

A2 Organic Chemistry Notes

Typed version of Fahad Hameed's handwritten A2 Organic Chemistry notes for Cambridge International A Level Chemistry (9701). Every page of the original is typed in the same order, with drawn structures named and written as formulae, and drawn mechanisms written as numbered steps, so the notes can be searched and copied. The handwritten original is on the same page of megalecture.com.

Introduction to Organic Chemistry

Organic: chemistry of **carbon compounds**.

- biological molecules
- fossil fuels

Formulas

Molecular formula: $C_2H_4O_2$. Total number of atoms of elements in a molecule (no information about structure).

Structural formula

1. Fully displayed formula

All atoms and bonds shown.

- C: 4 bonds
- N: 3 bonds
- O: 2 bonds
- H: 1 bond
- Halogen: 1 bond

N and O: lone pairs can form dative bonds.

Displayed formulas drawn with every atom and bond shown:

- butanone, $CH_3COCH_2CH_3$
- $HOOCCH_2COOCH_3$ (a carboxylic acid group at one end and a methyl ester group at the other)

2. Condensed structural formula

The displayed formula $H-O-C(=O)-CH_2-C(=O)-O-CH_3$ is written as $HOOCCH_2COOCH_3$.

The displayed formula of 2-hydroxy-2,3-dimethylbutanoic acid, counted along the main chain with the branches (CH_3 , OH and CH_3) circled, is written as $CH_3CH(CH_3)C(OH)(CH_3)COOH$.

Aldehydes: $R-C(=O)-H$ is written as $R-CHO$.

3. Skeletal formula

C–C bonds shown only, and any functional group.

The same molecule, 2-hydroxy-2,3-dimethylbutanoic acid, $CH_3CH(CH_3)C(OH)(CH_3)COOH$, is drawn



again as a displayed formula with each carbon marked by a dot, and then as a skeletal formula: a zigzag carbon chain with a line for each methyl branch, an OH on carbon 2 and the C(=O)OH group at the end.

Naming (simple naming)

Prefix	Number of carbons
meth	1C
eth	2C
prop	3C
but	4C
pent	5C
hex	6C
hept	7C
oct	8C
non	9C
dec	10C

Then: **an** or **en**.

Family	Suffix
alkane	-ane
alkene	-ene (position of C=C)
alcohol	-ol (position of OH)
carboxylic acid	-oic acid
nitriles	-nitrile
aldehyde	-al
ketones	-one (position of C=O)

CH₃CH=CHCOOH, numbered 4, 3, 2, 1 starting from the COOH carbon: **but-2-enoic acid** (but / 2-en / oic acid).

CH₃COCH₂CH₃, with the C=O carbon as carbon 2: **butan-2-one**.

Counting is done from the side which gives the smaller number to the higher precedence group (the suffix).

RCOOH > nitriles > aldehyde > ketones > alcohols (hydroxy branch) > amines (amino branches) > C=C

OHC-CH(OH)-CH₂-COOH, numbered 4, 3, 2, 1 starting from the COOH carbon. The groups are labelled aldehyde (carbon 4), alcohol (hydroxy, carbon 3) and carboxylic acid (carbon 1).

3-hydroxybutan-4-aloic acid

$\text{CH}_3\text{—CH}(\text{NH}_2)\text{—CH}_2\text{—OH}$, numbered 3, 2, 1 starting from the carbon with OH. The groups are labelled amine and alcohol.

2-aminopropan-1-ol

Branches

Order of the name: position, branch (alphabetical), **longest carbon atom chain**.

Choosing the longest carbon atom chain:

- more substituent groups
- maximum C=C
- highest precedence group (ticked)

Example: $\text{CH}_3\text{CH}(\text{CHO})\text{CH}=\text{C}(\text{CH}_3)\text{CH}(\text{OH})\text{CH}_3$. The main chain is highlighted and numbered from the aldehyde carbon: carbon 1 is CHO, carbon 2 is CH, carbon 3 is CH=, carbon 4 is =C, carbon 5 is CH(OH), carbon 6 is CH_3 . Circled branches: methyl on carbon 2, methyl on carbon 4, hydroxy on carbon 5.

5-hydroxy-2,4-dimethylhex-3-enal

The same molecule is drawn as a skeletal formula: a six-carbon zigzag chain with the C=O and H of the aldehyde at carbon 1, a methyl branch on carbon 2, the double bond between carbons 3 and 4, a methyl branch on carbon 4 and HO on carbon 5.

Isomers

Structural isomers

Same molecular formula, different **structural formula** (different arrangement of atoms).

(a) Chain / branch isomers

C_5H_{12} :

- pentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
- 2-methylbutane, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$
- 2,2-dimethylpropane, $\text{C}(\text{CH}_3)_4$

(b) Positional isomer

Change position of a functional group.

- $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$, but-1-ene
- $\text{CH}_3\text{CH}=\text{CHCH}_3$, but-2-ene

(c) Functional group isomer

$\text{CH}_3\text{CH}_2\text{CHO}$, propanal	CH_3COCH_3 , propanone
$\text{CH}_3\text{CH}_2\text{COOH}$, carboxylic acid	$\text{CH}_3\text{COOCH}_3$, ester
$\text{CH}_3\text{CH}=\text{CH}_2$, alkene	cyclopropane, a ring of three CH_2 groups (C_3H_6), cycloalkane

Stereoisomers

Same molecular formula, same structural formula but different 3-dimensional geometry.

(a) Geometric isomers

- C=C present
- each C must be bonded to two different groups

1,2-dichloroethene, $\text{CHCl}=\text{CHCl}$, drawn with the pi bond shaded above and below the C=C:

- **cis**: both Cl atoms on the same side of the C=C (both H on the other side)
- **trans**: the two Cl atoms on opposite sides of the C=C

Rotation is restricted around a C=C / pi bond.

$(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}=\text{CHCl}$: the first C=C is marked with a cross, because one of its carbons carries two CH_3 groups (circled). The second C=C is marked with a tick, cis / trans, because each carbon carries two different groups (H and Cl circled).

- **cis**: $(\text{CH}_3)_2\text{C}=\text{CH}-$ and Cl on the same side of the C=C, the two H atoms on the other side
- **trans**: $(\text{CH}_3)_2\text{C}=\text{CH}-$ and Cl on opposite sides of the C=C

Unsymmetric molecule

$n \times (\text{C}=\text{C})$ with cis / trans $\rightarrow 2^n$ different geometric isomers.

e.g. $\text{Cl}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$: each C=C is cis / trans, so $2^2 = 4$.

First C=C	Second C=C
cis	cis
trans	trans
cis	trans
trans	cis

Optical isomers

(Enantiomers. A mixture of enantiomers $\rightarrow$ racemate / racemic mixture.)

Chiral carbon: sp^3 hybridised / tetrahedral, 109.5° . C makes 4 single bonds with 4 different groups.
 $\rightarrow$ two non-superimposable mirror images.

Butan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, drawn as two tetrahedral structures on either side of a mirror line. The chiral carbon (C^*) carries H, CH_3 , CH_2CH_3 (dashed bond) and OH (wedge bond). One is labelled (+) and its mirror image (-).

Both enantiomers rotate plane polarised monochromatic light in opposite directions (clockwise / anticlockwise).

Printed figure: a light source, a polariser and a sample tube, shown twice. Optically active compounds rotate the plane of the polarised light. Optically inactive compounds do not rotate the plane of the polarised light.

Skeletal drawing: two fused six-membered carbon rings with a Cl on one ring, two CH_3 branches on the other ring, and a side carbon carrying OH and CH_3 . The chiral carbons are circled on the original

drawing.

Small enantiomers usually have exactly the same chemical and physical properties.

- Large biologically / shape specific molecules will have drastically different functions if stereochemistry is changed.

Alkanes

Saturated hydrocarbons, C_nH_{2n+2} .

Displayed formula of 2-methylbutane, $CH_3CH_2CH(CH_3)CH_3$.

sp³ hybridisation: all single bonds, no π bond / double bond.

$2s^1, 2p_x^1, 2p_y^1, 2p_z^1$ (each crossed out) become sp^3, sp^3, sp^3, sp^3 , with one electron in each.

Hybridisation: mixing of orbitals to form new hybrid orbitals during bond formation.

Diagram: a carbon atom with four sp^3 orbitals, each holding one electron, each pointing towards an H atom.

Free radical substitution

Cl_2 or Br_2 + UV light.

- Substitute Cl or Br into **any** alkyl chain.

$CH_3CH_2COCOOH + Cl_2 \rightarrow CH_3CHClCOCOOH + HCl$ (Cl_2 + UV light). HCl is the by-product.

Another product drawn: $CHCl_2CHClCOCOOH$.

The number / position of H atoms being substituted is random / multiple products produced.

Mechanism

1. Initiation: free radicals are produced.

1. $Cl-Cl \rightarrow Cl\cdot + Cl\cdot$ (UV light). The $Cl-Cl$ bond breaks and one electron of the bonding pair goes to each Cl atom (one curly arrow from the bond to each Cl).

Free radical: species with an unpaired electron, very reactive.

2. Propagation: radicals attack H atoms.

1. $CH_3CH_2CH_3 + Cl\cdot \rightarrow CH_3CH_2CH_2\cdot + HCl$. A C-H bond on the end carbon breaks. One electron of that bond stays on the carbon, the other pairs with the unpaired electron of $Cl\cdot$ to form H-Cl. A propyl radical is formed.
2. $CH_3CH_2CH_2\cdot + Cl_2 \rightarrow CH_3CH_2CH_2Cl + Cl\cdot$. The unpaired electron on the carbon pairs with one electron of the $Cl-Cl$ bond to form a C-Cl bond. The other electron of the $Cl-Cl$ bond goes to the second Cl, so $Cl\cdot$ is regenerated.
3. $ClCH_2CH_2CH_3 + Cl\cdot \rightarrow ClCH_2CH_2CH_2\cdot + HCl$. A C-H bond on the carbon at the other end from the Cl breaks. One electron stays on the carbon, the other pairs with the unpaired electron of $Cl\cdot$ to form H-Cl.
4. $ClCH_2CH_2CH_2\cdot + Cl_2 \rightarrow ClCH_2CH_2CH_2Cl + Cl\cdot$. The unpaired electron on the carbon pairs with one electron of the $Cl-Cl$ bond to form a C-Cl bond, and $Cl\cdot$ is regenerated.

3. Termination: free radicals combine randomly.

1. $\text{CH}_3\text{CH}_2\text{CH}_2\cdot + \cdot\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (hexane). The unpaired electrons on the two end carbons pair up to form a new C–C bond, giving a six-carbon chain.
2. $\text{CH}_3\text{CH}_2\text{CH}_2\cdot + \cdot\text{Cl} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$. The unpaired electron on the carbon pairs with the unpaired electron of $\text{Cl}\cdot$ to form a C–Cl bond.

Crude oil

Source of most hydrocarbons.

Printed figure: Fractional Distillation of Crude Oil. Crude oil is heated until it evaporates. The vapour rises up the column and the fractions condense at different levels: the larger hydrocarbons with high boiling points turn back into liquids at the base, and the smaller hydrocarbons rise further up the column. Some hydrocarbons with low boiling points (between 20 °C and 70 °C) remain as gases at the top.

Fraction	Temperature	Use
Refinery gas	20 °C	Bottled gas
Petrol	70 °C	Petrol for vehicles
Naphtha	120 °C	Chemicals
Kerosene	170 °C	Jet fuel, paraffin for lighting and heating
Diesel	270 °C	Diesel fuels
Lubricating oil		Lubricating oils, waxes and polishes
Fuel oil		Fuel for ships, factories and central heating
Bitumen	340 °C	Roads and roofing

Small molecules (top of the column)	Large molecules (bottom of the column)
Low boiling point	High boiling point
Light in colour	Dark in colour
Easy to light	Hard to light
Runny	Thick

Cracking

Zeolites / pumice. Al_2O_3 + temperature > 450 °C.

From	Reagents and conditions	To
Long chain hydrocarbon	Zeolites / pumice, Al_2O_3 , temperature > 450 °C	Smaller chain: alkanes, alkene, hydrogen

Long chain hydrocarbon	Smaller chain products
not very useful	more flammable

big molecules / more van der Waals	less viscous
high melting point / boiling point / viscosity	low melting point / boiling point
low flammability	lesser van der Waals

Structure of Benzene and Alkene

Alkenes

"C=C"

Carbon is sp^2 hybridised.

$2s^1$, $2p_x^1$, $2p_y^1$ (struck through) become sp^2 , sp^2 , sp^2 . $2p_z^1$ is circled and left as it is.

Diagram: one carbon atom with three sp^2 orbitals, each holding one electron, arranged trigonal planar at 120° , and the p orbital above and below the plane.

Ethene, $CH_2=CH_2$, drawn with each carbon labelled sp^2 .

Orbital diagram of ethene:

- sp^2-sp^2 overlap between the two carbon atoms, holding two electrons
- sp^2-s overlap between each carbon and its two H atoms (four in total)
- p-p overlap above and below the plane, forming the π bond

The π bond has high electron charge density. It attracts electrophiles **VERY STRONGLY**.

Benzene

Simplified version / Kekulé structure (don't use this). (1 : 1 ratio is only possible in benzene.)

C_6H_6 : a ring of six carbon atoms, each bonded to one H, drawn with alternating single and double bonds between the carbons.

sp^2 hybridised (all carbon atoms in benzene).

Benzene, C_6H_6 , drawn as an orbital diagram: six carbon atoms in a ring, each bonded to one hydrogen, with a p orbital above and below every carbon overlapping sideways all round the ring. Beside it, benzene drawn as a hexagon of six C atoms, each with one H, and a circle inside the ring.

Hexagonal planar, 120° .

- C-C σ bonds: sp^2-sp^2 overlap.
- C-H σ bonds: sp^2-s overlap.
- π bonds: p-p overlap.

Ring of delocalised π electrons.

Electron density in the π electron cloud is significantly lower compared to an alkene π electron cloud.

Bond	Found in	Bond energy
C-C	alkane	350 kJ/mol

Carbon to carbon bond in benzene (between single and double)	benzene	520 kJ/mol
C=C	alkene	610 kJ/mol

Electrophilic Addition

Ethene, $\text{CH}_2=\text{CH}_2$, drawn with its π bond above and below the C–C bond, reacting with Br_2 .

High electron density π bond strongly polarises Br_2 .

1. A curly arrow starts from the π bond of ethene and goes to the nearer bromine atom, $\text{Br}^{\delta+}$, of the polarised $\text{Br}^{\delta+}-\text{Br}^{\delta-}$ molecule. A second curly arrow starts from the Br–Br bond and goes to $\text{Br}^{\delta-}$. This forms the carbocation $\text{CH}_2\text{Br}-\text{CH}_2^+$ and a bromide ion, Br^- .
2. A curly arrow starts from a lone pair on Br^- and goes to the positively charged carbon. This forms 1,2-dibromoethane, $\text{CH}_2\text{BrCH}_2\text{Br}$.

The same mechanism drawn with displayed formulae:

1. $\text{CH}_2=\text{CH}_2$: a curly arrow from the C=C double bond to $\text{Br}^{\delta+}$ of $\text{Br}^{\delta+}-\text{Br}^{\delta-}$, and a curly arrow from the Br–Br bond to $\text{Br}^{\delta-}$.
2. Carbocation intermediate, $^+\text{CH}_2-\text{CH}_2\text{Br}$: a curly arrow from the lone pair on Br^- to the C^+ .
3. Product: 1,2-dibromoethane, $\text{CH}_2\text{BrCH}_2\text{Br}$.

From	Reagents and conditions	To
Ethene, $\text{CH}_2=\text{CH}_2$	Br_2 . $\text{Br}_2(\text{aq})$ or in an inert solvent (CCl_4), r.t.p., absence of light	1,2-dibromoethane, $\text{CH}_2\text{BrCH}_2\text{Br}$ (also 2-bromoethanol, $\text{CH}_2\text{BrCH}_2\text{OH}$, if aqueous)
Ethene, $\text{CH}_2=\text{CH}_2$	$\text{H}_2\text{O}(\text{g})$. Acid catalyst H_3PO_4 , 60 atm pressure, 300 °C	Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ (the H and the OH added are circled)
Ethene, $\text{CH}_2=\text{CH}_2$	H_2 . Ni / Pt catalyst, 150 °C to 200 °C	Ethane, CH_3CH_3 (the two H atoms added are circled)
Ethene, $\text{CH}_2=\text{CH}_2$	HCl (or HBr, HI). r.t.p.	Halogenoethane, $\text{CH}_3\text{CH}_2\text{X}$. The product drawn is bromoethane, $\text{CH}_3\text{CH}_2\text{Br}$, with the H and the Br added circled

* Test for unsaturated compounds: red/orange Br_2 decolourises.

Unsaturated (smaller), low melting point → saturated (bigger), higher melting point.

(Unsaturated vegetable oil) → (margarine).

Markovnikov's Rule

Unsymmetric alkene → H gets bonded to the C in C=C which is already bonded to more H atoms.
MAJOR PRODUCT.

Propene, $\text{CH}_3\text{CH}=\text{CH}_2$, + HBr gives two products:

- 1-bromopropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (H added to the middle carbon, Br to the end carbon).
- 2-bromopropane, $\text{CH}_3\text{CHBrCH}_3$ (Br added to the middle carbon, H to the end carbon). Major product.

The two possible carbocations:

- $\text{CH}_3\text{CH}_2\text{CH}_2^+$, 1° carbocation.
- $\text{CH}_3\text{CH}^+\text{CH}_3$, 2° carbocation, stable.

Carbocations with more electron donating alkyl chains are more stable as they have a lower charge density.

Carbocation	Structure	Positive charge	Stability
1° carbocation	CH_3CH_2^+ , one CH_3 group (9 electrons) pushing electrons towards C^+	large	less stable
2° carbocation	$(\text{CH}_3)_2\text{CH}^+$, two CH_3 groups (9 electrons each) pushing electrons towards C^+	small	
3° carbocation	$(\text{CH}_3)_3\text{C}^+$, three CH_3 groups (9 electrons each) pushing electrons towards C^+	very small	stable

Less stable $\rightarrow$ stable, from the 1° carbocation to the 3° carbocation.

Electrophilic Substitution

Electrophilic Substitution in Benzene

From	Reagents and conditions	To
Benzene, C_6H_6	Br_2 , AlBr_3 / FeBr_3 catalyst	Bromobenzene, $\text{C}_6\text{H}_5\text{Br}$, + HBr
Benzene, C_6H_6	Cl_2 , AlCl_3 / FeCl_3 catalyst	Chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$, + HCl
Benzene, C_6H_6	Conc. HNO_3 + conc. H_2SO_4 (catalyst), $T = 55^\circ\text{C}$	Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$

Electrophilic Substitution Mechanism

1. Bromination (or chlorination)

Drawn on the orbital diagram of benzene with the catalyst FeBr_3 :

1. A curly arrow starts from the π electron cloud of benzene and goes to $\text{Br}^{\delta+}$ of the $\text{Br}^{\delta+}-\text{Br}^{\delta-}$ molecule. A curly arrow starts from the $\text{Br}-\text{Br}$ bond and goes to $\text{Br}^{\delta-}$, and an arrow goes from $\text{Br}^{\delta-}$ to the Fe of FeBr_3 .
Weak polarisation: the benzene π electron cloud has low charge density and does not repel the bonded electrons very strongly.
2. Intermediate: the ring carries a positive charge (+ drawn inside the ring) and one carbon is bonded to both Br and H. The other ion is $[\text{FeBr}_4]^-$, drawn as Br with a lone pair bonded to FeBr_3 , in brackets with a charge of -1. A curly arrow starts from $[\text{FeBr}_4]^-$ and goes to the H on that carbon, and a curly arrow starts from the $\text{C}-\text{H}$ bond and goes back into the ring.
1. Products: bromobenzene, $\text{C}_6\text{H}_5\text{Br}$, with the ring of delocalised π electrons restored, HBr , and FeBr_3 .

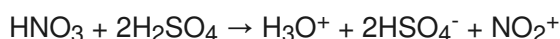
Exam mechanism

1. Benzene, C_6H_6 : a curly arrow from the ring to $Br^{\delta+}$ of $Br^{\delta+}-Br^{\delta-}$, a curly arrow from the $Br-Br$ bond to $Br^{\delta-}$, and an arrow from $Br^{\delta-}$ to the Fe of $FeBr_3$.
2. Intermediate: the ring drawn with a broken circle and a + charge, with one carbon bonded to both Br and H. A curly arrow from the lone pair on $[FeBr_4]^-$ to the H, and a curly arrow from the C-H bond back into the ring.
3. Products: bromobenzene, C_6H_5Br , + HBr, and $FeBr_3$ (regenerated).

Nitration mechanism

Benzene, $C_6H_6 \rightarrow$ nitrobenzene, $C_6H_5NO_2$ (conc. HNO_3 + conc. H_2SO_4 (catalyst), $T = 55\text{ }^{\circ}C$)

Conc. HNO_3 + conc. H_2SO_4 react:



NO_2^+ : nitronium electrophile.

Drawn on the orbital diagram of benzene:

1. A curly arrow starts from the π electron cloud of benzene and goes to NO_2^+ .
2. Intermediate: the ring carries a positive charge (+ drawn inside the ring) and one carbon is bonded to both NO_2 and H. A curly arrow starts from the lone pair on HSO_4^- and goes to the H, and a curly arrow starts from the C-H bond and goes back into the ring.
3. Products: nitrobenzene, $C_6H_5NO_2$, with the ring of delocalised π electrons restored, + H_2SO_4 . Catalyst regenerated.

Exam mechanism

1. Benzene, C_6H_6 : a curly arrow from the ring to NO_2^+ .
2. Intermediate: the ring drawn with a broken circle and a + charge, with one carbon bonded to both NO_2 and H. A curly arrow from the lone pair on HSO_4^- to the H, and a curly arrow from the C-H bond back into the ring.
3. Products: nitrobenzene, $C_6H_5NO_2$, + H_2SO_4 .

Electrophilic Substitution (2,4,6 and 3,5 Directing Groups)

Electrophilic Substitution of Benzene Derivatives

2,4(6) directing groups

1. Electrophilic Substitution of Arenes

Arene $\rightarrow$ benzene + alkyl chain.

- Ethylbenzene, $C_6H_5CH_2CH_3$.
- 1,3-dimethylbenzene, $C_6H_4(CH_3)_2$, with the CH_3 groups on carbons 1 and 3.

Printed extract: a benzene ring with a group X attached and positions 2, 3 and 4 numbered, C_6H_5X , + $Y^+ \rightarrow C_6H_4XY + H^+$.

X- groups that direct the incoming Y group to the 2- or 4- positions

X- groups that direct the incoming Y group to the 3- position

$-\text{NH}_2$, $-\text{NHR}$ or $-\text{NR}_2$	$-\text{NO}_2$
$-\text{OH}$ or $-\text{OR}$	$-\text{NH}_3^+$
$-\text{NHCOR}$	$-\text{CN}$
$-\text{CH}_3$, $-\text{alkyl}$	$-\text{CHO}$, $-\text{COR}$
$-\text{Cl}$	$-\text{CO}_2\text{H}$, $-\text{CO}_2\text{R}$

2,4(6) directing groups are electron donating groups.

Higher charge density at positions 2, 4 (6). Electrophiles will be strongly attracted to the 2, 4, 6 positions.

Orbital diagram of propylbenzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$, with positions 2, 4 and 6 of the ring marked. The alkyl chain, $\text{CH}_2-\text{CH}_2-\text{CH}_3$, has a slight electron donating effect towards the ring.

From	Reagents and conditions	To
Methylbenzene, $\text{C}_6\text{H}_5\text{CH}_3$	Br_2 . AlBr_3 / FeBr_3 catalyst	2-bromomethylbenzene and 4-bromomethylbenzene, $\text{CH}_3\text{C}_6\text{H}_4\text{Br}$, + HBr
Methylbenzene, $\text{C}_6\text{H}_5\text{CH}_3$	Cl_2 . AlCl_3 / FeCl_3 catalyst	2-chloromethylbenzene and 4-chloromethylbenzene, $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$ (drawn, not named on the page), + HCl
Methylbenzene, $\text{C}_6\text{H}_5\text{CH}_3$	Conc. HNO_3 + conc. H_2SO_4 (catalyst), $T = 55^\circ\text{C}$	2-methylnitrobenzene and 4-methylnitrobenzene, $\text{CH}_3\text{C}_6\text{H}_4\text{NO}_2$

Electrophilic Substitution of Phenols and Phenylamine

$-\text{OH}$, $-\text{NH}_2$: 2,4,6 directing groups.

- Phenol, $\text{C}_6\text{H}_5\text{OH}$ (not alcohol), with positions 2, 4 and 6 marked. The lone pair on O is drawn moving towards the ring: large electron donating effect.
- Phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, with positions 2, 4 and 6 marked. The lone pair on N is drawn moving towards the ring: large electron donating effect.

* Lone pair on O in the hydroxy group (or N in NH_2) overlaps with benzene's π electron cloud and significantly increases the π electron cloud density.

- Electrophiles (NO_2^+ / Br^+) will be strongly attracted to benzene.
- Faster reaction, milder conditions.

Halogenation

From	Reagents and conditions	To
Phenol, $\text{C}_6\text{H}_5\text{OH}$ (or $-\text{NH}_2$)	3Br_2 . Only $\text{Br}_2(\text{aq})$, no catalyst needed, r.t.p.	2,4,6-tribromophenol, $\text{C}_6\text{H}_2\text{Br}_3\text{OH}$ (or $-\text{NH}_2$), + 3HBr (white ppt formed)
Phenol, $\text{C}_6\text{H}_5\text{OH}$ (or $-\text{NH}_2$)	3Cl_2 . Only $\text{Cl}_2(\text{aq})$, no catalyst needed, r.t.p.	2,4,6-trichlorophenol, $\text{C}_6\text{H}_2\text{Cl}_3\text{OH}$ (or $-\text{NH}_2$), + 3HCl (white ppt formed)

Test for identification of phenols: red/orange $\text{Br}_2(\text{aq})$ decolourises and produces a white ppt.

Nitration, phenol / phenylamine

From	Reagents and conditions	To
Phenol, C_6H_5OH (or $-NH_2$)	Dilute HNO_3 , no catalyst needed	2-nitrophenol and 4-nitrophenol, $HOC_6H_4NO_2$ (or $-NH_2$)
Phenol, C_6H_5OH (or $-NH_2$)	Conc. HNO_3	2,4,6-trinitrophenol, $HOC_6H_2(NO_2)_3$ (or $-NH_2$) (yellow crystalline solid)

3(-5) directing groups

Electron withdrawing groups: NO_2 , CHO , $COOH$, $-NH_3^+$, CN .

Benzaldehyde, C_6H_5CHO , drawn with positions 3 and 5 marked and an arrow showing electrons drawn from the ring towards the CHO group.

Relatively higher electron density at position 3 (and 5).

Overall benzene becomes deactivated, electron density in the benzene π electron cloud is very less, less attraction for electrophiles, slower reactions / higher T / higher conc.

From	Reagents and conditions	To
Nitrobenzene, $C_6H_5NO_2$	Br_2 (ignore condition)	3-bromonitrobenzene, $BrC_6H_4NO_2$
Nitrobenzene, $C_6H_5NO_2$	Conc. HNO_3 (ignore conditions)	1,3-dinitrobenzene, $C_6H_4(NO_2)_2$

Electrophilic Substitution : Alkylation and Acylation

Alkylation

Attach an alkyl chain to benzene.

From	Reagents and conditions	To
Benzene, C_6H_6	2-chloropentane, $CH_3CHClCH_2CH_2CH_3$. $AlCl_3$ catalyst	(Pentan-2-yl)benzene, $C_6H_5CH(CH_3)CH_2CH_2CH_3$, + HCl
Benzene, C_6H_6	2-chloro-2-methylbutane, $(CH_3)_2CClCH_2CH_3$	(2-methylbutan-2-yl)benzene, $C_6H_5C(CH_3)_2CH_2CH_3$, + HCl

In the first reaction a curly arrow starts from the benzene ring and goes to the $C^{\delta+}$ bonded to Cl , and a curly arrow starts from the $C-Cl$ bond and goes to Cl . In the second reaction the carbon bonded to Cl is also marked $\delta+$.

Acylation

Reaction with acyl chloride, $RCOCl$.

From	Reagents and conditions	To
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Benzene, C_6H_6	Propanoyl chloride, CH_3CH_2COCl . $AlCl_3$ catalyst	1-phenylpropan-1-one, $C_6H_5COCH_2CH_3$, + HCl
-------------------	--	--

A curly arrow starts from the benzene ring and goes to the $C^{\delta+}$ of the $COCl$ group, and a curly arrow starts from the $C-Cl$ bond and goes to Cl .

Hydrolysis of Chlorinated Compounds

Hydrolysis of Cl related compounds

Chlorobenzene	Halogenoalkanes	Acyl chloride
C_6H_5Cl	Chloroethane, CH_3CH_2Cl	Propanoyl chloride, CH_3CH_2COCl
	$NaOH(aq)$, heat with reflux	Vigorous reaction even with cold water. White fumes of $HCl(g)$

No hydrolysis → strong hydrolysis, from chlorobenzene to acyl chloride.

No Hydrolysis of Chlorobenzene

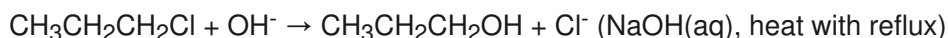
Chlorobenzene, C_6H_5Cl , drawn with the lone pairs on Cl and one lone pair overlapping with the ring. An OH^- ion and a water molecule ($O^{\delta-}$) are shown approaching and being repelled.

Lone pair on Cl overlaps with benzene's π electron cloud, which increases the strength of the $C-Cl$ bond, so the high charge density electron cloud repels OH^- ions / nucleophiles.

Negative ion is repelled by the high charge density π electron cloud.

Hydrolysis of Halogenoalkanes

1. Primary halogenoalkane, S_N2 → rate would depend on both reactants.



- 1-chloropropane, $CH_3CH_2CH_2Cl$, with the $C-Cl$ bond polarised $C^{\delta+}-Cl^{\delta-}$. A curly arrow starts from the lone pair on HO^- (nucleophile; also $:CN^-$, $:NH_3$) and goes to $C^{\delta+}$. A curly arrow starts from the $C-Cl$ bond and goes to Cl . This gives the transition state, in which the HO to C bond is partly formed and the C to Cl bond is partly broken (both drawn as dotted lines), with a curly arrow from the C to Cl dotted bond to Cl .
- Products: propan-1-ol, $CH_3CH_2CH_2OH$, + $:Cl^-$.

One step mechanism.

2. Tertiary halogenoalkane, S_N1



2 step mechanism:

- Step 1: 2-chloro-2-methylbutane, $CH_3CH_2C(CH_3)_2Cl$, with the $C-Cl$ bond polarised $C^{\delta+}-Cl^{\delta-}$. A curly arrow starts from the $C-Cl$ bond and goes to Cl . This forms the tertiary carbocation $CH_3CH_2C^+(CH_3)_2$ and $:Cl^-$.
- Step 2: a curly arrow starts from the lone pair on $:OH^-$ and goes to the C^+ . This forms 2-methylbutan-2-ol, $CH_3CH_2C(CH_3)_2OH$, with $:Cl^-$.

Easier to form a tertiary carbocation. More electron donating alkyl chains lower the positive charge density.

Strong Hydrolysis of Acyl chlorides

Propanoyl chloride, $\text{CH}_3\text{CH}_2\text{COCl}$, drawn with $\text{C}^{\delta+}$, $\text{O}^{\delta-}$ and $\text{Cl}^{\delta-}$, and a water molecule, H_2O , with a curly arrow from the lone pair on its O to the $\text{C}^{\delta+}$.

C in acyl chloride is attached to two very electronegative elements, oxygen and chlorine. So $\delta+$ charge density is very high. Nucleophiles, H_2O , are very strongly attracted.

$\text{CH}_3\text{CH}_2\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{HCl}$ (vigorous reaction even with cold water; white fumes of HCl)

Addition-Elimination Mechanism (Nucleophilic)

1. Propanoyl chloride, $\text{CH}_3\text{CH}_2\text{COCl}$, with $\text{C}^{\delta+}$, $\text{O}^{\delta-}$ and $\text{Cl}^{\delta-}$. A curly arrow starts from the lone pair on the O of H_2O (nucleophile) and goes to $\text{C}^{\delta+}$. A curly arrow starts from the $\text{C}=\text{O}$ double bond and goes to $\text{O}^{\delta-}$.
2. Intermediate: $\text{CH}_3\text{CH}_2\text{C}(\text{O}^-)(\text{Cl})(\text{O}^+\text{H}_2)$, the carbon bonded to O^- , to Cl and to the oxygen of the water molecule, which now carries a positive charge. A curly arrow starts from the lone pair on O^- and goes back to the $\text{C}-\text{O}$ bond to reform $\text{C}=\text{O}$. A curly arrow starts from the $\text{C}-\text{Cl}$ bond and goes to $\text{Cl}^{\delta-}$.
3. $\text{CH}_3\text{CH}_2\text{C}(=\text{O})-\text{O}^+\text{H}_2$ and $:\text{Cl}^-$. A curly arrow starts from the lone pair on $:\text{Cl}^-$ and goes to one H on the O^+ . A curly arrow starts from that $\text{O}-\text{H}$ bond and goes to O^+ .
4. Products: propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, and $\text{HCl}(\text{g})$.

Comparison of Weak Acids

Weak Acids

All organic acids are weak acids (partially ionise, produce fewer H^+ ions).

In order, from weakest acid to stronger acid:

1. alcohol, $\text{CH}_3\text{CH}_2\text{OH}$ (weakest acid)
2. water, H_2O
3. phenol, $\text{C}_6\text{H}_5\text{OH}$
4. carboxylic acid, $\text{CH}_3\text{CH}_2\text{COOH}$ (stronger acid)

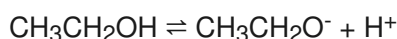
Type of reaction	Reagent	Alcohol, $\text{CH}_3\text{CH}_2\text{OH}$ (weak acid)	Phenol, $\text{C}_6\text{H}_5\text{OH}$	Carboxylic acid, $\text{CH}_3\text{CH}_2\text{COOH}$ (strongest acid)
Redox	Reactive metal, Na	Very slow reaction. $\text{CH}_3\text{CH}_2\text{O}^-\text{Na}^+ + \text{H}_2$	Sodium phenoxide, $\text{C}_6\text{H}_5\text{O}^-\text{Na}^+ + \text{H}_2$	$\text{CH}_3\text{CH}_2\text{COO}^-\text{Na}^+ + \text{H}_2$
Acid, base reactions	Strong base, NaOH	No reaction	Sodium phenoxide, $\text{C}_6\text{H}_5\text{O}^-\text{Na}^+ + \text{H}_2\text{O}$	$\text{CH}_3\text{CH}_2\text{COO}^-\text{Na}^+ + \text{H}_2\text{O}$
Acid, base reactions	Weak base, Na_2CO_3	No reaction	No reaction	$\text{CH}_3\text{CH}_2\text{COO}^-\text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2$

Acid, base reactions	Weak base, NH_3	No reaction	No reaction	$\text{CH}_3\text{CH}_2\text{COO}^-\text{NH}_4^+$
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Explaining acid strength

Alcohols are the weakest of the weak acids.

Ionises even less than water (water produces $1 \times 10^{-7} \text{ mol/dm}^3 \text{ H}^+$ ions).

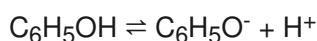


In the ethoxide ion, $\text{CH}_3\text{CH}_2\text{O}^-$: electron donating alkyl chain, large negative charge density on the oxygen.

The alkyl chain has an electron donating effect which increases the charge density on the $\text{CH}_3\text{CH}_2\text{O}^-$ ion, making it unstable. Stronger attraction for H^+ ions, less dissociation, O-H bond strength increases.

Phenols are slightly stronger acids compared to alcohols.

They can react with Na (reactive metal) and NaOH (strong bases).



In the phenoxide ion, $\text{C}_6\text{H}_5\text{O}^-$: a lone pair on the oxygen is drawn moving into the benzene ring. Lesser charge density on the oxygen, less attraction for H^+ . Relatively weaker conjugate base.

Lone pairs on the phenoxide ion, $\text{C}_6\text{H}_5\text{O}^-$, overlap with benzene's pi electron cloud. Charge density on the phenoxide ion decreases, making it more stable (less attraction for H^+ , the O-H bond weakens), hence more dissociation.

Comparison of acid strength within phenols

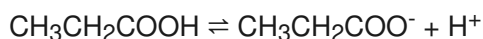
Phenol, $\text{C}_6\text{H}_5\text{OH}$, versus 4-propylphenol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OH}$.

Phenol	Ion formed	Notes
phenol, $\text{C}_6\text{H}_5\text{OH}$	$\text{C}_6\text{H}_5\text{O}^- + \text{H}^+$	
4-propylphenol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{O}^- + \text{H}^+$	The $\text{CH}_3\text{CH}_2\text{CH}_2$ group has an electron donating effect. Negative charge density is higher, unstable, stronger O-H bond, dissociates less / weaker.

Phenol, $\text{C}_6\text{H}_5\text{OH}$, versus 4-nitrophenol, shown as its ion $\text{O}_2\text{NC}_6\text{H}_4\text{O}^- + \text{H}^+$.

The O_2N group is electron withdrawing. Negative charge density is lesser, more stable, less attraction for H^+ ions, O-H bond becomes weaker.

Why are carboxylic acids (relatively) the strongest acid



The negative charge density on the O^- is small. An arrow is drawn from the O^- towards the $\text{C}=\text{O}$, and the ion is then drawn as $\text{CH}_3\text{CH}_2\text{COO}^-$ with the negative charge spread over both oxygens.

In carboxylic acids, a highly electronegative oxygen in $\text{C}=\text{O}$ has a strong electron withdrawing effect, which decreases the negative charge density in the RCOO^- ion, making it stable. Less attraction for H^+ ions, O-H bond strength decreases, more dissociation / relatively strong acid.

Alkyl chain length → carboxylic acid strength

Ethanoate ion, $\text{CH}_3\text{COO}^- + \text{H}^+$: the CH_3 group donates electrons.

Butanoate ion, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^- + \text{H}^+$: electron donating effect of the longer chain, larger charge density on the O^- , more attraction for H^+ .

Large electron donating effect in bigger alkyl chains.

Higher negative charge density in RCOO^- , making it unstable. More attraction for H^+ ions, stronger O-H bond, less ionisation → **weaker acid**.

Cl substituted carboxylic acid

More Cl, stronger acid (going down the list):

1. Ethanoate ion, $\text{CH}_3\text{COO}^- + \text{H}^+$.
2. Chloroethanoate ion, $\text{ClCH}_2\text{COO}^- + \text{H}^+$: Cl pulls electrons away from the COO^- , lesser charge density, less attraction for H^+ .
3. Trichloroethanoate ion, $\text{CCl}_3\text{COO}^- + \text{H}^+$: even lesser charge density, even less attraction for H^+ .

Cl has an electron withdrawing effect. RCOO^- charge density decreases, becomes more stable, O-H is weaker, less attraction for H^+ → stronger acid, more ionisation.

Position of Cl

3-chloropropanoate ion, $\text{ClCH}_2\text{CH}_2\text{COO}^- + \text{H}^+$: the Cl is further from the COO^- .

2-chloropropanoate ion, $\text{CH}_3\text{CHClCOO}^- + \text{H}^+$: smaller charge density on the O^- . **Stronger acid**.

Cl is closer, more electron withdrawing effect. RCOO^- becomes more stable, lower charge density, less attraction for H^+ . O-H bond becomes weaker → more dissociation.

Comparison of Weak Bases

Strength of bases (all are weak)

Nitrogen bases accept H^+ ions.

$\text{NH}_3 + \text{H}^+ \rightarrow [\text{NH}_4]^+$ (the lone pair on N forms a dative bond to the H^+)

In order, from not basic to strongly basic:

1. amides, for example $\text{CH}_3\text{CONHCH}_3$ (not basic)
2. phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$
3. ammonia, NH_3
4. ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$ (strongly basic)

Compound	Basicity	Explanation
Amides, $\text{CH}_3\text{CONHCH}_3$	Not basic	The lone pair on N in the amide overlaps with the π electron cloud in C=O , as oxygen has a strong electron withdrawing effect. The lone pair on N is not available to accept H^+ ions.

Phenylamine, $C_6H_5NH_2$	Weakly basic	The lone pair on N overlaps with benzene's π electron cloud and its charge density decreases. Hence weaker attraction for H^+ ions, weakly basic. $C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3^+$ (phenylammonium ion) + Cl^-
Ethylamine, $CH_3CH_2NH_2$	Strongly basic	The alkyl chain has an electron donating effect. Charge density on the lone pair on N increases, more attraction for H^+ ions, stronger base.

All Redox Reactions (Including AS)

Redox Reactions

Hydrogenation of benzene

benzene, $C_6H_6 \rightarrow$ cyclohexane, C_6H_{12} ($H_2(g)$, Ni / Pt catalyst, $150^\circ C$)

Oxidation of Arenes

1-ethyl-3-methylbenzene, $CH_3C_6H_4CH_2CH_3 \rightarrow$ benzene-1,3-dicarboxylic acid, $HOOC C_6H_4 COOH$
 ($KMnO_4 / H^+$ + heat, reflux)

Oxidation of Alkenes

1. Mild oxidation

propene, $CH_3CH=CH_2 \rightarrow$ propane-1,2-diol, $CH_3CH(OH)CH_2OH$ (cold / dilute $KMnO_4$)

2. Strong oxidation (hot, concentrated, acidified $KMnO_4$)

The $C=C$ bond is broken.

	From	To
(a)	$=CH_2$	$CO_2 + H_2O$
(b)	$=CHR$	$RCHO$ (aldehyde) $\rightarrow$ $RCOOH$ (carboxylic acid)
(c)	$=CR_2$	$R_2C=O$

Examples:

- 2-methylbut-2-ene, $(CH_3)_2C=CHCH_3 \rightarrow$ propanone, $(CH_3)_2C=O$, and ethanoic acid, CH_3COOH .
- 1-methylcyclohexene $\rightarrow$ the ring opens at the $C=C$ to give 6-oxoheptanoic acid, $CH_3CO(CH_2)_4COOH$.
- 3,4-dimethylpenta-1,3-diene, $(CH_3)_2C=C(CH_3)CH=CH_2$ (as read from the sketch) $\rightarrow$ propanone, $(CH_3)_2C=O$, and 2-oxopropanoic acid, $CH_3COCOOH$, and $CO_2 + H_2O$.

Primary Alcohol $\rightarrow$ aldehyde $\rightarrow$ carboxylic acid

Primary alcohol (propan-1-ol, $CH_3CH_2CH_2OH$) $\rightarrow$ oxidation $\rightarrow$ aldehyde $\rightarrow$ oxidation $\rightarrow$ carboxylic acid.

From	Reagents and conditions	To	Type of reaction
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Primary alcohol	1. $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$, reflux, heat. Orange to green. 2. $\text{KMnO}_4 / \text{H}^+$, reflux, heat. Purple to colourless.	Aldehyde	Oxidation
Aldehyde	1. $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$, reflux, heat. Orange to green. 2. $\text{KMnO}_4 / \text{H}^+$, reflux, heat. Purple to colourless. 3. Tollens' reagent, $[\text{Ag}(\text{NH}_3)_2]^+$. Silver mirror / black ppt. 4. Fehling's reagent + heat. $\text{Cu}^{2+} \rightarrow \text{Cu}_2\text{O}$, brick red ppt of copper(I) oxide.	Carboxylic acid	Oxidation

To stop at the aldehyde and prevent further reaction: not reflux $\rightarrow$ distillation.

Aldehydes have much lower melting and boiling points as they don't form hydrogen bonds, and they evaporate easily.

Only two carboxylic acids are oxidised.

Most carboxylic acids are resistant to oxidation.

1. Methanoic acid, $\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$, with any of:

1. $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+ / \text{reflux}$
2. $\text{KMnO}_4 / \text{H}^+ / \text{reflux}$
3. Tollens' reagent, $[\text{Ag}(\text{NH}_3)_2]^+$
4. Fehling's solution + heat

2. Ethanedioic acid (oxalic acid), $\text{HOOC-COOH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ ($\text{KMnO}_4 / \text{H}^+$, reflux)

Secondary Alcohols $\rightarrow$ Ketones

From	Reagents and conditions	To	Type of reaction
Secondary alcohol, R_2CHOH	1. $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$, reflux, heat. Orange to green. 2. $\text{KMnO}_4 / \text{H}^+$, reflux, heat. Purple to colourless.	Ketone, $\text{R}_2\text{C=O}$	Oxidation

Tertiary alcohols

No oxidation.

Example

1-(hydroxymethyl)cyclohexane-1,3-diol (a cyclohexane ring where carbon 1 carries an OH and a CH_2OH group, and carbon 3 carries an OH) $\rightarrow$ 1-hydroxy-3-oxocyclohexane-1-carboxylic acid (acidified $\text{K}_2\text{Cr}_2\text{O}_7$, reflux)

- The OH on carbon 1 of the ring is a tertiary alcohol: no change.
- The CH_2OH group is a primary alcohol: becomes a carboxylic acid, COOH .
- The OH on carbon 3 of the ring is a secondary alcohol: becomes a ketone, C=O .

Reduction

From	Reagents and conditions	To
Carboxylic acid	LiAlH_4 (lithium hydrido aluminate)	Aldehyde
Aldehyde	LiAlH_4 / NaBH_4	Primary alcohol
Ketones	LiAlH_4 / NaBH_4	Secondary alcohol

Reduction of Nitrobenzene

nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2 \rightarrow$ phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$ (Sn + conc. HCl + heat)

Reduction of Amides

amide, $\text{RCONHR} \rightarrow$ amine, RCH_2NHR (LiAlH_4). The C=O becomes CH_2 : loses O, gains 2H.

Reduction of nitriles

nitrile, $\text{RC}\equiv\text{N} \rightarrow$ alkyl amine, RCH_2NH_2 (H_2 + Ni catalyst, 150°C , or LiAlH_4)

Dye Stuff : Azo Dyes

Dye Stuff / Azo Dyes

"Paints" $\rightarrow$ azo dyes are very stable.

From	Reagents and conditions	To	Type of reaction
benzene, C_6H_6	conc. HNO_3 , conc. H_2SO_4 , $T = 55^\circ\text{C}$	nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$	Electrophilic substitution
nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$	Sn + conc. HCl + heat	phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$	
phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$	$\text{NaNO}_2 + \text{HCl}$ (HNO_2), $T < 10^\circ\text{C}$	diazonium ion, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ ($\text{C}_6\text{H}_5-\text{N}\equiv\text{N Cl}^-$), an electrophile, very unstable	
diazonium ion, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$	hydrolysis, decomposes if $T > 10^\circ\text{C}$, H_2O	phenol, $\text{C}_6\text{H}_5\text{OH} + \text{N}_2$	

Azo dye formation

The diazonium ion electrophile attacks an activated benzene (benzene + OH / NH_2 , electron donating).

1. The lone pair on the oxygen of phenol, $\text{C}_6\text{H}_5\text{OH}$, is drawn into the ring, so the ring is activated (shown shaded as electron rich).
2. A curly arrow goes from the activated ring of phenol to the end nitrogen of the diazonium ion, $\text{C}_6\text{H}_5-\text{N}^+\equiv\text{N}$. Conditions: $T < 10^\circ\text{C}$, NaOH(aq) .
3. The product is $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{OH}$ (4-hydroxyazobenzene, with the OH opposite the $\text{N}=\text{N}$). The $-\text{N}=\text{N}-$ is the azo group.

Just as an Example

Printed chart of dye structures, with the --N=N-- azo group highlighted in each azo dye:

Dye	Type
Acid Red 27	azo dye
Disperse Red 60	anthraquinone dye
Direct Blue 86	phthalocyanine dye
Disperse Blue 60	anthraquinone dye
Acid Orange 7	azo dye
Direct Green 1	azo dye

Find original reactants

Acid Orange 7 (azo dye): $\text{Na}^+ \text{ } ^-\text{O}_3\text{S--C}_6\text{H}_4\text{--N=N--C}_{10}\text{H}_6\text{--OH}$, a benzene ring carrying a sodium sulfonate group, joined through the azo group to a naphthalene ring system that carries an OH next to the azo group.

$\text{--N}^+\equiv\text{N}$, that comes from the inactive benzene.

The molecule is split by a line drawn next to the N=N , on the side of the ring that carries the OH. The two original reactants are:

- the diazonium ion, $\text{Na}^+ \text{ } ^-\text{O--S(=O)}_2\text{--C}_6\text{H}_4\text{--N}^+\equiv\text{N}$ (a benzene ring with the sodium sulfonate group opposite the diazonium group)
- naphthalen-2-ol, $\text{C}_{10}\text{H}_7\text{OH}$ (two fused benzene rings with an OH group)

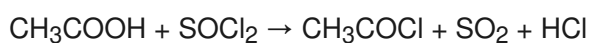
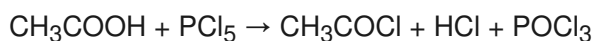
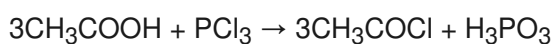
Formation of Acyl Chlorides

Acyl chlorides

R--C(=O)--Cl , written RCOCl .

Formation

From	Reagents and conditions	To
carboxylic acid, R--C(=O)--OH	PCl_3 + heat SOCl_2 + heat PCl_5 (+ heat)	acyl chloride, R--C(=O)--Cl

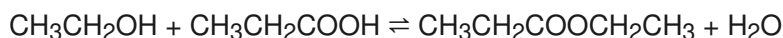


Esters & Amides

Formation of Esters

1. Alcohol + carboxylic acid $\rightleftharpoons$ ester + H_2O

- Forward reaction: addition-elimination, "condensation". Conc. H_2SO_4 + reflux.
- Reverse reaction: dilute H_2SO_4 / $NaOH$, reflux (acid or alkaline hydrolysis).



1. A curly arrow goes from the lone pair on the oxygen of the alcohol, CH_3CH_2OH , to the δ^+ carbon of the $C=O$ in the acid, CH_3CH_2COOH .
2. The OH of the acid and the H of the alcohol's OH are crossed out. They leave as H_2O .
3. The product is $CH_3-CH_2-C(=O)-O-CH_2-CH_3 + H_2O$. The $-C(=O)-O-$ is the ester link.

Naming: the $CH_3CH_2C(=O)-$ part is "propanoate" and the $-CH_2CH_3$ part is "ethyl", so the ester is ethyl propanoate.

A diol with two carboxylic acids:

1. Reactants: carboxylic acid, 2-methylpropanoic acid, $(CH_3)_2CHCOOH$, on each side of a diol, ethane-1,2-diol, $HOCH_2CH_2OH$.
2. The OH of each carboxylic acid and the H of each OH on the diol are crossed out.
3. Product: $(CH_3)_2CHCOOCH_2CH_2OOCCH(CH_3)_2$, with an ester group at each end of the diol.

Forming a ring:

1. Two molecules of 4-hydroxybutanoic acid, $HOCH_2CH_2CH_2COOH$, are drawn facing each other, the OH end of one next to the $COOH$ end of the other.
2. At both places the OH of the $COOH$ and the H of the alcohol OH are crossed out.
3. Product: a ring containing two ester groups, $-O-CH_2CH_2CH_2-C(=O)-O-CH_2CH_2CH_2-C(=O)-$ joined end to end (a cyclic diester).

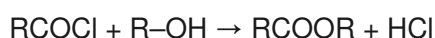
Alkaline hydrolysis of Esters produces soaps

The ester $R-C(=O)-O-R$ is split between the C of the $C=O$ and the O :

- $R-C(=O)-OH$, which reacts with alkali to give $R-C(=O)-O^- Na^+$
- $R-OH$

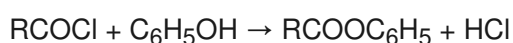
Acyl chlorides + alcohols $\rightarrow$ Ester + HCl

Fast vigorous reaction, no conditions needed.



1. A curly arrow goes from the lone pair on the oxygen (δ^-) of the alcohol, $H-O-R$, to the δ^+ carbon of the $C=O$ in the acyl chloride, $R-C(=O)-Cl$.
2. The Cl of the acyl chloride and the H of the alcohol are circled together. They leave as HCl .
3. The product is the ester $R-C(=O)-O-R + HCl$.

Phenols **only** form Esters with acyl chlorides

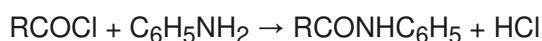


1. The carbon of the $C=O$ in the acyl chloride, $R-C(=O)-Cl$, is δ^+ with a high charge density.

2. A curly arrow goes from the lone pair on the oxygen of phenol, $\text{H}-\text{O}-\text{C}_6\text{H}_5$, to this δ^+ carbon. A second small arrow shows the lone pair on the oxygen moving towards the benzene ring.
3. The product is the ester $\text{R}-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_5 + \text{HCl}$.

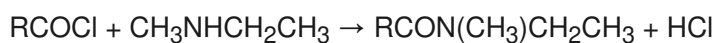
The lone pair on phenol overlaps with the benzene pi electron cloud, unavailable for ester formation with carboxylic acid.

Acyl chlorides form amides with phenylamine



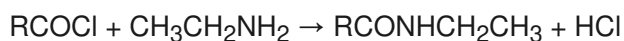
1. A curly arrow goes from the lone pair on the nitrogen of phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, to the δ^+ carbon of the $\text{C}=\text{O}$ in the acyl chloride, $\text{R}-\text{C}(=\text{O})-\text{Cl}$. A second small arrow shows the lone pair on the nitrogen moving towards the benzene ring.
2. The Cl of the acyl chloride and one H on the nitrogen are circled together. They leave as HCl.
3. The product is $\text{R}-\text{C}(=\text{O})-\text{N}(\text{H})-\text{C}_6\text{H}_5 + \text{HCl}$. The $-\text{C}(=\text{O})-\text{N}(\text{H})-$ group is boxed and labelled amide.

With a secondary amine:



1. A curly arrow goes from the lone pair on the nitrogen of the secondary amine, $\text{CH}_3-\text{NH}-\text{CH}_2-\text{CH}_3$, to the δ^+ carbon of the $\text{C}=\text{O}$ in $\text{R}-\text{C}(=\text{O})-\text{Cl}$.
2. The Cl and the H on the nitrogen are circled together. They leave as HCl.
3. The product is $\text{R}-\text{C}(=\text{O})-\text{N}(\text{CH}_3)-\text{CH}_2-\text{CH}_3 + \text{HCl}$.

With a primary amine:



1. A curly arrow goes from the lone pair on the nitrogen of the primary amine, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_3$, to the δ^+ carbon of the $\text{C}=\text{O}$ in $\text{R}-\text{C}(=\text{O})-\text{Cl}$.
2. The Cl and one H on the nitrogen are circled together. They leave as HCl.
3. The product is $\text{R}-\text{C}(=\text{O})-\text{N}(\text{H})-\text{CH}_2-\text{CH}_3 + \text{HCl}$.

Acid / alkaline hydrolysis of amides

The amide $\text{R}-\text{C}(=\text{O})-\text{N}(\text{H})-\text{R}$ is split between the C of the $\text{C}=\text{O}$ and the N:

- $\text{R}-\text{C}(=\text{O})-\text{OH}$ (alkaline hydrolysis: $\text{R}-\text{C}(=\text{O})-\text{O}^- \text{Na}^+$)
- $\text{H}-\text{N}(\text{H})-\text{R}$, which is RNH_2 (acid hydrolysis $\rightarrow \text{RNH}_3^+$)

Amino Acids, Polymerisation

Amino Acids

Amino acids (monomer) $\rightarrow$ Protein (polymer)

General structure: $\text{H}_2\text{N}-\text{CH}(\text{R})-\text{COOH}$. The NH_2 group and the COOH group are circled. Only the R is different.

- alanine, $\text{H}_2\text{N}-\text{CH}(\text{CH}_3)-\text{COOH}$

- valine, $\text{H}_2\text{N}-\text{CH}(\text{CH}(\text{CH}_3)_2)-\text{COOH}$
- $\text{H}_2\text{N}-\text{CH}(\text{CH}_2\text{COOH})-\text{COOH}$ (not named on the page; this is aspartic acid)
- $\text{H}_2\text{N}-\text{CH}((\text{CH}_2)_4\text{NH}_2)-\text{COOH}$ (not named on the page; this is lysine)

Primary Structure / simple polypeptide (Condensation Polymers)

1. Four amino acids are drawn in a row: alanine, $\text{H}_2\text{N}-\text{CH}(\text{CH}_3)-\text{COOH}$, then valine, $\text{H}_2\text{N}-\text{CH}(\text{CH}(\text{CH}_3)_2)-\text{COOH}$, then $\text{H}_2\text{N}-\text{CH}(\text{CH}_2\text{COOH})-\text{COOH}$, then $\text{H}_2\text{N}-\text{CH}((\text{CH}_2)_4\text{NH}_2)-\text{COOH}$.
2. Between each pair, the OH of one COOH group and an H of the next NH₂ group are circled together.
3. Condensation polymer: the circled atoms are removed and the C of each C=O joins to the N of the next amino acid, giving $\text{H}_2\text{N}-\text{CH}(\text{CH}_3)-\text{C}(=\text{O})-\text{N}(\text{H})-\text{CH}(\text{CH}(\text{CH}_3)_2)-\text{C}(=\text{O})-\text{N}(\text{H})-\text{CH}(\text{CH}_2\text{COOH})-\text{C}(=\text{O})-\text{N}(\text{H})-\text{CH}((\text{CH}_2)_4\text{NH}_2)-\text{COOH}$.

$-\text{C}(=\text{O})-\text{N}(\text{H})-$ is the amide / peptide link.

Condensation Polymerisation

1. Polyester

From a diacyl chloride and a diol (□ stands for the rest of each molecule):

1. The monomers are drawn alternately: diacyl chloride, $\text{Cl}-\text{C}(=\text{O})-\square-\text{C}(=\text{O})-\text{Cl}$, then diol, $\text{HO}-\square-\text{OH}$, then diacyl chloride, then diol.
2. A curly arrow goes from the lone pair on an oxygen of the diol to the δ^+ carbon of a C=O in the diacyl chloride.
3. Each Cl of the diacyl chloride and each H of the diol's OH groups are crossed out.
4. Condensation gives the chain $-\text{C}(=\text{O})-\square-\text{C}(=\text{O})-\text{O}-\square-\text{O}-\text{C}(=\text{O})-\square-\text{C}(=\text{O})-\text{O}-\square-\text{O}-$ + HCl + HCl + HCl. The $-\text{C}(=\text{O})-\text{O}-$ group (boxed) is the ester linkage.

From a dicarboxylic acid and a diol:

1. The monomers are drawn alternately: dicarboxylic acid, $\text{HO}-\text{C}(=\text{O})-\square-\text{C}(=\text{O})-\text{OH}$, then diol, $\text{HO}-\square-\text{OH}$, then dicarboxylic acid, then diol.
2. Each OH of the dicarboxylic acid and each H of the diol's OH groups are crossed out.
3. Condensation gives the chain $-\text{C}(=\text{O})-\square-\text{C}(=\text{O})-\text{O}-\square-\text{O}-\text{C}(=\text{O})-\square-\text{C}(=\text{O})-\text{O}-\square-\text{O}-$ + H₂O + H₂O + H₂O. The $-\text{C}(=\text{O})-\text{O}-$ group (boxed) is the ester linkage.

Repeat unit: $-\text{C}(=\text{O})-\text{O}-\square-\text{O}-\text{C}(=\text{O})-\square-$

Examples

- Terylene, fabric, clothing
- natural polyesters, fats

Printed diagram of a fat: glycerol joined through three $-\text{O}-\text{C}(=\text{O})-$ groups to three long fatty acid chains, one of which contains a C=C double bond. Key: glycerol, carboxyl group, fatty acid, double bond.

2. Polyamide

1. The monomers are drawn alternately: diacyl chloride (or dicarboxylic acid), $\text{Cl}-\text{C}(=\text{O})-\square-\text{C}(=\text{O})-\text{Cl}$, then diamine, $\text{H}_2\text{N}-\square-\text{NH}_2$, then diacyl chloride, then diamine.
2. A curly arrow goes from the lone pair on a nitrogen of the diamine to the δ^+ carbon of a $\text{C}=\text{O}$ in the diacyl chloride.
3. Each Cl of the diacyl chloride and one H on each nitrogen of the diamine are crossed out.
4. Condensation / addition-elimination gives the chain $-\text{C}(=\text{O})-\square-\text{C}(=\text{O})-\text{N}(\text{H})-\square-\text{N}(\text{H})-\text{C}(=\text{O})-\square-\text{C}(=\text{O})-\text{N}(\text{H})-\square-\text{N}(\text{H})-$ + $\text{HCl} + \text{HCl} + \text{HCl}$. The $-\text{C}(=\text{O})-\text{N}(\text{H})-$ group (boxed) is the amide linkage.

Repeat unit: $-\text{[N}(\text{H})-\text{C}(=\text{O})-\square-\text{C}(=\text{O})-\text{N}(\text{H})-\square]-_n$

Examples

Kevlar, Nylon, natural proteins.

Addition Polymers

monomer = alkene

Propene, $\text{CH}_3-\text{CH}=\text{CH}_2$. The $\text{C}=\text{C}$ is boxed. The CH_3 group and the H at the two ends are circled, with arrows showing them redrawn below the $\text{C}=\text{C}$ carbons.

1. Five propene molecules are drawn side by side, each as $\text{C}(\text{H})(\text{CH}_3)=\text{C}(\text{H})(\text{H})$ with the CH_3 and one H drawn below the $\text{C}=\text{C}$.
2. Addition: each $\text{C}=\text{C}$ becomes $\text{C}-\text{C}$ and the molecules join to each other, giving the chain $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-$, polypropene.

Repeat unit: $-\text{[CH}(\text{CH}_3)-\text{CH}_2]-_n$

Addition Polymers vs Condensation Polymers

Addition Polymers	Condensation Polymers
inert, non biodegradable	very polar linkages: $-\text{C}(=\text{O})-\text{O}-$ and $-\text{C}(=\text{O})-\text{N}(\text{H})-$, with the C δ^+ , the O of the $\text{C}=\text{O}$ δ^- and the N δ^-
PVC, Polyethene, Polypropene	very reactive, hydrolyse easily
linkage $\rightarrow$ non-polar carbon chain, very stable and unreactive	heat / boil with dilute acid or dilute alkali

Checked by Mega Lecture

Typed from the handwritten original, page by page. Drawn structures are given as names and formulae, and mechanisms as numbered steps; names for structures the original leaves unnamed were added by us. Seven slips of the pen were put right: the product of ethene with a hydrogen halide is written as a halogenoethane (page 14); the 3-directing group is typed as $-\text{NH}_3^+$ (page 18); chlorination of phenol gives 3HCl (page 19); the acid from hydrolysis is $\text{CH}_3\text{CH}_2\text{COOH}$ (page 23); phenylamine with HCl gives the phenylammonium ion (page 30); Tollens' reagent is $[\text{Ag}(\text{NH}_3)_2]^+$ (page 32); a diazonium ion warmed with water gives phenol and N_2 (page 36); and a diacyl chloride with a diol loses HCl (page 43). Two printed pictures taken from other sources (a crude oil distillation diagram and a chart of commercial dyes) are summarised, not copied. Spotted a mistake? Tell us on WhatsApp: +92 336 780 1123.