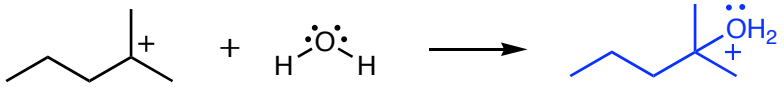
Learning Guide for Chapter 8 - Organic Reactions II

I. Substitution, Addition, and Elimination Reactions
II. Oxidation and Reduction Reactions
III. Radical Reactions
IV. Reactive Intermediates
V. Stereochemistry of Reactions

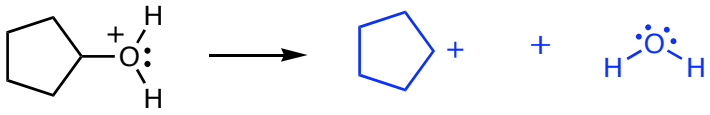
I. Substitution, Addition, and Elimination Reactions

In the previous chapter, we learned to use association, dissociation, and displacement to describe Lewis acid/base reactions. Complete the following reactions.

association 

where did the C+ come from?

how will this compound become neutral?

dissociation 

how did the alcohol become protonated?

what will happen to the C+?

displacement 

how did the alcohol get deprotonated?

Are these complete reactions?

no - reactions usually start and end with neutral molecules

these are steps in the mechanism of a reaction

What do the following terms mean?

substitution: a bond to one group is substituted for a bond to another group

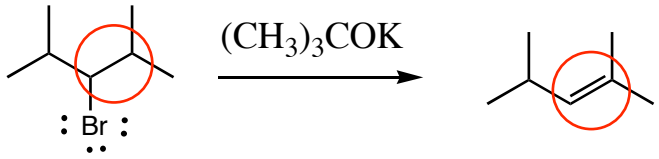
addition: new atoms are added to a molecule, and a double bond is lost

elimination: atoms are lost from a molecule, and a double bond is gained

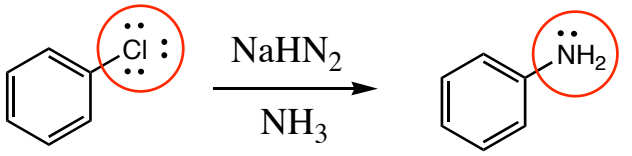
How are they different from the terms above?

they refer to the end result of a reaction, not what happens to the electrons

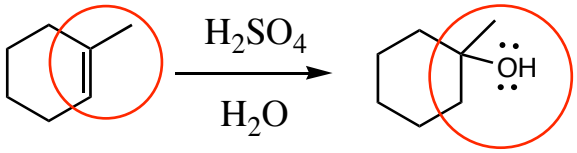
Match the following reactions with one of the three descriptions on the previous page.



elimination



substitution



addition

Which of these involve C=C?

addition starts with a C=C

elimination ends with a C=C

II. Oxidation and Reduction Reactions

How is oxidation defined in general chemistry?

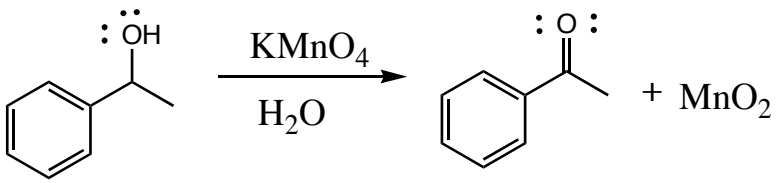
oxidation - loss of electrons (decrease in charge) $\overset{0}{Ag} \rightarrow \overset{+2}{AgO}$

reduction - gain of electrons (increase in charge) $\overset{+7}{KMnO_4} \rightarrow \overset{+4}{MnO_2}$

Why won't this work in organic chemistry?

compounds can be oxidized or reduced without changing charge

oxidation states are more difficult to calculate



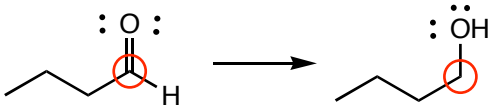
Mn was reduced, so the organic compound must have been oxidized

How are oxidation and reduction defined in organic chemistry?

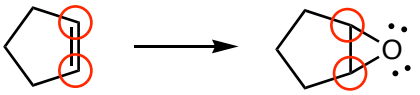
oxidation: gaining bonds to O and/or losing bonds to H

reduction: losing bonds to O and/or gaining bonds to H

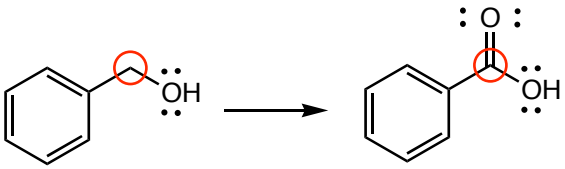
Which of the following is occurring in each of these transformations?



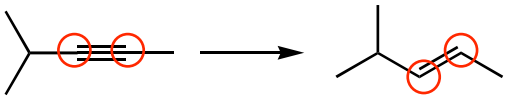
C loses bonds to O and gains a bond to H
reduction



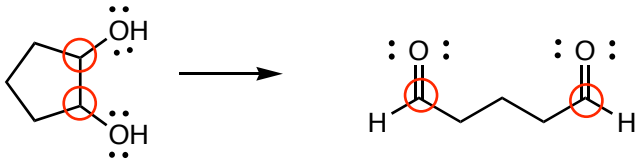
both C's lose a bond to H and gain a bond to O
oxidation



C gains 2 bonds to O
oxidation



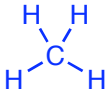
both C's gain a bond to H
reduction

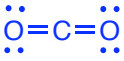


both C's gain a bond to O
oxidation

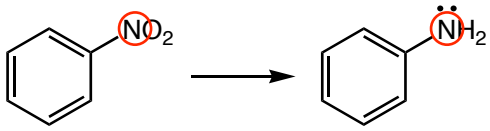
called oxidative cleavage because a C-C was also broken

What are the highest and lowest oxidation states of carbon?

lowest - methane 

highest - carbon dioxide 

Can atoms other than carbon be oxidized or reduced? yes

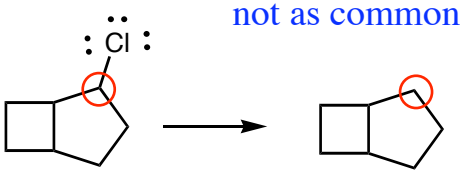


N loses 3 bonds to O, gains 2 bonds to H
reduction

Is only oxygen involved?

no - any other atom which is more electronegative than C counts (N, halogens)

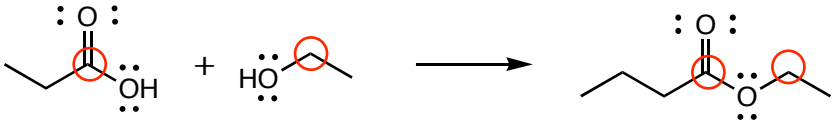
not as common to use these terms



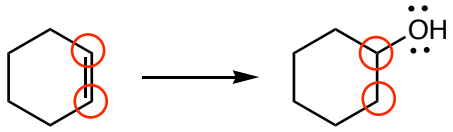
C lost a bond to Cl, gained a bond to H
reduction

Are all reactions oxidation and reductions?

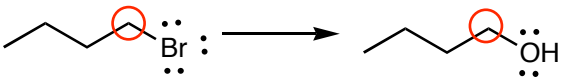
no - sometimes the starting material and product are in the same oxidation state



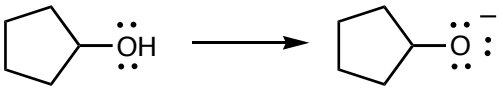
1st C stays at 3 bonds to O
2nd C stays at 1 bond to O
no change



1 C gained a bond to O,
1 C gained a bond to H
no net change



C lost a bond to Br, gained a bond to O
both are more EN than C
no change



loss of H and change of charge means
no change in oxidation state

acid/base reactions are not redox reactions

What is an oxidizing agent?

a compound which is easily reduced, oxidizes other compounds

What are some common oxidizing agents, and how can you recognize them?

Na_2CrO_4 sodium chromate

$KMnO_4$ potassium permangante

} metal atom in a high oxidation state, lots of O's

H_2O_2 hydrogen peroxide

O_3 ozone

} O bonded to itself

What is a reducting agent, and how can you recognize them?

a compound which is easily oxidized, reduces other compounds

H_2 hydrogen gas

$NaBH_4$ sodium borohydride

$LiAlH_4$ lithium aluminum hydride (LAH)

} hydride reagents (H bonded to group III atoms)

Na sodium metal

Sn tin metal

} metals in elemental state

III. Radical reactions

What is a radical?

hydroxyl radical

bromine radical

carbon radical

an atom (or molecule) with an unpaired electron

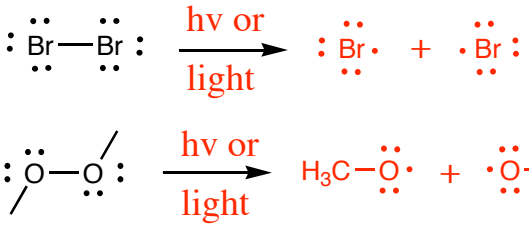
Are radicals very reactive?

yes! they have an incomplete octet

Are radicals dangerous?

yes - when they are formed inside the body, they can react with proteins and DNA and cause damage to cells; they are thought to play a part in aging

How are radicals formed?



initiation steps

a molecule with a weak bond absorbs energy from heat or light and breaks homolytically

What kinds of molecules form radicals in this way?

molecules with two highly EN and/or large atoms bonded to each other

What are reactions like this called?

initiation steps - bonds break to form radicals

How are carbon radicals formed?

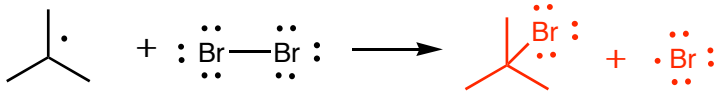
they react with radicals formed by initiation steps

What is this type of reatction called?

propogation - one radical creates another

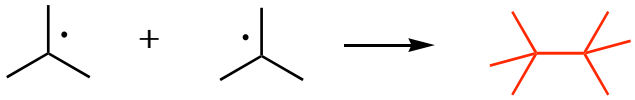
How do carbon radicals become stable again?

2 ways:



1) they take atoms from stable molecules, forming new radicals

another propagation step



2) two radicals come together

What are these kinds of reactions called?

termination - two radicals come together

Which of these two is more likely?

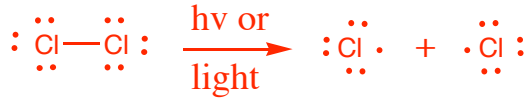
a radicals are very reactive, very short lived, radical reactions are very fast

so a radical is more likely to collide with a stable molecule than a radical

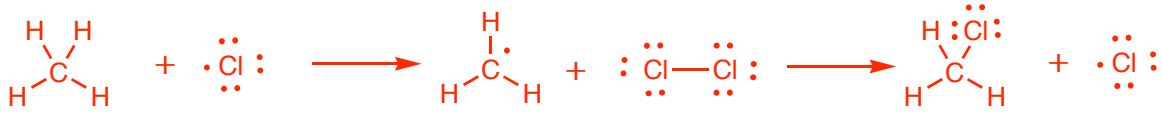
The halogenation of alkanes is a radical reaction. What does its mechanism look like?

$$CH_4 + Cl_2 \xrightarrow[\text{or heat}]{h\nu} CH_3Cl + HCl$$

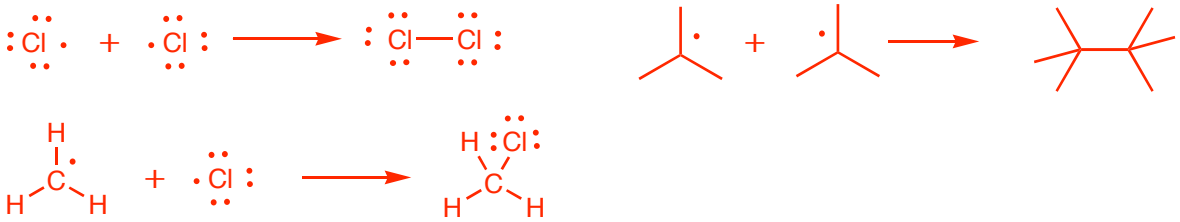
Initiation step:



Propagation steps:



Termination steps:



What role does the initiation step play?

gets the reaction started - no light or heat, nothing happens

Why are many chemicals stored in dark bottles in cool places?

to prevent radicals from forming

What role do the propagation steps play?

organic compound reacts and forms the product - main steps

What role do termination steps play?

they are side reactions
they slow the reaction down
one recreates SM, one creates product, one creates a side product
they occur mostly at the end when no reagents are left
we don't always worry about these

Does the reaction stop at the product shown? What other products would be formed?

nope - the product could react with another Cl radical

CH_2Cl, $CHCl_3$, CCl_4

Many radical reactions are also chain reactions. Is this one? How can you tell?

yes! the radical needed to react with the alkane is regenerated by the propagation steps; initiation only has to happen once
(this is referred to as high quantum yield - lots of product for less light)

How are reactions involving radicals different from reactions of acids and bases or nucleophiles and electrophiles?

electrons don't move in pairs

How are the arrows different?

they are single-headed; they flow in opposite directions

Which is more common in organic chemistry?

only a few reactions in this course have a radical mechanism

they seem to be common as unwanted reactions

IV. Reactive Intermediates

What is a reactive intermediate?

a high energy molecule which is formed and then quickly reacts

Why are they important?

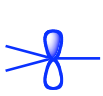
anything which affects their stability will have a big impact on the reaction

Fill in the chart below.

	description	example	charge	hybridization	why reactive?
stable carbon	four bonds		0	sp^3, sp^2, sp	
carbocations	3 bonds empty orbital		+	sp^2	no octet
carbanions	3 bonds e- pair		-	sp^2	low EN
carbon radicals	3 bonds unpaired e-		0	sp^2	no octet
carbenes	2 bonds e- pair empty orbital		0	sp^2	no octet

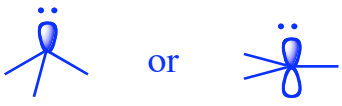
What do their molecular orbitals look like? What is the geometry of the substituents?

carbocation



trig planar

carbanion



trig pyramid or trig planar (resonance)

carbon radical

trig planar

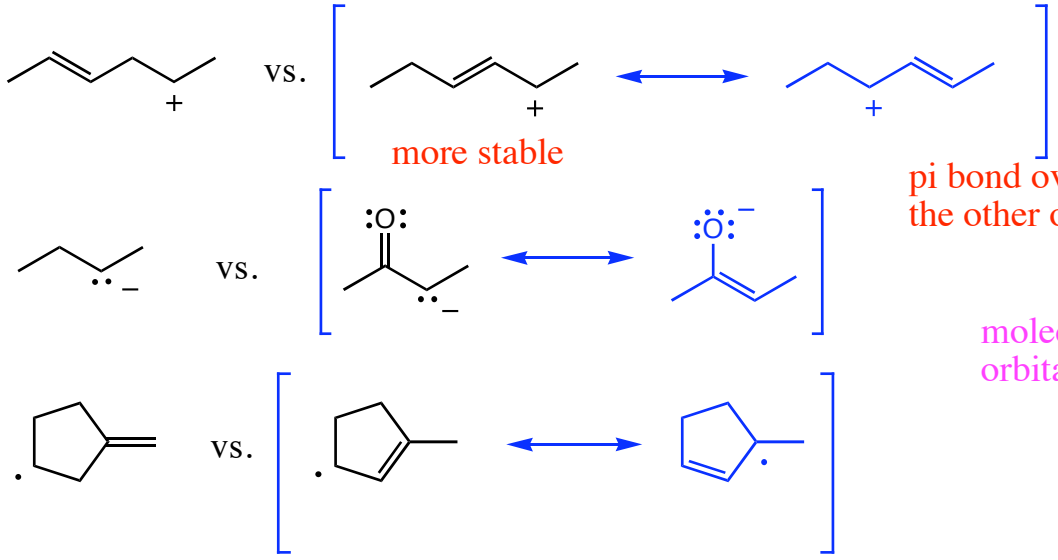
carbene

bent

Stabilization

How does resonance stabilize carbocations, carbanions, and radicals?

the positive charge, negative charge, or unpaired electron are spread over more than one atom



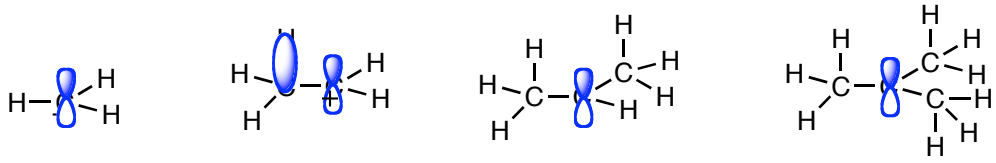
molecular orbital models

What does the molecule have to have in order for resonance to occur?

a double bond one atom away from the unstable atom

How does having alkyl substituents stabilize carbocations and radicals?

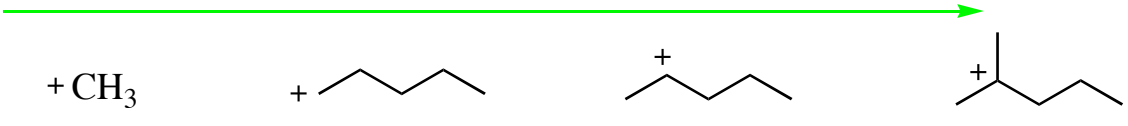
the sigma bonds overlap with the electron-deficient orbital and donate some electron density to it - called hyperconjugation



methyl	primary 1°	secondary 2°	tertiary 3°
no alkyl substituents	1 alkyl substituent	2 alkyl substituents	3 alkyl substituents

In which direction does stability increase?

more stable



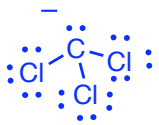
$+CH_3$			
methyl doesn't form	1° doesn't form	2° less stable but can form	3° most stable

Does hyperconjugation stabilize carbanions?

no - that orbital is not electron-deficient, so sharing e- density doesn't help

How can electronegative atoms stabilize carbanions?

they draw e- density away from the C

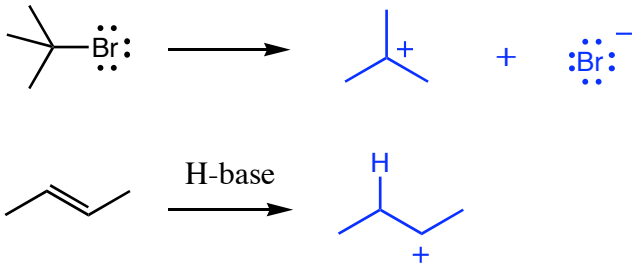


Why aren't carbenes stabilized by either resonance or alkyl substitution?

they usually don't have any other groups attached

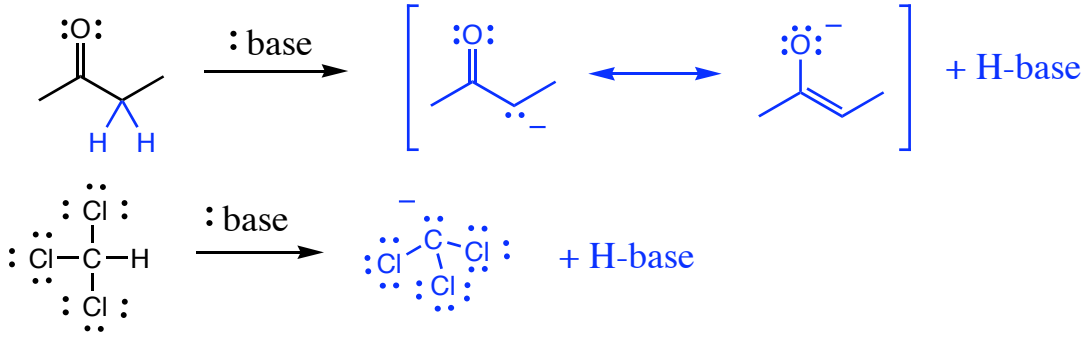
Formation

How are carbocations formed?



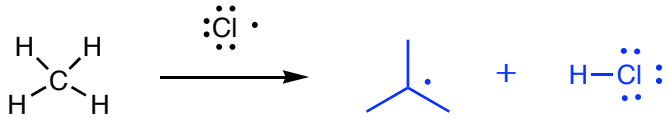
dissocation or reaction of alkenes with acid

How are carbanions formed?



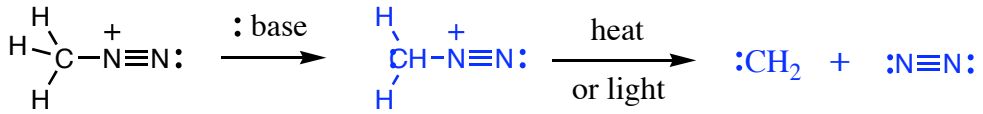
by removing a H from a C

How are carbon radicals formed?



by reacting with existing radicals in propagations steps

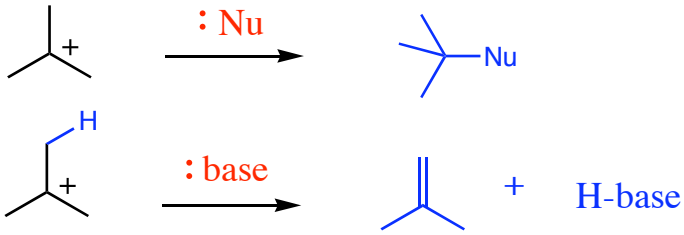
How are carbenes formed?



base takes a H, then dissocation

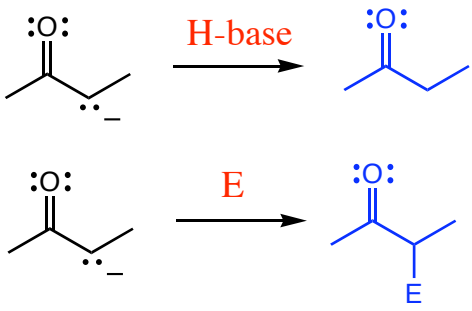
<u>Reactivity</u>

How do carbocations react?



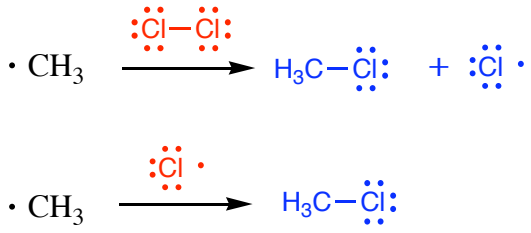
as electrophiles or acids

How do carbanions react?



as nucleohiles or bases

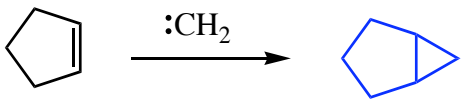
How do carbon radicals react?



take atoms from other molecules (propagation)

combine with other radicals (termination)

How do carbenes react?



electrocyclic reactions (both give and receive e-)

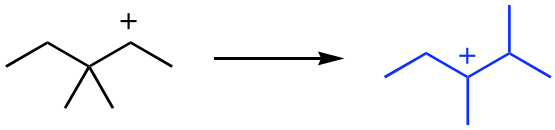
Summary

	Stabilization	Formation	Reactivity
carbocations	resonance hyperconjugation	dissociation or C=C + acid	E or acid
carbanions	resonance induction	base takes a H	Nu or base
carbon radicals	resonance hyperconjugation	react with another radical	propagation, termination
carbenes	N/A	lose an H, then dissociate	electrocyclic reactions

Rearrangements of Carbocations

What happens to a carbocation when it undergoes rearrangement?

a bond moves into the empty orbital, leaving the positive charge on another atom



Is this resonance, or a chemical reaction? a reaction - atoms moved!

Why do rearrangements occur?

so that the C+ can become more stable

Which of the carbocations commonly undergoes rearrangements?

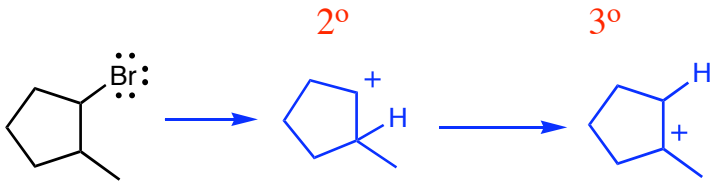
1º - doesn't form

* 2º - wants to become 3º

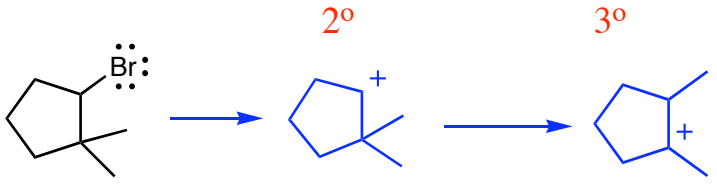
3º - already stable

What are the two ways in which a carbocation can rearrange?

hydride shift, alkyl shift



hydride shift
H moves with its e-



alkyl shift
carbon moves with its e-

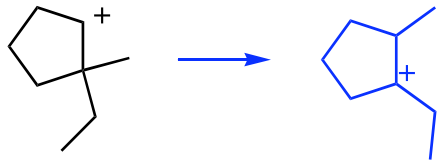
Why can't the following carbocation rearrange?

equally stable

less stable

too far away
can't happen

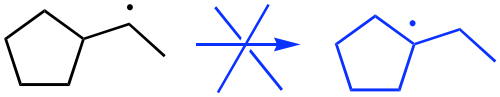
What is the most likely rearrangement of the following carbocation?



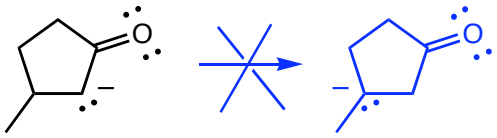
smallest group is most likely to move

methyl shifts are most common

Why don't radicals, carbanions, or carbenes rearrange?



Ea too high? rate too slow compared to reaction with another molecule?



not stabilized by alkyl substitution
can only be formed on a C stabilized by resonance or induction by EN atoms

$:CH_2$ nowhere to go
can't shift e- pair and empty orbital at the same time anyway

V. Stereochemistry of Reactions

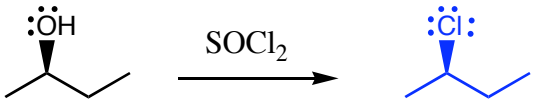
What are the two conditions under which the stereochemistry of the reaction is important?

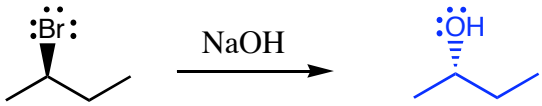
stereocenter is involved in a reaction

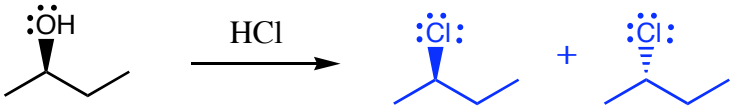
stereocenter(s) created

<u>Existing stereocenter undergoes a reaction</u>

What three things can happen to a stereocenter involved in a reaction?

conserved:  same orientation

inverted:  opposite orientation

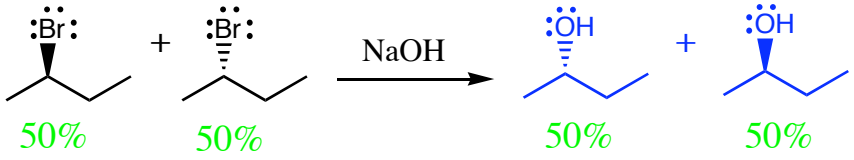
racemized:  both orientations are formed

What determines which of these occurs?

the mechanism of the reaction

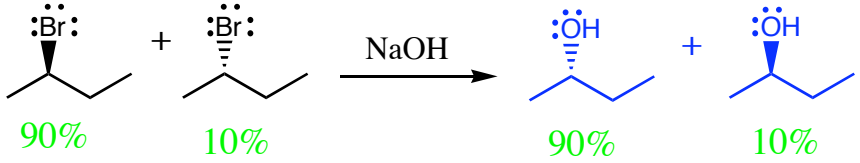
What happens if the compound isn't enantiomerically pure?

racemic mixture



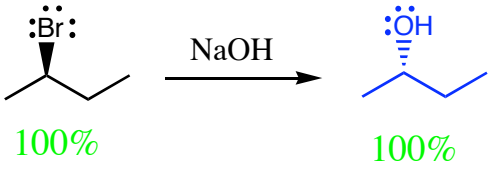
no effect

80% o.p.



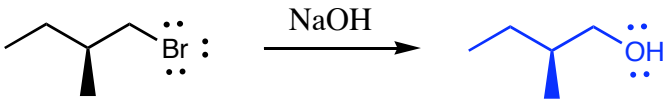
opposite preference

enantiomerically pure



totally switched

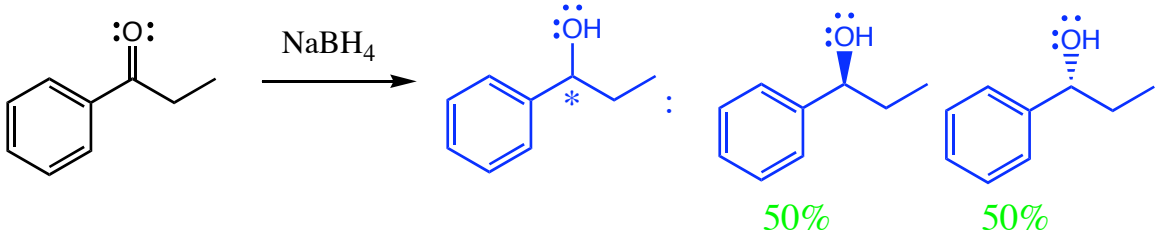
What if the stereocenter isn't involved in the reaction?



it doesn't change!

<u>One new asymmetric carbon</u>

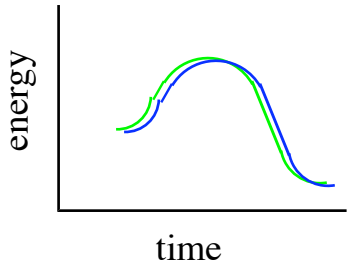
When only one new stereocenter is formed, how many stereoisomers can result?



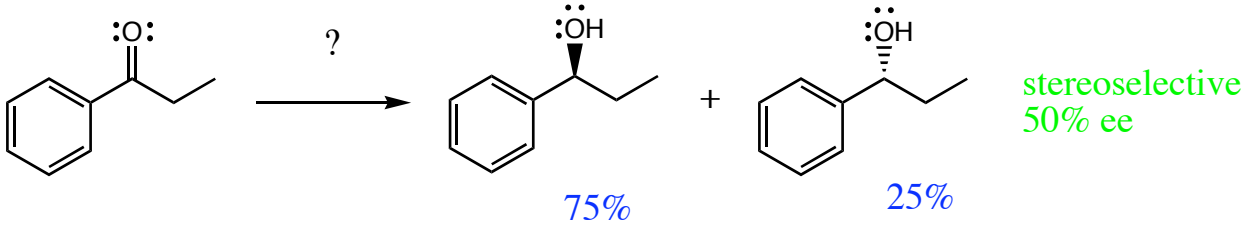
2

What mixture will you usually get, and why? racemic

reactions have the same Ea
same ΔH
formed at the same rate

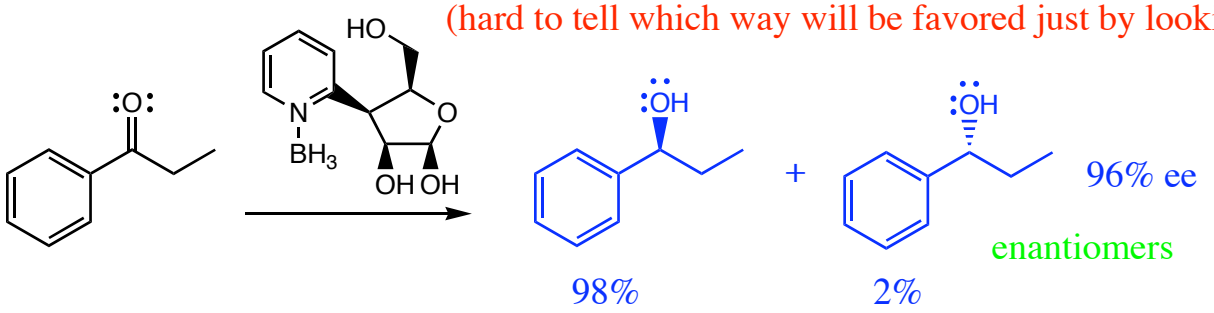


What could we do to favor one enantiomer over the other?

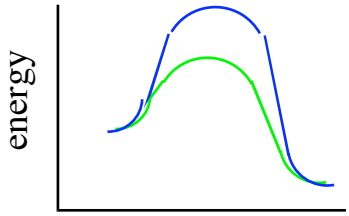


1) use an enantiomerically pure reagent

(hard to tell which way will be favored just by looking)

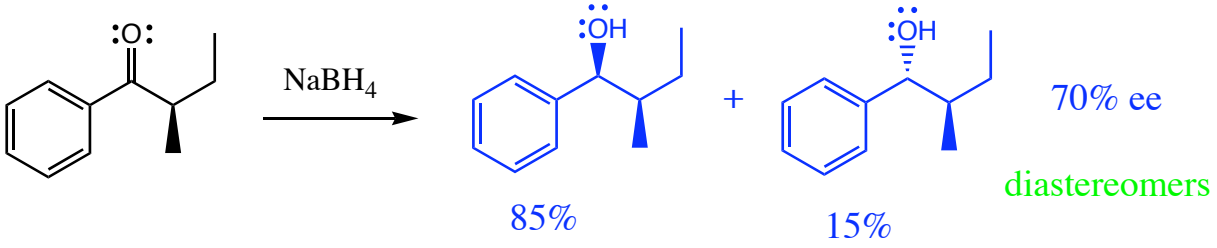


different Ea
same ΔH
one will be formed faster

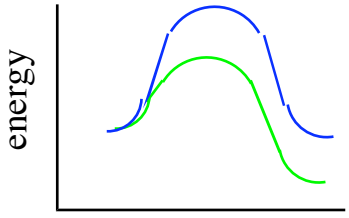


2) use an enantiomerically pure starting material with the stereocenter nearby

(less crowded one is favored)



different Ea,
different ΔH
one will be formed faster
and favored more



What is this kind of reaction called, and why is it useful?

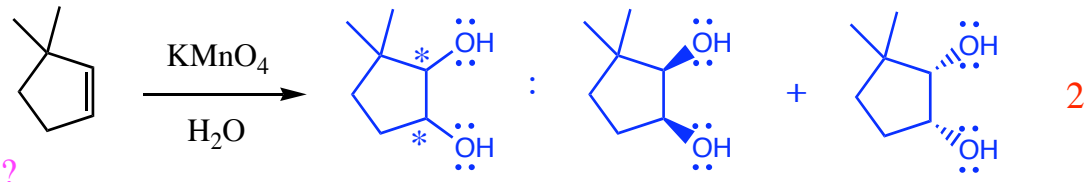
stereoselective reactions - useful for making enantiomerically pure compounds like pharmaceuticals!

Two new asymmetric carbons

When two new stereocenters are formed, how many stereoisomers can result?

4 are possible, but some reactions give only 2 (depends on the mechanism)

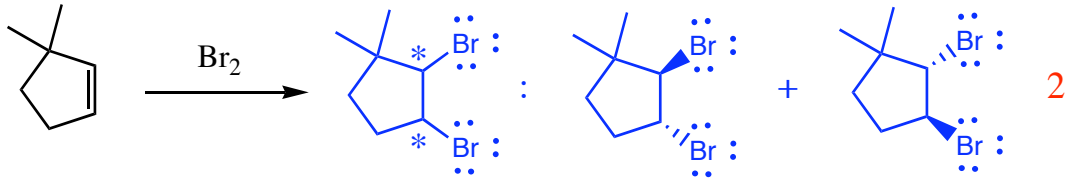
syn addition



what if no methyls?
single meso compound

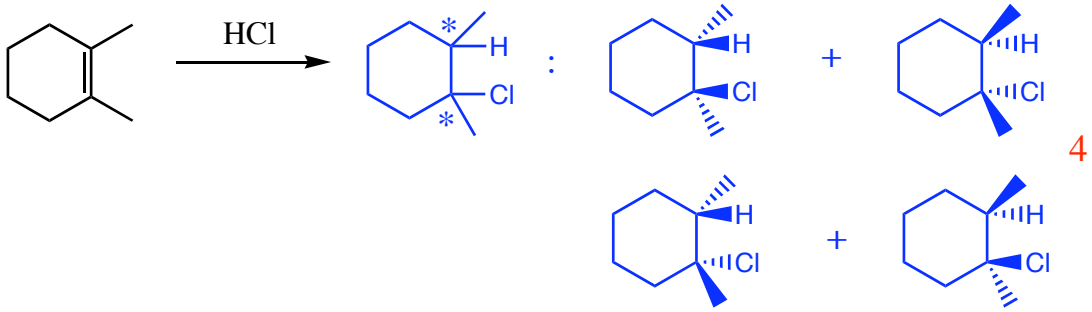
new substituents on the same side
1 pair of enantiomers
or a meso compound

anti addition



new substituents on opposite sides
1 pair of enantiomers

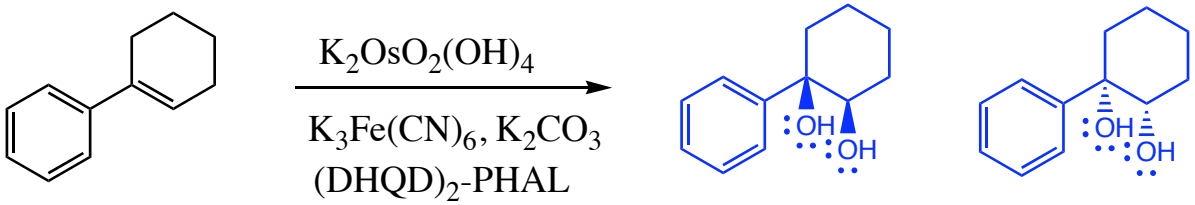
nonselective



all possible stereoisomers
(2 pairs of enantiomers)

Can these reactions be stereoselective? yes!

use a chiral reagent or a chiral starting material



98% 2%

chiral reagent