

BOOKS

- 1) Organic Chemistry Structure and Function, K. Peter C. Vollhardt, Neil Schore, 6th Edition
- 2) Organic Chemistry, T. W. Graham Solomons, Craig B. Fryhle
- 3) Organic Chemistry: A Short Course, H. Hart, L. E. Craine, D. J. Hart, C. M. Hadad,
- 4) Organic Chemistry: A Brief Course, R. C. Atkins, F.A. Carey

3. ALKENES

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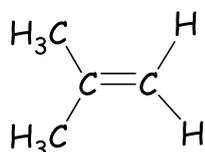
3.1 Nomenclature of Alkenes

Alkenes are named using the same general naming rules for alkanes, except that the suffix is now -ene.

C_3H_6 , $CH_3-CH=CH_2$ propene (common name is, propylene)

C_4H_8 , $CH_3-CH_2-CH=CH_2$ 1-Butene (common name is, butylene)

C_4H_8 $CH_3-CH=CH-CH_3$ 2-Butene (common name is, butylene)

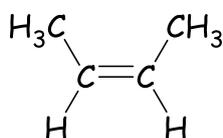


2-Methylpropene

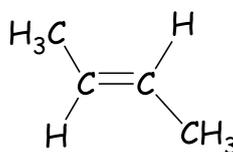
- If more than one double bond is present, the prefixes di-, tri-, tetra-, etc. are used before the -ene.

C_6H_{10} , $CH_3-CH=CH-CH_2-CH=CH_2$ 1,4-Hexadiene

- Cis/trans used for 1,2-disubstituted ethene. For example, there are two 2-butenes, which are geometric isomers:



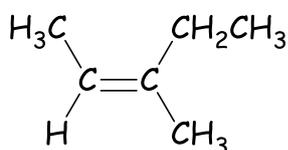
cis-2-butene



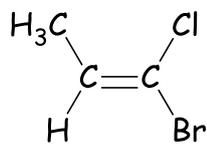
trans-2-butene

- For tri- and tetrasubstituted alkenes, it is necessary to use E, Z (or cis/trans) nomenclature to indicate which isomer it is.

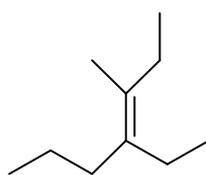
- E/Z system is recommended by IUPAC for the designation of geometric isomerism.



(Z)-3-methyl-2-pentene
(3-methyl-*cis*-2-pentene)



(E)-1-bromo-1-chloropropene



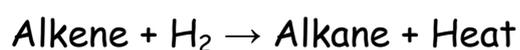
(E)-4-ethyl-3-methylhept-3-ene

3.2 Isomers of Alkenes

The presence of a carbon-carbon double can create two possible structures; *cis* isomer - two similar groups on same side of the double bond and *trans* isomer similar groups on opposite sides.

3.3 Relative Stabilities of Alkenes

The relative stabilities of alkenes can be measured using the exothermic heats of hydrogenation. Heat of hydrogenation:

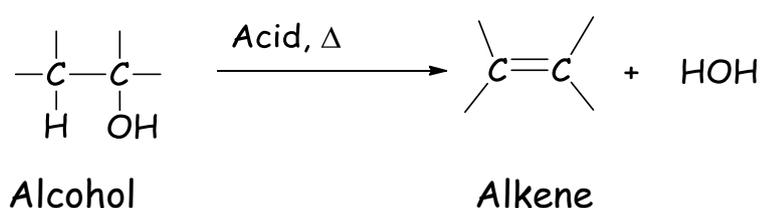


Generally *cis* alkenes are less stable than *trans* alkenes because of steric hindrance. Internal alkenes are more stable than terminal alkenes.

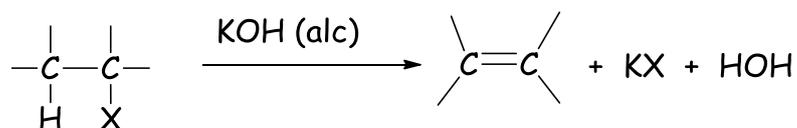
3.4 Synthesis of alkenes:

3.4.1 Dehydration of Alcohols

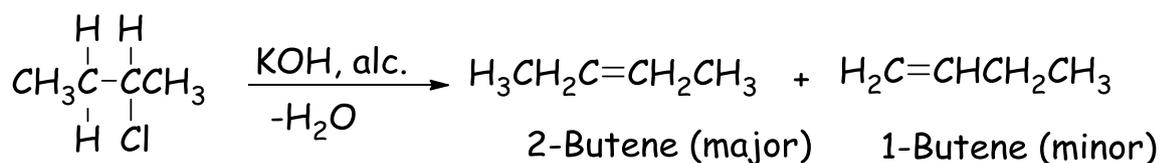
The reaction is acid catalyzed dehydration of alcohols and elimination is favored over substitution at higher temperatures. Typical acids used in dehydration are sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4).



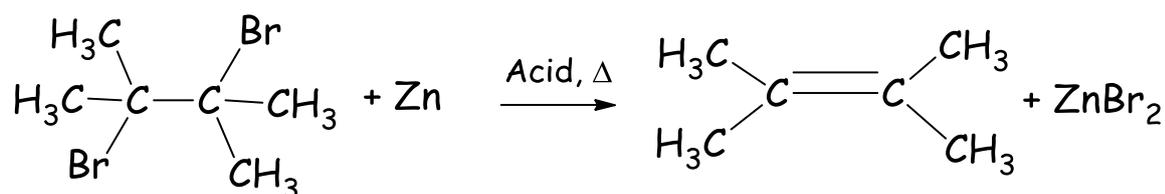
3.4.2 Dehydrohalogenation of alkyl halides



Alkoxide bases such as sodium ethoxide or potassium *tert*-butoxide are used as base in these reactions. Some hydrogen halides can eliminate to give two different alkene products.

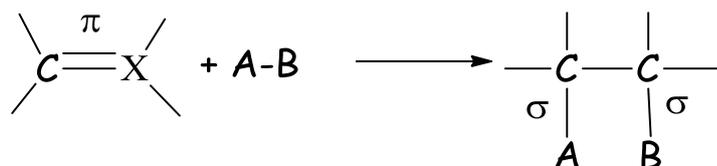


3.4.3 From Dihalalkanes- dehalogenation



3.5 Reactions of Alkenes

Alkenes contain the unsaturated $C=C$ functional group which characteristically undergo addition reactions. Electrophilic addition reactions of alkenes:



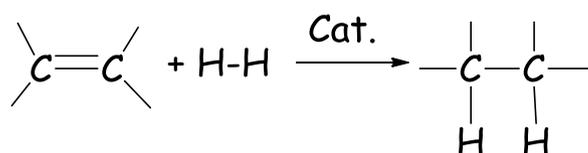
3.5.1 Combustion Reactions

Alkenes burn in presence of oxygen to produce carbon dioxide and heat.



3.5.2 Hydrogenation of Alkenes

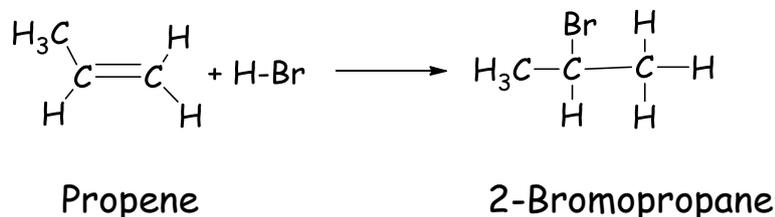
Hydrogen adds to alkenes in the presence of metal catalysts. This process is called a reduction or hydrogenation. An unsaturated compound becomes a saturated (with hydrogen) compound.



Catalysts : Pt, Pd, or Ni

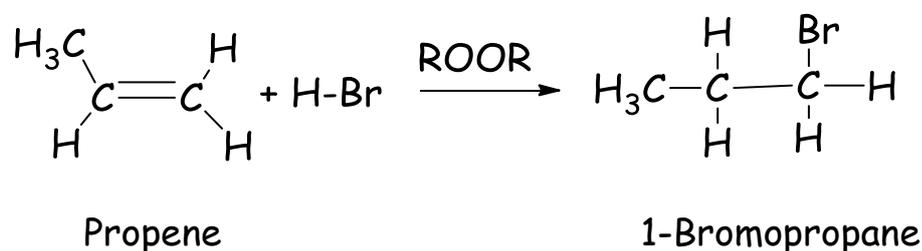
3.5.3 Addition of Hydrogen Halides

Hydrogen halide reactivity order is $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.



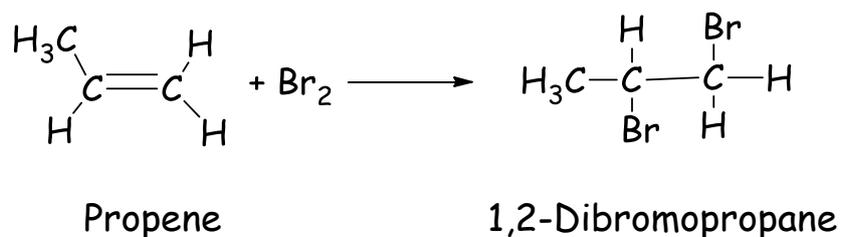
3.5.4 Free Radical addition to Alkenes

It is possible to obtain anti-Markovnikov products when HBr is added to alkenes in the presence of free radical initiators such as peroxide. Only HBr has the most suitable bond energy for this reaction HCl and HI do not give this reaction.

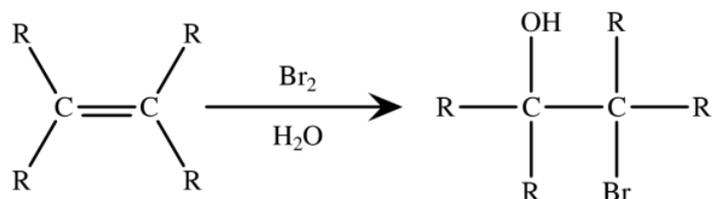


3.5.5 Addition of Halogens

X-X (Cl, Br) is non-polar molecule, but gets polarized during approach to alkene. Addition products are vicinal dihalides.

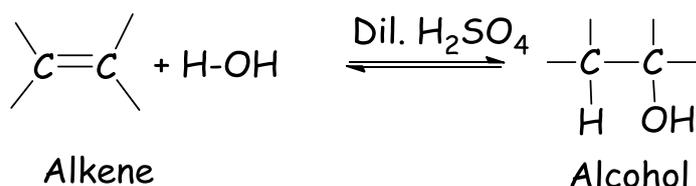


Halogens in aqueous solution: When chlorine and bromine reacts with alkenes in aqueous media, the product is a halohydrine containing hydroxyl and halogen on adjacent carbons.



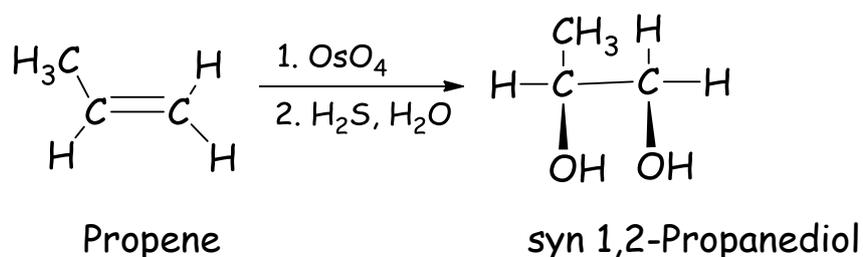
3.5.6 Addition of Water

Alkenes can be converted to alcohols in the presence of an acid such as diluted H_2SO_4 . It is the reverse reaction of the dehydration of alcohols to give alkenes.



3.5.7. Oxidation of Alkenes

The two most common reagents are osmium tetroxide with hydrogen peroxide, or potassium permanganate and hydroxide ion. Syn hydroxylation of alkenes gives syn 1,2-diols.

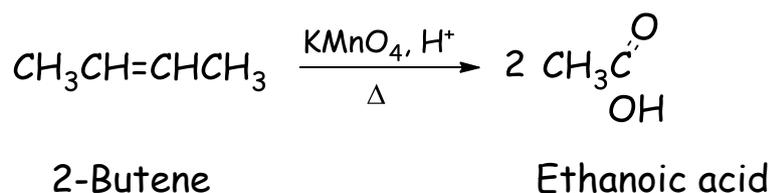


3.5.8 Oxidative Cleavage of Alkenes

Mild oxidizing conditions will not break the alkene's double bond. Strong oxidizing conditions will break the alkene's double bond.

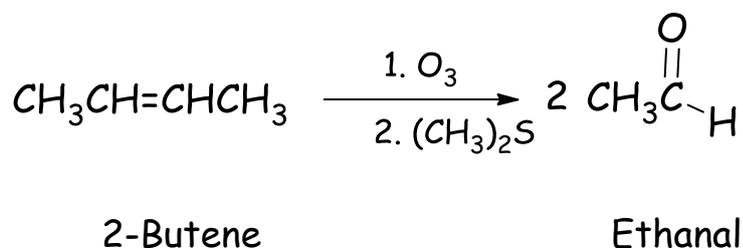
3.5.8.1 Reaction of an alkene with hot KMnO_4

The aldehydes further oxidize to carboxylic acids. This can be used as a chemical test for alkenes in which the purple color of the KMnO_4 disappears and forms brown MnO_2 residue if alkene(or alkyne) is present.



3.5.8.2 Ozonolysis of Alkenes

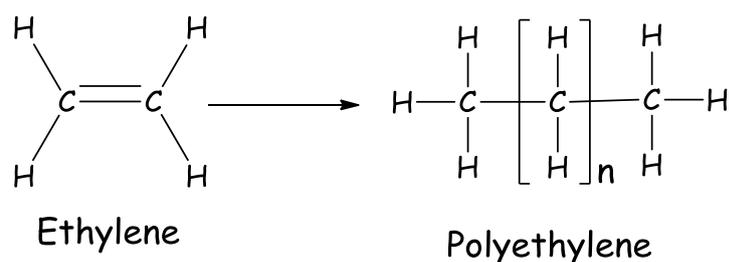
Cleavage of alkenes with ozone and workup with zinc in acetic acid leads to less highly oxidized carbons than products from cleavage with hot KMnO_4 .



3.5.9 Polymerization of Alkenes

Polymerization is a process by which an organic compound reacts with itself to form a high-molecular-weight compound composed of repeating units of the original compound.

The polymerization of ethene :



3.5.10 Addition to Conjugated Alkadienes

Dienes undergo electrophilic addition reactions in a similar manner to simple alkenes, but two addition products are possible. These differ based on the relative positions of H and X in the products. The distribution of the products depends on the reaction conditions.

