ALKENES

Prof Alaa Hayallah

31/10/2023 06:50 م

Nomenclature

For straight chain alkenes, it is the same basic rules as nomenclature of alkanes except change the suffix to "-ene."

1. Find the longest carbon chain that contains the carbon carbon double bond. If you have two ties for longest Carbon chain, and both chains contain a carbon carbon double bond, then identify the most substituted chain.

2. Number the chain so as to include both carbon atoms of the double bond, and begin numbering at the end of the chain nearer the double bond. Designate the location of the double bond by using the number of the first atom of the double bond as a prefix.

1 2 3 4

$H_2C{=}CH{-}CH_2{-}CH_3$

1-butene

(not 3-butene)

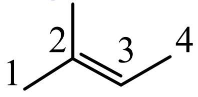
1 2 3 4 5 6

$H_3C{-}HC{=}CH{-}CH_2{-}CH_2{-}CH_3$

2-hexane

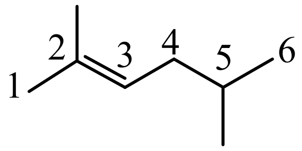
(not 4-hexene)

3. Add substituents and their position to the alkene as prefixes. Of course remember to give the lowest numbers possible. And remember to name them in alphabetical order when writing them.



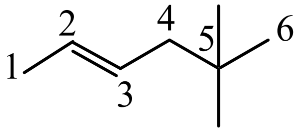
2-methyl-2-butene

(not 3-methyl-2-butene)

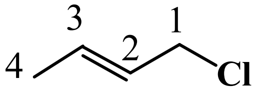


2,5-dimethyl-2-hexene

(not 2,5-dimethyl-4-hexene)

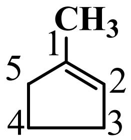


5,5-dimethyl-2-hexene



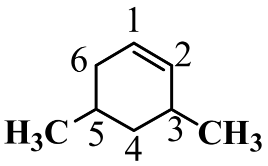
1-chloro-2-butene

4. Number substituted cycloalkenes in the way that gives the carbon atoms of the double bond the 1 and 2 positions and that also gives the substituent groups the lower numbers at the first point of difference



1-methylcyclopentene

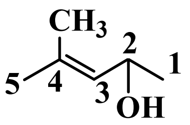
(not 2-methylcyclopentene)



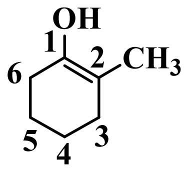
3,5-dimethylcyclohexene

(not 4,6-dimethylcyclohexene)

5. Name compounds containing a double bond an alcohol group as alkenols (or cycloalkenol) and give the alcohol carbon the lower number.



4-methyl-3-penten-2-ol

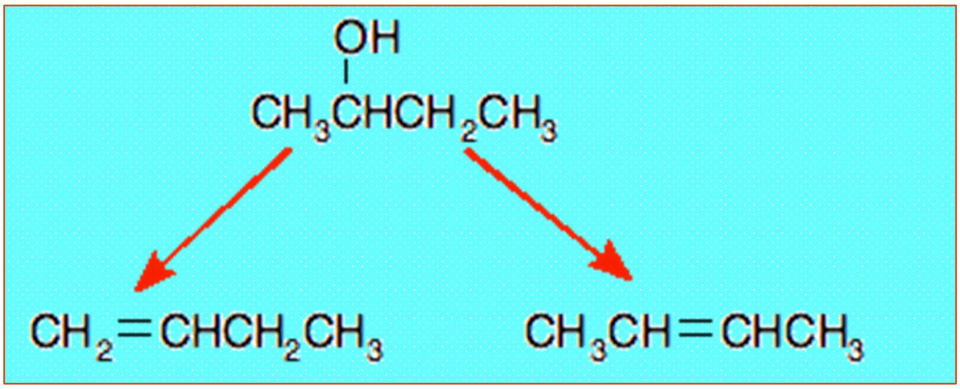


2-methyl-2-cyclohexen-1-ol

Synthesis of alkenes

A. Dehydration of alcohol using aluminum oxide as a radical

Examples



⟶

Methanol < primary < secondary < tertiary

↑ The relative reactivity of alcohols in dehydration reaction

---

Mechanism

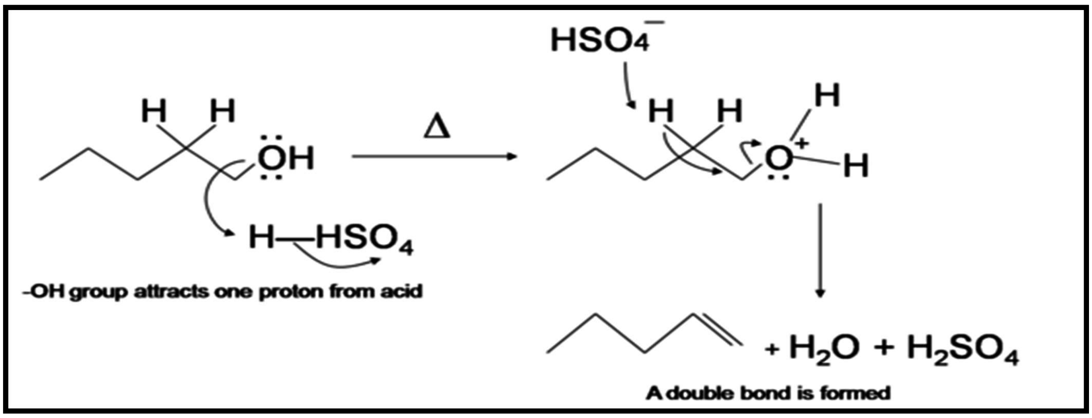
1. the –OH group in the alcohol donates two electrons to H^+ from the acid reagent, forming an alkyloxonium ion. This ion acts as a very good leaving group which leaves to form a carbocation.
2. The deprotonated acid (the nucleophile) then attacks the hydrogen adjacent to the carbocation and form a double bond.

Note

- ❑ **Primary alcohols undergo bimolecular elimination (E2 mechanism)**
- ❑ **secondary and tertiary alcohols undergo unimolecular elimination E1 mechanism)**

E2 mechanism (1^{ry} alcohol)

1) Oxygen donates two electrons to a proton from sulfuric acid H_2SO_4, forming an alkyloxonium ion.
2) The nucleophile HSO_4^- back-side attacks one adjacent hydrogen and the alkyloxonium ion leaves in a concerted process, making a double bond.

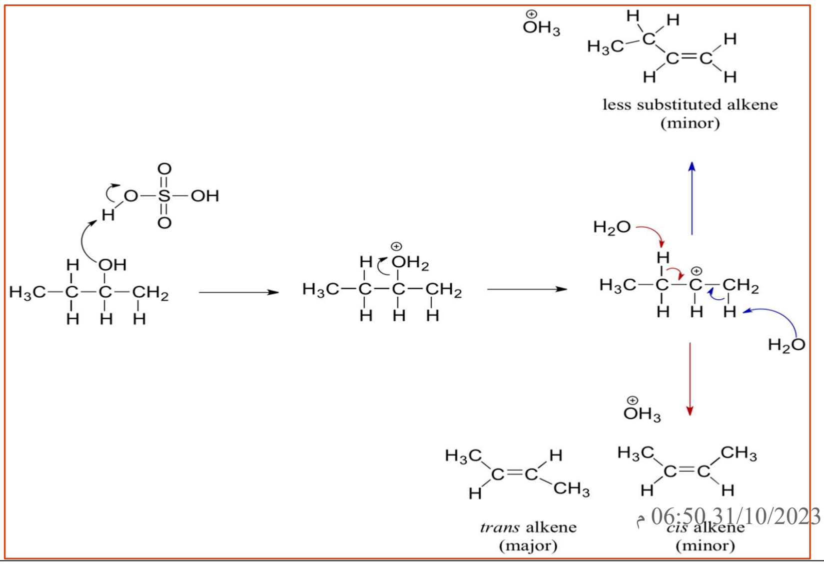


-OH group attracts one proton from acid

A double bond is formed

E1 mechanism (2^{nd} & 3^{ry} alcohol)

1) (OH) protonates to form alkyloxonium ions.
2) the ion leaves first and forms a carbocation as the reaction intermediate.
3) The water molecule (which is a stronger base than the HSO_{4^-} ion) then abstracts a proton from an adjacent carbon, forming a double bond.



❖**Notes:**

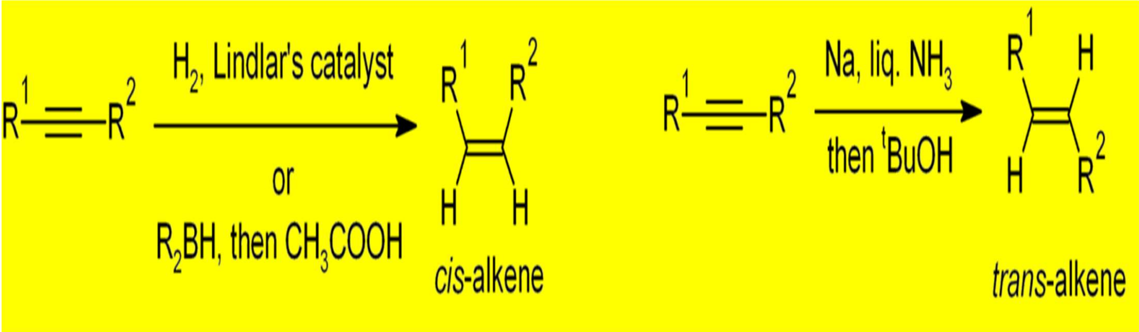
- The red arrows show formation of the more substituted 2-butene, while the blue arrows show formation of the less substituted 1-butene.

- More substituted alkenes are more stable than less substituted alkenes, and *trans* alkenes are more stable than *cis* alkenes.

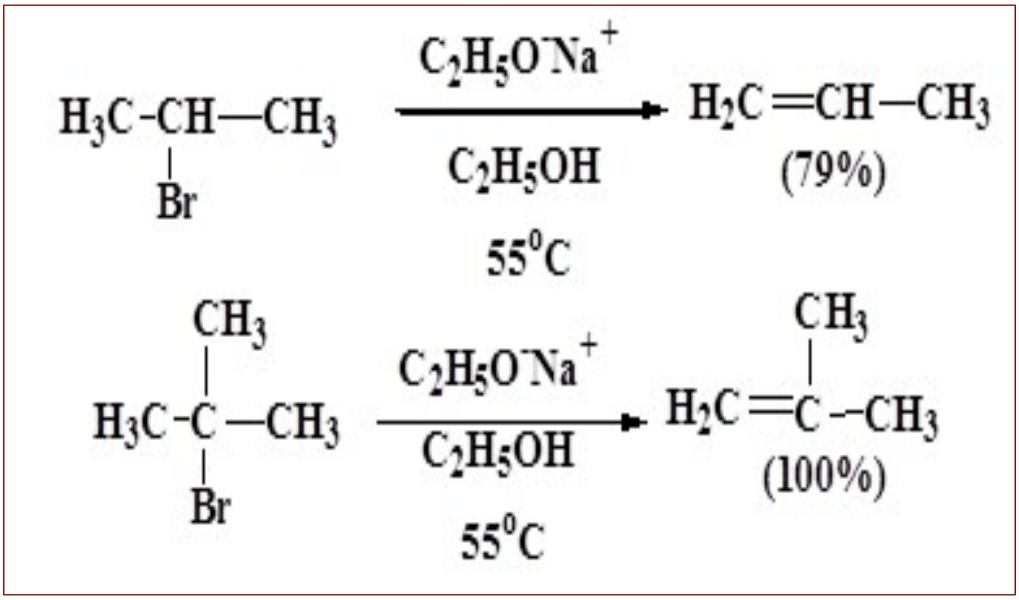
B) From Alkynes (stereoselective synthesis)

If the *cis*-alkene → hydrogenation in the presence of Lindar's catalyst (palladium deposited on calcium carbonate) or hydroboration followed by hydrolysis

If the *Trans*-alkene → Reduction of the alkyne by sodium metal in liquid ammonia gives the *trans*-alkene



c- Dehydrohalogenation of alkyl halides (haloalkanes):



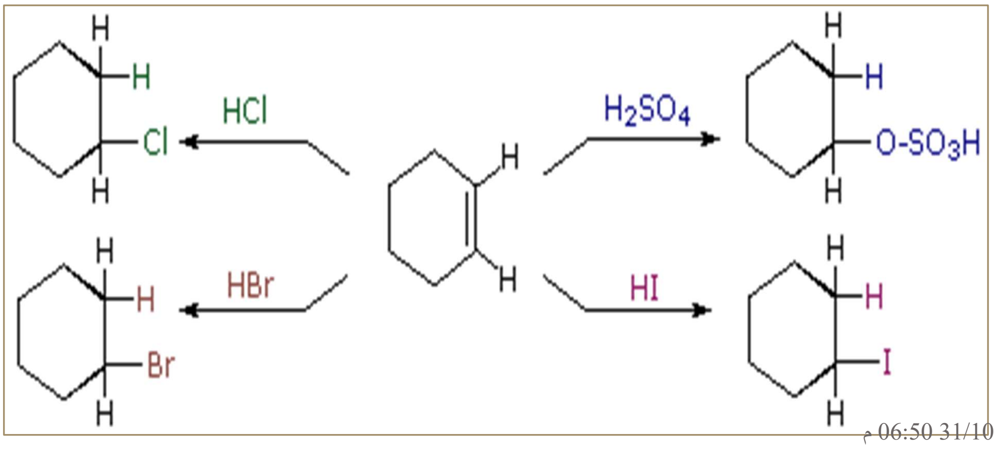
Addition Reaction

(Exothermic reaction)

1- Addition of Strong Bronsted Acids

a) Strong Bronsted acids such as HCl, HBr, HI & H_2SO_4

b) When added to the C=C of alkenes, new covalent bonds are formed to hydrogen and to the conjugate base of the acid

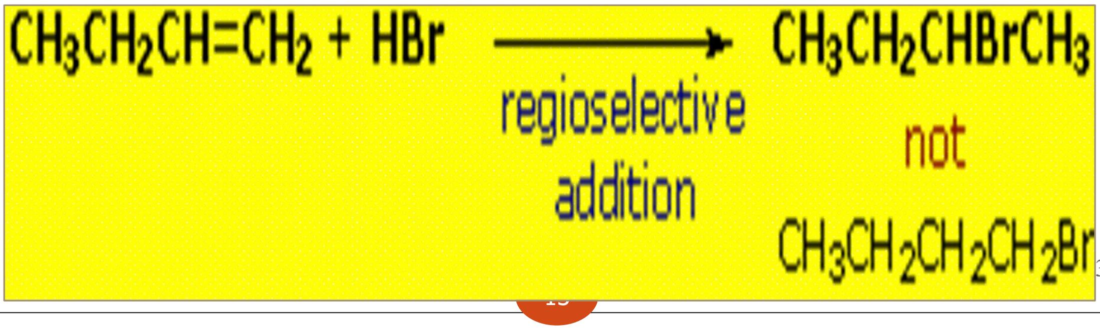


Note…. Weak Bronsted acids such as water (pK_a = 15.7) and acetic acid (pK_a = 4.75) do not normally add to alkenes. However, the addition of a strong acid serves to catalyze the addition of water, and in this way alcohols may be prepared from alkenes

$$CH_2{=}CH_2 + H_3O^{(+)} \longrightarrow HCH_2{-}CH_2OH + H^{(+)}$$

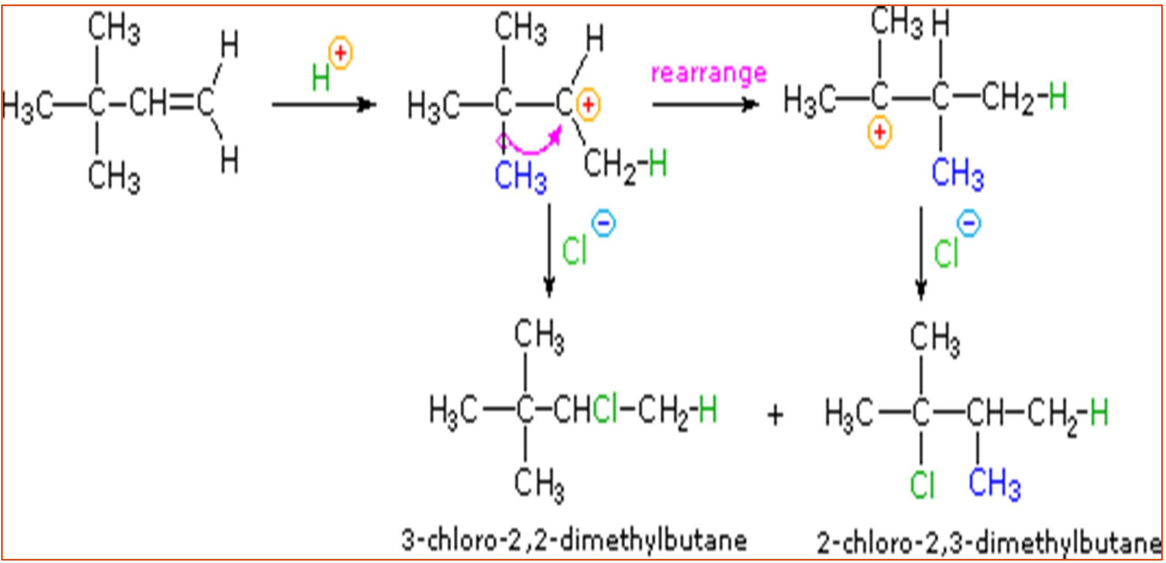
Regioselectivity and the Markovnikov Rule

When addition reactions to such unsymmetrical alkenes are carried out, we find that one of the two possible constitutionally isomeric products is formed preferentially. Selectivity of this sort is termed regioselectivity


$$CH_3CH_2CH{=}CH_2 + HBr \xrightarrow[\text{addition}]{\text{regioselective}} CH_3CH_2CHBrCH_3 \text{ not } CH_3CH_2CH_2CH_2Br$$

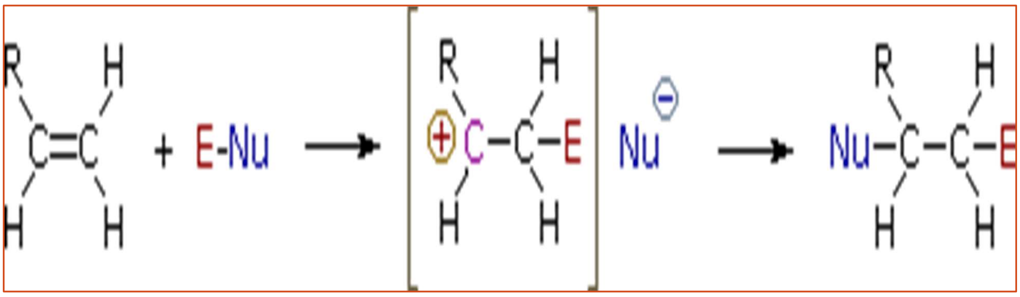
2-Rearrangement of Carbocations

Rearrangement of the initially formed 2º-carbocation to a 3º-carbocation by a 1,2-shift of a methyl group (a shift of a neighboring alkyl group or hydrogen)



3-Addition of Lewis Acids (Electrophilic Reagents)

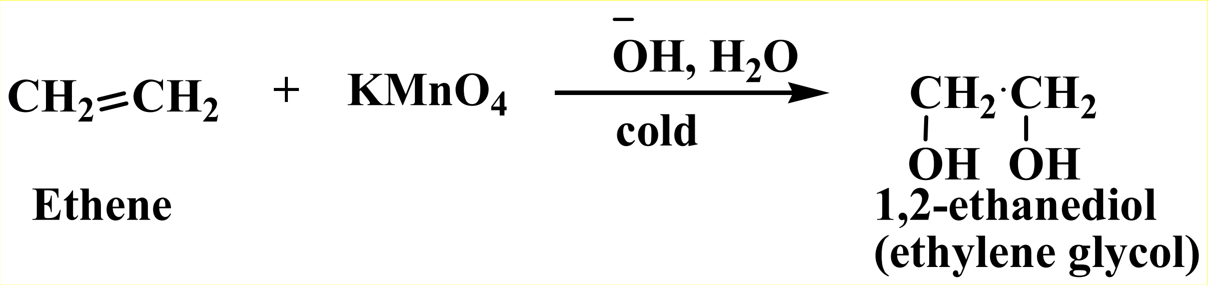
Lewis acids like the halogens, boron hydrides and certain transition metal ions are able to bond to the alkene pi-electrons, and the resulting complexes rearrange or are attacked by nucleophiles to give addition products



4- Oxidation of alkenes

Alkenes undergo a number of reactions in which the carbon-carbon double bond is oxidized. Several oxidizing agents, e.g. $KMnO_4$, $K_2Cr_2O_7$, O_3, and peroxy acids may be used.

(a) Oxidation by potassium permanganate to glycol



$$CH_2{=}CH_2 + KMnO_4 \xrightarrow[\text{cold}]{\bar{O}H,\ H_2O} \underset{OH}{CH_2}\cdot\underset{OH}{CH_2}$$

Ethene

1,2-ethanediol
(ethylene glycol)

(b) Oxidation by ozone to ozonoid(ozonolysis of alkenes) .