

PRINCIPLES OF ORGANIC CHEMISTRY

REACTIVE INTERMEDIATES

CARBOCATION



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Aim:

- To understand the concept on formation, geometry, stability and applications of carbocation's.

Objectives:

- Comparing the stability of 1° , 2° , 3° , allylic and benzylic carbocation based on the effects.
- Explaining the importance of carbocation in various chemical reactions like addition, elimination and rearrangement.

Outcome:

After completing this topic, you should be able to:

- Describe the geometry of a given carbocation.
- Describe the stability of the carbocation based on the effects.
- Describe the reactions of carbocation.

Prerequisites:

- Generation of the reactive intermediate carbocation.
- Stability of carbocation.
- Chemical reactions of carbocation.

INTRODUCTION

- An organic species which has a carbon atom bearing only six electrons in its outermost shell and has a positive charge is called **carbocation**.
- The positively charged carbon of the carbocation is sp^2 hybridized.
- The unhybridized p-orbital remains vacant.
- They are highly reactive and act as reaction intermediate.
- They are also called carbonium ion.

FORMATION

- A carbocation is an organic species, an intermediate, that forms as a result of the loss of two valence electrons, normally shared electrons, from a carbon atom that already has four bonds.
- This leads to the formation of a carbon atom bearing a positive charge and three bonds instead of four. The whole molecule holding the positively charged carbon atom is referred to as a **carbocation intermediate**.

FORMATION

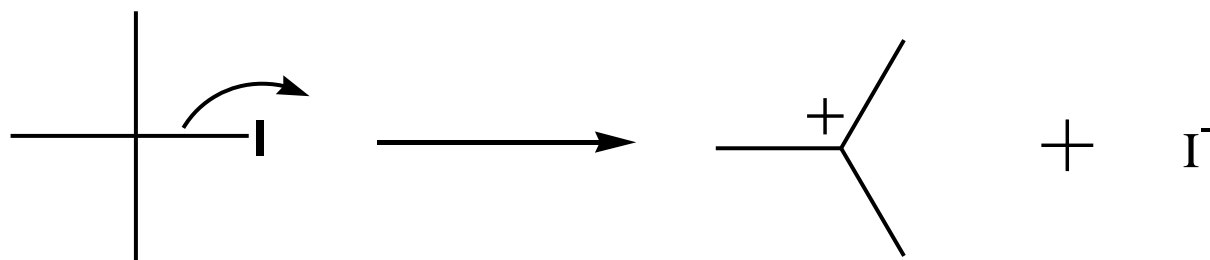
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graph TD; A[FORMATION] --- B[HETEROLYTIC BOND CLEAVAGE]; A --- C[PROTONATION]
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HETEROLYTIC
BOND
CLEAVAGE

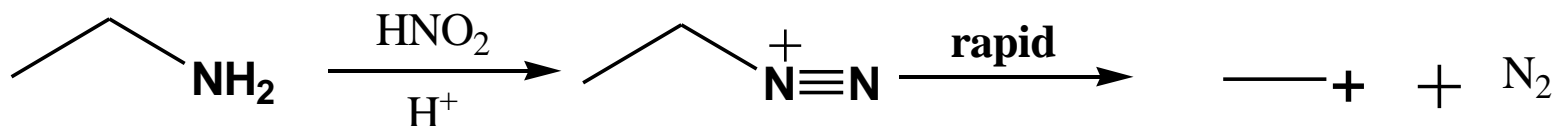
PROTONATION

HETROLYTIC BOND CLEAVAGE

1) Ionization of alkyl halide:

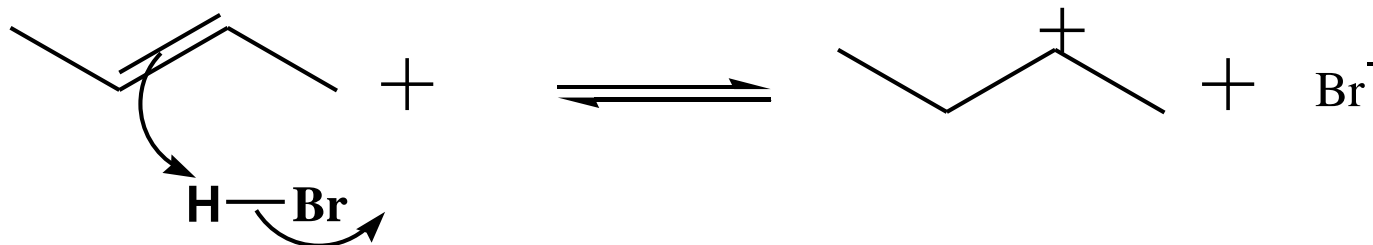


2) Determination of amine by nitrous acid:

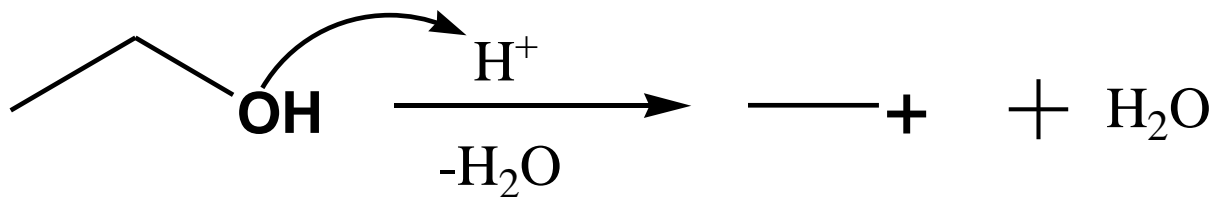


PROTONATION

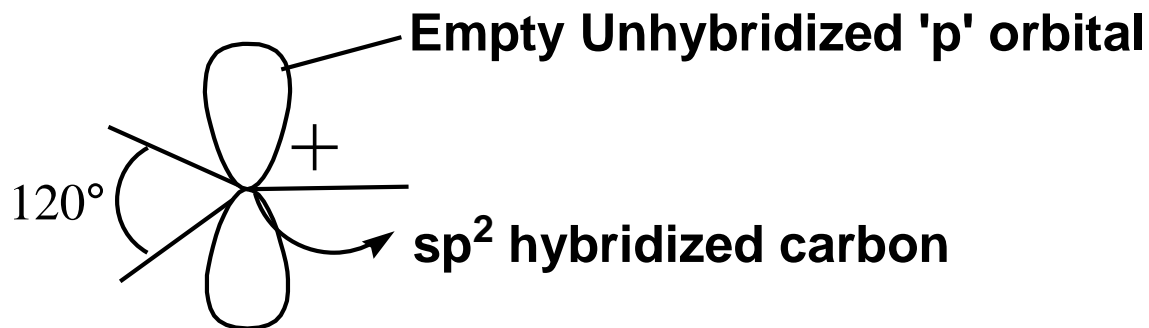
1) Protonation of alkenes:



2) Protonation of alcohols followed by dehydration:



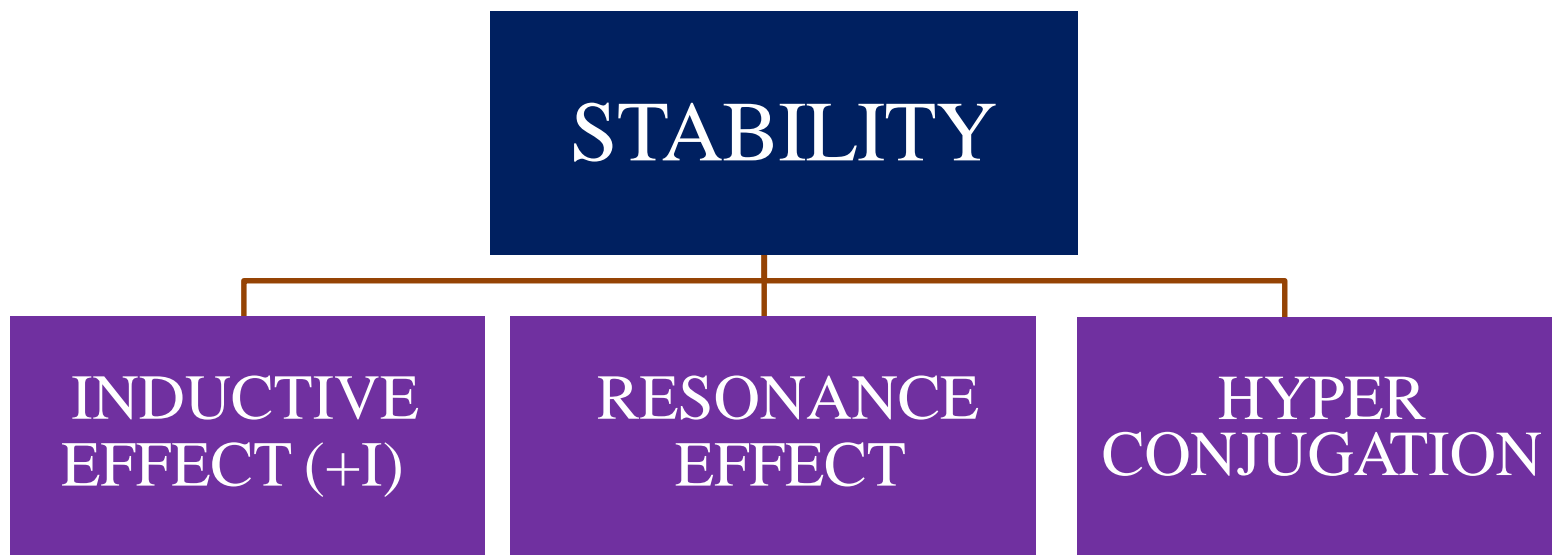
STRUCTURE



- The positively charged carbon of the carbocation is sp^2 hybridized.
- This carbon uses the three sp^2 hybridized orbitals for single bonding to 3 substituents.
- The unhybridized p -orbital remains vacant.
- Due to sp^2 hybridization, the carbocation possesses a planar structure with a bond angle of 120° between them.

STABILITY OF CARBOCATION

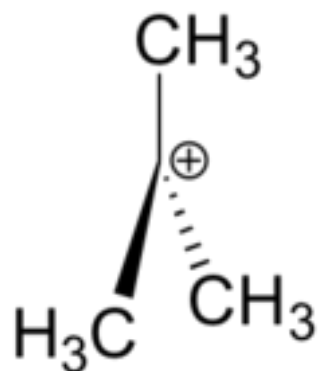
- Generally stability of carbocation depends upon three factors:



1) Stability of alkyl carbocation:

Order of stability due to +I Effect:

most stable \Longrightarrow least stable



tertiary



secondary



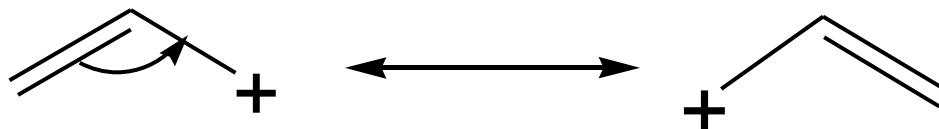
primary



methyl

2) Stability of allyl carbocation:

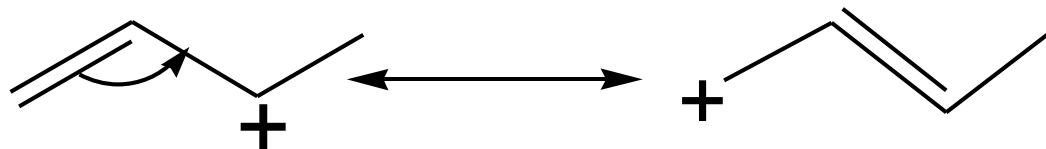
➤ Primary allylic carbocation:



Two resonating structures

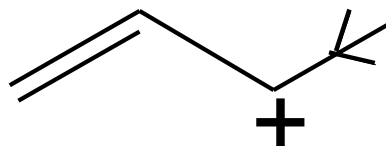
➤ Secondary allylic carbocation:

Resonance effect:



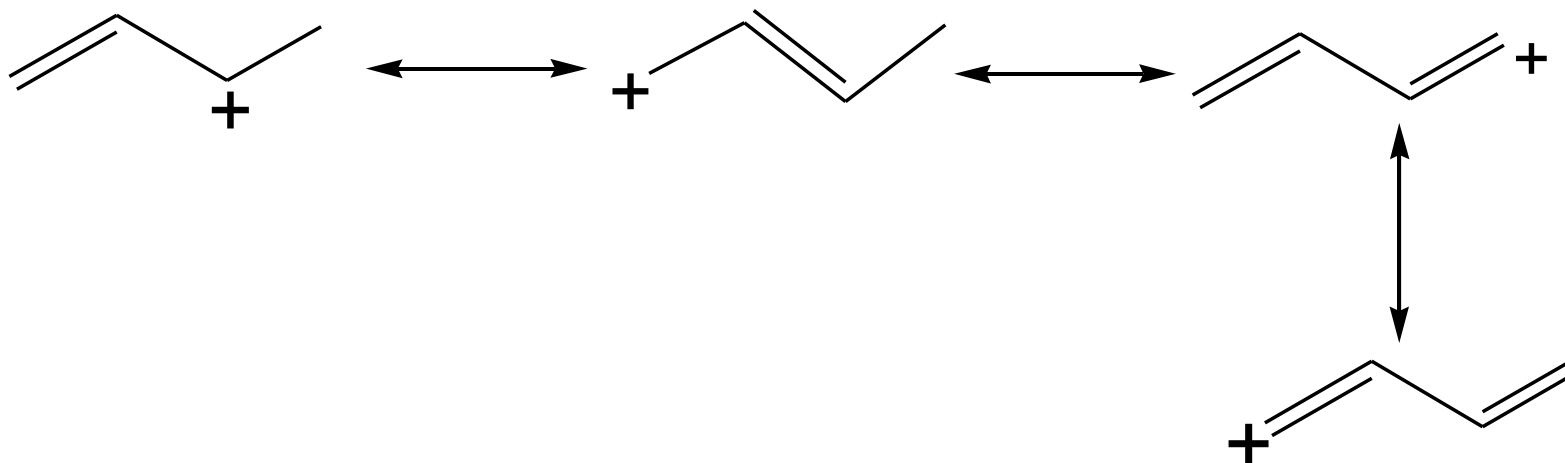
Two resonating structures

Inductive effect:



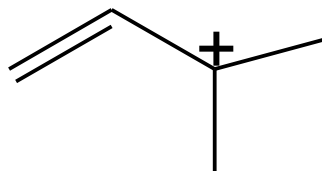
e^- - deficiency is reduced by the +I effect of alkyl group attached to the carbocation

Hyperconjugation effect:

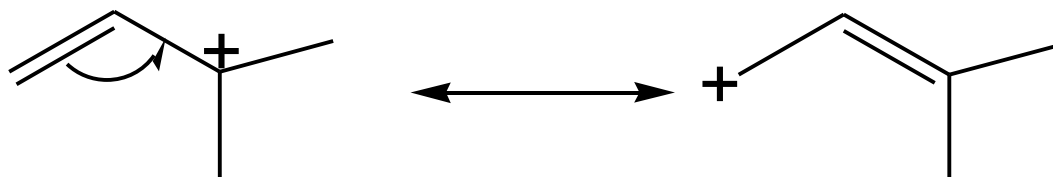


Four resonating structure due to hyper conjugation effect

➤ Tertiary allylic carbocation:

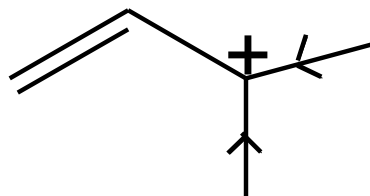


Resonance effect:



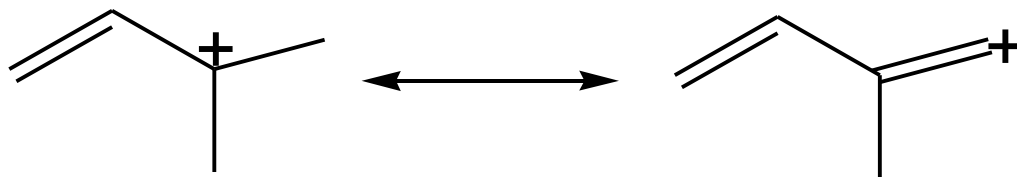
Two resonating structures

Inductive effect:



e^- - deficiency of the trivalent carbon is reduced by the two alkyl groups

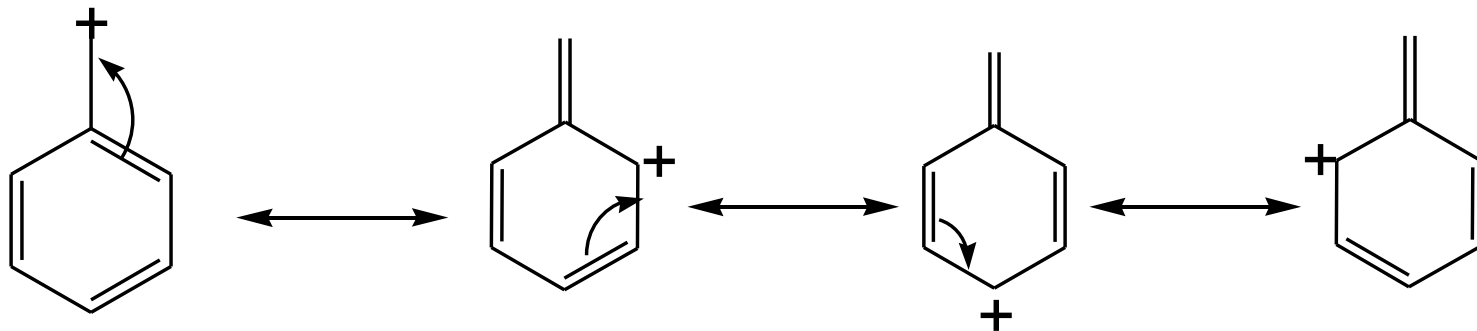
Hyperconjugation effect:



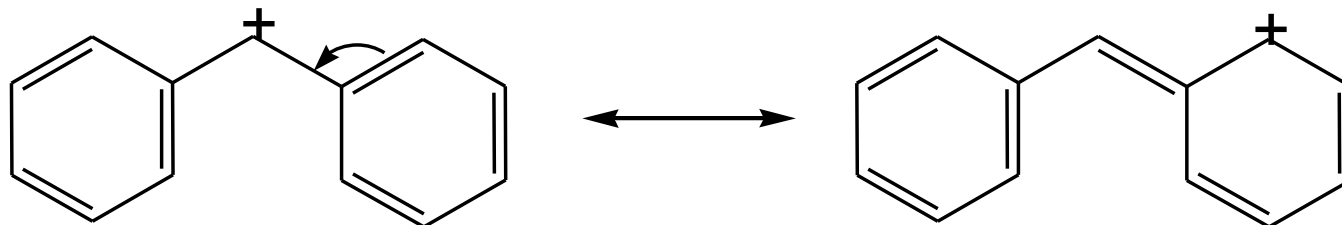
Totally seven resonating structures

3) Stability of benzyl carbocation:

Resonance effect of 1°-benzyl :

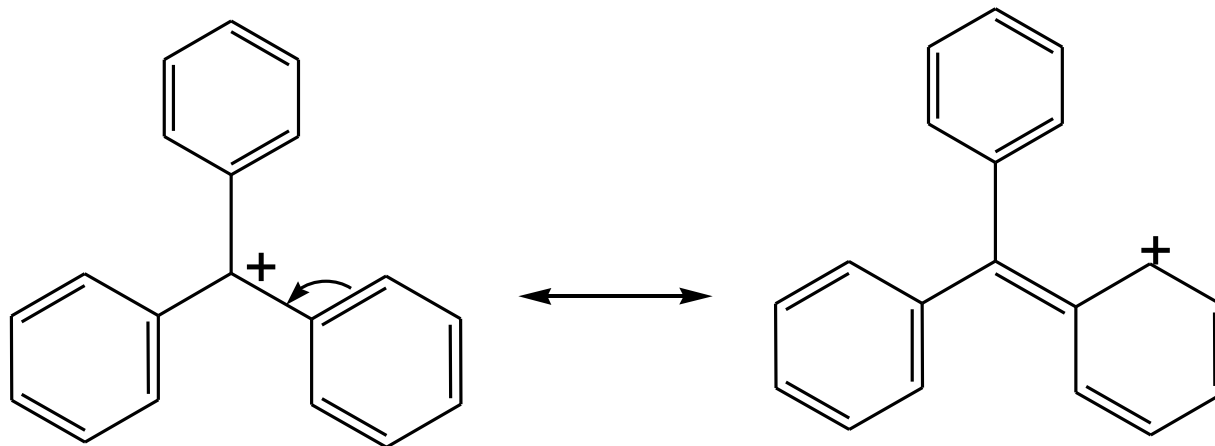


Resonance effect of 2°- benzyl :



Totally seven resonating structures

Resonance effect of 3°- benzyl:



Totally ten resonating structures

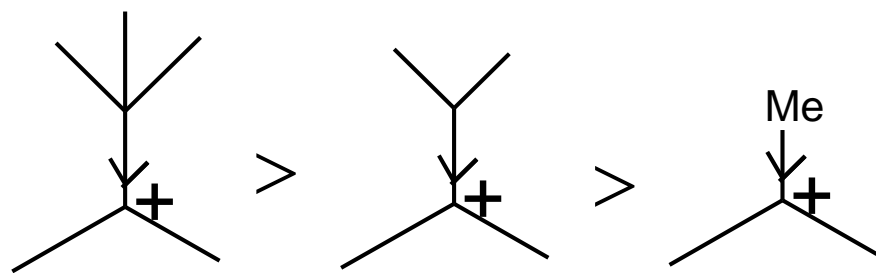
Stability of Carbocation:

We have seen all the possible carbocation's like alkyl, allylic and benzylic carbocation. In all the carbocation's the tertiary carbocation found to be **more stable** based on the possible effects.

The role of substituents in the stability of the carbocation:

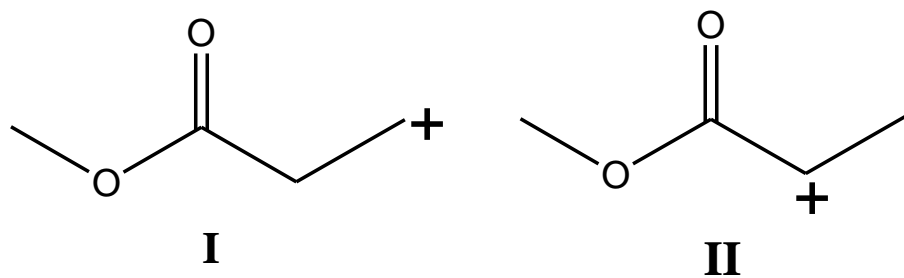
Consider an **electron donating** group has substituted in a carbocation, for eg: methyl, methoxy group or hydroxy group etc.

Since the carbocation's are electron deficient, thus any group which donates electron density to the **carbocationic center** of electron poverty will **help to stabilize it**.



It is not accurate to say, however, that carbocations with higher substitution are always more stable than those with less substitution.

Like electron donating, **electron withdrawing** group destabilize the carbocation. For eg: carbonyl group, ester group etc.,



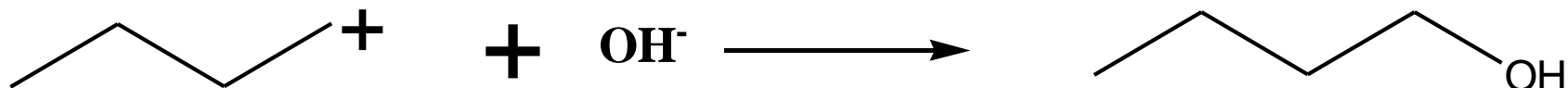
In the above structures, The structure – I is primary carbocation and structure – II is secondary carbocation. Based on the effect, we expect the structure – II is more stable. But in these case structure – I is more stable. This is due to the presence of electron withdrawing carbonyl group. In structure – II the carbocation is nearer or adjacent to the electron withdrawing group, hence it destabilize the carbocation. Hence structure – II is less stable compare to structure – I. The effect decreases with distance.

Based on all the consideration the stability order of the carbocations is as follows:

$1^\circ \text{alkyl} < 2^\circ \text{ alkyl} = 1^\circ \text{ allylic} < 1^\circ \text{ benzylic} < 3^\circ \text{ alkyl} < 2^\circ \text{ Allylic} = 2^\circ \text{ Benzylic} < 3^\circ \text{ Allylic} = 3^\circ \text{ Benzylic}.$

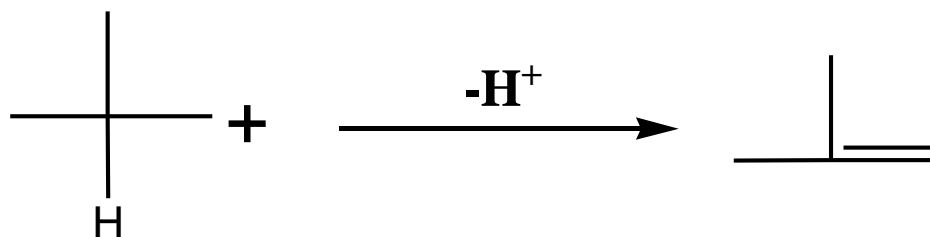
Reactions of Carbocation:

1) Substitution Reaction:

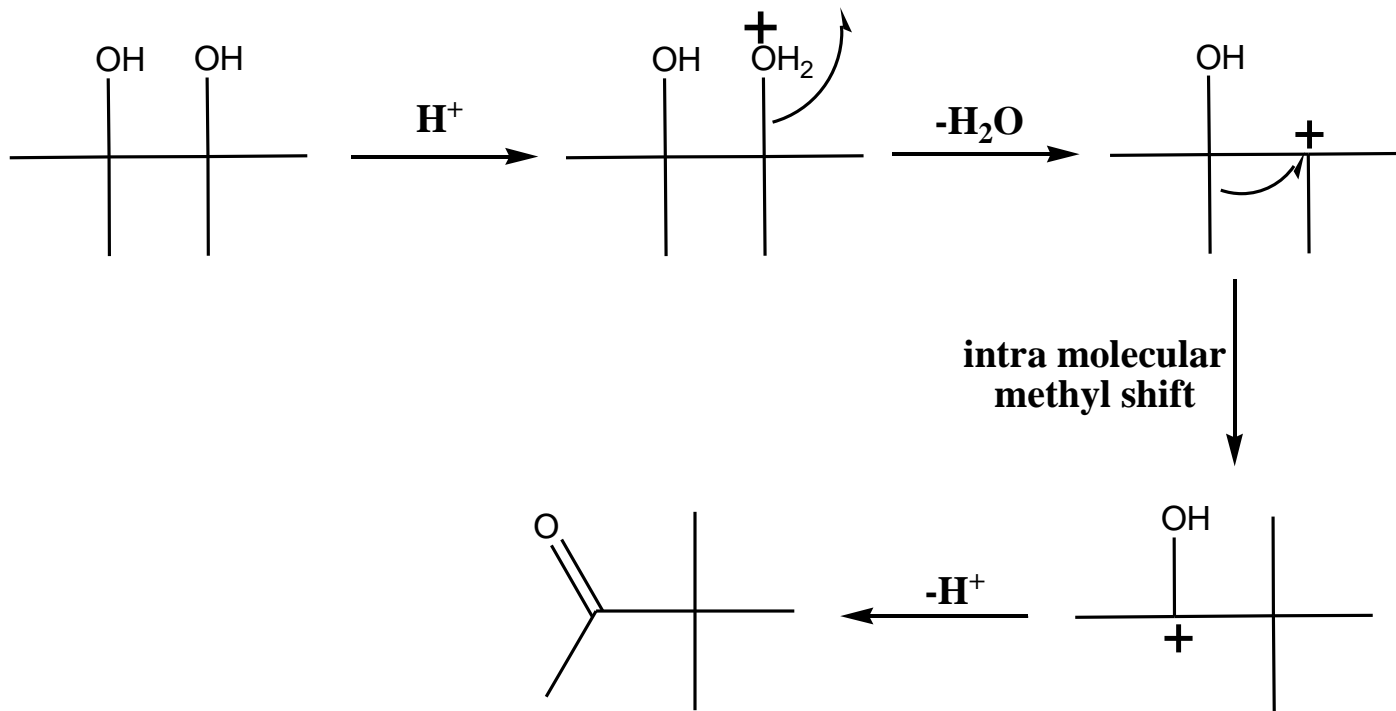
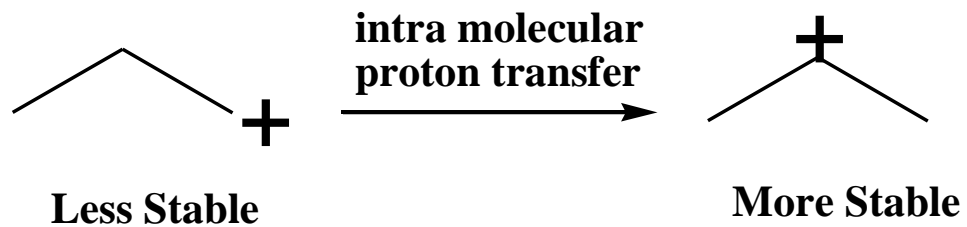


All nucleophilic S_N type reactions are best examples.

2) Elimination Reaction:



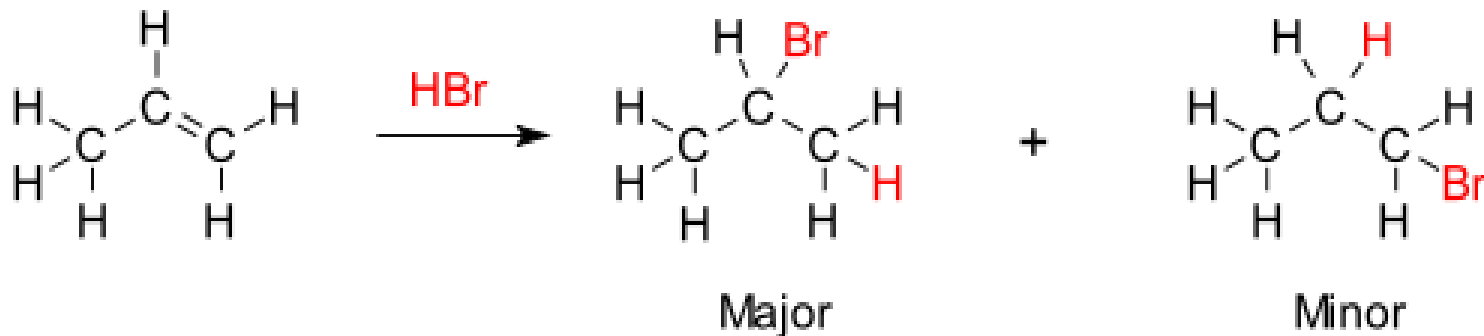
3) Rearrangement Reaction:



4) Addition Reaction:

Markovnikov's rule:

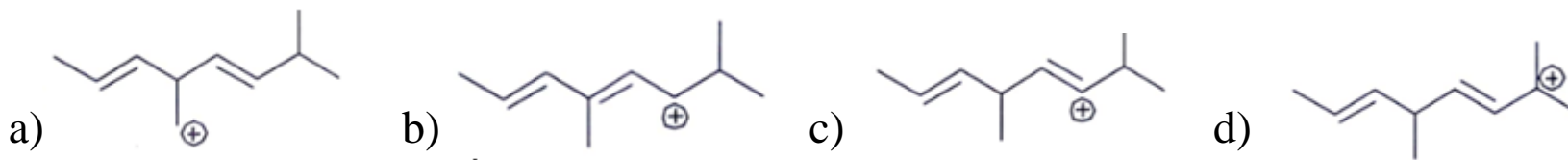
The rule states that with the addition of a protic acid HX to an asymmetric alkene, the acid hydrogen (H) gets attached to the carbon with more hydrogen substituents, and the halide (X) group gets attached to the carbon with more alkyl substituents. Alternatively, the rule can be stated that the hydrogen atom is added to the carbon with the greatest number of hydrogen atoms while the X component is added to the carbon with the least number of hydrogen atoms.



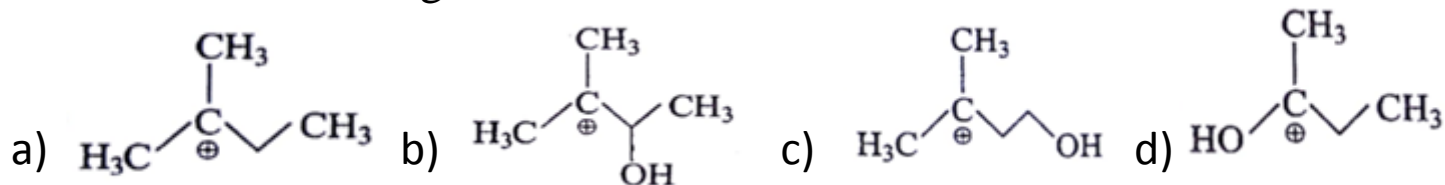
Work Out Examples

- 1) The hybridisation of carbocation is _____
a) Sp b) Sp^2 c) Sp^3 d) Sp^3d
- 2) The shape of carbocation is _____
a) Pyramidal b) Bent c) Linear d) Trigonal planar
- 3) The formal charge at the carbocation is equal to _____
a) -1 b) 0 c) +1 d) +2
- 4) Arrange the following carbocations in the order of increasing stability.
a) Benzyl > 3^0 > 2^0 > 1^0 b) Benzyl > 1^0 > 2^0 > 3^0 c) 3^0 > 2^0 > 1^0 > Benzyl
d) 1^0 > 2^0 > 3^0 > Benzyl

- 5) Which carbocation is the most stable?



- 6) Which of the following is most stable intermediate?



REFERENCES

INTERNET LINKS:

- [https://socratic.org/questions/how-is carbocation-formed](https://socratic.org/questions/how-is-carbocation-formed)
- <https://www.sanfoundry.com/engineering-chemistry-questions-answers-carbocations/>
- <https://www.sanfoundry.com/organic-chemistry-questions-answers-reaction-intermediates/>

BOOKS:

- Advanced organic chemistry, by Dr. Jagdamba Singh & Dr. L.D.S. Yadav.
- Organic Reactions and Mechanism by V.K. Ahluwalia