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Organic chemistry: a survival guide for students

Ethan C. Levine
Northeastern University

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Organic Chemistry: A Survival Guide for Students

Ethan C. Levine, Sociology Major, College of Arts and Sciences
Northeastern University
Boston, Massachusetts
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Faculty Advisor: Professor Philip Le Quesne

Abstract
This project reviews material from undergraduate Organic Chemistry I and II. It is meant to function as a supplement to the textbook and lecture material for the course as it is taught in universities throughout the United States. Complex ideas are broken down into simpler ones. Material is presented in conversational language, using as little scientific jargon as possible.

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Alkenes

Now that we've learned how to name and describe some properties of organic compounds, it's time to look at some reactions! Some texts and review books, including this one, jump straight into alkenes (with carbon-carbon double bonds). Others begin with alkanes (single bonds). Check out sections 9-11 for alkane reactions.

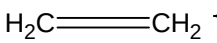
Nomenclature and Structure

Double bonds can be treated as functional groups in and of themselves, and they sometimes take priority over other groups when naming compounds. If a double bond is in the parent chain of a molecule, indicate the location of the double bond and use the suffix 'ene.' Be careful to use the lowest number possible!

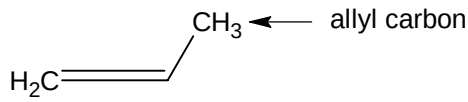
$CH_3CH_2CH_2CH_3$
butane

$CH_3CH_2CH{=}{=}CH_2$
1-butene

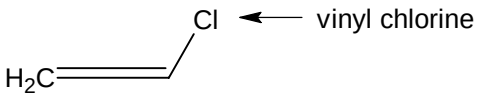
The carbons in and adjacent to double bonds have special names. These names can also refer to substituents attached to these carbons.

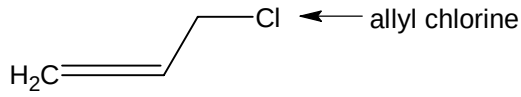


vinyl group

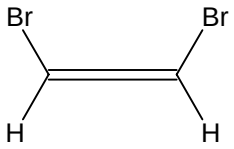


allyl group

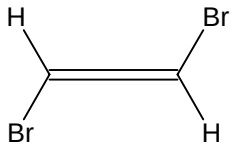




Structure plays a role in naming alkenes. If each carbon in a double bond is attached to similar groups (each C is attached to one H and one Br, for example), we can describe the bond with cis and trans nomenclature. In a **cis configuration**, similar groups are on the same side of the bond. In a **trans configuration**, they are on opposite sides. This is similar to the cis/trans nomenclature of cyclohexane (see section two). To name the compound, add 'cis-' or 'trans-' to the IUPAC name:



cis-1,2,-dibromoethene

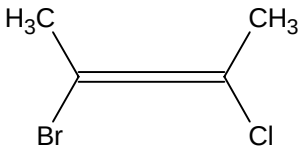


trans-1,2,-dibromoethene

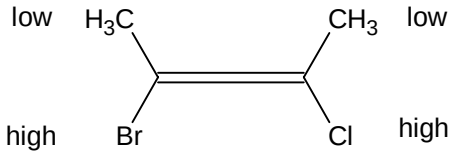
Things get more complicated when the carbons are attached to three or four different groups. When this happens, we must use E/Z nomenclature. The first step is to assign priorities to the groups on each carbon, using atomic number (higher atomic number = higher priority). When the first atoms in each group are identical, we work our

way through the chain, looking at every bond. In a **Z configuration**, groups with similar priorities are on the same side (similar to cis). In an **E configuration**, groups with similar priorities are on opposite sides (similar to trans).

Example one:

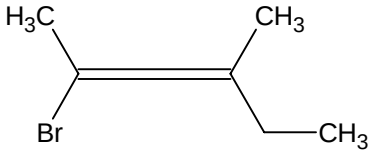


Br has an atomic number of 35 and C has an atomic number of 6. This makes Br the high priority and C (CH_3) the low priority group for the first carbon. Cl has an atomic number of of 17, making it the high priority for the second carbon.

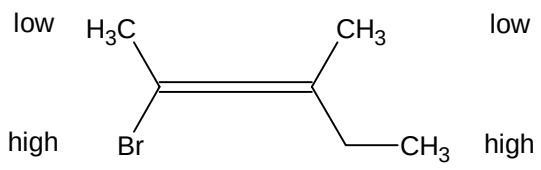


This molecule is in a Z configuration.

Example two:

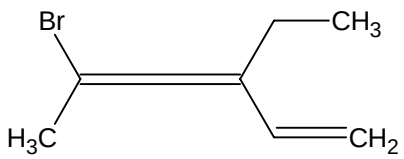


When we look at the substituents on the second carbon, both begin with C (atomic number = 6). We need to go further into the substituents to assign priorities. In the CH_3 group, carbon is attached to H(1), H(1), and H(1). In the CH_2CH_3, carbon is attached to H(1), H(1), and C(6). This gives CH_2CH_3 a higher priority.

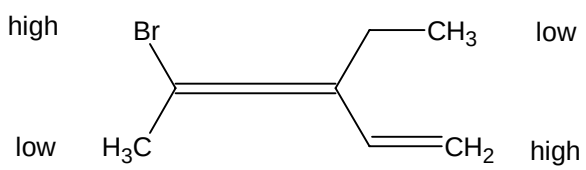


This molecule is in a Z configuration.

Example three:



Once again, the atoms directly attached to the second carbon are identical, making it necessary to go farter into the substituents. In CH_2CH_3, the carbon is attached to H(1), H(1), and C(6). In CH==CH_2, we treat every bond as a separate group – that is, we describe the carbon as attached to H(1), C(6), and C(6).

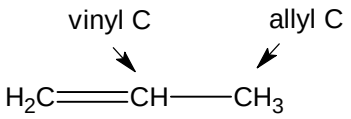


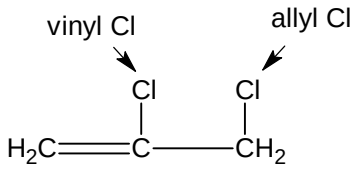
This molecule is in the E configuration.

*Note about stability: as we learned in section two, organic molecules like to keep bulky and electron-rich groups as far apart as possible. This means that trans and E isomers will generally be more stable than cis and Z isomers.

The carbons involved in double bonds are sp^2 hybridized (see section two). Remember that sp^2 carbons' bonds are planar! The bond angles in a double bond are approximately 120˚ (carbon is attached to three substituents, and divides the full circle of 360˚ among them). In ethene, the simplest alkene, bond angles are exactly 120˚.

The C's in double bonds, as well as groups attached to them, are called **vinyl C's and groups**. The C's adjacent to double bonds, as well as groups attached to them, are called **allyl C's and groups**.

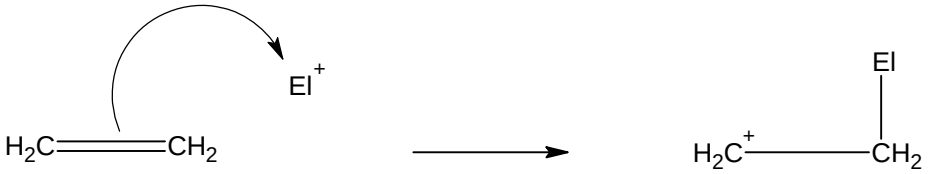




Basic Reaction Mechanism

Throughout this course, most of the alkene reactions you encounter will change alkenes to alkanes, or convert the double bond into a single bond. Each carbon needs to find something else to hold on to for this to work. The basic reaction here is called **electrophilic addition**.

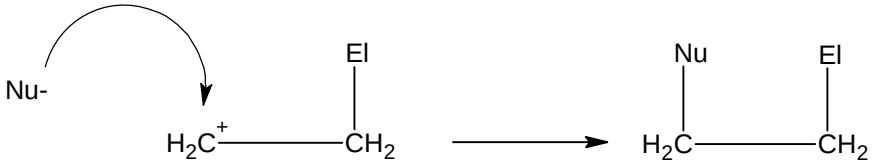
Double bonds are made up of electrons, which are negatively charged. As a result, bonds are attracted to positively-charged (or at least electron-poor) atoms. The electrons of the double bond attack an **electrophile**, or electron-loving group, in the first step of this reaction:



By the end of this step, one carbon still has four bonds (it's simply moved the double bond into a different position). The other carbon, however, has lost a bond. Losing contact with electrons (negatively charged) leaves this carbon with a positive charge – it has become a **carbocation**. Conversely, he electrophile loses its charge when it bonds

with electrons. Note that *net charge is conserved* – we began with one positive charge, and we end with one positive charge.

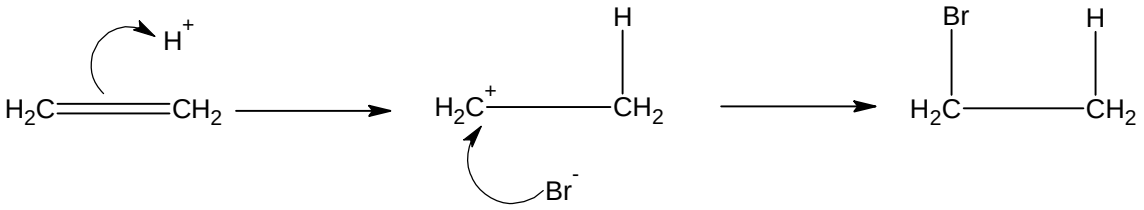
Now, a **nucleophile** (attracted to positive charges, like the protons in an atom's nucleus) steps in to finish the job:



The rest of the reactions we explore in this section will follow this basic pattern (double bond attacks electrophile, C+ forms, nucleophile attacks C+). Mechanisms vary somewhat among reactions.

HX (HBr, HCl, HI) and Some Complications

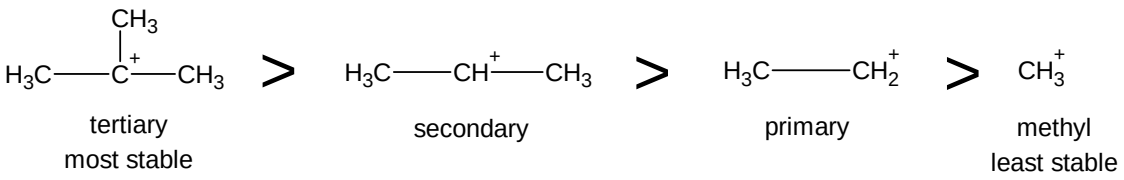
HBr follows the basic reaction with H^+ as an electrophile and Br^- as a nucleophile:



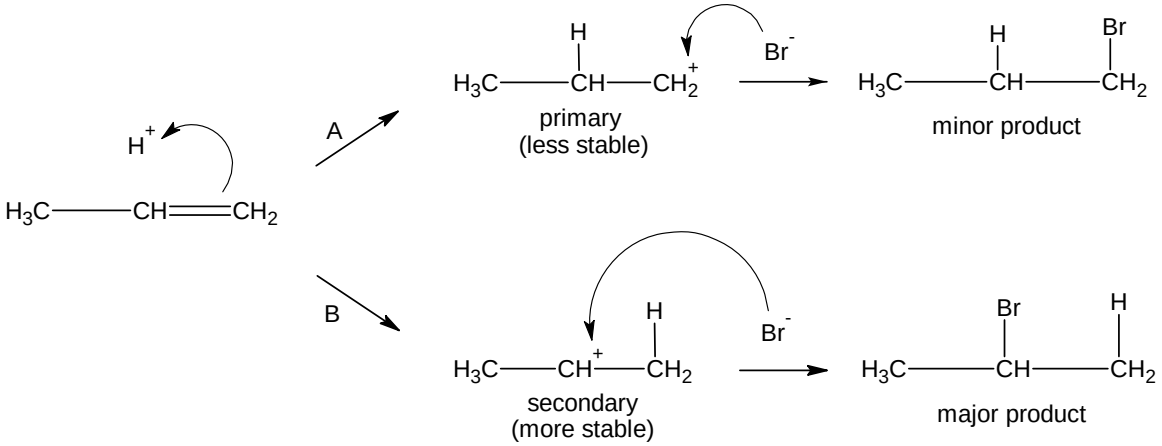
This is all well and good when working with ethene, but what if the alkene isn't symmetrical? What if the two carbons are different? To solve these problems, we need to look at carbocation stability.

Carbocations are positively charged. Ideally, molecules want to share their charges among several atoms (see section six on resonance) or at least balance them out. Remember that like charges repel. A C^+ surrounded by hydrogen atoms, which are basically protons (H's electron is busy maintaining its bond to carbon), will be unstable. A C^+ surrounded by a mixture of carbons and hydrogens, or all carbons, will fare better.

Carbocations, like neutral carbons, are classified as methyl, primary, secondary, or tertiary, depending on how many carbons they are directly attached to.



Let's apply this to a reaction. If I want to react HBr with $CH_3CH{=}{=}CH_2$, the reaction can precede in one of two ways:

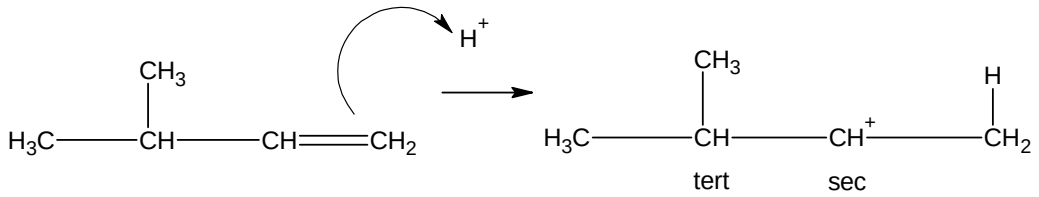


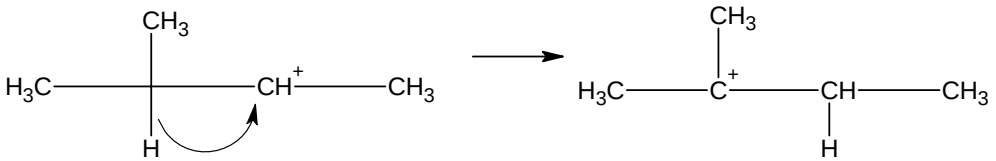
In reaction A, H^+ adds to the secondary carbon. As a result, the primary carbon loses a bond and becomes positive. Primary carbocations are very unstable. In reaction B, H^+ adds to the primary carbon. As a result, the secondary carbon loses a bond and forms a more stable, secondary carbocation. Sounds like reaction B is the winner! This being the case, H^+ will show **regioselectivity**, or a preference for one particular carbon in the double bond (regio = region, H^+ selectively adds to one particular region of the molecule). The product formed by the more stable reaction pathway, reaction B in this case, is the **major product**. The product formed by the less stable reaction pathway is the **minor product**.

A chemist named Vladimir Markovnikov noticed this pattern, and produced what has become known as **Markovnikov's Rule**: H adds to the carbon with the most H's on it (the least substituted carbon). He was slightly mistaken. As we will see, the electrophile in a reaction adds to the carbon with the most H's, and H is not always the electrophile. Reactions are described as either **Markovnikov or anti-Markovnikov reactions**, depending on whether they follow this rule.

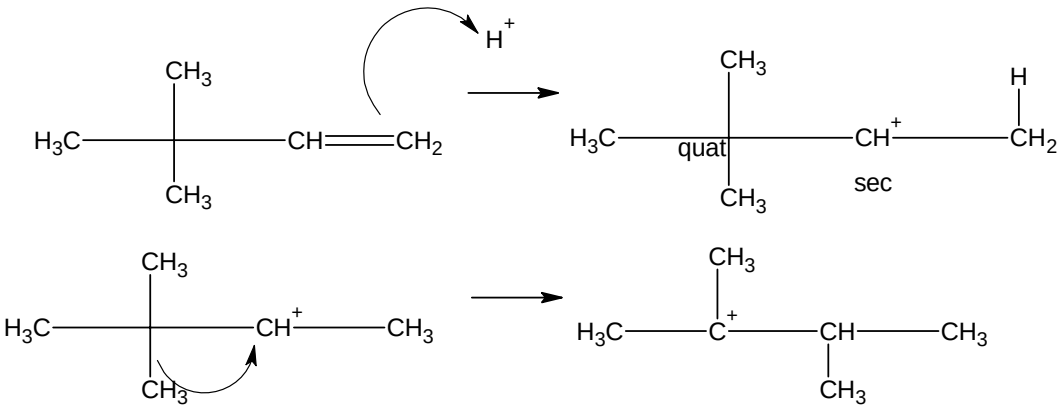
Sometimes, in a more dramatic effort to form the most stable C^+ possible, molecules will move H's and C-groups around. This is called **rearrangement**. If possible, it is best to move an H (along with its bond to C) – this is known as a **hydride shift**. Otherwise, it is possible to move a CH_3 group (**methyl shift**), a larger carbon group, or even to add another carbon to a ring. In this last type of rearrangement, known as a **ring expansion**, five- and six-membered rings are typically formed. The atom that gains a bond (C^+) becomes neutral, and the atom that loses a bond becomes positively charged. To determine whether rearrangement will happen, add H^+ to form the most stable carbocation possible, and then see whether adjacent carbons are more substituted.

1) Hydride Shift

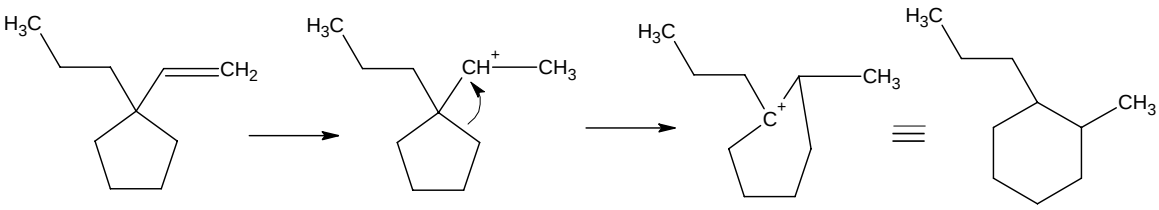




2) Methyl Shift

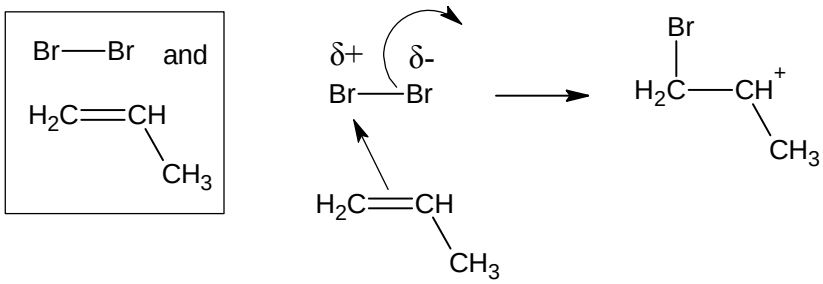


3) Ring Expansion (this is the hardest one!)



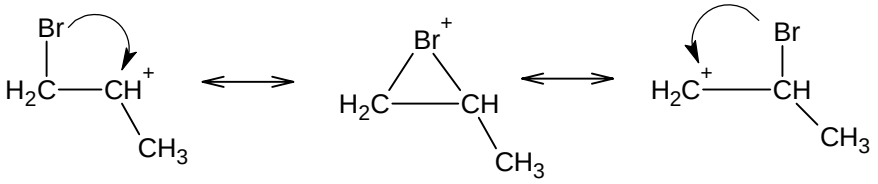
Br_2 and Avoiding Rearrangement

It is possible to add Br_2 to a double bond. This may seem strange, as Br_2 does not have a clear electrophile or nucleophile – the electrons are evenly split by both atoms! Remember that like charges repel. When the pi bond attacks, it pushes the electrons in the Br—Br bond away, creating partially positive (δ+) and partially negative (δ-) sides. The alkene then takes the δ+ atom, separating it from the δ- atom. This type of bond-breaking, in which one atom claims both electrons, is called **heterolytic cleavage**.

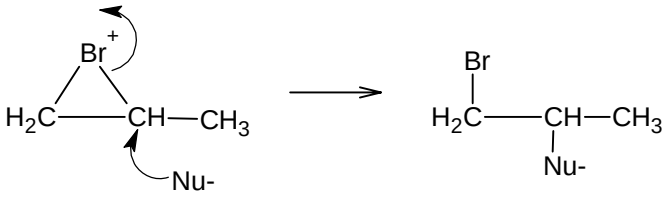


Br is a halogen, meaning that it has seven valence electrons. One of these is lost by the electrophile when the Br-Br bond breaks, but that still leaves six electrons (or three lone

pairs). They are attracted to the C+, and attack it. This forms a triangle intermediate. Although the molecule will go back and forth between linear and triangular shapes, the triangle is the most stable (and thus dominates). This prevents rearrangement by keeping the positive charge away from carbon.



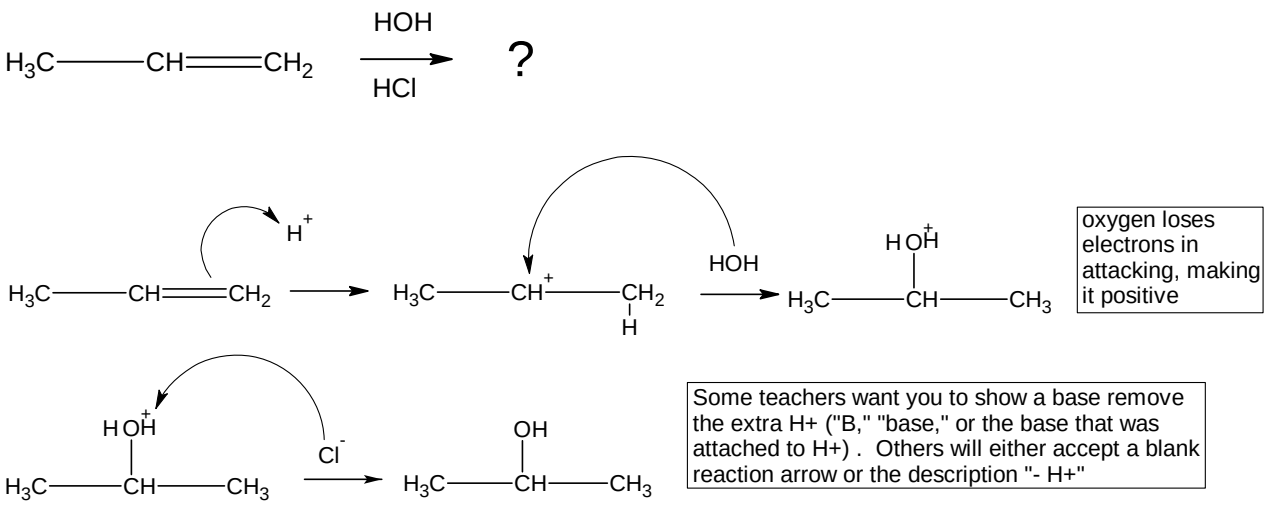
Finally, the nucleophile attacks. If Br_2 is the only nucleophile source in the mixture, then a Br^- (left over from the beginning) will attack the most stable carbocation – in this case, the secondary carbon. If another nucleophile source, such as OH^- or Cl^- is present (often introduced via HOH and NaCl), that nucleophile will typically attack.



Water (HOH) and Alcohols (ROH)

1) With Acid

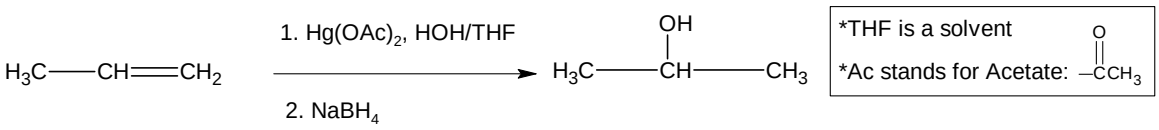
Think back to our review of general chemistry – an acid is a proton (H^+) donor. As such, when an acid is present in our solution, chances are that the donated H^+ will be our electrophile. Commonly used acids include HCl (H^+Cl^-) and H_2SO_4 ($H^+HSO_4^-$). Sometimes, the H^+ is written on its own, rather than as part of a larger compound. These reactions follow the basic reaction mechanism, with the added step of removing an H^+ at the end. Let's figure out the mechanism and major product for this reaction:

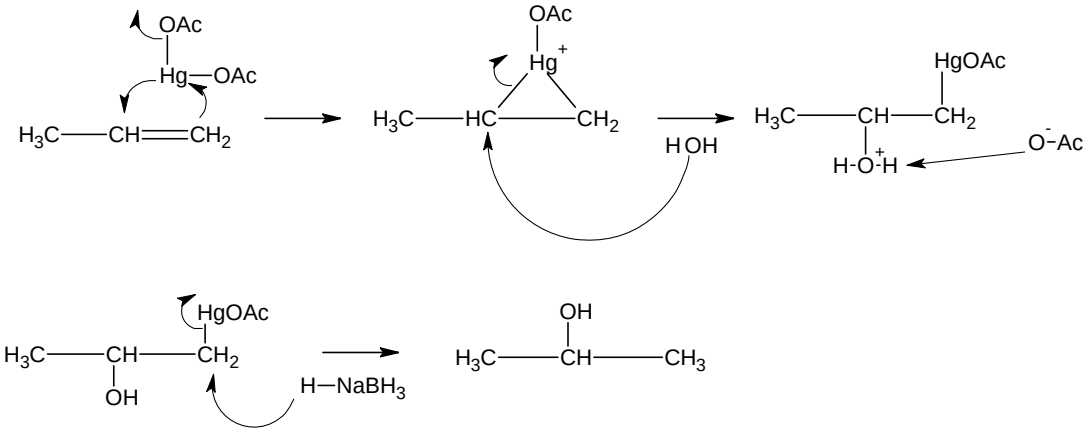


To perform this reaction with an alcohol, simply substitute a carbon group for one of the H's in water!

2) With Mercury: Avoiding Rearrangement

As we saw with HBr, any reaction that follows the basic mechanism risks rearrangement – but, as we saw with Br_2, it is possible to avoid rearrangement by forming a triangle intermediate. Adding water or alcohol with mercury, a process called **oxymercuration** for water and **alkoxymercuration** for alcohols, accomplishes the same thing. Mercury acts as an electrophile at first, and must be replaced with an H. This process is called **reduction**. Overall: oxymercuration-reduction (what a mouth full!). Here is the process, again using water as an example.

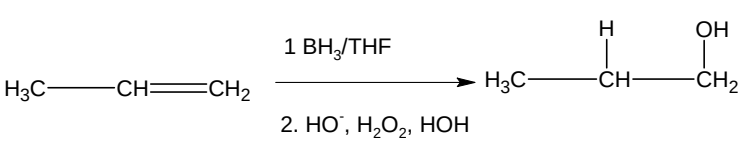




3) With Boron: Anti-Markovnikov!

This last reaction is for water only. Every now and then, we might want to add H to the least substituted carbon. You can think of it as adding water backwards, the wrong way, an unusual way – or in an anti-Markovnikov reaction, if you're feeling fancy. In order to pull this off, we need to find something else to act as an electrophile – and BH_3 is more than willing to do so. This reaction is called **hydroboration/oxidation**.

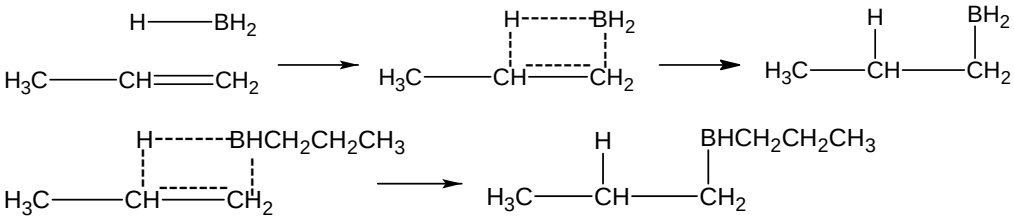
Generally, you will only need to know which reactants to use for this process:

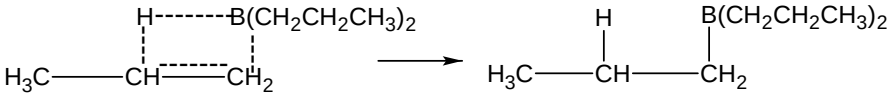


*THF is a solvent

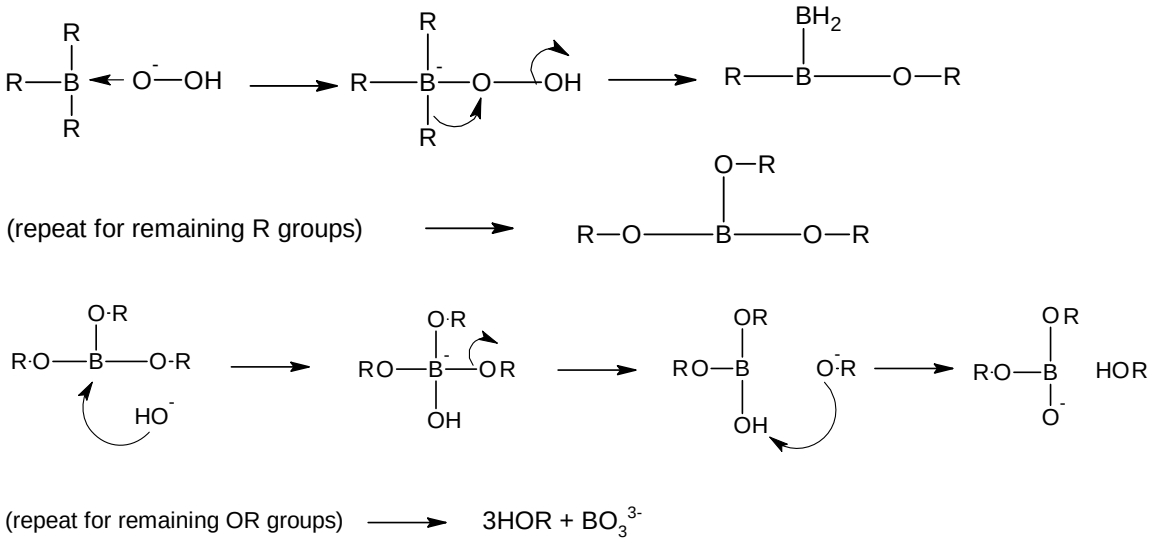
*In step 2, HOH is not always written out. HO^- and H_2O_2 make HOH

Some teachers may want you to know the mechanism. It's long, but manageable. Boron (B) basically acts as an electrophile, and alkenes keep attacking until there isn't any room left. Each time, a ring of partial bonds forms before B and H officially join the molecule.



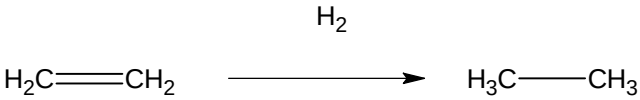


Then oxygen steps in. To save space, we will use 'R' to represent the carbon chains attached to B – feel free to do that during an exam as well, as long as you draw out the final product!



Hydrogen

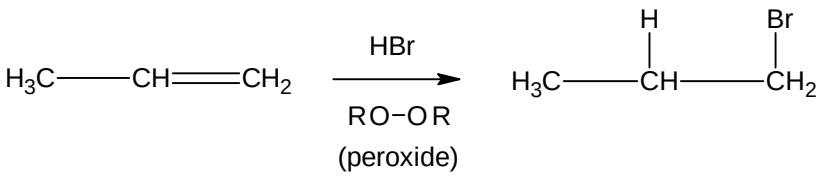
This reduces a double bond to a single bond without adding functional groups. Chances are that you won't need to learn the mechanism for this reaction during the first year of organic chemistry (and the only year, for some of you!), so we will just list the catalysts involved: Pd/C, Pt, Ni



Breaking the Markovnikov Rule with HBr

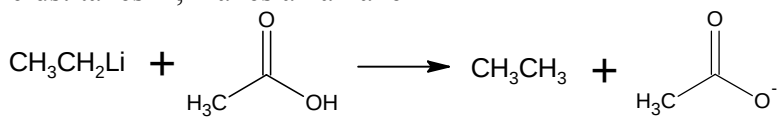
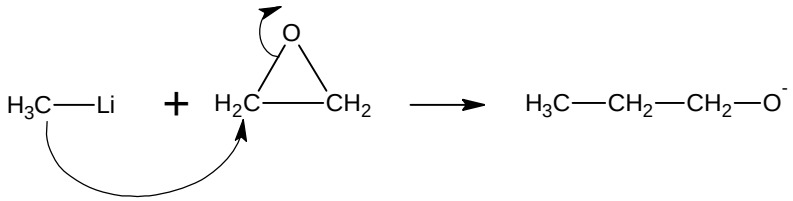
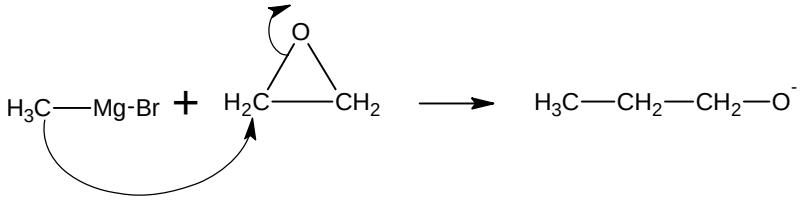
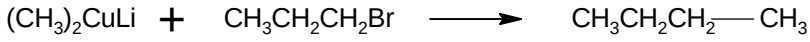
It is possible to add HBr in a way that places the H on the most substituted carbon. The mechanism for this involves radicals, or unpaired electrons. For the time

being, we will just learn which reactants are involved. See section eight for information on radicals, including the mechanism of this reaction.



*See section five for the stereochemistry associated with alkene reactions!

ORGANOMETALLIC COMPOUNDS

Compound	Formation	Reactions
Organolithium: RLi	RBr + Li → R—Li + LiBr (need 2Li per RBr, but it may not be written this way on an exam!)	1) Acids: takes H, makes an alkane  2) Expoxides: opens ring 
Grignard: RMgX	RBr + Mg → RMgBr	Epoxides: opens ring 
Gilliman: R_2CuLi	2RLi + CuI →	Coupling; Replaces a Halogen (similar to S_N) 

	R_2CuLi + LiI	

Glossary

Many textbooks have an extensive glossary that can be helpful when learning new concepts and reviewing for exams. They are a wonderful, but underused resource! This list is limited primarily to the words that appeared in bold in this book.

1,2 addition	see 'direct addition'
1,4 addition	see 'conjugate addition'
Acetal	two OR groups one the same C. formed when alcohols attack aldehydes
Acetylene	simplest alkyne: HC≡≡CH. alkynes are sometimes referred to as substituted acetylenes.
Acid	generally interpreted as 'Bronsted-Lowry acid,' i.e. a proton donor
Acidity	acid strength (determined ability to donate a proton, stability after donating that proton)
Activating substituent	makes a compound more reactive
Acyl	C==O group attached to C and/or H
Acyl halide	C==O attached to a halogen
Alcohol	ROH molecule, an alkyl group attached to an OH
Aldehyde	C==O group attached to one H and one alkyl group
Aldol Addition	first step of the Aldol Condensation
Aldol Condensation	two steps: 1) the α C of a ketone/aldhyde attacks the C==O of another ketone/aldehyde, 2) dehydration
Alkane	HC molecule with exclusively single bonds
Alkene	HC molecule with at least one double bond
Alkoxymercuration	technique for adding an alcohol (ROH) to a double or triple bond without allowing for rearrangement. followed by reduction.
Alkyl groups	see hydrocarbon groups
Alkyl halide	RX molecule, an alkyl group is attached to a halogen
Alkyne	HC molecule with at least one triple bond
Allyl	adjacent to a double bond (either an adjacent C or a substituent attached to it)
Alpha (α) C	adjacent to a C with a functional group
Amide	contain carbonyl groups attached to N
Amine	alkyl group attached to a N-group. Can be primary, secondary, tertiary, or quaternary depending on how many C's are attached to N
Angle strain	the result of unstable bond angles. 3-membered rings have considerable angle strain. 5-membered rings have very little angle strain, and 6-membered rings have none (when in their most stable arrangements)
Anhydride	two C==O groups separated by O
Anion	negatively-charged atom
Anti	substituents are 180° apart from one another
Anti addition	two groups add to opposite sides of a molecule
Anti-aromatic compound	cyclic, planar, contains an even number of pairs of pi electrons. resonance can occur throughout the ring. very unstable

Anti-bonding orbital	higher-energy molecular orbitals, produced by out-of-phase overlap
Anti-Markovnikov Reaction	violates Markovnikov's rule
Aprotic	does not contain protons that it can donate, an aprotic solvent does not have protons that will interact with molecules in the solution
Aromatic compound	cyclic, planar, contains an odd number of pairs of pi electrons. resonance can occur throughout the ring. very stable
Aromatic electrophilic substitution	an electrophile replaces an atom/group in an aromatic compound
Arrhenius Equation	calculates the rate constant of a reaction
Aryl group	benzene or substituted benzene
Asymmetric carbon	chiral carbon, attached to four different groups
Atomic number	the number of protons in an atom
Atomic weight	combined total of protons and neutrons in an atom
Axial	vertical, groups are pointing straight up or straight down
Base	generally interpreted as 'Bronsted-Lowry base,' i.e. a proton accepter
Base peak	in a mass spectrum: represents the most abundant fragment. set at an arbitray value of 100 (relative to the other peaks)
Basicity	base strength (determined by ability to attract a proton, stability after accpeting that proton)
Bending vibration	a bond's angle changes when it is exposed to radiation
Benzyl group	benzene ring and one adjacent C
Benzyne	benzene ring in which one of the double bonds is replaced by a triple bond
Bonding orbital	lower-energy molecular orbitals, produced by in-phase overlap
Bronsted-Lowry acid	proton donor
Bronsted-Lowry base	proton accepter
Carbocation	positively-charged C
Carbonyl	C==O group
Carboxyl group	COOH (a carbonyl and an OH)
Carboxylic acid	RCOOH molecule, an alkyl group attached to a carboxyl group
Carboxylic acid ester	see 'ester'
Catalyst	increases a reaction's speed without being consumed or used up
Cation	positively-charged atom
Chair conformation	most stable conformation for cyclohexane
Chemical shift	in NMR: a measure of each signal's frequency, relative to a reference compound
Chemically equivalent protons	attached to the same C or in symmetrical positions on a molecule. produce the same signal in an NMR graph
Chiral center	molecule attached to four different groups
Cis	pointing in the same direction (both up/towards you or both down/away). in cis double bonds, similar groups are pointing in the same direction.
Claisen Condensation	the α C of an ester attacks the C==O of another ester
Concerted	all-at-once
Condensed structures	written like text, no bonds drawn out
Conformational	bonds are arranged differently due to rotation (e.g. staggered vs. eclipsed)

isomers

Conformations	see 'conformers'
Conformers	different spatial arrangements of individual bonds, determined by rotation. see staggered, eclipsed, and skewed.
Conjugate acid	a base becomes its conjugate acid by accepting a proton
Conjugate addition	electrophilic addition to conjugated double bonds, in which resonance occurs between the electrophile adding and the nucleophile adding. the groups wind up at C1 and C4, if the first C in the conjugated system is labeled C1
Conjugate base	an acid becomes its conjugate base by donating a proton
Conjugated	separated by one single bond
Constitutional isomers	connected differently (e.g. straight-chain vs. branched)
Coupling	reaction of organometallic compounds that creates new C-C bonds
Covalent bonds	bonds formed by sharing electrons. stronger than ionic bonds.
Cumulated	adjacent - not separated by one single bond
Cumulene	contains consecutive double bonds
Cyclic compound	contains a ring
Deactivating substituent	makes a compound less reactive
Debye (D)	units of measurement for dipole moment, 1D = 1 x 10-18esu cm
Degree of unsaturation	total of pi bonds (one pi bond per double bond, two per triple bond) and rings within a molecule
Dehydration	removal of HOH
Dextrorotatory	rotates polarized light in a clockwise direction
Diastereomers	versions of the same chiral molecule that are different, but not enantiomers (e.g. RR and RS). include at least 2 chiral centers
Diastereotopic hydrogens	two H's on the same C - replacing one will produce an S chiral center, replacing the other will produce an R stereocenter. overall results will be 2 diastereomers (there must be another chiral center in the molecule already!)
Dipole moment	a measure of bond polarity determined by multiplying the charge on either atom (*e*) by the distance between them (*d*)
Direct addition	electrophilic addition to conjugated double bonds, in which the electrophile and nucleophile add to the same bond. the groups wind up at C1 and C2, if the first C in the conjugated system is labeled C1
E configuration	in double bonds: high-priority groups are pointing in opposite directions, similar to trans
Eclipsed	least stable arrangement for bonds, in which substituents are lined up with one another
Electron delocalization	see 'resonance'
Electron releasing groups (ERG)	donate electrons to a system or molecule, either through resonance or induction
Electron withdrawing groups (EWG)	pull electrons away from a system or molecule, either through resonance or induction
Electronegativity	tendency of an atom to attract electrons
Electrophile	electron-loving, a molecule or atom that is attracted to negative charges
Electrophilic addition	an electrophile is attacked by the molecule it's being added to. in alkenes, this is followed by a nucleophile attacking the molecule.

Elimination	removal of atoms/groups, creates a double bond
Enamine	double bond (ene) and N-group (amine) attached to the same C
Enantiomeric excess	excess of one enantiomer that is present in a mixture of 2 enantiomers
Enantiomers	chiral molecules that are non-superimposable mirror images of each other. S and R versions of the same molecule are enantiomers.
Enantiotopic hydrogens	two H's on the same C - replacing one will produce an S chiral center, replacing the other will produce an R stereocenter. overall results will be 2 enantiomers.
Endergonic	a reaction that consumes more energy than it releases. will have a positive $\Delta G°$
Endo product	placement for substituents: closer to the longer or less saturated bridge
Endothermic	a reaction that absorbs heat
Enol	one double bond (ene) and one OH group (ol) attached to the same C
Enthalpy (H)	heat, $\Delta H°$ = (heat of the products) – (heat of the reactants)
Entropy (S)	disorder or chaos, increased by going from solid to liquid to gas or by increasing the number of molecules
Epoxide	contains a 3-membered ring with 2C and 1O
ERG	see 'electron releasing groups'
Equatorial	diagonal, groups are slanting upwards or downwards
Ester	RCOOR' molecule in which an alkyl group is attached to a COOR' group (like a carboxyl group with R' instead of H)
Ether	ROR molecule, two alkyl groups with one O between them
EWG	see 'electron withdrawing groups'
Excited state	higher-energy state, electrons may jump up to higher-energy orbitals
Exergonic	a reaction that releases more energy than it consumes. will have a negative $\Delta G°$
Exo product	placement for substituents: closer to the shorter or more saturated bridge
Exothermic	a reaction that releases heat
Fingerprint region	unique to each molecule, it is next to impossible to recognize a molecule simply by looking at its fingerprint region (without the help of a computer!)
First-order reaction	one molecule in the rate-determining step
Formal charge	the charge on an individual atom in a molecule
Functional group	reactive part(s) of a molecule; refers to anything except for saturated alkyl groups
Functional group region	region in an IR spectroscopy chart in which most functional groups appear
Gauche	substituents are 60° apart from one another
Gauche interactions (G)	strain from groups being close together. see section two for instructions on measuring this.
Geminial dihalide	two halogens attached to the same C
Gibbs free energy change ($\Delta G°$)	overall change in energy after a reaction: (free energy of the products) – (free energy of the reactants)
Gillman reagent	R_2CuLi, an organometallic compound containing 2 R-groups, copper, and lithium
Grignard reagent	RMgX, an organometallic compound containing magnesium and a halogen

Ground state	lowest-energy state, all electrons in lowest-energy orbitals
Haloform reaction	the α H's in a methyl ketone/aldehyde are all replaced by halogens. the CX3 group can then be replaced by an OH
Halogen	column 7 in the periodic table: F, Cl, Br, I
Hammond's Postulate	compares the transition state to reactants and products. The transition state (TS) represents the highest-energy point of a reaction. Therefore, the TS is similar to the reactants in reactions that releases energy (exergonic) and similar to the products in reactions that consume energy (endergonic).
Hemiacetal	one OH group and one OR group on the same C. the C is attached to an H and an R-group. formed when an alcohol attacks an aldehyde
Hemiketal	one OH group and one OR group on the same C. the C is attached to an H and an R-group. formed when an alcohol attacks a ketone
Heterocyclic compound	contains a ring that is not exclusively composed of C's (may include an N or O)
Heterolytic cleavage	a bond breaks, with both electrons going to one atom
Highest occupied molecular orbital (HOMO)	highest-energy molecular orbital that contains electrons
HOMO	see 'highest occupied molecular orbital'
Homolytic cleavage	a bond breaks, with one electron going to each atom
Huckel's Rule	aromatic compounds must have (4n + 2) pi electrons in their resonance systems, where n = any integer
Hybrid orbitals	combinations of s and p orbitals that allow molecules to bond in certain ways. sp orbitals, for example, allow C to have two double bonds or one triple and one double bond
Hydrate	C attached to two OH groups, forms when HOH attacks a ketone or aldehyde
Hydride shift	H, along with its bond, moves during a reaction to create a more stable carbocation
Hydroboration	technique for anti-Markovnikov addition of water, in which the H goes to the most substituted C
Hydrocarbon (HC) groups	molecules, or sections of molecules, composed of C and H. often labeled 'R' groups
Imine	contains C==N bond
Infrared spectroscopy	method for identifying molecules that involves exposing them to infrared (IR) radiation and measuring bonds' vibrations
Iniation	first step in a radical substitution reaction: no radicals to radicals
In-phase	orbitals overlap favorably to produce bonding orbitals
Internal alkyne	triple bond is somewhere in the middle of the molecule
Inversion of configuration	stereochemistry changes during a reaction: S becomes R, R becomes S
Ion	charged atom
Ionic bonds	bonds between oppositely-charged atoms. weaker than covalent bonds. bond is based on attraction between ions, not shared electrons.
Isolated	separated by more than one single bond
Isomers	molecules with the same chemical formula that are structurally different. see constitutional, conformational, and stereoisomers.
Isotopes	atoms of the same element that have different numbers of neutrons and,

	therefore, different atomic weights
IUPAC names	scientific names for molecules, based on the rules established by the International Union of Pure and Applied Chemistry
Kekule structures	use lines to represent covalent bonds, may include dots to represent lone pairs
Ketal	two OR groups one the same C. formed when alcohols attack ketones
Keto-enol tautomerism	interconversion of ketone/aldehyde and enol tautomers
Ketone	C==O group attached to two alkyl group
Kinetic control	reactions proceed as quickly as possible, without regard to how stable the products will be
Kinetic product	forms the fastest
Kinetic stability	reactions are kinetically stable when they proceed slowly, and have high energy difference between the reactants and transition states
LCAO	see 'linear combination of atomic orbitals'
LDA	lithium-diisopropyl amide, a very strong base
Leaving group	replaced in a substitution reaction
Levorotatory	rotates polarized light in a counterclockwise direction
Lewis acid	accepts a pair of electrons
Lewis base	donates a pair of electrons
Lewis structure	diagrams in which the valence electrons of an atom are drawn around its chemical symbol
Lindlar's catalyst	stops hydrogenation of an alkyne to form a cis double bond
Linear combination of atomic orbitals (LCAO)	essentially, we need to end with the same number of orbitals we begin with. For C, we begin with 4 orbitals (s p p p), and we need to end with 4 orbitals after hybridization
Lone pairs	pairs of electrons that aren't used in bonding
Lowest occupied molecular orbital (LUMO)	lowest-energy molecular orbital that does not contain electrons
LUMO	see 'lowest unoccupied molecular orbital'
m/z	mass/charge
Major product	most likely to form, either because it is the most stable product (thermodynamic conditions) or the fastest to form (kinetic conditions)
Markovnikov Reaction	obeys Markovnikov's rule
Markovnikov's Rule	in electrophilic addition, H adds to the C with the most H's (the least substituted C).
Mass spectrometry	method for identifying molecules; involves exposing a molecule to an energy beam, which causes it to break into radical and cation fragments. the cations' masses and relative abundance are measured
Mass spectrum	a graph of the relative amounts of each fragment obtained through mass spectroscopy
Meso compound	chiral molecule that is its own mirror image, and has no enantiomer. must include at least 2 chiral centers, each of which is attached to the same groups, and be either RS or SR. has a plane of symmetry, which may or may not be obvious from the picture.
Meta	arrangement of substituents on benzene: 2 groups are 2 C's away from each other
Meta director	substituent on benzene that causes the next atom/group to add to a meta position
Methyl shift	methyl group, along with its bond, moves during a reaction to create a

	more stable carbocation
Minor product	less likely to form, either because it is less stable (thermodynamic control) or forms more slowly than the major product (kinetic control)
Molecular orbitals	formed when the orbitals of different atoms within one molecule overlap
Newman projections	look directly down an individual bond, useful in studying different arrangements that bonds can get into when they rotate
Nodes	regions where we do not find electrons, created by out-of-phase interactions
Non-aromatic compound	neither aromatic nor anti-aromatic
Nonpolar bonds	covalent bonds in which electrons are shared equally (or almost equally) between atoms
Nuclear magnetic resonance spectroscopy (NMR)	method for identifying molecules that involves exposing them to a magnetic field; specific atoms will show signals. 'NMR' usually means 'proton NMR'
Nucleophile	nucleus-loving, a molecule or atom that is attracted to positive charges (the nucleus includes positive-charged protons!). nucleophiles are bases.
Nucleophilic Acyl Substitution (S_NAc)	a nucleophile replaces an atom/group attached to a C==O.
Nucleophilic Aromatic Substitution (S_NAr)	a nucleophile replaces an atom/group in an aromatic compound
Nucleophilic Substitution (S_N)	nucleophile replaces an atom or group
Observed specific rotation	degree to which a sample rotates polarized light
Optical activity	ability of a molecule to rotate polarized light; chiral molecules are optically active
Optical purity	excess of one enantiomer that is present in a mixture of 2 enantiomers
Orbitals	region around the nucleus in which an electron is most like to be present
Organic compounds	contain C
Organometallic compound	contains C and a metal
Ortho	arrangement of substituents on benzene: 2 groups are on adjacent C's
Ortho-para director	substituent on benzene that causes the next atom/group to add to an ortho or para position
Out-of-phase	orbitals overlap unfavorably to produce anti-bonding orbitals
Oxidation	several equivalent terms: losing H; increase in CO, CN, and CX bonds, loss of electrons
Oxymercuration	technique for adding HOH to a double or triple bond without allowing for rearrangement. followed by reduction.
Para	arrangement of substituents on benzene: 2 groups are 3 C's away from each other
Parent chain	longest chain of consecutive carbons in a molecule. used to determine the name of a compound.
Pericyclic	concerted reaction that involves the cyclic rearrangement of electrons (e.g. Diels-Alder)
Phenyl group	benzene ring
Pi bonds	combinations of p orbitals, produce double and triple bonds
pKa	a measure of acid strength - the lower the pKa, the stronger the acid
Polar bonds	covalent bonds in which electrons are not shared equally between atoms.

	these bonds have partially negative and partially positive ends.
Propogation	middle of a radical substitution reaction: radicals to radicals. this is where the radical chain reaction occurs
Pro-R hydrogen	replacing this H with a functional group will produce an R chiral center
Pro-S hydrogen	replacing this H with a functional group will produce an S chiral center
Protecting group	preserve a functional group while a molecule undergoes reactions that would otherwise change it. afterwards, the functional group can be restored by removing the protecting group.
Protic	contains protons that it can donate, a protic solvent had protons that can interact with other molecules in solution
Proton-transfer reactions	acid-base reactions in which one molecule (acid) donates a proton to another (base)
Racemate	equal mixure of 2 different enantiomers
Racemic mixture	see 'racemate'
Radical chain reaction	during propogation, radicals produce new radicals that can start the whole process over again
Radical initiator	substance used to create radicals necessary for a reaction. the initiator does not participate in the reaction.
Radical substitution reactions	one atom or group replaces another through a radical reaction
Rate constant	determines the speed at which reactions proceed (along with the number of molecules in the rate-determining step)
Rate-determining step (RDS)	slowest step of a reaction, determines the rate at which the whole reaction can proceed
Reactivity-selectivity principle	as reactivity increases, selectivity decreases
Rearrangement	H's and C's shift in order to produce a more stable carbocation
Reduction	several equivalent terms: gaining H, replacing a funcitonal group with H, addition of electrons
Regioselectivity	preference for which region a reaction (or a step in a reaction) occurs in. when adding to a double bond, an electrophile may have a preference for a particular C.
Resonance	electrons moving within a molecule, not trapped between 2 atoms
Resonance contributors	different theoretical structures a molecule can acquire through resonance
Retention of configuration	stereochemistry does not change during a reaction: S stays S, R stays R, cis stays cis, trans stays trans
Retrosynthetic analysis	a method of solving synthesis problems that involves working backwards from the product
R-groups	any part of a molecule that isn't drawn out; often represents hydrocarbon groups
Ring expansion	rearrangement in which a C that was outside of a ring becomes part of a ring. most likely to occur when it can create a 5- or 6-membered ring
Ring flip	cyclohexanes can transition between 2 different chair conformations. causes axial groups to become equatorial and equatorial groups to become axial, but does NOT change cis and trans arrangements
Saturated	molecule with exclusively single bonds
Sawhorse projection	lines used to represent all bonds, including C-H
S-cis configuration	cis-arrangement around a single bond. in the Diels-Alder reaction, the

	double bonds in the diene need to be pointing in the same direction
Second-order reaction	two molecules in the rate-determining step
Shielding	in NMR: electrons can get in the way of the magnetic field, which weakens the protons' signals. weaker signals have lower frequencies.
Sigma bonds	combinations of s orbitals, produce single bonds (and the first bond in double and triple bonds)
Skeletal structures	lines indicate C-C bonds, H's are not specifically written out (zig-zag-like structures)
Skewed	somewhere in between staggeed and eclipsed
S_N	see 'nucleophilic substitution'
S_NAc	see 'nucleophilic acyl substitution'
S_NAr	see 'nucleophilic aryl substitution'
Specific rotation	degree to which a pure sample of an enantiomer will rotate polarized light
Staggered	comparatively stable arrangement for bonds, in which substituents and H's are as far apart as possible
Stereochemistry	3D chemistry, the arrangement of molecules in space
Stereoisomers	arranged differently in space, but connected in the same way (e.g. cis vs. trans)
Steric strain	occurs when substituents are close together. in general, groups and atoms like to have as much space to themselves as possible.
Strain	stress on molecules: see angle, steric, and torsional strain
Stretching vibration	a bond's length changes when it is exposed to radiation
Substituent	any group, other than H, that is attached to C
Syn addition	two groups add to the same side of a molecule
Tautomerism	rapid interconversion between tautomers
Tautomers	isomers with different arrangement of bonding electrons, different structures a molecule can take on through tautomerism (e.g. ketone and enol)
Terminal alkyne	triple bond is at the end of the molecule
Termination	end of a radical substitution reaction: radicals to no radicals
Tetrahedral Intermediate	forms when a carbonyl is attacked by a nucleophile. temporarily, the C has four bonds (tetrahedral structure)
Thermodynamic control	reactions produce the most stable products possible
Thermodynamic product	most stable
Thermodynamic stability	reactions produce the most stable products possible
Thioacetal	acetal formed with RSH groups instead of ROH groups
Thioketal	ketal formed with RSH groups instead of ROH groups
Torsional strain	electrons in different bonds (generally bonds to H or substituents) repel each other when they get too close - occurs in eclipsed conformations
Trans	pointing in opposite directions (one up/towards you and one down/away). in trans double bonds, similar groups are pointing in opposite directions.
Unsaturated	molecule with at least one double bond, possibly multiple double/triple bonds.
Valence shell	outermost shell of electrons

Vicinal dihalide	see 'geminal dihalide'
Vinyl	attached to a double bond (either a C in the bond or a substituent attached to it)
Workup	clean-up' that occurs at the end of reactions - separates the products from other materials, may protonate or de-protonate final products
Ylene	molecule in which a double bond could move onto one of its atoms, creating an ylide
Ylide	molecule with opposite charges on adjacent atoms
Z configuration	in double bonds: high-priority groups are pointing in the same direction, similar to cis

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