

INDEX

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[illegible]

10 mark Important concepts

① what do you mean by SN_1 & SN_2 reaction?
 Explain Mechanism, kinetics & Stereochemistry of SN_1 & SN_2 reaction.

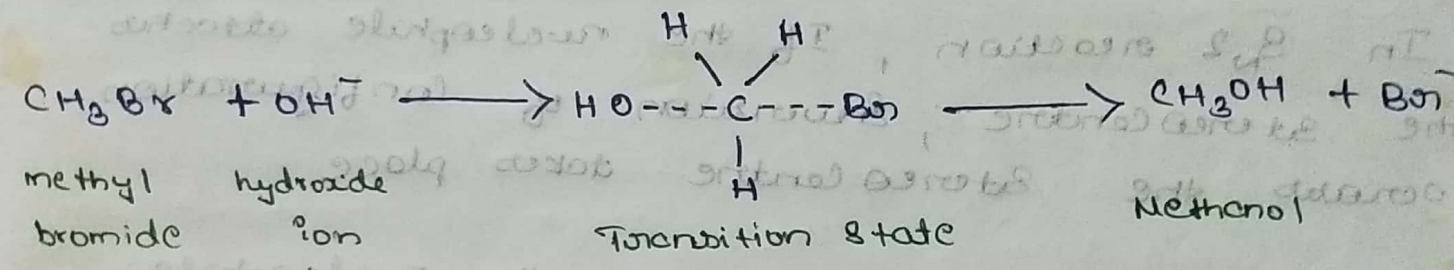
① SN_1 reaction
 unimolecular nucleophilic substitution reaction

where rate of reaction depends only upon alkyl halide

② SN_2 reaction
 bimolecular nucleophilic substitution reaction

where rate of reaction depends upon both of the reactants

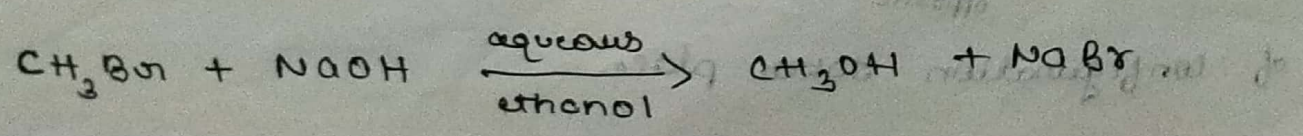
① mechanism of SN_2 reaction



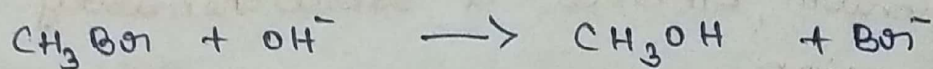
① It is a single step reaction, hydroxide ion reacts with methyl bromide to yield transition state

② In the transition state, OH & Br forms partial bond with carbon. OH develops partial positive & Br develops partial negative charge slowly. Bond b/w carbon & bromine breaks & give rise to bromide ions

SN_2 Reaction
 methyl bromide reacts with sodium hydroxide in aqueous ethanol to yield methanol



② Kinetics of S_N2 reaction



Since S_N2 reaction occurs from collision b/w Hydroxide ion and methyl bromide molecule, the rate of reaction depends upon the concentration of both reactants.

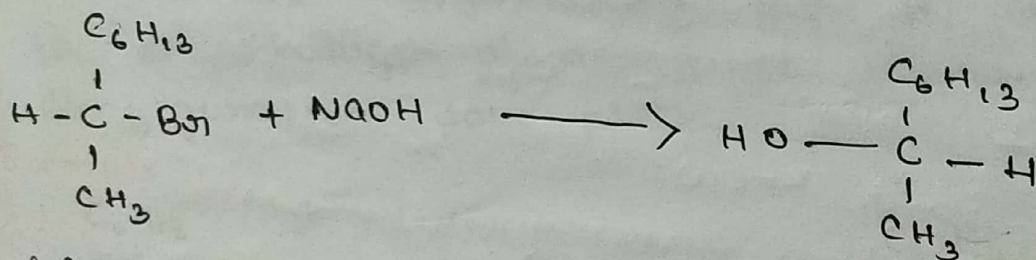
$$\text{rate} = k [CH_3Br] [OH^-]$$

If concentration of reactants are doubled, the rate of reaction is also doubled. If concentration is halved, then rate of reaction is also halved. It follows second order kinetics.

③ Stereochemistry of S_N2 mechanism

In S_N2 mechanism the nucleophile attacks the stereocentre from the side opp to the halogen atom. Hence inversion of configuration takes place.

Example:



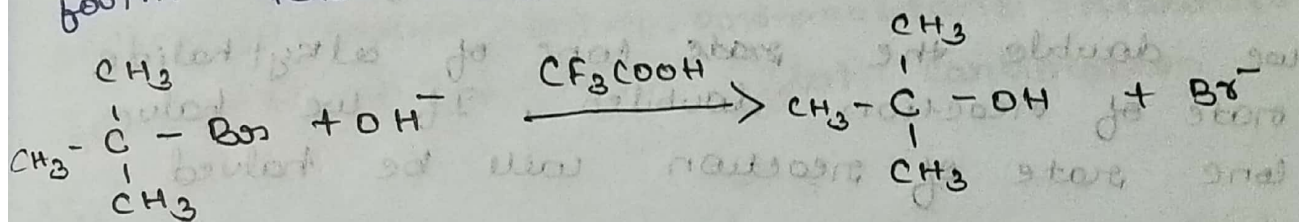
(-) 2-Bromooctane

(+) 2-octanol

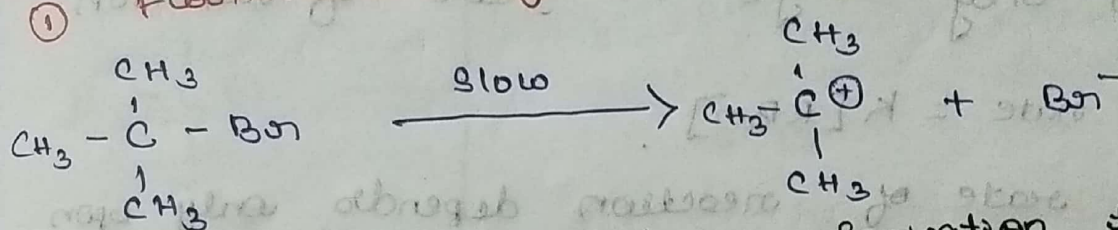
When (-)-2-bromooctane is heated with aqueous NaOH (+)-2-octanol is formed. Here OH group occupies the position opposite to that of bromine. Hence inversion of configuration takes place.

(2) Mechanism of S_N1 Reaction

tert-Butyl bromide reacts with hydroxide ion in presence of CF_3COOH (trifluoroacetic acid) to form tert-butyl alcohol.

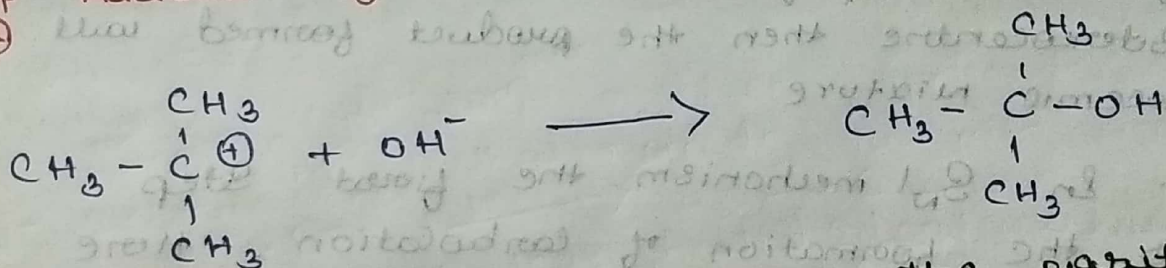


Step 1 Formation of carbocation



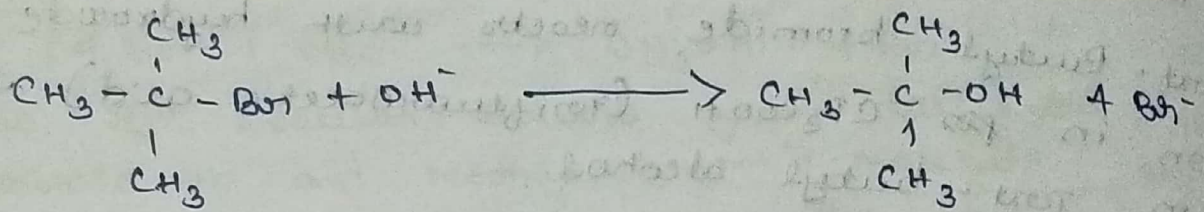
tert-Butyl bromide undergoes ionization to form tertiary carbocation & bromide ion. This is a slow step and hence is a rate determining step.

Step 2 Attack of nucleophile on carbocation



The nucleophile OH^- attacks the positive centre of carbocation from any one of the directions forming the final product, i.e. tert-butyl alcohol.

② Kinetics of S_N1 Reaction



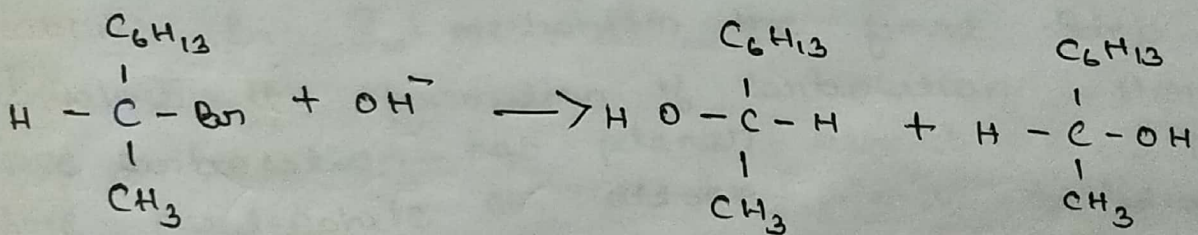
- ① If we double the conc of alkyl halide the rate of reaction doubles. If we halve the conc of alkyl halide the rate of reaction will be halved.
- ② If we double or halve the OH^- conc, there will be no change in rate of reaction.

$$\text{rate} = k[\text{RBr}]$$

Hence the rate of reaction depends only upon conc of alkyl halide. It follows first order kinetics.

③ Stereochemistry of S_N1 Reaction

Let us consider reaction of (-)-2-bromooctane with OH^- ion,



(-)-2-bromooctane

(+)-2-octanol

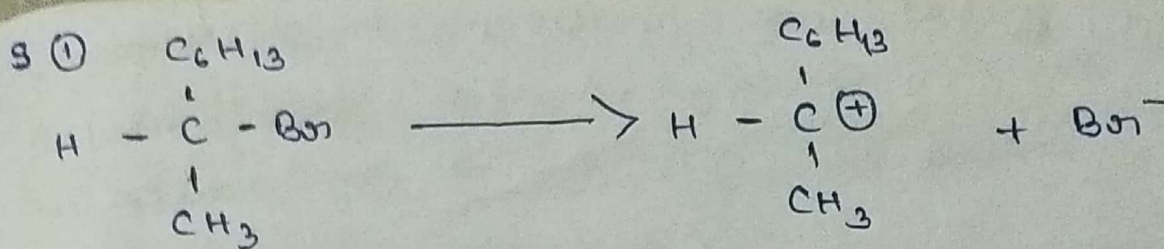
(-)-2-octanol

(75%)

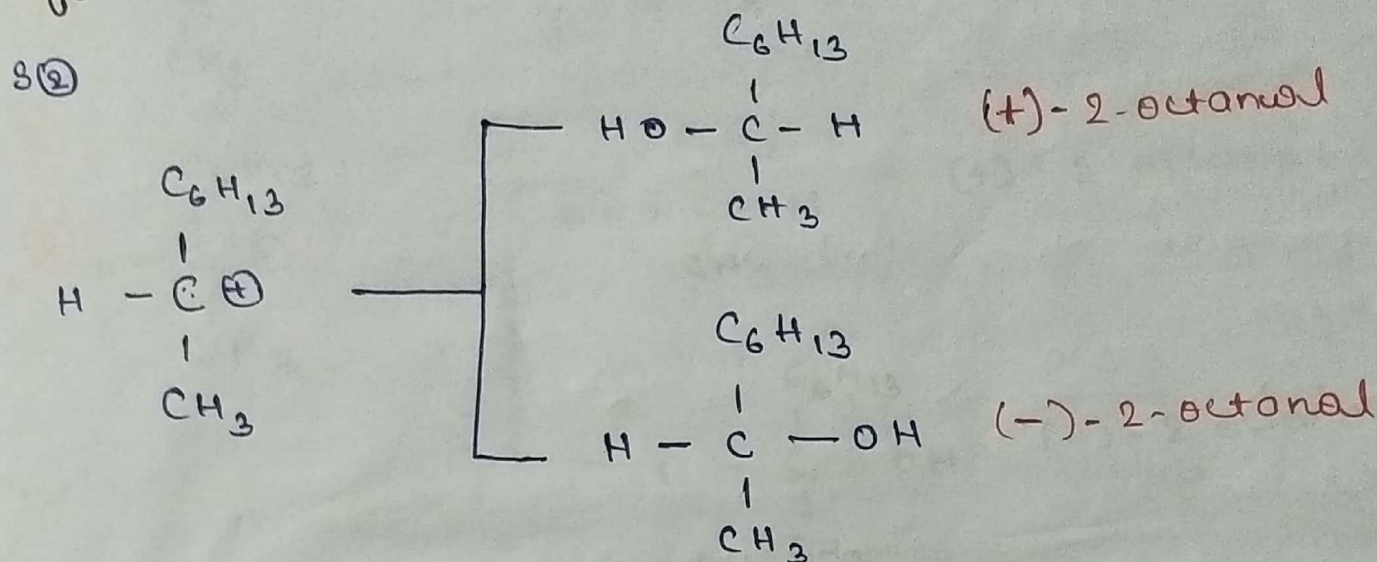
(25%)

(Inverted product)

(Retention product)



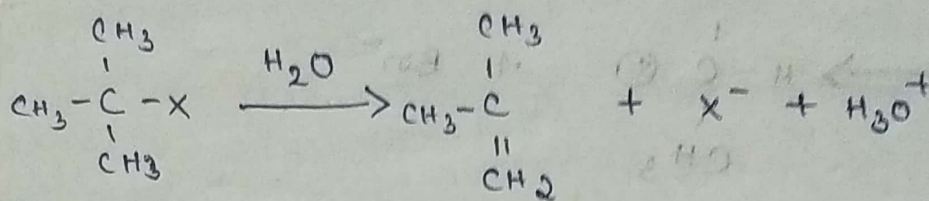
optically active (-)-2-bromooctane dissociates to form halide ion and flat carbocation.



The nucleophile Hydroxide ion attacks to either side of flat carbocation to yield two enantiomeric product.

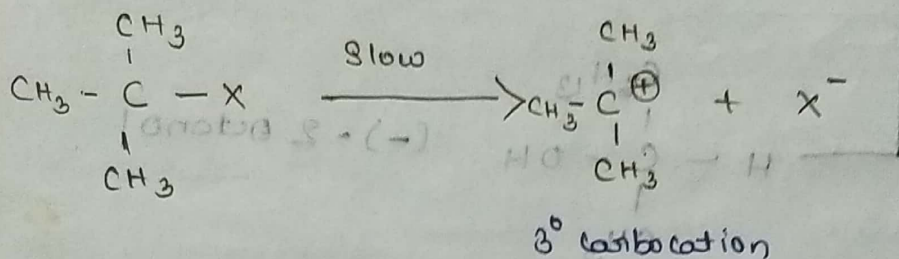
Q. Explain the mechanism, orientation, stereochemistry and reactivity of E_1 and E_2 reaction with appropriate examples.

E_1 Reaction (Dehydrohalogenation or β -elimination).

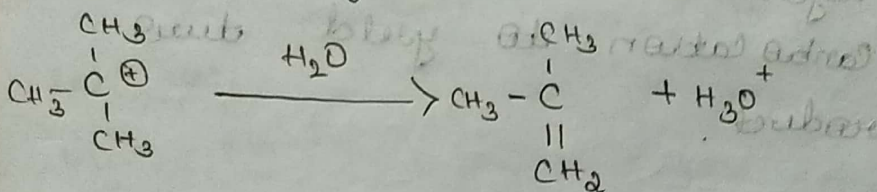


① Mechanism

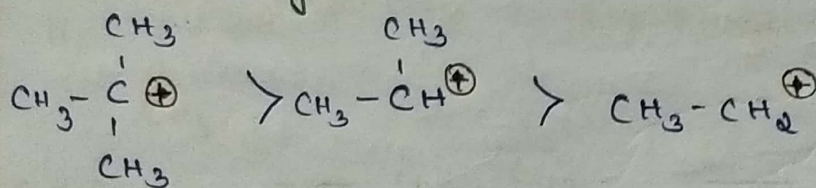
S① Formation of δ^+ carbocation



S② Attack of nucleophile



② Reactivity



① the more stable the carbocation, the more faster the E_1 reaction will be

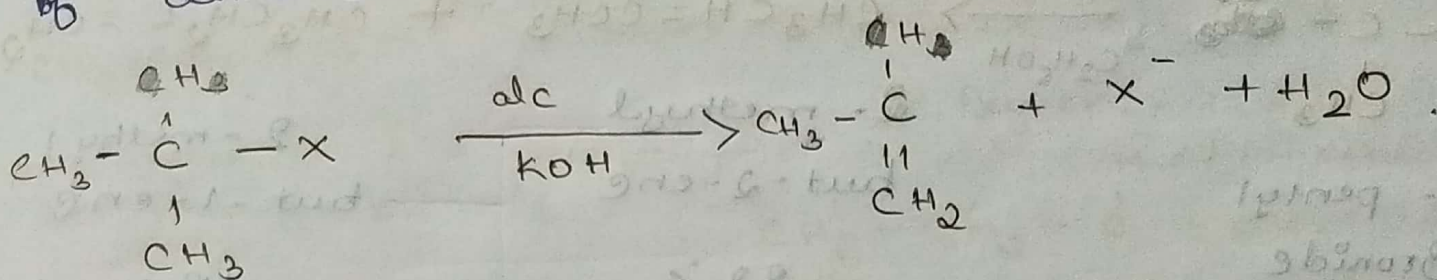
② By hyperconjugation, stability follows the order $3^\circ > 2^\circ > 1^\circ$.

③ the more stable

③ The product formation of alkyl halides follows the order $3^\circ > 2^\circ > 1^\circ > \text{CH}_3$

① STEREOCHEMISTRY

E_2 Reaction: (dehydrohalogenation or β -elimination)
It involves single step, base pulls a proton away from carbon, simultaneously halide ion departs resulting in the formation of alkene.



② Reactivity

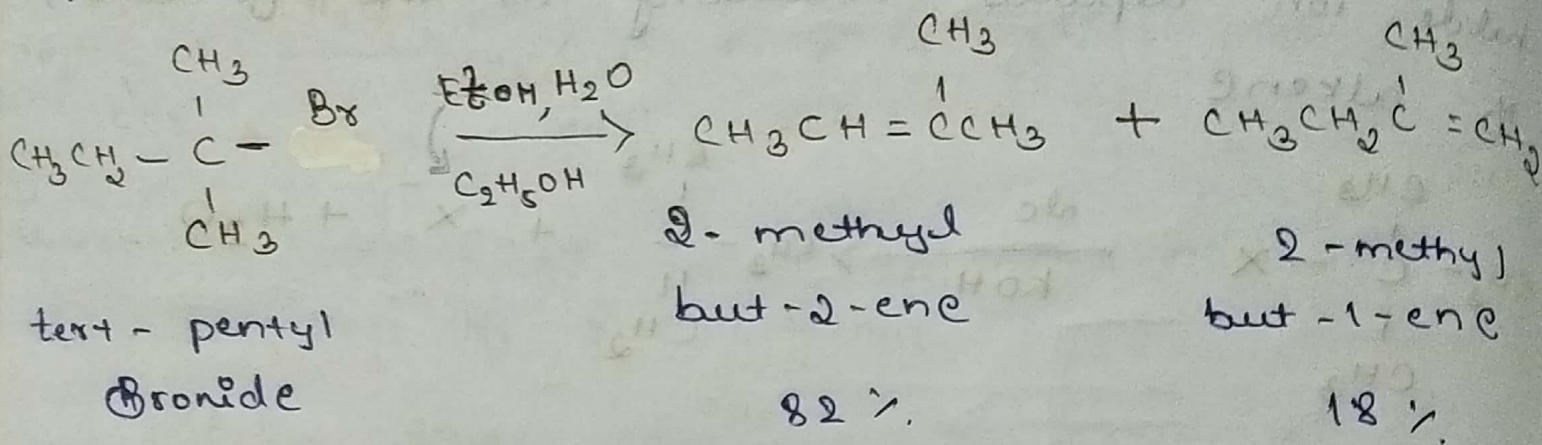
① When methyl groups involved in hyperconjugation, alkyl halide become more stable. Stability follows the order $3^\circ > 2^\circ > 1^\circ$.

② The more stable the alkyl halide, the more faster the E_2 reaction will be.

③ The product formation of alkyl halide follows the order $3^\circ > 2^\circ > 1^\circ$.

E₁ orientation.

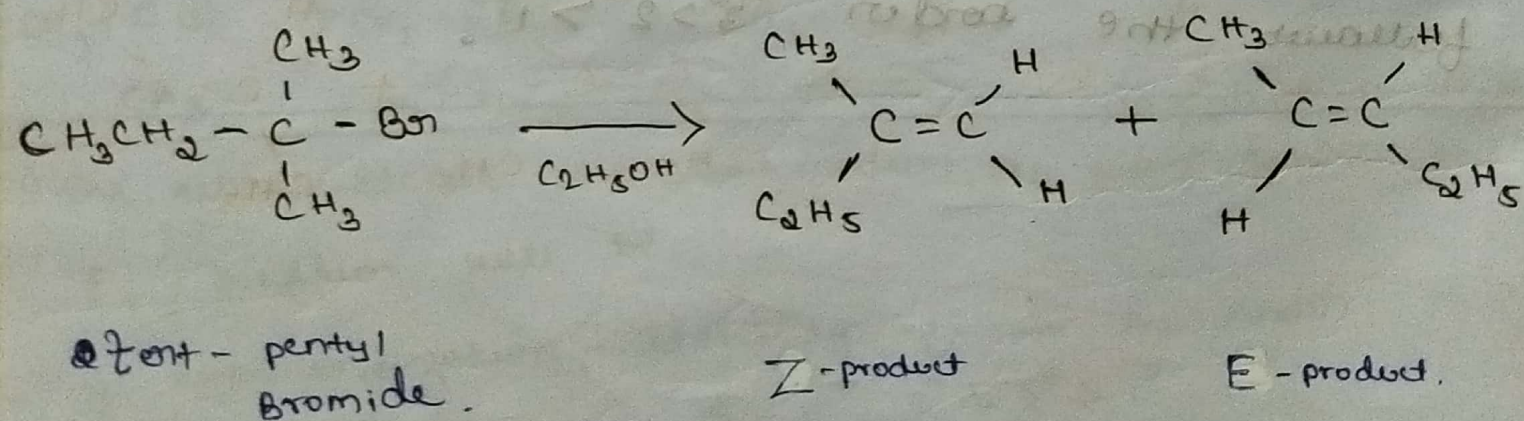
E₁ shows strong Saytzeff orientation when more than one alkene is formed, highly branched & more stable alkene is preferred product



Stereochemistry

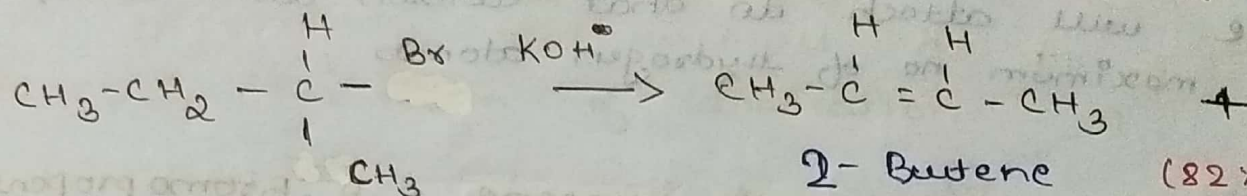
① with carbocation both syn and anti elimination occurs, so E₁ forms both E & Z product

[regardless of no of H atoms on β-carbon]
 ② product stability leads to stereoselectivity but not stereospecificity.]



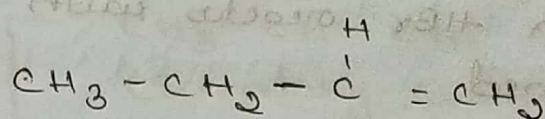
E₂ orientation: (Ex for Saytzeff Elimination)

sec-butyl bromide, on Attack by base at any β-hydrogen can lead to the formation of 1-butene & 2-butene. Among both 2-butene is the preferred product, follows Saytzeff rule.



2-Butene (82%)

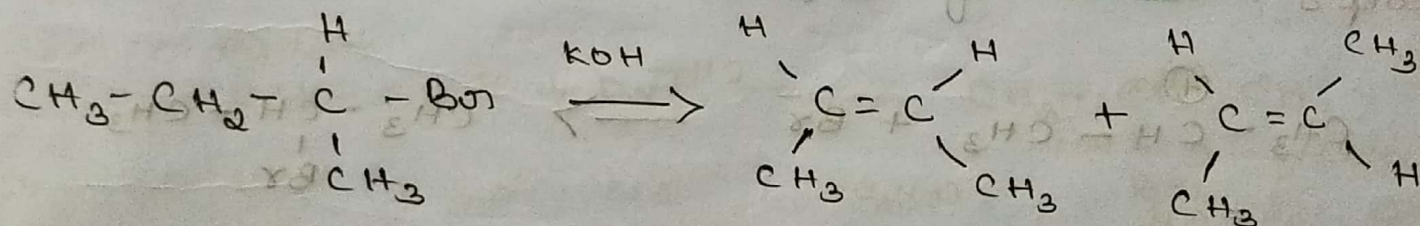
sec-butyl bromide



1-Butene (18%)

Stereochemistry.

① E₂ reaction is stereoselective but not stereospecific if 2 βH's are available on β-carbon



sec-butyl bromide.

Z-2-Butene

E-2-Butene

(82%)

(18%)

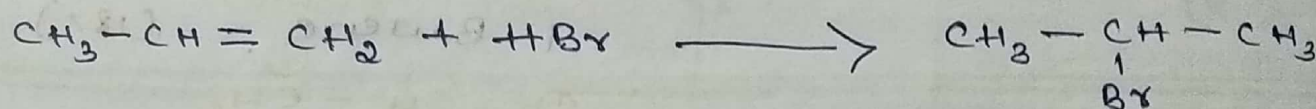
③ Explain Markovnikov's and Anti-Markovnikov's addition with examples.

① Markovnikov's rule

When an unsymmetrical molecule is added to an unsymmetrical alkene, the positive part of the molecule will attach to that carbon atom which contains maximum no. of hydrogen atoms.

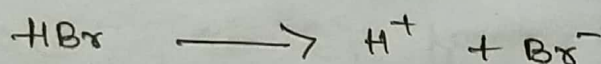
Example:

When HBr reacts with propene, 2-Bromopropane is formed.



Mechanism

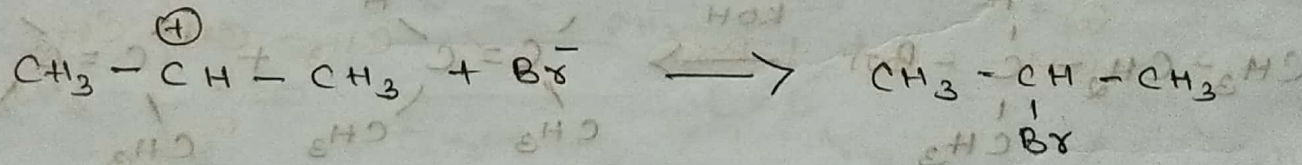
Step 1: Ionization of HBr



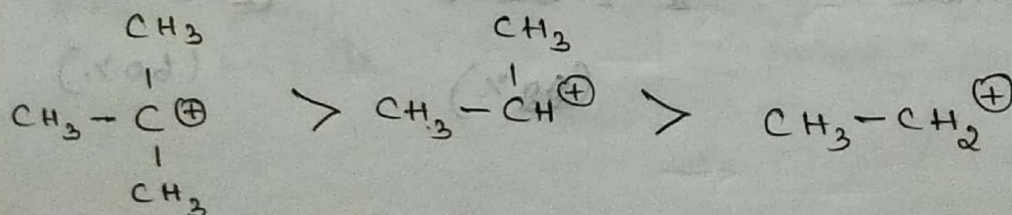
Step 2: Formation of carbocation



Step 3: Attack of Bromide ion on carbocation



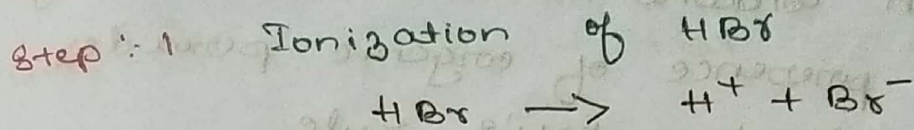
Reactivity



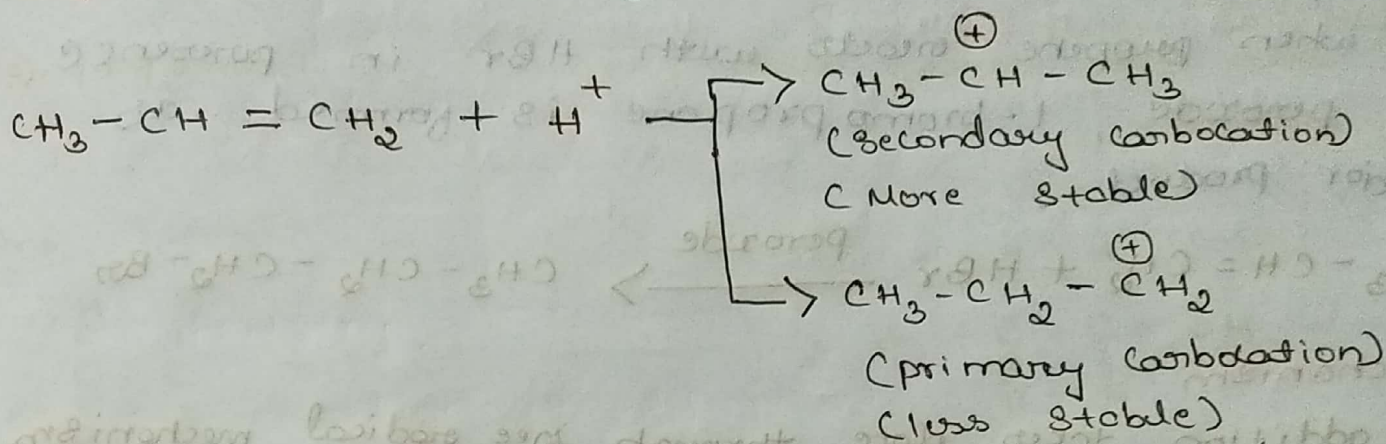
① The more stable the carbocation, the more faster the reaction will be.

② By hyperconjugation stability follows the order $3^\circ > 2^\circ > 1^\circ$

Orientation

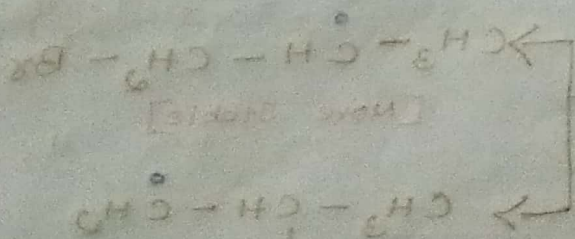
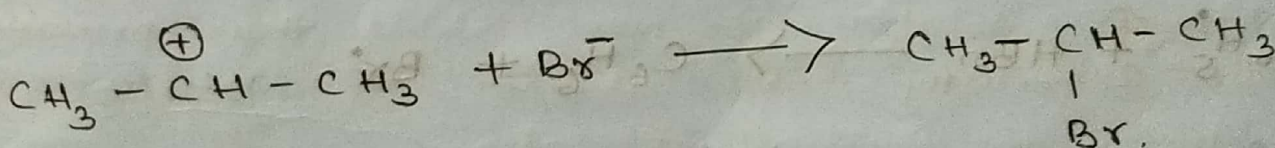


Step: 2 Formation of carbocation



Secondary carbocation is more stable than primary carbocation. Hence secondary carbocation is formed in preference to primary carbocation.

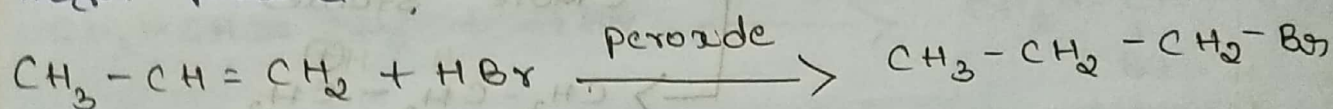
Step: 3 Attack of Bromide ion on carbocation forming final product 2-bromopropene



② Antimarkownikoff's Addition [peroxide effect]
 when an unsymmetrical molecule is added to unsymmetrical alkene, the positive part of the molecule will attach to the carbon atom which contains minimum number of H-atoms, in the presence of organic peroxides, which is opp to Markownikoff's rule.

Example:

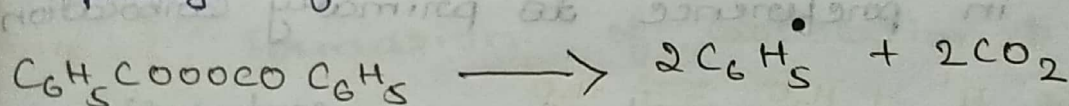
when propene reacts with HBr in presence of peroxide, 1-bromopropane is formed as major product.



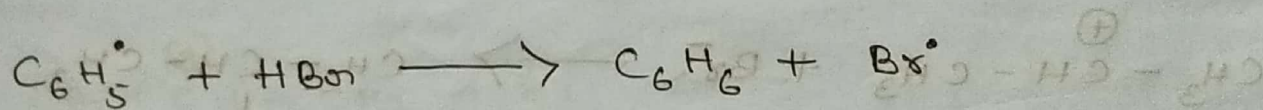
Mechanism

addition takes place through free radical mechanism

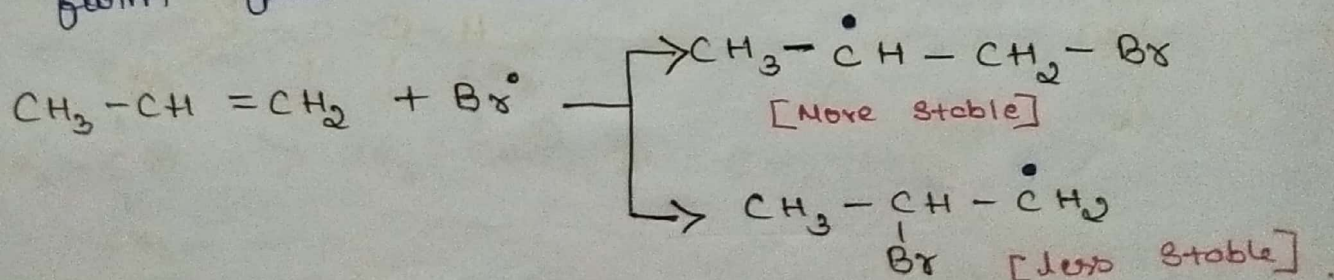
① Decomposition of Benzoyl peroxide to give phenyl free radical



② phenyl free radical abstracts HBr & yield bromine free radical



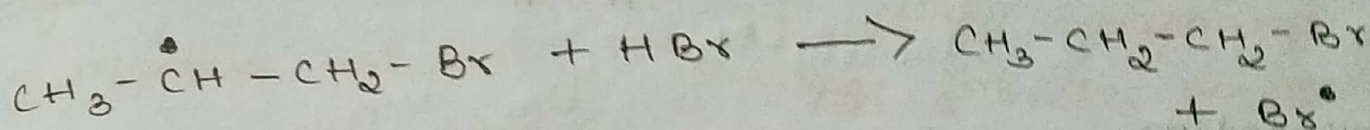
③ Bromine free radical attacks alkene to form free radicals



The Secondary free radical is more stable than primary free radical. Hence secondary free radical

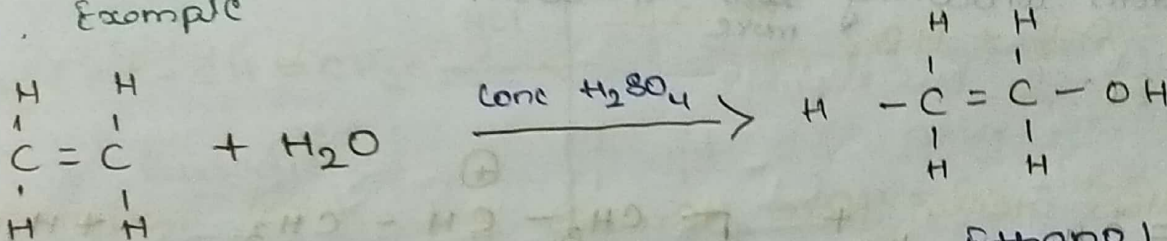
is formed in preference with primary free radical

3④ Secondary free radical attacks another molecule of HBr to form 1-Bromopropane



④ Explain the mechanism & orientation involved in hydration of alkenes

Ans. Example

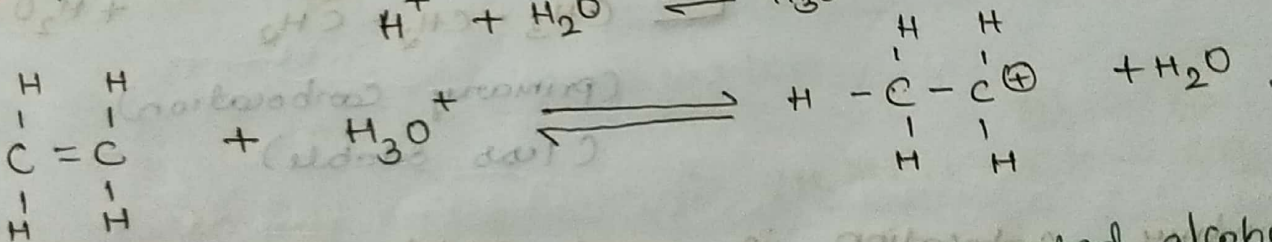


Ethene

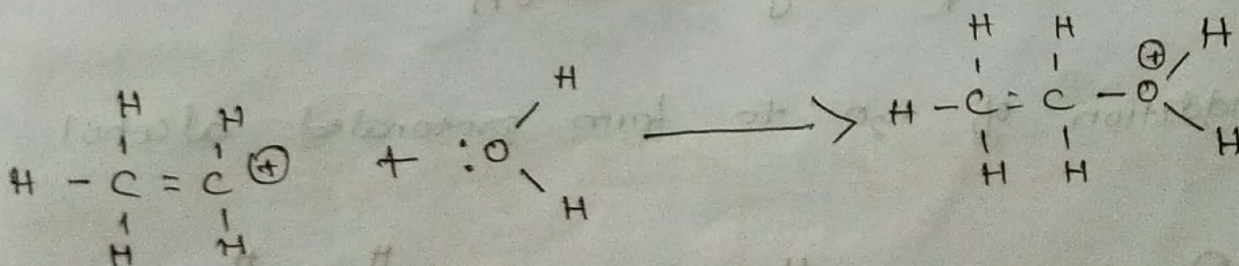
Ethanol

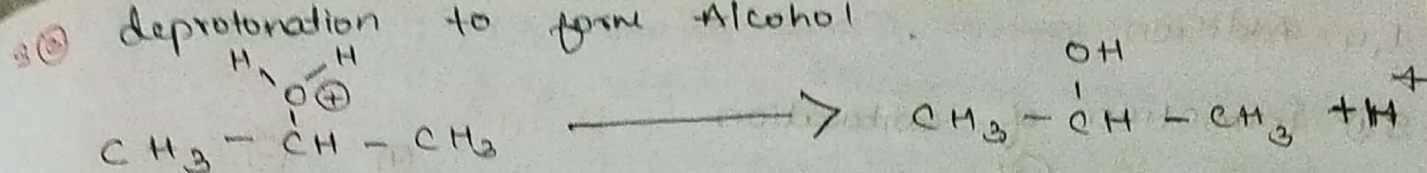
Mechanism

8① protonation of alkene to form carbocation



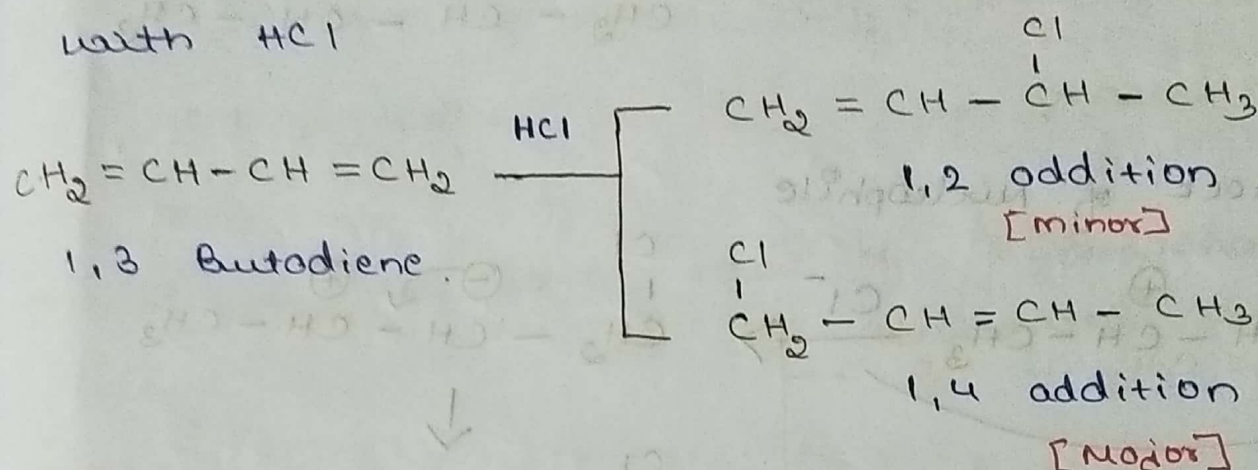
8② Addition of H_2O to form protonated alcohol





5. Explain 1,2 and 1,4 addition in conjugated dienes with mechanism. Add a note on effect of temperature.

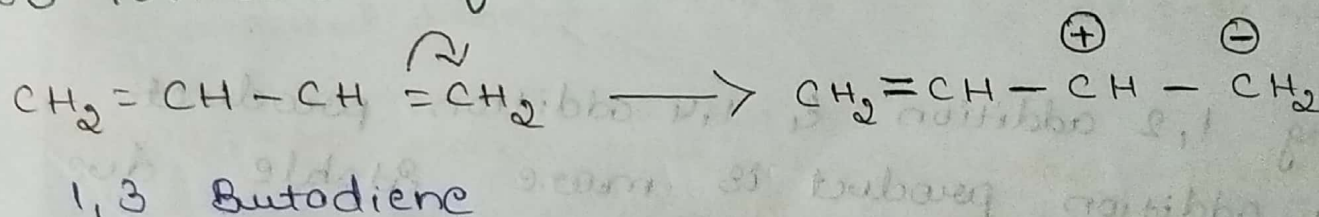
Ans: Let us consider reaction of 1,3-Butadiene with HCl



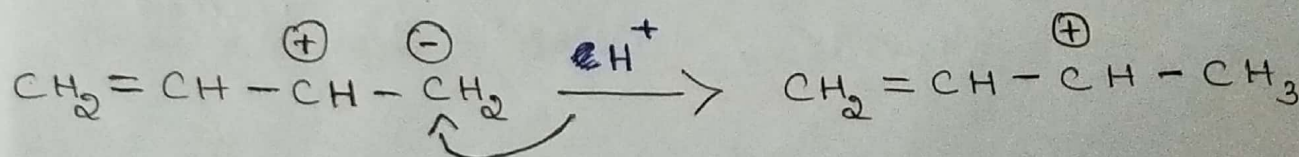
Mechanism

1,2 addition

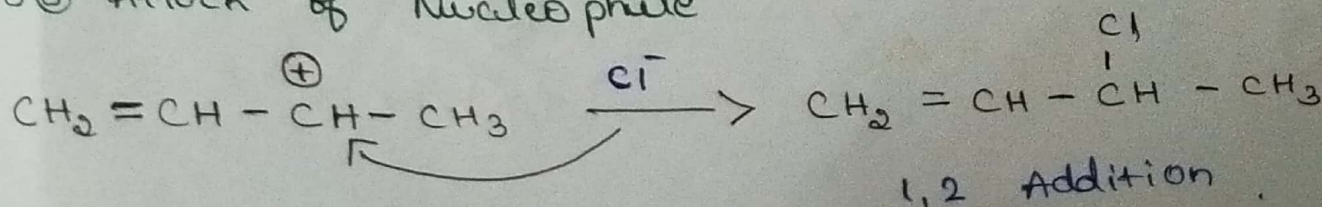
3① Formation of Carbocation



3② Attack of Electrophile

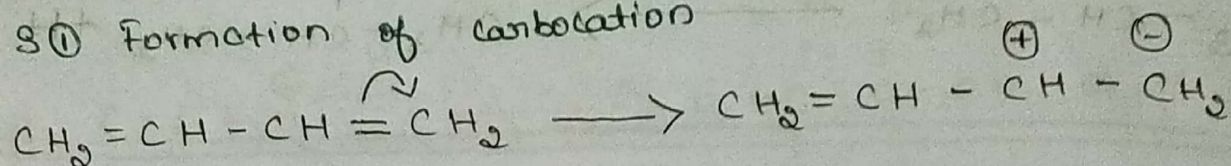


3③ Attack of Nucleophile

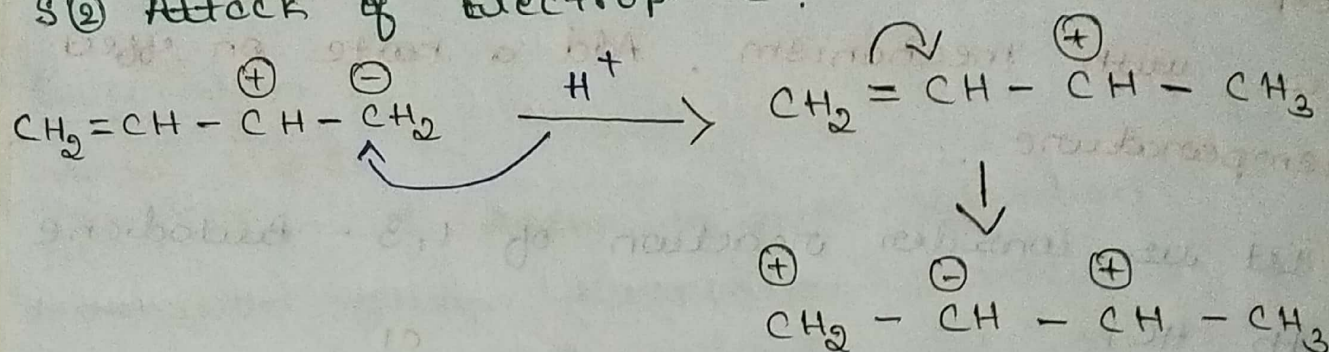


1,4 Addition

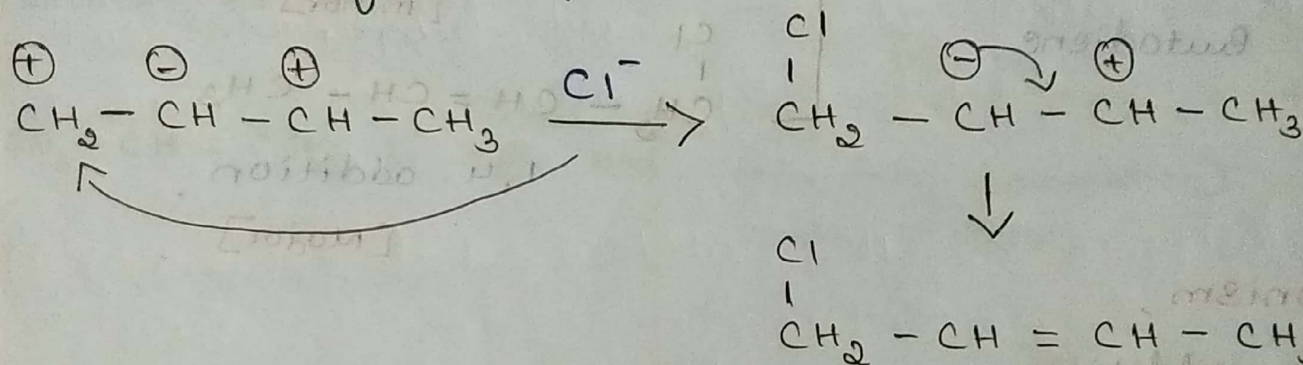
S① Formation of Conjugation



S② Attack of Electrophile



S③ Attack of Nucleophile



1,4 addition

Among 1,2 addition & 1,4 addition product, 1,4 addition product is more stable due to hyperconjugation

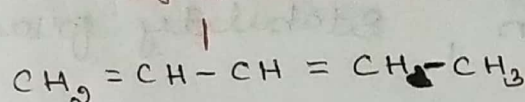
⑥ Explain why 1,3-pentadiene is more stable than 1,4-pentadiene?

① Conjugated dienes are more stable than isolated dienes because

An sp^2-sp^2 single bond is stronger than

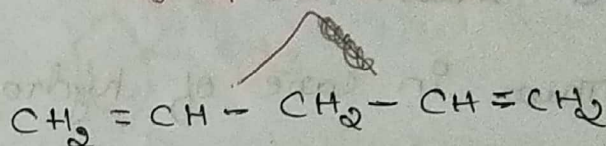
sp^3-sp^2 single bond

single bond formed
by sp^2-sp^2 overlap



1,3 pentadiene

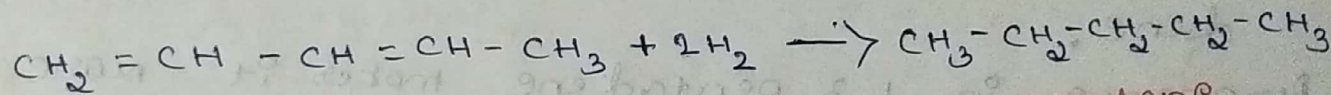
single bonds formed
by sp^3-sp^2 overlap



1,4 pentadiene

② Let us consider heat of hydrogenation of conjugated and non-conjugated dienes.

i)



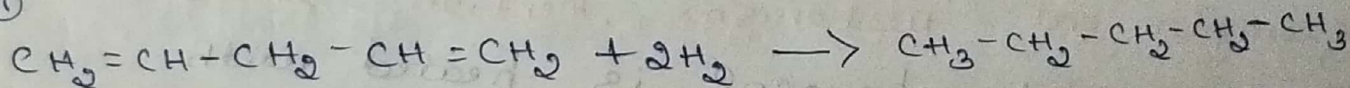
1,3 pentadiene

n-pentane

(conjugated diene)

$$\Delta H = -54 \text{ kcal/mol}$$

ii)

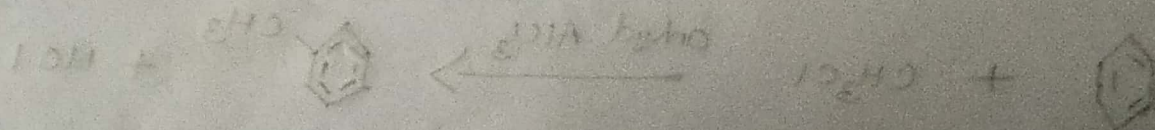


1,4 pentadiene

n-pentane

(non conjugated diene)

$$\Delta H = -61 \text{ kcal/mol}$$



- ① Both reaction (i) & (ii) consumes 2 moles of hydrogen to yield same product n-pentane
- ② But reaction (i) releases lesser energy than reaction (ii)
- ③ This is because 1,3 pentadiene which is conjugated diene contains less energy and thus more stable than 1,4-pentadiene
- ④ Thus in case of hydrogenation, stability follows the order

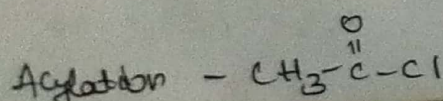
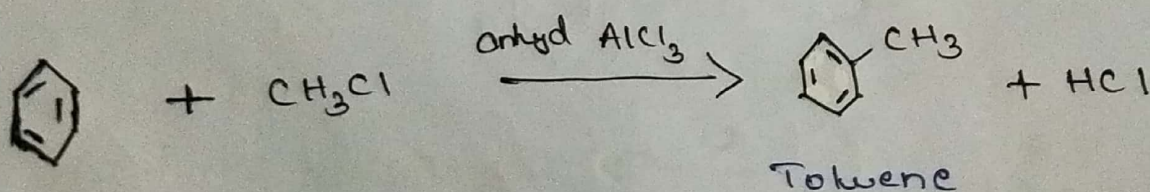
conjugated dienes > non-conjugated dienes

Thus conjugated dienes reacts faster with hydrogen than non-conjugated dienes

- ⑤ Resonance also stabilizes the conjugated diene.

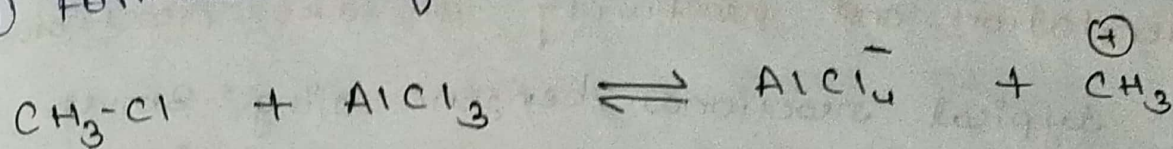
Resonance in 1,3 pentadiene makes it more stable than 1,4 pentadiene

- ⑦ Discuss Friedel Crafts alkylation with examples and mechanisms, mention limitations
- Ans when benzene is heated with methyl chloride in presence of anhydrous aluminium chloride Toluene is formed.

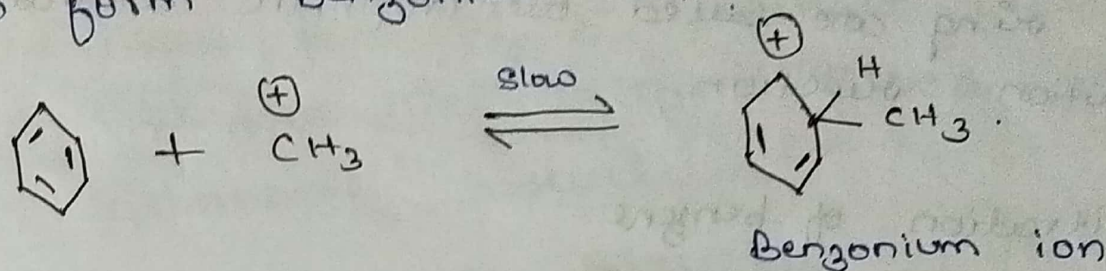


Mechanism.

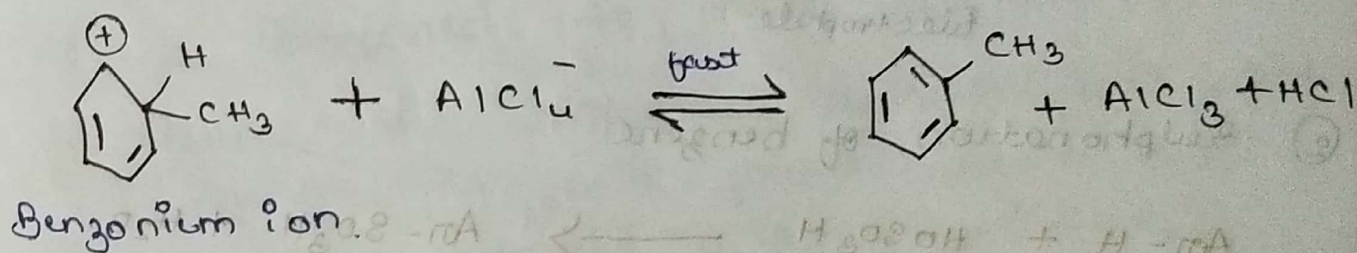
① Formation of carbocation.



② Attack of carbocation on benzene ring to form benzonium ion.



③ Deprotonation of Benzonium ion.



Limitations

① The halide must be alkyl halide, vinyl and aryl halides do not react.

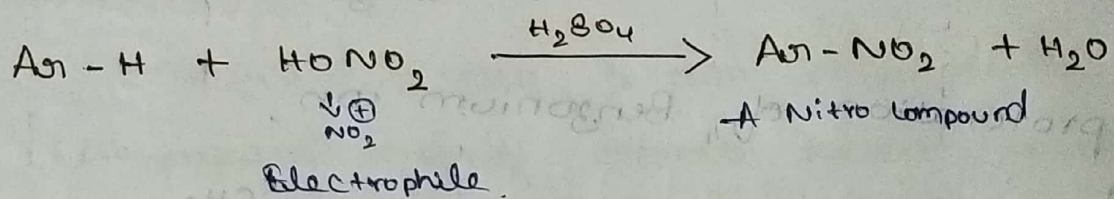
② Deactivated benzenes are not reactive to Friedel-Crafts condition

③ presence of meta-directing group in the aromatic ring hinders friedel-craft's alkylation. Reason: meta-directing group being deactivating group lowers electron density. Thus nitrobenzene does not react to friedelcraft alkylation.

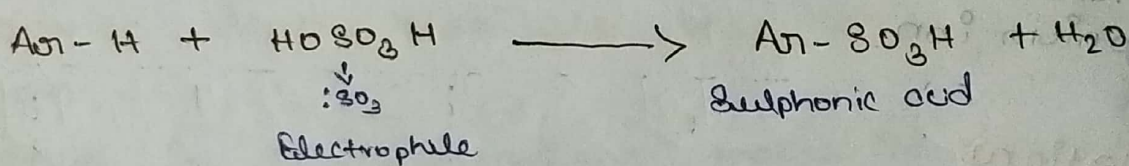
⑧ what are electrophilic aromatic substitution reaction ? Explain the effect of substituents on orientation and reactivity in these reactions

Ans: In typical reactions benzene ring serves as source of electrons, i.e. as a base. Hence the reaction b/w Electrophilic acids and benzene ring are called Electrophilic aromatic Substitution reaction.

Eg: ① Nitration of benzene

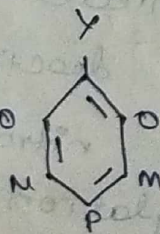


② Sulphonation of benzene



Determination of orientation

① In case of substituted benzene 6 positions are available to attack by electrophile i.e. 2 ortho, 2 meta and 1 para.



Y → Substituent

- ① The orientation can be explained using Resonance theory
- ② The electron donating group attached to the benzene ring contains a lone pair of e^-
- ③ The lone pair of e^- interact with πe^- of the benzene ring. This gives rise to resonance structures
- ④ In the resonance structures, the ortho and para positions contain more e^- density compared to meta position.
- ⑤ Therefore the Incoming Substituent, which is an electrophile, will prefer ortho and para positions compared to meta position. Hence ortho-para product is formed.
- ⑥ In presence of e^- withdrawing group, the meta positions contain relatively high e^- density compared to ortho & para position
- ⑦ Therefore Incoming Substituent which is an electrophile will prefer meta position compared to the ortho-para position.

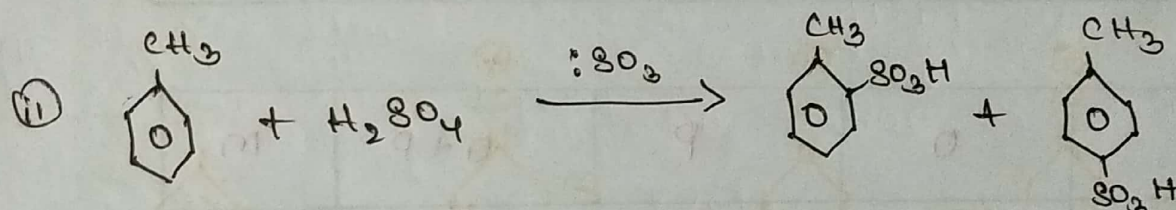
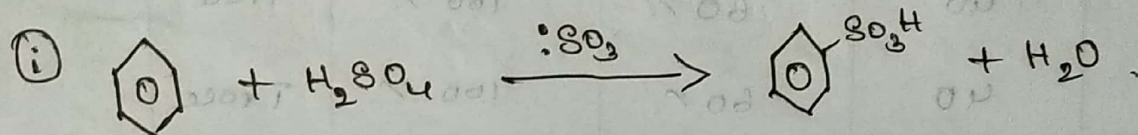
③ If δ^- withdrawing groups like $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{CHO}$, $-\text{SO}_3\text{H}$ electrophile substitution takes place at meta position.

Relative reactivity.

① A group is said to be activating group if it is more reactive than benzene.

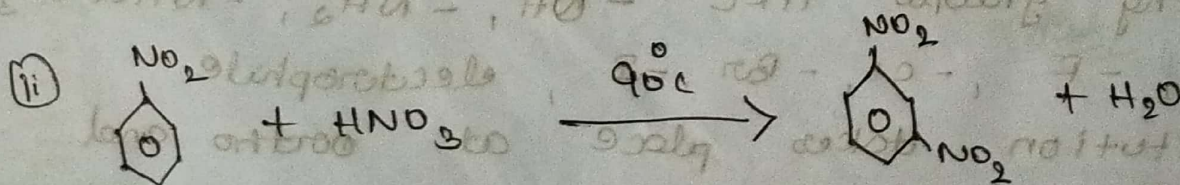
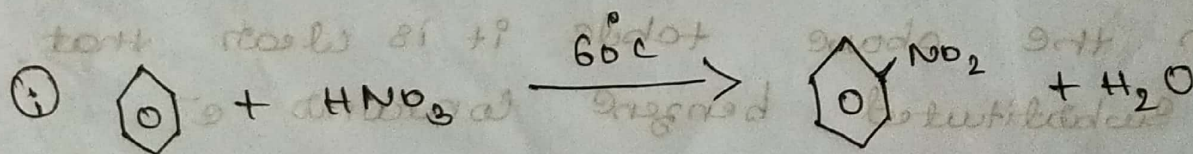
② Relative reactivity of benzene and substituted benzene can be found by time and condition required for the reaction.

③ Let us consider Sulphonation of Benzene and Toluene under same condition.



(ii) reaction requires $\frac{1}{10}$ less time compared to (i). Thus methyl group is activating group.

④ Let us consider Nitration of Benzene and Nitrobenzene.



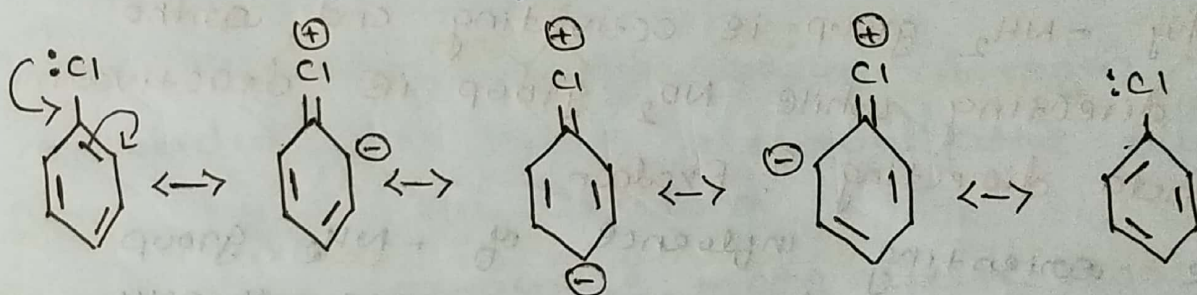
(ii) reaction requires more temp compared to reaction (i), This means Nitro benzene is relatively less reactive than benzene towards Nitration.

(9) why chloro group is deactivating yet ortho-para directing? Explain

(1) The orienting influence of -Cl group can be explained using resonance theory.

(2) The Cl atom attached to the benzene ring contains a lone pair of electrons

(3) This lone pair of electrons interact with π electrons of the benzene ring. This give rise to following resonance structures.



(4) In the above steps, ortho and para positions contain more electron density compared to the meta position

(5) Therefore the incoming substituent, which is an electrophile, will prefer ortho-para position compared to meta position. Hence ortho-para product is formed.

(6) Therefore chlorine acts as ortho-para directing group

⑦ on the contrary it acts as a ring deactivator. This is because of the high electronegativity of the chlorine atom.

⑧ Since the chlorine atom is highly electronegative it withdraws the π electrons of the benzene ring resulting in the decrease in the electron density of the benzene ring (Inductive effect).

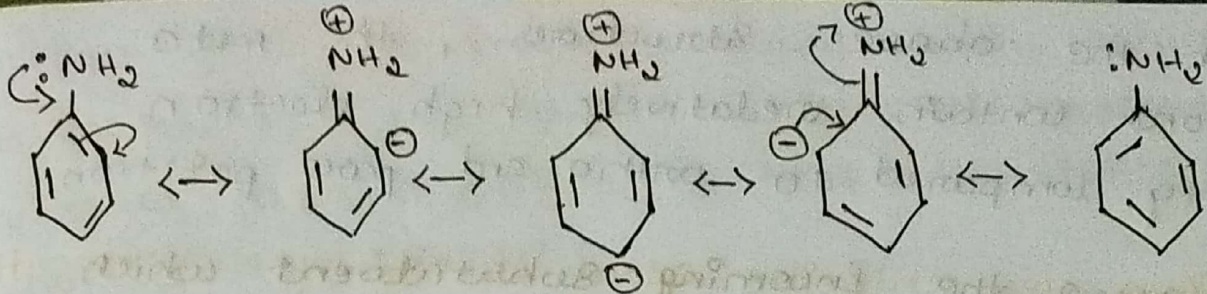
⑨ out of these two effects, electron donating (mesomeric effect) and electron withdrawing (inductive) electron withdrawing nature predominates. Hence $-Cl$ acts as ring deactivator.

⑩ why $-NH_2$ group is activating and ortho-para directing while $-NO_2$ group is deactivating and meta directing. 9. Explain.

① The orienting influence of $-NH_2$ group can be explained using resonance theory.

② The $-NH_2$ attached to the benzene ring contains a lone pair of electrons.

③ This lone pair of electrons interact with π electron of the benzene ring. This gives rise to following resonance structures.



④ In the above structures, the ortho and para positions contain more electron density compared to the meta position.

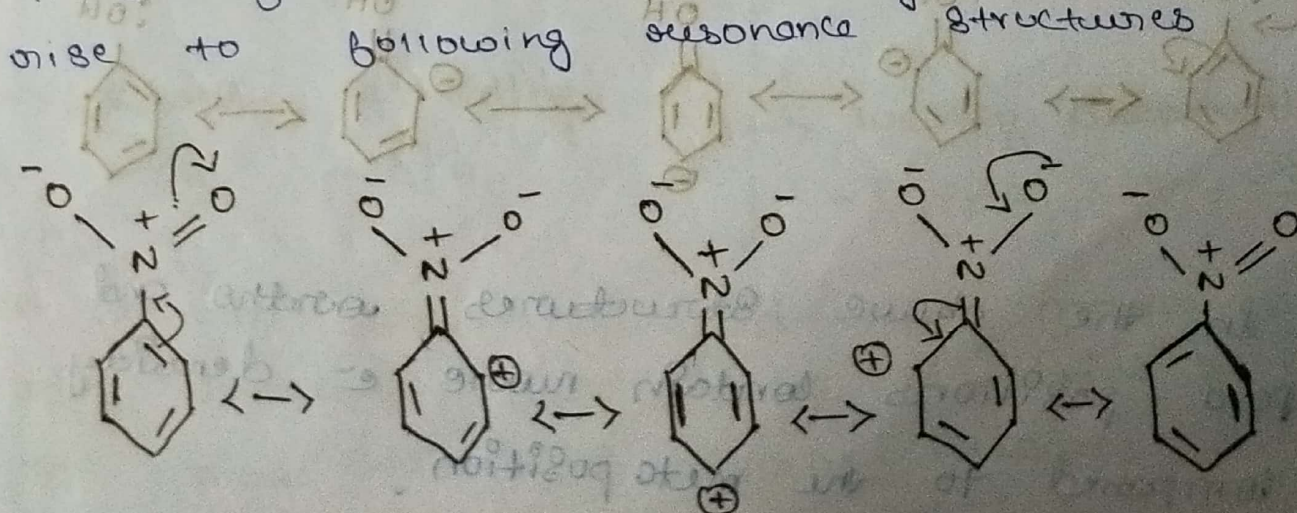
⑤ Therefore the incoming substituents, which is an electrophile, will prefer ortho and para position compared to meta position. Hence ortho - para product is formed.

⑥ Therefore $-NH_2$ acts as ortho - para directing group.

① The key atom of the $-NO_2$ is nitrogen. It is bonded to more electronegative oxygen atom by a double bond.

② Since the oxygen is more electronegative than nitrogen, bonded e^- are pulled towards oxygen. In turn Nitrogen alone pulls the

πe^- from the benzene ring. This gives rise to the following resonance structures.



③ In the above structures, the meta positions contain relatively high electron density compared to ortho and para position.

④ Therefore the incoming substituent which is an electrophile will prefer meta position compared to the ortho-para position.

⑤ Therefore NO_2 acts as deactivating and meta directing group.

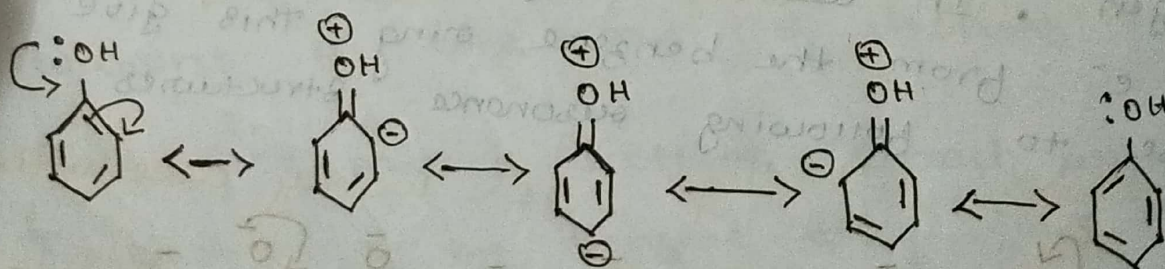
⑩ Discuss orientation & reactivity of hydroxyl group in benzene.

Ans:

① The orienting influence of $-\text{OH}$ group can be explained using resonance energy.

② The $-\text{OH}$ atom attached to benzene ring contains a lone pair of electrons.

③ This lone pair of e^- interact with πe^- of benzene ring. This give rise to following resonance structures.



④ In the above structures, ortho and para positions contain more e^- density compared to the meta position.

⑤ Therefore the Incoming Substituent, which is an electrophile, will prefer ortho-para position compared to meta position. Hence ortho-para product is formed.

⑥ Therefore $-OH$ acts as ortho-para directing group.

⑪ Classify substituent group based on orientation & reactivity?

Substituents

Activating

- ① Electron donating grp
- ② ortho-para directing

→ Strongly activating.
 $-NH_2$, $-OH$

→ Moderately activating.
 $-NHCOCH_3$, $-OCH_3$

→ weakly activating
 $-CH_3$, $-C_2H_5$

Deactivating

- ① Electron withdrawing group
- ② meta directing.

→ Strongly Deactivating
 $-NO_2$, $-CF_3$

→ Moderately Deactivating
 $-CN$, $-COOH$, $-CHO$

→ weakly deactivating
 $-F$, $-Cl$, $-Br$, $-I$

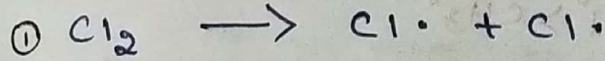
In general ortho para directing groups are ring activators and meta directing groups are ring deactivator except halogens.

5 mark important concepts

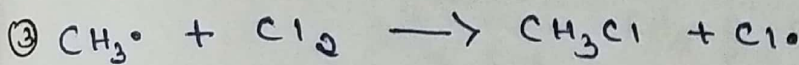
① describe chlorination of methane with mechanism and energy graph / free radical halogenation

Ans: The chlorination of methane is an example of chain reaction, a reaction that involves a series of steps, where each step generates reactive substances.

① chain - Initiating Step

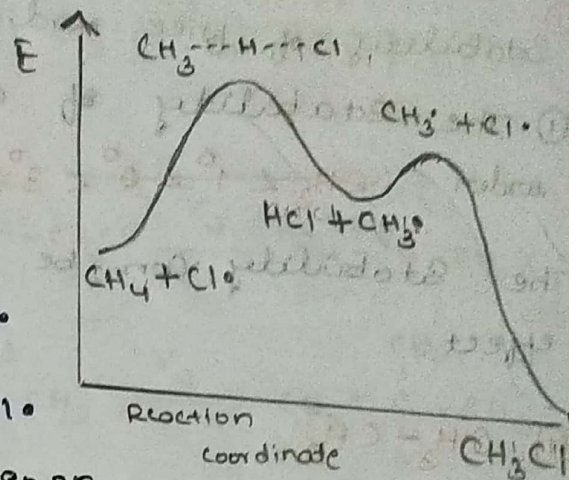
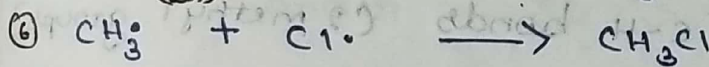
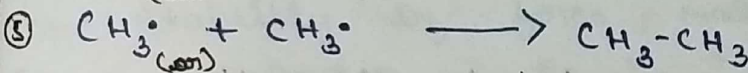
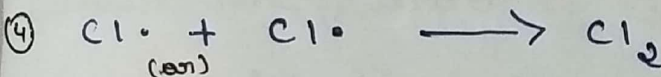


② chain - propagating step



then (2), (3), (2), (3), etc, so on

③ chain - terminating step



① chain Initiating step: Halogen undergoes homolysis in presence of UV light to produce halide free radical.

② chain propagating step: ① In first step of chain propagation halide free radical reacts with alkane molecule to form a alkyl free radical

② alkyl free radical reacts with Halogen to form Alkyl halide and halide free radical.

③ chain-terminating step: In this step two similar or a different free radical will react together to form a stable molecule

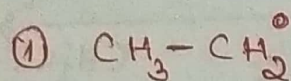
① what is free radical & classify and give order of stability & relative reactivity

Ans. Free radical are species carrying an unpaired e^-

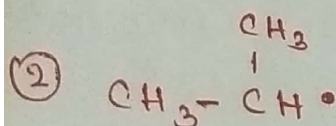
① Stability of free radical.

① The stability of alkyl free radical is in the order $\text{CH}_3 < 1^\circ < 2^\circ < 3^\circ > 2^\circ > 1^\circ > \text{CH}_3^\bullet$

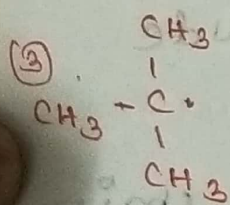
The stability can be explained using hyperconjugative effect.



1° free radical has 3 C-H bonds (3 CH_3 groups) involved in hyperconjugation to stabilize it.



2° free radical has 6 C-H bonds (2 methyl groups) involved in hyperconjugation to stabilize it.

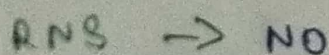
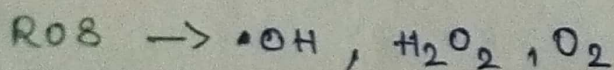


3° free radical has 9 C-H bonds (3 methyl groups) involved in hyperconjugation to stabilize it.

Hence maximum stabilization occurs in 3° free radical.

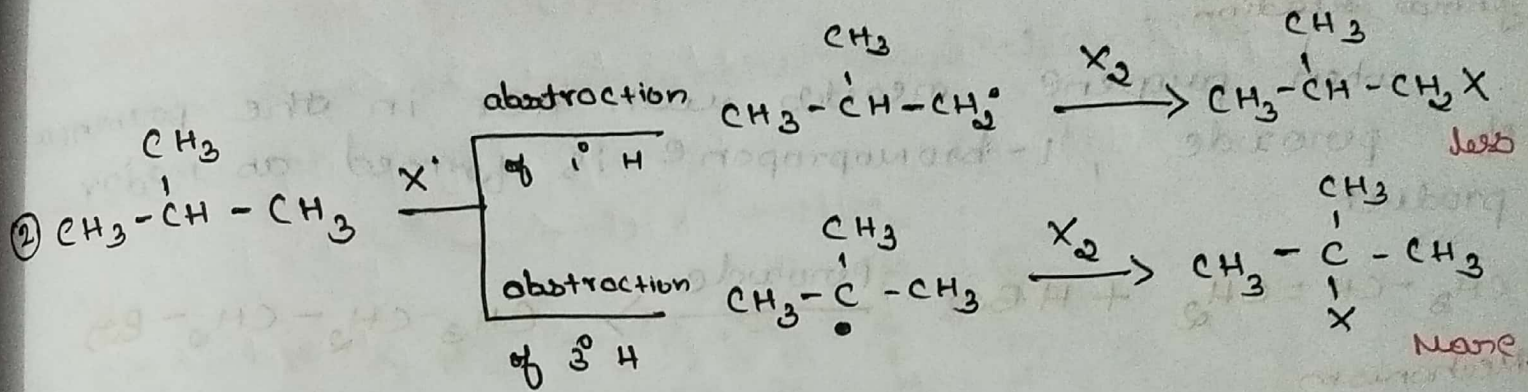
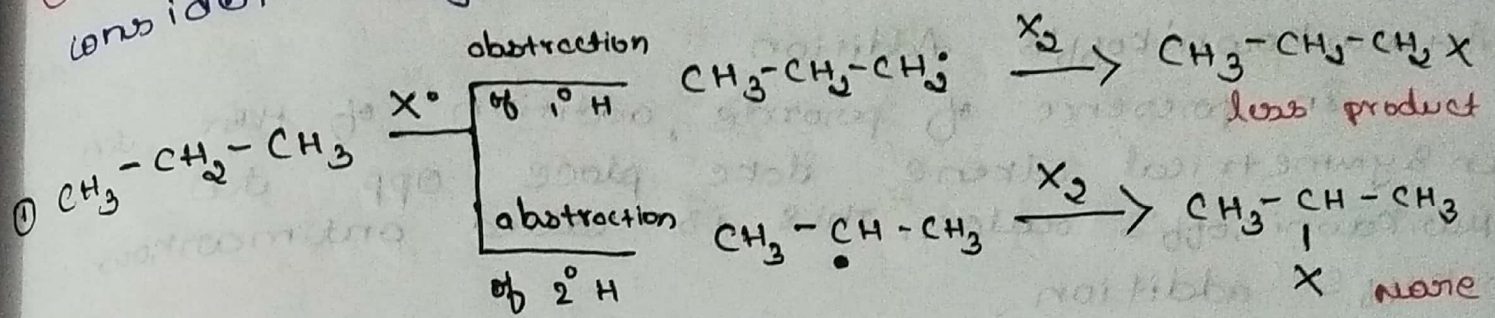
② Classification of free radical

Free radical can be classified as Reactive oxygen Species (ROS) and Reactive nitrogen Species (RNS)



③ Reactivity of free radical

consider halogenation reactions



- The rate of abstraction of hydrogen atom follows the order $3^\circ > 2^\circ > 1^\circ > \text{CH}_4$
- The stability of free radical follows the order $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^\bullet$
- The more stable the free radical the more easily it is formed
- Thus product formation of alkyl halides follows the order $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{X}$

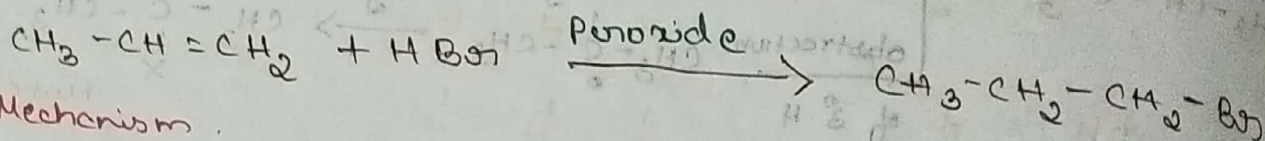
③ Explain the mechanism of free radical addition reaction with suitable examples.

Antimarkownikoff's Addition

In presence of peroxide, addition of HBr to unsymmetrical alkene take place opp to Markownikoff's rule. This is called antimarkownikoff's addition.

General reaction.

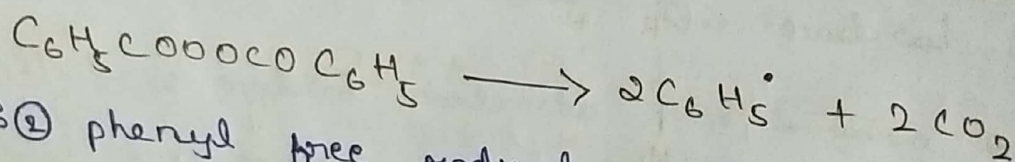
when propene reacts with HBr in the presence of peroxide, 1-bromopropane is formed as major product.



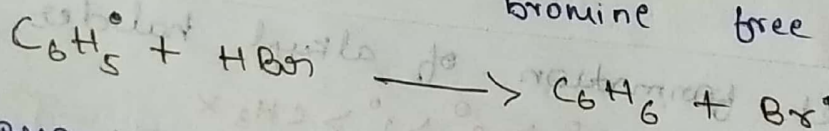
Mechanism.

addition takes place through free radical mechanism.

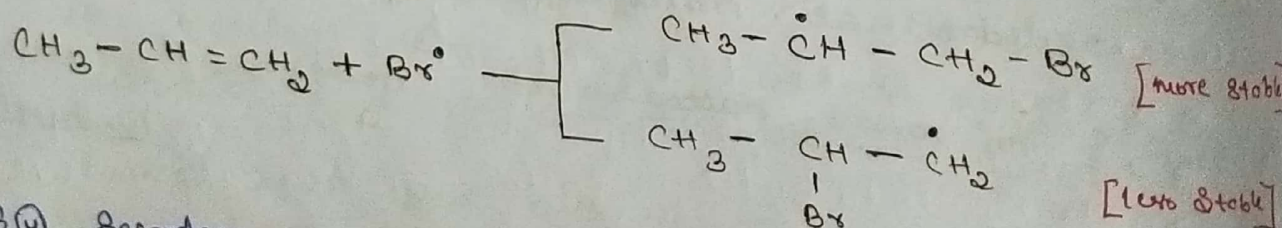
①. Decomposition of Benzoyl peroxide to give phenyl free radical



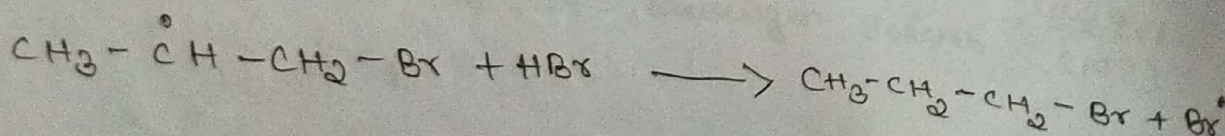
② phenyl free radical abstracts HBr & yield bromine free radical



③ Bromine free radical attacks alkene to form free radicals

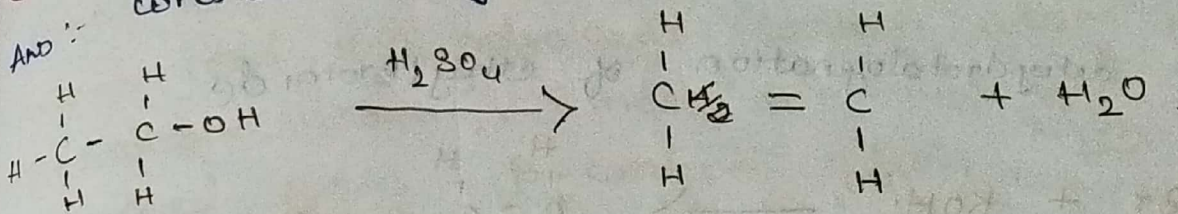


④ Secondary free radicals attacks another molecule of HBr to form 1-bromopropane



Describe mechanism of dehydration of alcohol.

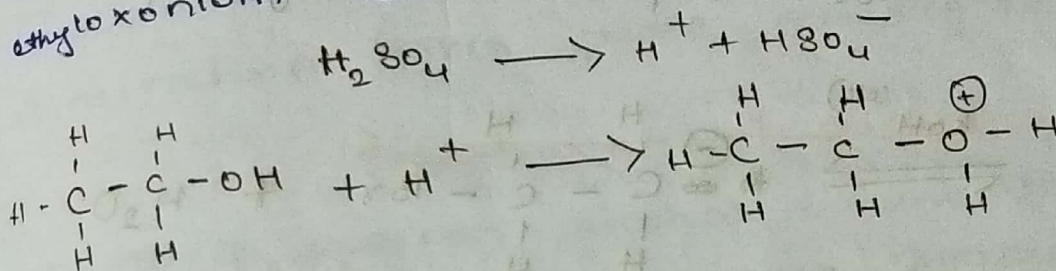
(u) consider dehydration of ethyl alcohol



mechanism

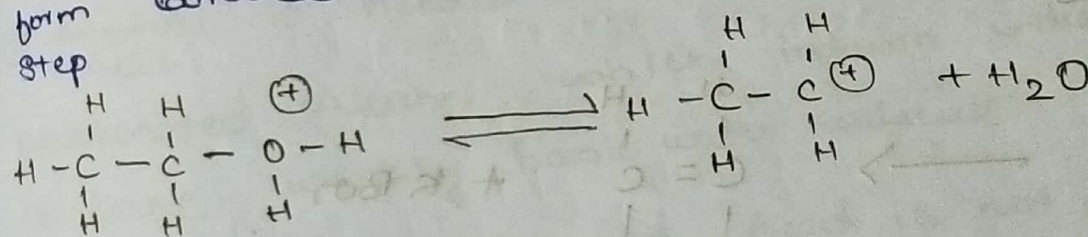
8① Protonation of alcohol

Concentrated H_2SO_4 protonates ethyl alcohol to form ethyloxonium ion



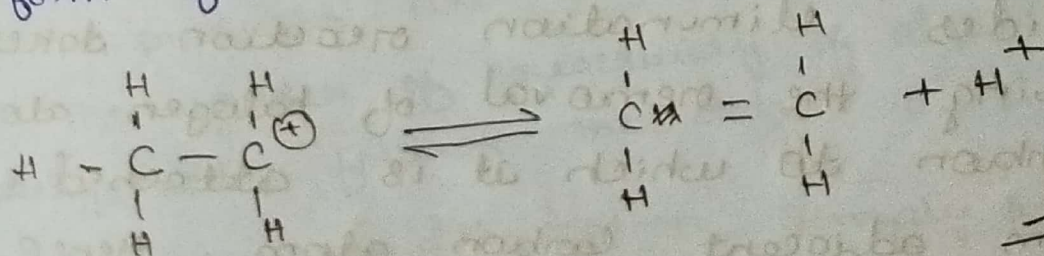
8② Formation of carbocation

The oxonium ion formed loses water molecule to form carbocation. This is slowest step & rate determining step



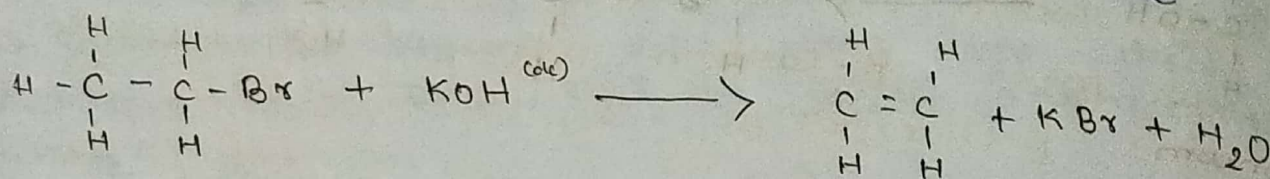
8③ Elimination of proton

The carbocation formed loses a proton to form final product ethene



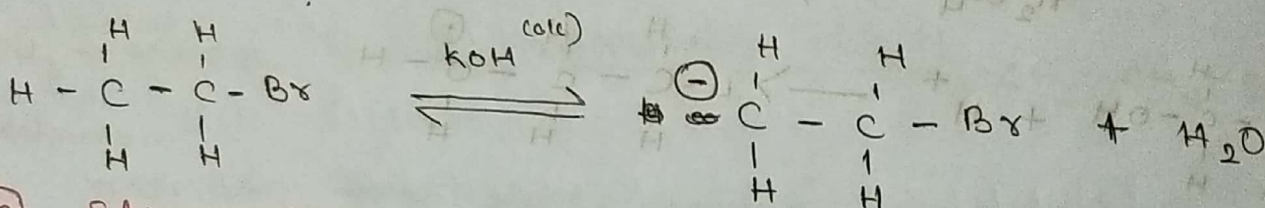
⑤ Describe Dehydrohalogenation of Alkyl Halide.

Sol: Consider dehydrohalogenation of ethyl bromide



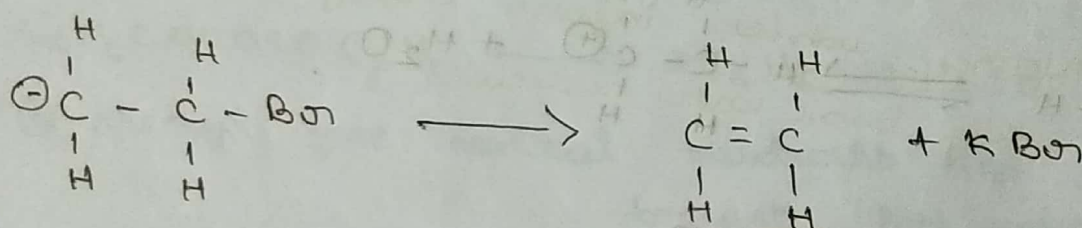
8① Formation of carbanion Follow E₂

The substrate loses a proton to form carbanion



8② Elimination of halogen

8② The carbanion loses halide ion to yield alkene



① These are the reaction that involve removal of groups from a substrate molecule

② In alkyl halides elimination reaction takes place involving the removal of halogen atom from the carbon to which it is attached & hydrogen from adjacent carbon atom, hence this process is called dehydrohalogenation

③. During dehydrohalogenation, if isomeric alkenes results, then alkene with maximum no of alkyl groups attached to carbon atom containing double bond will be the major product.

④ In alkyl halides the carbon atom containing halogen atom is called α carbon atom, and the adjacent carbon atom is called β -carbon atom. Since the hydrogen is removed from β -carbon atom, the reaction is called β -elimination.

⑤ Here when alkyl halide heated with alcoholic potash alkenes are formed. This type of reaction is called elimination reaction. The elimination takes place according to Saytzeff's rule.

⑥ Note on dehydration of alcohols?

- ① In this process, alcohol is converted into alkene by dehydration. It requires presence of acid & the application of heat.
- ② Alcohol is needed to convert the alcohol into the protonated Alcohol, which then undergo heterolysis to lose weakly basic water molecule.
- ③ It being acid catalysed, Acid is not consumed. It is regenerated in Step ③.
- ④ Each step of dehydration are reversible. Dehydration products are quite volatile.
- ⑤ The order of reactivity of alcohols towards dehydration follows the order $3^\circ > 2^\circ > 1^\circ$.
- ⑥ Orientation of dehydration strongly follows Saytzeff's rule.

(6) Evidence for E_1 mechanism

- (1) Follows first order kinetics ✓ (1)
- (2) are not accompanied by primary hydrogen isotope effect (2)
- (3) shows same effect of structure on reactivity as S_N1 reaction
- (4) where structure permits, are accompanied by rearrangement (3)

(7) Evidence for E_2 mechanism

- (1) Follows second order kinetics ✓ (1)
- (2) are not accompanied by rearrangements (3)
- (3) show a large hydrogen isotope effect (2)
- (4) are not accompanied by hydrogen exchange
- (5) show a large element effect (4)

S_N2

- ① second order kinetics
- ② order of reactivity of alkyl halide
 $1^\circ > 2^\circ > 3^\circ$
- ③ concentration of nucleophile should be high
- ④ nucleophile should be strong in nature
- ⑤ solvent can be low polarity since ionization is not required
- ⑥ Nucleophile attacks from the side opposite to halogen atom
- ⑦ Inversion of configuration

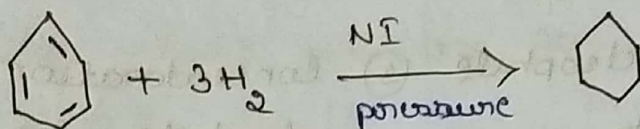
S_N1

- ① Follows first order kinetics
- ② order of reactivity of alkyl halide
 $3^\circ > 2^\circ > 1^\circ$
- ③ concentration of nucleophile can be low
- ④ Nucleophile can be mild in nature
- ⑤ solvent should be high polarity since ionization is required
- ⑥ Nucleophile can attack from both the side
- ⑦ Retention of configuration

⑧ Describe any five methods of preparation of cycloalkanes

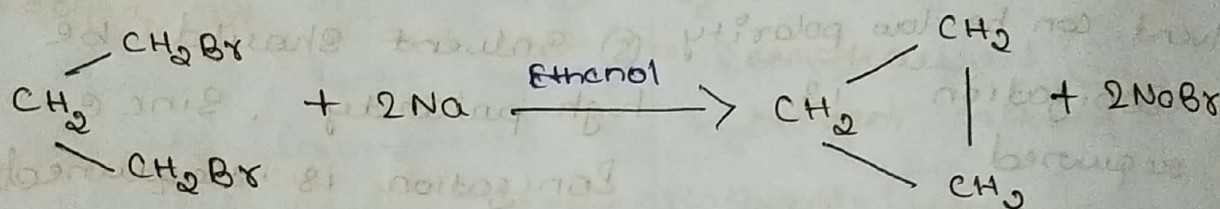
① From Aromatic compounds

Benzene is catalytically hydrogenated at higher temperature and pressure to yield cyclohexane



② From dihalogen compounds

Suitable dihalogen compounds on treating with sodium gives corresponding cyclohexane

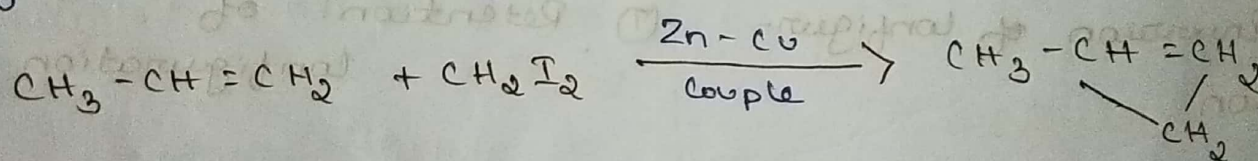


1,3 dibromopropane

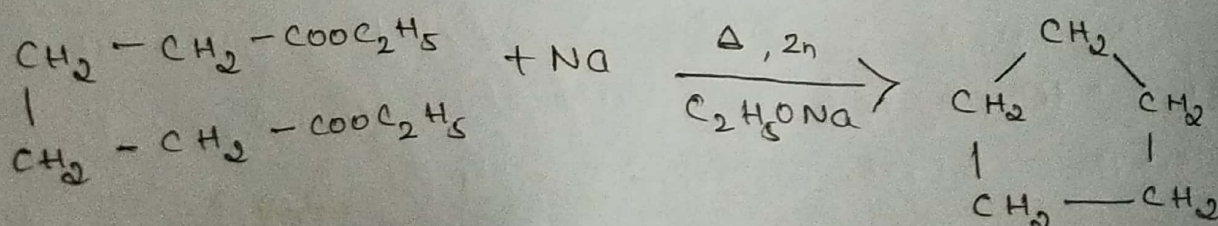
Cyclopropane

③ From Alkenes

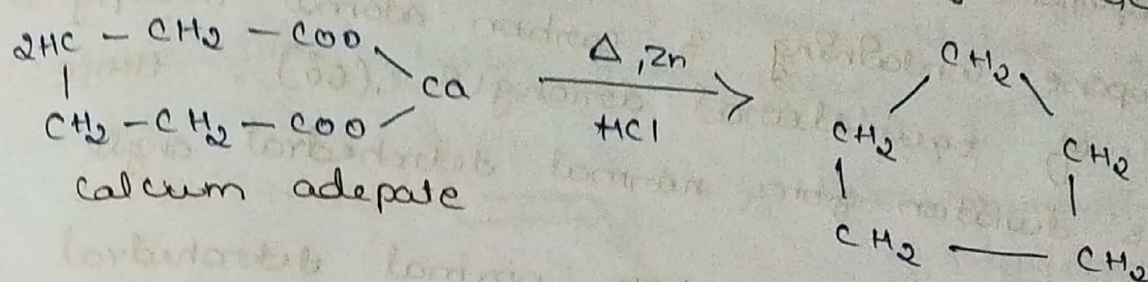
Alkenes on treating with CH_2I_2 in presence of Zn-Cu couple gives cycloalkanes



④ From Esters of Dicarboxylic acid
cyclic ketone on reduction yields corresponding cycloalkane



⑤ From calcium salt of Dicarboxylic acid



Calcium adipate readily converted into corresponding cycloalkane by means of Clemmensen reduction.

⑥ Explain Bayers strain theory and limitations.

Ans: Bayes observed different bond angle for different cycloalkanes. on this basis, he proposed angle strain theory.

ASSUMPTION.

- ① This Theory explains reactivity and stability of cycloalkanes.
- ② He assumed all the carbon atoms in cycloalkanes are planar.
- ③ Any deviation in bond-angle of ring carbon from ideal tetrahedral angle develops strain called bond-angle strain.
- ④ The stability of cycloalkane depends upon bond angle strain. The greater the angle strain, less is its stability.
- ⑤ Bond angle strain is expressed in terms of angle deviation.

$$\text{Angle deviation (d)} = \frac{1}{2} (109^\circ 28' - \text{bond angle})$$

Ex: cyclopropane

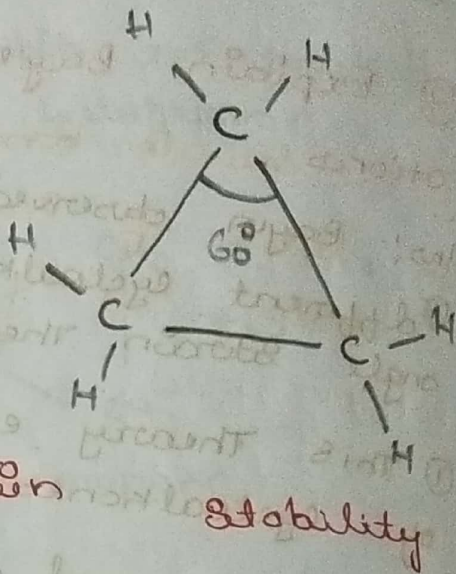
① cyclopropane containing 3 carbon atoms occupy corners of equilateral triangle (60°) . Hence there is deviation from normal tetrahedral angle.

② Bond angle deviation from normal tetrahedral angle produce strain. greater the strain less is its stability.

$$(\text{Angle strain}) \quad d = \frac{1}{2} (109^\circ 28' - 60^\circ)$$

$$= \frac{1}{2} (49^\circ)$$

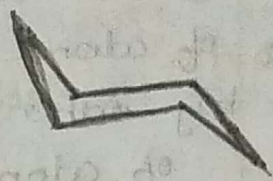
$$= 24^\circ 44'$$



Compound	Bond angle	Angle strain (d)	Stability
Cyclopropane	60°	$24^\circ 44'$	very less stable
Cyclobutane	90°	$9^\circ 44'$	less stable
Cyclopentane	108°	$0^\circ 44'$	stable
Cyclohexane	120°	$-5^\circ 16'$	less stable

Now if we go to higher cycloalkanes with more than 5-C atoms they are not planar structure & hence they have less bond angle strain. Hence they are also stable like cyclopentane. This become limitation for Baeyer's Strain Theory.

cyclohexane is more stable than cyclopentane because it is having more stable chair conformation with bond angle 109° .

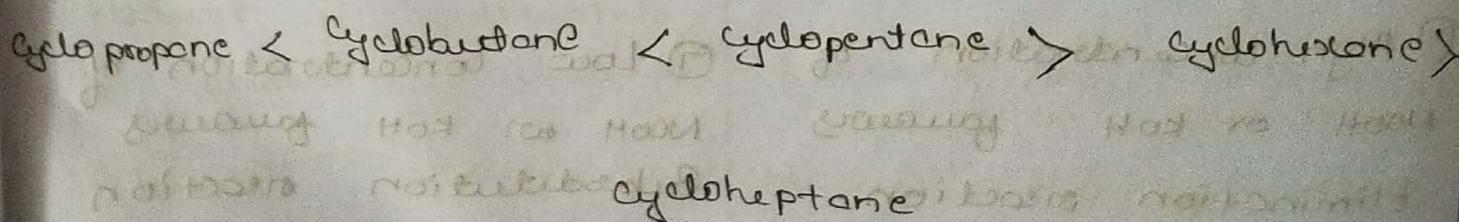


→ chair conformation of cyclohexane.

Limitations.

- ① It explains only relative stability of small ring compounds and fails to explain relative stabilities of higher cycloalkanes.
- ② C-C double bond known to form easily. But on basis of Baeyer's theory it is difficult to form highly reactive compounds.
- ③ Acc to Baeyer's theory heat of combustion should increase with the size. But higher cycloalkanes have negligible heat of combustion which means compounds are stable.
- ④ Acc to Baeyer's strain theory, higher cycloalkanes should be unstable but they are quite stable which is explained by strainless theory.

The stability of cycloalkanes is in the order

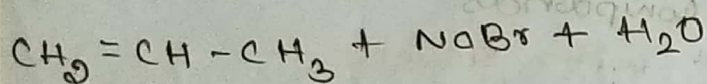
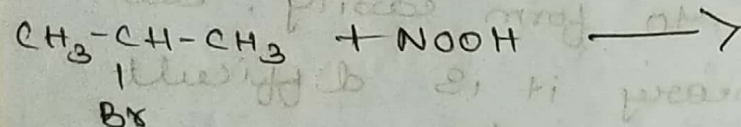


Elimination

① Two atoms are eliminated from the two adjacent carbons to form alkenes

② There is no substitution of atom in Elimination reaction

③ Example of Elimination



④ Tertiary alkyl halide favours Elimination reactions

⑤ Ethanol Encourages Elimination

⑥ Higher Temperature Encourages Elimination reaction

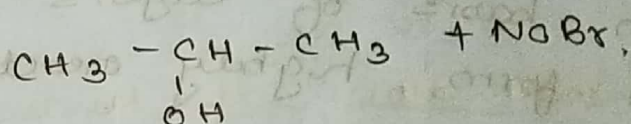
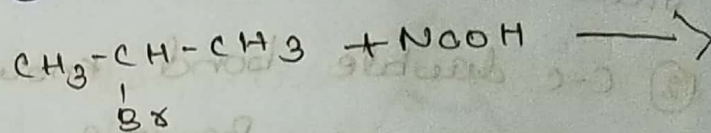
⑦ High concentration of NaOH or KOH favours Elimination reaction

Substitution

① one atom or group of atom is substituted by other atom or group of atoms

② There is no elimination of atom or group of atom

③ Example of Substitution



④ primary alkyl halide favours Substitution reaction

⑤ water Encourages Substitution

⑥ lower temperature Encourages Substitution reaction

⑦ Low concentration of NaOH or KOH favours Substitution reaction

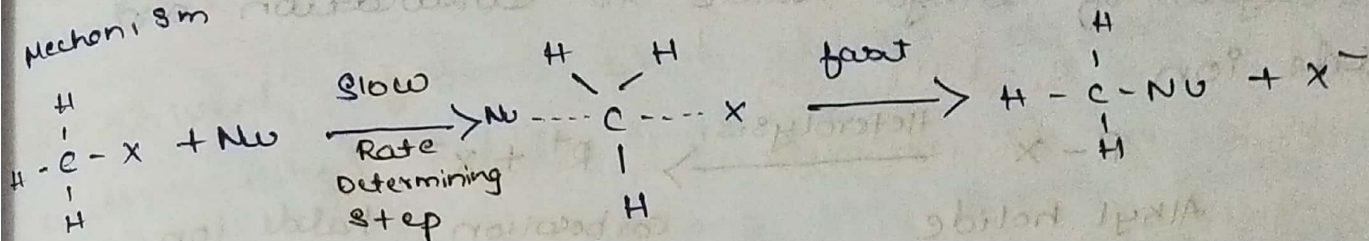
11. Explain effects of Nucleophile in S_N reaction.

① S_N2 Reaction.

① Nucleophile participate in rate determining step

$$\text{rate} = k [RX] [Nu]$$

Mechanism



② Conc of Nucleophile
Higher conc of Nucleophile favours S_N2 Reactions

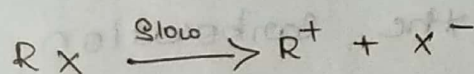
③ Nature of Nucleophile
Stronger Nucleophile favours S_N2 Reaction

④ Interaction of Nucleophile with solvent
Nucleophile is negatively charged. If we use polar solvent, polar solvent forms strong ion-dipole with Nucleophile. Thus lowers rate of reaction

② S_N1 Reaction.

① No effect on rate of reaction

$$\text{rate} = k [RX]$$



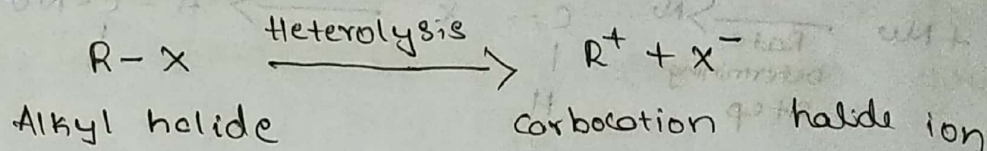
② Conc of Nucleophile
Lower conc of Nucleophile favours S_N1 Reaction

③ Nature of Nucleophile
weaker Nucleophile favours S_N1 Reaction.

12. Explain the Effects of Solvent in S_N Reactions.

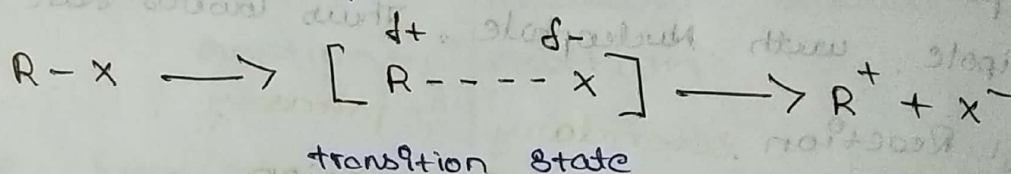
① S_N1 Reaction

① In S_N1 Reaction rate determining step is heterolysis of alkyl halide to carbocation and halide ion.



Since it is a bond breaking step requires more energy. This energy is comes from dipole-dipole bonds b/w reactant & solvent molecules.

② polar protic solvents used in S_N1 Reaction form dipole-dipole bond with transition state. Thus stabilizes transition state.



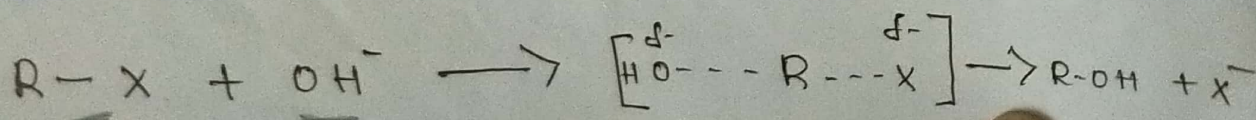
Polar Protic

③ Solvent forms weak ion dipole bond with carbocation & stabilizes the carbocation.

④ polar protic solvent involves in solvation of anions by forming hydrogen bonding.

② S_N2 Reaction

① polar Aprotic solvents used in S_N2 Reaction stabilizes the transition state.



② polar Aprotic Solvents don't contain proton, such as DMF. It accelerates the rate of S_N2 reaction by solvating the cations, thus making the nucleophile more available to react.

③. Solvent forms weak dipole-dipole bond with Alkyl halide.

④. Solvent forms strong ion-dipole bond with Nucleophile carrying full negative charge.

13. Factors Influencing S_N1 & S_N2 Reactions?

①. Nature of Substrate S_N1

① As there is formation of carbocation in S_N1 mechanism, more stable the carbocation, greater the reaction rate.

② Tertiary > Secondary > primary.

③ only tertiary halide react by S_N1 mechanism.

S_N2 .

①. Methyl > primary > Secondary > Tertiary.

② Factor behind this order of reactivity is steric hindrance.

③ Bulky groups hinder the formation of required transition state.

② Nature of leaving group

- ① weaken the base stronger the leaving group
- ② In both S_N1 & S_N2 reaction leaving group begin to acquire negative charge in transition state
- ③ weaken the bond b/w carbon & leaving group more easy to carry out S_N1 & S_N2 reaction

③ Nature of solvent

S_N1

S_N2

polar protic solvent

polar Aprotic

① can donate H^+ ions

① cannot donate H^+ ions

② solvate both Anions & cations

② solvate only cations

Eg: CF_3COOH

Eg: Acetone, DMF

④ Nature of nucleophile

S_N1

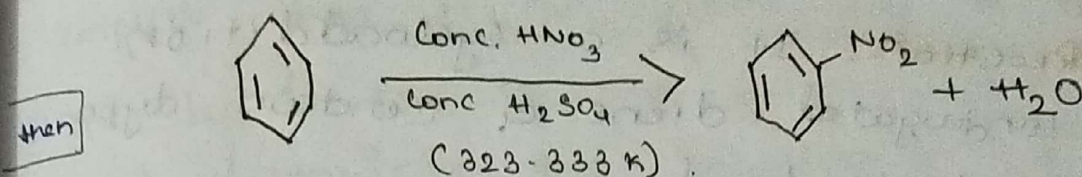
Stronger & Higher conc of nucleophiles favour S_N2 reaction

S_N2

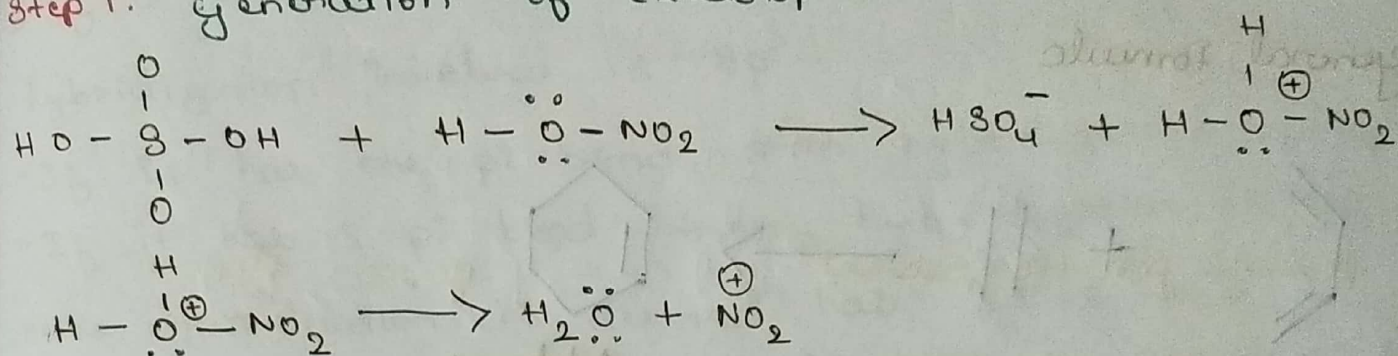
Nucleophile has no effect on rate of reaction, generally weaker & lower conc of Nucleophiles favours S_N2 reaction

(14). Mechanism of nitration of benzene?

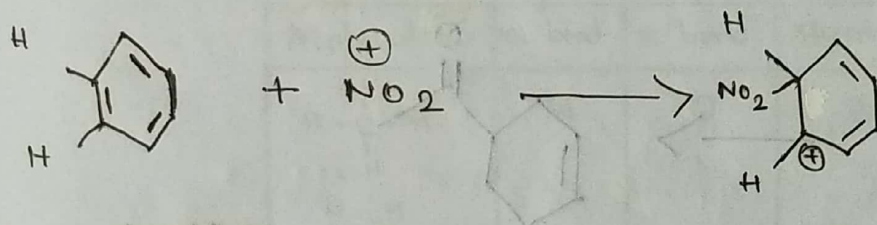
Substituting nitro ($-NO_2$) group to benzene ring is called as Nitration of benzene



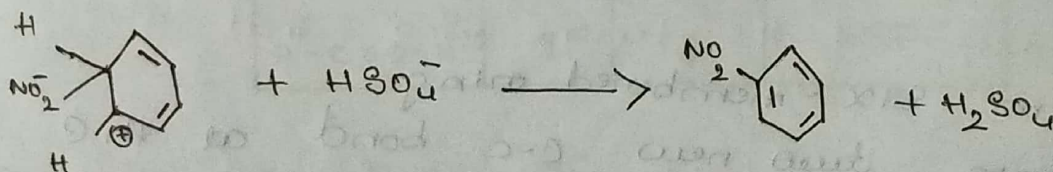
Step 1. Generation of Electrophile



Step 2. Formation of Carbocation



Step 3. Deprotonation

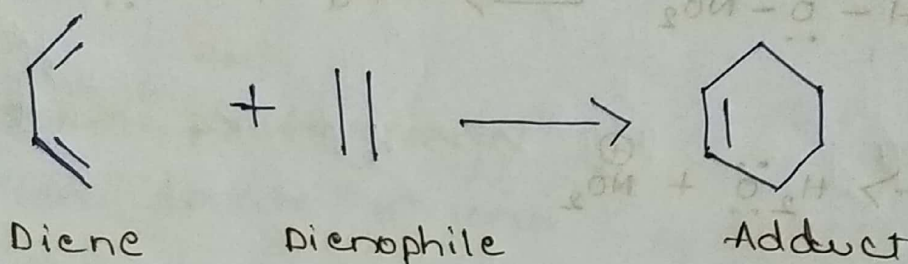


⑧ Explain cycloaddition reaction ?

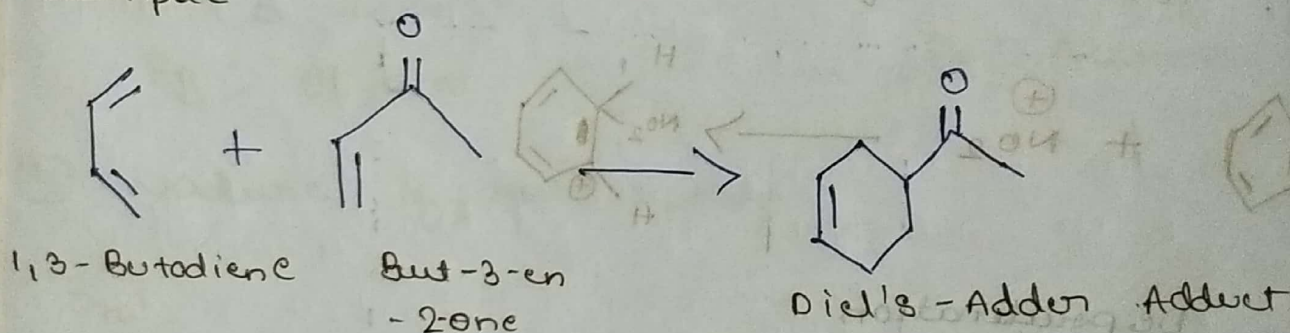
Ans: cycloaddition Reaction: A Reaction in which two reactants add together in a single step to form a cyclic product.

Diels Alder Reaction: It is a cycloaddition reaction of conjugated diene & contain type of double & triple bond.

General Formula



Example



- ① They form six-membered ring
- ② They form two new C-C bond at the same time
- ③ They are stereospecific
- ④ There is no transition state

Q6) Explain the term Hybridization and Hyperconjugation with example?

① Hybridization.

① Carbon has the valency 4 in its compound. This implies that it can form only 4 bonds.

② The bond can be σ or π . The type of bond determines the hybridization of carbon atom.

③ If a carbon has all 4 sigma bonds then the hybridization involved is sp^3 .

- If it has one π bond then hybridization is sp^2 .

- If it has 2 π bonds then hybridization is sp .

Hence hybridization is defined as it is the concept of mixing atomic orbitals into new hybrid orbitals.

Molecules	σ bond	π bond	Hybridization
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	4	0	sp^3
$\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{C} & = & \text{C} \\ & \\ \text{H} & \text{H} \end{array}$	3	1	sp^2
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	2	2	sp

② Hyperconjugation. II

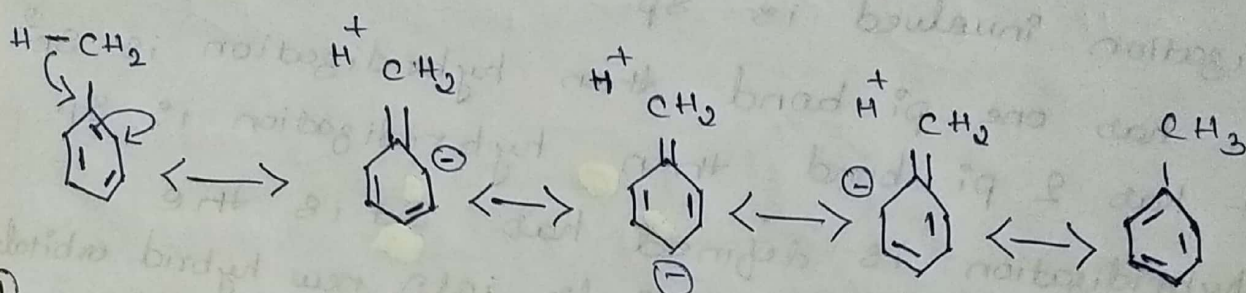
① It is the phenomenon in which electron displacement takes place resulting in the conjugation between π electrons & σ electrons.

② Only the e^- of C-H bond give rise to this type of effect.

Hyperconjugative effect is used to explain the following phenomenon

- ① orienting influence of $-CH_3$ group
- ② stability of carbocation
- ③ stability of free radicals.

Ex: orienting influence of CH_3



- ① The carbon atom of methyl group which is directly ~~attached~~ attached to the benzene ring does not contain lone pair of e^-
 - ② The ortho-para directing nature of $-CH_3$ group can be explained by hyperconjugative effect
 - ③ The $C-H$ bonds of $-CH_3$ group will interact with the π electrons of the benzene ring. That give rise to above resonance structures
 - ④ In this resonance hybrid the ortho and para positions contain more electron density compare to meta positions
 - ⑤ Therefore Incoming substituent group which is an electrophile will prefer ortho-para position compared to meta position
- $\therefore CH_3$ acts as ortho para directing group

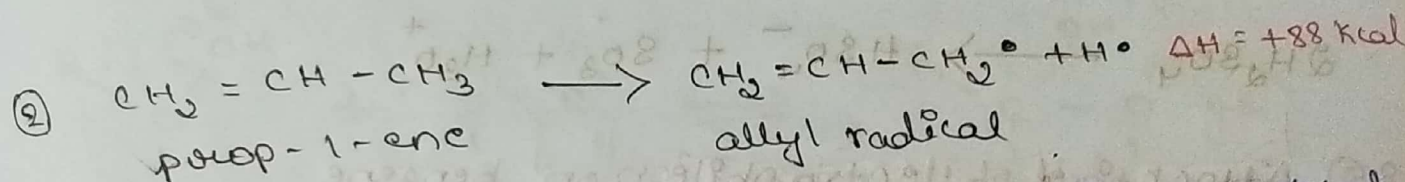
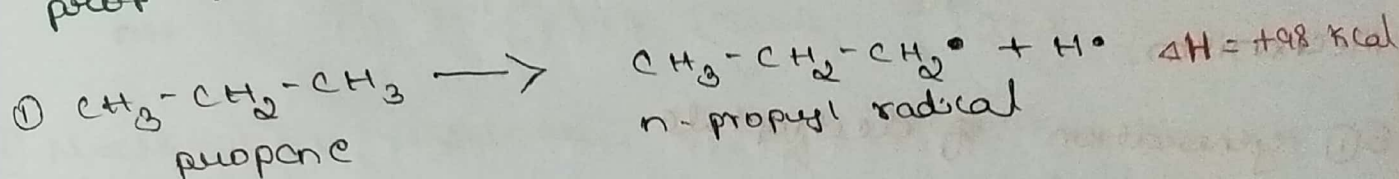
17) Explain the stability and resonance hybrid of allyl radical

① stability of allyl radical

① According to resonance theory, As a resonance hybrid, the allyl radical is more stable than either of the contributing structures

② The additional stability possessed by the molecule is referred as resonance energy.

Let us consider dissociation of propene and prop-1-ene

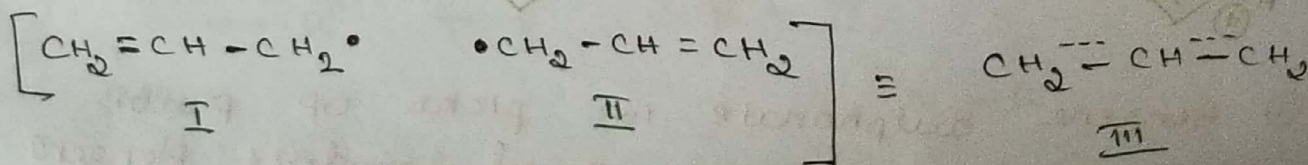


① The energy difference b/w ① & ② is 10 Kcal

② lower dissociation energy of eq ② is entirely due to resonance stabilization of allyl radical

③ Estimated resonance energy to be 10 Kcal.

② Allyl radical as resonance hybrid.



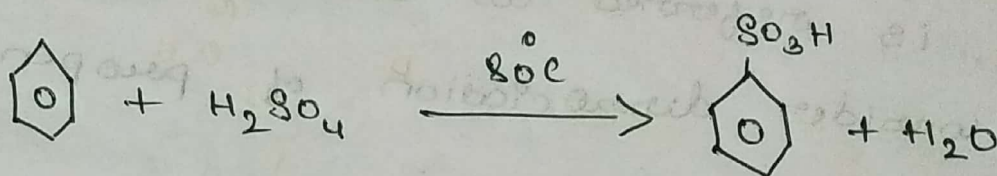
① Acc to theory of resonance, allyl radical is a resonance hybrid of two str I & II

② Allyl radical contain "hybrid bonds". It is said to possess one half single bond character and one-half double bond character.

③ odd electron is delocalized in the molecule. It is equally distributed over both terminal carbons, as represented in III.

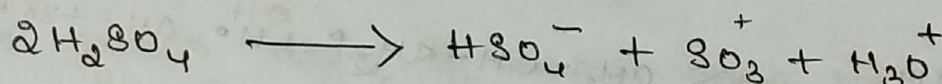
(18) Describe Sulphonation of benzene

Ans when benzene is heated with conc H_2SO_4 at 80°C benzene sulphonic acid is formed.

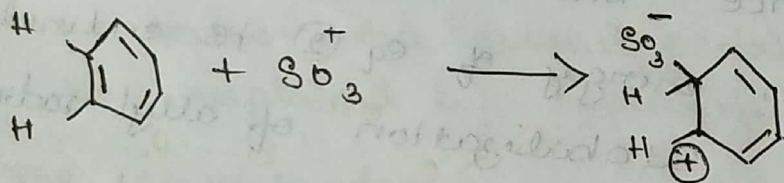


Mechanism.

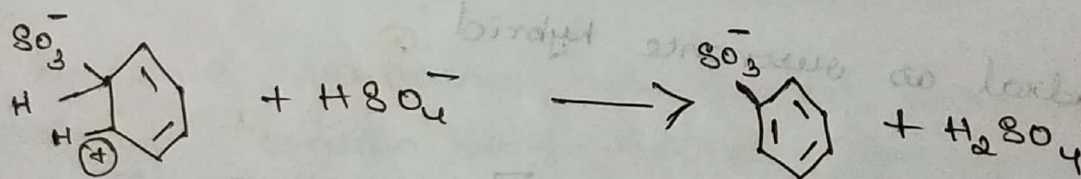
S① Generation of electrophile



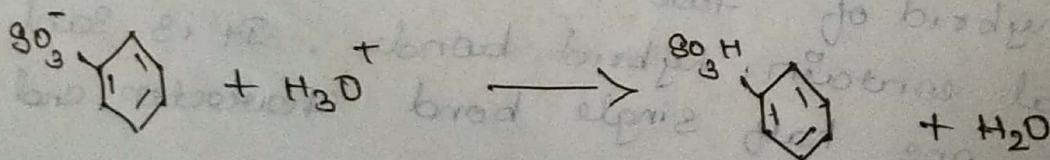
S② Formation of carbocation



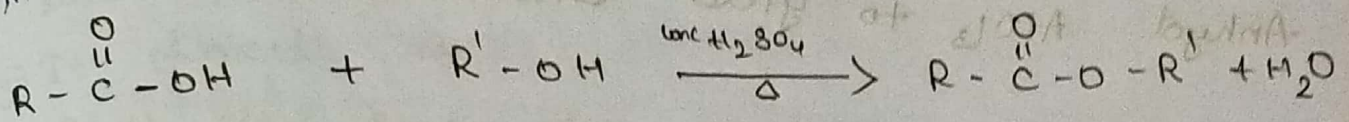
S③ Deprotonation



S④ Benzene Sulphonate ion picks up proton from H_3O^+ to form final product Benzene Sulphonic acid

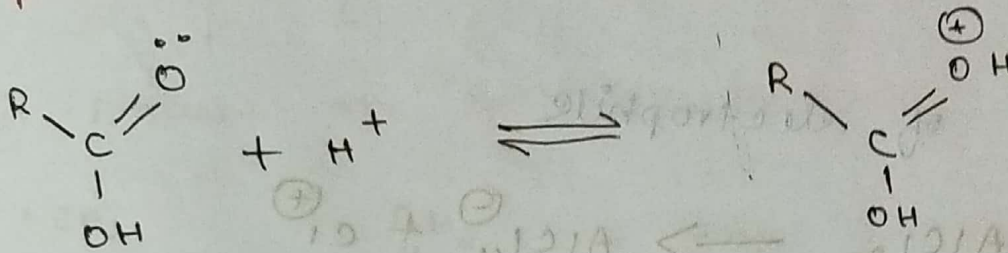


Q1) Explain esterification reaction with mechanism when carboxylic acids are heated with alcohols in the presence of conc H_2SO_4 , esters are formed.

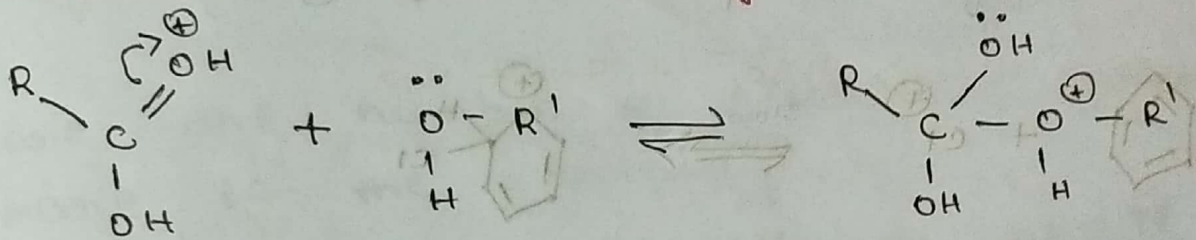


mechanism.

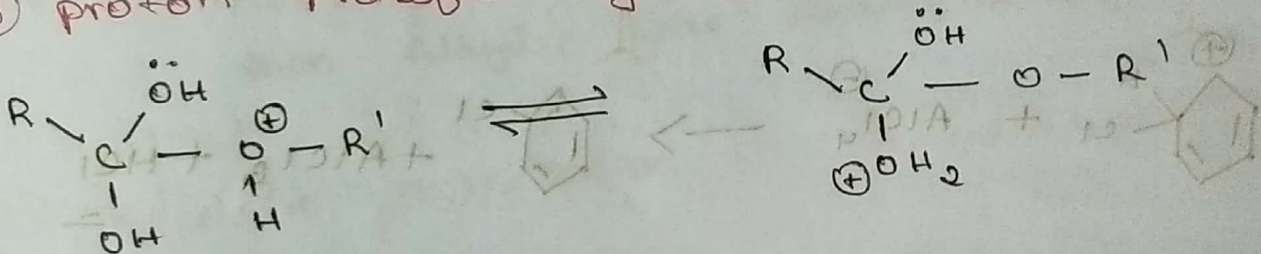
① protonation of carbonyl group



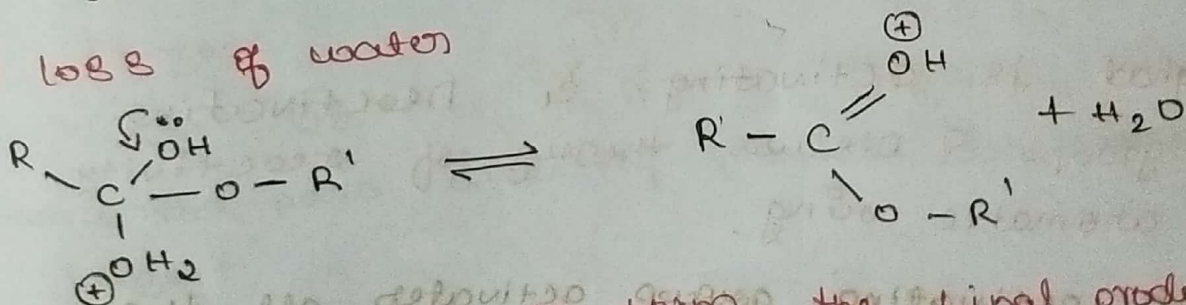
② Nucleophilic attack by alcohol



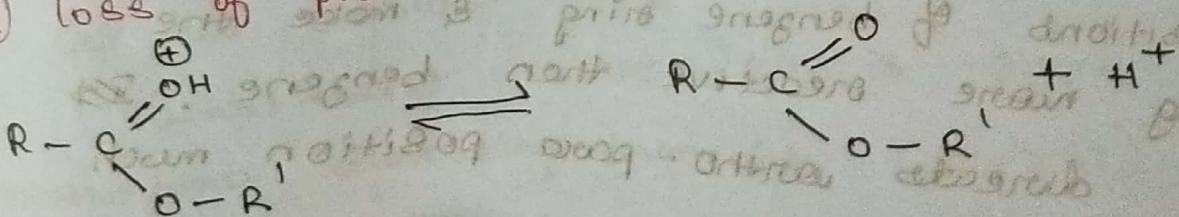
③ proton transfer by the intermediate



④ loss of water

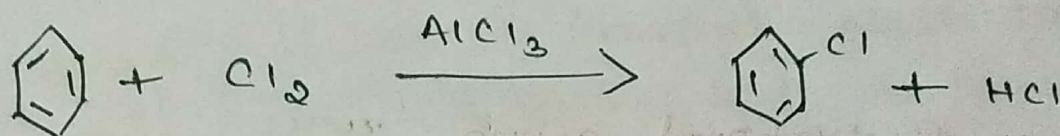


⑤ loss of proton to form the final product



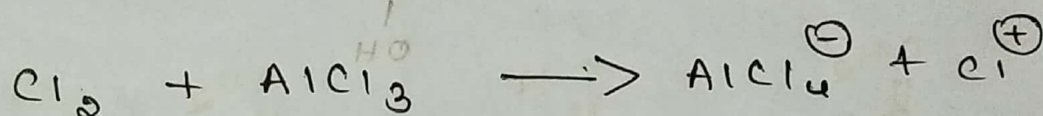
20 Chlorination of benzene.

Benzene react with chlorine in presence of Anhyd $AlCl_3$ to yield chlorobenzene

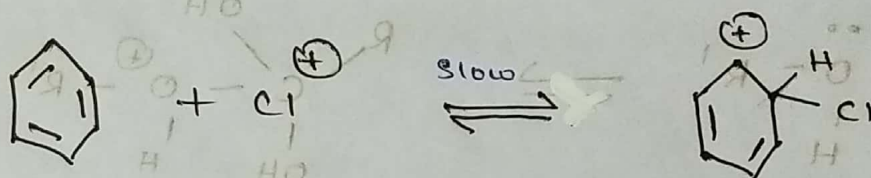


Mechanism.

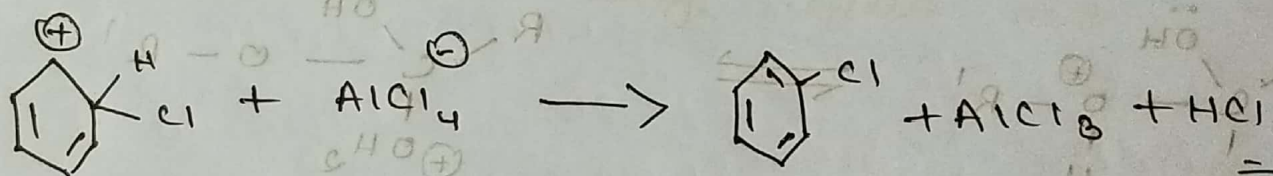
① Formation of electrophile



② Attack of electrophile on Benzene



③ Deprotonation to get chlorobenzene



Q1) what is activating & Deactivating groups? Discuss theory of reactivity in aromatic ring.

① An activating group activates all the positions of benzene ring & make the ring more reactive than benzene.

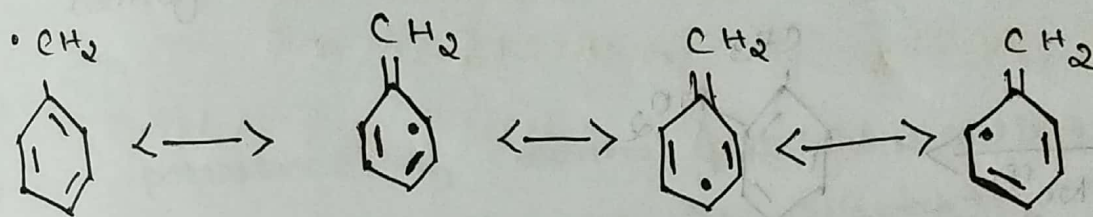
② It directs ortho - para position much more than meta

Ex: $-\text{NH}_2$, $-\text{OH}$

- ③ Deactivating group deactivates all the position of the ring & makes the ring less reactive than benzene. It directs meta position.
- Ex: $-\text{NO}_2$, $-\text{CF}_3$

For reactivity, write relative reactivity.

- ② Discuss the stability of Benzyl radical.



more the number of resonating structures more is the stability.

so Benzyl free radical is more stable than Alkyl free radical or any other.

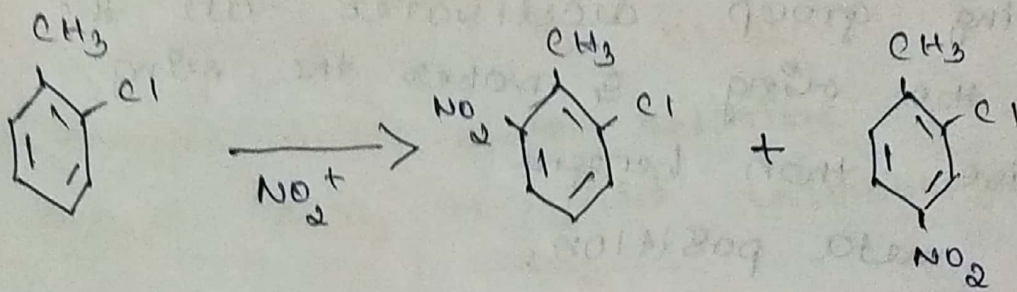
- ③ Explain orientation in Disubstituted benzene.

Ans Case ① In presence of ortho-para directing groups in disubstituted benzene.

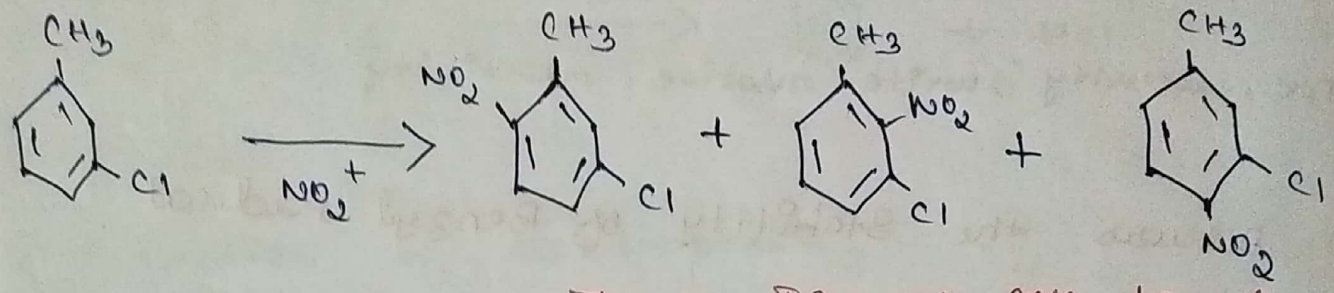
- ② Let us consider CH_3 & Cl has two substituents. where CH_3 is strong.

ortho para directing than Cl ($\text{CH}_3 > \text{Cl}$).

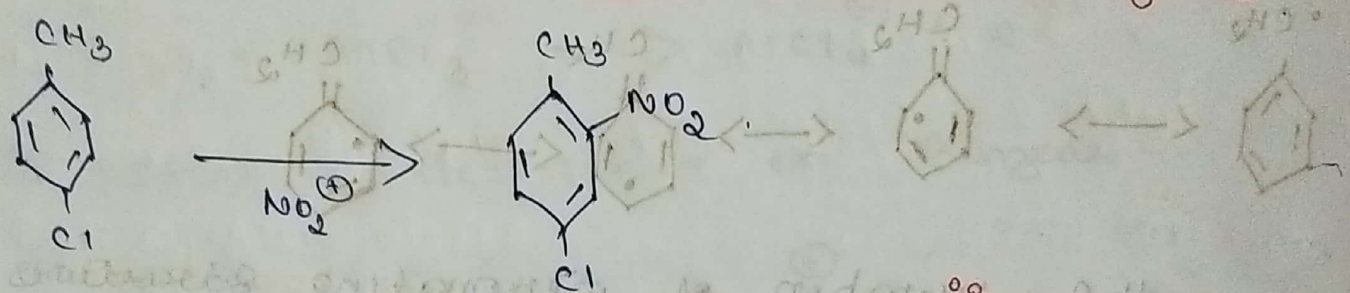
- ③ When disubstituted benzene undergo nitration reaction.



Two Isomers are formed



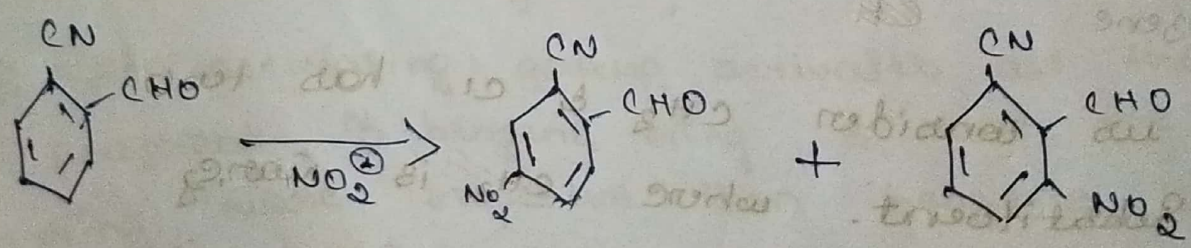
Three Isomers are formed



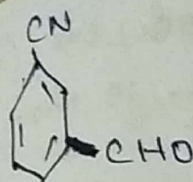
one Isomer is formed

Case (ii)

- ① In presence of meta-directing groups in disubstituted benzene
- ② Let us consider CN and CHO has two substituent, where CN is strong meta directing group than CHO ($\text{CN} > \text{CHO}$)
- ③ when disubstituted benzene undergo nitration reaction



Two Isomers are formed



one isomer is formed



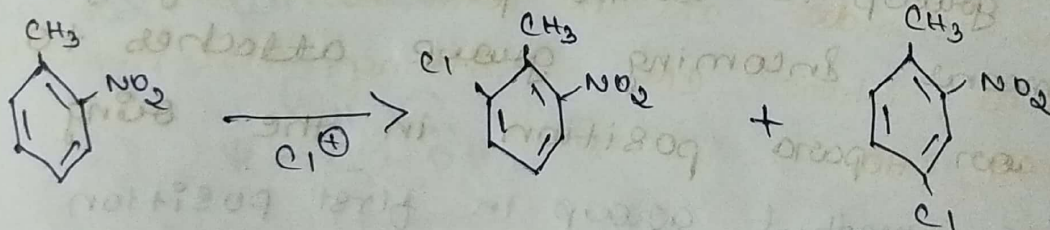
Two isomers are formed

Case (ii)

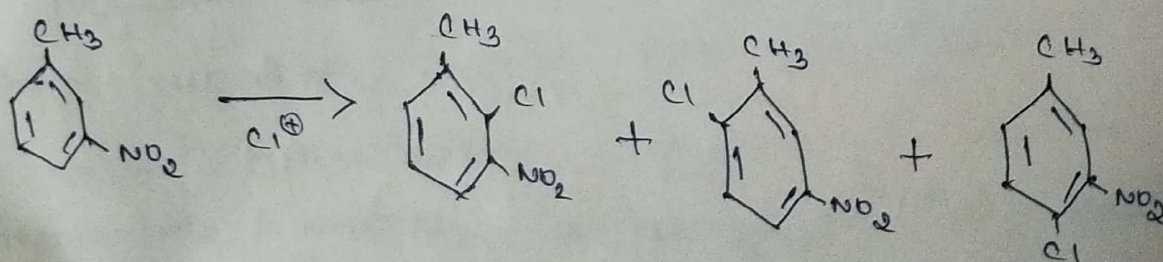
① In presence of ortho, para directing and meta directing groups in disubstituted benzene

② Let us consider CH_3 and NO_2 has two substituent, where CH_3 is strong ortho-para directing. ($\text{CH}_3 > \text{NO}_2$)

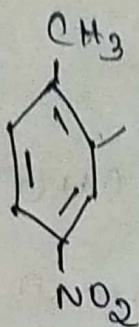
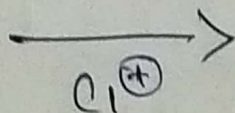
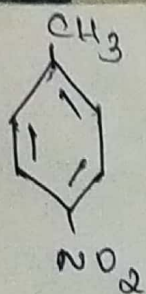
③ when disubstituted benzene undergo chlorination reaction



Two isomers are formed



Three isomers are formed

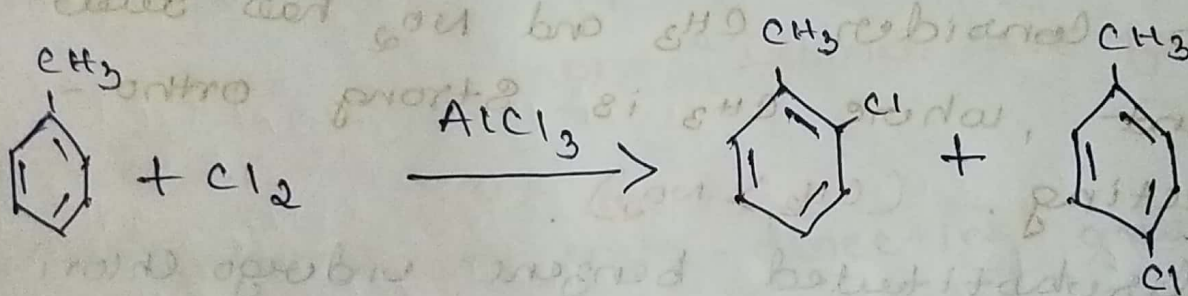


only one
str is enough

one isomer is formed

(24) Discuss Electrophilic aromatic Substitution in benzene with activating and side chain halogenation of alkyl benzene

Ans: Toluene react with chlorine in the presence of $AlCl_3$ to yield 2 chlorotoluene & p-chlorotoluene.



Methyl group is ortho-para directing group, which means incoming group attaches to ortho or para position in the ring assuming methyl group in first position =

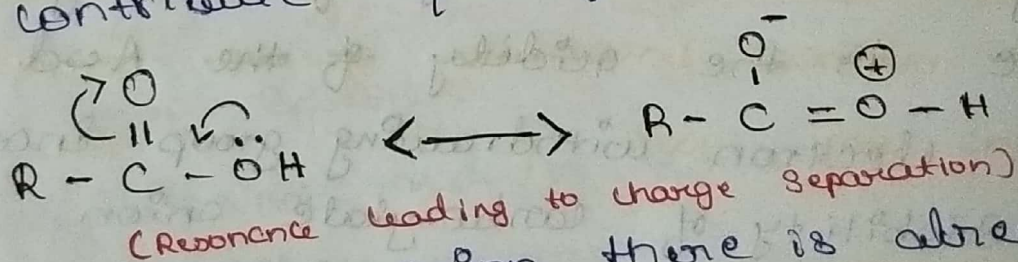
Q5. Explain the acidity of carboxylic acid. Add a note on effect of substituents.

Ans:- The acidic nature of carboxylic acids can be explained by the relative stability of carboxylic acid and carboxylate anion.

① Even though both carboxylic acid and carboxylate anions are resonance stabilized the resonance stabilization of carboxylate anion is more than carboxylic acid.

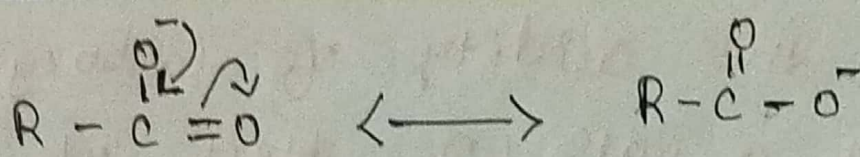
② This is because during resonance, acid group develops two opposite charges in it which leads to charge separation.

③ Hence both str's are not equivalent and do not contribute equally to the final structure.



④ In carboxylate anion there is already a negative charge. During resonance this negative charge gets distributed.

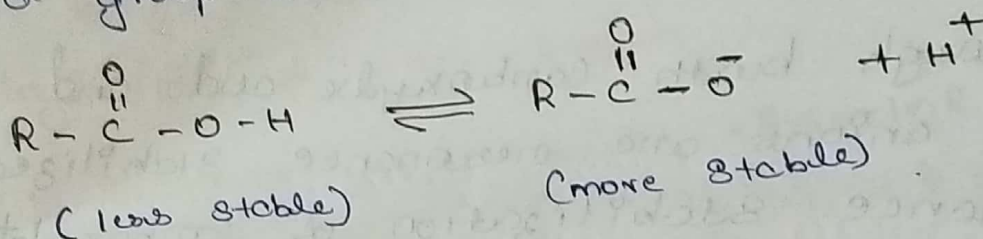
⑤ This distribution of charge as in resonance makes carboxylate ion stable than the carboxylic acid.



(Resonance leading to charge distribution)

Conclusion

Due to Resonance, Stability of carboxylate anion is more than that of carboxylic acid group. Hence carboxylic acid group donate proton and behaves as an acid



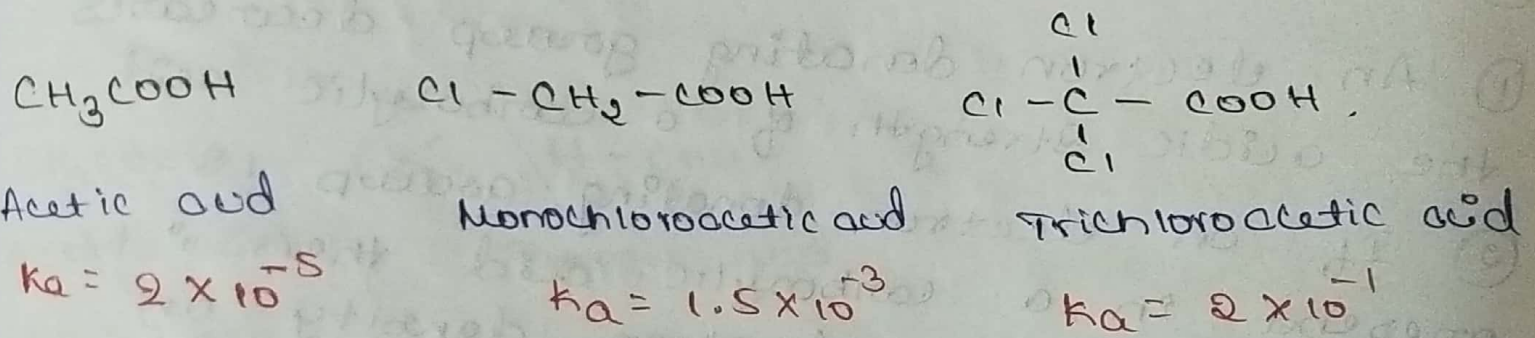
Effect of Substituents on the acidic strength:

- ① Electron withdrawing groups
- ① The acidic nature of carboxylic acids is due to the stabilisation of carboxylate anion.
- ② Higher the stability of carboxylate anion more is the acidity of the Acid
- ③ An electron withdrawing group increases the stability of carboxylate anion and hence increases the stability of carboxylic acid
- ④ This is because electron withdrawing group disperses the negative charge of -COO group there by increasing the stability of carboxylate anion.

① Higher the number of electron withdrawing group in a molecule, stronger is the acid.

① Trichloroacetic acid is stronger than monochloroacetic acid because trichloroacetic acid contains three e^- withdrawing chlorine groups

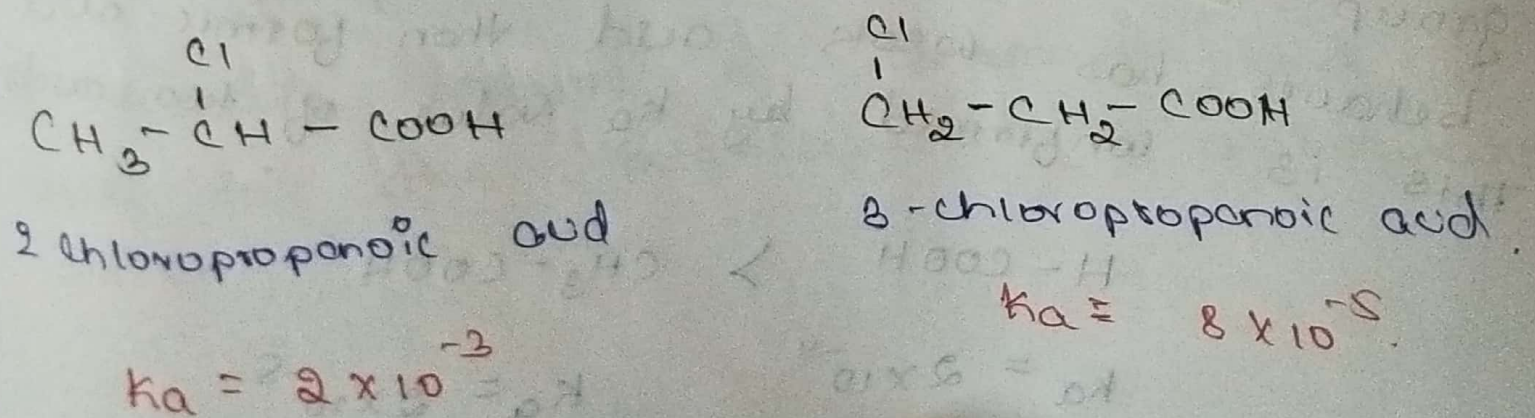
② Then monochloroacetic acid is stronger acid than Acetic acid because it contains one e^- withdrawing group



Higher the K_a value stronger is the acid

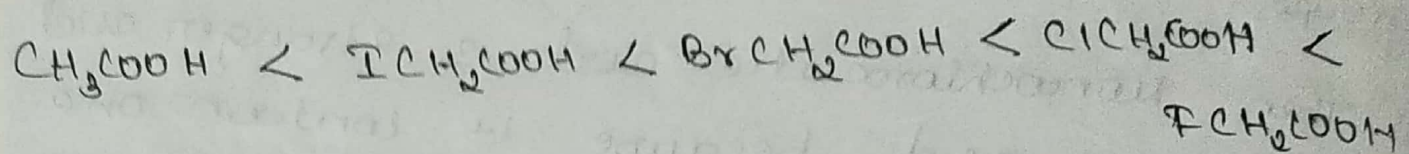
② Higher the electron-withdrawing group to $-\text{COOH}$ group stronger is the acid.

① 2-chloropropionic acid is stronger than 3-chloropropionic acid



(ii) Higher the electronegativity of the halogen atom, stronger is the acid.

Among various monohalo acetic acids fluoroacetic acid is the strongest acid and Iodoacetic acid is the weakest.



② Electron donating groups.

① An electron donating group decreases the acidic strength of a carboxylic acid.

② If an electron donating group is present in a carboxylic acid then it increases the electron density on carboxylate anion. This decreases the stability of carboxylate anion and hence the acidic strength decreases.

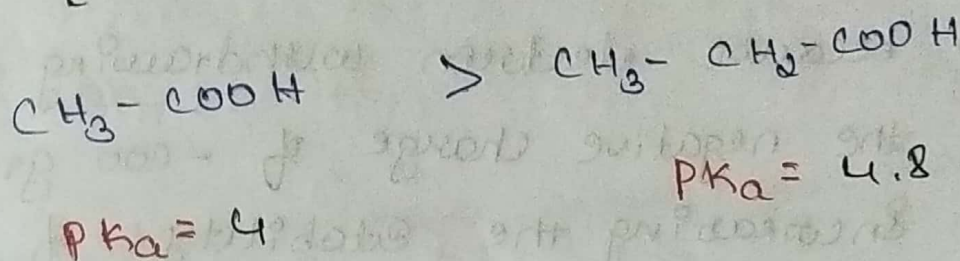
③²ⁿ presence of electron donating $-\text{CH}_3$ group. , Acetic acid behaves as weak acid than formic acid. This is confirmed by K_a value of two acids.



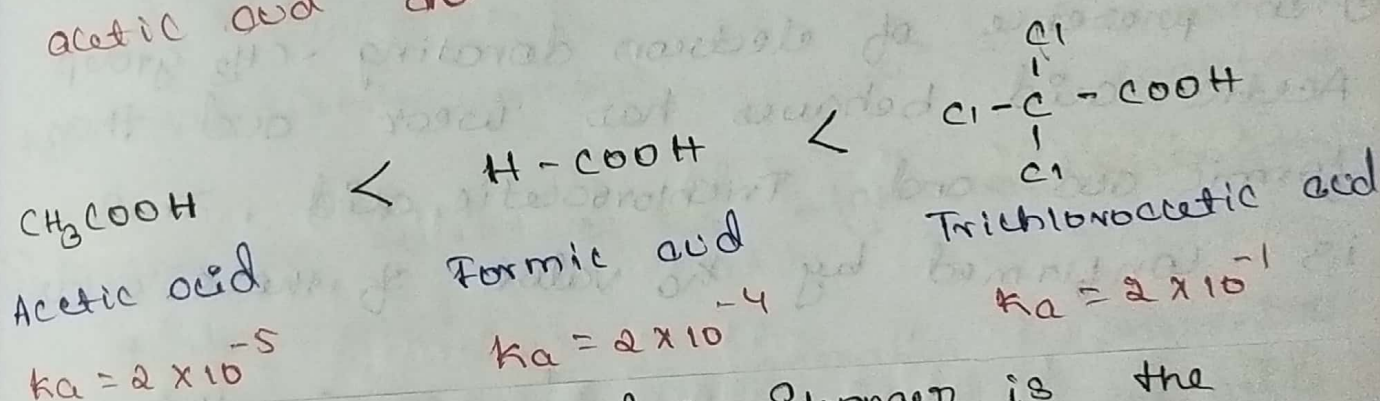
$$K_a = 2 \times 10^{-4}$$

$$K_a = 2 \times 10^{-5}$$

① The acidic strength decreases with increase in the size of the alkyl group hence propanoic acid is weaker acid than ethanoic acid.



② Compare the acidity among acetic acid and Trichloroacetic acid formic acid,



① Higher the K_a value stronger is the acid.

② Trichloroacetic acid is stronger than formic acid and Acetic acid because Trichloroacetic acid contains 3 e^- withdrawing groups.

③ Acidic nature of carboxylic acid is due to the stabilization of carboxylate anion.

④ An e^- withdrawing group increases the stability of carboxylate ion and hence increases the stability of carboxylic acids.

⑤ This is because electron withdrawing group disperses the negative charge of $-COO^-$ group, thereby increasing the stability of carboxylate ion.

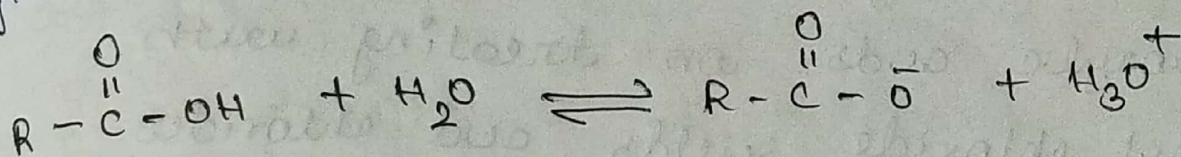
① In presence of electron donating $-CH_3$ group, Acetic acid behaves as weak acid than formic acid and Trichloroacetic acid. This is confirmed by K_a value of these acids.

② An e^- donating group decreases the acidic strength of a carboxylic acid.

③ If an electron donating group is present in a carboxylic acid then it increases the electron density on carboxylate anion. This decreases the stability of carboxylate anion and hence the acidic strength decreases.

27 Explain Ionisation of COOH .

① Carboxylic acids dissociate in water to give carboxylate anions and hydronium ion



Applying law of mass action for above equilibrium

$$K_{eq} = \frac{[\text{H}_3\text{O}^+][\text{RCOO}^-]}{[\text{H}_2\text{O}][\text{RCOOH}]}$$

$$K_a = K_{eq}[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{RCOO}^-]}{[\text{RCOOH}]}$$

K_{eq} = equilibrium constant

K_a = acid dissociation constant

② Higher the value of K_a higher the strength of the acid.

③ Strength of acid is generally represented by pK_a

$$pK_a = -\log K_a$$

④ Higher the value of pK_a weaker is the acid

Ex: ① propanoic acid
 $\text{CH}_3\text{CH}_2\text{COOH}$

$$pK_a = 5.$$

② Ethanoic acid
 CH_3COOH

$$pK_a = 4.5$$

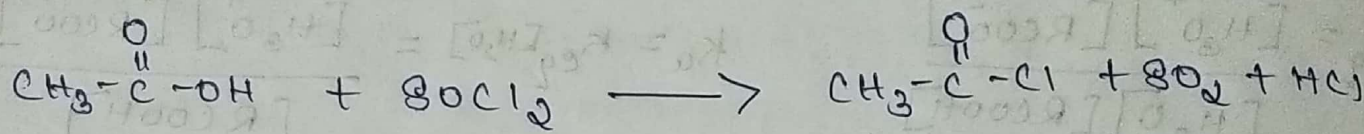
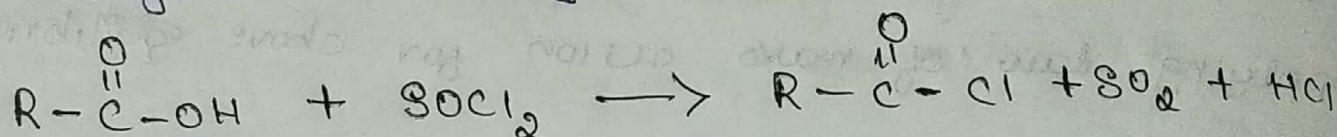
③ Fluoroethanoic acid
 CH_2FCOOH

$$pK_a = 2.5$$

Q8 Write the conversion of acid to acid chloride, amide, ester / preparation of various acid derivatives

① Conversion of Acid to Acid chloride.

Carboxylic acids on treating with thionyl chloride yields acid chlorides

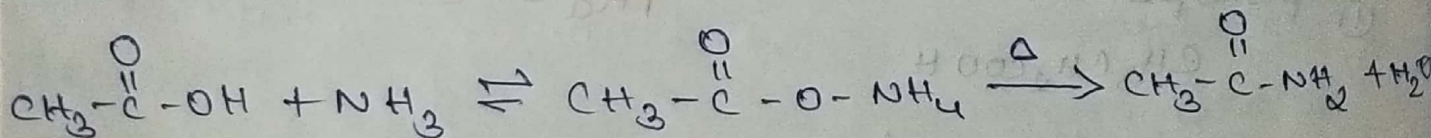
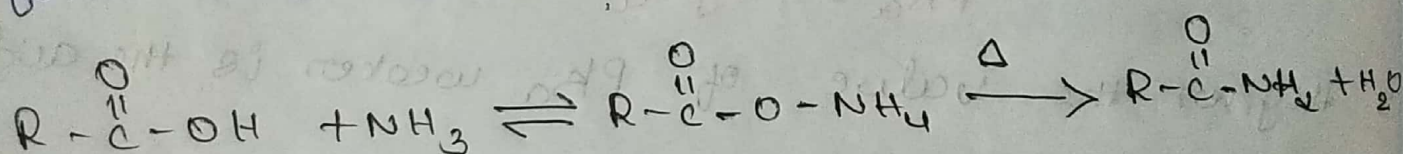


Acetic acid

Acetyl chloride

② Conversion of Acid to Amide

Carboxylic acids reacts with ammonia to form Ammonium salt of carboxylic acid which on heating undergoes dehydration to form acid amide

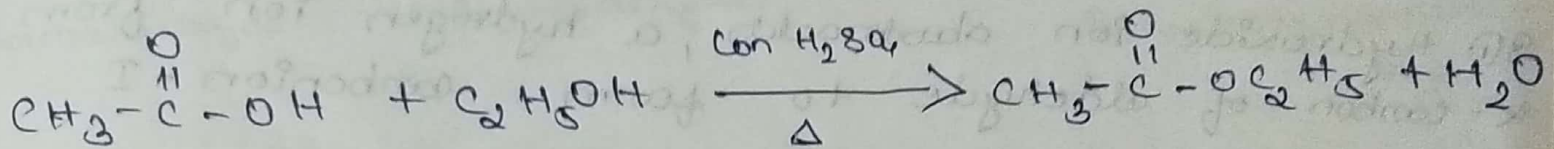
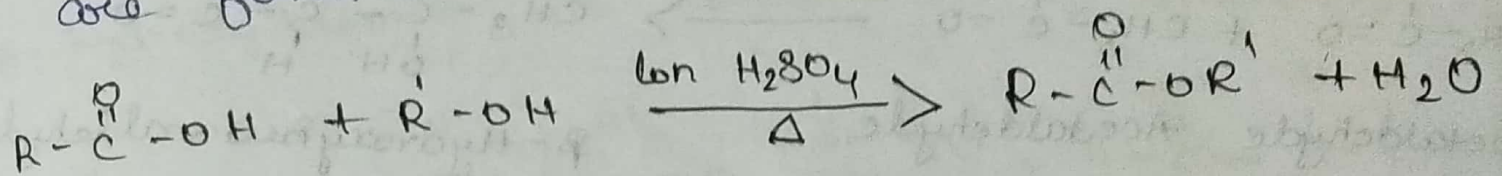


acetic acid

Ammonium
acetate

Acetanomide

③. Conversion of Acids to ester
 When carboxylic acids are heated with alcohols in presence of $\text{con H}_2\text{SO}_4$, esters are formed



Acetic acid

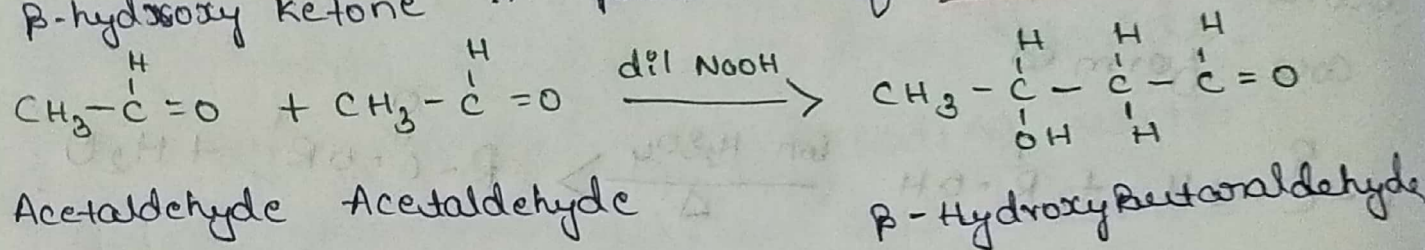
~~Ethanol~~

Ethyl alcohol

Ethyl acetate

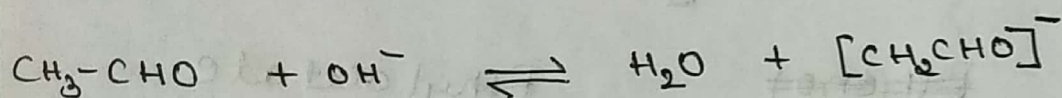
① Aldol condensation.

Two same molecules of Aldehyde or ketone may combine to form β -hydroxy aldehyde and β -hydroxy ketone in presence of dil base.

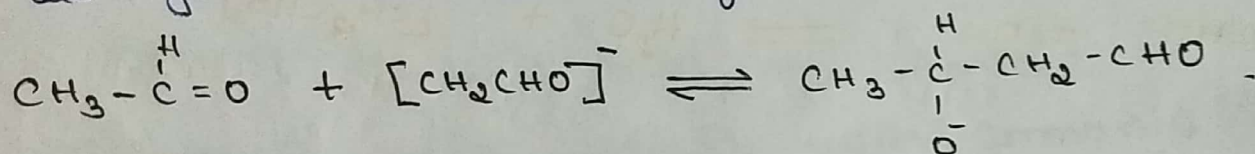


Mechanism.

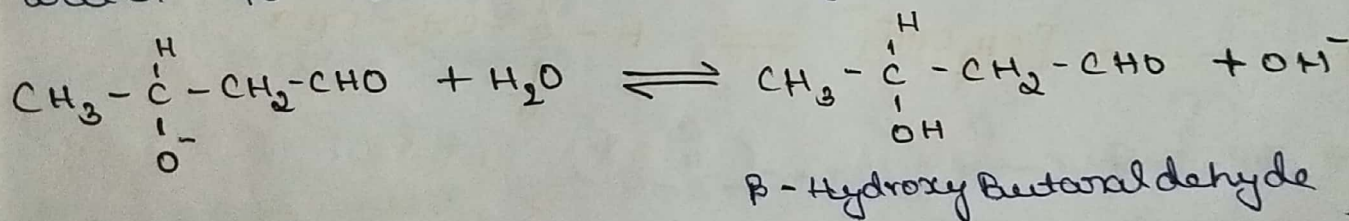
① Hydroxide ion abstracts a hydrogen ion from α -carbon of aldehyde to form carbanion - I



② Carbanion I ~~attacks~~ ^{is added to} carbon of second aldehyde molecule to form alkoxide ion.



③ Alkoxide ion abstracts hydrogen ion from water to form β -Hydroxy aldehyde.



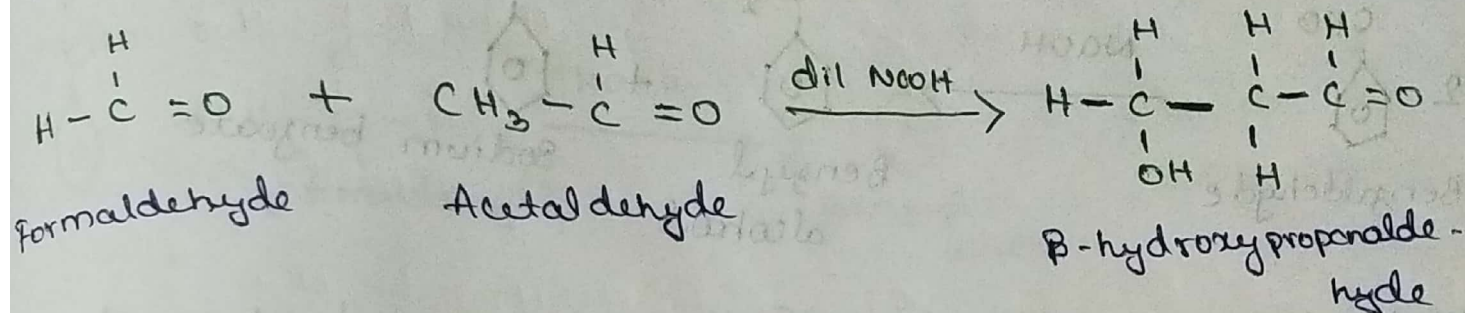
Abstraction

Addition

Abstraction

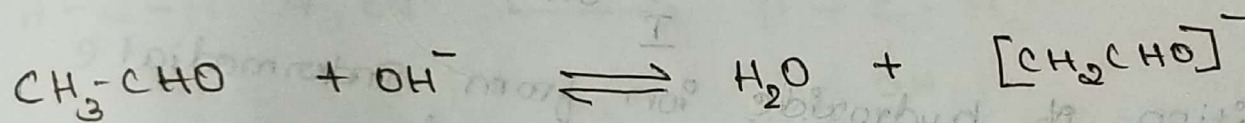
2) crossed Aldol condensation

Two different molecules of Aldehyde or ketone may combined to form β -Hydroxy aldehyde and β -hydroxy ketone in presence of dil base

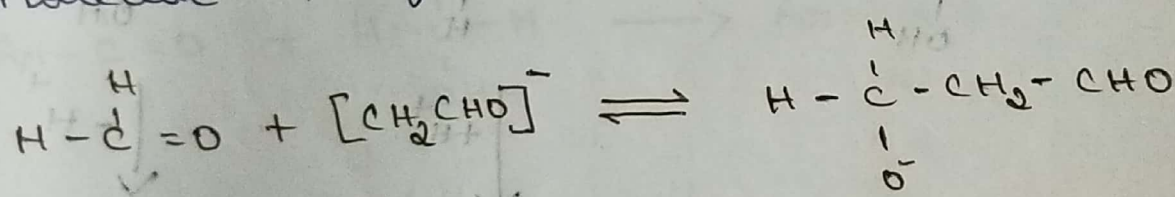


Mechanism.

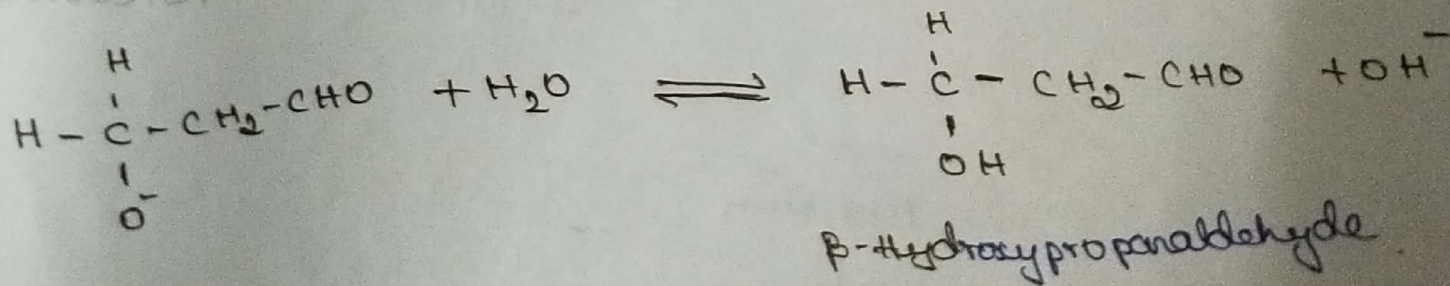
Step 1 Hydroxide ion abstracts a hydrogen ion from α -carbon of aldehyde to form carbanion - I



Step 2 Carbanion I attacks carbon of second aldehyde molecule to form alkoxide ion

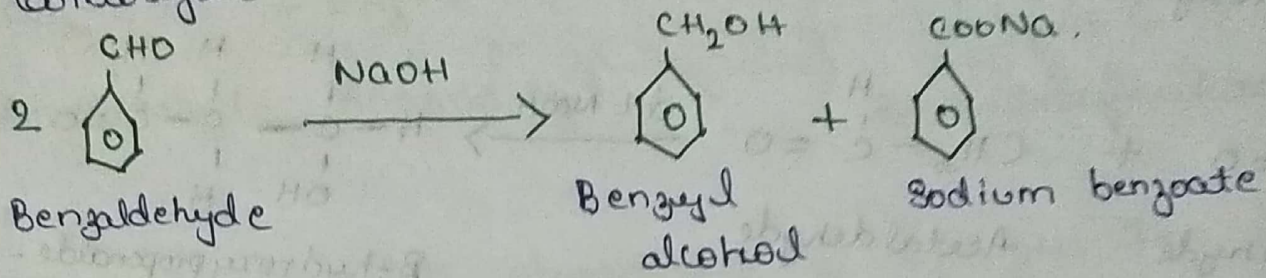


Step 3 Alkoxide ion abstracts hydrogen ion from water to form β -hydroxy aldehyde.



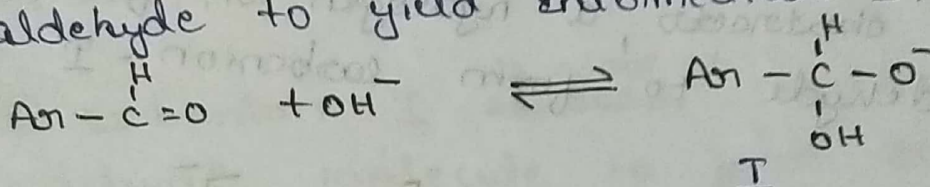
③ Cannizzaro reaction

Two same molecules of Aldehydes without α -hydrogen undergoes self oxidation and reduction to form mixture of alcohol and a salt of carboxylic acid in presence of conc base

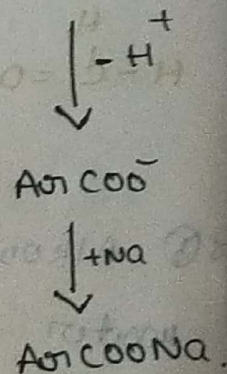
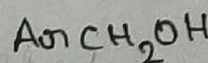
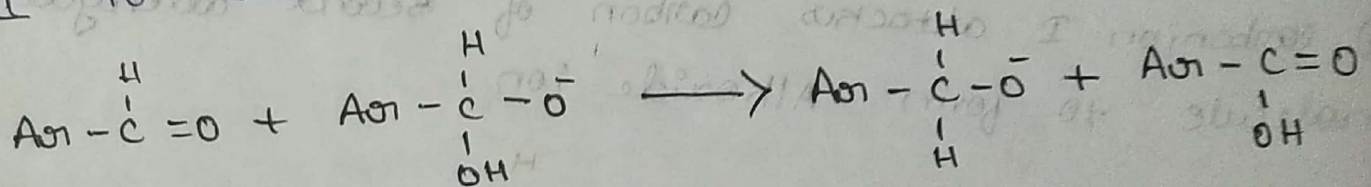


Mechanism

① Hydroxide ion is added to carbonyl carbon of aldehyde to yield Intermediate I.



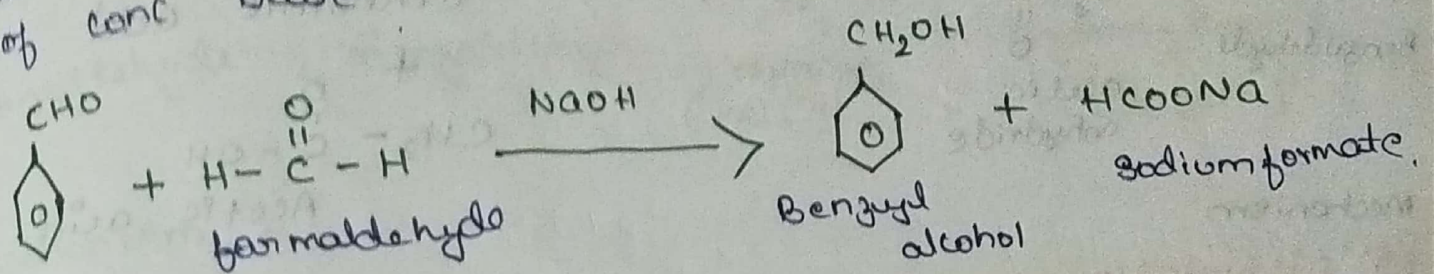
② Addition of hydrogen. H^+ ion from Intermediate I to second molecule of aldehyde



Addition

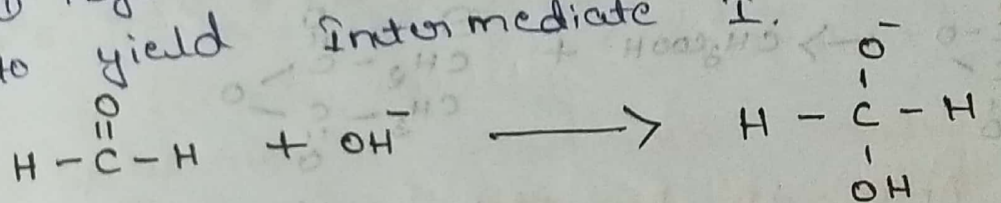
Addition

Cannizzaro reaction
 (a) Two different molecules of Aldehydes without α -hydrogen undergoes self oxidation and reduction to form mixture of alcohol and a salt of carboxylic acid, in presence of conc base.

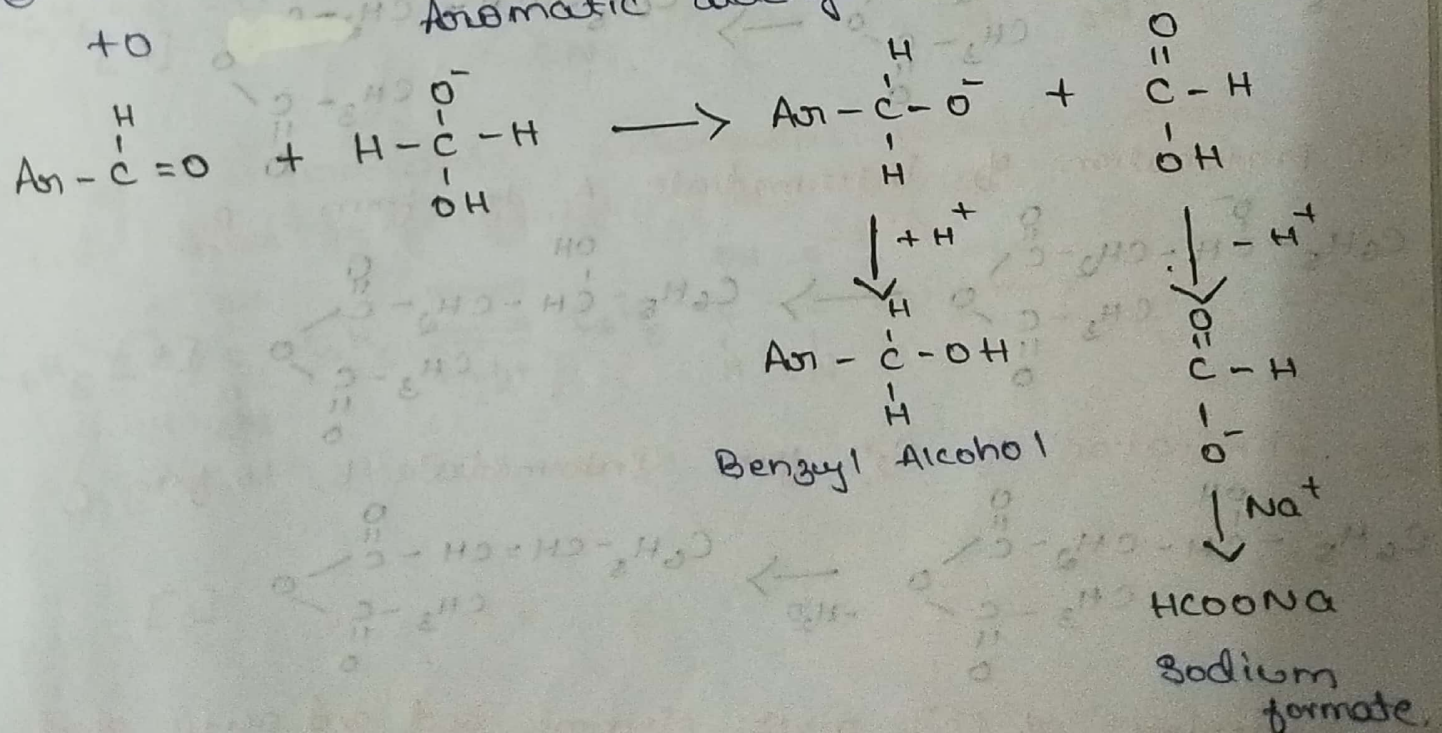


mechanism.

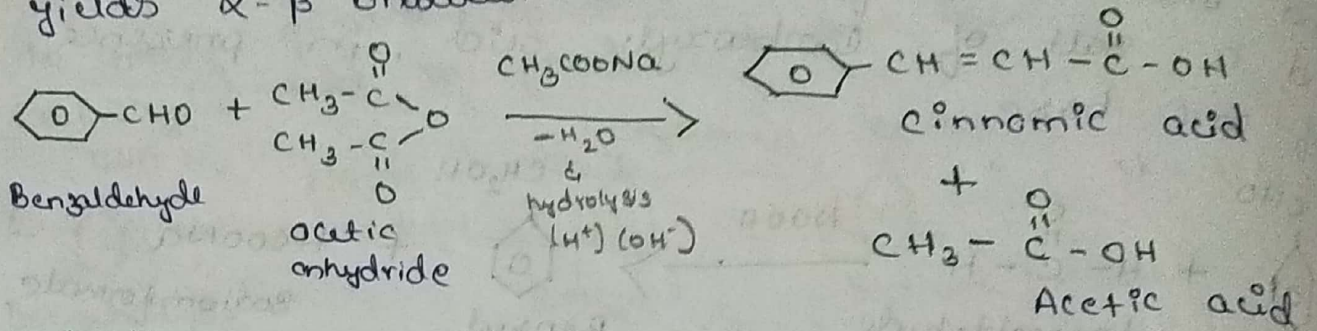
3① Hydroxide ion is added to aliphatic aldehyde to yield Intermediate I.



3② Addition of hydrogen ion from Intermediate I to Aromatic aldehyde

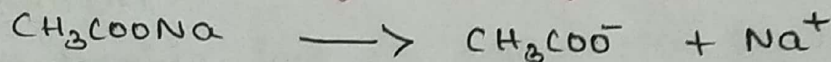


⑤ perkin condensation
Aromatic aldehyde when heated with the anhydride of an aliphatic acid & sodium salt of that acid yields α - β unsaturated acid

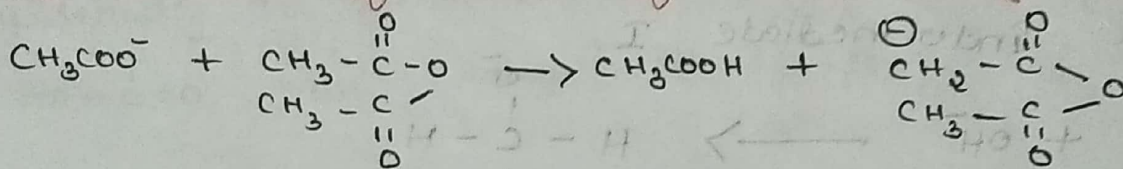


Mechanism.

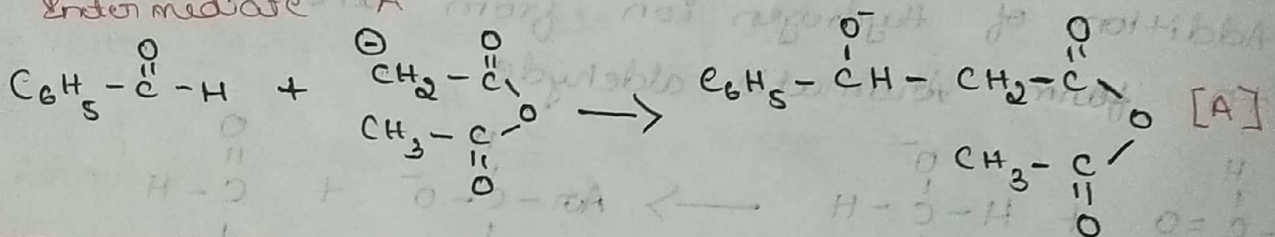
8① Dissociation of salt of acid



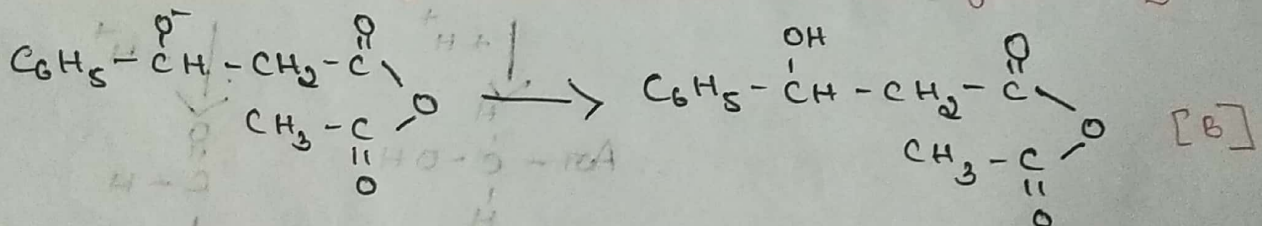
8② Formation of anion of acetic anhydride



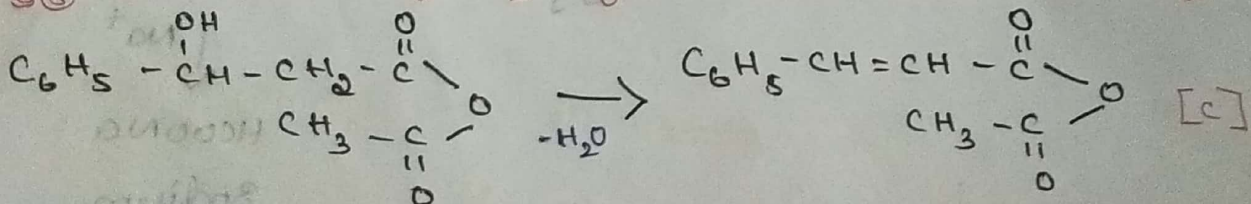
8③ Addition of Anion to Benzaldehyde to give Intermediate A



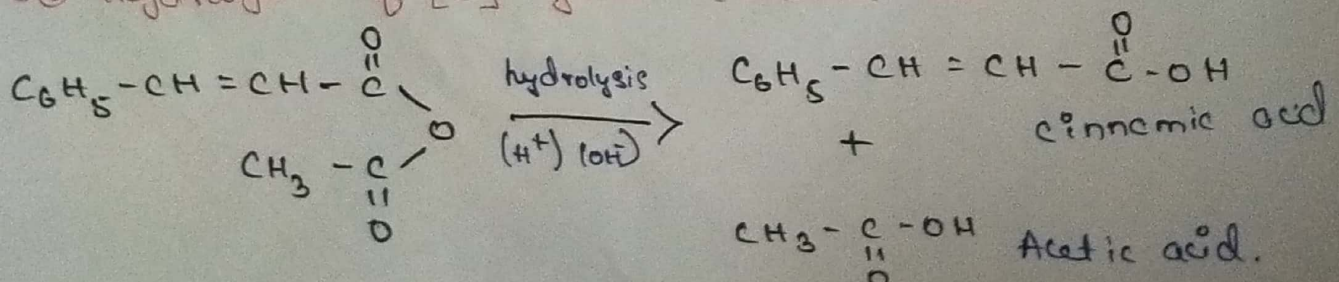
8④ Protonation of Intermediate A to form B



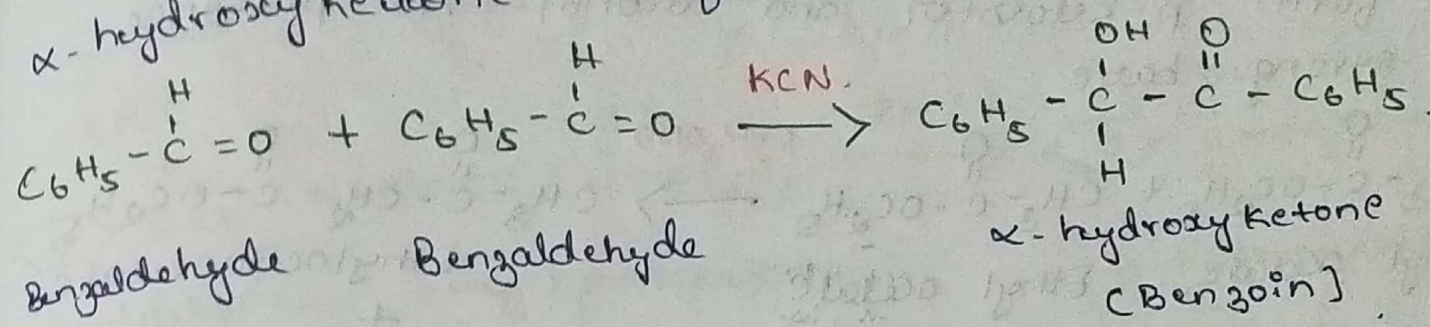
8⑤ Elimination of H_2O from Intermediate B to form C



8⑥ Hydrolysis of [C] gives cinnamic acid and acetic acid

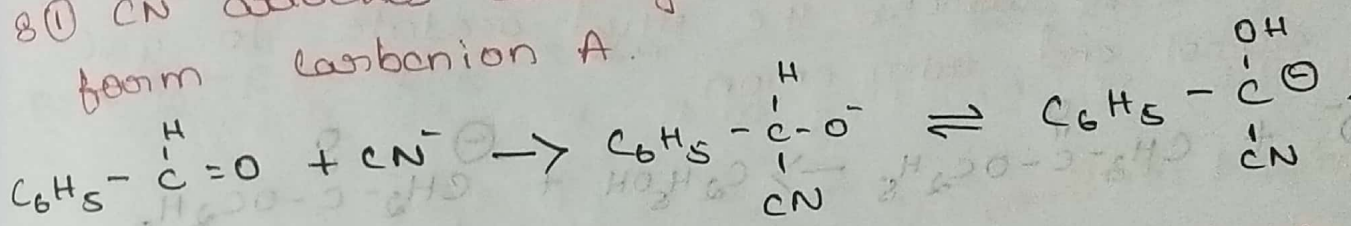


⑥ Benzoin condensation. ★
 when Aromatic aldehyde is heated with alc. KCN
 α -hydroxy ketone is formed

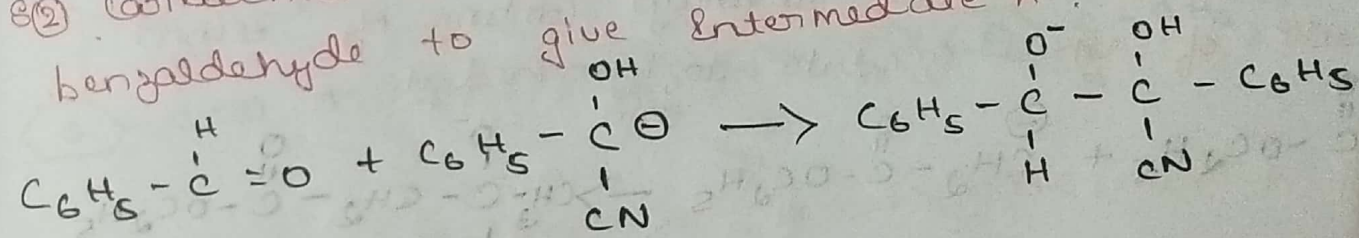


Mechanism

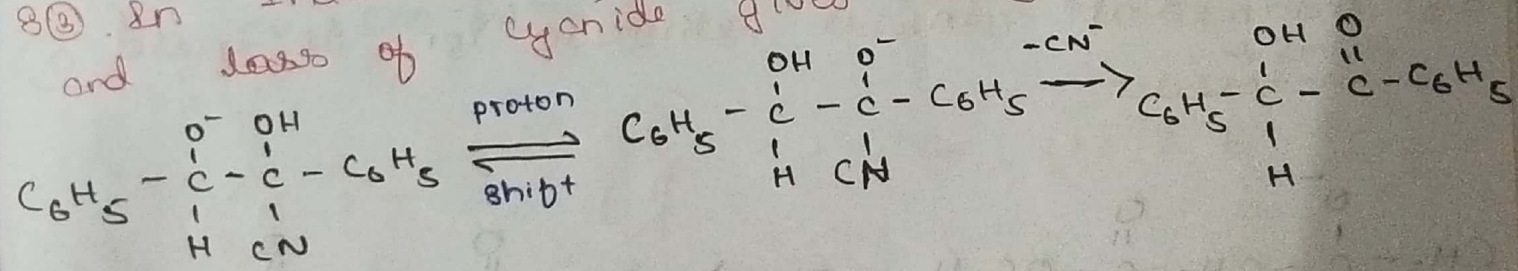
8① CN^- attacks carbonyl carbon of aldehyde to form carbanion A.



8② Carbanion A react with another molecule of benzaldehyde to give Intermediate A.

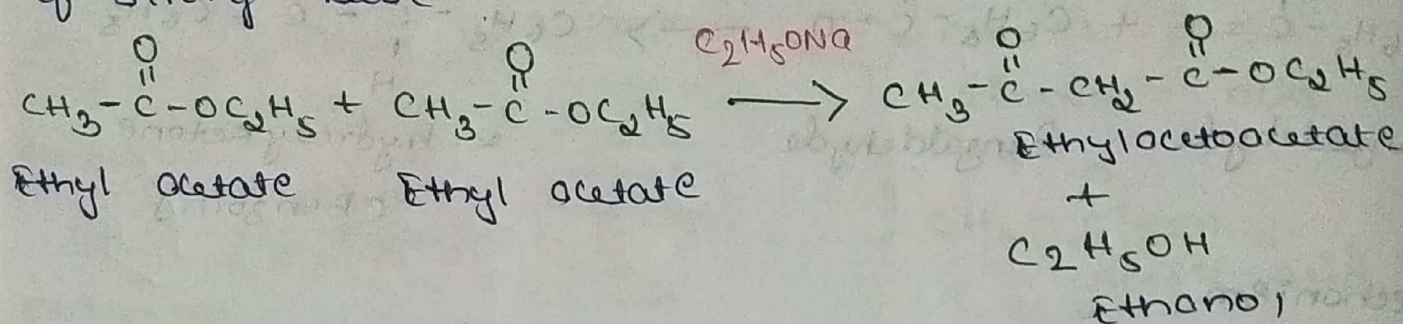


8③ In Intermediate, subsequent proton transfer and loss of cyanide gives benzoin



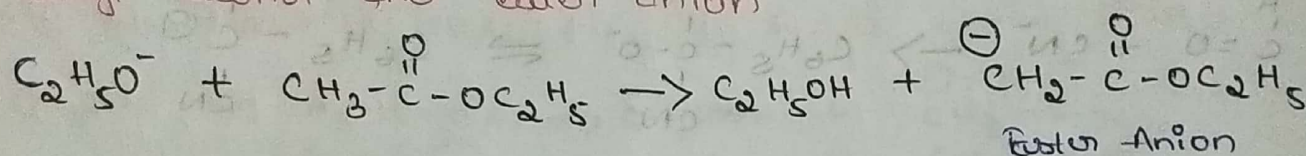
⑦ Claisen condensation

Two ester molecules with α -hydrogen combined to form β -ketoester and alcohol in presence of strong base

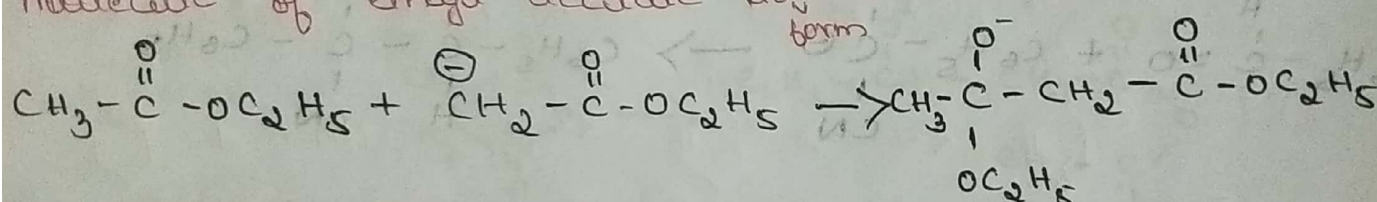


Mechanism

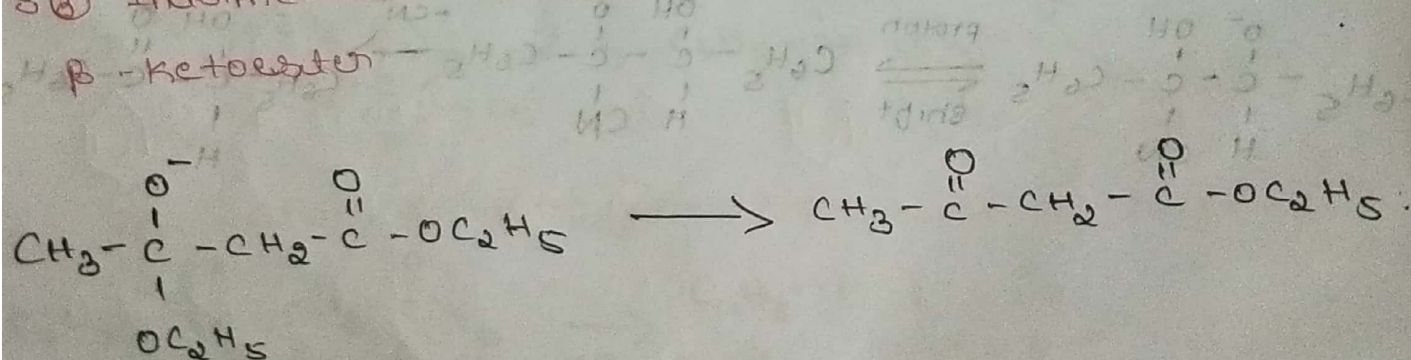
8① Ethoxide ion attacks the ethyl acetate to give ethyl alcohol and ester anion



8② Ester Anion attacks carbonyl carbon of second molecule of ethyl acetate to form intermediate

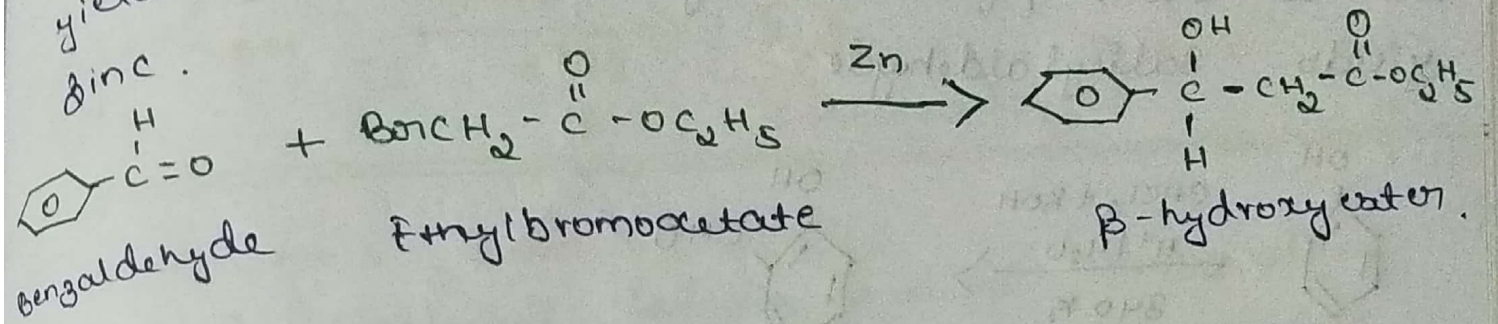


8③ Intermediate loses ethoxide ion to yield

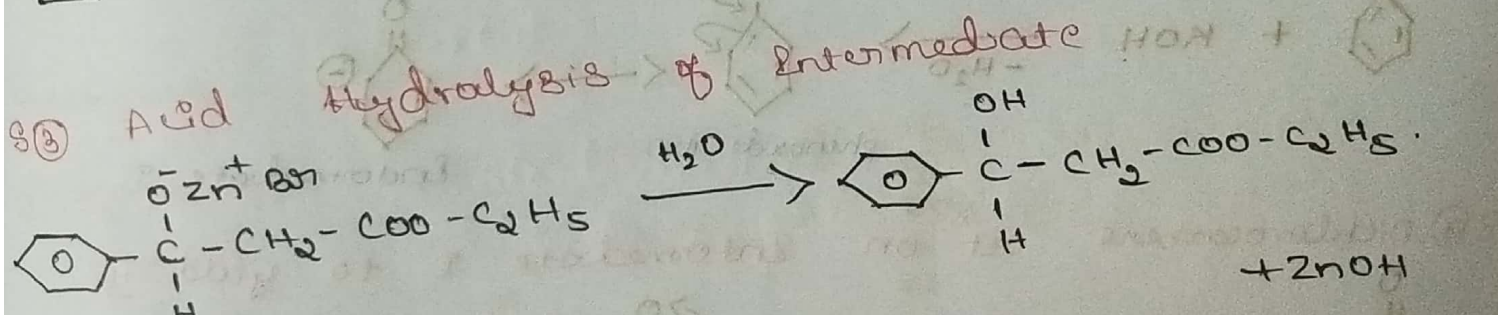
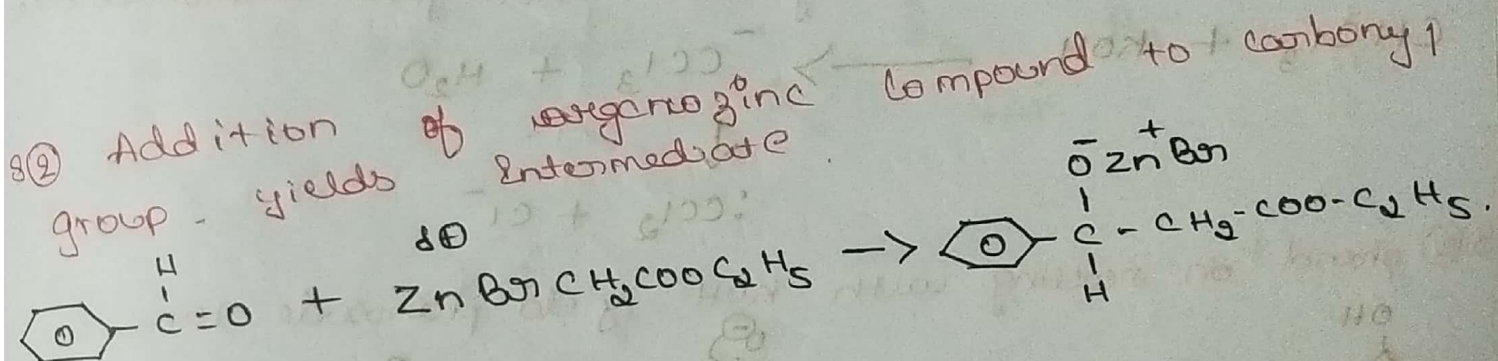
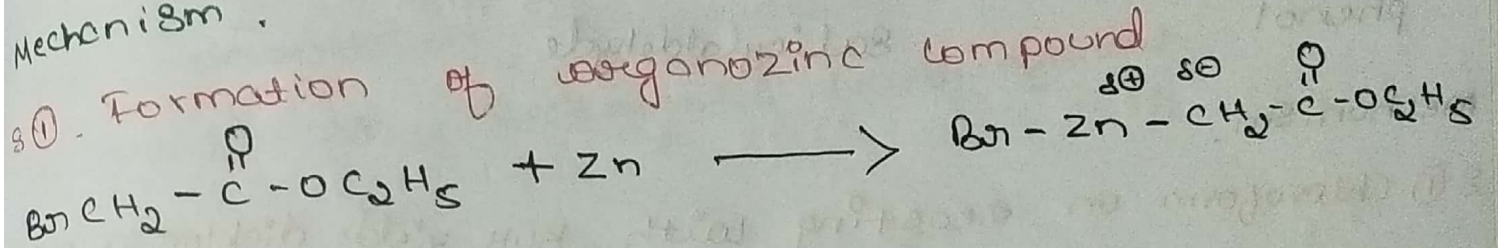


Reformatsky Reaction

Aromatic aldehyde when treated with α -Bromoester yields β -Hydroxyesters in presence of metallic zinc.

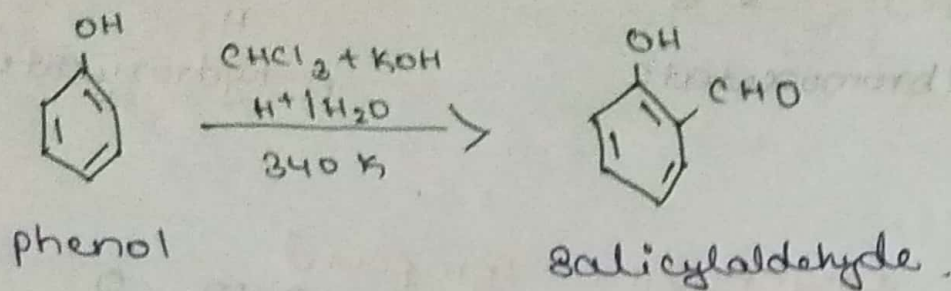


Mechanism.



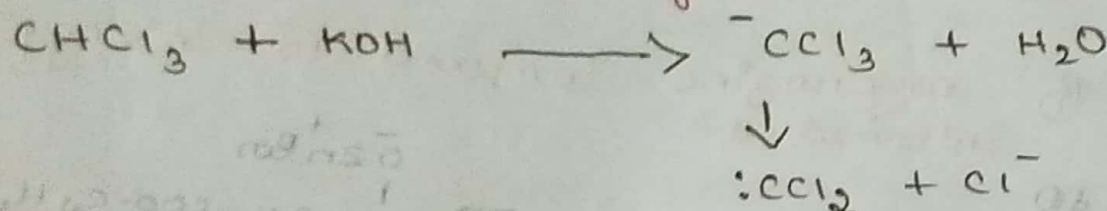
① Reimer Tiemann Reaction

phenol on reacting with chloroform in aq. KOH sol at 340 K, followed by acid hydrolysis yields Salicylaldehyde.

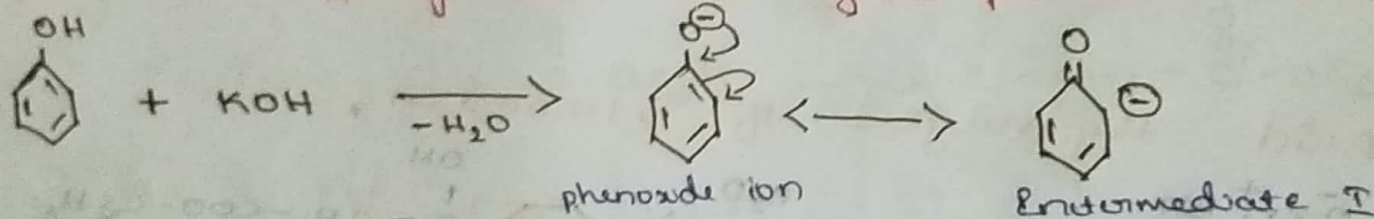


Mechanism:

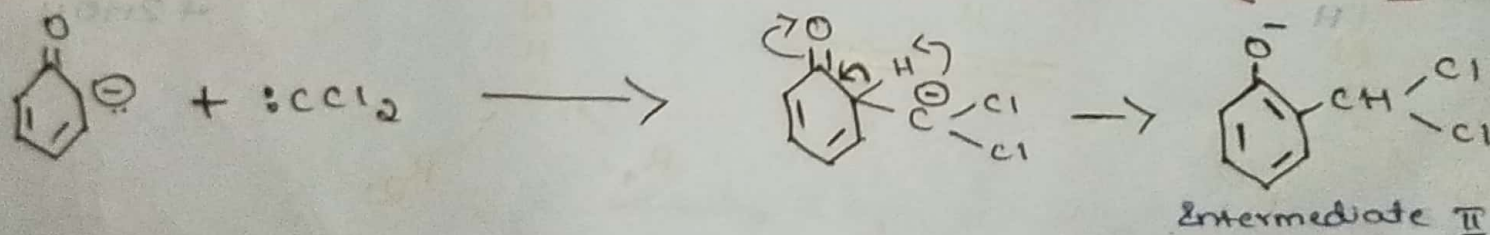
① Chloroform on reacting with KOH yields dichlorocarbene



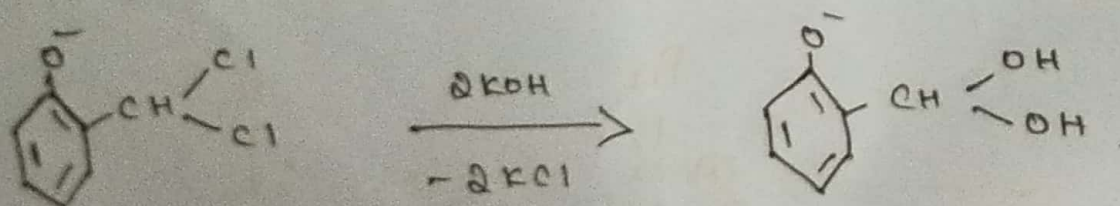
② phenol on reacting with KOH yield phenoxide ion.



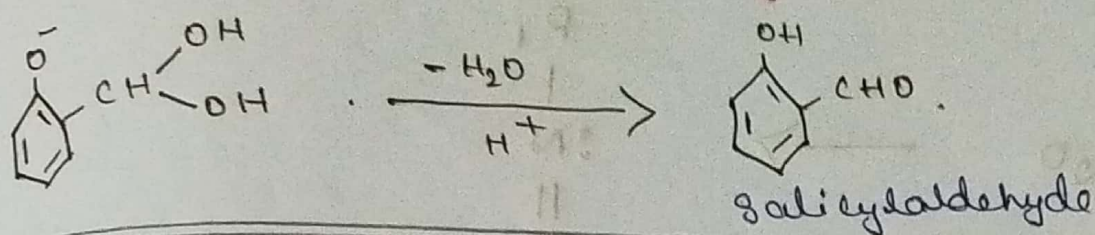
③ Dichlorocarbene act on Intermediate I to yield II



④ Intermediate II reacting with KOH yield III

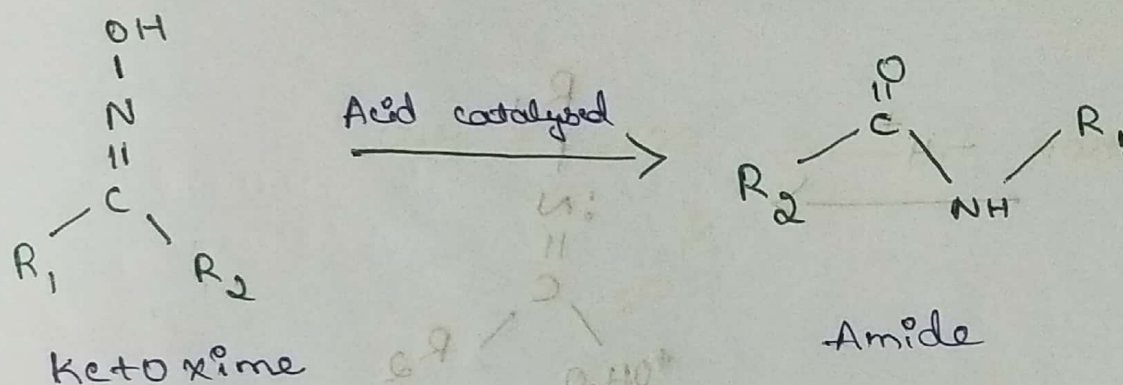


25) Dehydration followed by acid hydrolysis yield salicylaldehyde.



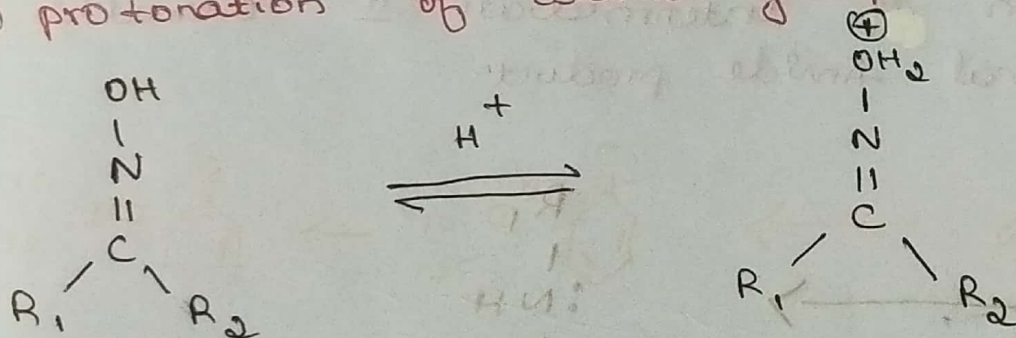
10) Beckmann's Rearrangement

The acid catalysed rearrangement involving the conversion of ketoxime to an amide is known as Beckmann's rearrangement.

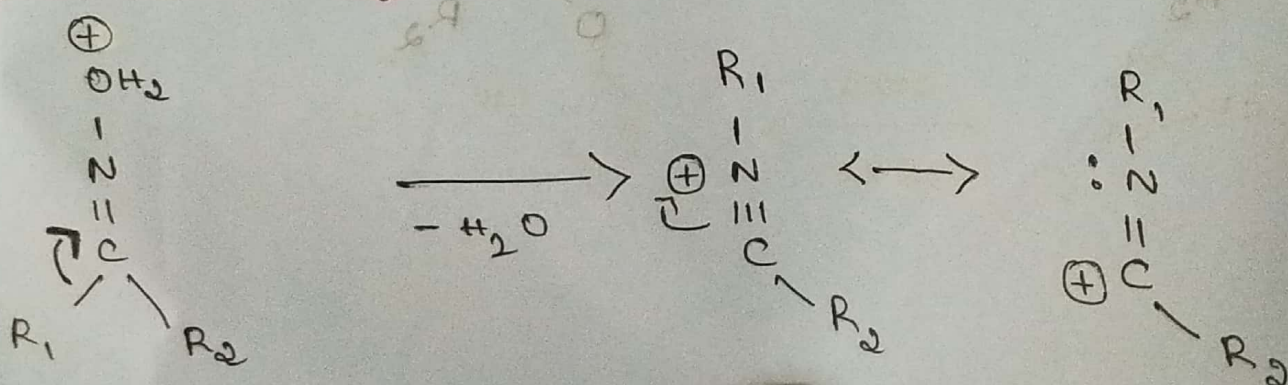


Mechanism.

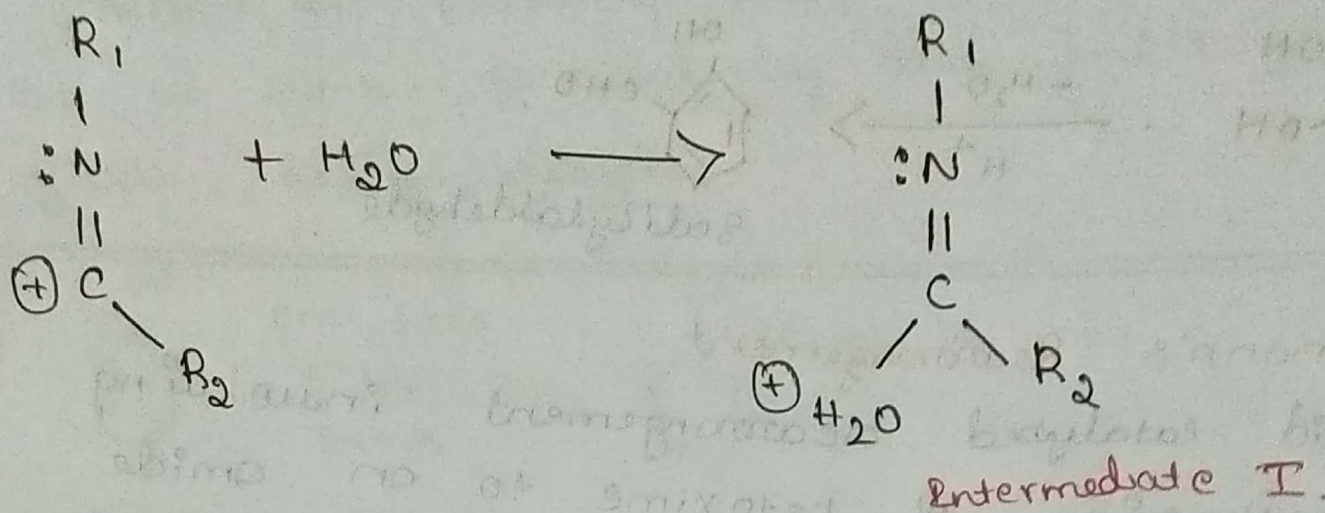
① protonation of alcohol group



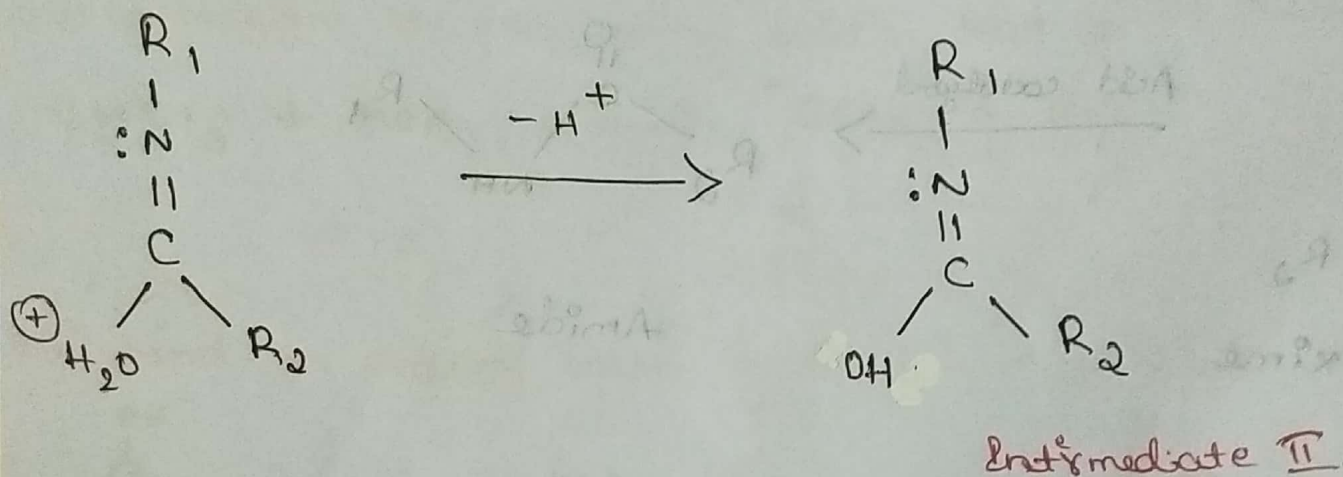
② Formation of carbocation by release of H_2O molecule



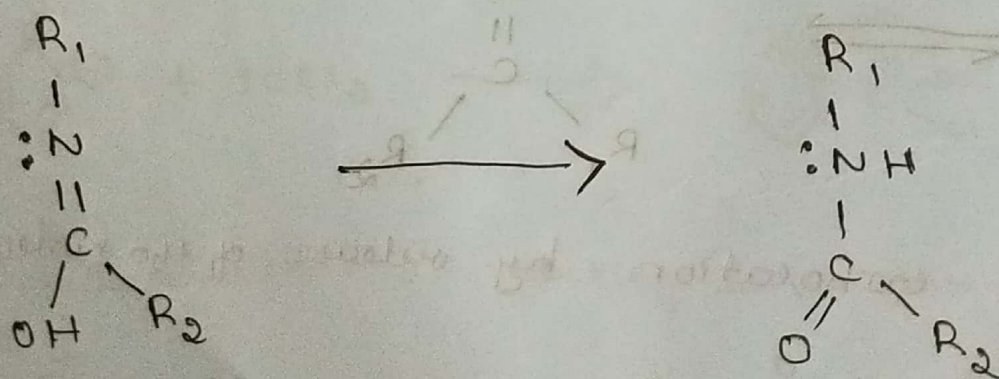
③ Attack of H_2O on carbocation to yield Intermediate I



④ Deprotonation of Entr I to form Entr II



⑤ Tautomerism of Intermediate II results in the final Amide product.



2 mark important concepts

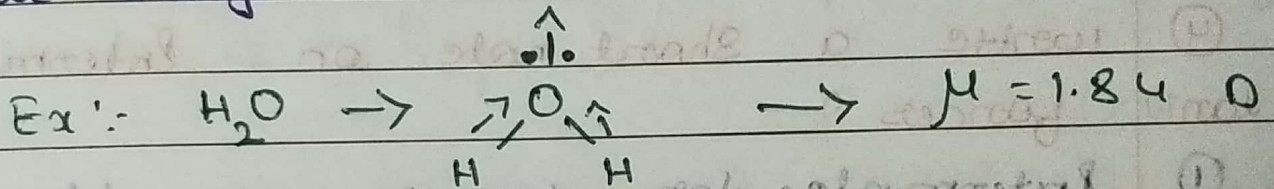
① Define polarity and dipole moment with ex

① A bond becomes polar covalent if the shared pair of e^- are unequally shared b/w the two atoms.

5

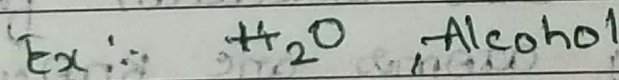
② It is the product of magnitude of the charge and distance b/w the centres of positive and negative charge

10

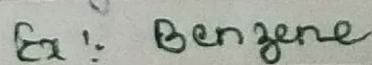


② What are protic and Aprotic Solvents? Give Ex

① Protic Solvents are the solvents containing H^+ ions which can be readily donated to other reagents



② Aprotic Solvents are the solvents which lack H^+ ions which do not donate or accept protons





③ Explain Lewis Theory of Acids & Bases.

① Lewis Acid: A species that accepts an electron pair.

5

② Lewis Base: A species that donates an electron pair.

④ Write a short note on Intermolecular forces.

① Intermolecular forces are attractive and repulsive forces operating b/w interacting atoms.

② 15 Attractive Intermolecular forces operating b/w interacting atoms are known as van der Waal's forces.

③ Dispersion force, Dipole-Dipole force, Dipole-Induced Dipole, Hydrogen bonding are some Attractive forces.

20

Q5) why CCl_4 & methane have 0 dipole moment

Ans ① In methane, there is no much difference in electronegativity of C and H. Hence the resultant dipole moment of all bonds is 0. Each bond has a very low dipole moment which is cancelled out by each other.

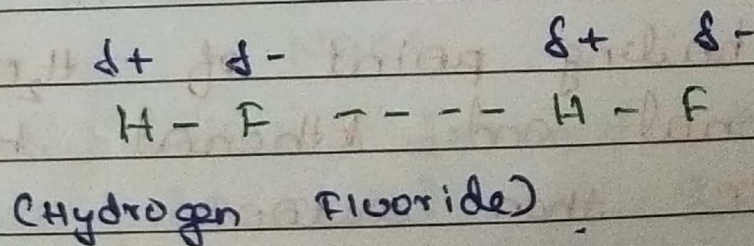
② In CCl_4 , there are four equivalent bonds, four dipole moments cancel out each other, hence the resultant dipole moment of all bonds is 0.

Q6) which molecule is polar & why? CH_3Cl & CH_4

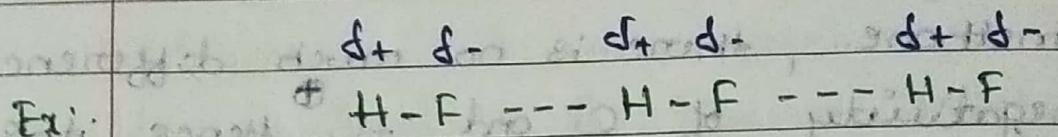
Ans In CH_3Cl , chlorine being most electronegative dipole moment b/w C and Cl is more. Hence the molecule is polar.

Q7) Define and classify hydrogen bond with examples.

Ans Attraction b/w hydrogen & electronegative atom of other molecule is called hydrogen bonding.

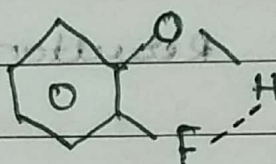


①. Intermolecular H-bonding - other molecule



②. Intermolecular H-bonding - same molecule

Ex. ortho fluorophenol.

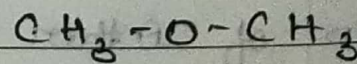
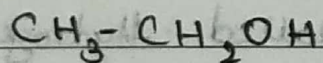


10

⑧. which is having more boiling point?
 Dimethyl ether or ethanol

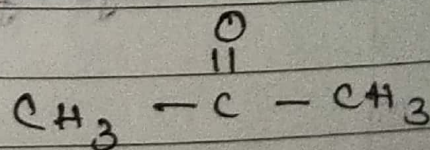
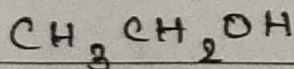
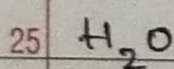
Ans Ethanol have more boiling point than Dimethyl Ether, Since Alcohol possess Hydrogen bonding, will have much higher boiling point.

15



20

⑨. why boiling point of H_2O is more than Ethanol and Ethanol boiling point is more than acetone

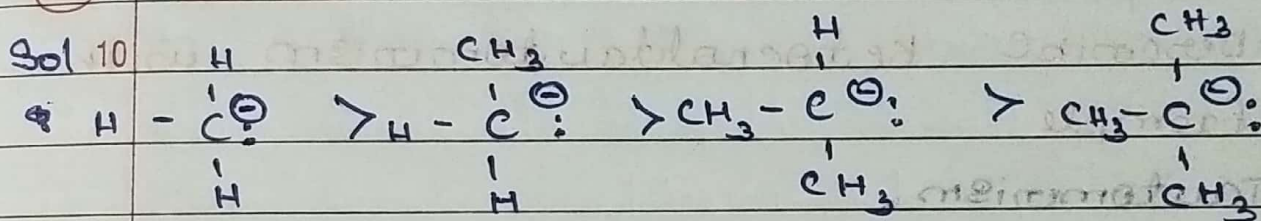


25

①. Hydrogen bonding b/w the molecules of H_2O is higher than the bonding b/w molecules of ethanol.

②. Hydrogen bonding b/w o and H is much stronger than in Ethanol, compare to Hydrogen bonding in Acetone

(10) Write stability of carbocation



Stability of carbocation decreases with increase in donating group

(11) Define ionic and non-ionic solutes give examples

① Solutes which exists as ions when dissolved in solvent are called ionic solvents
NaCl

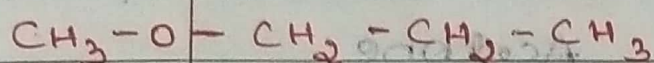
② Solutes which doesn't exists as ions when dissolved in solvents are called non-ionic solvents

25

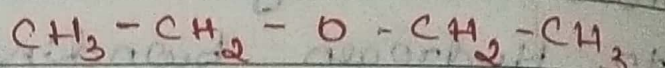
Methane, CCl_4

(12) Define metamerism with ex

Compounds having same molecular formulae but different distribution of alkyl group around functional group show metamerism



Methoxypropane

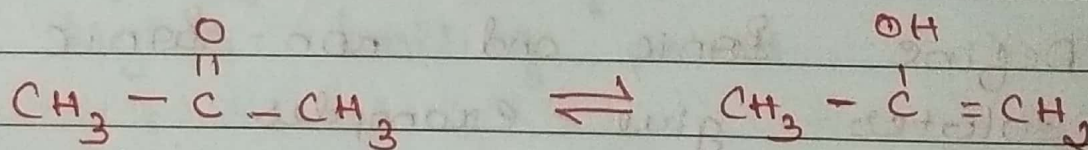


Ethoxyethane

(13) 10 Describe keto-enol tautomerism with example

Tautomerism

Compounds having same molecular formula but differ in the position of hydrogen atom and are in dynamic equilibrium. Show tautomerism



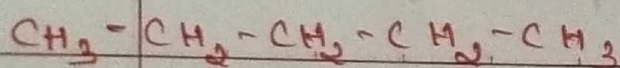
Acetone (propanone)

Prop-1-en-2-ol

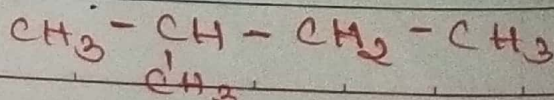
Keto form

Enol form

(14) Define structural formula, give ex. Compounds having same molecular formula but different structural formula show structural isomerism



n-pentane



2-methylbutane

(15) which of the following compounds would you predict to be able to form H-bonding?

① Ethanol

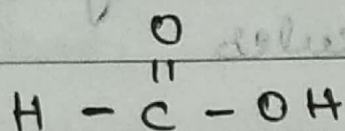
② Diethylether

Ans Ethanol, hydrogen bonding can occur b/w ethanol molecules

① write str & IUPAC Name of following compounds.

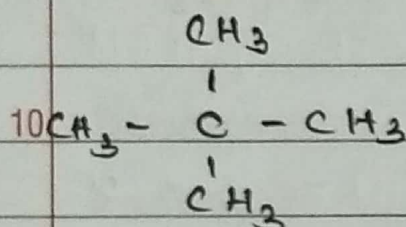
① Formic acid

5



methanoic acid

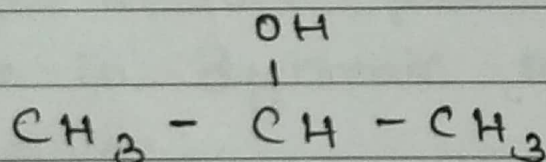
② Neopentane



2,2 dimethyl propane

③ Isopropyl alcohol

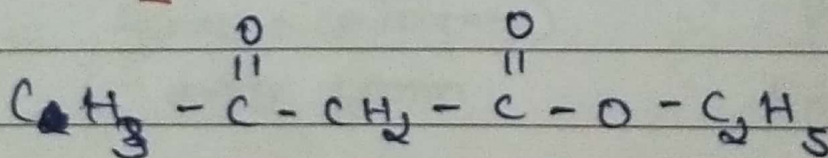
15



propan-2-ol

④ Ethyl acetoacetate

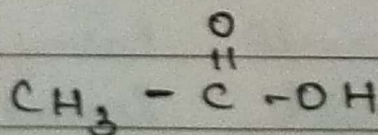
20



Ethyl-oxo-butyrate

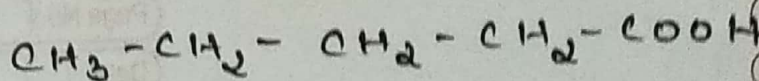
⑤ Acetic acid

25



Ethanoic acid

valeric acid



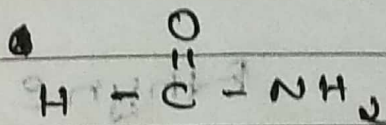
Page No.:



Date:

(6)

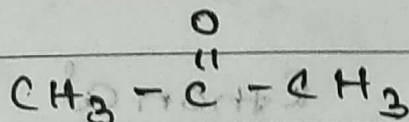
Formamide



methanamide

(7)

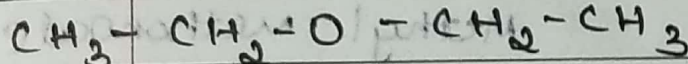
Acetone



propanone

(8)

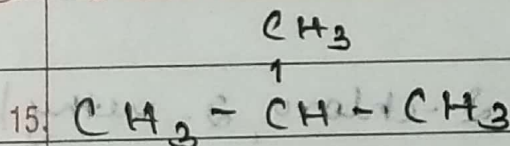
Diethyl ether



ethoxy ethane.

(9)

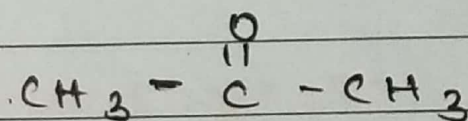
Isobutane



2-methyl propane

(10)

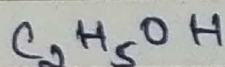
Dimethyl ketone (or) Acetone



propanone

(11)

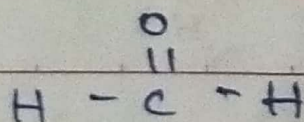
Ethyl alcohol



Ethanol

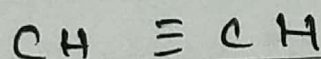
(12)

Formaldehyde



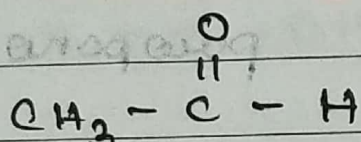
methanal

(12) Acetylene



Ethyne

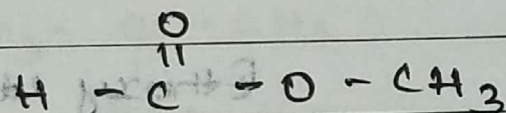
(13) 5 Acetaldehyde



Ethanal

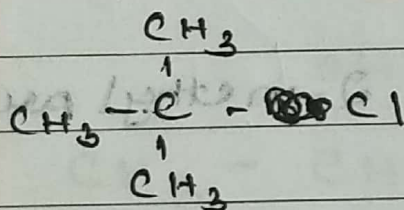
(14) Methyl formate

10

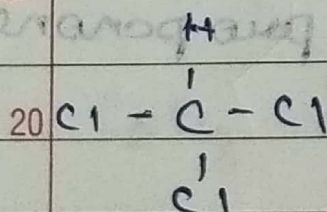


Methyl methanoate

(15) Tert - Butyl chloride

2-chloro, 2-methyl
propane

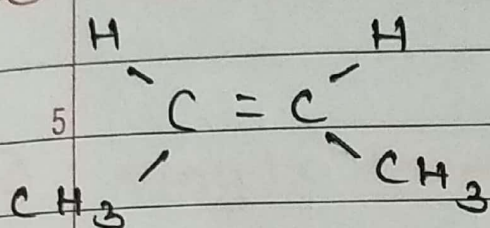
(16) Chloroform



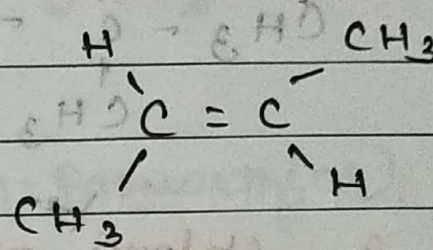
Trichloromethane

(2) write the Sdr of the following

(1) cis and trans - 2-butene

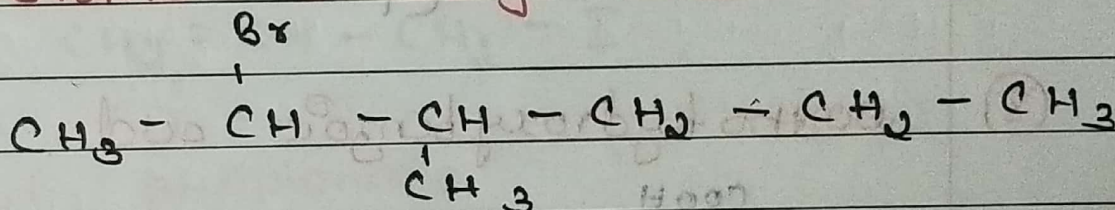


cis-2-Butene

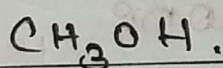


Trans - 2-Butene

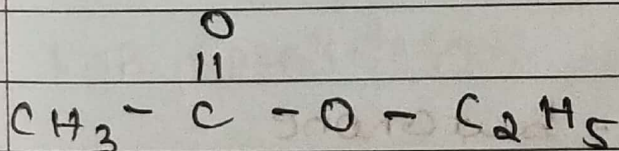
(2) 2-bromo-3-methyl hexane



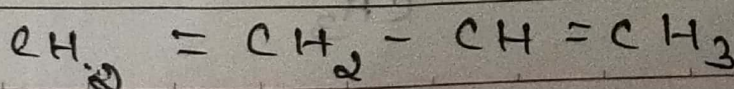
(3) Methanol



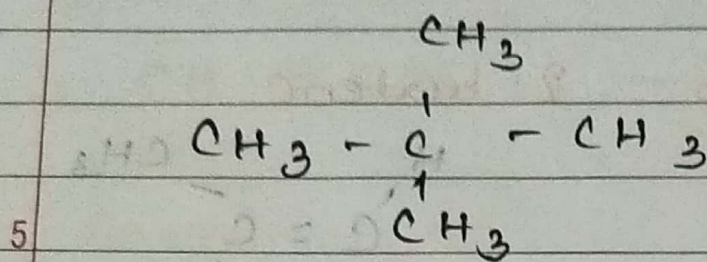
(4) Ethyl acetate



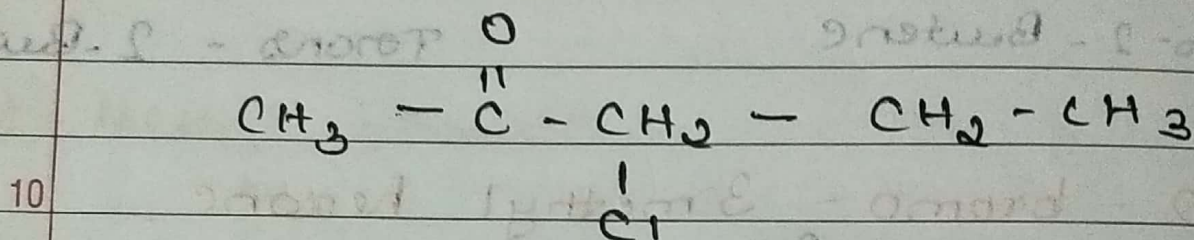
(5) 1,3 butadiene



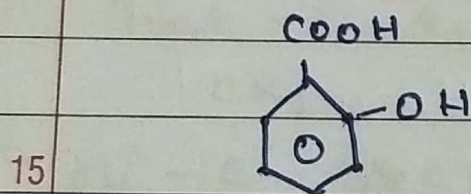
⑥ 2,2 Dimethyl propane



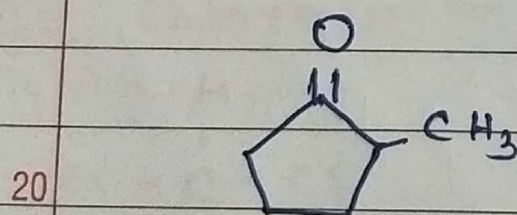
⑦ 3-chloro pentanone



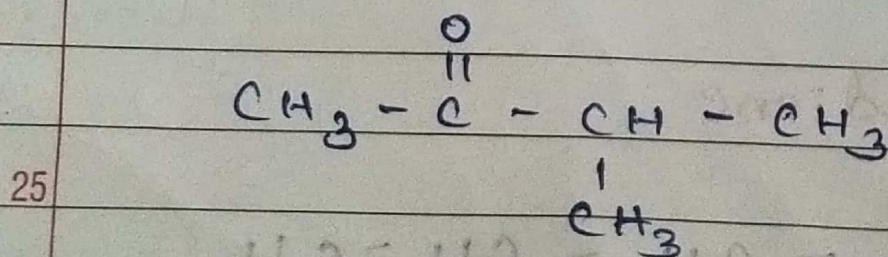
⑧ ortho hydroxy benzoic acid



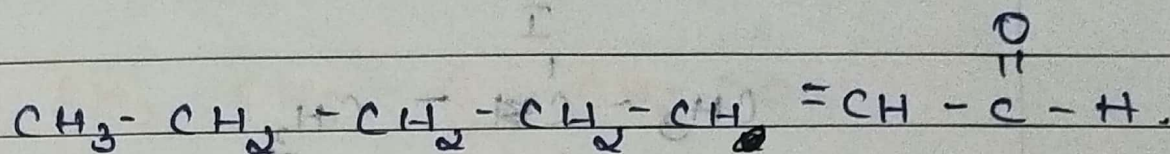
⑨ 2 methyl - cyclopentanone



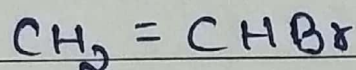
⑩ 3-methyl - 2-butanone



(11) 2-Hexenal



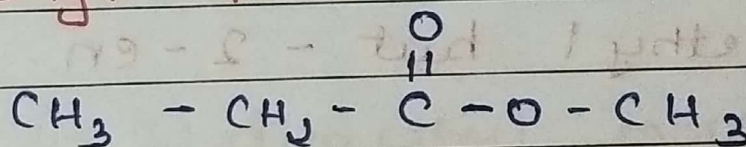
(12) vinyl bromide (1-Bromoethene)



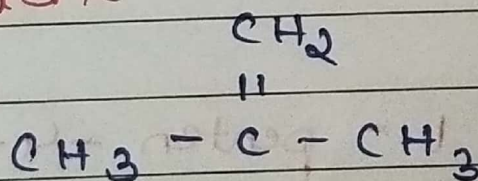
(13) allyl iodide (3-Iodopropene)



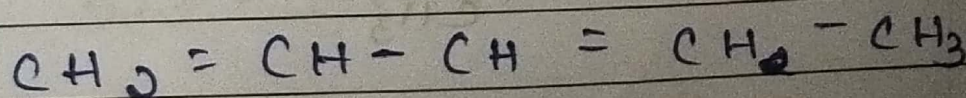
(14) Methyl propionate



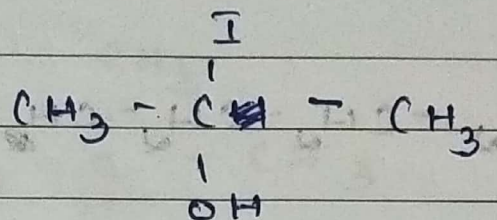
(15) Isobutene



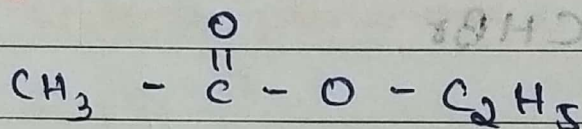
(16) 1,3-pentadiene



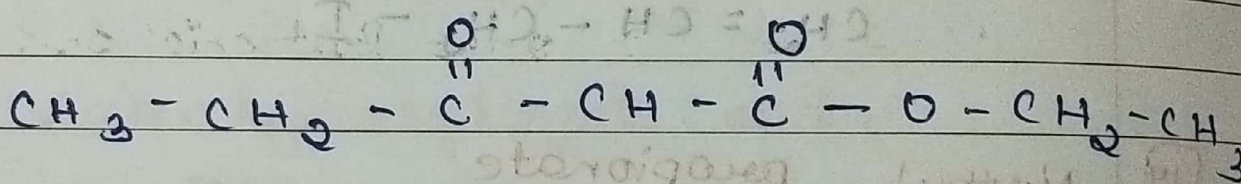
(17) 2-Iodo-2-propanol.



(18) Ethyl ethanoate

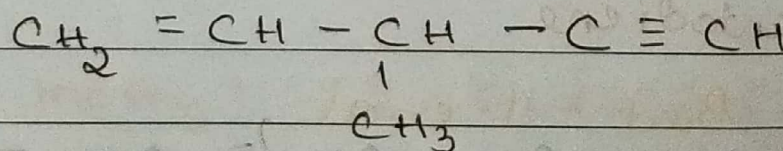


(19) 3-oxo-2-methyl pentanoic acid.

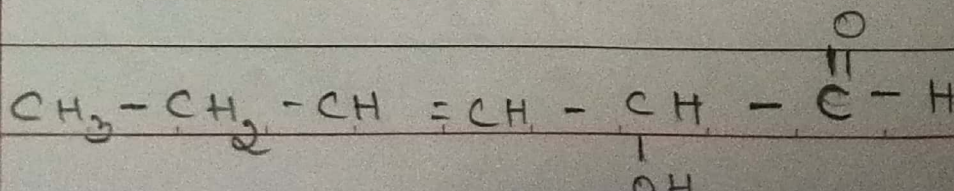


(20) 4-methyl but-2-en, 6-yne

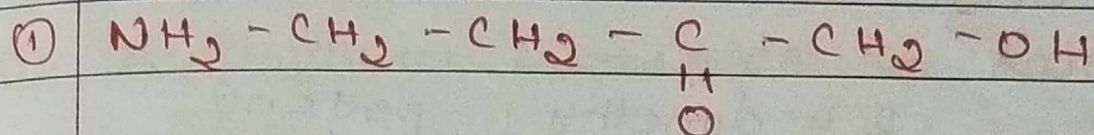
(21) 3-methyl-1-penten-4-yne



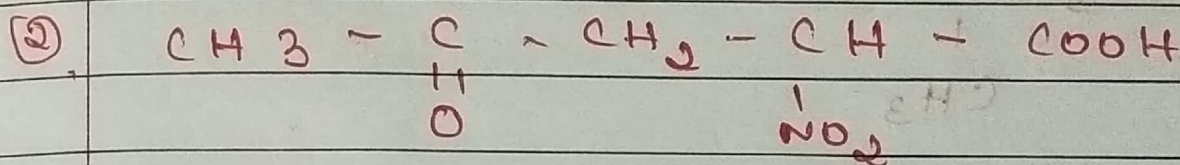
(22) 5-Hydroxy-3-hexenal



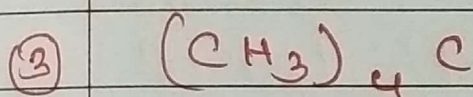
③ write IUPAC names



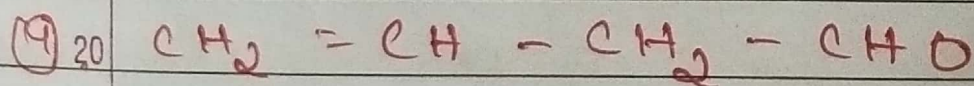
1-amino - 3-one - Butanol



4-Amino - 2-one - Butanoic acid

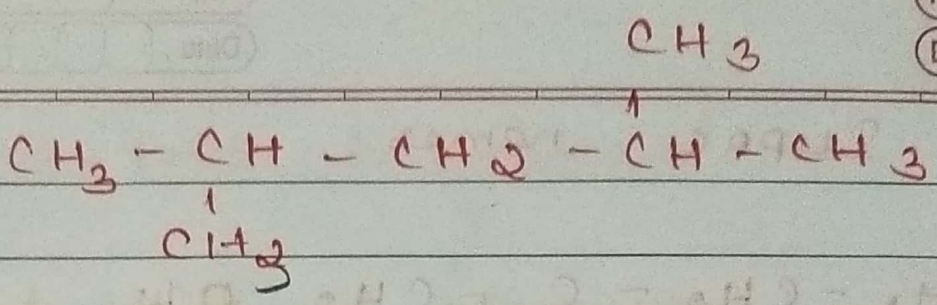


2,2 dimethyl propane



But - 1-enal

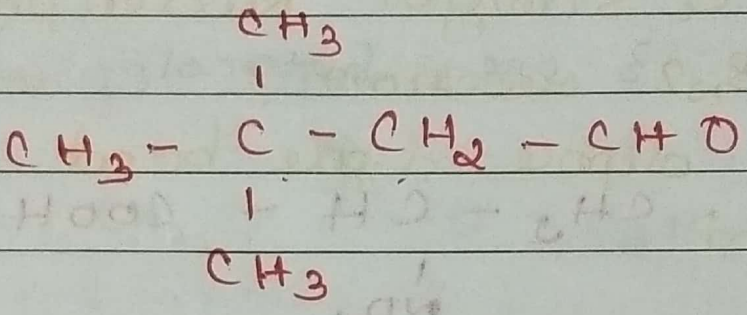
5



2,4-dimethyl 1-pentane

5

8



2,2-dimethyl propanal

10

15

① Role of Nucleophiles on S_N1 & S_N2

S_N2

- ① Nucleophiles participate in Rate determining Step.
- ② High conc & stronger Nucleophiles favours S_N2 reaction.
- ③ It forms dipole-dipole bond with Solvent.

10

S_N1

- ① low conc & weaker Nucleophiles favours S_N1 Reaction.

② Two Difference & Two Similarity b/w S_N1 & $E1$

15

$E1$

S_N1

- | | |
|---|--|
| <p>① Two atoms are Eliminated from Two adjacent carbons to form alkenes</p> <p>② There is no Substitution of atom</p> | <p>① One atom or group of atom is substituted by other</p> <p>② There is no Elimination of atom or group</p> |
|---|--|

F.1

S.1.

① Removal of halogen from Alkyl halide

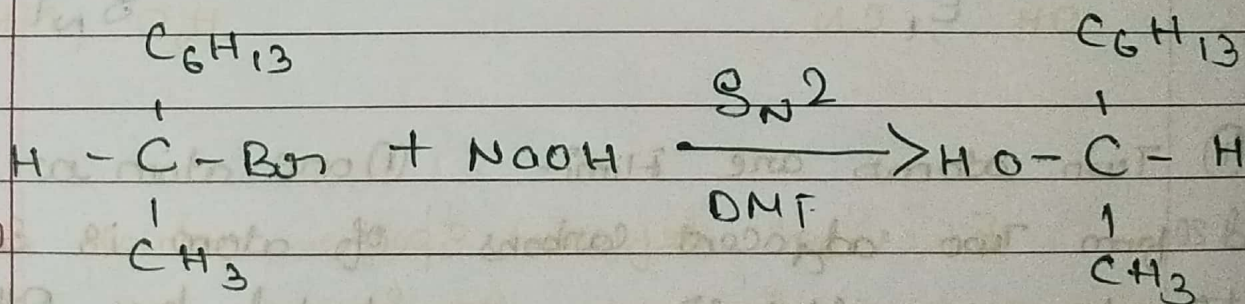
① Removal of Halogen

② Mechanism Involves formation of Carbocation

② Mechanism Involves formation of Carbocation

③ Walden Inversion

Ans. In a chemical reaction of organic compound containing chiral carbon, if it gives the product having opposite configuration that process called Walden Inversion



(-)-2-bromooctane

(+)-2-octanol

In $\text{S}_\text{N}2$ reaction of chiral organic compound, we get the product with complete Stereochemical Inversion

(14) which is stable, methyl carbocation or Tertiary butyl carbocation? give reason

Ans: Tertiary butyl carbocation is more stable.

(1) In Tertiary butyl carbocation there are three CH_3 groups which involve in hyperconjugation to stabilize it

(5)10 Define Nucleophiles, classify with ex Electrophiles

(1) Nucleophiles

Electron rich species which can donate electrons to Electron deficient species

Charged ions

Ex: OH^- , CN^-

Neutral Molecules

H_2O , NH_3

(2) Electrophiles

Electron deficient species which accepts e^- from e^- rich species

charged ions

H^+ , NO_2^+

Neutral molecules

Alkyl halide

$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$

⑥ Diff b/w E_1 & E_2

E_1

E_2

① 5 unimolecular Reaction

① Bimolecular Reaction

② Formation of carbocation

② No carbocation formation

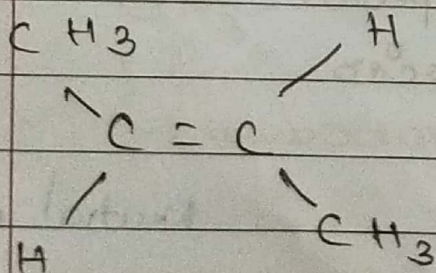
10 ③ It doesn't require strong base

③ It requires strong base

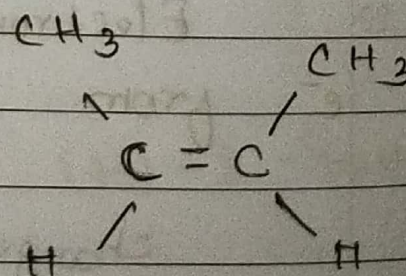
④ No stereochemistry

④ leaving group must be opp to H removed

⑦ which is more stable trans-2-butene or cis-2-butene?



trans

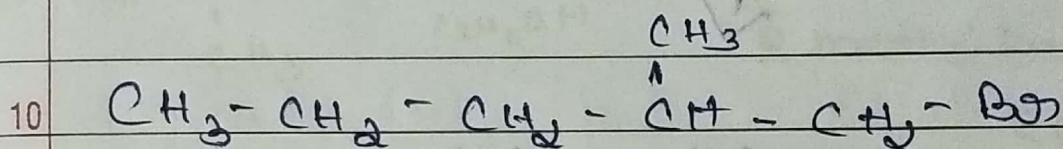


cis

- ① Trans - 2 - butene is more stable
 ② Due to steric hindrance of
 Me substituents in cis - 2 - butene
 it is less stable.

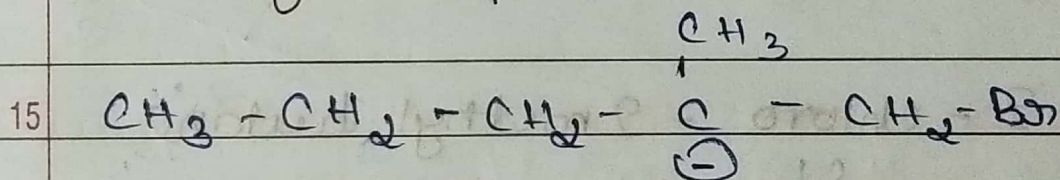
⑧ Dehydrohalogenation product of

- ① 1-bromo - 2 methyl pentane.

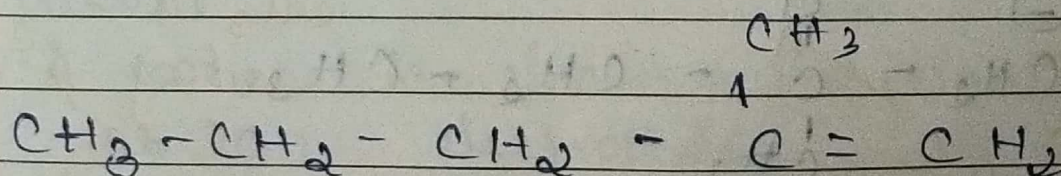


Mechanism

- ① Formation of carbanion by removing Hydrogen
 from β - carbon.



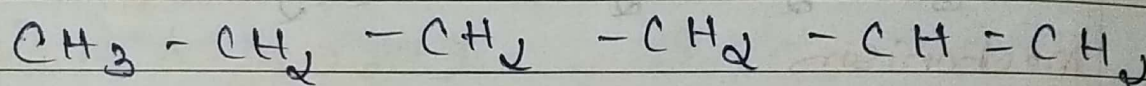
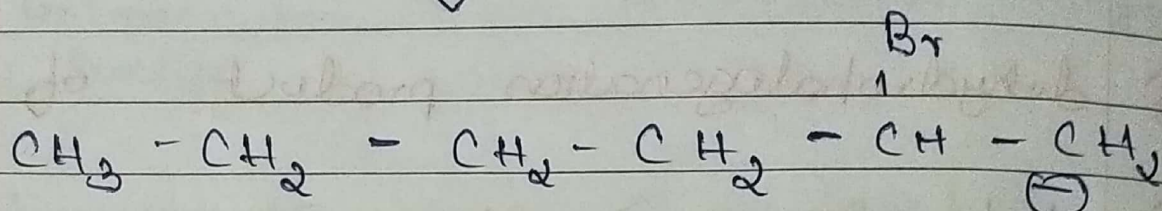
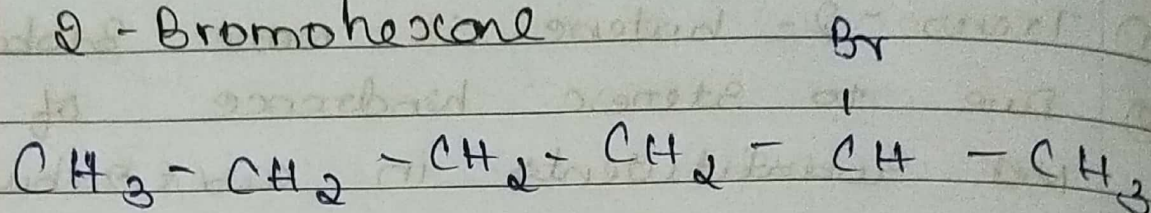
- ② Carbanion loses halide ion to yield
 alkene



2 Methylpent - 1 - ene

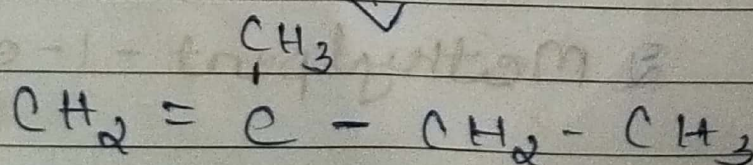
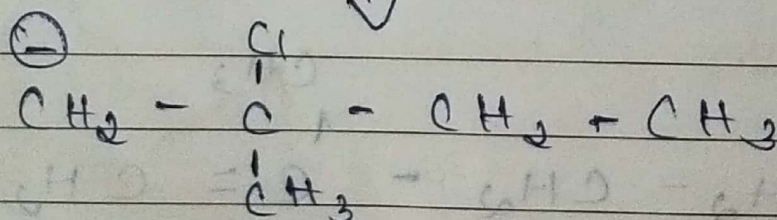
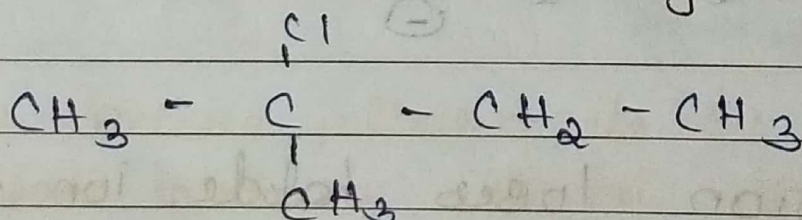


② 2-Bromohexane



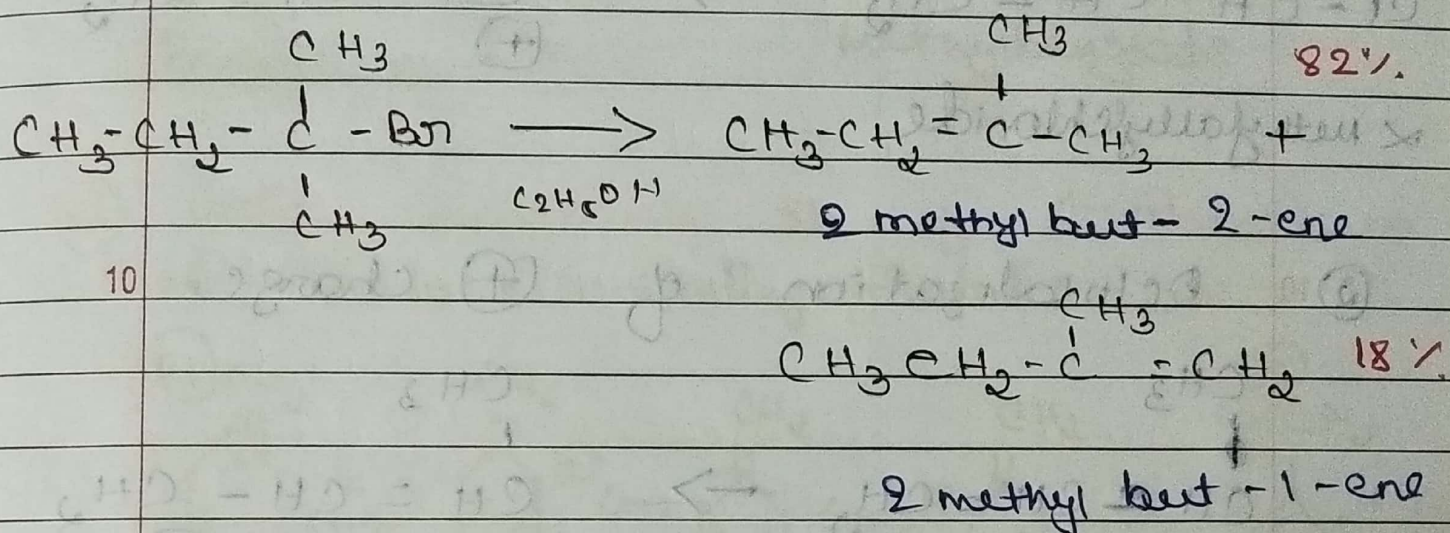
Hexene

⑥ 15 ~~2-chloro~~ 2-methyl butane



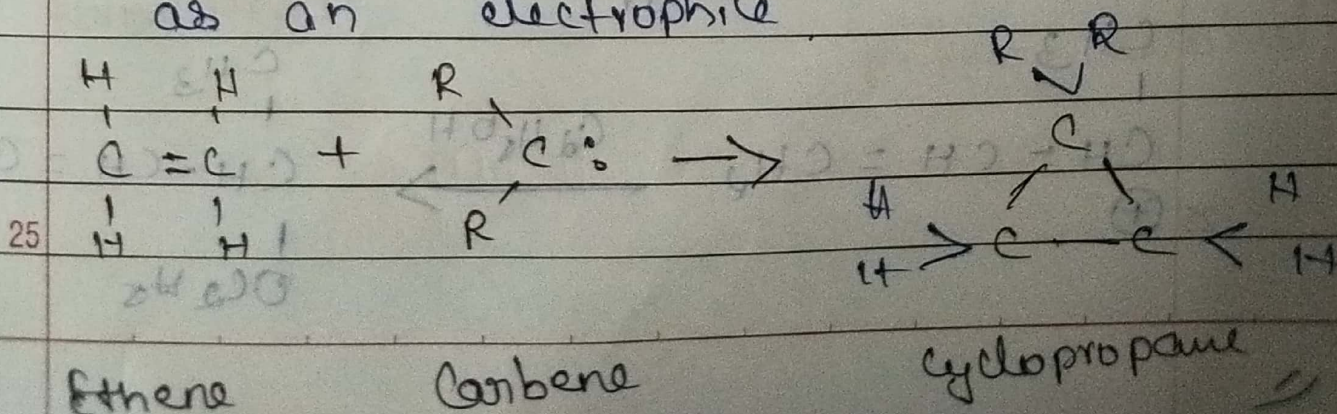
2-methylbut-1-ene

- (9) Saytzeff orientation
when more than one alkene is formed, highly branched and more stable alkene is preferred product.



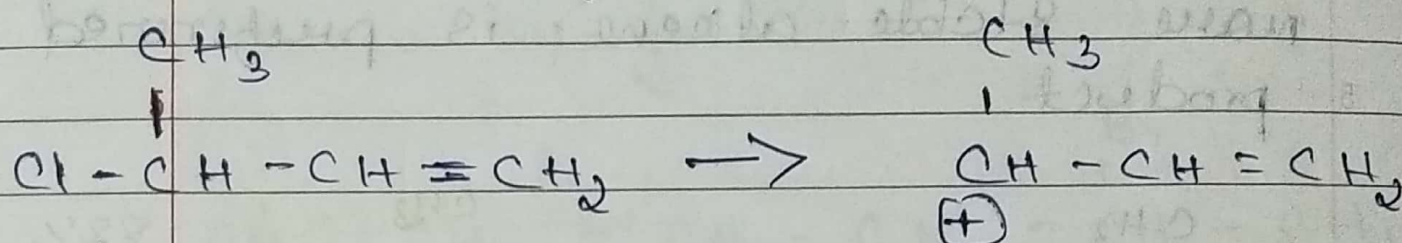
- (10) Write a note on addition of carbene to alkene

- (1) Carbene is electrically neutral with 8 valence electrons in the outer shell.
- (2) The carbene functional group is "half of alkene".
- (3) A carbene is electron-deficient and acts as an electrophile.



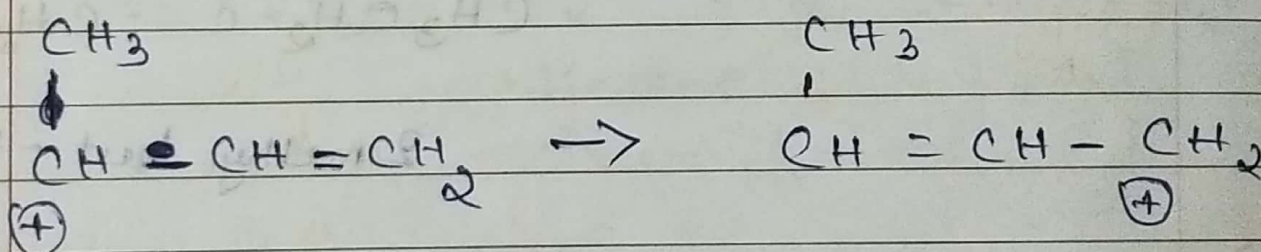
⑪ Allylic rearrangement with e^-

① Formation of carbocation

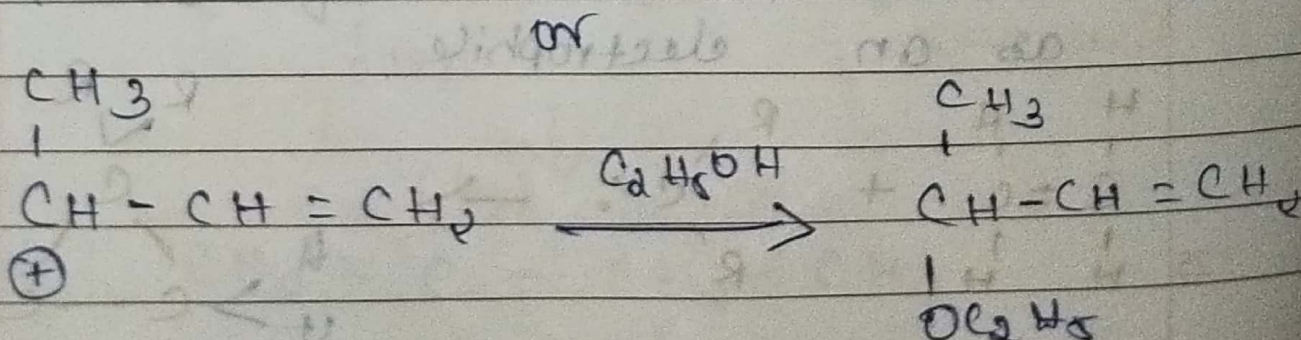
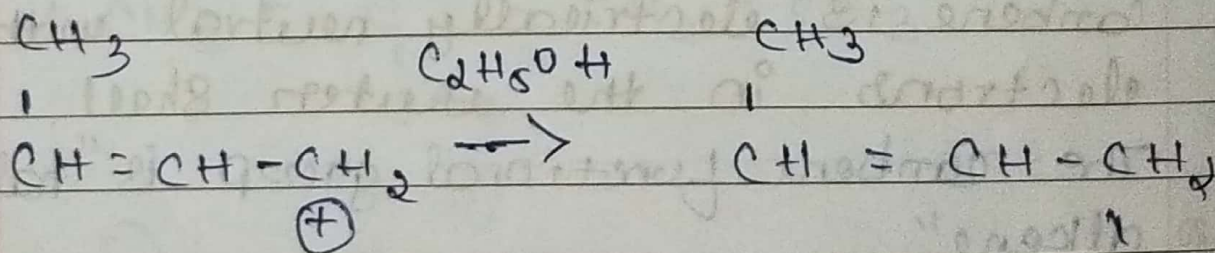


$\times$ methylallylchloride

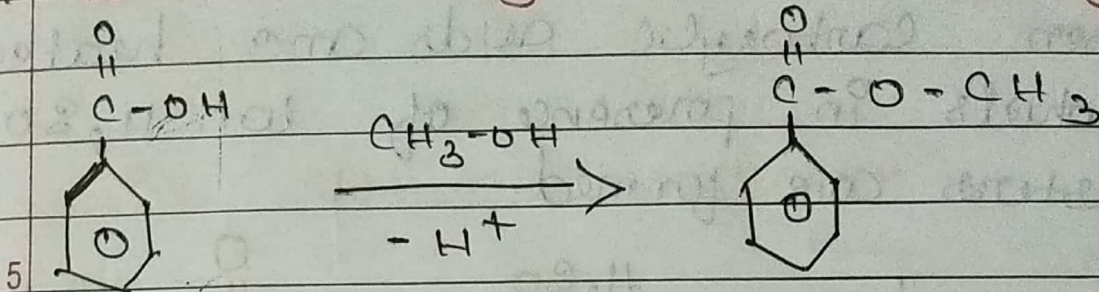
② Delocalization of $\oplus$ charge



③ Attack of nucleophile



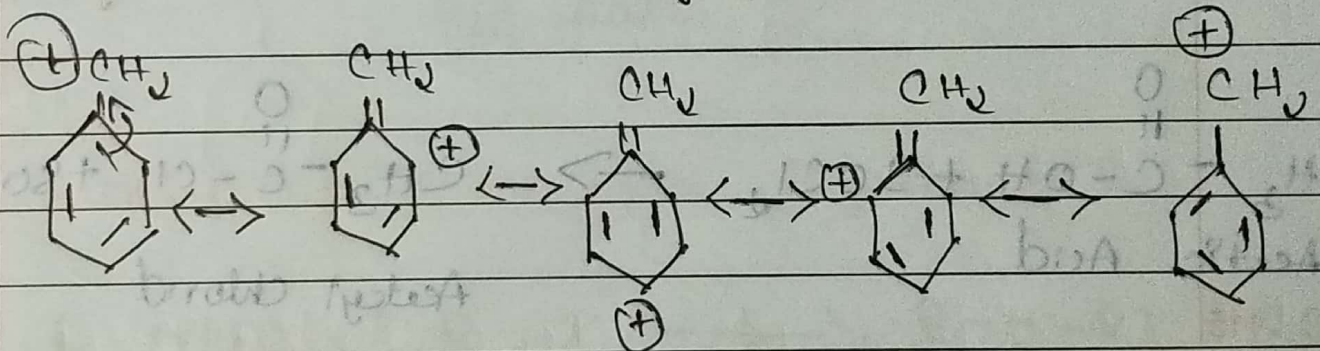
12. Convert benzoic acid to methyl benzoate



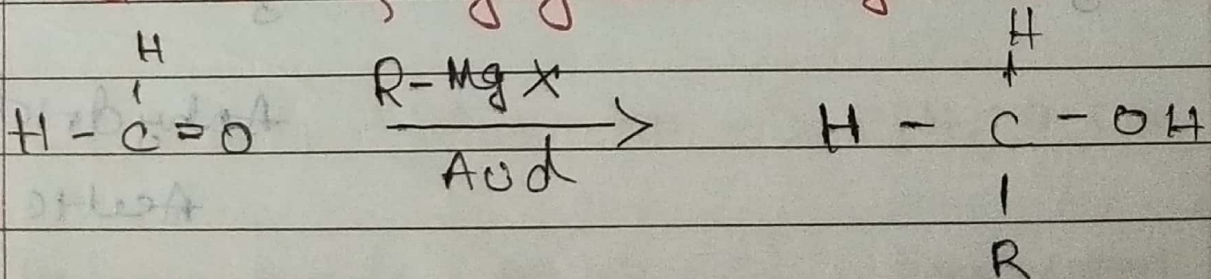
Benzoic acid

Methylbenzoate

13. write resonance str of carbonium
10 carbonium ion = containing trivalent C ion



14. Addition of grignard reagent to carbonyl carbon



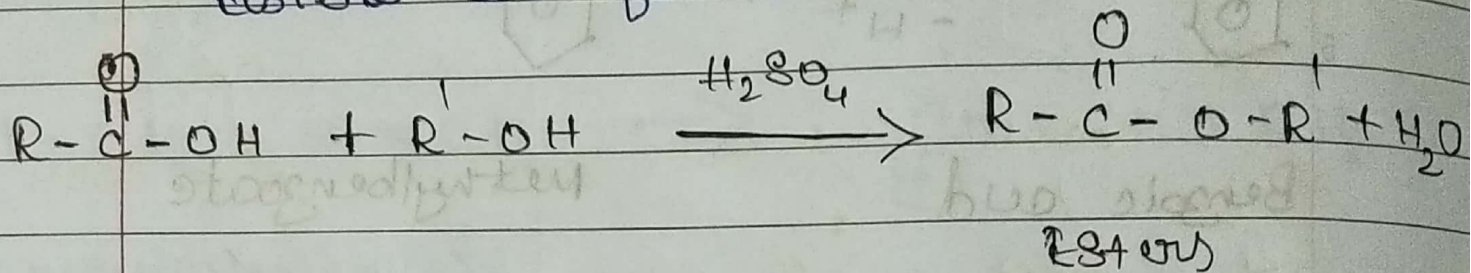
Formaldehyde

primary alcohol

15

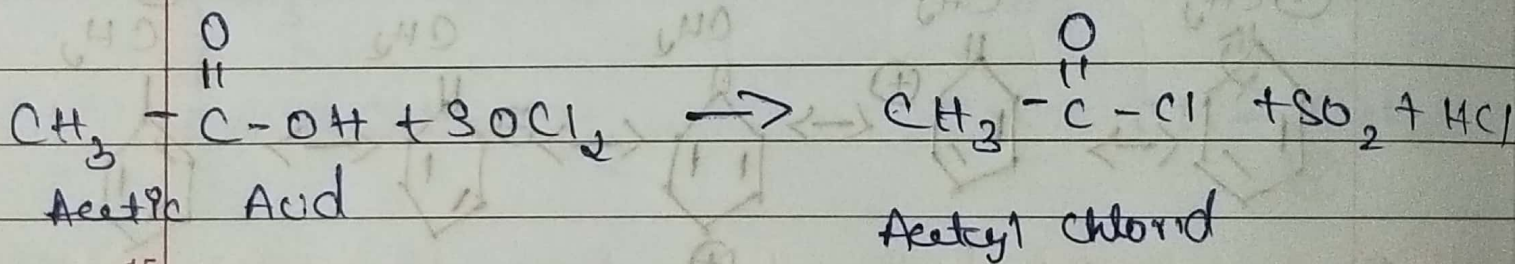
Esterification reaction

when carboxylic acids are heated with alcohols in presence of H_2SO_4 esters are formed

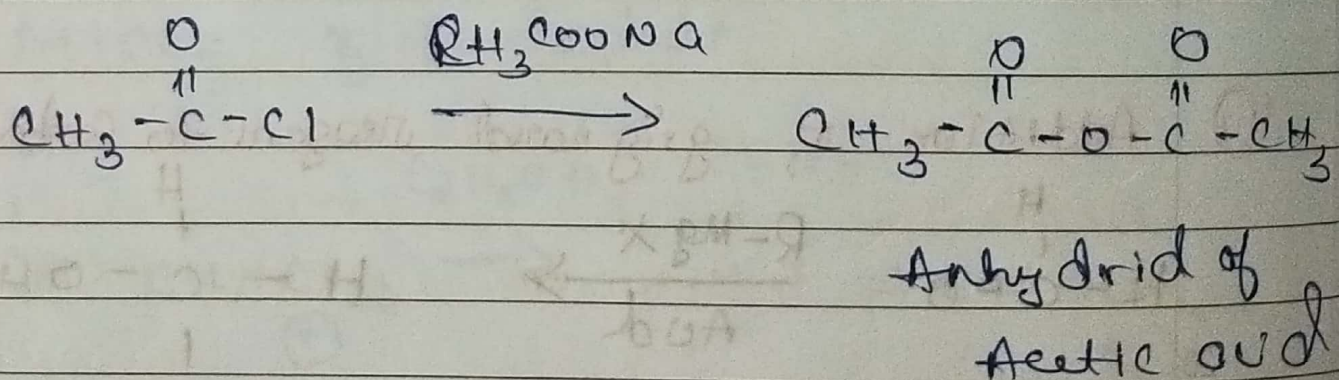


16 10

Conversion of Acid into anhydrides



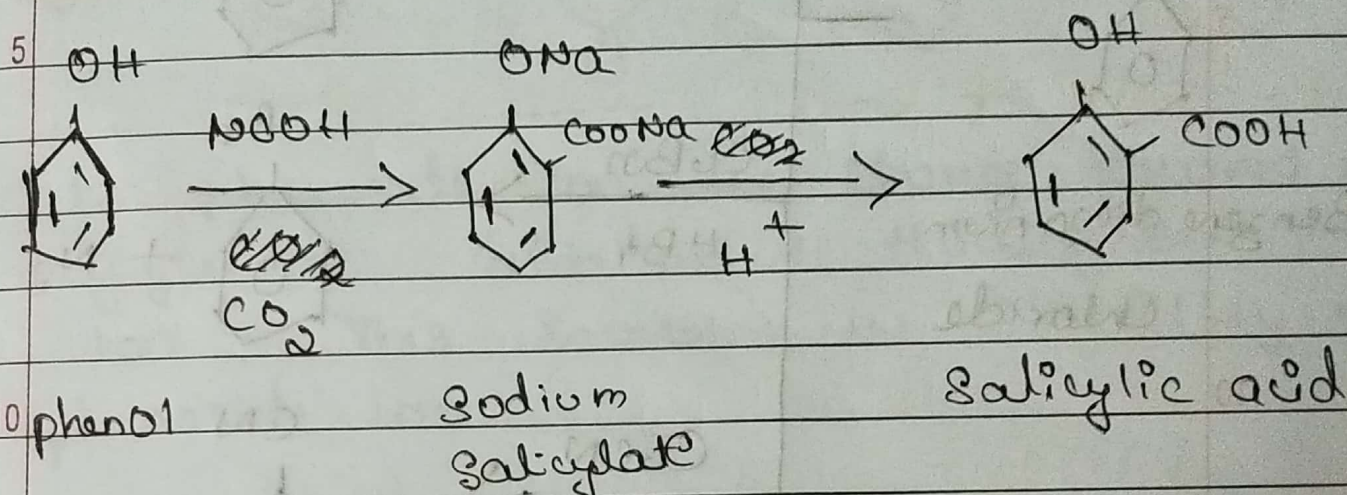
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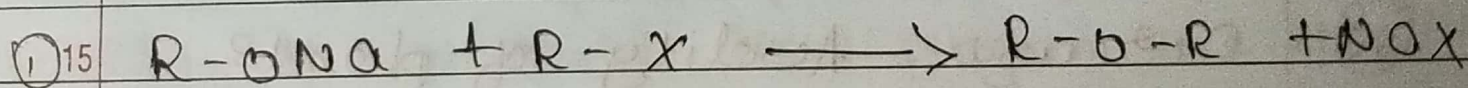
20

25

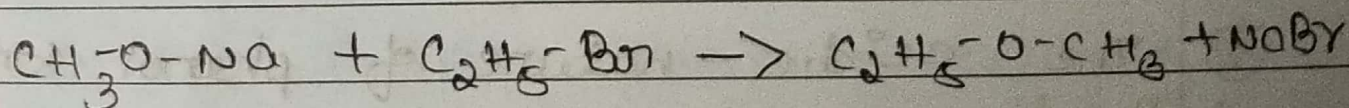
(17) How will you convert phenol into Salicylic acid & write reaction
or
write Kolbe's reaction



(20) write Williamson Synthesis

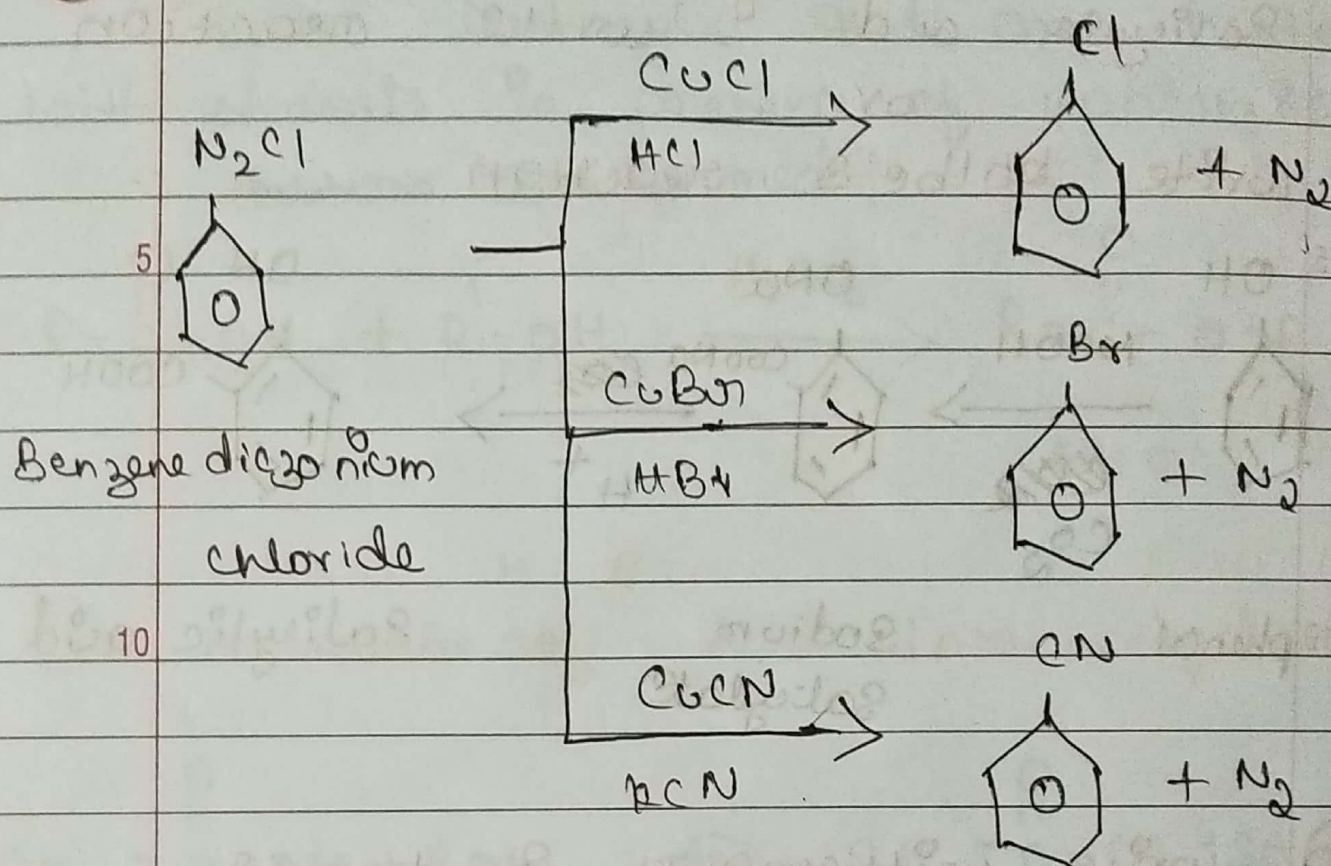


Sodium alkoxide alkyl halide Ether

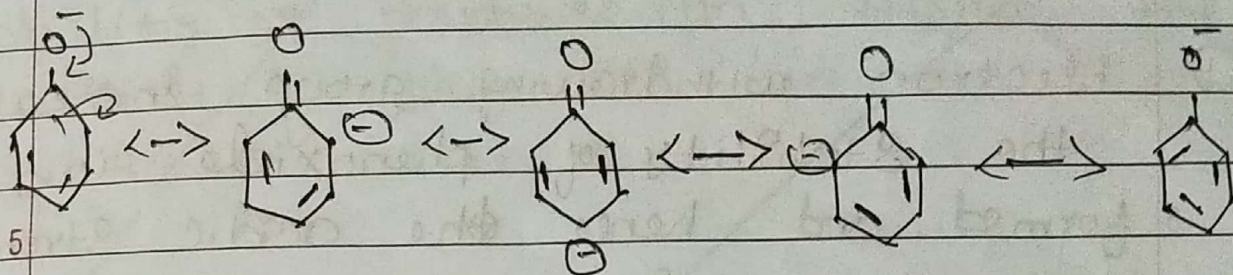


Sodium methoxide Ethyl Bromide Ethyl methyl Ether

(21) outline Sandmeyer's reaction



Resonance stabilization of phenoxide ion



In phenoxide ion the charge present on the oxygen is distributed throughout the ion. This increases the stability of phenoxide ion.

(23) Effect of substituents on acidity of phenols

Ans The acidity of phenol depends on stability of phenoxide ion. Higher the stability of phenoxide ion more is its acidic strength.

Electron donating group on acidity of phenols

① Electron donating group increases e^- density on benzene ring, thereby opposing the release of e^- from oxygen atom to the benzene ring. Hence stability of phenoxide ion decreases.

Ex: CH_3 , NH_2

Electron withdrawing group

- ① Electron withdrawing group increases the stability of phenoxide ion formed and hence the acidic strength of phenol increases.

Ex: NO_2 , $-\text{CHO}$, $-\text{COOH}$

Electron withdrawing group

- ① Electron withdrawing group decreases the e^- density on benzene ring. Hence benzene can effectively withdraw the electron from oxygen of phenoxide ion. Hence stability of phenoxide ion increases.

Ex: NO_2 , $-\text{CHO}$, $-\text{COOH}$

④ O-nitrophenol is more acidic than phenol

(i) The acidity of phenol depends on stability of phenoxide ion. Higher the stability of phenoxide ion more is its Acidic Strength.

5

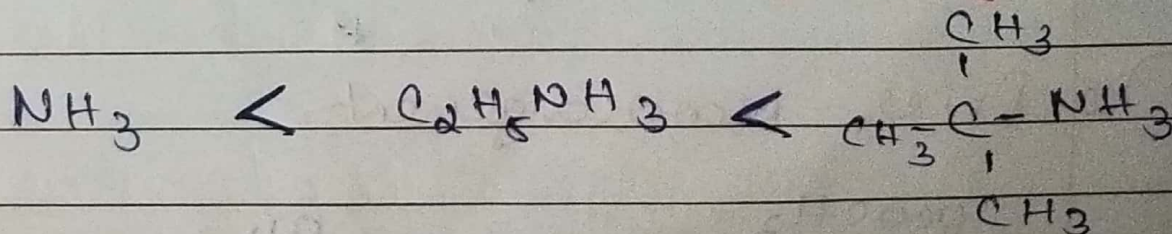
Even
(i) NO_2 group being even decreases e^- density on benzene ring. Hence benzene can effectively withdraw the e^- from oxygen of phenoxide ion. Hence stability of phenoxide ion increases in o-nitrophenol than in phenol.

15

Hence o-nitrophenol is more acidic than phenol.

(ii) Compare basicity among ammonia, ethylamine, tertiary butylamine.

20



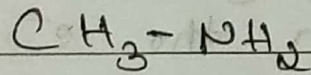
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Due to the presence of e^- donating group basic strength of aliphatic amines should increase with increase in the no of alkyl groups.

⑥ what are primary and secondary amine
give ex

① primary amines

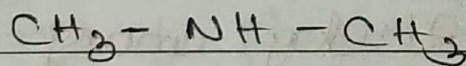
primary amines are obtained by replacing one H atom of ammonia (NH_3) by alkyl group.



Ex: Methylamine.

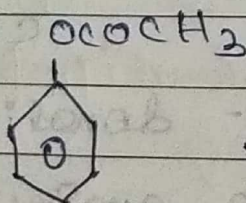
② Secondary amines

Secondary amines are obtained by replacing two H atoms of ammonia by alkyl group

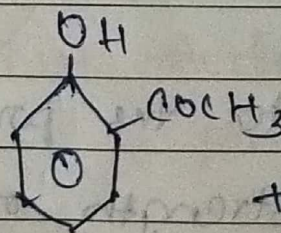
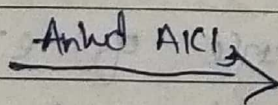


Ex: Dimethylamine

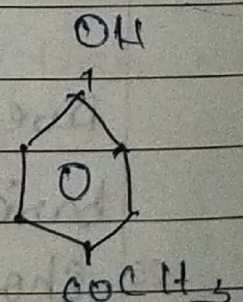
⑦ Fries Rearrangement



phenyl acetate

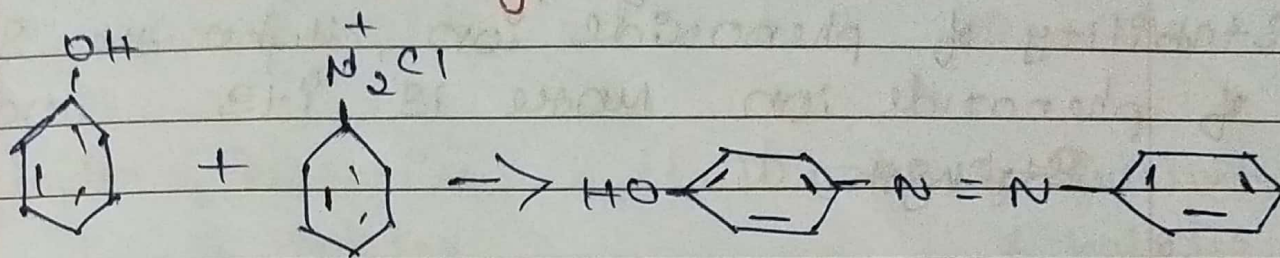


o-Hydroxy
acetophenone



p-Hydroxy
acetophenone

Q8) Diazocoupling reaction



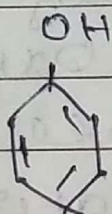
phenol

Benzene

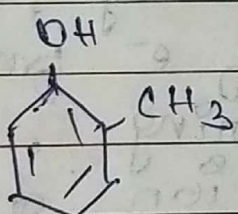
Diazonium

chloride

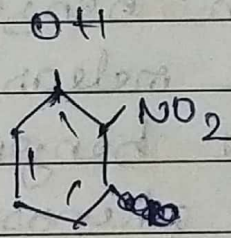
Q9) Arrange order of Acidic Strength phenol, o-cresol, o-nitrophenol, 2,4 dinitrophenol



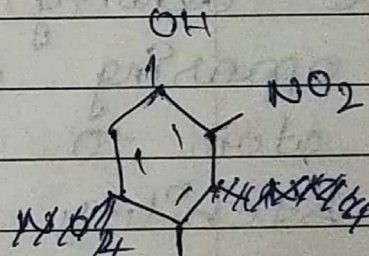
phenol



o-cresol



o-nitrophenol



2,4 dinitrophenol

20

2,4 dinitrophenol > o-nitrophenol > phenol > o-cresol

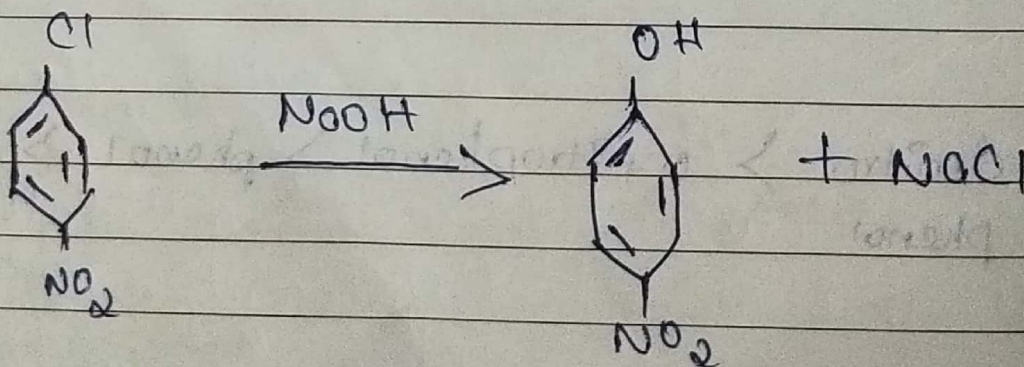
25

The acidity of phenol depends on stability of phenoxide ion. Higher the stability of phenoxide ion more is its acidic strength.

→ Electron withdrawing group decreases the e^- density on benzene ring. Hence benzene can effectively withdraw the e^- from oxygen of phenoxide ion. Hence stability of phenoxide ion increases.

→ Electron donating group increases the e^- density on benzene ring, thereby opposing the release of e^- from oxygen atom to the benzene ring. Hence stability of phenoxide ion decreases.

(10) Give one ex of Nucleophilic aromatic substitution.



p-Chloronitro
benzene

p-Hydroxy
Nitrobenzene.

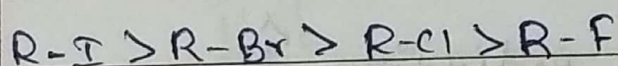
~~Nucleophilic~~~~Nucleophilic~~

(11) Aliphatic Substitution Reaction

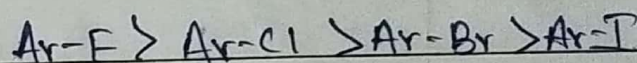
Aromatic Substitution Reaction

① order of reactivity of halides

5



① order of reactivity of halides.

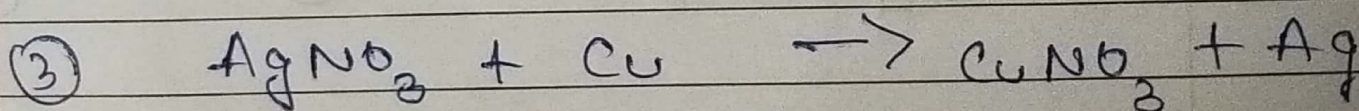
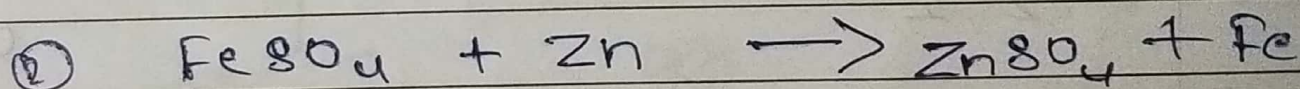
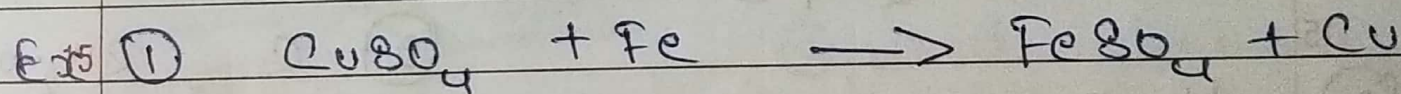


② formation pentavalent Transition State

10

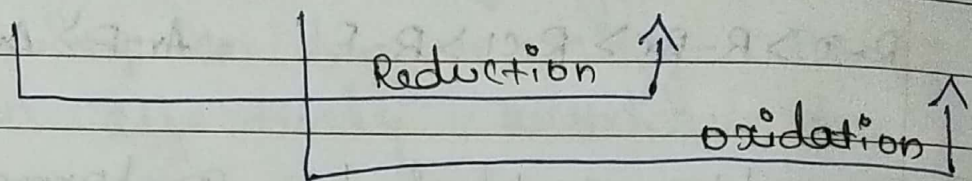
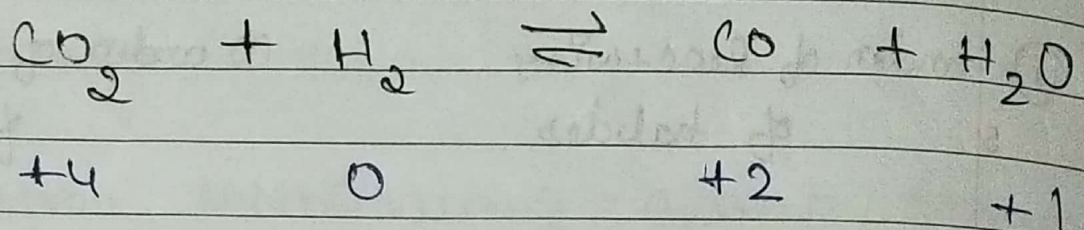
② formation of Trivalent Transition State

(12) Examples for displacement Reactions



20

13 give one ex of oxidation -
Reduction Reaction

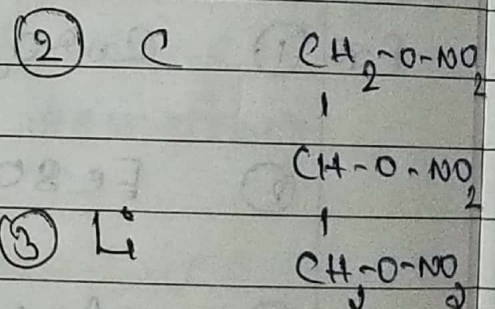


14 oxidizing agent Reducing agent

① Dichromate ion
($\text{Cr}_2\text{O}_7^{2-}$)

① CO

② H_2O_2



③ KMnO_4

③ Li

15 Write str & uses of

(i) Nonillan

(v) Lactic acid

(ii) nitroglycerin

(vi) Dimercaprol

(iii) Tartaric acid

(vii) SLS

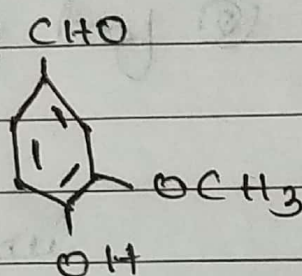
(iv) glyceryl trinitrate

(viii) ~~nephrenin~~
nephrenin

16) preparation & uses of Aspirin

1) vanillin

5



uses

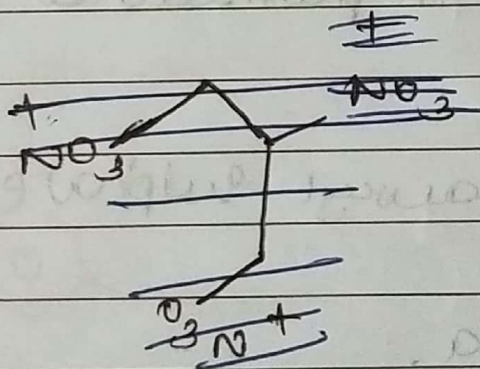
① used as flavouring agent

② used in perfumes

10

2) nitroglycerin [glyceryl trinitrate]

15



uses:

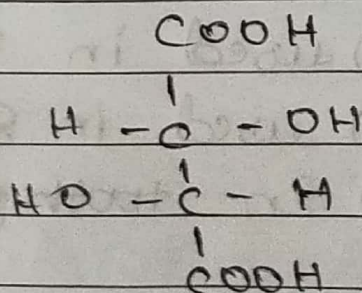
① used to prevent chest pain

~~②~~

② used as vasodilator

3) tartaric acid

25



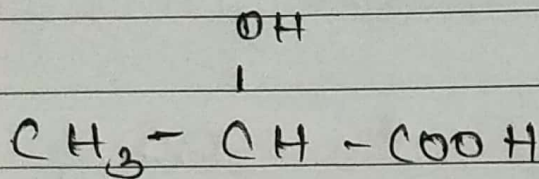
uses:

① used in baking powders

② Flavouring agent

(4) Lactic acid.

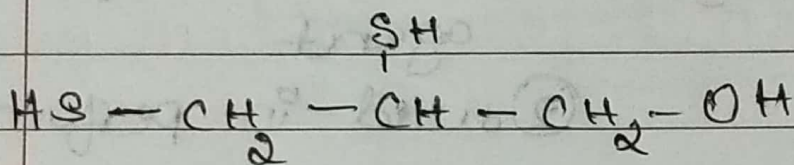
uses:-



- ① Flavouring agent
- ② food preservative

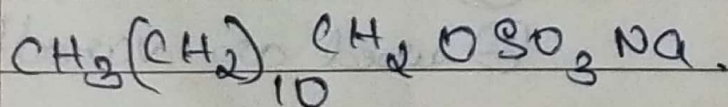
(5) Dimercaprol

uses:-



- ① used as antidote
- ② used as adjuvant in pharmaceutical preparation

(6) SLS (sodium lauryl sulphate)



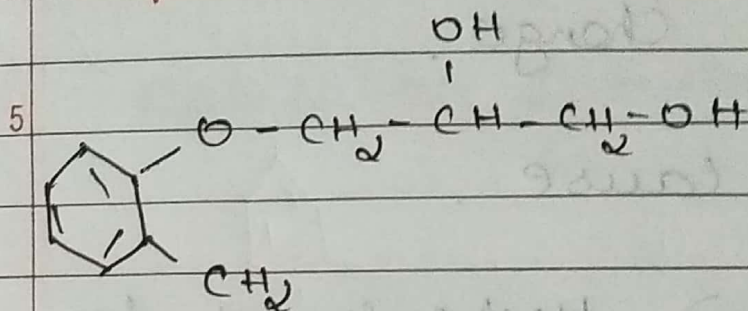
uses



- ① used in soap
- ② used in shampoos
- ③ in toothpaste

⑤ ~~Nephrensin~~

⑤ Nephrensin



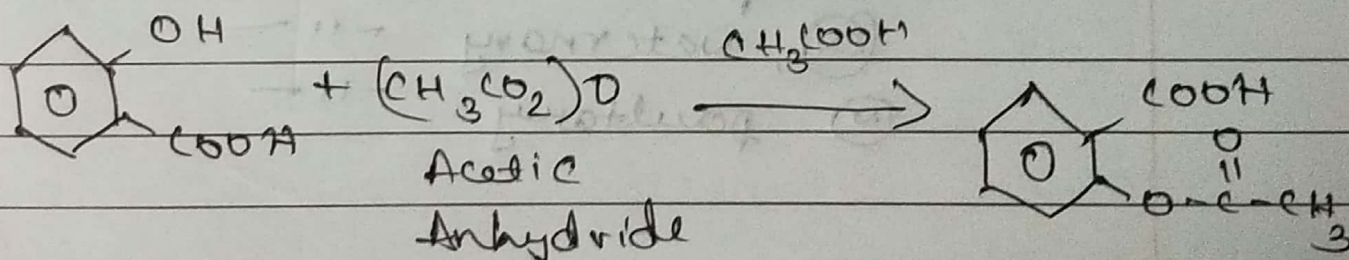
10

uses

① Reduces muscular tone

⑥ preparation of Aspirin

15



20

Salicylic
Acid

Aspirin

uses

① Analgesic

② Antipyretic