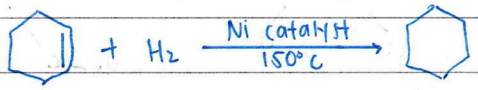
Date No.

ALKANES (saturated)

- aliphatic — C_nH_{2n+2} — From >4C, structural isomerism ✓
  - ⇝ due to branching
- cycloalkanes — C_nH_{2n}
  - stereoisomerism ✓
    - ⇝ optical isomerism
    - ⇝ geometrical isomerism
      - ↳ cycloalkanes
- sp^3 hybridised
- tetrahedral shape ≈ 109.5° bond angle

- As no. of C ↑, b.p. ↑.
  - ↳ electron cloud size increases and hence electron cloud becomes more easily polarised
  - ↳ id-id interactions are more extensive and stronger ⇒ more energy required to overcome...
- As branching ↑, b.p. ↓
  - ↳ molecule becomes more spherical and surface area for intermolecular interactions ↓
  - ↳ extent of id-id forces between molecules ↓ ⇒ less energy required to overcome...
- As more closely packed the molecules are, m.p. ↑
- mostly soluble in less polar organic solvents
- As Mr ↑, density ↑.
- Preparation of alkenes:  — generally UNREACTIVE (① non-polar ② saturated)

Reduction.

- Reactions:
  - ① Combustion
    - Complete: $C_xH_y + (x + \frac{y}{4})O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$
    - Incomplete: $C_xH_y + (\frac{x}{2} + \frac{y}{4})O_2(g) \rightarrow xCO(g) + \frac{y}{2}H_2O(l)$
      - or
      - $C_xH_y + \frac{y}{4}O_2(g) \rightarrow xC(s) + \frac{y}{2}H_2O(l)$
        - soot
  - ② Free-radical Substitution:

$CH_4 + Cl_2 \xrightarrow{uv/heat} CH_3Cl + HCl$

Initiation: $Cl\!-\!Cl \xrightarrow{uv/heat} 2Cl\cdot$

Propagation: $CH_4 + Cl\cdot \rightarrow \dot{C}H_3 + HCl$

$\dot{C}H_3 + Cl\!-\!Cl \rightarrow CH_3Cl + Cl\cdot$

Termination: $Cl\cdot + Cl\cdot \rightarrow Cl_2$

$\dot{C}H_3 + Cl\cdot \rightarrow CH_3Cl$

$\dot{C}H_3 + \dot{C}H_3 \rightarrow C_2H_6$ (trace)

* reactions should be in liquid or gaseous phase

X AQUEOUS ∴ water molecules will react

⇓

not a preferred synthesis method ∴ may result in multi-substitution.

(must use limited Cl_2 or excess alkane)

may lead differing positions too

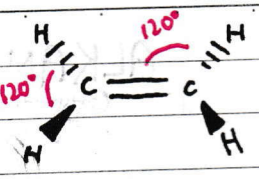
WHY LIGHT? to bring about homolytic fission of halogen molecule so that radicals produced would initate substitution reaction.

Date No.

ALKENES

→ trigonal planar about each C atom in the C(C=C) double bond

→ sp^2 hybridised

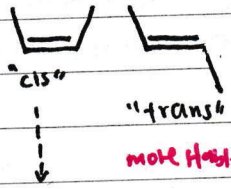


→ energy required to break C=C < 2x needed to break C-C ⇒ π bond weaker than σ bond

→ Geometrical Isomerism ⇒ side-on overlap of orbitals less effective than head-on overlap of orbitals

→ cycloalkene ✗

→ C joined to 2 different groups ✓

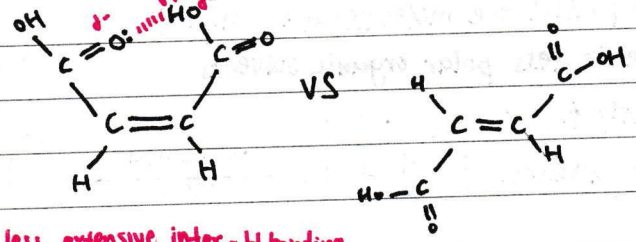


steric factor bet. groups ⇒ repulsion

- As C ↑, b.p ↑
- As branching ↑, b.p ↓, m.p. ↑
- cis b.p. >> trans. b.p.
- cis m.p. << trans. mp.

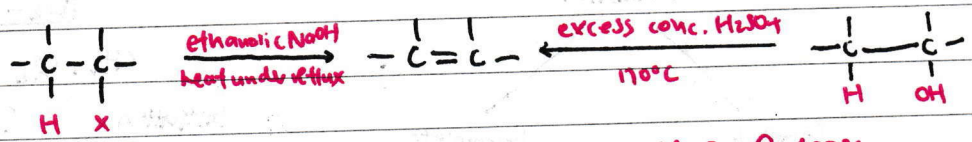
polar (pd-pd) | non-polar (id-id) | can pack better

* Beware of intramolecular H bonding!



less extensive inter-H bonding

- Preparation.



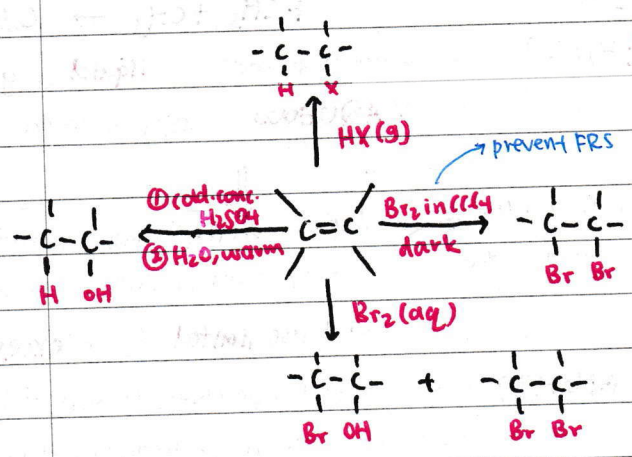
+ or Al_2O_3 @ 400°C

H_3PO_4 @ 250°C

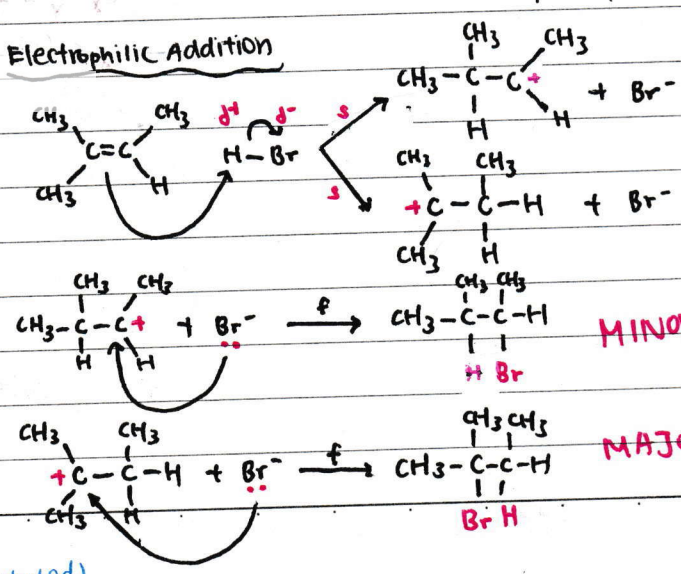
☆ Zaitsev's rule:

→ the more stable (substituted) alkene is the MAJOR product

Alkenes → high e⁻ density of C=C → π-electron cloud attracts electrophiles (electron-seeking) → have vacant orbitals that can accept e⁻ pair



Electrophilic Addition



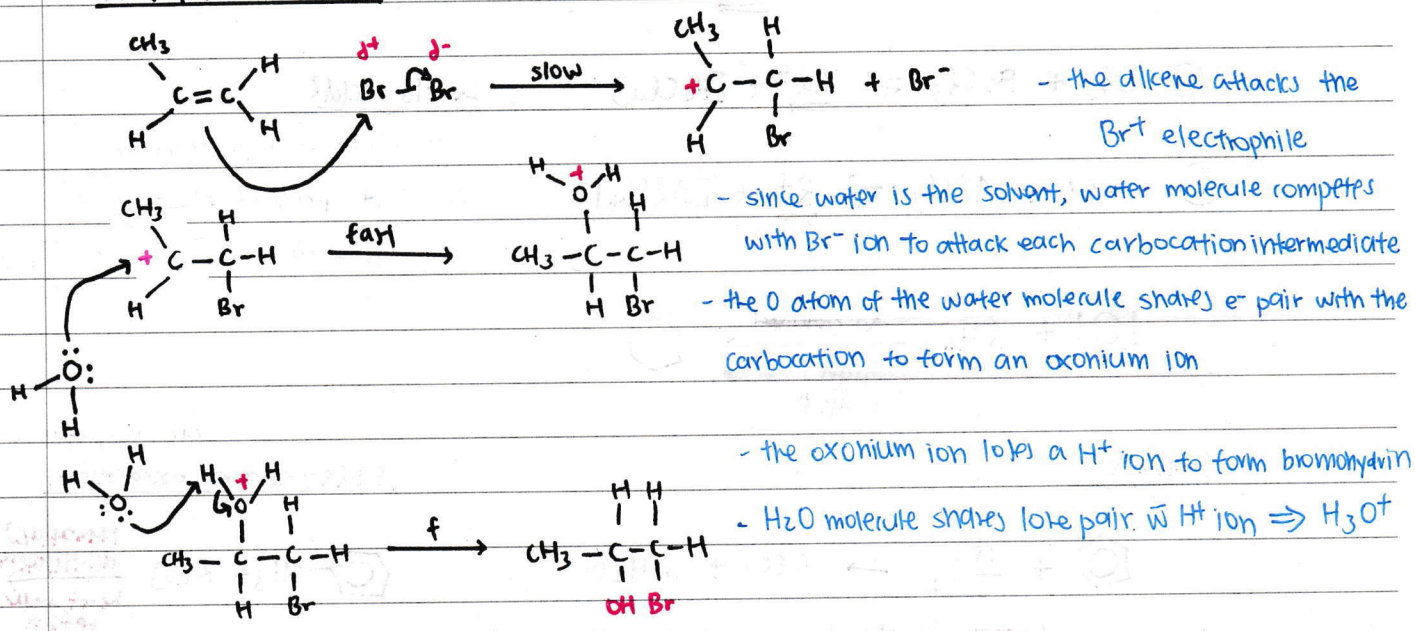
☆ Markovnikov's Rule:

- the more stable carbocation intermediate is formed (more substituted)
- the less electronegative binds to carbon with more H.

Date No.

* $CH_3CH=CH_2 + Br_2 + H_2O \longrightarrow CH_3CH(OH)CH_2Br + HBr$

Electrophilic addition



- the alkene attacks the Br^+ electrophile
- since water is the solvent, water molecule competes with Br^- ion to attack each carbocation intermediate
- the O atom of the water molecule shares e⁻ pair with the carbocation to form an oxonium ion
- the oxonium ion loses a H^+ ion to form bromohydrin
- H_2O molecule shares lone pair w/ H^+ ion ⇒ H_3O^+

Reduction: H_2 / Ni catalyst 150°C

✗ $LiAlH_4$ ∵ reduction involving $LiAlH_4$ is initiated by H^- nucleophile. Alkenes are e⁻ rich due to C=C ⇒ repel the H^- nucleophile which is e⁻ rich as well.

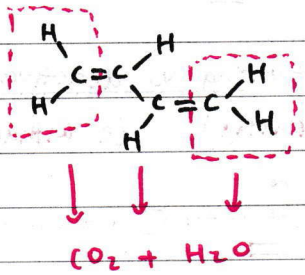
Oxidation: ① Mild

$KMnO_4(aq)$, $NaOH(aq)$, cold ⇒ forms a diol.

② Strong < Acidic / Basic

$KMnO_4(aq)$, $H_2SO_4(aq)$, heat under reflux ⇝ ketone / c. acid / $CO_2 + H_2O$

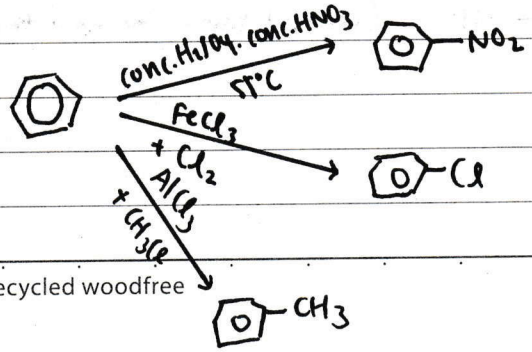
Combustion: $C_nH_{2n} + \frac{3n}{2} O_2(g) \rightarrow nCO_2(g) + nH_2O(l)$



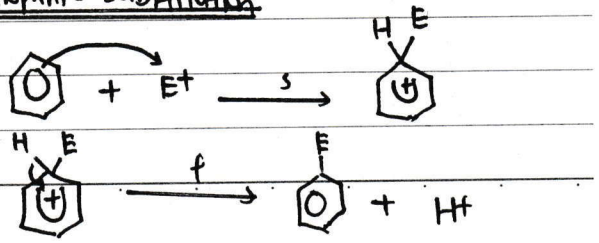
ARENES

↝ 6 delocalised electrons

- all C–C bond the same (1½ bond)
- sp^2 hybridised
- prefers **SUBSTITUTION** over **ADDITION** ⇒ destroy aromatic character and resonance stabilisation ⇝ becomes less stable.



Electrophilic Substitution



Date No.

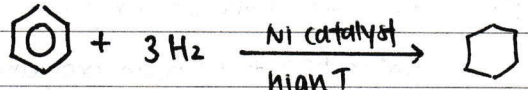
Generation of electrophile:

① $2H_2SO_4 + HNO_3 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$

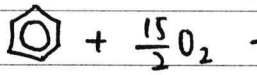
② $Cl_2 + FeCl_3 \rightleftharpoons Cl^+ + [FeCl_4]^-$

③ $R-Cl + AlCl_3 \rightleftharpoons R^+ + [AlCl_4]^-$

Lewis acid?
- an electron pair acceptor
⇒ accepts pair of electrons from halogen to generate Br^+ or Cl^+ electrophile

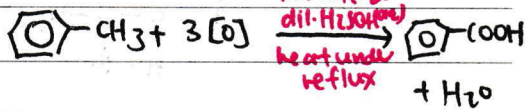


Combustion:



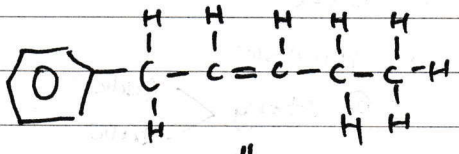
(sooty smoky flame ∵ high C:H ratio)

Side-chain oxidation: (decolourisation of purple KMnO4)

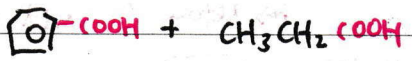


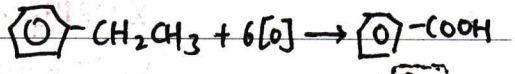
VS

Oxidative cleavage >> side-chain oxidation.



⇓





* Benzylic C atom must contain O/H atom to have side-chain oxidation.

Activating vs deactivating

(e⁻ donating) (e⁻ withdrawing)

↓ e⁻ density in the ⬡ and makes it less attractive for electrophiles
tends to intensify + charge → destabilisation of carbocation

* ↑ e⁻ density in the ⬡ and makes it more attractive to electrophiles
helps disperse + charge in intermediate carbocation → stabilisation of carbocation
∴ activating group activates ⬡ towards e⁻ attack ↑ reactivity

Orientation

2, 4 : $-NH_2$ $-OH$ $-CH_3$ $-Cl$

3 : $-COOH$ $-NO_2$ $-CHO$ (should know by now tbh)

Date No.

Halogenoalkanes

→ mono sub: $C_nH_{2n+1}X$

→ 1° 2° 3° (no. of alkyl / aryl groups attached to C)

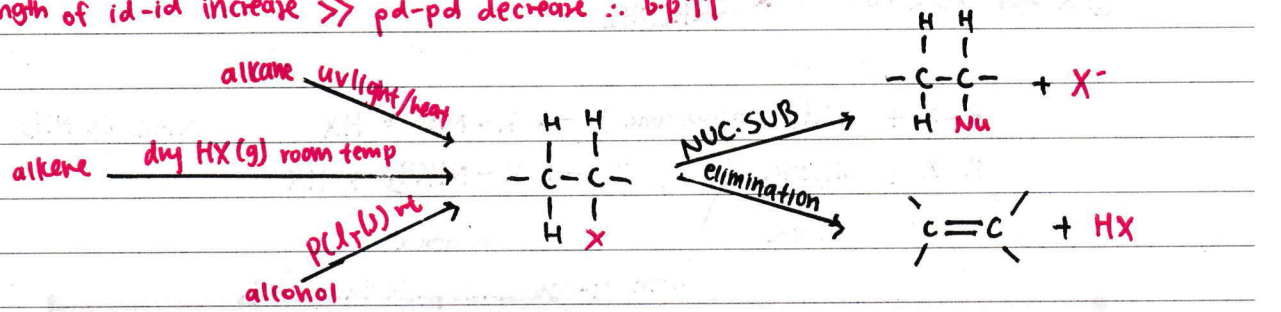
→ halogenoarenes (X directly attached to ⬡)

↑ b.p. ∵ pd-pd interactions

$CH_3CH_2F < CH_3CH_2Cl < CH_3CH_2Br < CH_3CH_2I$

(* soluble in non-polar solvent)

strength of id-id increase >> pd-pd decrease ∴ b.p ↑↑



- since the halogen is more electronegative than C, the α-carbon is said to be electron deficient ∴ susceptible to nucleophilic attack

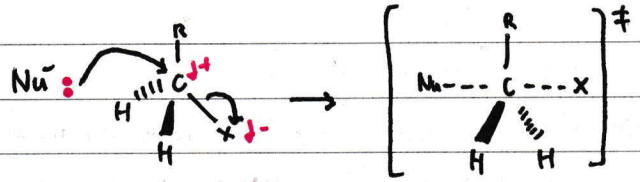
Nucleophiles: electron-rich species which have at least one pair of electrons

- negatively charged nucleophile always stronger than its conjugate acid.

S_N2

→ one step

→ rate = k[RX][nucleophile]



(If C is chiral, chiral centre is inverted compared w reactant)

- As energy required to break bond ↓, rate of S_N2 / S_N1 ↑ - favoured by less substituted halogenoalkanes

(slowest) $CH_3-F < CH_3-Cl < CH_3-Br < CH_3-I$ (fastest)

→ too strong ∴ chemically inert

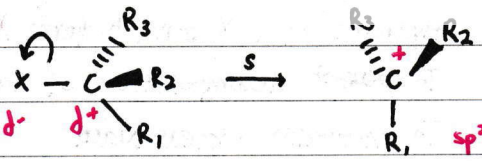
S_N1

→ two step

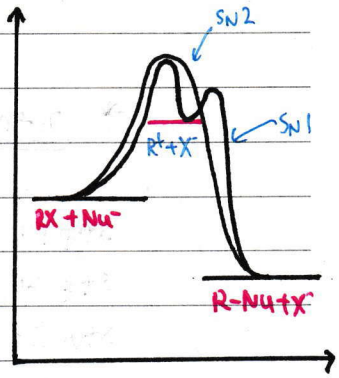
→ rate = k[RX]

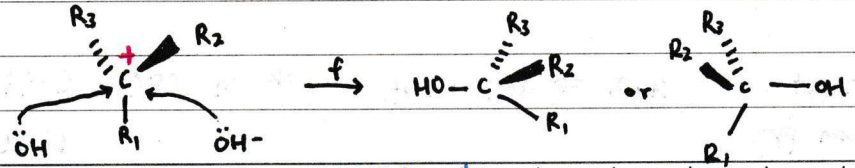
- favoured by factors that stabilise carbocation (more e⁻ donating)

- favoured by polar solvents



sp² trigonal planar





racemic mixture formed ⇒ resultant mixture is optically inactive*

equal likelihood of OH⁻ attacking from left or right

Date No.

- Examples of nucleophilic sub:

$R-X + OH^-(aq) \longrightarrow R-OH + X^-$ aqueous NaOH, heat.

$R-X + CN^- \longrightarrow R-CN + X^-$ ethanolic KCN, heat.

① HCl(aq) heat
② NaOH (aq) heat

hydrolysis

reduction

} $LiAlH_4$ in dry ether ;
Ni catalyst, H_2, heat

① RCOOH / ② $RCOO^-$ $R-CH_2NH_2$

$R-X + NH_3$ (excess, conc.) $\longrightarrow R-NH_2 + HX$ ethanolic NH_3, heat in sealed tube

$R-X + \underbrace{CH_3NH_2}_{1° \text{ amine}}$ " " $\longrightarrow R-\underbrace{NHCH_3}_{2° \text{ amine}} + HX$

even stronger nucleophile than NH_3

$R'-X + RO^- \longrightarrow R'-OR + X^-$ Na, R'OH, heat.

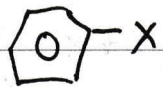
ether

NaCN

- Elimination (refer to alkenes)

* $RCH_2CH_2-X \xrightarrow[\text{heat}]{KOH(aq)} RCH_2CH_2OH + X^-$ nuc. sub.

$RCH_2CH_2-X \xrightarrow[\text{heat}]{KOH(alc)} RCH=CH_2 + H_2O + X^-$ elimination.



- less reactive to nucleophilic substitution

(a) the p orbital of the halogen atom overlap with the π-electron cloud of the benzene ring ⇒ partial double bond character in the C-X bond
↝ more energy required to break the C-X bond.

(b) electronic repulsion between electrons in the benzene ring and the approaching electron-rich nucleophile

* Distinguishing Test

Step 1: Heat RX with NaOH(aq)	Hydrolysis of C-X bond to form $X^-(aq)$
Step 2: Cool the mixture	To prevent decomposition of $AgNO_3$
Step 3: Acidify with dilute HNO_3	To neutralise excess NaOH.
Step 4: Add $AgNO_3$ (aq)	Test for presence of X^-.

AgCl ⇒ white ppt AgI ⇒ yellow ppt.

AgBr ⇒ cream ppt

* In CFCs: C-Cl + C-Br bonds broken

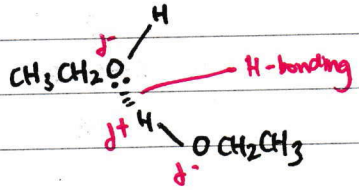
C-H & C-F bonds not broken → preferred replacement

Date No.

ALCOHOLS

→ $C_nH_{2n+1}OH$

→ 1° 2° 3°



- with same no. of e^-, b.p. of alcohol > alkanes ∵ H-bonding
- ↑ length of alkyl chain, bp ↑ ∵ ↑ ia-id ↑ branching, b.p ↓
- ↑ length of alkyl chain, solubility ↓ ∵ vdw forces become predominant

- alcohols have lower acidity than water

$ROH \rightleftharpoons RO^- + H^+$ --- (1)

$HOH \rightleftharpoons HO^- + H^+$ ---(2)

e^- donating alkyl group increases the e^- density on the oxygen in the alkoxide ion, RO^- and intensifies the negative charge ⇒ destabilises the alkoxide ion and makes it ready to accept protons

p.o.e for (1) lies more to the left compared to (2) ∴ weaker acid

↑ e^- donating alkyl group, ↓ acidity of alcohols

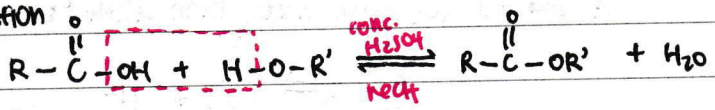
- can only react w Na(s) $C_2H_5OH + Na(s) \longrightarrow C_2H_5O^-Na^+(s) + \frac{1}{2}H_2(g)$ ↑ effervescence

ALKENE —hydration→ ALCOHOLS ←nuc. sub.— HALOGENOALKANE

ALCOHOLS —reduction→ c. acid / aldehyde / ketone

- Combustion (to give CO_2 & H_2O)

- Esterification



* slow & reversible.

① supply H^+ to catalyse reaction

② remove H_2O so shift p.o.e →

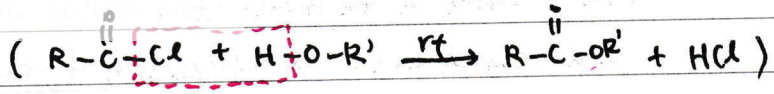
- Halogenation

$R-OH \rightarrow R-X$

⇝ dry HX gas + heat

⇝ PX_3

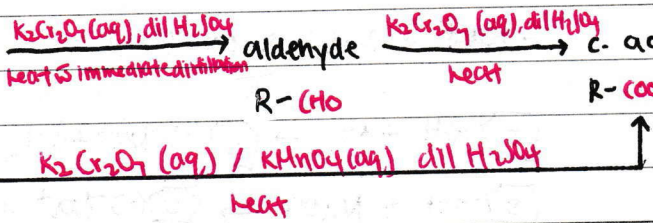
⇝ $PCl_5(s)$, $SOCl_2$

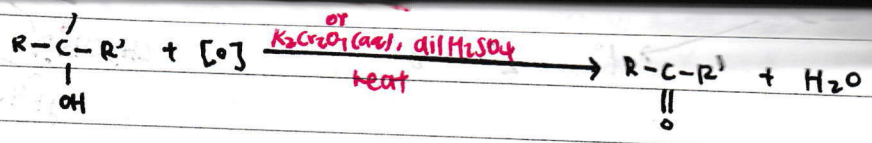


- Elimination (refer to alkene)

Oxidation

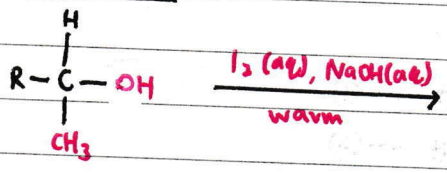
1° alcohols ⇝ $R-CH_2OH$



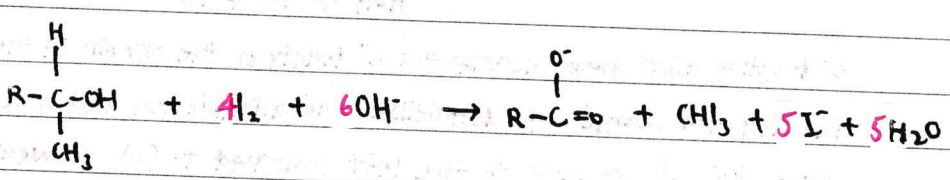


3° alcohol cannot be oxidised.

* **Iodoform test** (oxidation)



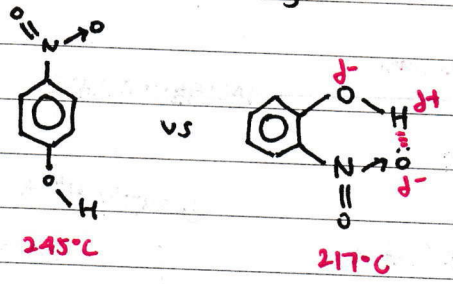
Balanced equation:



PHENOLS

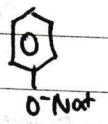
-high bp ∵ intermolecular H-bond

→ extent of H-bonding

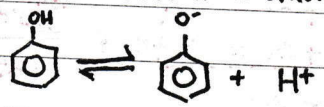


↓ extent of intermolecular H bonding

↑ solubility by heating with alkali



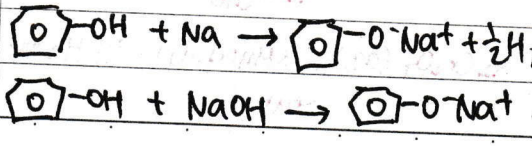
- phenols are more acidic than alcohol & water



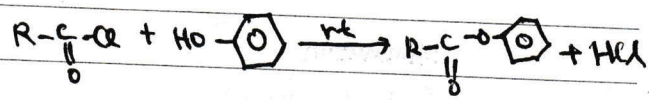
- the p orbital of the oxygen atom overlaps with the π-orbitals of the benzene ring to form a delocalised cloud → delocalisation of negative charge on O into ring

∴ phenoxide ion resonance stabilised.

- react w Na(s) & NaOH(aq)

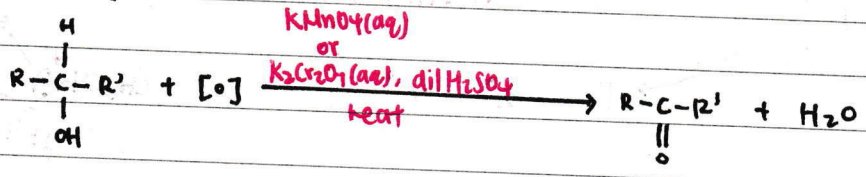


- react w acyl chloride



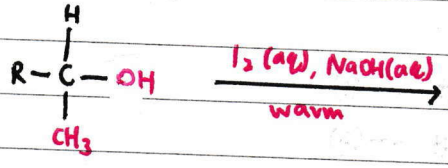
Date No.

2° alcohols

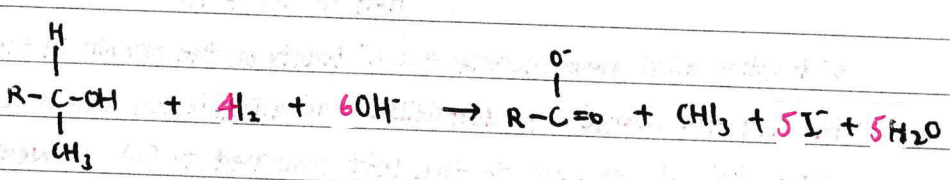


3° alcohol cannot be oxidised.

* Iodoform test (oxidation)

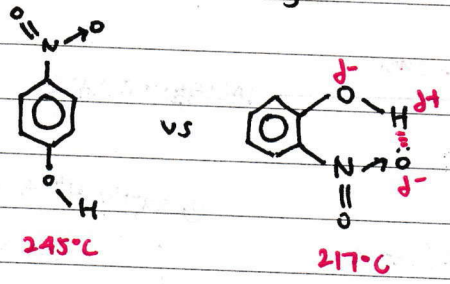


Balanced equation:



PHENOLS

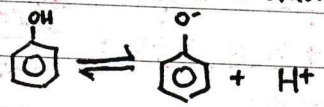
- high bp ∵ intermolecular H-bond
→ extent of H-bonding



↓ extent of intermolecular H bonding

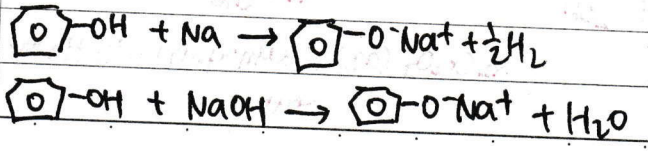
↑ solubility by heating with alkali

- phenols are more acidic than alcohol & water

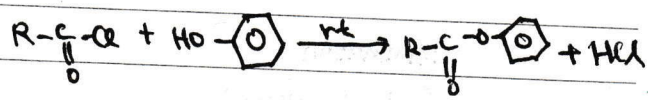


- the p orbital of the oxygen atom overlaps with the π-orbitals of the benzene ring to form a delocalised cloud → delocalisation of negative charge on O into ring
∴ phenoxide ion resonance stabilised.

- react w Na(s) & NaOH(aq)



- react w acyl chloride



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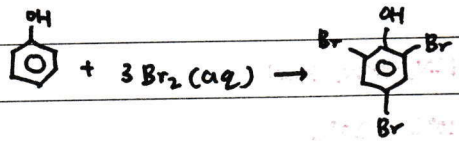
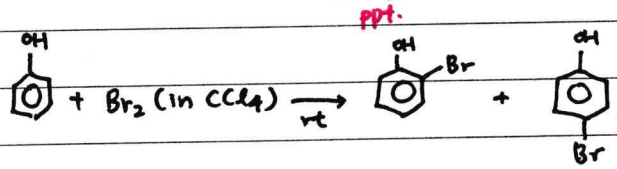
- electrophilic substitution



multi-sub

white ppt.

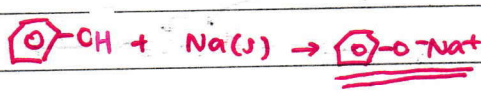


mono-sub.

conc. HNO_3 → tri-sub.

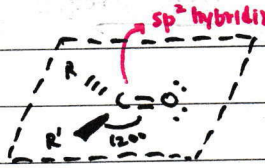
dil. HNO_3 → mono-sub.

* Test: Neutral $FeCl_3$ (aq)

* sometimes phenol can act as nucleophile 

CARBONYL COMPOUNDS → ketone / aldehyde.

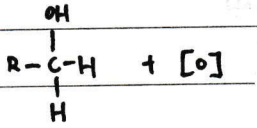
- planar molecule
- pd-pd interactions (m.p. and b.p.)
- lone pair of electrons on carbonyl O atom allows formation of H bond with protonic H atom of H_2O molecule.



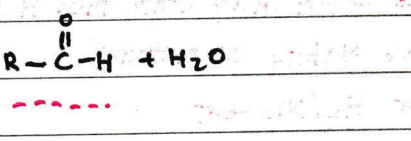
⇝ appreciable solubility

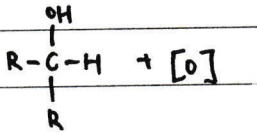
As C chain ↑, solubility in water ↓ due to increasing size of hydrophobic alkyl chain.

only way of forming ALDEHYDE.

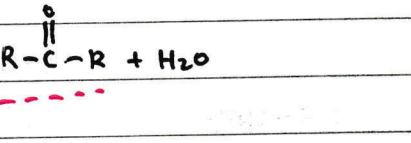
1° 

$K_2Cr_2O_7$ (aq), dil H_2SO_4
heat ⇝ immediate distillation



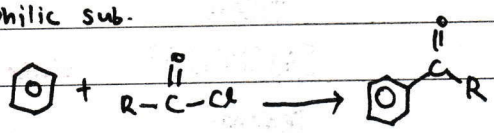
2° 

$K_2Cr_2O_7$ (aq), dil H_2SO_4
heat with reflux



oxidative cleavage of alkenes

electrophilic sub.



- C atom of the −C=O group has δ^+ ∵ bonded to e^- negative O

⇒ e^- rich nucleophiles attracted to this e^--deficient site

* aldehydes more reactive than ketone.

⇒ affected by:

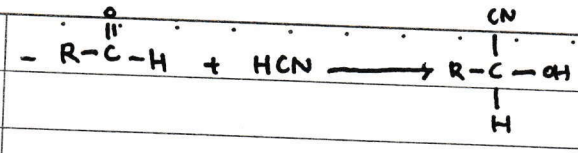
① Electronic factor

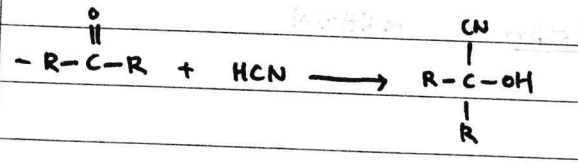
e^- donating groups reduce size of δ^+, hence decreasing attraction for nucleophiles + SUSCEPTIBILITY of nucleophilic attack

② steric factor

- hinder approach of attacking nucleophile -

Date No.



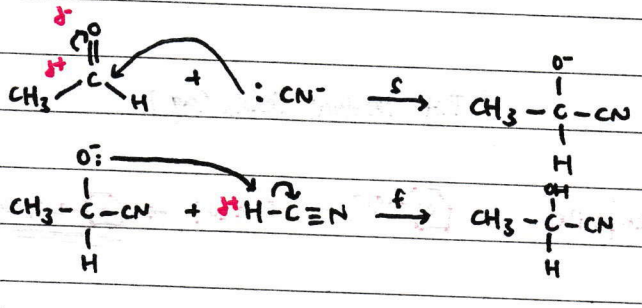


HCN, trace KCN

10°C – 20°C

Nucleophilic Addition

$KCN \rightarrow K^+ + :CN^-$

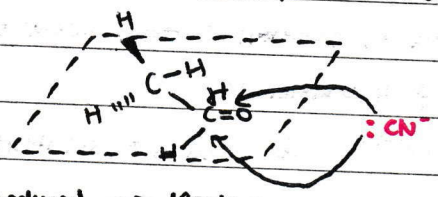


– use either KCN catalyst or NaOH

$HCN + OH^- \rightarrow H_2O + :CN^-$

→ geometry around sp^2 hybridized carbonyl carbon atom is trigonal planar

→ nucleophile can attack carbonyl carbon from either side to form racemic mixture.



aldehyde → reduced → 1° alc.

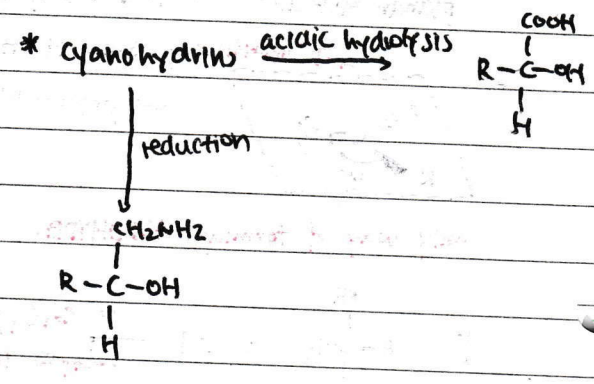
ketone → reduced → 2° alc.

* $LiAlH_4$ in dry ether, then H_2O @ r.t

or $NaBH_4$ in methanol

or H_2/Ni, heat

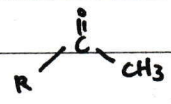
↳ cannot reduce alkenes



	R–CHO		R–COR
2,4-DNPH	✓ orange ppt	✓ orange ppt	✓ orange ppt
Tollen's $[Ag(NH_3)_2]^+$	✓ silver mirror	✓ silver mirror	✗ no formation
Fehling's Cu^{2+}	✓ reddish-brown ppt	✗ no ppt	✗ no ppt
$K_2Cr_2O_7$(aq) dil H_2SO_4, heat	✓ purple turns colourless	✓ purple turns colourless	✗ remains purple

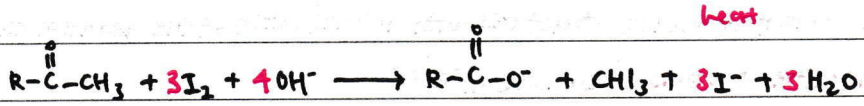
Date No.

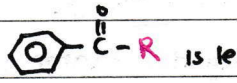
- Iodoform



$I_2(aq) + NaOH(aq)$

heat

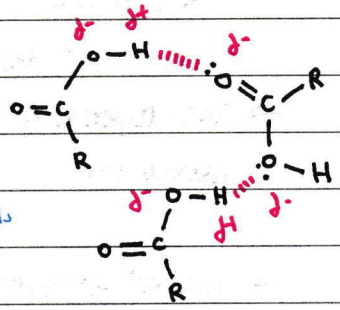


*  is less reactive towards nucleophilic attack as the carbonyl C atom is less e^- deficient due to interaction of the π electron cloud of the carbonyl group and those of the adjacent  . In addition, the bulky benzene ring poses steric hindrance to the approaching nucleophile.

Carboxylic Acids → carboxyl group (-COOH)

→ tend to have higher boiling points

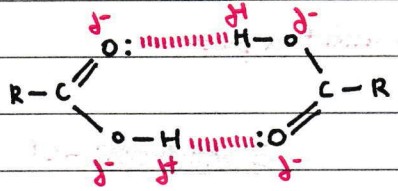
∵ intermolecular H bonding



- stronger intermolecular hydrogen bonds than alcohols

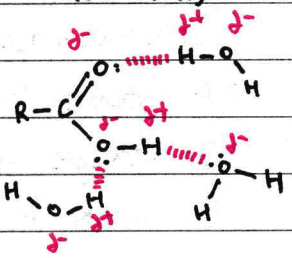
∵ -OH group more polarised due to presence of e^- withdrawing carbonyl group.

- tend to dimerise in vapour state and in non-polar solvents

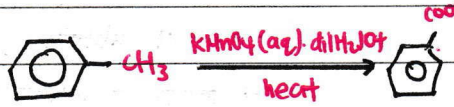


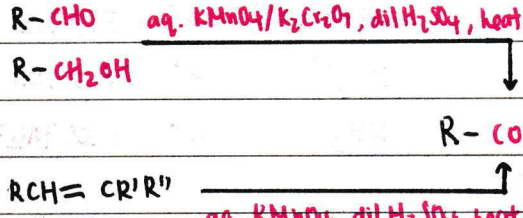
In polar solvents:

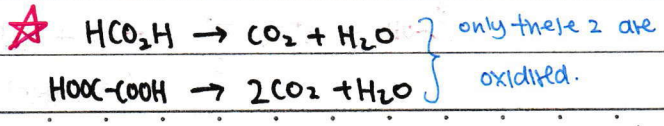
$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$



- ability of the -COOH group form H-bonds with water molecules
- partial dissociation in water forms H_3O^+ and $RCOO^-$ which are capable of forming ion-dipole interaction with water molecules
- As length of C↑, solubility ↓







☆ $HCO_2H \rightarrow CO_2 + H_2O$ } only these 2 are oxidised.

$HOOC\text{-}COOH \rightarrow 2CO_2 + H_2O$ }

Date No.

Acidity: $RCOOH \rightleftharpoons RCOO^- + H^+$

Generally, R-OH < water <  < R-COOH

(the more stable the conjugate base formed, the less likely it is to accept proton)

→ $RCOO^-$ forms 2 equivalent resonance structures with delocalisation of the negative charge over 2 highly electronegative O atoms (resonance effect)

→ This results in the carboxylate anion being greatly stabilised compared to the  and RO^- ion.

⇒ negative charge equally distributed between the 2 oxygen atoms

→ 

→ The p-orbital of O overlaps with the π-electron cloud of the benzene ring so that the negative charge on O delocalises into the benzene ring

→ The dispersal of negative charge stabilises the phenoxide ion so that it is more stable than the alkoxide ion.

→ $ROH \rightleftharpoons RO^- + H^+$

→ e^- donating alkyl group intensifies the negative charge on O atom

→ charge on RO^- ion also remains localised on a single e^- negative O

→ RO^- is most unstable and most likely to accept a proton.

E^- donating $-CH_3$	E^- withdrawing $-Cl$
① increase e^- density of ⊖ charge on carboxylate ion	① decrease " "
② intensify ⊖ charge on the carboxylate anion	② disperse " "
③ destabilise the c. base of the acid	③ stabilise " "
④ acidity ↓	④ acidity ↑

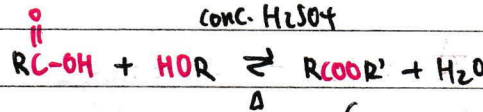
→ no. of substituents

→ position of substituents

Reactions ✓ :

$Na(s)$	✓	$RCOO^-Na^+ + \frac{1}{2}H_2$
$NaOH(aq)$	✓	$RCOO^-Na^+ + H_2O$
Na_2CO_3	✓	$2RCOO^-Na^+ + H_2O + CO_2$
NH_3	✓	$RCOO^-NH_4^+$ acid-base reaction

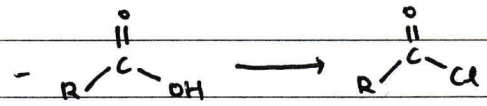
Esterification



$$RC(=O)-OH + HOR \underset{\Delta}{\overset{\text{conc. } H_2SO_4}{\rightleftharpoons}} RCOOR' + H_2O$$

(reversible)

Date No.



PCl_3, PCl_5, $SOCl_2$

at room temp.

- Reduction: RCOOH $\xrightarrow{LiAlH_4 \text{ in dry ether}}$ $RCH_2OH + H_2O$

X $NaBH_4$ in methanol

DERIVATIVES : acid → hydrolyse readily in water

acyl-chloride } lower bp than C. acid

ester

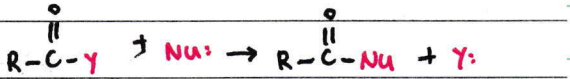
hydrolyses to amide

give HCl

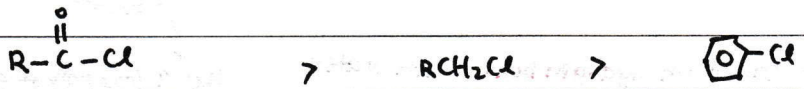
(pH=1)

Y: OH acid OR' ester

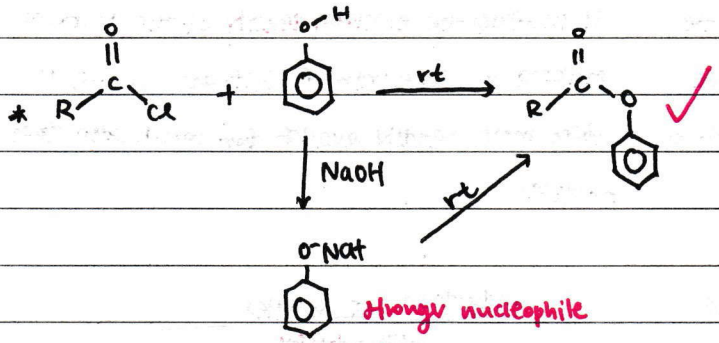
Cl acylchloride NH_2 amide



Ease of hydrolysis



higher $\delta+$ on C (bonded to 2 strongly e^- negative atoms, O & Cl)	lower $\delta+$ on C (only bonded to 1 e^- negative Cl atom)	overlapping of p-orbital on Cl atom with π-electron cloud of benzene
⇒ attracts nucleophile more strongly	⇒ attracts nucleophile less strongly	⇒ attracts nucleophile less strongly
highly polarised C–Cl cleaves easily	C–Cl cleaves only with heating	C–Cl does not cleave (partial double bond character)
sp^2 hybridised (less steric hindrance)	sp^3 hybridised (more steric hindrance)	



Strongly nucleophile

+ ammonia → 1° amide

+ 1° amine → 2° amide

+ 2° amine → 3° amide

X 3° amine

ester $\underset{\Delta}{\overset{HCl(aq)}{\rightleftharpoons}}$ C. acid + alcohol

ester $\xrightarrow[\Delta]{NaOH(aq)}$ C. acid salt + alcohol

Date No.

NITROGEN COMPOUNDS

- amide
- amine

sp^3 hybridised ; trigonal pyramidal

↑ in C chain, ↑ b.p.

$3° < 2° < 1°$ → pd-pd, id-id + H-bonding

- no H-bonding
- weaker pd-pd + less extensive H-bonding

b.p. of amines << b.p. of alcohol

→ N atom less e⁻ negative than O atom

→ N–H bond less polar than the O–H bond

Amine

has a lone pair of electrons on the N atom and is available to form dative covalent bond ῶ proton

Solubility: can form hydrogen bonds with water

↑ C, ↓ solubility

availability of the lone pair of electrons on the N-atom for co-ordination ῶ proton

$NH_2 < NH_3 < CH_3CH_2NH_2$

In phenylamine, the lone pair of e⁻ on the N atom is delocalised by interaction ῶ the π-electron cloud of the ⬡. ∴ lone pair less available for coordination to a proton.

In ethylamine, the $-CH_2CH_3$ group is e⁻ releasing. It increases the electron density at the N atom, making the lone pair of electrons on the N atom more readily available for coordination to a proton.

* substituents on the ⬡ affects too.

$R-X + NH_3 \xrightarrow[\text{heat in sealed tube}]{\text{excess. conc. } NH_3 \text{ (ethanolic)}} R-NH_2$

$R-X + R-NH_2 \longrightarrow R_2\ddot{N}H$

$R-X + R_2-NH \longrightarrow R_3\ddot{N}$

$R-X + R_3-N \longrightarrow R_4N^+X^-$

Reduction of nitriles

$R-C\equiv N \xrightarrow{LiAlH_4 \text{ in dry ether}} R-CH_2NH_2$

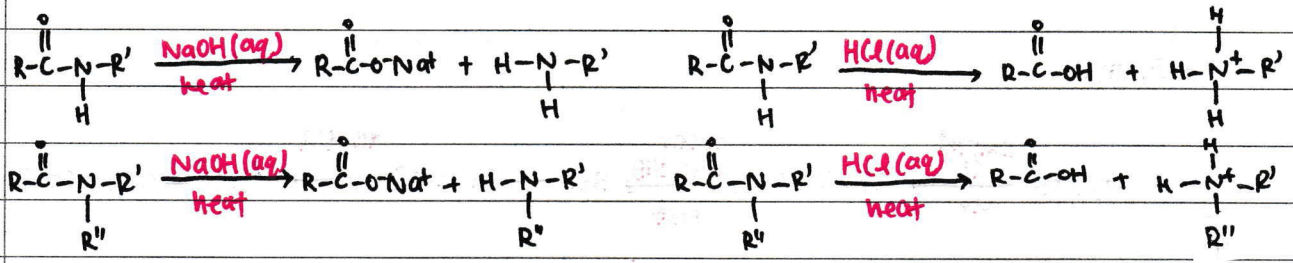
Reduction of amides $LiAlH_4$ in dry ether

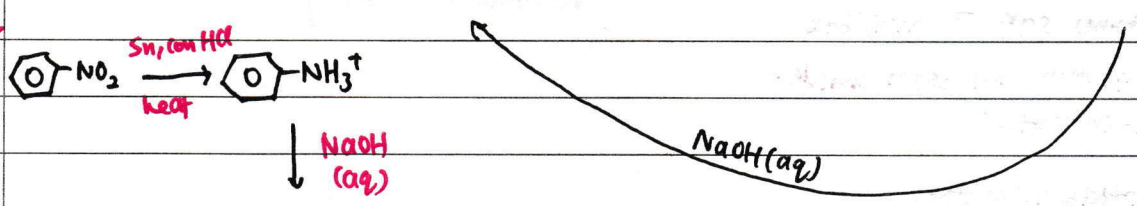
- 1° amide → 1° amine
- 2° amide → 2° amine
- 3° amide → 3° amine

Date No.

- Hydrolysis

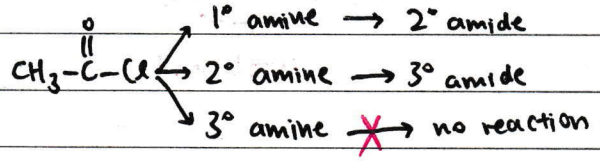
Basic **Acidic**

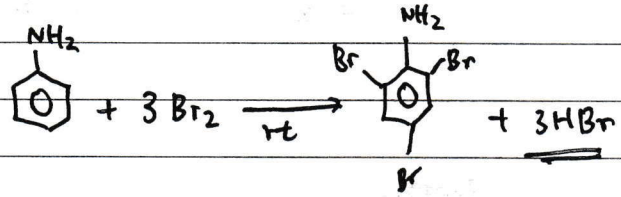




amine + acid → amine salt

amine salt + alkali → amine





* to mono-sub: ① acylation — reduce e⁻ density
② bromination
③ basic hydrolysis

1° & 2° amides ↑ bp ∵ H-bonding
3° amine no H-bonding

WHY ARE AMIDES NEUTRAL? the lone pair of electrons on the N atom interacts with the π-e⁻ cloud of the adjacent C=O bond and is delocalised, and hence not available for coordination to proton.

If no. of C < 5 in amines, pungent gas evolved turns moist red litmus blue.

Amino Acids — contain -COOH and -NH₂
- exist as zwitterions — held together by strong* ionic bonds ∴ ↑ m.p ↑ b.p.
- much more soluble in water
  - ⇝ can interact w/ H₂O molecules via ion-dipole interactions

amphoteric; optical isomerism (except glycine)

pI — pH at which amino acid exists predominantly as zwitterions & does not migrate under electric field
- separation by electrophoresis — different rate of movement due to different sizes and different net charges

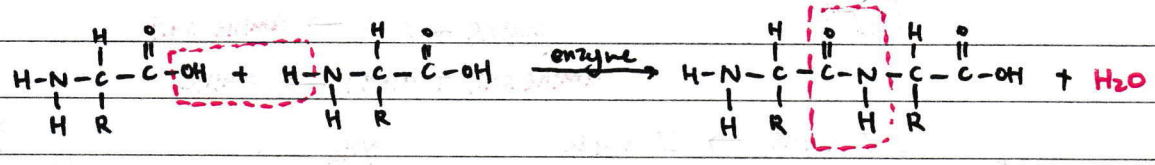
Date No.

- Titration curves

- Synthesis

$CH_3COOH \xrightarrow[\text{uv}]{\text{limited } Cl_2} Cl-CH_2COOH \xrightarrow[\text{heat}]{\text{excess conc. } NH_3} H_2N-CH_2COO^- \xrightarrow{\text{all HCl}} H_3N^+-CH_2-COO^-$

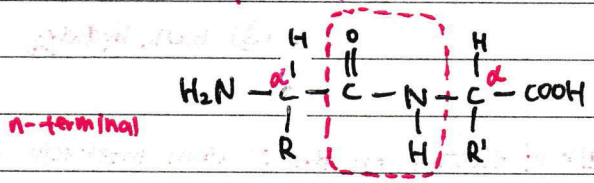
- Form salt w/ acid/base
- acylation can form amide.
- esterification
- Peptide formation



peptide bond

Proteins

1° structure — sequence of amino acids in the polypeptide chain



peptide bond

* peptides containing same amino acid residues but in different order are not identical

⇒ has partial double bond character

due to delocalisation of electrons

The C & N + 2 attached atoms → planar 120°

① complete hydrolysis → amino acids

② partial hydrolysis → smaller polypeptide fragments

acid-catalysed

- heating with concentrated HCl at 100°-120°C for 10-36 hours in evacuated tube

HCl, H_2SO_4(aq) NaOH(aq) heat under reflux for few hours

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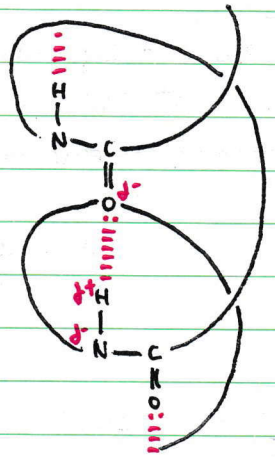
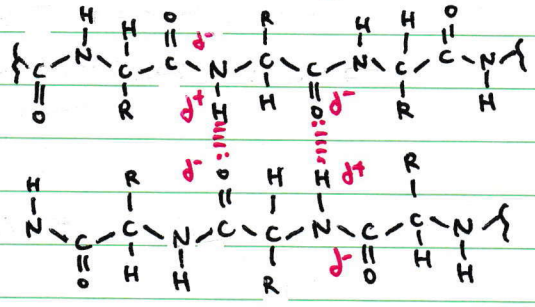
2° structure — the way in which segments of the polypeptide backbone orientate into a regular pattern through hydrogen bonding between the N-H and C=O groups of the peptide linkages in the polypeptide backbone

α-helix: regular coiled spiral polypeptide chain held in place by intra-chain hydrogen bonds between the C=O group of nth amino acid residue and the N-H group of (n+4)th amino acid residue. The R groups point outside of the helix and are perpendicular to the main axis of the helix.

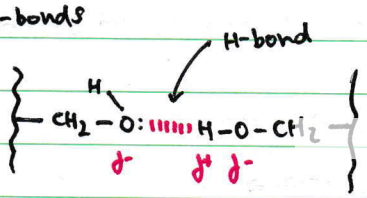


β-pleated sheet: all peptide linkages are involved in intra-chain hydrogen bonding. It is stabilized by hydrogen bonds between the C=O group of a peptide in one strand and the N-H group of another peptide in adjacent strand. The R groups project above and below the sheet perpendicularly.

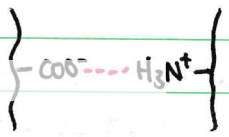


3° structure — the 3D arrangement of the protein due to the folding of the 2° structural elements together with the spatial disposition of the side-chains. Folding is due to R group interactions.

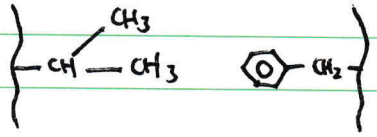
① H-bonds



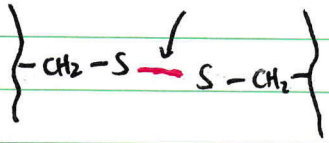
② Ionic interactions



③ Vander Waals' forces



④ Disulfide linkages



4° structure — the spatial arrangement and association of polypeptide subunits. It is the combination of several protein chains into a larger 3D-structure held together by R-group interactions

① H-bonding ② ionic interactions ③ van der Waal's forces ④ disulfide linkages

HAEMOGLOBIN:

- 2 α-subunits + 2 β-subunits
- each subunit dative covalently bonded to haem residue
- 1 haemoglobin molecule can bind to 4 O_2 molecules to form one molecule of HbO_8.

$$Hb + 4O_2 \underset{\text{low } [O_2]}{\overset{\text{high } [O_2]}{\rightleftharpoons}} HbO_8.$$

Denaturation: - the disruption of 2°, 3° or 4° structure of proteins by breaking the non-covalent interactions that hold these structures in their native conformation

⇒ loss of biological function.

→ for eg: conditions which disrupt specific interactions that maintain the conformation of the enzyme active site will usually lead to loss of catalytic activity

① ↑ in temp: - results in strong molecular vibrations which agitate the polypeptide chains enough to overcome the interactions that stabilise the protein conformation

⇒ Coagulation can occur as unfolded protein molecules get entangled and aggregate to form solid.

② Change in pH: - change ionic charges on amino acid residues and hence disrupt electrostatic attractions

low pH: protonation $-COO^- \rightarrow -COOH$

high pH: deprotonation $-NH_3^+ \rightarrow -NH_2$

} at one point, isoelectric. no net charge ⇒ no longer repel and: tend to coagulate and ppt out of solution

③ Heavy metal ions: - compete with +ve-charged groups for attraction to negatively charged groups, hence disrupting original ionic interactions

④ detergents: — contain hydrophobic and hydrophilic groups

hydrophobic → can disrupt association of hydrophobic side chains

hydrophilic → associate with surface of protein.