Organic Reactions

Question bank for Organic Reaction Chapter

Q1: What is the peroxideeffect? Explain it by example& discuss its mechanism.

OR

How will propene react with HBr in presence of peroxide? Write down the mechanism of this reaction.

OR

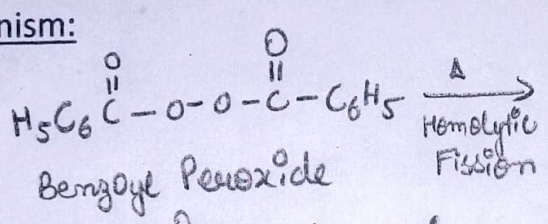
Discuss Anti Markonikov's rule.

Ans 1: Peroxide effect is used in case of alkenes and is also known by the name of the Anti Markovnikov's rule according to which the negative part of the chemical reagent to added to that carbon of the double bond which has the higher number of the hydrogen atoms.

Example: $CH_3-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3-CH_2-CH_2-Br$

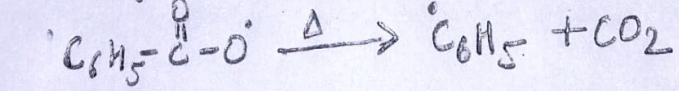
Mechanism:

Step 1:



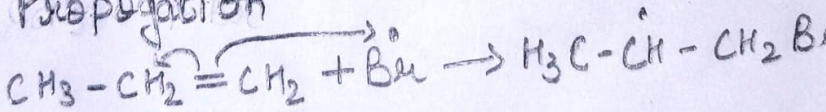
Benzoyl Peroxide — Homolytic Fission

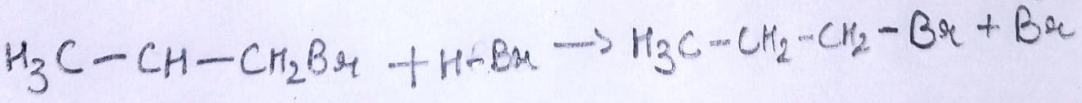
Step 2:



Step 3:

Step 4: Propagation

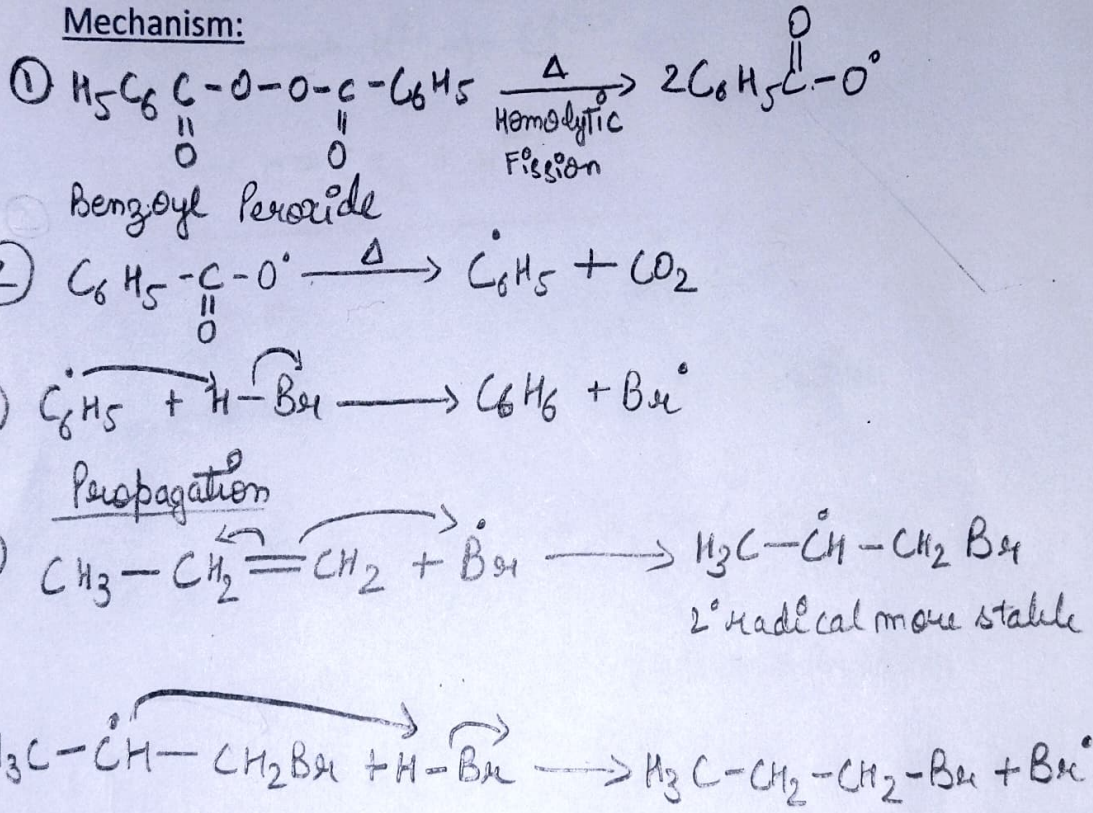




Ans 1 OR Part:When propene (C_3H_6) reacts with hydrogen bromide (HBr) in the presence of a peroxide, such as benzoyl peroxide $(C_6H_5COO)_2$, a different reaction pathway occurs compared to the reaction in the absence of peroxide.

Reaction in the presence of peroxide (peroxide effect):

Mechanism:



Overall reaction: Propene + HBr + Peroxide → 2-Bromopropane

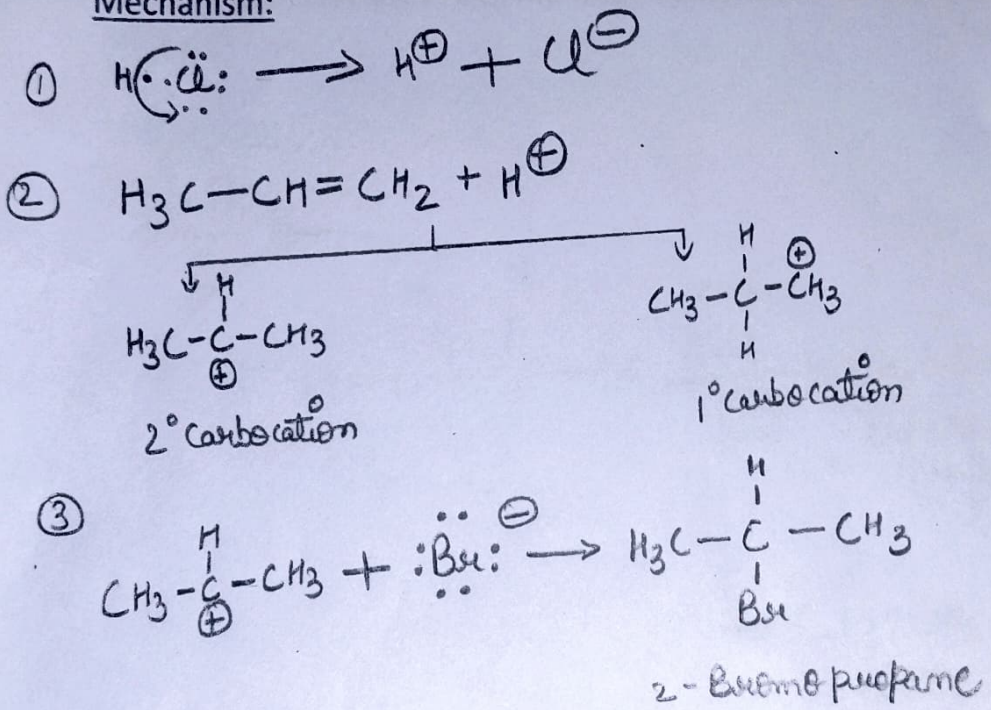
In the absence of any peroxide, the reaction between propene and HBr follows a different mechanism.

Q2: what is Markovnikov's rule? Give an example & discuss its mechanism.

Ans2:Markovnikov's rule states that when an unsymmetrical reagent adds to an unsymmetrical alkene, the more positive part of the agent goes to the carbon that has more hydrogen atoms.

Example:

Mechanism:



According to Markovnikov's rule, the hydrogen atom adds to the carbon atom of propene that already has more hydrogen substituents (the terminal carbon), resulting in the formation of 1-chloropropane. This rule holds true in many addition reactions to unsymmetrical alkenes or alkynes and provides a useful guideline to predict the major product formed in such reactions.

Q3: State Saytzeff's rule & illustrates it with example.

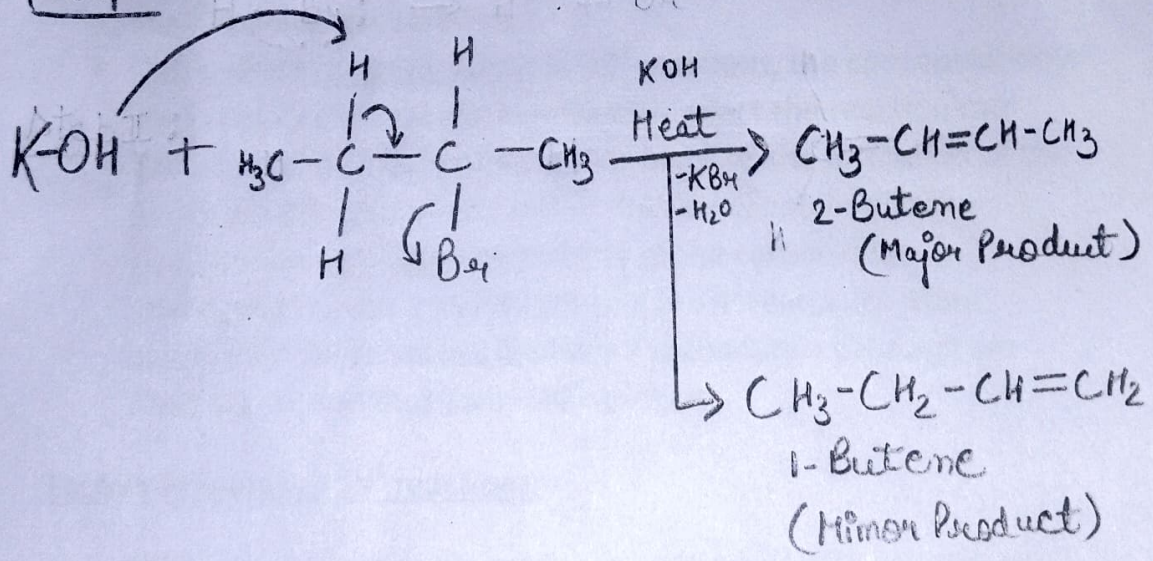
Ans3:According to Saytzeff's rule, "the favored product in dehydrohalogenation reactions is the alkene with the greatest amount of alkyl groups connected to the doubly bound carbon atoms."

Example: Dehydrohalogenation of 2-Bromobutane

According to Saytzeff's rule, the more substituted alkene is the major product.

Mechanism:

Step I:



This rule is based on the principle that the more substituted alkene is more stable due to the greater distribution of electron density and better delocalization of pi electrons, resulting in a lower energy state.

Q4: Name the factors which influence SN^1& SN^2 reaction.

Ans4:**Factors influencing SN1 reactions:**

1. **Substrate:** The nature of the substrate is crucial in SN^1 reactions. Substrates with a good leaving group (e.g., alkyl halides) tend to undergo SN^1 reactions more readily.
2. **Leaving group:** A good leaving group that can stabilize the negative charge after departure enhances SN^1 reactions.
3. **Solvent**: Polar protic solvents (e.g., water, alcohols) are typically favored in SN^1 reactions as they can solvate the cation intermediate and stabilize it.
4. **Nucleophile concentration:** In SN^1 reactions, the concentration of the nucleophile does not significantly affect the reaction rate because the rate-determining step involves the formation of the carbocation intermediate rather than nucleophilic attack.
5. **Carbocation stability:** The stability of the carbocation intermediate plays a significant role in SN^1 reactions. More substituted carbocations (tertiary > secondary > primary) are more stable and thus favor SN^1 reactions.

Factors influencing SN^2 reactions:

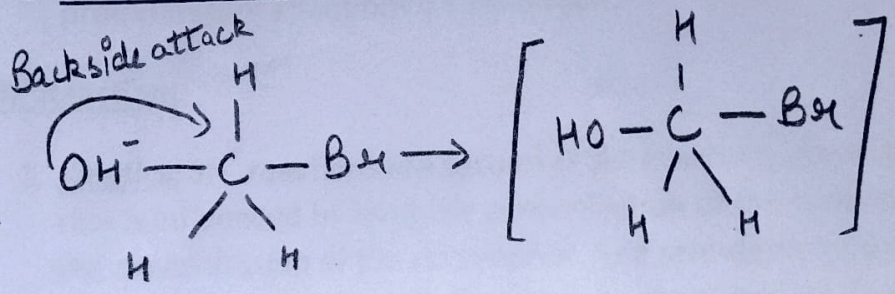
1. **Substrate:** SN^2 reactions predominantly occur with primary or methyl substrates due to their accessibility and lack of steric hindrance.
2. **Leaving group:** A good leaving group is necessary for SN^2 reactions to occur effectively.
3. **Nucleophile strength:** The strength and concentration of the nucleophile directly impact the rate of SN^2 reactions since the nucleophile directly participates in the rate-determining step.
4. **Solvent:** Polar aprotic solvents (e.g., acetone, DMSO) are preferred for SN^2 reactions as they do not solvate the nucleophile strongly, allowing it to readily approach the substrate.

5. **Steric hindrance:** Steric hindrance caused by bulky substituents around the reaction site hinders the approach of the nucleophile and favors SN^1 or other competing reactions over SN^2.

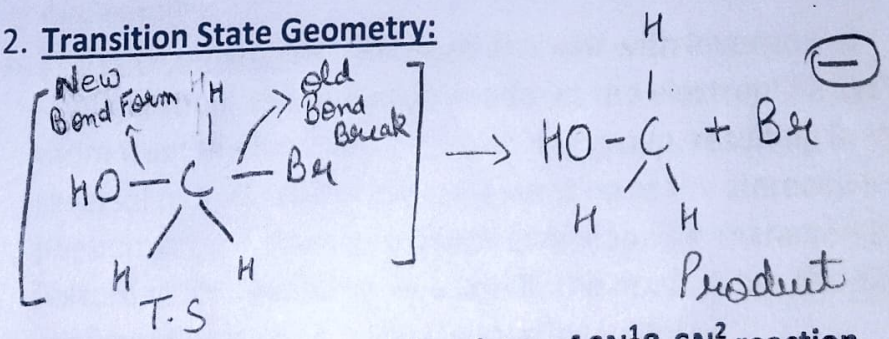
Q5: Justify that all SN^2 reactions proceed by inversion of configuration.

Ans 5:The stereochemical outcome of SN^2 reactions, which involves the simultaneous bond-making and bond-breaking steps, is governed by the mechanism itself and has been experimentally observed to proceed with inversion of configuration. Here are two key justifications for the inversion of configuration in SN^2 reactions:

1. **Backside Attack**:



2. **Transition State Geometry:**



Q6: Give the Kinetics & stereochemistry of SN^1 & SN^2 reaction.

Ans 6:The kinetics and stereochemistry of SN^1 (Substitution Nucleophilic Unimolecular) and SN^2 (Substitution Nucleophilic Bimolecular) reactions differ based on their reaction mechanisms.

SN1 Reaction:

1. **Kinetics:** SN^1 reactions are first-order reactions, meaning their rate depends solely on the concentration of the substrate. The rate-determining step involves the formation of a carbocation intermediate, which occurs independently of the nucleophile's concentration.
2. **Stereochemistry:** SN^1 reactions proceed with racemization or the retention of configuration at the chiral center. This is because the carbocation intermediate can be attacked from either side by the nucleophile, leading to the formation of both R and S enantiomers. The overall product is a racemic mixture unless there is a chiral auxiliary or a specific reaction condition that promotes one enantiomer's formation.

SN^2 Reaction:

1. **Kinetics:** SN^2 reactions are second-order reactions, meaning their rate is influenced by both the concentration of the substrate and the concentration of the nucleophile. The rate-determining step involves a bimolecular collision between the substrate and the nucleophile.
2. **Stereochemistry:** SN^2 reactions proceed with inversion of configuration. The nucleophile attacks the electrophilic carbon atom from the backside of the leaving group, resulting in the reversal or inversion of the configuration at the stereocenter. This phenomenon, known as Walden inversion, is a characteristic feature of SN^2 reactions. As a result, the product has the opposite configuration compared to the starting material.

Q7: Discuss the mechanism of SN^1 & SN^2 reactions.

Ans7

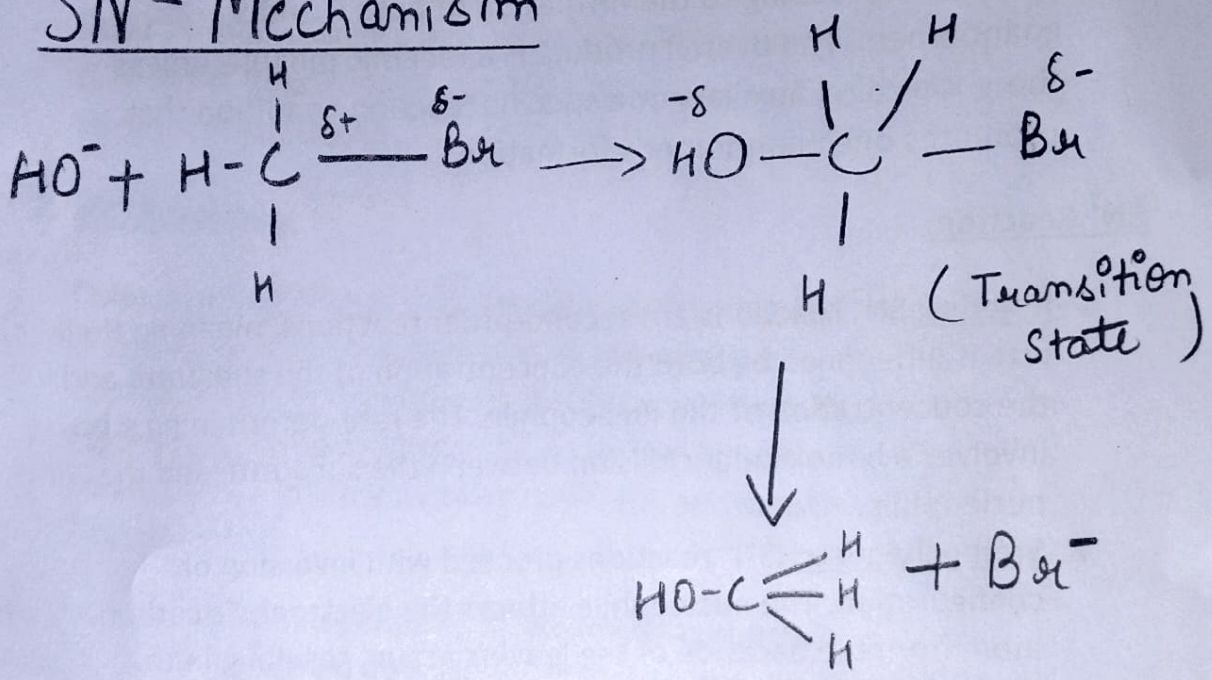
S_N1 Mechanism:

① $(CH_3)_3C^{\delta+}—Br^{\delta-} \xrightarrow{slow} (CH_3)_3C^{\oplus} + Br^{\ominus}$

② Step

$(CH_3)_3C^{\oplus} + OH^{\ominus} \xrightarrow{fast} (CH_3)_3C-OH$

S_N2 Mechanism



Q8: Discuss the effect of polarity of solvent on the rate of SN^1 & SN^2 reaction.

Ans8: The polarity of a solvent can significantly affects the rate of SN^1 and SN^2 reactions:

1. **SN^1 Reactions:**

- Polar protic solvents (e.g., water, alcohols) stabilize both the nucleophile and carbocation intermediate, slowing down the reaction rate.
- Polar aprotic solvents (e.g., acetone, DMF, DMSO) increase the rate of SN^1 reactions by not stabilizing the carbocation, allowing it to react more readily.

2. **SN^2 Reactions:**

- Polar aprotic solvents are generally preferred for SN^2 reactions as they promote the reaction rate by allowing the nucleophile to approach the electrophilic carbon without interference.
- Polar protic solvents hinder SN^2 reactions by solvating the nucleophile, reducing its nucleophilicity, and stabilizing the transition state.

The choice of solvent depends on factors such as substrate nature, nucleophile strength, and desired reaction outcome. Solvent polarity is one aspect to consider in optimizing reaction conditions.

Q9: What are E_1 & E_2 reactions? Give the mechanism of these reactions.

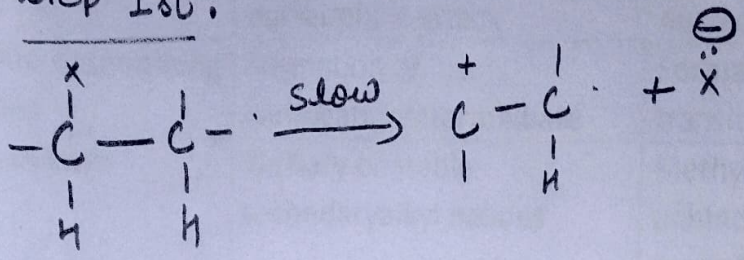
Ans9: E_1 and E_2 reactions are elimination reactions in organic chemistry:

- E_1 proceeds through the formation of a carbocation intermediate.

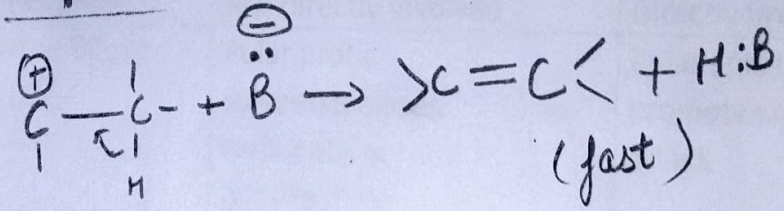
- E_2 occurs in a one-step concerted manner with the simultaneous removal of the leaving group and a hydrogen atom by a strong base.

E_1 Mechanism:

Step Ist:

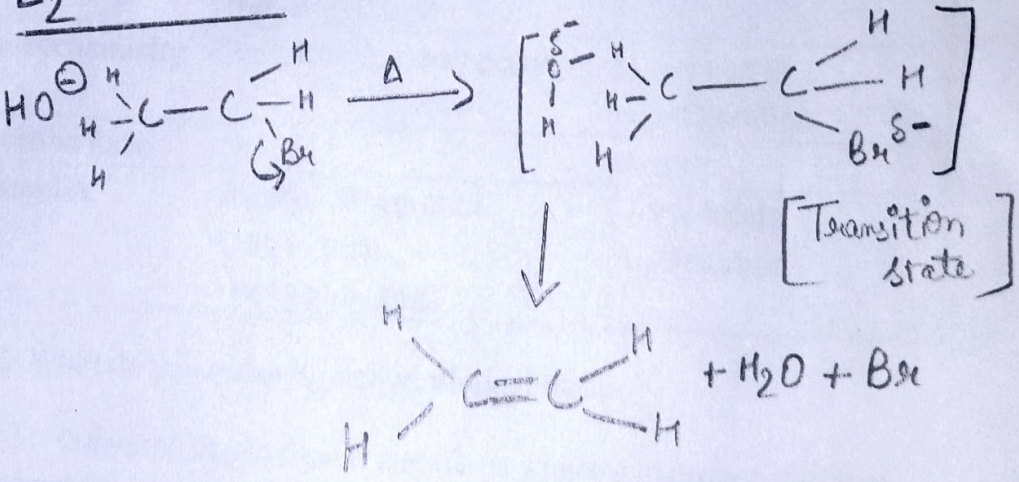


Step IInd:



(fast)

E_2 Mechanism:



Q10: Write the distinguishable features of SN^1& SN^2.

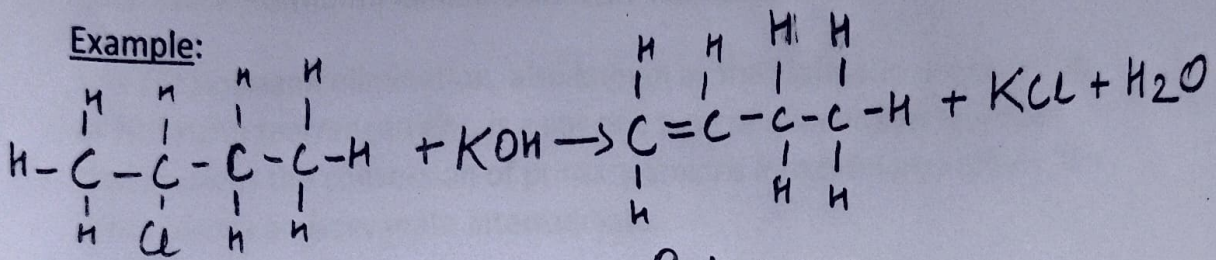
	SN^1 Reaction	SN^2 Reaction
Reaction Type	Unimolecular	Bimolecular
Mechanism	Two-step: Ionization and	One-step: Simultaneous
	nucleophilic attack	nucleophilic attack
Rate-determining Step	Formation of carbocationintermediate	Formation of transitionstate
Substrate	Tertiary or stable secondaryalkyl halides	Methyl, primary, or unhindered secondary
Steric Hindrance	Less significant	Significant
Nucleophile	Not directly involved	Directly involved
Solvent Effect	Polar protic solventstabilizes carbocation. intermediate	Polar aprotic solvent promotes nucleophile attack
Rearrangement	Can occur (carbocation rearrangement)	Does not occur
Stereochemistry	Racemization may occur	Inversion of configuration
Reaction Rate	Slower	Faster
Examples	Alcohol dehydration Carbocation rearrangements	Alkyl halide substitution

Q11: What do you mean by Dehydrohalogenation?

Ans11: Dehydrohalogenation is a reaction where a hydrogen halide is removed from an organic compound, leading to the formation of a double bond. It is an elimination reaction that occurs when an alkyl halide reacts with a strong base. The base abstracts a hydrogen atom

from the adjacent carbon while the halogen atom leaves, resulting in the formation of a double bond. This reaction is commonly used to synthesize alkenes from alkyl halides.

Example:



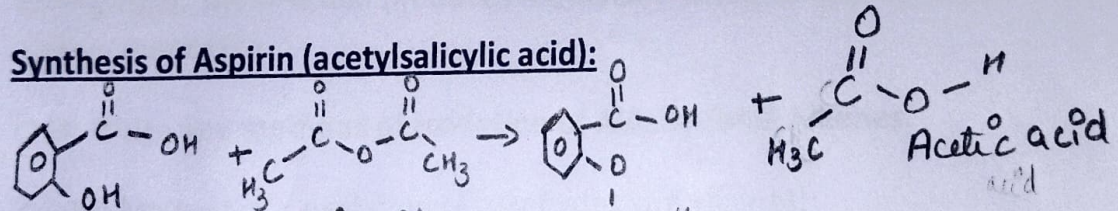
2-Chlorobutane

But-2-ene

Q12: Write down the reactions of synthesis of Aspirin & Acetaminophen.

Ans 12: The reactions for the synthesis of Aspirin and Acetaminophen:

Synthesis of Aspirin (acetylsalicylic acid):



Salicylic acid

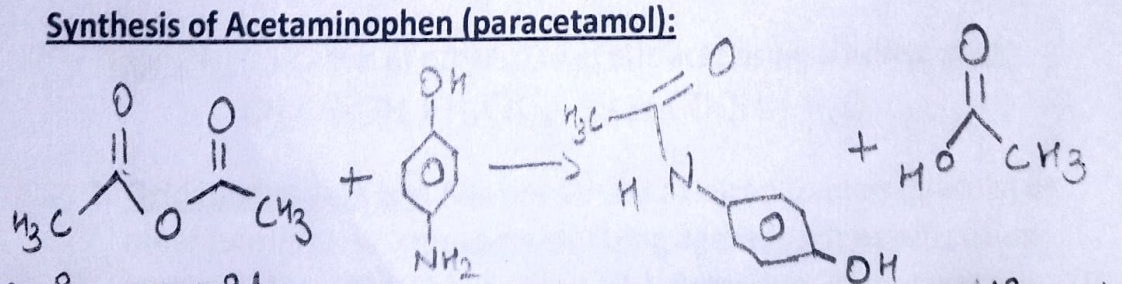
acetic acid

Acetylsalicylic acid

Acetic acid

In this reaction, salicylic acid reacts with acetic anhydride in the presence of a catalyst, typically a strong acid such as sulfuric acid. The result is the acetylation of salicylic acid, forming acetylsalicylic acid (Aspirin) and acetic acid.

Synthesis of Acetaminophen (paracetamol):



Acetic anhydride

P-amino-Phenol

→ acetaminophen + acetic acid

In this reaction, aminophenol reacts with Acetic anhydride to give acetaminophen(paracetamol) and acetic acid.

Q13: State Hoffmann elimination with example.

Ans 13: Hofmann elimination, also known as the Hofmann degradation or Hofmann rearrangement, is a specific type of elimination reaction that involves the conversion of primary amides into primary amines. It proceeds via an isocyanate intermediate.

Example:

$CH_3CONH_2 \rightarrow CH_3NH_2 + CO$

In this example, acetamide is subjected to Hofmann elimination using a strong base. The reaction produces methylamine (a primary amine) and carbon monoxide.

Q14: Write any methods of oxidation of Aldehydes & Alkenes.

Ans14: Methods for oxidation of aldehydes and alkenes:

1. **Oxidation of Aldehydes:** Aldehydes can be oxidized to carboxylic acids using oxidizing agents such as Tollens' reagent (Ag (NH3)2OH) or chromic acid (H2CrO4). Tollens' reagent forms a silver mirror while oxidizing the aldehyde, while chromic acid converts the aldehyde to a carboxylic acid.

   Example: Oxidation of ethanol to acetic acid using chromic acid:

   $$CH_3CH_2OH + H_2CrO_4 \rightarrow CH_3COOH + H_2O$$

2. **Oxidation of Alkenes:** Alkenes can be oxidized to diols (glycols) or other functional groups using oxidizing agents such as potassium permanganate ($KMnO_4$) or ozone (O_3). Potassium permanganate adds hydroxyl groups to both carbons of the double bond,

forming a diol. Ozone oxidation generates an ozonide, which can be further reduced to yield carbonyl compounds.

Example: Oxidation of propene to 1,2-propanediol using potassium permanganate:

$$CH_3CH=CH_2 + KMnO_4 \rightarrow HOCH_2CH_2CH_2OH$$

Q15: How will you do hydrogenation(reduction) of alkenes & carboxylic acids.

Ans 15: To perform hydrogenation (reduction) of alkenes and carboxylic acids, different conditions and catalysts are used for each reaction. methods for hydrogenation alkenes and carboxylic acids:

1. **Hydrogenation of Alkenes:** Alkenes can be reduced to alkanes by adding hydrogen gas (H_2) in the presence of a suitable catalyst, such as palladium (Pd), platinum (Pt), or nickel (Ni). The reaction typically takes place at elevated temperatures and pressures.

Example: Hydrogenation of ethene to ethane using a palladium catalyst:

$$CH_2=CH_2 + H_2 \rightarrow CH_3CH_3$$

2. **Hydrogenation of Carboxylic Acids:** Carboxylic acids can be reduced to primary alcohols by using strong reducing agents, such as lithium aluminum hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$). The reaction requires an appropriate solvent, usually anhydrous conditions, and can be carried out at room temperature or with mild heating.

Example: Reduction of acetic acid to ethanol using sodium borohydride:

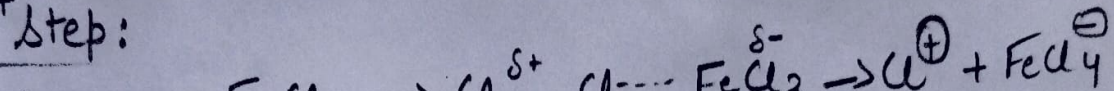
$$CH_3COOH + NaBH_4 \rightarrow CH_3CH_2OH + NaB(OH)_3$$

Q16: Write one reaction of electrophilic substitution. Give the mechanism of Electrophilic substitution.

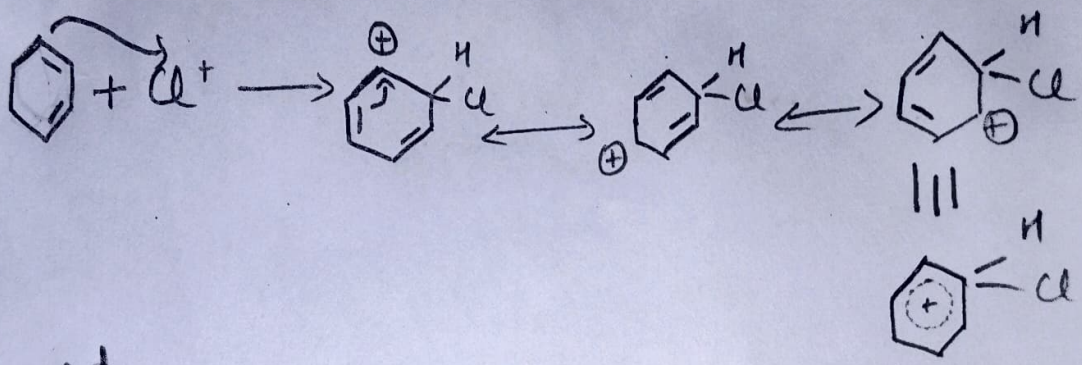
Ans: Reaction with Halogen

Mechanism:

1st Step:



2nd Step:



3rd Step:

Abstraction of H^+ from carbocation