THE P-BLOCK ELEMENTS

FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

***** Fundamental Concepts In Organic Reaction Mechanism:

Reaction Mechanism: Part-I

Reaction: Breaking of old bond and formation of new bond is known as chemical reaction



A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism. Reactants are of two types substrate and reagent.

Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both reactants supply carbon to the new bond, then choice is arbitrary and in that case the molecule on which attention is focused is called substrate.

Concepts To Understand Reaction Mechanism:

- (1) Bond cleavage (2) Attacking reagent
- (3) Reaction intermediate (4) Electronic effect
- 1. Type Of Bond Cleavage:
 - (a) Heterolytical cleavage/fission: Cleavage in which unequal distribution of electrons takes place during the bond cleavage is known as heterolytically cleavage. Due to unequal distribution of electrons, ions are formed. That's why it is also known as ionic cleavage or heterolytically cleavage.
 - (b) Homiletical cleavage/fission: Cleavage in which equal distribution of e-s takes place during the chemical reaction, is known as homiletical cleavage. Due to equal distribution of electrons, without charge unpaired electron containing species are formed, which are known as free radicals and cleavage is known as unironic cleavage/homiletical fission.



2. Types Of Attacking Reagents

These are of two types:

(A) Electrophilic reagent or electrophiles:

Electrophilic	+	phallic)	
	(electron	+	loving)

The reagent which attacks on the negative part of the molecule or having attraction for electrons are called electrophiles.

Electrophiles may be positively charged or neutral.

(i) Positively charged electrophiles:

$$\begin{array}{c} \bigoplus \\ H, \\ SO_{3}H, \\ NO, \\ NO_{2}, \\ X, \\ R, \\ R-C, \\ C_{6}H_{5}-N_{2} \\ \\ 0 \end{array} \right)$$

- (ii) Neutral electrophiles: central atom e- deficient
 - (a) All Lewis acids as:
 - BF3, A1Cl3, SO3, ZnC12, BeC12, FeC13, SnC12, CO2, SnC14.
 - (b) Free radicals, carbenes and nitrenes act as electrophiles

(B) Nucleophilic reagent or nucleophiles.

Which attacks on the positive site of the substrate or loves nucleus or having attraction towards nucleus.

Nucleophilic (Nucleon	+	phials)
	\downarrow	
(Nucleus	+	loving)
1	d :	

Nucleophiles may be negatively charged ions or possess a lone pair of electrons or πe^{-} .

(i) Negatively charged nucleophiles.

 $\overset{\scriptscriptstyle \Theta}{\mathrm{H}}, \overset{\scriptscriptstyle \Theta}{\mathrm{OH}}, \overset{\scriptscriptstyle \Theta}{\mathrm{OR}}, \overset{\scriptscriptstyle \Theta}{\mathrm{CN}}, \overset{\scriptscriptstyle \Theta}{\mathrm{X}}, \overset{\scriptscriptstyle \Theta}{\mathrm{R}}, \mathrm{R} - \mathrm{COO}, \overset{\scriptscriptstyle \Theta}{\mathrm{NH}}_2, \overset{\scriptscriptstyle \Theta}{\mathrm{SH}}$

(ii) All Lewis base which contains lone pairs or π e⁻.

H₂
$$\stackrel{\bullet}{\text{O}}$$
, R- $\stackrel{\bullet}{\text{O}}$ H, R- $\stackrel{\bullet}{\text{O}}$ -R, $\stackrel{\bullet}{\text{N}}$ H₃, R- $\stackrel{\bullet}{\text{N}}$ H₂,CH₂=CH₂, CH≡CH.

(iii) $\stackrel{*}{R}$ –Mg–X, LiAl $\stackrel{*}{H}_{4}$, NaB $\stackrel{*}{H}_{4}$

The star (*) indicates the atom which donates electrons to the substrate. **Ambident nucleophile: -** Nucleophiles which have two sites of electron rich centre or in which two or more atoms bear a lone pair of electrons.

Examples:- $K^{\bigoplus \Theta}O-N=0$, $\overset{\bullet}{N}H_2-\overset{\bullet}{O}H$, $\overset{\bullet}{N}a\overset{\bullet}{C}N$

3. Reaction Intermediate

Carbocation:

Cation in which positive charge is present on carbon atom is called carbocation.

- Due to electron deficiency, it acts as an electrophile and always attack on electron richer site.
- > It is incomplete octet species because it has six electrons in outer most shell.
- All electrons are paired.

Carbanions: Anion in which negative charge is present on carbon atom is called carbanion.

- > It has eight electrons in outermost shell so it is complete octet species.
- > It is an electron richer species because it has extra electron.
- > Due to presence of nonbonding electrons, it acts as a nucleophile.

Free Radical:

- Electrically neutral species in which unpaired electron is present on carbon atom is known as carbon free radical.
- It has seven electron or odd electron in outermost shell of unpaired electron containing carbon.
- > It is electron deficient species due to incomplete octet.

Cl Carbenes (CH₂:):

Carbenes are neutral carbon species in which the carbon atom is bonded to two monovalent atoms or groups and carries two nonbonded electrons.

- It behaves as an electrophile.
- ▶ 6 e⁻ in outermost shell.
- ➢ It is neutral.
- ➤ 4 e⁻ are bonded and two are non-bonded e⁻.

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Cl Nitrenes (-N:)

Nitrenes are neutral nitrogen species in which the nitrogen is bonded to one monovalent atom or group and carries four non-bonded electrons.

- \geq It is monovalent radical.
- \triangleright 6 e- in outermost shell.
- It is neutral. \geq
- \triangleright Two are bonded and four are nonbonded electrons

Electronic Effects: 4

There are four effects which affect the chemical reaction due to transfer of electron

- (1) Inductive effect
- (3) Hyperconjugation

- (2) Mesmeric effect
- (4) Electrometric effect

1. Inductive Effect (I-Effect):

Polarity induced in non-polar a bond due presence of adjacent polar bond is known as detective effect.

- > In I-effect there is partial displacement of $e^{\mathbb{Z}}$.
- > After 3 or 4 C-atom I-effect is considered to be zero.
- Inductive effect decreases on increasing distance. So, Magnitude of I effect $\propto \frac{1}{\text{distance}}$
- I-effect of hydrogen is considered as zero.

-I groups

$$\begin{array}{c} \bigoplus \\ -OR_2 \\ > \\ -NR_3 \\ > \\ -NH_3 \\ > \\ -NH_3 \\ > \\ -NH_3 \\ O \\ \end{array} \right) \begin{array}{c} sp \\ -C \\ \equiv N \\ O \\ \\ O \\ \end{array} \right) \begin{array}{c} Sp^z \\ -C \\ = OH \\ \\ \\ O \\ \end{array} \right)$$

$$-X > -OH > -OR > -C \equiv CH > -NH_2 > Ph > -CH = CH_2 > H(I \approx 0)$$

+I group

$$-\overset{\Theta}{NH} > -\overset{\Theta}{O} > -COO^{\Theta} > -\overset{CH_{3}}{-CH} - CH_{3} > -CH - CH_{3} > -CH_{2} - CH_{3} > -CT_{3}$$
$$-CD_{3} - CH_{3} > T > D > H(I \approx 0)$$

Chemistry



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Chemistry

Example:	
(i)	$CH_3 - CH_2 - COOH < Cl - CH_2 - COOH < F - CH_2 - COOH$
	$-H^{\oplus}$ $-H^{\oplus}$ $-H^{\oplus}$
	$\begin{array}{c} \downarrow & \ominus \\ CH_3 - CH_2 - COO \end{array} \qquad \begin{array}{c} \downarrow & \ominus \\ Cl - CH_2 - COO \end{array} \qquad \begin{array}{c} \downarrow & \ominus \\ F - CH_2 - COO \end{array} \qquad \begin{array}{c} \downarrow & \ominus \\ F - CH_2 - COO \end{array}$
	+ I of -CH3Maximum -I of -Fanion is less stableMaximum stable anionCorresponding acid isMaximum acidic.
(ii)	CCl ₃ – COOH > CBr ₃ – COOH > Cl ₃ –COOH Maximum –I of Cl So maximum acidic.
(iii)	$\begin{array}{ll} CH_3-CH_2-CH-COOH > CH_3-CH-CH_2-COOH > CH_2-CH_2-CH_2-CH_2-COOH \\ I \\ F \\ \end{array} \\ \begin{array}{l} F \\ \end{array} \\ \begin{array}{l} F \\ \end{array} \\ \begin{array}{l} F \\ F \\ \end{array} \\ \begin{array}{l} F \\ F \\ \end{array} \\ \begin{array}{l} F \\ \end{array} \\ \end{array} \\ \begin{array}{l} F \\ \end{array} \\ \begin{array}{l} F \\ \end{array} \\ \begin{array}{l} F \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{l} F \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{l} F \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{l} F \\ \end{array} $ \\ \begin{array}{l} F \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \end{array} \\ \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\
(iv)	$\begin{array}{ccc} CH_2 - COOH & > & CH_2 - COOH & > & CH_2 - COOH \\ I & I & I \\ NO_2 & H & & CH_3 \\ -I \ of \ NO_2 & & -I \ of \ -CH_3 \\ maximum \ acidic. \end{array}$
(v)	HCOOH > CH ₃ -COOH > CH ₃ -CH ₂ -COOH Maximum +I Minimum acidic
(vi)	$\begin{array}{c} \text{COOH} \\ \text{COOH} \end{array} > \begin{array}{c} \text{CH}_2 < \begin{array}{c} \text{COOH} \\ \text{COOH} \end{array} > \begin{array}{c} \text{CH}_2 - \text{COOH} \\ \text{CH}_2 - \text{COOH} \end{array}$ $\begin{array}{c} \text{maximum distance of -COOH from other} \\ \text{maximum -I of -COOH on other} \\ \text{maximum acidic} \end{array}$



Basic strength \propto + I effect $\propto \frac{1}{-\text{Ieffect}}$

Ex.: (1) CH_3NH_2 (Ans. 4 > 3 > 2 > 1Maximum +I so maximum basic

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(2) $C_2H_5NH_2$ (3) $C_3H_7NH_2$ (4) $C_4H_9NH_2$

H⁺ acceptor

2. Resonance Or Misopedic Effect

Delocalization of πe^- is called as resonance or complete transfer of πe^- from one shell to another shell is called as **Resonance**.

Conditions For Resonance

(1) If there are two π bonds in conjugation then e⁻ of one π bond is transferred towards another π bond.

Ex. (i)
$$CH_2 = CH - CH = CH_2 \leftrightarrow CH_2 - CH = CH - CH_2 \leftrightarrow CH_2 - CH = CH - CH_2 \leftrightarrow CH_2 - CH = CH - CH_2$$

(b) (a) (b)

(ii)
$$CH_2 = CH - C-H + CH_2 - CH = C - H$$

- (2) If there is lone pair or a negative charge and n bond are in conjugation the lone pair of e⁻ or negative charge are transferred towards n bond.
- **Ex.** (i) $CH_2 = CH OH \iff OH = OH$

(ii)
$$CH_2 = CH - OH_2 \longrightarrow CH_2 - CH = CH_2$$

(3) If there is positive charge (vacant orbital) and 1t bond are in conjugation then e- of 1t bond are transferred towards positive charge.

Ex.
$$CH_2 = CH - CH_2 \longleftrightarrow CH_2 - CH = CH_2$$

(4) If there is free e^- and π bond is in conjugation.

Ex.
$$CH_2 = CH = CH_2$$
 \longleftrightarrow $CH_2 - CH = CH_2$

(5) If there is lone pair or negative charge and positive charge (vacant orbital) are in conjugation then e⁻ of lone pair or negative charge are transferred towards positive charge.

Ex.
$$\stackrel{\oplus}{\operatorname{CH}}_2 \stackrel{\frown}{-} \stackrel{\odot}{\operatorname{OH}} \stackrel{\longleftarrow}{\longrightarrow} \operatorname{CH}_2 = \stackrel{\oplus}{\operatorname{OH}}$$

- ➤ In resonance only e⁻ are delocalized not atoms.
- The number of e⁻ or number of unpaired or paired e⁻ in all resonating structures should be same.
- ➤ It is permanent effect.
- > All the resonating or canonical structures must follow the Lewis structures

Draw resonating structures:



or EDG) is known as 'M' effect.

(1) +M effect: - Group that donates the electron pair to conjugated system is known as +M effect exerting groups and the phenomena is known as +M effect.

+M group: Lone pair containing group like **e**.g.

–
$$\ddot{N}H_{2}$$
, – $\ddot{O}H$, – $\ddot{O}R$, – $\ddot{N}R_{2}$, – $\ddot{S}H$, – $\ddot{N}HR$, – \ddot{X} , – $\ddot{N}HCOCH_{3}$

e.g.



-OH, group lone pair donor So +M of -OH group

(2) -M effect: - Group, that withdraws electron pair from the conjugated system, is known as -M

effect exerting groups and the phenomena is known as –M effect.

-M group: -CHO, -COOH, -COOR, -COR, -NO₂, -CN, -COX, -CONH₂, -SO₃H

E.g.



-CHO group with drawing e- So -CHO is -M group

APPUCATIONS OF RESONANCE EFFECT:

- (1) Stability of carbocation.
- Ex. Give stability order for: -

(i) $CH_2 = CH - \overset{\oplus}{CH}_2 > CH_3 \rightarrow CH_2 - \overset{\oplus}{CH}_2 > CH_2 = CH \leftarrow CH - \overset{\oplus}{CH}_2$ Stabilized by Resonance (SBR) +I of Alkyl group -I of Alkenyl groups

(ii)

$$\begin{array}{ll} CH_3 - \bigoplus_{l=1}^{\bigoplus} CH_2 = CH_2 \\ H_3 \\ SBR \text{ and } + I \text{ of two } -CH_3 \end{array} > \begin{array}{l} CH_3 - \bigoplus_{l=1}^{\bigoplus} CH_2 = CH_2 \\ SBR \text{ and } + I \text{ of two } -CH_3 \end{array} > \begin{array}{l} \bigoplus_{l=1}^{\bigoplus} CH_2 - CH_l = CH_2 \\ SBR \text{ and } + I \text{ of one } -CH_3 \end{array} > \begin{array}{l} \bigoplus_{l=1}^{\bigoplus} CH_2 - CH_l = CH_2 \\ SBR \text{ and } + I \text{ of one } -CH_3 \end{array}$$

(iii)

$$\begin{array}{c} \bigoplus \\ (C_{6}H_{5})_{3} \stackrel{\oplus}{C} > (C_{6}H_{5})_{2} \stackrel{\oplus}{CH} > C_{6}H_{5} \stackrel{\oplus}{CH}_{2} > CH_{2} = CH - CH_{2} > (CH_{3})_{3} \stackrel{\oplus}{C} > (CH_{3})_{2} \stackrel{\oplus}{CH} > \\ (CH_{3} - CH_{2} > \stackrel{\oplus}{CH}_{3} > CH_{2} = \stackrel{\oplus}{CH} > CH \equiv \stackrel{\oplus}{C} \end{array}$$

(iv)



Maximum resonance

(v)







Ex. Give stability order for:

- (i) I. $CH_2=CH-\dot{C}H_2$ II. $CH_2-\dot{C}H$ III. $CH_2=CH-\dot{C}H-CH=CH_2$ Less reso. No. reso. More reso. Stability order III > I > II
- (ii) $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > (C_6H_5)\dot{C}H > CH_2 = \dot{C}H_2 > (CH_3)_3\dot{C} >$ $(CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

(4) Stability of resonating structures (R.S) Rules:

- (i) Complete octet R.S. is more stable than incomplete octet.
- (ii) Nonpolar R.S. is more stable than polar resonating structures.
- (iii) For charged R.S. negative charge on more EN and positive charge on less EN is more stable.
- **Ex.** Arrange the following for stability order.

 $\begin{array}{ccc} R-C-OH & > & R-C= \overset{\bigoplus}{O} -H & > & R-\overset{\bigoplus}{C} = O-H \\ \| & & & |_{\ominus} \\ Complete \ octet, \ nonpolar & Complete \ octet, \ polar & Incomplete \ octet \end{array}$ (i) R - C - OH $R - \overset{\Theta}{C} = OH$ > (ii) Less EN atom With more EN atom with incomplete octet incomplete octet R - C - OH $R - C \equiv \overset{\bigoplus}{O}$ (iii) < Incomplete octet complete octet $CH_2 - CH - O$ $\stackrel{\Theta}{CH_2}$ – CH=O < (iv) (Negative charge (Negative charge on less EN) on more EN) Aromaticity (Hickel's rule): Cyclic, planar and completely conjugated system

(5) Aromaticity (Hickel's rule): Cyclic, planar and completely conjugated system with $(4n+2)\pi$ electrons (where n = 0, 1, 2, 3, ...) is known as aromatic compounds, these compound gains extra stability which is known as aromaticity.

Note: $[4n + 2] \pi$ electrons. (Odd number of 1t electron pairs) means

If

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n = 0	2π electrons	or 1 pair
n = 1	6π electrons	or 3 pairs
n = 2	10 π electrons	or 5 pairs
n = 3	14 π electrons	or 7 pairs

S. No	Compound	Cyclic	Planner	Cyclic	Heckel Rule	Aromatic
1.	Ř	√	✓	√ √	22e-	Yes
	\bigtriangleup					
2.	$\overset{\odot}{\bigtriangleup}$	~	~	\checkmark	4⊡e-	No
3.	₽ □	~	~	\checkmark	42e-	No
4.		✓	~	~	62e-	Yes
5.		~	✓	✓	6?e-	Yes
6.		~	×	×	42e-	No
7.	$\overset{\oplus}{\bigcirc}$	~	~	✓	6⊡e-	Yes
8.	, ji	~	✓	~	6⊡e-	Yes
9.		~	✓	~	6⊡e-	Yes
10.	N N H	~	~	✓	6⊡e-	Yes
11.		~	~	✓	6 2e -	Yes
12.		~	~	✓	10⊡e-	Yes
13.		~	~	√	14 2e -	Yes
14.		√	~		62e-	Yes

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- (6) Acidic and Basic strength:
- (a) Acidic strength: (Acidic strength \propto stability of conjugate base (anion) $\propto \frac{-M,-I}{+M,+I}$)

Illustrations

Illustration 1. Carboxylic acids are more acidic than phenols, why? **Solution.**



2, equal R.S. more stable anion so corresponding acid is more acidic. Here, carboxylate ion is more

stable than phenoxide ion.

5, unequal R.S. less stable anion since –ve charge is being shared by oxygen is less electronegative carbon.

Note: The molecule having equivalent R.S. has more stability than the molecule having non-equivalent R.S.

Illustration 2. Phenol is more acidic than alcohols why?

Solution.



(b) Basic strength order: -Tendency to donate the electron pair by an atom or group is known as its basic strength. Compounds in which electron pair is

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delocalized will be less basic while, those in which electron pair is localised will be more basic.

(Basic strength $\propto H^{\oplus}$ accepting tendency $\propto l.p.$ donating tendency $\propto \frac{+M,+I}{-M,-I}$)

Ex. Give basic strength order:



More resonance of I.p. so less basic

less resonance of l.p. so more basic

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Illustrations

Illustration 3. Give stability order of:



So, stability order IV > III > II > I



 $-M_0 = -M_P$ and $-M_m = 0$

but –I_0 > –I_m > –I_P, –M and –I increases positive charge stability order is IV > II > III > I

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-OH, group shown + M effect

$$\label{eq:main_stability} \begin{split} +M_0 &= +\ M_P\ \text{and} + M_m = 0\ \text{but}\ -I_0 > -I_m > -I_P\ \text{and} + M >> -I \\ \text{So, } +M\ \text{stability}\ \text{the carbocation}\ \text{by}\ \text{decreasing}\ \text{positive}\ \text{charge} \\ \text{Stability}\ \text{order}\ III > I > IV > II \end{split}$$



charge is minimum So stability order I>III>III>IV

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Illustration 4. Give acidic strength order for:



So acidic order is I > II > III > IV



Acidic order should be I > III > II > IV but correct order is III > I > II > IV

Reason: Due to intramolecular H-bonding in ortho nitrophenol, it is less acidic than para nitrophenol.





intermolecular H-bonding more association more B.P. less volatile more acidic more soluble in water

- intramolecular H-bonding
- less association
- ➢ less B.P.
- > more volatile
- ➢ less acidic
- ➤ less soluble in water

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Maximum -M and Maximum -I effect So, maximum acidic Acidic order I > II > III > IV



Acidic order is I > II > III > IV > V Н-СООН CH₃COOH C₆H₅-COOH I Π

COOH

Acidic order is I > III > II



(vi)

(v)

COOH

NO₂





only –I –I and –M Ortho effect Acidic order is \Rightarrow o > p > m > benzoic acid



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Acidic order is \Rightarrow o > m > p >benzoic acid

Illustration 5. Give basic strength order for:

-M and -I



Basic strength order is \Rightarrow aniline > m>p>o

+H and +I

Only +I



3. Hyperconjugation Effect (H-Effect)

Complete transfer of e⁻ of C–H σ bond towards π bond or positive charge or free electron is called as H-effect (permanent effect). It is also called as No bond resonance (given by Nathen and Baker).

Conditions Of H-Effect:

1. If there is C–H σ bond and positive charge are in conjugation Carbon which is attached to positively charged carbon is called as α -C and H which is attached to α -C is called as α -H. So, if number of α –H are more, then there will be a greater number of hyper conjugating structures, so more stable will be the carbocation.

$$H \xrightarrow{\alpha} C \xrightarrow{\Phi} CH_{2} \longleftrightarrow H \xrightarrow{H^{\oplus}} C = CH_{2} \longleftrightarrow H \xrightarrow{H^{\oplus}} C = CH_{2} \longleftrightarrow H^{\oplus} C = CH_{2} \xleftarrow{H^{\oplus}} H^{\oplus} C = CH_{2} \xleftarrow{H^{\oplus$$

all are called as hyper conjugating structures or canonical structures.

- 2. If there is C–H σ bond and free e– are in conjugation then there will be H-effect. Carbon, which is attached to C having unpaired e–, is called as α –C and H which are attached to α –C are called as α -H.
- 3. If there is C–H σ bond and π bond is in conjugation then there will be H-effect. sp³ carbon which is attached to double bonded C is called as α –C and H attached to α –C is called as α –H.

$$H \xrightarrow{\alpha} \stackrel{H}{\xrightarrow{C}} CH \xrightarrow{E} CH_{2} \xrightarrow{H} H \xrightarrow{C} C = CH \xrightarrow{C} CH_{2} \xrightarrow{H} H \xrightarrow{C} C \xrightarrow{H} H \xrightarrow{C} H \xrightarrow{C} C \xrightarrow{H} H \xrightarrow{L} H \xrightarrow$$

Note: If there is C–H σ bond and negative charge in conjugation then there will be no H-effect.

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$$H - C = C H_2 (No H - effect)$$

no shifting of C–H σ bond, because anion is having complete octet (8e⁻)

Apposition Of H-Effect

Stability of carbocation / Free Radical / Alkene

Stability oc No. of canonical structures \propto No. of α H.

Example: Give stability order for:

Heat of hydrogenation:

 $R-CH=CH_2 + H_2 \rightarrow R-CH_2-CH_3 + \Delta H$ (Heat of hydrogenation)

Heat evolved when any unsaturated hydrocarbon is hydrogenated is called heat of hydrogenation (ΔH)

(If alkene is more reactive towards hydrogen, then it will evolve more ΔH) So, Heat of hydrogenation $\propto \frac{1}{\text{stabilityofalkene}} \propto \frac{1}{\text{numberof}\alpha - H}$

4. Electrometric Effect: (E Effect)

Complete transfer of a shared pair of π -electrons from one atom to another atom in presence of attacking reagent, is known as 'E' effect.

(i) **Positive Electrometric Effect (+ E effect):** In this effect the π -electrons of the multiple bonds are transferred to that atom to which the reagent gets attached. For example:



(ii) Negative Electrometric Effect (-E effect): In this effect the 1t- electrons of the multiple bonds are transferred to that atom, to which the attacking reagent does not get attached.
For example

For example.

Shifting of π electrons:

- (i) $CH_2 = CH_2 \xrightarrow{\text{reagent}} CH_2 CH_2$
- (ii) $CH_3-CH=CH_2 \xrightarrow{\text{reagent}} CH_3-CH-CH_2 +I$

(iii)
$$CH_3-C = C-CH_3 \xrightarrow{reagent} CH_3-C = C-CH_3 \text{ or } CH_3-C = C-CH_3 \text{ or } CH_3-C = C-CH_3 \text{ (b)}$$

(iv) CCl₃-CH=CH₂
$$\xrightarrow{\text{reagent}}$$
 CCl₃-CH-CH₂ -I

5. Tautomerism or Dermographism

- Tautomer's have same molecular formula but different structural formula due to migration of active hydrogen from one polyvalent atom to another polyvalent atom. This phenomenon is known as tautomerism.
- Dermographism means bond turning. [Desmos = Bond; Troops =Turn]

$$\begin{array}{c} CH_2-C-H \\ I \\ H \\ H \\ \alpha-Hydragon \text{ or active H} \end{array} \qquad \alpha-H \text{ of carbonyl compound is active H}$$

Ex.
$$H - \begin{array}{c} H \\ - \begin{array}{c} C \\ - \end{array} \\ H \\ H \end{array} \\ H \\ 0 \end{array} \qquad H - \begin{array}{c} H \\ - \end{array} \\ H \\ - \begin{array}{c} C \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ H \\ 0 \\ - \end{array} \\ H \\ - \begin{array}{c} H \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - \begin{array}{c} H \\ - \end{array} \\ - H \\ - \end{array} \\ - \end{array} \\ - H \\ = H \\ - \bigg \\ - H \\ - \bigg \\ - H \\ - H \\ - H \\ = H \\ - H \\ = H \\ - H$$

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Ex.		$\begin{array}{ccc} CH_3 - C - CH_2 & \rightleftharpoons & CH_2 \\ H & H \\ O & H \\ keto \end{array}$	$H_3 - C = CH_2$ O - H ene + ol =enol	
Note:	(1) Taut (2) By sh	omer's exist in dynamic equilib hifting of H-atom, 1t bond also c	rium. hanges its positi	on.
(I) (a)	Condition For carb $(\alpha - H)$ s	on for Tautomerism: oonyl compounds: - Carbonyl co how tautomerism	ompounds havin	g at least one active-H
	(i)	$CH_3 - C - H$	3 α H,	Shows Tautomerism
	(ii)	$CH_3 - C - CH_3$	6 α H,	Shows Tautomerism
	(iii)	$\mathbf{CH}_3 - \mathbf{CH}_{\substack{ \\ CH_3 \\ 0}} - \mathbf{CH}_{\substack{ \\ 0 \\ 0}} - \mathbf{H}$	1αΗ,	Shows Tautomerism
	(iv)	H - C - H	No α H,	No Tautomerism
	(v)	о С-н	No α H,	No Tautomerism
		O C–CH ₃ (Acetophenone) 		
	(vi)		3 α H,	Shows Tautomerism
	(vii)	(Acetophenone) Ph – C – Ph (Benzophenone) Νο α Η,	No Tautomerism
	(viii)	$Ph - CH_2 - CH_2 - CH_2 - Ph$	2 α H,	Shows Tautomerism

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(b) For nitro compounds: Nitro compounds having at least one active -H (α -H) show tautomerism



(c) $H-C\equiv N$ and $H-N \xrightarrow{} C$ are tautomer's [also Functional isomers] while $R-C\equiv N$ and $R-N \xrightarrow{} C$ are only Functional isomers.

 $H-C≡N \rightarrow C \stackrel{\bullet}{=} N-H$ Active H

(d) H - N and H - O - N = O are tautomer's.

Note: Nitro compounds with at least one a-H are soluble in NaOH.

(II) Enol Content: 1. $\begin{array}{c} CH_2 - C - H \\ \downarrow \\ H \end{array} \rightleftharpoons \begin{array}{c} CH_2 - C - H \\ \bigcirc \\ OH \end{array} \rightleftharpoons \begin{array}{c} CH_2 - C - H \\ \bigcirc \\ OH \end{array}$ "Keto" ($\approx 99\%$) "enol" ($\approx 1\%$)

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- More active the H, more will be its participation in tautomerism.
- Stability of enol form depends on
 - (i) Resonance
 - (ii) H Bond
 - (iii) Aromaticity.

4 Type of Reactions:

Reaction is of mainly four types:

- 1. Addition reactions. 2. Substitution reactions.
- 3. Elimination reactions. 4. Isomerisation reactions
- 1. ADDITION REACTIONS: It is also of three types:
 - (A) Electrophilic addition reactions
 - (B) Free radical addition reactions
 - (C) Nucleophilic addition reactions
 - (A) Electrophilic addition reaction: Because of the presence of >C=C< bond in molecules, alkenes generally take part in the addition reactions.



From mechanism point of view, the addition in alkenes is generally **electrophilic in nature** which means that attacking reagent which carries the initial attack is an electrophile (E^+). This is quite expected also as there is high electron density in the double bond. The mechanism proceeds in two steps.

Step I: The π -electron cloud of the double bond causes the polarization of the attacking molecule (E-Nu) which cleaves to release the electrophile (E⁺) for the attack The double bond simultaneously undergoes electrometric effect and the attack by the electrophile is accomplished in slow step (also called rate determining step) to form a **carbocation** intermediate.

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$$>C = \underbrace{C} < + \underbrace{\overset{\delta}{F}}_{\text{Rate determing step (RDS)}}^{+} \xrightarrow{(Slow)} >C - \underbrace{C}^{\text{F}}_{\text{C}} + :Nu^{-} \xrightarrow{\text{Fast}}_{\text{F}} > \underbrace{C}_{\text{F}}_{\text{C}} - \underbrace{C}_{\text{C}}^{+}_{\text{F}} < :Nu^{-} \xrightarrow{\text{Fast}}_{\text{F}} > \underbrace{C}_{\text{F}}_{\text{F}} - \underbrace{C}_{\text{F}}_{\text{F}}$$

Step II: The nucleophile (: Nu⁻) released in the slow step combines with the carbocation to give the desired addition product in the fast step.
Reactivity for Electrophilic addition reaction ∝ stability of carbocation formed in RDS

(1) Addition of Halogen: It is an electrophilic addition reaction.

$$\begin{array}{c} X \\ I \\ R-CH=CH_2+X_2 \rightarrow R-CH-CH_2 \\ I \\ X \\ (Vicinal halides) \end{array}$$

- (a) The addition of Br₂ on alkenes provides a useful test for unsaturation in molecule. The brown colour of the bromine being rapidly discharged. Thus, decolorization of 5% Br₂ in CC1₄ by a compound suggest unsaturation in it. Colourless dibromo compound is formed.
- (b) 12 reacts with alkenes to form Vicinal di-iodides which are unstable and I₂ gets eliminated to give original alkene.

.

Mechanism:

$$CH_2 \stackrel{\frown}{=} \underbrace{CH_2}_{H_2} \stackrel{\delta+}{=} \underbrace{Br}_{H_2} \stackrel{\delta-}{=} \underbrace{Br}_{H_2} \stackrel{(Slow)}{\longrightarrow} \underbrace{CH_2}_{H_2} \stackrel{\ominus}{=} \underbrace{CH_2}_{H_2} \stackrel{\ominus}{=} \underbrace{Br}_{H_2} \stackrel{\ominus}{\longrightarrow} \underbrace{CH_2}_{H_2} \stackrel{\ominus}{=} \underbrace{CH_2}_{H_2} \stackrel{\ominus}{\to} \underbrace{CH_2}_{H_2} \stackrel{\bullet}{\to} \underbrace{CH_2} \stackrel{\bullet}{\to} \underbrace{CH_2} \stackrel{\bullet}{\to} \underbrace{CH_2} \stackrel{\bullet}{\to} \underbrace{$$

It is interesting to note that product which is mainly formed as a result of addition is trans in nature whereas the cis isomer is obtained in relatively smaller proportions. Since carbocation intermediate is planar (sp² hybridized), both cis and trans addition products must be formed almost in equal proportions. The trans product can be justified in case a cyclic halonium ion is formed by the initial electrophile attack.

$$\overset{\delta + \delta^{-}}{\text{Br} - \text{Br} + \text{CH}_{2} = \text{CH}_{2} \xrightarrow{(\text{Slow})} \overset{\Phi}{\underset{\text{CH}_{2} - \text{CH}_{2}}{\overset{\Theta}{\underset{\text{CH}_{2} - \text{CH}_{2}}{\overset{\Theta}{\underset{\text{Br}}}} \xrightarrow{\text{CH}_{2} - \text{CH}_{2}} \xrightarrow{\text{CH}_{2} - \text{CH}_{2}} \overset{\Theta}{\underset{\text{Br}}} \overset{\Theta}{\underset{\text{Halonium ion}}}$$

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$$\begin{array}{c} \bigoplus \\ Br + \\ H_2C \\ H_2C$$

E.g.
$$CH_3-CH-CH=CH_2 \xrightarrow{Br_2} CH_3-CH-CH-CH_2$$

 $H_1 \\ CH_3 \\ C$

No carbocation rearrangement and anti-addition product.

(2) Addition of halogen acid:

$$R - CH = CH - R + HX \longrightarrow R - CH_2 - CH - R$$

$$R - CH = CH_2 + HX \longrightarrow R - CH - CH_3$$

- > The order of reactivity of hydrogen halide is: HI > HBr > HCI
- > Addition on alkene proceeds via the formation of more~ stable carbonium ion.
- Addition of HX on unsymmetrical alkenes (R-CH=CH₂) takes place according to Markovnikov's rule. Carbocation rearrangement is observed in the reaction.

Rearrangement in. carbocation



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Markovnikov's Rule States:

(a) First Rule: When molecule of HX add up on unsymmetrical unsaturated hydrocarbon, the electrophile (H⁺) goes to the unsaturated carbon atom bearing a greater number of hydrogen atoms.

$$CH_3 - CH = CH_2 + HX \longrightarrow \begin{array}{c} X \\ H \\ CH_3 - CH - CH_2 \\ H \\ H \end{array}$$

Mechanism: It is electrophilic addition and is illustrated by the action of HCl to propene.

$$CH_{3} - CH = CH_{2} + H - Cl \xrightarrow{Slow} CH_{3} - CH - CH_{3} + Cl^{-}$$

Secondary carbocation
$$Cl^{-} + CH_{3} - CH - CH_{3} \xrightarrow{Fast} CH_{3} - CH - CH_{3}$$
$$CH_{3} - CH - CH_{3}$$
$$Cl_{2} - Chloropropane$$

Primary carbocation (CH₃-CH₂- $\overset{\oplus}{CH}_2$) cis also formed. but only in very small proportion since it less, Stable than the secondary carbocation. Markovnikov's rule is based on stability of carbocation.

Note; The electrophilic addition of HX to unsymmetrical alkenes always occurs through the formation of a more stable carbocation intermediate.

(b) Second Rule: In the addition of HX to vinyl halide and analogous compounds, the halogen attaches itself to the carbon atom, on which the halogen atom is already present.

$$CH_2 = CH - Cl + HCl \rightarrow CH_3 - CH - Cl$$

 $\downarrow Cl$
Ethylidene chloride

Mechanism:

$$CH_2 = CH - \stackrel{\bigcirc}{Cl}_{H} \xrightarrow{\bigoplus}_{H} CH_3 - \stackrel{\bigcirc}{CH} - \stackrel{\bigcirc}{Cl}_{Cl} \xrightarrow{\bigoplus}_{Cl} CH_3 - \stackrel{\cap}{CH} - Cl$$

All polar regents of the general structure $\stackrel{\oplus \emptyset}{YZ}$ (such as $\stackrel{\oplus}{Y} - \stackrel{\emptyset}{X}$, $\stackrel{\oplus}{H} - \stackrel{\emptyset}{OH}$ $\stackrel{\oplus}{H} - \stackrel{\Theta}{SO_3H}$, $\stackrel{\oplus}{X} \stackrel{\Theta}{OH}$) add on unsymmetrical unsaturated compound in accordance with Markovnikov's rules. Such additions are called normal Markovnikov's rule, whereas additions in the opposite manner are referred to as abnormal or **anti-Markovnikov's additions**.

(3) Addition of Hypohalous acid (or X₂/H₂O, or HOX): It is an electrophilic addition and follows Markovnikov's rule, and anti-addition.



(4) Addition of water (Hydration of alkenes): Propene and higher alkenes react with water in the presence of acid to form alcohol This reaction is known as acidic hydration reaction. Intermediate in this reaction is carbocation, so rearrangement may take place.

(ii) $CH_3-C=CH_2+H_2O \xrightarrow{H^+} CH_3-CH-CH_3$ $CH_3 \xrightarrow{CH_3} CH_3$ 2-Methylpropene 2- Methylpropene-2-ol

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Mechanism:

$$CH_{3}-CH = CH_{2}+H^{+} \xrightarrow{Slow} CH_{3}-CH-CH_{3}$$

$$CH_{3}-CH = CH_{3}+H-\ddot{\Box}-H \xrightarrow{Fast} CH_{3}-CH-CH_{3} \xrightarrow{-H^{+}} CH_{3}-CH-CH_{3}$$

$$H \stackrel{I}{\stackrel{O}{\leftarrow}} -H \xrightarrow{O-H} O \xrightarrow{H}$$

$$H \stackrel{I}{\stackrel{O}{\leftarrow}} -H \xrightarrow{O-H}$$

$$Propan-2-ol$$

(5) Addition of NOCl (Tilden reagent):

$$CI NO | | CH_3 - CH = CH_2 + NOCI \rightarrow CH_3 - CH - CH Propylene nitroso chloride$$

(6) Hydroboration Oxidation: Borane readily reacts with alkenes giving trialkyl boranes. The reaction is called hydroboration.

 BH_3 does not exist freely as monomer so a solvent THF (tetra hydro furane) is used to stabilized it.

Ex.
$$3CH_3-CH=CH_2+B \xrightarrow{\delta^+}_{H} \xrightarrow{H}_{H} \xrightarrow{THF} (CH_3-CH_2-CH_2)_3B$$

BHR₂ also can be taken.

Ex.
$$CH_3-CH=CH_2+BHR_2 \longrightarrow CH_3-CH_2-CH_2-BR_2$$

$$(CH_{3}-CH_{2}-CH_{2})_{3}B \rightarrow \xrightarrow{H_{2}O/H^{+}} 3CH_{3}-CH_{2}-CH_{3}+H_{3}BO_{3}$$

$$\bigcirc Propane$$

$$H_{2}O_{2}/OH \rightarrow 3CH_{3}-CH_{2}-CH_{3}+H_{3}BO_{3}$$

$$Propanol$$

$$(1^{\circ} alcohol)$$

$$\begin{array}{ccc} 3R-C \equiv C-R & \xrightarrow{BH_3} & (R-C=C-)_3B \\ & I & I \\ & H & R \end{array}$$

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- **Note:** The overall process appears to be addition of water according to anti-Markovnikov's rule and involves syn. addition.
- (7) Oxymercuration- demarcation: Mercuric acetate in water is treated with an alkene. The addition product on reduction with sodium Boro hydride in aqueous NaOH solution gives alcohol. It follows the Markovnikov's rule.

$$CH_3 - CH = CH_2 \rightarrow CH_3 - CH_3 - CH_3$$

(i) $(AcO)_2 Hg/H_2O$ (Mercuric acetate) or $(CH_3COO)_2Hg/H_2O$

(ii) NaBH₄

Mechanism:

 $\begin{array}{c} CH_{3}-COO \\ Hg \\ CH_{3}-COO \end{array} \xrightarrow{Hg} CH_{3}-COO^{-} + CH_{3}-COOHg^{+} (Electrophile) \end{array}$



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Note: Intermediate is cyclic cation so there is no rearrangement.



(B) Free radical addition reactions: - Addition of HBr on alkene or alkyne in presence of peroxide.

$$CH_3 - CH = CH_2 \xrightarrow[HBr(\triangle)]{HBr(\triangle)} CH_3 - CH_3 - CH_1 - CH_2$$

Anti-Markovnikov's rule or peroxide effect or Kharasch rule

(i) In the presence of peroxides, the addition of HBr on unsaturated unsymmetrical compound takes place contrary to Markovnikov's rule.

This is called peroxide effect and is due to the difference in the mechanism of the addition.

- (ii) In the normal Markovnikov's addition, the mechanism is ionic.
- (iii) In the presence of peroxide the addition of HBr takes place via free radicals.
- (iv) Peroxide effect is not observed in case of H–F, HCI and HI. Reactions follows electrophilic addition mechanism.



Mechanism:

(i) Chain initiation -

(a)
$$R-O-O-R \longrightarrow 2RO^{\bullet}$$

 $HBr + RO^{\bullet} \longrightarrow ROH + Br^{\bullet}$

(ii) Chain propagation

(iii) Chain termination: $R - \dot{C}H - CH_{2} - Br + B\dot{r} \longrightarrow R - CH(Br) - CH_{2}(Br)$ $R - \dot{C}H - CH_{2} - Br + R - \dot{C}H - CH_{2} - Br \longrightarrow R - CH - CH_{2} - Br$ $I = CH - CH_{2} - Br$ $R - \dot{C}H - CH_{3} - CH = CH_{2} \xrightarrow{HBr(\Delta)}_{ROOR} CH_{3} - CH_{3} - CH_{3}$

Ans. no effect simple EAR

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(C) Nucleophilic Addition Reaction: -

(C1) NAR in Alkyne: In these reactions some heavy metal cation like Hg⁺², Pb⁺², Ba⁺² is used. This cation attracts the π - e- of alkynes and decrease the e- density and hence a nucleophile can attack an alkyne.

(1) Addition of dil. H₂SO₄ (Hydration): The addition of water takes place in the presence of Hg⁺² and H₂SO₄ [1% HgSO₄ + 40% H₂SO₄].

$$CH \equiv CH + H - OH \rightarrow CH_2 = CH - OH \rightleftharpoons CH_3 - CHO$$
(Enol)

$$CH_{3} - C \equiv CH + H - OH \rightarrow CH_{3} - CH_{3} - CH_{3} = CH_{3} - C$$

Mechanism:

$$R - C \equiv CH \xrightarrow{Hg^{+2}} R - \overset{\bigoplus}{C} = \overset{\bigoplus}{CH} \rightarrow R - \overset{\bigoplus}{C} = \overset{\bigoplus}{CH} \rightarrow R - \overset{\bigoplus}{C} = \overset{\bigoplus}{CH} \rightarrow \overset{\bigoplus}{Hg^{+2}} \overset$$

$$R - C = CH \xrightarrow{H - O - H} R - C = CH \xrightarrow{-H^+} R - C = CH \xrightarrow{-H^+} R - C = CH \xrightarrow{H^-} Hg^{+--Hg^{+2}} H \xrightarrow{H^-} H \xrightarrow{H^-} H$$
(enol) (Keto more stable)

Ex.
$$CH_3 - C \equiv C - CH_3 \xrightarrow{H^+/H_2O} CH_3 - C = C - CH_3 \xrightarrow{OH} CH_3 - C = C - CH_3 \xrightarrow{OH} CH_3 - C - CH_2 - CH_3$$

(2) Addition of alcohols: In presence of BF₃ and HgO alkynes react with alcohols and form acetal and ketal.

$$CH \equiv CH + CH_{3}OH \xrightarrow{BF_{3}} CH_{2} = CHOCH_{3} \xrightarrow{CH_{3}OH} CH_{3} - CH \xrightarrow{OCH_{3}} OCH_{3}$$

Methylal (acetal)

$$R-C \equiv CH + CH_{3}-OH \xrightarrow{BF_{3}} R-C = CH_{2} = \xrightarrow{CH_{3}OH} R-C-CH_{3}$$

Ketal

(3) Addition of AsCl₃: - In presence of AlCl₃ or HgCl₂ acetylene combines with AsCl₃ to yield Lewisite gas. It is four times poisonous than mustard gas. $CH \equiv CH + Cl-AsCl_2 \longrightarrow CH-Cl$

$$I-AsCl_2 \longrightarrow CH-Cl \\ \parallel \\ CHAsCl_2$$

2-Chlorovinyl dichlorvos arsine (Lewisite gas)

(C₂) NAR ·in Aldehyde & Ketone: Due to strong electronegativity of Oxygen, the mobile π electrons pulled strongly towards oxygen, leaving the carbon atom deficient of electrons. Carbon is thus readily attacked by Nu. The negatively charged oxygen is attacked by electron deficient (electrophile) E⁺.

$$\frac{\partial}{\partial C} = 0^{\partial} \xrightarrow[RDS]{N_{u}}{RDS}} \xrightarrow[RDS]{\Theta} \xrightarrow[fast]{E^{\oplus}}{fast}} \xrightarrow[Ku]{C-OE} \xrightarrow[Nu]{N_{u}}{N_{u}}$$
Reactivity \propto Magnitude of ∂ +ve Charges of carbonyl group \propto -I effect $\propto \frac{1}{+I \text{ effect}}$

Illustrations

Solution.

Illustration 1. Arrange the following for reactivity in decreasing order.

(a)	I. $_{\rm H}^{\rm H}$ >C=0	II. $H^{CH_3} > C = O$	III. $CH_3 \\ CH_3 > C = 0$
(b)	I. CICH2CHO IV. CH3CH2CHO	II. NO2CH2CHO	III. CH3CHO
(c)	I. CH₃CHO IV. CCI₃CHO	II. CICH2CHO	III. HCCI2CHO
(b)	I. $\frac{CH_3}{CH_3}$ C=0 IV. $\frac{CH_3}{CH_3}$ C=0	II. CH ₃ CH ₂ C=0	III. (CH ₃)CH ₂ CH ₃ C=0
(a) (d)	I > II > III IV > I > II > III	(b) II > l > III > IV	(c) IV > III > II >

CH₃– is +I group, decreases the intensity of δ +ve charge on C-atom of >C=0 group.

Cl- is –I group increases the intensity of δ +ve charge on C-atom of >C=O group.

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(6) Reaction with glycol:



(7) **Reaction with H₂O:** It is a reversible reaction.



- **Note:** Chloral (Cl₃C–CH=O) forms stable hydrate [CCl₃–CH(OH₂) (chloral hydrate)]
- (8) Reaction with ammonia derivatives: These are condensation or addition elimination reaction. These precedes well in weakly acidic medium. $NH_3 \rightarrow NH_2Z$ (Ammonia derivative)

 $>C=O+H_2N-Z \xrightarrow{n} >C=N-Z+H_2O$ Addition- elimination (Condensation)

Ammonia derivatives (NH₂Z):

 $Z = OH \longrightarrow NHpH (Hydroxyl amine)$ $Z = NH_2 \longrightarrow NH_2NH_2 (hydrazine)$ $Z = NHC_6H_5 \longrightarrow NH_2NHC_6H_5 (Phenyl hydrazine)$ $Z = NH \longrightarrow NO_2 \longrightarrow NH_2-NH \longrightarrow NO_2$ $Z = NH \longrightarrow NO_2 \longrightarrow NH_2-NH \longrightarrow NO_2$ $Z = NH \longrightarrow NO_2 \longrightarrow NH_2-NH \longrightarrow NO_2$

 $Z = NHCONH_2 \rightarrow NH_2NHCONH_2$ Semi Carbazide



2. SUBSTITUTION REACTIONS: Reactions in which one atom or a group of substrates is replaced by other atom or group are called as substitution reactions.

On the basis of reaction conditions and attacking species, substitution reaction is also of three types:

- (A) Free radical substitution reactions
- (B) Electrophilic substitution reactions
- (C) Nucleophilic substitution reactions
- (A) Free radical substitution reactions: Substitution reaction in alkanes show free radical mechanism. They give following substitution reaction.
 (a) Halogenation: Replacement of H-atom by halogen atom

$$R-H + X_2 \rightarrow R-X + HX$$

Halogenation is made on exposure to (halogen + alkane) mixture to UV or at elevated temperature. The reactivity order for halogens shows the order.

$$F_2 > Cl_2 > Br_2 > I_2$$

Reactivity order of hydrogen atom in alkane is Tertiary C-H > Sec. C-H > primary C-H

- (i) Fluorination: Reacts explosively even in dark. Fluorination can be achieved without violence when alkane is treated with F₂ diluted with an inert gas like N₂.
- (ii) Chlorination:

 $CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$

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The monochord derivative of alkane is obtained as major product by taking alkane in large excess.

When chlorine is in excess then perchloro derivative is obtained as major product.

At 12 noon explosively $CH_4 + Cl_2 \rightarrow C + HCl$ **Mechanism** for $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ **Step-I Chain initiation step:** $Cl : Cl \xrightarrow{UV}_{orA} Cl^{\bullet} + Cl^{\bullet}$

Step-II Chain propagation step:



Step-III Chain termination step:

 $\operatorname{Cl}^{\bullet} + \operatorname{Cl}^{\bullet} \longrightarrow \operatorname{Cl}_{2}, \operatorname{CH}_{3}^{\bullet} + {}^{\bullet}\operatorname{Cl} \longrightarrow \operatorname{CH}_{3}\operatorname{Cl}, \operatorname{CH}_{3}^{\bullet} + {}^{\bullet}\operatorname{CH}_{3} \longrightarrow \operatorname{CH}_{3}\operatorname{CH}_{3}$

- (iii) Bromination: Br₂ reacts with alkanes in a similar manner but less vigorously.
- (iv) Iodination: Iodine reacts with alkanes reversibly. HI formed as the by product is a powerful reducing agent and is capable of reducing the CH₃I to CH₄.

Iodination may be carried out in the presence of an oxidising agent such as HIO₃, HNO₃, HgO etc. which decompose HI,

 $CH_4 + I_2 \Longrightarrow CH_3I + HI$

$$5\mathrm{HI} + \mathrm{HIO_3} \longrightarrow 3\mathrm{I_2} + 3\mathrm{H_2O}$$

Iodination is very slow because energy of activation of the reaction is very large

$$CH_4 + I^{\bullet} \longrightarrow HI + CH_3$$

(b) Nitration: (Vapour phase nitration) This involves the substitution of a hydrogen atom of alkane with –NO₂ group.

At ordinary temperature, alkanes do not react with HNO_3 But reacts with vapours of Conc. HNO_3 at $450^{\circ}C$ and in pressure.

$$R-H + HO-NO_2 \xrightarrow{400-500^{\circ}C} R-NO_2 + H_2O$$

Since the reaction is carried at high temperature and in pressure, so the C–C bonds of alkanes also break during the reaction and a mixture of nitroalkanes is formed.

Ex. $CH_3-CH_3 + HNO_3 \xrightarrow{450^{\circ}C} CH_3CH_2NO_2 + CH_3NO_2 + H_2O$

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(c) Sul phonation: Replacement of H atom of alkane by -SO₃H is known Sul phonation. Alkane react with fuming H_2SO_4 or oleum ($H_2S_2O_7$).

$$\begin{array}{ccc} CH_3 & CH_3 \\ | & & | \\ Ex. & CH_3 - C - H + HO - SO_3H & \longrightarrow & CH_3 - C - SO_3H + H_2O \\ | & & | \\ CH_3 & CH_3 & CH_3 \end{array}$$

2-Methy1 propane

[The reactivity order for Sul phonation is tart. H > Sec. H > prim. H] **Note:** The reaction is observed in higher alkanes and the alkanes having 3° H.

(d) Chlorosulphonation (Reed reaction): Reaction with a mixture of SO₂ and Cl₂ at ordinary temperature in the presence of UV light is called Chlorosulphonation.

$$C_{3}H_{8} + SO_{2} + Cl_{2} \xrightarrow{UV} C_{3}H_{7}SO_{2}Cl + HCl$$

Propane sulphonyl chloride

Allylic or benzylic substitution by Br2 (low concentration)/hv or NBS/hv

 $CH_{3}-CH=CH_{2} \xrightarrow{Br_{2}} CH_{2}-CH=CH_{2}+HBr$

Mechanism:

Chain initiation step: Ι

$$\operatorname{Br}_2 \xrightarrow{hv} \operatorname{Br} + \operatorname{Br}$$

Π Chain propagation step: $CH_3-CH=CH_2+Br \longrightarrow CH_2-CH=CH_2+HBr$ (stable by resonce)

$$\begin{array}{c} \cdot \\ CH_2 - CH = CH_2 + Br_2 \rightarrow CH_2 - CH = CH_2 + Br \\ | \\ Br \\ (product) \end{array}$$

Electrophilic substitution reaction [ESR]: Characteristic reaction of **(B)** arenes is ESR Mechanism:

Formation of $\stackrel{\oplus}{E}$ $E-Nu \xrightarrow{Catalyst} \stackrel{\oplus}{E} + \stackrel{\Theta}{Nu}$

Chemistry



Illustrations

Illustrations 2. Give reactivity order for electrophilic substitution reaction.

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Less EN of nitrogen So more +M so more e- density So more reactive



less +M of -OH due to more EN





More -M of $-NO_2$ & more -1So, e⁻ density decrease

(more) so less reactive



less -M of -CHO & less -1 So, e- density deceases (less) so more reactive.





CH₃

 $\underbrace{\bigcirc}_{+M}^{NH_2} \underbrace{\bigcirc}_{-M}^{-M} \underbrace{\bigcirc}_{\downarrow}^{-M}$





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Note:

(1) ortho/para directing group or activating group: Group which direct electrophile on ortho and para position is called as o/p directing group.

These group increases electron density or increases reactivity of benzene ring so are called activating group.

These groups are:

-NH2, -NHR, -NR2, -OH, -OR, -NHCOCH3. -SH, -OCOR, -CH3, -CH2CH3, -CH(CH3)2



Due to +M/+H of these groups' electron density at ortho and para position is increased so electrophile easily attack on ortho/para position.

(2) Meta directing or deactivating group: Due to -M/-H of groups electron density at ortho and para position is less but more at meta position so electrophile attack on meta position. So, groups

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which direct electrophile on meta position are called as meta directing groups.

These groups decrease electron density in benzene ring and decrease reactivity of benzene ring so are called as deactivating group.

These groups are:





More e^- density at meta position

- (3) Halogens are o/p directing group due to +M effect but are deactivating group due to -I > +M.
- (4) M and H effect does not depend on distance while I–effect depends on distance in given example
- (5) M-effect at meta position is considered zero.



no effect at meta position

Similarly:



no effect at meta position

(i) Halogenations:



Chemistry



Note: CH₃ group in toluene is o/p directing and activating group.

(ii) Nitration:



Formation of \mathbf{E}





(iii) Sul phonation:







Chemistry



(iv) Friedel crafts reaction [FCR]: Alkylation or acylation of arenes in presence of Lewis acid [FeCl₃, A1Cl₃ or ZnCl₂ ...] is called as FCR.



Intermediate carbocation is formed in FCR so rearrangement is possible.





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(vi) Gattermann's Koch Reaction:

Class-XI



(vii) Gattermann's Aldehyde synthesis:



The important electrophiles used in the aromatic substitution are the following –

Electrophilic reaction	Source	Name of substitution
		Chladiation
CI ⁺ (Chloronium)	CI2 + AICI3 OF FECI3	Chlorination
Br+ (Bromonium)	Br ₂ + AlBr ₃ or FeBr ₃	Bromination
NO ₂ + (Nitronium)	$(conc. HNO_3 + H_2SO_4)$	Nitration
SO ₃	conc. H ₂ SO ₄ , fuming	Sul phonation
(Sul p her trioxide)	sulphuric acid	
R ⁺ (Alkyl carbonium)	$RX + AIX_3 (X = Cl \text{ or } Br)$	Friedel crafts
	$ROH + H^+$	(Alkylation)
$\mathbf{P} \stackrel{\oplus}{\mathbf{C}} - \mathbf{O}$	$RCOCI + AlCl_3$	Friedel crafts
K = C = 0		(Aculation)
(Acyl carbonium)		(Acylation)

(C) Nucleophilic substitution reaction (S_N): Due to electronegativity



Thus, the C-atom of the $\overset{\delta_+}{C} - \overset{\delta_-}{X}$ bond becomes centre of attack by a nucleophile ($\overset{\Theta}{Nu}$).

Chemistry

 X^{Θ} ion from R–X molecule is substituted by a Nu. i.e.S_N reaction are the most common reactions in R–X.

$$R-X + \stackrel{\Theta}{Nu} \longrightarrow R-Nu + X^{\Theta}$$

Two mechanisms are observed in S_N reaction:

(a) S_{N^1} mechanism

(b) S_{N^2} mechanism

Mechanism of S_{N^1} and S_{N^2} :

 S_{N^1} **Mechanism:** S_{N^1} stands for uni molecular nucleophilic substitution. The mechanism involves two steps. Consider the hydrolysis of tert. butyl bromide with aqueous NaOH.

Step 1: The alkyl halide ionizes to give a planar carbonium ion. The carbonium ion is planar because the central positively charged carbon is sp² hybridized.





Step-2: The nucleophile can attack the planar carbonium ion from either side to give the product.



- (i) Ionisation is the rate determining step because it is the slow step. In other words, the rate at which alcohol is formed depends upon the concentration of tertiary alkyl halide alone.
- \therefore Rate = K[R₃C-Br]

Chemistry

It is obvious that the reaction follows first order kinetics, therefore reaction is called S_{N^1} .

- (ii) The reactivity order for S_{N^1} reaction \propto stability of carbocations formed by halides.
- ∴ reactivity order of halides (S_{N1}) varies as follows:
 Benzyl halide > Allyl3^o halide > Allyl 2^o halide > Allyl 1^o halide > 3^o halide > 2^o halide > 1^o halide > methyl halide.
- (iii) Remember that in case alkyl halide is optically active, S_{N^1}

reactions lead to racemization.

 S_{N^2} mechanism: S_{N^2} stands for bimolecular nucleophilic substitution. In this type of nucleophilic substitution reaction, bond making and bond breaking process occur simultaneously.



Transition state

- (i) Reactivity of alkyl halides in S_{N^2} substitution is governed by steric factors. The bulkier the group, that less reactive it will be.
- (ii) Reactivity order of alkyl halide varies as follows:
 allyl halide > CH₃f > 1^o halide > 2^ohalide > 3^o halide
- (iii) The order of reactivity among 1° alkyl halides is: $CH_3X > C_2H_5X > C_3H_7X$ etc.

Remember that in case alkyl halide is optically active, S_{N^1} reactions lead to Walden inversion.

- (iv) For a given alkyl group the order of reactivity is- (for S_{N^1} and S_{N^2} both): **RI** > **RBr** > **RCI** > **RF**
- (v) In addition to substitution reaction alkyl halide also undergo elimination reactions to form alkene with the removal of a molecule of hydrogen halide (dehydrohalogenation). In dehydrohalogenation, hydrogen and halogen atoms are eliminated from two adjacent carbon atoms, the reaction also known as β -elimination it may proceed by E¹ or E² mechanism (analogous, to S_{N^1} and S_{N^2} mechanism).

The order of elimination reaction is: **3º halides > 2º halides > 1º** halides

(1) Nucleophilic substitution reaction (S_N) in alkyl halide:



(g) Reaction with KCN and AgCN:

 $\stackrel{\delta_{+}}{R} \xrightarrow{\delta_{-}} + \stackrel{+}{KCN} \xrightarrow{Alc.} R \xrightarrow{-} C \equiv N + KX$ Ionic bond cyanide (major) $\stackrel{\delta^+}{R} - \stackrel{\delta^-}{X}$ $\frac{Alc.}{\Delta} \rightarrow R - N \equiv C + Ag - X$ + Ag-CN covalent bond isocyanide (major) Reaction with KNO₂ and AgNO₂: (h) $\overset{\delta_{+}}{R} - \overset{\delta_{-}}{X}$ $\dot{K} O = N = O$ $Alc. \rightarrow$ + R - O - N = O + KXIonic bond (Alkyl nitrites) (major) $R - N \langle O + Ag - X \rangle$ $\overset{\delta_{+}}{R} \xrightarrow{\delta_{-}} X + Ag \longrightarrow \overset{O}{-} \overset{N=O}{\longrightarrow} \xrightarrow{Alc.} \Delta$ covalent bond Nitroalkane (major)



(k) Reaction with
$$CH \equiv CNa$$
:
 $R \rightarrow X + CH \equiv CNa \xrightarrow{\Delta} R \rightarrow C \equiv CH + NaX$
If $CH_3 \rightarrow \stackrel{i}{C} \stackrel{i}{-} X + CH \equiv \overline{C} \stackrel{i}{N}a \xrightarrow{\Delta} CH_3 - C = CH_2 + NaX + CH \equiv CH_3$
 $IH_1 \cap \stackrel{i}{C} \stackrel{i}{-} X + CH \equiv \overline{C} \stackrel{i}{N}a \xrightarrow{\Delta} CH_3 - C = CH_2 + NaX + CH \equiv CH_3$
(Elimination is more)

NSR reaction of alcohol: -

(a) Reaction with HX:

e.g.
$$R-CH_2-OH \xrightarrow{H-X} RCH_2-X$$

Mechanism:



(Unstable)

(Product)

In this reaction, intermediate carbocation is formed so rearrangement can take place. any. ZnCl₂ act as dehydrating agent and absorbs H₂O from the reaction so good yield of halide is obtained.

Also, it generates H⁺ from HCI.

 $HCl + ZnCl_2 \longrightarrow ZnCl_3^{\Theta} + H^{\oplus}$

Reactivity order for alcohol:

[Reactivity \proptotic stability of intermediate carbocation], so reactivity order:

Tart. ale. > Sec. ale. > Pri. alc.

Reactivity order of H–X is: **HI** > **HBr** > **HCl** HI is maximum reactive so it reacts readily with 1°, 2° and 3° alcohols.

$$R-OH + HI \longrightarrow R-I + HP$$

HCl and also 1° alcohol are less reactive so ZnCl₂ or some amount of H₂SO₄ is needed to increase the reactivity.

 $CH_3-CH_2-OH + HCl \xrightarrow{ZnCl_2} CH_3-CH_2-Cl$

At normal condition:

e.g.

 $CH_3-CH_2-OH + HCl \longrightarrow \times (no reaction)$

Note: [HCI (conc) + ZnCl_{2(anhydrous)} is called as **lucas reagent**, alcohol gives turbidity with lucas reagent.

Chemistry

Reactivity towards lucas reagent (difference in 1° , 2° and 3° alcohol).

	1° alcohol	2° alcohol	3° alcohol
Time to	in 30 min.	in 5 min.	in 2-3 second
give turbidity	on heating		

(b) Reaction with phosphorus halides: -

 $R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCI$ $3R-OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$

PBr₃ and PI₃ are less stable, thus for bromides and Iodides, $(P + Br_2)$ Or $(P + I_2)$ mixture is used.

(c) Reaction with thionyl chloride-(Drazen's procedure): -

 $R-OH + SOCl_2 \xrightarrow{Pyridine} R-Cl + SO_2 + HCI$

One mole One mole

NSR reaction in ether: -

Reaction with HX: Reactivity of HX [HI > HBr > HCl]

- (A) Reaction with cold cone. HX: Ethers forms abandum. salt with cold and cone. HCI (less reactive) Cold cone. HI and HBr (more reactive) break C–O bond.
- (B) Reaction with cone. HI or cone. HBr:

 $CH_{3}CH_{2}-O-CH_{3} \xrightarrow{hot and conc.HI} CH_{3}CH_{2}-I + CH_{3}-I$

Illustrations

Illustrations 3.



Solution. Mechanism



Chemistry

If oxonium ion gives more stable carbocation $[Ph \overset{\oplus}{C}H_2, CH_2=CH-\overset{\oplus}{C}H_2, (CH_3)_3 \overset{\oplus}{C}]$ then SN¹ reaction occurs.

If oxonium ion gives less stable carbocation [$\stackrel{\oplus}{P}h$, CH₂= $\stackrel{\oplus}{C}H_2$, CH₃ $\stackrel{\oplus}{C}H_2$, (CH₃)₂ $\stackrel{\oplus}{C}H$] then SN² reaction occurs, and X $\stackrel{\ominus}{\ominus}$ attacks at less hindered carbon

Illustration 4. $CH_3CH_2-O-CH_2Ph \xrightarrow{Cold conc.}_{HI} CH_3CH_2-OH + PhCH_2-I, write mechanism of given reaction.$

Solution Mechanism:

$$CH_{3}CH_{2}\overset{\Box}{\Omega}CH_{2}Ph \xrightarrow{H^{\oplus}} CH_{3}CH_{2} \xrightarrow{\Phi} CH_{2}Ph \xrightarrow{H^{\oplus}} CH_{2}Ph \xrightarrow{H^{\oplus}} H$$

$$CH_{3}CH_{2}OH + Ph\overset{\oplus}{C}H_{2} \xrightarrow{I^{\Theta}} PhCH_{2}I + CH_{3}CH_{2}-OH \qquad (S_{N}1)$$

Illustration 5. $CH_3CH_2-O-CH_3 \xrightarrow{conc.andcoldHI} ?$ Solution.



Oxonium ion gives less stable carbocation $SN^2 \mbox{ reaction } I^\Theta \mbox{ attacks at less hindered carbon}.$

Illustration 6. CH_3 - CH_2 -O- $Ph \xrightarrow[HBr]{cold and conc.}$?

Solution. Mechanism:

$$CH_{3}-CH_{2}-\overset{\bullet}{O}-Ph-\overset{H^{+}}{\xrightarrow{H^{+}}} CH_{3}-\overset{\bullet}{CH_{2}}\overset{\bullet}{\xrightarrow{\Theta}}-Ph-\overset{Br}{\xrightarrow{Br}} CH_{3}CH_{2}Br+PhOH$$

Note: If excess of HI/ \triangle is used then two moles of alkyl halides are formed. CH₃CH₂-O-CH₂Ph $\xrightarrow{\text{HI}}_{\Delta}$ CH₃CH₂OH + PhCH₂I $\xrightarrow{\text{HI}}_{\Delta}$ CH₃CH₂-I + PhCH₂-I

Illustration 7. $C_2H_5-O-C_2H_5 \xrightarrow{hotandconc.HBr}$? +? Solution. $C_2H_5-Br + C_2H_5-Br$ Aromatic nucleophilic substitution:

NSR reaction in halobenzene: -

Class-XI



Presence of deactivating group at ortho and para position makes the nucleophilic substitution easier.

Reactivity Order: (Towards nucleophilic substitution)



Illustrations Which of the following undergoes Hydrolysis most easily:



Solution.If there is more e- withdrawing groups then there will be more
nucleophilic substitution reaction.Ans.(4)IllustrationThe product in the following reaction is:
 $Ph-Cl + Fe/Br_2 \longrightarrow Product$

(1) o- bromo-chloro benzene

	(2) p- bromo-chloro benzene
	(3) (1) and (2) both
	(4) 2, 4, 6-tribromo chloro benzene
Solution.	Since –Cl group is deactivating and o/p directing group so o–
	and p– products are formed.
Ans.	(3)

NSR in Acid derivatives:

Example: Hydrolysis of acid derivatives:



Here Z is a good leaving group

3. ELIMINATION REAC TIONS: These reactions are involving elimination of small molecule from the substrate



α-Elimination (1, 1-Elimination): Removal of H and X from one C-atom Example: CHCl₃ $\xrightarrow{\text{KOH}}$: CCl₂ (dichloro carbine) Mechanism:



Class-XI

α, **β** Elimination (b-elimination): Removal of H and X from adjacent



(a) Unimolecular elimination (E₁): -CH₃-CH₂-OH $\xrightarrow{95\%H_2SO_4}{443^{\circ}K}$ CH₂=CH₂

Mechanism of Reaction: The acidic dehydration of alcohol proceeds through the formation of a carbocation intermediate and is explained as follows:

Step I: Alcohol being a Lewis base accepts a proton (H⁺) from the acid in a reversible step as follows:

$$CH_3 - CH_2 - \ddot{O} - H + \ddot{H} \iff CH_3 - CH_2 - \ddot{O} - H$$

Ethanol (From acid) Protonated ethanol **Step II:** Due to presence of positive charge on electronegative oxygen, its electron accepting tendency increases. As a result, C–O bond becomes weak and cleaves as follows:



Ethyl carbocation

This is a slow and is regarded as **rate determining step in E1 reaction**. **Step III:** base removes $H\alpha$ (proton) form carbocation and changes it into ethene in a fast step as follows:

$$H - CH_2 - \overset{\oplus}{C}H_2 \xrightarrow{Base}{fast} CH_2 = CH_2$$

Ethene

Saytzeff rule: When two possible alkenes are obtained by the elimination reaction then that alkene containing maximum number of alkyl group on double bonded C-atoms is called Saytzeff product and formed as major product.

Chemistry

Note: The alkene having a smaller number of alkyl groups on double bonded C-atoms is called Hofmann's product.

Example:

(i)
$$CH_{3}-CH_{2}-CH_{-}CH_{3} \xrightarrow{H_{2}SO_{4}} CH_{3}-CH=CH-CH_{3}+CH_{3}-CH_{2}-CH=CH_{2}$$

2-butanol main product 1-butene
2-butene 80% 20%
(Saytzeff's product) (Hoffmann's product)
(ii) $CH_{3}-CH_{2}-CH_{2}-CH_{2}-OH \xrightarrow{-H_{2}SO_{4}}{\Delta} CH_{3}-CH=CH-CH_{3} + CH_{3}CH_{2}CH=CH_{2}$
1-butanol 2-butene80% 1-butene 20%
Main product

Mechanism: Acid catalyzed dehydration of alkanols proceeds via the formation of more stable carbonium ion.



Primary carbonium ion

Chemistry



Reactivity order of acidic dehydration of alcohols is $3^{\circ} > 2^{\circ} > 1^{\circ}$ R–OH

- \blacktriangleright Rate of reaction \propto [substrate]
- Molecularity of reaction = 1 (So reaction is called as E₁)
- In reaction intermediate carbocation is formed, so carbocation rearrangement is possible.

(b) Bimolecular elimination (E₂): Example:

 (i) Dehydrohalogenation of halides by alcoholic KOH/NaNH₂: CH₃-CH₂-Cl + KOH_(alc) → CH₂=CH₂ + KCl + H₂O Mechanism:



- Rate of reaction a [substrate] [base]
- Order of reaction = 2 (So reaction is E₂)
 In E₂ reaction intermediate (carbocation) is not formed. So, there will be no carbocation rearrangement.

Class-XI





(ii) Pyrolysis of tetra alkyl ammonium ion:



Class-XI

Ex.
$$CH_3 \xrightarrow{H_3} \beta \xrightarrow{H_2} CH_2 \xrightarrow{-OH} CH_2 = CH - CH_3$$
 (minor)
 $H_2 \xrightarrow{H_2} CH_2 \xrightarrow{-OH} CH_2 \xrightarrow{-OH} CH_2 = CH_2$ (major)

Note: Hoffmann's product is formed as major product. Competition between substitution and elimination reactions

Reactivity order of alkyl halides:

> SN^2/E^2 is favored by high conc. of good nucleophile or strong base. (CH₃O^{Θ}, HO^{Θ})

Rate of Reaction \propto (Substrate) (Reagent)

- SN¹/E¹ is favored by low conc. of poor nucleophile or weak base (CH₃OH, H₂O)
- If an alkyl halide, undergoes SN²/SN¹ then SN² reaction will be favored by high conc. of good nucleophile (negatively charged) in presence of polar aprotic solvent where as SN¹-reaction is favored by low conc. of poor nucleophile (neutral) in presence of polar protic solvent.
- Polar protic solvent: H₂O, CH₃OH, HCOOH
- ▶ Polar aprotic solvent: DMSO, CH₃CN, C₂H₅-O-C₂H₅, DMF
- **4. ISOMERIZATION REACTIONS:** This reaction involves the interconversion of one isomer into another isomer. For example:

(i)
$$CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{AICI_3} CH_3 - CH$$

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Chemistry

(ii)
$$CH_3 - CH_2 - CH = CH_2 \xrightarrow{Al_2(SO_4)_3} CH_3 - C = CH_2 + CH_3 - CH = CH - CH_3$$

 $\downarrow CH_3$

(iii)
$$CH_3 - CH_2 - C \equiv CH \xrightarrow{Alc.KOH} CH_3 - C \equiv C - CH_3$$

NaNH₂

REACTION AT A GLANCE:

S. N	Class of compounds	Types of reactions
(i)	Alkane	Free radical substitution
(ii)	Alkene, alkyne	Electrophilic addition
(iii)	Alkyl halide	Nucleophilic substitution
(iv)	Aldehyde, ketone	Nucleophilic addition
(v)	Acid and their derivatives	Nucleophilic substitution
(vi)	Aromatic compounds	Electrophilic substitution