

ALCOHOLS AND PHENOLS; ETHERS AND EPOXIDES; THIOLS AND SULFIDES

A STUDENT SHOULD BE ABLE TO:

1. Give the IUPAC name when given the structure, and draw the structure given the name of open-chain and monocyclic alcohols, phenols and ethers (alcohol nomenclature was first covered in Module 4; ethers are named as alkoxyalkanes). Also, draw the structure when given the common name, and name when given the structure of ethylene glycol, tetrahydrofuran, and simple alcohols and ethers containing any of the alkyl groups listed in the objectives for Module 4, Organic Chemistry I. Also, draw examples of, and identify the functional groups in, thiols, thioethers, and disulfides.

Note:

thiols, RSH (alcohols, ROH)
thioethers RSR (ethers ROR)
disulfides RSSR (peroxides ROOR)
sulfoxides RSOR (ketones RCOR)

2. Predict relative physical properties, including boiling points and relative solubilities, of alcohols, ethers, sulfur-containing compounds, and other compounds. The principles involved were covered in previous modules. Also, be able to predict the relative acidities of phenols and alcohols.
3. Given the starting materials and reaction conditions, predict the products of the following reactions involving alcohols and ethers.

Preparations of alcohols:

Substitution reactions: S_N1 , S_N2 (see Module 7, Organic Chemistry I)
Acid-catalyzed hydration of alkenes (see Module 9, Organic Chemistry I)
Hydroboration-oxidation (hydroboration is a *syn* addition; replacement of boron by OH in the oxidation step occurs with retention, and the overall process is also a net *syn* addition) (see Module 9, Organic Chemistry I)
Oxymercuration-Demercuration (see Module 9, Organic Chemistry I)
Reduction of ketones, aldehydes, carboxylic acids, and esters with $LiAlH_4$ (LAH) and of ketones and aldehydes with $NaBH_4$.
Reactions of Grignard reagents and alkyllithium reagents with acids, ethylene oxide, ketones, aldehydes, and esters. (Including the synthesis of the Grignard reagent via alkyl and aryl halides reacting with Mg in the presence of ether)
Grignard and alkyllithium reagents react with:
Formaldehyde to give 1° alcohols with one more carbon atom than the starting material
Ethylene oxide to give 1° alcohols with two more C's than the starting material
Aldehydes to give 2° alcohols
Ketones and esters to give 3° alcohols

Reactions of alcohols:

Acid-base reactions involving alcohols and their conjugate bases. The order of relative acidity is: mineral acids > carboxylic acids > water > alcohols > terminal alkynes > ammonia and amines > alkanes.

Oxidation of 1° and 2° alcohols using pyridinium chlorochromate (PCC); and of 1° and 2° alcohols and aldehydes using chromic acid.

Formation of sulfonate (e.g., tosylate) esters (see Module 7, Organic Chemistry I)

Formation of alkyl halides from alcohols using hydrogen halides, PBr₃, and SOCl₂

Preparation of ethers:

The Williamson synthesis of ethers (the S_N2 reaction of an alkoxide with an alkyl halide). Note that methyl and 1° alkyl halides give the ether as the product; 2° and 3° halides give alkenes by an E2 reaction.

- Using any of the above reactions, propose syntheses of compounds that can be made using alcohols as starting materials or intermediates. As always, synthesis problems may require any reaction that you have studied in the course so far.
- Propose mechanisms, and predict and explain experimental results using your knowledge of mechanism. Important reactions include:

Hydration and dehydration (covered in previous modules).

Reaction of alcohols with hydrogen halides.

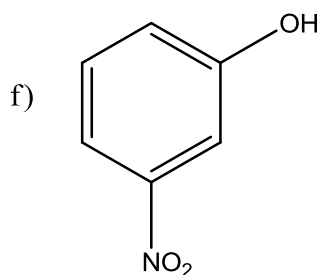
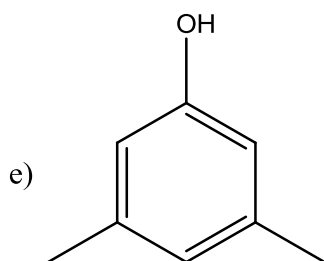
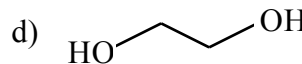
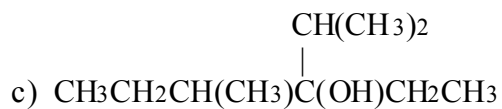
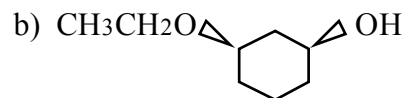
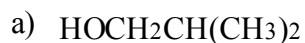
Hydride addition to a carbonyl

Organometallic addition to a carbonyl

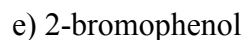
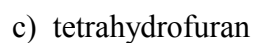
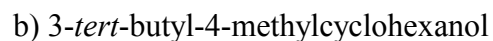
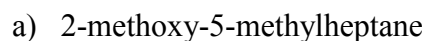
To best prepare for this module, please work Chapters 13 and 14 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGE SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

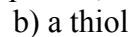
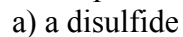
1.1 Name each of the following compounds.



1.2 Draw the structure of each of the following compounds.



1.3 Give an example of the following compounds. (Be specific; do not use R)



2.1 Which of the following compounds has the lowest boiling point?



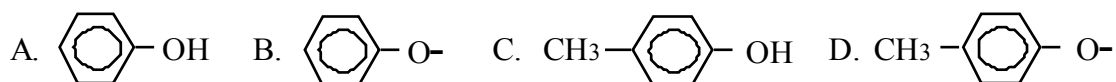
2.2 Which of the following compounds is the least soluble in water?

A. $\text{CH}_3\text{CH}_2\text{COOH}$ B. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ C. $\text{CH}_3\text{CH}_2\text{COONa}$ D. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$

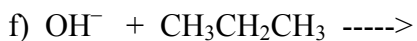
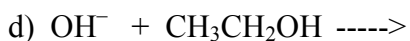
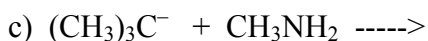
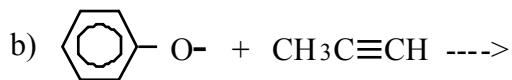
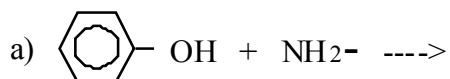
2.3 a) Which of the following is the strongest acid? b) Which is the strongest base?



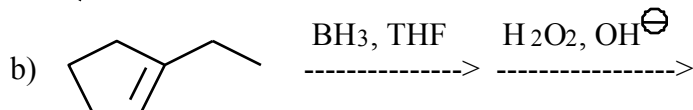
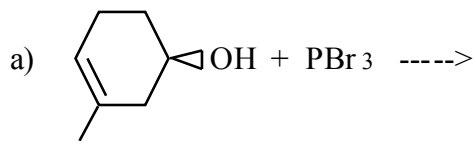
2.4 a) Which of the following is the strongest acid? b) Which is the strongest base?

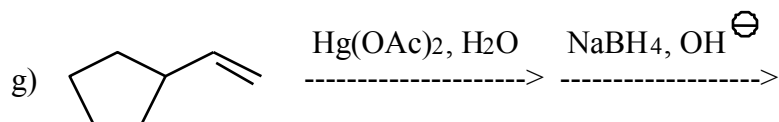
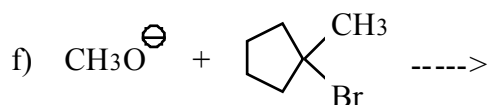
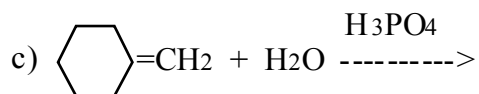


3.1 Predict the products of the reactions given below (if any).

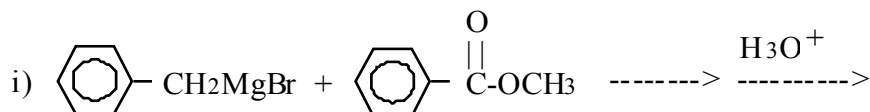
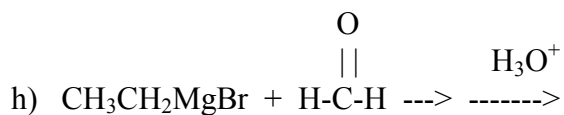
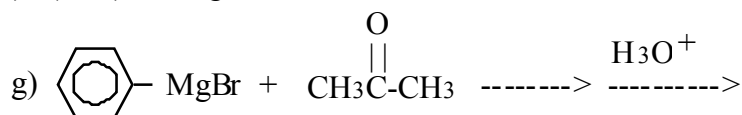
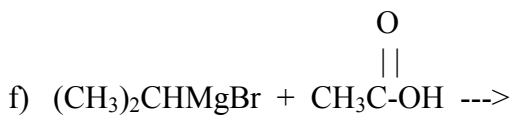
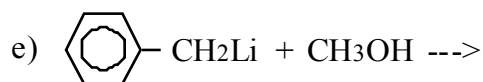
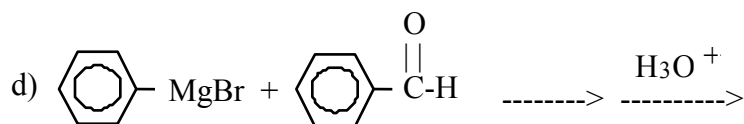
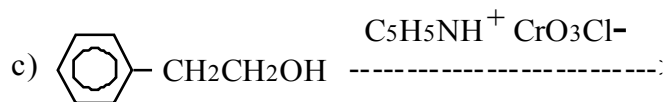
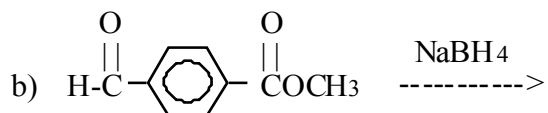
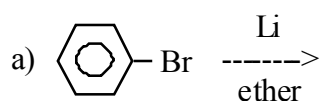


3.2 Predict the organic product(s) of the reactions given below, including stereochemistry whenever appropriate.

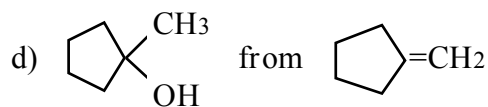
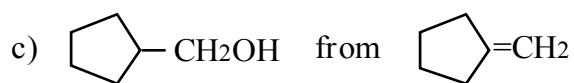
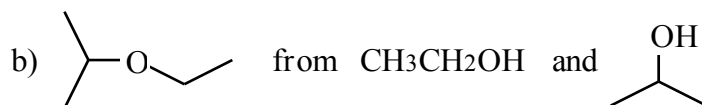
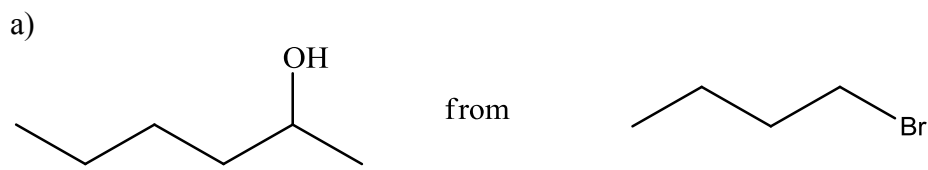




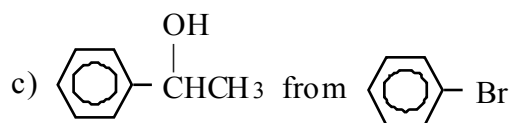
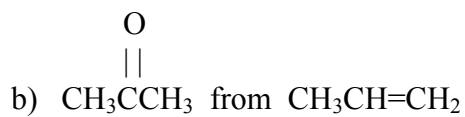
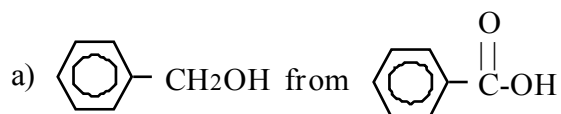
3.3 Predict the product(s) of each of the following reactions (if any).

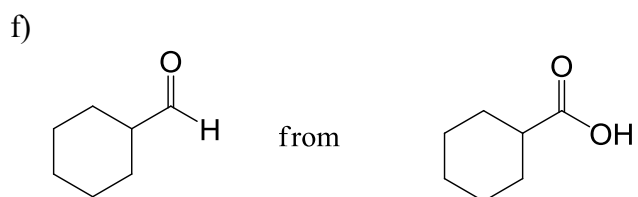
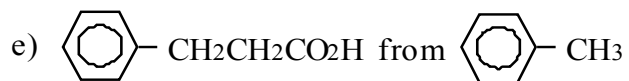
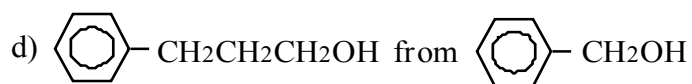


4.1 Propose a synthesis of each of the compounds shown, from the given starting materials and any other needed reagent

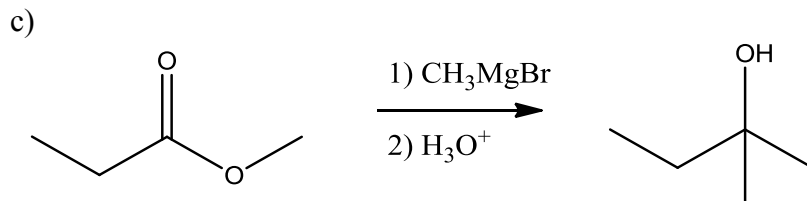
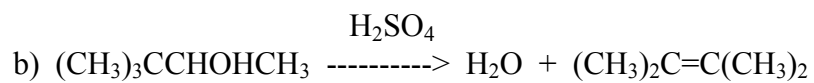
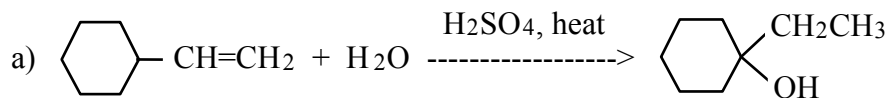


4.2 Propose syntheses of each of the following compounds, from the given starting material and any other needed reagents.





5. Propose a mechanism for each of the following reactions.



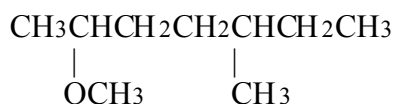
SOLUTIONS TO SAMPLE PROBLEMS:

1.1 Names of the compounds shown:

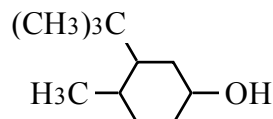
- | | |
|--|--------------------------------------|
| a) isobutyl alcohol or 2-methyl-1-propanol | b) <i>cis</i> -3-ethoxycyclohexanol |
| c) 3-ethyl-2,4-dimethyl-3-hexanol | d) ethylene glycol or 1,2-ethanediol |
| e) 3,5-dimethylphenol | f) 3-nitrophenol |

1.2 Structures of the compounds named:

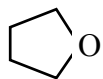
a) 2-methoxy-5-methylheptane



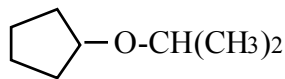
b) 3-*tert*-butyl-4-methylcyclohexanol



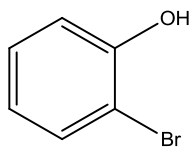
c) tetrahydrofuran



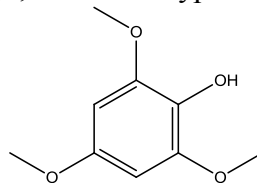
d) isopropoxycyclopentane



e) 2-bromophenol



f) 2,4,6-trimethoxyphenol



1.3 a) a disulfide: $\text{CH}_3\text{S-SCH}_2\text{CH}_3$

b) a thiol: $(\text{CH}_3)_2\text{CHSH}$

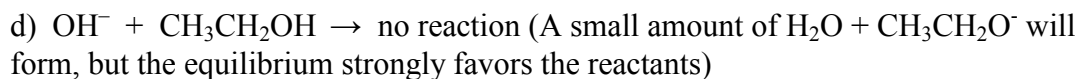
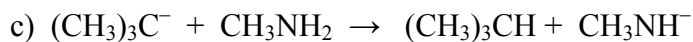
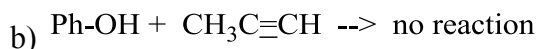
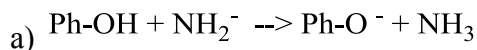
2.1 D

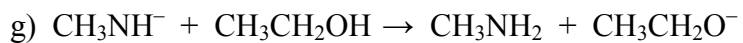
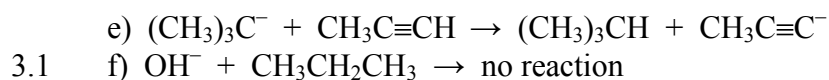
2.2 D

2.3 a) B b) C

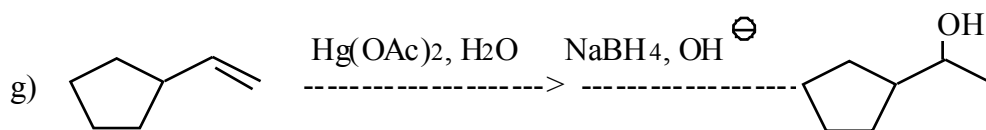
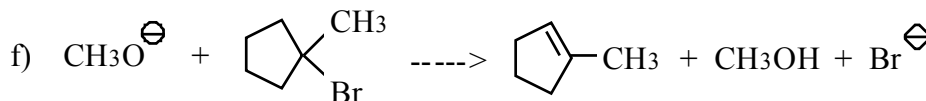
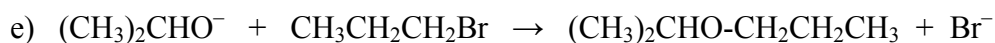
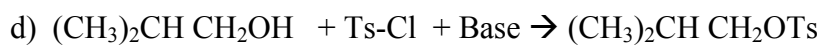
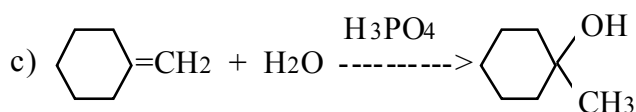
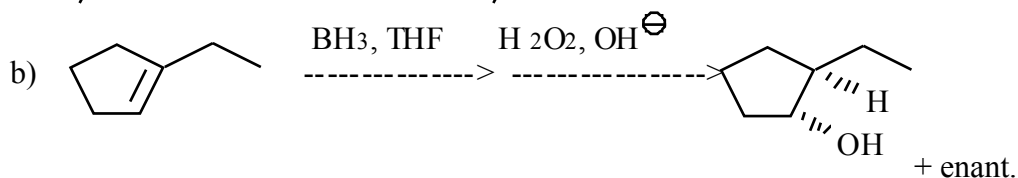
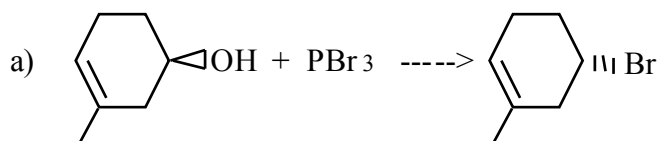
2.4 a) A b) D

3.1 Predict the products

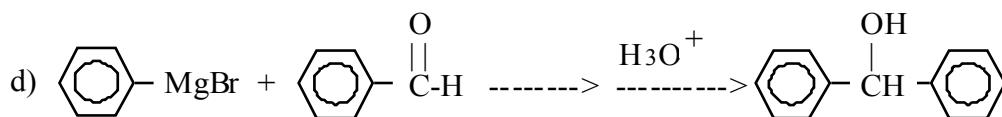
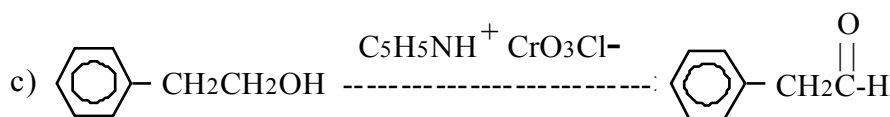
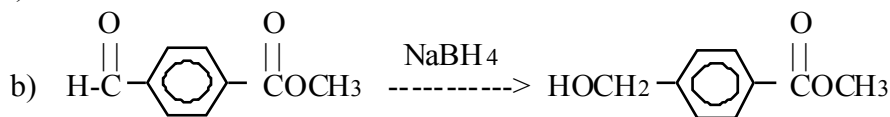
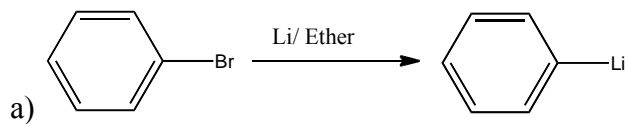




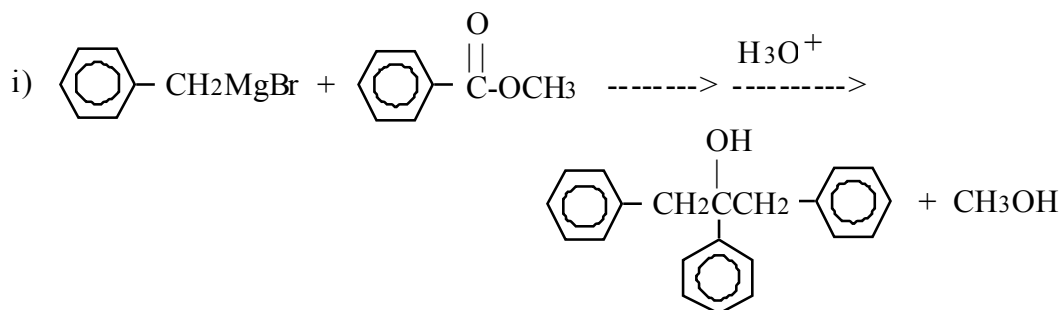
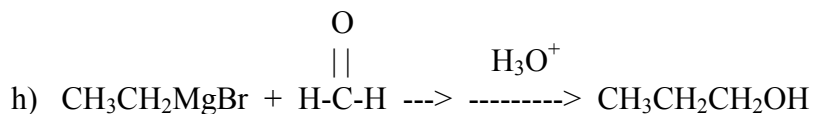
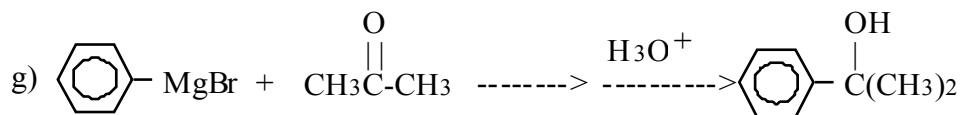
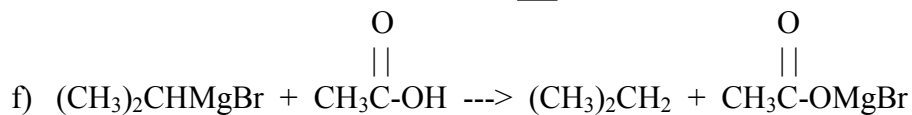
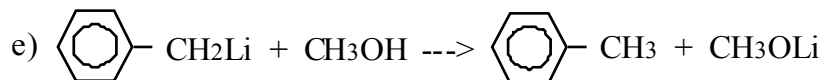
3.2 Predict the product(s) of the reactions given below, including stereochemistry whenever appropriate.



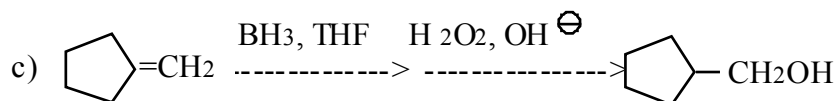
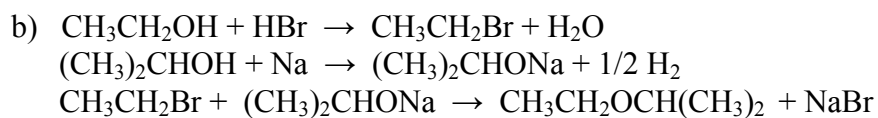
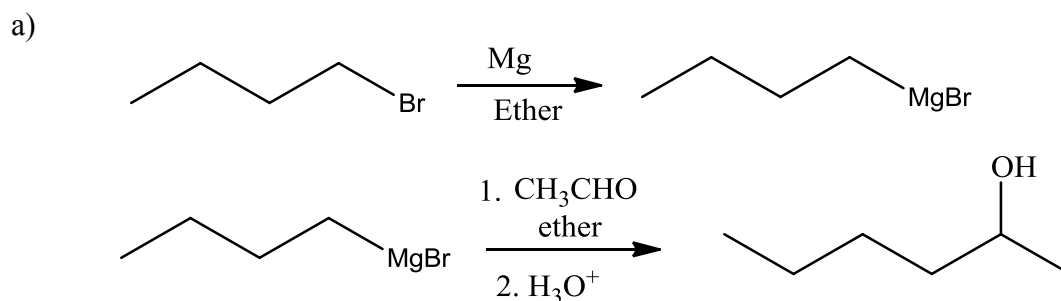
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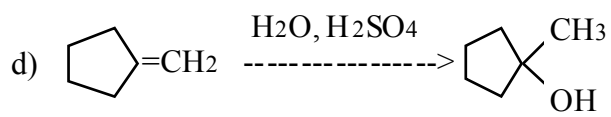


3.3

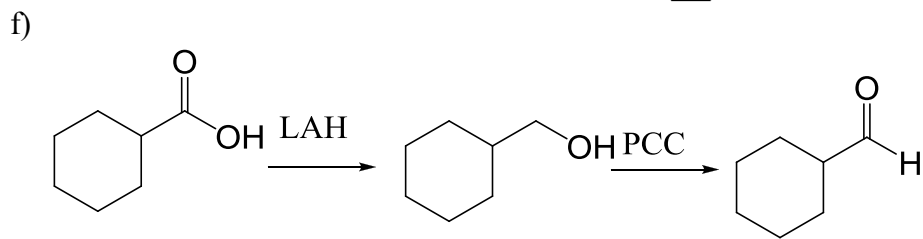
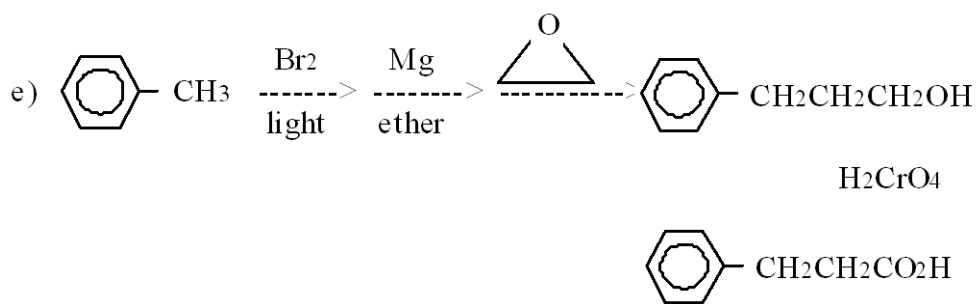
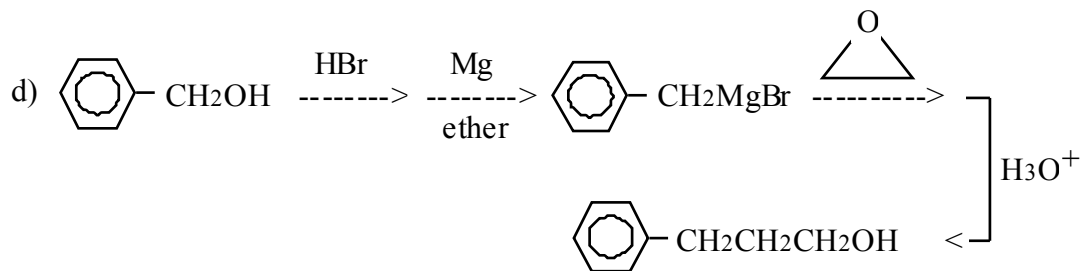
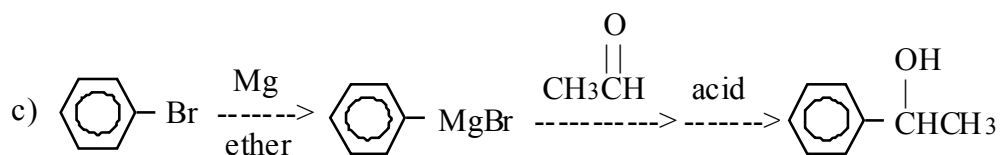
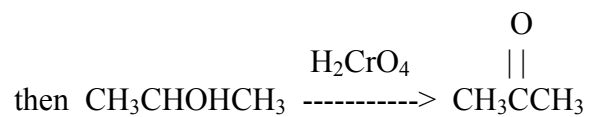
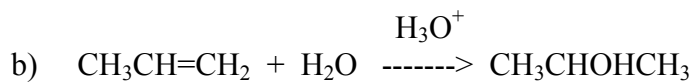
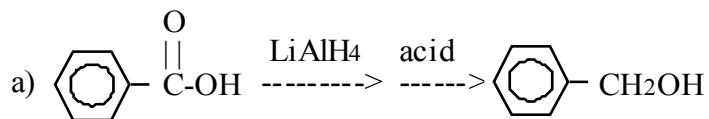


4.1 Syntheses:

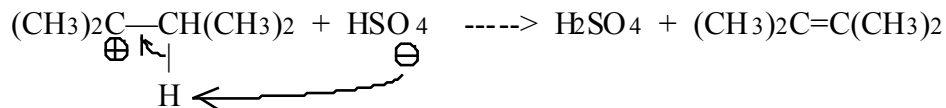
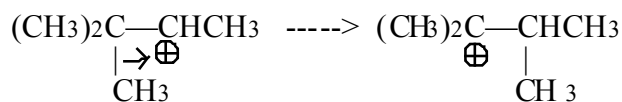
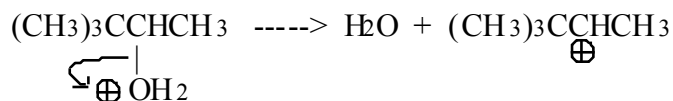
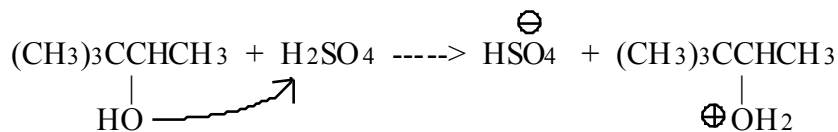
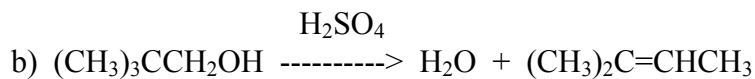
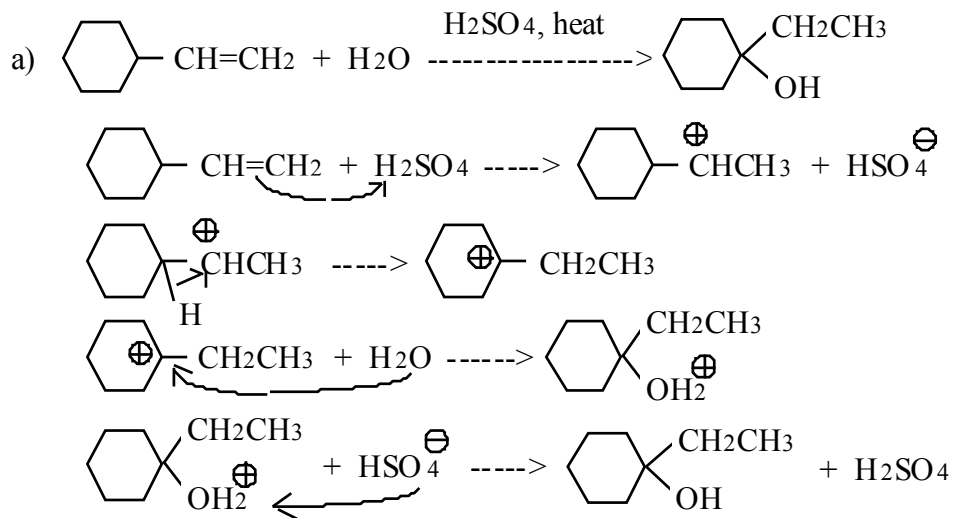




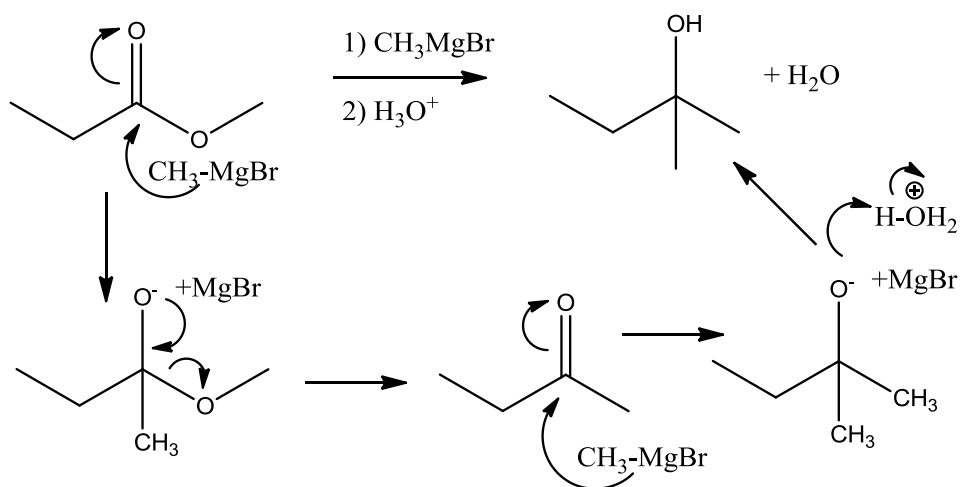
4.2 More syntheses:



5. Mechanisms:



c)

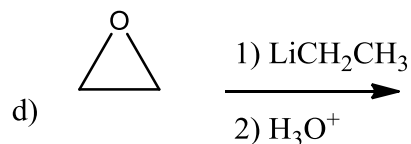
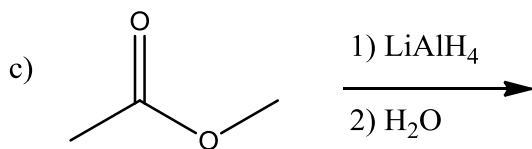
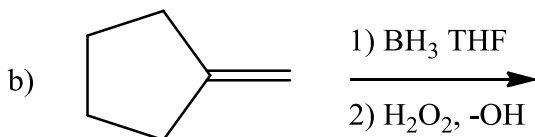
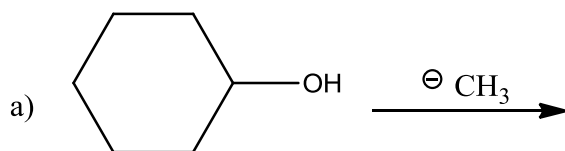


1. Draw: *cis*-3-isopropylcyclopentanol 2. Name: $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CHOCH}_2\text{CH}_3$
|
 $\text{CH}_2\text{CH}_2\text{CH}_3$

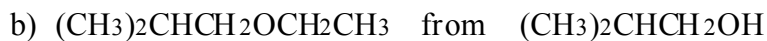
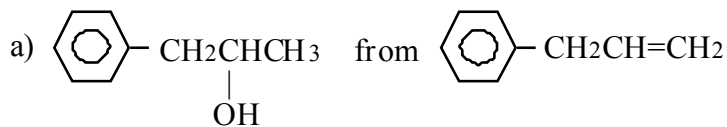
3. Which of the following compounds has the HIGHEST boiling point?



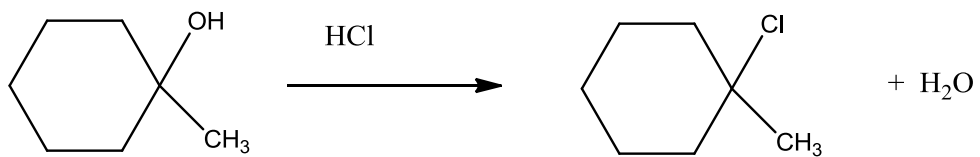
4. Predict the product or products of each of the following reactions.



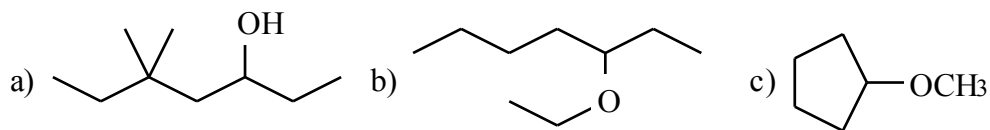
5. Propose a synthesis of each of the following compounds, beginning with the given starting material and using also any needed reagents or solvents.



6. Propose a mechanism for the reaction shown:



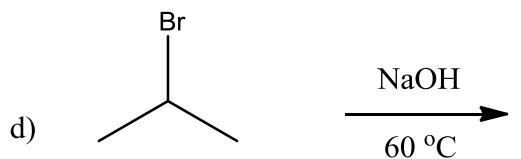
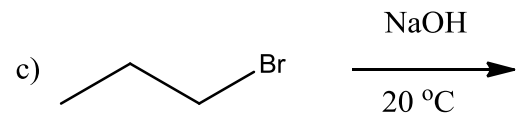
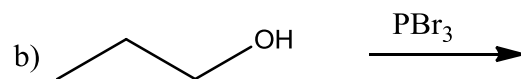
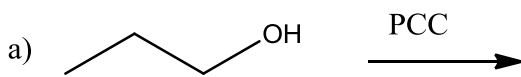
1. Give the IUPAC name of each of the following compounds.



2. Which of the following compounds has the LOWEST boiling point?



3. Predict the product of each of the following reactions.



4. Propose a synthesis of each of these compounds starting from 3,3-dimethyl-1-butene and any other needed reagents.

a) 3,3-dimethyl-1-butanol

b) 3,3-dimethyl-2-butanol

5. Propose a mechanism for the following reaction:

