

## Stereochemistry (*direction of bond changes*) in Chemical Reactions

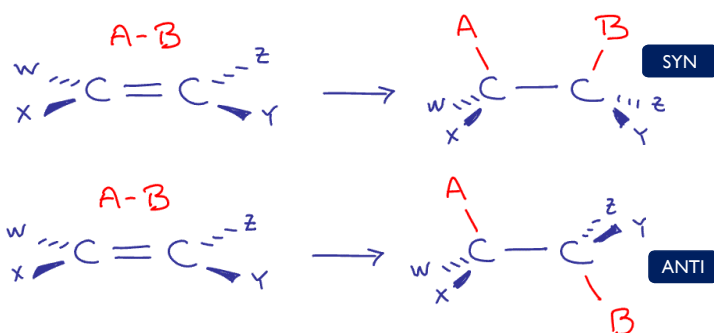
Ch 7 (finish)

### Overview

- ▶ Definitions for describing “directions” of bond changes
- ▶ Applications
  - ▶ Alkene Additions
- ▶ Reactant Stereochemistry vs. Product Distribution

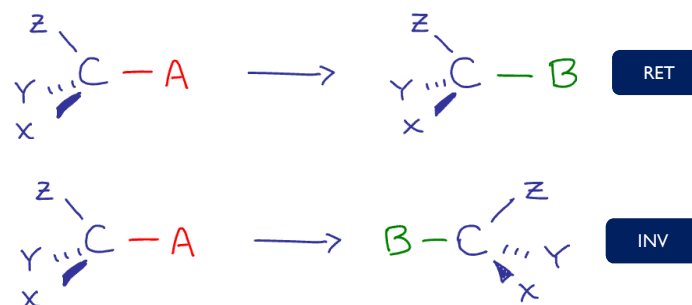
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Definition:  
**SYN** v. **ANTI** addition



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Definition:  
**RET**ention v. **INV**ersion of configuration

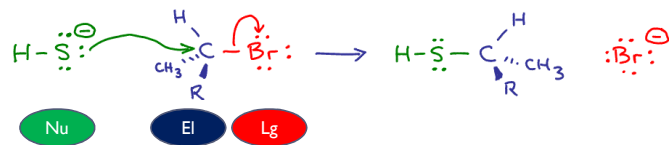


R/s labels don't matter here →  
just pay attention to locations of XYZ relative to A/B

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## Nucleophilic Substitution

### ▶ Example

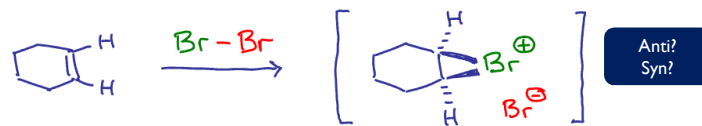


### ▶ Observation

- ▶ always INVersion of configuration at Ei
- ▶ **"BACKSIDE** (away from Lg) **ATTACK** by Nu"

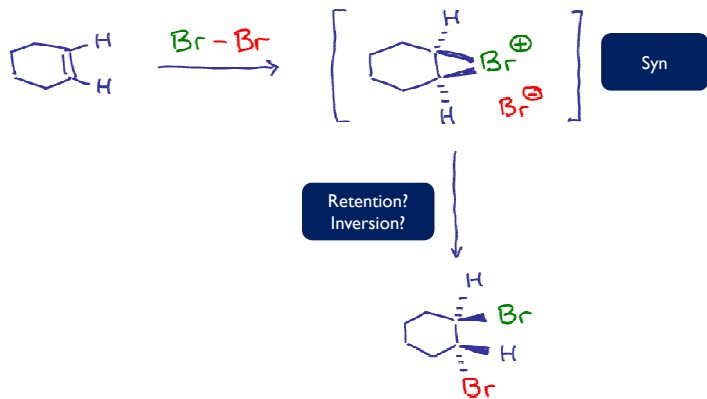
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## Bromination



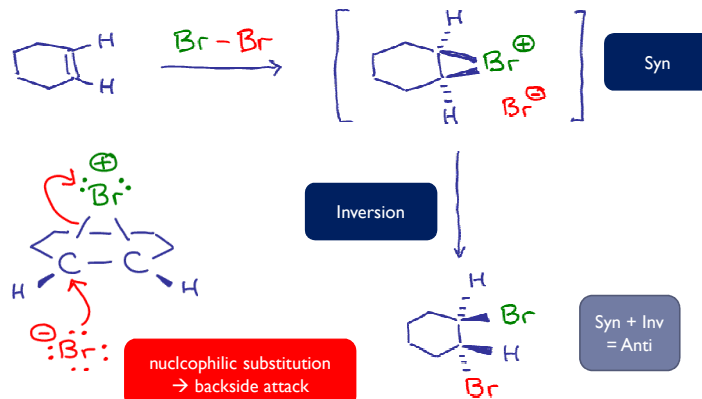
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## Bromination



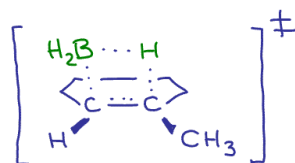
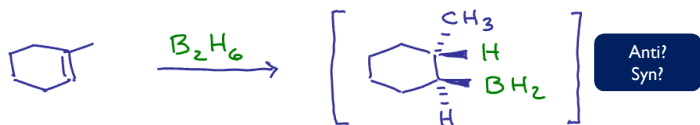
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## Bromination



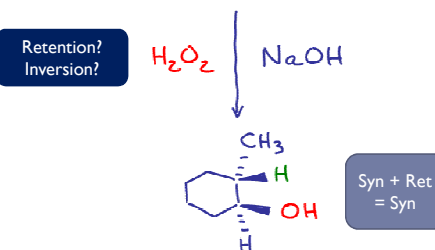
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## Hydroboration-Oxidation



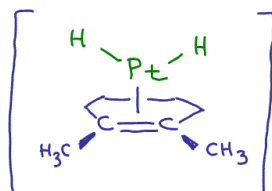
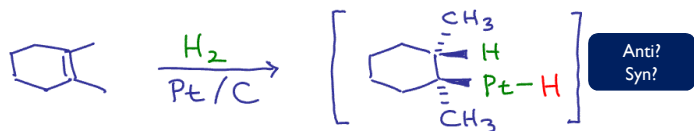
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## Hydroboration-Oxidation



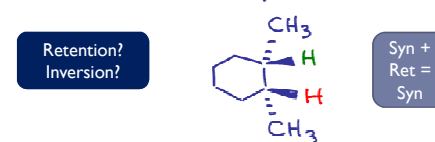
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## Catalytic Hydrogenation



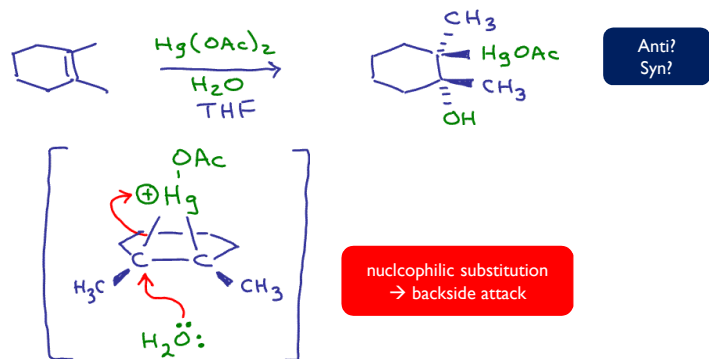
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## Catalytic Hydrogenation



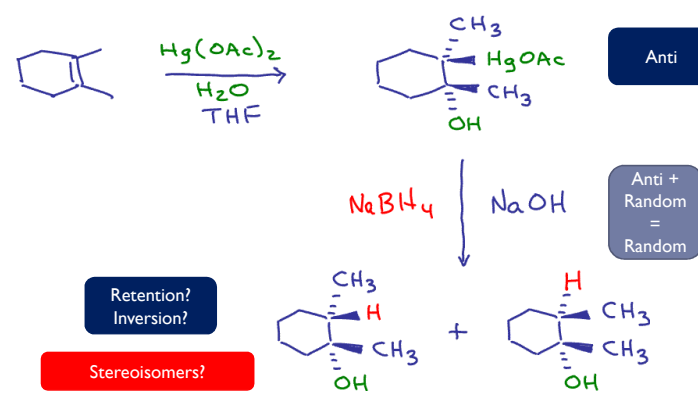
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## Oxymercuration-Demercuration



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## Oxymercuration-Demercuration



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Stereochemical Outcomes Vary →  
Learn Each Reagent's (Step's) Peculiarities

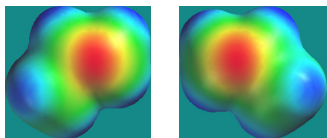
- ▶ Bromination
  - ▶ Br adds **SYN**
  - ▶ Br (or OH) replaces Br w/ **INV** → nuc.subst.
- ▶ Hydroboration
  - ▶ H & B add **SYN**
  - ▶ OH replaces B w/ **RET** → not nuc. subst.
- ▶ Hydrogenation
  - ▶ Pt adds **SYN**
  - ▶ H replaces Pt w/ **RET** (twice) → not nuc. subst.
- ▶ Oxymercuration
  - ▶ Hg adds **SYN**
  - ▶ OH replaces Hg w/ **INV** → nuc. subst.
  - ▶ H replaces Hg **randomly** → not nuc. subst.

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## Reactant Possibilities

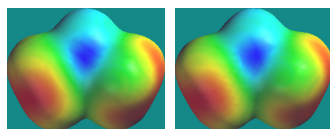
- ▶ Achiral
  - ▶ What if reaction creates asymmetric atoms or stereocenters?
- ▶ Chiral
  - ▶ How will each enantiomer behave?
  - ▶ How will mixture of enantiomers behave?
  - ▶ What if asymmetric atom(s) not involved in reaction?
  - ▶ What if asymmetric atom(s) or stereocenters involved?
- ▶ Remember
  - ▶ **Enantiomers** (molecules, intermediates, transition states) have **identical energies**
  - ▶ **Diastereomers** have **different energies**

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Alkenes & Carbocations  $\rightarrow$  2 Reactive Sides

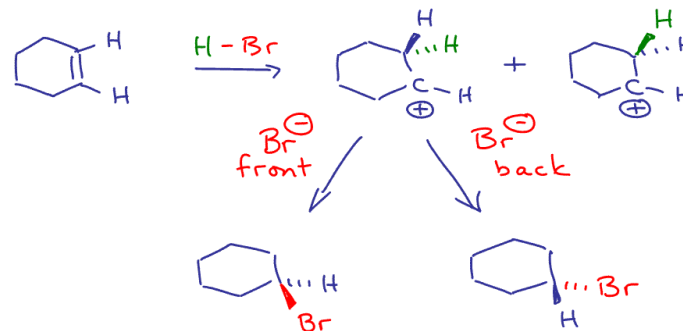
two sides of  $\text{CH}_3\text{CH}=\text{CH}_2$  are identical  
(related by plane of symmetry)

two sides of  $\text{CH}_3\text{CH}^+\text{CH}_3$  are identical  
(related by axis of symmetry)



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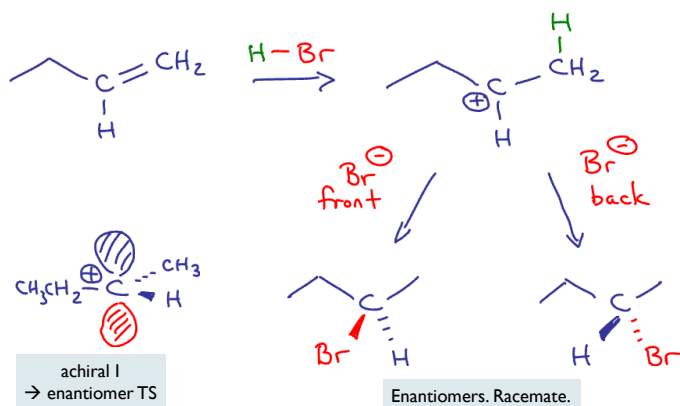
## HBr Addition



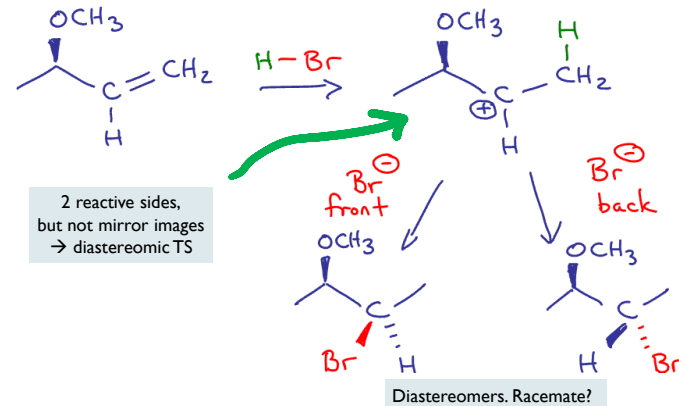
All products identical. No asymmetric atoms. Not exciting.

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## HBr forms asymmetric atom



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Alkene contains asymmetric atom &  
HBr forms asymmetric atom

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