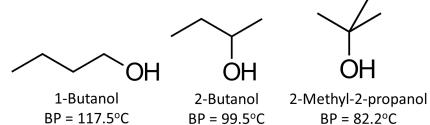


Quiz CH203 **Organic Chemistry Alcohols: Synthesis and Reactions** Lucas Monteiro Nogueira

PROBLEMS

Problem 1 (McMurry, 2008, w/ permission)

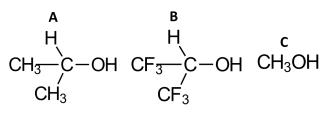
The following data for isomeric four-carbon alcohols show that there is a decrease in boiling point with increasing substitution of the OH-bearing carbon. How might you account for this trend?



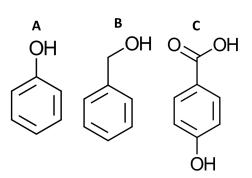
BP = 82.2°C

Problem 2 (McMurry, 2008, w/ permission)

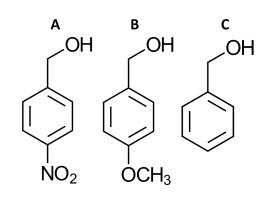
Rank the following substances in order of increasing acidity. 2.1.



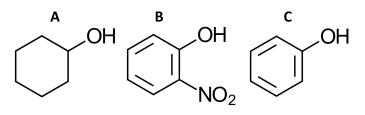
2.2.



2.3.



2.4.



Problem 3 (Carey, 2008, w/ permission) Evaluate the feasibility of the route

$$RH \xrightarrow{Br_2} RBr \xrightarrow{KOH} ROH$$

as a method of preparing

3.1. 1-Butanol from butane

3.2. 2-Methyl-2-propanol from 2-methylpropane

3.3. Benzyl alcohol from toluene

3.4. (*R*)-1-Phenylethanol from ethylbenzene

▶ Problem 4

Show the alcohols obtained from addition of methylmagnesium bromide to the following compounds.

4.1. Cyclopentanone

$$() \qquad (1) CH_3MgBr \\ 2) H_3O^+$$
?

4.2. Benzophenone (diphenyl ketone)

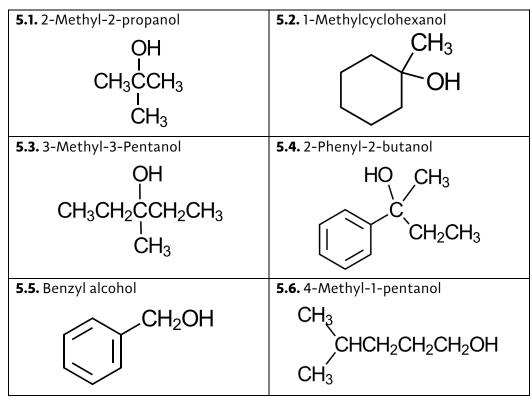
$$(1) CH_3MgBr ?$$

4.3. 3-Hexanone

$$CH_{3}CH_{2}CH_{2}CCH_{2}CCH_{3} \xrightarrow{1) CH_{3}MgBr} ?$$

▶ Problem 5

Show how you would use a Grignard reaction to produce the following alcohols.



Problem 6 (Carey, 2008, w/ permission)

Write equations showing how 1-phenylethanol ($C_6H_5CHOHCH_3$) could be prepared from each of the following starting materials.

- 6.1. Bromobenzene
- **6.2.** Benzaldehyde
- 6.3. Benzyl alcohol
- **6.4.** Acetophenone
- 6.5. Benzene

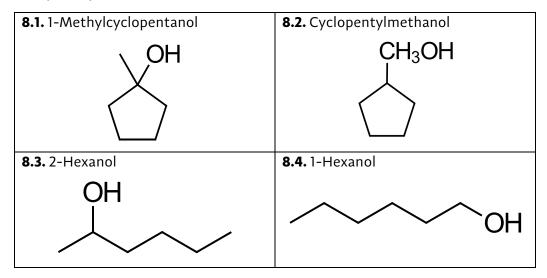
Problem 7 (Carey, 2008, w/ permission)

Write equations showing how 2-phenylethanol (C₆H₅CH₂CH₂OH) could be prepared from each of the following starting materials.

- 7.1. Bromobenzene
- 7.2. Styrene
- 7.3. 2-Phenylethanal (C₆H₅CH₂CHO)
- 7.4. Ethyl 2-phenylethanoate (C₆H₅CH₂CO₂CH₂CH₃)
- **7.5.** 2-Phenylethanoic acid (C₆H₅CH₂CO₂H)

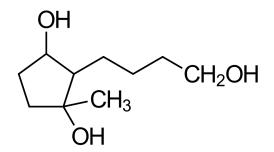
▶ Problem 8 (Wade and Simek, 2016, w/ permission)

Predict the major products of dehydration of the following alcohols catalyzed by sulfuric acid.



Problem 9 (Wade and Simek, 2016, w/ permission)

Predict the products you expect when the following starting material undergoes oxidation with an excess of each of the reagents listed below.



9.1. Chromic acid

9.2. PCC (pyridinium chlorochromate)

- **9.3.** Sodium hypochlorite/acetic acid
- **9.4.** DMSO and oxalyl chloride
- 9.5. DMP (periodinane) reagent

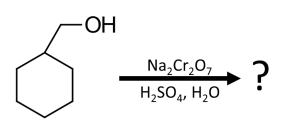
▶ Problem 10

Predict the major product for each of the following reactions.

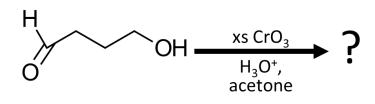
10.1.

$$\bigcirc OH \xrightarrow{Na_2Cr_2O_7} ?$$

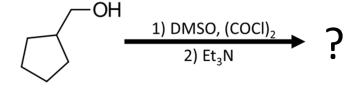
10.2.



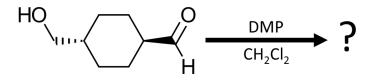
10.3.



10.4.



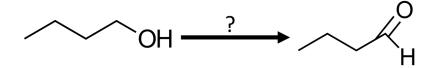
10.5.



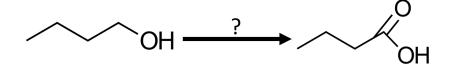
Problem 11 (Klein, 2017, w/ permission)

Starting with 1-butanol, show the reagents you would use to prepare each of the following compounds.

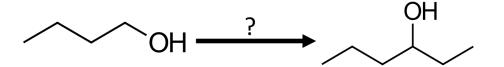
11.1. How does one convert 1-butanol to butanal?



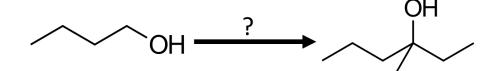
11.2. How does one convert 1-butanol to butanoic acid?



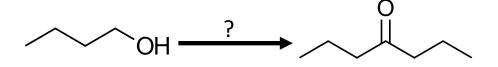
11.3. How does one convert 1-butanol to 3-hexanol?



11.4. How does one convert 1-butanol to 3-methyl-3-hexanol?



11.5. How does one convert 1-butanol to 4-heptanone?



Problem 12 (Wade and Simek, 2016, w/ permission)

Show how you would convert 2-methylcyclopentanol to the following products. Any of these products may be used as the reactant in any subsequent part of this problem.

12.1. 1-Methylcyclopentene

12.2. 2-Methylcyclopentyl tosylate

12.3. 2-Methylcyclopentanone

12.4. 1-Methylcyclopentanol

12.5. 1,2-Dimethylcyclopentanol

12.6. 1-Bromo-2-methylcyclopentane

12.7. 2-Methylcyclopentyl acetate

12.8. 1-Bromo-1-methylcyclopentane

▶ Problem 13

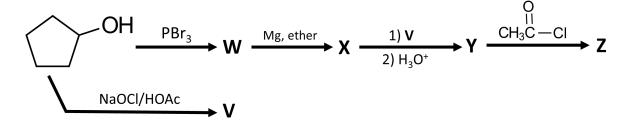
Predict the major products (including stereochemistry) when *cis*-3methylcyclohexanol reacts with the following reagents. **13.1.** PBr₃ **13.2.** SOCl₂ **13.3.** Lucas reagent **13.4.** Concentrated HBr **13.5.** TsCl/Pyridine, then NaBr

Problem 14

Predict the major products of the following reactions, including stereochemistry where appropriate. **14.1**. (*R*)-Butan-2-ol + TsCl in pyridine **14.2**. Cyclooctanol + NaOCl/HOAc **14.3**. Cyclopentylmethanol + CrO₃ · pyridine · HCl **14.4**. Cyclopentylmethanol + Na₂Cr₂O₇/H₂SO₄ **14.5**. Cyclopentanol + HCl/ZnCl₂ **14.6**. *Cis*-3-methylcyclopentanol + HCl/ZnCl₂ **14.7**. *n*-Butanol + HBr **14.8**. Cyclooctylmethanol + CH₃CH₂MgBr **14.9**. Cyclopentanol + H₂SO₄/heat **14.10**. Product from reaction above + OsO₄/H₂O₂, then HIO₄ **14.11**. 1-Octanol + DMSO + oxalyl chloride **14.12**. 4-Cyclopentyl-1-hexanol + DMP reagent

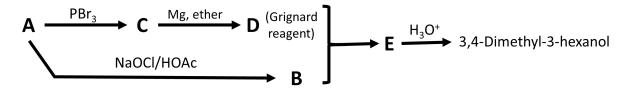
Problem 15 (Wade and Simek, 2016, w/ permission)

Starting with cyclopentanol, give the structures of the intermediates and products V through Z.



Problem 16 (Wade and Simek, 2016, w/ permission)

Compound A is an optically active alcohol. Treatment with chromic acid converts A into a ketone, B. In a separate reaction, A is treated with PBr₃, converting A into compound C. Compound C is purified, and then is allowed to react with magnesium in ether to give a Grignard reagent, D. Compound B is added to the resulting solution of the Grignard reagent. After hydrolysis of the initial product, labeled E, this solution is found to contain 3,4-dimethyl-3hexanol. Propose structures for compounds A, B, C, D, and E.



SOLUTIONS

P.1 → Solution

In general, the boiling points of a series of isomers decrease with branching. The more nearly spherical a compound becomes, the less surface area it has relative to a straight chain compound of the same molecular weight and functional group type. A smaller surface area allows fewer van der Waals interactions, the weak forces that cause covalent molecules to be attracted to each other.

In addition, branching in alcohols makes it more difficult for hydroxyl groups to approach each other to form hydrogen bonds. A given volume of 2-methyl-2-propanol therefore contains fewer hydrogen bonds than the same volume of 1=butanol, and less energy is needed to break them in boiling.

P.2 → Solution

2.1: Compound A has the alcohol carbon hindered by two methyl groups, and hence should make for a poor acid. Compound B in turn has the alcohol carbon linked to two CF_3 groups; these are electron-withdrawing groups, which should increase the acidity of the molecule substantially. Compound C, methanol, should have an intermediate acidity relatively to A and B. The correct order, from least acid to most acid, is A < C < B.

2.2: Since the molecules are similar, we may use the generalization $K_a(alcohol) < K_a(phenol) < K_a(carboxylic acid)$. That is, benzyl alcohol is less acidic than phenol, which in turn is less acidic than *p*-hydroxybenzoic acid. The correct order, from least acid to most acid, is **B** < **A** < **C**.

2.3: A nitro group is electron-withdrawing. Since electron-withdrawing groups stabilize phenoxide anions, *p*-nitrobenzyl alcohol is more acidic than benzyl alcohol. The methoxyl group, which is electron-donating, destabilizes an alkoxide ion, making *p*-methoxybenzyl alcohol less acidic than benzyl alcohol. The correct order, from least acid to most acid, is B < C < A.

2.4: Cyclohexanol is the least acidic because its conjugate base is not resonance stabilized. The other two compounds are much more acidic, because each of them generates a resonance-stabilized phenolate ion upon deprotonation. Among these two compounds, 2-nitrophenol is more acidic, because its conjugate base has an additional resonance structure in which the negative charge is placed on an oxygen atom of the nitro group. The correct order, from least acid to most acid, is **A** < **C** < **B**.

P.3 → Solution

3.1: The suggested synthesis

$$CH_{3}CH_{2}CH_{2}CH_{3} \xrightarrow{Br_{2}} CH_{3}CH_{2}CH_{2}Br \xrightarrow{KOH} CH_{3}CH_{2}CH_{2}OH$$

is a poor one because bromination of butane yields a mixture of 1-bromobutane and 2-bromobutane, 2-bromobutane being the major product.

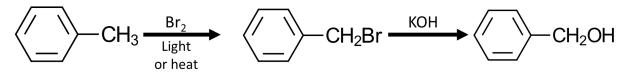
$$CH_{3}CH_{2}CH_{2}CH_{3} \xrightarrow{Br_{2}} CH_{3}CH_{2}CH_{2}Br + \begin{array}{c} CH_{3}CHCH_{2}CH_{3} \\ I \\ Br \\ (Minor product) \end{array}$$

3.2: The suggested synthesis

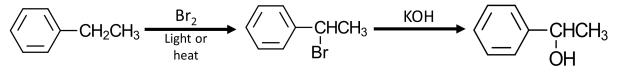
$$(CH_3)_3CH \xrightarrow{Br_2}_{\text{Light or}} (CH_3)_3CBr \xrightarrow{KOH} (CH_3)_3COH$$

will fail because the reaction of 2-bromo-2-methylpropane with potassium hydroxide will proceed by elimination rather than by substitution. The first step in the process, selective bromination of 2-methylpropane to 2-bromo-2methylpropane, is satisfactory because bromination is selective for substitution of tertiary hydrogens in the presence of secondary and primary ones.

3.3: Benzyl alcohol, unlike 1-butanol and 2-methyl-2-propanol, can be prepared effectively by the pathway in question.



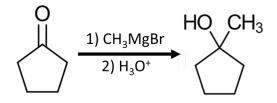
Free radical bromination of toluene is selective for the benzylic position. Benzyl bromide cannot undergo elimination, and so nucleophilic substitution of bromide by hydroxide will work well.



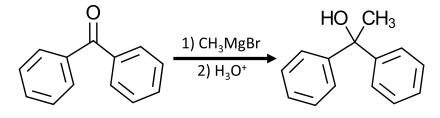
fails because it produces more than one enantiomer. The reactant ethylbenzene is achiral and although its bromination will be highly regioselective for the benzylic position, the product will be a racemic mixture of (R) and (S)-1-bromo-1-phenylethane. The alcohol produced by hydrolysis will also be racemic. Furthermore, the hydrolysis step will give mostly styrene by an E2 elimination, rather than 1-phenylethanol by nucleophilic substitution.

P.4 → Solution

4.1: Cyclopentanone reacts with methylmagnesium bromide to yield 1-methylcyclopentanol.



4.2: Benzophenone reacts with methylmagnesium bromide to yield 1,1diphenyl-1-ethanol.



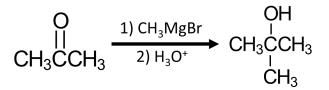
4.3: 3-Hexanone reacts with methylmagnesium bromide to yield 3-methyl-3-pentanol.

$$CH_{3}CH_{2}CH_{2}CCH_{2}CH_{3} \xrightarrow{1) CH_{3}MgBr} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3} \xrightarrow{1) CH_{3}MgBr} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3}$$

P.5 → Solution

McMurry suggests the following strategy. First, identify the type of alcohol. If the alcohol is primary, it can only be synthesized from formaldehyde plus the appropriate Grignard reagent. If the alcohol is secondary, it is synthesized from an aldehyde and a Grignard reagent. (Usually, there are two combinations of aldehyde and Grignard reagent). A tertiary alcohol is synthesized from a ketone and a Grignard reagent. If all three groups on the tertiary alcohol are different, there are often three combinations of ketone and Grignard reagent. If two of the groups on the alcohol carbon are the same, the alcohol may also be synthesized from an ester and two equivalents of Grignard reagent.

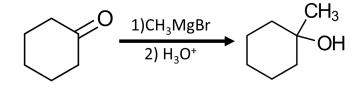
5.1: 2-Methyl-2-propanol is a tertiary alcohol. To synthesize a tertiary alcohol, start with a ketone; in this case, reaction of propanone with methylmagnesium bromide should do the trick.



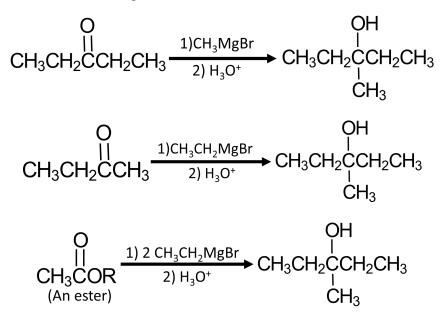
Recall that, if two or more alkyl groups bonded to the carbon bearing the -OH group are the same, an alcohol can be synthesized from an ester and a Grignard reagent.

$$\begin{array}{c} O \\ || \\ CH_3COR \\ (An ester) \end{array} \xrightarrow{1) 2 CH_3MgBr} CH_3CH_3 \\ \xrightarrow{1) 2 (H_3O^+)} CH_3CH_3 \\ \xrightarrow{1} CH_3 \end{array}$$

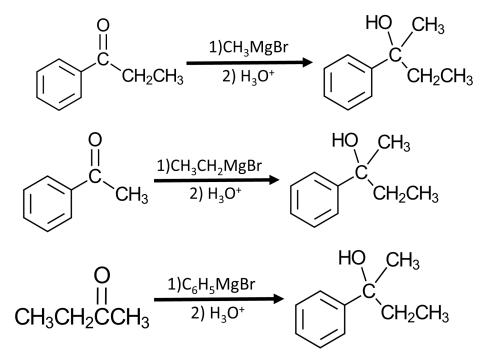
5.2: 1-Methylcyclohexanol is a tertiary alcohol. To synthesize a tertiary alcohol, we start with a ketone.



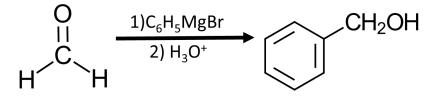
5.3: 3-Methyl-3-pentanol is a tertiary alcohol. Thus, this alcohol can be produced by reaction of a ketone with a Grignard reagent. Since two of the three groups bonded to the alcohol carbon are the same, another option is to use an ester as the starting material.



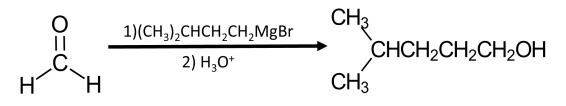
5.4: Once again, we have a tertiary alcohol. Three combinations of ketone and Grignard reagent can be used in this case.



5.5: Formaldehyde must be used to synthesize this primary alcohol.



5.6: As in the previous problem, formaldehyde must be used to synthesize this primary alcohol.



P.6 → Solution

6.1: 1-Phenylethanol is a secondary alcohol and so can be prepared by the reaction of a Grignard reagent with an aldehyde. One combination is phenylmagnesium bromide and ethanal (acetaldehyde).

$$C_6H_5MgBr + H-C \stackrel{\frown}{\leftarrow} H \xrightarrow{C_6H_5CHCH_3} OH$$

Grignard reagents – phenylmagnesium bromide in this case – are always prepared by reaction of magnesium metal and the corresponding halide. Starting with bromobenzene, a suitable synthesis is described by the following sequence.

$$C_{6}H_{5}Br \xrightarrow{Mg} C_{6}H_{5}MgBr \xrightarrow{1) H-C \leftarrow H} C_{6}H_{5}CHCH_{3}$$

6.2: Another way to obtain 1-phenylethanol via a Grignard reaction is to use benzaldehyde and a methyl Grignard reagent.

$$C_{6}H_{5}CH + CH_{3}MgI \longrightarrow C_{6}H_{5}CHCH_{3}$$

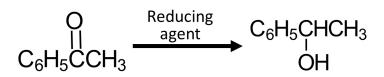
Starting with iodomethane, 1-phenylethanol can be synthesized with the following sequence. Benzaldehyde is used in the Grignard reaction.

$$CH_{3}I \xrightarrow[ether]{Mg} CH_{3}MgI \xrightarrow[2]{1}C_{6}H_{5}CH CH_{3}H_{3}O^{+} OH C_{6}H_{5}CHCH_{3}$$

6.3: Aldehydes are, in general, obtainable by oxidation of the corresponding primary alcohol. By recognizing that benzaldehyde can be obtained by oxidation of benzyl alcohol with PCC, we propose the following synthesis.

$$C_{6}H_{5}CH_{2}OH \xrightarrow{PCC} C_{6}H_{5}CH \xrightarrow{1) CH_{3}MgI} C_{6}H_{5}CHCH_{3}$$

6.4: The conversion of acetophenone to 1-phenylethanol is a reduction reaction.



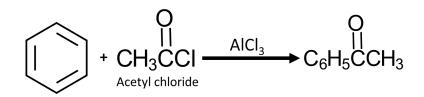
According to Carey, at least three reducing agent preparations can be used to achieve this conversion, namely:

1. NaBH4, CH3OH;

2. LiAlH₄ in diethyl ether, then H₂O;

3. H₂ and a Pt, Pd, Ni, or Ru catalyst;

6.5: Benzene can be employed as a starting material in the synthesis of 1-phenylethanol. Friedel-Crafts acylation of benzene gives acetophenone, which can then be reduced as in Problem 6.4.



P.7 → Solution

7.1: As a primary alcohol having two more carbons than bromobenzene, it can be formed by reaction of a Grignard reagent, phenylmagnesium bromide, with ethylene oxide.

$$C_6H_5MgBr + H_2C - CH_2 \longrightarrow C_6H_5CH_2CH_2OH$$

Starting with bromobenzene, the appropriate reaction sequence is the following.

$$C_{6}H_{5}Br \xrightarrow{Mg} C_{6}H_{5}MgBr \xrightarrow{1)} H_{2}C \xrightarrow{-CH_{2}} C_{6}H_{5}CH_{2}CH_{2}OH$$

7.2: Hydration of styrene with a regioselectivity contrary to that of Markovnikov's rule is required. This is accomplished readily by hydroboration-oxidation.

$$C_{6}H_{5}CH \longrightarrow CH_{2} \xrightarrow{1) B_{2}H_{6}, \text{ diglyme}} C_{6}H_{5}CH_{2}CH_{2}OH$$

7.3: Reduction of aldehydes yields primary alcohols. 2-Phenylethanol can be synthesized by reduction of 2-phenylethanal.

$$C_{6}H_{5}CH_{2}CH \xrightarrow{Reducing}{agent} C_{6}H_{5}CH_{2}CH_{2}OH$$

As mentioned in Problem 6.4, three reducing agent preparations can be used to achieve this conversion, namely:

1. NaBH₄, CH₃OH;

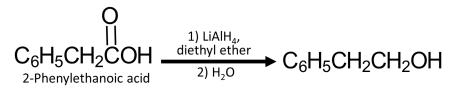
2. LiAlH₄ in diethyl ether, then H_2O ;

3. H₂ and a Pt, Pd, Ni, or Ru catalyst;

7.4: Esters are readily reduced to primary alcohols with lithium aluminum hydride.

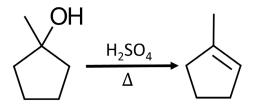
$$C_{6}H_{5}CH_{2}COCH_{2}CH_{3} \xrightarrow{1) \text{ LiAlH}_{4}, \\ \stackrel{\text{diethyl ether}}{\longrightarrow} C_{6}H_{5}CH_{2}CH_{2}CH_{2}OH \\ \hline C_{6}H_{5}CH_{2}CH_{2}CH_{2}OH$$

7.5: The only reagent that is suitable for the direct reduction of carboxylic acids to primary alcohols is lithium aluminum hydride.

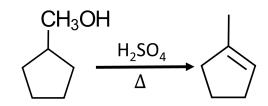


P.8 → Solution

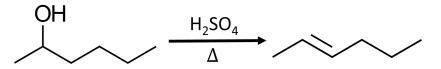
8.1: The main dehydration product of 1-methylcyclopentanol is 1-methylcyclopentene.



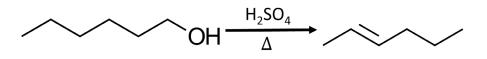
8.2: Cyclopentylmethanol is rearranged to yield 1-methylcyclopentene as the main dehydration product.



8.3: 2-Hexanol is dehydrated to yield 2-hexene as the main dehydration product.

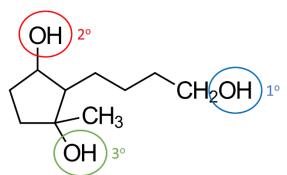


8.4: 1-Hexanol is rearranged to yield 2-hexene as the main dehydration product.

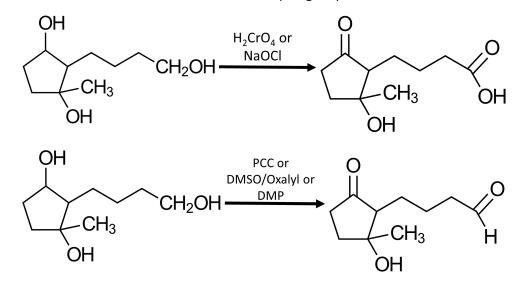


P.9 → Solution

9.1 to 9.5: This molecule serves as an interesting substrate for study of oxidation reactions because it contains a primary alcohol group, a secondary alcohol group, and a tertiary alcohol group.

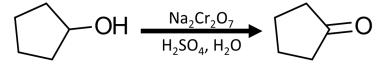


None of the five oxidation reagents affects the tertiary alcohol. All five oxidize the 2° alcohol to a ketone. Chromic acid and excess NaOCl oxidize the 1° alcohol to a carboxylic acid group, while PCC, DMSO/oxalyl chloride (Swern), and DMP oxidize the 1° alcohol to an aldehyde group.

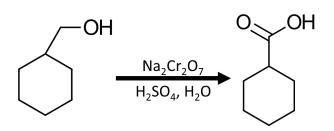


P.10 Solution

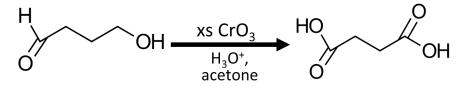
10.1: The alcohol in this case is secondary. Chromic acid will oxidize the alcohol to give a ketone.



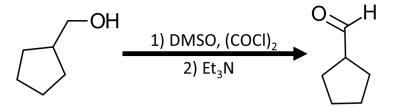
10.2: The alcohol in this case is primary. Chromic acid will oxidize the alcohol to give a carboxylic acid.



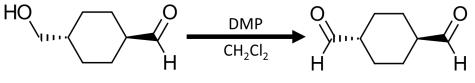
10.3: The alcohol in this case is primary. This alcohol is oxidized upon treatment with chromic acid to give a carboxylic acid group. The aldehyde group already present in the molecule is also oxidized to yield a second carboxylic acid group.



10.4: The alcohol in this case is primary. A Swern oxidation will oxidize the alcohol to give an aldehyde.

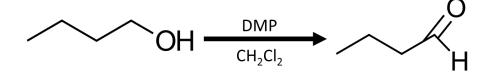


10.5: The alcohol in this case is primary. Dess-Martin periodinane (DMP) will oxidize the alcohol to give an aldehyde. The aldehyde function already present in the substrate is unchanged.

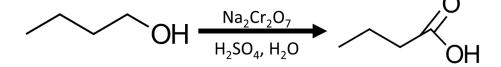


P.11 Solution

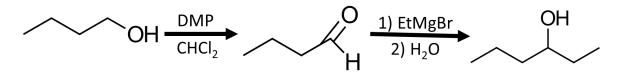
11.1: The aldehyde in question can be synthesized in one step by oxidizing butanol with PCC (pyridinium chlorochromate) or DMP (Dess-Martin periodinane), or by Swern oxidation.



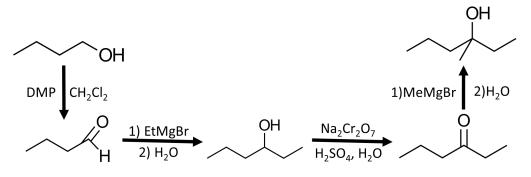
11.2: The carboxylic acid in question can be prepared in one step, using chromic acid as the oxidizing agent.



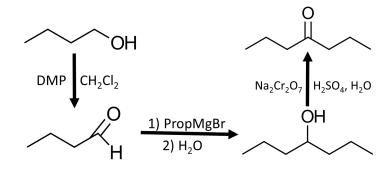
11.3: The alcohol in question can be prepared by first converting butanol into an aldehyde with DMP, PCC, or Swern oxidation, then by submitting it to a Grignard reaction with ethyl magnesium bromide.



11.4: This problem is similar to 11.3, but in this case two alkyl groups – one methyl and one ethyl – must be installed to the starting alcohol. Each alkyl group can be installed using the same procedure from the previous problem (oxidation followed by a Grignard reaction). The first oxidation procedure can be performed with DMP (or PCC, or Swern oxidation) to give an aldehyde. The second oxidation procedure can be achieved with chromic acid.

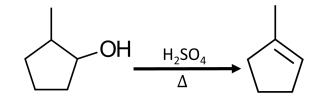


11.5: Oxidation of the starting molecule with DMP (or PCC, or by Swern oxidation) gives an aldehyde, which can then be treated with a Grignard reagent to yield a secondary alcohol. Oxidation of this alcohol gives the desired ketone.

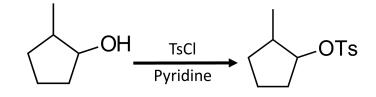


P.12 → Solution

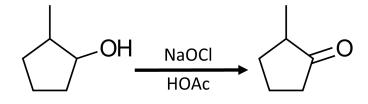
12.1: Dehydrating 2-methylcyclopentanol with sulfuric acid and heat should yield this alkene.



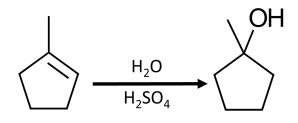
12.2: 2-Methylcyclopentanol can be converted to the desired tosylate by reacting it with TsCl in pyridine.



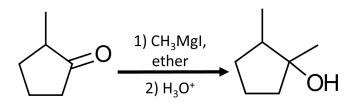
12.3: 2-Methylcyclopentanol can be converted to the desired ketone by oxidizing it with NaOCI/HOAc. Chromic acid, PCC, DMP, or Swern oxidation work just as well.



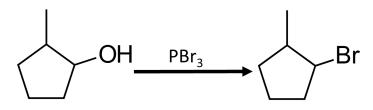
12.4: We first dehydrate 1-methylcyclopentanol as we did in Problem 12.1. Then, we hydroxylate the ensuing alkene.



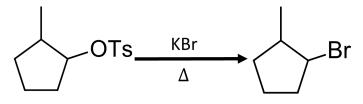
12.5: We first oxidize 1-methylcyclopentanol as we did in Problem 12.3. Then, we react the ensuing ketone with methylmagnesium iodide, followed by hydrolysis.



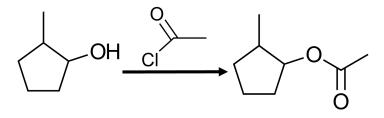
12.6: 2-Methylcyclopentanol can be converted to the desired alkyl halide by reacting it with phosphorus tribromide (PBr_3) .



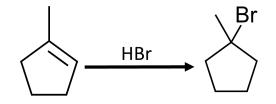
Another option is to use the alkyl tosylate obtained in Problem 12.2 and heat it with potassium bromide (KBr).



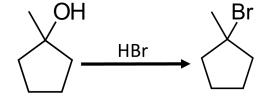
12.7: The ester in question can be obtained by reacting 2-methylcyclopentanol with acetyl chloride.



12.8: We first dehydrate 1-methylcyclopentanol as we did in Problem 12.1. Then, we react the ensuing alkene with HBr.



Another option is to treat the alcohol obtained in Problem 12.4 with HBr.

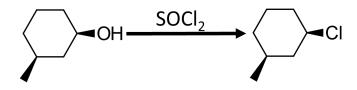


P.13 → Solution

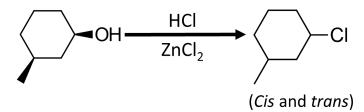
13.1: *Cis*-3-methylcyclohexanol reacts with phosphorus tribromide with inversion to yield an alkyl bromide.



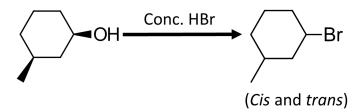
13.2: *Cis*-3-methylcyclohexanol reacts with thionyl chloride to yield an alkyl chloride. Stereochemistry is retained.



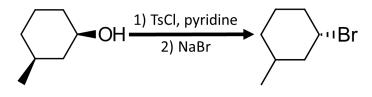
13.3: *Cis*-3-methylcyclohexanol reacts with Lucas reagent by S_N 1 substitution to yield *cis* and *trans* stereoisomers of an alkyl chloride.



13.4: *Cis*-3-methylcyclohexanol reacts with concentrated HBr by S_{N1} substitution to yield *cis* and *trans* stereoisomers of an alkyl bromide.

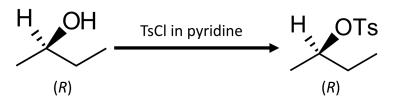


13.5: This sequence of reactions ultimately yields an alkyl bromide by $S_N 2$ substitution. As with any $S_N 2$ substitution, the reaction proceeds with inversion of configuration.

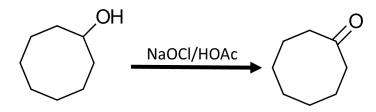


P.14 → Solution

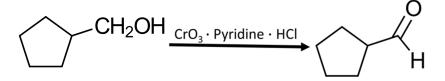
14.1: Reaction of butan-2-ol with tosyl chloride in pyridine cleaves the hydroxyl proton and substitutes it with Ts, creating an alkyl tosylate. Regiochemistry is conserved.



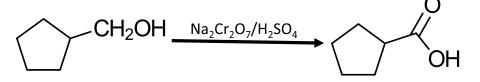
14.2: Cyclooctanol, a secondary alcohol, reacts with NaOCl/HOAc to yield a ketone.



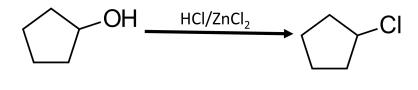
14.3: In this reaction, the primary alcohol is oxidized to an aldehyde.



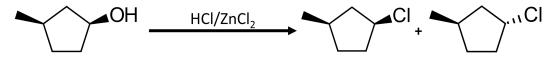
14.4: In this reaction, the primary alcohol is oxidized to a carboxylic acid.



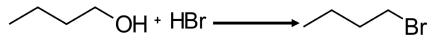
14.5: Cyclopentanol reacts with the Lucas reagent to have its hydroxyl group replaced with a chloride group.



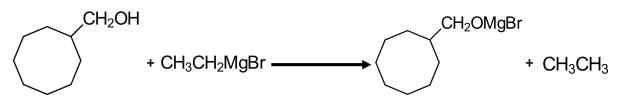
14.6: Cis-3-methylcyclopentanol reacts with Lucas reagent to have its hydroxyl group replaced with a chloride group. The reaction is a S_N1 substitution, and a racemic mixture of enantiomers is formed as the carbocation intermediate can be attacked from either side by chloride.



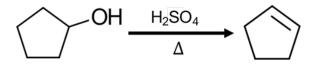
14.7: *n*-Butanol reacts with HBr to have its hydroxyl group replaced with a bromide group.



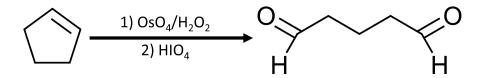
14.8: This reaction yields an organometallic compound and ethane.



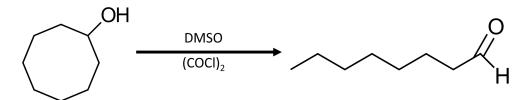
14.9: Cyclopentanol is dehydrated upon being heated with sulfuric acid.



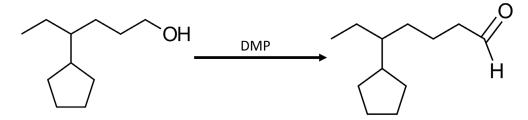
14.10: Cyclopentene formed in the previous reaction is dihydroxylated and oxidized to yield a dialdehyde.



14.11: 1-Octanol undergoes Swern oxidation to yield an aldehyde.

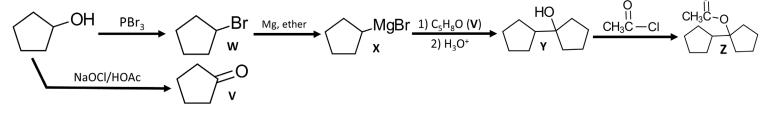


14.12: 4-Cyclopentyl-1-hexanol is oxidized with DMP reagent to yield an aldehyde.



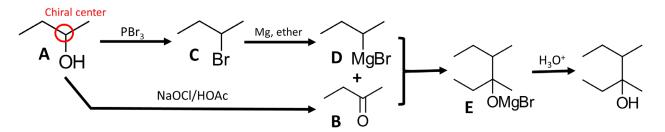
P.15 → Solution

Cyclopentanol is oxidized with NaOCI/HOAc to yield cyclopentanone; this is compound V. Cyclopentanol reacts with phosphorus tribromide to yield bromocyclopentane; this is compound W. Reaction of bromocyclopentane with magnesium in ether gives cyclopentyl magnesium bromide; this is compound X. Cyclopentyl magnesium bromide reacts with cyclopentanone (compound V) to undergo a Grignard reaction and produce the bicyclic alcohol 1,1bi(cyclopentyl)-1-ol; this is compound Y. Lastly, reaction of compound Y with acetyl chloride produces a bicyclic ester, which is compound Z.



P.16 Solution

Compound A is 2-butanol. Oxidation of this alcohol with NaOCl/HOAc yields butanone, which is compound B. Reaction of 2-butanol with phosphorus tribromide yields 2-bromobutane, which is compound C. Treatment of 2-bromobutane with magnesium in ether produces *sec*-butylmagnesium bromide, which is compound D. Compounds B and D react to yield compound E, which is finally hydrolyzed to produce 3,4-dimethyl-3-hexanol.



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- MCMURRY, J. (2008). Organic Chemistry. 7th edition. Belmont: Thomson.
- WADE, L. and SIMEK, J. (2016). *Organic Chemistry*. 9th edition. Upper Saddle River: Pearson.



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