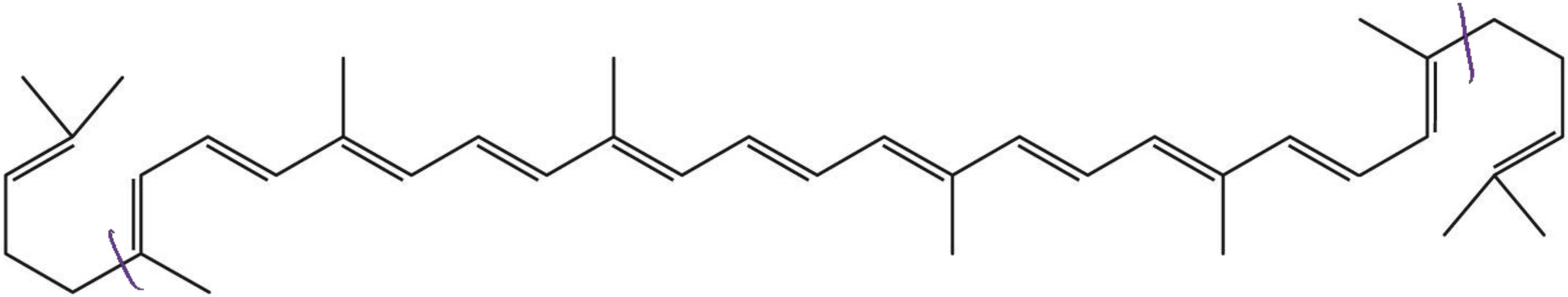
Chapter 3: Alkenes and Alkynes



lycopene

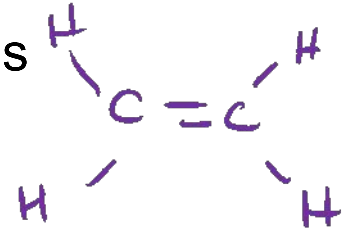
Conjution
(alternating double bonds)

Hydrogenation of Alkenes and Alkynes

Hydrocarbons that have carbon-carbon double bond are called alkenes; those with a carbon-carbon triple bond are alkynes

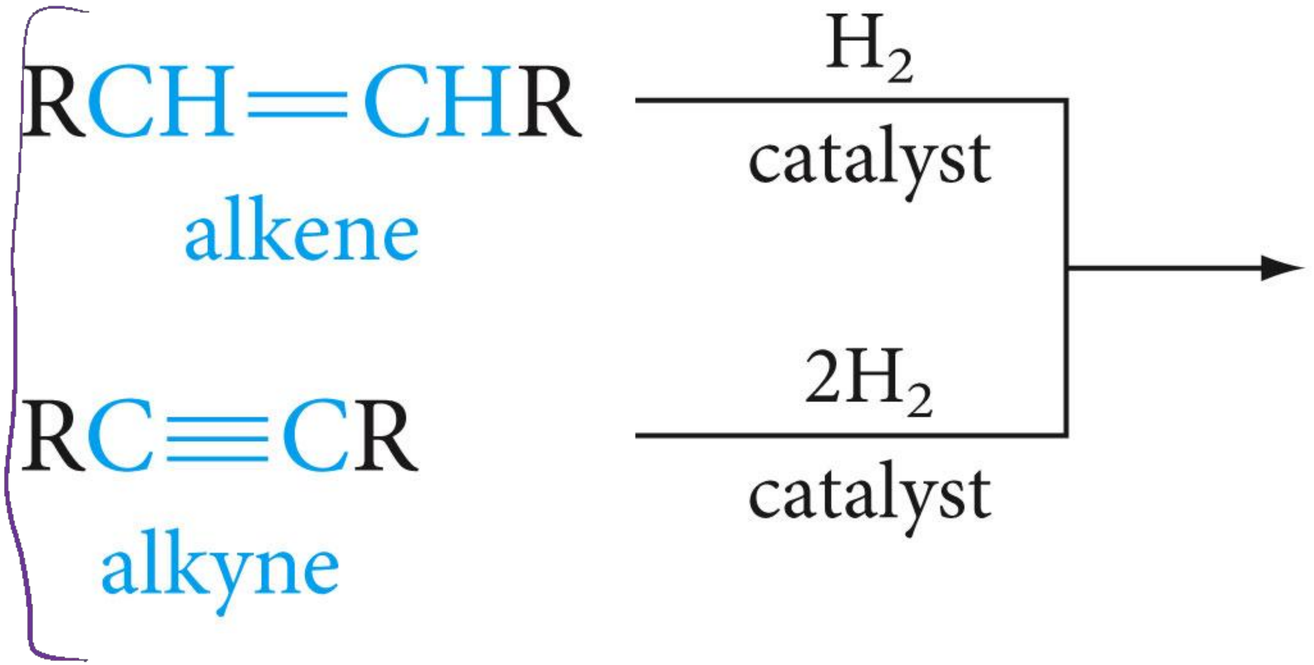
Their general formulas are **C_nH_{2n} alkenes** and **C_nH_{2n-2} alkynes**

Both alkenes and alkynes are unsaturated hydrocarbons



C_2H_4

ethene [Ethylene]



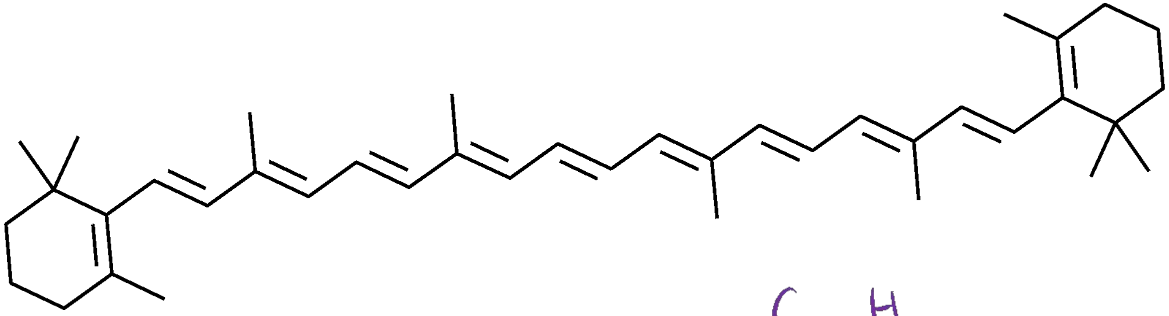
RCH_2CH_2R

alkane

$H-C\equiv C-H$

C_2H_2

Compounds with more than one double or triple bonds exist. Multiple double bonds may lead to dienes, trienes, tetraenes and polyenes. β-carotene and lycopene are examples of polyenes



$C_{40}H_{56}$

11 C-C double bonds

When two or more multiple bonds re present in a molecule, they can be classified depending on the relative positions of the bonds

$C{=}\overset{sp}{C}{=}C$

$C{=}C{=}\overset{sp}{C}{=}\underset{sp^2}{C}$

cumulated

$C{=}C{-}C{=}C$ ✓

$C\overset{\pi}{\underset{\sigma}{=}}C{-}C\overset{2\pi}{\underset{\sigma}{\equiv}}C$ ✓

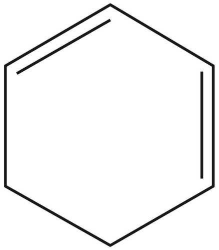
conjugated

$C{=}\overset{sp^2}{C}\underline{{-}\overset{sp^3}{C}{-}}\overset{sp}{C}{=}C$

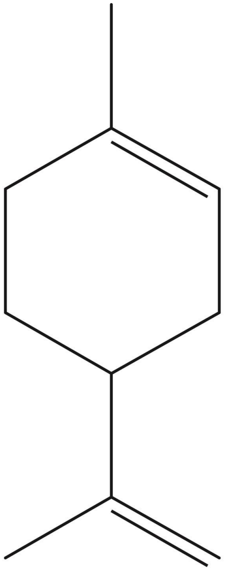
$C{\equiv}C{-}C{-}C{-}C{\equiv}C$

nonconjugated (isolated)

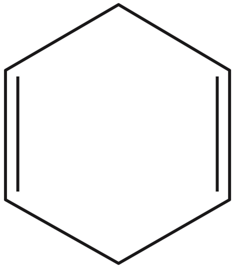
Which of the following compounds have conjugated multiple bonds?



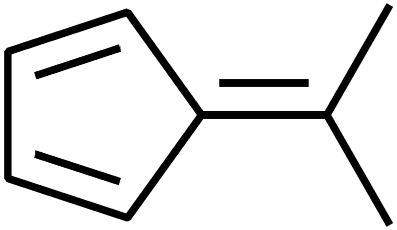
Conjugated



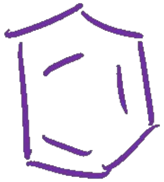
No



NO



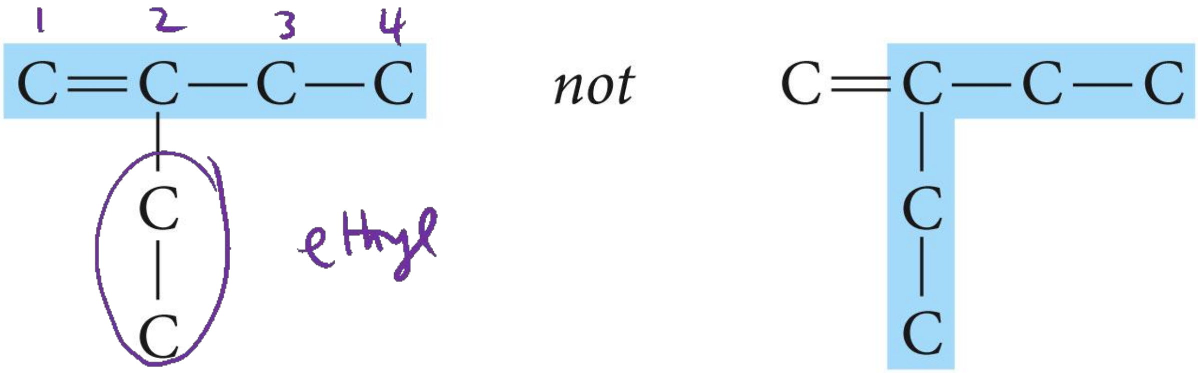
✓



yes

Nomenclature

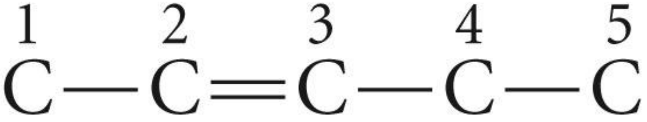
1. The ending –*ene* is used to designate carbon-carbon double bond. When more than one double bond is present, the ending is –*diene, triene, tetraene* and so on. The ending –yne is used for triple carbon-carbon bond.
2. Select the longest chain that includes both carbons of the double bond or triple bond.



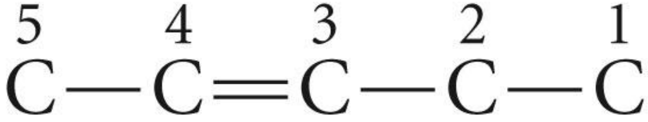
named as a butene, not as a pentene

2-ethyl-1-butene

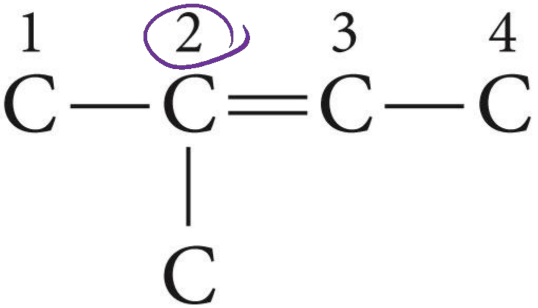
Number the chain from the end nearest the multiple bond so that the carbon atoms in that bond have the lowest possible numbers.


$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$

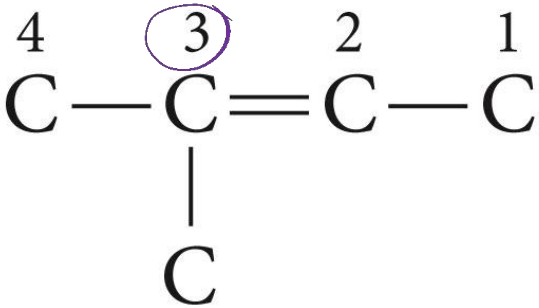
not


$\overset{5}{C}-\overset{4}{C}=\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$

If the multiple bond is equidistant from both ends of the chain, number the chain from the end nearest the first branch point.



not



2-methyl-2-butene

Indicate the position of the multiple bond using the lower numbered carbon atom of that bond.

$\overset{1}{C}H_2{=}\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3$ 1-butene, *not* 2-butene

If more than one multiple bond is present, number the chain from the end nearest the first multiple bond.

$\underrightarrow{\overset{1}{C}{=}\overset{2}{C}{-}\overset{3}{C}{=}\overset{4}{C}{-}\overset{5}{C}}$ *not* $\underleftarrow{\overset{5}{C}{=}\overset{4}{C}{-}\overset{3}{C}{=}\overset{2}{C}{-}\overset{1}{C}}$

= END =

If the double bond and the triple bond are equidistant from the end of the chain, the double bond receives the lowest number.

alkene takes priority over alkyne

$\overset{1}{C}=\overset{2}{C}-\overset{3}{C}\equiv\overset{4}{C}$ ✓ *not* $\overset{4}{C}=\overset{3}{C}-\overset{2}{C}\equiv\overset{1}{C}$ X

The root name is from the longest carbon chain containing the multiple bond

CH_3CH_3
ethane

$CH_2{=}CH_2$
ethene ✓

$HC{\equiv}CH$
ethyne ✓

$CH_3CH_2CH_3$
propane

$CH_2{=}CHCH_3$
propene ✓

$HC{\equiv}CCH_3$
propyne ✓

$CH_3CH_2CH_2CH_3$

$CH_2=CHCH_2CH_3$ 1-butene

$CH_3-CH=CHCH_3$ 2-butene

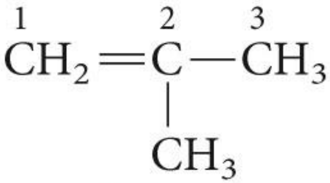
so are
1-butyne and
2-butyne

$\overset{1}{\mathrm{CH_2}}=\overset{2}{\mathrm{CH}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$
1-butene

$\overset{1}{\mathrm{CH_3}}\overset{2}{\mathrm{CH}}=\overset{3}{\mathrm{CH}}\overset{4}{\mathrm{CH_3}}$
2-butene

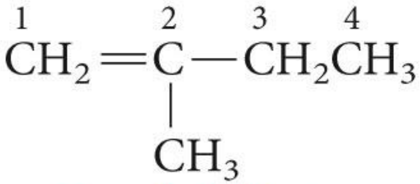
$\overset{1}{\mathrm{HC}}\equiv\overset{2}{\mathrm{C}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$
1-butyne

$\overset{1}{\mathrm{CH_3}}\overset{2}{\mathrm{C}}\equiv\overset{3}{\mathrm{C}}\overset{4}{\mathrm{CH_3}}$
2-butyne



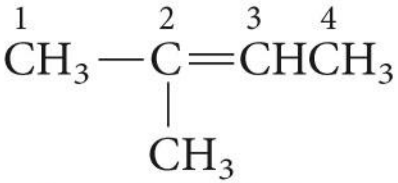
$$\overset{1}{\mathrm{CH_2}}=\underset{\mathrm{CH_3}}{\underset{|}{\overset{2}{\mathrm{C}}}}-\overset{3}{\mathrm{CH_3}}$$

methylpropene
(isobutylene)



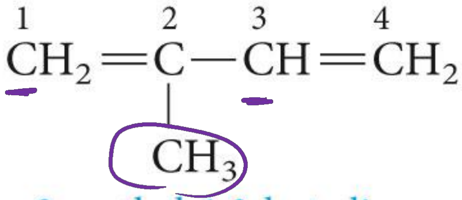
$$\overset{1}{\mathrm{CH_2}}=\underset{\mathrm{CH_3}}{\underset{|}{\overset{2}{\mathrm{C}}}}-\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$$

2-methyl-1-butene
↑



$$\overset{1}{\mathrm{CH_3}}-\underset{\mathrm{CH_3}}{\underset{|}{\overset{2}{\mathrm{C}}}}=\overset{3}{\mathrm{CH}}\overset{4}{\mathrm{CH_3}}$$

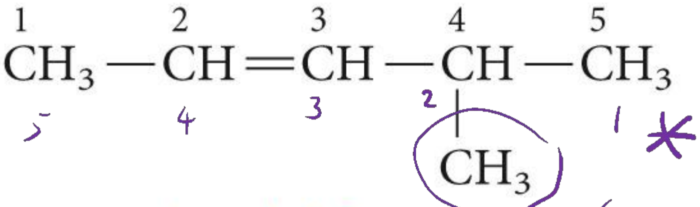
2-methyl-2-butene



$$\underline{\overset{1}{\mathrm{CH_2}}}=\underset{\mathrm{CH_3}}{\underset{|}{\overset{2}{\mathrm{C}}}}-\underline{\overset{3}{\mathrm{CH}}}=\overset{4}{\mathrm{CH_2}}$$

2-methyl-1,3-butadiene
(isoprene)

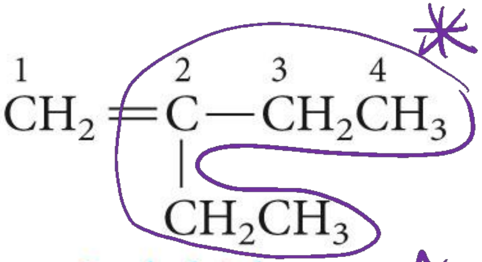
The numbering rules applied



$$\overset{1}{\mathrm{CH_3}}-\overset{2}{\mathrm{CH}}=\overset{3}{\mathrm{CH}}-\underset{\displaystyle \mathrm{CH_3}}{\overset{4}{\mathrm{CH}}}-\overset{5}{\mathrm{CH_3}}$$

4-methyl-2-pentene

(*Not* 2-methyl-3-pentene; the chain is numbered so that the double bond gets the lower number.)



$$\overset{1}{\mathrm{CH_2}}=\underset{\displaystyle \mathrm{CH_2CH_3}}{\overset{2}{\mathrm{C}}}-\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$$

2-ethyl-1-butene

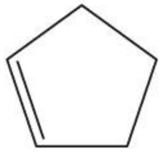
(Named this way, even though there is a five-carbon chain present, because that chain does not include both carbons of the double bond.)

$$\overset{1}{\mathrm{CH_2}}=\overset{2}{\mathrm{CH}}-\overset{3}{\mathrm{CH}}=\overset{4}{\mathrm{CH_2}}$$

1,3-butadiene

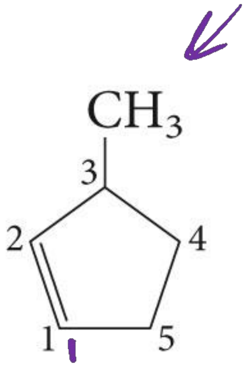
(Note the *a* inserted in the name, to help in pronunciation.)

With the cyclic hydrocarbons, we start numbering the ring with the carbons of the multiple bond.



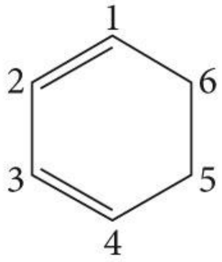
cyclopentene

(No number is necessary, because there is only one possible structure.)

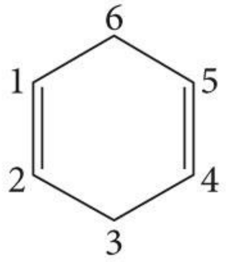


3-methylcyclopentene

(Start numbering at, and number through the double bond; 5-methylcyclopentene and 1-methyl-2-cyclopentene are incorrect names.)



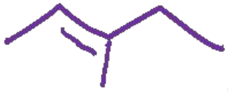
1,3-cyclohexadiene



1,4-cyclohexadiene

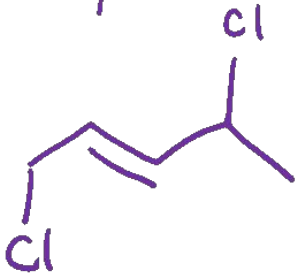
Write the structural formula for

3-methyl-2-pentene

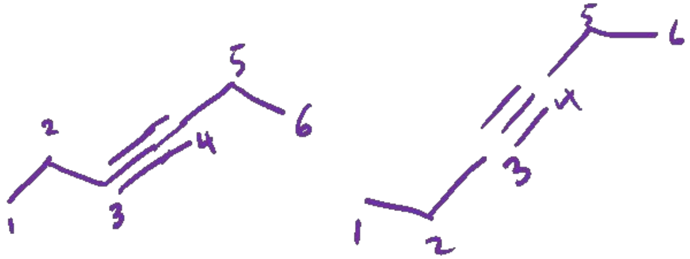


$-C\equiv C-$

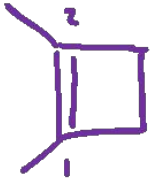
1,4-dichloro-2-pentene



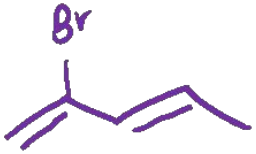
3-hexyne



1,2-dimethylcyclobutene



2-bromo-1,3-pentadiene

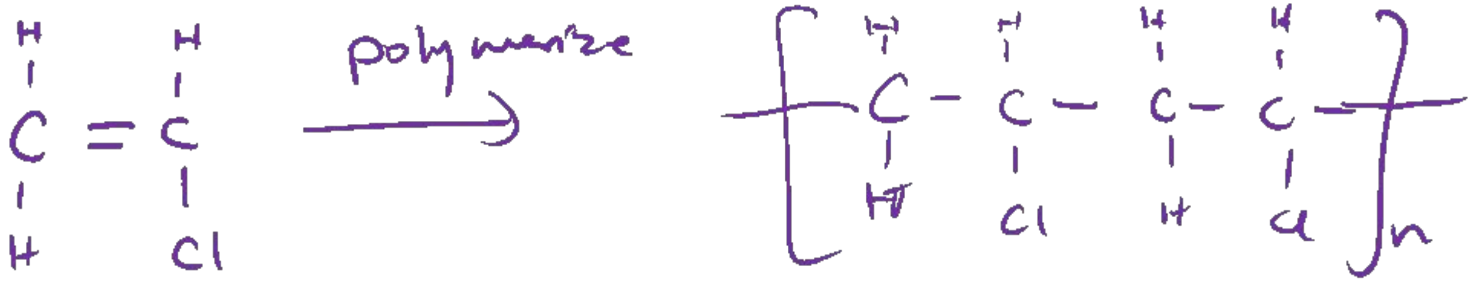


Some Common names

$CH_2{=}CH_2$
ethylene
(ethene) ✓

$HC{\equiv}CH$
acetylene
(ethyne) ✓

$CH_3CH{=}CH_2$
propylene
(propene)



$CH_2{=}CH—$

vinyl

(ethenyl)

$CH_2{=}CHCl$

vinyl chloride

(chloroethene)

$CH_2{=}CH—CH_2—$

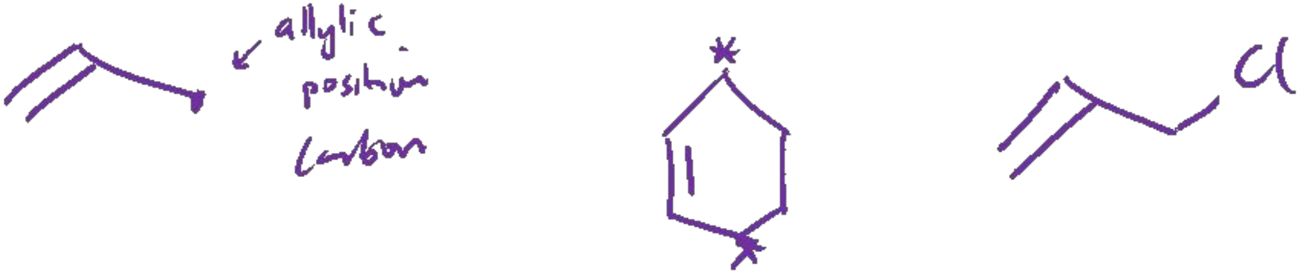
allyl

(2-propenyl)

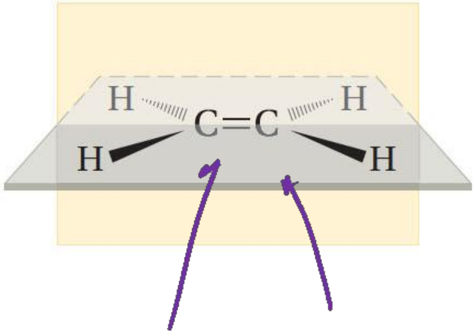
$CH_2{=}CH—CH_2Cl$

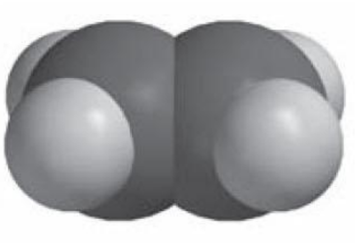
allyl chloride

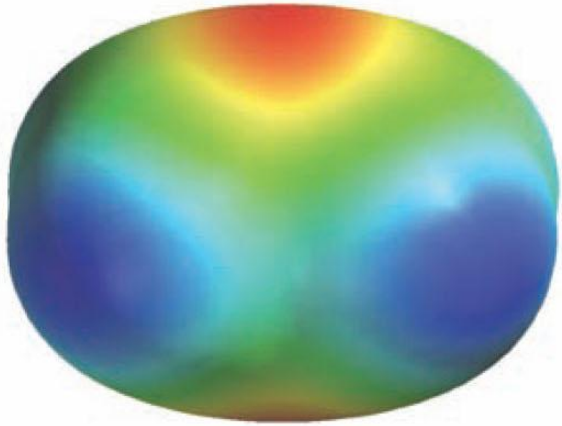
(3-chloropropene)



Some Facts about Double Bonds

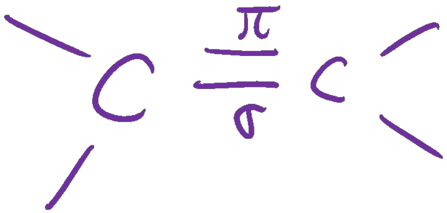






sp^2 sp^2

trigonal planer
120°



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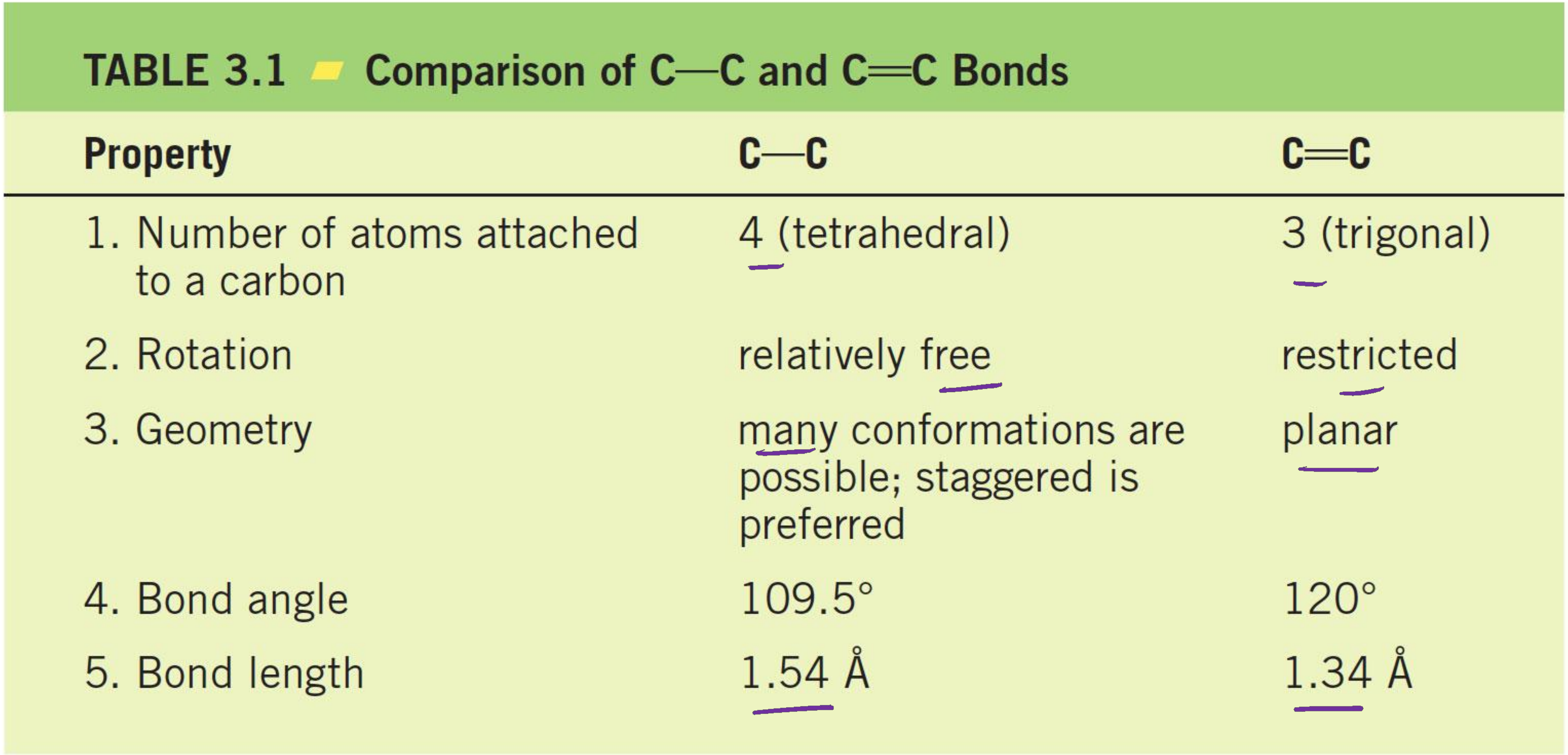
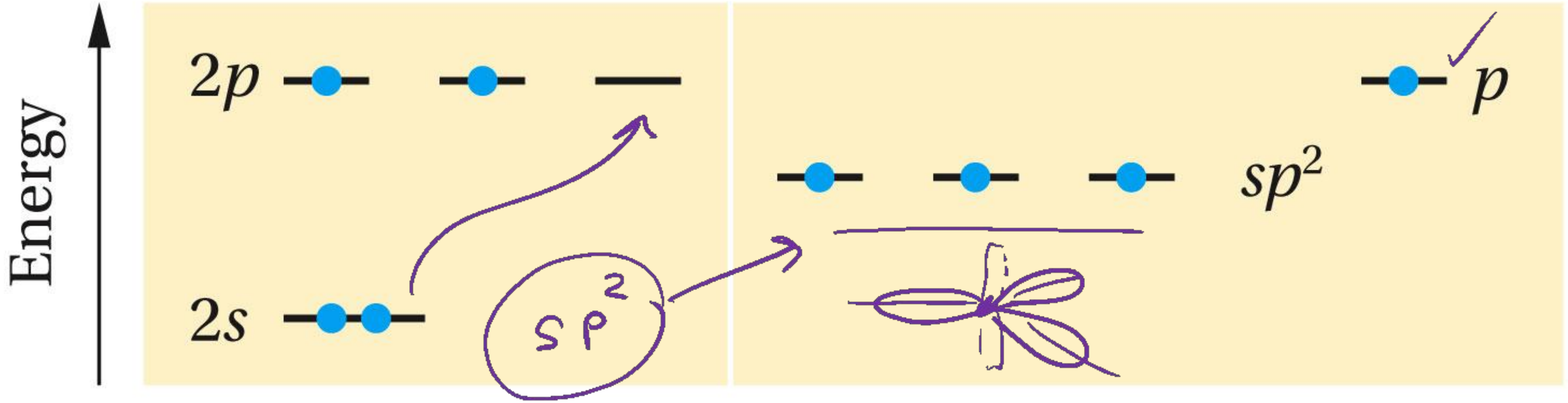


TABLE 3.1 Comparison of C—C and C═C Bonds

Property	C—C	C═C
1. Number of atoms attached to a carbon	4 (tetrahedral)	3 (trigonal)
2. Rotation	relatively free	restricted
3. Geometry	many conformations are possible; staggered is preferred	planar
4. Bond angle	109.5°	120°
5. Bond length	1.54 Å	1.34 Å

The Orbital Model of a Double Bond; the pi Bond

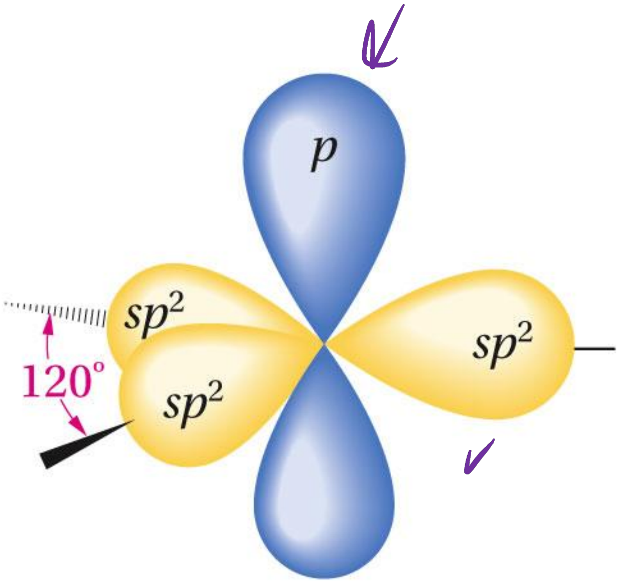


Atomic orbitals of carbon

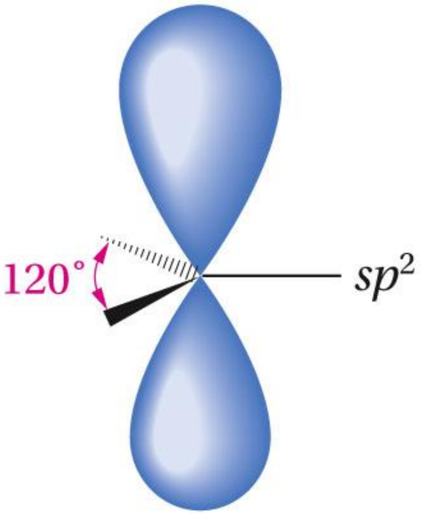
The 2*s* and two 2*p* orbitals are combined to form three hybrid *sp*² orbitals, leaving one electron still in a *p* orbital.

^{6}C

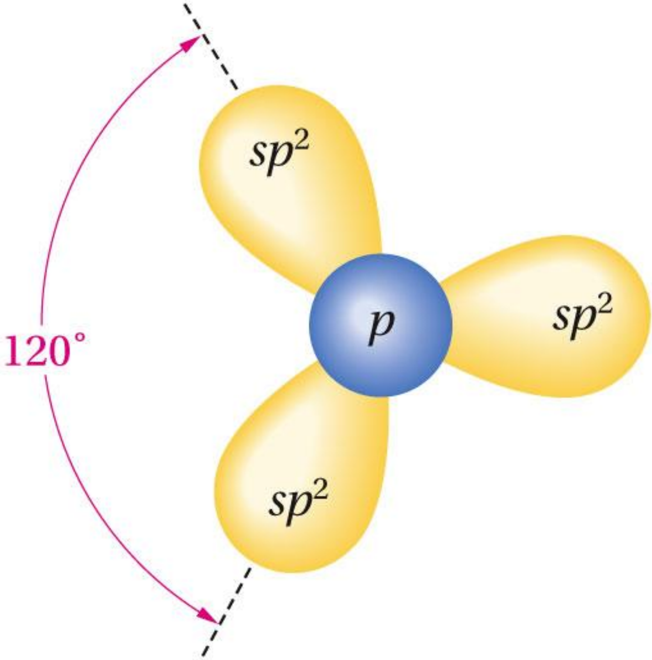
$1s^2, \underbrace{2s^2\, 2p^2}$



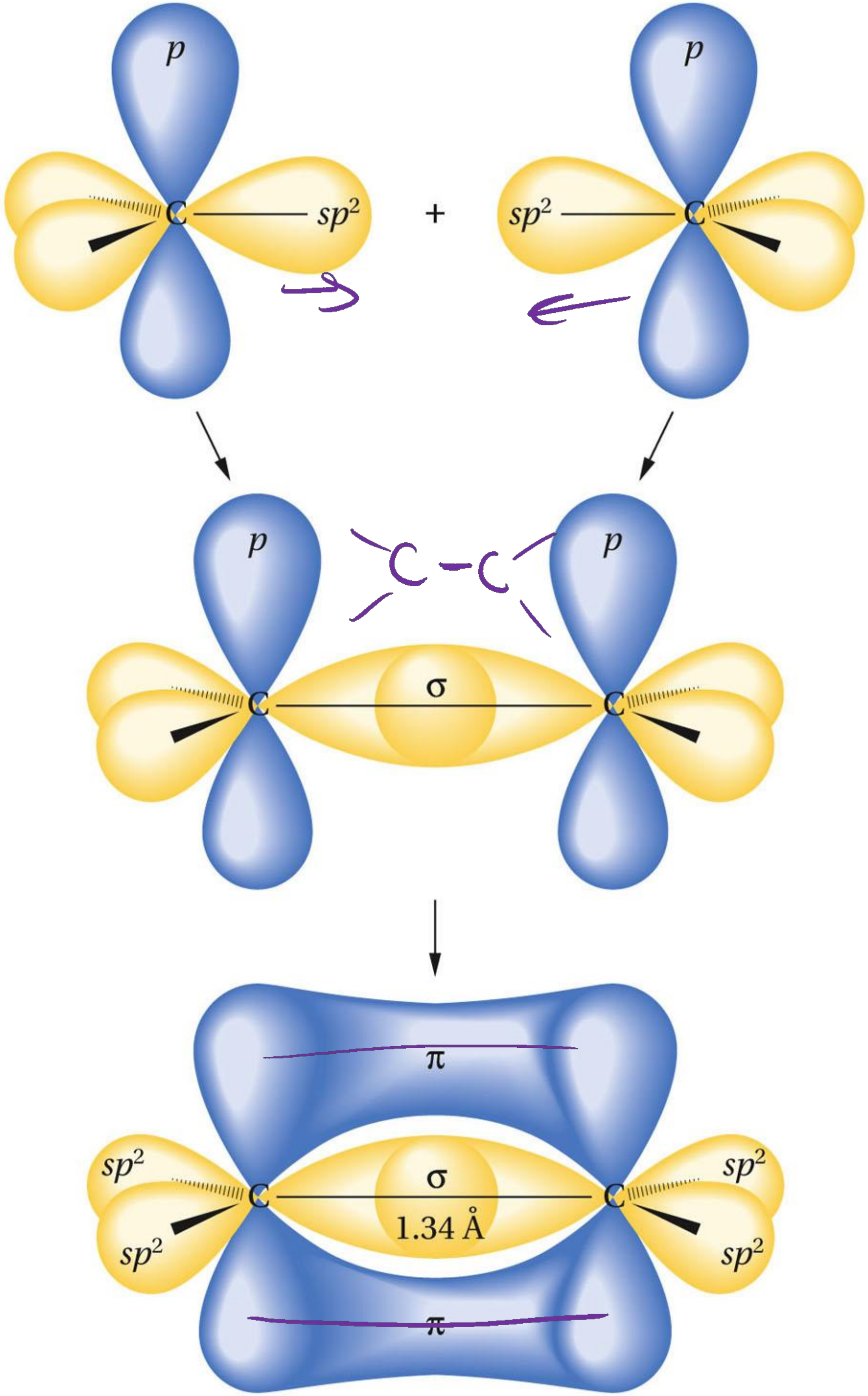
side view



side view with the sp^2 orbitals represented by lines



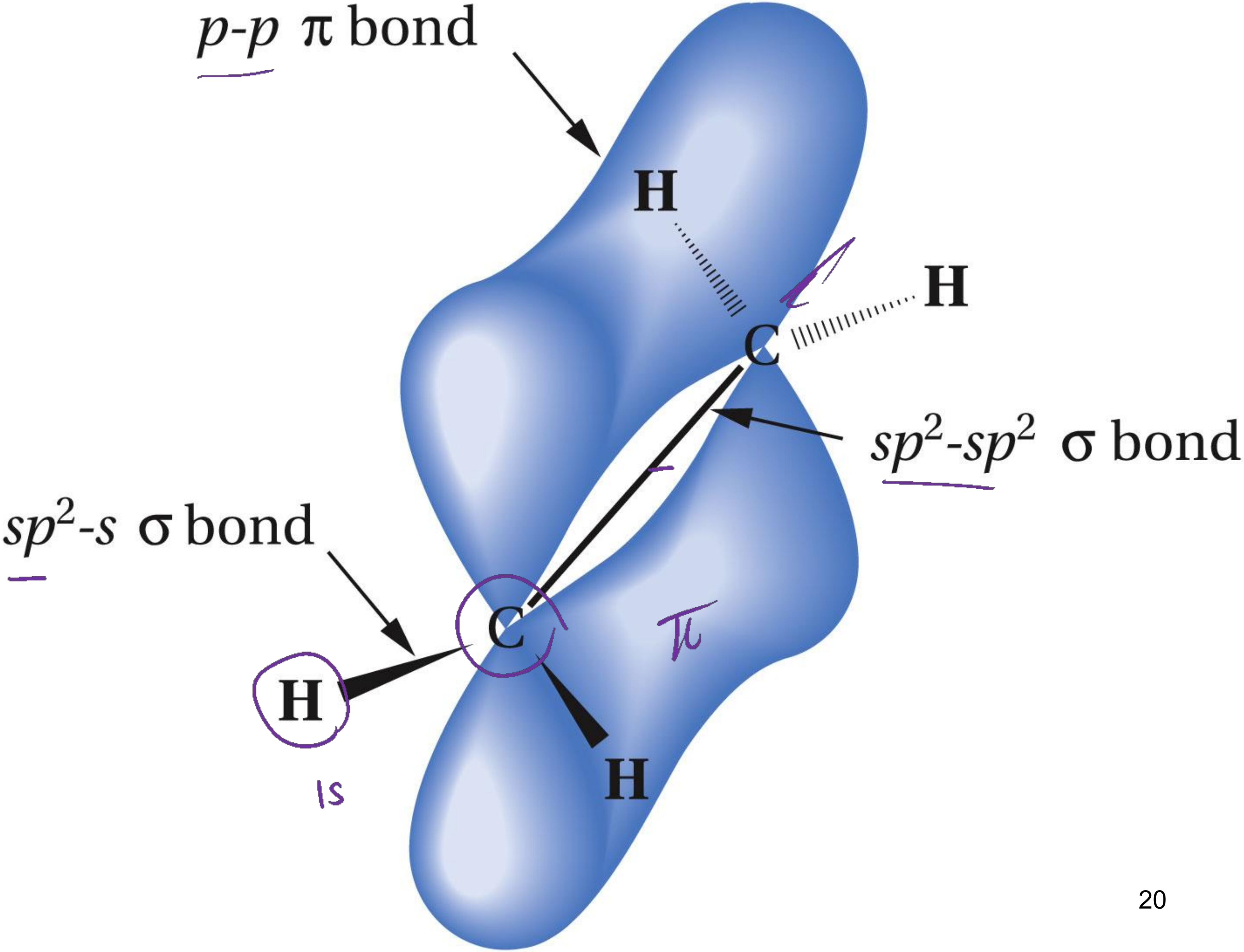
top view



two sp^2-hybridized carbons with *p* orbitals parallel

the σ bond is formed by two electrons in overlapping sp^2 orbitals

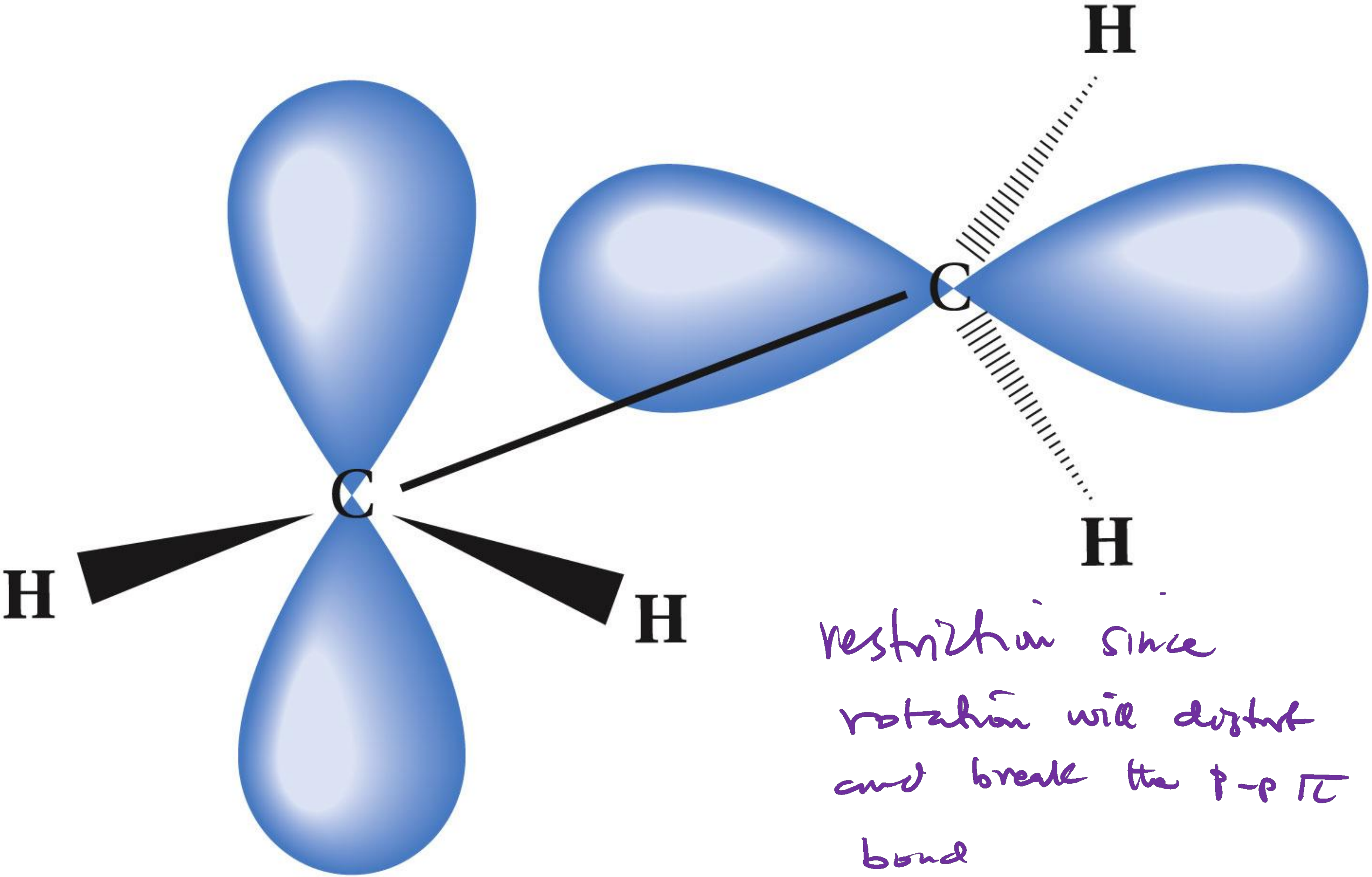
the π bond is formed by two electrons in overlapping parallel *p* orbitals



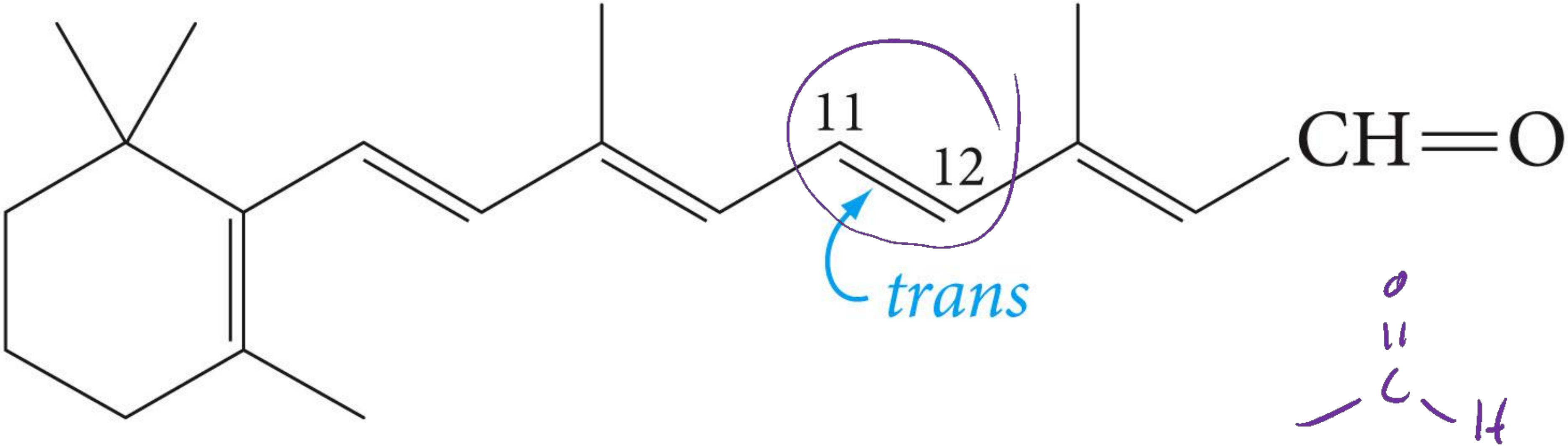
p-*p* π bond

sp^2-*sp*^{2} σ bond

sp^2-*s* σ bond

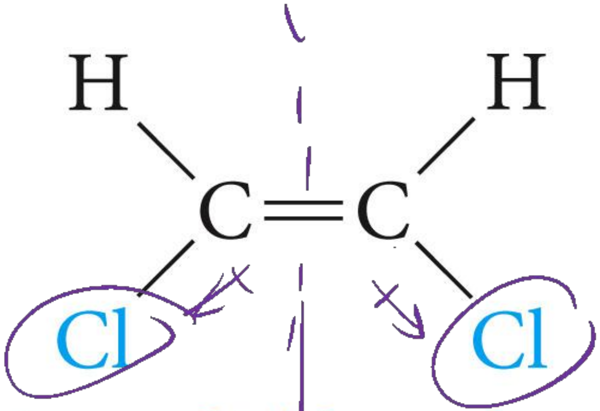


restriction since rotation will distort and break the p-p π bond



trans-retinal

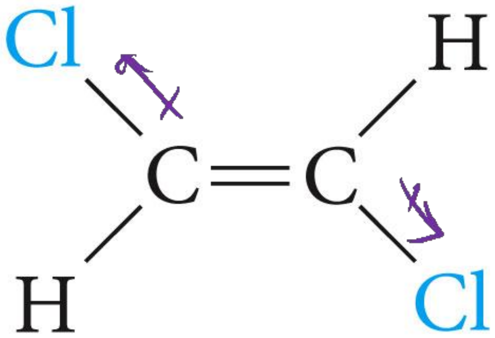
Cis-Trans Isomerism in Alkenes



cis-1,2-dichloroethene

bp 60°C, mp −80°C

polar

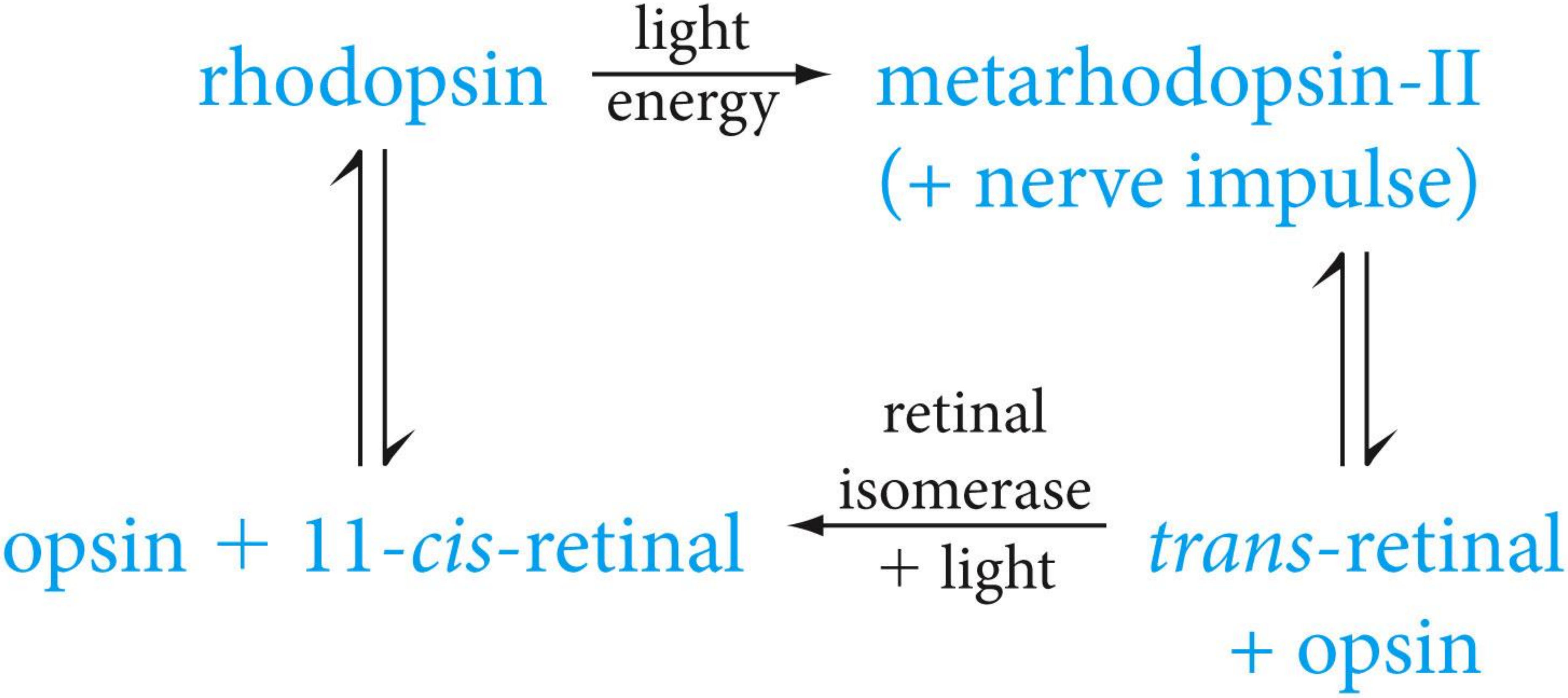


trans-1,2-dichloroethene

bp 47°C, mp −50°C

not polar

The Chemistry of Vision

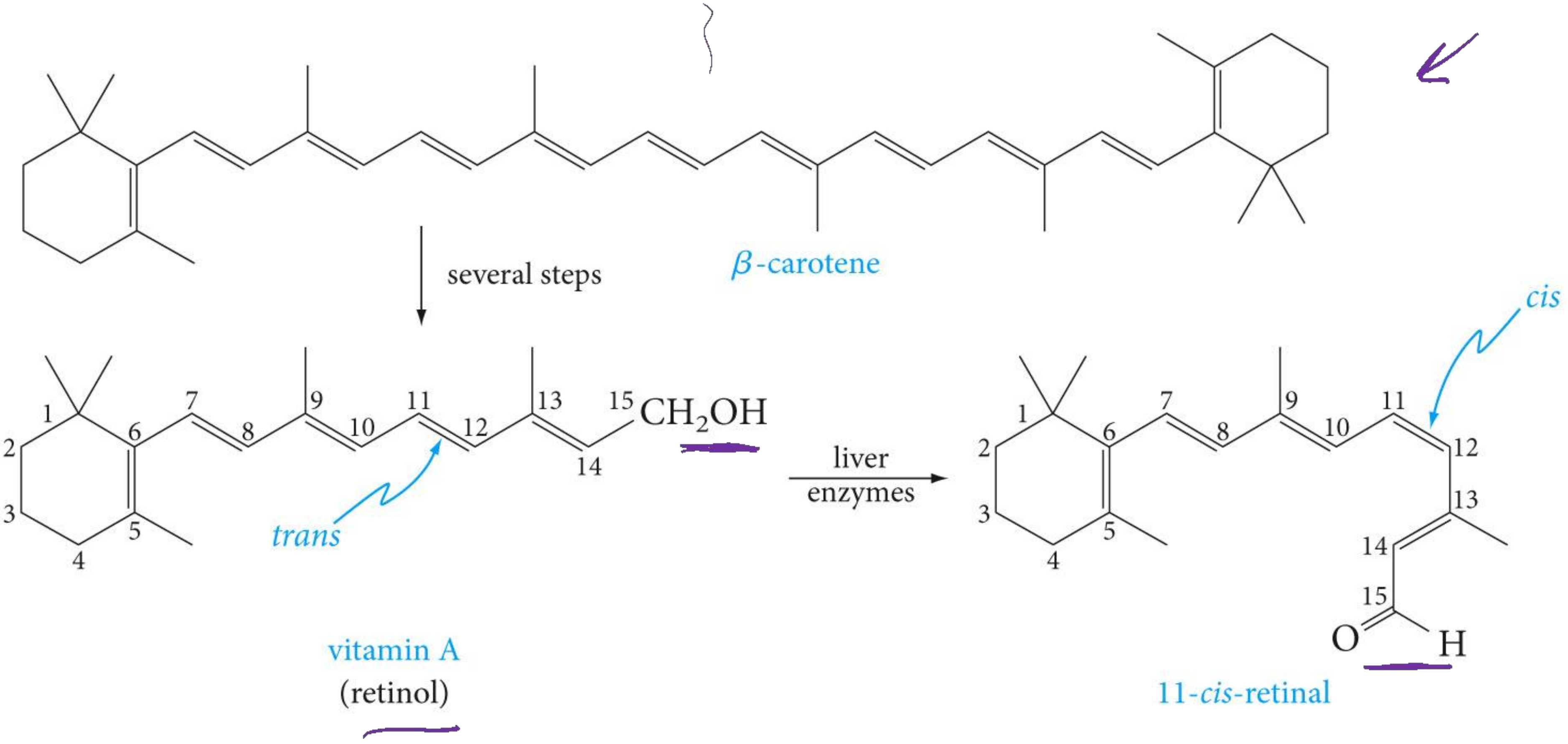


rhodopsin $\xrightarrow[\text{energy}]{\text{light}}$ metarhodopsin-II (+ nerve impulse)

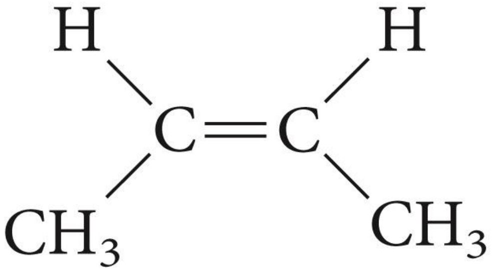
metarhodopsin-II ⇌ *trans*-retinal + opsin

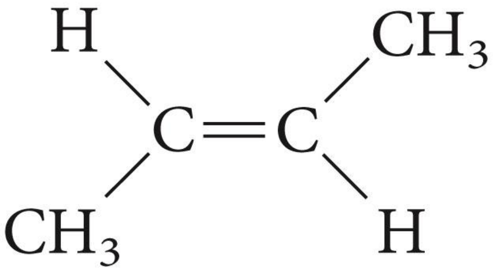
trans-retinal + opsin $\xrightarrow[\text{+ light}]{\text{retinal isomerase}}$ opsin + 11-*cis*-retinal

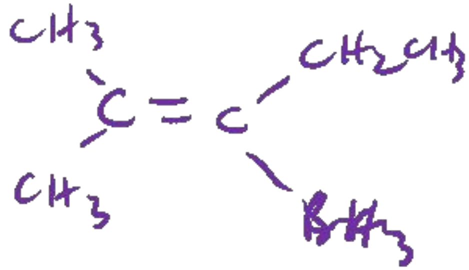
opsin + 11-*cis*-retinal ⇌ rhodopsin

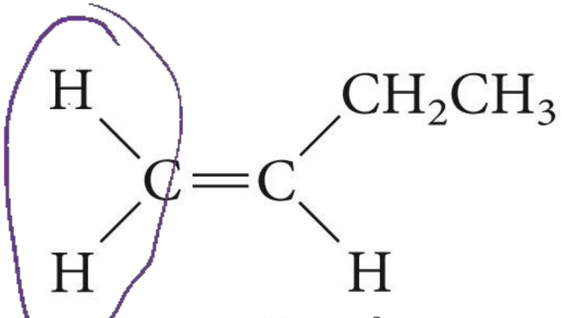

β-carotene
several steps
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
CH_2OH
trans
vitamin A
(retinol)
liver
enzymes
cis
O
H
11-*cis*-retinal

Are cis-trans isomers possible for 1-butene and 2-butene?

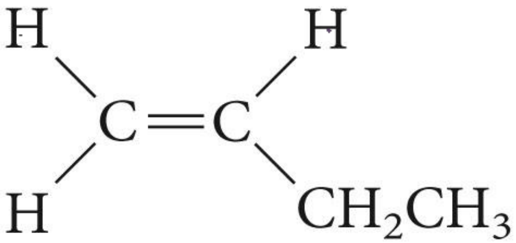

cis-2-butene
bp 3.7°C, mp −139°C


trans-2-butene
bp 0.3°C, mp −106°C



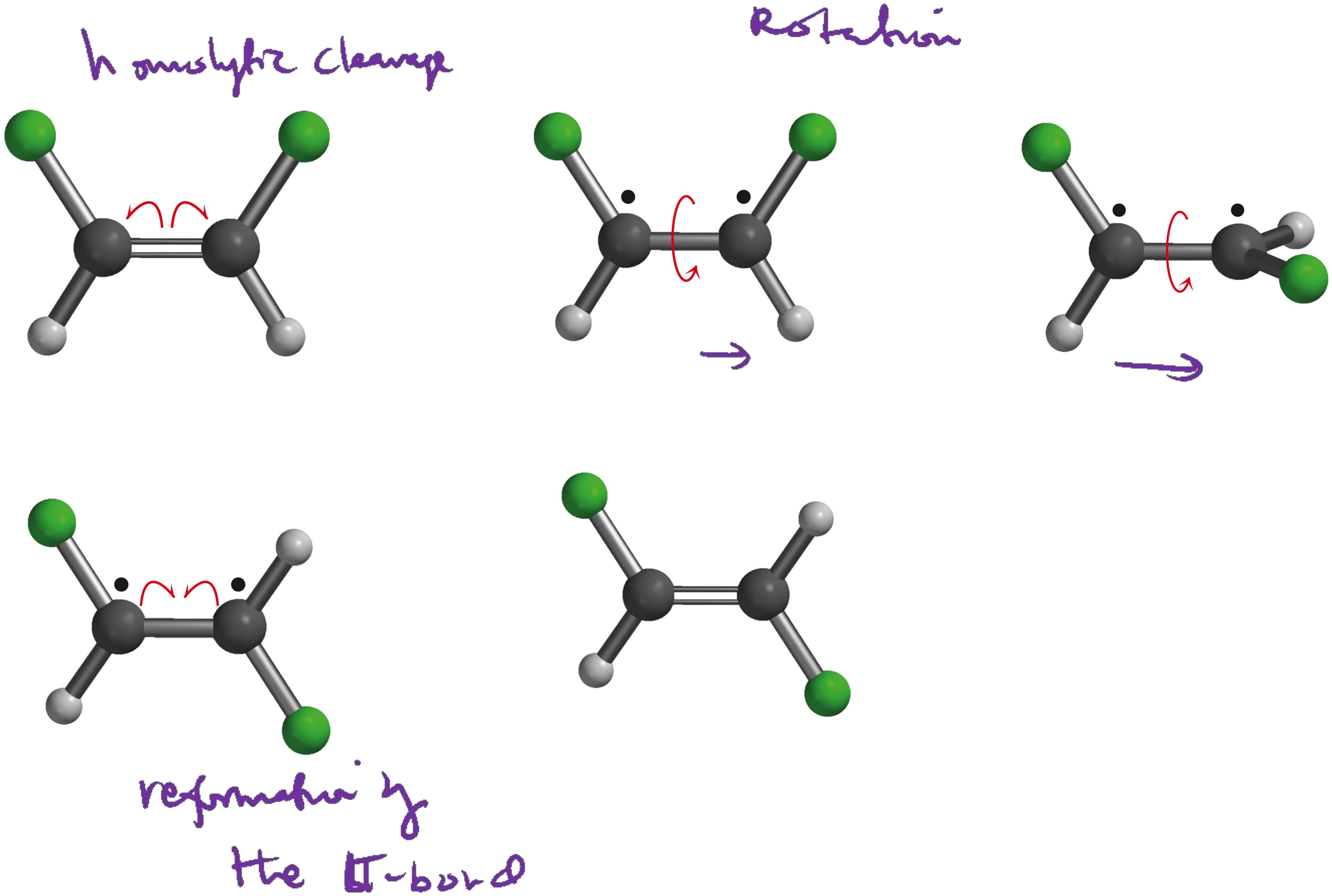

1-butene

is identical to


1-butene

Whenever you have identical grps on one side of C=C bond, ⇒ NO possibili of cis/trans

Geometric isomers of alkenes can be interconverted if sufficient energy is supplied to break the pi bond and allow rotation about the remaining sigma bond.

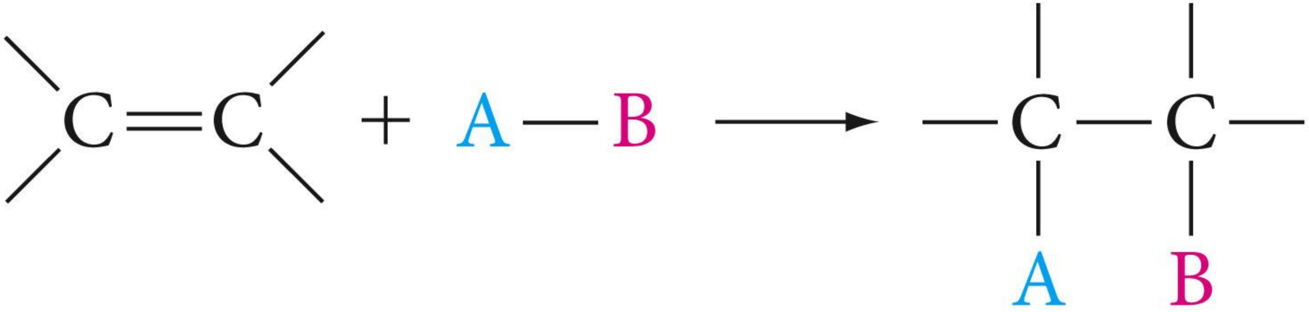


homolytic cleavage

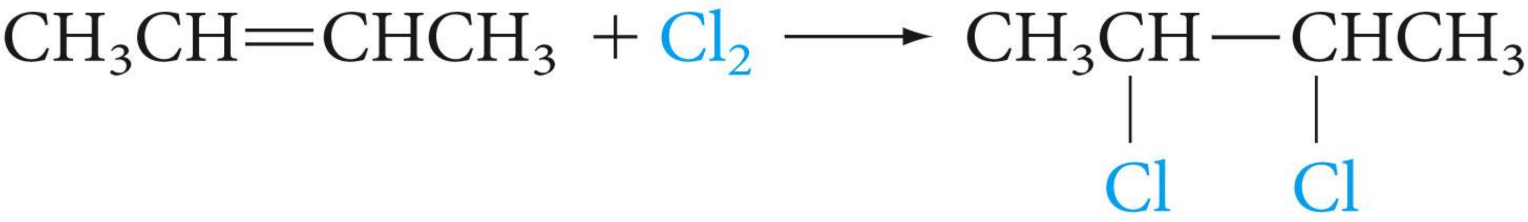
Rotation

reformation of the π-bond

Addition and Substitution Reactions Compared



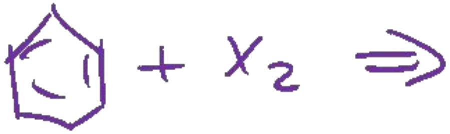
Addition of halogens X_2 $(Br_2, Cl_2, I_2, \overset{?}{F_2})$



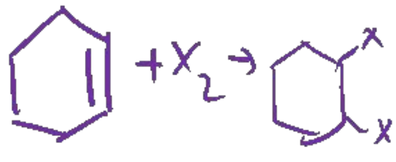
$$CH_3CH{=}CHCH_3 + Cl_2 \longrightarrow CH_3\underset{\overset{|}{Cl}}{CH}-\underset{\overset{|}{Cl}}{CH}CH_3$$

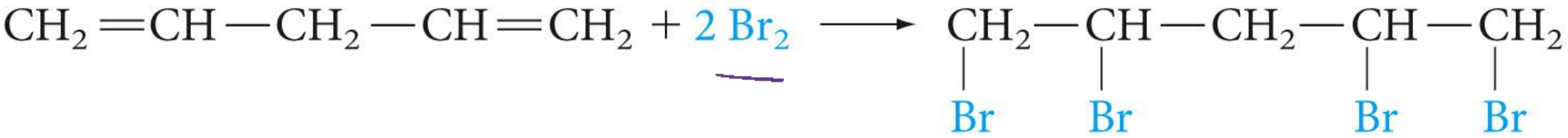
2-butene
bp 1–4°C

2,3-dichlorobutane
bp 117–119°C



Do not undergo addition rxn

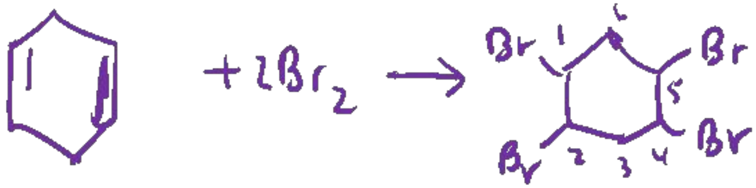




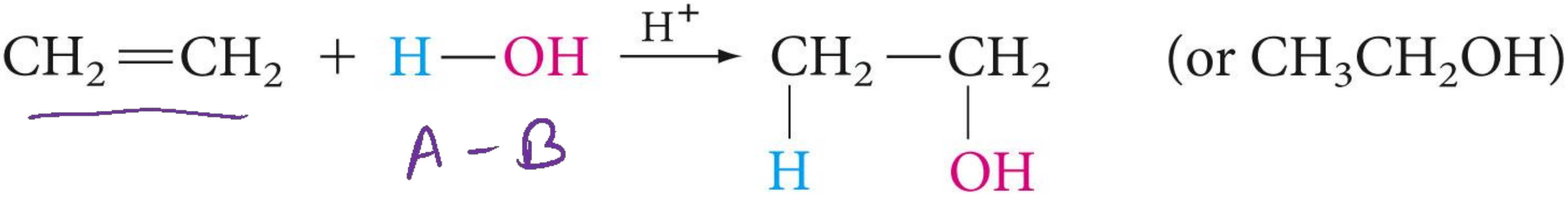
$$CH_2{=}CH{-}CH_2{-}CH{=}CH_2 + \underline{2\,Br_2} \longrightarrow \underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH}}-CH_2-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}$$

1,4-pentadiene
bp 26.0°C

1,2,4,5-tetrabromopentane
mp 85 – 86°C

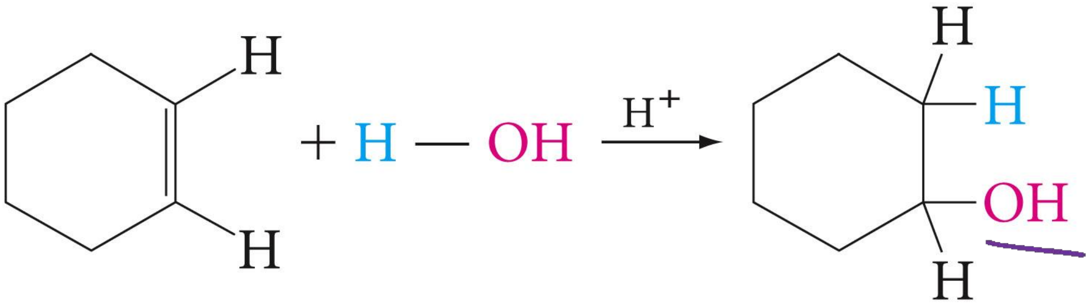


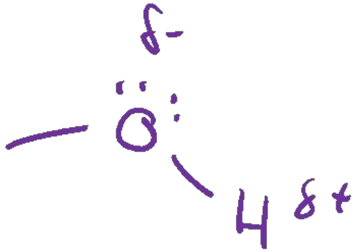
Addition of Water (Hydration)



$$\underline{CH_2{=}CH_2} + \underset{A-B}{H{-}OH} \xrightarrow{H^+} \underset{H}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}} \qquad (\text{or } CH_3CH_2OH)$$

ethanol





cyclohexene
bp 83.0°C

Unsaturated cycloalkane

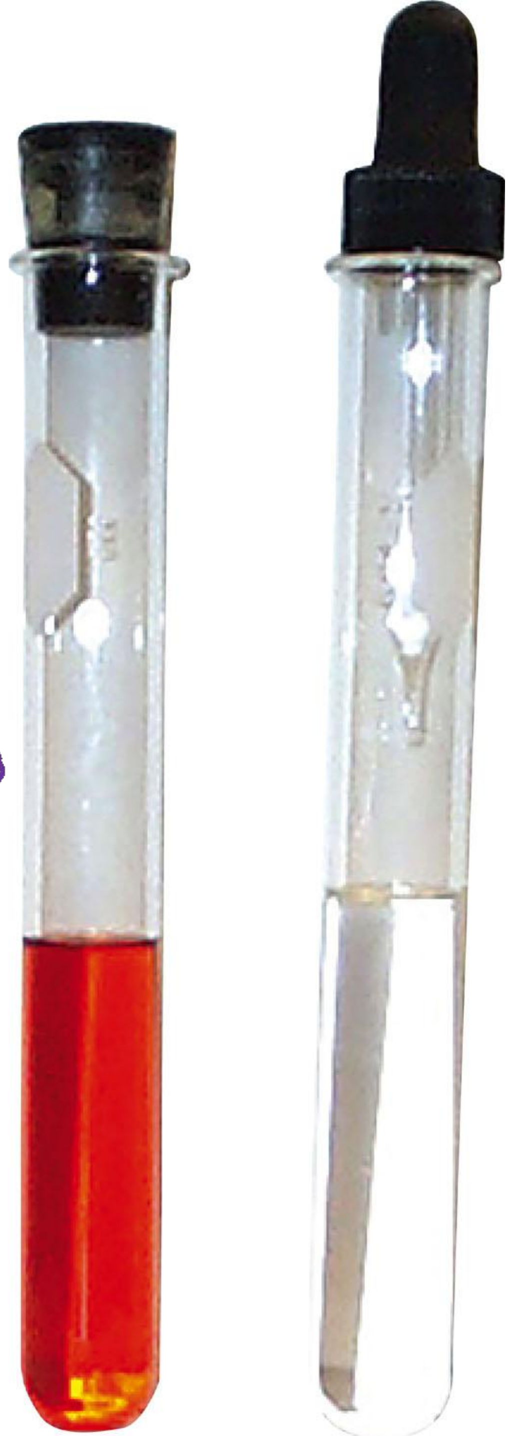
non polar

cyclohexanol
bp 161.1°C

alcohol

polar ⇒ hydrogen bonding

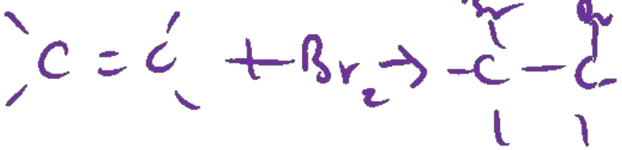
Bromine added
to
saturated



Br2 to

unsaturated Hydroca

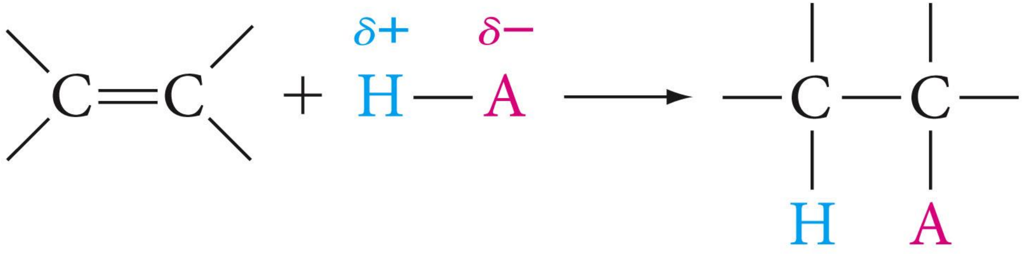
alkene
alkyne



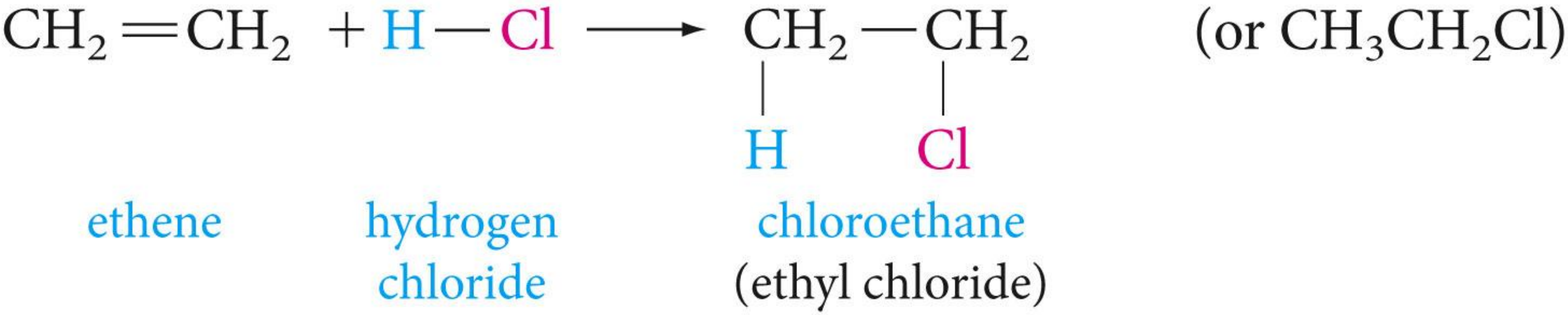
$$>C=C< + Br_2 \rightarrow -\overset{Br}{\underset{|}{\overset{|}{C}}}-\overset{Br}{\underset{|}{\overset{|}{C}}}-$$

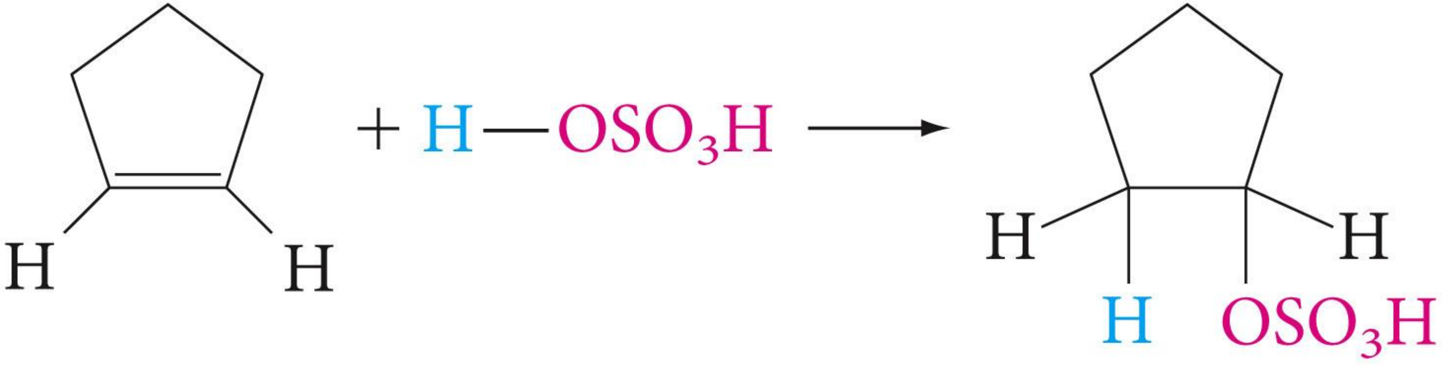
- END -

Addition of Acids



Acids that add this way are the hydrogen halides (H-F, H-Cl, H-Br, H-I) and sulfuric acid ($H\text{-}OSO_3H$)


$$CH_2{=}CH_2 + H{-}Cl \longrightarrow \underset{H}{\underset{|}{CH_2}}{-}\underset{Cl}{\underset{|}{CH_2}} \qquad (\text{or } CH_3CH_2Cl)$$



cyclopentene

sulfuric acid

cyclopentyl hydrogen sulfate

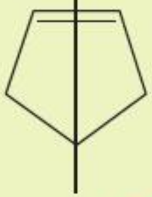
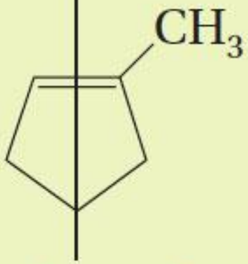
Write the equation for each of the following reactions

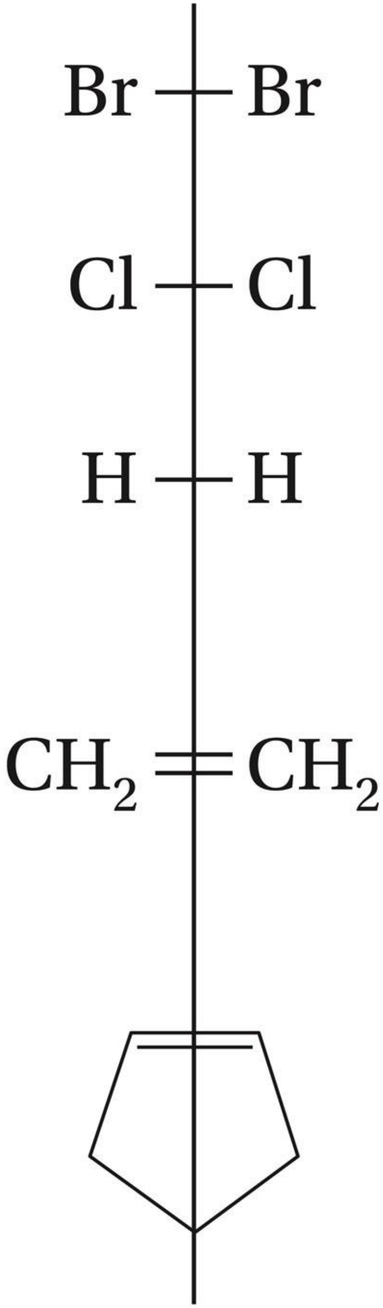
a)2-butene + HCl

b)3-Hexene + HI

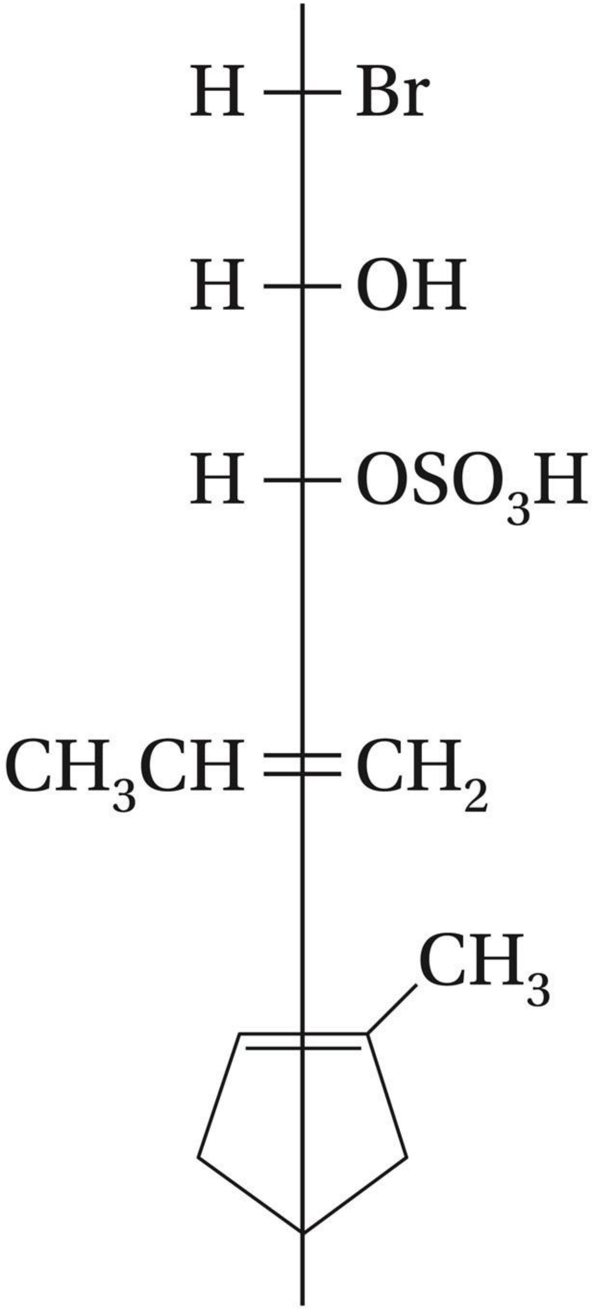
c)4-methylcyclopentene + HBr

Table 3.2 ▰ Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

	Symmetric	Unsymmetric
Reagents	$Br-Br$	$H-Br$
	$Cl-Cl$	$H-OH$
	$H-H$	$H-OSO_3H$
Alkenes	$CH_2=CH_2$	$CH_3CH=CH_2$
		
	mirror plane	not a mirror plane

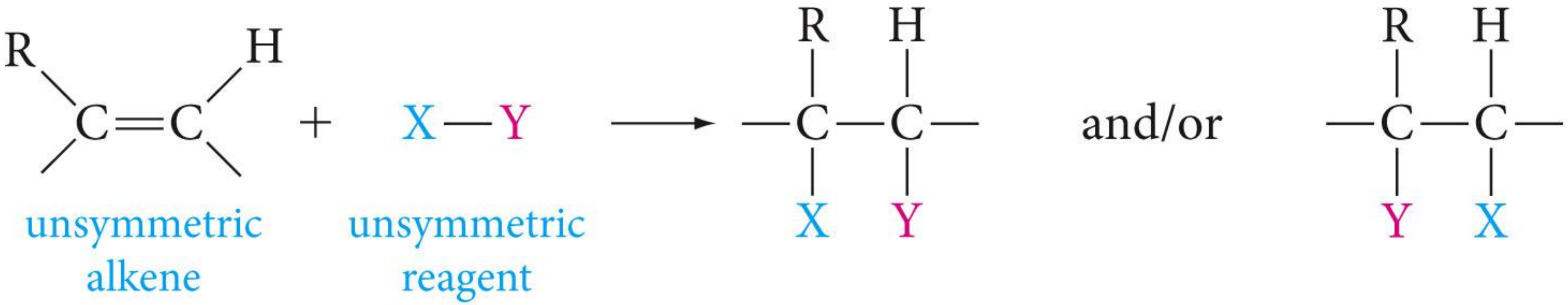


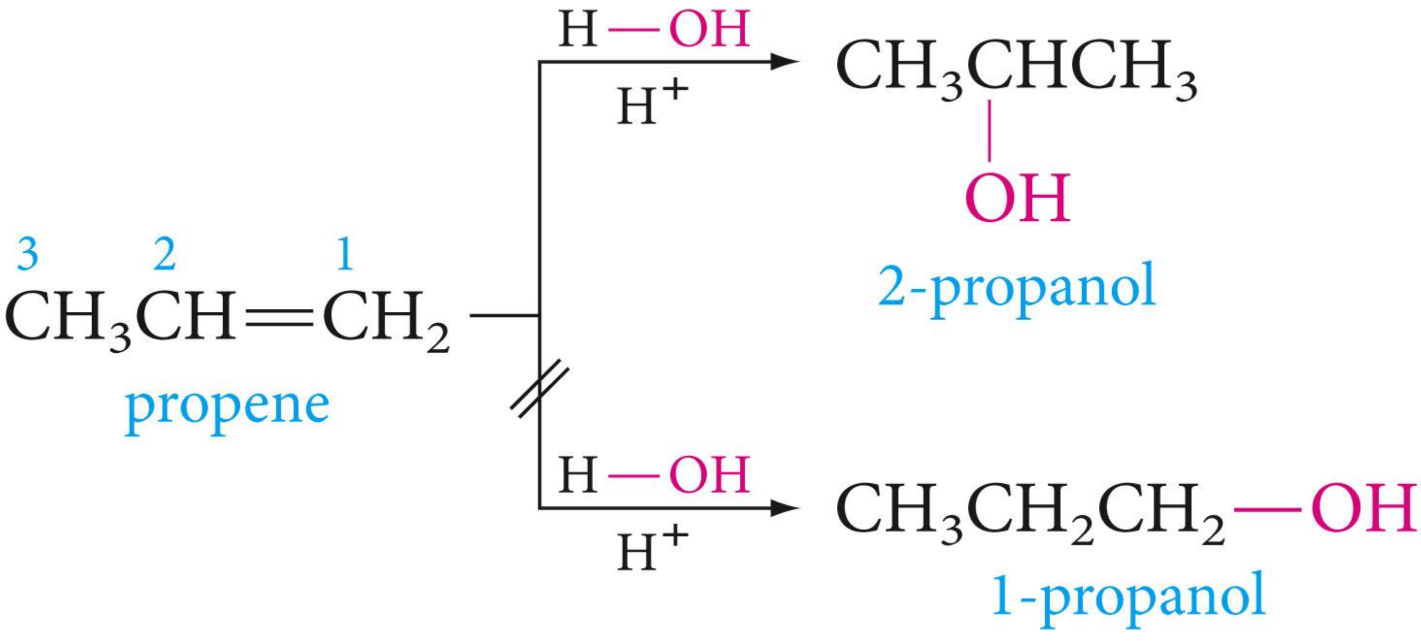
mirror plane



not a mirror plane

Addition of Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule





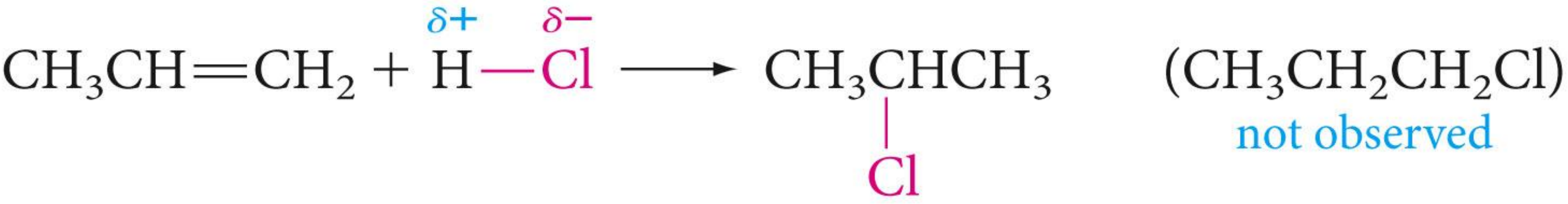
$$\overset{3}{C}H_3\overset{2}{C}H{=}\overset{1}{C}H_2 \xrightarrow[H^+]{H-OH} CH_3\underset{\displaystyle OH}{\underset{|}{C}H}CH_3$$

propene

2-propanol

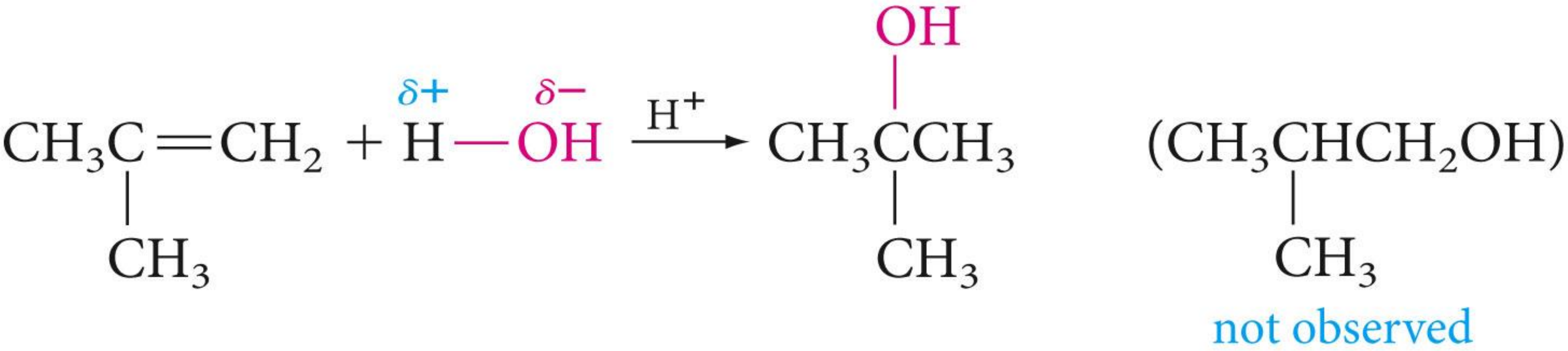
$$CH_3CH{=}CH_2 \not\xrightarrow[H^+]{H-OH} CH_3CH_2CH_2-OH$$

1-propanol



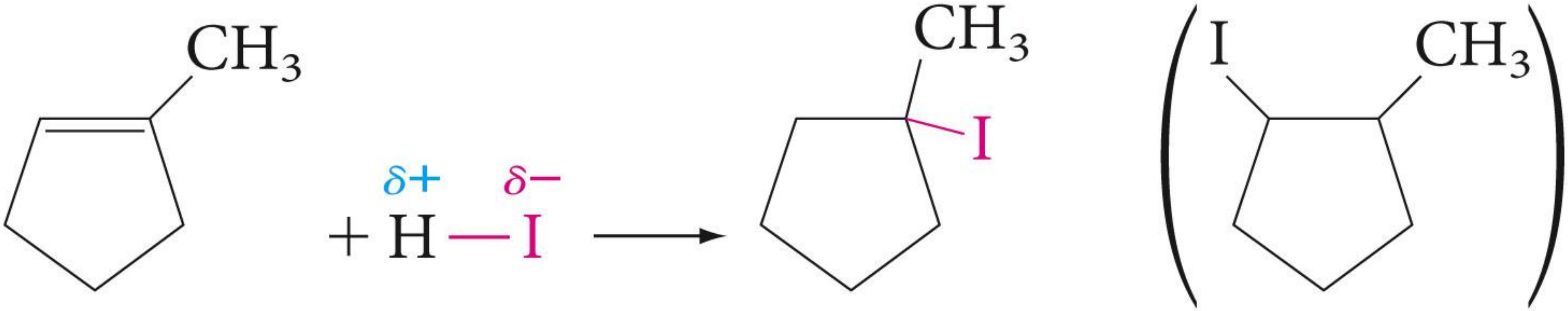
$$CH_3CH{=}CH_2 + \overset{\delta+}{H}{-}\overset{\delta-}{Cl} \longrightarrow CH_3\underset{\underset{\displaystyle Cl}{|}}{C}HCH_3 \qquad (CH_3CH_2CH_2Cl)$$

not observed



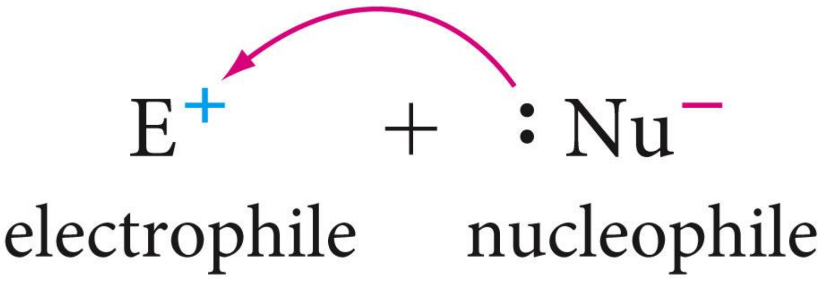
$$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2 + \overset{\delta+}{H}{-}\overset{\delta-}{OH} \xrightarrow{H^+} CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_3 \qquad (CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2OH)$$

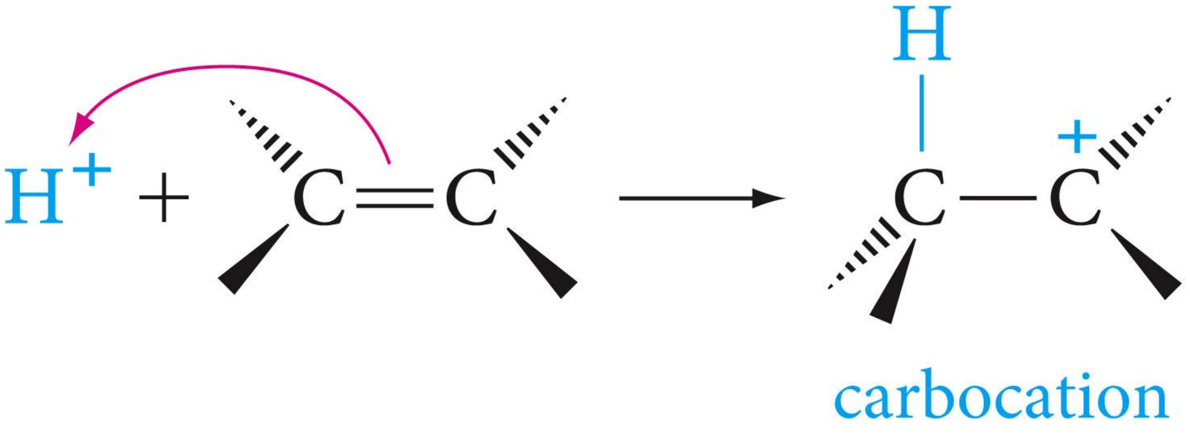
not observed

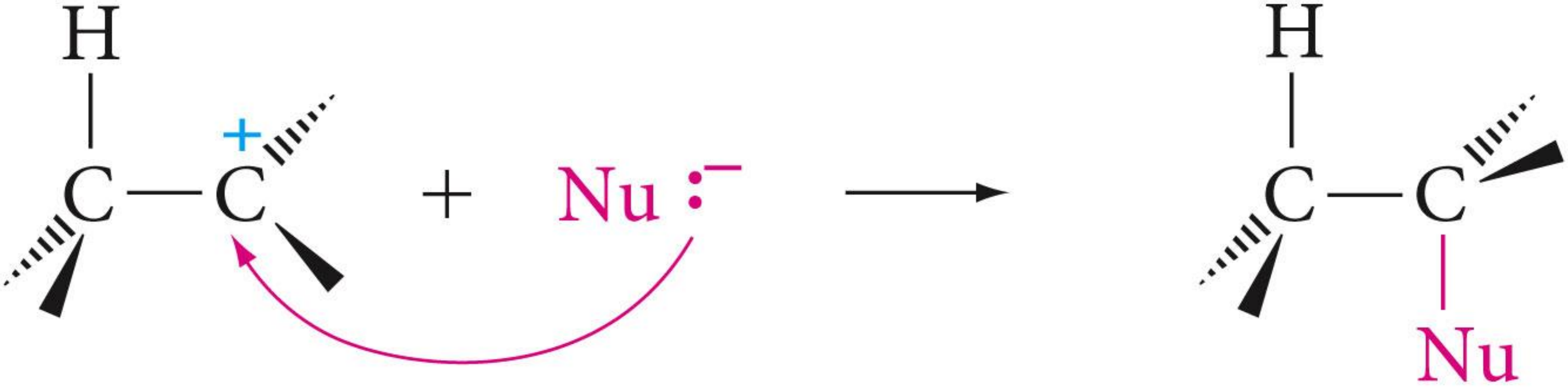


not observed

Mechanism of Electrophilic Addition to Alkenes

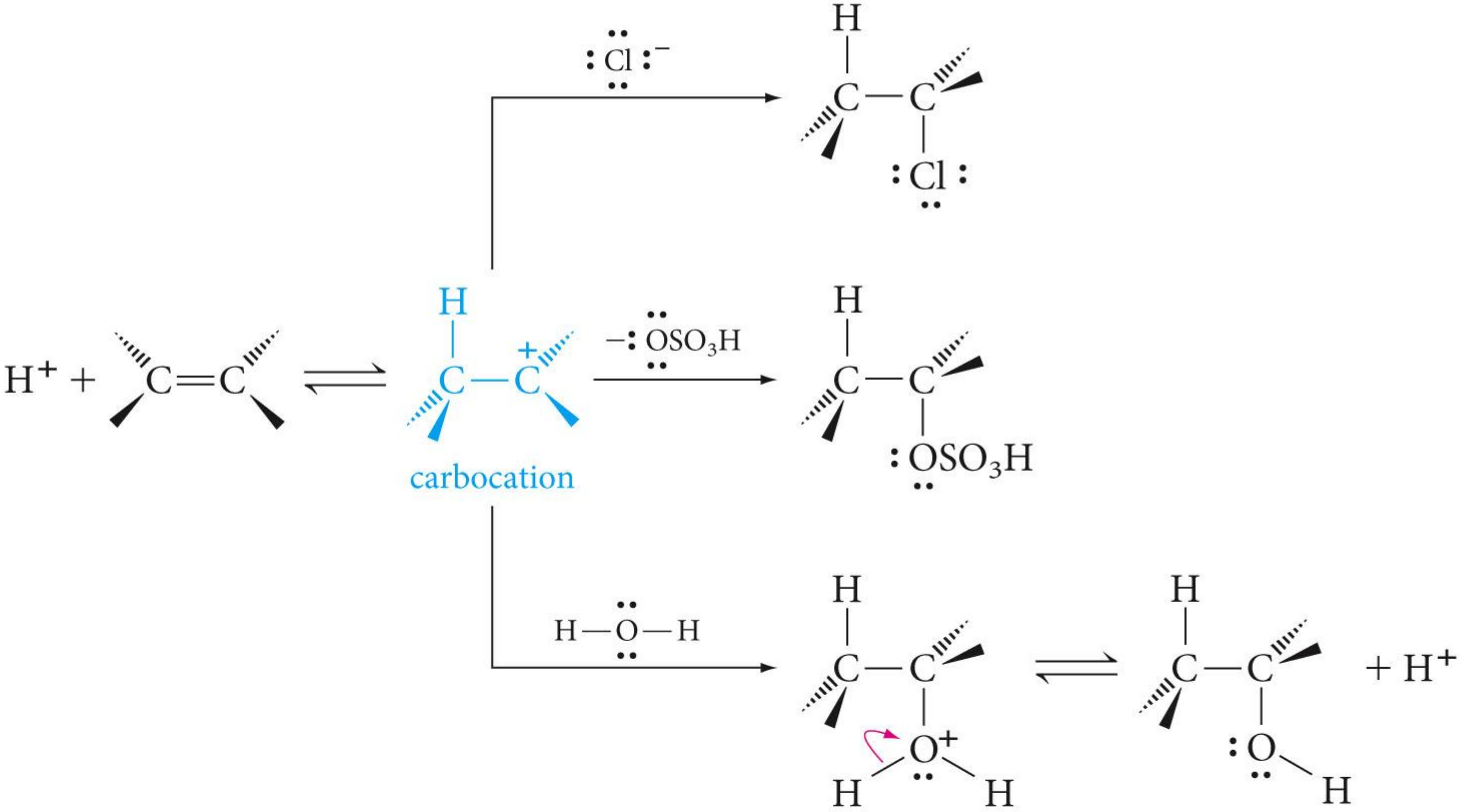






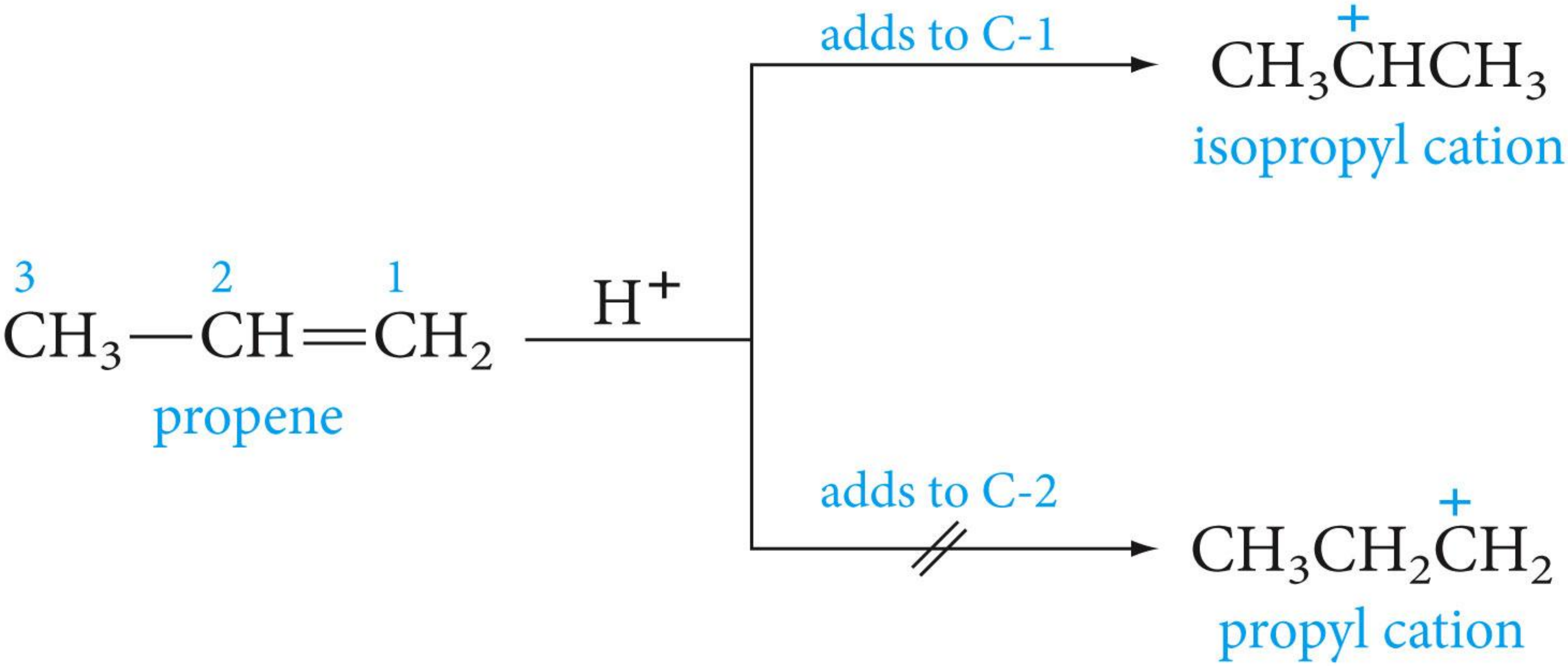
nucleophile

product of addition
of H—Nu to an alkene



H+ +
C=C
H
C—C+
carbocation
:Cl:−
−:OSO3H
H—O—H
H
C—C
:Cl:
H
C—C
:OSO3H
H
C—C
O+
H
H
H
C—C
:O
H
+ H+

Markovnokov’s Rule Explained



$\overset{3}{\mathrm{CH_3}}-\overset{2}{\mathrm{CH}}=\overset{1}{\mathrm{CH_2}}$

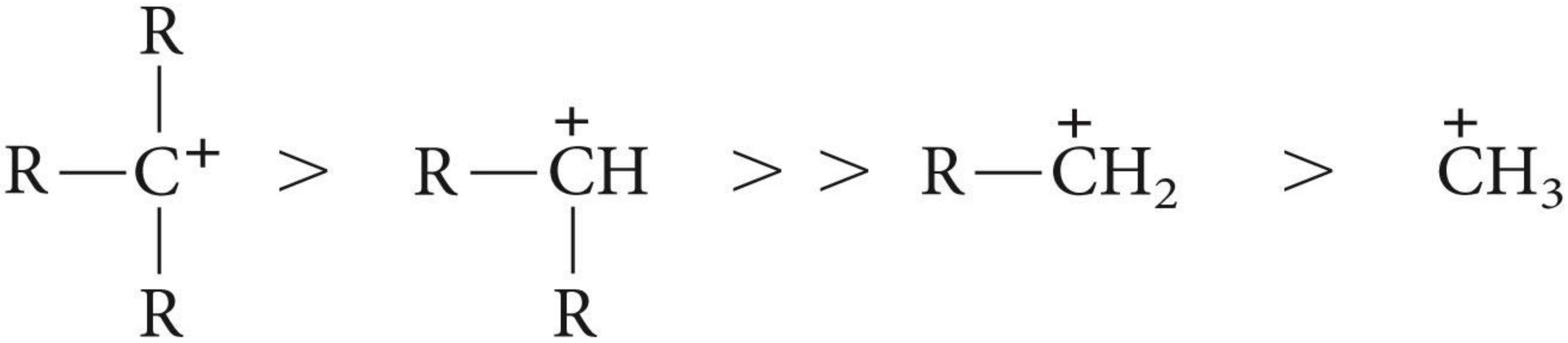
propene

$$\xrightarrow{H^+}\ \xrightarrow{\text{adds to C-1}}\ \mathrm{CH_3\overset{+}{C}HCH_3}$$

isopropyl cation

$$\xrightarrow{H^+}\ \overset{\text{adds to C-2}}{\not\longrightarrow}\ \mathrm{CH_3CH_2\overset{+}{C}H_2}$$

propyl cation

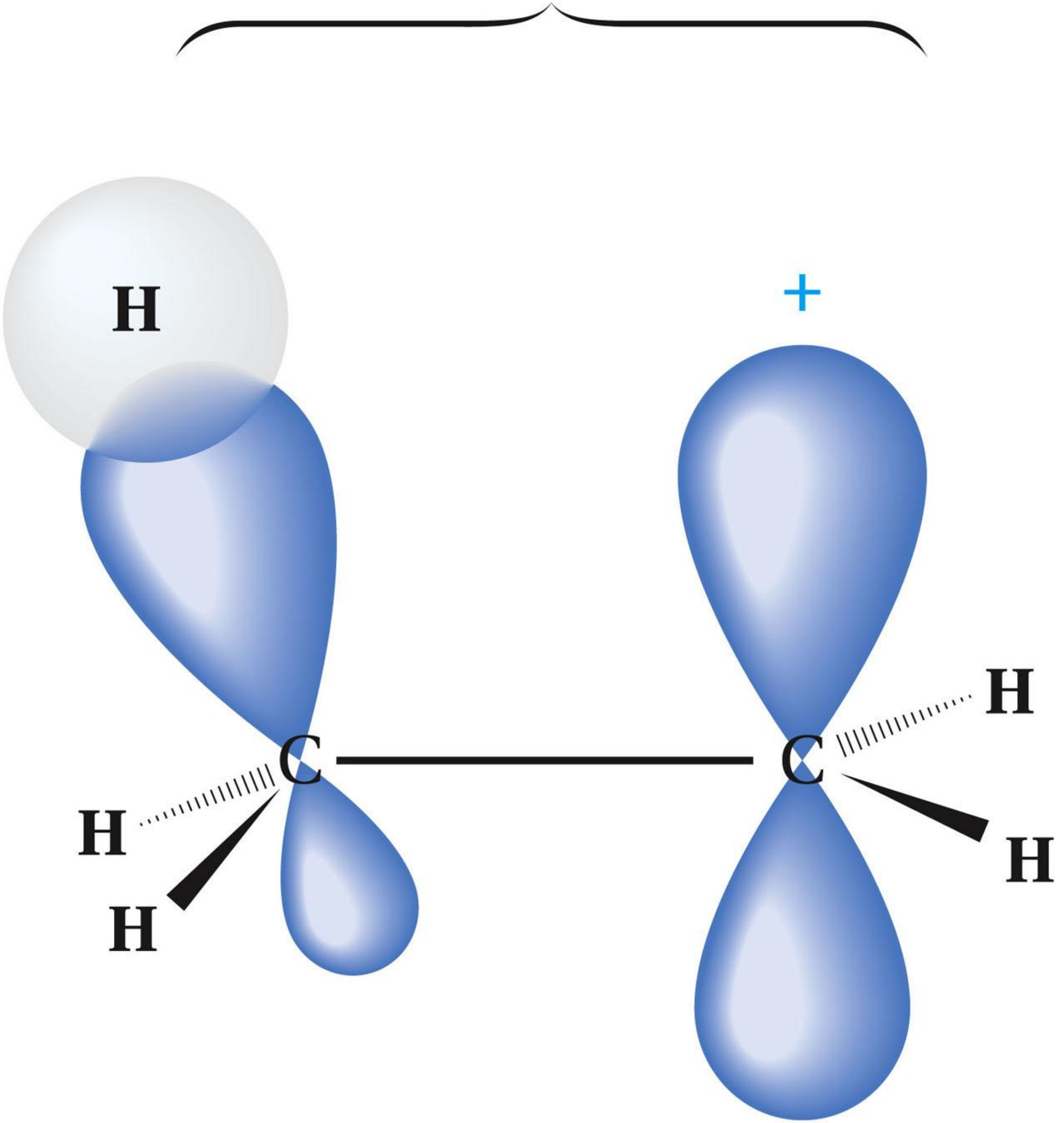


$$\mathrm{R}{-}\overset{\overset{\displaystyle \mathrm{R}}{|}}{\underset{\underset{\displaystyle \mathrm{R}}{|}}{\mathrm{C}^{+}}} \;>\; \mathrm{R}{-}\overset{+}{\underset{\underset{\displaystyle \mathrm{R}}{|}}{\mathrm{C}}}\mathrm{H} \;>>\; \mathrm{R}{-}\overset{+}{\mathrm{C}}\mathrm{H}_2 \;>\; \overset{+}{\mathrm{C}}\mathrm{H}_3$$

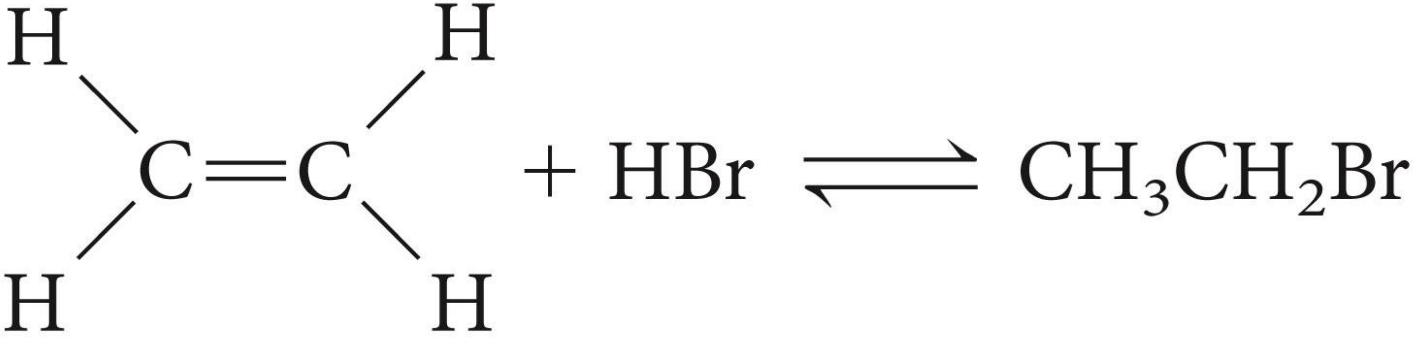
tertiary (3°) secondary (2°) primary (1°) methyl (unique)

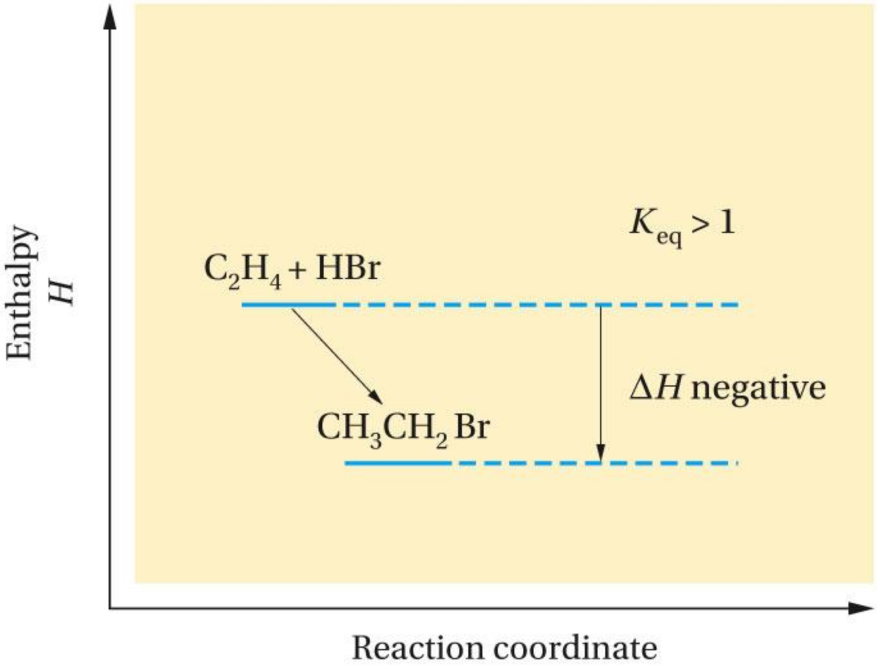
most stable → least stable

C-H σ-*p* overlap

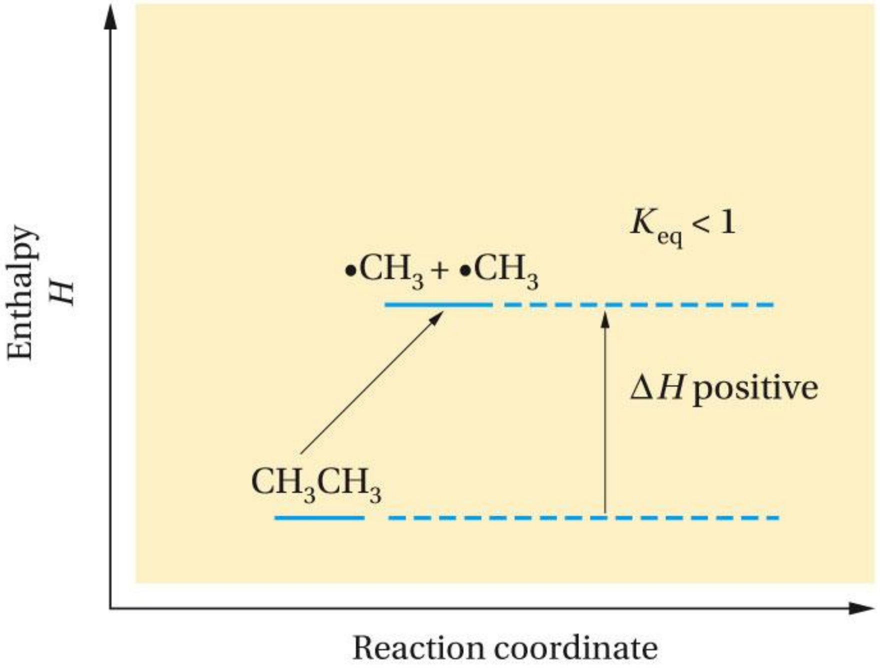


Reaction Equilibrium

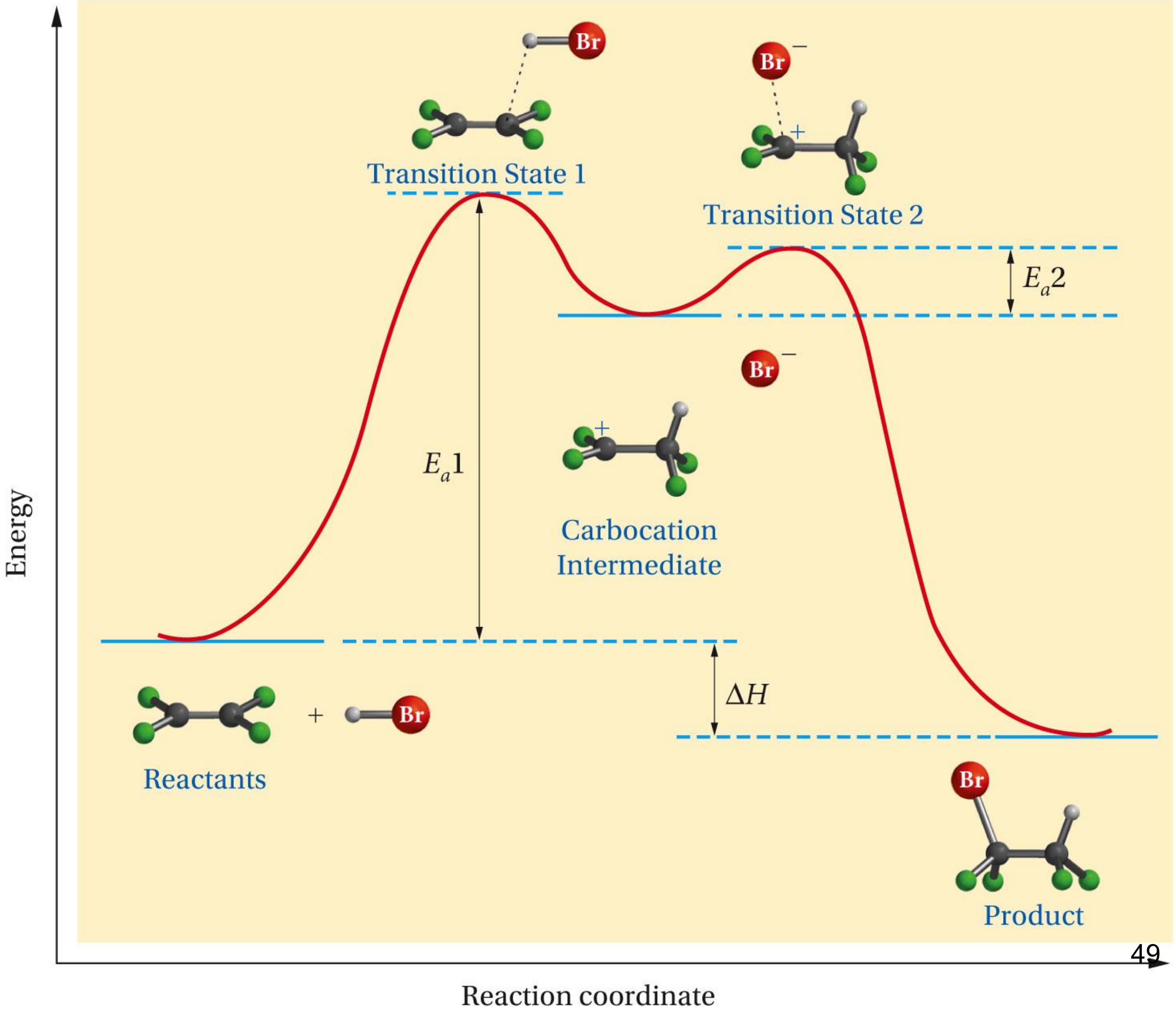


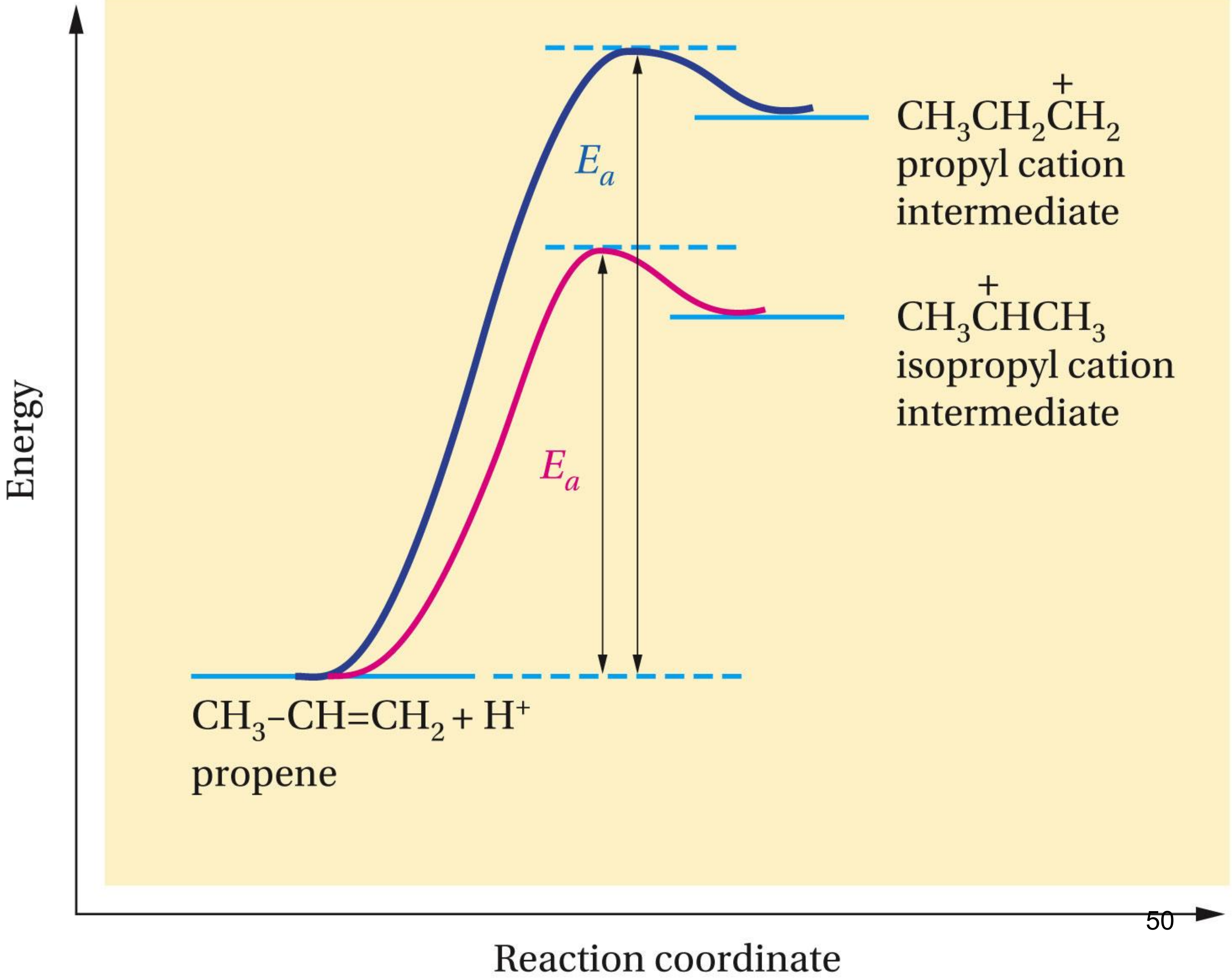

Enthalpy
H
$K_{eq} > 1$
$C_2H_4 + HBr$
CH_3CH_2Br
ΔH negative
Reaction coordinate

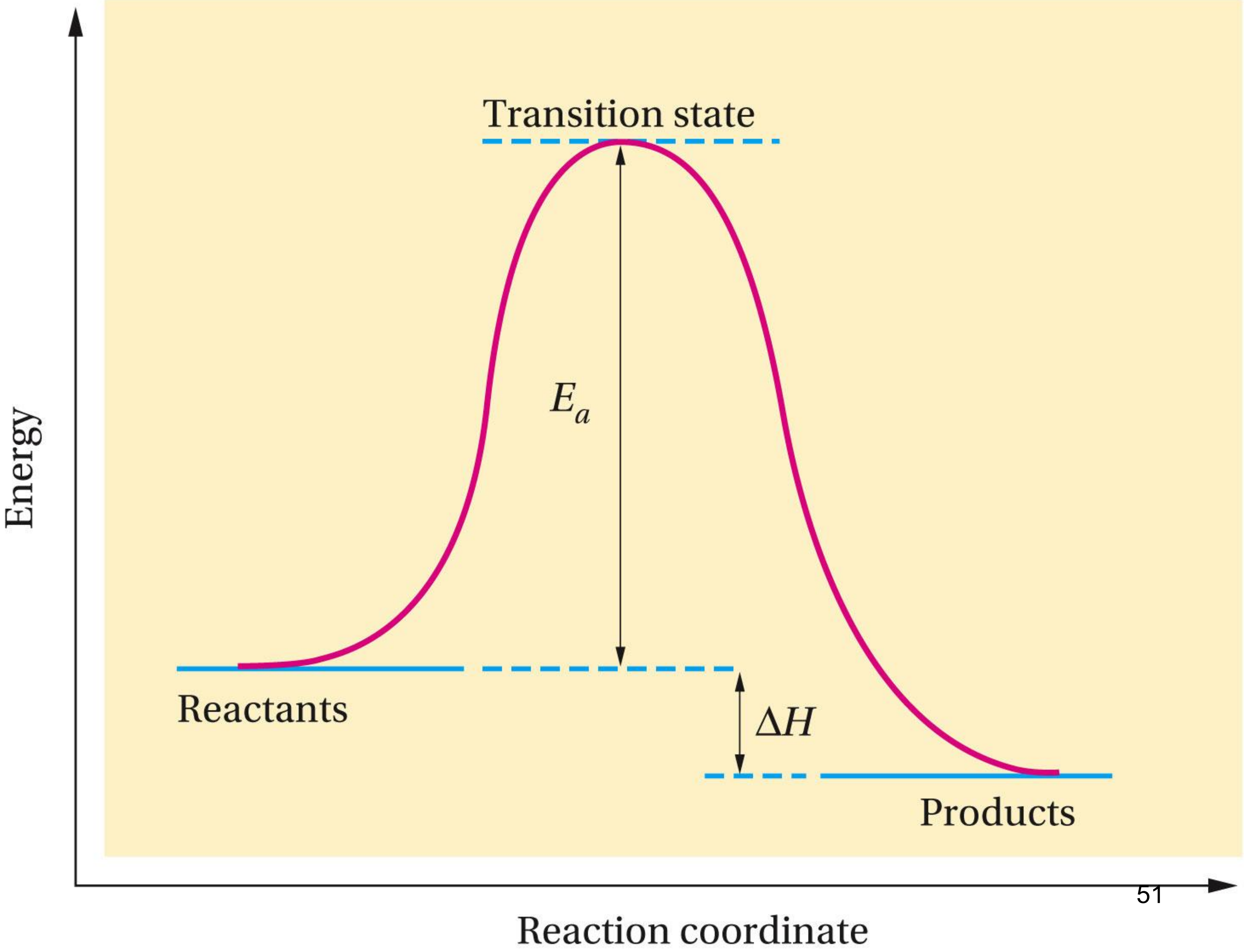
(a)


Enthalpy
H
$K_{eq} < 1$
$\bullet CH_3 + \bullet CH_3$
ΔH positive
CH_3CH_3
Reaction coordinate

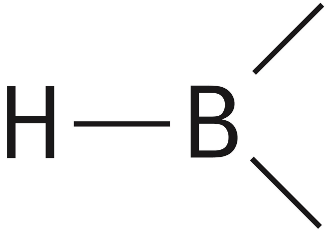
(b)

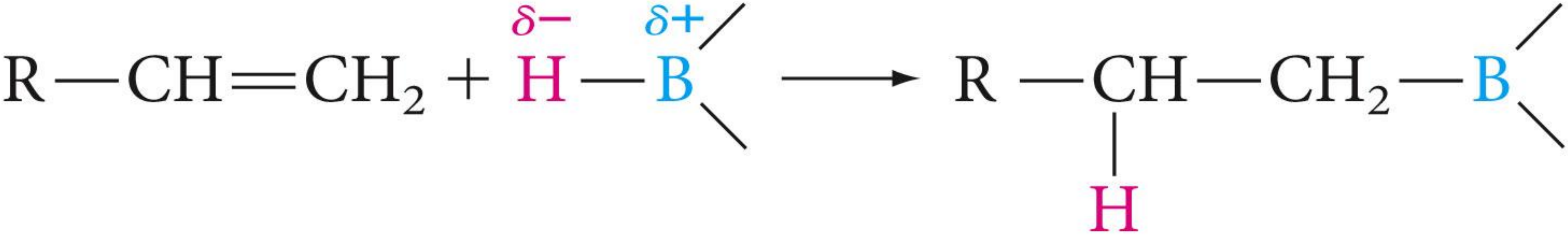

Br
Transition State 1
Br
−
+
Transition State 2
E_a2
Br
−
E_a1
+
Carbocation Intermediate
ΔH
Br
+
Br
Reactants
Br
Product
Energy
Reaction coordinate

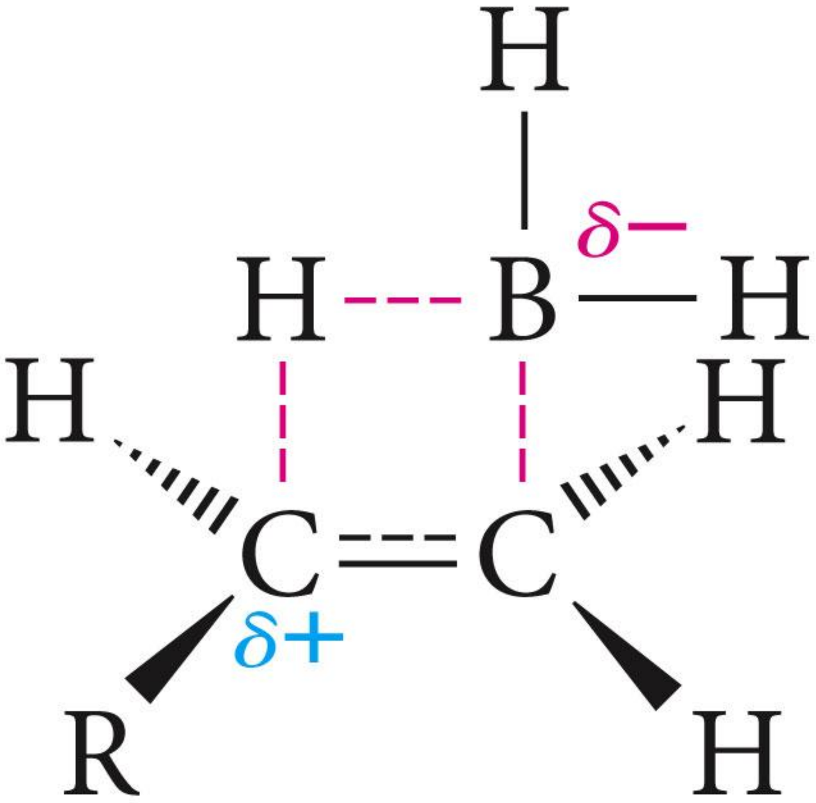

Energy
E_a
E_a
$CH_3CH_2\overset{+}{C}H_2$
propyl cation
intermediate
$CH_3\overset{+}{C}HCH_3$
isopropyl cation
intermediate
$CH_3–CH=CH_2 + H^+$
propene
Reaction coordinate


Transition state
E_a
Energy
Reactants
ΔH
Products
Reaction coordinate

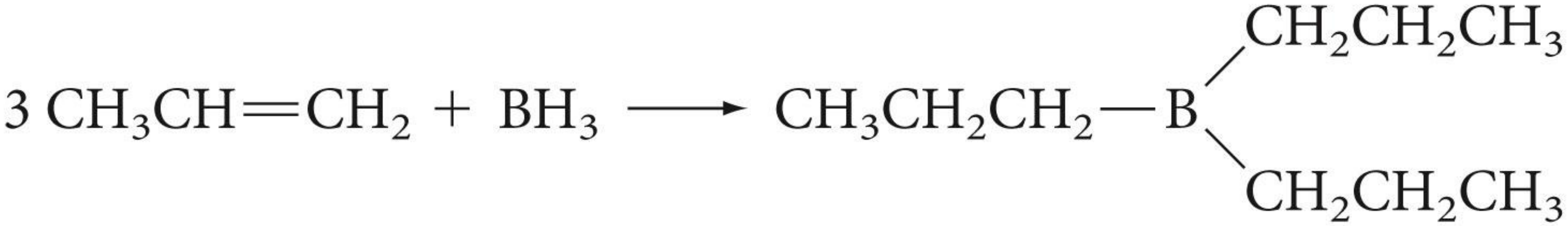
Hydroboration of Alkenes







transition state
for hydroboration



$$3\ CH_3CH{=}CH_2 + BH_3 \longrightarrow CH_3CH_2CH_2{-}B(CH_2CH_2CH_3)_2$$

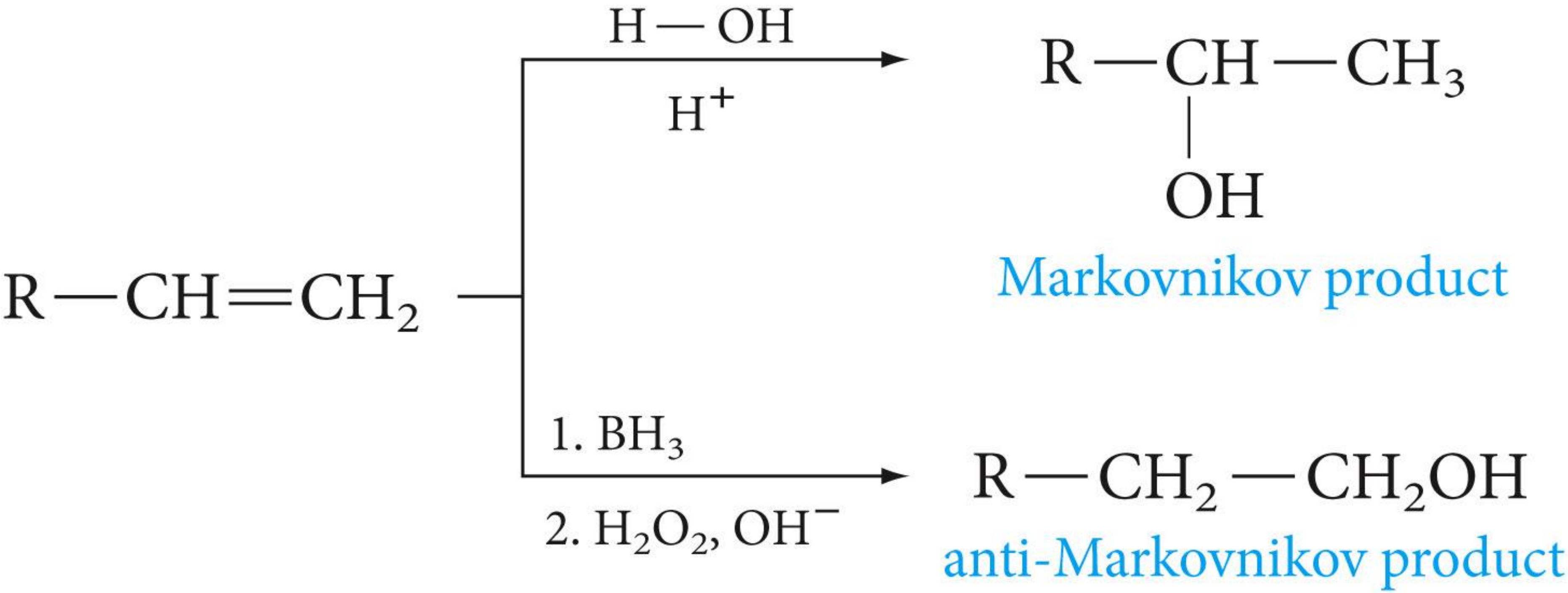
propene borane tri-*n*-propylborane

$$(CH_3CH_2CH_2)_3B + 3\ H_2O_2 + 3\ NaOH \longrightarrow$$

tri-*n*-propylborane

$$3\ CH_3CH_2CH_2OH + Na_3BO_3 + 3\ H_2O$$

n-propyl alcohol sodium borate

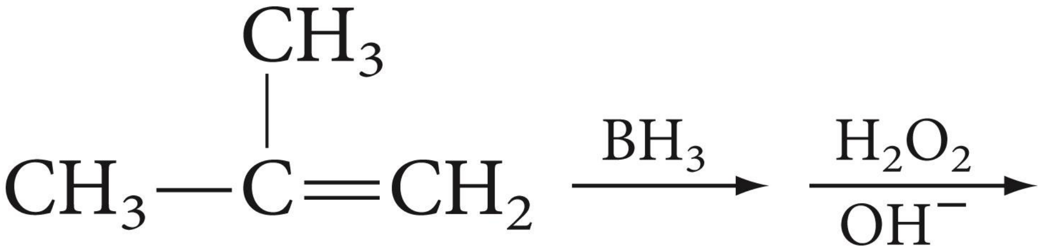


$$R-CH=CH_2 \xrightarrow[H^+]{H-OH} R-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

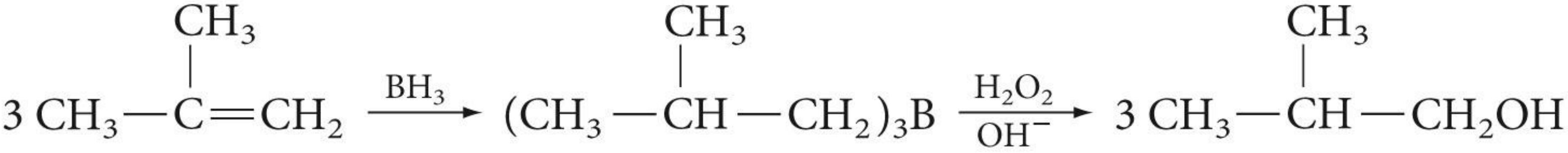
Markovnikov product

$$R-CH=CH_2 \xrightarrow[2.\ H_2O_2,\ OH^-]{1.\ BH_3} R-CH_2-CH_2OH$$

anti-Markovnikov product

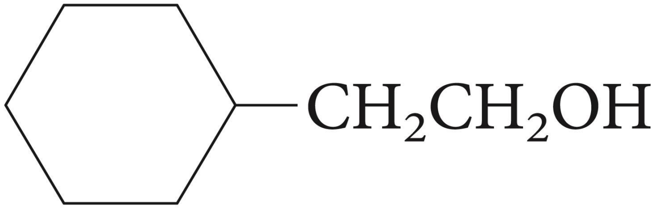


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \xrightarrow{BH_3} \xrightarrow[OH^-]{H_2O_2}$$

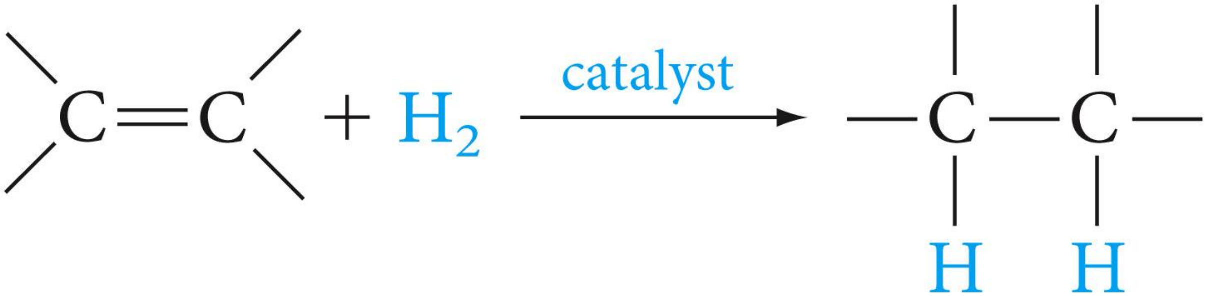


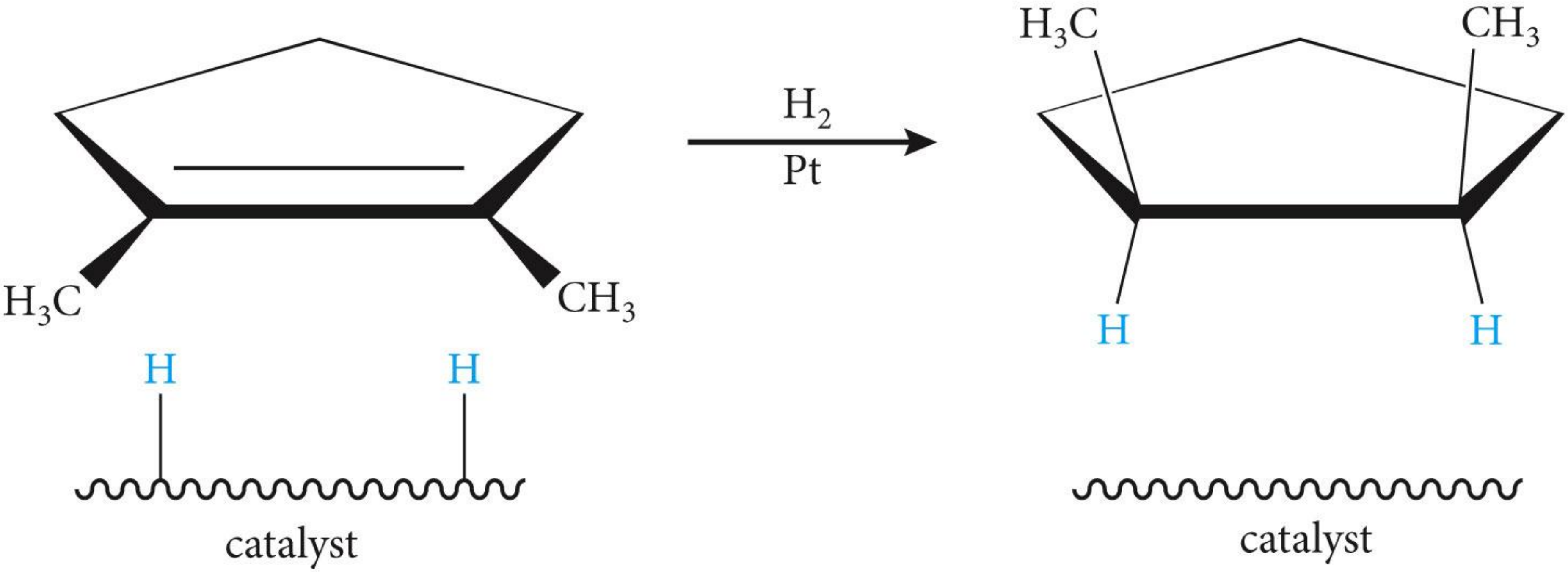
$$3\,\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2} \xrightarrow{\mathrm{BH_3}} \mathrm{(CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2)_3B} \xrightarrow[\mathrm{OH^-}]{\mathrm{H_2O_2}} 3\,\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2OH}$$

What alkene is needed to obtain he alcohol below via hydroboration-oxidation sequence, what product would this alkene give with acid-catalyzed hydration.

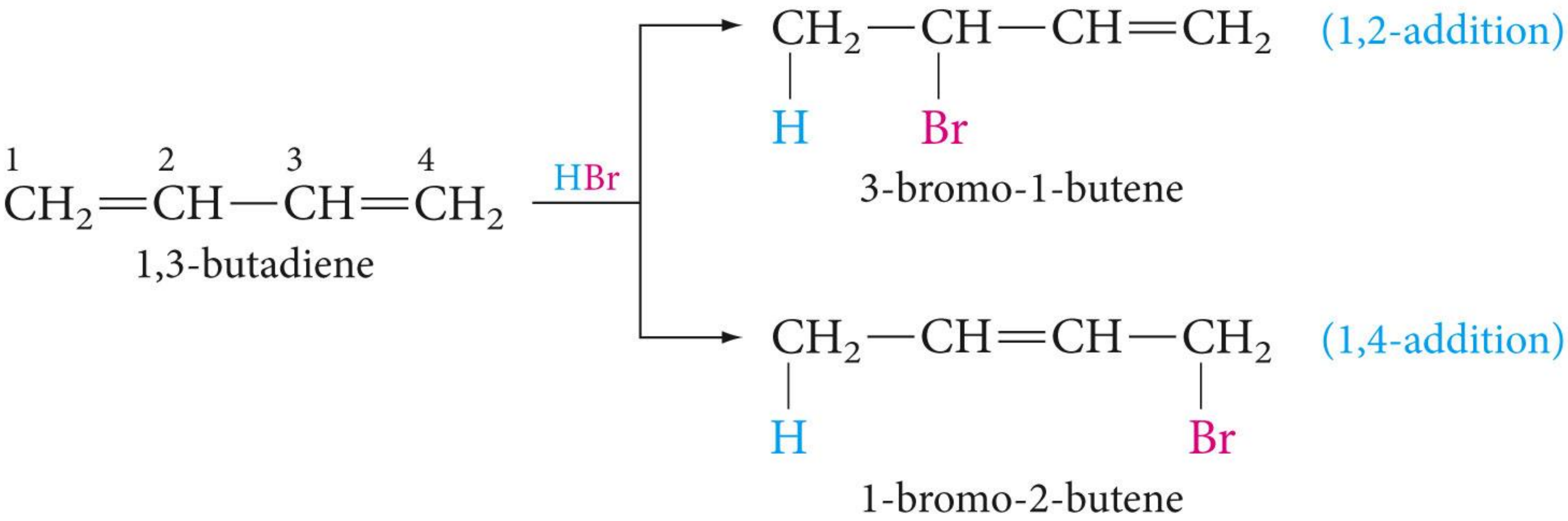


Addition of Hydrogen




H$_3$C
CH$_3$
H
H
catalyst
H$_2$
Pt
H$_3$C
CH$_3$
H
H
catalyst

Addition to Conjugated Systems



$$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH}{=}\overset{4}{CH_2} \xrightarrow{HBr}$$

1,3-butadiene

$$\underset{H}{CH_2}{-}\underset{Br}{CH}{-}CH{=}CH_2$$

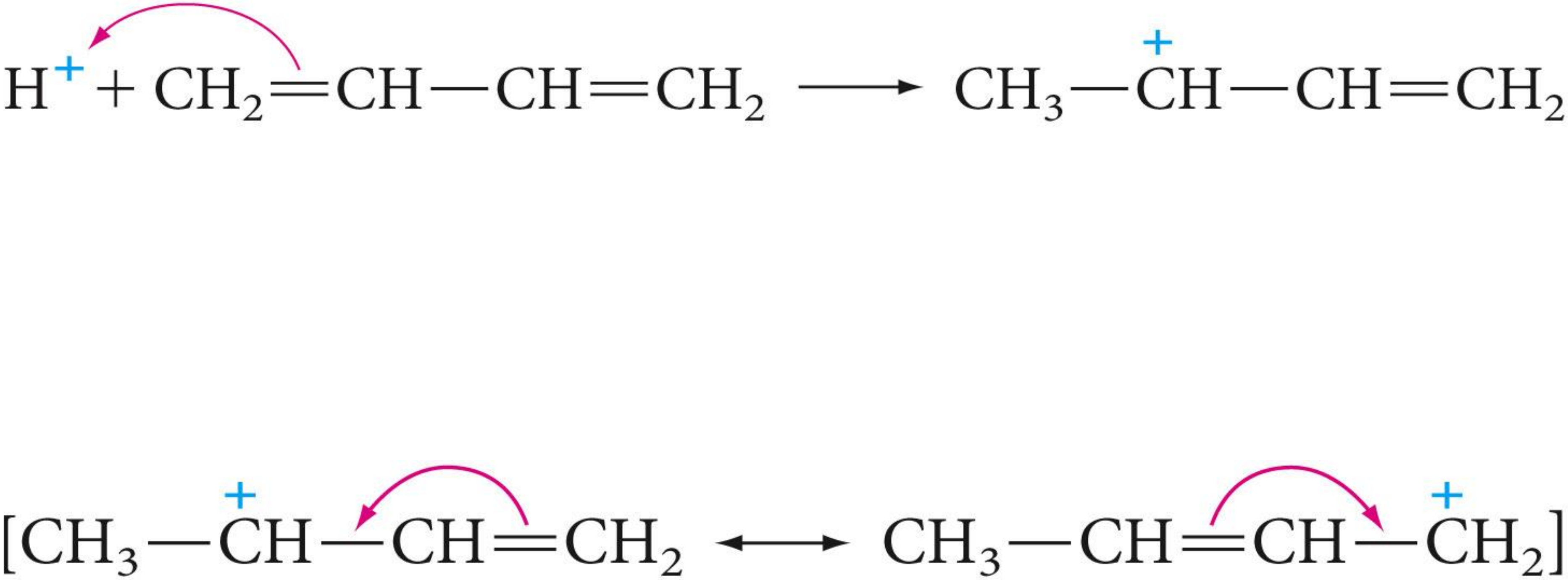
3-bromo-1-butene

(1,2-addition)

$$\underset{H}{CH_2}{-}CH{=}CH{-}\underset{Br}{CH_2}$$

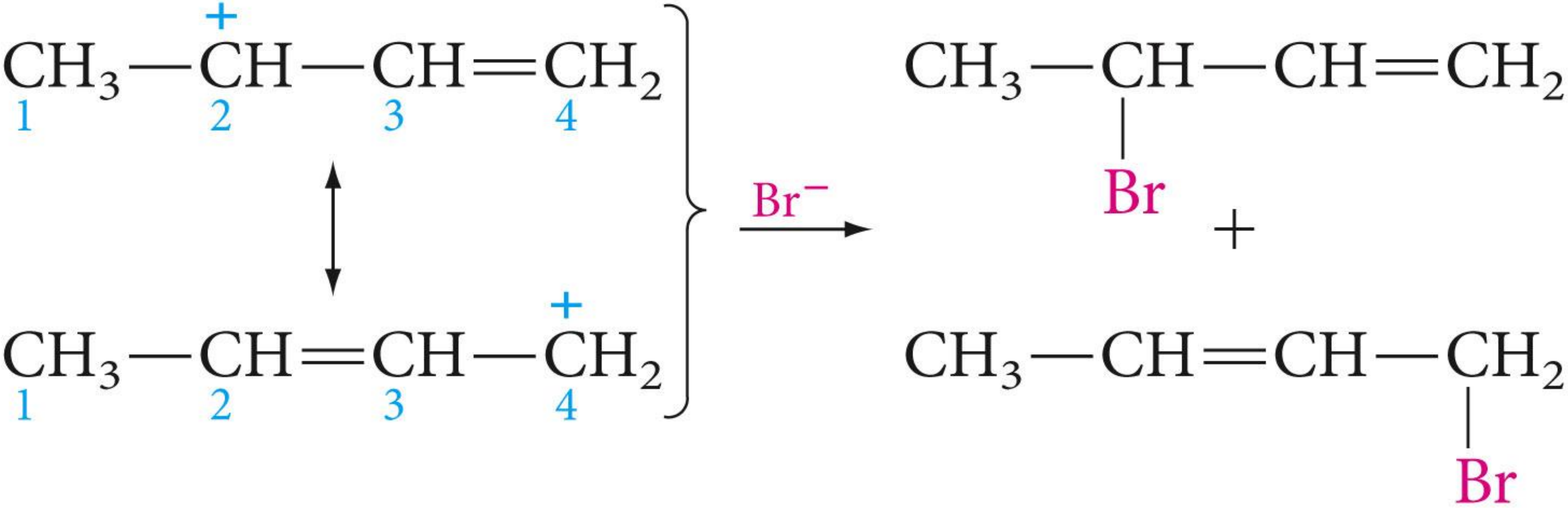
1-bromo-2-butene

(1,4-addition)

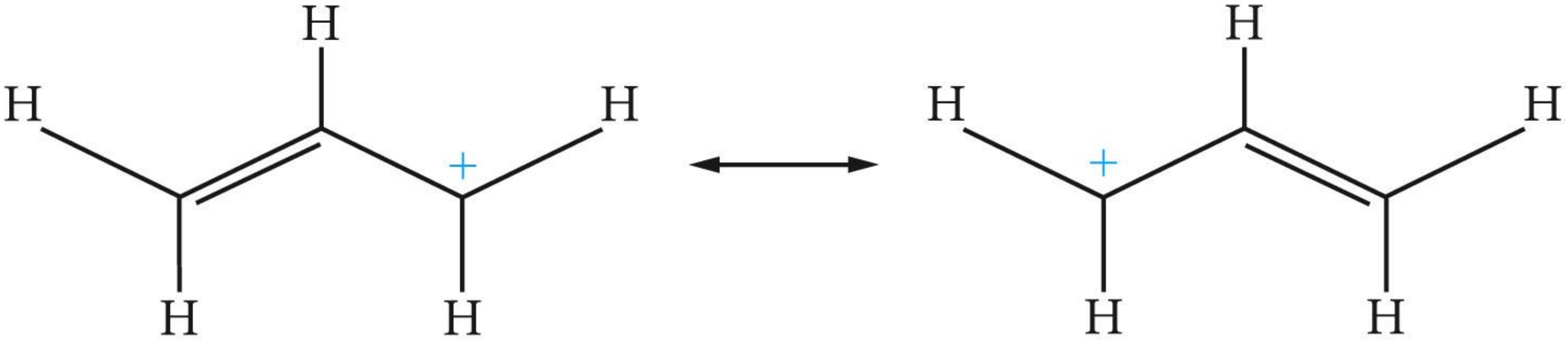


$$H^{+} + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow CH_3{-}\overset{+}{C}H{-}CH{=}CH_2$$

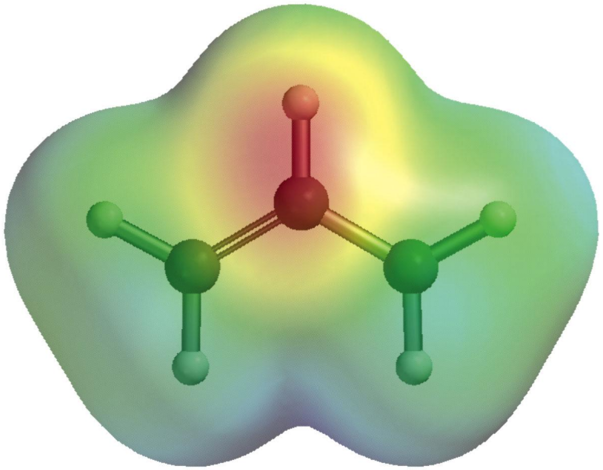
$$[CH_3{-}\overset{+}{C}H{-}CH{=}CH_2 \longleftrightarrow CH_3{-}CH{=}CH{-}\overset{+}{C}H_2]$$

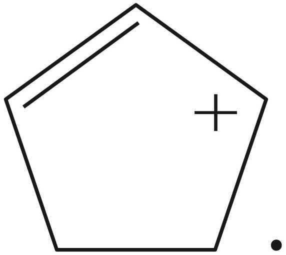


$$\left.\begin{array}{c} \underset{1}{\mathrm{CH_3}}{-}\underset{2}{\overset{+}{\mathrm{C}}\mathrm{H}}{-}\underset{3}{\mathrm{CH}}{=}\underset{4}{\mathrm{CH_2}} \\ \updownarrow \\ \underset{1}{\mathrm{CH_3}}{-}\underset{2}{\mathrm{CH}}{=}\underset{3}{\mathrm{CH}}{-}\underset{4}{\overset{+}{\mathrm{C}}\mathrm{H_2}} \end{array}\right\} \xrightarrow{\mathrm{Br^-}} \begin{array}{c} \mathrm{CH_3}{-}\underset{\mathrm{Br}}{\mathrm{CH}}{-}\mathrm{CH}{=}\mathrm{CH_2} \\ + \\ \mathrm{CH_3}{-}\mathrm{CH}{=}\mathrm{CH}{-}\underset{\mathrm{Br}}{\mathrm{CH_2}} \end{array}$$

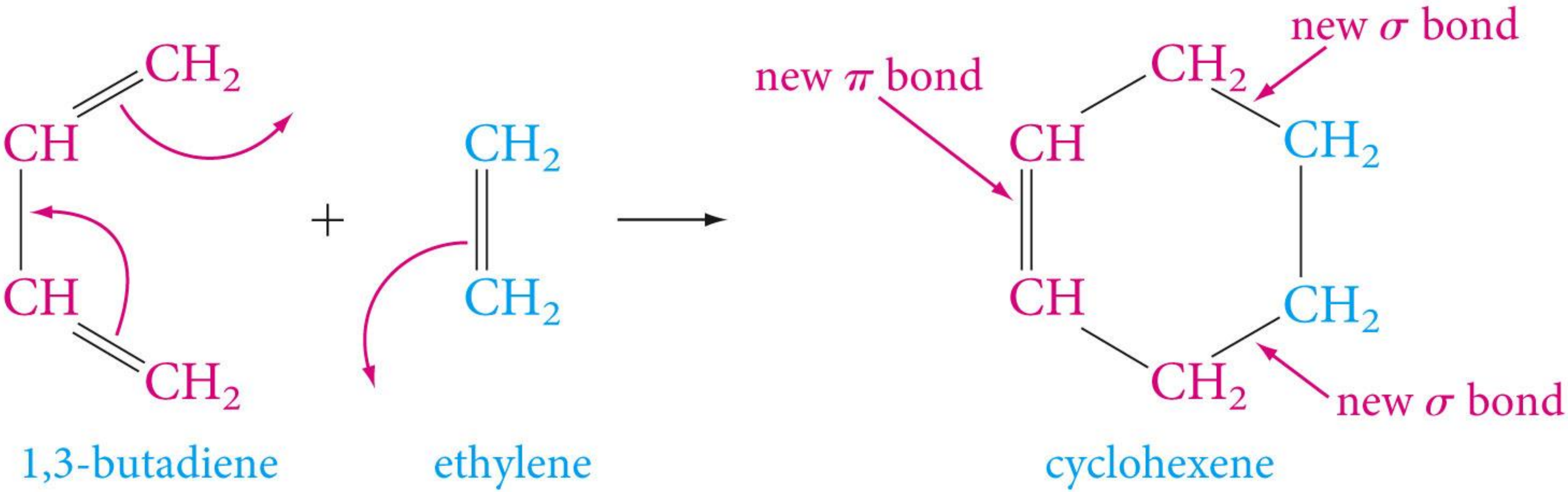


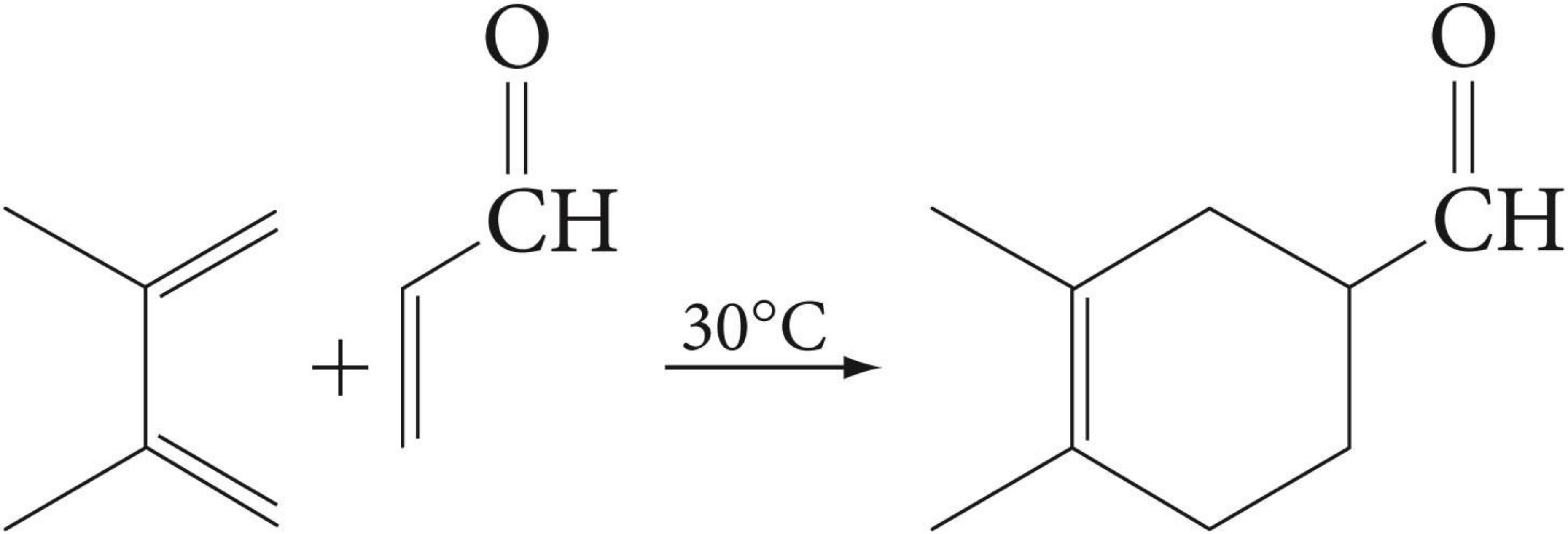
the allyl carbocation

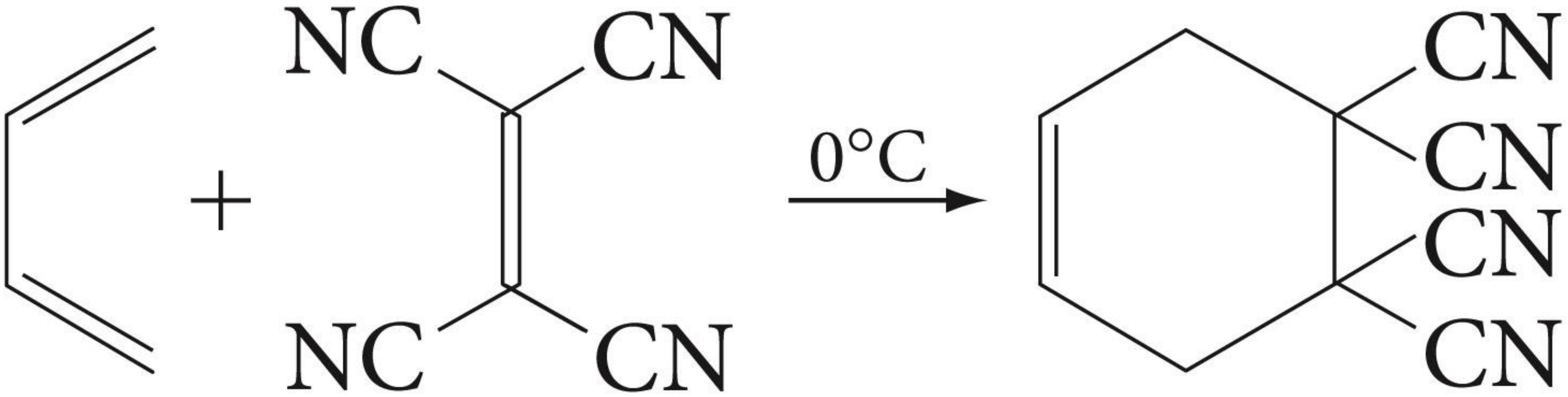


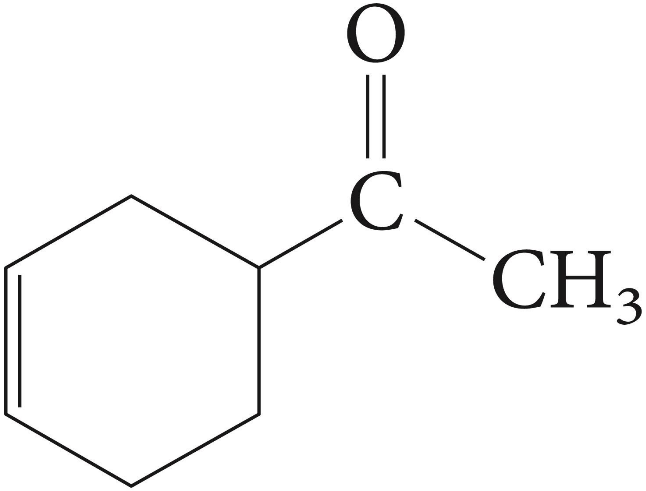


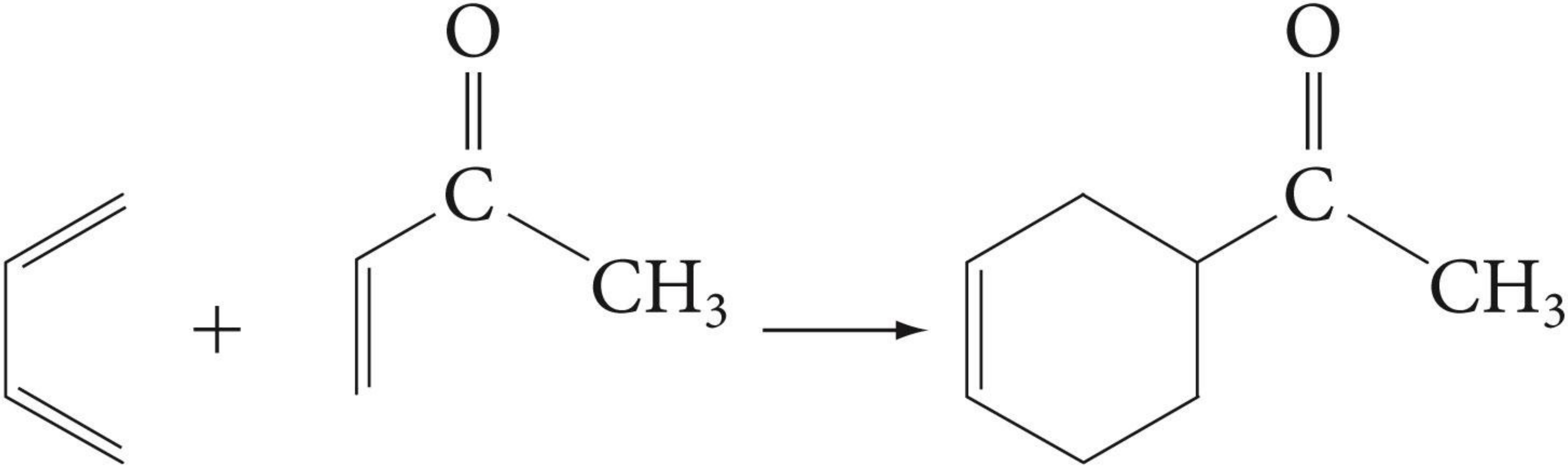
Cycloaddition to Conjugated Dienes: **Diels-Alder Reaction**

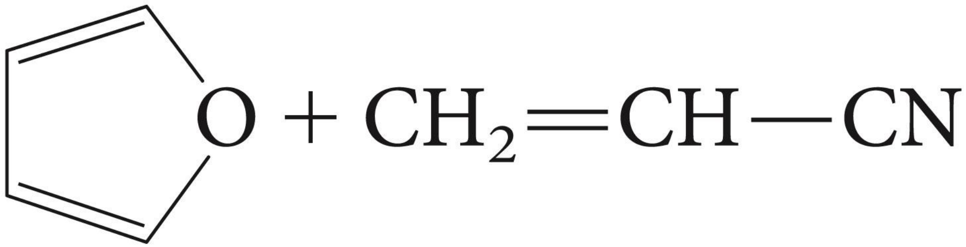



O
CH
30°C
O
CH


NC
CN
NC
CN
0°C
CN
CN
CN
CN



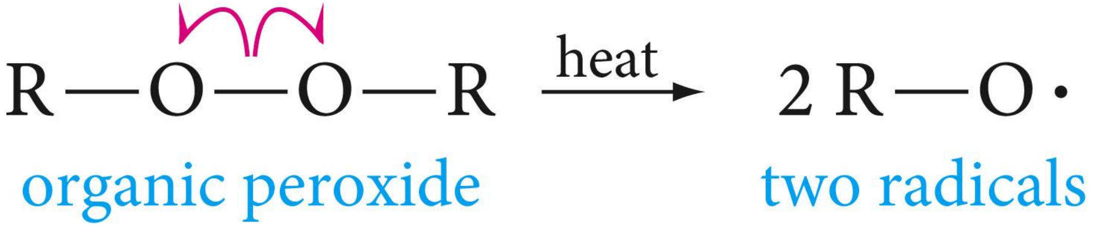

O
C
CH3
+
O
C
CH3


O
+ $CH_2{=}CH{-}CN$

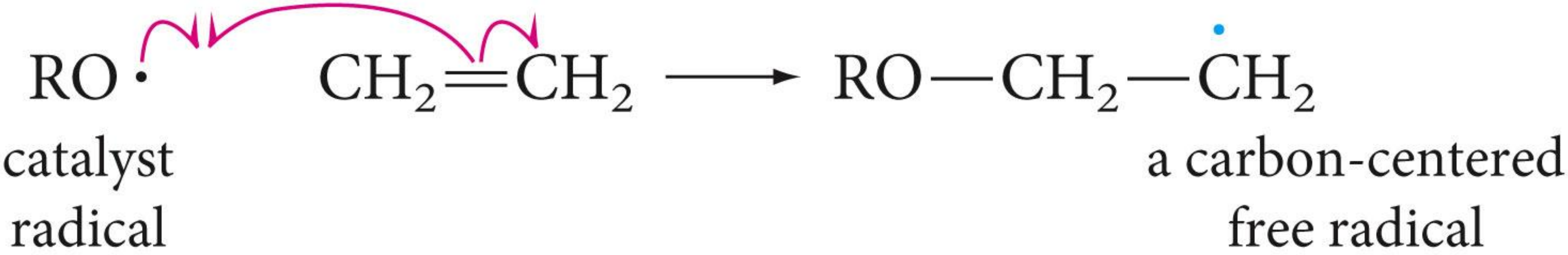
Free-Radical Additions; Polyethene

$$\underset{\text{ethylene}}{CH_2{=}CH_2} \xrightarrow[\text{1000 atm, >100°C}]{\text{ROOR}} \underset{\text{polyethylene}}{\left(CH_2{-}CH_2\right)_n}$$

(n = several thousand)

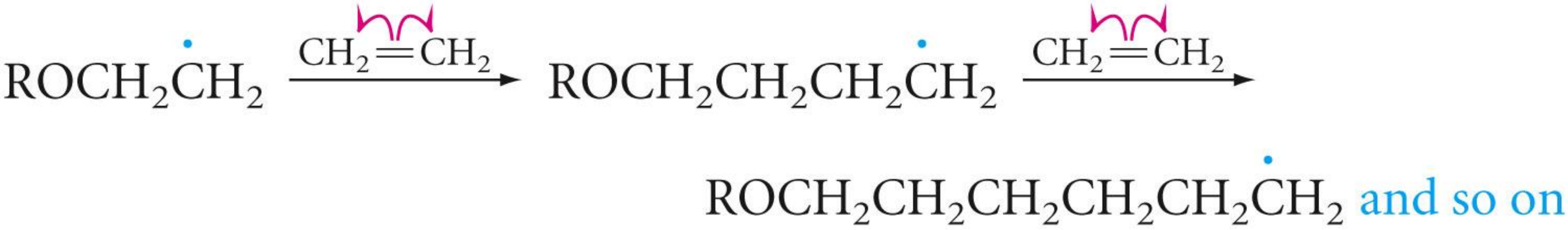


$$\underset{\text{organic peroxide}}{R{-}O{-}O{-}R} \xrightarrow{\text{heat}} \underset{\text{two radicals}}{2\,R{-}O\cdot}$$



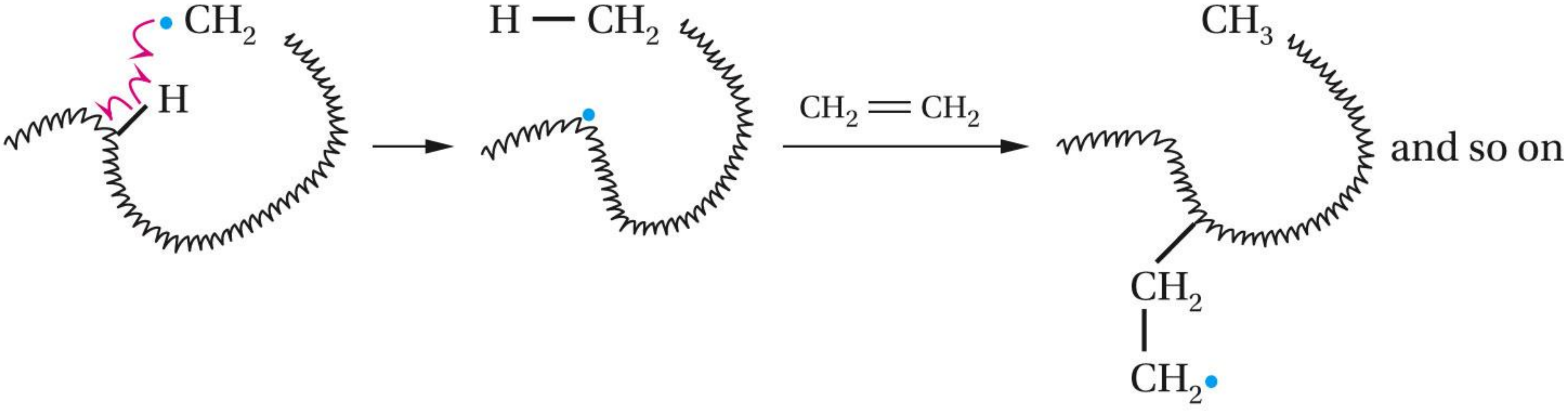
$$RO\cdot \qquad CH_2{=}CH_2 \longrightarrow RO{-}CH_2{-}\dot{C}H_2$$

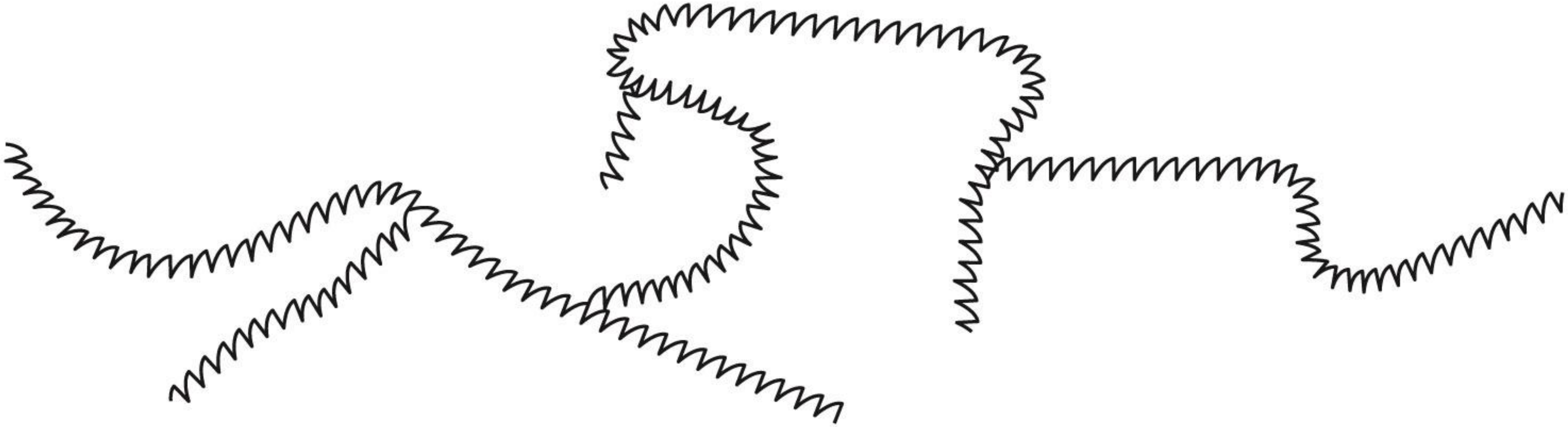
$$ROCH_2\dot{C}H_2 \xrightarrow{CH_2=CH_2} ROCH_2CH_2CH_2\dot{C}H_2 \xrightarrow{CH_2=CH_2}$$



$$\mathrm{RO CH_2\dot{C}H_2} \xrightarrow{\mathrm{CH_2{=}CH_2}} \mathrm{ROCH_2CH_2CH_2\dot{C}H_2} \xrightarrow{\mathrm{CH_2{=}CH_2}} \mathrm{ROCH_2CH_2CH_2CH_2CH_2\dot{C}H_2}$$

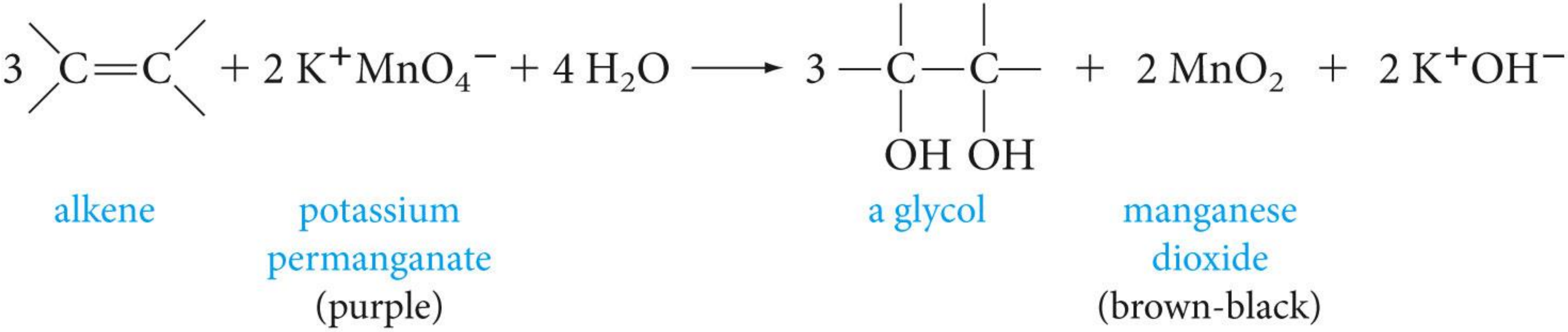
and so on



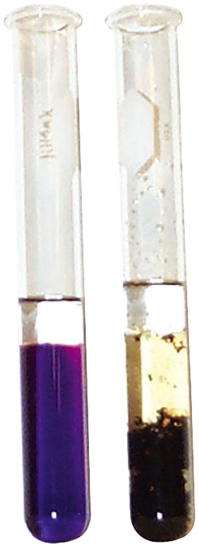


branched polyethylene

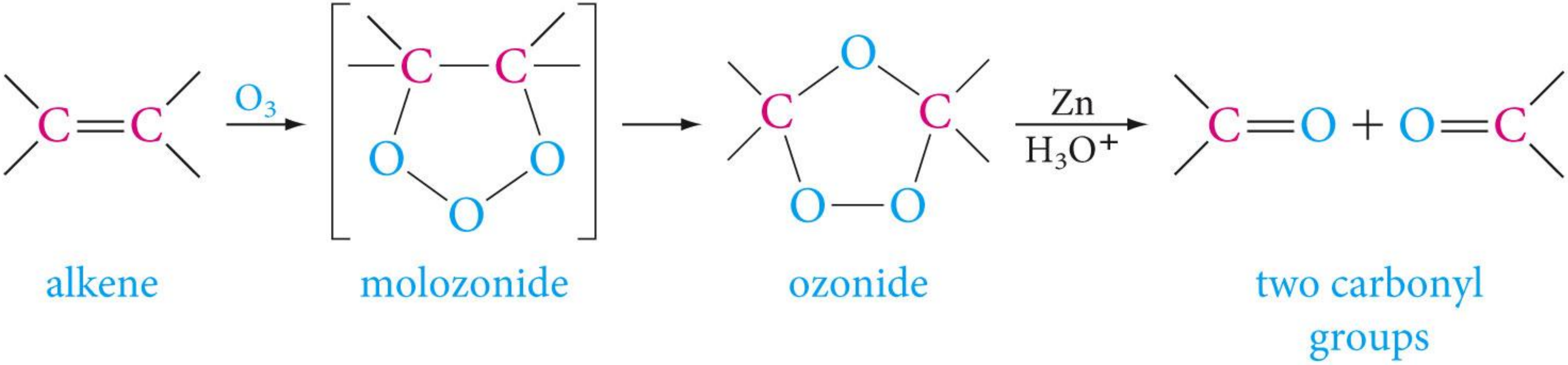
Oxidation with permanganate; a Chemical Test



$$3\ \mathrm{>C{=}C<} + 2\,\mathrm{K^+MnO_4^-} + 4\,\mathrm{H_2O} \longrightarrow 3\ \mathrm{-\underset{OH}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-} + 2\,\mathrm{MnO_2} + 2\,\mathrm{K^+OH^-}$$

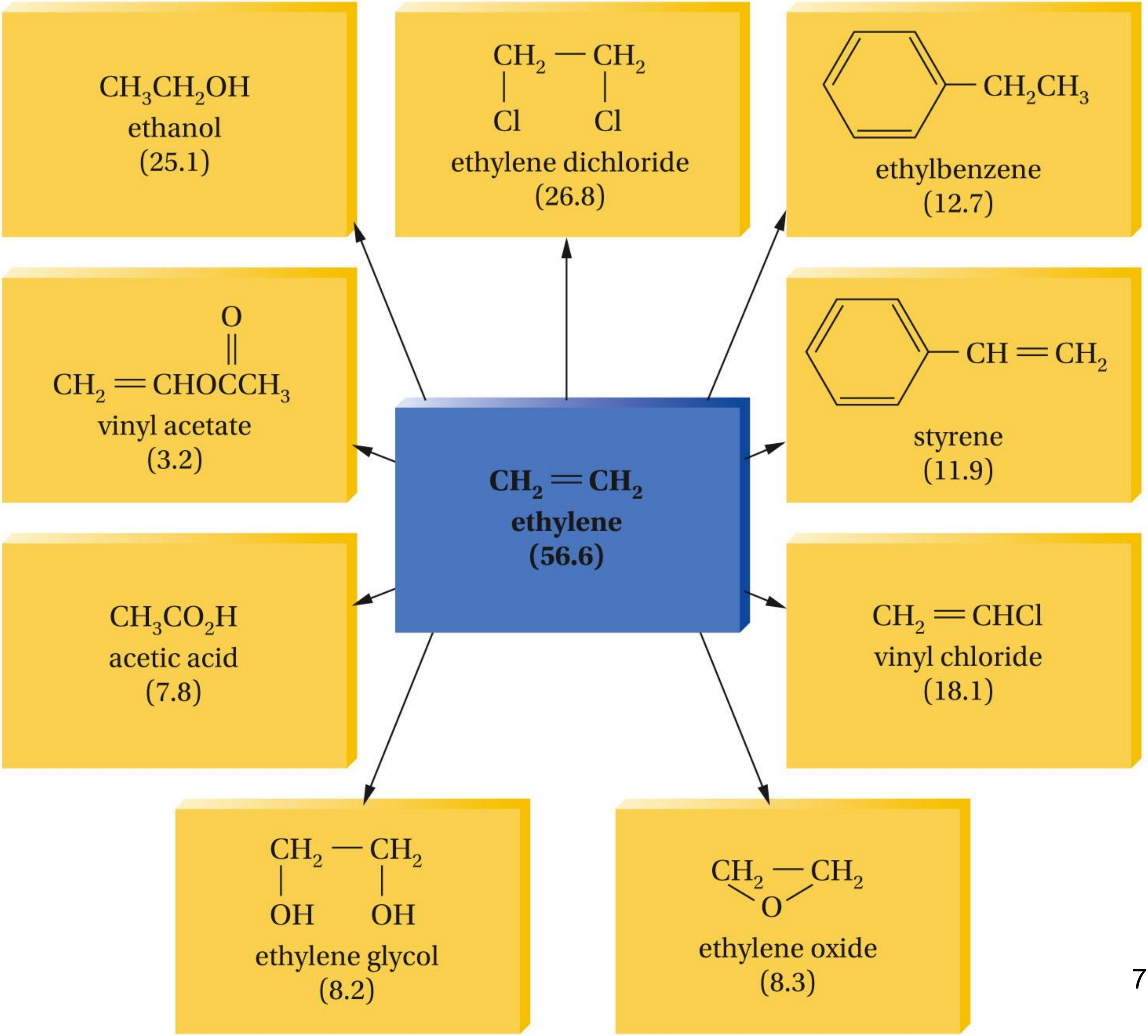


Ozonolysis of Alkenes



$$\underset{\text{1-butene}}{CH_2{=}CHCH_2CH_3} \xrightarrow[\text{2. Zn, H}^+]{\text{1. O}_3} \underset{\text{formaldehyde}}{CH_2{=}O} \quad \underset{\text{propanal}}{O{=}CHCH_2CH_3}$$

$$\underset{\text{2-butene}}{CH_3CH{=}CHCH_3} \xrightarrow[\text{2. Zn, H}^+]{\text{1. O}_3} \underset{\text{ethanal}}{2\ CH_3CH{=}O}$$



$CH_2{=}CH_2$
ethylene
(56.6)

CH_3CH_2OH
ethanol
(25.1)

$\underset{\displaystyle Cl}{CH_2}-\underset{\displaystyle Cl}{CH_2}$
ethylene dichloride
(26.8)

ethylbenzene
(12.7)

$CH_2{=}CHO\overset{\displaystyle O}{\overset{\|}{C}}CH_3$
vinyl acetate
(3.2)

styrene
(11.9)

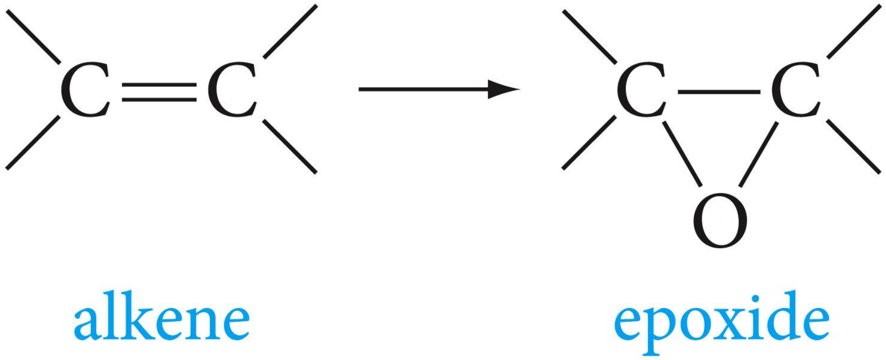
CH_3CO_2H
acetic acid
(7.8)

$CH_2{=}CHCl$
vinyl chloride
(18.1)

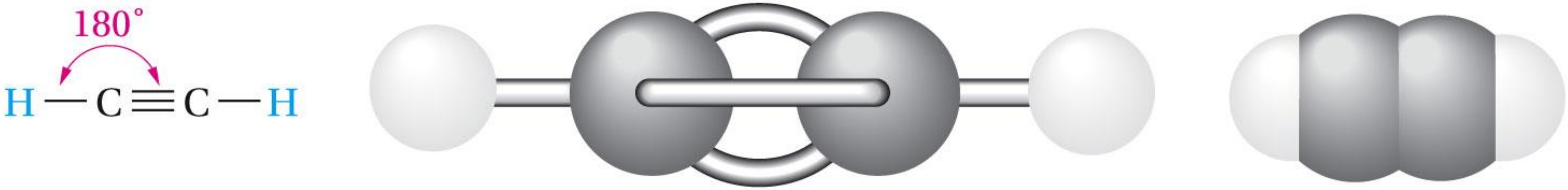
$\underset{\displaystyle OH}{CH_2}-\underset{\displaystyle OH}{CH_2}$
ethylene glycol
(8.2)

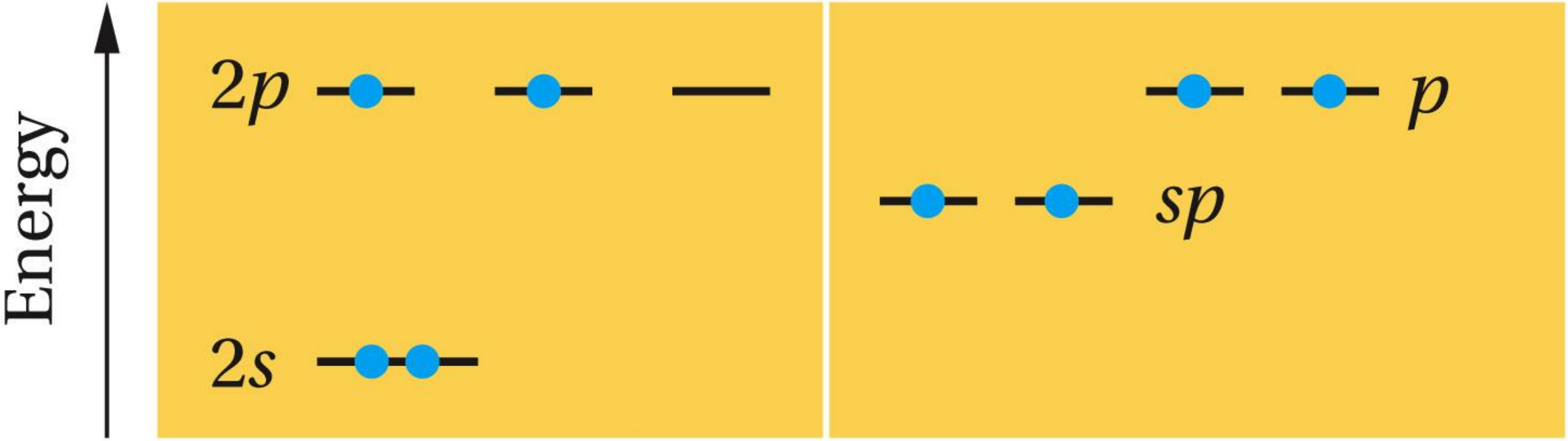
CH_2-CH_2 with O bridging (epoxide)
ethylene oxide
(8.3)

Other Alkene Oxidations



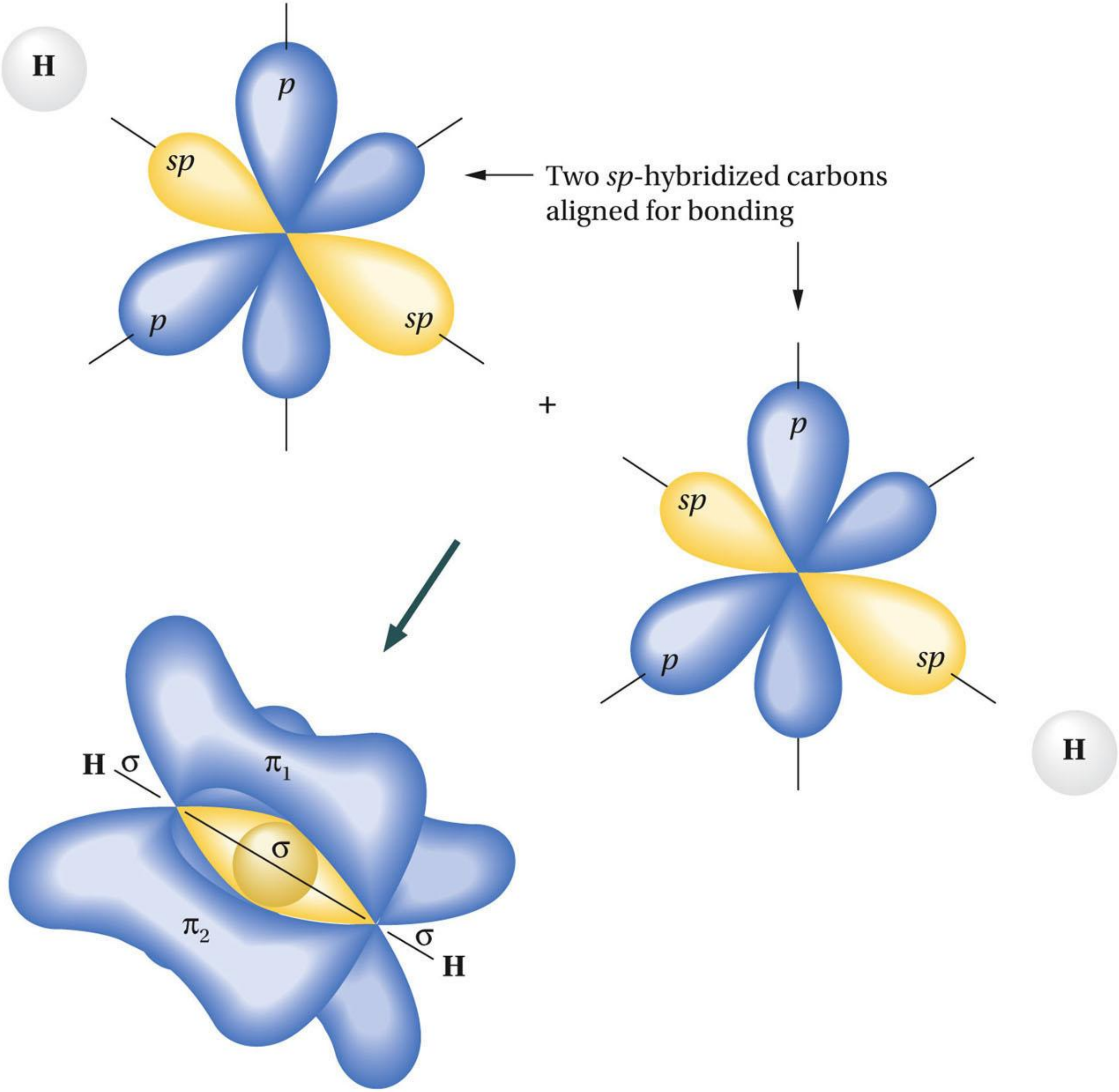
$$\mathrm{C}_n\mathrm{H}_{2n} + \frac{3n}{2}\,\mathrm{O}_2 \longrightarrow n\mathrm{CO}_2 + n\mathrm{H}_2\mathrm{O}$$


180°
H—C≡C—H



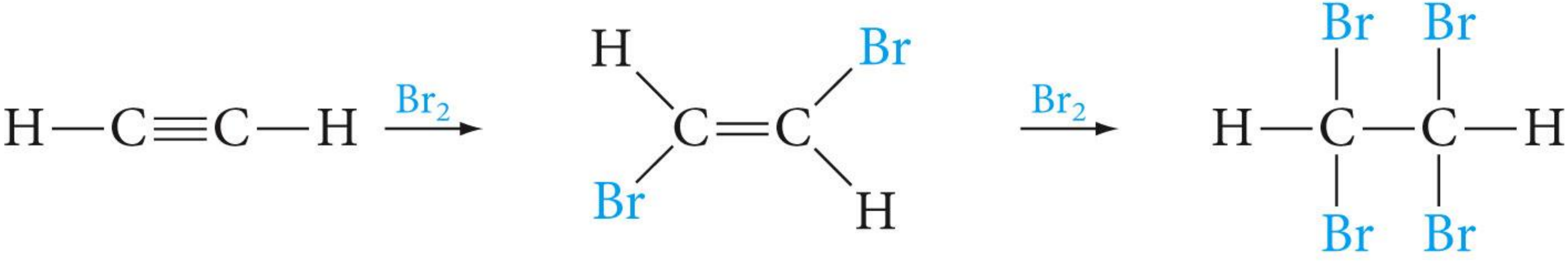
Atomic orbitals of carbon

The 2*s* and one 2*p* orbital are combined to form two hybrid *sp* orbitals, leaving one electron in each of two *p* orbitals.



Two *sp*-hybridized carbons aligned for bonding

The resulting carbon–carbon triple bond, with a hydrogen atom attached to each remaining *sp* bond. (The orbitals involved in the C—H bonds are omitted for clarity.)



ethyne *trans*-1,2-dibromoethene 1,1,2,2-tetrabromoethane

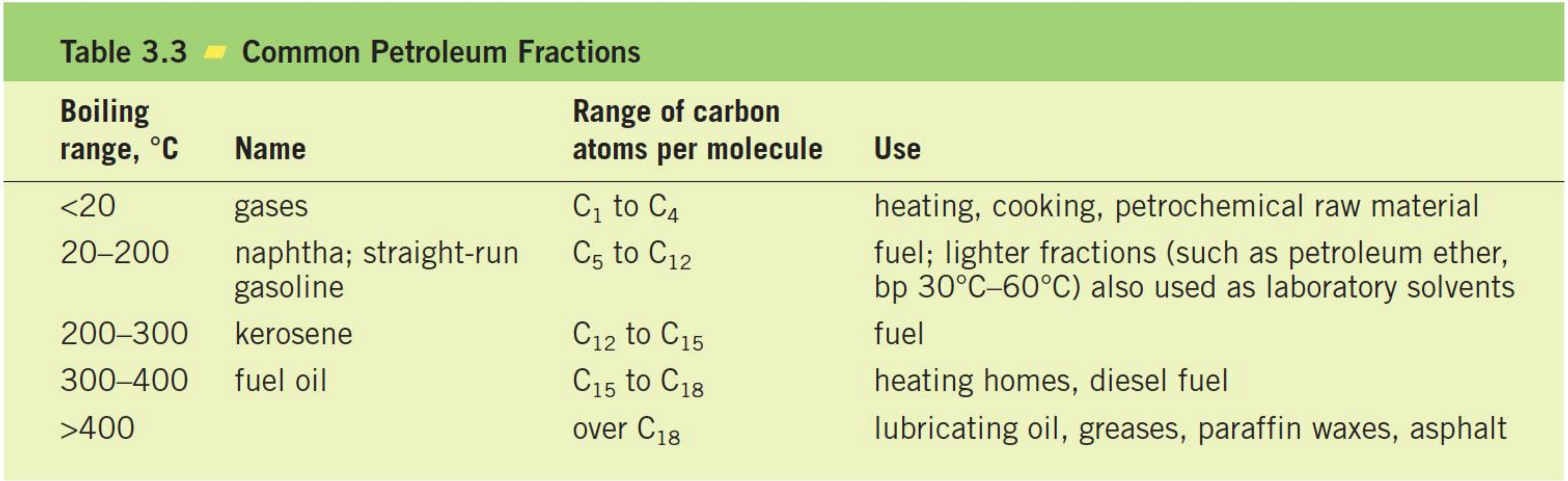
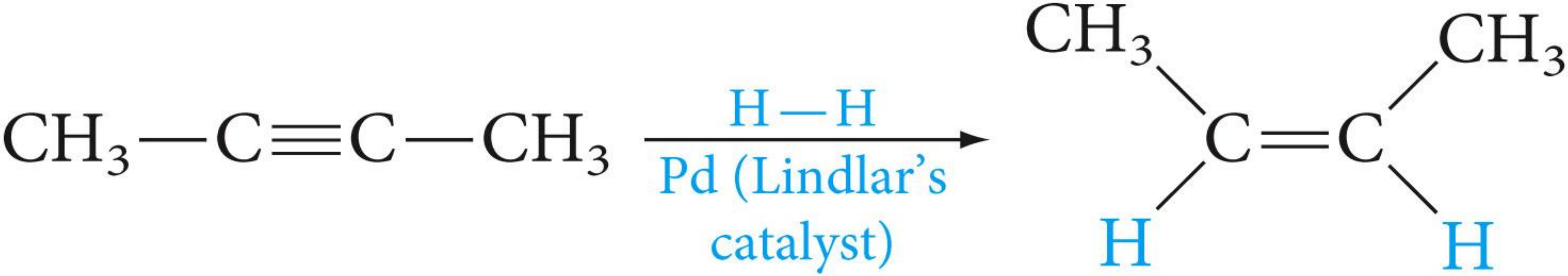


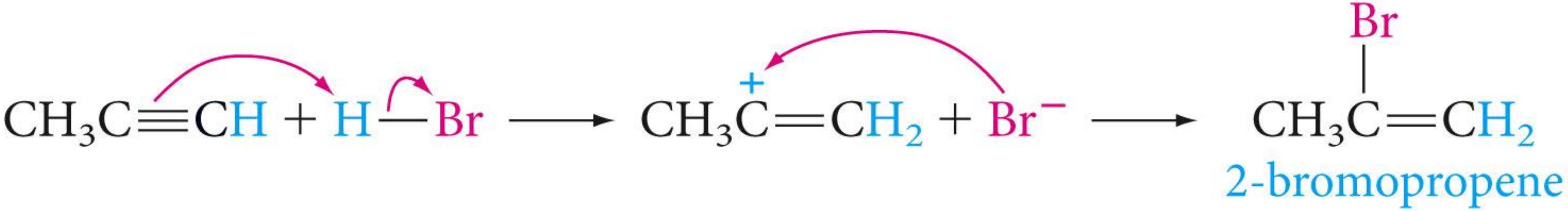
Table 3.3 Common Petroleum Fractions

Boiling range, °C	Name	Range of carbon atoms per molecule	Use
<20	gases	C_1 to C_4	heating, cooking, petrochemical raw material
20–200	naphtha; straight-run gasoline	C_5 to C_{12}	fuel; lighter fractions (such as petroleum ether, bp 30°C–60°C) also used as laboratory solvents
200–300	kerosene	C_{12} to C_{15}	fuel
300–400	fuel oil	C_{15} to C_{18}	heating homes, diesel fuel
>400		over C_{18}	lubricating oil, greases, paraffin waxes, asphalt

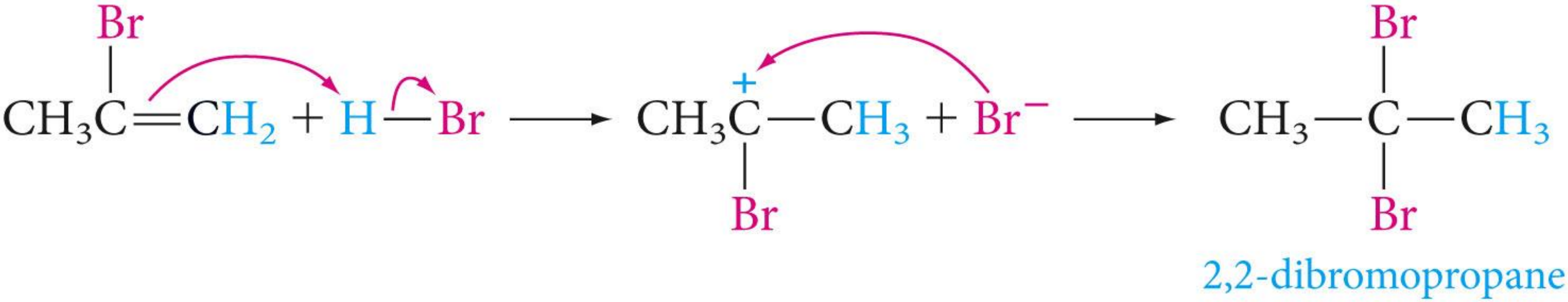


2-butyne
bp 27°C

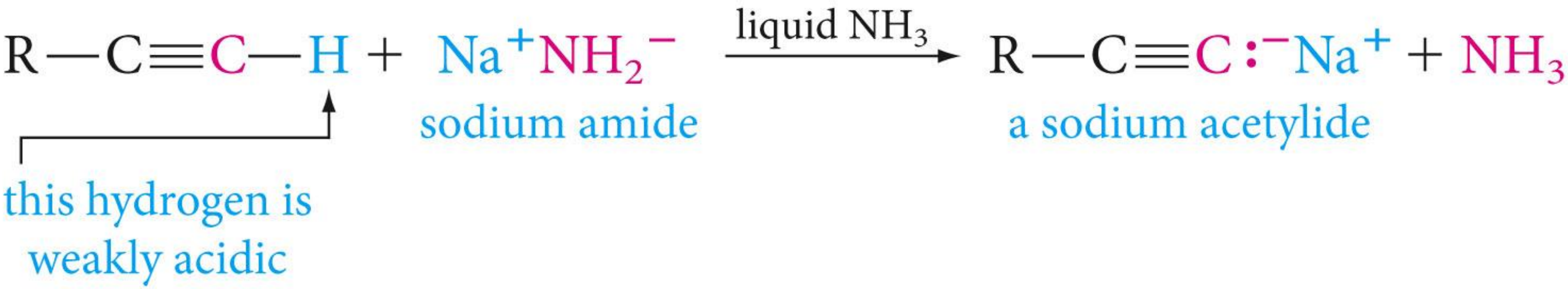
cis-2-butene
bp 3.7°C



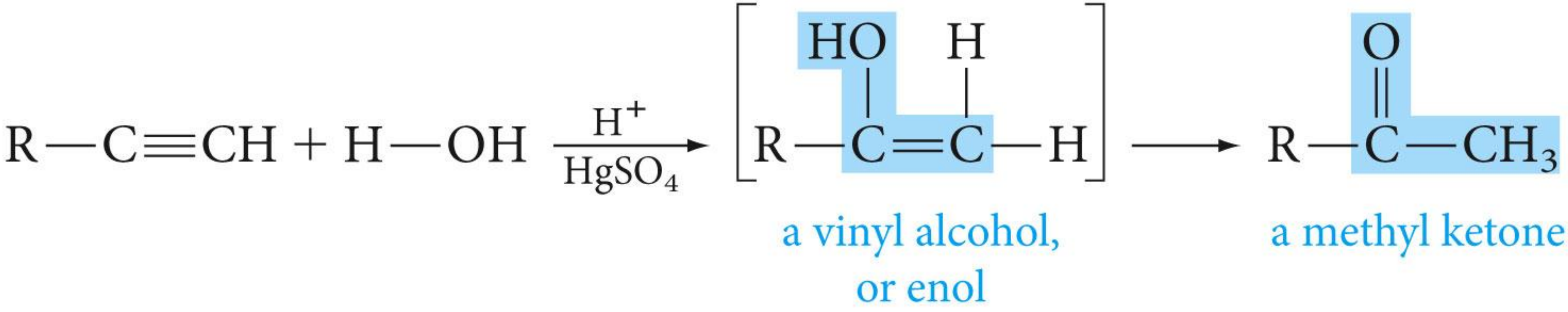
$$CH_3C{\equiv}CH + H{-}Br \longrightarrow CH_3\overset{+}{C}{=}CH_2 + Br^- \longrightarrow CH_3\overset{\overset{Br}{|}}{C}{=}CH_2$$



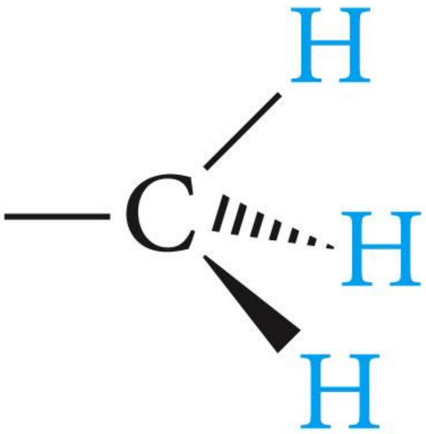
$$CH_3\overset{\overset{Br}{|}}{C}{=}CH_2 + H{-}Br \longrightarrow CH_3\underset{\underset{Br}{|}}{\overset{+}{C}}{-}CH_3 + Br^- \longrightarrow CH_3{-}\underset{\underset{Br}{|}}{\overset{\overset{Br}{|}}{C}}{-}CH_3$$



$$R-C\equiv C-H + Na^+NH_2^- \xrightarrow{\text{liquid } NH_3} R-C\equiv C:^-Na^+ + NH_3$$



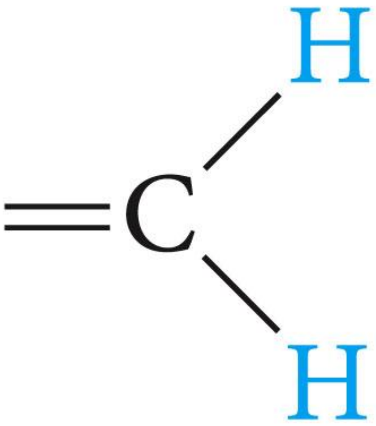
$$R-C\equiv CH + H-OH \xrightarrow[HgSO_4]{H^+} \left[R-\overset{HO}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H \right] \longrightarrow R-\overset{O}{\overset{\|}{C}}-CH_3$$



sp^3

25% *s*,

75% *p*



sp^2

$33\frac{1}{3}$% *s*,

$66\frac{2}{3}$% *p*

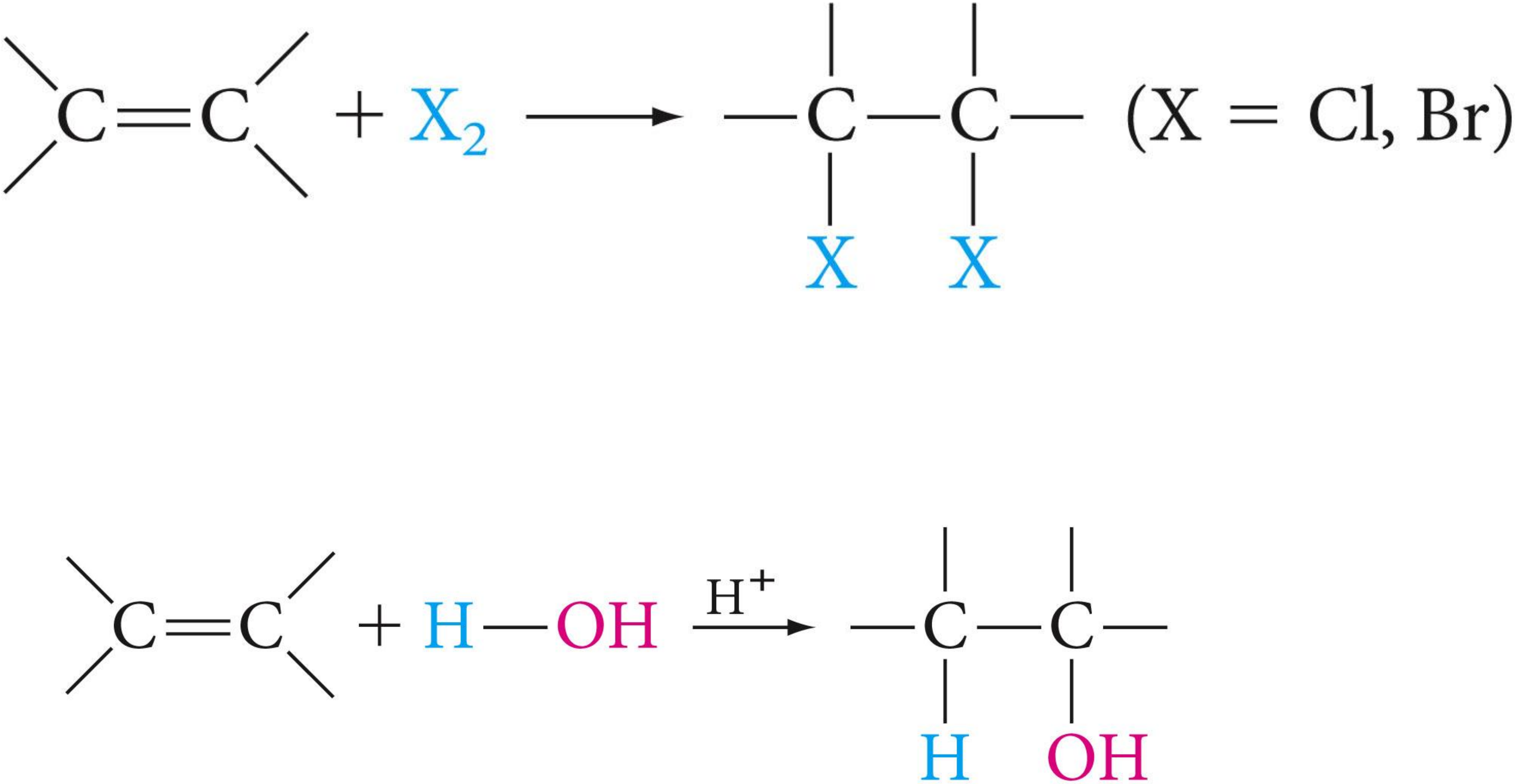
sp

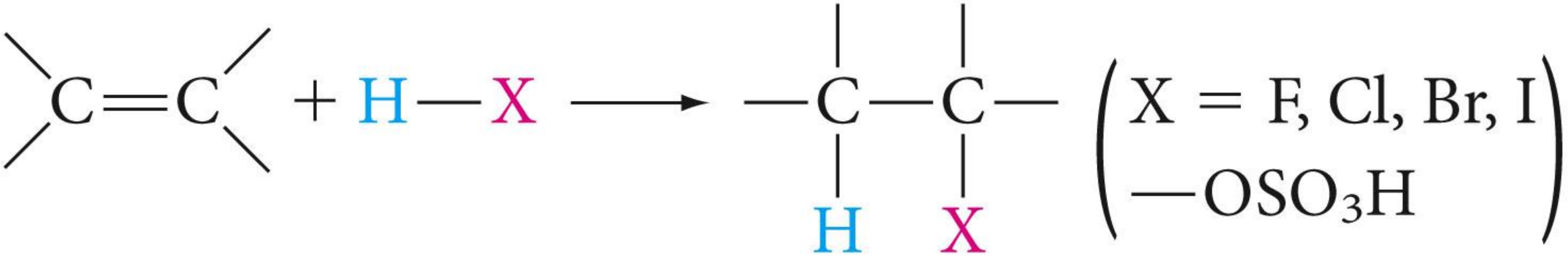
50% *s*,

50% *p*

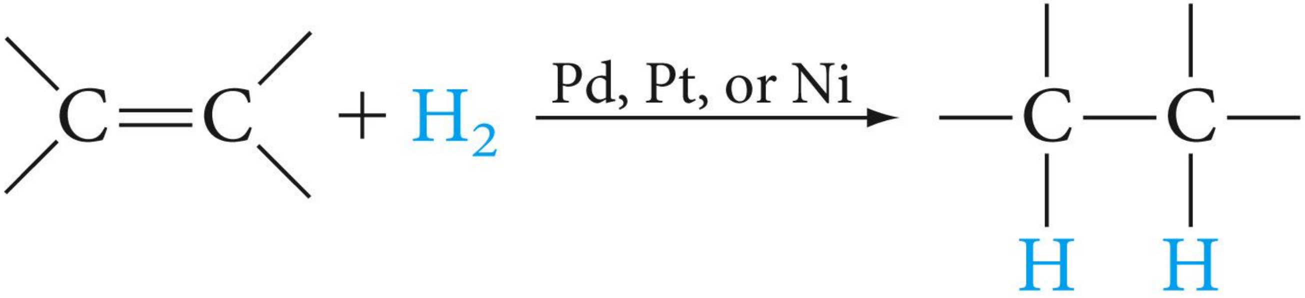
increasing acidity →

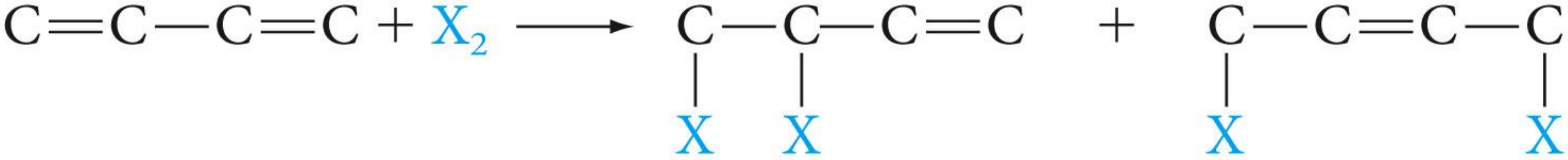
REACTIONS SUMMARY





$$3\ \mathrm{RCH{=}CH_2} \xrightarrow{\mathrm{BH_3}} \mathrm{(RCH_2CH_2)_3B} \xrightarrow[\mathrm{HO^-}]{\mathrm{H_2O_2}} 3\ \mathrm{RCH_2CH_2OH}$$

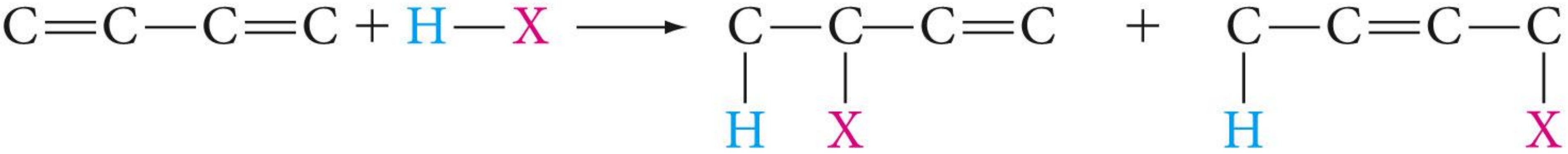




$$\mathrm{C{=}C{-}C{=}C} + X_2 \longrightarrow \underset{X}{\mathrm{C}}-\underset{X}{\mathrm{C}}-\mathrm{C{=}C} \quad + \quad \underset{X}{\mathrm{C}}-\mathrm{C{=}C}-\underset{X}{\mathrm{C}}$$

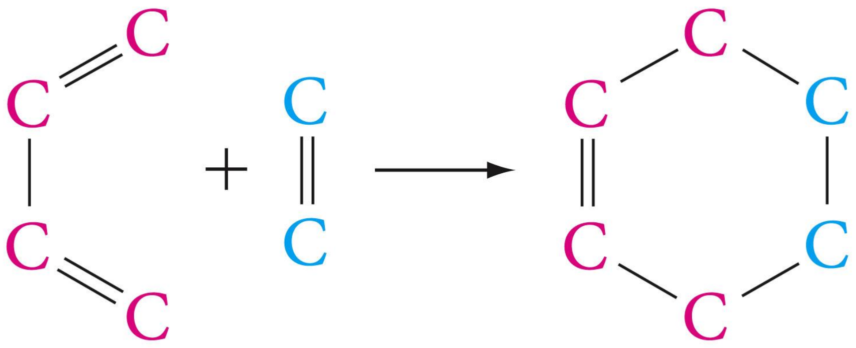
1,2-addition

1,4-addition

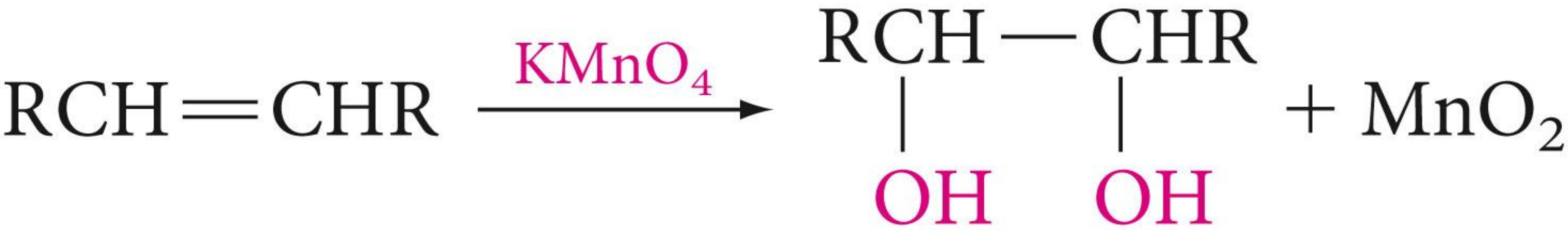


$$\mathrm{C{=}C{-}C{=}C} + \mathrm{H{-}X} \longrightarrow \underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}{-}\underset{\mathrm{X}}{\underset{|}{\mathrm{C}}}{-}\mathrm{C{=}C} \quad + \quad \underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}{-}\mathrm{C{=}C}{-}\underset{\mathrm{X}}{\underset{|}{\mathrm{C}}}$$

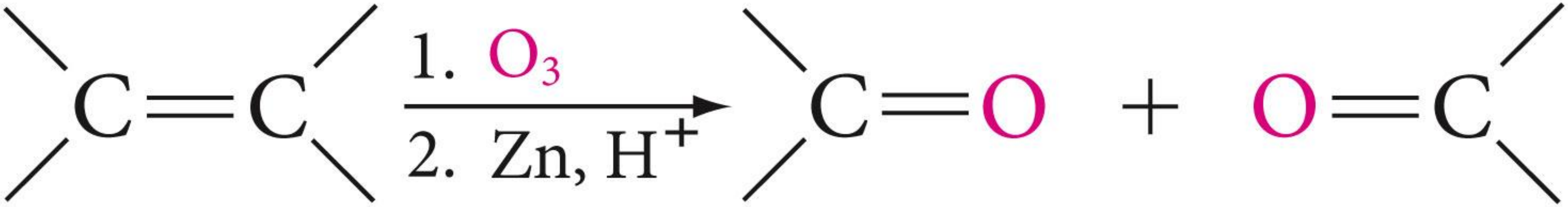
(X = Cl, Br) 1,2-addition 1,4-addition

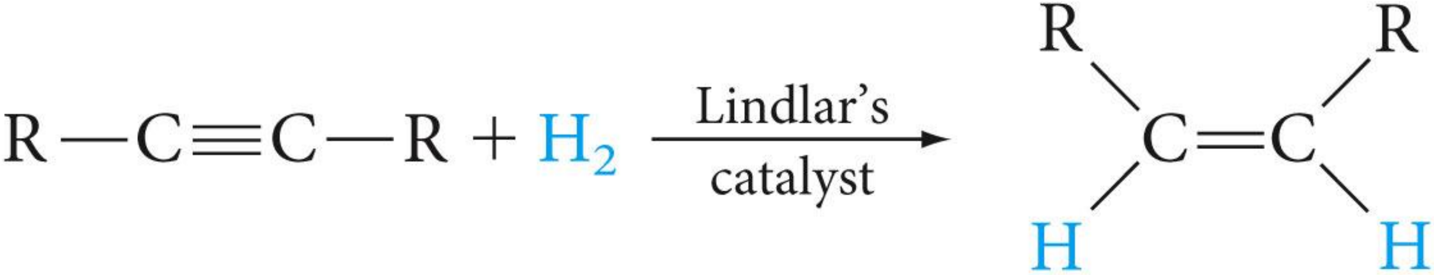


$$n\,H_2C{=}CH_2 \xrightarrow{\text{catalyst}} \left(CH_2{-}CH_2 \right)_n$$

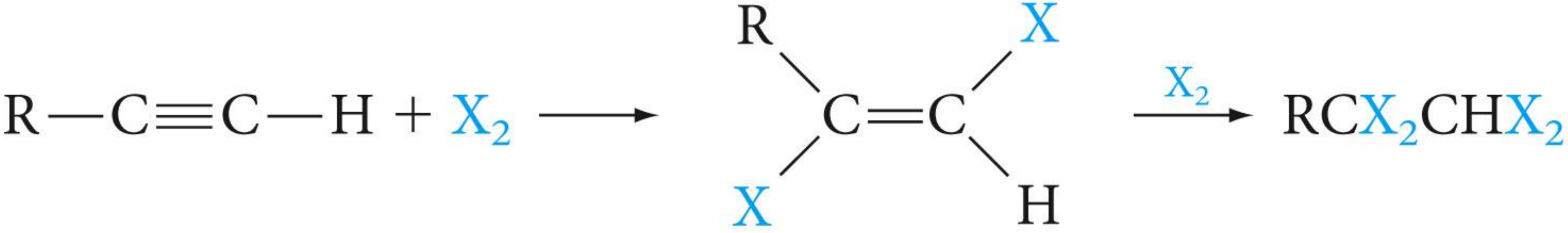


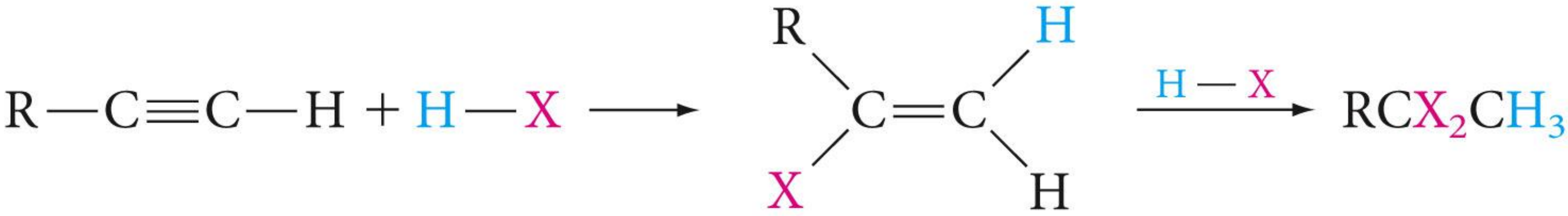
$$RCH{=}CHR \xrightarrow{KMnO_4} \underset{\displaystyle OH}{\underset{|}{RCH}}{-}\underset{\displaystyle OH}{\underset{|}{CHR}} + MnO_2$$

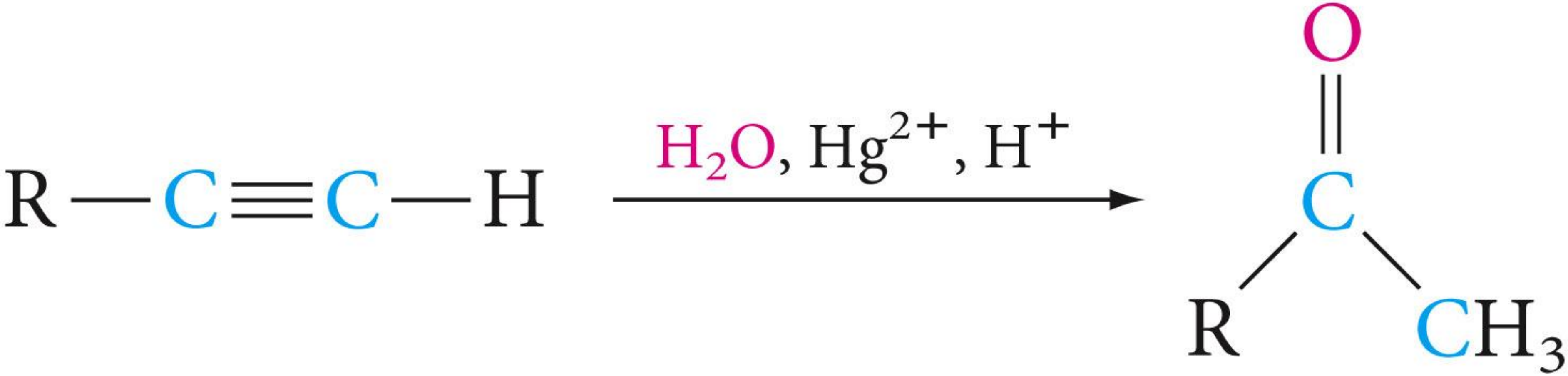




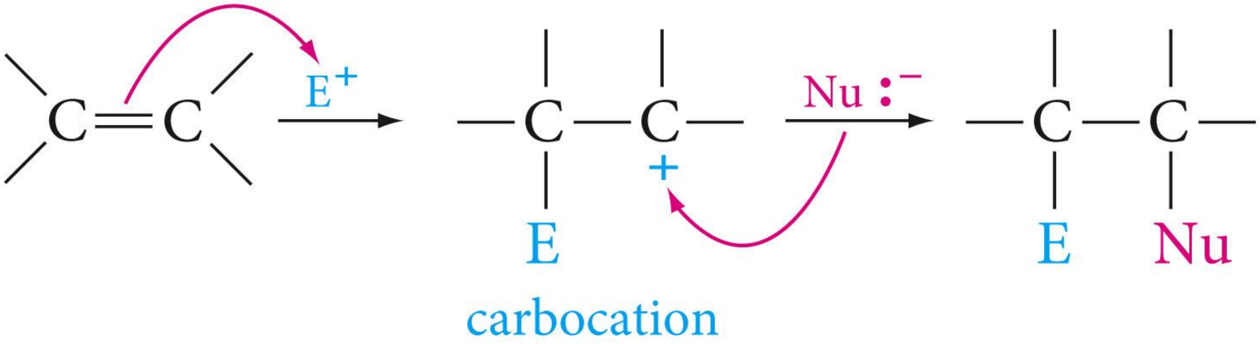
(*cis* addition)

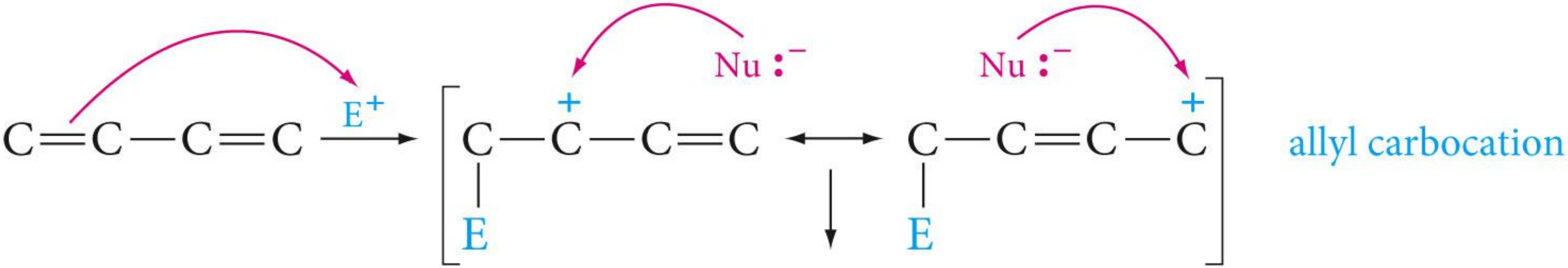

R—C≡C—H + X₂
R
X
C=C
X
H
X₂
RCX₂CHX₂

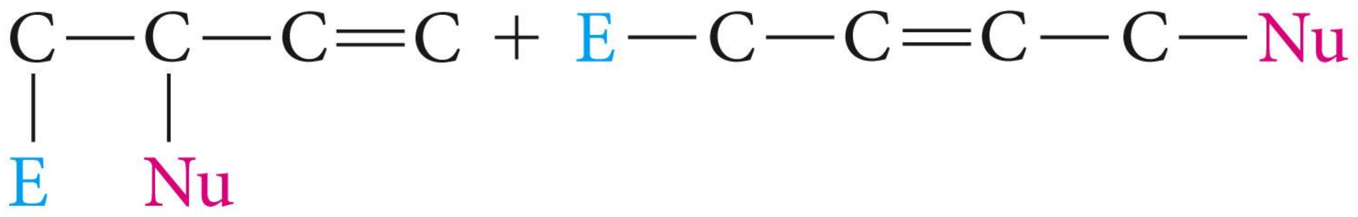

R—C≡C—H + H—X
R
H
C=C
X
H
H—X
RCX₂CH₃



$$\mathrm{R{-}C{\equiv}C{-}H} + \mathrm{Na^{+}\,NH_2^{-}} \xrightarrow{\mathrm{NH_3}} \mathrm{R{-}C{\equiv}C{:}^{-}\,Na^{+}} + \mathrm{NH_3}$$

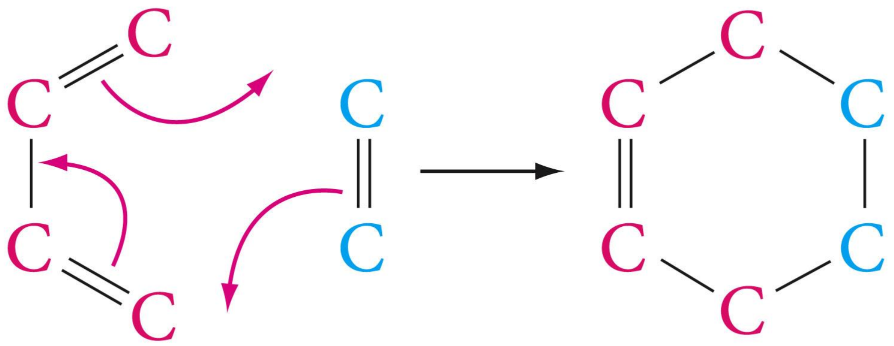

E+
Nu :−
E
Nu
carbocation

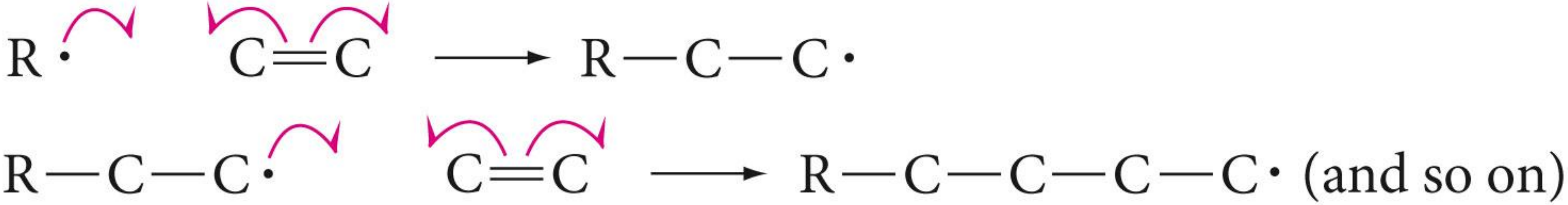

E+
Nu :−
Nu :−
E
E
allyl carbocation



$$\underset{\text{E}}{\text{C}}-\underset{\text{Nu}}{\text{C}}-\text{C}=\text{C} + \text{E}-\text{C}-\text{C}=\text{C}-\text{C}-\text{Nu}$$

1,2-product 1,4-product




R·
C=C
R—C—C·
R—C—C·
C=C
R—C—C—C—C· (and so on)