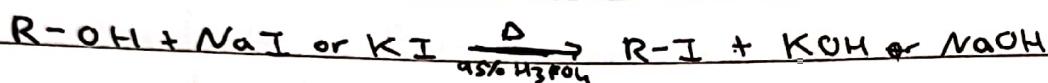
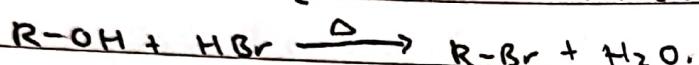
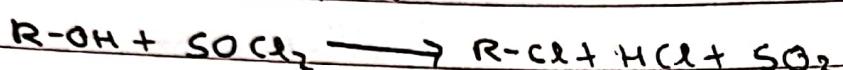
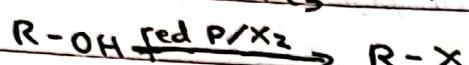
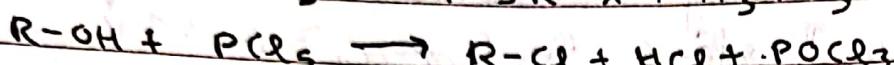
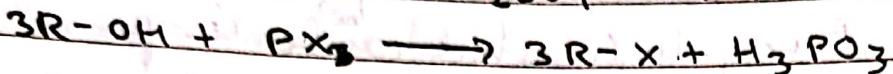
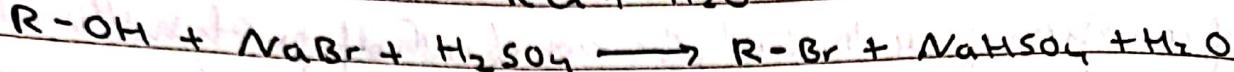
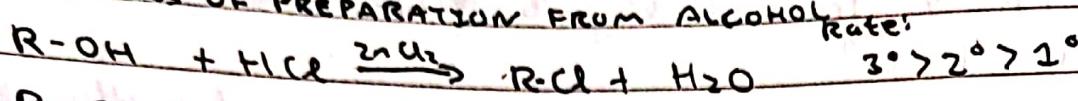


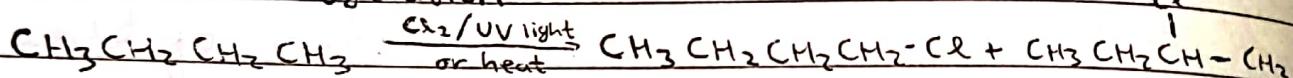
HALOALKANES

METHODS OF PREPARATION FROM ALCOHOL

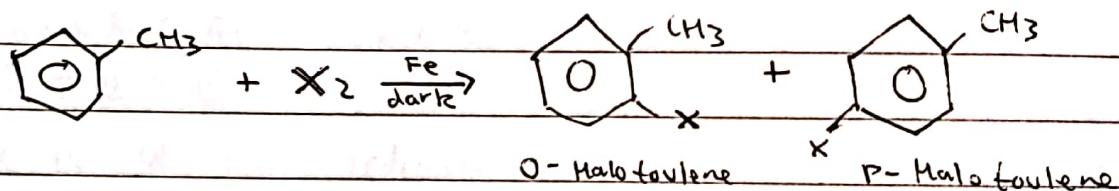


METHODS OF PREPARATION FROM HYDROCARBONS

(a) Free radical halogenation



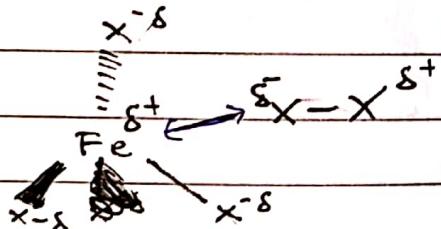
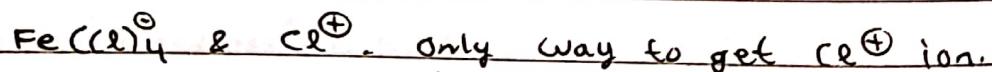
(b) By electrophilic substitution

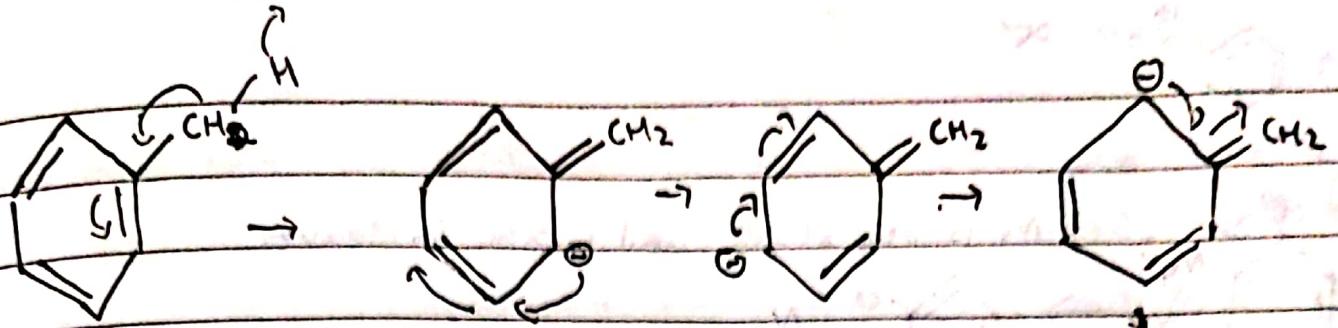


It is ortho-para directing.

*Note: Excess X_2 in $Fe(\text{III}) \rightarrow FeX_3$

which will give



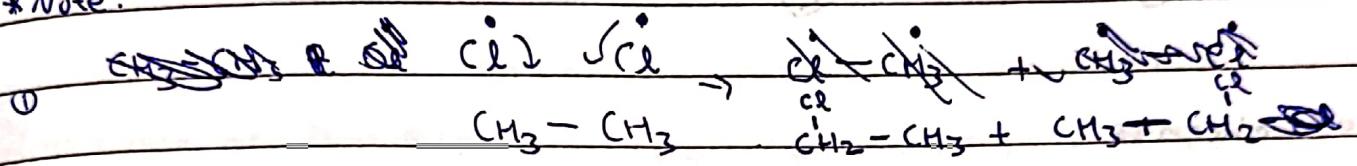


Negative charge on ortho & para locations

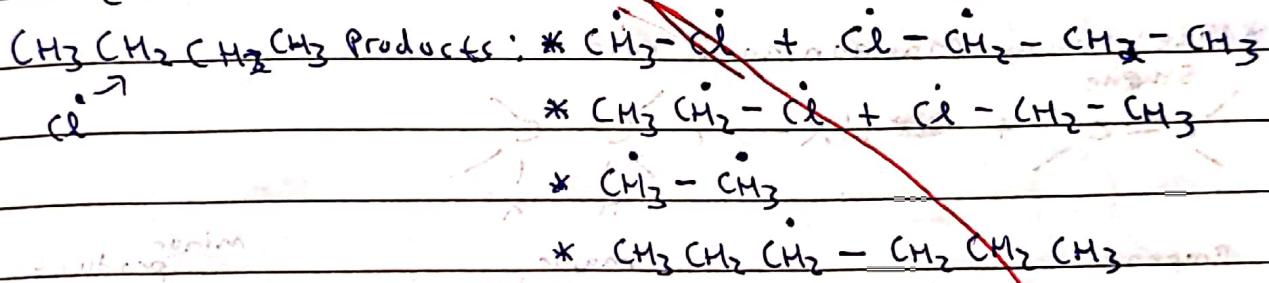
attracts X^+



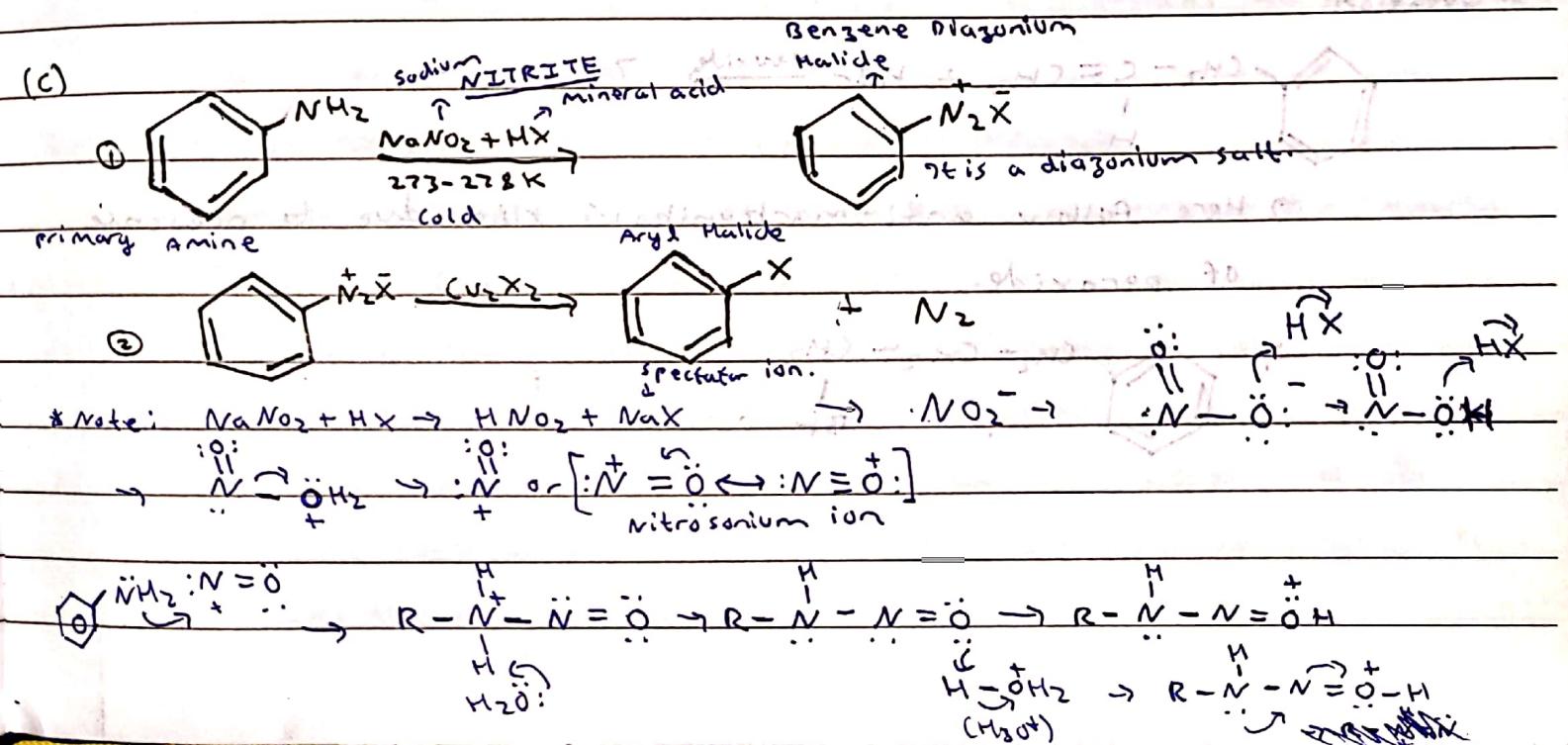
(a) *Note:

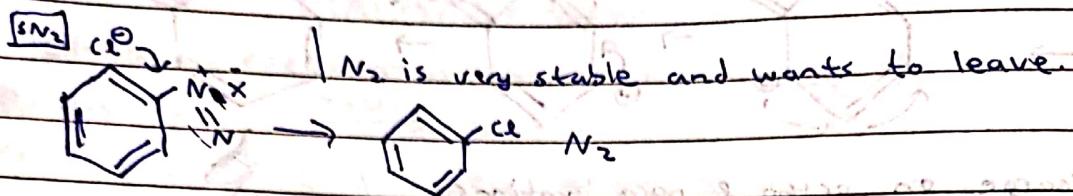
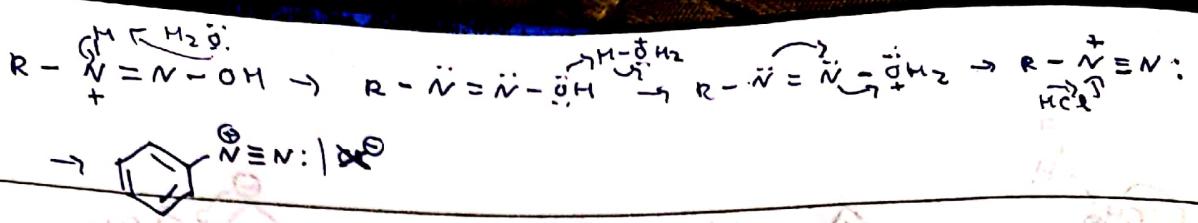


② (Cl) Different ways to break CH_3 ($\text{H}_2\text{CH}_2\text{CH}_3$) radically



Radical Cl^\cdot ions break the ~~hydrogen~~ C-H bonds radically and hence all possible combinations of bonds are formed





For iodine,

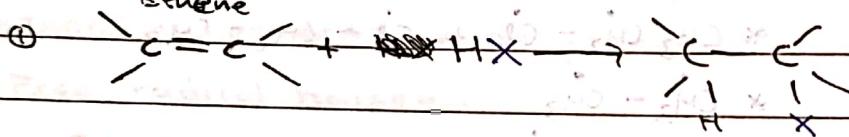


(d) From alkenes

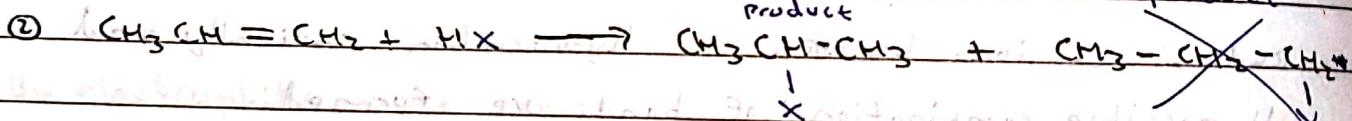
(i) Addition of hydrogen halides

* Note: Follow Markonikov's rule.

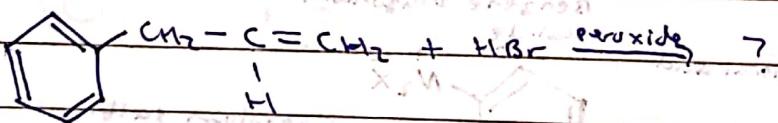
Ethene



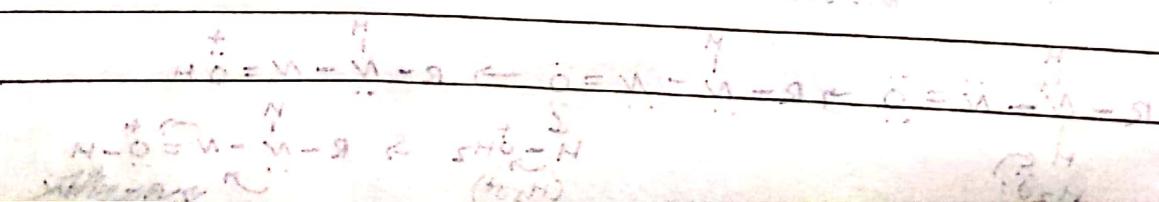
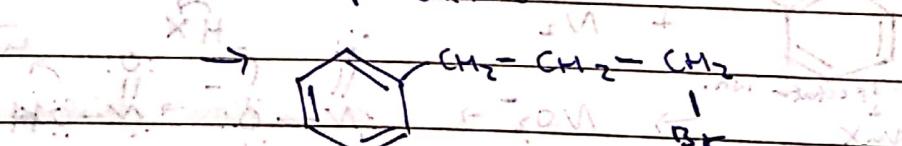
Propene ($\text{CH}_3\text{CH}=\text{CH}_2$) $\xrightarrow{\text{HX}}$ major product minor product



* Question:



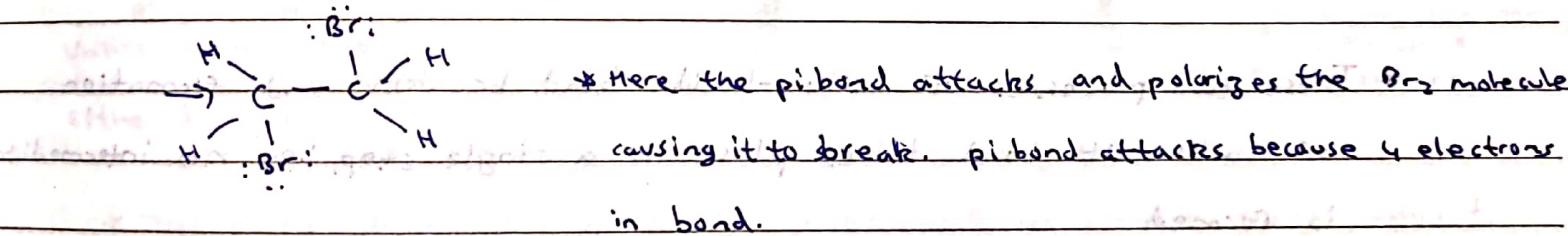
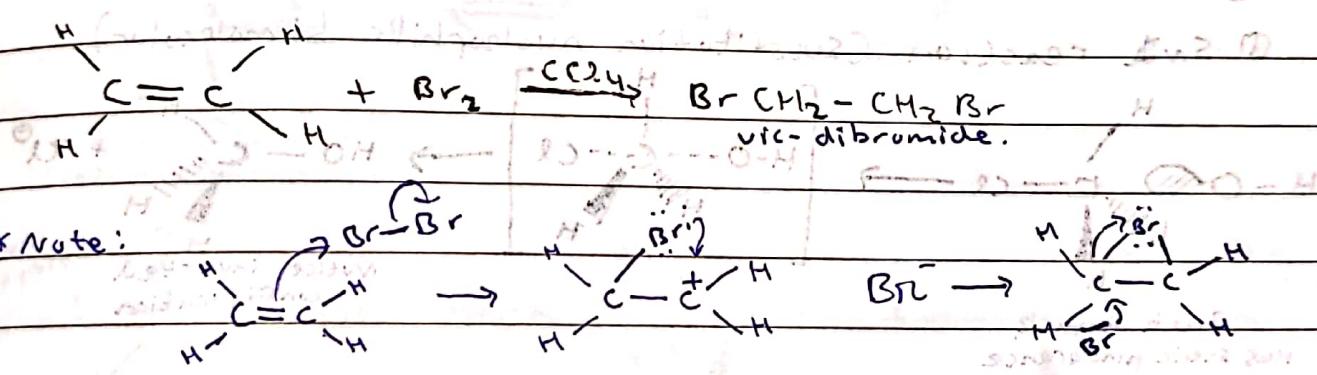
→ Here follow anti-Markonikov's rule due to presence of peroxide.



* **Markonikov's rule:** When an alkene reacts with an electrolyte, the negative addendum is added to the carbon containing lesser number of hydrogen atoms.

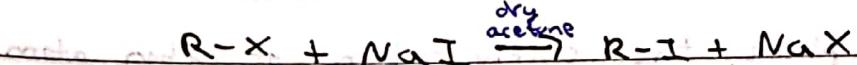
* **Anti-Markonikov's rule:** When an alkene reacts with an electrolyte, in the presence of peroxide, the negative addendum is added to the carbon containing more number of hydrogen atoms.

(ii) Addition of halogens



METHODS OF PREPARATION BY HALOGEN EXCHANGE

(i) Finkelstein reaction (Alkyl chloride/bromide with NaI in dry acetone)



For 1° & 2° R, it undergoes $\text{S}_{\text{N}}2$ reaction.

For 3° R, it undergoes $\text{S}_{\text{N}}1$ reaction.

(ii) Swarts reaction (heating alkyl chloride/bromide in the presence

of a metallic fluoride like AgF , Mg_2F_2 , CaF_2 or SbF_3)



For 1° or 2° R, $S\text{N}2$ reaction.

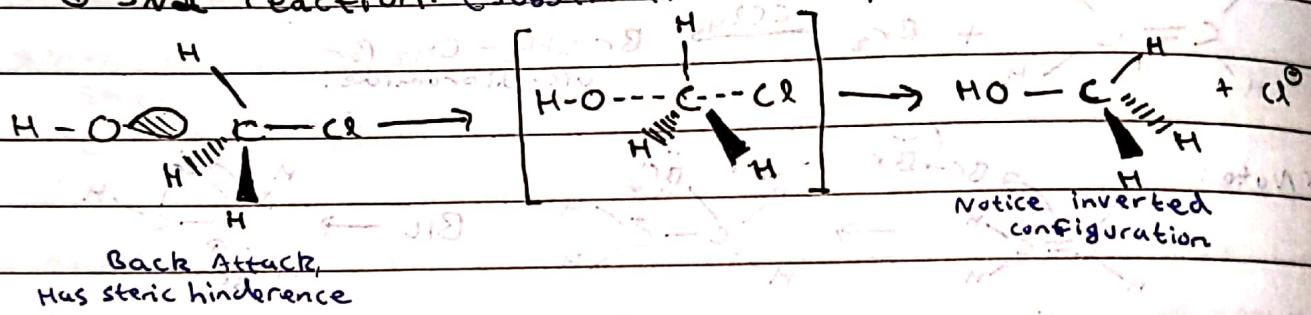
For 3° R, $S\text{N}1$ reaction

REACTIONS OF HALOALKENES

(i) Nucleophilic substitution reaction.

MECHANISMS:

① $S\text{N}2$ reaction. (Substitution nucleophilic bimolecular)



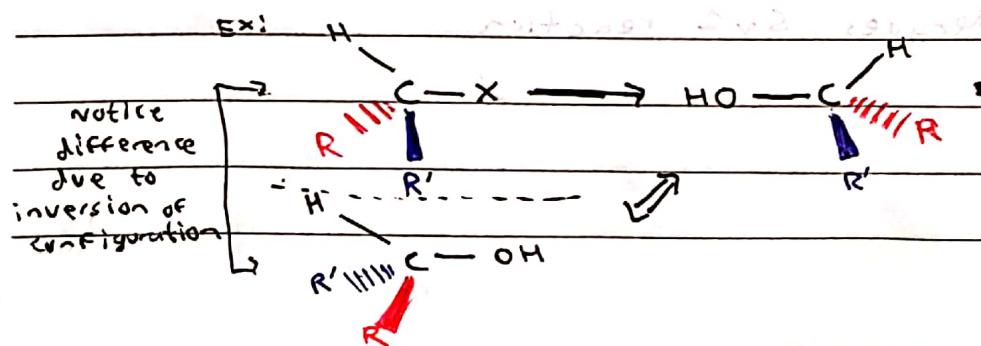
* These two processes of carbon-halide bond breaking and formation of carbon-OH bond takes place in a single step, i.e., no intermediate is formed

* It follows second-order kinetics, i.e., rate depends on concentration of both the reactants.

* As this process takes place, the configuration of carbon atom under attack inverts. This process is called inversion of configuration.

REQUIREMENTS:

- 1° or 2° Alkyl Halide
- Good Nucleophile
- Aprotic polar solvent



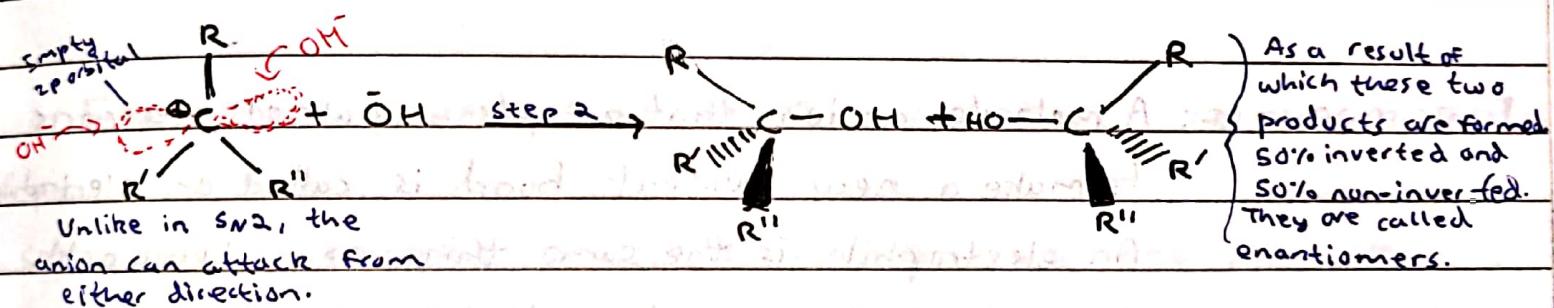
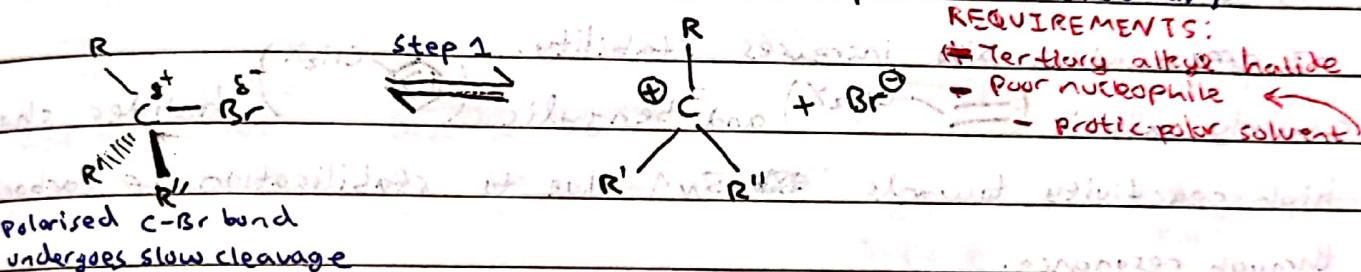
* Because this reaction involves the approach of the nucleophile to the carbon bearing the leaving group, rate of reaction will depend upon steric hindrance around that carbon atom as well.

∴ for S_N2 reaction,

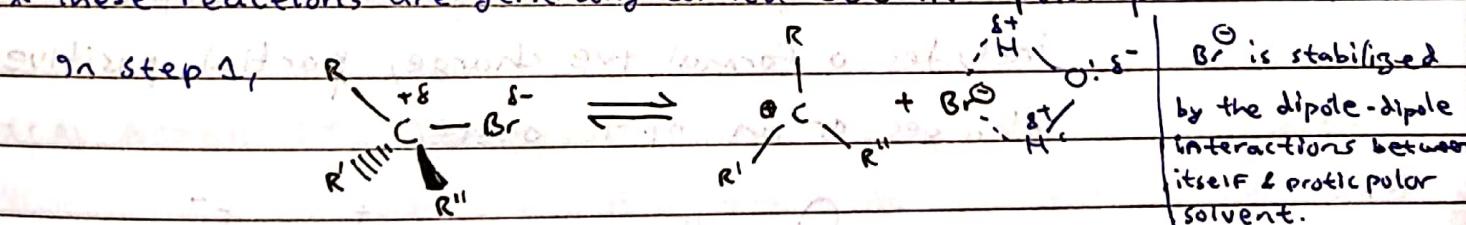
Rate of reaction \rightarrow Methyl-X $>$ 1° halide $>$ 2° halide $>$ 3° halide.

In fact, S_N2 reaction never occurs for 3° (tertiary) halides.

② S_N1 reaction (Substitution ~~not~~ nucleophilic unimolecular)



* These reactions are generally carried out in polar protic solvents.



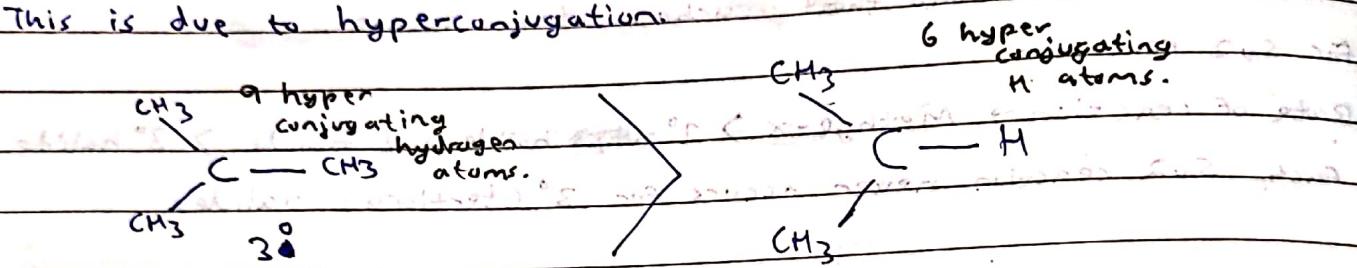
Hence rate is faster in protic polar solvents.

* It follows first-order kinetics, i.e., rate depends on concentration of substrate, i.e., the alkyl halide. It occurs in two steps. Step 1 is the slowest and is hence the rate determining step (RDS).

* Greater the stability of the carbocation the greater the ease of

formation from the alkyl halide and hence faster the rate of reaction.
In general 3° halides $> 2^\circ$ halides $> 1^\circ$ halides for stability.

This is due to hyperconjugation:



This is a general rule. Must be checked. CH_3 groups give

$+I$ effect which also increases stability.

* Similarly allylic ($=\text{CH}_2\text{X}$) and benzylic ($\text{C}_6\text{H}_5\text{CH}_2\text{X}$) halides show high reactivity towards $\text{S}_{\text{N}}1$ due to stabilisation of carbocation through resonance.

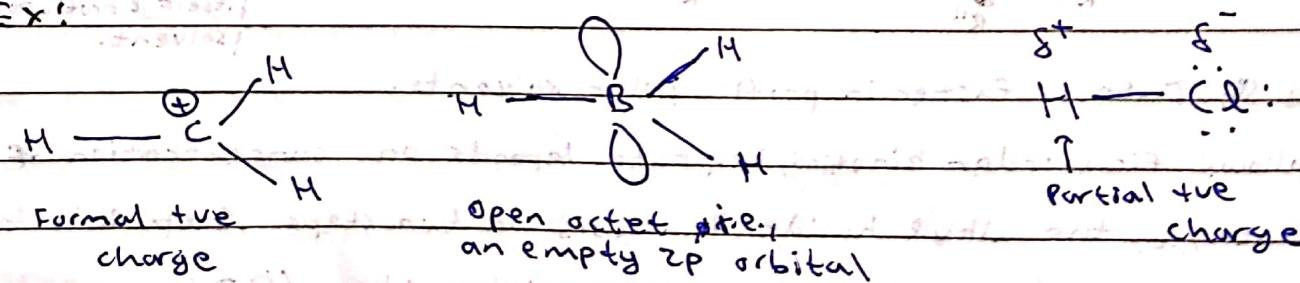
ELECTROPHILE: A molecule or ion that accepts a pair of electrons to make a new covalent bond is called an electrophile.

An electrophile is the same thing as a Lewis acid.

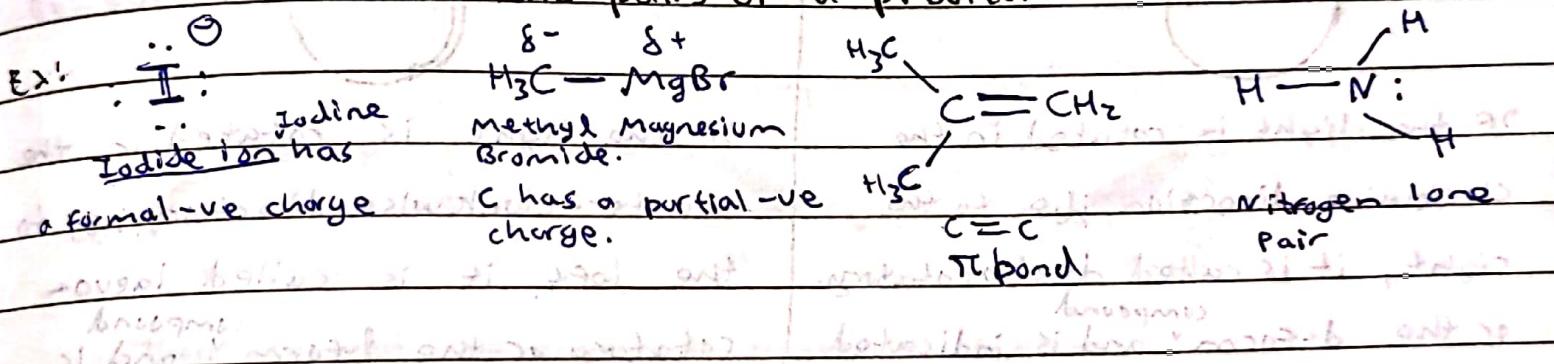
Any molecule, ion or atom that is electron deficient

in some way can behave as an electrophile. This includes a formal +ve charge, partial positive charges or an open octet.

Ex:



NUCLEOPHILE: A molecule or ion that donates a pair of electrons to form a new covalent bond is called a nucleophile. A nucleophile is the same thing as a Lewis base. Any molecule, ion or atom that has electrons that can be shared can be a nucleophile. This includes a formal negative charge, partial-ve charges & lone pairs or a pi-bond.

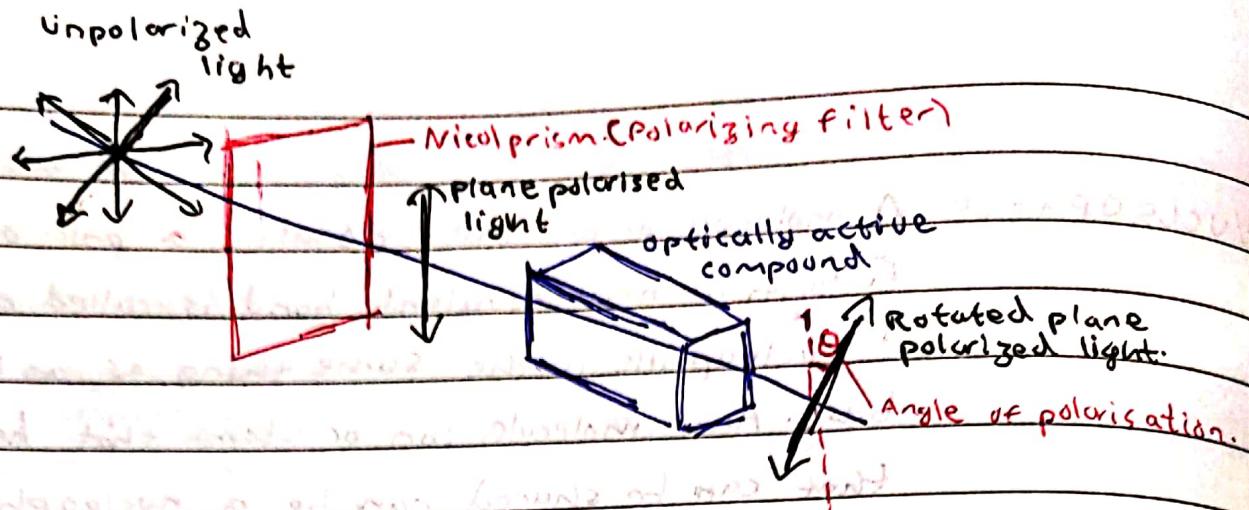


(-) ELECTRONS ALWAYS FLOW FROM NUCLEOPHILE TO ELECTROPHILE

STEREOCHEMISTRY: The branch of chemistry concerned with the spatial arrangement of atoms and molecules and the effect of this on chemical reactions.

OPTICAL ACTIVITY: The property shown by certain (optically active) solutions of compounds to rotate the plane of plane polarized light is called optical activity.

POLARIMETER measures the angle by which the plane polarised light is rotated.



OPTICAL ROTATION

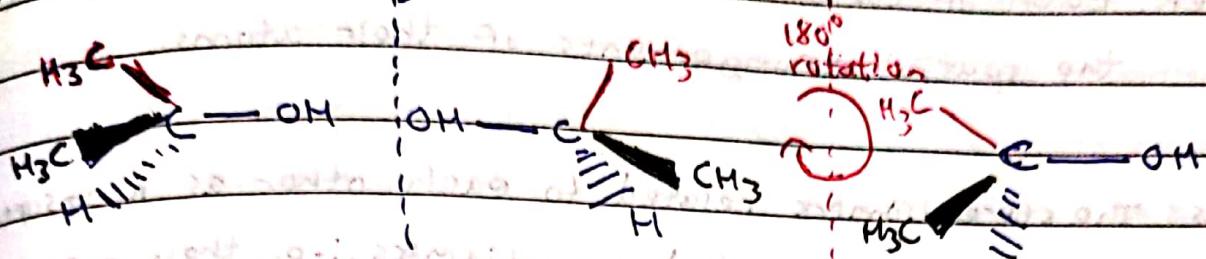
If the light is rotated in the clockwise direction i.e., to the right, it is called dextrorotatory or the d-form^{compound} and is indicated by placing a positive (+) sign before the angle of rotation.

If the light is rotated in the counter-clockwise direction i.e., to the left, it is called laevorotatory or the l-form^{compound} and is indicated by placing a negative (-) sign before the angle of rotation.

Such (+) & (-) isomers of a compound are called optical isomers and the phenomenon is termed as optical isomerism.

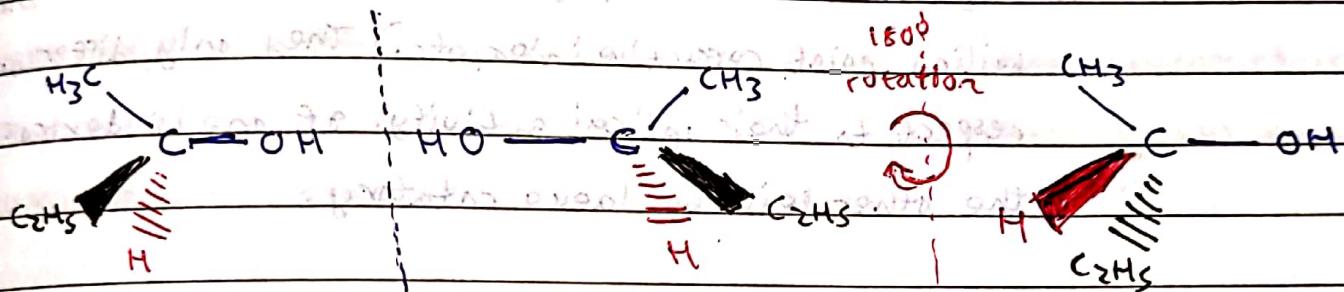
CHIRALITY: An object that cannot be superimposed with its mirror image is called chiral. This property is known as chirality. Objects which are superimposable on their mirror images are called achiral. Chiral molecules are optically active whereas achiral molecules are optically inactive.

Ex: Propan - 2 - ol



They are superimposable. Hence it is achiral.

Ex: Butan - 2 - ol



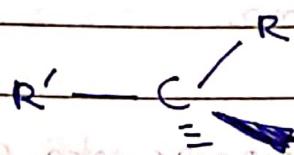
They are not superimposable. Hence it is chiral.

MOLECULAR ASYMMETRY: An asymmetric carbon atom is a carbon atom in a molecule that is attached to four different types of atoms or groups of atoms.

All asymmetric carbons are chiral, i.e., they either have optical activity or are optically inactive.

*Note! Asymmetric carbons are also called stereocenters.

Ex:



STEREOISOMER: Each of two or more compounds differing only in the spatial arrangements of their atoms.

ENANTIOMERS: The stereoisomers related to each other as non-superimposable mirror images are called enantiomers, i.e., they refer to any two molecules that are non-superimposable mirror images of each other.

*note: They have identical physical properties (ex: melting point, boiling point, refractive index, etc.) They only differ with respect to their optical activity. If one is dextro-rotatory, the other will be laevo-rotatory.

RACEMIC MIXTURE: A mixture containing two enantiomers in equal proportions is called a racemic mixture or racemic modification. Such a mixture will have zero optical rotation, as the rotation due to one isomer will be equal in magnitude but opposite in direction to the optical rotation due to the other isomer, thus cancelling each other and producing 0 optical rotation.

*note: A racemic mixture is denoted by prefixing D or (±) before the name.

Ex: (±) butan-2-ol.

The process of conversion of enantiomer into a racemic mixture is known as racemisation.

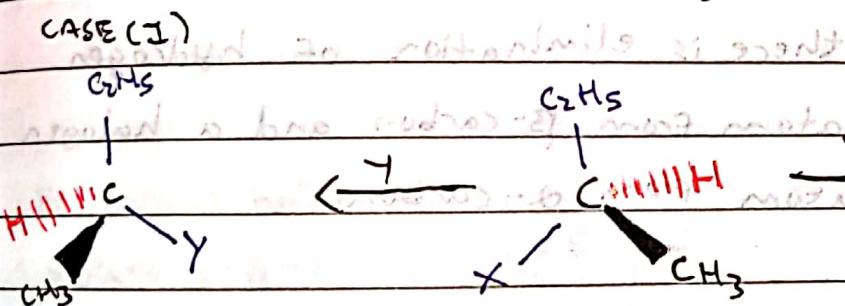
RETENTION: Retention of configuration is the preservation of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation.

* Note: In general, if no bond to the stereocentre is broken during a chemical reaction, the product will have the same general configuration as the reactant, i.e., configuration is retained.

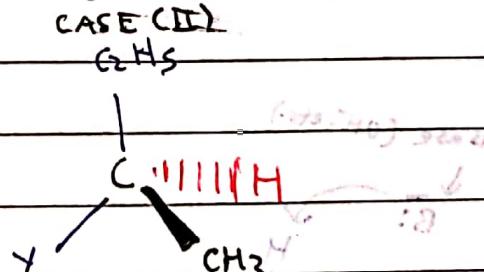
INVERSION: If a bond directly linked to the asymmetric carbon is broken, then 3 different outcomes for the reaction are possible.

* Given replacement of group X by Y in the following reaction,

CASE (I)



CASE (II)



Product A

Product B

CASE (III)

Product A + Product B

CASE (I) \rightarrow Product A \rightarrow Retention of configuration

CASE (II) \rightarrow Product B \rightarrow Inversion of configuration

CASE (III) \rightarrow Product A + Product B \rightarrow If a 50:50 mixture of A & B

is obtained, the process is

called racemisation.

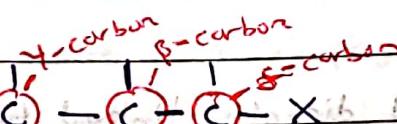
$\text{CH}_3\text{CH}(\text{H})\text{CH}_2\text{CH}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}(\text{Y})\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}(\text{H})\text{CH}_2\text{CH}_3$

$\text{CH}_3\text{CH}(\text{H})\text{CH}_2\text{CH}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}(\text{Y})\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}(\text{H})\text{CH}_2\text{CH}_3$

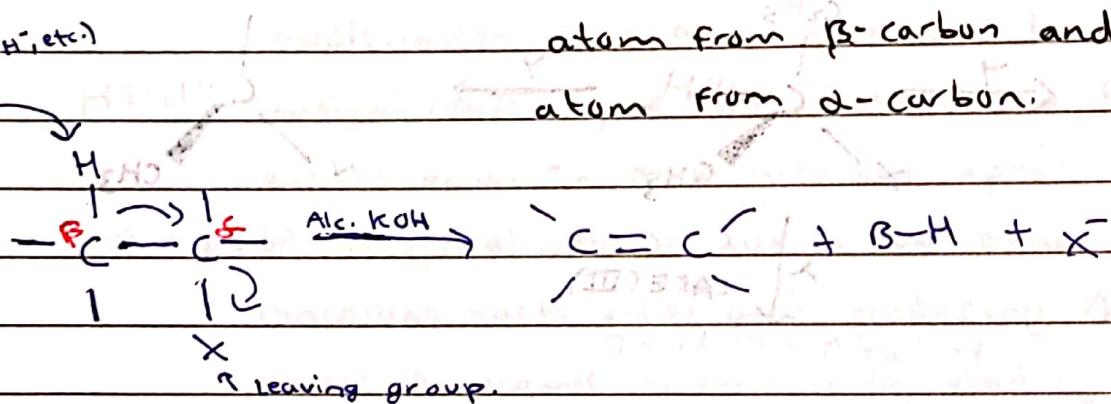
α & β -carbons: Carbon on which halogen atom is directly attached is called α -carbon.



Carbon on which halogen atom adjacent to this carbon is called β -carbon



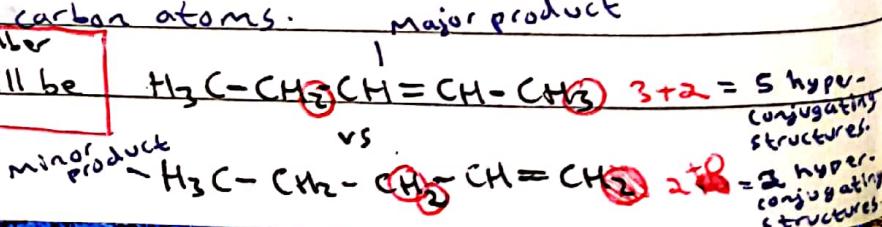
ELIMINATION REACTIONS: When a haloalkane with β -hydrogen atom is heated with alcoholic KOH, there is elimination of hydrogen atom from β -carbon and a halogen atom from α -carbon.



*Note: This reaction is also called β -elimination or dehydrohalogenation.

*Note: If there is possibility of formation of more than one alkene due to availability of more than one β -hydrogen atom, the preferred product is that alkene which has greater number of alkyl groups attached to the doubly bonded carbon atoms.

*Note: Whichever product has more number of hyperconjugating structures will be the major product.



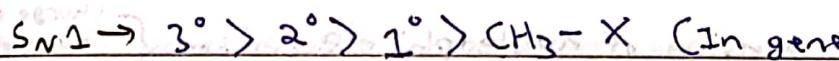
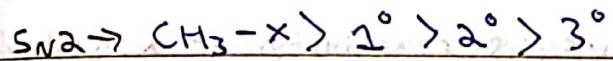
ELIMINATION VS SUBSTITUTION

A reaction tends to go in that direction which is easiest for them, i.e., results in the lowest energy state possible. For an alkyl halide with β -hydrogen atoms that is reacted with a nucleophile (base), three different reactions are possible. S_N1 & S_N2 substitution & elimination reactions all involve a nucleophile ~~attacking~~ reacting with an alkyl halide.

Which reaction takes place depends upon the nature of the alkyl halide, strength and size of the nucleophile (^{1/base} nucleophilicity) and reaction conditions (~~type of solvent~~ (basicity)).

Ex: A bulkier nucleophile will prefer to act as a base and abstract a proton rather than approach a tetravalent carbon atom (due to steric hindrance). Similarly, a primary alkyl halide will prefer a S_N2 reaction.

For alkyl halides:



*Note: Depends on stability of carbocation (No. of hyperconjugating & resonance structures)

Elimination \rightarrow

LEAVING GROUP APTITUDE: how easily a halogen leaves.

For both S_N1 & S_N2 and elimination, $R-I > R-Br > R-Cl > R-F$

Two reasons: ① C-X bond enthalpy decreases as we go down the group (Due to increase in size of ion). Hence, C-X bond enthalpy is $(-F) > (-Cl) > (-Br) > (-I)$. Hence it is easier to break the C-I bond as compared to the C-F bond.

③ The leaving group which forms the most stable anion is the best leaving group.

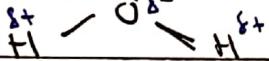
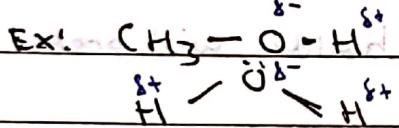


(since I^\ominus has the largest size, its charge is the most delocalised, and hence it is the most stable)

POLAR SOLVENTS

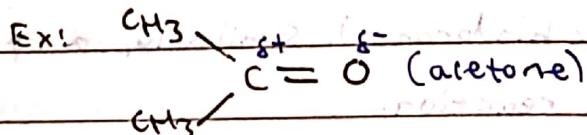
PROTIC POLAR

They are polar solvents which can perform hydrogen bonding.



APROTIC POLAR

They are non-polar solvents which cannot exhibit hydrogen bonding.



NUCLEOPHILICITY: The ability of a nucleophile to attack the carbon nucleus, i.e., reactivity of a nucleophile.

It depends on:

① Charge density of nucleophile (depends on charge of nucleophile)

② Size of Nucleophile (size of nucleophile)

③ Solvent (size of nucleophile)

* Greater the charge on the nucleophile, greater the nucleophilicity.

* Greater the size of the nucleophile, lower the nucleophilicity.

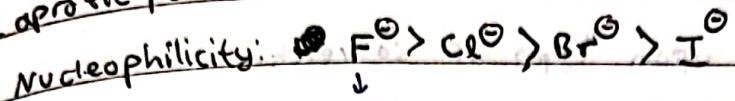
But,

* Rate of $\text{S}_{\text{N}}2$ reaction will be less in protic polar solvents due to

poor nucleophilicity of the nucleophile as a consequence of hydrogen bonding with protic polar solvent. In aprotic polar solvents, due to absence of hydrogen bonding, nucleophilicity will be high.

Therefore, rate of reaction is greater in aprotic polar solvent.

In aprotic polar solvent:



↓
Highest charge density & least size.

In protic polar solvent:



F^\ominus with max. charge density accumulates max. no. of solvent molecules around it due to hydrogen bonding. Hence nucleophilicity decreases due to steric factor whereas I^\ominus having min. charge density will accumulate min. no. of solvent molecules around it due to H-bonding as a result of which, nucleophilicity will be maximum.

(4) An anion containing a negative charge on less electronegative atom will be a better nucleophile than that containing the negative charge on more electronegative atom.



* This is because it is more difficult to donate a pair of electrons on a more electronegative atom than one on a less electronegative atom.

BASICITY: The ability of an anion to donate an electron pair / accept H^+ .

accept H^+ . of anion

It depends on: ① Charge density. (Only)

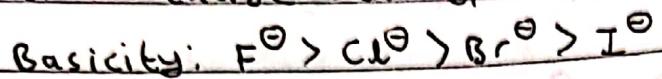
* Note: A strong acid will have a weak and very stable conjugate base.

A weak acid will have a strong and unstable conjugate base.



Charge density is very less.

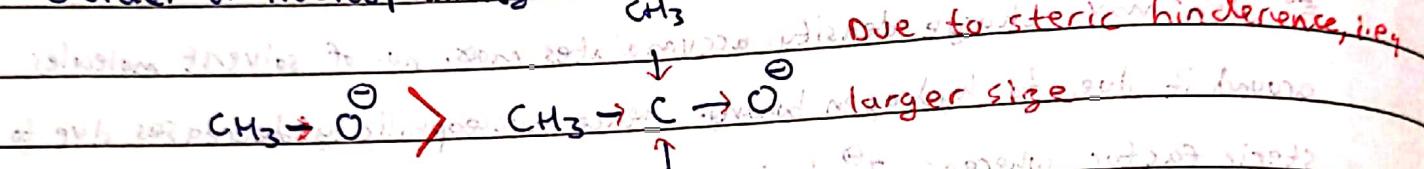
Based on charge density,



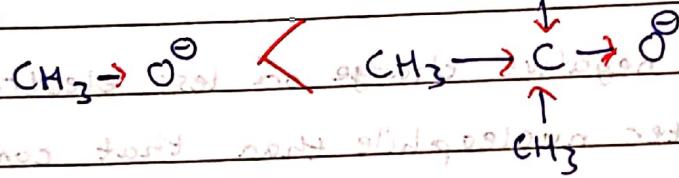
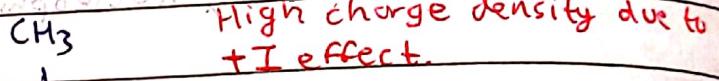
*note: Basicity does not depend upon type of solvent.

*Question!

① Order of nucleophilicity



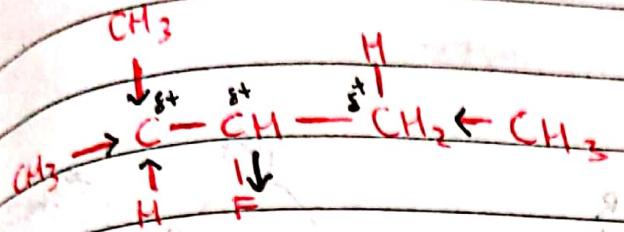
② Order of basicity



JEE NOTES

*In beta-hydrogen elimination reactions, the major product is generally the most substituted alkene, i.e., the alkene with more no. of hyperconjugating H atoms. But, when the leaving group is F or ^{+ methyl}NMe₂, the major product will be the least substituted alkene.

REASON: When the leaving group is a highly electronegative atom like F, it induces a delta positive charge on the β -carbon's too. On the carbon with more hyperconjugating H atoms, this δ^+ charge is more countered by the +I effect from the ~~surrounding~~ C atoms.



The greater δ^+ charge gets countered by the leaving H^+ ion which leaves a lone pair behind which participates least substituted alkene.

* Elimination reaction is endothermic.

REASON: because two strong σ bonds ($C-H$ & $C-X$) are broken to form one weak π bond.

*For stability: Resonance > Hyperconjugation > Inductive Effect

Inductive effect happens due to the movement of e^- in a σ bond towards the more electronegative atom.

Hyperconjugation involves the movement of electrons from the σ -bond to forming a π bond ($c=c$)

Resonance involves the movement of electrons across π bonds.

σ bond is stronger than π bonds, hence it is less facilitating.

for the movement of electrons through it. Hence contribution of

resonance is the reason for stability is the most and inductive

effect is the least.

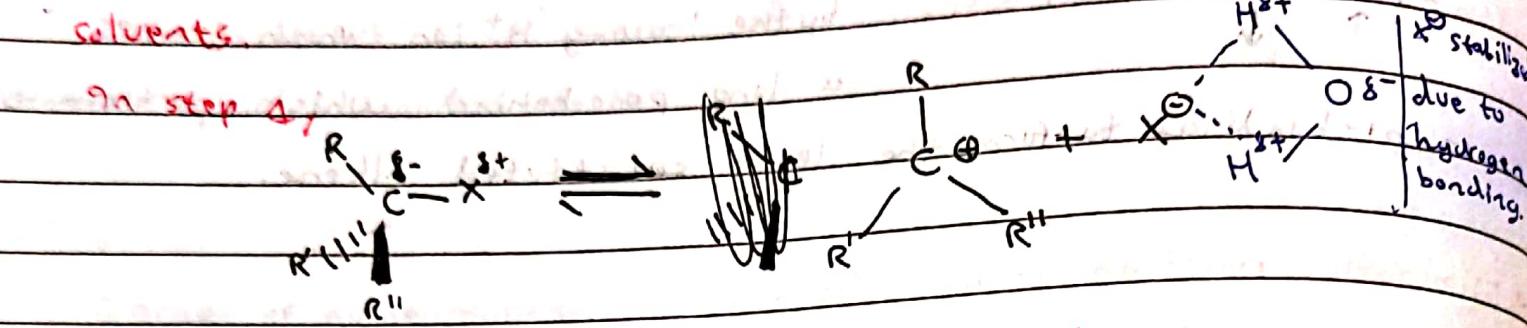
Elimination unimolecular reaction (E')

* It requires a 3° alkyl halide, weak base and elevated temperatures to occur. The mechanism occurs in two steps.

(ii) Formation of carbocation (RNS)

(ii) Removal of β -Hydrogen by base.

* These reactions are generally carried out in ~~protic~~ protic polar solvents.



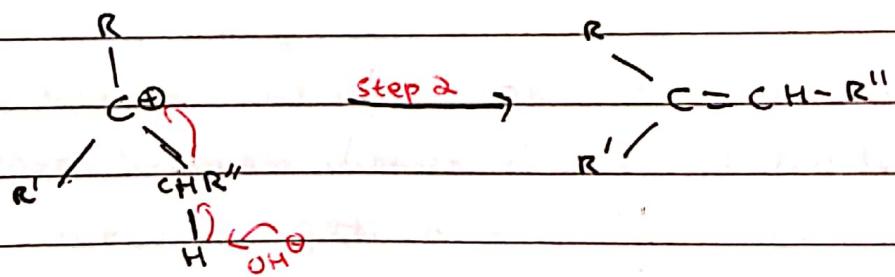
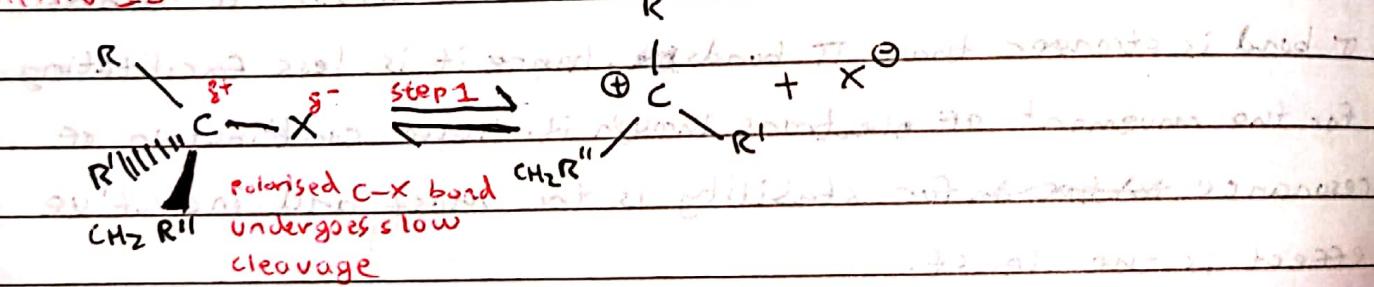
Hence rate is faster in protic polar solvents.

* It follows first order kinetics, i.e., rate only depends upon the concentration of the substrate, i.e., the alkyl halide.

* Rate also depends upon stability of carbocation. Since generally $3^\circ > 2^\circ > 1^\circ$ alkyl halides for stability this reaction generally only takes place for 3° alkyl halides.

* Similarly allylic ($=\text{CH}_2\text{X}$) and benzylic ($\text{C}_6\text{H}_5\text{CH}_2\text{X}$) show high reactivity towards E^- due to high stability of carbocation.

MECHANISM:



* Most substituted alkene is the major product. Always. Regardless of leaving group.

~~S_N2 AND E₁~~ SUBSTITUTION & ELIMINATION REACTIONS

These reactions are generally given together because they generally occur together.

This is because both S_N2 and E₁ mechanisms share the common first (RDS) step of carbocation formation. After this step, the route the reaction takes depends upon nucleophilicity & temperature.

* All weak bases are inadvertently, weak nucleophiles. This is due to the low charge density possessed by weak bases. But if the nucleophile is both a weak base (low charge density) ^{strong base} AND bulky (steric hindrance) S_N2 will be less favoured and Elimination product will be major product.

→ ~~S_N2~~ → E₁



* Elevated temperatures give preference to / aid elimination reaction. Hence, at higher temperatures, elimination product will be major product.

To facilitate ~~S_N2~~ E₁:

- Use bulky ~~weak~~ base. Ex: $\text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^-$ ion. Weak base due to low charge density & poor nucleophilicity due to large size.

E₁ → Carry out the reaction at high temperatures.

To facilitate S_N2:

- Use anion's like: $\text{Cl}^- (\text{HCl})$, $\text{Br}^- (\text{HBr})$ etc. Weak base ~~weak~~ (low charge density) & good nucleophilicity (small size).

S_N2 → Carry out reactions at low temperatures.

* Alc. KOH performs S_N2 (Acts as nucleophile)

* Alc. KOH performs E₁ (Acts as base)

Methyl carbocation $\rightarrow 0^\circ$ Hyperconjugating atoms.

1° carbocation $\rightarrow 3$ Hyperconjugating atoms

2° carbocation $\rightarrow 6$ Hyperconjugating atoms

3° carbocation $\rightarrow 9$ Hyperconjugating atoms

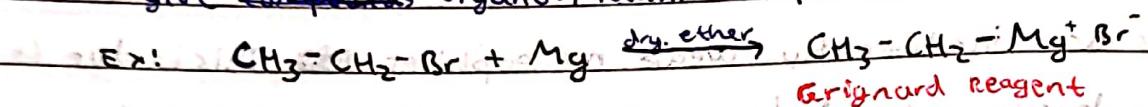
& nucleophile

Hence carbocation formation occurs for 1° , 2° & 3° alkyl halides too. Hence E₁ can occur for 1° alkyl halides too. (If using weak base). In this case, E₁ will compete with S_N2. For 1° & 2° alkyl halides, E₁ vs S_N2 depends upon stability of carbocation formed (Hyperconjugating atoms) & steric hindrance produced by alkyl halide.

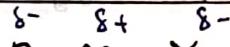
REACTIONS WITH METALS

ORGANO-METALLIC COMPOUNDS: Compounds containing carbon-metal bonds are called organo-metallic compounds.

* Note: Most organic chlorides, bromides and iodides react with certain metals to give organo-metallic compounds.



Mechanism: $\text{Mg} \rightarrow \text{Mg}^+ + e^-$ loss of one electron



R-Mg X R-Mg bond is covalent but highly polar.

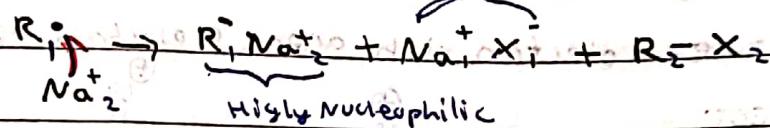
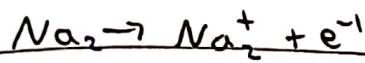
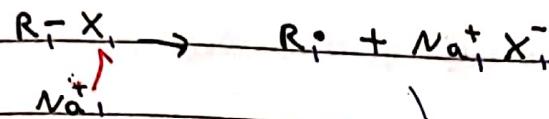
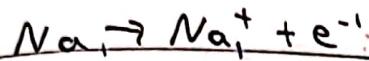
Grignard reagent Mg X bond is essentially ionic.

Hence, Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Water, alcohols & amines are sufficiently acidic to convert them to corresponding hydrocarbons.

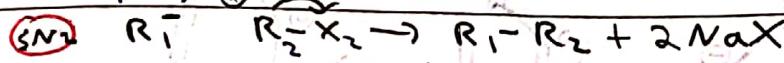


WURTZ REACTION

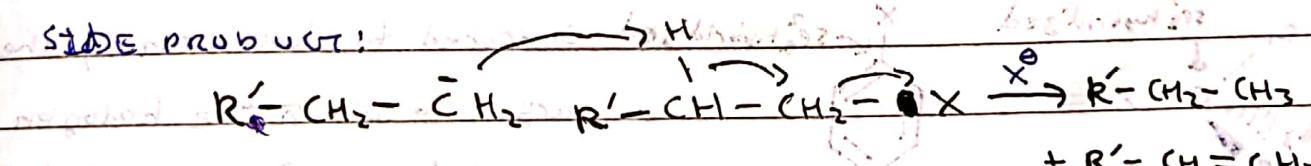
Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide.



substitution reaction



Note: However, $R\cdot$ is also extremely basic and hence if the alkyl halide $R-X$ is bulky in nature, elimination will ~~not~~ overpower substitution & more of the side product will be formed (alkene). Hence this method generally fails for tertiary (3°) alkyl halides.



Reaction is generally carried out with symmetric alkanes since (alkene)
mixture of alkene products are formed when dissimilar alkyl halides
are reacted (yield is low & mixture is difficult to separate)

REACTIONS OF HALOARENES

Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

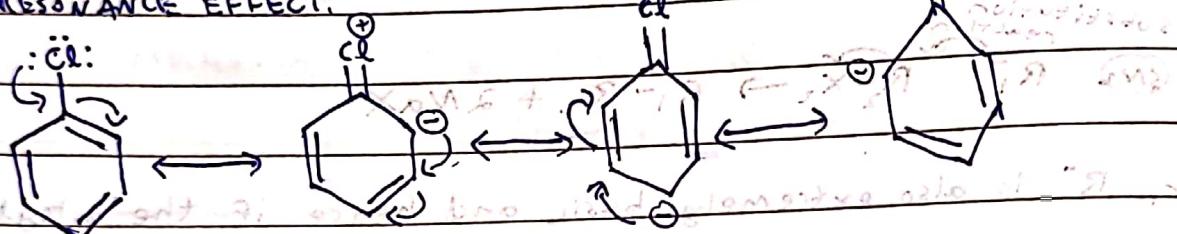
- (i) Resonance effect
- (ii) sp^2 hybridized carbon

(iii) Unstable phenyl cation

(iv) Repulsion between electron rich arene & electron rich nucleophile

(i) RESONANCE EFFECT:

Ex:

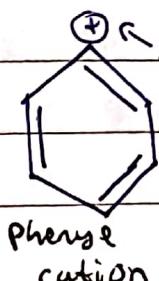


Electron pairs on halogen atom are in conjugation with π -electrons of the ring (resonance). Hence the C-X bond has partial double bond character. Hence bond cleavage becomes more difficult and hence they are less reactive to nucleophilic substitution.

(ii) sp^2 HYBRIDIZED CARBON:

R_1 sp^3 hybridized X sp^2 Hybridized Compared to haloalkynes, the carbon to which the halogen is bonded is sp^2 hybridized, instead of sp^3 . Hence, the s character in the C-X bond of haloarenes is more. Therefore the C-X bond length in haloarenes is less than C-X bond length in halo-alkanes. Shorter bonds are more difficult to break.

(iii) UNSTABLE PHENYL CATION:

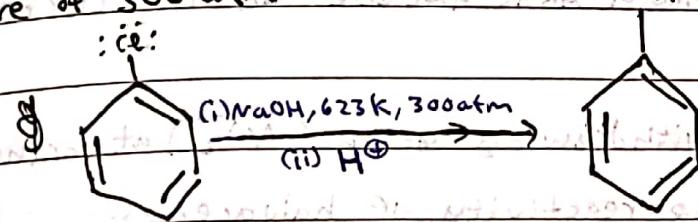


Not resonance stabilized. Hence self-ionisation does not occur. S_N1 never occurs. [Even if double bond breaks & carbon obtains lone pair it'll still only have 6 electrons i.e., incomplete octet]

(iv) REPULSION BETWEEN ELECTRON RICH ARENES & ELECTRON RICH NUCLEOPHILE
 Arenes have pi-electrons. ~~so~~ It is hence electron rich. Nucleophiles, by definition are electron rich. Hence there is possibility of repulsion between their electrons when they approach each other.

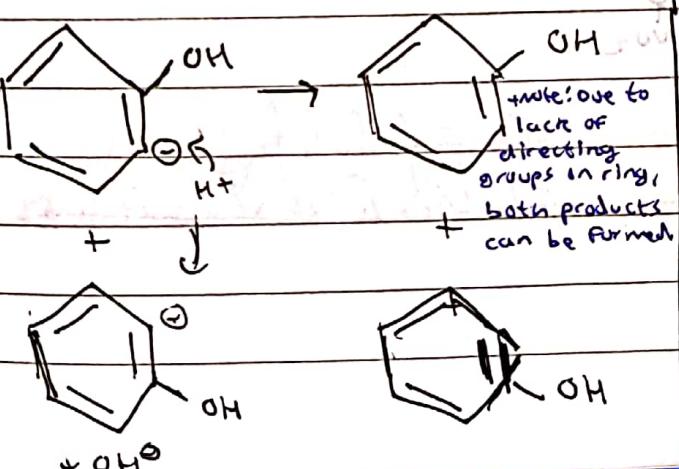
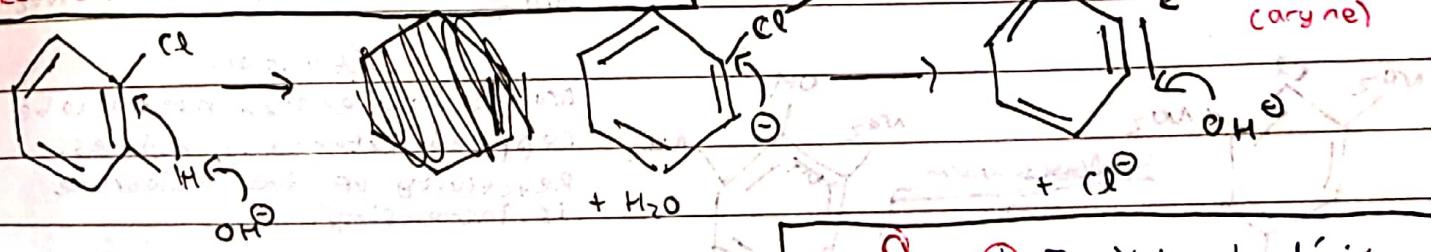
NUCLEOPHILIC SUBSTITUTION REACTION (SNAr)

Chlorobenzene can be converted into phenol by heating ~~at~~ in aqueous sodium hydroxide solution at a temperature of 623 K & a pressure of 300 atm. ~~reaction only occurs at very high temperatures & pressure.~~



Note: The presence of an electron withdrawing group at ortho & para positions increases reactivity of halobenzenes & reduces the temperature & pressure required for the reactions to occur.

ELIMINATION-ADDITION MECHANISM



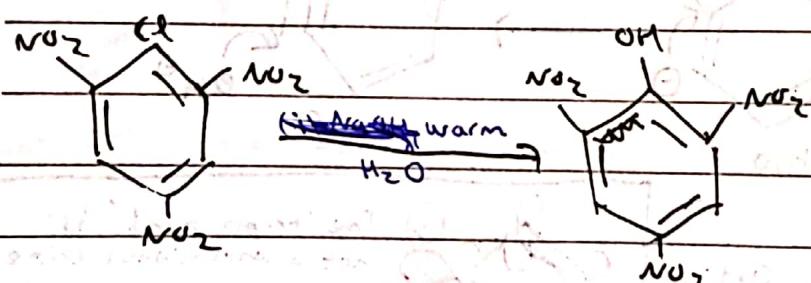
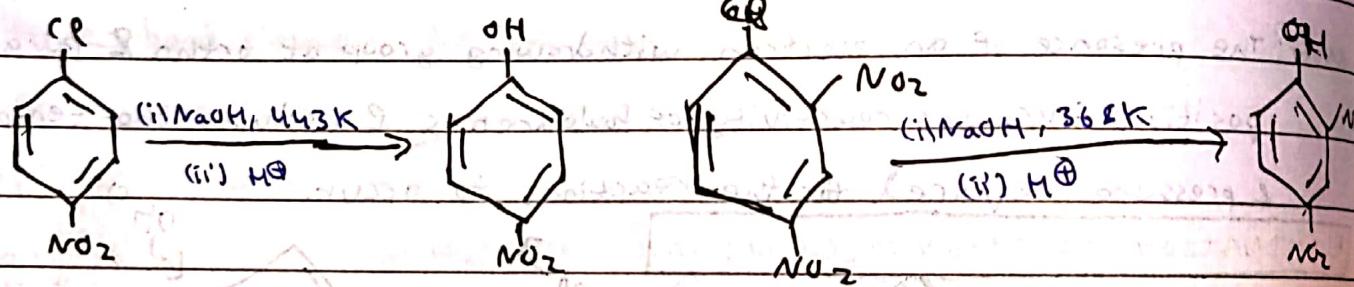
The 'triple bond' is not a conventional triple bond since linear geometry with sp carbons cannot be achieved in a 6 membered ring. Hence the 2 electrons of the 'triple bond' occupy the sp^2 orbitals of the carbons involved in the triple bond that are not involved in any σ or π bond. These however are not parallel to each other & hence cannot form a true π bond. Therefore, the 'triple bond' of arynes are HIGHLY reactive.

*Note: Initially OH^- acts as a base & removes the H^+ from the ring. Then once the aryne is formed, the lone pair on C forms attacks the halogen & forms the aryne. Now, OH^- acts as a nucleophile & reacts with the highly reactive aryne to form the substituted aryl halide. It finally undergoes protonation to remove the negative charge & attain stability. Hence rate of reaction depends on basicity of substituting group & leaving group aptitude of halogen.

$\text{Ex: } \text{OH}^-, \text{NH}_2^-$ [good]

REPLACEMENT OF HALOGEN FROM ARYL HALIDE WITH ELECTRON WITHDRAWING GROUPS.

The presence of an electron withdrawing group (NO_2) at ortho- & para- positions increases the reactivity of haloarenes.

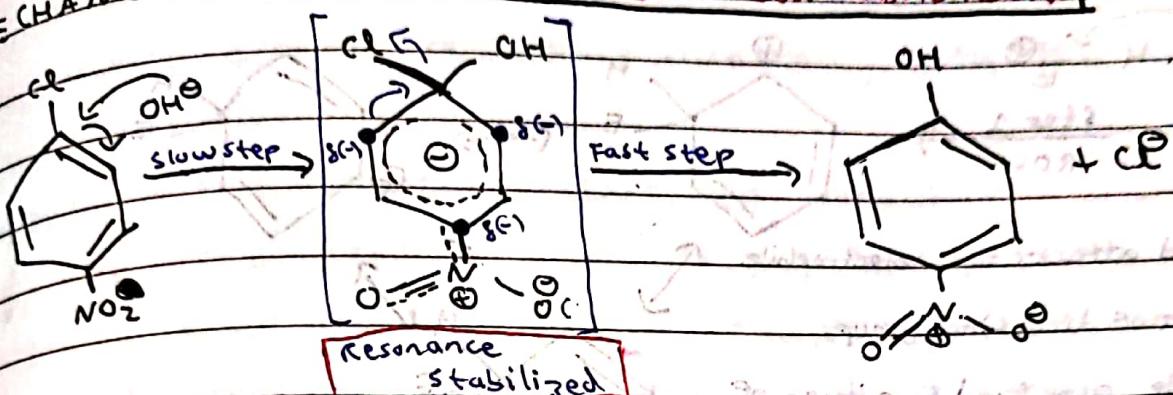


activation
Notice how energy needed to be supplied externally reduces. Reactivity of the haloarene is increasing.

~~Electro-withdrawing groups tend to deplete electron density of the ring.~~

~~Electro-withdrawing groups tend to withdraw electron density from the ring.~~

MECHANISM: ADDITION-ELIMINATION REACTION



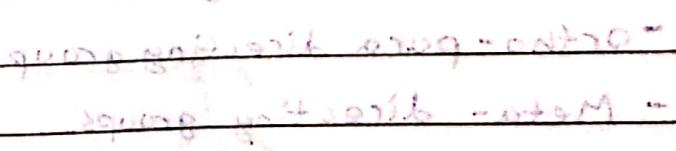
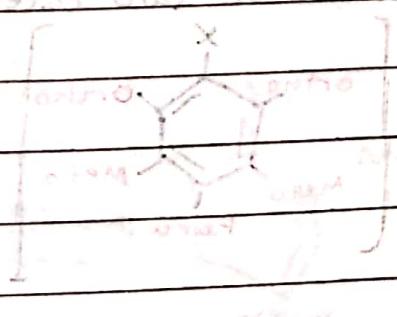
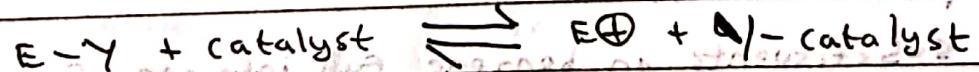
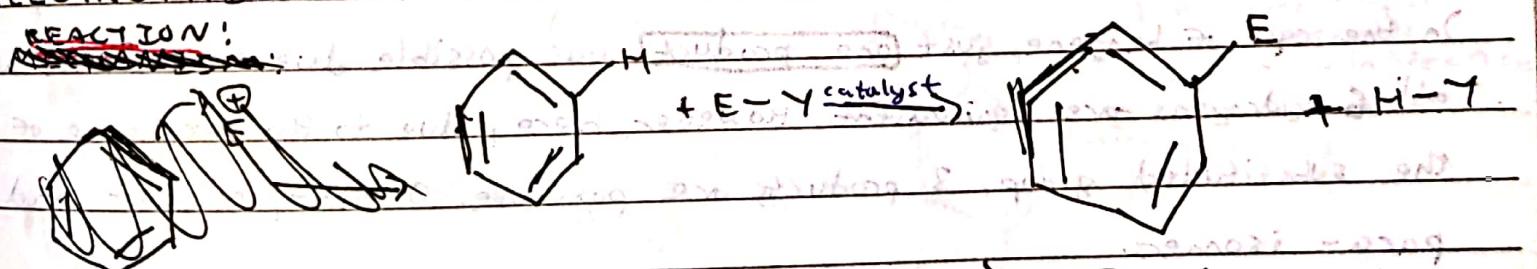
*Note: Here, addition-elimination takes place instead of elimination-addition due to high stability of resonance stabilized carbanion. ~~With electron~~

The effect is pronounced when the electron-withdrawing group is at ortho-⁻ and para-⁻ positions. However, no effect on reactivity is seen when it is at metaposition. This is because at meta-position the electron-withdrawing group does not contribute much to the resonance stabilization of the carbanion.

*Note: It is a two-step process. The substituting group must be a good nucleophile.

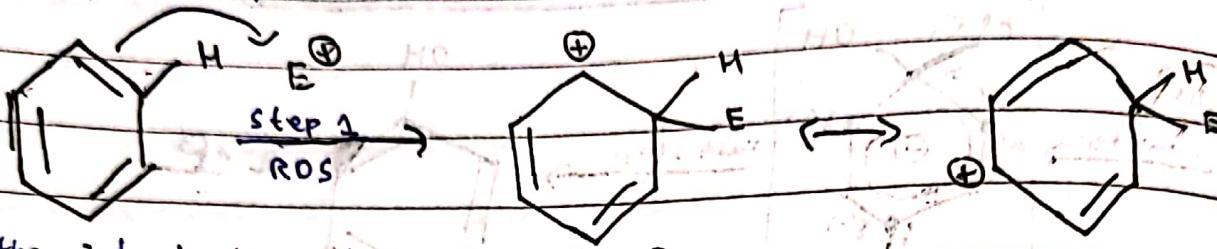
ELECTROPHILIC AROMATIC SUBSTITUTION REACTION

REACTION:



MECHANISM:

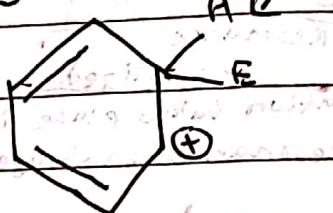
* Carbocation is resonance stabilized.



* Here, the pi-bond attacks the electrophile.

* Due to the lack of directing groups,

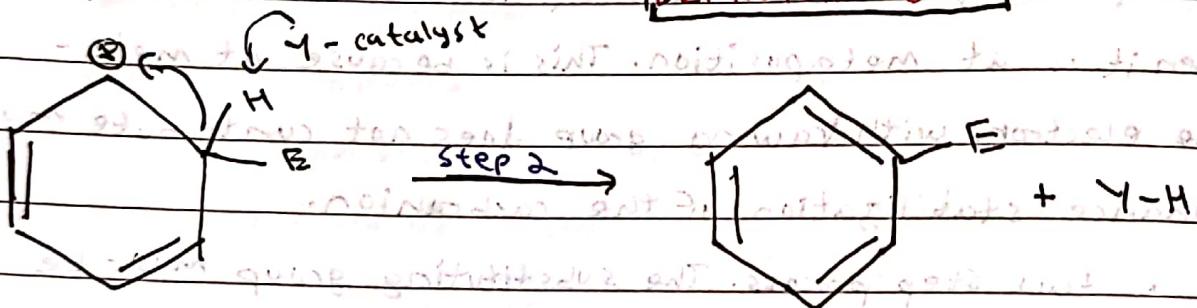
the electrophile can bond to either of the carbons involved in the pi-bond.



* Any of the pi-bonds can attack the electrophile.

DEPROTONATION

Removal of H⁺

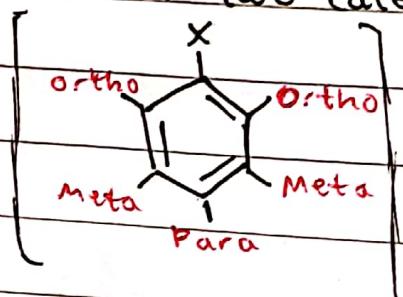


ELECTROPHILIC AROMATIC SUBSTITUTION ON A MONO-SUBSTITUTED BENZENE DERIVATIVE:

In the case of benzene, just one product was possible due to the fact that all 6 hydrogens are equivalent. However, here, due to the presence of the substituted group, 3 products are possible. Ortho-, meta- and para-isomers.

Substituents on benzene fall into one of two categories:

- Ortho-para directing groups
- Meta-directing groups



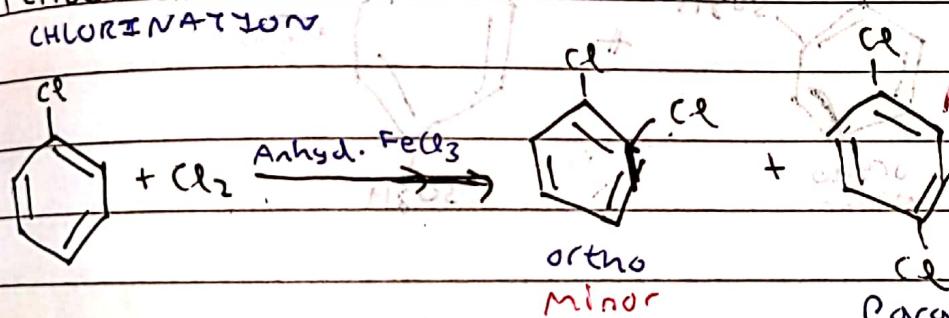
All activating groups are ortho-para directors and all deactivating groups are meta-directors, with the one exception being the halogens.
* Halogens are deactivating ortho-para directors.

Activating groups tend to donate electron density to the ring ($+I_g + R$)
deactivating groups tend to withdraw electron density from the ring ($-I_g - R$)
* However for halogens, while they have strong $-I$ effect, they also have a $+R$ effect due to their lone pairs which causes their resonance structures to have a charge on the ortho & para positions thus causing the benzene ring to be more reactive towards ortho & para positions for electrophilic aromatic substitution (EAS).

Ex:

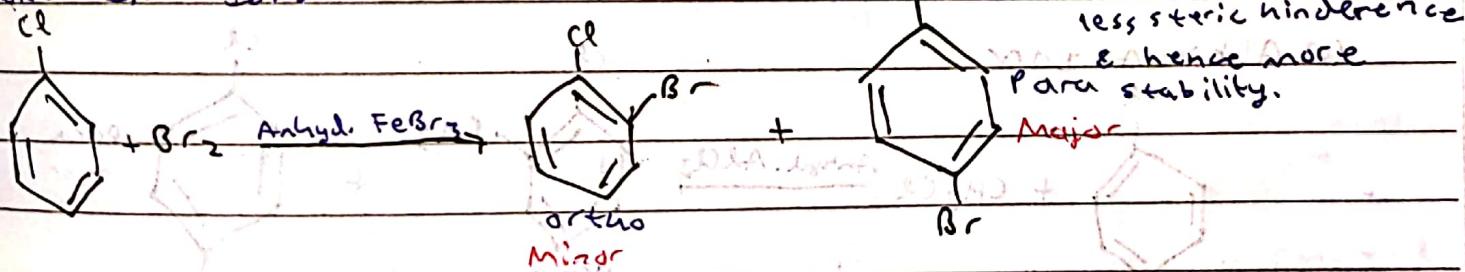
~~CHLORINATION~~ (i) HALOGENATION:

CHLORINATION:



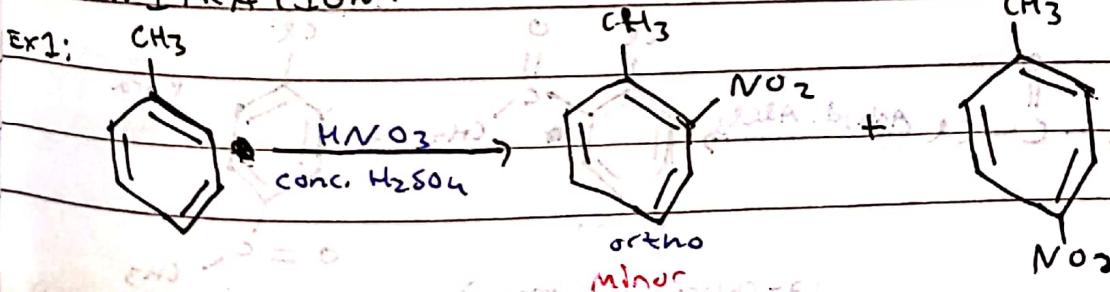
* Cl_2, CH_3 , etc are all activating groups and hence ortho and para products are formed.

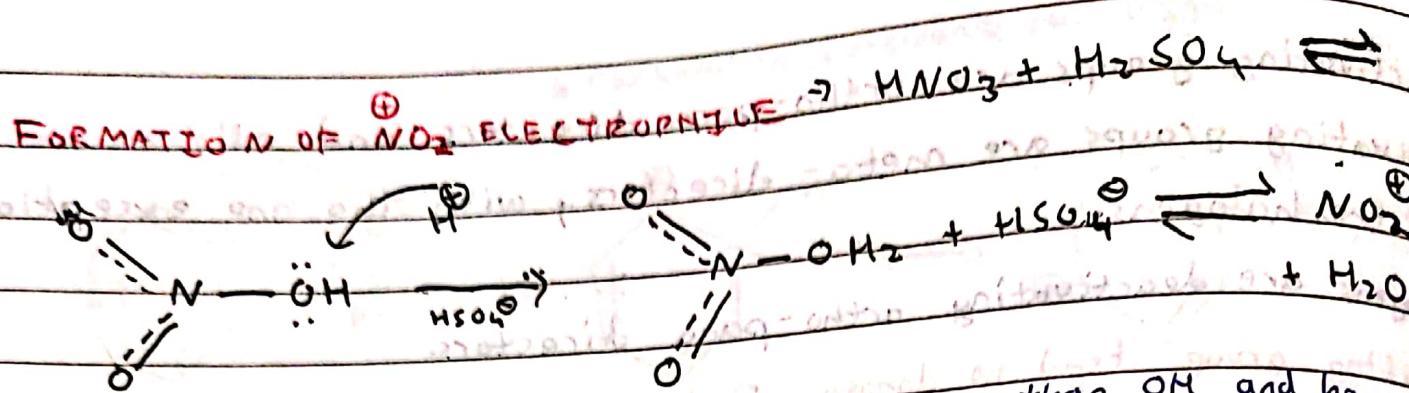
BROMINATION



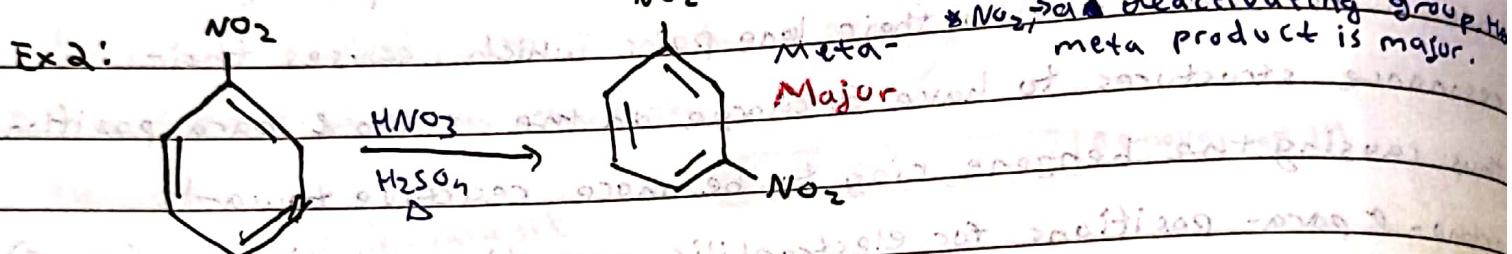
* Para products are generally major since there is less steric hindrance and hence more para stability.

(ii) NITRATION:

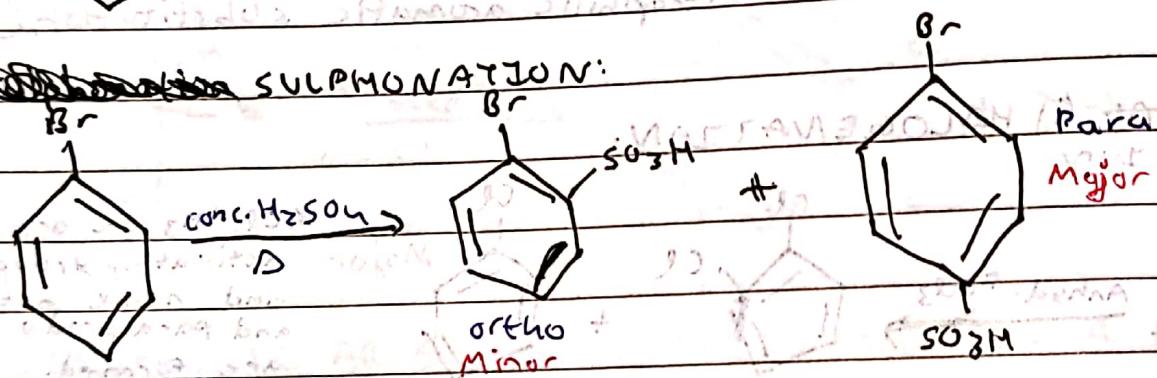




* Note: $\text{OH}_2(\text{H}_2\text{O})$ is a much better leaving group than OM and hence leaves N to form the NO_2^+ electrophile.

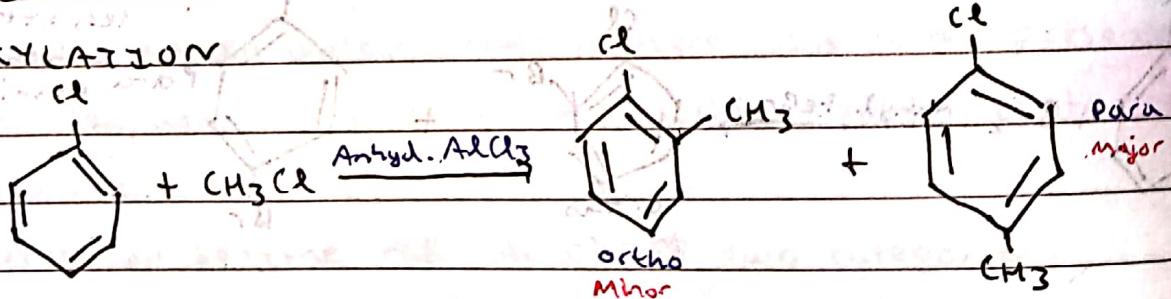


(iii) SULPHONATION:

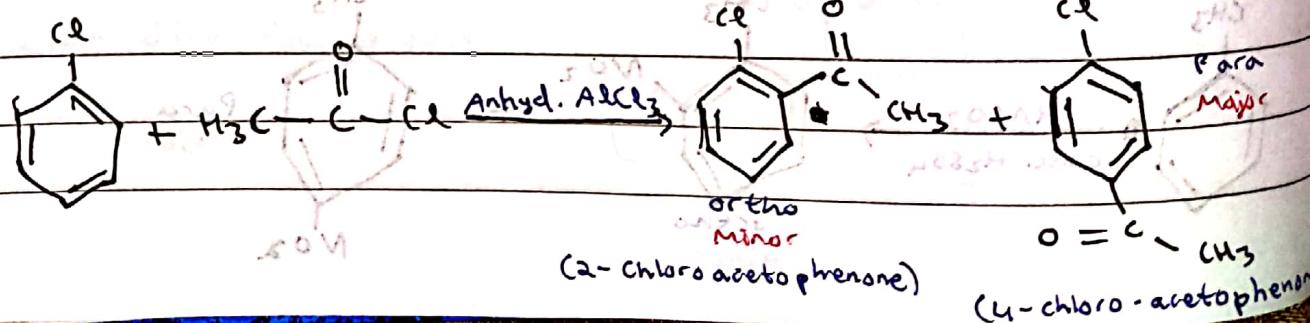


IV FRIEDEL-CRAFTS REACTIONS

(a) ALKYLATION



(b) ACYCLATION

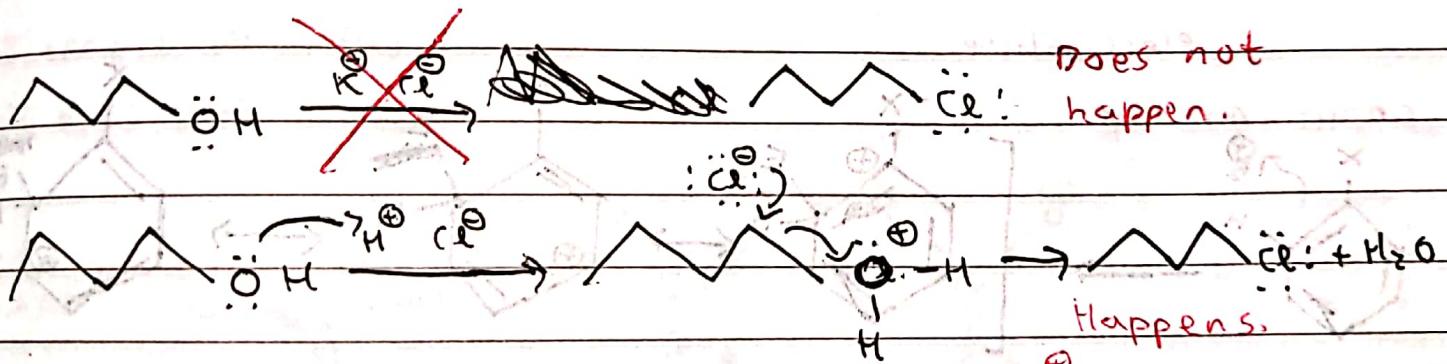


JEE NOTES

THE CONJUGATE ACID IS ALWAYS A BETTER LEAVING GROUP:
One of the key factors that determines whether a nucleophilic substitution reaction will happen or not is the identity of the leaving group. Good leaving groups are the ones which form stable anions, i.e., weak bases (Cl^- , Br^- , etc.). However, functional groups like OH^- are a bad leaving group and hence cannot be substituted easily via nucleophilic substitution reactions.

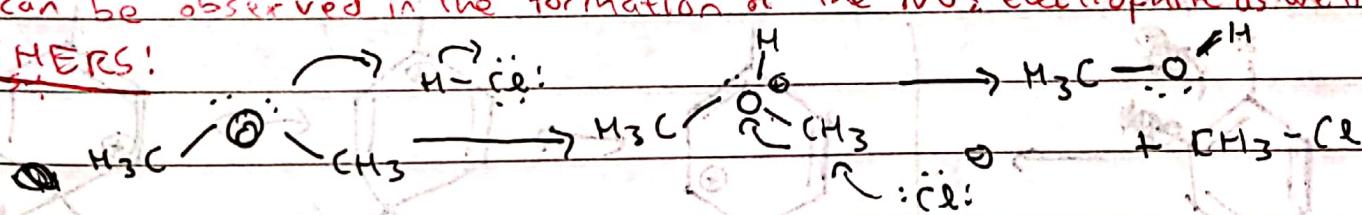
* To make groups like OH^- participate in substitution reactions we need to convert it to a weak base. This is done by removing some of its electron density. The best way to do this is to treat it with acid.

This makes the conjugate acid of our leaving group, which will be a weaker base & hence a better leaving group.



* This can be observed in the formation of the NO_2^+ electrophile as well.

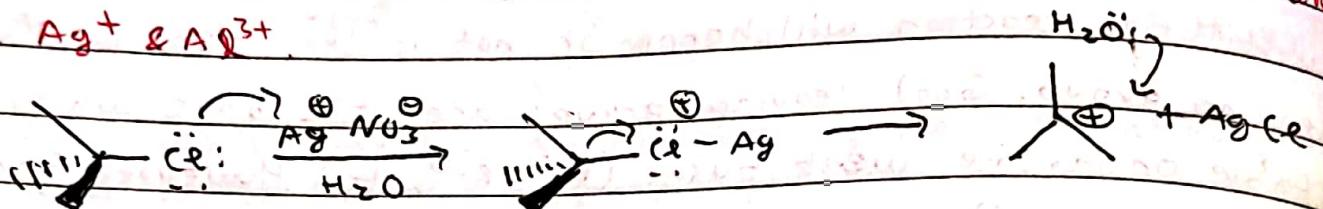
~~FOR ETHERS:~~



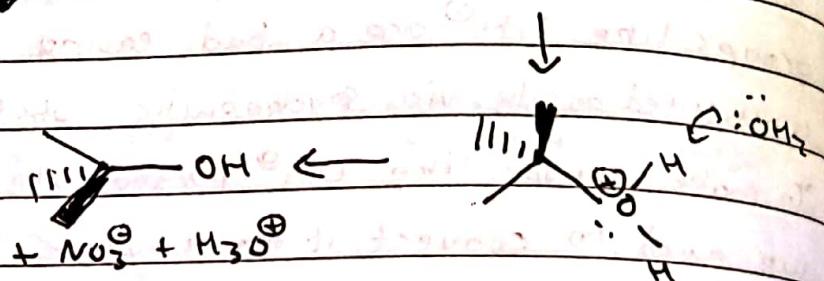
* Hence Lewis acids generally act as catalyst for these reactions.

* This phenomenon can be used to make halogens even better leaving groups as well. Halogens don't react with H^+ as readily as alcohols & ethers but they react very well with other Lewis acids like Ag^+ & Al^{3+} .

Ex:



An added benefit is that silver halides are insoluble in water thus pushing the reaction to completion.

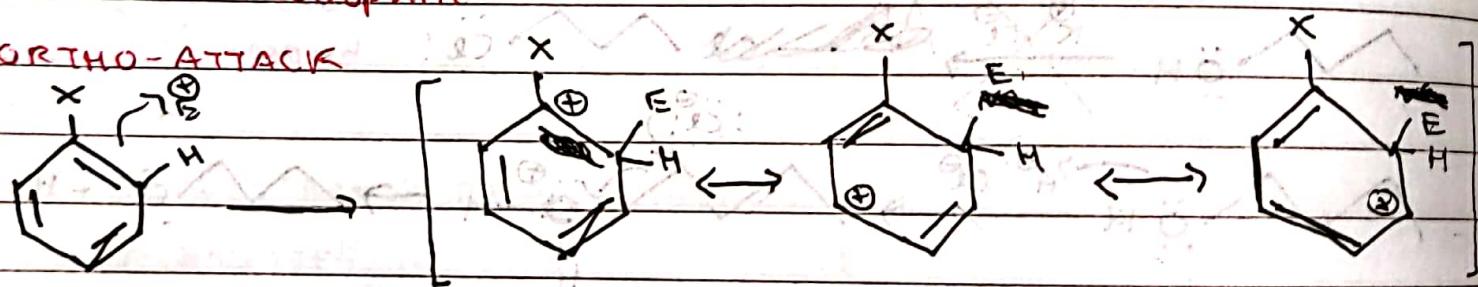


ACTIVATING GROUPS \rightarrow ORTHO, PARA

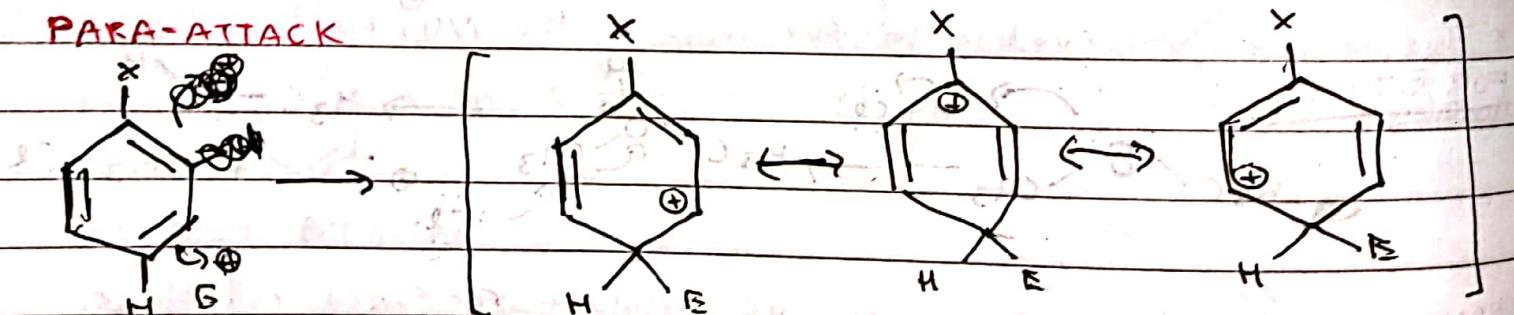
DEACTIVATING GROUPS \rightarrow META

REASON: Let X be any substituent group. Let E be the electrophile.

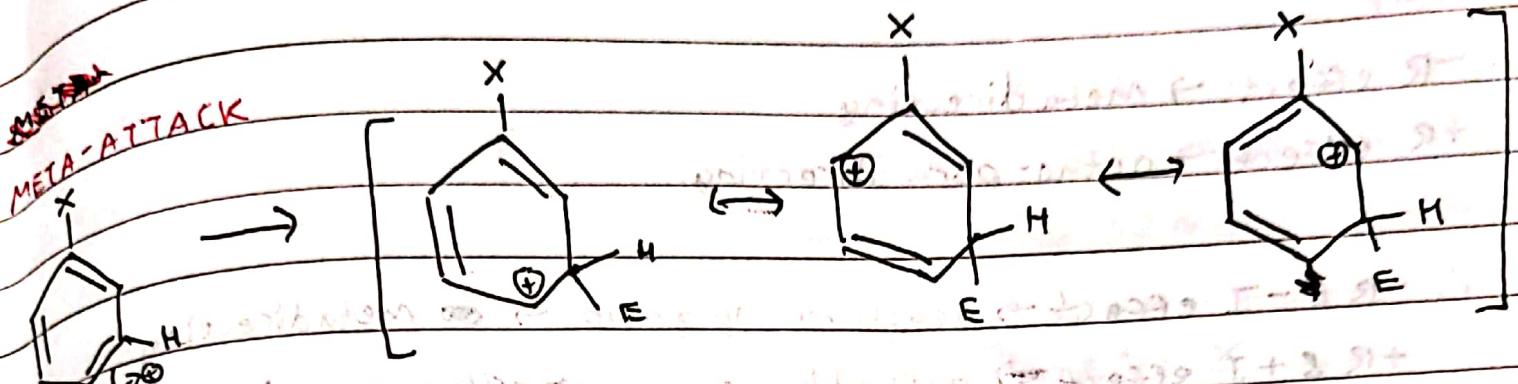
ORTHO-ATTACK



PARA-ATTACK



If the electrophile attacks ortho & para positions, in its resonance structures the +ve charge is on the carbon connected to X .

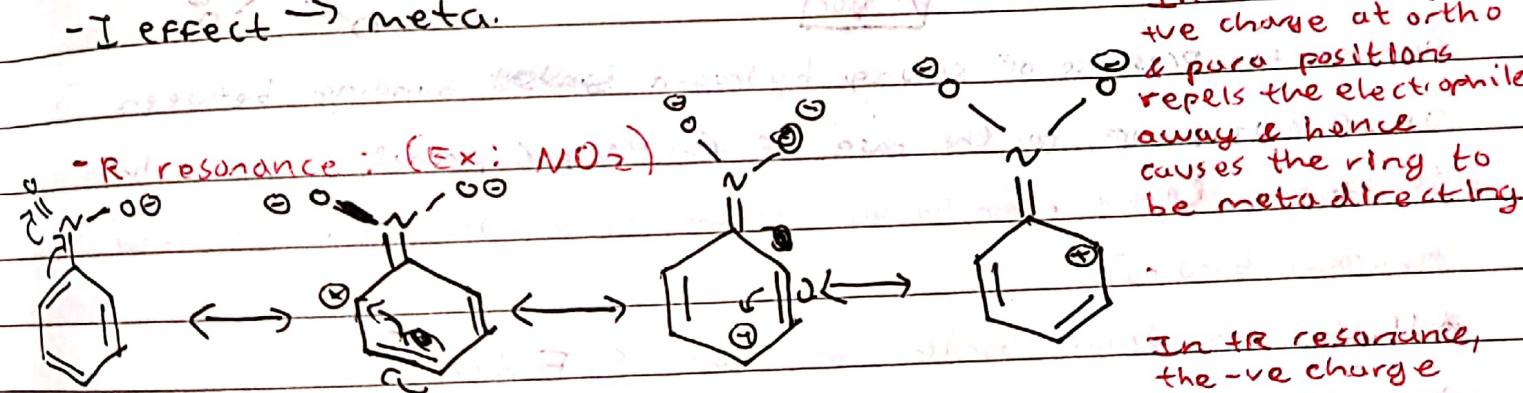


If the electrophile attacks meta position, in its resonance structure the +ve charge is ~~not~~ not on the carbon connected to X. If X gives +I effect; In the case of ortho & para attack it counters the +ve charge & helps stabilize the carbocation. If X gives -I effect; In the case of ortho & para attack, it intensifies the +ve charge leading to instability. Hence meta attack is more stable.

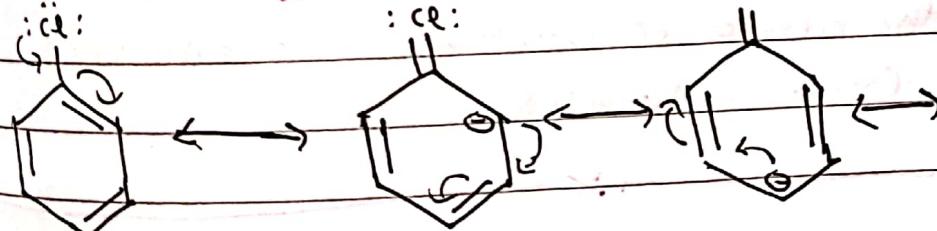
Hense:

+ effect \rightarrow ortho-para

-I effect \rightarrow meta.



+ R resonance; (Ex: Cl)



In -R resonance, the
positive charge at ortho
& para positions
repels the electrophile
away & hence
causes the ring to
be meta directing

In the resonance, the -ve charge occupies the ortho & para positions thus attracting the electrophile towards ortho & para positions & hence makes the ring, ortho-para directing.

Hence,

-R effect \rightarrow meta-directing

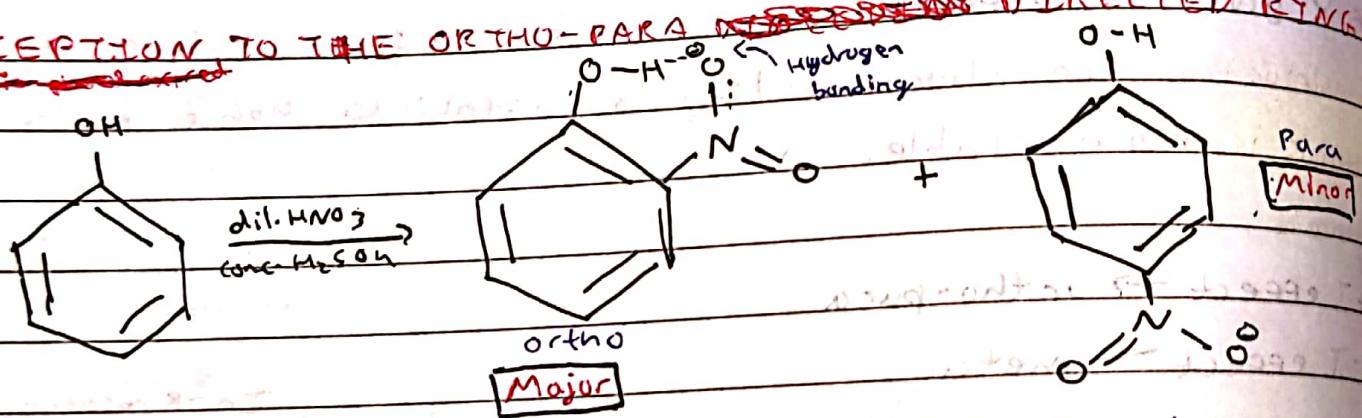
+R effect \rightarrow ortho-para directing.

\therefore -R & -I effect \rightarrow deactivating groups \rightarrow metadirecting.

+R & +I effect \rightarrow activating groups \rightarrow ortho-para directing

* With the exception of halides. Even though they are deactivating groups due to strong -I effect, their +R resonance structures cause them to be ortho-para directing.

~~EXCEPTION TO THE ORTHO-PARA DIRECTED RINGS~~



Due to the presence of strong hydrogen bonding between OH & NO₂ group, for the case of dil. HNO₃ & phenol, ortho product is major. (Not true for halogens or other compounds that do not show hydrogen bonding)

* H shows hydrogen bonding only with O, F & N.

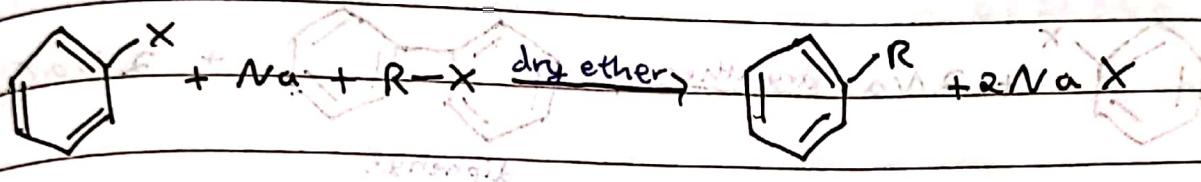
* This reaction takes place in the presence of dil. HNO_3 & not conc. HNO_3 . In the presence of conc. HNO_3 , a tri-substituted ring will be formed (More in Alcohols)

REACTIONS WITH METALS

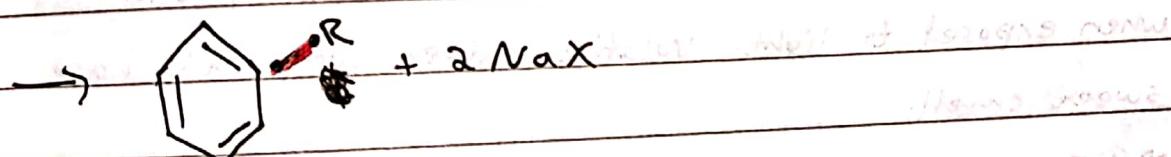
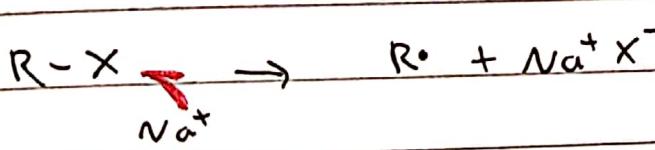
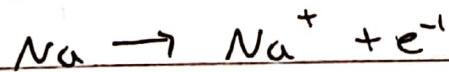
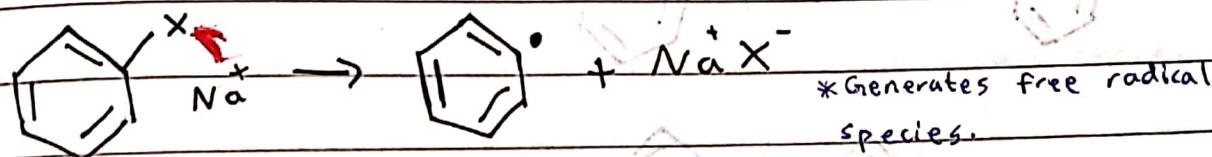
MONTAGUE SULTAN

WURTZ-FITTIG REACTION

A mixture of ~~any~~ an aryl halide & an alkyl halide gives an alkyl arene when treated with sodium in dry ether

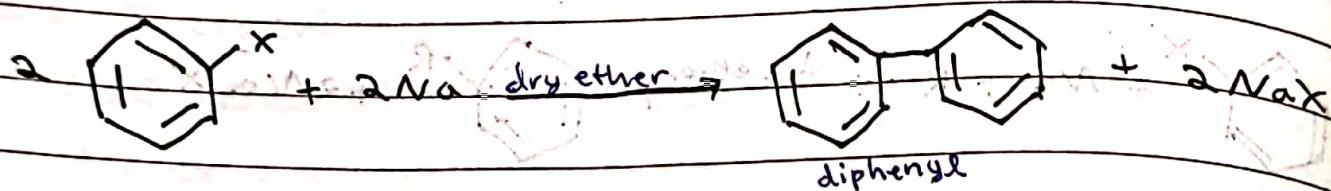


MECHANISM:

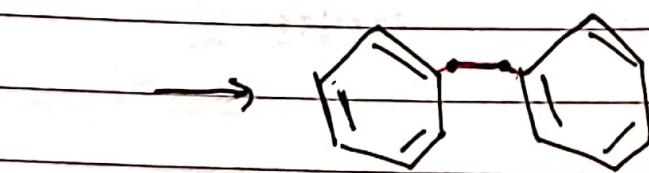
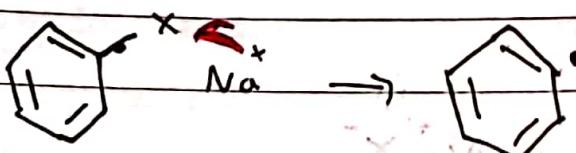


FITTIG REACTION

Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together.



MECHANISM:

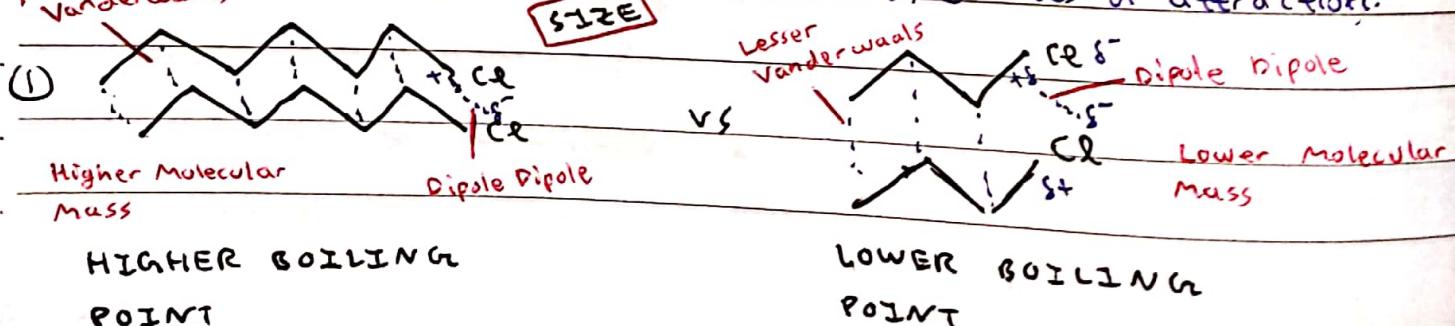


PHYSICAL PROPERTIES

Alkyl halides \rightarrow colourless when pure. But, bromides & iodides develop color when exposed to light. Volatile halogen compounds have sweet smell.

Boiling point \rightarrow ① Forces of attraction ② Molecular mass

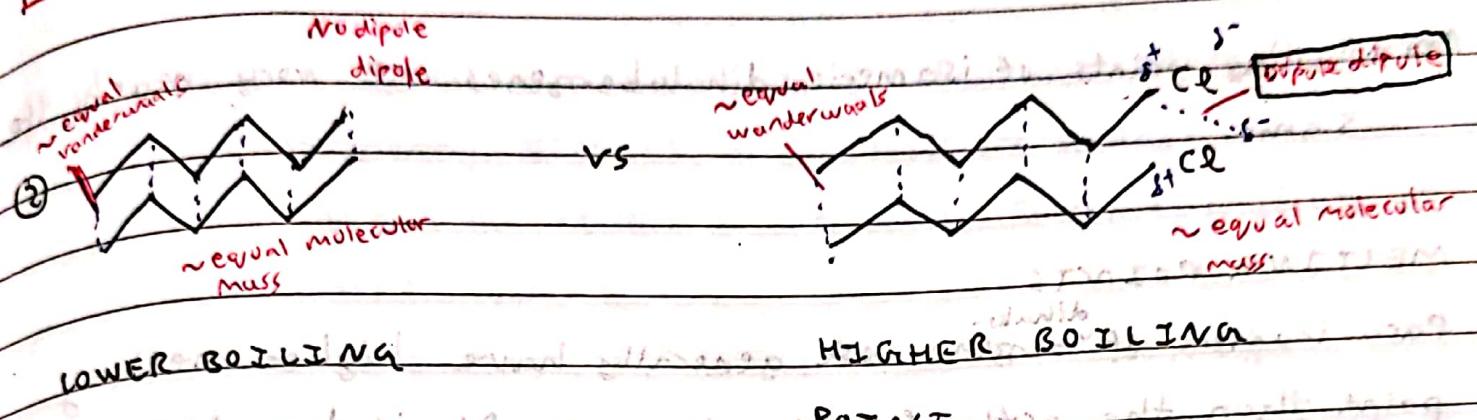
Melting point \rightarrow ① Symmetry (compressibility) ② Forces of attraction.



HIGHER BOILING POINT

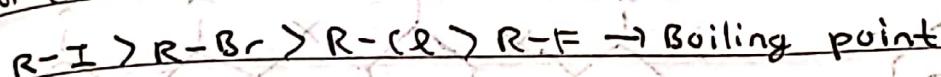
LOWER BOILING POINT

ALKYL HALIDE VS HYDROCARBON



HALOGEN GROUP

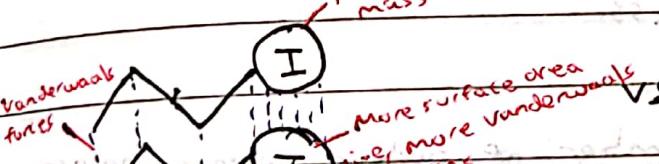
for the same alkyl group: R,



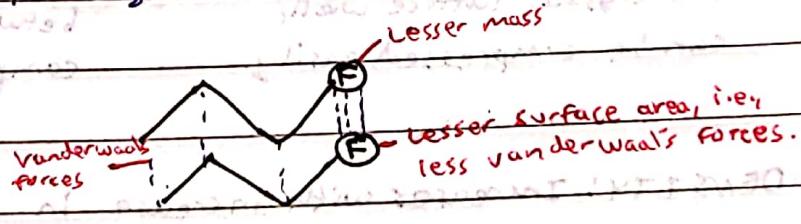
* Molecular mass of R-I > R-Br > R-Cl > R-F.

* Size of I > Br > Cl > F. Hence surface area is more i.e., more space

/area for vanderwaal's forces (i.e., stronger vanderwaal's forces).



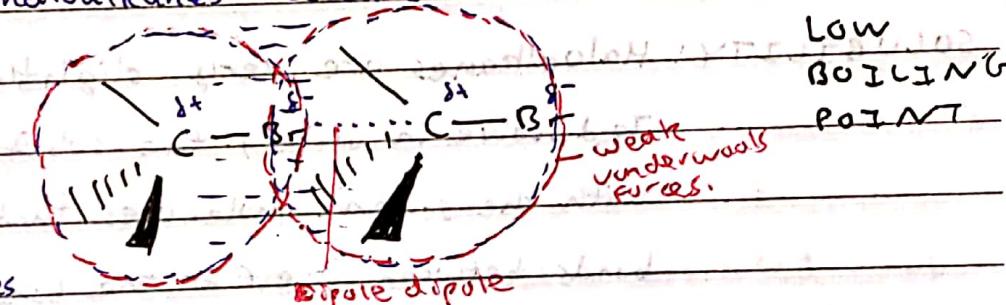
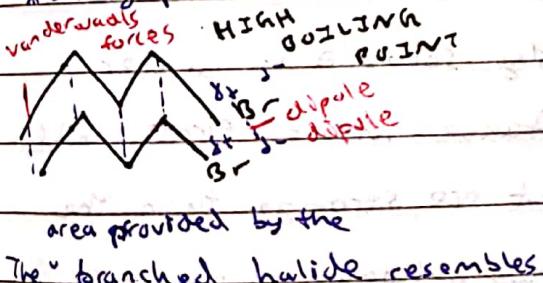
HIGH BOILING POINT



LOWER BOILING POINT.

ISOMERS

* Boiling points of isomeric haloalkanes decrease with increase in branching

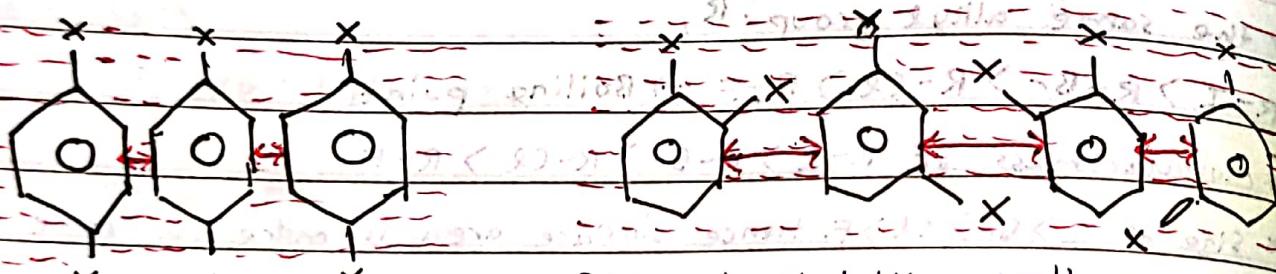


The branched halide resembles the surface area of sphere, i.e., minimum surface area which results in weaker vanderwaal forces.

* Boiling points of isomeric dihalobenzenes are very nearly the same.

MELTING POINTS:

Para isomers of benzene ^{dihalo-} generally have higher melting point than the ortho- & meta-isomers. It is due to symmetry. Para-isomers fit the crystal lattice better as compared to ortho- & meta-isomers.



Fits crystal lattice well,
can be compressed easily.

Does not fit lattice well, more space
between the compounds. Harder to
compress.

DENSITY: Increases with increase in number of carbon atoms, halogen atoms & mass of halogen atoms.

Mainly, density & mass.

SOLUBILITY: Haloalkanes are very slightly soluble in water

To dissolve in water, the substance must form bonds with the solvent molecules that are stronger than the bonds between itself or the bonds between solute molecules.

This is because, energy is required to ~~break~~ overcome the bonds between the haloalkane molecules & to overcome the hydrogen bonds between water molecules. Energy

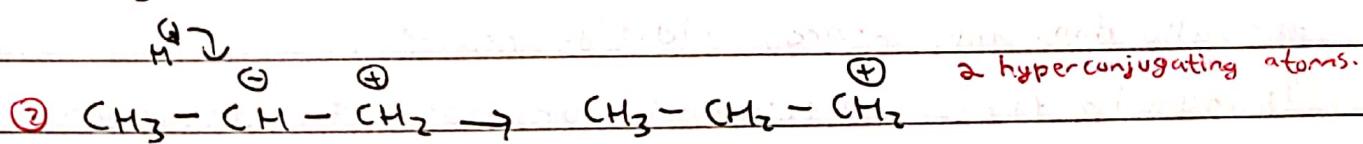
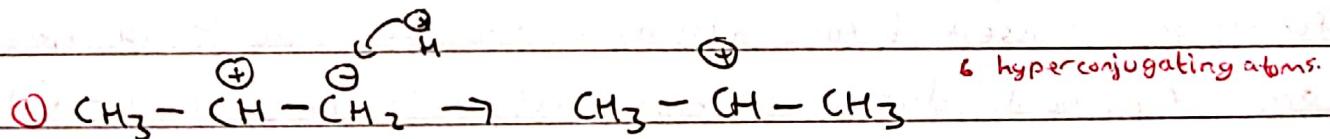
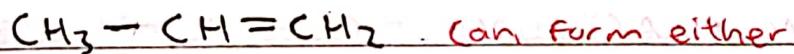
released by the formation of ~~other~~ haloalkane-solvent bonds is lesser than energy absorbed; i.e. the bonds are weaker. Hence ΔH is +ve and thus the reaction is unfavorable. Therefore, solubility of haloalkanes in water is low.

However, haloalkanes tend to dissolve in non-polar/organic solvents because the bonds between haloalkane-solvent that are being formed are mostly of the same type as the bonds being broken or stronger. Hence, energy released is equal to or more than energy absorbed. So, $\Delta H \approx 0$ or -ve, therefore the reaction occurs. & they tend to dissolve.

JEE NOTES

* Markonikov's rule works due to carbocation stability.

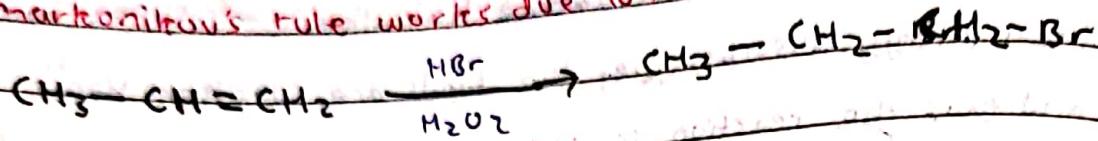
Ex:



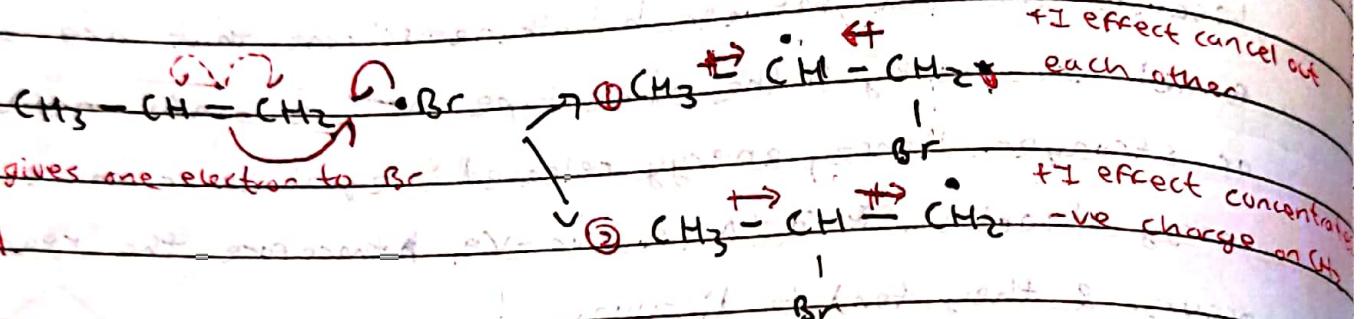
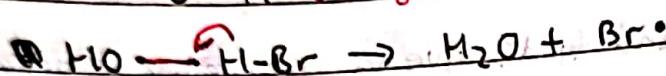
Hence 1 is more stable. Therefore, carbon with lesser number of hydrogen atoms will bond with the negative addendum.

→ The negative addendum will bond to the most substituted carbon

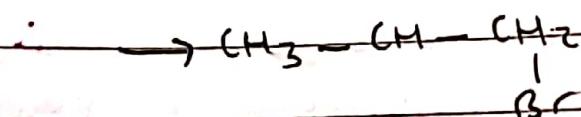
* Antimarkonnikov's rule works due to free radical addition



$\text{H}-\text{O}-\text{O}-\text{H}$ undergoes homolytic bond cleavage. $\rightarrow 2\text{H}_2\text{O}$.



Hence ① is more stable than ②.

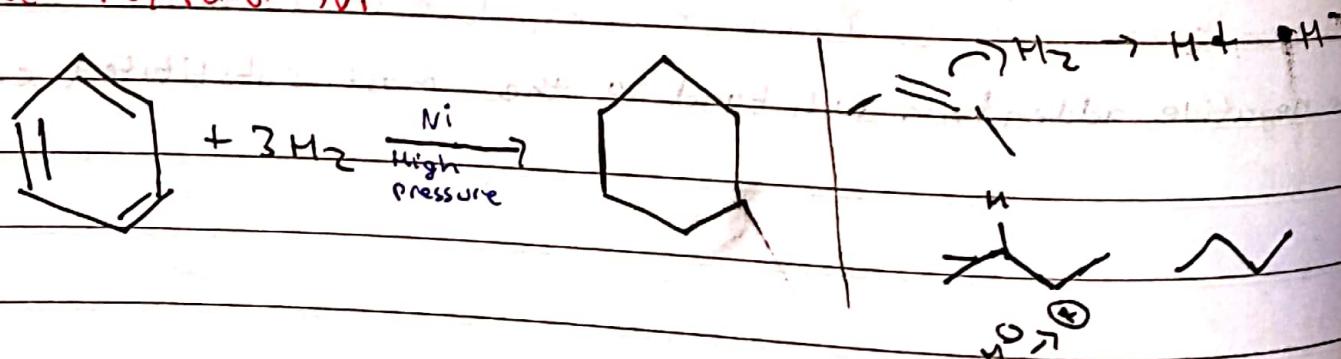


NUCLEOPHILIC ADDITION REACTIONS FOR ARYL HALIDES.

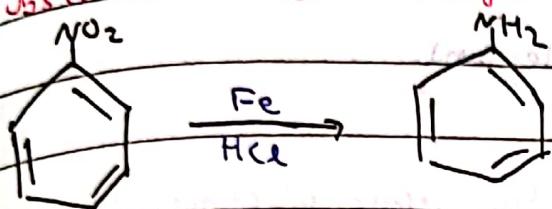
* For reasons discussed before, although the benzene ring has an array of pi-bonds, due to its aromaticity it is very stable and hence generally does not undergo addition reactions.

It instead performs electrophilic aromatic substitution.

* However at high pressure & temp, in the presence of catalysts like Pt, Pd or Ni

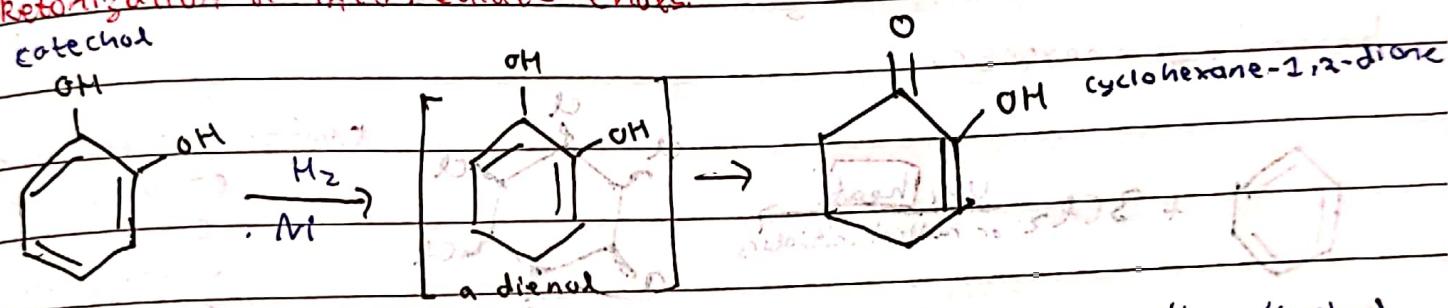


* Substituted benzene rings may also be reduced ~~to this form~~

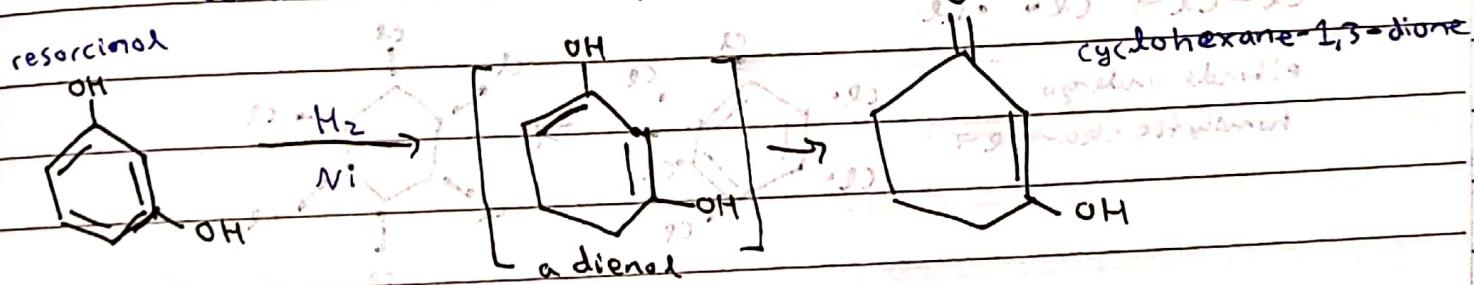


Mechanism in amines.

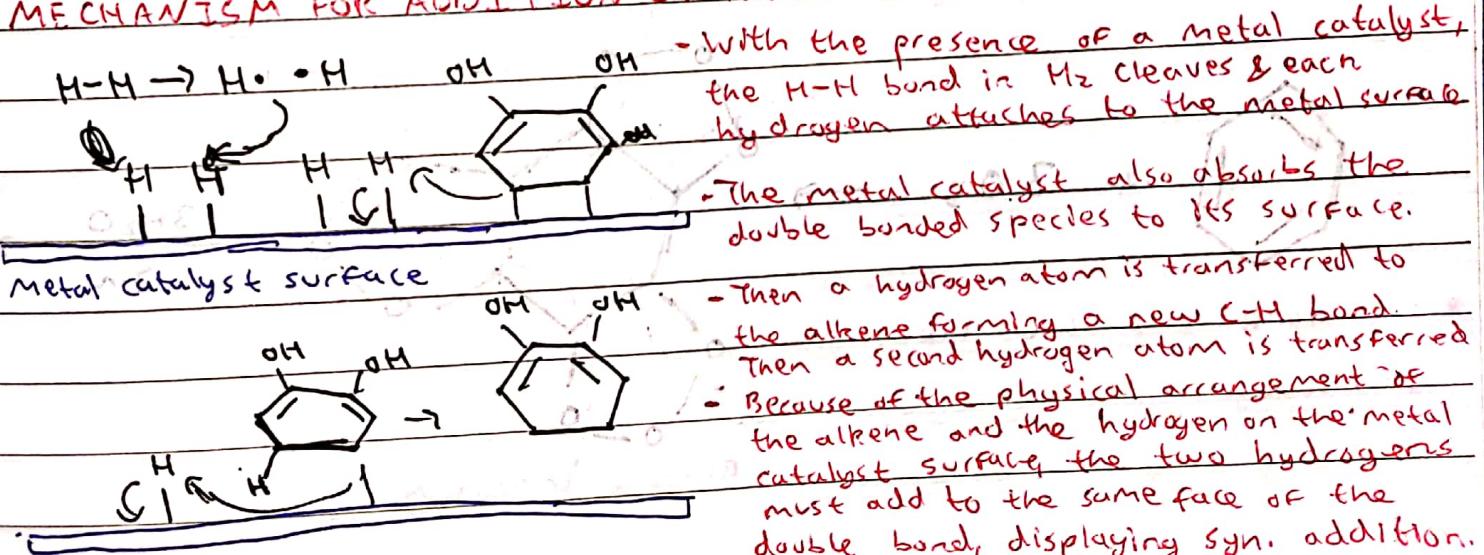
* Hydroxy substituted compounds like phenol, catechol and resorcinol give carbonyl ($\text{R}'\text{C}\text{O}\text{R}''$) resulting from fast ketonization of intermediate enols.



dienol \rightarrow Any compound having a hydroxy (-OH) group directly attached to a diene (-C=C-)



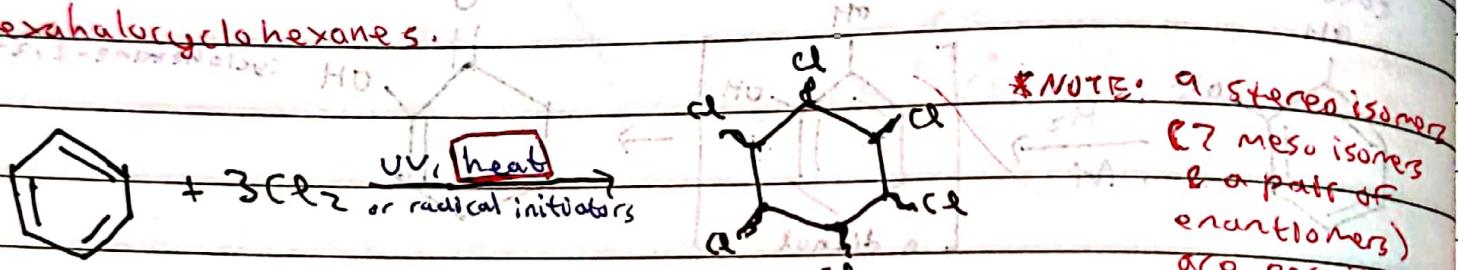
MECHANISM FOR ADDITION OF HYDROGEN:



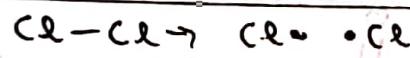
Syn addition \rightarrow it is the addition of two substituents to the same side or face of a double bond or triple bond.

RADICAL ADDITION REACTION.

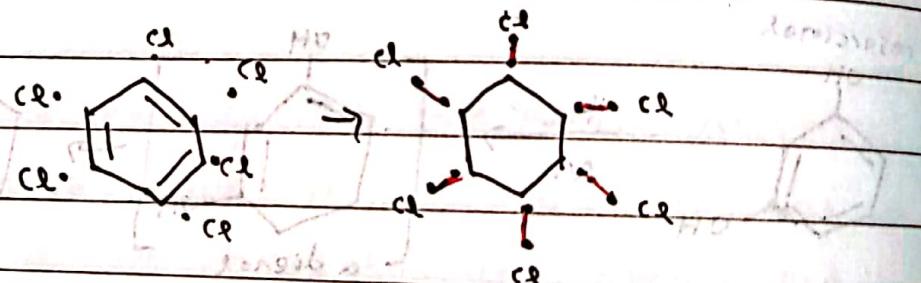
Benzene is more susceptible to radical addition than electrophilic addition. Benzene does not react with chlorine or bromine in the absence of a catalyst and heat. In strong sunlight or with radical initiators, benzene adds those halogens to give hexahalocyclohexanes.



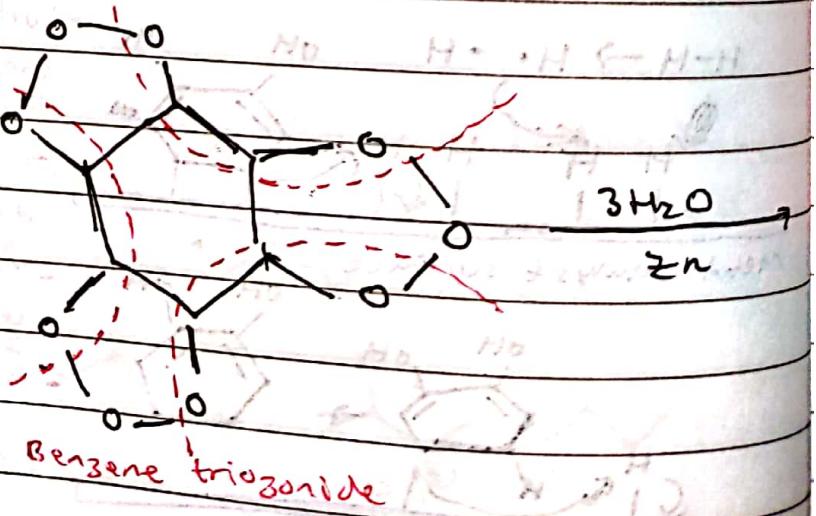
MECHANISM: With HO^{\cdot} (hydroxyl radical) participation, mixed hexa- and hepta-

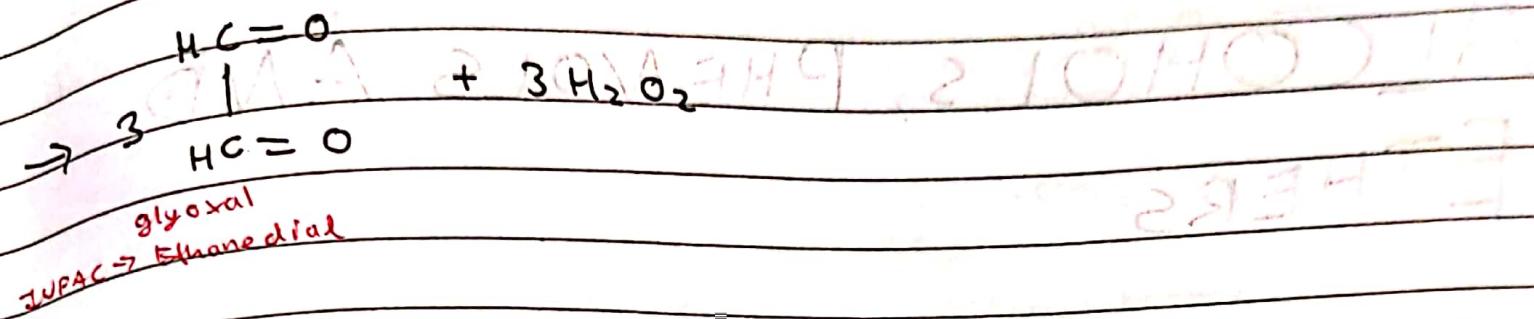


π bonds undergo homolytic cleavage \rightarrow

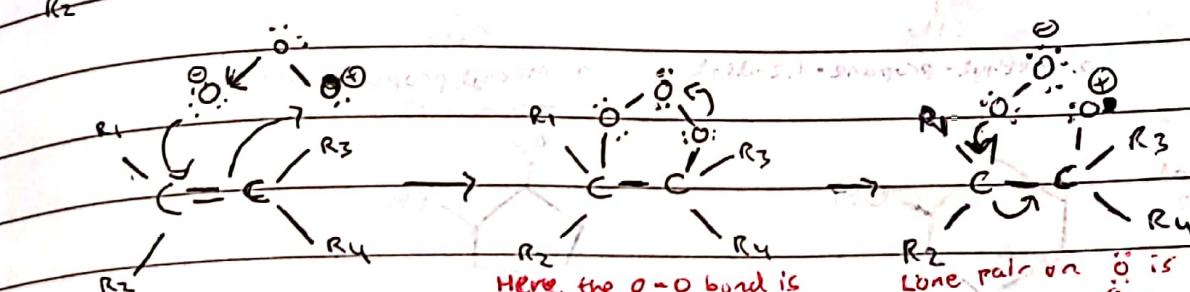
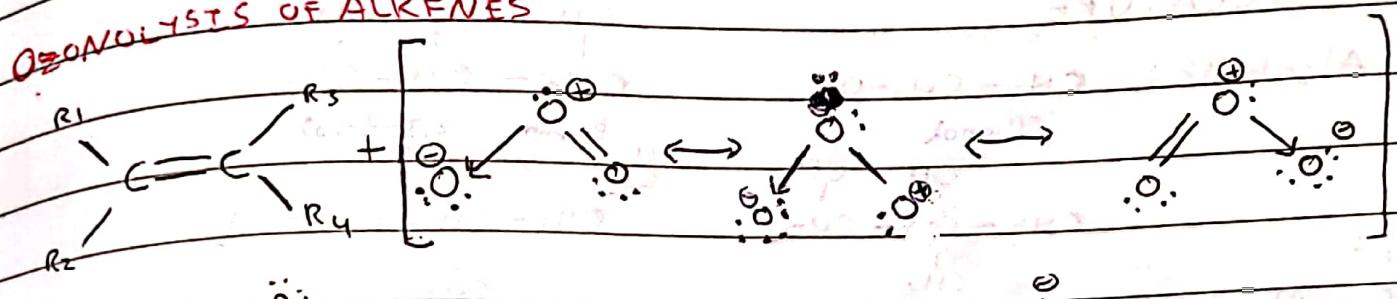


OZONOLYSIS OF BENZENE





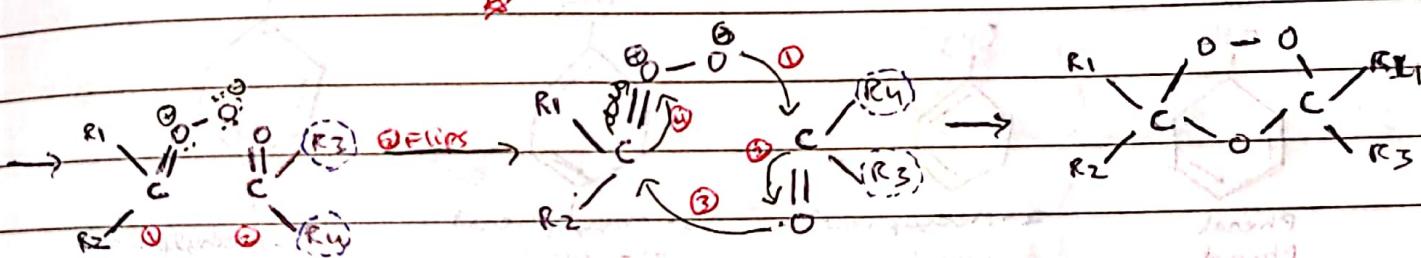
OZONOLYSIS OF ALKENES



* Intermediate might favor most substituted carbon.

Here the O-O bond is unstable & hence breaks. Direction does not matter since it is symmetric.

R₂ lone pair on O is repelled by -ve charge on O⁺ & hence attacks C-C bond. C-C bond breaking also helps neutralize +ve charge on O⁺



After this, depending on medium it undergoes either a reductive or oxidative workup to produce carboxylic acids or ketones. (Mechanism in adducts of ketones)

