Date: 02-09-2024

Alky halide

alkyl halide

When H-atom of alkane is replaced by halogen atom (X), the compound formed will be alkyl halide.

haloalkane

The compound containig mono, di°, Tri, tetra or poly halogens into alkane carbon.

Monoalkane

→ When one atom (H) of carbon is replaced by halogen. This is also known alkyl halide.

MDCAT

alkyl halide are rare nature mostly are synthetic. and mosHy they have oily nature.

General formula

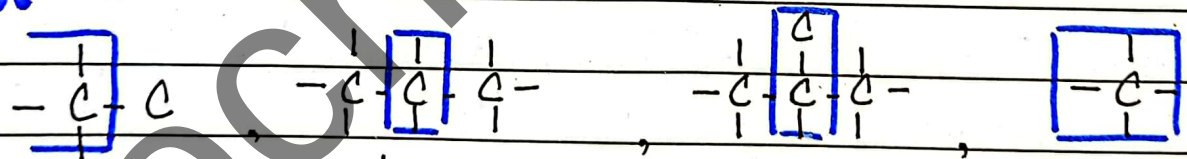
$C_nH_{2n+1}X$

representation

R-X → halogen (F, Cl, Br, I).

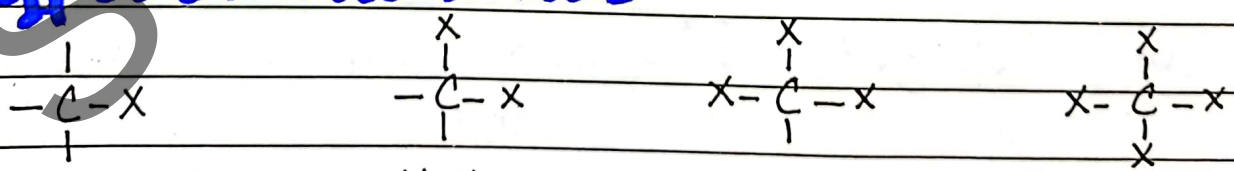
↳ alky group

Types of Carbon



1°/Primary , 2°/Secondary , 3°/tertiary , Quaternary/4°

Types of haloalkane



monohaloalkane ; dihaloalkane ; Trihaloalkane ; tetrahaloalkane

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Classification

- There are 3 main Types :-

1- Primary alkyl halide An alkyl halide in which halogen atom is bonded with Primary Carbon. (1°, i, pri).

example:

$CH_3-\overset{*}{C}H_2-Cl$; $CH_3-CH_2-\overset{*}{C}H_2-Cl$.

- methyl chloride (C.P.N)
- Chloromethane (IUPAC)

- 1-chloropropane. (IUPAC)
- Pri-Propyl chloride (C.N).

$CH_3-CH_2-CH_2-\overset{*}{C}H_2Br$

- 1-Bromobutane. (IUPAC)
- 1°-Butylbromide (C.N).

2- Secondary alkyl halide An alkyl halide in which halogen atom is bonded with secondary carbon. (2°, sec).

example:

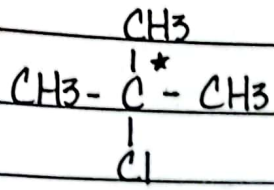
$CH_3-\overset{*}{C}H(Cl)-CH_3$; $CH_3-\overset{*}{C}H(Br)-CH_2-CH_3$

2-chloropropane. (IUPAC)
2°-propyl chloride. (C.N).
iso propyl chloride

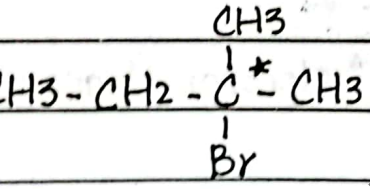
2-Bromobutane. (IUPAC)
2°butyl bromide. (C.N)
isobutyl bromide

3- Tertiary alkyl halide An alkyl halide in which halogen atom is boned with tertiary carbon (3°, ter).

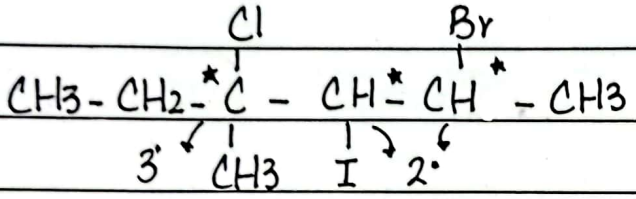
example :



-- 2- chloro -2- methylpropane (IUPAC)
-- tertiary prbutyl chloride (C·N).



-- 2-bromo-2-methylbutane.
-- terbutylbromide.
-- neobutyl bromide.



-- 2-bromo - 4-chloro-3-ido-4-methyl hexane (IUPAC)
* No C.N.

Physical Properties

-- The alkyl halide have high melting & boiling point.
-- The reason is that alkane itself is completely non-polar but when halogen gets attach to it, molecular dipole is produced due to high E·N of halogen.
-- This makes alkyl halide polar.
-- Increasing boiling & melting point.

C — F Vs C - C
2.5 4.0 = 1.5 2.5 2.5 = 0.

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$\overset{+S}{C}-\overset{-S}{F}$

★ ↳ electron charge density Towards halogen 'F.'

Preparation of R-X

1- Alcohol

•- Rxn with halogen acid :-

alcohol treated with HCl in presence of anhydrous ZnCl

★ $CH_3CH_2-OH + HCl(conc.) \xrightarrow[\Delta]{ZnCl_2(anhydrous)} CH_3-CH_2Cl + H_2O$

ethyl chloride.

★ $CH_3CH_2-OH + HBr(conc.) \xrightarrow[\Delta]{ZnCl_2(anhydrous)} CH_3-CH_2Br + H_2O$

ethyl bromide.

★ $CH_3CH_2-OH + HI(conc.) \xrightarrow[\Delta]{ZnCl_2(anhydrous)} CH_3-CH_2I + H_2O$

ethyl iodide.

★ $CH_3CH_2-OH + HF(conc.) \xrightarrow[\Delta]{ZnCl_2(anhydrous)} CH_3-CH_2F + H_2O$

ethyl flouride

Date:

.- RxN with thionyl chloride

Reaction of alcohol with thionyl chloride in presence of pyridine as solvent.

* $CH_3CH_2-OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3CH_2-Cl + HCl + SO_2$.
  ($SOCl-Cl$).
  1°- chloro ethane.

This method is Recommended as best method of Preparation becoz HCl & SO_2 are in gaseous state & will evolved whereas 100% alkyl halide can be obtained.

.- RxN with phosphorus chloride :

* $3CH_3-CH_2-OH + PCl_3 \longrightarrow 3CH_3-CH_2Cl + HBPO_13$
  (Phosphorus trichloride) (Phosphoric acid).

* $CH_3-CH_2-OH + PCl_5 \longrightarrow CH_3-CH_2Cl + HCl + POCl_3$
  (phosphorus Penta chloride) Phosphorus oxychloride.

* $3CH_3-CH_2-OH + PCl_5 \longrightarrow 3CH_3-CH_2Cl + HCl + HP_3PD_3$
  (phosphoric acid).

"PI_3 is most reactive bond than PF_3, PCl_5 etc & will do fast rxn."

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* HI is more acidic.

* $PI_3 + 3CH_3CH_2OH \longrightarrow 3CH_3CH_2I + H_3PO_3$

* $3CH_3CH_2OH + PBr_3 \longrightarrow 3CH_3CH_2I + H_3PO_3$.

2. alkane

$CH_3 - CH_3 + Cl_2 \xrightarrow{h\nu} CH_3 - CH_2Cl + HCl$. (continue till all H-replaced)

Not best reaction becoz mixture of haloalkane is produced which a difficult task.

last product will be C_2Cl_6.

$CCl_3 - CCl_3$.

Reactivity

The reactivity of alkyl halide depend upon bond energy that's experimentally determined.

→ Bond polarity of C-X bond

Electronegativity difference b/w 2 bonded atoms is called bond polarity.

Bond polarity ∝ Reactivity.

- C-F = 2.5 - 4.0 → 1.5
- C-Cl = 2.5 - 3.0 → 0.5
- C-Br = 2.5 - 2.8 → 0.3
- C-I = 2.5 - 2.5 → 0.

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→ R-F is more reactive than others.

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

Bond energy

→ amount of energy required to break 1 mol of bond.

Bond energy $\propto \frac{1}{\text{reactivity}}$

-· C-F = 467 KJ/mol

-· C-Cl = 346 KJ/mol

-· C-Br = 290 KJ/mol

-· C-I = 228 KJ/mol.

→ R-I is most reactive.

RI > R-Br > R-Cl > R-F

→ Different experimental rxn have shown that reactivity of alkyl halide depends upons bond energy not bond polarity.

→ Overall reactivity order :-

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

rxn of alkyl halide

→ undergo 2 types of rxns.

1. Nucleophillic subsitution rxn (S.N)
2. Elimination rxn.

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Nucleophilic Substitution rxn

→ Nu^-

↳ nucleous loving because it's +.

↳ may be additional e^- or lone pair in case of neutral atoms.

$Nu^- + \overset{+\delta}{C}\text{-}\overset{-\delta}{X} \longrightarrow C\text{-}Nu + X^-$ → nucleophile.

(nucleophilic) (substrate) (product) (leaving grp.)

" Reaction in which halogen atom of alkyl halide is replaced by strong nucleophile."

becox bond b/w C-X is quite strong.

Important Concept

1. Nucleophilic (Nu^-) :-

* substance which is e^- rich.
* Nucleus loving (+)
* Neutral having Lone pair
* Negatively charged.

CN^- OH^- Cl^- , $\ddot{N}H_3$ $H_2\ddot{O}:$ $H_2\ddot{S}:$

anions central atom e^- rich.

2. Electrophile (E^+) :-

* Substance which is e^- deficient
* e^- loving (e^-).
* Neutral (but actually due to high E.N, the e^- will be deficient to central atom).

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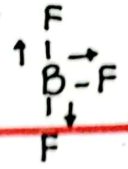
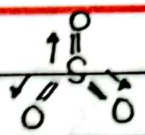


* Postively charged.

NO_2^+ Cl^+ CH_3^+ $CH_3-\overset{O}{\overset{\|}{C}}{}^+$, BF_3 $AlCl_3$ SO_3



cations — central atom should be e^- deficient.

3. Substrate:

- Substance on which Nucleophilic or electrophile attack.

" alky halide molecule on which Nu^- attacks".

4. Leaving group:

" Atom or group of atom which departs from the molecule"

→ Good leaving group is a group which become stable after departure.

and usually :-

atomic size ∝ leaving group.

* Cl^-, Br^-, I^-, CH_3COO^- → easily removed.
($8e^-$)

" flourine is not included becoz it's high E.N & small size & strong C-F bond which does n't allow it to leave easily."

→ Bad leaving group is a group which doesn't like to departure because of strong bond with carbon.

* OH^-, OR^-, NH_2^- → difficult to remove.

acidic strength

HI > HBr > HCl > HF

easily reactive & Low E.N

bond strength

HF > HCl > HBr > HI.

Br → Br^- stable

Strong bond ∝ 1 / acidic strength

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Carbocation

"Ion having positive charge on carbon atom."

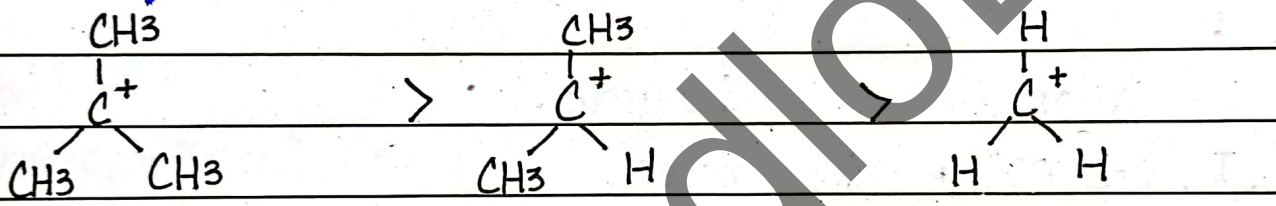
factor affecting C^+

* Resonance
* hyperconjugation
* Inductive effect

} $\propto$ Stability of C^+.

Resonance > Hyperconjugation > Inductive effect

example



3°- carbocation > 2°- carbocation > 1°- carbocation.

Resonance:-

- The delocalization of e^-.
- The carbocations donot resonates becoz it itself lock the e^- how it can ~~resonane~~ resonate.
- They have diff structure but same position e^-.
- This carbocation donot contribute these facts so, Resonance don't occur.

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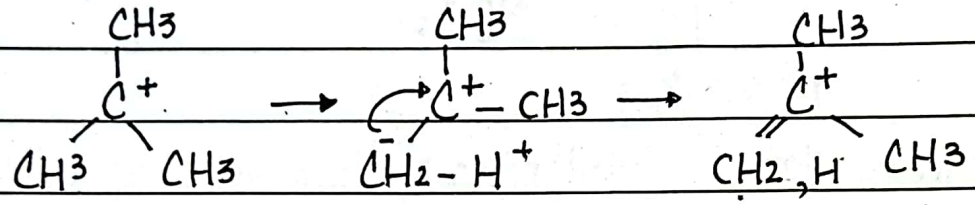
hyperconjugation:

- The phenomena in which C-break bond with H & become neg charge and share it with C^+ to form = bond.
- Temporary process.



* Hyperconjugation ∝ no. of alpha H.
* These methyl grp are attached to carbocation grp so, methyl carbon are alpha carbon & its hydrogen are alpha hydrogen.
* These CH_3 grp contain 3 hydrogen means three times H.C.

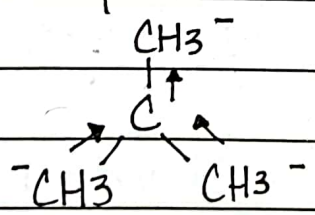
3°-carbocation > 2°-carbocation > 1°-carbocation.

9 H.C 6 H.C 3 H.C.

→ 3° > 2° > 1°

Inductive effect:

- Any group which attract e^- (with-drawing) or donate e^- and causes δ polarity is Inductive effect.
- Temporary.
- The + ion donot finishes but remains becoz there's no permanent shifting e^-.



→ 3° IE > 2° IE > 1° IE

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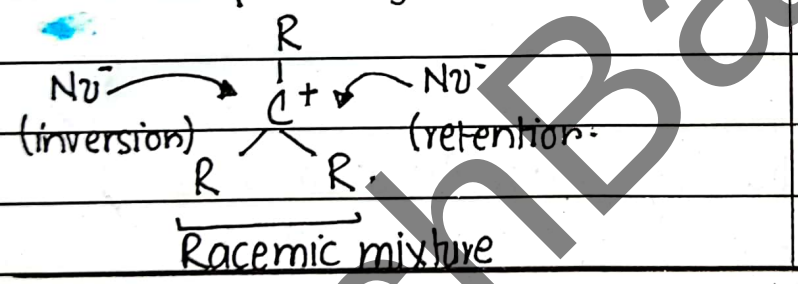
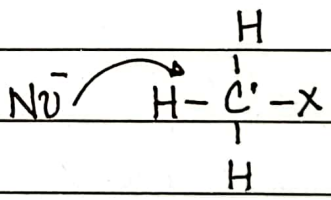
diff b/w SN_1 & SN_2

SN_1	SN_2
Meaning	
Substitution Nucleophilic unimolecular.	Subsitution Nucleophilic bimolecular.
rate determining step	
1 mol take part in rate determining slow step.	2 molecule will take part in rate determining step.
Mechanism	
2- step.	1-step.
Product Configuration	
50% of configuration & 50% retention of configuration. 	100% inversion of configuration. 
alkyl halide	
3° alkyl halide favours SN1 mechanism due to stability of C^+	1° alkyl halide favours SN_2 mechanism due to steric repulsion.
2° alkyl halide	
2°- alkyl halide undergo SN1 in presence of polar solvent. (H_2O, ethanol, methanal) → moist Ag_2O, Ag, $AgNO_3$ ↓ solvolysis.	2° R-X undergo SN_2 is presence of non-polar solvent. CCl_4, hexane, C_6H_6.

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Stability of carbocation

1° R-X donot undergo SN1 mechanism becox of unstable.	3°-R-X donot undergo SN2 mechanism becox of steric repulsion.

mechanism order

These reaction first order. rate = K[R-X] = 1.	These reaction 2 order. rate = K [R-X][Nu⁻] = 2

RxN solvent

take place in polar solvent (C^+)	take place in non-polar solvent (Transition complex)

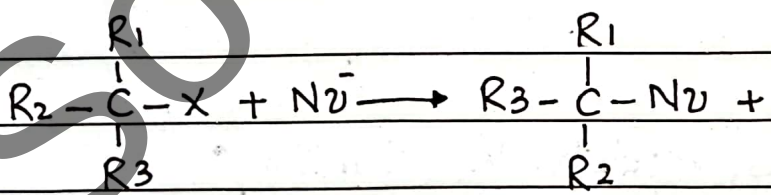
RxN Base

Rxn take place in presence of strong base or weak base.	take place in presence of strong base.

SN1

→ Unimolecular substitution rxn

→ 2 step reactions
- R-X ionizes reversibly to C^+ ion (slow step)
- C^+ ion combines with Nu^- (fast step).

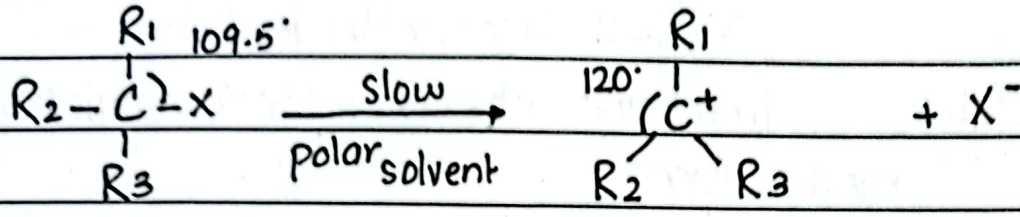


3°-alkyl halide.

Date: _____

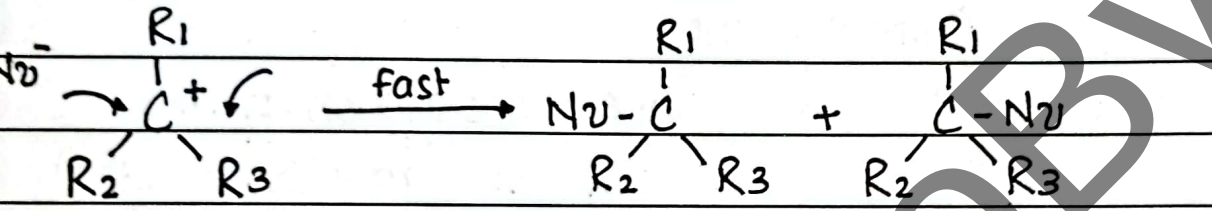
Mechanism:

formation of carbonium ion C^+



3°- alkyl halide 3°- Carbonium ion.

attack of nucleophile on α-C



50% Inversion Configuration 50% Retention Configuration

Racemic mixture.

Kinetic evidence:

→ depend upon only on Conc. of alky halide.

→ change in conc. of attacking Nucleophile has no effect.

Rate = $K[R-X]$

order = 1.

Points:

→ 3° alky halide stable in ion form.

→ Carbocation form.

→ in Sp^2 structure, angle is less, repulsion less, stability ↑

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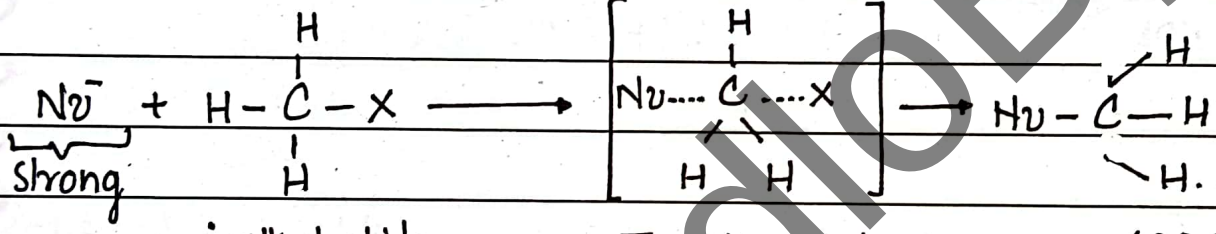
S_N2

→ Bimolecular structure
→ Only in 1 step
→ attack & depature occurs

$CH_3-X + Nu^- \xrightarrow{\text{non-polar}} CH_3-Nu + X^-$

i-alkyhalide

Mechanism:



* Transition state
* Activated complex

100% Inversion.

Kinetic evidence:

Rate $\propto [Nu^-][R-X]$

Rate $= K[Nu^-][R-X]$

order = 2.

Points:

→ The nucleophile can't attack from right side beoz of X group.
→ This is behaving life bulky group creating hindrance & repulsion.

Conclusion:

- Compound having more branches will favour SN1
- Compound having less branches will favour SN_2.

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Elimination rxn

Reaction in which 2 groups (halogen and β-hydrogen form alkyl halide) are eliminated from 2 adjacent carbon atoms to form carbon–carbon double bond. & form unsaturation.

example:

$$CH_3\overset{\beta}{-}\underset{Cl}{CH_2}\overset{\alpha}{} + KOH \xrightarrow{\text{alcohol}} CH_2 = CH_2 + KCl + H_2O.$$

Point:

→ β-hydrogen is necessary for elimination. That's why it's also called β-elimination.

types

E1 = Elimination unimolecular

E2 = Elimination bimolecular

difference

E1-elimination	E2-elimination
meaning	
elimination unimolecular	elimination bimolecular
rate-determining step	
1 molecule take part.	2 molecule take part

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Types of alkyl halide

Most 3°-alkyl halide.	Most 1°-alkyl halide.

Mechanism

2-step mechanism	1-step mechanism

reaction order

first order = 1	2end order = 2

E1

General:

$$R_2-CH_2-\underset{\underset{R_3}{|}}{\overset{\overset{R_1}{|}}{C}}-X + KOH \xrightarrow{\text{alcohol}} R_2-CH=\underset{\underset{R_3}{|}}{\overset{\overset{R_1}{|}}{C}} + KX + H_2O.$$

Mechanism

Step #1 : Ionization of alkyl halide

Carbocation form & halide ion reversibily.

$$R_2-CH_2-\underset{\underset{R_3}{|}}{\overset{\overset{R_1}{|}}{C}}-X^{-\delta} \overset{\text{Slow}}{\rightleftharpoons} R_2-CH_2-\underset{\underset{R_3}{|}}{\overset{\overset{R_1}{|}}{C^+}} + X^-$$

3°-RX. 3°-carbocation

Step #2 : Removal of β-H

$$OH^- + R-CH_2-\underset{\underset{R_3}{|}}{C^+} \xrightarrow{\text{fast}} R-CH=\underset{\underset{R_3}{|}}{\overset{\overset{R_1}{|}}{C}} + H_2O.$$

Date:

* B-H becomes acidic.

Kinetic evidence

Rate $\propto$ [R-X]

Rate = K [R-X]

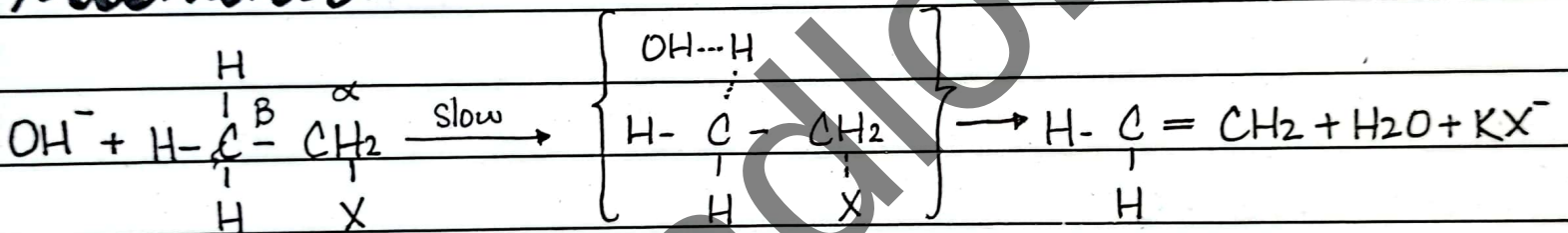
order = 1st.

E2

General:

$CH_3\overset{\beta}{-}CH_2\overset{\alpha}{-}X + KOH \xrightarrow{\text{alcohol.}} CH_2=CH_2 + H_2O + KX$

Mechanism



Kinetic equation

Rate = K [Nu][R-X]

order = 1+1 = 2

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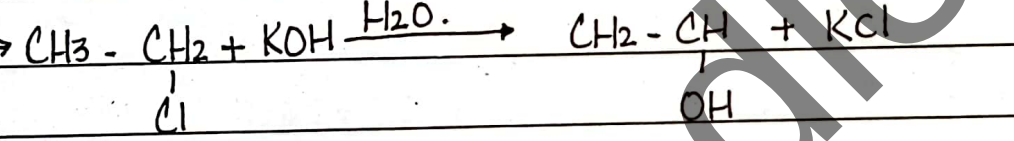
Substitution vs elimination

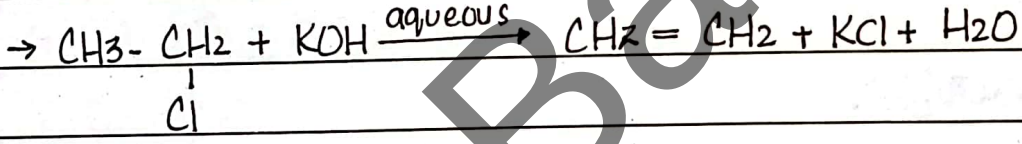
- Alkyl halide is of dual nature giving both subsitution and elimination reaction.

examples:

Subsitution:



elimination:



Point:

- Mostly product is substitution becoz substitution does not require β-hydrogen condition.

factors

1- Structure of Carbon Substrate

- More alkylated R-X (more branch) undergo elimination reaction and less alkylated R-X (less branch) undergo substitution.
- The reason is it will difficult for nucleophile to attack on less branched.

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Less alkylated:

with KOH

$CH_3-CH_2-X + KOH \xrightarrow{H_2O} CH_3-CH_2-OH + KX$ (substitution)

$CH_3-CH_2-X + KOH \xrightarrow{alc} CH_2=CH_2 + KX + H_2O$ (elimination)

with C_2H_5ONa

$CH_3-CH_2-X + C_2H_5ONa \xrightarrow{H_2O} CH_3-CH_2-C_2H_5O + NaX$

S = (88%)

$CH_3-CH_2-X + C_2H_5ONa \xrightarrow{C_2H_5OH} CH_2=CH_2 + C_2H_5OH + NaX$

E = (12%).

2- Nature of base

- Strong bases = OH^-, NH_2^-, $\bar{O}R$ gives elimination.
- High polarizable nucleophile or weak base = I^-, $R\bar{S}$ gives substitution.

Strong base:

with $\bar{O}H$

$CH_3-CH_2-X + \bar{O}H \longrightarrow CH_2=CH_2 + H_2O + X^-$

with $\bar{N}H_2$

$CH_3-CH_2X + \bar{N}H_2 \longrightarrow CH_2=CH_2 + NH_3 + X^-$

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with $\bar{O}R$

$$CH_3-\underset{\underset{X}{|}}{CH_2} + \bar{O}R \longrightarrow CH_2=CH_2 + HOR + X^-$$

base weak:

with I^-

$$CH_3-\underset{\underset{X}{|}}{CH_2} + I^- \longrightarrow CH_2-\underset{\underset{I}{|}}{CH_2} + X^-$$

with RS^-

$$CH_3-\underset{\underset{X}{|}}{CH_2} + RS^- \longrightarrow CH_3-\underset{\underset{SR}{|}}{CH_2} + X^-$$

with CH_3COO^-

$$CH_3-\underset{\underset{X}{|}}{CH_2} + CH_3COO^- \longrightarrow CH_3-\underset{\underset{CH_3COO}{|}}{CH_2} + X^-$$

3- Nature of leaving group

* Only effect SN_2 & E_2 reactions becoz L.G doesn't leave itself.

→ Good leaving = Substitution

→ bad leaving grp = Elimation

Good Leaving:

$$C_{16}H_{33}-CH_2-CH_2-X + (CH_3)_3C\bar{O}K^+ \longrightarrow C_{16}H_{33}-CH_2-CH_2-(CH_3)_3C\bar{O} + KX$$

Leaving Bad:

$$C_{16}H_{33}-CH_2-CH_2-X + (CH_3)_3C\bar{O}K^+ \longrightarrow C_{16}H_{33}CH=CH_2 + (CH_3)_3COH + KX.$$

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★ Size big =

4- Nature of solvent

Elimination reacts by lowering solvent polarity.

- The alcoholic KOH = Less polarity favours = elimination.
- The aqueous KOH = More polarity favours = substitution.

→ In E1 is favoured by polar solvent like SN1.

→ In E2 is favoured by non-polar.

Polar solvent: Substitution

$$CH_3-\underset{Cl}{CH_2} + KOH \xrightarrow{H_2O} CH_3-\underset{OH}{CH_2} + KCl$$

Non-polar solvent: Elimination

$$CH_3-\underset{Cl}{CH_2} + KOH \xrightarrow{Alc} CH_2=CH_2 + KCl + H_2O$$

5- Effect of temp

Increase temp = elimination beoz it requires reorganization.

Decrease temp = Substitution beoz it donot requires reorganization.

At 45°C

$$2CH_3-\underset{Br}{CH}-CH_3 + 2NaOH \xrightarrow{45^\circ C} CH_3-CH=CH_2 + NaBr + H_2O + CH_3-\underset{OH}{CH}-CH_3$$

E = 53%.

NaBr.

S = 47%.

At 100°C

$$2CH_3-\underset{Br}{CH}-CH_3 + 2NaOH \xrightarrow{100^\circ C} CH_3-CH=CH_2 + NaBr + H_2O + CH_3-\underset{OH}{CH}-CH_3$$

E = 64%.

NaBr

S = 36%.

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Organometal Compound

"Organic Compound in which metal is bounded with Carbon."

example:

$\underbrace{R-Li}_{\text{alkyl grp + metal}}$, $C_2H_5-\underset{\displaystyle C_2H_5}{\overset{\displaystyle \cdot\cdot}{Pb}}-C_2H_5$, $\underbrace{C-Mg}_{\text{alkyl grp + metal}}$

Triethyllead

important point

→ Derivatives of alkyl halide

→ Belong to organometallic comp family

→ Chemical name is alkyl magnesium halide

→ Victor Grignard (1900) discovered most reactive organic comp in chem.

→ Used to identify starting ~~meta~~ materials of any organic reaction.

→ All rxn of grignard's are exothermic.

reactivity

$\overset{-5}{R}-\overset{+5}{Mg}-X$

"Grignard is reactive due to polarity of R-Mg bond."

- R = more electronegative = act as nucleophile
- Mg = Less electronegative = act as electrophile.
- Carbon atom $\propto \frac{1}{\text{reactivity}}$

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• Now how?

→ Cov R grp are e^- donating which gives e^- reducing charging, hence decrease polarity, in result reactivity decreases.

$CH_3-Mg-X > C_2H_5-Mg-X > C_3H_7-Mg-X$

↓ less e^- donating

↓ more e^- donating.

→ polarity ∝ reactivity

Now X grp?

$RI > RBr > RCl > RF$ → Vigorous.

↓ more reversible & slow rxn

more intermediate & reactive.

Preparation

$$R-X + Mg \xrightarrow[\Delta]{\text{dry ether}} R-Mg-X$$

dry ether: gaseous form (should be free from moisture & impurity)

$$CH_3-CH_2-Br + Mg \xrightarrow[\Delta]{\text{dry ether}} CH_3-CH_2-Mg-Br$$

ethyl bromide — ethyl magnesium bromide

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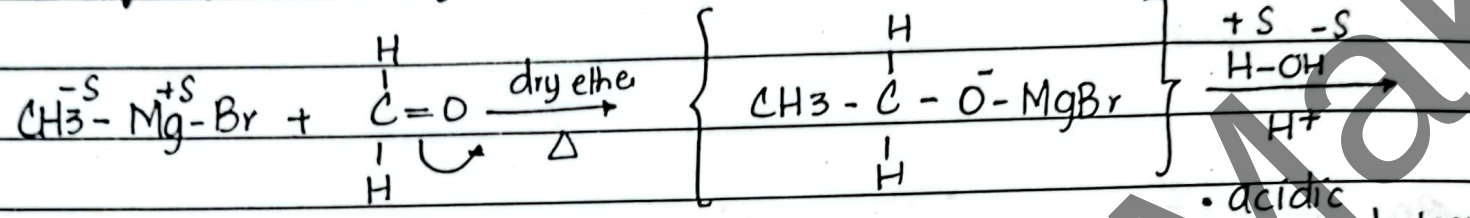
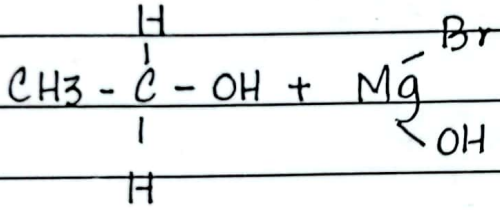
Reactions : aldehyde and ketone

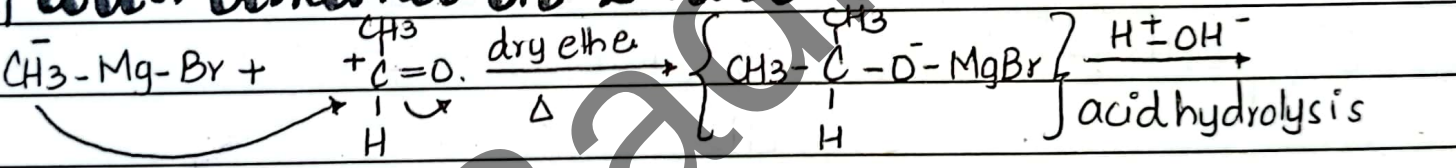
1) with methanal (formaldehyde) or Preparation of alcohol

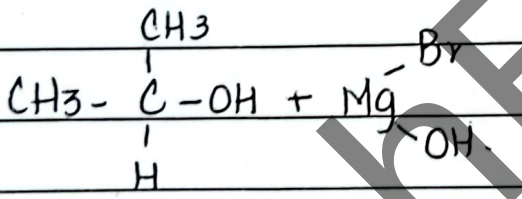




- ethanal
- i- Alcohol

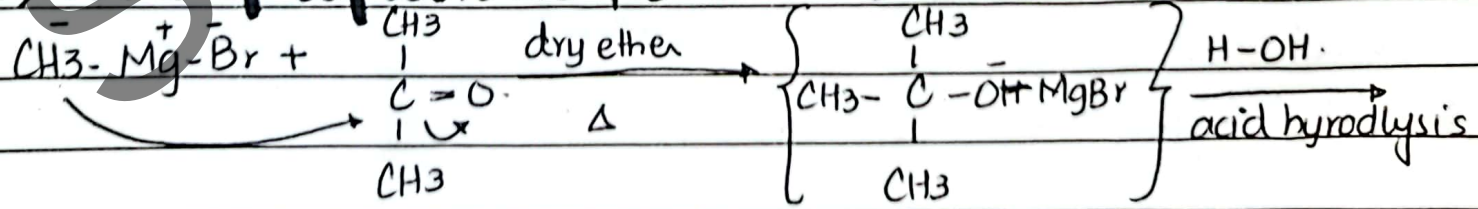
2) with ethanal or 2° alcohol





- 2°- alcohol.
- 2°-Propanol.

3) with Propanone (acetone) or 3° alcohol



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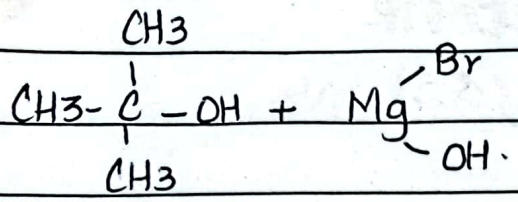
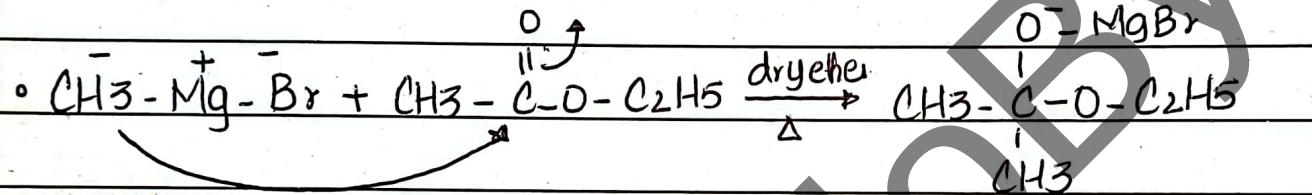


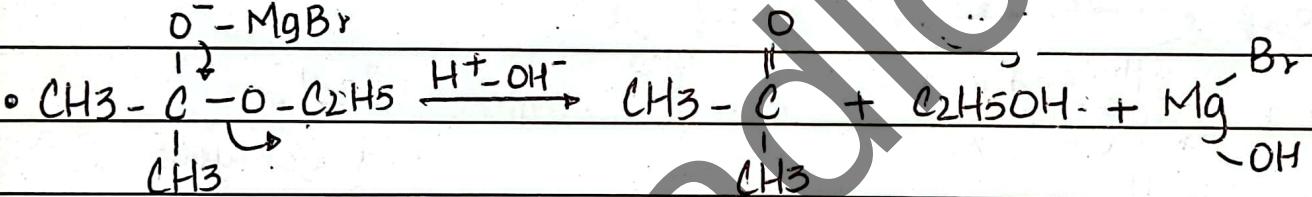
2-Methyl-2-propanol
3° alcohol

reaction with esters or 3° alcohol

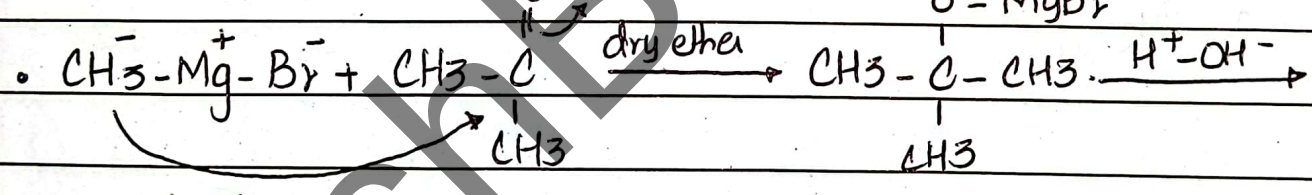
mechanism

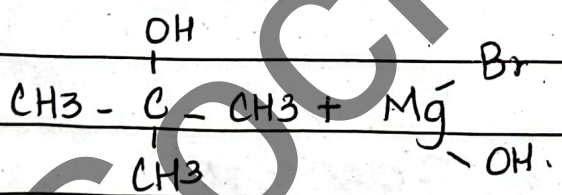
excess of grignard reagent reacts with ester or ethyl acetate :-





Propanone





3° - alcohol
2° - Methyl - 2 - propanol.

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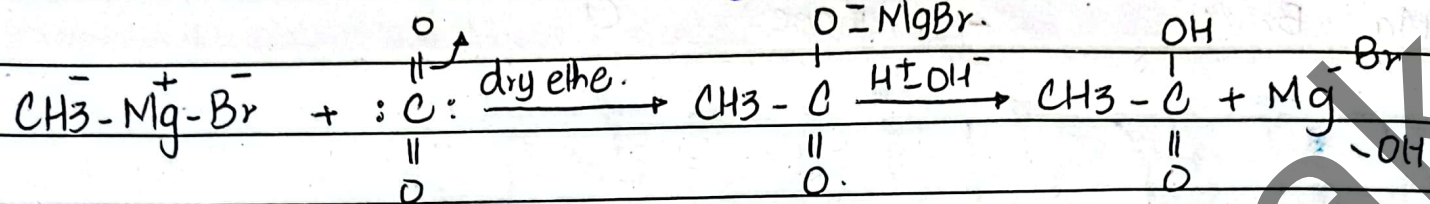
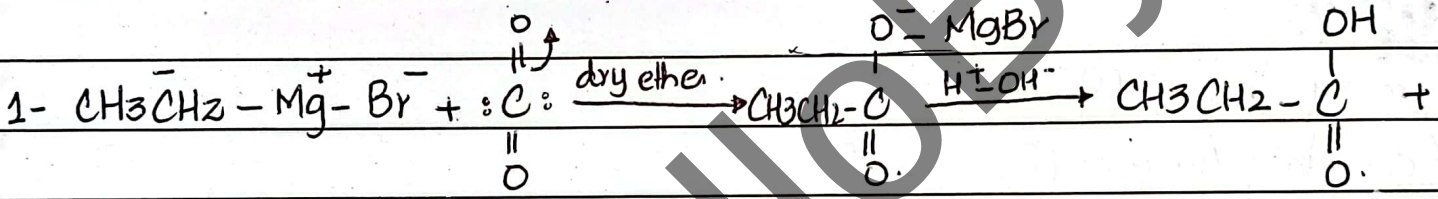
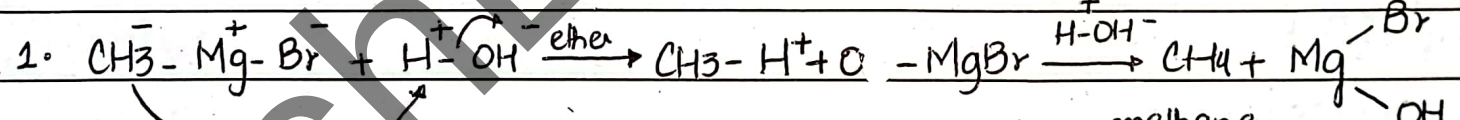
reaction with CO_2 or formation CO_2

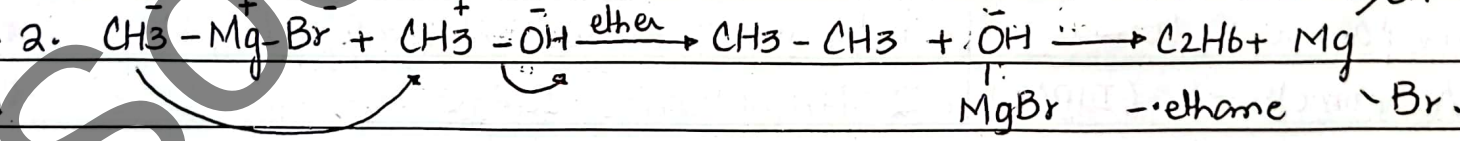


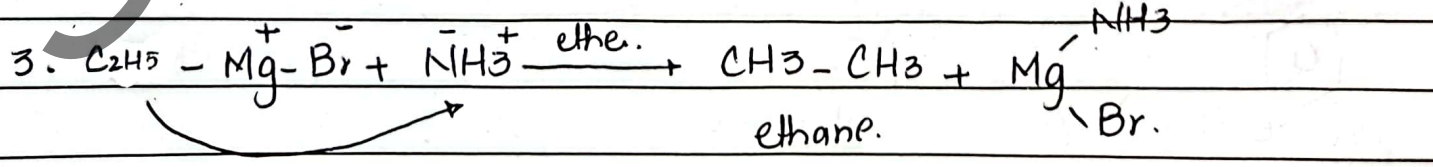
Practice



alkane formation:

1. 

2. 

3. 

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4- $CH_3 + H\overset{+}{Cl} \longrightarrow CH_4 + MgBrCl$

Mg Br. — methane.

Amines

→ derivates of NH_3.

→ When H-atoms of NH_3 is replaced by alkyl group compounds formed are called Amines

types

→ Primary Amines ($R-NH_2$).

→ Secondary Amines ($R-NH-R$)

→ Tertiary Amines. ($R-\overset{R}{\underset{R}{N}}-R$)

Primary Amine

When one H-atom of NH_3 is reploced by one alkyl group, the compound formed is 1° Amine.

IUPAC

examples :-

CH_3-NH_3.	$CH_3-CH_2-CHNH_2-CH_3$.
∘ Methylamine (C.N)	∘ butylamine. or Sec. butylamine (C.N).
∘ Aminomethane (IUPAC)	∘ 2-Aminobutane (IUPAC).

∘ 

aniline (C.N) / Sec. phenyl amine.

Aminobenzene (IUPAC).

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Secondary amine

- When 2-H atom of NH_3 are removed & replaced by 2 alkyl group.

Compound formed is 2° amine.

IUPAC

examples

$CH_3-NH-CH_3$.	$CH_3-NH-CH_2-CH_3$.
∘ Dimethyl amine. (C.N).	∘ Ethylmethyl amine. (C.N).
∘ N-Methyl aminomethane (IUPAC).	∘ N-ethylaminomethane.

- methylphenylamine. (C.N).
- N- aminobenzene (IUPAC)
- N-methyl~~amino~~Aniline (IUPAC).

Tertiary amine

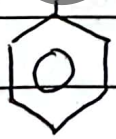
- When 3H-atom of NH_3 is replaced by 3 alkyl group.

IUPAC

examples:

$CH_3-N(CH_3)-CH_3$	$CH_3-N(CH_2CH_3)-CH_2CH_3$:
∘ Trimethylamine (C.N).	∘ ethylmethyl n-propyl amine (C.N).
∘ N,N-Dimethyl amino methane (IUPAC)	∘ N-ethyl-N-methylamino Propane (IUPAC).

$CH_3-N-CH_2-CH_3$



ethyl~~amine~~methyl phenyl amine (C.N)

N-ethyl-N-methylaminobenzene. / N-ethyl-N-methylaniline. (IUPAC).

(IUPAC)

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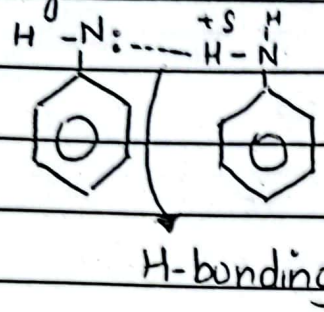
Physical Properties

1) They show H-bonding with eachothe.



2) They high B.P & M.P compare to analogous alkane.

more B.P & M.P

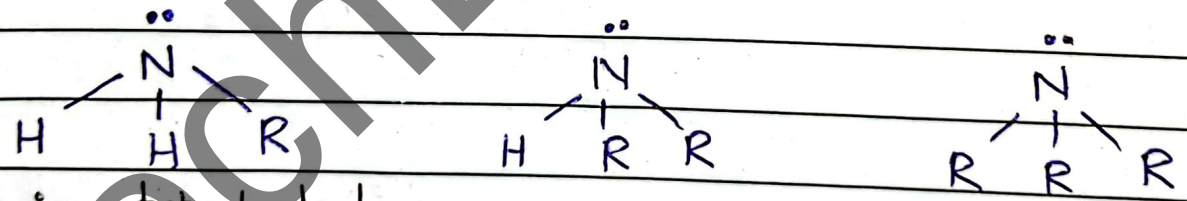
$CH_3 - NH_2$ & CH_4 → less B.P & M.P.

same carbon.

H-bonding — London dispersion forces

3) More Soluble than alkane due to slight polarity in water.

Structure



- 4e⁻ pair = tetrahedral.
- final geometry is trigonal pyrimidal
- sp^3
- 3° amine is optical active.
- 107.5° angle.

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Preparation

Alkylation of NH_3 with R-X or aminolysis

- $C_2H_5I + H\text{-}NH_2 \longrightarrow C_2H_5NH_2 + HI$

  limited excess — Pri-amino

  Aminoethane.

- if you want to stop the rxn at 1° amine C_2H_5I in limited amino & NH_3 in excess.
- If you want to produce all types 1°, 2°, 3° amine take C_2H_5I in excess.
- $C_2H_5\text{-}I\,(excess) + H\text{-}NH_2\,(excess) \longrightarrow C_2H_5\text{-}NH_2 + HI$
- $C_2H_5\text{-}NH\text{-}C_2H_5 + I\text{-}C_2H_5 \longrightarrow C_2H_5\text{-}NH\text{-}C_2H_5 + HI$

  2° amine.

- $C_2H_5\text{-}NH\text{-}C_2H_5 + I\text{-}C_2H_5 \longrightarrow C_2H_5\text{-}N(C_2H_5)\text{-}C_2H_5$

  3° amine.

Salt formation by 3° amine

$C_2H_5\text{-}\ddot{N}(C_2H_5)\text{-}C_2H_5 + I\text{-}C_2H_5 \longrightarrow [C_2H_5\text{-}N^{+}(C_2H_5)\text{-}C_2H_5]\,I^{-}$

(coordinate covalent bond; ionic bond)

mixture of 1°, 2°, 3° & salt separated by fractional distillation.

tetraethylammonium iodide.

Quaternay ethyl ammonium iodide

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Reduction of N containing functional group

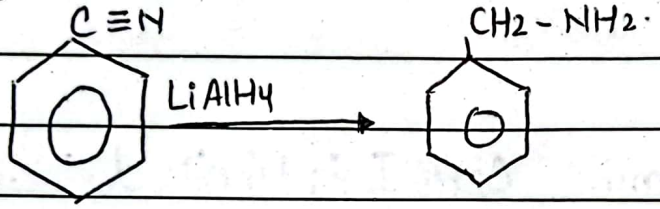
By Reducing agent:

reducing agent
Lithium aluminium hydride

$CH_3 - C \equiv N \xrightarrow{LiAlH_4} CH_3 - CH_2 - NH_2$

- methyl cyanide.
- cyanide ethane

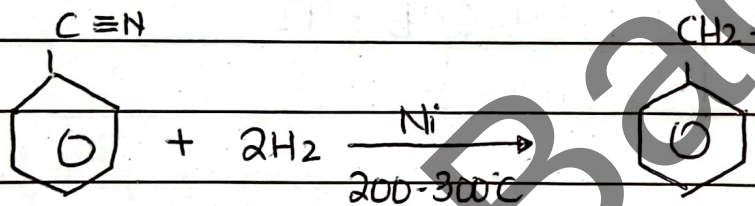
i- ethylamine.



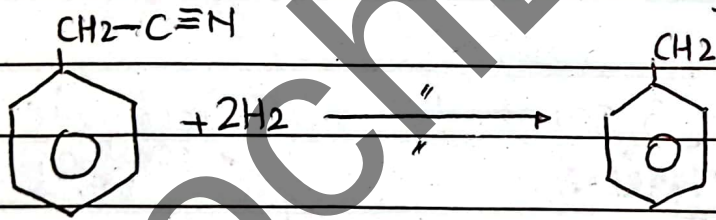
Benzylamine
arylamine.

By catalytic reduction:

$CH_3 - C \equiv N + 2H_2 \xrightarrow[200-300^\circ C]{Ni} CH_3 - CH_2 - NH_2$



Benzylamine.

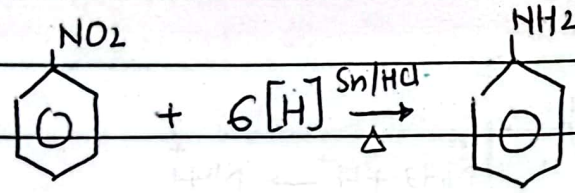


Date:

Reducing agent of nitro comp NO_2

Reducing agent:
Sn/HCl, H_2/Ni, Pt, Pd
Fe/H_2SO_4, Na/ethanol

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



Reduction of amide $R-\overset{O}{\overset{\|}{C}}-NH_2$

a) by Reducing agent

$$CH_3-CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4} CH_3-CH_3-CH_2-NH_2$$

Propane amide. → Propane amine

b) by Hoffmann degradation reaction.

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2/KOH2} CH_3-CH_2-NH_2 + 2KBr + CO_2 + H_2O$$

$Br_2 + NaOH/KOH$.

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basicity

- Basicity of Amine depend on 2 factors :-

1- Relative availibity of lone pair ∝ Basicity

2- Relative stability of NH_4^+ ion ∝ Basicity

3- $Pkb \propto \frac{1}{\text{basicity}}$

$Pkb = NH_3 = 4.76$

$Pkb = CH_3-NH_2 = 3.38$ (more stable)

$\ddot{N}H_3 + H^+ \longrightarrow NH_4^+$

$CH_3-\ddot{N}H_2 + H^+ \longrightarrow CH_3-NH_3^+$

inductive effect ↓ e⁻ donating so giving more support.

compare

2° amine > 1° amine > 3° amine

$R-\ddot{N}H-R$
- ↳ Stable NH^+ ion
- ↳ availibity of L.P.

$R-\ddot{N}H_2$
- ↳ less +ve charge
- ↳ attachment failure to L.P.
- ↳ Polarity decrease due to R-group

$R-\ddot{N}(R)-R$
- ↳ more steonic repulsion
- ↳ difficulty for r+n of L.P.

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Reaction

reaction of 1° amine with R-X, alkylation of 1° amine (ammonolysis)

→ $R-NH_2 + R-X \longrightarrow R-NH-R + HX$

1°-amine → 2°amine

→ $R-NH-R + R-X \longrightarrow R-\underset{\underset{R}{|}}{N}-R + HX$

2°-amine → 3°-amine

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

Quaternary salt

reaction with acid halide ($R-\overset{\overset{O}{\|}}{C}-X$)

$R-\overset{\overset{O}{\|}}{C}-X + H-NH-R \xrightarrow{+H} R-\overset{\overset{O}{\|}}{C}-NH-R$

1°amine → 2°amide.

$CH_3-\overset{\overset{O}{\|}}{C}-Cl + H-NH-CH_2-CH_3 \xrightarrow{H^{+}} CH_3-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_3$

acetyl chloride + ethylamine → N-ethylacetamide

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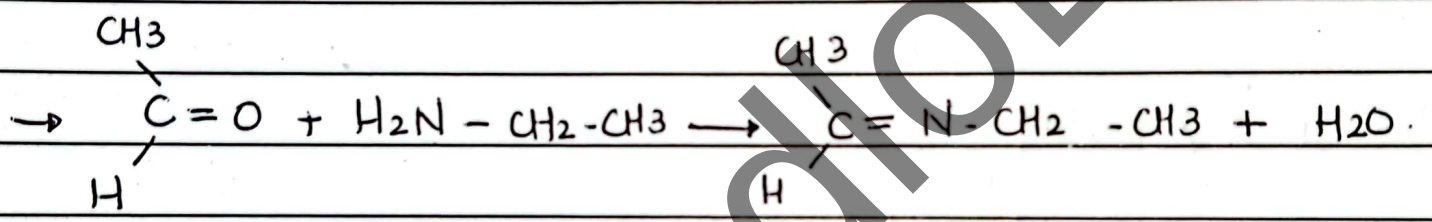
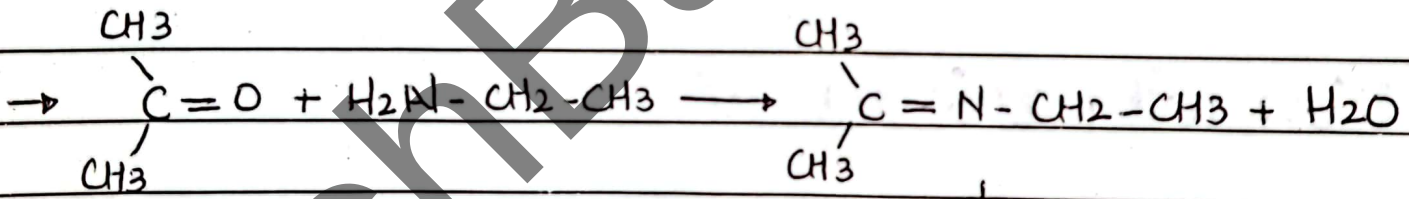
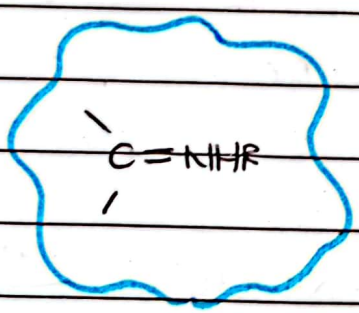
o $R-\overset{O}{\overset{\|}{C}}-NH_2$ (1° Amide)	$R-NH_2$ (1-amine)
o $R-\overset{O}{\overset{\|}{C}}-NH-R$ (2° Amide)	$R-NH-R$ (2° amine)
o $R-\overset{O}{\overset{\|}{C}}-\underset{R}{N}-R$ (3° Amide	$R-\underset{R}{N}-R$ (3° amine)

1°-amine with aldehyde and ketone (Schiff's base)



acetaldehyde (imine) (Schiff's base).





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reaction with nitrous acid (Diazonium salt)

or ↳ HNO_2

Preparation of diazonium salt/ion

$$R\text{-}NH_2 + HONO \xrightarrow[0\text{-}5^\circ C]{NaNO_2+HCl} R\text{-}N^+\equiv N + OH^- + H_2O$$

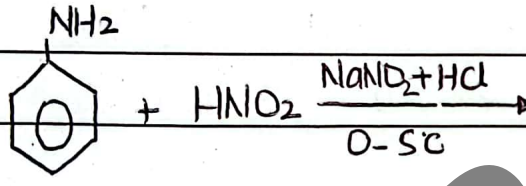
i-amine — nitrous acid — (diazonium ion).

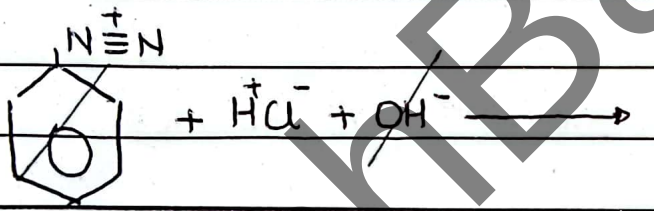
$$R\text{-}N^+\equiv N + H^+Cl^- + OH^- \longrightarrow [R\text{-}N^+\equiv N]Cl^- + H_2O$$

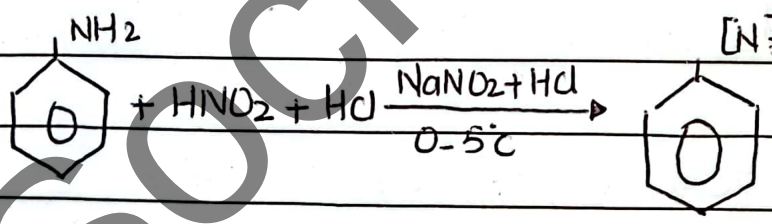
(diazonium salt)

$$R\text{-}NH_2 + HNO_2 \xrightarrow[0\text{-}5^\circ C]{NaNO_2+HCl} [R\text{-}N^+\equiv N]Cl^- + 2H_2O.$$

reaction with nitrous acid







HNO_3 (+5) = nitric acid

HNO_2 (+3) ↳ nitrous acid

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Revision Q18

Amines are more basic then analogous alcohols why?

It's due to several reasons. Some of them are below?

electron density:

- Nitrogen has lone pairs of e^- that are avalible for donation compared to oxygen in alcohol.
- In amines, this lone pair is less tightly bonded then Oxygen due to less electronegativity.

Resonance and Inductive effects:

- In alcohol, the lone pair on Oxygen can be involved in resonance with hydroxyl group which in turn reduces availibity of that lone pair for bonding with H^+
- But amines donot possess the resonance stabilization that delocalizes lone pair keeping it more avaliable for protonation.

Steric and Solvation:

- Sometimes, substituents can hinder the availibility of amines or alcohol to interact with H^+.
- Therefore, amines are more basic in less sterically hindered environment.

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How to Convert ethyl chloride To:-

a) ethyl cyanide:

$$CH_3-CH_2-Cl + KCN \text{ or } NaCN \longrightarrow CH_3CH_2CN + KCl$$

b) ethanal:

$$CH_3-CH_2-Cl + KOH \xrightarrow{H_2O} CH_3-CH_2-OH + KCl$$

c) Propane:

$$CH_3-Mg-Cl + CH_3-CH_2Cl \xrightarrow{\text{dry ether}} CH_3-CH_2-CH_3 + Mg\begin{matrix}-Cl\\-Cl\end{matrix}$$

d) n-butane

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

(wurtz synthesis double C-atom).

e) tetraethylead

$$4C_2H_5-Cl + Na_4Pb \longrightarrow (C_2H_5)_4Pb + 4NaCl$$

Amines are reduced by $LiAlH_4$. Give mechanism.

$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4} R-CH_2-NH_2.$$

Mechanism:

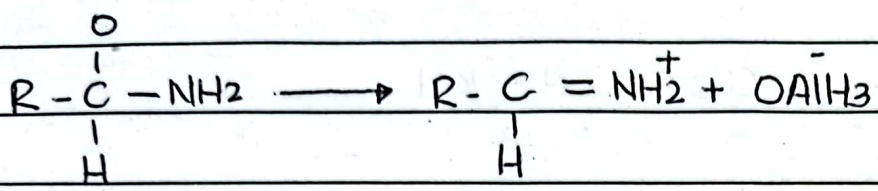
$LiAlH_4 \rightleftharpoons Li^+ + AlH_4^-$ (source of hydride ion)

Step #1

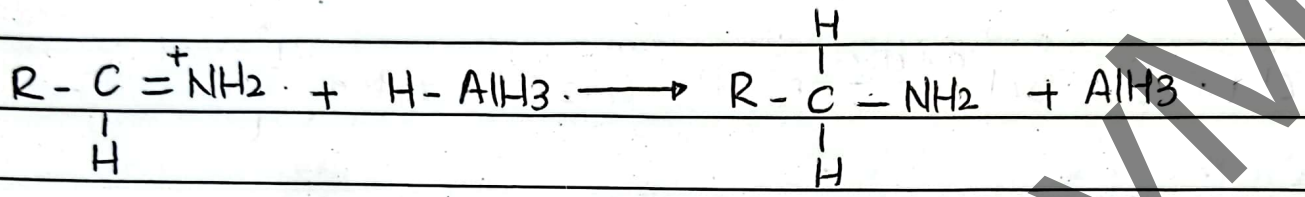
$$R-\overset{\overset{O}{\|}}{C}-NH_2 + H-AlH_3^- \longrightarrow R-\overset{\overset{OAlH_3}{|}}{C}-NH_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H$$

Date:

Step 2



Step 3



What are the main features that increases basicity of Amines?

Lone pair avalibity:

The more bne pair avaliable, the more protonation meaning more basicity.

electronegativity:

Nitrogen is less electronegative, which mean it holdē less tightly. make avalible to proton.

Subsituent effects:

- alkyl groups: electron-donating alkyl grap can increase basicity by donating e^- to N, making it more reactive.
- steric hindrance: Smaller substituents can ~~eh~~ enhance basicity.

hybridization:

sp^3 amines are more basic then sp^2 or sp because lone pair is in an orbitals that are more avalible for bonding.

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Quick Quiz 2

Protonation

A chemical process where proton (H^+ ion) is added to an atom, molecule or ion resulting in the formation of conjugate acid

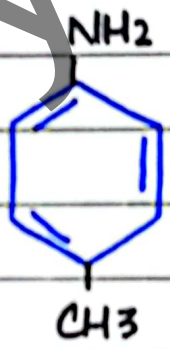
example

$$CH_3\text{-}Mg\text{-}Br + H\text{-}OH \xrightarrow{ether} CH_3\text{-}H^+ + O\text{-}MgBr \xrightarrow{H^+OH^-} CH_4 + Mg(Br)(OH)$$

3

toluidine

- chemical compound with formula C_7H_9N
- Molecule contain total 17 bonds including 8 non H-bonds, 6 multiple bonds and 6 aromatic bonds.
- It also contain 1 six-membered ring and 1 primary amine (aromatic).



p. toluidine.

17 bonds =
- 6 = C-C bond (benzene)
- 5 = C-H bond (benzene)
- 1 = C-N bond (amine)
- 2 = N-H bond (amine)
- 1 = C-C bond (methyl)
- 3 = C-H bond (methy)

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SLO

Why halogenation is not best method for Preparation of alkyl halides?

Halogenation is not the best Method because it often leads to a mixture of Products including different isomers and Polyhalogenated compounds making it difficult to obtain Single pure alkyl halide.

What is Reactivity order of alkyl halide in terms of bond polarity?

The reactivity order is :-

$$R\text{-}I < R\text{-}Br < R\text{-}Cl < R\text{-}F$$

because

→ Polarity $\propto$ Reactivity.

What is the Reactivity order of alkyl halides in terms of bond energy?

Reactivity order is :-

$$R\text{-}I > R\text{-}Br > R\text{-}Cl > R\text{-}F$$

Because

→ Bond energy $\propto \frac{1}{\text{reactivity}}$

Date:

Why Nucleophile is nucleus loving Specie?

Nucleophile is nucleus loving specie because it's electron-rich specie.

Why is electrophile electron loving specie?

Electrophile is electron loving specie due to deficiency of electrons

What is the effect of atomic size on leaving group?

Atomic Size ∝ Leaving group.

- a Large atom such as Iodide (I^-) Proves to be a good leaving group.
- A smaller atom like F^- hold on negative charge more tightly and it's a polar leaving group.

There are 2 molecules, one with hyperconjugation and one with Inductive effect but hyperconjugation one is more stable. Why?

The molecule with hyperconjugation is more stable because hyperconjugation allow it's electron density to spread over effectively and stabilize the molecule. Unlike inductive effect weakens quickly over distance and is less effective at stabilization.

Why Racemic mixture of Product is produced in SN1 reaction.

In SN1 reaction, planar carbocation is produced that can be attacked by the Nucleophile from either side, This result in 2 different enantiomers being formed in equal amounts creating a racemic mixture.

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When will alkyl halide go under substitution and elimination reactions.

- In case of aqueous KOH, substitution reaction takes place while in presence of alcoholic KOH elimination reaction happens.

Which compound is the most reactive in Organic chemistry?

Grignard Reagent is among the highly reactive Compound is Organic chemistry.

Why methyl amine is more basic than NH_3?

Methyl amine is more basic than ammonia (NH_3) because Methyl group donates electron density through inductive effect making nitrogen more electron rich and better at accepting protons. This increased electron density on Nitrogen in methyl amine enhance its ability to bond with H^+ making it stronger base than ammonia.

Why amines have high melting and boiling point than analogous alkanes?

Amines can form H-bonds due to nitrogen atoms that has lone pairs. H-bonding is stronger than L.D.F present in alkanes leading to stronger IMF in amines & higher M.P & B.P than alkanes.

Date:

Why Solubility of amine is greater than alkane?

Amines can form hydrogen bonds with water molecules so they interact more favourably with water & more soluble. On the other hand, alkanes can only interact with water through LDF which are sufficient for solubility.

In Grignard Reagent carbon is Nucleophile but in R-X carbon is electrophile. Why?

- In Grignard Reagent carbon is linked with Mg. Mg is less electronegative than carbon so magnesium develops partial +ve charge while carbon is partial negative.
- In alkyl halide, carbon is linked with halogen, halogen is more electronegative than carbon therefore carbon develops partial positive charge.

Aryl diazonium is more stable than alkyl diazonium.

Aryl diazonium salt is more stable because the aryl comp meaning benzene posses property of Resonance & hyperconjugation which makes diazonium a good supporter than alkyl which does not possess such property.

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- Primary alkyl or aryl amines yield diazonium salts.

Exercise

1. Select the right answer from the choices given with each question.

i. In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms;

a. Two b. Three c. One d. Four

ii. SN_2 reactions can be best carried out with:

a. Primary alkyl halides b. Secondary Alkyl halides

c. Tertiary alkyl halides d. All the three

iii. For which mechanisms, the first step involved is the same;

a. E_1 and E_2 b. E_2 and SN_2 c. E_1 and SN_2 d. E_1 and SN_1

iv. The rate of E_1 reaction depends upon;

a. the concentration of substrate

b. the concentration of nucleophile.

c. the concentration of substrate as well as nucleophile

d. None of the above.

. **Alkyl halides are considered to be very reactive compounds towards nucleophiles, because:**

a. they have an electrophilic carbon

b. they have an electrophilic carbon and a good leaving group

c. they have an electrophilic carbon and a bad leaving group

d. they have a nucleophilic carbon and a good leaving group

i. **Which one of the following is not a nucleophile:**

a. H_2O b. H_2S c. BF_3 d. NH_3

i. **Double bond is formed as a result of;**

a. Substitution reactions b. Elimination reactions

c. Addition reactions d. Rearrangement reactions

ii. **Which of the following alkyl halides cannot be formed by direct reaction of alkanes with halogen**

a. RBr b. RCl c. RF d. RI

. **Grignard's reagent gives alkane with;**

a. Water b. Ethylamine c. Ethanol d. All of these

Action of alkyl halides with Na metal yield;

a. Alkanes b. Alcohols c. Alkenes d. Phenols

. **Alkyl halides react with excess of ammonia to give;**

a. 1^0-amine b. 2^0-amine c. 3^0-amine d. all

i. **Among the alkyl halides the primary alkyl halides always follow the mechanism;**

a. SN_1 b. SN_2 c. Both a and b d. None of these

nswer the following questions briefly.