



Chapter 10: Organic chemistry – fast facts

10.1 Fundamentals of organic chemistry

Organic chemistry focuses on the chemistry of compounds containing carbon.

- A homologous series is a series of compounds with the same general formula, where each member differs from the successive member by $-\text{CH}_2-$. Members of the same homologous series show a trend in their physical properties and have similar chemical properties.
- Different formulas are used to describe an organic compound:
 - empirical formula is the simplest ratio of atoms present in a molecule
 - molecular formula is the actual number of atoms present in a molecule
 - condensed structural formula gives the minimum information to describe the molecule non-ambiguously
 - full structural formula shows all the bonds in a molecule
 - stereochemical formula shows the 3-dimensional arrangement of the atoms.
 (Note: skeletal formula is not a structural formula as it does not include all the hydrogen atoms.)
- Saturated compounds contain single bonds only, and unsaturated compounds contain double or triple bonds.
- IUPAC nomenclature is used to describe organic compounds.
- Stem: named for the longest carbon chain where:
 - C1 = meth-, C2 = eth-, C3 = prop-, C4 = but-, C5 = pent-, C6 = hex-, C7 = hept-, C8 = oct-
- Suffix used for the functional group ending:
 - ene, -anol, -anal, -anone, -anoic acid, -anoate, -amide, -amine, -anenitrile, -benzene
- Prefix used for substituent groups, using the smallest number to denote the main-chain C atom.
 - methyl-, ethyl-, propyl-, fluoro-, chloro-, bromo-, iodo-, amino-
- The functional group is the reactive part of a molecule. It defines the class of compound e.g. the hydroxyl group defines the class, the alcohols.
- Structural isomers are molecules with the same molecular formula but different structural formulas. They contain atoms attached in a different order, and have distinct physical and chemical properties. Structural isomers can be straight/branched chains or differ in the position or nature of the functional group.
- Primary, secondary, and tertiary carbon atoms are attached to a functional group, and differ in the number of hydrogen atoms to which they are also attached. Primary, secondary, and tertiary compounds e.g. alcohols and haloalkanes, show some different chemical properties.
- Arenes contain the benzene ring. They are known as aromatic compounds. Organic compounds without the benzene ring are known as aliphatic compounds.
- Benzene has distinct properties due to its delocalized pi electrons, which give it an extra stability. It is a planar, non-polar molecule, which does not readily undergo addition reactions despite being highly unsaturated.
- The volatility of organic compounds depends on:
 - the size of the molecule/length of the hydrocarbon chain and
 - the functional group.
- The larger members of a homologous series are less volatile due to stronger London (dispersion) forces.

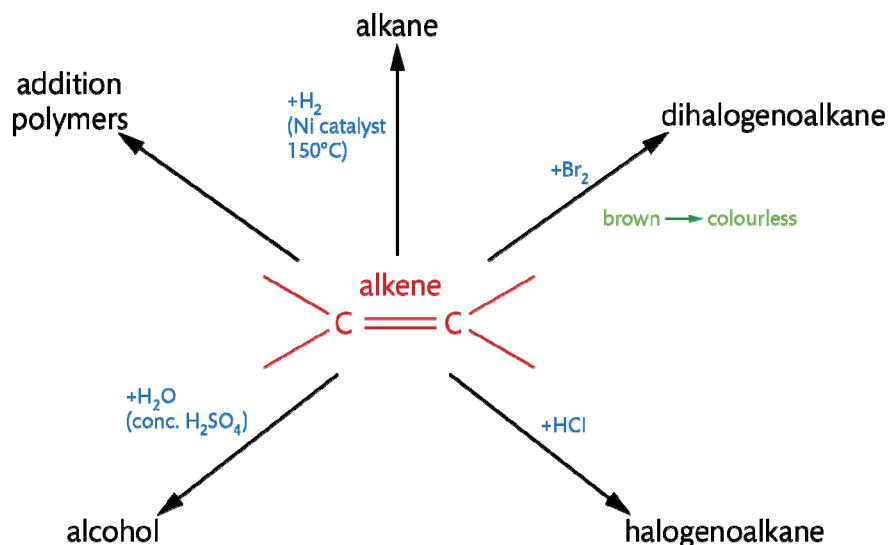


- More polar functional groups decrease the volatility of the compound.

10.2 Functional group chemistry

Structure, bonding and chemical reactions involving functional group interconversions are key strands in organic chemistry.

- Hydrocarbons contain carbon and hydrogen only. Alkanes, alkenes, alkynes, and benzene are hydrocarbons.
- Hydrocarbons undergo combustion and release significant energy. These reactions have high activation energy.
- In excess O_2 , hydrocarbons burn to produce CO_2 and H_2O . In limited O_2 , they undergo incomplete combustion and produce CO or C .
- The products of burning hydrocarbons have harmful effects on the environment and health.
- Alkanes are saturated hydrocarbons. They have low reactivity as the $C-C$ and $C-H$ bonds are strong.
- Alkanes undergo substitution reactions with halogens in UV light. The halogen undergoes photochemical homolytic fission to produce free radicals in the initiation step. The radicals substitute for H in the alkanes in propagation reactions that also produce free radicals. The reaction produces a mixture of substituted products. Termination steps involve two free radicals joining together.
- Alkenes are unsaturated hydrocarbons containing a carbon-carbon double bond. The double bond is the site of reactivity as the pi bond breaks relatively easily, and so alkenes are more reactive than alkanes.
- Alkenes undergo addition reactions, by breaking their double bond.
- Addition reactions of alkenes include:
 - addition of H_2 (hydrogenation) \Rightarrow alkanes
 - addition of halogens \Rightarrow dihalogenoalkane
 - addition of hydrogen halide (hydrohalogenation) \Rightarrow halogenoalkane
 - addition of H_2O (hydration) \Rightarrow alcohol
- Alkenes decolorize bromine water in the dark or light, and this colour change can be used to distinguish between alkanes and alkenes.
- Alkenes undergo addition reactions to form addition polymers by breaking their double bonds. The repeat unit shows the structure of the monomer with open bonds on each side.





- Alcohols are fuels and, like hydrocarbons, yield products that depend on the amount of oxygen available.
- Alcohols differ in their ability to be oxidized. Oxidizing agents include acidified potassium dichromate(VI) or potassium manganate(VII) and the reaction is heated.
 - Primary alcohols are oxidized first to aldehyde, and with prolonged oxidation to carboxylic acid. The aldehyde product can be separated by distillation as it has the lowest boiling point in the mixture. For prolonged oxidation to carboxylic acid, reflux is used. The oxidizing agent changes colour as it is reduced.
 - Secondary alcohols are oxidized to the ketone. The oxidizing agent changes colour as it is reduced.
 - Tertiary alcohols are not oxidized under these conditions. The oxidizing agent does not change colour.
- Alcohols react with carboxylic acids to produce an ester and water. Concentrated sulfuric acid is used as a catalyst in the reaction. It is a condensation/esterification reaction.

$$\text{acid} + \text{alcohol} \rightarrow \text{ester} + \text{water}$$

$$\text{RCOOH} + \text{R}'\text{OH} \rightarrow \text{RCOOR}' + \text{H}_2\text{O}$$
- Halogenoalkanes contain the polar bond C–halogen, and so are more reactive than alkanes.
- Halogenoalkanes are susceptible to attack by nucleophiles at the electron-deficient carbon of the C–halogen bond. Nucleophiles are species that possess a lone pair of electrons, and can also possess a negative charge.
- Halogenoalkanes undergo substitution reactions where the halogen is replaced by a nucleophile.
- Halogenoalkanes react with NaOH(aq) to form an alcohol.

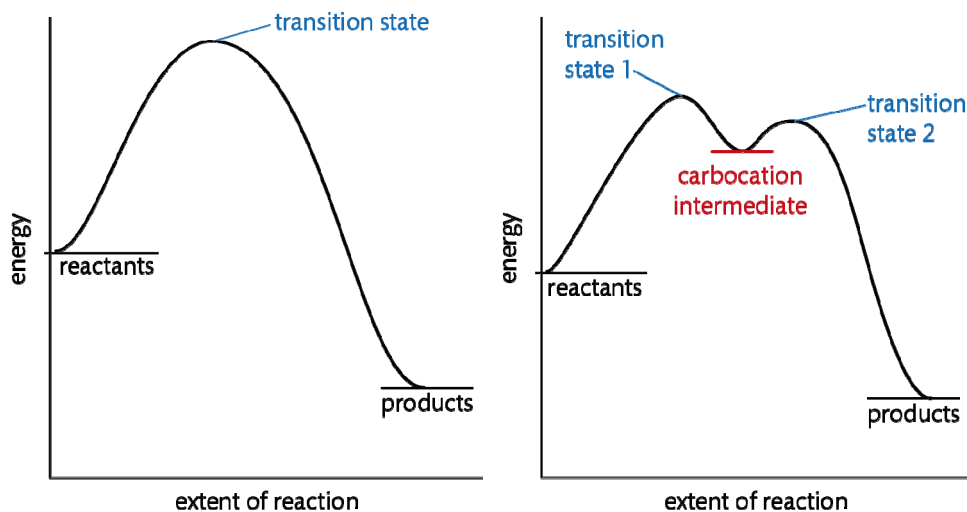
$$\text{e.g. RCl} + \text{NaOH} \rightarrow \text{ROH} + \text{NaCl}$$
- Benzene does not readily undergo addition reactions, but instead undergoes substitution reactions that preserve the stable ring structure. These reactions are carried out by electrophiles, electron-deficient species that are attracted to the electron-dense benzene ring. They are known as electrophilic substitution reactions.

20.1 Types of organic reactions

Key organic reaction types include nucleophilic substitution, electrophilic addition, electrophilic substitution, and redox reactions. Reaction mechanisms vary and help in understanding the different types of reaction taking place.

Nucleophilic substitution reactions

- Between halogenoalkanes and NaOH.
- $\text{S}_{\text{N}}1$ mechanism = substitution reaction, nucleophilic, unimolecular. Proceeds via a carbocation intermediate formed by heterolytic fission of the C–halogen bond. Favoured by tertiary halogenoalkanes due to stability of the tertiary carbocation. Carried out in protic polar solvents.
- $\text{S}_{\text{N}}2$ mechanism = substitution reaction, nucleophilic, bimolecular. Proceeds in one concerted step via a transition state. The reaction is stereospecific. Carried out in aprotic, polar solvents.
- OH^- is a stronger nucleophile than H_2O as it has a negative charge, in addition to lone pairs.



Electrophilic addition reactions

- Alkene + Br₂ / interhalogens / hydrogen halides
- The pi bond in alkenes is an electron-dense area, to which electrophiles are attracted. Electrophiles are electron-deficient species, generated by heterolytic fission, e.g. Br⁺ from Br₂.
- The reaction involves breaking the pi bond of the double bond, creating two new bonding positions for the addition product.
- The major product of the reaction of addition of unsymmetrical reagents to unsymmetrical alkenes can be predicted from Markovnikov's rule. This prediction is based on the favoured mechanism proceeding via the more stable carbocation.

tertiary carbocation > secondary carbocation > primary carbocation in stability

Electrophilic substitution reactions

- Benzene + HNO₃/H₂SO₄
- The delocalized ring of pi electrons in benzene is an electron-dense area, to which electrophiles are attracted.
- Substitution reactions in benzene substitute a hydrogen atom of the ring for the electrophile, which preserves the stability of the benzene ring structure.
- Nitration of benzene uses a nitrating mixture of the concentrated acids HNO₃ and H₂SO₄. This generates the electrophile NO₂⁺ that substitutes in benzene.

Reduction reactions

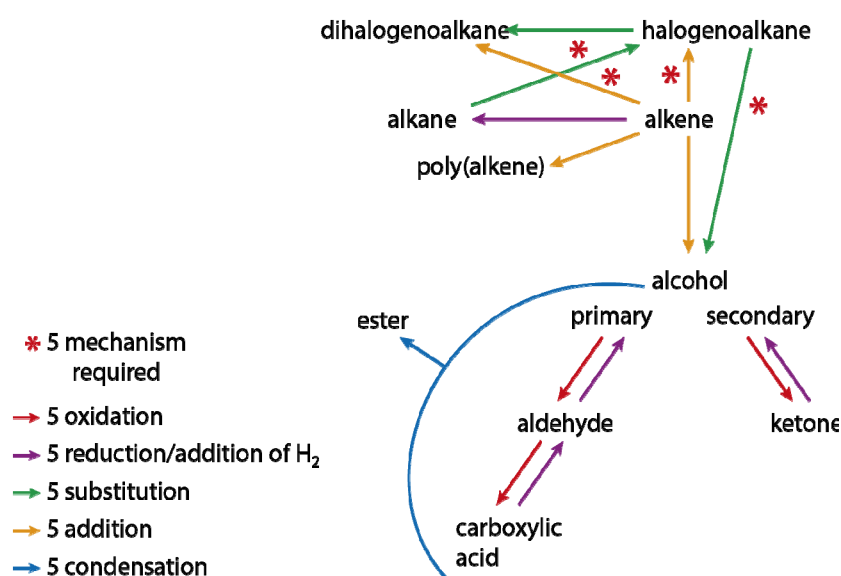
- These are often defined in terms of gain of H/loss of O in organic chemistry.
- Reducing agents for carbonyl compounds are NaBH₄ or LiAlH₄, which both produce H⁻:
 - carboxylic acid is reduced to aldehyde
 - aldehyde is reduced to primary alcohol
 - ketone is reduced to secondary alcohol
- Reducing agents for nitrobenzene are Sn/conc. HCl. Nitrobenzene is reduced to phenylammonium ions, and then to phenylamine.



20.2 Synthetic routes

Organic synthesis is the systematic preparation of a compound from a widely available starting material or the synthesis of a compound via a synthetic route that often can involve a series of different steps.

- Organic chemistry often involves converting an available starting material into a required product in a multi-step process.
- Retro-synthesis involves working backwards from a desired product, and deducing the precursor molecules that can react to form the target molecule.
- Functional group chemistry determines reaction conversions in synthetic routes.



20.3 Stereoisomerism

Stereoisomerism involves isomers which have different arrangements of atoms in space but do not differ in connectivity or bond multiplicity (i.e. whether single, double, or triple) between the isomers themselves.

- Stereoisomers differ in the spatial/three-dimensional arrangement of the atoms in a molecule.
- Configurational isomerism refers to stereoisomers that cannot be interconverted without breaking sigma bonds and so have a permanent difference in their geometry.
- cis-trans* isomers and *E/Z* isomers occur where there is a restriction on rotation around substituted groups. This occurs in (i) cyclic and (ii) double-bonded molecules, as here there is no free rotation.
- Where there are only two types of substituents the isomers are called *cis* and *trans* – *cis* has the same groups on the same side, and *trans* has them on opposite sides of the reference plane.
- Where there are more than two different substituents, the *E/Z* nomenclature must be used, which has broader application. Using priority rules, each group attached to each C atom of the ring or double bond is assigned a priority based on atomic number. The *E* isomer has the two groups of highest priority on the same side of the double bond or ring, and the *Z* group has them on the opposite sides.
- Optical isomers occur when a molecule contains a chiral/asymmetric carbon atom. This is attached to four different groups, and gives rise to enantiomers that are non-superimposable mirror images of each other.



- Optical isomers differ in the direction in which they rotate plane-polarized light. This can be measured using a polarimeter.
- A racemic mixture contains equal amounts of the two enantiomers and is optically inactive.
- Diastereoisomers arise when a molecule has more than one chiral centre, and has different configurations in some but not all of these positions. Diastereoisomers are not mirror images of each other.
- Enantiomers differ from each other in their direction of rotation of plane-polarized light, and in their reactivity with other chiral molecules. This is important in living cells, as all biochemical reactions are stereospecific.

Get it straight

- Free radicals have an unpaired electron but do not carry a charge; ions carry a charge.
- Homolytic fission generates free radicals; heterolytic fission generates ions.
- Combustion refers to complete oxidation of the molecule and involves destruction of the carbon chain. Oxidation of an organic compound refers to a chemical change at a functional group, which leaves the carbon structure of the molecule intact.