

Halogenation Of Alkenes

from chapter(s) _____ in the recommended text

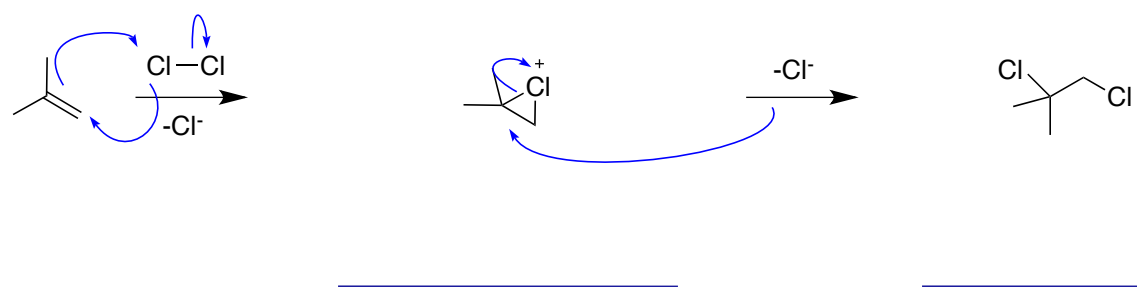
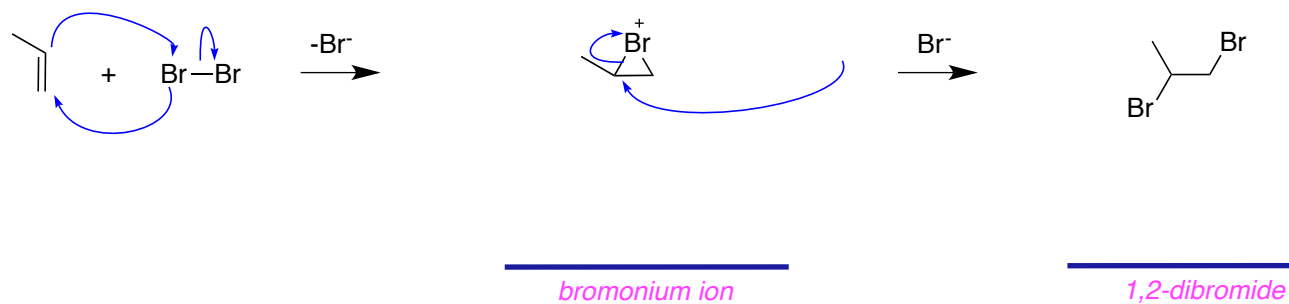
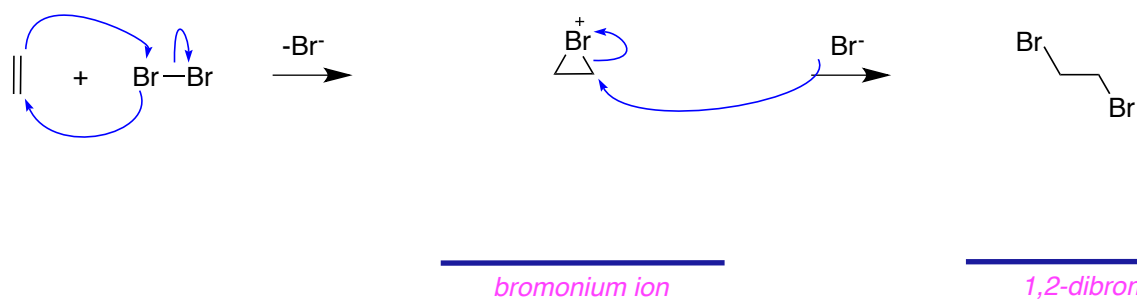
A. Introduction

B. Mechanism

parallel
polarized
positively
is

Chlorination and Bromination

intermediates.



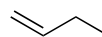
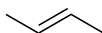
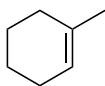
Halogens (X₂) are electrophiles

Nucleophiles

electrophile

becomes polarized in the presence of high electron density.

electrophilic
nucleophilic
faster

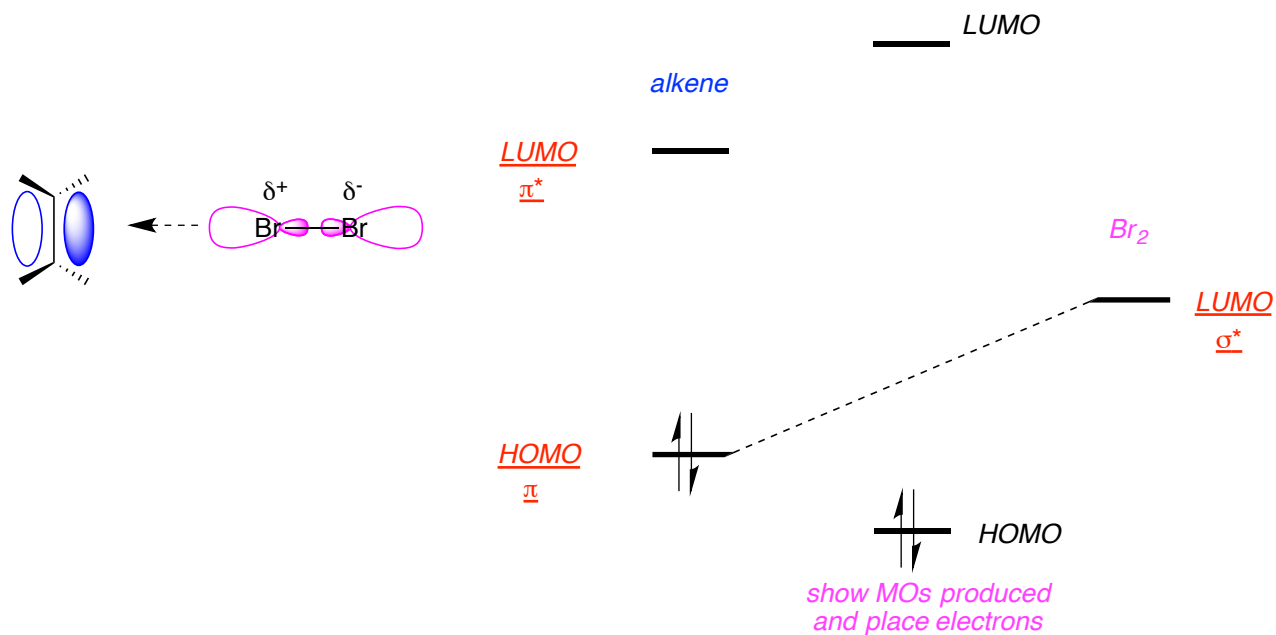


fastest bromination

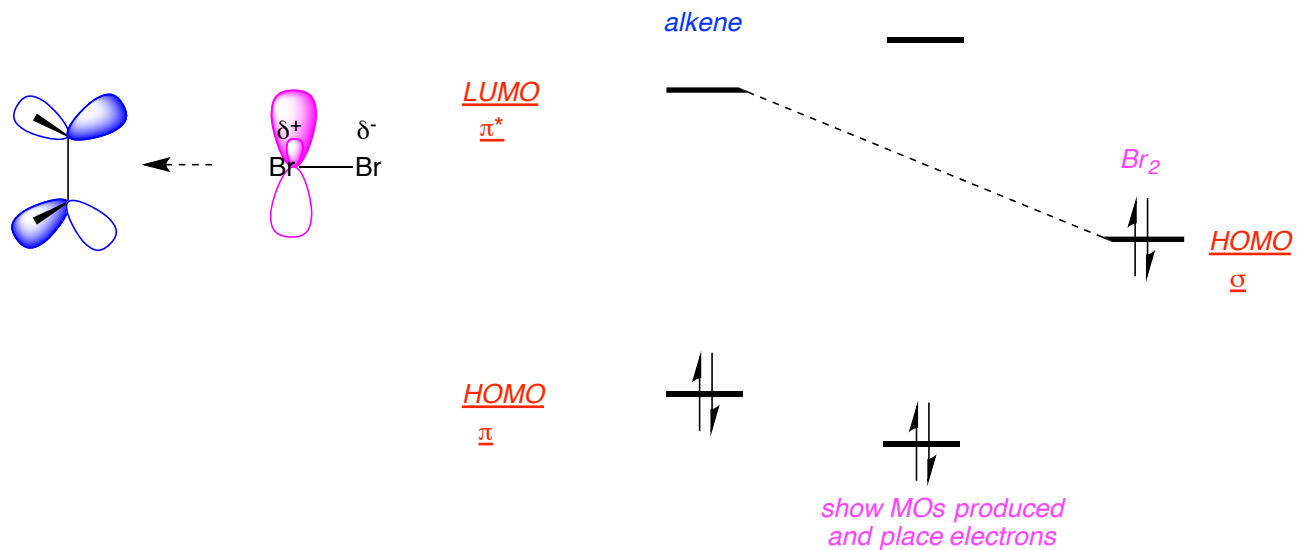
slowest bromination

addition

A MO View Of Halogenations



stabilizing,
primary
secondary



do not

Stereospecificity

S_N2

anti

endocyclic

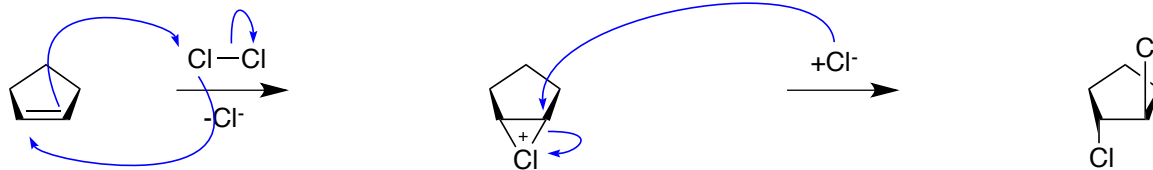
trans-

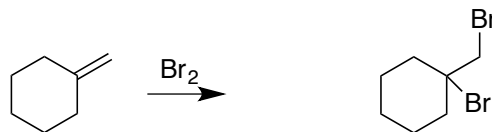
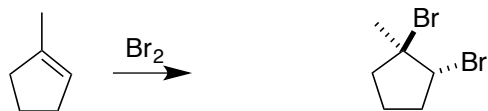
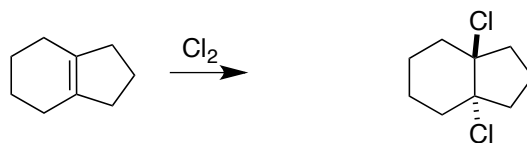
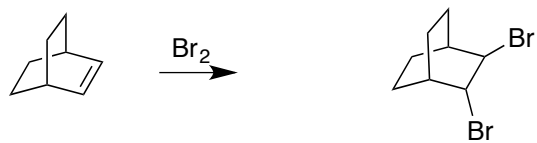
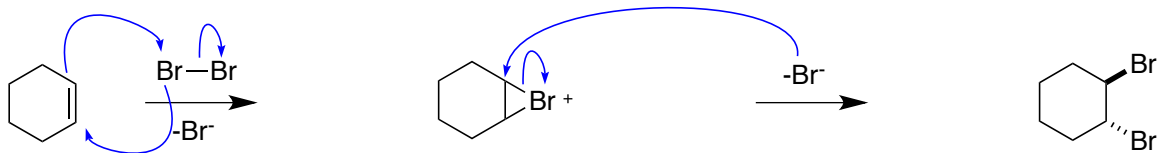
mostly trans-

opposite

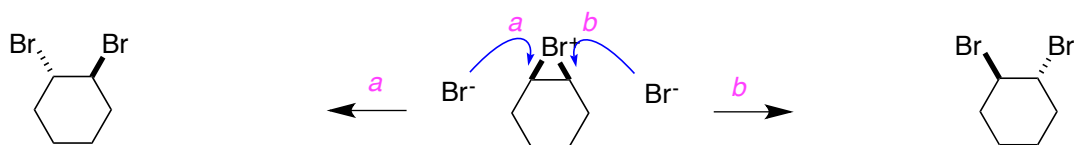
stereospecifically-

always





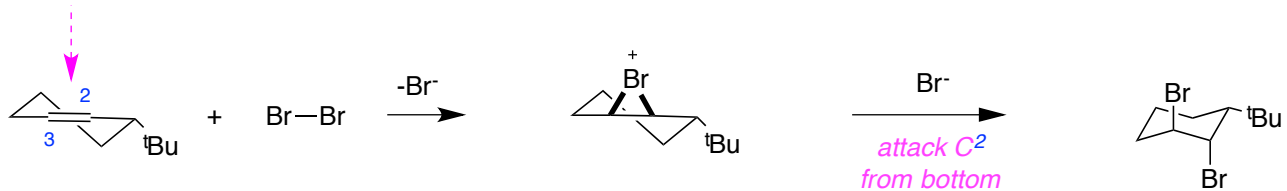
enantiomers



S,S

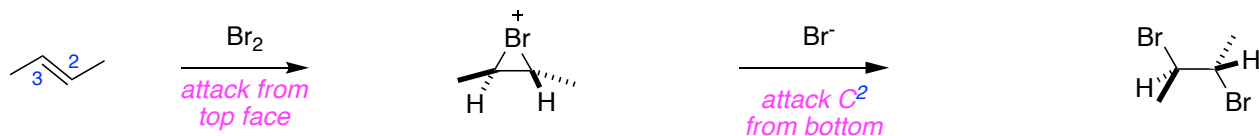
R,R

equal
a racemate
is not

equalbromonium ion
formation

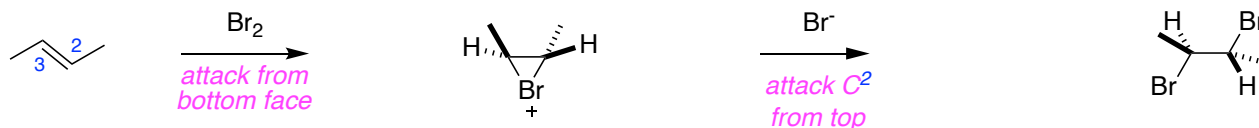
bromonium ion

1,2-dibromide



bromonium ion

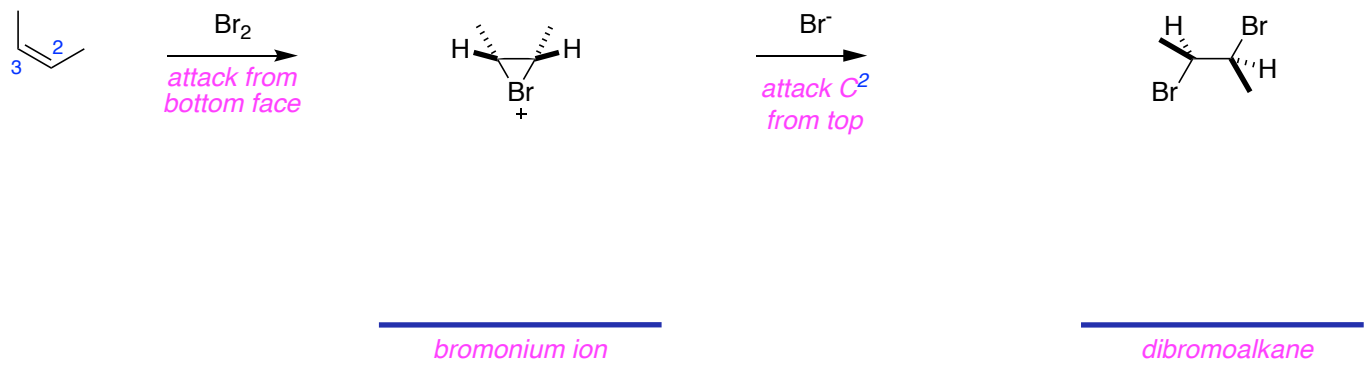
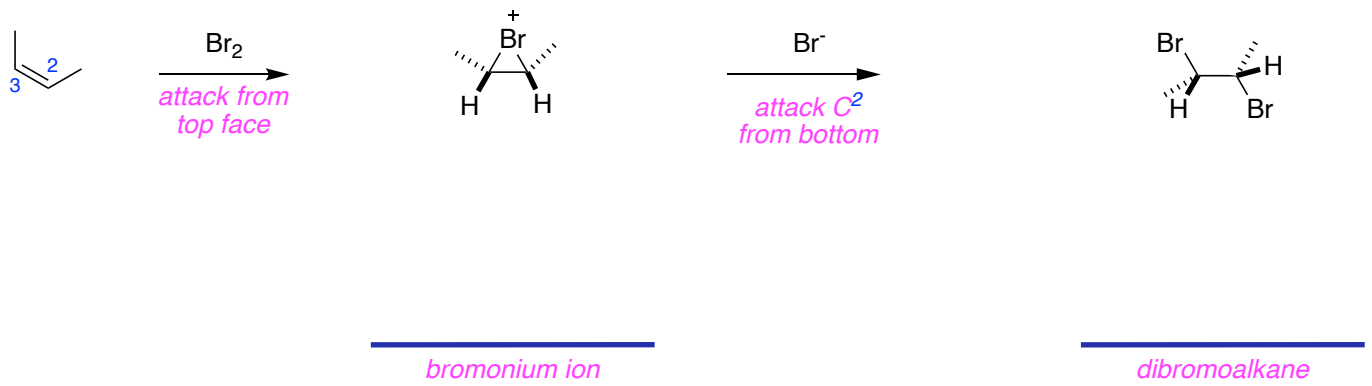
dibromoalkane



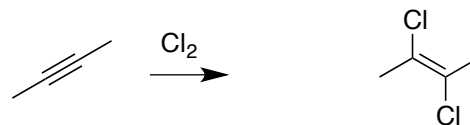
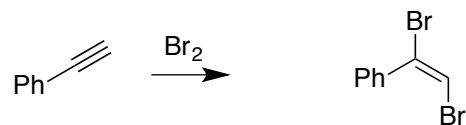
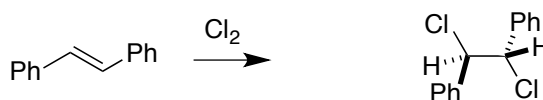
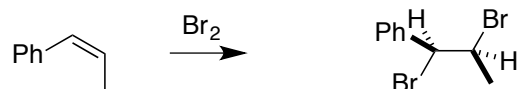
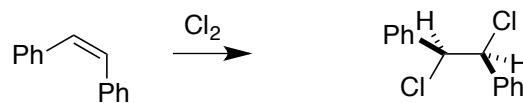
bromonium ion

dibromoalkane

identical.

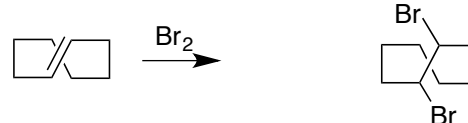


diastereomers.



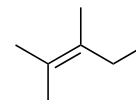
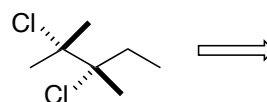
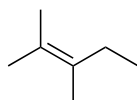
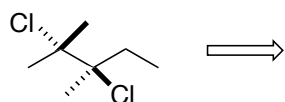
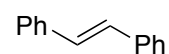
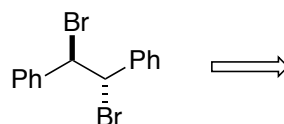
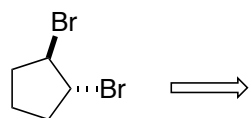
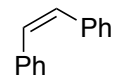
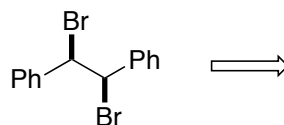
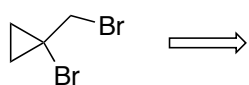
trans-1,2-dibromophenylethene

trans-2,3-dichlorobut-2-ene



trans-

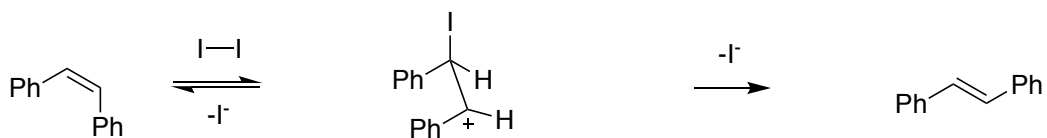
cis-



Iodination

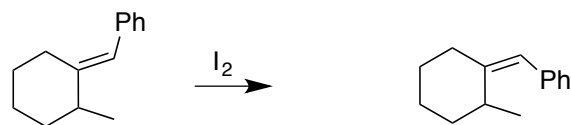
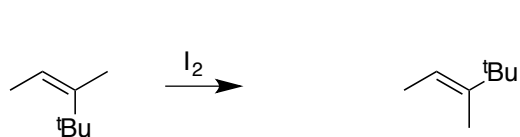
the product is thermodynamically unstable relative to ethene and iodine.

Following question in first edition is confusing so the question/answer will be simplified in the second edition to this:

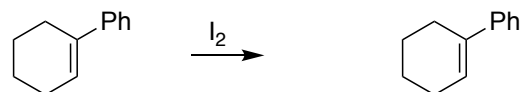
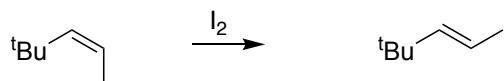


carbocation

E-1,2-diphenylethene

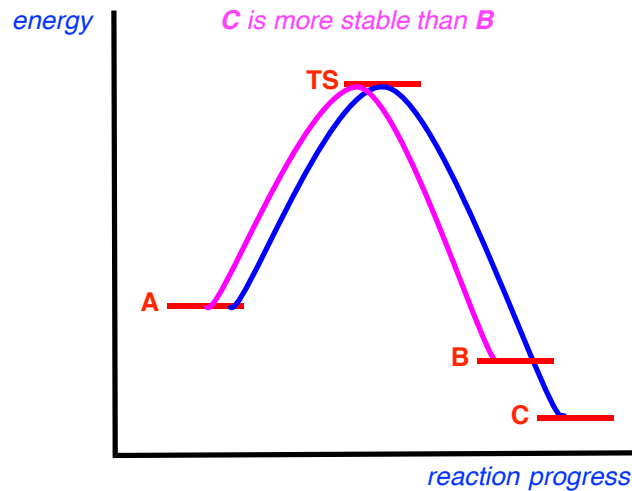
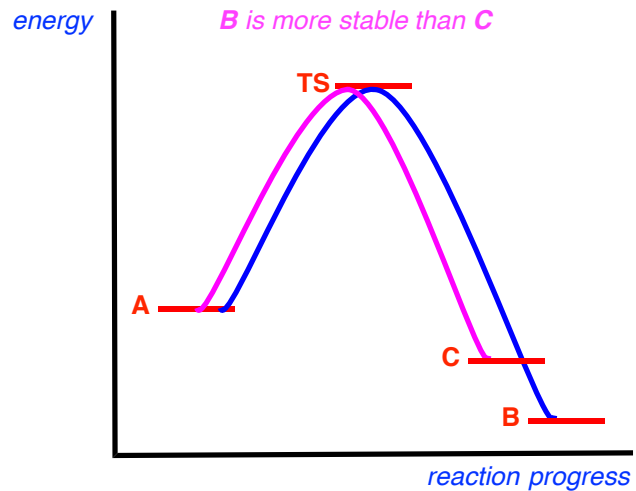


new question for 2nd edition

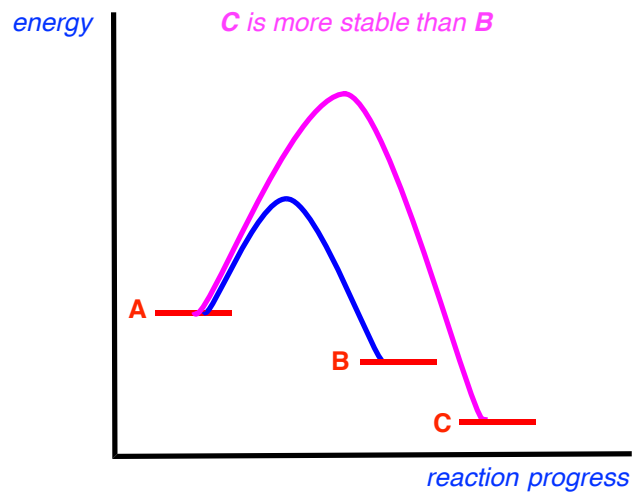
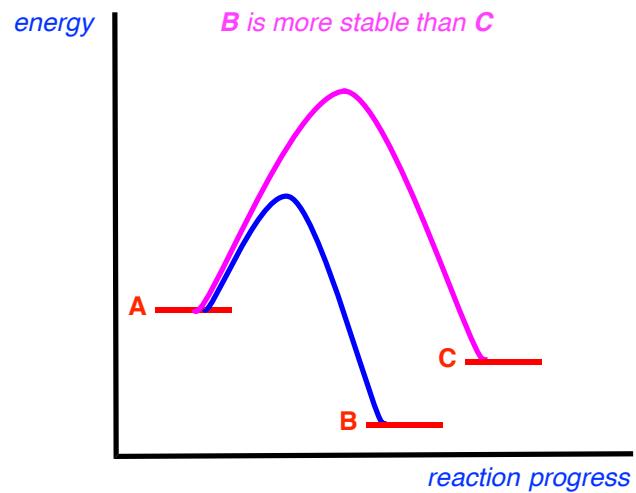


C. Kinetic And Thermodynamic Control

Kinetic Control



lower
cannot
is not
is dictated
1, and when C is more stable than B it will be 1.



rates of formation,
be invariant
kinetic one.

Thermodynamic Control

reversible

>1.

will not

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

is another

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

independent of

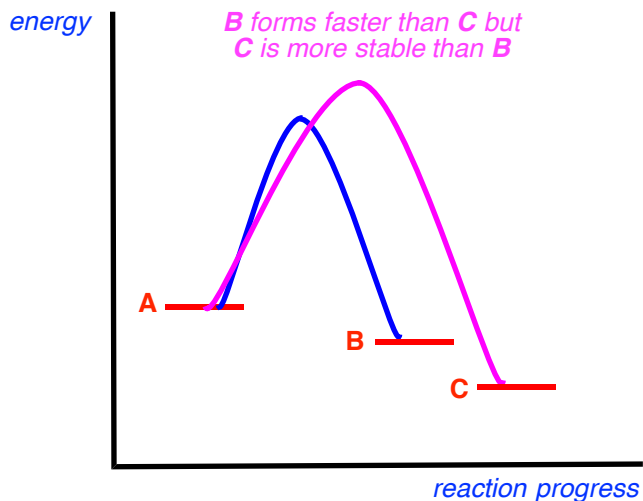
coincident

activation energy barriers

stabilities of the products.

These ratios are different

Non-coincident Kinetic And Thermodynamic Control



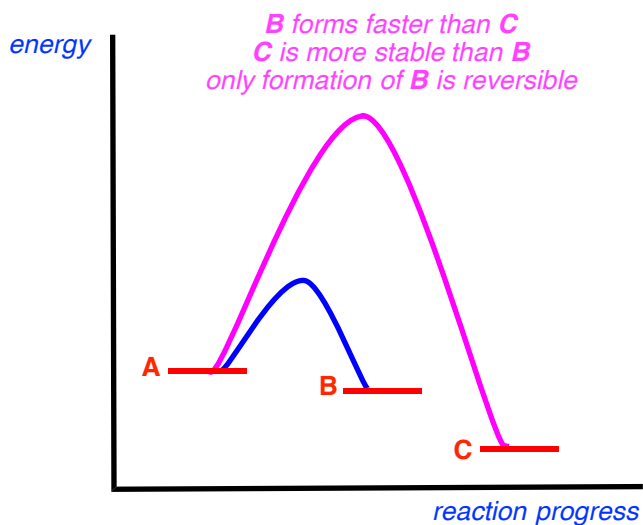
kinetic

reversibly.

thermodynamic

reversibly.

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



kinetic product; only **B** forms reversibly.

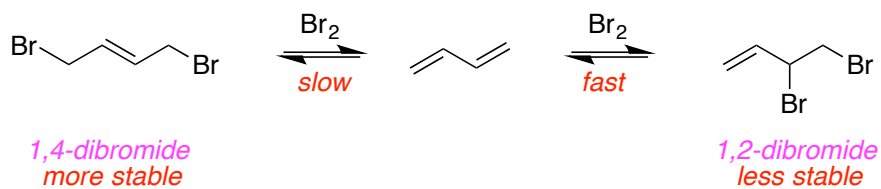
thermodynamic product; it forms irreversibly.

not be observed because it will revert as the reaction proceeds and irreversibly

kinetic

thermodynamically

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



kinetic

decreases

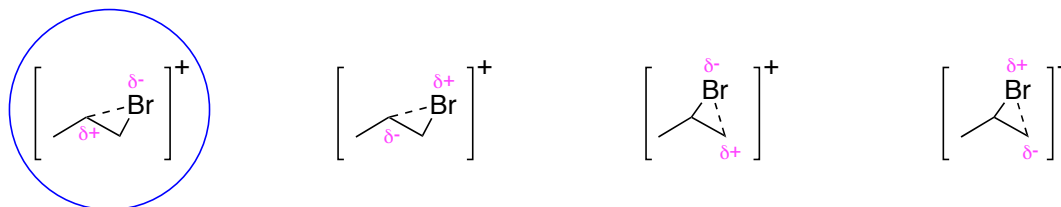
increases.

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

less

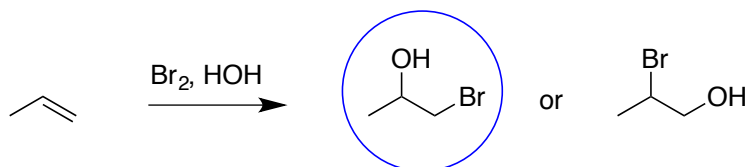
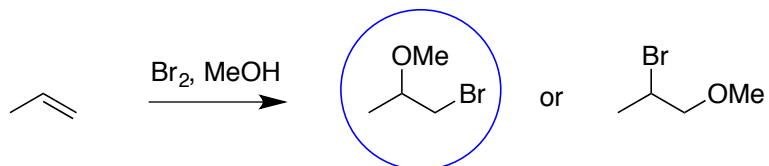
does not proceed

D. Halogenations In Nucleophilic Solvents



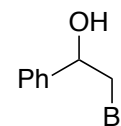
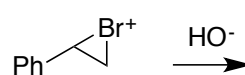
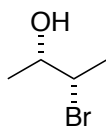
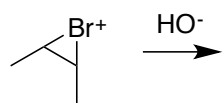
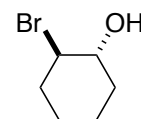
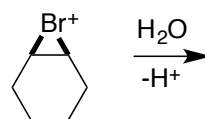
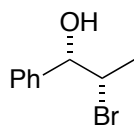
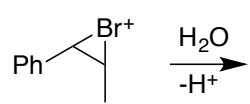
best

Regio--selectivity
regioisomers.



halohydrin

this is the precursor to the most stable cation.



are