

Unit V- S7

SLO-1: Elimination reaction

SLO-2: Oxidation reaction

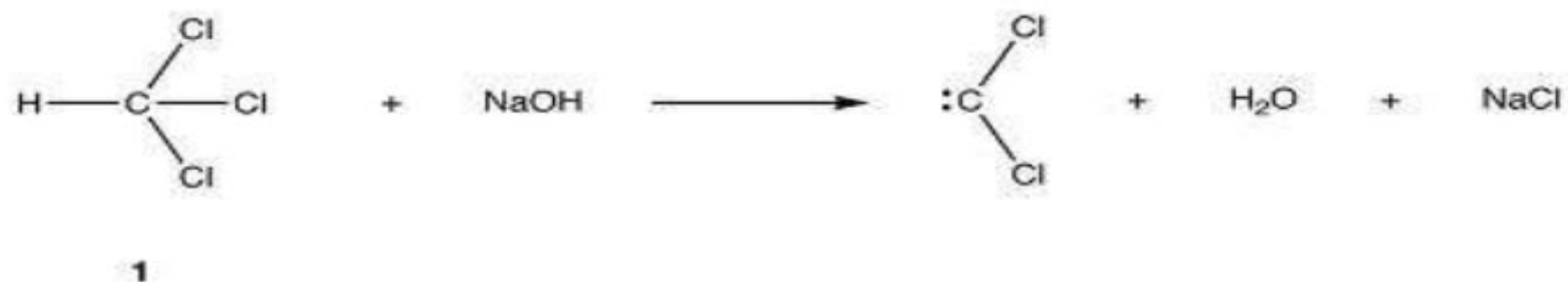
Dt. 24/12/2021

Elimination reaction

It involves loss of two atoms from the substrate molecule leading to the formation of multiple bond.

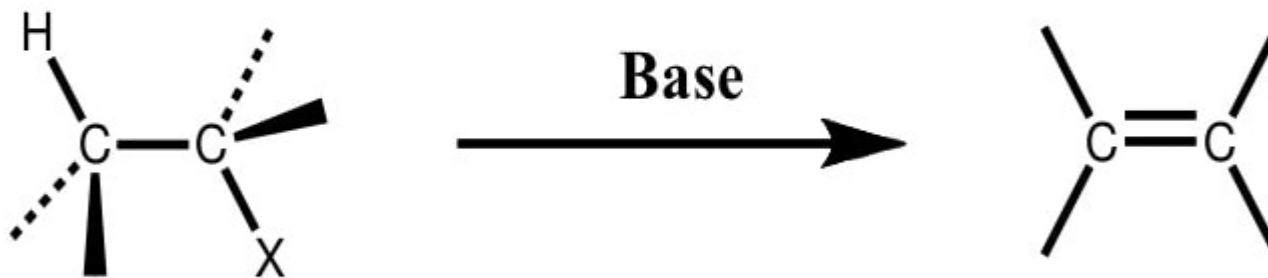
Molecular weight of product is less than the starting materials/substrate

➤ **α -eliminations** in which two groups are eliminated from the same atom.



In this case unstable species are formed which undergo further reactions.

- **β -eliminations** in which groups on adjacent atoms are eliminated with the formation of multiple bonds.



β -eliminations

β -eliminations proceeds through two mechanisms which are

- E2 bimolecular elimination reactions
- E1 unimolecular elimination reaction

The E2 and E1 mechanisms differ in the timing of bond cleavage and bond formation, analogous to the S_N2 and S_N1 mechanisms.



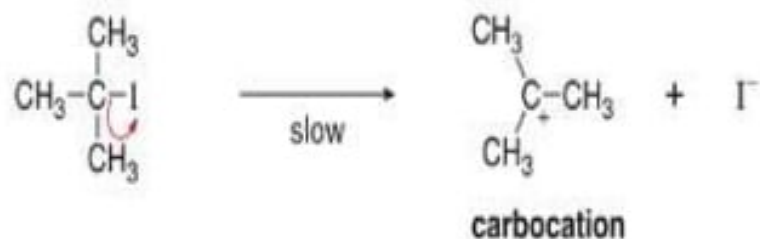
E1, Unimolecular Elimination Reactions

E1 indicates a **elimination, unimolecular** reaction. The E1 reaction proceeds via a two-step mechanism: the bond to the leaving group breaks first before the π bond is formed. The slow step is unimolecular, involving only the alkyl halide.



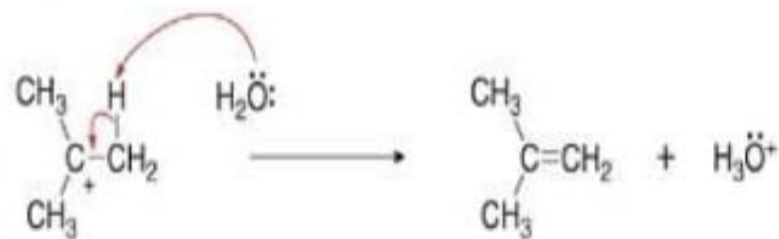
The dehydrohalogenation of $(\text{CH}_3)_3\text{CI}$ with H_2O to form $(\text{CH}_3)_2\text{C}=\text{CH}_2$ can be used to illustrate the E1 mechanism.

Step [1] The C–I bond is broken.



- **Heterolysis of the C–I bond** forms an intermediate **carbocation**. This is the same first step as the $\text{S}_{\text{N}}1$ mechanism. It is responsible for the first-order kinetics because it is rate-determining.

Step [2] A C–H bond is cleaved and the π bond is formed.



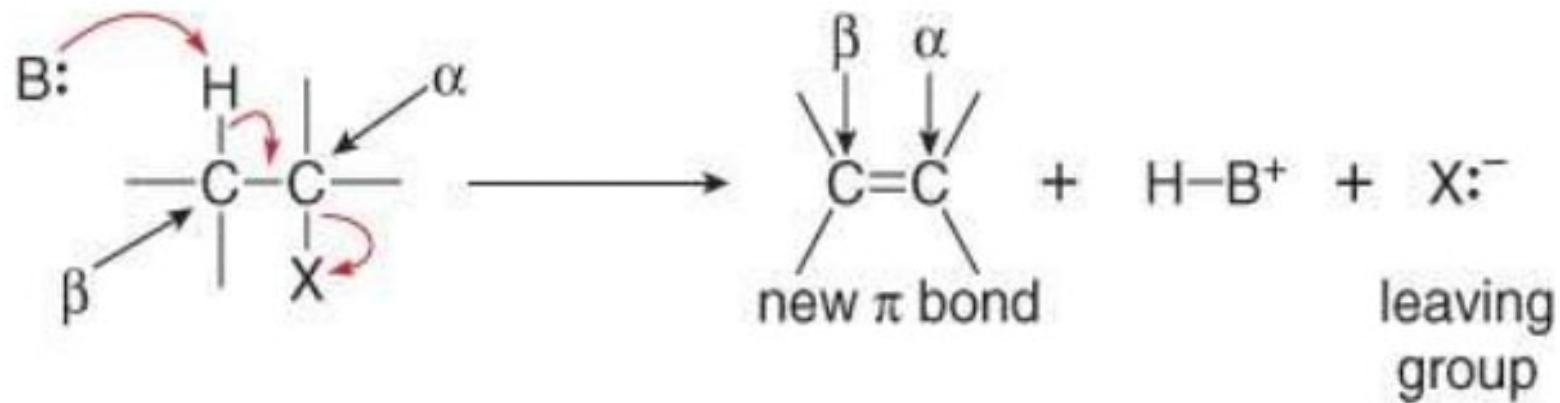
- **A base** (such as H_2O or I^-) **removes a proton from a carbon adjacent to the carbocation** (a β carbon). The electron pair in the C–H bond is used to form the new π bond.

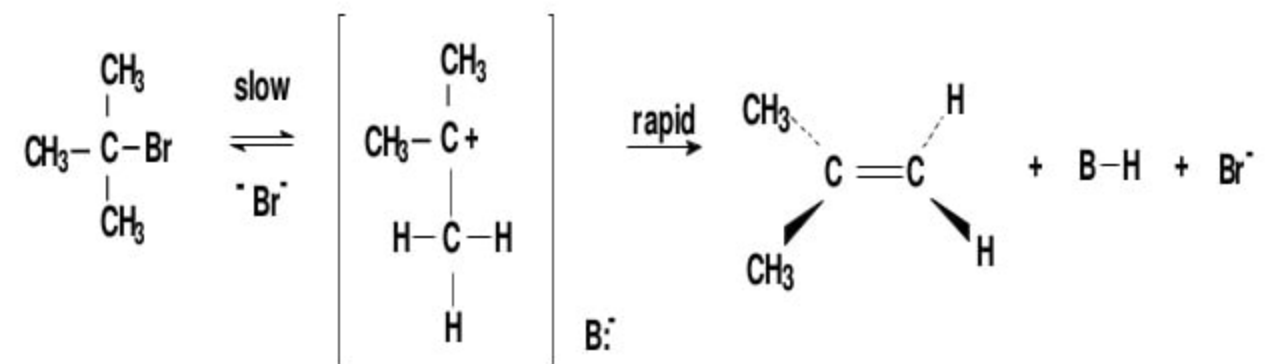
Types of elimination reactions:

1. Dehydrohalogenation (-HX) and
2. Dehydration ($\text{-H}_2\text{O}$)

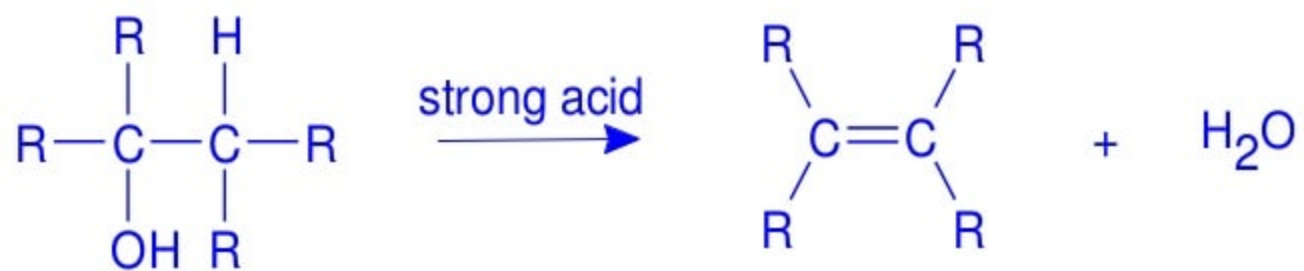


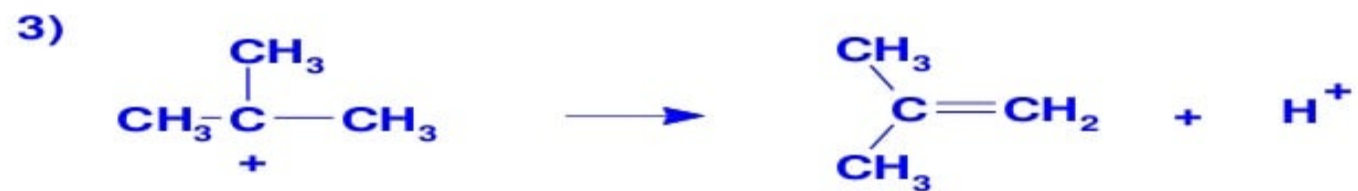
1. Dehydrohalogenation (-HX)





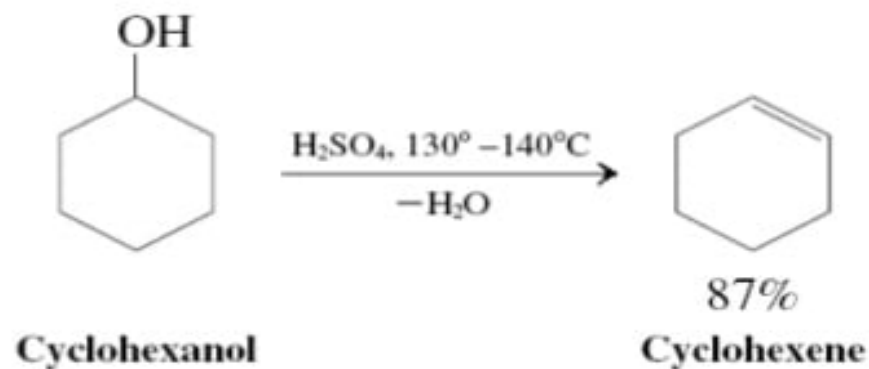
2. Dehydration (-H₂O)



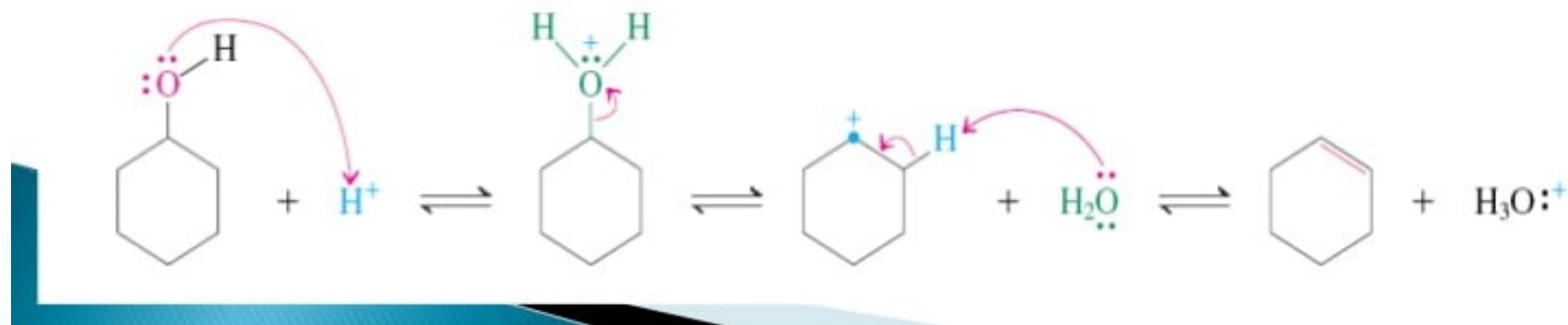


Alcohols also undergo Elimination under Acidic Conditions:

Alcohol Dehydration by the E1 Mechanism



Mechanism of the Dehydration of Cyclohexanol



1) Substrate effect:

The order of the reactivity of the alkyl groups is

Tertiary > Secondary > Primary

This is because the rate determining step is the formation of carbocation and the stability of these ions increases.



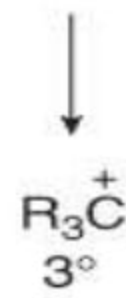
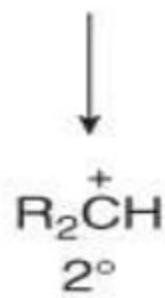
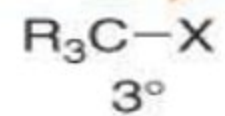
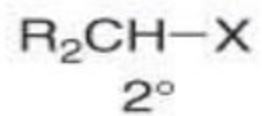
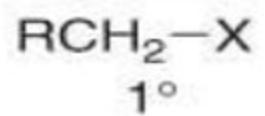
Order of stability of Carbocation

Tertiary (3°) > secondary (2°) > primary (1°)

It is hard (but not impossible) to get primary compounds to go by E1. The reason for this is that primary carbocations are not stable!

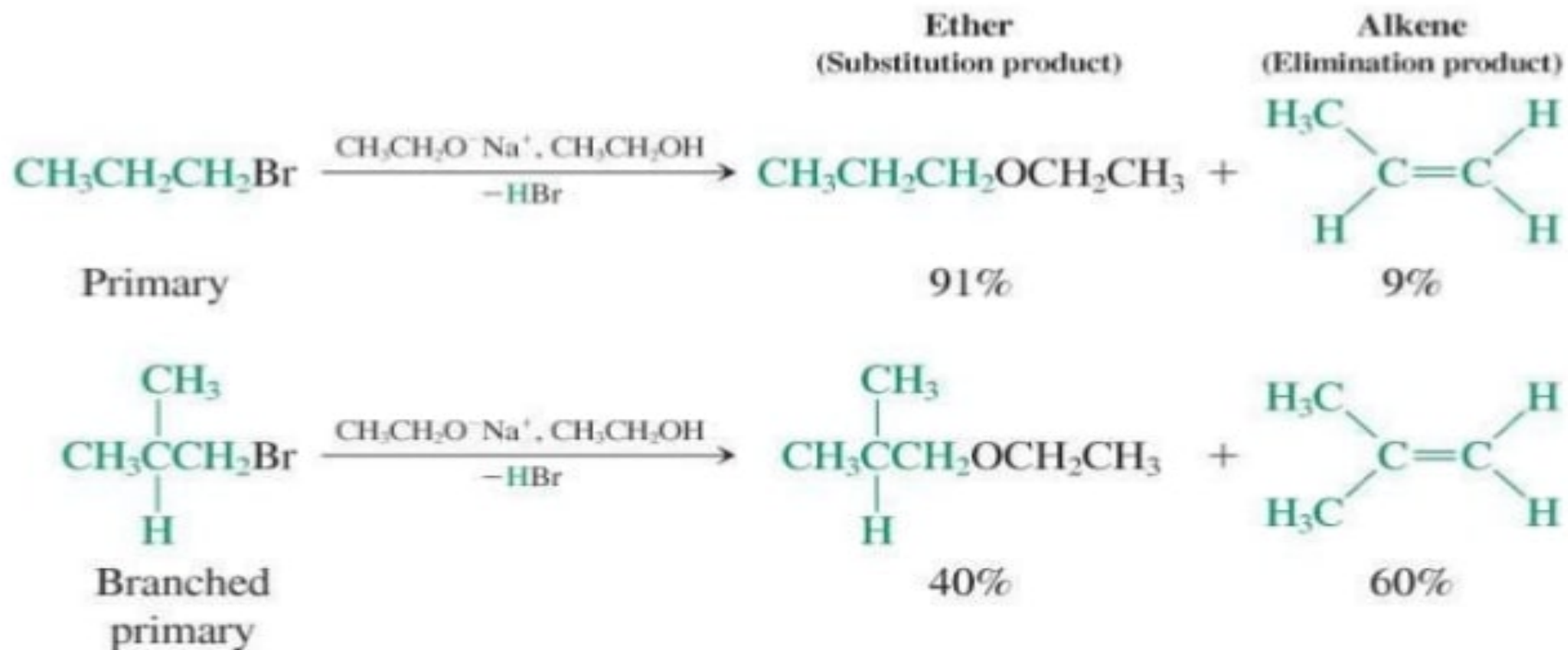


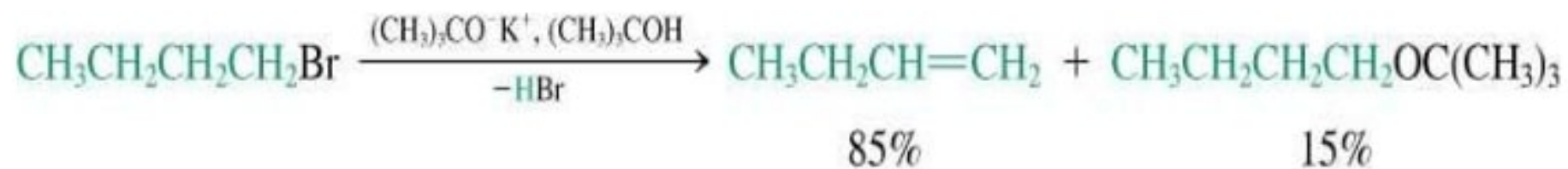
Increasing rate of an E1 reaction



Increasing carbocation stability

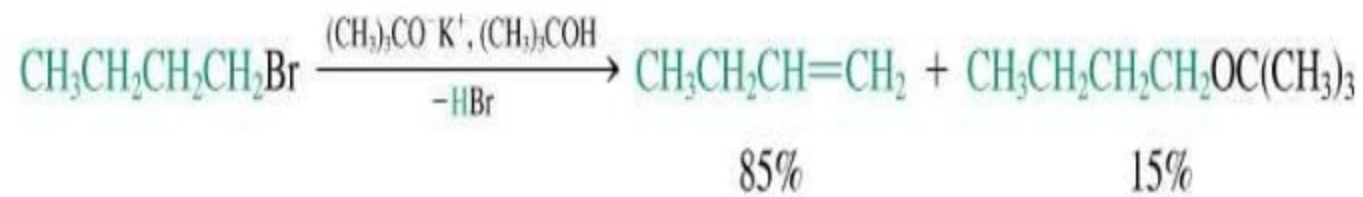
Increased Substitution Favors Elimination



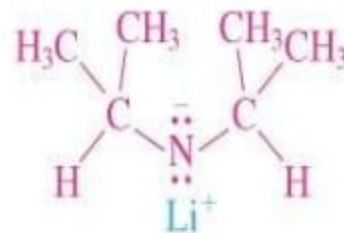
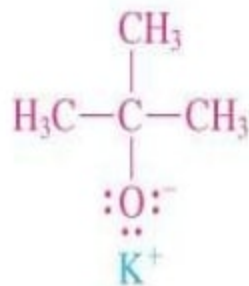


2) Base effect:

► Bulky Bases Favor Elimination

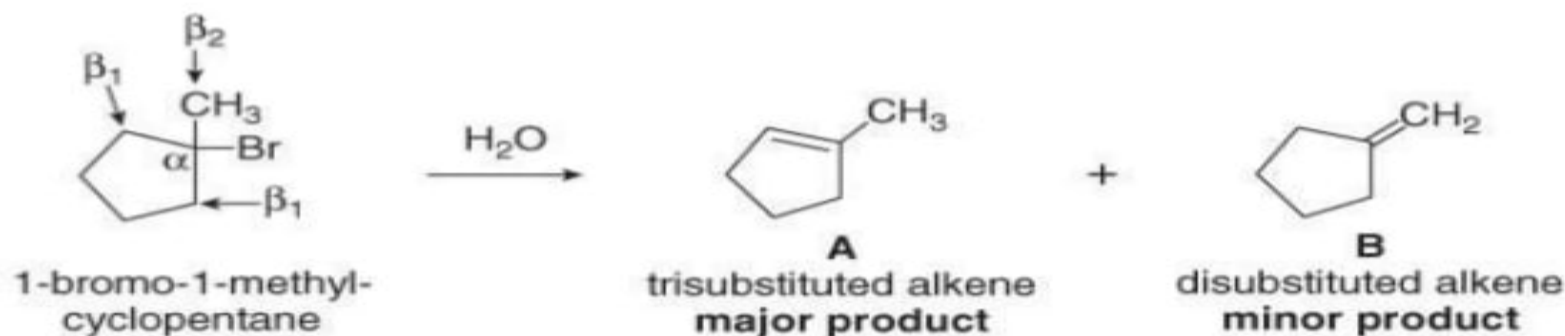


Sterically Hindered Bases



4. Orientation of elimination: Regiochemistry/ Zaitsev's Rule

- ▶ E1 reactions faithfully follow Zaitsev's rule!
- ▶ This means that the major product should be the product that is the most highly substituted.



two different β carbons
labeled β_1 and β_2

- ▶ In reactions of removal of hydrogen halides from alkyl halides or the removal of water from alcohols, the hydrogen which is lost will come from the more highly-branched carbon.



Nucleophile vs base

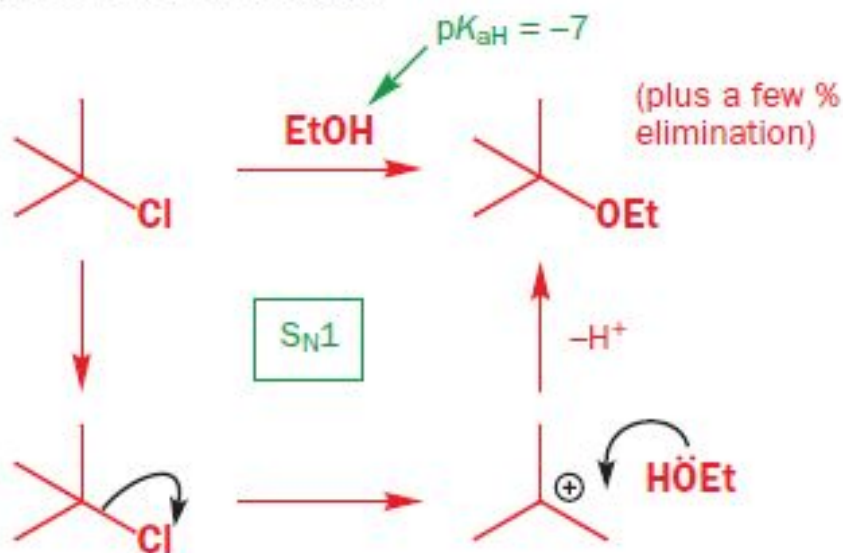
How the nucleophile affects elimination versus substitution

Basicity

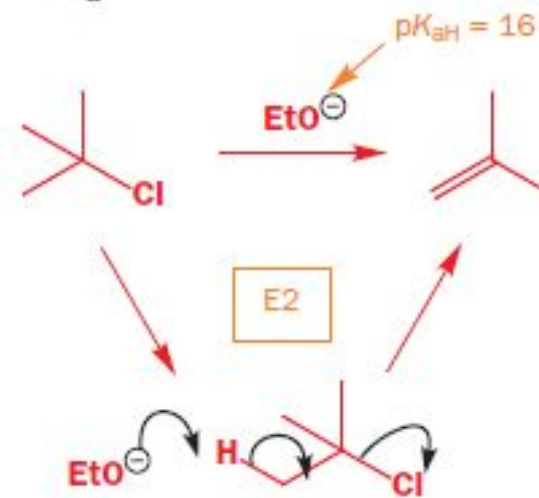
You have just seen molecules bearing leaving groups being attacked at two distinct electrophilic sites: the carbon to which the leaving group is attached, and the hydrogen atoms on the carbon adjacent to the leaving group. Attack at carbon leads to substitution; attack at hydrogen leads to elimination. Since strong bases attack protons, it is generally true that, the more basic the nucleophile, the more likely that elimination is going to replace substitution as the main reaction of an alkyl halide.

Here is an example of this idea at work.

weak base: substitution



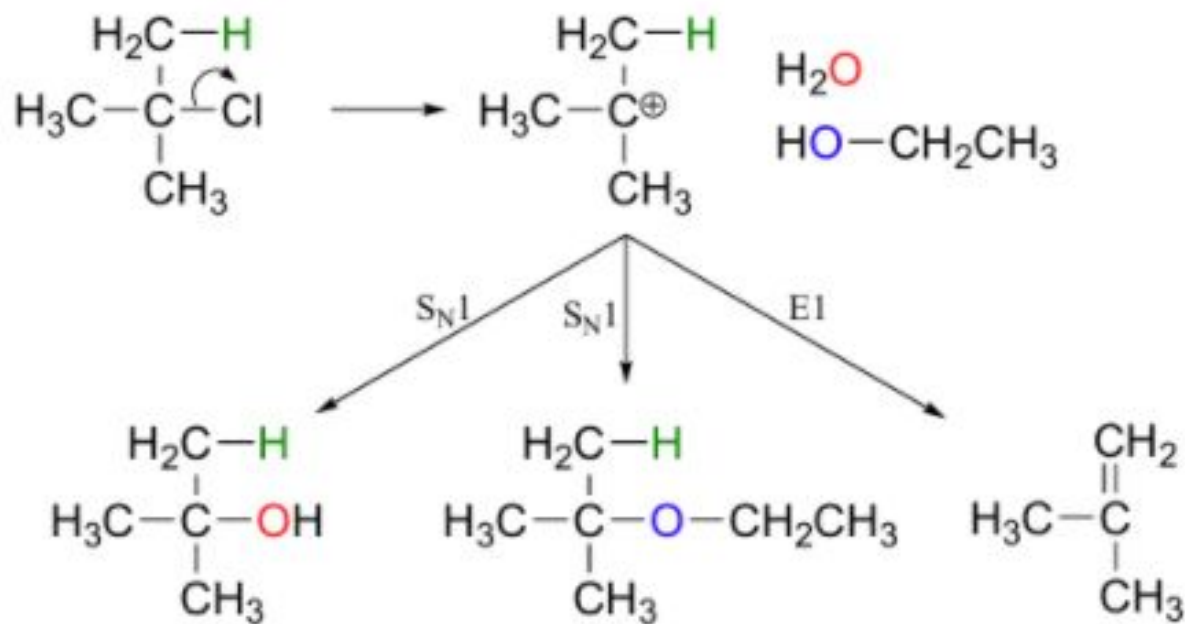
strong base: elimination



Elimination reaction unimolecular- E1

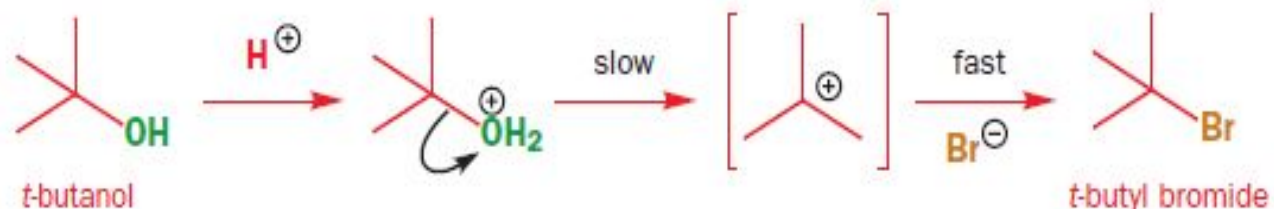
E1 reactions occur by the same kinds of carbocation-favoring conditions that have already been described for S_N1 reactions: a **secondary or tertiary substrate**, a **protic solvent**, and a **relatively weak base/nucleophile**.

In fact, E1 and S_N1 reactions generally occur simultaneously, giving a mixture of substitution and elimination products after formation of a common carbocation intermediate. When tert-butyl chloride is stirred in a mixture of ethanol and water, for example, a mixture of S_N1 products (tert-butyl alcohol and tert-butyl ethyl ether) and E1 product (2-methylpropene) results.



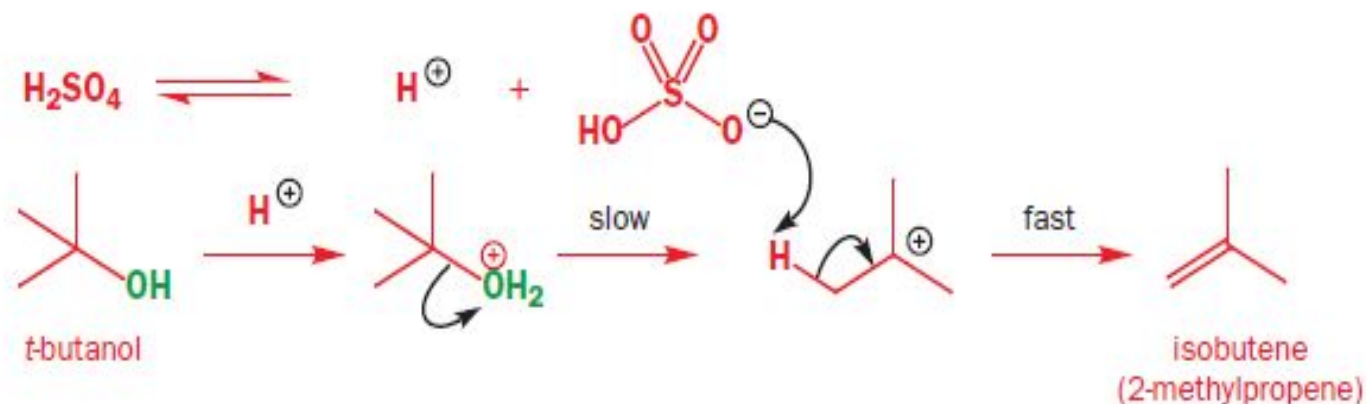
Elimination reaction unimolecular- E1

nucleophilic substitution of *t*-BuOH with HBr



Bromide, the nucleophile, is not involved in the rate-determining step, so we know that the rate of the reaction will be independent of the concentration of Br^- . But what happens if we use an acid whose counterion is such a weak nucleophile that it doesn't even attack the carbon of the carbocation? Here is an example—*t*-butanol in sulfuric acid doesn't undergo substitution, but undergoes elimination instead.

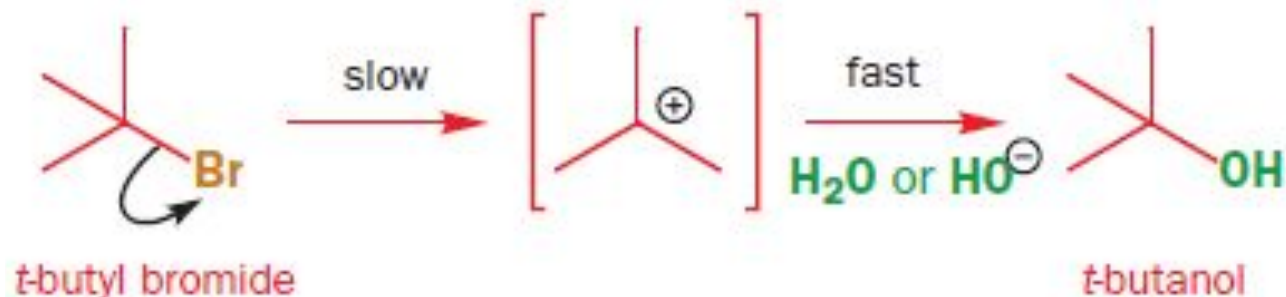
E1 elimination of *t*-BuOH in H_2SO_4



E1 describes an elimination reaction (E) in which the rate-determining step is unimolecular (1) and does not involve the base. The leaving group leaves in this step, and the proton is removed in a separate second step

Elimination reaction bimolecular- E2

nucleophilic substitution reactions of *t*-BuBr

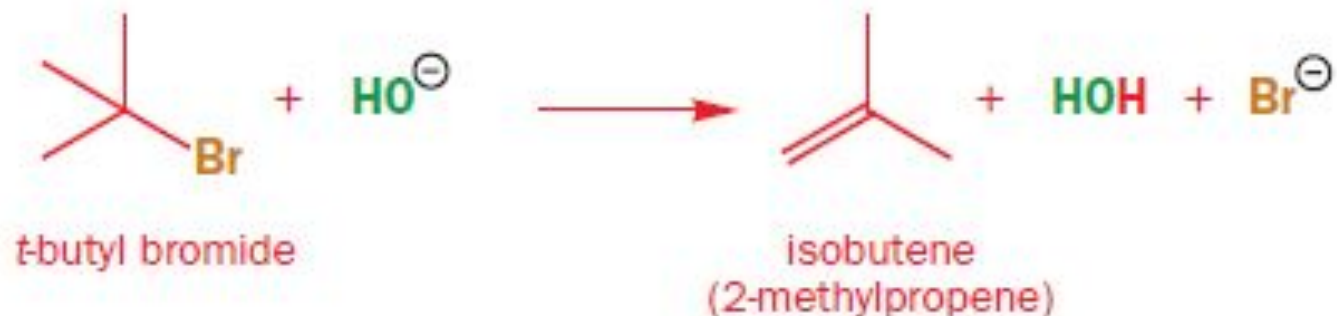


$$\text{rate} = k[\text{t-BuBr}]$$

reaction goes at the same rate whatever the nucleophile

You'd also be wasting your alkyl halide. This is what actually happens if you try the substitution reaction with a *concentrated* solution of sodium hydroxide.

reaction of *t*-BuBr with concentrated solution of NaOH



$$\text{rate} = k[\text{t-BuBr}][\text{HO}^-]$$

elimination reaction
forms alkene

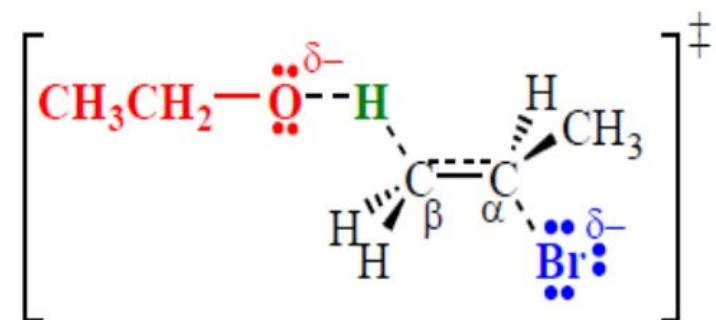
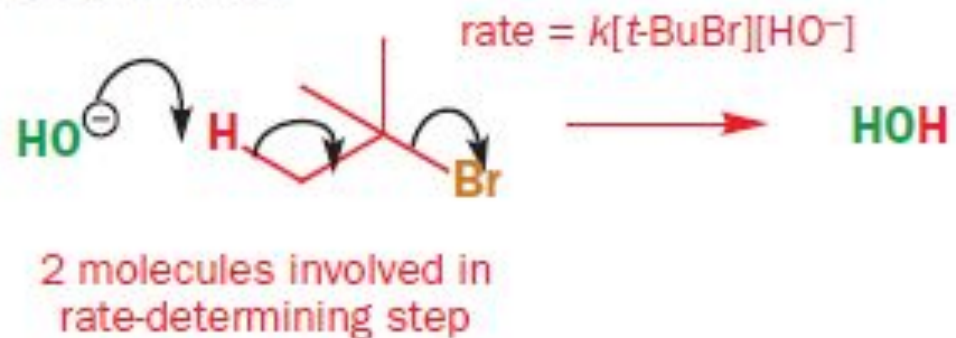
Elimination reaction bimolecular- E2

E2 describes an elimination (E) that has a bimolecular (2) rate-determining step that must involve the base. Loss of the leaving group is simultaneous with removal of the proton by the base



The loss of the leaving group and removal of the proton are **concerted**.

E2 elimination



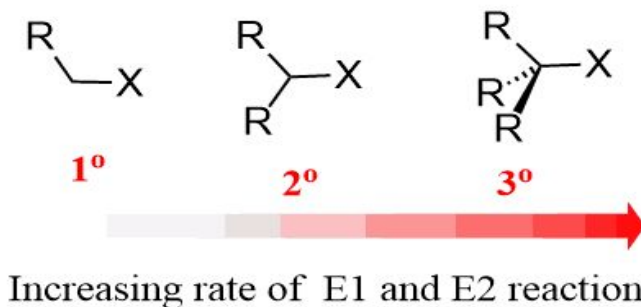
Transition state

Comparing the E1 and E2 mechanisms

	E1	E2
Rate Law	Unimolecular (depends on concentration of substrate)	Bimolecular (depends on concentration of both substrate and base)
"Big Barrier"	Formation of carbocation $3^\circ > 2^\circ \gg 1^\circ$	None
Requires strong base?	No	Yes
Stereochemistry	No requirement	Leaving group must be <i>anti</i> to hydrogen removed

Choosing between the E1 and E2 mechanisms

Choosing between E1 and E2 is easier since the reactivity pattern is the same for both; the rate of E1 and E2 increase with the degree of substitution.



1° substrates can only do E2

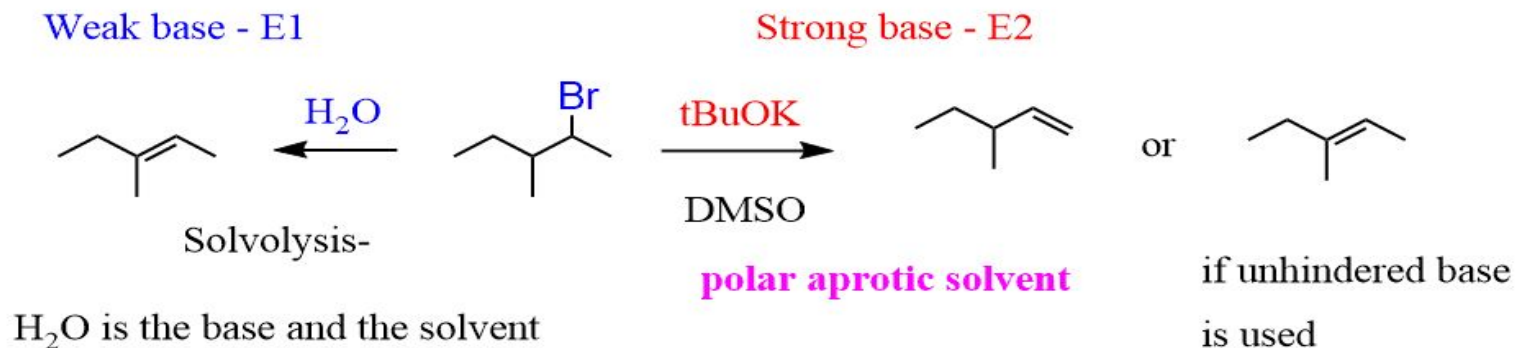
- no carbocation

Methyl substrates, obviously, cannot do elimination - only one carbon.

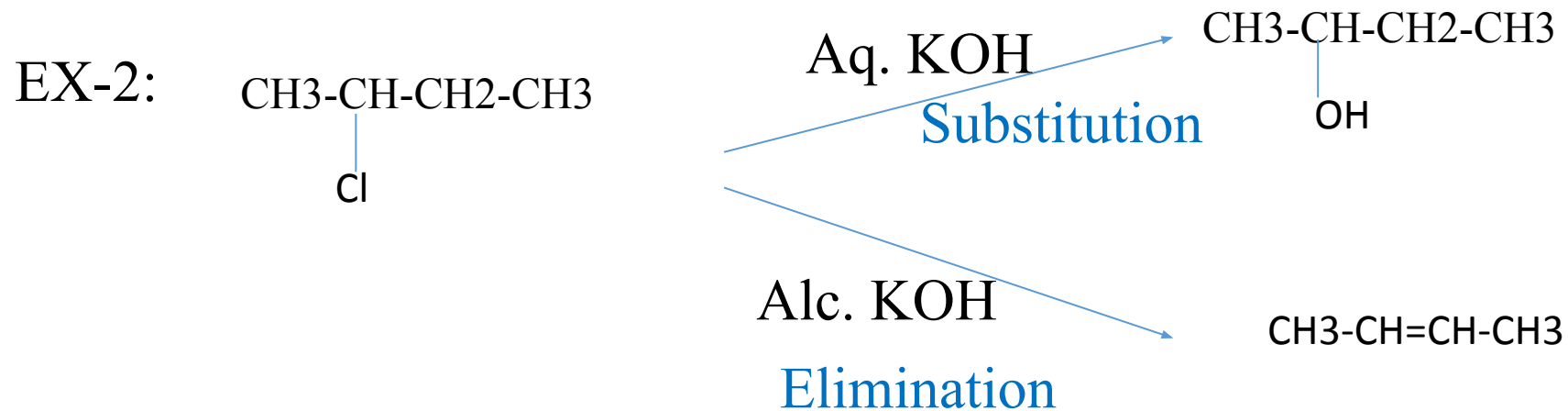
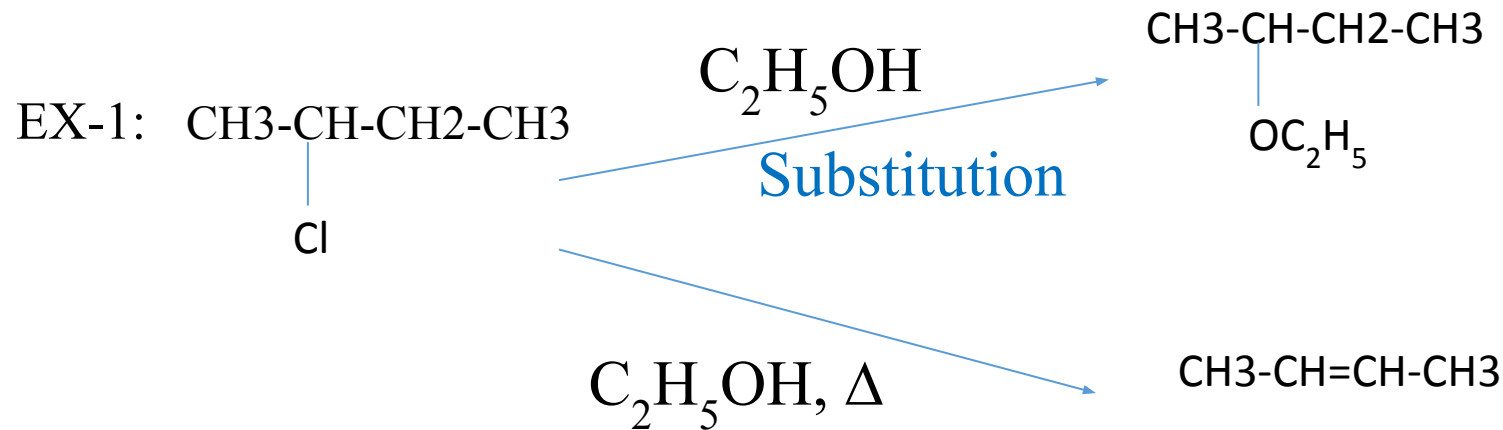
E1 or E2 ? The key factor here is the strength of the base.

E2 reactions are favored by strong bases. E1 reactions are favored by weak bases.

Also, **polar aprotic solvents** favor the **E2** mechanism since it is a bimolecular mechanism.



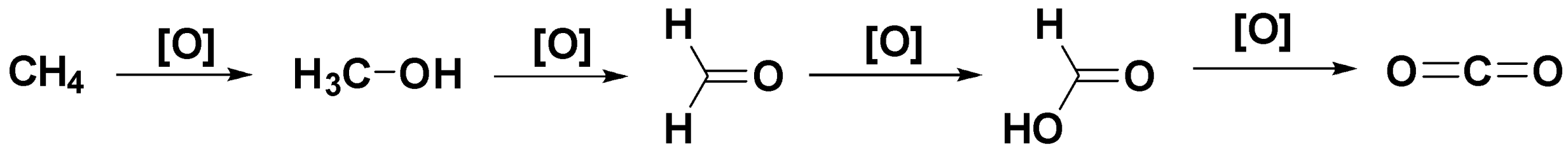
Substitution vs. Elimination



S_N1, S_N2, E1 and E2

	SN1	SN2	E1	E2
Mechanism	2 or more steps involving carbocation intermediate	1 step bimolecular process	2 or more steps involving carbocation intermediate	1 step bimolecular process
Kinetics	First order in substrate	Second order, first in substrate and nucleophile	First order in substrate	Second order, first in substrate and base
Substrate Dependence	Those substrates that form stable carbocations. 3°, allylic, benzylic	Those substrates that are uncluttered at the reaction site: 1°, 2°. Good nucleophiles.	Those substrates that form stable carbocations. 3°, allylic, benzylic	Requires strong base and any substrate with beta proton.
Stereochem	Racemization.	Stereospecific inversion.	Usually mixtures.	Stereospecific involving antiperiplanar relationship of beta-proton and leaving group.
Importance of Base/nucleophile	Not involved in RDS, but less basic form of nucleophile will limit E2.	Reactivity of nucleophile is important since it is involved in RDS.	If a good, non-basic nucleophile is present (halides, bisulfate) then SN1.	Strong, non-nucleophilic bases (KOtBu, LDA) best to limit SN2.
Importance of Leaving group	Involved in RDS so is important.	Involved in RDS so is important.	Involved in RDS so is important.	Involved in RDS so is important.
Competes with..	E1 and E2	E2 when basic nucleophiles employed.	SN1	SN2
Solvent	Polar protic best	Polar aprotic best	Polar protic best	Varies.

Oxidation reaction



0

1

2

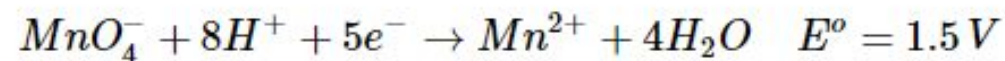
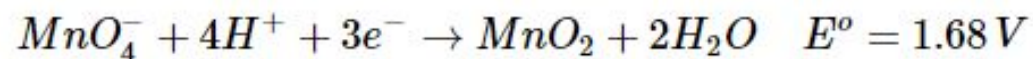
3

4

Oxidation states of Carbon

KMnO₄ oxidation

Mn(VII) is reduced under acidic conditions to Mn(IV) or Mn(II) according to the [half-reactions](#) shown below, with the indicated cell potentials.



[General Reactivity with Organic Molecules](#)

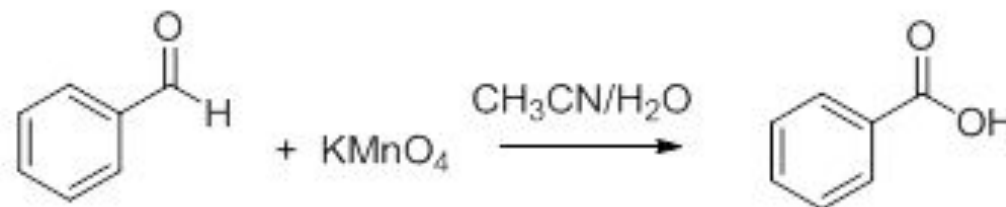
KMnO₄ is able to oxidize carbon atoms if they contain sufficiently weak bonds, including

1. Carbon atoms with $\pi\pi$ bonds, as in [alkenes](#) and [alkynes](#)
2. Carbon atoms with weak C-H bonds, such as
 - C-H bonds in the alpha-positions of substituted [aromatic rings](#)
 - C-H bonds in carbon atoms containing C-O bonds, including [alcohols](#) and [aldehydes](#)
3. Carbons with exceptionally weak C-C bonds such as
 - C-C bonds in a [glycol](#)
 - C-C bonds next to an aromatic ring and an oxygen
 - KMnO₄ also oxidizes phenol to para-benzoquinone.

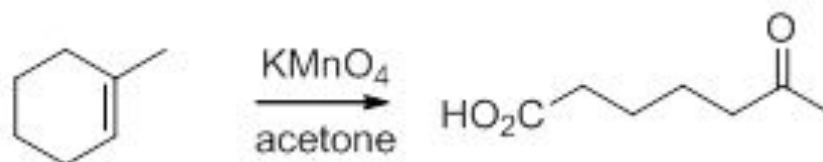
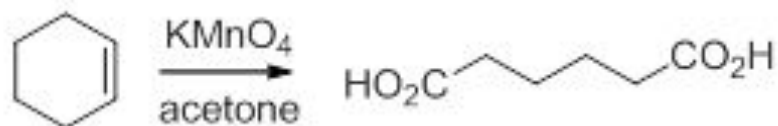
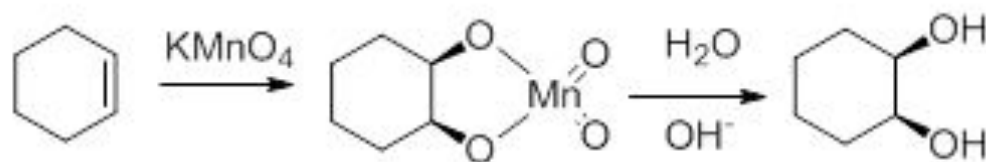
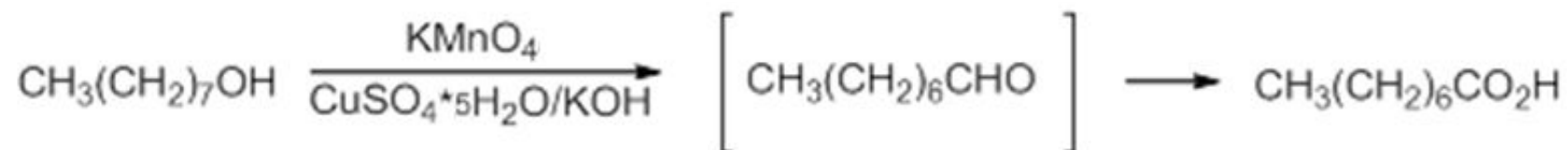
KMnO₄ oxidation

Aldehydes

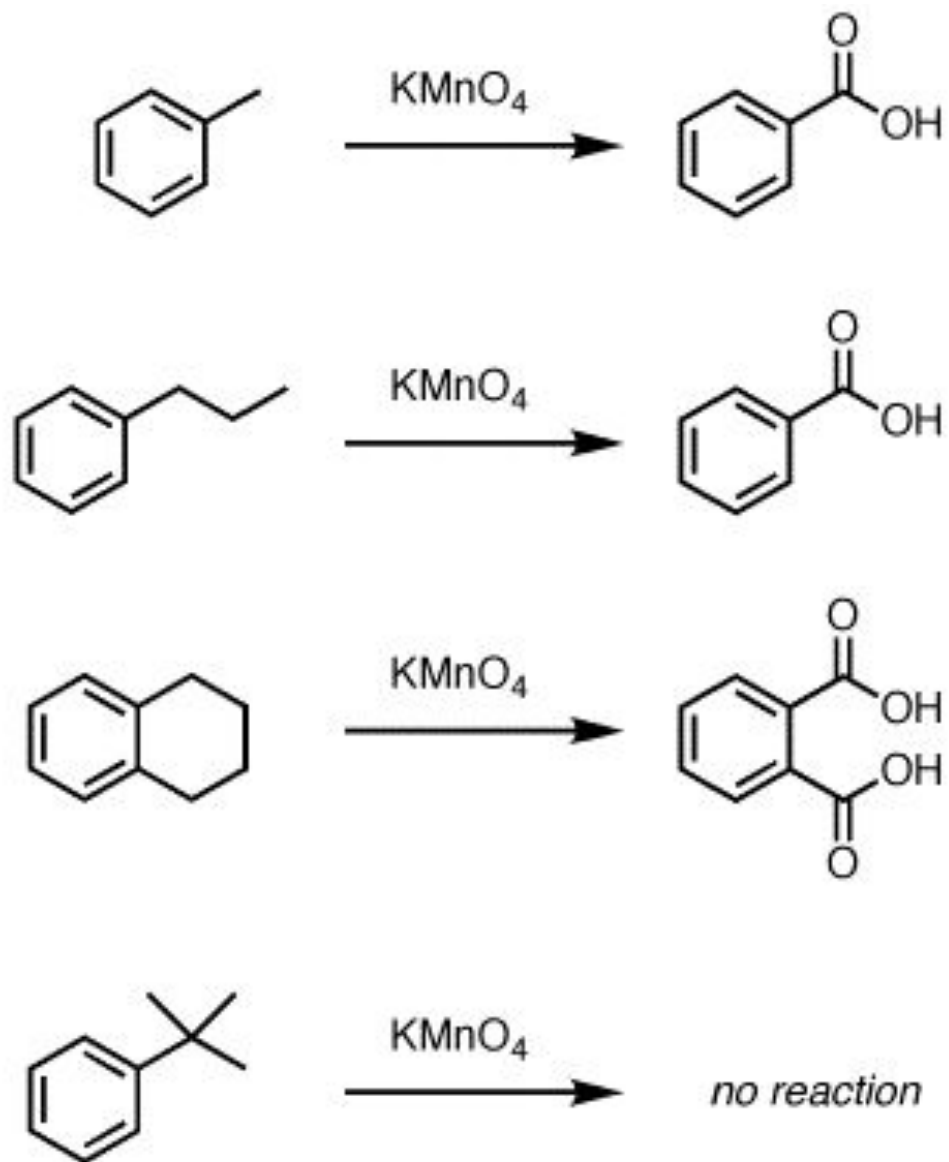
Aldehydes RCHO are readily oxidized to carboxylic acids.



Alcohols



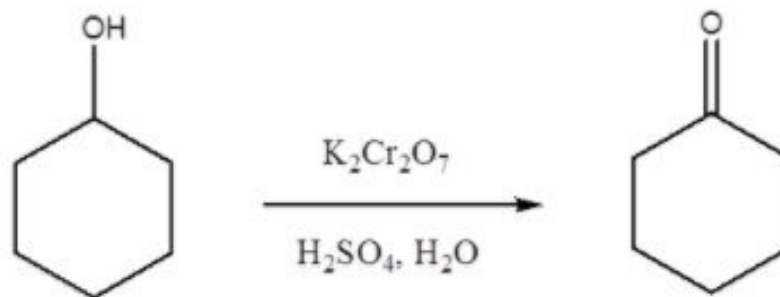
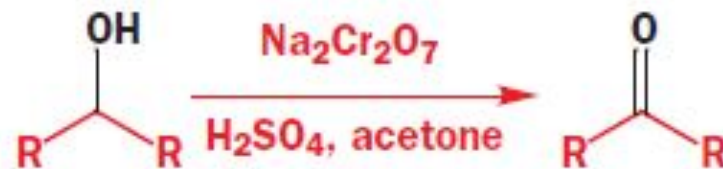
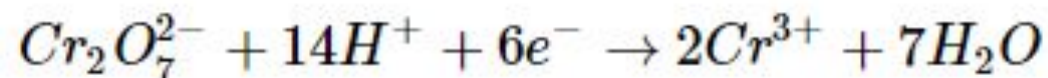
Oxidation in Aromatic molecules



$K_2Cr_2O_7$ oxidation

The oxidizing agent commonly shown is a solution of sodium or potassium dichromate(VI) acidified with dilute sulfuric acid. If oxidation occurs, the orange solution containing the dichromate(VI) ions is reduced to a green solution containing chromium(III) ions.

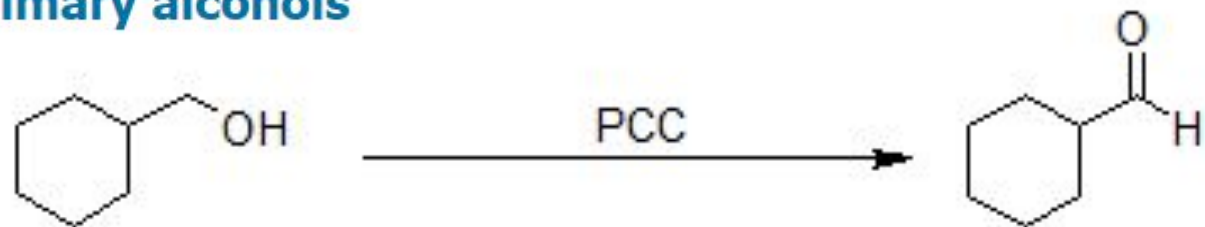
The electron-half-equation for this reaction is:



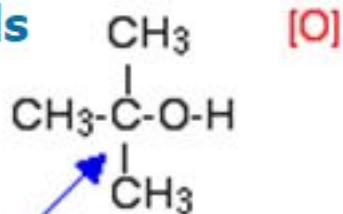
Different form of chromate



Primary alcohols



Tertiary alcohols



There is no hydrogen attached to this carbon for the oxygen to remove.

Secondary alcohols

