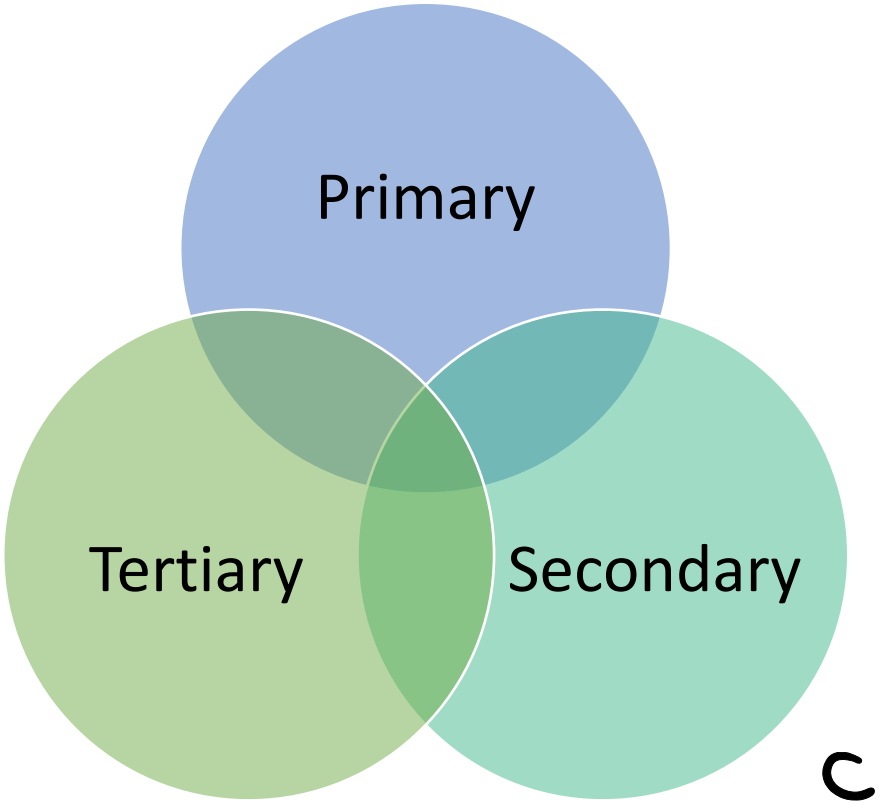
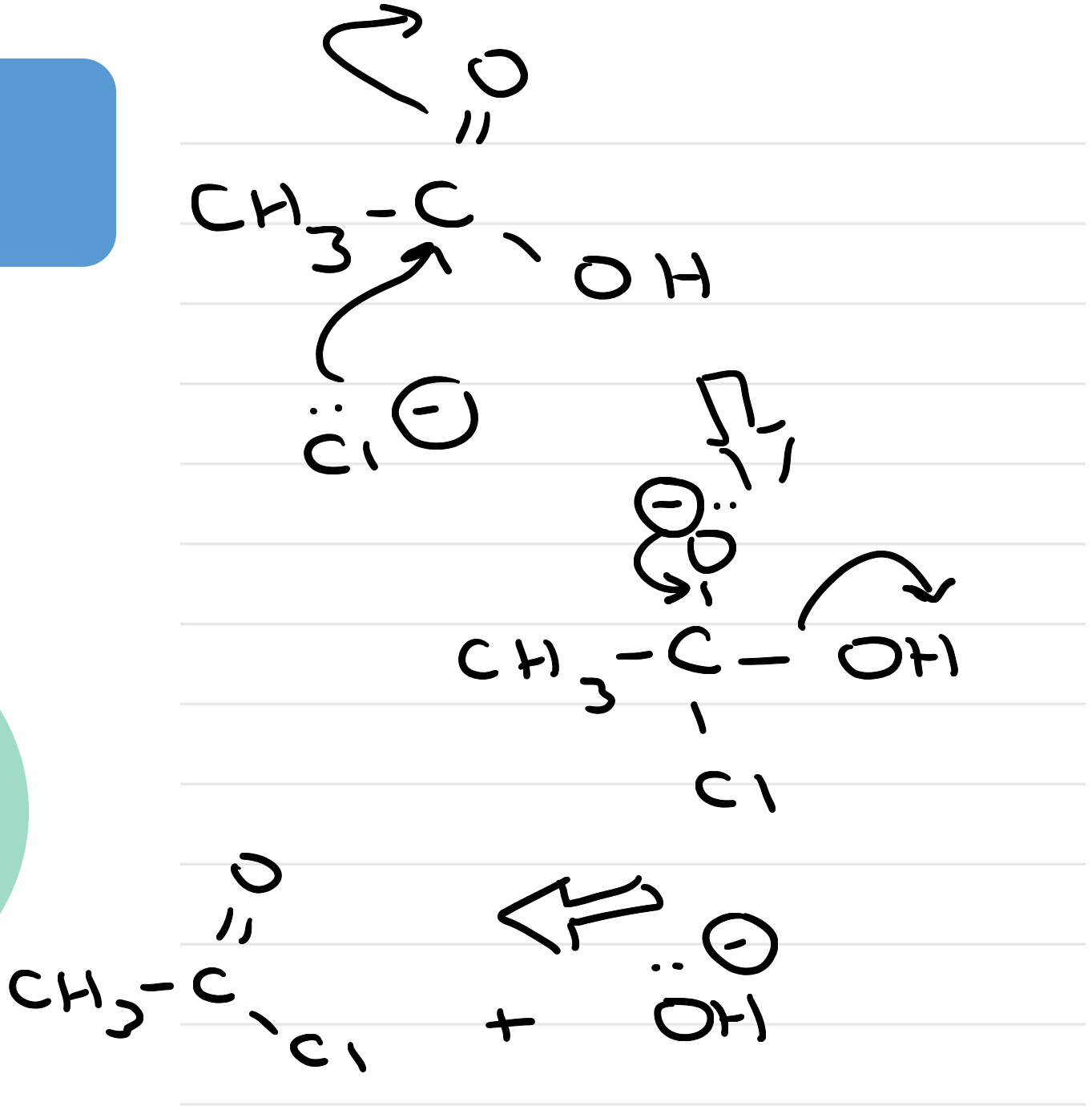
Amines

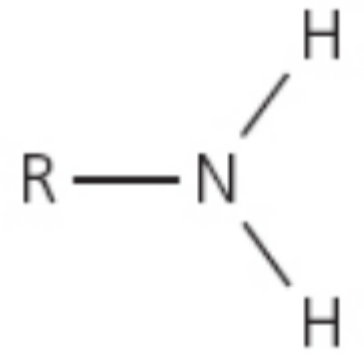
- The structure of amines
- Naming amines
- Preparation of primary amines
- Preparation of aromatic amines
- Base properties of amines
- Nucleophilic properties of amines

The structure of amines





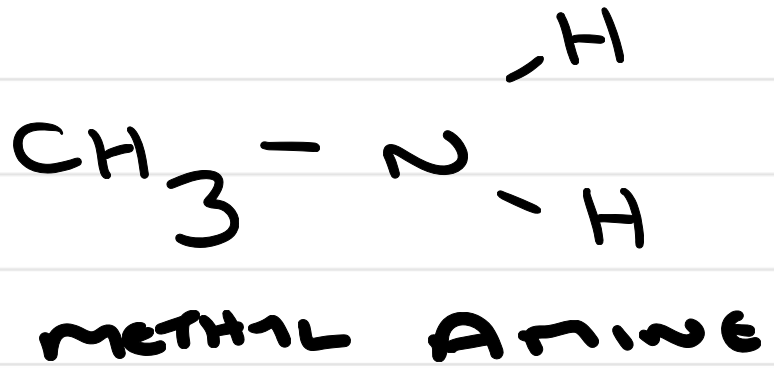
Primary



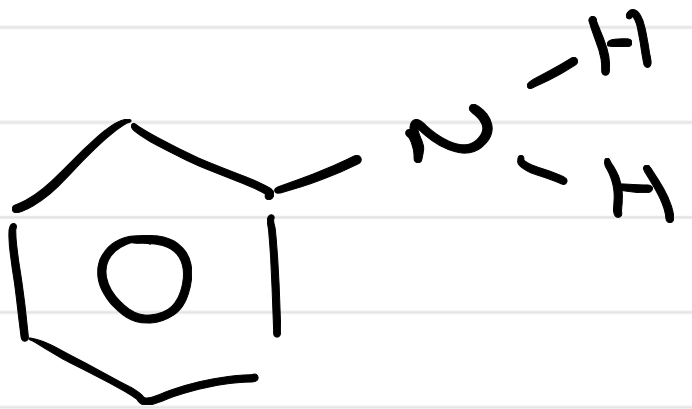
1 alkyl group

OR

1 ARYL.

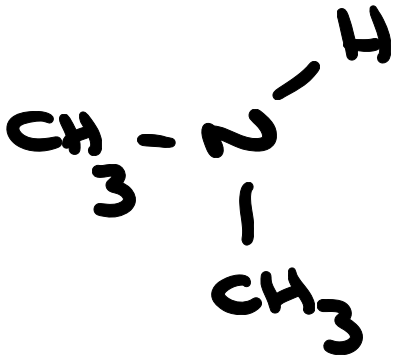


METHYL AMINE

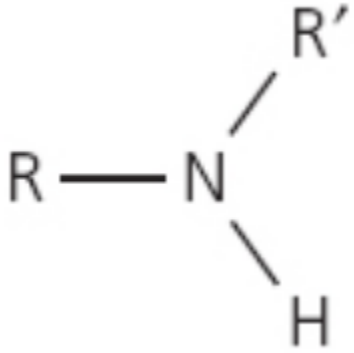


PHENYL AMINE

Secondary

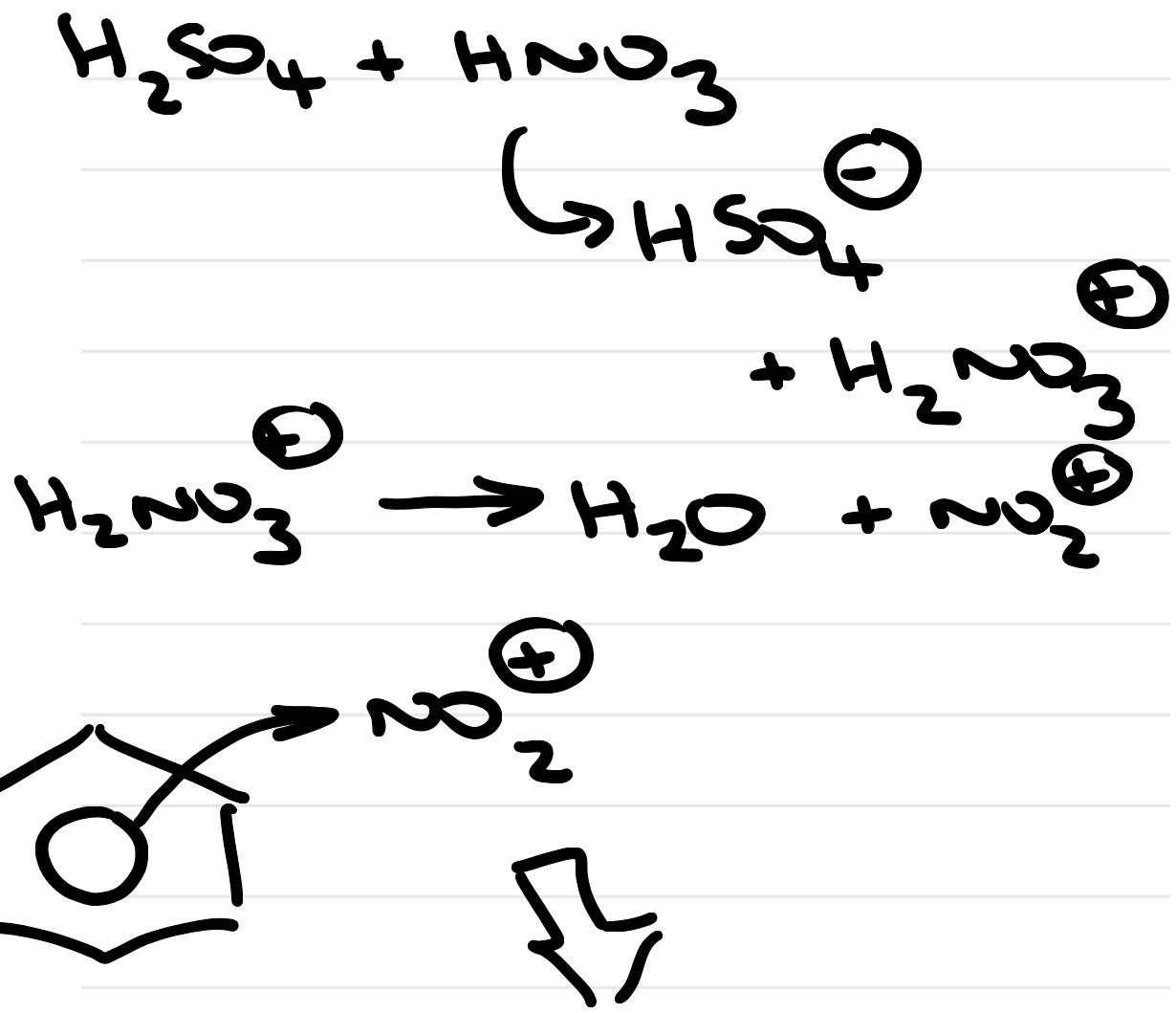


Di-methyl-amine



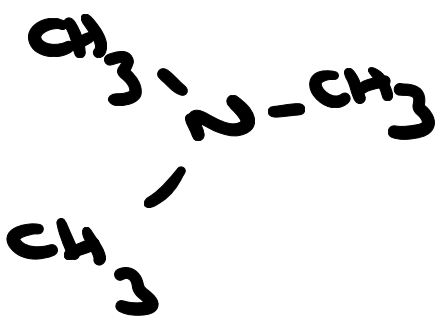
2 alkyl groups

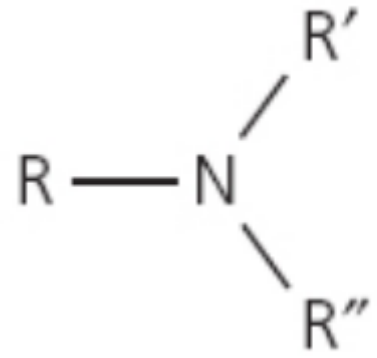
Nitrobenzene



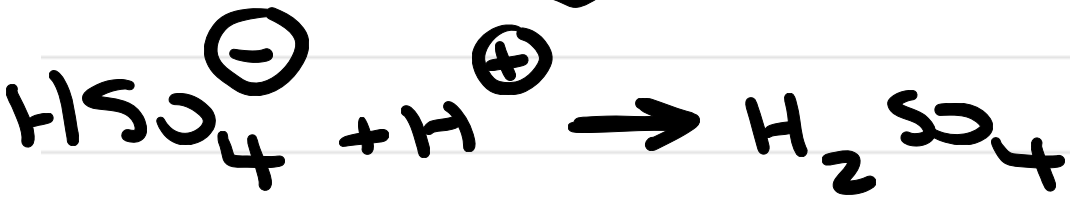
Tertiary

TRI-METHYL-AMINE





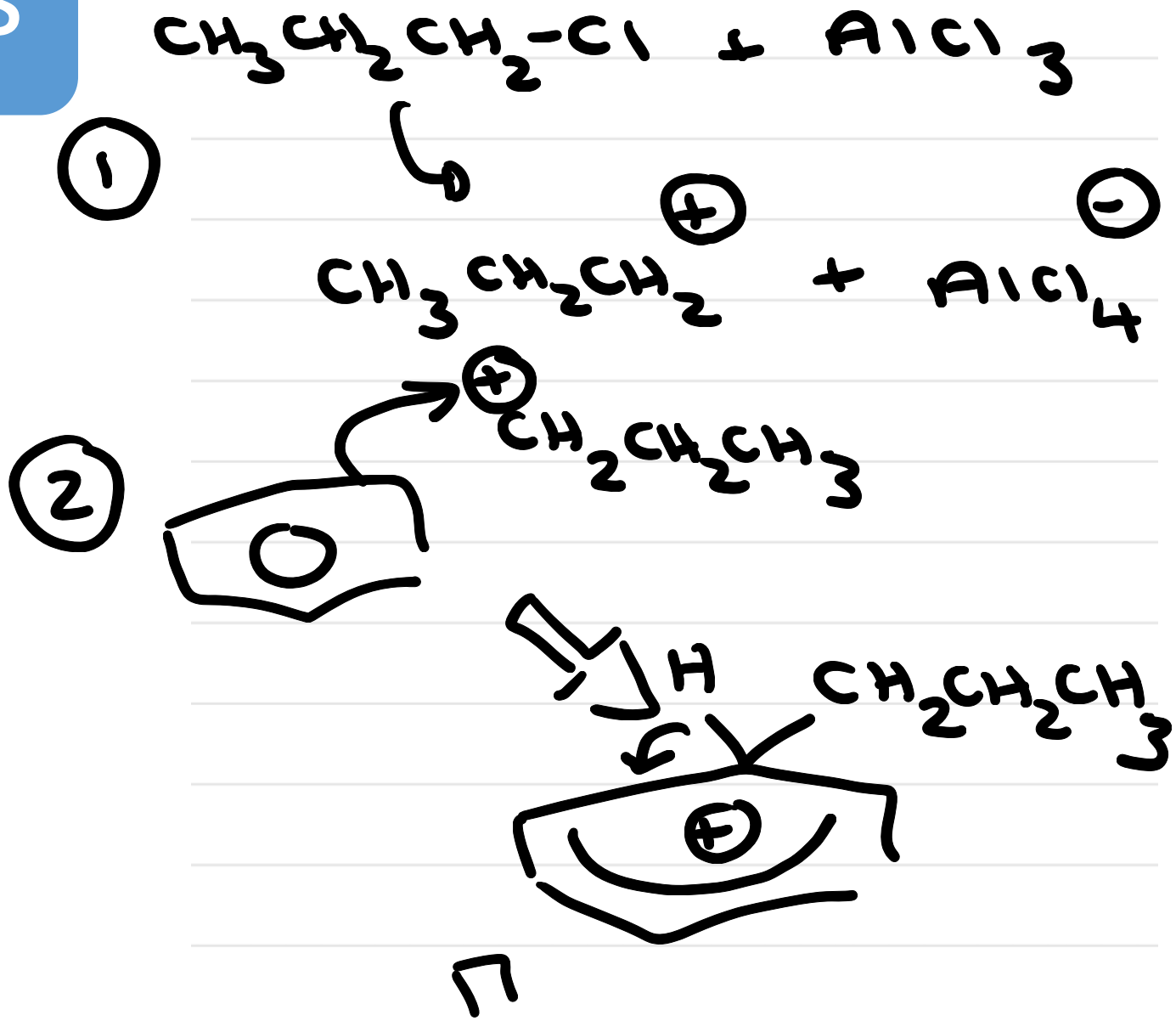
3 alkyl groups



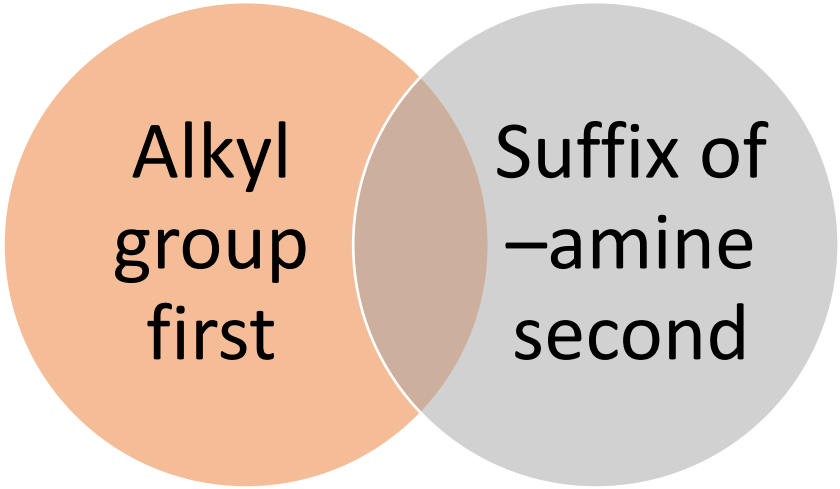
F.C. CATALYST

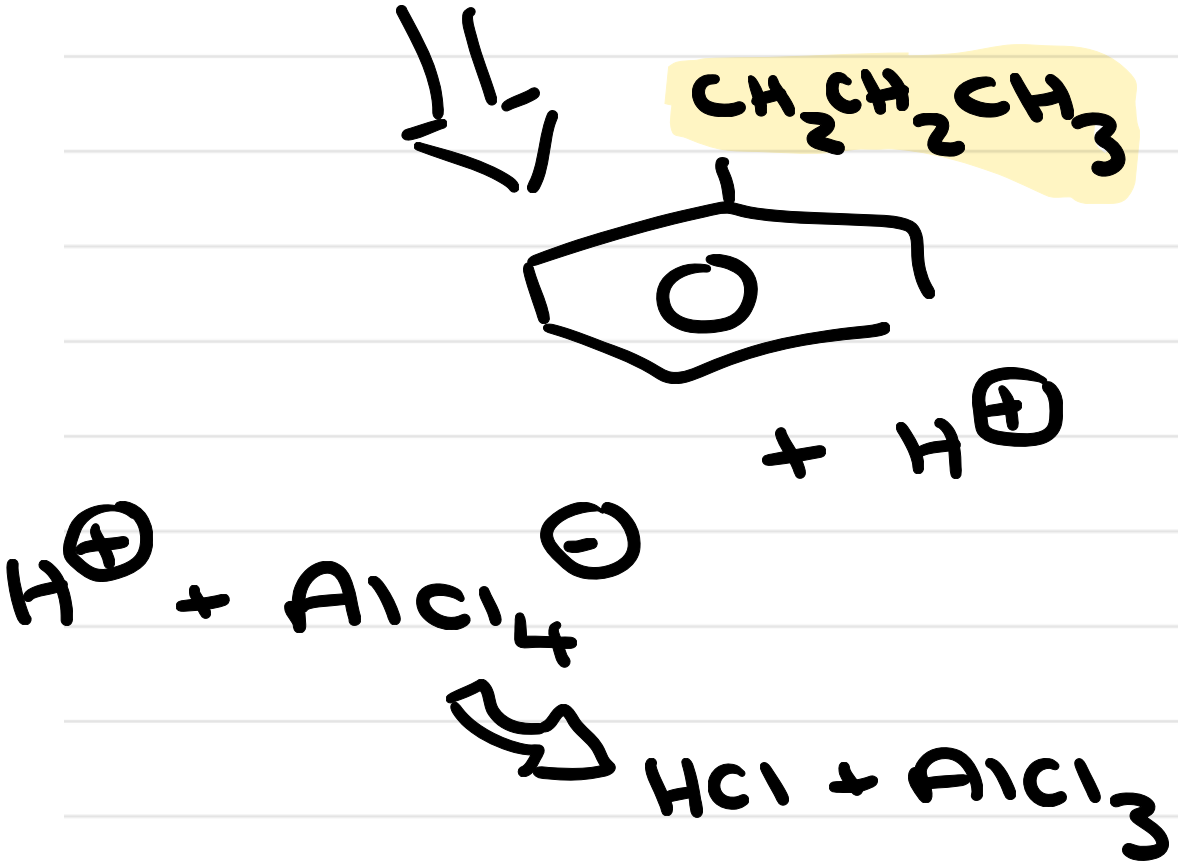
Naming amines

- Rules
- Simple alkanes
- Using amino
- Using *N*-
- Hierarchy of organic compounds



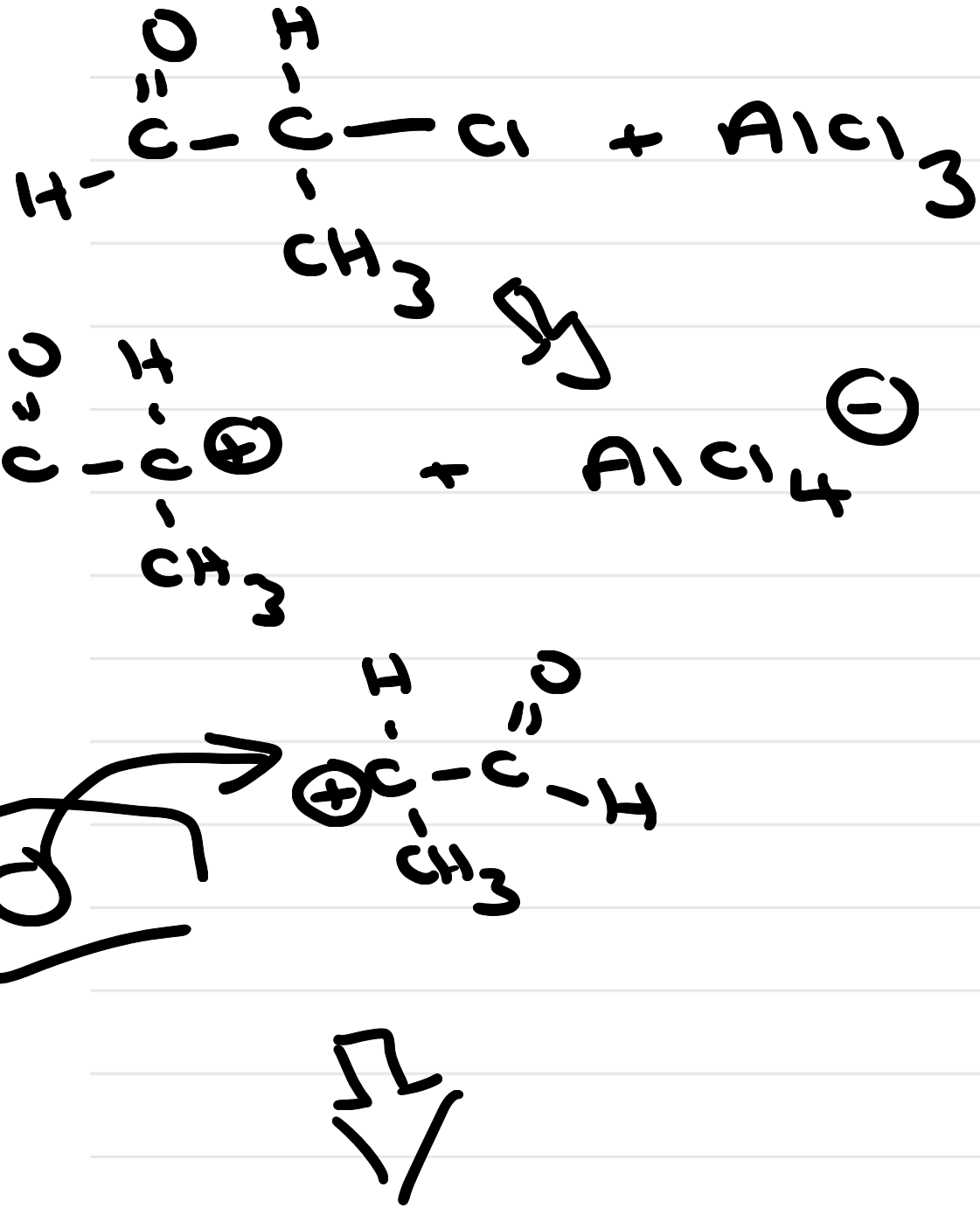
Naming rules

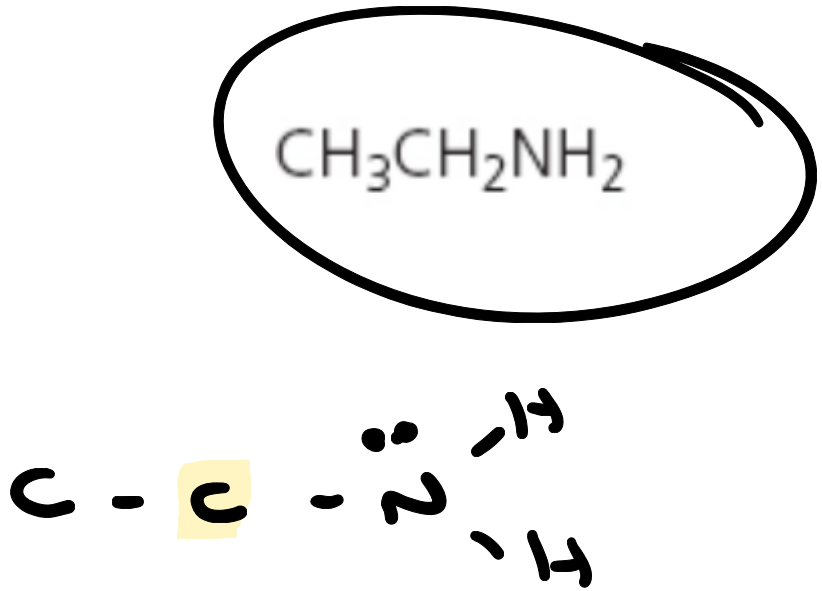




EXAMPLE 2

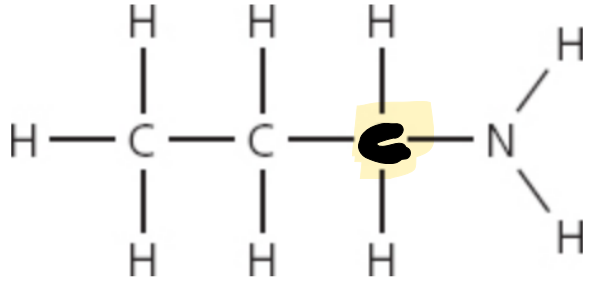
Ethyl amine



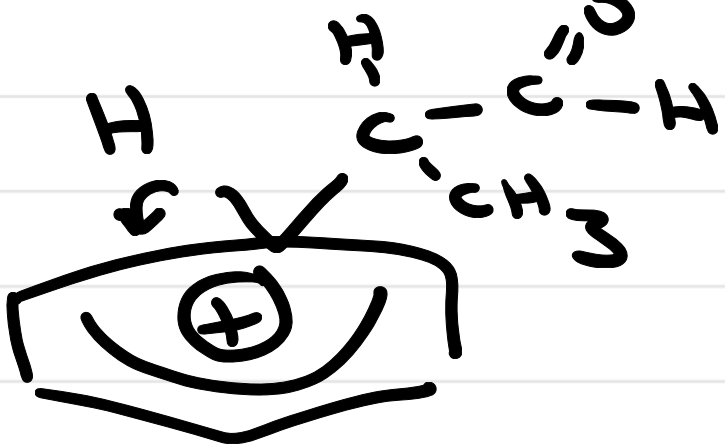


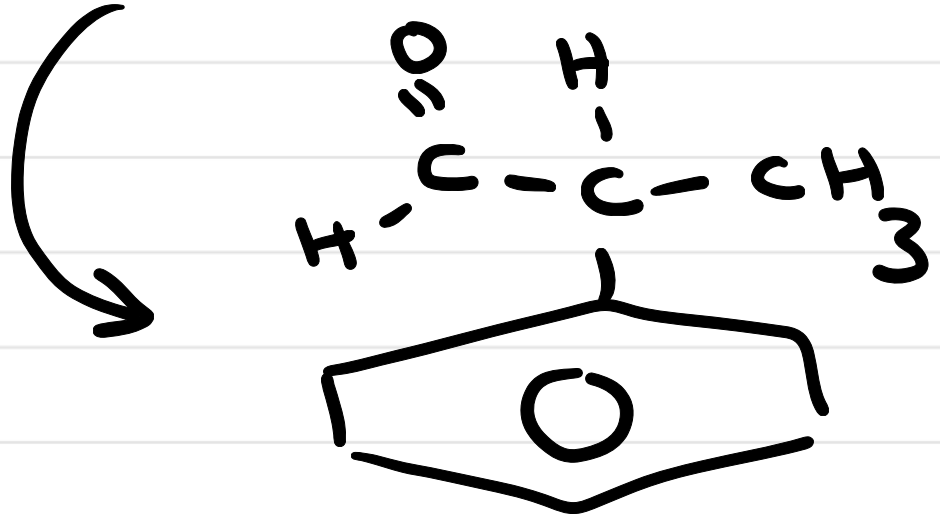
Primary

Propyl amine



Primary





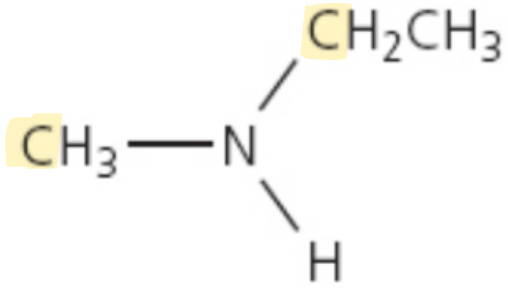
More primary amines

Butyl Amine

Pentyl - Amine

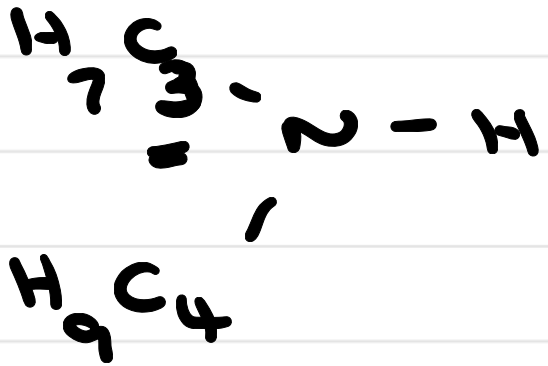
Pentyl - Amine

Ethyl methyl amine



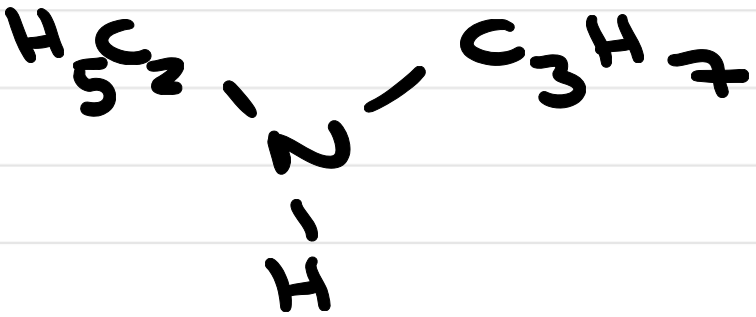
(Secondary)

ALPHABETICAL

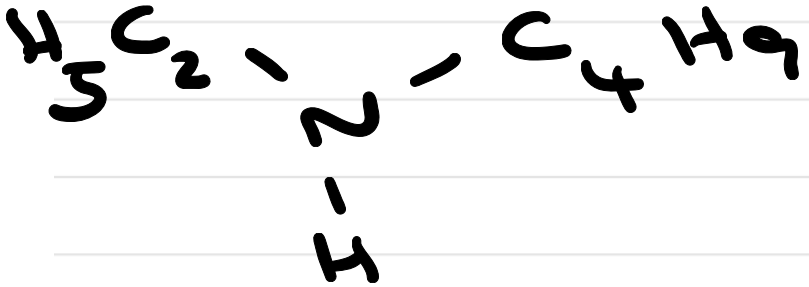


+ Butyl Propyl Amine

More secondary amines

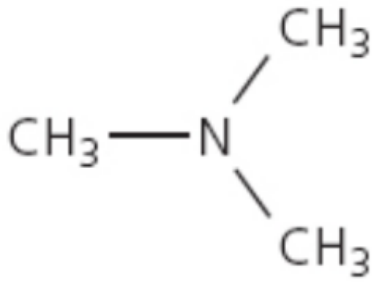


Ethyl Propyl Amine



Butyl Ethyl Amine

Tri methyl amine



1 4

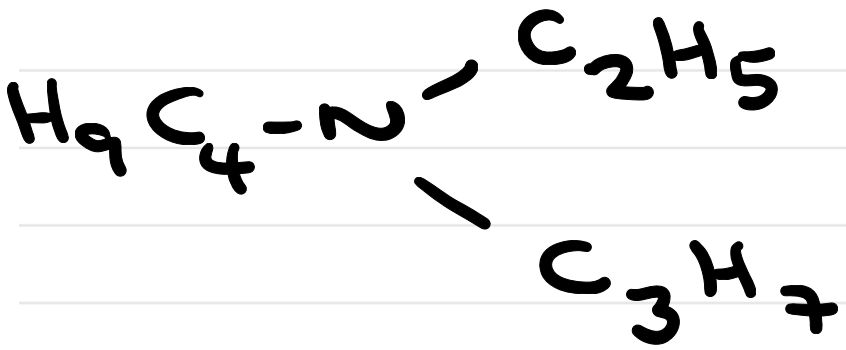
C - C - C - C

|

NH_2

2 - AMINO - BUTANE

Naming tertiary amines

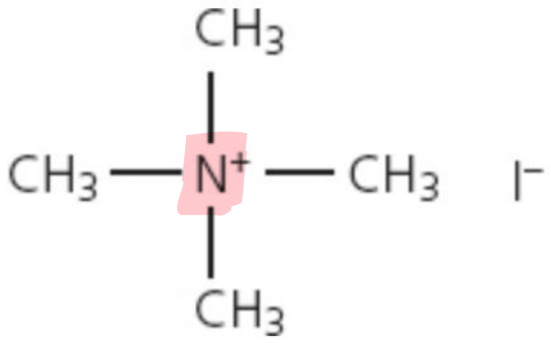


Butyl Ethyl Propyl Amine

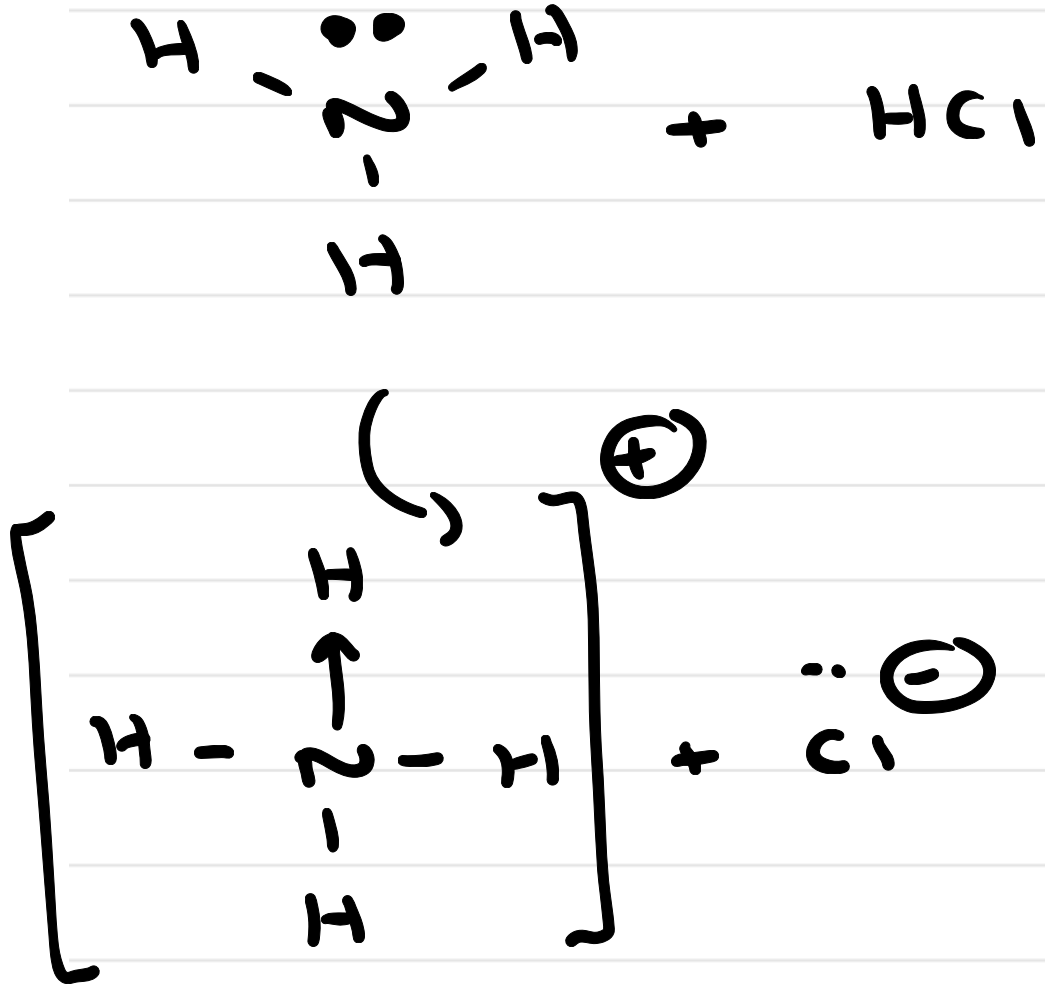
Classify as primary, secondary or tertiary

Amine	Primary	Secondary	Tertiary
methylamine	✓		
ethylamine	✓		
dimethylamine		✓	
phenylamine	✓		
triethylamine			✓

Quaternary ammonium compounds



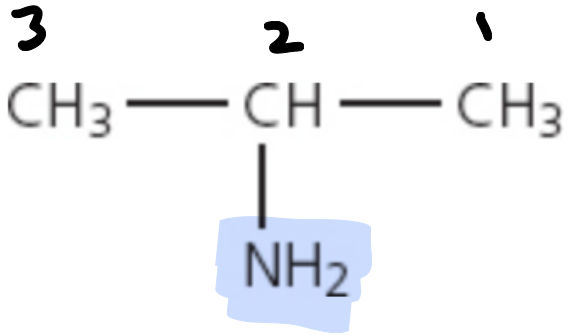
Produced from tertiary amines when nitrogen's lone pair forms a dative bond



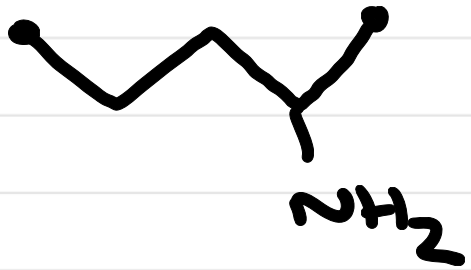
Using amino

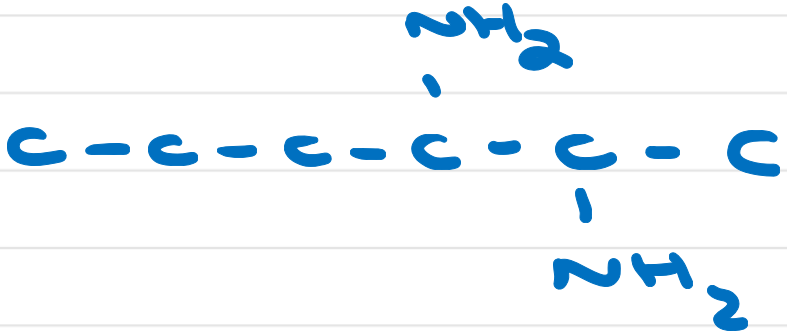
If you need to show the position of the NH_2 group use the *amino* form of naming

2-amino propane



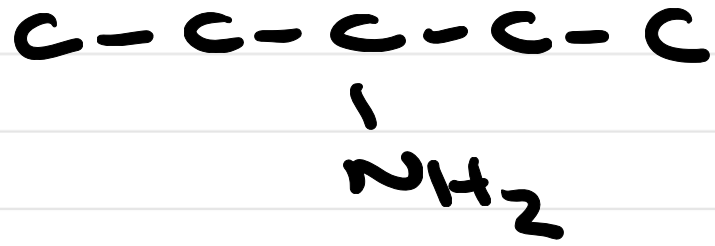
Draw structure for 2-amino pentane



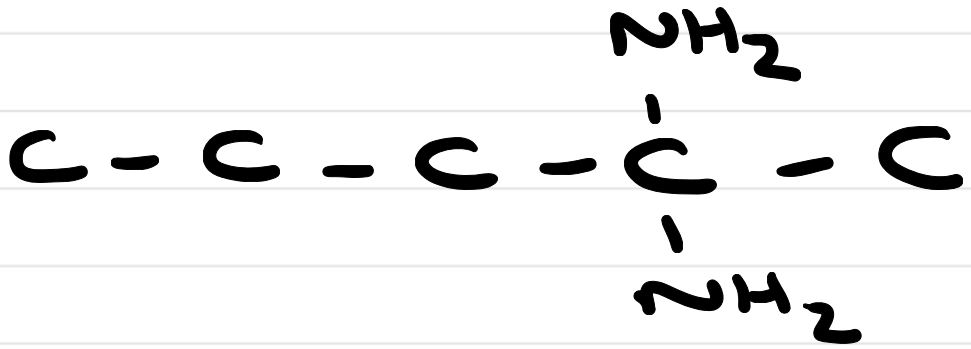


2,3 DIAMINO HEXANE

Draw structure for 3-amino pentane

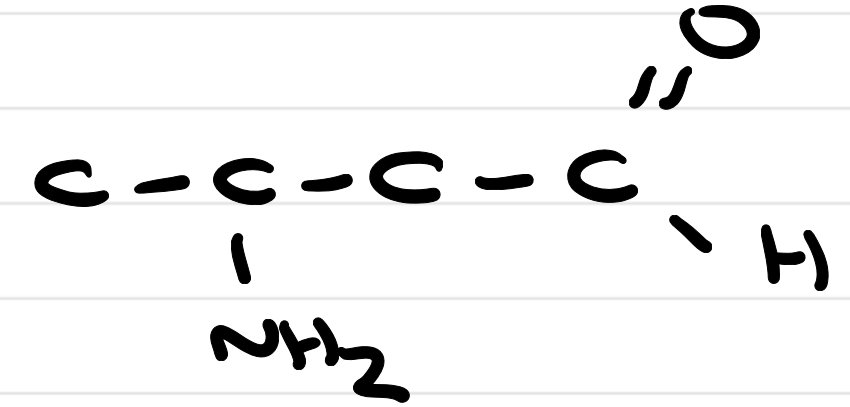


2,2 di amino pentane

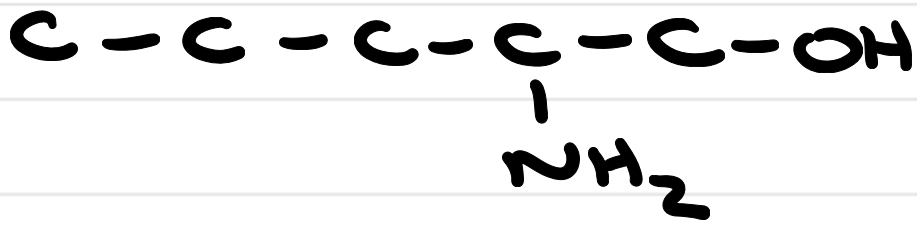


Hierarchy of organic chemistry

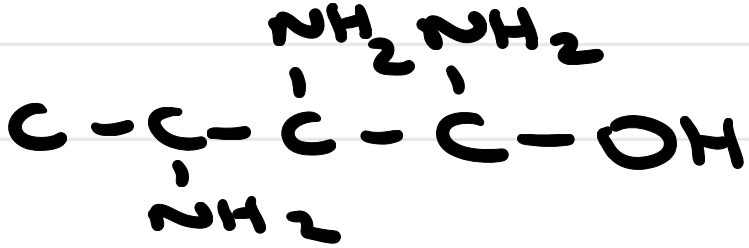
1 carboxyl (–COOH)
2 aldehyde (–CHO)
3 ketone (–CO–)
4 hydroxyl (–OH)
5 amines (–NH_2, –RNH, –R_2N)
6 alkene (–C=C–)



3 AMINO BUTANAL



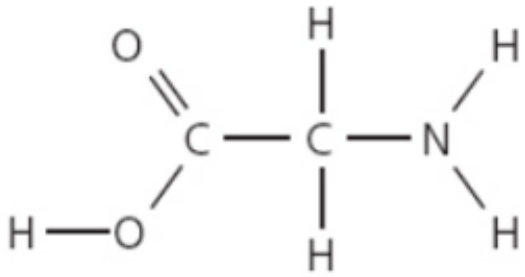
2 AMINO PENTANOL

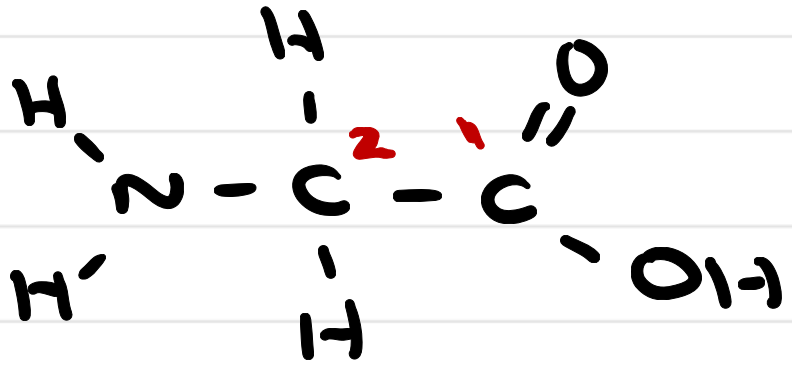


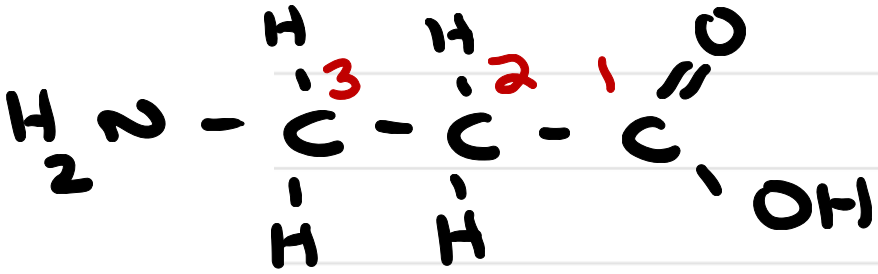
2,3,4 TRI AMINOBUTANOL.

Amino ethanoic acid

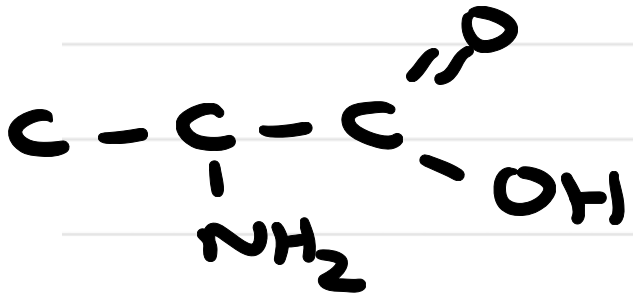
Less priority | Top priority



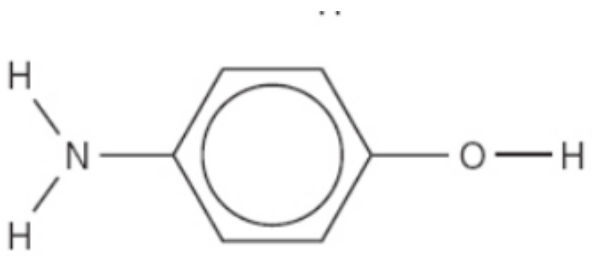


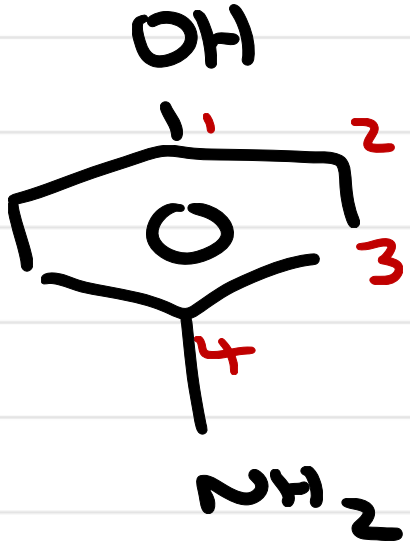


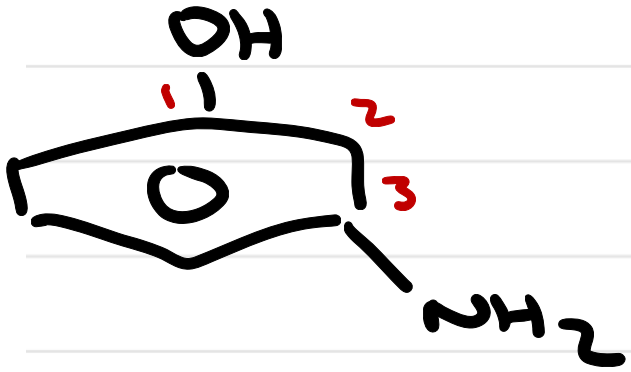
3 Amino Propanoic Acid



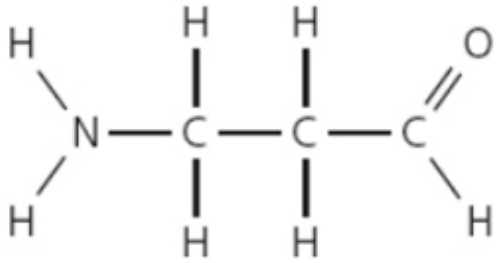
4 –amino phenol

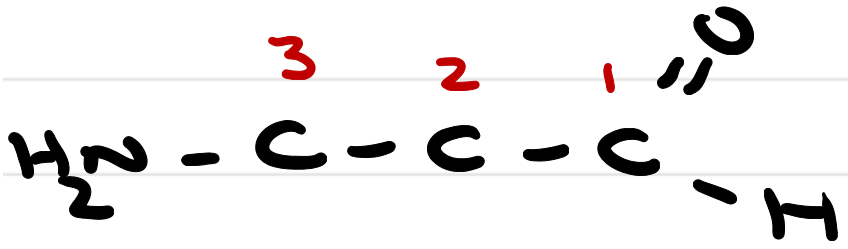


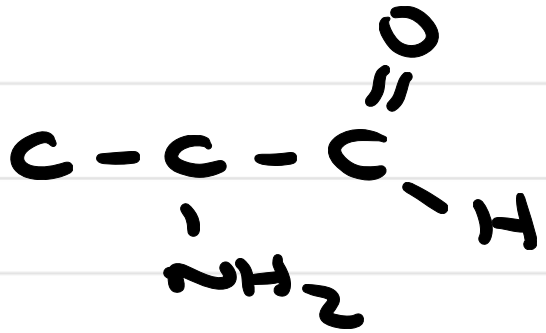




3-amino propanal



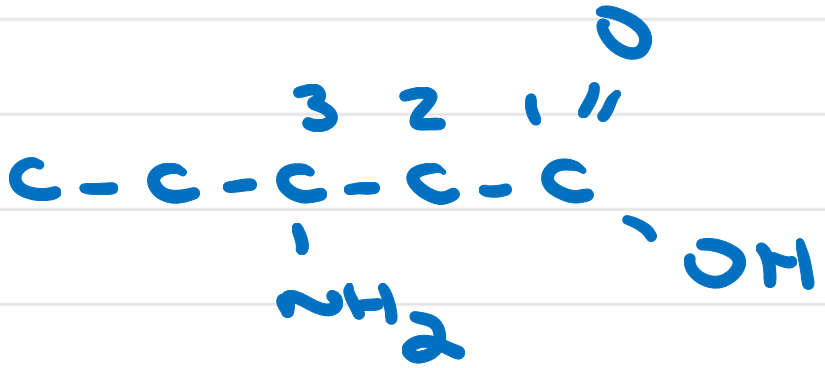




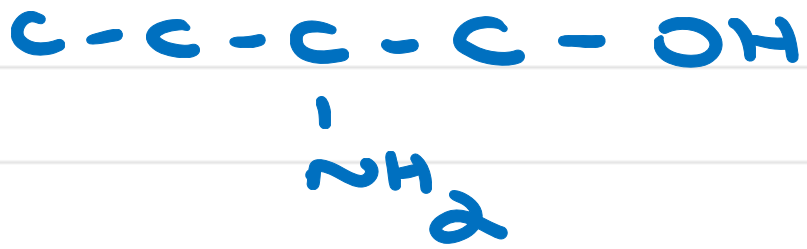
Using *N*-

The prefix *N*- is used to show that the alkyl group is attached to the main chain via the nitrogen atom

3 Amino Pentanoic Acid

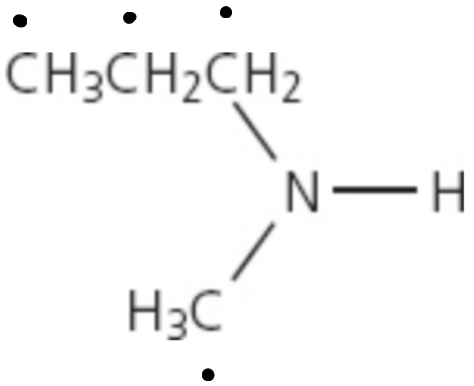


2 Amino Butan-1-ol

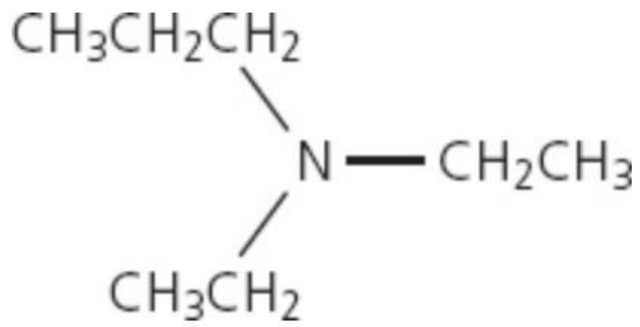


N-methyl propyl amine

N - METHYL PROPYL AMINE



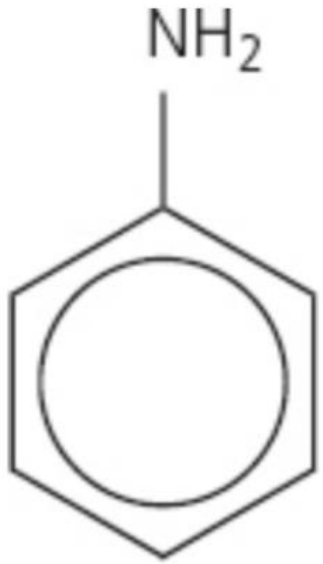
N,N-di ethyl propyl amine



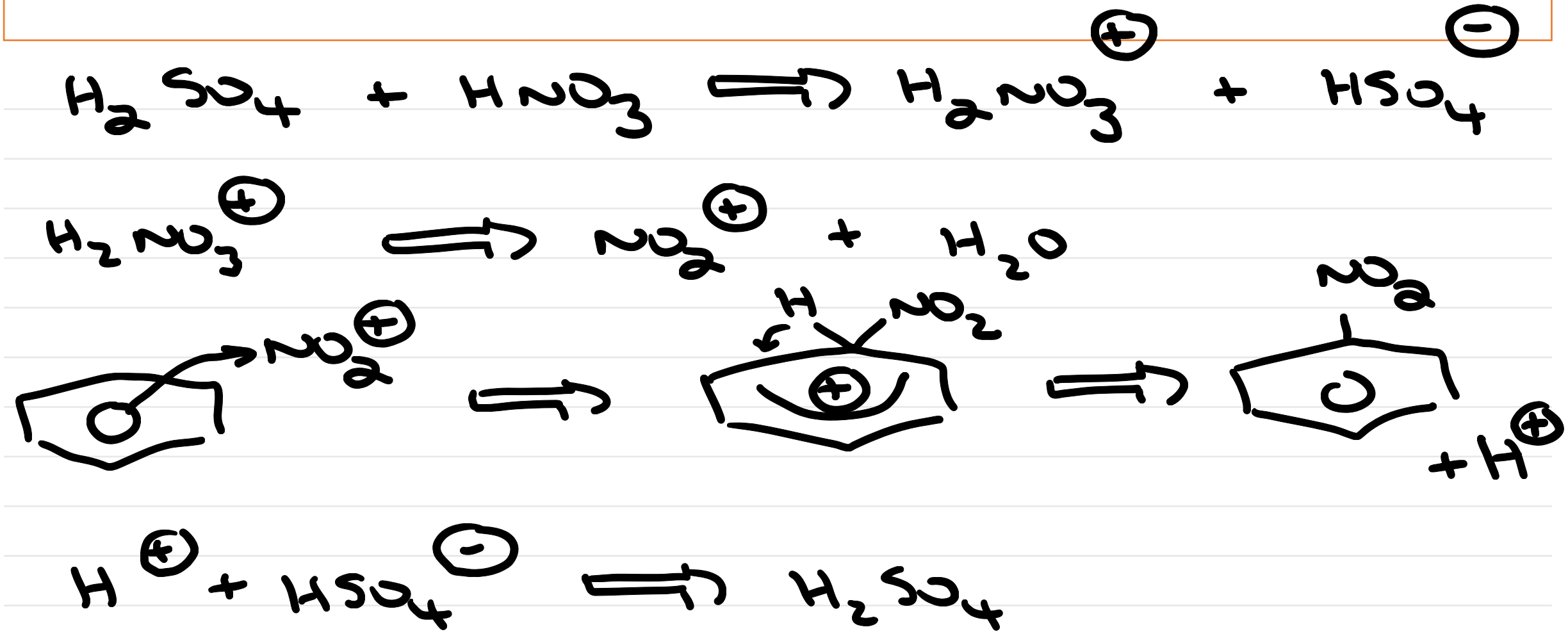
Using *Phenyl*

The prefix phenyl is used to show that the nitrogen is joined to a benzene ring

Phenyl amine



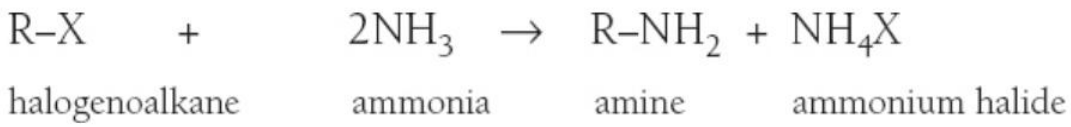
Notes:


$H_2SO_4 + HNO_3 \rightleftharpoons H_2NO_3^{\oplus} + HSO_4^{\ominus}$
$H_2NO_3^{\oplus} \rightleftharpoons NO_2^{\oplus} + H_2O$
NO_2
H
NO_2
$+ H^{\oplus}$
$H^{\oplus} + HSO_4^{\ominus} \rightleftharpoons H_2SO_4$

Preparation of primary amines

- From haloalkanes
- From nitriles
- Sn/HCl
- $LiAlH_4$/ether

Producing amines haloalkanes



Haloalkanes react with ammonia to produce amines

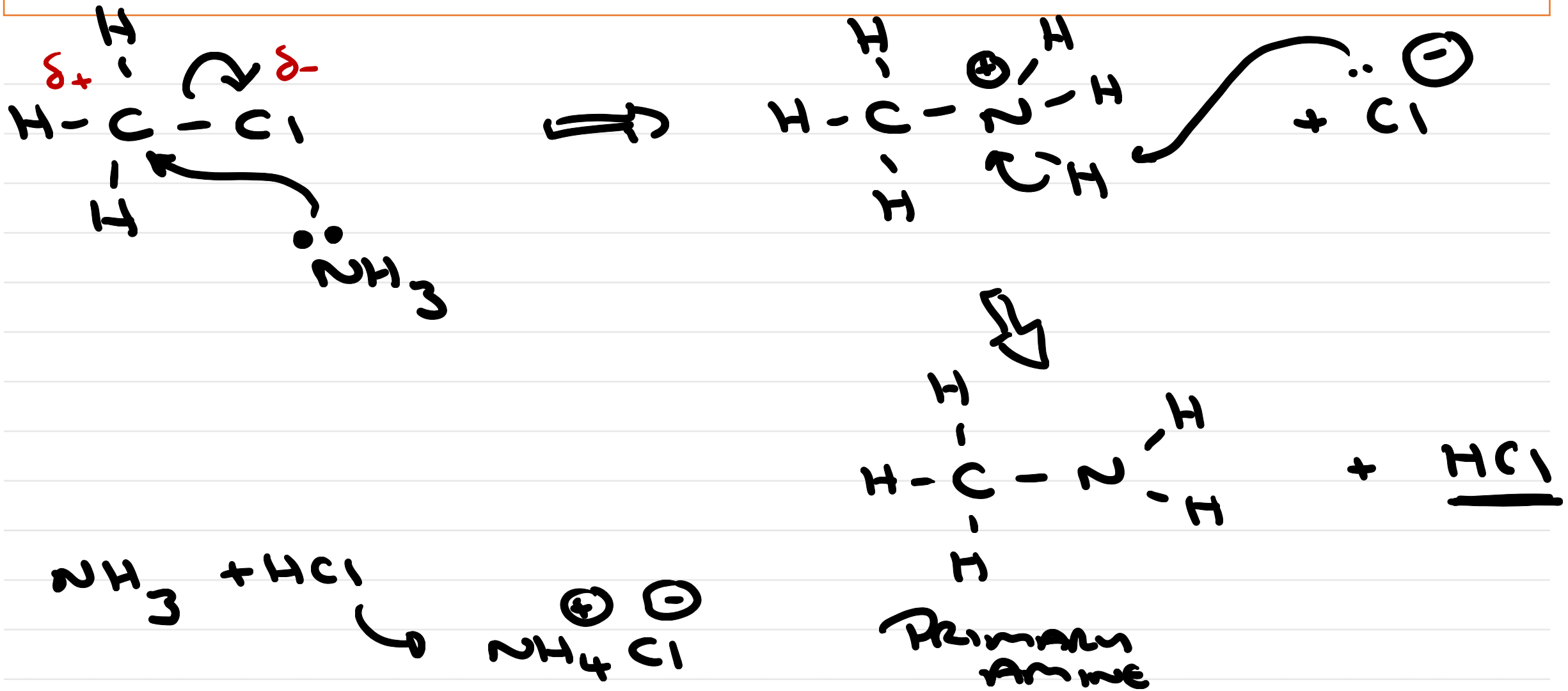
Sealed flask

Excess ammonia in ethanol

Nucleophilic substitution

Notes:

must use Excess of Ammonia.

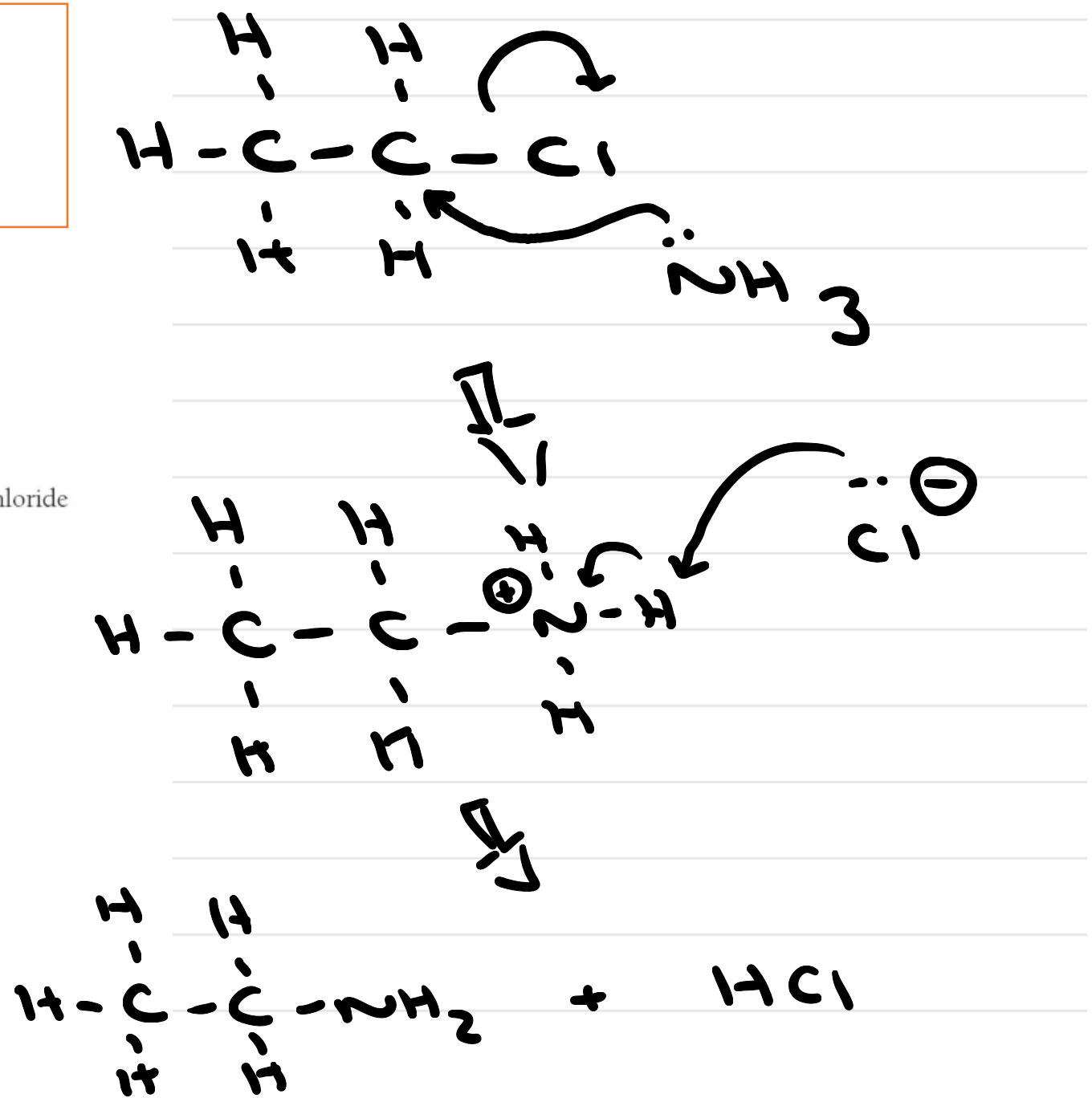


Preparation of ethylamine

$$CH_3CH_2Cl + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Cl$$

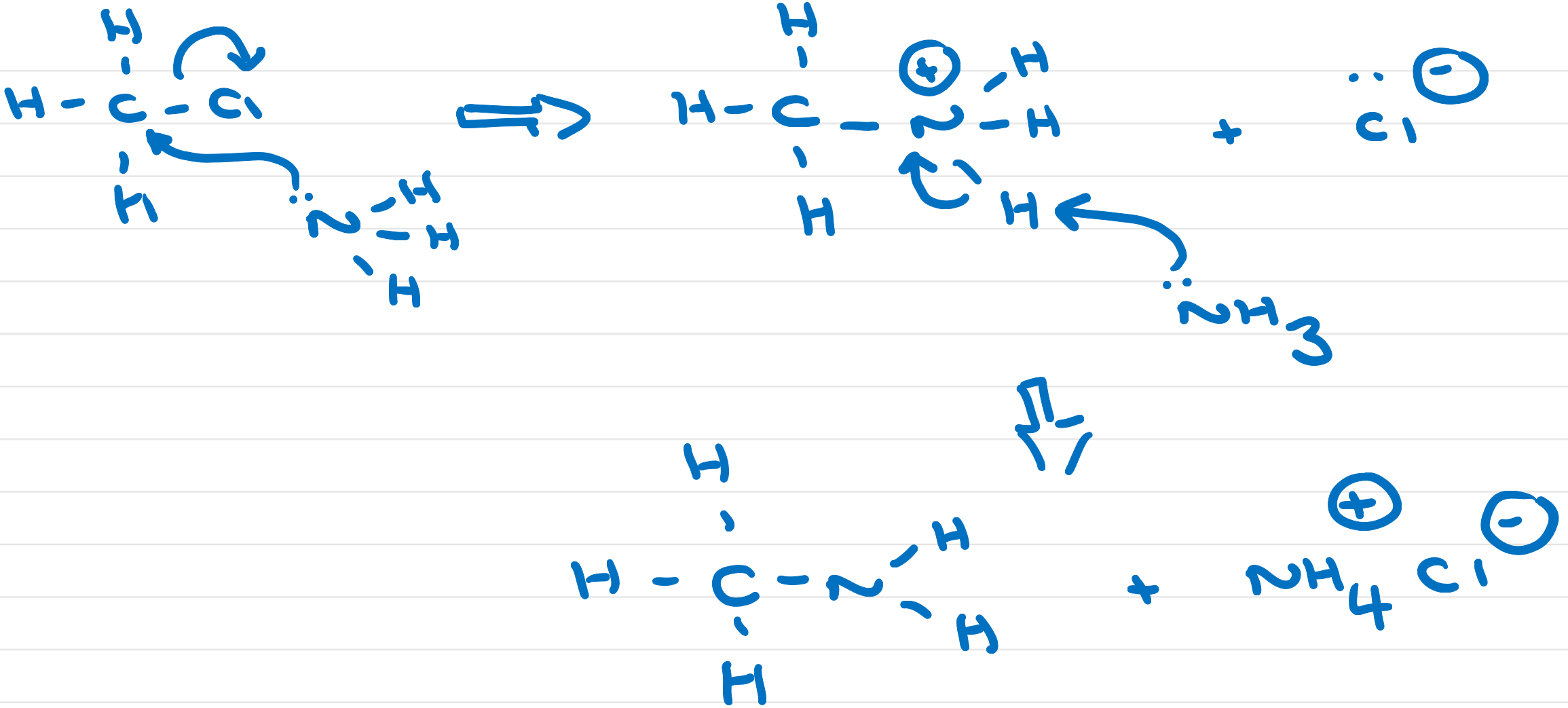
chloroethane — ammonia — ethylamine — ammonium chloride

Excess ammonia needs to be used



Mechanism for preparation of ethylamine

Notes:

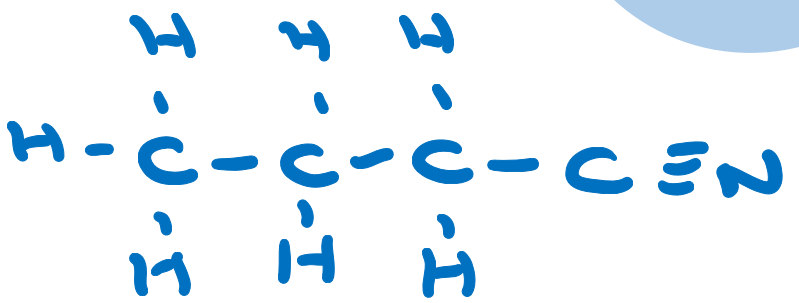


Producing amines from nitriles by reduction using H_2

$$R-C\equiv N + 2H_2 \rightarrow R-CH_2NH_2$$

Conditions: Hydrogen and Nickel catalyst

ETHANE NITRILE



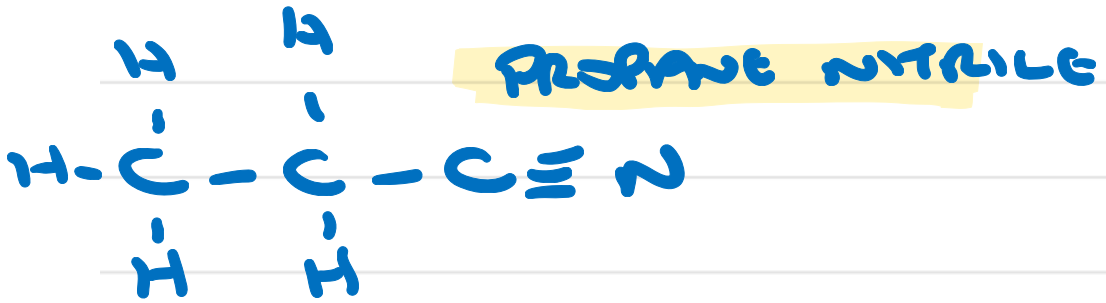
BUTANE NITRILE

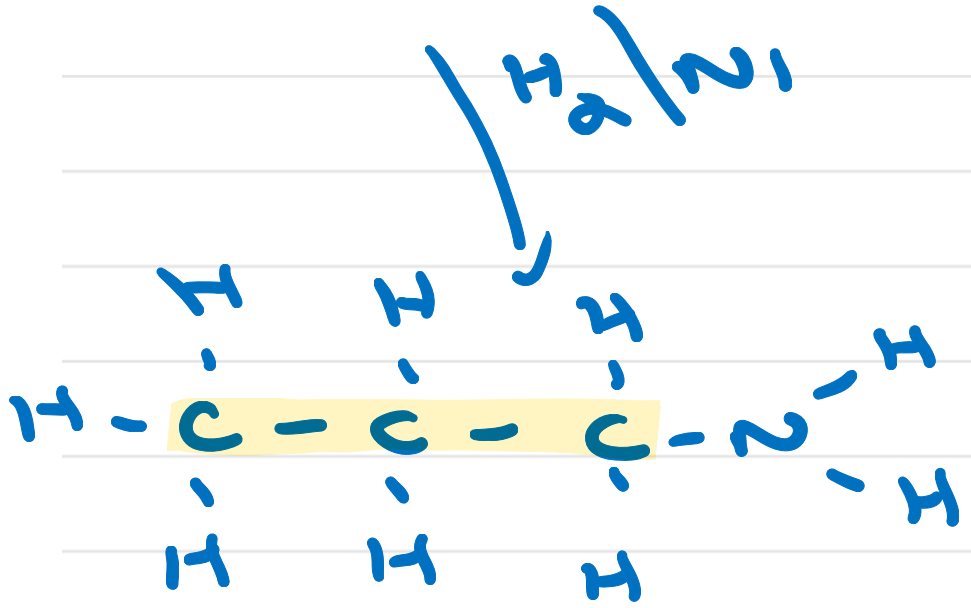
Preparation of ethylamine using H_2/Ni

$$CH_3CN + 2H_2 \rightarrow CH_3CH_2NH_2$$

ethanenitrile — ethylamine

HYDROGENATION





1 AMINO PROPANE OR PROPYL AMINE

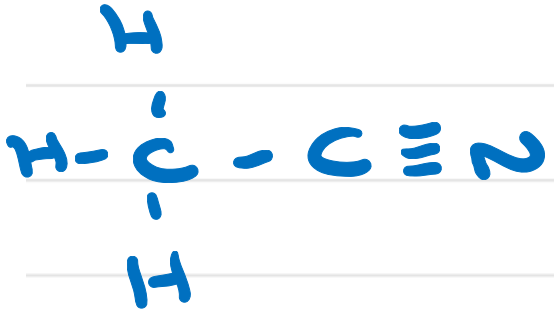
Producing amines from nitriles by reduction using $LiAlH_4$ - ALIPHATIC

(LITHIUM ALUMINIUM HYDRIDE)

$$R - C \equiv N + 4[H] \rightarrow R - CH_2NH_2$$

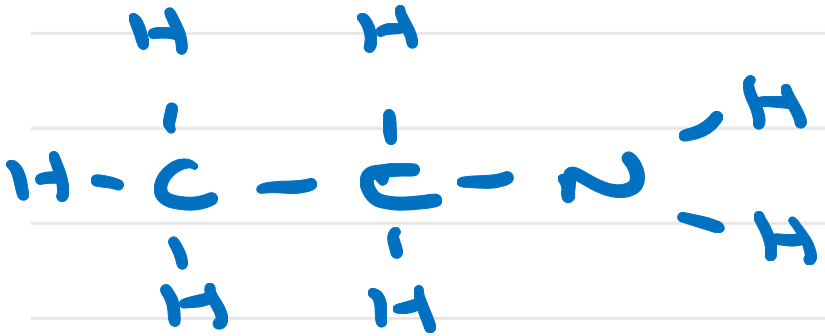
Conditions: $LiAlH_4$ in dry ether

Preparation of propylamine using $LiAlH_4$/ether



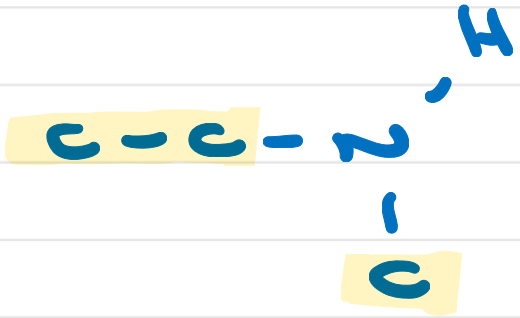
$$CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2NH_2$$

propanenitrile propylamine

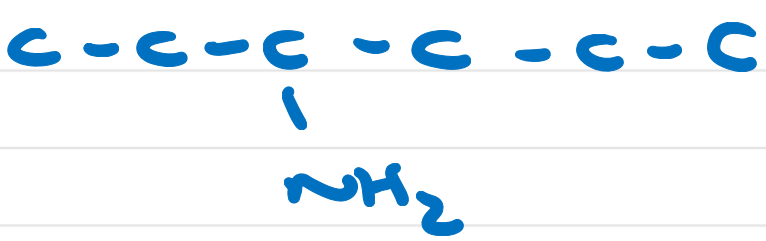


* COUNT THE NUMBER OF HYDROGENS!

Notes:



ETHYL METHYL AMINE



3 AMINO 1-HEXANE

Preparation of aromatic amines

- Production of phenylamine
- Phenyl ammonium ion
- Removing phenyl ammonium ion
- Benzene to phenylamine

OR

Butyl Amine

1 Amino Butane

Production of phenylamine

Exams

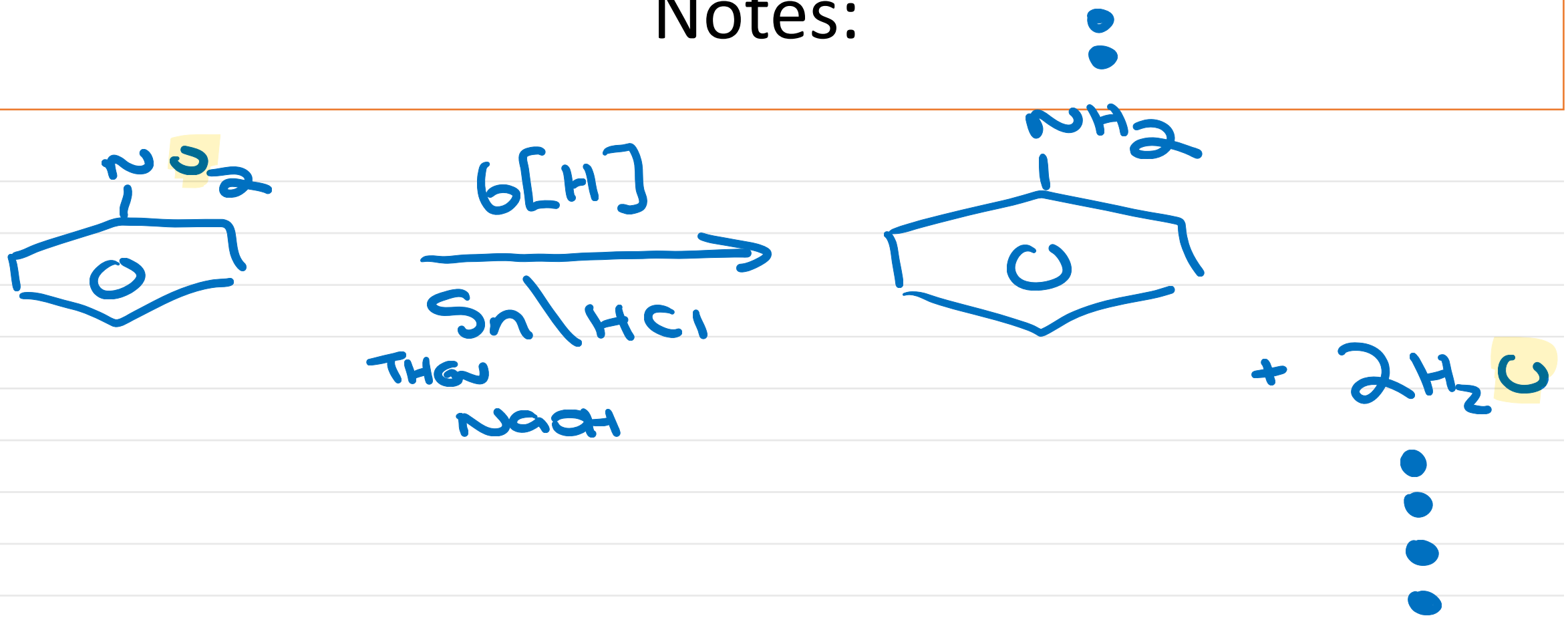
nitrobenzene phenylamine

Reduction of nitrobenzene

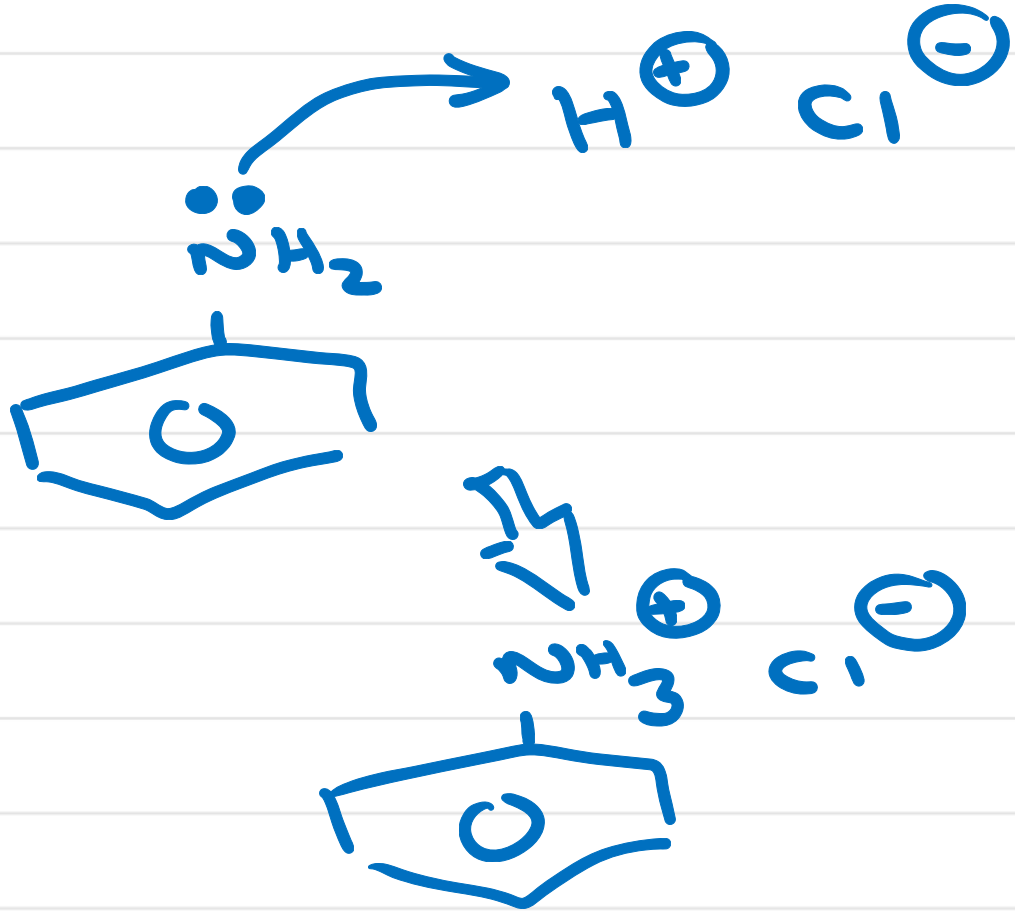
Sn/excess HCl followed by conc. NaOH

Remember this.

Notes:

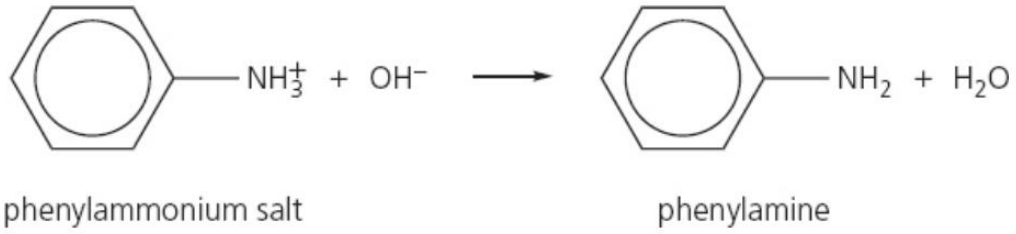


Phenylammonium ion

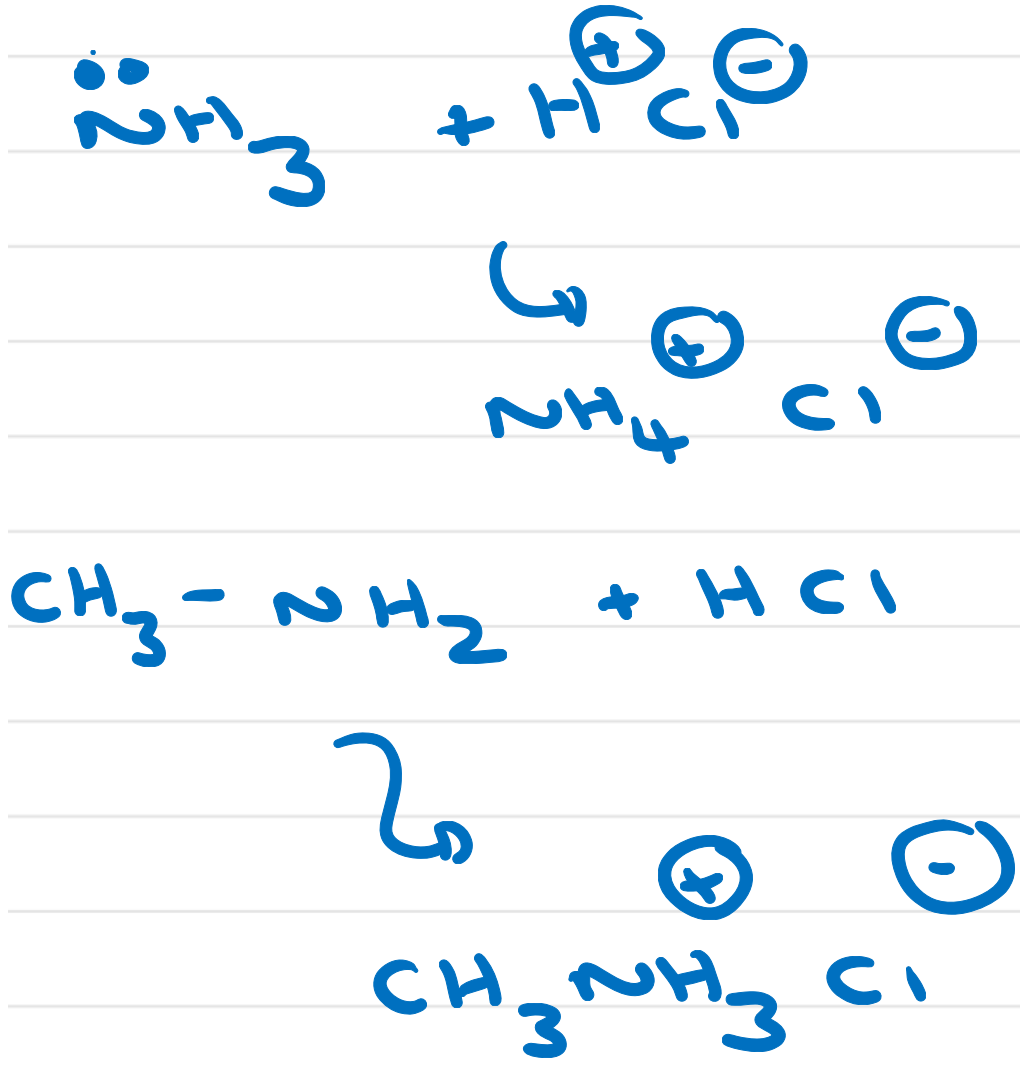


This is produced because of the excess of acid

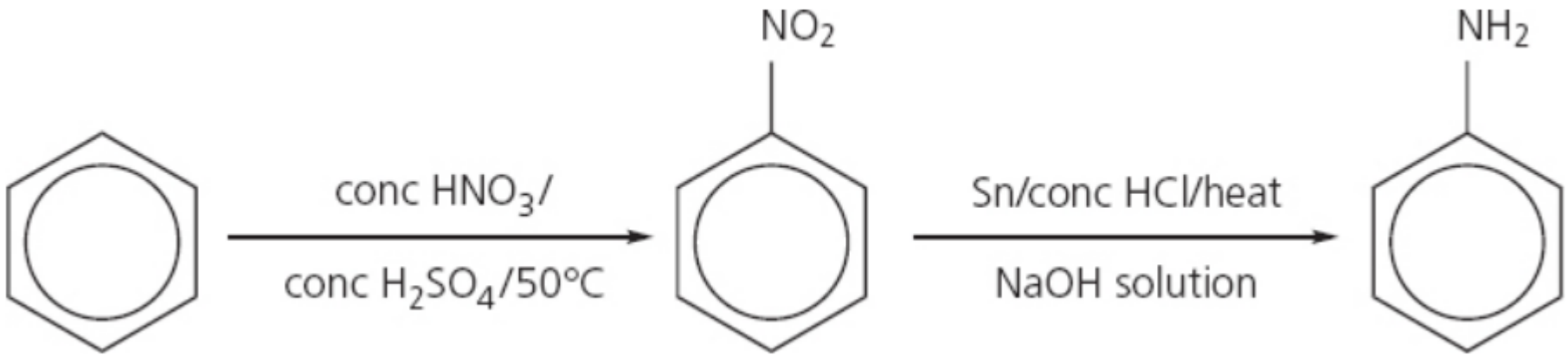
Removing the phenylammonium ion



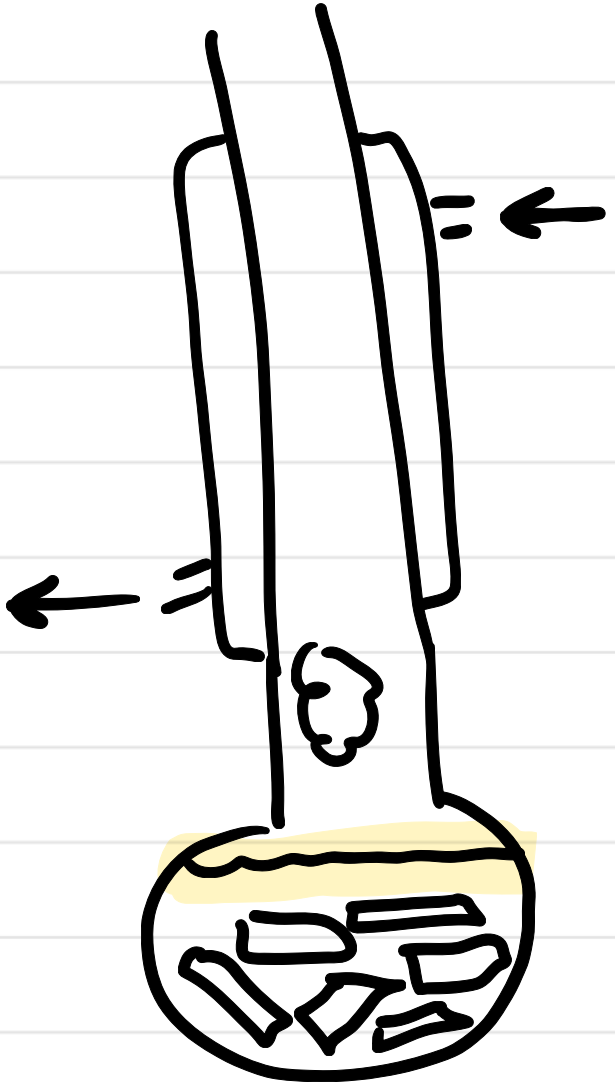
Add sodium hydroxide



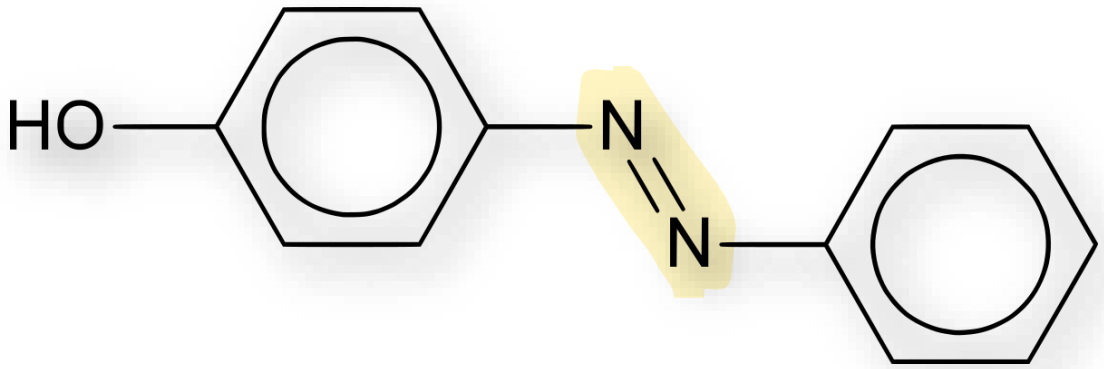
Popular exam synthetic pathway



Azo dyes



Azo bridge



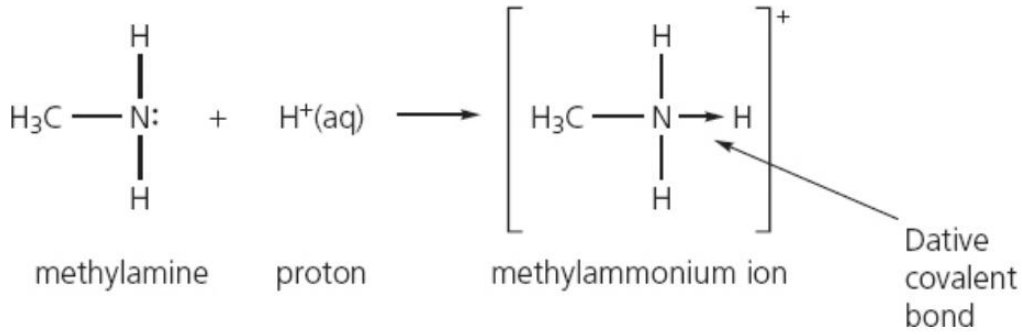
Base properties of amines

- Bases
- Dative bonds
- Base reactions of amines
- Ammonia + acids
- Amine + acid
- Ammonia + water
- Amine + water
- Mechanisms
- Basic strength

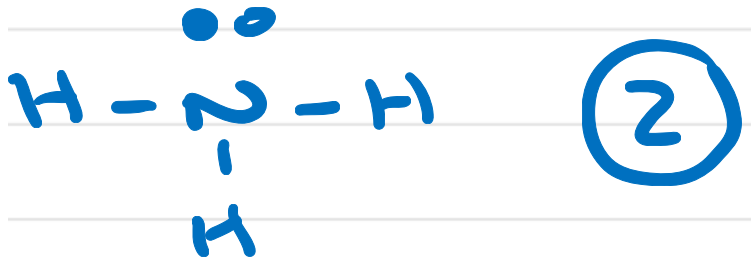
Bases

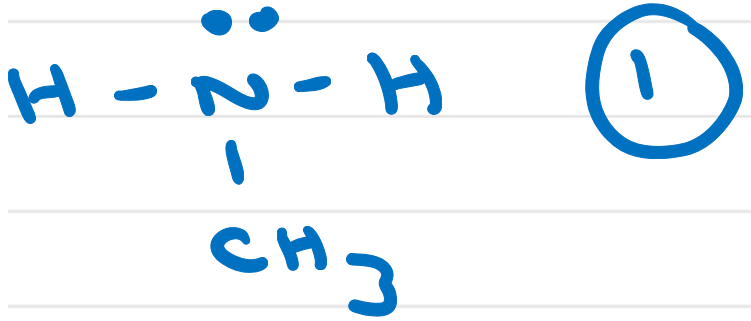
A base is a proton acceptor

Dative bonds

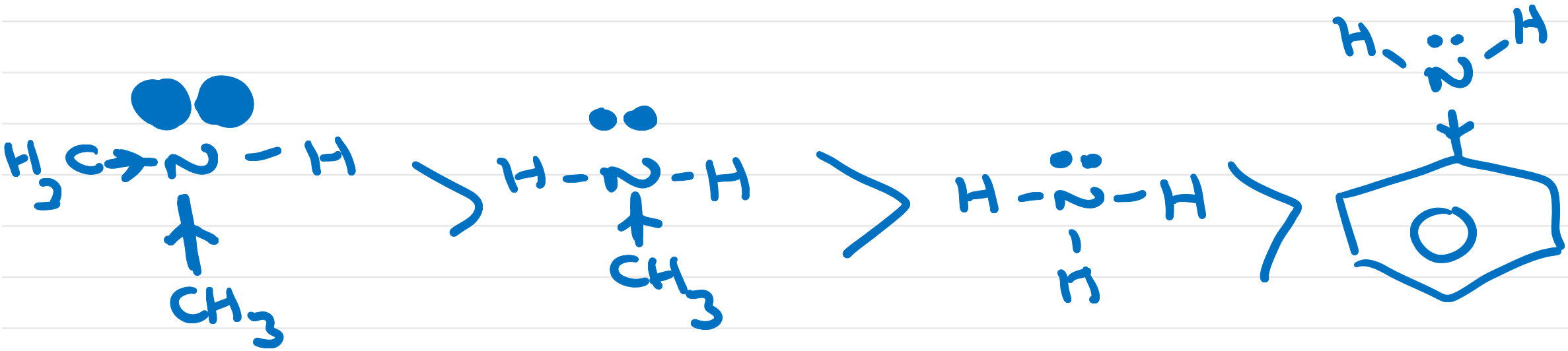


The lone pair on nitrogen forms dative bonds with protons





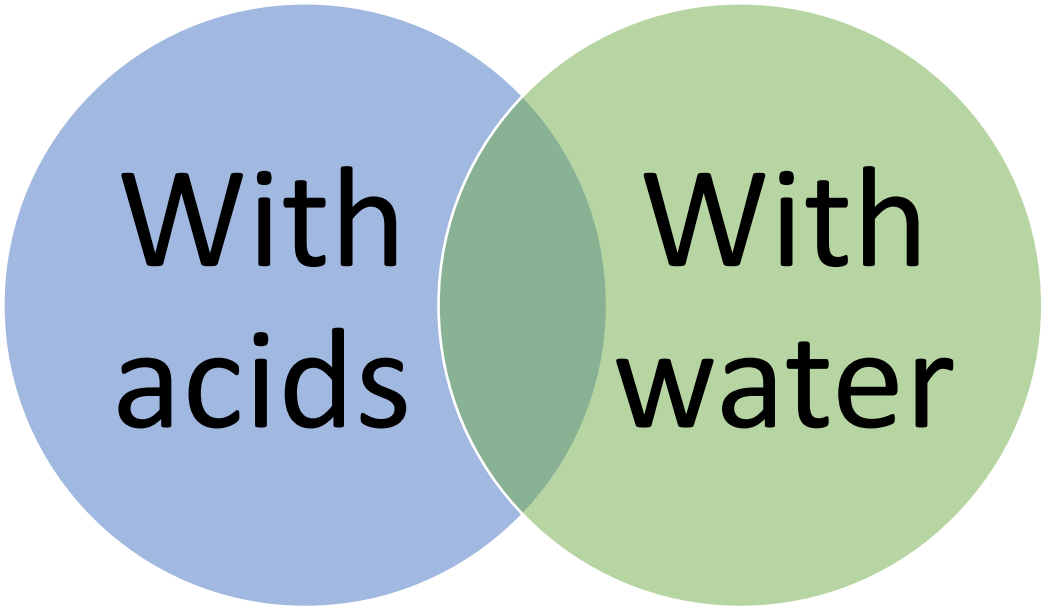
Notes:



POSITIVE INDUCTIVE EFFECT

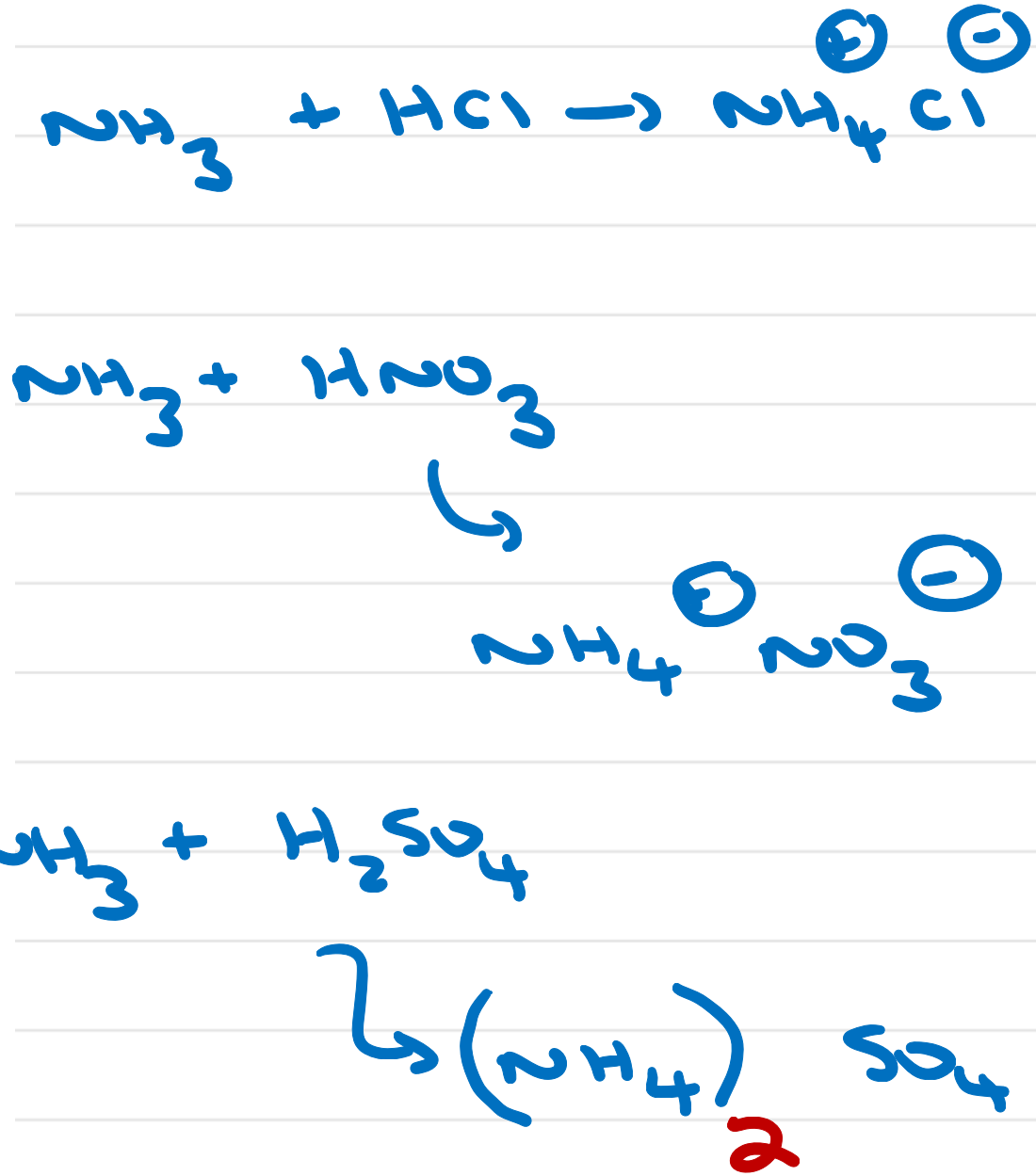
NEGATIVE INDUCTIVE EFFECT.

Basic reactions of amines



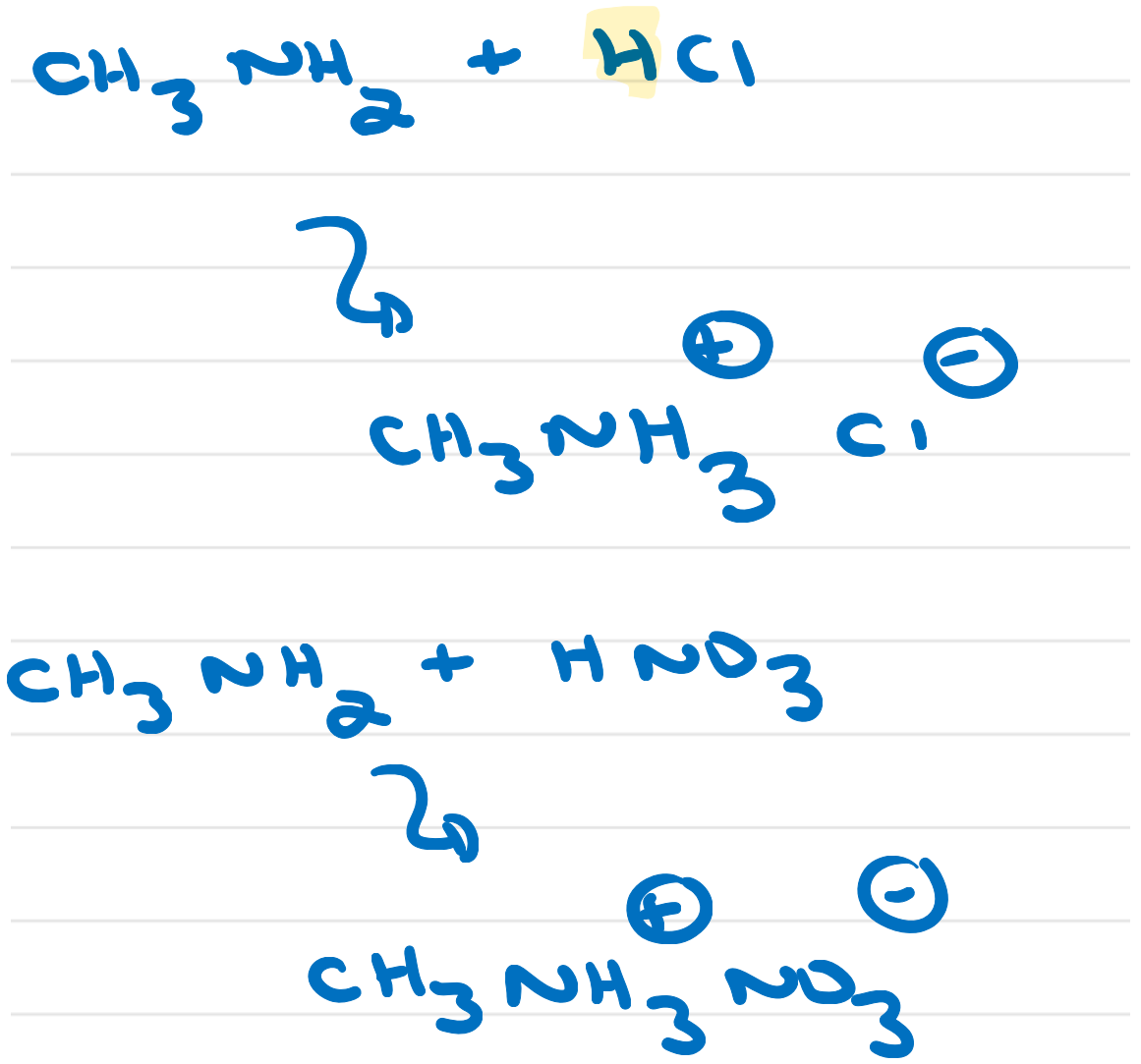
Ammonia + acids

ammonia + acid → ammonium salt



Amine + acid

amine + acid → alkyl ammonium salt



Preparation of methylammonium chloride

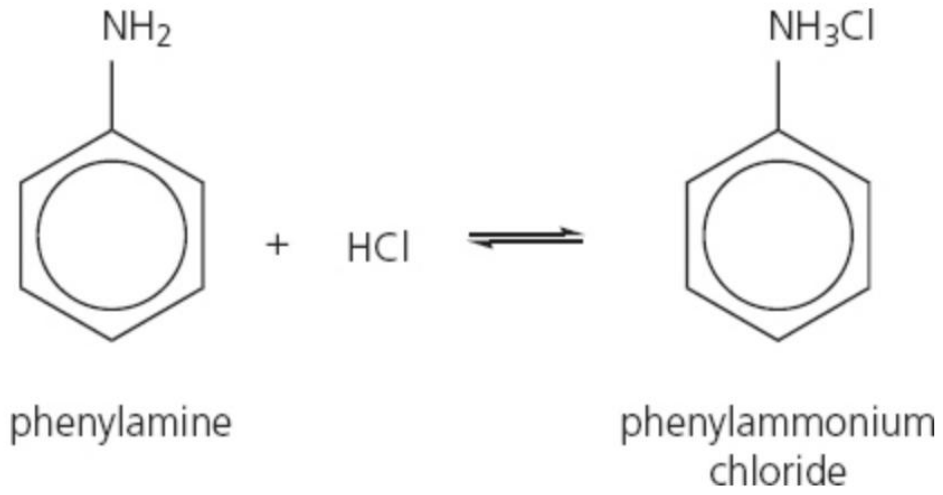
$2CH_3NH_2 + H_2SO_4$

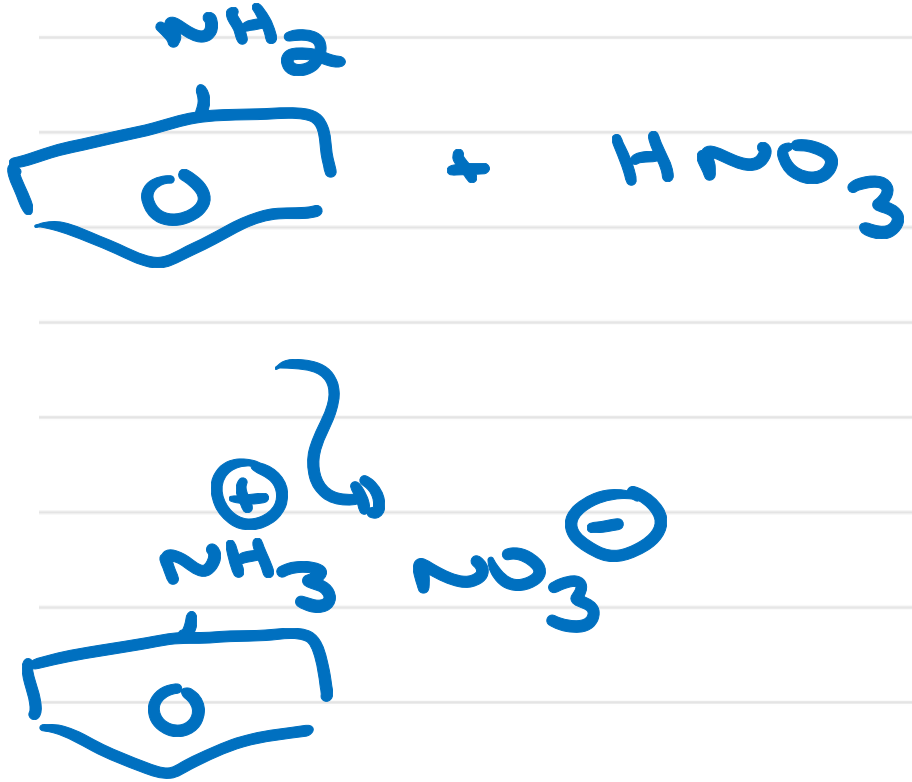
$\rightarrow (CH_3NH_3)_2SO_4$

$$CH_3NH_2 + HCl \rightleftharpoons CH_3NH_3^+Cl^-$$

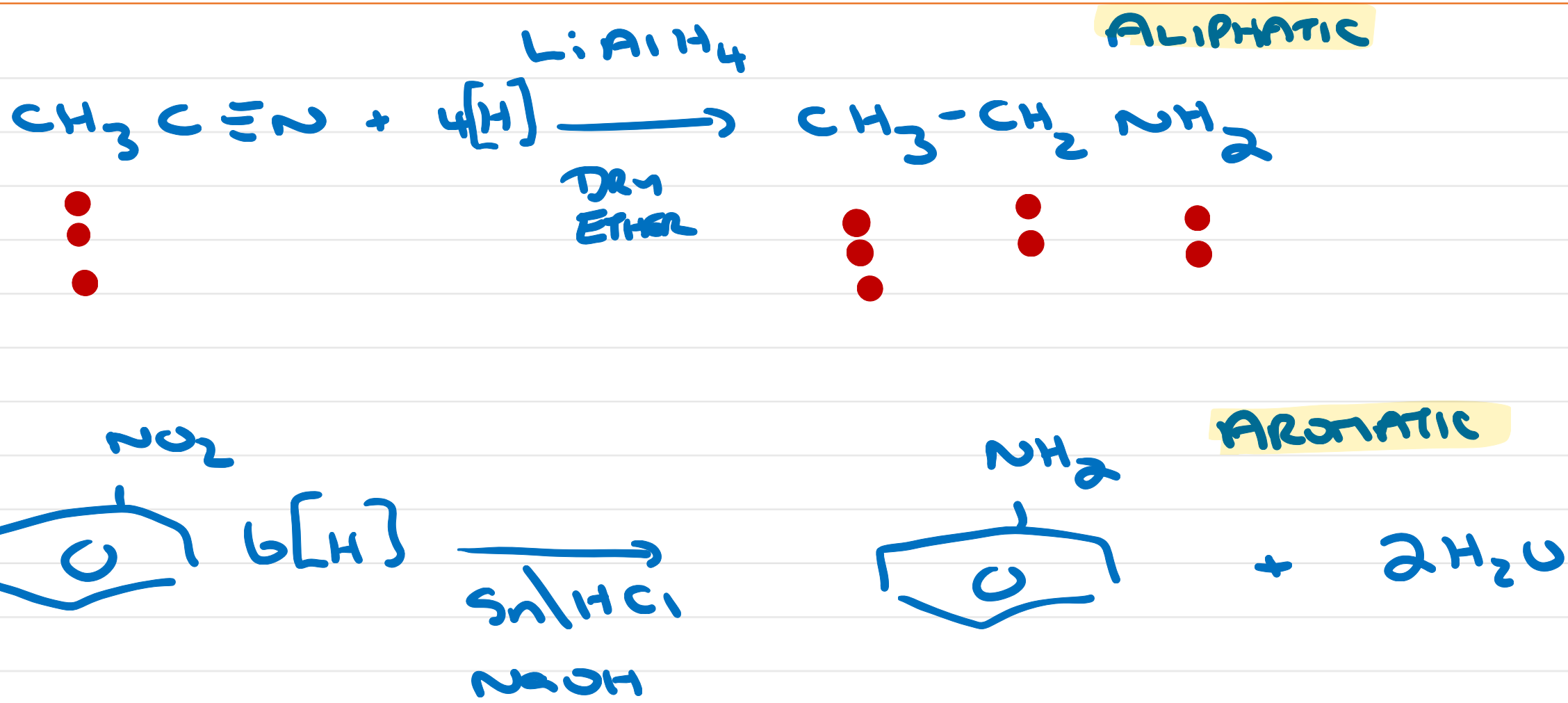
methylamine — methylammonium chloride

Preparation of phenylammonium chloride





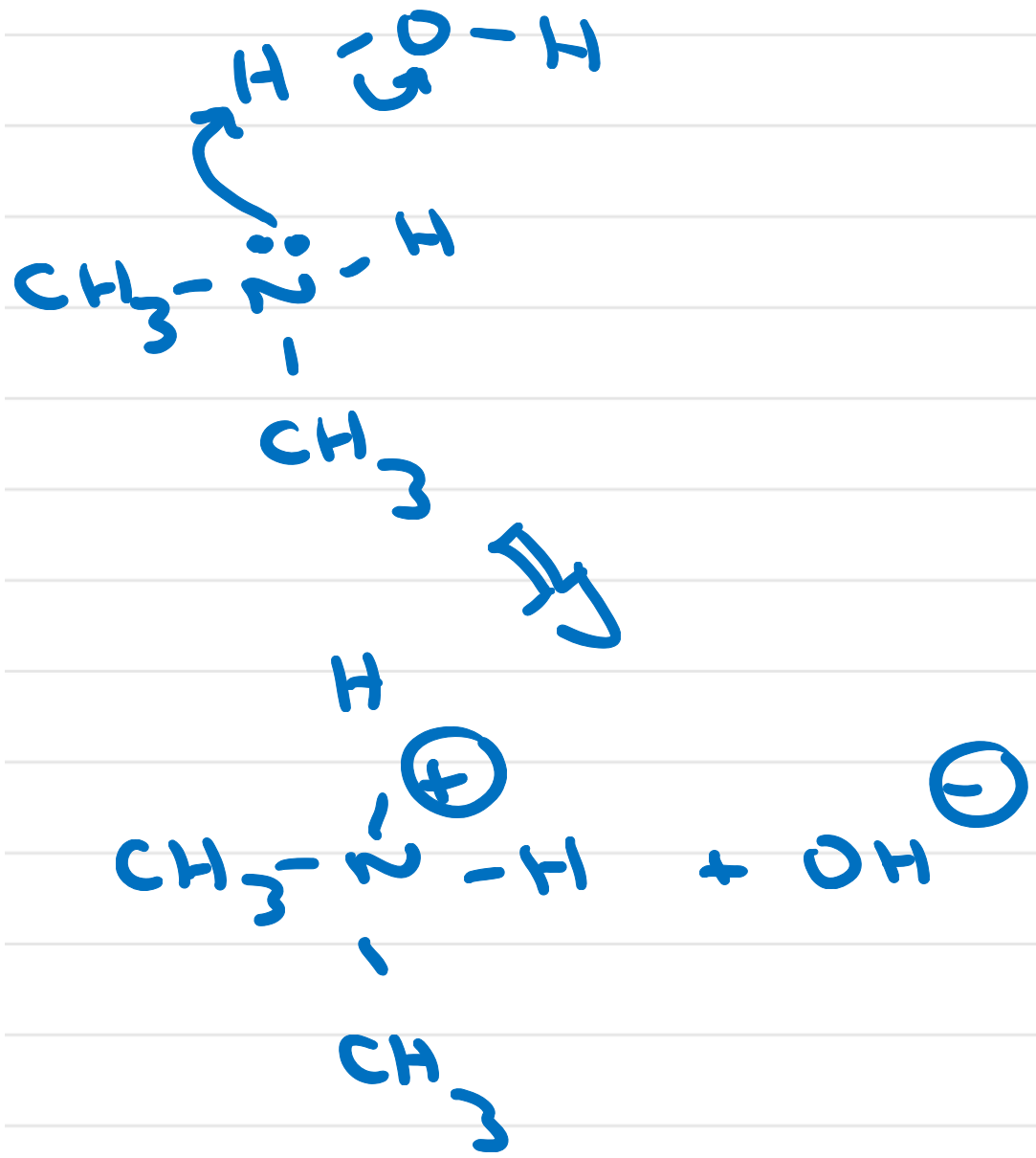
Notes:


ALIPHATIC
LiAlH4
4[H]
DRY ETHER
AROMATIC
NO2
6[H]
Sn/HCl
NaOH
NH2
+ 2H2O

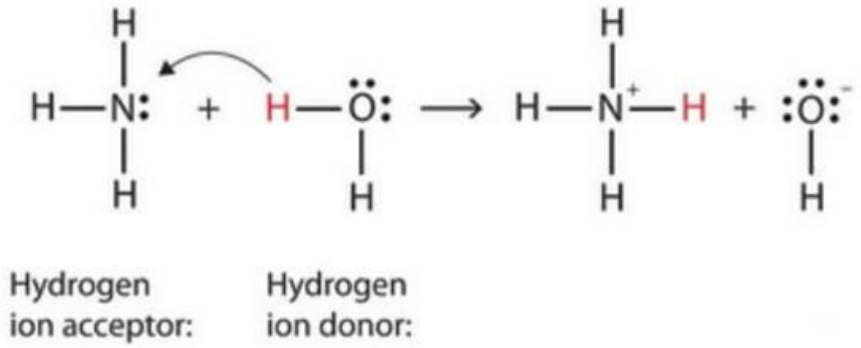
Reacting methylamine with water

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

methylamine — methylammonium ion



Mechanism



Comparison base strength

TERTIARY ALIPHATIC AMINE

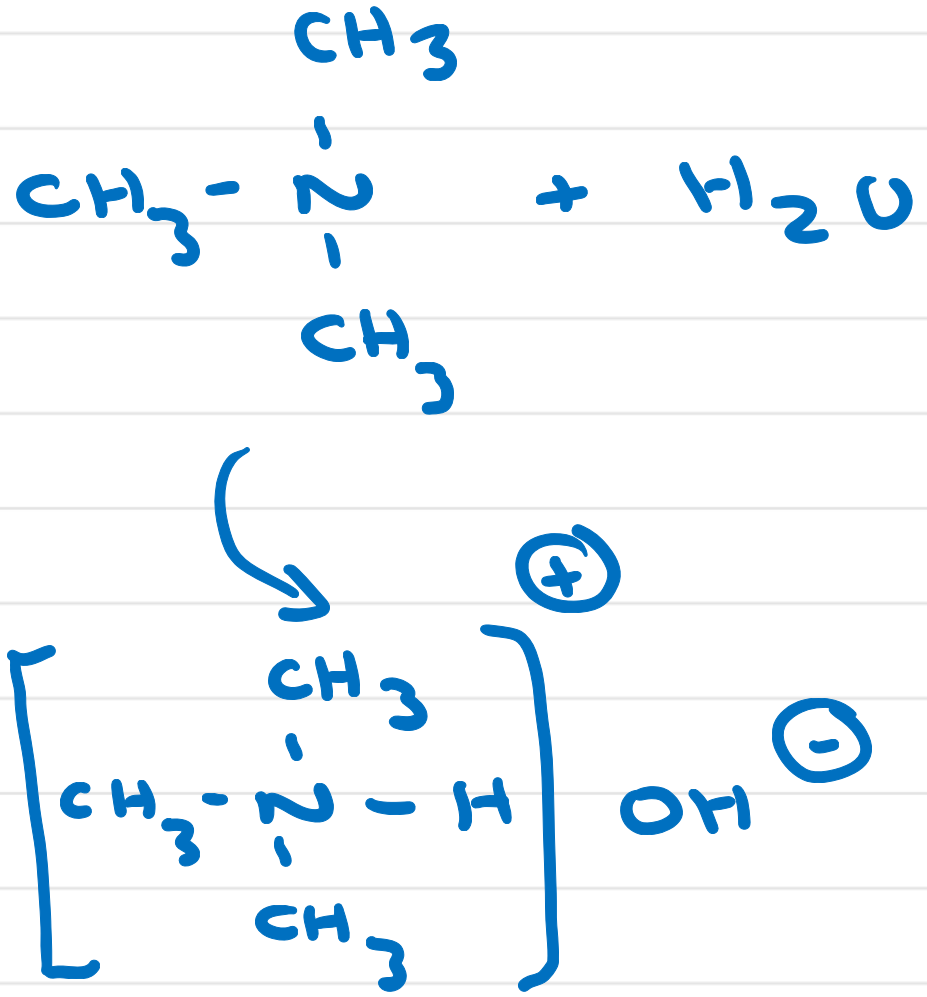
SECONDARY ALIPHATIC AMINE

Primary aliphatic amine

Ammonia

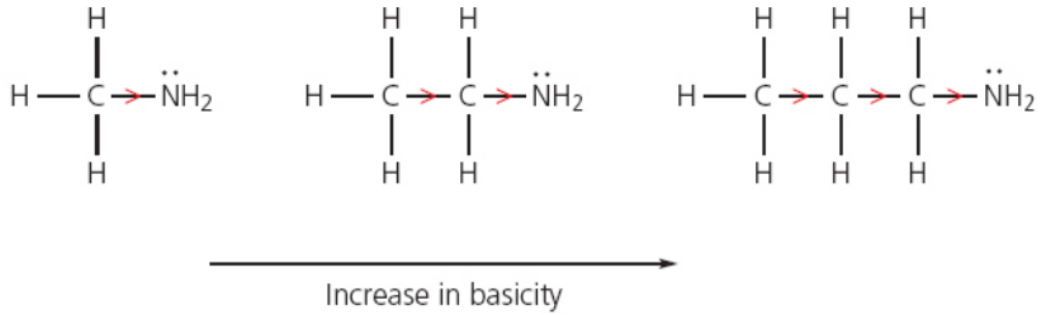
Primary aromatic amine

Basic strength decreases



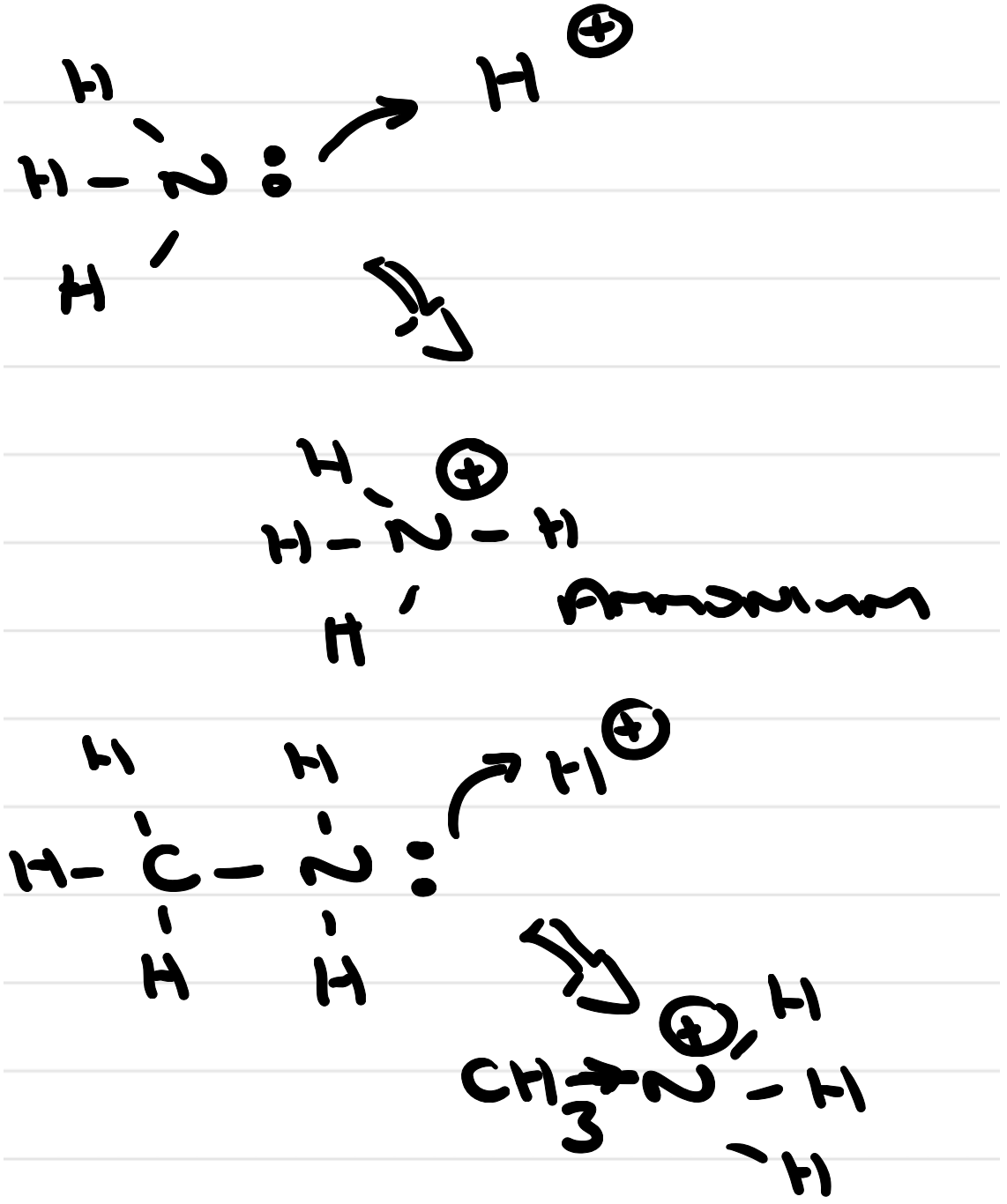
Basicity depends on the availability of the lone pair

Basicity of primary amines

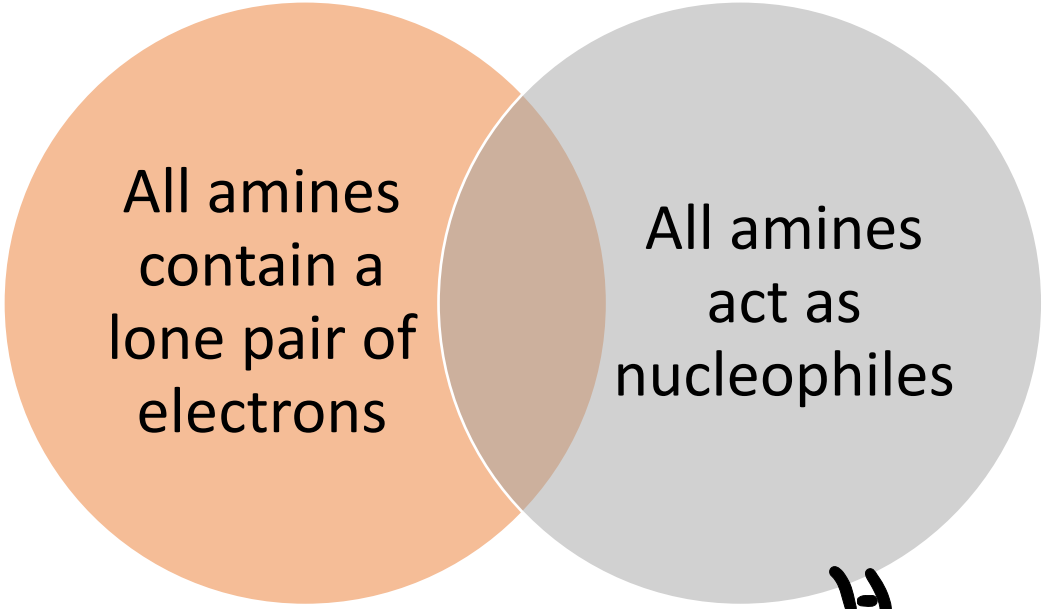


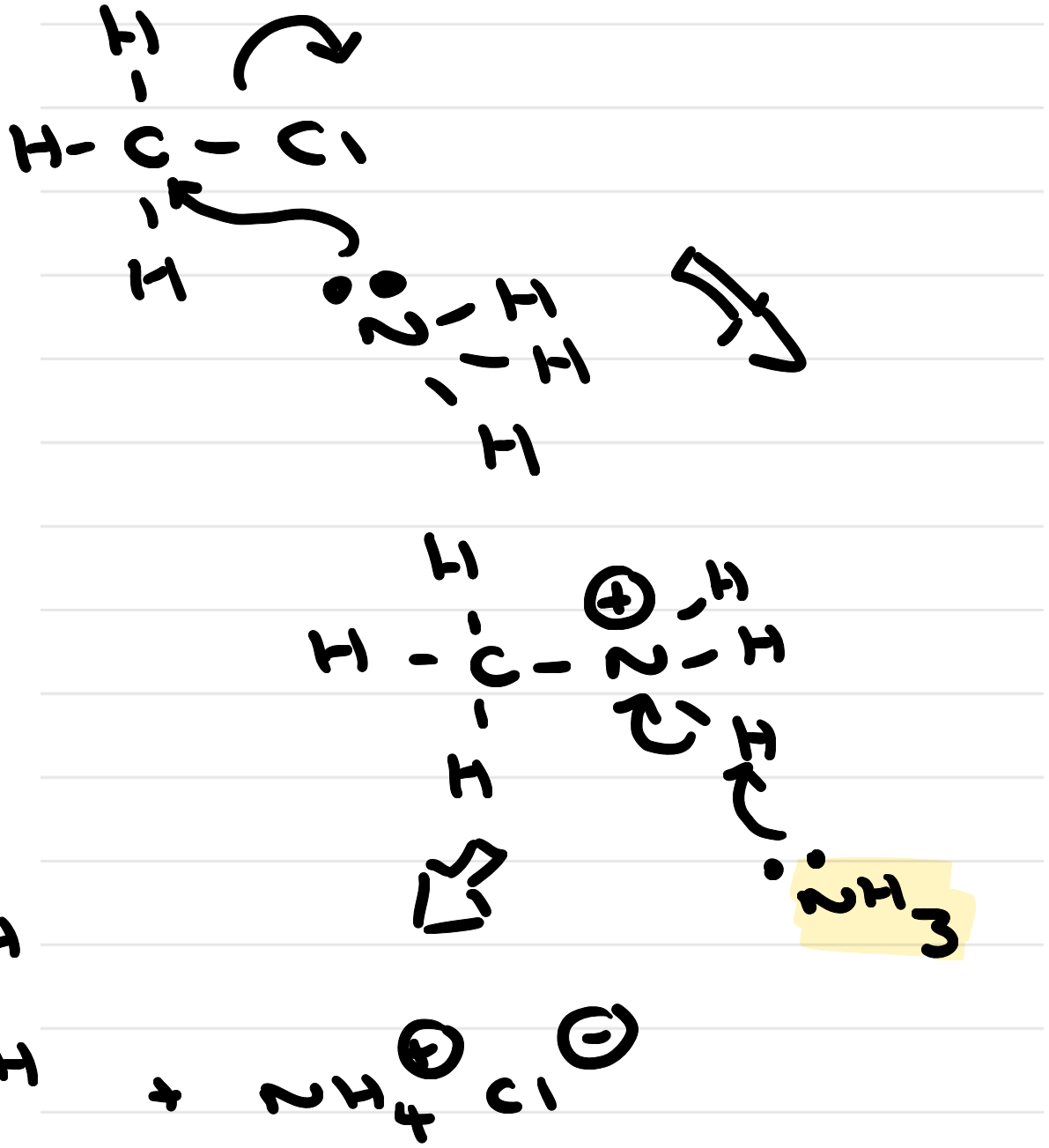
Nucleophilic properties of amines

- Introduction
- Making primary amines
- Making secondary amines
- Making tertiary amines
- Making quaternary salts
- Mechanisms



Introduction





Making primary amines

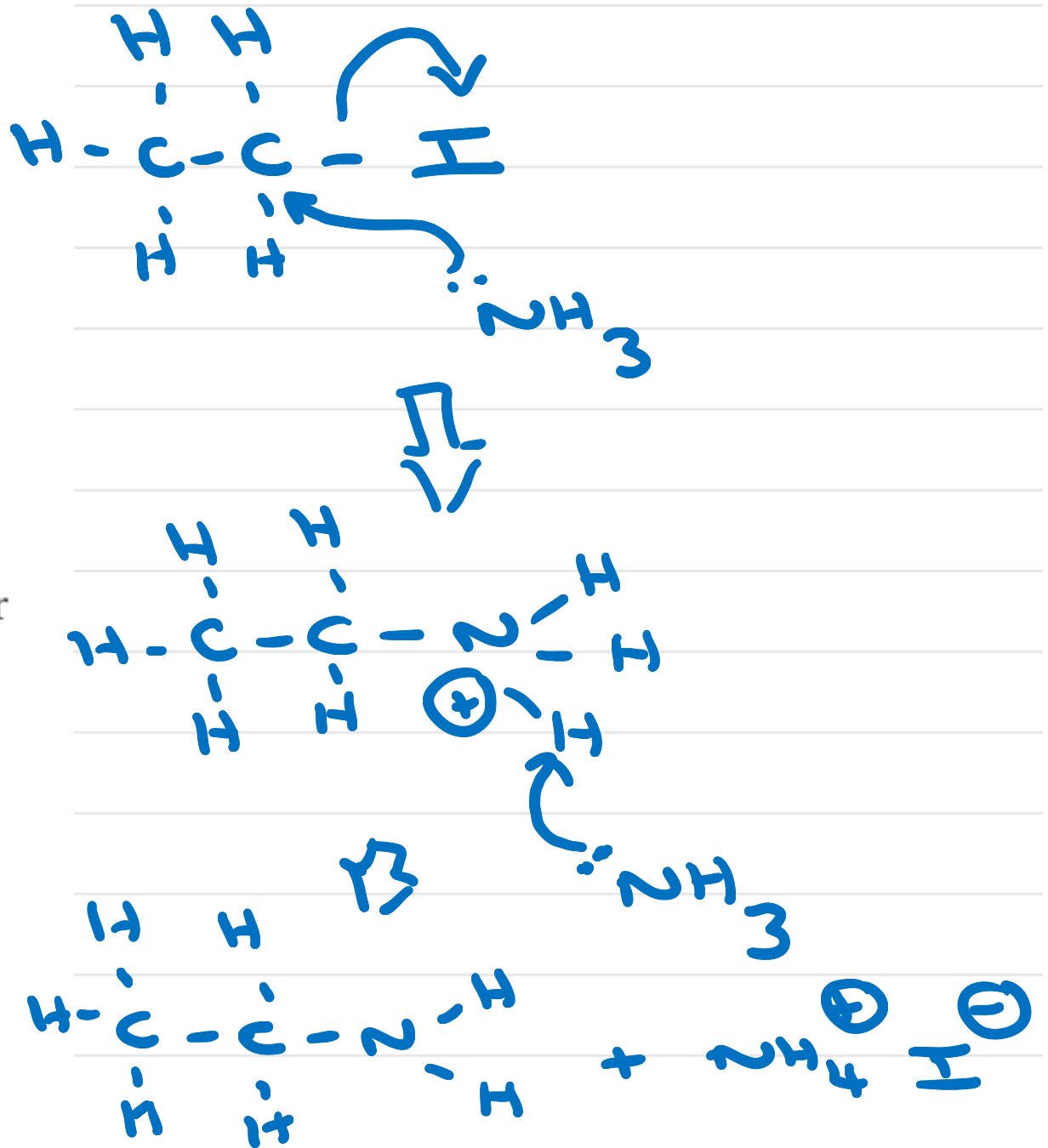
$$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_3Br$$

ethylammonium bromide

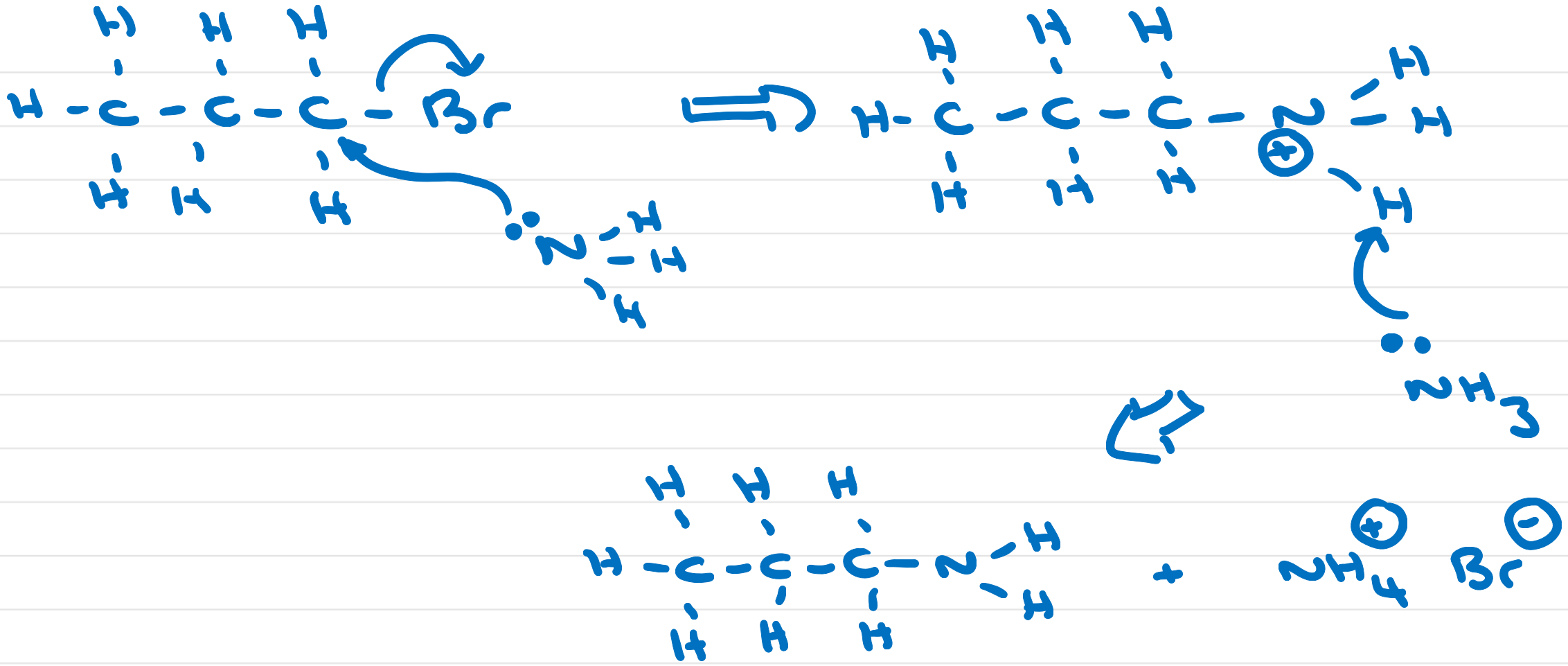
$$CH_3CH_2NH_3Br + NH_3 \rightleftharpoons CH_3CH_2NH_2 + NH_4Br$$

ethylamine
(primary amine)

Primary amines are formed if excess ammonia is used (see earlier)

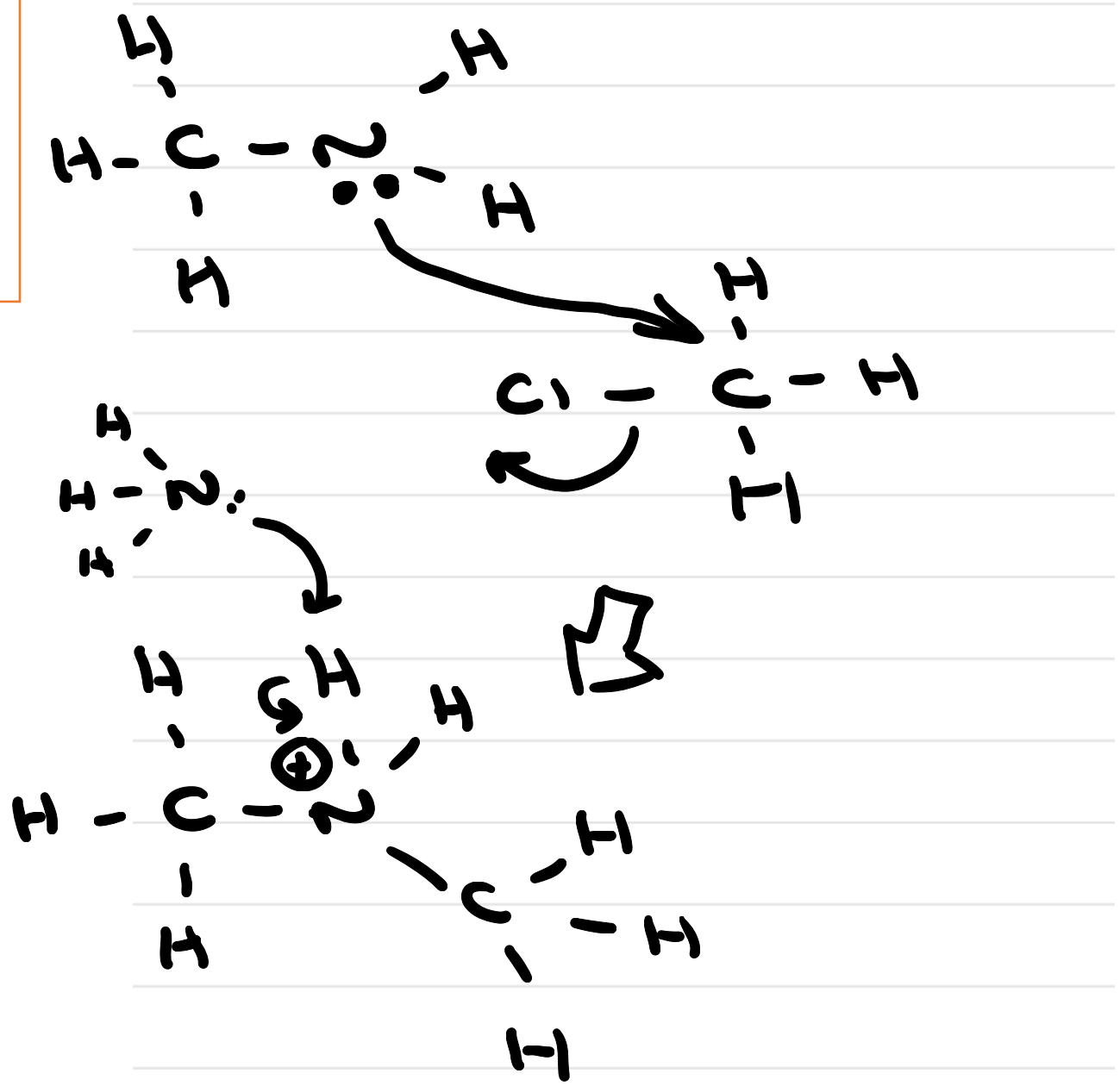


Notes:



Di ethyl amine and tri ethyl amine production

If excess haloalkane is used then successive substitution reactions occur



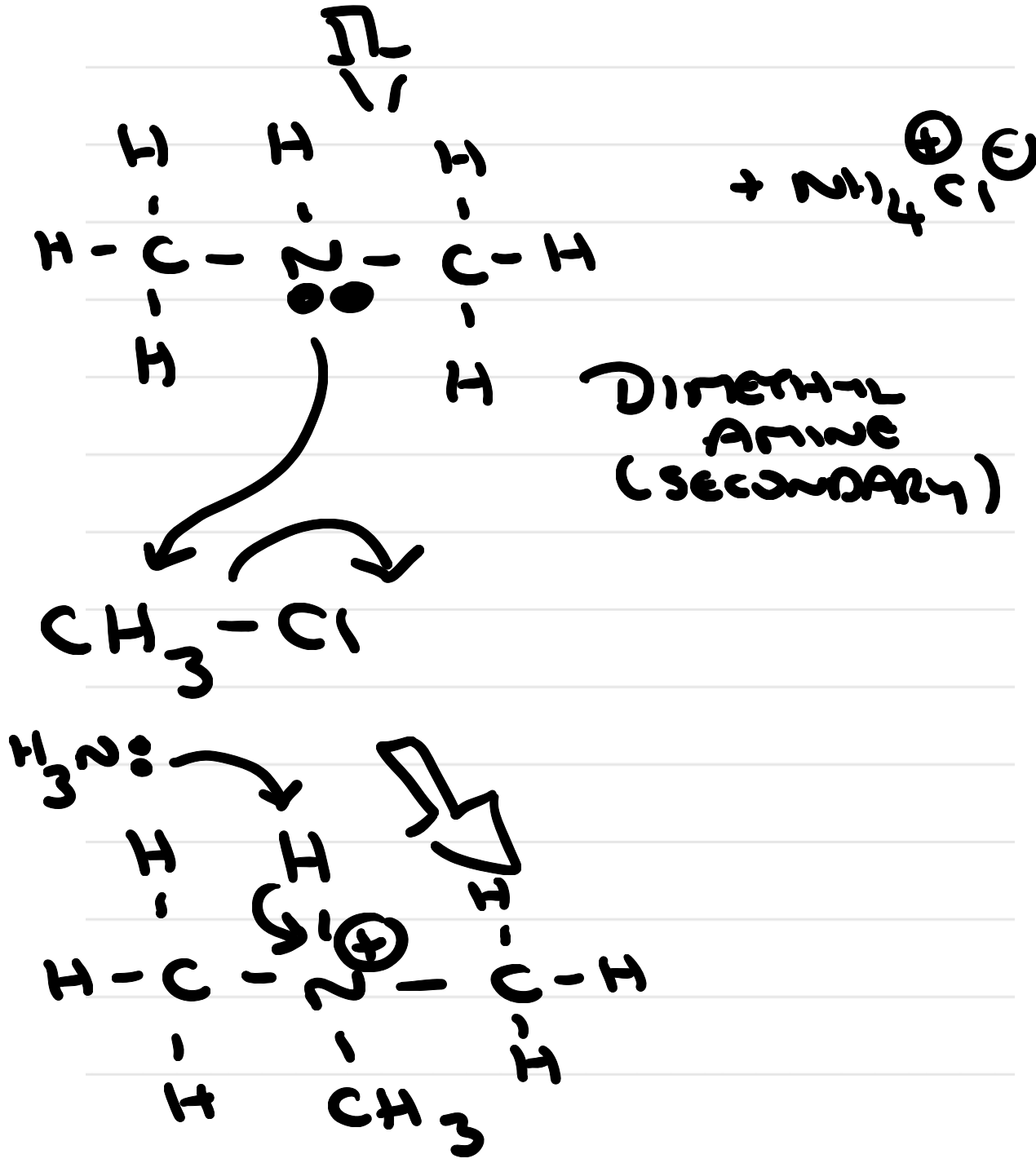
Making secondary amines

$$CH_3CH_2Br + CH_3CH_2NH_2 \rightarrow (CH_3CH_2)_2NH_2Br$$

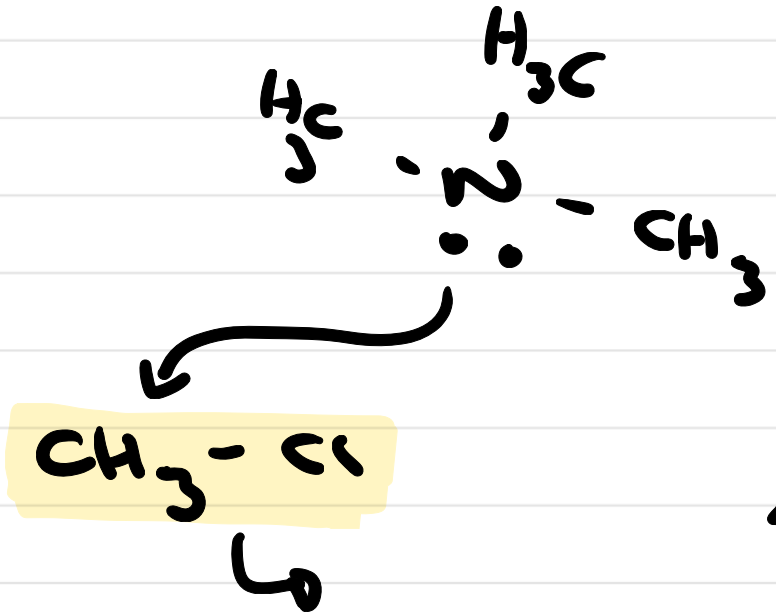
$$(CH_3CH_2)_2NH_2Br + NH_3 \rightleftharpoons (CH_3CH_2)_2NH + NH_4Br$$

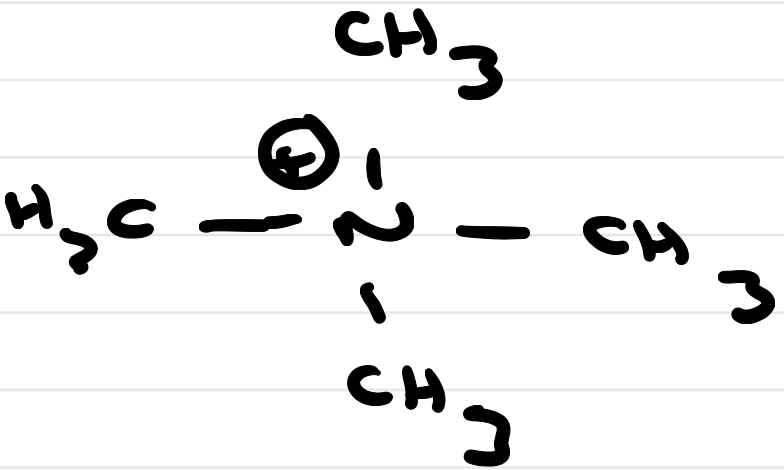
diethylammonium bromide — diethylamine (secondary amine)

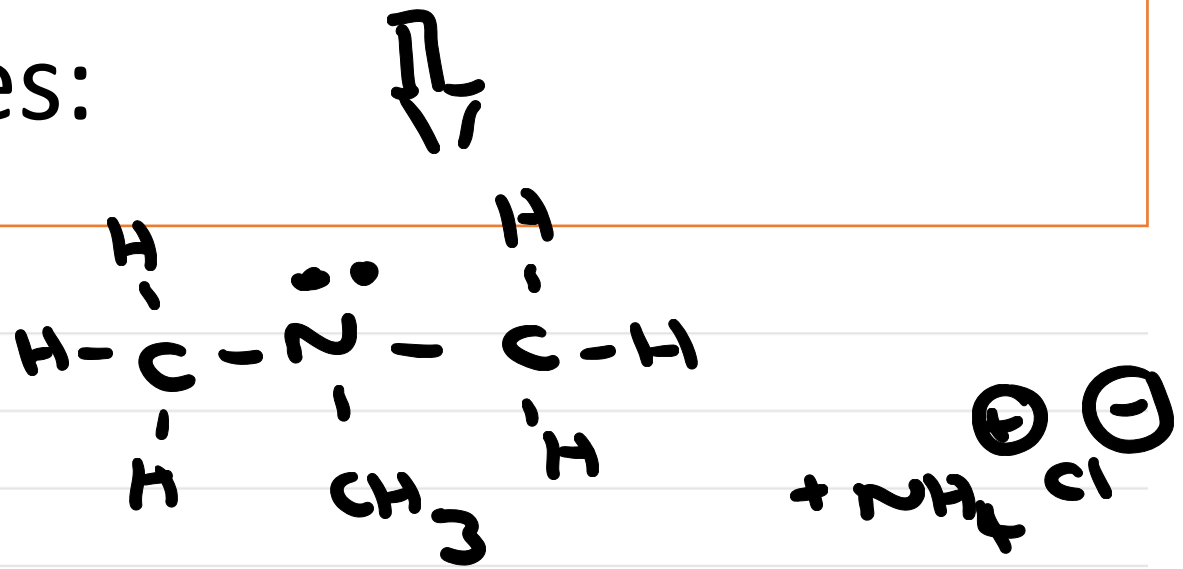
Secondary amine are formed if excess haloalkane is used



Notes:





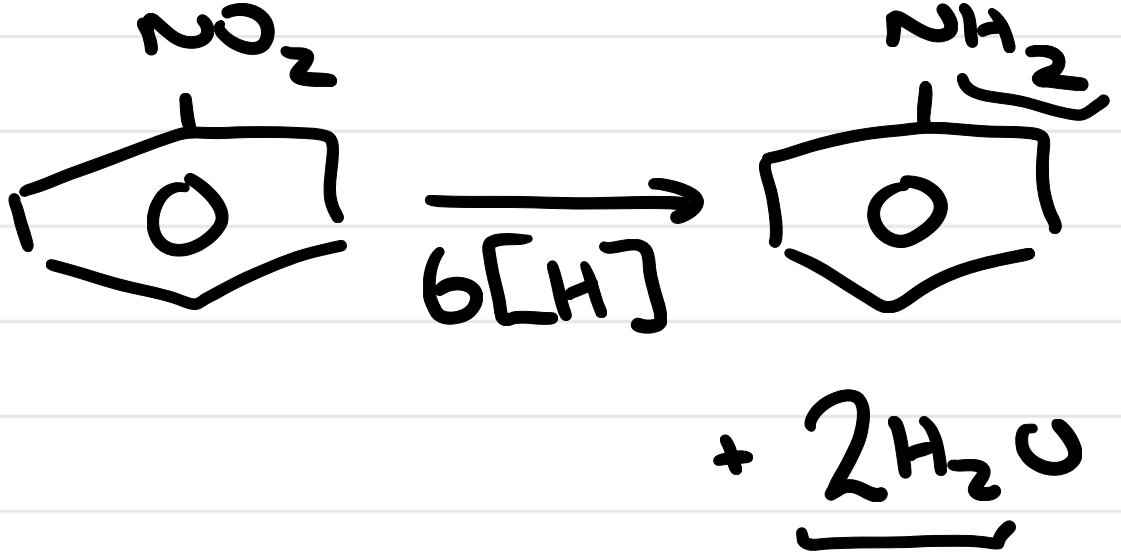


Making tertiary amines

$$CH_3CH_2Br + (CH_3CH_2)_2NH \rightarrow (CH_3CH_2)_3NHBr$$

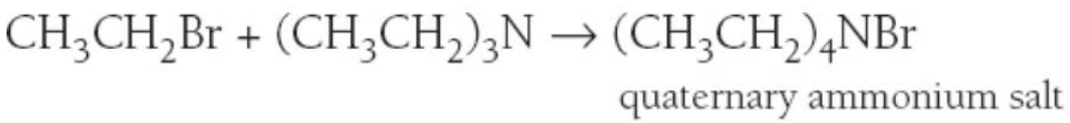
$$(CH_3CH_2)_3NHBr + NH_3 \rightleftharpoons (CH_3CH_2)_3N + NH_4Br$$

triethylamine
(tertiary amine)



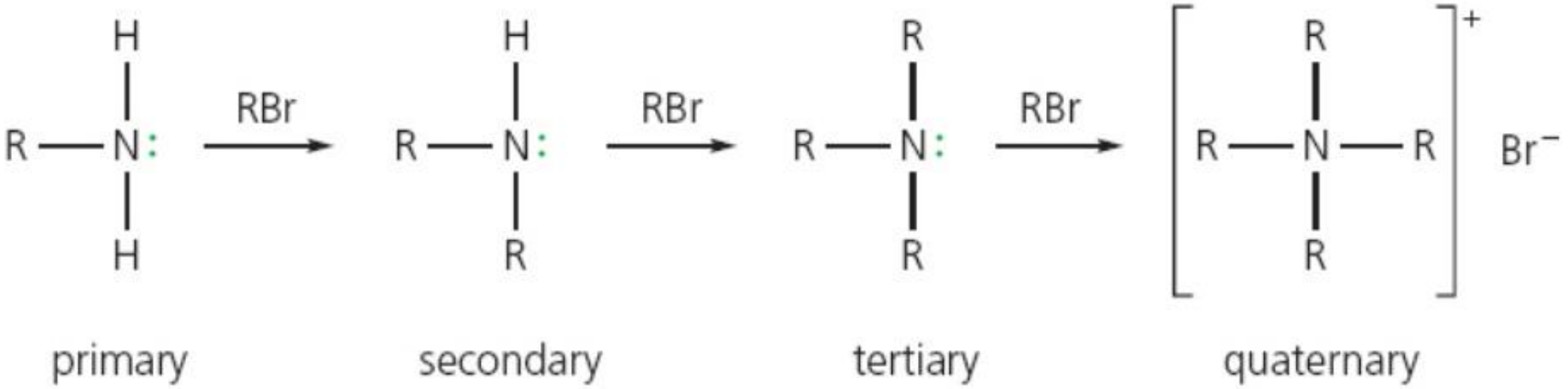
Tertiary amine are formed if excess haloalkane is used

Making quaternary salt

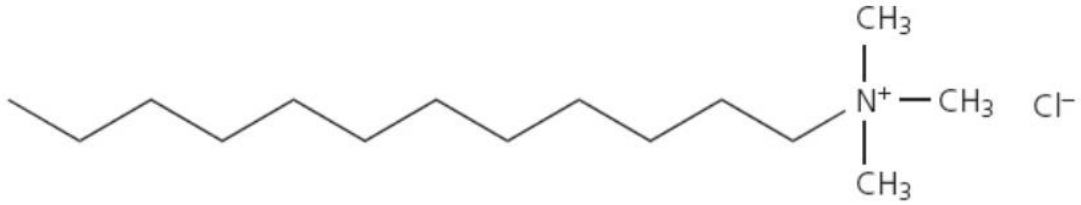


Tertiary amine are formed if excess haloalkane is used

Summary of amine production



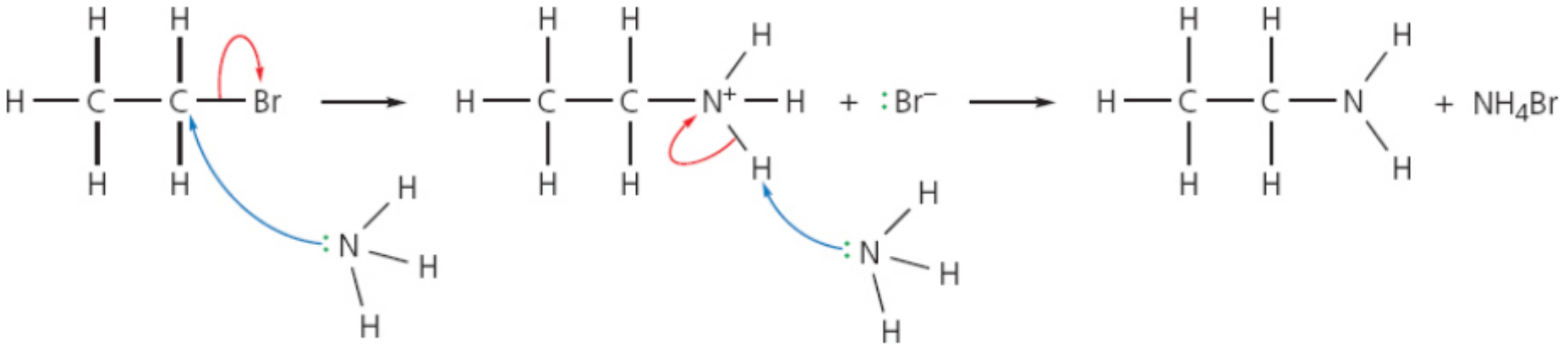
Use of quaternary ammonium salts



Used in hair conditioners to reduce static charge due to electrons

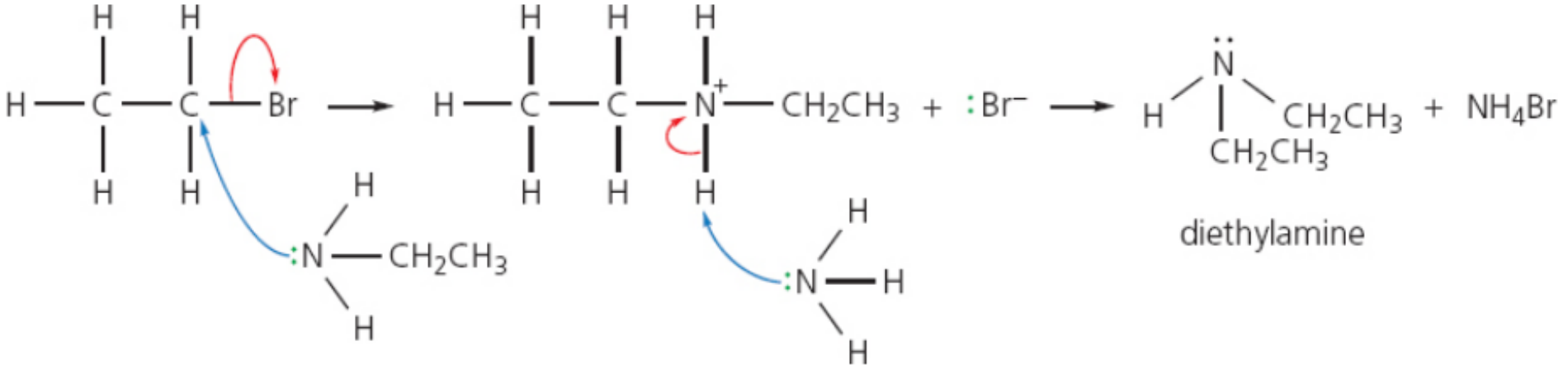
Mechanism: primary amine production

Excess Ammonia



Mechanism: secondary amine production

EXCESS HALOALKANE



Mechanism: quaternary amine production

Excess haloalkane