4. Reactions of Alkenes and Alkynes

Addition reaction of X–Y to the C=C and C=C multiple bonds



4.1 Addition of HX to Alkenes: Hydrohalogenation



The reaction is *regiospecific* – only one of the two possible directions of addition occurs.

Markovnikov's Rule

In the addition of HX to an alkene, the H attaches to the carbon with fewer alkyl substituents, and the X attaches to the carbon with more alkyl substituents The more highly substituted carbocation intermediate is formed.

$$\begin{array}{cccc} & & & H & & H \\ CH_3 - \overset{+}{C} - CH_2 & vs & CH_3 - \overset{+}{C} - \overset{+}{C}H_2 \\ CH_3 & & CH_3 \end{array}$$

chapter_04_01_Markov.ppt (Markovnikov vs Anti-Markovnikov addition)

Carbocation Stablity

Carbocation stability increases with increasing alkyl substitution: more highly substituted carbocations are more stable than less substituted ones because <u>alkyl</u> groups tend to donate electrons to the positively charged carbon atom.

chapter_04_02_carbocation.ppt

4.2 Addition of H₂O to Alkenes: Hydration

Water adds to alkenes to yield alcohols, ROH, a process called hydration.

 $\begin{array}{c} H & H \\ C = C & + \\ H & H \end{array} + H_2O \xrightarrow{H_3PO_4 \text{ catalyst}}{250 \circ C} \qquad CH_3CH_2OH$

The addition of water to an unsymmetrical alkene follows **Markovnikov's rule**, giving the more highly substituted alcohol as product.



Step 1. The alkene double bond reacts with H⁺ to yield a carbocation intermediate.

Step 2. Water acts as a nucleophile to donate a pair of electrons to form a carbon-oxygen bond and produce **a protonated alcohol intermediate**.

Step 3. Loss of H⁺ from the protonated alcohol intermediate then gives the neutral alcohol product and **regenerates the acid catalyst**.

Reaction energy diagram



The reaction conditions are so severe that molecules are sometimes destroyed by the high temperatures and strongly acidic conditions.

Some mild procedures for hydration.

(a) Oxymecuration-demercuration (Markovnikov addition)



(b) Hydroboration-oxidation (Anti-Markovnikov addition)



chapter_04_03_Hydration.ppt

4.3 Addition of X₂ to Alkenes: Halogenation

Addition of Br₂ acts as a simple and rapid laboratory test for unsaturation.



Anti-stereospecific addition reaction – the two Br atoms add to opposite face of the cyclopentene double bond.

The reaction intermediate is not a true carbocation but is instead **a bromonium ion**, $R-Br^+-R$, formed by overlap of bromine lone-pair electrons with the vacant *p* orbital of the neighboring carbon.



The bromine atom effectively "shield" one side of the molecule, reaction with Br⁻ ion in the second step occurs from the opposite side to give the anti product. <u>chapter 04 04 halogenation.ppt</u>

4.4 Addition of H₂ to Alkenes: Hydrogenation

Addition of H₂ to the C=C bond in the presence of a catalyst (Pd, PtO₂).

Heterogeneous process – the hydrogenation reaction occurs on the surface of solid catalyst particles rather than in solution.

Syn stereochemistry – both hydrogens add to the double bond from the same side.



chapter_04_05_hydrogenation.ppt

4.5 Oxidation of Alkenes: Hydroxylation and Cleavage

Hydroxylation of an alkene – the addition of an –OH group to each of the alkene carbons producing 1,2-diol (glycol) can be carried out by the reaction with potassium permanganate, KMnO₄, in basic solution.

Syn stereochemistry



When oxidation of the alkene is carried out with KMnO₄ in acidic solution, cleavage of the double bond occurs



4.6 Conjugated Dienes

Multiple bonds that alternate with single bonds are said to be **conjugated**. There is an **electronic interaction** between the two double bonds of a conjugated diene: *p* **orbital overlap across the central single bond – extra stabilization**.



conjugated diene



chapter_04_06_Conjugation.ppt

Addition reaction with electrophiles (1,2- vs 1,4-addition)



Allylic means "next to a double bond."

Stability of Allylic Carbocations: Resonance

The positively charged carbon atom has a vacant p orbital that can overlap the p orbitals of the neighboring double bond.

An allylic carbocation is symmetrical.

All three carbon atoms are sp^2 -hybridized, and each has a p orbital. The p orbital on the central carbon can overlap equally well with p orbitals on either of the two neighboring carbons, and the two electrons are free to move over the entire three-orbital array.





symmetrical

Neither of the resonance structure is correct by itself; the true structure of the allylic carbocation is somewhere between the two (two C-C bonds are equivalent).

An allylic carbocation has a single, unchanging structure called a resonance hybrid.

The greater the number of possible resonance forms, the greater the stability.

Resonance forms are imaginary.

Resonance forms differ only in the placement of their π or non-bonding electrons.

Resonance leads to stability.

chapter_04_07_allylic.ppt

4.7 Alkynes and Their Reactions

1. Nomenclature

The suffix -yne is used in the parent hydrocarbon name to denote an alkyne.

The position of the triple bond is indicated by its number in the chain – Numbering begins at the chain end nearer the triple bond.

$$\begin{array}{c} 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 \\ CH_3CH_2 - CHCH_2C \equiv CCH_2CH_3 \\ - & - & - \\ CH_3 \end{array}$$

6-Methyloct-3-yne

Compounds containing both double and triple bonds are called enynes.

Numbering of the hydrocarbon chain starts from the end <u>nearer the first multiple</u> <u>bond</u>, whether double or triple (double bonds receive lower numbers than triple <u>bonds</u>).

$$\begin{array}{c} \begin{array}{c} 7 & 6 & 5 & 4 & 3 & 2 & 1 \\ HC \equiv CCH_2CH_2CH_2CH = CH_2 \\ Hept-1-en-6-yne \end{array} \qquad \begin{array}{c} CH_3 \\ HC \equiv CCH_2CH - CH_2CH_2CH = CHCH_3 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ \hline 4-Methylnon-7-en-1-yne \end{array}$$

2. Addition of H₂



3. Addition of HX (HCI, HBr, and HI) – Markovnikov addition

 $\operatorname{CH}_3\operatorname{CH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{C}=\operatorname{CH} + \operatorname{HBr} \longrightarrow \operatorname{CH}_3\operatorname{CH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{C}=\operatorname{CH}_2$

4. Addition of X₂ (Br₂, Cl₂) – anti stereochemistry

$$CH_{3}CH_{2}CH_{2}CH_{2}C \equiv CH + Br_{2} \xrightarrow{CCl_{4}} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2} \xrightarrow{Br} CH_{3}CH_{2}$$

5. Addition of H₂O – Markovnikov addition

When an alkyne is treated with aqueous sulfuric acid in the presence of mercuric sulfate catalyst.

$$CH_{3}CH_{2}CH_{2}C \equiv CH + H_{2}O \xrightarrow{H_{2}SO_{4}} \begin{bmatrix} OH \\ CH_{3}CH_{2}CH_{2}C = CH_{2} \end{bmatrix} \xrightarrow{O} CH_{3}CH_{2}CH_{2}CCH_{3}$$

enol form keto form 78%

6. Formation of Acetylide Anions

Acidity of terminal alkynes (R-C=C-H): pK_a of 25

When a terminal alkyne is treated with a strong base such as sodium amide, NaNH₂, an **acetylide anion** is formed. Acetylide anions react only with <u>primary alkyl halides</u> to give alkylation products.

$$R-C \equiv \widehat{C} - H + \widehat{N}H_2 \stackrel{+}{Na} \longrightarrow R-C \equiv \widehat{C} \stackrel{-}{\otimes} \stackrel{+}{Na} + NH_3$$

$$Acetylide anion$$

$$R-C \equiv \widehat{C} \stackrel{-}{\otimes} \stackrel{+}{Na} + R'CH_2Br \longrightarrow R-C \equiv C-CH_2R'$$

$$chapter \ 04 \ 08 \ Alkynes.ppt$$