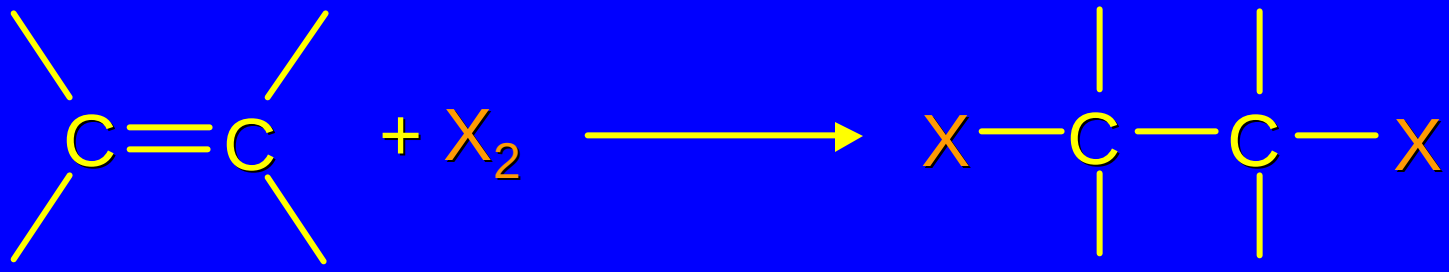
6.14
Addition of Halogens to Alkenes

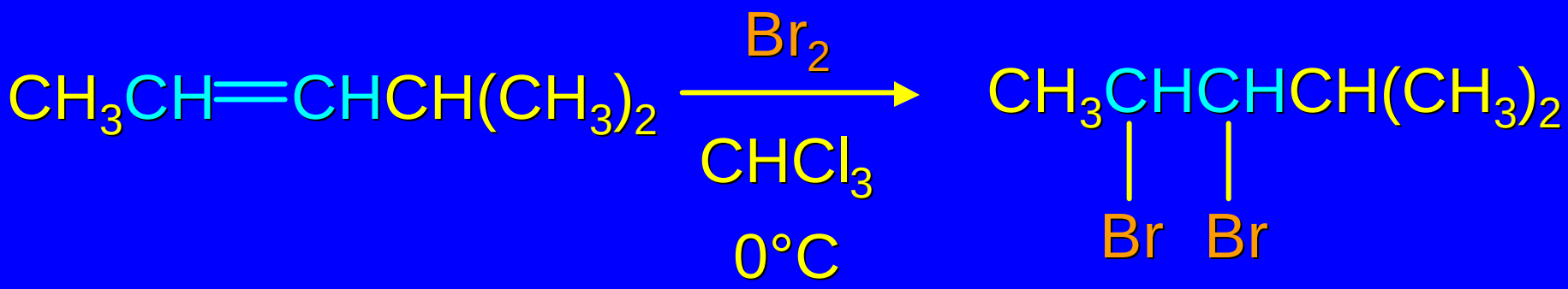
General features



electrophilic addition to double bond

forms a vicinal dihalide

Example



(100%)

Scope

limited to Cl_2 and Br_2

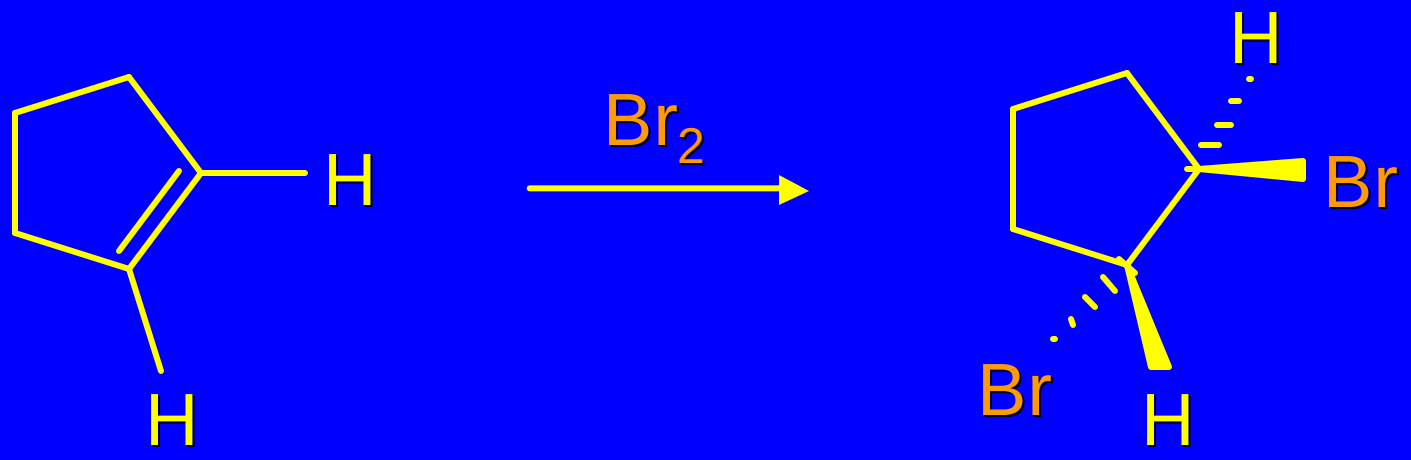
F_2 addition proceeds with explosive violence

I_2 addition is endothermic: vicinal diiodides dissociate to an alkene and I_2

6.15
Stereochemistry of Halogen Addition

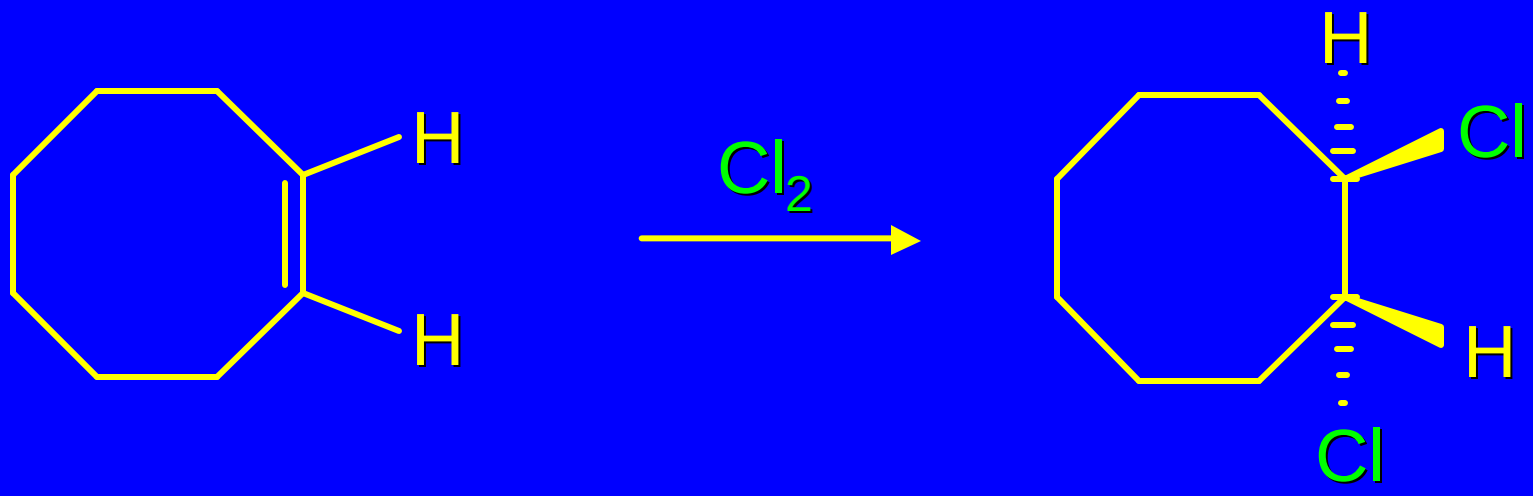
anti addition

Example



trans-1,2-Dibromocyclopentane
80% yield; only product

Example



trans-1,2-Dichlorocyclooctane
73% yield; only product

6.16
Mechanism of Halogen Addition to Alkenes: Halonium Ions

Mechanism is electrophilic addition

Br_2 is not polar, but it is polarizable

two steps

(1) formation of bromonium ion

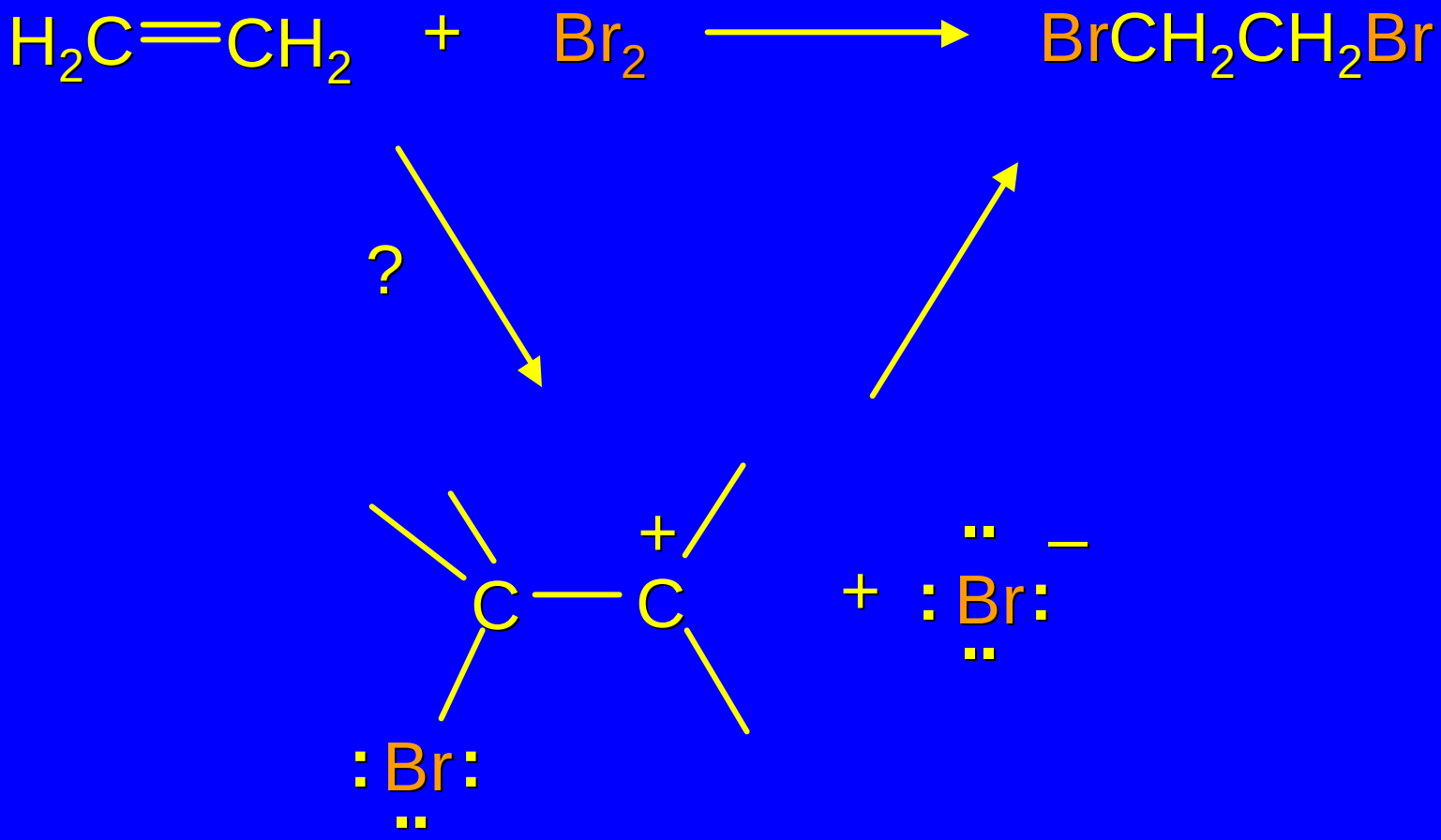
(2) nucleophilic attack on bromonium ion by bromide

Relative Rates of Bromination

ethylene	$H_2C=CH_2$	1
propene	$CH_3CH=CH_2$	61
2-methylpropene	$(CH_3)_2C=CH_2$	5400
2,3-dimethyl-2-butene	$(CH_3)_2C=C(CH_3)_2$	920,000

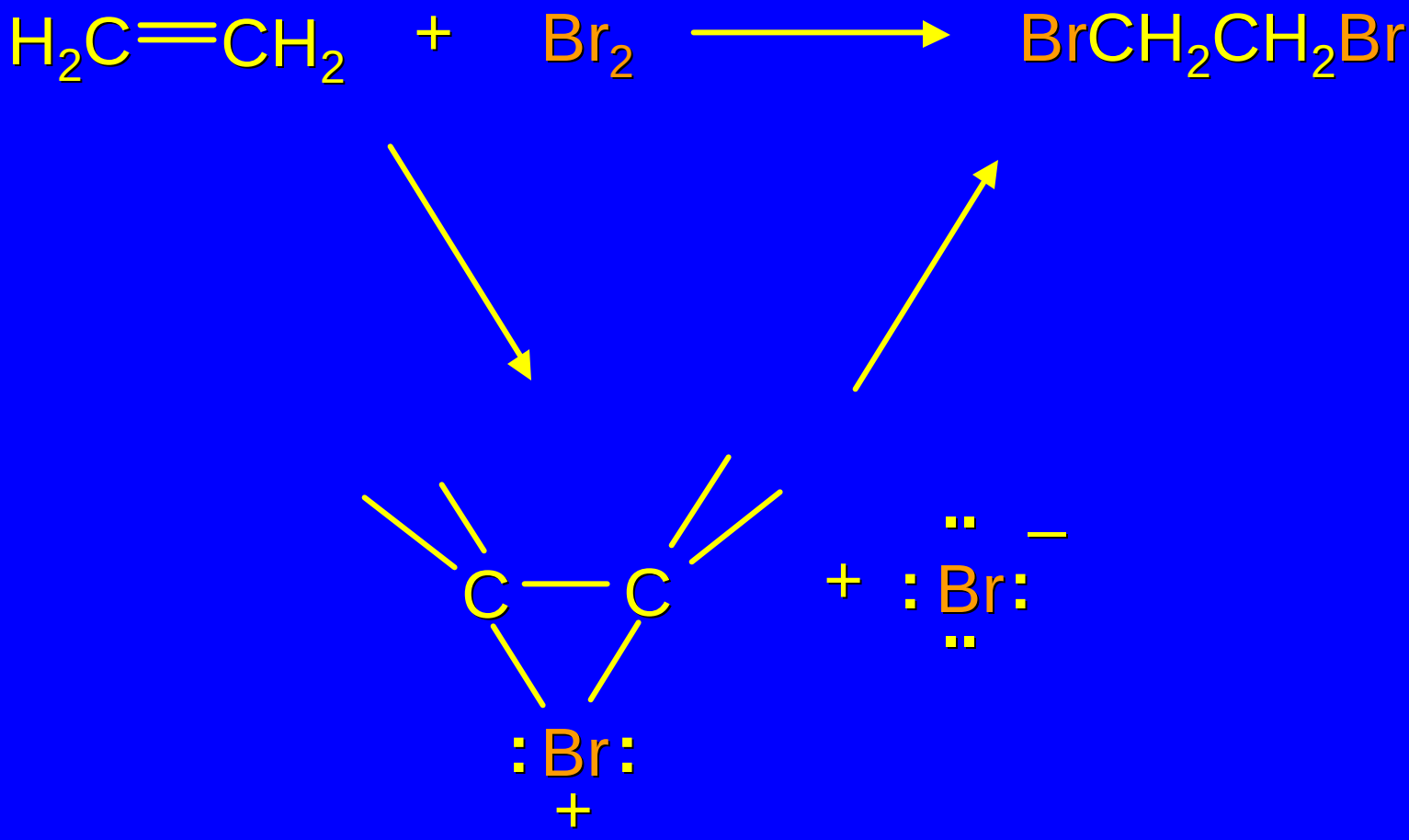
More highly substituted double bonds react faster.
Alkyl groups on the double bond make it more "electron rich."

Mechanism?



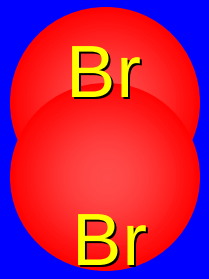
No obvious explanation for anti addition provided by this mechanism.

Mechanism

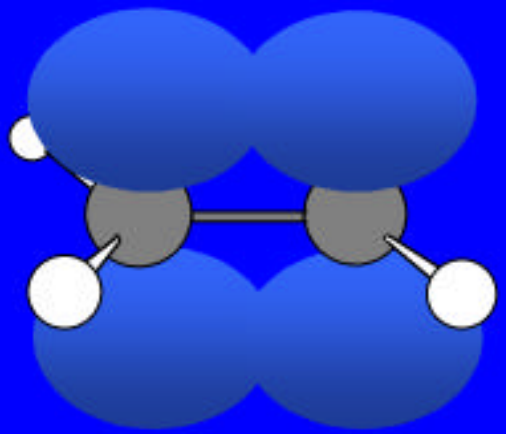


Cyclic bromonium ion

Formation of Bromonium Ion

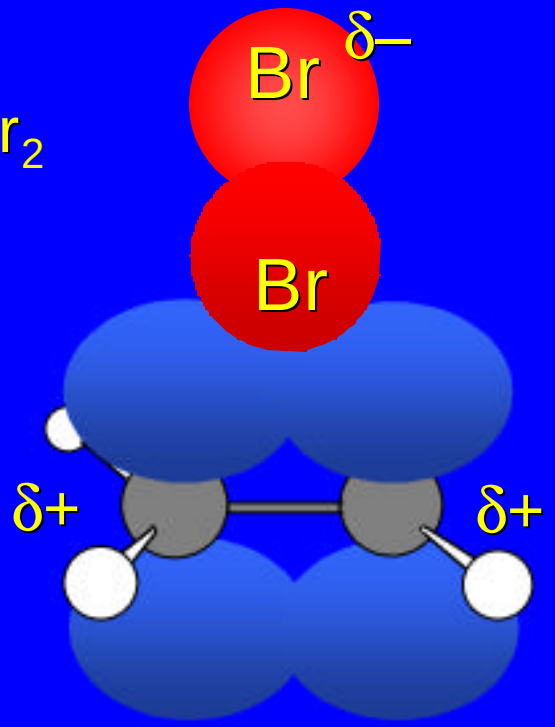


Mutual polarization
of electron distributions
of Br_2 and alkene



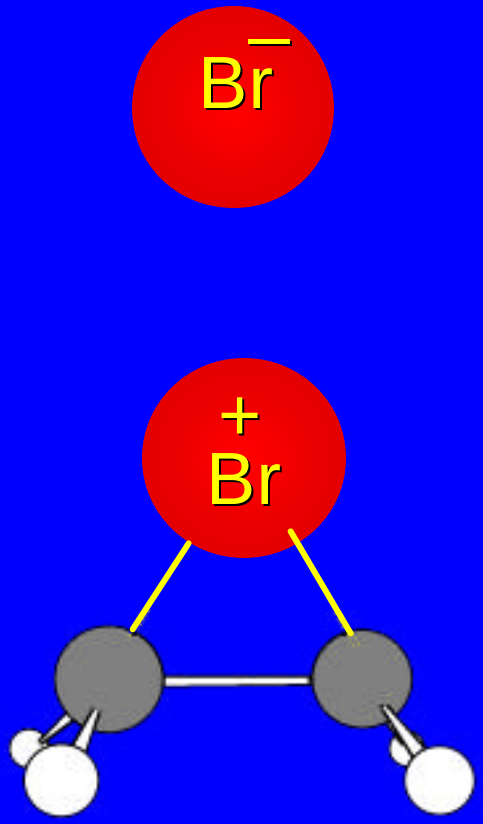
Formation of Bromonium Ion

Electrons flow
from alkene toward Br_2

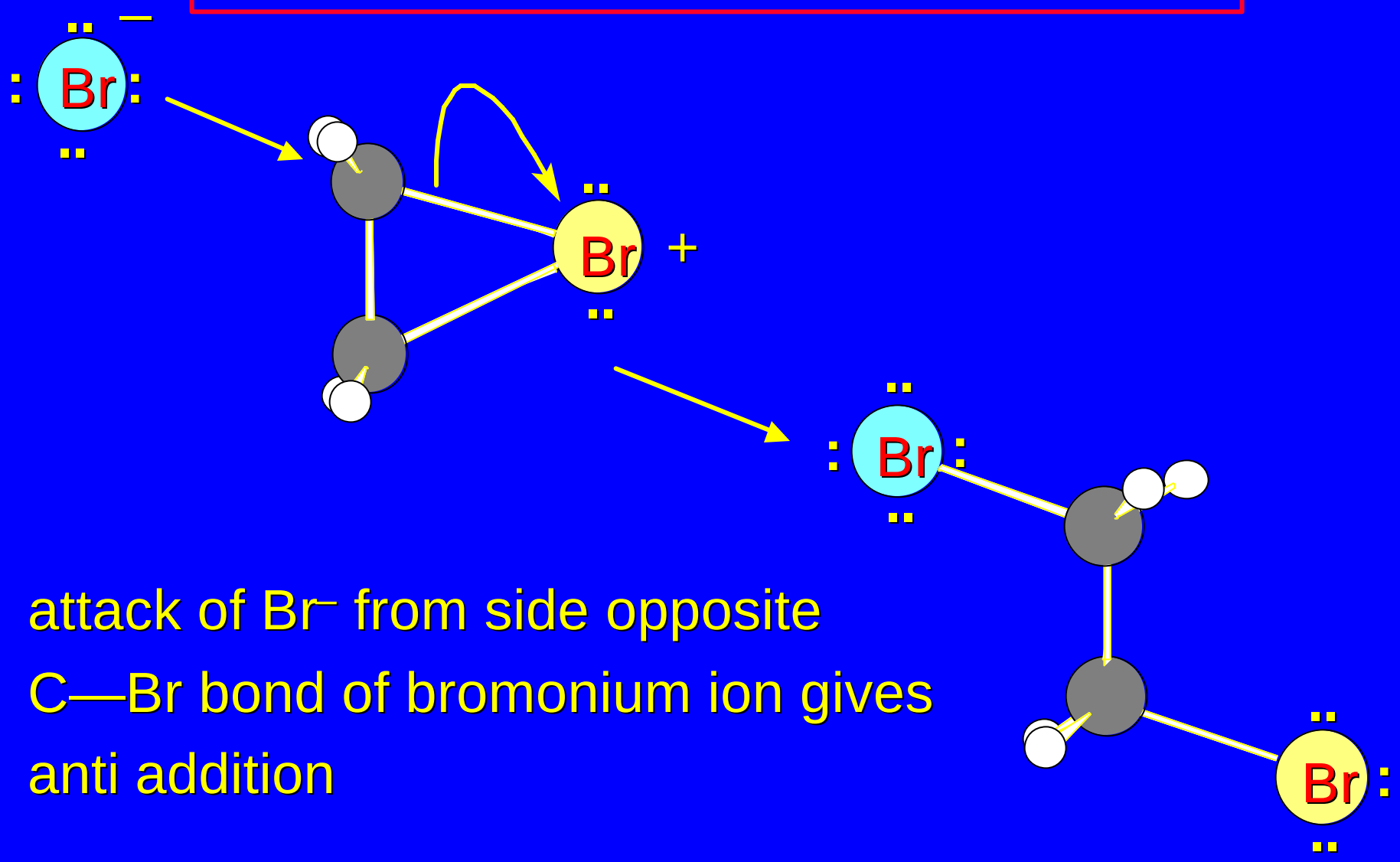


Formation of Bromonium Ion

π electrons of alkene displace Br^- from Br



Stereochemistry

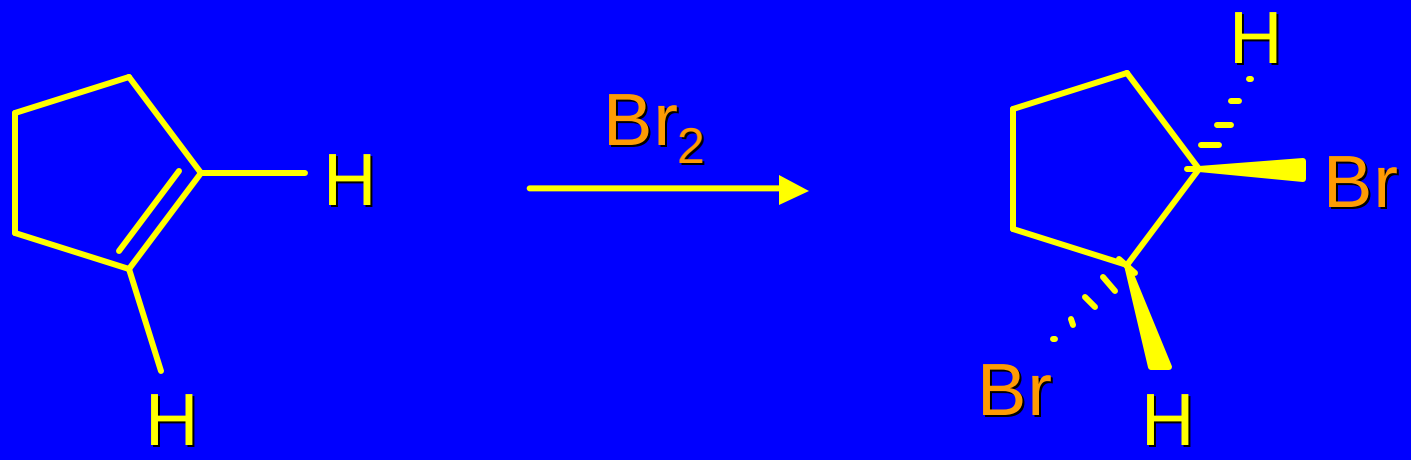


attack of Br^- from side opposite

C—Br bond of bromonium ion gives

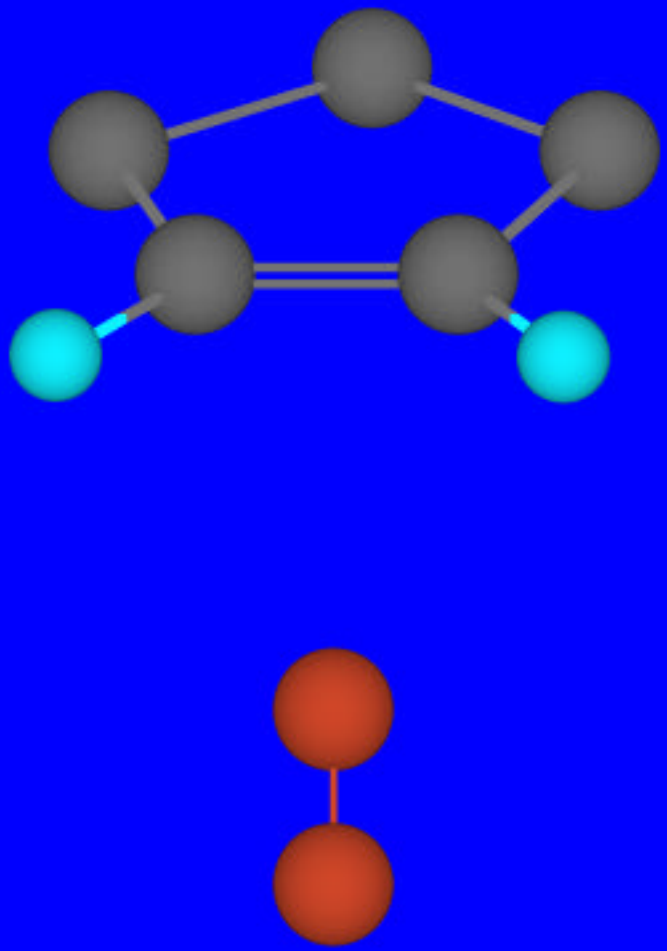
anti addition

Example

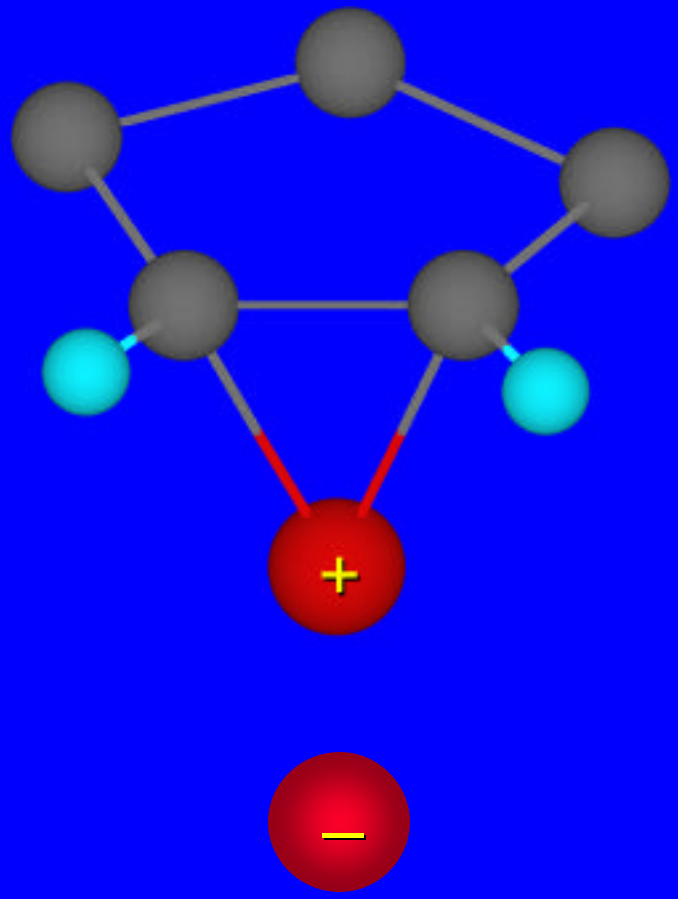


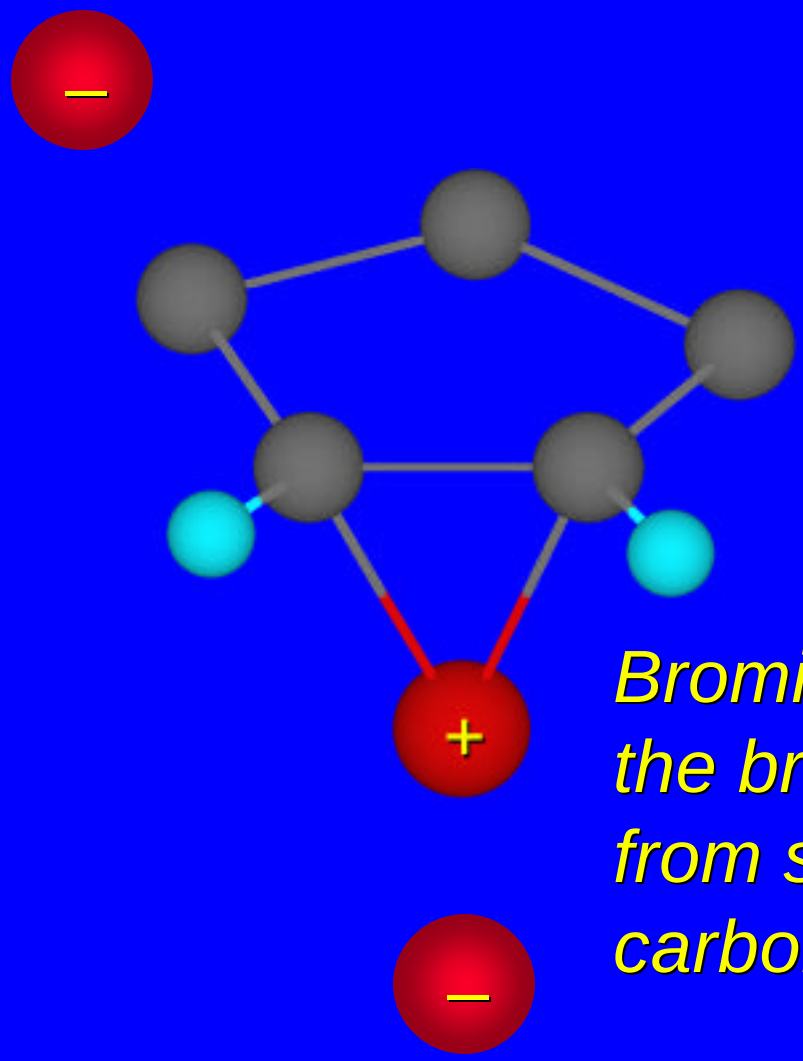
trans-1,2-Dibromocyclopentane
80% yield; only product

Cyclopentene +Br_2

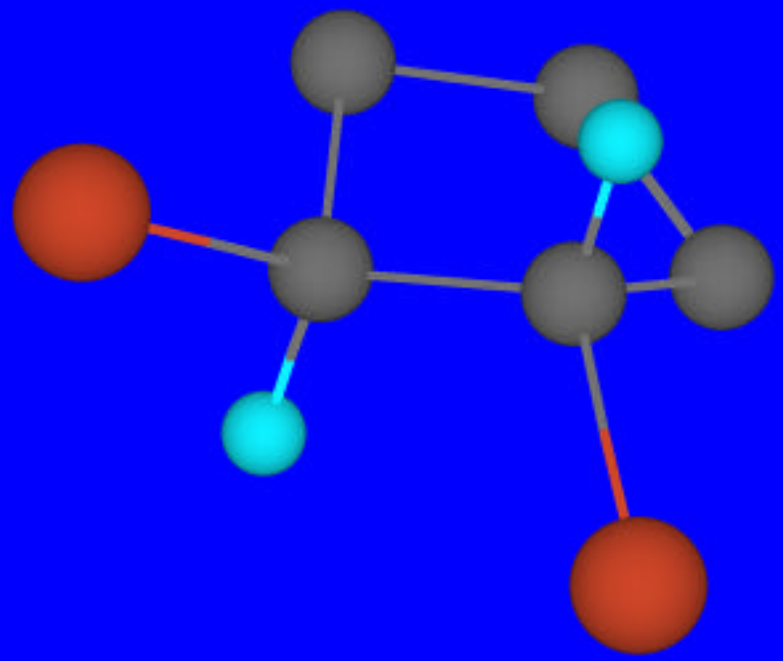


Bromonium ion



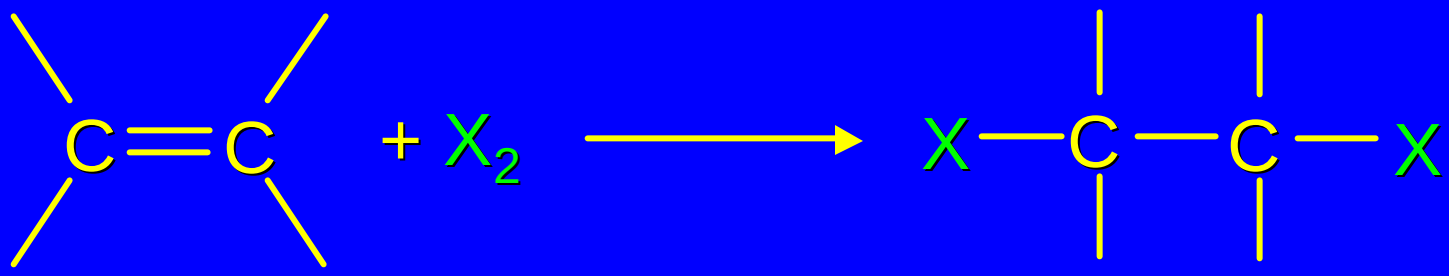


Bromide ion attacks the bromonium ion from side opposite carbon-bromine bond

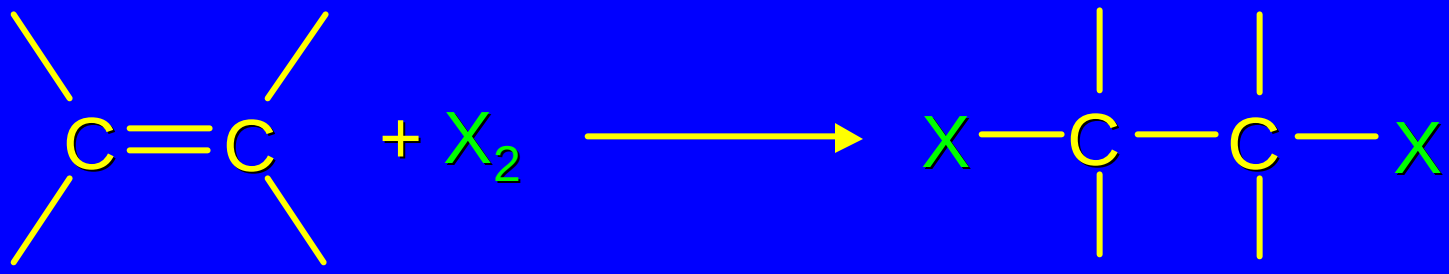


trans-Stereochemistry in vicinal dibromide

6.17
Conversion of Alkenes to Vicinal Halohydrins

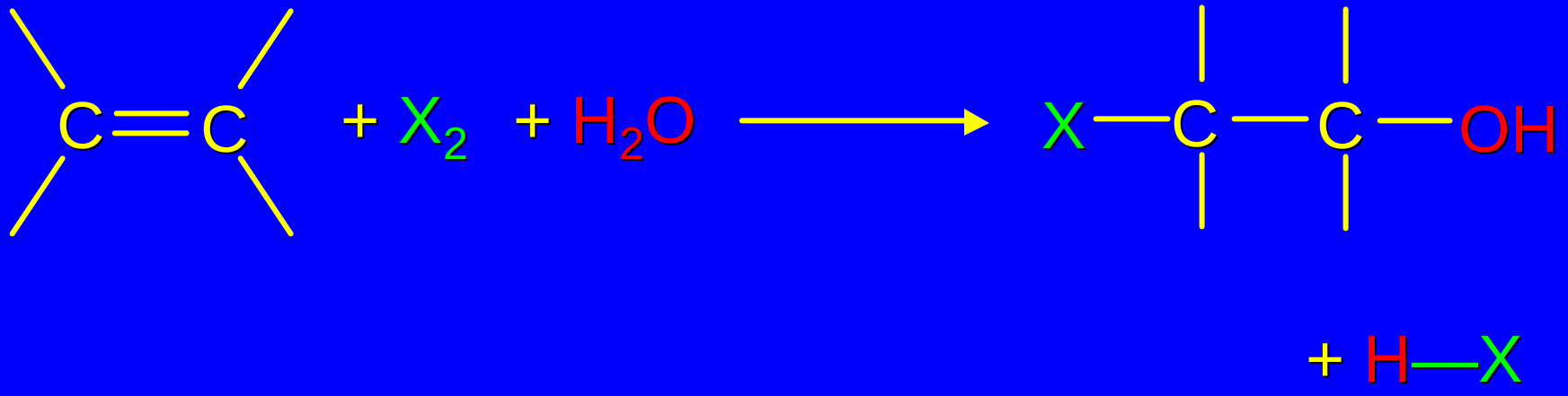


alkenes react with X_2 to form vicinal dihalides

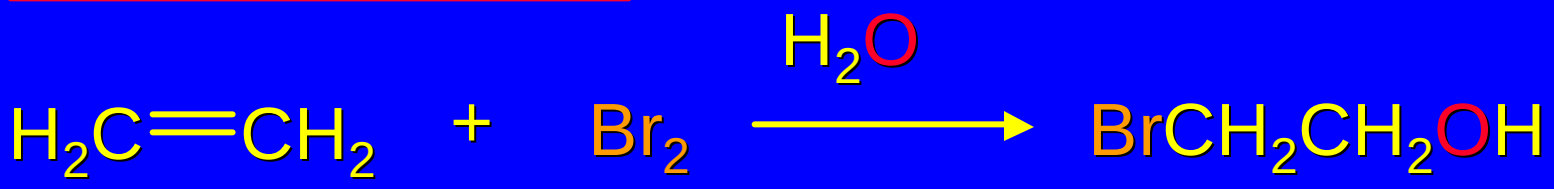


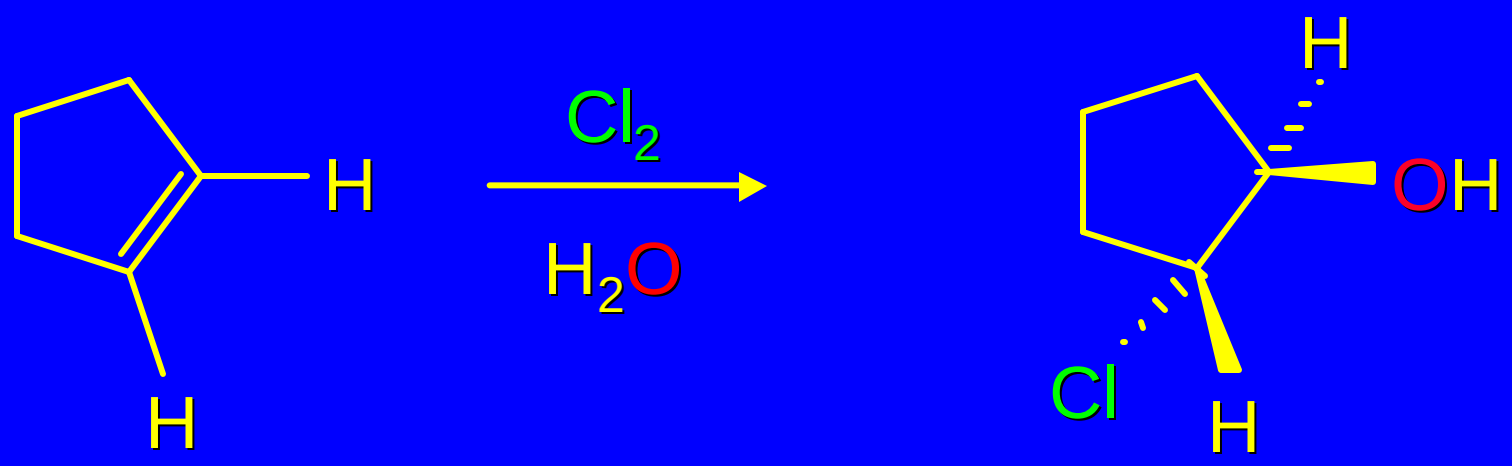
alkenes react with X_2 to form vicinal dihalides

alkenes react with X_2 in water to give vicinal halohydrins



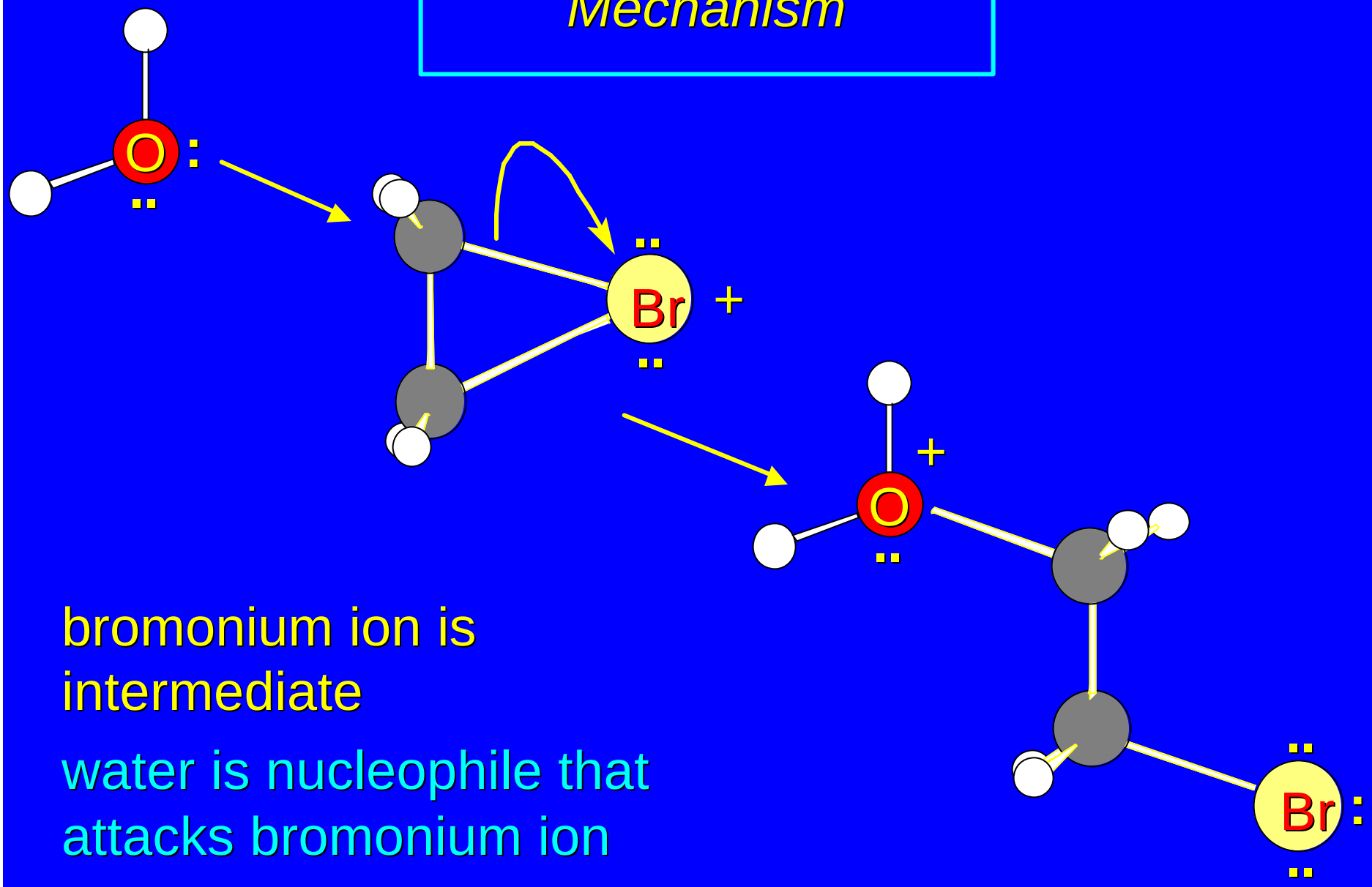
Examples





anti addition: only product

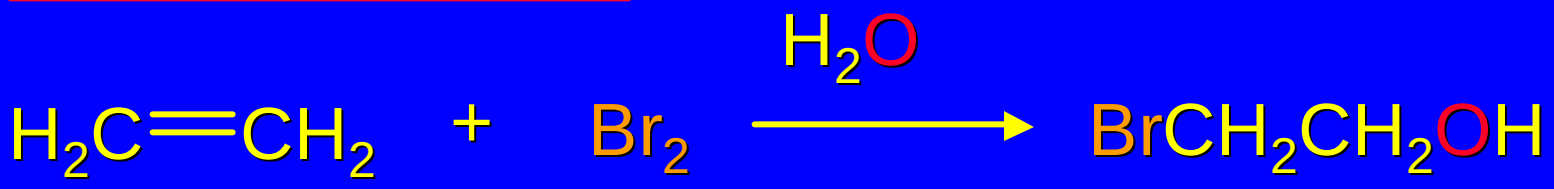
Mechanism

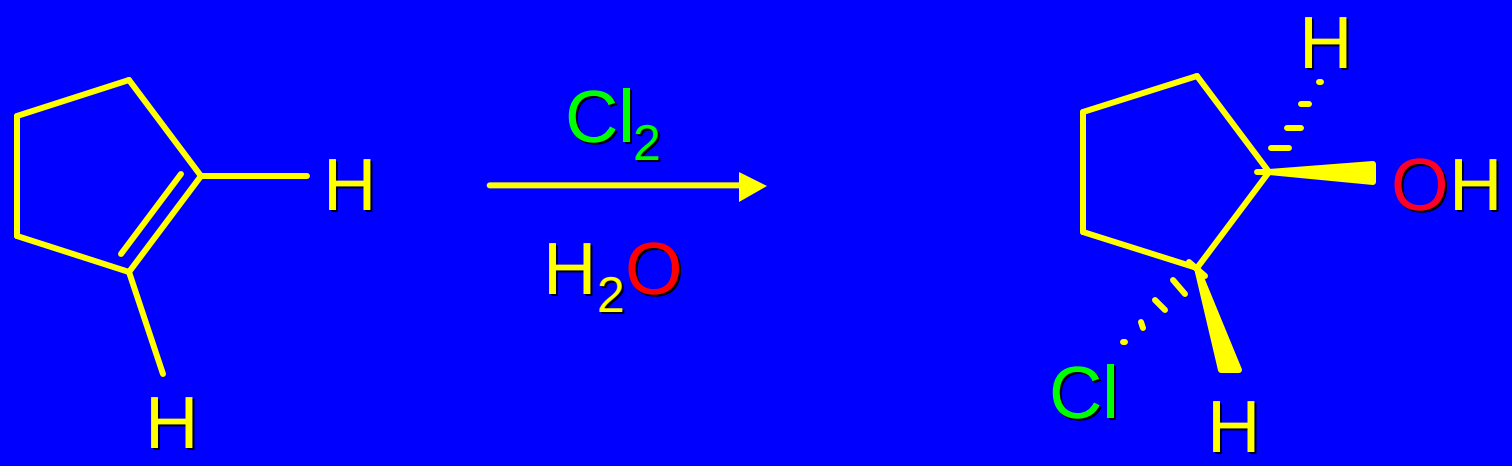


bromonium ion is intermediate

water is nucleophile that attacks bromonium ion

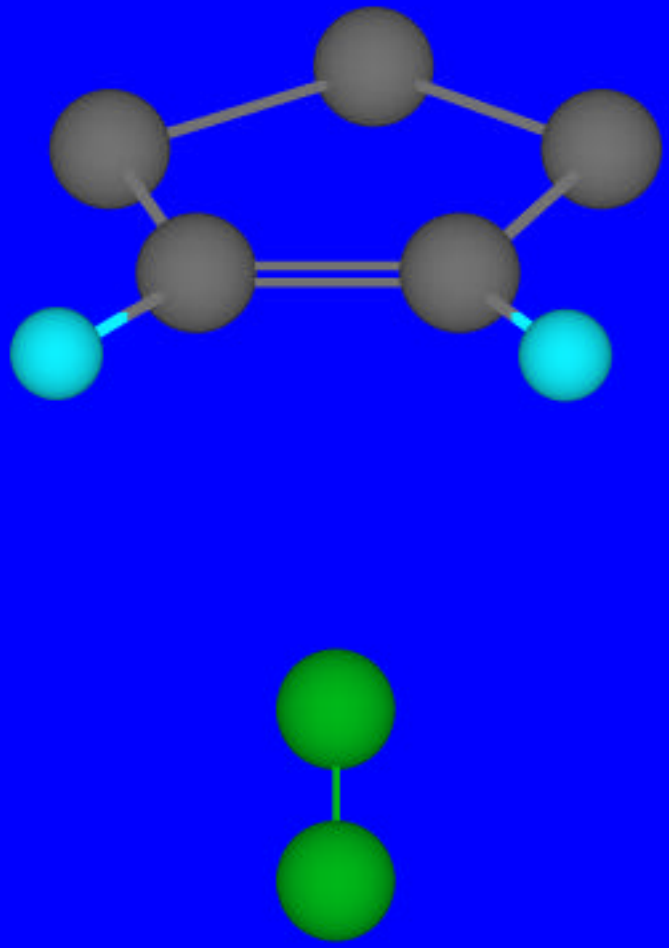
Examples



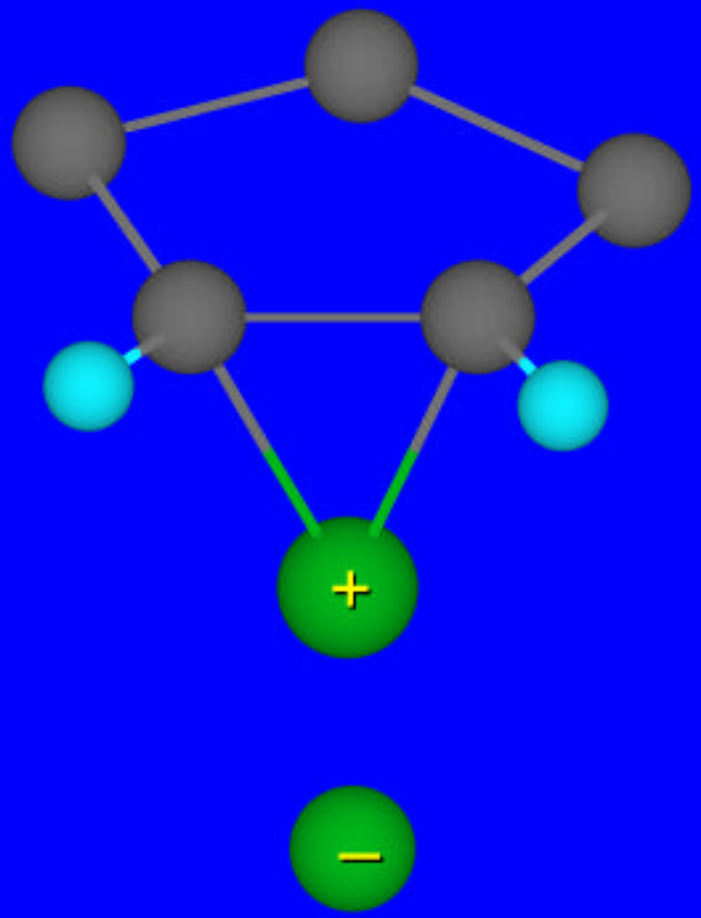


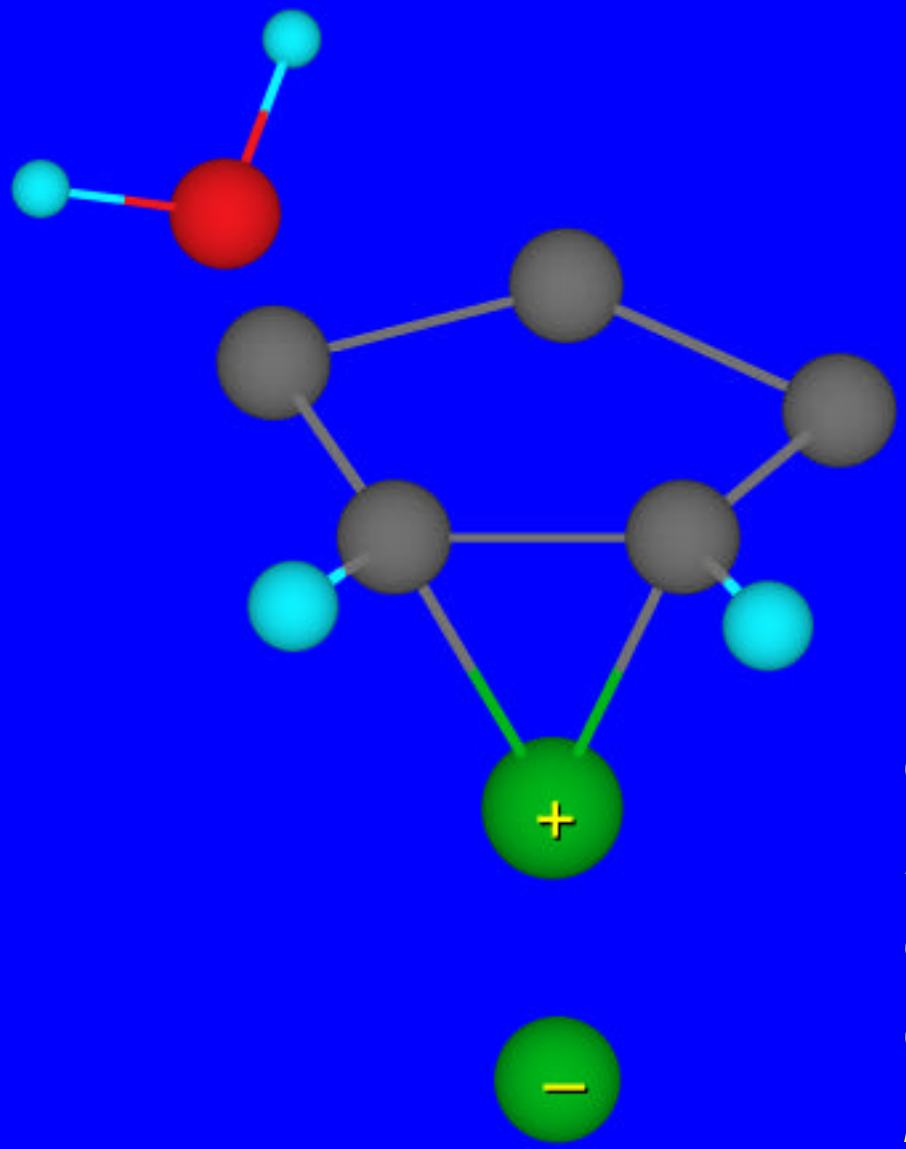
anti addition: only product

Cyclopentene + Cl_2



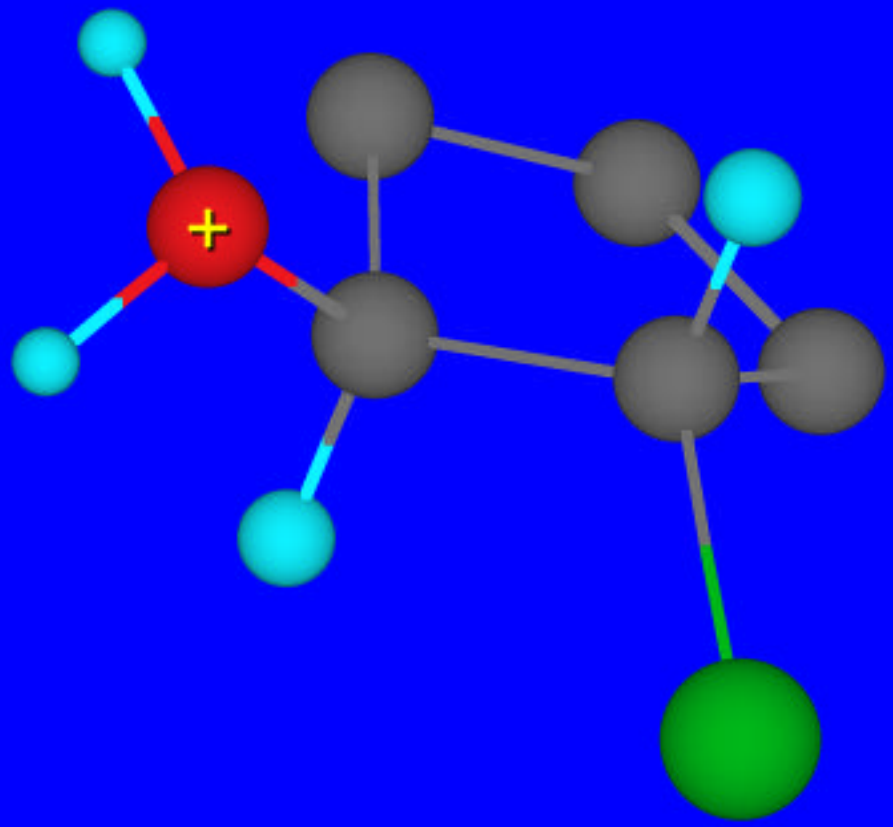
Chloronium ion

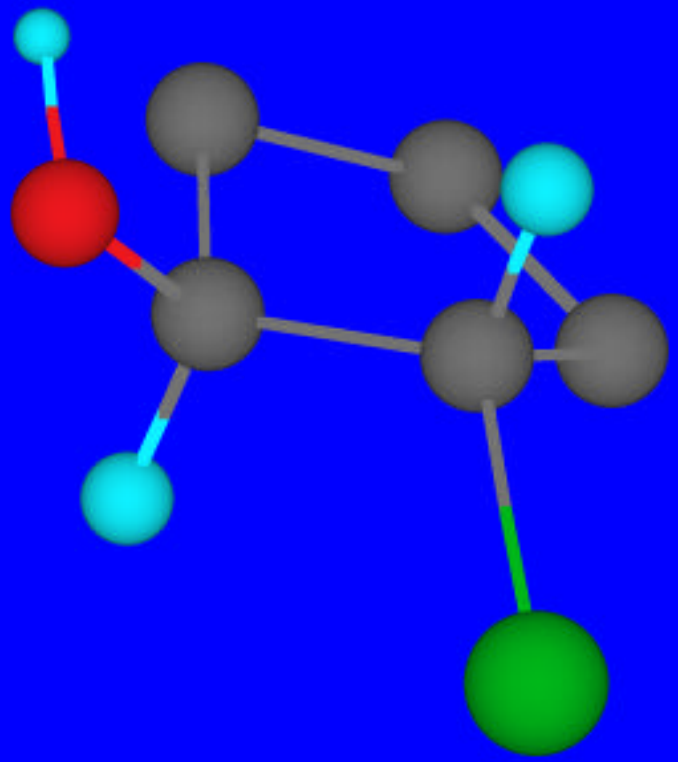




Water attacks chloronium ion from side opposite carbon-chlorine bond

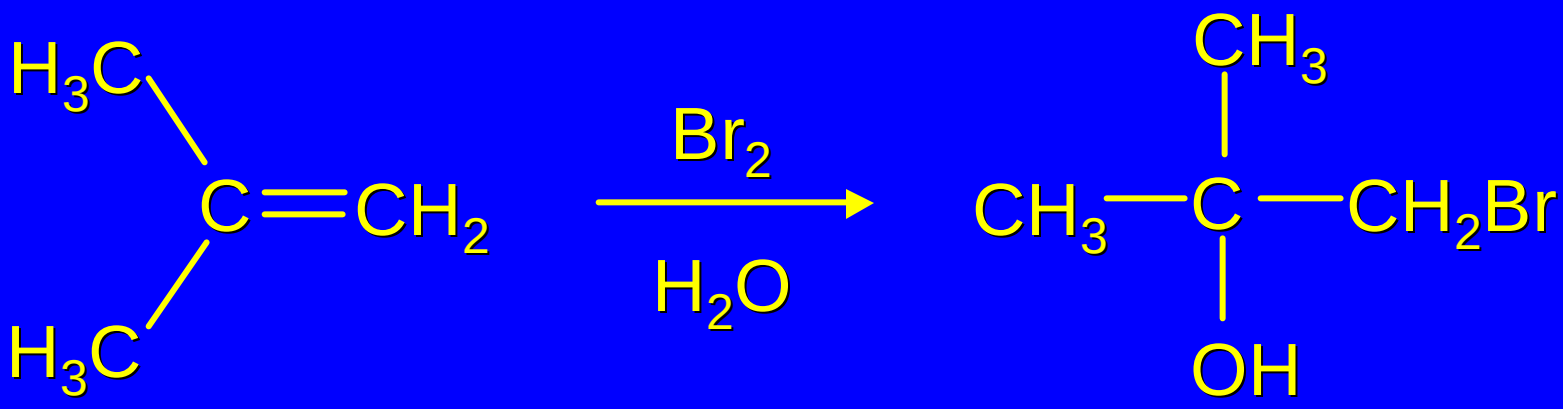
trans-Stereochemistry
in oxonium ion





trans-2-Chlorocyclopentanol

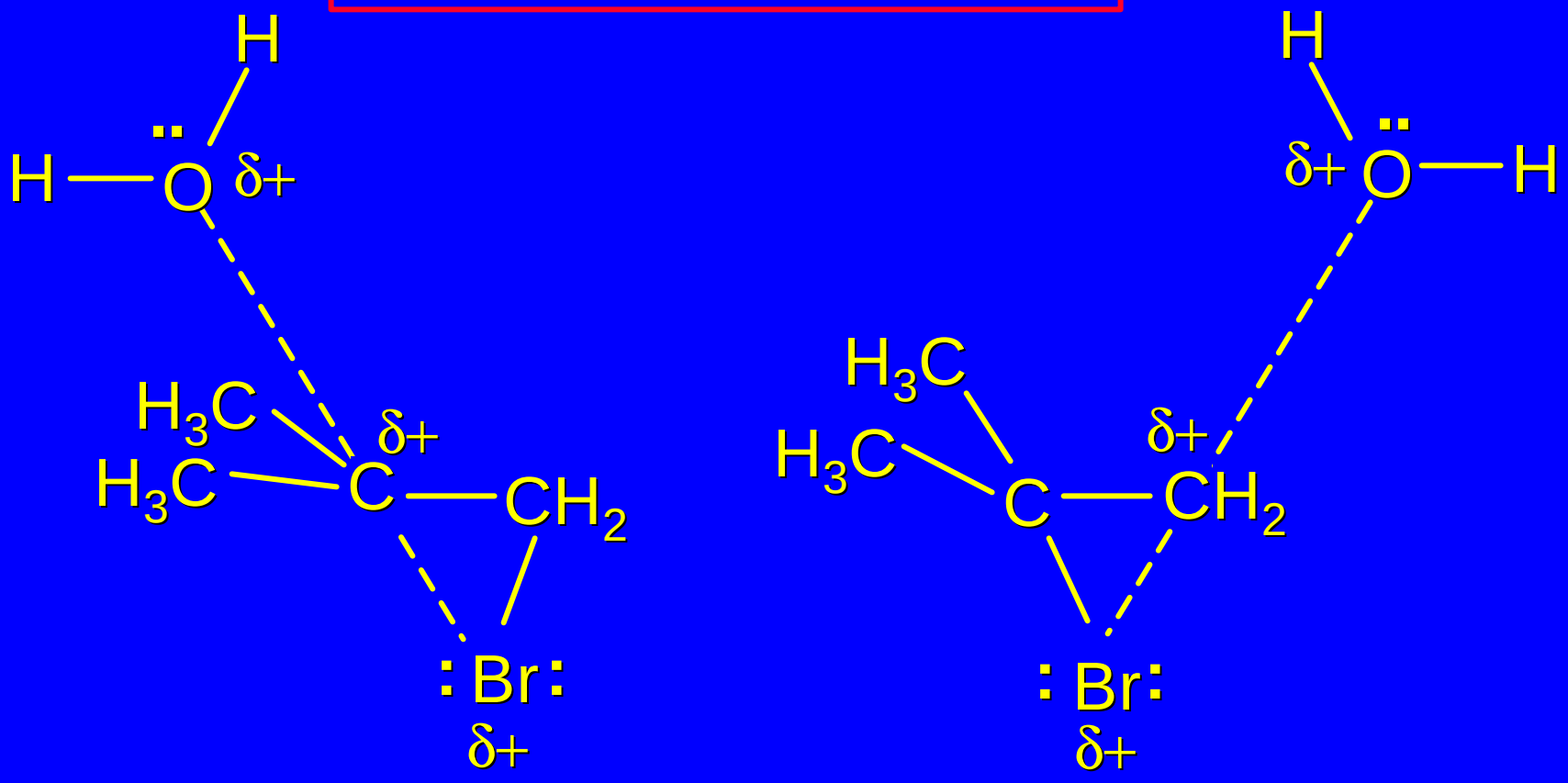
Regioselectivity



(77%)

Markovnikov's rule applied to halohydrin formation: the halogen adds to the carbon having the greater number of hydrogens.

Explanation



transition state has for attack of water on bromonium ion has carbocation character; more stable transition state (left) has positive charge on more highly substituted carbon