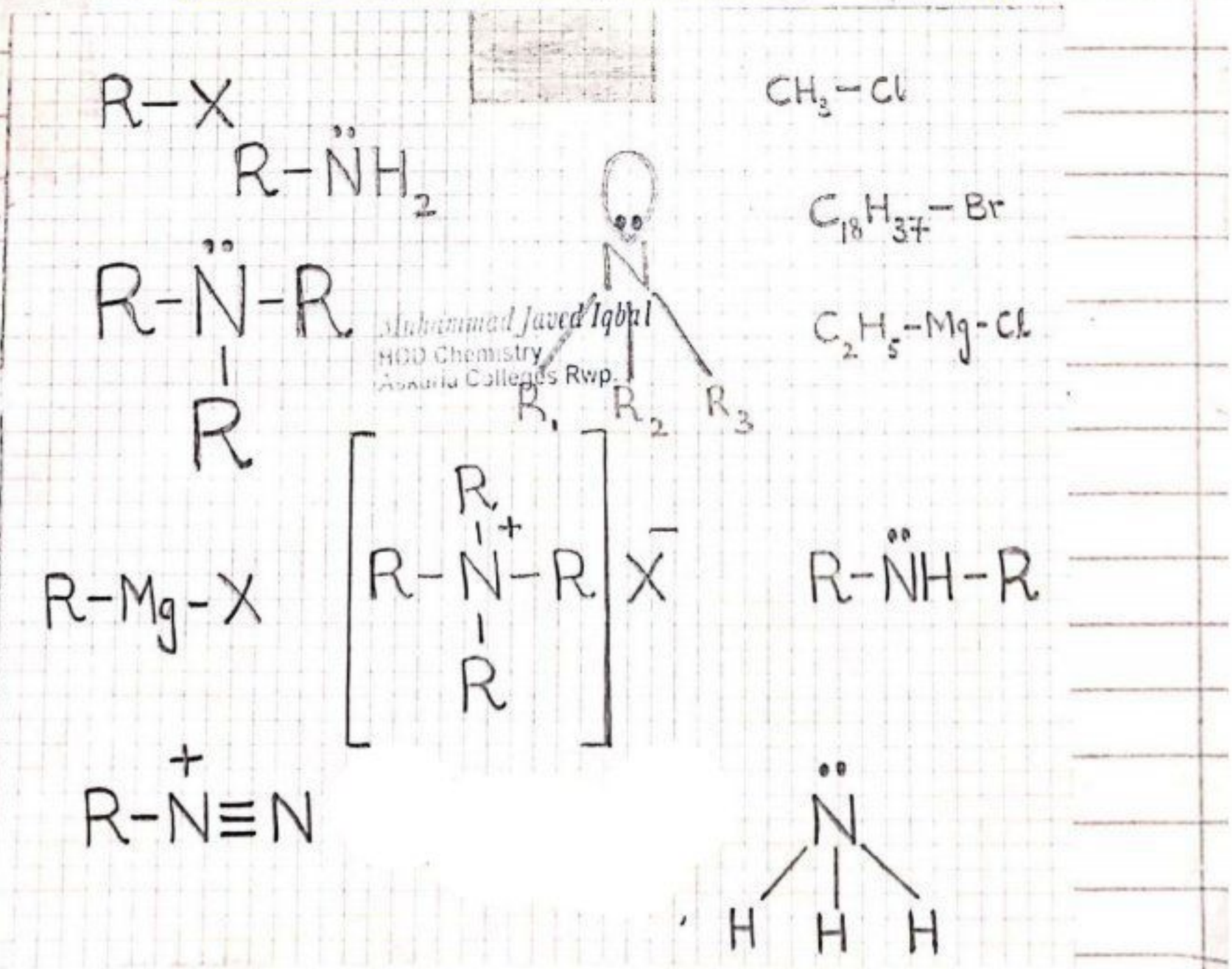
Chapter NO. 17
Alkyl halides & Amines

A+ - PRODUCTIONS F.Sc Part II

Chemistry Notes

Ch. 17

Alkyl Halides And Amines



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Alkyl Halides :- (Halo alkanes)

Alkyl halides are the compounds, formed by the replacement of hydrogen atom by halogen atom in Alkanes.

They are denoted by (R-X) where (-R) is alkyl group and (X) is Halogen.

-R (-CH_3 , -C_2H_5 , -C_3H_7 .....)

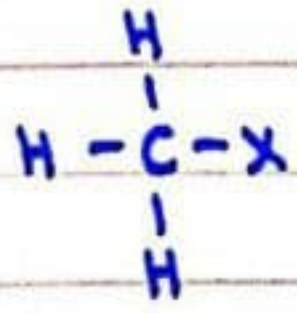
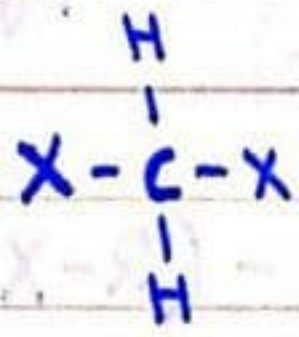
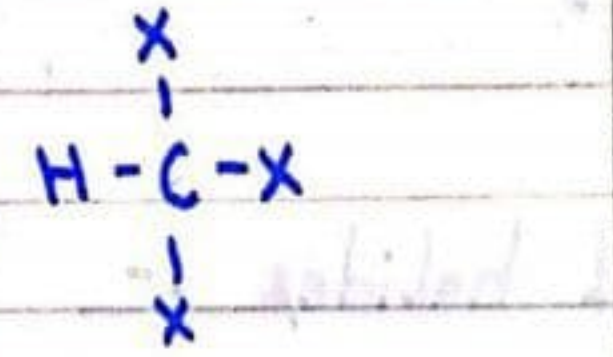
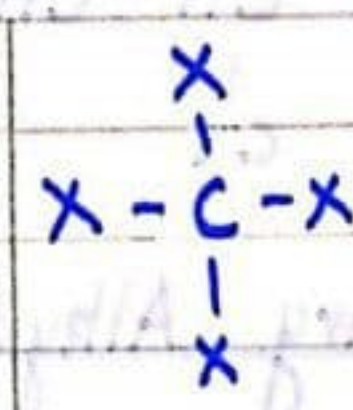
-X (-F, -Cl , -Br , -I)

General formula of alkyl group (-R) is C_nH_{2n+1}

Alkyl halides are the derivatives of Alkanes.

Alkyl halides are also called as Halo alkanes. They may be mono, di, tri, or poly halo alkanes depending upon the no. of Halogen atoms.

for example:-

			
Mono	Di	Tri	tetra

$\Longrightarrow$ $CH_3-CH_2-CH_2-Cl$ Propyl chloride (C.N).
or Chloro propane (IUPAC).

$\Longrightarrow$ CH_3-CH_2-Br Ethyl Bromide (C.N).
or Bromo Ethane (IUPAC).

Types :-

There are 3 types of Alkyl halides

1- Primary Alkyl halides :- 1° - (R-X)

The Alkyl halides in which Halogen Atom is attached with Primary Carbon (carbon attached directly with one other Carbon atom) is called Primary Alkyl Halides

$CH_2(Br) - CH_2 - CH_3$ Pri - Propyl Bromide.

(1 - Bromo Propane)

2- Secondary Alkyl halides :- 2° - (R-X)

The Alkyl halides in which Halogen atom is attached with the Secondary Carbon (Carbon atom directly attached with two other Carbon atoms) are called Secondary Alkyl halides.

$CH_3 - CH(Cl) - CH_3$ Sec - Propyl chloride

(2 - chloro Propane)

3- Tertiary Alkyl halides :- 3° - (R-X)

The Alkyl halides in which Halogen atom is attached with the Tertiary Carbon (Carbon atom directly attached with other three Carbon atoms) are Called Tertiary Alkyl halides.

$CH_3 - C(CH_3)(CH_3) - Br$ Ter - Butyl Bromide

(2 - Methyl - 2 - Bromo Propane).

Methods of Preparation.

Best Methods

① From Alcohols:-

a- Reaction of Alcohol with Halogen Acid:-

When Alcohol is reacted with Halogen Acid in the presence of anhydrous $ZnCl_2$ as a Catalyst, Alkyl halide is obtained.

$$R-OH + HX \xrightarrow[\Delta]{ZnCl_2} R-X + H_2O$$

$$CH_3-OH + HCl \xrightarrow[\Delta]{ZnCl_2} CH_3-Cl + H_2O$$

b- Reaction of Alcohol with thionyl chloride:- (chlorinating agent) $(SOCl_2)$

When Alcohol is reacted with $(SOCl_2)$ in the presence of Pyridine as a Solvent, Alkyl halide is obtained. In this Method, By-Product is obtained in Gaseous form.

$$CH_3-CH_2-OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3-CH_2-Cl + HCl_{(g)} + SO_{2(g)}$$

c- Reaction of Alcohol with Phosphorus halide (PBr_3, PX_5):- (Brominating agent)

$$3CH_3-CH_2-OH + PBr_3 \longrightarrow 3CH_3-CH_2-Br + H_3PO_3$$

$$CH_3-CH_2-OH + PBr_5 \longrightarrow CH_3-CH_2-Br + HBr + POBr_3$$

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Not a Best Method

(2) Halogenation of Alkane :-

$$C_2H_6 + Cl_2 \xrightarrow{h\nu} C_2H_5Cl + HCl$$

(F) reacts Volantly, while (I) reacts slowly
So, they are not Used generally.

Nucleophilic substitution reactions.

Reactivity of Alkyl Halides

Reactivity of Alkyl Halides depends upon following factors

1- Bond Polarity of C-X bond
2- Bond Energy of C-X bond

1- Bond Polarity:-

Electronegativity of Halogens is greater than Carbon.
The Molecules of Alkyl Halides becomes polarized due to Electronegativity difference b/w [C] and [X].
Hence Carbon got partial positive and Halogens acquires partial negative charge.
This is Called bond polarity.

Reactivity $\propto$ Bond polarity.

Halogens become nucleophilic in character due to partial (-ive) charge.

Atoms	F	Cl	Br	I	C	H
E·N	4.0	3.0	2.8	2.5	2.5	2.1

In C-F ΔE·N= 1.5
In C-Cl ΔE·N= 0.5
In C-Br ΔE·N= 0.3

On the Basis of Bond Polarity, Reactivity Order of Alkyl Halides is,

R-F > R-Cl > R-Br > R-I

2- Bond Energy :-

Amount of Energy required to Break 1 mole of Bond is called Bond Energy.

$$\text{Reactivity} \propto \frac{1}{\text{Bond Energy}}$$

Lesser will be the bond Energy, Higher will be the reactivity and Vice Versa.
Experiments have shown that, the Bond Energy is the main factor which decides the reactivity, not the Polarity of Molecule.

Bond	R-F	R-Cl	R-Br	R-I
Bond Energy	467 KJ/mol	346 KJ/mol	290 KJ/mol	228 KJ/mol

Reactivity order is given by

R-I > R-Br > R-Cl > R-F

Imp. Concepts

1- Nucleophile (Nu^-) :-

Nucleophile is a specie, which is electron rich and has an unshared electrons available for bonding. It is basic in most cases. It may be neutral or negatively charged. It may be called as Base.

Negatively charged ($\bar{N}u$)	Neutral ($\bar{N}u$)
Examples, $\bar{O}H$, $C_2H_5\bar{O}$, $H\bar{S}$; $\bar{Br}$, $\bar{N}H_2$, $S\bar{C}N$ etc	Examples , $H_2\ddot{O}:$, $\ddot{N}H_3$ etc

2- Electrophile:- (E^+)

A substance which is Electron deficient is called Electrophile. It is Electron loving. It may be neutral or positively charged.

Denoted by (E^+).

Examples

NO_2^+ ; CH_3^+ are positively Charged Electrophiles	SO_3 , BF_3 , $AlCl_3$ are neutral Electrophiles.

3- Leaving Group:-($\bar{L}G$) or ($\bar{L}$)

Group which Departs from the molecule as a result of an attack by a nucleophide which must be stronger than that group, is called a Leaving group. It is also a nucleophile because it contains a negative charge.

Denoted by ($\bar{L}G$) or ($\bar{L}$)

Good Leaving Groups ($C\bar{l}$, $B\bar{r}$, $\bar{I}$, HSO_4^-)

Poor Leaving Groups (OH^- , $O\bar{R}$, NH_2^-)

($\bar{I}^-$) iodide is a good leaving group as well as a good Nucleophide.

Good ($\bar{L}G$) are those which favours Leaving more, whereas poor ($\bar{L}G$) acquires much Energy, Conditions to leave the molecule.

Here is a table classifying Some Common ($\bar{L}G$):-

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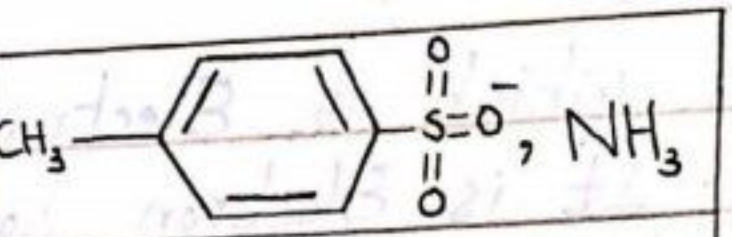
Excellent	 , NH_3
Very Good	I^- , $H_2\ddot{O}:$
Good	Br^-
Fair	Cl^-
Poor	F^-
Very Poor	$\bar{O}H$, NH_2^- , $\bar{O}R$

4 **Substrate:-** (S)

Alkyl halide molecules on which a nucleophile attacks, is called Substrate.

In General,

Any Molecule on which a Nucleophile or an Electrophile attacks in a Reaction Mechanism is Called a Substrate, denoted by (S).

e.g

Alcohols, Benzene, Ethers, Aldehydes etc.

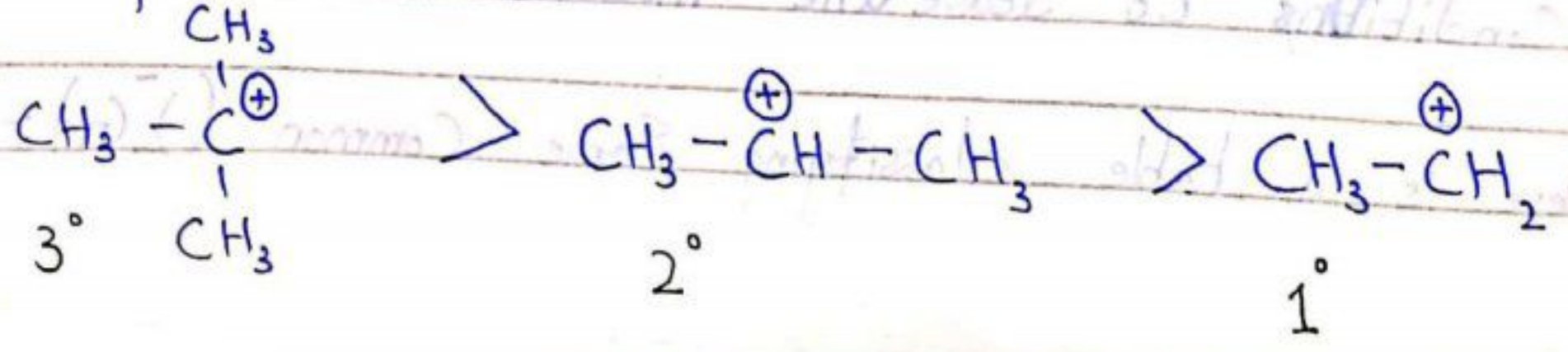
5- **(Carbocation or Carbonium ion) and its stability :-**

Positively charged Carbon ion (C^+) in an organic radical or a molecule is called Carbocation or Carbonium ion. They may be Primary (1°), Secondary (2°) and Tertiary (3°).

Stability order of (C^+) is given by :-

$3^\circ > 2^\circ > 1^\circ$

Example



$\overset{\oplus}{CH_3}$: [Methyl Carbonium ion] is the least stable Carbonium ion.

Its stability depends upon two aspects.

1- Hyper Conjugation
2- Inductive Effect.
3- Resondnce (If present).

Nucleophilic Substitution Reactions (SN reactions)

There are two types of (SN) reactions:-

1- SN_1
2- SN_2

Difference

SN_1 Mechanism	SN_2 Mechanism
1- SN_1 Stands for Substitution Nucleophilic Unimolecular.	1- SN_2 Stands for Substitution Nucleophilic Bimolecular.
2- Only One molecule take part in rate determining step, in these reactions.	2- Two Molecules take part in rate determining step, in these reactions.
3- These Reactions Undergo two step Mechanism.	3- These Reactions are Single step Mechanism.
4- Reaction takes place in the Presence of Polar Solvent.	4- Reaction takes place in the presence of non-polar Solvent.
5- Reaction can occur in strong as well as weak base.	5- Reaction can only Occur in strong base.

Stereo Chemical Evidence	Stereo Chemical Evidence
6 Each (C^+) is sp^2 hybridized and have one emply p-orbital. So, the Nucleophile can attack from both sides of Carbon with Equal ease. As a result, a product is formed Called racemic Mixture. It Contains 50% [Inversion of Configuration] and 50% [Retention of Configuration].	6 The Carbocation (C^+) in transition state is sp_2-hybridized and is planar. So, Nucleophile always attacks from opposite Side of the **leaving** Groups and therefore 100% inversion of Configuration will occur.
Kinetic Evidence	**Kinetic Evidence**
7 In SN_1, rate of reaction depends only on the Conc. of Substrate Rate $\propto$ [Substrate] Rate $= k[R-X]$ Order = 1	7 In SN_2, rate of reaction depends upon Conc. of Substrate and Nucleophile. Rate $= k[Nu][R-X]$ Order = 2
8 3°-[R-X] undergoes SN_1 and produces best yield due to stability of Carbocation.	8 1°-[R-X] Undergoes SN_2 due to less stearic repulsion.
9 2°-[R-X] undergoes (SN_1) in the presence of Polar Solvent.	9 2°-[R-X] Undergoes SN_2 in the presence of non-polar Solvent.
10 1°-[R-X] do not Undergo SN_1 due to unstability of (C^+)	10 3°-[R-X] do not undergo SN_2, due to bulky groups.

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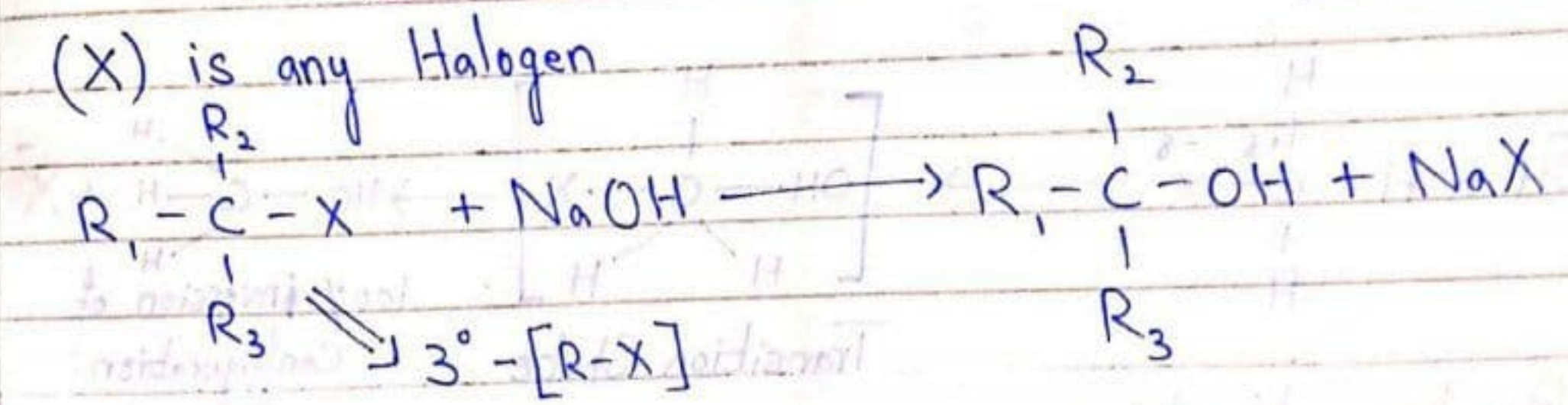
SN_1 Mechanism :-

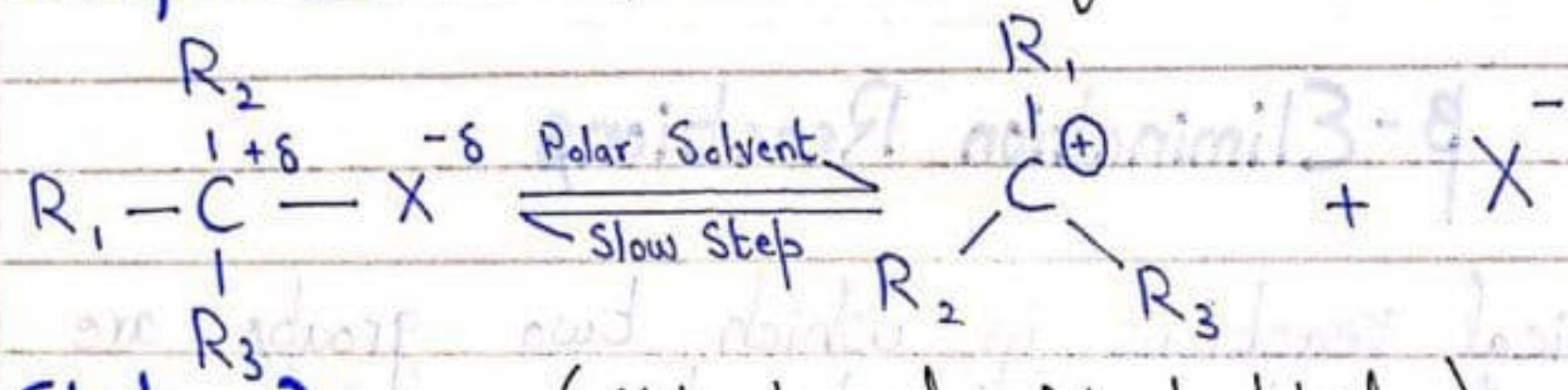
(X) is any Halogen



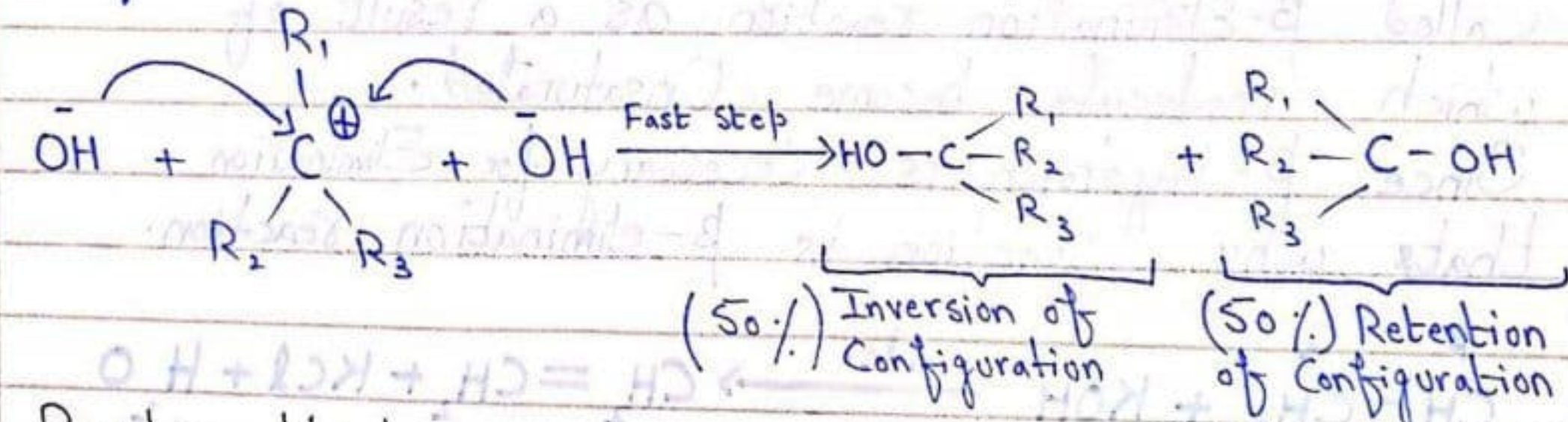
3° - [R-X]

Mechanism :-

Step - 1 (Formation of Carbocation)



Step - 2 (Attack of Nucleophile)



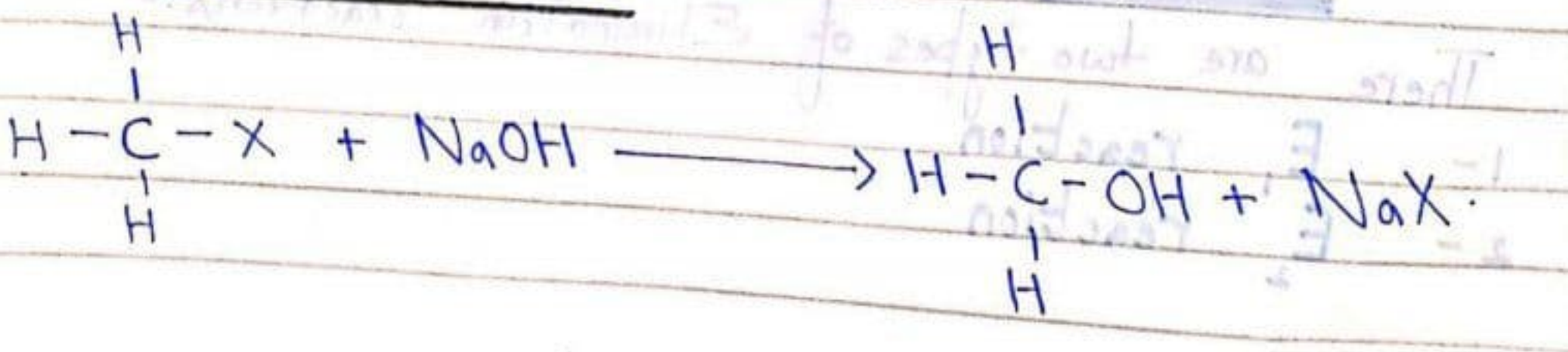
Reaction Kinetics :-

$$\text{Rate} \propto [\text{Substrate}]^1$$

$$\text{Rate} = k[\text{Substrate}]^1$$

Order = 1

SN_2 Reaction :-



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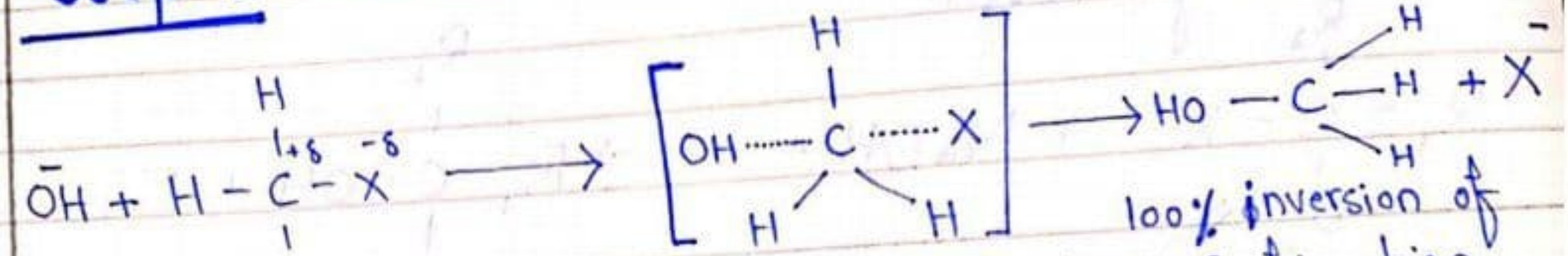
Mechanism:-

Step-1:-



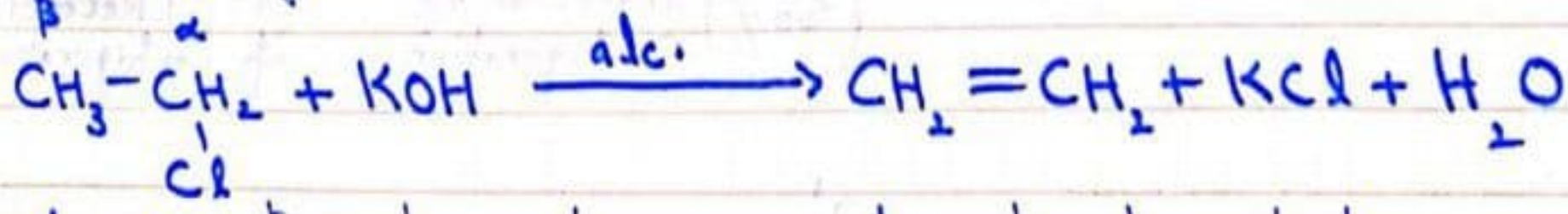
Reaction Kinetics:-

Rate = k [Nu] [Substrate]

Order = 1+1 = 2

β-Elimination Reactions

The Chemical reactions in which two groups are Eliminated from two adjacent atoms is Called β-Elimination reaction as a result of which molecule become Unsaturated.
Since β-Hydrogen is Necessary for Elimination that's why reaction is β-elimination reaction.



Note:- β-Hydrogen become acidic due to electron Withdrawing effect of Halogen atom.

Types

There are two types of Elimination reactions:-

1- E_1 reaction
2- E_2 reaction

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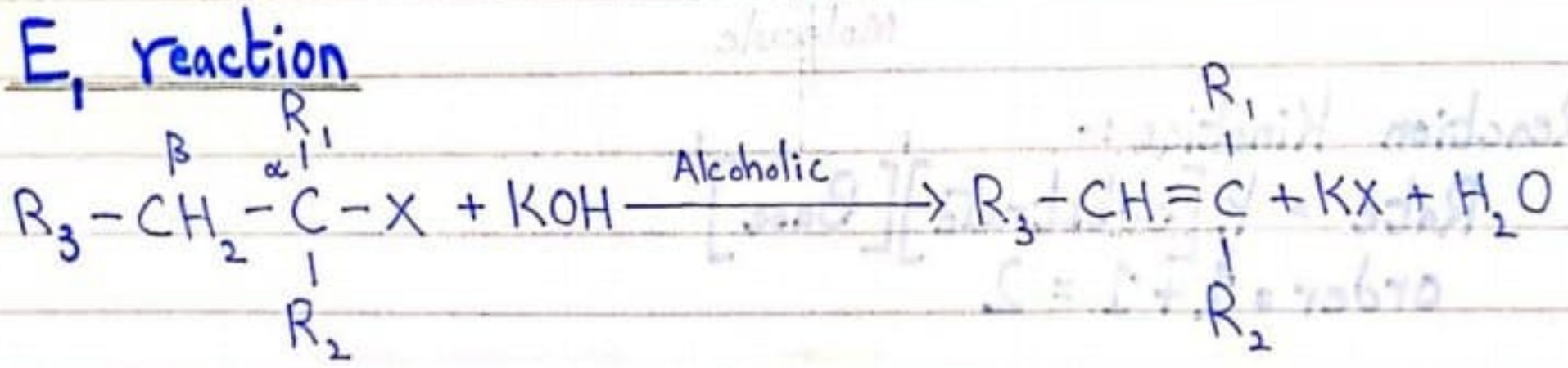
Difference

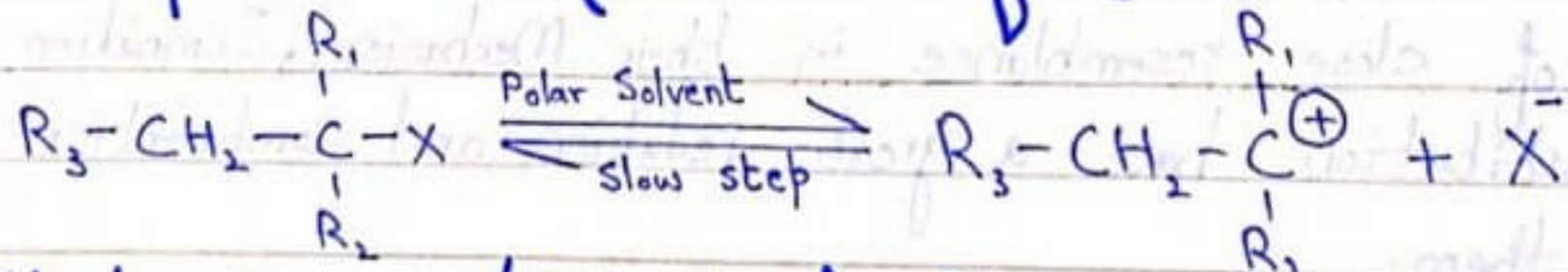
	E_1 reactions	E_2 reactions
1-	It is a Unimolecular two step Eliminating reaction.	It is a bimolecular One step Eliminating reaction.
2-	Reaction depends upon the Conc. of Substrate.	Reaction depends upon the Conc of Substrate and the Base.
3-	3°-(R-X) Undergoes E_1 Mechanism.	1°-(R-X) Undergoes E_2 Mechanism.
4-	In E_1, only one molecule take part in rate determining step.	In E_2, two molecules are undergoing a change in transition state.
5-	Order Kinetics = 1	Order Kinetics = 2

E_1 reaction

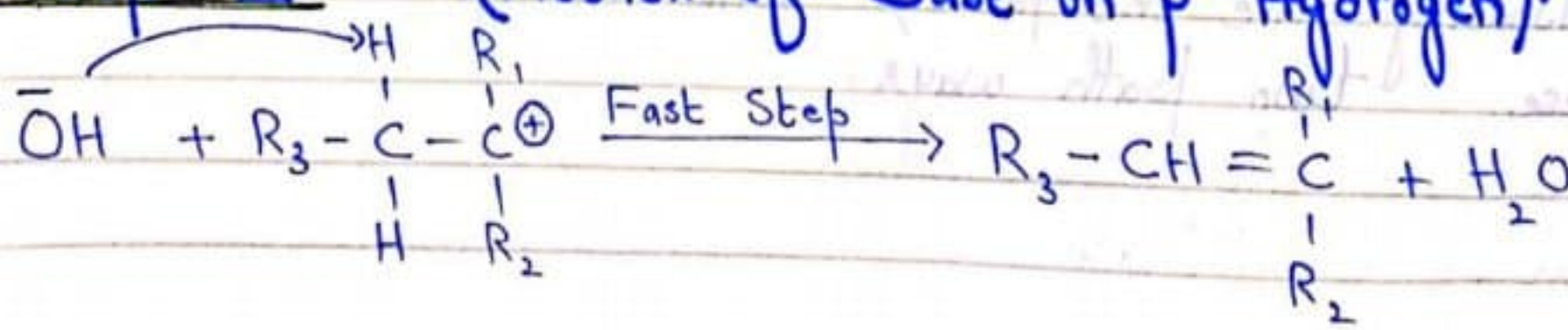


Mechanism:-

Step-1 (Formation of Carbonium ion).



Step-2 (Attach of Base on β-Hydrogen).



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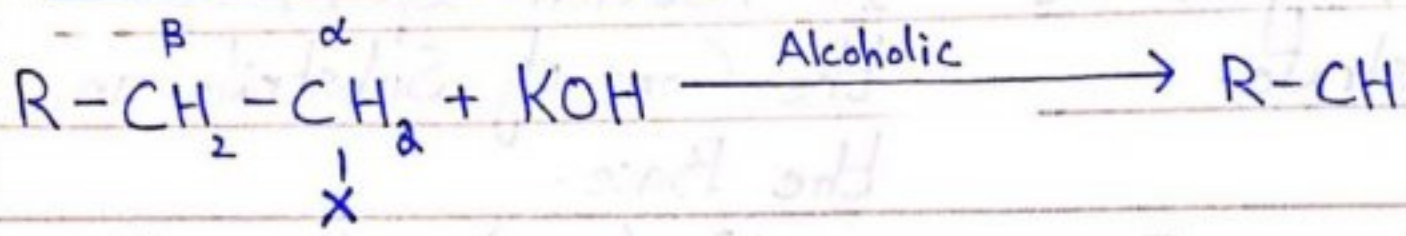
Reaction Kinetics

Rate = k[Substrate]

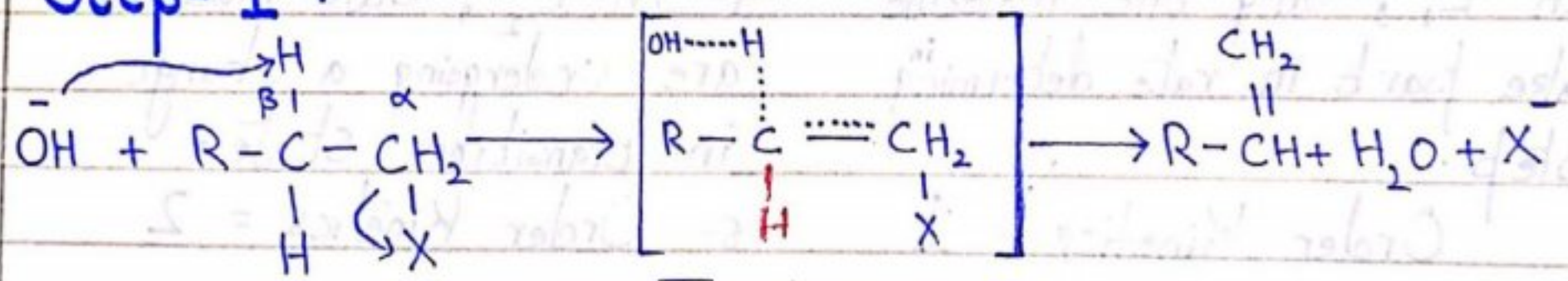
Order = 1

E_2 - reaction :-



Mechanism:-

Step-1 :-



Reaction Kinetics :-

Rate = k[Substrate]^1[Base]^1

order = 1+1 = 2

Substitution Versus Elimination

Because of close resemblance in their Mechanism, Elimination and Substitution have a great relation and competition between them.

Following are the factors which help to compare these two path ways.

1. Structure of Substrate
2. Nature of Base.

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3- Nature of Leaving Groups.
4. Nature of Solvent
5- Effect of Temperature

i Structure of Substrate

More Crowded Substrate favours Elimination and less crowded Substrate favours Substitution over Elimination because the nucleophile cannot approach to α-Carbon in more crowded Substrate for Substitution. e.g

$$CH_3-CH_2-Cl + C_2H_5ONa \xrightarrow{C_2H_5OH} \underset{\text{Substitution (88\%)}}{CH_3-CH_2-OC_2H_5} + \underset{\text{Elimination (12\%)}}{CH_2=CH_2} + NaCl$$

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-Br + C_2H_5ONa \longrightarrow \underset{\text{Substitution (39\%)}}{CH_3-\underset{\underset{CH_3}{/\quad\backslash}}{\overset{H}{C}}-OC_2H_5} + \underset{\text{Elimination (61\%)}}{CH_3-CH=CH_2} + NaBr$$

ii Nature of Base :-

E_2 is a dominant reaction when the electron pair donor is a strong base like $\bar{O}H$, $\bar{O}R$ etc.
SN_2 is a side reaction in this case.
When the nucleophile is a weak base like $\bar{X}$, RS- etc, Main reaction will be Substitution and E_2 will be the side reaction.

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$$CH_3-CH_2-\underset{Cl}{\underset{|}{}} + \bar{O}H \xrightarrow{E_2} CH_2=CH_2 + H_2O + \bar{X}(\bar{Cl})$$

(strong base) (Elimination) mainly

$$CH_3-CH_2-Cl + CH_3COO^- \xrightarrow{SN} CH_3-CH_2-OCOCH_3 + \bar{Cl}$$

(weak base) (Substitution) mainly

3 Nature of Leaving Group:-

In Unimolecular reactions, Leaving Group does not affect the mechanism of both Elimination and Substitution products because both are decided by Carbonium ion. However, in the biomolecular reactions the nature of product greatly depends upon the nature of leaving group.

e.g

$$C_{18}H_{37}-X + (CH_3)_3COK \xrightarrow[\text{Alcohol}]{(CH_3)_3COH} C_{16}H_{33}CH=CH_2 + \text{(Elimination)}$$

$$C_{18}H_{37}OC(CH_3)_3 \text{ (Substitution)}$$

If X = Br	E_2 = 85%	SN_2 = 15%
If X = OTS	E_2 = 1%	SN_2 = 99%

4 Nature of Solvent :-

Less polar Solvent favours Elimination more than Substitution like (alcoholic KOH). and More polar Solvent favours Substitution more than Elimination like (aqueous KOH).

$$CH_3-CH_2-\underset{Cl}{\underset{|}{}} + KOH \xrightarrow{\text{aqueous}} CH_3-CH_2-OH + KCl$$

$$\xrightarrow{\text{Alcoholic}} CH_2=CH_2 + H_2O + KCl$$

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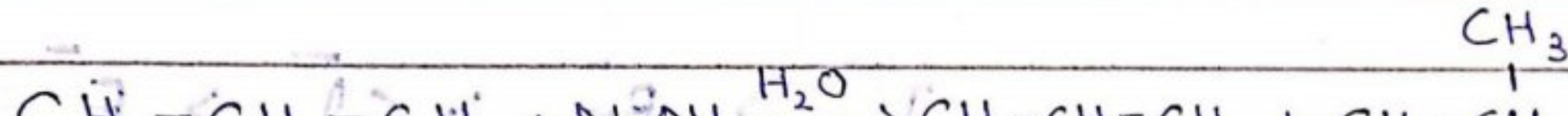
Effect of Temperature:-

Increase in Temperature will favour Elimination more than Substitution because Substitution reaction involve less re organization of bonds. E.g -



	(Bimolecular)	E_2	SN_2
At 45°C		53%	47%
At 100°C		64%	36%

Organo Metallic Compounds (Grignard's reagents)

R-Mg-X

Alkyl Magnesium halide is called Grignard reagent. It is a derivative of Alkyl halide and belongs to Organo Metallic Compound family. It was prepared by Victor Grignard in 1900. It has

Preparation of Grignard's Reagents:

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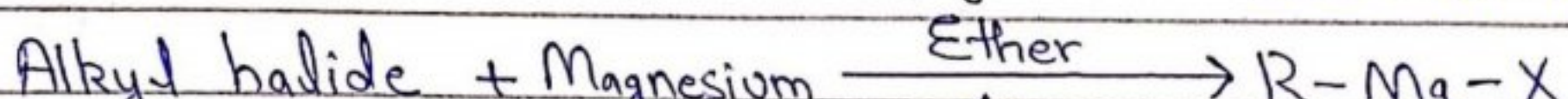

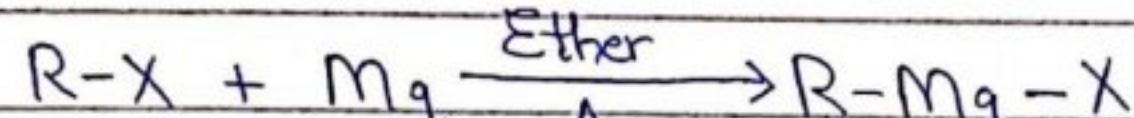

When (Mg) metal cut into small pieces is added to a Solution of an Alkyl halide in the presence of a dry Ether, and heated Grignard's reagent is produced.

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Reactivity :-

Grignard reagent is a very reactive Organic Compound due to a polarity of $C^{-\delta} - Mg^{+\delta}$ bond Its reactivity depends upon

1- Nature of Halogen (X)

Reactivity order of (X) in Grignard's reagent is Given by :-

$$I^- > Br^- > Cl^- > F^-$$

2- Nature of Alkyl Group :-

As, length of Alkyl Group increases, reactivity of Grignard's reagent decreases and Vice Versa!

Methyl Magnesium Iodide is the most reactive Compound of Grignard's Reagent :

$$CH_3-I + Mg \xrightarrow[\Delta]{Ether} CH_3-Mg-I$$

Note

They behave as nucleophile because they contain Nucleophilic Carbon due to more Electronegativity as compared to (Mg) atom.

$$\overset{-\delta \quad +\delta}{CH_3-Mg-Br} + \overset{+\delta \quad -\delta}{H-OH} \xrightarrow{Ether} CH_4 + Mg\begin{matrix}/\,OH \\ \backslash\,Br\end{matrix}$$

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Reactions of Grignard's Reagent

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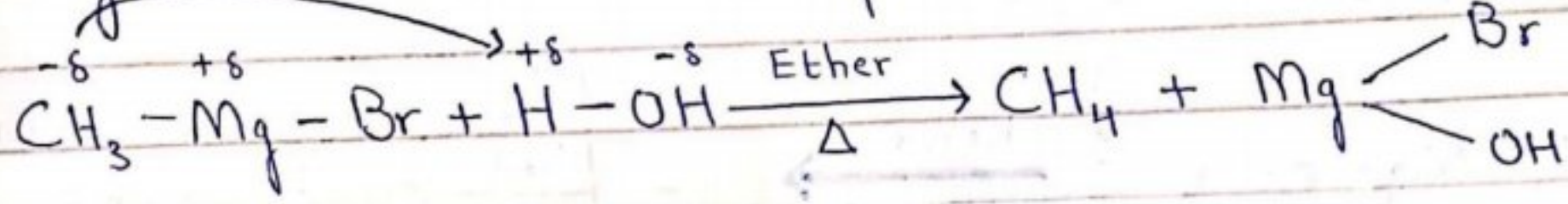
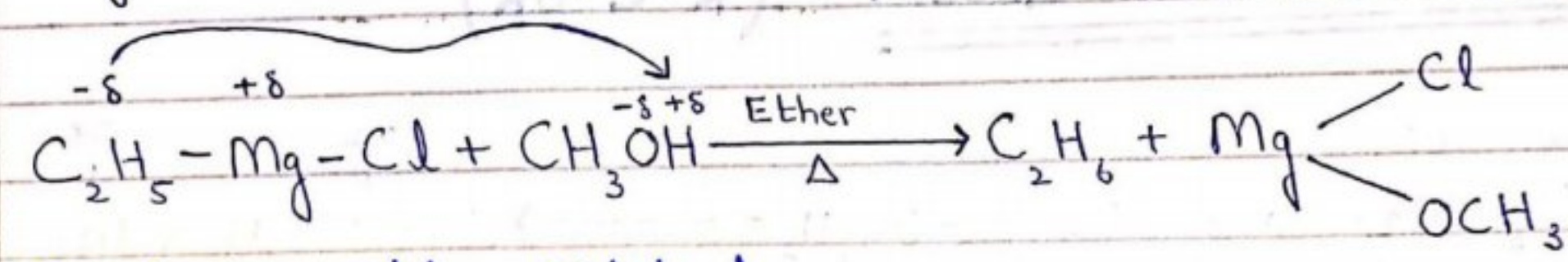
1- Reaction with Water (H_2O)

They react with Water to produce Alkanes . e.g



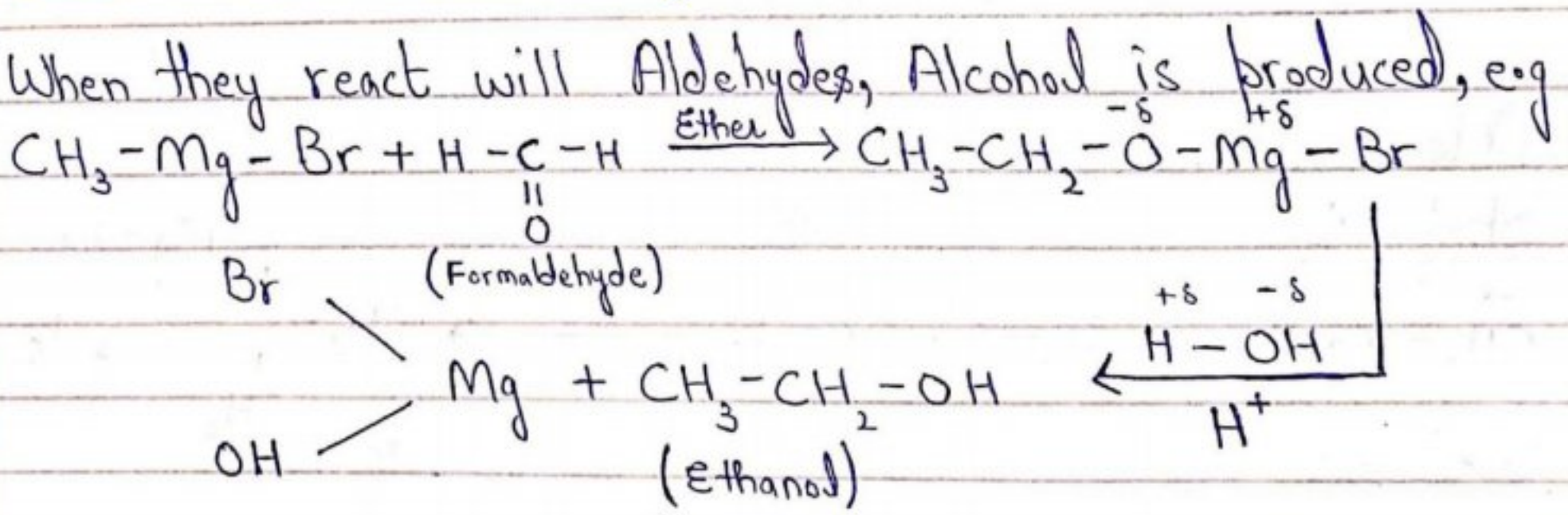
2 Reaction with Alcohol :-

They react with Alcohol to produce Alkanes e.g

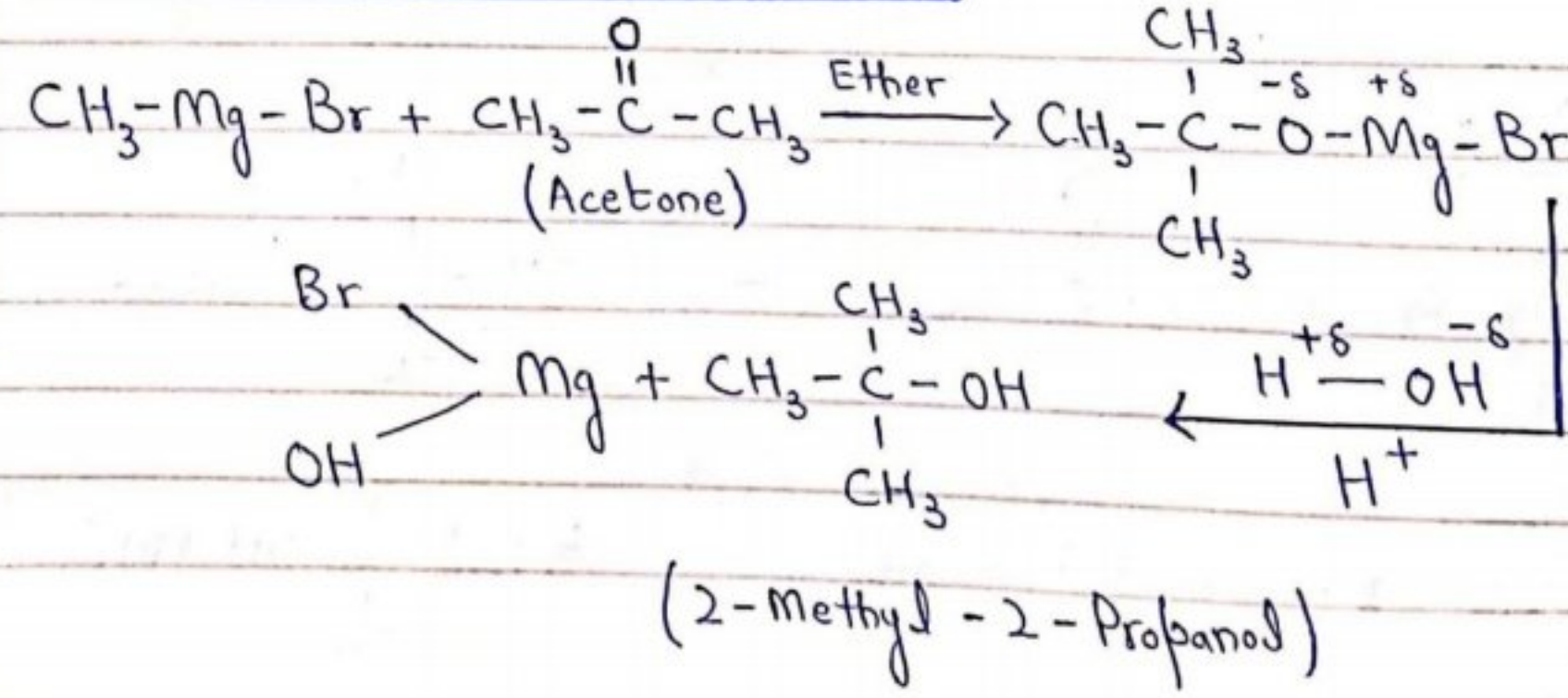


3 Reaction with Aldehydes :-

When they react will Aldehydes, Alcohol is produced, e.g



4 Reaction with Ketones :-



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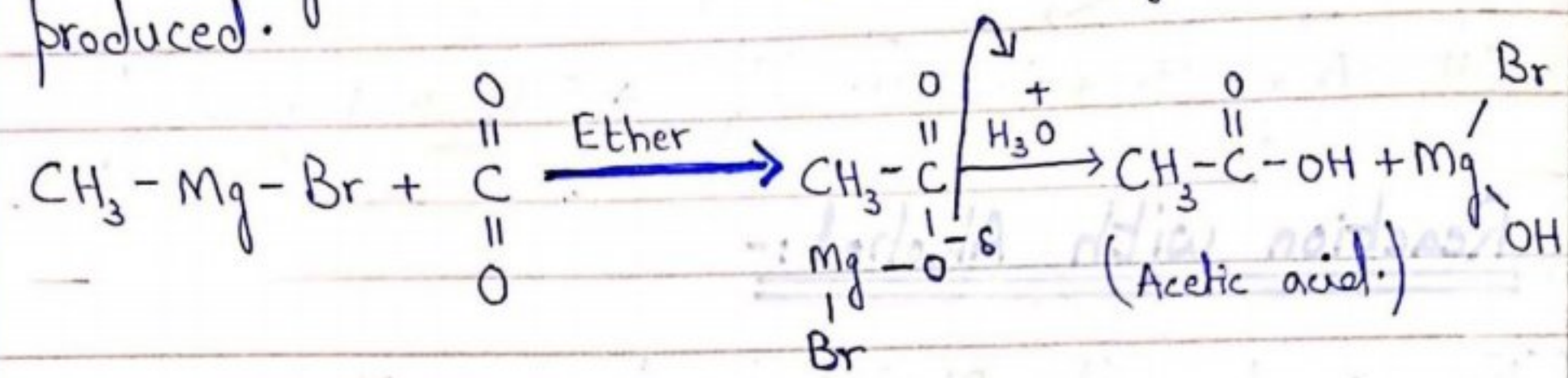
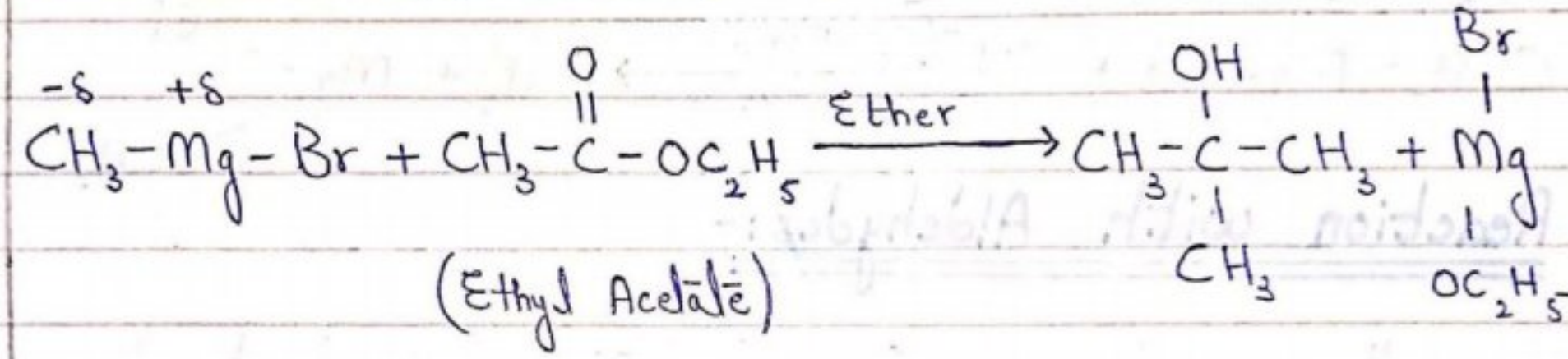
(20)

5 Reaction with CO_2

When they react with CO_2, Carboxylic Acid is produced.

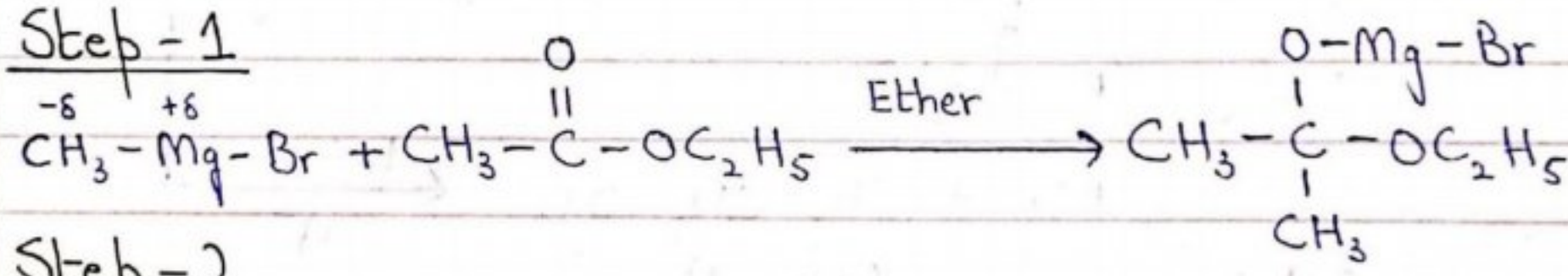


6 Reaction with Ester :- ($R-\overset{O}{\overset{\|}{C}}-OR$)

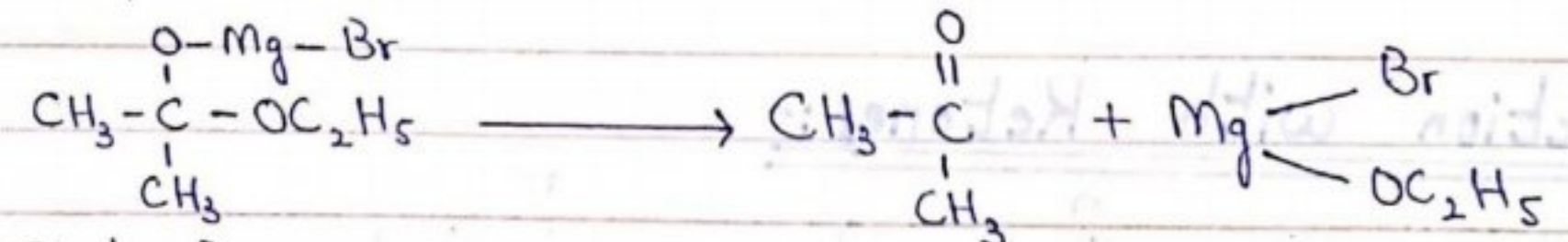


Mechanism :-

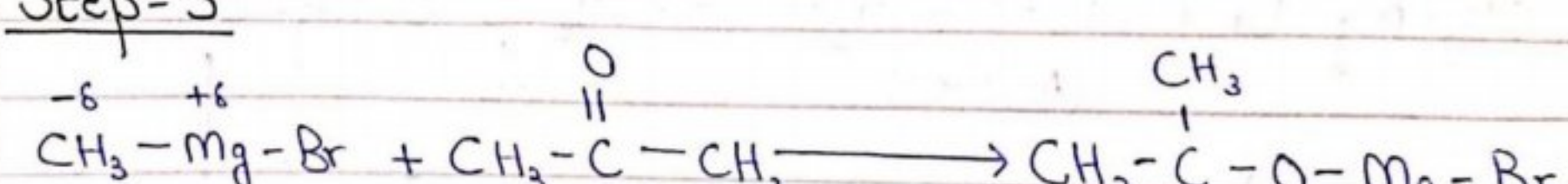
Step - 1



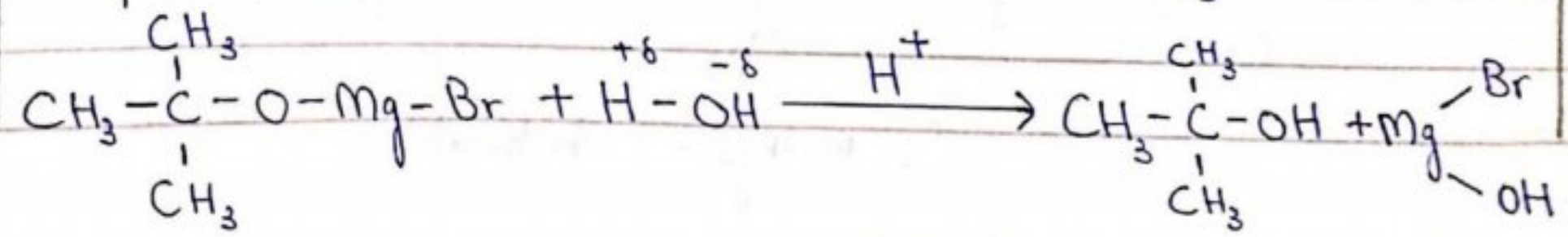
Step - 2



Step - 3



Step - 4



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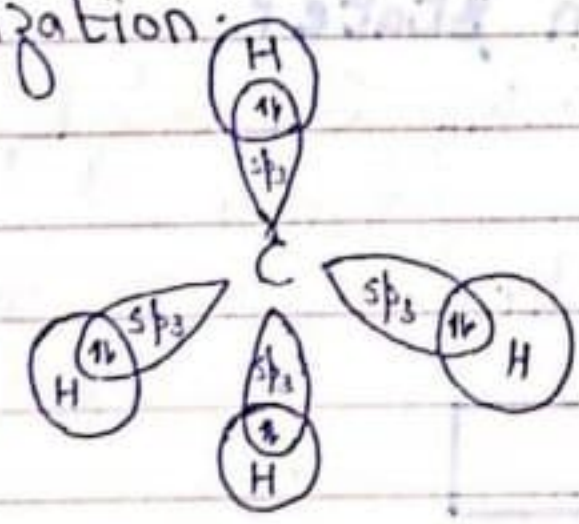
Quick Quiz - 1

(Q1 , Q2 , Q3 , Q4) concerned notes

Q5 What is sp_3 - hybridization?

One S - orbital and 3 (p - orbitals), when mix into each other and produce four hybrid orbitals. This process is called sp_3 - Hybridization.



sp_3 - Hybridization.

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(Q6, Q7 , Q8 , Q9) Concern Notes.

Q10 What is Inductive Effect?

An inductive effect is an electrostatic effect due to the polarization of σ-bonds within a molecule due to the great Electronegativity difference b/w bonded atoms like

C - Cl bond where $\Delta E.N = 0.5$ | O - H bond where $\Delta E.N = 1.4$

(Q11) See ch. 16

Q11 :- What is resonating effect?

Ans :- The Effect in aromatic Hydrocarbons which

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increases the stability of that compound by increasing the resonance contributing structures. Due to resonating effect, Benzene has resonance Energy of 152 KJ/mol.

Q12 What is racemization?

When nucleophile attacks the Substrate under SN_1 Mechanism and form racemic mixture which contains 50% Inversion and 50% relention of Configuration. This process is Called racemization.

Q13 What is transition state?

The State of a molecule during SN_2 and E_2 Mechanism at which the bonds are forming and breaking within the radical or molecule. This is an Unstable State which converts into other molecules (stable) within no time.

Quick Quiz - 2

(Q1 , Q4 , Q5) See notes

Q2 Define Protonation?

Ans. Protonation is defined as the addition of Proton which means Hydrogen. It is also known has hydrogenation (Addition of Hydrogen).

Q3 formula of Organo Lithium.

$$\overset{-\delta}{R}-\overset{+\delta}{Li}$$

e.g CH_3-Li , C_2H_5-Li etc.

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Amines

When one or more than one Hydrogen atom of Ammonia is replaced by Alkyl group, Compound formed are called Amine.

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Classification:-

They are classified in 3 groups:-

1 Primary Amine:-

When one Hydrogen atom of Ammonia is replaced by Alkyl groups, Primary Amine is formed.

$CH_3 - NH_2$ Methyl Amine.

2 Secondary Amine:-

When two H-atoms of NH_3 are replaced by Alkyl group, Secondary Amine is formed.

$CH_3 - NH - CH_2 - CH_3$
Ethyl Methyl Amine.

3. Tertiary Amine:-

When All H-atoms of NH_3 are replaced by Alkyl group, Tertiary Amine is formed.

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}} - CH_3$$

Trimethyl Amine.

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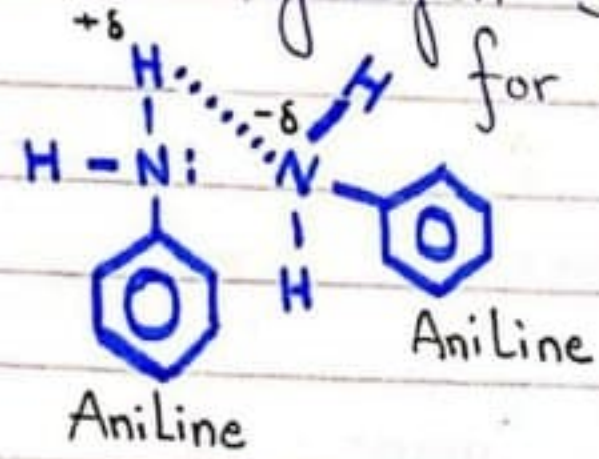
Physical properties of Amines:-

1- They have High Melting and Boiling Points as Compared to Alkanes.

2- They are highly Soluble in Polar Solvents like ($H_2\ddot{O}:$)

3- They show Hydrogen-Bonding with each other. for e.g



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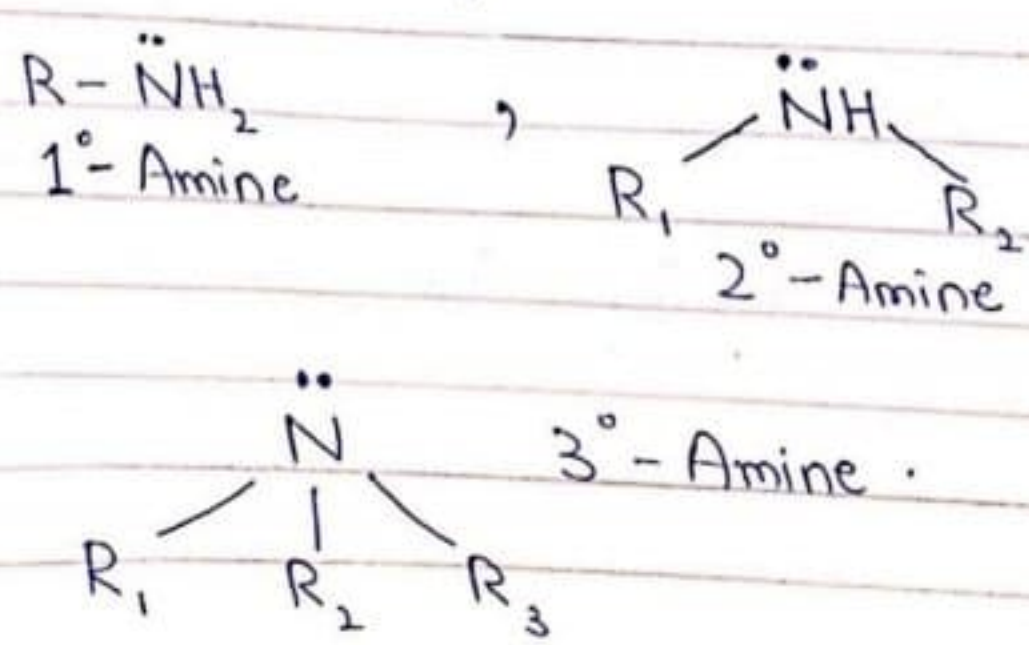
Structure:-

1- In Amines, Nitrogen is sp_3-Hybridized.

2- If All Alkyl groups in Amines are different, It becomes optically Active

3- The non-bonding Electron pair in Amines at Nitrogen makes it reactive and produces basic and nucleophilic characters in Amines.



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Basicity :- Basic chacter of amines depends upon following factors

i) Availability of lone pairs ∝ Stability of amines

ii) Stability of ammonium ion ∝ Stability of amines

Amines behaves as base in the presence of Acid and behaves as nucleophile in the presence of Electrophile.

Amines are more basic than Ether & Alcohol.

Basic character Order of Amines are

Secondary Amine > Primary- Amine > Tertiary - Amine

Preparation of Amines

Alkylation of Ammonia by Alkyl halide (Aminolysis)

or

Hoffmann's method fore Amine preparation

General Method

$$R-\boxed{X + H}-\ddot{N}H_2 \longrightarrow R-\ddot{N}H_2 + HX$$

Pri - Alkyl Amine

$$R-\ddot{N}H-\boxed{H + X}-R \longrightarrow R-\ddot{N}H-R + HX$$

Sec - Alkyl Amine

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$$R-\underset{\underset{H}{|}}{\ddot{N}}-R + X-R \longrightarrow R-\underset{\underset{R}{|}}{\ddot{N}}-R + HX$$

Ter - Alkyl Amine

$$R-\underset{\underset{R}{|}}{\ddot{N}}-R + {}^{\delta+}X-{}^{\delta-}R \longrightarrow \left[R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{\overset{\oplus}{N}}}-R\right] X^{-}$$

Quarternary Alkyl Ammonium halide (Salt)

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2- Reduction of Nitrogen Containing Functional Group :-

i- Reduction of Nitrile :-

Organic Compounds Containing Cyanide group ($-CN$) are Called Nitride.

They are reduced to Amine in the presence of H_2/Pd , $Al_2O_3 \cdot Rh$

E.g

$$R-C\equiv N + 2H_2 \xrightarrow[\Delta]{Pd} R-CH_2-NH_2$$

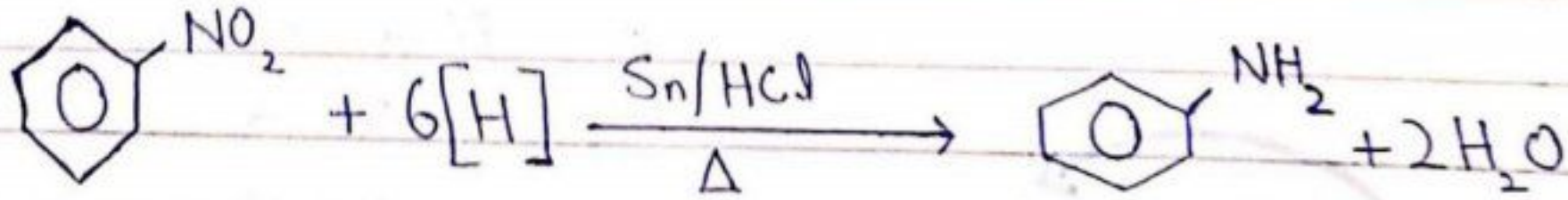
$$CH_3-C\equiv N + 2H_2 \xrightarrow[\Delta]{Pd} CH_3-CH_2-NH_2$$

ii- Reduction of Nitro Compounds :-

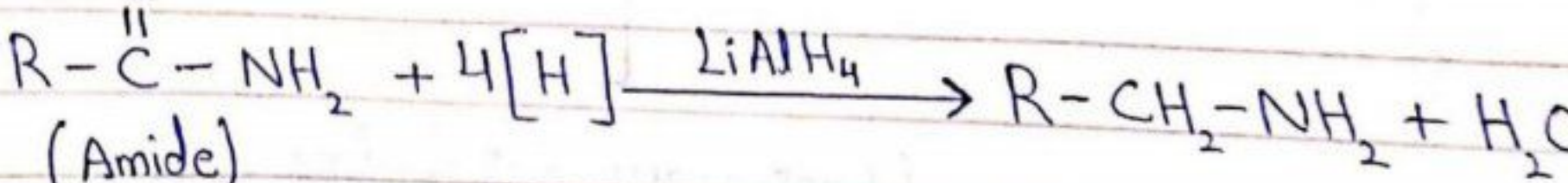
Nitro groups are reduced to Amine in the Presence of following reducing agents.

i- Sn/HCl
ii- Fe/H_2SO_4
iii- H_2/Pd

$$CH_3-NO_2 + 6[H] \xrightarrow[\Delta]{Sn/HCl} CH_3-NH_2 + 2H_2O$$



iii- Reduction of Amide :-



Reactivity:-

1- Amines are basic and nucleophiles because of non-bonding pair of electron on Nitrogen.
2- Amines are more basic than Ammonia.
3- Its reactivity also depends upon extent of Salvation, Hydrogen bonding, and Resonance Stabilization.

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Reaction of Amines

1- Reaction of Amine with Alkyl halide :-

$$CH_3-Cl + CH_3-NH_2 \longrightarrow CH_3-NH-CH_3 + HCl$$

$$CH_3-NH-CH_3 + CH_3-Cl \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle \ddot{}}{N}}-CH_3 + HCl$$

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle \ddot{}}{N}}-CH_3 + CH_3-Cl \longrightarrow \left[\begin{array}{c} CH_3 \\ | \\ CH_3-N^{\oplus}-CH_3 \\ | \\ CH_3 \end{array}\right] Cl^{\ominus}$$

Quarternary Methyl Ammonium Chloride
(Salt)

2- Reaction with Carbonyl Compounds :-

$$\diagdown C=O + H_2N-R \longrightarrow \diagdown C=N-R + H_2O$$

Imine

$$CH_3\diagdown \quad \diagup CH_3$$
$$C=O + H_2N-CH_3 \longrightarrow C=N-CH_3 + H_2O$$
$$H\diagup \quad \quad H$$

Imine
(schiff base)

therefore much more stable than its aliphatic Counterparts. Nevertheless, it decomposes readily above 10°C.

Quick Quiz - 3

(Q1, Q2, Q3) See Ch. 16

Q4:- Write the eq. for CH_4 preparation?

1- $CH_3-Mg-Br + H-OH \longrightarrow CH_4 + Mg\begin{matrix}Br\\OH\end{matrix}$

2- $CH_3OH + CH_3-Mg-Br \longrightarrow CH_4 + Mg\begin{matrix}Br\\OCH_3\end{matrix}$

3- $CH_3-Mg-Br + NH_3 \longrightarrow CH_4 + Mg\begin{matrix}Br\\NH_2\end{matrix}$

(Q5, Q6, Q7) See ch 16

(Q8) concern notes

Q9 Why halogen of Vinyl Chloride is inert?

Formula of Vinyl Chloride is

$[CH_2=CH-Cl]$

Though, the Electronegativity Difference b/w C-Cl bond creates polarity but due to the presence of π-bond in Vinyl chloride in addition with δ-bond b/w Carbon atoms, the Molecule become inert.

Exercise

MCQ's :-

i	c	vi	c	xi	a
ii	a	vii	b	xii	d
iii	d	viii	d	xiii	b
iv	a	ix	d	xiv	b
v	b	x	d	xv	a

Q2 Give brief Answers :-

(i-), (iii-), (iv), (v), (viii), (x), (vi), (vii)
Concern Notes.

ii- Why (R-I) cannot be prepared by directly heating iodine with Alkane?

Alkyl Iodide (R-I) cannot be prepared by direct halogenation of Alkane because reaction is slow and reversible. In this Case, Alkane are converted to Alkyl Iodide and Side reaction will produce Hydrogen Iodide (HI).

(HI) is a powerful reducing agent, therefore It will convert the product into Original Reactant again.

Therefore, Best Method for the preparation of Alkyl Iodide is

Reaction of

"Alkyl chloride or Alkyl Bromide with Sodium Iodide"-

$$R\text{-}Cl + NaI \longrightarrow R\text{-}I + NaCl$$

ix- **Amines are more basic than Alcohols ? Why**

Due to an Unshared electron pair, the Amines have more basic and nucleophilic Characters than Alcohols.

Q3

(i, ii, iii, iv, vi, vii, viii, ix, x)

Concern Notes.

(v) **Conversion**

a- **Ethyl chloride ⟶ Ethyl cyanide**

$$CH_3-CH_2-Cl + KCN \longrightarrow CH_3-CH_2-CN + KCl$$

b- **Ethyl chloride ⟶ Ethanol**

$$CH_3-CH_2-Cl + KOH_{(aq)} \longrightarrow CH_3-CH_2-OH + KCl$$

c- **Ethyl chloride ⟶ Propane**

$$CH_3-CH_2-Cl + Mg \xrightarrow{Ether} CH_3-CH_2-Mg-Cl$$

$$CH_3-CH_2-\overset{-\delta}{Mg}-\overset{+\delta}{Cl} + \overset{+\delta}{CH_3}-\overset{-\delta}{Cl} \xrightarrow{Ether} CH_3-CH_2-CH_3 + MgCl_2$$

d- **Ethyl chloride ⟶ n-butane.** (m./mp)

$$CH_3-CH_2-Cl \longrightarrow CH_3-CH_2-CH_2-CH_3$$

Wurtz Method :-

When Alkyl halide is reacted with Sodium Metal,

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Ether is Used as a Solvent, Symmetrical Alkanes are formed e.g

$$2CH_3-CH_2-Cl + 2Na \xrightarrow{Ether} CH_3-CH_2-CH_2-CH_3 + 2NaCl$$

n-butane

c Ethyl chloride → Tetra ethyl Lead fmp

$$4C_2H_5Cl + Na_4Pb \rightarrow (C_2H_5)_4Pb + 4NaCl$$

(T.E.L)

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COMPLETE

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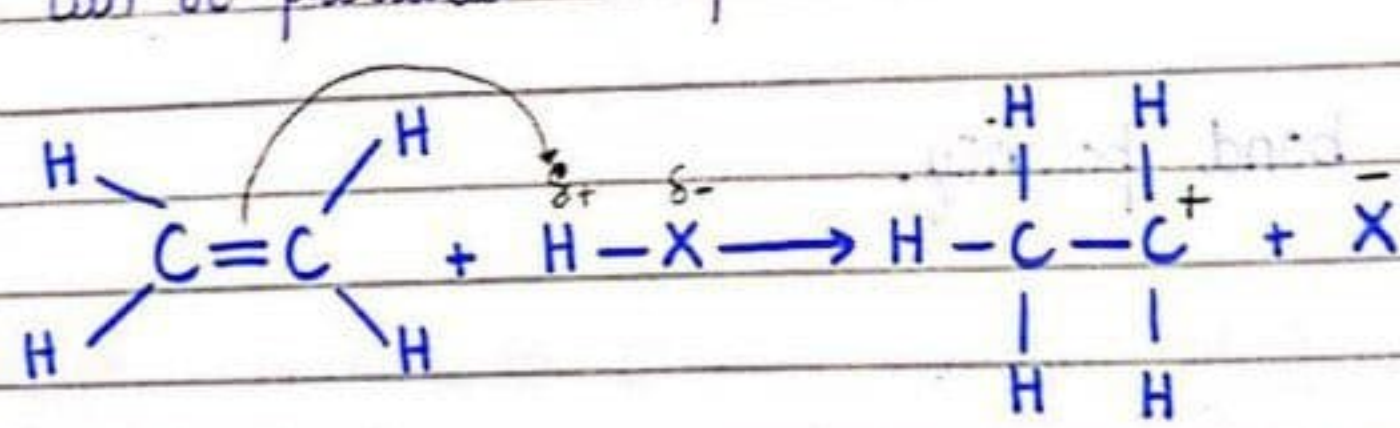
"QUICK QUIZ"

"CHAPTER NO # 17"

"QUICK QUIZ # 01"

1. What is Carbonium Ion?

A carbenium Ion is a reaction intermediate. It is a trivalent with a positive charge on carbon atom. It can be produced as follows:



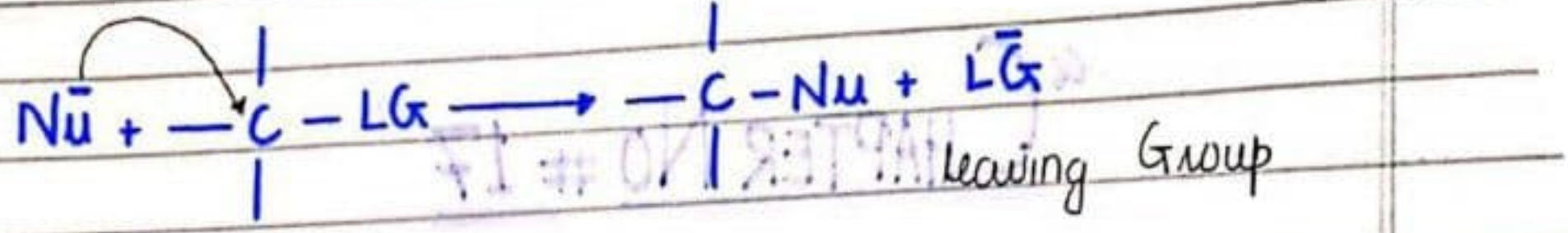
Carbonium Ion

Another term use for such species is called carbocation.

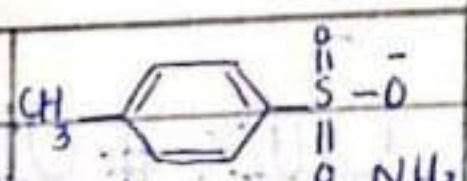
2. What is leaving Group?

Group which depart from the molecule during substitution reaction is called leaving group. It is also called nucleophile.
The incoming nucleophile must be stronger than the

leaving group. Iodid ($-\bar{I}$) is a good leaving group as well as a good nucleophile.



"TABLE"

EXCELLENT	 , NH_3
VERY GOOD	I^-, H_2O
GOOD	Br^-
FAIR	Cl^-
POOR	F^-
VERY POOR	$H\bar{O}$, NH_2^-, $R\bar{O}$

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3- Define bond polarity.

Electronegativity difference between two bonded atom is called bond polarity. Higher will be the bond polarity higher will be the reactivity and vice versa.

Example:

The bond between H and Cl is polar due to electronegativity difference between H^+ and $C\bar{l}$.

4- Define bond energy.

Amount of energy required to break 1 mole of

bond is called bond energy. Less will be the bond energy, higher will be the reactivity and vice versa.

Example:

$$H_2 \longrightarrow 2H$$

$$\Delta H = 435\ KJ/mol$$

Thus, bond energy of H-H bond is 435 KJ/mol.

5- What is nucleophile?

Nucleophile means nucleus loving. Substance which is election rich is called nucleophile. It may be neutral or negatively charged.

Example:

$\ddot{N}H_3$, $H_2\ddot{O}$, $\bar{C}l$, $\bar{O}H$ etc.

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6- What is electrophile?

Substance which is election deficient is called an electrophile or specie in seach of negative charge is called electrophile. It is positively charged.

Example:

NO_2^+, $B\acute{r}^+$, CH_3^+ etc.

7- What are primary, secondary and tertiary carbon atom?

→ PRIMARY CARBON ATOM:

The carbon atom which is directly bonded with one carbon atom or no carbon atom is called primary carbon atom.

Example:

C–C–C–C ; –C

↓

Primary C-atom (1° - C-atom)

→ SECONDARY CARBON ATOM:

The carbon atom which is directly bonded with two carbon atom is called secondary carbon atom.

Example: C–C–C–C

↓

Secondary C-atom (2° - C-atom)

→ TERTIARY CARBON ATOM:

The carbon atom which is directly bonded with three carbon atom is called tertiary carbon atom.

Example:

C

|

C–C–C–C

↓

Tertiary carbon atom (3° - C-atom)

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"QUICK QUIZ #02"

1- What are organometallic compounds ?

The compound containing at least one bond between Carbon atom of organic compound and a metal atom are called organometallic compounds.

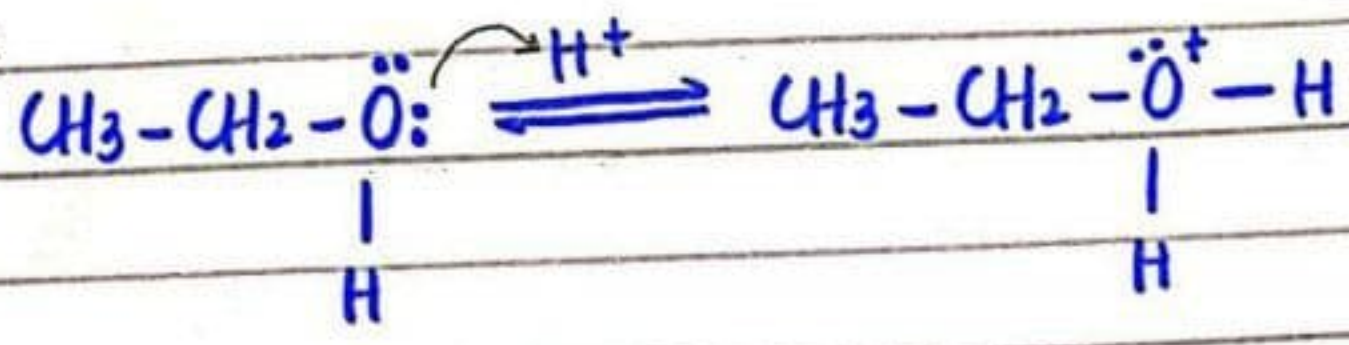
Examples:

* Grignard's Reagent: $CH_3 - Mg - Cl$
* Alkyl Lithium compounds: $CH_3 - Li$

2- Define protonation.

The addition of a proton (H^+) to an atom, molecule or an ion, forming its conjugate acid is called protonation.

Example:



3- How "RMgX" reacts with CO_2 ?

REACTION WITH CO_2:

4- Write the formula of Grignard's Reagent.

The general formula of Grignard's Reagent is:

"R-Mg-X"

where, "R" is any alkyl group and "X" is halogen atom.

Examples:

* Methyl magnesium Chloride: $CH_3-Mg-Cl$
* Ethyl magnesium Bromide: $CH_3-CH_2-Mg-Br$

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