

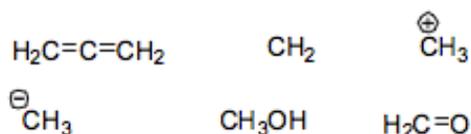
## Structure and Bonding

**Reading:** Most of the general texts (you should certainly consult Clayden, Greeves, Wothers and Warren – Organic Chemistry) carry decent sections on this work but probably the best is Peter Sykes, "A Guidebook to Mechanism in Organic Chemistry", you should also look at Hornby and Peach and other general texts.

**Notes and Questions:** Use your textbooks (e.g. Hornby and Peach) to summarize the rudiments of hybridisation, which is the approach Organic Chemists prefer to use to explain molecular structure.

Explain the structures of **methane**, **ethane**, **ethene** (ethylene) and **ethyne** (acetylene). This will introduce you to sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds. Explain the **rotation barriers** around **single** and **double** bonds. You need to appreciate the basis of **atomic** and **molecular orbitals** using the **Pauli exclusion principle** and **Hund's rules**.

1. Predict the likely shapes of the following molecules: for the ions think about the hybridisation the molecules may adopt in order to stabilise charge; for the carbene ( $\text{CH}_2$ ) think about possible hybridisation then ways of putting the electrons in these orbitals.



Organic Chemistry is a three dimensional subject and a molecular model kit is very useful for this piece of work. You need to understand the vocabulary which we use to describe molecules and try to get to grips with the rules of stereochemistry. Get into the habit of drawing clear diagrams which give good representation of the 3D structures which will make life a lot easier. Learn to use the various conventions such as Newman, Fischer and sawhorse projections.

**Conjugation:** The electrons which form the p component of the double bond in ethene are in the plane which is perpendicular to the atomic plane. Suppose we have another double bond (or lone pair atom) adjacent to the double bond. This can lead to the existence of an extended  $\pi$  system through **conjugation**. There are two ways to describe this phenomenon – either by a simple **molecular orbital description** or, much more commonly and usefully for Organic Chemists by using the concept of **RESONANCE** and using **resonance hybrids** (See "How to use curly arrows" – in particular frames 5-7, and "A problem oriented approach to acidity and basicity", and general text books). Make sure you are familiar with this extremely important concept and...

2. Draw the important resonance form(s) of the following molecules:



## Stereochemistry

**Reading:** "Stereochemistry at a Glance" – J. Eames and J. M. Peach. Lots of other texts have excellent sections on stereochemistry – March has a very good chapter. "Stereochemistry of Organic Compounds" Eliel and Wilen has an excellent glossary.

Cover the following topics in the form of concise revision notes. You must be able to give a definition of and understand the differences between terms mentioned. (An illustrative example of each in your notes is ESSENTIAL: and think of others which are *not* the examples given in the book!)

**A. ISOMERISM** – distinguish first between structural isomers and stereoisomers. Geometric isomers (*cis / trans*, *E / Z*). Stereoisomers (enantiomer, diastereomer, epimer, meso, dl pair, racemic mixture). Configuration (absolute and relative).  
Selectivity: the meaning of chemoselective, regioselective, enantioselective, diastereoselective.

### **B. CAHN – INGOLD – PRELOG RULES**

Learn these, and be able to use *R / S* terminology for a stereogenic centre: also learn *E / Z* terminology for double bond geometry.

### **C. OPTICALLY ACTIVE COMPOUNDS WITHOUT STEREOGENIC CENTRES**

Understand the definition of chirality and the structural features required. We do not necessarily need tetrahedral carbon for molecules to be chiral. Look at hindered biphenyls, allenes, cumulenes, sulfoxides etc. How do we use the Cahn, Ingold, Prelog rules for these compounds? (Norman has a few good illustrative examples for this section).

### **D. CONFORMATION**

Understand the difference between **configuration** and **conformation**. Consider restricted rotation about single bonds in acyclic molecules and the conformations of flexible ring compounds (i.e. cyclohexane; chair and boat forms; axial and equatorial sites). Practise using Newman projections, especially for acyclic compounds.

### **E. AMINO-ACIDS**

Look up the simple chemistry of amino acids. Include resolution, racemisation and synthesis, e.g. by the Strecker and other methods.

### **Questions**

1. Write definitions, with real examples and drawings for illustration, to explain the meaning of the following;

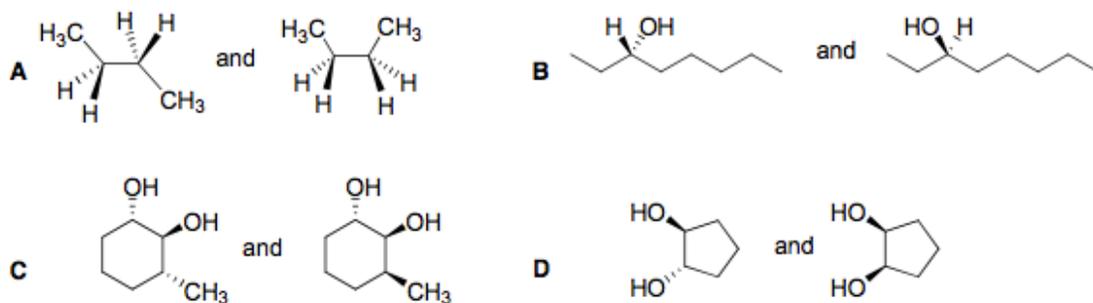
a) Enantiomer, diastereomer, meso, racemic, epimer, erythro/threo, diastereotopic, prochiral, achiral.

b) Configuration and conformation, relative and absolute configuration; *d / l*, *D / L*, (+) / (-); the *R/S* and *E/Z* system of nomenclature.

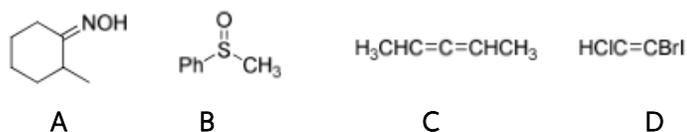
c) Resolution, giving methods used; also racemisation. d) Chemoselective, regioselective, stereoselective, enantioselective

NB **Definitions** should be short and accurate.

2. Using the following pairs of molecules as your examples, define and explain the following stereochemical terms: configuration, conformation, diastereomer, eclipsed, enantiomer, epimer, meso and racemic.

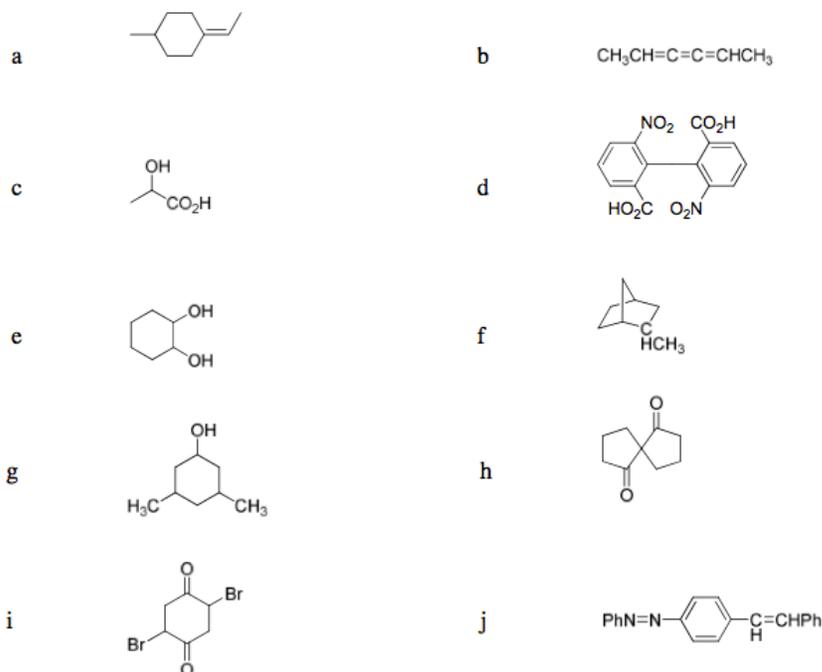


3. Identify the stereoisomers (other than conformational) of **all** of the following compounds:



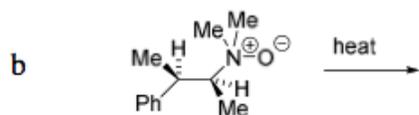
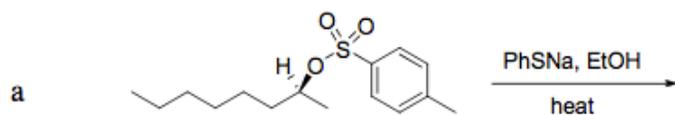
Use any of the compounds **A-B** to illustrate the stereochemical descriptors *R* and *E*.

4. Draw the stereoisomers of the following compounds:

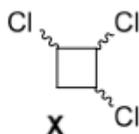


5 a) Draw the three-dimensional representation of all the various stereoisomers (excluding conformers) of 2,3,4-trihydroxybutanal  $[\text{HOCH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CHO}]$  and identify the enantiomeric and diastereomeric relationships. For each of your structures assign absolute configuration to the respective stereocentres using the Cahn-Ingold-Prelog (*R* and *S*) convention.

b) Giving your reasons, predict what you might expect to occur in the following reactions, paying particular attention to the stereochemical outcome.



6 a) How many stereoisomers of 1,2,3-trichlorobutane **X** are there?



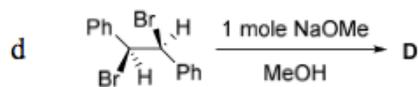
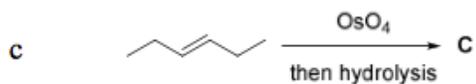
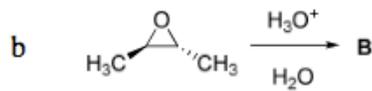
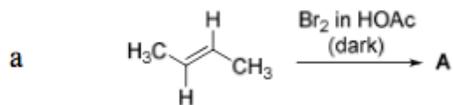
Draw out three-dimensional representations of them indicating, where relevant, diastereomeric, and enantiomeric relationships.

b) Draw out a three-dimensional representation of (2*S*,3*S*)-3-bromobutan-2-ol [gross structure:  $\text{Me.CHBr.CHOH.Me}$ ]. On treatment of (2*S*,3*S*)-3-bromobutan-2-ol with  $\text{HBr}$ , racemic 2,3-dibromobutane is obtained; explain.

What would you expect to be the result of treating (2*S*,3*R*)-3-bromobutan-2-ol with  $\text{HBr}$  under the same conditions?

## Further Questions

7. Discuss stereochemical features of the following reactions and identify the product(s).



8. From the following molecules, pick out: a) two which are achiral and contain no chiral centres; b) two which are achiral and contain chiral centres; c) two which are chiral and contain chiral centres; d) two which are chiral and contain no chiral centres.

