CHEM 109A
Organic Chemistry

https://labs.chem.ucsb.edu/zakarian/armen/courses.html

Chapter 6

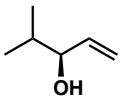
1. **The Reactions of Alkenes**
2. **The Stereochemistry of Addition Reactions**

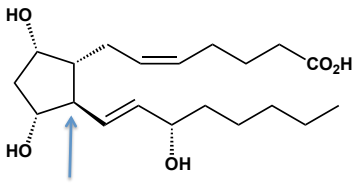
Midterm 3, Wednesday March 7

Chapter 5: 5.6 – 5.12 inclusively (~~5.13, 5.14~~)

Chapter 6: all sections

Chapter 7: 7.1 – 7.6 (inclusively)



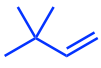


Practice Questions

What is the major product obtained by addition of HBr to the following alkenes

a.

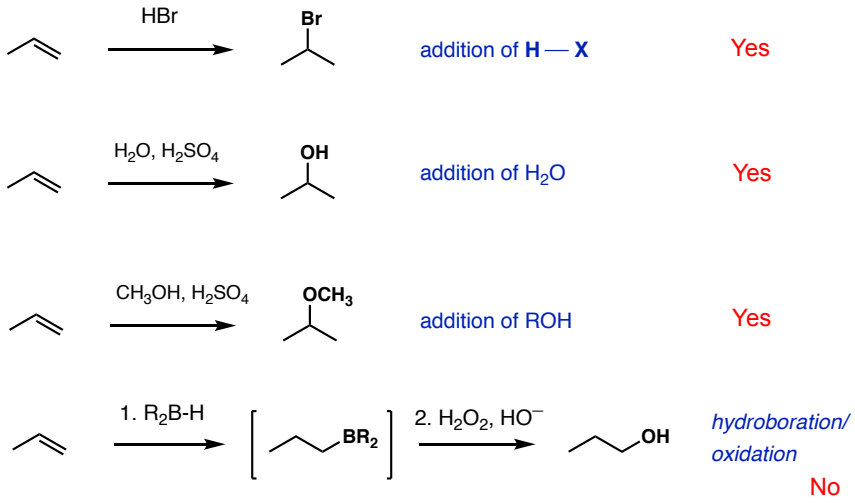
b.

c. 

summary of reactions

electrophilic addition; H — element

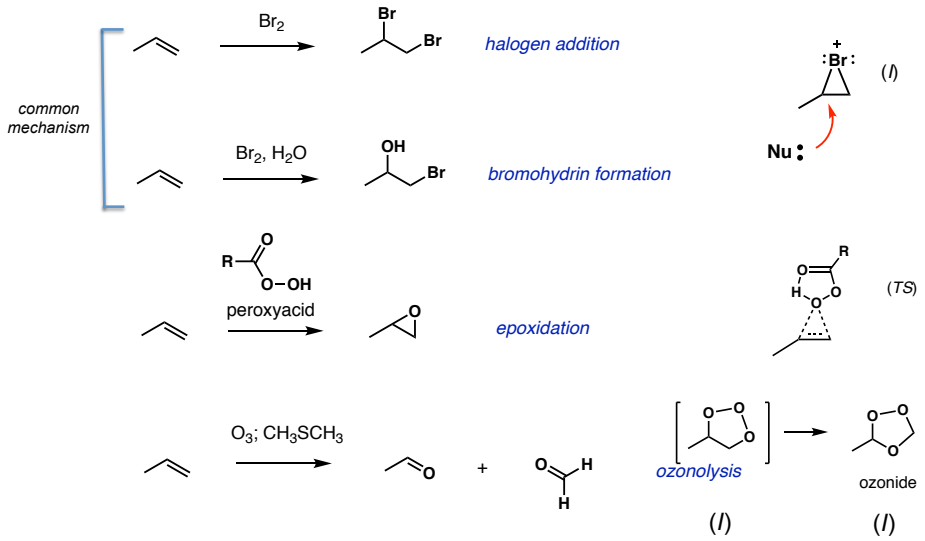
carbocation?



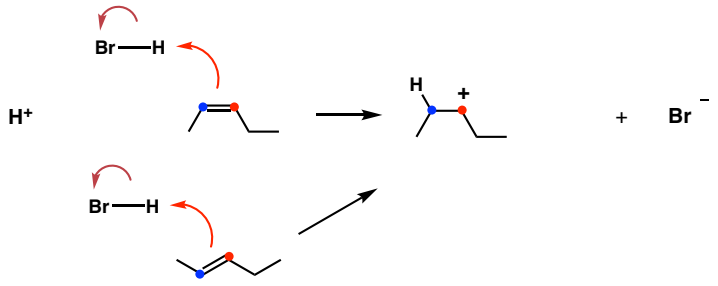
summary of reactions

electrophilic addition; element — element

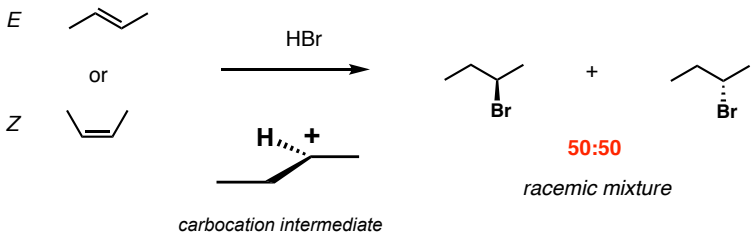
intermediate/
transition state



summary of reactions

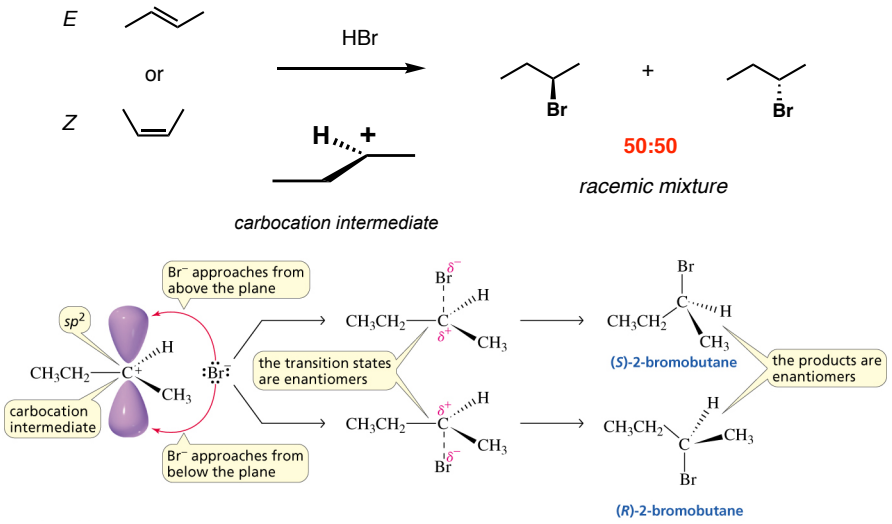


Racemic Mixture is Formed from Simple Alkenes



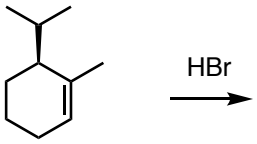
If the reactant does not have an asymmetric center and the reaction forms a product with an asymmetric center, the product will be a racemic mixture.

Racemic Mixture is Formed from Simple Alkenes



If the reactant does not have an asymmetric center and the reaction forms a product with an asymmetric center, the product will be a racemic mixture.

Alkene now has an asymmetric center



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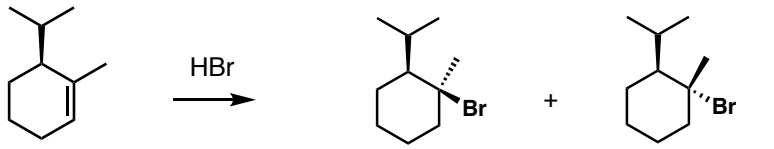
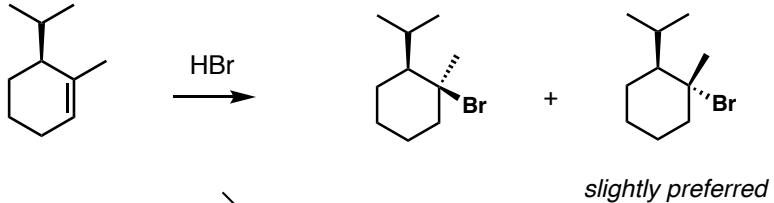


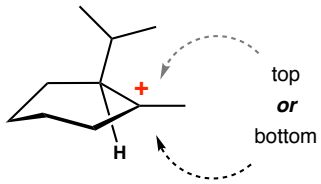
slightly preferred

If the starting compound has an asymmetric center
and the reaction forms a product with a new asymmetric center,
the product will be a **pair of diastereomers**.

Alkene now has an asymmetric center



slightly preferred



If the starting compound has an asymmetric center
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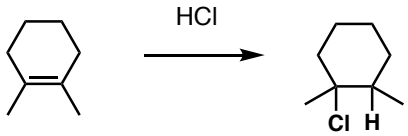
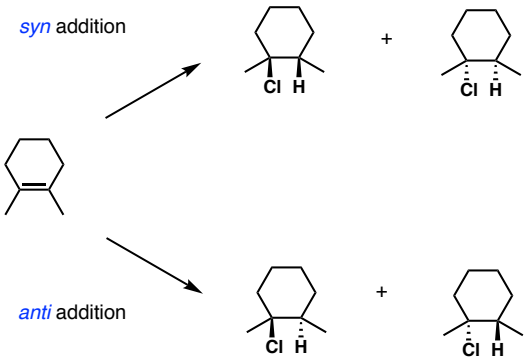
How many new Asymmetric Centers are formed?

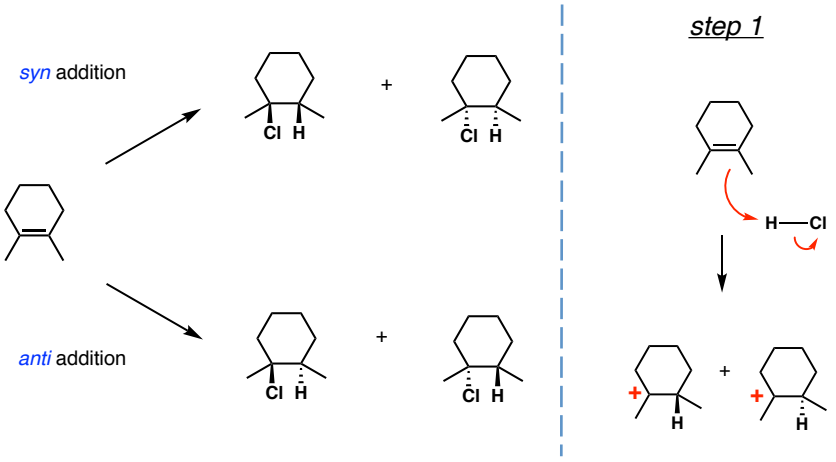


Syn and *Anti* Additions



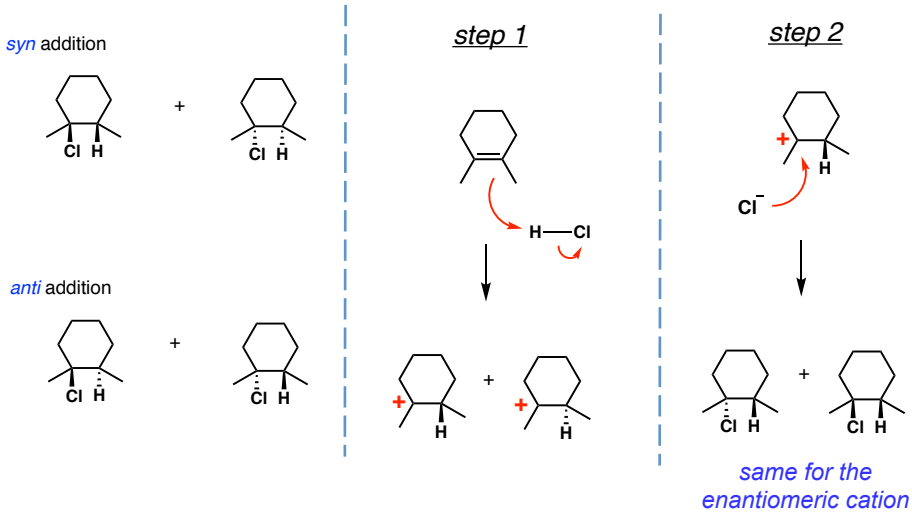
syn addition: new bonds on the same side of the double bond
anti additions: new bonds on the opposite side of the double bond

Four Stereoisomers are Obtained if the Reaction Forms a Carbocation Intermediate



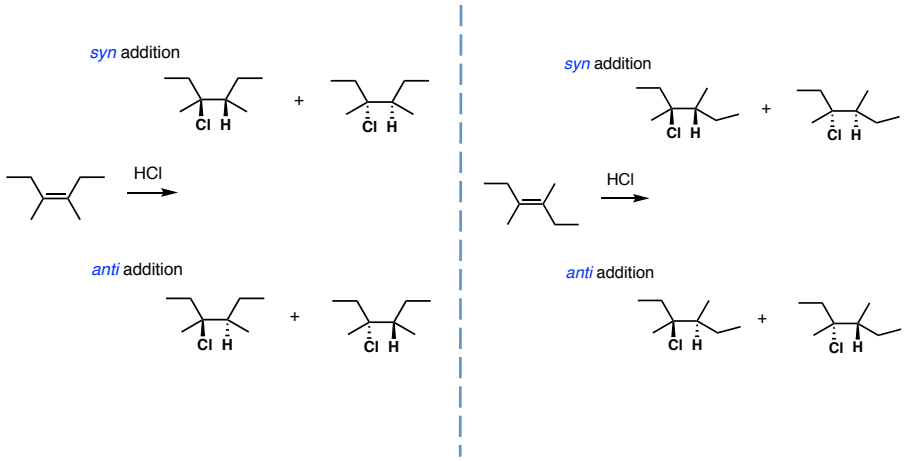
The stereoisomers obtained as products depend on the mechanism of the reaction.

Four Stereoisomers are Obtained if the Reaction Forms a Carbocation Intermediate

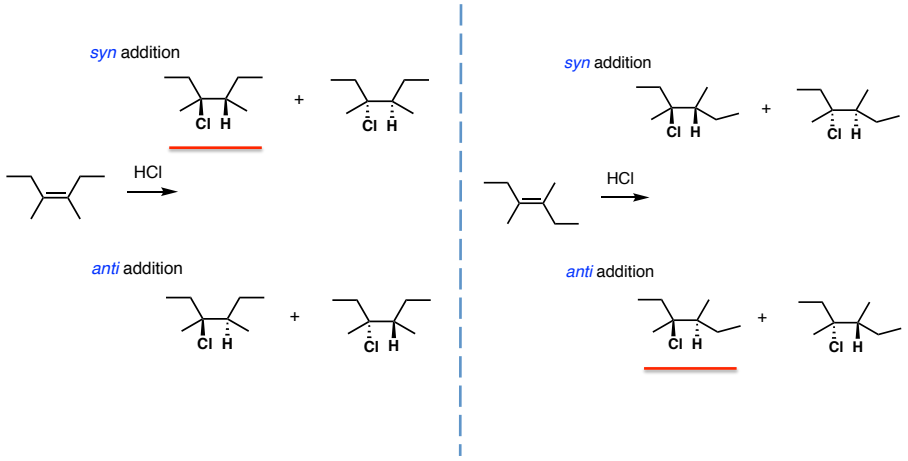


The stereoisomers obtained as products depend on the mechanism of the reaction.

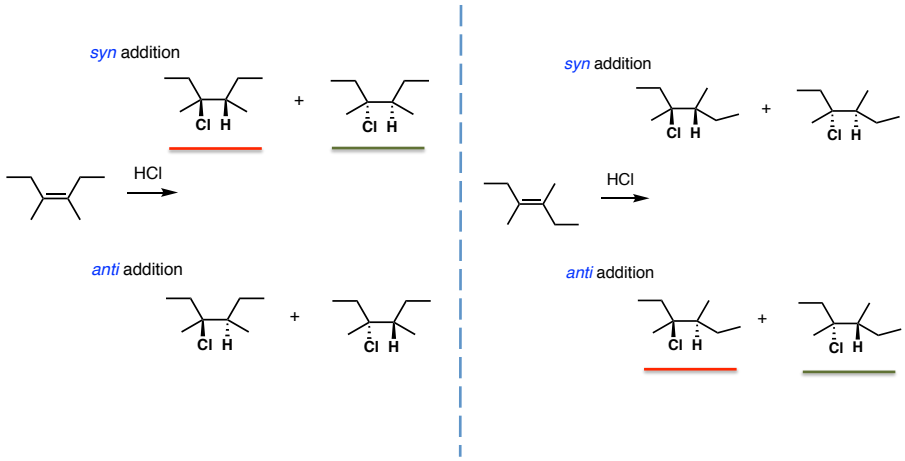
syn and *anti* additions: same with acyclic substrates



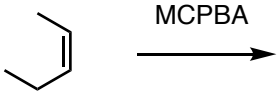
Same with acyclic substrates



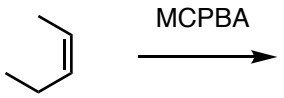
Same with acyclic substrates

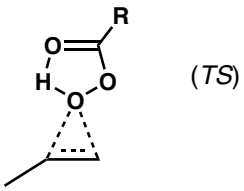


syn **or** ***anti*** **addition?**



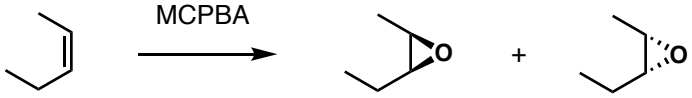
epoxidation: *syn* or *anti* addition?

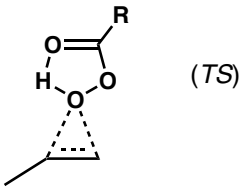




(*TS*)

epoxidation: *syn* or *anti* addition?





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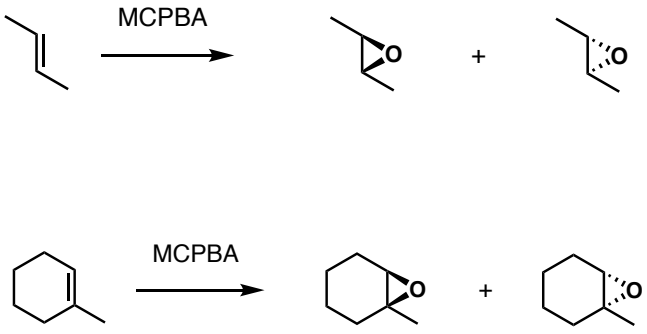
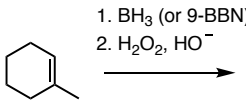
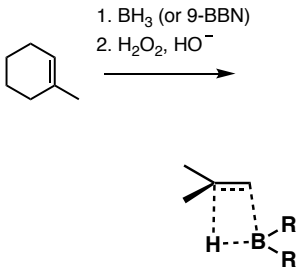


only syn addition

syn or *anti* addition?



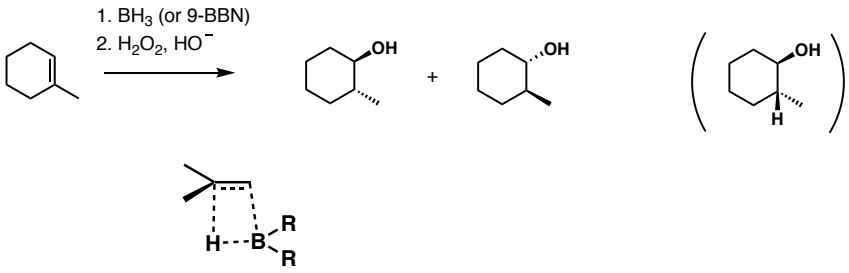
hydroboration/oxidation: *syn* or *anti* addition?



preferred

more stable transition state

hydroboration/oxidation: *syn* or *anti* addition?

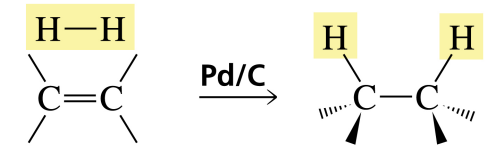


preferred

more stable transition state

only syn addition

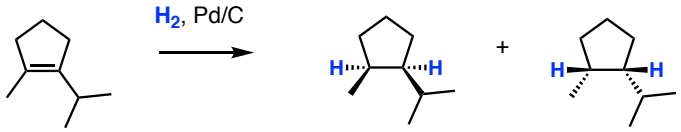
The Stereochemistry of Hydrogen Addition

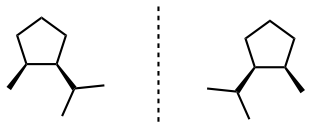


addition of H_2 is a syn addition

only syn addition

Syn H_2 Addition Forms Only the Cis Stereoisomers..

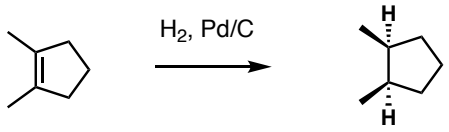


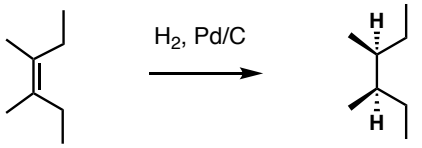


mirror

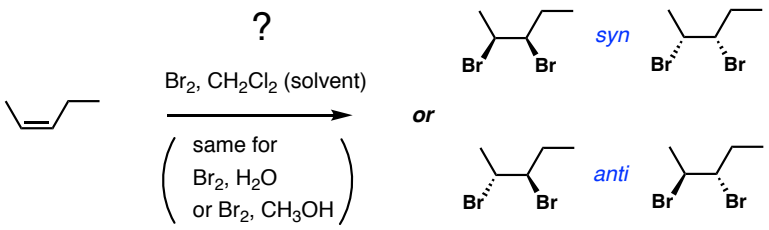
The products can also be seen as mirror images.

If the Substituents are the Same, The Cis Stereoisomer gives a *Meso* compound



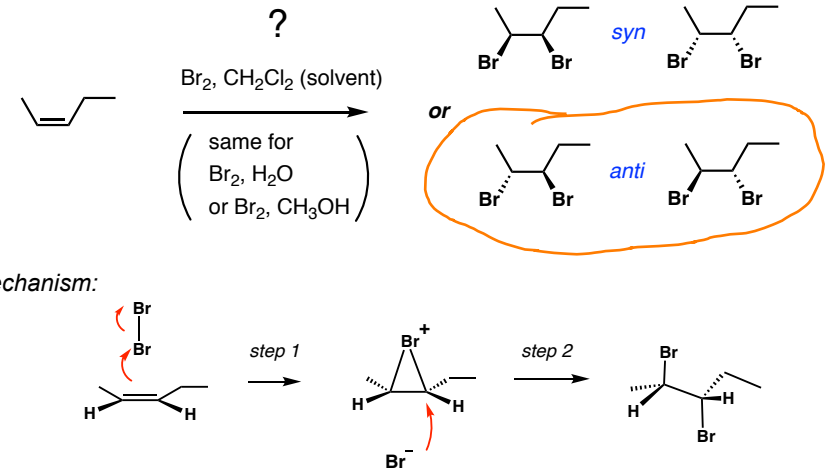


syn or *anti* addition?



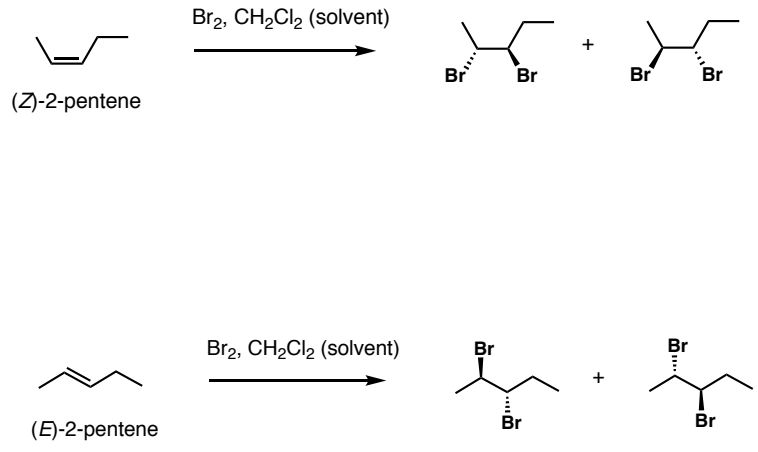
mechanism:

bromonium ion: *anti* addition

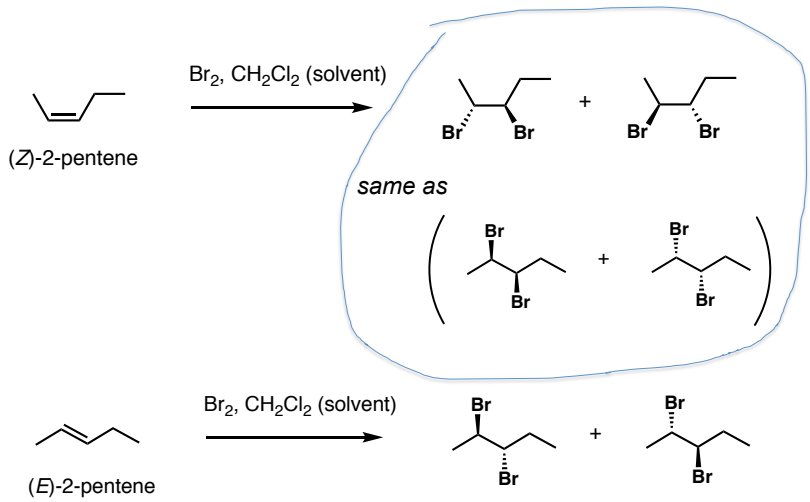


only anti addition

bromonium ion: *anti* addition

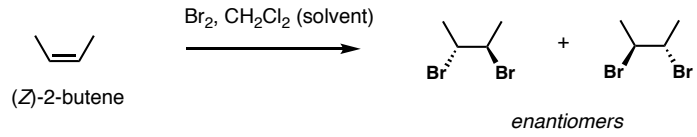


bromonium ion: *anti* addition

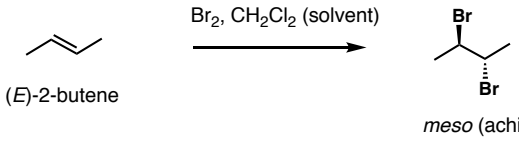


Br_2 *addition is a stereospecific reaction*

If the Substituents are the Same, the Cis (or Z) alkene gives is a Meso Compound



enantiomers



meso (achiral)

Anti Addition to a Cis Isomer Forms Only the Trans Stereoisomers

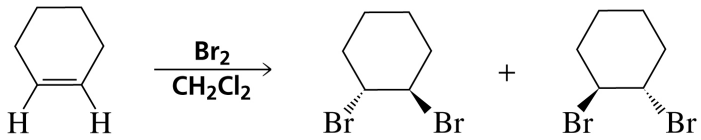


Table 6.1 Stereochemistry of Alkene Addition Reactions

Reaction	Type of addition	Stereoisomers formed
Addition reactions that create one asymmetric center in the product		If the reactant does not have an asymmetric center, then a racemic mixture is formed.
		If the reactant has an asymmetric center, then unequal amounts of a pair of diastereomers are formed.
Addition reactions that create two asymmetric centers in the product		
Addition of reagents that form a carbocation intermediate	syn and anti	Four stereoisomers are formed; the cis and trans isomers each form the same products.
Addition of H_2	syn	cis → erythro or cis enantiomers*
Addition of a peroxyacid	syn	trans → threo or trans enantiomers
Addition of BH_3 or BHR_2	syn	
Addition of Br_2, $Br_2 + H_2O$, Br_2 + ROH (any reaction that forms a cyclic bromonium or chloronium ion intermediate)	anti	cis → threo or trans enantiomers trans → erythro or cis enantiomers*

*An acyclic compound forms the erythro enantiomers; a cyclic compound forms the cis enantiomers. If the two asymmetric centers have the same substituents, a meso compound will be formed instead of the pair of erythro or cis enantiomers.

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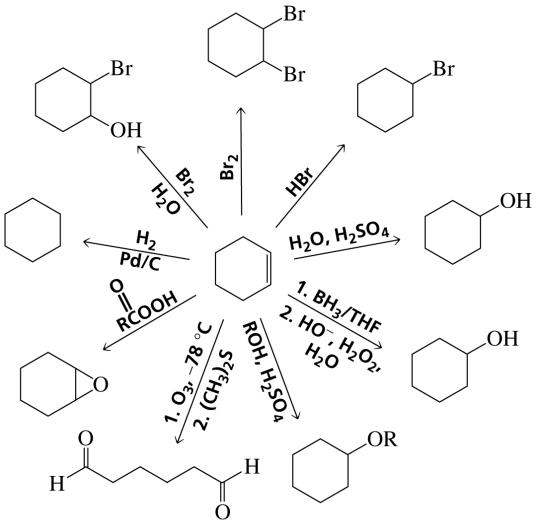
Compounds That Can Be Formed From an Alkene