

Chapter 12: Alcohols

This week! – Chap. 12 Alcohols

Next Week! Give Thanks, Family & Celebratory foods of choice, etc.

Wednesday 11/29 EXAM #3!!

Chapter 12: Alcohols

Today – Chapter 12 Sections

12.1 Alcohols and Phenols

12.2 Acidity of Alcohols (Ch. 3?)

12.3 Preparation of Alcohols (Ch. 7? Ch.8?)

12.5 Preparation of Diols (8.9, 8.10)

12.9 Reactions of Alcohols

Wednesday – Reactions with Alcohols

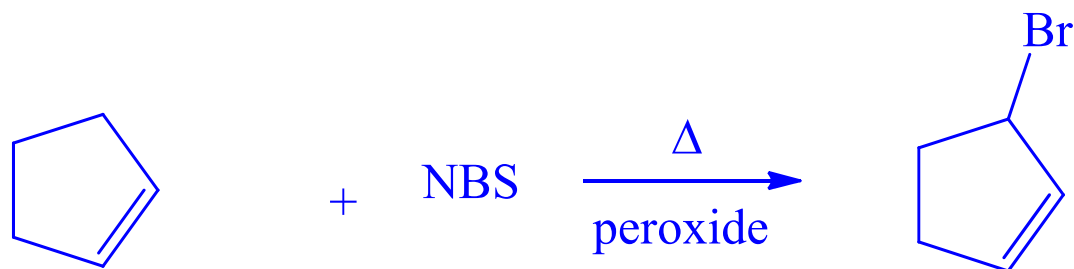
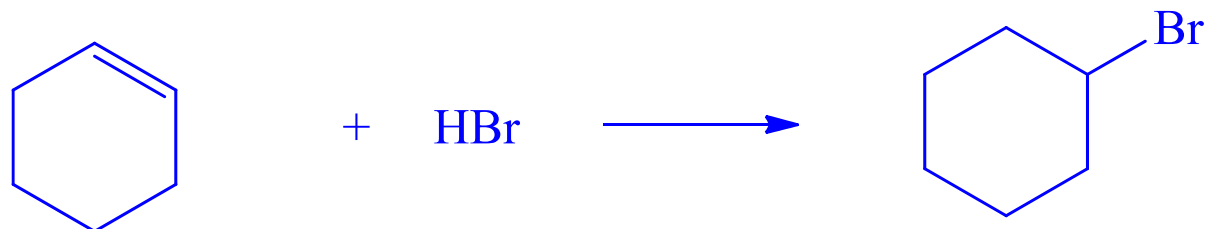
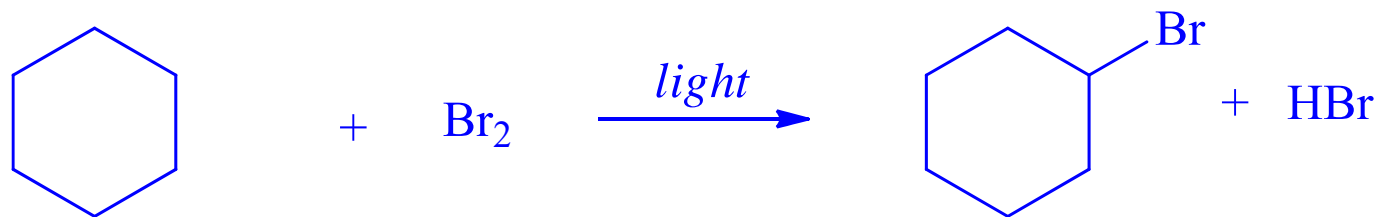
12.4 Preparation of Alcohols by Reduction

12.6 Preparation of Alcohols with Grignard

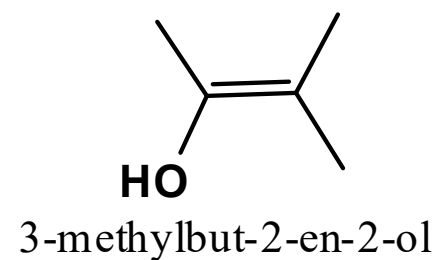
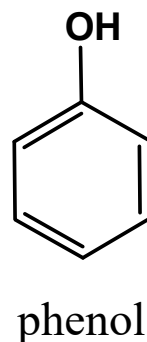
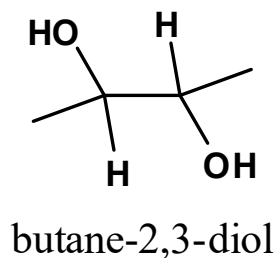
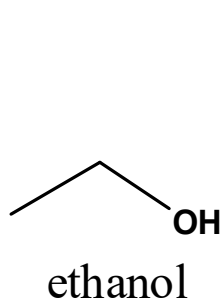
12.9 Reactions of Alcohols

12.10 Oxidation of Alcohols

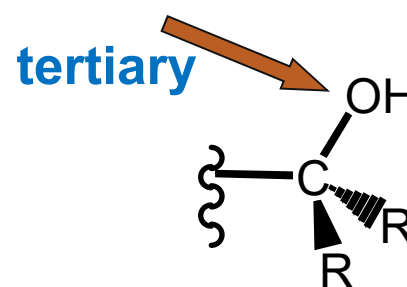
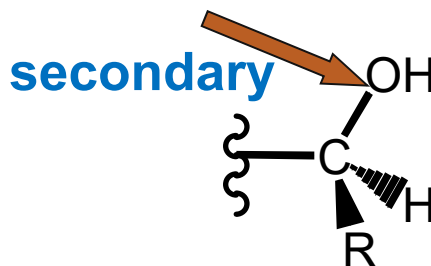
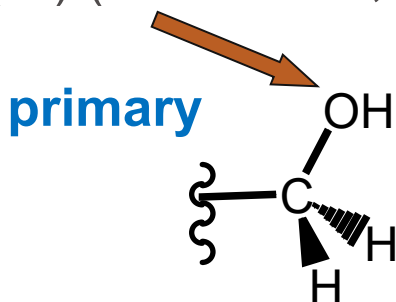
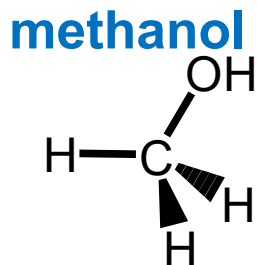
Reactions of Cyclic Compounds



Alcohols, Diols, Phenols, and Enols



- Alcohols possess a hydroxyl group (-OH).
- General classifications of alcohols based on substitution on C to which OH is attached
 - Methyl (C has 3 H's)
 - Primary (1°) (C has two H's, one alkyl group)
 - Secondary (2°) (C has one H, two alkyl groups)
 - Tertiary (3°) (C has no H, 3 alkyl groups),

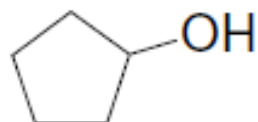


Alcohols and Phenols – Nomenclature

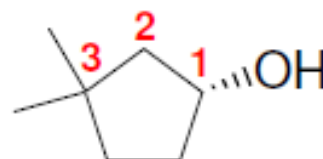
- Alcohols are named using the same procedure we used in Chapter 4 to name alkanes with minor modifications:
 1. Identify the parent chain, which should include the carbon that the –OH is attached to.
 2. Identify and name the substituents.
 3. Assign a locant (and prefix if necessary) to each substituent. Give the carbon that the –OH is attached to the lowest number possible.
 4. List the numbered substituents before the parent name in alphabetical order. Ignore prefixes (except iso) when ordering alphabetically.
 5. The –OH locant is placed either just before the parent name or just before the -ol suffix.

Alcohols and Phenols – Nomenclature

- For cyclic alcohols, the –OH group should be on carbon 1, so often the locant is assumed and omitted.

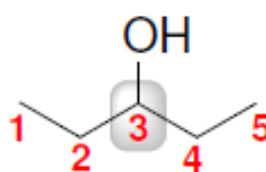


cyclopentanol



(R)-3,3-dimethylcyclopentanol

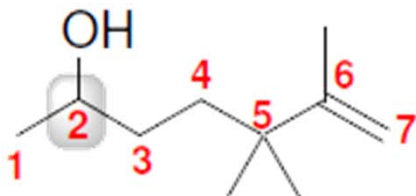
- The –OH locant is placed either just before the parent name or just before the -ol suffix.



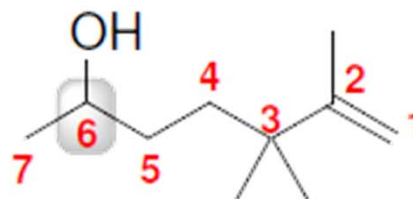
3-pentanol
or
pentan-**3**-ol

- Give the carbon that the –OH is attached to the lowest number possible **taking precedence over C=C double bonds**.

CORRECT

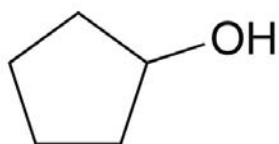


INCORRECT

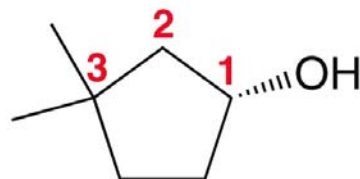


Alcohol Nomenclature

- For **cyclic alcohols**, the **–OH group is always carbon 1**

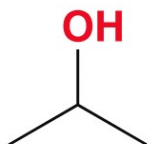


Cyclopentanol

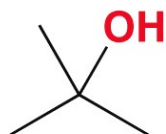


(*R*)-3,3-Dimethylcyclopentanol

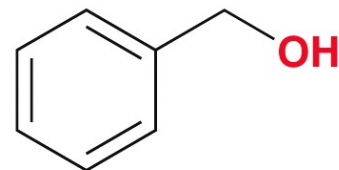
- Common names** for some alcohols are also frequently used



Isopropyl alcohol
(2-propanol)



tert-Butyl alcohol
(2-methyl-2-propanol)



Benzyl alcohol
(phenylmethanol)

Commercially Important Alcohols

Methanol (CH_3OH) is the simplest alcohol

With a suitable catalyst, about 2 billion gallons of methanol is made industrially from CO_2 and H_2 every year

Methanol is poisonous, but it has many uses: Solvent, chemical syntheses, Fuel

Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), produced by fermentation of grains or fruits

Industrially, ethanol is made via acid-catalyzed hydration of ethylene (5 billion gallons/year in the U.S. alone)

Ethanol has many uses: Solvent, chemical syntheses, Fuel,

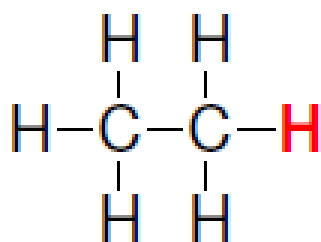
Isopropanol $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, a.k.a. rubbing alcohol.

Isopropanol is made industrially from the acid-catalyzed hydration of propylene

Isopropanol is poisonous, but it has many uses: solvent, antiseptic, additive to gasoline

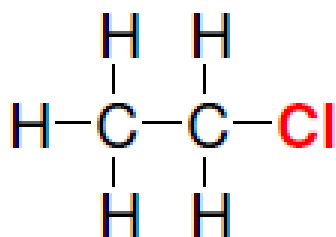
Alcohols and Phenols – Physical Properties of Alcohols

- The –OH of an alcohol can have a big effect on its physical properties.
- Compare the boiling points below.



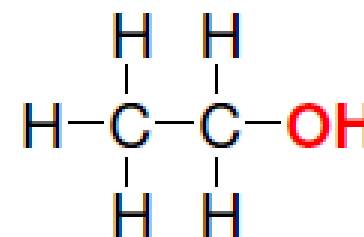
ethane

bp = -89°C



chloroethane

bp = 12°C

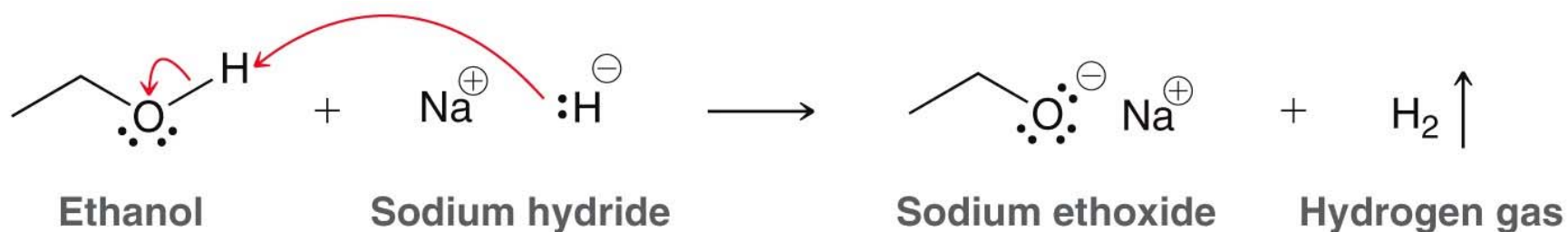


ethanol

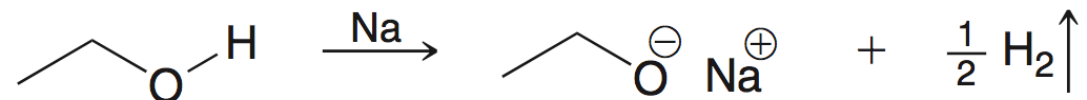
bp = 78°C

Acidity of Alcohols and Phenols

- A strong base is necessary to deprotonate an alcohol. NaH is often used to generate the corresponding **alkoxide**:

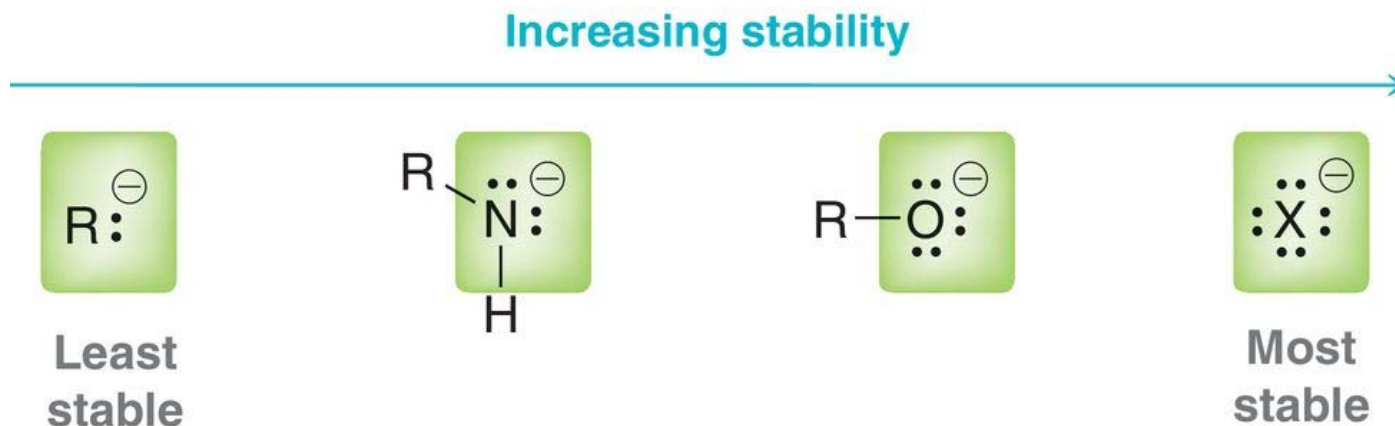


- Na, K, or Li metal is often used as well:

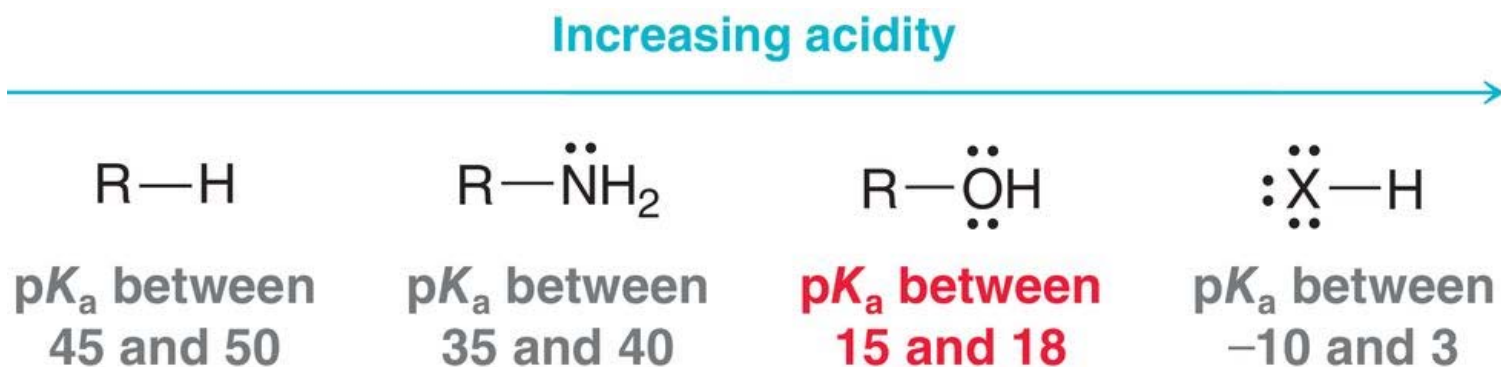


Acidity of Alcohols and Phenols

- **Alkoxide** – conjugate base of an alcohol

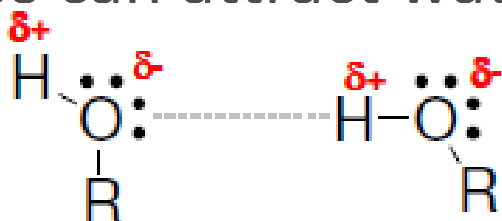


- Remember ARIO... to rationalize the relative acidity of an alcohol

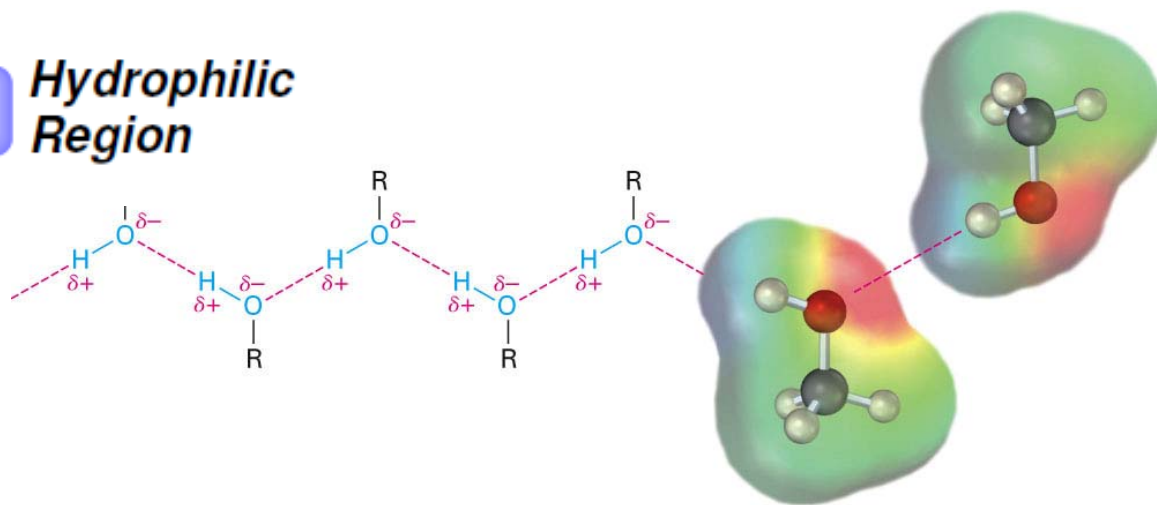
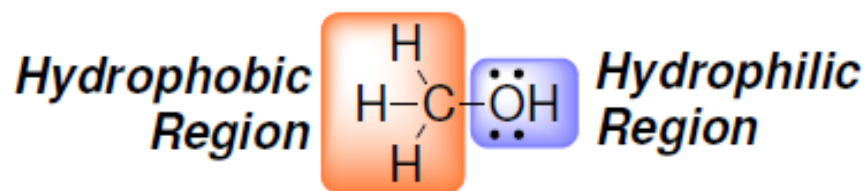


Alcohols and Phenols – Physical Properties of Alcohols

- Because they can hydrogen- (H-) bond, hydroxyl groups can attract water molecules strongly.

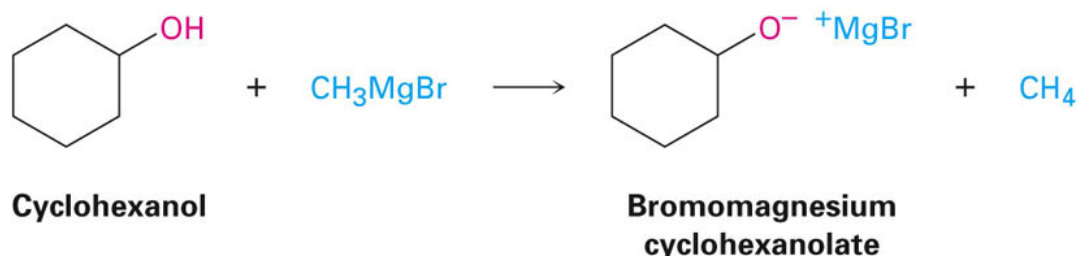
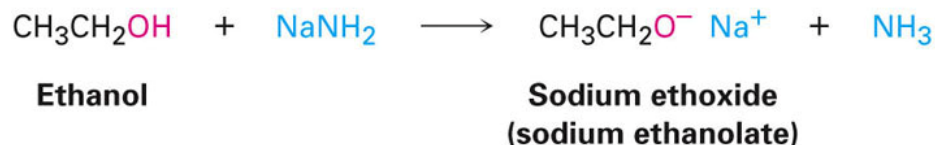
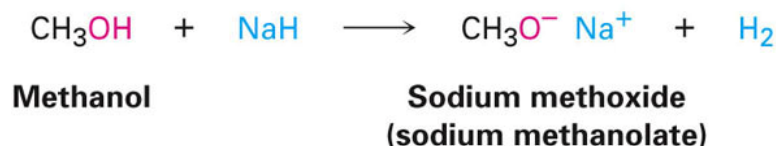
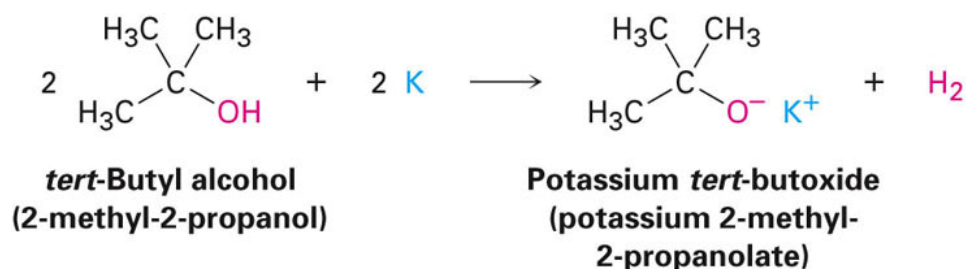


- Alcohols with small carbon chains are miscible in water
- Alcohols with large carbon chains do not readily mix with water.



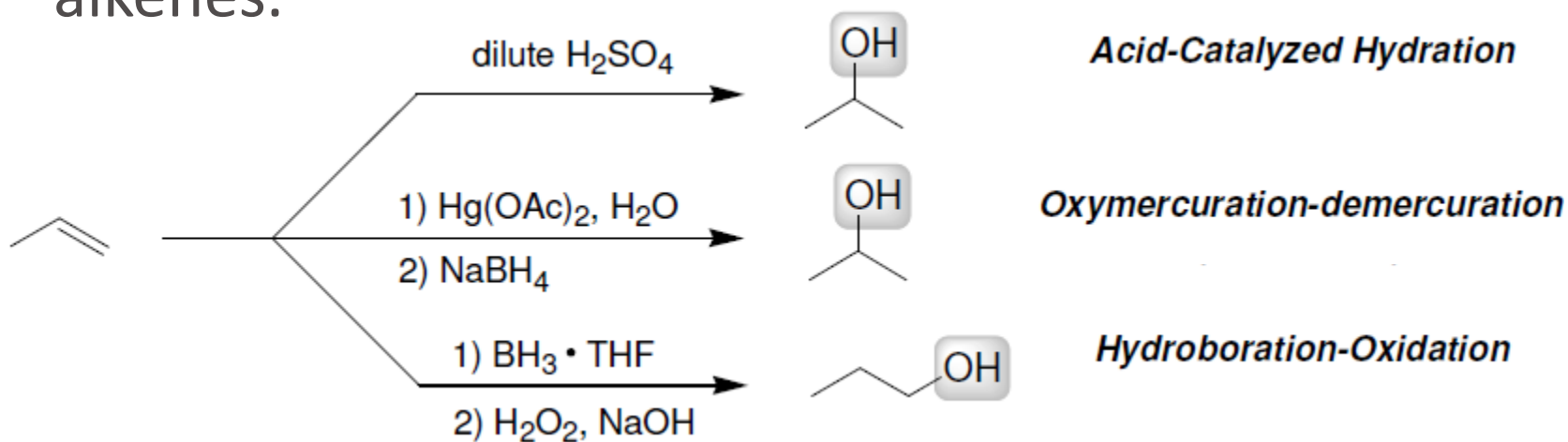
Generating Alkoxides from Alcohols

- Alcohols are weak acids
- It requires a strong base such as NaH, sodium amide NaNH_2 , to form alkoxides – which is then a **strong** base



Preparation of Alcohols

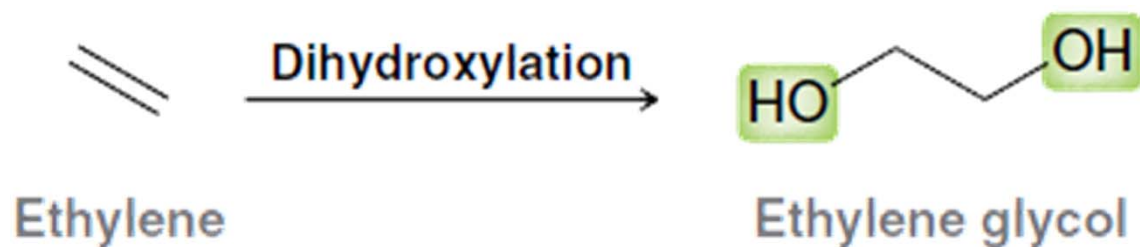
- In Chapter 8, we learned how to make alcohols from alkenes.



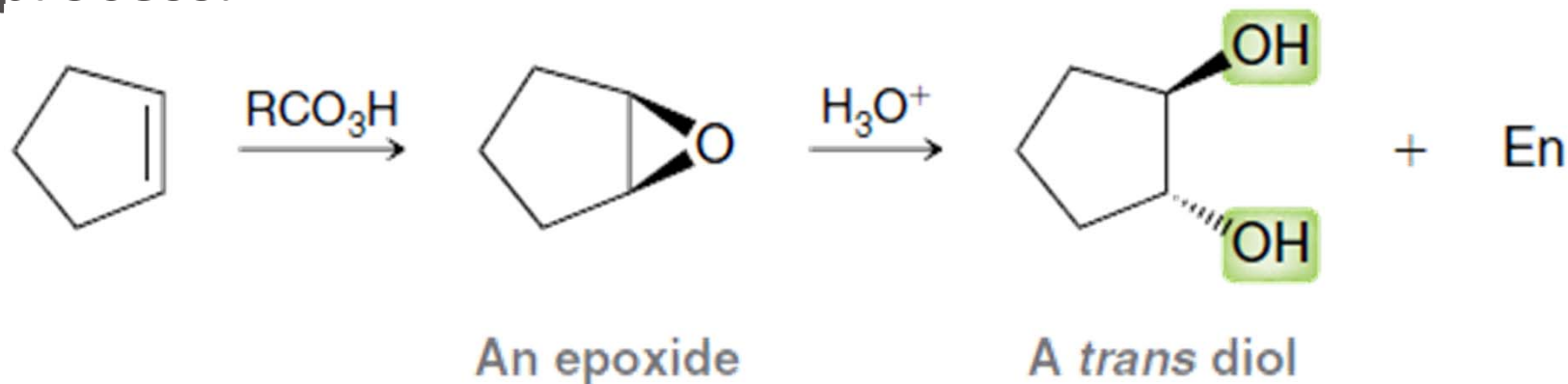
- Recall that acid-catalyzed hydration proceeds through a carbocation intermediate that can possibly rearrange.
- REMEMBER - How do you avoid rearrangements?

Anti Dihydroxylation

- Dihydroxylation occurs when two –OH groups are added across a C=C double bond.

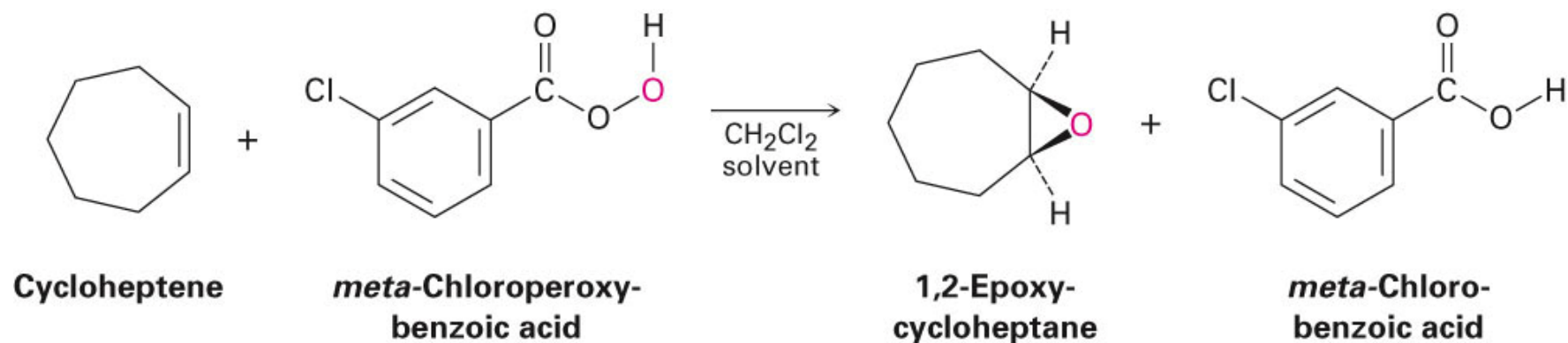


- ANTI dihydroxylation is achieved through a multi-step process.

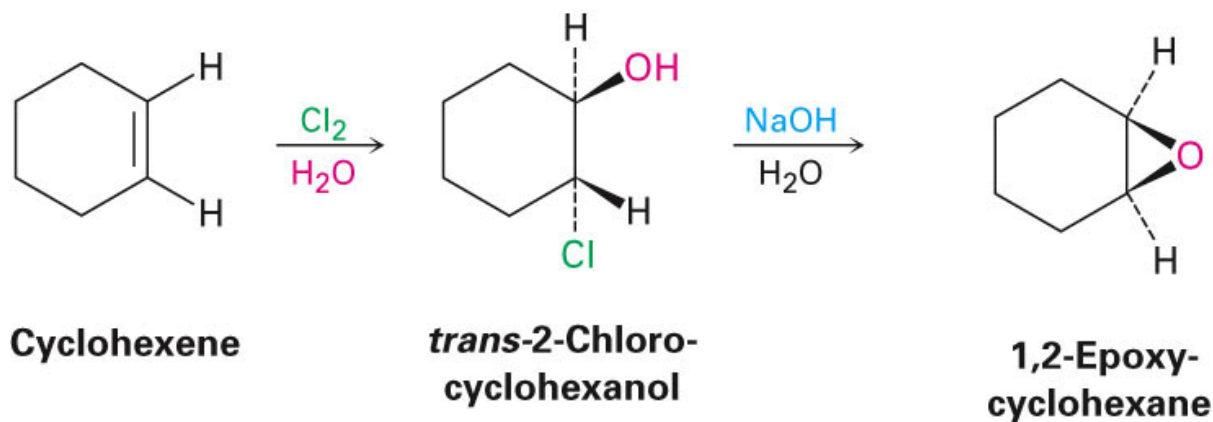


Preparation of Epoxides:

- Treatment of an alkene with a peroxyacid gives an epoxide

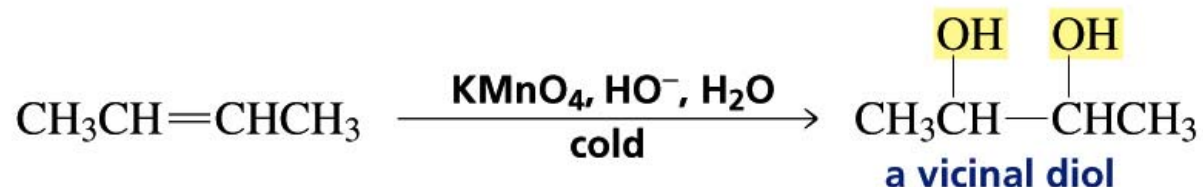


- Treatment of a halohydrin with base gives an epoxide



A three membered ring ether is called an **Epoxide** or an oxirane

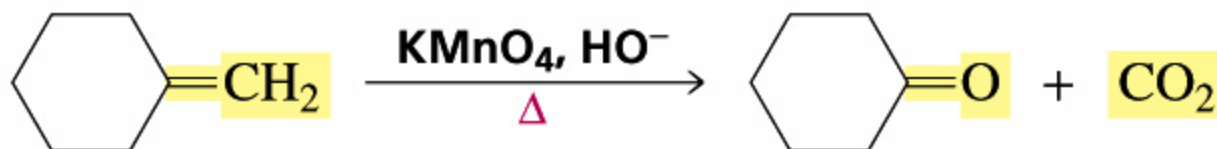
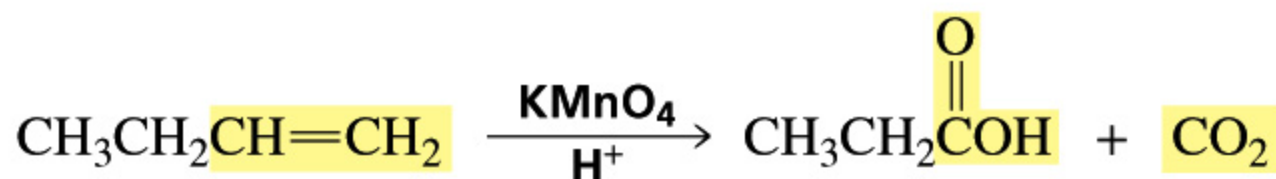
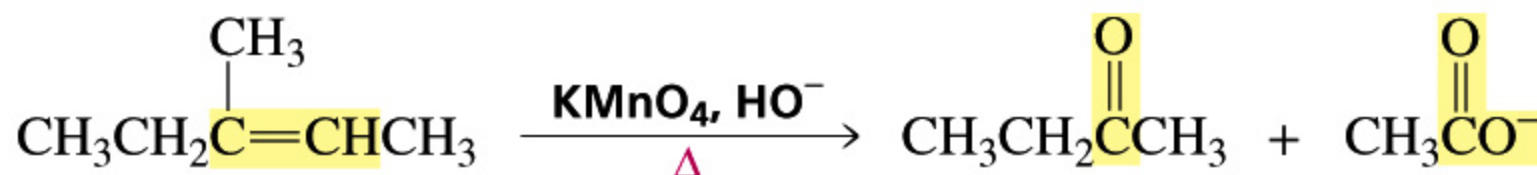
Syn Dihydroxylation



Mechanism for *cis*-Glycol Formation?



Syn Dihydroxylation

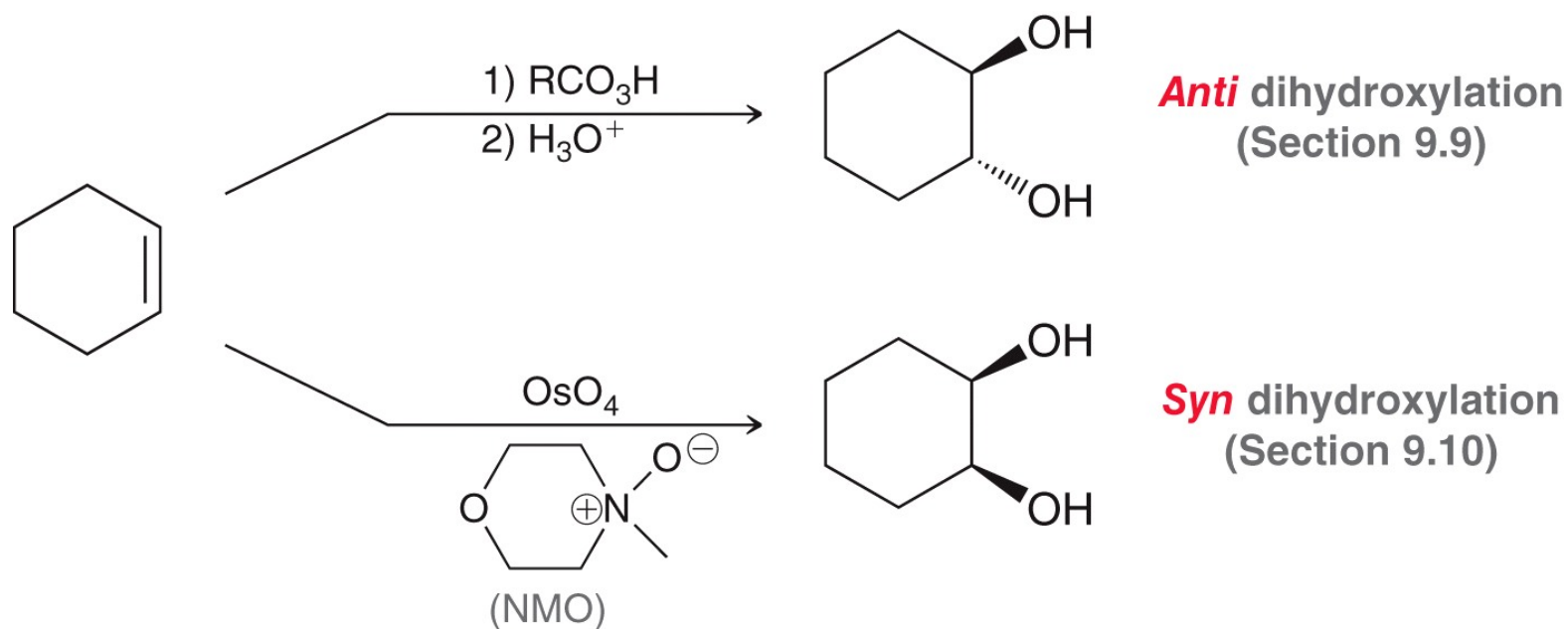


A peroxyacid, OsO_4 , and (cold basic) KMnO_4 break only the π bond of the alkene

Ozone and acidic KMnO_4 break both the π bond and the σ bond

Preparation of Diols

- Recall the methods we discussed in chapter 9 to convert an alkene into a diol



For Next Time....

Suggested Homework Problems Chapter 9

1, 7, 9, 13, 18, 20, 32-37, 41, 44, 52, 57

Suggested Homework Problems Chapter 10

1, 2, 12, 16, 23, 24, 33, 42

Suggested Homework Problems Chapter 12!

1, 4, 5, 7, 13, 17, 27-32, 34, 43-45