HERTFORD COLLEGE
FIRST YEAR ORGANIC CHEMISTRY TUTORIALS
2006-2007

Attendance at all first year lectures for Biochemists and tutorials in organic chemistry are compulsory.

RECOMMENDED STANDARD TEXTBOOKS

1. **'Organic Chemistry'**; Clayden, Greeves, Warren and Wothers; OUP. This will be the standard text from which reading will be set and has most of the material we will cover and is user friendly. It is relatively inexpensive but copies should be available from the College or Hooke libraries.
2. **'A guidebook to Mechanism in Organic Chemistry'**; R. Sykes; Longman is useful for many aspects of mechanism.
3. **'Chemistry of the Carbonyl Group (A Programmed Approach)'**; S.Warren; J.Wiley.
4. **'Foundations of Chemical Biology'**; Oxford Chemistry Primer; Dobson, Pratt, Gerrard; OUP.

You will also need a set of past papers for the preliminary examination in Organic Chemistry (2000-present; note not all questions are relevant to the current course-consult your tutors) and a set of molecular models.

TUTORIAL PLANNING

The tutorial work is designed to cover a general area of the organic chemistry course and will (approximately) follow the lecture course. Problems will be issued in advance to test your knowledge of each topic. A reading and keyword list will be attached from which you should make brief notes, which should ultimately be combined with you lecture notes to make a single set. ***Always do the reading and note preparation before attempting any of the problems***. All problem solutions should be submitted to your tutor by midday on the day preceding each tutorial. A tutorial will normally consist of the following:

i) Return of submitted problem scripts.
ii) A general discussion of the topic to assist with areas of difficulty.
iii) Discussion of the set problems.
iv) Tutorial problems.
v) Distribution of work for the next tutorial.

TOPICS TO BE COVERED IN THE FIRST FOUR TUTORIALS OF THE FIRST YEAR WILL INCLUDE:

1. Principles of Organic Chemistry (including acids and bases).
2. Stereochemistry.
3. Nucleophilic Substitution and Elimination.
4. Alkanes/ Dienes/ Alkynes/ Allenes/ Alkenes.

TUTORIAL ONE: INTRODUCTION TO ORGANIC CHEMISTRY

Material to be covered beforehand.

Keywords:
Atomic orbitals; molecular orbitals; lone pair; hybridisation; chemical structure; valence bonding; electron pair repulsion; bond lengths and strengths; conjugation; mesomeric effects; aromaticity (introduction); Lewis acids and bases; electronegativity; inductive effects; steric effects; electrophilic and nucleophilic behaviour; principles of mechanism in terms of electron flow; pKa's of acids, bases and carbon centred species; factors affecting acidity/ basicity; basic reaction types (Substitution/ Addition/ Elimination/ Rearrangement); generalised structure of reactive intermediates (Carbanions/ Carbocations/ Carbenes/ Radicals).

Reading:
CGWW; Chapters 1, 2, 4, 5, 7.
Sykes; Chapters 1, 3, 10.

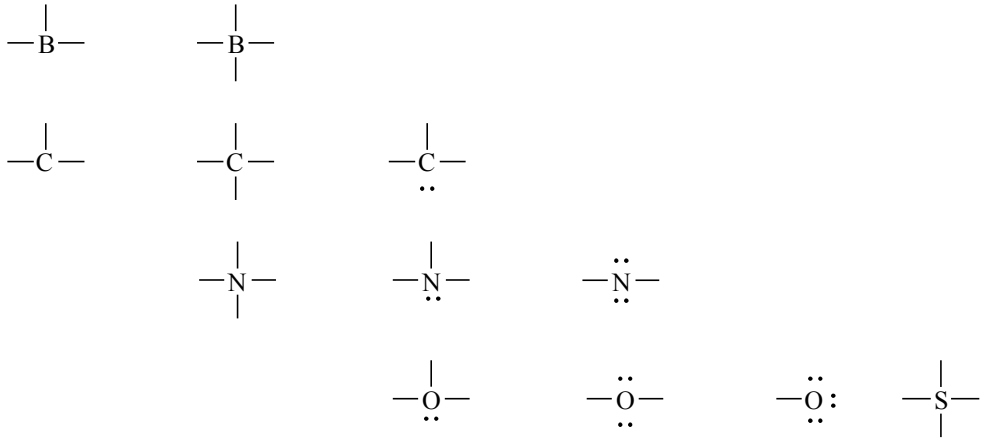
Note: it is very important you get to grips with the concepts introduced in this first few tutorials - they underpin the whole of organic chemistry. Even if you don't fully appreciate everything first time round persevere because this is the really important stuff - all of the rest stems from these basic principles.

Please also don't be afraid to give more than one answer to questions – if you are unsure of the answer say why.

EXERCISES ONE

A) INTRODUCTION TO BONDING

1. Assign formal charges to the following atomic groups:



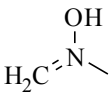
2. Assign lone pairs and charges to each of the atoms in the following structures:

a) 

b) $H_2C{=}C{=}O$

c) $H_2C{=}N{=}N$

d) $H_2B{=}NH_2$

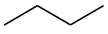
e) 

3. Draw all the possible neutral isomers for the following molecular formulas:

a) $C_2Br_2Cl_2$ b) $C_2H_4Cl_2$ c) C_2H_3N

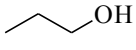
4. Which of the following substances are likely to be soluble in concentrated sulfuric acid?

a) 

b) 

c) 

d) H_2

e) 

5. There are three possible isomers with the formula $C_2H_2Cl_2$. Draw them and indicate which isomer has a zero dipole moment.

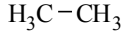
6. List the atoms that can form hydrogen bonds. Explain why they only occur with first row elements. Which of the following pure compounds is likely to form hydrogen bonds in the liquid state? Of the compounds which do not form hydrogen bonds, which can form hydrogen bonds with water. How will this affect their solubility?

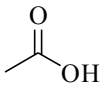
a) 

b) 

c)

d) 

e) 

f) 

7. An organic chemist attempted to prepare methanol labelled with ^{18}O ($H_3C^{18}OH$) by dissolving 1 equivalent of $Na^{18}OH$ in distilled water and adding methyl bromide. He obtained methanol that contained almost no label. Explain this result.

8. Methyl bromide reacts with a variety of Lewis bases (nucleophiles), including those shown below. For each reaction, describe the electronic change that occurs at C-Br and at the reactive atom of the Lewis base. Represent the bonding changes for each, using curved arrows:

(a) $CH_3Br + NaSH \longrightarrow CH_3SH + NaBr$

(b) $CH_3Br + NaI \longrightarrow CH_3I + NaBr$

(c) $CH_3Br + NaCN \longrightarrow CH_3CN + NaBr$

B) ACIDITY AND BASICITY

The concept of acidity/basicity are vital in many reactions mechanisms. Although a little 'old-fashioned', Sykes is a good text on the acidity of organic compounds.

1. Define what is meant by pKa and write down the equilibria which define the pKa of ethanol, phenol and acetic acid. What are the relative proportions of phenol and the phenoxide ion (PhO^-) in aqueous solutions at pH 7, 9 and 10? (The pKa of phenol is ca. 9).

2. List the factors which affect the acidity of organic compounds (include entropy). Explain how the relative stabilities of the acids and their conjugate bases can be useful in rationalising the acid/ base properties of organic compounds.

3. Giving reasons, arrange the following compounds in order of increasing acidity:
CH_3CO_2H, CH_3SO_3H, CH_3CH_3, CH_3CHO, CH_3CH_2OH, $CH_2{=}CH_2$, HCCH

4. Explain with reasoning which of the following pairs is the stronger acid (a to e) or base (f to i):

a) $ClCH_2CO_2H$ vs CH_3CO_2H

b) PhCCH vs $PhCH{=}CH_2$

c) $CH_3CH_2CO_2H$ vs $HCCCO_2H$

d) $[Ph_3P^+CH_2CH_3]\ Br^-$ vs $[Ph_3N^+CH_2CH_3]\ Br^-$ (hint; think about d orbitals)

e) CH_3CN vs Et_3N

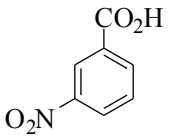
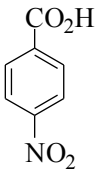
f) $PhCONH_2$ vs $PhSO_2NH_2$

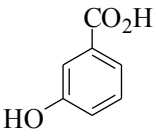
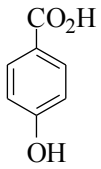
g) CH_3CONH_2 vs $H_2N(CO)NH_2$ vs $H_2N(C{=}NH)NH_2$

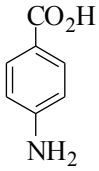
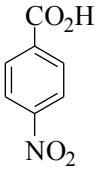
h) Comment on the fact that the pKa values in water of the conjugate acids of NH_3, CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ are 9.25, 10.64, 10.77 and 9.80, respectively.

5. Write down and <u>memorise</u> the approximate pKa values (to nearest unit) for the following: carboxylic acid, alcohol, thiol, phenol, ketone, aldehyde, and the protonated forms of imidazole, primary amine and anniline.

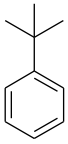
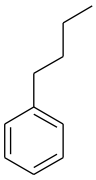
6. Explain with reasoning which of the following pairs is the stronger acid.

a)  vs 

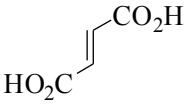
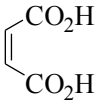
b)  vs 

c)  vs 

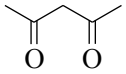
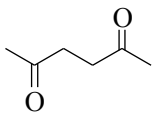
d)  vs 

e)  vs 

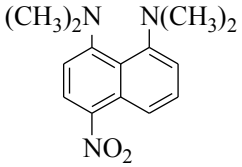
f)  vs 

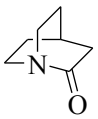
g)  vs 

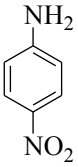
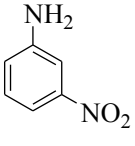
(first and second ionisations) for both

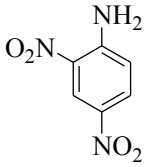
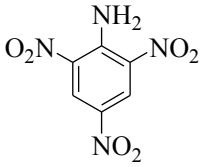
h)  vs 

7. Explain with reasoning which of the following pairs is the stronger base.

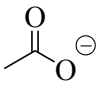
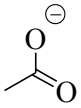
a) $PhN(CH_3)_2$ vs 

b) CH_3CONH_2 vs 

c)  vs 

d)  vs 

7. Which of the following pairs of structures do not constitute resonance structures? Name all functional groups shown.

a)  vs 

b)  vs 

c) $^{+}CH_2$-CH=CH_2 and CH_2=CH-CH_2^{+}

d) CH_2=CH-CHO and $^{+}CH_2$-CH=CH-O^{-}

e) CH_3CH=$CHCH_3$ and CH_3CH_2CH=CH_2

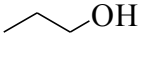
f) H_2C=C=CH_2 and CH_3CCH

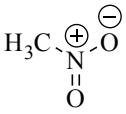
g) H-CN^{+}H and H-$^{+}$C=NH

h) CH_3-N=C=O and CH_3O-CN

i) CH_3-N=C=O and $CH_3{}^{+}NC$-O^{-}

j) $^{-}$O-$^{+}$O=O and O=O^{+}-O^{-}

k)  and 

l)  and