Alkenes: Geometrical Isomerism, Electrophilic Addition and Addition of Hydrogen

NEET UG Chemistry — Study Notes

1. Geometrical Isomerism in Alkenes

Definition

Geometrical isomerism is a type of stereoisomerism arising from restricted rotation around a carbon–carbon double bond, resulting in different spatial arrangements of groups.

The C=C double bond consists of one sigma (σ) bond and one pi (π) bond. Rotation around it would break the π bond, so free rotation is restricted.

Conditions for geometrical isomerism

Each carbon atom of the double bond must have **two different groups** attached to it.

For example, but-2-ene shows geometrical isomerism, but but-1-ene does not.

Example: But-2-ene

Cis-but-2-ene: The two methyl groups are on the same side of the double bond.

Trans-but-2-ene: The two methyl groups are on opposite sides of the double bond.

Property	Cis-but-2-ene	Trans-but-2-ene
Position of methyl groups	Same side	Opposite sides
Molecular formula	C_4H_8	C_4H_8
Connectivity	Same	Same
Dipole moment	Generally non-zero	Approximately zero due to cancellation
Stability	Generally less stable	Generally more stable because of lower steric repulsion

When cis/trans naming is insufficient

For alkenes with four different substituents, use the **E/Z system** based on priority rules.

- **Z (zusammen):** Higher-priority groups are on the same side.
- **E (entgegen):** Higher-priority groups are on opposite sides.

Priority is assigned using the Cahn–Ingold–Prelog rules: the atom with the higher atomic number receives higher priority.

NEET point: A double-bond carbon attached to two identical groups prevents geometrical isomerism around that double bond.

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2. Electrophilic Addition to Alkenes

What is electrophilic addition?

Electrophilic addition is a reaction in which an electrophile attacks the electron-rich double bond of an alkene, and two new sigma bonds form as the π bond is broken.

Alkenes undergo this reaction because their π electrons are relatively accessible and attract electrophiles.

General reaction

\[\mathrm{C=C + A-B \longrightarrow A-C-C-B} \]

Here, A and B represent the groups added across the double bond.

Mechanism: Addition of HBr to propene

\[\mathrm{CH_3CH=CH_2 + HBr \longrightarrow CH_3CHBrCH_3} \]

The major product under ordinary ionic conditions is **2-bromopropane**.

Step 1: Protonation of the double bond

The π electrons attack H^+ from HBr. Hydrogen attaches to the terminal carbon, producing the more stable secondary carbocation:

\[\mathrm{CH_3CH=CH_2 + H^+ \longrightarrow CH_3-C^+H-CH_3} \]

Step 2: Nucleophilic attack

The bromide ion attacks the carbocation:

\[\mathrm{CH_3-C^+H-CH_3 + Br^- \longrightarrow CH_3CHBrCH_3} \]

Why is 2-bromopropane the major product?

The reaction preferentially forms the more stable **secondary carbocation** rather than a primary carbocation.

This illustrates **Markovnikov's rule**:

> In the addition of HX to an unsymmetrical alkene, hydrogen generally attaches to the carbon already bearing more hydrogen atoms, while X attaches to the other carbon.

This rule applies to ordinary ionic addition of HX; radical addition of HBr under peroxide conditions is an important exception.

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3. Addition of Hydrogen: Hydrogenation of Alkenes

Definition

Hydrogenation is the addition of hydrogen (H_2) across the carbon–carbon double bond of an alkene to form an alkane.

It is an example of an **addition reaction** and is commonly used to convert unsaturated hydrocarbons into saturated hydrocarbons.

General reaction

$$\boxed{\mathrm{Alkene + H_2 \xrightarrow{Ni/Pt/Pd} Alkane}}$$

The reaction is usually carried out using a finely divided metal catalyst such as **nickel (Ni), platinum (Pt), or palladium (Pd)**.

Examples

1. Hydrogenation of ethene

$$\mathrm{CH_2=CH_2 + H_2 \xrightarrow{Ni} CH_3-CH_3}$$

Ethene → Ethane

2. Hydrogenation of propene

$$\mathrm{CH_3-CH=CH_2 + H_2 \xrightarrow{Ni} CH_3-CH_2-CH_3}$$

Propene → Propane

3. Hydrogenation of but-2-ene

$$\mathrm{CH_3-CH=CH-CH_3 + H_2 \xrightarrow{Ni} CH_3-CH_2-CH_2-CH_3}$$

But-2-ene → Butane

Mechanism of catalytic hydrogenation

1. Hydrogen molecules adsorb onto the metal catalyst's surface.
2. The H–H bond weakens and hydrogen atoms become available on the surface.
3. The alkene adsorbs onto the catalyst through its π bond.
4. Hydrogen atoms add across the double bond.
5. The alkane formed leaves the catalyst surface.

Hydrogenation is generally an **exothermic reaction**.

Importance and uses

- Converts unsaturated hydrocarbons into saturated hydrocarbons.
- Is used in the manufacture of various chemicals.
- Hydrogenation of vegetable oils can increase their saturation and alter their physical properties. Partial hydrogenation may produce trans fats, which are undesirable in the diet.

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4. Quick Comparison for NEET

Feature	Geometrical isomerism	Electrophilic addition	Hydrogenation
Type	Stereoisomerism	Chemical reaction	Chemical reaction
Main cause	Restricted rotation around C=C	Attack by an electrophile	Addition of H_2 across C=C
Requirement	Each double-bond carbon has two different groups	Electron-rich C=C bond	Alkene and hydrogen
Product	Different spatial isomers	Addition product	Alkane
Example	Cis- and trans-but-2-ene	Propene + HBr	Ethene + H_2

5. NEET Practice MCQs

1. Which alkene exhibits geometrical isomerism?

A. Ethene
B. Propene
C. But-1-ene
D. But-2-ene

2. The major product of propene reacting with HBr under ordinary ionic conditions is:

A. 1-Bromopropane
B. 2-Bromopropane
C. 1,2-Dibromopropane
D. Propane

3. Which catalyst can be used for hydrogenation of alkenes?

A. NaCl
B. H_2SO_4
C. Ni
D. NaOH

4. Hydrogenation of ethene produces:

A. Ethyne
B. Ethane
C. Ethanol
D. Ethanal

5. In electrophilic addition of HX to an unsymmetrical alkene, the major product under ordinary ionic conditions generally follows:

A. Markovnikov's rule
B. Saytzeff's rule
C. Huckel's rule
D. Hund's rule

Answer key

1. **D** — But-2-ene
2. **B** — 2-Bromopropane
3. **C** — Ni
4. **B** — Ethane
5. **A** — Markovnikov's rule