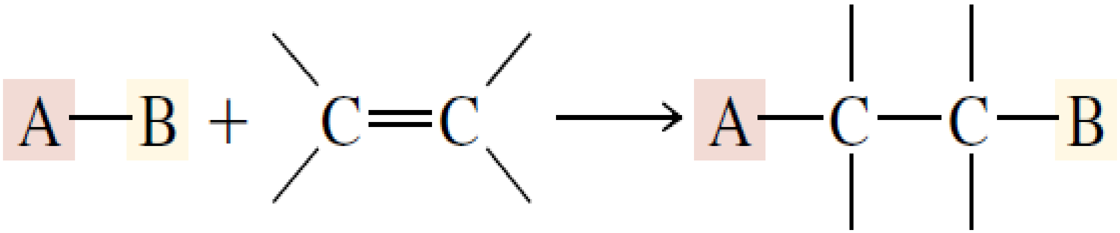
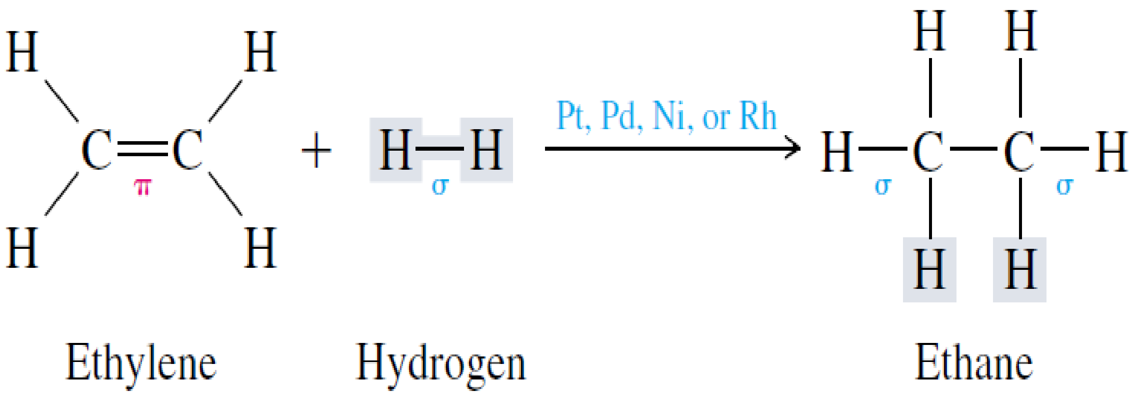
Reactions of alkenes

Unsaturated compounds



Addition reaction

Hydrogenation reaction

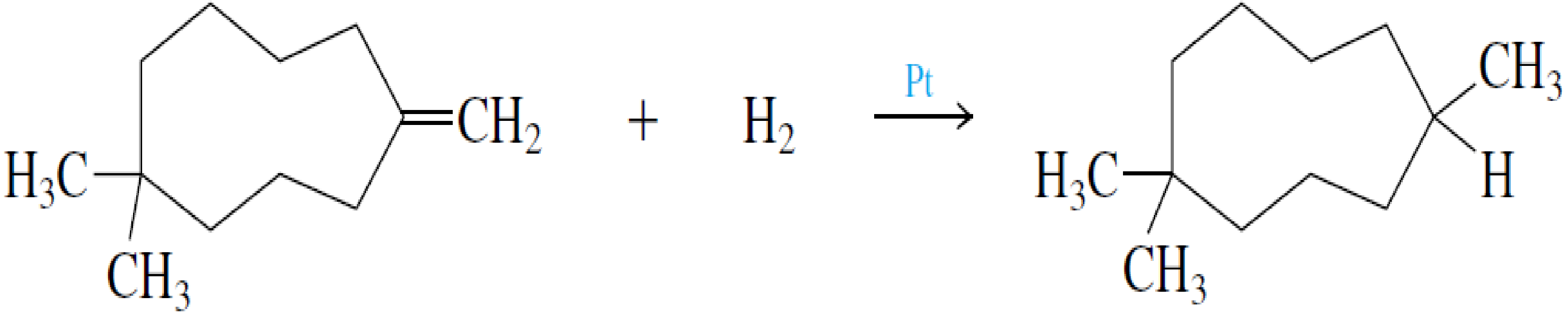


$\Delta H^\circ = -136\ \text{kJ}$
$(-32.6\ \text{kcal})$

Exothermic reaction; Heat of hydrogenation

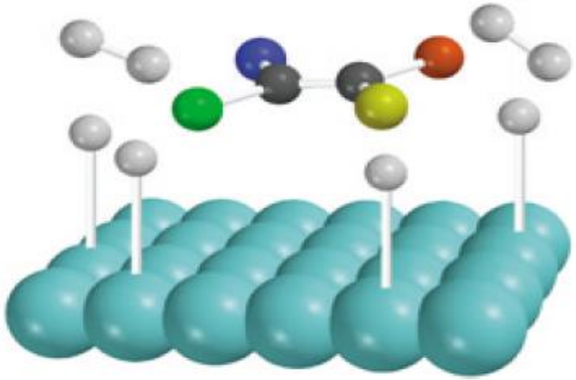
$$(CH_3)_2C{=}CHCH_3 + H_2 \xrightarrow{Pt} (CH_3)_2CHCH_2CH_3$$

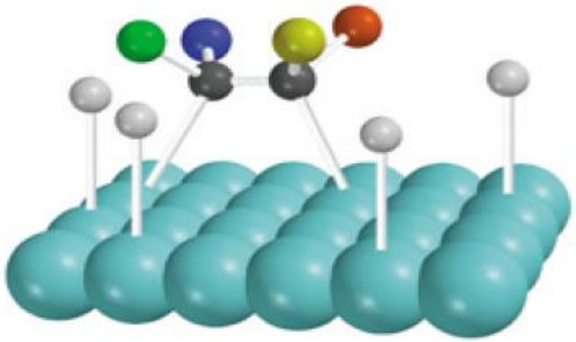
2-Methyl-2-butene Hydrogen 2-Methylbutane (100%)



5,5-Dimethyl(methylene)cyclononane Hydrogen 1,1,5-Trimethylcyclononane (73%)

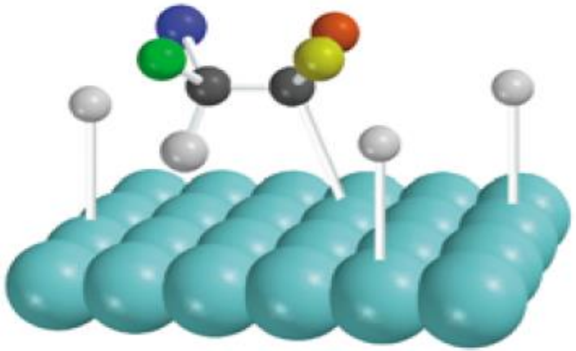
1. Heterogeneous reaction; 2. Homogeneous reaction





Step 3: A hydrogen atom is transferred from the catalyst surface to one of the carbons of the double bond.

Step 4: The second hydrogen atom is transferred, forming the alkane. The sites on the catalyst surface at which the reaction occurred are free to accept additional hydrogen and alkene molecules.



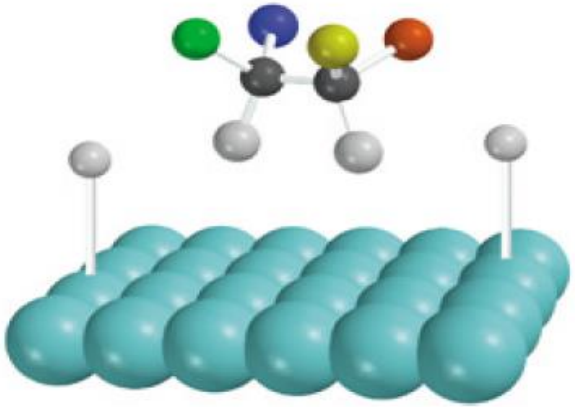


FIGURE 6.2 Heats of hydrogenation of butene isomers plotted on a common scale. All energies are in kilojoules per mole.

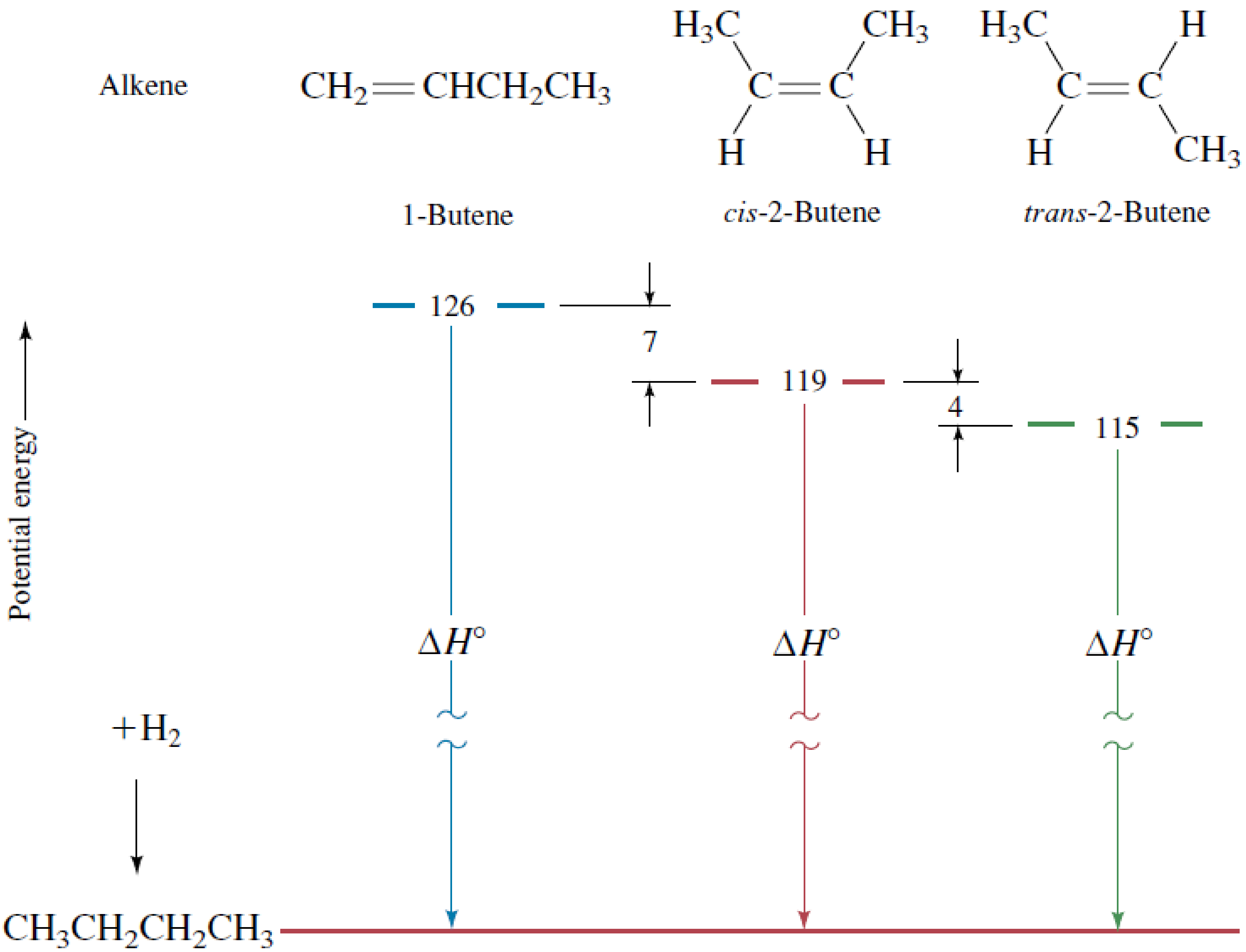
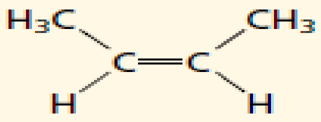
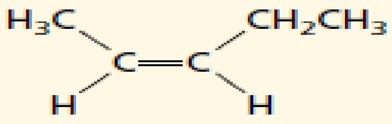
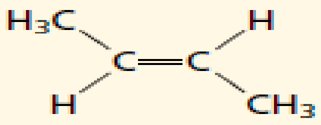
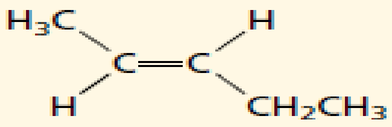
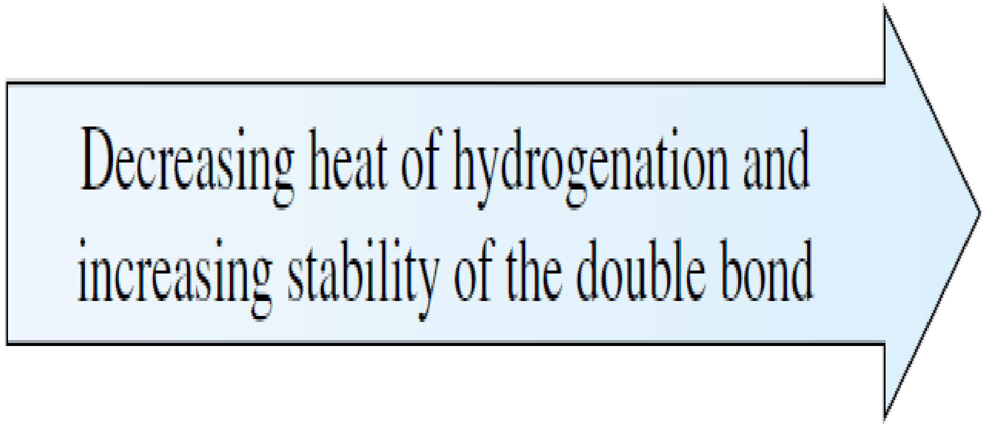


TABLE 6.1 Heats of Hydrogenation of Some Alkenes

Alkene	Structure	Heat of hydrogenation kJ/mol	Heat of hydrogenation kcal/mol
Ethylene	$CH_2{=}CH_2$	136	32.6
Monosubstituted alkenes			
Propene	$CH_2{=}CHCH_3$	125	29.9
1-Butene	$CH_2{=}CHCH_2CH_3$	126	30.1
1-Hexene	$CH_2{=}CHCH_2CH_2CH_2CH_3$	126	30.2
Cis-disubstituted alkenes			
cis-2-Butene		119	28.4
cis-2-Pentene		117	28.1
Trans-disubstituted alkenes			
trans-2-Butene		115	27.4
trans-2-Pentene		114	27.2
Trisubstituted alkenes			
2-Methyl-2-pentene	$(CH_3)_2C{=}CHCH_2CH_3$	112	26.7
Tetrasubstituted alkenes			
2,3-Dimethyl-2-butene	$(CH_3)_2C{=}C(CH_3)_2$	110	26.4

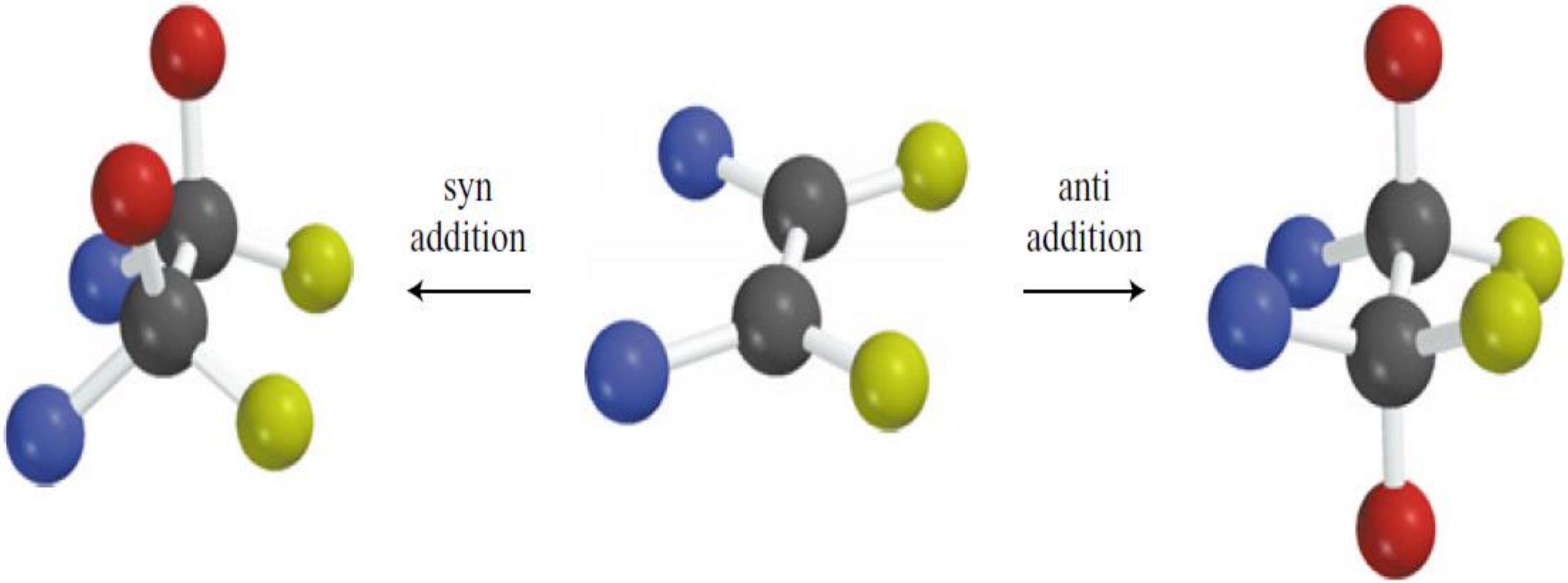


Decreasing heat of hydrogenation and increasing stability of the double bond

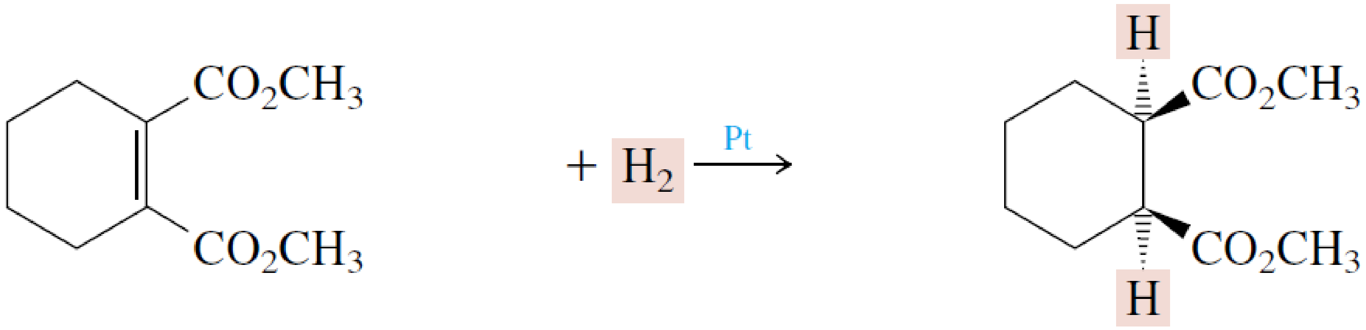
$CH_2{=}CH_2$	$RCH{=}CH_2$	$RCH{=}CHR$	$R_2C{=}CHR$	$R_2C{=}CR_2$
Ethylene	Monosubstituted	Disubstituted	Trisubstituted	Tetrasubstituted

Stereochemistry of alkenes hydrogenation

1. Syn addition
2. Anti addition

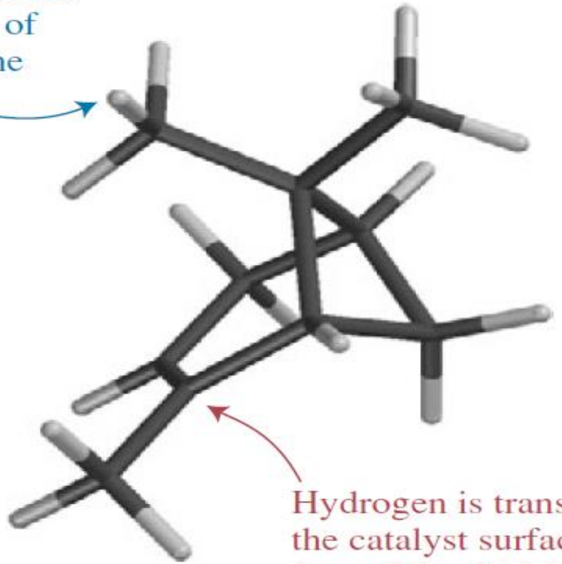


Stereoselective reaction



Dimethyl cyclohexene-1,2-dicarboxylate

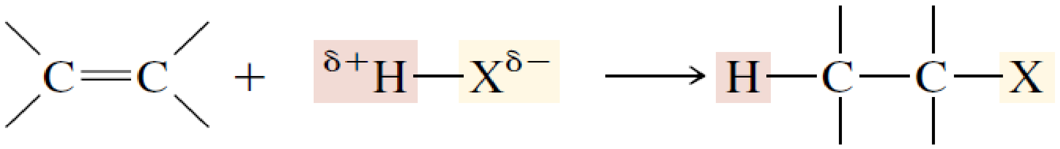
Dimethyl
cyclohexane-*cis*-1,2-dicarboxylate (100%)

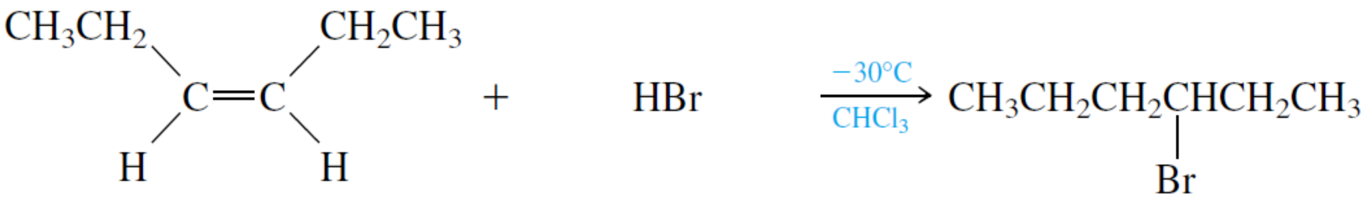


This methyl group blocks approach of top face of the double bond to the catalyst surface

Hydrogen is transferred from the catalyst surface to the bottom face of the double bond—this is the "less hindered side"

Electrophilic addition reactions





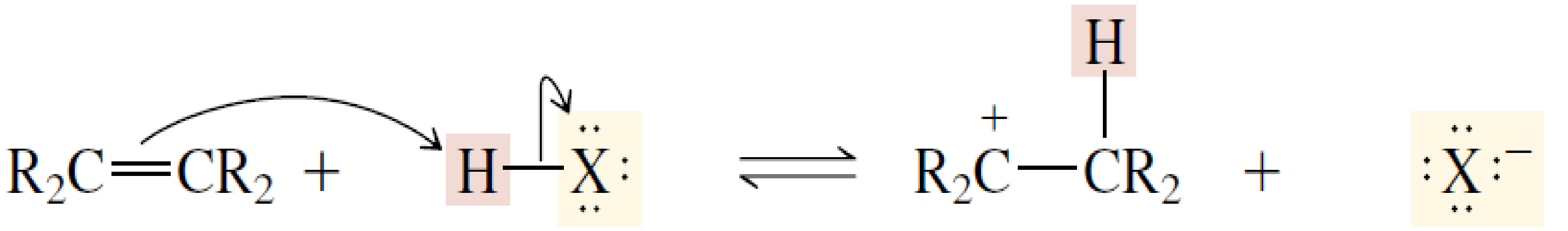
Increasing reactivity of hydrogen halides in addition to alkenes

$HF << HCl < HBr < HI$

Slowest rate of addition;
least acidic

Fastest rate of addition;
most acidic

Regioselectivity

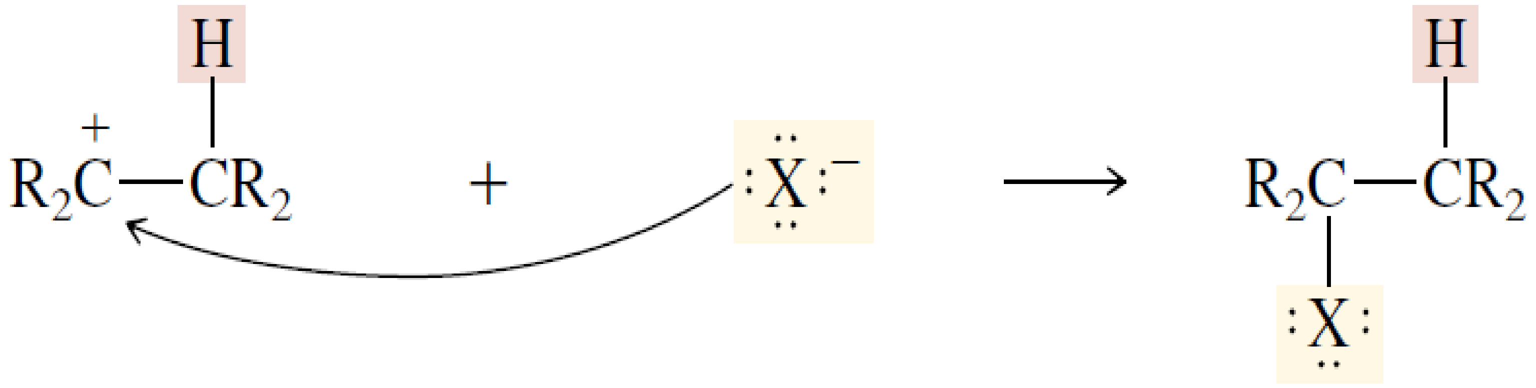


Alkene (base)

Hydrogen halide (acid)

Carbocation (conjugate acid)

Anion (conjugate base)

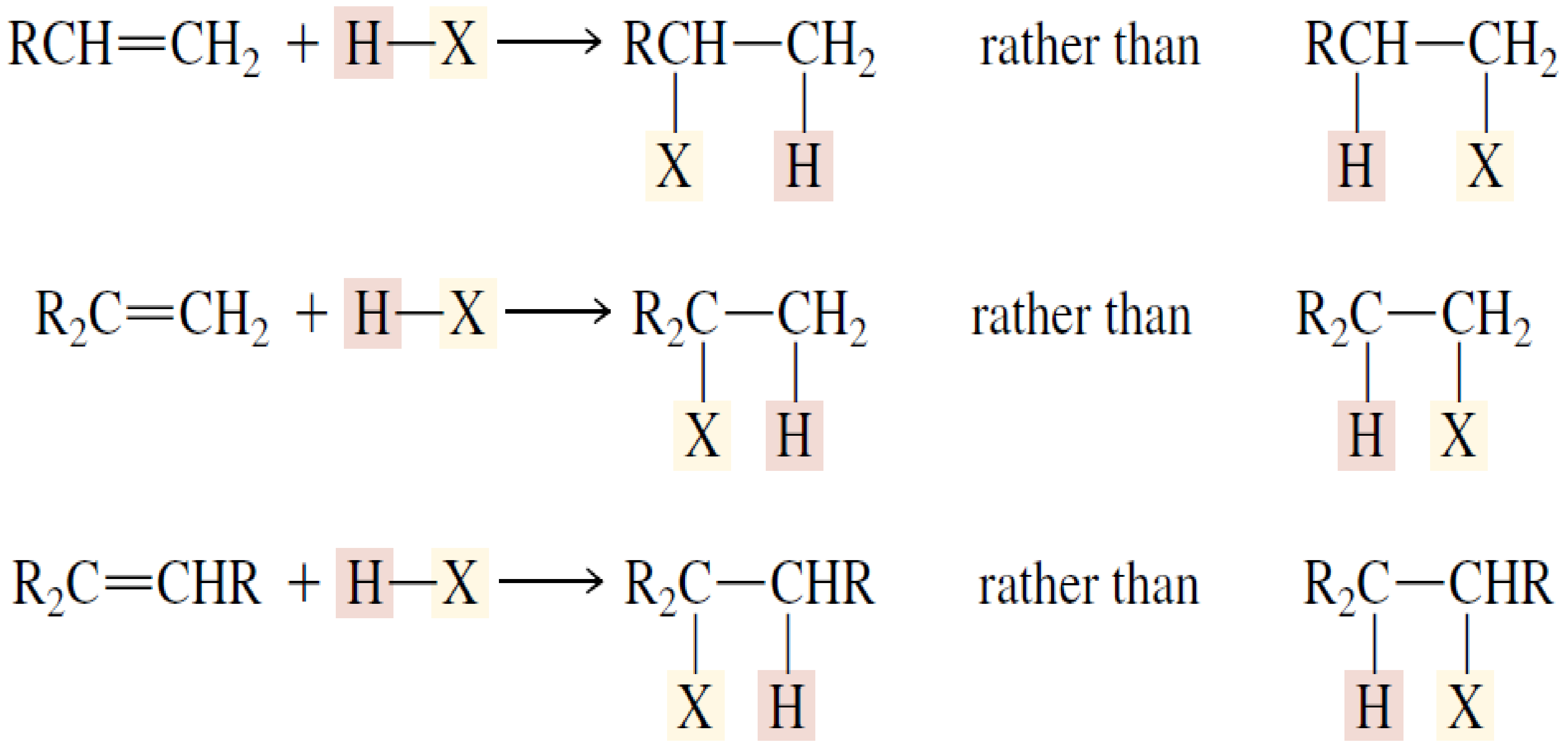


Carbocation (electrophile)

Halide ion (nucleophile)

Alkyl halide

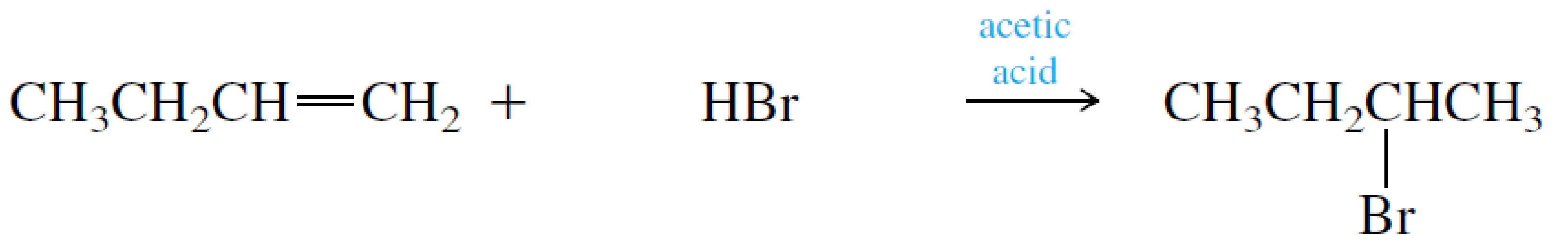
Markovnikov’s rule



$$\mathrm{RCH{=}CH_2} + \mathrm{H{-}X} \longrightarrow \underset{\mathrm{X}}{\mathrm{RCH}}{-}\underset{\mathrm{H}}{\mathrm{CH_2}} \quad \text{rather than} \quad \underset{\mathrm{H}}{\mathrm{RCH}}{-}\underset{\mathrm{X}}{\mathrm{CH_2}}$$

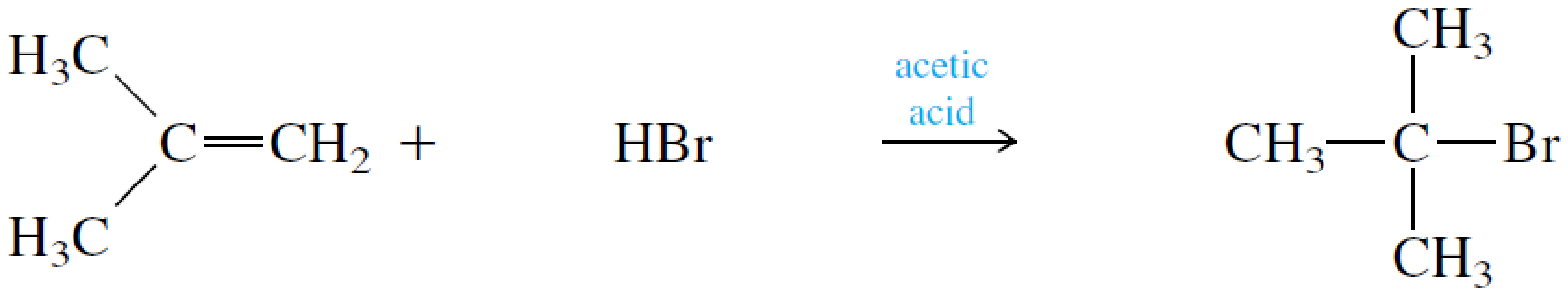
$$\mathrm{R_2C{=}CH_2} + \mathrm{H{-}X} \longrightarrow \underset{\mathrm{X}}{\mathrm{R_2C}}{-}\underset{\mathrm{H}}{\mathrm{CH_2}} \quad \text{rather than} \quad \underset{\mathrm{H}}{\mathrm{R_2C}}{-}\underset{\mathrm{X}}{\mathrm{CH_2}}$$

$$\mathrm{R_2C{=}CHR} + \mathrm{H{-}X} \longrightarrow \underset{\mathrm{X}}{\mathrm{R_2C}}{-}\underset{\mathrm{H}}{\mathrm{CHR}} \quad \text{rather than} \quad \underset{\mathrm{H}}{\mathrm{R_2C}}{-}\underset{\mathrm{X}}{\mathrm{CHR}}$$



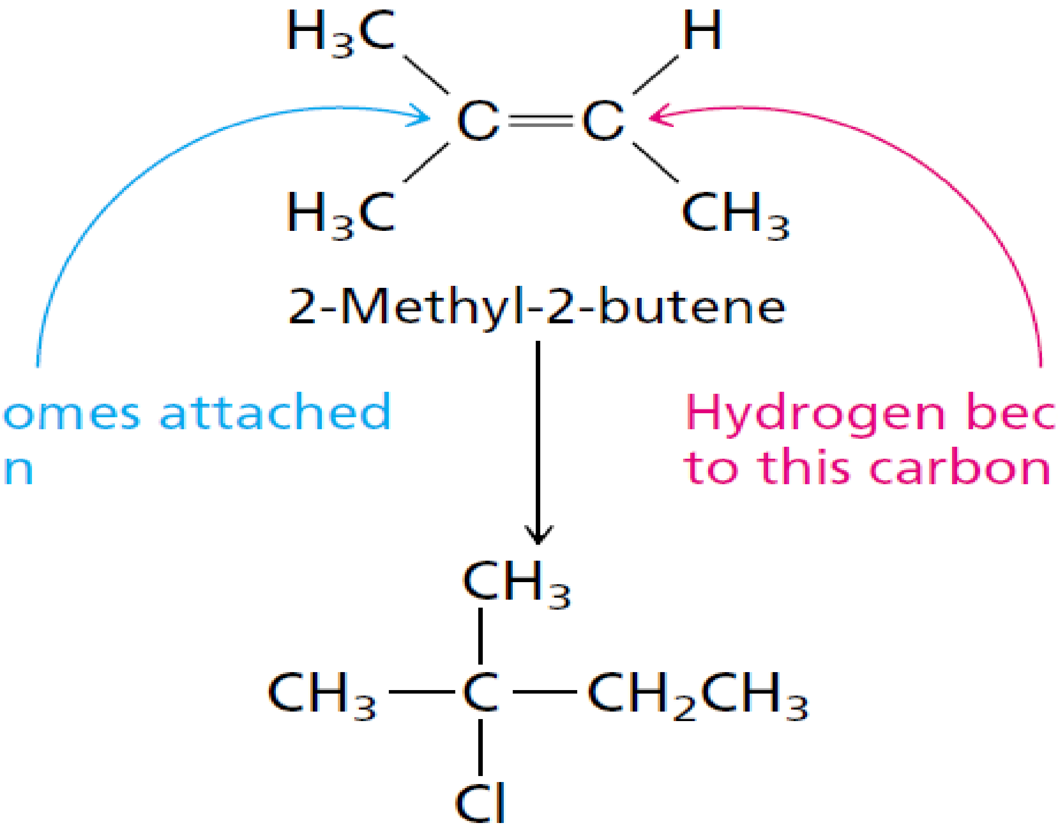
$$CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{acetic acid}} CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$$

1-Butene Hydrogen bromide 2-Bromobutane (80%)



2-Methylpropene Hydrogen bromide 2-Bromo-2-methylpropane (90%)

1-Methylcyclopentene Hydrogen chloride 1-Chloro-1-methylcyclopentane (100%)



2-Methyl-2-butene

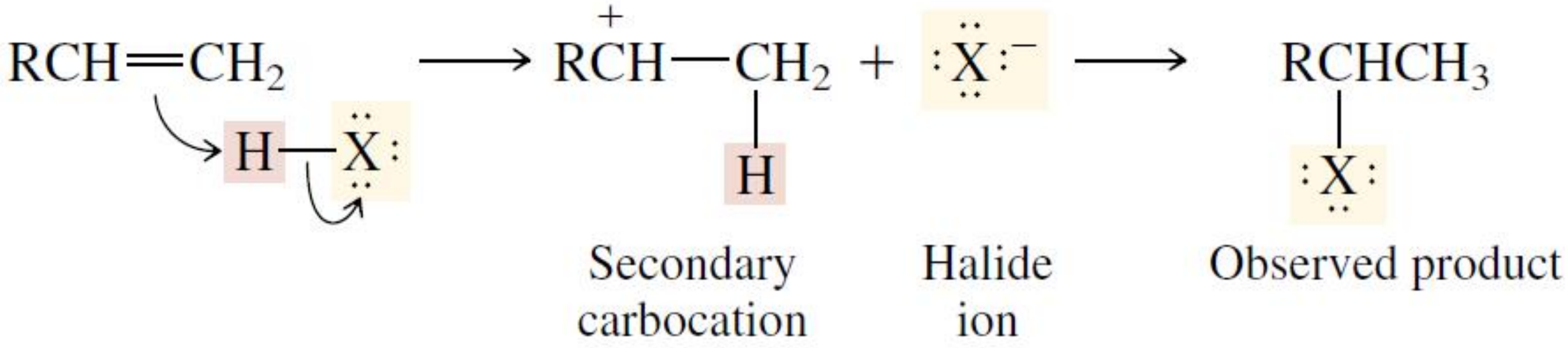
Chlorine becomes attached to this carbon

Hydrogen becomes attached to this carbon

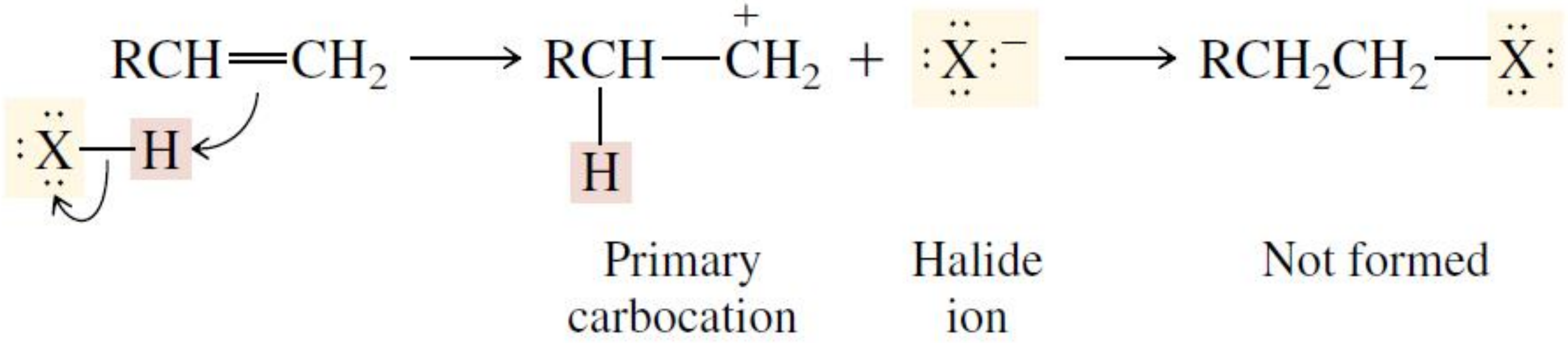
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-CH_2CH_3$$

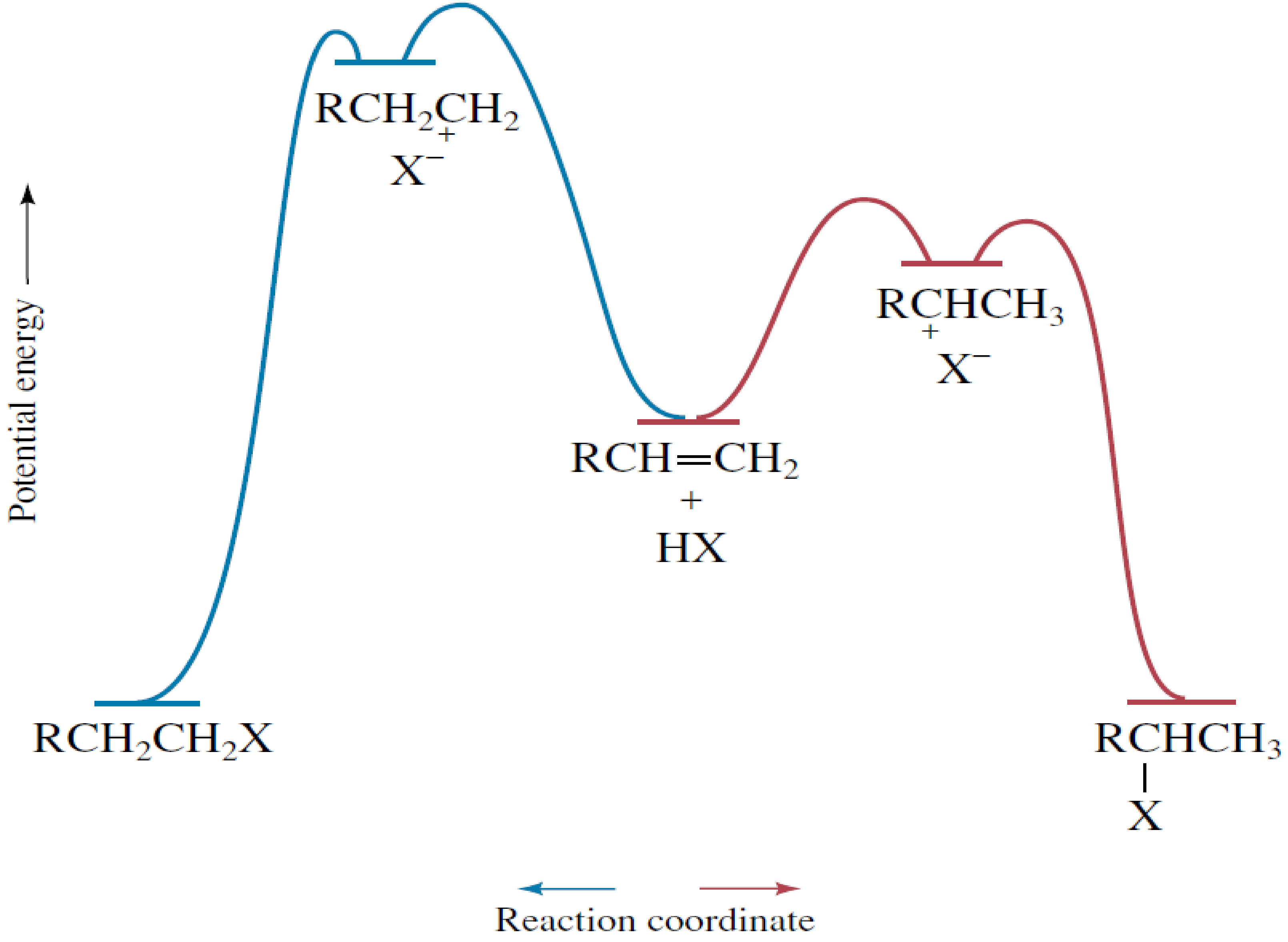
2-Chloro-2-methylbutane
(major product from Markovnikov addition of hydrogen chloride to 2-methyl-2-butene)

Mechanism



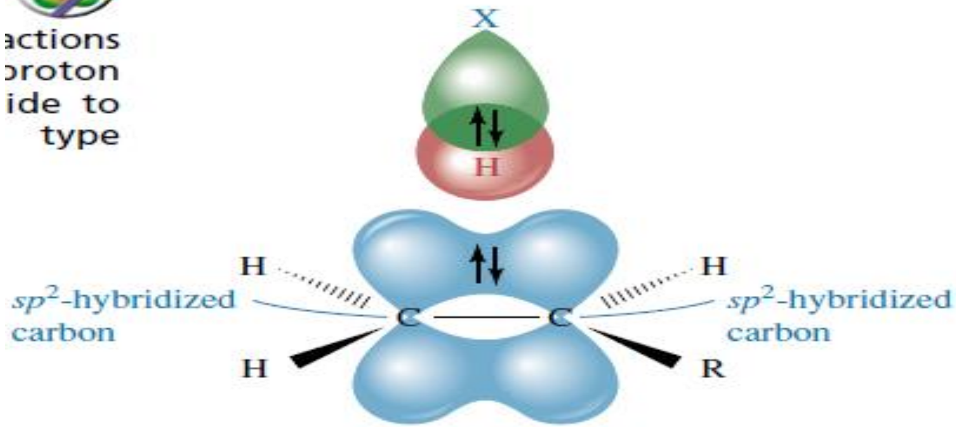
(b) *Addition opposite to Markovnikov's rule:*



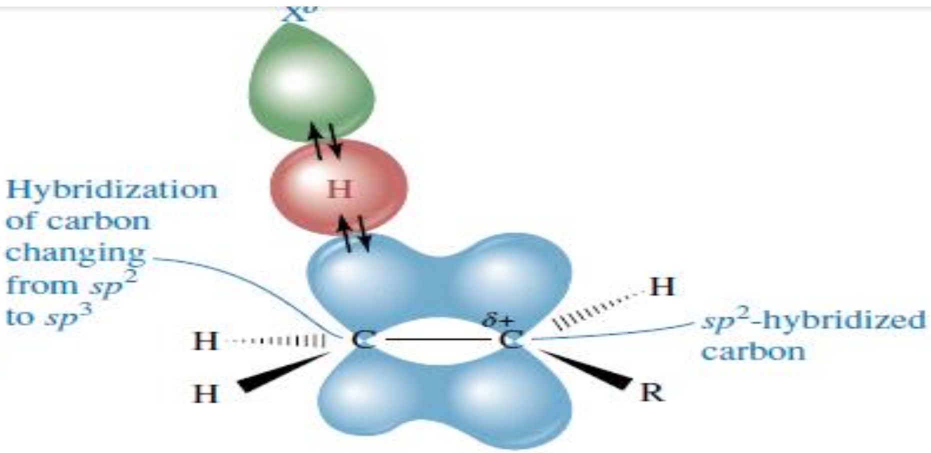


Potential energy
RCH2CH2X
RCH2CH2 + X−
RCH=CH2 + HX
RCHCH3 + X−
RCHCH3 | X
Reaction coordinate

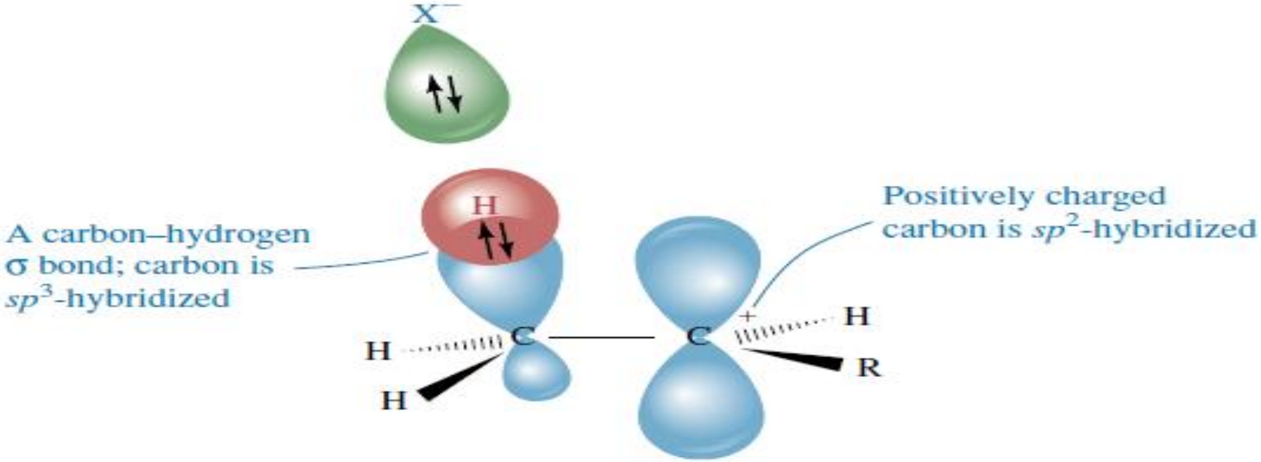
actions
roton
ide to
type



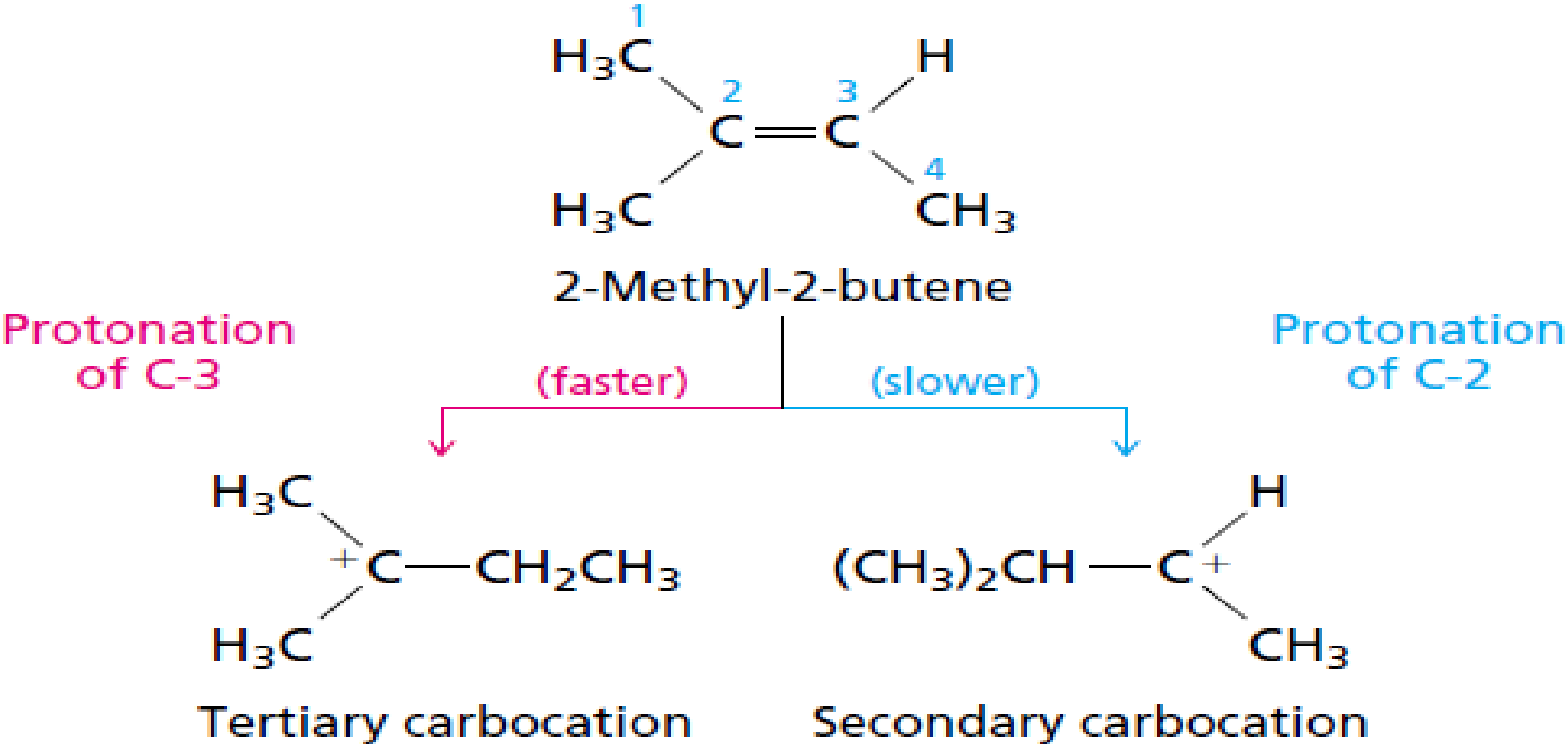
(*a*) The hydrogen halide (HX) and the alkene ($CH_2{=}CHR$) approach each other. The electrophile is the hydrogen halide, and the site of electrophilic attack is the orbital containing the σ electrons of the double bond.



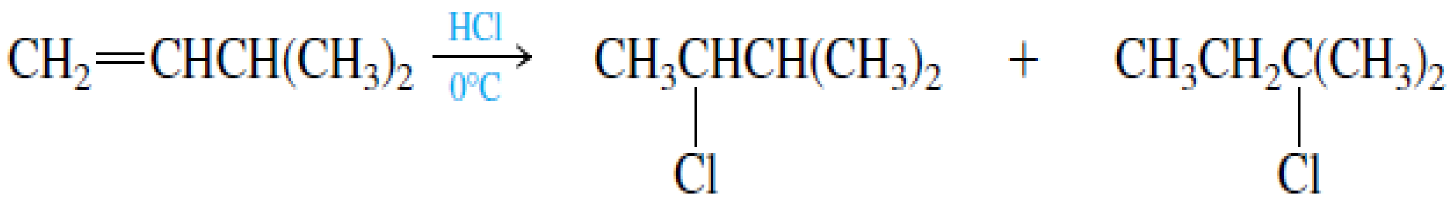
(*b*) Electrons flow from the π orbital of the alkene to the hydrogen halide. The π electrons flow in the direction that generates a partial positive charge on the carbon atom that bears the electron-releasing alkyl group (R). The hydrogen–halogen bond is partially broken and a C—H σ bond is partially formed at the transition state.



(*c*) Loss of the halide ion (X^-) from the hydrogen halide and C—H σ bond formation complete the formation of the more stable carbocation intermediate $CH_3\overset{+}{C}HR$.


1
2
3
4
H₃C
H₃C
H
CH₃
2-Methyl-2-butene
Protonation of C-3
(faster)
(slower)
Protonation of C-2
Tertiary carbocation
Secondary carbocation
(CH₃)₂CH

Rearrangement



$$\mathrm{CH_2{=}CHCH(CH_3)_2 \xrightarrow[0^\circ C]{HCl} CH_3\underset{\mid\atop Cl}{C}HCH(CH_3)_2 + CH_3CH_2\underset{\mid\atop Cl}{C}(CH_3)_2}$$

3-Methyl-1-butene

2-Chloro-3-methylbutane (40%)

2-Chloro-2-methylbutane (60%)

$$\mathrm{CH_3\overset{+}{C}H{-}\underset{\mid\atop H}{C}(CH_3)_2 \xrightarrow{hydride\ shift} CH_3\underset{\mid\atop H}{C}H{-}\overset{+}{C}(CH_3)_2}$$

1,2-Dimethylpropyl cation (secondary)

1,1-Dimethylpropyl cation (tertiary)

Free radical reactions

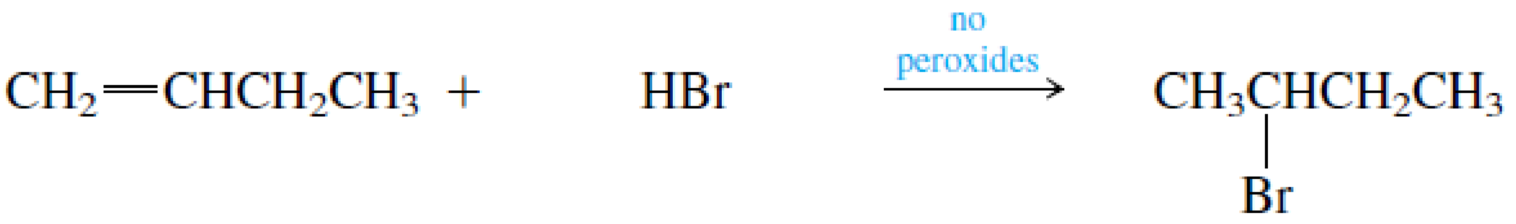
$$CH_2{=}CHCH_2CH_3 + HBr \xrightarrow{\text{peroxides}} BrCH_2CH_2CH_2CH_3$$

1-Butene

Hydrogen bromide

1-Bromobutane

(only product; 95% yield)



$$CH_2{=}CHCH_2CH_3 + HBr \xrightarrow{\text{no peroxides}} CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$$

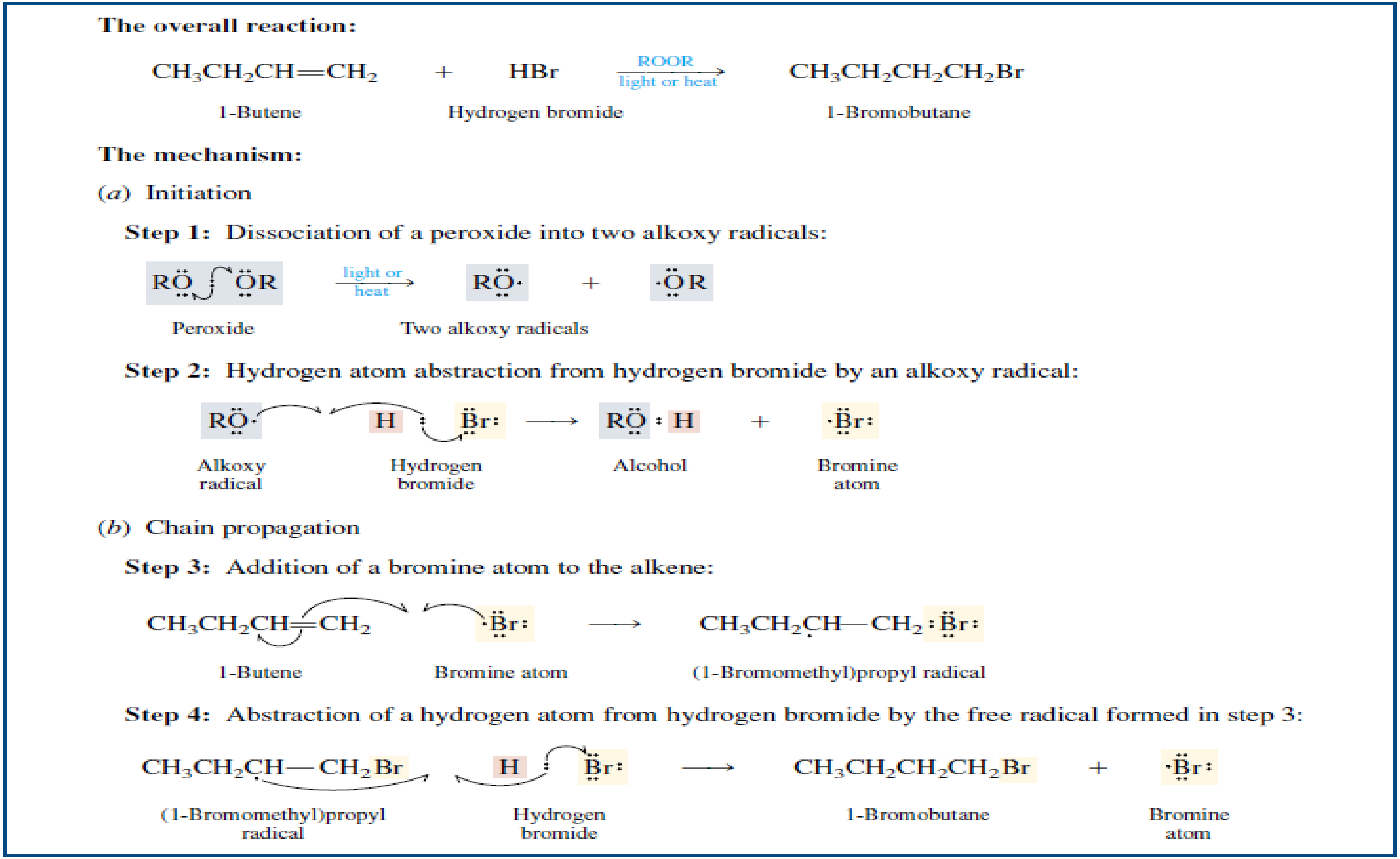
1-Butene

Hydrogen bromide

2-Bromobutane

(only product; 90% yield)

Peroxide effect (R-O-O-R); Anti Markovnikov’s rule; Kharash’s rule



The overall reaction:

$$CH_3CH_2CH{=}CH_2 \quad + \quad HBr \quad \xrightarrow[\text{light or heat}]{ROOR} \quad CH_3CH_2CH_2CH_2Br$$

1-Butene — Hydrogen bromide — 1-Bromobutane

The mechanism:

(*a*) Initiation

Step 1: Dissociation of a peroxide into two alkoxy radicals:

$$R\ddot{O}{-}\ddot{O}R \xrightarrow[\text{heat}]{\text{light or}} R\ddot{O}\cdot \; + \; \cdot\ddot{O}R$$

Peroxide — Two alkoxy radicals

Step 2: Hydrogen atom abstraction from hydrogen bromide by an alkoxy radical:

$$R\ddot{O}\cdot \quad H{:}\ddot{B}r{:} \longrightarrow R\ddot{O}{:}H \; + \; \cdot\ddot{B}r{:}$$

Alkoxy radical — Hydrogen bromide — Alcohol — Bromine atom

(*b*) Chain propagation

Step 3: Addition of a bromine atom to the alkene:

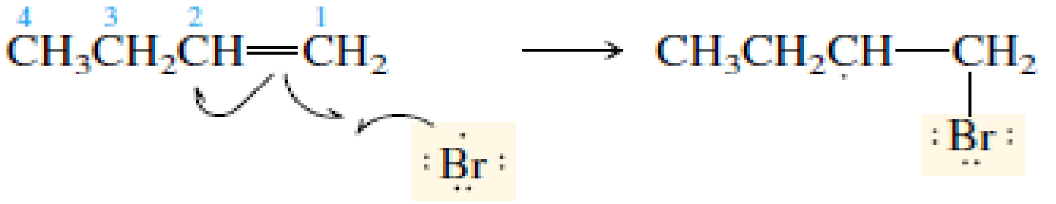
$$CH_3CH_2CH{=}CH_2 \quad \cdot\ddot{B}r{:} \longrightarrow CH_3CH_2\dot{C}H{-}CH_2{:}\ddot{B}r{:}$$

1-Butene — Bromine atom — (1-Bromomethyl)propyl radical

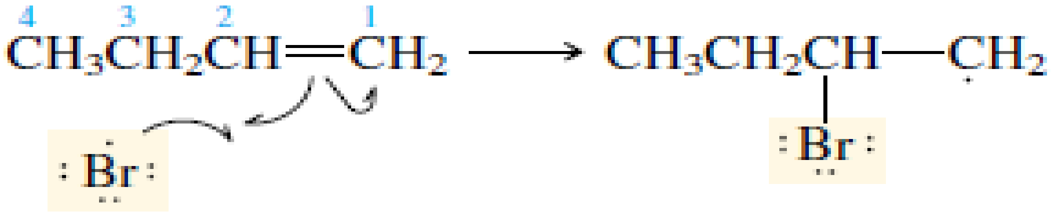
Step 4: Abstraction of a hydrogen atom from hydrogen bromide by the free radical formed in step 3:

$$CH_3CH_2\dot{C}H{-}CH_2Br \quad H{:}\ddot{B}r{:} \longrightarrow CH_3CH_2CH_2CH_2Br \; + \; \cdot\ddot{B}r{:}$$

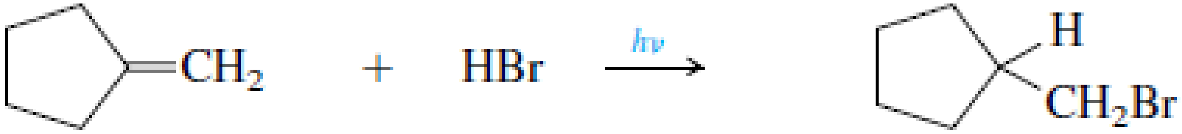
(1-Bromomethyl)propyl radical — Hydrogen bromide — 1-Bromobutane — Bromine atom



Secondary alkyl radical



Primary alkyl radical

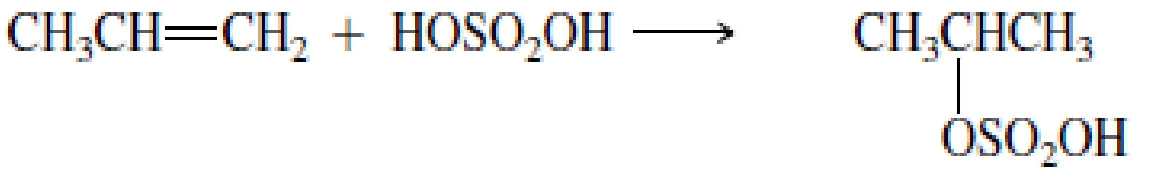


Methylenecyclopentane

Hydrogen bromide

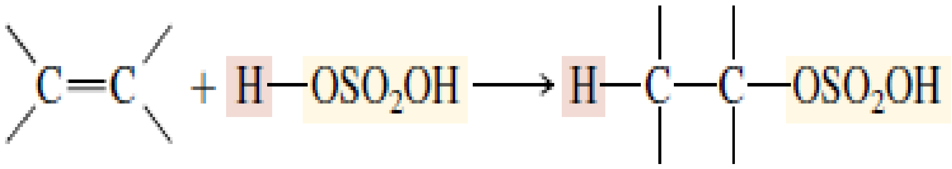
(Bromomethyl)cyclopentane (60%)

Addition of sulfuric acid

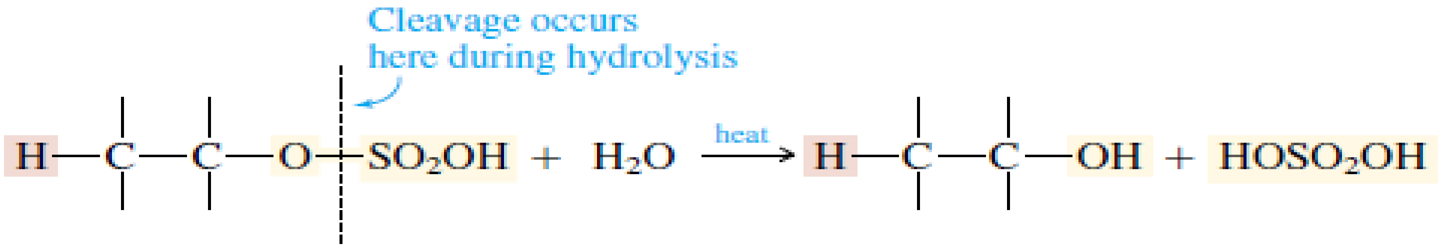


$$CH_3CH{=}CH_2 + HOSO_2OH \longrightarrow \underset{\displaystyle OSO_2OH}{CH_3\underset{|}{C}HCH_3}$$

Propene Sulfuric acid Isopropyl hydrogen sulfate



Alkene Sulfuric acid Alkyl hydrogen sulfate



Cleavage occurs here during hydrolysis

Alkyl hydrogen sulfate Water Alcohol Sulfuric acid

The overall reaction:

$$CH_3CH{=}CH_2 \quad + \quad HOSO_2OH \quad \longrightarrow \quad (CH_3)_2CHOSO_2OH$$

Propene — Sulfuric acid — Isopropyl hydrogen sulfate

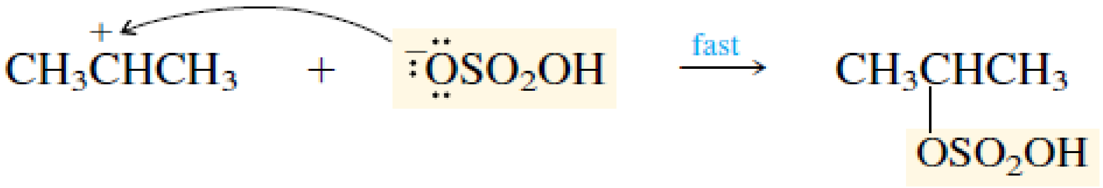
The mechanism:

Step 1: Protonation of the carbon–carbon double bond in the direction that leads to the more stable carbocation:

$$CH_3CH{=}CH_2 \quad + \quad H{-}\ddot{\underset{..}{O}}SO_2OH \quad \overset{\text{slow}}{\rightleftharpoons} \quad CH_3\overset{+}{C}HCH_3 \quad + \quad {}^{-}\!:\!\ddot{\underset{..}{O}}SO_2OH$$

Propene — Sulfuric acid — Isopropyl cation — Hydrogen sulfate ion

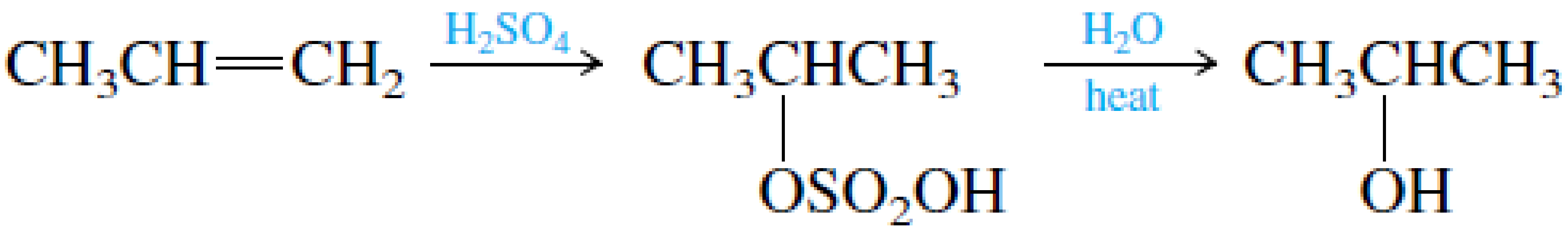
Step 2: Carbocation–anion combination



$$CH_3\overset{+}{C}HCH_3 \quad + \quad {}^{-}\!:\!\ddot{\underset{..}{O}}SO_2OH \quad \xrightarrow{\text{fast}} \quad CH_3\underset{\displaystyle OSO_2OH}{\underset{|}{C}}HCH_3$$

Isopropyl cation — Hydrogen sulfate ion — Isopropyl hydrogen sulfate

Hydration

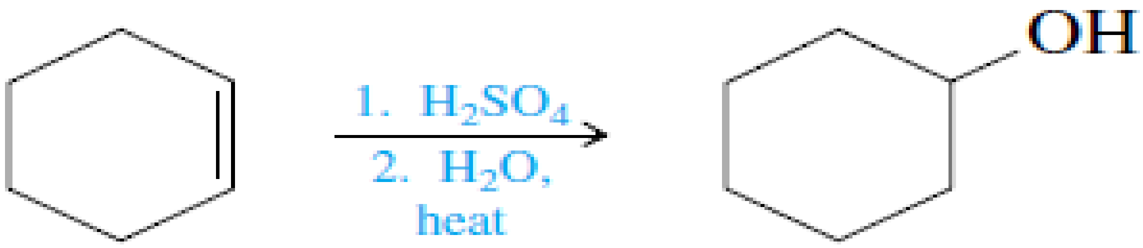


$$\mathrm{CH_3CH{=}CH_2} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{CH_3}\underset{\substack{|\\ \mathrm{OSO_2OH}}}{\mathrm{CH}}\mathrm{CH_3} \xrightarrow[\text{heat}]{\mathrm{H_2O}} \mathrm{CH_3}\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH}}\mathrm{CH_3}$$

Propene

Isopropyl hydrogen sulfate

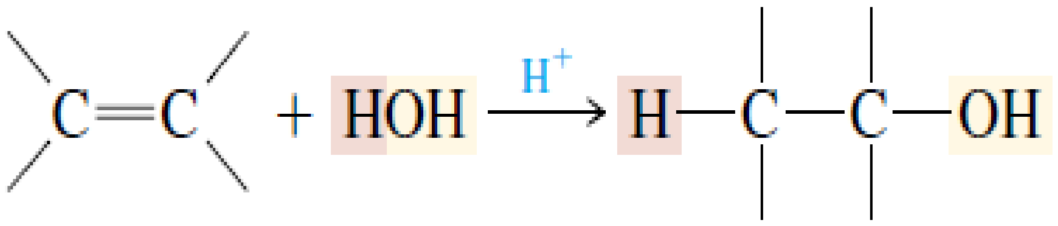
Isopropyl alcohol



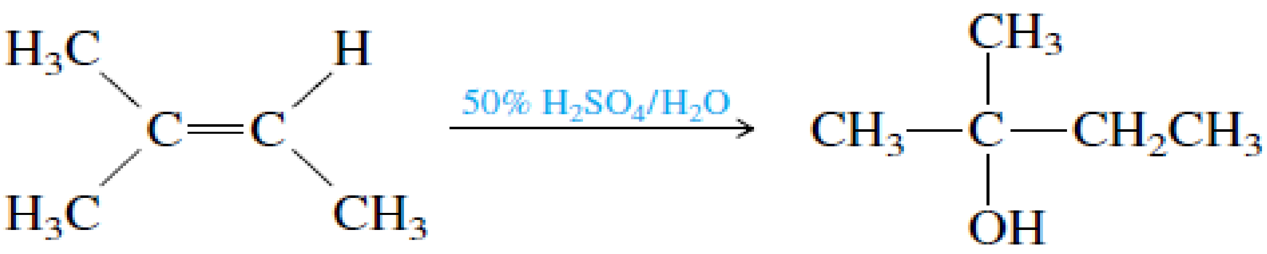
Cyclohexene

Cyclohexanol (75%)

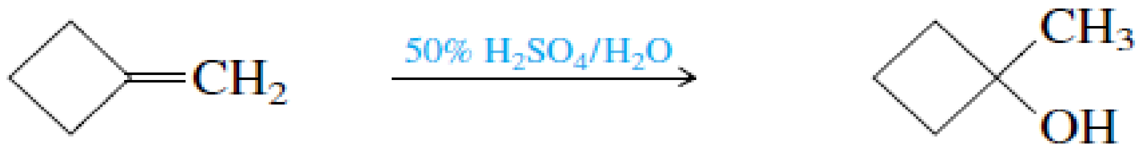
Acid catalyzed hydration



Alkene Water Alcohol



2-Methyl-2-butene 2-Methyl-2-butanol (90%)



Methylenecyclobutane 1-Methylcyclobutanol (80%)

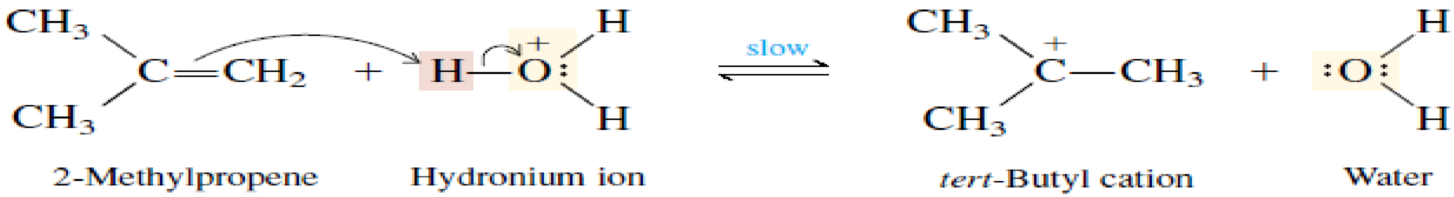
The overall reaction:

$$(CH_3)_2C{=}CH_2 \quad + \quad H_2O \xrightarrow{H_3O^+} (CH_3)_3COH$$

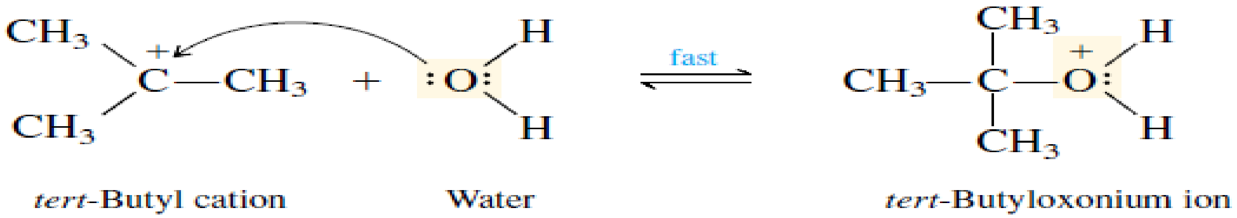
2-Methylpropene   Water   *tert*-Butyl alcohol

The mechanism:

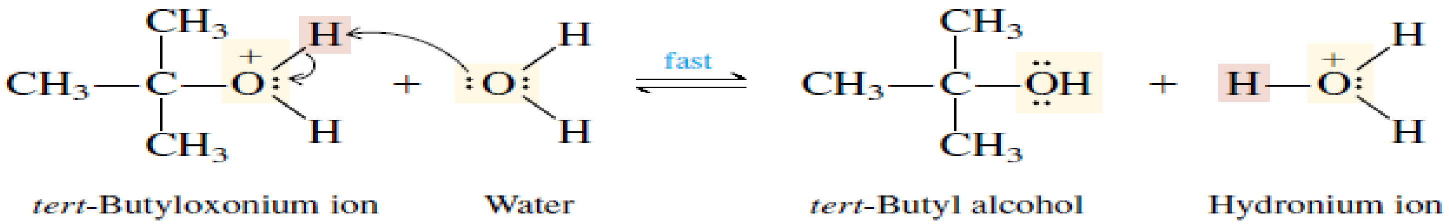
Step 1: Protonation of the carbon–carbon double bond in the direction that leads to the more stable carbocation:



Step 2: Water acts as a nucleophile to capture *tert*-butyl cation:



Step 3: Deprotonation of *tert*-butyloxonium ion. Water acts as a Brønsted base:



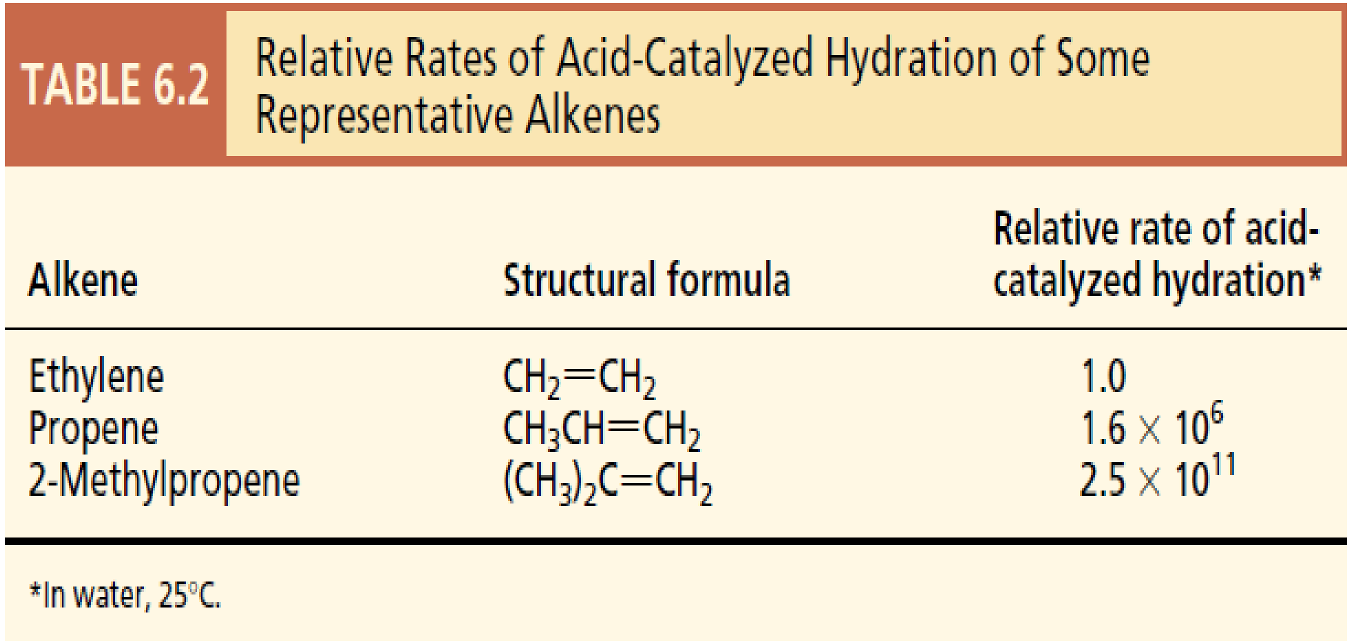
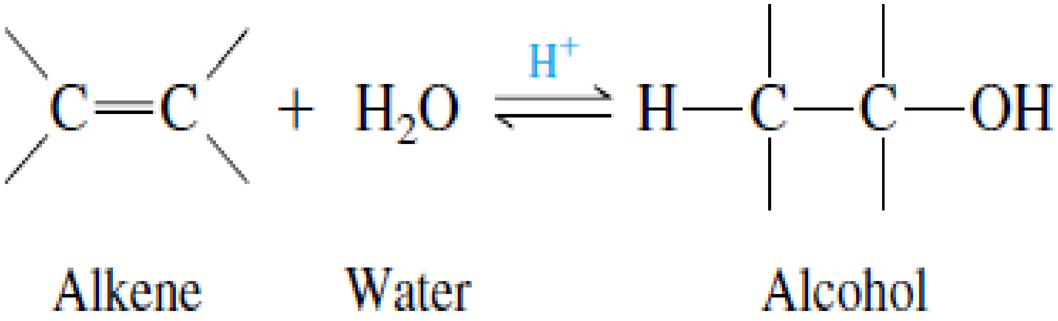


TABLE 6.2 Relative Rates of Acid-Catalyzed Hydration of Some Representative Alkenes

Alkene	Structural formula	Relative rate of acid-catalyzed hydration*
Ethylene	$CH_2{=}CH_2$	1.0
Propene	$CH_3CH{=}CH_2$	1.6×10^6
2-Methylpropene	$(CH_3)_2C{=}CH_2$	2.5×10^{11}

*In water, 25°C.



Principle of microscopic reversibility

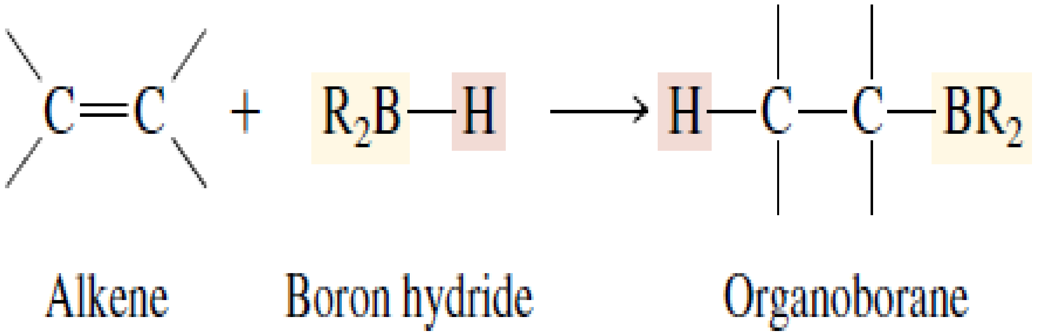
Le Chatelier’s principle

Hydroboration-oxidation

$$CH_3(CH_2)_7CH{=}CH_2 \longrightarrow CH_3(CH_2)_7CH_2CH_2OH$$

1-Decene 1-Decanol

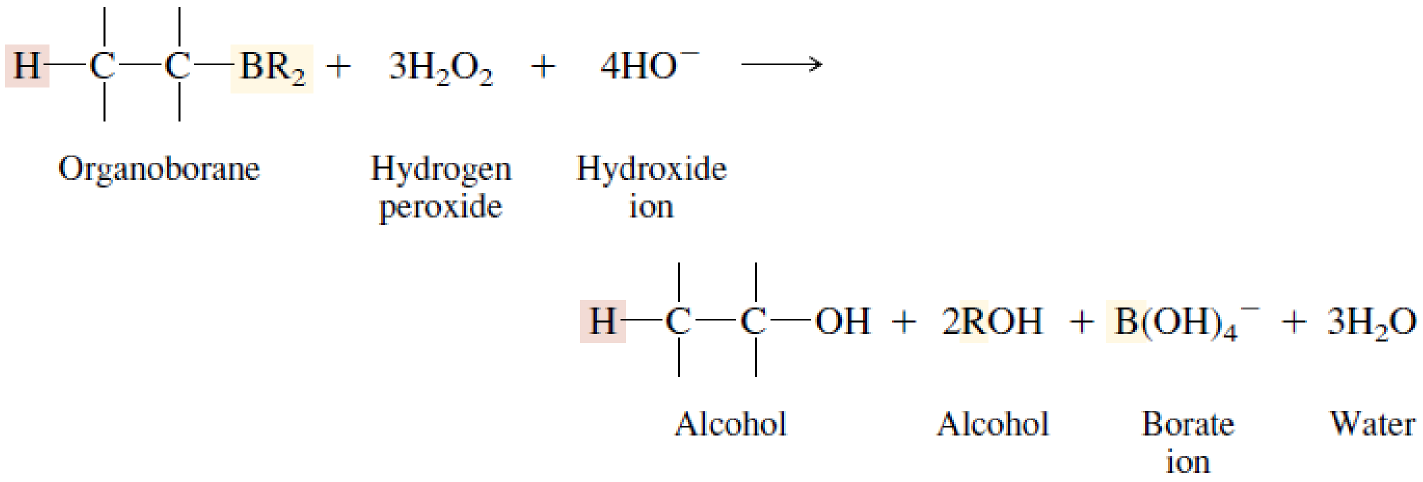
Hydroboration



$$>C{=}C< + R_2B{-}H \longrightarrow H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}BR_2$$

Alkene Boron hydride Organoborane

Oxidation



$$H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}BR_2 + 3H_2O_2 + 4HO^- \longrightarrow$$

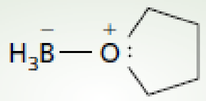
Organoborane Hydrogen peroxide Hydroxide ion

$$H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OH + 2ROH + B(OH)_4^- + 3H_2O$$

Alcohol Alcohol Borate ion Water

$$\underset{\text{1-Decene}}{6CH_3(CH_2)_7CH{=}CH_2} + \underset{\text{Diborane}}{B_2H_6} \xrightarrow{\text{diglyme}} \underset{\text{Tridecylborane}}{2[CH_3(CH_2)_7CH_2CH_2]_3B}$$

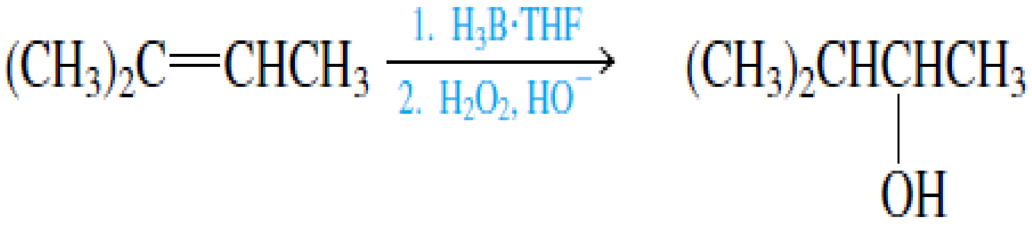
$$\underset{\text{Tridecylborane}}{[CH_3(CH_2)_7CH_2CH_2]_3B} \xrightarrow[\text{NaOH}]{H_2O_2} \underset{\text{1-Decanol}}{CH_3(CH_2)_7CH_2CH_2OH}$$



Borane-tetrahydrofuran complex

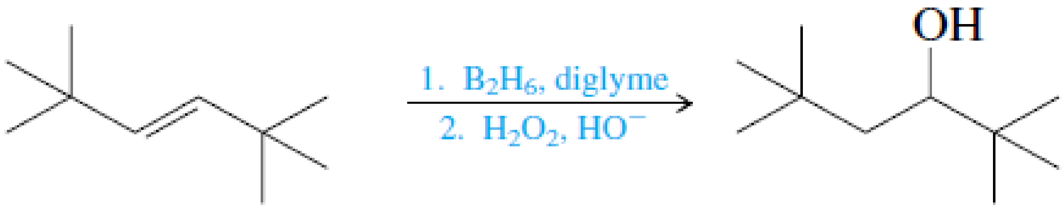
$$\mathrm{CH_3(CH_2)_7CH{=}CH_2} \xrightarrow[\text{2. } \mathrm{H_2O_2,\ HO^-}]{\text{1. } \mathrm{B_2H_6}\text{, diglyme}} \mathrm{CH_3(CH_2)_7CH_2CH_2OH}$$

1-Decene → 1-Decanol (93%)



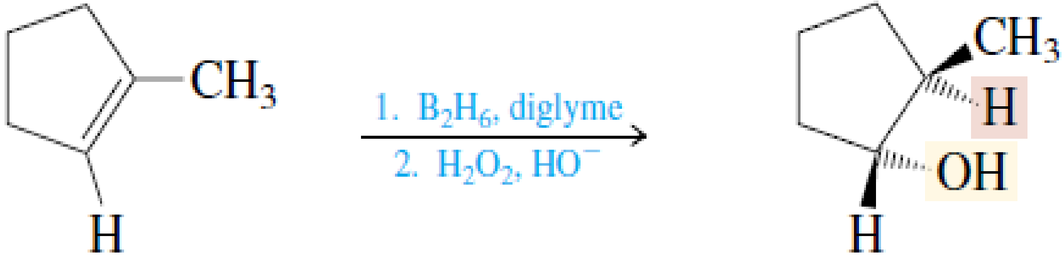
$$\mathrm{(CH_3)_2C{=}CHCH_3} \xrightarrow[\text{2. } \mathrm{H_2O_2,\ HO^-}]{\text{1. } \mathrm{H_3B{\cdot}THF}} \mathrm{(CH_3)_2CH\underset{\displaystyle OH}{\underset{|}{C}}HCH_3}$$

2-Methyl-2-butene → 3-Methyl-2-butanol (98%)



(*E*)-2,2,5,5-Tetramethyl-3-hexene → 2,2,5,5-Tetramethyl-3-hexanol (82%)

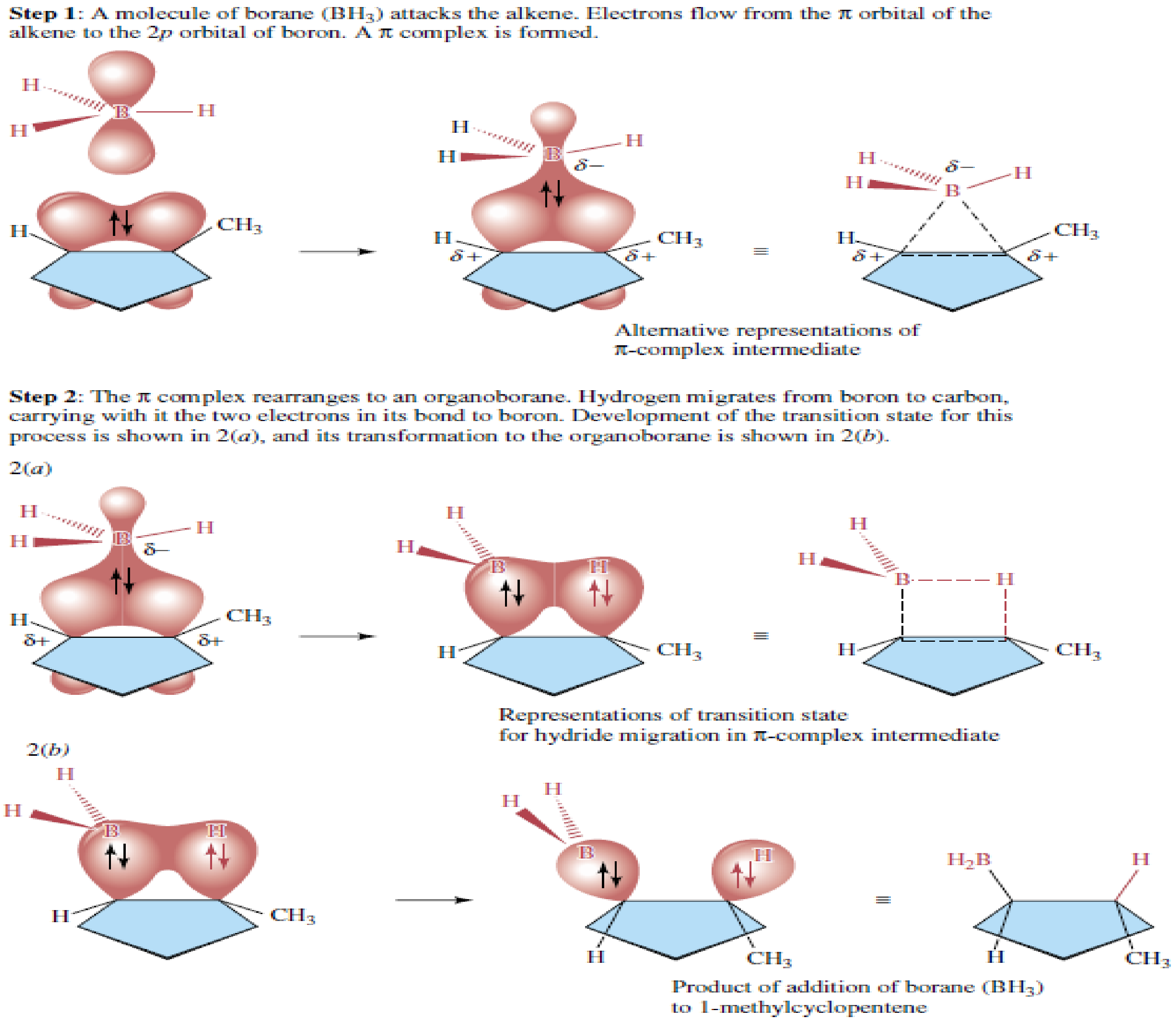
Stereochemistry of hydroboration-oxidation



1-Methylcyclopentene

trans-2-Methylcyclopentanol
(only product, 86% yield)

Mechanism:



Step 1: A molecule of borane (BH_3) attacks the alkene. Electrons flow from the π orbital of the alkene to the $2p$ orbital of boron. A π complex is formed.

Alternative representations of π-complex intermediate

Step 2: The π complex rearranges to an organoborane. Hydrogen migrates from boron to carbon, carrying with it the two electrons in its bond to boron. Development of the transition state for this process is shown in 2(*a*), and its transformation to the organoborane is shown in 2(*b*).

2(*a*)

Representations of transition state for hydride migration in π-complex intermediate

2(*b*)

Product of addition of borane (BH_3) to 1-methylcyclopentene

Step 1: Hydrogen peroxide is converted to its anion in basic solution:

$H—O—O—H + {}^{-}OH \rightleftharpoons H—O—O^{-} + H—O—H$

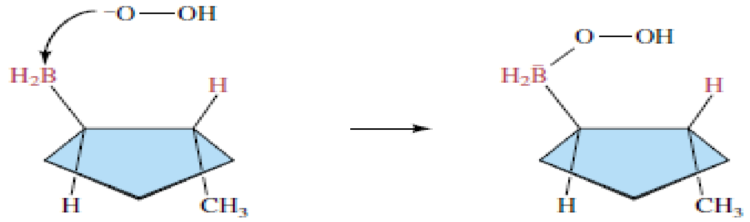
Hydrogen peroxide

Hydroxide ion

Hydroperoxide ion

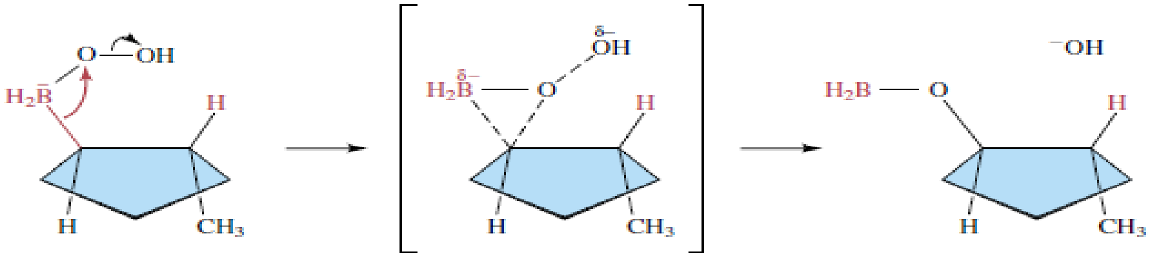
Water

Step 2: Anion of hydrogen peroxide acts as a nucleophile, attacking boron and forming an oxygen–boron bond:



Organoborane intermediate from hydroboration of 1-methylcyclopentene

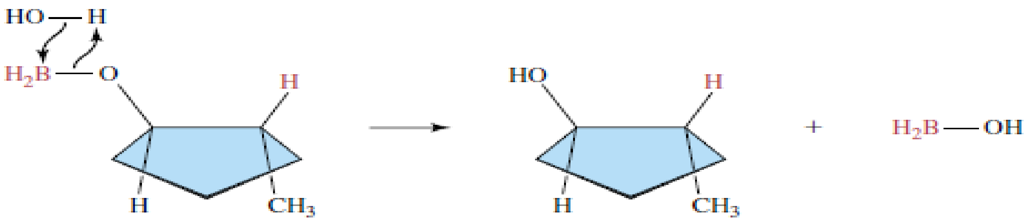
Step 3: Carbon migrates from boron to oxygen, displacing hydroxide ion. Carbon migrates with the pair of electrons in the carbon–boron bond; these become the electrons in the carbon–oxygen bond:



Representation of transition state for migration of carbon from boron to oxygen

Alkoxyborane

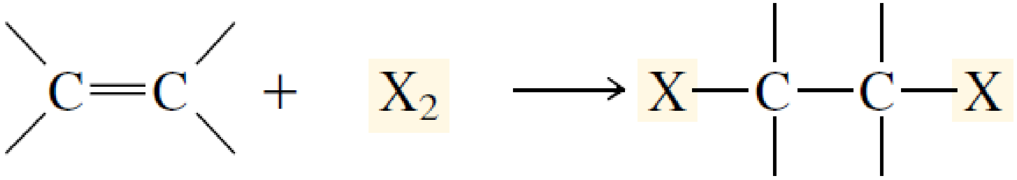
Step 4: Hydrolysis cleaves the boron–oxygen bond, yielding the alcohol:



Alkoxyborane

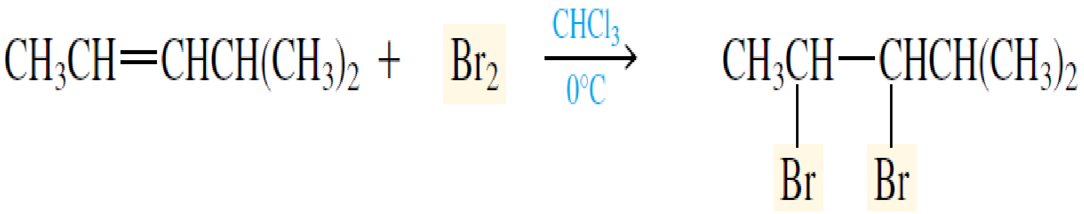
trans-2-Methylcyclopentanol

Addition of halogen



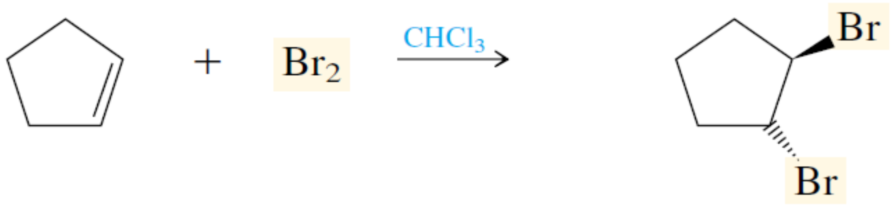
Alkene Halogen Vicinal dihalide

Stereochemistry of halogen addition

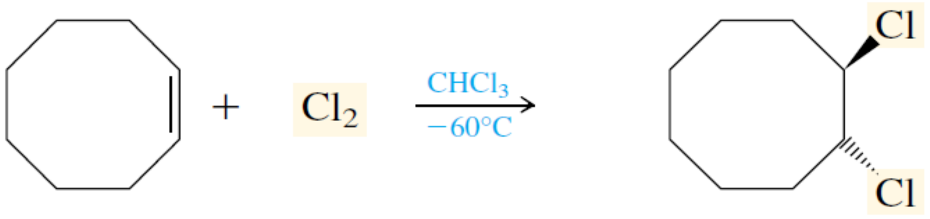


$$CH_3CH{=}CHCH(CH_3)_2 + Br_2 \xrightarrow[0°C]{CHCl_3} CH_3\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}CH(CH_3)_2$$

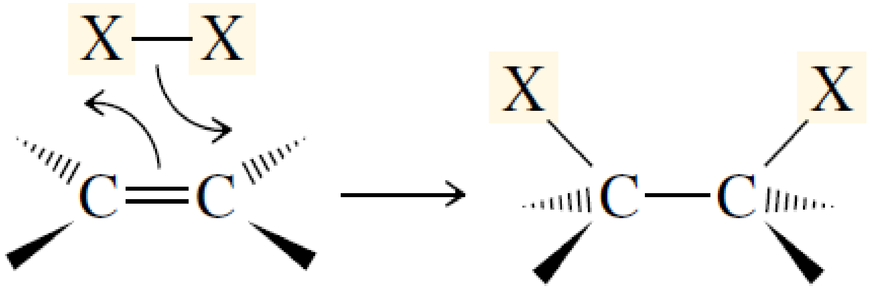
4-Methyl-2-pentene Bromine 2,3-Dibromo-4-methylpentane (100%)

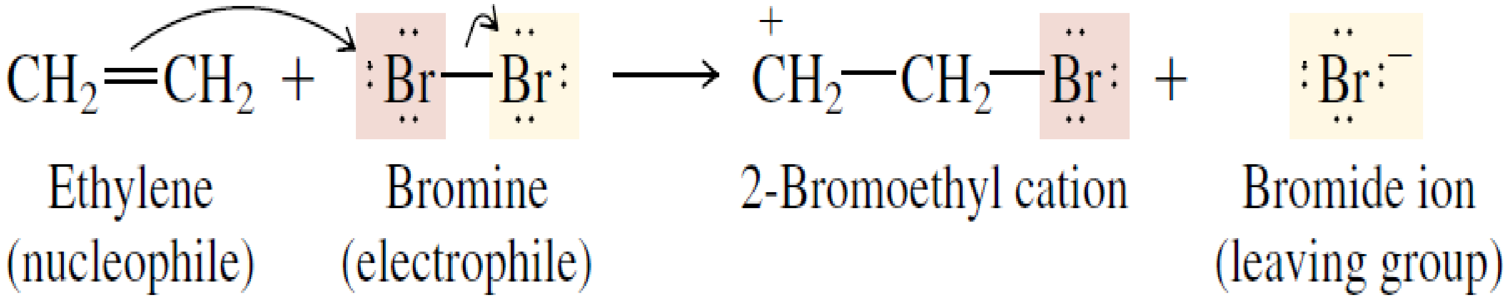


Cyclopentene Bromine *trans*-1,2-Dibromocyclopentane (80% yield; none of the *cis* isomer is formed)

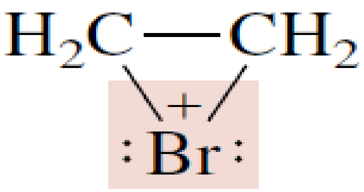


Cyclooctene Chlorine *trans*-1,2-Dichlorocyclooctane (73% yield; none of the *cis* isomer is formed)





Cyclic bromonium ion



Ethylenebromonium ion

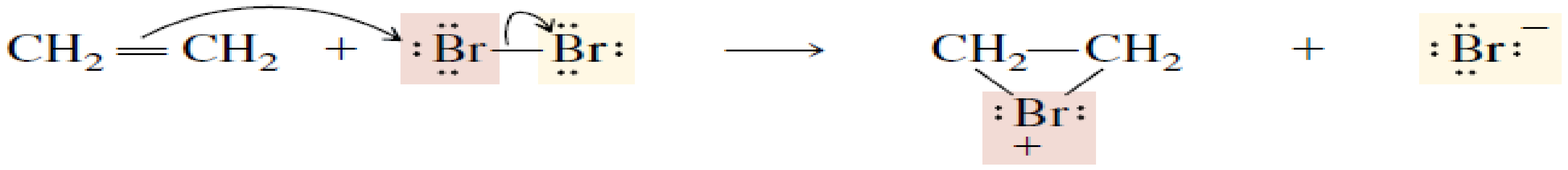
The overall reaction:

$$CH_2{=}CH_2 \quad + \quad Br_2 \quad \longrightarrow \quad BrCH_2CH_2Br$$

Ethylene Bromine 1,2-Dibromoethane

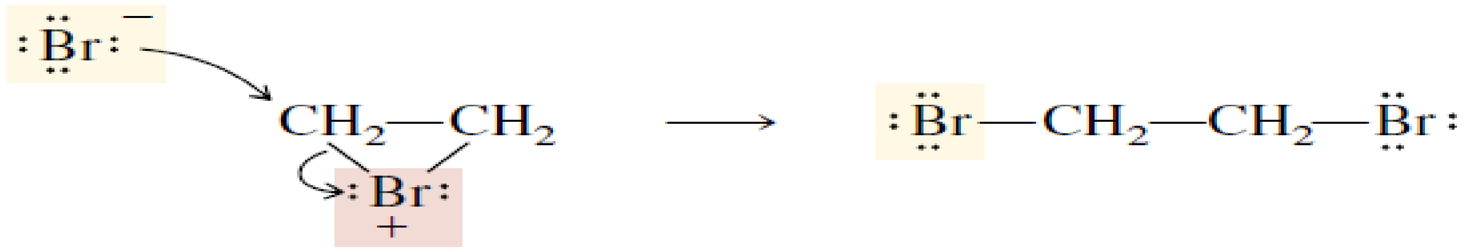
The mechanism:

Step 1: Reaction of ethylene and bromine to form a bromonium ion intermediate:



Ethylene Bromine Ethylenebromonium ion Bromide ion

Step 2: Nucleophilic attack of bromide anion on the bromonium ion:



Bromide ion Ethylenebromonium ion 1,2-Dibromoethane

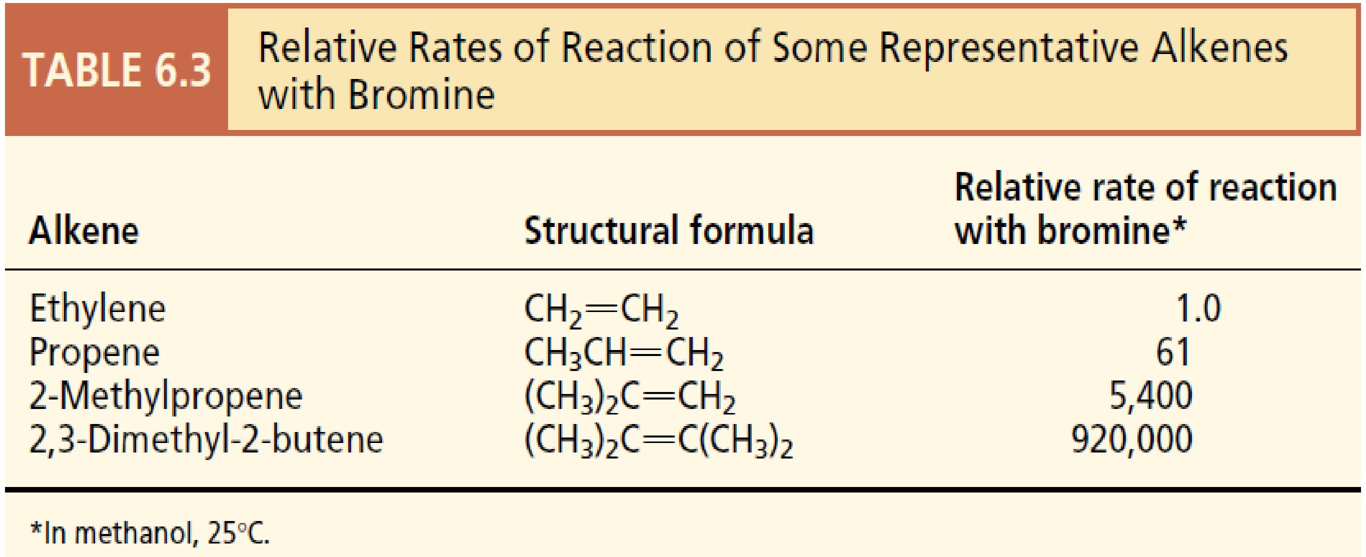
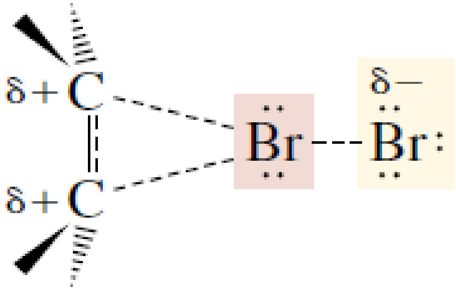


TABLE 6.3 Relative Rates of Reaction of Some Representative Alkenes with Bromine

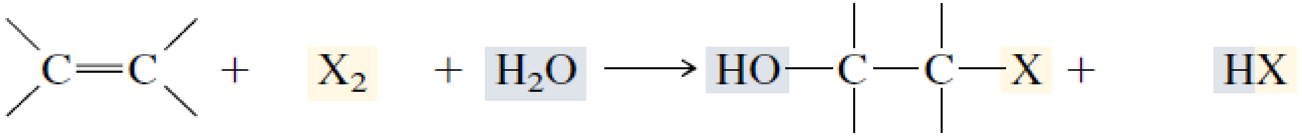
Alkene	Structural formula	Relative rate of reaction with bromine*
Ethylene	$CH_2{=}CH_2$	1.0
Propene	$CH_3CH{=}CH_2$	61
2-Methylpropene	$(CH_3)_2C{=}CH_2$	5,400
2,3-Dimethyl-2-butene	$(CH_3)_2C{=}C(CH_3)_2$	920,000

*In methanol, 25°C.

Transition state for bromonium ion formation from an alkene and bromine



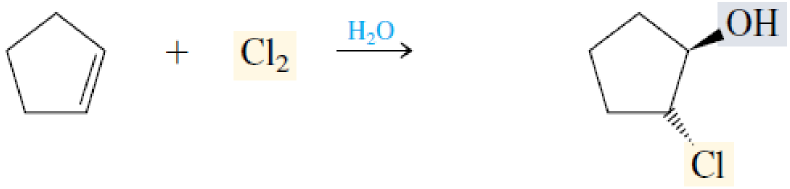
Halohydrin



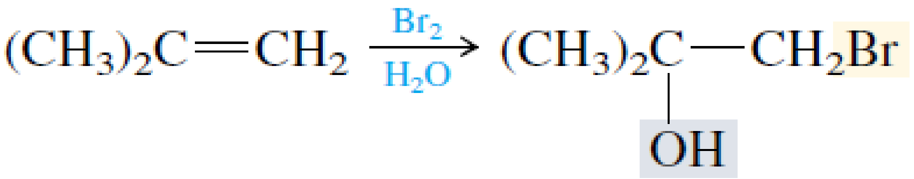
Alkene Halogen Water Halohydrin Hydrogen halide

$$CH_2{=}CH_2 + Br_2 \xrightarrow{H_2O} HOCH_2CH_2Br$$

Ethylene Bromine 2-Bromoethanol (70%)

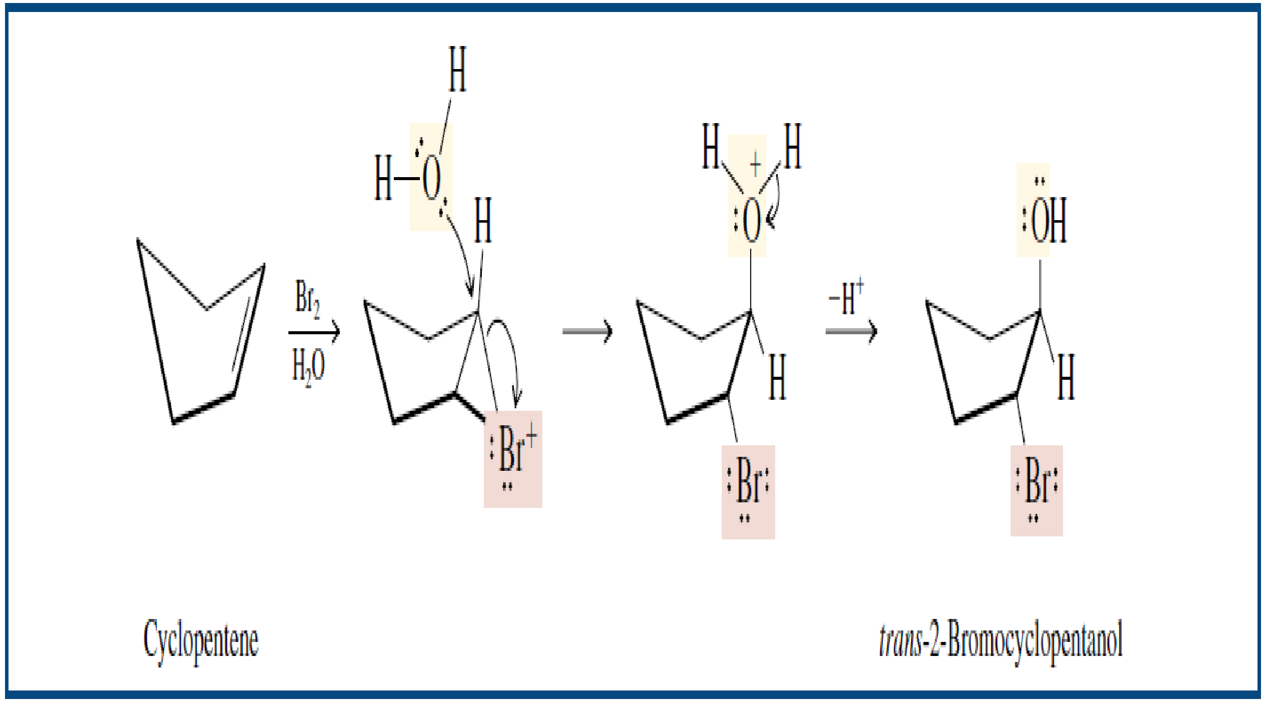


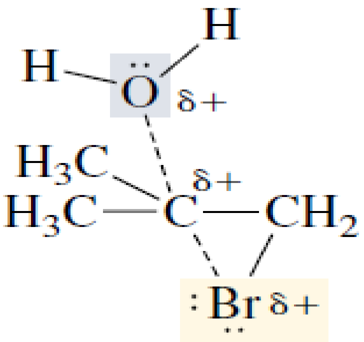
Cyclopentene Chlorine *trans*-2-Chlorocyclopentanol
(52–56% yield; cis isomer not formed)



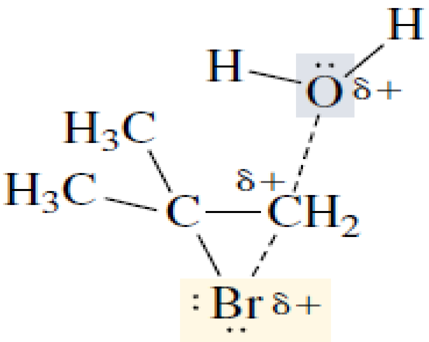
$$(CH_3)_2C{=}CH_2 \xrightarrow[H_2O]{Br_2} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}{-}CH_2Br$$

2-Methylpropene 1-Bromo-2-methyl-2-propanol (77%)



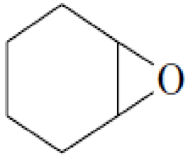


More stable transition state;
has some of the character
of a tertiary carbocation

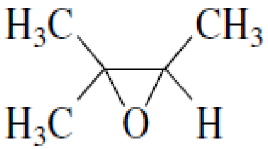


Less stable transition state;
has some of the character
of a primary carbocation

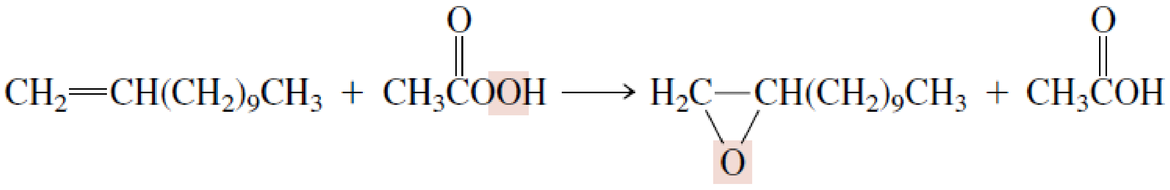
Epoxidation of alkenes



1,2-Epoxycyclohexane

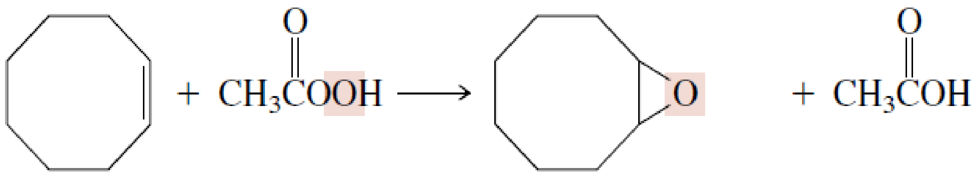


2-Methyl-2,3-epoxybutane

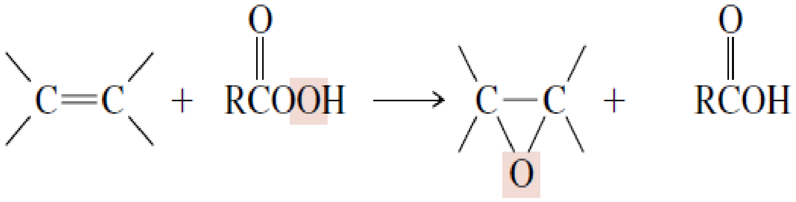


$$CH_2{=}CH(CH_2)_9CH_3 + CH_3\overset{O}{\overset{\|}{C}}OOH \longrightarrow \underset{\diagdown O \diagup}{H_2C{-}CH}(CH_2)_9CH_3 + CH_3\overset{O}{\overset{\|}{C}}OH$$

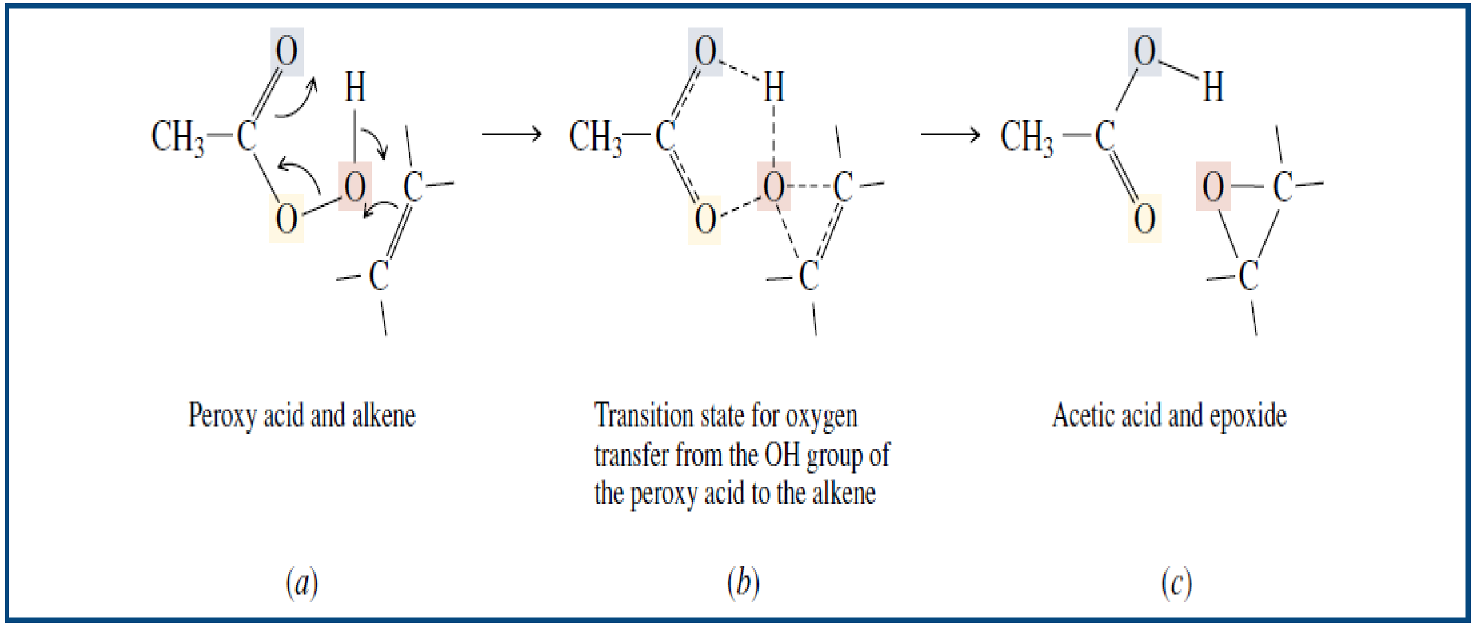
1-Dodecene Peroxyacetic acid 1,2-Epoxydodecane (52%) Acetic acid



Cyclooctene Peroxyacetic acid 1,2-Epoxycyclooctane (86%) Acetic acid



Alkene Peroxy acid Epoxide Carboxylic acid



Peroxy acid and alkene

(*a*)

Transition state for oxygen transfer from the OH group of the peroxy acid to the alkene

(*b*)

Acetic acid and epoxide

(*c*)

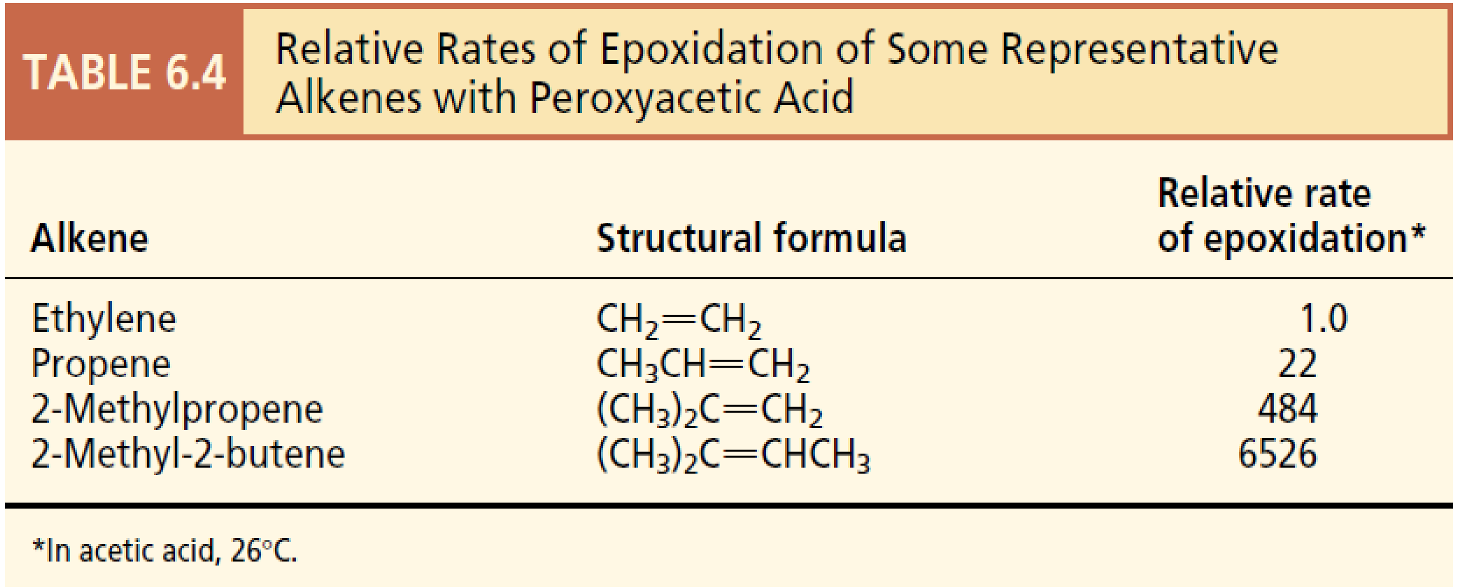
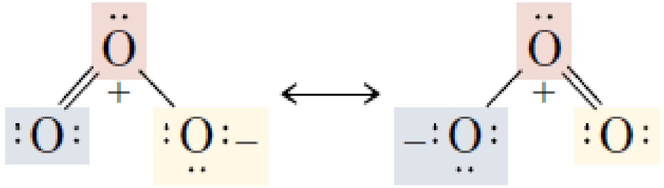


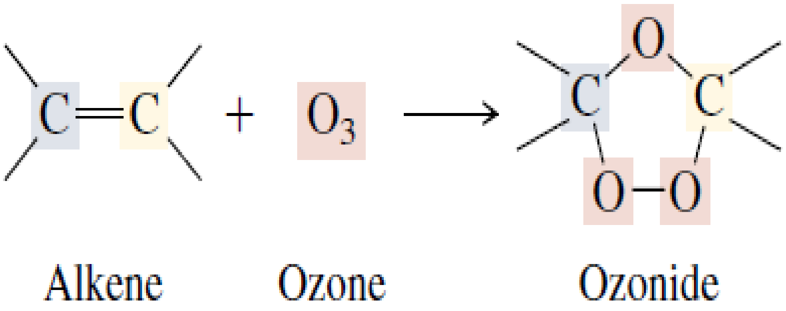
TABLE 6.4 Relative Rates of Epoxidation of Some Representative Alkenes with Peroxyacetic Acid

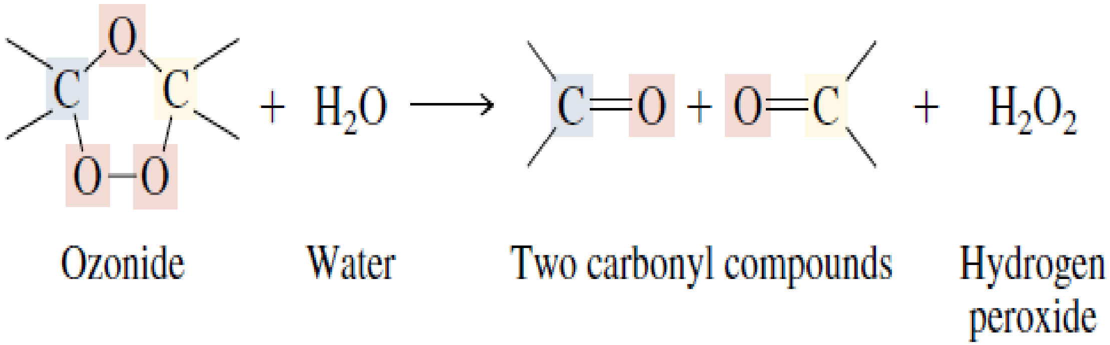
Alkene	**Structural formula**	**Relative rate of epoxidation***
Ethylene	$CH_2{=}CH_2$	1.0
Propene	$CH_3CH{=}CH_2$	22
2-Methylpropene	$(CH_3)_2C{=}CH_2$	484
2-Methyl-2-butene	$(CH_3)_2C{=}CHCH_3$	6526

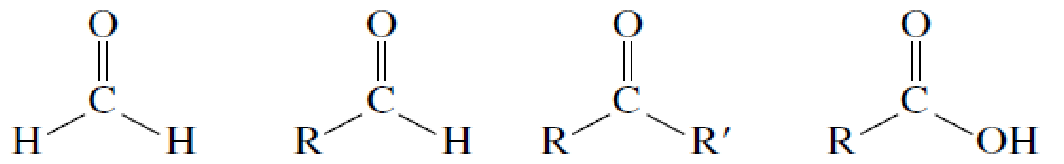
*In acetic acid, 26°C.

Ozonolysis of alkenes

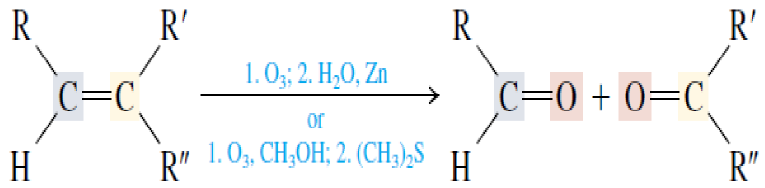




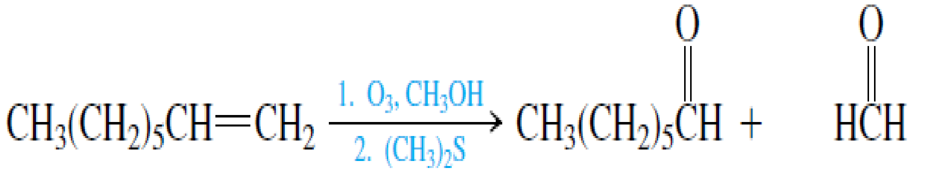




Formaldehyde Aldehyde Ketone Carboxylic acid

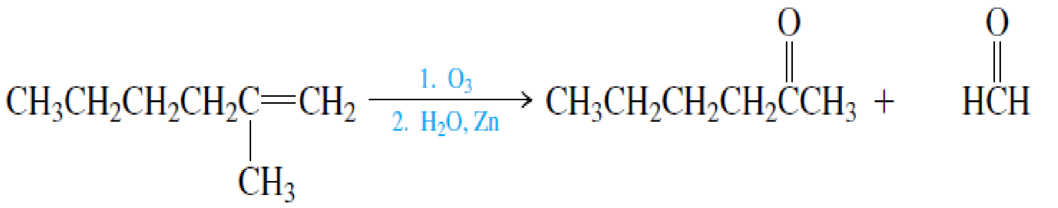


Alkene Aldehyde Ketone



$$CH_3(CH_2)_5CH{=}CH_2 \xrightarrow[2.\ (CH_3)_2S]{1.\ O_3,\ CH_3OH} CH_3(CH_2)_5\overset{O}{\overset{\|}{C}}H + H\overset{O}{\overset{\|}{C}}H$$

1-Octene Heptanal (75%) Formaldehyde

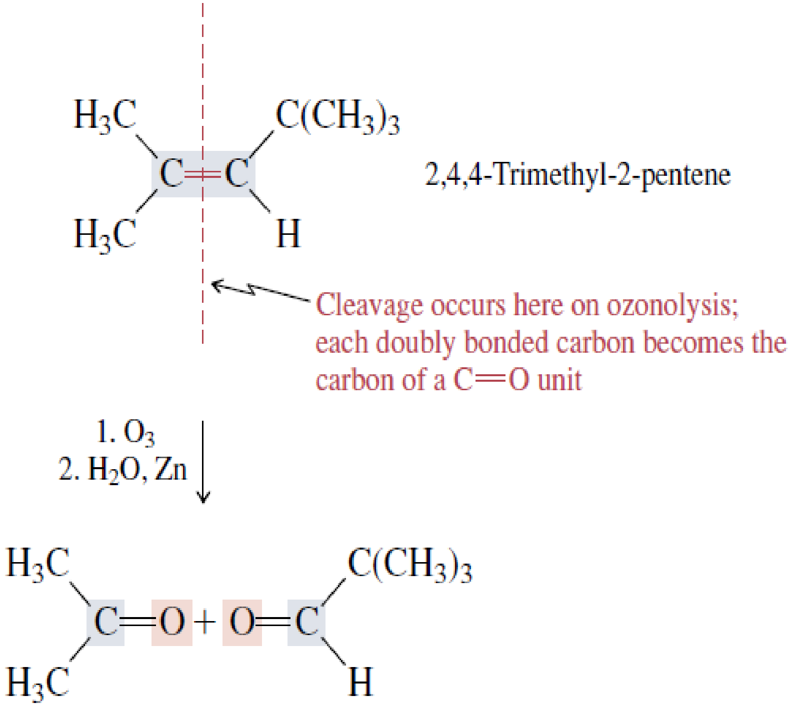


$$CH_3CH_2CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \xrightarrow[2.\ H_2O,\ Zn]{1.\ O_3} CH_3CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH_3 + H\overset{\displaystyle O}{\overset{\|}{C}}H$$

2-Methyl-1-hexene

2-Hexanone (60%)

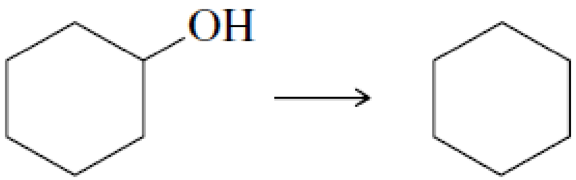
Formaldehyde



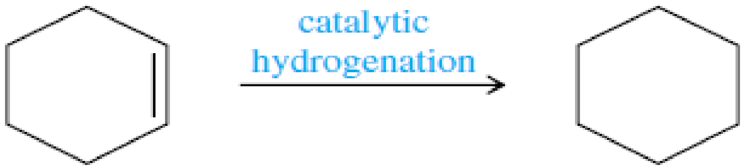
2,4,4-Trimethyl-2-pentene

Cleavage occurs here on ozonolysis; each doubly bonded carbon becomes the carbon of a C=O unit

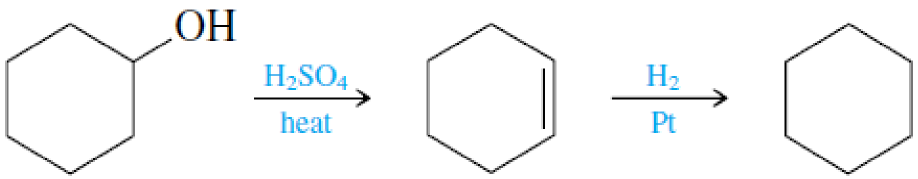
Synthesis



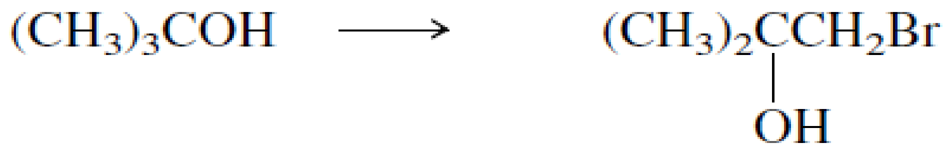
Cyclohexanol Cyclohexane



Cyclohexene Cyclohexane

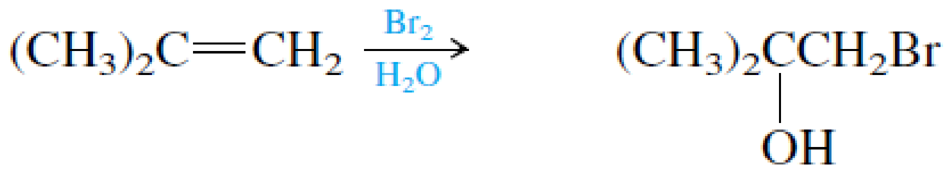


Cyclohexanol Cyclohexene Cyclohexane



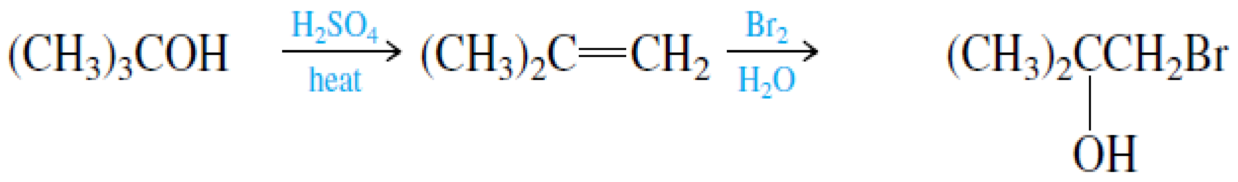
$$(CH_3)_3COH \longrightarrow (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2Br$$

tert-Butyl alcohol 1-Bromo-2-methyl-2-propanol



$$(CH_3)_2C{=}CH_2 \xrightarrow[H_2O]{Br_2} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2Br$$

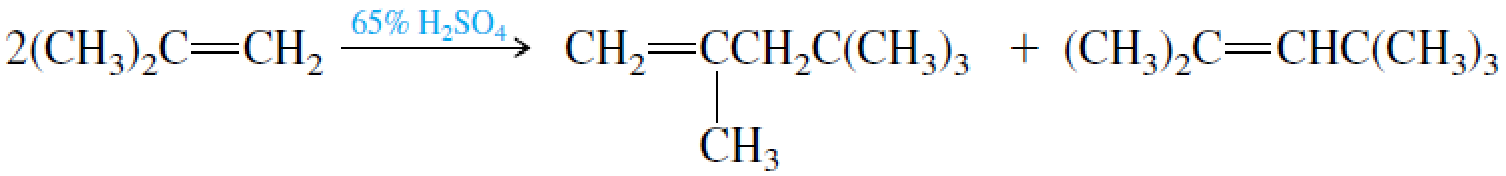
2-Methylpropene 1-Bromo-2-methyl-2-propanol



$$(CH_3)_3COH \xrightarrow[heat]{H_2SO_4} (CH_3)_2C{=}CH_2 \xrightarrow[H_2O]{Br_2} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2Br$$

tert-Butyl alcohol 2-Methylpropene 1-Bromo-2-methyl-2-propanol

Reactions of alkene with alkenes



$$2(CH_3)_2C{=}CH_2 \xrightarrow{65\%\ H_2SO_4} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2C(CH_3)_3 + (CH_3)_2C{=}CHC(CH_3)_3$$

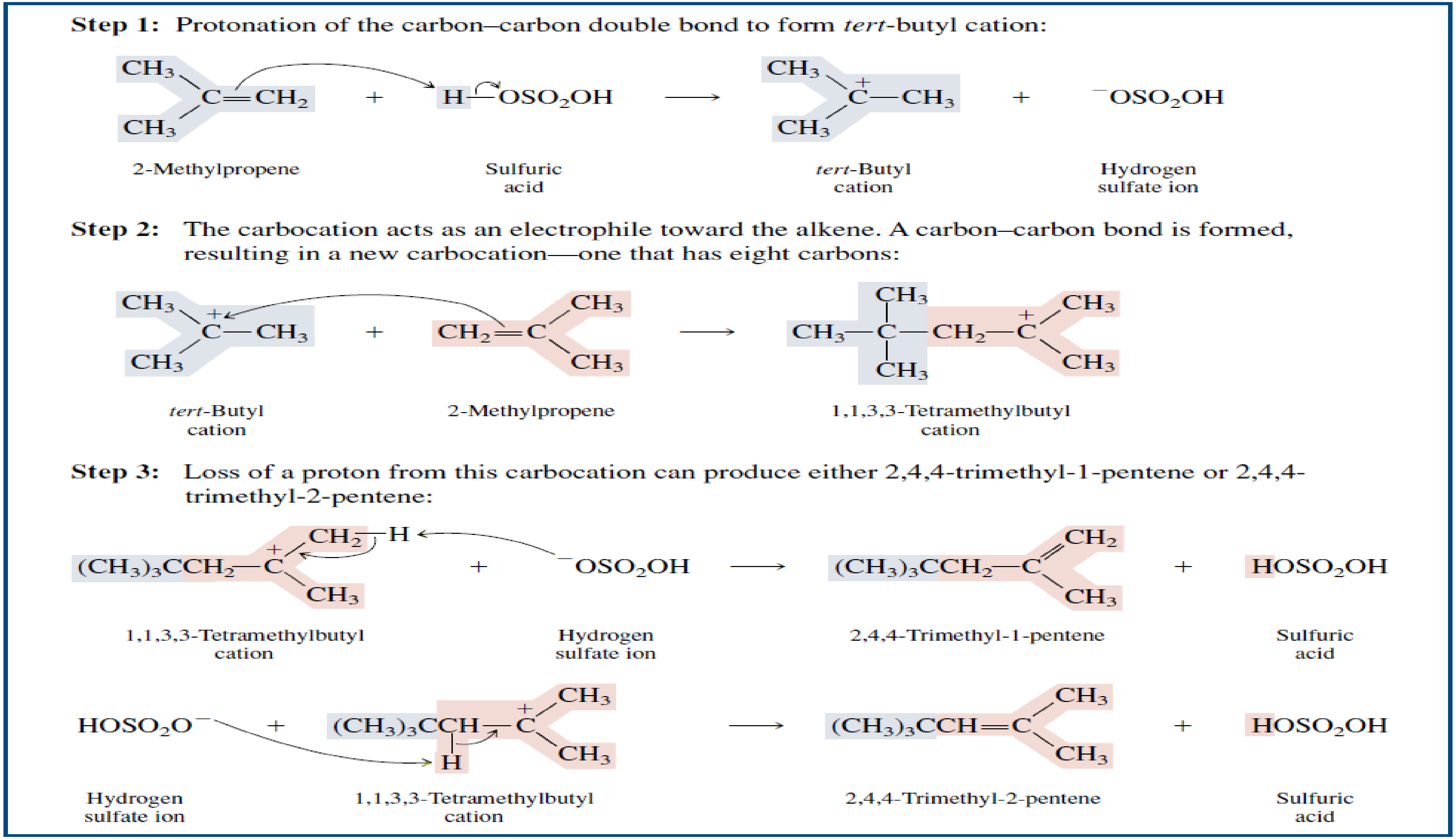
2-Methylpropene 2,4,4-Trimethyl-1-pentene 2,4,4-Trimethyl-2-pentene

Dimer, trimer and polymer

$$nCH_2{=}CH_2 \xrightarrow[\text{O}_2\text{ or peroxides}]{200°C,\ 2000\text{ atm}} {-}CH_2{-}CH_2{-}(CH_2{-}CH_2)_{n-2}{-}CH_2{-}CH_2{-}$$

Ethylene Polyethylene

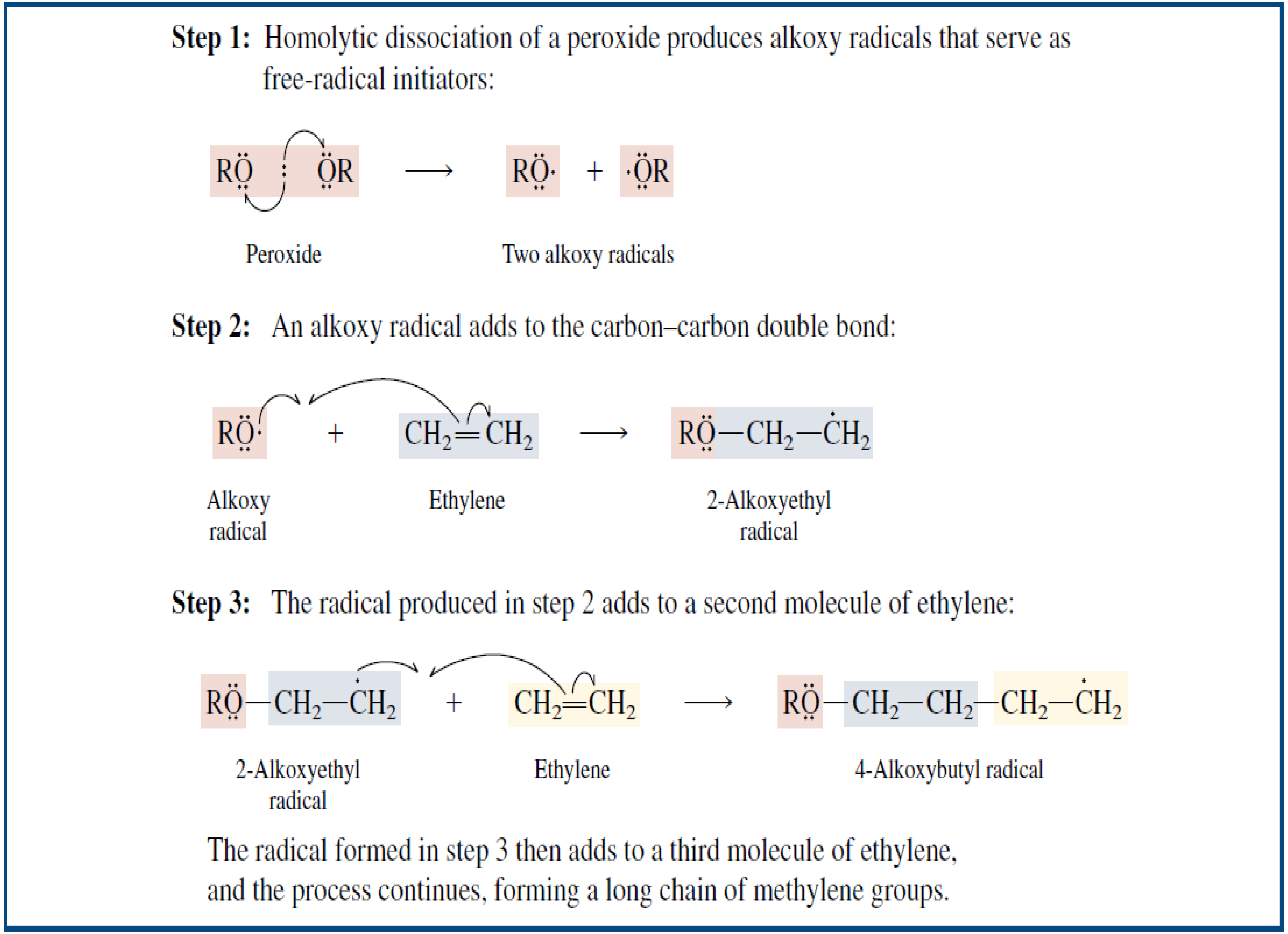
Cationic polymerization; Anionic polymerization; Free-radical polymerization



Step 1: Protonation of the carbon–carbon double bond to form *tert*-butyl cation:

Step 2: The carbocation acts as an electrophile toward the alkene. A carbon–carbon bond is formed, resulting in a new carbocation—one that has eight carbons:

Step 3: Loss of a proton from this carbocation can produce either 2,4,4-trimethyl-1-pentene or 2,4,4-trimethyl-2-pentene:



Step 1: Homolytic dissociation of a peroxide produces alkoxy radicals that serve as free-radical initiators:

$$\mathrm{R\ddot{O}}:\mathrm{\ddot{O}R} \longrightarrow \mathrm{R\ddot{O}}\cdot + \cdot\mathrm{\ddot{O}R}$$

Peroxide — Two alkoxy radicals

Step 2: An alkoxy radical adds to the carbon–carbon double bond:

$$\mathrm{R\ddot{O}}\cdot + \mathrm{CH_2{=}CH_2} \longrightarrow \mathrm{R\ddot{O}{-}CH_2{-}\dot{C}H_2}$$

Alkoxy radical — Ethylene — 2-Alkoxyethyl radical

Step 3: The radical produced in step 2 adds to a second molecule of ethylene:

$$\mathrm{R\ddot{O}{-}CH_2{-}\dot{C}H_2} + \mathrm{CH_2{=}CH_2} \longrightarrow \mathrm{R\ddot{O}{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H_2}$$

2-Alkoxyethyl radical — Ethylene — 4-Alkoxybutyl radical

The radical formed in step 3 then adds to a third molecule of ethylene, and the process continues, forming a long chain of methylene groups.

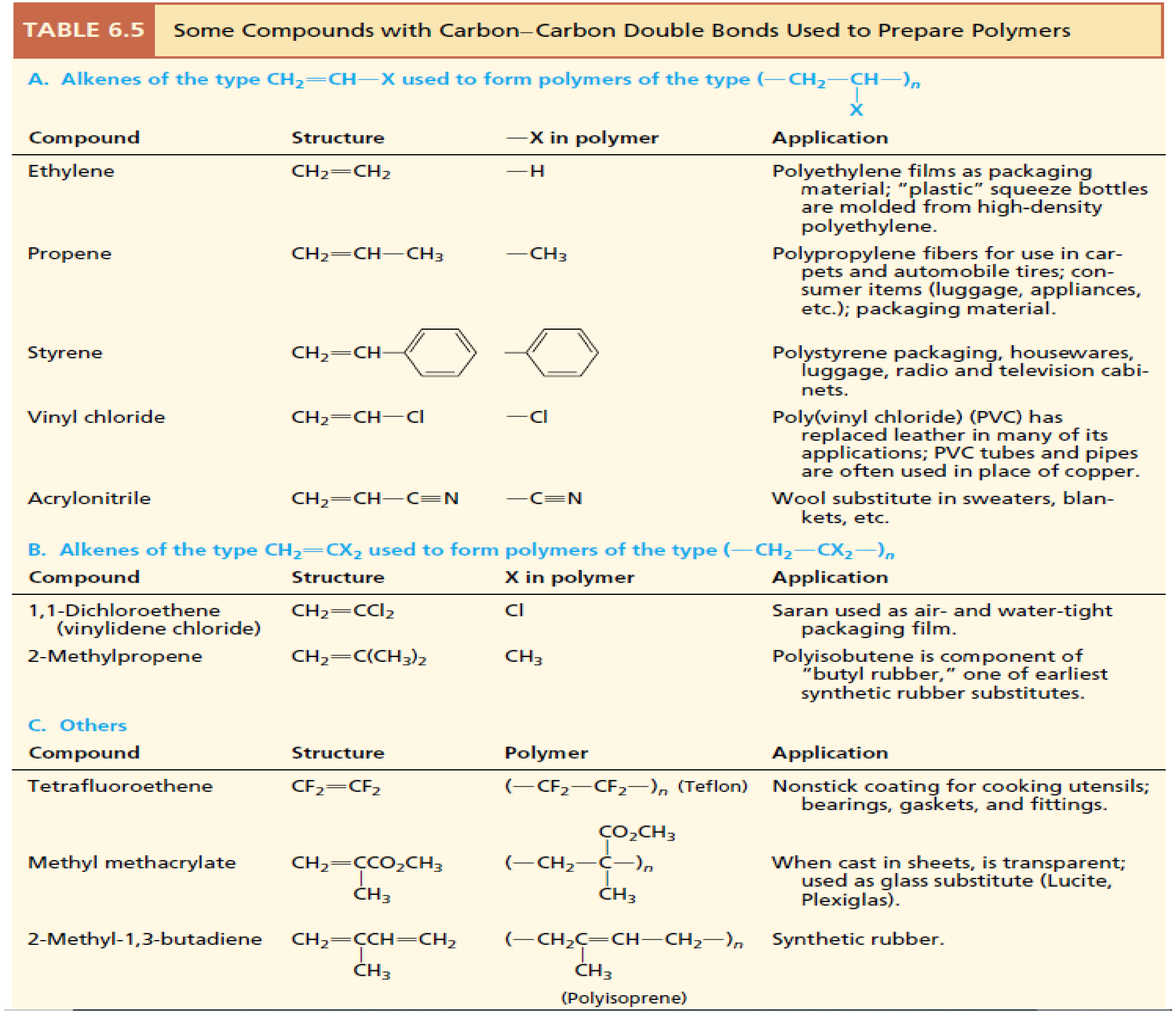


TABLE 6.5 Some Compounds with Carbon–Carbon Double Bonds Used to Prepare Polymers

A. Alkenes of the type $CH_2{=}CH{-}X$ used to form polymers of the type $(-CH_2-\underset{X}{\underset{|}{CH}}-)_n$

Compound	Structure	—X in polymer	Application
Ethylene	$CH_2{=}CH_2$	—H	Polyethylene films as packaging material; "plastic" squeeze bottles are molded from high-density polyethylene.
Propene	$CH_2{=}CH{-}CH_3$	$-CH_3$	Polypropylene fibers for use in carpets and automobile tires; consumer items (luggage, appliances, etc.); packaging material.
Styrene	$CH_2{=}CH-$		Polystyrene packaging, housewares, luggage, radio and television cabinets.
Vinyl chloride	$CH_2{=}CH{-}Cl$	—Cl	Poly(vinyl chloride) (PVC) has replaced leather in many of its applications; PVC tubes and pipes are often used in place of copper.
Acrylonitrile	$CH_2{=}CH{-}C{\equiv}N$	$-C{\equiv}N$	Wool substitute in sweaters, blankets, etc.

B. Alkenes of the type $CH_2{=}CX_2$ used to form polymers of the type $(-CH_2-CX_2-)_n$

Compound	Structure	X in polymer	Application
1,1-Dichloroethene (vinylidene chloride)	$CH_2{=}CCl_2$	Cl	Saran used as air- and water-tight packaging film.
2-Methylpropene	$CH_2{=}C(CH_3)_2$	CH_3	Polyisobutene is component of "butyl rubber," one of earliest synthetic rubber substitutes.

C. Others

Compound	Structure	Polymer	Application
Tetrafluoroethene	$CF_2{=}CF_2$	$(-CF_2-CF_2-)_n$ (Teflon)	Nonstick coating for cooking utensils; bearings, gaskets, and fittings.
Methyl methacrylate	$CH_2{=}\underset{CH_3}{\underset{\vert}{C}}CO_2CH_3$	$(-CH_2-\overset{CO_2CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-)_n$	When cast in sheets, is transparent; used as glass substitute (Lucite, Plexiglas).
2-Methyl-1,3-butadiene	$CH_2{=}\underset{CH_3}{\underset{\vert}{C}}CH{=}CH_2$	$(-CH_2\underset{CH_3}{\underset{\vert}{C}}{=}CH-CH_2-)_n$ (Polyisoprene)	Synthetic rubber.