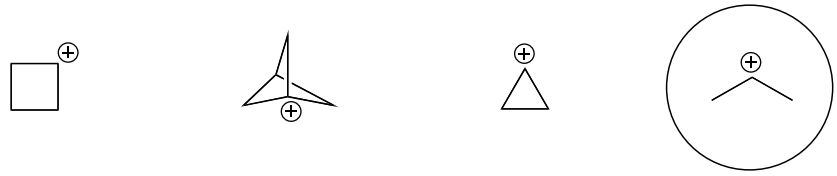
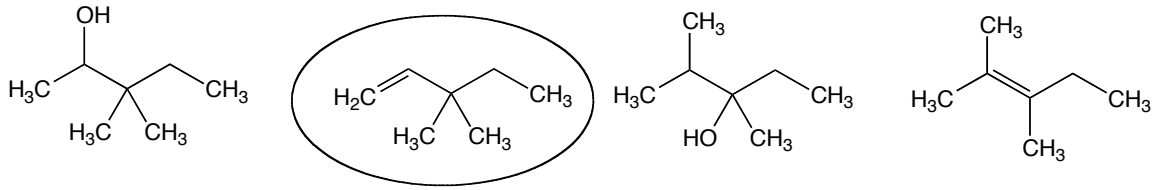
1. Molecules that have internal mirror planes are always: *Circle the correct answer*

chiral **achiral** meso enantiomers

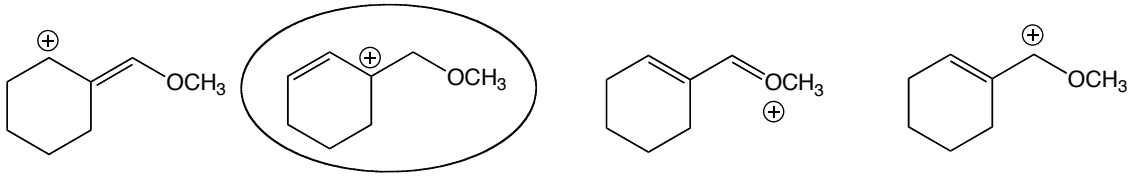
2. The most stable carbocation shown below is:



3. The major product formed when 2-bromo-3,3-dimethyl-pentane is reacted with aqueous NaOH is:



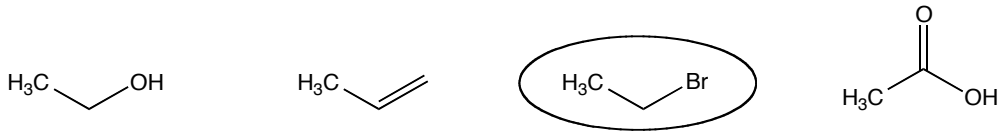
4. Which of the following carbocations is **not** a resonance structure of the other three?



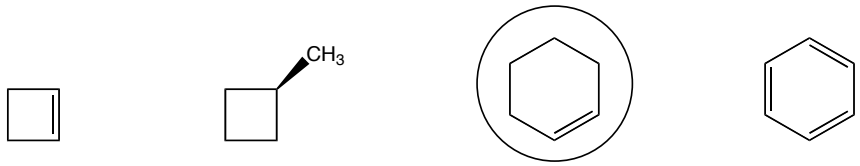
5. Circle the strongest acid from the list below.

water ammonia methane hydroxide

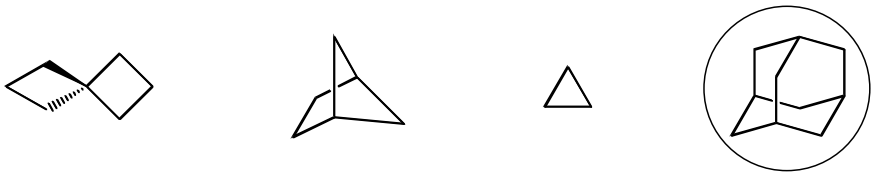
6. Which of the following can be reacted with sodium ethoxide to form diethyl ether?



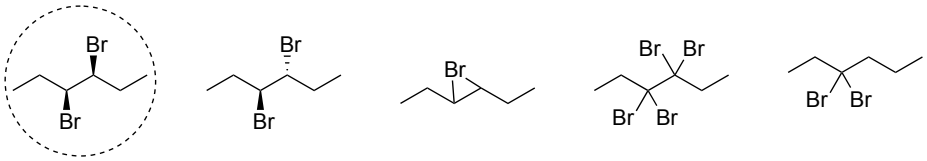
7. Which of the following compounds has 3 signals in its ^{13}C NMR spectrum?



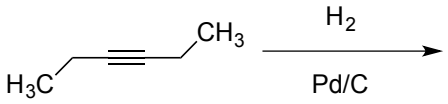
8. Circle the compound below that contains the least ring strain.

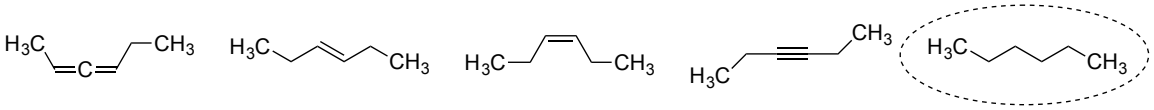


9. Circle the product of Br_2 addition (Br_2, CH_2Cl_2) to *cis*-3-hexene.



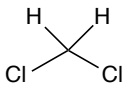
10. Circle the product formed when 3-hexyne is hydrogenated with H_2 (g) using a palladium catalyst on graphite (reaction shown below).



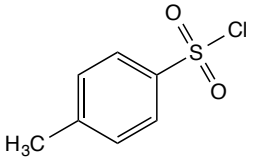


11. Provide clear structural drawings for the following compounds.

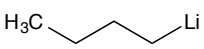
a) methylene chloride:



b) *para*-toluene sulfonyl chloride (tosyl chloride):



c) butyllithium:

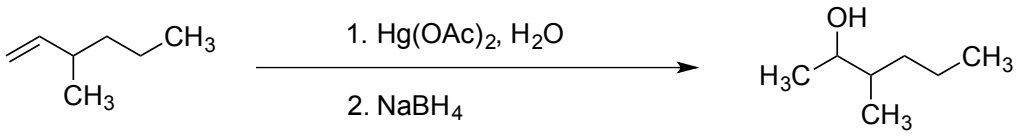


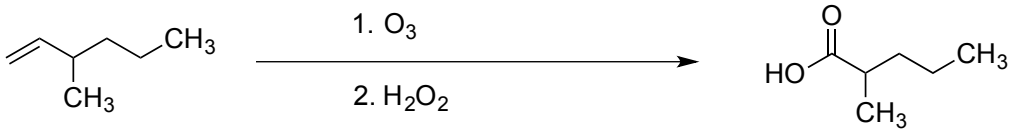
12. Briefly explain why rotation around the central bond of 1,3-butadiene requires greater energy than rotation around the central bond of butane. *Both molecules are shown below with arrows pointing to the bonds undergoing rotation.*

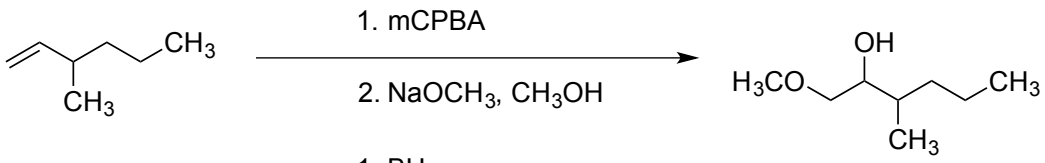
1,3-butadiene butane

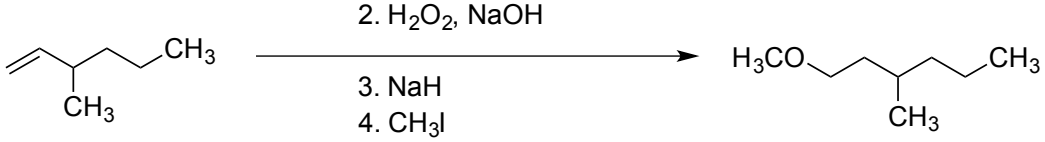
The diene is conjugated, and rotation around the central bond disrupts the overlap between the two indicated pi-bonds and causes loss of conjugative stabilization.

13. Supply missing reagents (over the arrows) and compound structures (in the boxes) to complete the following transformations. *Multiple reagents/steps may be needed. Be sure to pay attention to stereochemistry.*

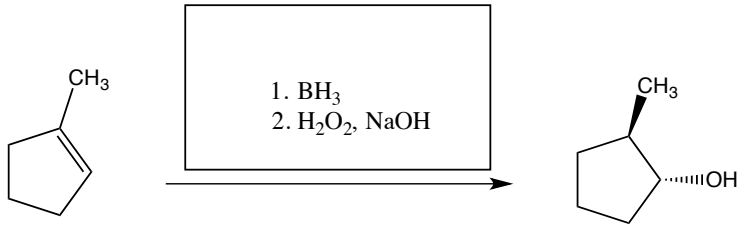
d) 

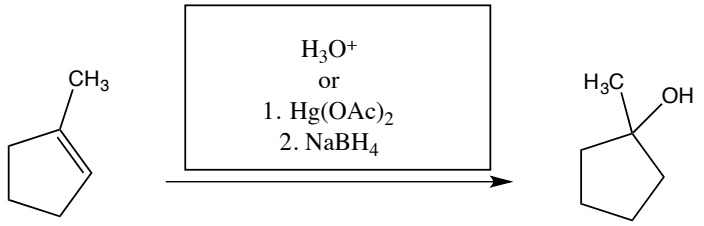
e) 

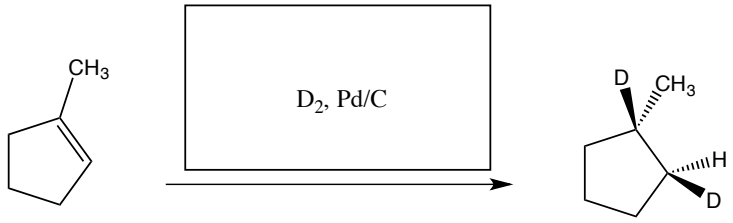
f) 

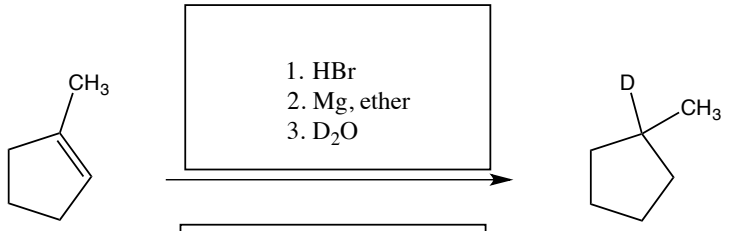
g) 

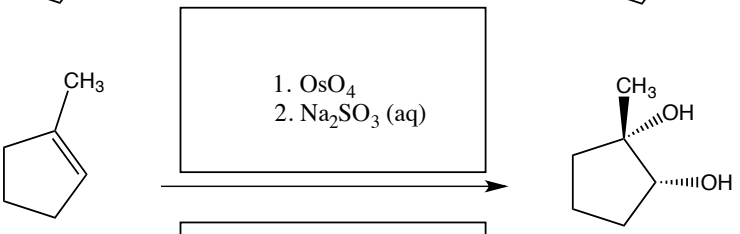
14. Starting with 1-methylcyclopentene, provide the missing reagent(s) to carry out each of the following reactions. *Multiple steps may be needed*.

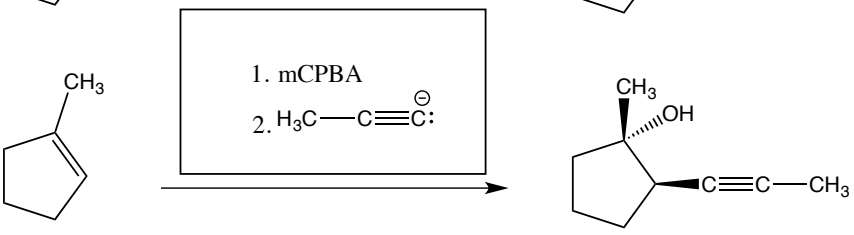
a) 

b) 

c) 

d) 

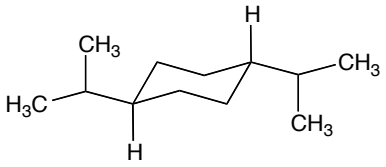
e) 

f) 

15. You have a sample of a chiral compound. If the optical rotation of the (+)-enantiomer is reported at +50.0° and your sample has an optical rotation of +20.0°, what percent of your sample is the (+)-enantiomer?

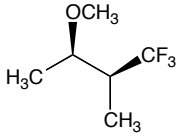
70% (+)-enantiomer

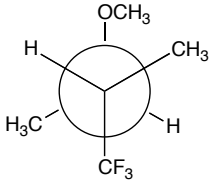
16. Draw *trans*-1,4-diisopropylcyclohexane in its lowest-energy conformation.



17. Classify each pair of compounds as **structural isomers, enantiomers, diastereomers, or identical**.

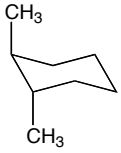
a)

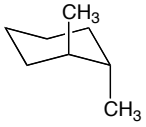




Answer: ***identical***

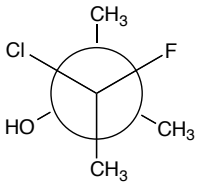
b)

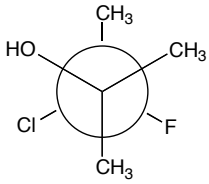




Answer: ***identical***

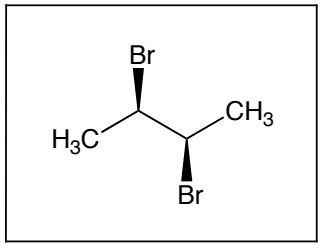
c)





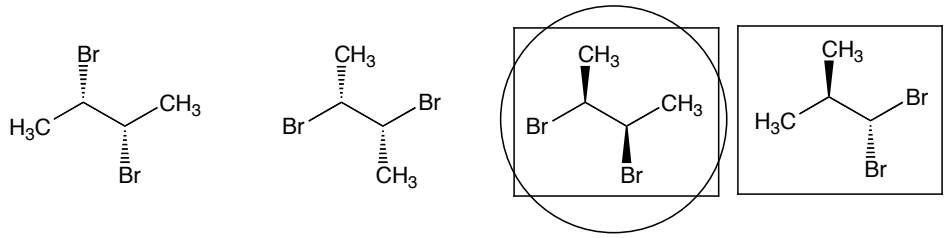
Answer: ***identical***

18. a) Provide a name for the compound (chemical formula $C_4H_8Br_2$) that is shown in the box below. Remember to assign configuration to all stereocenters

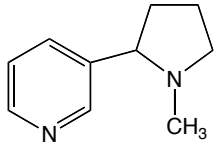


Name____**(2*R*,3*R*)-2,3-dibromobutane** _____

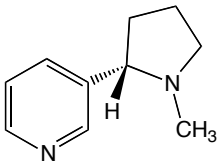
b) Four structures with the formula $C_4H_8Br_2$ are shown below. Circle each compound that is a diastereomer of the compound in the box above. Put a square around each achiral compound.



19. The structure of nicotine, a highly addictive substance found in tobacco, is shown below.



a) Draw nicotine with its stereocenter in the naturally occurring (*S*)-configuration.



b) Is nicotine more likely to act as an acid or a base? Explain your answer.

Nicotine is a base – amines are basic using their lone pair of electrons. Note: Nicotine contains 2 amines, and both are basic but the sp^3-hybridized nitrogen atom is more basic.

20. An unknown compound gives the following spectral data:

Mass spec: Molecular ion region has the following series of 4 peaks (values are given as mass/charge ratios with relative intensities as percentages): 212 (100%), 213 (10%), 214 (97%), 215 (9%).

IR: multiple absorbances between 3080-2900 cm^{-1}, strong absorbance at 1692 cm^{-1}, weaker absorbance at 1588 cm^{-1}.

^{1}H NMR in $CDCl_3$: doublet at 7.83 ppm (integration = 1), doublet at 7.60 ppm (integration = 1), quartet at 2.97 ppm (integration = 1), triplet at 1.22 ppm (integration = 1.5).

a) What information can you deduce from the mass spectral data?

MW = 212/214 (Br isotopes)
M+2 peak indicates: 1 bromine atom is present
M+1 peak indicates approx. 9 carbon atoms

b) What information can you deduce from the IR data?

3080-2900: C-H absorptions, both sp2 and sp3 carbon
1692: a carbonyl (non-conjugated amide or conjugated carbonyl of some other type)
1588: likely a benzene ring (or maybe a highly conjugated C=C)

c) What information can you deduce from the NMR data?

Integration suggests 9 hydrogen atoms

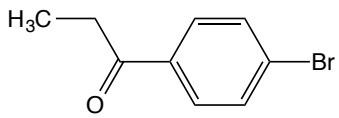
Four benzene hydrogens (signals at 7.83 ppm and 7.60 ppm), and the ring must be para-disubstituted since there are only two signals and they are doublets

Signals at 2.97 ppm and 1.22 ppm suggest an ethyl group

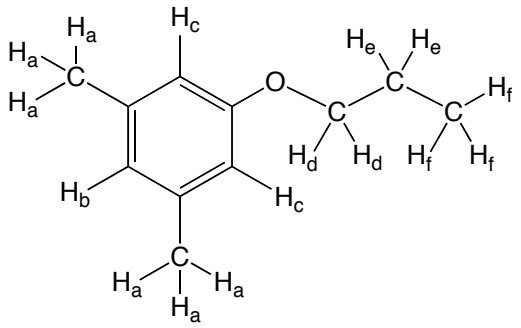
The methylene at 2.97 ppm is attached to something reasonably electronegative

d) What is the identity of the unknown compound?

The only structure consistent with all the above data is:



21. On the drawing of the compound below, place a label on each hydrogen atom (showing that they are chemically equivalent or inequivalent), and complete the chart describing the compound's ^{1}H NMR spectrum (the methyl group hydrogens have been identified for you, please follow this format).



Signal	Integration	Multiplicity	Approximate Chemical Shift (δ)
H_a	6 Hydrogens	Singlet	2.1 ppm
H_b	***1 Hydrogen***	***triplet***	***7.0 ppm***
H_c	***2 Hydrogens***	***doublet***	***7.0 ppm***
H_d	***2 Hydrogens***	***triplet***	***4.0 ppm***
H_e	***2 Hydrogens***	***quartet of triplets (multiplet)***	***2.0 ppm***
H_f	***3 Hydrogens***	***triplet***	***1.0 ppm***

22. You calculate the energies (heats of formation) of two species in conformational equilibrium:

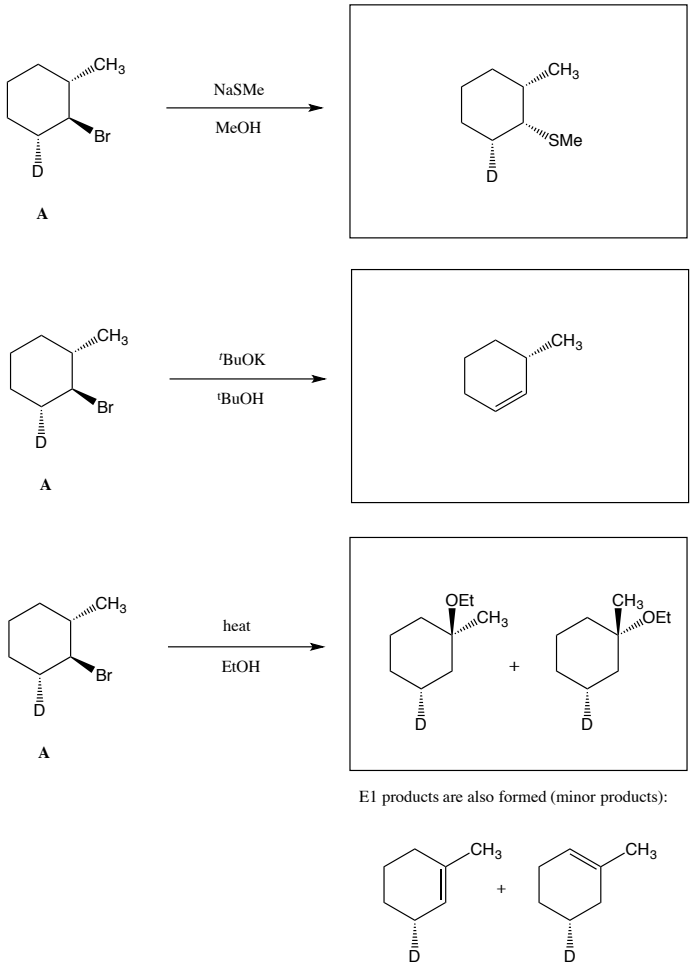
A ⇌ **B**

Calculated energies:
conformer **A**: –24.6 kcal/mol
conformer **B**: –23.3 kcal/mol

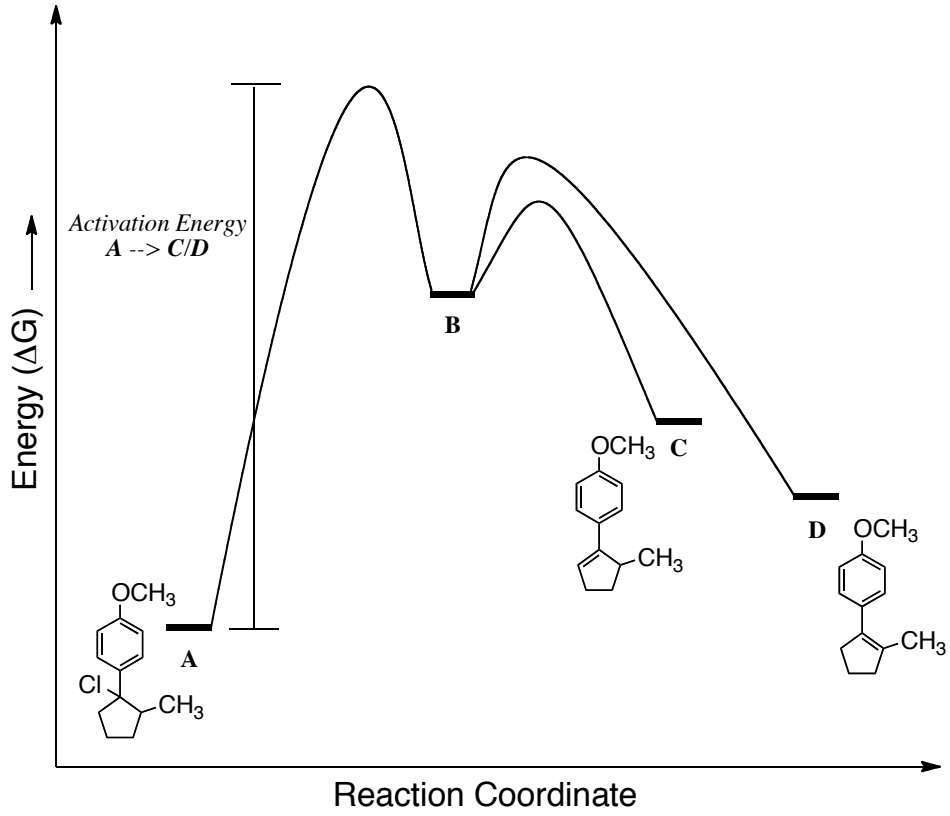
a) What is the approximate equilibrium constant (k) at 25 °C for the equation shown above? *Circle your answer from the choices provided below*.

k = 10 **k = 1** **k = 0** **k = 0.1** **k = 0.01**

23. Identify the major product produced when **A** is treated with the following reagents. Be sure to pay close attention to stereochemistry where appropriate.



24. Consider the following E1 reaction coordinate diagram:



a) On the above diagram, label the activation energy for the overall reaction of **A** → **C/D**

b) Is the reaction from **A** → **C/D** endergonic or exergonic?

endergonic

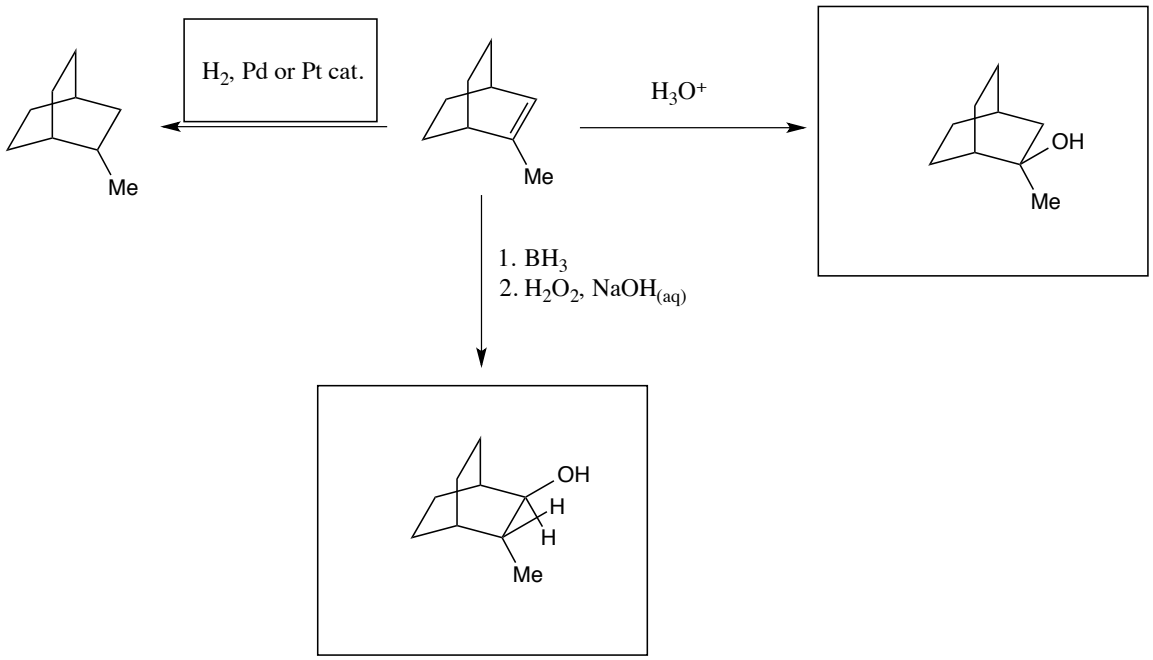
c) If this reaction proceeds under thermodynamic control, at the end of the reaction what species would be in the highest amount, **A**, **B**, **C**, or **D**?

A

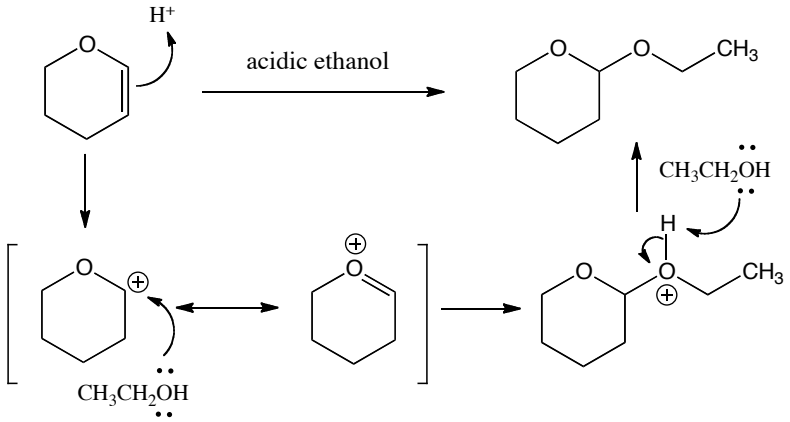
d) If this reaction proceeds under thermodynamic control, at the end of the reaction what species would be in the smallest amount, **A**, **B**, **C**, or **D**?

B

25. In the boxes provided, fill in the missing reagents and compound structures to complete the synthetic sequences.



26. Provide a complete mechanism for the following transformation. *Draw all relevant intermediates, including resonance structures.*



27. Heating of the secondary iodide shown below in acetic acid leads to the two indicated products (these are the major products). Provide a mechanism for the formation of each product. *Be sure your mechanism describes the formation of both observed products. Acetic acid is both a reagent in the reaction and the solvent.*