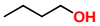
Organic Chemistry – The Functional Group Approach

alkane
(no F.G.)

non-polar (grease, fats)

tetrahedral



alcohol

polar (water soluble)

tetrahedral

halide

non-polar (water insoluble)

tetrahedral

alkene

non-polar (water insoluble)

trigonal

alkyne

non-polar (water insoluble)

linear

aromatic

non-polar (water insoluble)

flat

aldehyde/ketone

polar (water soluble)

trigonal

imine

polar (water soluble)

trigonal

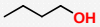
YSU

Organic Chemistry – The Functional Group Approach

alkane
(no F.G.)

non-polar (grease, fats)

tetrahedral



alcohol

polar (water soluble)

tetrahedral

halide

non-polar (water insoluble)

tetrahedral

alkene

non-polar (water insoluble)

trigonal

alkyne

non-polar (water insoluble)

linear

aromatic

non-polar (water insoluble)

flat

aldehyde/ketone

polar (water soluble)

trigonal

imine

polar (water soluble)

trigonal

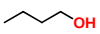
YSU

Organic Chemistry – The Functional Group Approach

alkane
(no F.G.)

non-polar (grease, fats)

tetrahedral



alcohol

polar (water soluble)

tetrahedral

halide

non-polar (water insoluble)

tetrahedral

alkene

non-polar (water insoluble)

trigonal

alkyne

non-polar (water insoluble)

linear

aromatic

non-polar (water insoluble)

flat

aldehyde/ketone

polar (water soluble)

trigonal

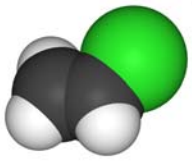
imine

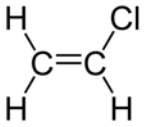
polar (water soluble)

trigonal

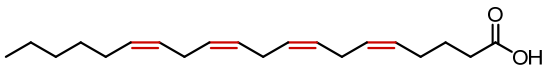
YSU

Carey Chapter 5 – Structure and Preparation of Alkenes

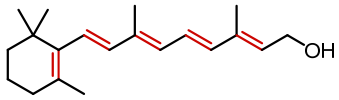




Vinyl chloride



Arachidonic acid



Vitamin A

YSU

Carey Chapter 5 – Structure and Preparation of Alkenes

Double bond - now dealing with sp^2 hybrid carbon

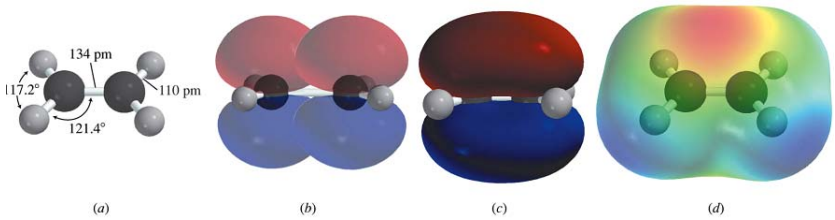


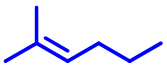
Figure 5.1 – Different representations of the C=C motif

YSU

5.1 Structure and Nomenclature of Alkenes

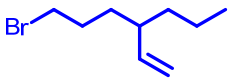
1-butene

1-hexene

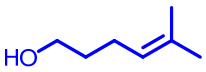


2-methyl-2-hexene

2,3-dimethyl-2-butene



6-bromo-3-propyl-1-hexene

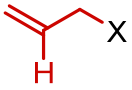


5-methyl-4-hexen-1-ol

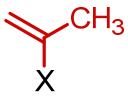
YSU

5.1 Common Alkene Substituents

vinyl

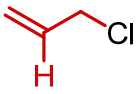


allyl

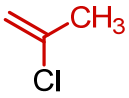


isopropenyl

Vinyl chloride



Allyl chloride

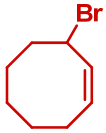


Isopropenyl chloride

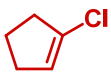
YSU

5.1 Cycloalkenes – Structure and Nomenclature

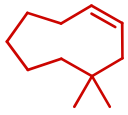
cyclohexene



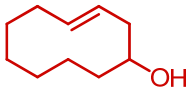
3-bromocyclooctene



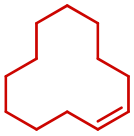
1-chlorocyclopentene



cyclohexene



3-bromocyclooctene



1-chlorocyclopentene

YSU

5.2 Structure and Bonding in Ethylene

Double bond - now dealing with sp^2 hybrid carbon

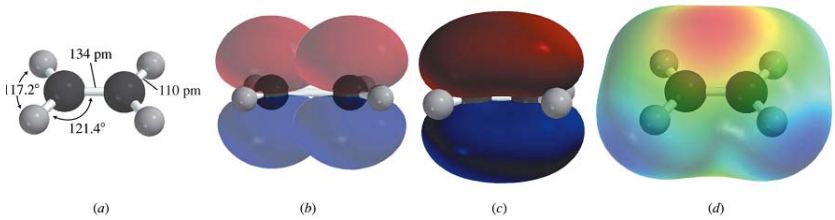
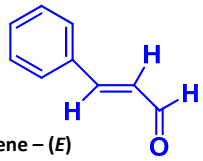


Figure 5.1 – Different representations of the C=C motif

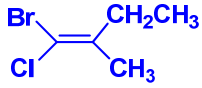
YSU

5.3-5.4 *cis-trans* Isomerism in Alkenes

1-butene **2-methylpropene** ***cis*-2-butene** ***trans*-2-butene**



***trans* alkene – (*E*)**

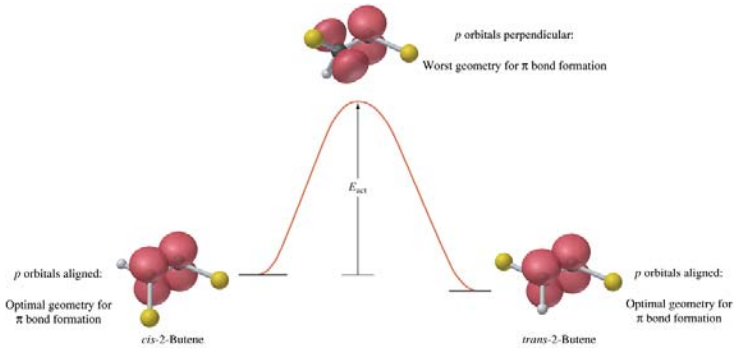


***cis* alkene (*Z*)**

See Table 5.1 for priority rules

YSU

Interconversion of *cis* and *trans*-2-butene



YSU

5.5-5.6 Heats of combustion of isomeric C_4H_8 alkenes

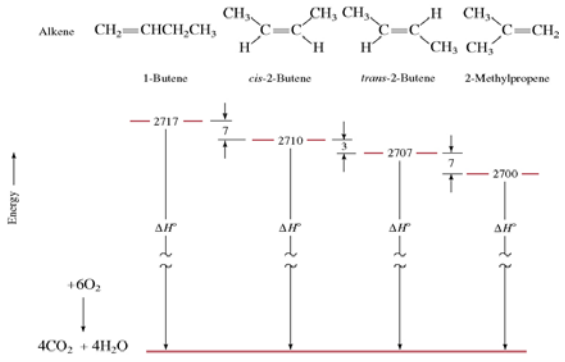


Figure 5.3

YSU

5.5-5.6 Relative Stabilities of Regioisomeric Alkenes

Generally, the more substituted an alkene, the more stable

sp^2-hybridized carbons of an alkene are more electronegative than sp^3-hybridized carbon and are stabilized by electron-donating substituents.

Methyl group is a better electron-donating substituent than hydrogen.

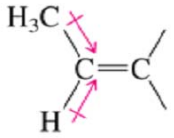


Figure 5.2 – **Inductive effect of alkyl groups contributing to alkene stability**

YSU

Molecular models of *cis*-2-butene and *trans*-2-butene

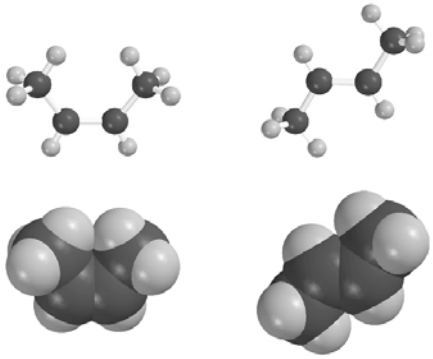
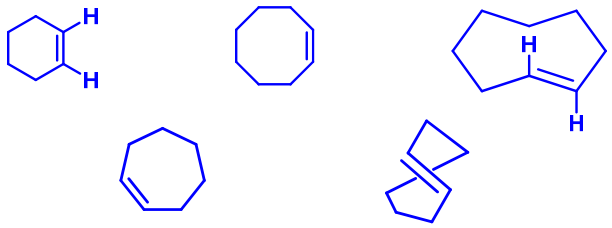


Figure 5.4

YSU

5.7 Cycloalkenes - *trans* not necessarily more stable than *cis*

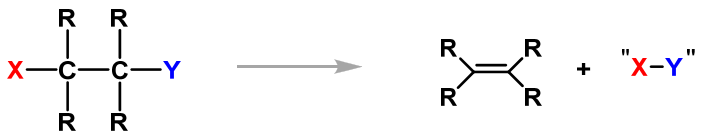


***Cis*-cycloheptene and *trans*-cycloheptene**

C-12 *cis* and *trans* ~ equal in energy

YSU

5.8 Preparation of Alkenes - Elimination reactions

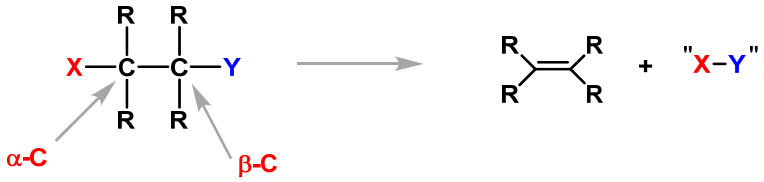


Involves loss of atoms or groups from adjacent carbons

X often = H; Y = good leaving group

YSU

5.8 Preparation of Alkenes - Elimination reactions

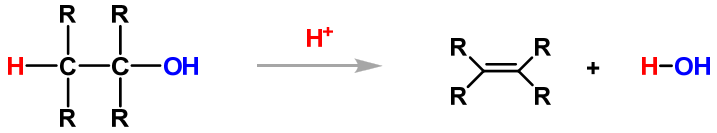


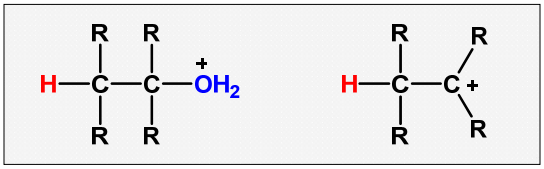
Involves loss of atoms or groups from adjacent carbons

X often = H; Y = good leaving group

YSU

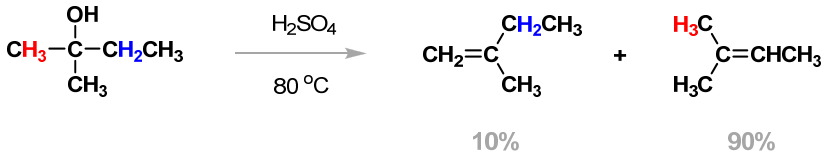
5.9 Dehydration of Alcohols – Acid-Catalysis





YSU

5.10 Zaitsev Rule - Regioselectivity

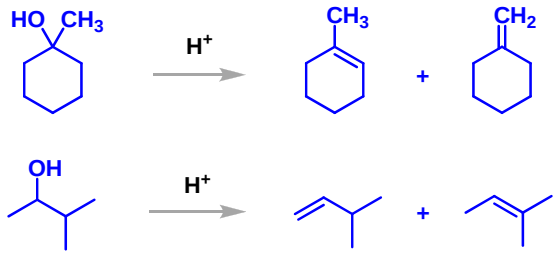


10% 90%

Dehydration usually results in more highly substituted alkene being major product - Zaitsev rule (*regioselectivity*)

YSU

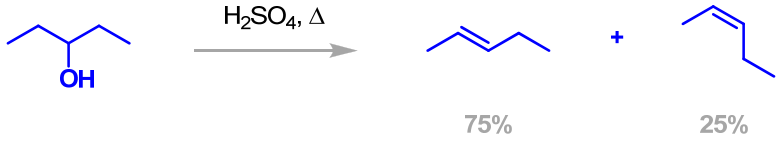
5.10 Zaitsev Rule - Regioselectivity



YSU

5.11 Stereoselectivity in Alcohol Dehydration

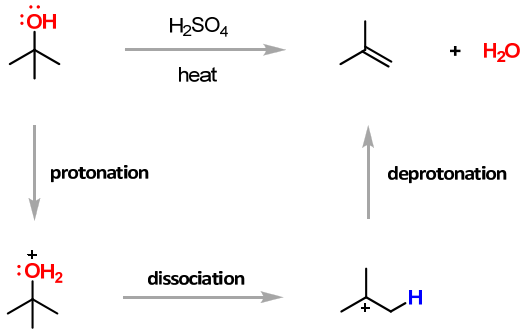
One stereoisomer is usually favoured in dehydrations



When *cis* and *trans* isomers are possible in this reaction and the more stable isomer is usually formed in higher yield

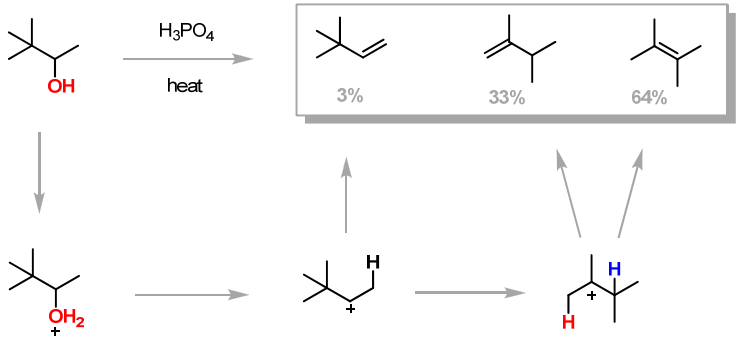
YSU

5.12 Acid-catalyzed Alcohol Dehydration – E1



YSU

5.13 Carbocation Rearrangements in E1 Reactions



YSU

Orbital representation of methyl migration

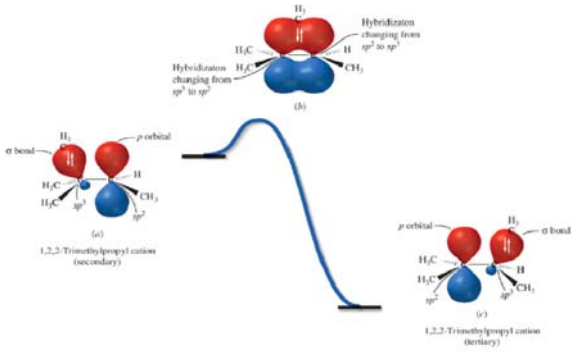
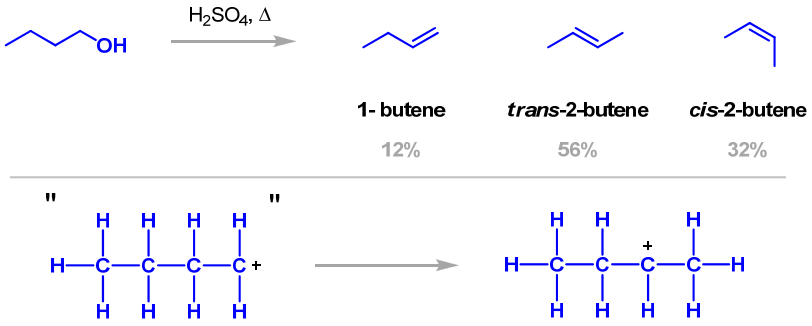


Figure 5.6

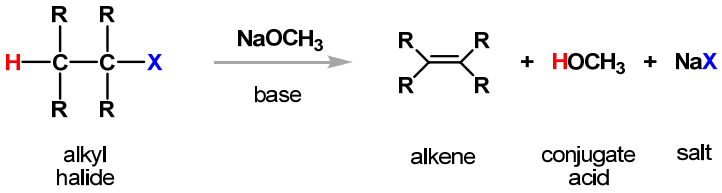
YSU

5.13 Hydride shifts to more stable carbocations



YSU

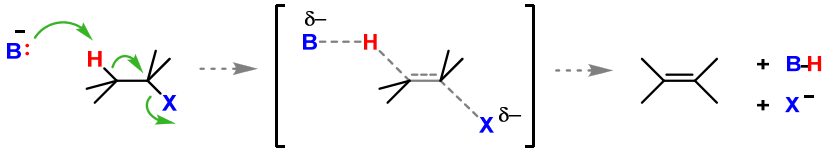
5.14 Dehydrohalogenation - Elimination with loss of H-X



Zaitsev rule followed for regioisomers when a small base such as $NaOCH_3$, $NaOCH_2CH_3$ is used. *Trans* usually favoured over *cis*.

YSU

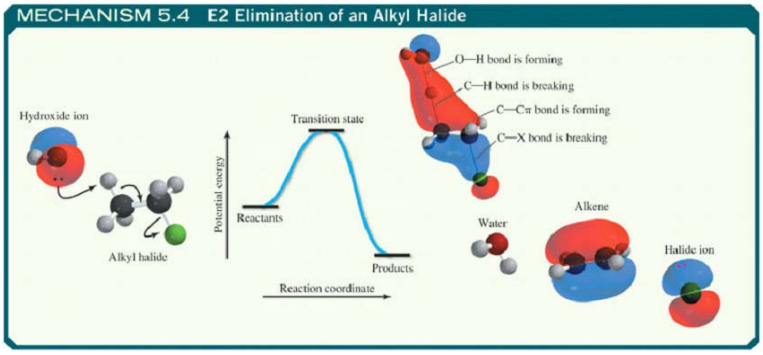
5.15 The E2 Mechanism - Bimolecular Elimination



- ✓ Reaction is concerted
- ✓ Rate depends on [base][alkyl halide] i.e. Bimolecular - E2
- ✓ Bond-forming & bond-breaking events all occur at the same time

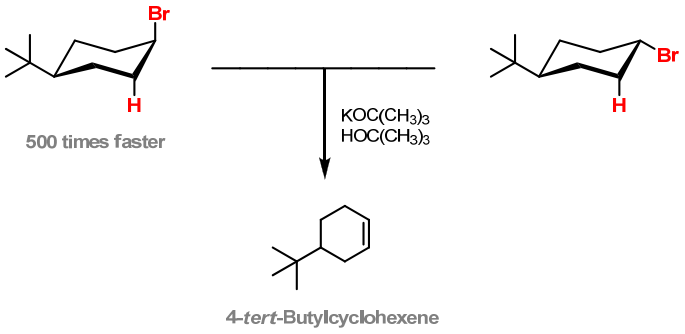
YSU

5.15 The E2 Mechanism - Bimolecular Elimination



YSU

5.16 Anti Elimination faster than Syn Elimination



YSU

Conformations of *cis*- and *trans*-4-*tert*-butylcyclohexyl

cis-4-*tert*-Butylcyclohexyl bromide

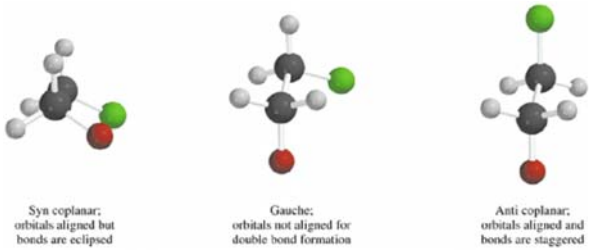
Axial halide is in proper orientation for anti elimination with respect to axial hydrogens on adjacent carbon atoms. Dehydrobromination is rapid.

trans-4-*tert*-Butylcyclohexyl bromide

Equatorial halide is gauche to axial and equatorial hydrogens on adjacent carbon; cannot undergo anti elimination in this conformation. Dehydrobromination is slow.

YSU

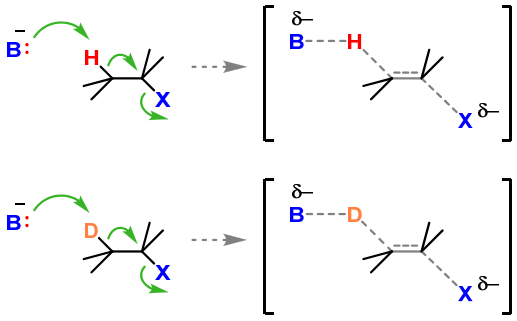
Favourable conformations for fast elimination



E2 Elimination usually faster when H and leaving group are *anti periplanar* as opposed to *syn periplanar*.

YSU

5.17 Kinetic Isotope Effects and the E2 Mechanism



C-D bond is stronger than C-H

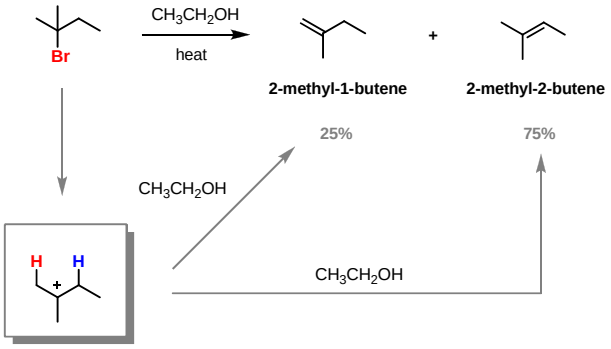
Breaking of C-D is slower and, if this occurs in the R.D.S., a kinetic isotope effect (k.i.e.) is observed:

k.i.e. = (K_H/K_D)

Typically 3-8 if the event occurs in the R.D.S. of a reaction, e.g. E2

YSU

5.18 Different Halide Elimination Mechanism - E1



YSU