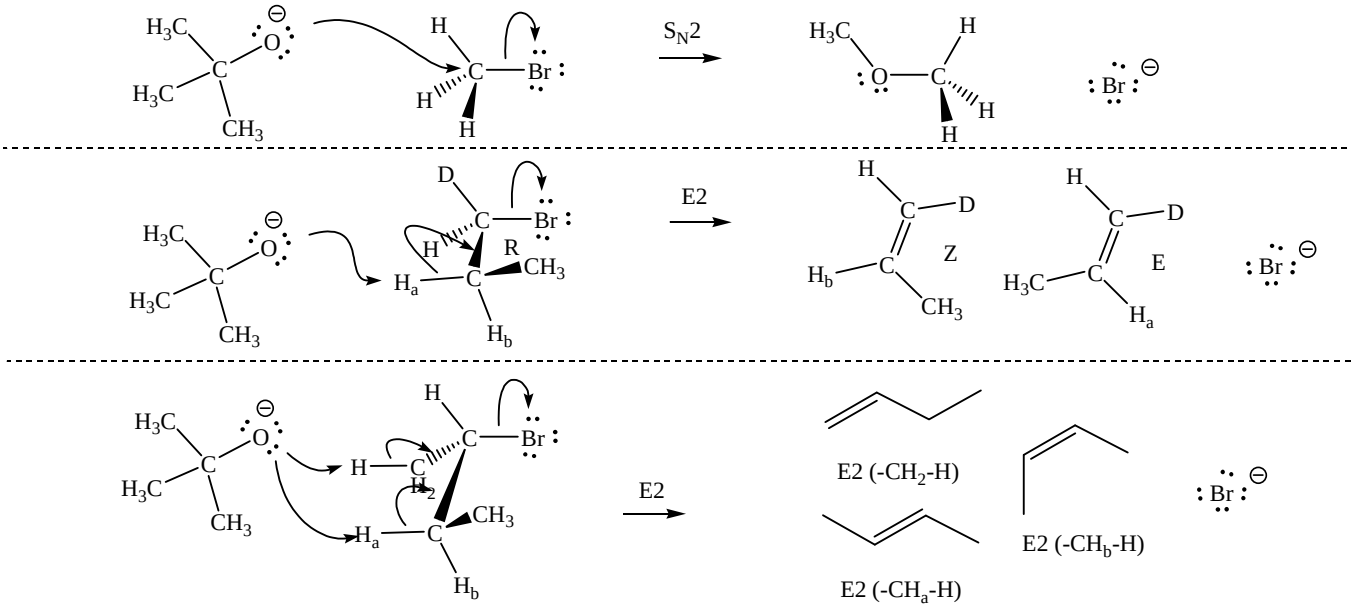
Organic Reactions Summary
Alkenes, alkynes and variations

For Use as a Study Guide

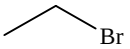
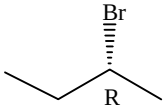
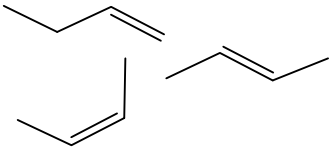
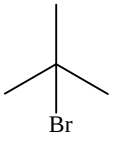
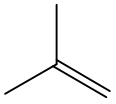
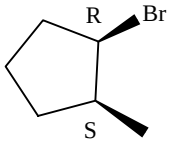
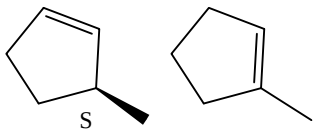
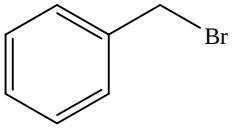
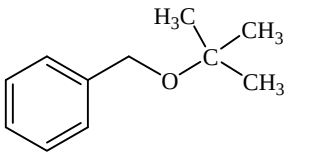
Beauchamp

Making alkenes and alkynes

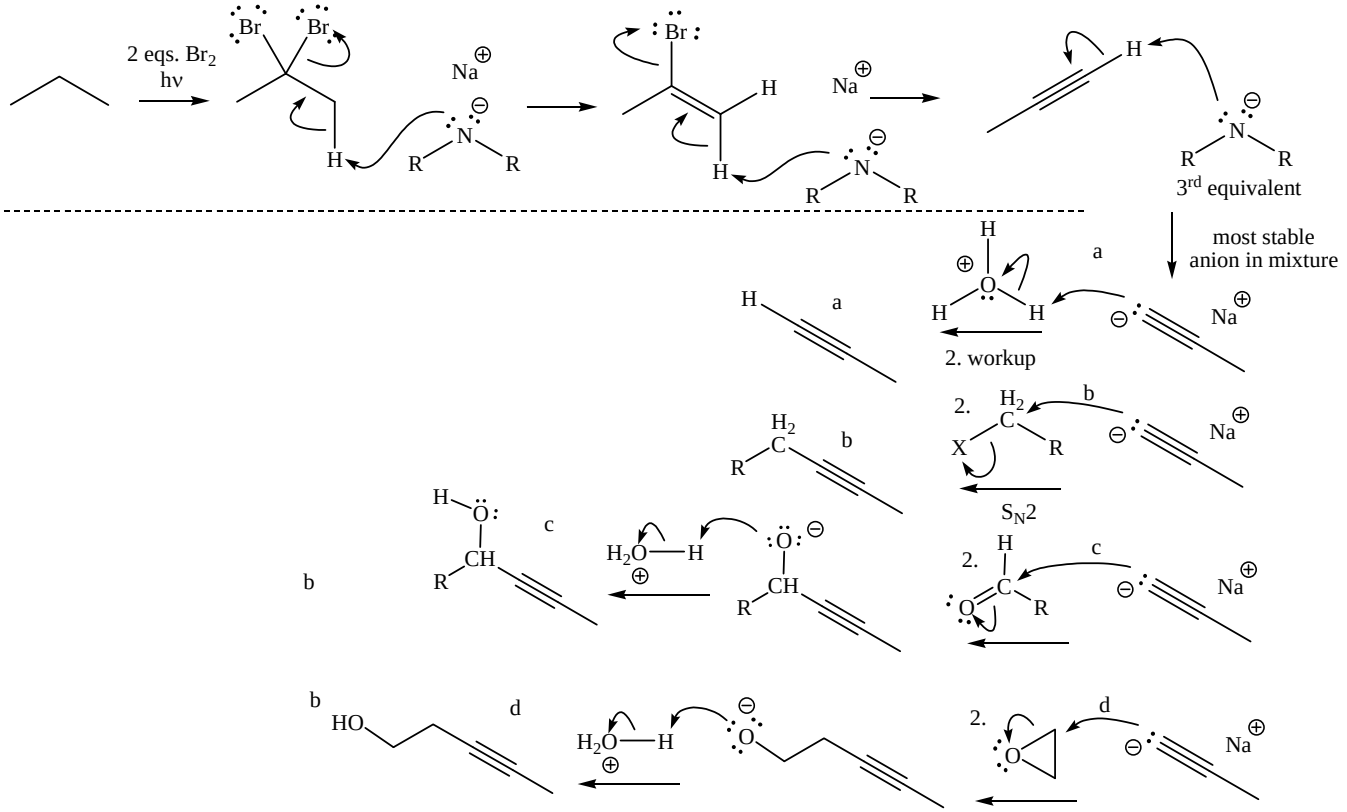
a. mechanism using potassium t-butoxide, $KOC(CH_3)_3$, S_N2 at and E2 at 1°, 2° and 3° RBr,



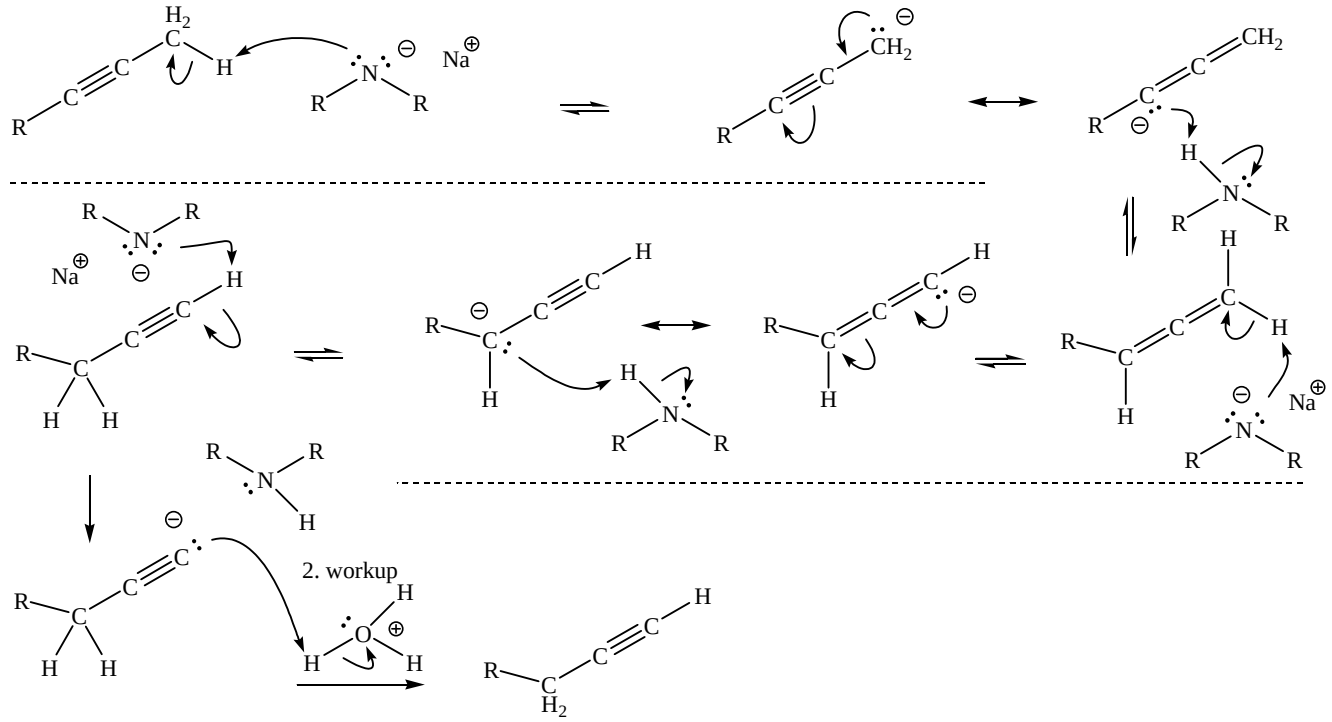
Example reactions

	$KOC(CH_3)_3$	 E2 > S_N2 anti elimination
	$KOC(CH_3)_3$	 E2
	$KOC(CH_3)_3$	 E2
	$KOC(CH_3)_3$	 E2
	$KOC(CH_3)_3$	 S_N2 no other option

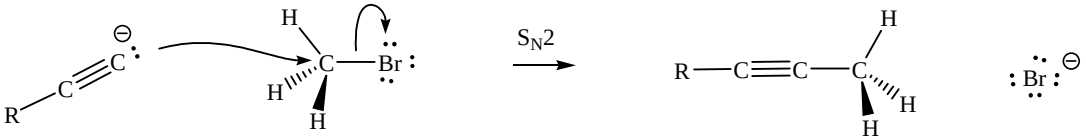
b. Double elimination from dibromoalkanes to form alkynes and terminal acetylides used in many additional reactions (S_N2 with RBr, C=O addition to aldehyses and ketones, and reaction with epoxides)

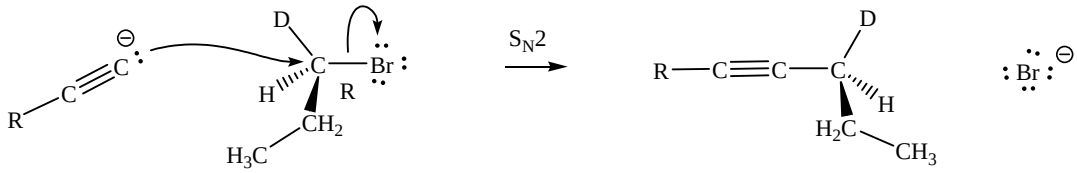


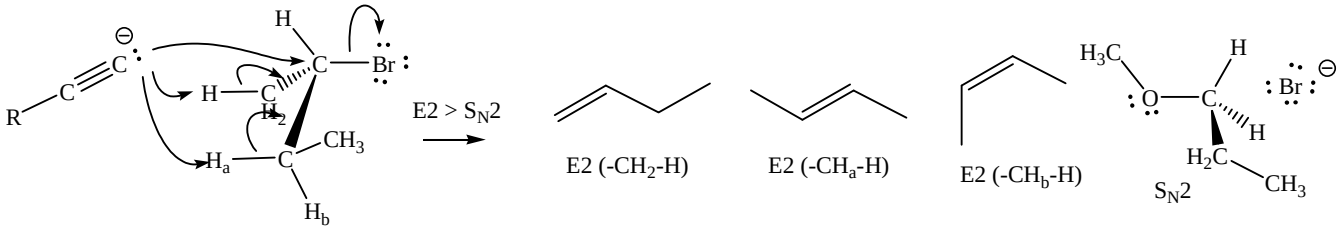
The zipper reaction moves a triple bond in an unbranched linear chain to the end and allows all of the above reactions.



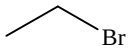
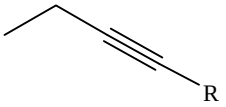
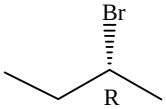
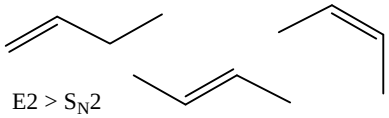
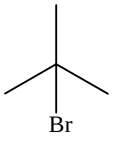
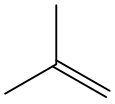
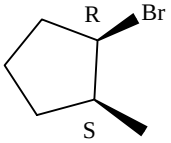
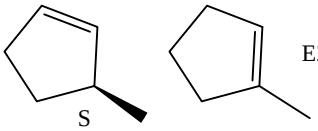
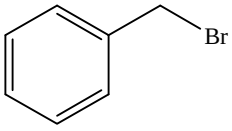
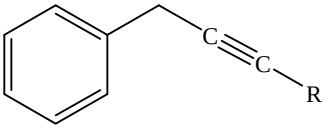
c. mechanism using NaCC-R to make a bigger alkyne, S_N2 at methyl, 1° and 2° RBr and only E2 at 3° RBr,



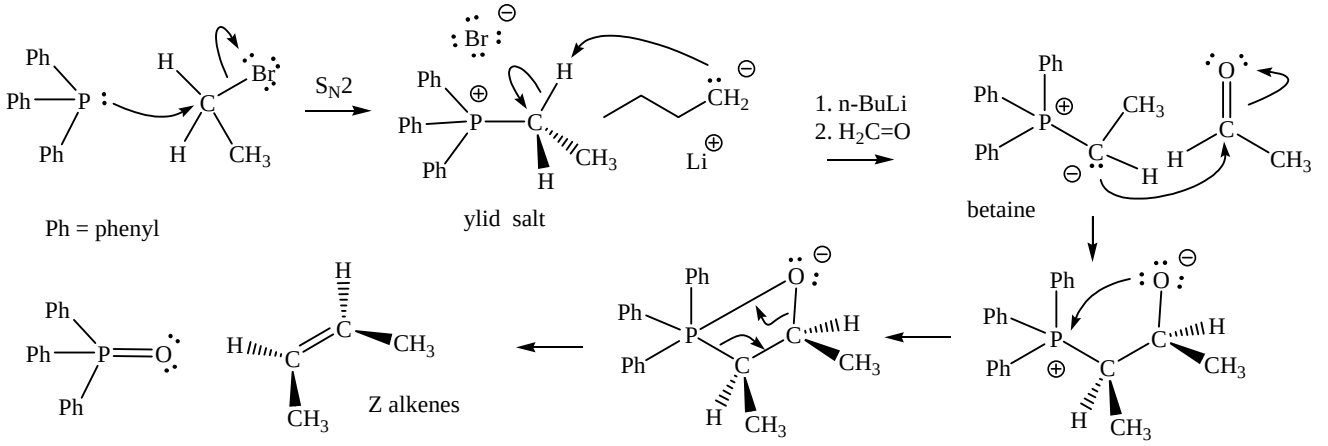


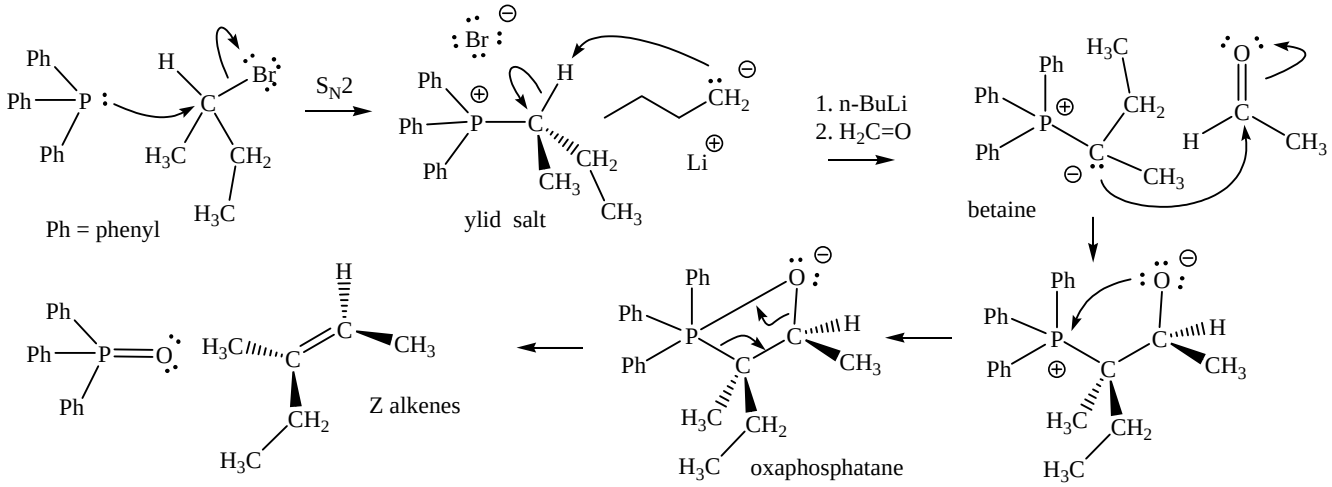


Example reactions

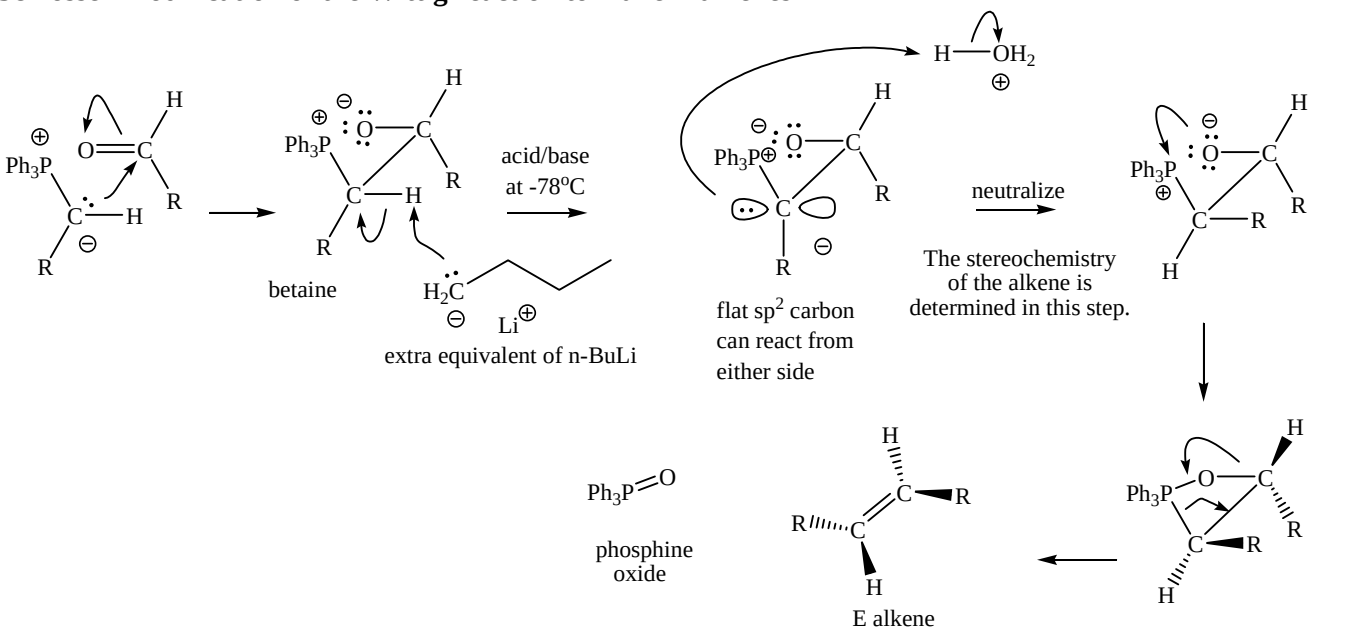
	NaCC-R →	 S_N2 inversion of configuration
	NaCC-R →	 $E2 > S_N2$
	NaCC-R →	 E2
	NaCC-R →	 $E2 > S_N2$
	NaCC-R →	 achiral S_N2

d. mechanism using triphenylphosphine to make triphenylphosphonium salt, S_N2 at methyl, 1° and 2° RBr and only E2 at 3° RBr, used to make a triphenylphosphonium ylid to make Z and E alkenes with aldehydes and ketones.

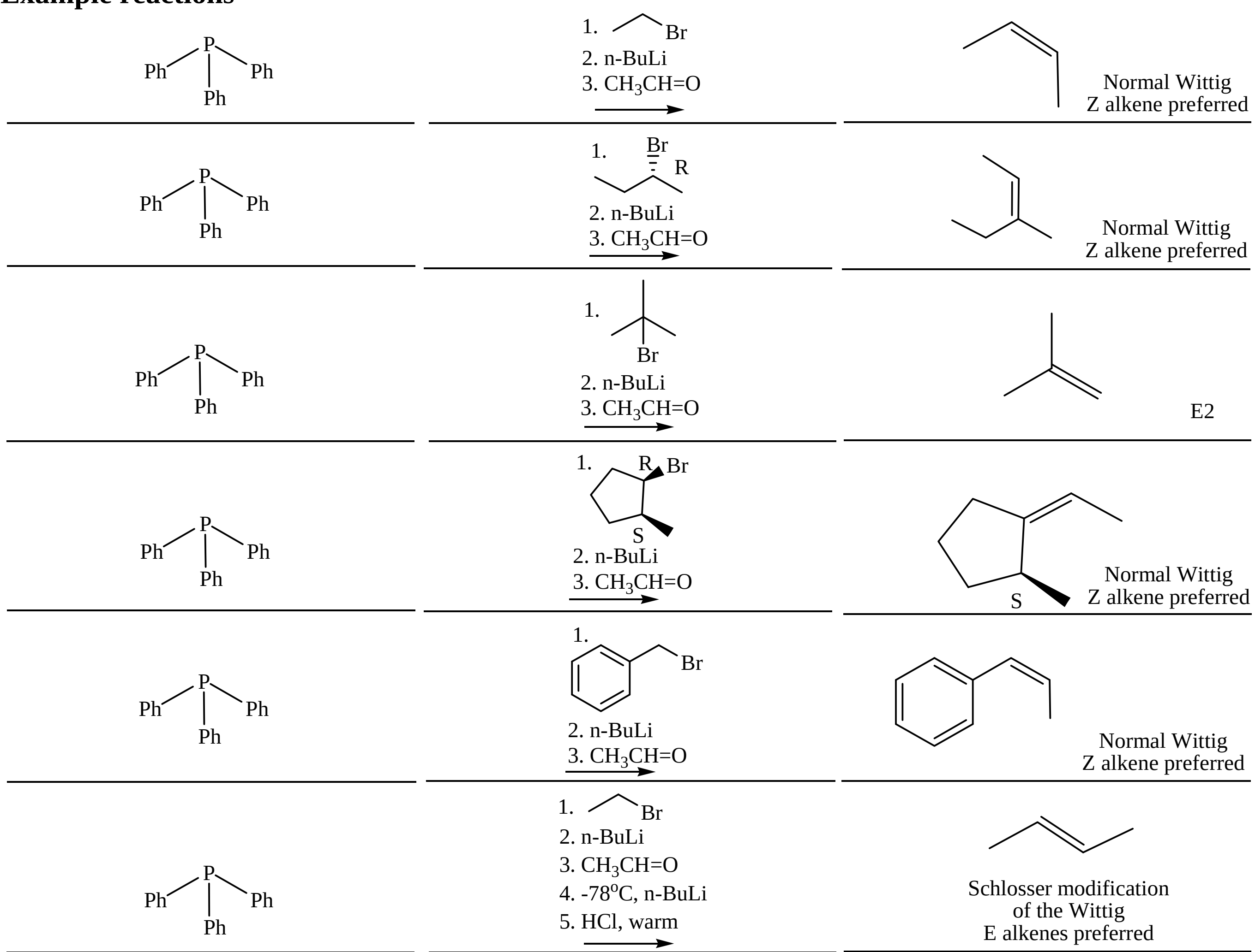




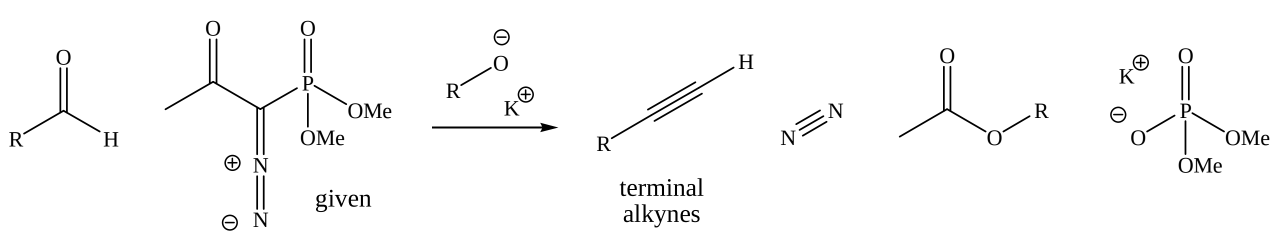
Schlosser Modification of the Wittig reaction to make E alkenes



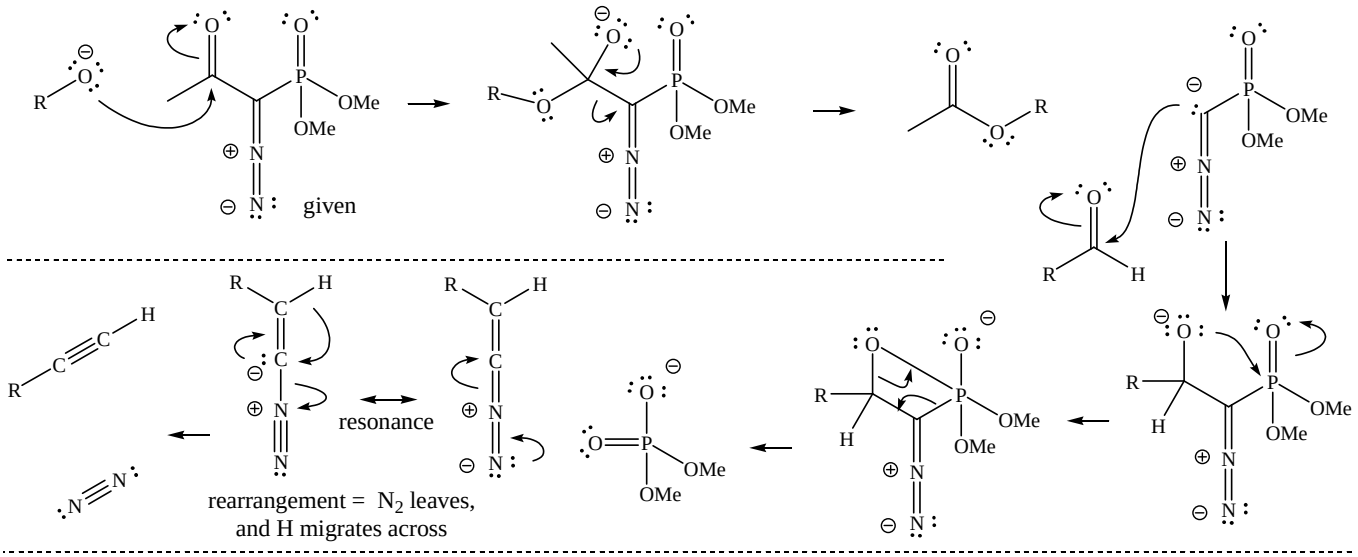
Example reactions



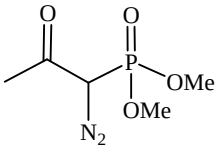
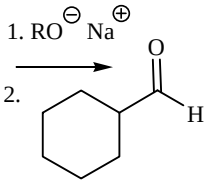
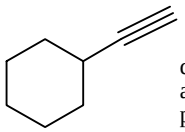
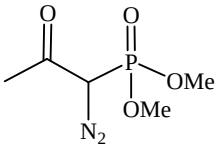
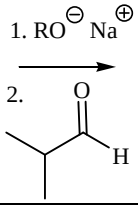
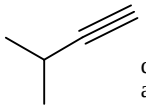
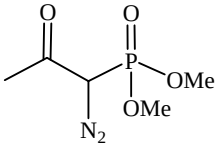
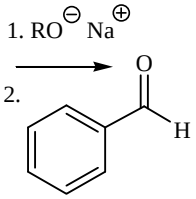
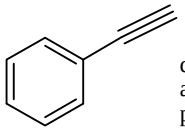
e. Ohira-Bestmann modification of the Seyferth-Gilbert reaction (makes terminal alkynes from aldehydes and a special ‘Wittig’ reagent). Overall reaction from aldehyde to the terminal alkyne – simplified Ohira-Bestmann reaction



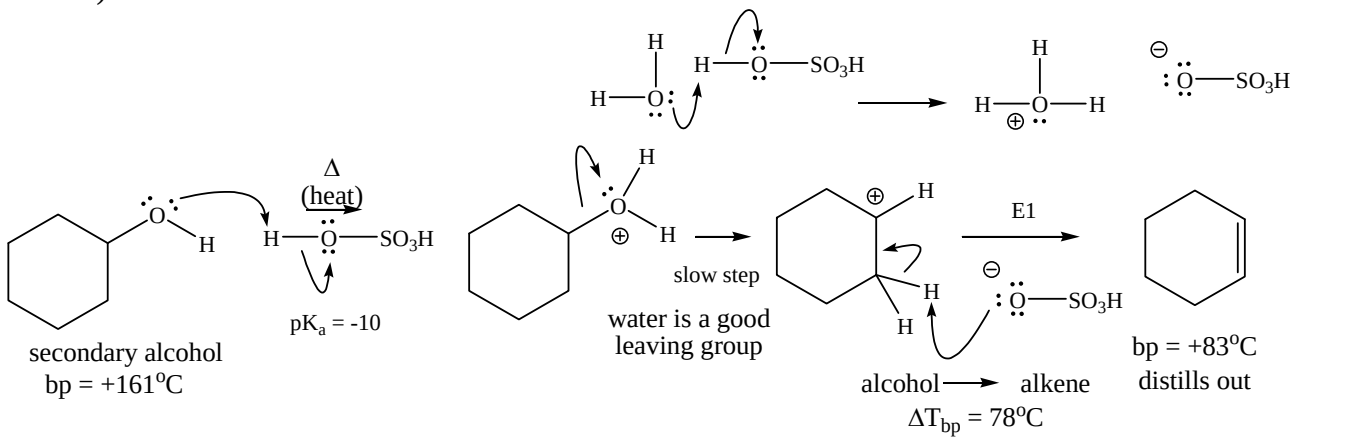
Possible mechanism – with mechanism details

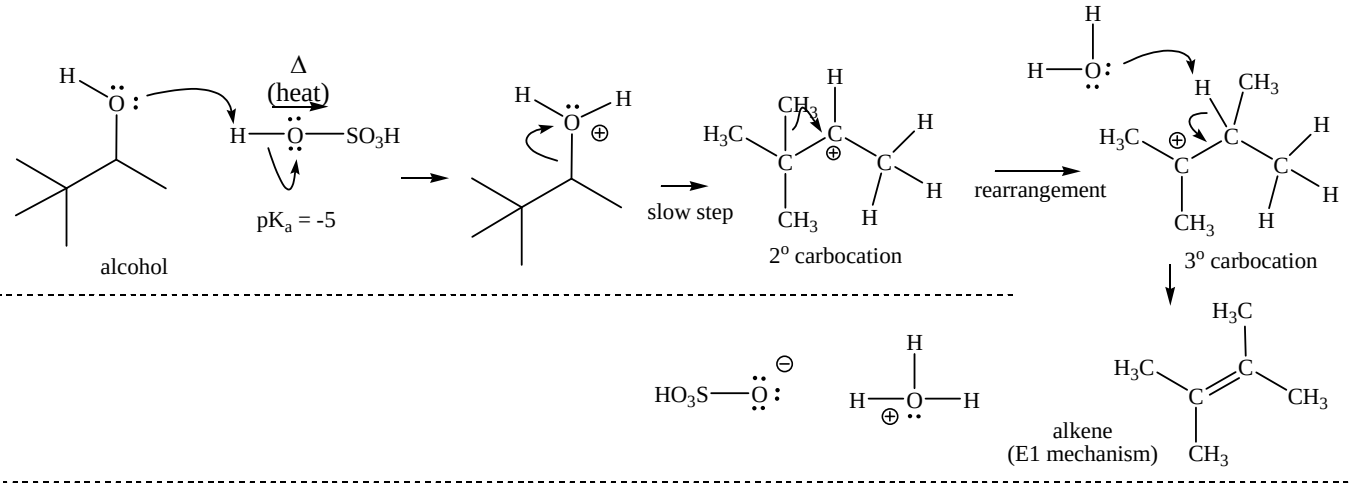


Example reactions

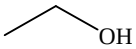
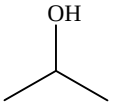
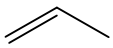
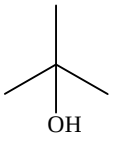
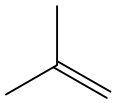
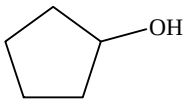
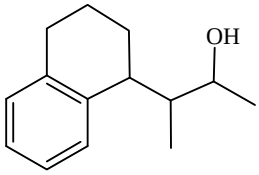
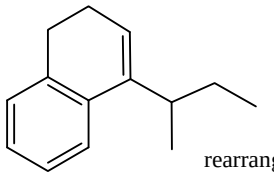
		 difficult to make alkyne at branch point
		 difficult to make alkyne at branch point
		 difficult to make alkyne at branch point

f. ROH with sulfuric acid / heat. Synthesis of alkenes (our only useful E1 reaction. Rearrangement is possible).



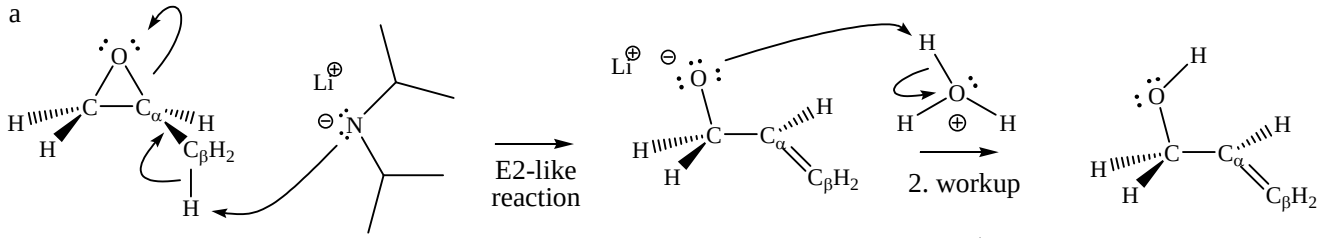


Example reactions

	H_2SO_4 / Δ →	 probably E2
	H_2SO_4 / Δ →	 E1
	H_2SO_4 / Δ →	 E1
	H_2SO_4 / Δ →	 E1
	H_2SO_4 / Δ →	 E1 rearrangement

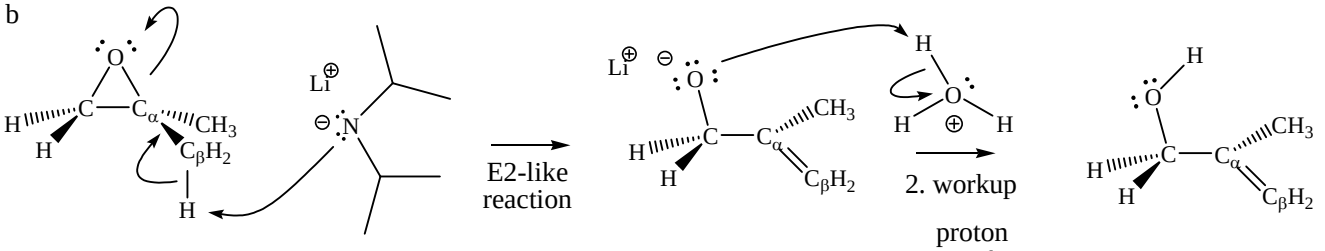
g. Making Allylic Alcohols from Epoxides using LDA (E2 reaction using LDA + epoxides)

a



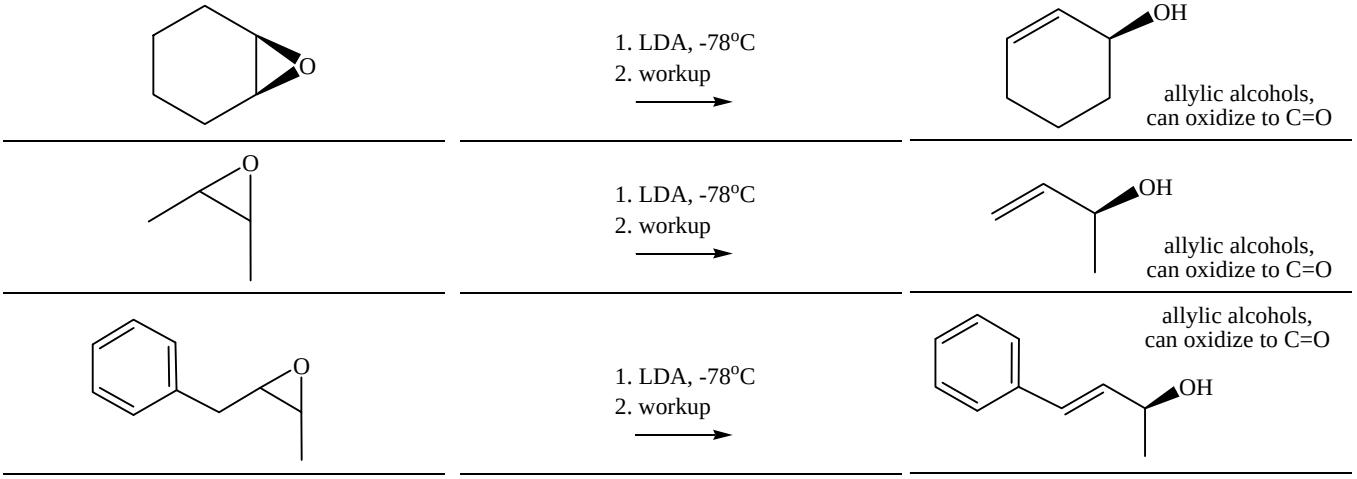
LDA, lithium diisopropyl amide (always a base in our course)

b



LDA, lithium diisopropyl amide (always a base in our course)

Example reactions

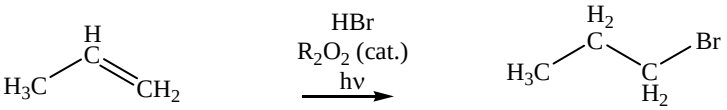


Reactions of alkenes, alkynes and conjugated variations

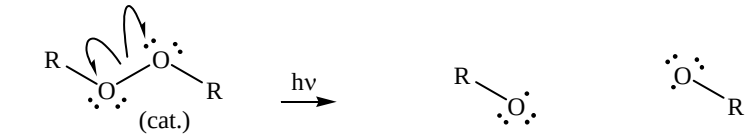
a. RBr from alkenes (anti-Markovnikov addition of HBr using free radical chemistry):

mechanism using HBr / ROOR / hν for free radical addition to alkane pi bonds (anti-Markovnikov addition = Br adds to less substituted position to form most stable free radical intermediate, and then H adds to more substituted position)

overall reaction



1. initiation (two steps)

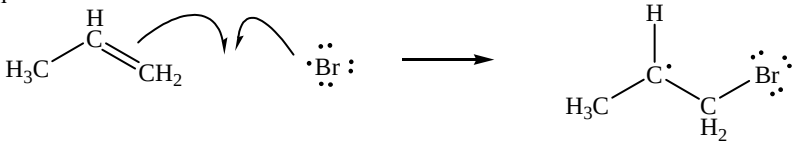


ΔH = 40 kcal/mole

BE = +88 kcal/mole
BE = -111 kcal/mole

ΔH = -23 kcal/mole

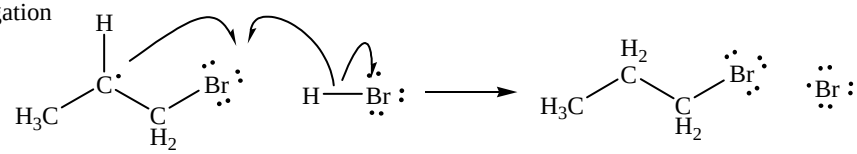
2a propagation



BE = +63 kcal/mole
BE = -68 kcal/mole

ΔH = -5 kcal/mole

2b propagation



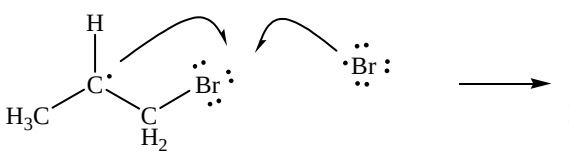
BE = +88 kcal/mole
BE = -98 kcal/mole

ΔH = -10 kcal/mole

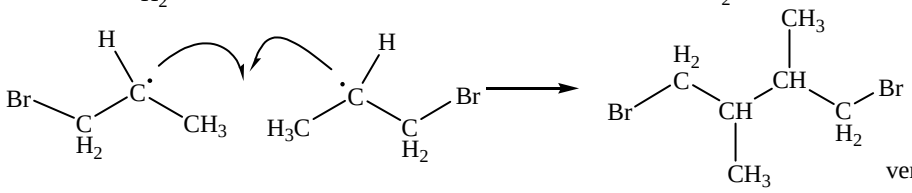
ΔH = -15

both steps (2a + 2b)

3. termination = combination of two free radicals - relatively rare because free radicals are at low concentrations



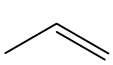
ΔH = -68 kcal/mole



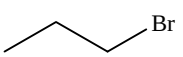
ΔH = -80 kcal/mole

very minor products

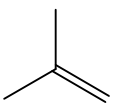
Example reactions



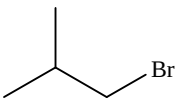
H-Br / hν
ROOR (cat.)



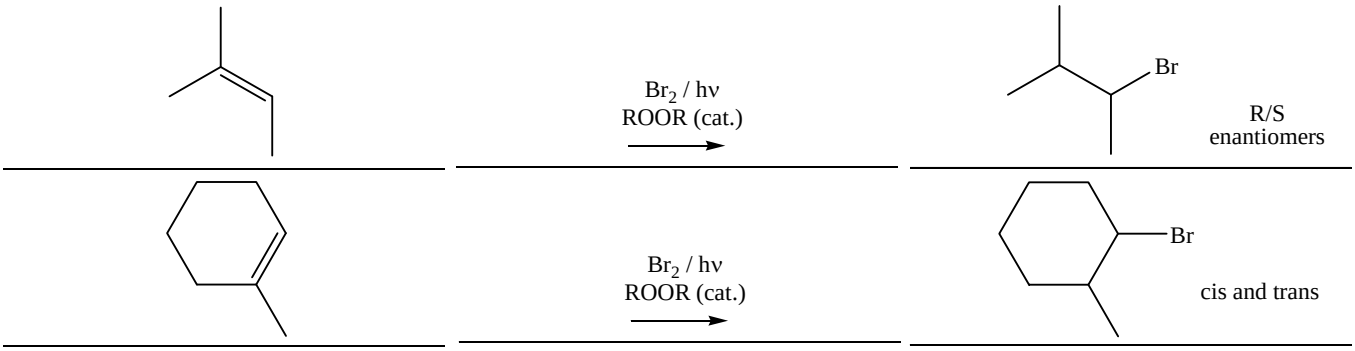
achiral



Br_2 / hν
ROOR (cat.)

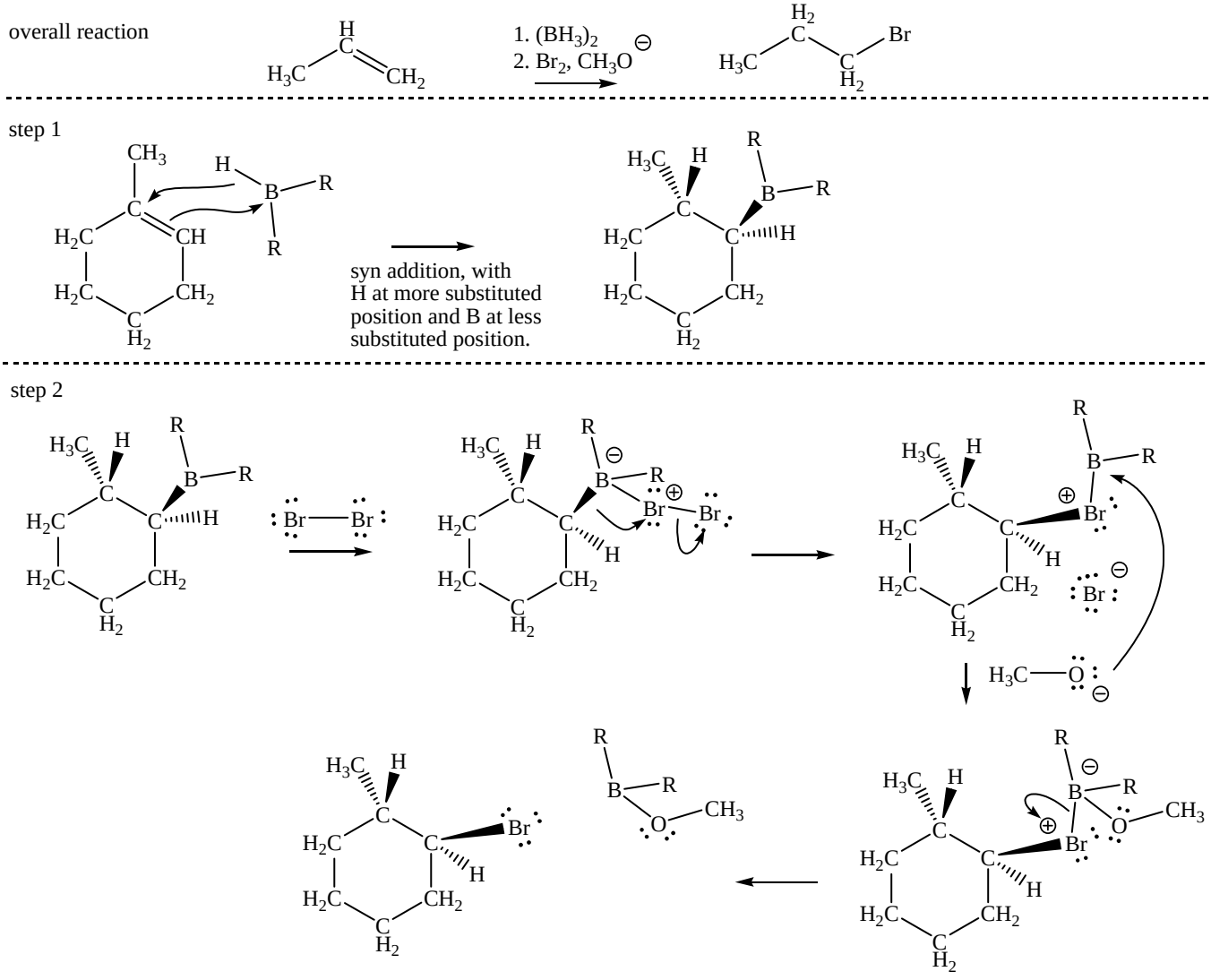


achiral

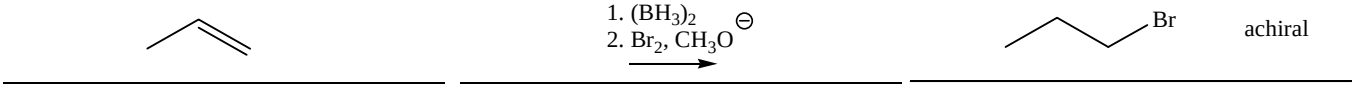


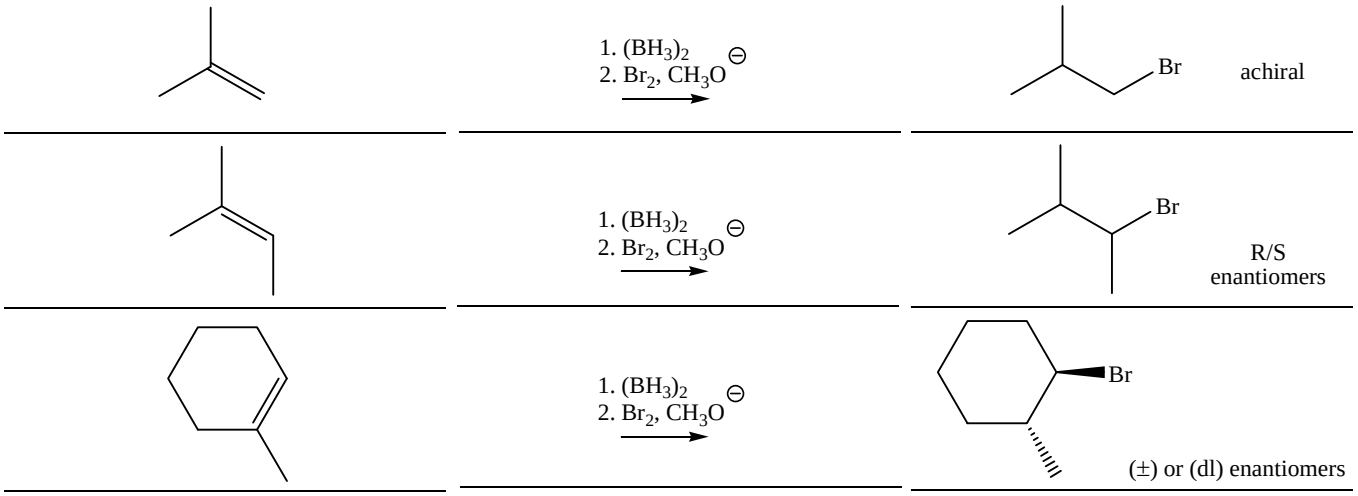
b. RBr from alkenes (anti-Markovnikov addition of HBr using borane chemistry):

mechanism using 1. BH_3 2. Br_2 / CH_3O^- for anti-Markovnikov addition of H-Br to alkane pi bonds (concerted, syn addition of H-BH_2 to alkene pi bond, followed by complex with Br_2 and migration of R group to Br)

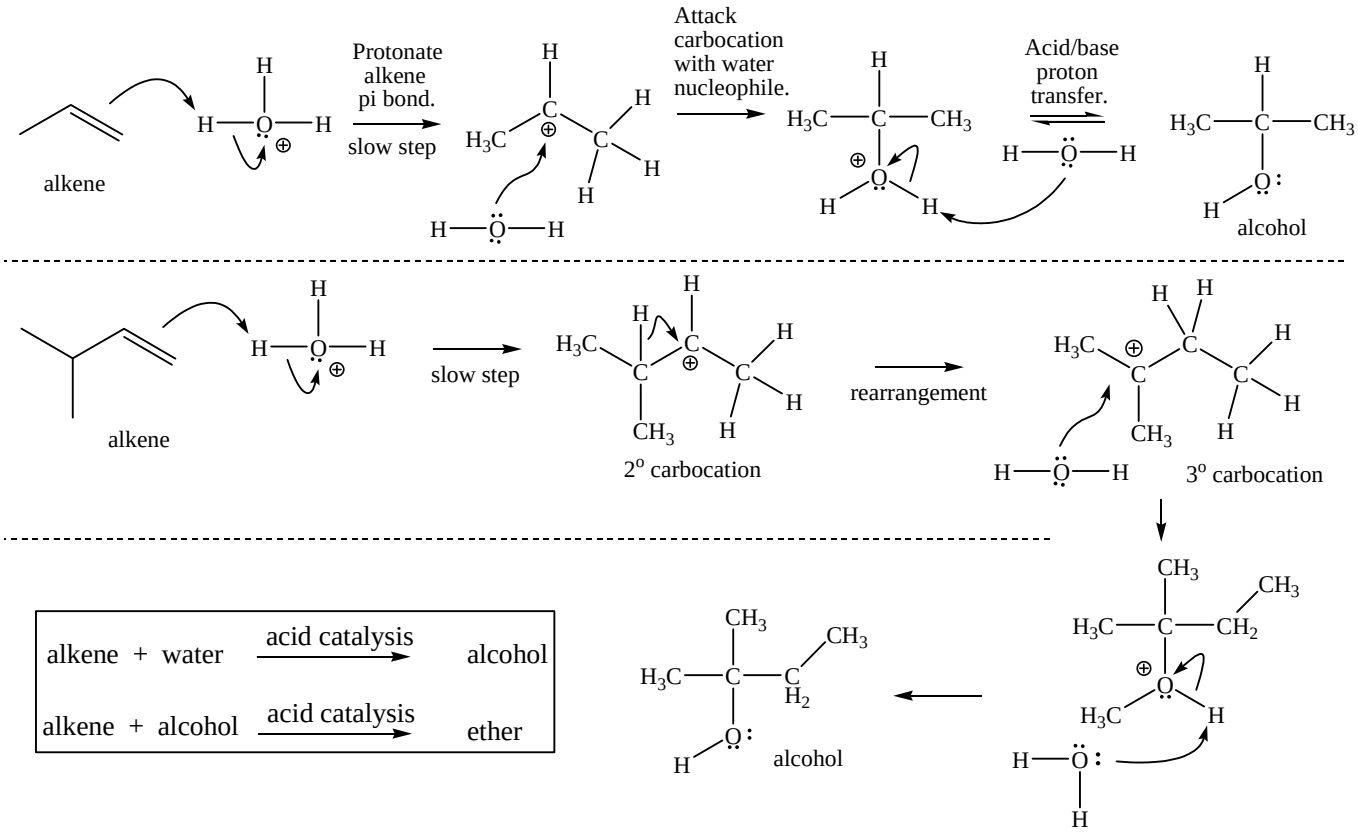


Example reactions

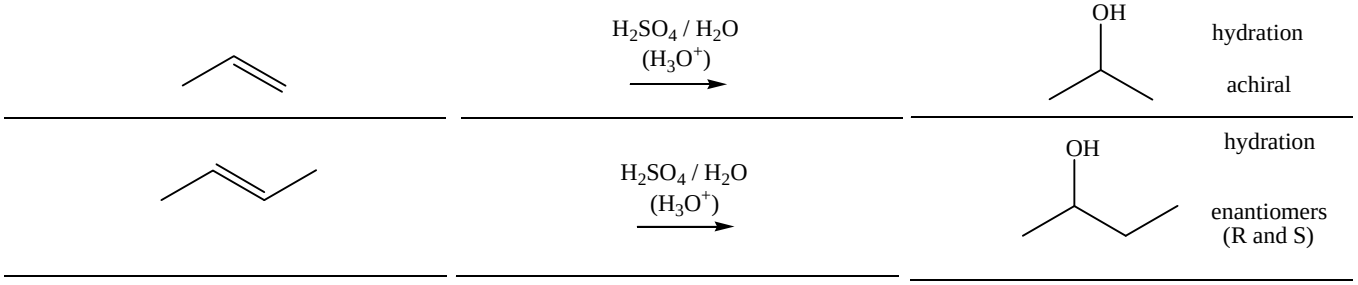


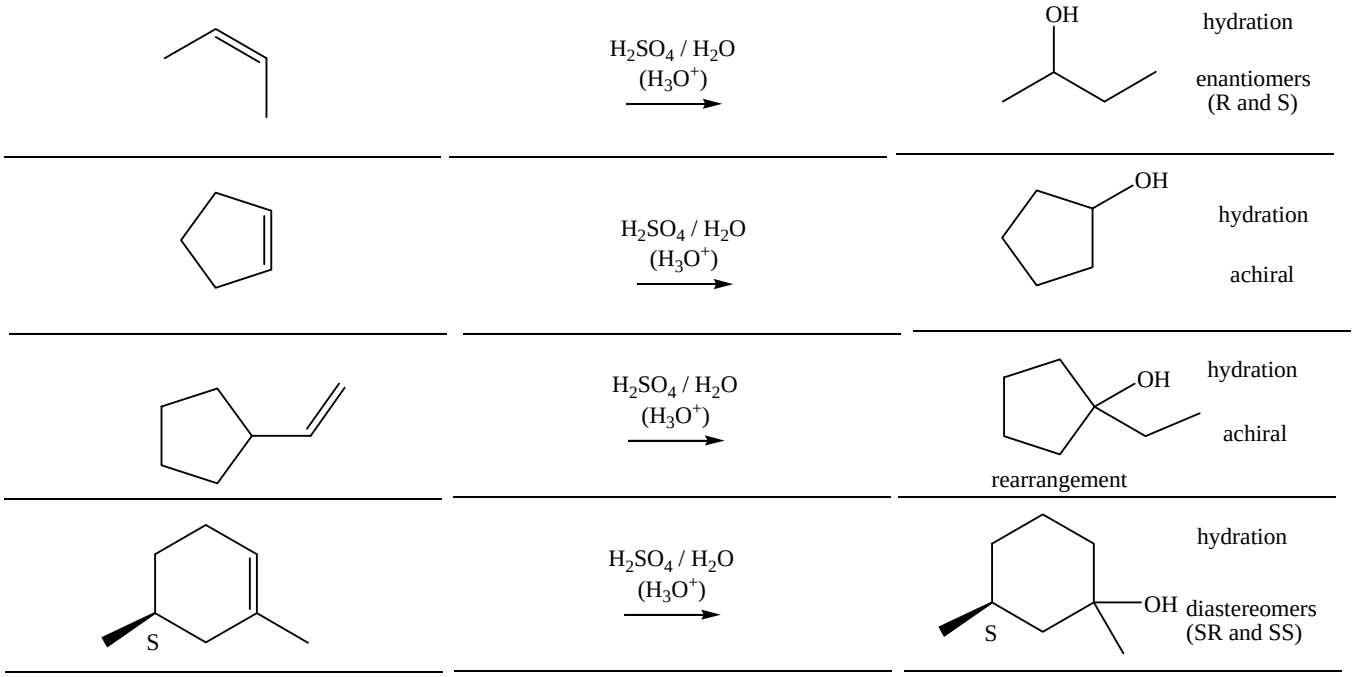


c. Alkenes with aqueous sulfuric acid. Alcohol synthesis (Markovnikov addition, rearrangements are possible).

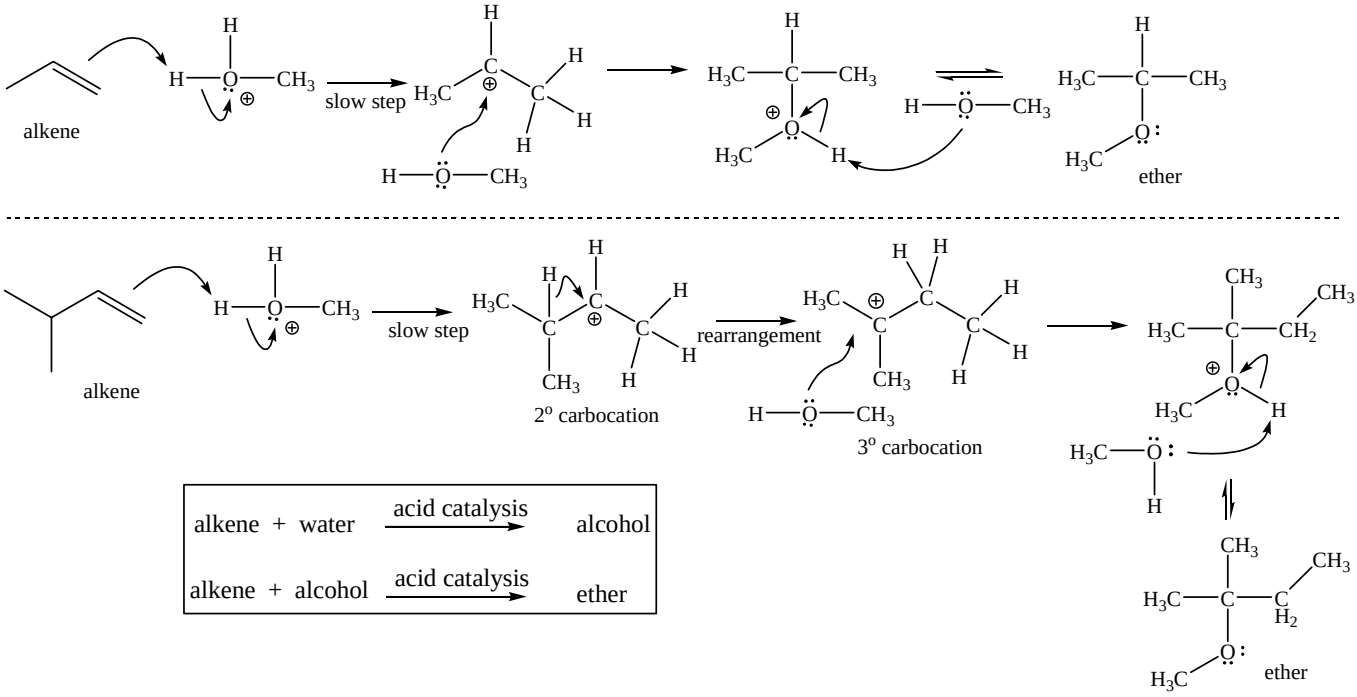


Example Reactions

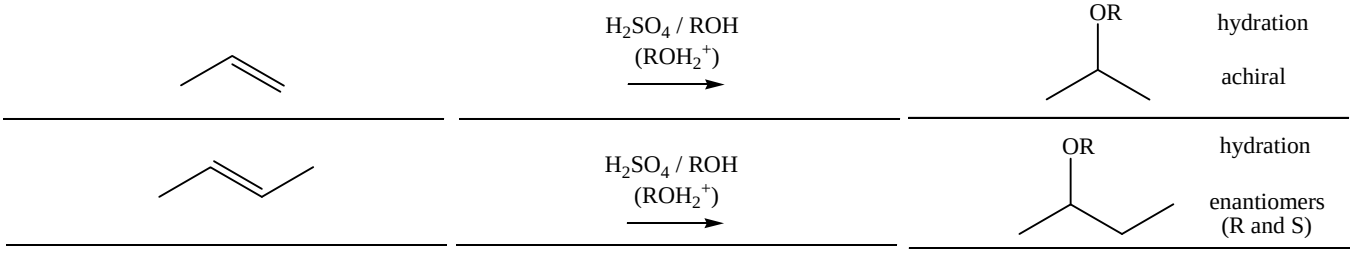


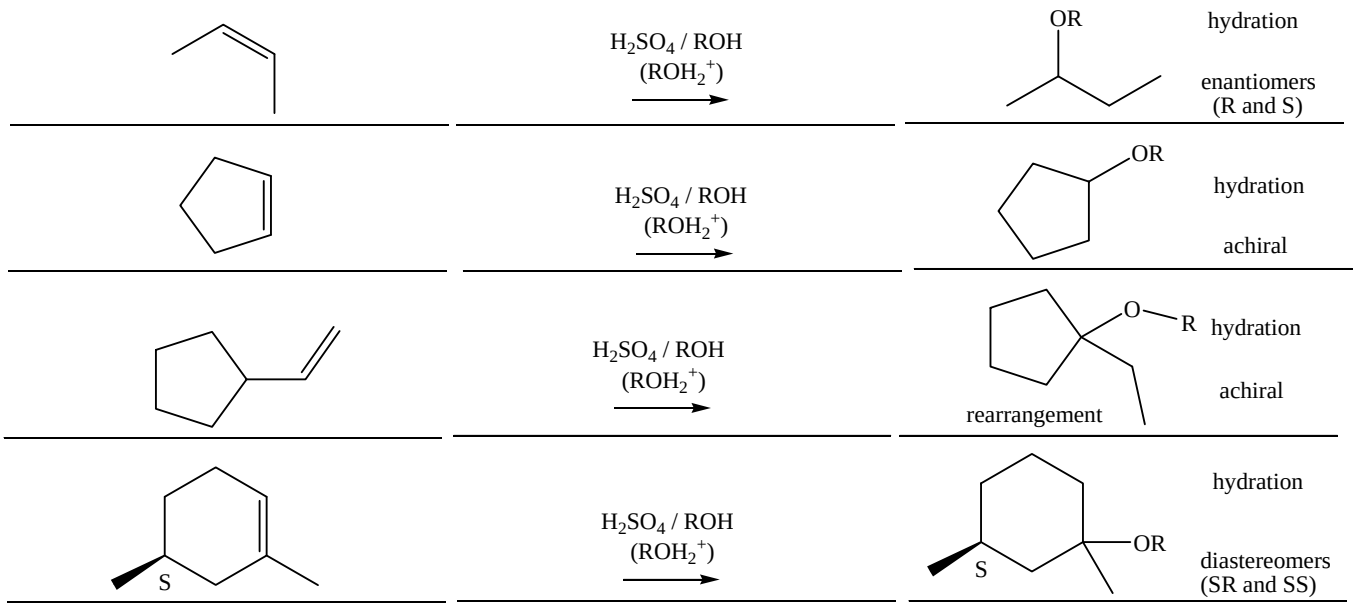


d. Alkenes with alcohol + sulfuric acid. Markovnikov addition, ether synthesis (rearrangements are possible).

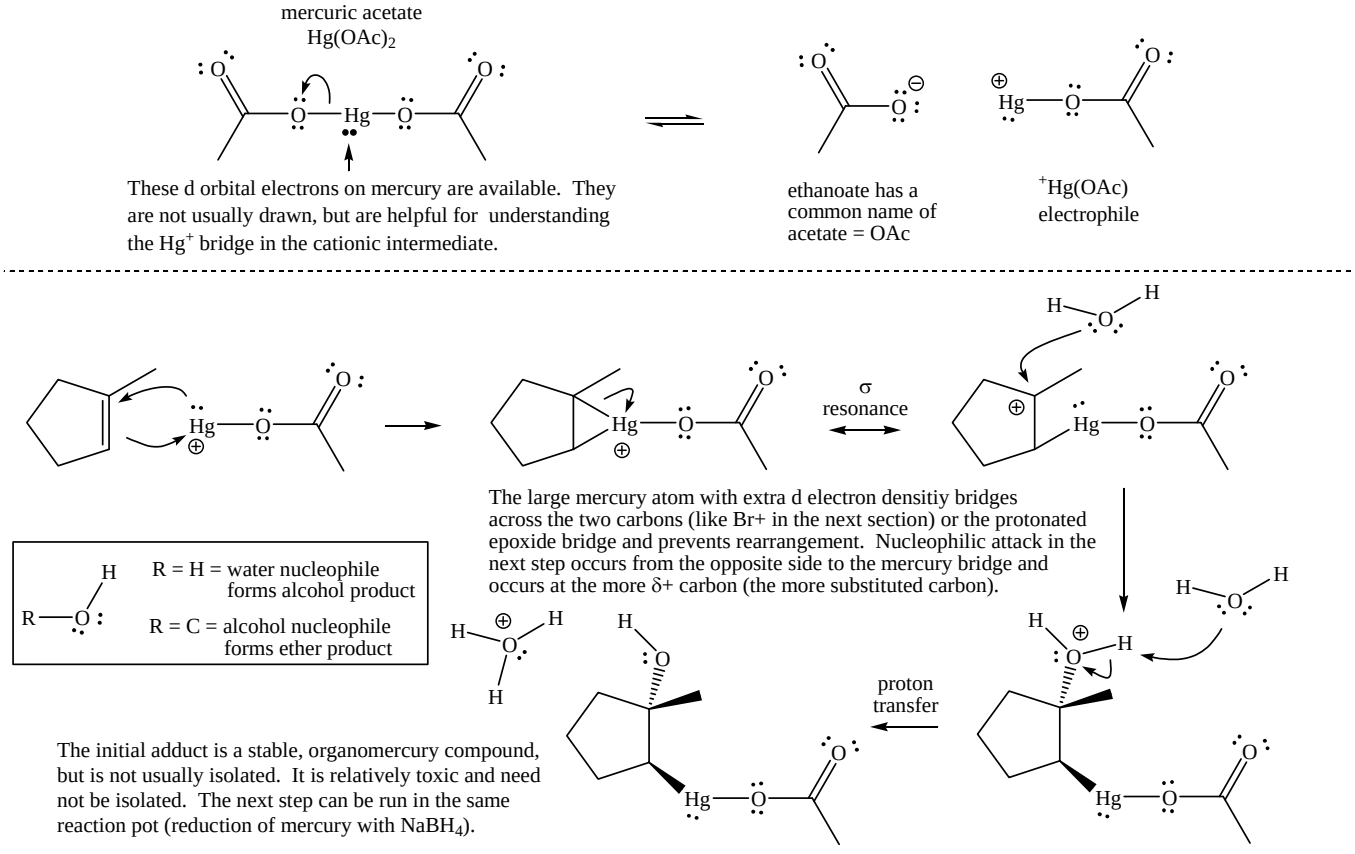


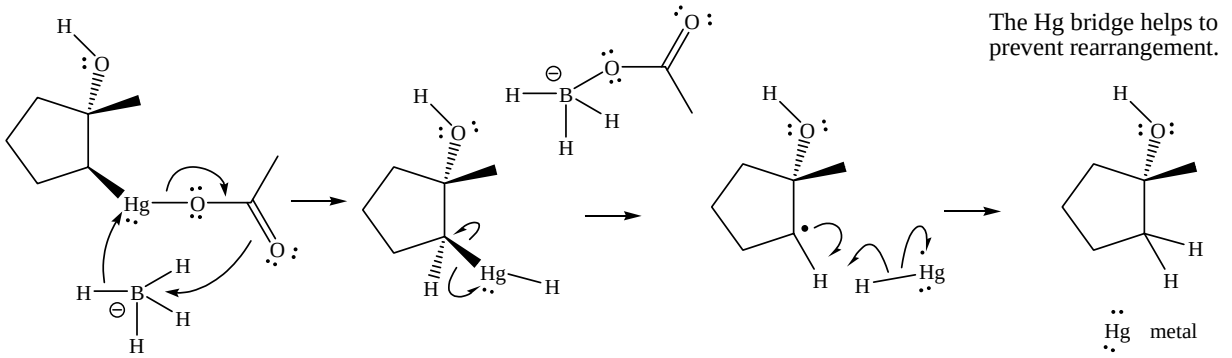
Example Reactions





e. Alkenes with 1. HgX_2 / H_2O 2. $NaBH_4$. Alcohol synthesis with minimal rearrangements (Markovnikov).



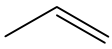
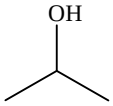
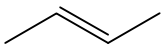
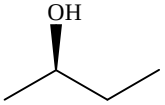
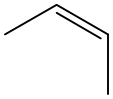
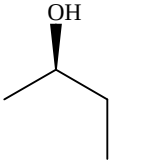
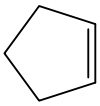
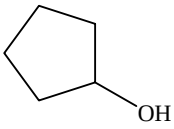
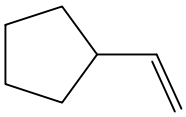
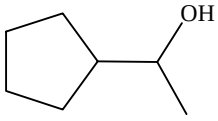
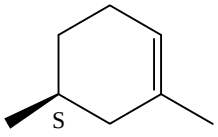
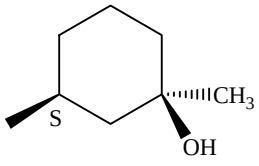


S_N2 nucleophilic attack by hydride at the mercury atom displaces acetate as the leaving group. Acetate can complex at boron taking the place of the transferred hydride. This keeps boron with an octet, which also is negatively charged.

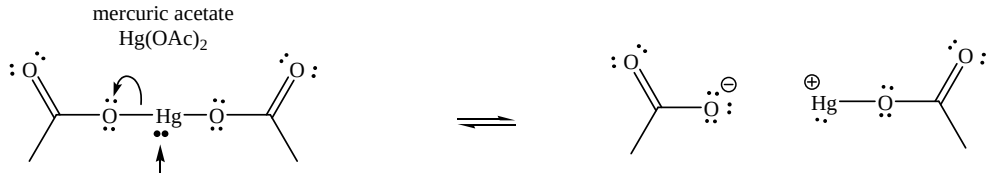
Free radical dissociation of the weak Hg-C bond occurs. Other free radical reactions are possible here, but not emphasized in our course.

A hydrogen atom is abstracted from the mercury by the highly reactive carbon free radical. This forms mercury metal as one of the products. No stereoselectivity is observed here because of the sp^2 free radical carbon.

Example Reactions

	1. HgX_2 / H_2O 2. $NaBH_4$		achiral
	1. HgX_2 / H_2O 2. $NaBH_4$		enantiomers R and S
	1. HgX_2 / H_2O 2. $NaBH_4$		enantiomers R and S
	1. HgX_2 / H_2O 2. $NaBH_4$		achiral
	1. HgX_2 / H_2O 2. $NaBH_4$		achiral no rearrangement
	1. HgX_2 / H_2O 2. $NaBH_4$		diastereomers SR and SS

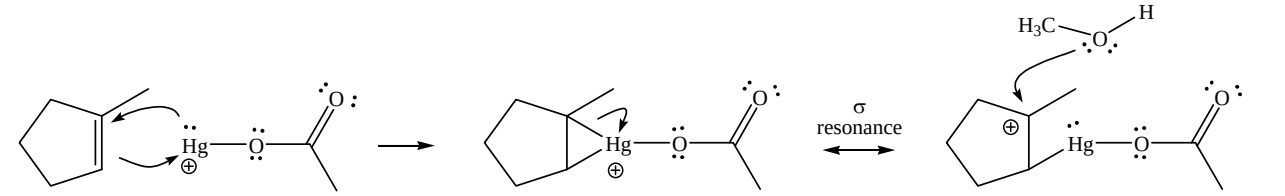
f. Alkenes with 1. HgX_2 / ROH 2. $NaBH_4$. Ether synthesis with minimal rearrangements (Markovnikov).



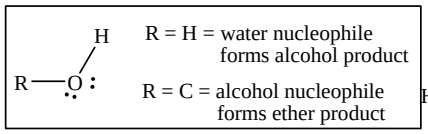
These d orbital electrons on mercury are available. They are not usually drawn, but are helpful for understanding the Hg^+ bridge in the cationic intermediate.

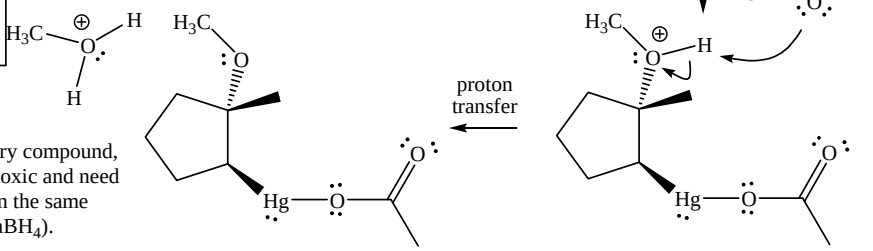
ethanoate has a common name of acetate = OAc

$^+$Hg(OAc) electrophile

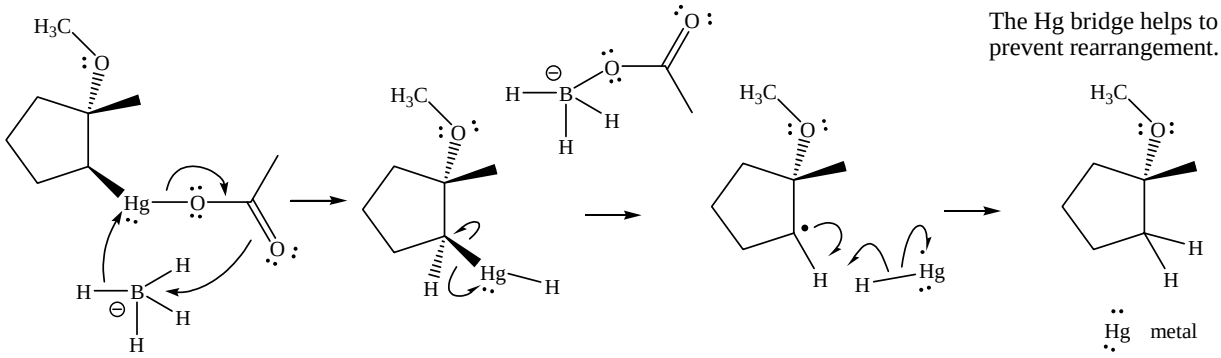


The large mercury atom with extra d electron densitiy bridges across the two carbons (like Br+ in the next section) or the protonated epoxide bridge and prevents rearrangement. Nucleophilic attack in the next step occurs from the opposite side to the mercury bridge and occurs at the more δ+ carbon (the more substituted carbon).





The initial adduct is a stable, organomercury compound, but is not usually isolated. It is relatively toxic and need not be isolated. The next step can be run in the same reaction pot (reduction of mercury with $NaBH_4$).



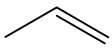
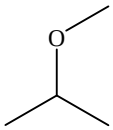
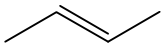
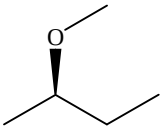
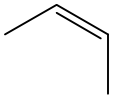
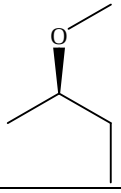
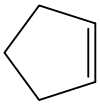
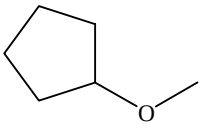
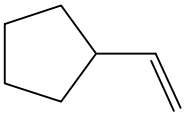
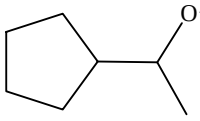
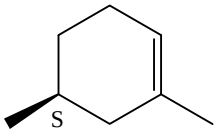
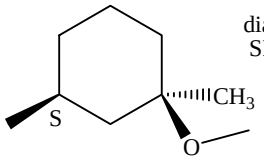
The Hg bridge helps to prevent rearrangement.

S_N2 nucleophilic attack by hydride at the mercury atom displaces acetate as the leaving group. Acetate can complex at boron taking the place of the transferred hydride. This keeps boron with an octet, which also is negatively charged.

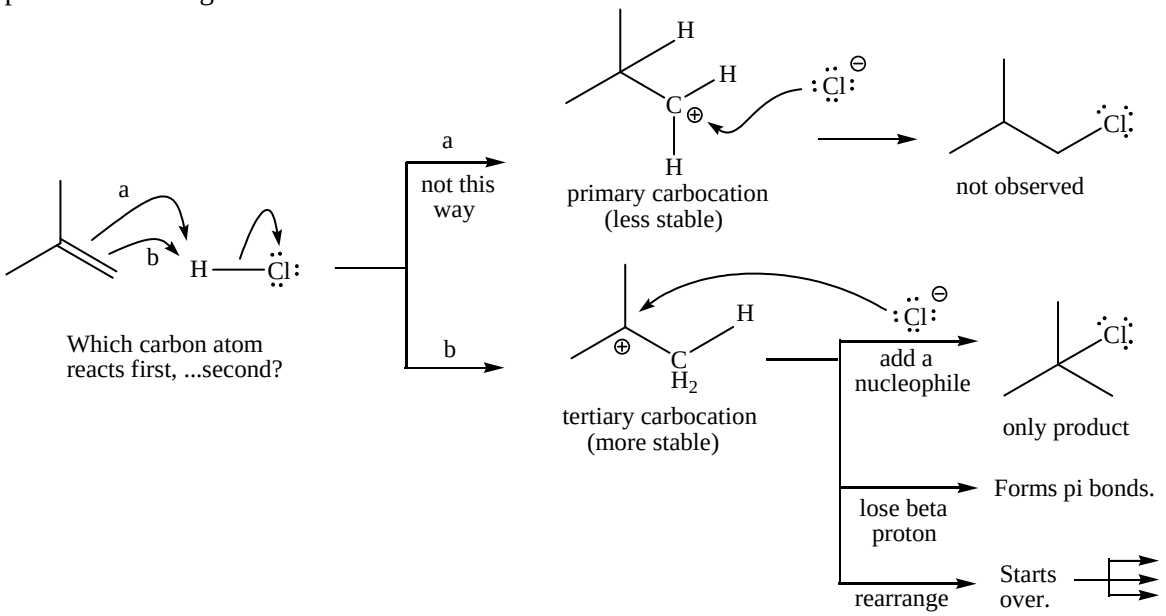
Free radical dissociation of the weak Hg-C bond occurs. Other free radical reactions are possible here, but not emphasized in our course.

A hydrogen atom is abstracted from the mercury by the highly reactive carbon free radical. This forms mercury metal as one of the products. No stereoselectivity is observed here because of the sp^2 free radical carbon.

Example Reactions

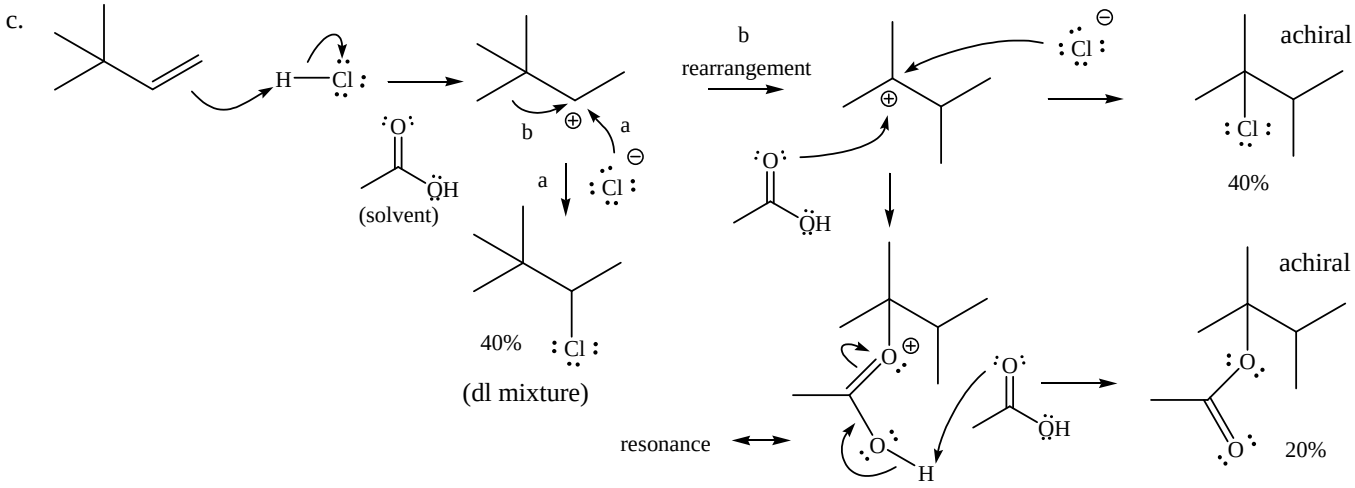
	1. HgX_2 / CH_3OH 2. $NaBH_4$		achiral
	1. HgX_2 / CH_3OH 2. $NaBH_4$		enantiomers R and S
	1. HgX_2 / CH_3OH 2. $NaBH_4$		enantiomers R and S
	1. HgX_2 / CH_3OH 2. $NaBH_4$		achiral
	1. HgX_2 / CH_3OH 2. $NaBH_4$		achiral no rearrangement
	1. HgX_2 / CH_3OH 2. $NaBH_4$		diastereomers SR and SS

g. Electrophilic addition of HCl, HBr, HI to alkenes = Markovnikov addition, synthesis of RX compounds with possibile rearrangements

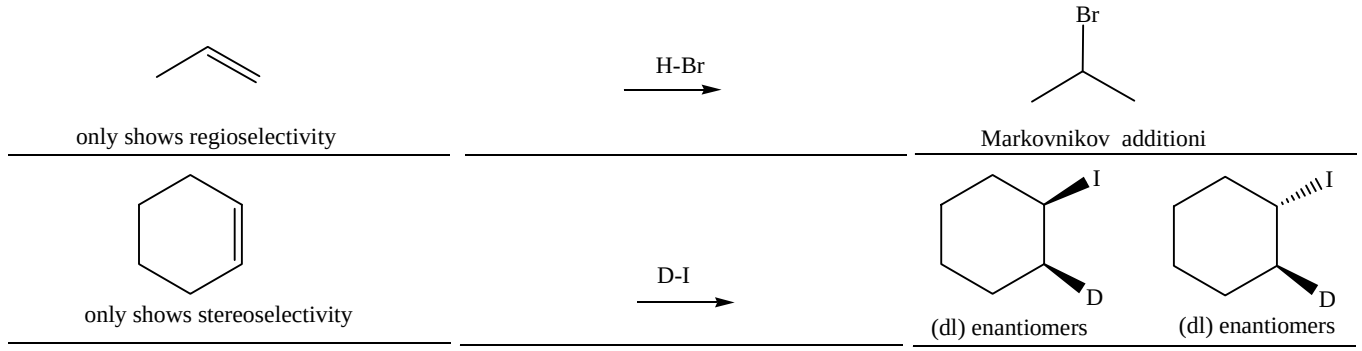


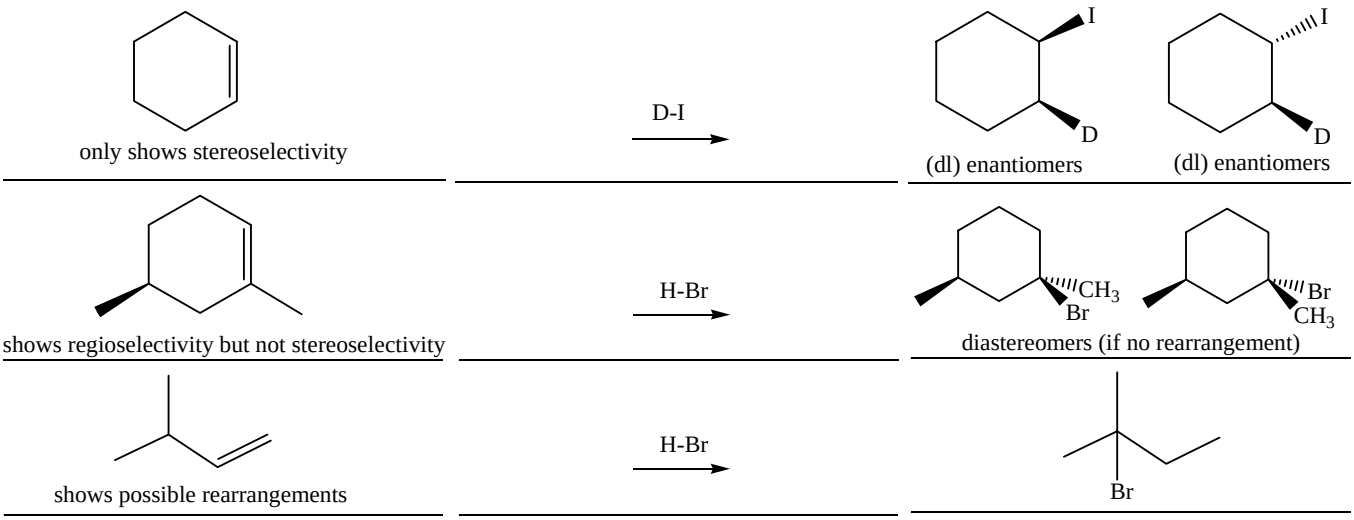
There are two carbon choices for an electrophile to react with. Which carbon gives up the electrons and becomes a carbocation is based on the most stable carbocation that can form (leading to a regioselective reaction). Such a reaction is generally not stereoselective because the flat carbocation allows attack of the nucleophile to both faces. We expect three possible reactions from the carbocation, add a nucleophile, lose a beta proton or rearrange.

c.

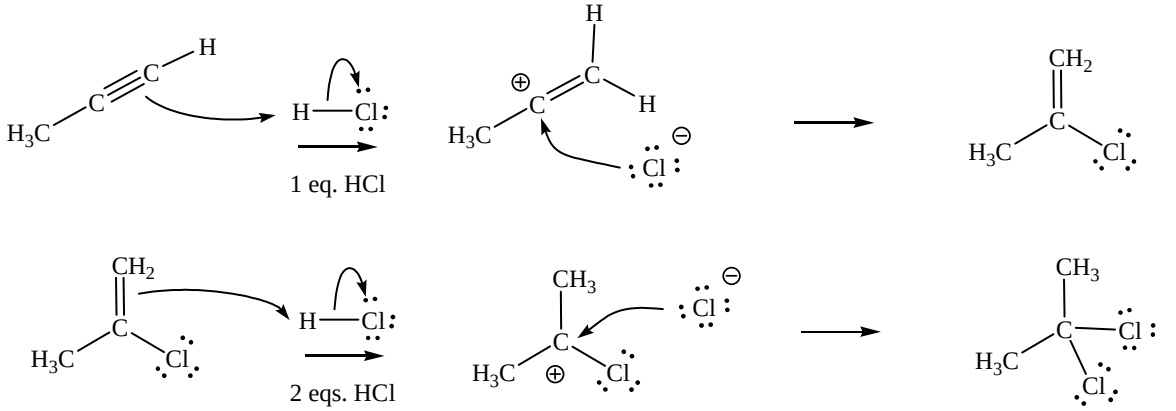


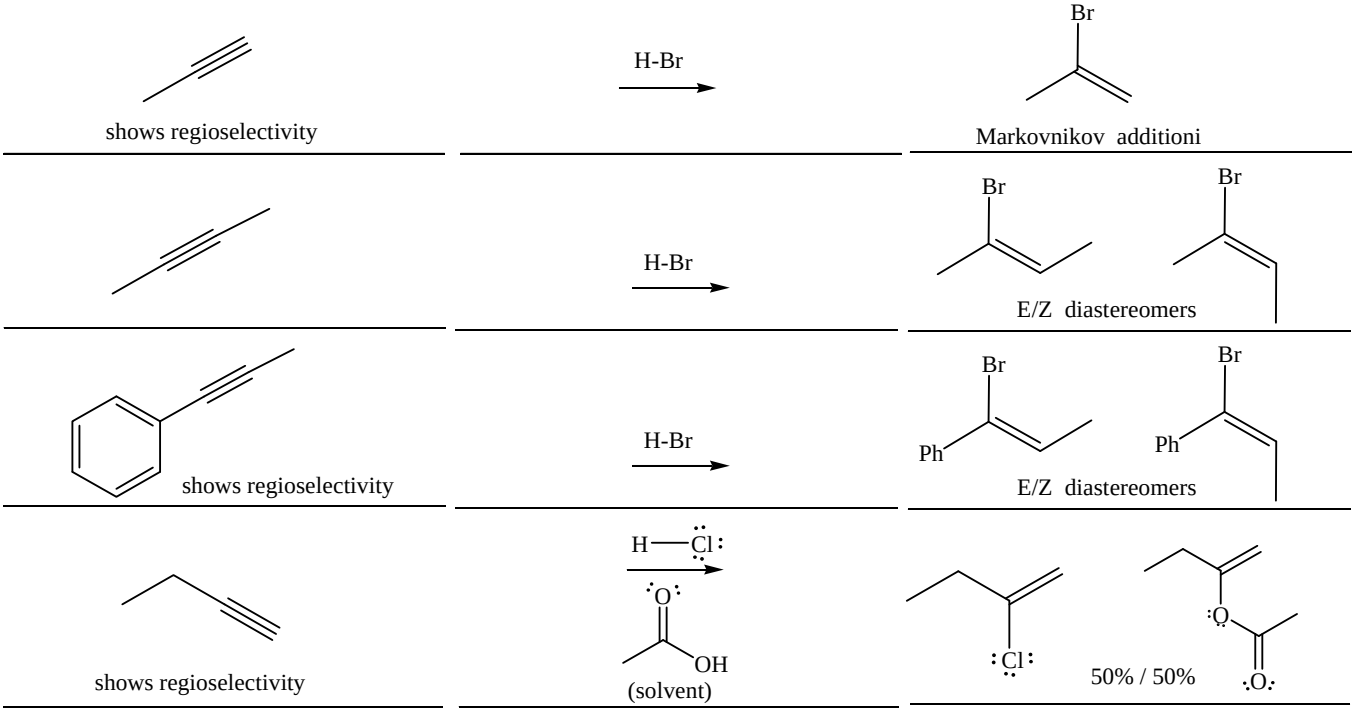
Example Reactions



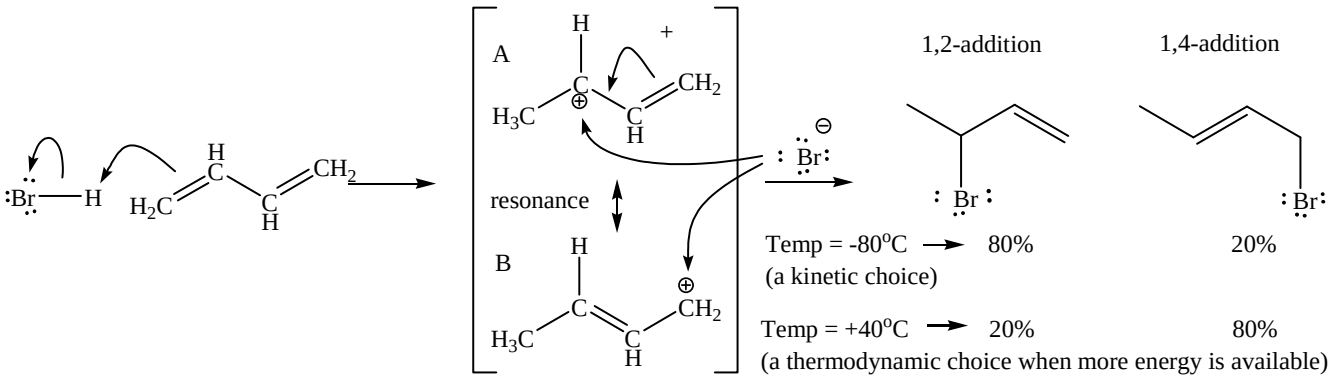


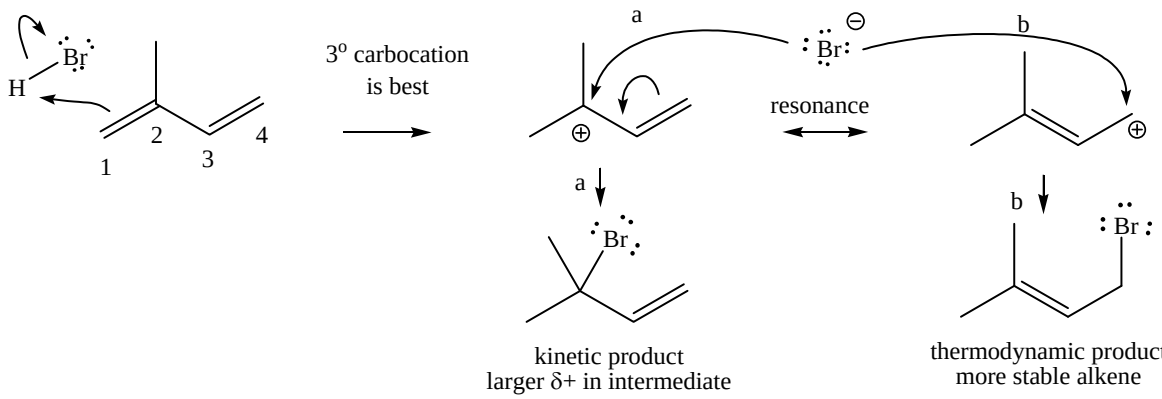
h. Electrophilic addition of HCl, HBr, HI to alkynes = Markovnikov addition, synthesis of RX compounds, can use 1 equivalent or 2 equivalents

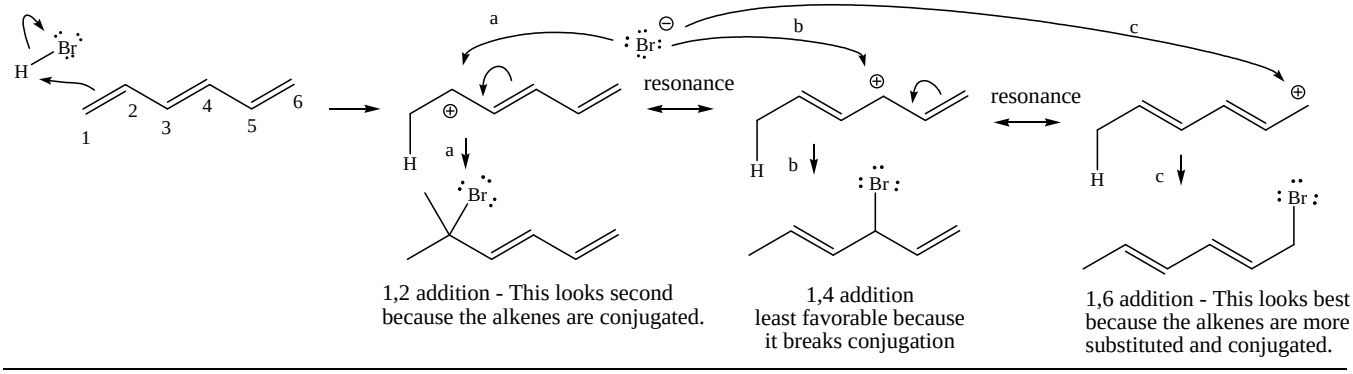




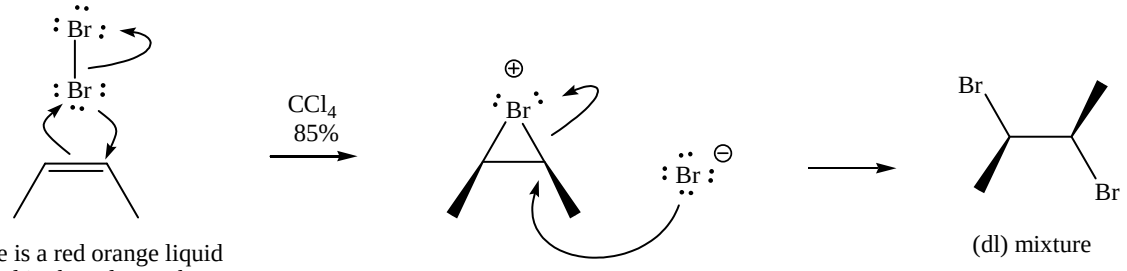
i. Electrophilic addition of HCl, HBr, HI to conjugated diene or triene = Markovnikov addition, synthesis of RX compounds, can use 1 equivalent or 2 equivalents





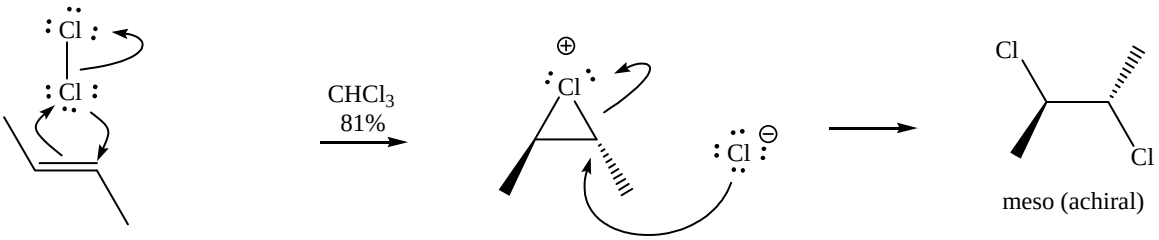


j. Alkenes with Br_2 or Cl_2. Synthesis of vicinal dihalide (anti addition).



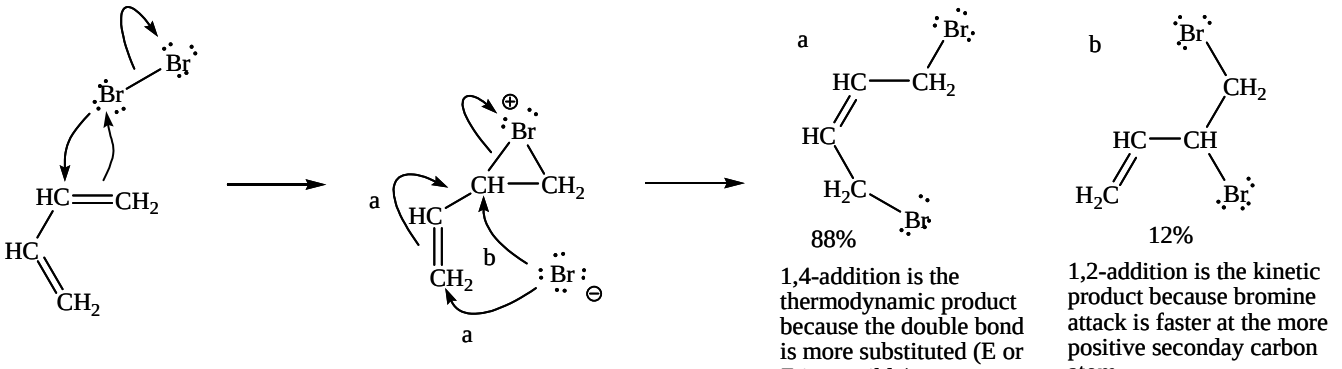
bromine is a red orange liquid dissolved in the solvent, the color disappears as it is added

(dl) mixture



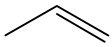
chlorine is a green gas, dissolved in the solvent

meso (achiral)

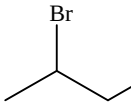


1,4-addition is the thermodynamic product because the double bond is more substituted (E or Z is possible)

1,2-addition is the kinetic product because bromine attack is faster at the more positive seconday carbon atom.

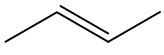


Br—Br (or Cl_2)

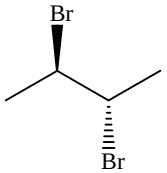


bromination

enantiomers R and S

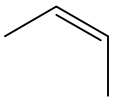


Br—Br (or Cl_2)

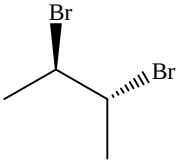


bromination

meso, RS

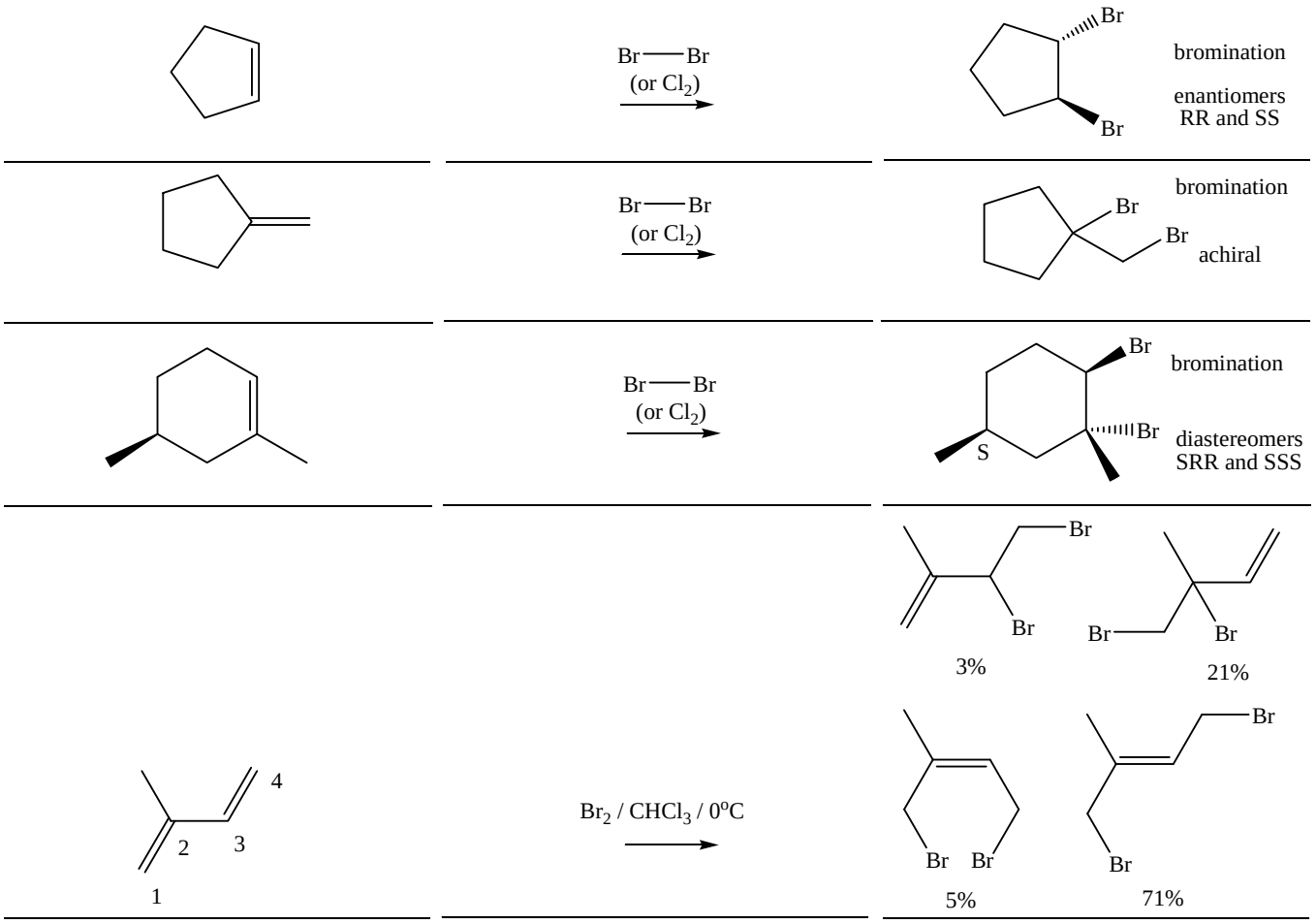


Br—Br (or Cl_2)

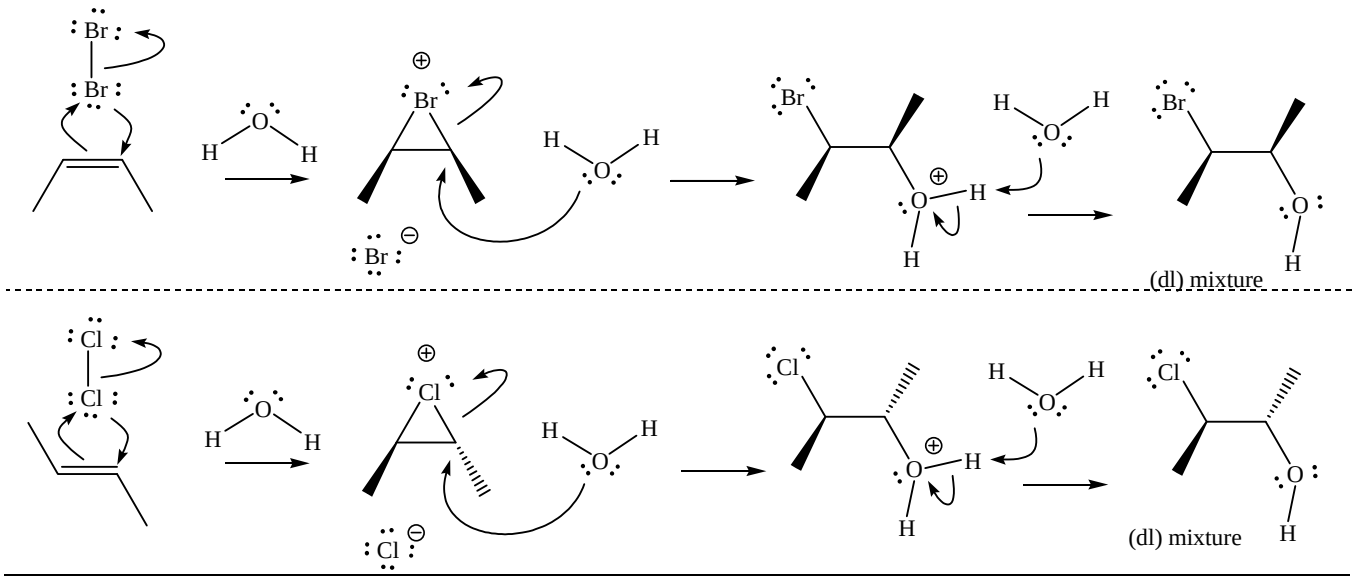


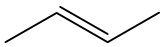
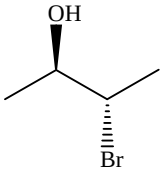
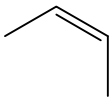
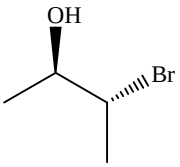
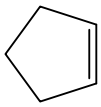
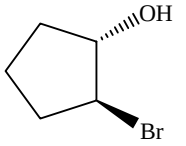
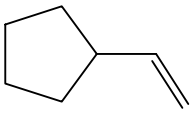
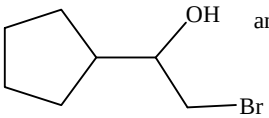
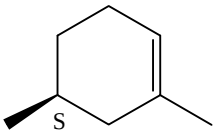
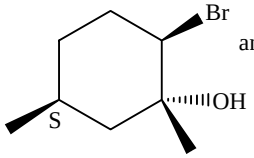
bromination

enantiomers RR and SS

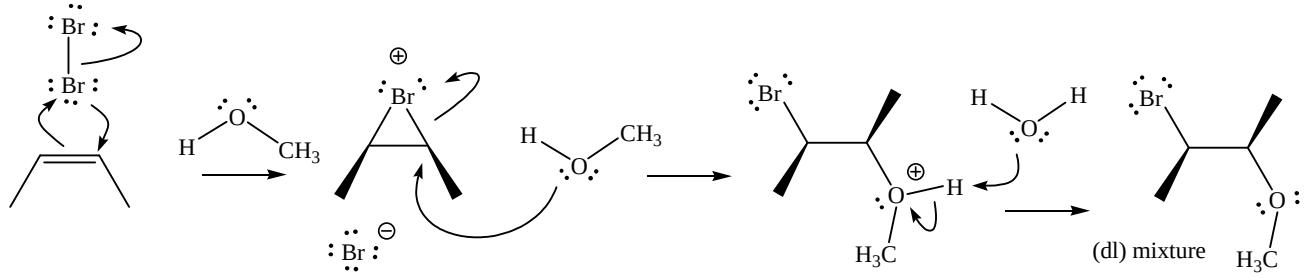


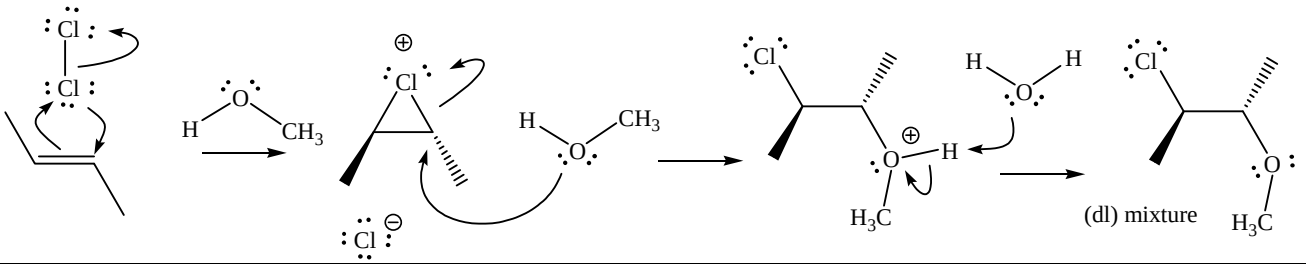
k. Alkenes with Br_2/H_2O or Cl_2/H_2O. Synthesis of bromohydrin or chlorohydrin (anti + Markovnikov addition).

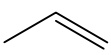
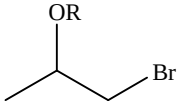


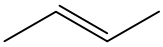
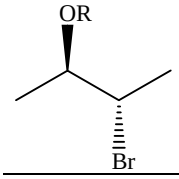
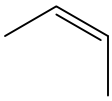
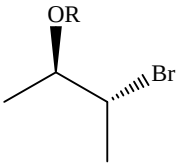
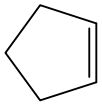
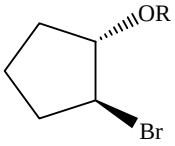
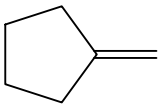
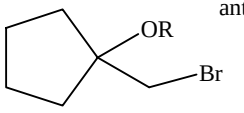
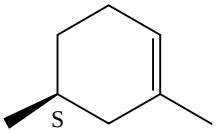
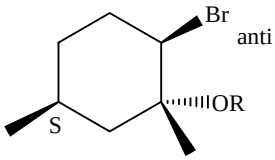
	Br_2 / H_2O (or Cl_2 / H_2O)		anti + Markovnikov addition enantiomers RS and SR
	Br_2 / H_2O (or Cl_2 / H_2O)		anti + Markovnikov addition enantiomers RR and SS
	Br_2 / H_2O (or Cl_2 / H_2O)		anti + Markovnikov addition enantiomers RR and SS
	Br_2 / H_2O (or Cl_2 / H_2O)		anti + Markovnikov addition achiral no rearrangement
	Br_2 / H_2O (or Cl_2 / H_2O)		anti + Markovnikov addition diastereomers SRR and SSS

l. Alkenes with Br_2/ROH or Cl_2/ROH. Synthesis of bromo or chloro "ethers".



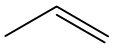
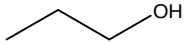
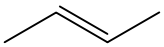
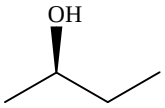
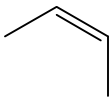
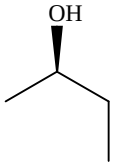
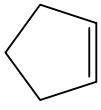
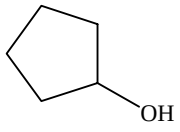


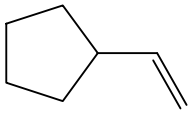
	Br_2 / ROH (or Cl_2 / ROH)		anti + Markovnikov addition enantiomers R and S

	Br_2 / ROH (or Cl_2 / ROH)		anti + Markovnikov addition enantiomers RS and SR
	Br_2 / ROH (or Cl_2 / ROH)		anti + Markovnikov addition enantiomers RR and SS
	Br_2 / ROH (or Cl_2 / ROH)		anti + Markovnikov addition enantiomers RR and SS
	Br_2 / ROH (or Cl_2 / ROH)		anti + Markovnikov addition achiral
	Br_2 / ROH (or Cl_2 / ROH)		anti + Markovnikov addition diastereomers SRR and SSS

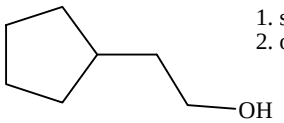
m. Alkenes with 1. BH_3 2. H_2O_2/HO^{--}. Hydroboration/oxidation = anti-Markovnikov alcohols.

The mechanism for this reaction is given at the beginning of this document.

	1. BH_3 2. H_2O_2 / $HO^{\ominus}$		1. syn addition 2. oxidation achiral
	1. BH_3 2. H_2O_2 / $HO^{\ominus}$		1. syn addition 2. oxidation enantiomers R and S
	1. BH_3 2. H_2O_2 / $HO^{\ominus}$		1. syn addition 2. oxidation enantiomers R and S
	1. BH_3 2. H_2O_2 / $HO^{\ominus}$		1. syn addition 2. oxidation achiral

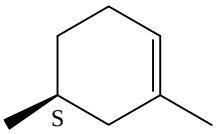


1. BH_3
2. H_2O_2 / $HO^{\ominus}$

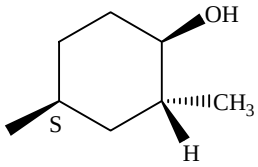


1. syn addition
2. oxidation

achiral



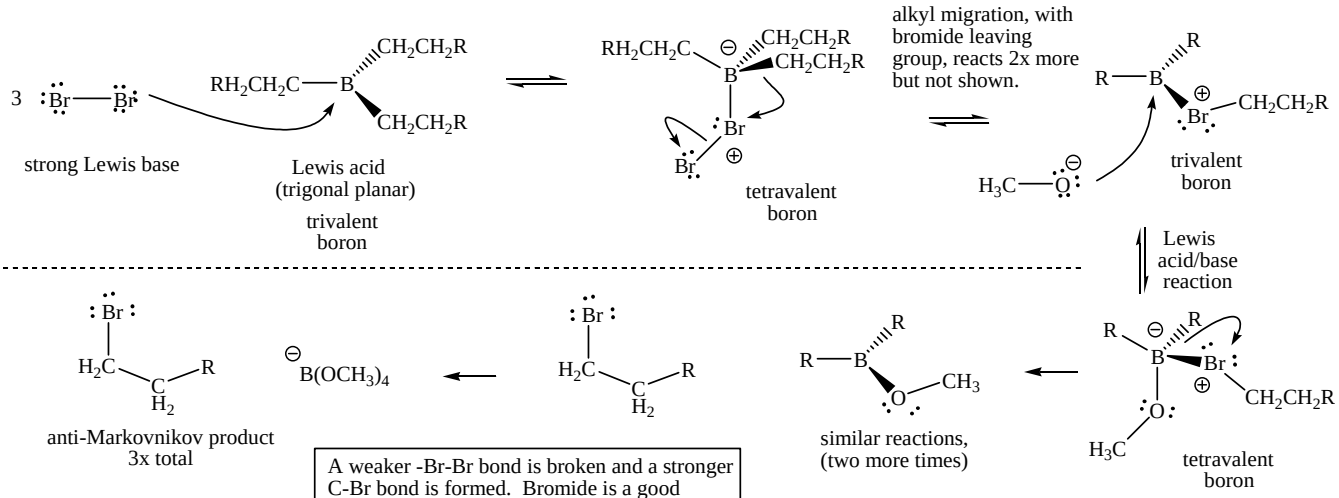
1. BH_3
2. H_2O_2 / $HO^{\ominus}$

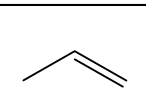


1. syn addition
2. oxidation

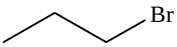
diastereomers
SRR and SSS

n. Alkenes with 1. BH_3 2. Br_2/CH_3O^{-}. Hydroboration/bromination = anti-Markovnikov R-Br.



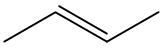


1. BH_3
2. Br_2 / $CH_3O^{\ominus}$

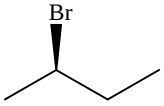


1. syn addition
2. bromination

achiral

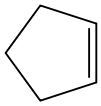


1. BH_3
2. Br_2 / $CH_3O^{\ominus}$

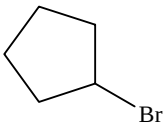


1. syn addition
2. bromination

enantiomers
R and S

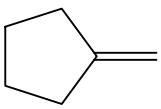


1. BH_3
2. Br_2 / $CH_3O^{\ominus}$

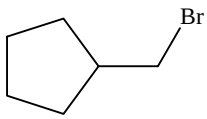


1. syn addition
2. bromination

achiral

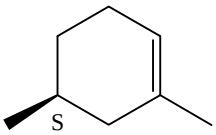


1. BH_3
2. Br_2 / $CH_3O^{\ominus}$

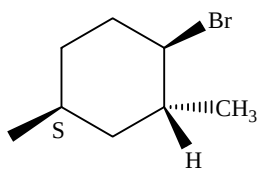


1. syn addition
2. bromination

achiral



1. BH_3
2. Br_2 / $CH_3O^{\ominus}$

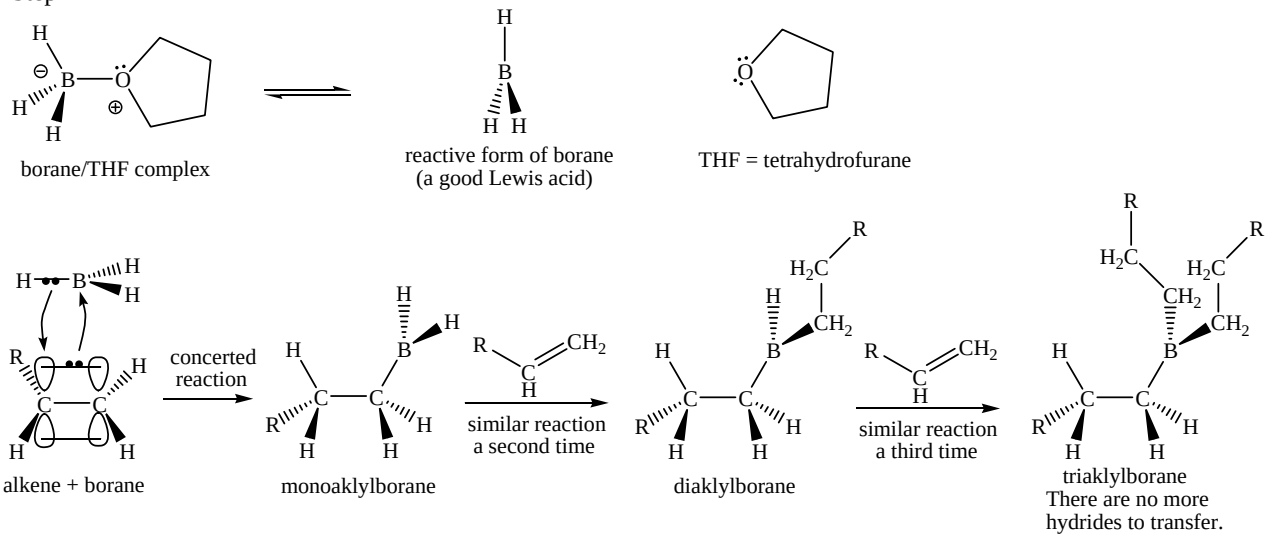


1. syn addition
2. bromination

diastereomers
SRR and SSS

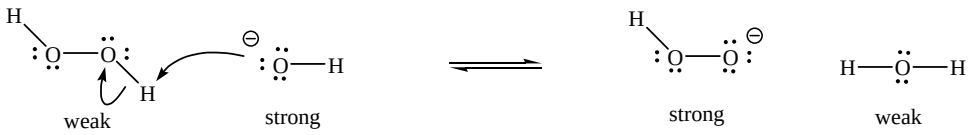
o. Alkynes with 1. HBR_2 2. H_2O_2/HO^-. Hydroboration/oxidation = anti-Markovnikov aldehydes.

Step 1

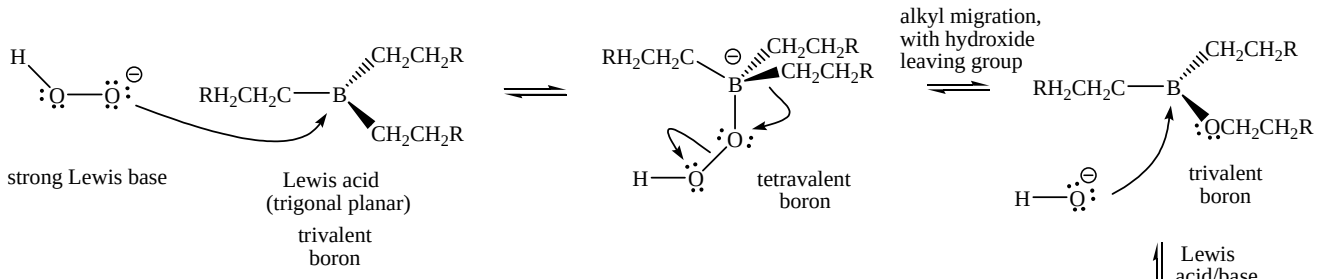


The transfer of two electron pairs is concerted. The boron and hydrogen atom add from the same face (syn), so this reaction is stereoselective. The boron adds at the less substituted carbon so this reaction is also regioselective. In subsequent reactions the boron can be converted to another group in exactly the same position, so whereever the boron ends up will indicate the position of the actual group introduced (OH or Br for us).

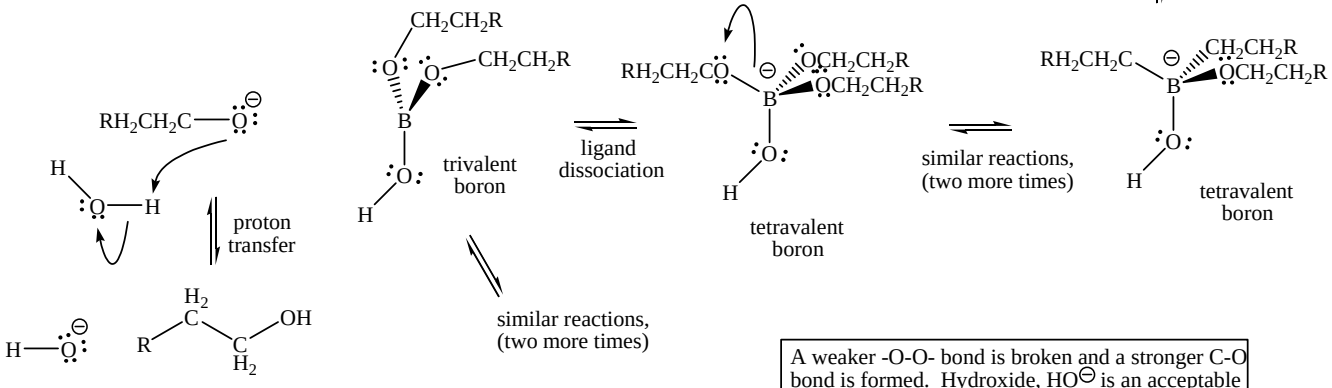
Step 2



There is a strong electron pair donor on each side of the equilibrium equation that can complex with trivalenet boron, but only the peroxide anion reacts further. All of these are present.

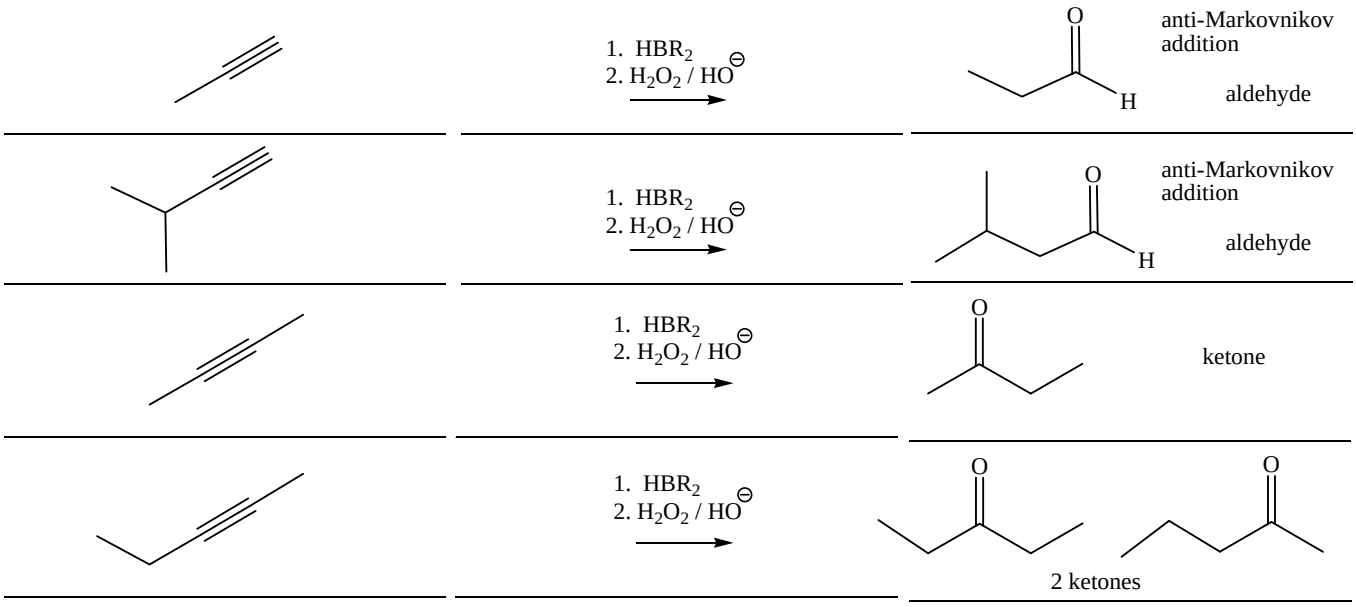


Lewis acid/base reaction

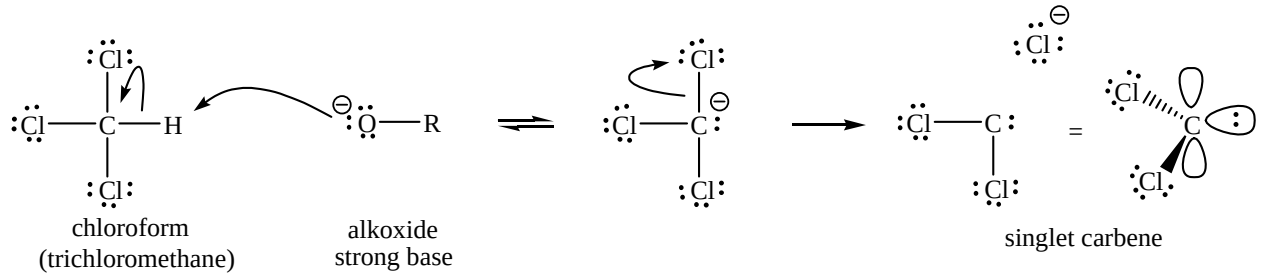


Anti-Markovnikov alcohol is formed in a regioselective and stereoselective manner.

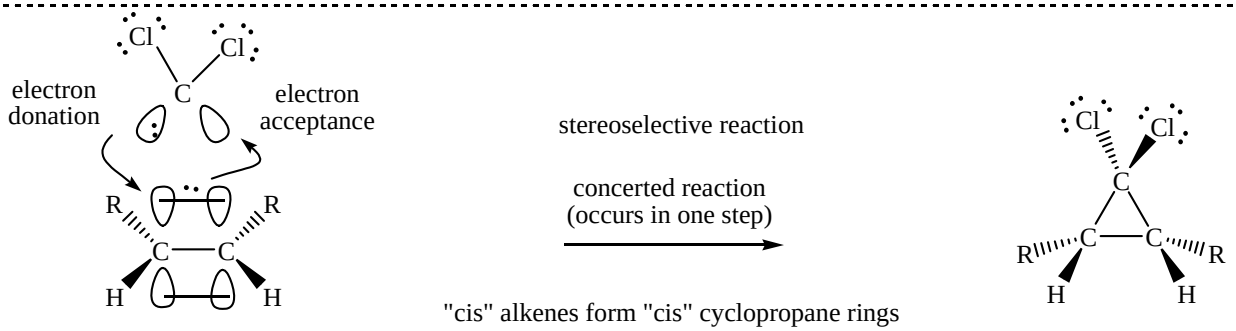
A weaker -O-O- bond is broken and a stronger C-O bond is formed. Hydroxide, $HO^{\ominus}$ is an acceptable leaving group in the strongly basic solution (compatible with the reaction conditions).



p. Alkenes with $CHCl_3$ / RO^{--} or $CHBr_3$ / RO^{--}. Carbene synthesis of dihalocyclopropanes.



A different type of elimination reaction.

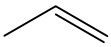
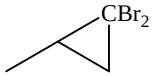
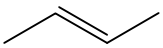
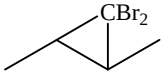
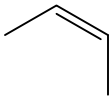
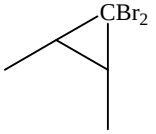
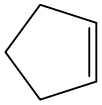
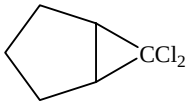
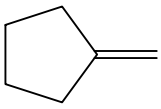
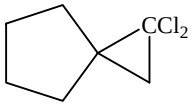
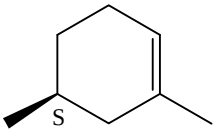
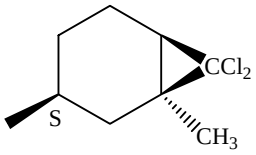


"cis" alkenes form "cis" cyclopropane rings

"trans" alkenes form "trans" cyclopropane rings

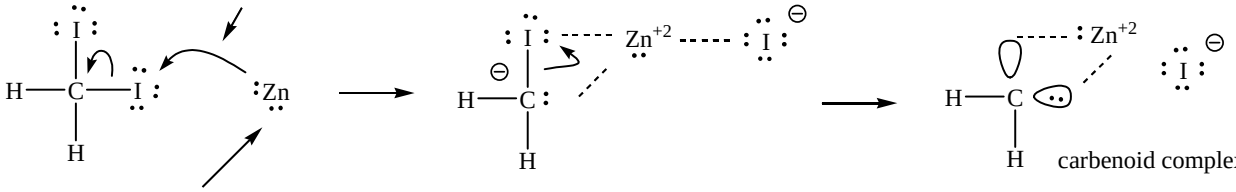
q. Alkenes with CH_2I_2 / Zn (Simmons-Smith Rxn). Carbenoid synthesis of cyclopropanes.

Example Reactions

	$CHBr_3$ / NaOH		syn addition enantiomers R and S
	$CHBr_3$ / NaOH		syn addition enantiomers RR and SS
	$CHBr_3$ / $KOC(CH_3)_3$		syn addition meso RS and SR
	$CHCl_3$ / NaOH		syn addition meso RS and SR
	$CHCl_3$ / NaOH		syn addition achiral
	$CHCl_3$ / $KOC(CH_3)_3$		syn addition diastereomers SSR and SRS

The first pair of dots represents easily lost 4s electrons on zinc, that reduce a C-I bond.

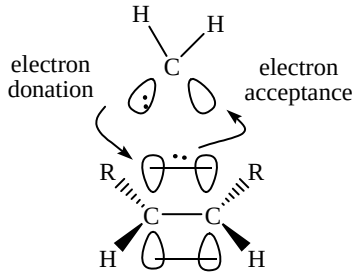
Simmons-Smith reaction



carbenoid complex

The second pair of dots represents 3d electrons on zinc that are invoked in the metal complex.

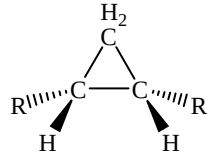
The stabilization by the metal makes the complex more stable, and less reactive. This makes the carbenoid complex more selective for the desired reaction.



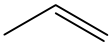
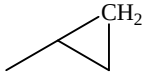
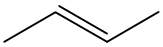
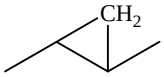
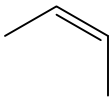
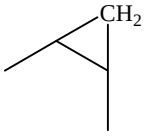
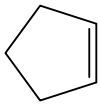
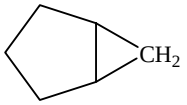
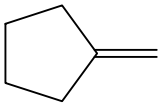
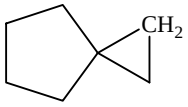
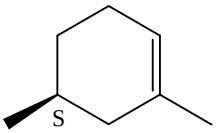
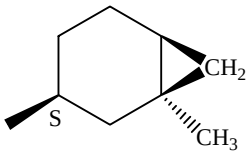
concerted reaction (occurs in one step)

"cis" alkenes form "cis" cyclopropane rings

"trans" alkenes form "trans" cyclopropane rings

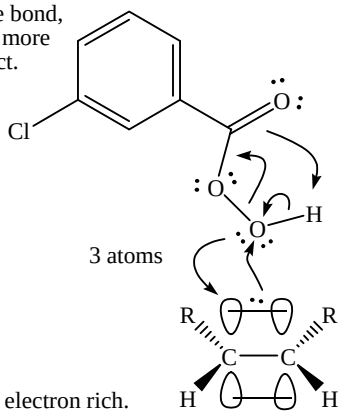


Example Reactions (Simmons-Smith reaction)

	$CH2I_2$ / Zn(Cu)		syn addition enantiomers R and S
	$CH2I_2$ / Zn(Cu)		syn addition enantiomers RR and SS
	$CH2I_2$ / Zn(Cu)		syn addition meso RS and SR
	$CH2I_2$ / Zn(Cu)		syn addition meso RS and SR
	$CH2I_2$ / Zn(Cu)		syn addition achiral
	$CH2I_2$ / Zn(Cu)		syn addition diastereomers SSR and SRS

r. Alkenes with meta chloroperbenzoic acid (mCPBA). Synthesis of epoxides.

mCPBA (peroxyacid) has two electron poor oxygen atoms in the peroxide bond, and the meta-Cl makes them even more electron poor by its inductive effect.

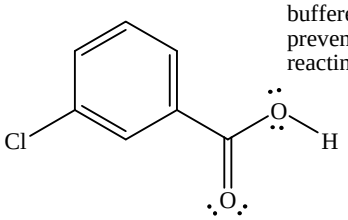


View this complicated group of arrows as two different groupings in the transition state, one of five atoms and one of three atoms. It might be easier to think about this way.

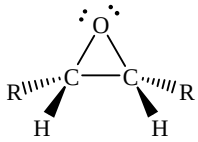
The alkene is electron rich.

5 atoms

buffered solution prevents acid from reacting with epoxide



one step concerted reaction



The reaction can occur from either the top face or the bottom face.

costs (bond energy in kcal/mole)

C=O (even trade) = +176
O-H (even trade) = + 110
O-O (very weak) = +45
C=C (weak pi bond) = +64
ring strain of an epoxide is also a cost = + 27
Total = + 422

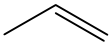
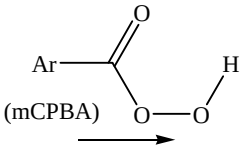
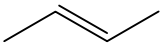
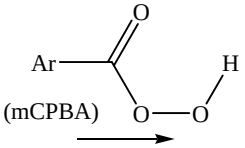
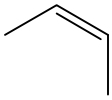
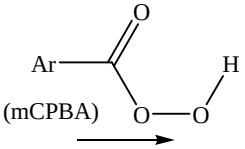
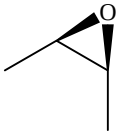
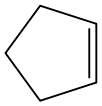
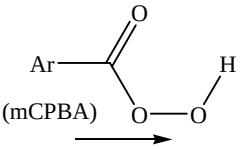
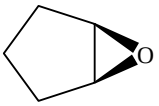
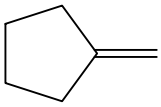
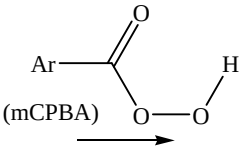
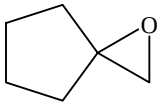
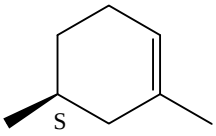
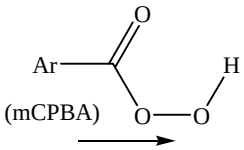
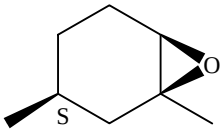
changes in energy

gains (bond energy in kcal/mole)

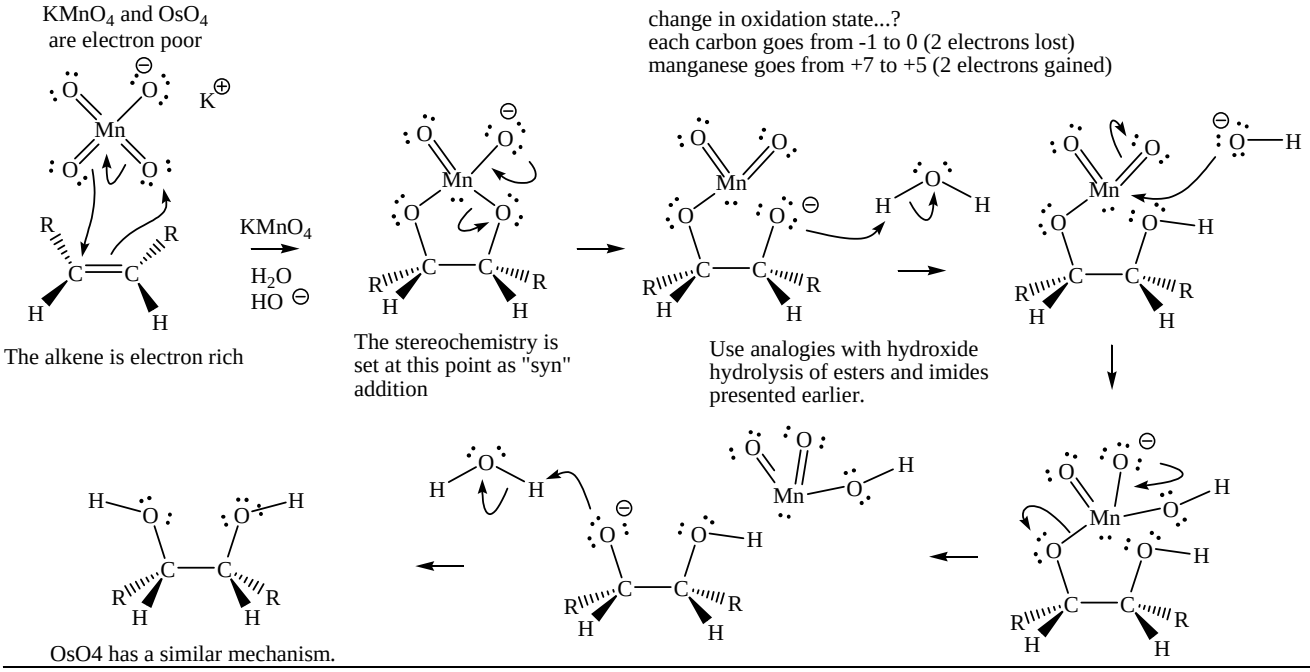
C=O (even trade) = -176
O-H (even trade) = - 110
C-O (very weak) = -90
C-O (very weak) = -90
Total = - 466

ΔH = -44 kcal/mole
exothermic, even with ring strain

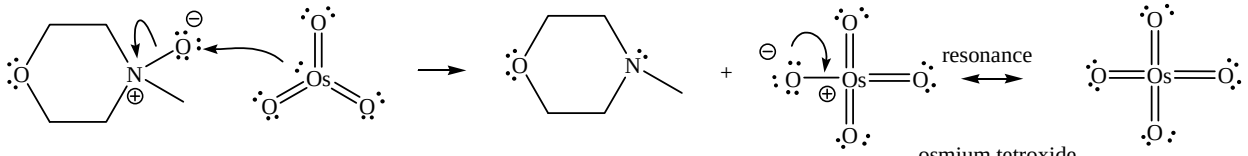
Example Reactions (mCPBA)

		 syn addition enantiomers R and S
		 syn addition enantiomers RR and SS
		 syn addition meso RS and SR
		 syn addition meso RS and SR
		 syn addition achiral
		 syn addition diastereomers SSR and SRS

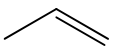
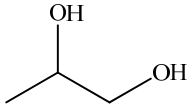
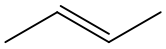
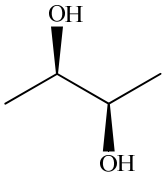
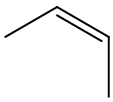
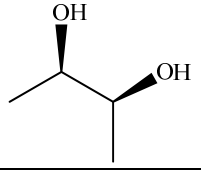
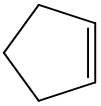
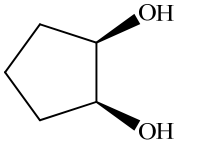
s. Alkenes with OsO_4 or $KMnO_4$. "Syn" synthesis of vicinal diols.

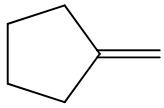


Very expensive OsO_4 can be continually reoxidized with an inexpensive amine oxide (like morpholine N-oxide)

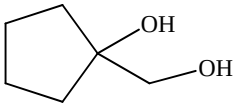


Example Reactions

	OsO_4 or $KMnO_4$ →		syn addition enantiomers R and S
	OsO_4 or $KMnO_4$ →		syn addition enantiomers RR and SS
	OsO_4 or $KMnO_4$ →		syn addition meso RS and SR
	OsO_4 or $KMnO_4$ →		syn addition meso RS and SR

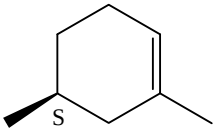


OsO_4 or $KMnO_4$ →

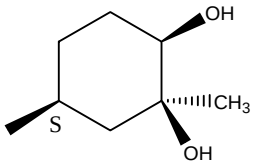


syn addition

achiral



OsO_4 or $KMnO_4$ →

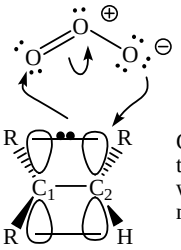


syn addition

diastereomers SSR and SRS

t. Alkenes with 1. O_3 / -78°C 2. CH_3SCH_3 or Zn. Synthesis of aldehydes or ketones.

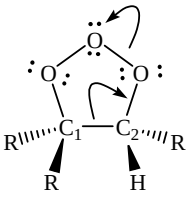
Ozone is an electron poor oxidizing reagent.



Simple alkenes are electron rich.

-78°C →

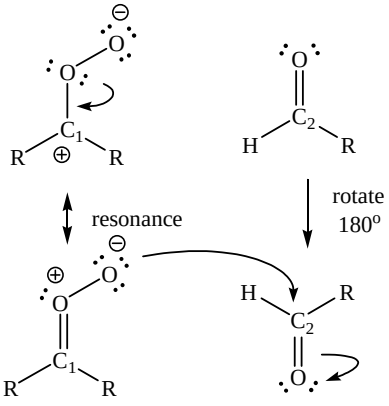
Cyclic five atom transition state with six electron movement.



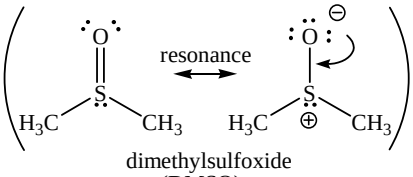
Molozonide is highly unstable, even at -78°C and rearranges to a more stable ozonide with only one peroxide bond.

-78°C →

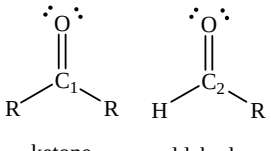
Peroxide bond ruptures (shown).



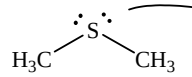
Rejoins with only one peroxide bond (use polarities).

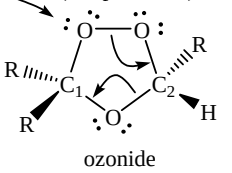


dimethylsulfoxide (DMSO)



ketone aldehyde

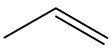




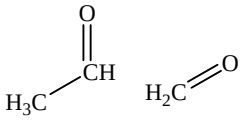
ozonide

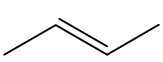
The C=C is completely cleaved at -78°C. The second step decides what will happen to the ozonide. In this example, it is reduced by DMS to two carbonyl compounds, (an aldehyde and a ketone).

Example Reactions

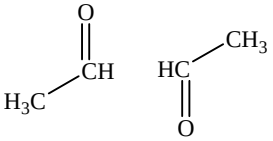


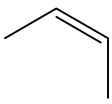
1. O_3 / -78°C
2. CH_3SCH_3 →



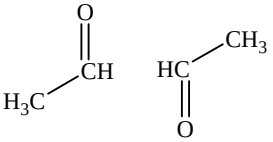


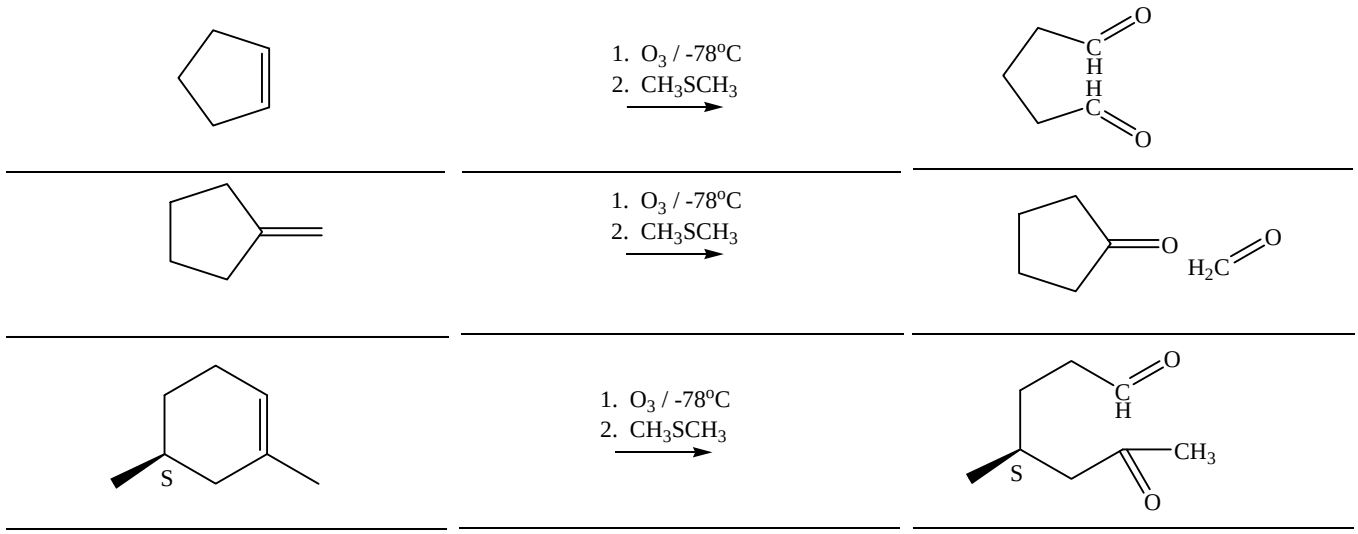
1. O_3 / -78°C
2. CH_3SCH_3 →



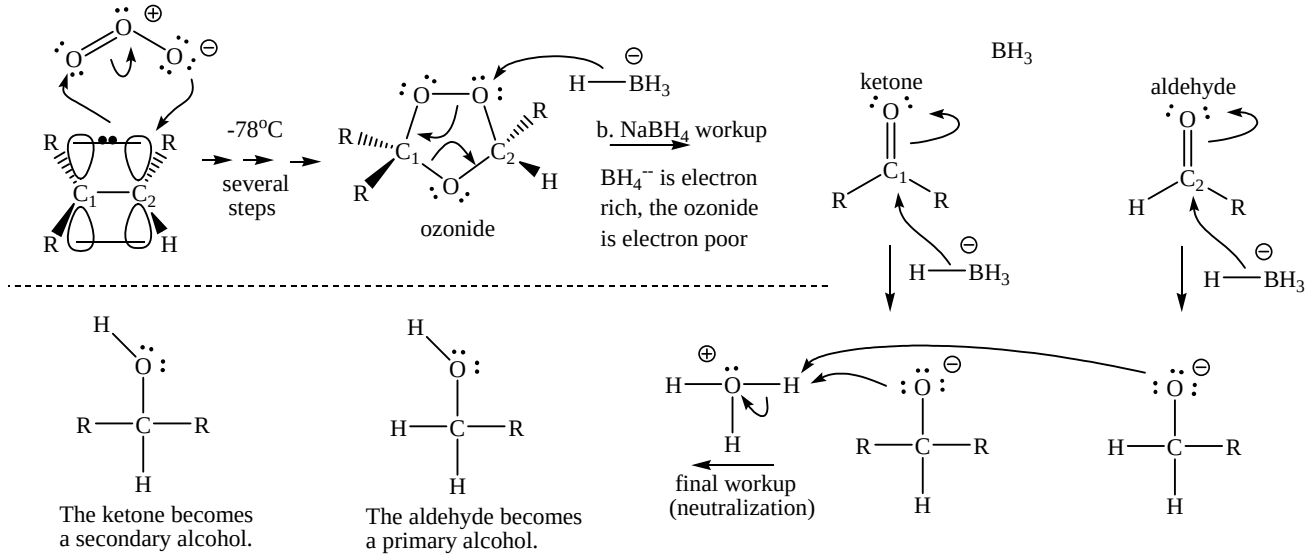


1. O_3 / -78°C
2. CH_3SCH_3 →

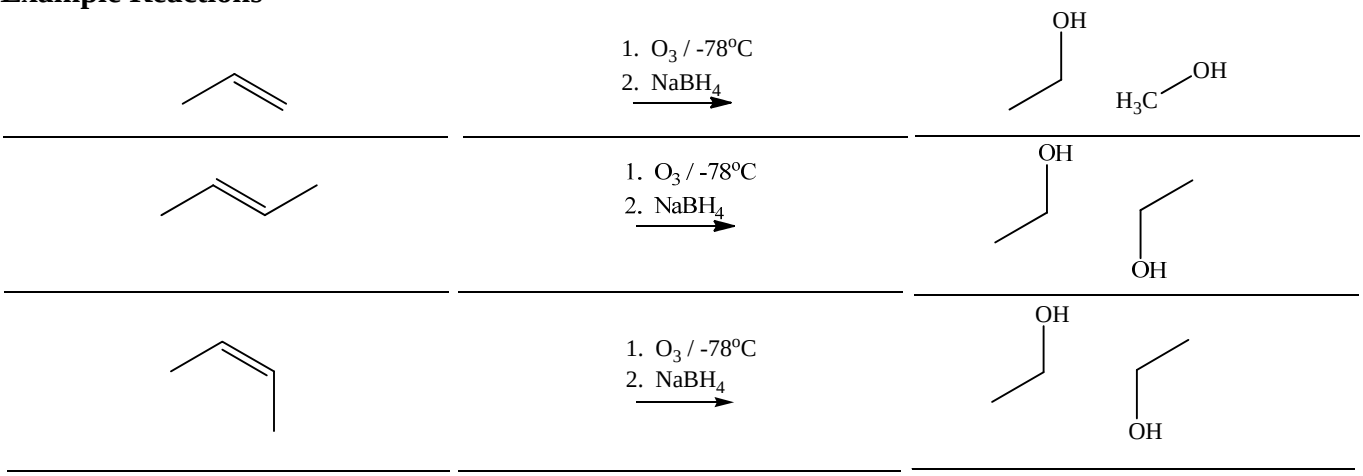


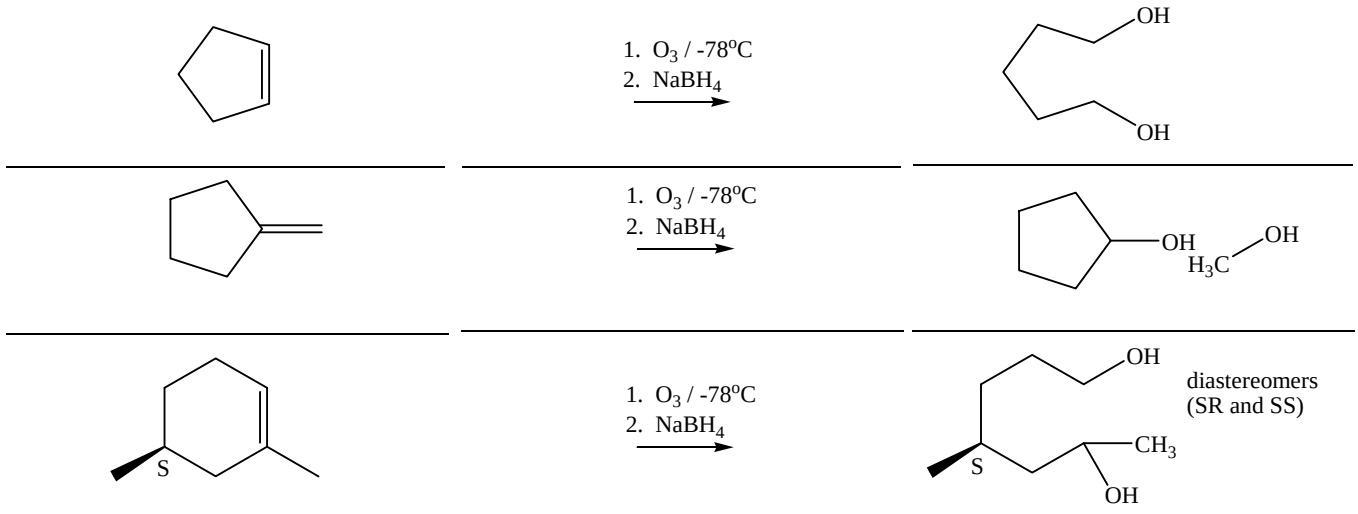


u. Alkenes with 1. O_3 / -78°C 2. $NaBH_4$. Synthesis of alcohols.

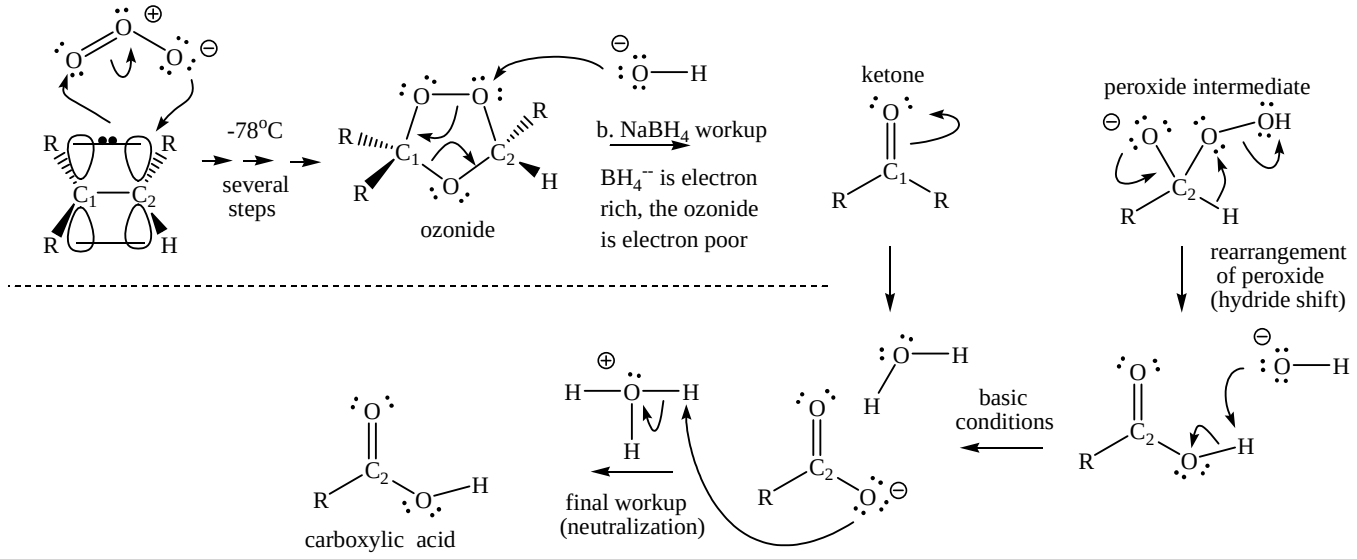


Example Reactions

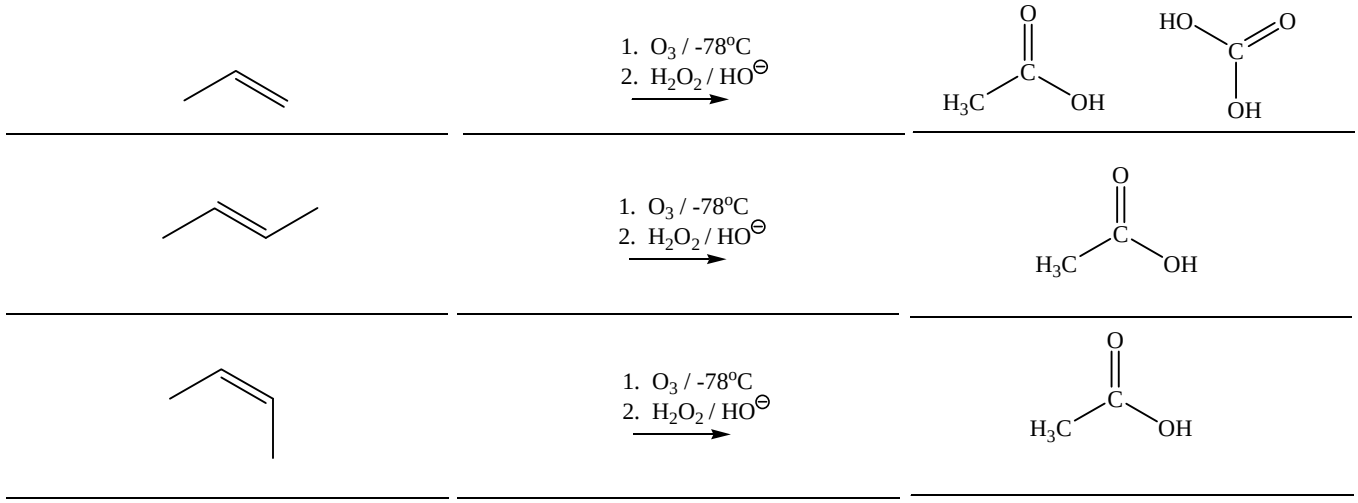


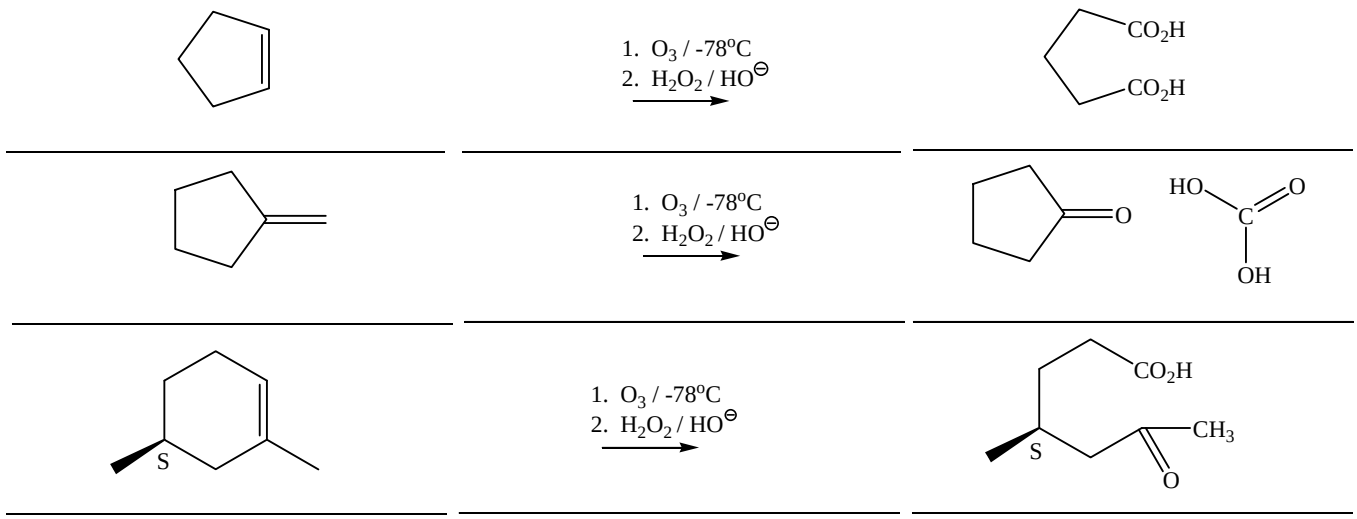


v. Alkenes with 1. O_3 / -78°C 2. H_2O_2 / HO^{--}. Synthesis of carboxylic acids or ketones.

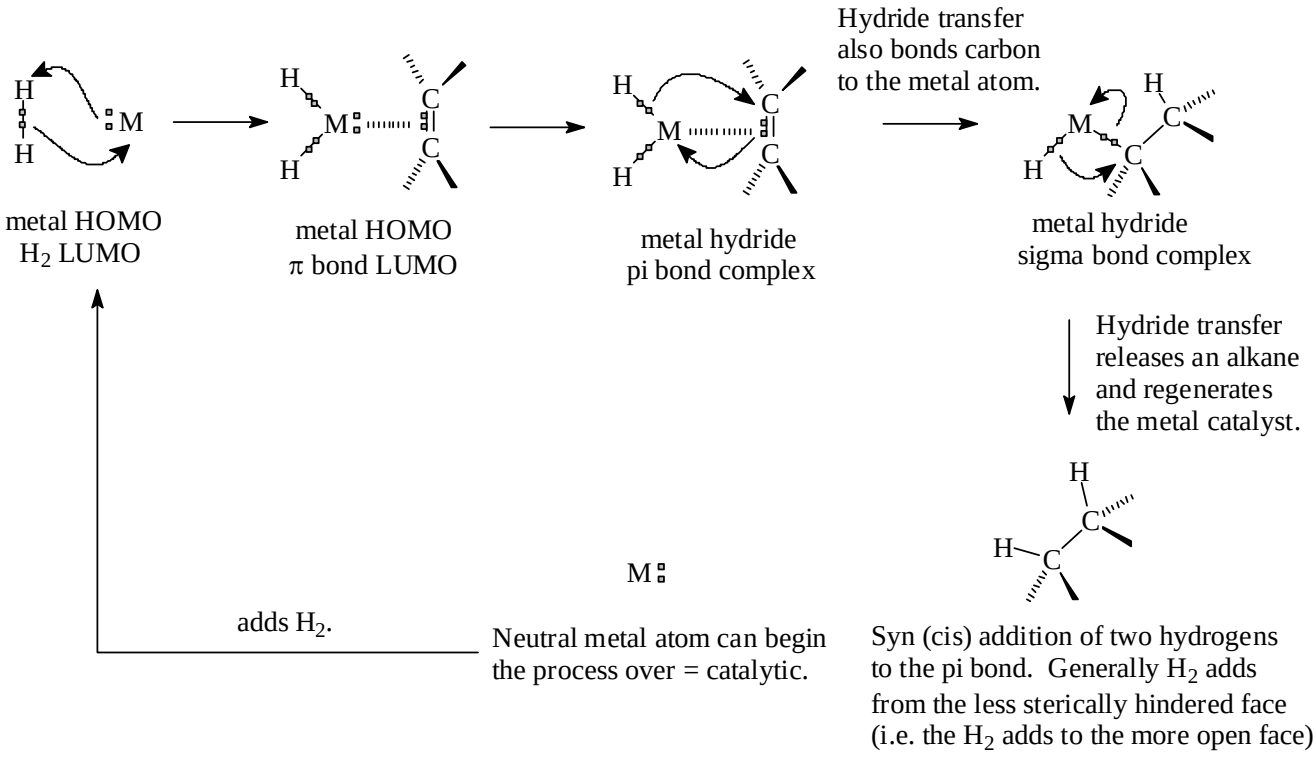


Example Reactions

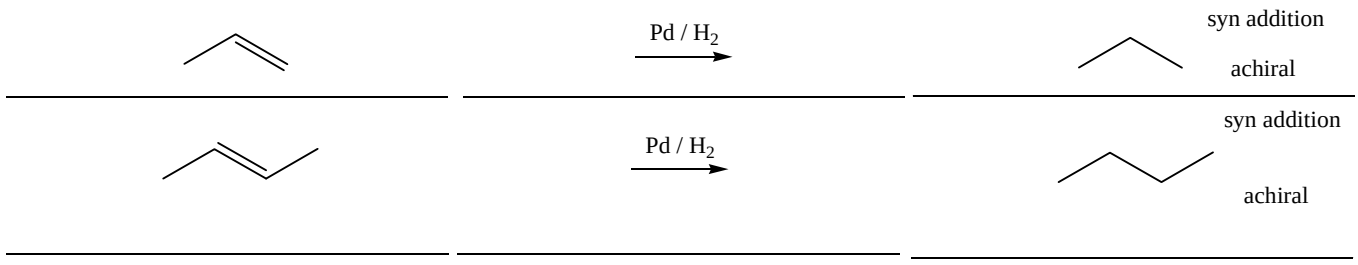


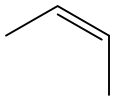
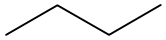
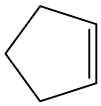
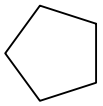
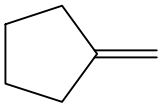
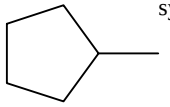
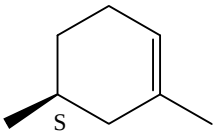
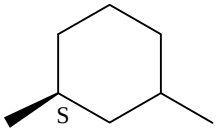


w. Alkenes with Pd / H_2. Synthesis of "alkane" from "alkene" (hydrogenation). Simplistic mechanism:



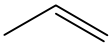
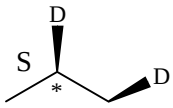
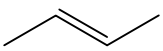
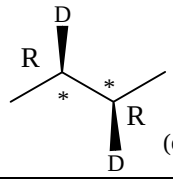
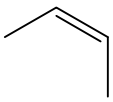
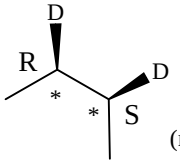
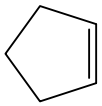
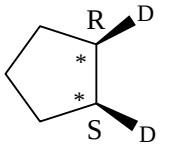
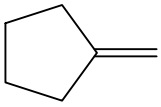
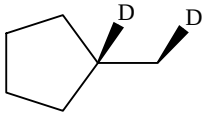
Example reactions

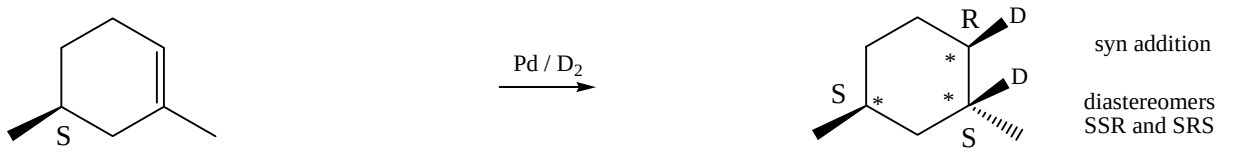


	Pd / H_2	 syn addition achiral
	Pd / H_2	 syn addition achiral
	Pd / H_2	 syn addition achiral
	Pd / H_2	 syn addition diastereomers SR and SS

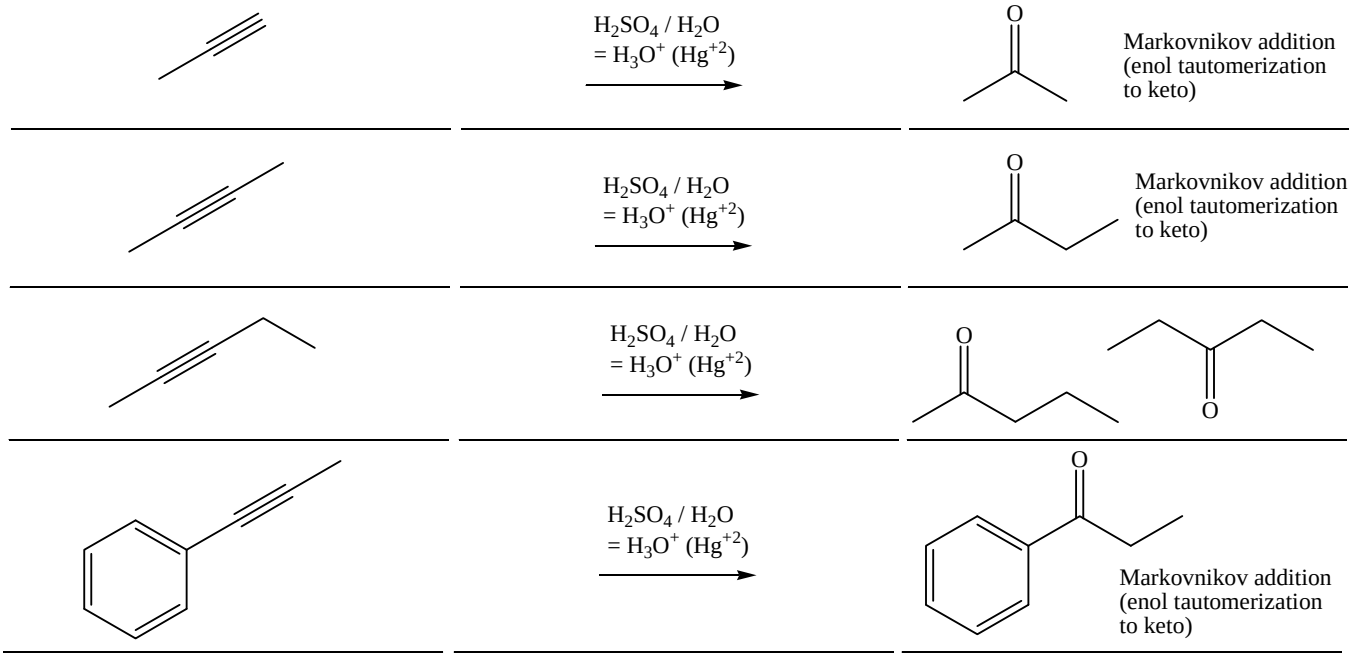
x. Alkenes with Pd / D_2. Same hydrogenation reactions with deuterium from "alkene" (hydrogenation w/"D" = deuterium).

* = chiral center

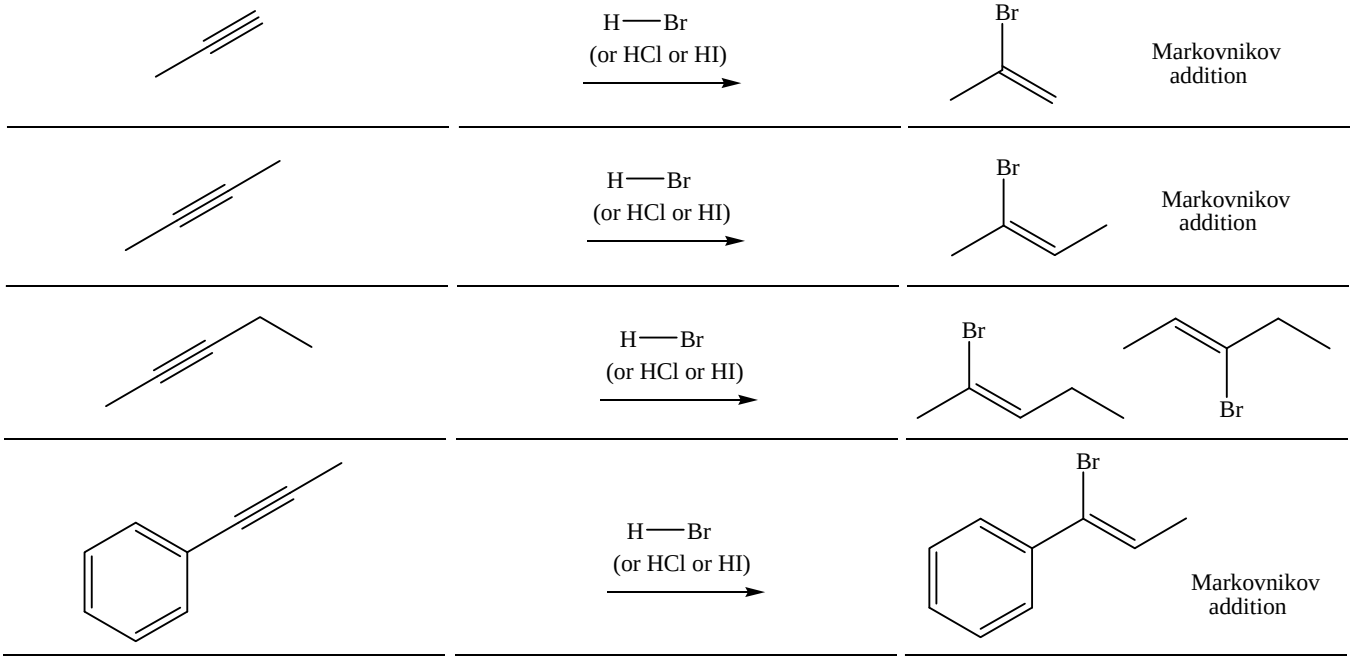
	Pd / D_2	 syn addition R / S
	Pd / D_2	 syn addition RR and SS (enantiomers)
	Pd / D_2	 syn addition RS and SR (meso,achiral)
	Pd / D_2	 syn addition RS and SR (meso,achiral)
	Pd / D_2	 syn addition achiral



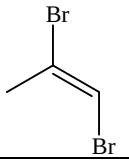
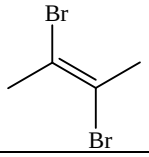
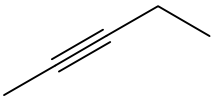
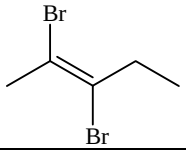
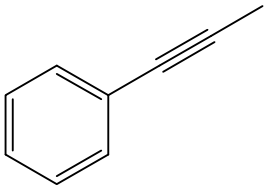
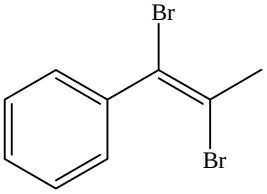
y. Alkynes with aqueous sulfuric acid (plus some Hg^{+2} catalyst). Synthesis via enols (Markovnikov addition).



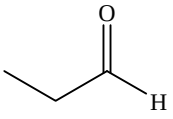
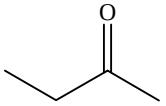
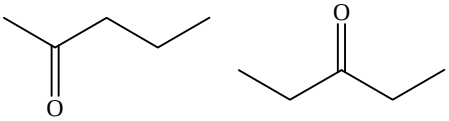
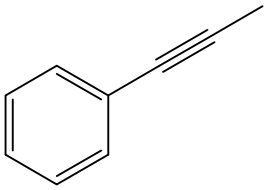
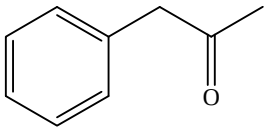
y. HX addition to alkynes. Markovnikov addition.



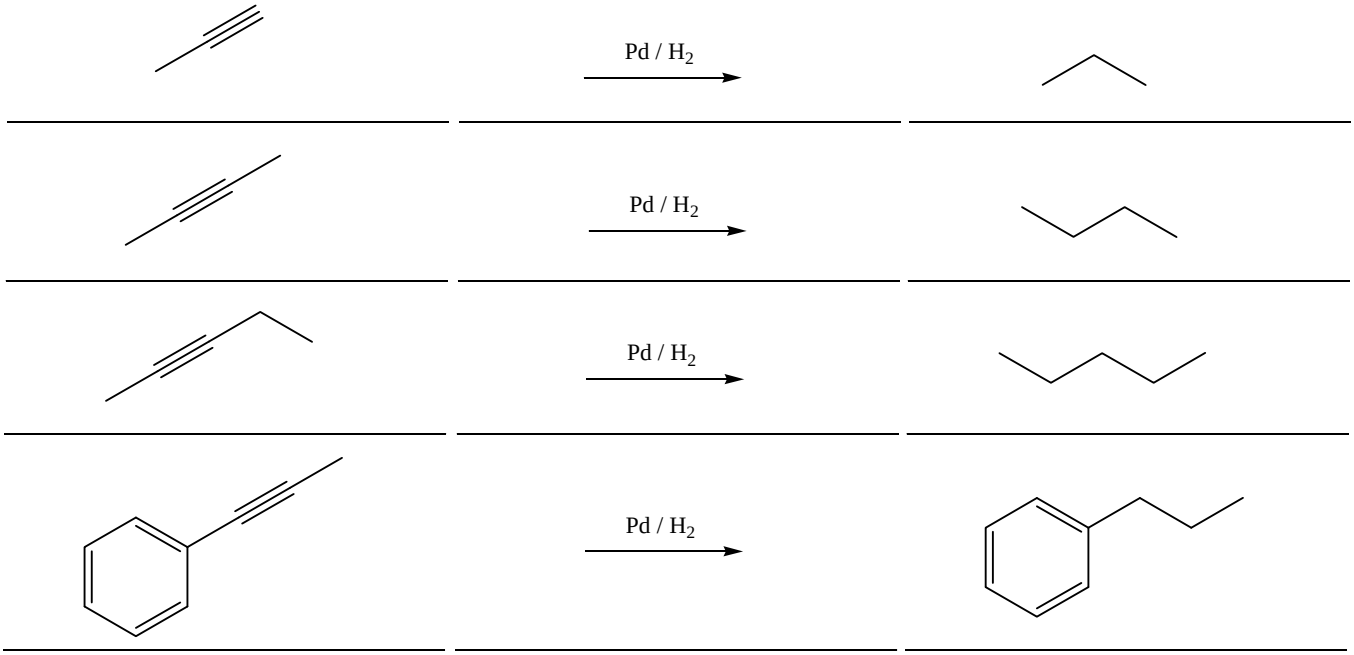
z. Bromination (or chlorination) of alkynes. Bridging bromonium ion.

	Br_2 or Cl_2		anti addition
	Br_2 or Cl_2		anti addition
	Br_2 or Cl_2		anti addition
	Br_2 or Cl_2		anti addition

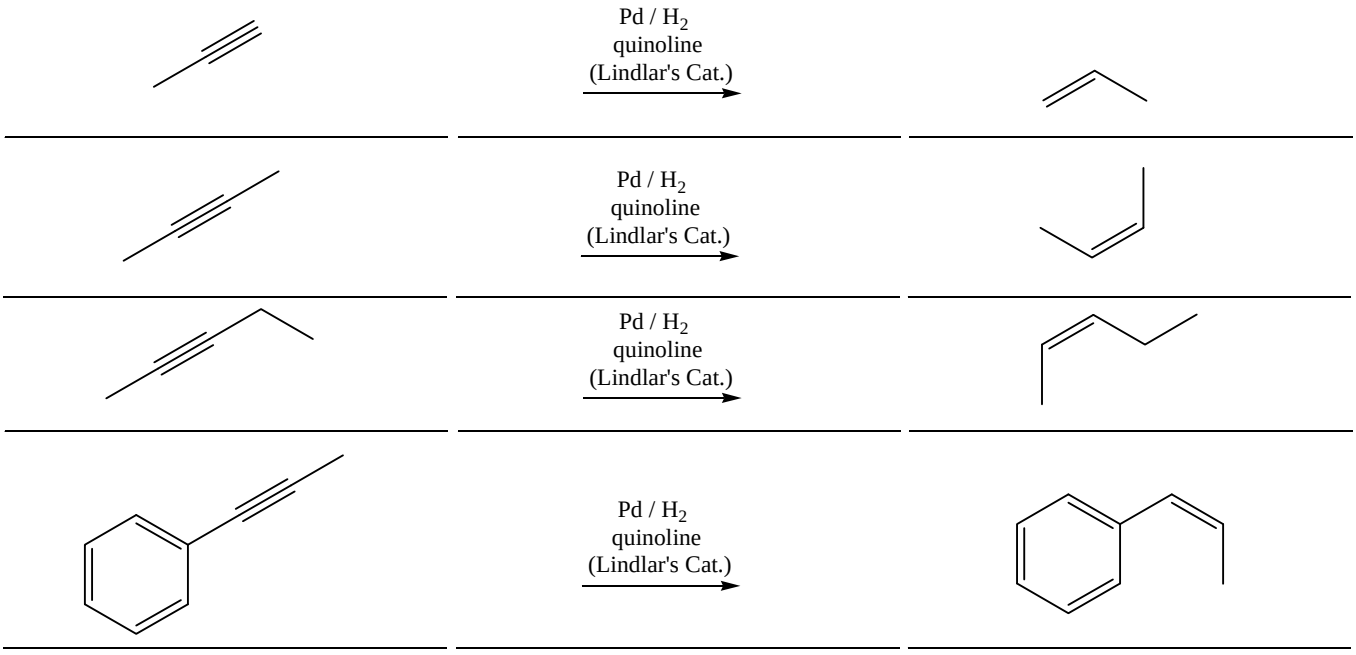
aa. 1. Hydroboration 2. oxidation of alkynes (anti-Markovnikov addition makes aldehydes or ketones via enolate).

	1. HBR_2 2. H_2O_2 / $HO^{\ominus}$		anti Markovnikov addition
	1. HBR_2 2. H_2O_2 / $HO^{\ominus}$		anti Markovnikov addition
	1. HBR_2 2. H_2O_2 / $HO^{\ominus}$		
	1. HBR_2 2. H_2O_2 / $HO^{\ominus}$		anti Markovnikov addition

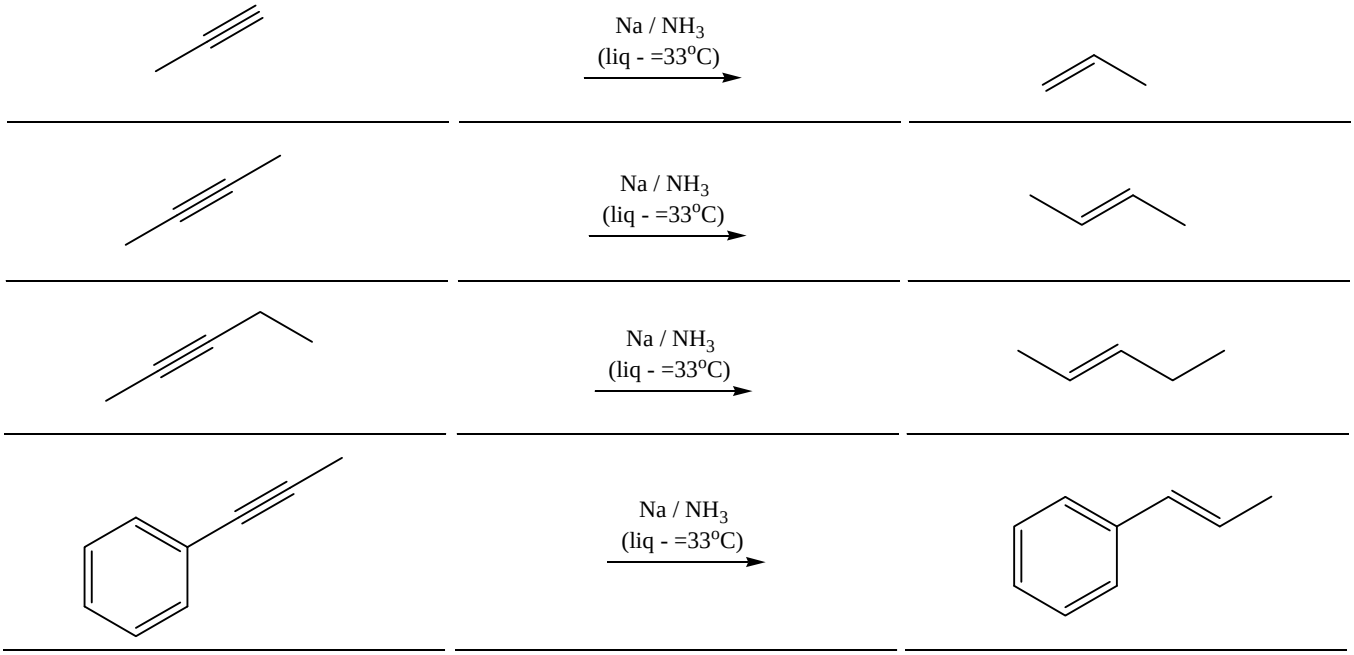
bb. Catalytic hydrogenation reduces triple bond to “alkane”.



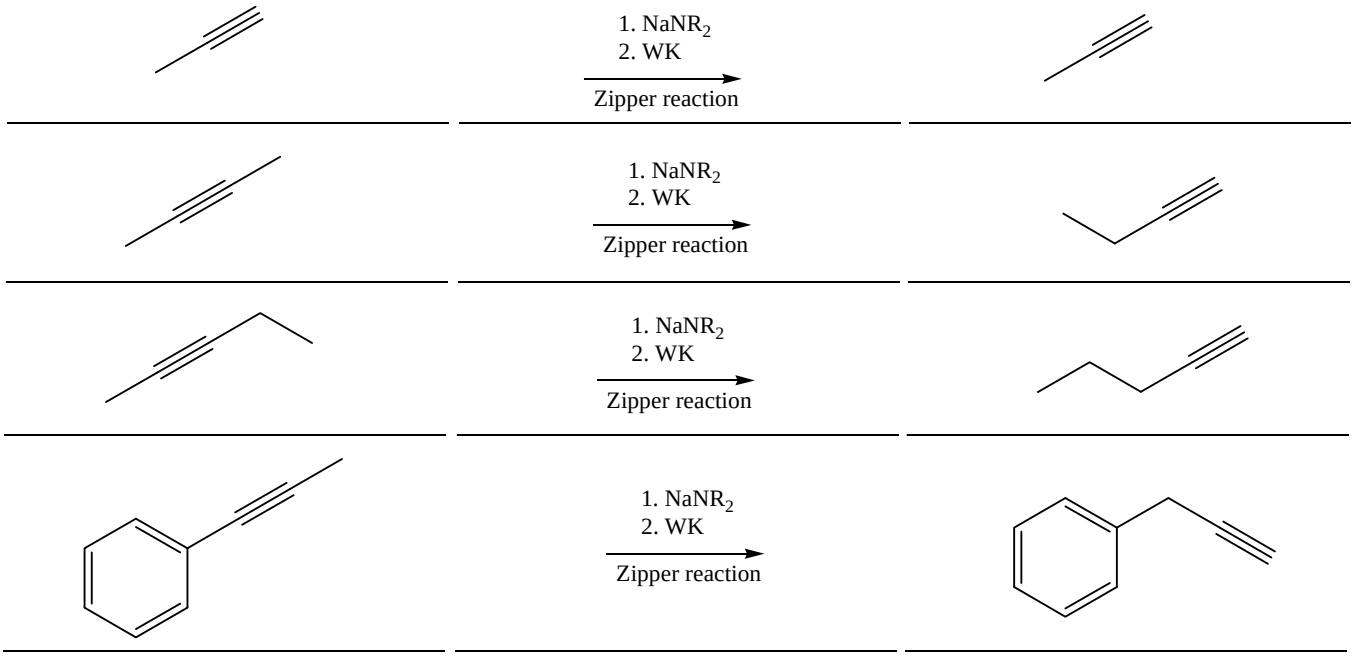
cc. Catalytic hydrogenation with quinoline “poison” of Pd catalyst reduces triple bond to Z alkene (syn addition).



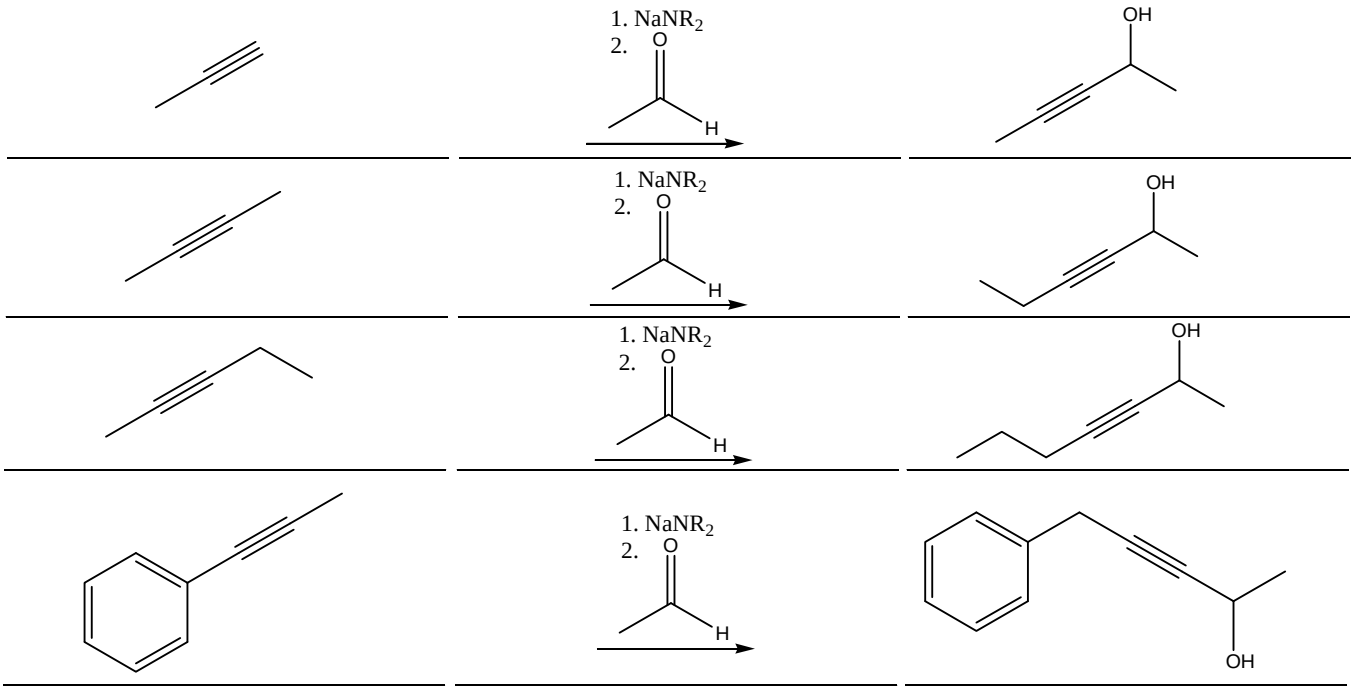
dd. Sodium metal + liquid ammonia reduction of triple bond to E alkenes.



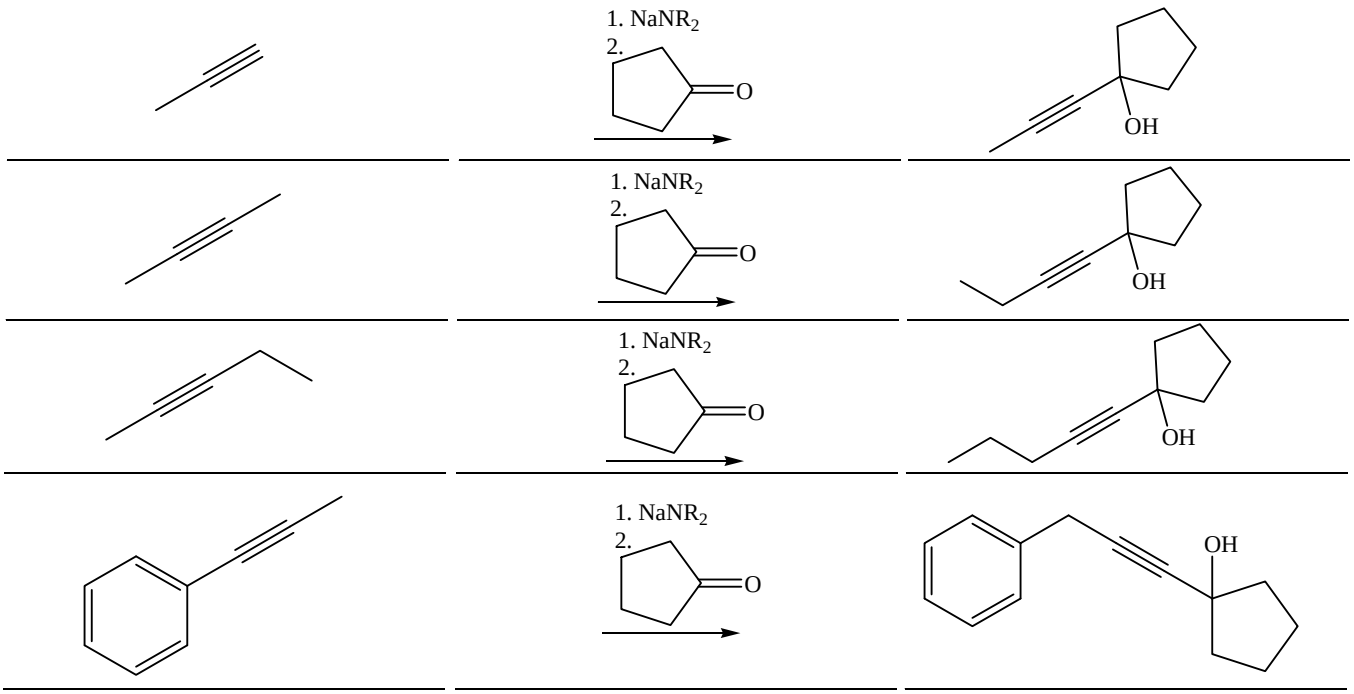
ee. Zipper reaction moves triple bond to terminal position where it can be removed to form sp carbanion nucleophile.



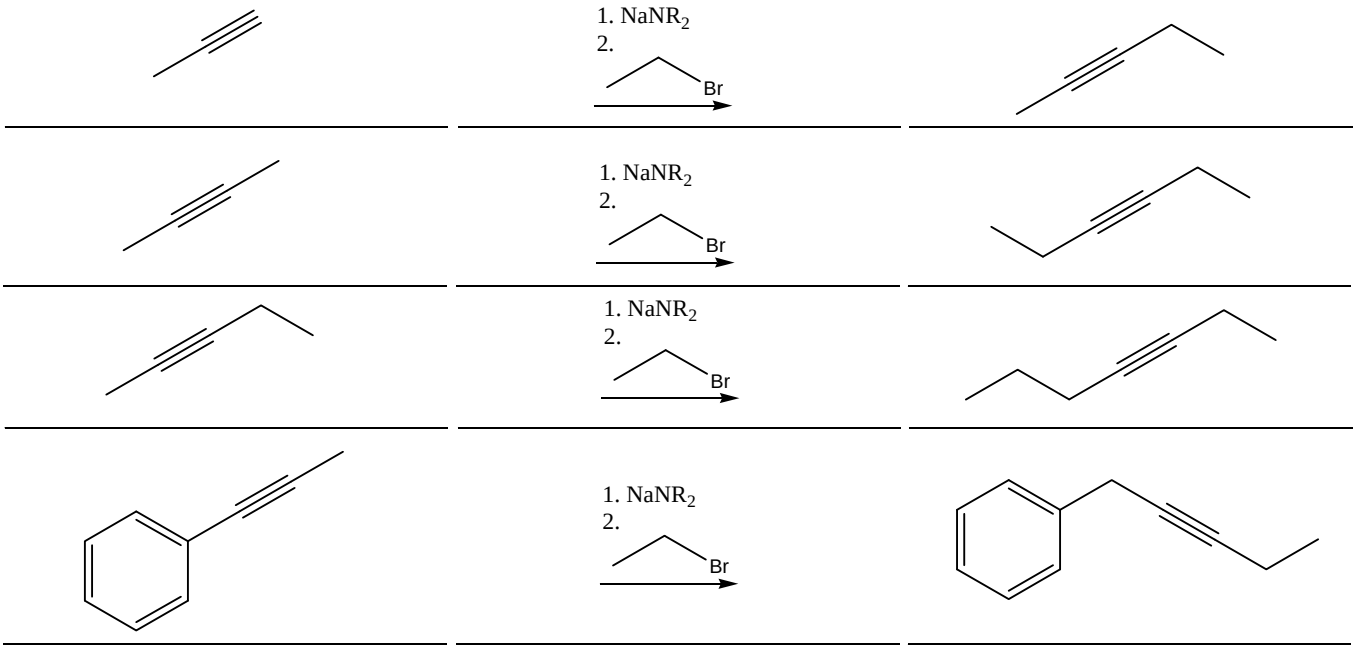
ff. Formation of conjugate base + addition of aldehyde electrophile forms propargyl alcohol.



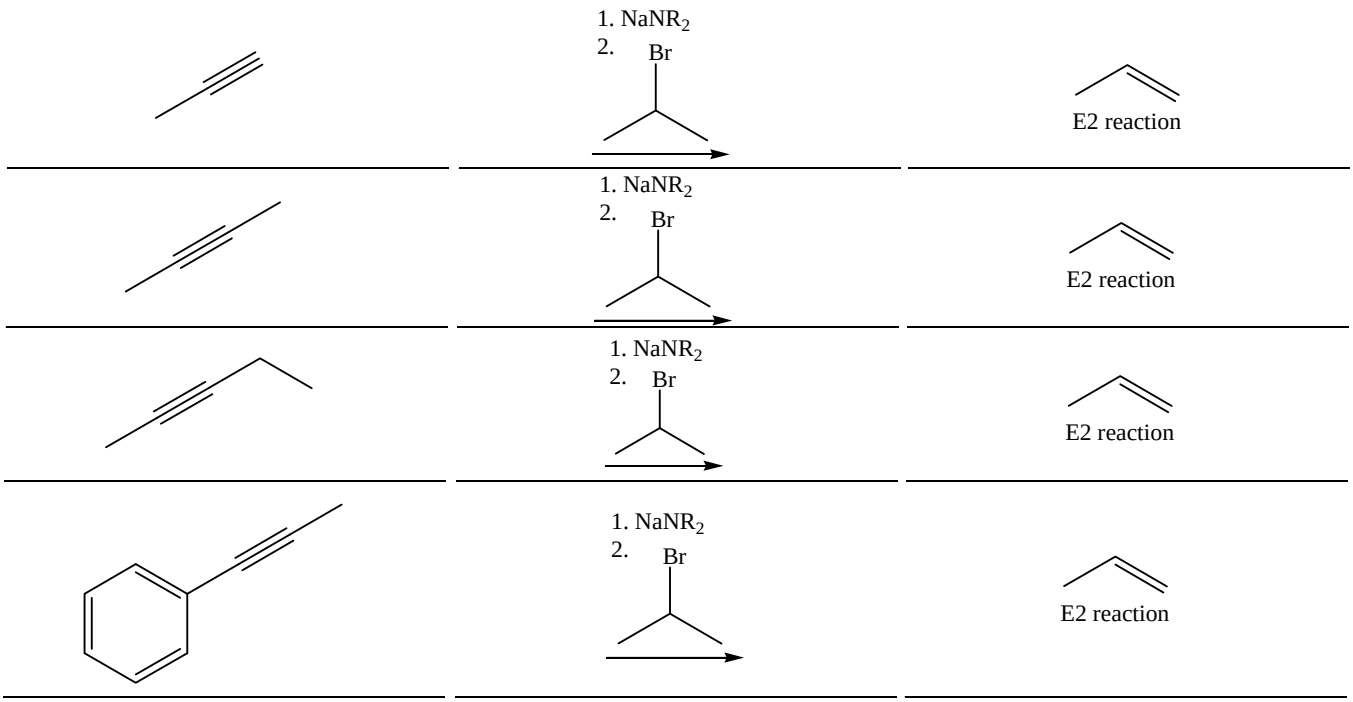
gg. Formation of conjugate base + addition of ketone electrophile forms propargyl alcohol.



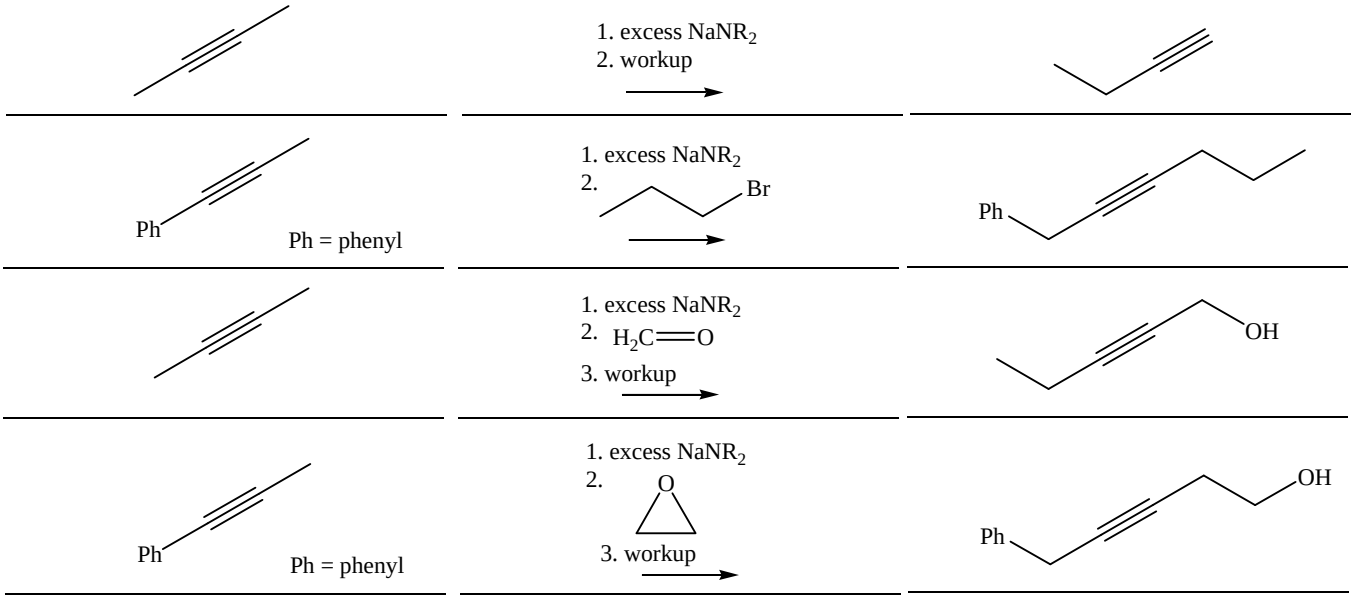
hh. Formation of conjugate base + addition of methyl or primary RX electrophile forms a longer alkyne.



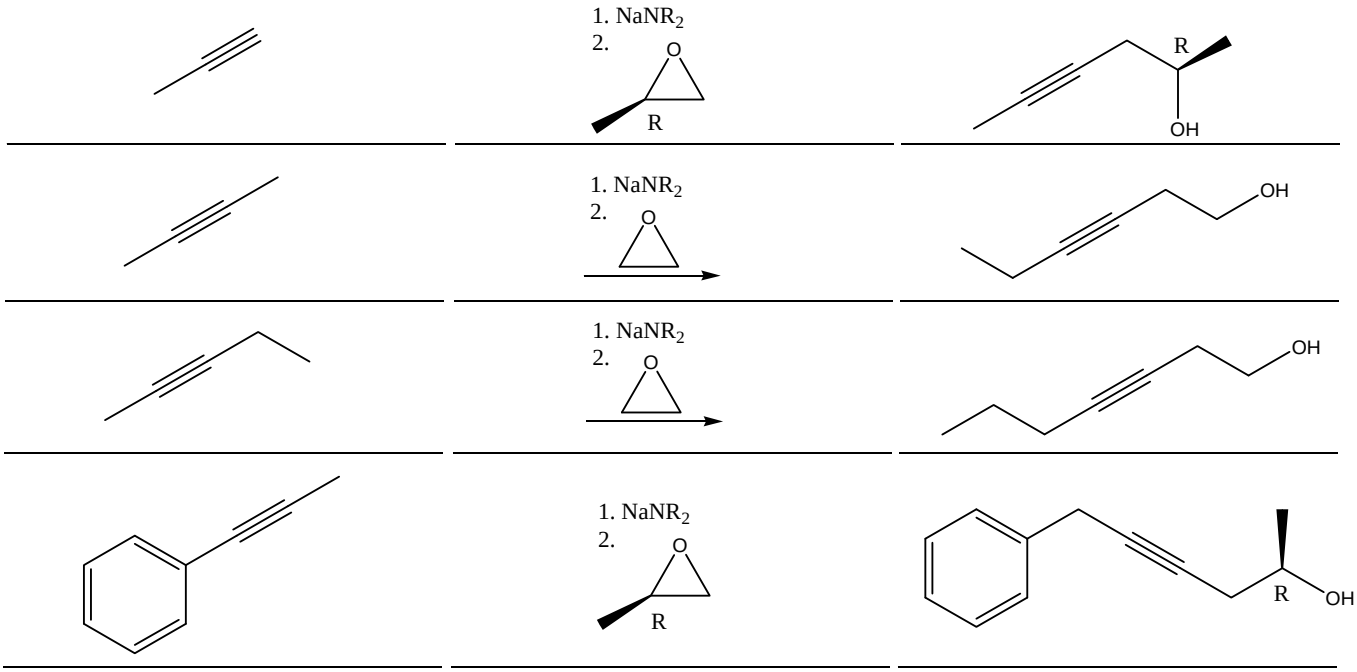
ii. Formation of conjugate base + addition of secondary electrophile reacts in a nonproductive E2 reaction.



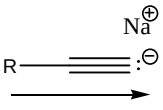
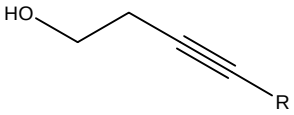
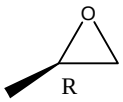
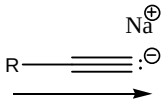
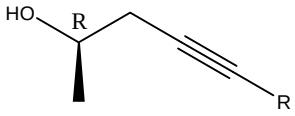
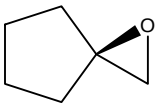
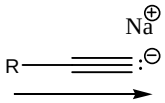
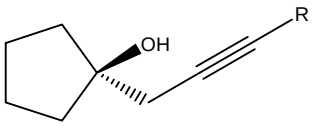
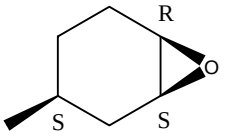
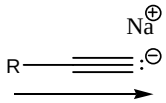
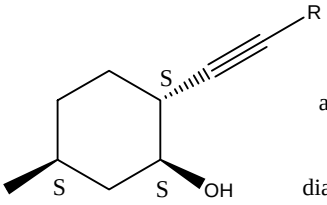
jj. Use zipper reaction to move alkyne through a linear chain to the end position. Work up 4 ways: a. with mild acid to generate the terminal alkyne, b. with an MeX or primary RCH2X to make a longer alkyne, c. with an aldehyde or ketone compound (C=O) or d. with an epoxide.



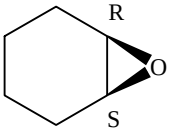
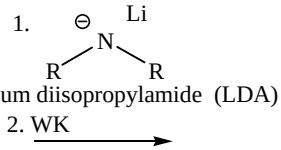
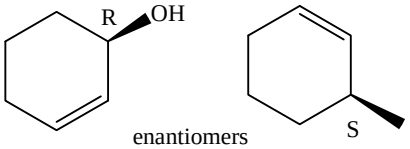
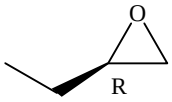
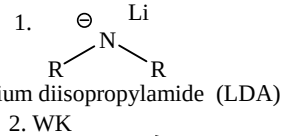
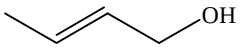
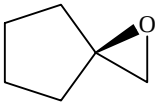
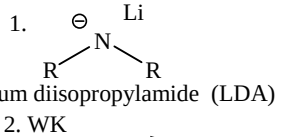
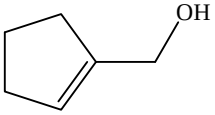
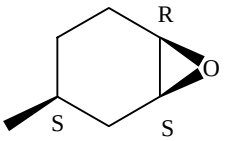
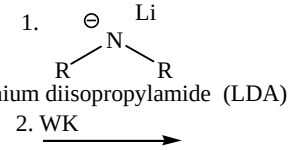
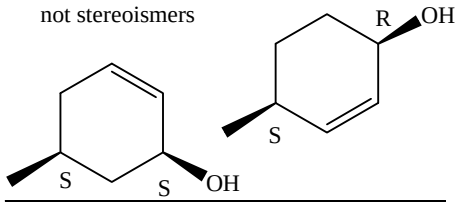
kk. Formation of conjugate base + addition of epoxide electrophile forms an alkynyl alcohol via S_N2 reaction.



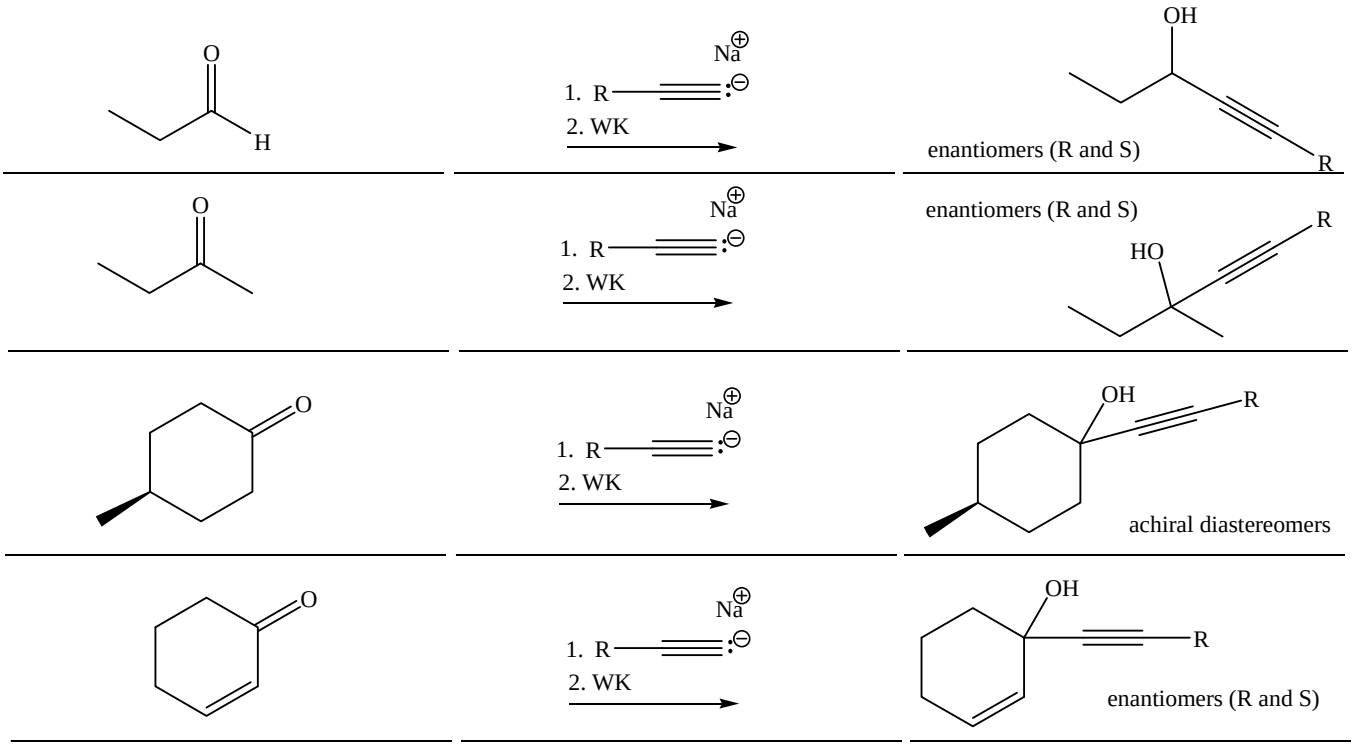
ll. Epoxides with terminal acetylides (followed by workup = neutralization).

		 achiral
		 chiral
		 achiral
		 and SRR diastereomers

mm. Epoxides with lithium diisopropyl amide (LDA, followed by workup = neutralization).

		 enantiomers
		 achiral
		 achiral
		not stereoismers 

nn. Aldehydes and ketones with terminal acetylides.



oo. Aldehydes and ketones with secondary amines (enamine synthesis, alkylation, hydrolysis).