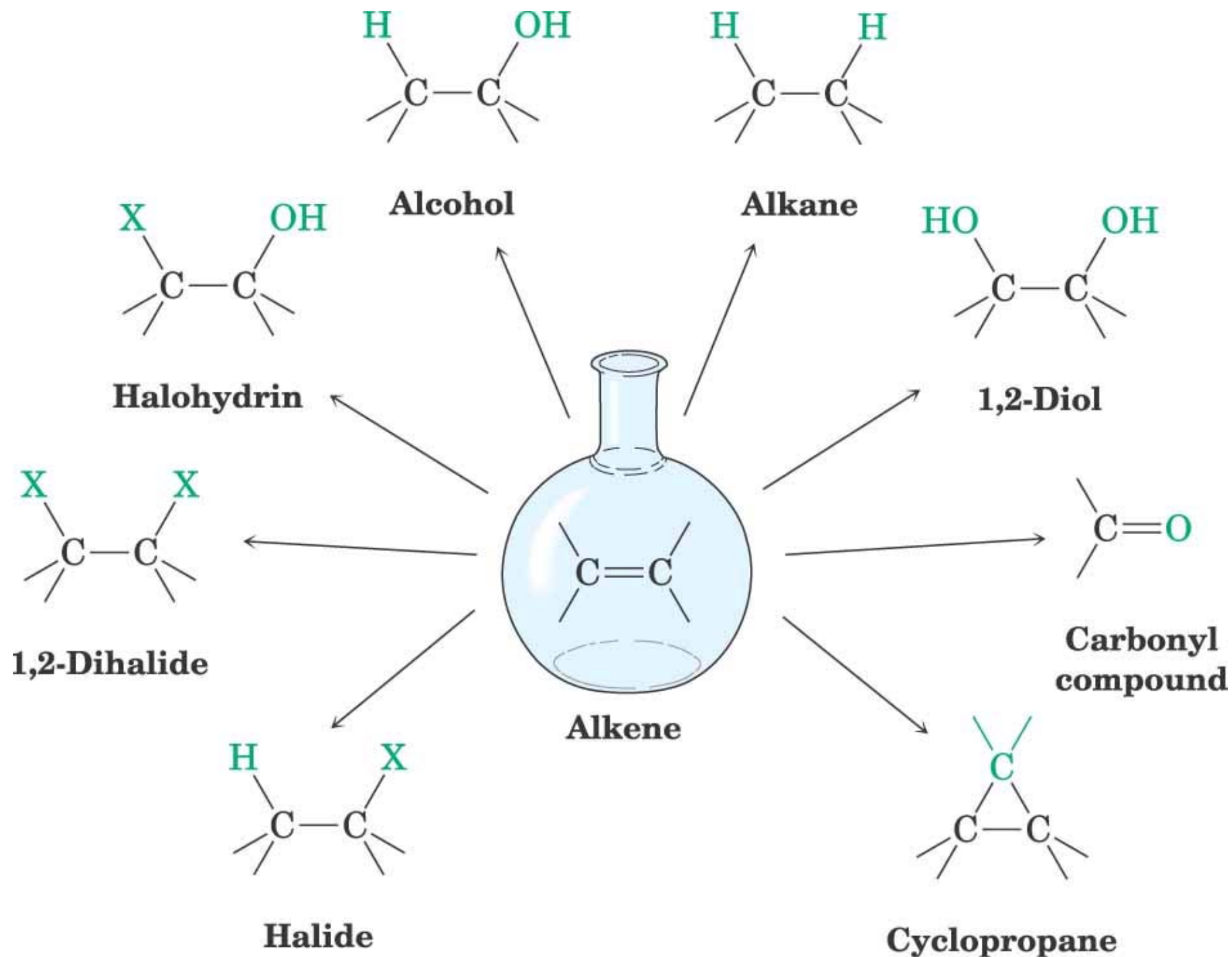
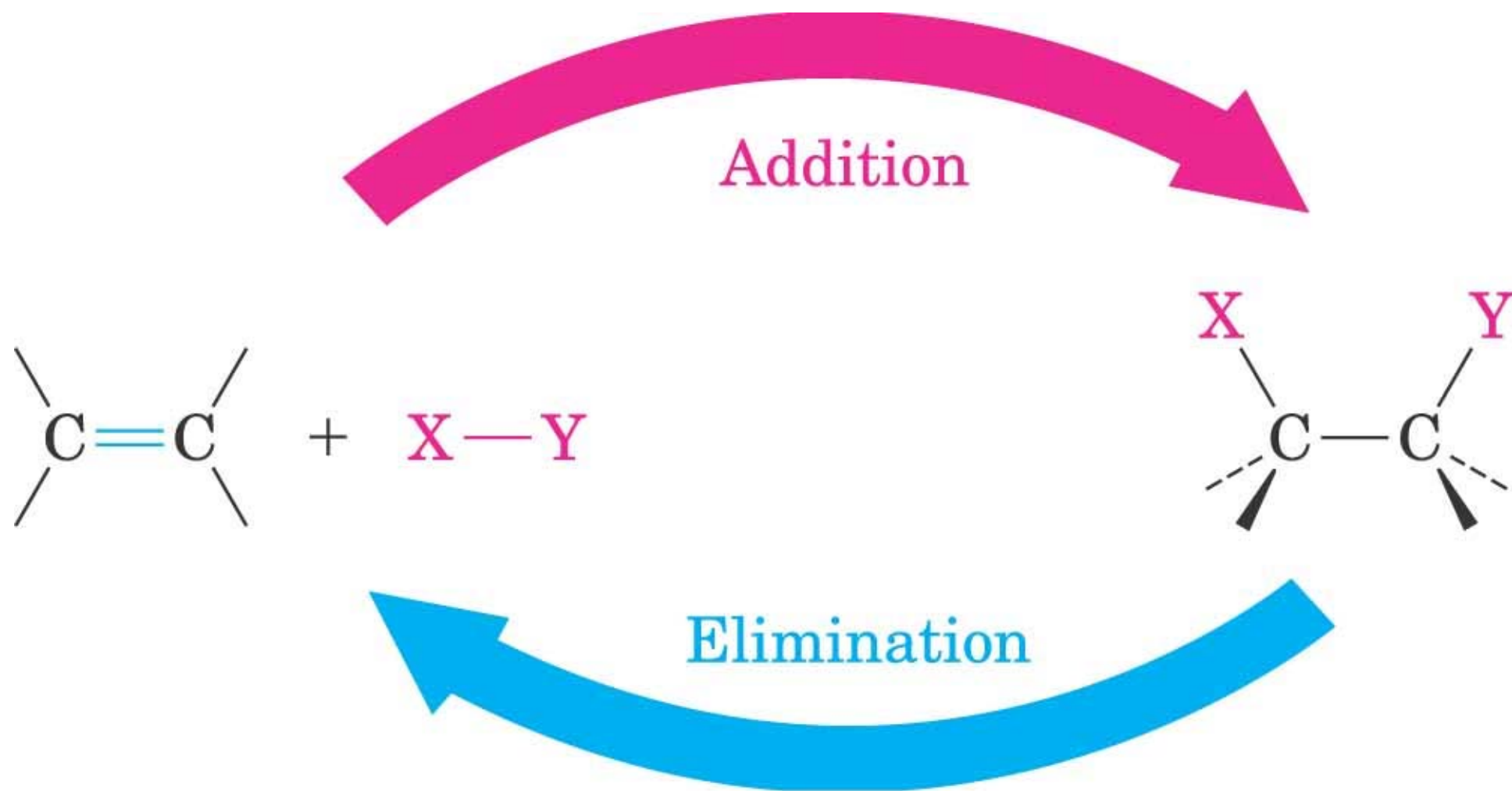


7. Alkenes: Reactions and Synthesis

Diverse Reactions of Alkenes

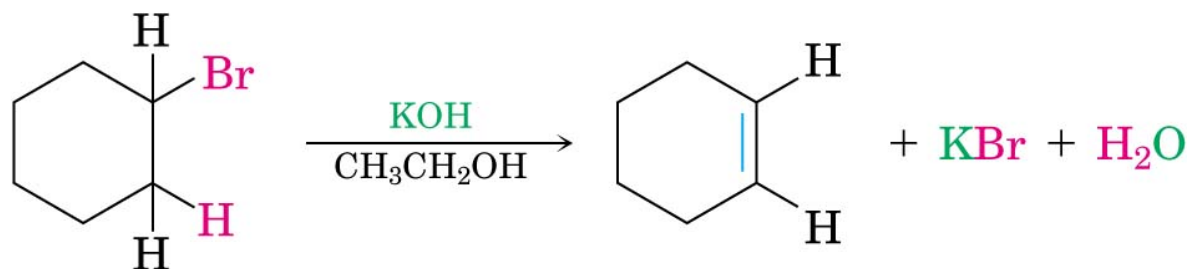
- Alkenes react with many electrophiles to give useful products by addition (often through special reagents)
 - alcohols (add H-OH)
 - alkanes (add H-H)
 - halohydrins (add HO-X)
 - dihalides (add X-X)
 - halides (add H-X)
 - diols (add HO-OH)
 - cyclopropane (add :CH₂)





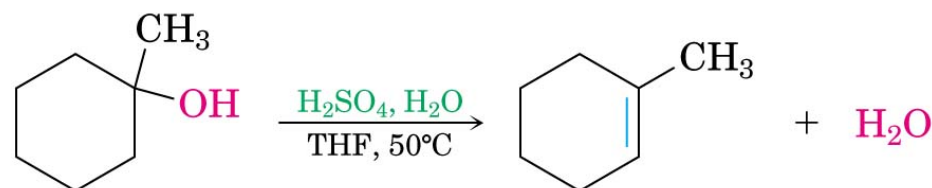
7.1 Preparation of Alkenes: A Preview of Elimination Reactions

- Alkenes are commonly made by
 - elimination of HX from alkyl halide (**dehydrohalogenation**)
 - Uses heat and KOH
 - elimination of H-OH from an alcohol (**dehydration**)
 - require strong acids (sulfuric acid, 50 °C)



Bromocyclohexane
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Cyclohexene (81%)



1-Methylcyclohexanol

1-Methylcyclohexene (91%)

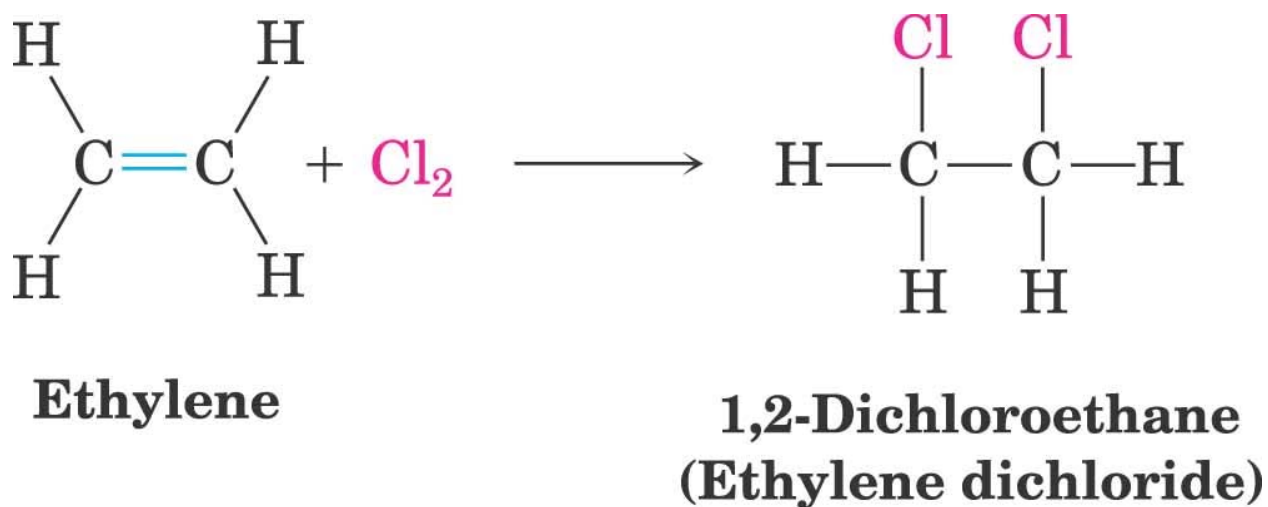


7.2 Addition of Halogens to Alkenes

Bromine and chlorine add to alkenes to give 1,2-dihalides, an industrially important process. (already saw addition of HX to alkenes, Markovnikov)

F₂ is too reactive and I₂ does not add

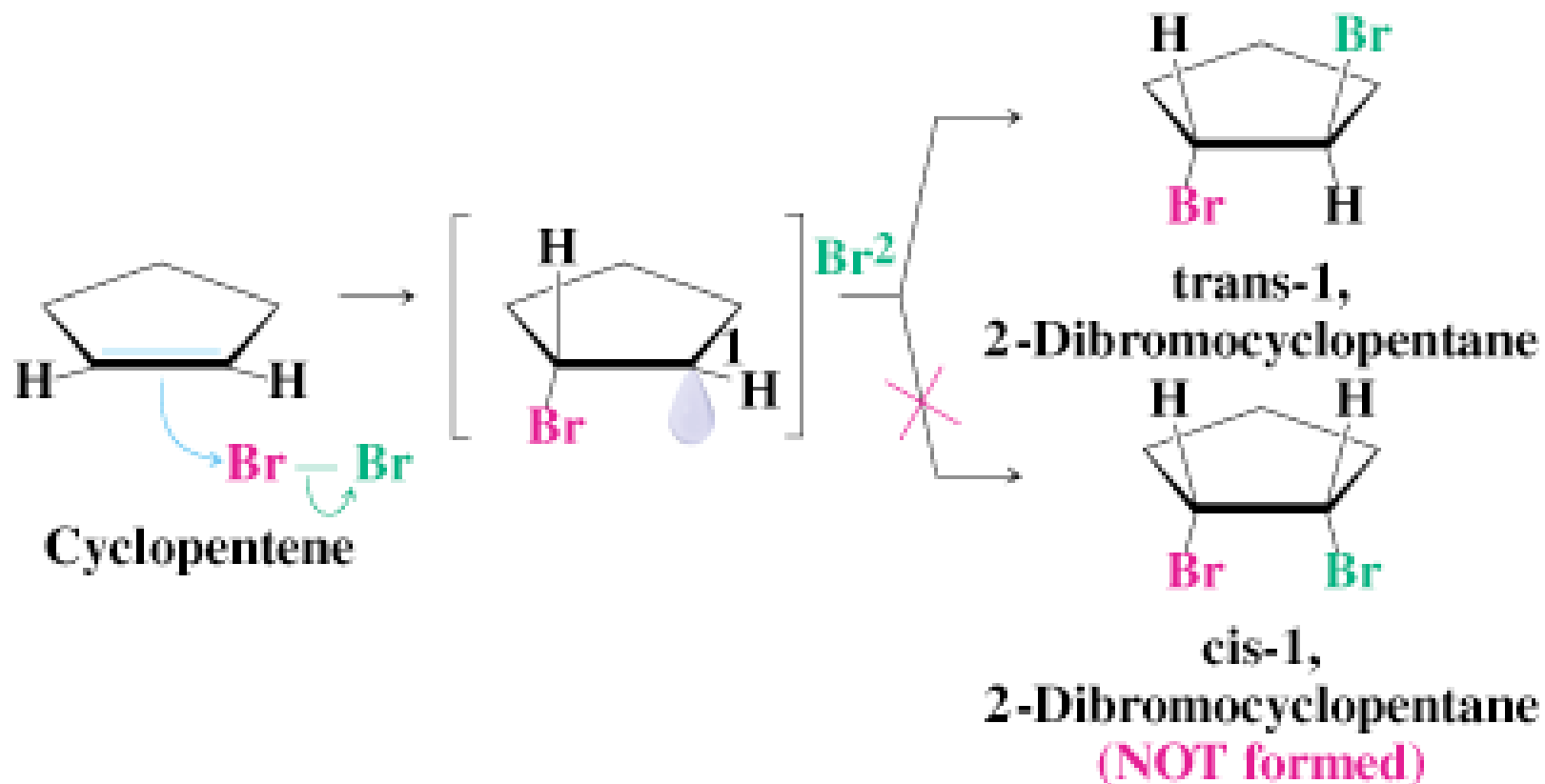
Cl₂ reacts as Cl⁺ Cl⁻, Br₂ is similar (Via chloronium & bromonium ion bridge)



Addition of Br₂ to Cyclopentene

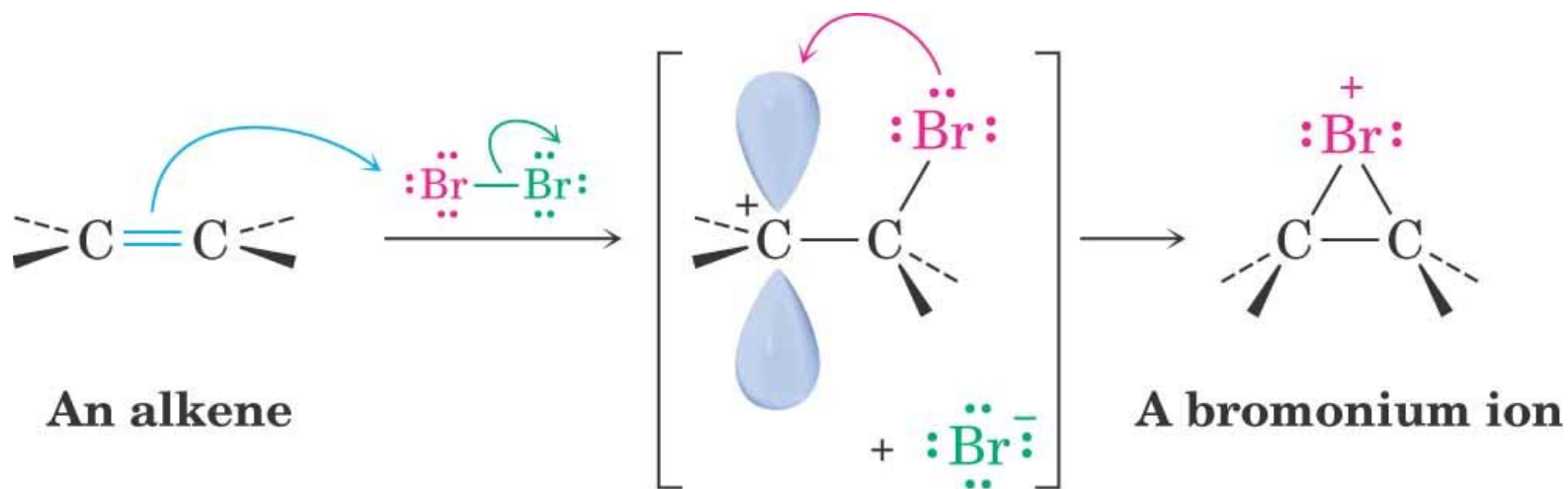
Addition is exclusively trans (mechanism & product are trans)

Reaction occurs with anti stereochemistry.



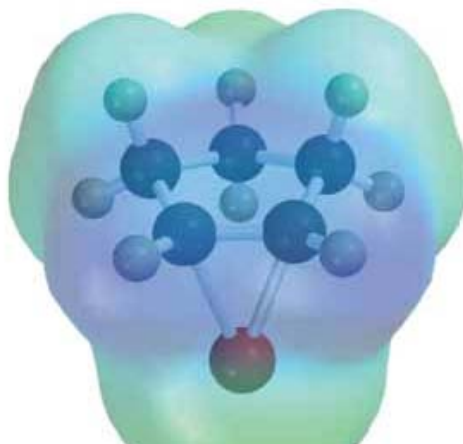
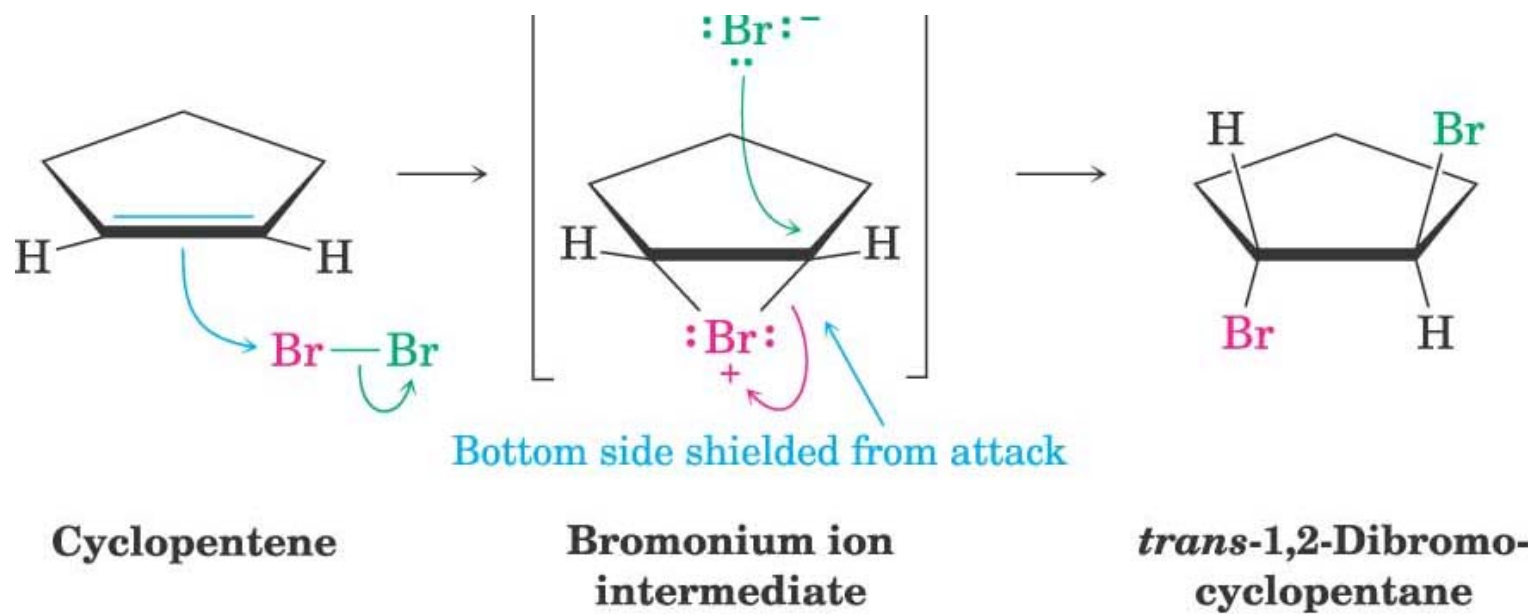
Mechanism of Bromine Addition

- Br^+ adds to an alkene producing a cyclic ion
- Bromonium ion, bromine shares charge with carbon
 - Gives trans addition

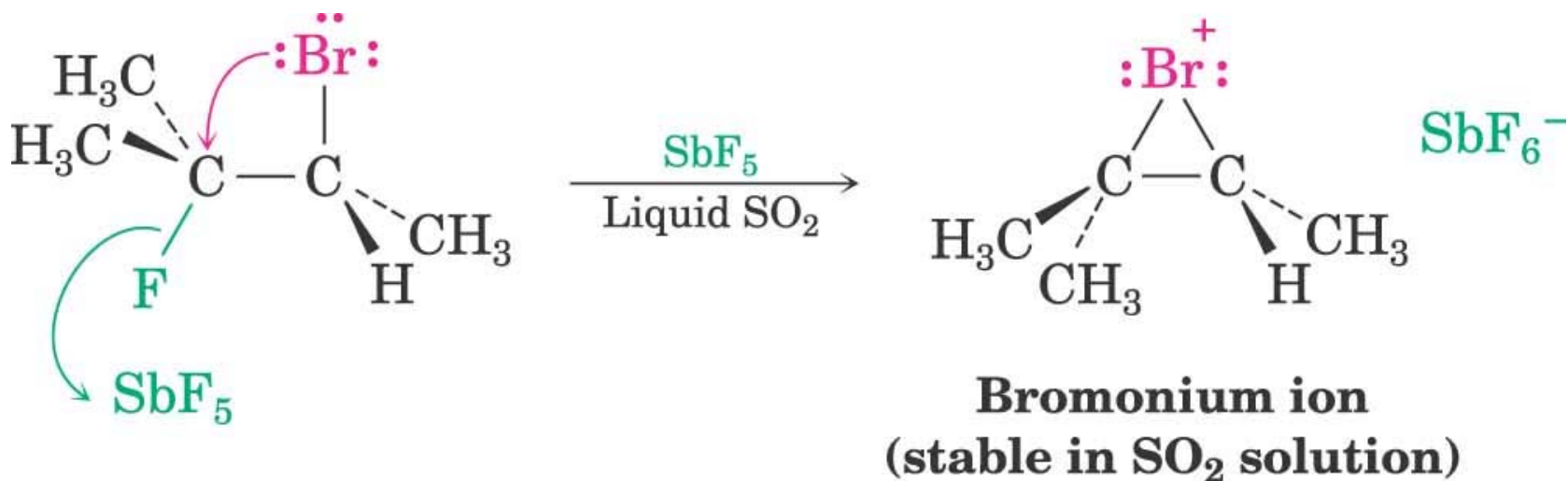


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Electrophilic addition of bromine to give a cation is followed by cyclization to give a *bromonium ion*. This bromonium ion is a reactive electrophile and bromide ion is a good nucleophile



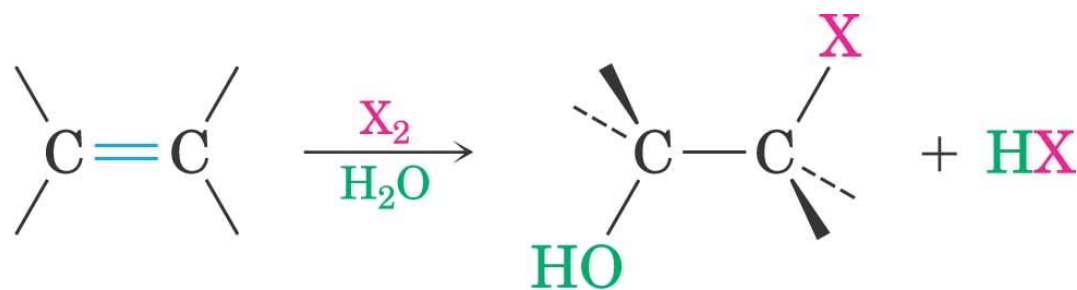
There is strong evidence nowadays for the existence of a bromonium ion structure.



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7.3 Halohydrin Formation

- This is formally the addition of HO-X to an alkene to give a 1,2-halo alcohol, called a halohydrin
- The actual reagent is the dihalogen (Br_2 or Cl_2 in water in an organic solvent)



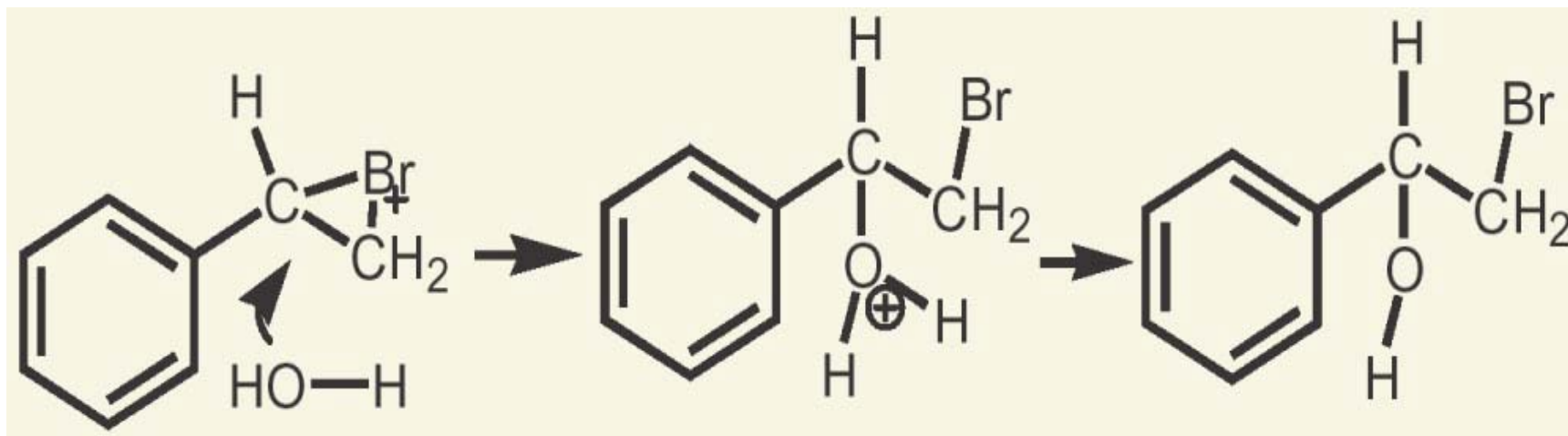
An alkene

A halohydrin

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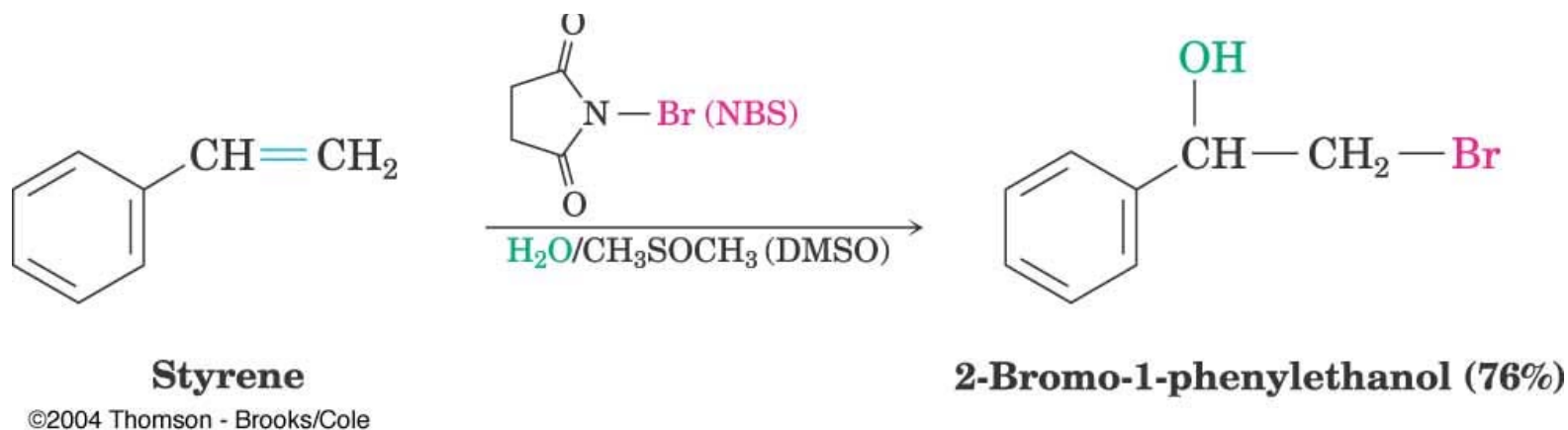
Mechanism of Bromohydrin Formation

- Br_2 forms bromonium ion, then water adds
 - Orientation toward stable C^+ species, (Aromatic rings do not react)



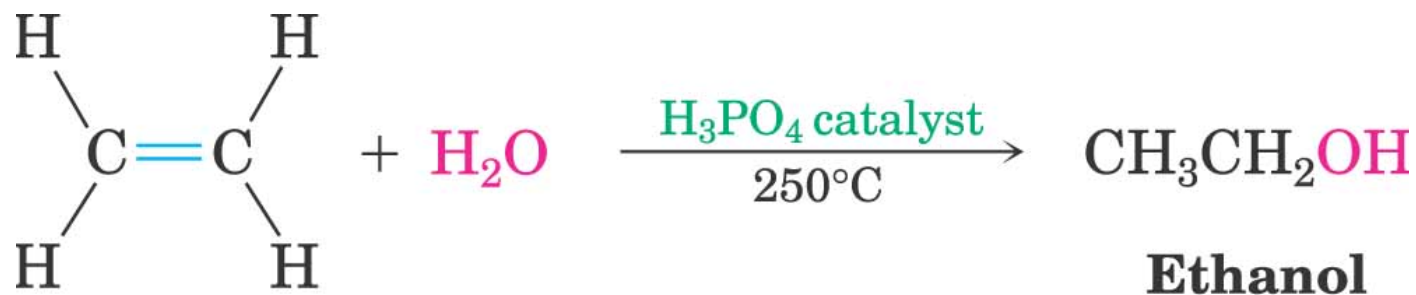
An Alternative to Bromine

- Bromine is a difficult reagent to use for this reaction
- N-Bromosuccinimide (NBS) produces bromine in water and is a safer source of bromine



7.4 Addition of Water to Alkenes/ Oxymercuration

- **Hydration of an alkene** is the addition of $\text{H}-\text{OH}$ to to give an alcohol
- Acid catalysts are used in high temperature industrial processes: ethylene is converted to ethanol



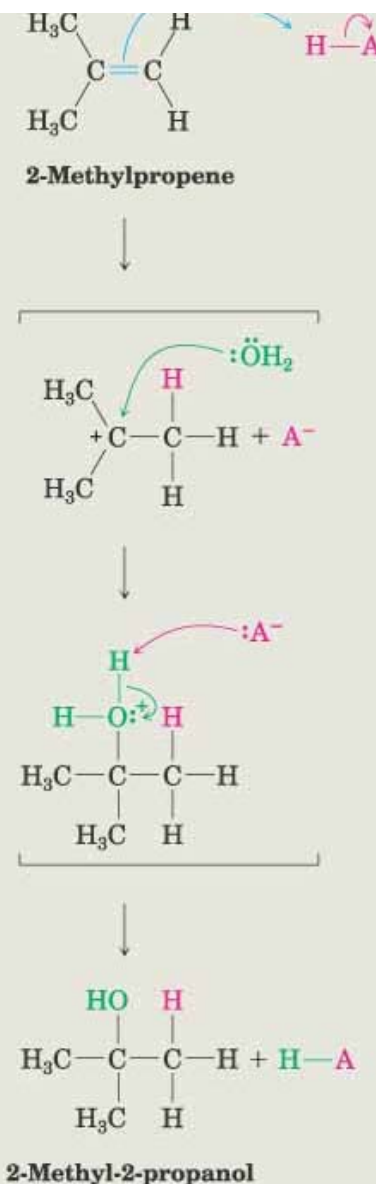
Ethylene

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Reaction of an alkene with acid (HA) yields a carbocation intermediate.

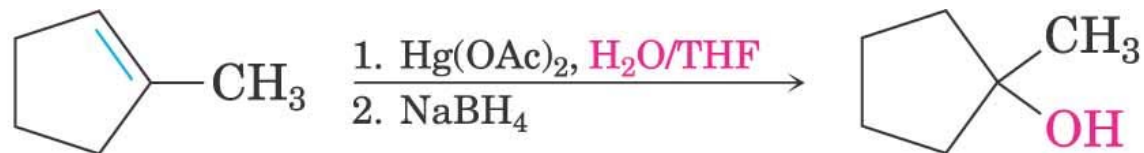
Water acts as a nucleophile, using a lone pair of electrons on oxygen to form a bond to carbon. The oxygen atom, having donated electrons, is now trivalent and has the positive charge.

Loss of an H^+ from oxygen then yields the neutral alcohol product and regenerates the acid catalyst HA.



Oxymercuration Intermediate

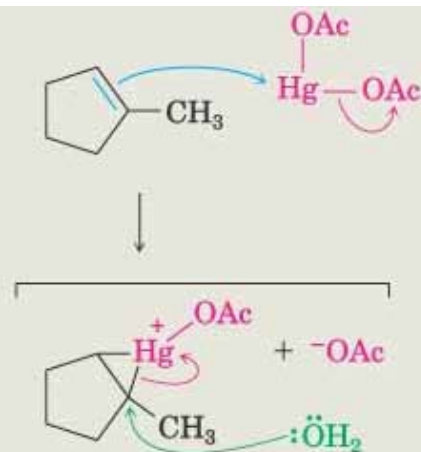
- For laboratory-scale hydration of an alkene
- Use mercuric acetate in THF followed by sodium borohydride
- Markovnikov orientation (*via* mercurinium ion)



1-Methylcyclopentene

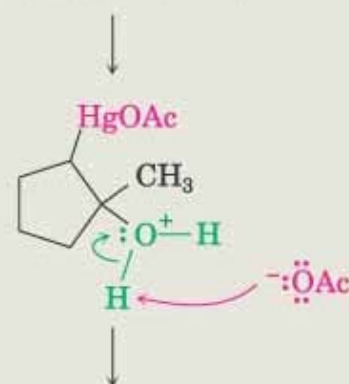
**1-Methylcyclopentanol
(92%)**

Electrophilic addition of mercuric acetate to an alkene produces an intermediate, three-membered mercurinium ion.

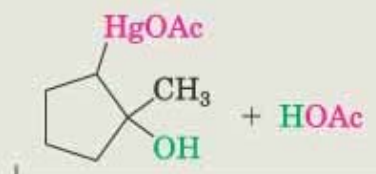


Water as nucleophile then displaces mercury by back-side attack at the more highly substituted carbon, breaking the C-Hg bond.

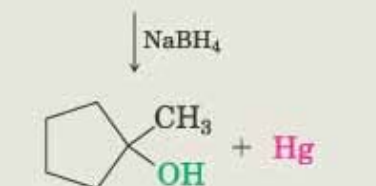
A mercurinium ion



Loss of H^+ yields a neutral organo-mercury addition product.

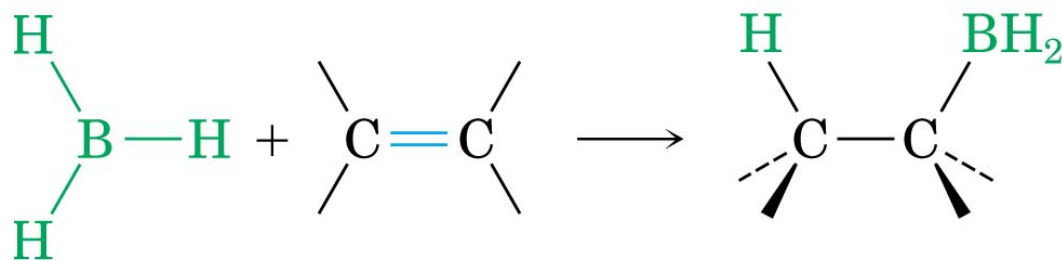


Treatment with sodium borohydride replaces the $-\text{Hg}$ by $-\text{H}$ and reduces the mercury, yielding an alcohol product.



7.5 Addition of Water to Alkenes: Hydroboration

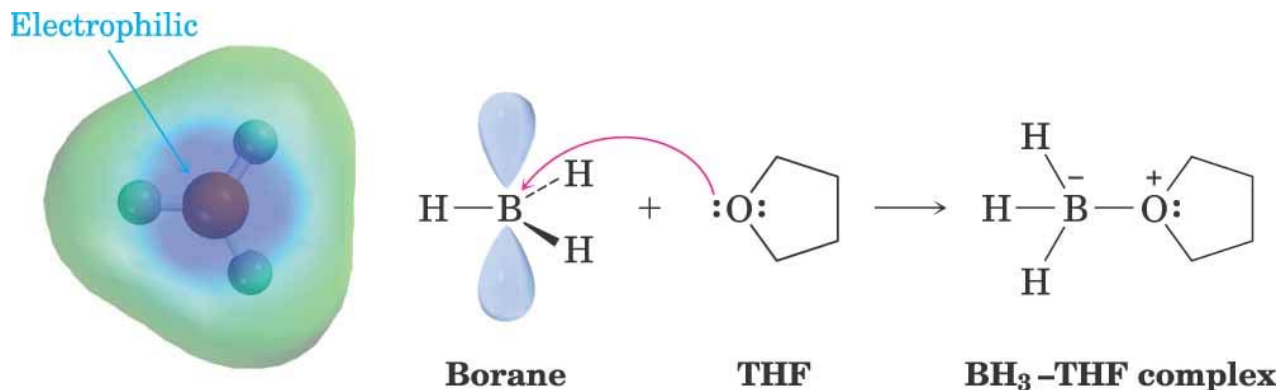
- Herbert Brown (HB) invented hydroboration (HB)
- Borane (BH_3) is electron deficient and thus a Lewis acid
- Borane adds to an alkene to give an organoborane



Borane
© Thomson - Brooks Cole

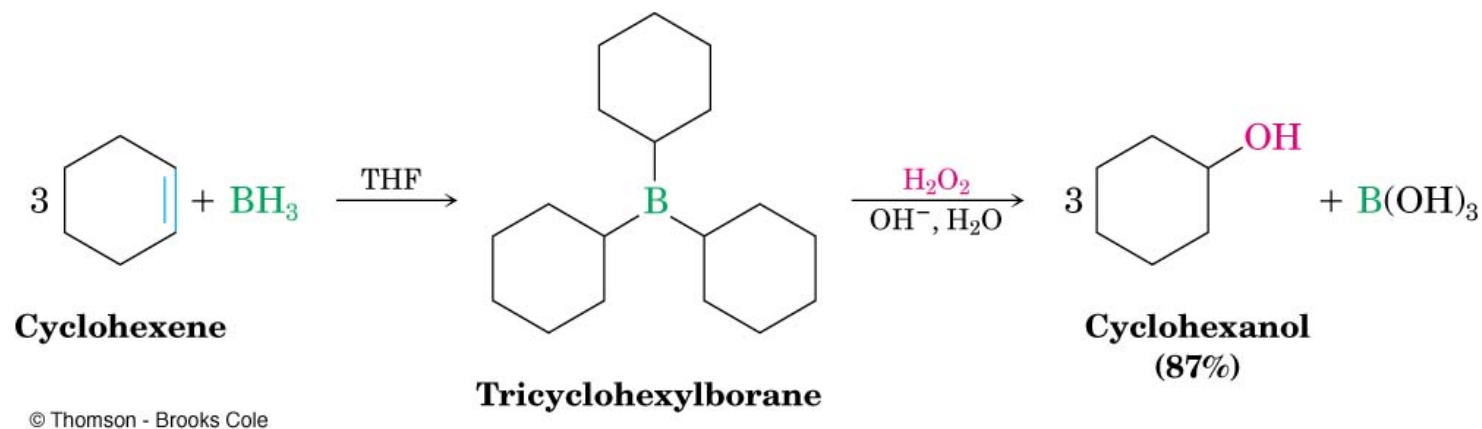
An organoborane

- Six electrons in outer shell
- Coordinates to oxygen electron pairs in ethers



Hydroboration-Oxidation Forms an Alcohol from an Alkene

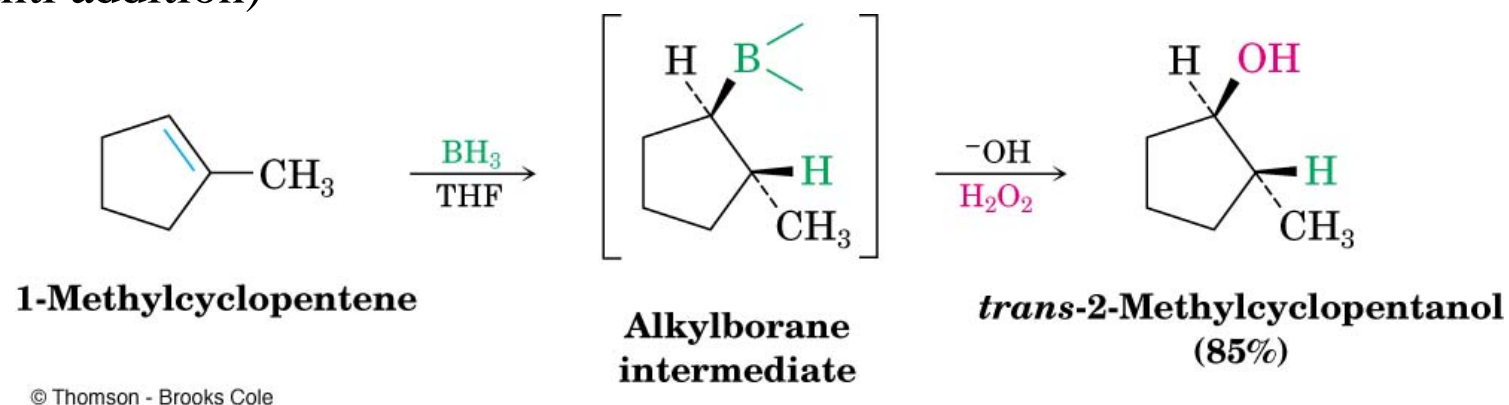
- Addition of H-BH₂ (from BH₃-THF complex) to three alkenes gives a trialkylborane
- Oxidation with alkaline hydrogen peroxide in water produces the alcohol derived from the alkene



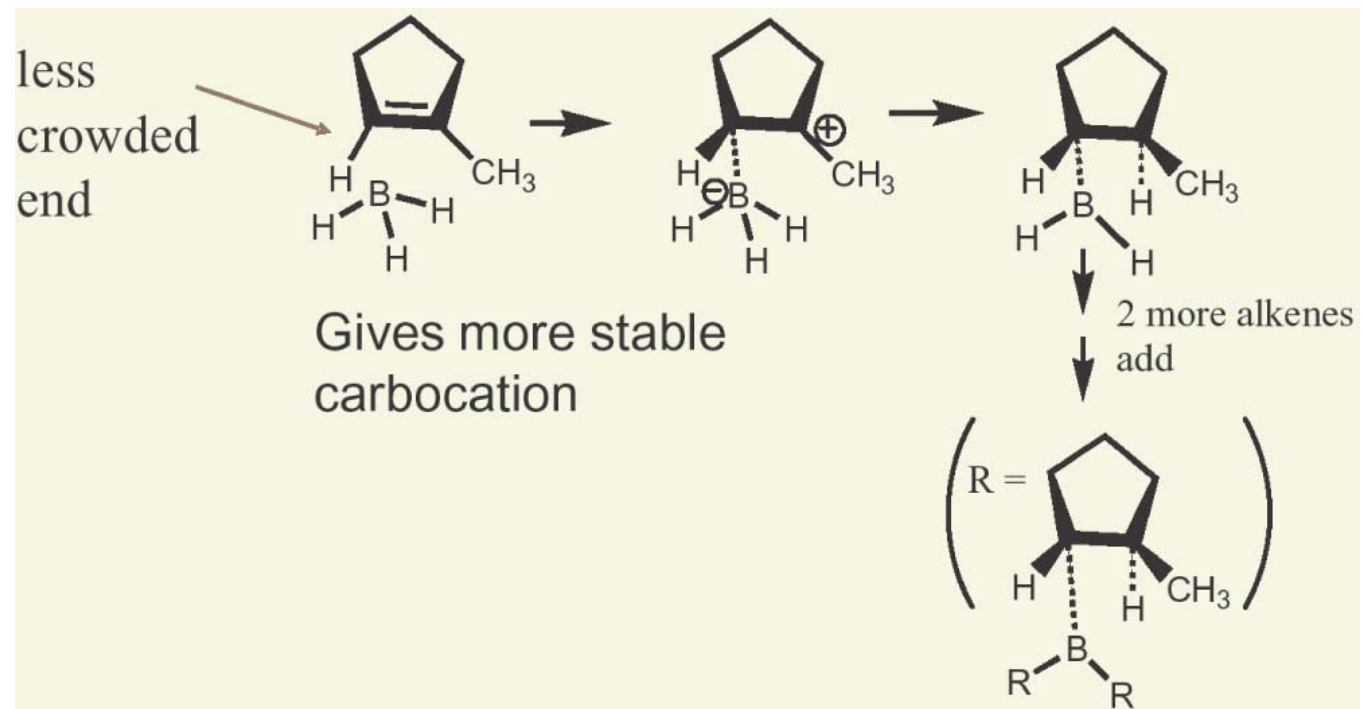
- Regiochemistry is opposite to Markovnikov orientation
 - OH is added to carbon with most H's

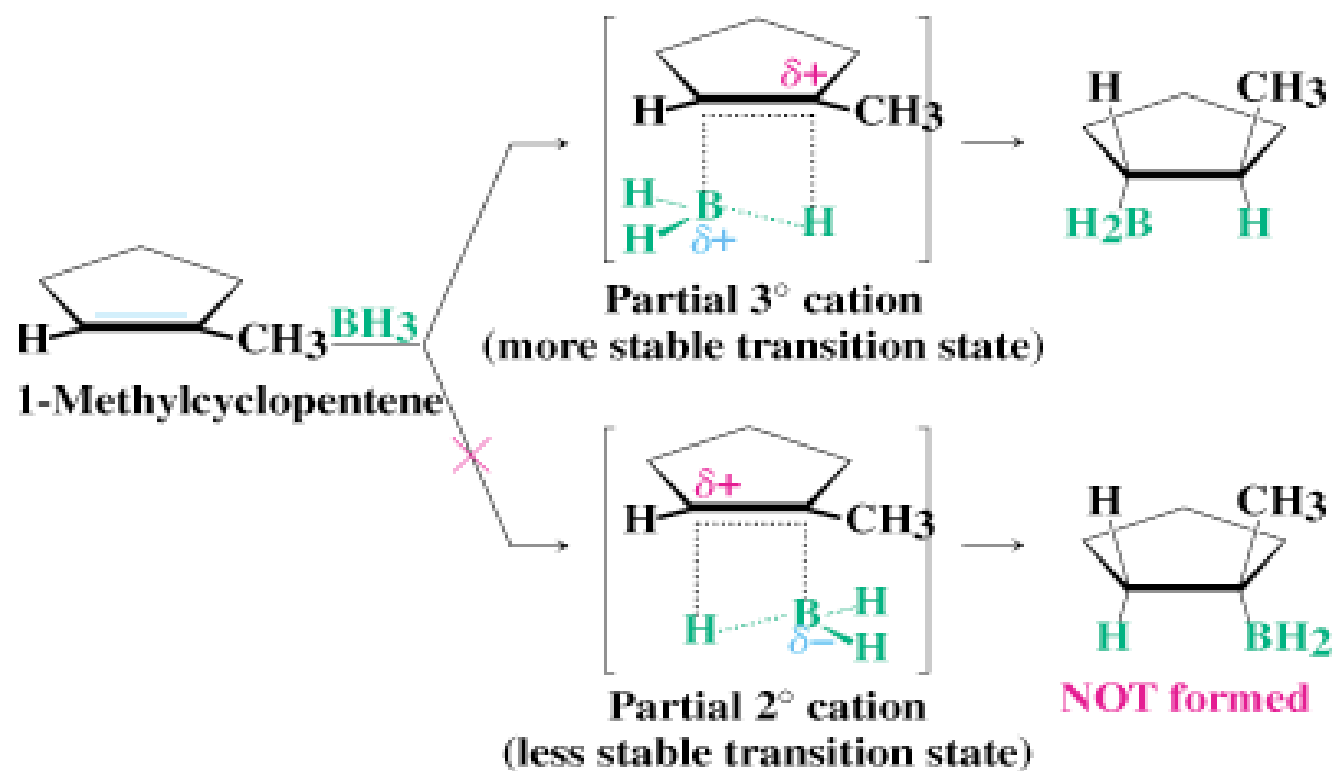
■

- H and OH add with **syn stereochemistry**, to the same face of the alkene (opposite of anti addition)

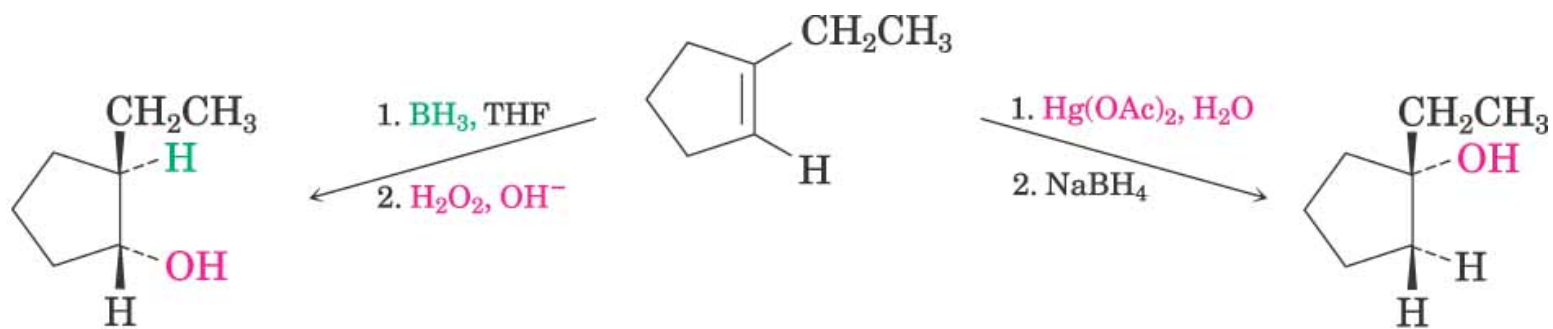
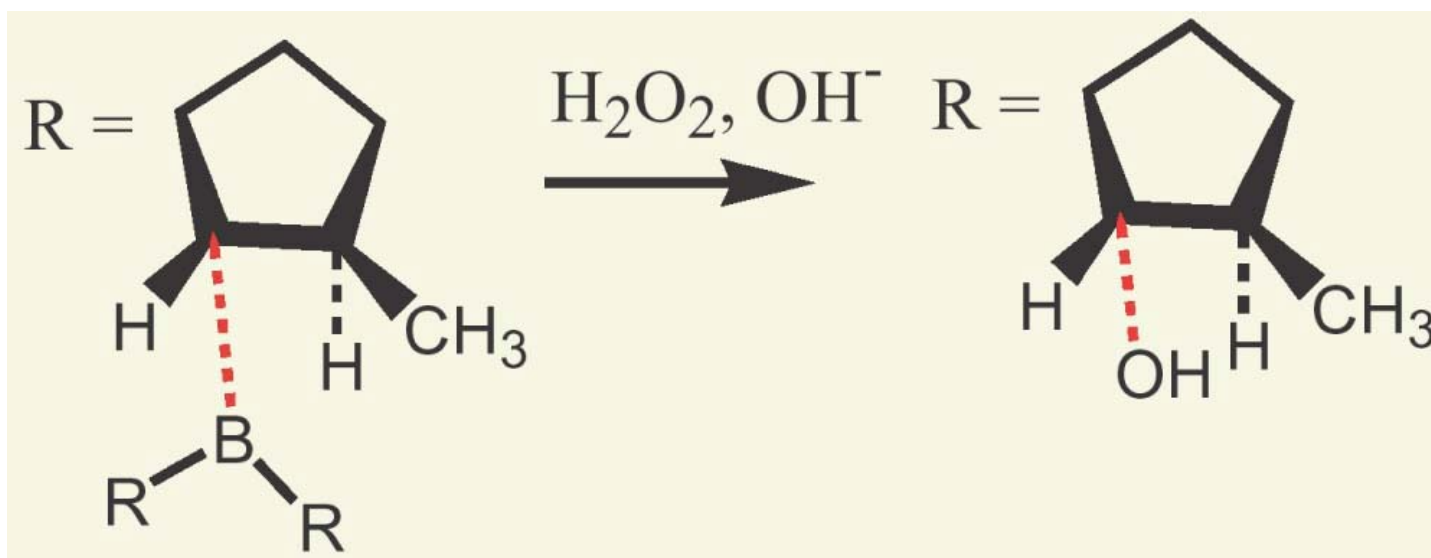


- Addition to the least crowded carbon
- Addition also is via most stable carbocation





- H_2O_2 , OH^- inserts OH in place of B
- Retains syn orientation

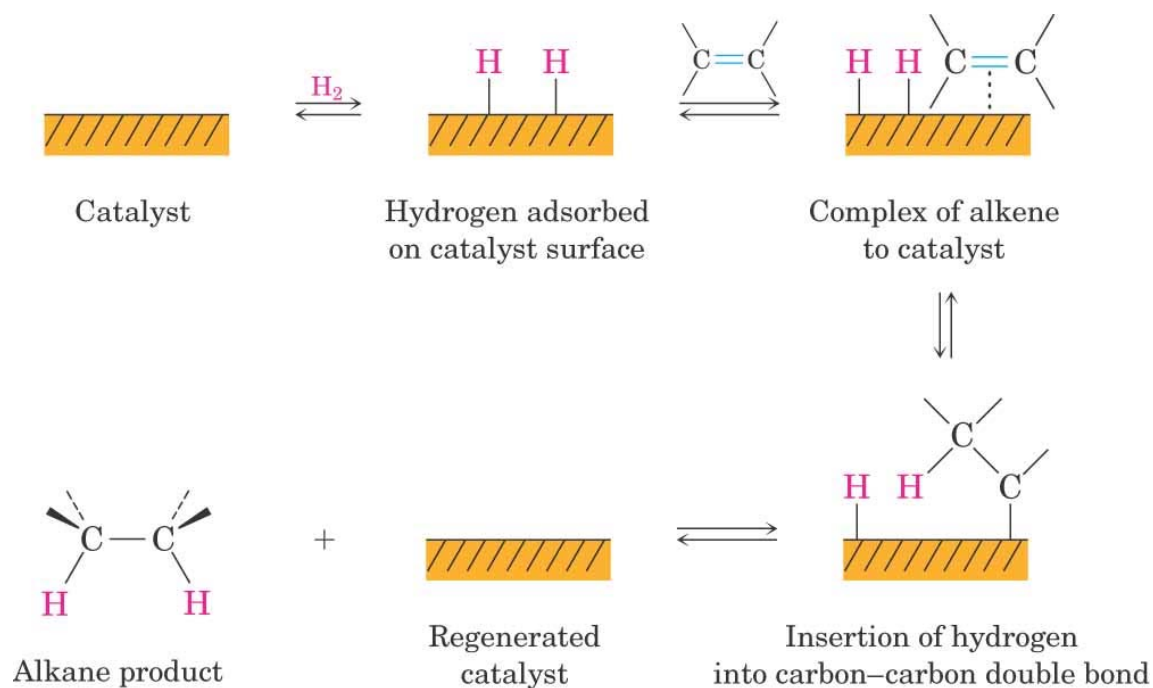


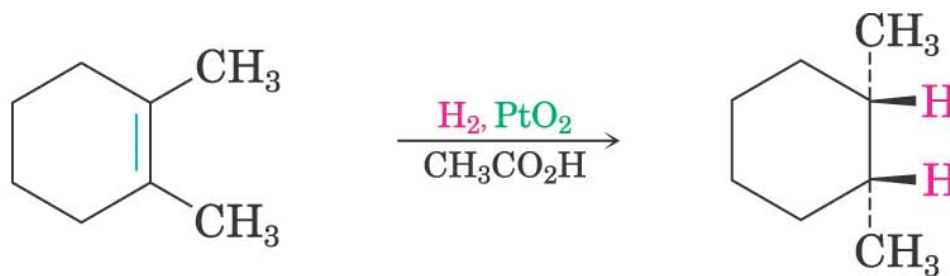
(a) Syn, non-Markovnikov
addition of H_2O

(b) Markovnikov
addition of H_2O

7.7 Reduction of Alkenes: Hydrogenation

- Addition of H-H across C=C
- Reduction in general is addition of H₂ or its equivalent
- Requires Pt or Pd as powders on carbon and H₂
- Hydrogen is first adsorbed on catalyst. Stereochemistry of addition is syn
- Reaction is heterogeneous (process is not in solution)





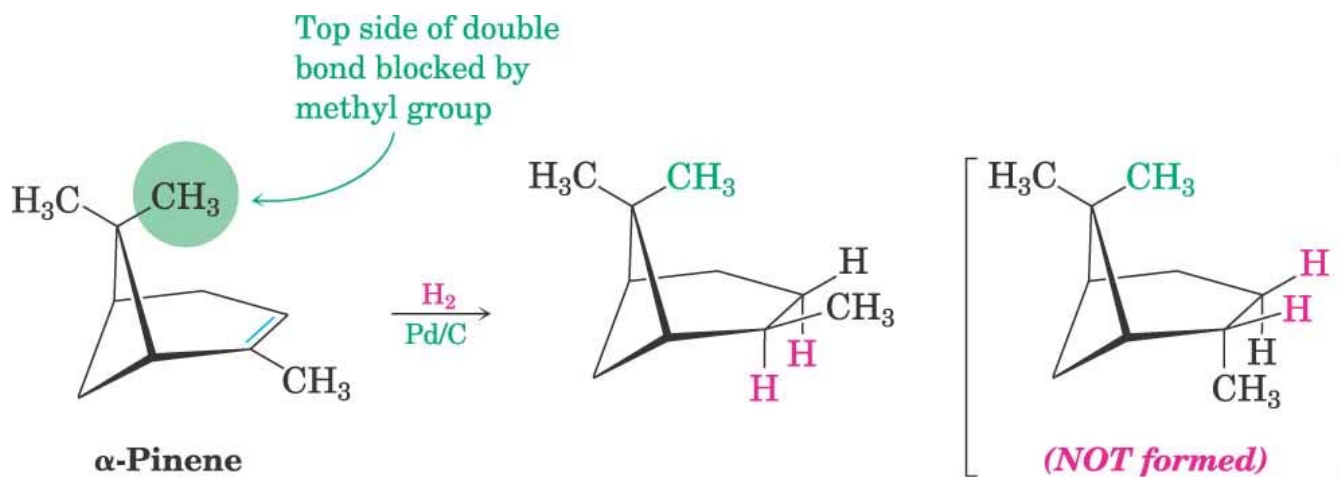
1,2-Dimethylcyclohexene

***cis*-1,2-Dimethylcyclohexane
(82%)**

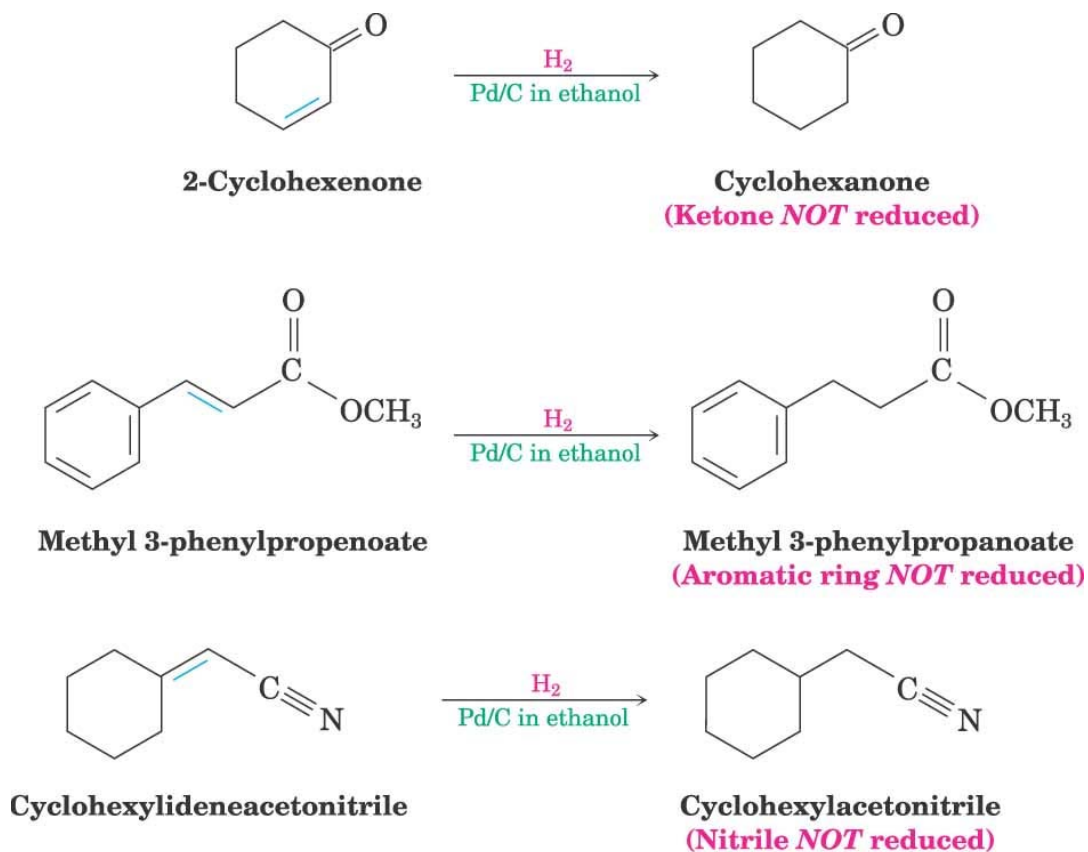
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Hydrogen Addition- Selectivity

- Selective for C=C. No reaction with C=O, C=N
- Polyunsaturated liquid oils become solids
- If one side is blocked, hydrogen adds to other



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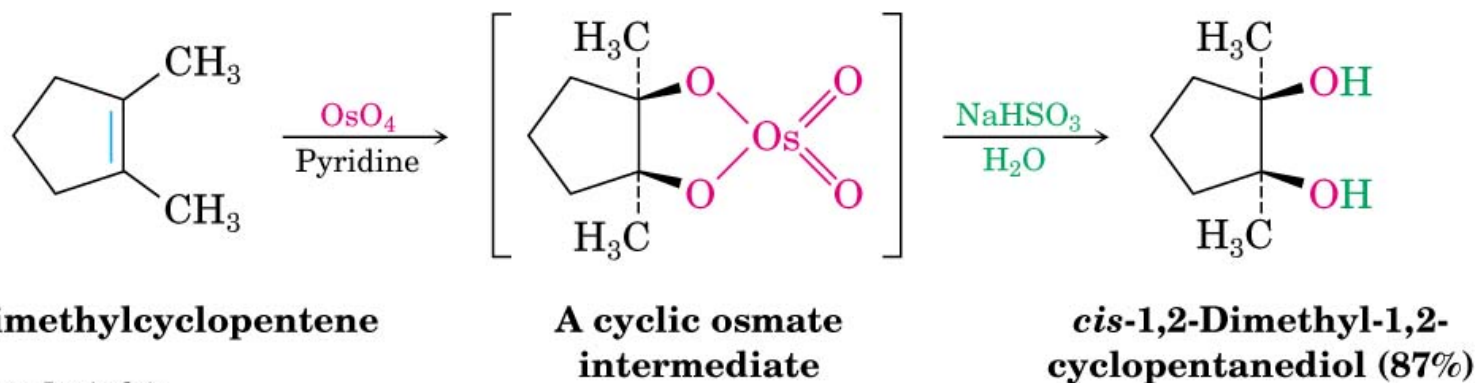


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7.8 Oxidation of Alkenes: Hydroxylation and Cleavage

- Hydroxylation adds OH to each end of C=C
- Reaction between osmium tetroxide and the alkene
- Stereochemistry of addition is syn
- Product is a 1,2-dialcohol or **diol** (also called a **glycol**)

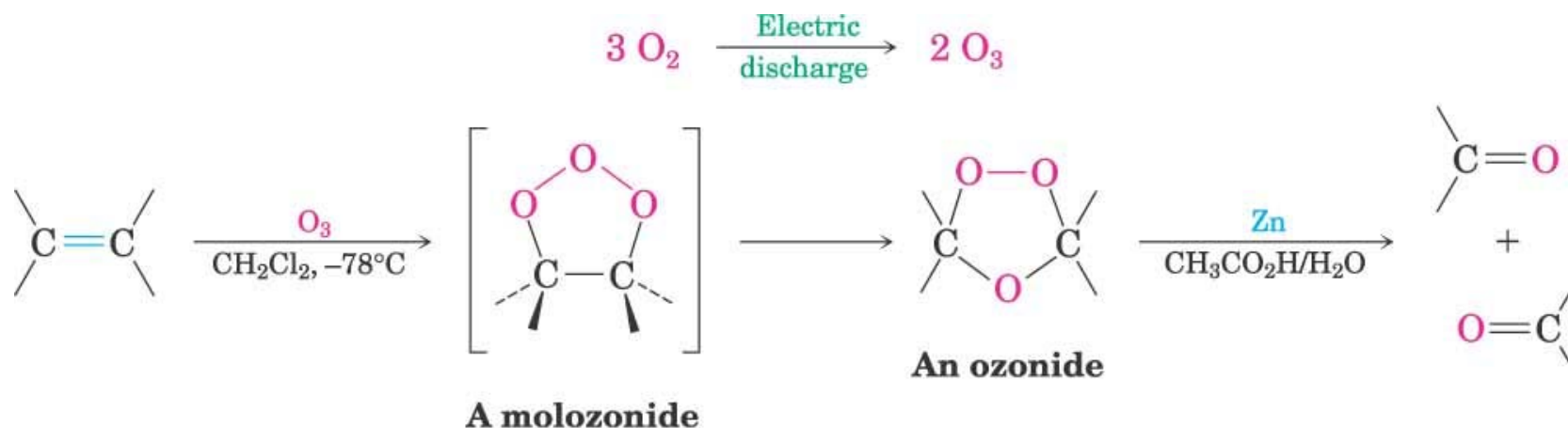
- Hydroxylation – converts an alkene to syn-diol
- Osmium tetroxide, then sodium bisulfate
- Via cyclic osmate di-ester



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Alkene Cleavage: Ozone

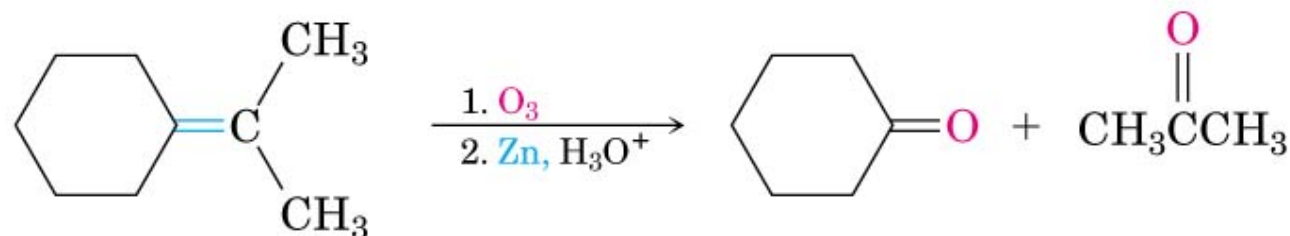
- Ozone, O₃, adds to alkenes to form molozonide
- Reduce molozonide to obtain ketones and/or aldehydes



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Examples of Ozonolysis of Alkenes

Used in determination of structure of an unknown alkene

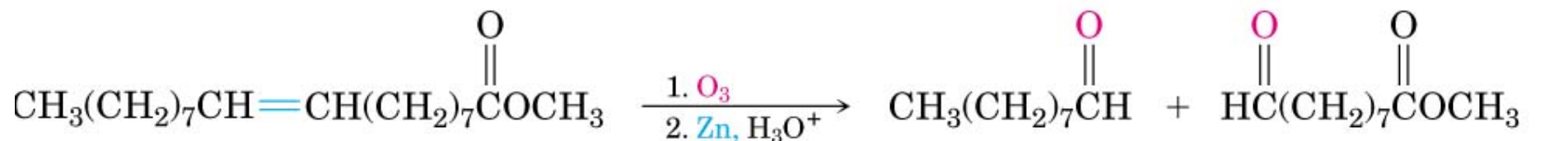


Isopropylidenecyclohexane
(tetrasubstituted)

Cyclohexanone

Acetone

84%; two ketones



Methyl 9-octadecenoate
(disubstituted)

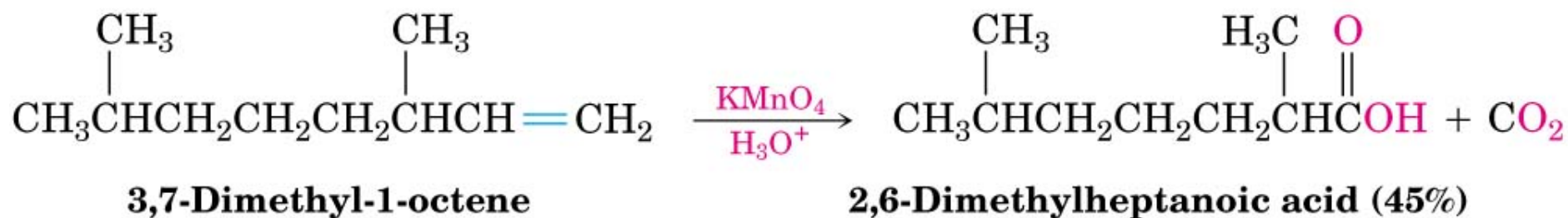
Nonanal

Methyl 9-oxononanoate

78%; two aldehydes

Permanganate Oxidation of Alkenes

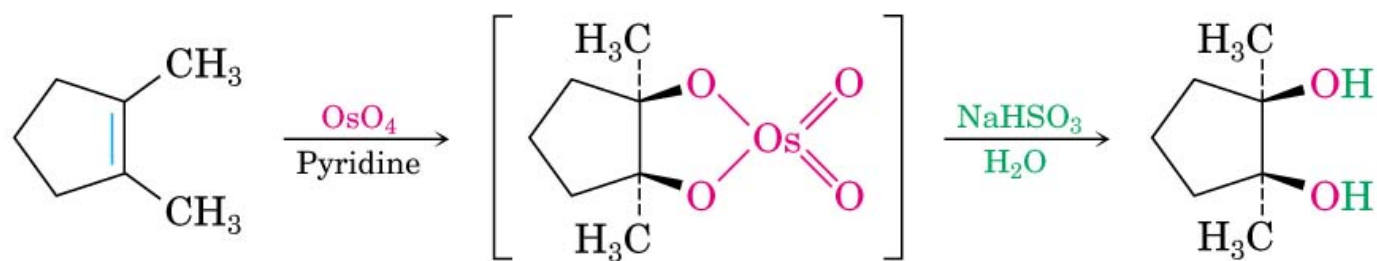
- Oxidizing reagents other than ozone also cleave alkenes
- Acidic or neutral Potassium permanganate (KMnO₄) can produce carboxylic acids and carbon dioxide if H's are present on C=C



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Cleavage of 1,2-diols (prepared from OsO₄ oxidation of alkenes)

- Reaction of a 1,2-diol with periodic (*per-iodic*) acid, HIO₄, cleaves the diol into two carbonyl compounds
- Sequence of diol formation with OsO₄ followed by diol cleavage is a good alternative to ozonolysis

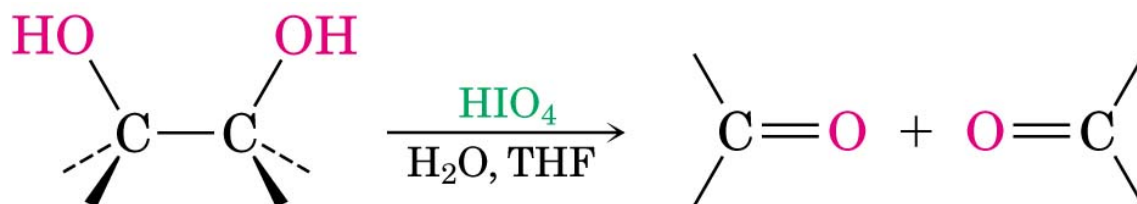


1,2-Dimethylcyclopentene

**A cyclic osmate
intermediate**

***cis*-1,2-Dimethyl-1,2-
cyclopentanediol (87%)**

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A 1,2-diol

Two carbonyl compounds

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■ Mechanism (not required) is via a cyclic periodate intermediate

