ORGANIC CHEMISTRY

A. STRUCTURE AND ISOMERISM

1. Structure

- (a) number of bonds to C, H, O, N and halogen
- (b) chain formation *via* C–C bonds
- (c) straight and branched chains isomerism
- (d) general formulae for alkanes, cycloalkanes, alkenes and alkynes
 - units of unsaturation (double-bond equivalents)

2. Structural isomerism

- (a) chain isomerism
- (b) positional isomerism
- (c) functional group isomerism

3. Geometric (cis-trans) isomerism

(a) in cycloalkanes

(b) in alkenes

4. **Optical isomerism**

in compounds with an asymmetric (chiral) carbon atom

B. FUNCTIONAL GROUPS AND IUPAC NOMENCLATURE

(see also the NAMING program in the Chemistry Lab)

- 1. Alkanes and Cycloalkanes
- 2. Alkenes and Cycloalkenes
- 3. Alkynes

4. **Aromatic compounds**

- (a) monosubstituted (including toluene, phenol, aniline, benzaldehyde & benzoic acid
- (b) disubstituted (1,2-, 1,3, 1,4 and o-, m-, p-)
- (c) polysubstituted (1,2,4-, etc.)
- 5. Halogen derivatives
- 6. Alcohols
 - (a) monohydric (one OH), dihydric (diols; two OH), trihydric (triols; three OH).
 - (b) primary (1°) , secondary (2°) , tertiary (3°) .
- 7. **Ethers** (acyclic only)

as dialkyl ethers, alkyl alkyl ethers and alkoxy alkanes

- 8. Aldehydes
- 9. **Ketones**
- 10. Carboxylic acids and derivatives (salts, esters, anhydrides & amides)
 - (a) monoacids, diacids, etc.

(b) esters

11. Amines

- (a) as alkyl amines and alkanamines
- (b) primary (1°) , secondary (2°) and tertiary (3°)

C. ORGANIC REACTIONS (Reaction type in italics; see Section D)

1. Alkanes

- (a) combustion (oxidation) O₂/heat
- (b) halogenation (substitution) Br₂ or Cl₂/light or heat

2. Alkenes

- (a) hydrogenation (addition) H₂/Pd
- (b) halogenation (addition) Br₂ or Cl₂
- (c) hydrohalogenation (addition) HBr or HCl
- (d) hydration (addition) H₂O/H⁺
- (e) hydroxylation (oxidation) cold dil. alkaline KMnO₄
- (f) oxidation to ketones and acids (oxidation) hot conc. KMnO₄

3. Alkynes

- (a) hydrogenation (addition) H₂/Pd
- (b) halogenation (addition) Br₂ or Cl₂
- (c) hydrohalogenation (addition) HBr or HCl

4. Aromatic compounds

- (a) halogenation (substitution)- Br₂ or Cl₂/Fe
- (b) conversion of alkyl substitutents to COOH (oxidation) hot KMnO₄

5. Alcohols

- (a) reaction with alkali metals (reduction) Na, Li or K
- (b) dehydration (elimination) conc. H₂SO₄
- (c) 1° to aldehydes & acids (oxidation) KMnO₄
- (d) 2° to ketones (oxidation) KMnO₄
- (e) ester formation (substitution) acids or anhydrides/H⁺

6. Aldehydes

- (a) conversion to acids (oxidation) KMnO₄
- (b) conversion to 1° alcohols (reduction or addition) H₂/Pd

7. **Ketones**

conversion to 2° alcohols (reduction or addition) - H₂/Pd

8. Carboxylic acids

- (a) reaction with base (acid-base) NaHCO₃ or NaOH
- (b) ester formation (substitution) alcohol/H⁺
- (c) amide formation (substitution) amine or ammonia

9. Esters

hydrolysis (substitution) - H₂O and H⁺ or HO⁻

10. Amides

hydrolysis (substitution) - H₂O and H⁺ or HO⁻

11. Amines

- (a) reaction with acid (acid-base) e.g. HCl, CH₃COOH, etc.
- (b) amide formation (*substitution*) carboxylic acids/heat

12. Phenols

- (a) reaction with strong base (acid-base) NaOH
- (b) ester formation (*substitution*) anhydrides/H⁺

D. TYPES OF ORGANIC REACTIONS

1. Addition

Reaction in which a reagent is added to the double (or triple) bond between two carbon atoms or the double bond between a carbon atom and an oxygen atom.

(a) hydrogenation (H_2/Pd)

i) alkene or alkyne to the corresponding alkane

ii) aldehyde or ketone to the corresponding alcohol

O
$$+$$
 $H_2(excess)$ Pd HO HO OH

(b) *halogenation* (Cl₂ or Br₂)

alkene or alkyne to the corresponding alkyl dihalide or tetrahalide

$$+ Cl_{2}$$

$$+ Br_{2}(excess)$$

$$+ Br_{3}(excess)$$

$$+ Br_{4}(excess)$$

(c) hydrohalogenation (HCl or HBr)

i) alkene to the corresponding alkyl halide (Markovnikov)

$$+ \qquad HBr \qquad \longrightarrow \qquad \boxed{\qquad } Br$$

ii) alkyne to the corresponding alkyl dihalide (Markovnikov)

(d) hydration (H_2O/H^+)

alkene to the corresponding alcohol (Markovnikov)

$$+$$
 H_2O \longrightarrow OH

2. Elimination

Removal of a small molecule from a compound to produce a double or triple bond.

 $dehydration (H_2SO_4)$

alcohol plus concentrated acid to the corresponding alkene

$$O$$
H $\frac{\text{concentrated}}{\text{H}_2\text{SO}_4}$

3. **Substitution**

Exchange of an atom (or group of atoms) for another

- (a) halogenation (Cl₂ or Br₂)
 - (i) alkane to the corresponding alkyl halide

$$+$$
 Br₂ $\xrightarrow{\text{heat or}}$ Br

(ii) benzene (with Fe catalyst) to the corresponding aryl halide

$$\leftarrow$$
 + Cl_2 \leftarrow Fe \leftarrow Cl

- (b) *esterification/amide formation*
 - (i) alcohol plus carboxylic acid to the corresponding ester

(ii) amine plus carboxylic acid to the corresponding amide

$$O$$
 H + CH_3NH_2
 $heat$
 NH + H_2O

- (c) ester/amide hydrolysis
 - (i) ester plus aqueous acid (or base) to the corresponding alcohol plus carboxylic acid

(ii) amide plus aqueous acid (or base) to the corresponding amine plus carboxylic acid

4. Acid/Base

Transfer of H⁺ ion from an acidic compound to a basic compound

neutralization

(i) carboxylic acid plus a base to the corresponding salt

$$O$$
 H + NaHCO₃ O Na⁺ + H₂O + CO₂

(ii) phenol plus a strong base to the corresponding salt

$$\bigcirc$$
 O-H + NaOH \longrightarrow \bigcirc O- Na⁺ + H₂O

(iii) amine plus an acid to the corresponding salt

$$CH_3CH_2NH_2 + HCl$$
 \longrightarrow $CH_3CH_2NH_3^+ Cl^-$

5. Oxidation-Reduction

1. Oxidation

Reaction with an oxidizing agent to produce a compound which, in many cases, contains a carbon oxygen double bond

- (a) oxidation of alcohols
 - (i) primary alcohol to the corresponding aldehyde (mild conditions) or the corresponding carboxylic acid (hot)

(ii) secondary alcohol to the corresponding ketone

$$H$$
 O
 $KMnO_4$
 O

- (b) oxidation of alkenes
 - (i) alkene to the corresponding diol

(ii) alkene to the corresponding carboxylic acid or ketone

$$+ KMnO_4(hot) + CO + O$$

$$+ KMnO_4(hot) + CO$$

(c) *oxidation of alkylbenzenes* alkyl benzene to the corresponding benzoic acid

2. Reduction

- (a) reduction of aldehydes and ketones to alcohols see 1 (a) (ii) (hydrogenation of aldehyde or ketone)
- (b) active metal plus alcohol to the corresponding salt

$$O \sim H$$
 + Na \rightarrow H_2