

The first week of  
January in  
Yellowstone →

-11° F





The first week of  
January on the  
Texas coast →

+70° F





Geminal  
Dihaloalkanes

Vicinal  
Tetrahaloalkanes

Alkynes (DFW)

Carboxylic  
Acids



Aldehydes,  
Ketones

Vicinal  
Diols

Vicinal or Geminal  
Dihaloalkanes (Waco)

Epoxides

Alkenes (Austin)

Alcohols

Halohydrins

Allylic  
Halides

Haloalkanes (S.M., N.B.)

Ethers

Thiols

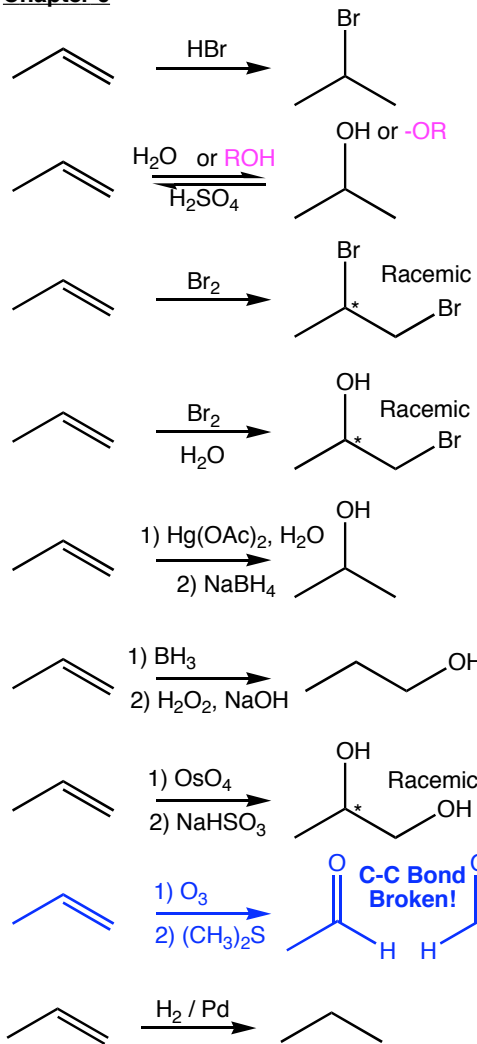


Alkyl  
Sulfonates

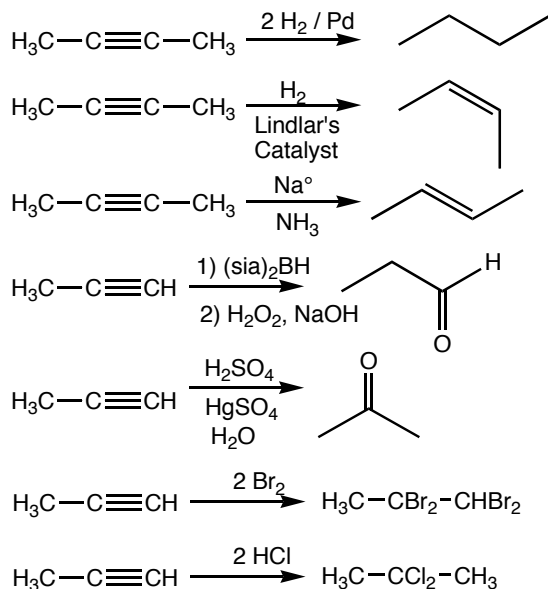
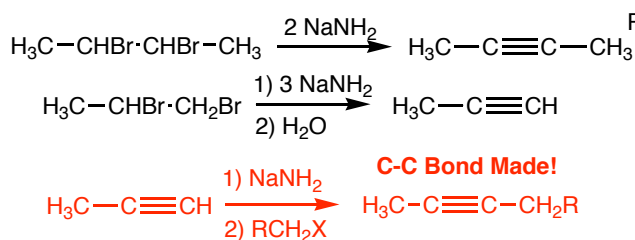
Alkanes (S.A.)



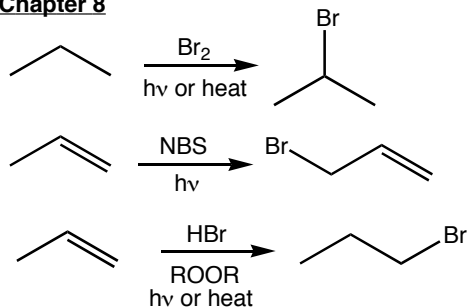
### Chapter 6



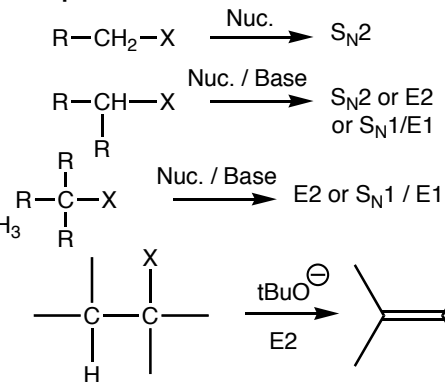
### Chapter 7



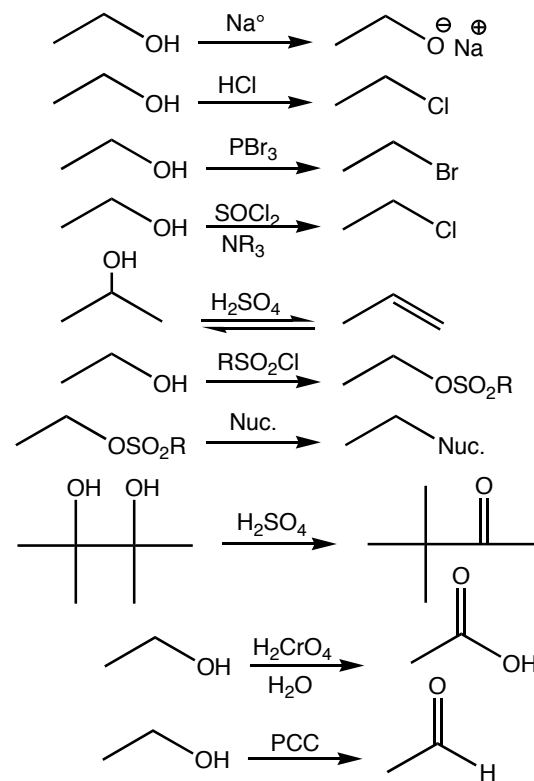
### Chapter 8



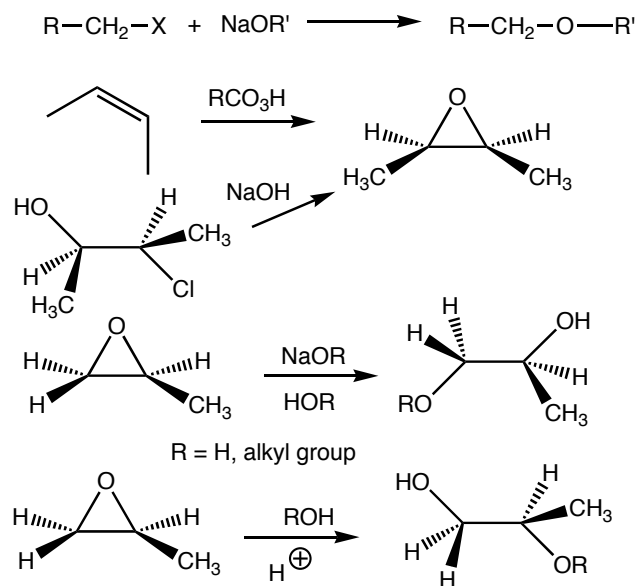
### Chapter 9



### Chapter 10



### Chapter 11

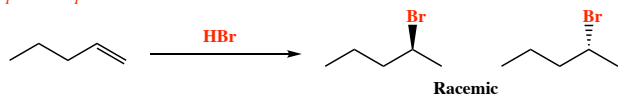


## Chapter 6

### 1) Reaction of Alkenes with HX to Give Haloalkanes

Mechanism Keys: **Carbocation intermediate (rearrangement possible)**, add the proton to make the more stable carbocation **when there is a difference** Regiochemistry: **Markovnikov** Stereochemistry: **Mixed**

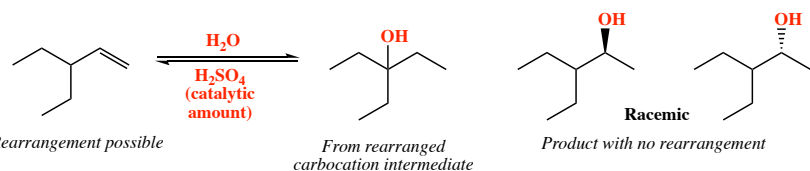
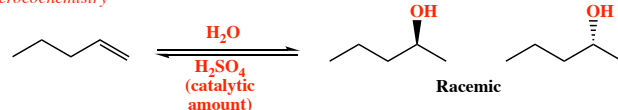
Replace the pi bond with bonds to X on the more substituted carbon and H on the less substituted carbon with mixed stereochemistry



### 2) Acid-Catalyzed Hydration of Alkenes to Give Alcohols

Mechanism Keys: **Carbocation intermediate (rearrangement possible)** add the proton to make the more stable carbocation **when there is a difference** Regiochemistry: **Markovnikov** Stereochemistry: **Mixed**

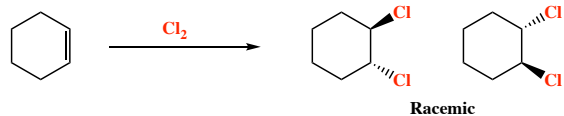
Replace the pi bond with bonds to OH on the more substituted carbon and H on the less substituted carbon with mixed stereochemistry



### 3) Halogenation of Alkenes to Give Vicinal Dihalooalkanes

Mechanism Keys: **Three-membered ring halonium ion intermediate** Regiochemistry: **N/A** Stereochemistry: **Anti**

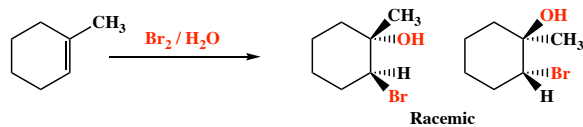
Replace the pi bond with bonds to X with anti stereochemistry only



### 4) Hydrohalogenation of Alkenes to Give Halohydrins

Mechanism Keys: **Three-membered ring halonium ion intermediate**, water will attack the more highly substituted carbon **because that has more positive charge** Regiochemistry: **Markovnikov** Stereochemistry: **Anti**

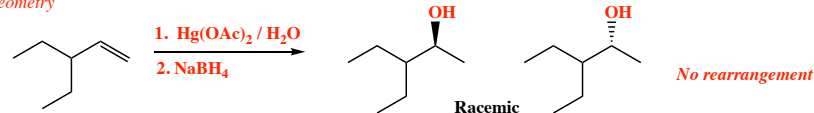
Replace the pi bond with bonds to OH on the more substituted carbon and X on the less substituted carbon with anti stereochemistry only



### 5) Oxymercuration-Reduction of Alkenes to Give Alcohols

Mechanism Keys: **Does not rearrange**, the OH ends up on the more highly substituted carbon Regiochemistry: **Markovnikov** Stereochemistry: **Mixed**

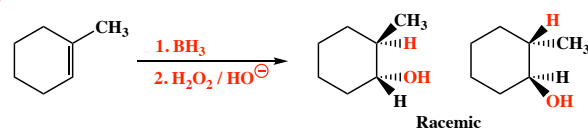
Replace the pi bond with bonds to OH on the more substituted carbon and H on the less substituted carbon with mixed geometry



### 6) Hydroboration-Oxidation of Alkenes to Give Alcohols

Mechanism Keys: **Four-membered ring transition state as H and B atoms add simultaneously to same face of pi bond**, the H atom goes on the more substituted carbon atom Regiochemistry: **non-Markovnikov** Stereochemistry: **Syn**

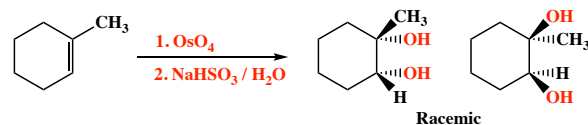
Replace the pi bond with bonds to H on the more substituted carbon and OH on the less substituted carbon with syn geometry only



### 7) Geminal Dihydroxylation of Alkenes to Give Vicinal Diols (the Oszy Osbourne reaction)

Mechanism Keys: **Cyclic osmate ester intermediate makes it so both OH groups are added to the same face of the double bond** Regiochemistry: **N/A** Stereochemistry: **Syn**

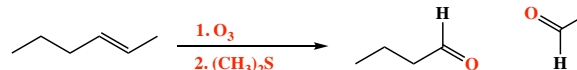
Replace the pi bond with bonds to OH with syn geometry only



### 8) Ozonolysis of Alkenes to Give Aldehydes and Ketones

Mechanism Keys: **Malozonide that then rearranges into an ozonide intermediate**, explaining why the carbon-carbon bond is broken Regiochemistry: **N/A** Stereochemistry: **N/A**

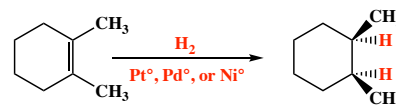
Replace the carbon-carbon double bond with two double bonds to an O atom (C=O) while **BREAKING THE C=C!**



### 9) Hydrogenation of an Alkene to Give Alkanes

Mechanism Keys: **Alkene and H2 adsorb on metal surface**, then new bonds form to both carbon atoms essentially **simultaneously** so the H atoms add to the same face Regiochemistry: **N/A** Stereochemistry: **syn**

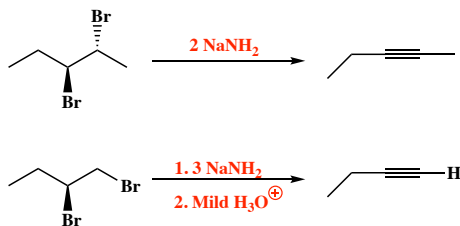
Replace the pi bond with bonds to H with syn geometry only



## Chapter 7

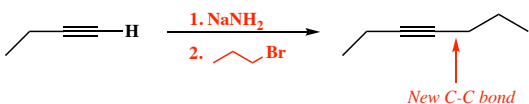
### 10) Reaction of Vicinal Dihalides with Base to Give Alkynes

Mechanism Keys: **Double E2 reaction**. For terminal alkynes, 3 equivalents of base are needed because the terminal H atom is also removed and must be replaced in mild acid. Regiochemistry: N/A Stereochemistry: N/A  
Replace the bonds to X with two pi bonds to give an alkyne



### 11) Reaction of Terminal Alkynes with Base then a Primary Haloalkane to Give an Alkyne with a New C-C Bond

Mechanism Keys: **S<sub>N</sub>2 reaction**. Haloalkane must be primary to avoid E2. Regiochemistry: N/A Stereochemistry: N/A  
Replace the terminal C-H bond with a new C-C bond to the carbon that had the C-X bond.

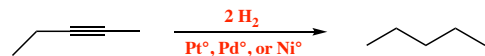


### 12) Hydrogenation of Alkynes to Give Alkanes

Mechanism Keys: Alkyne and H<sub>2</sub> adsorb on metal surface, then new bonds form to both carbon atoms essentially simultaneously. Happens twice and cannot be stopped because alkenes produced as intermediates react faster than alkynes

Regiochemistry: N/A Stereochemistry: N/A

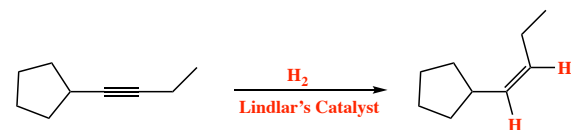
Replace the two pi bonds with four bonds to H atoms



### 13) Reduction of Alkynes with H<sub>2</sub> and Lindlar's Catalyst to Give Z Alkenes

Mechanism Keys: Alkene and H<sub>2</sub> adsorb on metal surface, then new bonds form to both carbon atoms essentially simultaneously. Pb and quinoline poison the catalyst so the reaction stops at a Z alken. Regiochemistry: N/A Stereochemistry: Syn

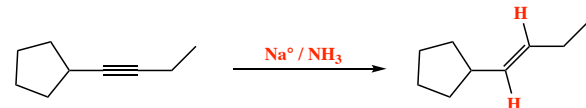
Replace one pi bond of an alkyne with bonds to H atoms to give only a Z product



### 14) Reduction of Alkynes with Na<sup>0</sup> and NH<sub>3</sub> to Give E Alkenes

Mechanism Keys: Radical mechanism, two one-electron transfers from Na<sup>0</sup>, followed by adding two protons from NH<sub>3</sub>, the more stable trans alkene (less steric strain) predominates. Regiochemistry: N/A Stereochemistry: Anti

Replace one pi bond of an alkyne with bonds to H atoms to give only an E product

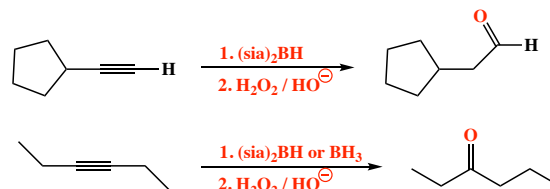


### 15) Hydroboration-Oxidation of Terminal Alkynes to Give Aldehydes (Using the "Antler" Reagent)

Mechanism Keys: Four-membered ring transition state as H and B atoms add to same face of pi bond, enol intermediate followed by enol-keto tautomerization, "antlers" ensure regiochemical control so that H adds to more substituted carbon.

Regiochemistry: non-Markovnikov Stereochemistry: N/A

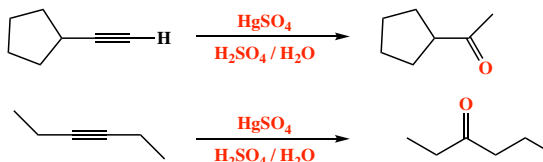
Replace the two pi bonds of a terminal alkyne with double bonds to an O atom to give an aldehyde. When the alkyne is not terminal, a ketone is the product.



### 16) Oxymercuration-Reduction of Alkynes to Ketones

Mechanism Keys: Enol intermediate followed by enol-keto tautomerization. O atom ends up bonded to more substituted carbon. Regiochemistry: Markovnikov Stereochemistry: Mixed

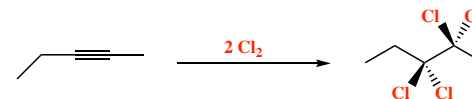
Replace the two pi bonds of an alkyne with double bonds to an O atom to give a ketone. When the alkyne is terminal the internal carbon ends up as the C=O



### 17) Reaction of Alkynes with X<sub>2</sub> to Give Tetrahaloalkanes

Mechanism Keys: X<sub>2</sub> reacts with both pi bonds. Regiochemistry: N/A Stereochemistry: N/A

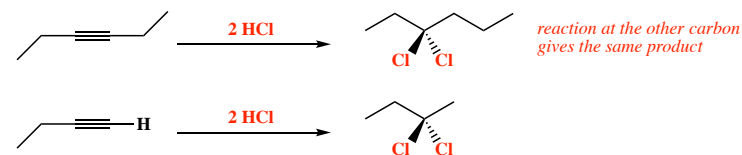
Replace both pi bonds with 2 bonds to X atoms for each carbon atom.



### 18) Reaction of Alkynes with HX to Give Geminal Dihalalkanes

Mechanism Keys: HX reacts with both pi bonds, and both X atoms always end up on the same carbon atom, which is the internal carbon of terminal alkynes. Regiochemistry: Markovnikov Stereochemistry: N/A

Replace both pi bonds on one carbon with 2 bonds to X atoms, and the other carbon with 2 bonds to H. For terminal alkynes, the internal carbon gets the two bonds to X and the terminal carbon gets the two bonds to H

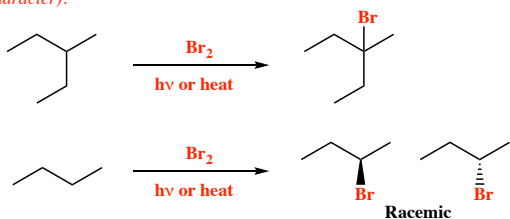


## Chapter 8

### 19) Free Radical Halogenation of Alkanes to Give Haloalkanes

Mechanism Keys: **Free radical chain process, initiation when Br<sub>2</sub> is exposed to light (hv) or heat to give Br radicals that abstracts an H atom on the most substituted carbon during the propagation step** Regiochemistry: **Br ends up on most substituted C atom** Stereochemistry: **N/A**

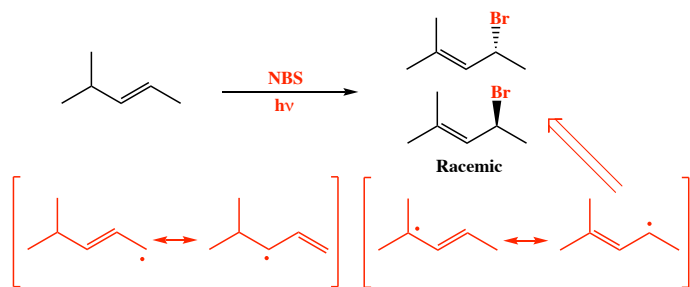
*On the most substituted carbon with an H atom, replace one C-H bond with a C-Br bond. Use Br<sub>2</sub> because it is more selective than Cl<sub>2</sub> (Hammonds postulate: The Br<sub>2</sub> reaction has an endothermic first step so the transition state has more radical character).*



### 20) Allylic Halogenation of Alkenes to Give Haloalkanes

Mechanism Keys: **Free radical chain process, initiation when NBS is exposed to light (hv) to give Br radicals that abstracts an H atom on the carbon adjacent to the C=C to create allylic radical intermediates that add a Br atom to make the most stable product (most highly substituted alkene)** Regiochemistry: **Br ends up on the carbon adjacent to the most stable possible alkene product** Stereochemistry: **N/A**

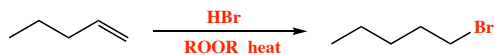
*Analyze both of the contributing structures for both allyl radicals that are possible, consider adding a Br atom to the location of each carbon radical on each contributing structure, analyze each of these possible products and choose the most stable alkene (most substituted alkene) as the predominant product*



### 21) Reaction of Alkenes with HBr in the Presence of H<sub>2</sub>O<sub>2</sub> and Heat to Give Haloalkanes

Mechanism Keys: **Radical mechanism initiated by peroxide and hv or heat, product comes from most stable radical** Regiochemistry: **non-Markovnikov** Stereochemistry: **Mixed**

*Replace the pi bond with bonds to Br on the less substituted carbon and H on the more substituted carbon with mixed geometry*



## Chapter 9

### 22) Substitution vs. Elimination of Haloalkanes to Give Various Substitution Products and Alkenes From Elimination

**S<sub>N</sub>2**: Nucleophile attacks backside of carbon-leaving group bond as the leaving group departs

Regiochemistry: **N/A** Stereochemistry: **INVERSION**

**E2**: Base removes H atom on carbon adjacent to leaving group as the leaving group departs. The H atom being removed and the leaving group must be in an antiperiplanar geometry for reaction to take place

Regiochemistry: **Zaitsev product (most highly substituted alkene)** Stereochemistry: **determined by antiperiplanar transition state requirement**

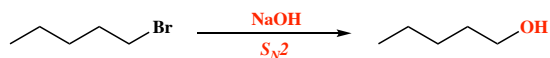
**S<sub>N</sub>1**: Leaving group departs to give carbocation intermediate then nucleophile binds to carbocation

Regiochemistry: **N/A** Stereochemistry: **Scrambled (not quite racemic)**

**E1**: Leaving group departs to give carbocation intermediate that loses a proton on an adjacent carbon to give an alkene

Regiochemistry: **Zaitsev product (most highly substituted alkene)** Stereochemistry: **N/A**

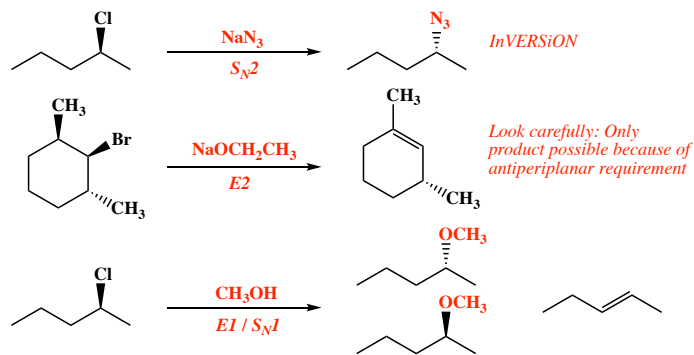
**Primary haloalkane - S<sub>N</sub>2 only (except when KOtBu is the base)**



**Secondary haloalkane - S<sub>N</sub>2 when nucleophile is not strong or very weak base**

**E2 when nucleophile is a strong base**

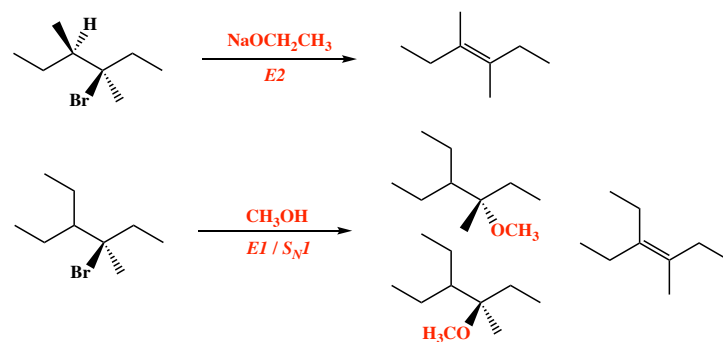
**E1/S<sub>N</sub>1 when nucleophile is a very weak base**



**Tertiary haloalkane - S<sub>N</sub>2 never**

**E2 when nucleophile is anything but a very weak base**

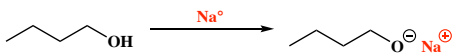
**E1/S<sub>N</sub>1 when nucleophile is a very weak base**



## Chapter 10

### 23) Reaction of Alcohols with Alkali Metals ( $\text{Na}^\ominus$ , $\text{Li}^\ominus$ ) to Give Alkoxides

Mechanism Keys: **Alkali metals react with alcohols to make alkoxides and  $\text{H}_2$**  Regiochemistry: *N/A* Stereochemistry: *N/A*  
Replace the *H* atom of an *OH* group with a negative charge



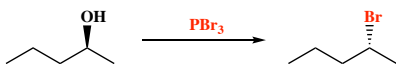
### 24) Reaction of Alcohols with HX to Give Haloalkanes

Mechanism Keys: **Alcohols react with HX by protonating the OH group (thus creating a good leaving group), then the halide anion reacts via an  $\text{S}_{\text{N}}2$  mechanism for primary alcohols and via an  $\text{S}_{\text{N}}1$  mechanism for secondary/tertiary alcohols, to give a haloalkane** Regiochemistry: *N/A* Stereochemistry: **InVERSiON** for  $\text{S}_{\text{N}}2$  and scrambled for  $\text{S}_{\text{N}}1$   
Replace the alcohol *OH* group with *X*. This reaction must be used with tertiary alcohols as  $\text{PBr}_3$  and  $\text{SOCl}_2$  only work with primary and secondary alcohols.



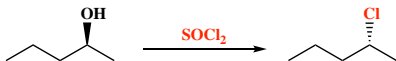
### 25) Reaction of Alcohols with $\text{PBr}_3$ to Give Bromoalkanes

Mechanism Keys: **Primary and secondary alcohols react with  $\text{PBr}_3$  to give an intermediate with an O-P bond (thus creating a good leaving group), that reacts with bromide anion via an  $\text{S}_{\text{N}}2$  mechanism to give a haloalkane** Regiochemistry: *N/A* Stereochemistry: **InVERSiON**  
Replace the alcohol *OH* group with *Br* with **InVERSiON** of any stereochemistry at the carbon that was bonded to the *OH* group of the original alcohol. Primary and secondary alcohols only because tertiary alcohols cannot react via  $\text{S}_{\text{N}}2$ .



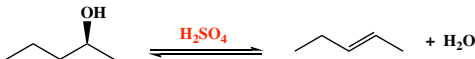
### 26) Reaction of Alcohols with $\text{SOCl}_2$ to Give Chloroalkanes

Mechanism Keys: **Primary and secondary alcohols react with  $\text{SOCl}_2$  to give an intermediate with an O-S bond (thus creating a good leaving group), that reacts with chloride anion via an  $\text{S}_{\text{N}}2$  mechanism to give a haloalkane** Regiochemistry: *N/A* Stereochemistry: **InVERSiON**  
Replace the alcohol *OH* group with *Cl* with **InVERSiON** of any stereochemistry at the carbon that was bonded to the *OH* group of the original alcohol. Primary and secondary alcohols only because tertiary alcohols cannot react via  $\text{S}_{\text{N}}2$ .



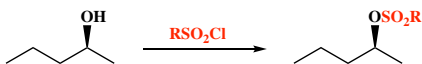
### 27) Reaction of Alcohols with Sulfuric Acid to Give Alkenes

Mechanism Keys: **Alcohols react with  $\text{H}_2\text{SO}_4$  to give alkenes via a carbocation intermediate, in a mechanism that is the exact reverse of hydration of an alkene, this is a reversible equilibrium process (*Le Chatlier*)** Regiochemistry: **Zaitsev** Stereochemistry: *N/A*  
Replace the alcohol *OH* group with a new  $\pi$  bond chosen to make the **Zaitsev** product (most substituted alkene)



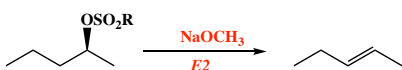
### 28) Reaction of Alcohols with Sulfonyl Chlorides to Give Sulfonyl Esters

Mechanism Keys: **Alcohols react as nucleophiles with sulfonyl chlorides to give sulfonyl esters, a good leaving group** Regiochemistry: *N/A* Stereochemistry: **Retention (not InVERSiON)**  
Replace the alcohol *OH* group with a new sulfonyl ester, without changing the stereochemistry



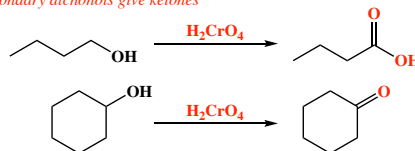
### 29) Reaction of Sulfonyl Esters with Nucleophiles to Give Various Substitution and Elimination Products

Mechanism Keys: **Sulfonyl esters react with nucleophiles and bases analogous to haloalkanes** Regiochemistry: **E2** and **E1** give **Zaitsev** product alkene Stereochemistry:  $\text{S}_{\text{N}}2$  gives **InVERSiON**,  $\text{S}_{\text{N}}1$  scrambled, **E2** gives product based on **antiperiplanar** transition state  
Replace the sulfonyl ester with a nucleophile with **InVERSiON** or carry out an elimination to give the **Zaitsev** alkene (most substituted) based on the same rules used with haloalkanes



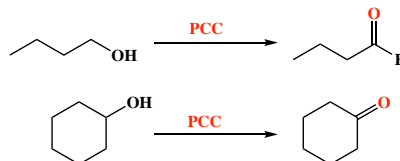
### 30) Reaction of Alcohols with Chromic Acid (Jones Reagent) to Give Carboxylic Acids and Ketones

Mechanism Keys: **The mechanism with primary alcohols involves a chromate ester intermediate then loss of an H atom on the carbon of the original alcohol to give an aldehyde, that adds water then reacts again. Secondary alcohols react once to give a ketone** Regiochemistry: *N/A* Stereochemistry: *N/A*  
Replace every *H* atom on the carbon attached to the *OH* group with bonds to *O* atoms. Primary alcohols give carboxylic acids, secondary alcohols give ketones



### 31) Reaction of Alcohols with PCC (Pyridinium Chlorochromate) to Give Aldehydes and Ketones

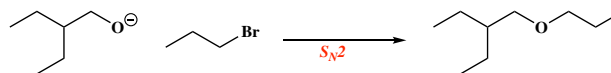
Mechanism Keys: **The mechanism with primary alcohols involves a chromate ester intermediate then loss of an H atom on the carbon of the original alcohol to give an aldehyde, and because there is no water it stops there. Secondary alcohols react once to give a ketone** Regiochemistry: *N/A* Stereochemistry: *N/A*  
Replace an *H* atom on the carbon attached to the *OH* group with a  $\pi$  bond to an *O* atom. Primary alcohols give aldehydes, secondary alcohols give ketones



## Chapter 10

### 32) Reaction of Alkoxides with Primary Haloalkanes to Give Ethers (Williamson Ether Synthesis)

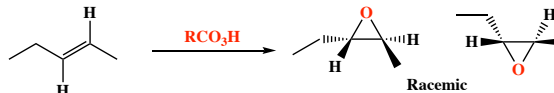
Mechanism Keys: **Alkoxides and primary haloalkanes react via an  $\text{S}_{\text{N}}2$  mechanism. The haloalkane must be primary to avoid **E2**.** Regiochemistry: *N/A* Stereochemistry: *N/A*  
Choose the alkoxide and haloalkane so the haloalkane is primary



### 32) Reaction of Alkenes with Peroxides to Give Epoxides

Mechanism Keys: **Alkenes react with peroxides in a single concerted step to give the epoxide and a carboxylic acid** Regiochemistry: *N/A* Stereochemistry: *N/A*

Create the epoxide from the alkene, making sure to keep the groups consistent (groups that are *cis* on the alkene stay *cis* in the epoxide) and add the *O* atom to both the top and bottom faces of the alkene



### 33) Reaction of Halohydrins with Base to Give Epoxides

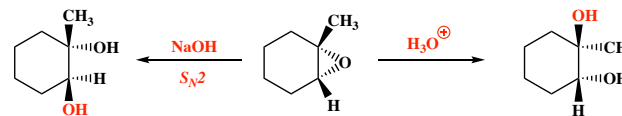
Mechanism Keys: **Halohydrins react with base to deprotonate the OH group and give an alkoxide intermediate, which attacks the backside of the C-X bond in a single step to give the epoxide** Regiochemistry: *N/A* Stereochemistry: *N/A*  
Create the epoxide from the halohydrin by lining up the *OH* group to be antiperiplanar to the *X* before making the new bond from *O* to the carbon of the original C-X bond



### 34) Reaction of Epoxides in Acid or Base to Give Vicinal Diols

Mechanism Keys: **Epoxides react with hydroxide from the backside of the C-O bond via an  $\text{S}_{\text{N}}2$  mechanism at the less-hindered carbon, and in acid epoxides are protonated to give a positively-charged intermediate analogous to the halonium ion intermediate, so water attacks the more substituted carbon** Regiochemistry: **In base**, **OH** adds to less-hindered carbon atom, in **acid** **OH** adds to the more substituted carbon atom Stereochemistry: **Anti** (backside attack on epoxide C-O bond)

Create the vicinal dihalide by adding the *OH* from the less-hindered side in base and more hindered side in acid, inverting the chiral center at the carbon of the attack and retaining stereochemistry at the carbon that keeps the *O* atom of the original epoxide, always giving trans product in both cases



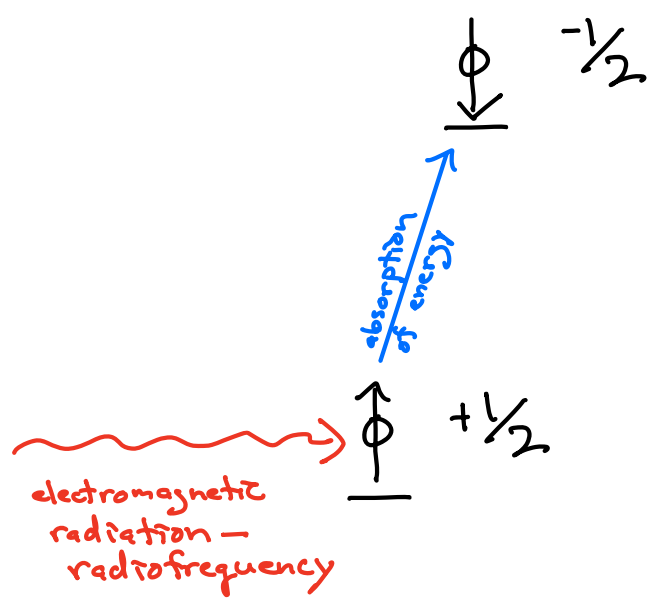
A) Moving charge generates a magnetic field  
Moving magnetic fields cause charges to move

B) Atomic nuclei, just like electrons, can have a quantum mechanical property called "spin"

→ Can be thought of as the positively-charged protons of the atomic nucleus "spinning" to create a small magnetic moment

C)  $^1\text{H} \rightarrow$  spin of  $\frac{1}{2}$

NMR experiment → place sample of a molecule in a very strong magnetic field



The energy absorption/nuclear spin flipping phenomenon is called "Resonance"

The  $^1\text{H}$  nucleus of spin state  $+\frac{1}{2}$  absorbs a quantum of energy of precisely the correct frequency and the nucleus is "excited" to the  $-\frac{1}{2}$  spin state

### In the classic $^1\text{H}$ -Nuclear Magnetic Resonance ( $^1\text{H}$ -NMR) experiment:

1. A sample of the molecule of interest is placed in solvent (the solvent has deuterium atoms in place of H atoms so the solvent molecules will not show up in the spectra).
2. The solution is put in a spinning tube in a very strong magnetic field.
3. The sample is exposed to radiofrequency irradiation and if it is of exactly the right frequency, energy is absorbed and spins flip from  $+1/2$  to  $-1/2$  spin states (the energy absorption/spin flipping process is called resonance).
4. The absorbed energy is plotted on the spectra as a function of wavelength, normalized by using the parts per million (ppm) scale.
5.  $^1\text{H}$  nuclei in different functional groups come into resonance at different and characteristic values of ppm and adjacent  $^1\text{H}$  nuclei split signals in predictable ways, allowing for chemical structures to be determined based on  $^1\text{H}$  NMR spectra.

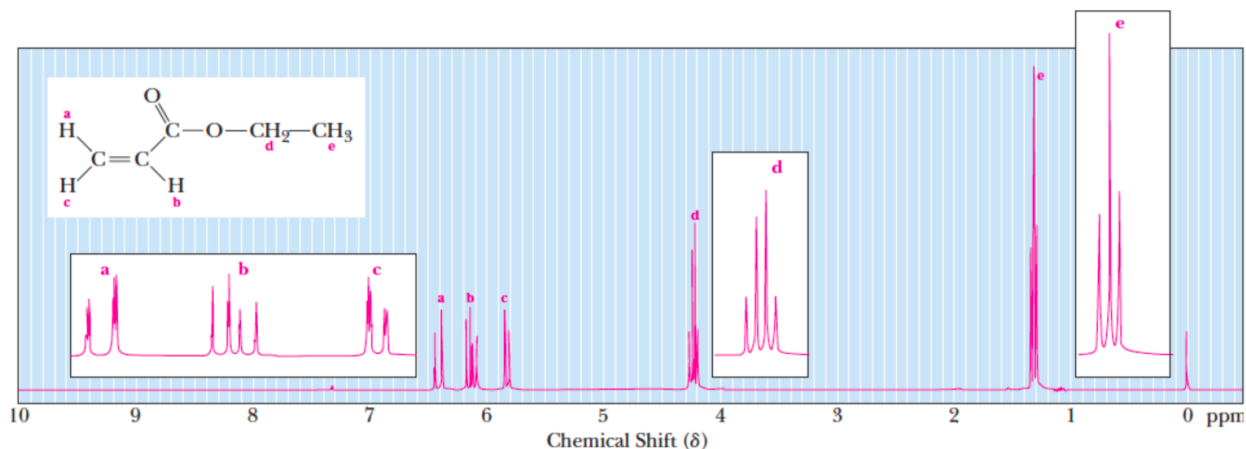
### The old way to carry out an NMR experiment:

1. Scan wavelengths (ex. High to low wavelengths) of radiofrequency electromagnetic radiation.
2. Measure absorbance during the scan and plot the amount of energy absorbed versus wavelength using the normalized ppm scale.
3. This is NOT used any more.

What we did not tell you: After a nuclear spin is flipped back from  $+1/2$  to  $-1/2$ , it will relax back to the  $+1/2$  spin state and EMIT a photon of the same wavelength it absorbed in the first place.

### How modern NMR works:

1. The sample is irradiated with all wavelengths simultaneously with a short blast. All of the  $^1\text{H}$  spins are flipped at once.
2. The sample is monitored for emitted photons as the  $^1\text{H}$  nuclear spins “relax” back to the  $+1/2$  spin state.
3. The emitted photons are analyzed using a technique called Fourier Transform (FT) to extract frequency and intensity information.
4. The frequency and intensity information is plotted on the ppm scale.
5. This process is repeated hundreds or thousands of times with the same sample to dramatically improve signal-to-noise.



**Figure 13.21**  
300 MHz  $^1\text{H}$ -NMR spectrum of ethyl propenoate.

**MRI** – ~~Nuclear~~ Magnetic Resonance Imaging – Produces a 3-d image inside the body.

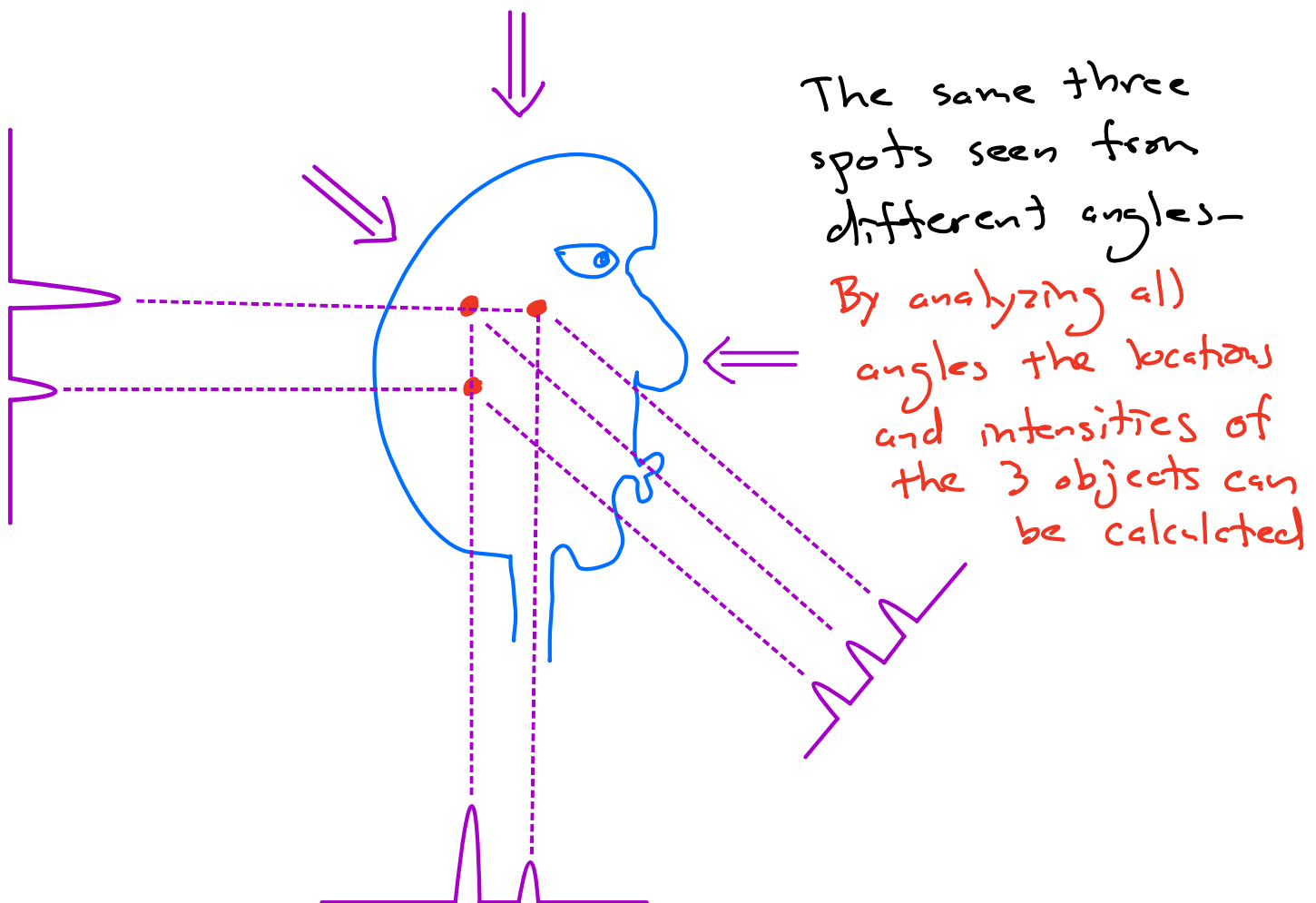
**MRI** is similar in approach, but complementary to, a CAT scan, which uses X-rays for imaging.

**MRI** is therefore safer than a CAT scan (no X-rays or other damaging radiation is used). Radiofrequency electromagnetic radiation does not cause DNA damage or any other kind of damage.

**MRI** primarily visualizes soft-tissue and especially cancer tumors while a CAT scan primarily visualizes bones or Calcium based dyes drunk to visualize the digestive tract.

**MRI** uses the same principles and NMR.

- 1) The patient is placed in a very strong magnetic field. Creating this very strong magnetic field is technically very demanding, explaining MRI machines are so expensive (~ 0.5 – 1.5 \$ million)
- 2) The patient is irradiated with radiofrequency electromagnetic radiation.
- 3) The flipping (resonance) of  $1H$  nuclear spins is monitored – Actually emitted photons are measured using the FT method.
- 4) Magnetic field gradients are used to gain imaging information. The magnetic field gradients are rotated around a central point and measurements are taken at each angle around  $360^\circ$  to gain 2-dimensional information. This technique is called **tomography**.



The overall **MRI** imaging approach involves looking at each 2-dimensional slice.

Each slice is added to give a 3-dimensional stack (analogous to stacking DVD's or CD's).

Each slice is shaded to indicate differences in the amount of  $^1\text{H}$  atoms in different areas/tissues.

Water and fat have the highest density of  $^1\text{H}$  atoms, so these are primarily being monitored in an **MRI** image.

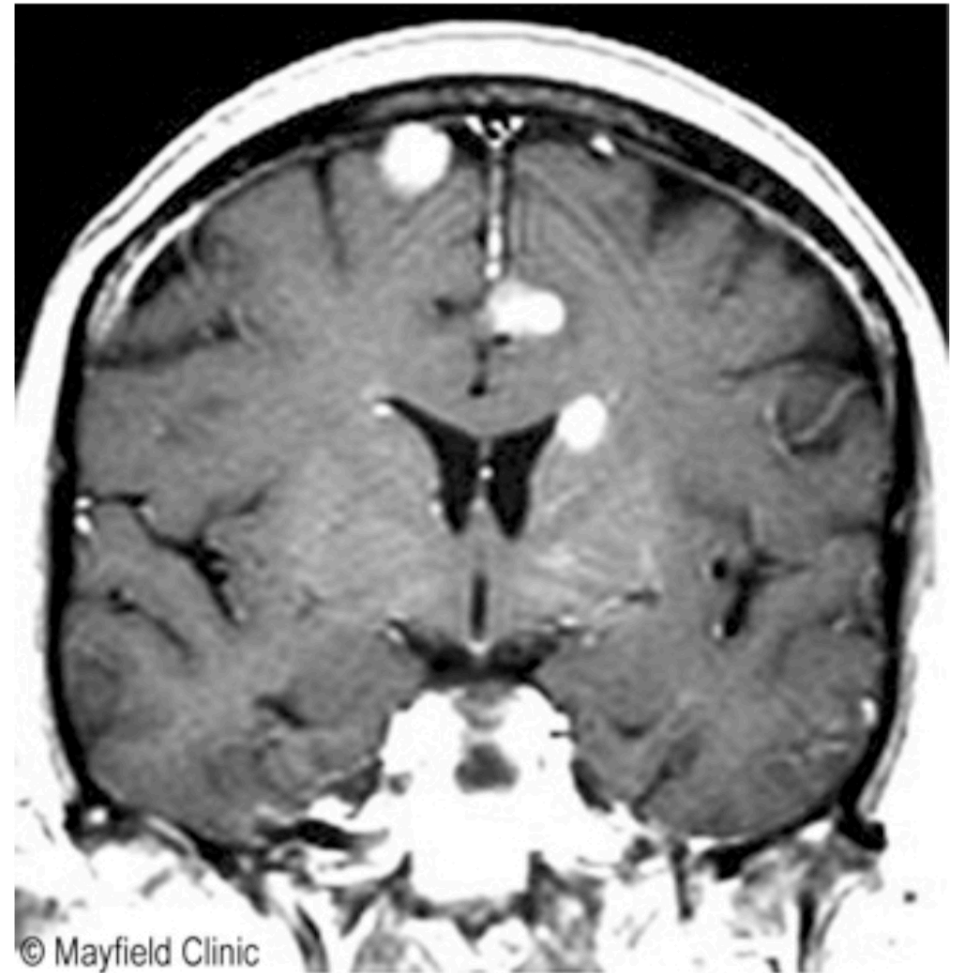
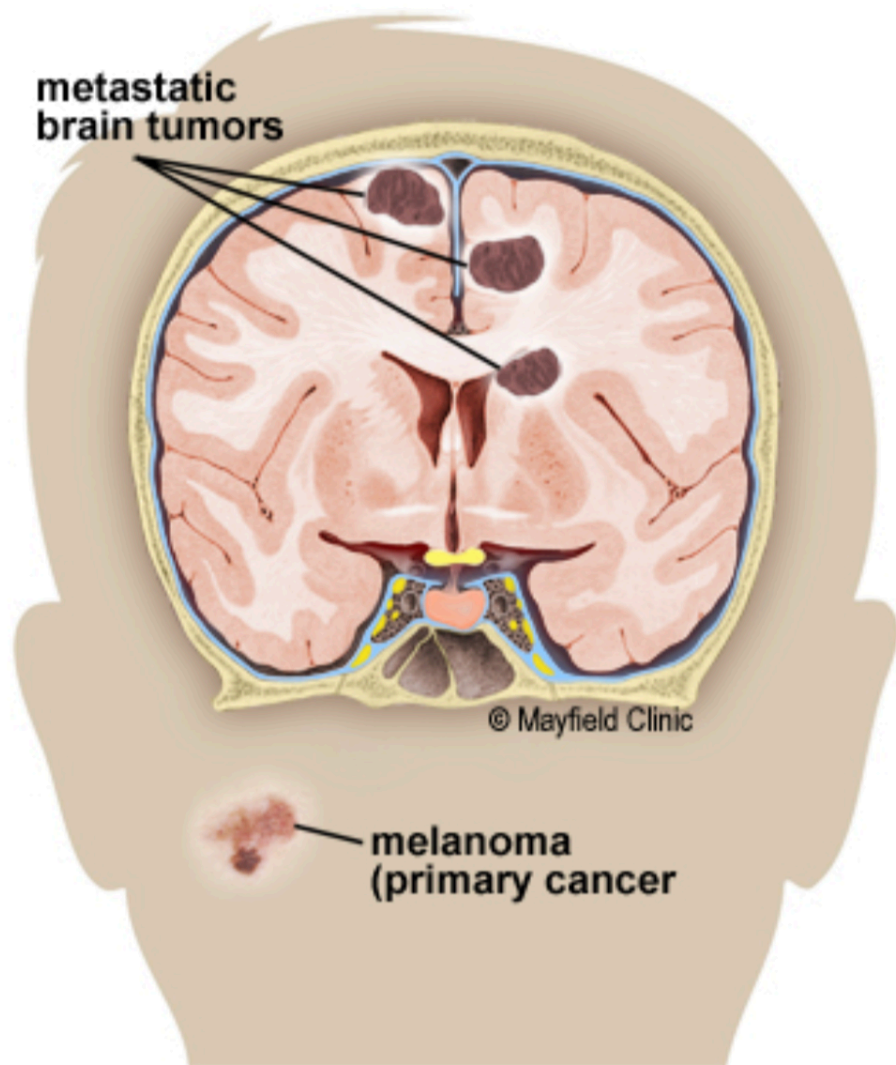
The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on **the same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of H atoms by radio frequency irradiation** when a patient is placed in **a strong magnetic field**. **Magnetic field gradients are used to gain imaging information**, and rotation of the gradient around the center of the object gives imaging in an entire plane (i.e. slice inside patient). In an MRI image, you are looking at **individual slices that when stacked make up the three-dimensional image of relative amounts of H atoms**, especially the H atoms from **water and fat, in the different tissues** [Memorize the preceding passage, as it will be worth 14 points on the next midterm. No I am not kidding, I just gave you 14 points right there.]



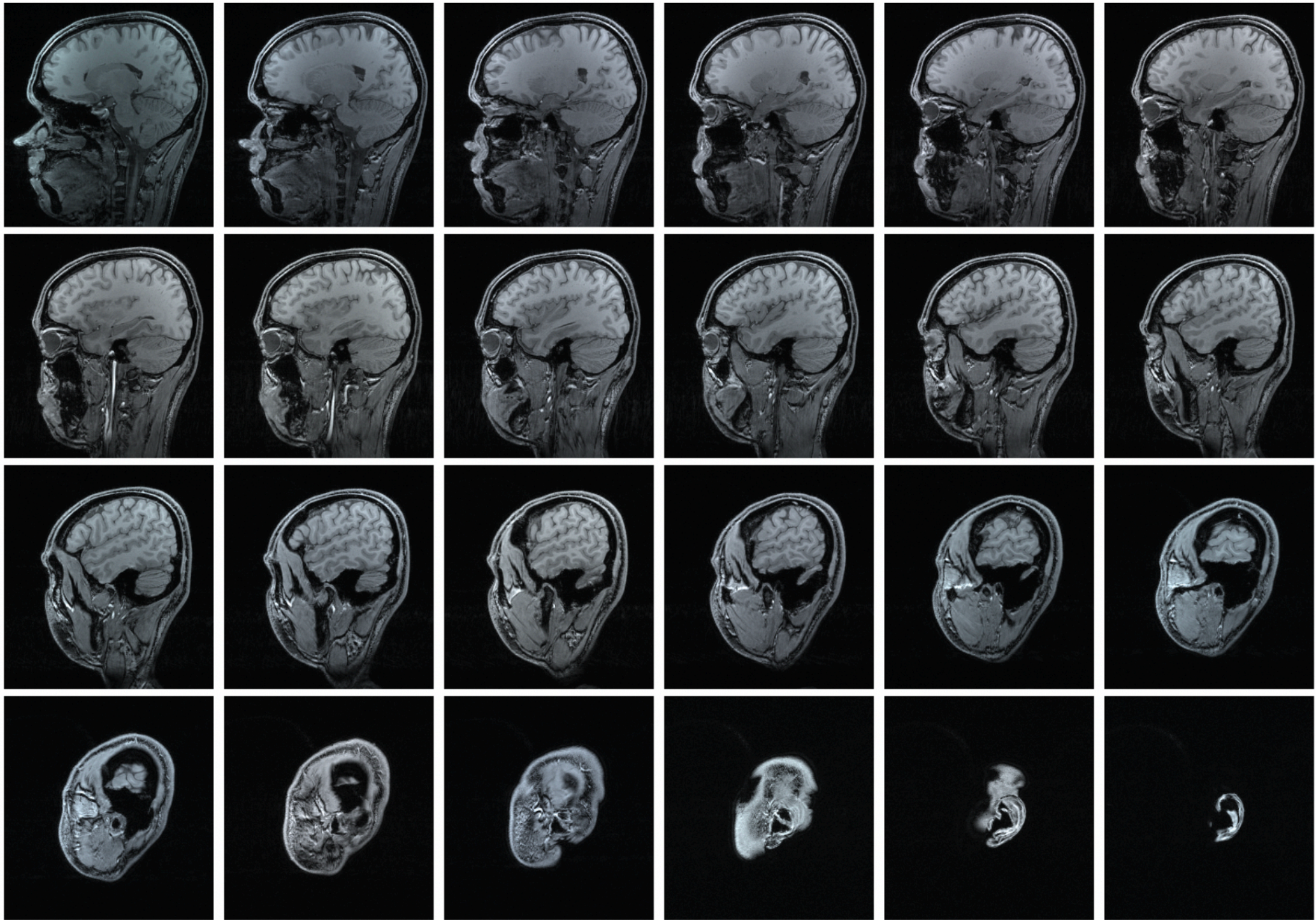


The popular medical diagnostic technique of magnetic resonance imaging (MRI) is based on the same principles as NMR, namely the flipping (i.e. resonance) of nuclear spins of H atoms by radio frequency irradiation when a patient is placed in a strong magnetic field. Magnetic field gradients are used to gain imaging information, and rotation of the gradient around the center of the object gives imaging in an entire plane (i.e. slice inside patient). In an MRI image, you are looking at individual slices that when stacked make up the three-dimensional image of relative amounts of H atoms, especially the H atoms from water and fat, in the different tissues.





**Figure 1. Illustration and MRI of multiple metastatic brain tumors that have spread from the melanoma skin cancer on the face.**



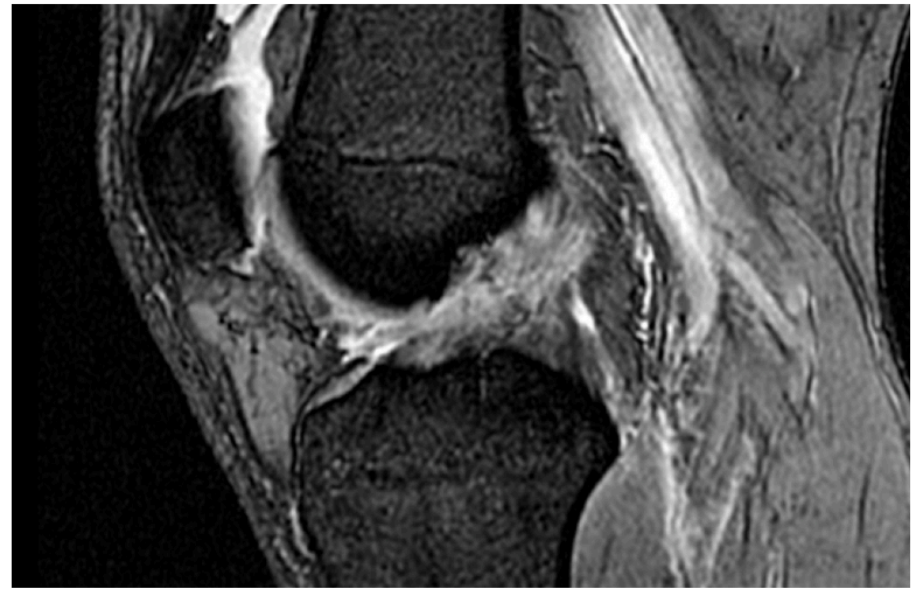
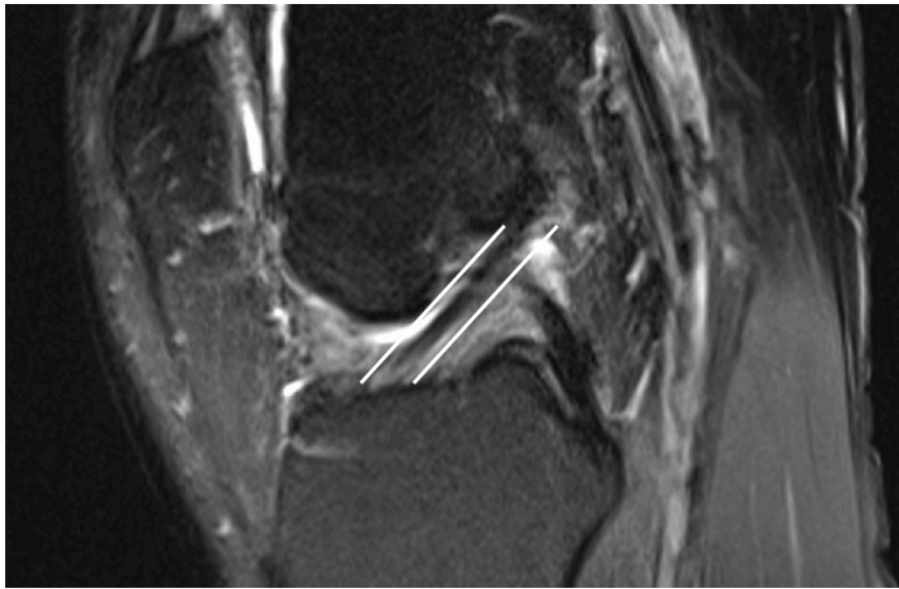


Image 13-16: MRI images of a normal ACL (between white lines), ruptured ACL (ligament not clearly visible), bone marrow oedema (white arrows) and anterior tibial translation.

**Organic Chemistry is the study of carbon-containing molecules. This class has two points.**

*The first point of the class is to understand the organic chemistry of living systems. We will teach you how to think about and understand the most amazing molecules on the planet!!*

You will learn how MRI scans work. 1/14/26

You will learn the basic principles of pharmaceutical science and how many drugs work.

You will learn about the special bond that holds carbohydrates such as glucose in six-membered rings, connects carbohydrate monomers together to make complex carbohydrate structures and is critical to DNA and RNA structure.

You will learn how soap is made from animal fat and how it works to keep us clean.

You will learn the important structural reason proteins, the most important molecular machines in our bodies, can support the chemistry of life.

You will learn how important antibiotics like penicillins work, including ones that make stable covalent bonds as part of their mode of action.

You will learn why carrots are orange and tomatoes are red.

You will learn the very cool reason that the DNA and RNA bases are entirely flat so they can stack in the double helix structure.

You will learn how energy drinks work.

You will learn even more about why fentanyl is such a devastating part of the opioid problem and how Naloxone is an antidote for a fentanyl overdose.

You will learn even more details about why Magic Johnson is still alive, decades after contracting HIV, and how the same strategy is being used to fight COVID.

You will learn about the surprising chemical reason the Pfizer and Moderna mRNA vaccines elicit strong immune responses.

*The second point of organic chemistry is the synthesis of complex molecules from simpler ones by making and breaking specific bonds, especially carbon-carbon bonds.*

You will learn how carbon-metal bonds lead to new carbon-carbon bonds.

You will learn how most reactions of carbonyl compounds involve only the four common mechanistic elements operating in only a few common patterns.

You will learn how, by simply adding a catalytic amount of base like  $\text{HO}^-$  to aldehydes or ketones, you can make new carbon-carbon bonds, giving complicated and useful products.

You will learn a reaction that can convert vinegar and vodka into a common solvent.

You will learn why molecules with six-membered rings and alternating double bonds are stable.

You will learn a reaction that can turn model airplane glue into a powerful explosive.

Most important, you will develop powerful critical thinking skills:

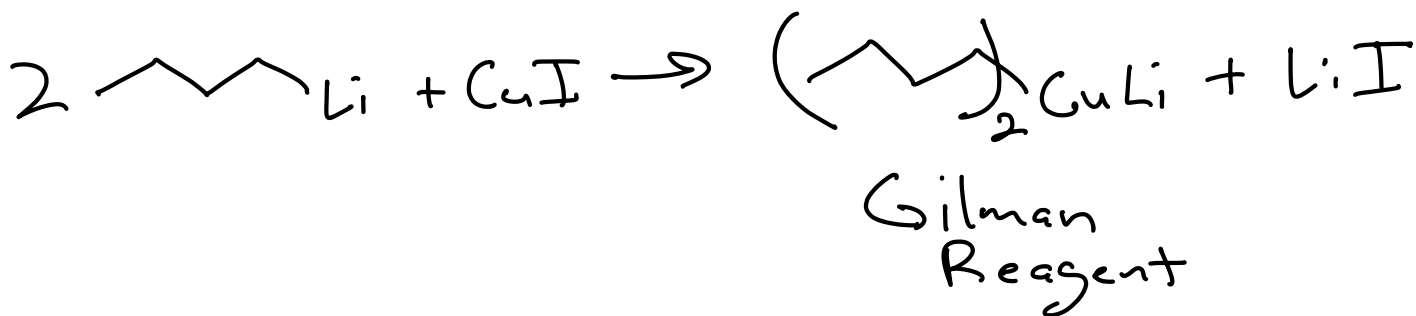
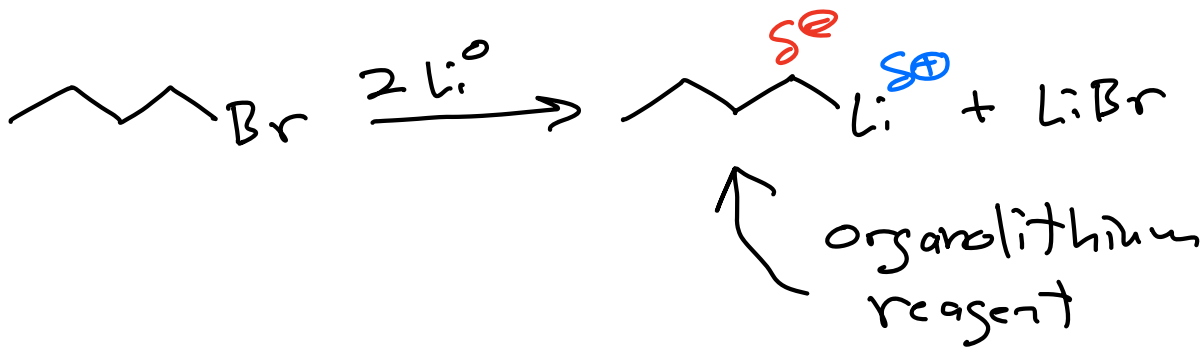
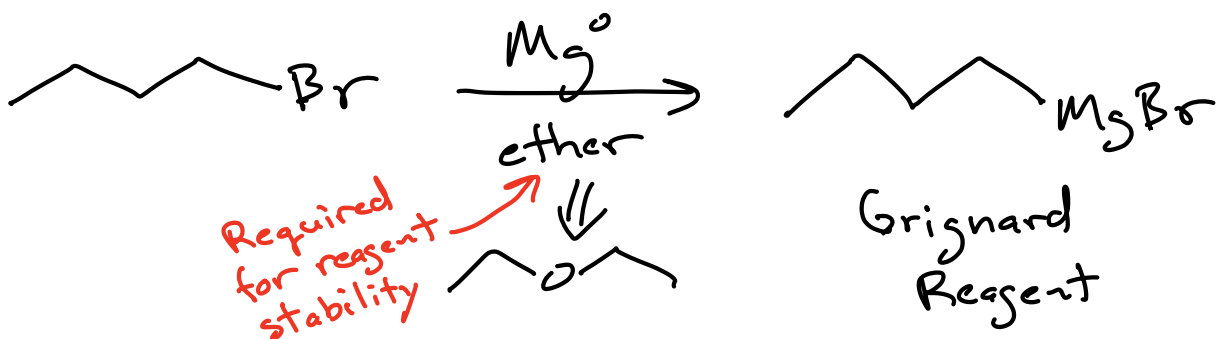
1. You will learn how to look at a molecule and accurately predict which atoms will react to make new bonds, and which bonds will break during reactions.
2. You will learn how to analyze a complex molecule's structure so that you can predict ways to make it via multiple reactions starting with less complex starting molecules.

# Preparation of Organometallic Reagents

C-metal bonds are more ionic than pure covalent bonds like C-C bonds

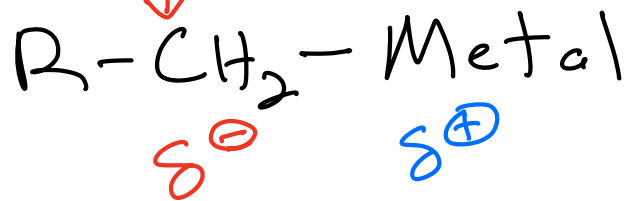
C-metal bond!

Prepared from haloalkanes



You are not responsible for these mechanisms!

More electronegative



The C-metal bond is polarized so the majority of electron density is on C.

⇒ The carbon atom of organometallic reagents is nucleophilic!

The electron density of the C-metal bond acts as a source for an arrow!

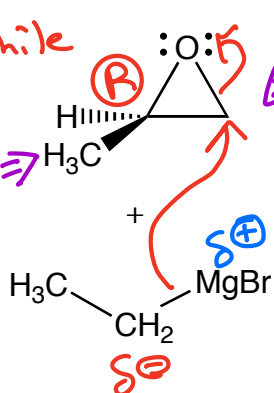


Organolithium and Gilman reagents react the same as Grignard reagents with epoxides

### Grignard Reagent Reacting with an Epoxide

Electrophile

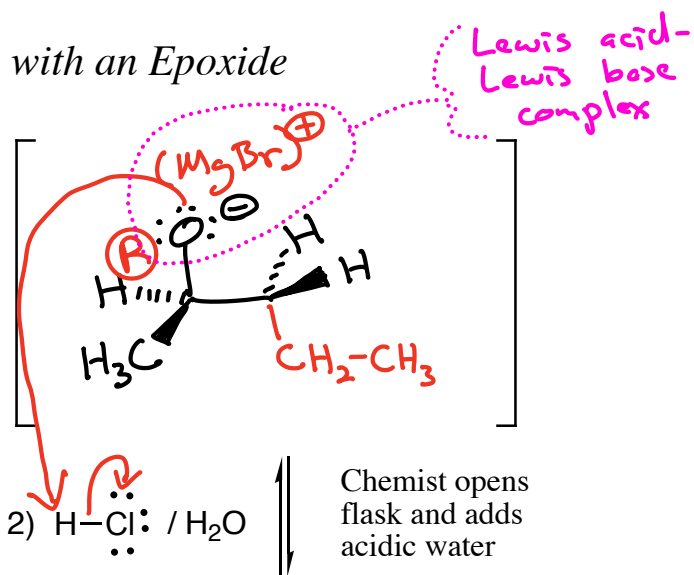
Methyl group blocks reaction on this side (steric strain)



Nucleophile

Less hindered side so reaction happens on this side

Make a bond



Key Recognition Element (KRE):

There is a new C-C bond that is two carbons from the -OH group

