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Organic chemistry

Alkenes

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Introduction to Alkenes

- ✓ Alkenes are a class of hydrocarbons .They are unsaturated compounds with at least one carbon-to-carbon double bond. The double bond makes Alkenes more reactive than alkanes. Olefin is another term used to describe alkenes.
- □ The graphic shows three alkenes. The more complex alkene is commonly known as 1menthene, but its full proper IUPAC name is 1-methyl-2-(1-methylethyl)-cyclohexene..



Structure of Ethene - the Simplest Alkene

✓ Ethene is often written as CH2=CH2 which stands for:



- □ The double bond is shared by the two carbon atoms and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C2H4, whereas that for ethane is C2H6.
- Ethene is not a very complicated molecule. It is made up of four 1s1 hydrogen atoms and two 2s2 2px1 2py1 carbon atoms. These carbon atoms already have four electrons, but they each want to get four more so that they have a full eight (octet) in the valence shell. Having eight valence electrons around carbon gives the atom the same electron configuration as neon, a noble gas. Carbon wants to have the same configuration as neon because when it has eight valence electrons carbon is at its most stable, lowest energy state.

Nomenclature of Alkenes

F IUPAC Rules for Alkene Nomenclature

- 1. The ene suffix (ending) indicates an alkene or cycloalkene.
- 2. The longest chain chosen for the root name must include both carbon atoms of the double bond.
- 3. The root chain must be numbered from the end nearest a double bond carbon atom. If the double bond is in the center of the chain, the nearest substituent rule is used to determine the end where numbering starts.
- 4. The smaller of the two numbers designating the carbon atoms of the double bond is used as the double bond locator.
- 5. If more than one double bond is present the compound is named as a diene, triene or equivalent prefix indicating the number of double bonds, and each double bond is assigned a locator number.
- 6. Substituent groups containing double bonds are:
 - H₂C=CH- Vinyl group
 - H₂C=CH-CH₂- Allyl group





3-Ethyl-1-butene

5-Methyl-1,3-hexadiene



Naming Cycloalkenes



Preparation of Alkenes

Preparation of Alkenes by Partial Reduction

Alkynes on partial reduction with H_2 in the presence of suitable catalysts yield alkenes. Reduction of alkynes in the presence of palladised charcoal partially deactivated with poison such as PbCO₃, S or quinoline predominantly gives **cis-alkenes**. This catalyst is known as **Lindlar's catalyst**. In contrast, Na in liquid ammonia is used to obtain **trans isomers**.



Preparation of Alkenes from Alkyl Halides

Haloalkanes, also known as alkyl halides, on heating with a strong base such as alcoholic solution of potassium hydroxide eliminate one molecule of halogen acid (HCl, HBr or HI) to form alkenes. This reaction is known as **dehydrohalogenation**.

$$H - \begin{array}{c}H & H & H & H & H \\ \beta I & \alpha I & I & I \\ C & C & C & H & \xrightarrow{alc. KOH} & H - C = C - H \\ I & I & H & X \end{array}$$

Since in this reaction, hydrogen is removed from beta carbon, this reaction is also known as β -elimination. Some important points regarding this reaction such as Saytzeff rule are discussed in Elimination reactions in haloalkanes.

Preparation of Alkenes from Vicinal Dihalides

In vicinal dihalides, two halogens are attached to adjacent carbon atoms. Vicinal dihalides on reaction with Zn lose a molecule of ZnX_2 to form alkenes.



$$CH_{3} - CH - CH_{2} - Br + Zn \longrightarrow CH_{3} - CH = CH_{2} + ZnBr_{2}$$

Br

Preparation of Alkenes from Alcohols

Alcohols containing a β -hydrogen on heating with concentrated sulphuric acid (H₂SO₄) lose a molecule of water to form alkenes. Due to the elimination of water and use of acid, this reaction is known as **acidic dehydration of alcohols.** Since a hydrogen atom is eliminated from β -carbon, this reaction is an example of β -elimination.

$$CH_3CH_2OH \xrightarrow{\text{conc. H}_3SO_4} CH_2 = CH_2 + H_2O$$

Alternatively, the vapours of alcohols are passed over heated alumina at 623K-633K to form alkenes with the elimination of one molecule of water.



Physical Properties of Alkenes

Physical State and Odour of Alkenes

The first three members of alkenes — ethene, propene and butene are colourless gases; the next fourteen members are liquids, and the higher ones are solids. Alkenes are colourless and odourless with an exception of ethene which is a colourless gas with pleasant smell.

Boiling Points of Alkenes

The boiling point increases as the size increases. In fact, the boiling point increases by 20-30K with every $-CH_2$ group added (if we leave out first few members). Among isomers, the boiling point decreases with increase in branch. Amongst the alkenes that show geometrical isomerism, cis-alkenes have higher boiling points than the corresponding trans-isomers because cis-isomers being polar have stronger dipole-dipole interactions.

Dipole Moments of Alkenes

In symmetrical trans-alkenes, the dipole moments of individual groups is equal and opposite resulting in zero dipole moment. Unsymmetrical alkenes, however, have some net dipole moment because the individual groups are not equal.

Solubility of Alkenes

Alkenes being either non-polar or weakly polar molecules are insoluble in water and other polar solvents but are fairly soluble in non-polar solvents such as benzene, CCl₄, petroleum ether.

Density of Alkenes

All alkenes are lighter than water.

Reactions of Alkenes

Addition of Halogens to Alkenes

When halogens such as bromine, chlorine are added to alkenes, vicinal dihalides are formed. Iodine does not show addition reaction under normal conditions while fluorine reacts with alkenes too rapidly to be controlled in the laboratory.

Bromine test : The addition of bromine to unsaturated compounds in an organic solvent such as CCl₄ results in the disappearance of reddish-orange colour of bromine. Because of this reason, this reaction is used to test unsaturation.

$$CH_{2} = CH_{2} + Br_{2} \xrightarrow{CCl_{*}} CH_{2} - CH_{2}$$

Ethene reddish-
orange Br Br
1,2-Dibromoethane
colourless

Addition of hydrogen halides to Alkenes

The addition of hydrogen halides (HCl, HBr, HI) to alkenes yields alkyl halides (haloalkanes). The order of reactivity of the hydrogen halides is HCl > HBr > HI.



Markovnikov's rule

Markovnikov's rule states that in the addition reactions of unsymmetrical alkenes, the negative part of reagent gets attached to the carbon having lesser number of hydrogen atoms. Let us apply Markovnikov's rule to the above reaction :



Anti Markovnikov's rule

When HBr is added to unsymmetrical alkenes such as propene **in the presence of peroxide**, the negative part gets attached to the carbon which posses more number of hydrogen atoms. Since the rule is contrary to the Markovnikov's rule, it is called **Anti Markovnikov's rule**. This rule is also termed as **peroxide effect** or **Kharash effect**.

$$CH_3 - CH = CH_2 + HBr \xrightarrow{Peroxide} CH_3 - CH_2 - CH_2 - Br$$

Addition of Sulphuric Acid to Alkenes

The addition of cold conc. sulphuric acid to alkenes produces alkyl hydrogen sulphate. Unsymmetrical alkenes follow Markovnikov's rule.

$$CH_{2} = CH_{2} + \overset{+}{H} OSO_{2}OH \longrightarrow CH_{3} - CH_{2} - OSO_{2}OH$$

$$CH_{3} - CH = CH_{2} + HOSO_{2}OH \longrightarrow CH_{3} - CH - CH_{3}$$

$$I \\ OSO_{2}OH$$

$$Propyl hydrogen sulphate$$

The OSO₂OH in the above reaction can alternatively be written as HSO₄. For example :

 $C_2H_5OSO_2OH = C_2H_5HSO_4$

Addition of Water to Alkenes

Alkenes react with water in the presence of mineral acids to form alcohols in accordance with the Markonikov's rule. Since a molecule of water is added in this reaction, this reaction is termed as **hydration of alkenes**.



Ozonolysis of Alkenes

Ozonolysis of alkenes involves the addition of an ozone molecule (O_3) to alkene to form *ozonide* which are reduced with zinc dust and water to give smaller molecules.

