Lecture 3

Reaction types: substitution (SN, SE, SR), addition (AE, AN), elimination (E), rereagment.

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Aim and Objectives

Aim: to study the main types of organic reactions, their mechanisms, and the structural changes in molecules.

1. Classify the main types of organic reactions
2. Explain nucleophilic, electrophilic and free-radical substitution
3. Describe electrophilic and nucleophilic addition
4. Investigate elimination reactions and their products
5. Understand molecular rearrangements
6. Compare mechanisms using equations and examples

Classification of Organic Reactions

Reactions in which bonds are broken, formed or rearranged to give new substances.

Substitution

SN · SE · SR

Replacement of an atom or group

Addition

AE · AN

Atoms add across a multiple bond

Elimination

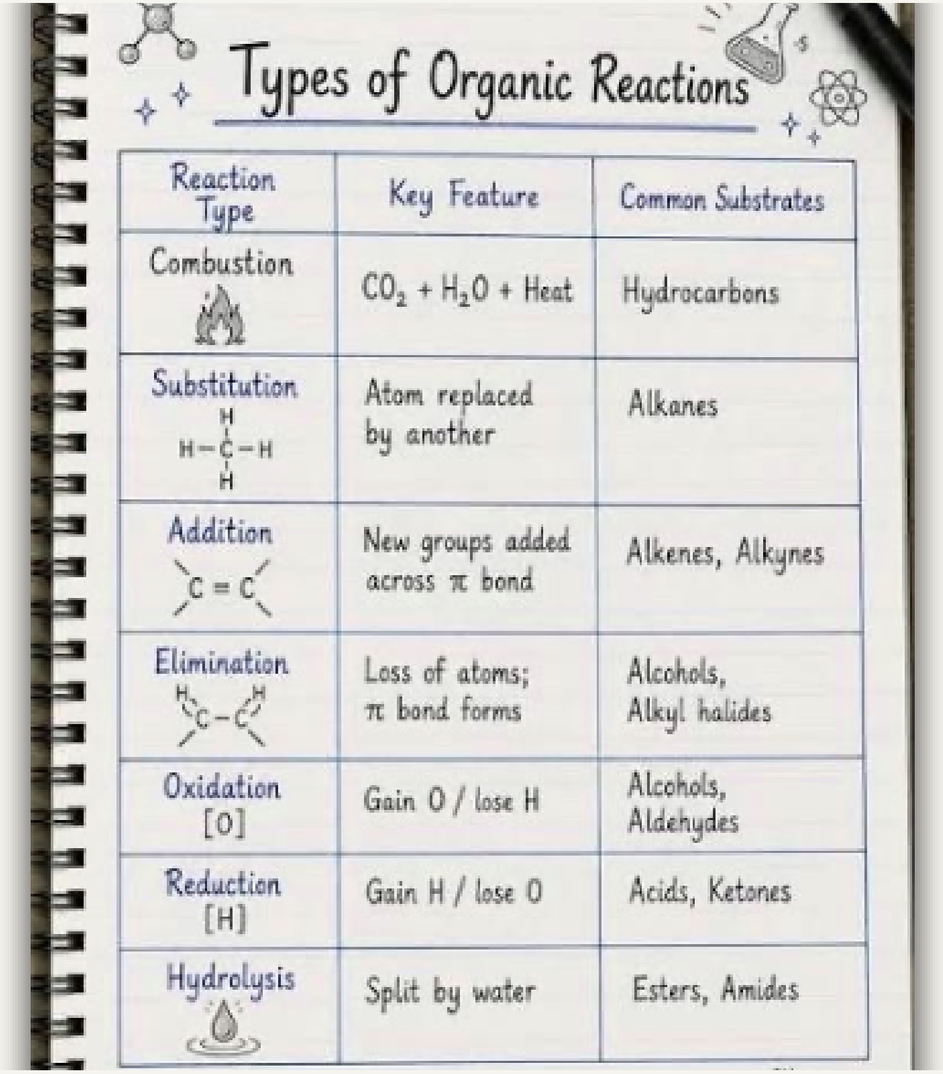
E1 · E2

Removal of atoms to form a multiple bond

Rearrangement

Migration

Reorganization of molecular structure



Substitution Reactions

One atom or group is replaced by another.

$R–X + Y \rightarrow R–Y + X$

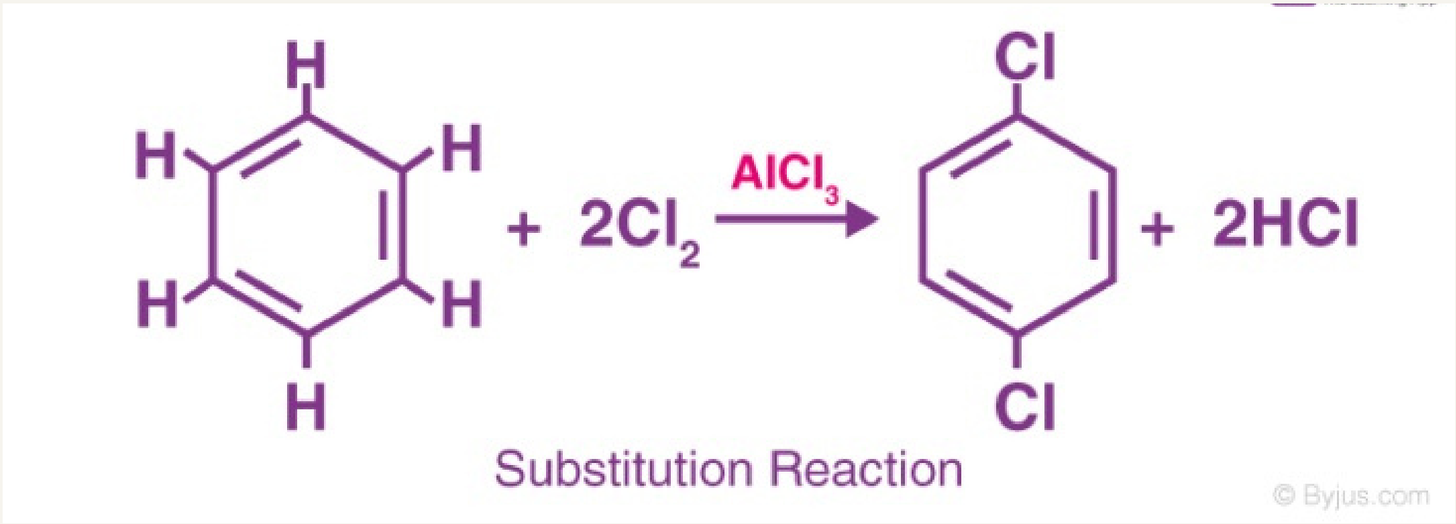
R: organic group · X: leaving group · Y: incoming group

SN
Nucleophilic

SE
Electrophilic

SR
Free-radical

Example: $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$ (bromomethane gives methanol)



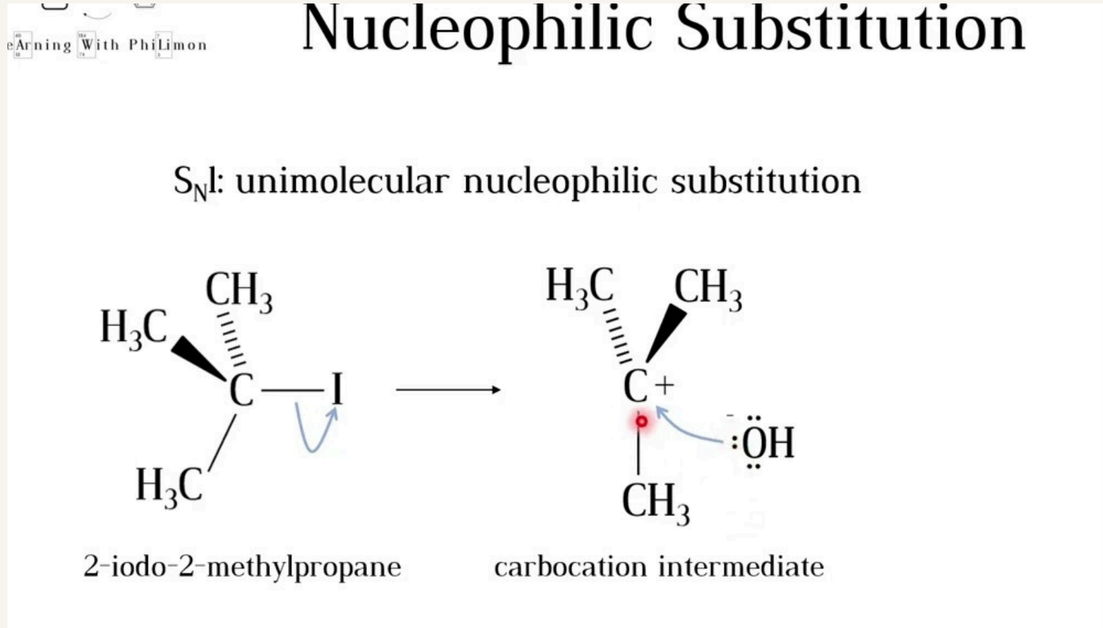
Nucleophilic Substitution (SN)

An electron-rich nucleophile attacks an electron-deficient carbon and replaces a leaving group.

	SN1	SN2
Steps	Two-step	One-step, concerted
Intermediate	Carbocation	None
Kinetics	First-order	Second-order
Favored by	Tertiary substrates	Methyl and primary substrates

SN1: $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$

SN2: $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$



Electrophilic Substitution (SE)

An electrophile replaces an atom, usually hydrogen, typically in aromatic compounds such as benzene.

1

Generate electrophile E^+

2

Attack on aromatic π-electrons

3

Arenium ion forms

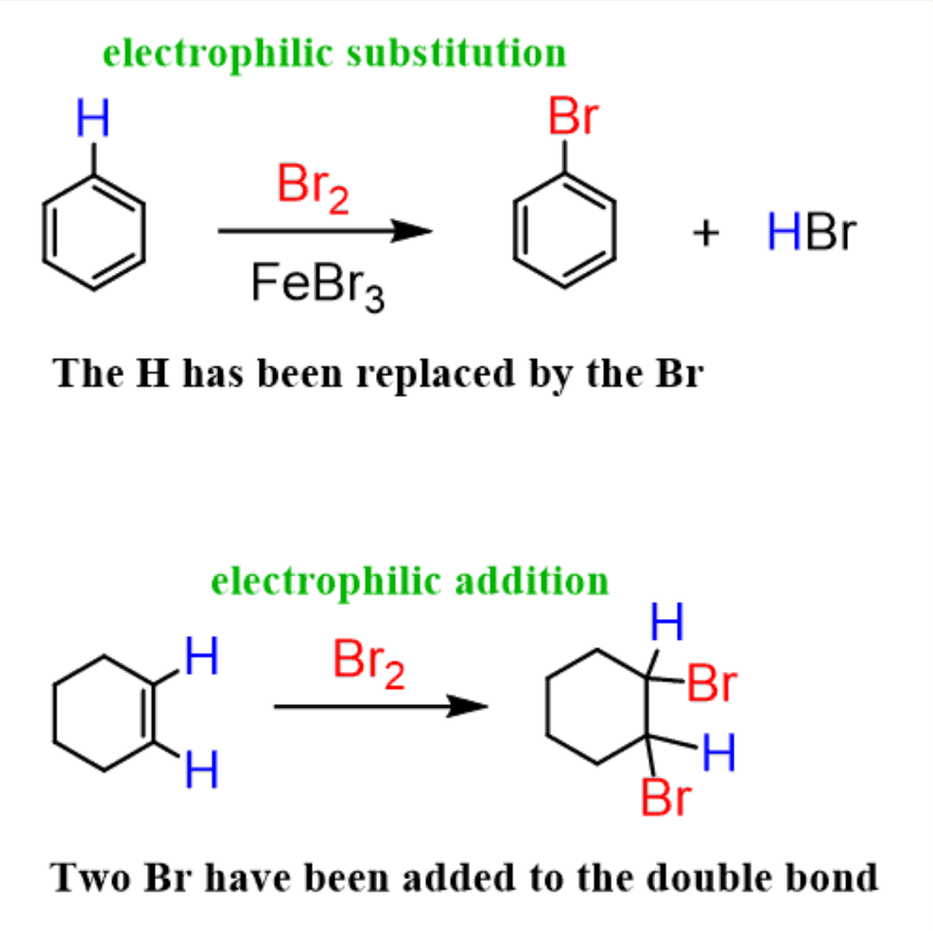
4

Proton loss restores aromaticity

Benzene nitration:

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

Used for dyes, medicines and aromatic compounds.



Free-Radical Substitution (SR)

Highly reactive species with unpaired electrons, often under UV light or heat.

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

Initiation

$Cl_2 \xrightarrow{h\nu} 2Cl\bullet$

Propagation

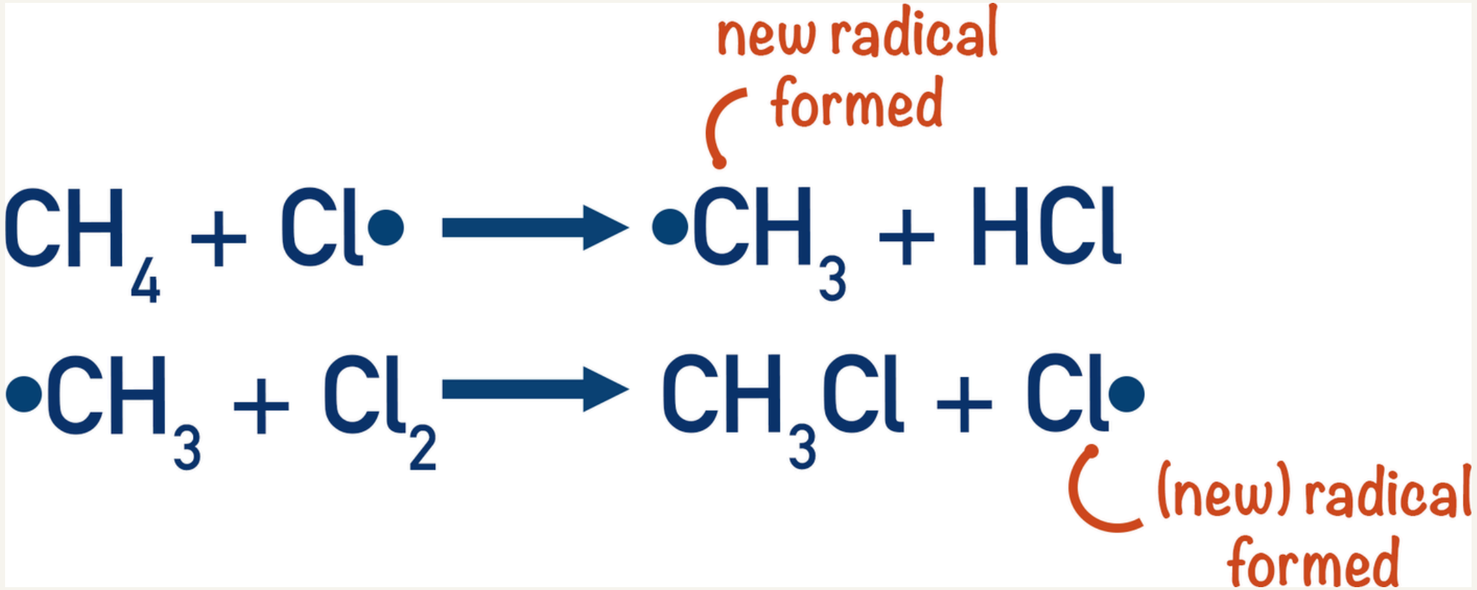
$Cl\bullet + CH_4 \rightarrow HCl + CH_3\bullet$

$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

Termination

$Cl\bullet + Cl\bullet \rightarrow Cl_2$

Important in halogenation and industrial synthesis.



Addition Reactions

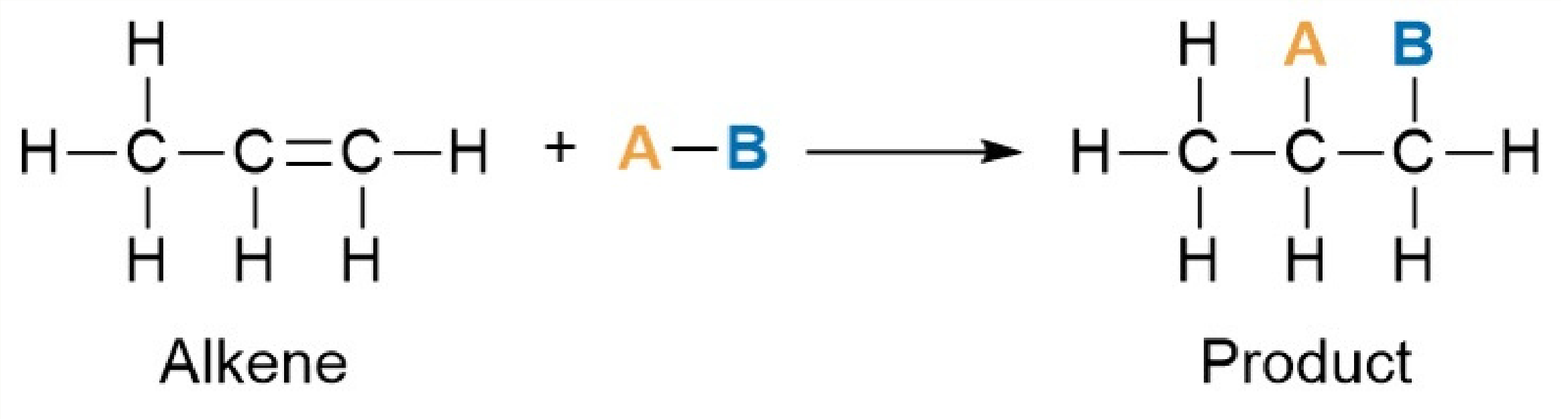
Two atoms or groups add to an unsaturated molecule, usually across a double or triple bond.

C=C + A–B → A–C–C–B

AE: electrophilic addition · AN: nucleophilic addition

Example: $CH_2=CH_2 + H_2 \xrightarrow{Ni} CH_3–CH_3$

- Multiple bonds become single bonds
- New σ bonds form
- Compounds become more saturated



Electrophilic Addition (AE)

Typical of alkenes and alkynes: the electrophile attacks the electron-rich π-bond, then a nucleophile adds.

$$CH_3CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3$$

1

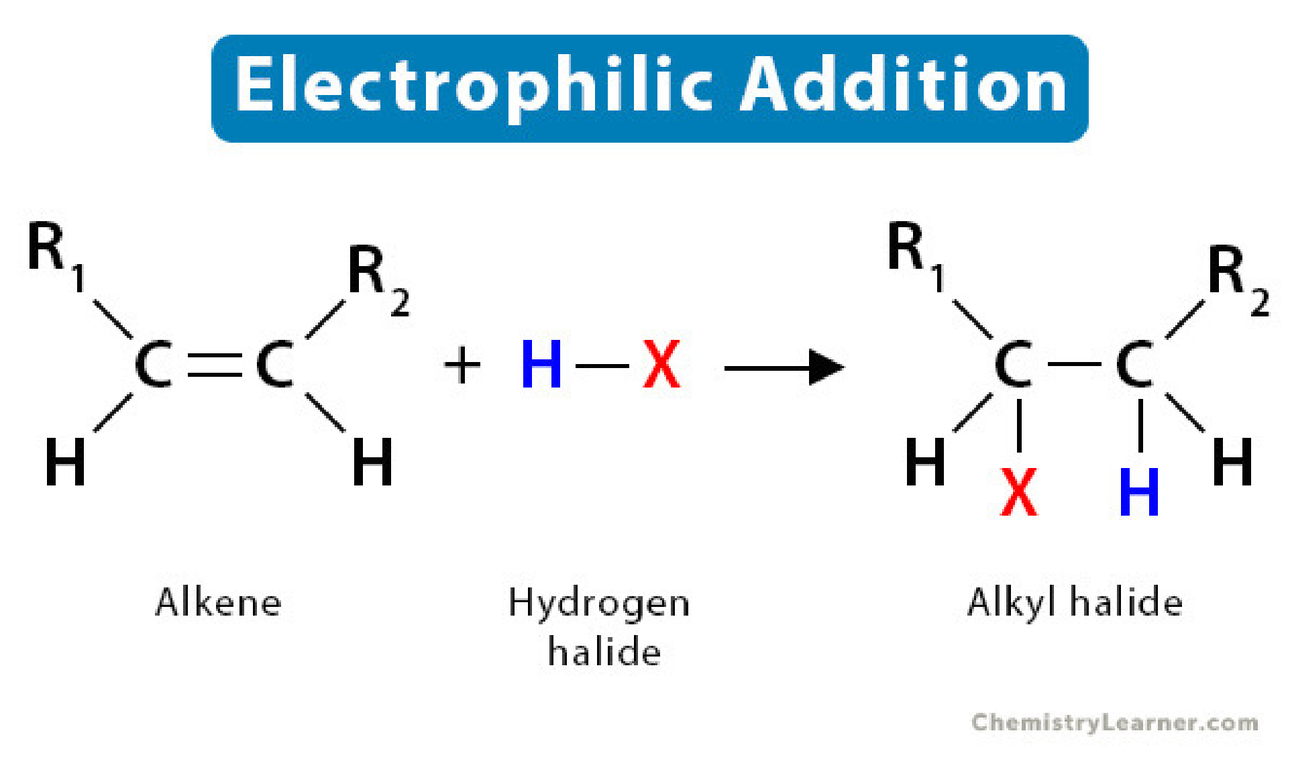
Propene + HBr; H^+ attacks

2

Secondary carbocation forms

Br^- attacks → 2-bromopropane

3

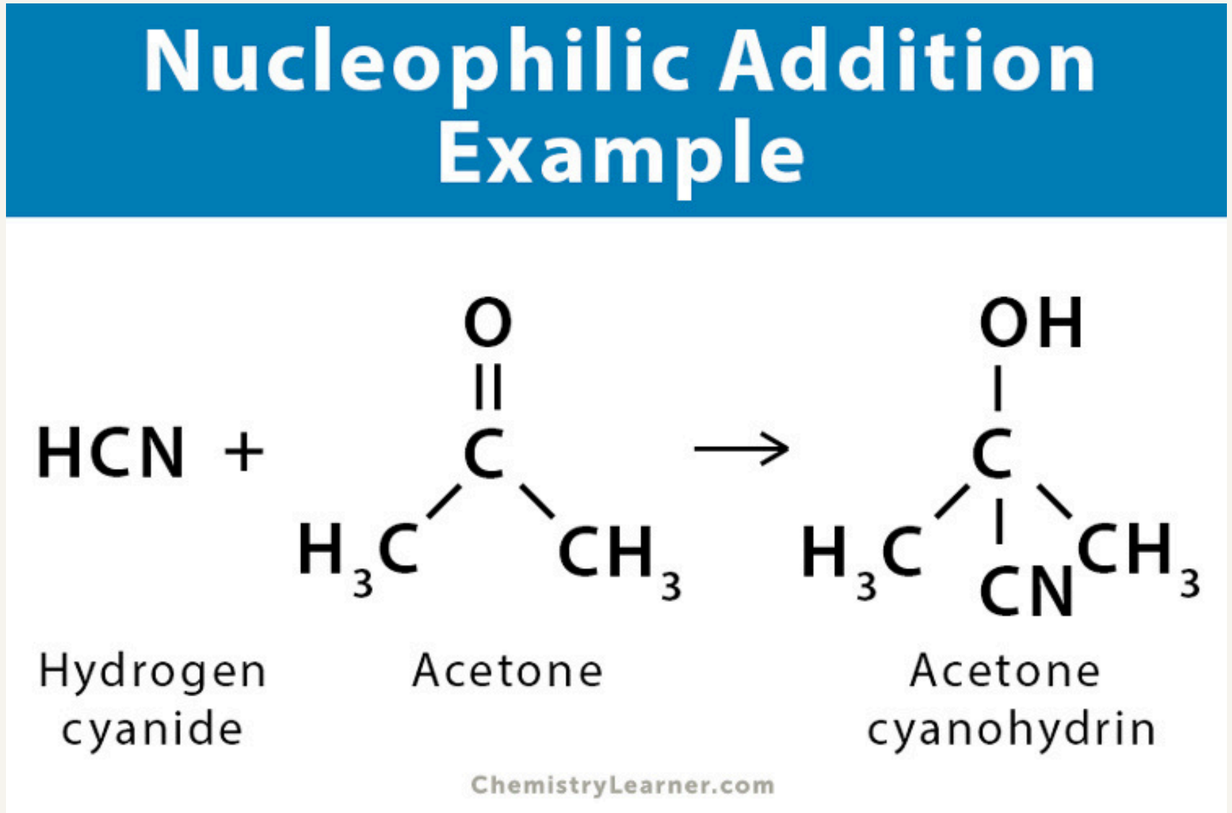


Markovnikov's rule: in HX addition to an unsymmetrical alkene, hydrogen generally goes to the carbon that already has more hydrogens.

Nucleophilic Addition (AN)

Typical of polar carbonyl groups (aldehydes, ketones): a nucleophile attacks the partly positive C=O carbon.

$$R_2C{=}O + Nu^- \rightarrow R_2C(O^-)Nu$$



The alkoxide intermediate is protonated to give an alcohol derivative.

Example: $CH_3CHO + HCN \rightleftharpoons CH_3CH(OH)CN$ (a cyanohydrin)

Used to make alcohols, cyanohydrins and pharmaceutical intermediates.

Elimination Reactions (E)

Two atoms or groups are removed, forming a multiple bond.

$$CH_3CH_2Br + KOH \xrightarrow{EtOH,\ \Delta} CH_2{=}CH_2 + KBr + H_2O$$

	E1	E2
Steps	Two-step	One-step, concerted
Intermediate	Carbocation	None
Kinetics	First-order	Second-order
Favored by	Tertiary substrates	Strong bases

Gives alkenes or alkynes; competes with substitution.

Elimination Mechanisms: E1 and E2

E1

$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$

$(CH_3)_3C^+ \rightarrow (CH_3)_2C{=}CH_2 + H^+$

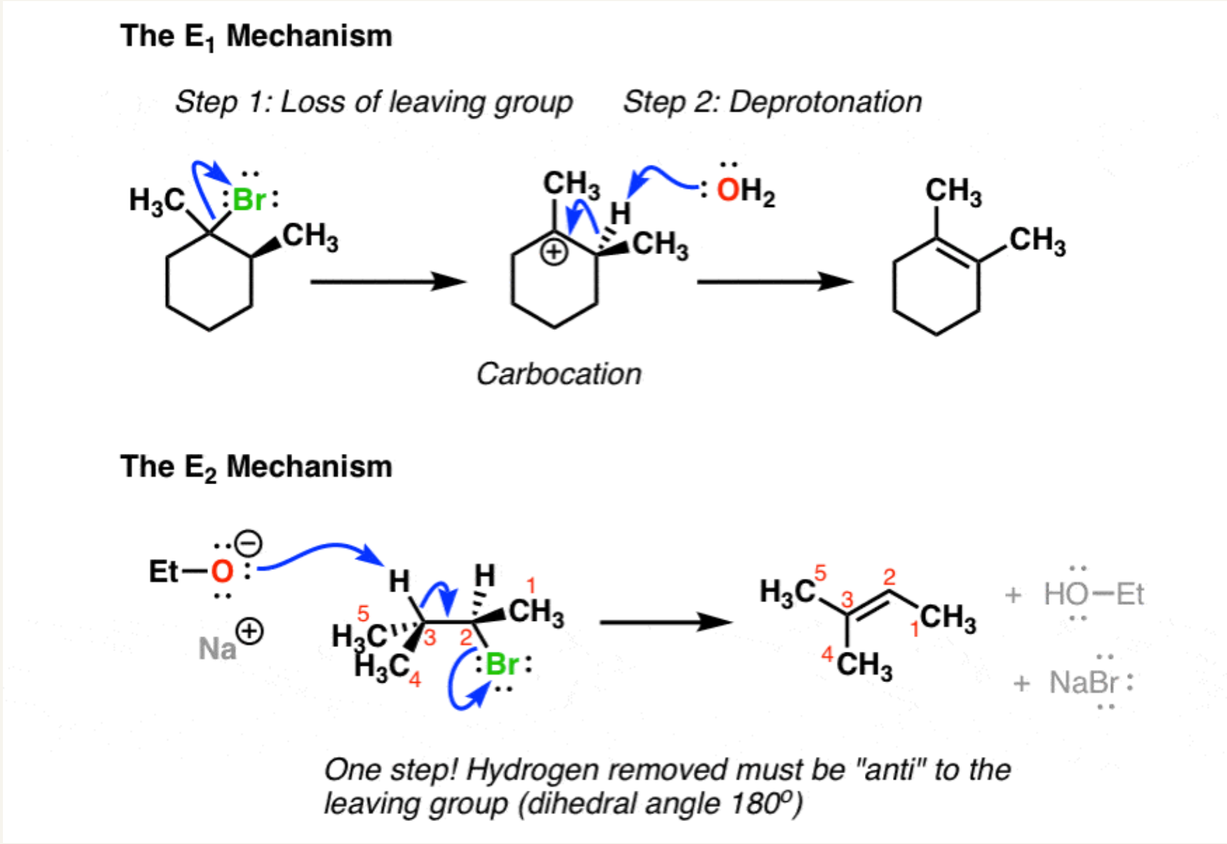
The leaving group departs first, giving a carbocation; then a base removes a proton.

E2

$CH_3CHBrCH_3 + OH^- \rightarrow CH_3CH{=}CH_2 + H_2O + Br^-$

A base removes a β-hydrogen while the leaving group departs at the same time.

Zaitsev's rule: the more substituted alkene is often the major product, though exceptions occur.



Rearrangement Reactions

Atoms or groups migrate within a molecule to give a new structure.

Hydride shift

Alkyl shift

Pinacol

Beckmann

Pinacol rearrangement:

$$(CH_3)_2C(OH)–C(OH)(CH_3)_2 \xrightarrow{H^+} CH_3COC(CH_3)_3 + H_2O$$

Pinacol → pinacolone. Useful for ketones, complex molecules and pharmaceuticals.

Comparison of Reaction Types

Type	Main process	Typical reactants	Example
SN	Replacement by nucleophile	Alkyl halides	$CH_3Br + OH^-$
SE	Replacement by electrophile	Aromatic compounds	Benzene nitration
SR	Radical replacement	Alkanes	Methane chlorination
AE	Electrophile adds to π-bond	Alkenes	Propene + HBr
AN	Nucleophile adds to C=O	Aldehydes, ketones	Ethanal + HCN
E	Removal of atoms/groups	Haloalkanes	Dehydrohalogenation
Rearr.	Internal reorganization	Alcohols, carbocations	Pinacol

Conclusion

1. Substitution replaces atoms or functional groups
2. Addition is typical of unsaturated compounds and polar multiple bonds
3. Elimination often yields alkenes
4. Rearrangement changes structure by intramolecular migration
5. Mechanisms depend on structure, reagents, solvents and conditions

Knowing reaction types and mechanisms lets us predict products, design syntheses and develop new compounds.

References: Clayden, Greeves & Warren; McMurry; Smith (March’s Advanced Organic Chemistry)