

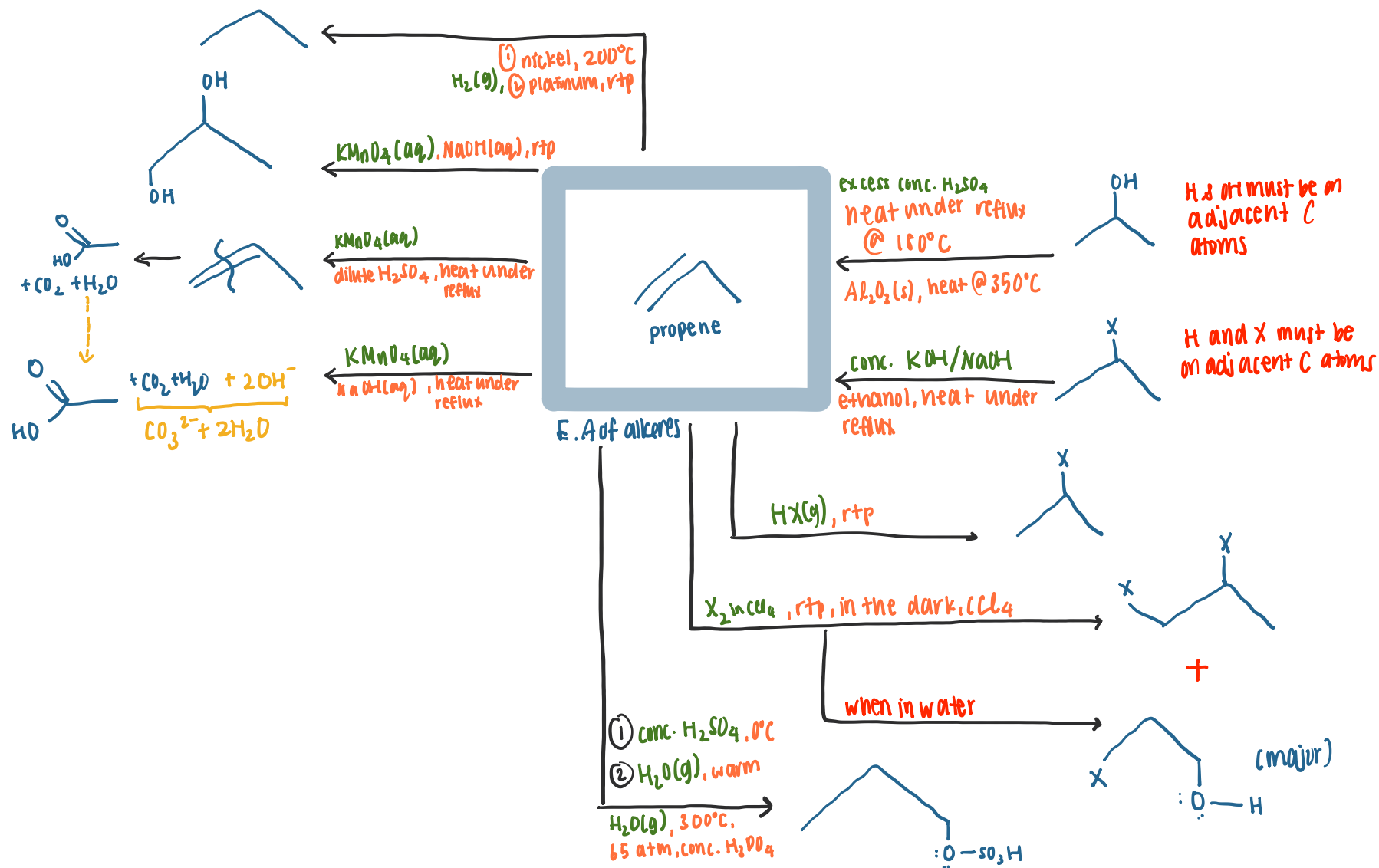
disclaimer:

this set of notes is only comprehensive for the following sub-topics of organic chemistry for H2:

- alkenes
- arenes
- halogen derivatives
- alcohols & phenols
- carbonyl compounds

However, the mind maps included are comprehensive of all the organic chemistry reactions in the 9729 syllabus, minus free radical substitution of alkanes.

ALKENES



Physical properties

Trend of boiling points down the homologous series (applicable to all):

- As the number of carbon atoms increase, the size of the electron cloud increases, and becomes more polarisable.
- The strength of id-id increases, so more energy is required to overcome the id-id, leading to higher boiling points.

cis vs trans isomer:

- cis isomers have higher boiling points, as they have a net dipole moment
- individual dipole moments cancel each other out in trans isomers
- cis isomer is a polar molecule held together by pd-pd, while trans isomers are held together by id-id
- more energy is required to overcome pd-pd than id-id
- trans isomers have better symmetry than cis isomers, allowing them to pack together more efficiently in the solid state
- closer packing allows for stronger id-id between molecules, which require more energy to overcome

soluble in non-polar solvents

- alkenes can form favourable id-id attractions with the solvent

insoluble in water and other highly polar solvents

- energy released from the id-id formed between alkenes and water molecules are insufficient to compensate for the energy required to overcome the id-id between alkene molecules and hydrogen bonding between water molecules.

Saytzeff's Rule

: When there is more than one alkene that can be formed from elimination, the major product is the alkene with the greatest number of alkyl groups bonded to C atoms in the C=C double bond.

Markovnikov's Rule

: The electrophile is added to the C=C bond in a way such that the most stable carbocation intermediate is produced.

FAQ

Why is XXX the major product?

- the ___ carbocation has more electron-donating alkyl groups attached to the positively-charged C atom
- positive charge on the C atom becomes more dispersed, so the carbocation is more stable, hence (major product) is more likely to be formed

Explain why the resulting mixture is optically inactive even though the product contains a chiral carbon.

- the carbocation is trigonal planar wrt the positively-charged C atom
- The _ nucleophile can attack the positively-charged C atom from either side of the plane with equal probability
- equal amounts of both enantiomers are formed, forming a racemic mixture
- the 2 enantiomers rotate plane-polarised light by the same extent but in

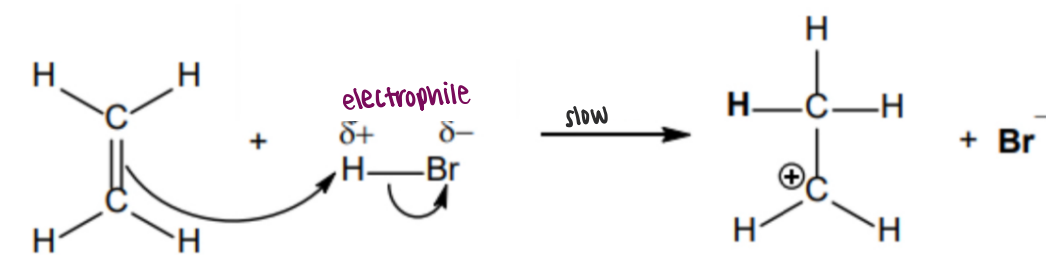
Mechanisms to know

: Electrophilic Addition

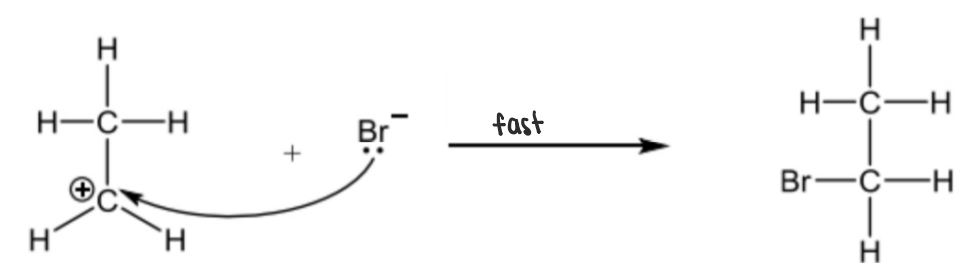
Mechanism for HBr(g)

Electrophilic Addition

Step 1 (slow step)



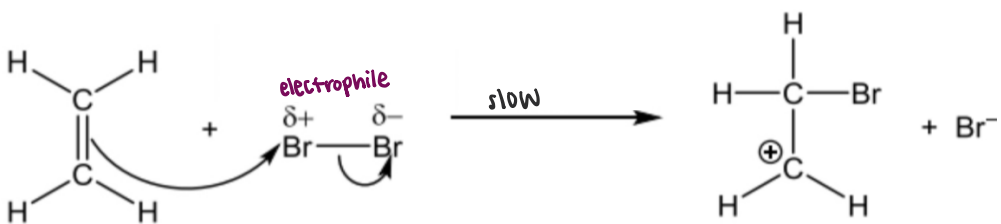
Step 2 (fast step)



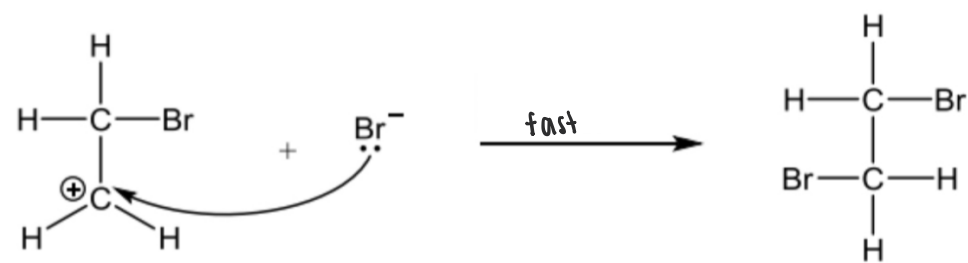
Mechanism for Br₂ in CCl₄

Electrophilic Addition

Step 1 (slow step)



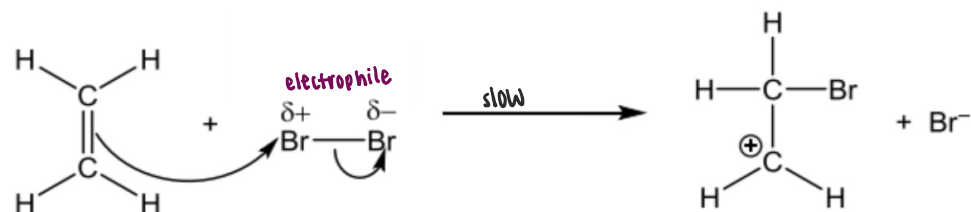
Step 2 (fast step)



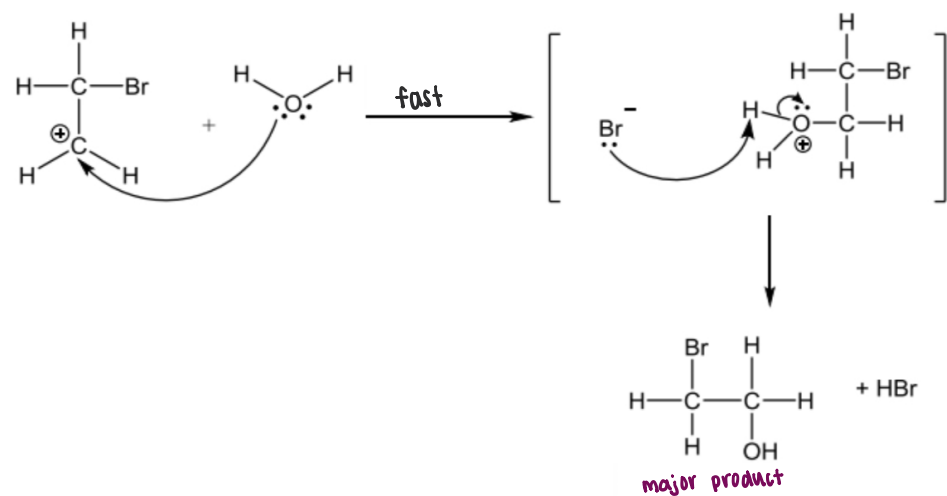
Mechanism for Br₂(aq)

Electrophilic Addition

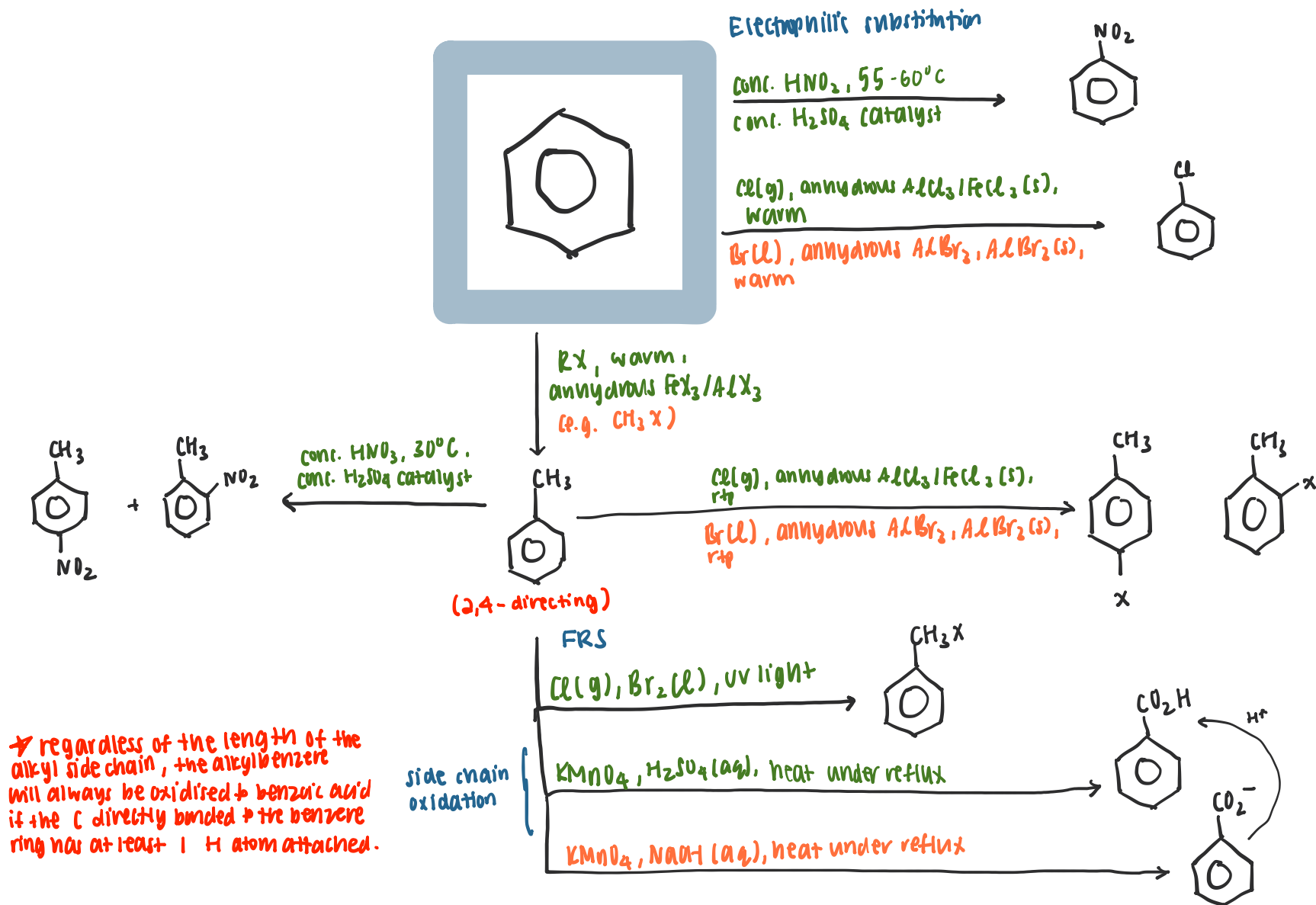
Step 1 (slow step)



Step 2 (fast step)



ARENES



Resonance

: the p orbitals of carbon atoms in a benzene ring overlap sideways with one another, creating a continuous overlap of unhybridised p orbitals throughout the benzene ring. The π electrons delocalise across the benzene ring, creating a delocalised π electron cloud.

identical C-C bond lengths

- due to the delocalised electron cloud in benzene, all 6 C-C bond lengths are in between the C-C bond length in alkanes and C=C bond length in alkenes
- due to partial double bond character of C-C bond in benzene

planar molecule

- all 6 C atoms are sp² hybridised = all are trigonal planar shaped
- = entire molecule is planar

substitution reactions

- substitution reactions preserve the resonance stability of the benzene ring while addition reactions disrupt it
- benzene ring undergoes substitution reactions instead of addition ones as they are more energetically feasible.

Physical properties

low melting & boiling point

- benzene is a non-polar simple molecule, held together by weak id-id

soluble in non-polar organic solvents

- form favourable id-id interactions with each other

insoluble in polar solvents like water

- energy released to form id-id between benzene and water molecules is insufficient to compensate for the energy required to overcome the id-id between benzene molecules and strong hydrogen bonding between water molecules

FAQ

Why is conc. H₂SO₄ catalyst necessary for the electrophilic substitution of benzene but not for the electrophilic addition of alkene?

- alkenes contain an electron-rich C=C bond that can attack electrophiles with a partial positive charge
- due to resonance stability of benzene, electrophiles with partial positive charges are too weak to react with benzene
- hence, concentrated H₂SO₄ catalyst reacts with HNO₃ to generate NO₂⁺, which is a much stronger electrophile that can react with benzene

Why must AlCl₃ Lewis acid catalyst be added in anhydrous conditions?

- H₂O contains LP of electrons on the O atom, so AlCl₃ might accept an electron pair from H₂O instead of Cl, preventing Cl⁺ electrophile from forming and electrophilic substitution with benzene cannot occur.

Resonance effect vs Inductive effect on substituted benzenes

Inductive effect: present when there is a difference in electronegativity between the 2 atoms in a sigma bond.

Resonance effect: present when there is an overlap of p orbitals between the C atoms of benzene ring and the substituent bonded to it.

Resonance effect > Inductive effect

: electrons are delocalised throughout the π electron cloud in resonance effect, while electrons only move within one sigma bond in inductive effect

Inductive effect > Resonance effect

: For -Cl, -Br, and -I substituent groups, the 3p orbital overlaps less effectively with the 2p orbitals of the C atoms in the benzene ring.

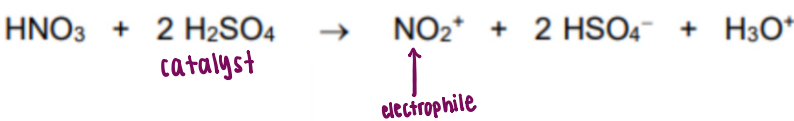
Mechanisms to know

: Electrophilic Substitution

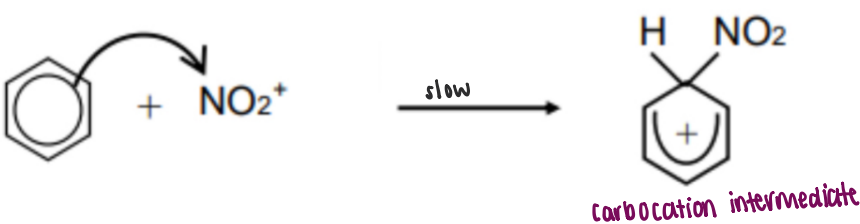
Mechanism for nitration

Electrophilic Substitution

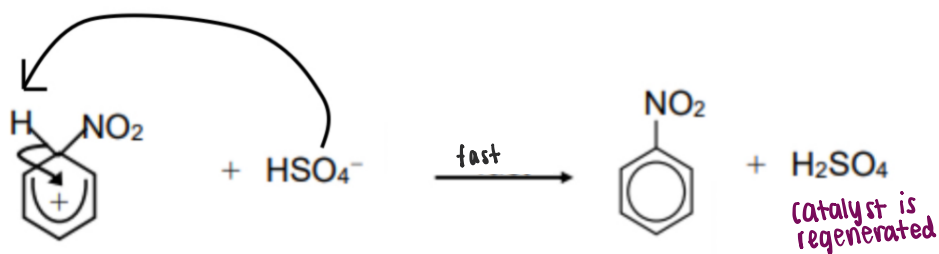
Step 1 (Generation of electrophile NO₂⁺)



Step 2 (Formation of carbocation intermediate, slow step)



Step 3 (Restoration of benzene aromaticity)



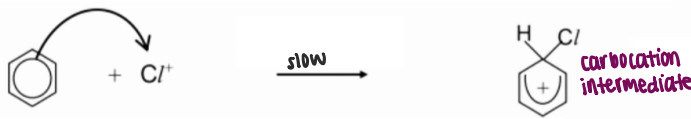
Mechanism for halogens

Electrophilic Substitution

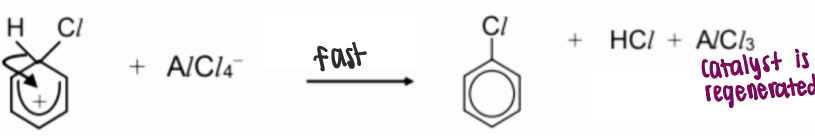
Step 1 (Generation of electrophile Cl⁺)



Step 2 (Formation of carbocation intermediate, slow step)



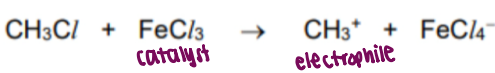
Step 3 (Restoration of benzene aromaticity)



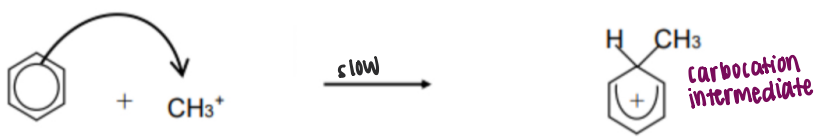
Mechanism for alkylation

Electrophilic Substitution

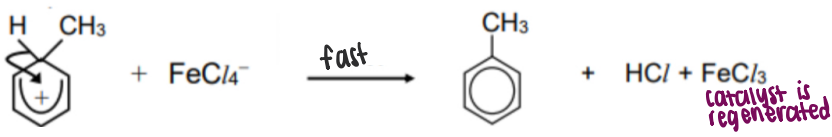
Step 1 (Generation of electrophile CH₃⁺)



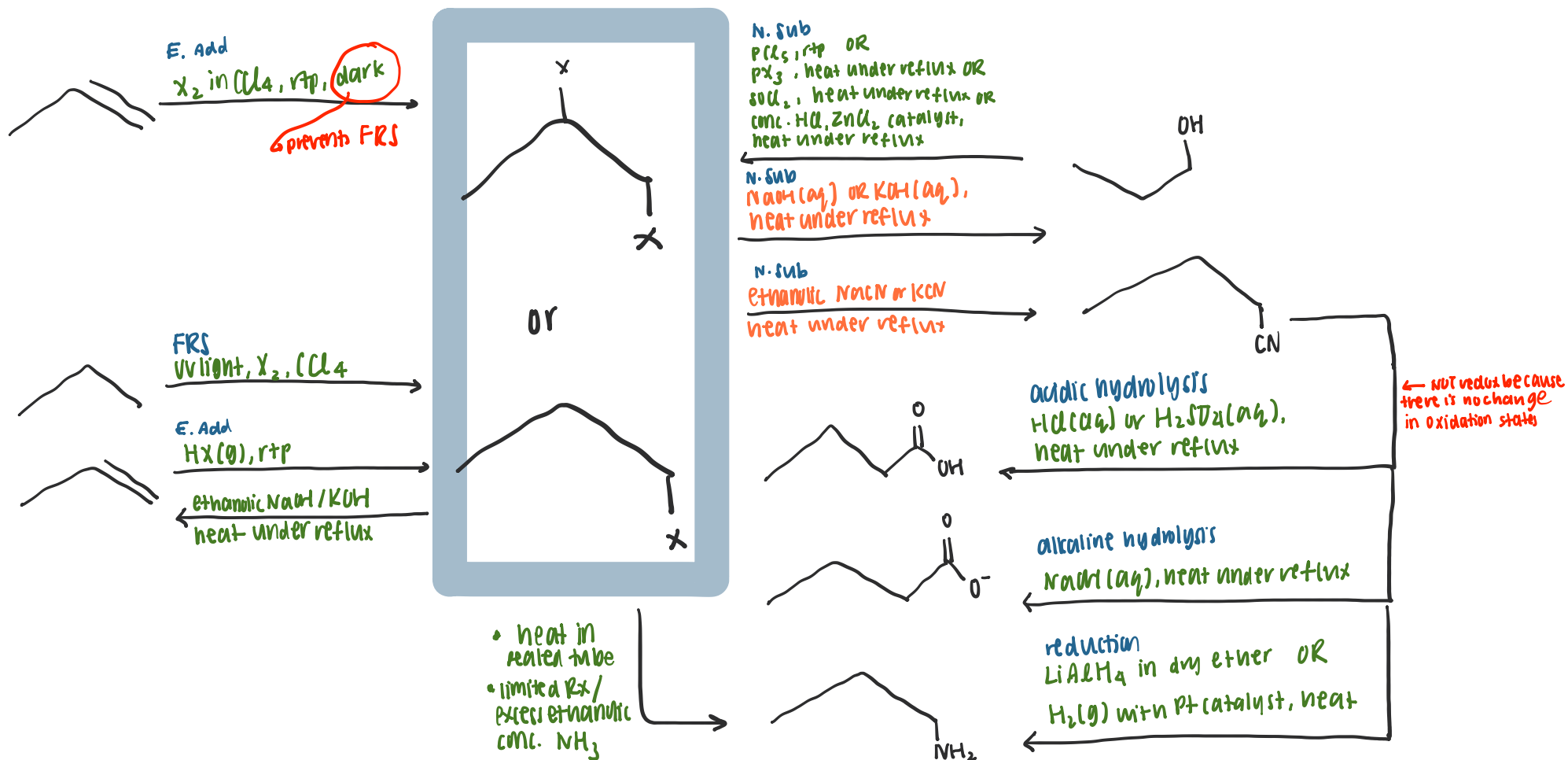
Step 2 (Formation of carbocation intermediate, slow step)



Step 3 (Restoration of benzene aromaticity)



HALOGEN DERIVATIVES



PHYSICAL PROPERTIES

: simple molecular structure, pd-pd

comparison of melting./boiling points between halogenoalkanes with different halogens

- iodoalkanes have the largest electron cloud size, most easily polarised
- iodoalkanes hence have the strongest id-id, more energy is required to overcome the id-id

insoluble in water

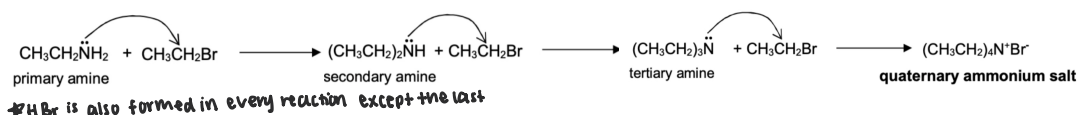
- the energy released to form pd-pd between halogenoalkanes and water molecules is insufficient to compensate for the energy required to overcome the strong hydrogen bonding between water molecules and pd-pd between halogenoalkane molecules

soluble in non-polar organic solvents

- the energy released to form id-id between the non-polar organic solvent molecules and halogenoalkanes is sufficient to compensate for the energy required to overcome the id-id between non-polar organic solvent molecules and pd-pd between halogenoalkanes.

Multi-substitution of ammonia

: once the amine is formed, further substitution can occur where the lone pair on the N atom of the amine is used to initiate another nucleophilic substitution reaction. This can be prevented by ensuring ammonia is in excess and the reaction is done in a sealed tube.



	S _N 1	S _N 2
rate equation	rate = [RX]	rate = [RX][nucleophile]
no. of steps	2	1
stereochemistry	racemic mixture (if chiral C is present in the <u>product</u>)	inversion (if chiral C is present in the <u>reactant</u>)
favoured by <u>halogenoalkanes</u>	tertiary (carbocation stability)	primary (low steric hindrance)

FAQ

Why do products of SN1 form a racemic mixture?

- The intermediate carbocation is trigonal planar wrt to the electron-deficient carbon, so the nucleophile is able to attack the top and bottom faces of the carbocation with equal probability.
- equal amounts of each enantiomer is formed, no net rotation of plane-polarised light, hence a racemic mixture is formed.

What factors affect the rate of nucleophilic substitution?

1. steric hindrance

- as the number of alkyl groups bonded to the C atom in the C-X bond increases, steric hindrance increases, rate of reaction decreases.

2. stability of carbocation

- as the number of alkyl groups bonded to the C atom in the C-X bond increases, the stability of the carbocation formed in step 1 increases, rate of reaction increases

3. type of halogen atoms in the C-X bond

- ease of nucleophilic substitution depends on the ease of breaking the C-X bond
- as the bond energy of the C-X bond decreases down the group, halogenoalkanes react more readily.

Why are halogenoarenes inert to nucleophilic substitution?

1. partial double bond character

- p-orbital of the halogen atom overlaps with the π electron cloud system of the benzene ring.
- the lone pair of electrons on halogen atoms can be delocalised into the benzene ring, giving the C-X bond partial double bond character, making it stronger and harder to break.

2. interelectronic repulsion

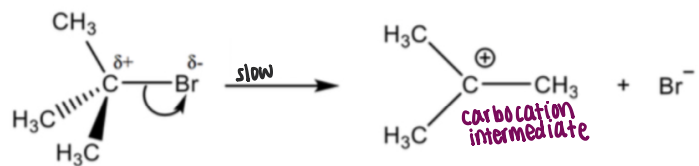
- nucleophiles face interelectronic repulsion with the π electron cloud system of the benzene ring.
- the benzene ring also provides high steric hindrance.

Mechanisms to know

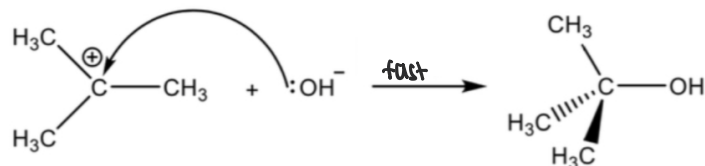
: Nucleophilic Substitution

S_N1 (Unimolecular nucleophilic substitution)

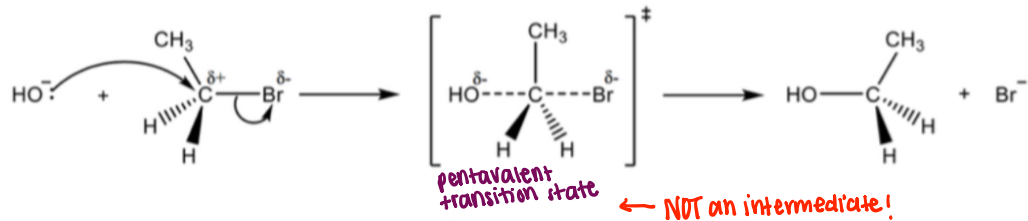
Step 1 (Formation of carbocation intermediate, slow step)



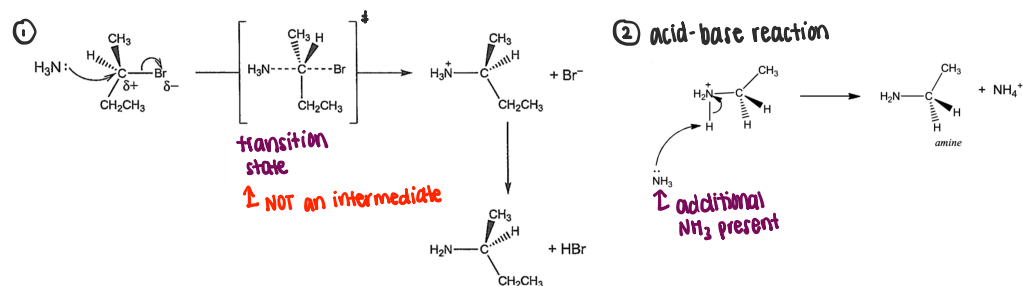
Step 2 (Nucleophile attacks carbocation intermediate)



S_N2 (Bimolecular nucleophilic substitution)



with NH₃:

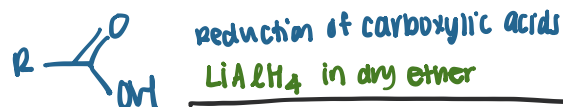
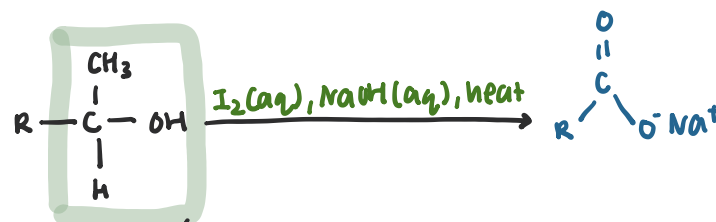


Distinguishing tests

test	observations
1. Add NaOH (aq) and heat: nucleophilic substitution to release halide from halogenoalkane 2. Add excess dilute HNO₃ after cooling: Neutralise excess OH⁻, prevents formation of Ag(OH) 3. Add AgNO₃ (aq): Forms ppt OR 1. Add 1cm³ of organic compound in a test tube 2. Add 1cm³ of ethanolic AgNO₃ and place test tube in a hot water bath	Use aqueous ammonia to more clearly differentiate between the halides Chloroalkane → white ppt of AgCl, soluble in excess aqueous ammonia Bromoalkane → Cream ppt of AgBr, partially soluble in excess aqueous ammonia Iodoalkane → Yellow ppt of AgI, insoluble in excess aqueous ammonia

ALCOHOLS

iodoform test:



E.A of alkenes

① cold conc. H_2SO_4 , ② boil, H_2O
 OR

$\text{H}_2\text{O}(\text{g})$, conc. H_3PO_4 , 300°C , 65 atm

excess conc. H_2SO_4 , 170°C OR Al_2O_3 , 350°C
 OR conc. H_3PO_4

Reduction of aldehydes & ketones

LiAlH_4 in dry ether

OR NaBH_4 in methanol

OR $\text{H}_2(\text{g})$ with Ni catalyst

★ see also in reduction of alkenes

N.S. of halogenoalkanes

$\text{NaOH}(\text{aq}) / \text{KOH}(\text{aq})$, heat under reflux

R-OH

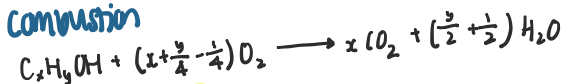
$\sim \text{OH}$

N.S. to form
 halogenoalkanes

$\text{R}-\text{Br}$ ← $\text{NaBr}(\text{s})$ or $\text{KBr}(\text{s})$,
 conc. H_2SO_4 , heat under reflux

$\text{R}-\text{I}$ ← $\text{NaI}(\text{s})$ or $\text{KI}(\text{s})$,
 conc. H_2SO_4 , heat under reflux

combustion

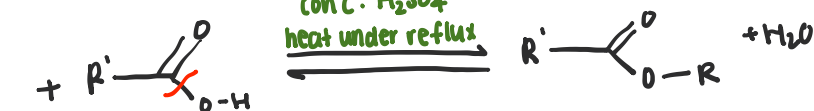


Redox
 $\text{Na}(\text{s})$

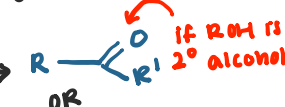
★ alcohols are not
 acidic enough to react w/ NaOH



conc. H_2SO_4
 heat under reflux



$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{H}_2\text{SO}_4(\text{aq})$, heat under reflux
 OR KMnO_4 , $\text{H}_2\text{SO}_4(\text{aq})$, heat under reflux



$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{H}_2\text{SO}_4(\text{aq})$, heat w/ immediate distillation

prevents aldehydes from
 being oxidised to carboxylic acids



PCl_5 , rt/p

SOCl_2 , heat under reflux

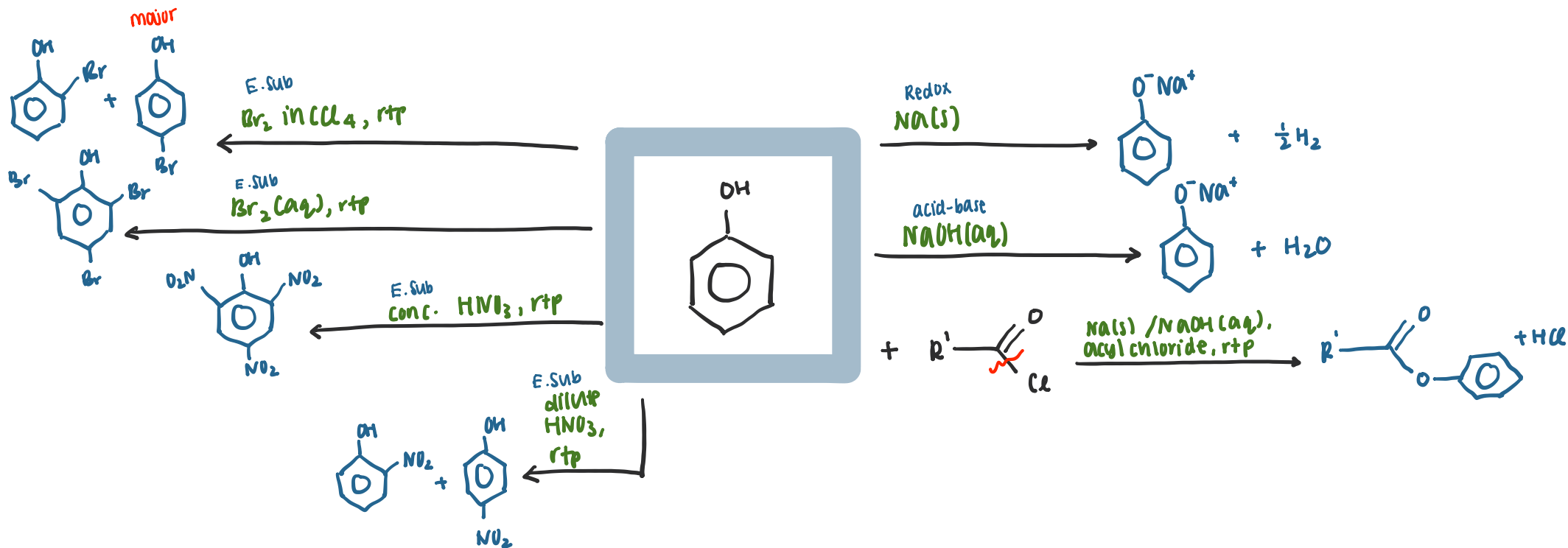
conc. HCl , ZnCl_2 , heat under reflux

PX_3 , heat under reflux

R-Cl

R-X

PHENOLS



PHYSICAL PROPERTIES

: simple molecular structure, hydrogen bonding

soluble in water

- energy released when hydrogen bonding is formed between water molecules and alcohol molecules is sufficient to compensate for the energy required to overcome the hydrogen bonding between alcohol molecules and hydrogen bonding between water molecules.

soluble in non-polar organic solvents

- energy released when id-id is formed between non-polar organic solvent molecules and alcohol molecules is sufficient to compensate for the energy required to overcome the hydrogen bonding between alcohol molecules and id-id between non-polar organic solvent molecules.

ACIDITY

: acidity of a compound is dependent on the stability of the conjugate base. The more stable the conjugate base, the stronger the acid.

- to achieve stability, the charge on the ion must be dispersed. The lower the charge, the less reactive and more stable the ion is.

- electron-withdrawing substituents help to disperse negative charges while electron-donating ones intensify them.

COMPARISON OF ACIDITY

: water as an 'invisible standard'

alcohols are weaker acids than water

- the electron-donating alkyl group intensifies the negative charge on the alkoxide ion, destabilising the conjugate base

phenols are stronger acids than water

- lone pair of electrons on O atom is delocalised into the benzene ring due to the p orbital of the O atom overlapping with the π electron cloud system of the benzene ring

- negative charge on the phenoxide ion is dispersed, stabilising the conjugate base

FAQ

Why is there a need to heat with immediate distillation to produce aldehydes from primary alcohols?

- if aldehydes are left in the mixture, they can be further oxidised into carboxylic acid.

- distillation is required to separate the aldehyde from the oxidising agent as soon as it is formed to prevent further oxidation.

- distillation can be done as aldehydes have a lower boiling point than alcohols and vaporise much more quickly.

Why do tertiary alcohols not undergo oxidation?

- absence of H atoms on the C atom bonded to the -OH group.

Why are phenols unable to react with carboxylic acids to form esters?

- phenols are poor nucleophiles compared to alcohols.

- carboxylic acids are not as reactive as acyl chlorides.

Why are phenols more reactive than the benzene ring?

- the -OH group is an electron-donating group as the O atom carries a lone pair of electrons that can delocalise into the benzene ring, increasing electron density in the benzene ring, making it more susceptible to electrophiles.

- the -OH group is considered an activating group and causes the phenol to be more reactive than benzene.

Why are phenols inert to nucleophilic substitution?

1. partial double bond character

- p orbital of the O atom overlaps with the π electron cloud system of the benzene ring, causing lone pair of electrons on O atom to delocalise into the benzene ring, giving the C-OH bond partial double bond character, making it stronger and harder to break.

2. interelectronic repulsion

- nucleophiles face interelectronic repulsion with the π electron cloud system of the benzene ring.

- the benzene ring also provides high steric hindrance.

Why does phenol form multi-substituted products with Br₂ (aq) but only monosubstituted products with Br₂ in CCl₄?

- Br₂ (aq) is more electrophilic because water is a more polar solvent, polarising the electron cloud of Br₂, forming partial positive charges on the Br atom, making Br₂ (aq) more susceptible to nucleophilic attacks.

- ketose sugars are not reducing sugars as they cannot be further oxidised easily

Distinguishing test:

works on all aldehydes except benzaldehyde / as long as an aliphatic aldehyde is present

aliphatic aldehyde

ketone

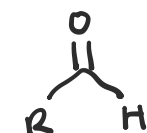
aromatic aldehyde



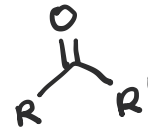
$K_2Cr_2O_7, H_2SO_4(aq)$,
heat w/ immediate distillation

oxidation

$\text{KMnO}_4 / \text{K}_2\text{Cr}_2\text{O}_7$,
 H_2SO_4 (aq), heat under reflux



aldely des



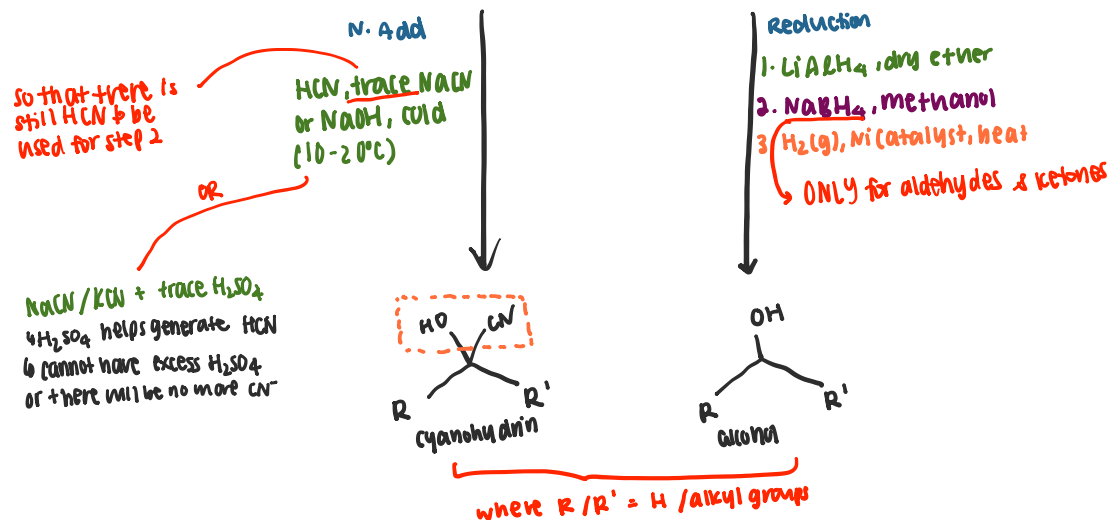
ketones



$K_2Cr_2O_7 / KMnO_4, H_2SO_4(aq)$
heat under reflux

oxidative cleavage

$H_2SO_4 / NaOH(aq)$,
 $KMnO_4$, heat under reflux



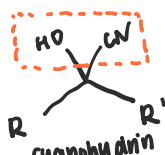
so that there is still HCN to be used for step 2

or

NaCN / KCN + trace H_2SO_4
 $4H_2SO_4$ helps generate HCN
 ↳ cannot have excess H_2SO_4
 or there will be no more CN^-

N. Add

HCl, trace NaCN
or NaOH, cold
(10-20°C)



cuanyu anin

where $R/R' = H$ /alkyl groups

Reduction

1. LiAlH_4 , dry ether

2. NaBH_4 , methanol

$$3 \text{H}_2(\text{g}), \text{Ni (catalyst, heat)}$$

ONLY for aldehydes & ketones

PHYSICAL PROPERTIES

: simple molecular structure, pd-pd due to C=O group

soluble in water

- the energy released to form hydrogen bonding between aldehyde / ketone molecules and water molecules is sufficient to compensate for the energy required to overcome the pd-pd between aldehyde / ketone molecules and the hydrogen bonding between water molecules.

soluble in non-polar organic solvents

- the energy released to form id-id between the non-polar organic solvent molecules and aldehyde / ketone molecules is sufficient to compensate for the energy required to overcome the pd-pd between aldehyde / ketone molecules and the hydrogen bonding between water molecules.

FAQ

Why are LiAlH₄ and NaBH₄ unable to reduce alkenes?

- they provide a H- nucleophile that attacks the electron-deficient C atom of the reactant, hence cannot be used to reduce alkenes which have an electron-rich C=C region.

Why is LiAlH₄ a stronger reducing agent than NaBH₄?

- Al is less electronegative than B and H, so the Al-H bond is more polar than the B-H bond, so H- is more readily produced.
- NaBH₄ can only reduce aldehydes and ketones.

Why are aldehydes generally more reactive than ketones in N. Addition?

1. steric hindrance

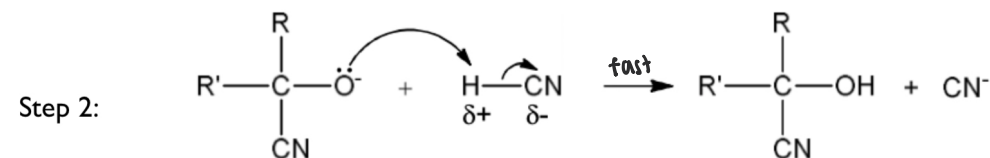
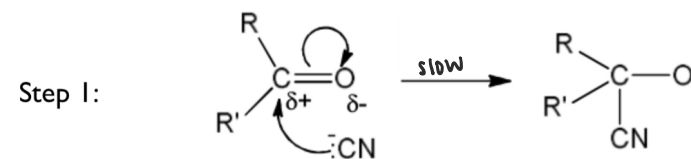
- aldehydes have 1 bulky alkyl group bonded to the carbonyl carbon while ketones have 2, so the attacking nucleophile approaches the carbonyl carbon in aldehydes more readily due to lower steric hindrance than in ketones.

2. electronic factor

- aldehydes have 1 electron-donating alkyl group while ketones have 2, hence the carbonyl carbon of aldehydes have a higher partial positive charge than ketones, making it more susceptible to nucleophilic attack.

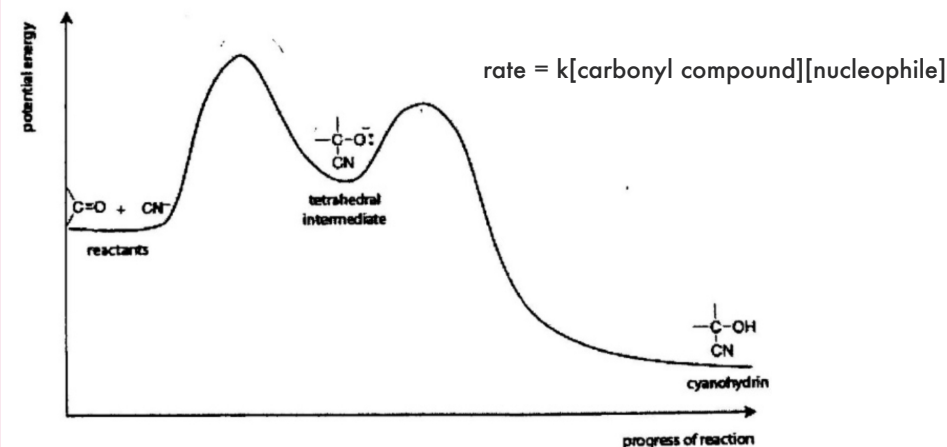
Mechanisms to know

: Nucleophilic Addition



- if the final product is chiral, a racemic mixture could be formed.
- there is equal probability of the CN⁻ nucleophile to attack either side of the trigonal planar carbonyl carbon, producing a racemic mixture with equal amounts of both enantiomers.

Kinetics of Nucleophilic Addition



Role of NaCN in Nucleophilic addition

: acts as a catalyst; NaCN completely dissociates to provide a high [CN⁻], CN⁻ is regenerated at the end of the reaction.

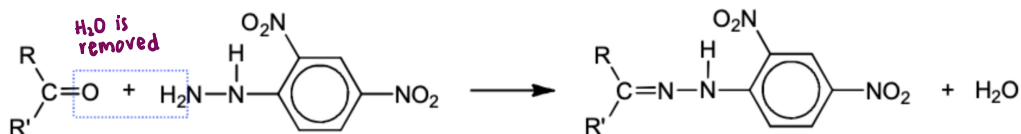
Role of NaOH in Nucleophilic addition

: NaOH reacts with H⁺ formed from HCN via an acid-base reaction, causing [H⁺] to decrease and the POE of dissociation of HCN to shift right, producing more CN⁻ and increasing the rate of reaction.

Distinguishing tests

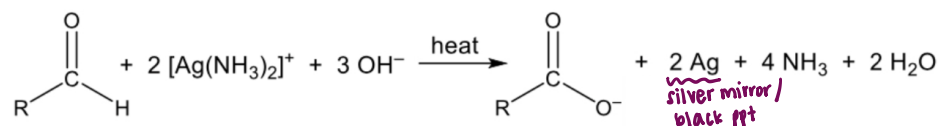
1. 2,4-DNPH (2,4-dinitrophenylhydrazine)

- condensation reaction
- positive test: orange ppt of 2,4-dinitrophenylhydrazone
- all carbonyl compounds

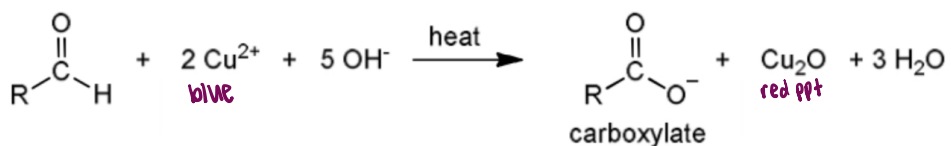


2. Tollens' Reagent

- oxidation reaction
- positive test for **ALL ALDEHYDES**: silver mirror / black ppt of Ag formed

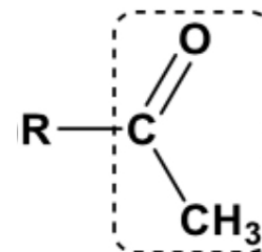


3. Fehling's Solution

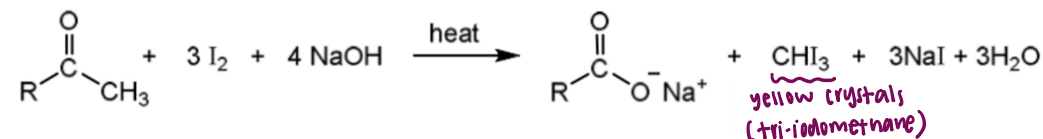


4. Iodoform test

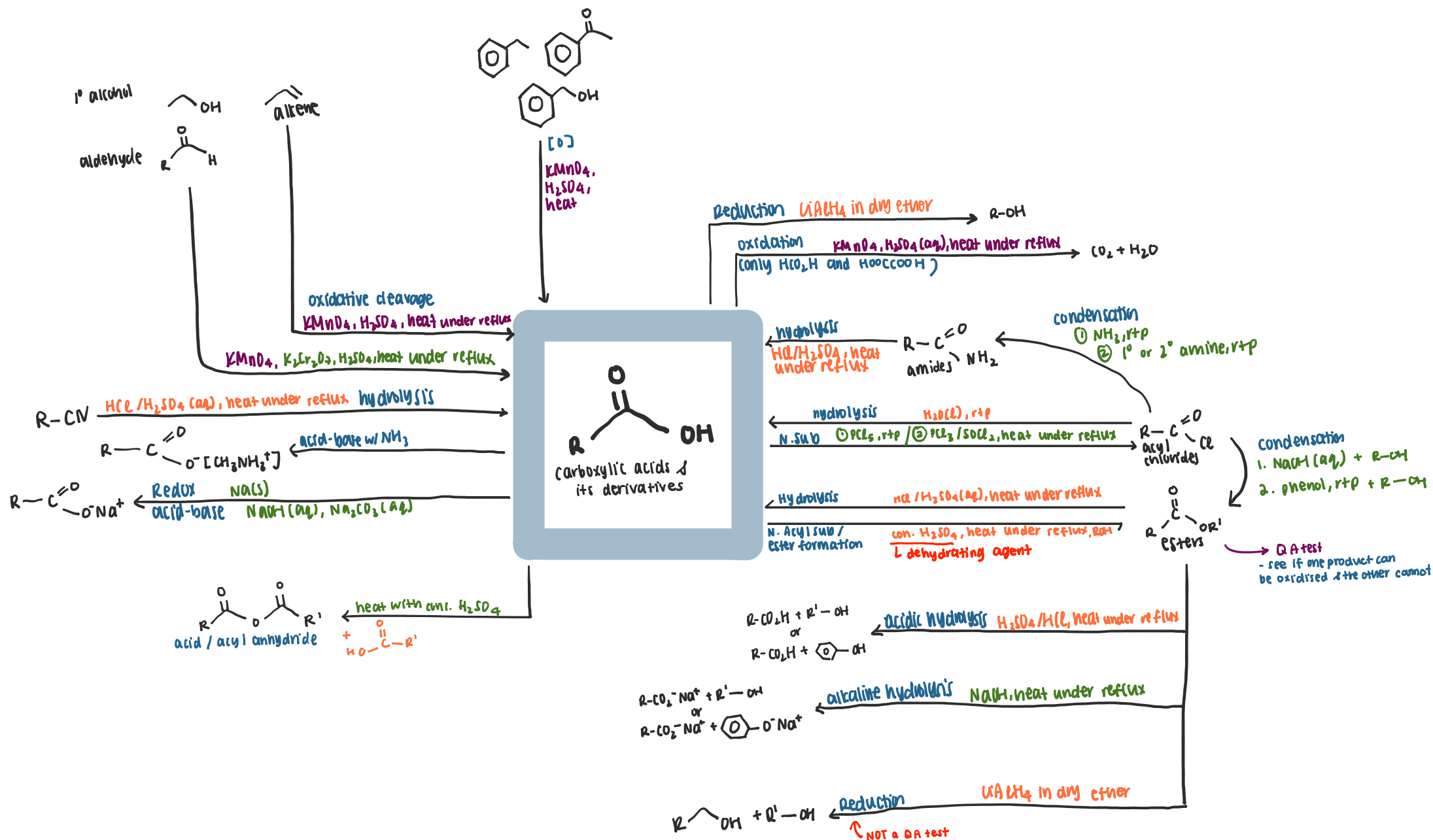
- R&C: I₂ (aq), NaOH (aq), heat
- oxidation reaction
- for aldehydes and ketones with the following structure, where R = H or alkyl group:



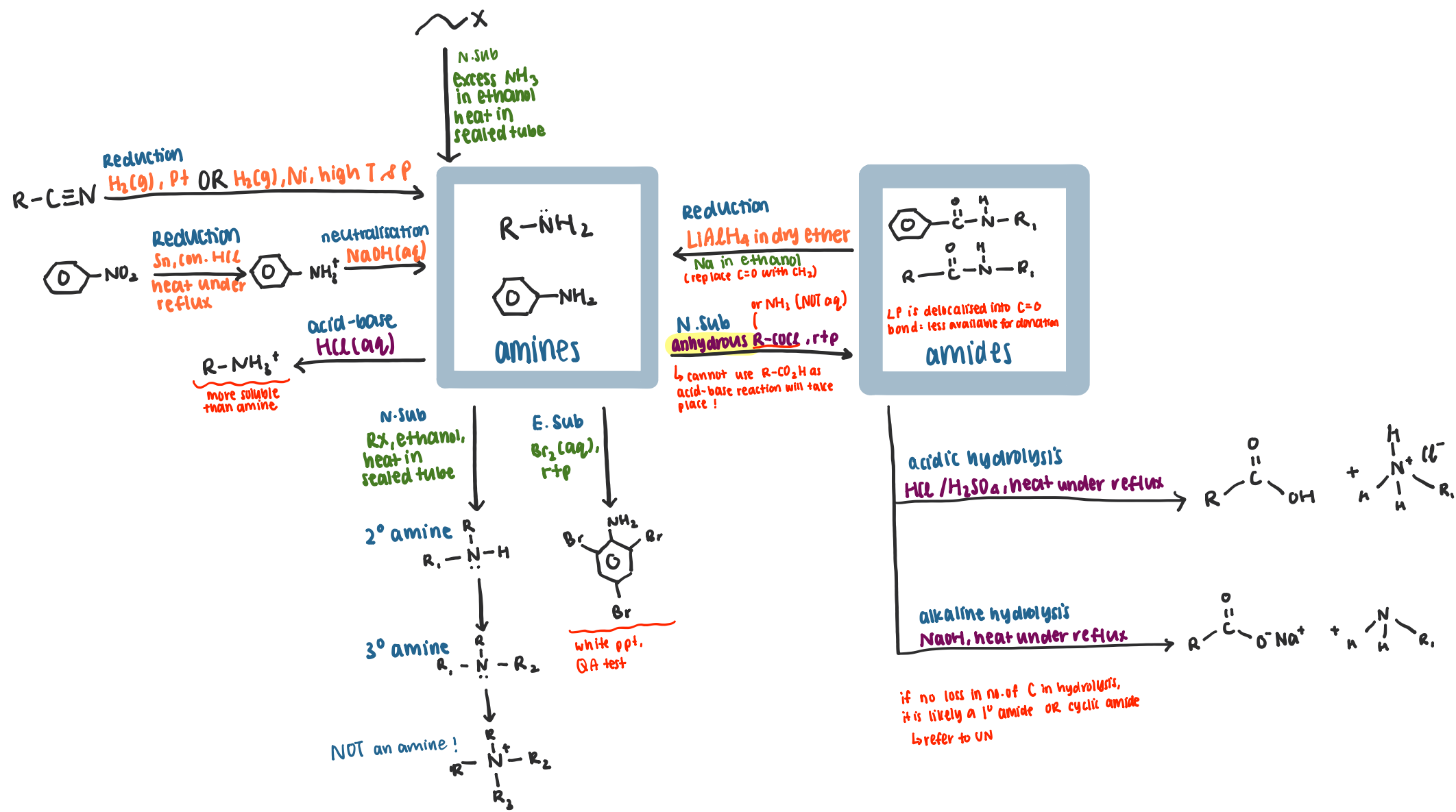
- positive test: yellow ppt of CHI₃
- for **KETONES**
- the only aldehyde that undergoes positive iodoform test is **ethanal**.
- a **step-down** reaction



CARBOXYLIC ACID & DERIVATIVES



NITROGEN COMPOUNDS



AMINO ACIDS

1. Acid strength:



- $\alpha\text{-CO}_2\text{H}$ is closer to the $\alpha\text{-NH}_3^+$ than $\text{R-CO}_2\text{H}$
 - $\alpha\text{-NH}_3^+$ exerts an **electron-withdrawing inductive effect**
 - further dispersal of negative charge on $\alpha\text{-COO}^-$
- $\text{-CO}_2\text{H}$ is more acidic than -NH_3^+ due to **resonance stabilisation** of -COO^- produced
- $\alpha\text{-NH}_3^+$ is closer to $\alpha\text{-COO}^-$ group than R-NH_3^+
 - $\alpha\text{-COO}^-$ exerts an **electron-withdrawing inductive effect**
 - intensifies positive charge on $\alpha\text{-NH}_3^+$, destabilising it.

2. lower pK_a = stronger acid = lose H^+ first

3. $\text{pH} < pK_a$: protonate
 $\text{pH} > pK_a$: deprotonate

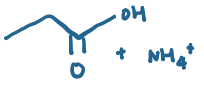
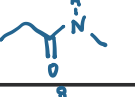
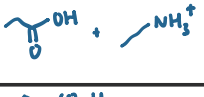
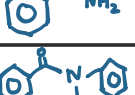
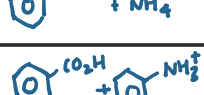
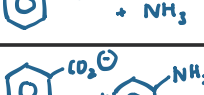
4. $\text{pH} > pI$: solution is basic (-ve charge)
 $\text{pH} < pI$: solution is acidic (+ve charge)

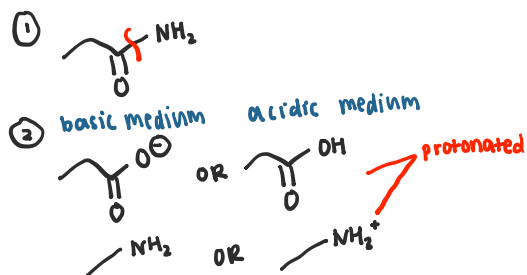
5. 1 product at equivalence point

6. isoelectric point = equivalence pt.
 $pI = \frac{1}{2}(pK_{a1} + pK_{a2})$

7. if an amino acid has 2 pK_a values, it is neutral

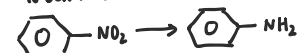
AMIDE HYDROLYSIS

amide	acidic products	alkaline products
		
		
		
		



- volatile amines: 4C and below

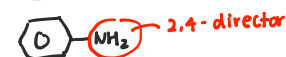
- to balance



↳ use H_2O to balance O

↳ use CH_4 to balance H

- Take note:



STRUCTURAL ELUCIDATION

- Deductions: include **ALL** reactions
- if there are substituents, include the **positions** of them
- take note of which groups are **3-directing** / **2,4-directing**
- use **degree of unsaturation (DoU)** formula:

$$\frac{2C + 2 - H - \text{Hal} + N}{2}$$

C - no. of C atoms

H - no. of H atoms

Hal - no. of halogen atoms

N - no. of N atoms

1 DoU = 1 double bond or 1 ring (e.g DoU of cyclohexene is 2; 1 for the ring structure, 1 for the C=C bond)

OTHERS

functions of electron-withdrawing groups:

- can weaken another bond to the extent that it breaks
- disperses the negative charge on a conjugate base, stabilising the conjugate base
- makes lone pairs less available for coordination to a proton

functions of electron-donating groups:

- makes lone pairs more available for coordination to a proton
- disperses the positive charge on a conjugate acid, stabilising the conjugate acid

AI Overview

An alpha (α) amino acid is an organic compound where the amino group ($-\text{NH}_2$) is attached to the alpha-carbon atom, which is the carbon atom immediately next to the carboxyl group ($-\text{COOH}$). These α -amino acids are the fundamental building blocks of proteins, with their unique side chains (R groups) determining their specific properties and functions.

