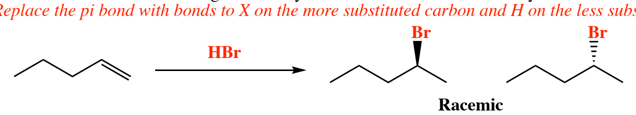
Chapter 6

1) Reaction of Alkenes with HX to Give Haloalkanes

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

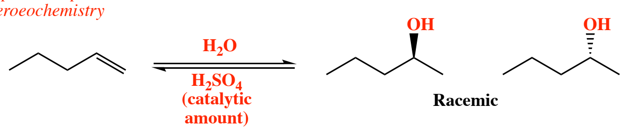
Replace the pi bond with bonds to X on the more substituted carbon and H on the less substituted carbon with mixed stereochemistry

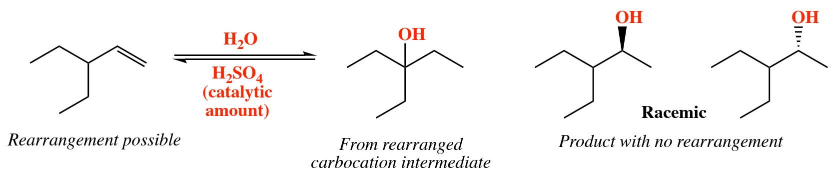


2) Acid-Catalyzed Hydration of Alkenes to Give Alcohols

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

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

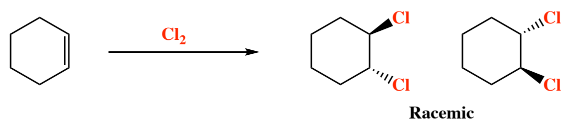




3) Halogenation of Alkenes to Give Vicinal Dihaloalkanes

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

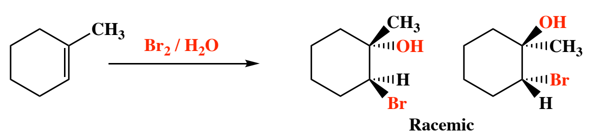
Replace the pi bond with bonds to X with anti stereochemistry only



4) Hydrohalogenation of Alkenes to Give Halohydrins

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

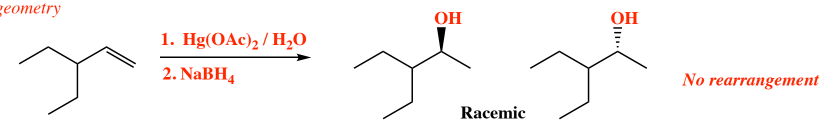
Replace the pi bond with bonds to OH on the more substituted carbon and X on the less substituted carbon with anti stereochemistry only



5) Oxymercuration-Reduction of Alkenes to Give Alcohols

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

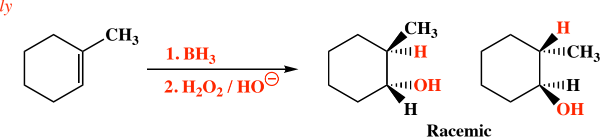
Replace the pi bond with bonds to OH on the more substituted carbon and H on the less substituted carbon with mixed geometry



6) Hydroboration-Oxidation of Alkenes to Give Alcohols

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

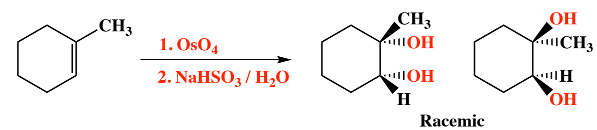
Replace the pi bond with bonds to H on the more substituted carbon and OH on the less substituted carbon with syn geometry only



7) Geminal Dihydroxykation of Alkenes to Give Vicinal Diols (the Ozzy Osbourne reaction)

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

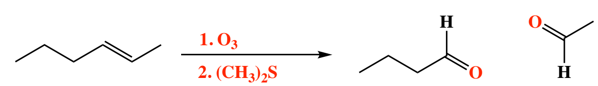
Replace the pi bond with bonds to OH with syn geometry only



8) Ozonolysis of Alkenes to Give Aldehydes and Ketones

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

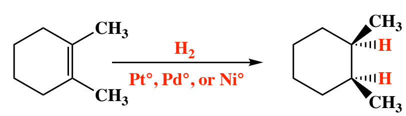
Replace the carbon-carbon double bond with two double bonds to an O atom (C=O) while BREAKING THE C=C!



9) Hydrogenation of an Alkene to Give Alkanes

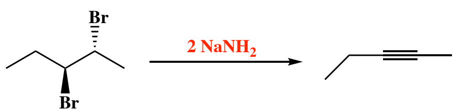
Mechanism Keys: **Alkene and H_2 adsorb on metal surface, then new bonds form to both carbon atoms essentially simultaneously so the H atoms add to the same face** Regiochemistry: **N/A** Stereochemistry: **syn**

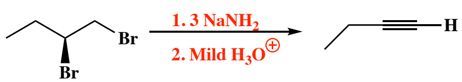
Replace the pi bond with bonds to H with syn geometry only



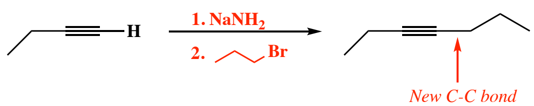
Chapter 7

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

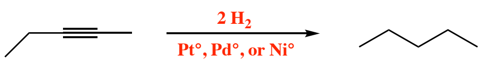




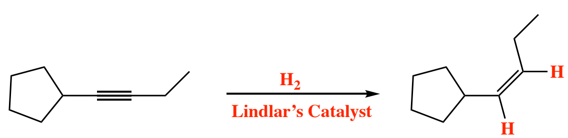
11) Reaction of Terminal Alkynes with Base then a Primary Haloalkane to Give an Alkyne with a New C-C Bond
Mechanism Keys: **S$_N$2 reaction. Haloalkane must be primary to avoid E2.** Regiochemistry: **N/A** Stereochemistry: **N/A**
Replace the terminal C-H bond with a new C-C bond to the carbon that had the C-X bond.



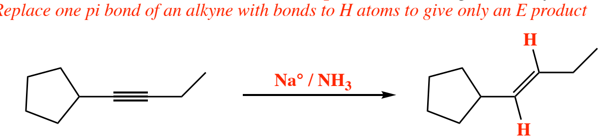
12) Hydrogenation of Alkynes to Give Alkanes
Mechanism Keys: **Alkyne and H$_2$ adsorb on metal surface, then new bonds form to both carbon atoms essentially simultaneously. Happens twice and cannot be stopped because alkenes produced as intermediates react faster than alkynes**
Regiochemistry: **N/A** Stereochemistry: **N/A**
Replace the two pi bonds with four bonds to H atoms



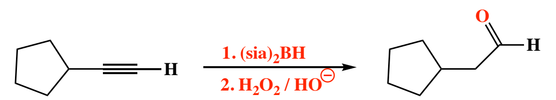
13) Reduction of Alkynes with H$_2$ and Lindlar's Catalyst to Give *Z* Alkenes
Mechanism Keys: **Alkene and H$_2$ adsorb on metal surface, then new bonds form to both carbon atoms essentially simultaneously. Pb and quinoline poison the catalyst so the reaction stops at a Z alken** Regiochemistry: **N/A**
Stereochemistry: **Syn**
Replace one pi bond of an alkyne with bonds to H atoms to give only a Z product

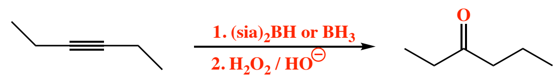


14) Reduction of Alkynes with Na° and NH$_3$ to Give *E* Alkenes
Mechanism Keys: **Radical mechanism, two one-electron transfers from Na°, followed by adding two protons from NH$_3$, the more stable *trans* alkene (less steric strain) predominates.** Regiochemistry: **N/A** Stereochemistry: **Anti**
Replace one pi bond of an alkyne with bonds to H atoms to give only an E product

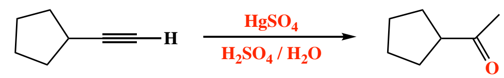


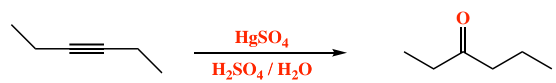
15) Hydroboration-Oxidation of Terminal Alkynes to Give Aldehydes (Using the "Antler" Reagent)
Mechanism Keys: **Four-membered ring transition state as H and B atoms add to same face of pi bond, enol intermediate followed by enol-keto tauatomerization, "antlers" ensure regiochemical control so that H adds to more substituted carbon.**
Regiochemistry: **non-Markovnikov** Stereochemistry: **N/A**
Replace the two pi bonds of a terminal alkyne with double bonds to an O atom to give an aldehyde. When the alkyne is not terminal, a ketone is the product.



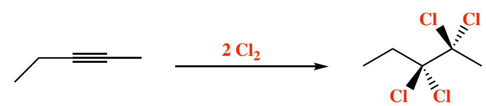


16) Oxymercuration-Reduction of Alkynes to Ketones
Mechanism Keys: **Enol intermediate followed by enol-keto tauatomerization. O atom ends up bonded to more stubstituted carbon** Regiochemistry: **Markovnikov** Stereochemistry: **Mixed**
Replace the two pi bonds of an alkyne with double bonds to an O atom to give a ketone. When the alkyne is terminal the internal carbon ends up as the C=O



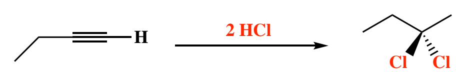


17) Reaction of Alkynes with X$_2$ to Give Tetrahaloalkanes
Mechanism Keys: **X$_2$ reacts with both pi bonds** Regiochemistry: **N/A** Stereochemistry: **N/A**
Replace both pi bonds with 2 bonds to X atoms for each carbon atom.



18) Reaction of Alkynes with HX to Give Geminal Dihaloalkanes
Mechanism Keys: **HX reacts with both pi bonds, and both X atoms always end up on the same carbon atom, which is the internal carbon of terminal alkynes** Regiochemistry: **Markovnikov** Stereochemistry: **N/A**
Replace both pi bonds on one carbon with 2 bonds to X atoms, and the other carbon with 2 bonds to H. For terminal alkynes, the internal carbon gets the two bonds to X and the terminal carbon gets the two bonds to H

reaction at the other carbon gives the same product

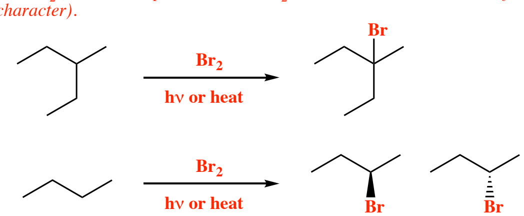


Chapter 8

19) Free Radical Halogenation of Alkanes to Give Haloalkanes

Mechanism Keys: **Free radical chain process, initiation when Br_2 is exposed to light (hν) or heat to give Br radicals that abstracts an H atom on the most substituted carbon during the propagation step** Regiochemistry: **Br ends up on most stubstituted C atom** Stereochemistry: **N/A**

On the most substituted carbon with an H atom, replace one C-H bond with a C-Br bond. Use Br_2 because it is more selective than Cl_2 (Hammonds postulate: The Br_2 reaction has an endothermic first step so the transition state has more radical character).

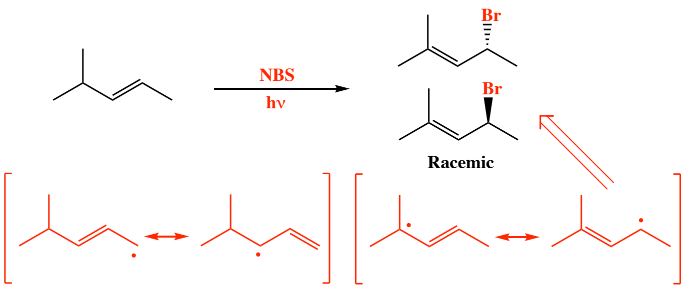


Racemic

20) Allylic Halogenation of Alkenes to Give Haloalkenes

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

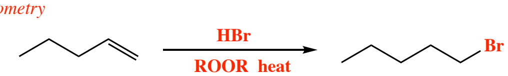
Analyze both of the contributing structures for both allyl radicals that are possible, consider adding a Br atom to the location of each carbon radical on each contributing structure, analyze each of these possible products and choose the most stable alkene (most substituted alkene) as the predominant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



21) Reaction of Alkenes with HBr in the Presence of H_2O_2 and Heat to Give Haloalkanes

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

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



Chapter 9

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

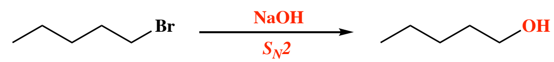
S_N2: Nucleophile attacks backside of carbon-leaving group bond as the leaving group departs
Regiochemistry: **N/A** Stereochemistry: **InVERSiON**

E2: Base removes H atom on carbon adjacent to leaving group as the leaving group departs. The H atom being removed and the leaving group must be in an antiperiplanar geometry for reaction to take place
Regiochemistry: **Zaitsev product (most highly substituted alkene)** Stereochemistry: **determined by antiperiplanar transition state requirement**

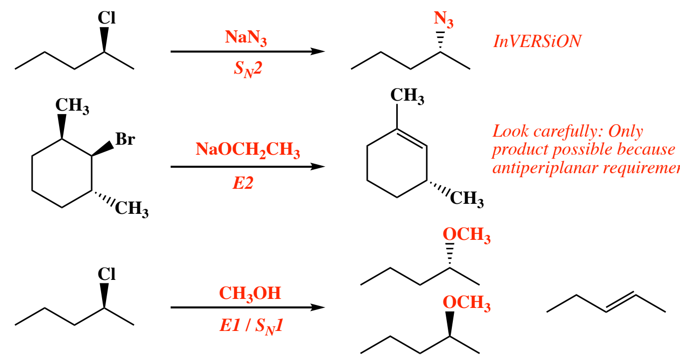
S_N1: Leaving group departs to give carbocation intermediate then nucleophile binds to carbocation
Regiochemistry: **N/A** Stereochemistry: **Scrambled (not quite racemic)**

E1: Leaving group departs to give carbocation intermediate that loses a proton on an adjacent carbon to give an alkene
Regiochemistry: **Zaitsev product (most highly substituted alkene)** Stereochemistry: **N/A**

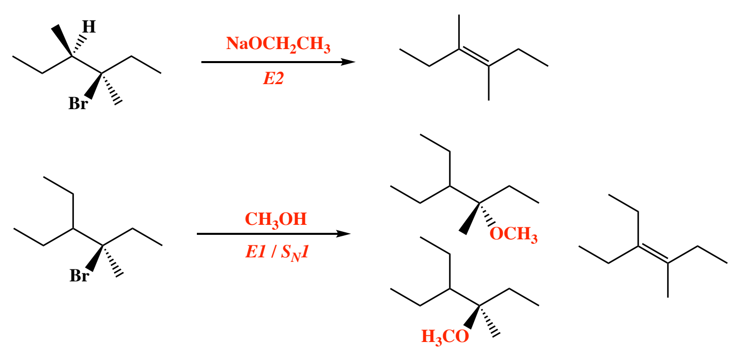
Primary haloalkane - *S_N2 only (except when KOtBu is the base)*



Secondary haloalkane - *S_N2 when nucleophile is not strong or very weak base*
E2 when nucleophile is a strong base
E1/S_N1 when nucleophile is a very weak base



Tertiary haloalkane - *S_N2 never*
E2 when nucleophile is anything but a very weak base
E1/S_N1 when nucleophile is a very weak base

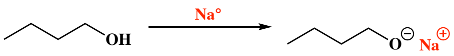


Chapter 10

23) Reaction of Alcohols with Alkali Metals (Na°, Li°) to Give Alkoxides

Mechanism Keys: **Alkali metals react with alcohols to make alkoxides and H_2** Regiochemistry: **N/A** Stereochemistry: **N/A**

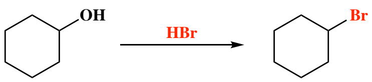
Replace the H atom of an OH group with a negative charge



24) Reaction of Alcohols with HX to Give Haloalkanes

Mechanism Keys: **Alcohols react with HX by protonating the OH group (thus creating a good leaving group), then the halide anion reacts via an S_N2 mechanism for primary alcohols and via an S_N1 mechanism for secondary/tertiary alcohols, to give a haloalkane** Regiochemistry: **N/A** Stereochemistry: **InVERSiON for S_N2 and scrambled for S_N1**

Replace the alcohol OH group with X. This reaction must be used with tertiary alcohols as PBr_3 and $SOCl_2$ only work with primary and secondary alcohols.

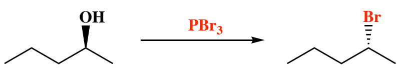


25) Reaction of Alcohols with PBr_3 to Give Bromoalkanes

Mechanism Keys: **Primary and secondary alcohols react with PBr_3 to give an intermediate with an O-P bond (thus creating a good leaving group), that reacts with bromide anion via an S_N2 mechanism to give a haloalkane**

Regiochemistry: **N/A** Stereochemistry: **InVERSiON**

Replace the alcohol OH group with Br with InVERSiON of any stereochemistry at the carbon that was bonded to the OH group of the original alcohol. Primary and secondary alcohols only because teertiary alcohols cannot react via S_N2.



26) Reaction of Alcohols with $SOCl_2$ to Give Chloroalkanes

Mechanism Keys: **Primary and secondary alcohols react with $SOCl_2$ to give an intermediate with an O-S bond (thus creating a good leaving group), that reacts with chloride anion via an S_N2 mechanism to give a haloalkane**

Regiochemistry: **N/A** Stereochemistry: **InVERSiON**

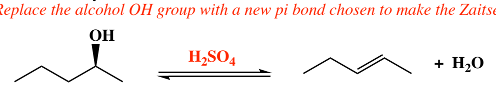
Replace the alcohol OH group with Cl with InVERSiON of any stereochemistry at the carbon that was bonded to the OH group of the original alcohol. Primary and secondary alcohols only because teertiary alcohols cannot react via S_N2.

27) Reaction of Alcohols with Sulfuric Acid to Give Alkenes

Mechanism Keys: **Alcohols react with H_2SO_4 to give alkenes via a carbocation intermediate, in a mechanism that is the exact reverse of hydration of an alkene, this is a reversible equilibrium proces (*Le Chatlier*)** Regiochemistry: **Zaitsev**

Stereochemistry: **N/A**

Replace the alcohol OH group with a new pi bond chosen to make the Zaitsev product (most substituted alkene)



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

Mechanism Keys: **Alcohols react as nucleophiles with sulfonyl chlorides to give sufonyl esters, a good leaving group**

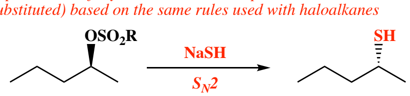
Regiochemistry: **N/A** Stereochemistry: **Retention (not InVERSiON)**

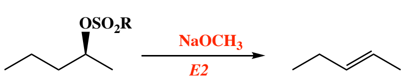
Replace the alcohol OH group with a new sulfonyl ester, without changing the stereochemistry

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

Mechanism Keys: **Sulfonyl esters react with nucleophiles and bases analogous to haloalkanes** Regiochemistry: **E2 and E1 give Zaitsev product alkene** Stereochemistry: **S_N2 gives InVERSiON, S_N1 scrambled, E2 gives product based on antiperiplanar transistion state**

Replace the sulfonyl ester with a nucleophile with InVERSiON or carry out an elimination to give the Zaitzev alkene (most substituted) based on the same rules used with haloalkanes

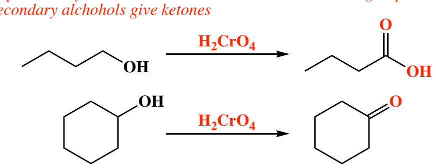




30) Reaction of Alcohols with Chromic Acid (Jones Reagent) to Give Carboxylic Acids and Ketones

Mechanism Keys: **The mechanism with primary alcohols involves a chromate ester intermediate then loss of an H atom on the carbon of the orginal alcohol to give an aldehyde, that adds water then reacts again. Secondary alchohols react once to give a ketone** Regiochemistry: **N/A** Stereochemistry: **N/A**

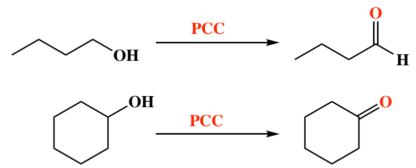
Replace every H atom on the carbon attached to the OH group with bonds to O atoms. Primary alcohols give carboxylic acids, secondary alchohols give ketones



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

Mechanism Keys: **The mechanism with primary alcohols involves a chromate ester intermediate then loss of an H atom on the carbon of the orginal alcohol to give an aldehyde, and because there is no water it stops there. Secondary alchohols react once to give a ketone** Regiochemistry: **N/A** Stereochemistry: **N/A**

Replace an H atom on the carbon attached to the OH group with a pi bond to an O atom. Primary alcohols give aldehydes, secondary alchohols give ketones

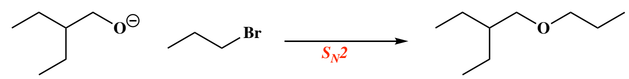


Chapter 10

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

Mechanism Keys: **Alkoxides and primary haloalkanes react via an S_N2 mechanism. The haloalkane must be primary to avoid E2.** Regiochemistry: **N/A** Stereochemistry: **N/A**

Choose the alkoxide and haloalkane so the haloalkane is primary

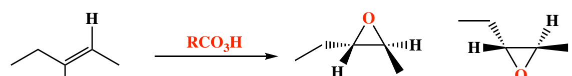


32) Reaction of Alkenes with Peracids to Give Epoxides

Mechanism Keys: **Alkenes react with peracids in a single concerted step to give the epoxide and a carboxylic acid**

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

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



Racemic

33) Reaction of Halohydrins with Base to Give Epoxides

Mechanism Keys: **Halohydrins react with base to deprotonate the OH group and give an alkoxide intermediate, which attacks the backside of the C-X bond in a single step to give the epoxide** Regiochemistry: **N/A** Stereochemistry: **N/A**

Create the epoxide from the halohydrin by lining up the OH group to be antiperiplanar to the X before making the new bond from O to the carbon of the originall C-X bond

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

Mechanism Keys: **Epoxides react with hydroxide from the backside of the C-O bond via an S_N2 mechanism at the less-hindered carbon, and in acid epoxides are protonated to give a positively-charged intermediate analogous to the halonium ion intermediate, so water attacks the more substituted carbon** Regiochemistry: **In base, OH adds to less-hindered carbon atom, in acid OH adds to the more substituted carbon atom** Stereochemistry: **Anti (backside attack on epoxide C-O bond)**

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