ORGANIC CHEMISTRY-SEM-3H

Reactions of Alkenes-1

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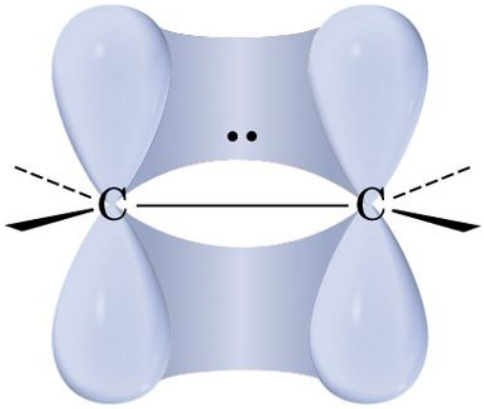


Carbon–carbon π bond:
weaker: more accessible electrons

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.

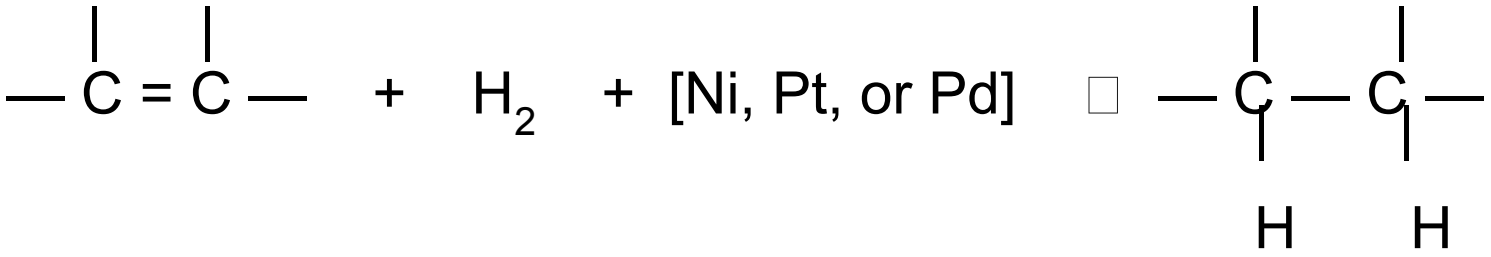
=>

Reactions, alkenes:

1. Addition of hydrogen (reduction).
2. Addition of halogens.
3. Addition of hydrogen halides.
4. Addition of sulfuric acid.
5. Addition of water (hydration).
6. Addition of aqueous halogens (halohydrin formation).
7. Oxymercuration-demercuration.

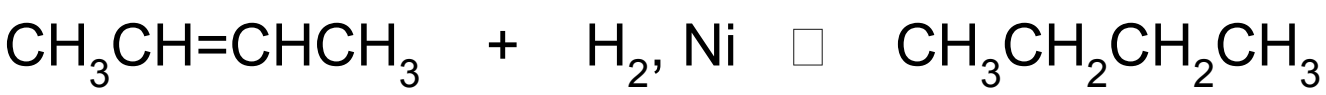
8. Hydroboration-oxidation.
9. Addition of free radicals.
10. Addition of carbenes.
11. Epoxidation.
12. Hydroxylation.
13. Ozonolysis.
14. Vigorous oxidation.

1. Addition of hydrogen (reduction).



a) Requires catalyst.

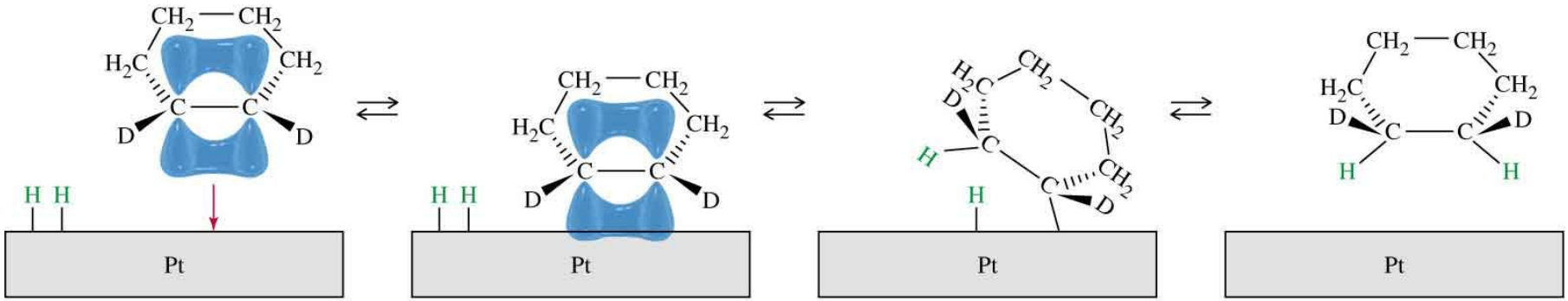
b) #1 synthesis of alkanes



2-butene *n*-butane

Hydrogenation

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



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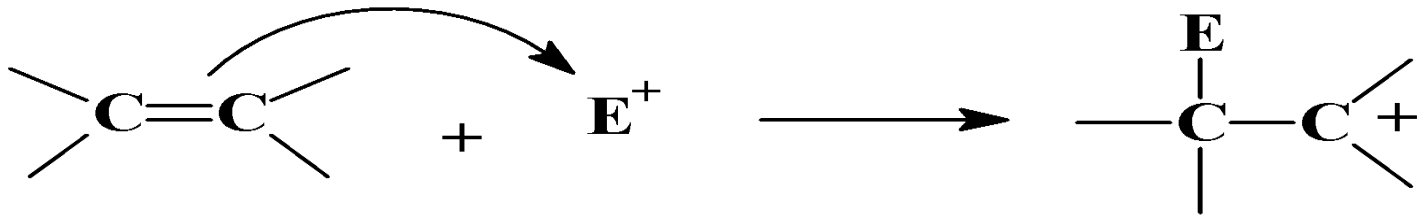
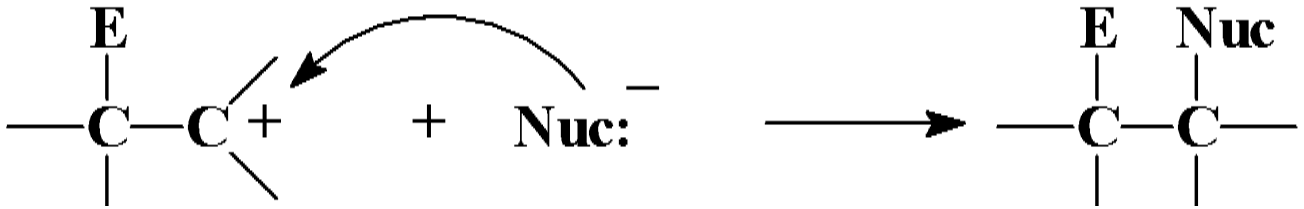
Electrophilic Addition

- Step 1: Pi electrons attack the electrophile.



- Step 2: Nucleophile attacks the carbocation.



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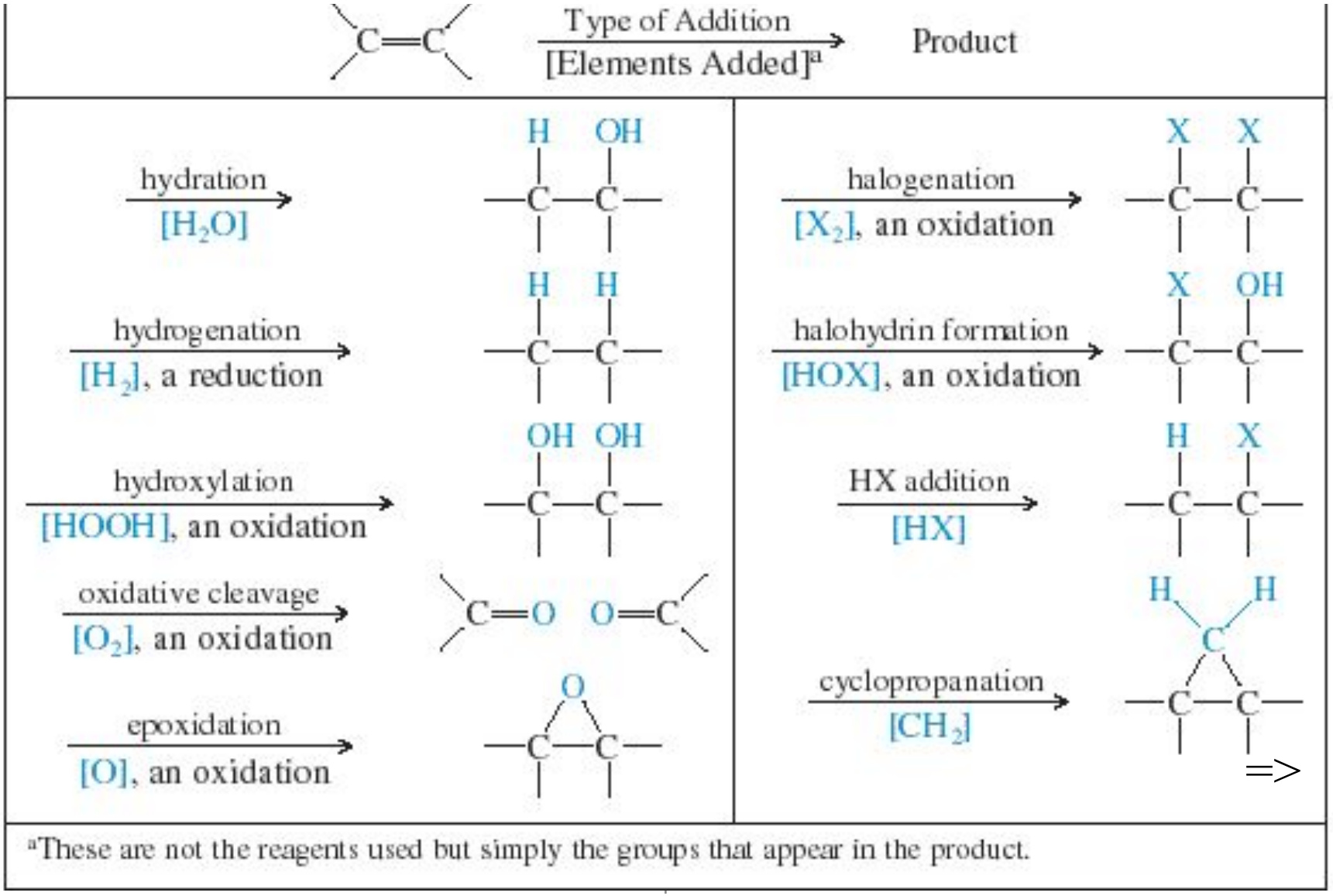
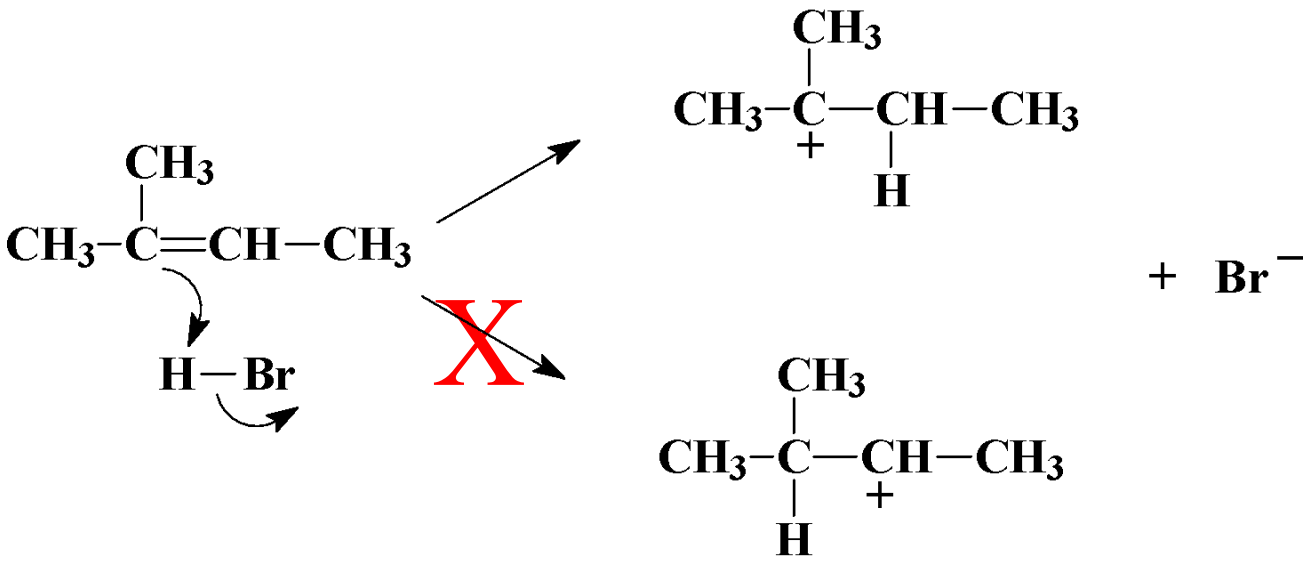
Types of Additions



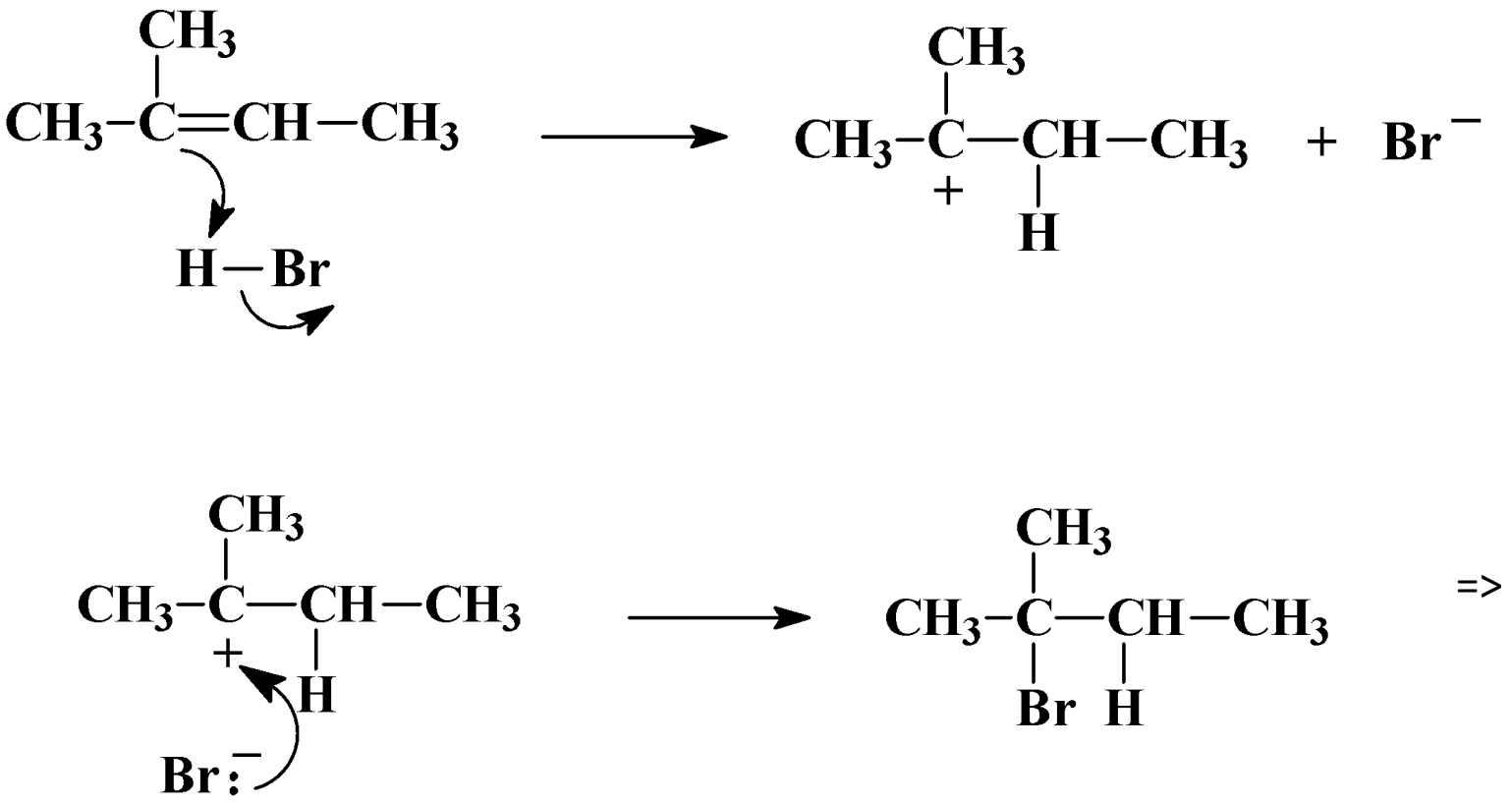
aThese are not the reagents used but simply the groups that appear in the product.

Addition of HX (1)

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



Addition of HX (2)



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.

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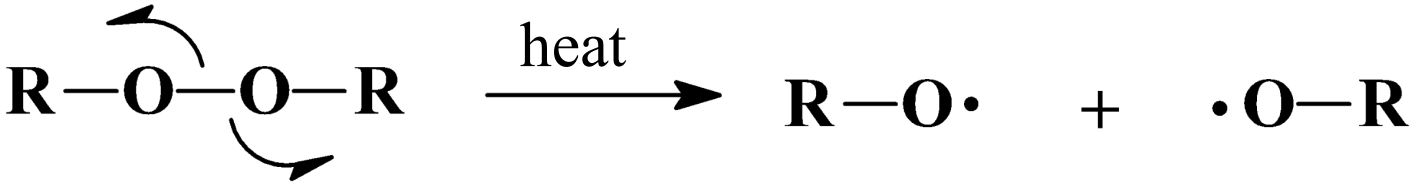
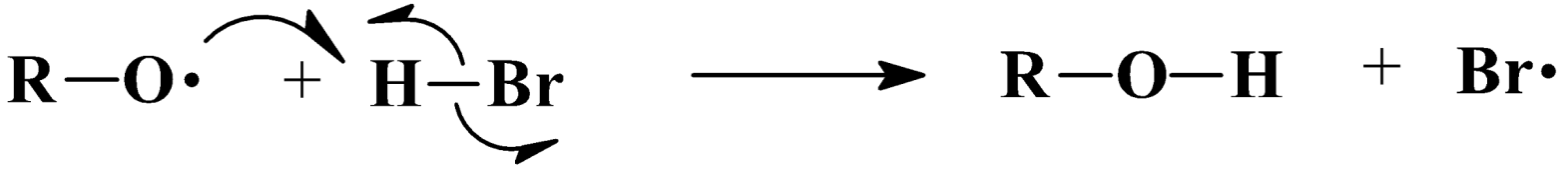
Free Radical Initiation

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



- Hydrogen is abstracted from HBr.



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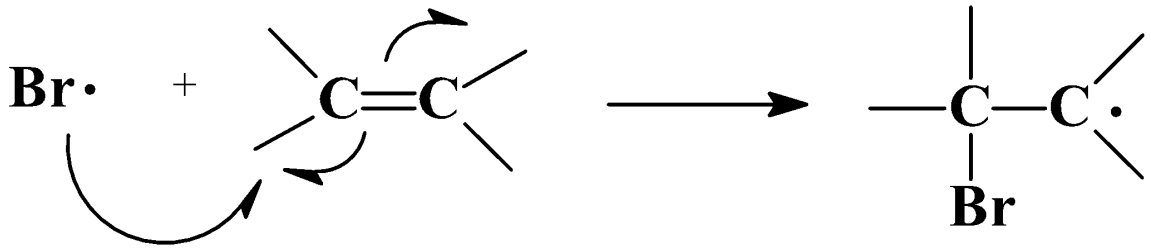
Electrophile

Propagation Steps

- Bromine adds to the double bond.



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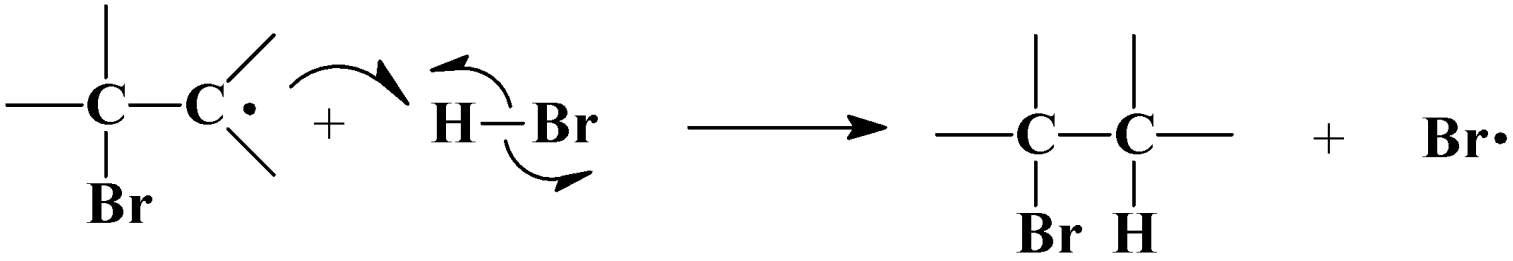
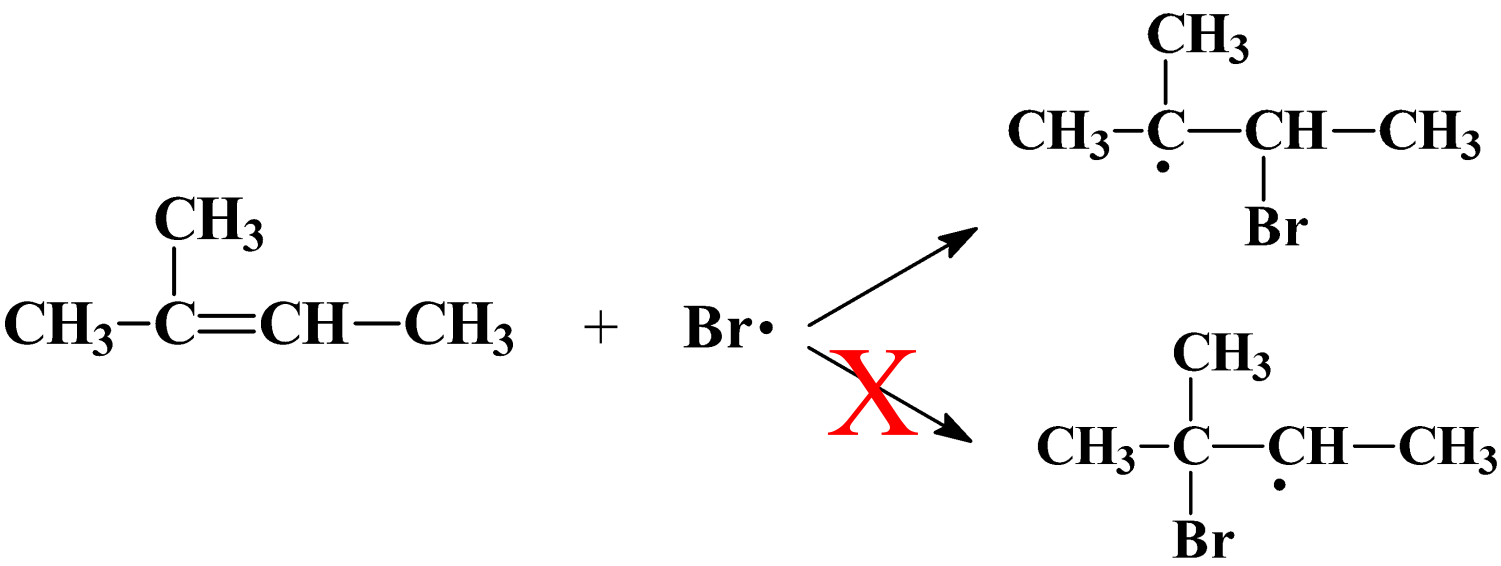


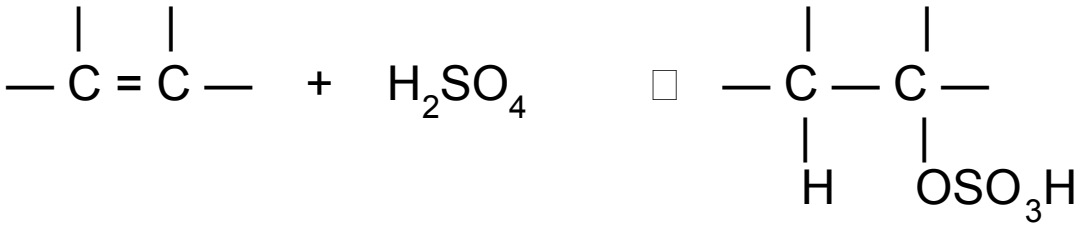
Electrophile =>

Anti-Markovnikov ??



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

4. Addition of sulfuric acid.



alkyl hydrogen sulfate

Markovnikov orientation.