Calculations using combustion data:

Using formula:
$C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + (y/2)H_2O$

Percentage yield:

Percentage yield = (Actual mass of product formed / Theoretical mass) x 100%

Calculations using volume of gas:

Condition	Temperature	Pressure	Molar volume
s.t.p. (standard temperature and pressure)	273K	1 atm	22.4 dm^3
r.t.p. (room temperature and pressure)	298K	1 atm	24 dm^3

Note: For a gas, volume ration = mole ratio

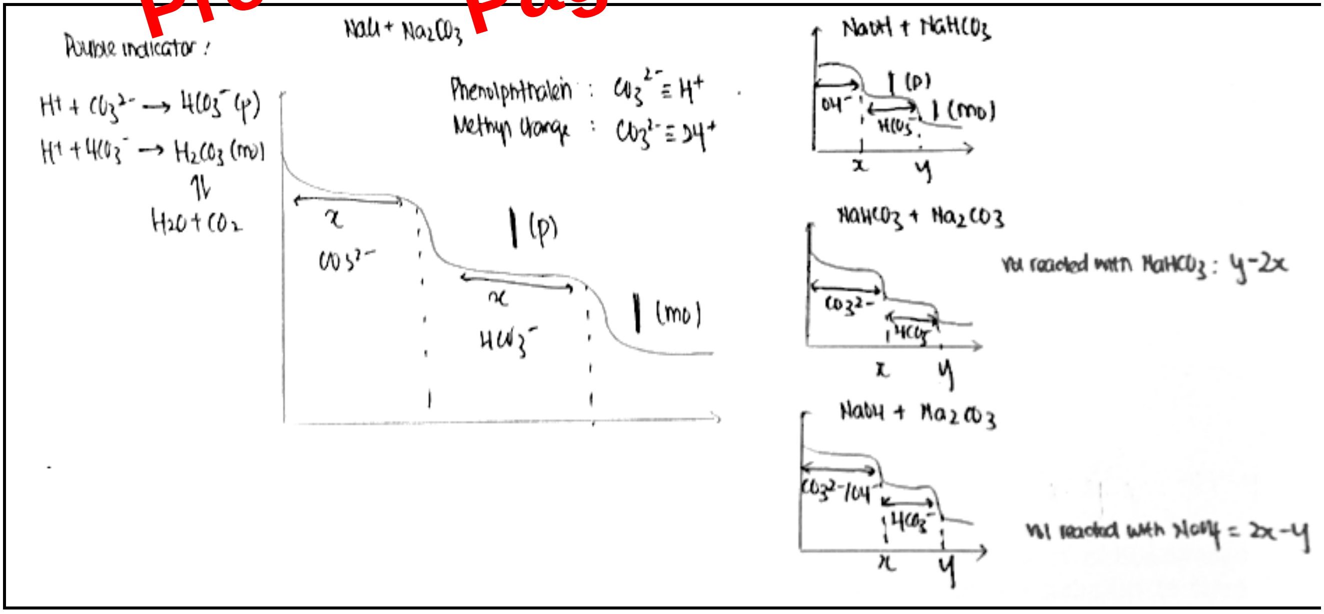
Titration and Back Titration:

Steps for back titration –

1. Determine amount of C required in titration
2. Using stoichiometry, find amount of A that reacted with C in the titration
3. Hence, amount of A that reacted with B = total amount of A (in excess) – amount that reacted with C
4. Thus determine amount of A that reacted with B, and thus amount of B

Summary: ηA = ηA that reacted with B + ηA that reacted with C

Double indicators:
Sometimes double indicators are used for the titration of dibasic acids

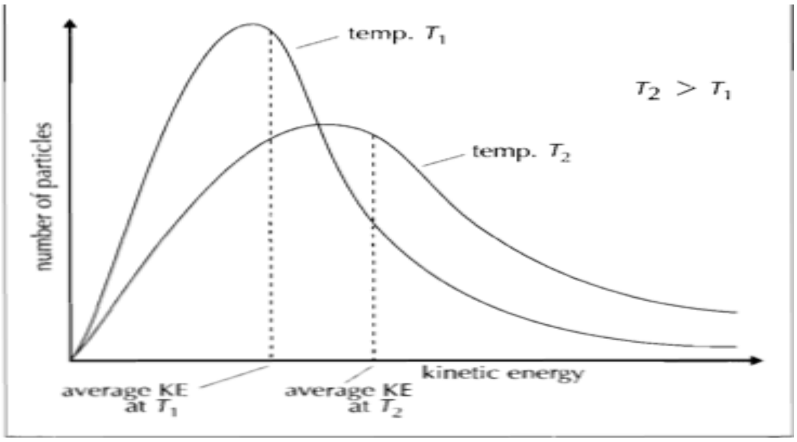


Assumptions of ideal gas:

1. Gas particles behave as rigid spheres
2. Gas particles have negligible volumes compared to volume of the container
3. Intermolecular forces of attraction and repulsion between gas particles are negligible
4. Collision between gas particles and walls of container are perfectly elastic
5. Average KE of gas particles is directly proportional to absolute temperature

- **Note:** Assumption 2 and 3 are most important, can bring up 4 if needed

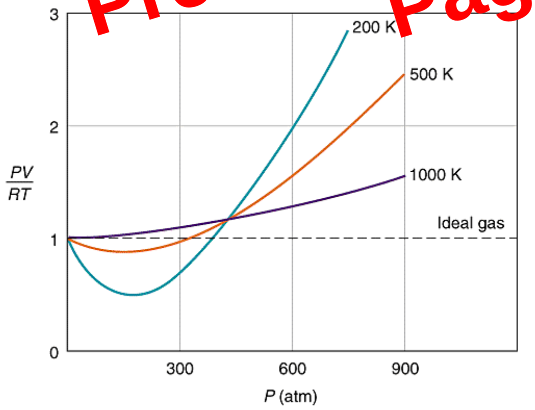
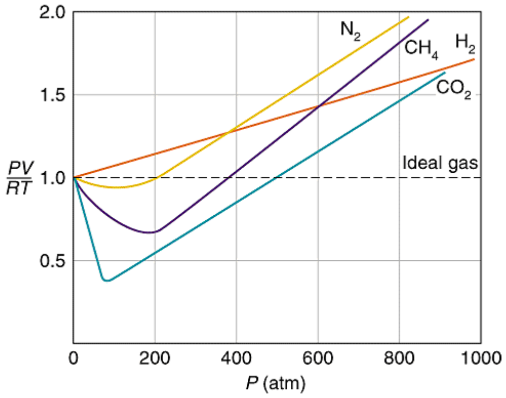
Boltzmann distribution curve:



Things to note:

- Peak of each curve represents most probably speed
- As temperatures increase, curve shifts right and peak decreases in height

Real gas and deviation from ideal behavior:

Temperature	**Pressure**
	

Hence, deviation is minimal when

1. High temperatures
2. Low pressure

Chapter 5: Intro to Organic Chemistry

Definitions:

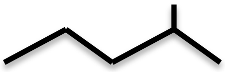
Homologous series: series of organic compounds where each successive member increases by the unit –CH_2

Distinguishing test: chemical test that aims to confirm presence of a particular compound, or differentiate between organic compounds

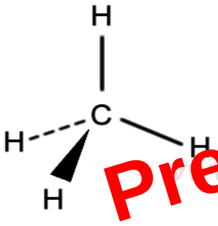
Types of formulae:
Structural formula is the most often used formula in organic chemistry

1. Displayed formula / full structural formula

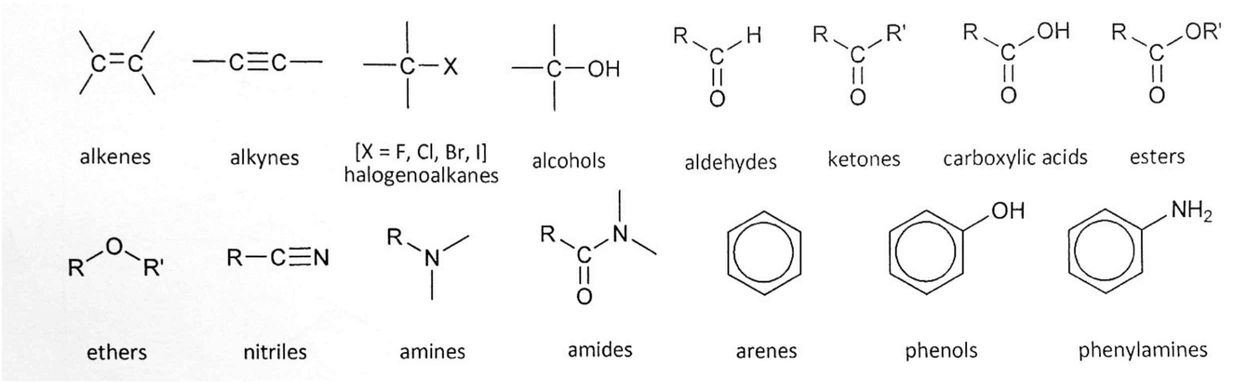
2. Condensed structural formula [$CH_3CH_2CH_2Br$]
3. Skeletal formula



4. Stereochemical formula



Overview of functional groups:



Chapter 6: Alkanes

Naming of Alkanes:

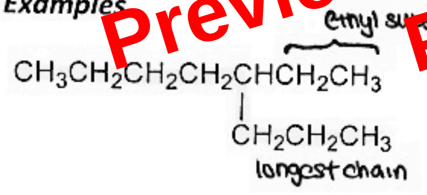
Straight Chain alkanes
They are named according to the number of carbon atoms

Number of carbons (n)	Name	Formula (C_nH_{2n+2})	Number of carbons (n)	Name	Formula (C_nH_{2n+2})
1	Methane	CH_4	6	Hexane	C_6H_{14}
2	Ethane	C_2H_6	7	Heptane	C_7H_{16}
3	Propane	C_3H_8	8	Octane	C_8H_{18}
4	Butane	C_4H_{10}	9	Nonane	C_9H_{20}
5	Pentane	C_5H_{12}	10	Decane	$C_{10}H_{22}$

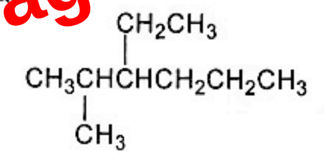
Branched (or substituted alkanes)

They are named according to the IUPAC rules:
1. Locate longest continuous chain of carbon atoms
2. Number the longest chain beginning with the end closer to the substituent
3. Use the number allocated to determine the position of the substituent
4. When 2 or more substituents are present, give them a number corresponding to their location
5. When 2 substituents are present on the same carbon, use that number twice
6. When 2 or more substituents are identical, indicate by using prefix of di-, tri-, tetra-

Examples



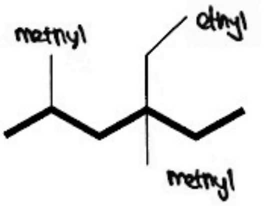
4–ethyloctane



3–ethyl–2–methylhexane

alphabetical order

between number and alphabet must have "–"



4–ethyl–2,4–dimethylhexane

between numbers use ","

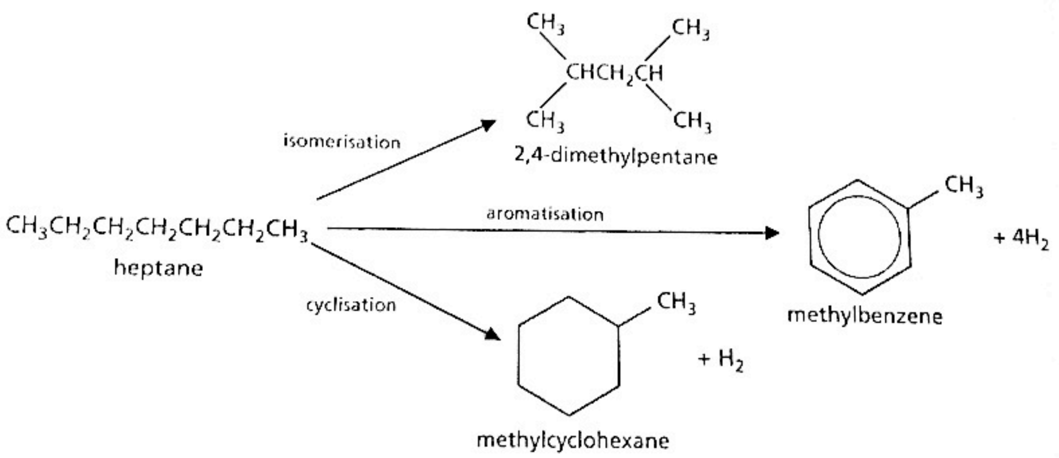
Physical properties of alkanes:
The molecules of alkanes are non-polar due to the C-H bonds and are held together mainly by weak dispersion forces

Boiling point – Increase with number of carbon atoms due to increasing size of electron cloud and thus stronger dispersion forces between molecules
- Branched-chain alkanes have lower boiling point than straight chains due to smaller surface area of contact between molecules
- Thus dispersion forces between branched-chain alkanes are weaker

Catalytic Reforming

Reforming straight-chain alkanes is done by changing straight-chain alkanes into branched-chain alkanes and cyclic hydrocarbons without loss of any carbon atoms

Done by passing vaporized alkane mixture over platinum-coated aluminum oxide catalyst at 500°C and moderately high pressure



Environmental consequences of burning fuel:

Carbon monoxides and unburnt hydrocarbons

They arise primarily due to incomplete combustion of fuel

Carbon monoxide: binds irreversibly to haemoglobin in blood and forms a stable complex, thus reducing capacity of haemoglobin to transport oxygen

Unburnt hydrocarbons: in the presence of sunlight, they react with oxygen, ozone and oxides of nitrogen to form photochemical smog

Oxides of nitrogen

NO_x are formed inside the combustion chambers of motor vehicles. At high temperatures of combustion, atmospheric oxygen and nitrogen combine to form NO and later oxidized to NO_2

$$N_2 + O_2 \rightarrow 2NO$$
$$2NO + O_2 \rightarrow 2NO_2$$

They irritate lungs, cause pneumonia and lower resistance to respiratory infections. They also result in the formation of photochemical smog which has a harmful effect on plants

Formation of nitrous and nitric acid: $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

Formation of sulfuric acid: $2SO_2 + NO_2 \rightarrow 2SO_3 + NO$; $NO + \frac{1}{2}O_2 \rightarrow NO_2$

HNO_3 and H_2SO_4 are strongly acidic and form acid rain which causes corrosion of buildings and man made structures, and also harms marine life and agriculture

Greenhouse effect

It is the heating of the earth due to the presence of greenhouse gases, which causes radiation to be trapped in the atmosphere and increase in global temperature

Greenhouse gases:

- Natural: Carbon dioxide, Methane, Water vapor and Nitrous oxides
- Manmade: Chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs)

Catalytic converters

It removes pollutant gases from the exhaust by oxidizing or reducing them, where the gases passes through a converter containing an alloy of platinum or rhodium (heterogeneous catalyst)

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$
$$2CO + O_2 \rightarrow 2CO_2$$

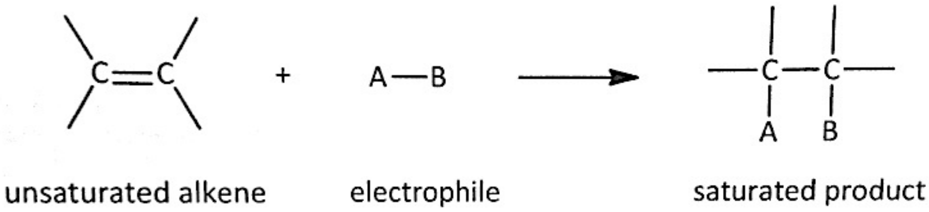
However, catalytic converters only work with unleaded petrol as lead poisons the catalyst by binding permanently to it

~ END ~

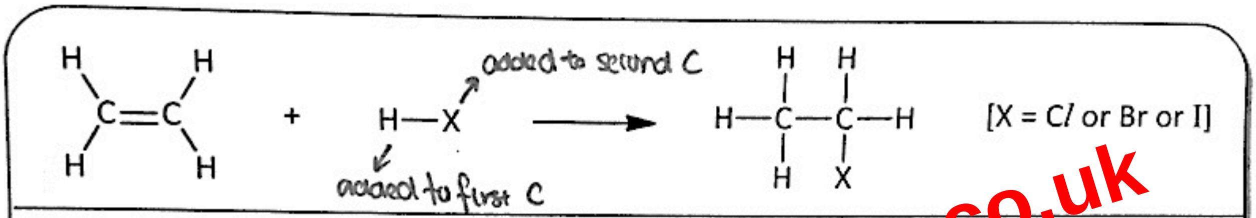
Chemical properties of Alkenes:

Alkenes are more reactive than alkanes due to the electron rich C=C where the π bond (electron cloud) attracts electrophiles

During a reaction, the weaker π bond is broken instead in the C=C bond, forming two strong bonds in the product. This reaction is known as **electrophilic addition**



Electrophilic addition of hydrogen halides (H–X):



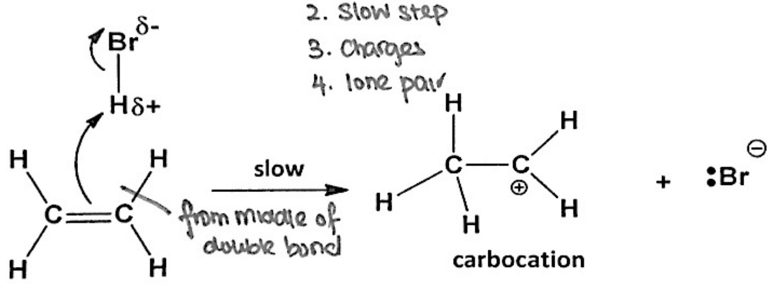
Reagents and conditions: Gaseous HCl, HBr or HI, room temperature

markovnikov rule (appendix)

Step 1: Rate determining step

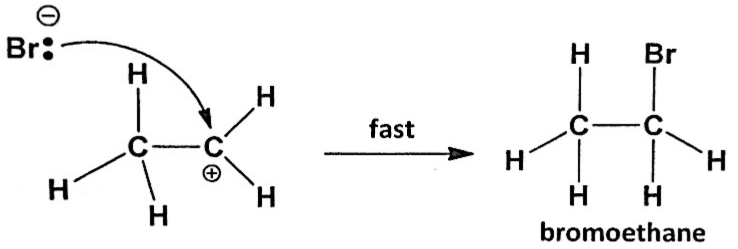
Polar HBr approaches the π electron cloud, the high electron density of π electron cloud "attacks" electron deficient H atom on HBr

1. Arrows
2. Slow step
3. Charges
4. lone pair

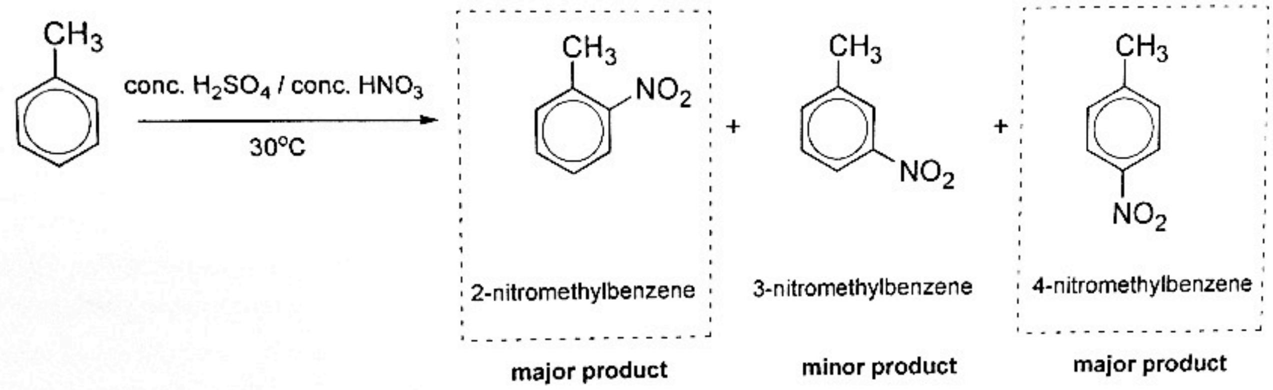


Step 2:

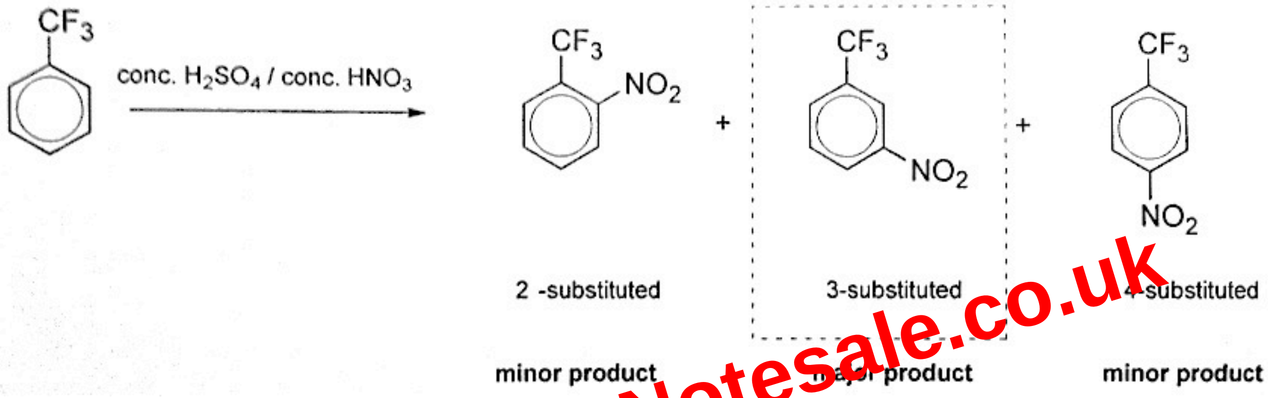
Bromide anion acts as nucleophile and attacks unstable carbocation



More than one product forms too, however 3 products can actually form instead of 2



However, nitration of trifluoromethylbenzene results in only 1 product.



This can be explained through the resonance and inductive effect

Effects on reactivity of benzene ring:

Activating groups: Electron-donating substituents increase electron density of benzene ring and thus increase reactivity
Deactivating groups: Electron-withdrawing substituents decrease electron density

There are 2 ways which electrons can be donated or withdrawn from the benzene ring –
1. Through the sigma bond → inductive effect
2. Through the pi bond → resonance effect

Substituent	**Inductive effect**	**Resonance effect**	**Overall effect on reactivity**	**Overall effect on position of incoming group**
Alkyl groups	Electron donating	-	Activating	2,4-directing
-OH, -NH$_2$, -OCH$_3$	Electron withdrawing	Electron donating	Activating	2,4-directing
-F, -Cl, -Br, -I	Electron withdrawing	Electron donating	Weakly Deactivating	2,4-directing
-CHO, -NO$_2$, -CO$_2$H, -CN	Electron withdrawing	Electron withdrawing	Deactivating	3-directing

Uses of halogenoalkanes:

Chlorofluorocarbons (CFCs) are used as refrigerants, aerosol propellants and fire extinguishers and have some useful properties

1. They are inert and non-flammable
2. They are non-toxic
3. They are compounds that liquefy under pressure and thus vaporize readily when pressure is released
4. They are odorless

Effect of CFCs on ozone:

Normally, ozone is formed when oxygen atoms are produced as O_2 absorbs UV light
$O_2 + O \rightarrow O_3$

However, CFCs deplete this ozone layer when they drift upwards to the atmosphere
$CF_3Cl + uv \rightarrow Cl\bullet + \bullet CF_3$

The chlorine radical then acts to destroy the ozone by removing O_3 and O from the atmosphere
$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$
$ClO\bullet + O \rightarrow Cl\bullet + O_2$

Measures to protect the ozone layer:

1. Reduce the usage of CFCs
2. Use substitutes such as hydrocarbons, hydrofluorocarbons or fluorocarbons

~ END ~

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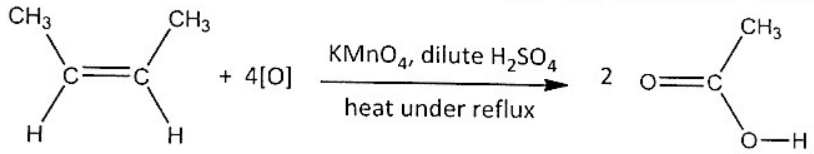
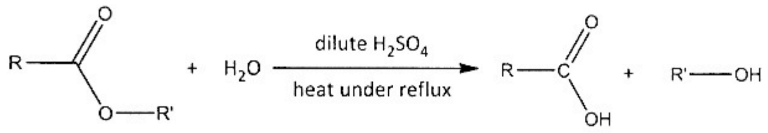
4. Oxidative cleavage of alkenes



Reagents and conditions: $KMnO_4$, dilute H_2SO_4, heat under reflux

Observations: ~~Orange solution ($Cr_2O_7^{2-}$) turns green (Cr^{3+})~~
Purple solution (MnO_4^-) decolourises (Mn^{2+})

5. Hydrolysis of esters



Reagents and conditions: dilute H_2SO_4, heat under reflux

Remarks: Esters can also be hydrolysed by bases like dilute NaOH, heat under reflux followed by acidification with dilute H_2SO_4 at room temperature and pressure.

Chemical reactions of carboxylic acids:
The C=O and O–H group are so close in proximity that carboxylic acids do not behave like aldehydes, ketones or alcohols

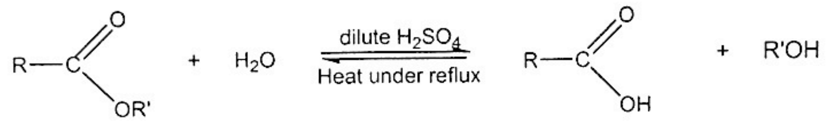
Carboxylic acids are stronger acids than alcohols and they do not undergo nucleophilic addition like aldehyde and ketones

- The flow of electrons from the O–H group makes the carboxyl carbon less electron deficient

There are 3 main types of reactions that carboxylic acids can undergo:

1. Acid-metal/Acid-base reaction
2. Nucleophilic acyl substitution reaction
3. Reduction of the CO_2H group

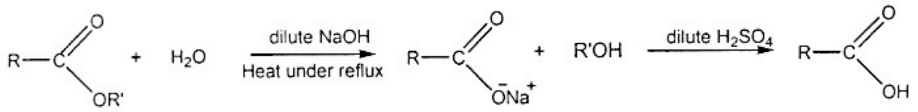
Acid hydrolysis of esters:



Reagents and conditions: dilute H_2SO_4, heat under reflux

Remarks: The reaction is reversible. A large excess of water (dilute acid) is used to ensure equilibrium lies to the right. Notice that this is the reverse reaction of esterification.

Base hydrolysis of esters:



Reagents and conditions: dilute NaOH, heat under reflux followed by acidification with dilute H_2SO_4 at room temperature and pressure

Remarks: The reaction is rapid and irreversible. Resonance-stabilised RCO_2^- ion is formed that has little tendency to react with alcohol, thus the reaction goes to completion. To obtain the carboxylic acid, aqueous acid is added to the mixture at the end of the reaction.

Commercial uses of esters:

Esters are prepared industrially mainly for use as essence, perfumes or artificial flavoring. Esters are also widely used as organic solvents.

~ **END** ~

Chapter 12: Carbonyl Compounds

Introduction:

A carbonyl (–C=O) functional group is probably the most important functional group in organic and biological chemistry

The two simplest types of carbonyl compounds are aldehydes and ketones

Carbonyl compounds are named the following manner –

1. For **aldehydes,** find the longest parent chain containing the –CHO group and number the carbonyl carbon
2. Aldehydes with the –CHO attached directly to a ring system are named by adding the suffix -carbaldehyde
3. For **ketones,** parent chain is the longest one containing the ketone group and numbering begins at the end nearer the carbonyl carbon
4. Aldehydes end with a –al and ketones end with –one

Isomerism:

Saturated aliphatic aldehydes and ketones have the general formula $C_nH_{2n}O$ and thus they are structural isomers if they have the same number of carbon atoms in the compound

Physical properties of aldehydes and ketones:

Nature of carbonyl carbon – it is sp^2 hybridized and bonded to 3 other atoms, and are thus planar

- C=O bonds are polarized as O is more electronegative than C
- Hence carbon has partial +ve charge and oxygen has partial –ve charge

Boiling points – they have higher boiling points than non-polar hydrocarbons of similar relative Mr but lower than alcohols and carboxylic acids

- Alkanes are non-polar, only have weak dispersion forces, but carbonyl group is polar and hence pd-pd interactions between molecules
- However alcohols and carboxylic acids can form H-bonds between molecules

Solubility in water – they have polar and non-polar regions, able to act as a solvent for both

- Lower aliphatic aldehydes and ketones are soluble in water due large to their ability to form hydrogen bonds with water molecules

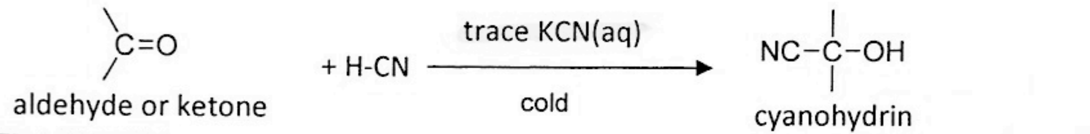
Nucleophilic addition and condensation reactions of aldehydes and ketones:

The C=O bond is similar to the C=C bond as both react to saturate the double bond by addition

- However in C=O, O is much more electronegative and withdraws electron density to itself
- Thus the carbonyl carbon has a partial +ve charge and can be attacked by nucleophiles, resulting in nucleophilic addition or condensation reactions

Nucleophilic addition:

Reaction with Hydrogen Cyanide, HCN

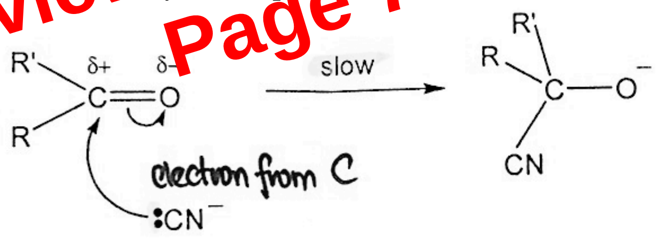


Reagents and conditions:	HCN with trace KCN(aq), cold (10-20°C)
Comments:	KCN is used as a catalyst; CN^- ion is regenerated at the end of the reaction.

Note: HCN is a toxic gas and is generated in situ through the following reaction

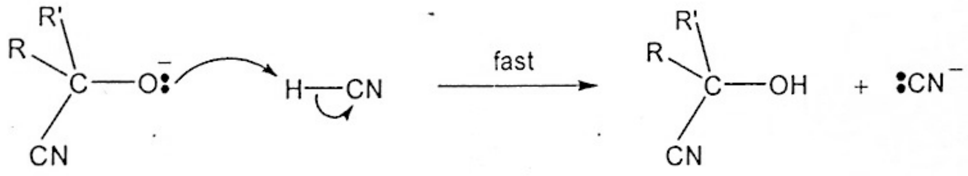
- $2KCN + H_2SO_4 \rightarrow K_2SO_4 + 2HCN$

Step 1: Carbonyl carbon attack by nucleophile CN^-



- CN^- ion acts as nucleophile and attacks electron-deficient carbonyl carbon and leads to formation of stable tetrahedral intermediate anion (alkoxide)

Step 2: Protonation of intermediate to give a cyanohydrin

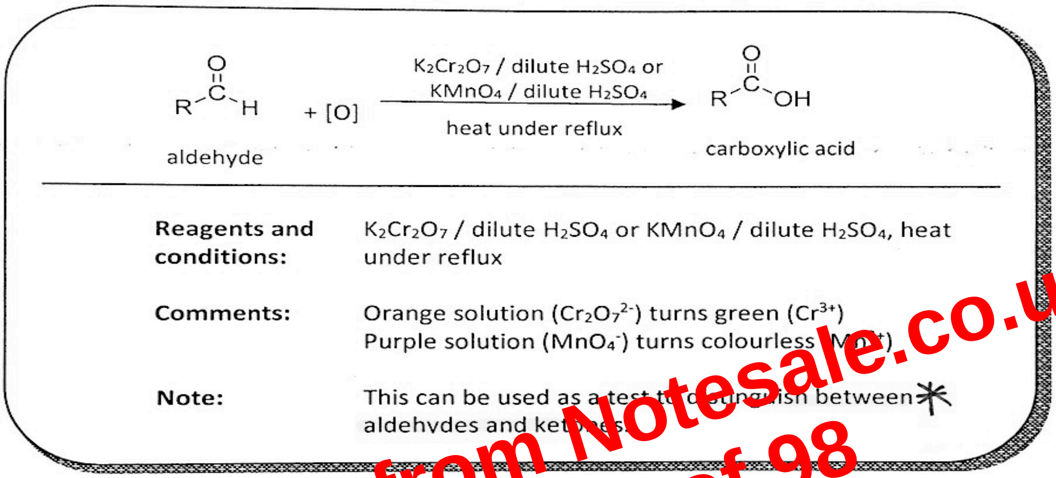


- The CN^- ion is regenerated

Functional groups	**Ability to be reduced by**		
	H_2 / Ni	$LiAlH_4$ in dry ether	$NaBH_4$ in methanol
Alkenes	+	-	-
Carboxylic Acids	-	+	-
Esters	-	+	-
Nitriles	+	+	-
Aldehydes	+	+	+
Ketones	+	+	+

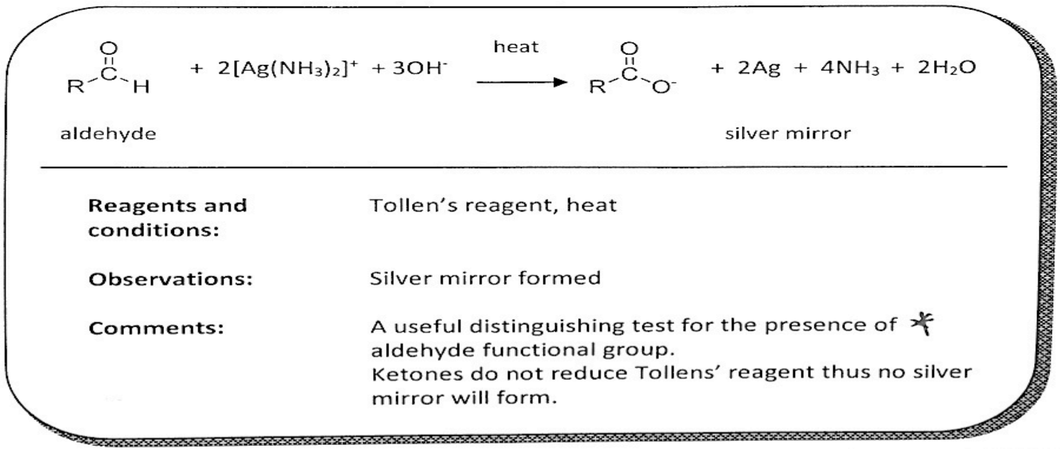
Oxidation:

With acidified potassium dichromate (VI)
Only for aldehydes as they contain a hydrogen attached directly to the carbonyl carbon



Reagents and conditions:	$K_2Cr_2O_7$ / dilute H_2SO_4 or $KMnO_4$ / dilute H_2SO_4, heat under reflux
Comments:	Orange solution ($Cr_2O_7^{2-}$) turns green (Cr^{3+}) Purple solution (MnO_4^-) turns colourless (Mn^{2+})
Note:	This can be used as a test to distinguish between aldehydes and ketones

With Tollens' Reagent (Silver Mirror Test)
All aldehydes reduce Ag^+ in Tollens' reagent to silver metal and deposit on the walls



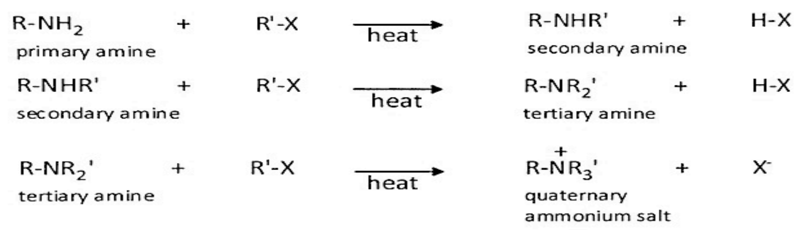
Reagents and conditions:	Tollen's reagent, heat
Observations:	Silver mirror formed
Comments:	A useful distinguishing test for the presence of aldehyde functional group. Ketones do not reduce Tollens' reagent thus no silver mirror will form.

Tollens' reagent contains $[Ag(NH_3)_2]^+$ ions and is highly unstable, thus it should be freshly prepared using the following method

- 1 drop of dilute NaOH to about $3cm^3$ of $AgNO_3$ to produce brown ppt of Ag_2O
- Dilute NH_3 then added drop wise until brown ppt first formed dissolves – contains $[Ag(NH_3)_2]^+$

Reaction with halogenoalkanes (as a nucleophile)

Primary, secondary and tertiary amines can react with halogenoalkanes to form secondary amines, tertiary amines and quaternary ammonium salts



$$R\text{-}NH_2 + R'\text{-}X \xrightarrow{heat} R\text{-}NHR' + H\text{-}X$$

$$R\text{-}NHR' + R'\text{-}X \xrightarrow{heat} R\text{-}NR_2' + H\text{-}X$$

$$R\text{-}NR_2' + R'\text{-}X \xrightarrow{heat} R\text{-}\overset{+}{N}R_3' + X^-$$

Reagents & conditions: Halogenoalkane, heated in sealed tube

Comment: To prevent multiple substitutions, excess amine is used.

Reaction with acyl chlorides (as a nucleophile)

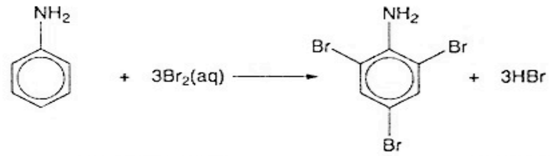
They can react with acid chlorides to form amides

Reagents & conditions: Acyl chlorides, room temperature

Comment: Tertiary amines do not contain a replaceable H atom on the N, so they are incapable of forming amides.

Reaction with bromine

Only for phenylamines due via an electrophilic substitution mechanism to form a white ppt



(tri-substitution)

Reagents & Conditions: Aqueous bromine, room temperature

↳ polar solvent, ↑e⁻phile

(non-polar solvent, poor e⁻) liquid bromine to get monosubstitution

Observations: Yellow-orange solution decolourise; white ppt formed

Comments: No Lewis acid catalyst (halogen carrier) is required for this reaction, unlike bromination of benzene (which requires $AlCl_3$ or $FeCl_3$). $-NH_2$ group is 2, 4-directing.

Explanation: Like phenol, the lone pair of electrons on the nitrogen atom is delocalised into the benzene ring, the electron density in the ring is greatly increased, making it much more susceptible to electrophilic attack than benzene. Hence, the presence of the $-NH_2$ group highly activates the benzene ring towards electrophilic substitution and no catalyst is required.

Physical properties of amino acids:

Formation of zwitterions gives amino acids some unusual properties

- Amino acids are crystalline solids with high melting points due to strong electrostatic forces of attraction between dipolar zwitterions in solid lattice structure
- They are more soluble in water than organic solvents due to strong ion-dipole interaction

Peptide bond formation:

Amide linkage between amino acids is called a peptide bond and is formed from the condensation reaction between –CO_2H and –NH_2

Features of polypeptide chain:

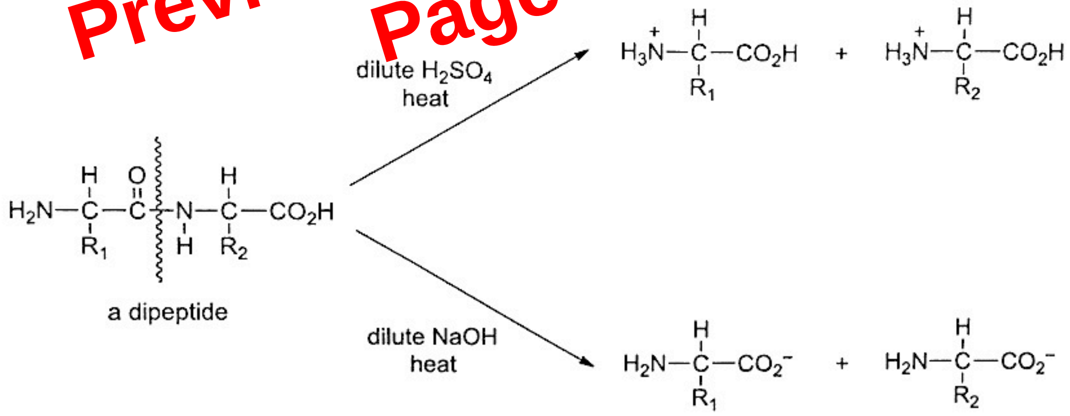
- Backbone is the main chain of polypeptide which includes everything but the side chains that are the R-groups of each amino acid residue
- Amino acid residues are amino acids condensed together in a polypeptide chain
- Peptide bonds which arise from the condensation reaction between adjacent amino acids
- N- and C- termini where there is an uncondensed amino group and one uncondensed carboxylic aid group
- Polypeptide chains are always written from the N-terminus to the C-terminus

PROTEINS

They are formed when a large number of amino acids are condensed together to form a long polypeptide chain

Hydrolysis of proteins:

Proteins can be hydrolyzed into their constituent amino acids by an enzyme or heating in the presence of dilute acid or alkali for several hours



$$\text{polypeptide / protein} \underset{\textit{condensation}}{\overset{\textit{hydrolysis}}{\rightleftharpoons}} \text{amino acids}$$