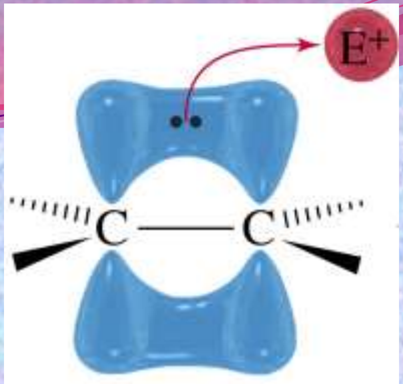
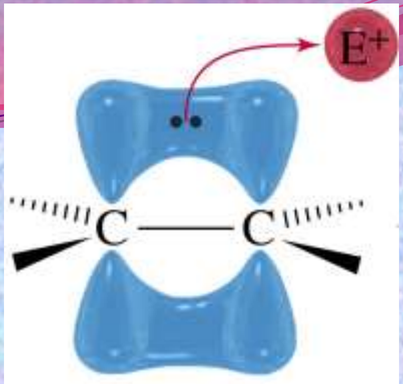


Reactions of Alkenes

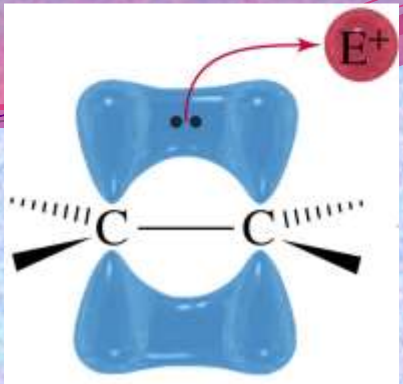
Reactivity of C=C



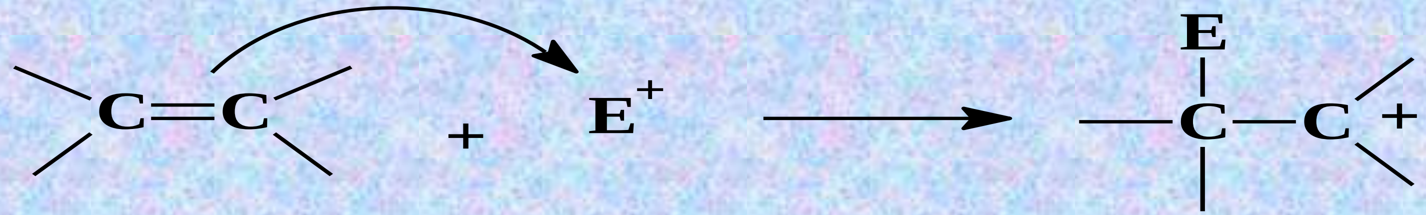
- Electrons in pi bond are loosely held.
- Electrophiles are attracted to the pi electrons.
- Carbocation intermediate forms.
- Nucleophile adds to the carbocation.
- Net result is addition to the double bond.

=>

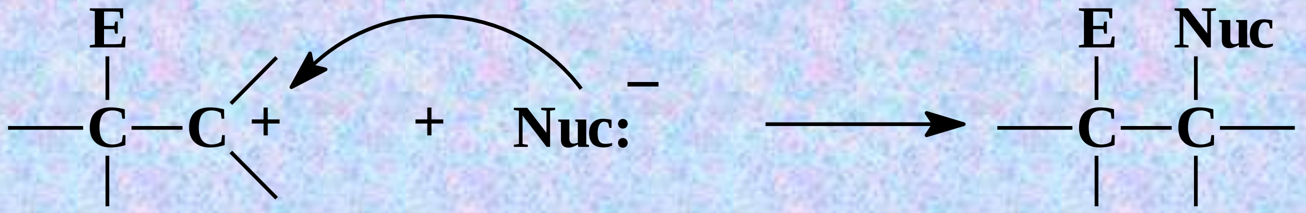
Electrophilic Addition



- Step 1: Pi electrons attack the electrophile.

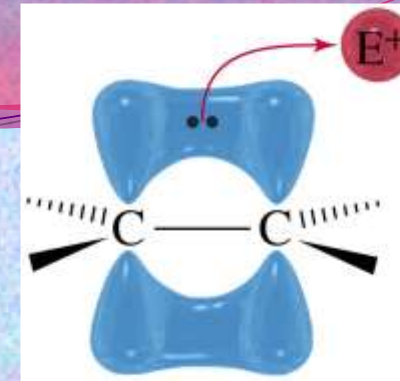


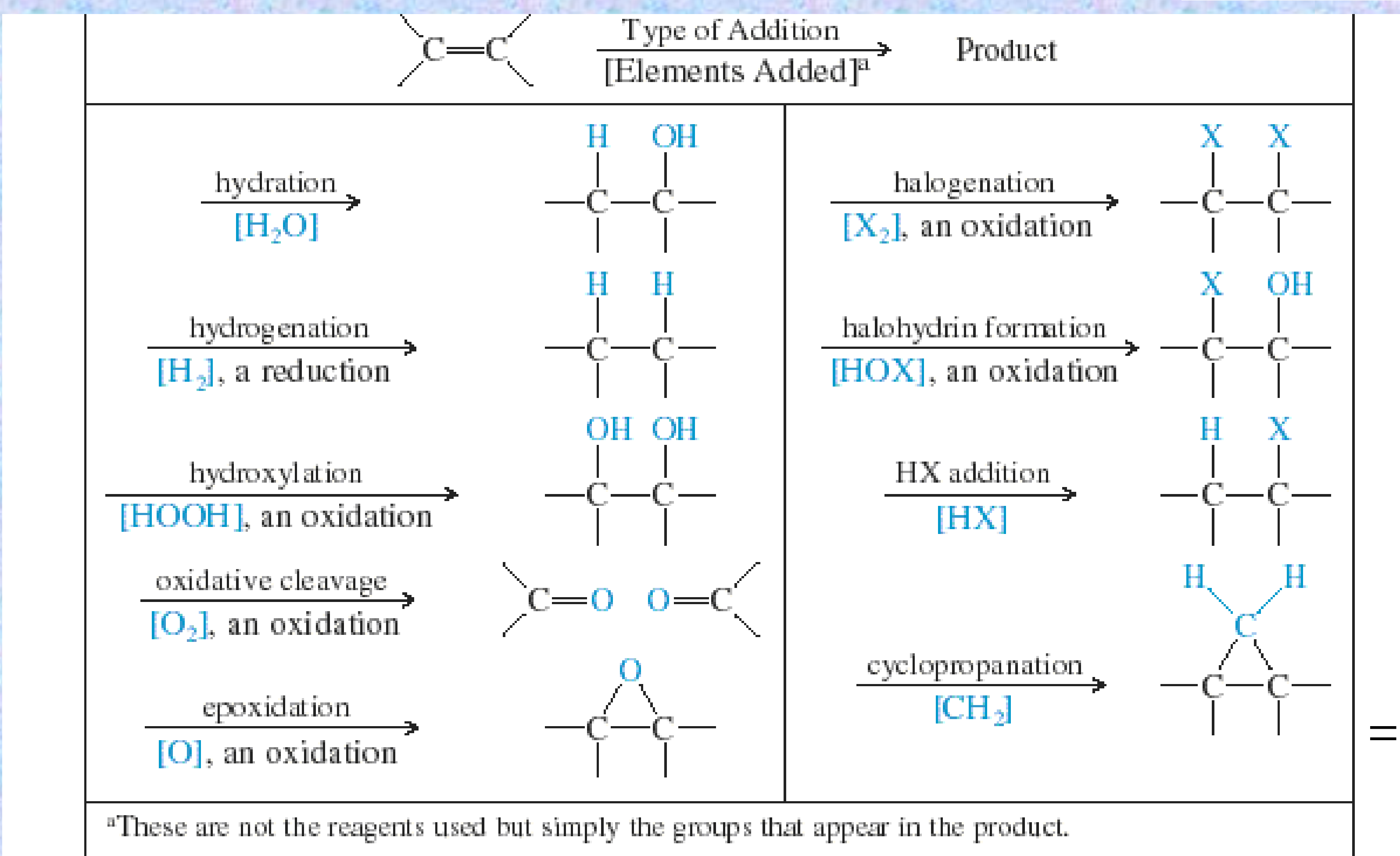
- Step 2: Nucleophile attacks the carbocation.



=>

Types of Additions





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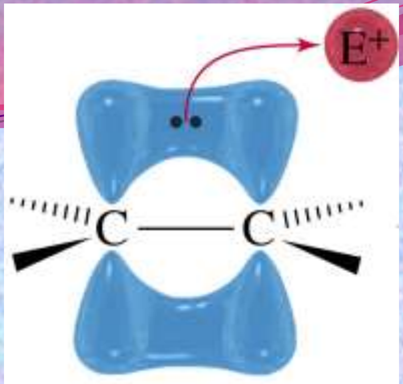
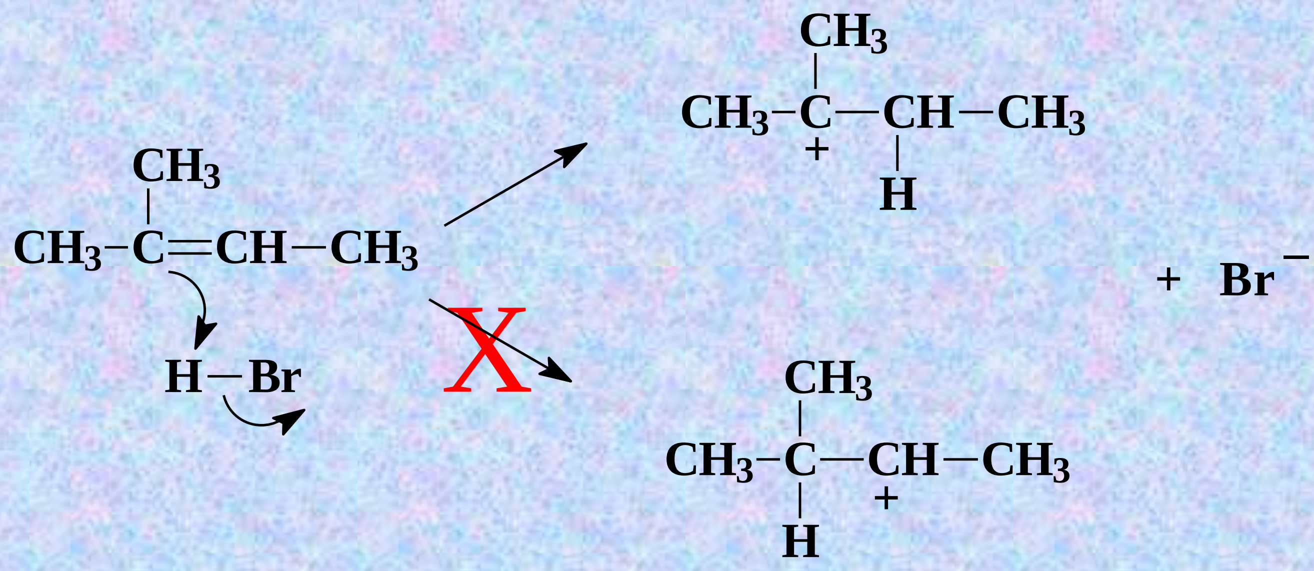
Addition of HX (1)



Protonation of double bond yields the most stable carbocation. Positive charge goes to the carbon that was not protonated.



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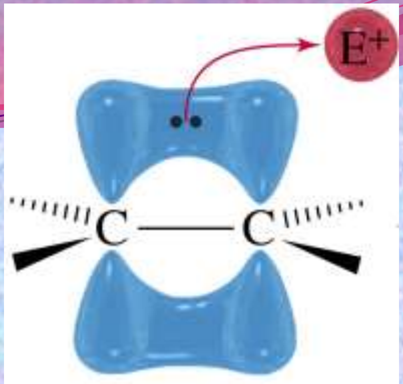
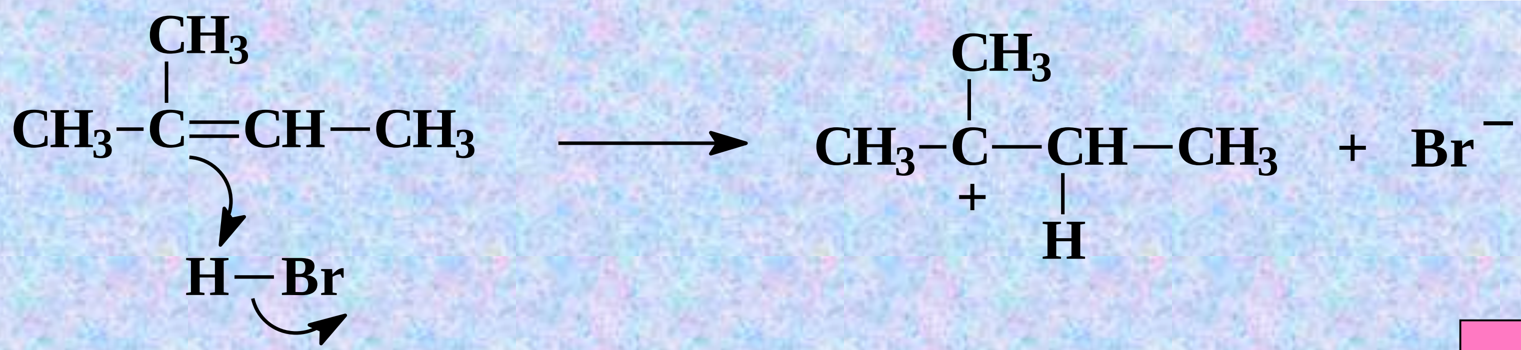
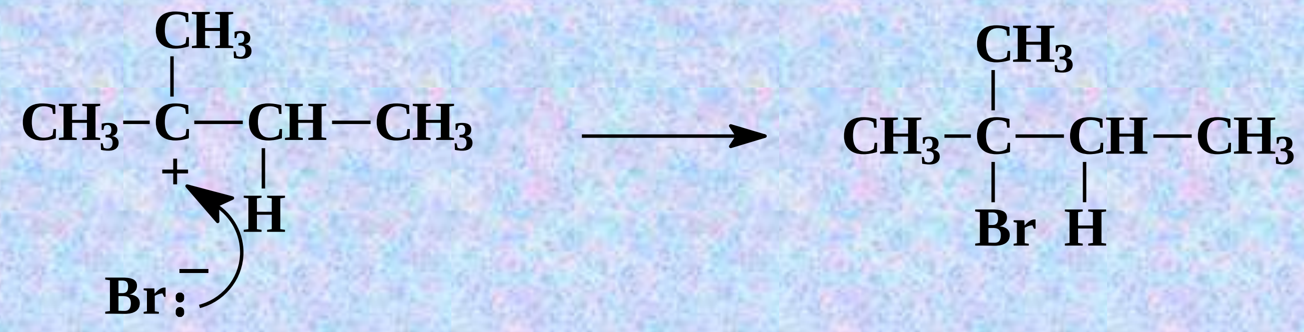
Addition of HX (2)







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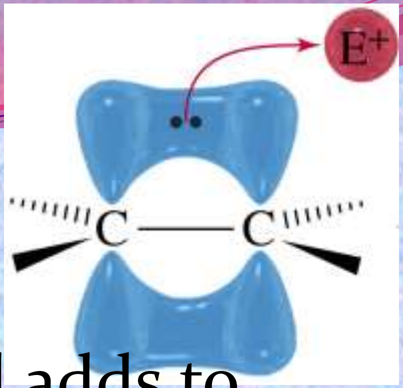
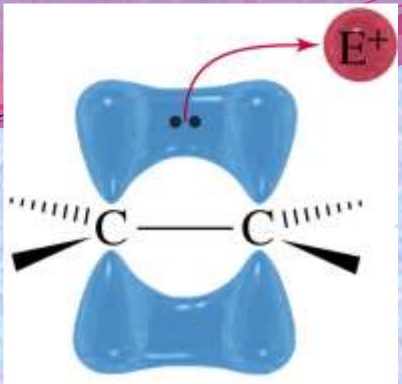
Regiospecificity



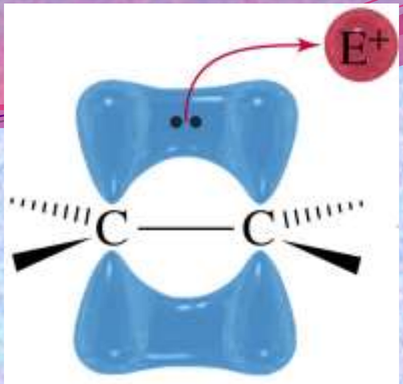
- Markovnikov's Rule: The proton of an acid adds to the carbon in the double bond that already has the most H's. "Rich get richer."
- More general Markovnikov's Rule: In an electrophilic addition to an alkene, the electrophile adds in such a way as to form the most stable intermediate.
- HCl, HBr, and HI add to alkenes to form Markovnikov products. =>

Free-Radical Addition of HBr



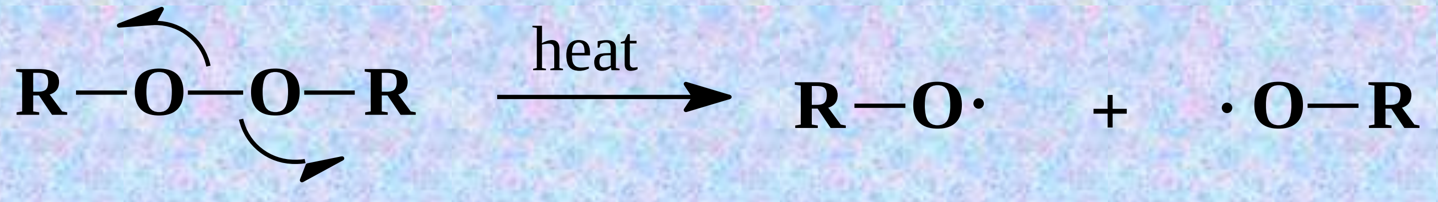
- In the presence of peroxides, HBr adds to an alkene to form the "anti-Markovnikov" product.
- Only HBr has the right bond energy.
- HCl bond is too strong.
- HI bond tends to break heterolytically to form ions.

=>

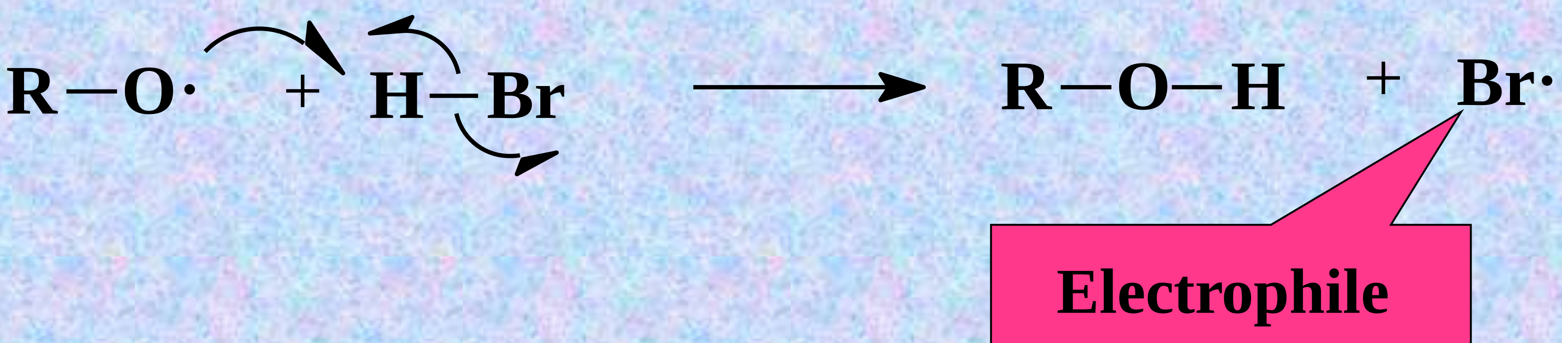


Free Radical Initiation

- Peroxide O-O bond breaks easily to form free radicals.



- Hydrogen is abstracted from HBr.



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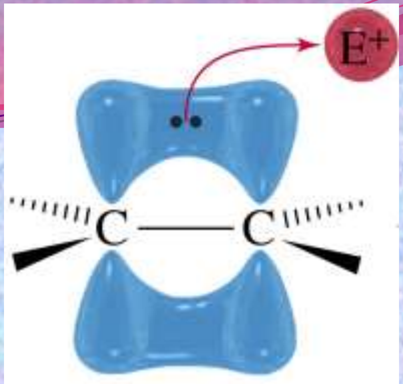
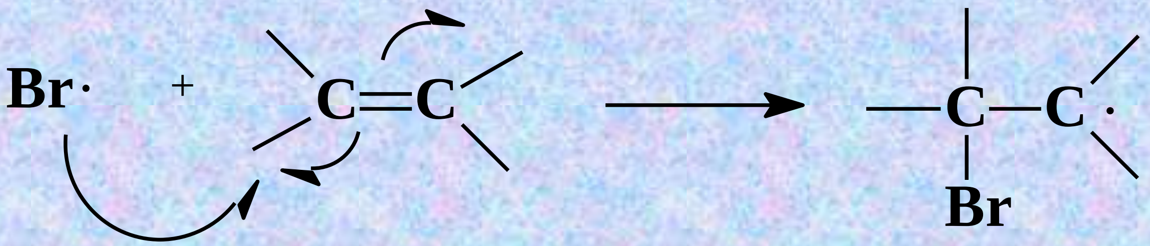
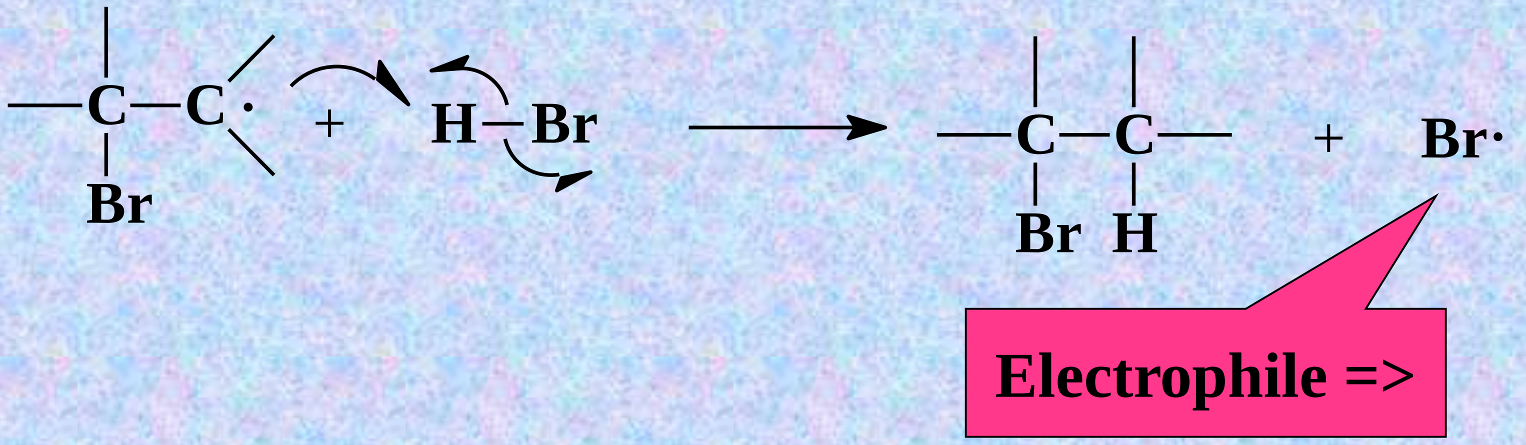
Propagation Steps



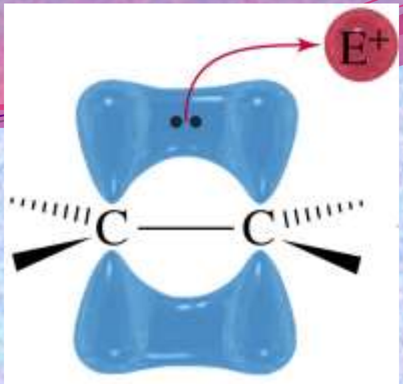
- Bromine adds to the double bond.

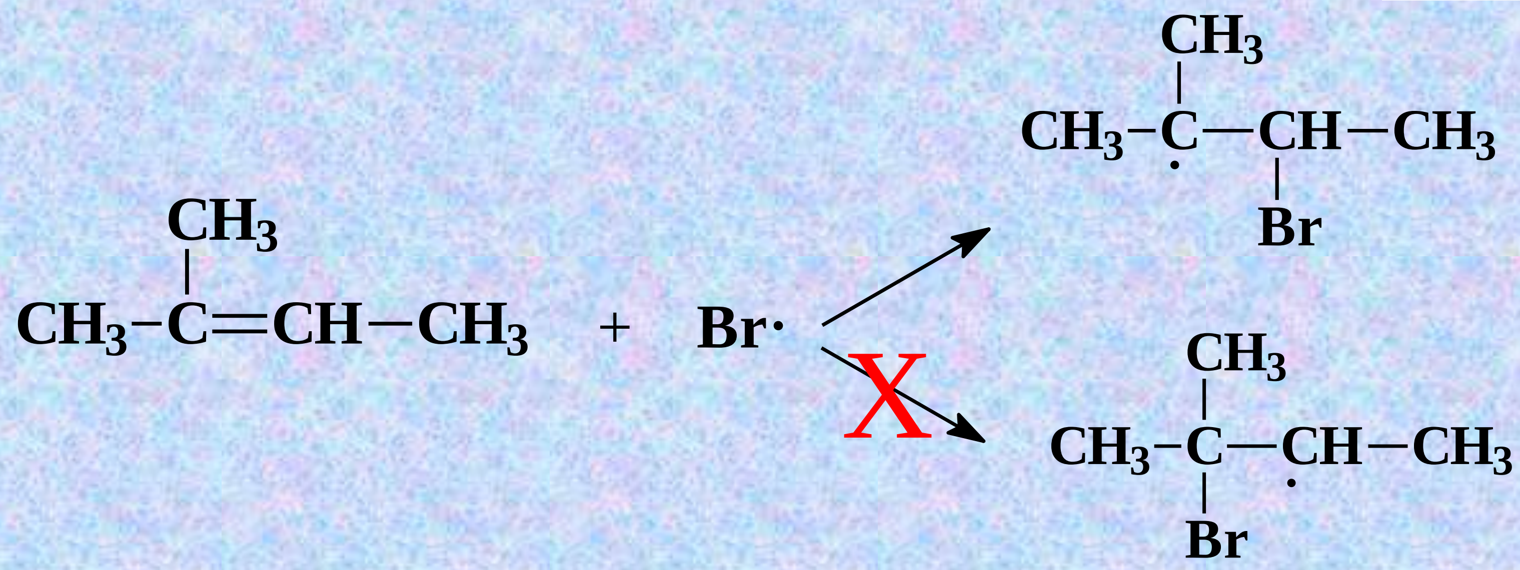


- Hydrogen is abstracted from HBr.



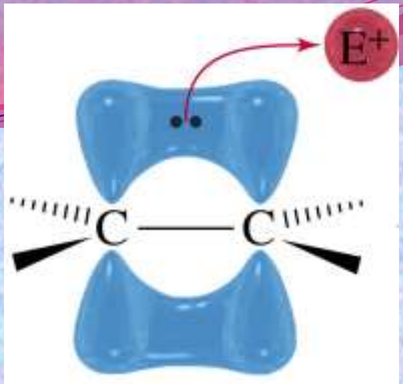
Anti-Markovnikov ??

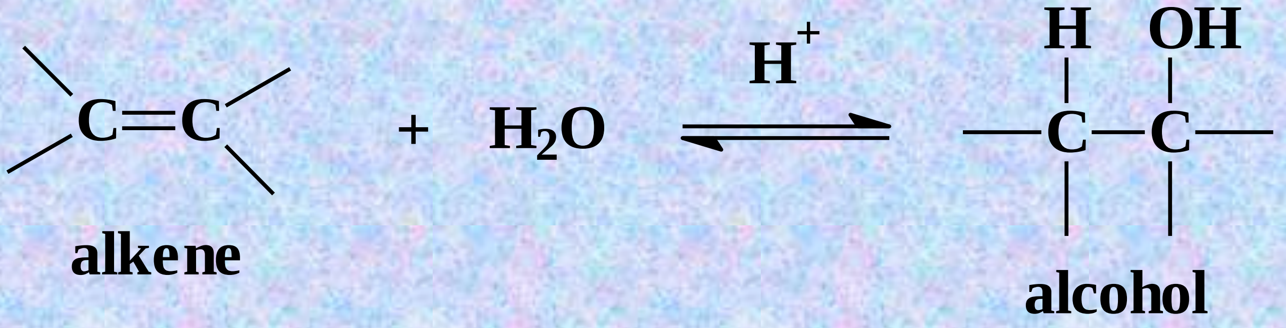




- Tertiary radical is more stable, so that intermediate forms faster. =>

Hydration of Alkenes

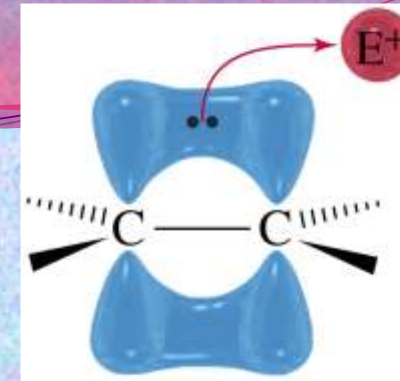


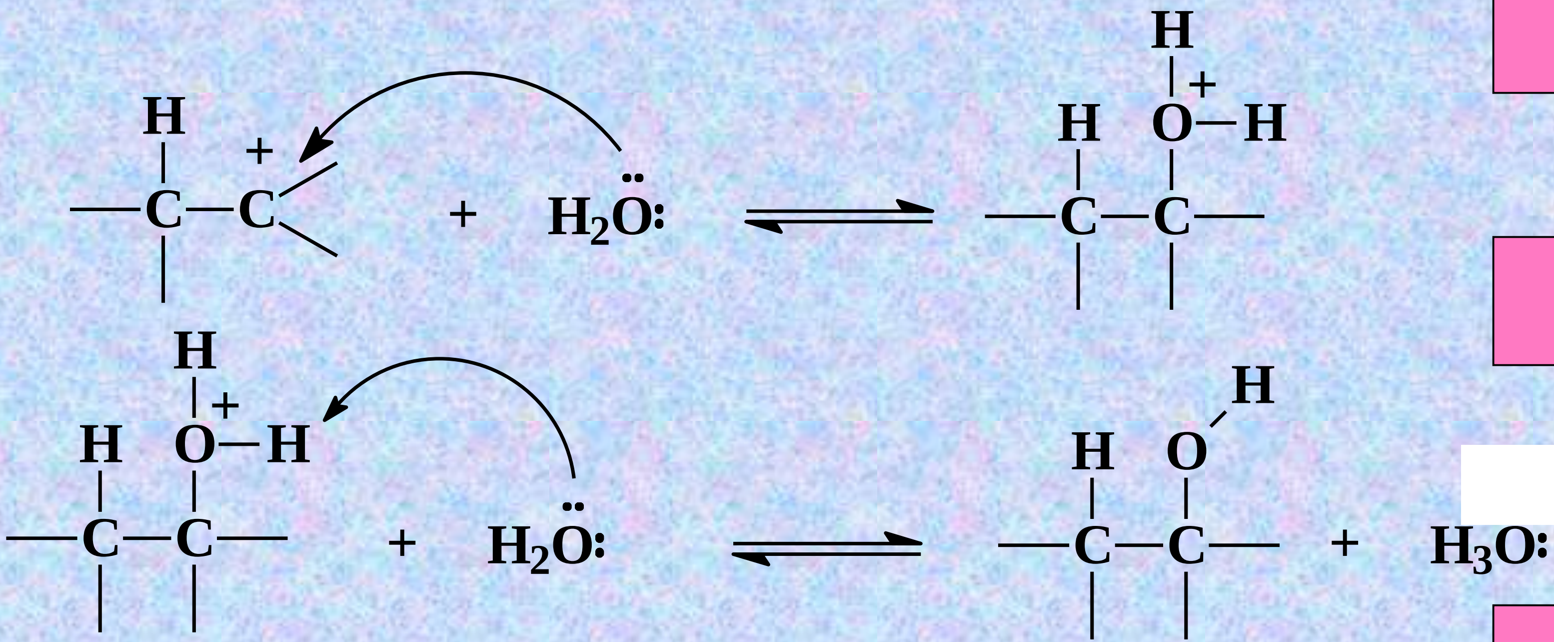


- Reverse of dehydration of alcohol
- Use very dilute solutions of H_2SO_4 or H_3PO_4 to drive equilibrium toward hydration.

=>

Mechanism for Hydration





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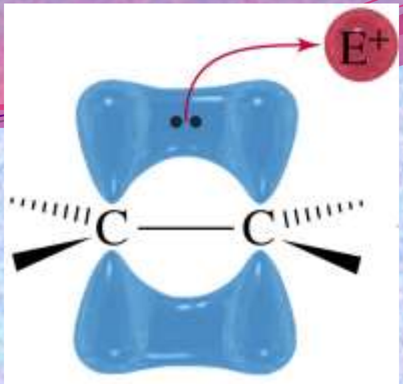
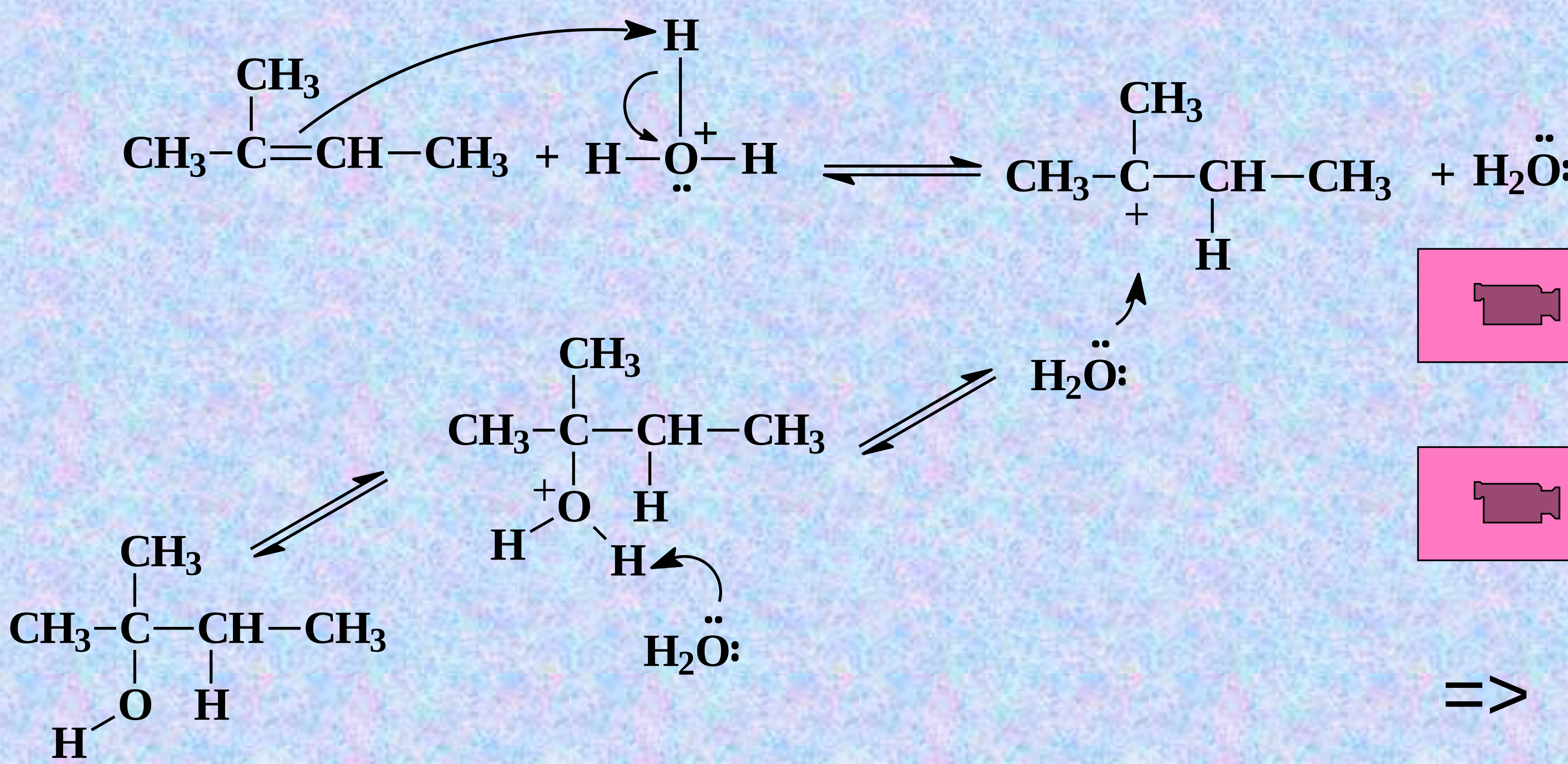
Orientation for Hydration



- Markovnikov product is formed.



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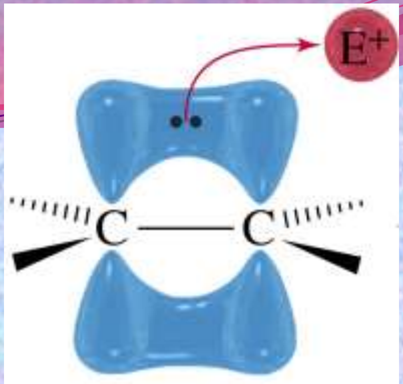
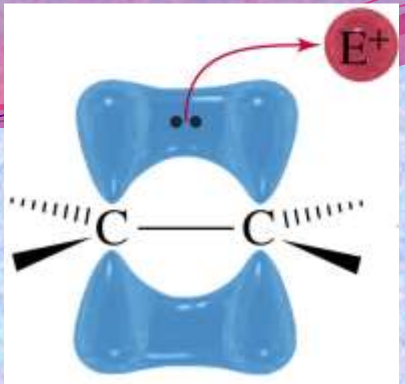
Indirect Hydration



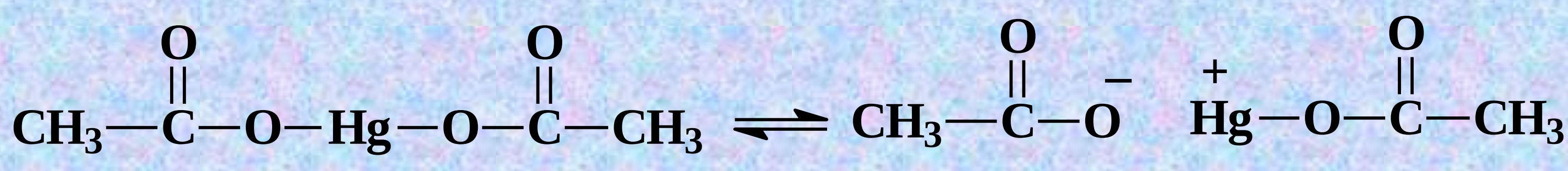
- Oxymercuration-Demercuration
  - Markovnikov product formed
  - Anti addition of H-OH
  - No rearrangements
- Hydroboration
  - Anti-Markovnikov product formed
  - Syn addition of H-OH

=>

Oxymercuration (1)



- Reagent is mercury(II) acetate which dissociates slightly to form $^{+}$Hg(OAc).
- $^{+}$Hg(OAc) is the electrophile that attacks the pi bond.



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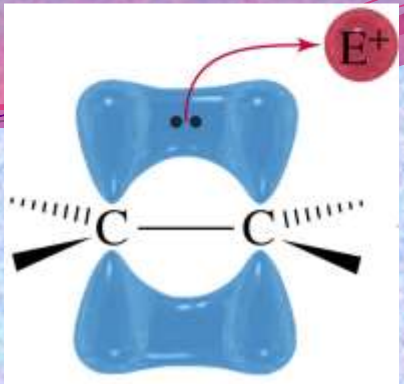
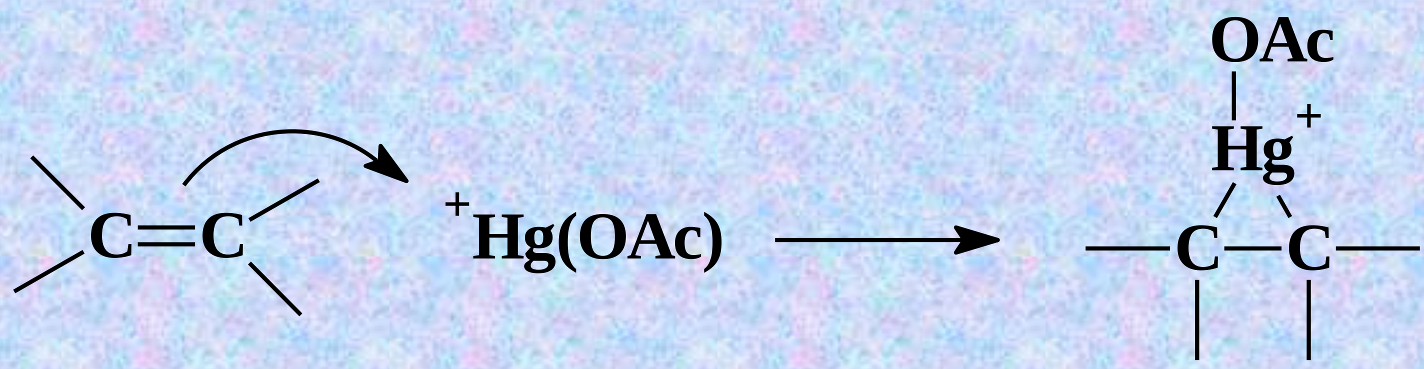
Oxymercuration (2)



The intermediate is a cyclic mercurinium ion, a three-membered ring with a positive charge.



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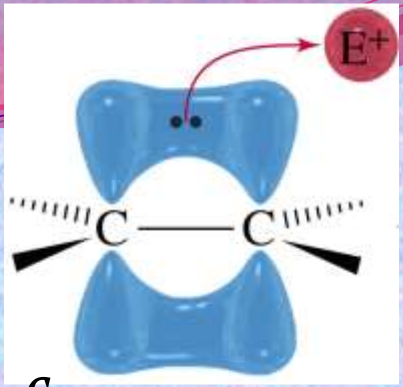
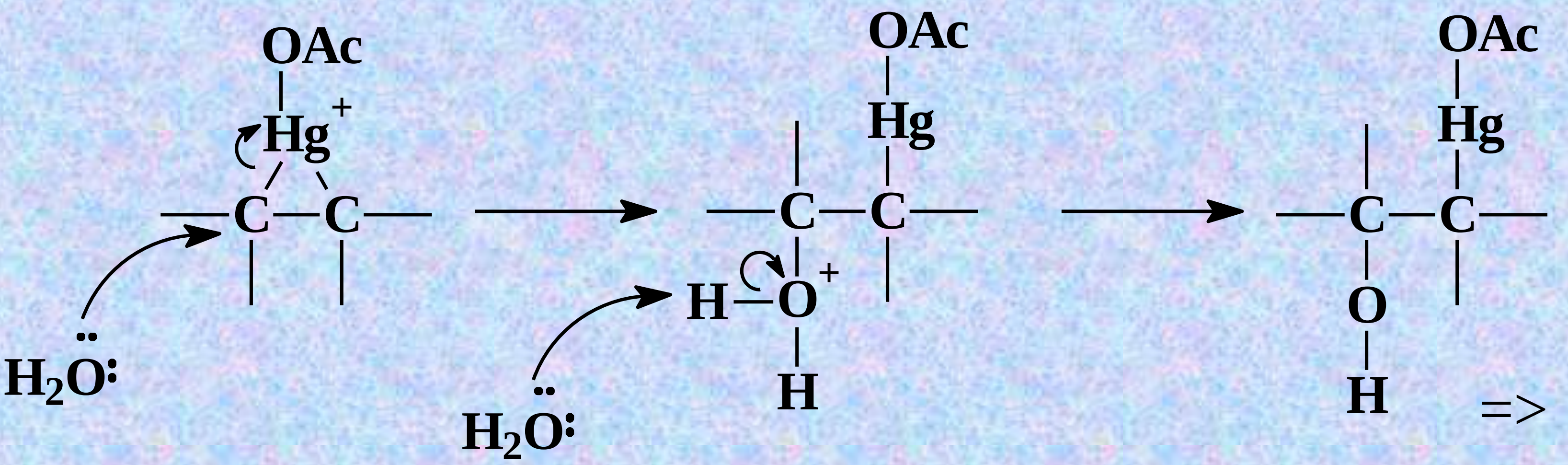
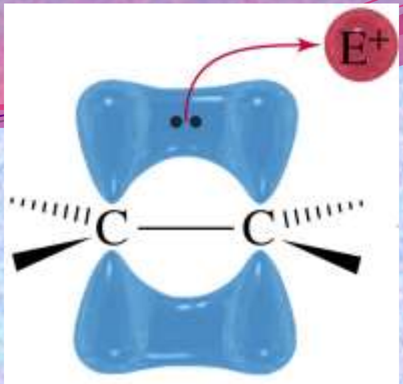
Oxymercuration (3)



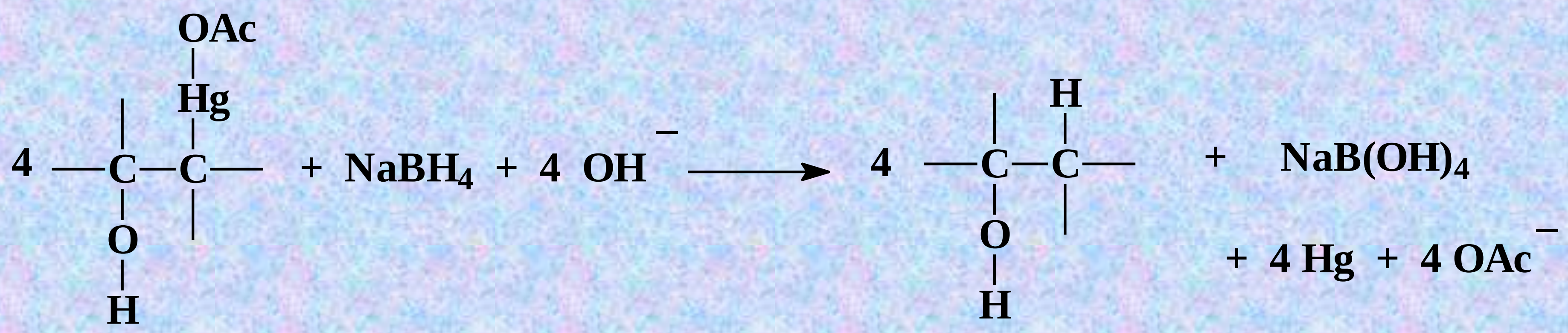
- Water approaches the mercurinium ion from the side opposite the ring (anti addition).
- Water adds to the more substituted carbon to form the Markovnikov product.





Demercuration

Sodium borohydride, a reducing agent, replaces the mercury with hydrogen.



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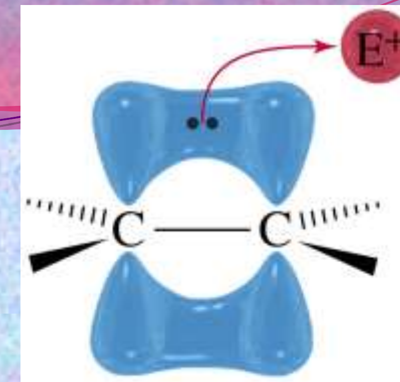
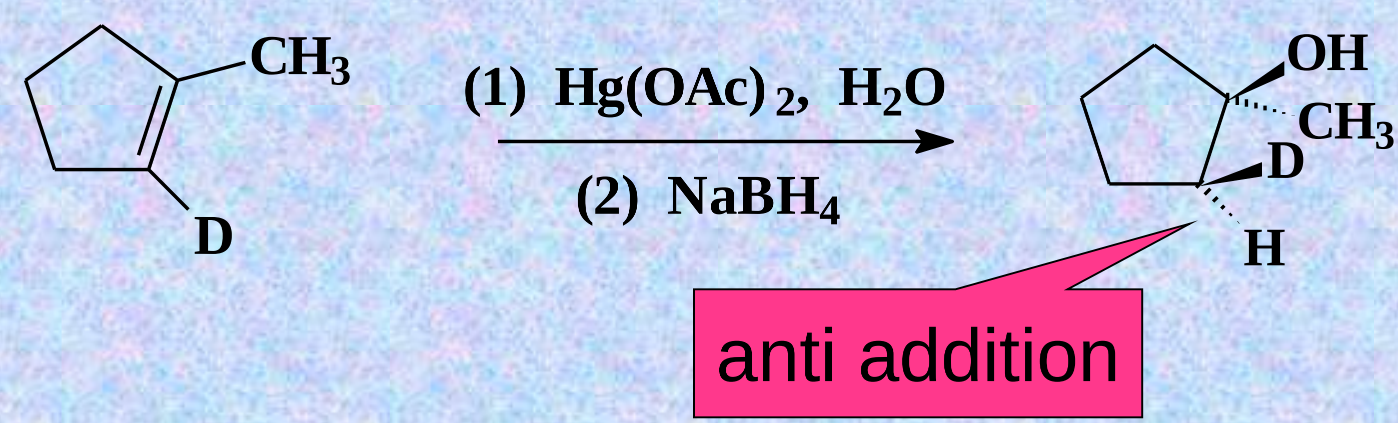
Predict the Product



Predict the product when the given alkene reacts with aqueous mercuric acetate, followed by reduction with sodium borohydride.



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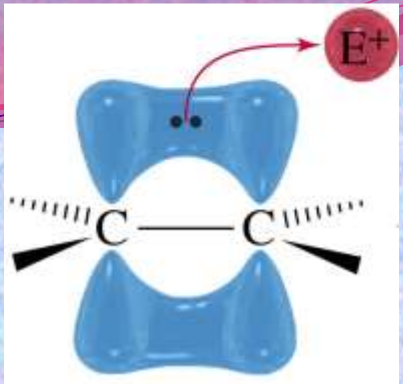
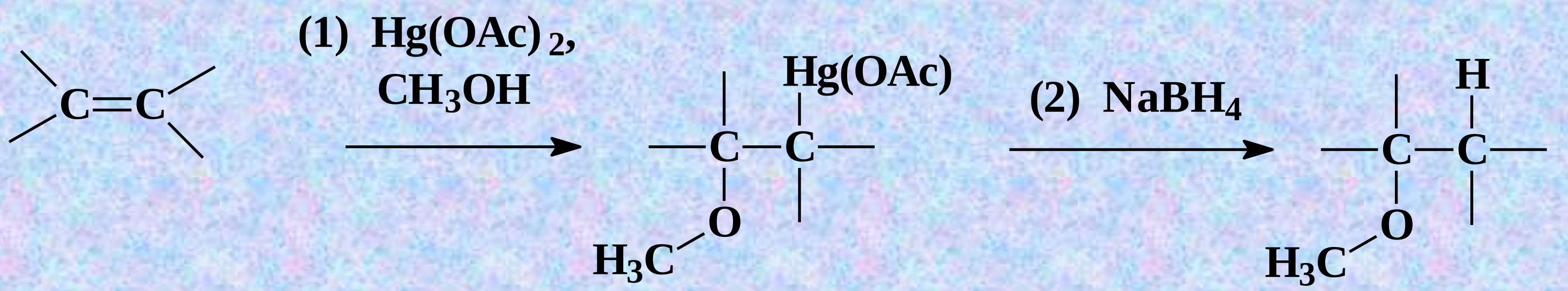
Alkoxymercuration - Demercuration



If the nucleophile is an alcohol, ROH, instead of water, HOH, the product is an ether.



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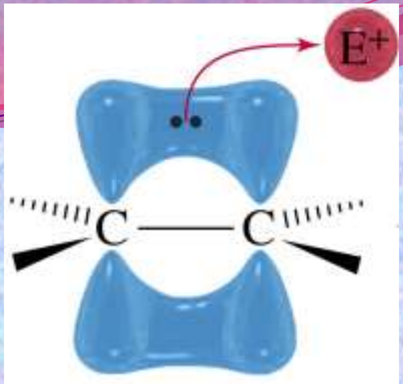
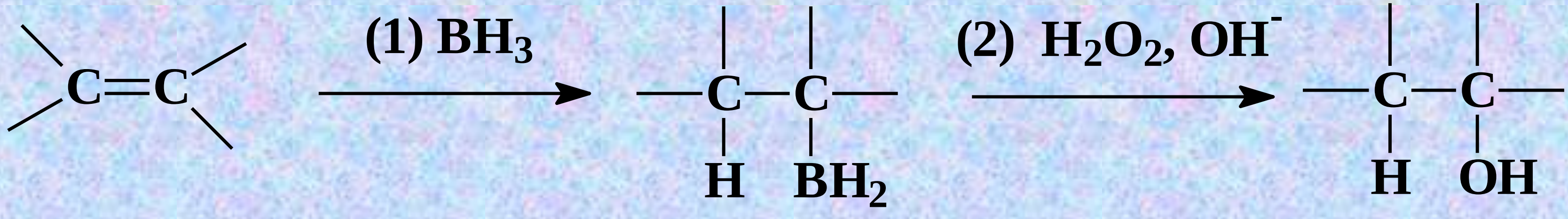
Hydroboration



- Borane, BH_3, adds a hydrogen to the most substituted carbon in the double bond.
- The alkylborane is then oxidized to the alcohol which is the anti-Mark product.



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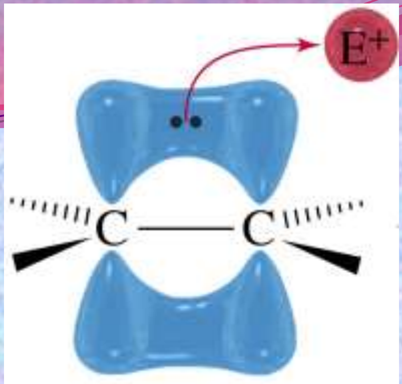
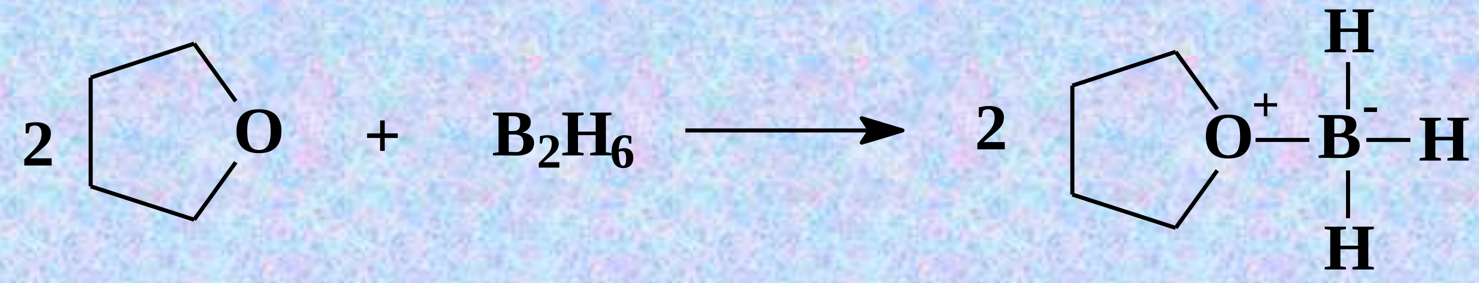


Borane Reagent

- Borane exists as a dimer, B_2H_6, in equilibrium with its monomer.
- Borane is a toxic, flammable, explosive gas.
- Safe when complexed with tetrahydrofuran.



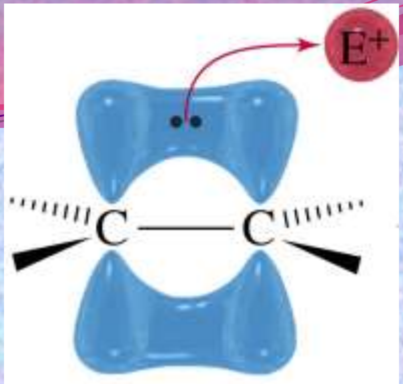
THF

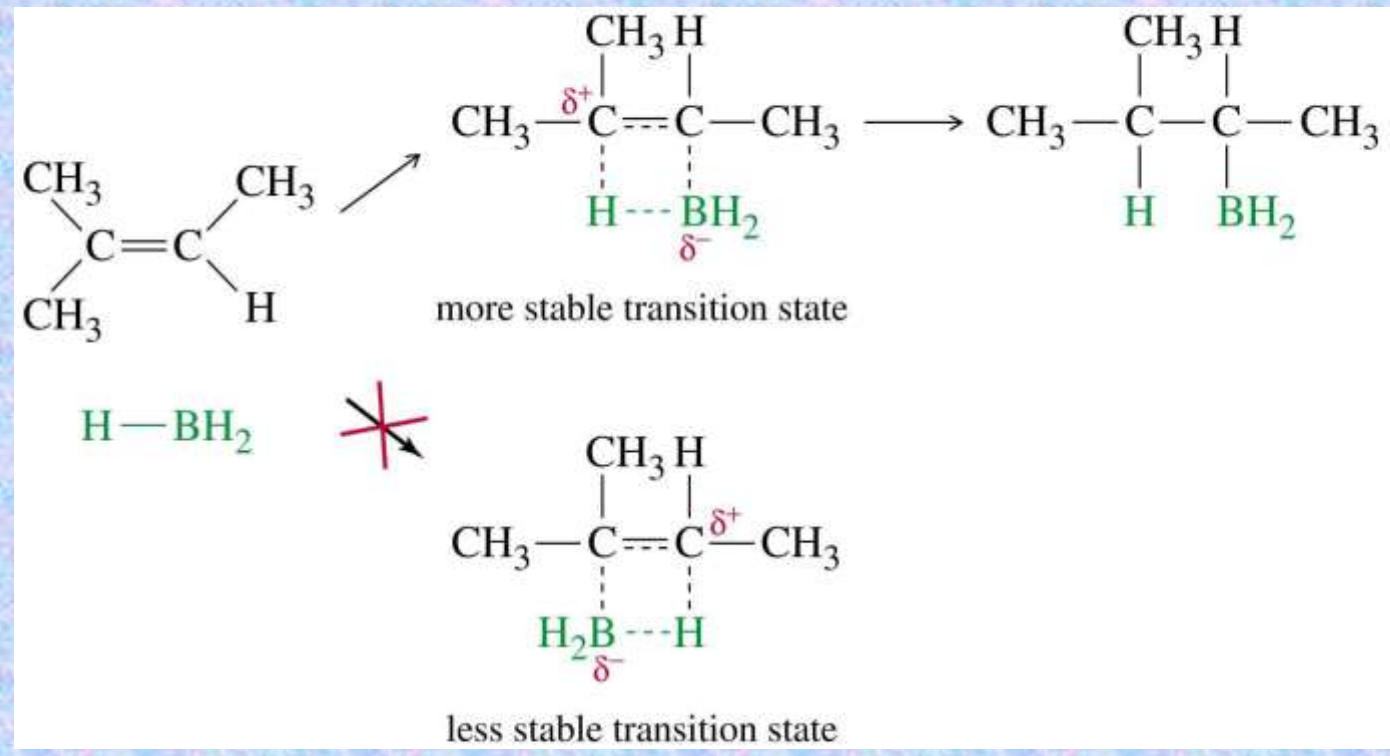
THF · BH_3

=>

Mechanism

- The electron-deficient borane adds to the least-substituted carbon.
- The other carbon acquires a positive charge.
- H adds to adjacent C on same side (syn).





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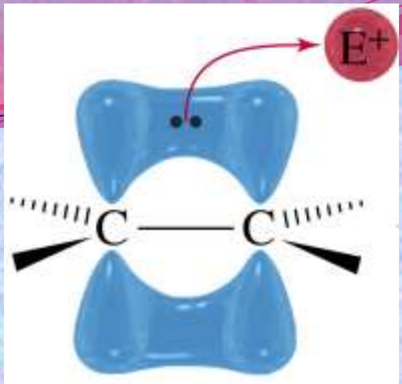
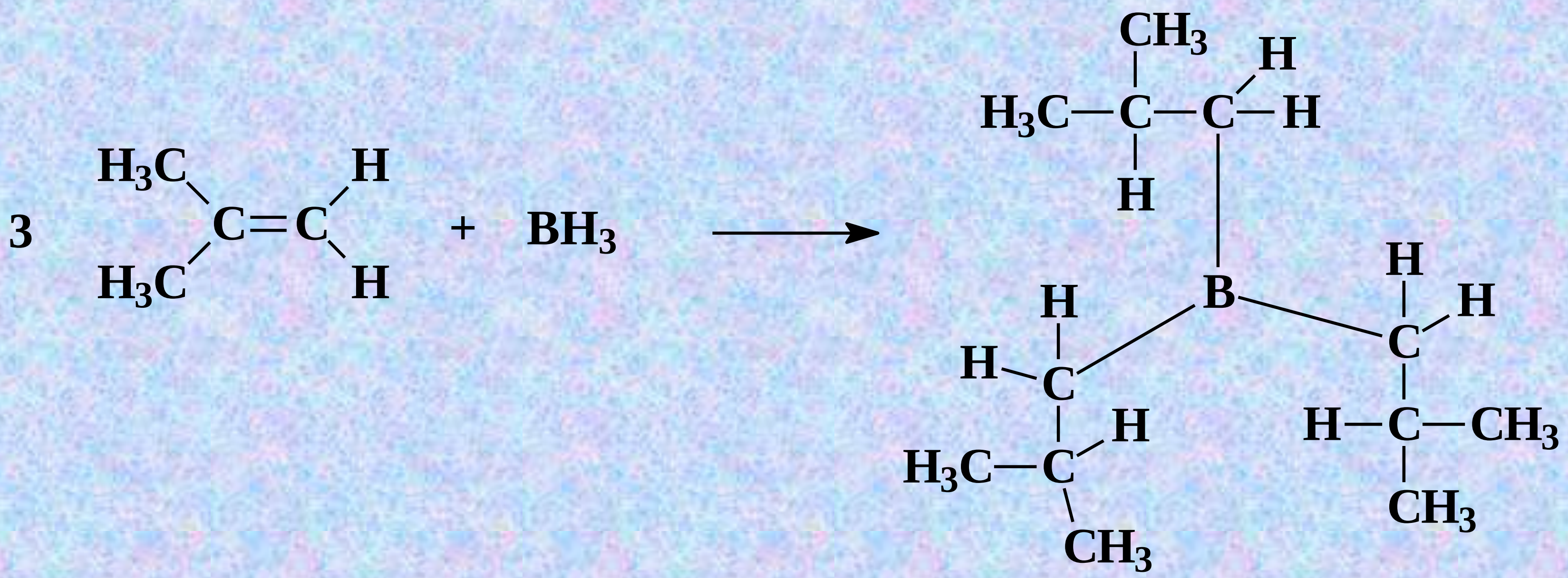
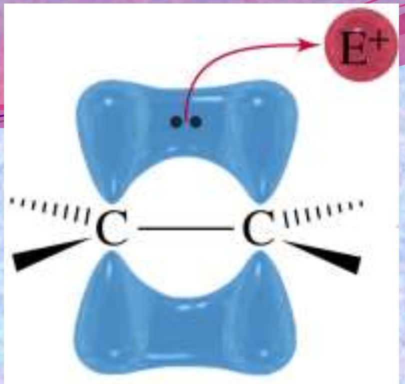


Actually, Trialkyl



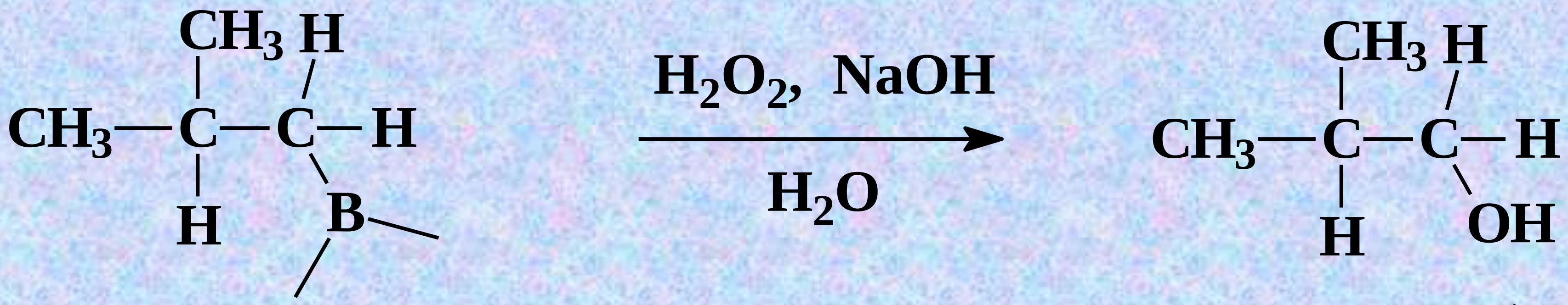
Borane prefers least-substituted carbon due to steric hindrance as well as charge distribution.

=>



Oxidation to Alcohol

- Oxidation of the alkyl borane with basic hydrogen peroxide produces the alcohol.
- Orientation is anti-Markovnikov.



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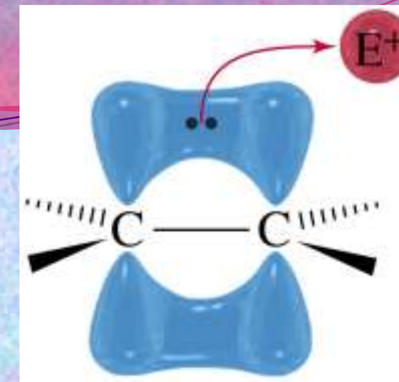
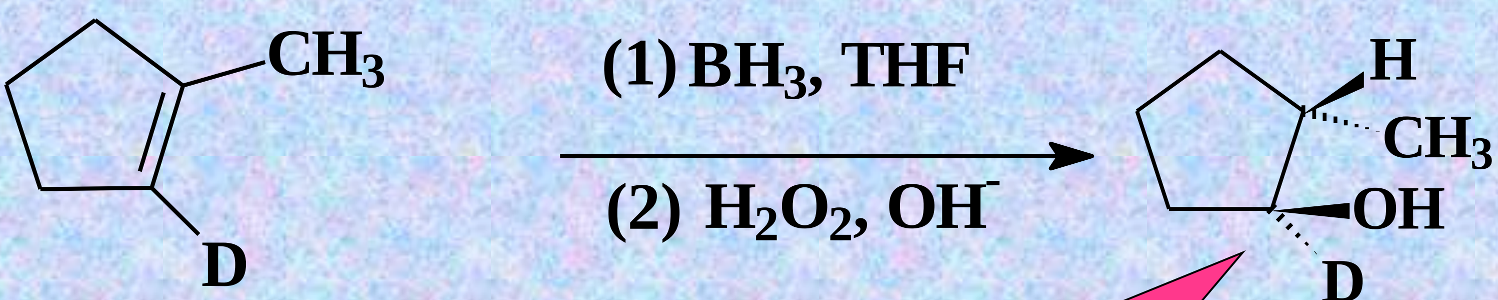


Predict the Product

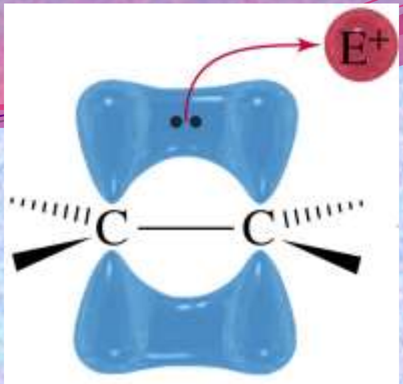
Predict the product when the given alkene reacts with borane in THF, followed by oxidation with basic hydrogen peroxide.



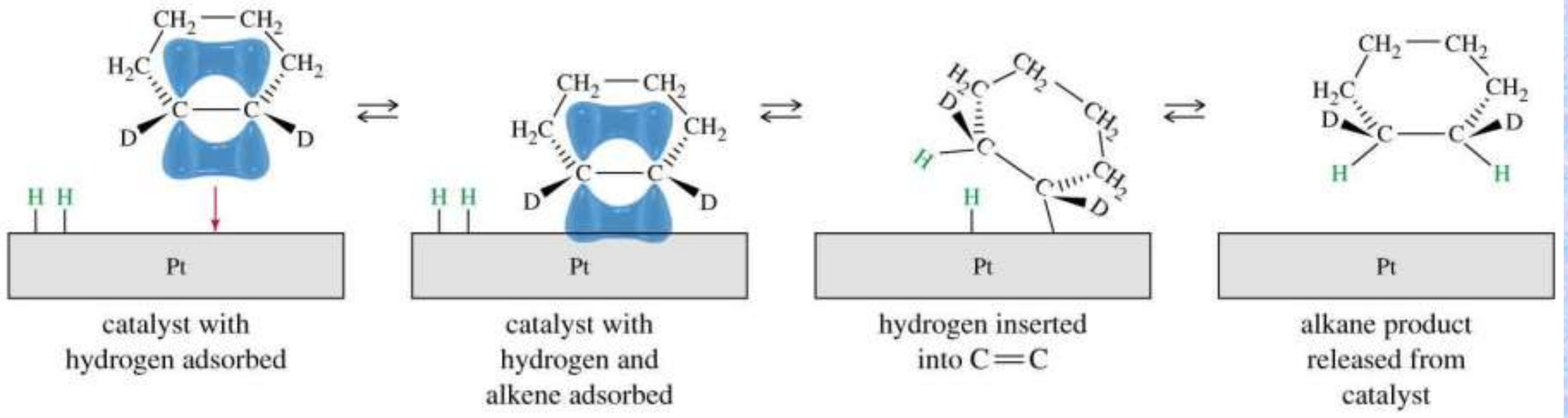
syn addition

=>

Hydrogenation



- Alkene + H_2 $\rightarrow$ Alkane
- Catalyst required, usually Pt, Pd, or Ni.
- Finely divided metal, heterogeneous
- Syn addition



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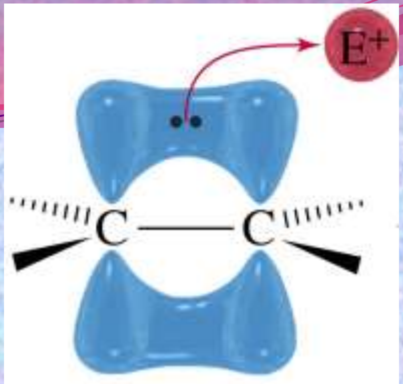
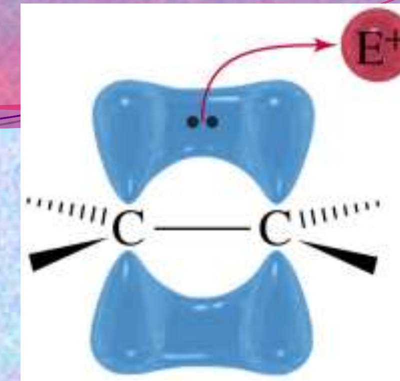
Addition of Carbenes

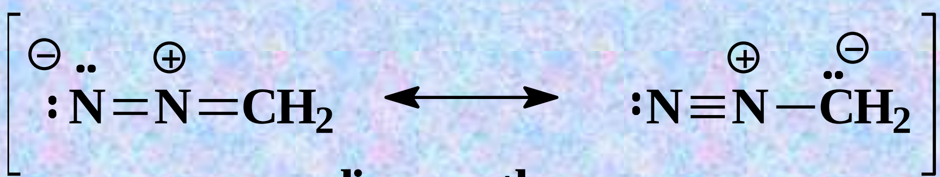


- Insertion of $-CH_2$ group into a double bond produces a cyclopropane ring.
- Three methods:
  - Diazomethane
  - Simmons-Smith: methylene iodide and Zn(Cu)
  - Alpha elimination, haloform

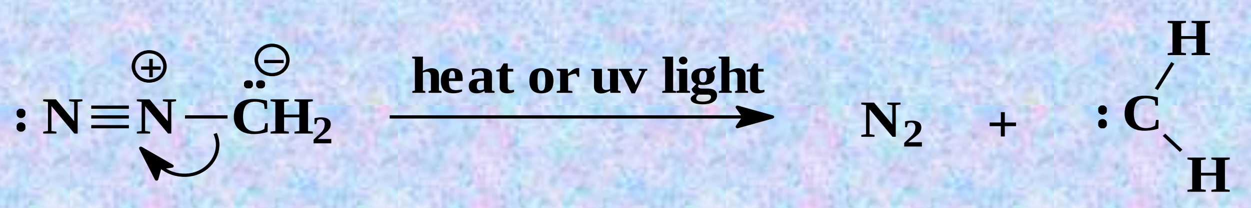
=>

Diazomethane

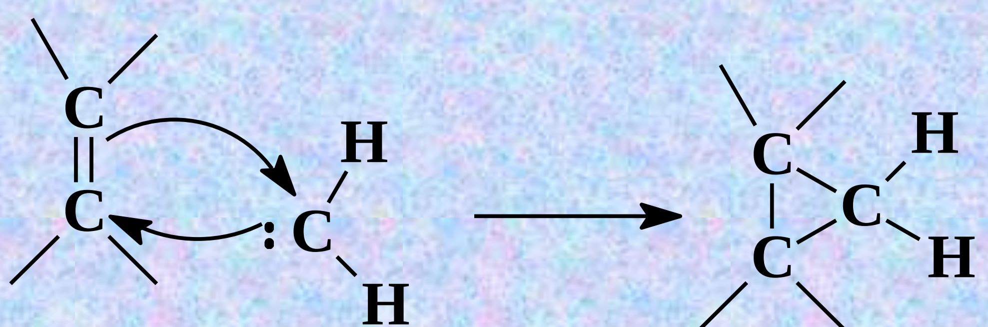




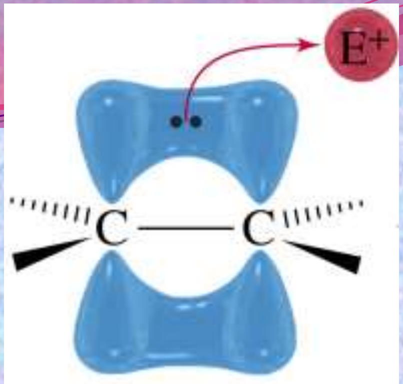
diazomethane



carbene



Extremely toxic and explosive. =>

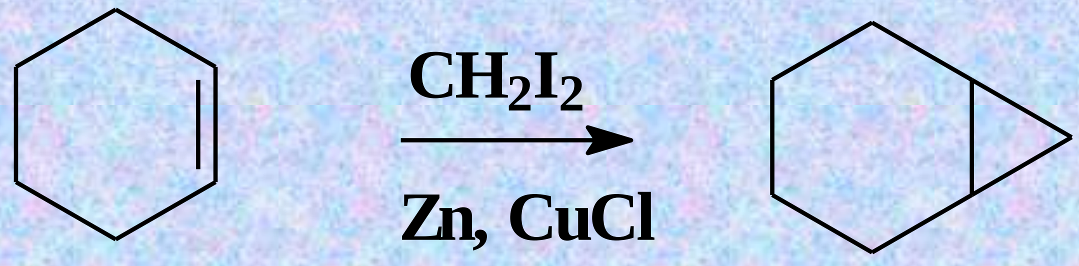


Simmons-Smith

Best method for preparing cyclopropanes.

$$CH_2I_2 \quad + \quad Zn(Cu) \longrightarrow ICH_2ZnI$$

a carbenoid



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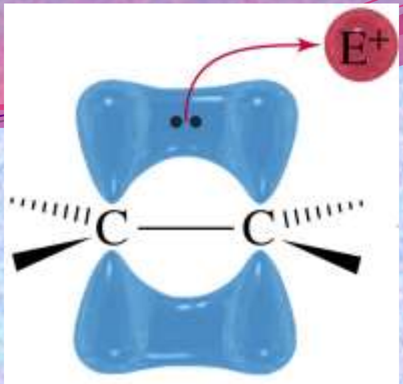
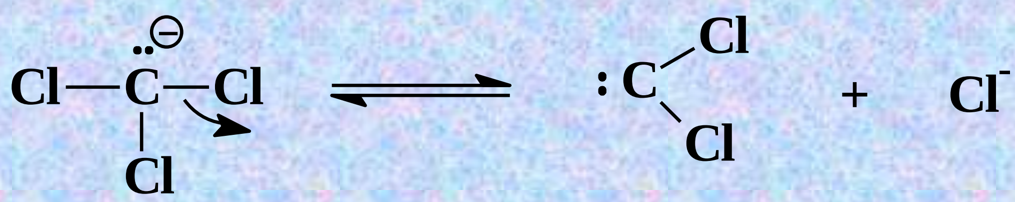
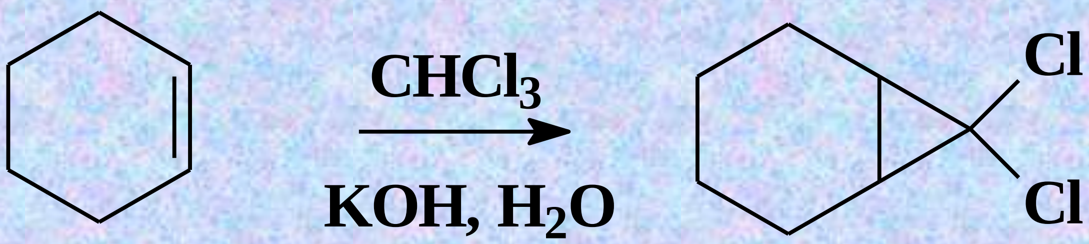
Alpha Elimination



- Haloform reacts with base.
- H and X taken from same carbon

$$CHCl_3 + KOH \rightleftharpoons K^{+}\ {}^{-}CCl_3 + H_2O$$





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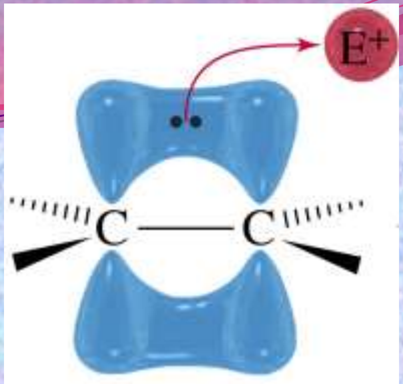
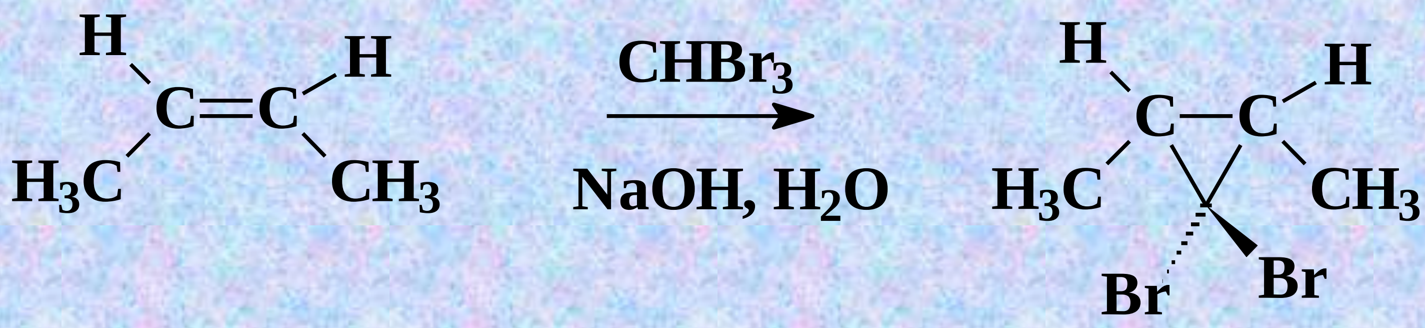
Stereospecificity



Cis-trans isomerism maintained around carbons that were in the double bond.



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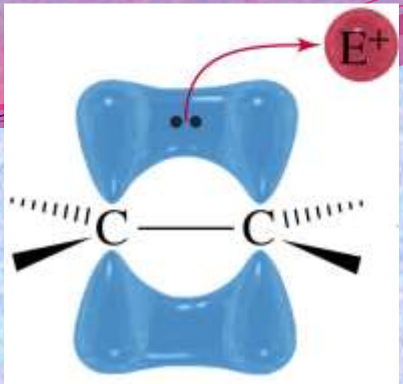
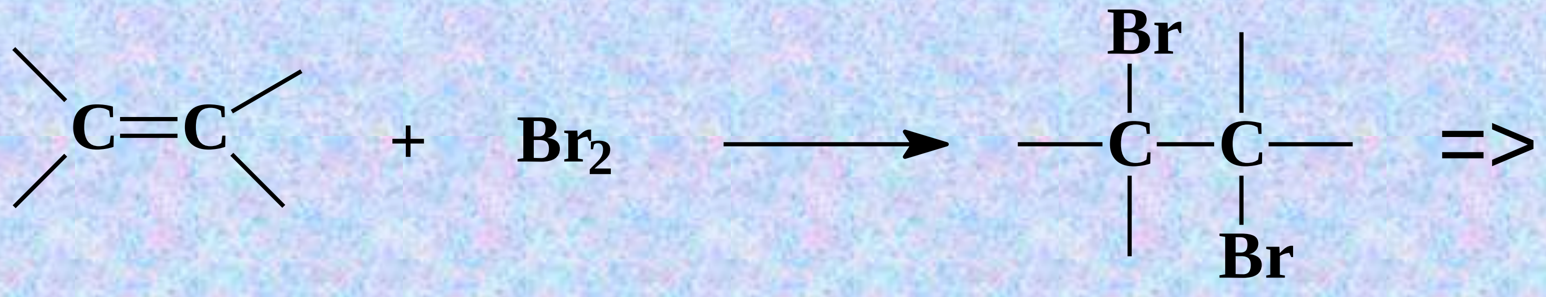
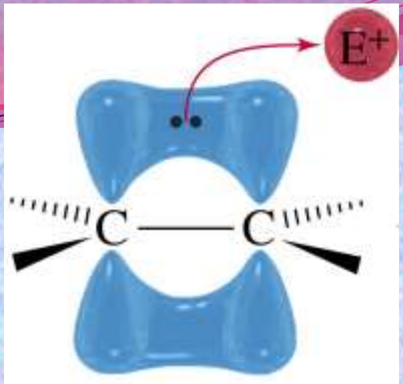
Addition of Halogens



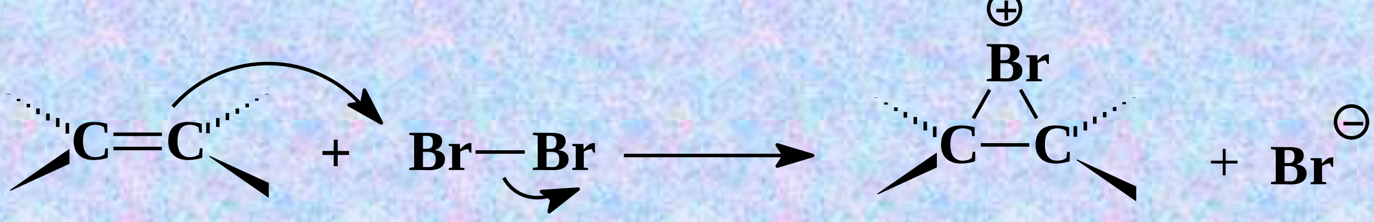
- Cl_2, Br_2, and sometimes I_2 add to a double bond to form a vicinal dibromide.
- Anti addition, so reaction is stereospecific.



Mechanism for Halogenation



- Pi electrons attack the bromine molecule.
- A bromide ion splits off.
- Intermediate is a cyclic bromonium ion.



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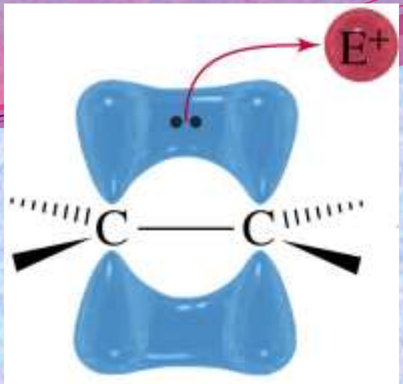
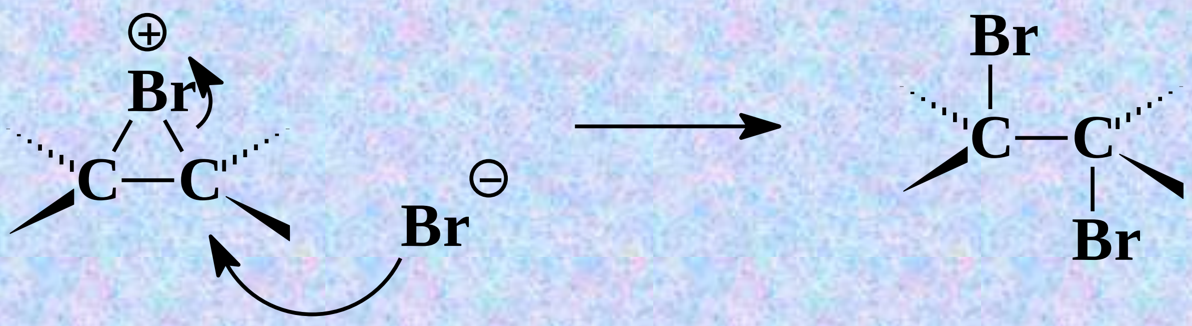
Mechanism (2)



Halide ion approaches from side opposite the three-membered ring.



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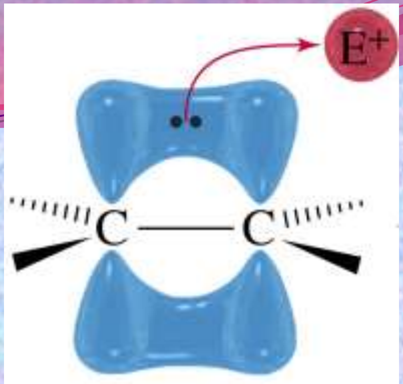
Test for Unsaturation



- Add Br_2 in CCl_4 (dark, red-brown color) to an alkene in the presence of light.
- The color quickly disappears as the bromine adds to the double bond.
- “Decolorizing bromine” is the chemical test for the presence of a double bond.

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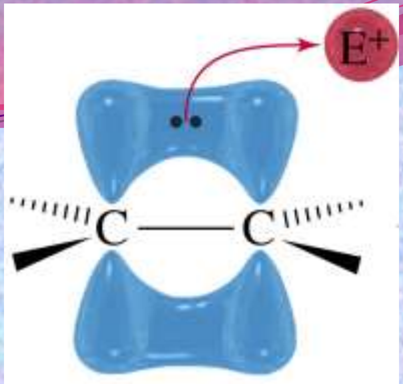
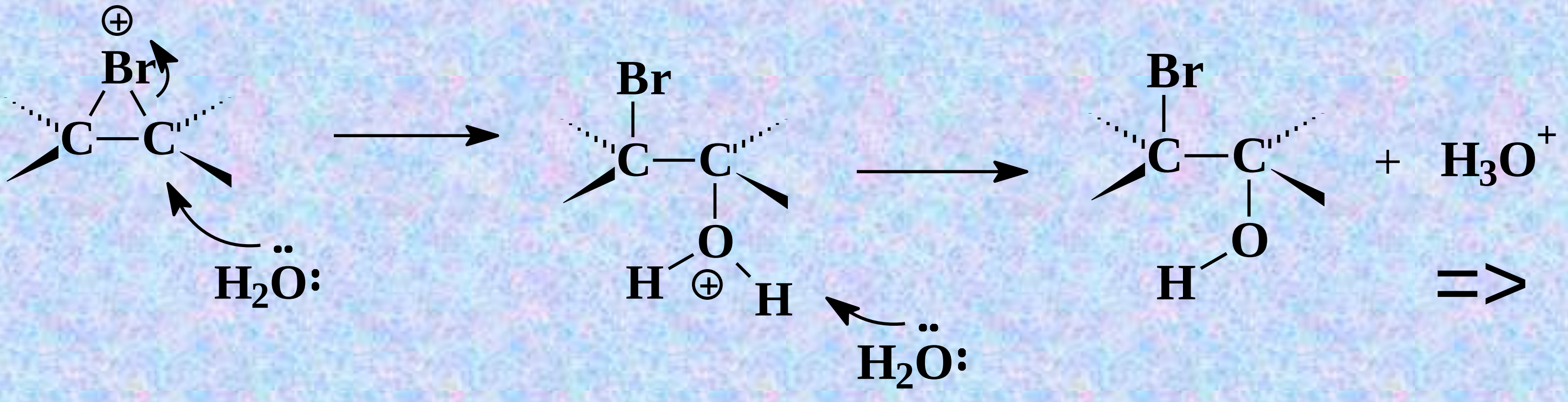
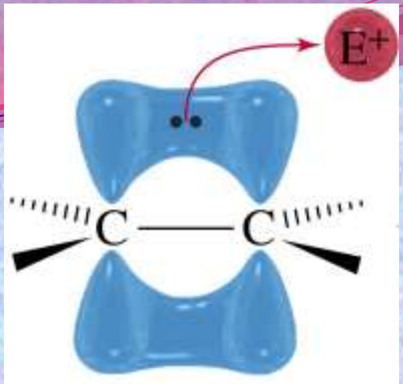
Formation of Halohydrin



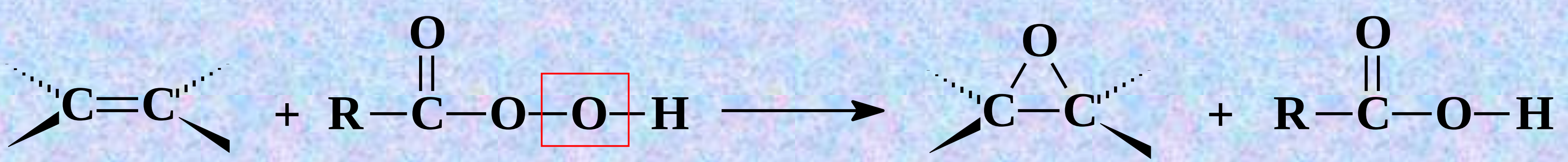
- If a halogen is added in the presence of water, a halohydrin is formed.
- Water is the nucleophile, instead of halide.
- Product is Markovnikov and anti.



Epoxidation



- Alkene reacts with a peroxyacid to form an epoxide (also called oxirane).
- Usual reagent is peroxybenzoic acid.



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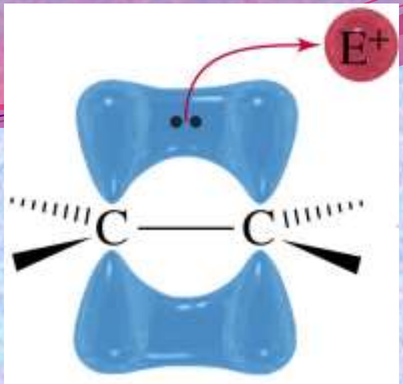
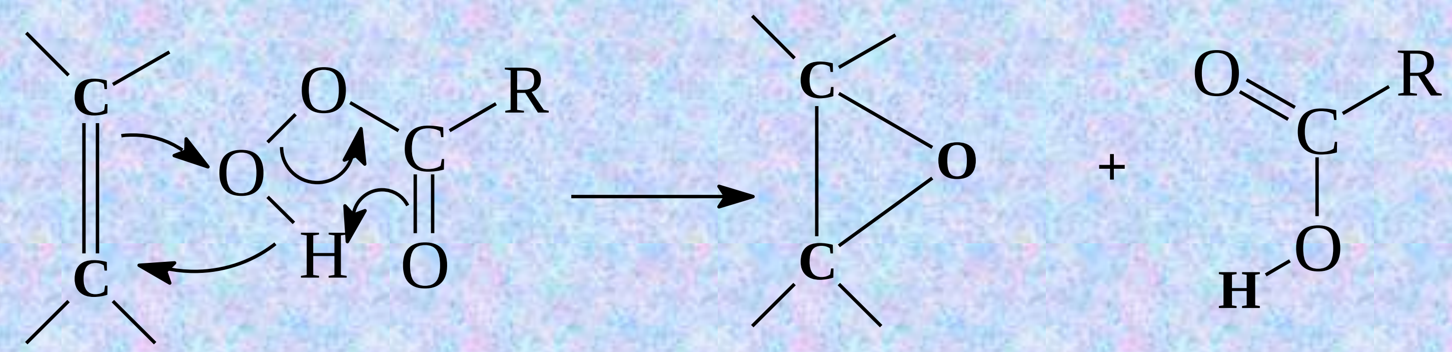
Mechanism



One-step concerted reaction. Several bonds break and form simultaneously.



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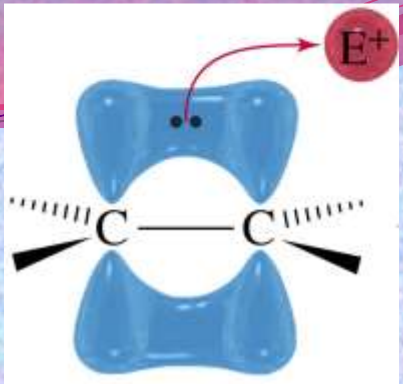
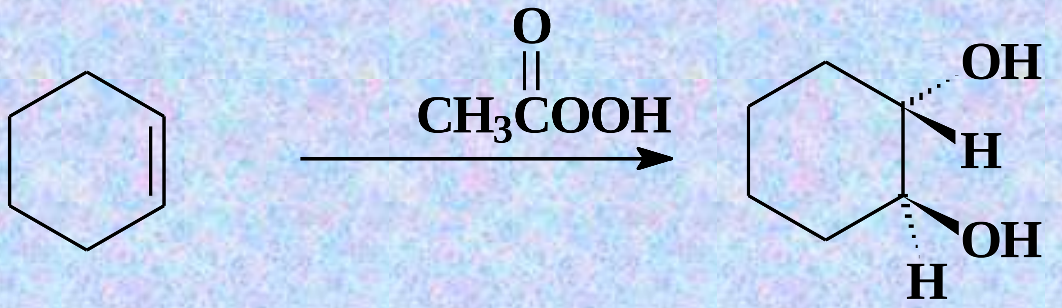
One-Step Reaction



- To synthesize the glycol without isolating the epoxide, use aqueous peroxyacetic acid or peroxyformic acid.
- The reaction is stereospecific.



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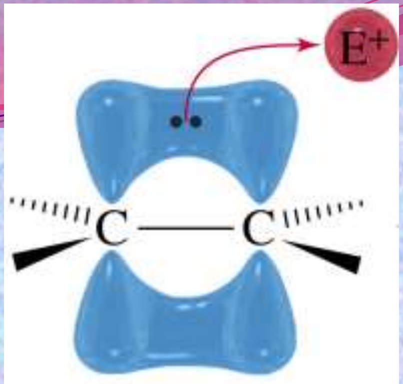
Syn Hydroxylation of Alkenes



- Alkene is converted to a *cis*-1,2-diol,
- Two reagents:
  - Osmium tetroxide (expensive!), followed by hydrogen peroxide *or*
  - Cold, dilute aqueous potassium permanganate, followed by hydrolysis with base

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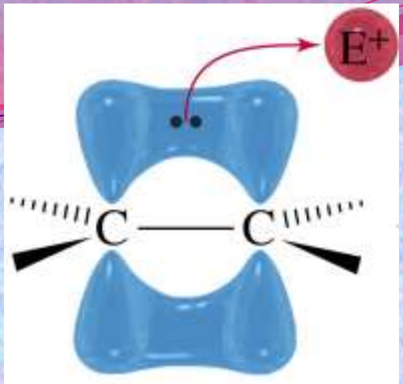
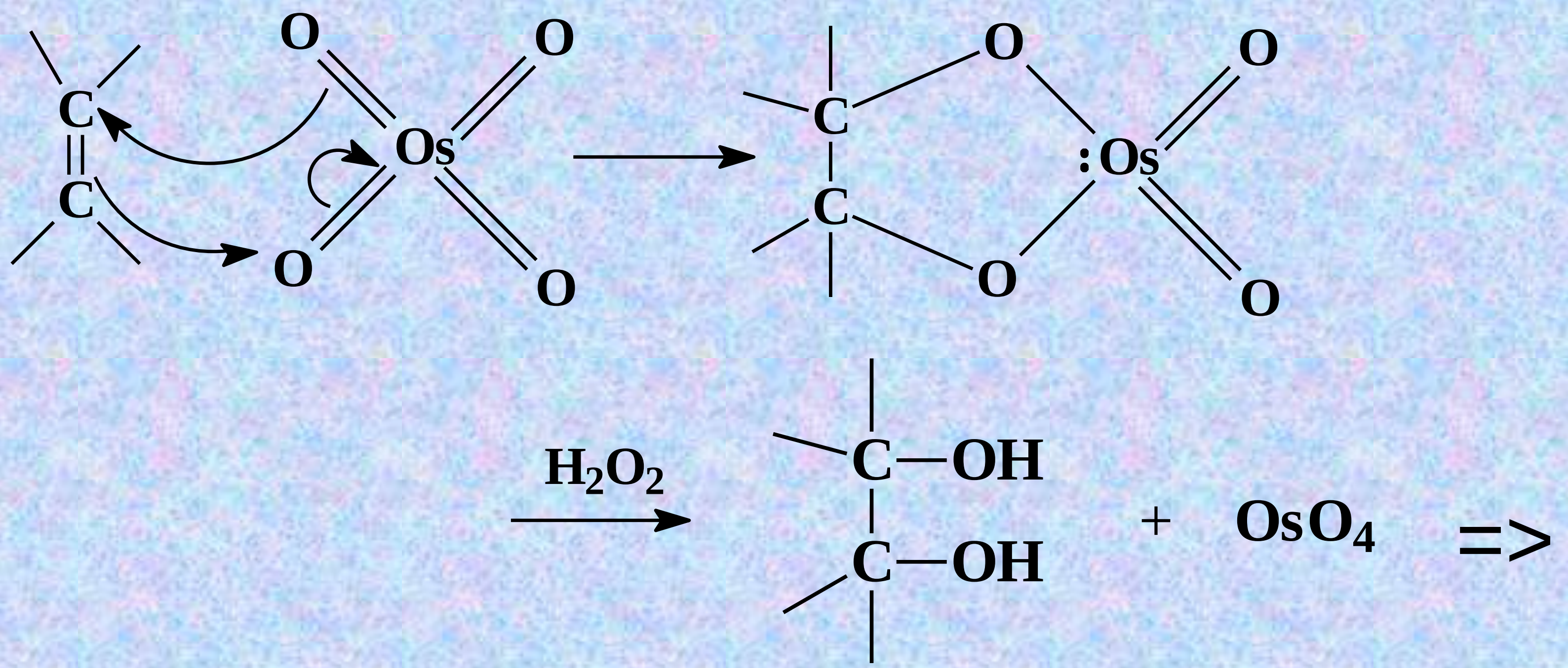
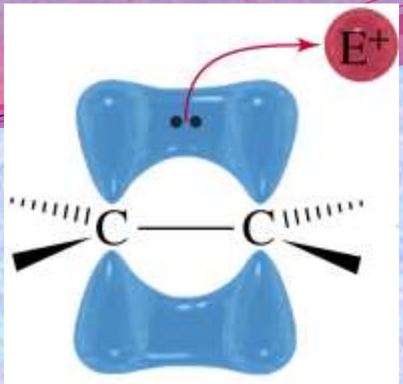


Mechanism with OsO_4

Concerted *syn* addition of two oxygens to form a cyclic ester.



Oxidative Cleavage



- Both the pi and sigma bonds break.
- C=C becomes C=O.
- Two methods:
  - Warm or concentrated or acidic $KMnO_4$.
  - Ozonolysis
- Used to determine the position of a double bond in an unknown.

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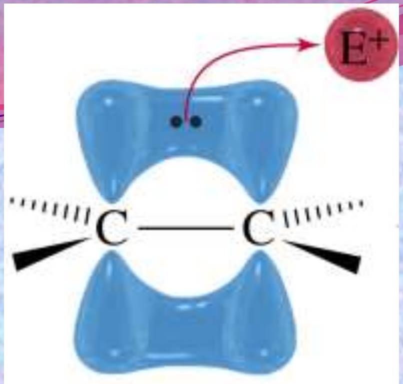
Cleavage with MnO4⁻



- Permanganate is a strong oxidizing agent.
- Glycol initially formed is further oxidized.
- Disubstituted carbons become ketones.
- Monosubstituted carbons become carboxylic acids.
- Terminal $=CH_2$ becomes CO_2.

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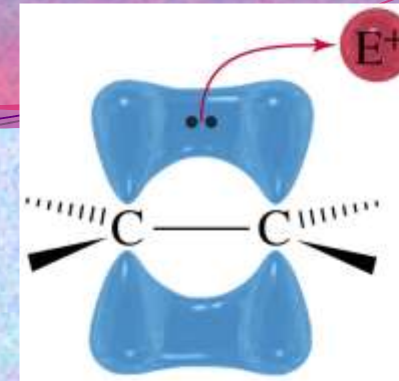
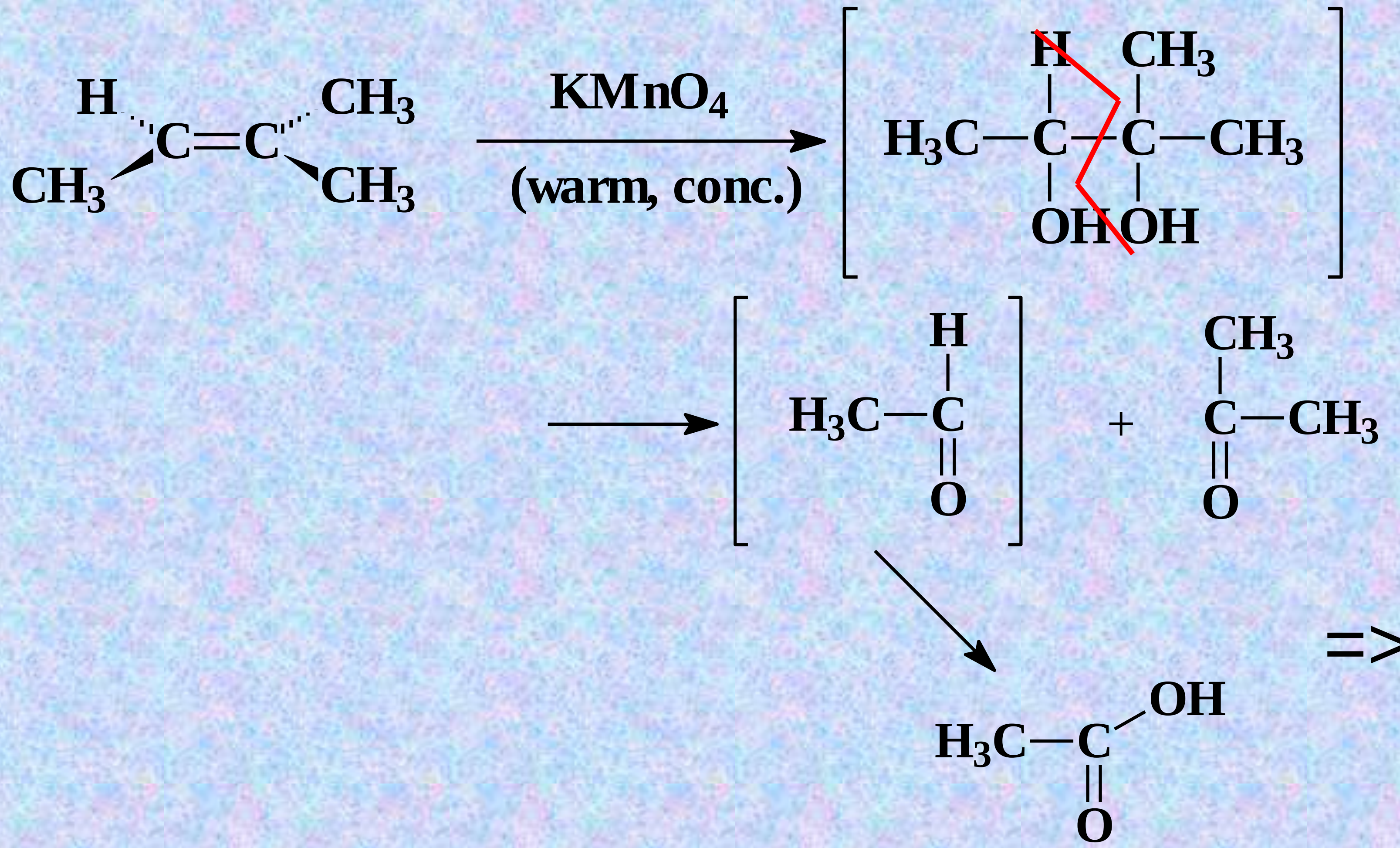
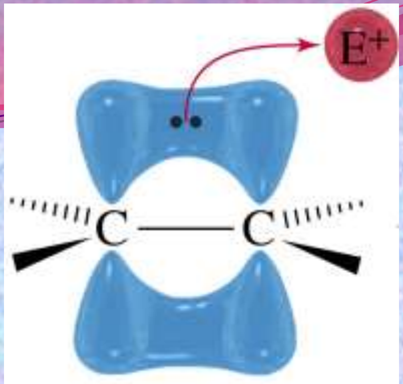
Example





Ozonolysis



- Reaction with ozone forms an ozonide.
- Ozonides are not isolated, but are treated with a mild reducing agent like Zn or dimethyl sulfide.
- Milder oxidation than permanganate.
- Products formed are ketones or aldehydes.

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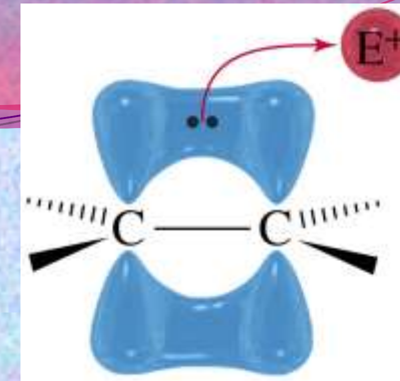
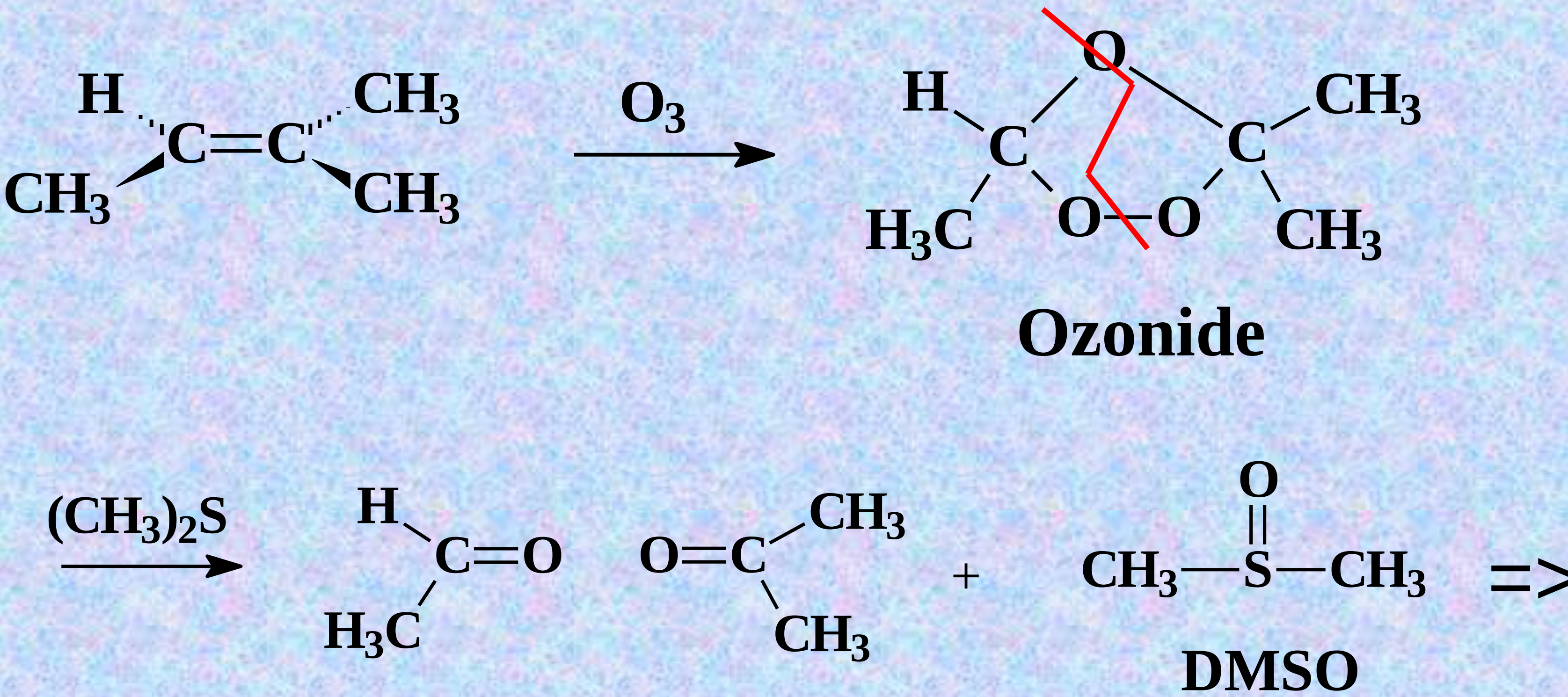
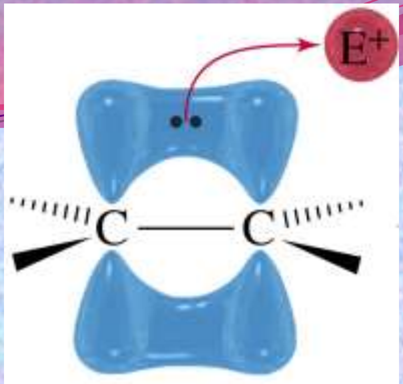
Ozonolysis Example







THANKS

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