

## Organic Summary

### Acidity:

Stronger acids have a stable conjugate base

#### *Electronegativity:*

If the atom that bears the charge is electronegative – stable base ∴ strong acid

If there is another electronegative atom, it spreads out  $e^-$  density stabilising the conjugate base.

#### *Hybridisation:*

Higher s character, stronger acid as it can stabilise  $-ve$  charge.

#### *Resonance:*

If the base is resonance stabilised, acid will be stronger.

### Basicity:

Depends on stability of the conj. acid and the availability of a lone pair for bonding to a H.

#### *Electronegativity:*

The less electronegative the atom, the better it can handle the  $+ve$  charge - stronger base.

#### *Hybridisation:*

Lower s character means  $e^-$  further from nucleus, so more available for bonding – stronger base

#### *Resonance:*

If resonance stabilized,  $e^-$  less available – weaker base

### Nucleophilic substitution:

Nucleophile attacks a carbon and displaces a leaving group.

Requires a good leaving group

#### *S<sub>N</sub>1:*

Depends only on conc. of electrophile

Two step: ionisation, nucleophilic attack

Goes via an achiral, planar carbocation – racemic product

Requires stable carbocation to occur

#### *S<sub>N</sub>2:*

Depends on conc of both nucleophile and electrophile

Single step

Walden inversion – gives opposite enantiomer

Will not occur if hindered

### Elimination reactions:

Nucleophile attacks, kicking off a leaving group resulting in a double bond.

#### *E1:*

Two steps: ionisation and deprotonation

Free rotation of intermediate – racemate formed

- *Zaitsev's rule:* the most substituted alkene will be the major product

Requires stable carbocation intermediate

#### *E2:*

One step

Requires leaving group to be antiperiplanar to the leaving hydrogen – single diastereoisomer formed

## Electrophilic addition:

Systems with  $\pi$  e<sup>-</sup> (double bonds) are attacked by an electrophile, the intermediate is then attacked by a nucleophile.

The most stable carbocation intermediate will form the major product.

### *Markovnikov's rule:*

The hydrogen is the electrophile, the halogen is the nucleophile

The most substituted product will form ("the rich get richer")

## Electrophilic aromatic substitution:

Aromatic rings'  $\pi$  system is attacked by electrophiles

Two step reaction – addition and elimination (H eliminated to retain aromaticity)

Reactivity is influenced by substituents.

### *Reagents:*

Sulphonation:  $\text{H}_2\text{SO}_4/\text{HSO}_3^+$

Nitration:  $\text{H}_2\text{SO}_4/\text{HNO}_3$

Friedel-Craft alkylation:  $\text{R-X}/\text{AlCl}_3$

Friedel-Craft acylation:  $\text{R-OX}/\text{AlCl}_3$

### *Substituents:*

Electron donating:

- have lone pair
- have O, N or S directly next to ring
- direct o/p

Electron withdrawing:

- +ve charge (formal or in resonance form)
- direct m

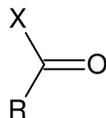
Halides are electron withdrawing, but have lone pairs: - deactivating but o/p directing.

## Nucleophilic aromatic substitution:

If there is a strong e<sup>-</sup> withdrawing group on ring ortho/para to leaving group, it can undergo nucleophilic substitution.

## Nucleophilic addition and substitution at unsaturated carbons:

Carbonyl group:



If X is a poor leaving group – addition resulting in alcohol

If X is good leaving group – substitution via addition/elimination

If X is a poor leaving group and the nucleophile bears an acidic proton, substitution on double bond.

Grignard:

Mg polarises C-Mg bond, forms very powerful nucleophiles.

Creates C-C bonds

Aldehyde - 2° alcohol

Ketone - 3° alcohol

Carboxylic acid – ester

Ester - 2° alcohol

## Oxidation/Reduction:

Oxidising agents:

Oxygen rich molecules

H<sub>2</sub>O<sub>2</sub>, KMnO<sub>4</sub>, CrO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>/CrO<sub>3</sub> or O<sub>2</sub> & Pt/Pd

Reducing agents:

Hydrogen rich molecules

NaBH<sub>4</sub>, LiAlH<sub>4</sub> or H<sub>2</sub> & Pt/Pd

Oxidation:

Substituted aromatics:

- will convert any hydrocarbon substituent to a carboxylic acid

Alcohols:

- 1° → aldehyde → carboxylic acid
- 2° → ketone
- 3° → no reaction

Reduction:

Alkenes:

- removes double bond

Carbonyl:

- acid → 1° alcohol
- ketone → 2° alcohol
- aldehyde → 1° alcohol