

## 17.S: ALCOHOLS AND PHENOLS (SUMMARY)

### CONCEPTS & VOCABULARY

#### 17.0 Introduction

- Alcohols have hydroxide groups (OH) bonded to an  $sp^3$  carbon.
- Enols have a hydroxide bonded to an  $sp^2$  carbon that is not part of an aromatic ring, a vinyl carbon.
- Phenols have a hydroxide bonded to an  $sp^2$  carbon that is part of an aromatic ring, an aryl carbon.

#### 17.1 Naming Alcohols and Phenols

- Alcohols can be described as methyl, primary, secondary or tertiary, based on the number of alkyl groups attached to the carbon bonded to OH.
- Alcohols are named following IUPAC rules, by dropping the -e of an alkane and replacing with -ol.

#### 17.2 Properties of Alcohols and Phenols

- Alcohols, enols and phenols all have significantly higher boiling points than alkanes, due to hydrogen bonding.
- Small alcohols are soluble in water.
- Alcohols are amphoteric, they act as an acid when reacting with bases and as a base when reacting with acids.
- Phenols are more acidic than alcohols due to resonance delocalization of the negative charge in the phenoxide conjugate base.
- Substituent groups on an aromatic ring that withdraw electron density increase the acidity of phenols, while substituent groups that donate electron density decrease acidity of phenols.

#### 17.3 Preparation of Alcohols: A Review

- Alcohols can be prepared from alkyl halides by reacting with hydroxide.
- Alcohols can be prepared from alkenes by reaction with acid/water or oxymercuration to form the more substituted alcohol.
- Alcohols can be prepared from alkenes by hydroboration/oxidation to form the less substituted alcohol.
- Diols can be prepared from alkenes by first forming an epoxide, then ring opening the epoxide to form an anti-diol.
- Diols can be prepared from alkenes by reacting with osmium tetroxide, then reducing off the osmium to form syn-diols.

#### 17.4 Alcohols from Carbonyl Compounds: Reduction

- Organic reduction can be defined by increasing the number of bonds to hydrogen.
- Aldehydes and ketones can be reduced to alcohols with several different hydride donor reagents.
- NADH is an example of a biological reducing agent, which donates a hydride to carbonyl groups, reducing them to an alcohol.
- Carboxylic acids and esters can be reduced to alcohols with a strong reducing agent such as lithium aluminum hydride  $LiAlH_4$ .

#### 17.5 Alcohols from Carbonyl Compounds: Grignard Reaction

- One of the most important organometallic groups of molecules are Grignard reagents, which are alkyl magnesium halides.
- Grignard reagents, like other organometallic compounds, include a nucleophilic alkyl group that can react with many different electrophiles.
- Grignard reagents will add to aldehydes and ketones forming alcohol products.
- Grignard reagents will add twice to ester molecules, forming alcohol products.
- Grignard reagents are strong bases, therefore they will not undergo nucleophilic addition reactions with molecules that have protons that are even slightly acidic such as: alcohols, carboxylic acids, alkynes, and amines or amides that have an N-H bond.

#### 17.6 Reactions of Alcohols

- Alcohols can be converted into alkyl halides directly by reaction with strong hydrogen halides. This works best for  $3^\circ$  alcohols.
- Conversion of  $1^\circ$  and  $2^\circ$  alcohols into alkyl halides commonly use thionyl chloride ( $SOCl_2$ ) or phosphorus tribromide ( $PBr_3$ ).
- To activate an alcohol in order to make the hydroxide a good leaving group, tosylates (toluenesulfonates) and mesylates (methanesulfonates) can be formed.
- Alcohols can be dehydrated by heating in strong acid solution to form an alkene.
- Alcohols react with acid chlorides to form esters.

#### 17.7 Oxidation of Alcohols

- Primary and secondary alcohols can be oxidized with various chromium reagents, while tertiary alcohols are not.
- Secondary alcohols are oxidized to ketones.
- Primary alcohols are oxidized to carboxylic acids using chromium trioxide or dichromate compounds.
- Primary alcohols can be stopped in their oxidation at aldehydes by reacting with pyridinium chlorochromate or Dess-Martin periodinane.

### 17.8 Protection of Alcohols

- Protection of a functional group is useful when that functional group may interfere with an intended reaction.
- Protection converts a functional group into a non-interfering derivative molecule through a reaction that can be easily reversed to remove the protecting group.
- Protection consists of a series of reactions that include protect, perform intended reactions, and deprotect.
- Alcohols can be protected as silyl ethers by reacting with chlorotrialkyl silanes.

### 17.9 Phenols and Their Uses

- Phenols can be prepared from chlorobenzene or isopropylbenzene.
- Phenol and phenol derivatives (such as resorcinol) are used as germicides and antiseptics.
- Bisphenol A (BPA) has controversially been used to create polycarbonate plastics such as water bottles.

### 17.10 Reactions of Phenols

- Phenols can react with strong electrophiles (such as in Friedel-Crafts reactions).
- Phenols react with strong oxidizing agents including Jones reagent or silver oxide to form quinones.

### 17.11 Spectroscopy of Alcohols and Phenols

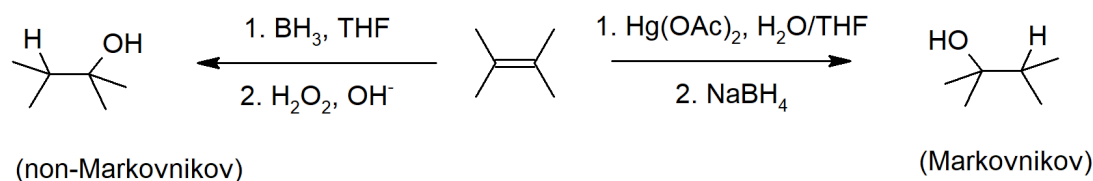
- Alcohols are among the most identifiable functional groups in infrared spectroscopy due to the strong, wide absorbance around  $3400\text{ cm}^{-1}$ .
- Alcohol peaks are much more difficult to recognize in  $^1\text{H}$  NMR, since OH hydrogens are relatively reactive and can exchange with hydrogens from the solvent, they are often weak absorptions without strong, sharp peaks.
- Hydroxide protons are not split in  $^1\text{H}$  NMR.
- Loss of hydroxide in mass spectroscopy can lead to loss of a fragment with  $17\text{ m/z}$ .

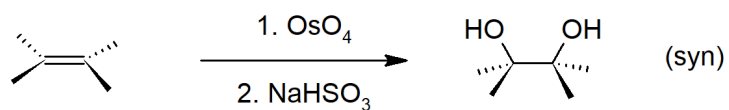
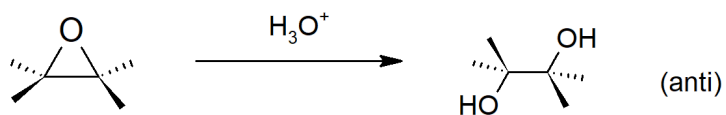
## SKILLS TO MASTER

- Skill 17.1 Identify types of alcohols.
- Skill 17.2 Name molecules with hydroxide groups using IUPAC rules.
- Skill 17.3 Describe properties related to intermolecular forces (including hydrogen bonding).
- Skill 17.4 Explain acid-base properties of alcohols and phenols.
- Skill 17.5 Describe how additional functional groups affect the acidity of phenols.
- Skill 17.6 Draw mechanisms to form alcohols from alkyl halides.
- Skill 17.7 Draw mechanisms to form alcohols from alkenes.
- Skill 17.8 Draw mechanisms to form alcohols by reduction reactions.
- Skill 17.9 Draw mechanisms to form alcohols by reaction of carbonyl compounds with Grignard reagents (and other organometallics).
- Skill 17.10 Draw mechanisms for conversion of alcohols to alkyl halides.
- Skill 17.11 Draw mechanisms for conversion of alcohols to tosylates.
- Skill 17.12 Draw mechanisms for dehydration of alcohols to alkenes.
- Skill 17.13 Draw mechanisms for conversion of alcohols to esters.
- Skill 17.14 Draw mechanisms for oxidation of alcohols to aldehydes, ketones, and carboxylic acids.
- Skill 17.15 Write out syntheses that incorporate protection and deprotection of alcohols.
- Skill 17.16 Identify presence of alcohols by IR, NMR and MS.

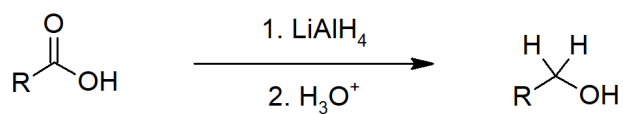
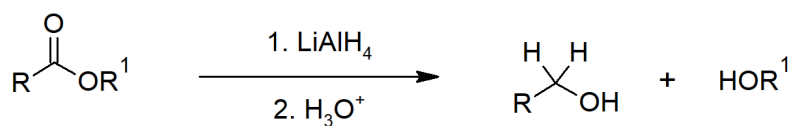
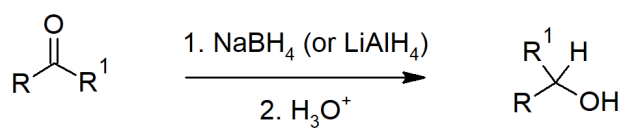
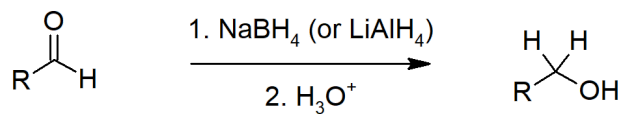
## SUMMARY OF REACTIONS

### Alcohol Preparation (Hydrolysis)

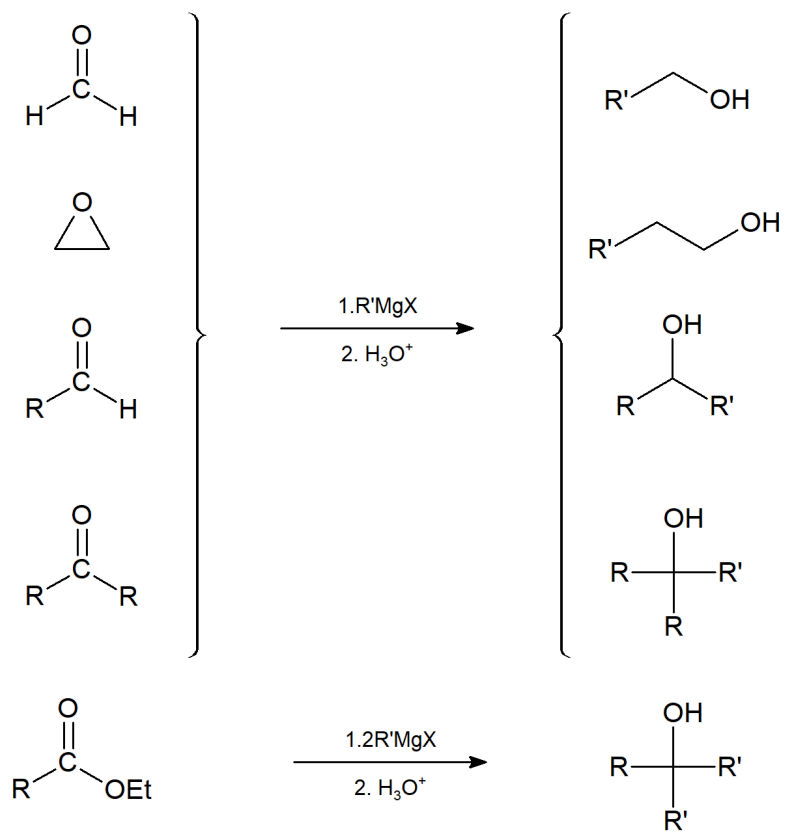




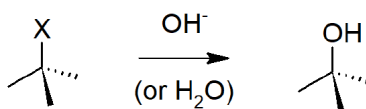
#### Alcohol Preparation (Reducing the Carbonyl)



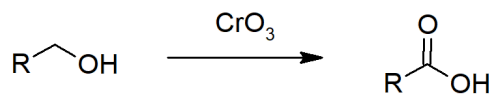
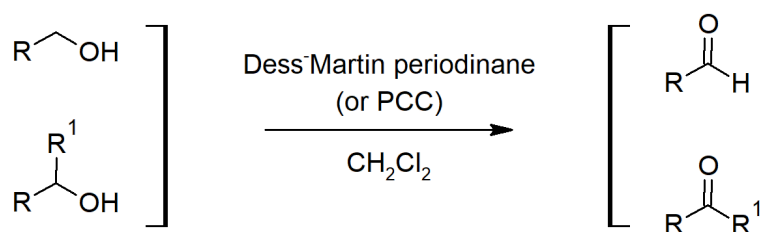
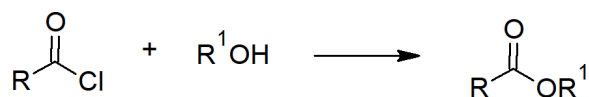
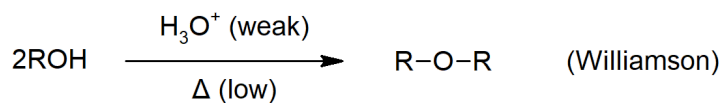
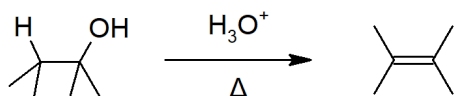
#### Alcohol Preparation (Grignard Additions)



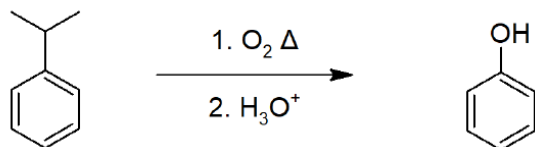
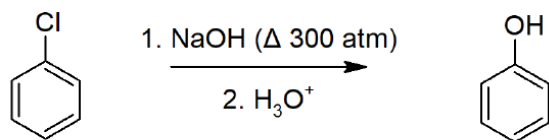
#### Alcohol Preparation (from Organohalide)



#### Alcohol Reactions



#### Phenol Preparation



#### CONTRIBUTORS AND ATTRIBUTIONS

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