

CHEM 2425. Chapter 17. Alcohols and Phenols (homework) W

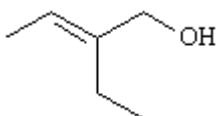
Short Answer

Drawing Instructions: Draw structures corresponding to each of the given names.

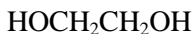
1. Draw: 3-methyl-2-buten-1-ol
2. Draw: 2-phenyl-2-propanol
3. Draw: glycerol
4. Draw: 2, 4, 6-trinitrophenol

IUPAC Naming Instructions: Provide proper IUPAC names.

5. Name:



6. Name:

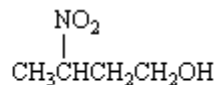
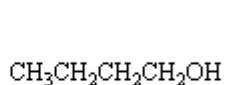
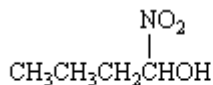
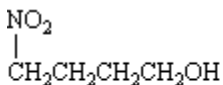


7. Name:

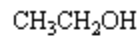
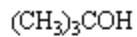
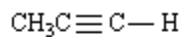


Exhibit 17-1

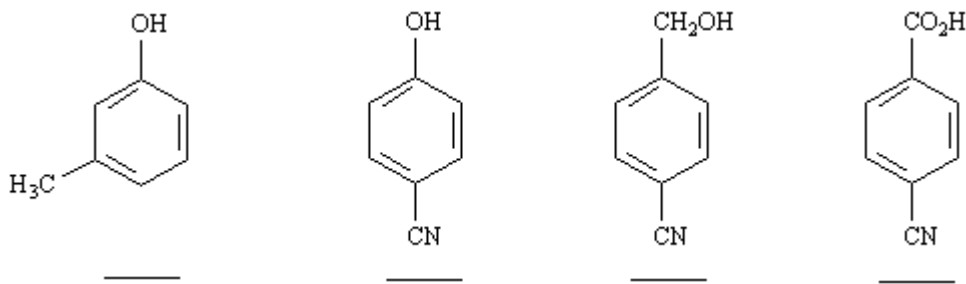
Rank the following groups of compounds from most acidic (1) to least acidic (4). Place the number corresponding to the compound's relative rank in the blank below the structure.



8. _____ _____ _____ _____



9. _____ _____ _____ _____



11. Explain why nonafluoro-2-methyl-2-propoxide is a much weaker base than *tert*-butoxide.

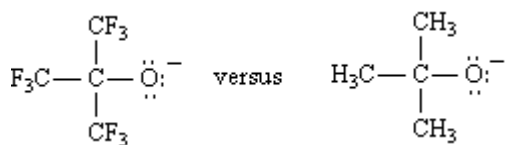
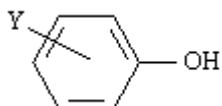


Exhibit 17-2

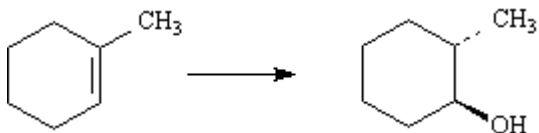
Refer to the data below to answer the following question(s).

pK _a s of Some Phenols	<u>Y</u>	<u>pK_a</u>
	-H	9.89
	<i>m</i> -NO ₂	8.28
	<i>p</i> -NO ₂	7.17
	<i>m</i> -OCH ₃	9.65
	<i>p</i> -OCH ₃	10.21

12. Refer to Exhibit 17-2. How do you account for the difference in acidity between *meta* and *para*-nitrophenol?

Exhibit 17-3

To answer the following question(s), consider the reaction below:

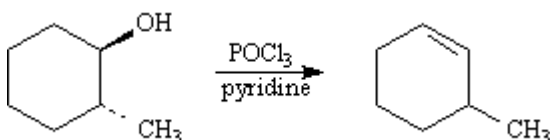


13. Refer to Exhibit 17-3. The alcohol product is classified as a:

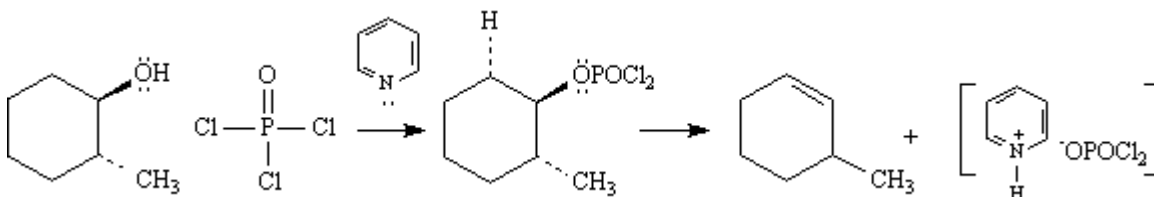
- 1° alcohol
- 2° alcohol
- 3° alcohol
- 4° alcohol

Exhibit 17-4

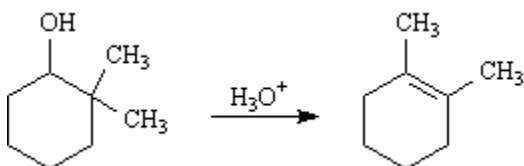
To answer the following question(s), consider the reaction below:



14. Refer to Exhibit 17-4. On the structures provided below, draw arrows which account for the complete stepwise mechanism for this reaction.



15. Refer to Exhibit 17-4. Why is 3-methylcyclohexene the major product of this reaction instead of 1-methylcyclohexene?
16. Acid-catalyzed dehydration of 2,2-dimethylcyclohexanol yields 1,2-dimethylcyclohexene as one of the major products. Write the complete stepwise mechanism for this reaction. Show all electron flow with arrows and show all intermediate structures.

**Exhibit 17-5**

To answer the following question(s), consider the reaction below:

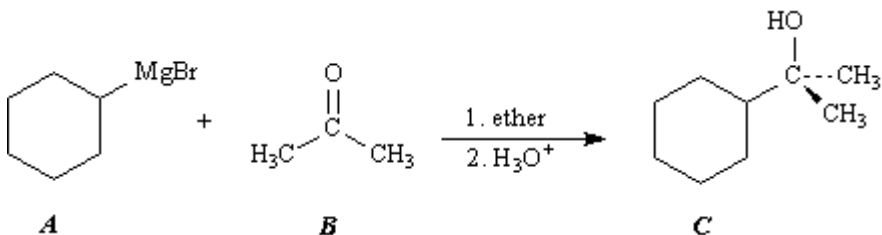


17. Refer to Exhibit 17-5. Provide the complete IUPAC name for the starting material in this reaction.
18. Refer to Exhibit 17-5. Write the complete stepwise mechanism for the reaction. Show all intermediates and all electron flow with arrows.
19. Refer to Exhibit 17-5. The conversion of an alcohol into an alkyl chloride by reaction with SOCl₂ is an example of:
- a. an E1 process

- b. an S_N1 process
- c. an E2 process
- d. an S_N2 process

Exhibit 17-6

Consider the Grignard reaction below to answer the following question(s).



20. Refer to Exhibit 17-6. The nucleophile in this reaction is:
21. Refer to Exhibit 17-6. The alcohol product can be classified as a:
- a. 1° alcohol
 - b. 2° alcohol
 - c. 3° alcohol
 - d. 4° alcohol

Exhibit 17-7

A highly useful and general method for the synthesis of alcohols is the addition of Grignard reagents to carbonyl compounds. Show what Grignard reagent and what carbonyl compound you would start with to prepare each alcohol below. List all possibilities.

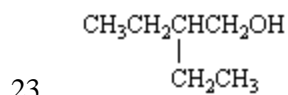
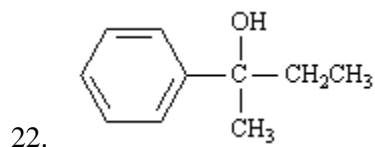
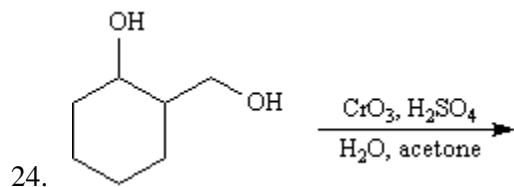


Exhibit 17-8

Give the major organic product(s) of the following reactions or sequences of reactions. Show all relevant stereochemistry.



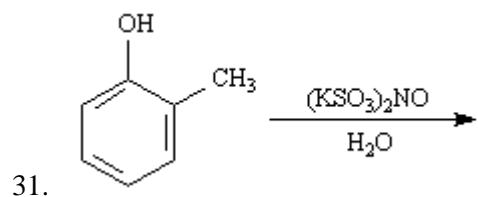
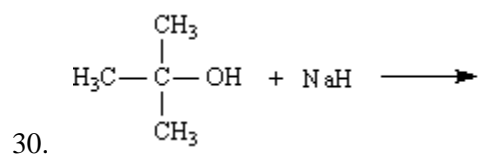
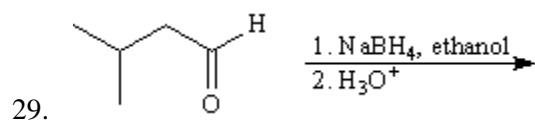
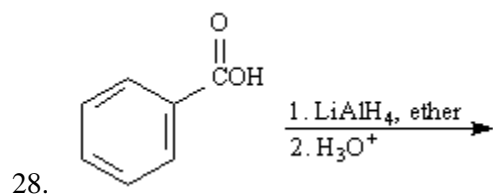
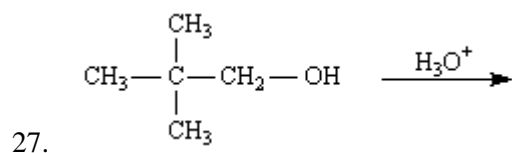
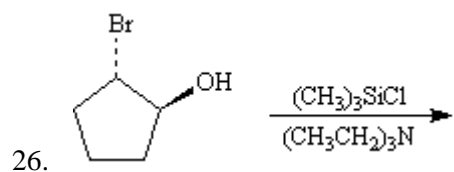
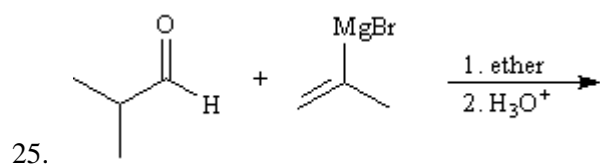


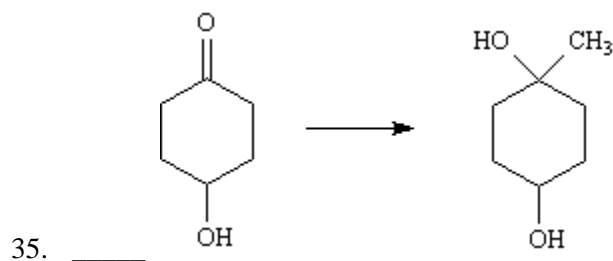
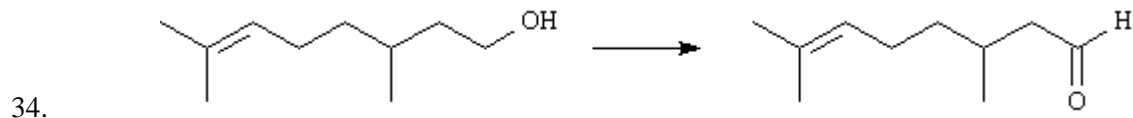
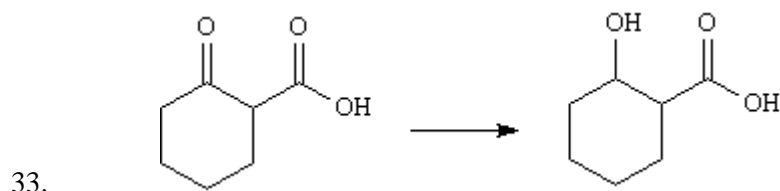
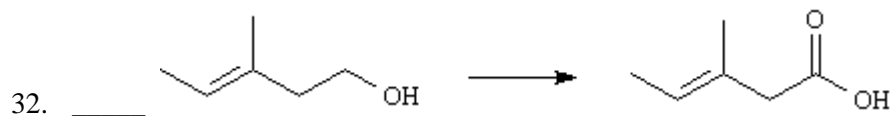
Exhibit 17-9

Choose the *best* reagent(s) for carrying out the following conversions from the list provided below. Place the letter of the best choice in the blank to the left of the conversion. Reagents may be used more than once.

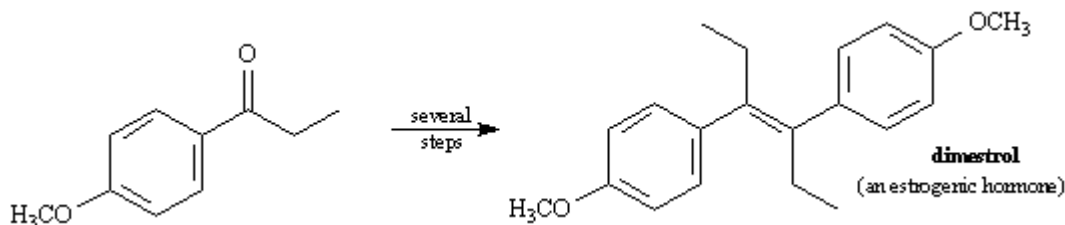
- a. 1. CH_3MgBr , ether
2. H_3O^+

- e. 1. *p*-TosCl, pyridine
2. NaOH

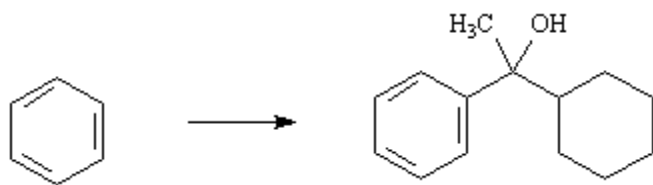
- b. 1. PBr_3
 2. NaOH
- c. 1. $(\text{CH}_3)_3\text{SiCl}$, $(\text{CH}_3\text{CH}_2)_3\text{N}$
 2. CH_3MgBr , ether
 3. H_3O^+
- d. 1. LiAlH_4 , ether
 2. H_3O^+
- f. CrO_3 , H_2SO_4 , H_2O
- g. 1. NaBH_4 , ethanol
 2. H_3O^+
- h. Dess–Martin periodinane, CH_2Cl_2



36. Propose a synthesis of Dimestrol starting from *p*-methoxypropiophenone as the only source of carbon.



37. Outline the synthetic steps necessary to carry out the conversion below. You may use any organic or inorganic reagents you need. Show the structures of all intermediate compounds that would probably be isolated during the course of your synthesis, and show all necessary reagents.



38. Synthesize the following alcohol starting with cyclohexene and bromocyclopentane as the only organic starting materials. Show all reagents and all intermediates in your synthesis.

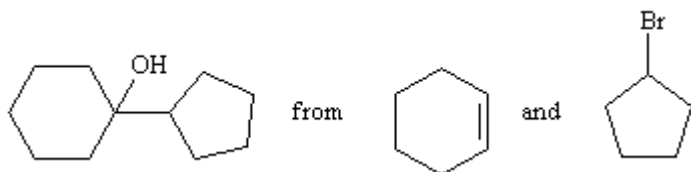
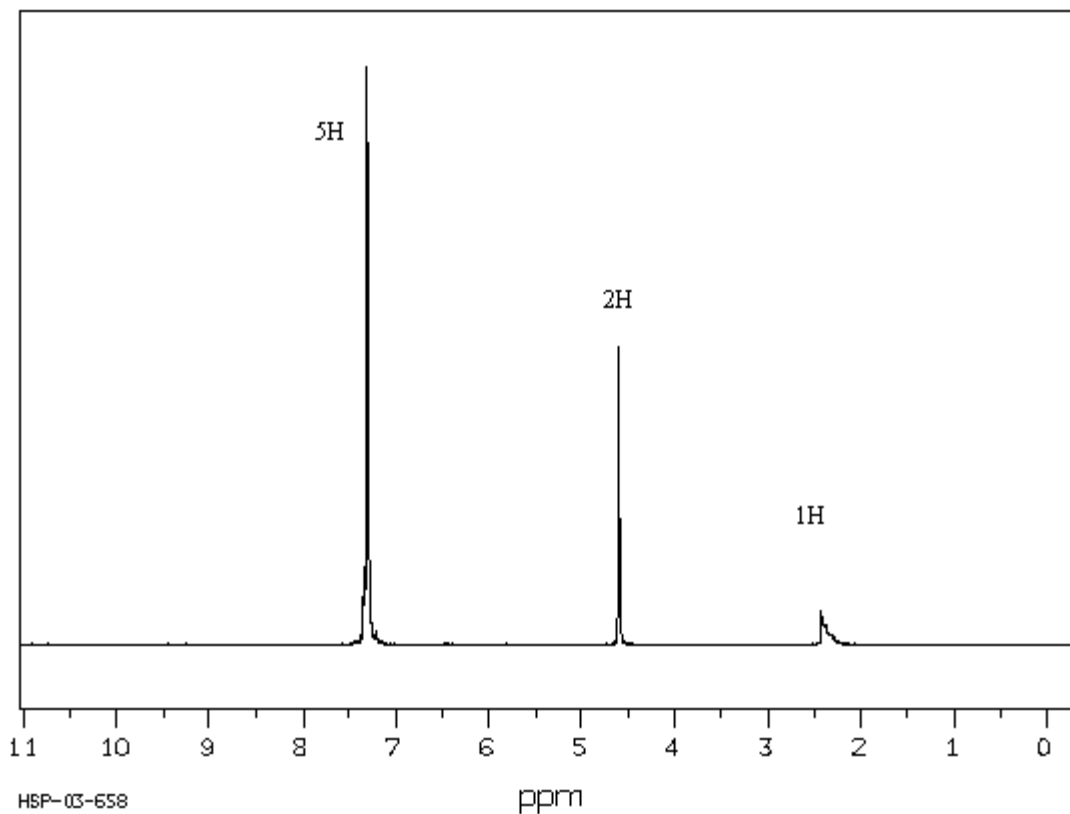


Exhibit 17-10

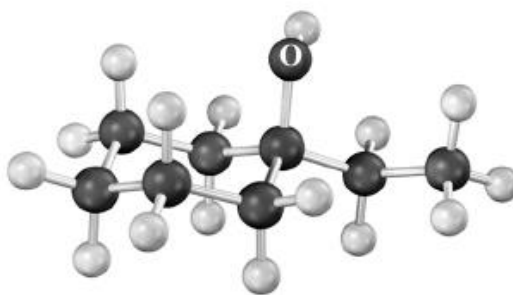
Propose structures for alcohols that have the following ^1H NMR spectra.

39. $\text{C}_7\text{H}_8\text{O}$ (neat solution; no solvent)



Spectrum obtained from: SBDSWeb: <http://www.aist.go.jp/RIODB/SDBS>

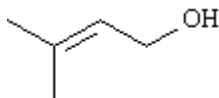
40. Give the IUPAC name for the following compound.



Answer Section

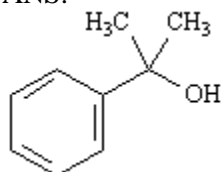
SHORT ANSWER

1. ANS:



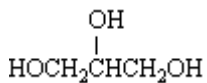
PTS: 1

2. ANS:



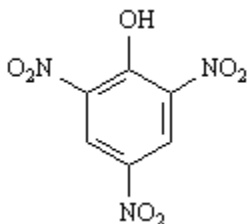
PTS: 1

3. ANS:



PTS: 1

4. ANS:



PTS: 1

5. ANS:

(E)-2-ethylbut-2-en-1-ol

PTS: 1

6. ANS:

1, 2-ethanediol or ethylene glycol

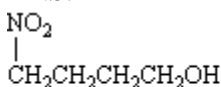
PTS: 1

7. ANS:

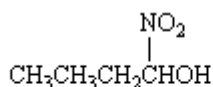
allyl alcohol or 2-propen-1-ol

PTS: 1

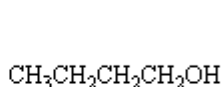
8. ANS:



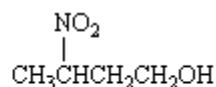
3



1



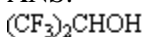
4



2

PTS: 1

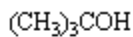
9. ANS:



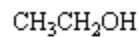
1



4



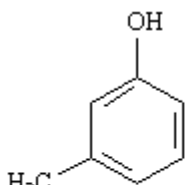
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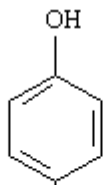
2

PTS: 1

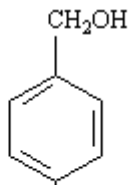
10. ANS:



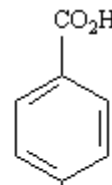
3



2



4



1

PTS: 1

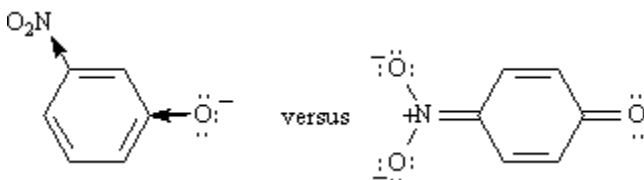
11. ANS:

Nonafluoro-2-methyl-2-propoxide anion is more stable than *tert*-butoxide anion because the electron-withdrawing fluoride atoms inductively delocalize the negative charge. Since nonafluoro-2-methyl-2-propoxide is more stable than *tert*-butoxide, it is a weaker base.

PTS: 1

12. ANS:

In *m*-nitrophenol, the *inductive effect* of the electron-withdrawing nitro group helps to stabilize the negative charge on oxygen. However, when the nitro group is *para* to the oxygen, direct conjugation of the negative charge on oxygen with the nitro group can occur. *p*-Nitrophenolate ion is, thus, more stable than *m*-nitrophenolate ion, and, as a result, forms more readily.



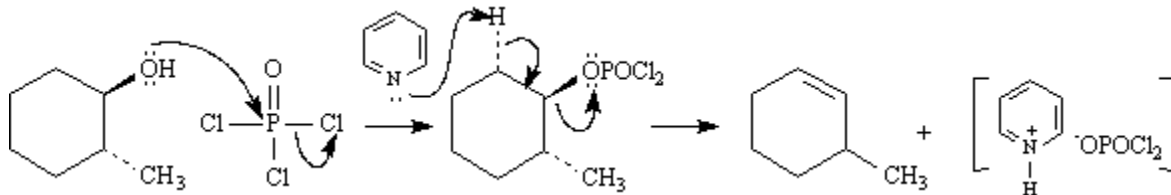
PTS: 1

13. ANS:

b

PTS: 1

14. ANS:



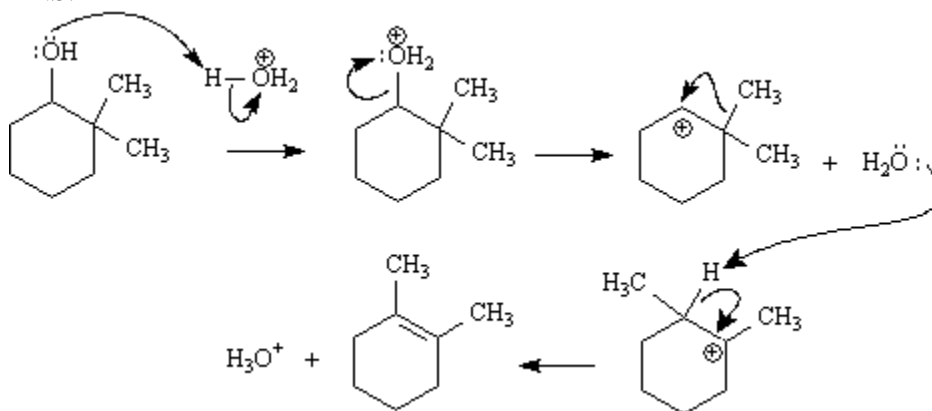
PTS: 1

15. ANS:

In E2 elimination, dehydration proceeds most readily when the two groups to be eliminated have a trans-diaxial relationship. In this compound, the only hydrogen with the proper geometric relationship to the -OH group is at C₆ so the major product of this reaction is 3-methylcyclohexene.

PTS: 1

16. ANS:



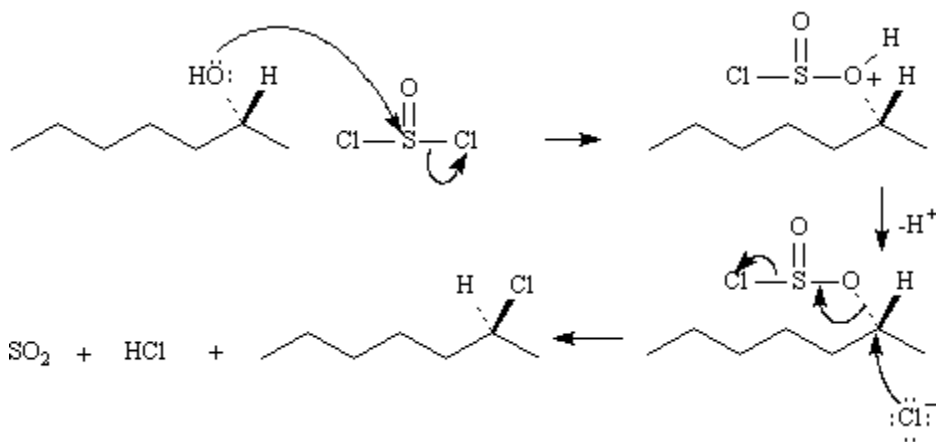
PTS: 1

17. ANS:

(R)-2-heptanol

PTS: 1

18. ANS:



PTS: 1

19. ANS:

d

PTS: 1

20. ANS:

A

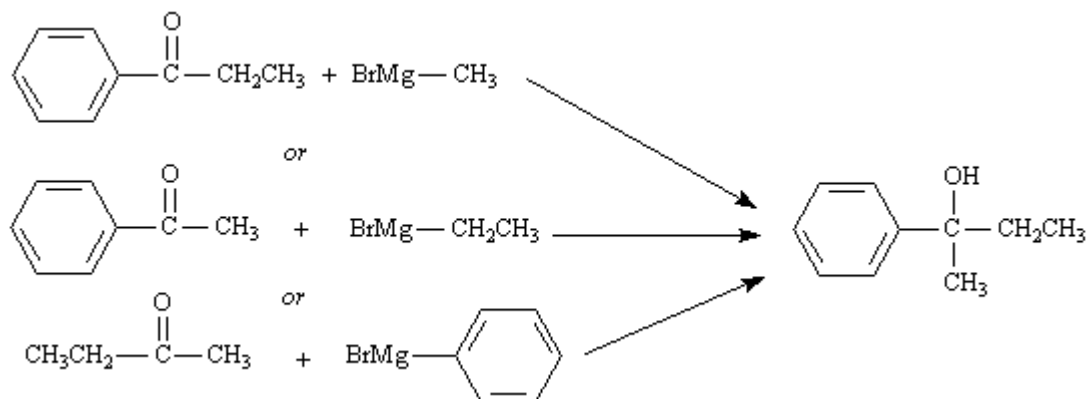
PTS: 1

21. ANS:

c

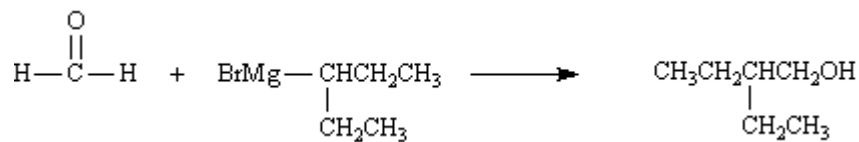
PTS: 1

22. ANS:

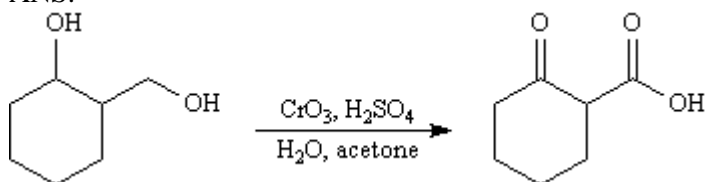


PTS: 1

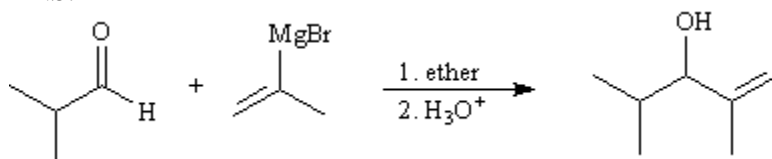
23. ANS:



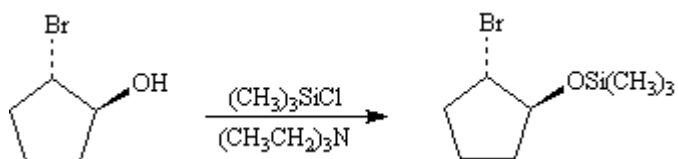
PTS: 1
24. ANS:



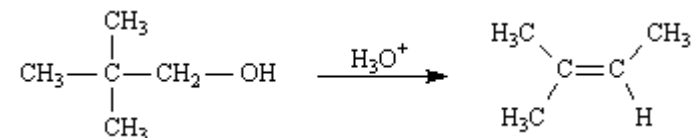
PTS: 1
25. ANS:



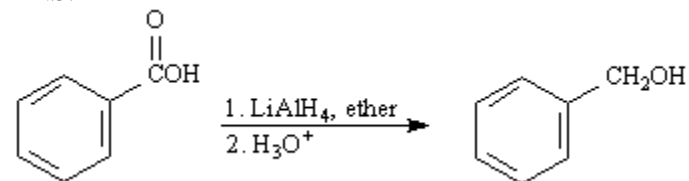
PTS: 1
26. ANS:



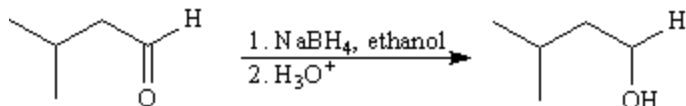
PTS: 1
27. ANS:



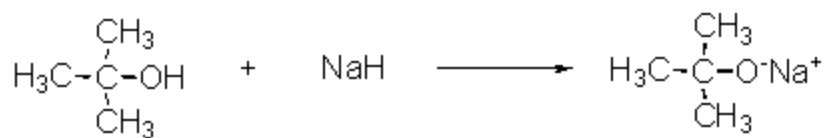
PTS: 1
28. ANS:



PTS: 1
29. ANS:

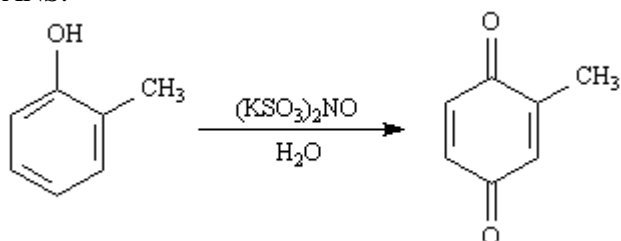


PTS: 1
30. ANS:



PTS: 1

31. ANS:



PTS: 1

32. ANS:

f

PTS: 1

33. ANS:

g

PTS: 1

34. ANS:

h

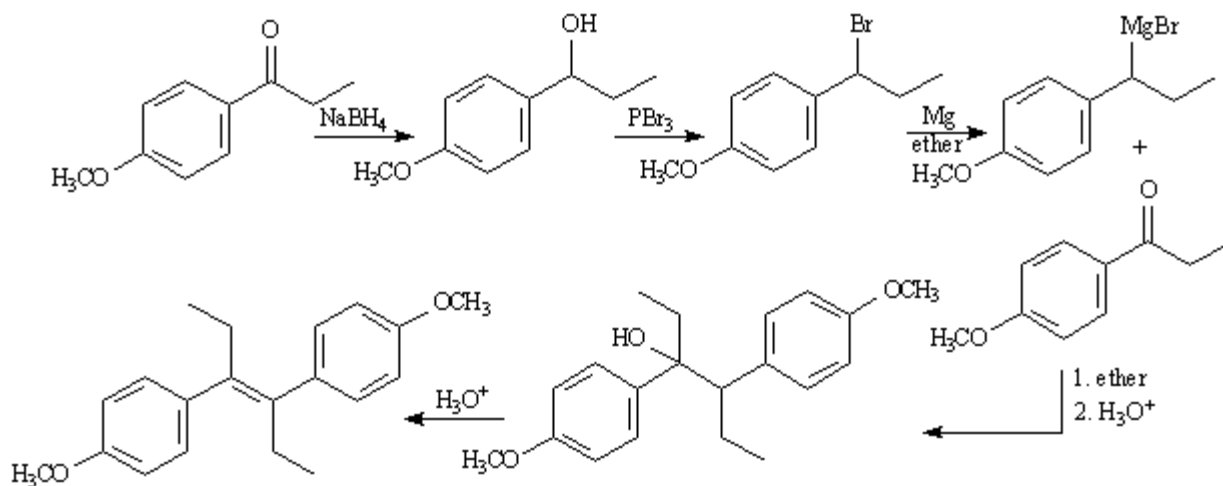
PTS: 1

35. ANS:

c

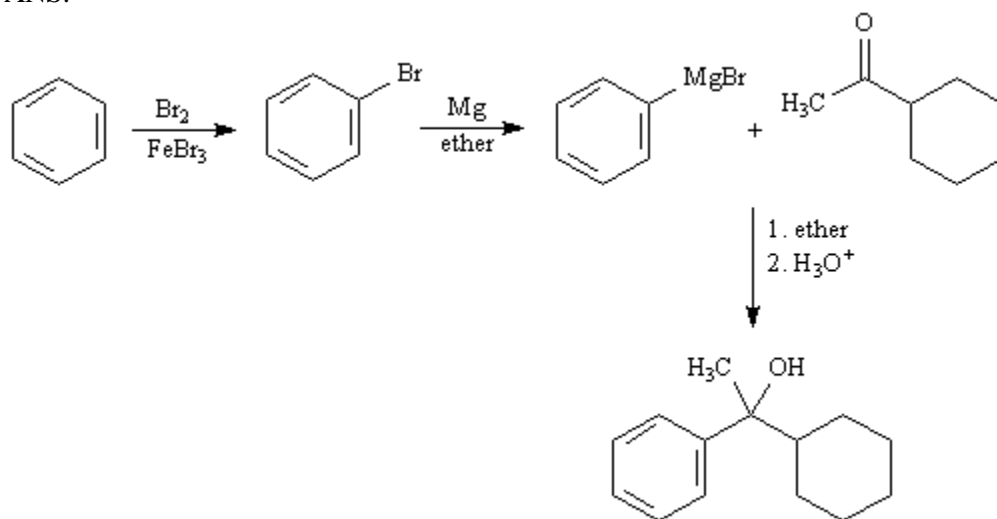
PTS: 1

36. ANS:



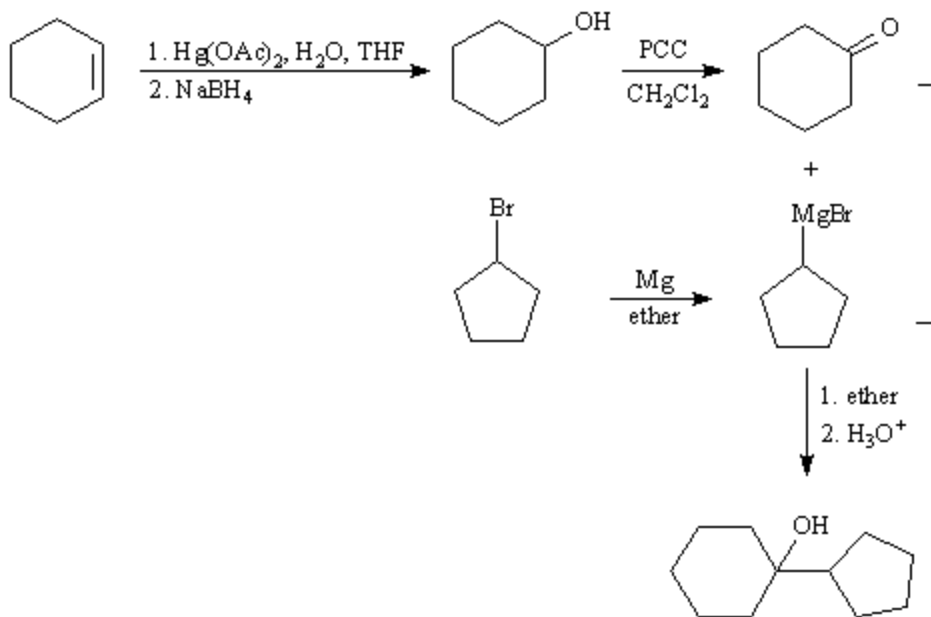
PTS: 1

37. ANS:



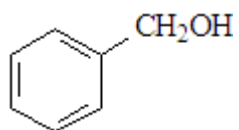
PTS: 1

38. ANS:



PTS: 1

39. ANS:
benzyl alcohol



PTS: 1

40. ANS:
1-ethylcyclohexanol

PTS: 1