

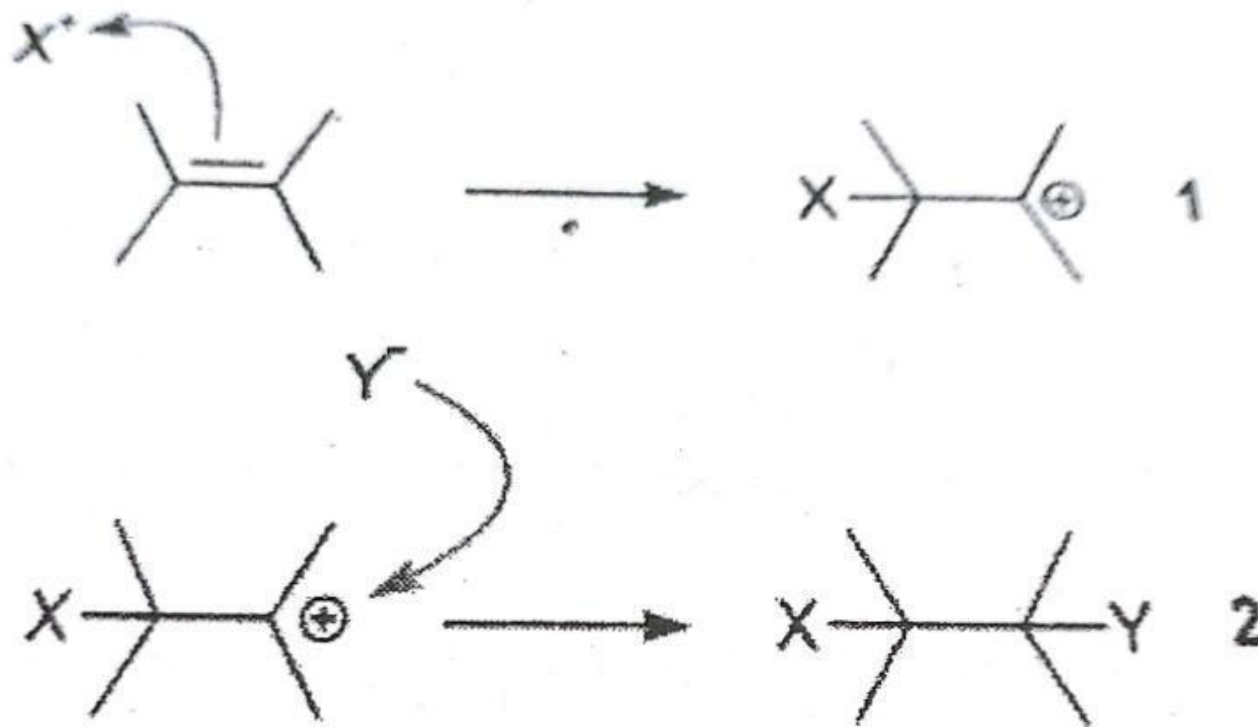
ELECTROPHILIC ADDITION REACTION IN ALKENES

- In this type of reaction chemical compound, pi-bond is broken and two new sigma bonds are formed. The substrate of an electrophile addition reaction must have double or triple bond.
- Alkenes have pi-electrons so they easily attracted by electrophile and gets attach to double bonded carbon atom.

ELECTROPHILIC ADDITION REACTION IN ALKENES (contd..)

- The driving force for this reaction is the formation of an electrophile that forms a covalent bond with an electron rich unsaturated carbon atom.

ELECTROPHILIC ADDITION REACTION IN ALKENES (contd..)



ELECTROPHILIC ADDITION REACTION IN ALKENES (contd..)

- Hydrogenation, hydrohalogenation, hydration are some examples of this type of reactions. The reactions follows the Markovnikov's rule which states that positive part will add on that carbon atom of alkene which has more H atoms. It occurs in syn or anti-direction.

ELECTROPHILIC ADDITION REACTION IN ALKENES (contd..)

- Major conditions for electrophilic addition are;
- Presence of double covalent bond in reactant molecule
- Presence of electrophile
- Reactions conditions like solvent which can stabilize the polar carbocation intermediate.

FREE RADICAL ADDITION IN ALKENES

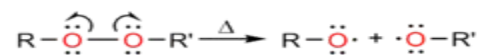
- Free-radical addition reactions free radicals.
- The addition may occur between a radical and a non-radical, or between two radicals.
- In this reaction, a catalytic amount of organic peroxide is needed to abstract the acidic proton from HBr and generate the bromine radical; however a full molar equivalent of alkenes and acid is required for completion.
- In the presence of a peroxide initiator, hydrogen halide add to alkene via an Anti-Markovnikov, free radical mechanism.

FREE RADICAL ADDITION IN ALKENES (contd..)

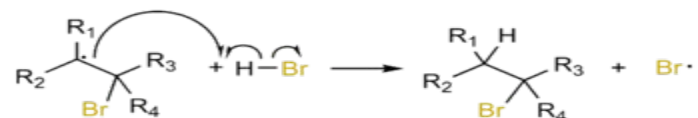
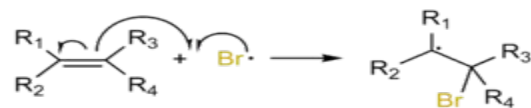
- The basic steps with example of free radical reaction are;
- **Initiation by radical indicator**
- **Chain propagation**
- **Chain termination**

FREE RADICAL ADDITION IN ALKENES (contd..)

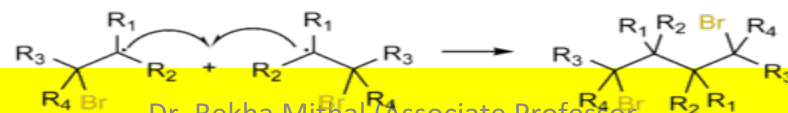
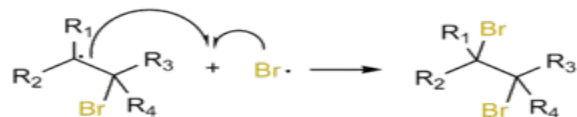
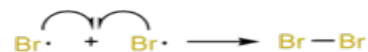
Initiation



Propagation



Termination

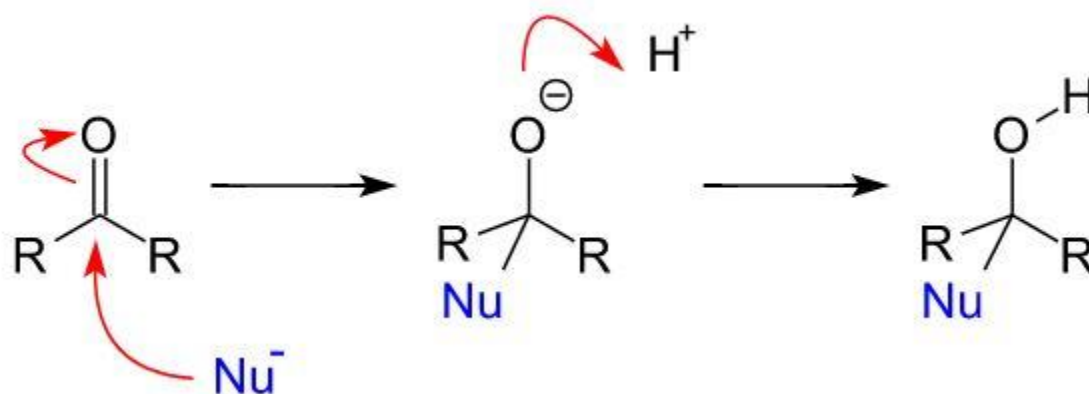


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NUCLEOPHILIC ADDITION IN ALDEHYDE AND KETONE

- It is a type of chemical reaction where a chemical compound with an electron-deficient or electrophilic double or triple bond, a pi-bond reacts with electron rich reactant, termed as nucleophile, with disappearance of the double bond and formation of two single bonds.
- These types of bonds are polar in nature and carries a partial positive charge.

NUCLEOPHILIC ADDITION IN ALDEHYDE AND KETONE (contd..)



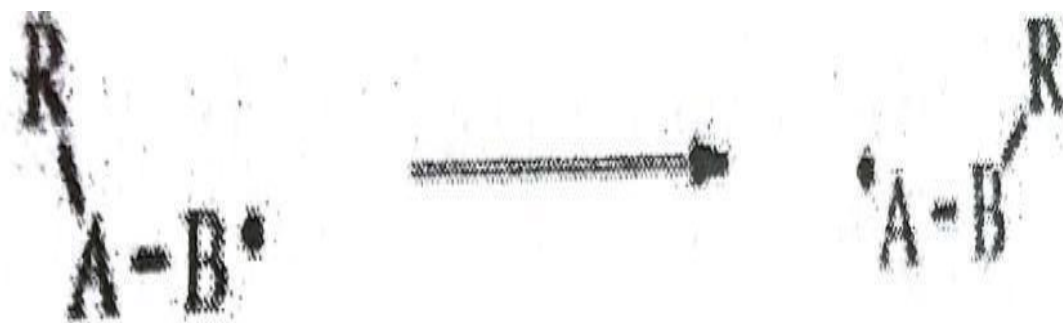
NUCLEOPHILIC ADDITION IN ALDEHYDE AND KETONE (contd..)

- Variety of Nucleophile:
- Grignard Reagents
- Alcohols
- Amines
- Alkyl Lithium Reagents
- Acetylide Ions

FREE RADICAL REARRANGEMENTS

- A 1,2-rearrangement or 1,2-migration or 1,2-shift is an organic reaction where a substituent moves from one atom to another one. The rearrangement is intramolecular and the starting compound and reaction product are structural isomers. A rearrangement involving a hydrogen atom is called 1,2-hydride shift.

FREE RADICAL REARRANGEMENTS (contd..)



FREE RADICAL REARRANGEMENTS (contd..)

- If the substituent being rearranged is an alkyl group, it is named according to alkyl group's anion: i.e. 1,2-methanide shift, 1,2-ethanide shift, etc.
- The most common way of generating free radicals for the purpose of detection of rearrangements is by decarboxylation of aldehydes.

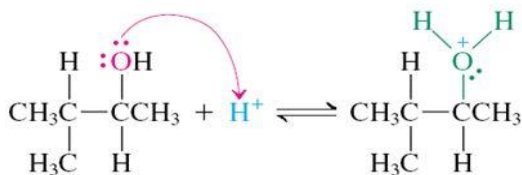
FREE RADICAL REARRANGEMENTS (contd..)

- **CARBOCATION REARRANGEMENT**
- These are defined as the movement of a carbocation from an unstable state to a stable state through the use of various structural reorganized “shifts” within the molecule.
- A carbocation holds a positive charge. There are two types of rearrangement: hydride shift or alkyl shift.

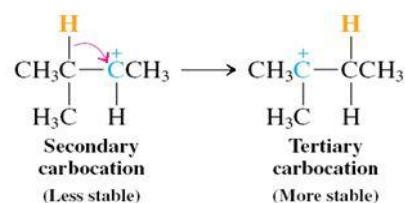
FREE RADICAL REARRANGEMENTS (contd..)

Rearrangement of an initial secondary carbocation to the more stable tertiary carbocation by a hydride shift results in a rearranged product.

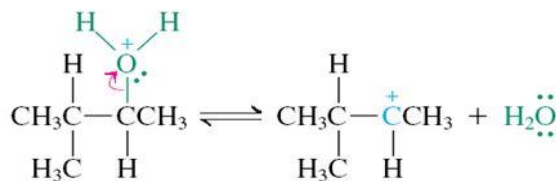
STEP 1. Protonation



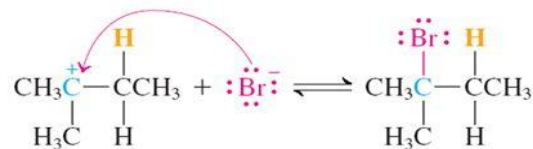
STEP 3. Hydride shift



STEP 2. Loss of water



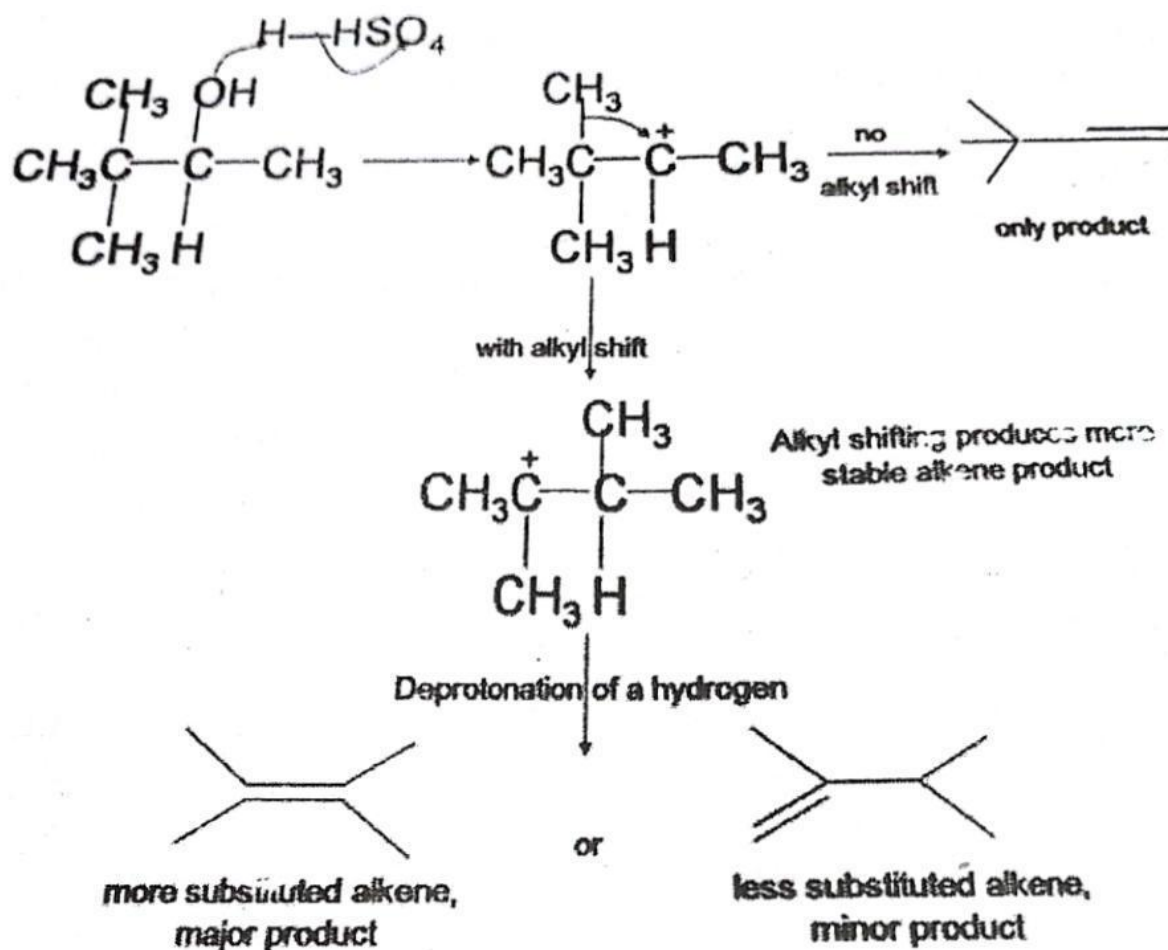
STEP 4. Trapping by bromide



HYDRIDE SHIFT OR ALKYL SHIFT

- The phenomenon of hydride shift typically with the reaction of an alcohol and hydrogen halides, which includes HCl, HBr and HI. HF is typically not used because of its instability and its fast reactivity rate.
- The hydrogen and the carbocation formally switch position.
- The Cl atom can now attack the carbocation, in which it forms most stable structure because of hyperconjugation.

HYDRIDE SHIFT OR ALKYL SHIFT (contd..)



HYDRIDE SHIFT OR ALKYL SHIFT (contd..)

- Tertiary cation is more stable than secondary cation, which in turn is more stable than primary cation due to a phenomenon known as hyperconjugation, where the interaction between the filled orbitals of neighbouring carbons and the singly occupied p orbital in the carbocation stabilizes the positive charge in carbocation.

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