

scores:

- 1)
- 2)
- 3)
- 4)

This is a closed-book "open model" exam. You may use models, but no notes or books. Please put all your answers on the test. Use the backs of the pages for scratch. There are additional scratch sheets at the end of the exam.

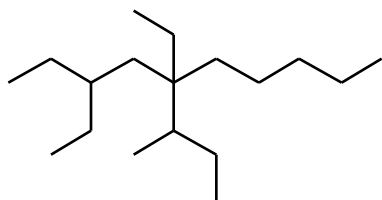
PLEASE read the questions carefully!

Partial Periodic Table

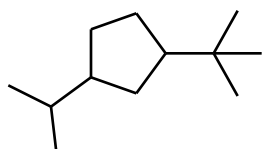
		1 H							8A 2 He
1A	2A			3A	4A	5A	6A	7A	
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne		
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar		
						35 Br			
						53 I			

1) (24 pts) a) Draw a molecular graph (bond line formula) for each of the following molecules ignoring Euclidean geometry (i.e. no wedges and dashes).

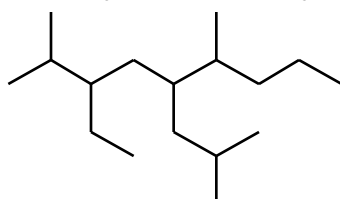
i) 5-sec-Butyl-3,5-diethyldecane



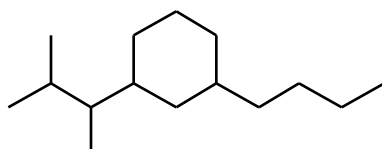
ii) 1-tert-Butyl-3-isopropylcyclopentane



iii) 3-Ethyl-5-isobutyl-2,6-dimethylnonane



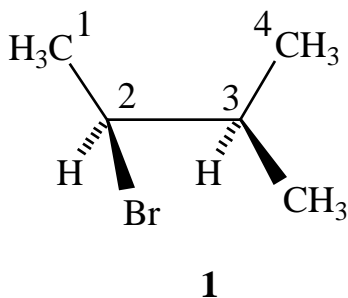
iv) 1-n-Butyl-3-(1,2-dimethylpropyl)cyclohexane



b) For each of the following pairs of compounds, circle the compound with the higher boiling point.

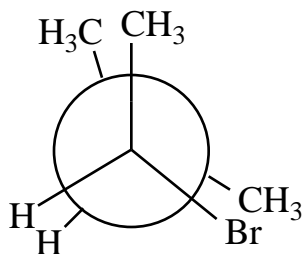
CH_4	CH_3F

2) (25 pts) A wedges and dashes structure for an eclipsed conformation of 2-bromo-3-methylbutane is shown below, with the main chain carbon atoms numbered.



a) What is the C1-C2-C3-C4 dihedral angle for conformation 1?

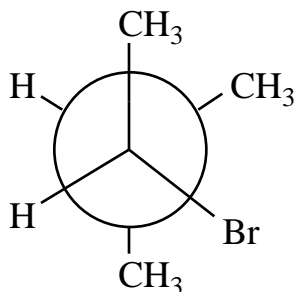
b) Carefully draw a Newman projection for conformation 1 sighting down the C2-C3 bond with C2 in front.



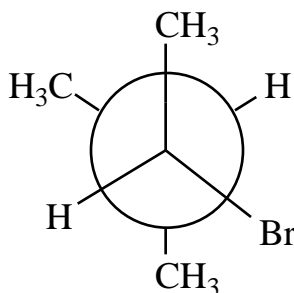
2) Continued

c) Carefully draw Newman projections for the three staggered conformations of 2-bromo-3-methylbutane generated by rotating carbon 3 (the "back" carbon) clockwise.

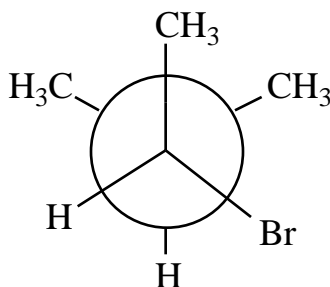
Staggered conformation I: C1-C2-C3-C4 dihedral = 60°



Staggered conformation II: C1-C2-C3-C4 dihedral = 180°



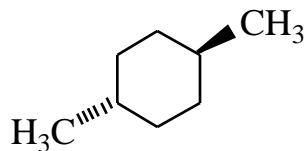
Staggered conformation III: C1-C2-C3-C4 dihedral = 300°



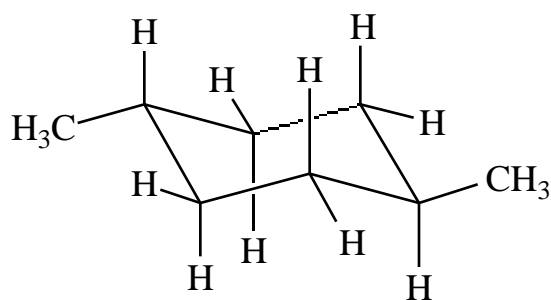
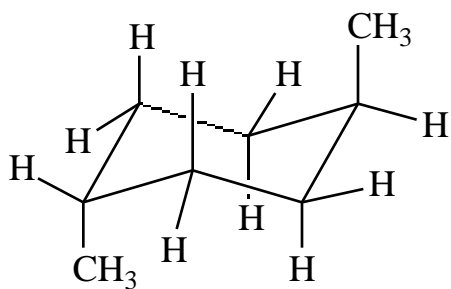
d) Given that a bromine is almost the same size as a CH_3 group, circle the most stable conformation of 2-bromo-3-methylbutane. Give a short explanation of why you made your choice.

Conformation II is the most stable because it has less steric strain. This is due to the fact that conformation II has only two "gauche butane" interactions, while both conformations I and III have three such interactions.

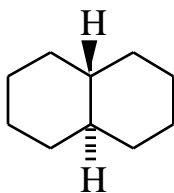
3) (25 pts) a) Carefully draw the two chair conformations of trans-1,4-dimethylcyclohexane (1), abbreviating the methyl groups with a CH₃ but showing all the H atoms on the rings. If one conformation is more stable than the other, circle the more stable conformation. If the conformations are of equal stability, then circle both.



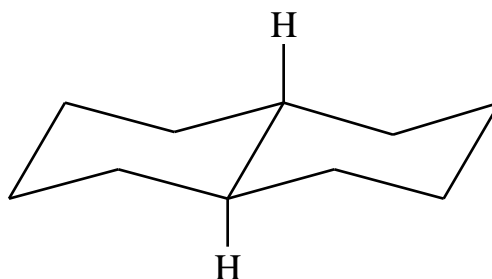
1



b) Carefully draw the single possible chair-chair conformation of trans decaline (2). For this drawing, only show the two H atoms indicated in structure 2.



2

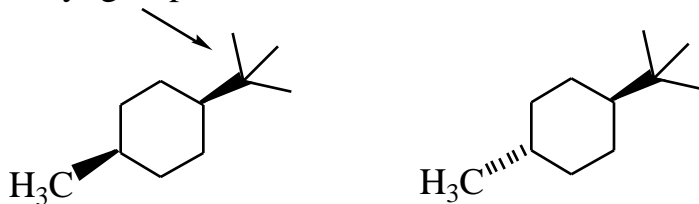


3) Continued

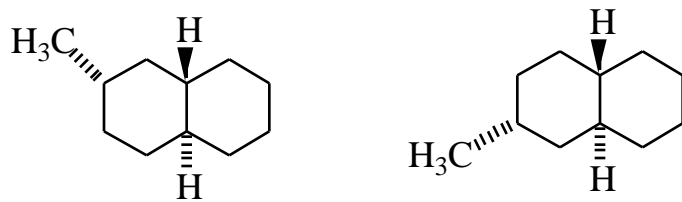
c) For each of the following pairs of isomers circle the more stable isomer (for these isomers one is always more stable than the other), and label the pair as constitutional isomers or stereoisomers.

I)

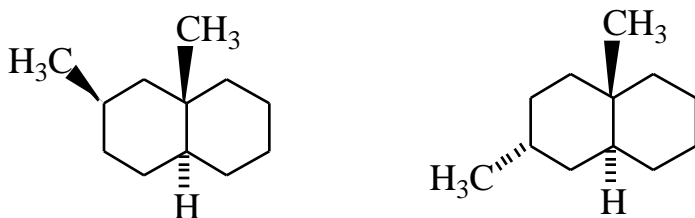
tert-butyl group



II)



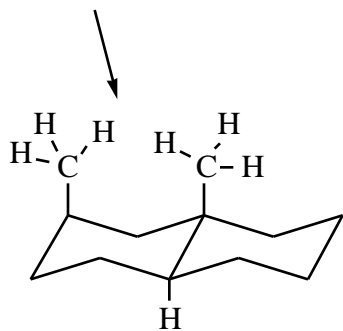
III)



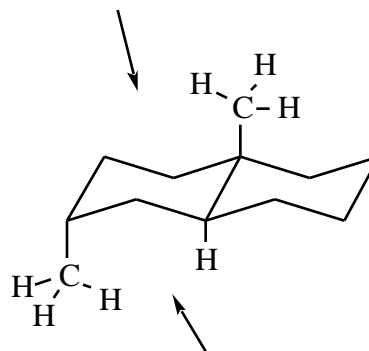
d) For part III above, give a brief explanation for your choice (you should use perspective chair drawings in your answer).

Both isomers have two axial methyl groups. The isomer on the right has two 1,3-diaxial $\text{CH}_3\text{-H}$ interactions. These cause about the same amount of steric strain as four gauche butanes. The isomer on the left, however, has a 1,3-diaxial $\text{CH}_3\text{-CH}_3$ interaction, where the methyl groups are seriously bumping into each other, plus they also have two gauche butane interactions. Since the 1,3-diaxial $\text{CH}_3\text{-CH}_3$ interaction is much worse than two gauche butanes, the isomer on the right is more stable (see drawings on next page).

1,3-diaxial $\text{CH}_3\text{-CH}_3$
(much worse than four
gauche butane interactions)

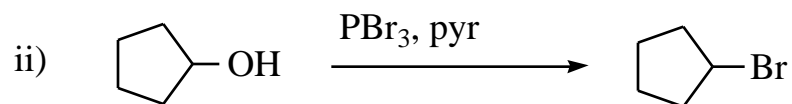
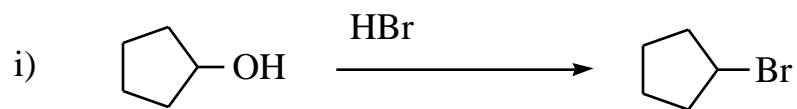


1,3-diaxial H-CH_3
(equiv. to two gauche
butane interactions)

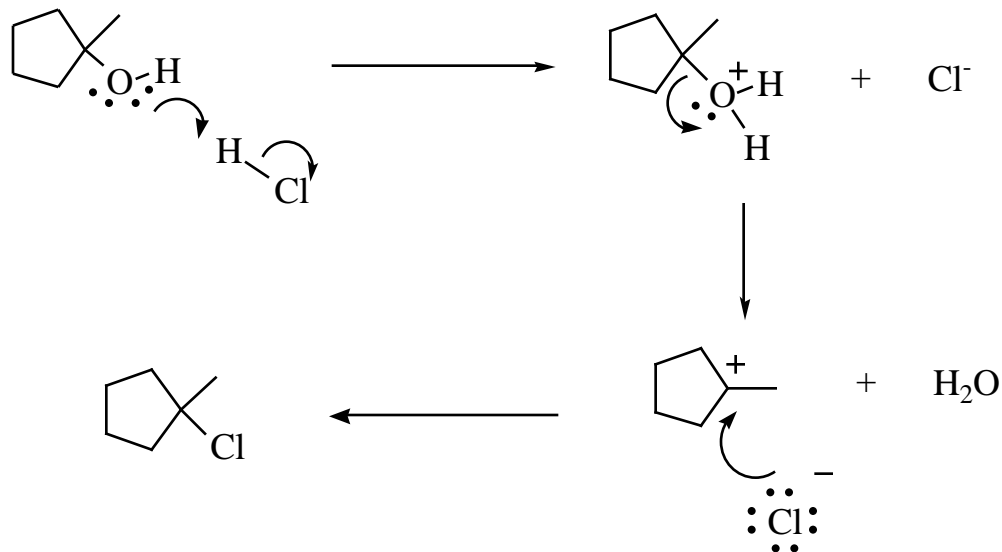
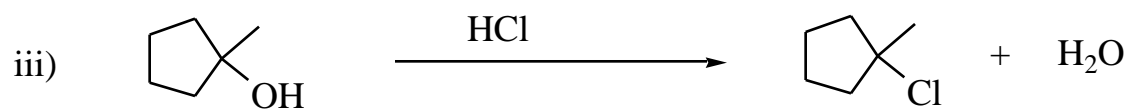


1,3-diaxial H-CH_3
(equiv. to two gauche
butane interactions)

4) (26 pts) a) Propose two different ways to accomplish the following transformation.

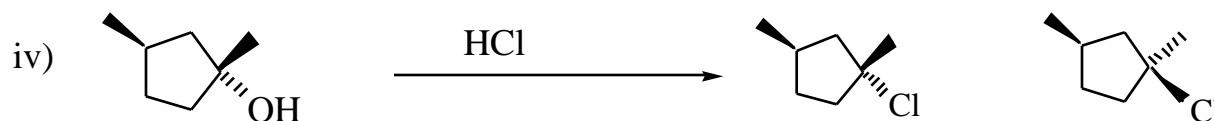


b) Propose an arrow-pushing mechanism for the following transformation. Carefully draw the structure of each intermediate with lone pairs and formal charges.

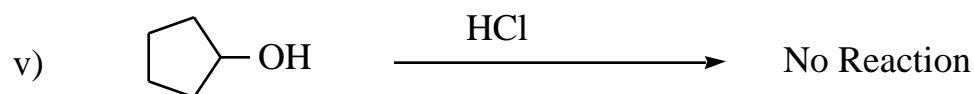


4) Continued

c) Reaction iv) below gives TWO alkyl chloride products! Propose structures for these two products.



d) When treated with HCl under the same conditions as for reactions iii) and iv) above, cyclopentanol gives no reaction, as indicated in reaction v) below (actually there is a reaction, but it is too slow). Using energy diagrams, explain why reaction iii) proceeds to give a new product, while v) does not give a new product.



As shown in the following energy diagrams, the rate determining step for reactions iii and iv is formation of the 3° carbocation, while for reaction v the rate determining step is formation of the 2° cation. The transition states for these steps look structurally similar to the cation products since the reactions are highly endothermic (Hammond's postulate). Since a 2° cation is less stable than a 3° cation, the transition state for formation of the 2° cation is less stable than that for formation of the 3° cation, so reaction v proceeds more slowly than reactions iii and iv.