Lecture 11

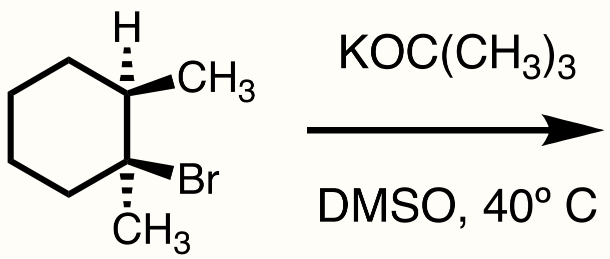
Organic Chemistry 1

Professor Duncan Wardrop

February 16, 2010

Self Test Question

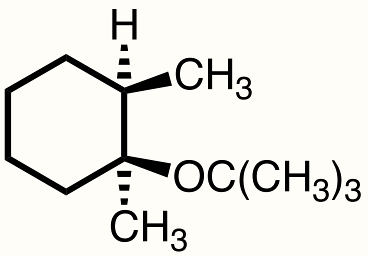
What is the product(s) of the following reaction?



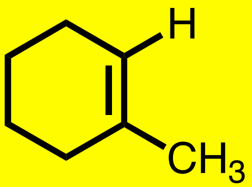
$KOC(CH_3)_3$

DMSO, 40° C

A



B



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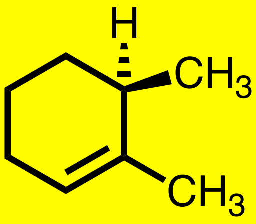
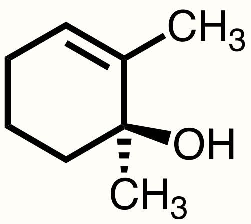
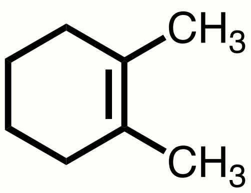


D



E

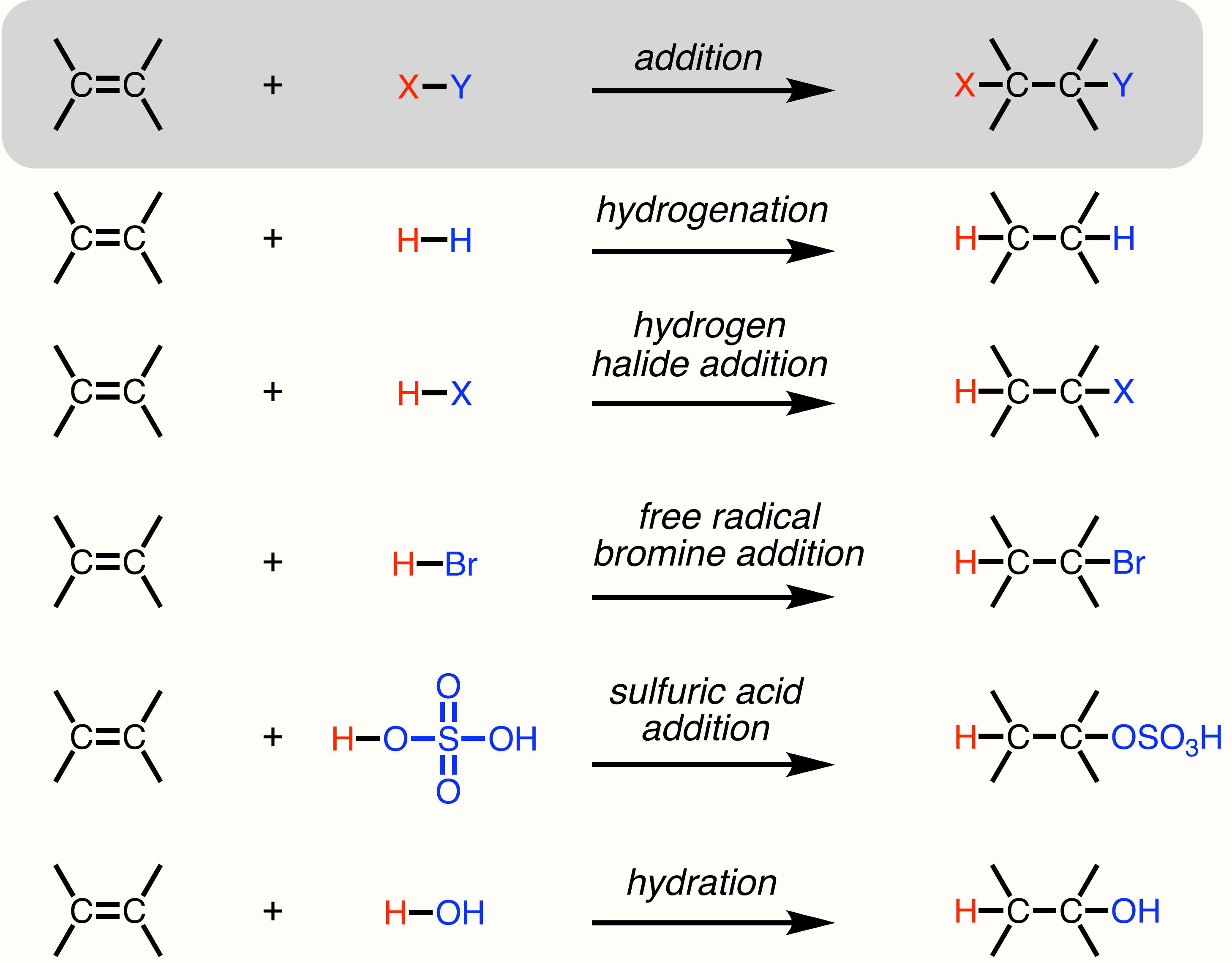


Addition Reactions of Alkenes

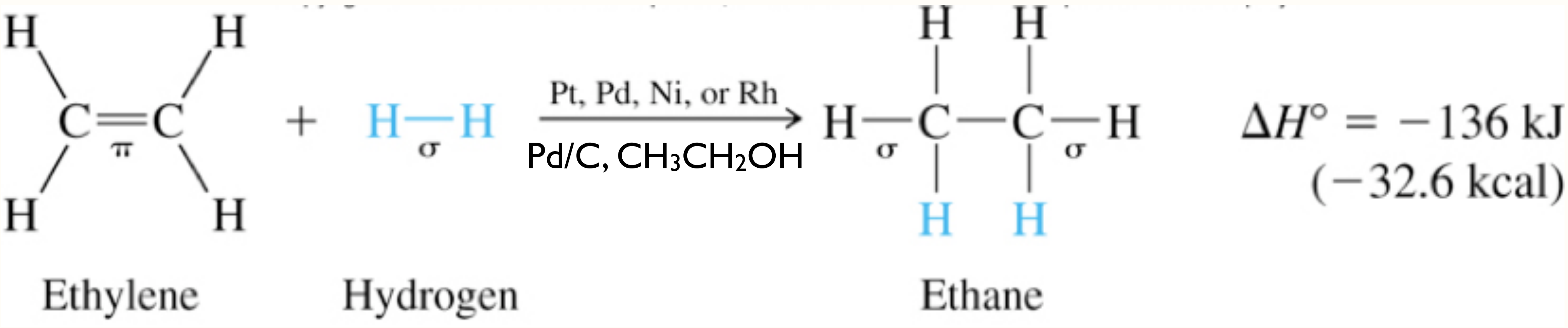
Section 6.1-6.10

You are responsible for Section 6.11.

Addition Reactions of Alkenes

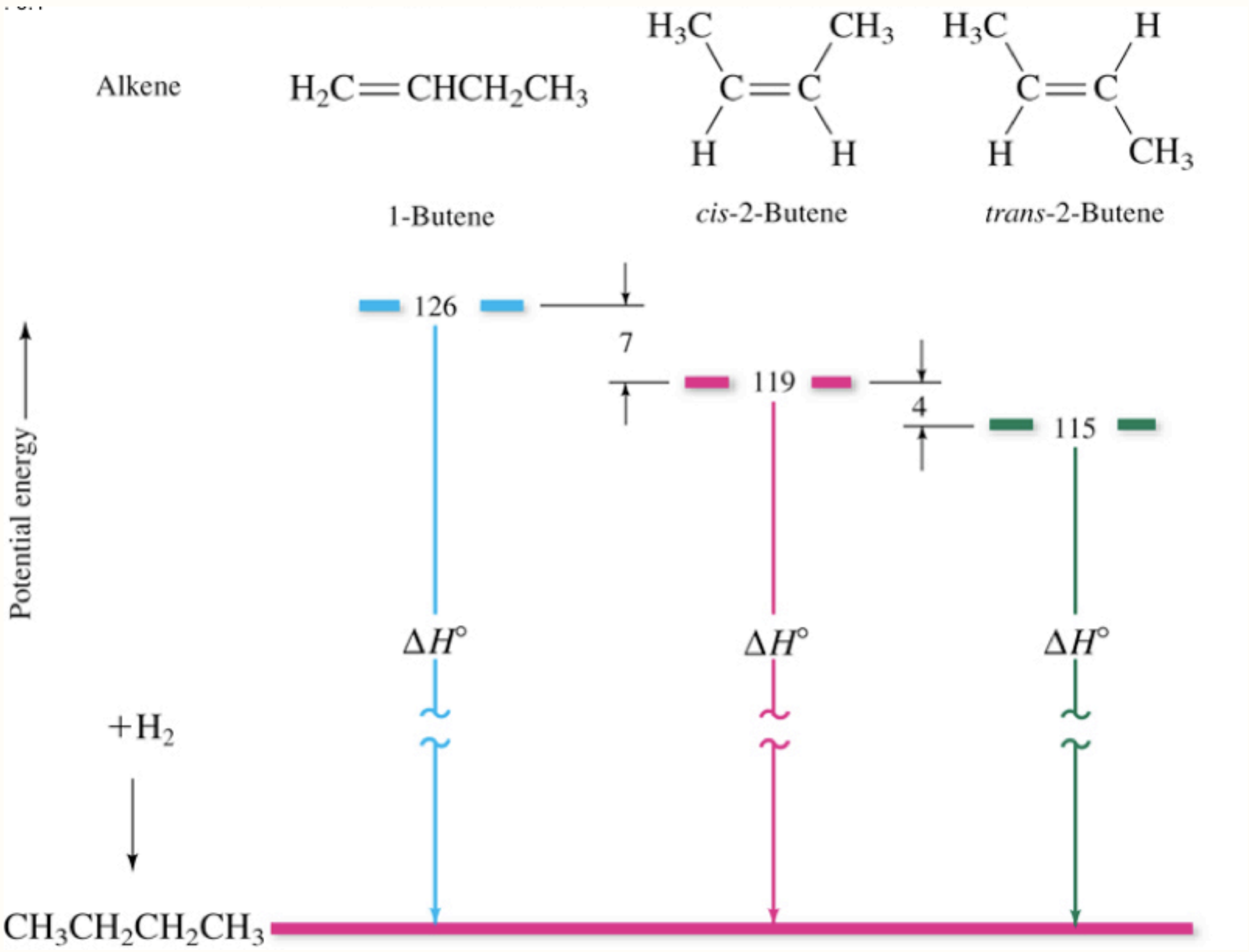


Hydrogenation



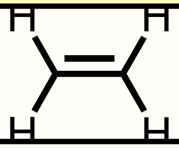
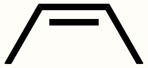
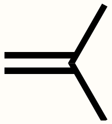
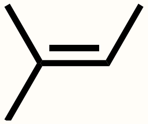
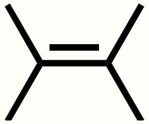
- exothermic reaction (-ΔHº), but high E_{act} - catalyst required
- catalysts are heterogeneous transition metals (Pd, R
- solvent is typically an alcohol (e.g. ethanol, CH_3CH_2OH)
- metals are insoluble (heterogeneous mixture)
- heat of hydrogenation = -ΔHº

Heat of Hydrogenation (-ΔHº)

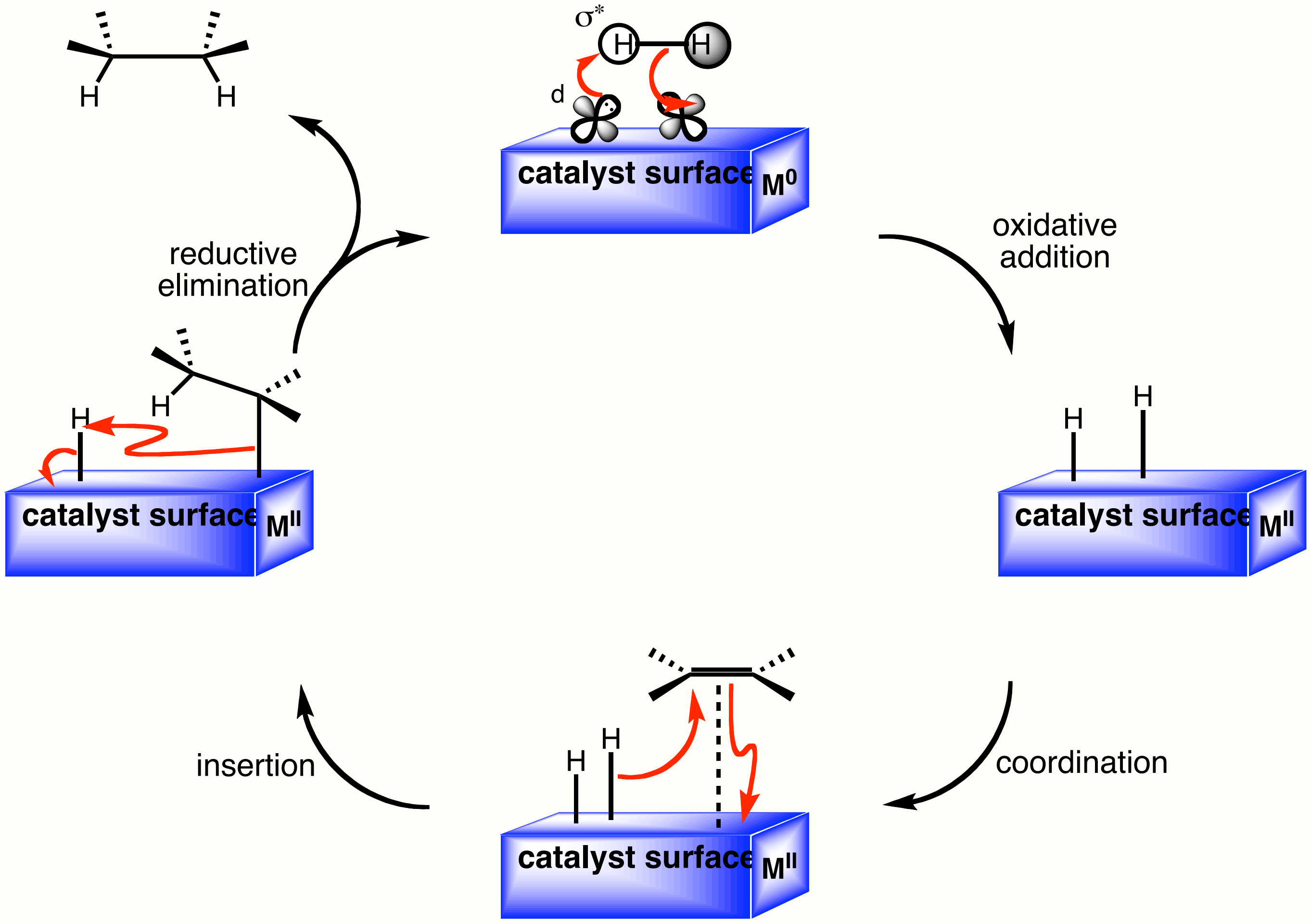


Heat of Hydrogenation (-ΔHº)

Since only the double bond is undergoing the reaction, heat of hydrogenation is independent of the number of carbon atoms in the molecule

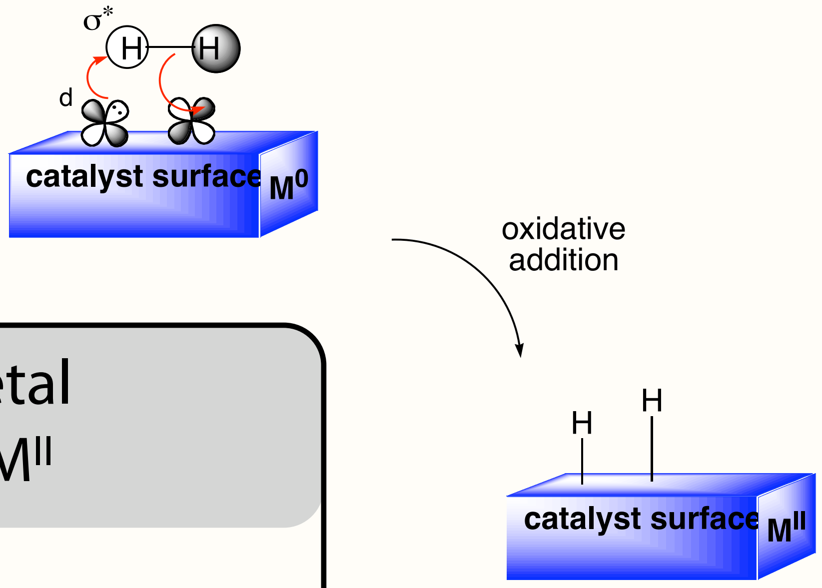
Alkene	-ΔHº (kJ/mol)	example
ethylene	136	
monosubstituted	126	
cis-disubstituted	119	
terminally disubstituted	117	
trisubstituted	112	
tetrasubstituted	110	

General Mechanism for Heterogenious Hydrogenation

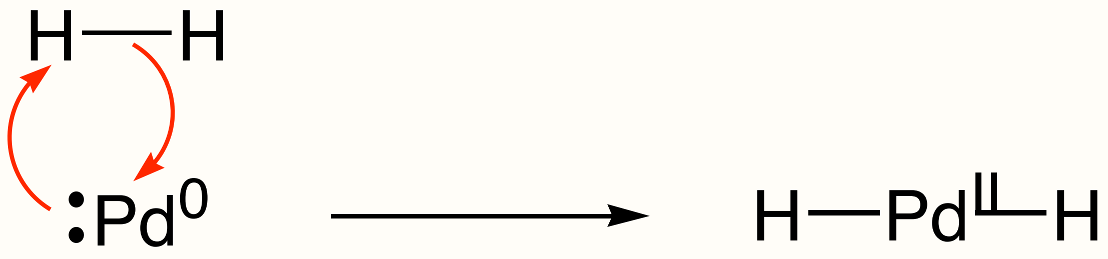


reaction takes places at the surface of the catalyst (many metal atoms combined)

Step 1: Oxidative Addition

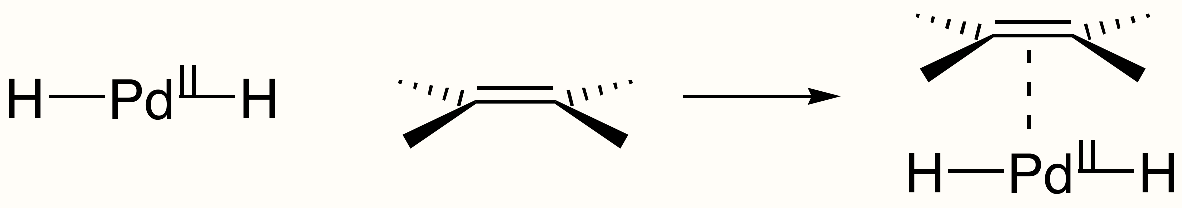


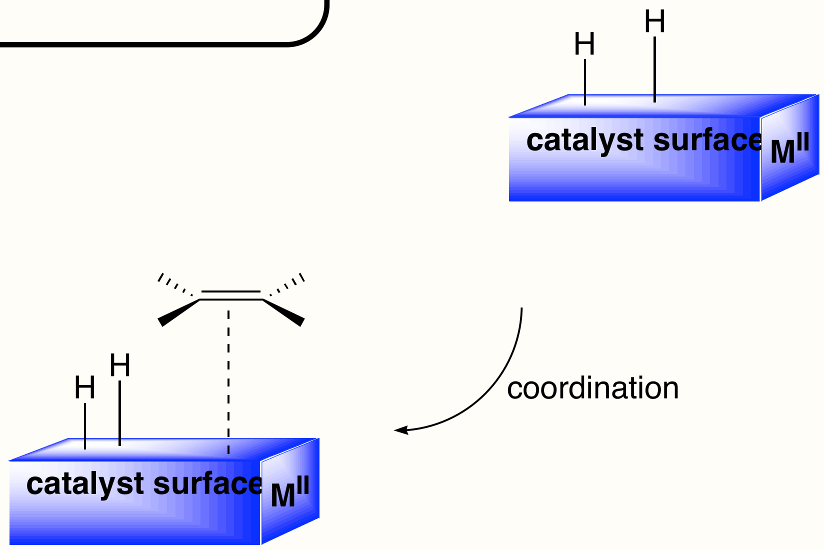
- hydrogen (H_2) is added to metal
- metal is oxidized from M^0 to M^{II}



Step 2: Coordination

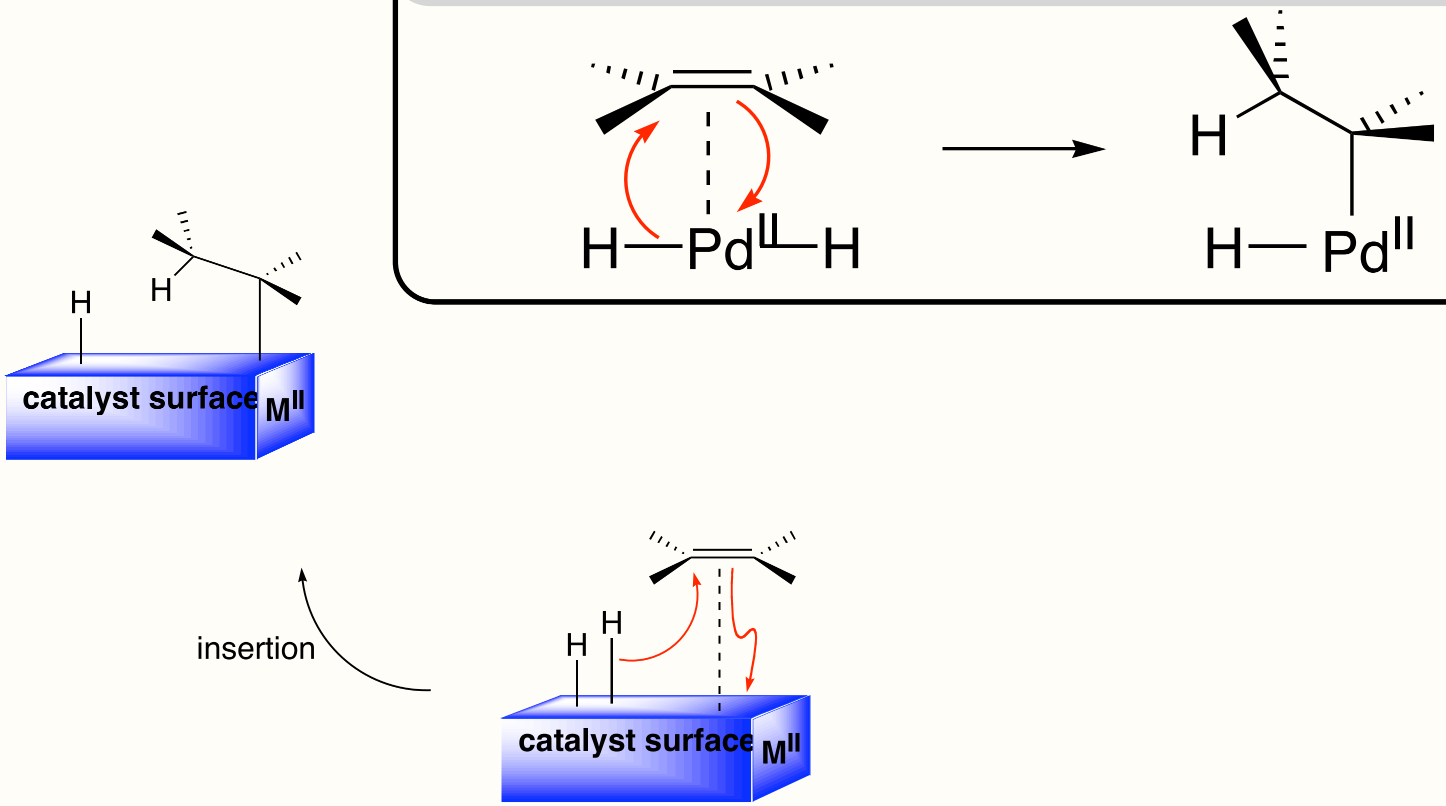
- metal is a Lewis acid (electron acceptor)
- π-bond is a lewis base (electron donor)
- coordination = Lewis acid/base complex



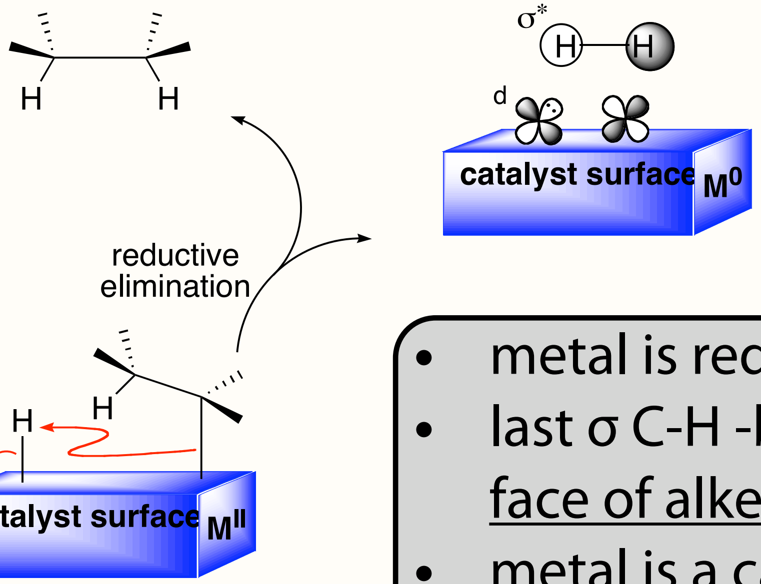


Step 3: Insertion

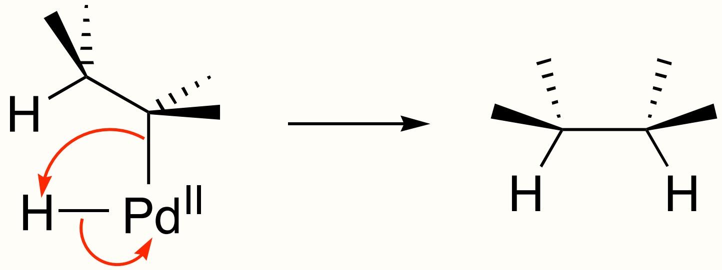
- two carbon atoms inserted between Pd-H
- formation of a weak metal-carbon σ-bond
- formation of a strong C-H σ-bond
- break a weak metal-H σ-bond



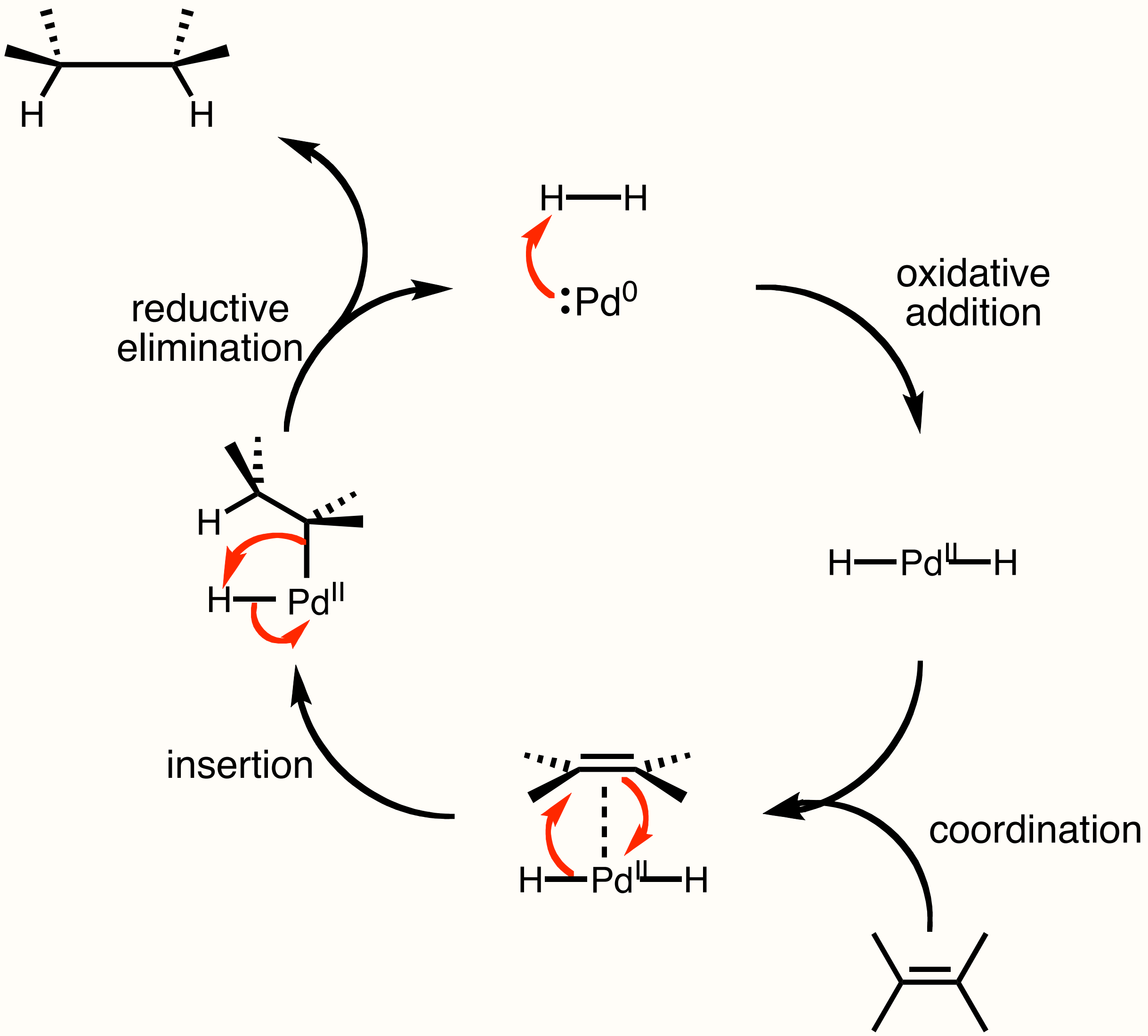
Step 4: Reductive Elimination



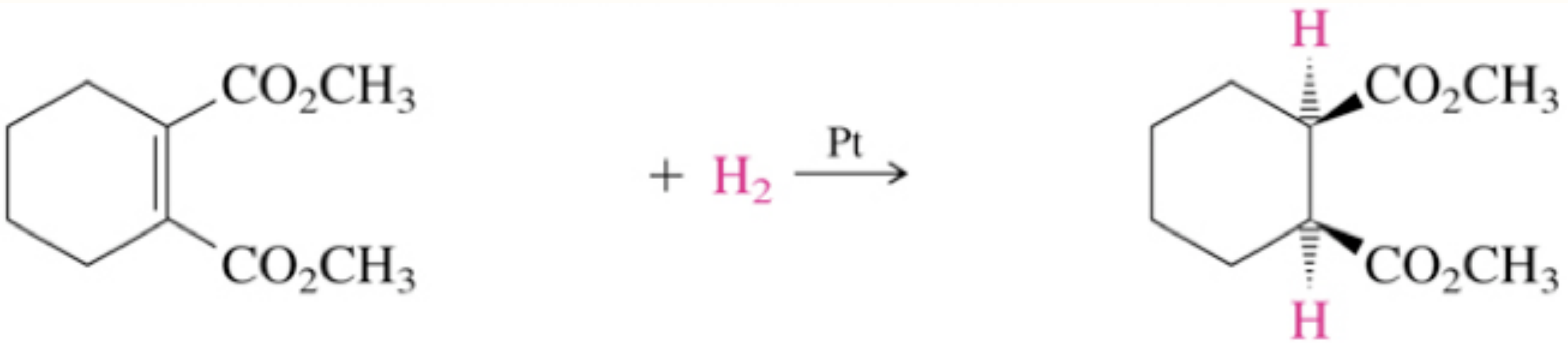
- metal is reduced from M^{II} to M^0
- last σ C-H -bond is formed from the <u>same face of alkene</u> as previous
- metal is a catalyst; it is regenerated



Complete Mechanism



Syn Addition of Hydrogen



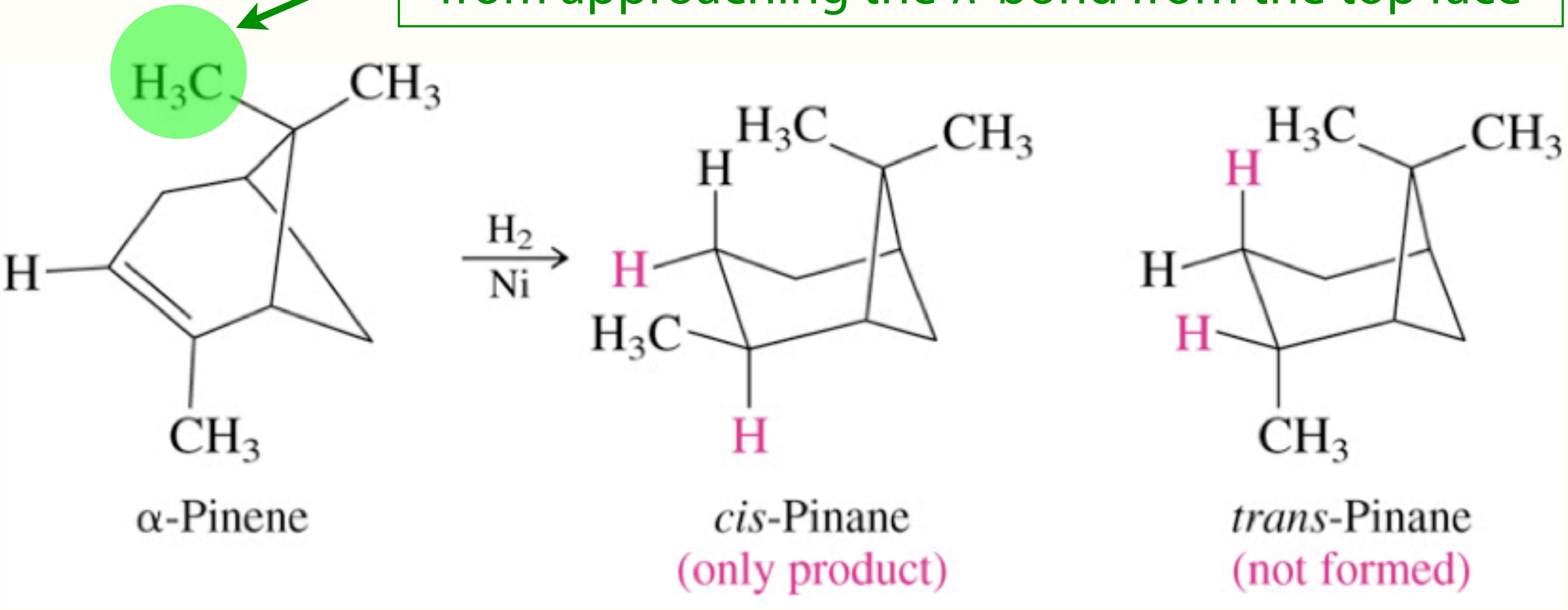
Dimethyl cyclohexene-1,2-dicarboxylate

Dimethyl cyclohexane-*cis*-1,2-dicarboxylate (100%)

- as a consequence of mechanism, both hydrogens are added to the same face of the π-bond: *syn* addition
- no *anti*-addition products are formed (addition of hydrogen to opposite faces)

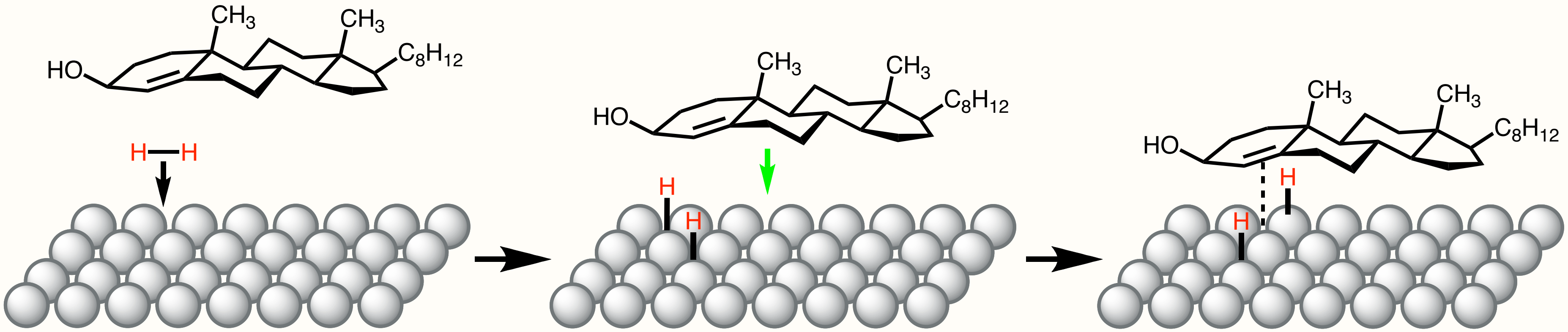
Hydrogenation is Stereoselective

This methyl group sterically hinders hydrogen from approaching the π-bond from the top face



- both products are arise from *syn* additions of hydrogen to alkene
- stereoselective: preference for one stereoisomer when two or more are possible

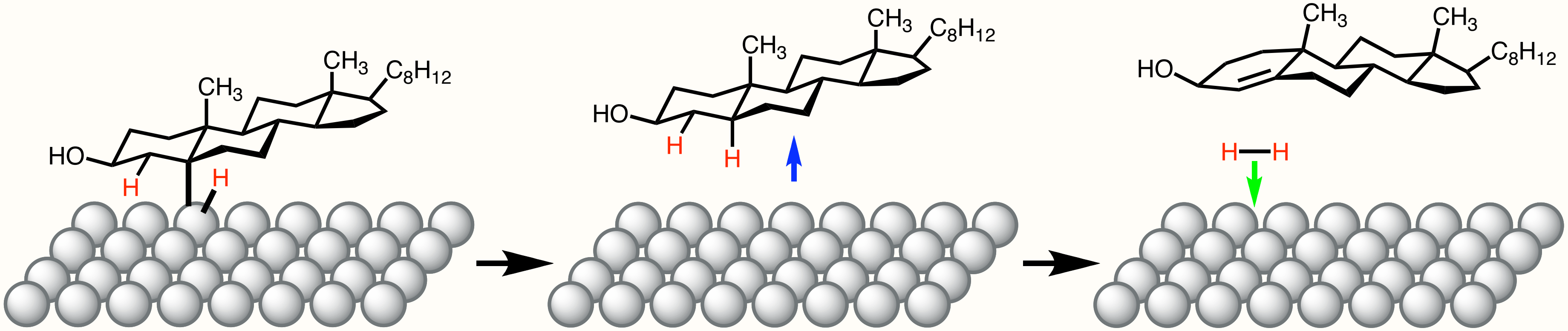
Example of *Syn* Addition



1. Diatomic hydrogen and alkene are present in solution phase. No reaction occurs.

2. Hydrogen absorbed on to catalyst surface. H-H bond cleaved.

3. π–System of alkene coordinates catalyst surface.



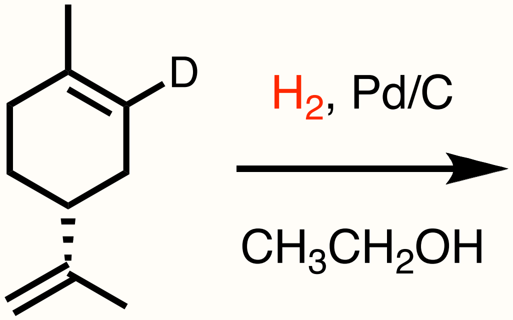
4. One hydrogen atom is transferred to alkene, forming C-catalyst bond.

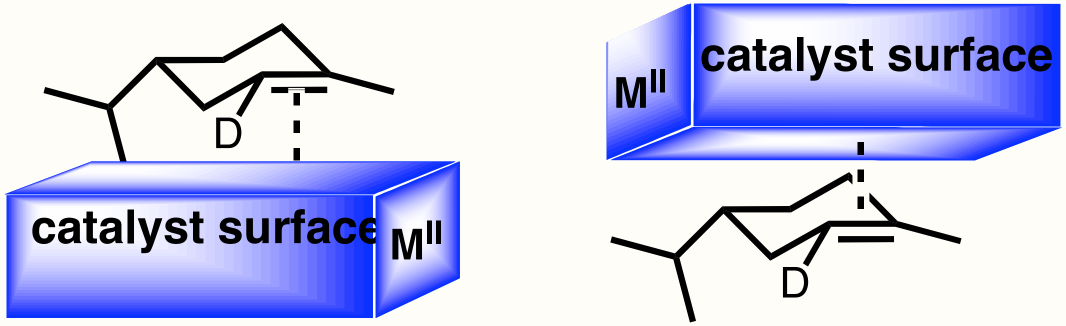
5. Second hydrogen atom is transferred, breaking substrate-catalyst bond. Alkane diffuses away from catalyst.

6. Steps **1-5** are repeated.

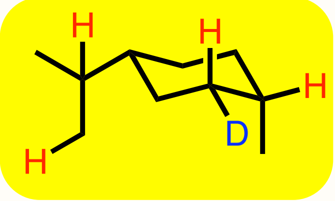
Self Test Question

What is the major product of the following hydrogenation reaction?

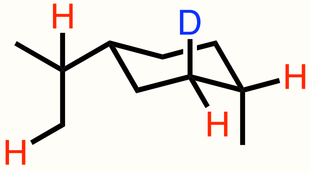




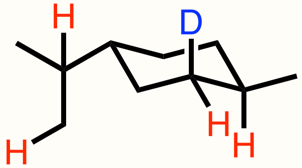
A.



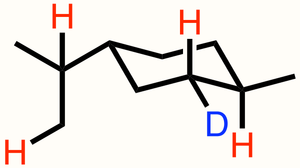
B.



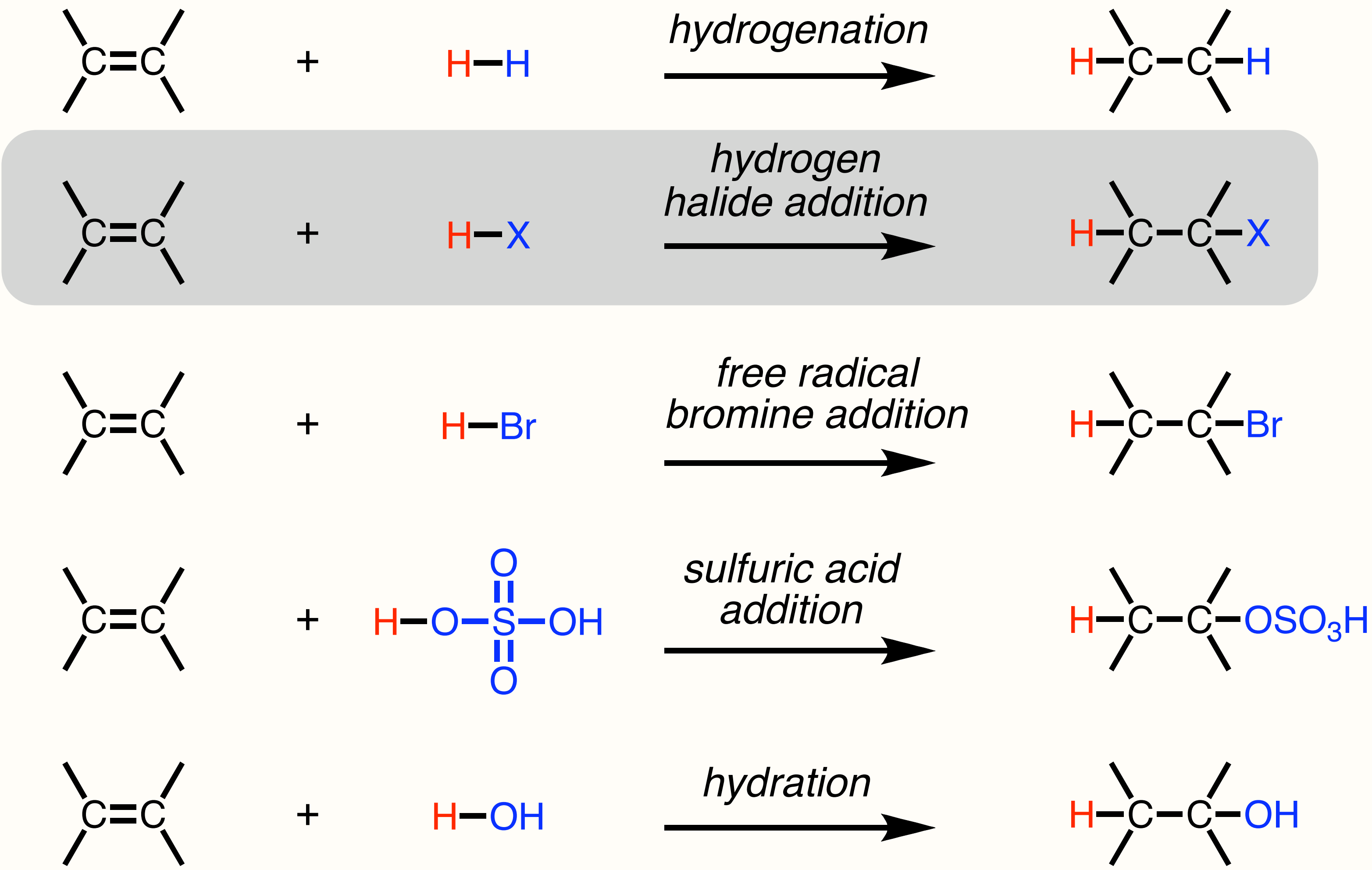
C.



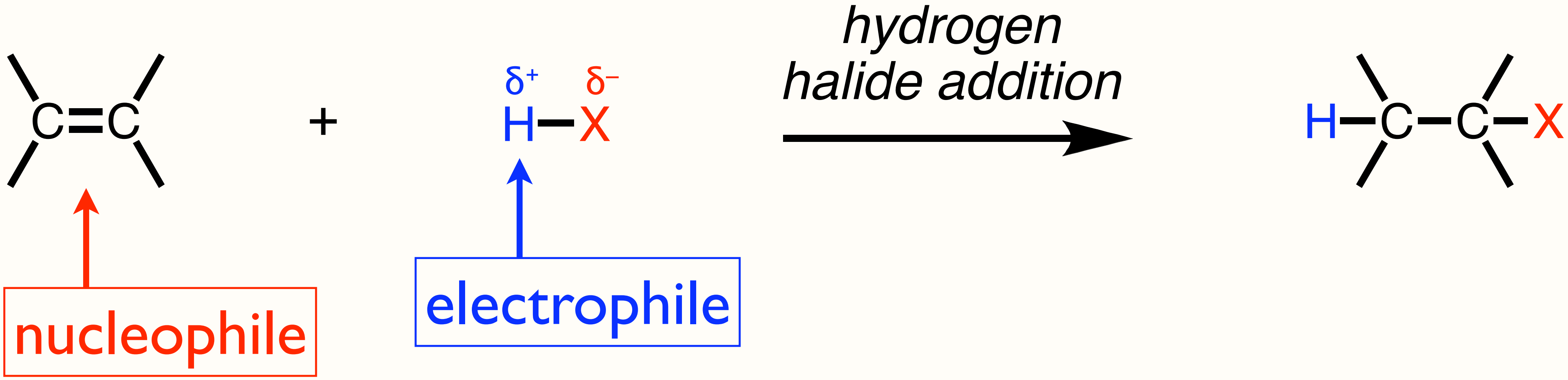
D.



Addition of Electrophiles to Alkene

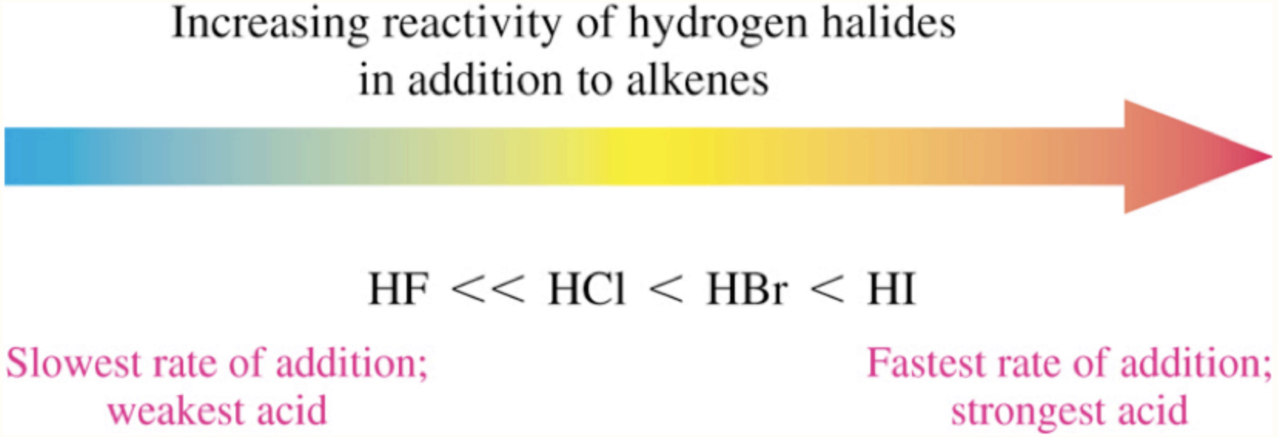


Electrophilic Addition of HX



nucleophile

electrophile



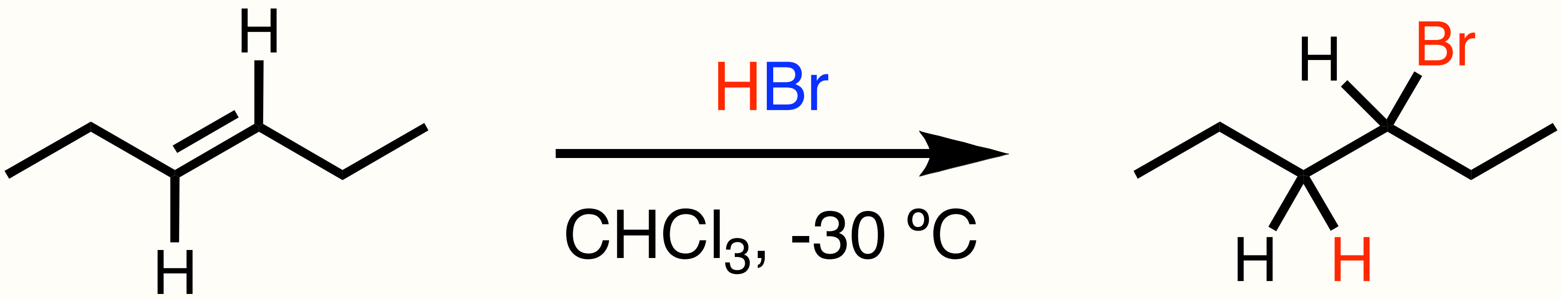
Increasing reactivity of hydrogen halides in addition to alkenes

HF << HCl < HBr < HI

Slowest rate of addition; weakest acid

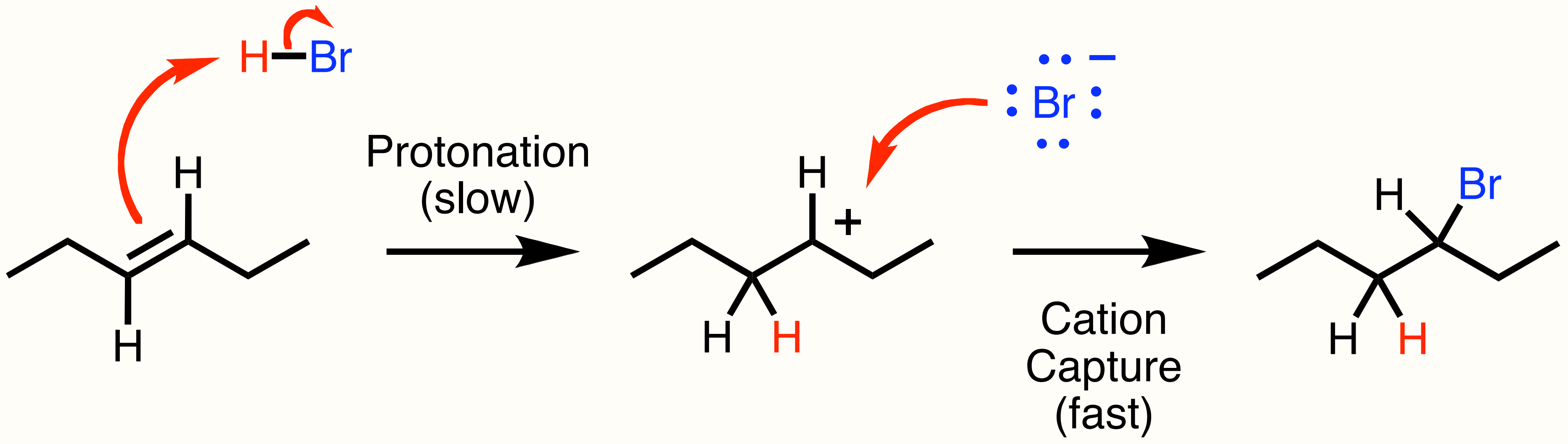
Fastest rate of addition; strongest acid

Reaction Conditions



- hydrogen halide: HX
- common solvents: chloroform ($CHCl_3$) ,dichloromethane (CH_2Cl_2), pentane, acetic acid
- generally performed at low temperature (below 0 °C)
- generally a fast reaction

Electrophilic Addition (Ad_E) Mechanism



- electrophilic addition: AdE
- RDS = protonation of carbon
- rate = k[alkene][hydrogen halide]
- unlike oxygen and nitrogen, protonation of carbon is slow
- proceeds through carbocation intermediate

HX Addition is Regioselective

Regioselectivity

Preferential reaction at one site of a single functional group over other sites that could undergo the same reaction

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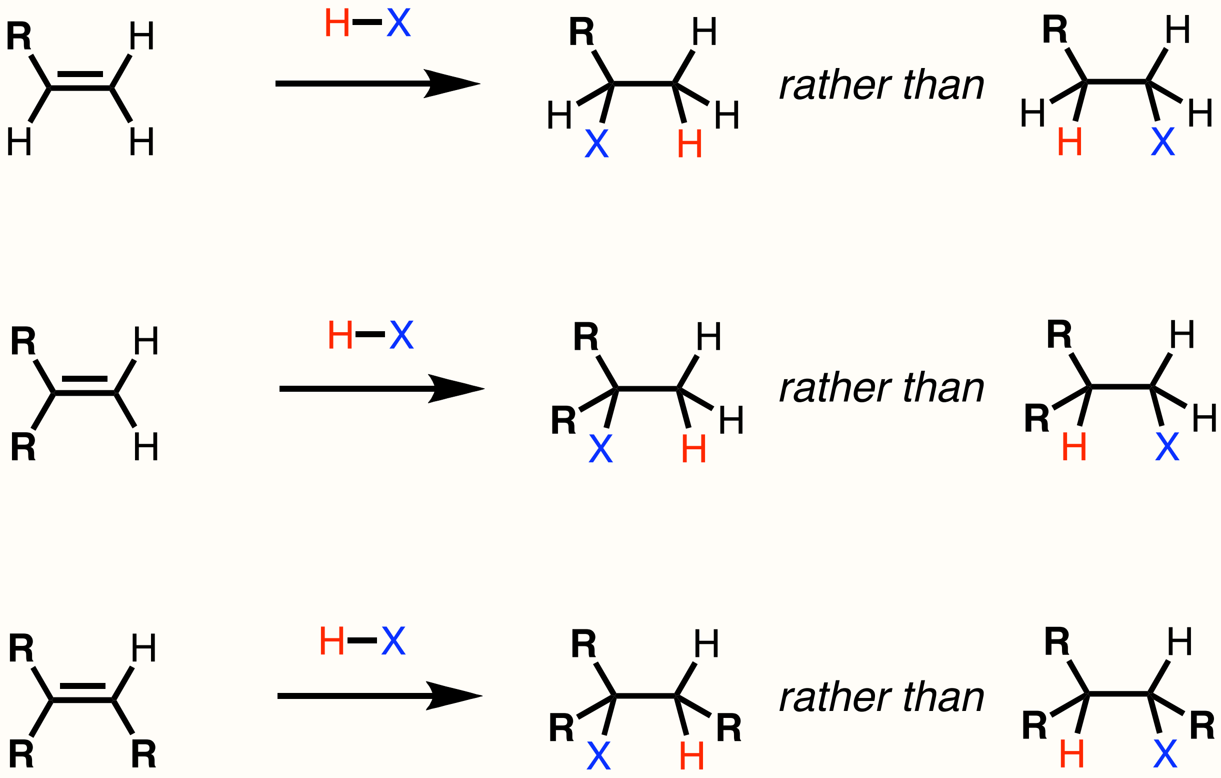
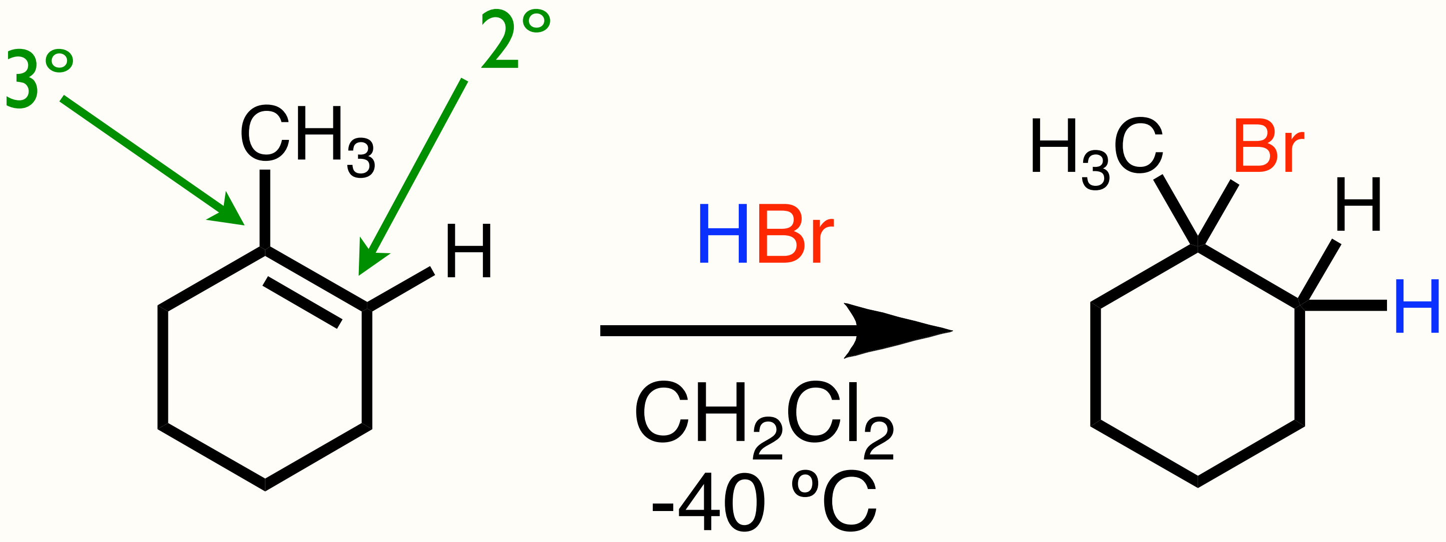
CHEM 232 Definition, 2010



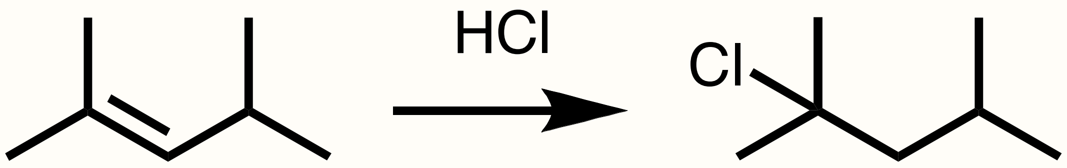
Markovnikov’s Rule



addition of HX to an unsymmetrically substituted alkene proceeds so that hydrogen (H) adds to the least substituted carbon and the halide (X) adds to the most substituted carbon atom

Self Test Question

Predict the product when 2,4-dimethyl-2-pentene is treated with HCl?



A. 3-chloro-2,4-dimethylpentane

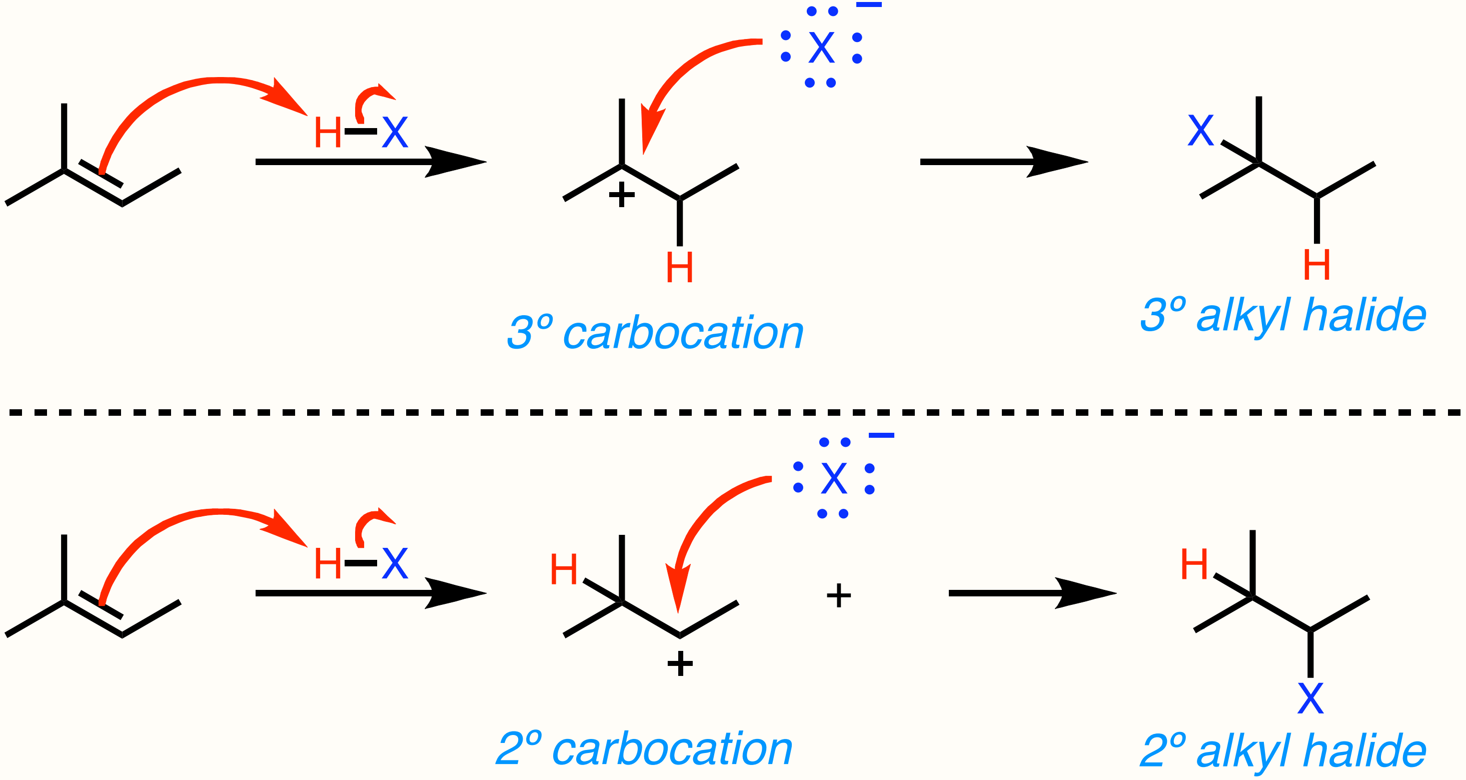
B. 2-chloroohexane

C. 2,3-dichloro-2,4-dimethylpentane

D. 2-chloro-2,4-dimethylpentane

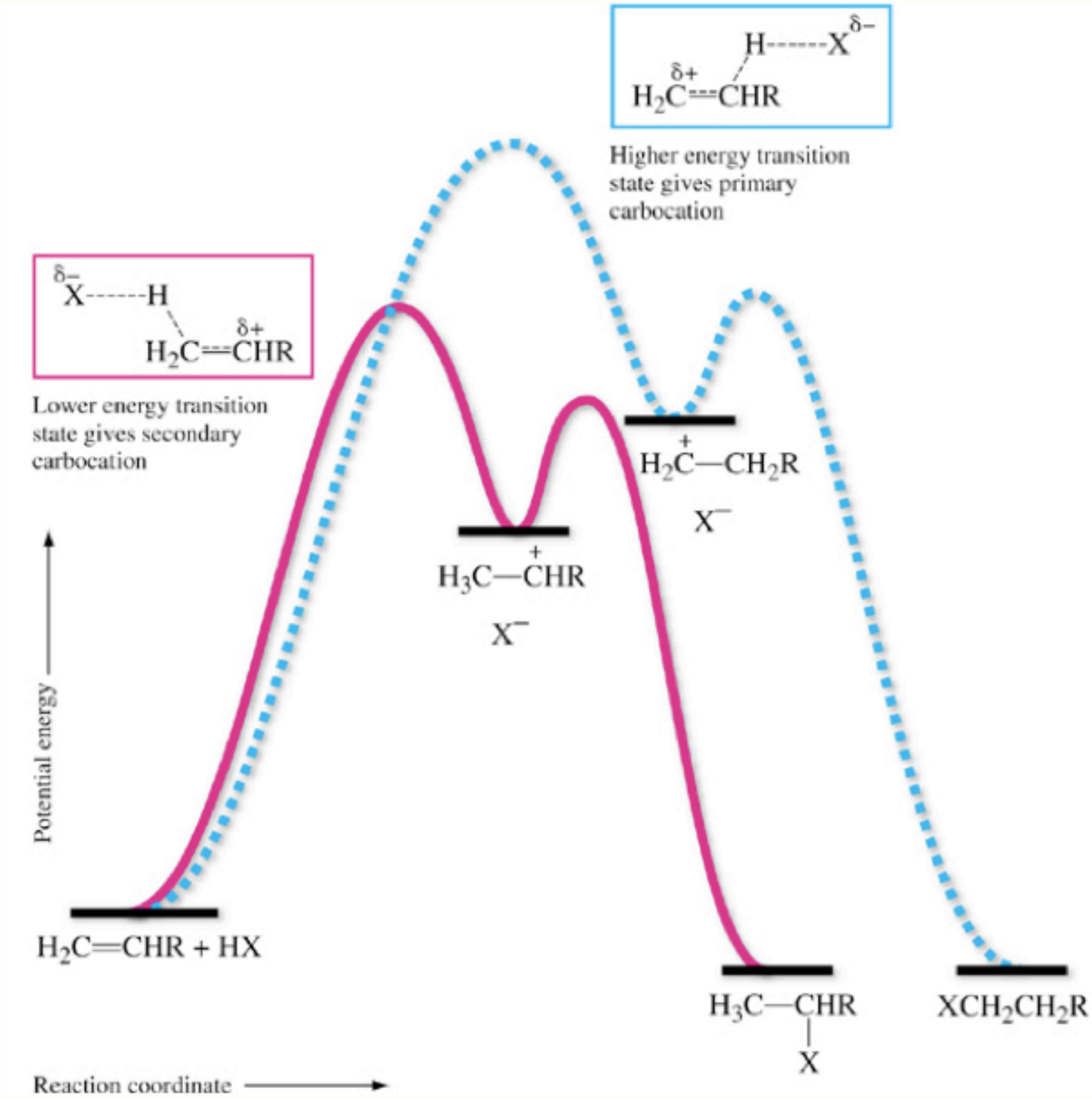
E. 1-chloro-2,4-dimethylpentane

Mechanistic Basis for Markovnikov’s Rule



- curved arrows do not indicate which carbon is protonated
- fastest protonation leads to more stable (more substituted) carbocation
- more substituted carbocation = more substituted alkyl halide

Mechanistic Basis for Markovnikov's Rule

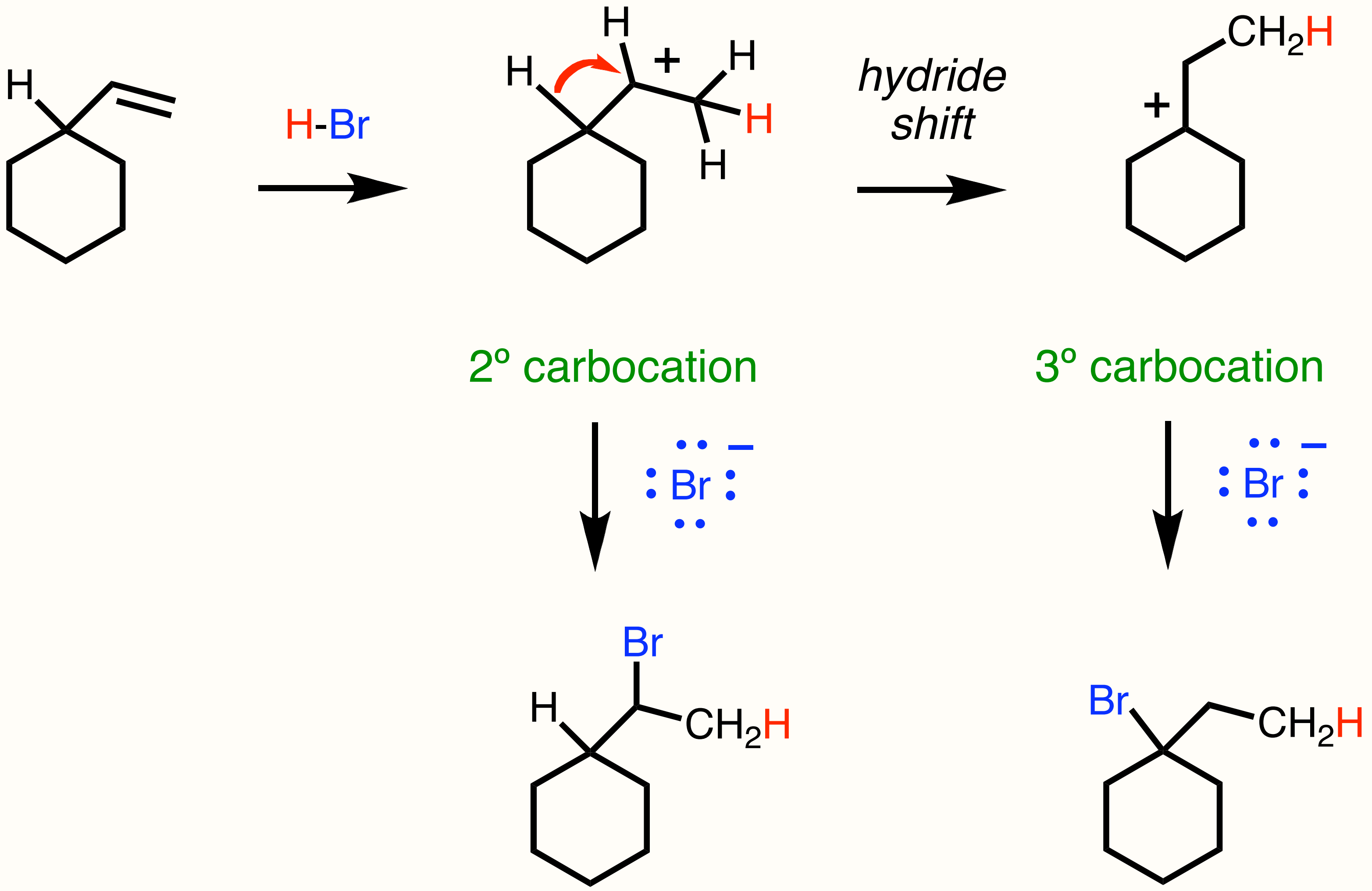


Hammond Postulate:

transition state structure resembles closest energy intermediate

- transition state resembles carbocation for endothermic RDS (late transition state)
- what stabilizes carbocation also stabilizes transition state
- lowest energy transition state leads to more substituted carbocation

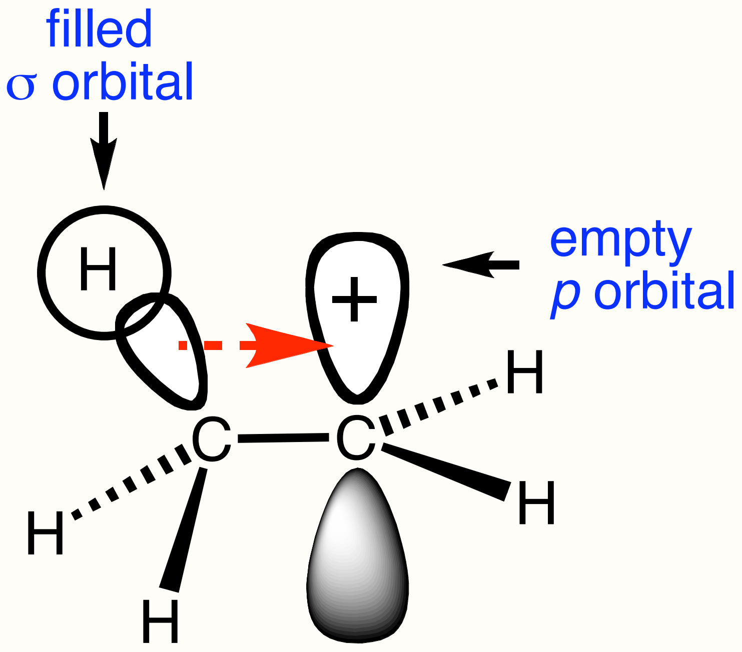
Rearrangement Can Precede Addition



Stability of Carbocations (Lecture 8)

2. Hyperconjugation

stabilizing interaction that results from the interaction of the electrons in a σ-bond (C–H or C–C bond) with an adjacent empty (or partially filled) orbital. Leads to the formation of an extended molecular orbital that increases the stability of the system

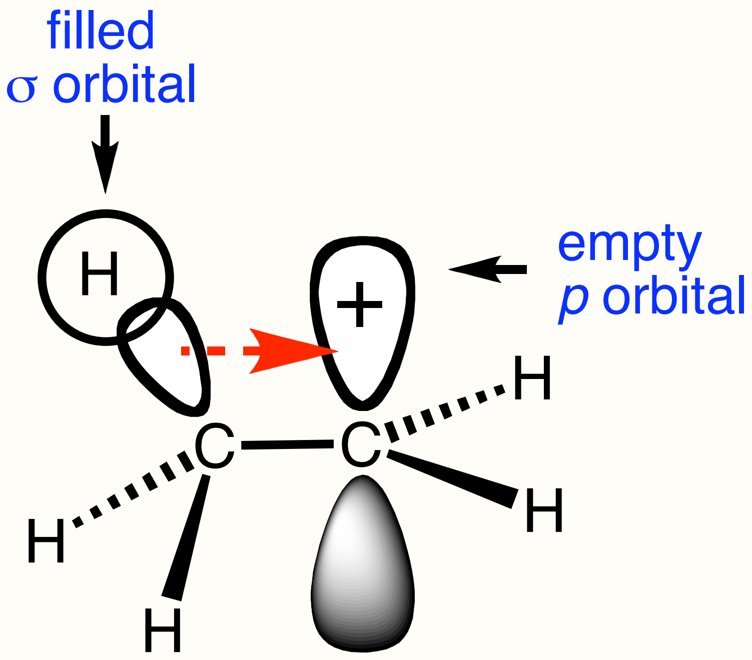


1° cation

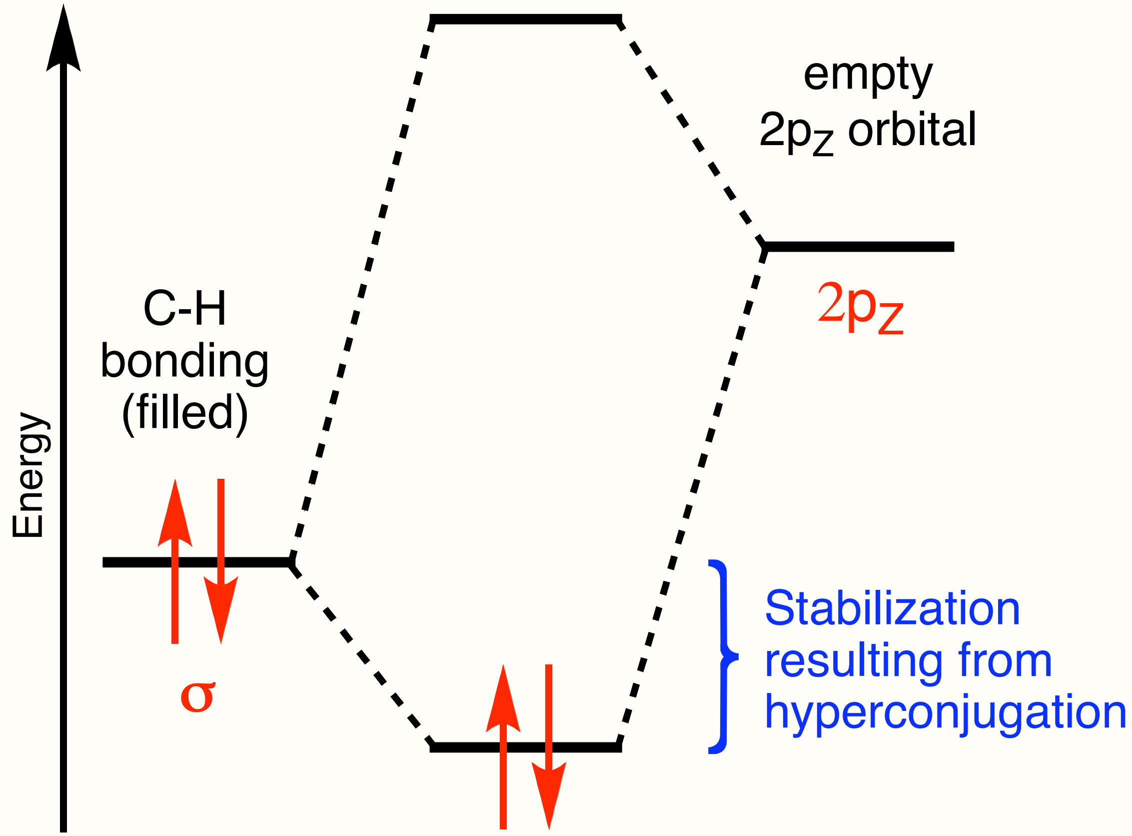
- stabilization results from σ-donation to empty p orbital of planar carbocation
- electron donation through σ-bonds toward carbocation delocalizes charge (spreads out)
- methyl cations cannot be stabilized by hyperconjugation since σ-bonds are perpendicular to the empty p orbital

Stability of Carbocations (Lecture 8)

2. Hyperconjugation


filled σ orbital

empty *p* orbital


empty $2p_Z$ orbital

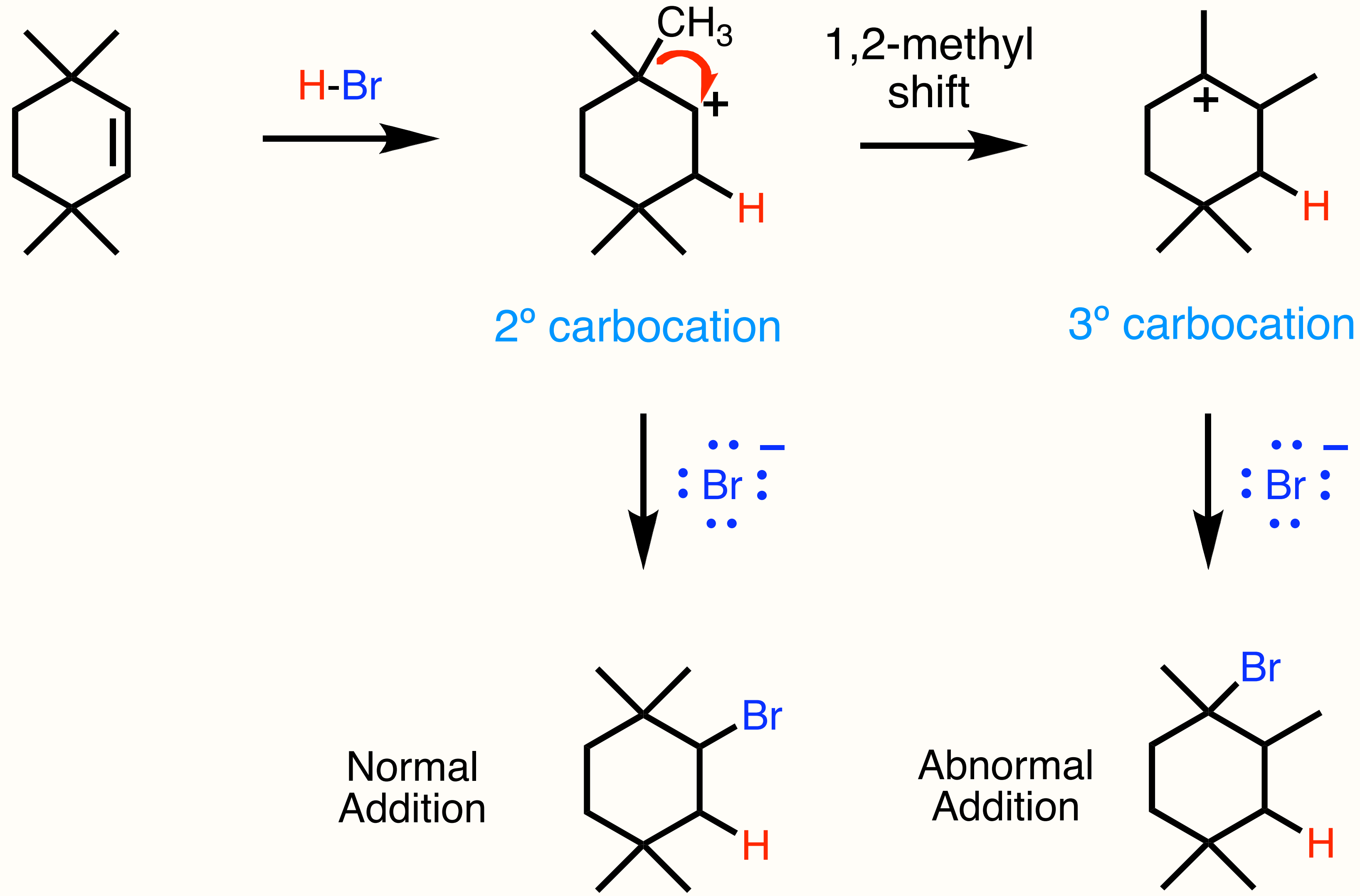
C-H bonding (filled)

$2p_Z$

σ

Stabilization resulting from hyperconjugation

Rearrangement Can Precede Addition



2° carbocation

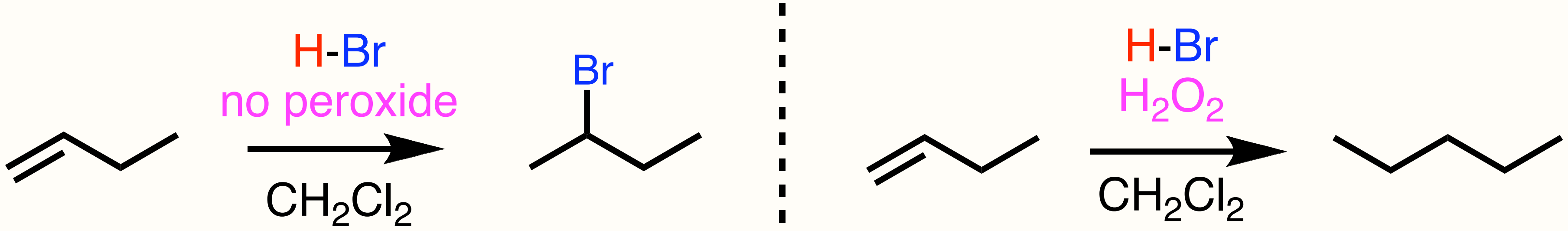
3° carbocation

Normal Addition

Abnormal Addition

Reversal of Addition Regioslectivty

The Peroxide Effect

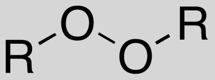
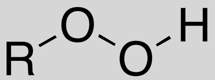
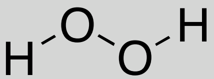


1-butene

2-bromobutane
(90% yield)

1-butene

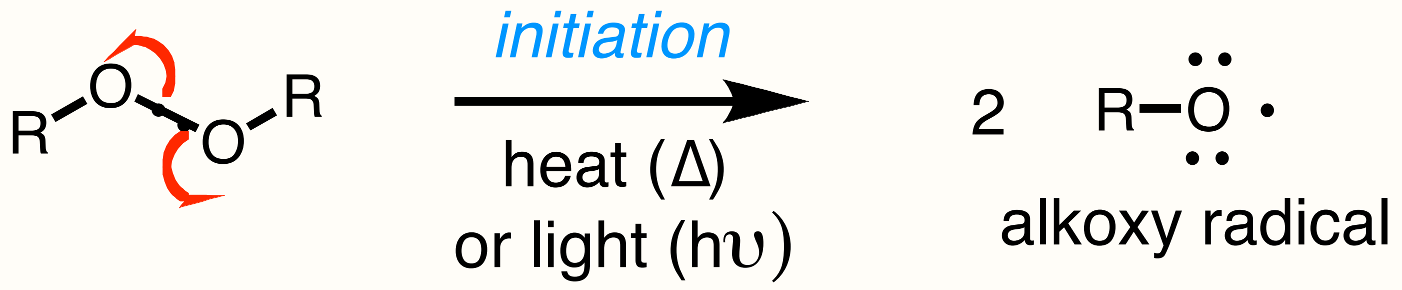
1-bromobutane
(95% yield)

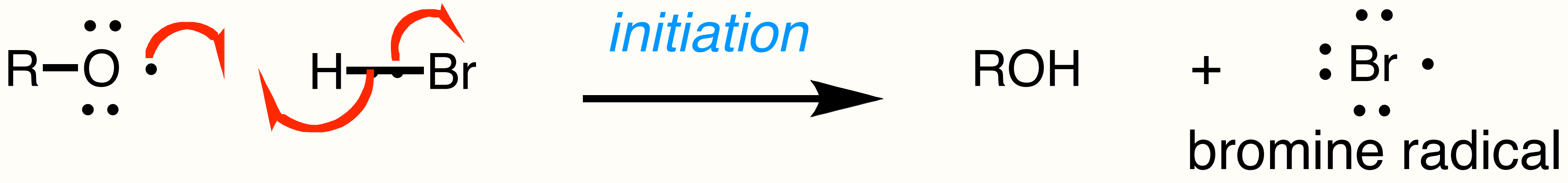
	peroxide
	hydroperoxide
	hydrogen peroxide

- alkyl peroxides easily fromed from alkanes/ alkenes by reaction with O_2 in the air
- presence of peroxides leads to anti-Markovnikov product (least substituted alkyl bromide)
- peroxide effect only operates when HBr

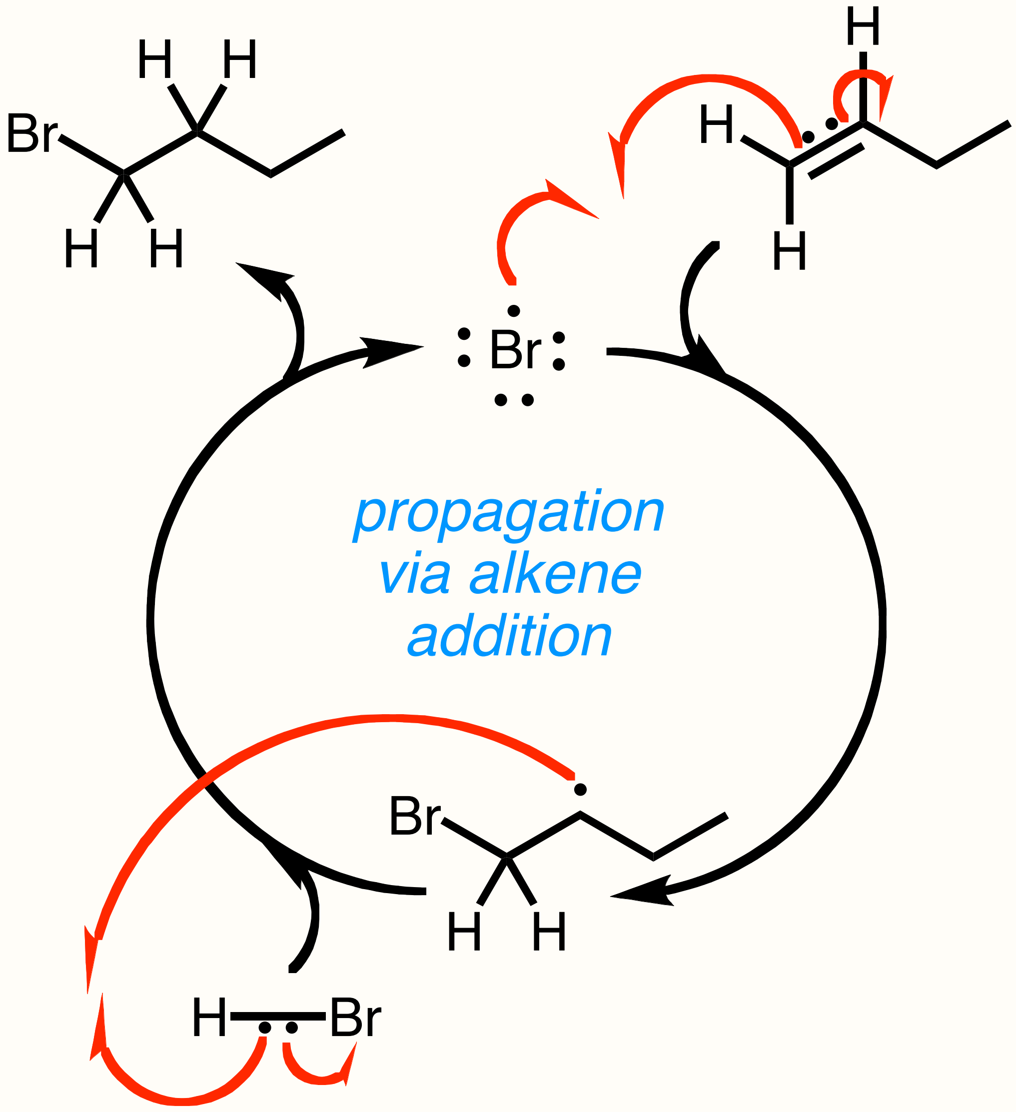
Mechanistic Rationale for Peroxide Effect

peroxides are radical *initiators*: they undergo homolysis to generate alkoxy radicals, which begin the chain mechanism



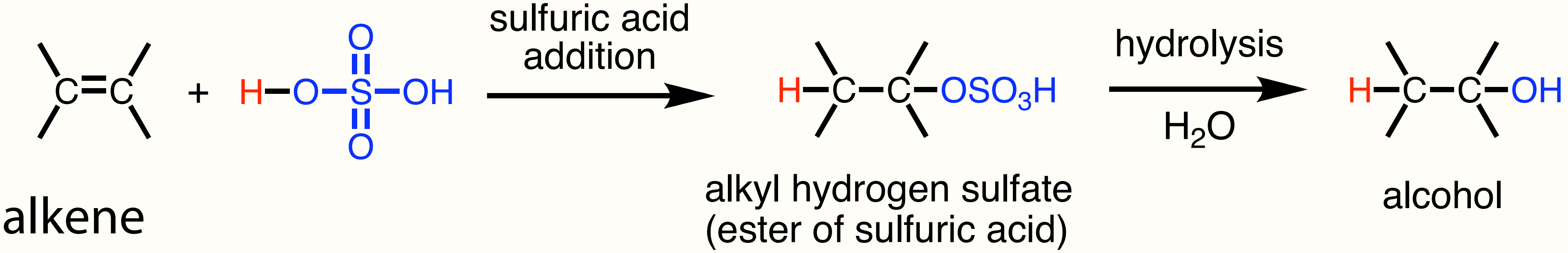


Mechanistic Rationale for Peroxide Effect



- bromine radical adds to the least substituted carbon of alkene
- this generates the most substituted and most stable alkyl radical
- alkyl radical undergoes hydrogen abstraction from HBr to generate a new bromine radical (chain mechanism)

Addition of Sulfuric Acid to Alkenes

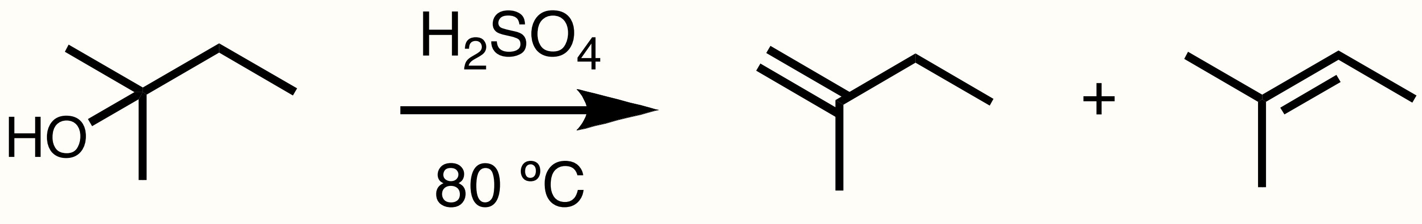


alkene

alkyl hydrogen sulfate
(ester of sulfuric acid)

alcohol

compare to:

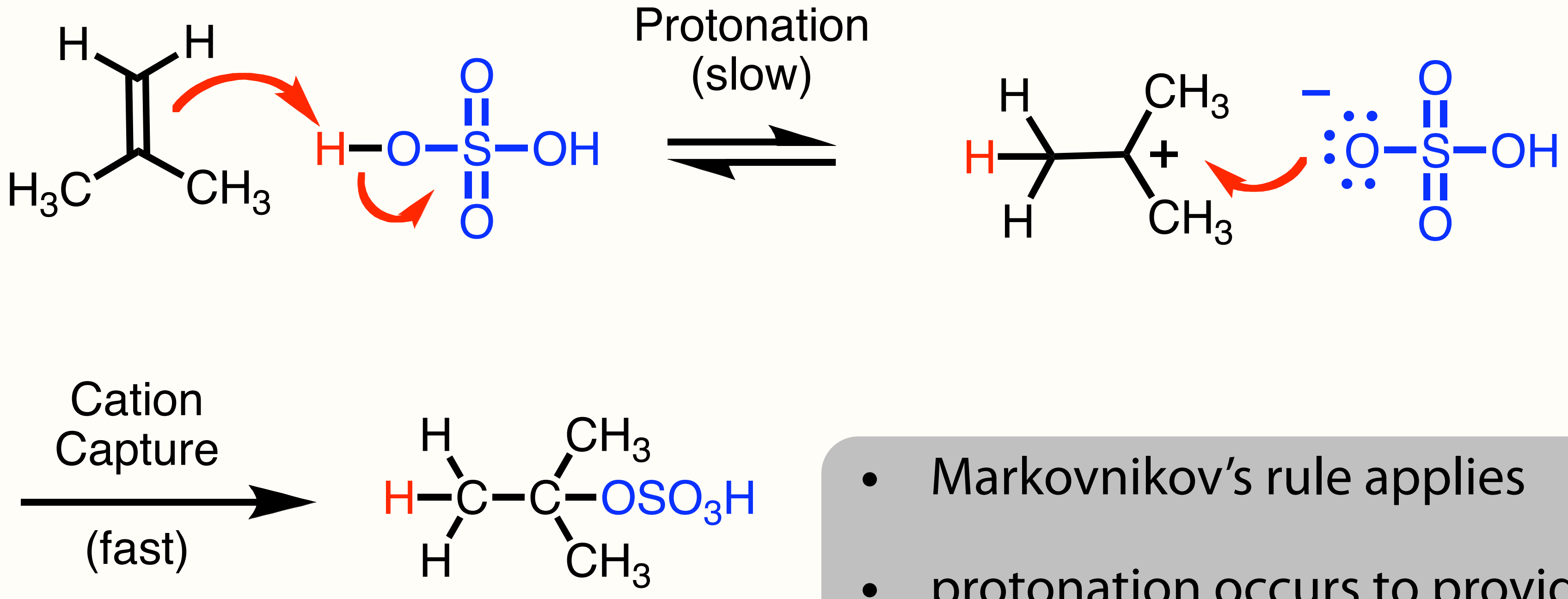


alcohol

elimination

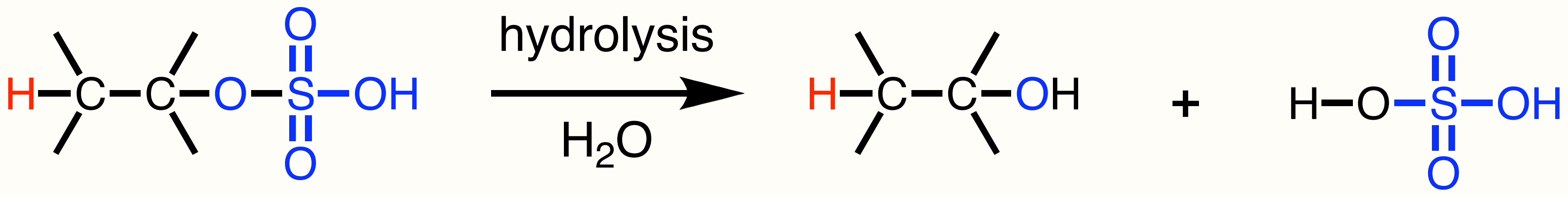
alkene(s)

Sulfuric Acid Addition: Ad_E Mechanism



- Markovnikov's rule applies
- protonation occurs to provide most stable (most substituted) carbocation
- leads to formation of most substituted alkyl hydrogen sulfate

Hydrolysis of Alkyl Hydrogen Sulfates



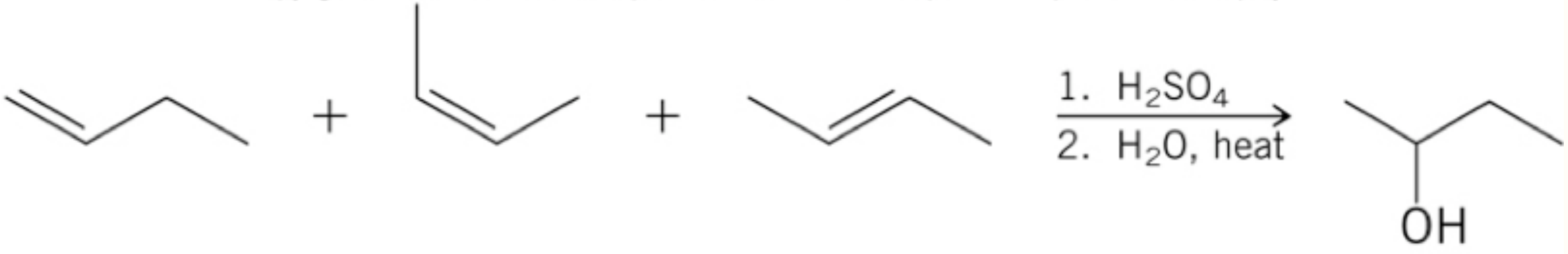
alkyl hydrogen sulfate
(ester of sulfuric acid)

alcohol

sufuric acid

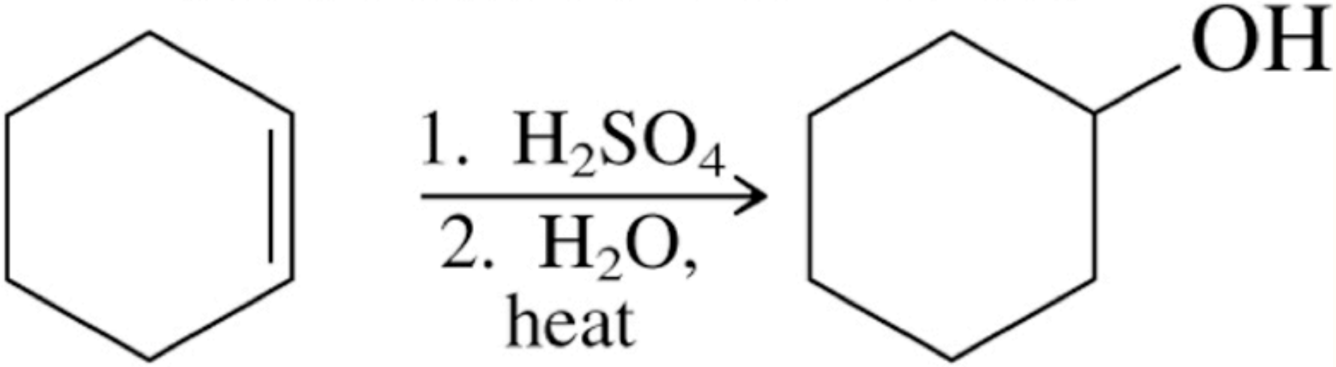
- don’t worry about mechanism for hydrolysis
- only requires hot water
- cleavage of the O-S bond
- substitution of S with H

Examples of Alkene Hydration



Mixture of 1-butene, *cis*-2-butene, and *trans*-2-butene

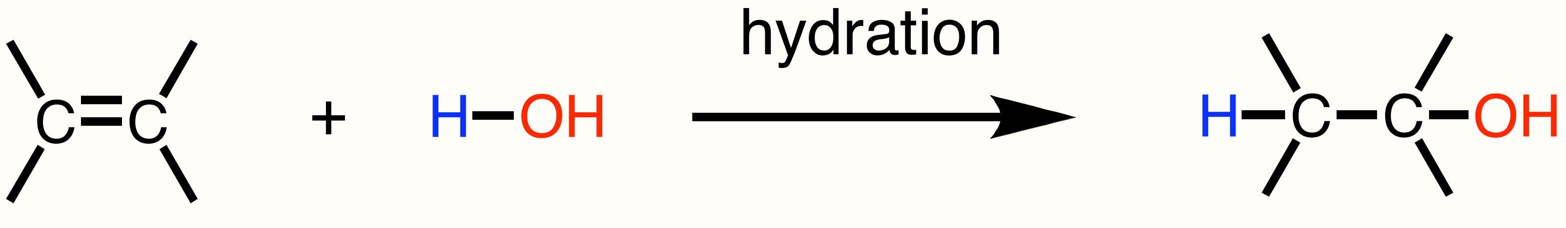
2-Butanol



Cyclohexene

Cyclohexanol
(75%)

Hydration of Alkenes (Addition of Water)

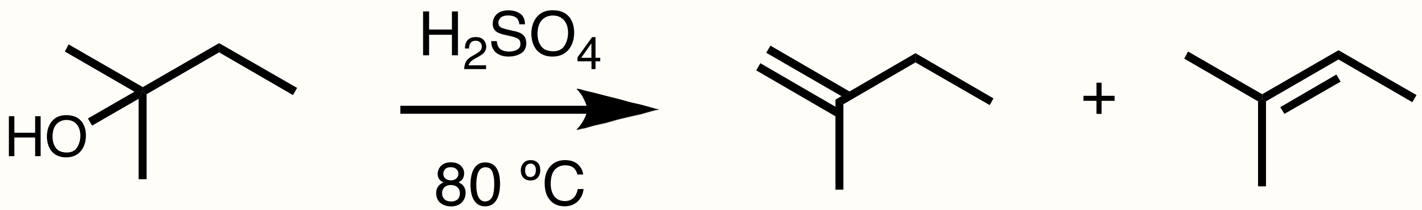


hydration

alkene

alcohol

compare to:



H_2SO_4

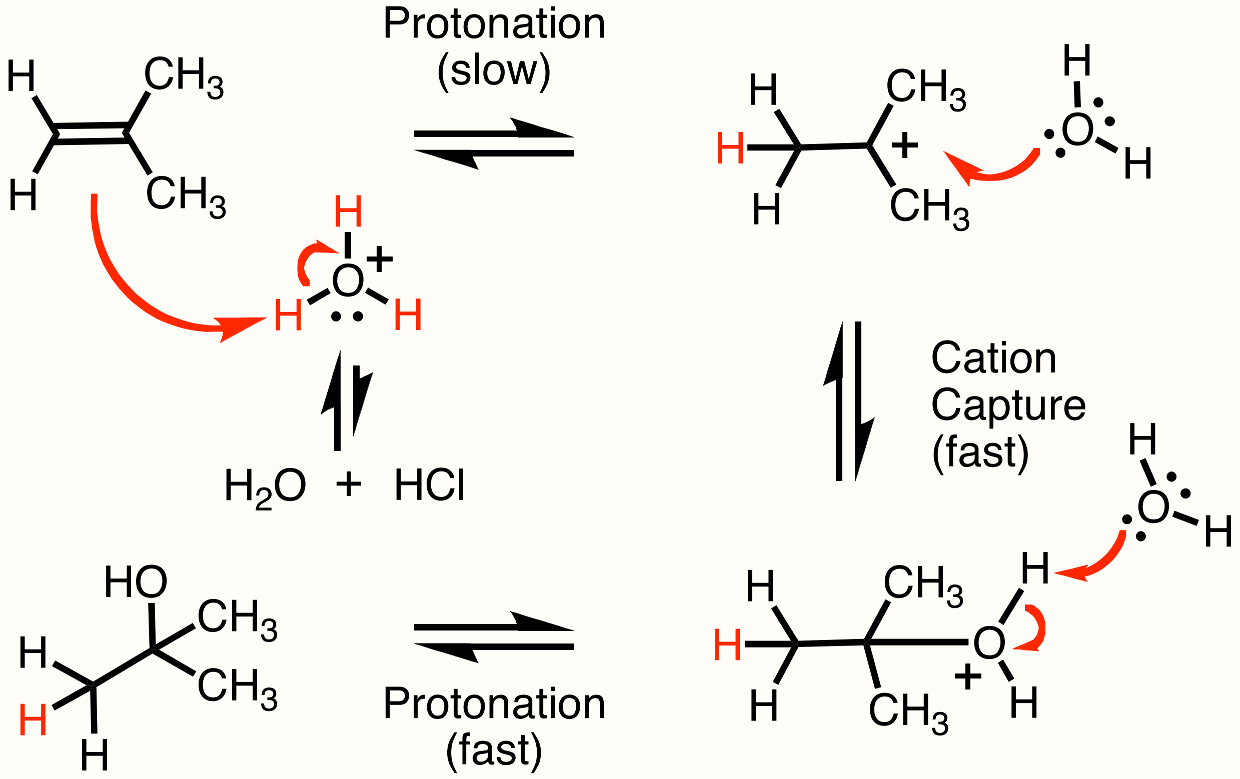
80 °C

alcohol

elimination

alkene(s)

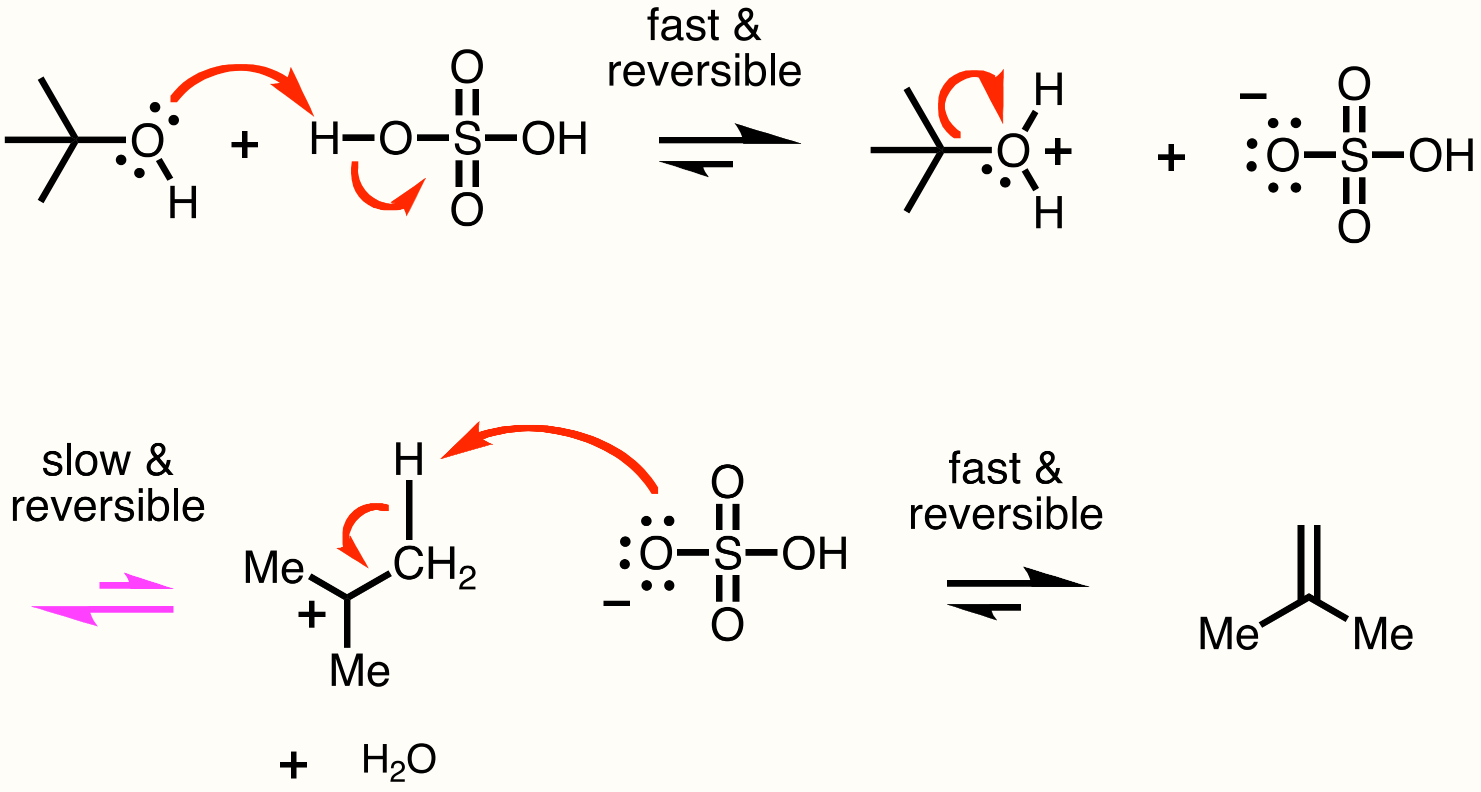
Hydration: Ad$_E$ Mechanism



Principle of Microscopic Reversibility

in an equilibrium, the forward mechanism is identical to the reverse mechanism

Hydration: Ad_E Mechanism



Principle of Microscopic Reversibility

in an equilibrium, the forward mechanism is identical to the reverse mechanism

Quiz ~~This~~ Next Week

- Topic = Chapter 5
- Alkenes Nomenclature
- Alkenes: Structure, Bonding & Stability
- Geometrical Isomerism of Alkenes (*E vs. Z*)
- Mechanism of E1 Eliminations
- Zaitsev's Rule (E1 & E2) & Stereoselectivity
- Rearrangement During Elimination
- Mechanism of E2 Eliminations

Next Lecture. . .

Chapter 6: Sections 6.12-6.22