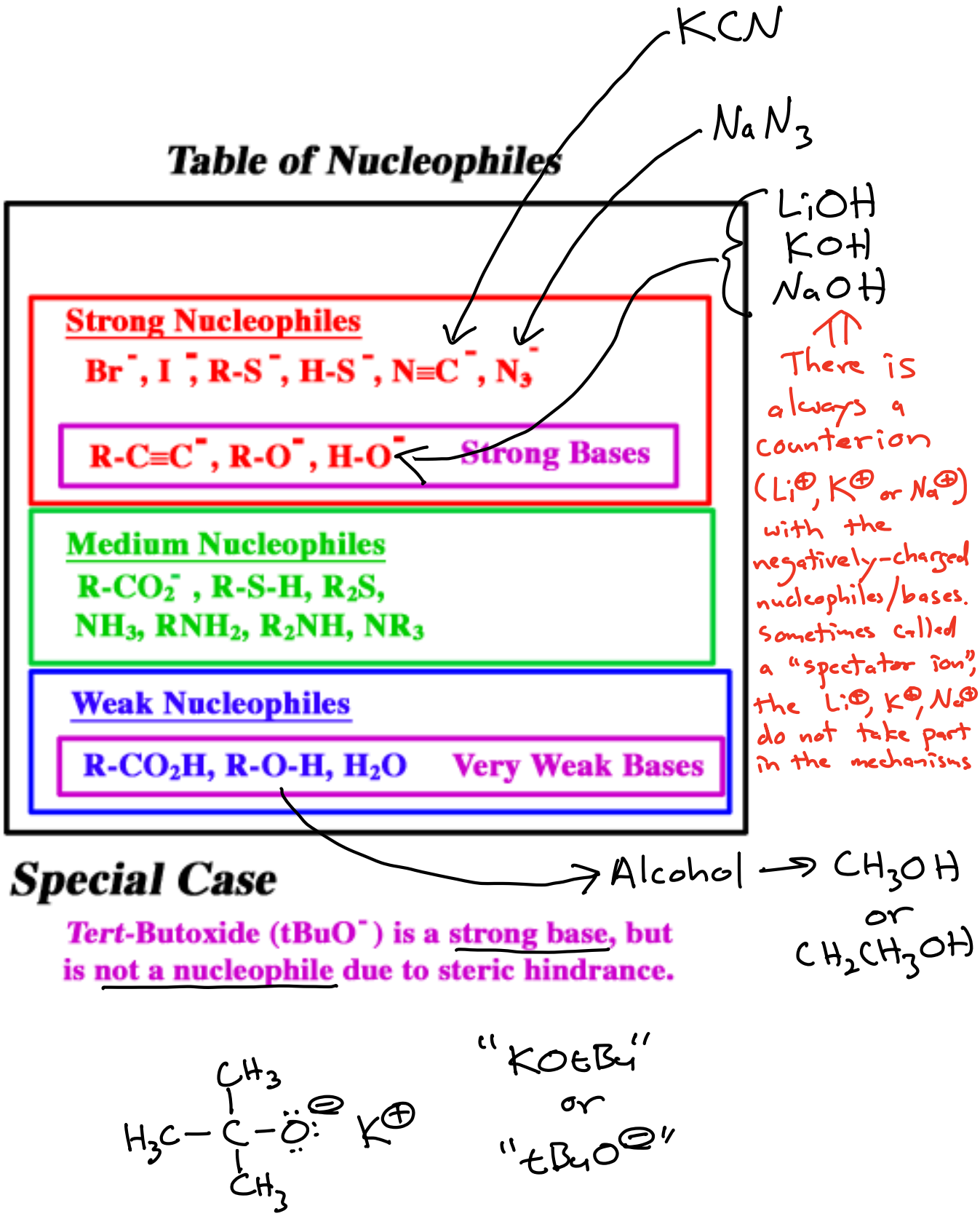
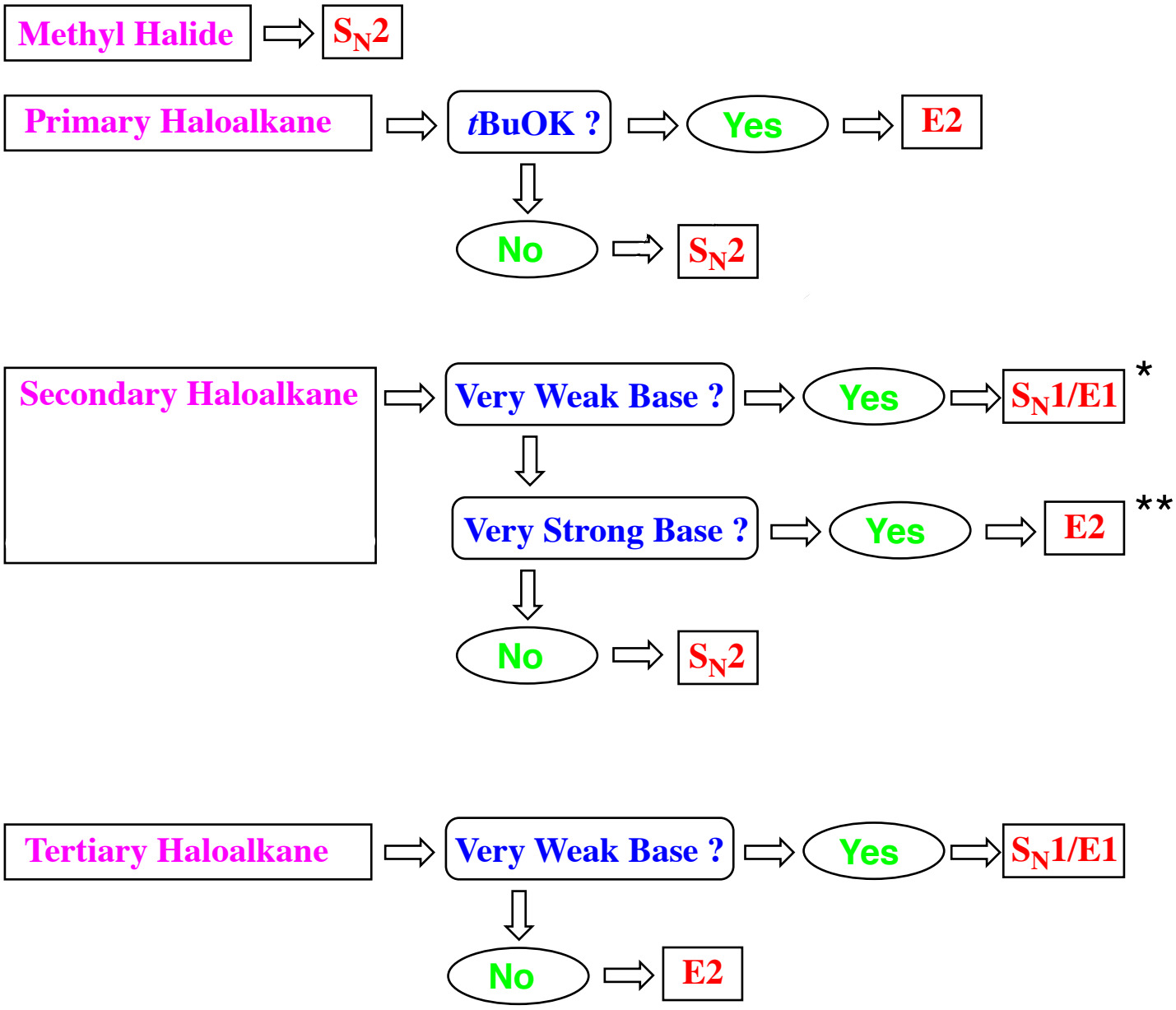

KCN
NaN3
LiOH
KOH
NaOH
Table of Nucleophiles
Strong Nucleophiles
Br-, I-, R-S-, H-S-, N≡C-, N3-
R-C≡C-, R-O-, H-O-
Strong Bases
Medium Nucleophiles
R-CO2-, R-S-H, R2S,
NH3, RNH2, R2NH, NR3
Weak Nucleophiles
R-CO2H, R-O-H, H2O
Very Weak Bases
There is always a counterion (Li⊕, K⊕ or Na⊕) with the negatively-charged nucleophiles/bases. Sometimes called a "spectator ion", the Li⊕, K⊕, Na⊕ do not take part in the mechanisms
Special Case
Alcohol → CH3OH or CH2CH3OH
Tert-Butoxide (tBuO-) is a strong base, but is not a nucleophile due to steric hindrance.
"KOtBu" or "tBuO⊖"

Substitution/Elimination Decision Map

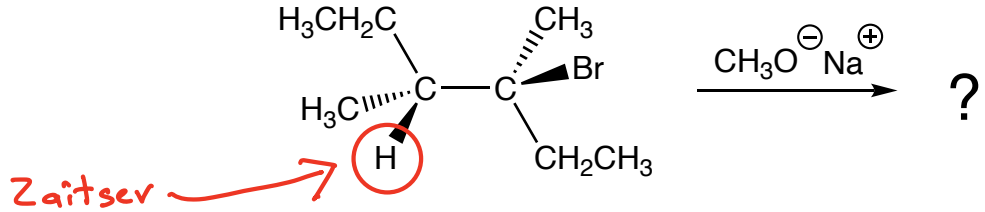


For S_N2 Remember Chiral Center InVERSiON
For E2 Remember anti-periplanar and Zaitsev
For S_N1 Remember Chiral Center Scrambling
For E1 Remember Zaitsev

* Note: With Very Weak Bases, SN2 can compete here, but for the purposes of this class, assume SN1 / E1 predominate

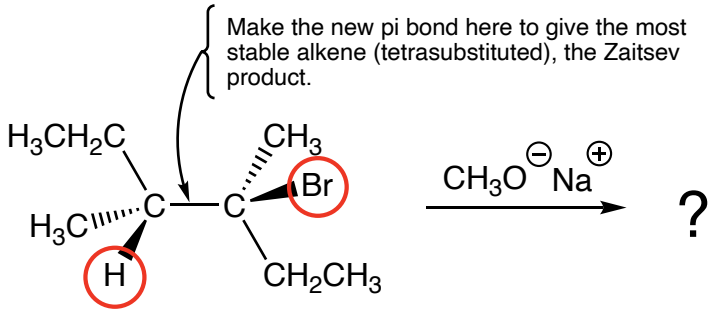
** Note: If tBuOK is the very strong base, an appreciable amount of a non-Zaitsev product can be formed because the bulky tBuOK will tend to react with the most accessible H atom.

E2 Reaction Considerations:



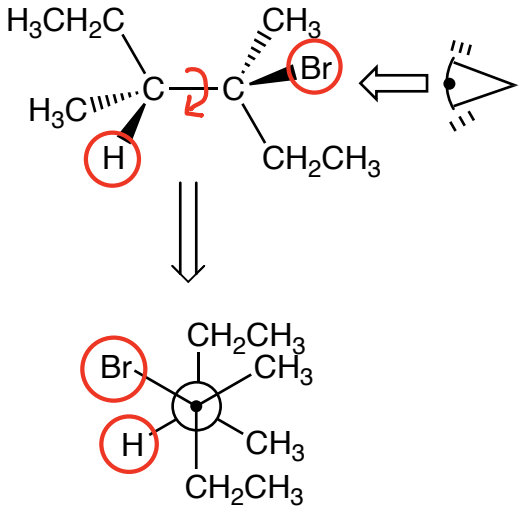
When analyzing highly substituted haloalkanes for a possible E2 reaction:

1. **You need to identify the most stable possible alkene (most highly substituted, *trans* over *cis*) that could be made (Zaitsev product).**



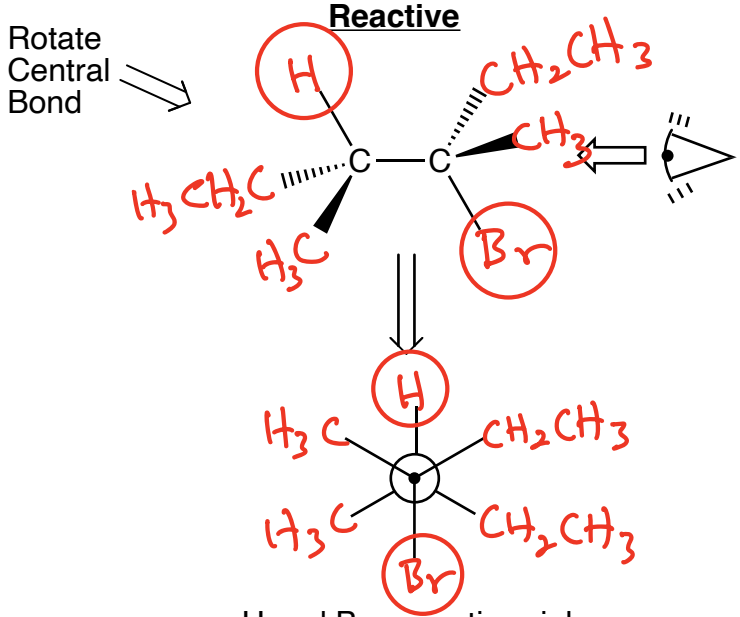
2. **Given the Zaitsev product you have identified, verify which anti-periplanar H atom(s) can be removed during the reaction to determine whether the product is E or Z.**
3. **You often need to rotate bonds to identify the particular H atom and configuration that reacts to give the alkene product.**

Not Reactive



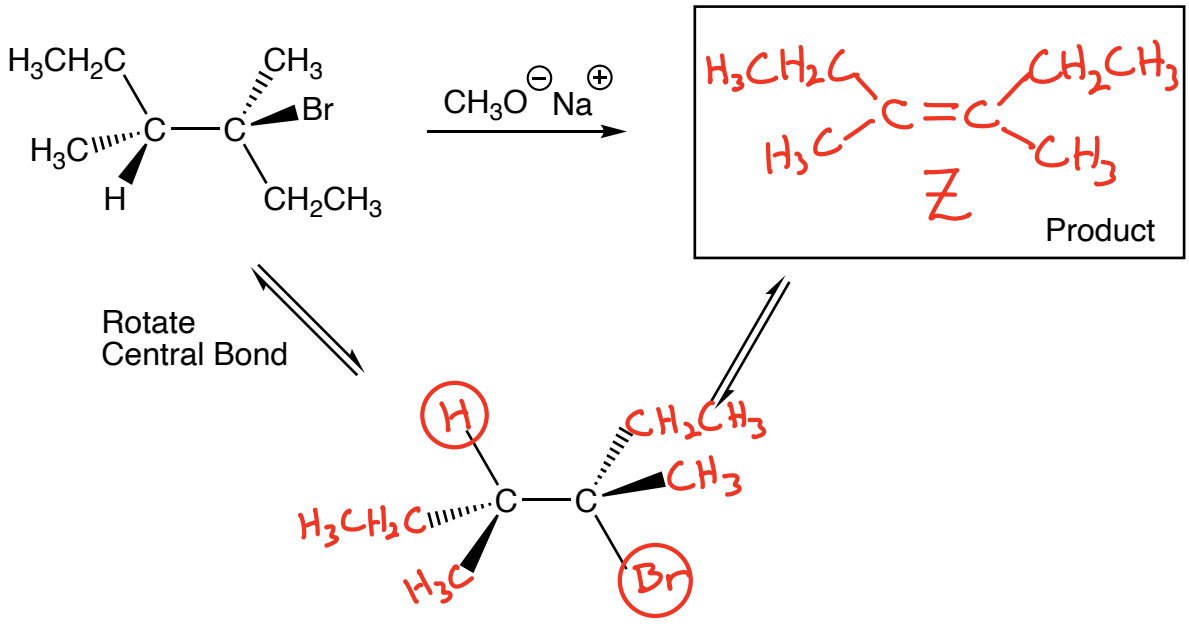
H and Br **not** anti-periplanar

Reactive

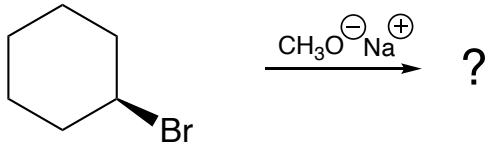


H and Br are anti-periplanar

Putting it all together:

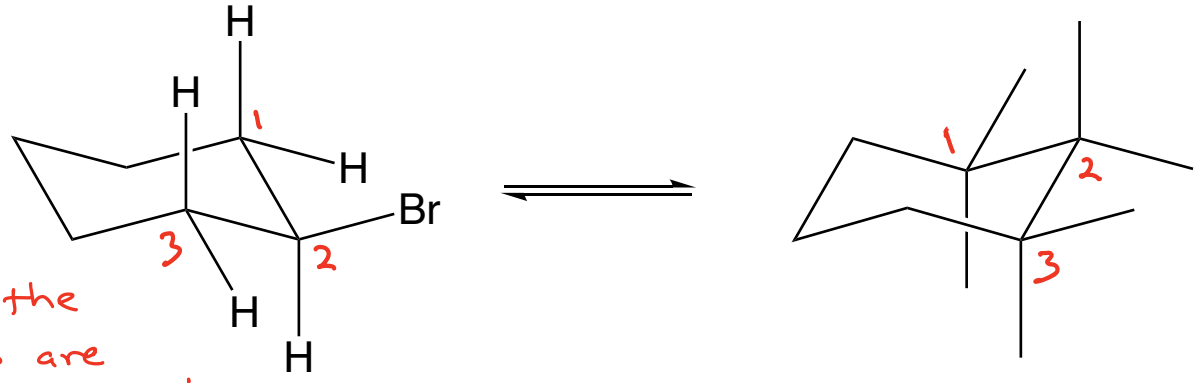


E2 Reaction of cyclohexane derivatives:



When analyzing highly substituted haloalkanes for a possible E2 reaction:

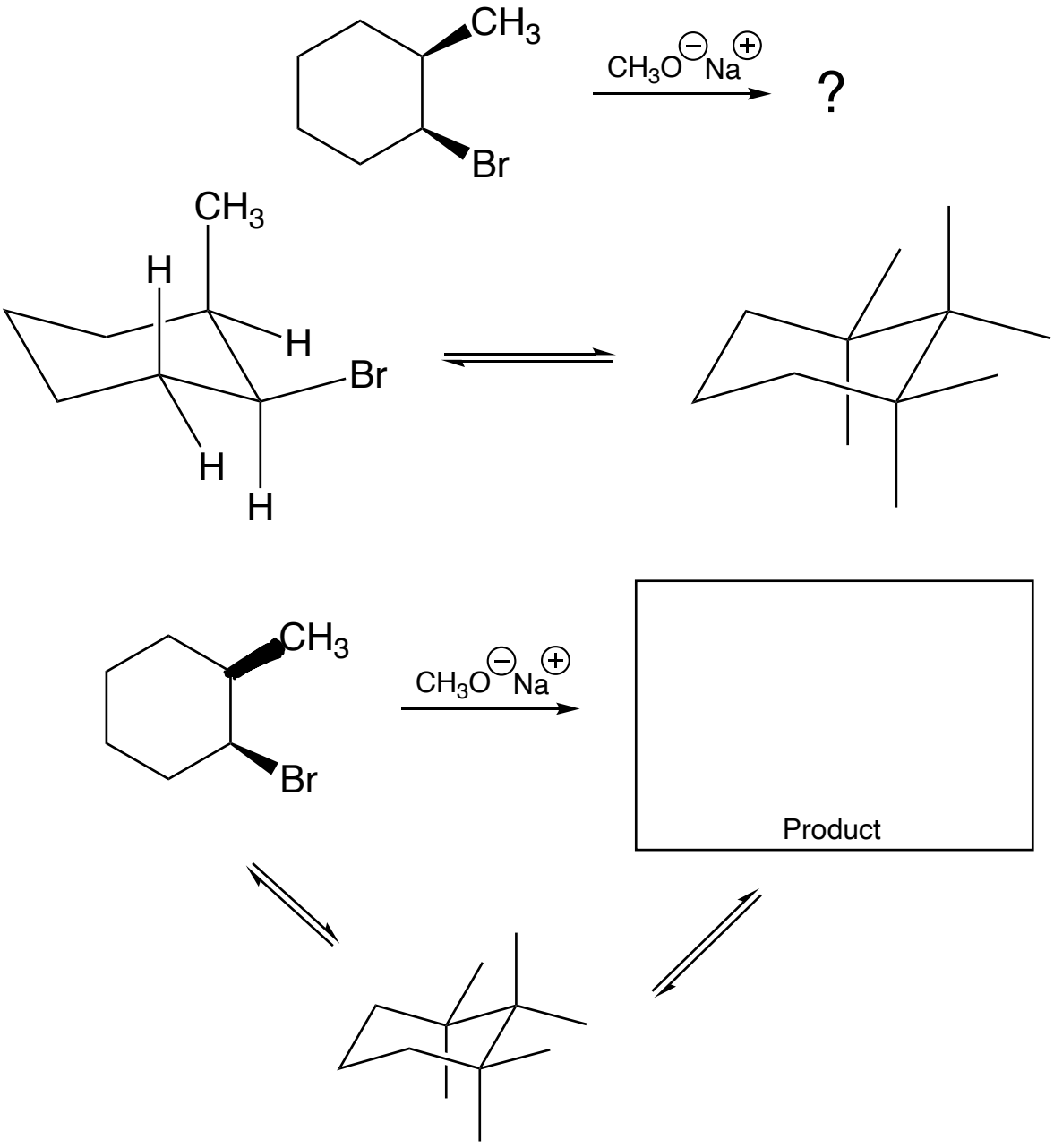
1. **You need to identify the most stable possible alkene (most highly substituted, *trans* over *cis*) that could be made (Zaitsev product).**
2. **Given the Zaitsev product you have identified, verify which anti-periplanar H atom(s) can be removed during the reaction to determine if that product can be made.**
3. **You often need to flip chairs in cyclohexane derivatives to identify the particular H atom and configuration that reacts to give the alkene product.**

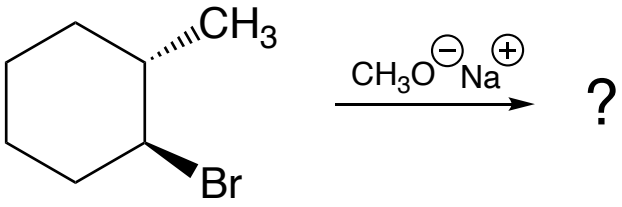


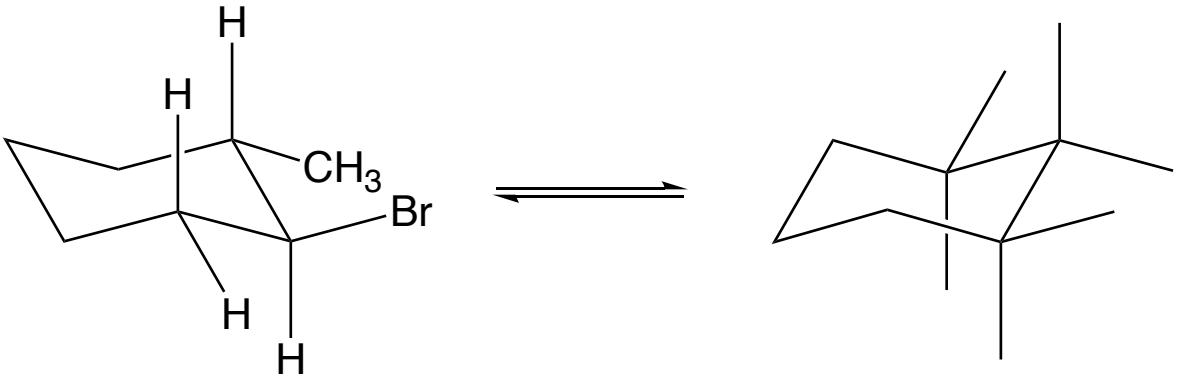
None of the H atoms are anti-periplanar to the Br atom!

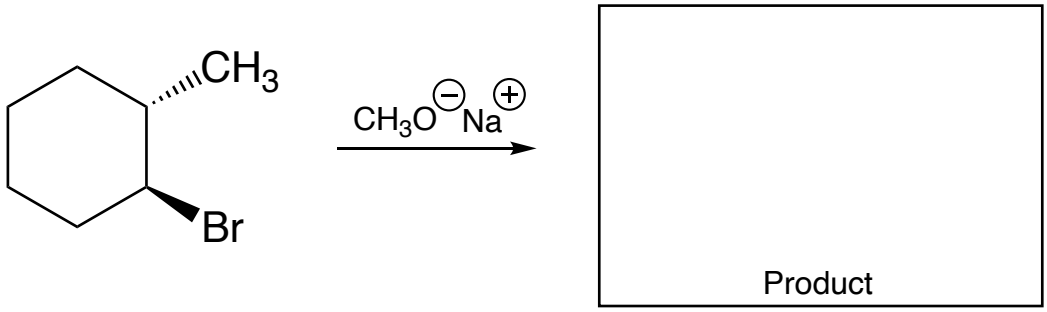
Rule: The halogen and H atom must both be AXIAL to react by an E2 mechanism.

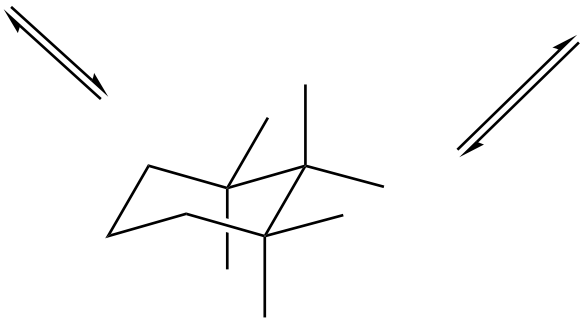
Classic Examples:



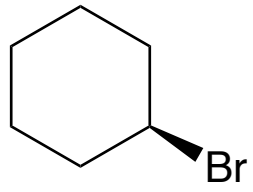

CH3
CH3O Na
Br
?


H
H
CH3
Br
H
H

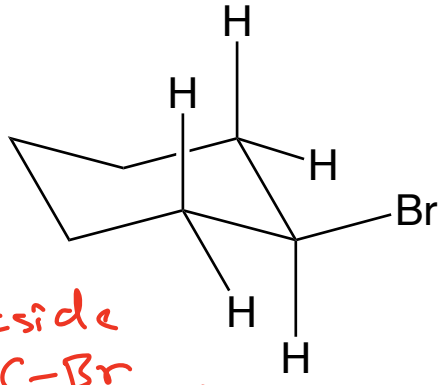

CH3
CH3O Na
Br
Product

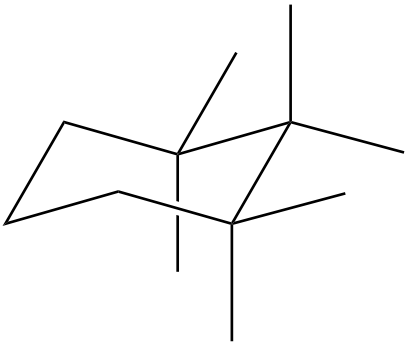


S_N2 Reactions of Cyclohexanes:

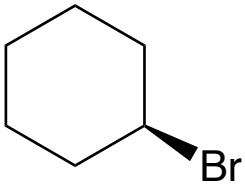


NaN_3 → ?



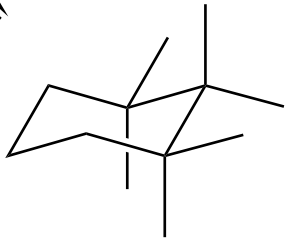


Backside of C–Br bond is blocked!



NaN_3 →

Product



Rule: The halogen must be AXIAL to react by an S_N2 mechanism.

"You can't stop the waves, but you can learn to surf"

Jon Kabat-Zinn


Alkanes
Alkenes
Alkynes
Haloalkanes
Vicinal dihaloalkanes
Ketones and Aldehydes
Carboxylic Acids
Alcohols
Where Electrons Are
Mechanisms
Roadmaps
Stereochemistry
Regiochemistry
ROTD
NIRRS
Motive
Opportunity
Carbocation
Radical
Pi-ways
Golden Rules
Make a Bond
Break a Bond
Add a Proton
Take a Proton
Nucleophiles and Electrophiles
Charge Delocalization
Hyperconjugation
Steric strain
Angle and Torsional Strain
Epoxides
Vicinal Diols
Radical Chain
SN2 vs. E2
SN1 and E1
Anti-periplanar
Markovnikov
Zaitsev

Geminal
Dihaloalkanes

Vicinal
Tetrahaloalkanes

Alkynes

Aldehydes/Ketones

Vicinal
Dihaloalkanes

Vicinal
Diols

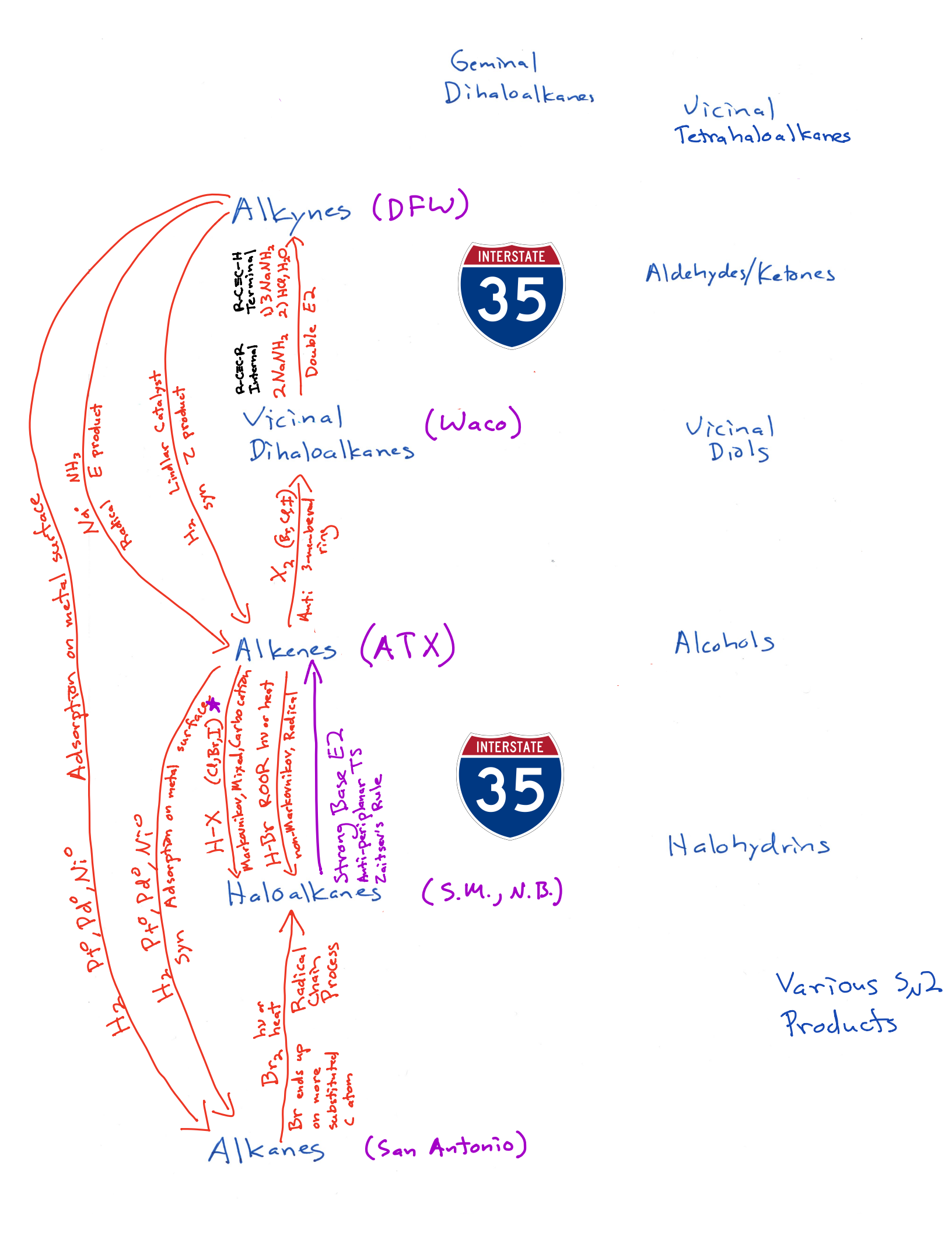
Alkenes

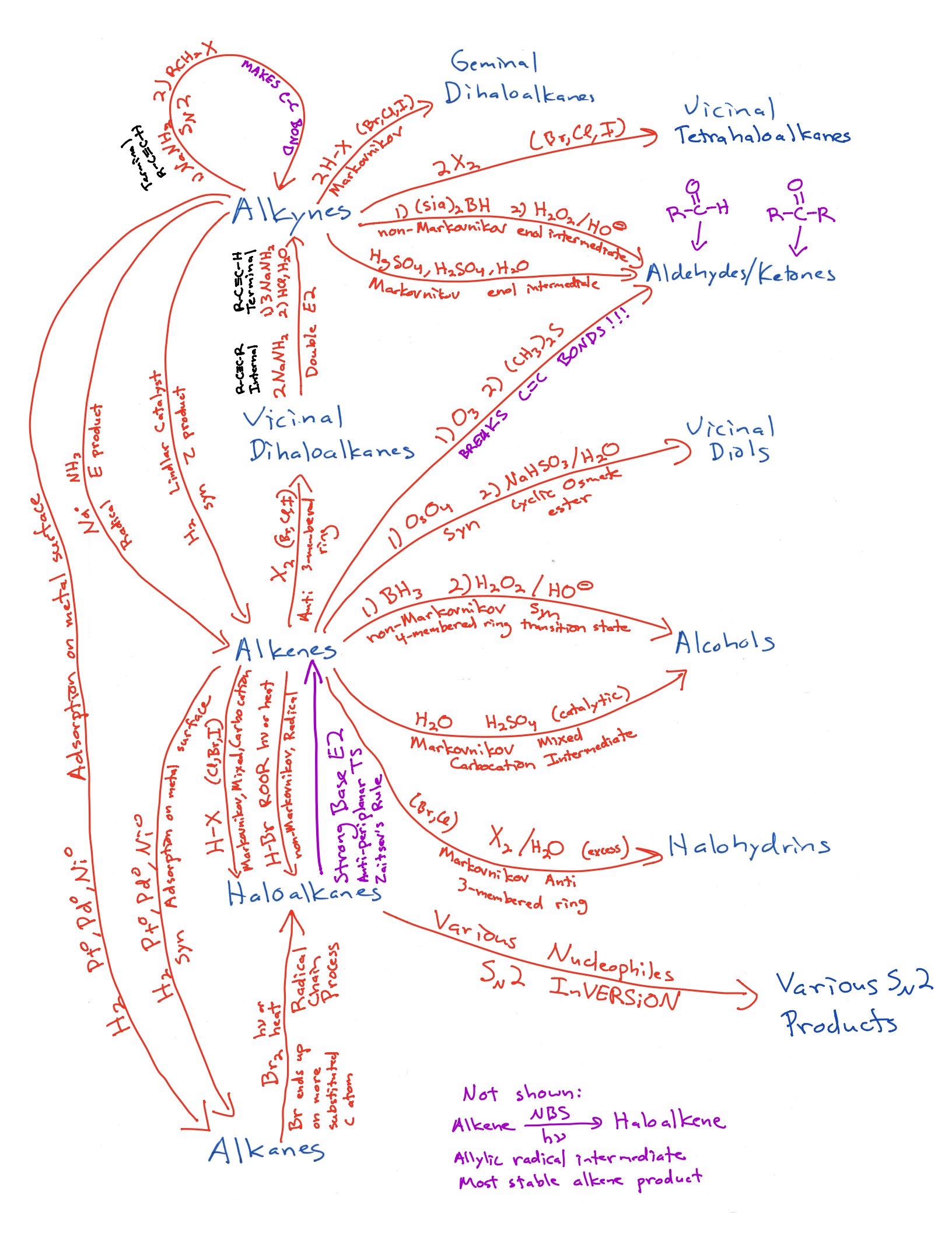
Alcohols

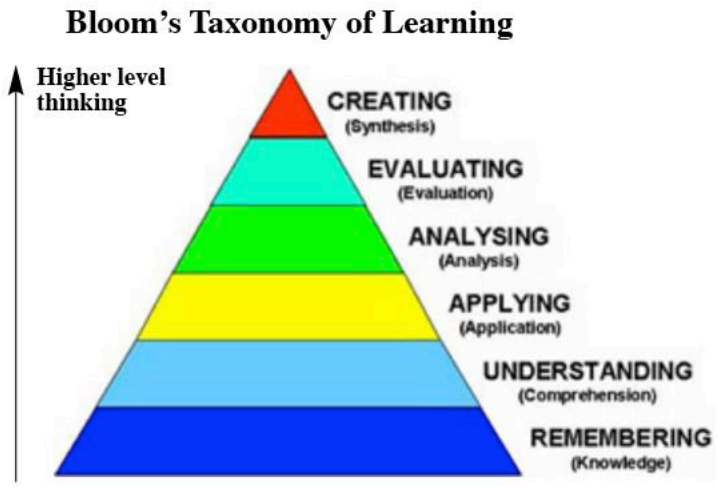
Halohydrins

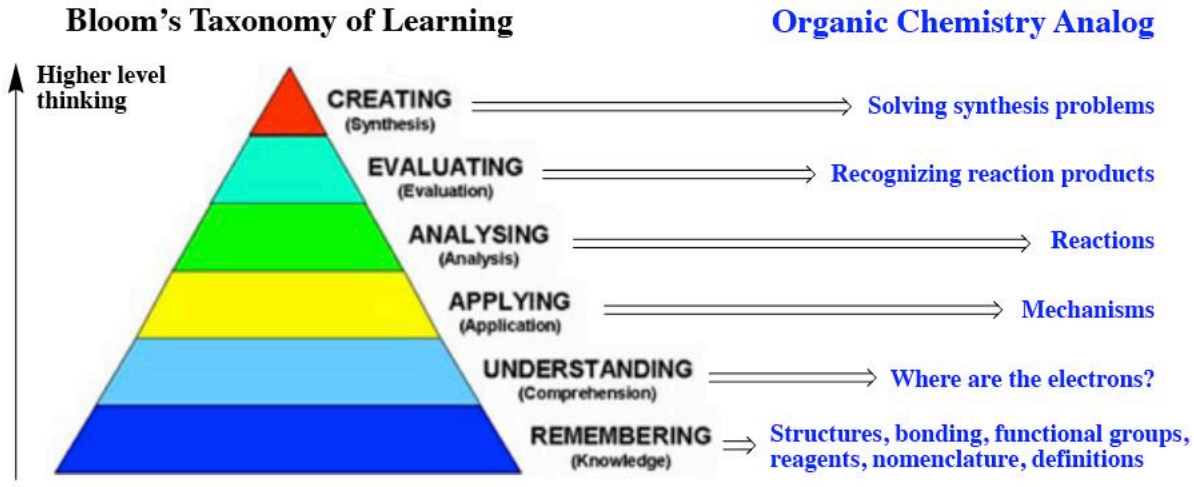
Haloalkanes

Alkanes


Geminal Dihaloalkanes
Vicinal Tetrahaloalkanes
Alkynes (DFW)
INTERSTATE 35
Aldehydes/Ketones
R-C≡C-H Terminal
1) 3 NaNH2
2) H2O, H2O
R-C≡C-R Internal
2 NaNH2
Double E2
Vicinal Dihaloalkanes
(Waco)
Vicinal Diols
Radical
Na° NH3
E product
Linear Catalyst
H2 syn
Z product
X2 (Br, Cl, I)
Anti
3-membered ring
Alkenes (ATX)
Alcohols
Adsorption on metal surface
Pt°, Pd°, Ni°
H2
Pt°, Pd°, Ni°
H2
syn
Adsorption on metal surface
H-X (Cl, Br, I)
Markovnikov, Mixed, Carbocation
H-Br ROOR hv or heat
non-Markovnikov, Radical
Strong Base E2
Anti-periplanar TS
Zaitsev's Rule
INTERSTATE 35
Haloalkanes
(S.M., N.B.)
Halohydrins
Br2
hv or heat
Radical Chain Process
Br ends up on more substituted C atom
Various SN2 Products
Alkanes
(San Antonio)


Geminal Dihaloalkanes
Vicinal Tetrahaloalkanes
Alkynes
Aldehydes/Ketones
Vicinal Dihaloalkanes
Vicinal Diols
Alkenes
Alcohols
Haloalkanes
Halohydrins
Alkanes
Various Products
Not shown:
Allylic radical intermediate
Most stable alkene product





A) **You must have your entire roadmap learned** so you can recite the NIRRS parameters for each reagent, i.e. Nature of overall transformation ("locations" on the roadmap), the Intermediate or transition state (carbocation, anti-periplanar etc.), the Reagents and how to designate them, as well as any Regiochemistry (Markovnikov, etc.) and any appropriate Stereochemistry (syn, anti, InVERSiON, scrambled, etc).

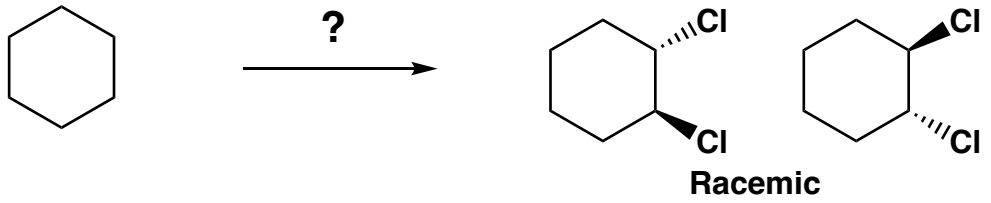
B) **Work backwards** (learn to RECOGNIZE the appropriate reagents and starting materials by looking at the products) from the final product. DO NOT try to work forward from the starting materials. Please trust me on this.

C) **Count carbons** in the starting material(s) and product(s) to see if any carbon-carbon bonds need to be broken or made, thereby zeroing in on key steps. This will be far more important next semester, so you should get used to doing this now.

D) **Pretty much all synthesis problems in OChem 1 involve traveling "north or south" on the so-called "I-35"** reactions (alkanes SA, haloalkanes NB/SM, alkenes ATX, vicinal dihaloalkanes Waco, alkynes DFW) at least part way at some point during the synthesis. This is not a promise or a rule, just an observation.

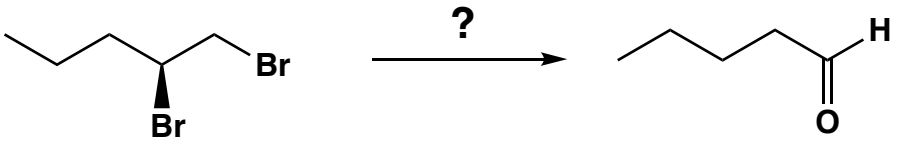
20. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

A) (7 pts)



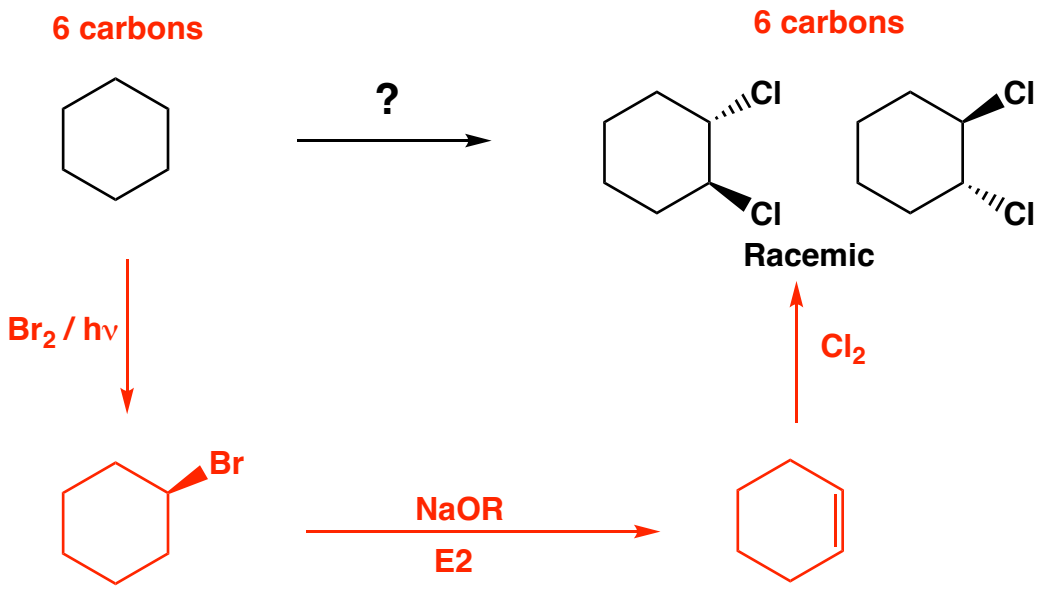
Racemic

B) (4 pts)

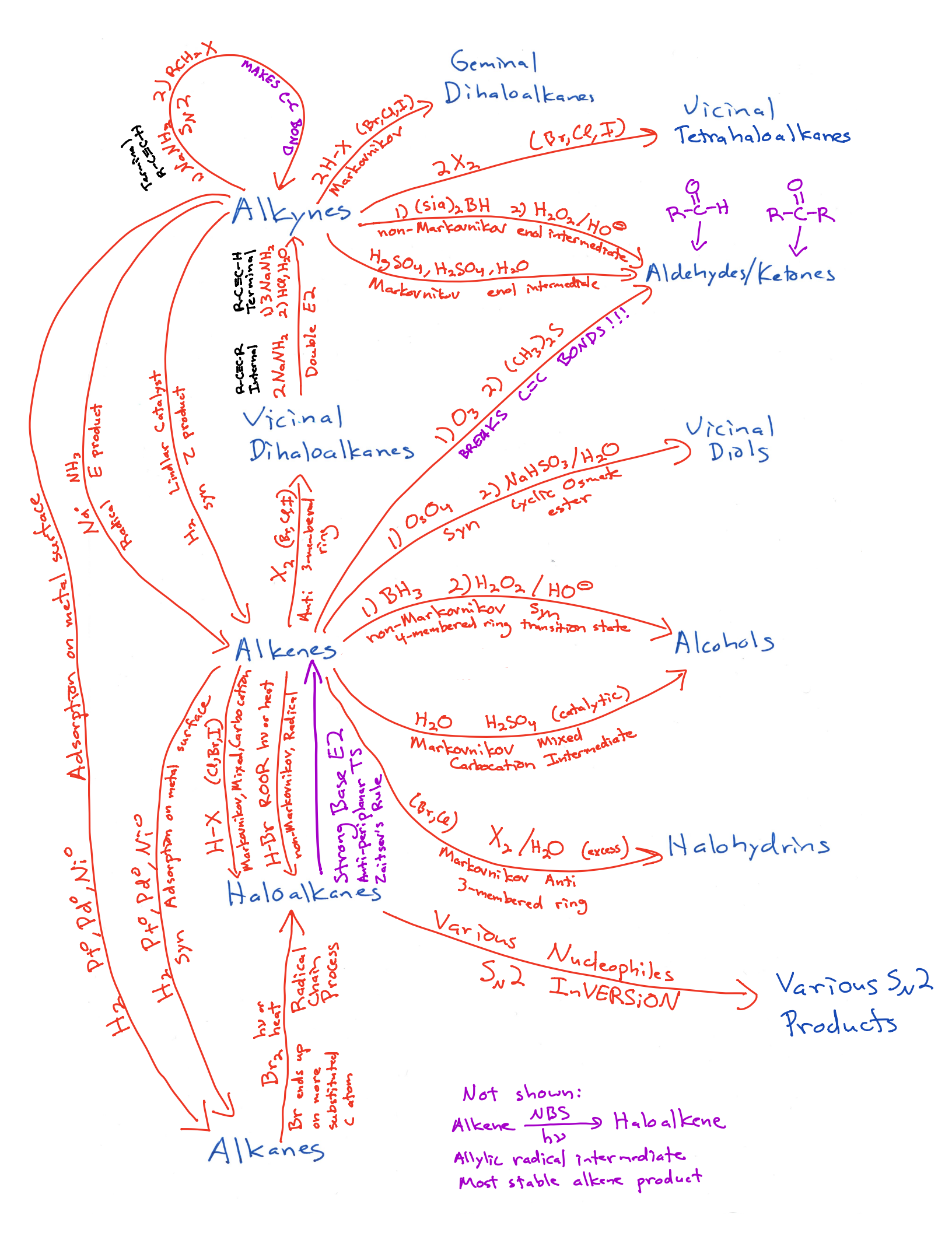


20. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

A) (7 pts)

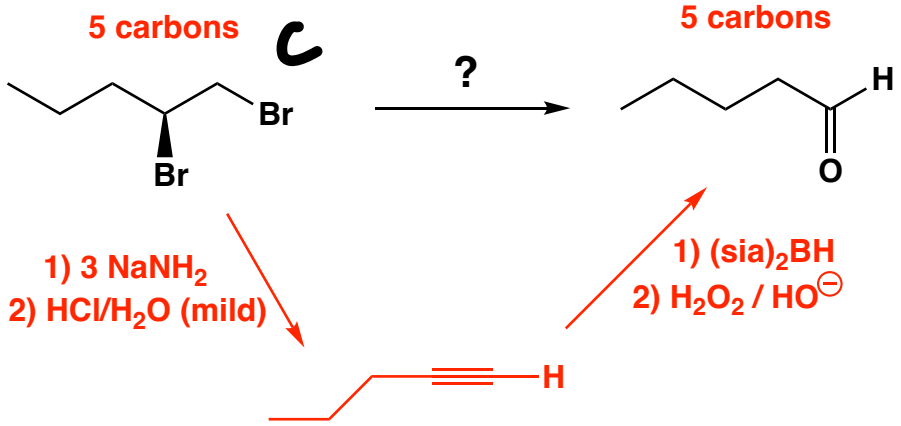


Recognize: The product is a *trans* dichlorocyclohexane tht must result from the reaction of an alkene (cyclohexene) with Cl_2. **Recognize**: The cyclohexene comes from the usual "I-35" combination of halogenation of an alkane with light (the only reaction that uses an alkane starting material) followed by an E2 in strong base such an alkoxide (NaOR).

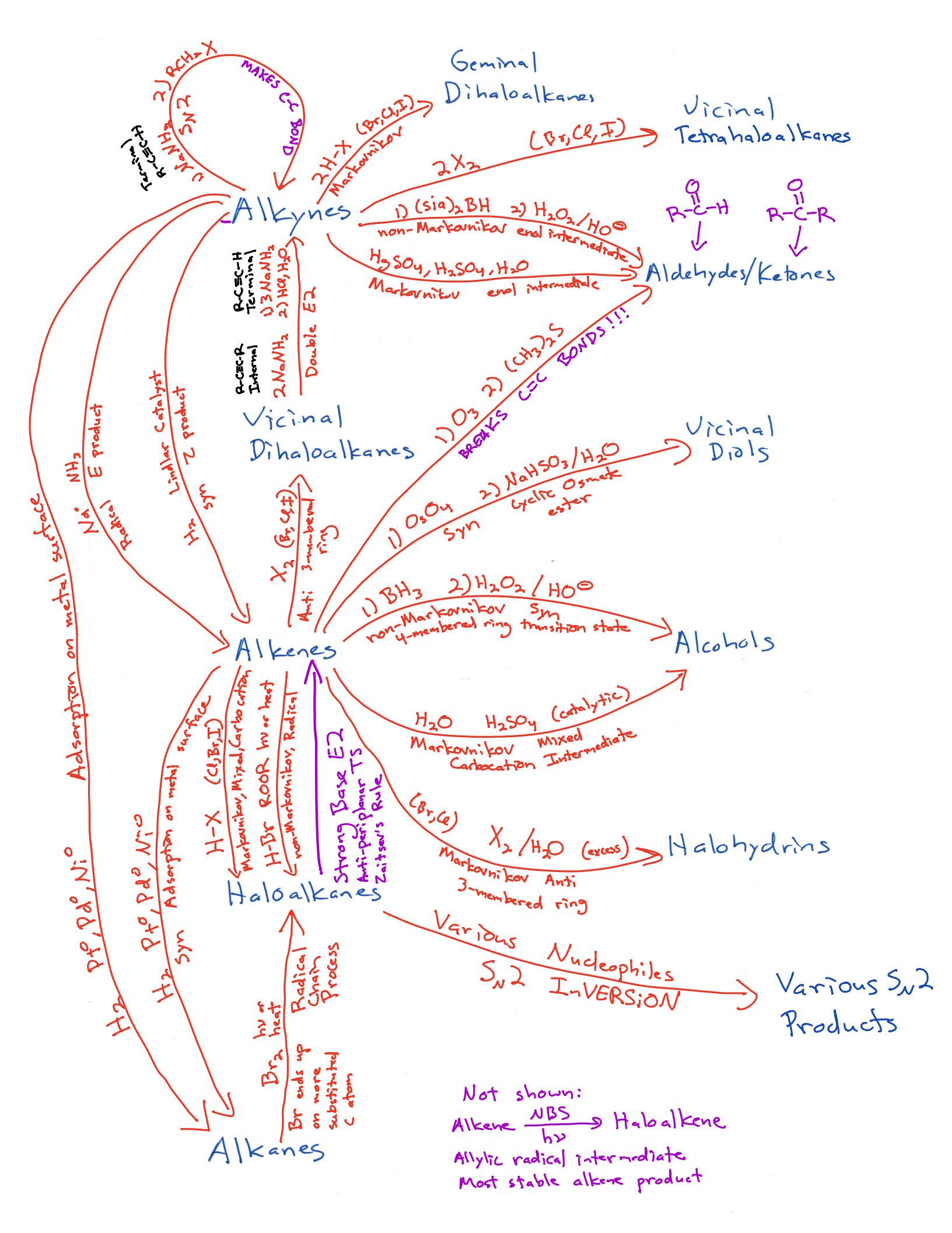

Alkynes
Terminal RC≡CH
1) NaNH2
2) RCH2X
SN2
MAKES C-C BONDS
Geminal Dihaloalkanes
2 H-X (Br,Cl,I)
Markovnikov
Vicinal Tetrahaloalkanes
(Br, Cl, I)
2 X2
1) (sia)2BH 2) H2O2/HO⊖
non-Markovnikov enol intermediate
H2SO4, H2SO4, H2O
Markovnikov enol intermediate
Aldehydes/Ketones
R-C(=O)-H
R-C(=O)-R
R-C≡C-H Terminal
1) 3 NaNH2
2) H⊕, H2O
R-C≡C-R Internal
2 NaNH2
Double E2
Vicinal Dihaloalkanes
1) O3 2) (CH3)2S
BREAKS C=C BONDS!!!
1) OsO4
2) NaHSO3/H2O
Syn
cyclic Osmate ester
Vicinal Diols
X2 (Br, Cl, I)
Anti
3-membered ring
1) BH3 2) H2O2 / HO⊖
non-Markovnikov
4-membered ring transition state
Syn
Alcohols
Alkenes
Adsorption on metal surface
Pt°, Pd°, Ni°
H2
Syn
Radical
Na° NH3
E product
Linear Catalyst
H2
Syn
Z product
H2O H2SO4 (catalytic)
Markovnikov
Mixed Carbocation Intermediate
(Br, Cl)
X2 / H2O (excess)
Markovnikov Anti
3-membered ring
Halohydrins
H-X (Cl, Br, I)
Markovnikov, Mixed, Carbocation
H-Br ROOR hv or heat
non-Markovnikov, Radical
Strong Base E2
Anti-periplanar TS
Zaitsev's Rule
Haloalkanes
Various Nucleophiles
SN2
INVERSION
Various SN2 Products
Br2
hv or heat
Radical Chain Process
Br ends up on more substituted C atom
Alkanes
Not shown:
Alkene NBS / hν → Haloalkene
Allylic radical intermediate
Most stable alkene product

20. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

B) (4 pts)



Recognize: The product is an aldehyde that can be made from a primary alcohol, ozonolysis of an alkene (breaks carbon-carbon bond so not possible here) or from an alkyne. Choose the latter because an alkyne can be made from the starting vicinal dihaloalkane using base, in this case three equivalents of $NaNH_2$ followed by mild acid workup because the product is a terminal alkyne.


Geminal Dihaloalkanes
Vicinal Tetrahaloalkanes
Alkynes
Terminal R-C≡C-H
1) NaNH2 2) RCH2X SN2
MAKES C-C BONDS
2H-X (Br,Cl,I) Markovnikov
(Br,Cl,I)
2X2
1) (sia)2BH 2) H2O2/HO⊖
non-Markovnikov enol intermediate
H2SO4, H2SO4, H2O
Markovnikov enol intermediate
Aldehydes/Ketones
R-C(=O)-H
R-C(=O)-R
R-C≡C-H Terminal
1) 3 NaNH2 2) HCl, H2O
R-C≡C-R Internal
2 NaNH2
Double E2
Vicinal Dihaloalkanes
1) O3 2) (CH3)2S
BREAKS C=C BONDS!!!
1) OsO4 2) NaHSO3/H2O
Syn
cyclic Osmate ester
Vicinal Diols
X2 (Br, Cl, ‡)
Anti
3-membered ring
Alkenes
1) BH3 2) H2O2 / HO⊖
non-Markovnikov Syn
4-membered ring transition state
Alcohols
H2O H2SO4 (catalytic)
Markovnikov Mixed Carbocation Intermediate
(Br,Cl)
X2 / H2O (excess)
Markovnikov Anti
3-membered ring
Halohydrins
Strong Base E2
Anti-periplanar TS
Zaitsev's Rule
H-X (Cl,Br,I)
Markovnikov, Mixed, Carbocation
H-Br ROOR hv or heat
non-Markovnikov, Radical
Haloalkanes
Various Nucleophiles
SN2 INVERSION
Various SN2 Products
Adsorption on metal surface
Pt°, Pd°, Ni°
H2
Syn
Adsorption on metal surface
Pt°, Pd°, Ni°
H2
Syn
Radical
Na° NH3
E product
Linear Catalyst
Z product
H2
Syn
Br2 hv or heat
Radical Chain Process
Br ends up on more substituted C atom
Alkanes
Not shown:
Alkene NBS / hν → Haloalkene
Allylic radical intermediate
Most stable alkene product

Alcohols → R–O–H

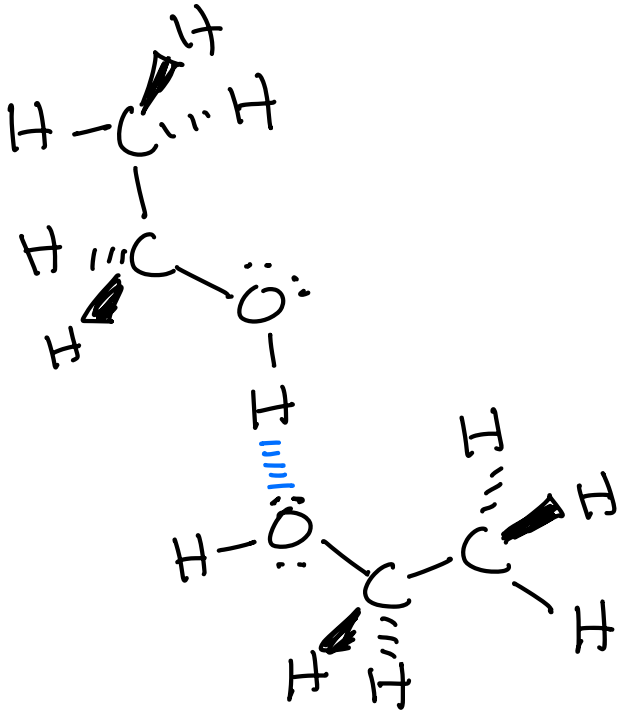


Table 10.1 **Boiling Points and Solubilities in Water of Five Groups of Alcohols and Hydrocarbons of Similar Molecular Weight**

Structural Formula	Name	Molecular Weight (g/mol)	Boiling Point (°C)	Solubility in Water
CH_3OH	Methanol	32	65	Infinite
CH_3CH_3	Ethane	30	−89	Insoluble
CH_3CH_2OH	Ethanol	46	78	Infinite
$CH_3CH_2CH_3$	Propane	44	−42	Insoluble
$CH_3CH_2CH_2OH$	1-Propanol	60	97	Infinite
$CH_3CH_2CH_2CH_3$	Butane	58	0	Insoluble
$CH_3CH_2CH_2CH_2OH$	1-Butanol	74	117	8 g/100 g
$CH_3CH_2CH_2CH_2CH_3$	Pentane	72	36	Insoluble
$HOCH_2CH_2CH_2CH_2OH$	1,4-Butanediol	90	230	Infinite
$CH_3CH_2CH_2CH_2CH_2OH$	1-Pentanol	88	138	2.3 g/100 g
$CH_3CH_2CH_2CH_2CH_2CH_3$	Hexane	86	69	Insoluble

General Rules of Solvents

Polar Protic

Polar protic solvents dissolve other polar molecules →

Polar protic solvents →

⇒ See the POTD for today for the main messages here

1) Solvation of cations and anions
2) Solvation of carbocations / anions in S_N1 / E1 reactions
3) Methanol dissolved in water
4) Why pentane and water do not mix

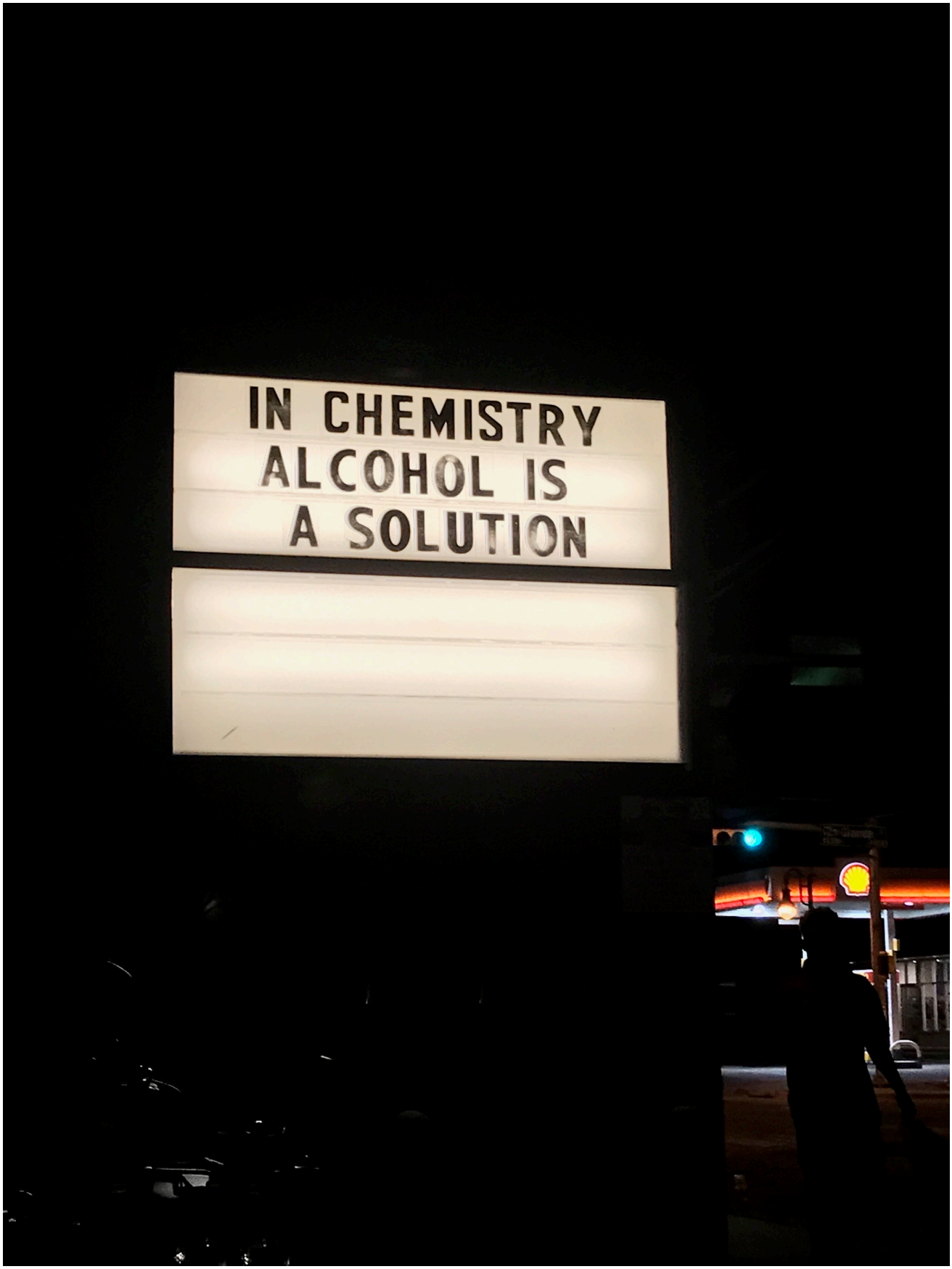

IN CHEMISTRY
ALCOHOL IS
A SOLUTION

Table of Nucleophiles

Strong Nucleophiles

Br^-, I^-, $R\text{-}S^-$, $H\text{-}S^-$, $N{\equiv}C^-$, N_3^-

$R\text{-}C{\equiv}C^-$, $R\text{-}O^-$, $H\text{-}O^-$ **Strong Bases**

Medium Nucleophiles

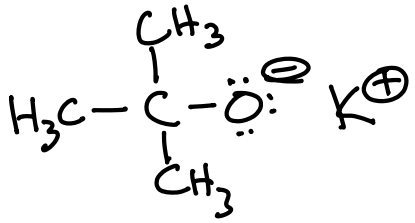
$R\text{-}CO_2^-$, R-S-H, R_2S,
NH_3, RNH_2, R_2NH, NR_3

Weak Nucleophiles

$R\text{-}CO_2H$, R-O-H, H_2O **Very Weak Bases**

Special Case

***Tert*-Butoxide ($tBuO^-$) is a strong base, but is not a nucleophile due to steric hindrance.**



"KOtBu"
or
"$tBuO^-$"

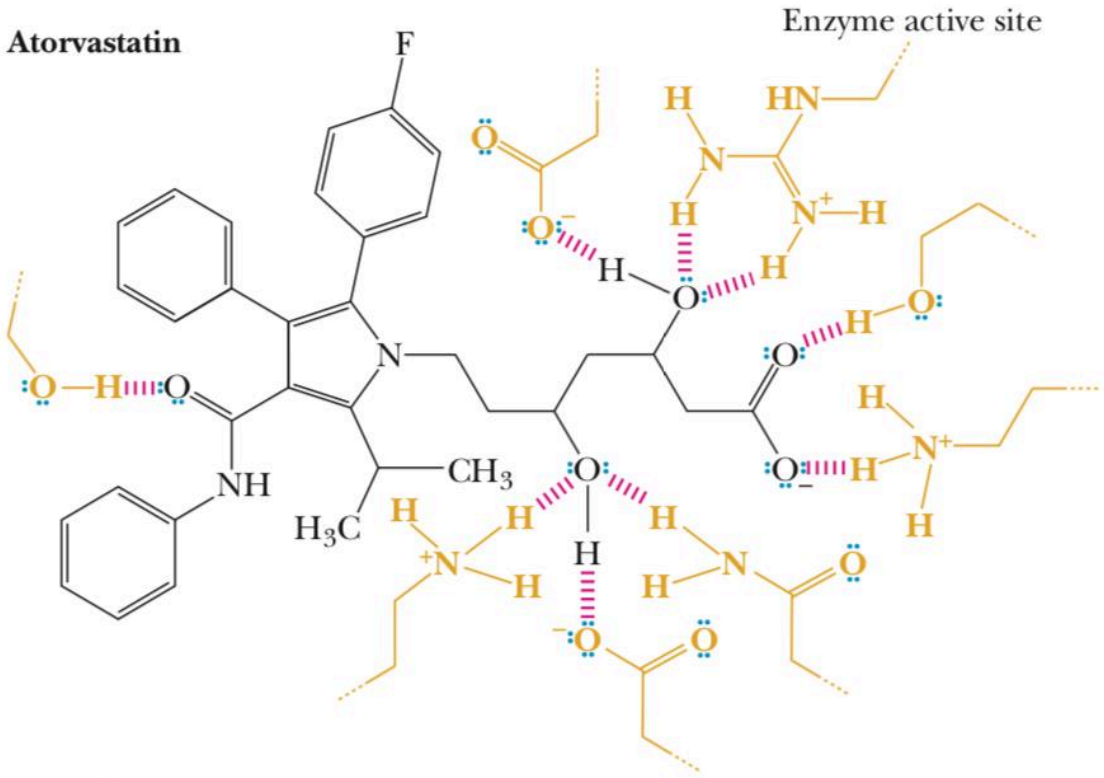


Figure 2

Hydrogen bonding (shown in red) between atorvastatin and the functional groups at the active site of the enzyme HMG-CoA reductase. The nine hydrogen bonds (shown in red), many of which involve hydroxyl groups on atorvastatin or the enzyme surface, help to provide the specificity that directs the binding of the drug to its target enzyme.

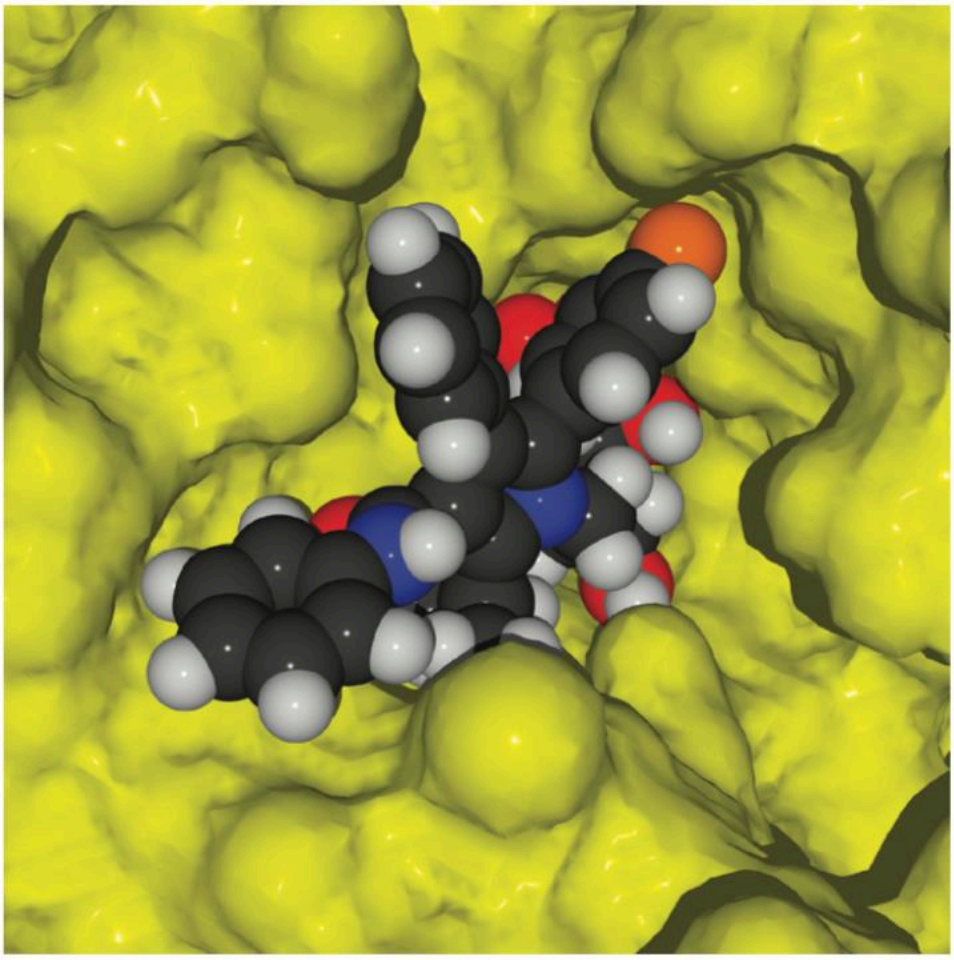


Figure 1

A space-filling model of the cholesterol-lowering drug atorvastatin (Lipitor) bound to the active site of its enzyme target HMG-CoA reductase (shown as a yellow surface). The shape of the drug is complementary to the active site of the enzyme.

<u>Organic Chemistry</u> is the study of carbon-containing molecules.

This class has two points.

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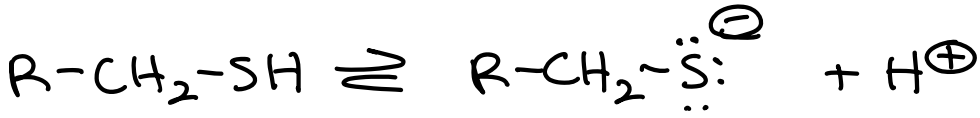
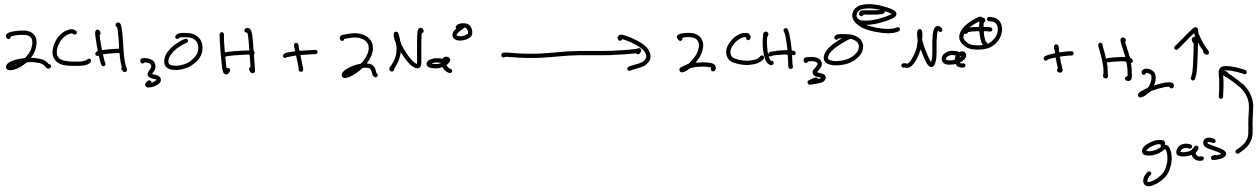
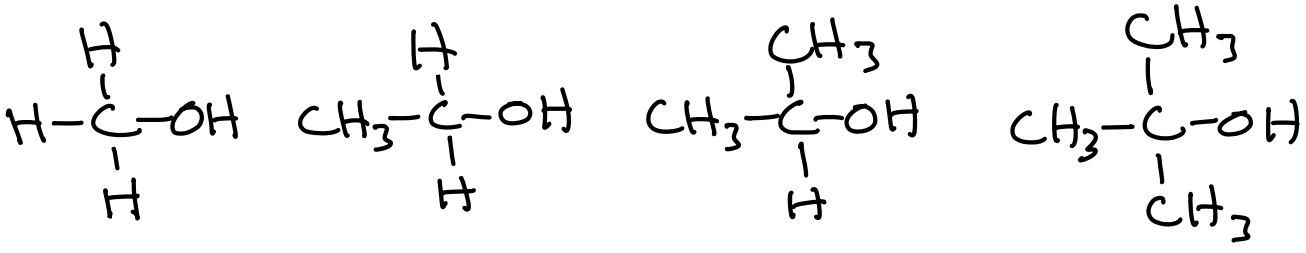
Alcohols → Acidity and Basicity



Notice This → $Na^{\circ}, K^{\circ}, Li^{\circ}$



Alcohols → Reaction mechanisms depend on the number of alkyl groups attached on the C atom of C-OH bond.

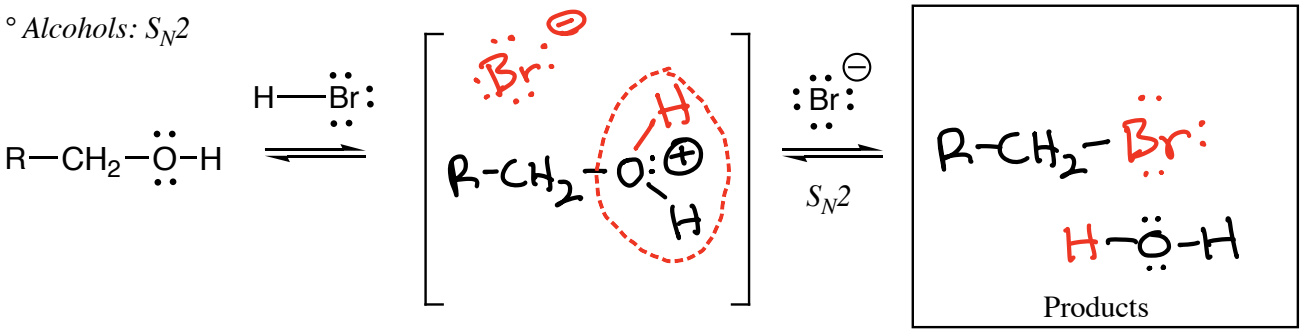


The -OH is not a leaving group but several reactions involve conversion of the -OH group into a good leaving group

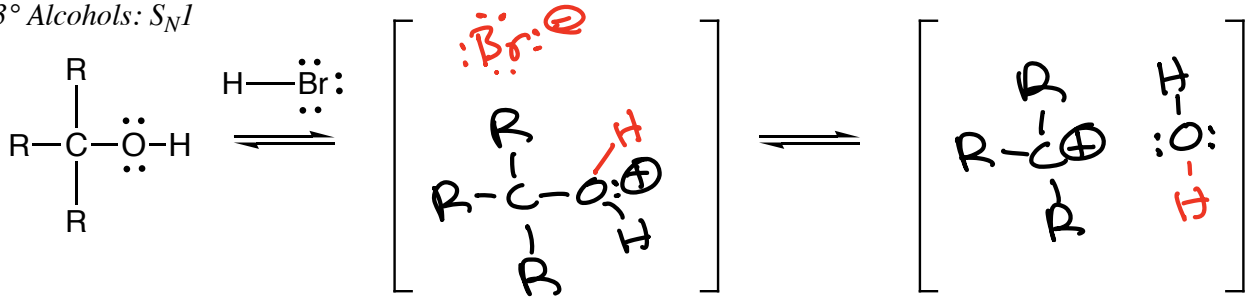
Recall, the -OH group is a weak nucleophile and weak base (in strong acid)

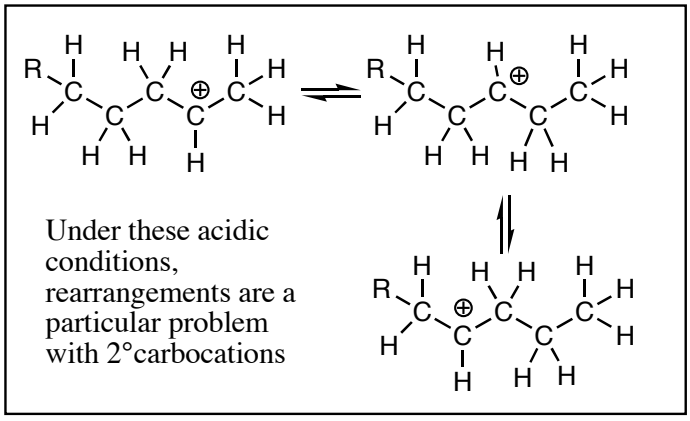
Alcohols + H-X

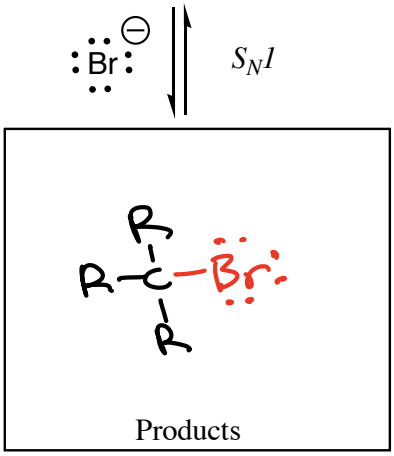
1° Alcohols: S_N2



2°/3° Alcohols: S_N1







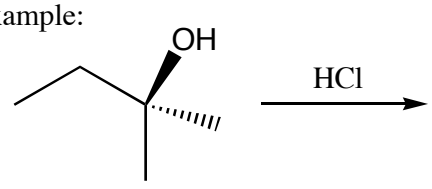
Summary:

Reaction of primary alcohols → S_N2
Reaction of secondary/tertiary alcohols → S_N1
The –OH group is converted to a good leaving group by protonation

Regiochemistry:

Stereochemistry:

Example:



Alcohols + H-X

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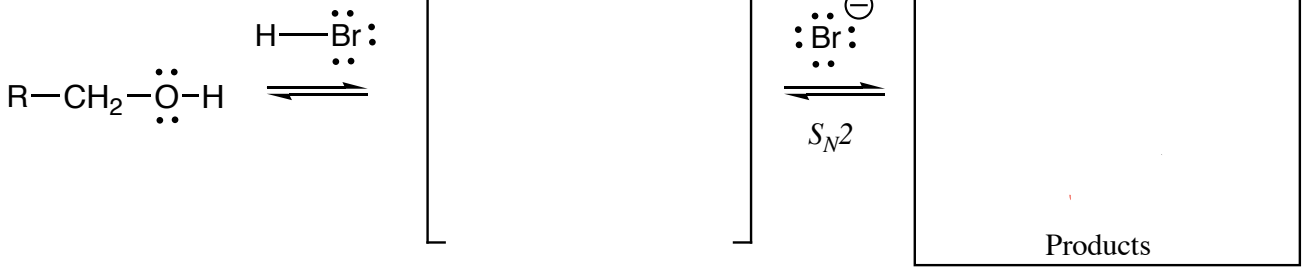
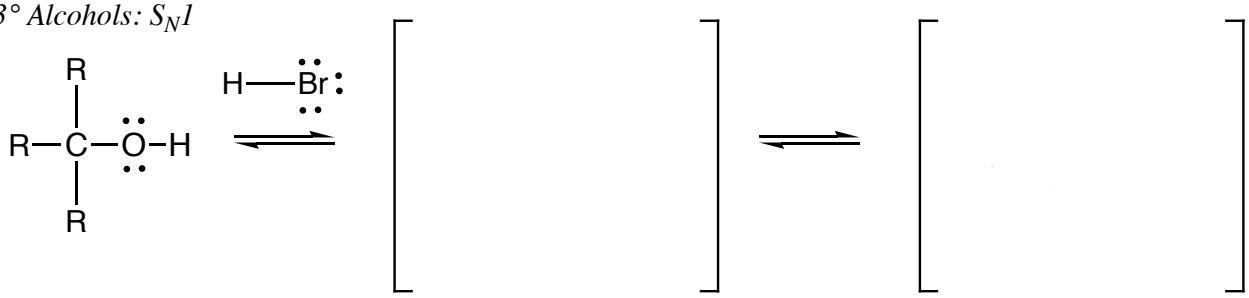
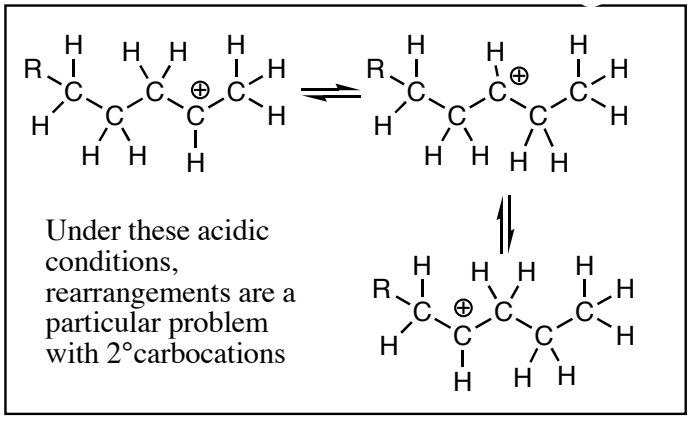
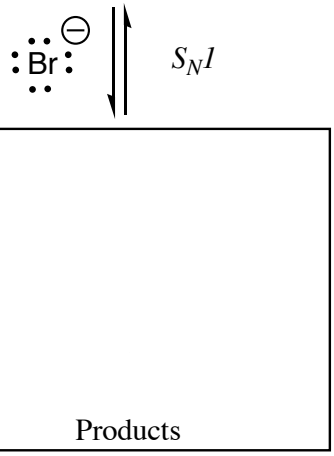


2°/3° Alcohols: S_N1







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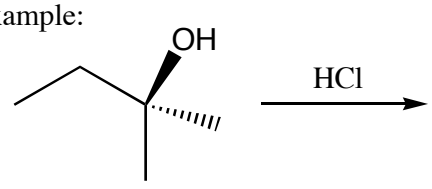
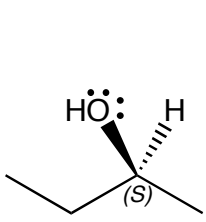
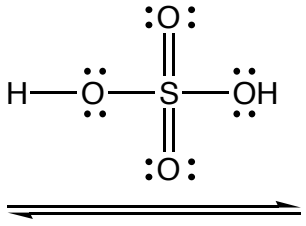
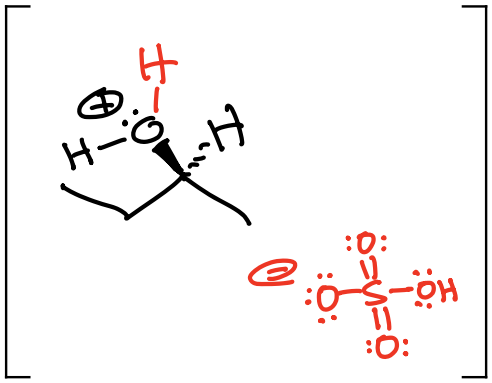


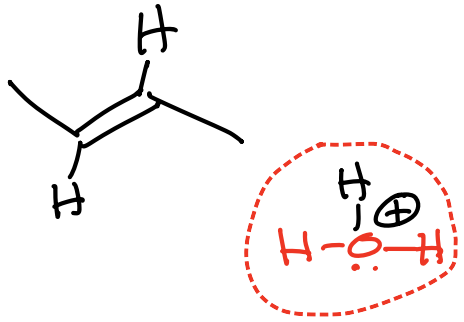
2° or 3° Alcohol Dehydration



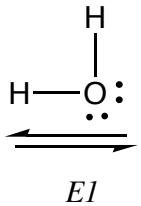
2° or 3° Alcohols



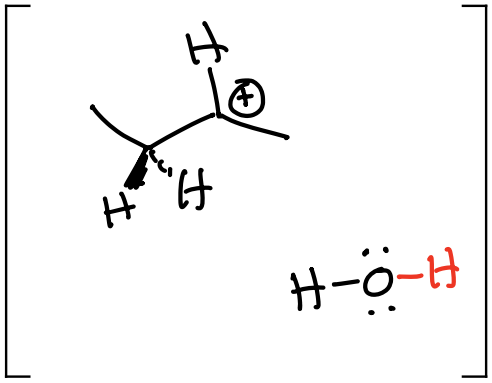




Products



E1

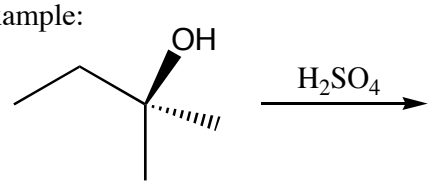


Summary: The OH group is protonated in strong acid to make a good leaving group (H_2O), which breaks a bond to give a carbocation that has a proton taken away → E1 (No S_N1!)

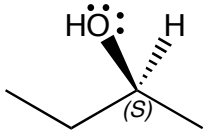
Regiochemistry:

Stereochemistry:

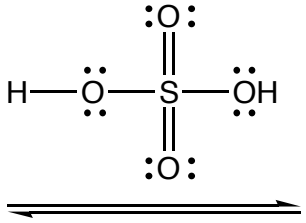
Example:

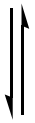


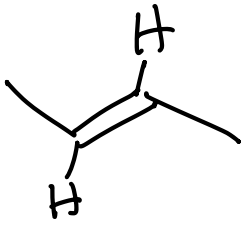
2° or 3° Alcohol Dehydration



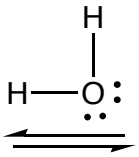
2° or 3° Alcohols







Products



E1

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Regiochemistry:

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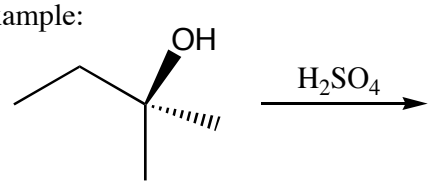
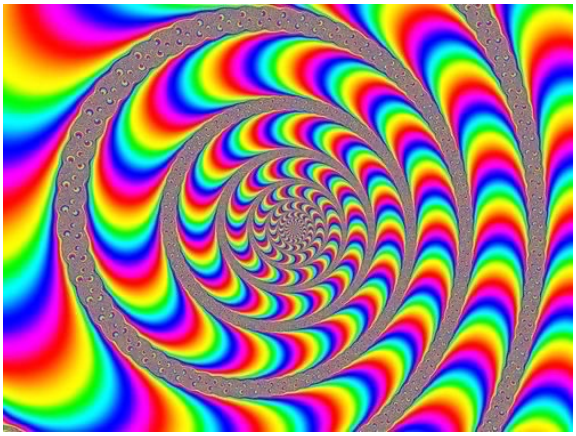
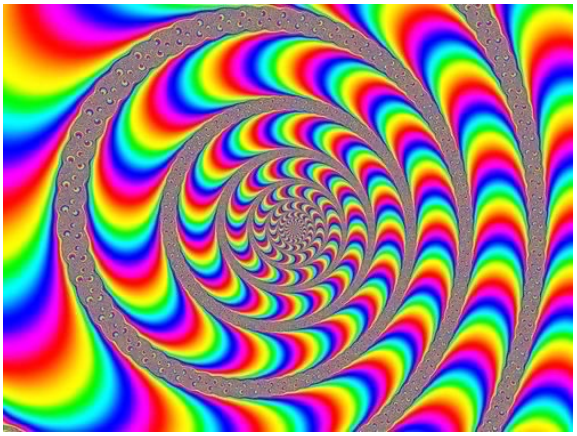
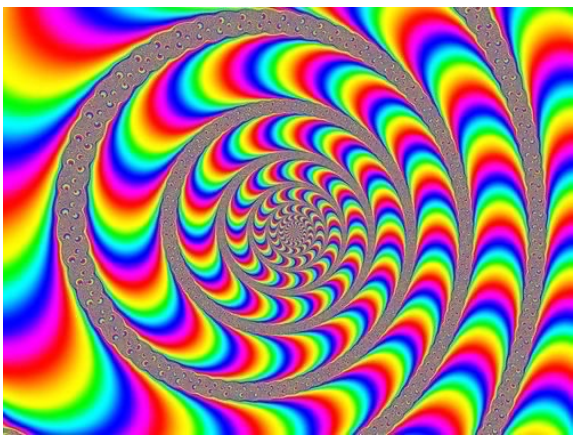
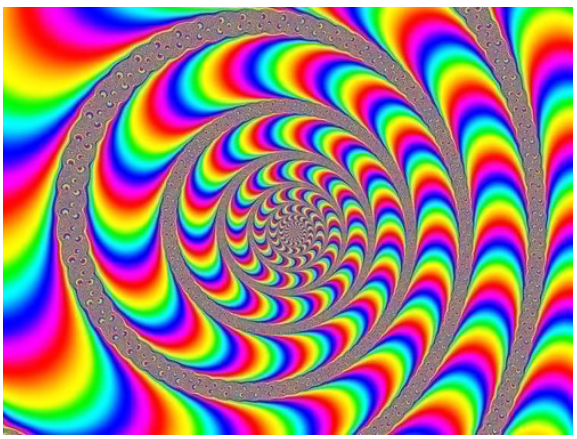


Flashback!!

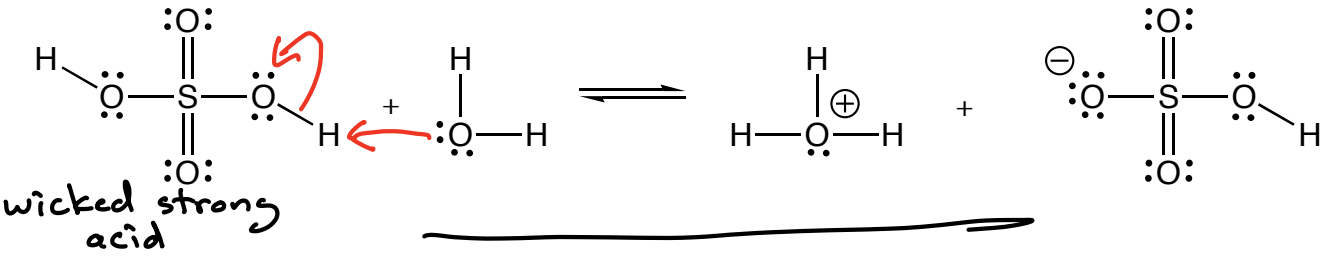


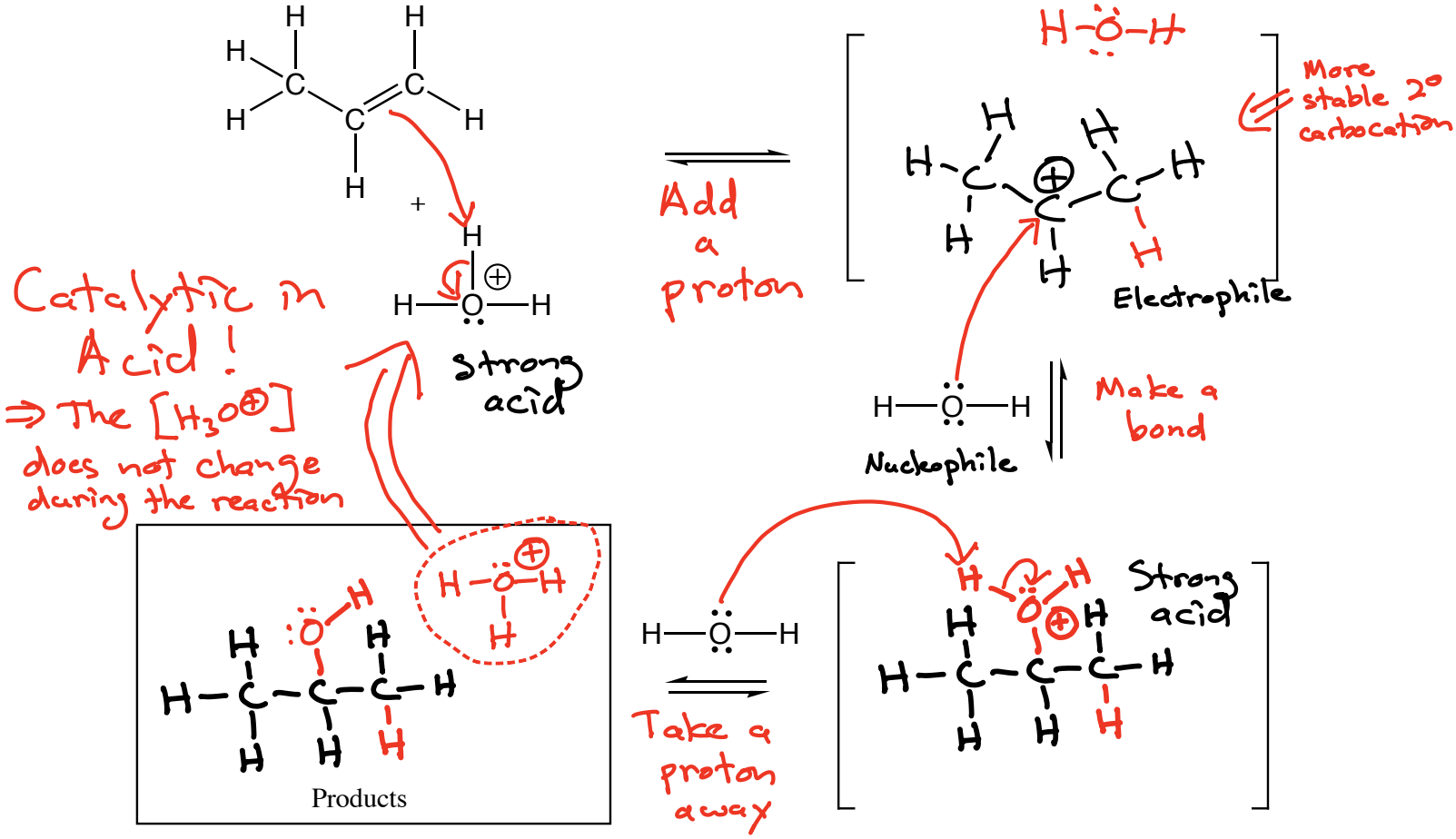






Acid-catalyzed Hydration of an Alkene



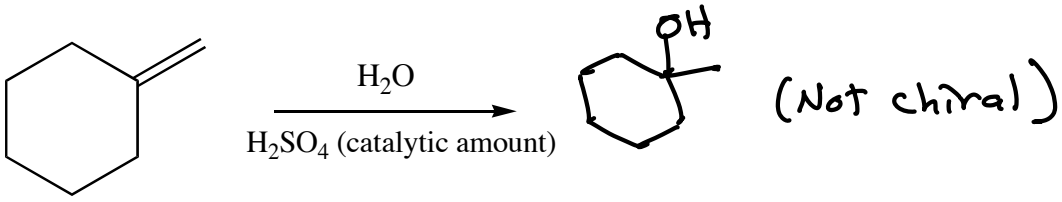


Summary: Proton adds to make a carbocation intermediate, water attacks to make a new bond, take a proton away to make the product alcohol. Catalytic in $H_3O^{\oplus}$

Regiochemistry: Markovnikov's Rule

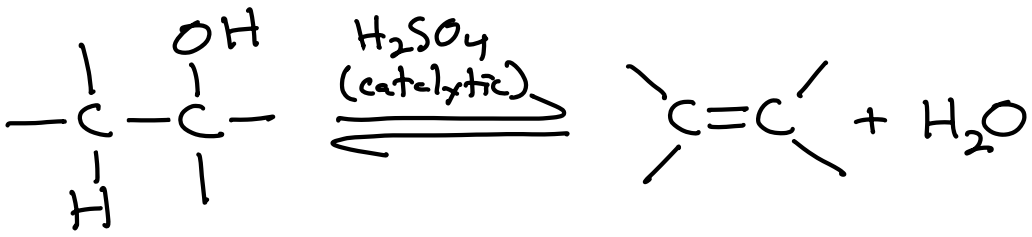
Stereochemistry: Mixed (time capsule)

Example:



-OH on more substituted C atom ⇒ Markovnikov's Rule

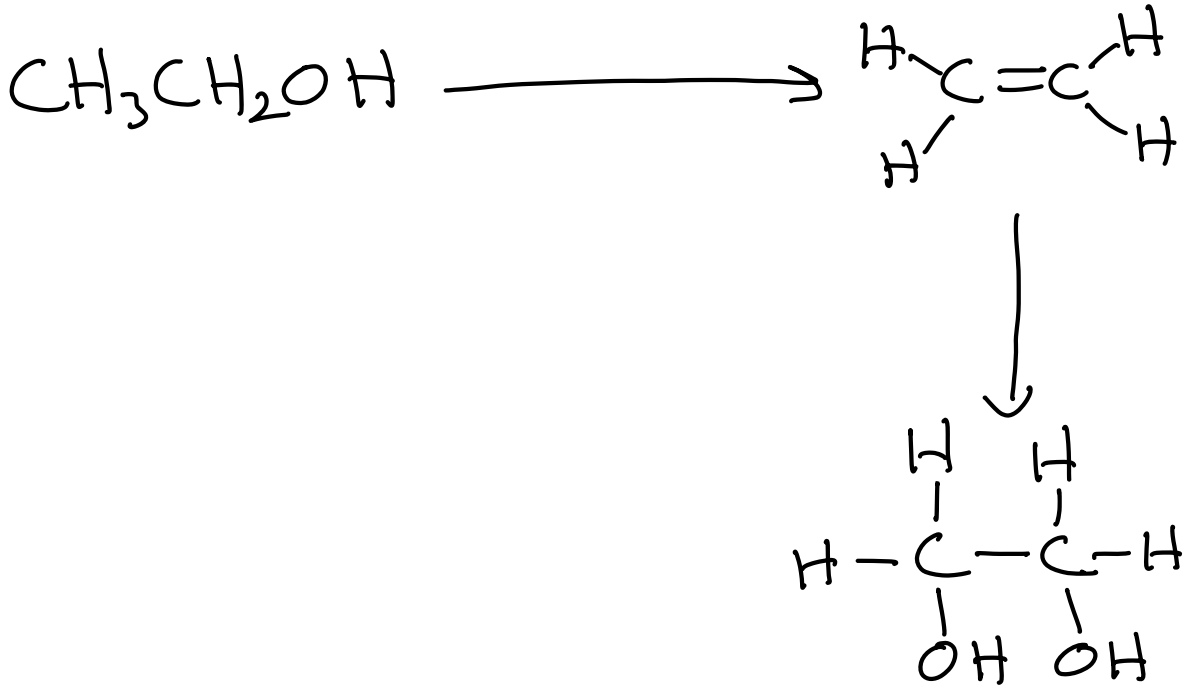
Microscopic Reversibility →



Le Chatlier's Principle ⇒

If we add water →

If we remove the water as it is formed →


CH3CH2OH
H
C
C
H
H
H
H
H
H
C
C
H
OH
OH

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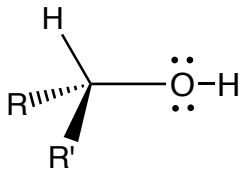
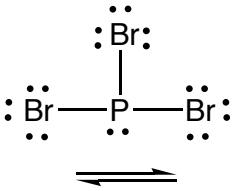
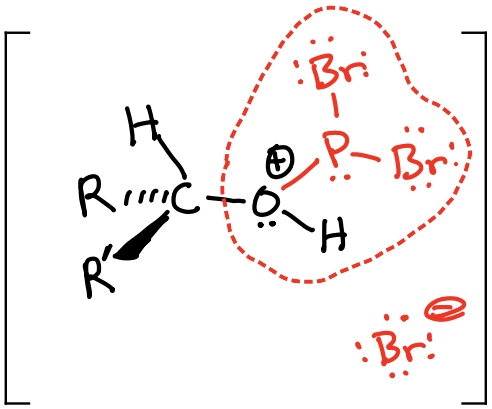
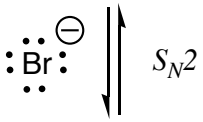
Alcohols + PBr_3



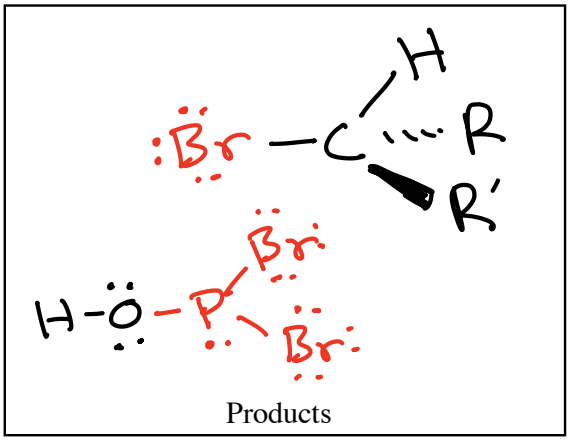
1° or 2° Alcohols







S_N2



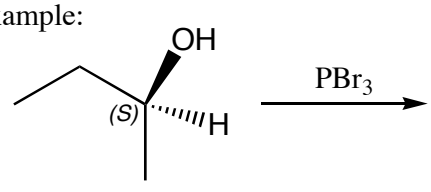
Products

Summary: 1° or 2° alcohols react with PBr_3 via an S_N2 reaction at the P atom to create a great leaving group that undergoes an S_N2 reaction with $Br^{\ominus}$ at the C atom

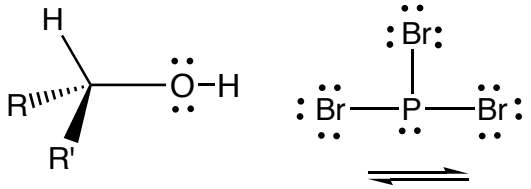
Regiochemistry:

Stereochemistry:

Example:



Alcohols + PBr_3



1° or 2° Alcohols

S_N2

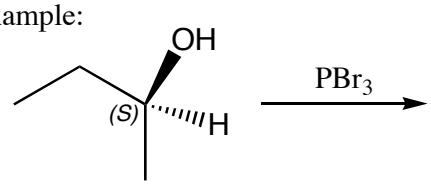
Products

Summary: 1° or 2° alcohols react with PBr_3 via an S_N2 reaction at the P atom to create a great leaving group that undergoes an S_N2 reaction with $Br^{\ominus}$ at the C atom

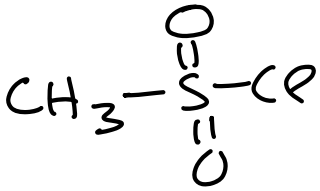
Regiochemistry:

Stereochemistry:

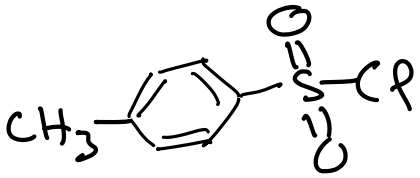
Example:



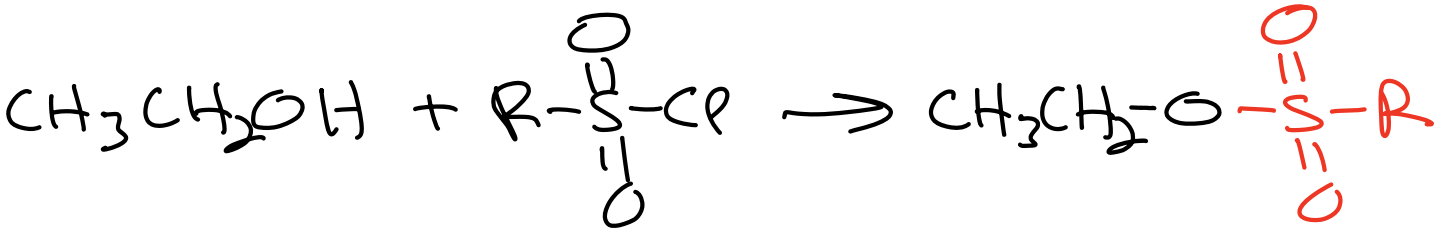
Alkyl Sulfonates



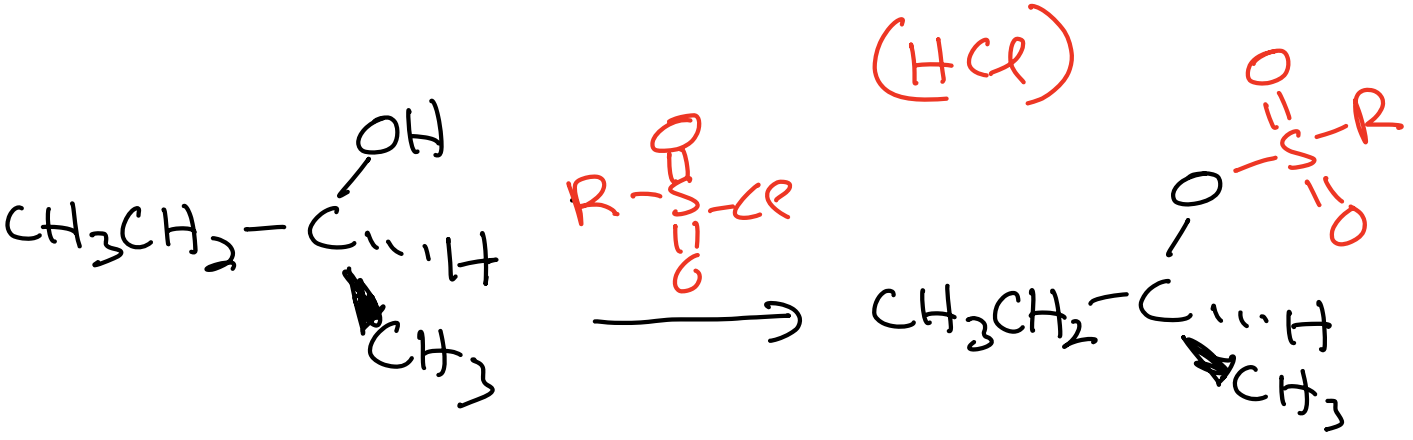
Methanesulfonyl Chloride

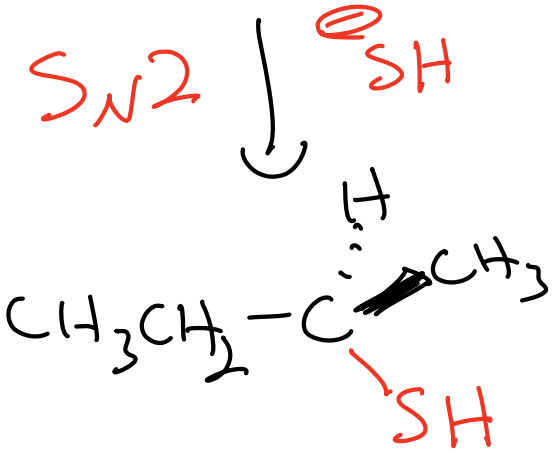


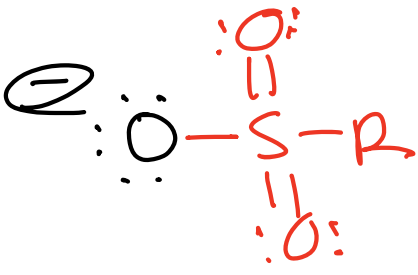
p-Toluenesulfonyl Chloride

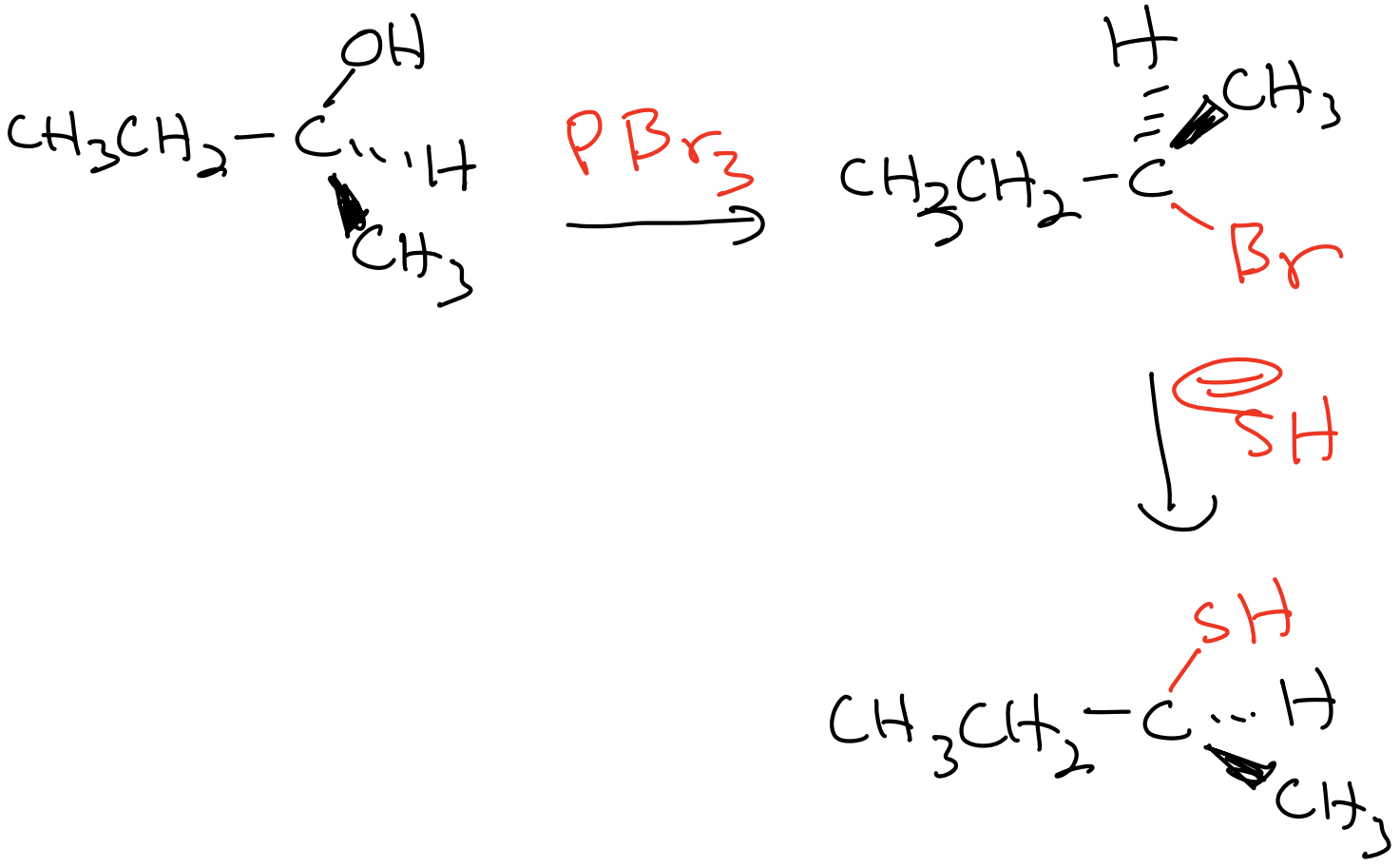


Stereochemistry







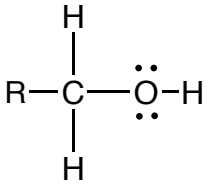


⟹ You can net invert or retain the stereochemistry of a chiral alcohol taking part in SN2 reactions

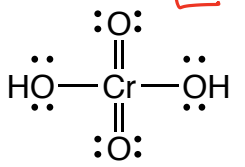
Chromic Acid Oxidation of Alcohols

Called "Jones Reagent" ($CrO_3 + H_2O$ or K_2CrO_7) + H_2SO_4

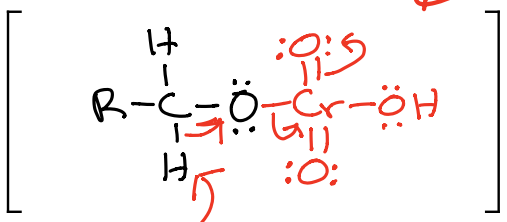
Not responsible for first step

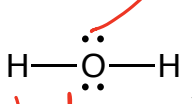


1° Alcohols



"H_2CrO_4" or "Chromic Acid"

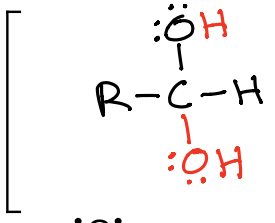




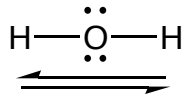
Take a proton away and break a bond

Aldehyde

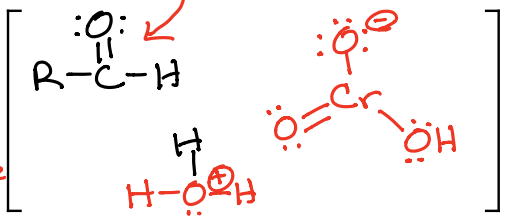
Not responsible for this step

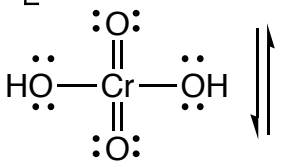


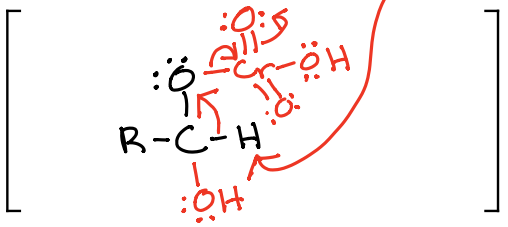
Called a geminal diol

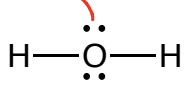


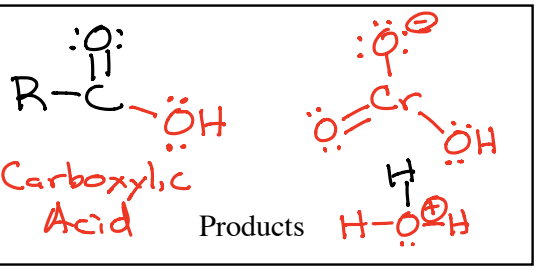
Water reacts with aldehyde – will learn next semester







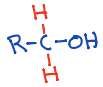




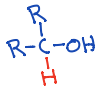
Carboxylic Acid

Products

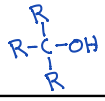
Summary:



1° alcohols ⇒ Carboxylic Acid → 



2° alcohols ⇒ Ketone → 

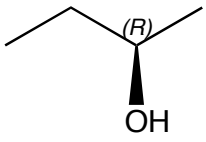


3° alcohols ⇒ NO REACTION

Regiochemistry: N/A

Stereochemistry: N/A

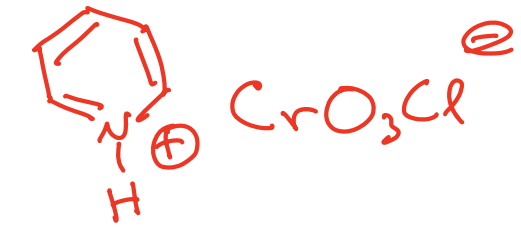
Example:



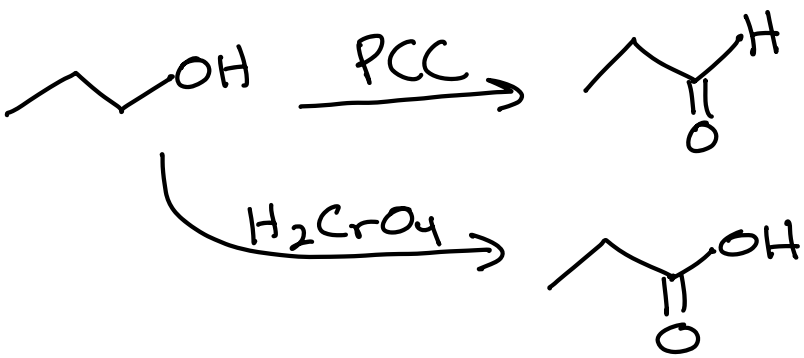
H_2CrO_4

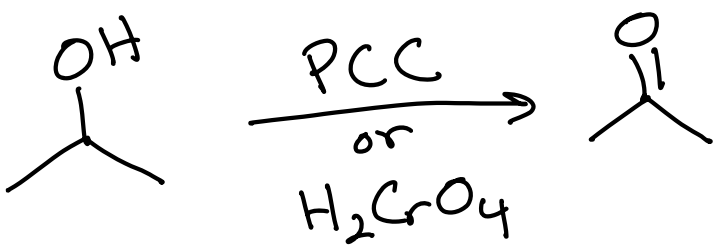
Ketone

A chromic acid-like reagent WITHOUT WATER will stop at the when using a as starting material



PCC





<u>Organic Chemistry</u> 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 things on the planet!!

Water is essential for life, you will learn why water has such special properties. 8/27/25

You will learn the secret structural reason proteins, the most important molecular machines in our bodies, can support the chemistry of life. 9/10/25

You will learn why when you take Advil for pain, exactly half of what you take works, and the other half does nothing. 9/24/25

You will learn how toothpaste works. 10/6/25

You will learn how a single chlorofluorocarbon refrigerant molecule released into the atmosphere can destroy many, many ozone molecules, leading to an enlargement of the ozone hole. 10/29/25

You will learn how medicines like Benadryl, Seldane, and Lipitor work. 11/10/25

You will learn how Naloxone is an antidote for an opioid overdose.

You will learn why Magic Johnson is still alive, decades after contracting HIV.

You will learn how MRI scans work.

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

You will learn how to understand movies of reaction mechanisms like alkene hydration. 10/8/25

You will learn reactions that once begun, will continue reacting such that each product molecule created starts a new reaction until all the starting material is used up. 10/29/25

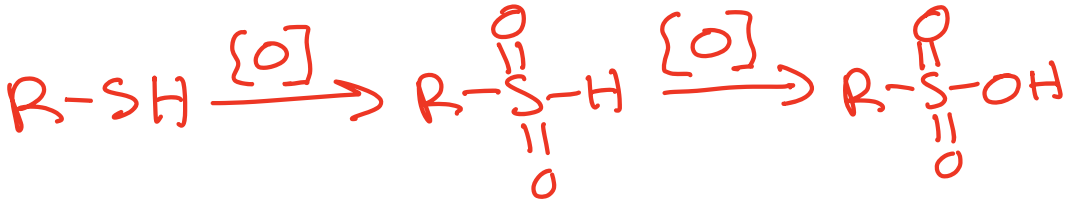
You will learn reactions that can make antifreeze from vodka. 11/12/25

You will learn a reaction that can make nail polish remover from rubbing alcohol.

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.

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.

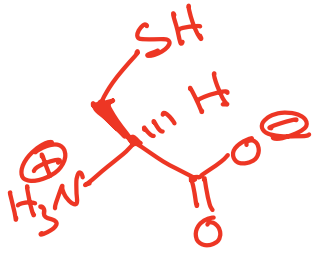
Thiols → R–S–H



In the presence of O_2:

$$2\ R\text{-}SH + \tfrac{1}{2}O_2 \longrightarrow R\text{-}S\text{-}S\text{-}R + H_2O$$

Dissulfide Bond



The amino acid cysteine (Cys)

Dissulfide bonds between cysteine residues that are far apart in the sequence, but overlap in three-dimensions, provide covalent links that stabilize folded protein structures