Formation of Carbocations:

There are different ways of forming carbocations using different substrates.

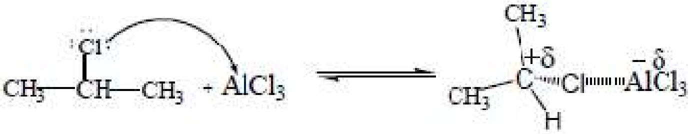
1- **From alkyl halides (Solvolysis of alkyl halides)**: The solvent used for the solvolysis must be **polar** solvents such as **water** or **alcohol**. The solvent plays **a dual role** in the solvolysis reaction: (a. Acts as **the solvent**, consequently **breaking of C-X bond** due to polarization, b. Acts as a **nucleophile** to **attack the carbocation formed**).

Example:

$$R\text{-}X \xrightarrow{\text{Solvent}} R^+ + X^- \xrightarrow{\text{Solvent}} R\text{-}OH$$

a- From alkyl halides with Lewis acid catalysts:

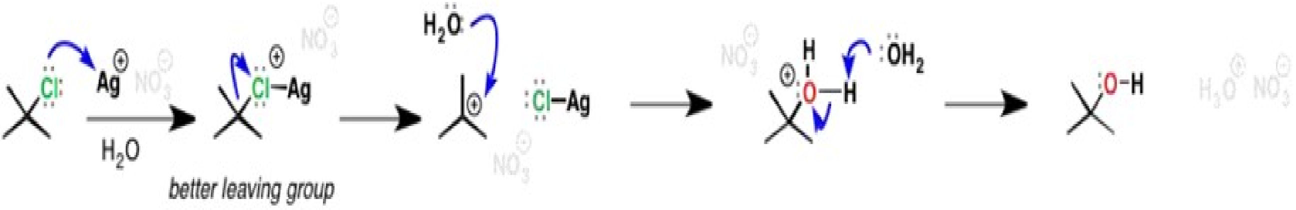
Example:



b- From alkyl halides with silver ion:

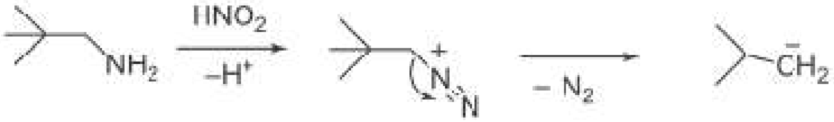
Example:

Mechanism:

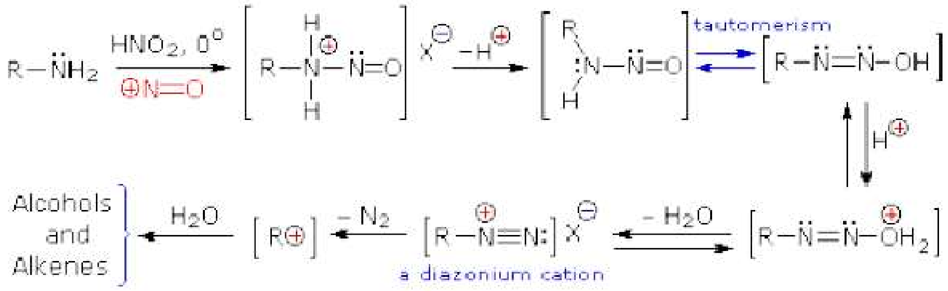


2- **From an amine (Using Diazonium salts)**: **Alkyl Diazonium ions** are **unstable** and **decomposed readily** to give **carbocations**.

Example:



Mechanism:



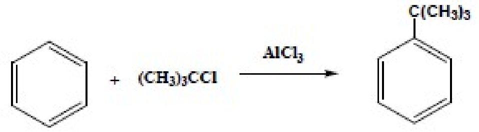
3- **From alcohol (Protonation of alcohols): Alcohols** are **easily protonated** using **dilute acids** and **carbocations** are **formed after losing water** molecules.

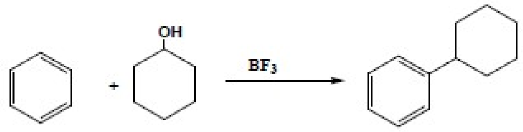
Examples:

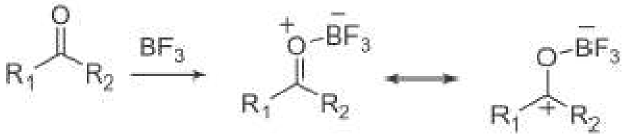
$$CH_3CH_2CH_2OH \xrightarrow{H^+} CH_3CH_2CH_2^+ + H_2O$$

4- **From Carbonyl compound:(Friedal Crafts acylation)**

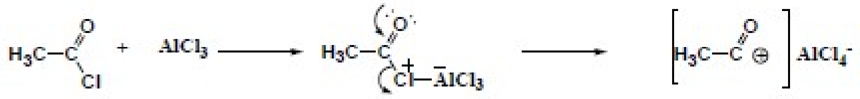
Example:







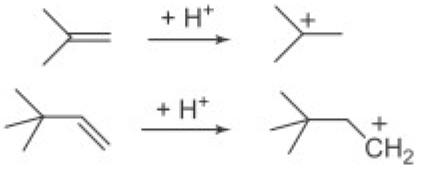
Mechanism: From **acyl chloride** when the **presence** of **Lewis acid** catalysts



5- **Addition of an electrophile to a π bond:**

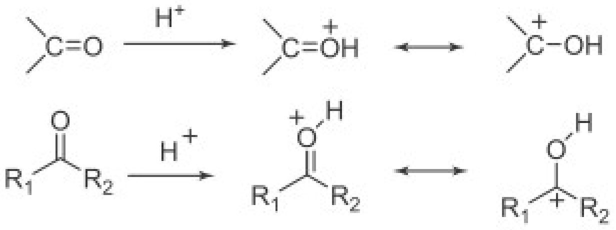
a- Protonation of an alkene:

Example:



b- Protonation of a carbonyl group:

Example:

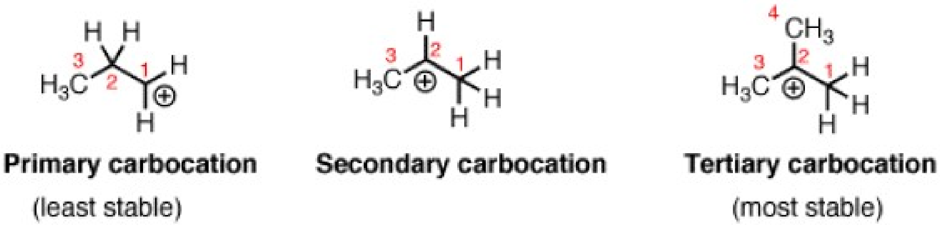


Reaction of Carbocation:

Many organic reactions proceed via carbocation intermediates. Therefore, carbocations are very important intermediates in organic synthesis.

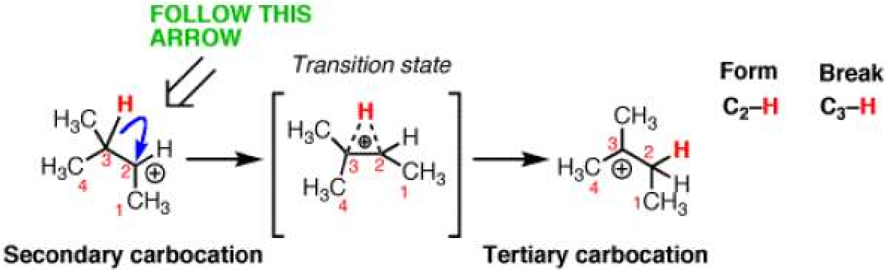
Carbocations are stabilized by neighboring carbon atoms:

The stability of carbocations increases as we go from primary to secondary to tertiary carbons. carbocations become more stable as you increase the number of electrons donating groups attached to them. **Alkyl groups are a perfect example:**

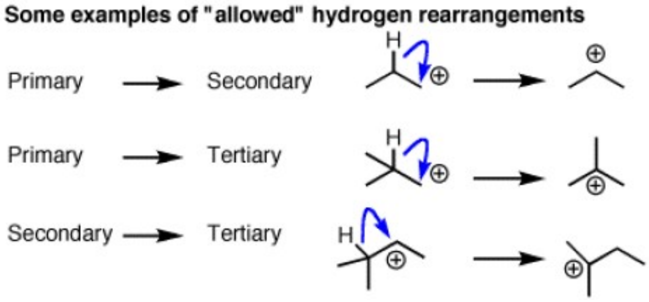


One rearrangement pathway where an unstable carbocation can be transformed into a more stable carbocation is called a **hydride shift**.

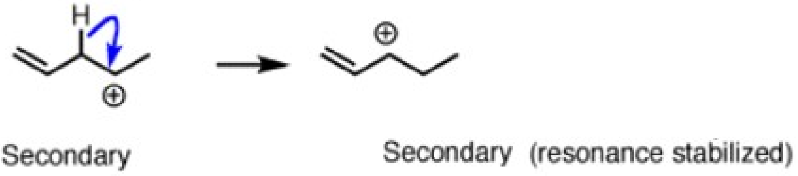
One pathway rearrangements can occur through is a *hydride shift.*



Example:

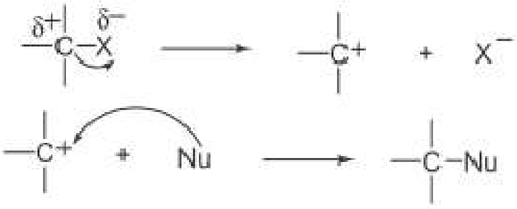


Note: **Carbocations with the same substitution pattern can rearrange if it results in a resonance-stabilized carbocation**

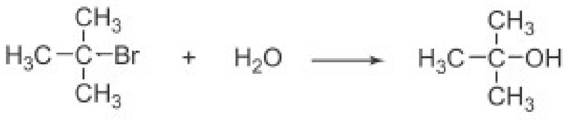


Now can show how the **rearrangement** reaction occurs with the **S_N1**.

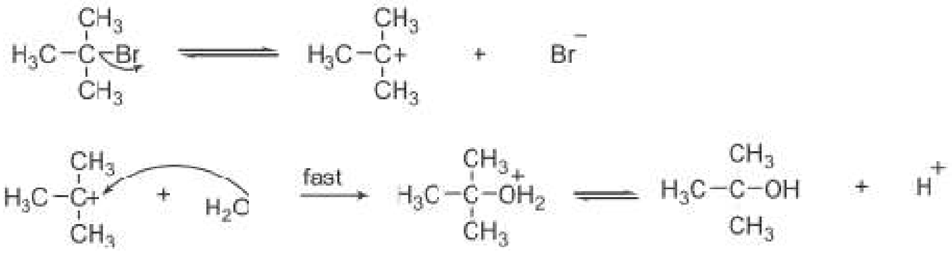
1- **Reaction with a Nucleophile: (e.g. S_N1 reaction)** the **first step** in the S_N1 is that the **leaving group leaves** to **give** a **carbocation**. In the case below, the **carbocation** that is **formed** is **secondary**, and there's a **tertiary carbon** next door. Therefore, a **rearrangement** can occur to **give** the **more stable tertiary carbocation**, which is then **attacked** by the **nucleophile (water in this case)**. Finally, the **water** is **deprotonated** to **give** the **alcohol**.



Example:

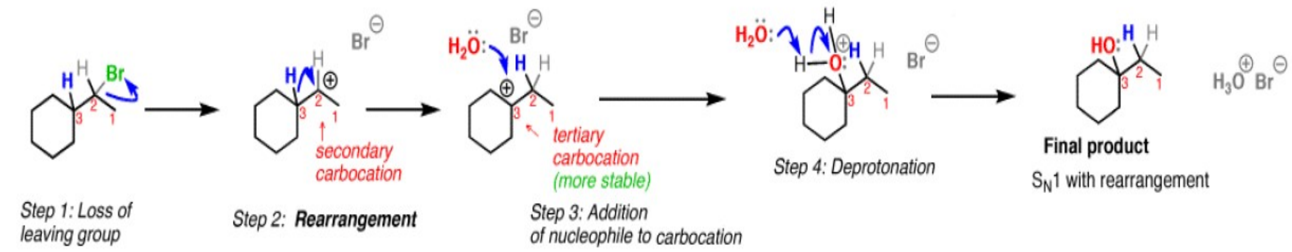

$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Br + H_2O \longrightarrow H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH$

Mechanism:


$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Br \rightleftharpoons H_3C-\overset{CH_3}{\underset{CH_3}{C}}{}^{+} + Br^-$

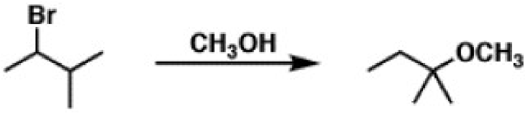
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}{}^{+} + H_2O \xrightarrow{fast} H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{O}H_2 \rightleftharpoons H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH + H^+$

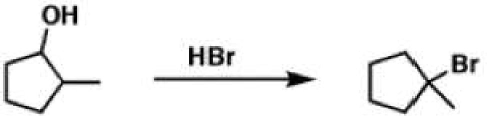
Example: the S_N1 reaction with **rearrangement**.

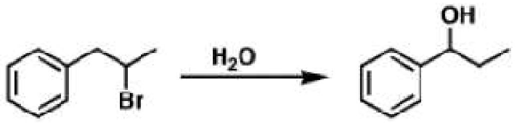


Rearrangements can accompany reactions where carbocations are formed, such as in the S_N1 reaction:

Examples:







$$R{-}I \; + \; {}^{\ominus}OH \longrightarrow R{-}OH \; + \; I^{\ominus}$$

$$\underset{\displaystyle Br}{CH_3CHCH_2CN} \xrightarrow[\text{acetone}]{\text{NaI}} \underset{\displaystyle I}{CH_3CHCH_2CN}$$

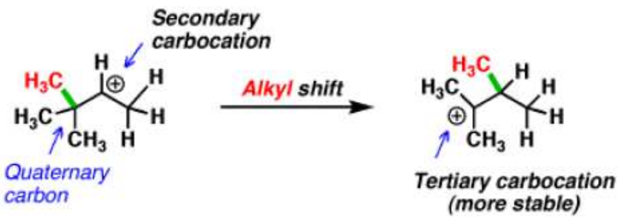
$$\underset{\displaystyle OTs}{CH_3CH(CH_2)_5CH_3} \; + \; PhS^- \xrightarrow{\text{ethanol}} \underset{\displaystyle SPh}{CH_3CH(CH_2)_5CH_3}$$

$$R{-}I \; + \; NMe_3 \longrightarrow R{-}\overset{+}{N}Me_3 \; I^{\ominus}$$

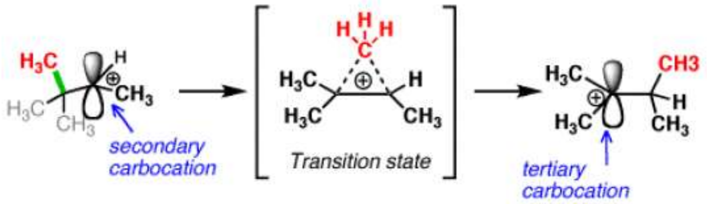
$$CH_3CH_2I \; + \; (CH_3CH_2CH_2CH_2)_3P \longrightarrow (CH_3CH_2CH_2CH_2)_3\overset{+}{P}\,CH_2CH_3\,I^-$$

$$PhC(CH_3)_2Cl \; + \; CH_3CH_2OH \longrightarrow PhC(CH_3)_2\underset{\displaystyle H}{\overset{+}{O}}CH_2CH_3 \xrightarrow[-H^+]{} PhC(CH_3)_2OCH_2CH_3$$

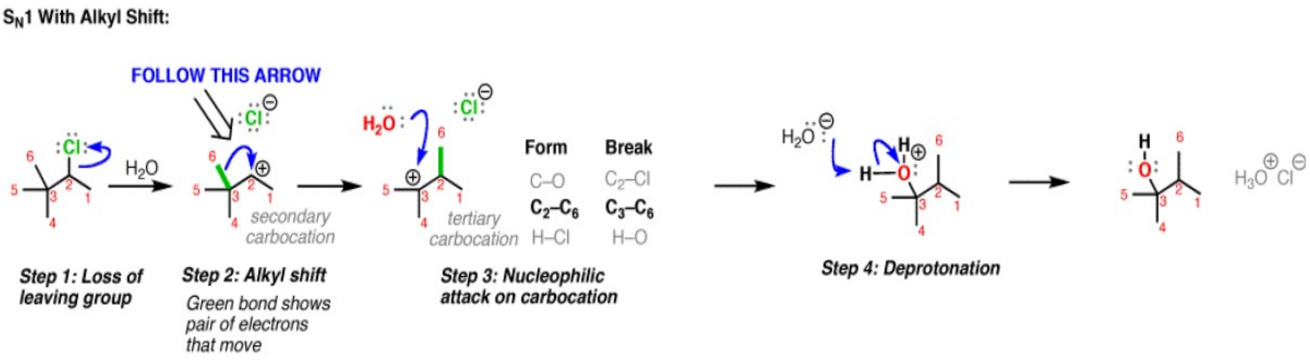
Note: The most common situation where **alkyl shifts** can occur is when a **quaternary carbon** (that's a **carbon attached to 4 carbons**) is **adjacent** to a **secondary carbocation**.



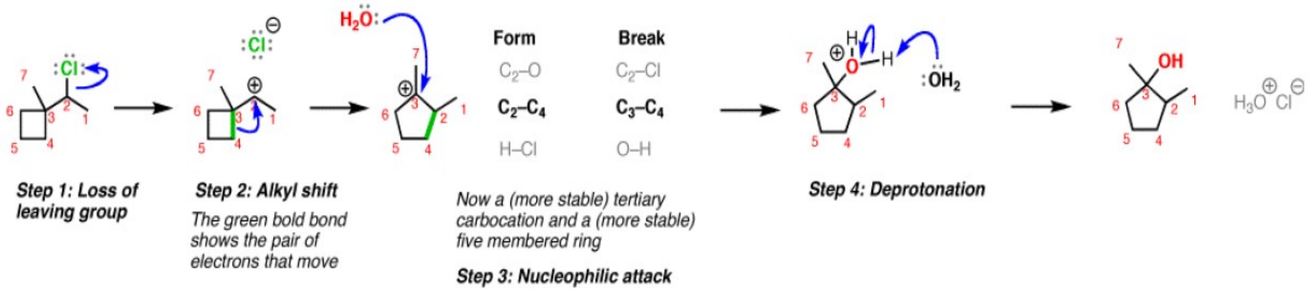
In the **transition state**, there are **partial bonds between** the carbon being transferred and each of the two adjacent carbon atoms. Then, as **one bond shortens and the other lengthens**, we end up with a (**more stable**) **tertiary carbocation**.



<u>Example:</u> CH_3 groups here are just shown as lines.

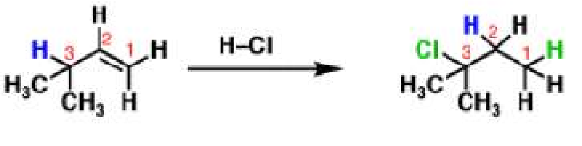


<u>Example:</u> **Alkyl shift leads** to **ring expansion**.



2- **<u>Addition reaction of Alkenes:</u>** The **alkene** is **gone**, and **two new bonds** have **formed** after rearrangement.

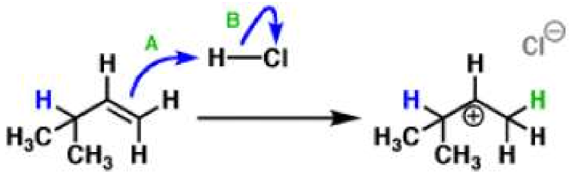
<u>Example:</u>



Form	Break
C_1–H	C_1–C_2 (π)
C_2–H	C_3–H
C_3–Cl	H–Cl

Mechanism:

Step 1 - attack of alkene on H-Cl (arrows A and B)



Form	Break
A C_1–H	A C_1–C_2 (π)
C_2–H	C_3–H
C_3–Cl	B H–Cl

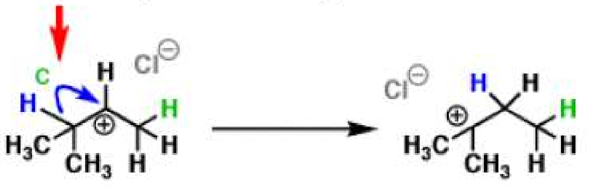
Observation: secondary carbocation

Step 2 - rearrangement (arrow C)

Recall the order of carbocation stability: tertiary > secondary > primary

Migration of the C-H bond from C_3 to C_2 results in a more stable carbocation!

This arrow says, "break the C_3–H bond and form a new C_2-H bond"



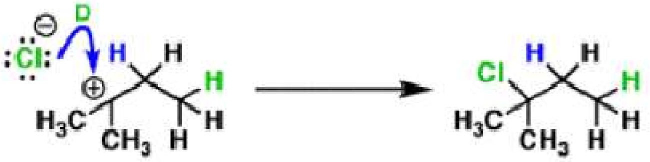
Secondary carbocation

Tertiary carbocation

a more stable carbocation

Form	Break
A C_1–H	A C_1–C_2 (π)
C C_2–H	C C_3–H
C_3–Cl	B H–Cl

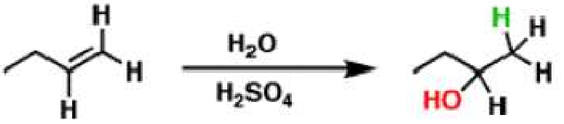
Step 3 - Attack of nucleophile (arrow D)



Tertiary carbocation

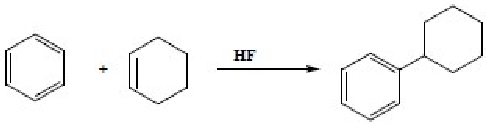
Form	Break
A C_1–H	A C_1–C_2 (π)
C C_2–H	C C_3–H
D C_3–Cl	B H–Cl

Example: Hydration of alkenes (with acid catalyst).

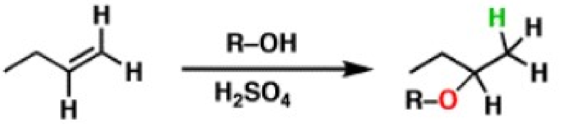


(often written $H_3O^{\oplus}$)

Form	Break
C–H	C–C (π)
C–OH	H–O



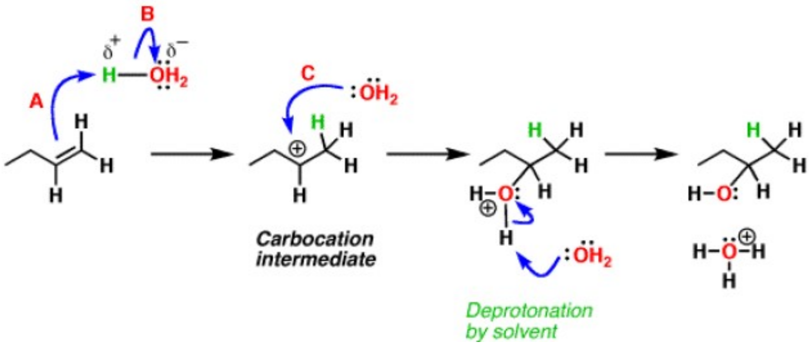
Example: Addition of alcohols to alkenes (with acid catalyst).



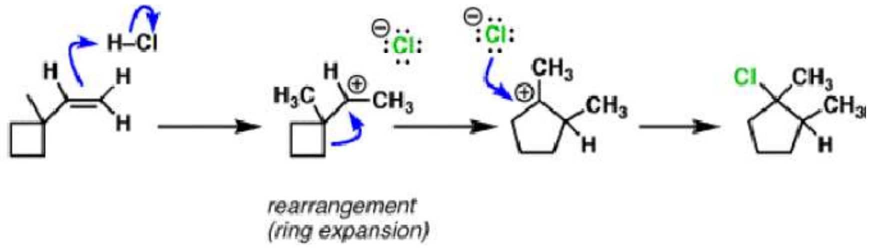
("$H^{\oplus}$" is often written as the acid here)

Form	Break
C–H	C–C (π)
C–OR	H–O

Example: Addition of water to alkenes (with acid catalyst).

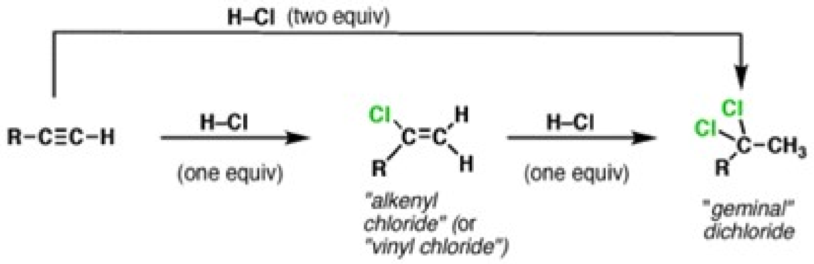


Example: Ring expansion.



3- Addition of acid to Alkynes:

Example:

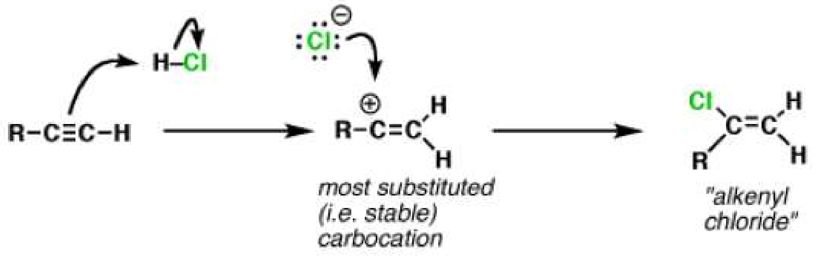


note: "Markovnikov" addition
(Cl adds to most substituted carbon)

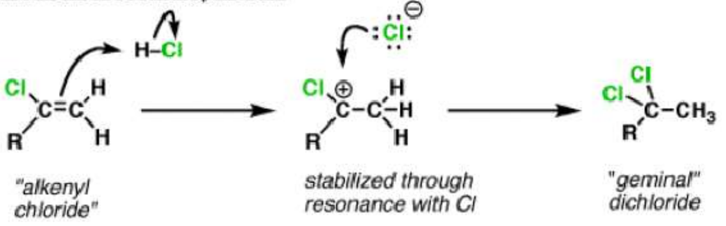
Same for HBr and HI

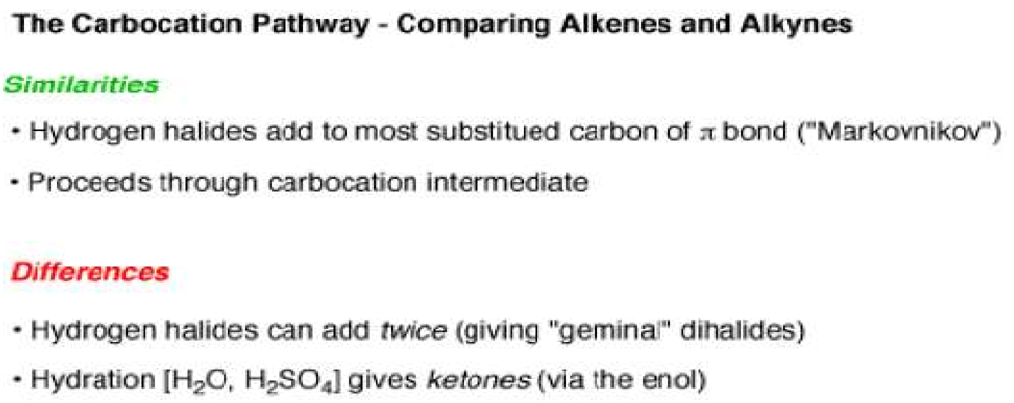
Mechanism:

Addition of first equivalent:



Addition of second equivalent:





The Carbocation Pathway - Comparing Alkenes and Alkynes

Similarities

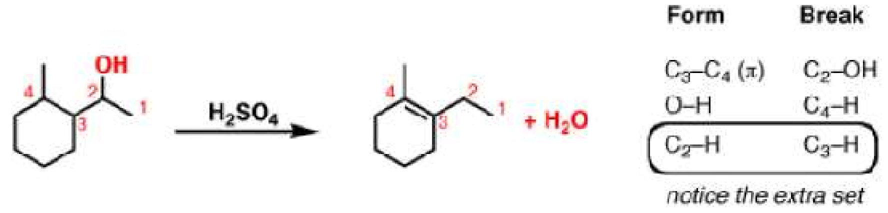
- Hydrogen halides add to most substitued carbon of π bond ("Markovnikov")
- Proceeds through carbocation intermediate

Differences

- Hydrogen halides can add *twice* (giving "geminal" dihalides)
- Hydration [H_2O, H_2SO_4] gives *ketones* (via the enol)

4- Elimination of a proton:(by E1 to form alkene)

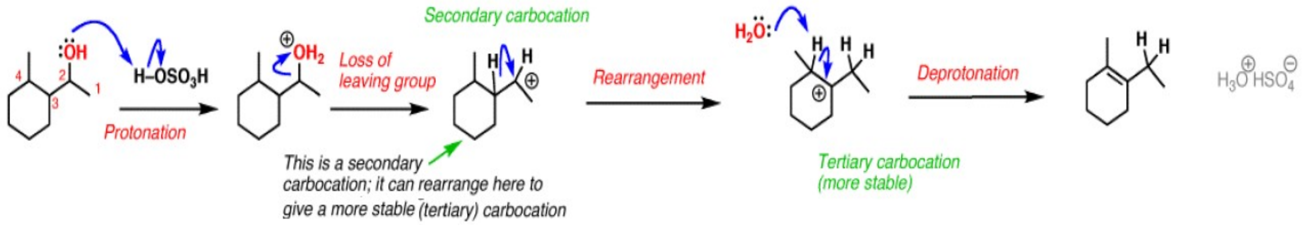
Example: **Elimination** with **rearranging** of **hydrogen**.



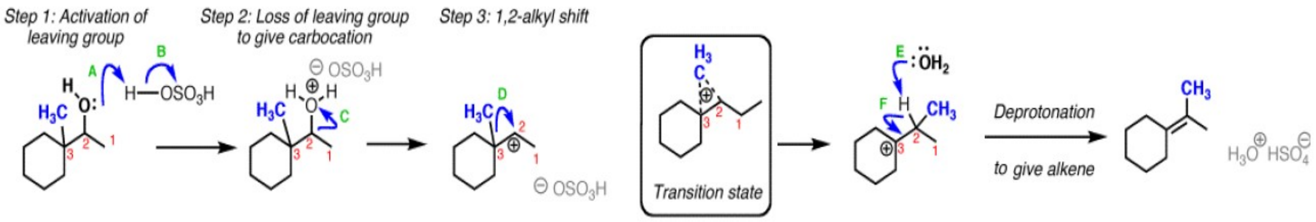
Form	Break
C_3–C_4 (π)	C_2–OH
O–H	C_4–H
C_2–H	C_3–H

notice the extra set

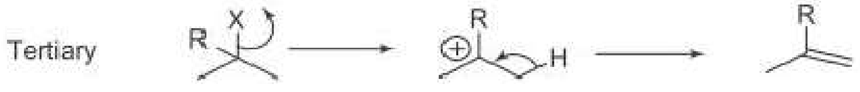
Mechanism: we start by protonating the alcohol. This allows for water to leave in the next step, which is going to form a secondary carbocation adjacent to a tertiary carbon. then the hydrogen (and its pair of electrons) were to migrate from C3 to C-2 to form tertiary carbocation, which is more stable. Then, a base (water) could remove C-H, forming the more substituted alkene (the Zaitsev product).

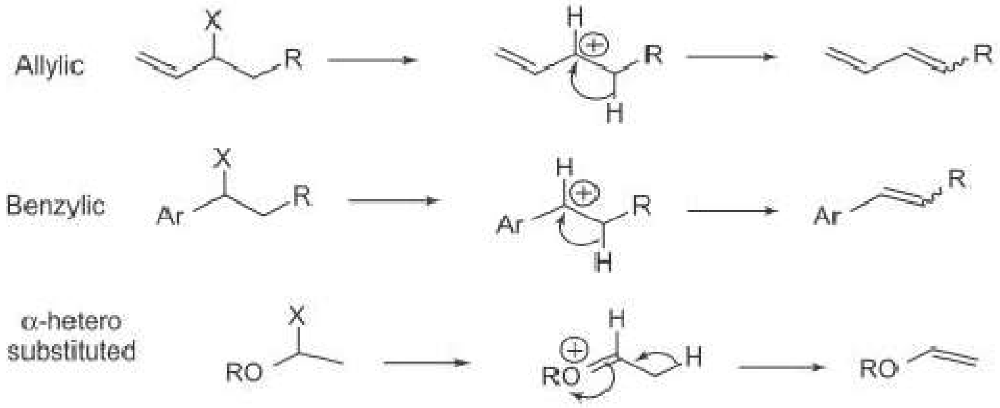


Example: **Elimination** with **rearranging** of **alkyl group**.

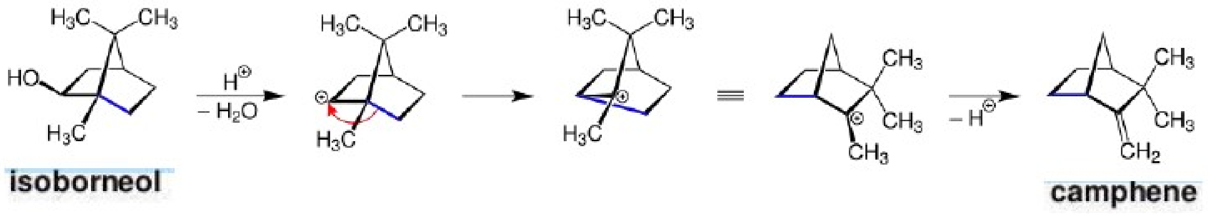


Examples:

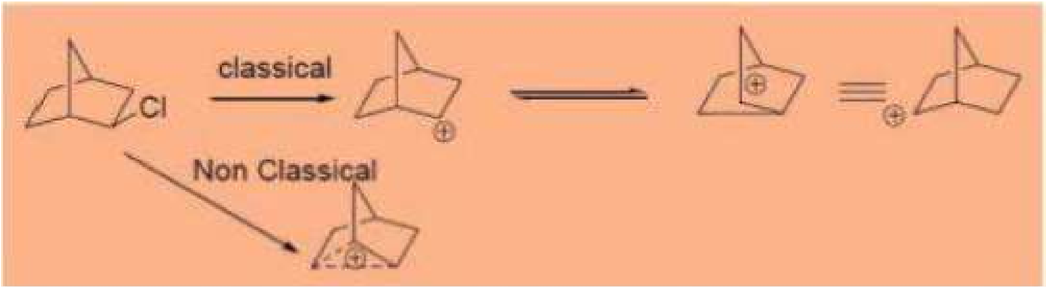




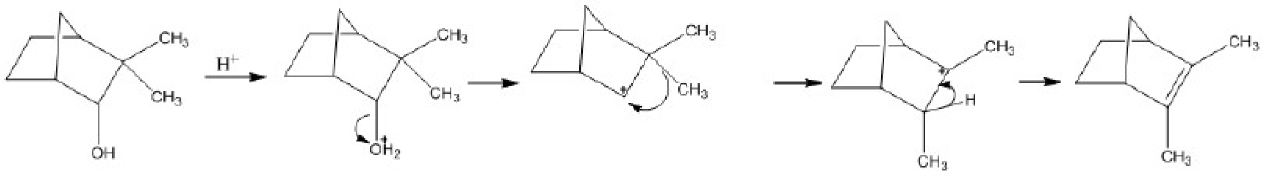
Wagner–Meerwein rearrangement: is a class of carbocation 1,2-rearrangement reactions in which a hydrogen, alkyl, or aryl group migrates from one carbon to a neighboring carbon. The rearrangement was first discovered in bicyclic terpenes for example the conversion of isoborneol to camphene.



Like **Meerweins rearrangement** of **norbomyl system**:

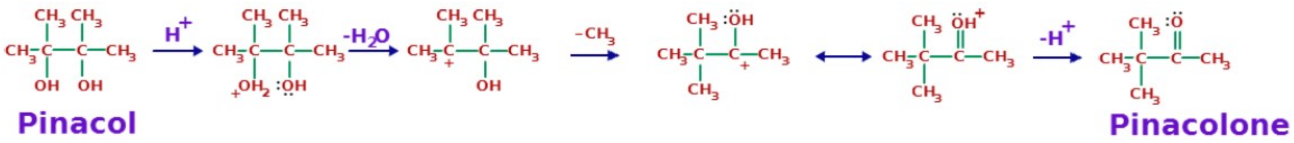


Example: Rearrangement of alcohols by **acid**.



5- **Rearrangement of carbocations (Pinacol / Pinacolon rearrangement):** Sometimes, unexpected products are formed. This is due to the rearrangement of the **first formed carbocation** into the most stable carbocation and undergoes the second reaction to form the product.

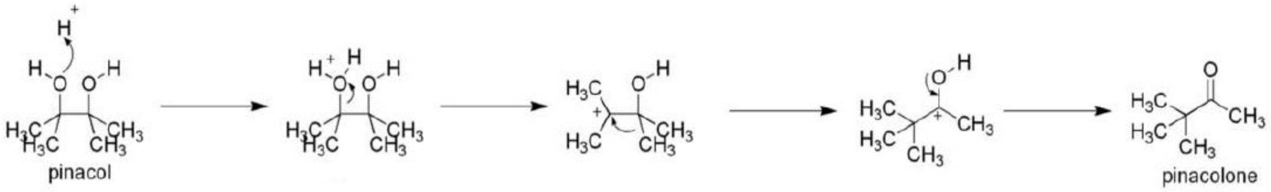
Example: 1,2-dihydroxy compounds.



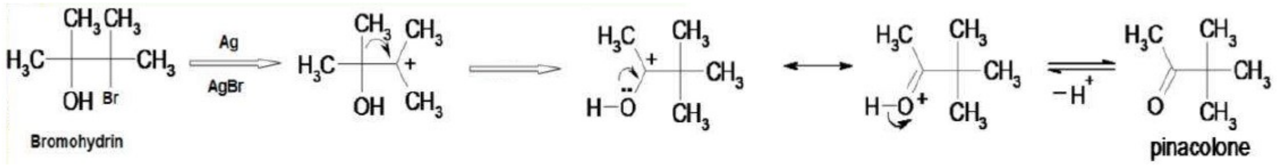
A carbocation is already tertiary, why should it rearrange?

Because the lone pair of electrons on the oxygen is another source to stabilize the carbocation. The carbocation formed as a result of the loss of H_2O pulls the migrating group, Lone pair of oxygen pushes the migrating group.

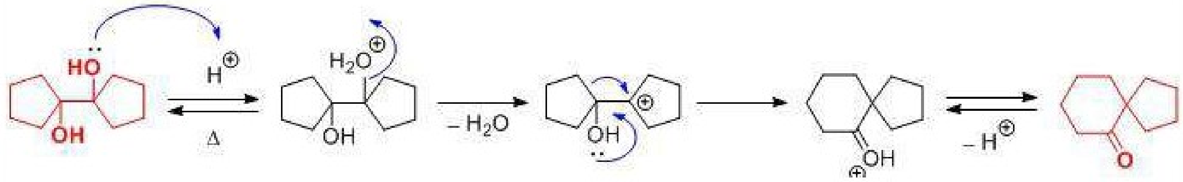
Mechanism:



Example: conversion of bromohydrin to pinacolone.

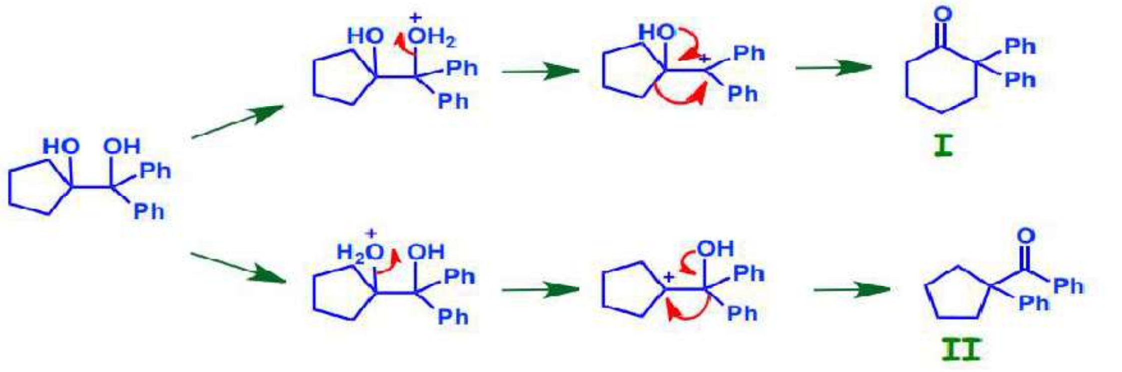


Example: Preparation of Spiro System:



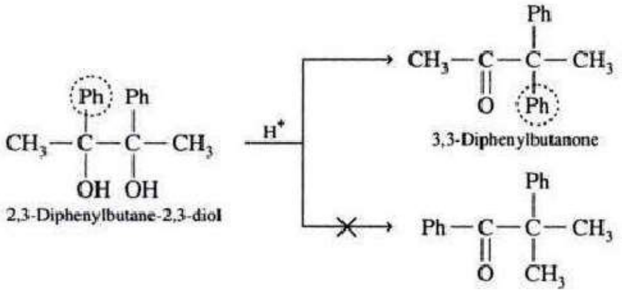
- **Migrating group preference:**

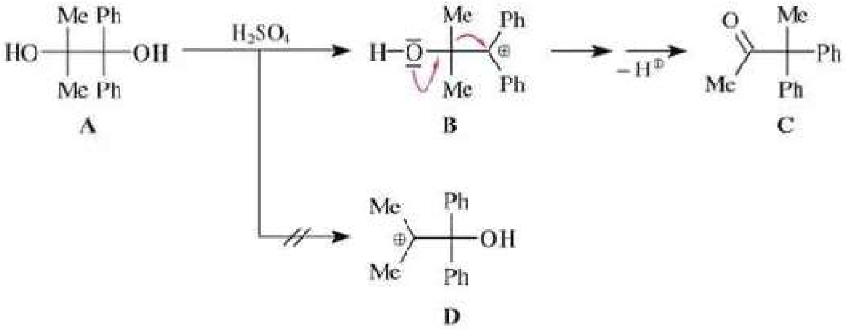
It doesn't matter when we have symmetrical diols & epoxides
It doesn't matter when we have unsymmetrical epoxides & diols



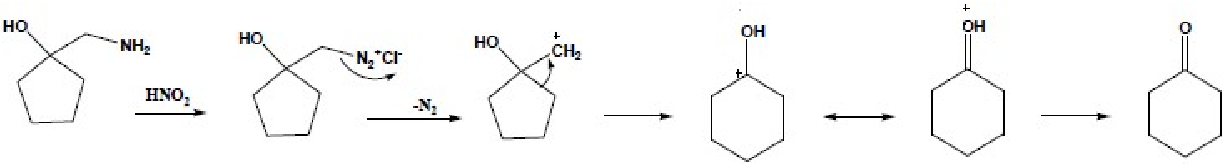
Only I is formed in quantitative amount because the carbocation is stabilized by two phenyl groups

Examples:



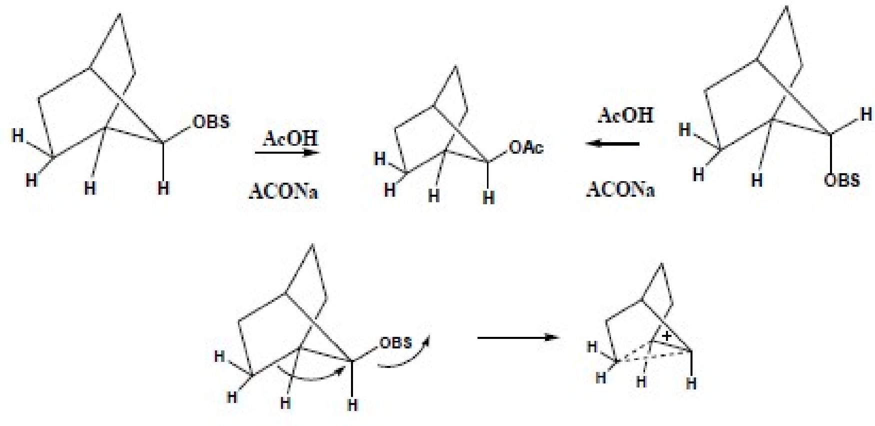


Example: Rearrangement by **Diazonium salt**.

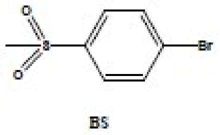


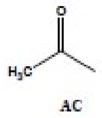
6- **Non-Classical Carbocation:** There are special types of carbocations called non-classical carbocations which show **special delocalization** through the **sigma bonds in 3-center-two electronic bonds in a bridging system**.

Example:

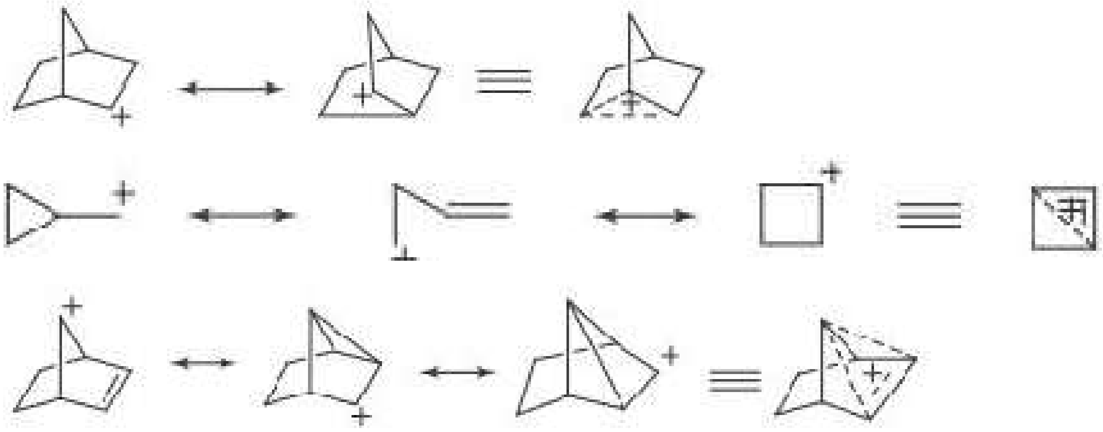


non-classical carbocation





Examples:



The acylation reaction shown above is 350 times faster than that of ter-butyl bromide. It is due to the reaction proceed through the non-classical carbocation.