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

- **alkyne**
  - non-polar (water insoluble)
  - linear

- **aromatic**
  - non-polar (water insoluble)
  - flat

- **aldehyde/ketone**
  - polar (water soluble)
  - trigonal

- **amine**
  - polar (water soluble)
  - trigonal

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Carey Chapter 5 – Structure and Preparation of Alkenes

- **Vinyl chloride**

- **Arachidonic acid**

- **Vitamin A**
Double bond - now dealing with \( sp^2 \) hybrid carbon

**Figure 5.1 – Different representations of the C=C motif**

### 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-hexene-1-ol
5.1 Common Alkene Substituents

- Vinyl
- Allyl
- Isopropenyl
- Vinyl chloride
- Allyl chloride
- Isopropenyl chloride

5.1 Cycloalkenes – Structure and Nomenclature

- Cyclohexene
- 3-bromocyclooctene
- 1-chlorocyclopentene
- 1-chlorocyclopentene
5.2 Structure and Bonding in Ethylene

Double bond - now dealing with \( sp^2 \) hybrid carbon

![Different representations of the C=C motif](image)

**Figure 5.1 – Different representations of the C=C motif**

5.3-5.4 cis-trans Isomerism in Alkenes

1-butene

2-methylpropene

\textbf{cis}-2-butene

\textbf{trans}-2-butene

\begin{align*}
\text{trans alkene} & \rightarrow (E) \\
\text{cis alkene} & \rightarrow (Z)
\end{align*}

\begin{align*}
\text{Br} & \quad \text{CH}_2\text{CH}_3 \\
\text{Cl} & \quad \text{CH}_3 \quad \text{CH}_3
\end{align*}

\text{See Table 5.1 for priority rules}
Interconversion of cis and trans-2-butene

5.5-5.6 Heats of combustion of isomeric C₄H₈ alkenes

Figure 5.3
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

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

Figure 5.4
5.7 Cycloalkenes - *trans* not necessarily more stable than *cis*

Cis-cycloheptene and *trans*-cycloheptene

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

5.8 Preparation of Alkenes - Elimination reactions

Involves loss of atoms or groups from adjacent carbons

X often = H; Y = good leaving group
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Involves loss of atoms or groups from adjacent carbons

\[ X \text{ often } = \text{H; } Y = \text{good leaving group} \]

5.9 Dehydration of Alcohols – Acid-Catalysis

\[ \text{H} - \text{C} - \text{C} - \text{OH} \xrightarrow{\text{H}^+} \text{R} - \text{C} = \text{C} - \text{OH}_2 \]
Dehydration usually results in more highly substituted alkene being major product - Zaitsev rule (regioselectivity)
5.11 Stereoselectivity in Alcohol Dehydration

One stereoisomer is usually favoured in dehydrations

\[
\text{cis} + \text{trans} \rightarrow \text{cis} + \text{trans} \quad \text{75%} + \text{25%}
\]

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

5.12 Acid-catalyzed Alcohol Dehydration – E1

\[
\text{protonation} \quad \text{deprotonation}
\]

\[
\text{dissociation}
\]
5.13 Carbocation Rearrangements in E1 Reactions

\[
\begin{align*}
\text{CH} & \xrightarrow{\text{H}_2\text{PO}_4, \text{heat}} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \\
\text{CH}_2 & \xrightarrow{\text{H}_2\text{PO}_4, \text{heat}} \text{CH}_2 \text{CH}_2 \text{CH} = \text{CH}_2
\end{align*}
\]

3% 33% 64%

Orbital representation of methyl migration

Figure 5.6
5.13 Hydride shifts to more stable carbocations

$$\text{OH} \xrightarrow{\text{H}_2\text{SO}_4, \Delta} \text{trans-2-butene}$$

1-butene    trans-2-butene    cis-2-butene
12%         56%            32%

5.14 Dehydrohalogenation - Elimination with loss of H-X

$$\text{R} - \text{C} - \text{C} - \text{X} \xrightarrow{\text{NaOCH}_3, \text{base}} \text{R} - \text{C} = \text{C} - \text{R} + \text{HOCH}_3 + \text{NaX}$$

Zaitsev rule followed for regioisomers when a small base such as NaOCH$_3$, NaOCH$_2$CH$_3$ is used. Trans usually favoured over cis.
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
5.16 Anti Elimination faster than Syn Elimination

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.
Favourable conformations for fast elimination

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

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:

\[
k.i.e. = \frac{K_H}{K_D}
\]

Typically 3-8 if the event occurs in the R.D.S. of a reaction, e.g. E2
5.18 Different Halide Elimination Mechanism - E1

\[
\begin{align*}
\text{Br} & \xrightarrow{\text{heat}} \text{CH}_2\text{CH}_2\text{OH} & \text{2-methyl-1-butene} & + & \text{2-methyl-2-butene} \\
\text{CH}_2\text{CH}_2\text{OH} & & & \text{CH}_2\text{CH}_2\text{OH} & \text{25%} & \text{75%} \\
\end{align*}
\]