These are the homework exercises to accompany the Textmap for McMurry's Organic Chemistry textbook.

17.0 Introduction

17.1 Naming Alcohols and Phenols

17.1 Exercises

Questions

Q17.1.1

Give IUPAC names for the following structures.

(a)

\[
\begin{align*}
\text{OH} \\
\text{CH}_2
\end{align*}
\]

(b)

\[
\begin{align*}
\text{OH} \\
\text{CH}_2
\end{align*}
\]

Indicate stereochemistry (c)

(d)

\[
\begin{align*}
\text{OH} \\
\text{C}_5
\end{align*}
\]
Q17.1.2

Name the following structures.

(a) \( \text{HO-CH}_2-\text{CH-} \)
(b) \( \text{HO} \)
(c) \( \text{HO} \)
(d) \( \text{NO}_2 \)
(e) \( \text{HO} \)
(f) \( \text{HO} \)

Q17.1.3

Draw and name all the alcohol isomers of C\(_3\)H\(_9\)O

Q17.1.4

Oleic acid, a commonly occurring fatty acid in vegetable oils, has the following structure. Name the compound, making sure to give the correct alkene geometry.

Q17.1.5

Creosols are naturally occurring compounds used building blocks for many molecules, they occur as three different isomers. Name each of the following isomers.
Solutions
S17.1.1

(a)

(b)

(c)

(d)

butan-2-ol

(1R,2R)-2-methylcyclohexan-1-ol

cyclopentylmethanol

2,6-di-tert-butyl-4-methylphenol
S17.1.2

(a) cyclohexane-1,2-diol  (b) trans-cyclobutane-1,3-diol  (c) cyclohexanol

(a) 4-nitrophenol  (b) prop-2-en-1-ol  (c) cyclopropanol

S17.1.3

propan-1-ol  propan-2-ol

or, 1-propanol and 2-propanol

S17.1.4

(9Z)-Octadec-9-enoic acid

S17.1.5

2-methylphenol  3-methylphenol  4-methylphenol
17.4 Exercises

Questions

Q17.4.1

Give the aldehyde, ketone, or carboxylic acid (there can be multiple answers) that could be reduced to form the following alcohols.

(a) 

(b) 

(c) 

(d)
Q17.4.2

Given the following alcohol, draw the structure from which it could be derived using only NaBH₄.

(a) 

(b) 

(c) 

(d)
Solutions

S17.4.1

(a)

(b)

(c) or

(d) or
Note, NaBH₄ is only a strong enough reducing agent to reduce ketones and aldehydes.

(a)

(b)

(c)

(d)
17.5 Alcohols from Reaction of Carbonyl Compounds: Grignard Reagents

17.5 Exercises

Questions

Q17.5.1

If allylmagnesium chloride were added to a solution of the following compound and then worked-up with acid, the product would contain a chiral center. Would the product be a racemic mixture or an enantiomerically pure product? Draw both enantiomers.

\[\text{[Chemical Structure]}\]

Q17.5.2

What combination of carbonyl compound and grignard (use MgBr) reagent would yield the following alcohols (after workup)?

(a) [Chemical Structure]

(b) [Chemical Structure]

(c) [Chemical Structure]
Q17.5.3

Fill in the blanks of the following reaction scheme.

Solutions

S17.5.1

The result would be a racemic mixture of the following.

s enantiomer

r enantiomer

S17.5.2

(a)
17.6 Reactions of Alcohols

17.6 Exercises

Questions

Q17.6.1

Draw the expected product of the reaction of cyclohexanol with the following reagents.

(a) CrO₃, H₂SO₄, H₂O  (b) Dess-Martin Periodinane  (c) SOCl₂  (d) NaH and 1-bromoethane  (e) PBr₃

Q17.6.2

Starting with cyclohexanol, describe how you would prepare the following?

(a) cyclohexyl acetate  (b) 1-allylcyclohexan-1-ol  (c) cyclohexene  (d) ethoxycyclohexane

Q17.6.3
In cyclohexanone, a ketone, indicate the polarity of the bond between oxygen and carbon.

Q17.6.4

In the dehydration of 1-methylcyclohexanol, which product is favored?

Q17.6.5

In the dehydration of this diol the resulting product is a ketone. Draw the mechanism of its formation. (Hint a rearrangement occurs)

Q17.6.6

Draw the mechanism of the reaction of thionylchloride with cyclohexanol, given below.

Q17.6.7

Draw an arrow pushing mechanism for the acid catalyzed dehydration of the following alcohol, make sure to draw both potential mechanisms. Assume no rearrangement for the first two product mechanisms. Which of these two would likely be the major product? If there was a rearrangement, draw the expected major product.

Q17.6.8
The following epoxide can be transformed into an alcohol using a grignard reagent, take for example allylmagnesium chloride. Draw the product of the treatment of this epoxide with this grignard after being worked up with H₂O. Note the stereochemistry and also remember that benzylic carbons are good Sn2 electrophiles.

\[ \text{Q17.6.9} \]

As seen in the previous example, there are many examples of chiral compounds containing alcohols. One common example of these are sugars, is the given the following sugar, allitol, also chiral?

\[ \text{Solutions} \]

\[ \text{S17.6.1} \]

(a)  

(b)  

(c)  

(d)
S17.6.2

a. This can be seen as a transesterification, acid and some other ester would be needed to form cyclohexylacetate

b. First, oxidize the alcohol to a ketone, take for example Dess-Martin Periodinane, then use an allyl grignard to form 1-allylcyclohexan-1-ol

c. Alcohols can dehydrate to form alkenes under acidic conditions, so using anhydrous acid and heat would yield cyclohexene

d. The alcohol can also be a nucleophile, perform a halogen substitution, using 1-X ethane, to yield ethoxycyclohexane

S17.6.3

Oxygen is more electronegative than carbon creating the polar bond. This is the basis for the carbon's electrophilicity.

S17.6.4

The more substituted alkene is favored, as more substituted alkenes are relatively lower in energy.

S17.6.5

This is also known as the Pinacol rearrangement.
Note how the carbocation after the rearrangement is resonance stabilized by the oxygen.
The major product of this mechanism would be the more highly substituted alkene, or the product formed from the red arrows.

Note the secondary carbocation adjacent a tertiary carbon center, if there were a hydride transfer (rearrangement) to form a tertiary carbocation the following would be the major product. The minor product being the same product as the one formed from the red arrows.

This compound actually has a plane of symmetry, the plane parallel to the carbon chain/backbone. So, it is not chiral, also called a meso compound.

---

17.7 Oxidation of Alcohols

17.7 Exercises
Questions

Q17.7.1

Draw the alcohol that the following ketones/aldehydes would have resulted from if oxidized. What oxidant could be used?

(a) 

(b)

Q17.7.2

Show the products of the oxidation of 1-propanol and 2-propanol with chromic acid in aqueous solution.

Solutions

S17.7.1

(a)

Any oxidant capable of oxidizing an alcohol to a ketone would work, such as the Jones reagent (CrO₃, H₂SO₄, H₂O), PCC, or Dess-Martin periodinane.

(b)

Since this is a primary alcohol, there are some precautions necessary to avoid formation of the carboxylic acid. Milder oxidants such as the Dess-Martin periodinane, and also PCC (there is no water to form the carboxylic acid) would work.

17.8 Protection of Alcohols

17.9 Phenols and Their Uses

17.10 Reactions of Phenols

17.10 Exercises

Questions

Q17.10.1

Predict the major product if the following reagents/reagents were used. No reaction is also a possible answer.

(a) 1 equivalent of PBr₃ (b) 1 equivalent of SOCl₂ (c) Dess–Martin periodinane (d) 3 equivalents of acetyl chloride and AlCl₃ as a catalyst

(e) Heat and H₂SO₄ (assume the phenol does not act as a nucleophile in this case)

Q17.10.2

Predict the major product if the following reagents/conditions were used. No reaction is also a possible answer.
(a) 2 equivalents of RMgBr and H$_3$O$^+$ work-up (b) LiAlH$_4$ and H$_3$O$^+$ work-up (c) NaBH$_4$ and H$_3$O$^+$ work-up

Solutions

S17.10.1
S17.10.2

(a)

(b)

(c) No reaction. NaBH$_4$ is milder oxidant than LiAlH$_4$. It typically only reduces ketones and aldehydes.

17.11 Spectroscopy of Alcohols and Phenols

17.11 Exercises

Questions

Q17.11.1

From mass spectroscopy analysis it was determined that a compound has the general formula C$_5$H$_{12}$O. Given the following $^1$H NMR spectrum, draw the structure. The integration values of each group of signals is given on the spectrum.
Q17.11.2

Given that alcohols are relatively acidic and the protons transfer in solution, what would you expect to happen to the NMR spectrum if D$_2$O was used as a solvent.

Q17.11.3

From mass spectroscopy analysis it was determined that a compound has the general formula C$_3$H$_8$O. Given the following $^1$H NMR spectrum, draw the structure. The integration values of each group of signals is given on the spectrum.

![NMR Spectrum](image)

Solutions

S17.11.1

![Structure](image)

S17.11.2

The alcohol proton signal's intensity in the $^1$H NMR would be expected to diminish and likely disappear. This is due to the fact that NMR can only probe the spin changes of nuclei with an odd number of protons.

S17.11.3

1-propanol

![Structure](image)