

Halogenation Of Alkenes

from chapter(s) _____ in the recommended text

A. Introduction

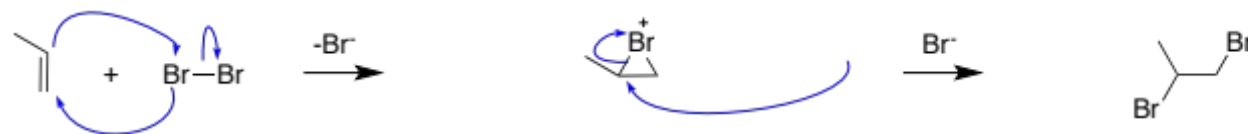
B. Mechanism

Like protons, halogens (X_2) tend to approach alkenes or alkynes *perpendicular* to the π -bond and an $X-X$ bond to become *polarized* until *halide* (X^-) and a halonium ion formed.

Halonium ions are *positively* charged; the *-ium* suffix in that name *is* indicative

Chlorination and Bromination

featuring halonium ion *intermediates*.



Halogen (X_2) are *electrophiles* while, because of their π -clouds, alkenes are *nucleophiles*. Bromine, for instance, is an *electrophile* because it *becomes polarized in the presence of high electron density*.

halogenation of alkenes involves rate-limiting *electrophilic* attack of the halogen
 this is *nucleophilic* attack of the alkene on the bromine.
 React *faster* than ones that have less or electron withdrawing substituents.

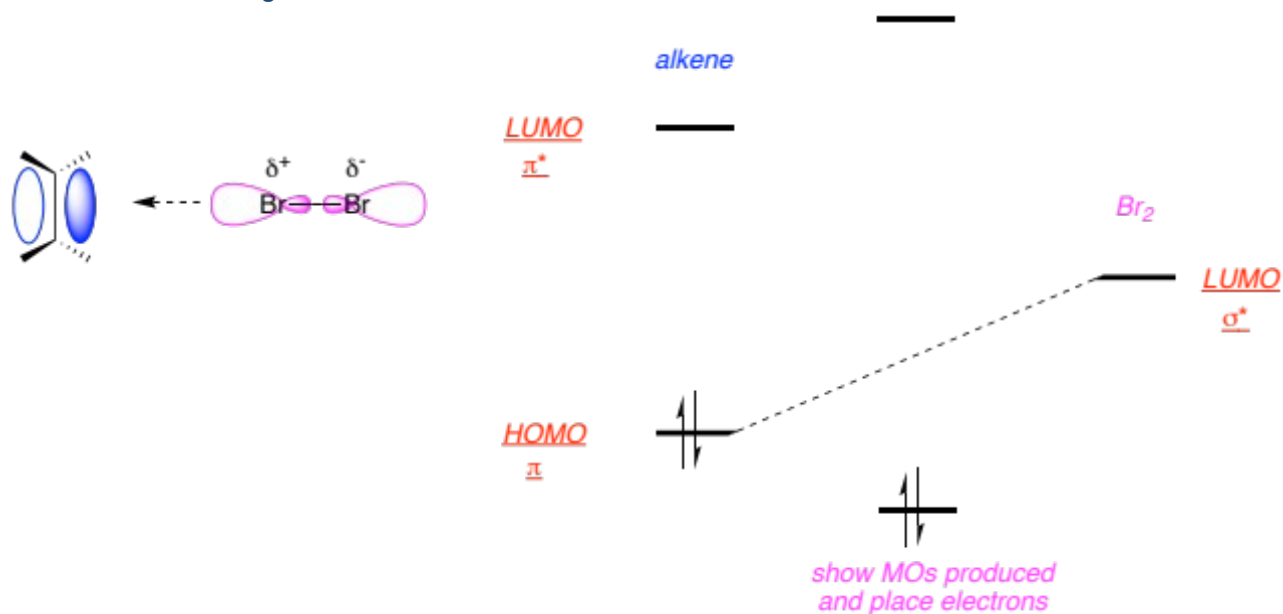


fastest bromination

slowest bromination

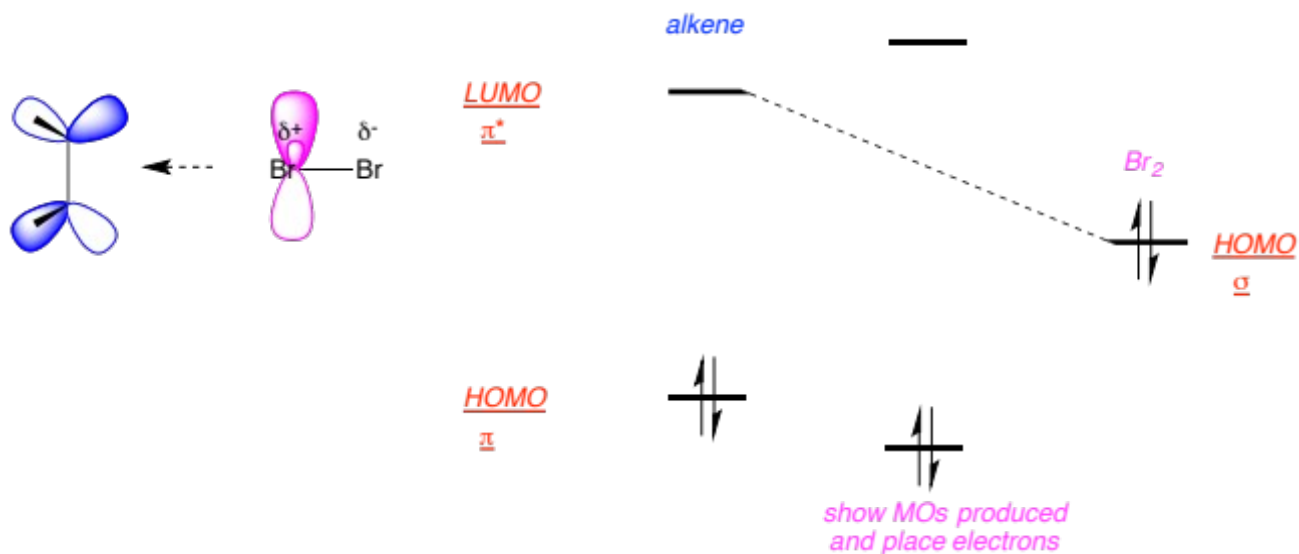
Halogenation of alkenes are *addition* reactions involving bonding of one X-

A MO View Of Halogenations



Perpendicular approach of halogens (X_2) to a symmetrical π -cloud is net *stabilizing*,
 halogenation is the most important orbital overlap so this is called the *primary* interaction.

Halogenation of alkenes is further stabilized by a *secondary orbital interaction* between the π^* -orbitals



Secondary interactions as shown above *do not* favor formation of bromonium ions.

Stereospecificity

Bromonium ions in bromination of alkenes, tend to be opened by S_N2 attack of bromide

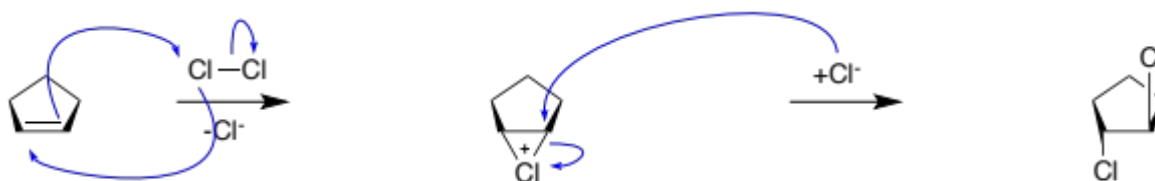
Nucleophilic attack on halonium ions occurs *anti* to the halogen atom

alkenes within a ring (*ie endocyclic* ones) give *trans*--dihalide products.

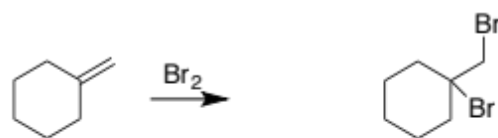
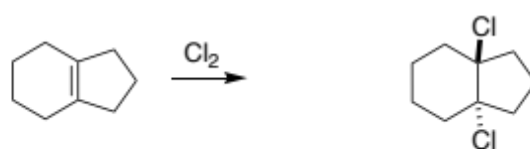
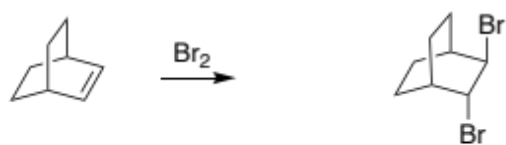
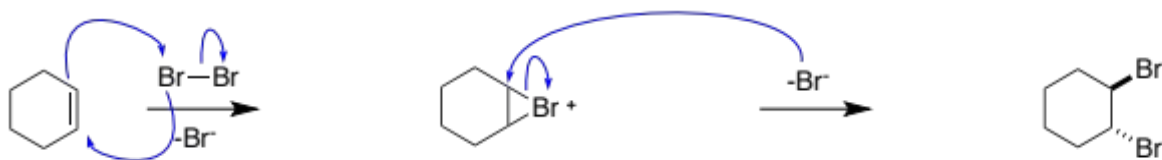
Bromination of cyclohexene *mostly* affords the *trans*--1,2-dibromocyclohexane

bromonium ion must occur from the *opposite* face of the bromine atom.

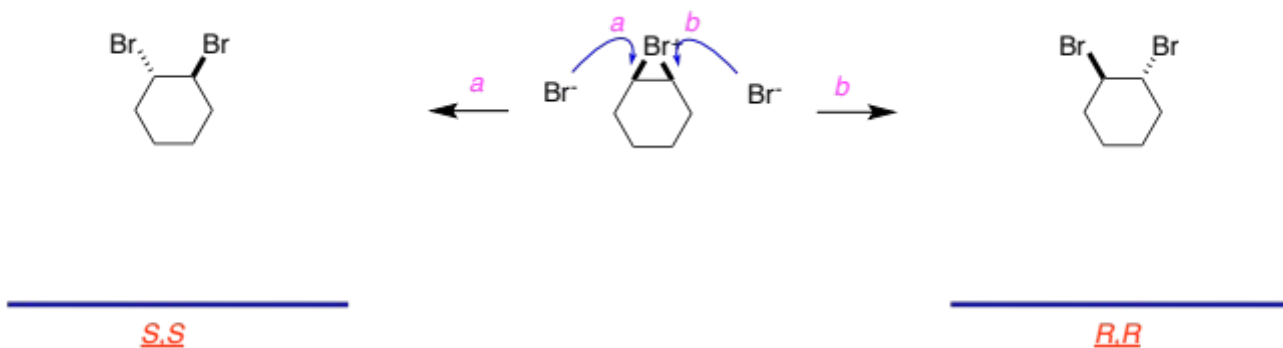
halogenation of *cis*-endocyclic alkenes is therefore *stereospecifically-trans*, meaning it *always* gives the *trans*-product.



Of course, if the product is chiral then a racemate is formed.



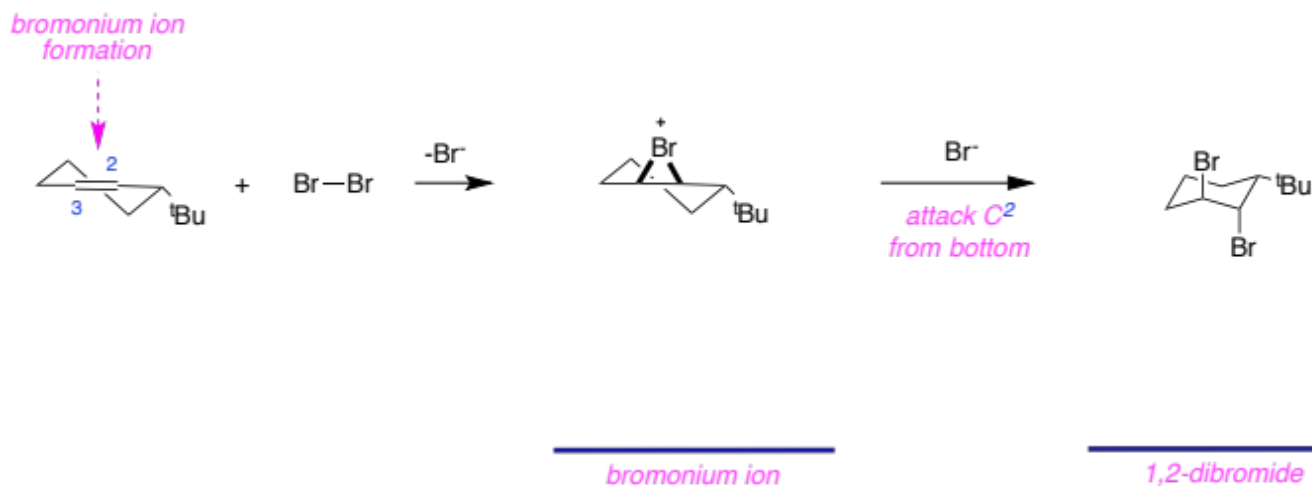
Nucleophilic attack on the following bromonium ion gives *enantiomers*.

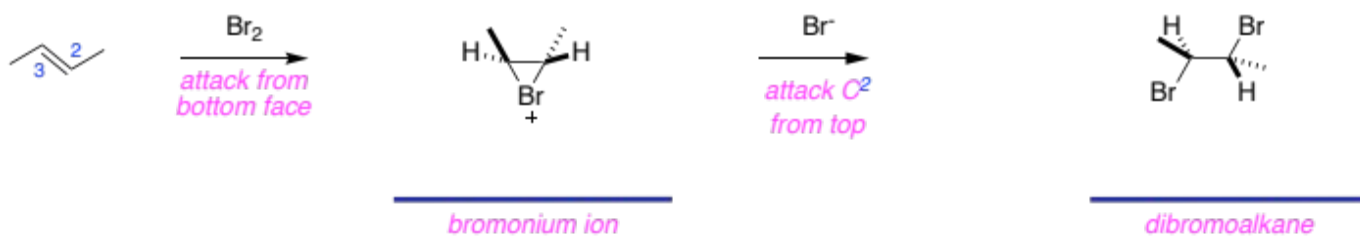
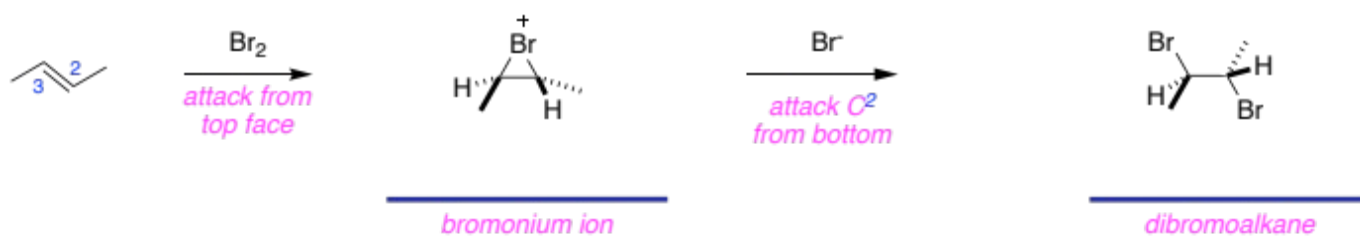


the ratio of the two enantiomers formed will be *equal*, ie the product will be a *racemate*

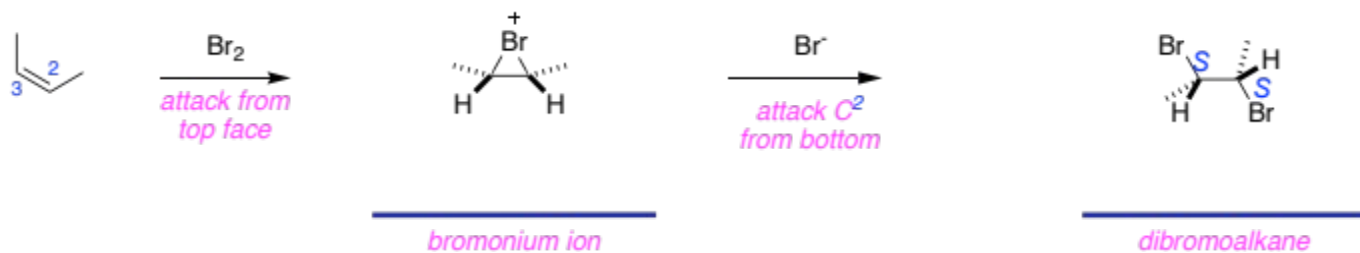
It *is not* possible to form *meso*-stereomers in this reaction.

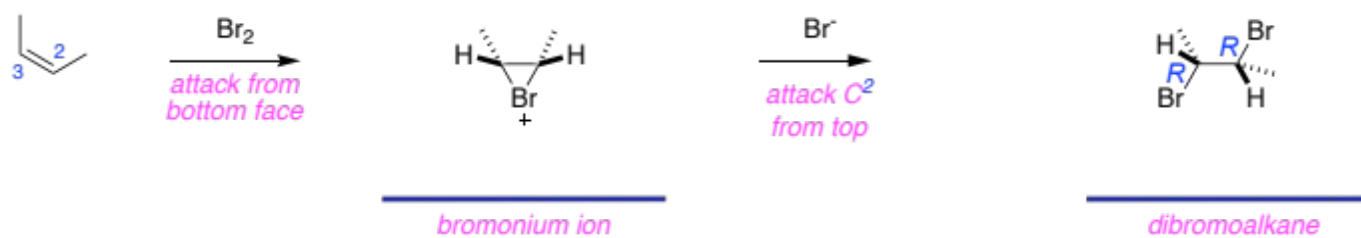
other one is formed in *equal* amounts; this is true



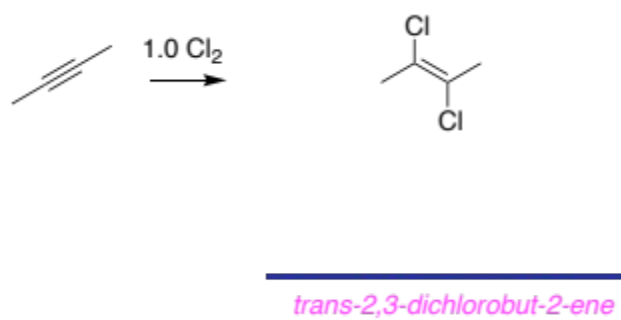
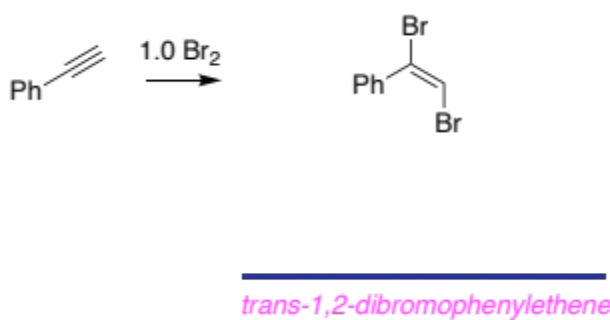
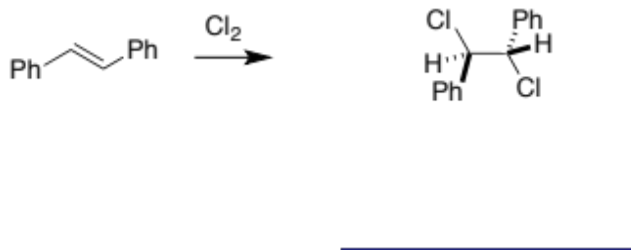
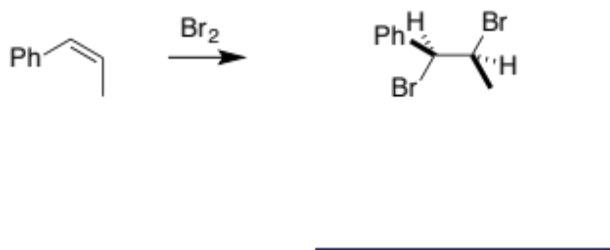
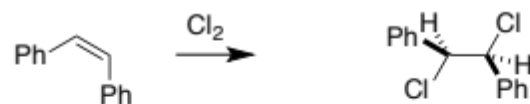
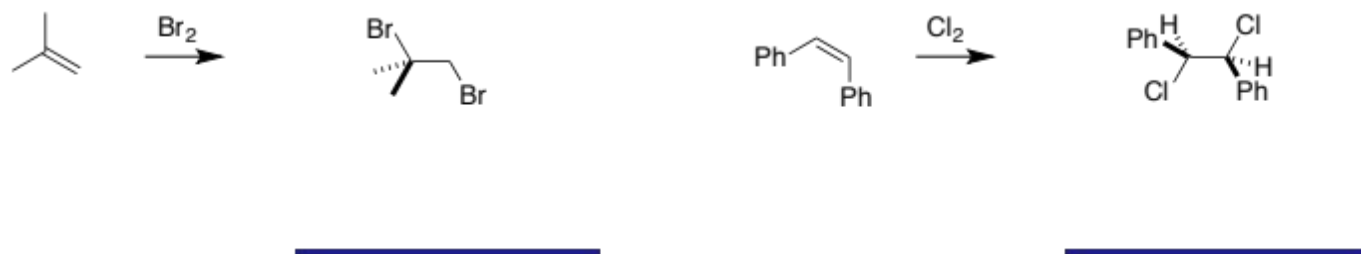


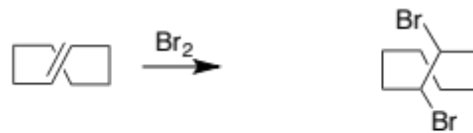
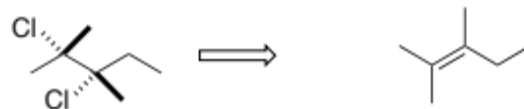
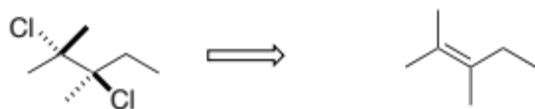
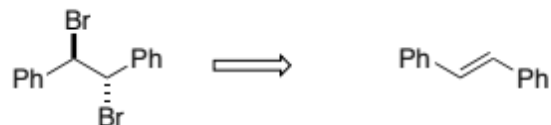
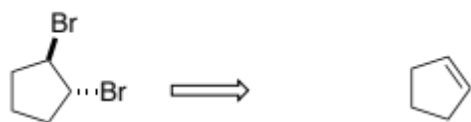
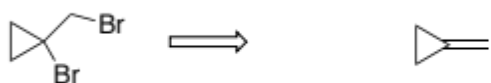
The products from these two reaction pathways are *identical*.





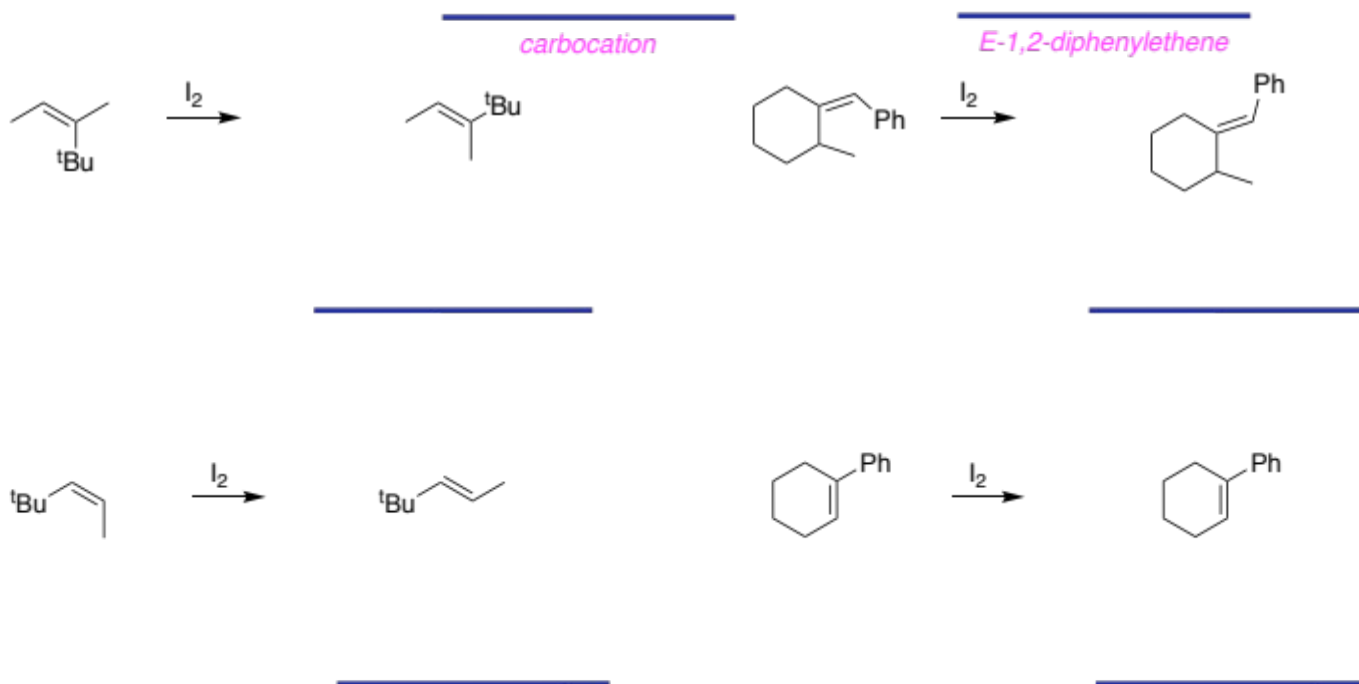
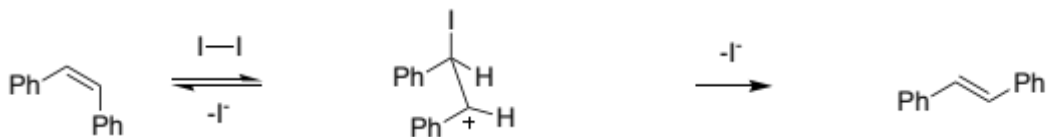
When *E*- and *Z*-2-butene react with bromine, the products are racemic *enantiomers*.



*trans-**cis-*

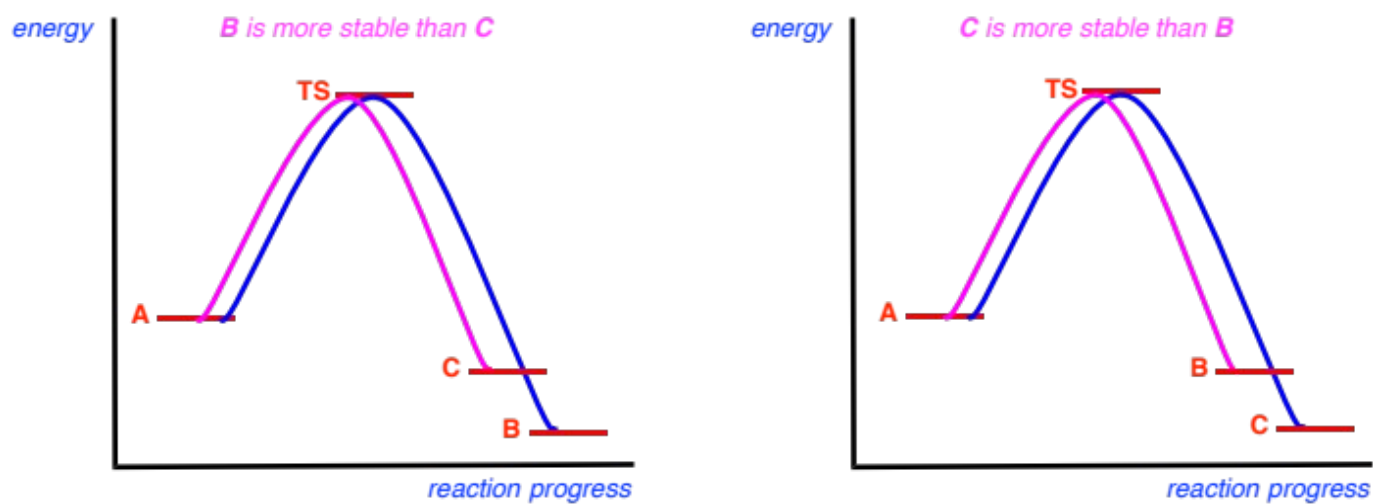
Iodination

iodination does not give product because *the product is thermodynamically unstable relative to ethene and iodine*.



C. Kinetic And Thermodynamic Control

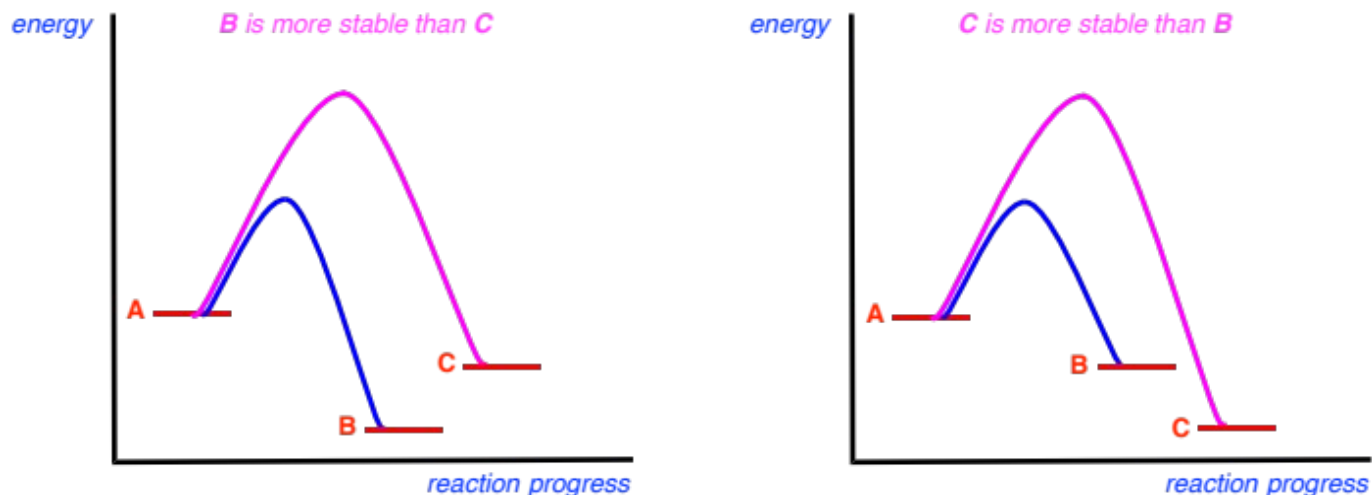
Kinetic Control



In both diagrams, **B** and **C** must be *lower* energy than **A** and the products *cannot* surmount the energy barrier

The rate of formation of **B** and **C** in this reaction *is not* dependent on the stabilities it *is* dictated by the energy barrier

B:C product ratio will be *1*, and when **C** is more stable than **B** it will be *1*.



B:C ratio will be determined by their relative *rates of formation*, and it will *be invariant*.
In this case the **B:C** ratio is a *kinetic* one.

Thermodynamic Control

A under the reaction conditions, *ie* the process is *reversible* and **B** and **C** have *different* energies
B:C will be *>1*, and *will* change as the reaction progresses.

$$K_B = [B] / [A] \quad \text{and} \quad K_C = [C] / [A]$$

At equilibrium, the K_B / K_C ratio *is* another constant, K_{BC} , where

$$K_{BC} = [B] / [C]$$

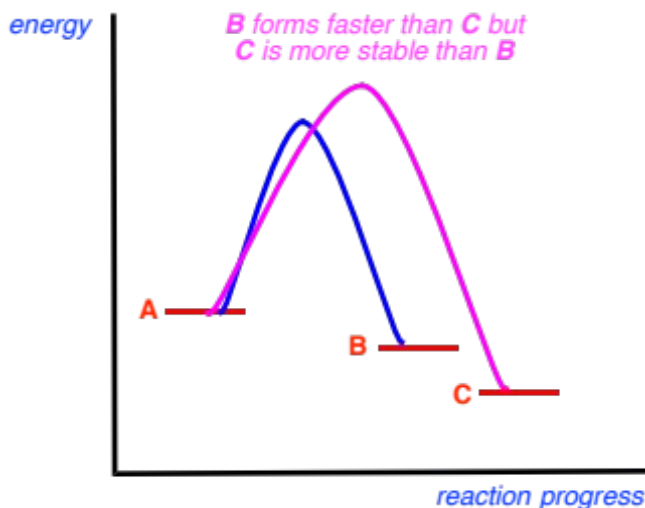
and the **B:C** ratio is *independent of* the concentration of **A**.

kinetic and thermodynamic controls are *coincident* insofar as they both

B:C ratio is determined by the relative *activation energy barriers* but at the end it is governed by the relative *stabilities of the products*.

These ratios are *different* but they both favor the same product.

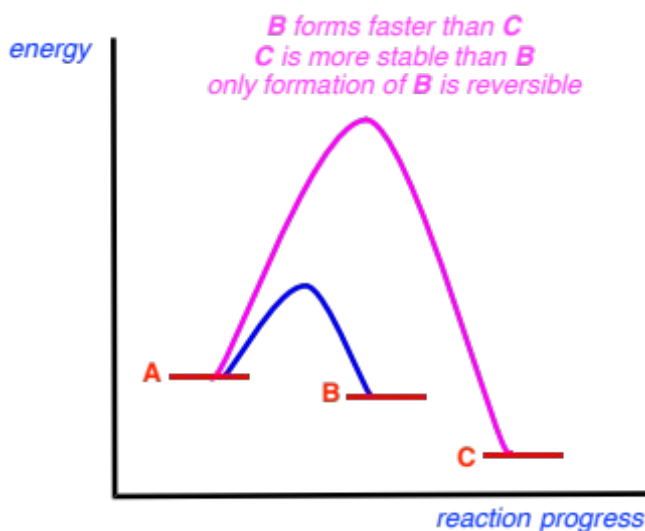
Non-coincident Kinetic And Thermodynamic Control



B forms faster than **C** so it is the *kinetic* product; it forms *reversibly*.

C is the *thermodynamic* product; it forms *reversibly*.

product **B** would *be disfavored* because it will revert as the reaction proceeds and *reversibly* forms **C**.



B forms faster than **C** so it is the *kinetic* product; only **B** forms *reversibly*.

C is the *thermodynamic* product; it forms *irreversibly*.

product **B** would *not be observed* because it will revert as the reaction proceeds and *irreversibly* forms **C**.

kinetic and thermodynamic control a *kinetic* product would form preferentially in the early stage transformed into a different *thermodynamically* controlled product later.

Bromination 1,3-Butadiene: Non-coincident Kinetic And Thermodynamic Control

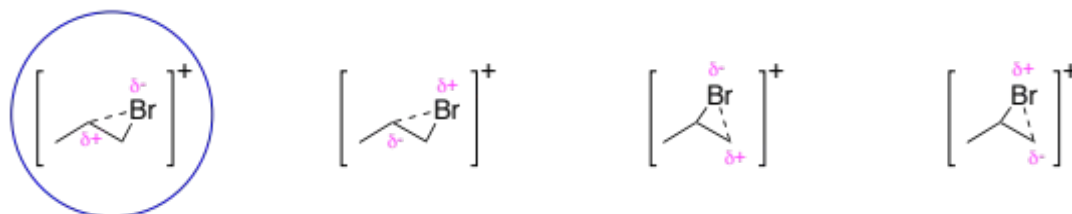
1,2-dibromide forms quickly in the early stages of the reaction, *ie* it is the *kinetic* product.

The amount of 1,2-dibromide *decreases* as the reaction time is extended, and the concentration of 1,4-dibromide *increases*.

the alkene products: *1,4-dibromide has two groups substituted on the alkene product while 1,2-isomer has only one group.*

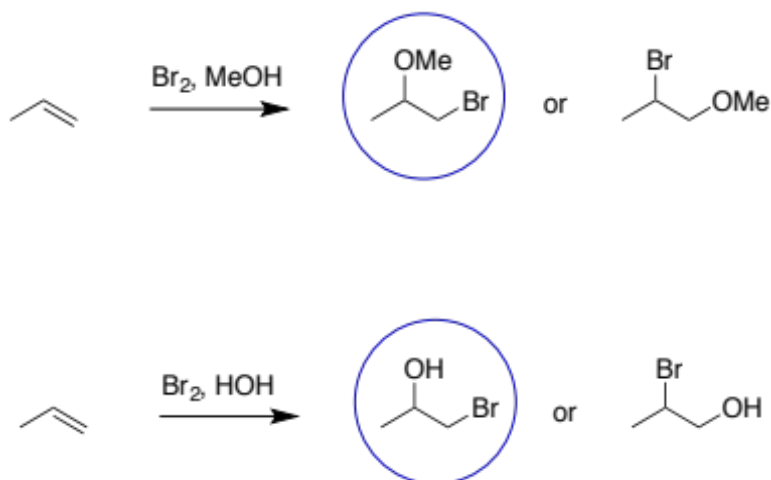
Nucleophilic attack on alkenes tends to be much *less* favorable than electrophilic attack it *does not* proceed unless there are electron-withdrawing groups

D. Halogenations In Nucleophilic Solvents

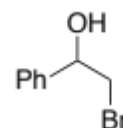
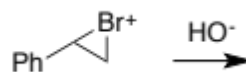
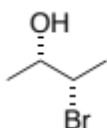
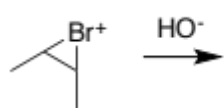
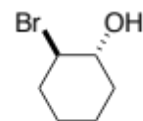
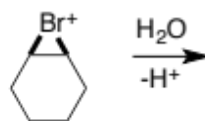
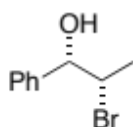
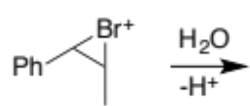


Nucleophiles add to the carbon of an unsymmetrical halonium ion that is *best* able to support

Regio-selectivity is important when bromination of unsymmetrical alkenes bromide because the reaction can produce different *regioisomers*.



Opening of bromonium or chloronium ions by water is called a *halohydrin* reaction. the halogen on the carbon least able to support a negative charge because *this is the precursor to the most stable cation*.



Considerations regarding potential carbocation stabilities *are* likely to apply to ring opening of epoxides.