

Introduction to the Organic Chemistry

Electron arrays of some basic elements

Valence Electrons

H (Hydrogen): $1s^1 \longrightarrow 1$ C (Carbon): $1s^2 2s^2 2p^2 \longrightarrow 4$ N (Nitrogen): $1s^2 2s^2 2p^3 \longrightarrow 5$ O (Oxygen): $1s^2 2s^2 2p^4 \longrightarrow 6$ F (Fluoro): $1s^2 2s^2 2p^5 \longrightarrow 7$

Valence electrons are the electrons present in the outermost shell of an atom.

Formal Charges

Formal charge = (Group number)
$$- \begin{pmatrix} number of electrons \\ in lone pairs \end{pmatrix} - \begin{pmatrix} number of \\ covalent bonds \end{pmatrix}$$



Electronegativity

Electronegativities generally increase from left to right across a period and decrease down a group.



Metals of Group I and Group II tends to give electrons

IA	ПА	 IIIA	IVA	VA	VIA	VIIA
Н 2.3						
Li 1.0	Be 1.5	В 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	AI 1.5	Si 1.8	P 2.2	S 2.5	CI 3.0
K 0.8						Br 2.8
Rb 0.8						I 2.5
Cs 0.7						

İndüktif Etki

The inductive effect: Effect on <u>electron density</u> in one portion of a <u>molecule</u> due to <u>electron-withdrawing</u> or <u>electron-donating groups</u> elsewhere in the <u>molecule</u>.

Substituents with -I inductive effects

If an element is more electronegative from hydrogen, the inductive effect of the element is (-) and is shown as –I.

—⊕ MH ₃	- F
–®R₃	<u>-C1</u>
-NO ₂	-Br
-CN	-OH
-COOH	-OR
-COOR	-SH
-CHO	-SR
-C=CH ₂	—C≡CH

Alkyl groups and alkali metals (Li, Mg) show +I inductive effect.

Less electronegative than hydrogen (electropositive)

Substituents with +I inductive effects





Various Arrow Used in Organic Chemistry

1) For a one-step reaction

2) In order to achieve the final product in more than one step,



3) In order to show that the final product can be synthesized from starting compound or the starting compound can be obtained from final product by using different reagents in a one-step reaction equation.

4) Equilibrium reactions

$$H_{3}C-C-OH + H_{3}C-OH - H_{3}C-C-OCH_{3}$$



6) Direction of movement of an electron

7) Direction of movement of two electrons



Mesomerism (Resonance)

1) Compounds with conjugated π bonds



2) Compounds bearing the unpaired electron pair on the atom adjacent to the π bond





3) Compounds bearing unpaired electron pair on an atom adjacent to a positively charged carbon



 4) The presence of a π bond (or conjugate π bonds) adjacent to the positive charge



5) The presence of a π bond between two different atoms



Benzaldehyde molecule:





the electrophilic substitution reaction takes place at the position of *meta*

Substituents with -M Effect



Substituents with -M Effect



The mesomeric effect is dominant from the inductive effect and the electrophilic substitution reaction occurs in *ortho, para* positions.

Substituents with +M Effect

Groups with + M effect active groups are usually heteroatoms with free electrons in their outer orbit.





There is no mesomeric effect since there is no π bond or empty p orbital.

Since a pair of unpaired electrons on the O atom are jointly used with the π bond, the mesomeric effect is + M

Nucleophiles

A nucleophile is a chemical species that donates an electron pair to an electrophile to form a chemical bond in relation to a reaction.

a) Anion: An anion may be defined as an atom or molecule that is negatively charged.

$$F^{\Theta} Cl^{\Theta} Br^{\Theta} HO^{\Theta} HS^{\Theta} RCOO^{\Theta} CH_3$$

b) Lewis bases: A Lewis base is a compound that has an electron pair.

 NH_3 H_3C-NH_2 H_3C-OH H_3C-SH

c) Double bond between carbon-carbon

$$H_2C=CH_2$$

Electrophile

Electrophiles are positively charged or neutral species having vacant orbitals that are attracted to an electron rich centre. It participates in a chemical reaction by accepting an electron pair in order to bond to a nucleophile.



Primary, Secondary, Tertiary ve Quaterner Terms

If the carbon atom bound to one carbon atom, it is **primer**, If the carbon atom bound to two carbon atom, it is **seconder**, If the carbon atom bound to three carbon atom, it is **tertiary**, If the carbon atom bound to four carbon atom, it is **quaterner**,



Primary, Secondary, Tertiary ve Quaterner Terms

In alkyl halides and in alcohols, the number of alkyl groups attached to the carbon atom to which the substituent is attached is checked.

H₃C-CH₂-Cl Primary alkyl halides





Tertiary alkyl halides

Primary, Secondary, Tertiary ve Quaterner Terms

• In amines, the number of alkyl groups attached to the nitrogen is checked.

$H_3C - CH_2 - NH_2$	Primary amine
H ₃ C—NH—CH ₃	Seconder amine
CH ₃	
H ₃ C—N—CH ₃	Tertiary amine
CH ₃	
H ₃ C [⊕] N−CH ₃	Quaterner amine
ĊH ₃	
	Primary aromatic amine
	i mary aromatic amine

Classification of Organic Reactions

Classification of Organic Reactions

a) Homolytic cleavage [Radical Reactions]:

In homolytic cleavage, the two electrons in the bond are divided equally between the products. Homolytic cleavage often produces <u>radicals</u>.

$$A : B \longrightarrow A + B$$
 Radical

b) Heterolytic cleavage [Ionic Reactions]:

In heterolytic cleavage, one atom gets both of the shared electrons. Heterolytic cleavage produces nucleophile and electrophile.

$$A : B \longrightarrow A + :B$$

Elektrofil Nükleofil

Organic reactions are classified as following:

A) Radical Reactions

a- Radical substitution (S_R)

b- Radical addition (A_R)

B) İonic Reactions

- a- Substitution reactions (S)
- b- Addition reactions (A)
- c- Elimination reactions (E)

C) Transposition Reactions

Substitution Reactions (S)

Substitution reaction is a chemical reaction during which one functional group in a chemical compound is replaced by another functional group. There are two types, electrophilic and nucleophilic.

Elektrophilic Substitution (SE)

These reactions are usually substitutions in aromatic structures and occur in three steps.

1. Formation of electrophilic unit

2. Addition of electrophilic unit to aromatic ring and rearomatisation of ring

3. neutralisation of leaving proton

Friedel-Crafts Alkylation







Friedel-Crafts Acylation





Synthesis of Bromobenzene





Sülfonation



Nucleophilic Substitution Reactions



Elimination Reactions (E):

It is the formation of a unsaturated compound from saturated molecule. There are two types, E_1 ve E_2 according to reaction kinetics. These reactions are parallel to the SN1 and SN2 reactions.









Reaction	Structure of RX	Reactivity of Nu:	Conc. Of Nu:	Solvent
SN2	1>2>3 Only this reaction and E2 will most likely react with a primary RX	Strong nucleophile favors reaction	High concentration of nucleophile favors reaction	Aprotic polar solvent favors a SN2 reaction if <u>either</u> of the reactants is charged ex: DMF DMSO Acetone
E2	3>2>1 Major product is more substituted alkene unless * the base is large * the alkyl halide is an alkyl flouride * the alkyl halide contains one or more double bonds	Strong Base favors reaction	High concentration of base favors reaction	Aprotic polar solvent favors a E2 reaction if <u>either</u> of the reactants is charged ex: DMF DMSO Acetone
SN1	3>2>1 Forms a carbocation	Not effected by strength of nucleophile but a weak nucleophile favors it by not favoring a SN2 reaction	Not effected but low concentration disfavors a SN2 reaction	Protic polar favors a SN1 reaction if the reactant is not charged. Ex: H2O, CH3OH, etc.
EI	3>2>1 Forms a carbocation	Weak base favors El reaction by disfavoring E2 reaction	Not effected but a low concentration of base favors E1 by disfavoring a E2 reaction	Protic polar favors a E1 reaction if the reactant is not charged. Ex: H2O, CH3OH, etc.

http://users.wfu.edu/wrightmw/chm122/handouts/sn1sn2e1e2%20summary.pdf

Electrophilic Addition(A_E):



Electrophilic Addition(A_E):



Nucleophilic addition (A_N):

Nucleophilic addition reactions are an important class of reactions that allow the interconversion of **C=O** into a range of important functional groups.



Nucleophiles involved in Nucleophilic addition reactions:



Addition of alchol to aldehyde give hemiacetal and acetal and hemiketale and ketale are obtained with the same reaction with ketone.



Reaction mechanism



Imine ve enamine formation

Addition of primary amines to aldehyde and ketone give imine $(R_2C=NR)$, while addition of secondary amine give enamine compounds.



Mechanism of imine formation



Mechanism of enamine formation



$$\longrightarrow$$
=0 + NH₂OH --- \longrightarrow \longrightarrow =N-OH + H₂O
Sikloheksanon Hidroksilamin Sikloheksanonoksim





Mechanism of grignard reaction formation





Nucleophilic addition