

Topic 20: Organic chemistry

12 hours

Essential idea: 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.

20.1 Types of organic reactions

Nature of science:

Looking for trends and discrepancies—by understanding different types of organic reactions and their mechanisms, it is possible to synthesize new compounds with novel properties which can then be used in several applications. Organic reaction types fall into a number of different categories. (3.1)

Collaboration and ethical implications—scientists have collaborated to work on investigating the synthesis of new pathways and have considered the ethical and environmental implications of adopting green chemistry. (4.1, 4.5)

Understandings:*Nucleophilic Substitution Reactions:*

- S_N1 represents a nucleophilic unimolecular substitution reaction and S_N2 represents a nucleophilic bimolecular substitution reaction. S_N1 involves a carbocation intermediate. S_N2 involves a concerted reaction with a transition state.
- For tertiary halogenoalkanes the predominant mechanism is S_N1 and for primary halogenoalkanes it is S_N2 . Both mechanisms occur for secondary halogenoalkanes.
- The rate determining step (slow step) in an S_N1 reaction depends only on the concentration of the halogenoalkane, rate = $k[\text{halogenoalkane}]$. For S_N2 , rate = $k[\text{halogenoalkane}][\text{nucleophile}]$. S_N2 is stereospecific with an inversion of configuration at the carbon.
- S_N2 reactions are best conducted using aprotic, non-polar solvents and S_N1 reactions are best conducted using protic, polar solvents.

Electrophilic Addition Reactions:

- An electrophile is an electron-deficient species that can accept electron pairs from a nucleophile. Electrophiles are Lewis acids.

International-mindedness:

- What role does green and sustainable chemistry, in relation to organic chemistry, play in a global context?

Utilization:

- Organic synthesis plays a vital role in drug design and drug uptake in medicine and biochemistry.
- Nutrition, food science and biotechnology also are underpinned by organic chemistry.

Syllabus and cross-curricular links:
 Topics 10.1 and 10.2—organic chemistry
 Topic 14.1—covalent bonding
 Topic 14.2—hybridization
 Option A.5 and A.9—polymers

Aims:

- **Aim 6:** Three-dimensional visualization of organic compounds using molecular models could be covered.

20.1 Types of organic reactions

- Markovnikov's rule can be applied to predict the major product in electrophilic addition reactions of unsymmetrical alkenes with hydrogen halides and interhalogens. The formation of the major product can be explained in terms of the relative stability of possible carbocations in the reaction mechanism.

Electrophilic Substitution Reactions:

- Benzene is the simplest aromatic hydrocarbon compound (or arene) and has a delocalized structure of π bonds around its ring. Each carbon to carbon bond has a bond order of 1.5. Benzene is susceptible to attack by electrophiles.

Reduction Reactions:

- Carboxylic acids can be reduced to primary alcohols (via the aldehyde). Ketones can be reduced to secondary alcohols. Typical reducing agents are lithium aluminium hydride (used to reduce carboxylic acids) and sodium borohydride.

Applications and skills:*Nucleophilic Substitution Reactions:*

- Explanation of why hydroxide is a better nucleophile than water.
- Deduction of the mechanism of the nucleophilic substitution reactions of halogenoalkanes with aqueous sodium hydroxide in terms of S_N1 and S_N2 mechanisms. Explanation of how the rate depends on the identity of the halogen (ie the leaving group), whether the halogenoalkane is primary, secondary or tertiary and the choice of solvent.
- Outline of the difference between protic and aprotic solvents.

Electrophilic Addition Reactions:

- Deduction of the mechanism of the electrophilic addition reactions of alkenes with halogens/interhalogens and hydrogen halides.

- **Aim 6:** A range of experiments of organic synthetic reactions exploring various types of reactions and functional group interconversions could be done. Core techniques of organic chemistry could include reflux, distillation, filtration, purification (including chromatographic techniques), separations and extractions.
- **Aim 6:** Synthesis (or reaction) in the laboratory of an example of a widely used drug or medicine (eg aspirin) or a household product (eg fading of tomato ketchup—electrophilic addition reaction of bromine).

20.1 Types of organic reactions

Electrophilic Substitution Reactions:

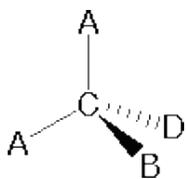
- Deduction of the mechanism of the nitration (electrophilic substitution) reaction of benzene (using a mixture of concentrated nitric acid and sulfuric acid).

Reduction Reactions:

- Writing reduction reactions of carbonyl containing compounds: aldehydes and ketones to primary and secondary alcohols and carboxylic acids to aldehydes, using suitable reducing agents.
- Conversion of nitrobenzene to phenylamine via a two-stage reaction.

Guidance:

- Reference should be made to heterolytic fission for S_N1 reactions.
- The difference between homolytic and heterolytic fission should be understood.
- The difference between curly arrows and fish-hooks in reaction mechanisms should be emphasized.
- Use of partial charges ($\delta+$ and $\delta-$) and wedge-dash three-dimensional representations (using tapered bonds as shown below) should be encouraged where appropriate in explaining reaction mechanisms.



- Typical conditions and reagents of all reactions should be known (eg catalysts, reducing agents, reflux etc.). However, more precise details such as specific temperatures need not be included.

Essential idea: 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.

| 20.2 Synthetic routes | |
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| Nature of science: Scientific method—in synthetic design, the thinking process of the organic chemist is one which invokes retro-synthesis and the ability to think in a reverse-like manner. (1.3) | |
| <p>Understandings:</p> <ul style="list-style-type: none"> The synthesis of an organic compound stems from a readily available starting material via a series of discrete steps. Functional group interconversions are the basis of such synthetic routes. Retro-synthesis of organic compounds. <p>Applications and skills:</p> <ul style="list-style-type: none"> Deduction of multi-step synthetic routes given starting reagents and the product(s). <p>Guidance:</p> <ul style="list-style-type: none"> Conversions with more than four stages will not be assessed in synthetic routes. Reaction types can cover any of the reactions covered in topic 10 and sub-topic 20.1. | <p>International-mindedness:</p> <ul style="list-style-type: none"> How important are natural products to developing countries? Explore some specific examples of natural products available in developing countries which are important to the developed world. <p>Theory of knowledge:</p> <ul style="list-style-type: none"> A retro-synthetic approach is often used in the design of synthetic routes. What are the roles of imagination, intuition and reasoning in finding solutions to practical problems? <p>Utilization:</p> <ul style="list-style-type: none"> Natural products are compounds isolated from natural sources and include taxol, mescaline and capsaicin. <p>Syllabus and cross-curricular links: Topics 10.1 and 10.2—organic chemistry</p> <p>Aims:</p> <ul style="list-style-type: none"> Aim 6: Multiple stage organic synthetic route series of experiments (up to a maximum of four stages). |

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

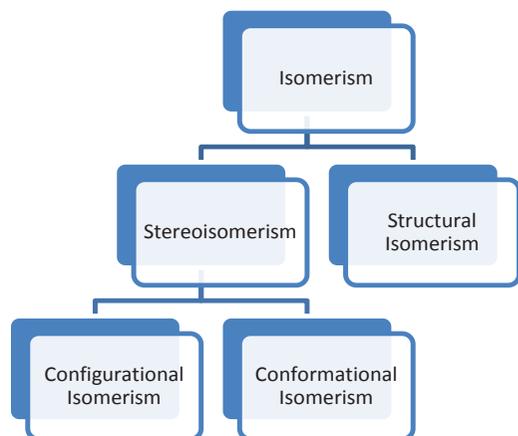
20.3 Stereoisomerism

Nature of science:

Transdisciplinary—the three-dimensional shape of an organic molecule is the foundation pillar of its structure and often its properties. Much of the human body is chiral. (4.1)

Understandings:

- Stereoisomers are subdivided into two classes—conformational isomers, which interconvert by rotation about a σ bond and configurational isomers that interconvert only by breaking and reforming a bond.



Configurational isomers are further subdivided into cis-trans and E/Z isomers and optical isomers.

International-mindedness:

- Have drugs and medicines in some countries been sold and administered as racemates instead of as the desired enantiomer with the associated therapeutic activity? Can you think of any drugs or medicines which may serve as good case studies for this?

Theory of knowledge:

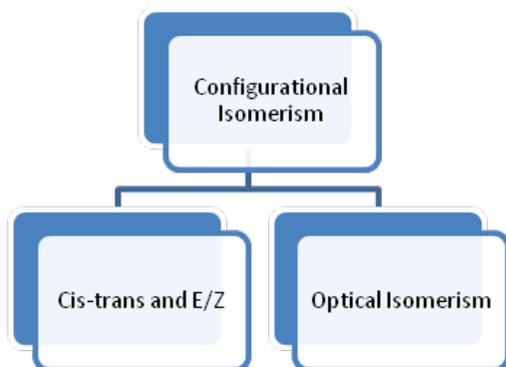
- The existence of optical isomers provide indirect evidence for a tetrahedrally bonded carbon atom. Which ways of knowing allow us to connect indirect evidence to our theories?
- Stereoisomerism can be investigated by physical and computer models. What is the role of such models in other areas of knowledge?
- One of the challenges for the scientist and the artist is to represent the three-dimensional world in two dimensions. What are the similarities and differences in the two approaches? What is the role of the different ways of knowing in the two approaches?

Utilization:

- Many of the drugs derived from natural sources are chiral and include nicotine, dopamine, thyroxine and naproxen.
- The role of stereochemistry in vision science and food science.
- In many perfumes, stereochemistry often can be deemed more important than chemical composition.

Syllabus and cross-curricular links:

20.3 Stereoisomerism



- Cis-trans isomers can occur in alkenes or cycloalkanes (or heteroanalogues) and differ in the positions of atoms (or groups) relative to a reference plane. According to IUPAC, E/Z isomers refer to alkenes of the form $R_1R_2C=CR_3R_4$ ($R_1 \neq R_2$, $R_3 \neq R_4$) where neither R_1 nor R_2 need be different from R_3 or R_4 .
- A chiral carbon is a carbon joined to four different atoms or groups.
- An optically active compound can rotate the plane of polarized light as it passes through a solution of the compound. Optical isomers are enantiomers. Enantiomers are non-superimposable mirror images of each other. Diastereomers are not mirror images of each other.
- A racemic mixture (or racemate) is a mixture of two enantiomers in equal amounts and is optically inactive.

Applications and skills:

- Construction of 3-D models (real or virtual) of a wide range of stereoisomers.
- Explanation of stereoisomerism in non-cyclic alkenes and C3 and C4 cycloalkanes.

Topics 10.1 and 10.2—organic chemistry
 Option B.4—carbohydrates
 Option B.10—stereochemistry in biomolecules
 Option D.7—importance of chirality and drug action

Aims

- **Aim 6:** Experiments could include the synthesis and characterization of an enantiomer (eg (-) menthol) or the resolution of a racemic mixture.

20.3 Stereoisomerism

- Comparison between the physical and chemical properties of enantiomers.
- Description and explanation of optical isomers in simple organic molecules.
- Distinction between optical isomers using a polarimeter.

Guidance:

- The term geometric isomers as recommended by IUPAC is now obsolete and cis-trans isomers and E/Z isomers should be encouraged in the teaching programme.
- In the E/Z system, the group of highest Cahn–Ingold–Prelog priority attached to one of the terminal doubly bonded atoms of the alkene (ie R1 or R2) is compared with the group of highest precedence attached to the other (ie R3 or R4). The stereoisomer is Z if the groups lie on the same side of a reference plane passing through the double bond and perpendicular to the plane containing the bonds linking the groups to the double-bonded atoms; the other stereoisomer is designated as E.
- Wedge-dash type representations involving tapered bonds should be used for representations of optical isomers.