

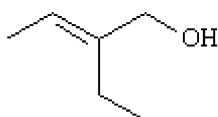
**Chem 2425 Review Test 2**

Draw structures corresponding to each of the given names.

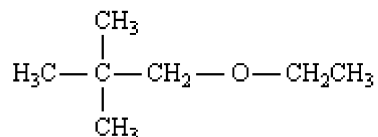
1. 2-phenyl-2-propanol
2. 2, 4, 6-trinitrophenol
3. tetrahydrofuran
4. allyl benzyl ether
5. diethyl ether
6. *trans*-3-isopropylcyclohexanecarbaldehyde

Provide proper IUPAC names.

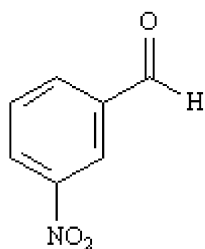
7. Name:



8. Name:



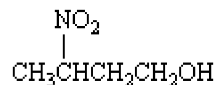
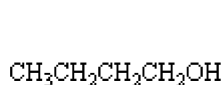
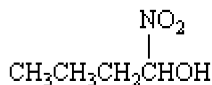
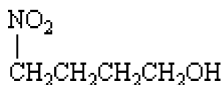
9. Name:



10. Name:



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.



11.        \_\_\_\_\_                                        \_\_\_\_\_                                        \_\_\_\_\_                                        \_\_\_\_\_

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

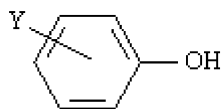
$\text{p}K_a$ s of Some Phenols

Y

$\text{p}K_a$

-H

9.89



*m*-NO<sub>2</sub>

8.28

*p*-NO<sub>2</sub>

7.17

*m*-OCH<sub>3</sub>

9.65

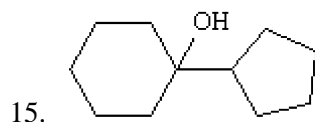
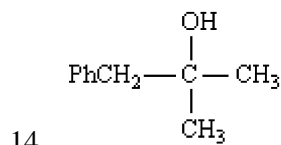
*p*-OCH<sub>3</sub>

10.21

12. The *weakest* acid in the table is:

13. How do you account for the difference in acidity between *meta* and *para*-nitrophenol?

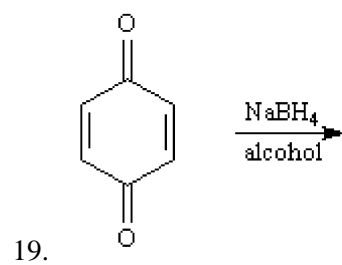
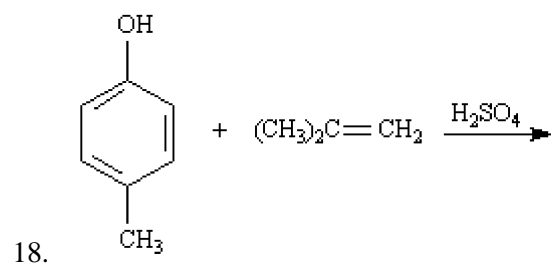
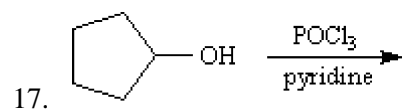
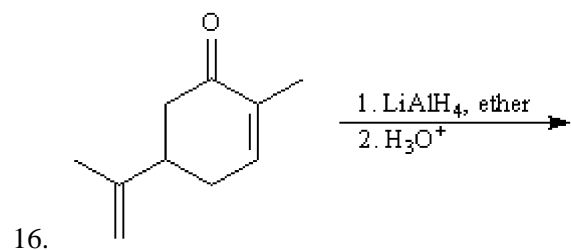
A highly useful and general method for the synthesis of alcohols is the addition of Grignard reagents to carbonyl compounds. Show what Grignard reagent and what carbonyl compound you would start with to prepare each alcohol below. List all possibilities.



Name: \_\_\_\_\_

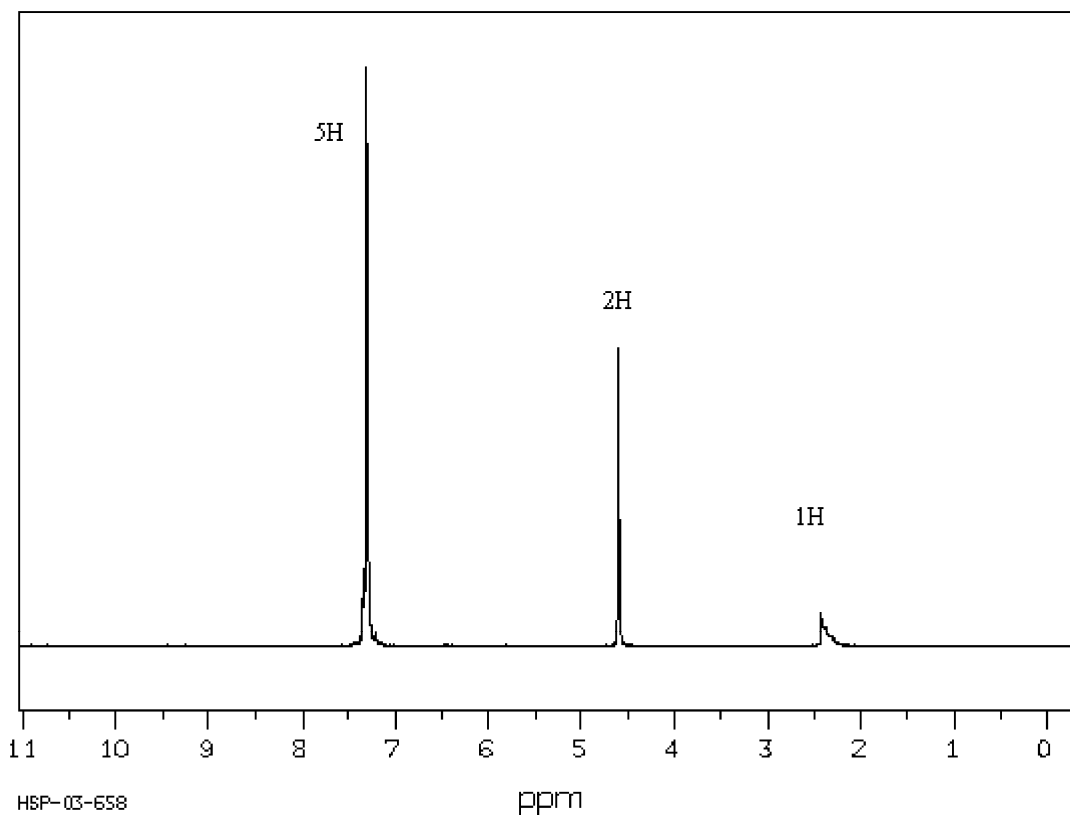
ID: A

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



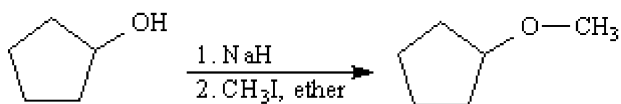
Propose structures for alcohols that have the following  $^1\text{H}$  NMR spectra.

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



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

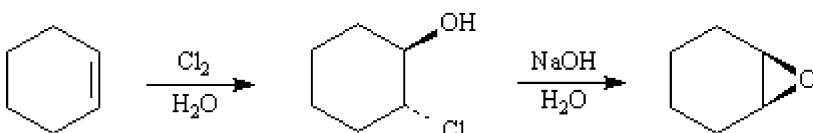
Consider the reaction below to answer the following question(s).



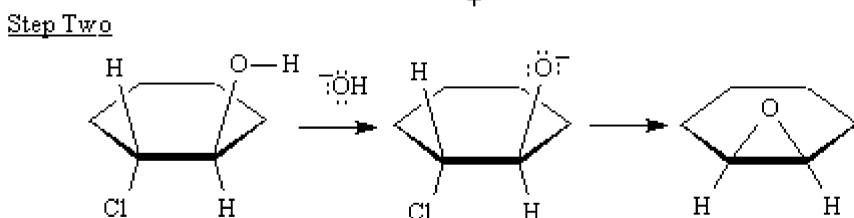
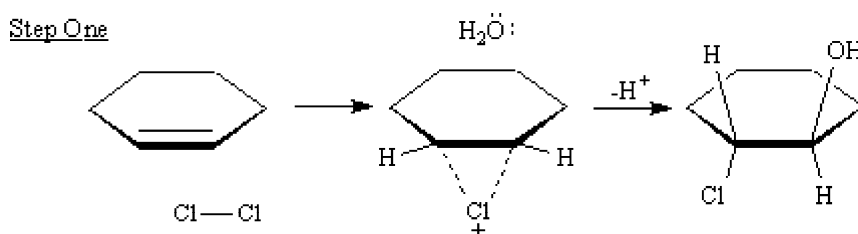
21. Mechanistically, the Williamson ether synthesis outlined above is:
- an  $\text{E1}$  process
  - an  $\text{S}_{\text{N}}1$  process
  - an  $\text{E2}$  process
  - an  $\text{S}_{\text{N}}2$  process
22. Alternatively, cyclopentyl methyl ether may be synthesized from cyclopentene. Outline a synthesis of cyclopentyl methyl ether from cyclopentene.

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

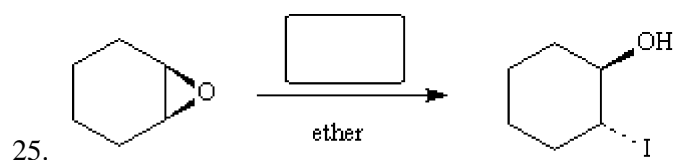
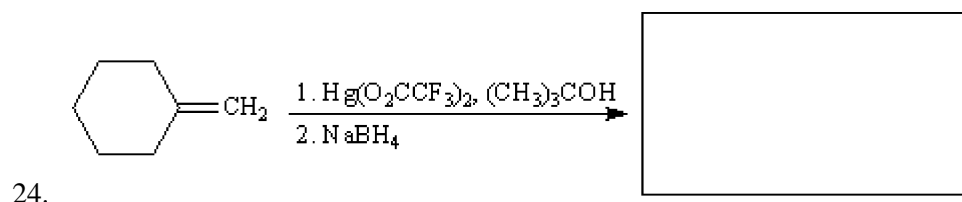
Epoxides are synthesized industrially in one step by silver oxide air oxidation of ethylene and on a laboratory scale in one step by treating an alkene with *m*-chloroperoxybenzoic acid. An alternative two step process converts alkenes to halohydrins, which are converted by treatment with base to epoxides.

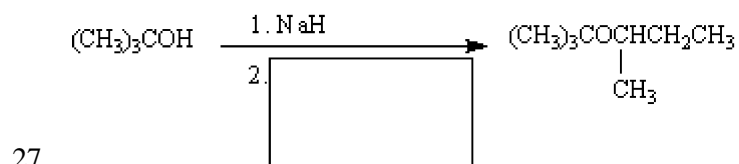
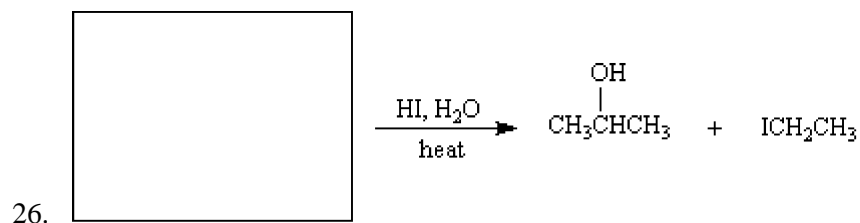


23. Show electron flow with arrows on the structures provided below for each step in the above transformation.

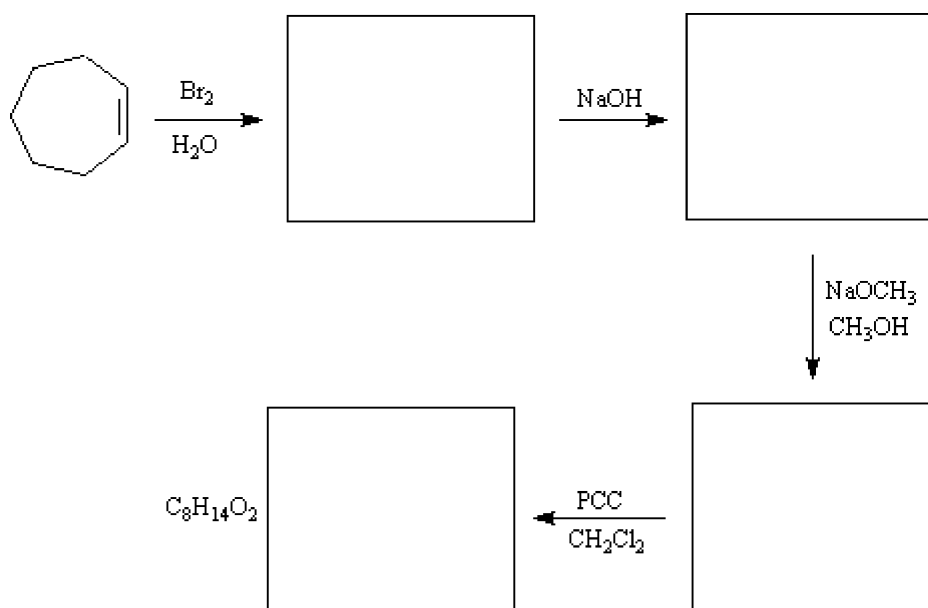


Propose structure(s) for the starting material(s), reagent(s), or major organic product(s) of the following reactions or sequences of reactions. Show all relevant stereochemistry.

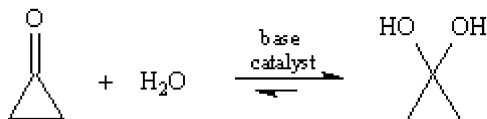




28. Complete the synthetic sequence below by drawing the structures of the reaction in the boxes provided.



Consider the reaction below to answer the following question(s):

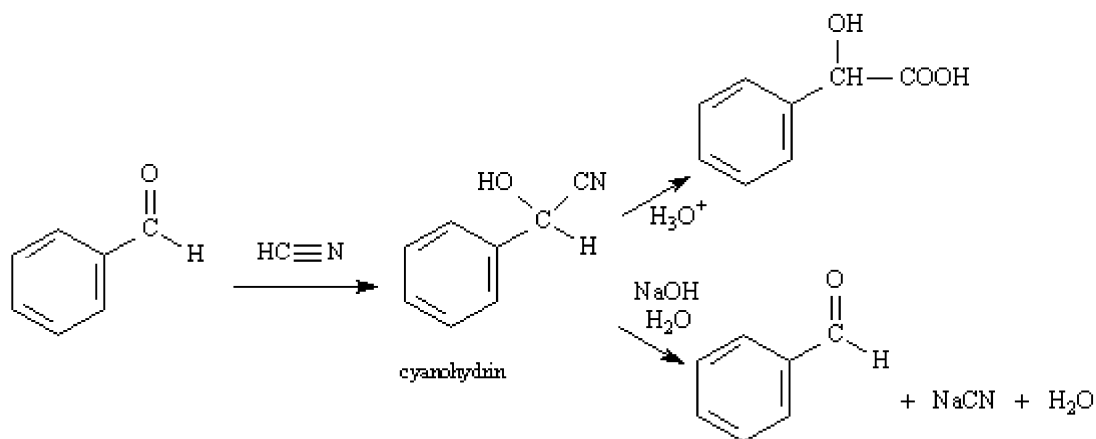


29. The substance formed on addition of water to an aldehyde or ketone is called a hydrate or a/an:

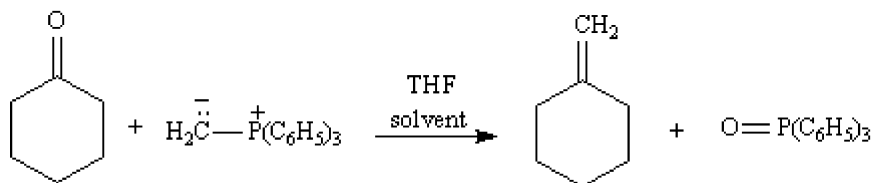
- vicinal diol
- geminal diol
- acetal
- ketal

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

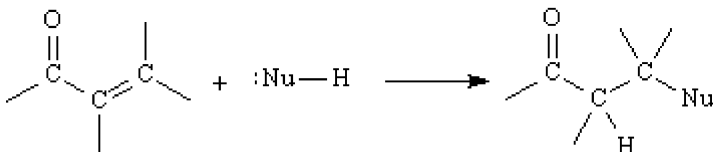
Cyanohydrins are important intermediates in the synthesis of  $\alpha$ -hydroxycarboxylic acids from ketones and aldehydes. The nitrile functional group can be hydrolyzed by aqueous acid to yield a carboxylic acid. Nitriles can also be hydrolyzed to carboxylic acids using aqueous base. Unfortunately, when a cyanohydrin is treated with aqueous base the original carbonyl compound is isolated.



30. The reaction of an aldehyde with hydrogen cyanide is an example of \_\_\_\_\_ reaction.
- a nucleophilic substitution
  - an electrophilic addition
  - an electrophilic substitution
  - a nucleophilic addition
31. In the Wittig reaction, a phosphorus ylide adds to a ketone or aldehyde to yield an alkene. Write the complete stepwise mechanism for the Wittig reaction shown below. Show all intermediate structures and all electron flow with arrows.

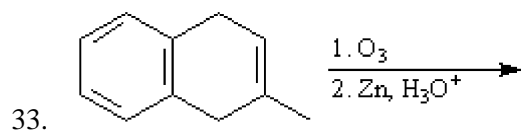


$\alpha,\beta$ -Unsaturated aldehydes and ketones can undergo reaction with nucleophiles at the  $\beta$  carbon, as shown below.

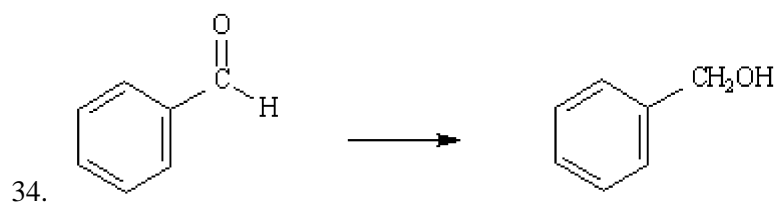


32. Draw a resonance form for the unsaturated carbonyl that accounts for this reactivity.

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



Choose the **BEST** reagent for carrying out each of the following conversions.



- $\text{NaBH}_4$ , ethanol
- $\text{CH}_2\text{PPh}_3$
- $\text{NaOH}, \text{H}_2\text{O}$
- All of the above

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

$\text{C}_7\text{H}_{14}\text{O}$

IR:  $1715 \text{ cm}^{-1}$

MS:  $\text{M}^+$  at  $m/z = 114$ ,  $\alpha$ -cleavage fragment at  $m/z = 71$ ,  
McLafferty rearrangement fragment at  $m/z = 86$ .

$^1\text{H NMR}$ :  $0.92 \delta$  (6H, triplet),  $1.59 \delta$  (4H, multiplet),  $2.36 \delta$  (4H, triplet)

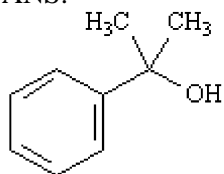
- What functional group is indicated by the IR data?
- Interpret the mass spectral data.



## Chem 2425 Review Test 2 Answer Section

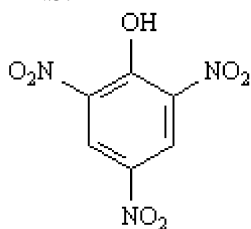
### SHORT ANSWER

1. ANS:



PTS: 1

2. ANS:



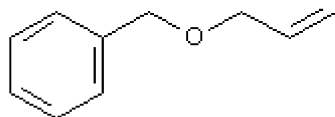
PTS: 1

3. ANS:



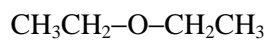
PTS: 1

4. ANS:



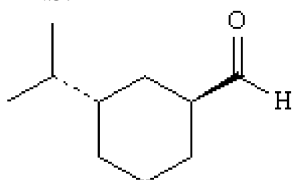
PTS: 1

5. ANS:



PTS: 1

6. ANS:



PTS: 1

7. ANS:  
(E)-2-ethylbut-2-en-1-ol

PTS: 1

8. ANS:  
1-ethoxy-2,2-dimethylpropane or ethyl neopentyl ether

PTS: 1

9. ANS:  
*m*-nitrobenzaldehyde

PTS: 1

10. ANS:  
4,8-dimethyl-7-nonen-2-one

PTS: 1

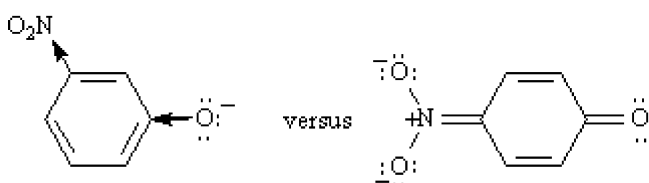
11. ANS:
- |  |   |   |   |
|--|---|---|---|
| $\begin{array}{c} \text{NO}_2 \\   \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \end{array}$ | $\begin{array}{c} \text{NO}_2 \\   \\ \text{CH}_3\text{CH}_3\text{CH}_2\text{CHOH} \end{array}$ | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ | $\begin{array}{c} \text{NO}_2 \\   \\ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{OH} \end{array}$ |
| <u>3</u>   | <u>1</u>  | <u>4</u>  | <u>2</u>  |

PTS: 1

12. ANS:  
*p*-methoxyphenol

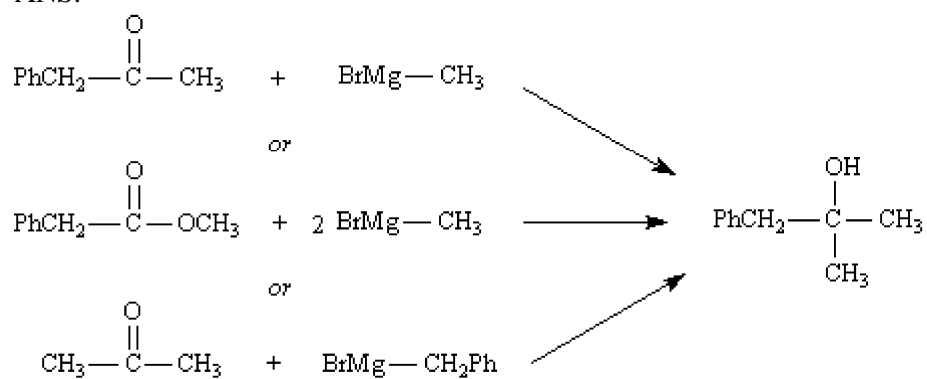
PTS: 1

13. 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.



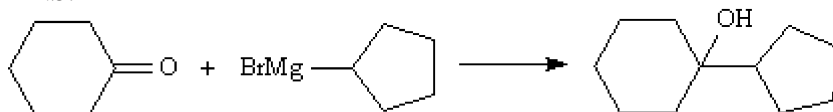
PTS: 1

14. ANS:



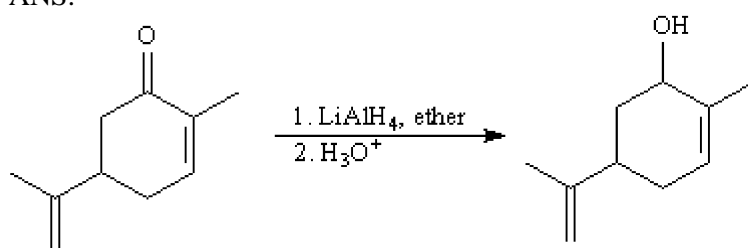
PTS: 1

15. ANS:



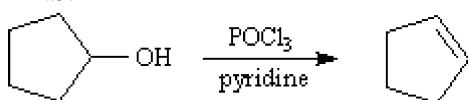
PTS: 1

16. ANS:



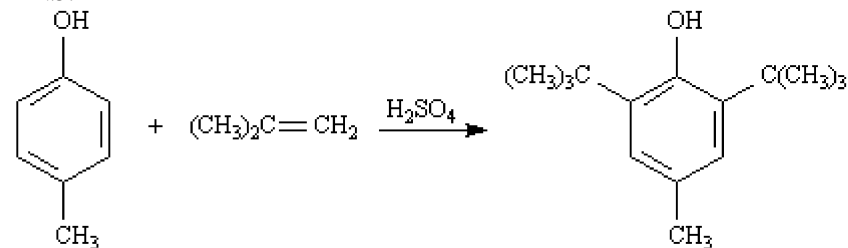
PTS: 1

17. ANS:



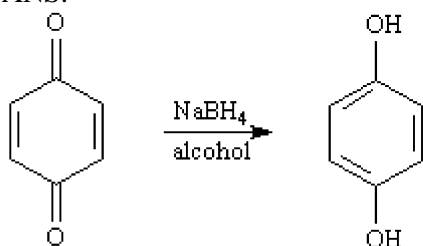
PTS: 1

18. ANS:



PTS: 1

19. ANS:



PTS: 1

20. ANS:

benzyl alcohol,  $\text{PhCH}_2\text{OH}$ 

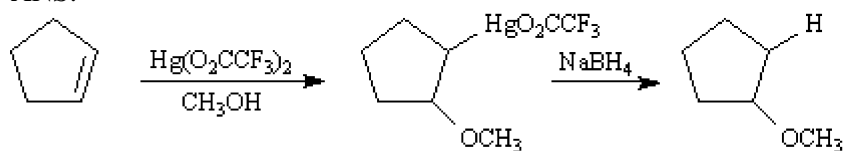
PTS: 1

21. ANS:

d

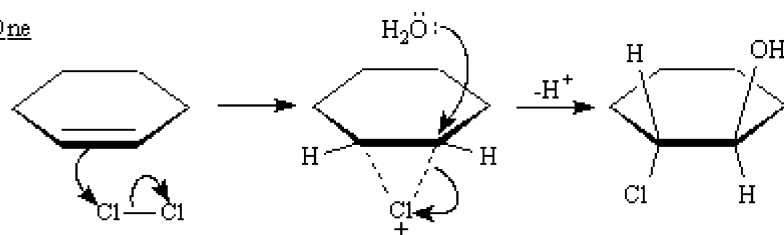
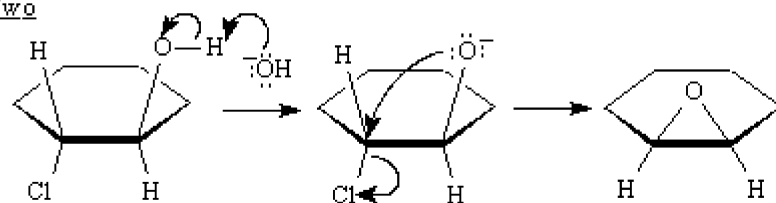
PTS: 1

22. ANS:



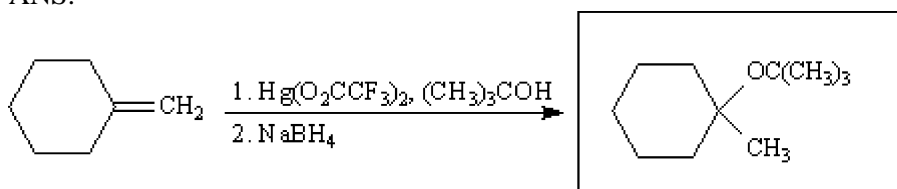
PTS: 1

23. ANS:

Step OneStep Two

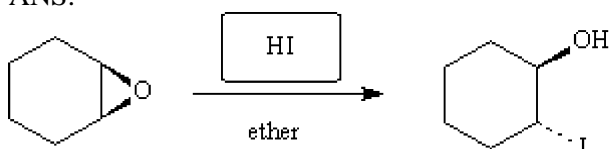
PTS: 1

24. ANS:



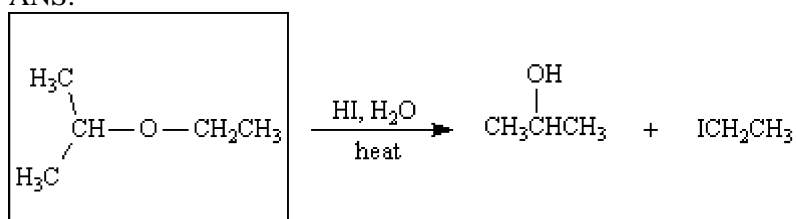
PTS: 1

25. ANS:



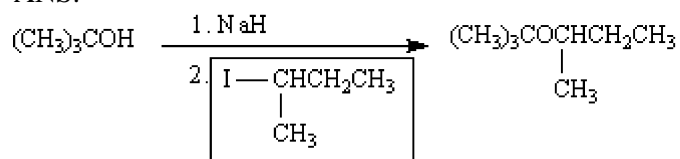
PTS: 1

26. ANS:



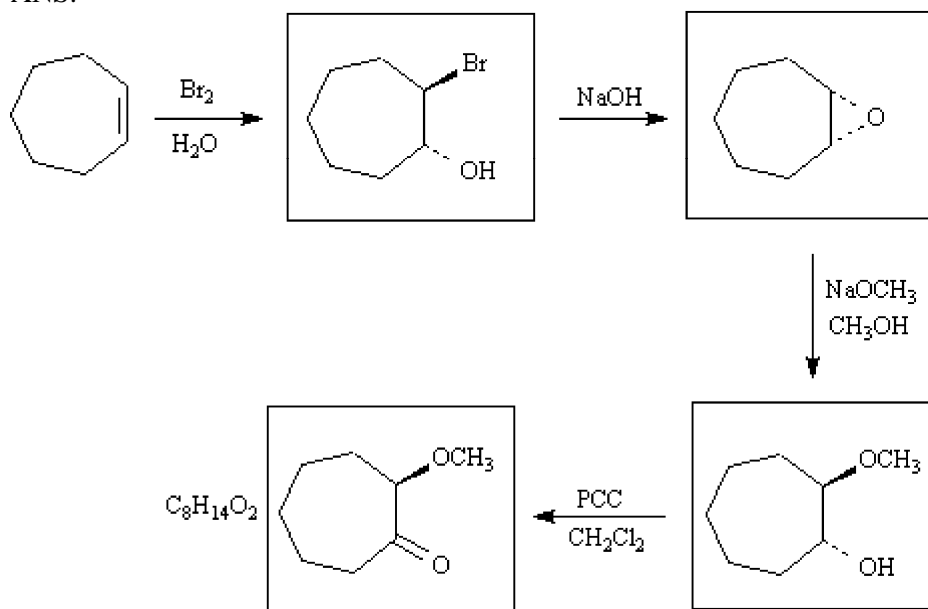
PTS: 1

27. ANS:



PTS: 1

28. ANS:



PTS: 1

29. ANS:

b

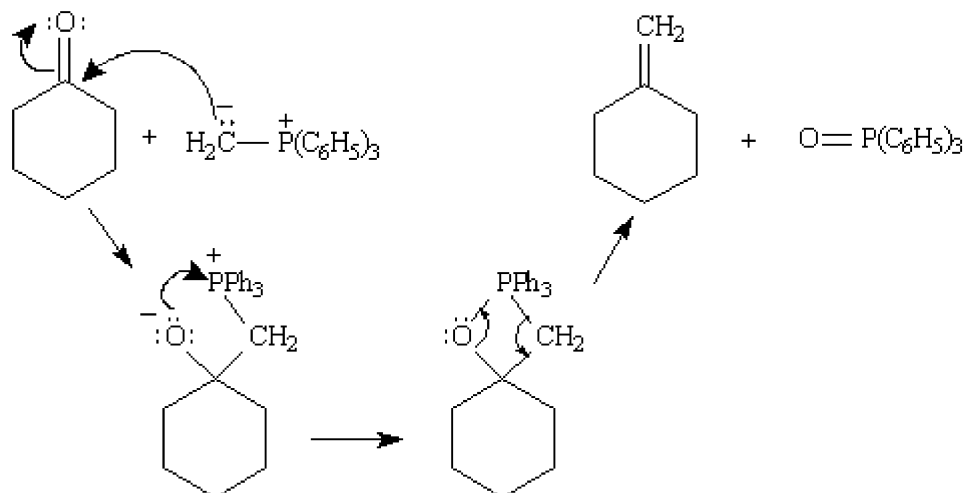
PTS: 1

30. ANS:

d

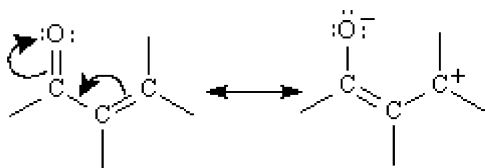
PTS: 1

31. ANS:



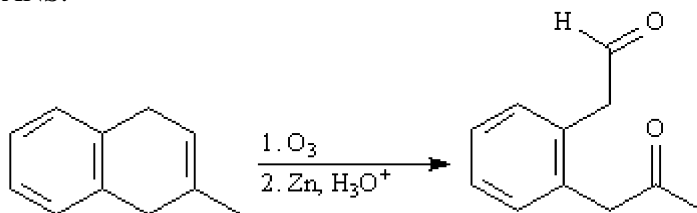
PTS: 1

32. ANS:



PTS: 1

33. ANS:



PTS: 1

34. ANS:

a

PTS: 1

35. ANS:

Absorption at  $1715\text{ cm}^{-1}$  in the infrared spectrum indicates the presence of a carbonyl compound, most probably a ketone.

PTS: 1

36. ANS:

A fragment at  $m/z = 71$  indicates a loss of 43, or a propyl group, from  $\alpha$ -cleavage. A fragment at  $m/z = 86$  indicates a loss of 28, or ethylene, from McLafferty rearrangement (transfer of a hydrogen atom from the gamma carbon to the carbonyl oxygen with concomitant breaking of the bond between the alpha and beta carbon).

PTS: 1