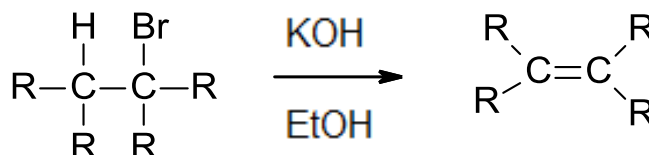


Ch 8 Alkene Reactions and Syntheses

Alkenes are prepared by the reverse of the electrophilic reactions in the last chapter. That is, they are prepared by elimination reactions.

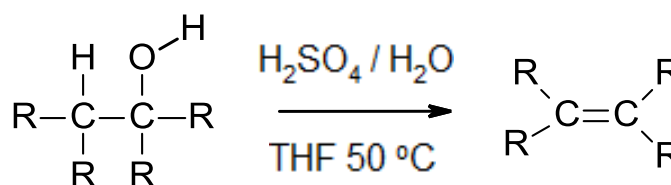
Dehydrohalogenation

- Mechanism can be either single-step or reverse of addition.



Dehydration

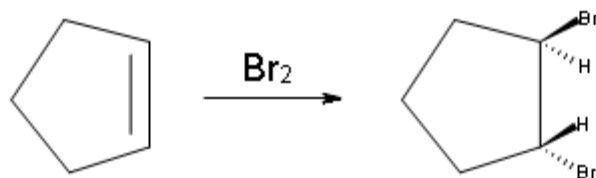
- Water molecule is expelled to create alkene.



Alkenes undergo **electrophilic addition** to form RX (as in Ch's 6 & 7), RX_2 , ROH, $\text{R}(\text{OH})_2$, C=O compounds, and cyclopropane rings.

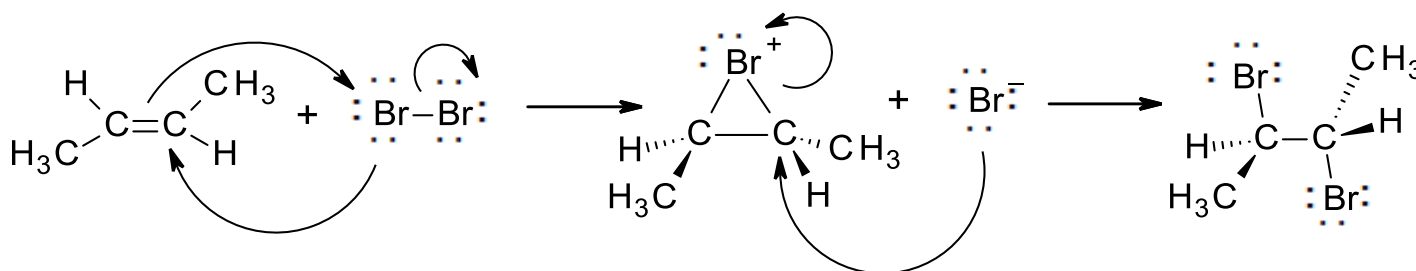
Halogen Addition

- Does not involve a carbocation, and forms only trans (anti stereochemistry).

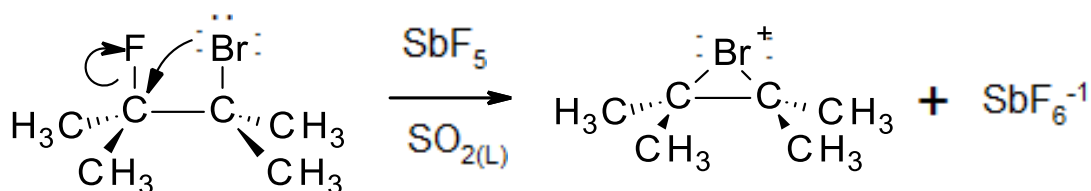


Bromonium Ion Intermediate – has Br^+ partially bonded to both C's

- This shields one side, so that Br^- must react on the other side.
- Cl and I form similar cationic intermediates (chloronium and iodonium).

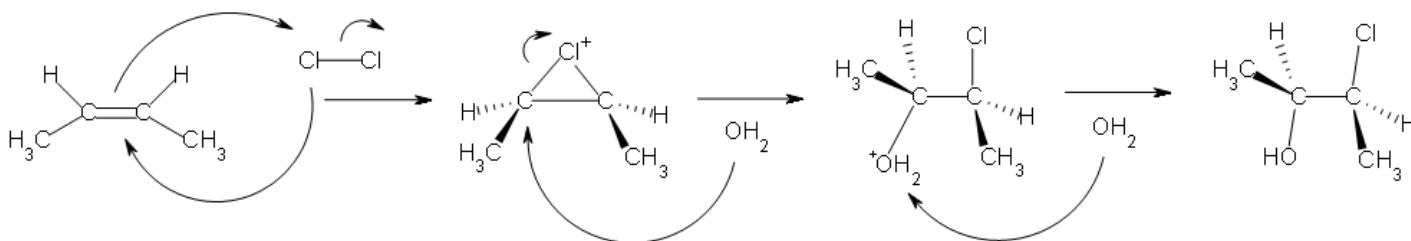


- A stable solid bromonium ion salt was first isolated in 1970 by reacting a fluorobromoalkane with antimony pentafluoride in liquid SO_2 solution:



Halohydrin Formation ($\text{XCH}_2\text{CH}_2\text{OH}$, where X is a Cl, Br, or I)

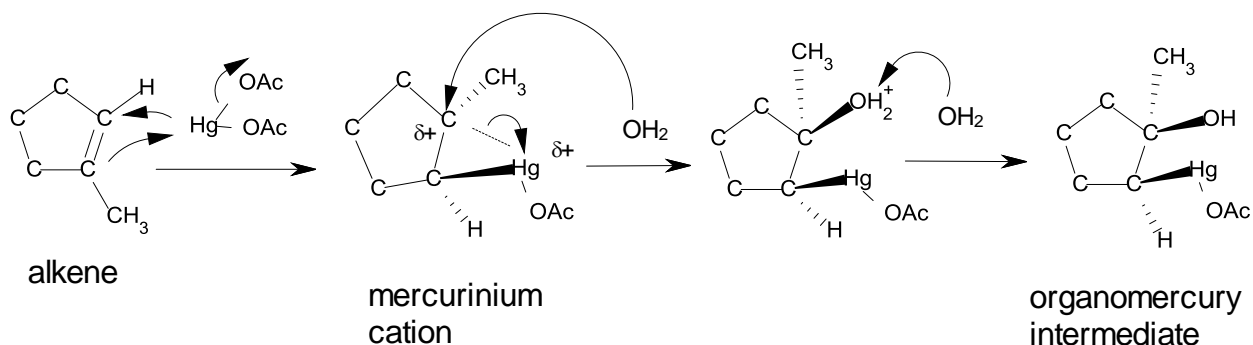
- Halohydrin formation is not done directly with XOH .
 H-O-Cl is hypochlorous acid, which is very acidic, and does not generate OH^- .
- Halohydrin formation is done with X_2 and H_2O .
- The first step forms a halonium cation (such as bromonium).
 Then, H_2O competes with X_2 as the Nu in the second step.
- Alkenes are not usually soluble in water, so dimethyl sulfoxide (DMSO or CH_3SOCH_3) is typically used as a solvent for the reaction, because it dissolves all of the reactants.
- N-bromosuccinamide (NBS) is used a stable, controlled, easy-to-handle source of Br_2 .
 Halogens (X_2) are very reactive, and not easy to handle.



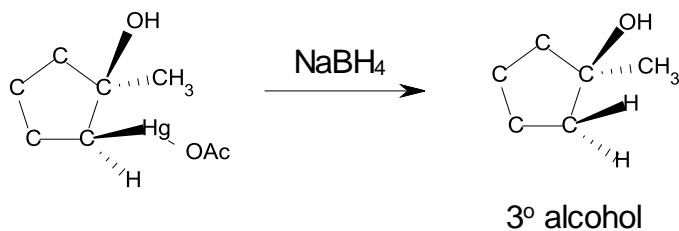
Addition of H₂O (**Hydration**) by **Oxymercuration**

- Follows Markovnikov's Rule, that is, the OH adds to the **more** substituted C.
- Better for creating 2° and 3° alcohols. 1° alcohols have their OH on the less substituted C.
- The first reaction (mercuration) uses mercury (II) acetate with water and tetrahydrofuran.
- Once one of the acetate ions (CH₃COO⁻¹ or OAc⁻¹) is removed, the Hg(OAc)⁺¹ adds to both C's by accepting the two π bond e⁻¹'s from one C with the Hg atom's empty 6s orbital, while donating a pair of e⁻¹'s from the Hg atom's 5d subshell to the other C.
- The three-membered mercurinium cation appears similar to the bromonium cation. But, the mercury atom is less strongly connected to the more substituted C, which shares the overall +1 positive charge with the mercury atom.
- Water adds to the partially positive C, then loses H⁺¹ to leave only an OH attached.
- The second reaction (demercuration) uses sodium borohydride (a reducing agent) to replace HgOAc with an H atom, which creates the alcohol product.

Mercuration with Hg(OAc)₂ / H₂O / THF

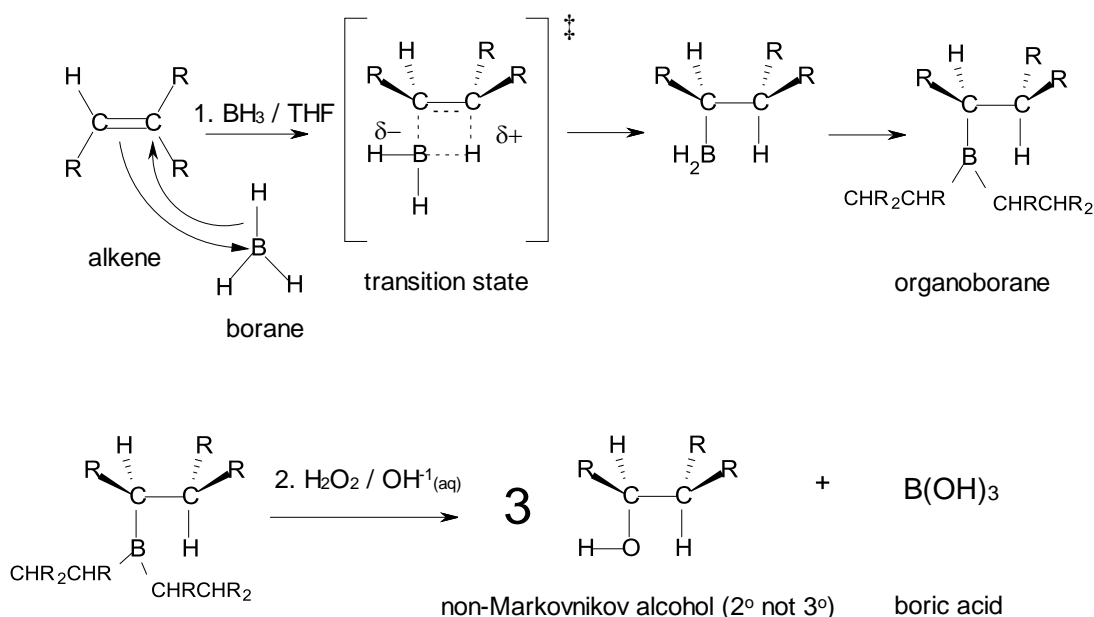


Demercuration with NaBH₄ (reducing agent)

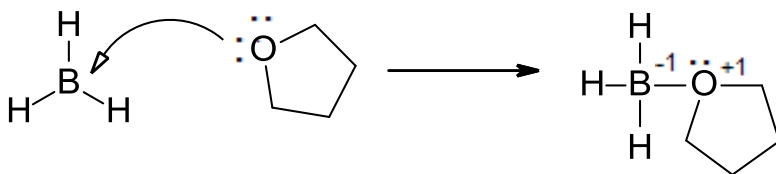


Addition of H₂O (Hydration) by Hydroboration

- Follows anti-Markovnikov orientation, that is, the OH adds to the **less** substituted C.
- Better for creating 1° alcohols, because they have their OH on the least substituted C.
- In the first reaction, BH₃ (borane) is added across the double bond so that BH₂ is bonded to the less substituted C, where the BH₂ group has less steric crowding.
The H removed from the BH₃ is added to the other C.
- Another reason for this orientation is that the more substituted C can better accommodate the δ⁺ H.
- The addition is “syn”. That is, both BH₂ and H are added to the same side.
For instance, both would be on the top or bottom of a ring together.
- Three alkene molecules add to the boron atom, replacing all three of its H atoms.
- In the second reaction, the boron atom is separated from the carbons and replaced with OH groups using H₂O₂ (an oxidizing agent) and OH⁻ (aq base). This creates the alcohol product.

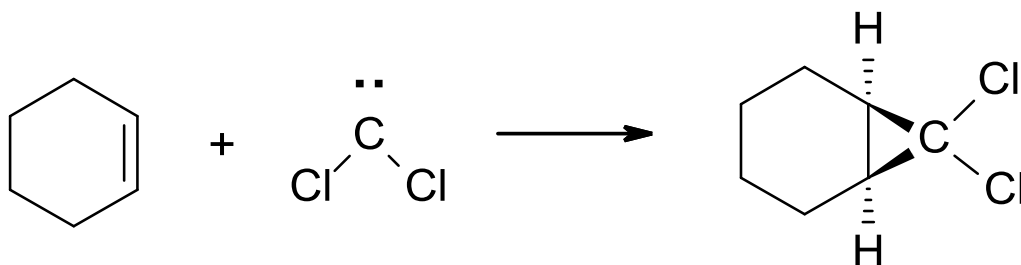
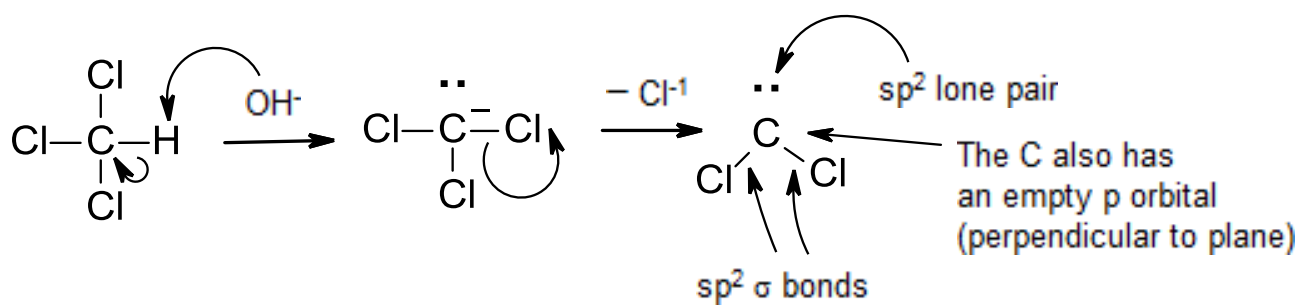


- Borane is normally a gas, but forms a stable acid-base complex when in solution with tetrahydrofuran (THF).
- The boron atom in BH₃ is an exception to the octet rule and has an empty orbital.
- As a result, BH₃ is a Lewis acid, and it accepts 2e⁻'s from the oxygen atom in THF, which is a Lewis base.

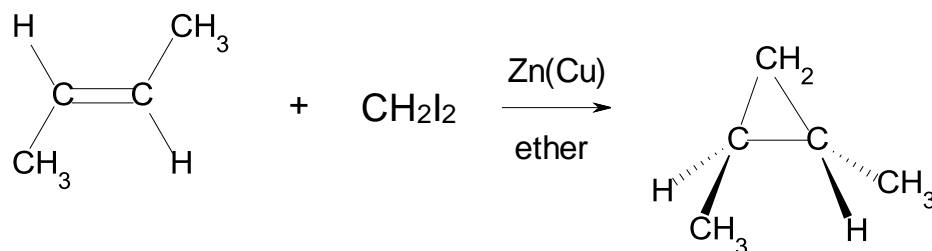
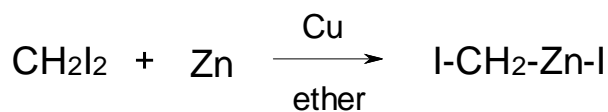


Carbene addition to Alkenes to form Cyclopropane Rings

- The C on the carbene ($R_2C:$) is neutral (with $6 e^{-1}$) and sp^2 .
- The lone pair is sp^2 , and the carbene has an empty p orbital.
- The empty p orbital is like an E^+ , and accepts the $2e^{-1}$'s from the Π bond.
- The filled sp^2 orbital is like a Nu^- , and donates $2e^{-1}$'s to the other alkene C.
- A substituted carbene ($Cl_2C:$) can be formed by treating chloroform with KOH.

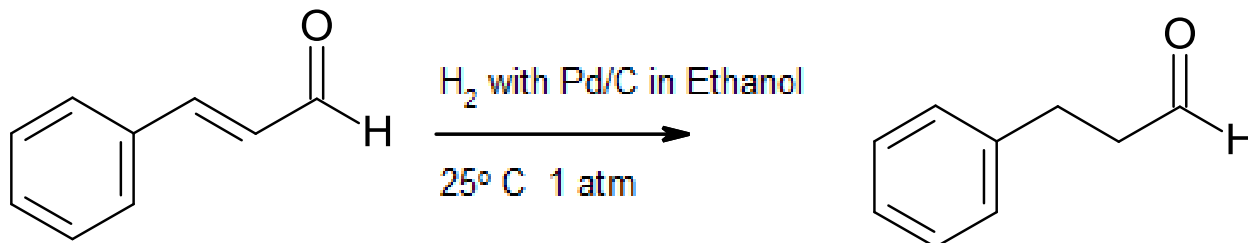


- **Simmons-Smith Reaction** uses a carbenoid to add a carbene to an alkene. The carbenoid is created when diiodomethane is treated with Zn powder (activated with Cu).



Catalytic Hydrogenation

- Reduction of an alkene with H_2 is catalyzed with Pd/C or PtO_2 (Adam's catalyst)
- The reaction is heterogeneous because the catalyst is solid and the reactants are fluids.
- Stereochemistry is syn, and is stereospecific to the side of the alkene with the least steric hindrance.
- Alkene Π bonds are more reactive than other Π bonds.
So, carbonyls ($C=O$), nitriles (RCN), and aromatic rings (below) are unaffected, unless a stronger catalyst or more vigorous conditions are used.

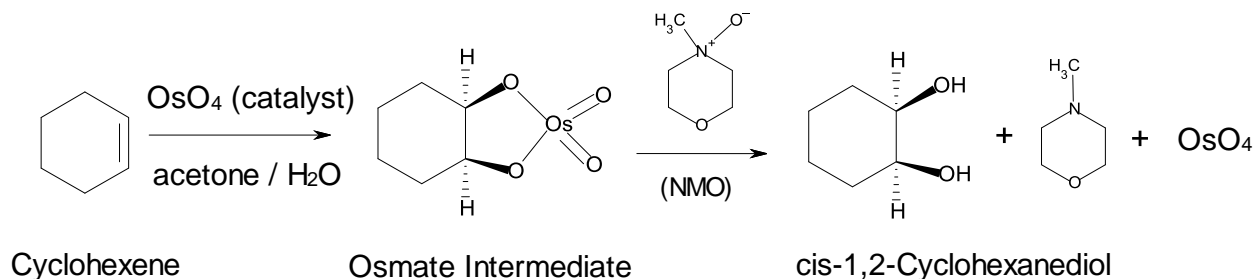


3-phenylprop-2-enal

3-phenylpropanal

Oxidation

- **Hydroxylation** creates a 1,2-diol from an alkene.
- The most efficient laboratory method uses OsO_4 (osmium tetroxide) as a catalyst, along with N-methylmorpholine N-oxide (NMO).
- NMO is converted to N-methylmorpholine when it cleaves the intermediate and regenerates the OsO_4 .
- As a result of the regeneration, only small catalytic amounts of OsO_4 are needed. This is important because osmium is not only expensive, but also very toxic and highly carcinogenic.
- The intermediate is cyclic and is called an **osmate**.
The osmate intermediate is not charged and is not a carbocation.
- Resulting from the osmate's cyclic structure, the reaction has **syn** stereochemistry. That is, both OH's are added to the same side of the ring.



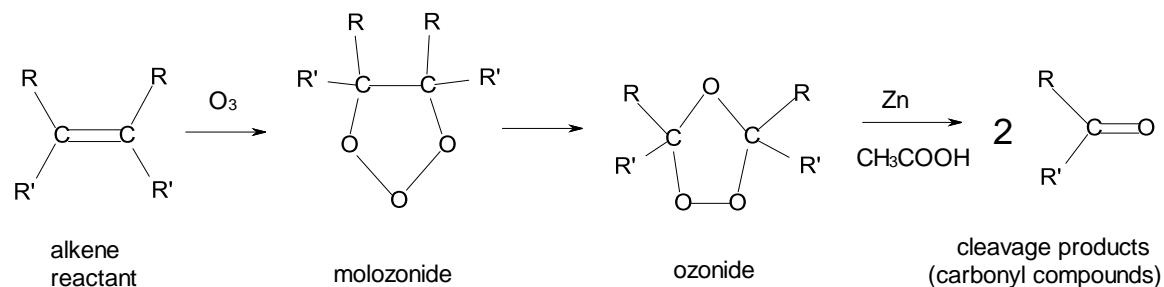
Cyclohexene

Osmate Intermediate

cis-1,2-Cyclohexanediol

Cleavage Split a C=C into two portions

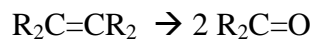
- Ozonation (with O_3 followed by Zn/CH_3COOH)



- Potassium Permanganate ($KMnO_4$) with H_3O^+
Splits C=C so that $H_2C=$ becomes CO_2 , $RHC=$ becomes $RCOOH$,



And $R_2C=$ becomes $R_2C=O$



- Diol Cleavage

HIO_4 (periodic acid) in H_2O and THF converts $R_2COHCOHR_2$ (**1,2-diol**) into two R_2CO (ketone) molecules by splitting the C-C bond between the two C's with OH's.

Biological Alkene Addition Reactions

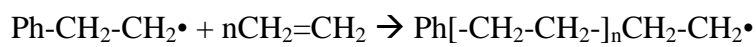
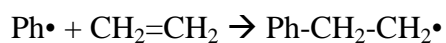
- Occurs in aqueous medium with enzyme catalysts
- Are usually stereoselective, often reacting with or forming only one stereoisomer
- Fumerase, for instance, reacts with Fumaric Acid (trans), but is inert to Maleic Acid (cis).

Radical Additions to Alkenes (forms polymers)

- $n\text{CH}_2=\text{CH}_2 \rightarrow [-\text{CH}_2-\text{CH}_2-]_n$
- A long hydrocarbon chain is created.
- The three steps are Initiation, Propagation, and Termination.
- Initiation is with benzoyl peroxide (BzOOBz) to create phenyl radicals (Ph•).



- Propagation converts one radical into a larger one (chain lengthening).



- Termination combines two radicals to create one larger molecule.

