Acid-Catalyzed Hydration of Alkenes

The reaction is acid catalyzed; typical hydration medium is 50% H₂SO₄, 50% H₂O.

Follows Markovnikov's Rule

Mechanism

Involves a carbocation intermediate.

The reaction is the reverse of acid-catalyzed dehydration of alcohols to alkenes.
Addition of Water to Alkene (alcohols)

Mechanism for the acid-catalyzed addition of water:

- Addition of the nucleophile
- Addition of the electrophile
- H₂O removes proton, regenerating the acid catalyst

CH₂=CH₂ + H₂O → CH₃CH₂OH

Principle of Microscopic Reversibility

In an equilibrium process, the same intermediates and transition states are encountered in the forward direction and the reverse, but in the opposite order.

H₂C
C=CH₂ + H₂O → CH₃CH₂OH

Addition of Water to Alkenes (alcohols)

Question

Which alkene will undergo acid-catalyzed hydrolysis at the fastest rate?

A) B) C) D)

H₂C
C=CH₂ + H₂O → CH₃CH₂OH

H₂C
C=CH₂ + H₂O → CH₃CH₂OH

Question

The product isolated from the acid-catalyzed hydration of (Z)-3-methyl-2-pentene is:

A) 2-ethyl-2-butanol
B) 2-ethyl-1-butanol
C) 3-methyl-2-pentanol
D) 3-methyl-3-pentanol
The product isolated from the acid-catalyzed hydration of (E)-3-methyl-2-pentene is:
A) chiral
B) achiral

Regiochemistry withstanding, in order to understand the stereochemistry of the product, you must consider two things:
(1) Stereochemistry of the starting alkene (cis or trans, Z or E)
(2) Stereochemistry of the addition (syn or anti)

Optically inactive reactants produce optically inactive products. (Racemic mixtures are optically inactive)
The corollary is that an optically active starting material MAY produce an optically active product depending on the mechanism.

The product isolated from the acid-catalyzed hydration of (E)- or (Z)-3-methyl-2-pentene is:
A) optically active
B) an optically inactive racemic mixture
C) an optically inactive enantiomer
Needed: a method for hydration of alkenes with a regioselectivity opposite to Markovnikov’s rule.

Suppose you wanted to prepare 1-decanol from 1-decene?

Two-step reaction sequence called hydroboration-oxidation converts alkenes to alcohols with a regiochemistry opposite to Markovnikov’s rule.

1. hydroboration
2. oxidation

Hydroboration can be viewed as the addition of borane (BH₃) to the double bond. But BH₃ is not the reagent actually used.

Diborane (B₂H₆) normally used in an ether-like solvent called “diglyme”

Hydroboration reagents:

Organoborane formed in the hydroboration step is oxidized with hydrogen peroxide.
Features of Hydroboration-Oxidation

- Hydration of alkenes
- Regioselectivity opposite to Markovnikov's rule
- No rearrangement
- Stereospecific syn addition

Example

\[
\text{1. BH}_3 \text{ diglyme} \\
\text{2. H}_2\text{O}_2 \text{ HO}^{-} \\
\]

Example

\[
\text{H}_2\text{C} \quad \text{C} = \text{C} \quad \text{CH}_3 \\
\text{H}_2\text{C} \quad \text{H} \\
\]

Example

\[
\text{1. BH}_3 \text{ diglyme} \\
\text{2. H}_2\text{O}_2 \text{ HO}^{-} \\
\]

Example

\[
\text{H}_3\text{C} \quad \text{C} \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{H} \\
\]

Features of Hydroboration-Oxidation

- Hydration of alkenes
- Regioselectivity opposite to Markovnikov's rule
- No rearrangement
- Stereospecific syn addition

6.13 Stereochemistry of Hydroboration-Oxidation
**Question**

Hydroboration-oxidation of which one of the following yields a primary alcohol as the major product?

A) ![Structure A]  
B) ![Structure B]  
C) ![Structure C]  
D) ![Structure D]

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**6.15**

Addition of Halogens to Alkenes

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**Question**

A) The product is achiral  
B) The product is optically active  
C) The product is a racemic mixture  
D) The product is a single enantiomer

---

**Syn Addition**

H and OH become attached to same face of double bond.

\[ \text{CH}_3\text{C}!=\text{CH}_3 + \text{B}_3\text{H}_6 \rightarrow \text{CH}_3\text{C}!\text{C}H_3 \]

Only product is trans-2-methylcyclopentanol (86% yield).

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**Introduction**

Hydroboration-oxidation adds the elements of water to an alkene. In the first step, borane adds from one side of the alkene. Click "Start" to begin.

\[ \text{CH}_3\text{C}!=\text{CH}_3 + 3\text{BH}_3 \rightarrow \text{CH}_3\text{C}!\text{CH}_3 \]

---

**Addition of Halogens**

\[ \text{CH}_3\text{C}!=\text{CH}_3 + 2\text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{C}!\text{OH} \]

---

**Conclusion**

A) The product is achiral  
B) The product is optically active  
C) The product is a racemic mixture  
D) The product is a single enantiomer
**General features**

Electrophilic addition to double bond forms a vicinal dihalide.

**Example**

\[
\text{CH}_3\text{CH} = \text{CHCH(\text{CH}_3)}_2 + \text{Br}_2 \xrightarrow{\text{CHCl}_3, 0^\circ \text{C}} \text{CH}_3\text{CHCHCH(\text{CH}_3)_2} \quad \text{(100%)}
\]

**Scope**

Limited to \(\text{Cl}_2\) and \(\text{Br}_2\).
- \(\text{F}_2\) addition proceeds with explosive violence.
- \(\text{I}_2\) addition is endothermic: vicinal diiodides dissociate to an alkene and \(\text{I}_2\).

**14a**

Halogen Addition to Alkenes

**6.16 Stereochemistry of Halogen Addition**

- **anti addition**

**Example**

\[
\text{trans-1,2-Dibromocyclopentane}
\]

80% yield; only product
trans-1,2-Dichlorocyclooctane 73% yield; only product

Mechanism of Halogen Addition to Alkenes: Halonium Ions

Br₂ is not polar, but it is polarizable

two steps:
1. formation of bromonium ion
2. nucleophilic attack on bromonium ion by bromide

Addition of Halogens to Alkenes

H₂C=CH₂ + Br₂ → H₂C=CH₂• Br₂ → H₂C=CHBr + H₂C=CHBr

The Halonium Ion 1

Relative Rates of Bromination

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Rate (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>1</td>
</tr>
<tr>
<td>Propene</td>
<td>61</td>
</tr>
<tr>
<td>2-Methylpropene</td>
<td>5400</td>
</tr>
<tr>
<td>2,3-Dimethyl-2-butene</td>
<td>920,000</td>
</tr>
</tbody>
</table>

More highly substituted double bonds react faster.
Alkyl groups on the double bond make it more electron rich.²

Question

Arrange the alkenes in order of decreasing rate of reaction toward bromine addition:
2-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene

A) 2-methyl-1-butene > 3-methyl-1-butene > 2-methyl-2-butene
B) 3-methyl-1-butene > 2-methyl-1-butene > 2-methyl-2-butene
C) 2-methyl-2-butene > 2-methyl-1-butene > 3-methyl-1-butene
D) 2-methyl-2-butene > 3-methyl-1-butene > 2-methyl-1-butene
Diastereomers

Diastereomers have different physical properties:
- BP, MP, density, refractive index, solubility
- Can be separated through conventional means (distillation, recrystallization, chromatography)

\[
\begin{align*}
\text{trans-1,2-dibromocyclopentane} & : \\
\text{80\% yield} & : \text{2 asymmetric carbon atoms,} \\
\text{Chiral product} & : \text{Optically inactive,} \\
\text{Racemic mixture, only products formed} & : \\
\text{CO}_2\text{H} & : \text{Br} \\
\text{H} & : \text{H} \\
\text{Br} & : \text{H} \\
\text{CO}_2\text{H} & : \text{Br} \\
\text{MP} = 158^\circ\text{C} & : \text{MP} = 256^\circ\text{C} \\
\end{align*}
\]

Diastereomers

In general, diastereomers fall into two categories:
- Geometric isomers
- Stereoisomers containing two or more asymmetric atoms; (that are not enantiomers)
- Geometric isomers (cis-trans)

\[
\begin{align*}
\text{cis-2,3-dibromobutane} & : \\
\text{2,3-dibromobutane} & : \\
\text{2,3-dibromobutane} & : \\
\text{Enantiomers} & : \text{Diastereomers} \\
\text{Same compound} & : \text{Meso} \\
\text{Only 3 stereoisomers for 2,3-dibromobutane.} & : \\
\end{align*}
\]

Diastereomers

A compound with "n" asymmetric carbon atoms can have a maximum of \(2^n\) stereoisomers.

\[
\begin{align*}
\text{2,3-dibromobutane} & : \\
\text{2,3-dibromobutane} & : \\
\text{2,3-dibromobutane} & : \\
\text{Enantiomers} & : \text{Diastereomers} \\
\text{Same compound} & : \text{Meso} \\
\text{Only 3 stereoisomers for 2,3-dibromobutane.} & : \\
\end{align*}
\]

Question

The addition of bromine to cis-2-butene produces:

A) A single enantiomer
B) A product with one asymmetric carbon atom
C) An optically inactive meso product
D) A racemic mixture
E) 4 different stereoisomers each with 2 chiral carbon atoms
Question

The addition of bromine to trans-2-butene produces:
A) A single enantiomer
B) A product with one asymmetric carbon atom
C) An optically inactive meso product
D) A racemic mixture
E) 4 different stereoisomers each with 2 chiral carbon atoms

Diastereomers

When naming compounds containing multiple chiral atoms, you must give the configuration around each chiral atom:
- position number and configuration of each chiral atom, separated by commas, all in ( ) at the start of the compound name
- (S) \(\text{CH}_3\)
  - \(\text{H}\) \(\text{Br}\) \(\text{Cl}\) \(\text{H}\)
  - (2S, 3S)-2-bromo-3-chlorobutane

Diastereomers

Which ones are chiral? Name each one. Give the stereochemical relationship between them.

All of them are chiral.

Diastereomers

A and B: enantiomers
C and D: enantiomers
A and C: diastereomers
A and D: diastereomers
B and C: diastereomers
B and D: diastereomers

Conversion of Alkenes to Vicinal Halohydrins
Addition of Halogens in the Presence of Water (halohydrins)

alkenes react with $X_2$ to form vicinal dihalides

alkenes react with $X_2$ in water to give vicinal halohydrins

Examples

$H_2C\equiv CH_2 + Br_2 \rightarrow BrCH_2CH_2Br$ (70%)

$\text{Fischer projections of the stereoisomers of 3-bromo-2-butanol}$

$H_2C\equiv CH_2 + Br_2 \rightarrow BrCH_2CH_2OH$

$\text{Examples}$

$H_2C\equiv CH_2 + Cl_2 \rightarrow BrCH_2CH_2OH$

$\text{(70%)}$

$\text{Fischer projections of the stereoisomers of 3-bromo-2-butanol}$

$H_2C\equiv CH_2 + X_2 \rightarrow X-C-C-X$

$X-C-C-OH$

$H_2O$
Regioselectivity

Markovnikov’s rule applied to halohydrin formation: the halogen adds to the carbon having the greater number of hydrogens.

Explanation

Transition state for attack of water on bromonium ion has carbocation character: more stable transition state (left) has positive charge on more highly substituted carbon.