Learning Guide for Chapter 14 - Alcohols (I)

I. Introduction to Alcohols and Thiols II. Acid/base Behavior of Alcohols, Phenols, and Thiols III. Nomenclature of Alcohols IV. Synthesis of Alcohols Previous reactions Reduction of C=O functional groups Organometallic reagents

I. Introduction to Alcohols and Thiols

What does an alcohol functional group look like?

How are alcohols different from carboxylic acids?



carboxylic acids ahve C=O on same carbon as OH, alcohols do not

What are some common alcohols?

wood alcohol; race car fuel; poisonous - causes blindness, methanol CH₃OH then death: treatment - IV of ethanol grain alcohol; found in alcoholic beverages; comes from ethanol ÖН fermenting sugars and starches; denatured for use in labs; poisonous over time or in high doses found in rubbing alcohol; used in first aid for disinfecting isopropanol -он What does a thiol functional group look like? SH What other name are they known by? mercaptan - captures mercury Why is their reactivity similar to alcohols? S and O are in the same family

What is the main difference in their reactivity? size - S is larger than O thiols are more acidic, stronger Nu

What is the most noticeable characteristic of thiols? stron

strong, disagreeable odor

What are some examples of this?



Physical Properties of Alcohols

Match up the following compounds with their boiling points and justify your answers.



Which of the following would you expect to be soluble in water?



soluble: 1-4 carbons with one OH; up to at least 6 C's with more than one OH

IR Spectra of Alcohols

Is IR a good way to identify alcohols? yes

Label the important bands in the following spectrum.





Label the peaks in the following spectrum.





a - 5H, m, 7ppm b - 2H, t, 2-3 ppm c - 2H, t, 3-4 ppm d - 1H, s, 1-5 ppm a > c > b > d

II. Acid-base Behavior of Alcohols, Phenols, and Thiols

What happens when an alcohol reacts with an acid?



What kind of acid would be required for this reaction to have a favorable equilibrium?

pKa less than 2.4
$$H_2SO_4 - 10$$
 HBr -8 HI -9 HCl -7

What would happen if the protonated alcohol came in contact with a base?

 $\stackrel{+}{\searrow}$ $\stackrel{\text{NaOH}}{\longrightarrow}$ $\stackrel{\stackrel{-}{\longrightarrow}}$ $\stackrel{+}{\longrightarrow}$ $\stackrel{+}{$

What happens when an alcohol reacts with an base?



What kind of base would be required for this reaction to have a favorable equilibrium?

pKa of the conjugate acid must be greater than 18

most commonly used base - NaH - pKa 36

How can alkali metals be used to form alkoxides?

by a redox reaction



What would happen if an alkoxide came in contact with an acid?



What would happen if a protonated alcohol and an alkoxide were reacted with each other?



they would neutralize each other

How does the acidity of alcohols vary?

methyl > 1° > 2° > 3°



Why are aryl alcohols more acidic than aliphatic alcohols?

conjugate base is stabilized by resonance



Why are thiols more acidic than alcohols?

sulfur is larger than oxygen, H is further away, easier to remove



Could NaOH be used as the base? ^{yes}



III. Nomenclature of Alcohols

Common names

Based on the common name for the following alkyl halide, deduce the common name of the alcohol shown.



Give the common names of the following alcohols.



IUPAC names

What are the four steps in naming an organic compound?

- 1. Determine stereochemistry, if any.
- 2. Choose the principle chain, give it a name.
- 3. Number the principle chain.
- 4. Name the substituents, alphabetize them, add them to the name.

What are the priorities for choosing the principle chain?

- 1. must contain the alcohol (or as many as possible)
- 2. double or triple bonds
- 3. longest chain
- 4. most substituents



How does the alkane name change for each of the following?



What are the priorities for numbering the principle chain?

- 1. lowest number to alcohol(s)
- 2. lowest number to double or triple bonds
- 3. lowest numbers to substituents (first point of difference)
- 4. lowest number to first substituent alphabetically

Number the following compounds.



If you have to name an alcohol as a substituent, what is it called? hydroxy

ю́н С 2-(1-hydroxyethyl)-1-cyclopentanol

Draw structures for the following names.



IV. Synthesis of Alcohols

Reactions from Previous Chapters

What reagents would be required to convert the following compounds to alcohols using the reaction given?



In this chapter, we will learn two more:

reduction of a C=O by adding hydrogen



ketones aldehydes carboxylic acids esters to ROH

reduction of a C=O by adding an alkyl group



ketone aldehyde ester acid chloride Reduction of C=O groups to form alcohols

How is oxidation defined in organic chemistry?

gaining bonds to O and/or losing bonds to H

How is reduction defined in organic chemistry?

losing bonds to O and/or gaining bonds to H

Which of these is occurring in the following reactions, and why?



What type of alcohol can be formed by the reduction of the following compounds?



ketone, aldehyde COOH, ester C≡C to C-C c = cC=O to C-OH C=O to C-OH H_2 , Pd/C yes no no most common yes NaBH₄ no no reagent for ald/ket LiAlH₄ yes most common no yes reagent for ester, COOH Raney Ni yes yes no

Which of the following reagents is effective in reducing the functional groups shown?

Which is more reactive, NaBH₄ or LiAlH₄? Why?



What is Raney Ni? What is the advantage of using it?

Ni catalyst with H₂ molecules absorbed onto it

it will also reduce C=C and C---C if they are present

What safety hazards exist with these materials?

LiAlH₄ reacts vigorously with water, releases H₂, can cause lab fires

Raney Ni is pyrophoric - spontaneously ignites in air

What reagent(s) could be used to accomplish the following reactions?



Addition of Organometallic Reagents to C=O Groups to form Alcohols

What is the advantage of using an organometallic reagent instead of a reducing agent to convert a C=O group to an alcohol?

reducing agent - same carbon structure

organometallic reagent - new carbon group added

What are the two most common kinds of organometallic reagents used in organic chemistry?



What polarity do these reagents have? How reactive are they, and why?

C - partially negative

highly reactive - C doesn't like to be -, usually formed and used, not stored

How are organometallic reagents formed?

alkyl halide + metal



What other kinds of halides can be used?





What are the two ways in which a Grignard or organolithium reagent can react?

How strong of bases are organometallic reagents? Why is this so?

conjugate acid - alkane pKa ~50

weakest acid - strongest base!

C has low EN, unstable with partial neg charge

What would happen if an organometallic reagent came in contact with water?

it would be protonated



What other kinds of compounds will react as acids with organometallic reagents?

alcohols, amines, amides, carboxylic acids, terminal alkynes

If this usually a reaction we desire? no - it ruins our reagent!

Is there any way in which it could be useful?

converts RX to alkane



In the absense of any compounds with acidic H's, organometallic reagents react as nucleophiles.

What type of compound will be formed when a Grignard or organolithium reagent is reacted with an aldehyde or ketone, followed by mild, aqueous acid?



What type of compound will be formed when a Grignard or organolithium reagent is reacted with an acid chloride, following by mild, aqueous acid?



Why doesn't this happen with aldehydes and ketones?

react once

What will happen to an ester? same thing



What type of compound is formed when a Grignard or organolithium reagent is reacted with ethylene oxide?



What reagents would be needed to complete the following reactions?



How could the following compound be synthesized?



Summary of methods for synthesizing alcohols:

S_N2:

1° alkyl halide + NaOH --> 1° alcohol

Acid-catalyzed hydration:

alkene + H_2SO_4 + H_2O --> 2° or 3° alcohol (more substituted side, rearrangements possible)

Oxymercuration-reduction:

alkene + 1. $Hg(OAc)_2$, H_2O 2. $NaBH_4$ --> 2° or 3° alcohol (more substituted side, no rearrangements)

Hydroboration-oxidation:

alkene + 1. BH₃-THF, 2. H_2O_2 , NaOH --> 1° or 2° alcohol (less substituted side, no rearrangements)

Reduction of an aldehyde or ketone:

aldehyde or ketone + NaBH₄, CH₃OH --> 1° or 2° alcohol

Reduction of a carboxylic acid or ester:

carboxylic acid or ester + $\text{LiAlH}_4 \rightarrow 1^{\circ}$ alcohol (ester has a second alcohol)

Addition of an organometallic reagent to an aldehyde or ketone

aldehyde or ketone + Grignard or organolithium reagent, 2. $H_3O^+ -> 2^\circ$ or 3° alcohol

Addition of an organometallic reagent to and acid chloride or ester:

acid chloride or ester + Grignard or organolithium reagent, 2. $H_3O^+ -->$ 3° alcohol with two identical groups

Addition of an organometallic reagent to an epoxide:

ethylene oxide + Grignard or organolithium reagent, 2. H₃O⁺ --> 1° alcohol