Halogenation Of Alkenes

from chapter(s) _____ in the recommended text

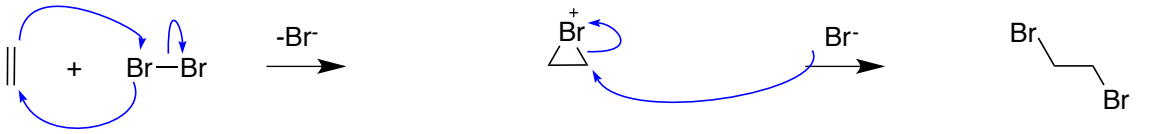
A. Introduction

B. Mechanism

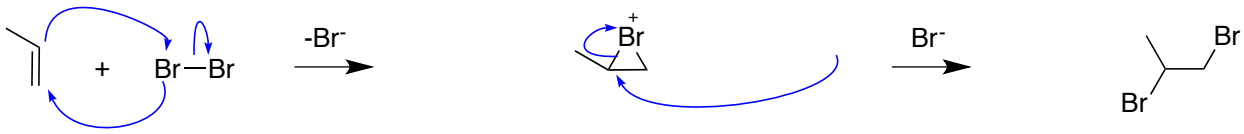
parallel
polarized
positively
is

Chlorination and Bromination

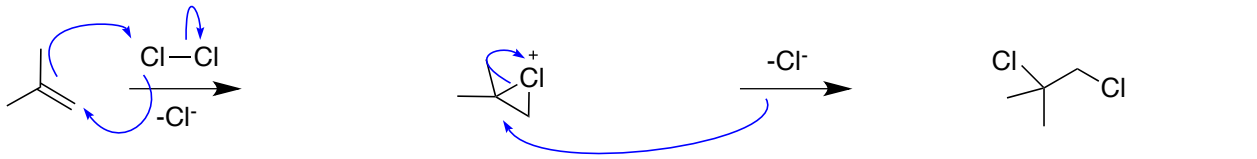
intermediates.



bromonium ion *1,2-dibromide*



bromonium ion *1,2-dibromide*



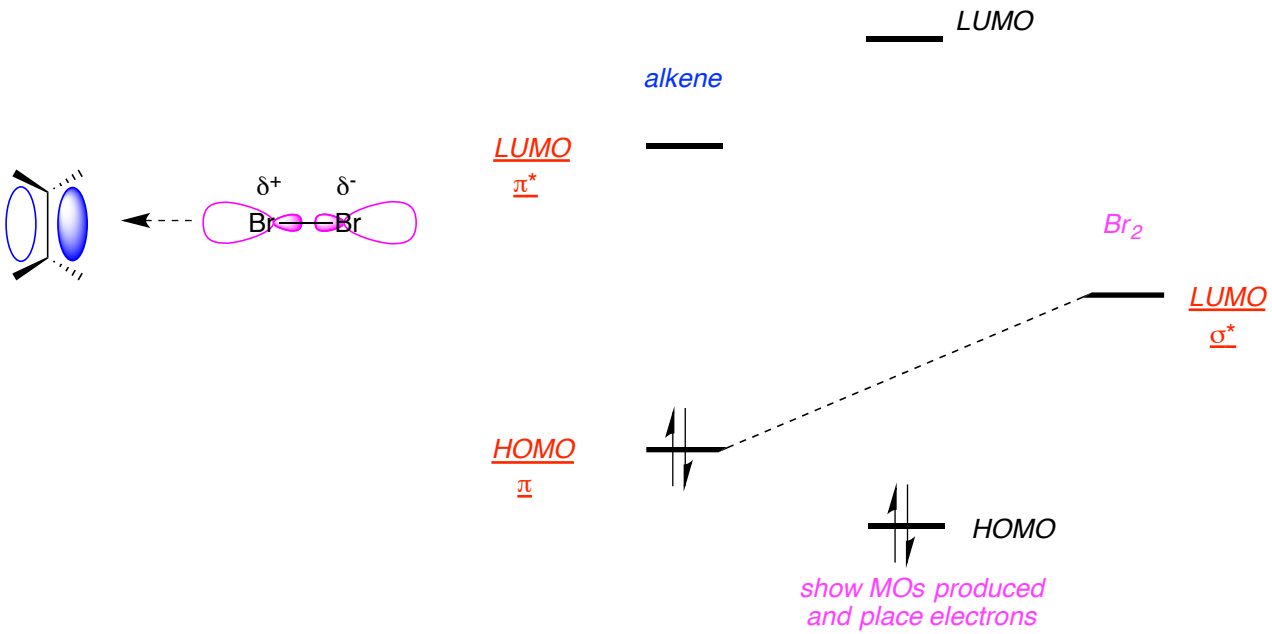
Halogens (X_2) are *electrophiles*
Nucleophiles
electrophile
has a dipole.

electrophilic
nucleophilic
faster

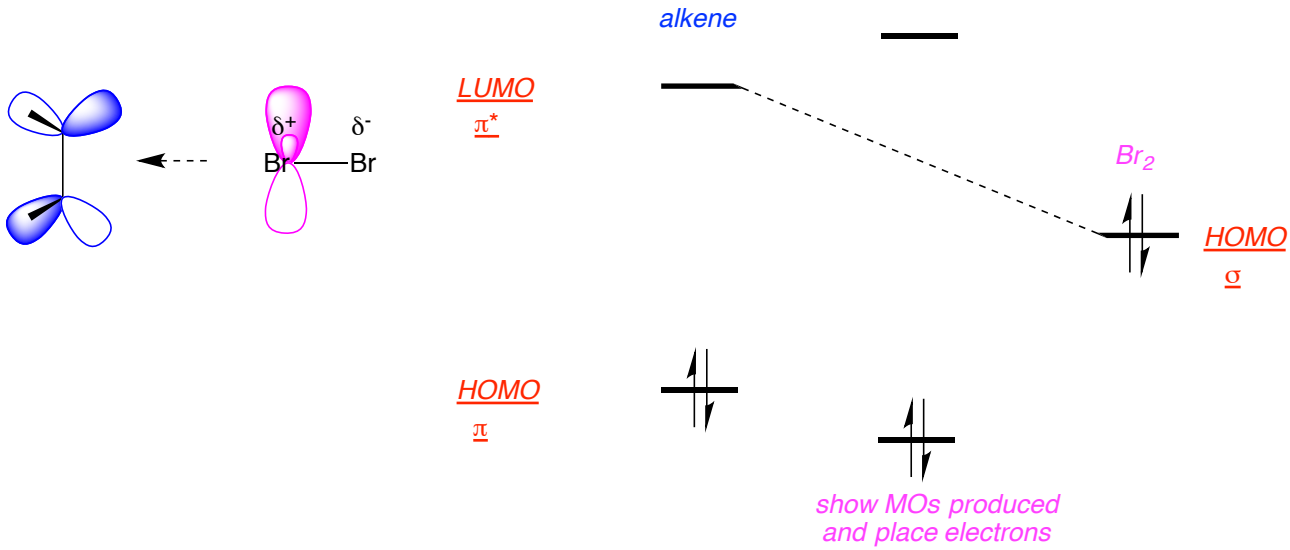
fastest bromination *slowest bromination*

addition

A MO View Of Halogenations



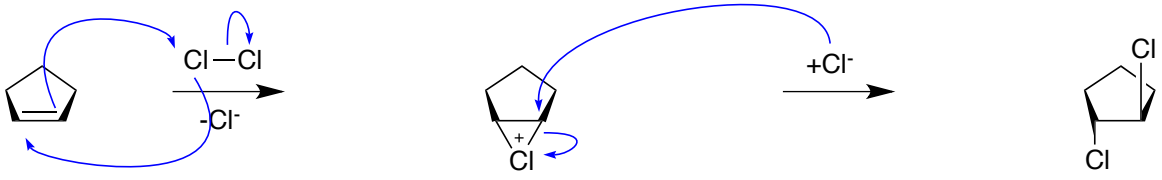
stabilizing,
primary
secondary

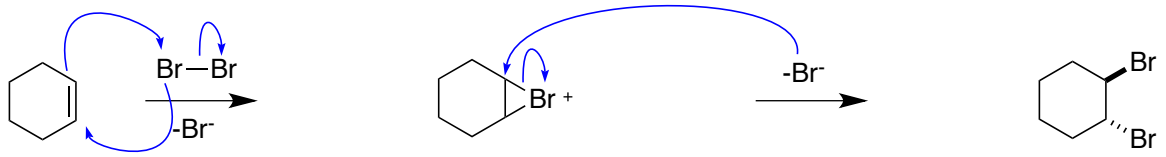


do not

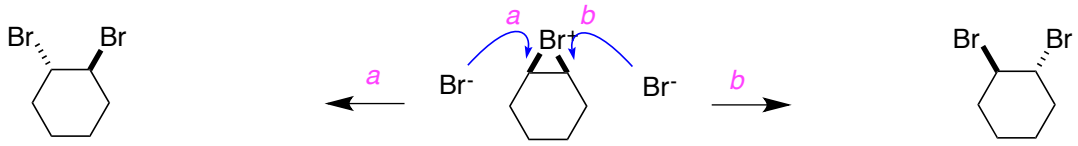
Stereospecificity
S_N2
anti
endocyclic
trans-

mostly trans-
opposite
stereoselectively-
always
.





enantiomers

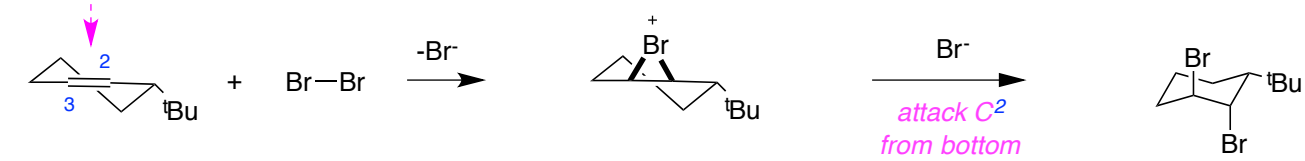


S,S *R,R*

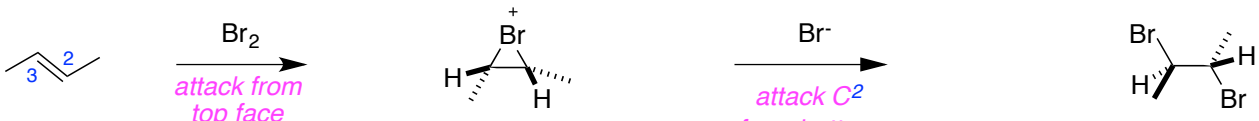
equal
a racemate
is not

equal

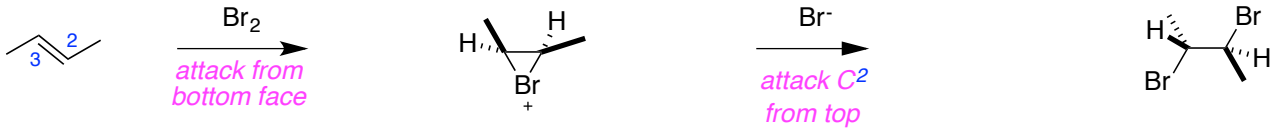
bromonium ion formation



bromonium ion *1,2-dibromide*



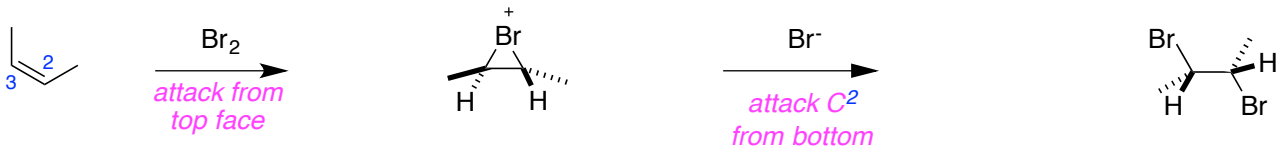
bromonium ion *dibromoalkane*



bromonium ion *dibromoalkane*

identical.

.



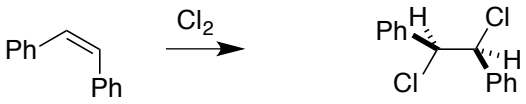
bromonium ion

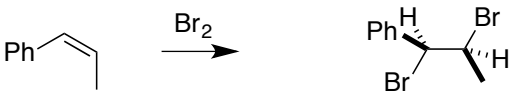
dibromoalkane

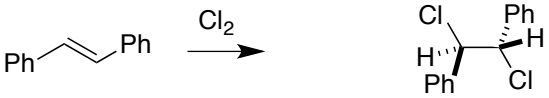
bromonium ion

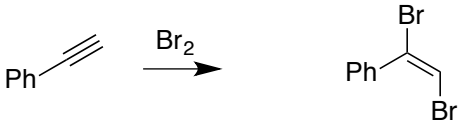
dibromoalkane

diastereomers.

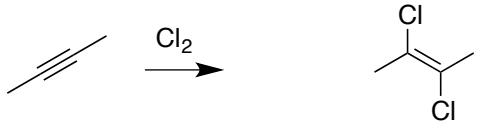






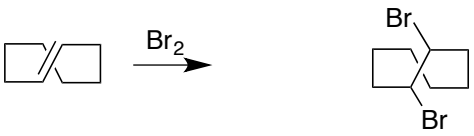


trans-1,2-dibromophenylethene

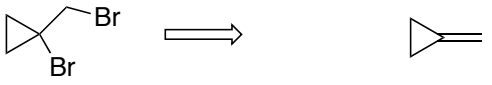


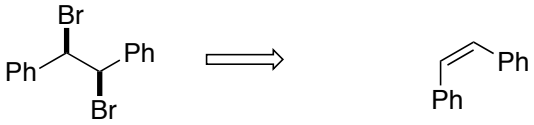
trans-2,3-dichlorobut-2-ene

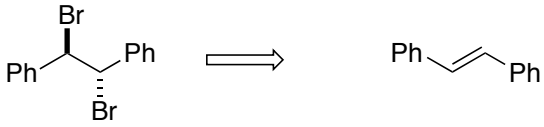
trans-

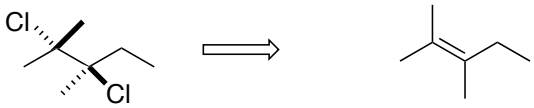


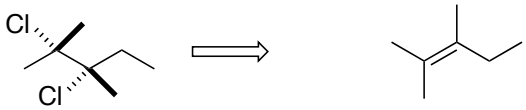
cis-





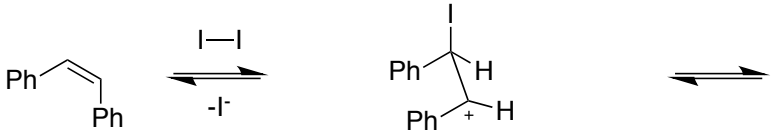




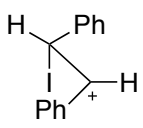


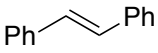
Iodination

the product is thermodynamically unstable relative to ethene and iodine.



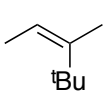
carbocation
in eclipsed conformation

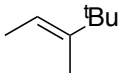


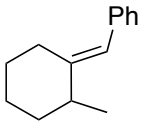


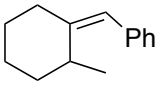
carbocation in anti conformation

E-1,2-diphenylethene



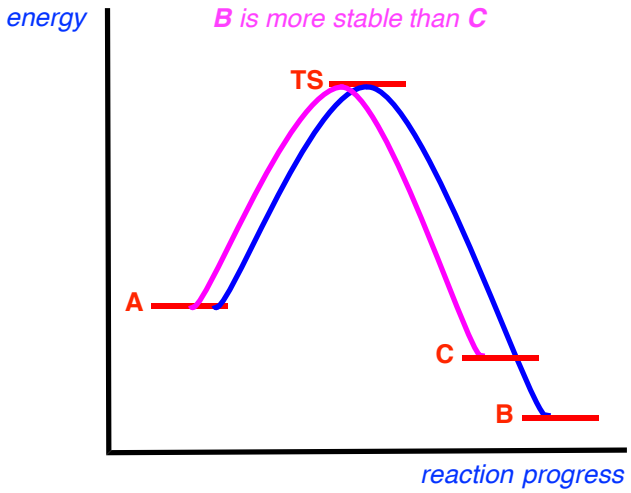


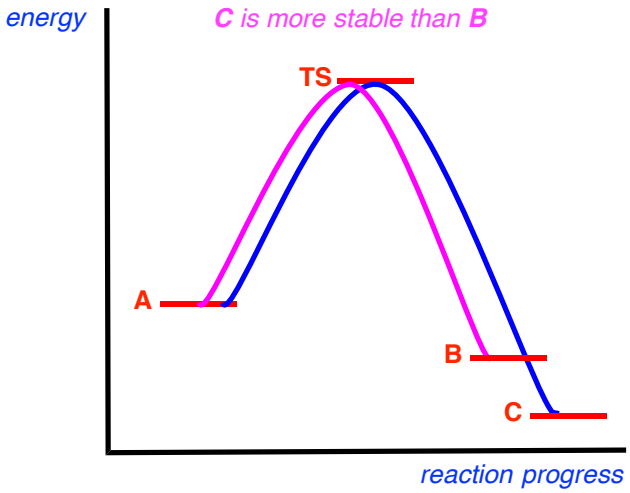




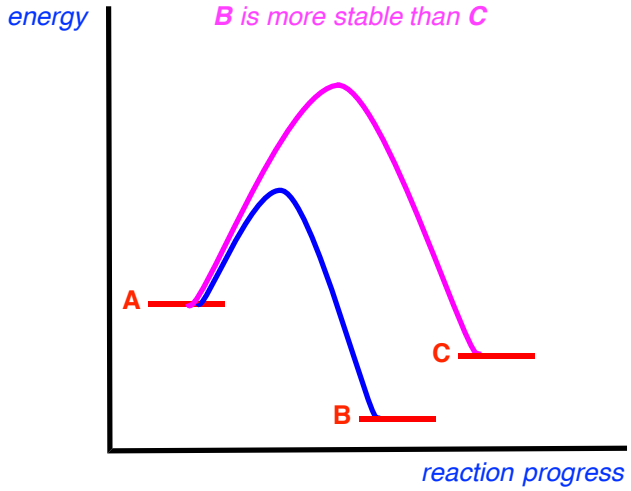
C. Kinetic And Thermodynamic Control

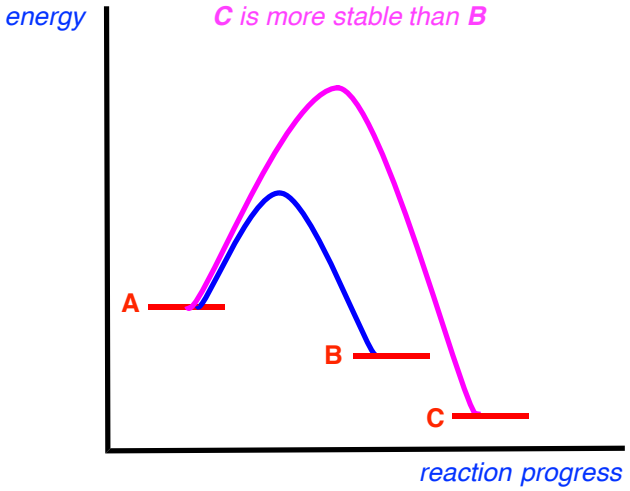
Kinetic Control





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

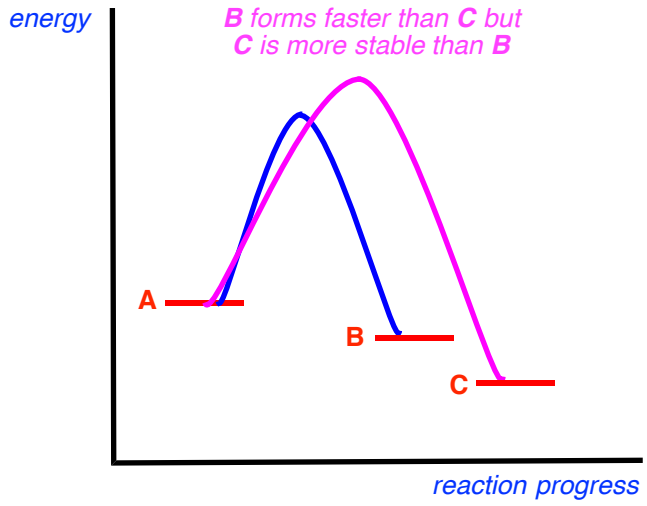
$$K_B = [\ B\ ] / [\ A\ ] \quad \text{and} \quad K_C = [\ C\ ] / [\ A\ ]$$

is another

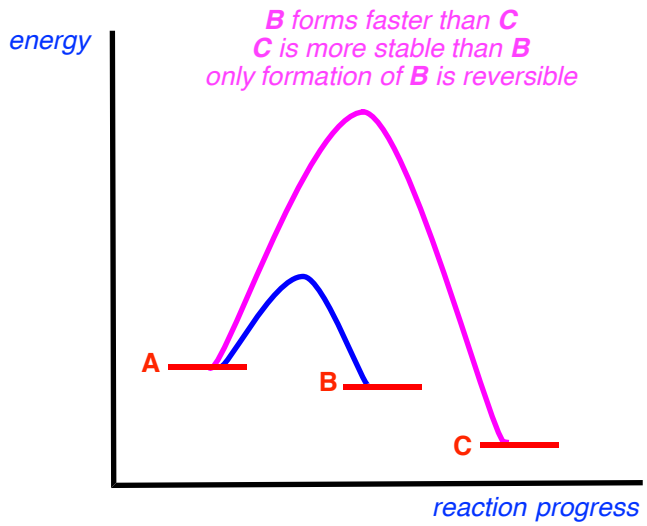
$$K_{BC} = [\ B\ ] / [\ C\ ]$$

independent of
coincident
activation energy barriers
stabilities of the products.
These ratios are *different*

Non-coincident Kinetic And Thermodynamic Control



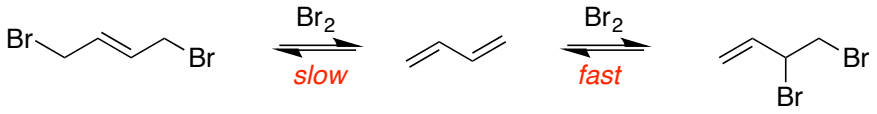
kinetic
reversibly.
thermodynamic
reversibly.
be disfavored because it will revert as the reaction proceeds and *reversibly* forms **C**.



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



1,4-dibromide more stable

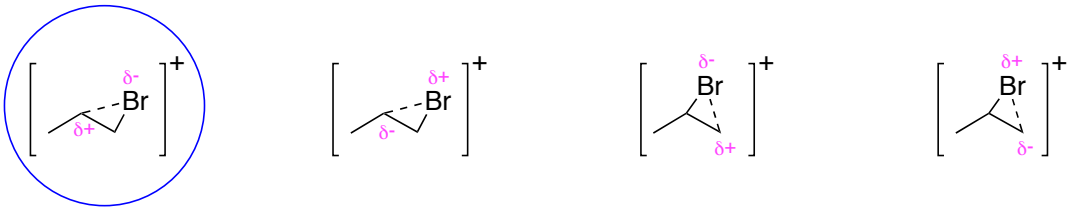
1,2-dibromide less stable

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.

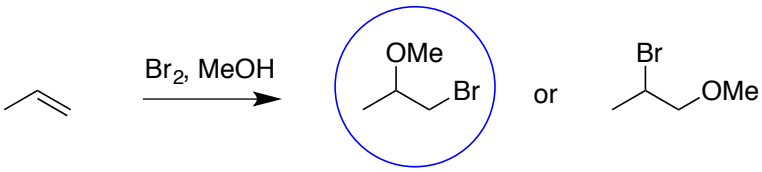
less
does not proceed

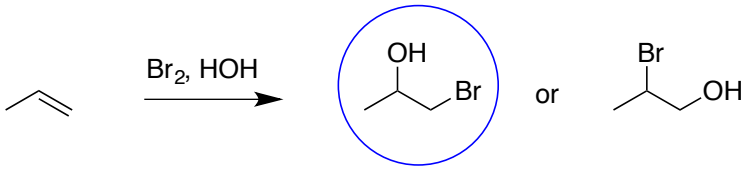
D. Halogenations In Nucleophilic Solvents



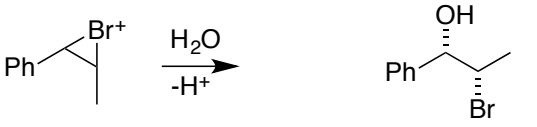
best

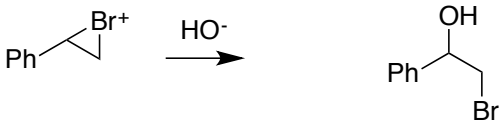
Regio--selectivity
regioisomers.





halohydrin
this is the precursor to the most stable cation.





are