

LEVEL 3 ORGANIC CHEMISTRY

AS91391 - Demonstrate understanding of the properties of organic compounds

Contents

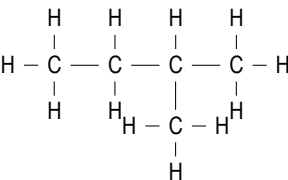
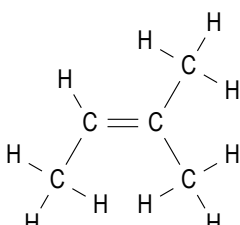
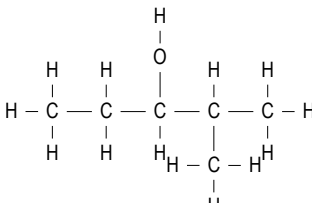
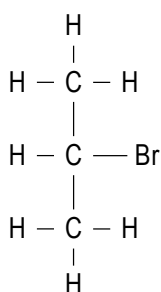
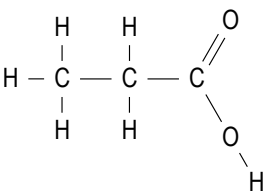
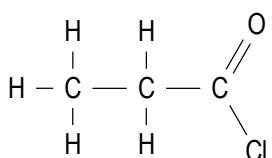
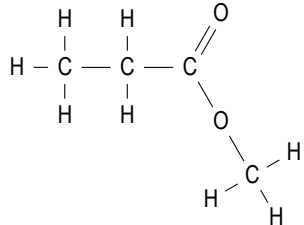
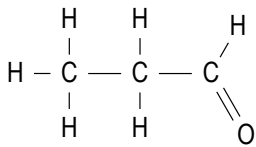
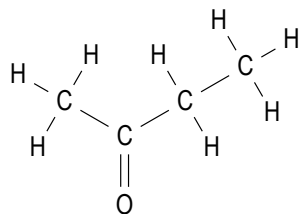
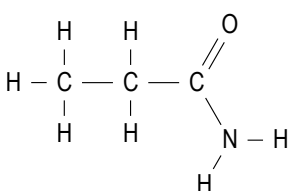
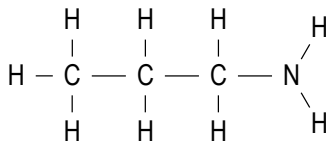
- Naming
- Functional Groups
- Formulae – types of
- Isomerism – types of
- Alkanes, alkenes, alkynes (in brief – Level 2 recap)
- Physical Properties & Reactions of alkanes and alkenes
- Polymerisation – addition & condensation polymerisation (including proteins)
- Haloalkanes – classification, physical properties, preparation, chemical reactions
- Alcohols – classification, physical properties, preparation, chemical reactions
- Aldehydes (revised for 2013)
- Ketones (revised for 2013)
- Carboxylic acids
- Acyl chlorides
- Amides
- Esters – naming, preparation & hydrolysis
- Triglycerides (new for 2013)
- Amines
- Reaction types

“Distinguishing between tests” will be covered in a separate document

Naming (IUPAC nomenclature)

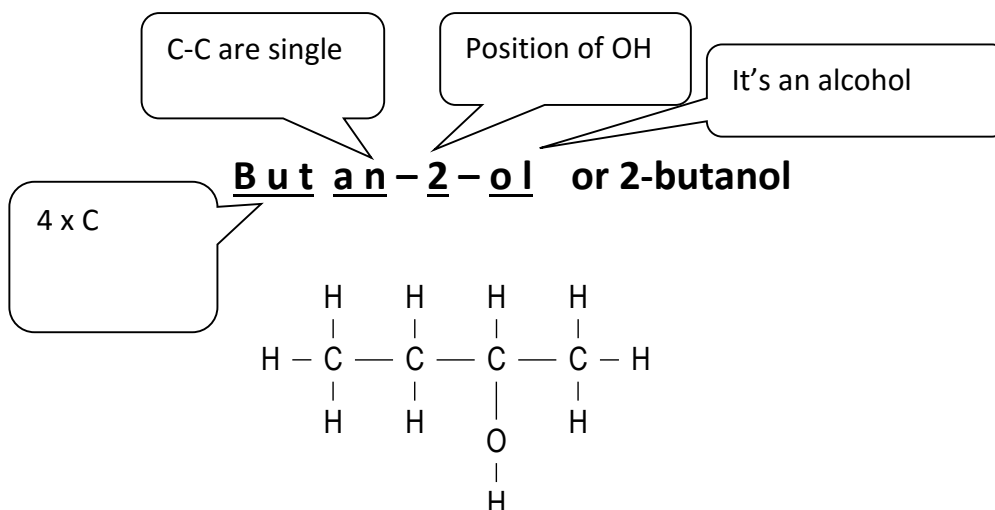
Place where a reaction takes place. Compounds with the same functional group have similar properties.

First the functional groups...

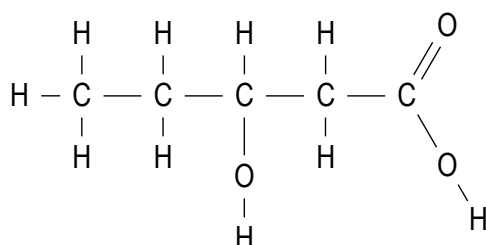
alkane -ane	alkene -ene	alcohol -anol	haloalkane bromo, chloro etc
		<p>hydroxyl group</p> 	
carboxylic acid -anoic acid	acid chloride -oyl chloride	ester -anoate	C-C C=C R-X R-OH R-COOH R-COCl R-COO-R' R-CHO R-CO-R' R-CONH ₂ R-NH ₂
			
aldehyd -anal	ketone -one	amide -amide	amine amino
			

N A M I N G

No. of carbons	Alkane name	Prefix	Side chain
1	methane	meth-	methyl-
2	ethane	eth-	ethyl-
3	propane	prop-	propyl-
4	butane	but-	butyl-
5	pentane	pent-	
6	hexane	hex-	



- Find longest carbon chain – base name on the parent alkane
- Number the C atoms in the chain to indicate position of any side chains or functional groups (number from end to give the lowest numbers)
- Give names and positions of functional groups eg 3-bromo, and 4-chloro (alphabetically)
- Where there's more than one functional group there is priority order for naming -anoic acid > hydroxyl (-OH) -ol > halo- -anoic acid > halo



3 – hydroxy pentanoic acid

FORMULAE

Molecular formula – gives the number of each type of atom in a molecule

Empirical formula: Simplest ratio formula.

Stoichiometric proportions of atoms only. E.g. CH_2O is the empirical formula of the molecule $\text{C}_3\text{H}_6\text{O}_3$

General Formula

$\text{C}_n\text{H}_{2n+2}$ alkanes

C_nH_{2n} alkenes

$\text{C}_n\text{H}_{2n-2}$ alkynes

$\text{C}_n\text{H}_{2n+1}\text{OH}$ alkanols (alcohols)

$\text{C}_n\text{H}_{2n+1}\text{Cl}$ chloroalkanes

$\text{C}_n\text{H}_{2n+1}\text{COOH}$ carboxylic acids

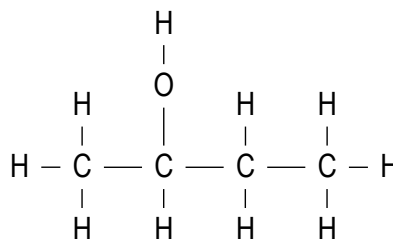
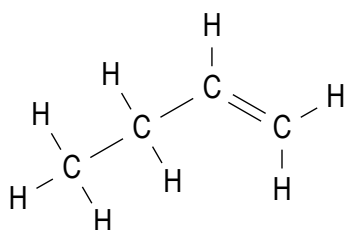
$\text{C}_n\text{H}_{2n+1}\text{COCl}$ acyl (acid) chlorides

$\text{C}_n\text{H}_{2n+1}\text{CONH}_2$ amides

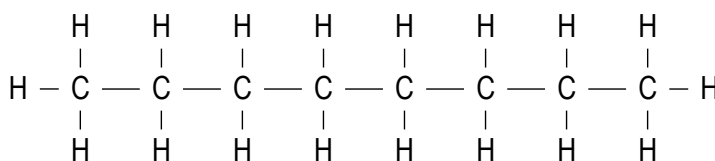
$\text{C}_n\text{H}_{2n+1}\text{NH}_2$ amines

Structural formula – gives the arrangement of atoms in a molecule, indicating how atoms are bonded together.

- **Expanded (all bonds shown)**



- **Condensed**



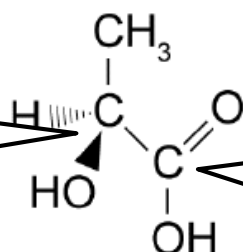
expanded

is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$

condensed

- **Stereochemistry** (3-D arrangement of atoms) is shown.

Tetrahedral arrangement around this C atom



Trigonal planar arrangement around this C atom



Structural isomers

- **Same number and type of atoms but arranged in different ways**

Structural isomers have the same molecular formula but they differ in the sequence in which the atoms are joined together.

Structural

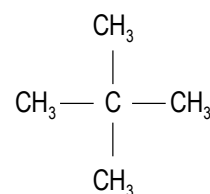
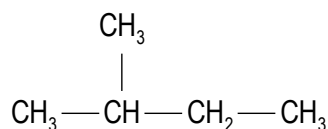
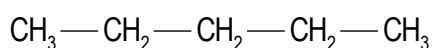
- Chain/branched chain
- Positional
- Functional group

Geometric

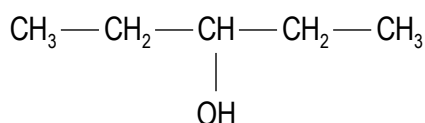
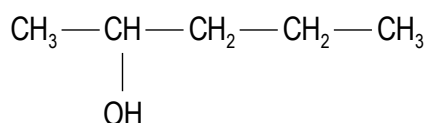
- Cis
- Trans

Optical

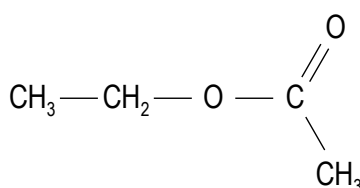
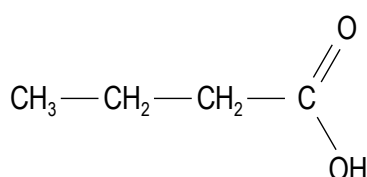
Chain/branched chain



Positional



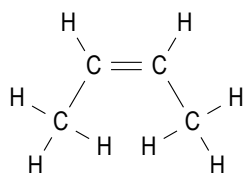
Functional group



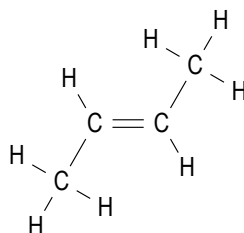
- **Geometric**

C=C double bond in alkanes is fixed and cannot be rotated (“is no free rotation about the C=C double bond”). This allows for different arrangements of the atoms/groups of atoms **in space**.

- groups on same side, cis-
- groups on opposite sides, trans

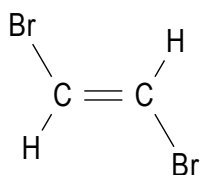


cis-

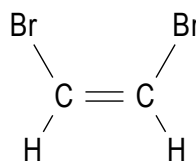


and *trans-*

Cis-trans (geometric) isomers exist where there is a C=C which **cannot freely rotate**. If there are two different groups bonded to the Cs of the double bond, two arrangements are possible.



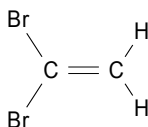
trans-



and *cis-*

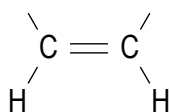
1,2-dibromoethene meets these requirements since each C of double bond has -H & -Br, i.e. different groups.

However, 1,1-dibromoethene does not meet these requirements since the two groups on the Cs of the double bond are the same, i.e. one C has two -H & the other two -Br.



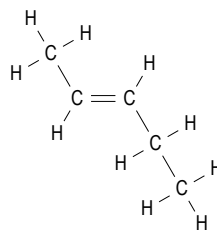
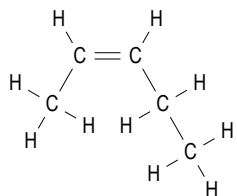
Drawing cis- and trans- isomers

Always start from a



shape;

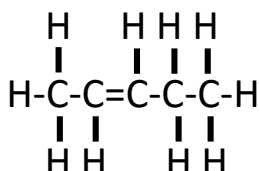
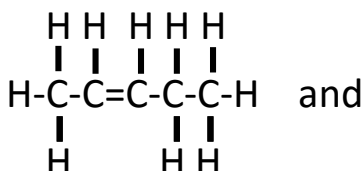
Right 😊



Using this way, you will clearly see the effect on the shape of the molecule.

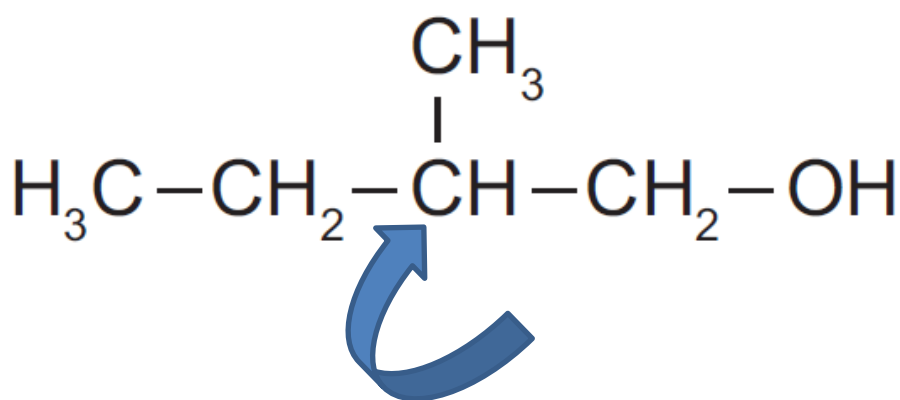
and

Wrong 😞

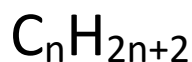


Optical isomerism

- 4 different atoms / groups attached to a C atom
- Chiral carbon or asymmetric carbon
- Are mirror images / non superimposable
- The isomers have identical chemical properties (but they may perform differently in biochemical systems) & physical properties *except*...the two isomers will rotate plane-polarised light in opposite directions (same $^{\circ}$ but one clockwise, the other anticlockwise).



ALKANES



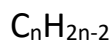
- single C-C bonds
- are saturated (no more H atoms can be added to their molecules)

ALKENES



- contain a C=C double bond
- are unsaturated (more H atoms (or other atoms) can be added to their molecules)

ALKYNES



- contain a C≡C triple bond
- are unsaturated (more H atoms (or other atoms) can be added to their molecules)

Physical properties of all

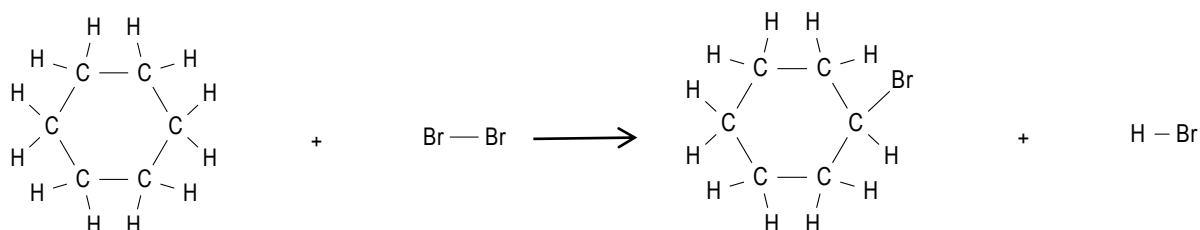
- as no. of C↑ go from being gas to liquid to solid at room temperature
- smell – have weak intermolecular forces
- low m.pt & b.pt – have weak intermolecular forces
- insoluble in water – hydrocarbons are non-polar
- good solvents for fats & oils – non-polar substances dissolve other non-polar substances
- don't conduct electricity – no electrons that are free to move

ALKANES

- Fairly unreactive (only C-C); reactions need heat and/or UV light.
- But they do BURN well 😊 see below

Substitution reactions: chlorination / bromination.

- React in presence of UV light and/or heat.



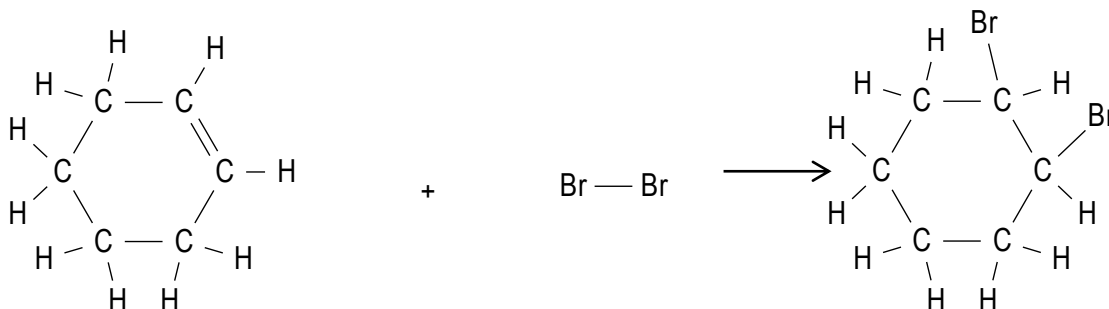
- The reaction is slow. Orange bromine is slowly decolourised.
- Chlorine reacts in a similar way.
- The reaction continues but normally we only write equations for “monosubstitution”.
- It is called a SUBSTITUTION reaction because one of the hydrogen atoms in the molecule is replaced by a bromine atom.

Combustion

- Complete; plentiful O₂. Products CO₂ & H₂O and lots of energy
- Incomplete; limited O₂. Products C (soot), CO & CO₂ & H₂O and less energy

ALKENES...

- More reactive than alkanes because of C=C
- Undergo ADDITION reactions
- C=C double bond replaced with C-C bond & 2 new bonds are made.

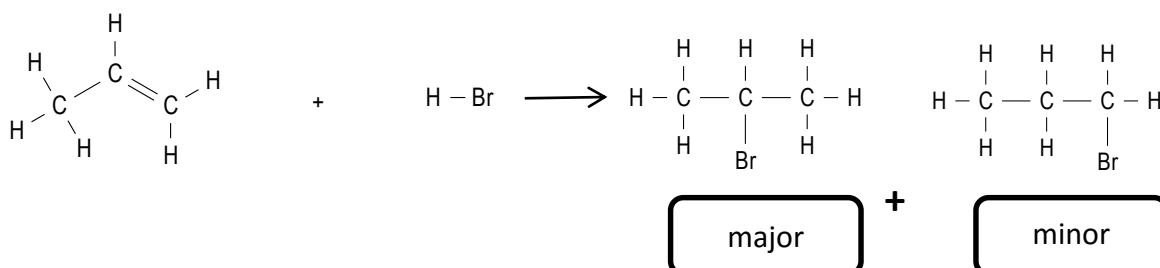
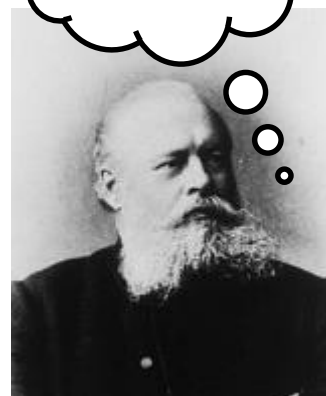


- Addition reactions can occur with
 - Hydrogen, H₂, Pt catalyst – hydrogenation
 - Water, conc H₂SO₄ then water & heat – hydration
 - Halogens, Cl₂ & Br₂ – halogenation (chlorination, bromination)
 - Hydrogen halides, HBr – hydrohalogenation
 - Themselves, monomer → polymer, polymerisation

The rich get richer!!!

Markovnikov's rule or Markownikoff's rule

- Addition of an unsymmetrical reagent (eg HCl, HBr, H₂O (H-OH)) to an unsymmetrical alkene eg propene or but-1-ene
- 2 possible products, one major one minor
- Predict using “the rich get richer”
- H atom adds to the C of the C=C that already has most H atoms

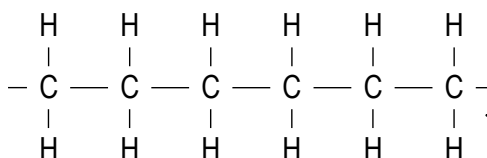
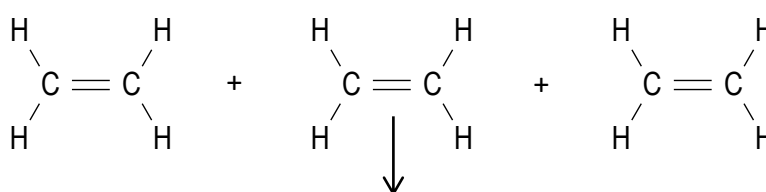


POLYMERISATION

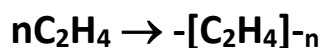


ADDITION POLYMERISATION

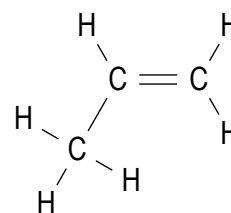
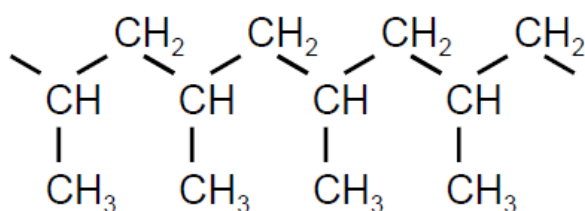
- Need high temperatures, pressure & catalyst
- Many monomer molecules → polymer molecule
- Addition reaction – called “addition polymerisation”
- E.g. ethene → polyethene, propene → polypropene
- Feature that allows this is the C=C double bond



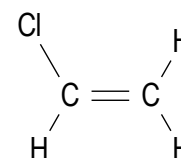
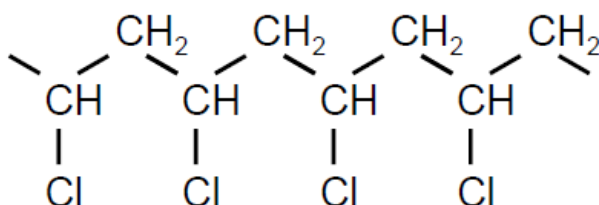
Now a saturated molecule but still called polyethene



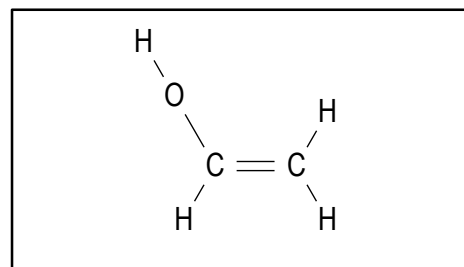
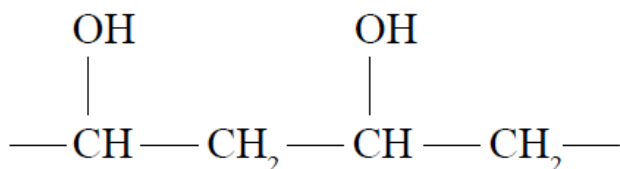
Polypropene



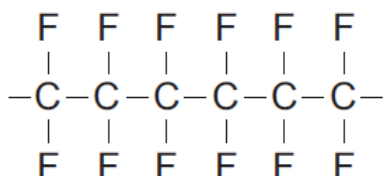
Polyvinyl chloride (PVC)



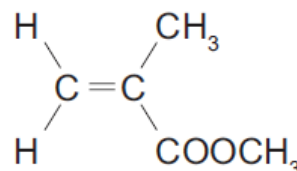
Polyvinyl alcohol



Polytetrafluoroethene (PTFE)



Perspex

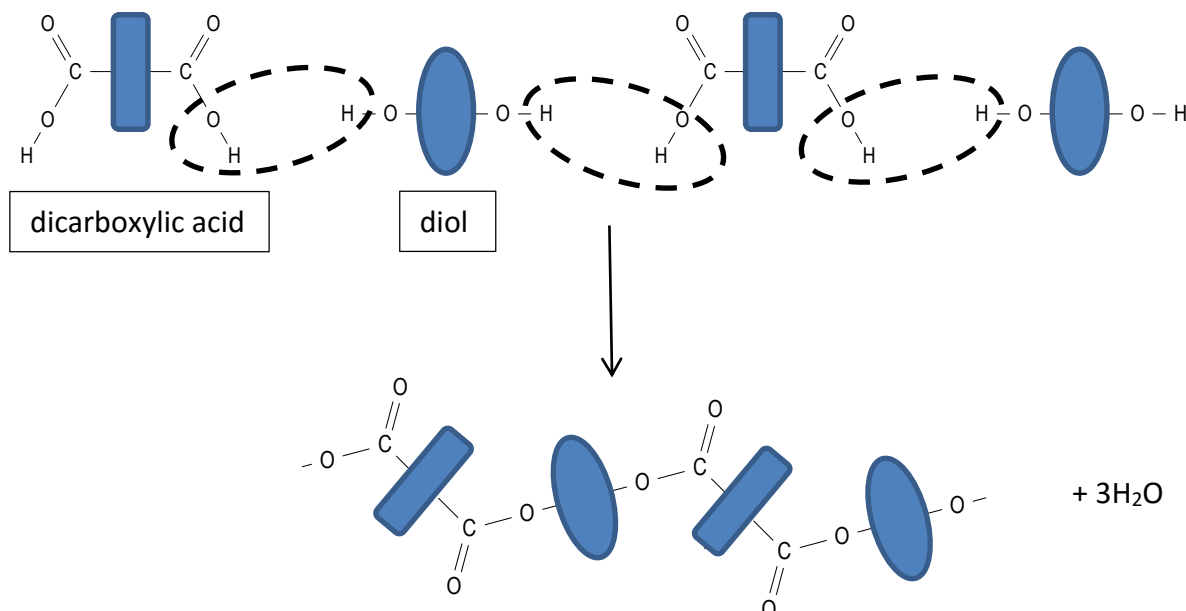


CONDENSATION POLYMERISATION

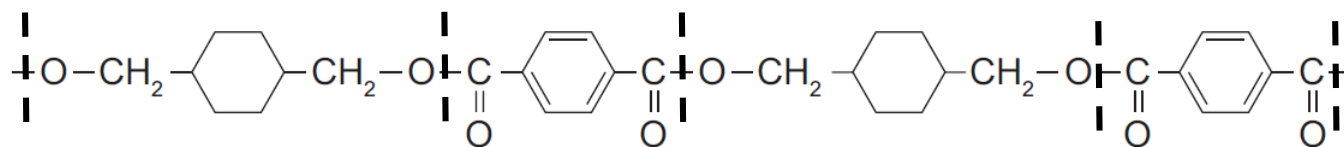
POLYESTERS: Remember....Esters are formed by the reaction of an alcohol and either a carboxylic acid or an acyl chloride.

They are made by reacting “double-ended” molecules such as a dicarboxylic acid and a diol. Eg terylene (You could also use a diacyl chloride and a diol).

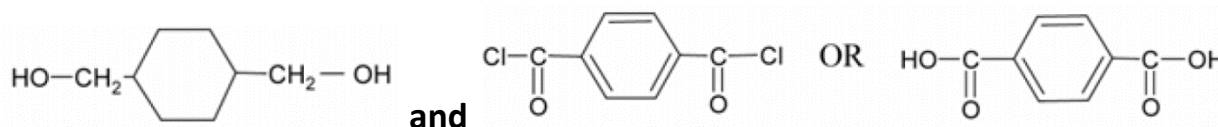
The polymer units alternate i.e. -A-B-A-B-A-B-A- etc and each time they join a small molecule such as H_2O or HCl is eliminated.



Example

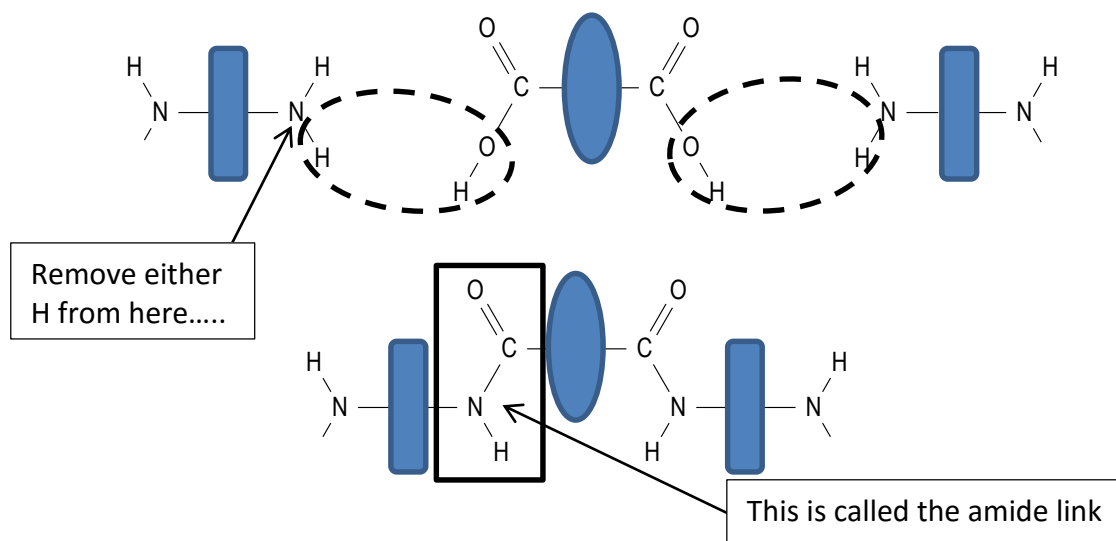
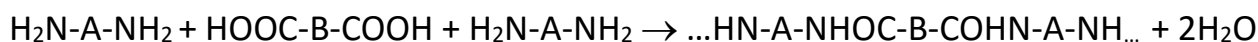


is made from monomers

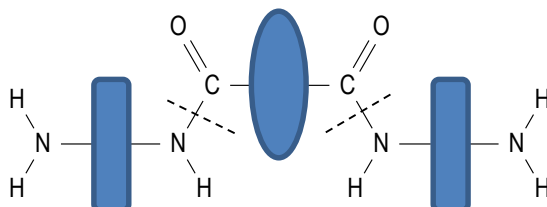


POLYAMIDES

Polyamides can be made by combining a diamine and a dicarboxylic acid or acyl chloride, E.g. nylon.



Polyamides can be hydrolysed under acid conditions ($\text{H}^+/\text{H}_2\text{O}$).



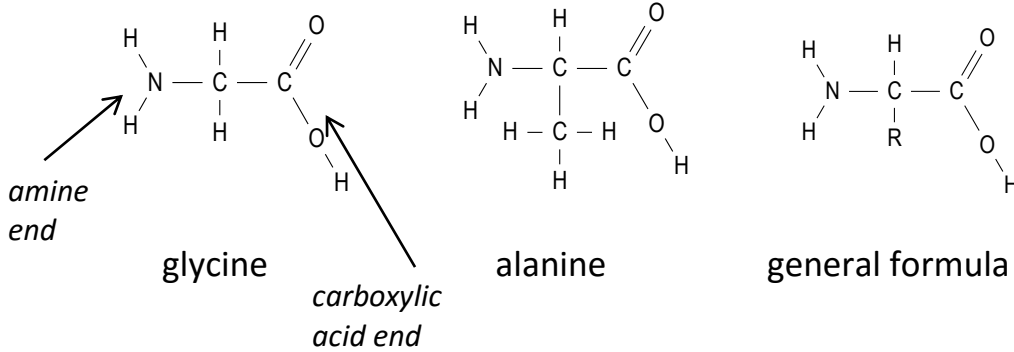
They are much more resistant to alkaline hydrolysis. Hydrolysis is faster at higher temperatures.

If you spill something like dilute sulfuric acid on a fabric made from nylon, the amide linkages are broken. The long chains break and you can eventually end up with the original monomers. Because you produce small molecules rather than the original polymer, the fibres are destroyed, and you end up with a hole!

Natural polymers e.g. carbohydrates, proteins, DNA etc.

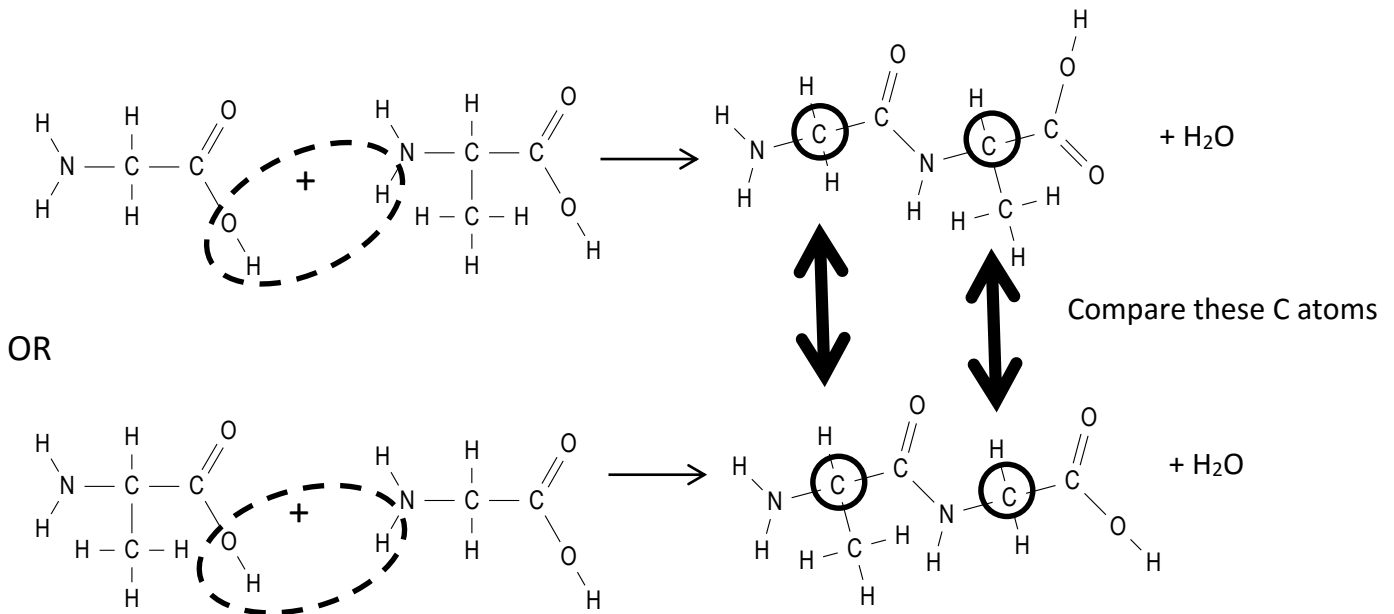
You need to know PROTEINS - **polymers** made of amino acid **monomers**. Each amino acid contains the NH_2 group of an amine and the COOH group of a carboxylic acid.

Examples of amino acids



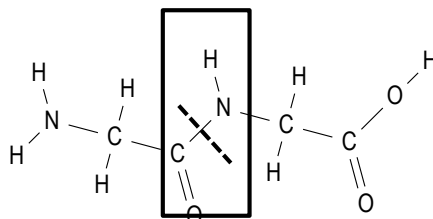
Apart from glycine, all amino acids have a *chiral carbon* (four different groups off it) and form optical isomers. Normally only one of the optical isomers is biologically important/useful.

Dipeptides – 2 amino acids joined together. The order matters as it can make 2 different dipeptides depending on which is the $-\text{NH}_2$ end and the other the $-\text{COOH}$ end e.g.



With THREE different amino acids the variation gets even bigger: 6 possible amino acids. Since amino acids can be assembled in any order it means an almost infinite number of different protein molecules. Most common proteins contain more than 100 amino acids

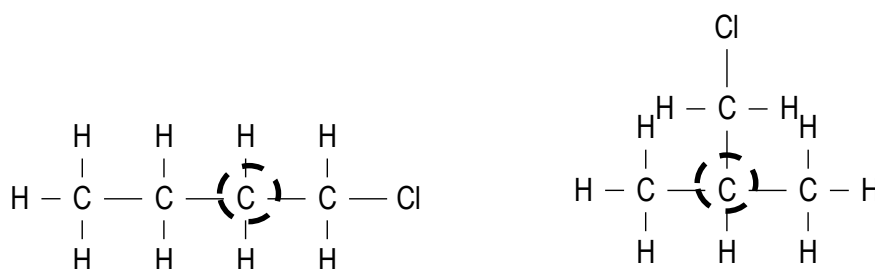
peptide link or amide link



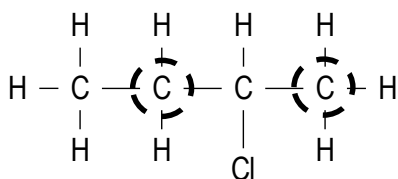
Proteins/peptides can be hydrolysed under acid conditions ($\text{H}^+/\text{H}_2\text{O}$). They "split" where they were formed, ie ----- to give the amino acids. (Important reaction in digestion).

HALOALKANES

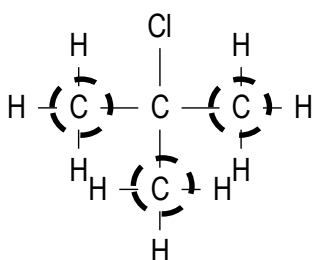
- R-X, where X – is F, Cl, Br or I (halogen)
- $C_nH_{2n+1}X$
- alkanes in which one (or more) hydrogen atoms have been replaced by halogen atoms
- classified as primary, secondary or tertiary like alcohols
- **Primary**



- **Secondary**



- **Tertiary**



How many C are attached to the C that has the halogen attached to it?

Physical properties

Chloromethane, bromomethane and chloroethane are colourless gases.

Low-mass haloalkanes are colourless, pleasant-smelling volatile liquids, often volatile.

Higher molar masses are solids.

Although polar, haloalkanes are only slightly soluble in water - no hydrogen bonding can occur.

Polarity causes b.pt to be higher than corresponding alkanes.

Preparation

Formed by-

- Substitution of an alkane (needs *uv* light and or heat)
- Addition of HX to an alkene
- Addition of X₂ to an alkene
- chlorination of an alcohol with HCl/ZnCl₂, PCl₃ or PCl₅ or SOCl₂

Best one
ever!!

Reactions

Nucleophilic substitution

C-X bond is polar; $\delta^+C-X\delta^-$ so C is vulnerable to attack by nucleophiles

A nucleophile

- is a species attracted to a positive charge.
- is a species carrying a negative charge or a lone pair of electrons

Examples: OH⁻(aq), H₂O and NH₃(alc).

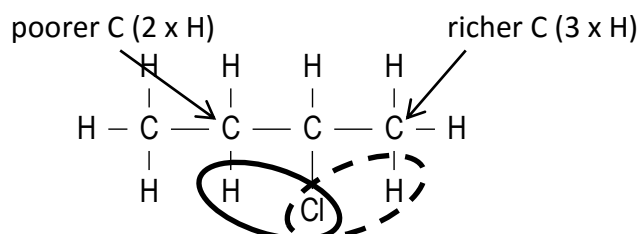
- R-X(l) + OH⁻(aq) → R-OH + X⁻(aq)
- R-X(l) + NH₃(alc) → R-NH₂ + HX(alc) - amine ; For NH₃ to act as a nucleophile it must be dissolved in alcohol, not in H₂O (which would produce NH₄⁺ and OH⁻: OH⁻ would react with the R—X instead of the NH₃).

Elimination reactions

Haloalkanes → alkenes, reagent OH⁻(alc)

R-X → R=C + HX

- KOH(alc) or NaOH(alc) - dissolved in alcohol to prevent nucleophilic substitution by OH⁻ (forming the alcohol)
- 3° haloalkanes > 2° haloalkanes > 1° haloalkanes to undergo elimination
- reverse of Markovnikov's rule applies: *the poor get poorer*.
- Will get a major & minor products if unsymmetrical haloalkane

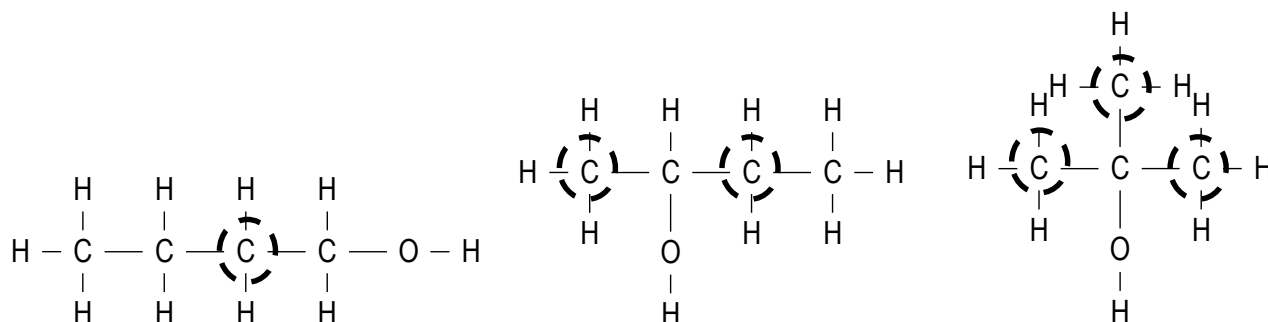


A L C O H O L S

important fuels
and solvents

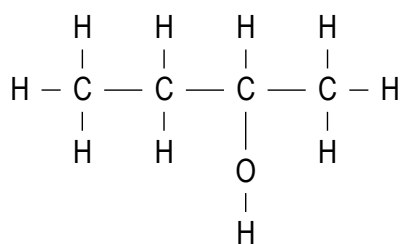


- -OH functional group
- $C_nH_{2n+1}OH$ or R-OH
- Position of -OH group decides primary, secondary or tertiary

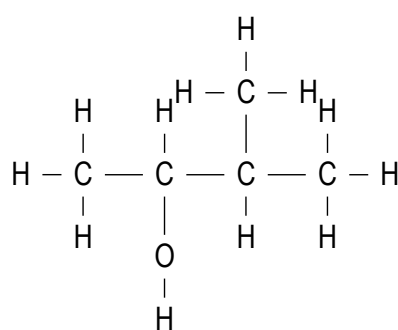


- Polar molecules due to -OH group; small ones (C 1 -3) are water soluble, larger ones not.

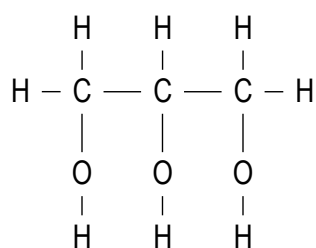
Naming - name or draw



propan-2-ol or 2-propanol

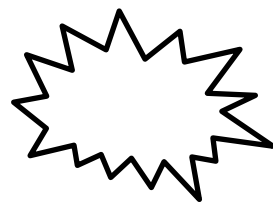


ethan-1,2-diol



2-chloro-butan-2-ol
or 2-chloro-2-butanol

Alcohols



Physical properties -

The lower alcohols are colourless, soluble in water due to polar $-OH$ group - allows for hydrogen bonding to adjacent molecules and to water

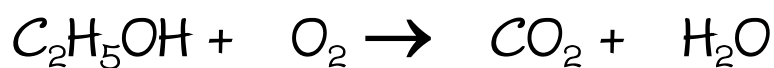
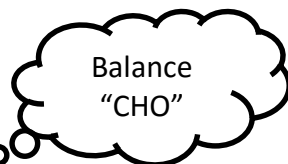
As no. of C \uparrow increases, the solubility rapidly \downarrow

Hydrogen bonding causes alcohols to have much higher m.pt and b.pt than the corresponding alkanes.

Chemical properties -

Combustion

Burn with a clean almost colourless flame, good fuels.



OXIDATION

Primary alcohols can be oxidised by heating them with either:

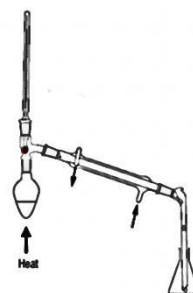
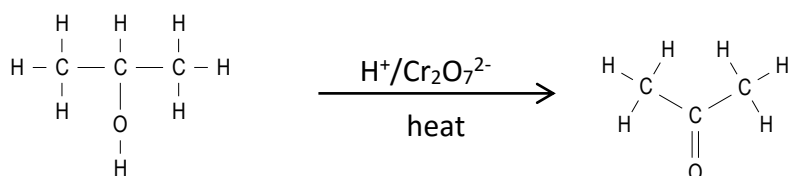
- Acidified dichromate ($H^+/Cr_2O_7^{2-}$): milder O.A. than MnO_4^-
colour change $Cr_2O_7^{2-}$ (orange) to Cr^{3+} (green)
- Acidified permanganate (H^+/MnO_4^-)
colour change MnO_4^- (purple) to Mn^{2+} (colourless)

The alcohols are oxidised to aldehydes* ($-CHO$) and then to carboxylic acids ($-COOH$ functional group)

(*To isolate the aldehyde it is necessary to distil it off as it forms)

Secondary alcohols can be oxidised, as above, to ketones

e.g.



Tertiary alcohols are not oxidised by common oxidising agents (but will still burn).

DEHYDRATION (an elimination reaction)

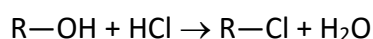
- Conc. H_2SO_4 & heat
- Alcohol \rightarrow alkene (3° easier than 2° , 2° easier than 1°)
- The poor get poorer

Substitution by chlorine (chlorination)

Alcohols can form chloroalkanes with three different reagents: PCl_5 , PCl_3 or SOCl_2

- thionyl chloride SOCl_2 – is best choice as works with 1° , 2° & 3° AND is useful as $\text{SO}_2(\text{g}) + \text{HCl}(\text{g})$ as bubble off, leaving RCl as the only product. $\text{ROH}(\text{l}) + \text{SOCl}_2(\text{l}) \rightarrow \text{RCl}(\text{l}) + \text{SO}_2(\text{g}) + \text{HCl}(\text{g})$
- with HCl/ZnCl_2 (Lucas reagent)

A mixture of conc HCl and anhydrous ZnCl_2 will react with 3° alcohols to form chloroalkanes.



Tests to distinguish between alcohols

Warm with acidified dichromate $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$

- Tertiary – no colour change (orange dichromate remains orange)
- Secondary AND primary – colour change orange to green as Cr^{3+} made

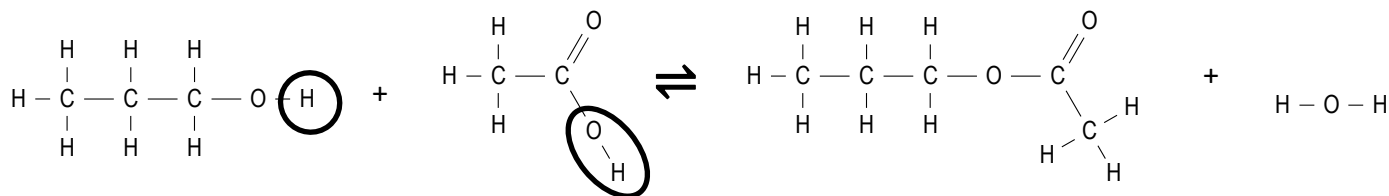
Lucas reagent – anhydrous ZnCl_2 / conc HCl

- Tertiary – cloudy* immediately
- Secondary – cloudy* after 10 minutes
- Primary – no change

*Due to formation of insoluble haloalkane

ESTERIFICATION (a condensation reaction, and also a substitution reaction)

Heat alcohol and carboxylic acid, with a little concentrated sulfuric acid H_2SO_4 (acts as catalyst and dehydrating agent).



It's a \rightleftharpoons reaction; eqm. position lies to left; removal of water by the conc acid (dehydrating agent) shifts the eqm. position in favour of the ester product.

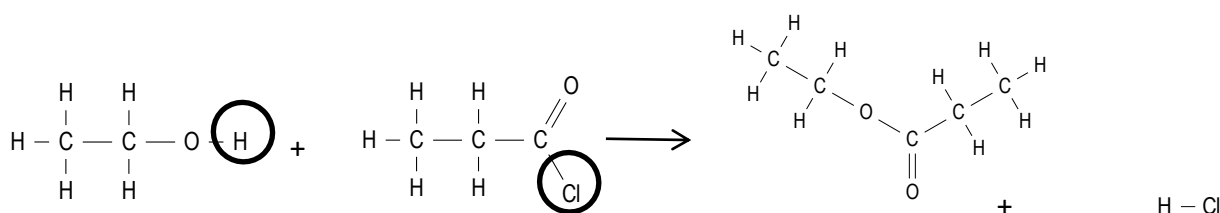
Small scale preparation of ester.

To make a small ester like ethyl ethanoate, you can gently heat a mixture of ethanoic acid and ethanol in the presence of concentrated sulfuric acid, and distil off the ester as soon as it is formed. The ester has the lowest boiling point of anything present because the ester is the only thing in the mixture which doesn't form hydrogen bonds, and so it has the weakest intermolecular forces.

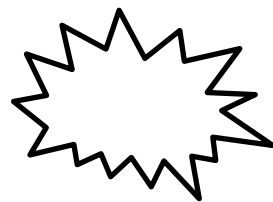
If you want a more pure product.....

- Mix alcohol & c.acid in a pear shaped flask and add conc. H_2SO_4 – catalyst.
- Heat gently under reflux – under reflux so the chemicals react but so the volatile reactants / product don't vaporise and escape. (vaporise – condense – vaporise – condense – etc).
- Add sodium carbonate solution to the mixture in a separating funnel – neutralises the acids. Need to release the pressure in separating funnel due to the CO_2 gas given off!
- Discard the aqueous layer – it's not wanted.
- Dry the organic layer (the ester!) with anhydrous $CaCl_2$ – removes traces of H_2O .
- Distil, collecting the fraction with the boiling point of the ester ($\pm 1-2^\circ C$).

Alcohols also form esters with acid/acyl chlorides – don't need heat or conc. sulfuric acid catalyst



Naming esters



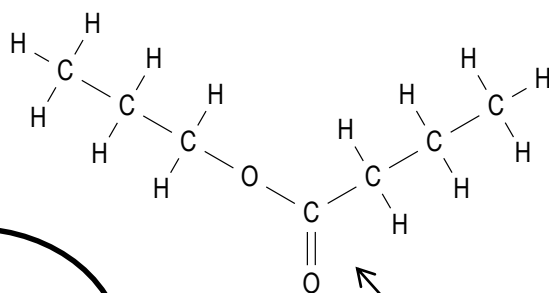
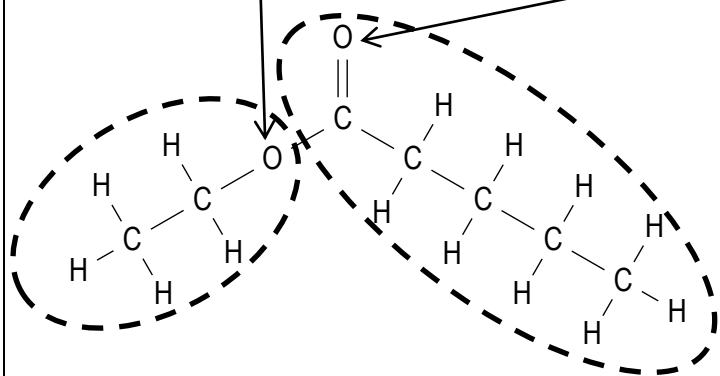
.....yloate

from the alcohol

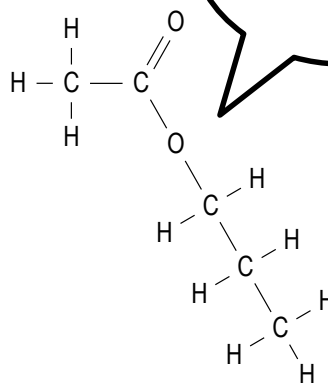
from the carboxylic acid
or acid/acyl chloride

(the "inline O")

(from the "stick-out=O")

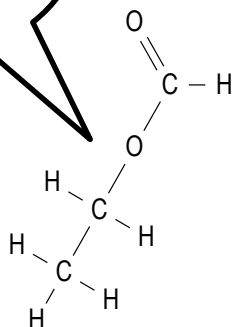


ethyl
methanoate

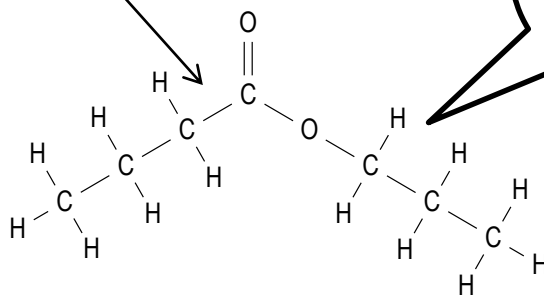


propyl
ethanoate

We are the same!!!

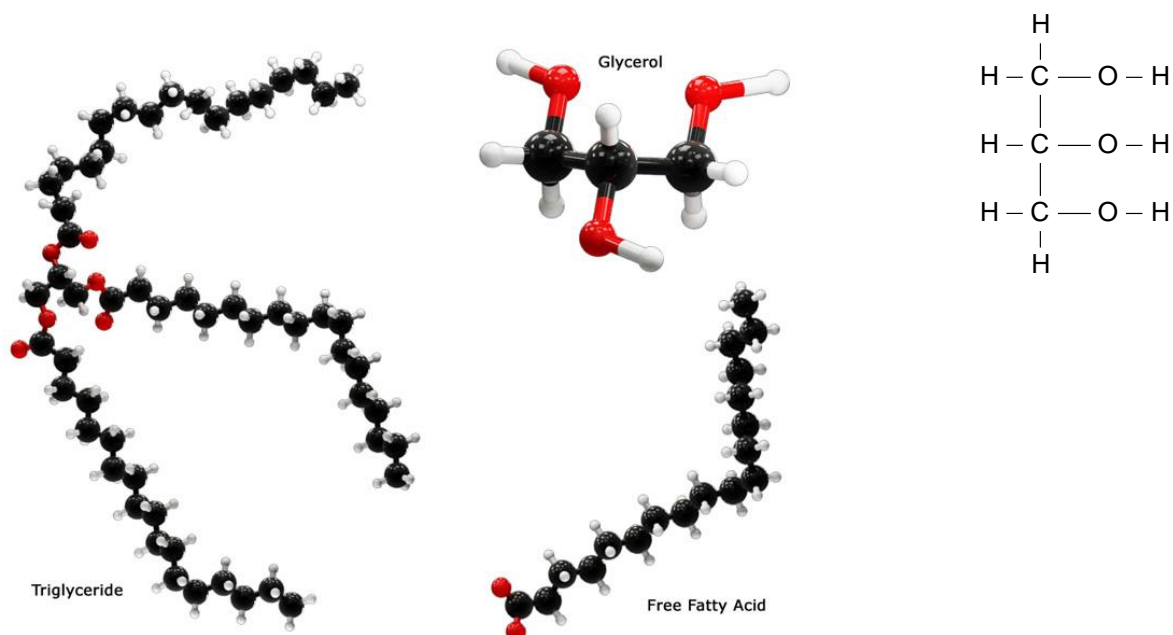


propyl
butanoate



TRIGLYCERIDES – fats and oils.

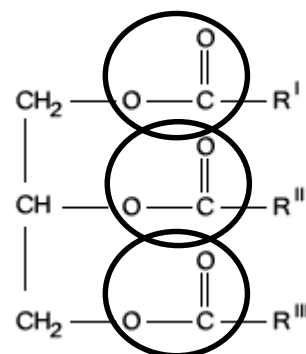
Most fats and oils are derived from propan-1,2,3-triol (glycerol) and a variety of long-chain carboxylic acids (known as fatty acids). Glycerol is a triol as it has 3 –OH groups.



They are also called triglycerides because they have 3 ester links and are based on glycerol.

The three fatty acids bonded to a single glycerol molecule need not be the same.

Solid fats contain a large proportion of saturated fatty acids, whereas oils have more unsaturated fatty acids.

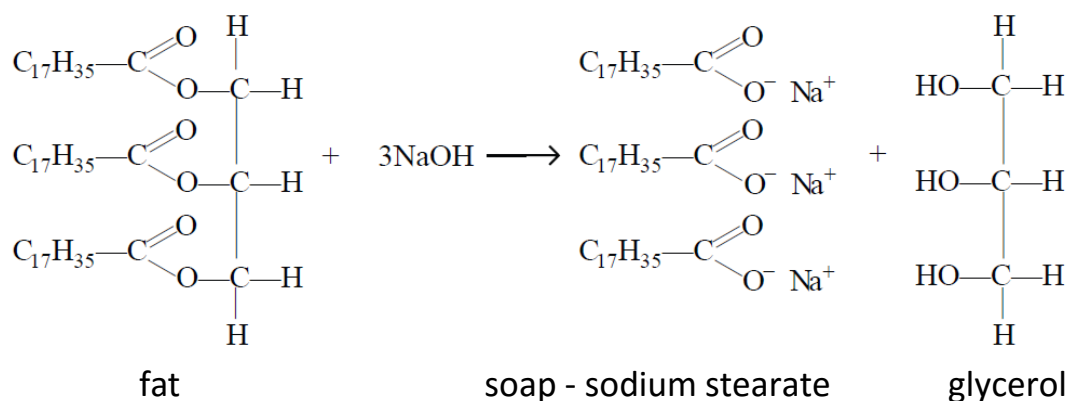


Soap making

Alkaline hydrolysis of fats / oils will form the sodium salts of the fatty acid and glycerol. The fat/oil is heated with NaOH solution. The reaction is alkaline hydrolysis but the process is also called **saponification** when the ester comes from a fat.

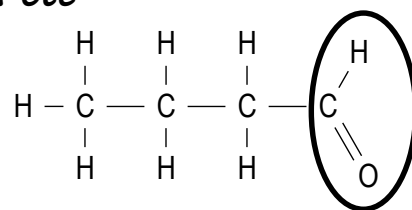
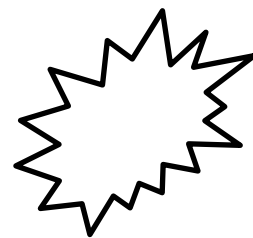
The sodium salts of the fatty acid are soluble in water.

E.g.



Aldehydes RCHO

- have the carbonyl group $C=O$ on the end C
- have names -anal! E.g. ethanal, butanal etc
- are structural isomers of ketones



Physical properties

- methanal is a gas at room temp, other low C atom aldehydes are liquids
- have unpleasant, pungent smells
- C1-4 soluble in water

Preparation

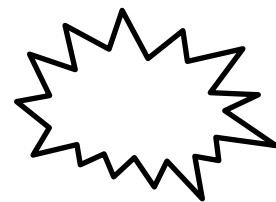
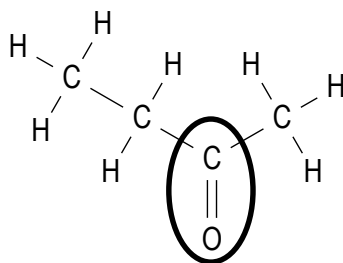
- oxidation of primary alcohols; heat with $H^+/Cr_2O_7^{2-}$. Aldehyde must be distilled off the mixture to prevent further oxidation to the carboxylic acid

Distinguishing between aldehydes and ketones – VERY IMPORTANT!

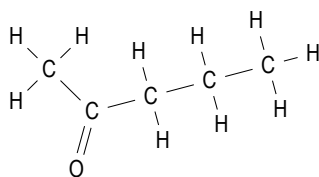
These reactions depend on the fact that **aldehydes can be oxidised to carboxylic acids but that ketones do not oxidise further** (except by combustion). Aldehyde gives POSITIVE result in the 3 tests below, but with the ketone... there are NO COLOUR CHANGES

- warm with acidified potassium dichromate/permanganate; ALDEHYDE oxidised to CARBOXYLIC ACID.
 - acidified $Cr_2O_7^{2-}$ (ORANGE) is reduced to Cr^{3+} (GREEN), or
 - acidified MnO_4^- (PURPLE) is reduced to Mn^{2+} (COLOURLESS)
- Warm with Tollens reagent – diammine silver complex $[Ag(NH_3)_2]^+$ or “ammoniacal silver nitrate”; ALDEHYDE oxidised to CARBOXYLIC ACID.
 - silver mirror seen on test tube as silver ion is reduced to silver. $Ag^+ + e^- \rightarrow Ag$
- Warm with Fehlings solution – Cu^{2+} ions in a complex; ALDEHYDE oxidised to CARBOXYLIC ACID.
 - forms copper(I) oxide (Cu_2O), which is a red-brown precipitate as the copper(II) ion is reduced to copper(I); $Cu^{2+} + e^- \rightarrow Cu^+$

Ketones RCOR



- carbonyl group $C=O$ on a middle (non-terminal) carbon.
- name ends in $-anone$.
- first member – propanone
- if more than 4 C, position of carbonyl group must be specified, eg pentan-2-one



- are structural isomers of aldehydes

Physical properties

- pleasant, sweet odours
- liquids at room temp
- C1-4 soluble in water

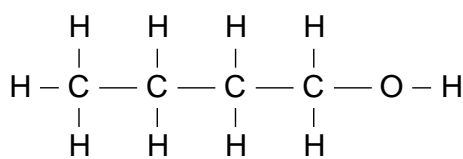
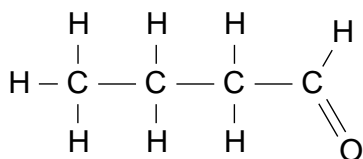
Preparation

- oxidation of a secondary alcohol

Reduction of aldehydes and ketones with $NaBH_4$.

The reduction of aldehydes and ketones with sodium borohydride $NaBH_4$ returns the carbonyl compound to the original alcohol.

- Aldehyde \rightarrow primary alcohol e.g. butanal to butan-1-ol



- Ketone \rightarrow secondary alcohol e.g. butanone to butan-2-ol

This reaction is a “must” to know for organic conversion questions.

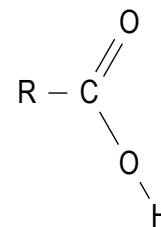
NEW
STUFF IN
AS91391

Carboxylic acids – count the “C”s ☺

HCOOH methanoic acid





CH₃COOH ethanoic acid

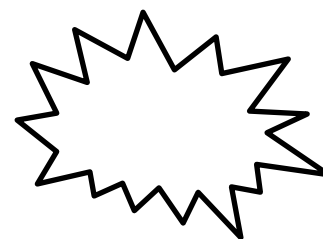
C₂H₅COOH propanoic acid



- contain the –COOH functional group - as it is on the end there is no need to number it.
- the -COOH group is very polar; C1-3 are soluble in water, C4 and above not (due to long hydrocarbon portion)
- Higher m.pt. and b.pt. than alcohols of similar mass due to stronger intermolecular attractions
- are weak acids – only partly ionised when placed in water
$$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$$
- are poor conductors of electricity as aq. solutions (as weak acids)

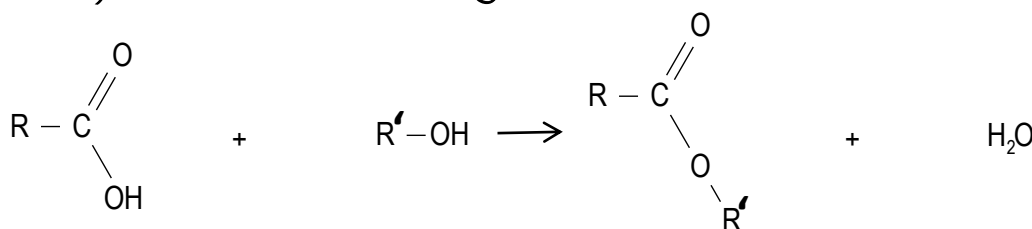
Reactions as acids

- turn  blue litmus  red
- turn  green UI paper  orange pH 3-4
- $\text{RCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{RCOO}^- + \text{H}_3\text{O}^+$ ie release H_3O^+ ions
- “Typical acids reactions”; react slowly with Mg, NaHCO_3 , CaCO_3 etc due to the low concentrations of H_3O^+ present
 - acid + metal \rightarrow salt + hydrogen eg Mg or Zn to produce bubbles of H_2 gas
 - acid + base \rightarrow salt + water eg NaOH
 - acid + carbonate \rightarrow salt + water + carbon dioxide eg Na_2CO_3 and CaCO_3 & hydrogen carbonates NaHCO_3 to produce bubbles of CO_2 gas

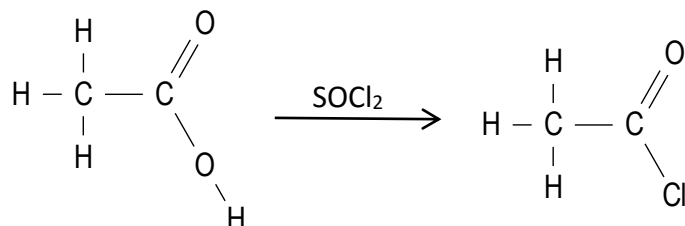


“Organic reactions”

Esterification (again!!!). Heat an alcohol and a carboxylic acid, with a little concentrated sulfuric acid H_2SO_4 (catalyst). It's also a **CONDENSATION** reaction.



Nucleophilic substitution: Carboxylic acids react to form acyl (acid)chlorides by nucleophilic substitution with PCl_3 or PCl_5 or SOCl_2 *. *Best as other products are gases SO_2 & HCl



Acyl chlorides

Acyl chlorides (a.k.a. acid chlorides) are derivatives of carboxylic acids where the $-\text{OH}$ group is replaced by Cl .

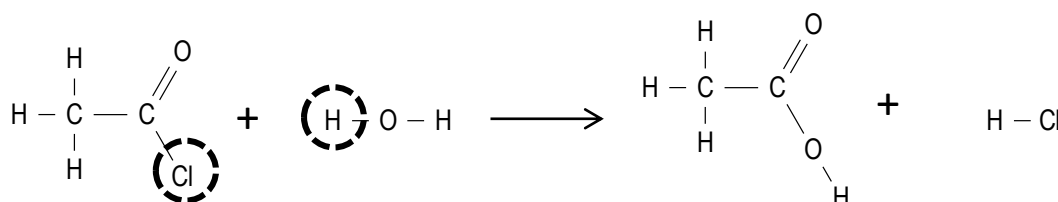
- Naming; end in $-\text{anoyl chloride}$, eg ethanoyl chloride, CH_3COCl .

Physical properties

- Colourless volatile liquids; low m. pt. (polar molecules but no hydrogen bonding)
- Pungent smell

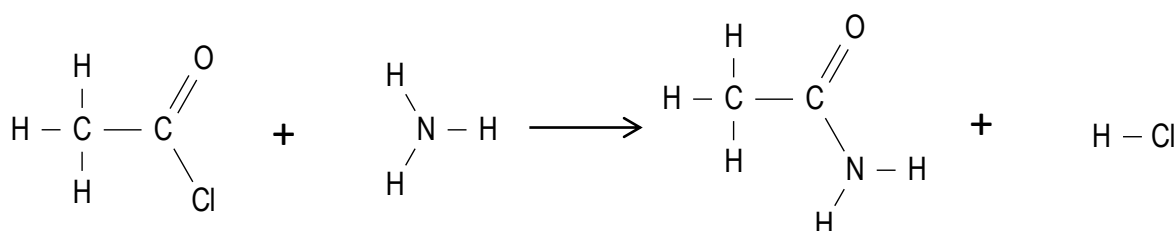
Chemical Properties

- Preparation; nucleophilic substitution of carboxylic acids by PCl_3 , PCl_5 and SOCl_2 .
- Very very reactive – react vigorously with water \Rightarrow carboxylic acid & HCl

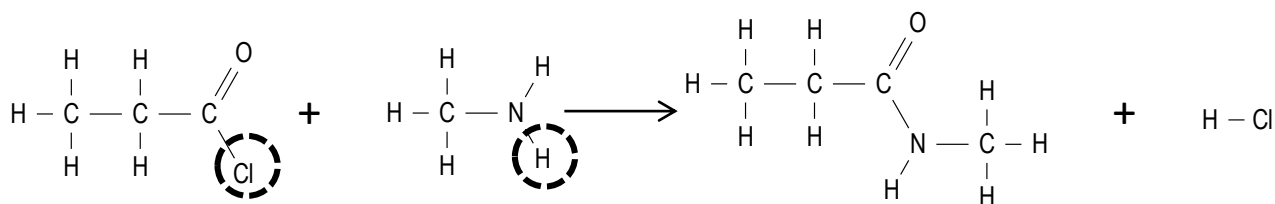


(Because of this they will fume if you take the lid off in moist air)

- Used to prepare esters, amides, secondary amides and carboxylic acids
 - Esters: condensation reaction where two “large” molecules combine, ejecting a small molecule, in this case HCl . Don't need heat or a catalyst.
 $\text{R}-\text{OH} + \text{R}'-\text{COCl} \rightarrow \text{R}-\text{O}-\text{CO}-\text{R}' + \text{HCl}$
 - Amides: Ammonia (a nucleophile) reacts with acyl chlorides to form amides
 $\text{CH}_3\text{CH}_2\text{COCl} + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CONH}_2 + \text{HCl}$ The NH_3 must be **dissolved in alcohol** – $\text{NH}_3(\text{alc})$ or the water would react and make a c. acid instead.

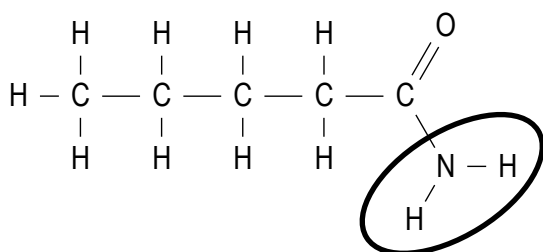


- Secondary amides: Amines (RNH_2) also contain the nucleophile $-\text{NH}_2$ and so react with acyl chlorides, this time to form secondary amides



- Carboxylic acids; Just add water ☺ $\text{R-COCl} + \text{H}_2\text{O} \rightarrow \text{R-COOH} + \text{HCl}$

AMIDES



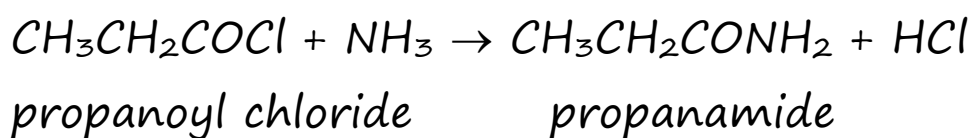
Are carboxylic acid derivatives. The $-\text{OH}$ from the acid is replaced by an:

- NH_2 (for primary amides) eg RCONH_2
- NH (for secondary amides) eg RCONHR or
- N (for tertiary amides) eg RCONR_2 .

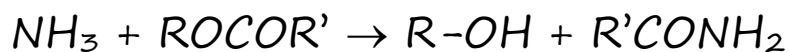
You only need to know how to name primary amides. Their names end in $-\text{anamide}$, eg CH_3CONH_2 is ethanamide

Amide formation

- ammonia (dissolved in alcohol) reacts with acyl chlorides to form amides:



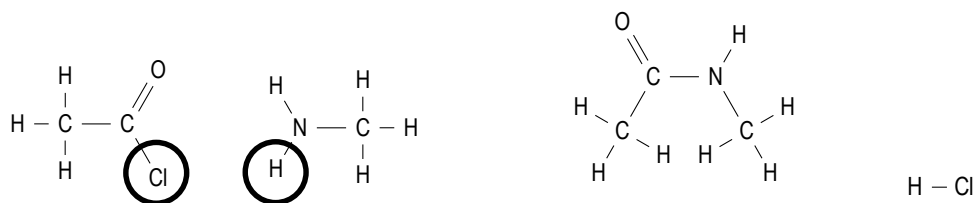
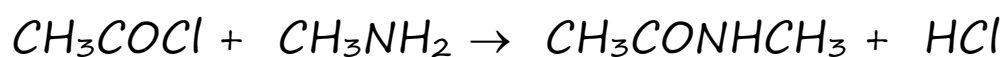
- ammonia (dissolved in alcohol) reacts (slowly) with ester



- thermal decomposition of the ammonium salt* of the carboxylic acid: $\text{RCOO}^-\text{NH}_4^+ \rightarrow \text{RCONH}_2 + \text{H}_2\text{O}$

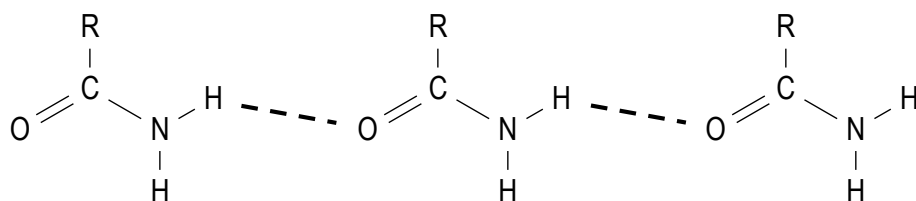
NOTE: Ammonia does not form an amide by reacting with the carboxylic acid directly. * $\text{RCOOH} + \text{NH}_3 \rightarrow \text{RCOO}^-\text{NH}_4^+$

- amines (R-NH_2) also react with acyl chlorides, this time to form secondary amides.



Physical properties

- methanamide (liquid @ room temp.)
- other amides - white crystalline solids @ room temp.
- no smell if pure
- the lower members are soluble in water
- the high melting points and boiling points due to hydrogen bonds between the O of one molecule and the amino H of another.



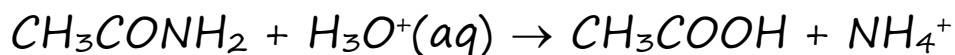
Chemical properties

Amides are much weaker bases than amines

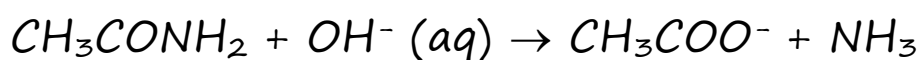
- amides are neutral to litmus
- do not react with hydrochloric acid to form salts.

Hydrolysis

Amides are hydrolysed by heating with acid e.g. HCl



They are also hydrolysed by heating with alkalis (eg NaOH):



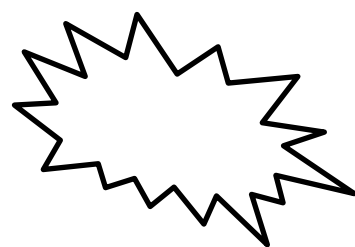
(NH₃ gas turns red litmus blue)

Esters – characteristics and reactions...

- little polarity so
 - insoluble in water (2 layers)
 - low melting points & boiling points
 - good solvents (for other non-polar substances)
- volatile; usually characteristic pleasant odours – many are “fruity”
- occur in fats and oils (see later)

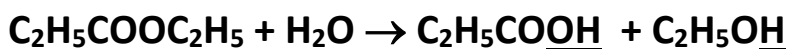
Hydrolysis of esters (reaction with water)

This is the reverse of esterification reaction!

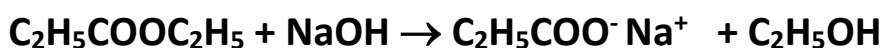


Since the nonpolar esters are insoluble in water they don't react “easily” with water, so need heat + acid OR heat + alkali.

Acid hydrolysis $\text{H}^+/\text{H}_2\text{O} + \text{heat}$



Alkaline hydrolysis $\text{NaOH}(\text{aq}) + \text{heat}$

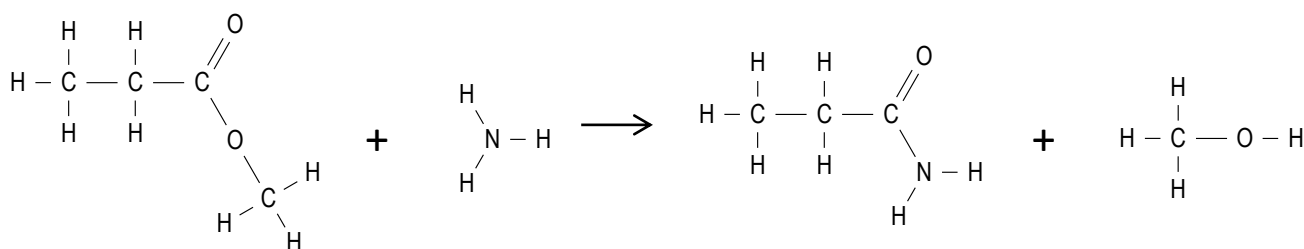
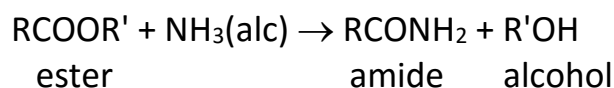


Products are the alcohol in both cases, but in acid hydrolysis you get the carboxylic acid while in alkaline hydrolysis you get the sodium salt of the carboxylic acid.

$\text{C}_2\text{H}_5\text{COO}^- \text{Na}^+$ can be written $\text{C}_2\text{H}_5\text{COONa}$ or $\text{NaC}_2\text{H}_5\text{COO}$ BUT DON'T WRITE $\text{C}_2\text{H}_5\text{COO}-\text{Na}$ (not a covalent bond between O and Na!!) Its name is sodium propanoate (since 3 x C atoms)

Reaction with ammonia

Esters react with alcoholic ammonia to form amides:



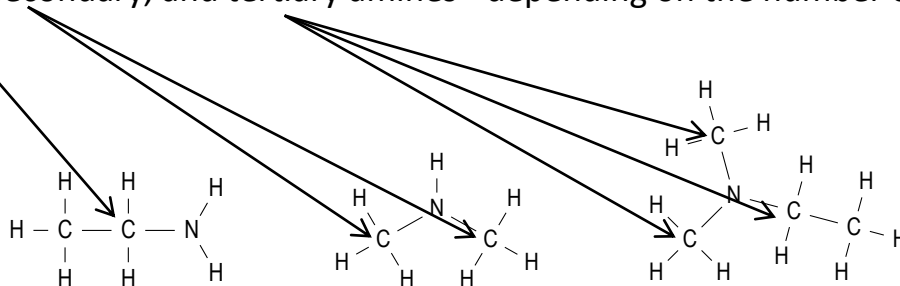
The reaction is slow, so the better method of forming amides is acyl chloride + $\text{NH}_3(\text{alc})$,
 $\text{RCOCl} + \text{NH}_3 \rightarrow \text{RCONH}_2 + \text{HCl}$

AMINES -NH₂ amino group

Essentially NH_3 with 1, 2 or 3 H atoms replaced with alkyl group(s)

- naming based on alkane so $\text{C}_2\text{H}_5\text{NH}_2$ is aminoethane (IUPAC) but also often called ethylamine

Are primary, secondary, and tertiary amines - depending on the number of C atoms the N is bonded to.



- nucleophiles due to lone pair on the N:
- weak bases since proton acceptors, $\text{R-NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{R-NH}_3^+ + \text{OH}^-$

Physical properties

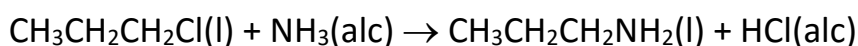
- Methylamine and ethylamine are gases; others low m.pt. volatile liquids; C > 5 are usually solids



- Characteristic “fishy” smell
- Low mass amines soluble in water – as form hydrogen bonds with water; larger ones insoluble. (Tertiary can't form hydrogen bonds as no H bonded to the N)

Preparation

Primary amines can be prepared by the nucleophilic substitution of a haloalkane by alcoholic ammonia.






For NH_3 to act as a nucleophile it must be dissolved in alcohol, not in H_2O as OH^- would react with the R-X instead of the NH_3).

Chemical reactions

Amines are bases - like ammonia.

- $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
- $\text{R-NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{R-NH}_3^+ + \text{OH}^-$

They turn damp  litmus paper  and universal indicator solution/paper blue. 

Reaction with HCl

As bases, amines react with acids such as HCl to form salts.

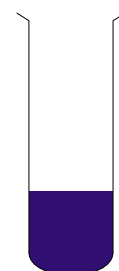
- $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4^+\text{Cl}^-(\text{s})$
- $\text{CH}_3\text{NH}_2(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{CH}_3\text{NH}_3^+\text{Cl}^-(\text{s})$ methyl ammonium chloride

These salts are colourless, crystalline solids, soluble in water and have no smell.

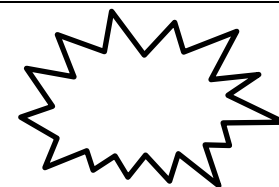
Reaction with copper sulfate

Just as copper sulfate reacts with ammonia, amines also react with Cu^{2+} solutions to give deep blue complexes which are soluble in water.

- $\text{Cu}^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq})$
- $\text{Cu}^{2+}(\text{aq}) + 4\text{C}_2\text{H}_5\text{NH}_2(\text{aq}) \rightarrow [\text{Cu}(\text{C}_2\text{H}_5\text{NH}_2)_4]^{2+}(\text{aq})$



TYPES OF REACTIONS



The list may look long & bewildering but that's just because some reactions can be called a number of things.....All of this has been previously covered in separate sections.

- **acid-base**
 - reaction involving a carboxylic acid & a base e.g. NaOH OR NH_3
 - reaction involving a carboxylic acid & a carbonate/hydrogen carbonate e.g. NaHCO_3
 - reaction between an amine & HCl
- **addition**
 - involves a small molecule joining across the C=C double bond of an unsaturated molecule (alkene/yne). The molecule becomes saturated.
 - no other product is made
- **bromination/chlorination**
 - addition of bromine/chlorine
- **condensation reaction**

two molecules combine, discarding a small one—often water or HCl. E.g. formation of an ester from an alcohol and an acid chloride, or when amino acids combine to make a protein.
- **dehydration**
 - removal of water (H and OH on adjacent C atoms) to form C=C bond
 - heat with conc. H_2SO_4 or pass over Al_2O_3 catalyst
 - since it involves removal it is also an elimination reaction
- **elimination**
 - removal of water: H & OH / water / removed from neighbouring C atoms in a molecule. A C=C double bond forms / forms an alkene / the molecule becomes unsaturated. Saytzeff's rule (a reverse of Markovnikov's rule) applies: the hydrogen tends to be eliminated from that carbon atom joined to the least number of hydrogen atoms. (also known as dehydration)
 - haloalkanes to alkenes – heat haloalkane with alcoholic KOH or NaOH to produce alkene and HX. (NaOH(aq) would cause substitution)

- **esterification**
 - reaction between alcohol & carboxylic acid to produce ester & water
 - needs conc. sulfuric acid (catalyst and dehydrating agent) & heat
- **halogenation (halogens are Cl₂, Br₂ etc)**
 - halogen added across the double bond of alkene (or C≡C of alkyne)
 - since it involves adding atoms it is also an addition reaction
 - chlorination, bromination & iodination are all halogenation reactions

OR

 - halogen swapped for an H on an alkane (alkane & halogen & UV light and/or heat). Since it involves replacing atoms it is also a substitution reaction
- **hydration**
 - water added across the double bond of alkene (alkene → alcohol)
 - since it involves adding atoms H and OH it is also an addition reaction
- **hydrogenation**
 - hydrogen added across double bond of alkenes, needs Pt or Ni catalyst
 - since it involves adding atoms it is also an addition reaction
- **hydrolysis – reaction with water**
 - acid hydrolysis of ester produces alcohol + carboxylic acid
 - hydrolysis of acyl chlorides produces HCl + carboxylic acid
 - acid hydrolysis of amides produces NH₄⁺ + carboxylic acid
 - alkaline hydrolysis of ester produces alcohol + sodium salt of carboxylic acid
 - alkaline hydrolysis of amides produces the carboxylate ion + NH₃
- **oxidation/reduction**
 - oxidation: conversion of primary alcohol to an aldehyde and then a carboxylic acid using heat and H⁺/Cr₂O₇²⁻ or H⁺/MnO₄⁻ (both oxidising agents)
 - oxidation: conversion of primary alcohol using heat and H⁺/Cr₂O₇²⁻ or H⁺/MnO₄⁻ to a ketone
 - oxidation: conversion of an alkene to a diol using H⁺/MnO₄⁻ (no heat needed)
 - reduction: conversion of an aldehyde to primary alcohol, and a ketone to secondary alcohol using NaBH₄.

- **polymerisation**
 - **addition**
 - i. unsaturated monomers joined to make a polymer (saturated)
 - ii. it is an addition reaction as the monomers add (and no other product made)
 - **condensation**: when condensation polymers form from monomers, a small molecule such as H_2O or HCl is lost at each join.
- **substitution** – one atom is removed and replaced with another atom
 - e.g. Cl_2 and an alkane: one hydrogen atom will be removed from the molecule and one chlorine atom will take its place. UV light is required for the process. HCl also formed.
 - Substitution reactions include esterification, condensation, hydrolysis, and polymerisation.

Add any others here that I have missed 😊

