

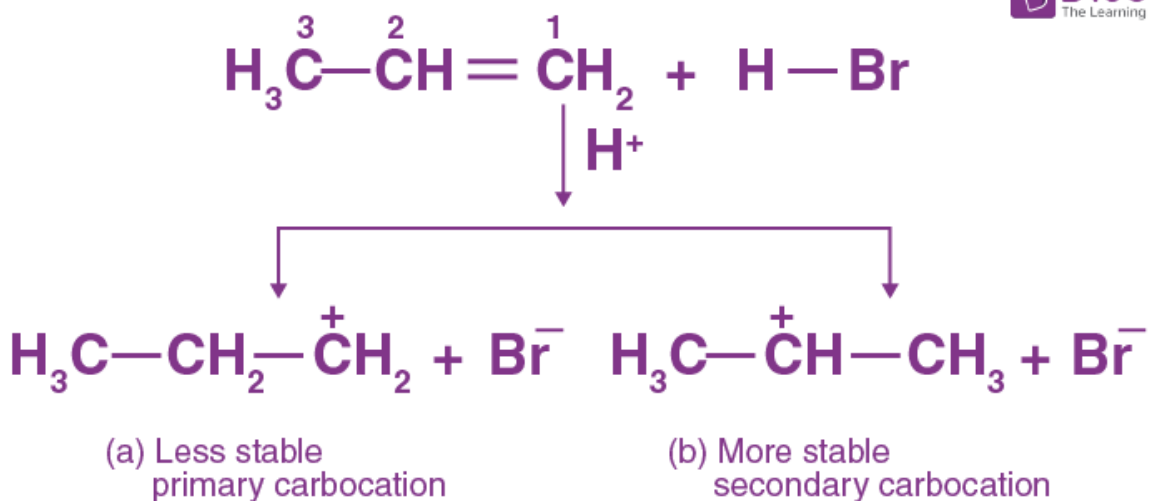
Markovnikov Rule Chemistry Questions with Solutions

Q-1: With the help of an appropriate example, write the steps of the Markovnikov rule mechanism.

Answer:

Step-1 Formation of carbocation

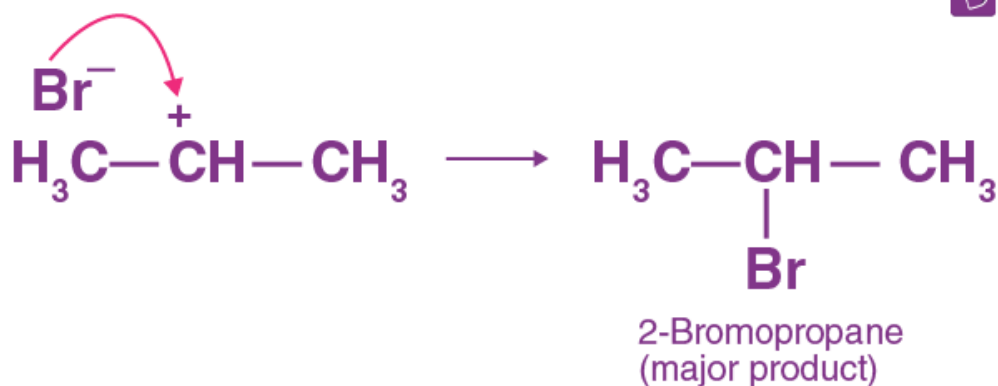
H^+ , an electrophile produced by hydrogen bromide, attacks the double bond of propene to form a carbocation, as shown below:



Because the secondary carbocation (b) is more stable than the primary carbocation (a), it takes precedence as it forms faster.

Step-2 Attack of Nu^-

The carbocation (b) is attacked by Br^- ion, resulting in the following product:



Q-2: State a rule that is the opposite of the Markovnikov rule.

Answer: When a polar molecule is introduced to an unsymmetrical alkene in the presence of organic peroxide, the negative part of the molecule is attached to the carbon atom that is coupled to more Hydrogen atoms than the other unsaturated carbon atom. This reaction is known as the peroxide or Kharash effect, or the anti-Markovnikov rule addition reaction.

Q-3: The Markovnikov rule is not followed in

- Reaction of alkenes with sulphuric acid
- Reaction of alkene with water
- Hydroboration-oxidation reaction
- Oxymercuration-Demercuration Reaction

Answer: c) Hydroboration-oxidation reaction

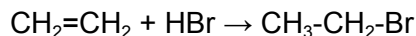
Explanation: The ultimate product of treating alkenes with borane (BH_3) in the presence of hydrogen peroxide or sodium hydroxide is an alcohol. The boron atom acts as an electrophile in this electrophilic addition process. The boron atom is mostly placed on the carbon which is less substituted. Therefore, it can be classified as an anti-Markovnikov reaction.

Q-4: Will the Markovnikov rule apply when adding HBr to a symmetrical alkene?

Answer: No

Explanation: Addition reactions of HBr to symmetrical alkenes (similar groups attached to double bond) take place by electrophilic addition mechanism.

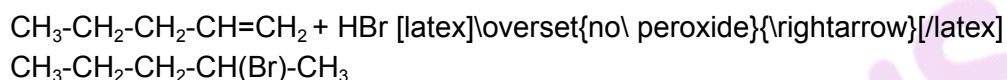
For example: Addition of HBr to ethene takes place as:



Because the system is symmetrical, there is no olefin carbon that can be classified as having fewer or more H-atoms.

Q-5: Write IUPAC name of the product obtained by addition reactions of HBr to pent-1-ene in the absence of peroxide.

Answer: The reaction follows the Markovnikov Rule in the absence of peroxide.



The IUPAC name of the product is 2-Bromopentane.

Q-6: Free radical addition reaction obey

- a) Markovnikov rule
- b) Kharash effect
- c) Hoffmann rule
- d) Saytzeff rule

Answer: b) Kharash effect

Q-7: When a hydrogen halide(HX) is introduced to an unsymmetrical alkene, an intermediate is

- a) Free Radical
- b) Carbocation
- c) Carbanion
- d) Nitrene

Answer: b) Carbocation

Explanation: The production of carbocation occurs when HX is added to an unsymmetrical alkene according to the Markovnikov rule. The product is generated after the nucleophile attacks the created carbocation.

Q-8: When two acid (H-X) equivalents are added to an aliphatic alkyne, what product is produced?(X= Cl, Br, I)

- a) Alkenyl halide
- b) Geminal dihalide
- c) Alkyl Halide
- d) Aryl halide

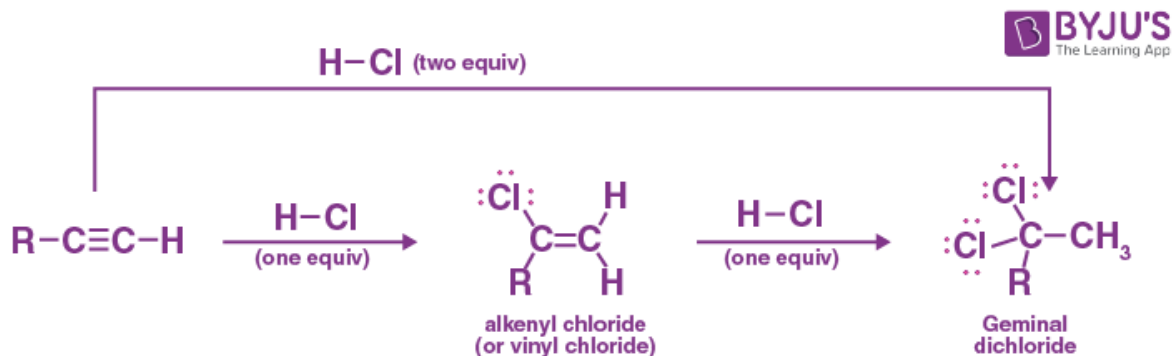
Answer: b) Geminal dihalide

Explanation:

One equivalent of an acid gives the alkenyl halide (vinyl halide)

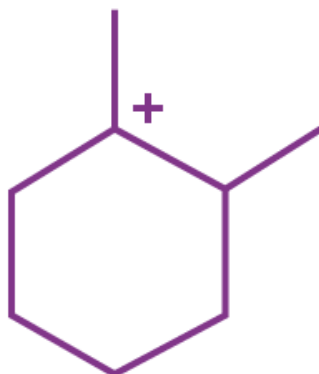
Two equivalent of an acid gives geminal dihalide.

The reaction illustration is shown below:



Same for HBr and HI

Q-9: What is the hybridisation of the following carbocation?



- a) sp^2
- b) sp^3
- c) sp
- d) p

Answer: a) sp^2

Explanation: Because the positive-charged carbon forms three sigma bonds, this is an example of sp^2 hybridisation.

Q-10: Sort the following chemicals in decreasing order of HBr reactivity: isobutene, ethene, and propene

Answer: Isobutene>propene>ethene

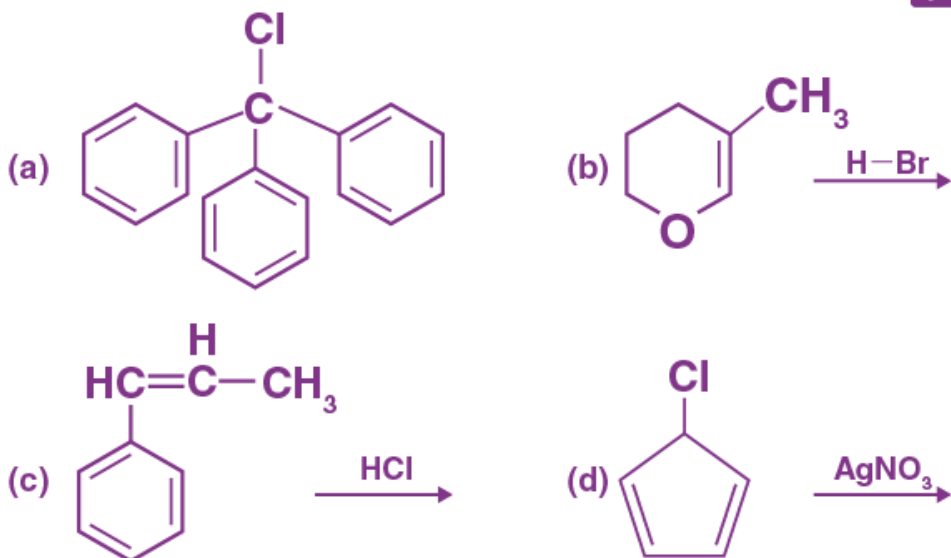
Explanation:

The stability of the carbocation produced determines the reactivity of alkenes towards HBr. Tertiary carbocation is more stable than secondary and primary carbocation.

Isobutene results in the formation of 3° carbocation, propene in 2° carbocation and ethene in 1° carbocation.

As a result, isobutene is the most reactive towards HBr, whereas ethene is the least reactive.

Q-11: Reaction which will give fastest carbocation



Answer: b)

Explanation:

In a) carbocation is formed by removal of chlorine and is resonance stabilised.

In b) the carbocation formed is mesomerically stabilised (lone pair donation of oxygen).

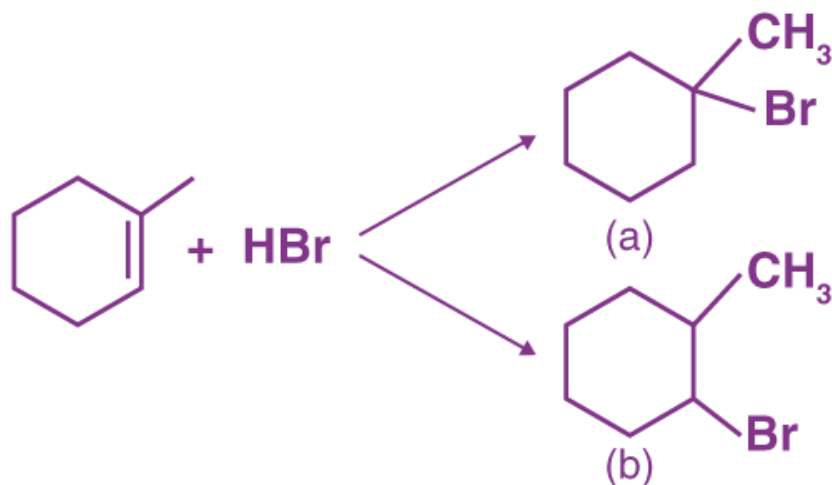
In c), proton released from HCl attacks the double bond and forms carbocation which is again resonance stabilised.

In d) carbocation formed after removal of chlorine forms an antiaromatic system, hence least stable.

The reaction that gives the most stable carbocation will proceed fast. Any carbocation which is stabilised by +M effect (back bonding) is the most stable.

Thus, reaction b) will give the fastest carbocation.

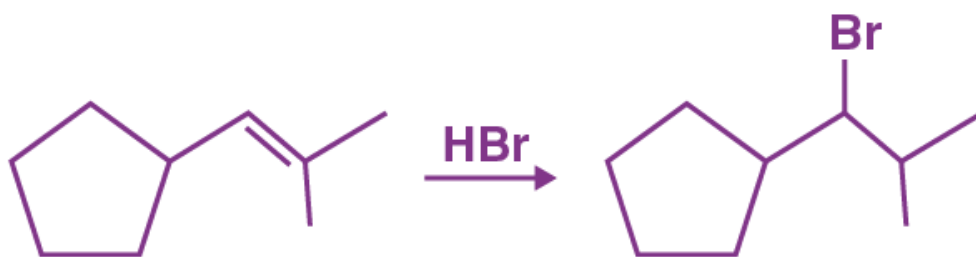
Q-12: What will be the primary product if the following reaction follows the Markovnikov rule?



Answer: a)

Explanation: According to Markovnikov, the acid's negative component (Br) adds to the more substituted olefinic carbon. As a result, product (a) is a major product.

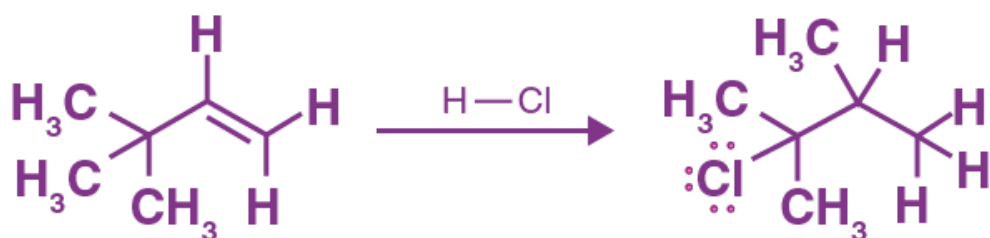
Q-13: Does the reaction follow Markovnikov rule?



Answer: No

Explanation: The halide component is added to the carbon in the product, which is less substituted. It is an anti markovnikov product.

Q-14: How do you explain the product like the one shown in the below reaction?

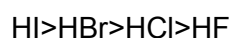


Answer: HCl will simply join its hydrogen to the olefin carbon with the greatest hydrogens and chlorine to the carbon with less hydrogen, according to markovnikov rule. But here, chlorine is added to the carbon other than olefinic. This is because of the rearrangement of the carbocation formed.

The methyl shift takes place which results in a more stable tertiary carbocation.

Q-15: What is the order of reactivity of hydrogen halides with alkenes?

Answer: Due to a decrease in bond (HX) dissociation energy, the stability of hydrogen halides diminishes along the group. The reactivity order is



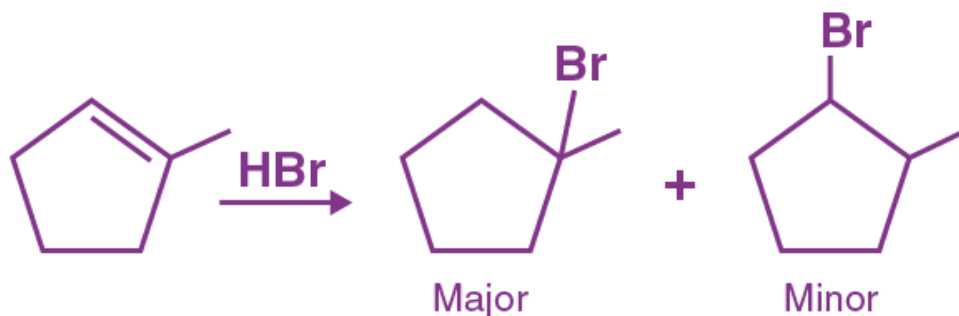
Practise Questions on Markovnikov Rule

Q1: How does Markovnikov's rule show that electrophilic addition reactions to alkenes are regioselective?

Answer:

The regioselectivity of HX addition to unsymmetrically substituted alkenes is predicted by the Markovnikov Rule. In chemical processes, regioselectivity arises when one reaction site is chosen over another. The halide component of HX prefers to bond to the carbon that is more heavily substituted, whereas the hydrogen prefers to bond to the carbon that already has more hydrogens.

The following reaction explains the regioselectivity in Markovnikov rule:



The preferred product is the major one which ultimately explains the regioselectivity.

Q-2: Markovnikov reaction is a

- a) Electrophilic substitution reaction
- b) Nucleophilic substitution reaction
- c) Electrophilic addition reaction
- d) SN1 reaction

Answer: c) Electrophilic addition reaction

Explanation: In organic chemistry, an electrophilic addition reaction occurs when a double or triple bond in a chemical molecule is broken, resulting in the production of two new sigma bonds.

Q-3: In the hydration of alkene, the rate determining step is

- a) Protonation of alkene
- b) Nucleophilic attack by water molecule
- c) Deprotonation to alcohol
- d) All of the above

Answer: a) Protonation of alkene

Explanation: The rate-determining step is the slowest step in a chemical reaction that controls how quickly the overall reaction proceeds.

The production of carbocation occurs when a double bond is protonated. The greater the stability of carbocation, the greater the reactivity, and the faster it will occur.

Q-4: List the factors that influence carbocation stability.

Answer: When determining the stability of carbocation, the following factors must be considered in order:

- Aromaticity: Any carbocation that is part of aromaticity is highly stable, that is, the system that follows Huckel rule.
- + M effect
- Resonance
- Hyperconjugation
- + I effect

Q-5: Addition of HCl to propyne leads to

- Vinyl carbocation
- Allyl carbocation
- Both of the above
- Sec-vinyl carbocation

Answer: d) Sec-vinyl carbocation

Explanation: A vinyl carbocation is the carbon atom with the open octet and positive formal charge is part of a carbon-carbon double bond.

When a positive-charged vinyl carbon atom is surrounded by two other carbon atoms, the prefix "sec" is used.

Addition of HCl to propyne follows Markovnikov addition. The carbocation formed after protonation of a triple bond is sec-vinyl carbocation as shown in the reaction below:

