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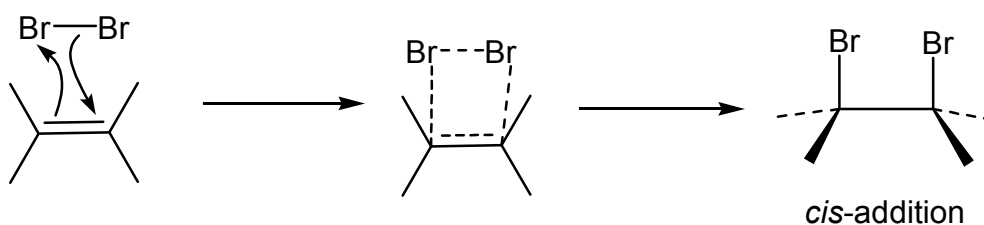
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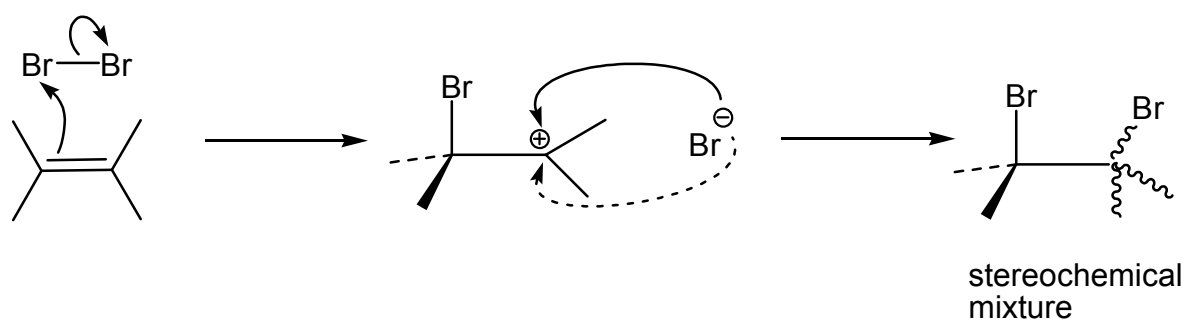
## Addition Reactions at $sp^2$ Carbons

Consider the addition of bromine to an alkene: what are some reasonable mechanisms?

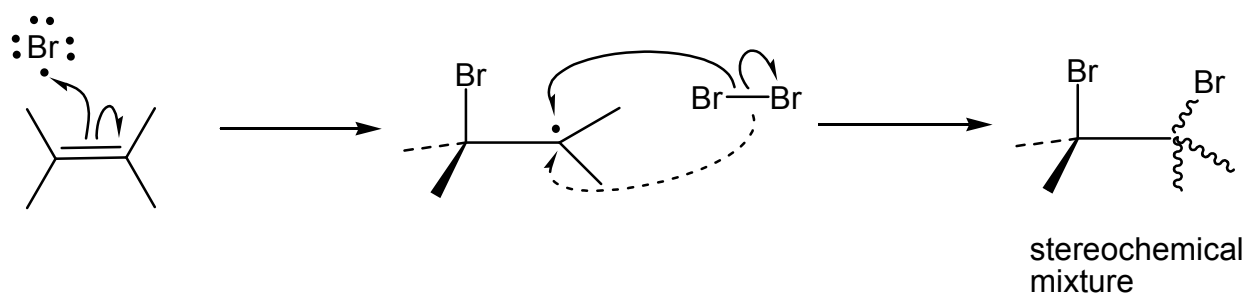
A concerted mechanism?



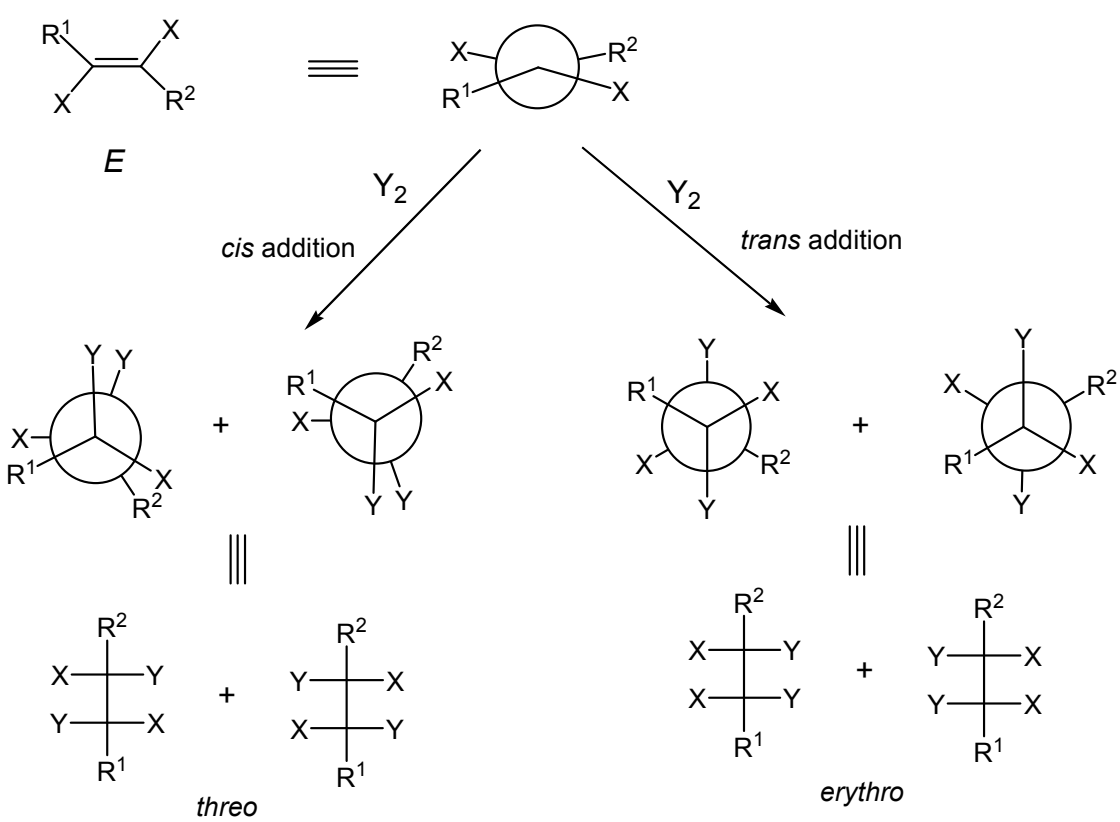
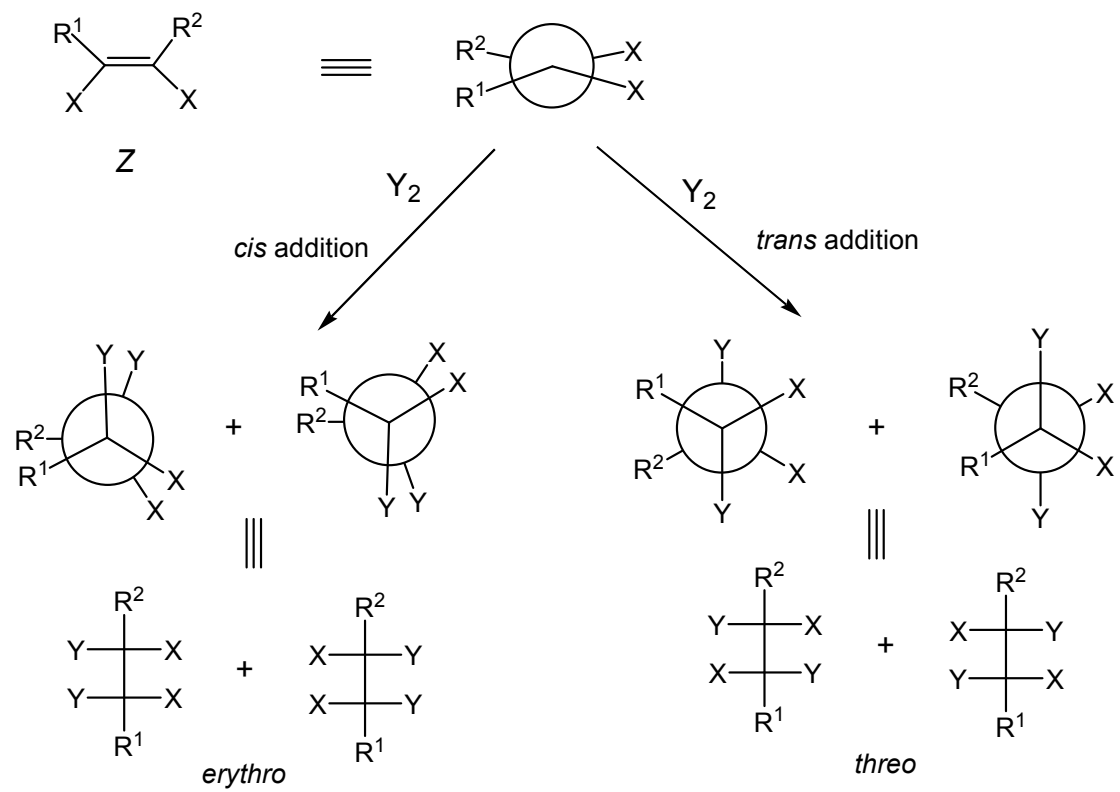
A stepwise polar mechanism?



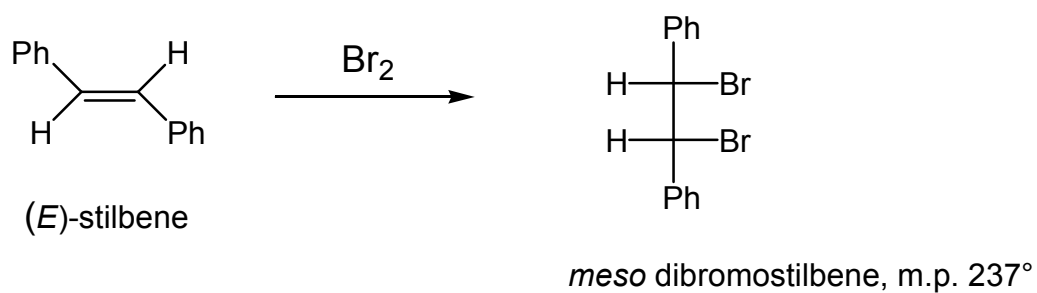
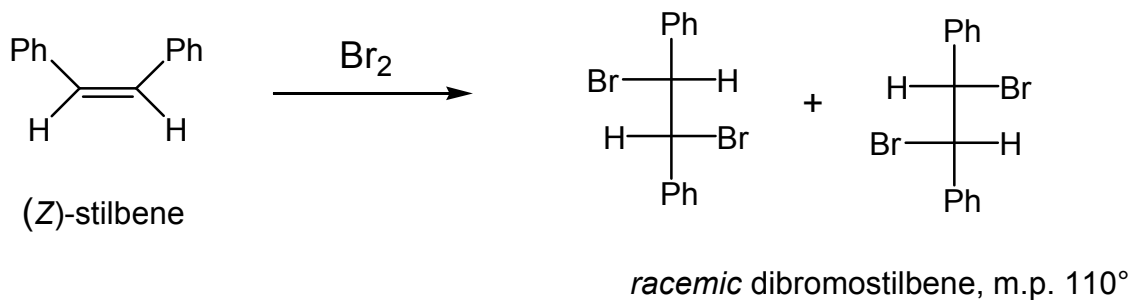
A stepwise radical mechanism?



# Stereochemical Possibilities

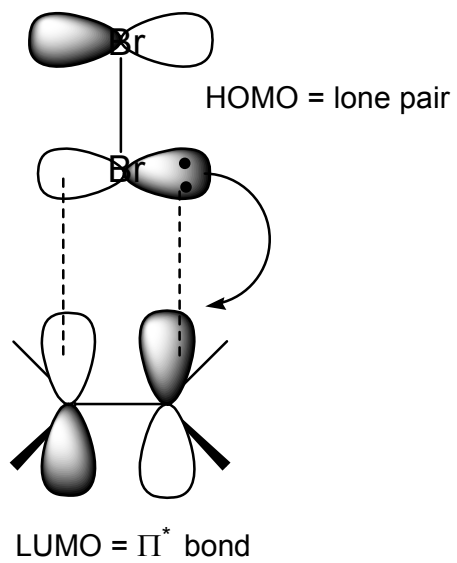
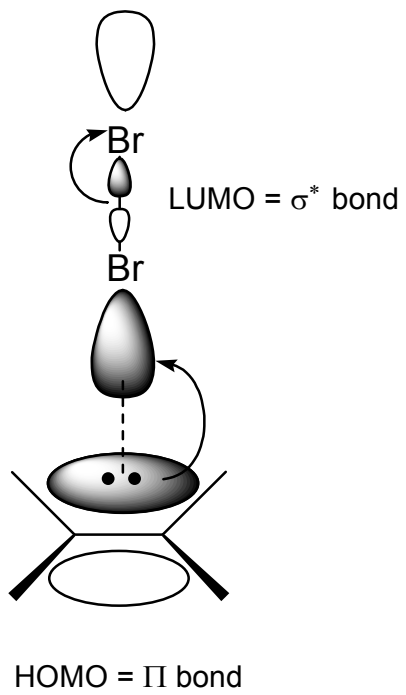


## Example

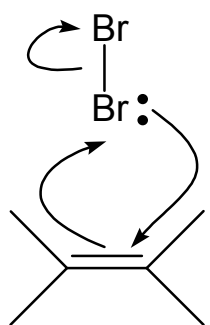


## Mechanism of Bromine Addition to Alkenes

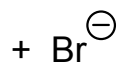
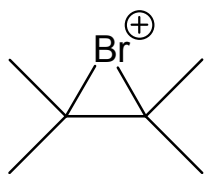
Two step reaction – first formation of a cyclic bromonium ion intermediate, then  $\text{S}_{\text{N}}2$  ring opening. Formation of the cyclic bromonium ion is **concerted**:

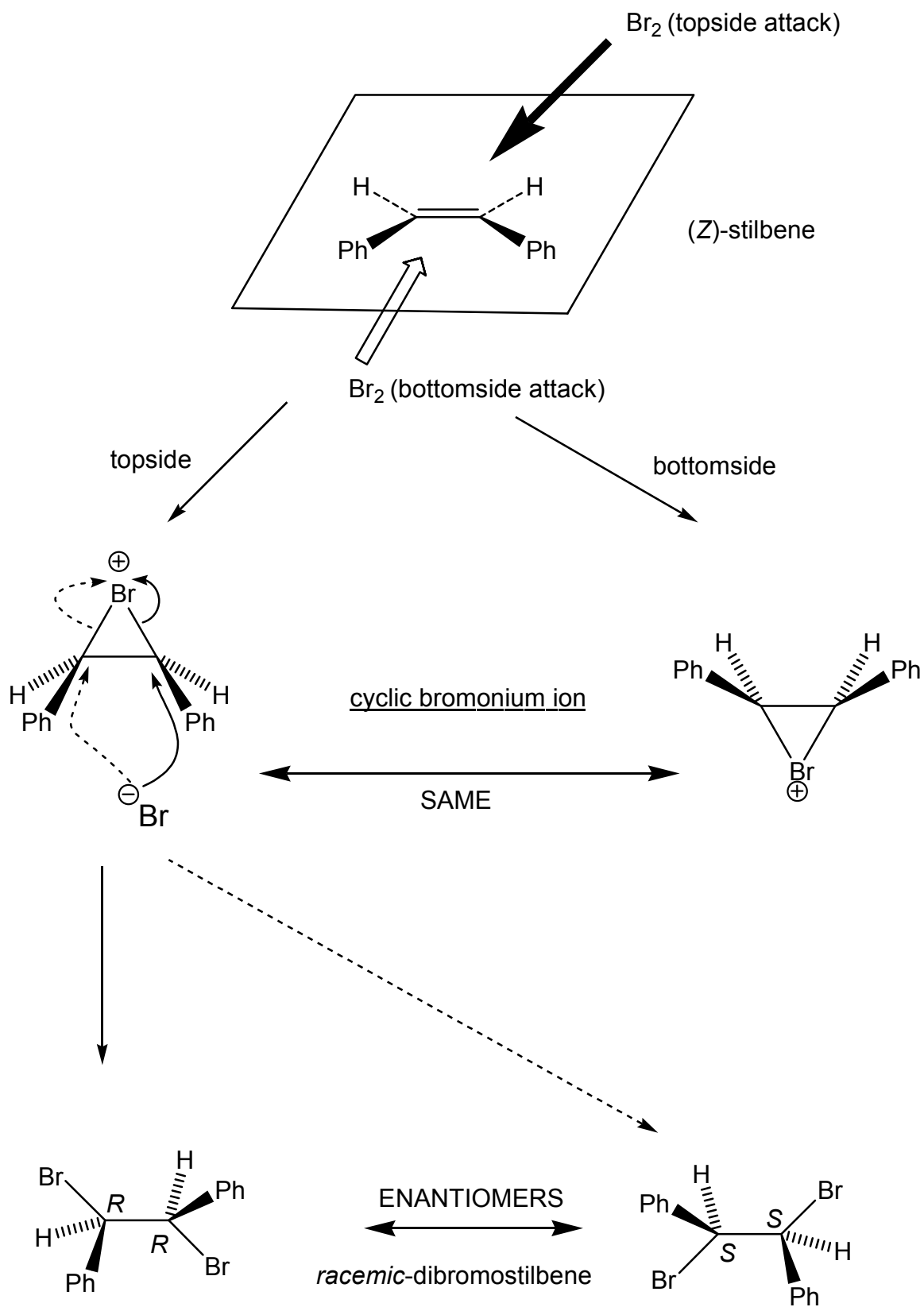


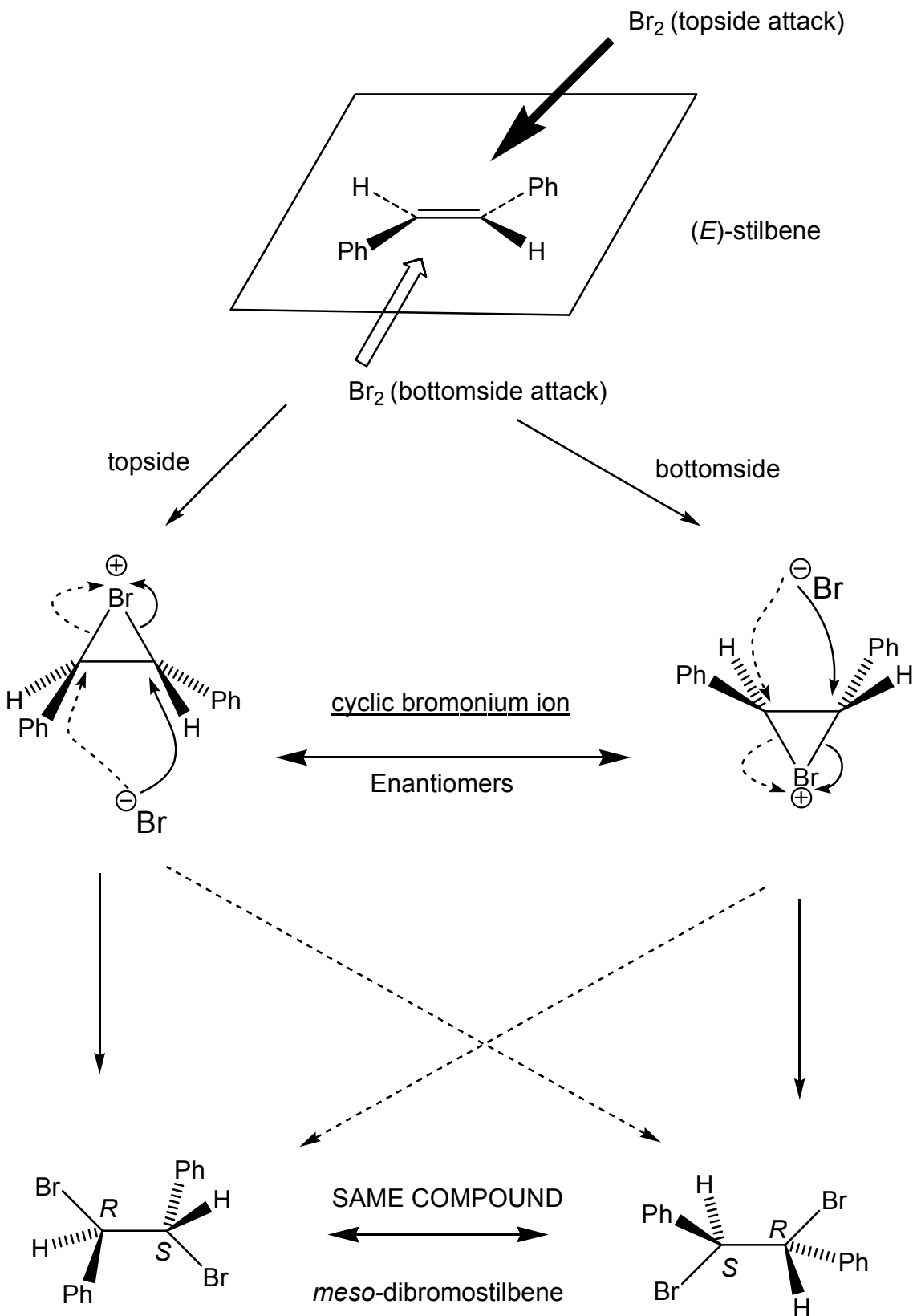
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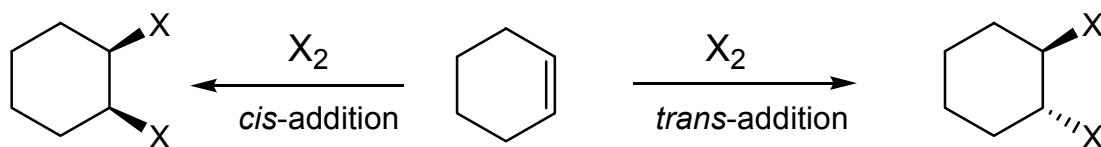




## Stereochemical Possibilities

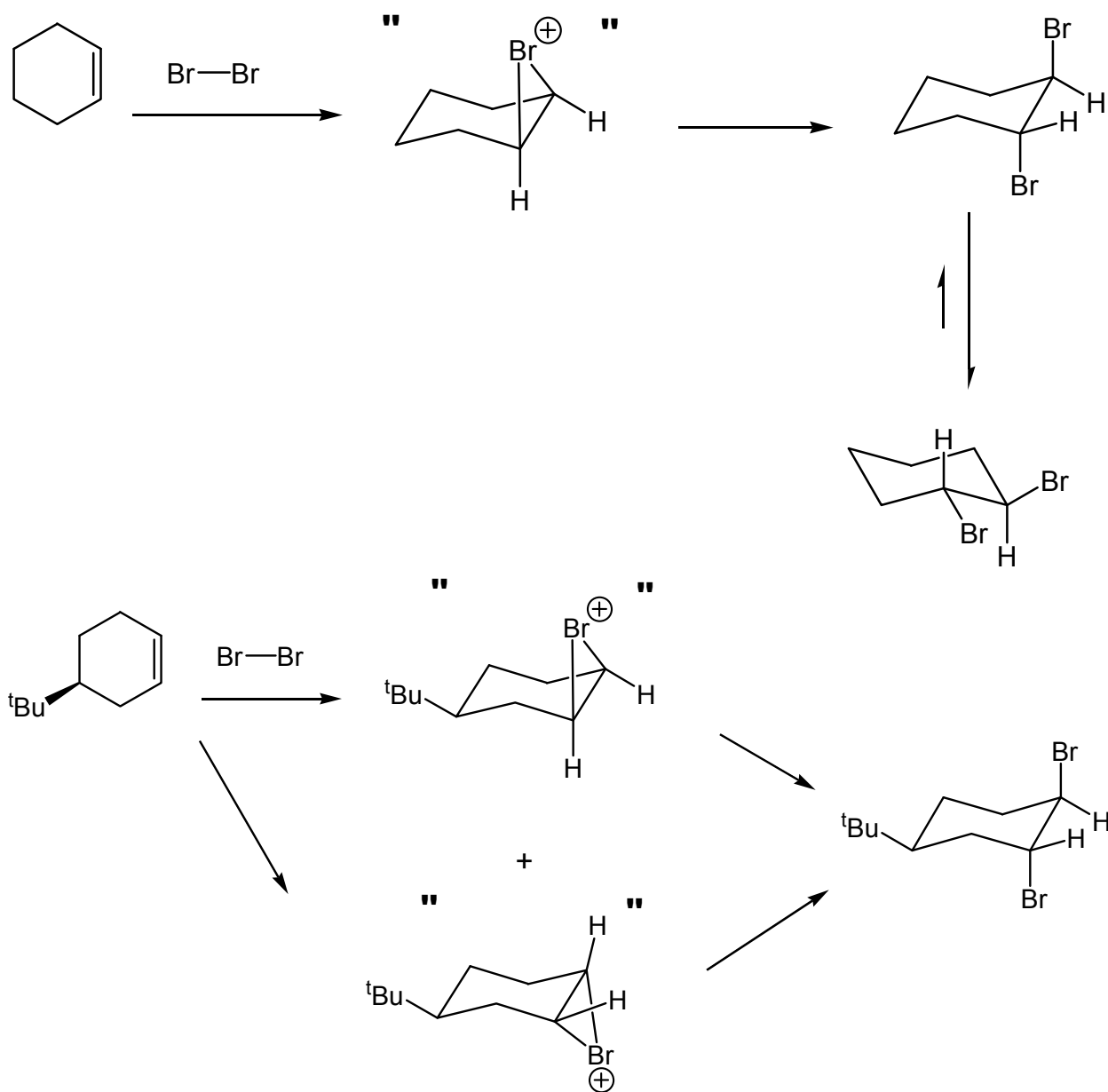
### Cyclic compounds

*Cis* and *trans* addition are defined with respect to the face of the ring:



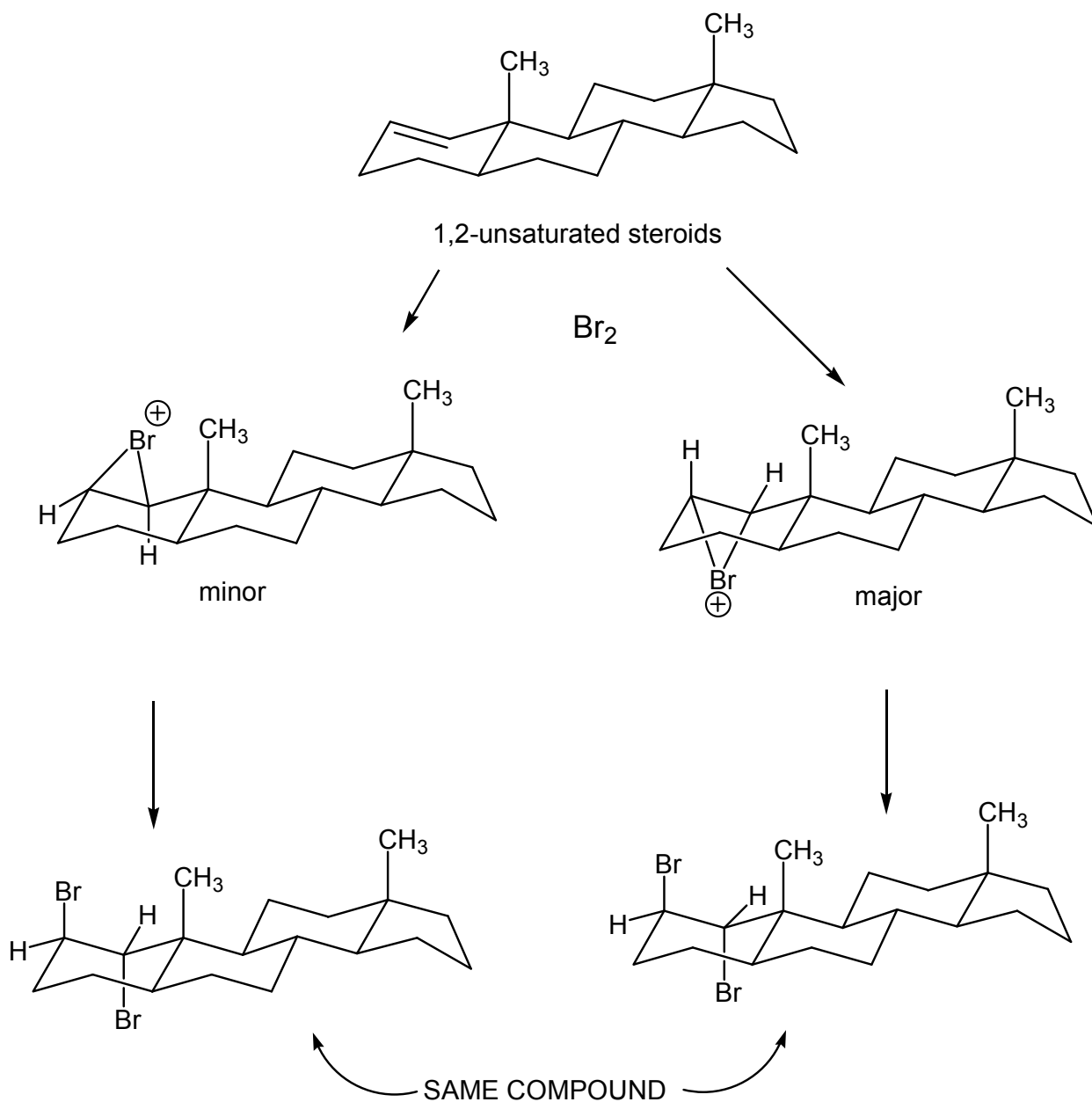
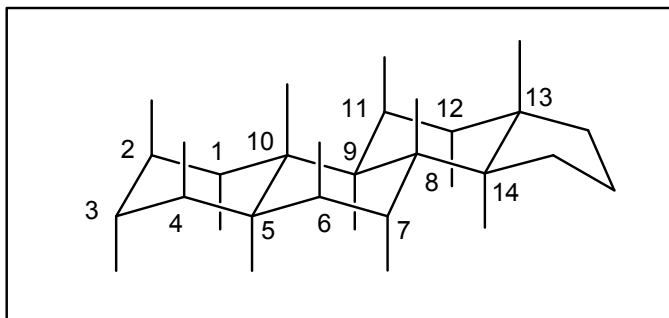
### Example

Bromination of cyclohexenes. The *anti*-periplanar requirement for  $S_N2$  ring opening of the cyclic bromonium ion leads to (at least initially) *trans*-diaxial products (see epoxides pg 39):





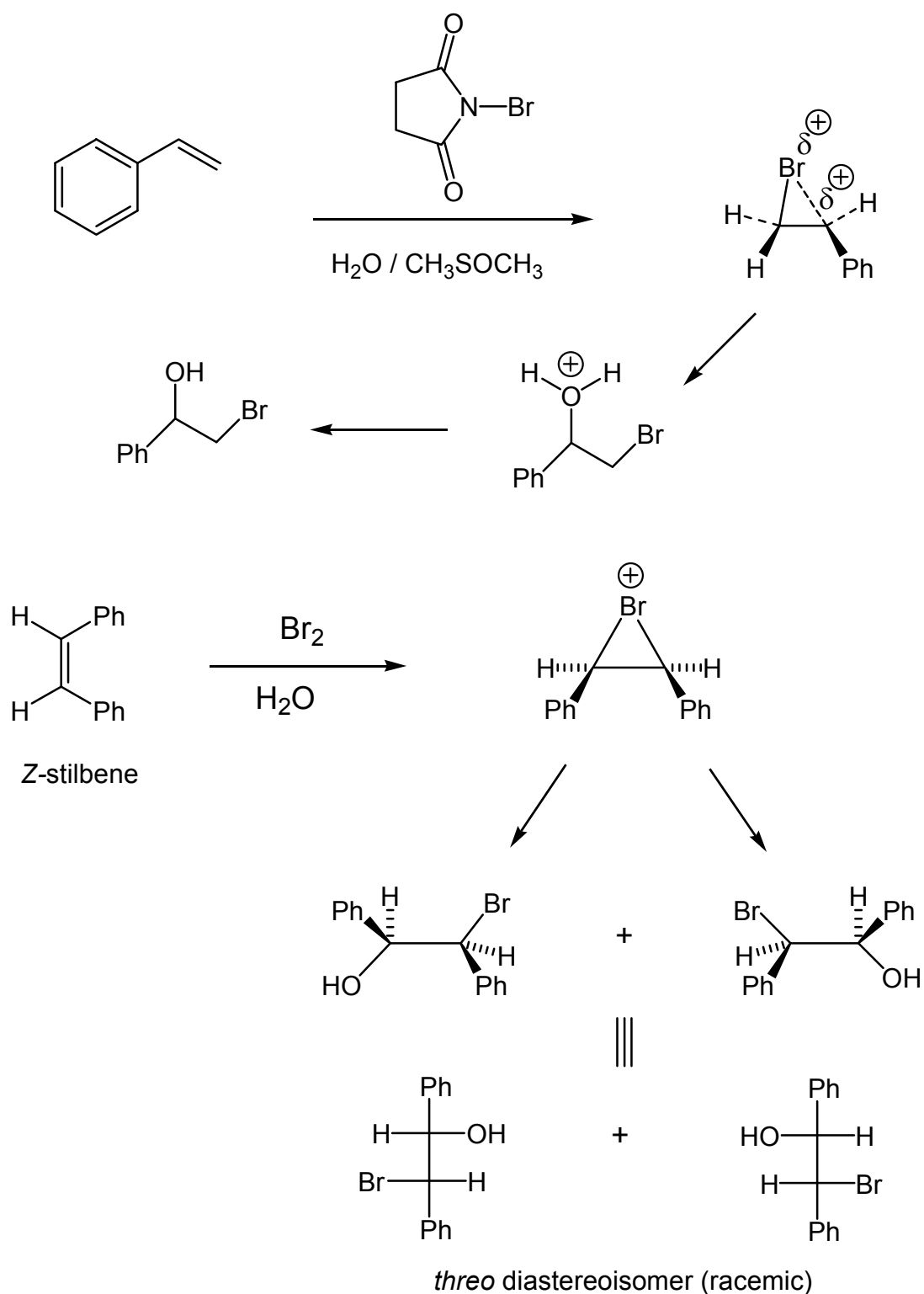
Since *trans*-diaxial products are formed it is important to know which are the axial positions at the various carbons in fused ring systems. For example in the steroid ring system the  $\beta$ -substituents (top face) at carbons 2,4,6,8,10,11,13 and 13 are axial, while the  $\alpha$ -substituents (bottom face) at carbons 1,3,5,7,9,12 and 14 are axial.

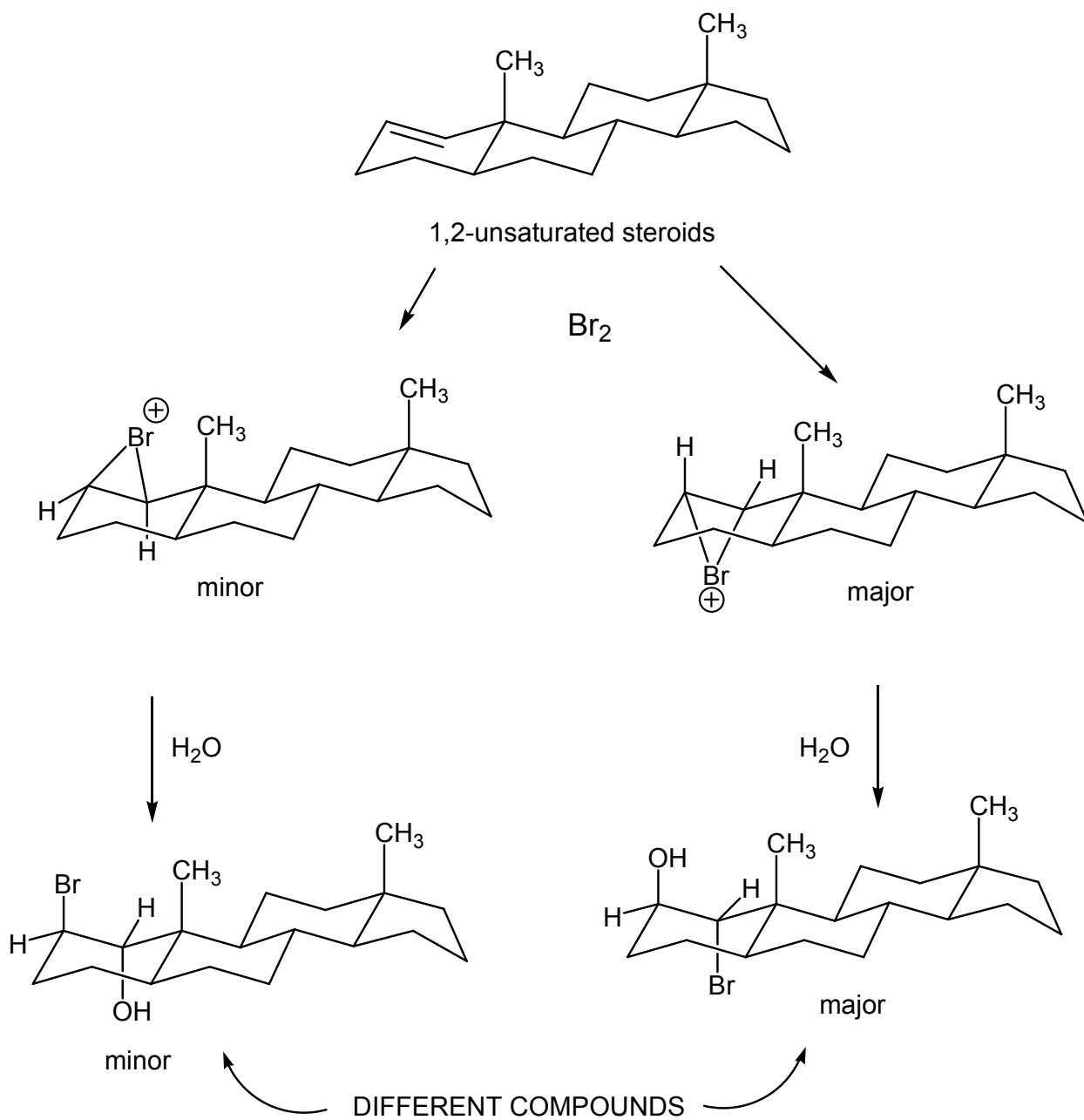


## Other Addition Reactions

### Bromohydrin Formation

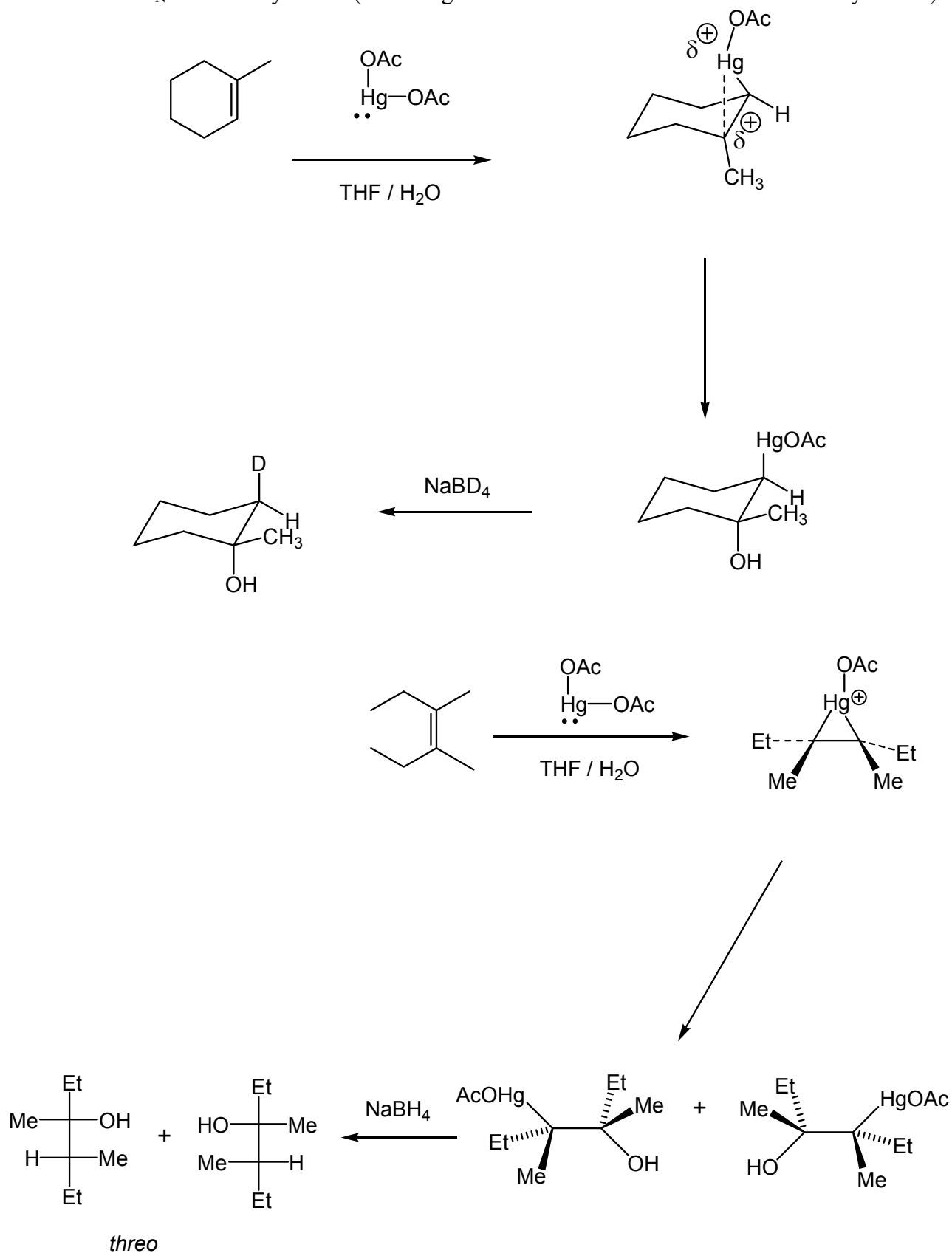
*Regiochemistry and Stereochemistry* – more substituted carbon of bromonium ion intermediate is attacked in an  $S_N2$  fashion by water (compare acid-catalysed epoxide ring opening – pg. 38).



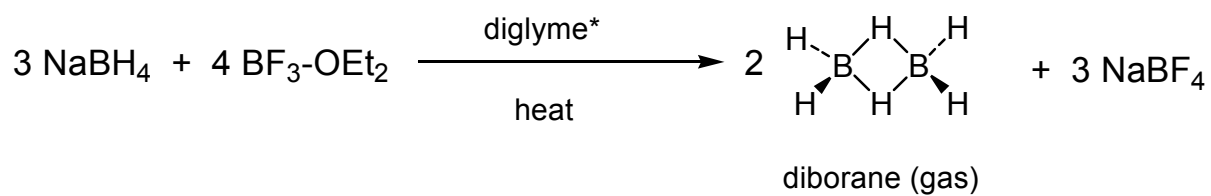


## Oxymercuration

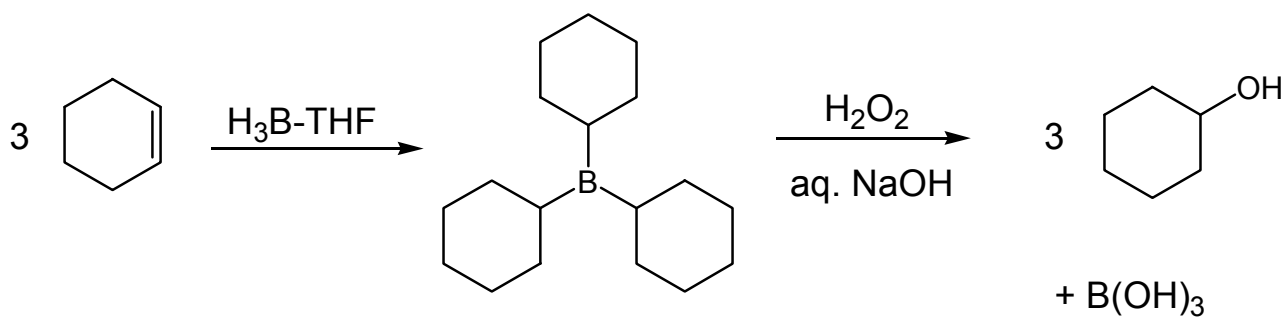
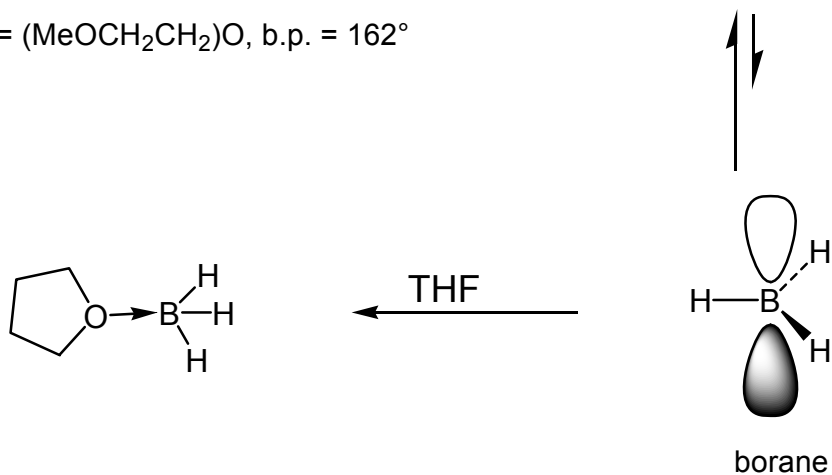
*Regiochemistry and Stereochemistry* – more substituted carbon of mercurinium ion intermediate is attacked in an S<sub>N</sub>2 fashion by water (following reduction leads to overall Markovnikov hydration).



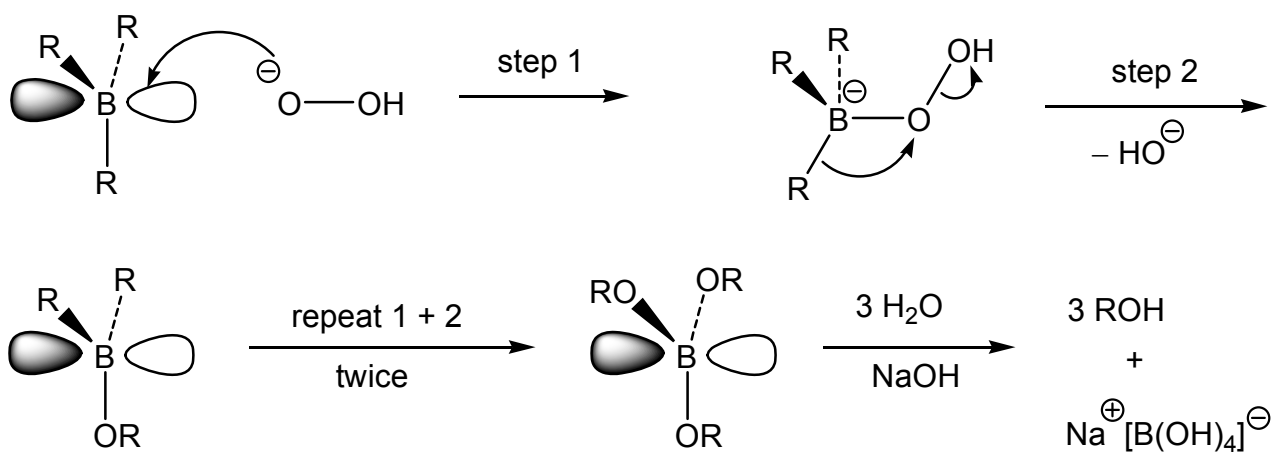
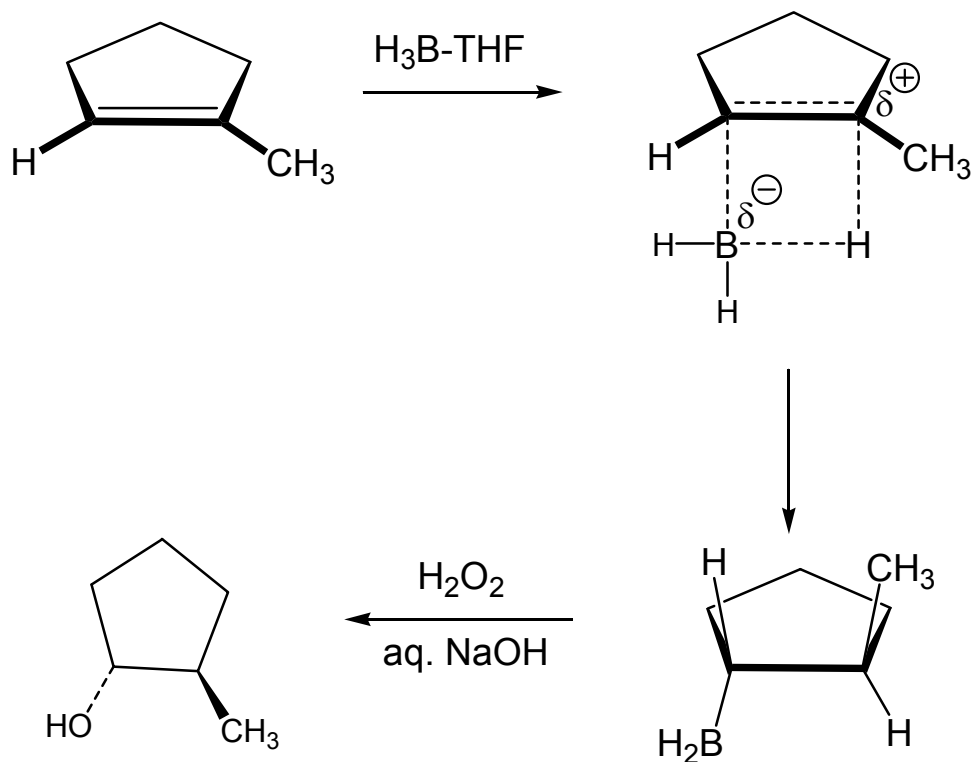
## Hydroboration

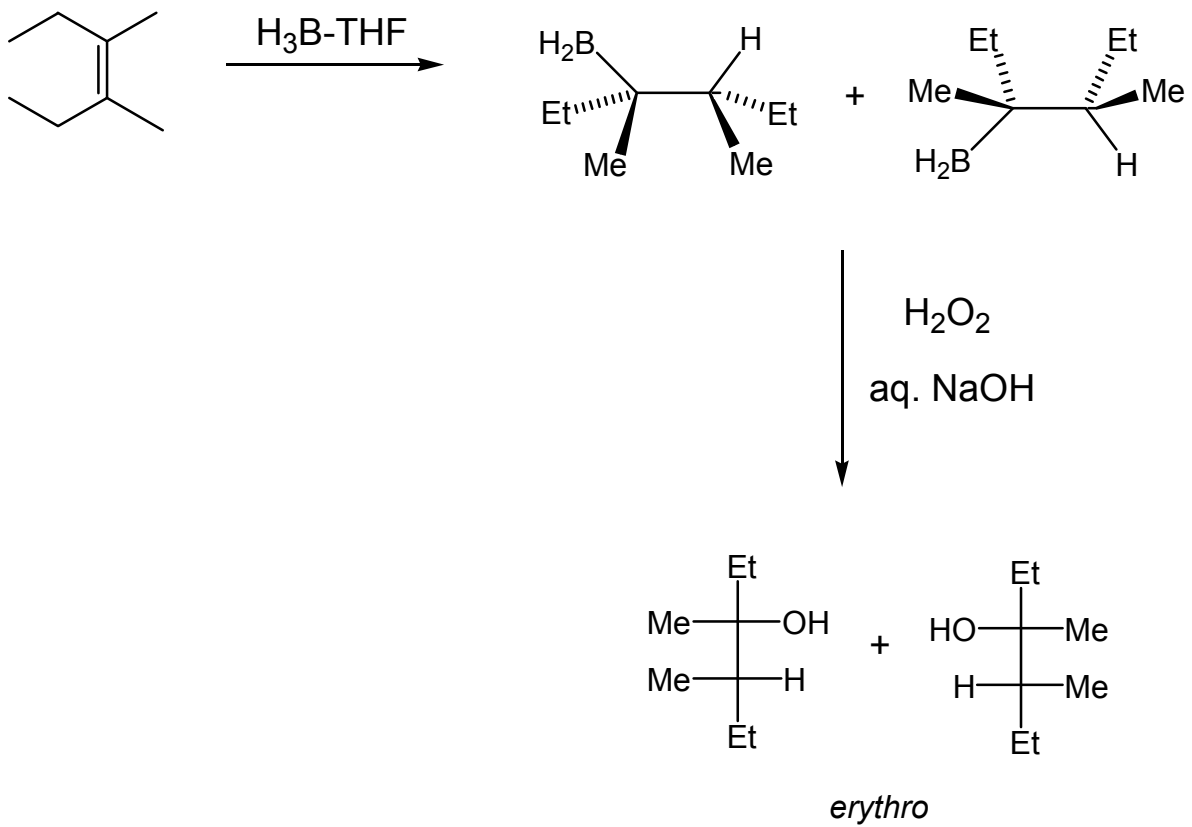


\*diglyme = (MeOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, b.p. = 162°

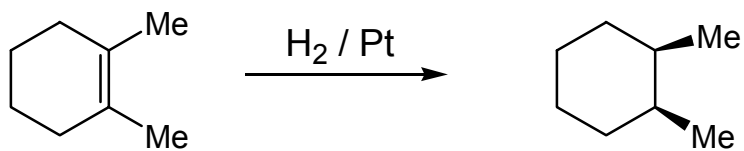


*Regiochemistry and Stereochemistry* – B—H adds *cis* across double bond with anti-Markovnikov regiochemistry (electronic and steric factors).





### Catalytic Hydrogenation



### Alkene Hydroxylation with OsO<sub>4</sub>

