# Alkanes

**combustion:**

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

## Free Radical Substitution

$Cl_2(g)$ / $Br_2(g)$ , UV light

- provide energy to initiate the homolytic fission of X–X bond to generate X· radicals
- brief exposure as UV light produces X· radicals that initiate chain reactions of propagation step to produce more radicals for rxn to sustain

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

↳ $CH_3Cl$ predominates w/ excess $CH_4$
$CCl_4$ predominates w/ excess $Cl_2$

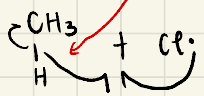
**mechanism**

Initiation

$$Cl-Cl \xrightarrow{UV} 2Cl\cdot$$

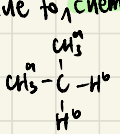
homolytic fission

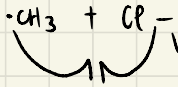
Propagation



$$\cdot CH_3 + H-Cl$$

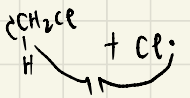
- different poss due to diff. chemical environments of H atoms



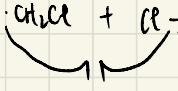


$$CH_3Cl + Cl\cdot$$

sub. $H^a$ atoms give 1-chloropropane while sub $H^b$ atoms give 2-chloropropane



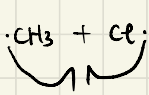
$$\cdot CH_2Cl + H-Cl$$



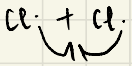
$$CH_2Cl_2 + Cl\cdot$$

} for disubstituted poss

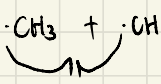
Termination (at least 3)



$$\cdot CH_3 + Cl\cdot \rightarrow CH_3-Cl$$



$$Cl\cdot + Cl\cdot \rightarrow Cl-Cl$$



$$\cdot CH_3 + \cdot CH_3 \rightarrow CH_3-CH_3$$

**Ratio of isomeric poss**

- ratio of poss calculated from number of H atoms of same chemical environment that can be substituted to form a particular isomer

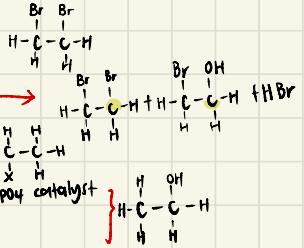
# Alkenes

## Reduction

- $H_2(g)$, Ni catalyst, heat
- $H_2(g)$, Pd/Pt catalyst, room temp

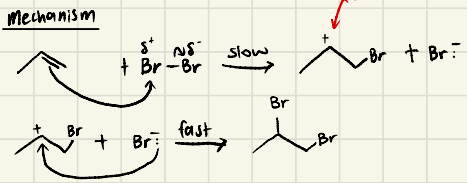
## Electrophilic Addition

- $Br_2$ in $CCl_4$, room temp
- $Br_2(aq)$, room temp
- $HX(g)$, room temp
- $H_2O(g)$, 300°C, 60atm, conc. $H_3PO_4$ catalyst (industrial)
- conc. $H_2SO_4$, $H_2O$, heat (laboratory)



## Mechanism

carbocation on C w/ more alkyl group / least e⁻ withdrawing groups (halogens)

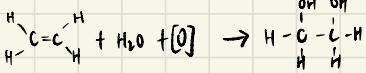



## Oxidation

purple $KMnO_4$ decol.

purple $KMnO_4$ decol.; brown ppt. of $MnO_2$

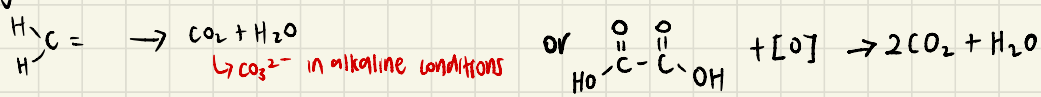
mild oxidation : $KMnO_4$, $H_2SO_4(aq)$, cold / $KMnO_4$, $NaOH(aq)$, cold



purple $KMnO_4$ decol.

purple $KMnO_4$ decol.; brown ppt. of $MnO_2$

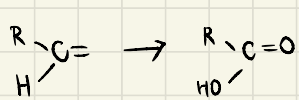
strong oxidation / oxidative cleavage : $KMnO_4$, $H_2SO_4(aq)$, heat under reflux / $KMnO_4$, $NaOH(aq)$, heat under reflux



$\rightarrow CO_2 + H_2O$

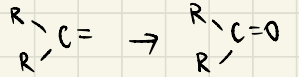
↳ $CO_3^{2-}$ in alkaline conditions

or $+[O] \rightarrow 2CO_2 + H_2O$



carb. acid

in alkaline conditions



ketone

# Arenes

$\Delta H$ of hydrogenation of  $= -354\ kJ\ mol^{-1}$

$\Delta H$ of hydrogenation of  $= -208\ kJ\ mol^{-1}$

diff in actual & expected value of $\Delta H = 146\ kJ\ mol^{-1}$

↳ resonance energy → measure of stability of benzene due to delocalisation of its π electrons.

## Benzene

### Electrophilic Substitution

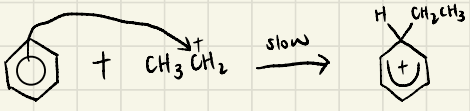
- $Br_2(l) / Cl_2(g)$, anhydrous $FeX_3$ / $AlX_3$ / finely divided Fe catalyst, room temp.
  - anhydrous $FeX_3$ / $AlX_3$: to prevent $FeX_3$ / $AlX_3$ from undergoing hydrolysis w/ water
  - finely divided Fe: reacts with $X_2$ to form $FeX_3$
- RCl, anhydrous $FeCl_3$ / $AlCl_3$ catalyst, room temp.
  - $FeCl_3$ / $AlCl_3$ acts as Lewis acid catalyst by accepting an electron pair from $Cl_2$
- conc. $HNO_3(aq)$, conc. $H_2SO_4(aq)$ catalyst, heat under reflux at 55°C
  - $H_2SO_4$ acts as a Bronsted-Lowry acid by donating a proton to $HNO_3$

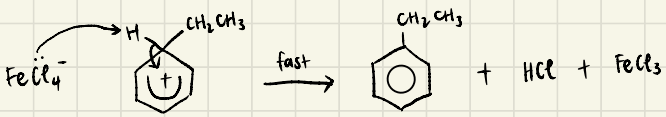
**Mechanism** (Lewis acid catalyst)

$$AlCl_3 + Cl_2 \rightleftharpoons AlCl_4^- + Cl^+$$

or

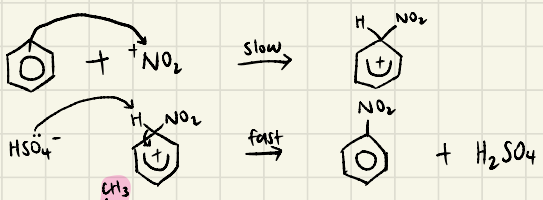
$$FeCl_3 + CH_3CH_2Cl \rightleftharpoons FeCl_4^- + CH_3^+CH_2$$




**Mechanism** (Bronsted-Lowry acid catalyst)

$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + H_2O + HSO_4^-$$




## methylbenzene, 

### Electrophilic Substitution

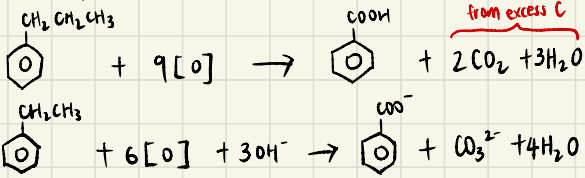
- conc. $HNO_3$, conc. $H_2SO_4$, 30°C → lower temp ∵ electron donating alkyl group ↑ reactivity
- $Br_2(l) / Cl_2(g)$, anhydrous $FeX_3$ / $AlX_3$ / finely divided Fe catalyst, room temp.

} substituted at 2,4 positions

- $Cl_2(g) / Br_2(g)$, uv light (FRS of $CH_3$ side chain)

## Oxidation

- $KMnO_4$ (aq), $H_2SO_4$ (aq), heat under reflux → purple $KMnO_4$ decol.
- $KMnO_4$ (aq), $NaOH$ (aq), heat under reflux → purple $KMnO_4$ decol., brown ppt of $MnO_2$

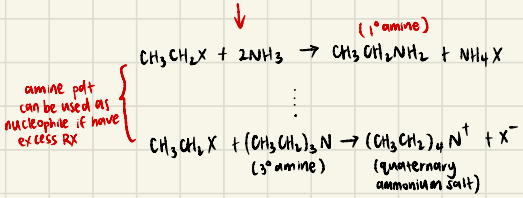



## Alkyl Halides

$RX + NaOH \rightarrow ROH + NaX$

### Nucleophilic Substitution

- NaOH (aq), heat under reflux
- ethanolic NaCN, heat under reflux
- excess ethanolic $NH_3$, heat in sealed tube




Further rxns for R-CN:

**Hydrolysis**

- HCl (aq)/$H_2SO_4$ (aq), heat under reflux
- NaOH (aq), heat under reflux

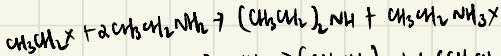
$R-CN + HCl + 2H_2O \rightarrow R-COOH + NH_4Cl$

$R-CN + NaOH + H_2O \rightarrow R-COO^-Na^+ + NH_3$

**Reduction**

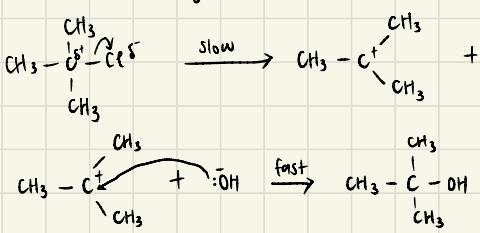
- $LiAlH_4$ in dry ether, room temp.
- Na in ethanol
- $H_2$ (g) w/ Ni/Pd/Pt catalyst (heat / room temp)

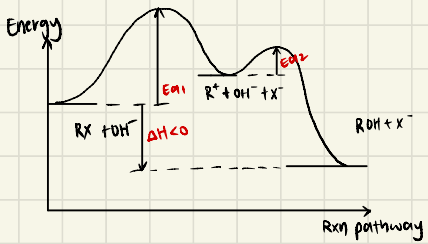
$R-CN + 4[H] \rightarrow R-CH_2NH_2$ → amine



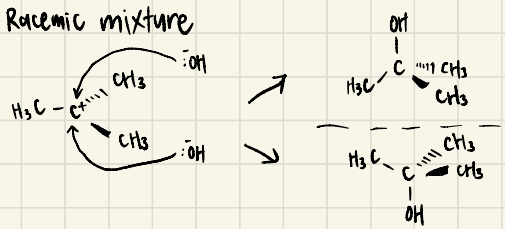

### Mechanism

**$S_N1$ (mostly tertiary RX)**

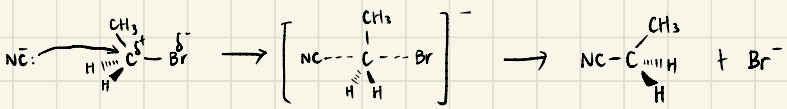


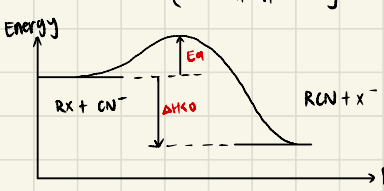




**Racemic mixture**



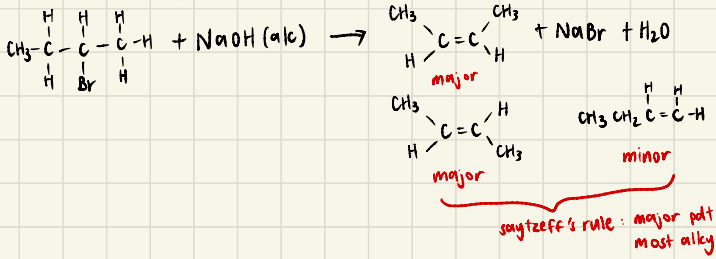
**$S_N2$ (mostly primary RX)**



## Elimination

- ethanolic NaOH, heat under reflux



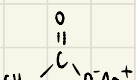

## Distinguishing Tests

### Find X in RX

Method 1:
- Add NaOH (aq), heat → nucleophilic sub of RX, release $X^-$ halide
- Add $HNO_3$ (aq) → remove excess $OH^-$ (prevent $Ag_2O$ ppt)
- Add $AgNO_3$ (aq) → form AgX ppt

R–I → immediate yellow ppt
R–Br → immediate cream ppt
R–Cl → immediate white ppt

 –X → no ppt

Method 2:
- Add ethanolic $AgNO_3$ / ethanolic silver ethanoate 
- warm mixture in water bath at 50°C

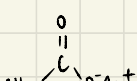
R–I → immediate yellow ppt
R–Br → cream ppt formed after a while
R–Cl → white ppt after a long time

 –X → no ppt

→ forms carboxylic acid

} rate of hydrolysis depend on strength of C–X bond

### Find 1°/2°/3° RX

- Add ethanolic $AgNO_3$ / ethanolic silver ethanoate 
- warm mixture in water bath at 50°C

1° RX → ppt formed after a long time
2° RX → ppt formed after a while, thickens w/ time
3° RX → ppt formed immediately

} - ethanol form hydrogen bonds w/ $H_2O$, hindering rxn
- rate of $S_N2$ depend on [Nu], ∵ ethanol slows down $S_N2$
- rate of $S_N1$ independent of [Nu]

# Hydroxy Compounds

## Alcohols

### Reduction

- Sodium metal at room temp.

$ROH + Na \rightarrow RO^-Na^+ + \frac{1}{2}H_2$

↳ strong nucleophile

→ very weak acid ∴ does not react w/ NaOH

### Condensation

- carboxylic acid, conc. $H_2SO_4$, heat under reflux → $RC(=O)-OH + R'OH \rightleftharpoons RC(=O)-O-R' + H_2O$ (ester)
- acyl chloride, room temp → $RC(=O)-Cl + R'OH \rightarrow RC(=O)-O-R' + HCl$

↳ e.g. methyl propanoate (alcohol + carb acid / acyl chloride)

### Oxidation

- $K_2Cr_2O_7(aq)$ / $KMnO_4(aq)$, $H_2SO_4(aq)$, heat under reflux
  - 1° alcohols → $R-C(=O)-OH$
  - 2° alcohols → $R-C(=O)-R'$ ketone
  - 3° alcohols → no rxn
- $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat with immediate distillation
  - ↳ controlled oxidation
  - 1° alcohols → $R-C(=O)-H$ aldehyde

orange $K_2Cr_2O_7$ turns green

### Elimination

- Excess conc. $H_2SO_4$, 170°C
- Heat w/ $Al_2O_3$, 350°C

} follow saytzeff's rule

### Nucleophilic Substitution (halogenation)

- $PCl_5$, room temp ($RX + POCl_3 + HCl$)
- $SOCl_2$, room temp ($RX + HCl + SO_2$) → preferred ∴ can separate RX from gaseous side products

} Cl

- dry HCl, anhydrous $ZnCl_2$ catalyst, heat under reflux

↳ * will undergo nucleophilic sub w/ alcohol BUT NOT carboxylic acid

- $PBr_3$ ($Br_2$ w/ red phosphorus), room temp.
- NaBr, conc. $H_2SO_4$, heat under reflux

} Br

- $I_2$ w/ red phosphorus, heat under reflux
- NaI, conc. $H_3PO_4$, heat under reflux

} I

### Iodoform Test (oxidation)

- NaOH(aq), $I_2$(aq), warm

$R-C(CH_3)(H)-OH + 4I_2 + 6NaOH \rightarrow CHI_3 + R-C(=O)-O^-Na^+ + 5NaI + 5H_2O$

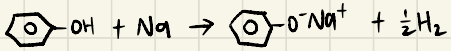
4655

methyl alcohol needed for rxn ($CH_3$ can be $CH_2I$, $CHI_2$ etc)

# Phenol

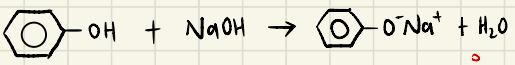
## Reduction

- Sodium metal at room temp.



## Acid-Base

- NaOH (aq), room temp.



## Condensation

- phenol w/ pyridine as solvent → for aliphatic acyl chloride → ∵ aliphatic undergo hydrolysis w/ NaOH easily ∴

- phenol w/ NaOH as solvent → for aromatic acyl chloride

## Electrophilic Substitution

- dilute $HNO_3$, room temp. } monosubstituted
- $Br_2$ in $CCl_4$, room temp. }
- conc. $HNO_3$, room temp. } multisubstituted (2,4,6-trinitro/bromophenol)
- $Br_2$ (aq), room temp }

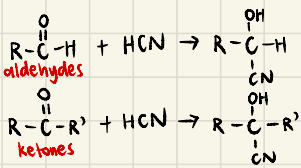
## Complex Formation

- neutral $FeCl_3$ (aq), room temp.
  - ↳ purple colouration observed

# Carbonyl Compounds

## Nucleophilic Addition

- HCN w/ trace amounts of NaOH / NaCN, 10-20°C

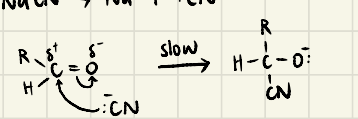


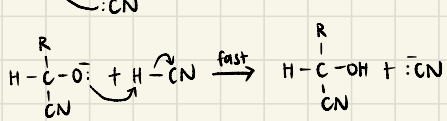

### Mechanism

$NaOH + HCN \rightarrow Na^+ + :\bar{C}N + H_2O$

OR

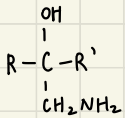
$NaCN \rightarrow Na^+ + :\bar{C}N$



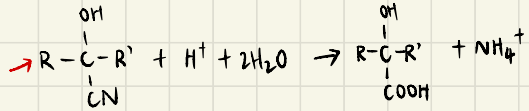



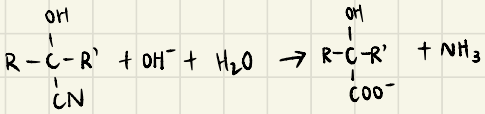
**cyanohydrin** 

**Reduction**
- $LiAlH_4$ in dry ether
- Na in ethanol
- $H_2$ w/ Pd/Pt, room temp. / $H_2$ w/ Ni, heat

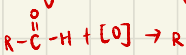


**Hydrolysis**
- Dilute HCl(aq) / $H_2SO_4$(aq), heat under reflux
- NaOH(aq) / KOH(aq), heat under reflux

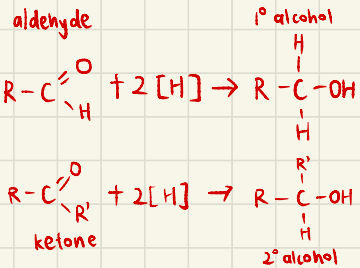




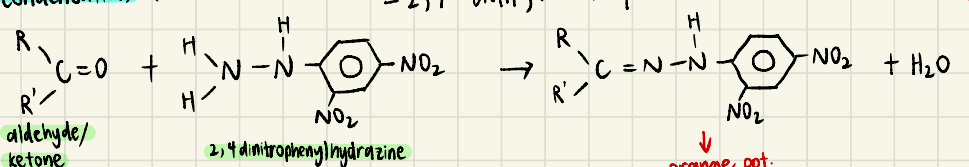
**Oxidation**
- $K_2Cr_2O_7$(aq) / $KMnO_4$(aq), $H_2SO_4$(aq), heat under reflux
  - ↳ aldehydes → carboxylic acid



**Reduction**
- $LiAlH_4$ in dry ether, room temp
- $NaBH_4$(aq) / $NaBH_4$ in methanol, room temp
- $H_2$ w/ Ni catalyst, heat / $H_2$ w/ Pd/Pt catalyst, room temp



**Condensation** (rxn w/ 2,4-DNPH) — 2,4-DNPH, room temp



aldehyde/ketone — 2,4 dinitrophenylhydrazine — orange ppt.

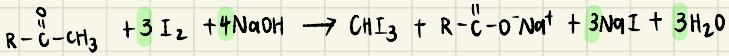
**Aldehyde vs Ketone Tests** (oxidation)

2513

- Fehling's solution, warm → brick red $Cu_2O$ ppt, blue sol. decol. $RCHO + 2Cu^{2+} + 5OH^- \rightarrow RCO_2^- + Cu_2O + 3H_2O$
  - ↳ only aliphatic aldehydes
- Tollens' reagent, warm → silver mirror $RCHO + 2Ag^+ + 3OH^- \rightarrow RCO_2^- + 2Ag + 2H_2O$
  - ↳ All aldehydes (aliphatic / aromatic) tve

2322

**Iodoform Test** (oxidation)
- NaOH(aq), $I_2$(aq), warm



# Carboxylic Acids & Derivatives

## Carboxylic Acids

### Reduction

- Na (or any reactive metal)

$CH_3CO_2H + Na \rightarrow CH_3CO_2^-Na^+ + \frac{1}{2}H_2$

### Neutralisation

- NaOH / KOH

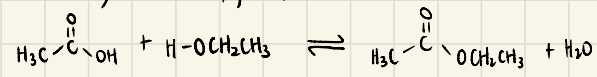
$CH_3CO_2H + NaOH \rightarrow CH_3CO_2^-Na^+ + H_2O$

- $Na_2CO_3$ (s) / (aq) / $NaHCO_3$

$2CH_3CO_2H + Na_2CO_3 \rightarrow 2CH_3CO_2^-Na^+ + CO_2 + H_2O$

### Condensation

- Alcohol, conc. $H_2SO_4$, heat under reflux



### Nucleophilic substitution (form Acyl Chloride)

- $PCl_3$, room temp.

$PCl_3 + 3CH_3CO_2H \rightarrow 3CH_3COCl + H_3PO_3$

- $PCl_5$, room temp.

$CH_3CO_2H + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

- $SOCl_2$, room temp.

$CH_3CO_2H + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$

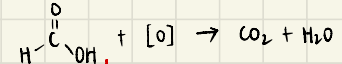
### Reduction (form Primary Alcohol)

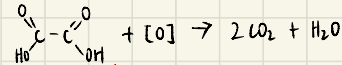
- $LiAlH_4$ in dry ether → NaBH4 / catalytic hydrogenation not strong enough RA

$CH_3CO_2H + 4[H] \rightarrow CH_3CH_2OH + H_2O$

### Oxidation (special cases)

- $KMnO_4$ (aq), $H_2SO_4$ (aq), heat under reflux



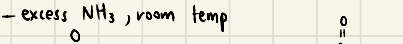

## Acyl Chlorides

### Hydrolysis

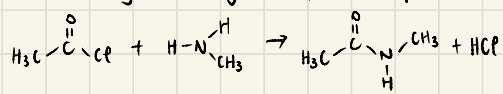
- $H_2O$, room temp.

## Condensation

- Alcohol, room temp.
- Phenol, pyridine as solvent (aliphatic acyl chloride)
- Phenol, NaOH as solvent (aromatic acyl chloride)
- excess $NH_3$, room temp



- excess primary / secondary amines, room temp.

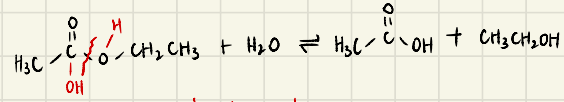


} form amide

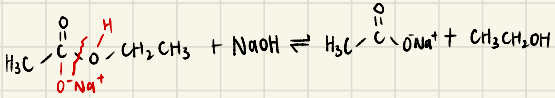
### Esters

#### Hydrolysis

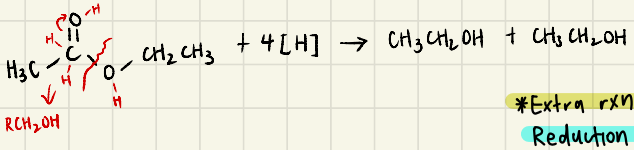
- Dilute $H_2SO_4$ / HCl (acid is catalyst, does not take part in rxn), heat under reflux (acidic hydrolysis)



- NaOH (aq) (not catalyst, takes part in rxn), heat under reflux (alkaline hydrolysis)



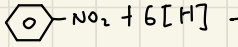
#### Reduction (not in syllabus, might be in data based)



*Extra rxn to form amine

**Reduction of nitrobenzene**

$H_2(g)$, Ni catalyst, heat / Sn in conc. HCl, heat under reflux, followed by NaOH(aq) at room temp.



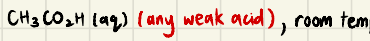
## Nitrogen Compounds

### Amines

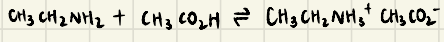
$R-NH_2$ / $R_1-\underset{\displaystyle R_2}{\underset{|}{N}}-H$ / $R_1-\underset{\displaystyle R_2}{\underset{|}{N}}-R_3$

#### Neutralisation

- HCl (aq) / $H_2SO_4$ (aq), room temp. (distinguishing test for amine (form white crystalline solid))



- $CH_3CO_2H$ (aq) (any weak acid), room temp.

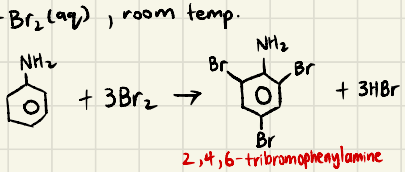


} amine salt can react w/ alkali to form back amine



#### Electrophilic Substitution (of phenylamine)

- $Br_2$ (aq), room temp.



2,4,6-tribromophenylamine

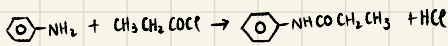
observations:

1. orange aq. $Br_2$ decolourises
2. white ppt. of 2,4,6-tribromophenylamine formed
3. white fumes of HBr
   - ↳ last resort only

## Condensation (to form 2°/3° amide)

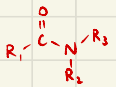
- acyl chloride, room temp.

$CH_3CH_2NH_2 + CH_3COCl \rightarrow CH_3CONHCH_2CH_3 + HCl$



3° amine cannot undergo condensation

## Amides



### Hydrolysis

- HCl (aq) / $H_2SO_4$ (aq), heat under reflux (acidic)

$CH_3CONH_2 + HCl + H_2O \rightarrow CH_3COOH + NH_4^+Cl^-$

$CH_3CONHCH_3 + HCl + H_2O \rightarrow CH_3COOH + CH_3NH_3^+Cl^-$

- NaOH (aq), heat under reflux (basic)

$CH_3CONH_2 + NaOH \rightarrow CH_3CO_2^-Na^+ + NH_3$

$CH_3CONHCH_3 + NaOH \rightarrow CH_3CO_2^-Na^+ + CH_3NH_2$

Distinguishing test:
1° amide produces pungent, colourless $NH_3$ gas, turns moist red litmus blue
↳ exception for 2° amides
- $CH_3CONHCH_3 \xrightarrow{\text{forms}} CH_3NH_2$ (g)
- $CH_3CONHCH_2CH_3 \xrightarrow{\text{forms}} CH_3CH_2NH_2$ (g)

### Reduction

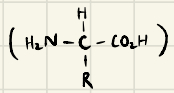
- $LiAlH_4$ in dry ether, room temp.

$CH_3CONH_2 + 4[H] \rightarrow CH_3CH_2NH_2 + H_2O$
1° amide → 1° amine

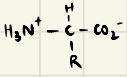
$CH_3CON(CH_3)_2 + 4[H] \rightarrow CH_3CH_2N(CH_3)_2 + H_2O$
3° amide → 3° amine

C=O $\xrightarrow{\text{reduced}}$ $CH_2$

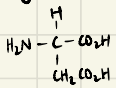
## Amino Acids



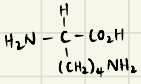
**zwitterion state**



**R group can also contain $-CO_2H$ or $-NH_2$ group**



aspartic acid



lysine

| no. of groups | acidic/basic | colour of universal indicator | colour of litmus |
|---|---|---|---|
| $-CO_2H > -NH_2$ | acidic | orange/yellow | red |
| $-CO_2H < -NH_2$ | basic | blue | blue |
| $-CO_2H = -NH_2$ | acidic | orange/yellow | red |

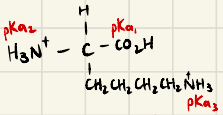
### Isoelectronic point (pI)

↳ pH at which amino acid no net charge

**At high pH (pH > pI)**
- amino acid deprotonated
- overall -ve charge
- move towards anode

**At low pH (pH < pI)**
- amino acid protonated
- overall +ve charge
- move towards cathode

↳ distance migrated ∝ $\frac{\text{charge}}{\text{mass}}$



think acidic ∴ (wA/conj A)
- pH < pKa
↳ protonated ($COOH$/$NH_3^+$)

think basic ∴ (wB/conj B)
- pH > pKa
↳ deprotonated ($COO^-$/$NH_2$)

to find out which group protonated → compare pKa of group to pH

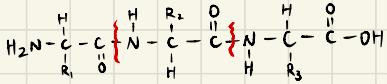
## Proteins

↳ formed via amino acids joined by peptide (-C(=O)-N(H)-) links

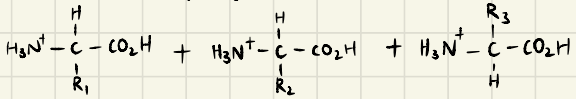
- 2 amino acids joined → dipeptide
- 3 amino acids joined → tripeptide
- >3 amino acids joined → polypeptide

## Hydrolysis

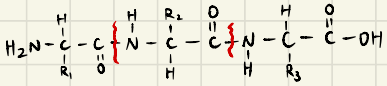
- HCl (aq) / $H_2SO_4$ (aq), heat under reflux for several hours (acidic)



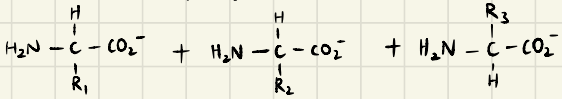
↓ hydrolysis



- NaOH (aq), heat under reflux for several hours (basic)



↓ hydrolysis



## Peptide Sequencing

- just overlap as much as possible

Eg 1:

Cys - Ser - Leu - Tyr - Gln - Leu | Tyr - Gln - Leu - Glu

Solution:

Cys - Ser - Leu - Tyr - Gln - Leu
Tyr - Gln - Leu - Glu
1 2 3 4 5 6 7

∴ Sequence is
Cys - Ser - Leu - Tyr - Gln - Leu - Glu

Eg 2:

Ala - Gly | Tyr - Lys | Ser - Ala | Gly - Tyr

Solution:

1 2 3 4 5
Ser - Ala
Ala - Gly
Gly - Tyr
Tyr - Lys

∴ Sequence is
Ser - Ala - Gly - Tyr - Lys