

**Lectures 7 & 8:** Special case where  $C=C + EI^+$  is followed by loss of  $H^+$  leads to  $S_EAr$ . Attack by neutral species I (carbenes, dienes) = pericyclic (should follow naturally from  $Br_2$  attack). Attack by neutral species II (radicals), orientation. Review of mechanism types setting the scene for the rest of the course. Redox concepts – prelude to carbonyl course.

**Electrophilic addition to alkenes:**

Recall the electrophilic addition of  $Br_2$  to an alkene proceeds via a bromonium ion (and *not* via a carbocation)

The bromonium ion undergoes nucleophilic attack from the backside of the C-Br bond. What are the consequences for stereochemistry?

This outcome provides evidence for the existence of the bromonium ion (and against a planar carbocation).

**Electrophilic Substitution:**

Aromatic molecules, e.g. benzene also react with  $Br_2$ , however, the product is not the 1,2-dibromide and instead only a single bromine atom is incorporated. This is an example of an aromatic electrophilic substitution ( $S_EAr$ ).

$S_EA_r$  mechanism:

Pericyclic mechanisms describe reactions that are “concerted”. It may be less clear which molecule which is the nucleophile and which the electrophile. However, FMO interactions are still relevant to our understanding of such reactions.

The Diels-Alder reaction (alkene + diene):

Diels-Alder mechanism:

Cyclopropanation (alkene + carbene):

Cyclopropanation mechanism:

**Radical reactivity:** Remember the use of “fish hook” curly arrows to indicate the movement of single electrons rather than electron pairs.

## Survey of Primitive Mechanism Types

In the preceding lectures all of the following were exemplified using curly arrow mechanisms and an FMO treatment:

a) Ionization and the reverse

e.g. nucleophilic substitution by the  $S_N1$  mechanism

b) Addition of nucleophile to  $\sigma^*$  leads to bond cleavage

e.g. nucleophilic substitution by the  $S_N2$  mechanism

c) Addition of nucleophile to  $\pi^*$  leads to a tetrahedral product

e.g. nucleophilic 1,2-addition

d) The reverse of c) is 1,2-elimination

e.g. bimolecular elimination by the E2 mechanism

e) Addition of an electrophile to a  $\pi$  bond

e.g. electrophilic 1,2 addition

f) Addition of  $H^+$  to a  $\pi$  bond may lead to elimination

e.g. elimination by the E1 mechanism

g) Addition of an electrophile to a benzene ring

e.g. electrophilic aromatic substitution by the  $S_{EAr}$  mechanism

h) Reactions of alkenes with dienes/carbenes

e.g. pericyclic reaction such as Diels-Alder cycloaddition

i) Reactions of alkenes with radical species

## Redox Concepts in Organic Chemistry

Recall that: Oxidation =

Reduction =

It is generally helpful to consider groupings in organic molecules in terms of those that are “at the same oxidation level”. Typically, this equates to how many bonds to heteroatoms (e.g. hal, N, O ...) there are.

Level 0

Level 1

Level 2

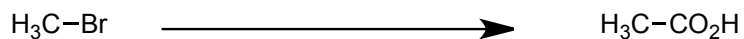
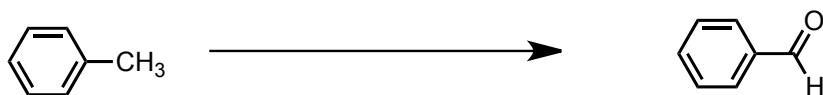
Level 3

Level 4

We can relate diverse molecules by imagining replacing each C-heteroatom bond with a bond to OH and then eliminating water to create a stable molecule

Unsaturated molecules can be so related by the hypothetical addition of water that can be useful when comparing synthetic equivalents later in the course.

How could we achieve the following synthetic transformations?



Orbitals and Mechanism 1

