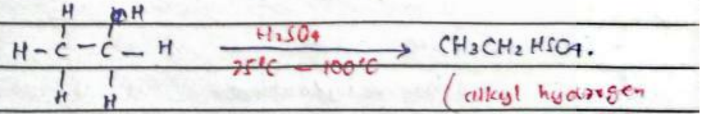


vi, $H-\overset{H}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-H \xrightarrow[140° \geq temp]{H_2SO_4} CH_3-CH_2-\boxed{OH + H}O-CH_2-CH_3$

↓

Intermolecular dehydration (self-condensation)

↳ SN_2-mechanism is followed.

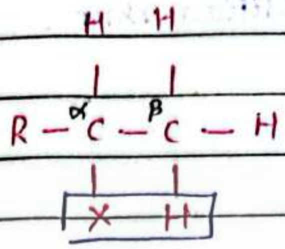


vii, $H-\overset{H}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-H \xrightarrow[~~75°C - 100°C~~]{H_2SO_4} CH_3CH_2HSO_4.$

(alkyl hydrogen sulphate)

Checked By: ______

2. Dehydrohalogenation of alkyl halides:



$R-\overset{\alpha}{C}-\overset{\beta}{C}-H \xrightarrow{\text{strong base}} R-HC=CH_2 + HX$

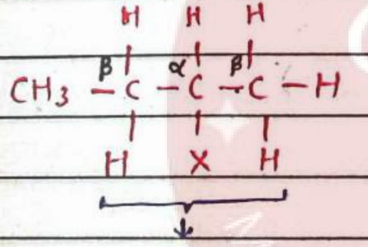
i) KOH in alcohol → more commonly used

ii) $Na_2O_2CH_5$ in alcohol

iii) $NaOCH_3$ in alcohol

→ It is a β- Elimination Rxn

- E1 (3° R-X)
- E2 (1° R-X)



$CH_3-\overset{\beta}{C}H_2-\overset{\alpha}{C}HX-\overset{\beta}{C}H_2-H \longrightarrow$

$CH_2-CH_2-HC=CH_2$ (1-Butene)

$CH_3-HC=CH-CH_3$ (2- Butene) (major product)

'H' is removed from the carbon having less no. of H-atoms.

↓

poor gets poorer/richer get richer.

▸ Acc. to Zeitzaev's Rule, more substituted alkene is more stable. (and)

▸ Elimination rxn favours more substituted product.

→ Order of Reactivity of H-X :-

HX : HF < HCl < HBr < HI

→ Reactions Of Alkenes :

1) Characteristic Rxns : Electrophilic Addition rxns

→ 2 step rxn :- 1) Add electrophile ($E^{\oplus}$)
2) Add nucleophile ($\ddot{Nu}^{\ominus}$)

→ It is called electrophilic addition bcz it is initiated by an electrophile.

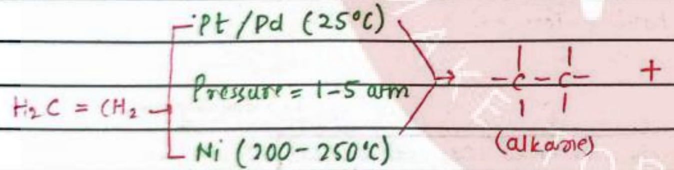
→ whereas alkene itself is a nucleophile.

1. Hydrogenation :

→ addition of H_2 (reduction)

→ catalytic hydrogenation

→ exothermic process (energy is released)
 L breaking of π bond
 L sigma bond breaking b/w H - H.


$H_2C=CH_2$ — Pt / Pd (25°C) / Pressure = 1-5 atm / Ni (200-250°C) → $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$ (alkane) +

$\Delta H_h = -ive$

ΔH_h for ethene = −136 kJ/mol (heat of hydrogenation)

→ the energy released per double bond (breaking) is generally 120 kJ/mol.

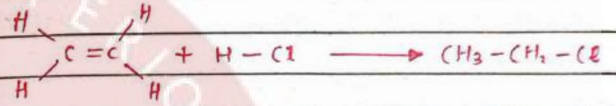
→ when stable bonds are formed, energy is released.

MCQ :- WOF is not efficient in hydrogenation?
(A) Ni (B) Pt / Pd
(requires high temperature)

2. Hydrohalogenation :-

→ addition of H and X, or HX.

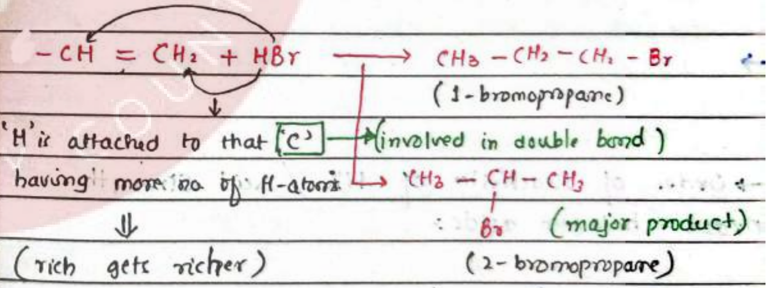
→ Preparation of alkyl halides.


$CH_2=CH_2 + H-Cl \longrightarrow CH_3-CH_2-Cl$

(for symmetric alkene and reagent only one product is possible).

→ for unsymmetric reagent Markonikov's Rule is followed :-

(unsymmetrical substrate + unsymmetrical reagent)


$-CH=CH_2 + HBr \longrightarrow CH_3-CH_2-CH_2-Br$ (1-bromopropane)

'H' is attached to that 'C' (involved in double bond) having more no of H-atoms

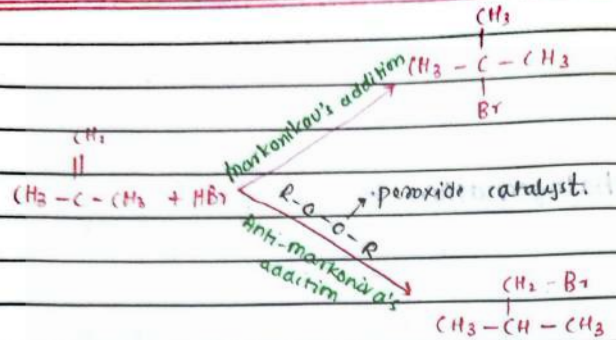
⇓

(rich gets richer)

$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$ (major product) (2-bromopropane)

→ 2 - step - rxn :-
 L ① Add electrophile. (H^+)
 L ② Add nucleophile (X^-)

Checked By: ______



'H' is attached to that carbon ← (Khrash Rule) (involved in (=) bond) having lesser no. of H-atoms (against the Markonikov's Rule).

Markonikov's Addition	Anti-markonikav's Addition
→ catalyst not used	→ catalyst is used.
→ carbocation (rxn intermediate ↓ ionic mechanism.	→ Free-radical is the rxn intermediate.

→ Only for HBr, antimarkonikav's rule can be applied.

→ Order of Reactivity of HX / Acid Strength

Order halogen acids :-

HI > HBr > HCl > HF

(least B.E) (High B.E)

→ Order of Reactivity of Alkenes :-

Nucleophile (Lewis base)

more substituted alkene → less reactive and vice versa.

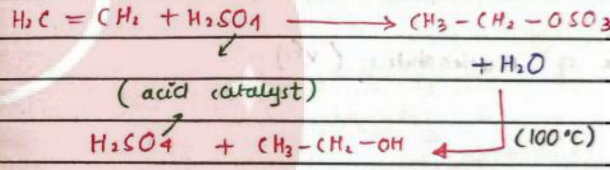
3. Hydration :-

→ addition of H_2O

→ $$\boxed{\text{Alkene} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} \text{alcohol}}$$

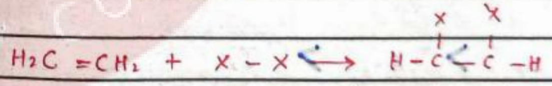
- acid catalyzed (both hydration & dehydration of alcohol)
- carbocation (rxn intermediate)
- Order of Reactivity of R-OH

$3° > 2° > 1° > CH_3-OH$



4. Halogenation :

→ Addition of halogen



$$H_2C=CH_2 + X-X \longrightarrow H-\overset{X}{\underset{|}{C}}-\overset{X}{\underset{|}{C}}-H$$

(vicinal dihalide)

→ when the electrophile approaches the halogen, it polarizes it and pushes its lone pair and the bond b/w X-X breaks.

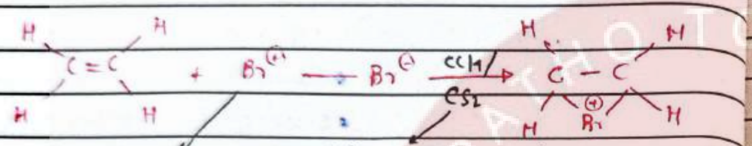
Checked By:

(halonium ion) $X^{\oplus}$ ↓ (electrophile)

$X^{\ominus}$ (halide ion) ↓ (nucleophile)

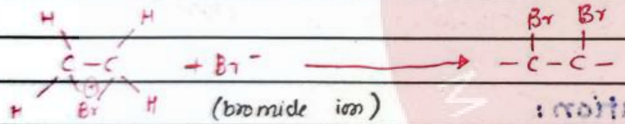
Mechanism :-

① Attack of Electrophile ($X^{\oplus}$):-



(electrophile) inert/non-polar ε solvent (cyclic halonium ion)

② Attack of Nucleophile. ($X^{\ominus}$) :-



→ Reactivity Order of Halogens :-

F_2 > Cl_2 > Br_2 > I_2

F_2 ↓ fast (create explosions)

I_2 ↓ (very slow)

→ Stability order of dihalides :-

dichlorides > dibromides > diiodides

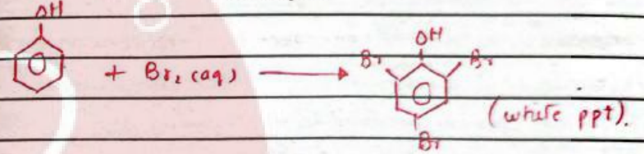
(stable at RTP) unstable at RTP

* F_2 → not mentioned bcs it create explosions.

→ Applications :-

Aqueous Br_2 (Br_2 water / Br_2 aq) test)
⇓
to detect unsaturation. / phenol.

C=C / C≡C + Br_2 (aq) ⟶ colourless (orange / brownish colour vanished)
↓
(brownish) orange.



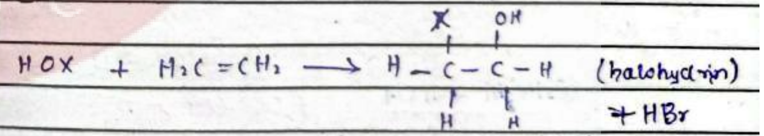
(white ppt).

5. Halohydration :-

→ Addition of Halogen (X) and (OH)

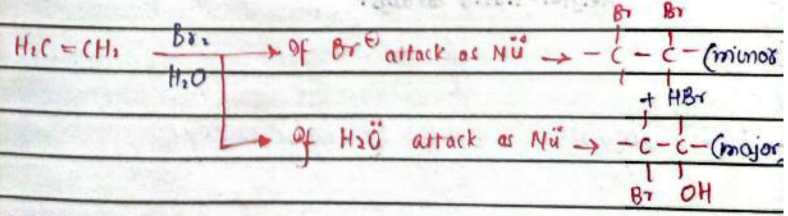
→ Mechanism :- HBr.

① (H)–OH + (X)–X ⟶ HOX (hypohalous acid)

② 

$$HOX + H_2C=CH_2 \longrightarrow H-\overset{X}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-H$$

(halohydrin) + HBr



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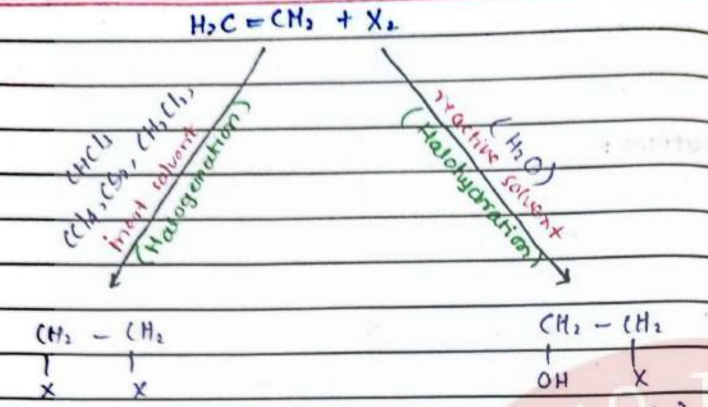


(vicinal dihalide)

(halohydrin)

$H_2C = CH_2 + Br_2 \xrightarrow{CCl_4} H_2C - CH_2$ (Br, Br)

(1,2 - Dibromoethane / Ethylene dibromide)

EDB

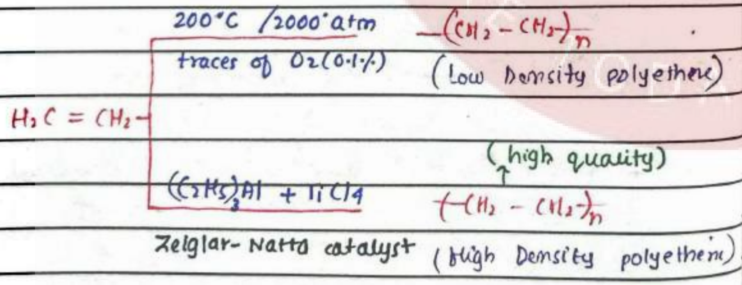
↓

used as

pesticide

soil fumigant

(c) Polymerization:



KP :-

200°C / 2000 atm + H_2O_2 (initiator catalyst).

FTB :-

$(C_2H_5)_3Al + TiCl_4$ + 400°C / 100 atm and traces of O_2 (0.1%).

→ thermodynamically feasible rxn.

→ exothermic

→ pi-bond convert into sigma bond.

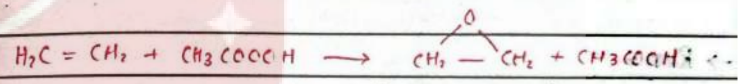
→ monomer converts → larger, longer and single molecule.

7. Epoxidation: (oxidation rxn)

alkenes + peroxyacids/ (peracid) ⟶ epoxides (cyclic ethers)

↓

e.g (oxyacetic acid / peroxy benzoic acid)

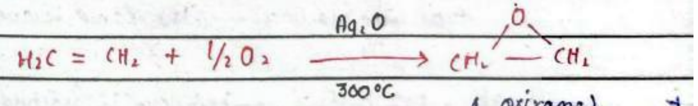


(ethylene oxide) / (epoxy ethane)

[oxirane]

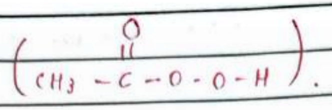
→ commonly used peracid is (peracetic acid)

→ On industrial scale ethylene oxide is prepared by the air oxidation of ethene with silver oxide catalyst at 300°C.



(oxirane)

→ epoxides are imp org compounds. On acid hydrolysis produces glycols.

Peracetic acid 
$\left(CH_3-\overset{O}{\overset{\|}{C}}-O-O-H\right).$

8. Ozonolysis :

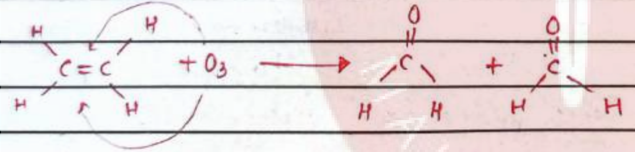
→ addition of O_3 → so oxidation rxn.

→ versatile rxn.

→ Applications :

1) to check unsaturation
2) to find the double bond position
3) to find unknown alkene
4) to prepare ketone, aldehyde, COOH.

→ Rxn :-

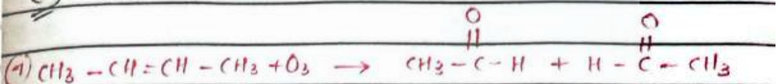


→ symmetrical alkene → 2 same compounds

two same aldehydes | two same ketones

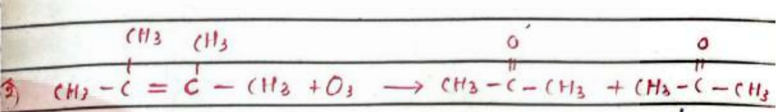
→ unsymmetrical alkene → two diff. compounds
- both can be aldehyde
- both can be ketone
- 1 aldo and 1 keto

e.g


$(1)\ CH_3-CH=CH-CH_3+O_3 \rightarrow \underbrace{CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-CH_3}$

2-butene
(symmetrical)

both aldehydes.


$(2)\ CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3+O_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

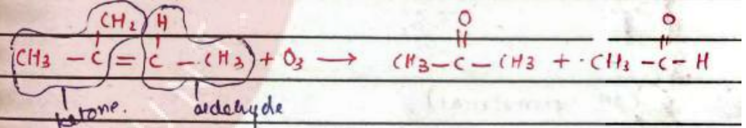
(2,3-dimethyl butene)
(unsymmetrical)

↳ both ketones ↵

→ substituent at double bond (both carbons) → always ketone

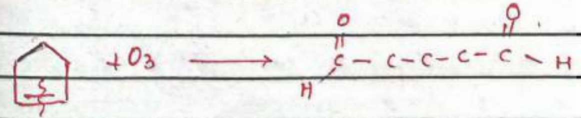
→ substituent at one carbon → 1 aldo and 1 keto.
side with substituent (ketone)
side without substituent (aldehyde)

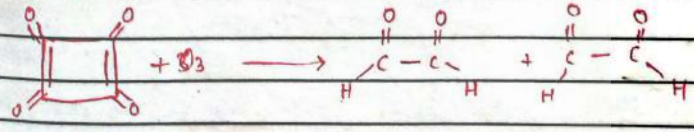
→ no substituent → both are aldo.


$CH_3-\overset{CH_2}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_3+O_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-H$

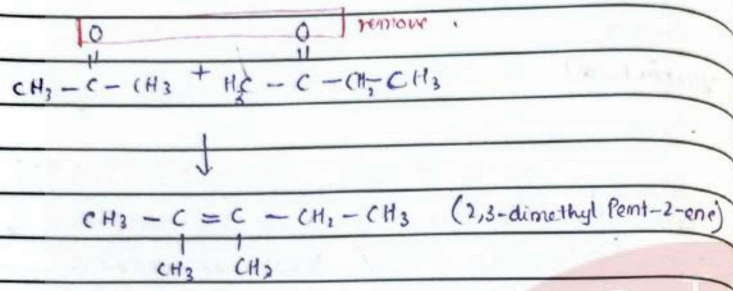
→ Rxn of cyclic Alkene and Ozone (O_3)

cyclic alkene + O_3 ⟶ dialdehyde





MCQ of an alkene (Y) reacts with ozone (O_3) and forms acetone + Butanone. Find the alkene.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H_3C-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

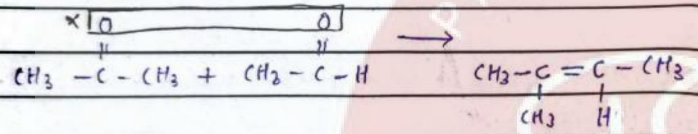
remove.

$$\downarrow$$

$$CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_2-CH_3$$

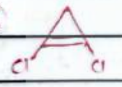
(2,3-dimethyl Pent-2-ene)

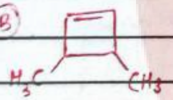
MCQ :- acetone + aldehyde $\xrightarrow{O_3}$ alkene ?



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3-\overset{\overset{O}{\|}}{C}-H \longrightarrow CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-CH_3$$

MCQ :- WOF can follow the MK-rule?

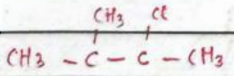
Ⓐ 

Ⓑ 

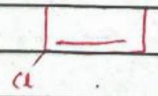
Ⓒ $CH_3-CH=CH-CH_3$

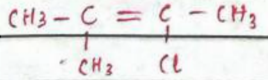
● none (all symmetrical)

★ MCQ :- WOF can't follow MK-rule?

Ⓐ 

$$CH_3-\overset{CH_3}{\overset{|}{C}}-\overset{Cl}{\overset{|}{C}}-CH_3$$

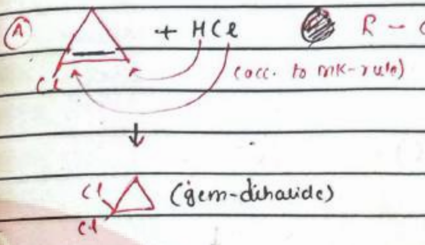
Ⓑ 

Ⓒ 

$$CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{Cl}{\underset{|}{C}}-CH_3$$

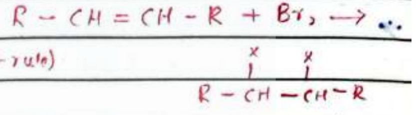
Ⓓ All Ⓔ None

★ MCQ :- WOF can give vicinal dihalide?

Ⓐ 

(acc. to MK-rule)

(gem-dihalide)

● 

$$R-CH=CH-R + Br_2 \longrightarrow R-\overset{X}{\overset{|}{C}H}-\overset{X}{\overset{|}{C}H}-R$$

(vicinal dihalide)

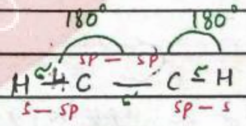
ALKYNES :- (acetylenes)

Acetylene (Alkyne),
- linear molecule hence geometrical isomers not possibl

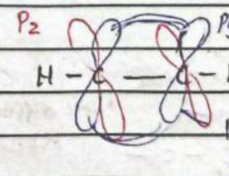
→ Hydrocarbons having → C ≡ C (FG, reaction site)
→ simplest alkyne (acetylene)
- C_2H_2
- HC ≡ CH (garlic-like odour)

$\boxed{C_nH_{2n-2}}$

→ Structure of Ethyne :



(Linear geometry /shape)



perpendicular to the sigma framework

Py − Py (1st π bond) and Pz − Pz (2nd π bond)

→ π electronic cloud is present cylindrically symmetrical about the bond axes.

→ 's'-orbital (closer to nucleus) → when they overlap both the C-atoms become very close to each other.

→ (C–C)	(C=C)	(C≡C)
(154 pm)	(134 pm)	(119 pm)
↓	↓	↓
(C–H)	(C–H)	(C–H)
(109.5 pm)	(108 pm)	(106 pm)
(ethane)	(ethene)	(ethyne)

→ % s-charachter inc↑ ; bond length dec↓

→ bond length dec↓ so bond strength inc↑.

→ Order of Reactivity:

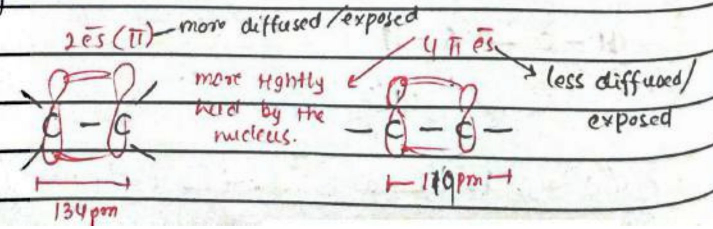
①

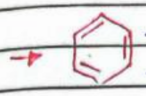
alkenes > alkynes > Benzene > alkanes

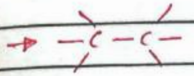
(for electrophilic rxns)

$\boxed{\ddot{Nu}^{\ominus} \longrightarrow E^{\oplus}}$

in alkene → π ēs are exposed → attack of electrophile is faster on alkene.




→ π ēs are extensively delocalized
→ strong $E^{\oplus}$ needed for locating π ēs


→ no π ēs
→ that's why the give free radical substitutio rxns

$$\boxed{\text{Bond Energy} \propto \text{Stability} \propto \frac{1}{\text{Reactivity}}}$$

① >C=C< (614 kJ/mol) → less stable / more reactive

② –C≡C– (839 kJ/mol) → more stable / less reactive.

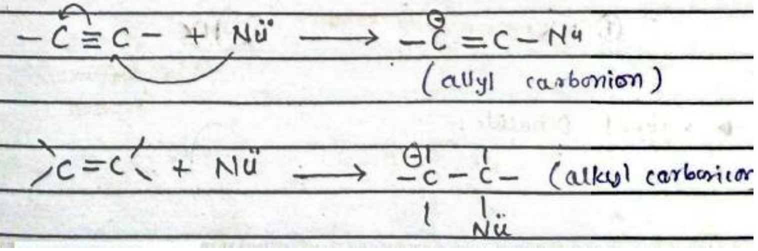
→ Alkenes } characteristic rxns (electrophilic addition rxns)
Alkynes }

→ Benzene } characteristic rxn (electrophilic substitution rxn)

② alkynes > alkenes for nucleophilic addition rxns.

i, catalytic hydrogenation

ii, Nucleophilic addition ($\ddot{Nu} = \overset{\ominus}{O}R$, $\overset{\ominus}{O}CH_3$)


$-C\equiv C- + \ddot{Nu} \longrightarrow -\overset{\ominus}{C}=C-Nu$ (allyl carbonion)

$>C=C< + \ddot{Nu} \longrightarrow -\overset{\ominus}{C}-C(\ddot{Nu})-$ (alkyl carbanion

→ allyl carbonium is more stable than alkyl carbonium therefore there are greater chances of allyl carbonium formation.

Hence → alkynes > alkenes.

→ Where there is a negative charge and a π-bond, there will be resonance.

→ alkyne (sp - hybridization)

→ Preparation of Alkynes:

→ can be prepared by dehydrohalogenation of vicinal & gem dihalides in the presence of some alkaline reagent

1. Dehydrohalogenation of Vicinal dihalides:

→ removal of HX

→ E_2 mechanism is followed.

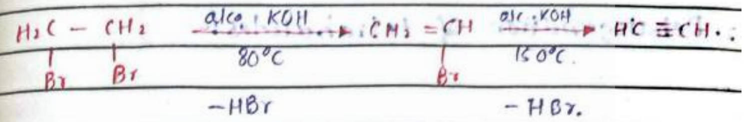
→ Dihalides
- vicinal · dihalides (vicinus $\xrightarrow{\text{Latin word}}$ adjacent)
- Geminal dihalides (Geminus $\xrightarrow{\text{latin word}}$ twins)

$$\text{dihalide} \xrightarrow[\text{80°C}]{\text{alc. KOH}} \text{vinyl halide} \xrightarrow[\text{150°C}]{\text{alc. KOH}} \text{alkyne}$$

① HX ② HX

→ Vicinal Dihalide :-

In the presence of strong base such as KOH and at high T, triple bond at terminal C-atom of higher alkynes migrate to give more disubstituted alkynes. Therefore alc. KOH is useful when rearrangement is not possible.



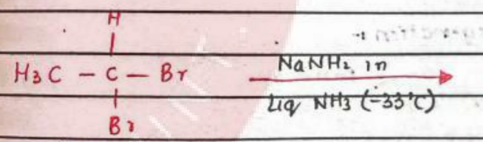
$$\underset{Br}{H_2C} - \underset{Br}{CH_2} \xrightarrow[\substack{80°C \\ -HBr}]{\text{alc. KOH}} CH_2 = \underset{Br}{CH} \xrightarrow[\substack{150°C \\ -HBr}]{\text{alc. KOH}} HC \equiv CH$$

→ to remove the acid (HX), a strong base is needed

→ strong base
- KOH (alcoholic) → KOH in C_2H_5OH
  - ↳ when used rxn completes in two steps. and 2nd step requires high temp/ (very strong base)
- $NaNH_2$ (sodium amide/ sodamide) in Liq NH_3 at -33 °C (very strong base) both rxns in single mixture)

(acc. to KP book : It is generally a two step rxn).

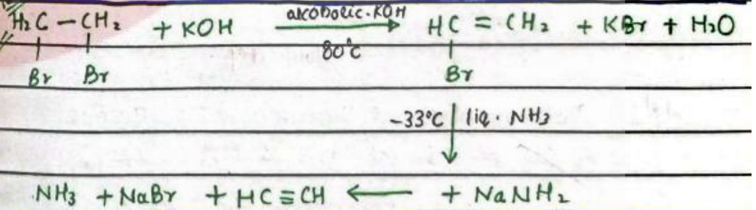
→ Geminal Dihalides :-



$$H_3C - \overset{H}{\underset{Br}{C}} - Br \xrightarrow[\text{Liq } NH_3 \ (-33°C)]{NaNH_2 \text{ in}} HC \equiv CH$$

× ———————— ×

KP Book



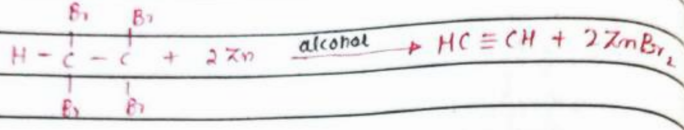
$$\underset{Br}{H_2C} - \underset{Br}{CH_2} + KOH \xrightarrow[\text{80°C}]{\text{alcoholic. KOH}} \underset{Br}{HC} = CH_2 + KBr + H_2O$$

$$\xrightarrow{-33°C \ | \ \text{liq. } NH_3}$$

$$NH_3 + NaBr + HC \equiv CH \longleftarrow + NaNH_2$$

Temp (FTB) → (100 - 120°C)

2. Dehalogenation of tetrahalides :-



$$H-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}} + 2Zn \xrightarrow{alcohol} HC\equiv CH + 2ZnBr_2$$

→ tetrahalides heated with Zn dust in alcohol → alkyne

→ Stability of Alkynes :

→ same as alkenes

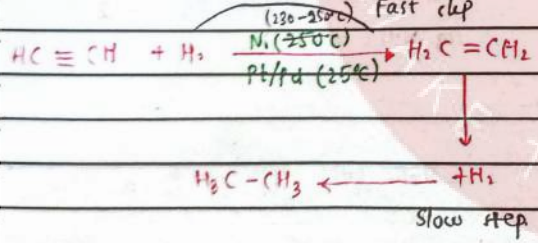
→ more substituted means mor

Acetylene is an unsaturated HC and shows addition rxns. It also undergoes substitution rxns due to easy cleavage of C-H bond. The π e's are present cylindrically symmetrical abt. the C-C sigma bond & the removal of terminal 'H' is possible without disturbing C-C bonding. Therefore, electrophilic substitution rxns are possible in 1-alkynes.

→ Reactions of Alkynes :

1. Hydrogenation :

(a) catalytic Hydrogenation :-

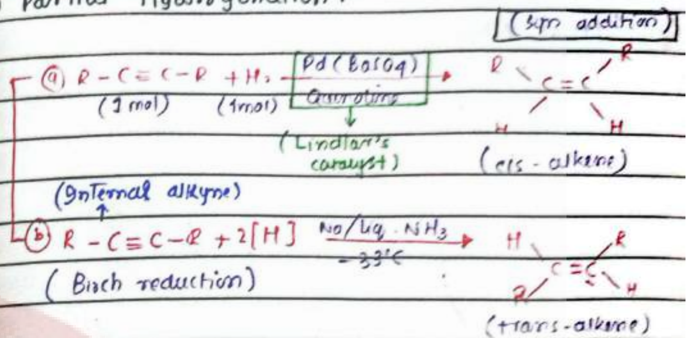


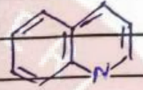
In catalytic hydrogenation; alkynes are more reactive than alkenes. (so 1st step = fast and 2nd step = slow)

ΔH_h = -ive (heat of hydrogenation)

ΔH_h of alkynes > ΔH_h of alkenes.

(b) Partial Hydrogenation :-




(Quinoline)

MCQ:- the hydrogenation at alkene stage can be stopped by:

[✓ (a) using $\overset{1}{\text{half}}$ mole of H_2] (B) Lindlar's catalyst

(C) Both (D) None

for complete hydrogenation $2H_2$ are needed.

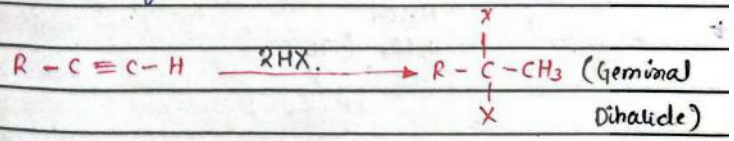
→ Termal Alkynes + acetylenes react with metals such as Na in liq. NH_3 to form salts called alkynides/ acetylides.

(Internal alkynes)

→ reduction of non-terminal alkynes to Trans alkenes (anti-addition) can be carried by the reduction of alkynes with Na metal in NH_3.

2. Hydrohalogenation :

→ addition of HX



$$R-C\equiv C-H \xrightarrow{2HX} R-\underset{X}{\overset{X}{C}}-CH_3 \text{ (Geminal Dihalide)}$$

Acetylene is an unsaturated HC and shows addition rxns. It also undergoes substitution rxns due to easy cleavage of C-H bond. The π ēs are present cylindrically symmetrical abt. the C-C sigma bond & the removal of terminal 'H' is possible without disturbing C-C bonding. Therefore, electrophilic substitution rxns are possible in 1-alkynes.

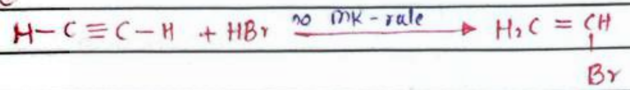
Relative Stabilities of Alkynes :

Alkynes are more stable as comp. to alkenes bcz of prence of an extra π - bond.

- this can be supported by the comparison of thermodynamic data
- ΔH of 1 - Hexyne = 290 kJ/mol
- ΔH of 1 - Hexene = 126 kJ/mol.

Symmetrical Alkyne :-

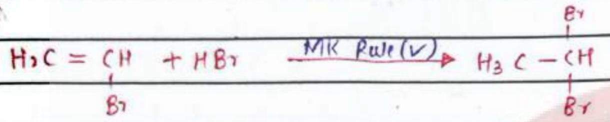
①



$H-C\equiv C-H + HBr \xrightarrow{\text{no MK-rule}} H_2C=CH(Br)$

(vinyl bromide)

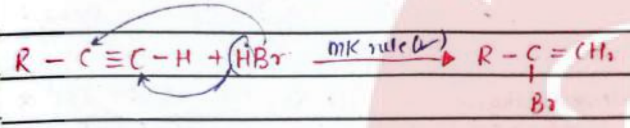
②



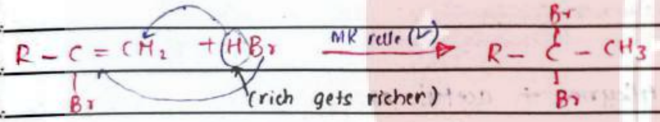
$H_2C=CH(Br) + HBr \xrightarrow{\text{MK Rule (✓)}} H_3C-CH(Br)_2$

Only 2nd step follow MK-Rule.

Asymmetrical Alkyne :-



$R-C\equiv C-H + HBr \xrightarrow{\text{MK rule (✓)}} R-C(Br)=CH_2$



$R-C(Br)=CH_2 + HBr \xrightarrow{\text{MK rule (✓)}} R-C(Br)_2-CH_3$

→ Both steps will follow MK-Rule.

3. Hydration :

→ addition of H_2O

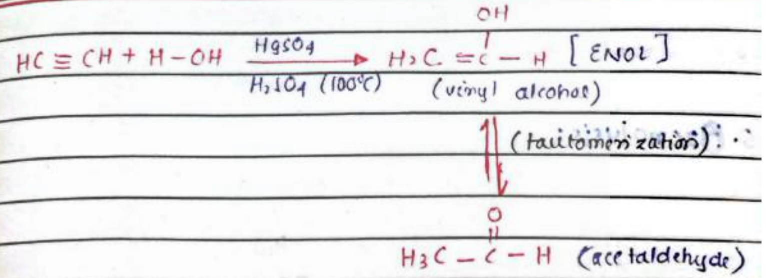
→ Reagent :- a mixture of mercuric sulfate in aqueous sulfuric acid.

→ $\text{alkyne} + H_2O \xrightarrow[\cancel{H_2SO_4\ (75^\circ C)}]{HgSO_4} \text{carbonyl compound}$

↓

KP (100°C)

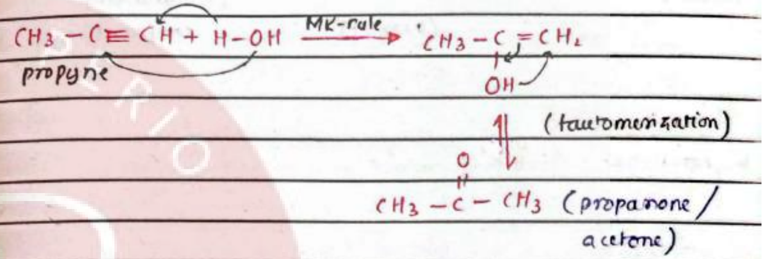
Alkyne + H_2O → alkenol $\overset{\text{tautomers}}{\rightleftharpoons}$ aldehyde/ketone



$HC\equiv CH + H-OH \xrightarrow[H_2SO_4\ (100^\circ C)]{HgSO_4} H_2C=C(OH)-H$ [ENOL] (vinyl alcohol)

$\rightleftharpoons$ (tautomerization)

$H_3C-C(=O)-H$ (acetaldehyde)



$CH_3-C\equiv CH + H-OH \xrightarrow{\text{MK-rule}} CH_3-C(OH)=CH_2$

propyne

$\rightleftharpoons$ (tautomerization)

$CH_3-C(=O)-CH_3$ (propanone / acetone)

→ Only Acetylene/Ethyne → aldehyde

→ Higher alkynes. → ketones (always)

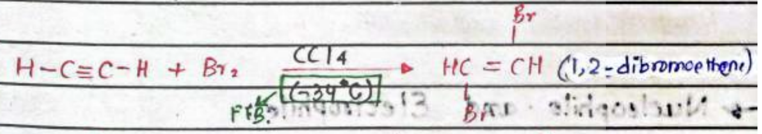
MCQ :- WOF will give aldehyde by hydration?

(A) 1-Butyne [✓ (B) Ethyne] (C) Propyne (D) all

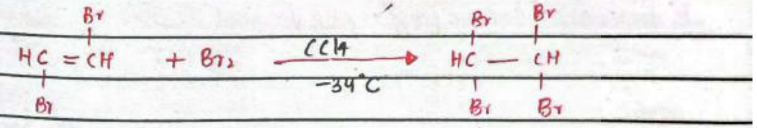
4. Halogenation (Bromination)

→ two step rxn

→ 1st dibromoalkene is formed and then tetrabromide (tetrabromoalkanes) :



$H-C\equiv C-H + Br_2 \xrightarrow[\boxed{(-34^\circ C)}]{CCl_4} HC(Br)=CH(Br)$ (1,2-dibromoethene)



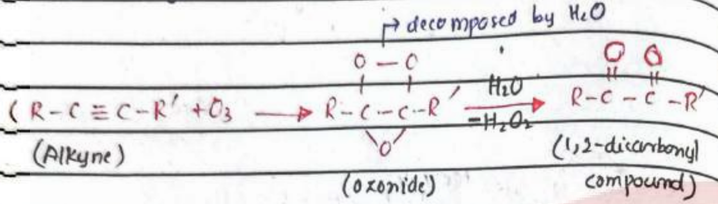
$HC(Br)=CH(Br) + Br_2 \xrightarrow[-34^\circ C]{CCl_4} HC(Br)_2-CH(Br)_2$

(1,2,~~3~~,4-tetrabromoethane)

Checked By:

→ Cl_2 reacts in the similar way.

5. Ozonolysis:



$$R-C\equiv C-R' + O_3 \longrightarrow \text{ozonide} \xrightarrow[-H_2O_2]{H_2O} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R'$$

$$R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{H_2O_2} R-\overset{O}{\overset{\|}{C}}-OH + R'-\overset{O}{\overset{\|}{C}}-OH$$

↳ produced in the rxn.

Terminal Alkynes + Acetylene

$$R-C\equiv C-H + O_3 \longrightarrow RCOOH + CO_2$$

$$HC\equiv CH + O_3 \longrightarrow HCOOH + CO_2$$

Non-Terminal Alkynes

$$R-C\equiv C-R + O_3 \longrightarrow \text{two } COOH.$$

→ Acidity of Terminal Alkynes:

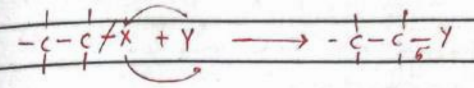
(MM-Notes) (after alkynes topic)

→ Nucleophile and Electrophile:

(MM-notes) (after alkynes topic)

Organic Reactions:

1. Substitution Rxns:-



$$-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-X + Y \longrightarrow -\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\underset{\sigma}{-}Y$$

- A σ bond is formed with the breaking of σ sigma bond in substrate.
- saturated compounds show substitution rxns.

Types:-

(i) Free Radical substitution rxns (alkanes)

(ii) Nucleophilic Substitution (SN) rxns.

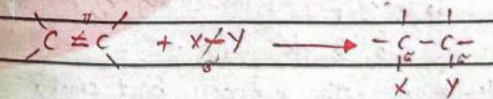
$$R-X + Nu^{\ominus} \longrightarrow R-Nu + X^{\ominus}$$

$$R-OH + HX \longrightarrow R-X + H_2O$$

$$R-\overset{O}{\overset{\|}{C}}-OH + OR/NH_2/X \longrightarrow R-\overset{O}{\overset{\|}{C}}-OR / R-\overset{O}{\overset{\|}{C}}-NH_2 / R-\overset{O}{\overset{\|}{C}}-X.$$

(iii) Electrophilic Aromatic substitution Rxns (Benzene)

2. Addition Rxns:-



$$>C=C< + X-Y \longrightarrow -\underset{X}{\underset{|}{\overset{|}{C}}}-\underset{Y}{\underset{|}{\overset{|}{C}}}-$$

→ a π-bond and a σ-bond break and 2 σ bonds are formed.

→ Unsaturated compounds show addition rxns.

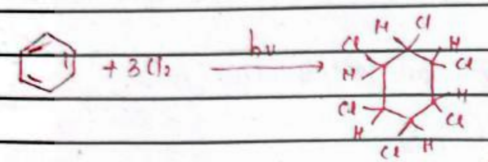
Types :-

i, Free - Radical addition rxns (rxns of anti-MK rule)

$R-HC=CH_2 + HBr \xrightarrow{Peroxide} R-CH_2-CH_2-Br$

↳ without catalyst the rxn will follow MK-Rule.

(anti MK Rule) / (Kharasch's Rule)



ii, Electrophilic Addition Rxns (alkenes, alkynes)

iii, Nucleophilic Addition Rxns (aldehydes & ketones)

BENZENE

– benzene and substituted benzene are called arenes.

1) colourless liq. with peculiar smell and burning taste
2) MP = 6°C and BP = 80°C
3) Insoluble in H_2O
4) Good solvent for → organic substances e.g fats, resins
   ↳ inorganic substances e.g. S, P and I_2 etc
5) highly inflammable. burns with luminous and smoky flame.
6) toxic and carcinogen.
7) Discovery :- Michael Faraday (1825) in a gas produced from the destructive distillation of vegetable oil.

* Hoffman (1845) discovered it in coal tar.

8) Empirical formula :- CH (determined by elemental analysis)
9) Molecular formula :- C_6H_6 (determined by vapour density method) (Molecular weight : 78)
10) Structure :-

(determined by X-ray studies)

└ cyclic, planar, regular hexagonal structure.

11) highly unsaturated compound (as shown by its molecular formula).

FAMILY	COMPOUND	C to H RATIO	H to C RATIO
Alkane	Hexane (C_6H_{14})	$\frac{6}{14} = 0.43$	$\frac{14}{6} = 2.33$
Alkene	Hexene (C_6H_{12})	$\frac{6}{12} = 0.5$	$\frac{12}{6} = 2$
Alkyne	Hexyne (C_6H_{10})	$\frac{6}{10} = 0.6$	$\frac{10}{6} = 1.67$
Arene	Benzene (C_6H_6)	$\frac{6}{6} = 1$	$\frac{6}{6} = 1$

→ Reason for soapy / sooty Flame of Benzene :-

higher C to H ratio i.e 1

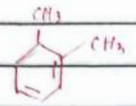
→ combustion of Benzene

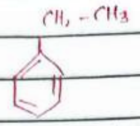
$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$

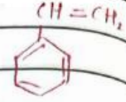
If benzene is placed in air ; air can't provide 15 mol O_2 so the unreacted C forms sooty flame.

→ monocyclic arenes :-


(toulene)

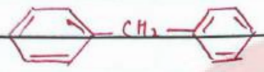

(o-xylene)

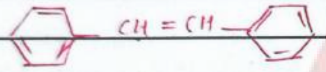

(ethylbenzone)


(styrene)

→ Polycylic Aromatic Hydrocarbons :-

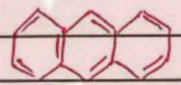

(biphenyl)

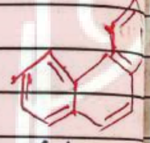

(difenylmethan)

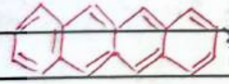

→ stilbene (1,2-diphenylethene)

→ Linear Fusion of Aromatic Rings:-


(naphthalene)


(anthracene)


(phenanth


(naphthacene)

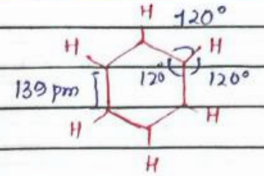
→ X-Ray Studies of Benzene Structure :-

1) cyclic regular hexagonal structure. (→ all sides are equal, → 120°)

↳ hexa (six) and corner (edges).

2) Planar structure [6 C-C bonds, 6 C-H bonds] → all bonds lie in one plane.

total = 12 bonds.



iii) C-C = 1.39 A°

C-H = 1.08 A°

iv) C-C bond is neither single nor double.

C - C (single bond) (154 pm) Band Order = 1

C = C (double bond). (134 pm) B.O = 2

C - C (in benzene) (139 pm) B.O = 1.5

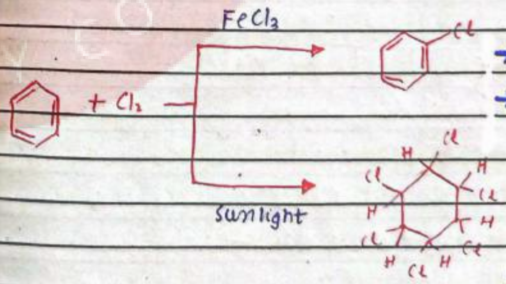
→ B.O in whole number (localized $\bar{e}$s)

→ B.O in fractional number (delocalized $\bar{e}$s)

→ delocalized π ės in benzene (6 $\bar{e}$s)

→ Benzene → preferably give substitution rxns (Saturated Nature)

→ reluctantly give addition rxns. (Unsaturated Nature)

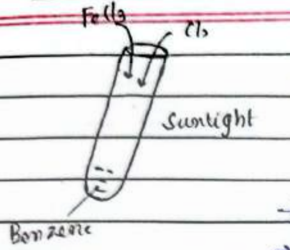


→ Substitution Rxn

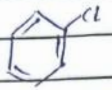
→ characteristic stability of benzene retain.

→ Addition rxn

→ Loss of stability



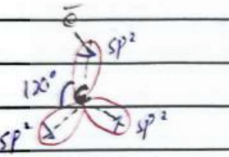
→ major product is chlorobenzene



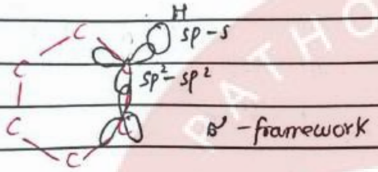
→ b/c it is more stable

→ showing that benzene preferably undergoes substitution rxns.

→ Atomic Orbital Treatment of Benzene



C – sp^2 – hybridized

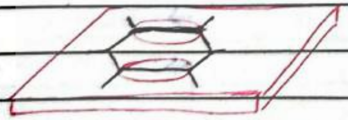


→ Extensive delocalization

→ Benzene is extraordinary stable.

1) All carbon sp^2 – hybridized.

2) All sigma bonds lie in one plane (sigma plane).



3) the unhybridized p-orbitals ($2P_z$) are perpendicular to the plane of hybridized orbitals.

4) Bond angle – 120°

5) Bond order = 1.5

6) Bond length (C – C) = 1.39 A° and C – H = 108 pm.

7) No of delocalized π bonds = 3

8) No of σ bonds – 12

9) All C – C bonds are somewhat in b/w double & single.

10) No of total double bonds on the ring = 0

11) No of total single bonds in the ring = 0

12) No true single / double bond present.

13) total no. of π $\bar{e}s$ = 6 $\bar{e}s$

14) total no. of σ $\bar{e}s$ = 24 $\bar{e}s$

15) Ratio b/w sigma and pi-bonds = $\cancel{12}:\cancel{3}$ = 4 : 1

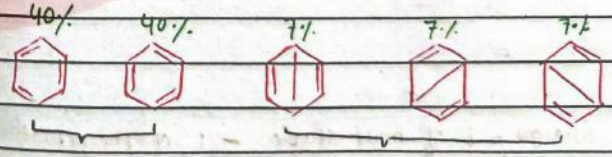
→ Resonance In Benzene : (Delocalization)

→ Defined as;

"Process in which two / more structures are written for a compound which differ only in the arrangement of $\bar{e}s$"

OR

"the possibility of different pairing schemes of valence $\bar{e}s$ of an atom within the molecule."



Kekule's structures (major part)

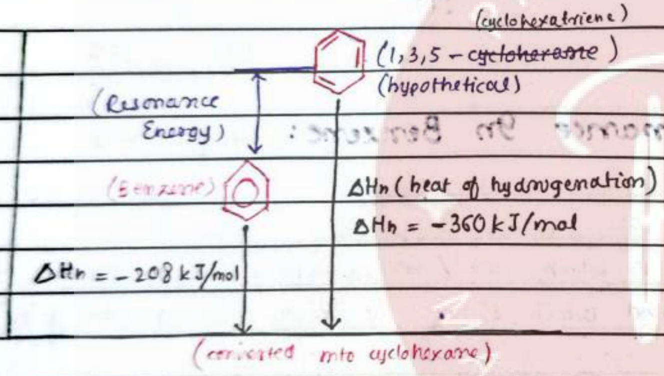
Dewar's structures (minor part)

Resonance
Canonical } Structures of benzene
Contributing

Resonance Hybrid / Robinson's Structure of Benzene.

→ Resonance Energy :-

Resonance Energy = $\Delta H_{h(obs)} - \Delta H_{h(calculated)}$



Resonance Energy = $-208\ kJ/mol - (-360\ kJ/mol)$

Resonance Energy = $152\ kJ/mol$

OR

Resonance Energy = E of most stable canonical form expected − E of the actual molecules

R-E = $360\ kJ/mol - 208\ kJ/mol = 152\ kJ/mol$ or

double bond ~ ... length length

Heat of hydrogenation $\propto \frac{1}{\text{stability of the molecule.}}$

→ Benzene is more stable than expected due to the extensive delocalization of π ēs.

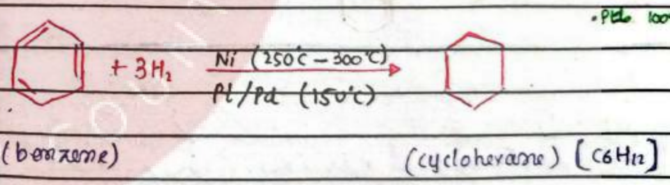
Reactions Of Benzene :-

→ Characteristic Rxns :- Electrophilic Aromatic Substitution Rxns.
↳ Substitution Elimination rxns
↳ Electrophilic Aromatic Substitution. rxn

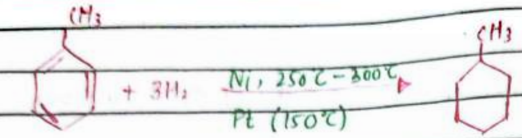
→ highly unsaturated ; still undergo the electrophilic substitution rxns rather than addition due to the extensive π ēs delocalization.

1. Catalytic Hydrogenation :

FTB
- Raney Ni / 200°C
- Pt/Pd 100°C / 10atm

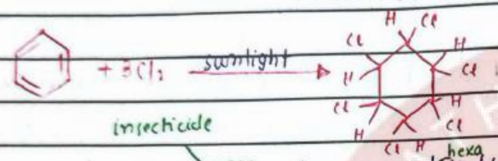


→ In case of alkenes Pt / Pd can react at room temp.
→ But in case of benzene , requires high temp. i.e. catalytic hydrogenation of benzene require vigourous conditions at the cost of stability of benzene.



(Toluene) (methylcyclohexane)

2. Halogenation:



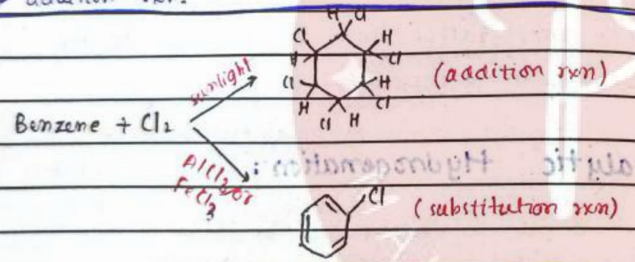
insecticide

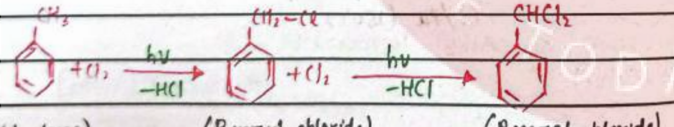
uses – (1,2,3,4,5,6-~~Hexa~~ hexachlorocyclohexane) (BHC)

antilice shampoo

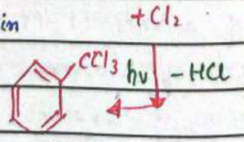
→ Free radical reaction/mechanism

→ addition rxn.





(toulene) (Benzyl-chloride) (Benzal chloride)



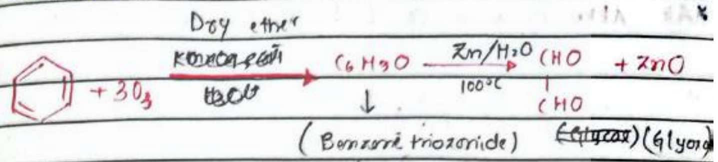
(Benzotrichloride)

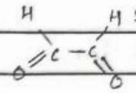
- halogenation occurs at aliphatic side chain
- rxn follows free radical addition mechanism instead of simple addition

Addition of Halogens :- (FTB)
Benzene can add 3 molecules of Cl_2 or Br_2 under the influence of sight.

- the reaction of F_2 with benzene is very vigorous, while with I_2 is very slow.

3. Ozonolysis :



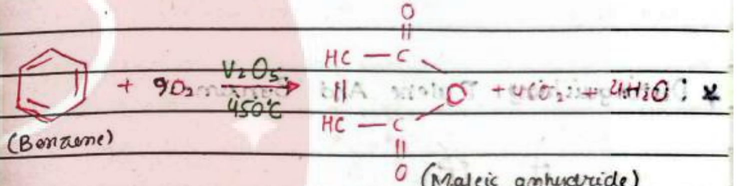


smallest dialdehyde

4. Oxidation :

→ Benzene is resistant to oxidation even in the presence of strong oxi. agents such as $K_2Cr_2O_7$ and $KMnO_4$ due to its stable nature. ✱

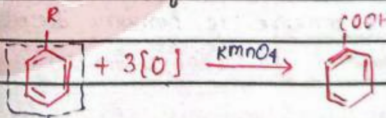
→ catalytic oxidation of Benzene is possible.



(Maleic anhydride)
(means with H_2O)

→ Maleic anhydride when dissolved in H_2O forms Maleic acid. (this is the commercial method for the preparation of maleic anhydride

→ Oxidation of Alkyl Benzene :- (side Chain Oxidation)



(Benzoic acid)

Benzene ring remains intact.

- alkaline or acidic $KMnO_4$ or $K_2Cr_2O_7$

→ R - group converts into COOH group.

Checked By:

rxn follows free radical mechanis

instead of $\overset{\text{simple}}{\text{addition}}$

Addition of Halogens:- (FTB)

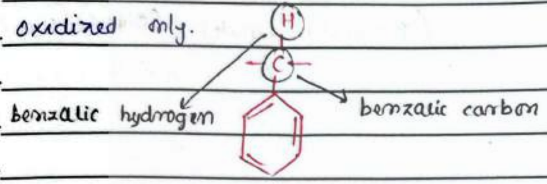
Benzene can add 3 molecules of Cl_2 or Br_2 under the influence of light. The reaction of F_2 with benzene is very vigorous, while with I_2 is very slow.

Conclusion:

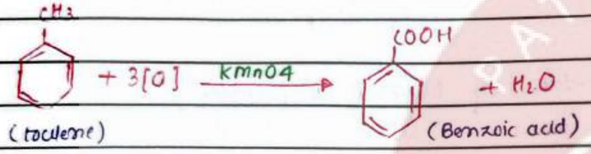
the add. rxn of H_2 and Cl_2 with benzene shows its unsaturated natur and that it has 3 double bonds.

***All Alkyl Benzene Can't Be Oxidized;**

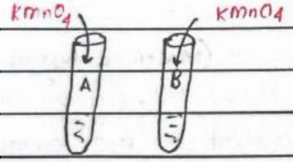
the alkyl benzene having benzalic-hydrogen can be oxidized only.



*** Oxidation of Toulene:-**



*** Distinguishing Toulene And Benzene:-**

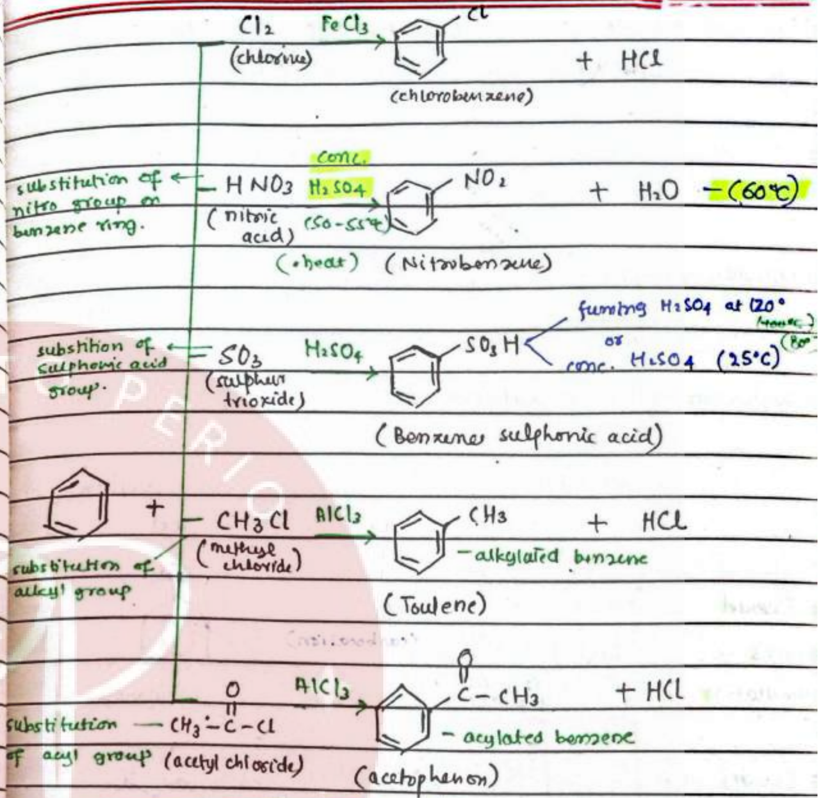


→ If purple colour of $KMnO_4$ discharges, it is toulene

→ If it doesn't then it is benzene. ie Benzene doesn't react with $KMnO_4$.

→ Weak electrophile can't attack benzene.

•ELETROPHILIC SUBSTITUTION RXNS OF BENZENE



HALOGENATION:- (FTB)

- chlorination and Brommination are normal rxns
- flourination is too vigorous to control.
- Iodine gives poor yield.

Chlorination of toulene - results in a mixture of isomeric o, p and m-chlorotoulenes.

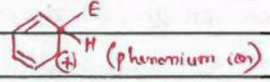
(o: 43%) (p: 55%) (m: 2%)

SULPHONATION:-

Fuming H_2SO_4 has free sulphur trioxide which e-deficient (electrophile)

• Steps of Electrophilic Substitution Rxn:

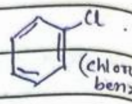
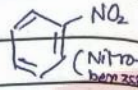
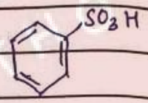
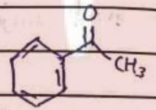
1) Formation of strong electrophile
2) Formation of phenonium ion
3) Regeneration of catalyst.



→ Isoelectronic with

→ Linear structure

→ N-atom is sp-hybridized.

REACTION	REAGENTS/ CATALYST	ELECTROPHILE	PRODUCT
1) Halogenation	[Cl_2, Br_2] {$FeCl_3$/$FeBr_3$} (25°C) Lewis acid catalyst	$Cl^{\oplus}$, $Br^{\oplus}$ (chlorinium ion)	 (chloro-benzene)
2) Nitration	[HNO_3] (conc. [H_2SO_4]) 60°C catalyst	$NO_2^{\oplus}$ (nitronium ion)	 (Nitro-benzene)
3) Sulphonation	[conc. H_2SO_4] 190°C or fuming H_2SO_4 25°C	SO_3	 Benzenesulphonic acid
4) Freidel Craft's alkylation	[CH_3Cl] ([$AlCl_3$]) Lewis acid catalyst	$CH_3^{\oplus}$ (carbocation)	 (toulene)
5) Freidel Craft's Acylation	$CH_3-\overset{\overset{O}{\|}}{C}-Cl$ ([$AlCl_3$])	CH_3CO^+ (acyleium ion/acetylium ion)	 (acetophenone)

By Products :-

1) Nitration (H_2O) 2) Halogenation (HCl

3) Sulphonation -(H_2O) when conc. H_2SO_4 is used.

4) Freidal craft alkylation (HCl)

5) Freidal craft acylation (HCl).

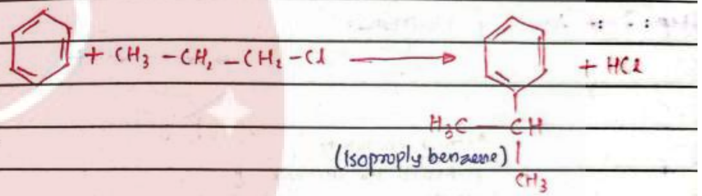
→ Friedal Craft Alkylation (Points Old-Book) :-

Benzene reacts with R-X in the presence of lewis acid catalyst to form alkyl benzene.

→ This rxn is useful due to the serious objections given below;

i) the rxn is not limited to monoalkylation. Usually di/tri alkylated benzene is formed.

ii) the alkyl groups often rearrange e.g treatment of benzene with n-propyl chloride gives isopropyl benzene rather than the expected n-propyl benzene.



this is bcz the rxn involves formation of carbonium ion which can undergo rearrangement before attacking the benzene ring.

thus, the possibility of rearrangement brings uncertainty about the actual product formed.

→ Freidal Craft's Acylation :-

Substitution of acyl ($-\overset{\overset{O}{\|}}{C}-R$) group.

Benzene + $CH_3-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{AlCl_3}$ Aromatic ketones.

→ can't produce aromatic aldehydes.

→ the rxn intermediate is acetylium / acylium ion.

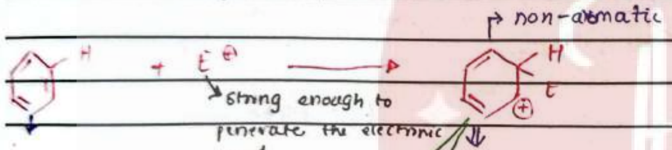
→ characteristics of the catalyst on Halogenation ($FeCl_3$ or $AlCl_3$)

1) ē-deficient / poor specie 2) electrophile
3) Lewis acid catalyst 4) ē-pair acceptor
5) generate the electrophile.

→ Mechanism of Rxns of Benzene

Step : 1 :- Formation of Electrophile.

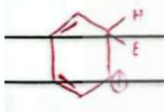
Step : 2 :- Attack of Electrophile



→ non-aromatic

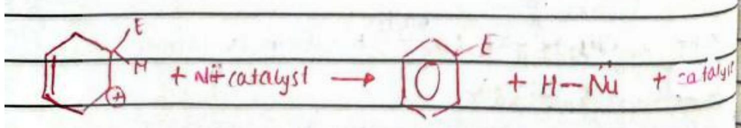
strong enough to penetrate the electronic cloud.

sp² - hybridized	carbon having substituent is chiral.	sp3-hybridized
120°		109.5°
trigonal planar	an intermediate, not transition-state	tetrahederal.



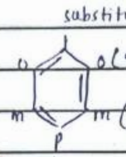
* phenonium ion / arenium ion / cyclohexadienyl / carbocation / carbonium ion / σ-complex / Benzenoium ion / (cyclohexadienyl carbocation)

Step : 3 :- Loss of H^+ / Regaining Aromaticity



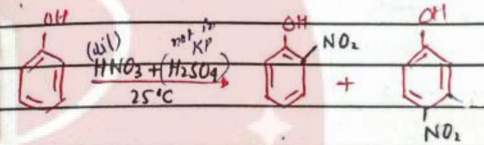
→ In the rxns of benzene, 2 transition states and 1 arenium ion is formed.

SUBSTITUENT EFFECT

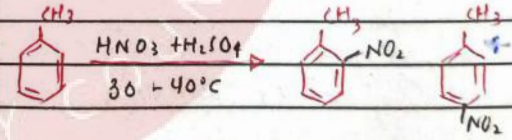


o (greek word means correctness / straightness)
m (greek word means in b/w / middle)
↳ para (greek word means beyond) :

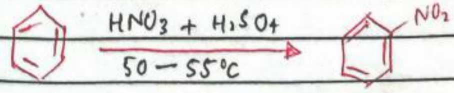
→ substituent effects / substituent has
i, orientation effect
ii, Reactivity Effect.

①


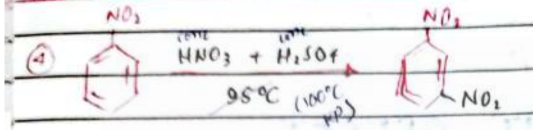
OH ┬ o/p director
  ├ ring activator group (inc↑ the reactivity)
  └ Rate of rxn = 1000.

②


CH_3 ┬ o/p director
  ├ ring activator
  └ Rate of rxn = 33

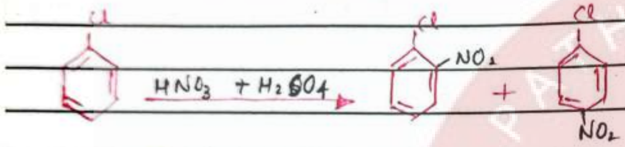
③


Rate = 1

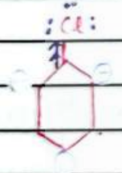
④


NO_2
- meta-directing group
- ring deactivator
- Rate = 10^{-4}

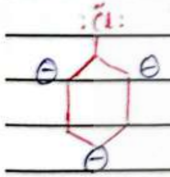
Exception: (Halogens)



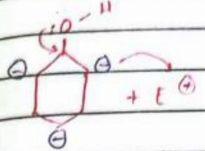
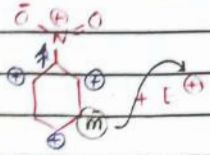
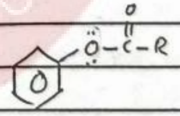
(X)
- o/p director
- ring deactivator
- rate = 0.33



→ due to the $\bar{e}$-withdrawing inductive effect it is ring deactivating group.

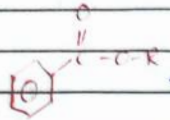


→ due to the $\bar{e}$-donating resonance effect it is o/p director.

O/P - Directing Groups	m - Directing Groups
	
(Ring activators)	(Ring deactivators)
→ $\bar{e}$-donating group	→ $\bar{e}$ - withdrawing group
→ Inct the availability of $\bar{e}s$ at ortho and para positions.	→ deficiency of $\bar{e}$ at ortho and para positions.
→ those with lone pair of $\bar{e}s$	→ those with a partial +ive charge.
• $\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$, $-\ddot{X}N_2$	$\overset{\oplus}{N}H_3$, $\overset{\oplus}{N}R_3$, $\overset{\oplus}{N}HR_2$ $\overset{\oplus}{N}H_2R$
• $\ddot{P}H_2$, $-\ddot{P}R_2$, $\ddot{P}HR$, PX_2.	$\overset{+}{P}H_3$, $\overset{\oplus}{P}R_3$, $\overset{+}{P}HR_2$, $\overset{+}{P}H_2R$
• $\ddot{O}H$, $\ddot{O}R$ ($\ddot{O}CH_3$, $\ddot{O}C_2H_5$)	$\overset{+}{O}H_2$, $\overset{+}{O}RH$, $\overset{+}{O}R_2$
$\ddot{O}COR$ (ester),  $\ddot{O}X$	SH_2, $\overset{+}{S}RH$, etc.
• $\ddot{S}H$, $\ddot{S}R$, $\ddot{S}-Ar$, $\ddot{S}COR$ (thioester)	→ (hetero atoms) with (unsaturated bonds.)
→ Alkyl groups due to hyper-conjugation are -e-donating groups. e.g CH_3, C_2H_5 etc.	→ those having carbonyl carbon. $\overset{O}{\overset{\Vert}{C}}-$ i, aldehyde

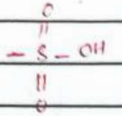
ii, Ketones' iii, COOH and its derivatives

iv, amides, acid halides, acid anhydrides



← vi, ester

$(-C\equiv N)$ ← vii, nitrile

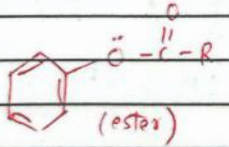


$-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$ ← viii, $-SOH_3$

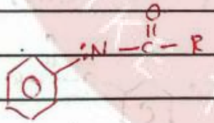
→ alkenes $(C=C)$, C_6H_5 (Benzene) :- $\bar{e}$-donating groups and o/p-directors. (ring activator)

→ alkynes $(-C\equiv C)$:- $\bar{e}$-withdrawing group and meta-directing. (ring deactivator)

→ if ester $(-\overset{\overset{O}{\|}}{C}-OR)$ and amide $(-\overset{\overset{O}{\|}}{C}-NH_2)$ are joined through O and N respectively then they $\bar{e}$-donating groups (ring activators) and o/p-directors

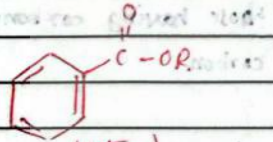


(ester)

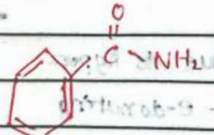


(o/p and $\bar{e}$-donating)

→ if both are joined through the carbonyl carbon, then they are $\bar{e}$-withdrawing and m-directing.



(ester)



(amide)

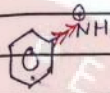
(m-directing and ring deactivators)

except halogens, which are pr
deactivators.
1) all meta-directing groups are deactivators.

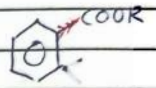
MCQs:-

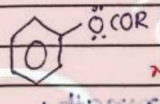
① WOF is more reactive than benzene / WOF is strongest nucleophilic benzene / WOF is more reactive towards electrophile or more reactive towards electrophilic substitution rxn / WOF is reducing agent (reducing benzene) / give faster rxn / o-p.

①

Ⓐ


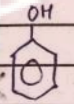
Ⓑ


Ⓒ


Ⓓ


(attached through (:) → e-donating → ring reactivity inc↑ than benzene - when reagent attacks, it reduces)

② WOF is the 'strongest' acid?

Ⓐ


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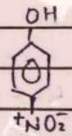

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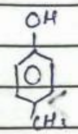

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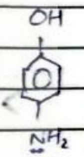


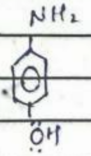
Acidity ∝ $\bar{e}$-withdrawing group

Basicity ∝ $\bar{e}$-donating group

③ WOF is the strongest base?

Ⓐ


(weak base)

Ⓑ


Ⓒ


Ⓓ

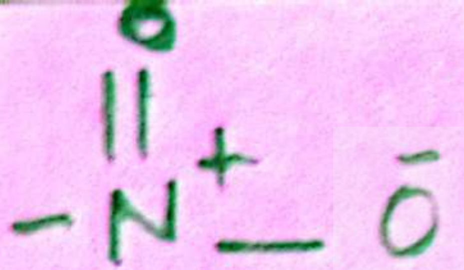

(weak base)

weak donar.

Determining the directive, activating and deactivating effects of the substituents:

1. All alkyl groups, phenyl groups having one/more non-bonding e^- pairs on the atom adjacent to the ring are ortho-para directing e.g $-R$, $-OH$, $-OR$, $-NH_2$, $-X$.

2) Substituents having a +ive or a partial +ive charge on the atom adjacent to the ring are meta-directing groups.

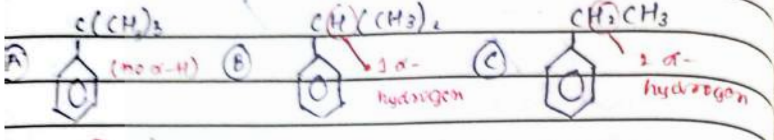


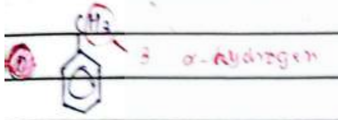
$-\overset{\overset{O}{\|}}{N^{+}}-\bar{O}$, $-\overset{+}{N}H_3-$, $-CN$

3) All o/p groups activate the ring except halogens, which are partial deactivators.

4) all meta-directing groups are deactivators.

3) W.O.F is more reactive than benzene (stronger donor)?





more α-hydrogen ; more $\bar{e}$-donating.

$C_6H_5-CH_3 > C_6H_5-CH_2-CH_3 > C_6H_5-CH(CH_3)_2 >$

$C_6H_5-C(CH_3)_3$

→ **Strongest e-withdrawing strength:**

$\left[-\overset{\oplus}{N}X_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -SO_3H\right]$

(strongest $\bar{e}$-withdrawing power)

$\left[> SO_3H > -CHO > -COOH > R-\overset{O}{\overset{\|}{C}}-Cl > -\overset{O}{\overset{\|}{C}}-OR >\right.$

$\left. R-\overset{O}{\overset{\|}{C}}-NH_2\ [\text{moderate}]\right]\ \left[> F > Cl > Br > I\right]$

weak

→ **Strongest e-donating strength:**

$\ddot{\underset{\cdot\cdot}{O}}^{\ominus} > \ddot{N}R_2 > NH_2 > \ddot{\underset{\cdot\cdot}{O}}H > \ddot{\underset{\cdot\cdot}{O}}R$

strong

$> \ddot{N}H-\overset{O}{\overset{\|}{C}}-R > \ddot{\underset{\cdot\cdot}{O}}COR$ (ester $>$

moderate

$> R >$  $> -C=CR_2$

weak

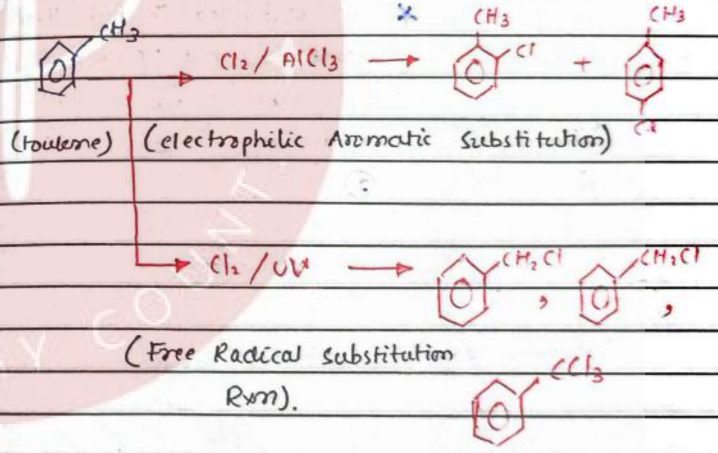
→ Relative Reactivity towards Electrophile :-

Alkene > Alkynes > Benzene > Alkanes

→ Relative Reactivity towards Nucleophile :-

Alkynes > Alkene > Benzene > Alkanes

→ **Chlorination of Benzene (toulene)**



(toulene) (electrophilic Aromatic Substitution)

(Free Radical substitution Rxn).