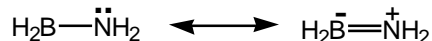
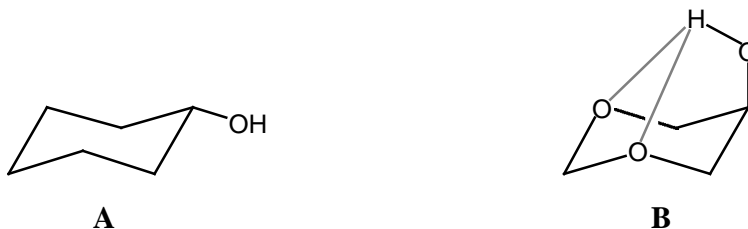


ANSWERS TO REVIEW PROBLEM SET
CH241-2001F

- [1] (a) The boron-nitrogen bond has some double bond character due to overlap of the filled orbital on nitrogen with the empty orbital on boron. Hence it is more difficult to rotate about this bond than the carbon-carbon bond in ethane.

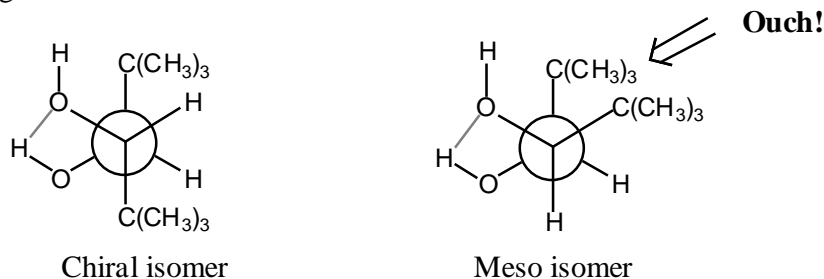


- (b) In **A** the hydroxy group occupies the more stable equatorial position for the usual steric reasons. In **B**, however, intramolecular hydrogen bonding stabilizes the axial hydroxy group.

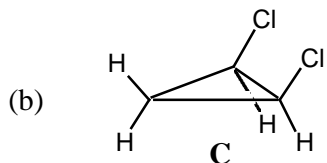
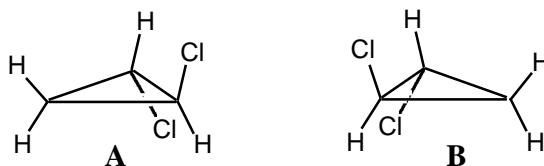


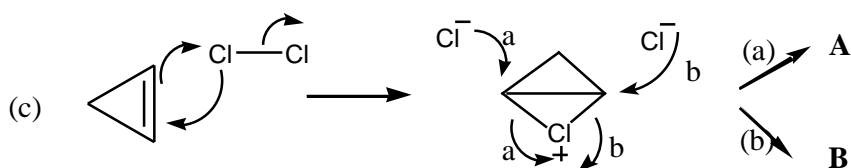
- (c) See problem # 11.17 on page 490 in text.

- (d) The chiral isomer is stabilized by intramolecular hydrogen bonding between the two gauche OH groups. Such an arrangement also keeps the bulky *tert*-butyl groups farther apart as they are anti to each other. In the meso isomer, however, putting the two OH groups gauche to each other also results in the *tert*-butyl groups becoming involved in sterically unfavorable gauche interactions

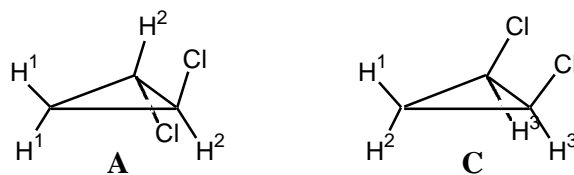


- [2] (a) **A** and **B** are enantiomers.

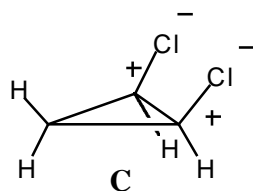




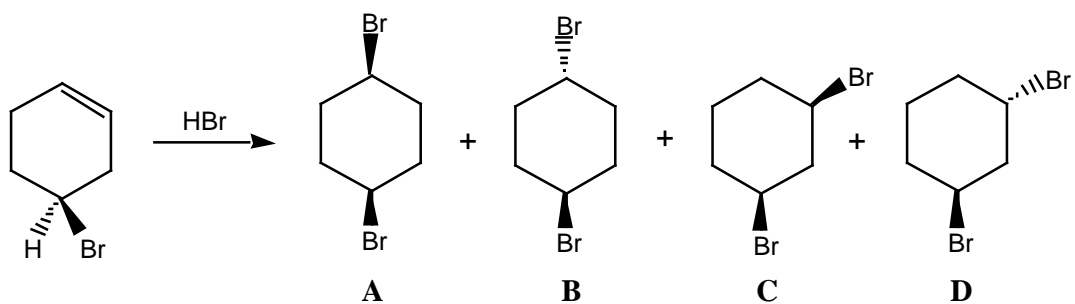
(d) As **A** and **B** are enantiomers they cannot be distinguished by ^1H NMR spectroscopy unless special chiral conditions are employed. **A** and **C**, however, are diastereomers which are readily distinguished. The ^1H NMR of **C** will show three different signals whereas **A** will show only two. Also there will be noticeable differences in J values as well with the cis coupling being larger than the trans.



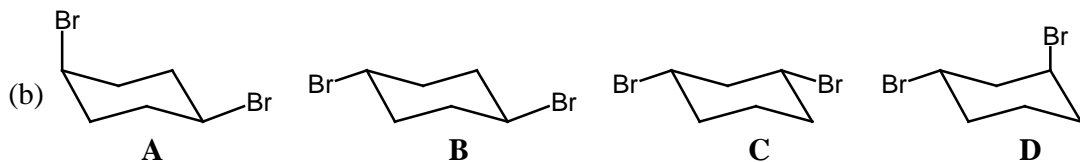
(e) **A** and **B**, being enantiomers of each other, are equally stable. **C** is the least stable of the three because: (1) the large chlorine atoms are eclipsing each other and (2) the negative ends of the carbon-chlorine dipoles are too close and hence destabilizing.



[3] The reaction gives four products as shown below.

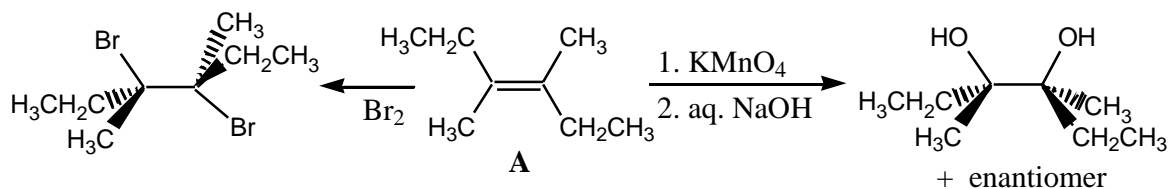


(a) S

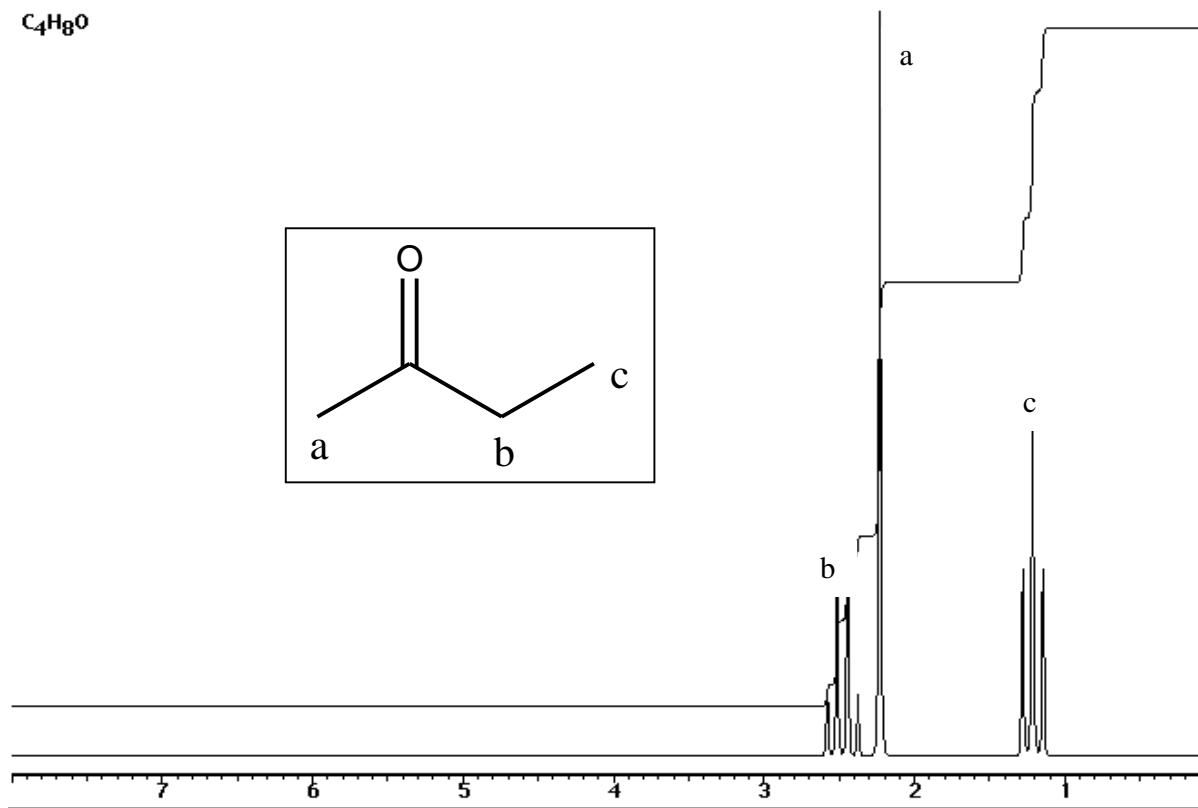


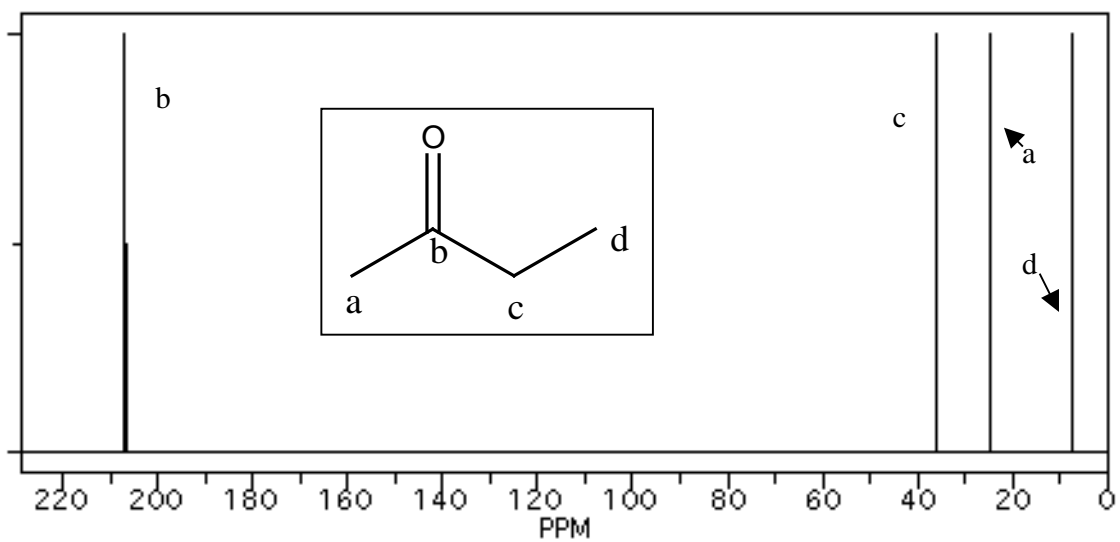
- (c) **A**, **B**, and **C** are achiral. **A** and **B** have a plane of symmetry that goes through the two bromine atoms. **C**, a meso compound, has a plane of symmetry that goes between the two bromine atoms. **D** is chiral.
- (d) **A** and **B** are diastereomers, as are **C** and **D**. Also, both **A** and **B** are structural isomers of **C** and **D**.

[4] The molecular formula of **A** indicates one degree of unsaturation. The fact that **A** reacts with bromine, KMnO_4 , and ozone suggests that the degree of unsaturation in **A** is due to a double bond. Furthermore, the fact that a single compound is produced upon ozonolysis indicates that both ends of the double bond in **A** are identically substituted! Also, the product of ozonolysis is a ketone not an aldehyde because the aldehyde proton signal (9 - 10 ppm) is missing in the ^1H NMR spectrum. Analysis of the chemical shifts, integrals, and splitting patterns in the ^1H NMR suggest that the ketone is 2-butanone (see assignments on spectrum). This is further confirmed by the ^{13}C NMR spectrum which shows four different carbons with the expected chemical shifts. Thus, **A** is as shown below. The *E* geometry is required by the stereochemical outcome of the bromination and KMnO_4 reactions.

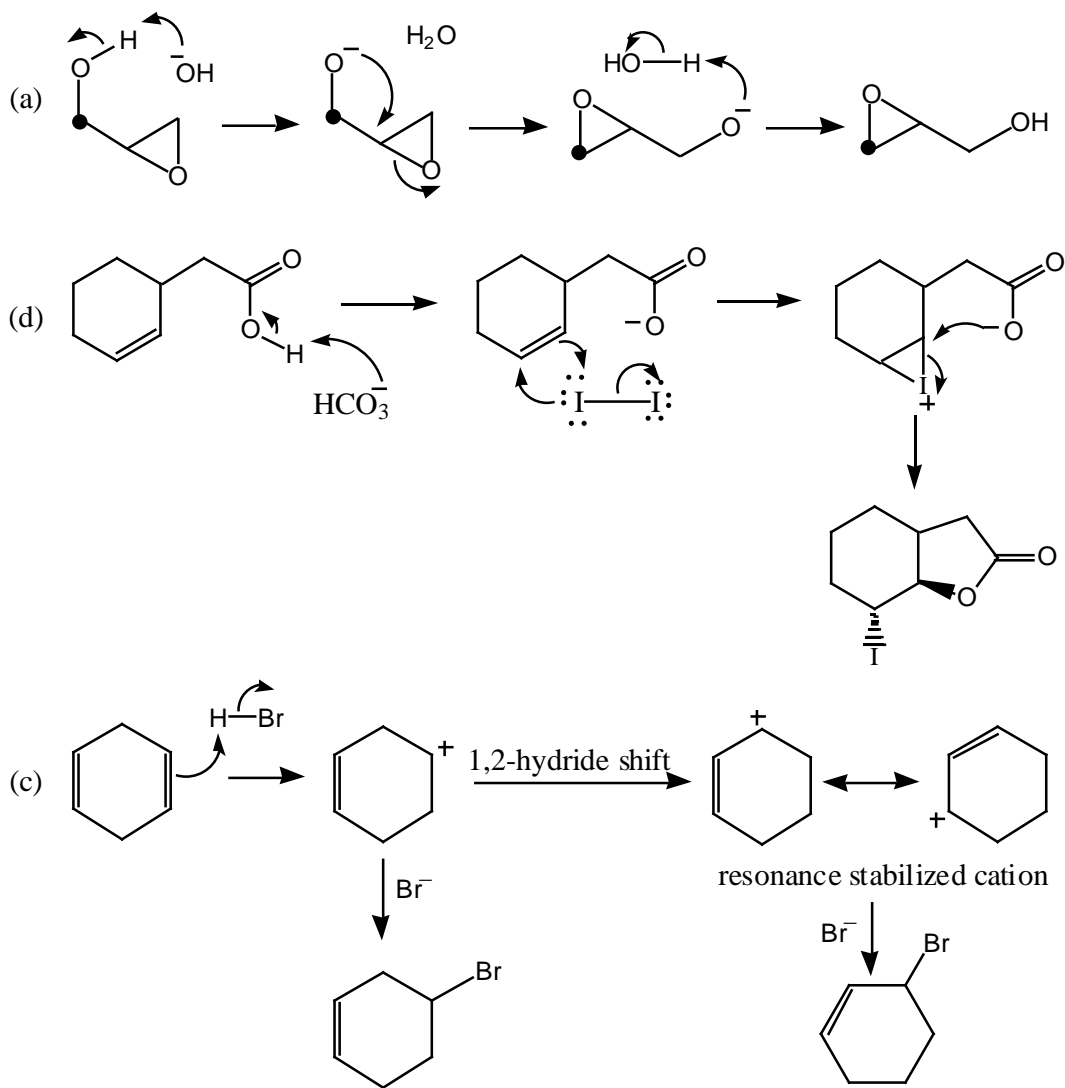


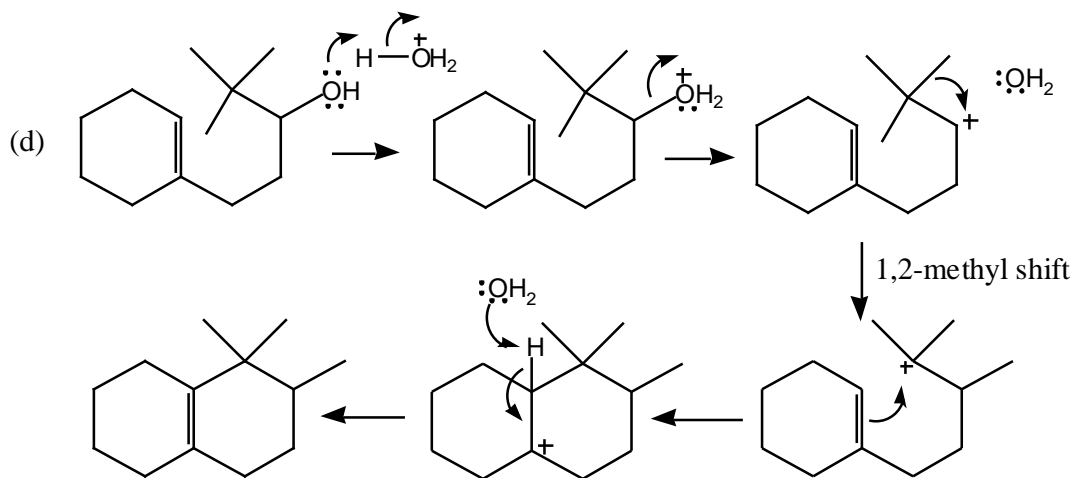
$\text{C}_4\text{H}_8\text{O}$



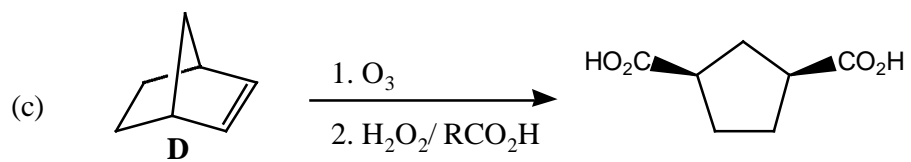
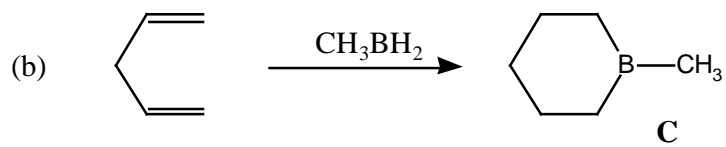
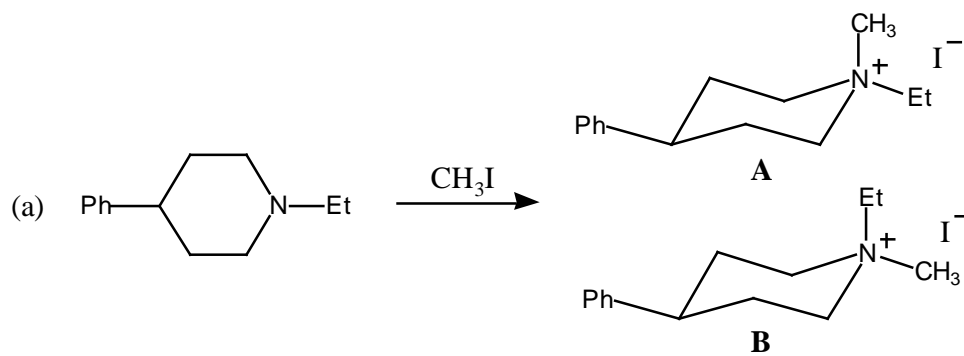


[5]

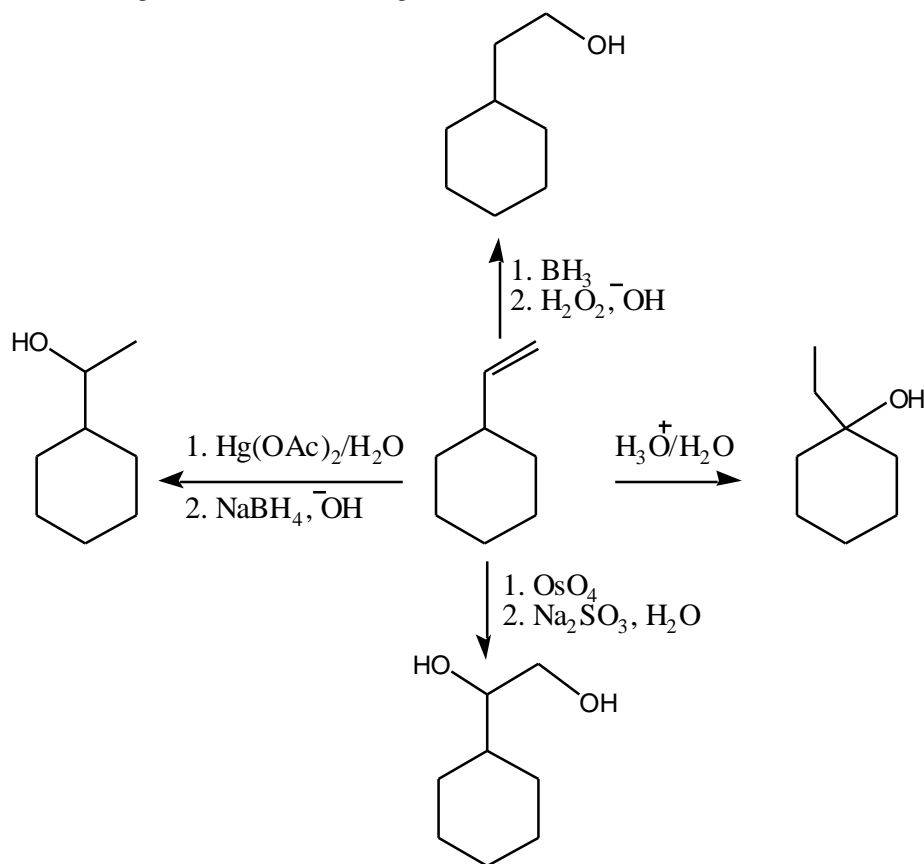




[6]



[7] Some ideas are given below. You might have other, correct answers.



[8] Again, some suggestions are given below. Alternative answers are possible.

