



ScienceGuyz

CHEM 2212

First Semester

Organic Chemistry Refresher

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- General Chemistry 2 - CHEM 1212
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- Physics 2 – PHYS 1112
- Organic Chemistry 1 - CHEM 2211
- Organic Chemistry 2 - CHEM 2212
- Biology 1 – BIOL 1107

For hours of operation, important dates and other info, check our regularly updated website:

www.scienceguyz.com

Introduction:

Welcome to your second semester of Organic Chemistry! This packet reviews the most important concepts from the first semester that you will likely see again in the course. This is by no means a comprehensive review of every topic in your first semester, but it is a great refresher of some useful naming rules, structural representations, and reactions. We encourage you to try this packet without the video to see what you recall, then check your answers! Happy studying.

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Nomenclature Rules from Organic 1

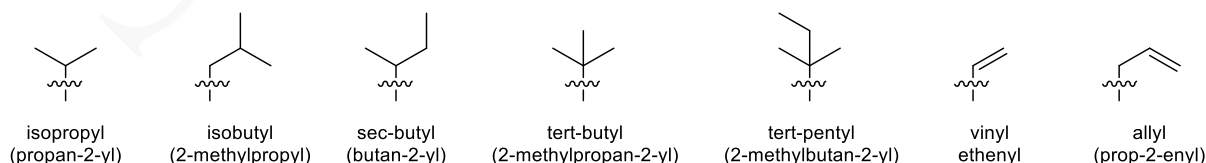
I. To Name a Compound:

- Determine if a priority group (alcohol) is present. Priority groups are listed at the end of the parent chain name.
- Find the longest continual chain of carbons that includes the priority group, if one is present.
 - If there is no priority group, identify the longest continual chain of carbons.
 - If a cyclic ring is present, it must be the parent chain, unless an alcohol is present on another chain.
 - If there are multiple chains of equal length, choose the chain with the greatest number of substituents.
- Number the longest chain such that the priority group has the lowest locant.
 - If there is no priority group, number the chain such that the substituents receive the lowest possible locant.
 - If you can number in either direction and the locants are the same, pick the direction that gives the first alphabetized substituent the lower locant.
- Identify and name the substituents with a locant in front, denoting where the substituent falls on the parent chain.
 - If there are multiple substituents of the same type, aggregate them together and include a prefix denoting the number, along with their locants (ex. 2,2,3-trimethyl).
- Assemble the name by alphabetizing the substituents, then adding the parent chain name, then the priority group at the end (if there is one).
 - Never alphabetize by prefixes (di, tri, etc.) unless the prefix is inside the parentheses of a complex substituent.
- Any stereochemistry present (R/S or E/Z) should be placed in front of the name inside parentheses.
 - If there is only one stereocenter of a type (ex. one chiral center), no locant is necessary.

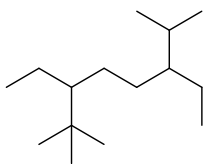
IUPAC Name Break Down:

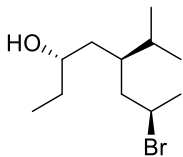
Stereochemistry	Substituents	Parent Chain	Saturation	Priority Group
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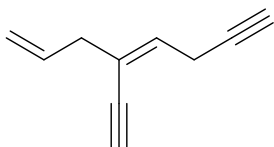
Complex Substituents with Common Names

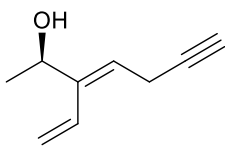


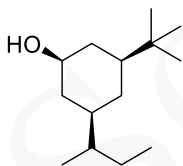
Example: Provide the IUPAC name for each of the following compounds.

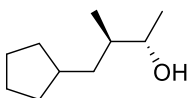






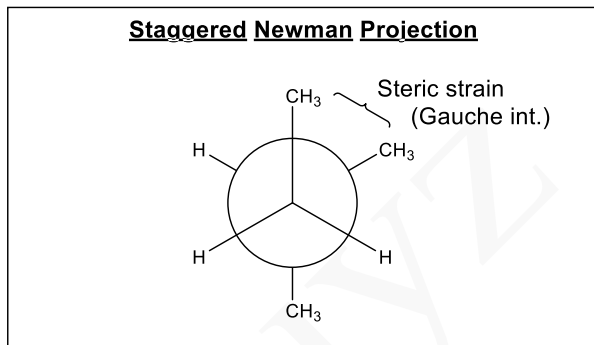
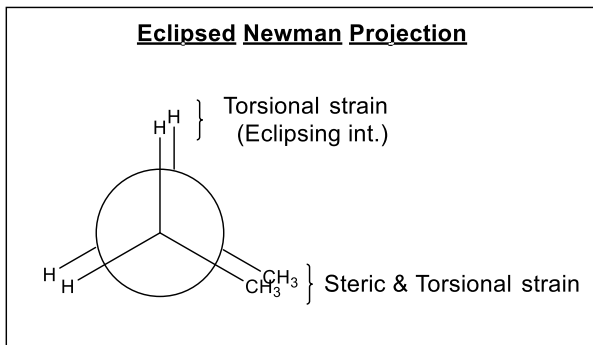




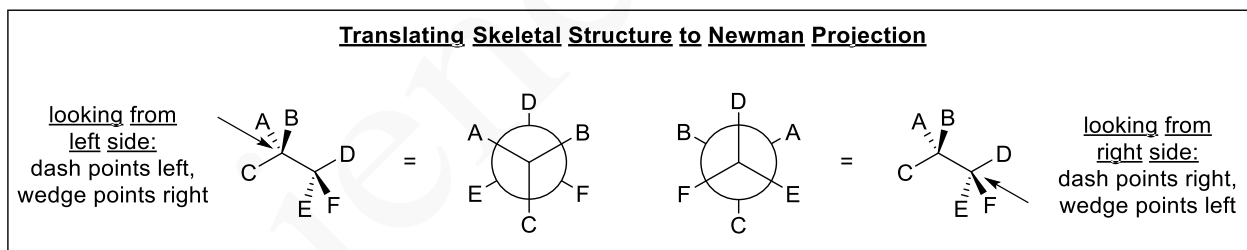
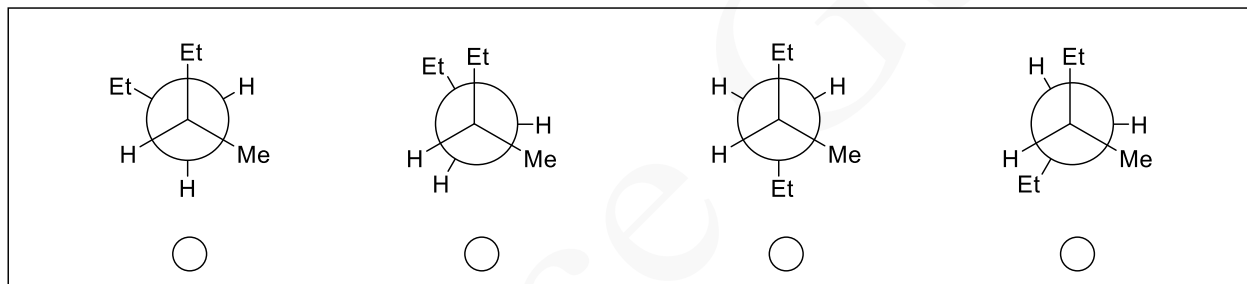


Structural Representations: Newman Projections

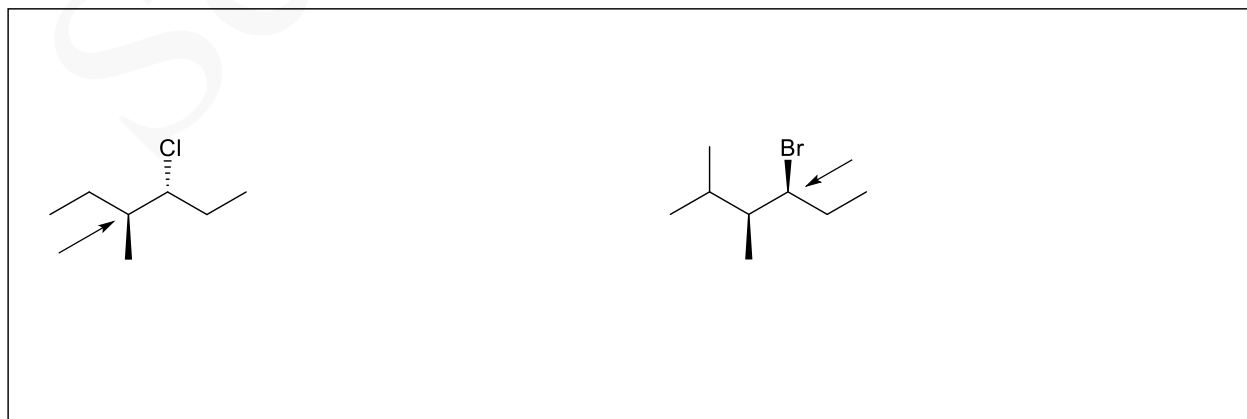
- I. **Newman Projections:** method of visualizing single bond rotation.
 - a. **Staggered Conformation:** more stable projection; places atoms/groups 60° apart.
 - b. **Eclipsed Conformation:** less stable projection due to overlapping bonds.



Example: Which projection represents the most stable conformation of 3-methylhexane?



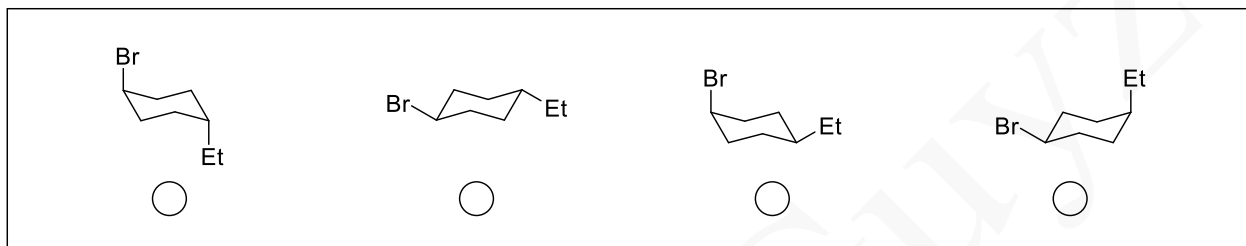
Example: Translate the following skeletal structures into Newman projections.



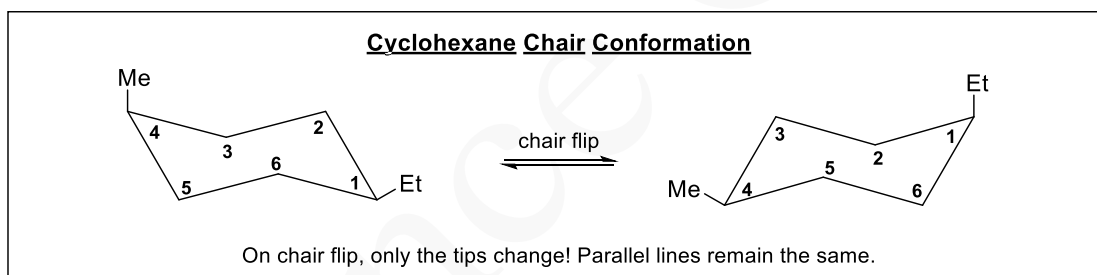
Structural Representations: Chair Conformation

- I. **Chair Conformation:** the most stable conformation of cyclohexane; minimizes all angle and torsional strain.
- Axial Bonds:** point straight up or straight down; give rise to 1,3-diaxial interactions (steric strain)
 - Equatorial Bonds:** point outwards and up or outwards and down (slanted); preferred bond for bulky substituents

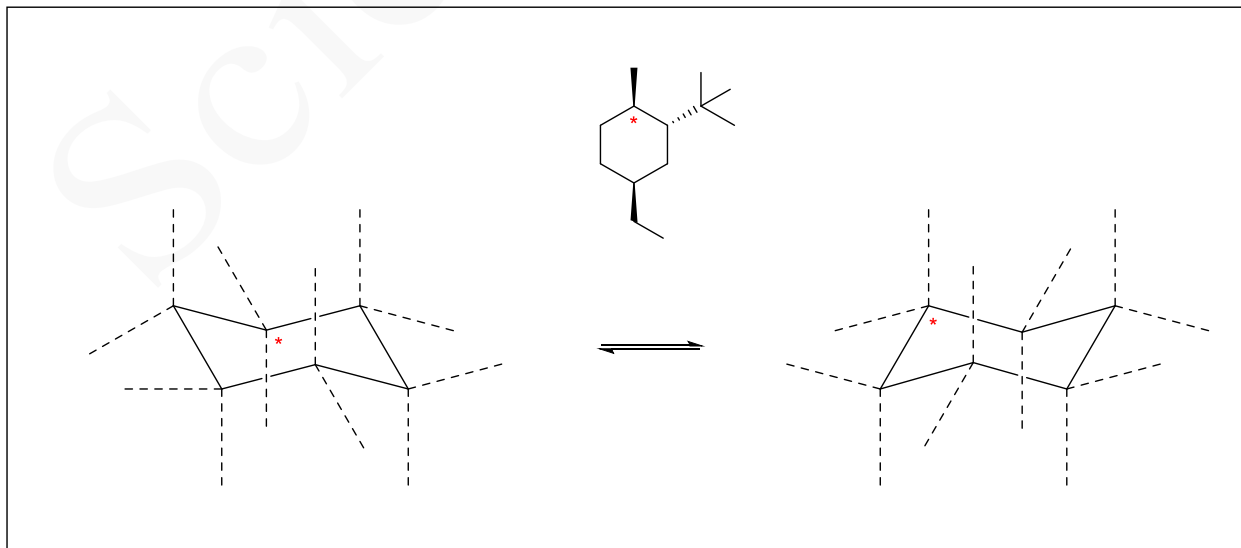
Example: Which represents the most stable conformation of *cis*-1-bromo-4-ethylcyclohexane?



- c. **Chair Flips:** method of rotating cyclohexane such that the axial bonds become equatorial and equatorial bonds become axial. On chair flip, direction (up vs down) does not change.



Example: Complete the following chair flip template by adding the missing substituents. Then, decide which chair is more stable. Do not include hydrogens in your answer.



Acids and Bases

I. Bronsted Acids and Bases:

- Bronsted Acids: proton (hydrogen with no electrons) donors
- Bronsted Bases: proton acceptors
 - Generally, are [neutral with a lone pair of electrons] or are [negatively charged with a lone pair of electrons]
 - Always Bases:** Any time an **alkali** or an **alkali earth** metal is attached to a non-metal, this species will always be the base (ex. NaOH, LiCH₃, etc.)


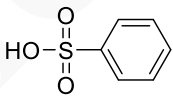

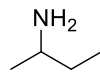


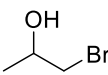
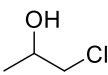
II. Lewis Acids and Bases:

- Lewis Acids: electron acceptors (usually group III making three bonds or transition metals).
 - Uncommon Lewis Acids: TiCl₄, FeBr₃, SnCl₂, AlCl₃, and BF₃. Remember that any of the halogens used in the list above can be exchanged with other halogens.
 - Other neutral Lewis Acids can accept a pair of electrons via a resonance form.
- Lewis Bases: electron donors

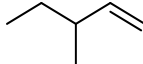

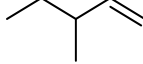
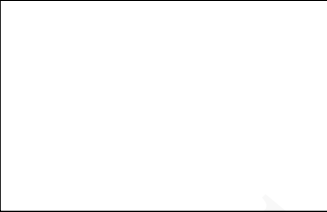
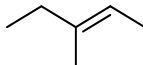

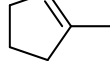
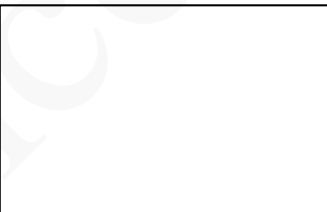
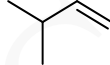

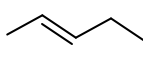
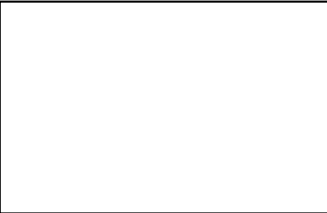
III. Ranking Acidity: Acidity can depend on several situations depending on the relationship between the atoms bearing the most acidic proton.

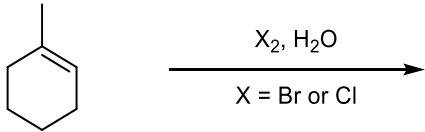
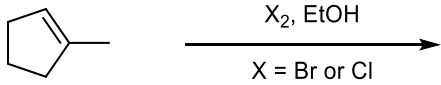
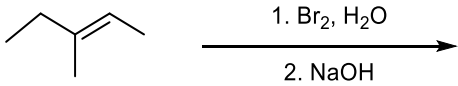
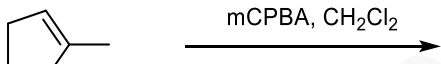
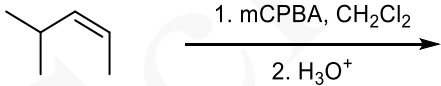
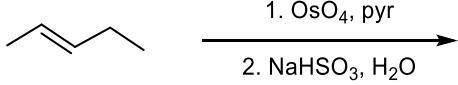
The Most Acidic Proton is Located On....	
Identical Atoms	Different Atoms
1. Hybridization: more s character = more acidic	1. Size: larger atom = more acidic
2. Resonance: more resonance = more acidic	2. Electronegativity: more EN = more acidic
3. Inductive Electron Withdrawal: more EN groups close to acidic proton = more acidic	

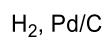
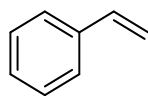
Example: Assess the pairs of compounds shown below and select the most acidic.

	vs.		vs.		vs.	
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	vs.		vs.		vs.	
<input type="radio"/>		<input type="radio"/>		<input type="radio"/>		<input type="radio"/>

Electrophilic Addition Reactions of Alkenes

Acid Catalyzed Hydration (Rearrangement Possible)	 $\xrightarrow{\text{H}_2\text{SO}_4, \text{H}_2\text{O (or H}_3\text{O}^+)}$		Stereochemistry: N/A Regiochemistry: Markovnikov Reactants: Alkene Products: Alcohol
Oxymercuration/Demercuration	 $\xrightarrow[2. \text{NaBH}_4]{1. \text{Hg(OAc)}_2, \text{H}_2\text{O, THF}}$		Stereochemistry: N/A Regiochemistry: Markovnikov Reactants: Alkene Products: Alcohol
Modified Oxymercuration/Demercuration	 $\xrightarrow[2. \text{NaBH}_4]{1. \text{Hg(OAc)}_2, \text{CH}_3\text{OH, THF}}$		Stereochemistry: N/A Regiochemistry: Markovnikov Reactants: Alkene Products: Ether
Hydroboration/Oxidation	 $\xrightarrow[2. \text{H}_2\text{O}_2, \text{HO}^-, \text{H}_2\text{O}]{1. \text{BH}_3, \text{THF}}$		Stereochemistry: Syn Regiochemistry: Anti-Mark Reactants: Alkene Products: Alcohol
Hydrohalogenation (Rearrangement Possible)	 $\xrightarrow[\text{X = Br, Cl, or I}]{\text{HX}}$		Stereochemistry: N/A Regiochemistry: Markovnikov Reactants: Alkene Products: Alkyl Halide
Halogenation	 $\xrightarrow[\text{X = Br or Cl}]{\text{X}_2, \text{CH}_2\text{Cl}_2}$		Stereochemistry: Anti Regiochemistry: Markovnikov Reactants: Alkene Products: Vicinal Dihalide

Halohydrin			<p>Stereochemistry: Anti</p> <p>Regiochemistry: Markovnikov</p> <p>Reactants: Alkene</p> <p>Products: Halohydrin</p>
Modified Halohydrin			<p>Stereochemistry: Anti</p> <p>Regiochemistry: Markovnikov</p> <p>Reactants: Alkene</p> <p>Products: Haloether</p>
Epoxidation via Halohydrin			<p>Stereochemistry: Syn</p> <p>Regiochemistry: N/A</p> <p>Reactants: Alkene</p> <p>Products: Epoxide</p>
Peroxyacid Epoxidation			<p>Stereochemistry: Syn</p> <p>Regiochemistry: Markovnikov</p> <p>Reactants: Alkene</p> <p>Products: Epoxide</p>
Trans Diol Formation			<p>Stereochemistry: Anti</p> <p>Regiochemistry: N/A</p> <p>Reactants: Alkene</p> <p>Products: Trans Diol</p>
Syn Diol Formation			<p>Stereochemistry: Syn</p> <p>Regiochemistry: N/A</p> <p>Reactants: Alkene</p> <p>Products: Syn Diol</p>

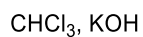
Catalytic Hydrogenation

Stereochemistry: Syn

Regiochemistry: N/A

Reactants: Alkene

Products: Alkane

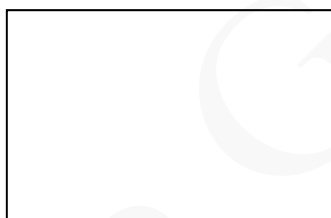
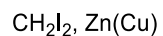
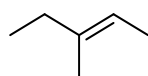
Cyclopropane Formation

Stereochemistry: Syn

Regiochemistry: N/A

Reactants: Alkene

Products: Cyclopropane

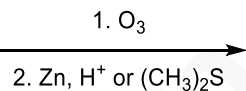
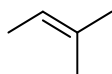
Simmons-Smith Reaction

Stereochemistry: Syn

Regiochemistry: N/A

Reactants: Alkene

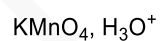
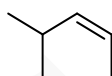
Products: Cyclopropane

Ozonolysis

0 H: Ketone

1 H: Aldehyde

2 H: Formaldehyde

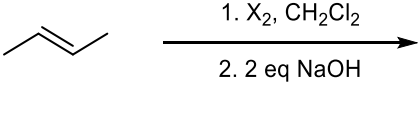
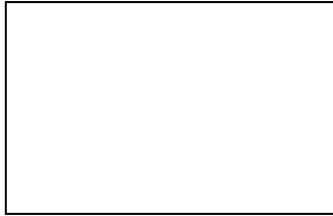
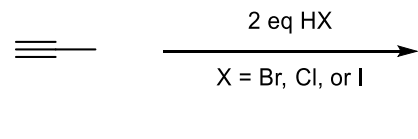
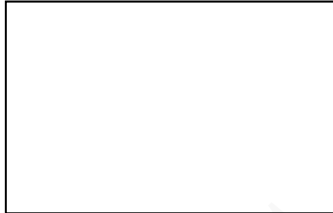
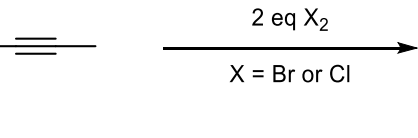

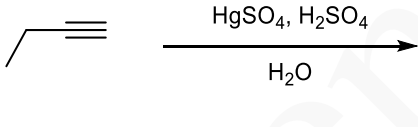

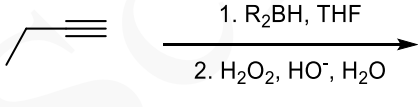
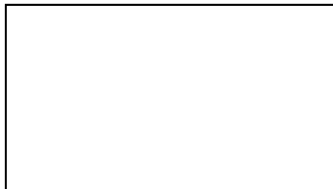
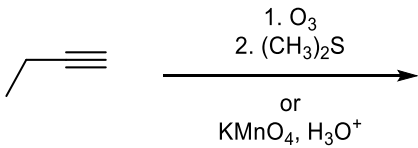

Oxidative Cleavage

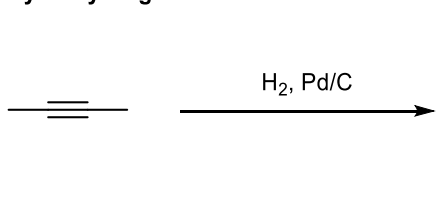
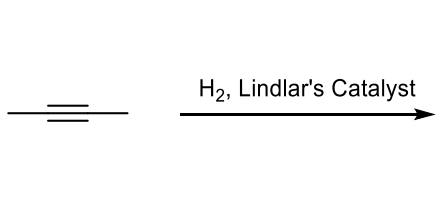
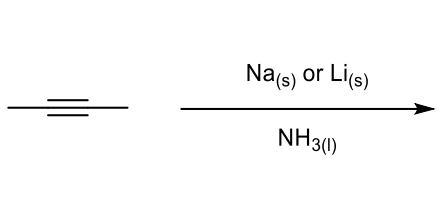
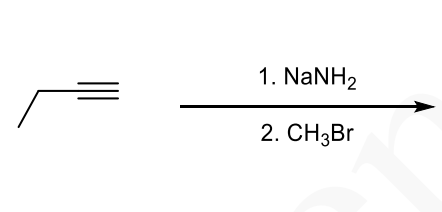
0 H: Ketone

1 H: Carboxylic Acid

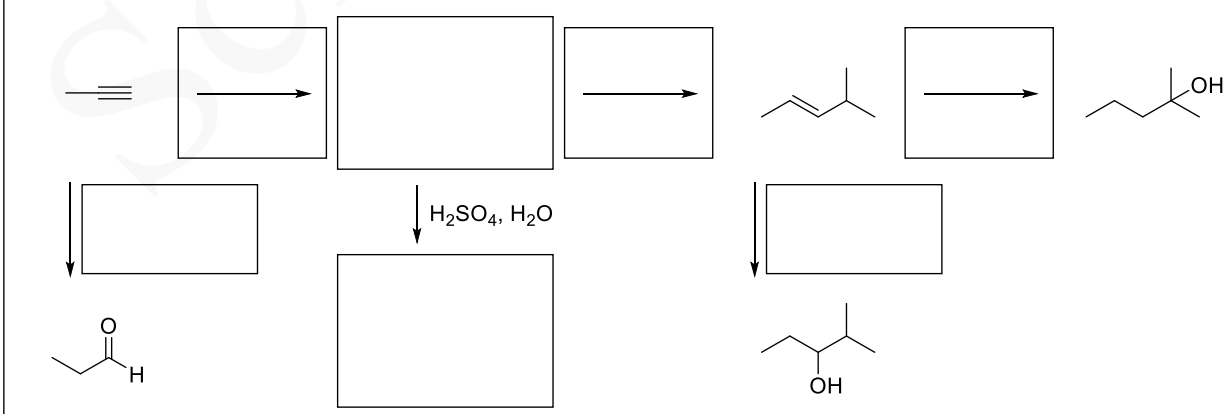
2 H: CO₂

Electrophilic Addition Reactions of Alkynes

<p>Alkyne Formation</p> 		<p>Stereochemistry: N/A Regiochemistry: Zaitsev Reactants: Alkene Products: Alkyne</p>
<p>Hydrohalogenation</p> 		<p>Stereochemistry: Anti (1 eq) Regiochemistry: Markovnikov Reactants: Alkyne Products: Geminal Dihalide</p>
<p>Halogenation</p> 		<p>Stereochemistry: Anti Regiochemistry: N/A Reactants: Alkyne Products: Tetrahalide</p>
<p>Mercury-Catalyzed Hydration</p> 		<p>Stereochemistry: N/A Regiochemistry: Markovnikov Reactants: Alkyne Products: Ketone</p>
<p>Hydroboration-Oxidation</p> 		<p>Stereochemistry: N/A Regiochemistry: Anti-Mark Reactants: Alkyne Products: Aldehyde</p>
<p>Ozonolysis / Oxidative Cleavage</p> 		<p>0 H: Carboxylic Acid 1 H: CO₂</p>

<p>Catalytic Hydrogenation</p> 	<p>Stereochemistry: Syn</p> <p>Regiochemistry: N/A</p> <p>Reactants: Alkyne</p> <p>Products: Alkane</p>
<p>Catalytic Hydrogenation with Poisoned Catalyst</p> 	<p>Stereochemistry: Syn</p> <p>Regiochemistry: N/A</p> <p>Reactants: Alkyne</p> <p>Products: Cis Alkene</p>
<p>Dissolving Metal Reduction</p> 	<p>Stereochemistry: Anti</p> <p>Regiochemistry: N/A</p> <p>Reactants: Alkyne</p> <p>Products: Trans Alkene</p>
<p>Chain-Extension of the Terminal Alkyne</p> 	<p>Reactants: Terminal Alkyne</p> <p>Products: Internal Alkyne</p> <p>1° or 2° Alkyl Halides Only</p>

Example: Complete the following guided synthesis by providing the missing reactants, reagents, or products.

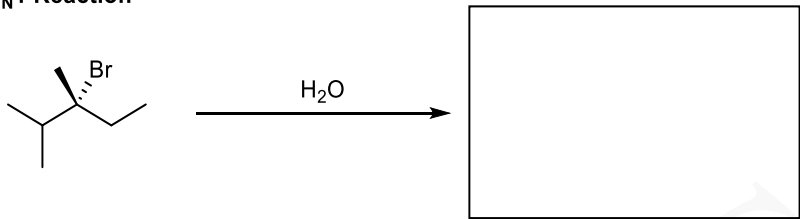
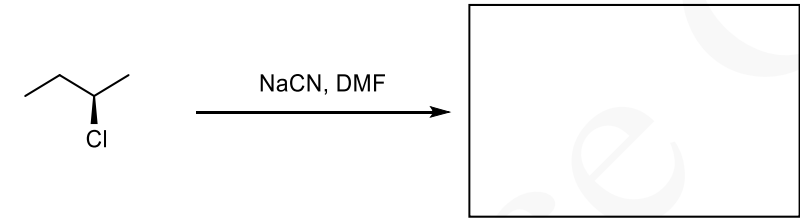
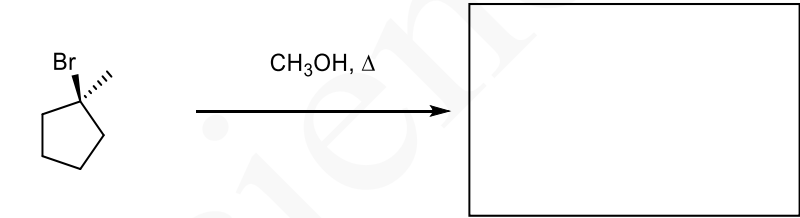
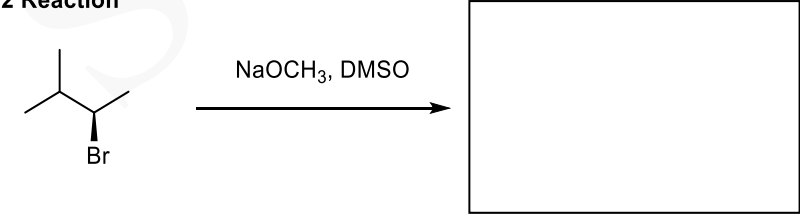


The synthesis flowchart consists of the following steps and components:

- Starting material: Terminal alkyne (1-butyne).
- Step 1: $\text{Alkyne} \xrightarrow{\text{[]}}$
- Step 2: $\text{[]} \xrightarrow{\text{[]}}$
- Step 3: $\text{[]} \xrightarrow{\text{[]}}$ 2-methyl-2-butene
- Step 4: $\text{2-methyl-2-butene} \xrightarrow{\text{[]}}$ 2-methyl-2-butanol
- Side branch 1: $\text{Alkyne} \xrightarrow{\text{[]}}$ Propanal $\xrightarrow{\text{[]}}$ 2-methyl-2-butanol
- Side branch 2: $\text{Alkyne} \xrightarrow{\text{[]}}$ [] $\xrightarrow{\text{H}_2\text{SO}_4, \text{H}_2\text{O}}$ [] $\xrightarrow{\text{[]}}$ 2-methyl-2-butanol

Substitution and Elimination of Alkyl Halides

<u>Strong Nucleophiles</u>	<u>Strong Bases</u>	<u>Leaving Groups</u>
1. Negatively charged 2. Not bulky	Negatively charged (C)arbon, (H)ydrogen, (O)xygen, (N)itrogen unless pi bonds are present	Weaker bases are better leaving groups
Ex. ^-Cl , ^-SH , ^-OAc , ^-CN	Ex. $^-CH_3$, ^-H , ^-OH , $^-NH_2$	$I^- > Br^- > Cl^- > F^-$

<p>S_N1 Reaction</p> 	<p>Electrophile: $3^\circ > 2^\circ \gg \gg 1^\circ$</p> <p>Mechanism: Carbocation Forming</p> <p>Stereochem: Racemic mix, slightly more inversion</p> <p>Favored By: Low temps, WN/WB, protic solvents</p>
<p>S_N2 Reaction</p> 	<p>Electrophile: $1^\circ > 2^\circ \gg \gg 3^\circ$</p> <p>Mechanism: Backside Attack</p> <p>Stereochem: Inversion</p> <p>Favored By: SN/WB, aprotic solvents</p>
<p>E1 Reaction</p> 	<p>Electrophile: $3^\circ > 2^\circ \gg \gg 1^\circ$</p> <p>Mechanism: Carbocation Forming</p> <p>Regiochem: Zaitsev</p> <p>Stereochem: E</p> <p>Favored By: High temps, WN/WB, protic solvents</p>
<p>E2 Reaction</p> 	<p>Electrophile: $3^\circ > 2^\circ > 1^\circ$</p> <p>Mechanism: Concerted</p> <p>Regiochem: Zaitsev</p> <p>Stereochem: Anti-Periplanar</p> <p>Favored By: WN/SB, aprotic solvents</p>

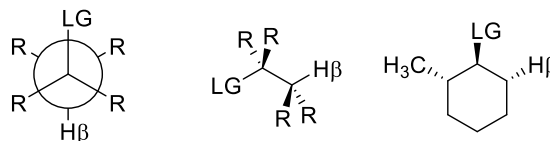
Zaitsev Exceptions

The least substituted beta-hydrogen will be removed if:

1. The leaving group is fluorine
2. A bulky base (tert-butoxide) is used in the elimination
3. If the more substituted beta-hydrogen cannot adopt anti-periplanar conformation (E2 on cyclic rings)

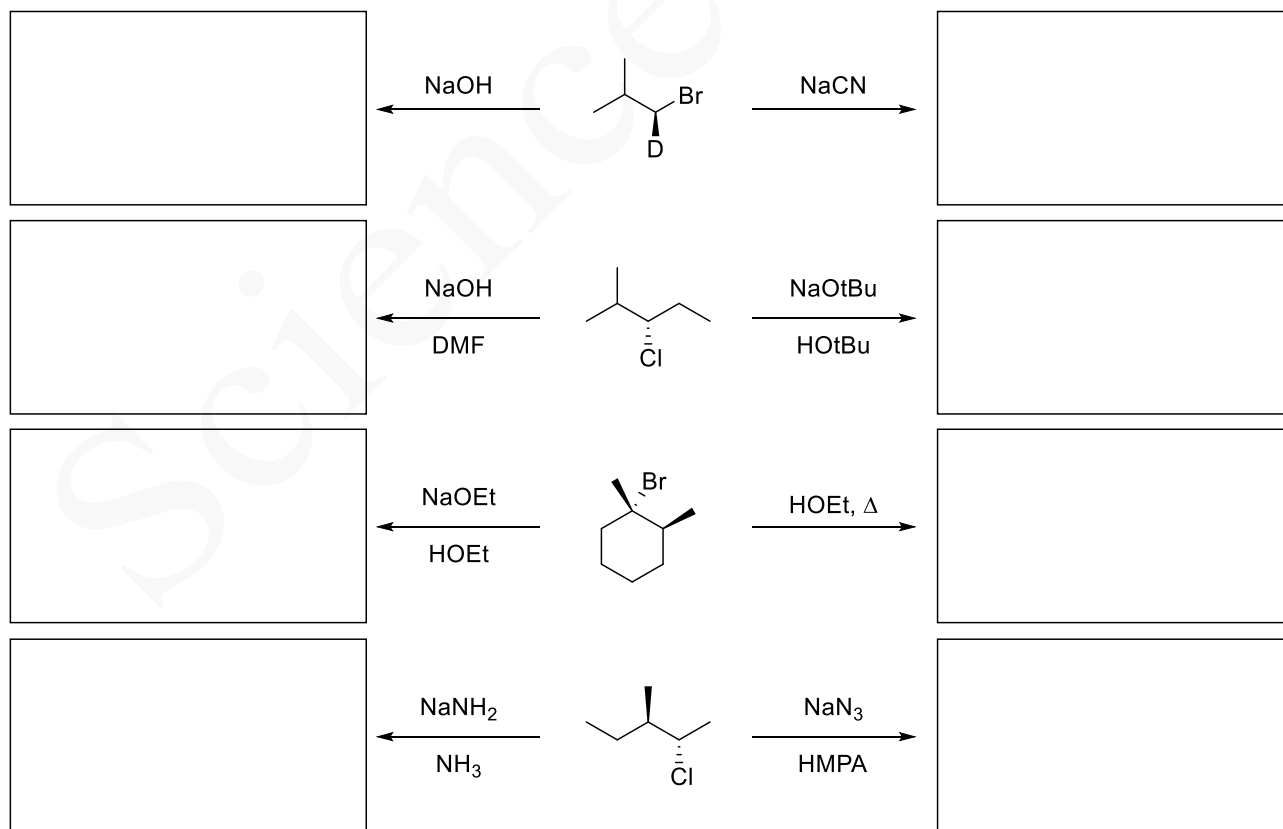
Anti-Periplanar (E2 Requirement)

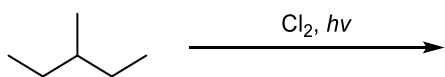
must do to predict E/Z outcome of reaction



Alkyl Halide Substitution	WN/SB		SN/SB		SN/WB		WN/WB	
	KOC(CH ₃) ₃ LDA NaH	DBU DBN	NaOH NaNH ₂	KOCH ₃ NaNR ₂	KCN NaN ₃ H ₂ S	NaBr NaOAc CH ₃ SH	H ₂ O	CH ₃ OH
1°	E2		S _N 2		S _N 2		-	
2°	E2		E2		S _N 2		-	
3°	E2		E2		S _N 1 &/or E1 (Δ)		S _N 1 &/or E1 (Δ)	

Example: Predict the major products to the reactions below.

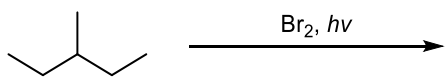


Radical Reactions**Free-Radical Chlorination**

H Reactivity: 1° - 1.0
2° - 3.8
3° - 5.0

Major Product: Statistically favored H

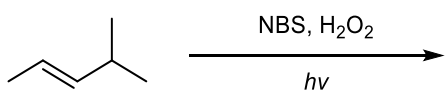
Stereochem: Racemic mixture

Free-Radical Bromination

H Reactivity: 1° - 1.0
2° - 82.0
3° - 1600

Major Product: Most sub H

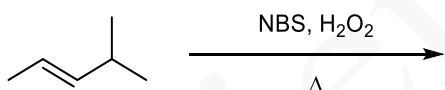
Stereochem: Racemic mixture

Allylic Bromination (low $[\text{Br}_2]$)

Major Product: Most sub allylic H

Stereochem: Racemic mixture

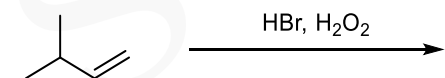
*Don't forget to resonate!



Major Product: Most sub allylic H

Stereochem: Racemic mixture

If catalyzed by heat,
thermodynamic product is major!

Anti-Markovnikov Bromination

Regiochem: Anti-Mark

Stereochem: Racemic mixture

Spectroscopy Summary Tables

