CHEM20020

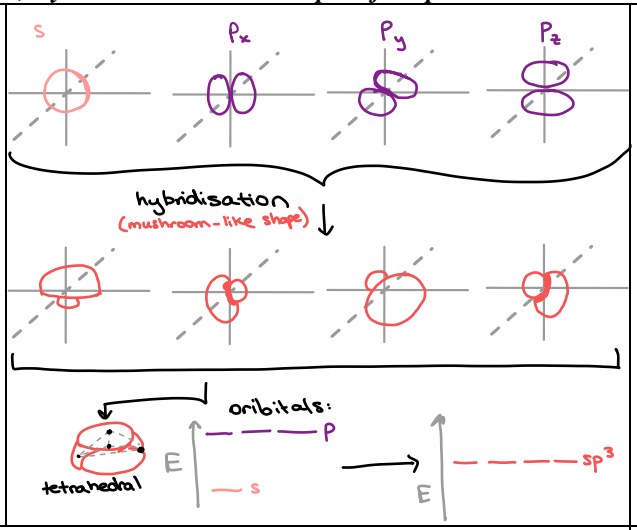
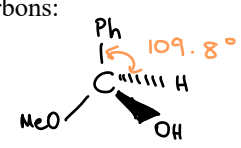
Chemistry – Structure and Properties

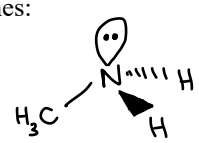
Week 1:

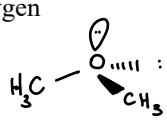
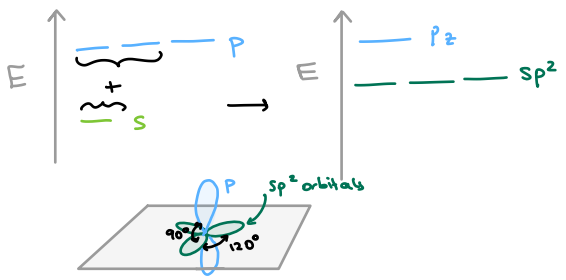
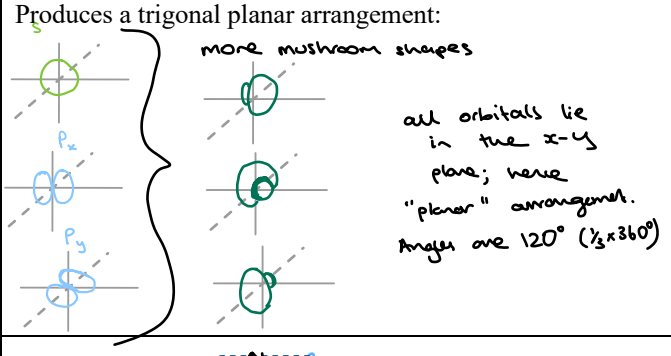
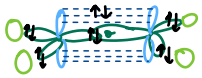
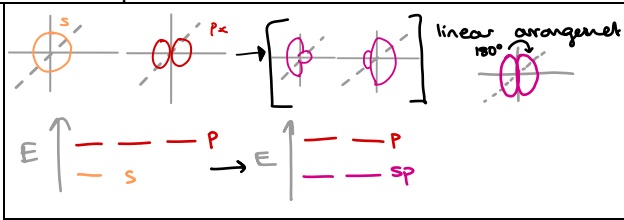
Reactivity and Mechanism

Chemical Reactions: formation and breaking of bonds
Mechanism: detail at the molecular level as to how the reaction takes place
Reactivity is dictated by bonding and stereochemistry.

Orbitals, Hybridisation and the shapes of simple molecules

<table>
<tr><td>sp^3</td><td> 
</td><td>Produces a tetrahedral arangement:
e.g., carbons:
 

e.g., amines:
 

e.g., oxygen
 
</td></tr>
<tr><td colspan="2">σ–bonds have conformational isomers, but since the bonds have free rotation, they interconvert and spend the most time in the staggered (less steric hinderance than the eclipsed)</td><td> 
</td></tr>
<tr><td>sp^2</td><td> 
</td><td>Produces a trigonal planar arrangement:
 
</td></tr>
<tr><td colspan="2">π-bonding (the double bond) does not have free rotation, and thus molecules with π bonds may possess geometric isomers. Atoms lie in the plane</td><td>  </td></tr>
<tr><td rowspan="2">sp</td><td> 
</td><td>e.g., CO_2 

e.g., nitrile: 

e.g., acylium: 
</td></tr>
<tr><td>Can produce two perpendicular π bonds, producing a triple bond.</td><td>No geometric isomers are possible</td></tr>
</table>

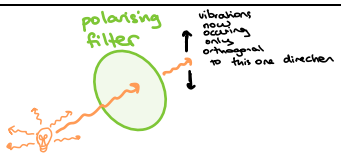
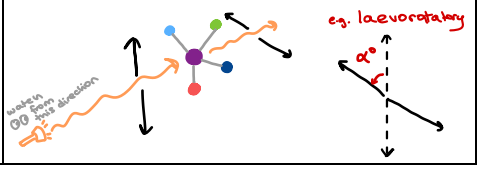
Stereochemistry

Isomers	Different compounds with the same molecular formula
Structural isomers	Same molecular formula but varying connectivity (i.e., different elements are bonded to different elements)

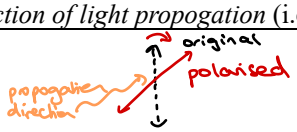
Stereoisomers	Same molecular formula, different arrangement in space (e.g., chiral molecules, geometric (E/Z) isomers)

Enantiomers
Non-superimposable mirror images. Molecules capable of existing as enantiomers are called chiral.
An sp^3 centre (most generally C) with four different substituents is termed a stereogenic centre.

Experimentally determining if a molecule is chiral:

A polarising filter isolates one plane of light	
A chiral molecule rotates the plane of polarised light $[\alpha]_D$ = specific rotation for a particular wavelength	

Look down the direction of light propogation (i.e., your eyes watch the torch beam away from you)

+  **Dextrorotatory** Linearly polarised light is rotated to the right	−  **Laevorotatory** Linearly polarised light is rotated to the left

⚠ **warning:** +/- notation is entirely indpendent of D/L or R/S assigned stereochemistry (R/S is only based on CIP nomenclature) ⚠

$[\alpha]_D$ varies depending on:
1. The concentration of optically active compounds
2. The length of the cell ()
3. The wavelegnth of light used

$$[\alpha]_D = \frac{\alpha}{l \times C}$$

When naming R/S compounds:
- Make a list of each connection on each substituent
- Remember that priority is only assigned on the basis of atomic number (and if atomic number is the same, then by isotope)
- Ensure the least priority is pointing towards the back
  (if it is pointing to the front, simply invert (i.e., 4 points to the front $\Longrightarrow R \leftrightarrow S$)

D/L nomenclature

Transforming a molecule into a Fischer projection:
1. Draw the parent chain vertically up the page
2. Position the most oxygenated (oxidised) carbon at the top of the paghe
3. Orient the molecule so that vertical bonds go INTO the page and horizontal bonds come OUT of the page
4. When the OH group [of a chiral carbon] points to the right it is D. If OH points to the left, it is L.

Example: glucose