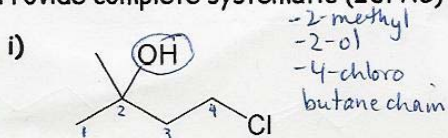


INTRODUCTORY ORGANIC CHEMISTRY I --- PROBLEM SET #2

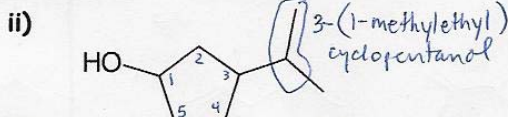
INSTRUCTIONS: HAND IN STAPLED, COMPLETED ASSIGNMENT (no extra pages please) AT THE BEGINNING OF CLASS on Tues. Oct. 25. LATE SUBMISSIONS WILL NOT BE ACCEPTED (EARLY IS OK). ANSWER ALL QUESTIONS. ALL MATERIAL WILL BE COVERED BEFORE THE DUE DATE. (QUESTIONS GRADED ARE HIGHLIGHTED.)

NOTE: In some questions, I have asked you to draw relevant structures/interactions/etc. to support your explanations. This should be standard practice any time you are asked to EXPLAIN anything. Next time, and on exams, I won't explicitly ask...

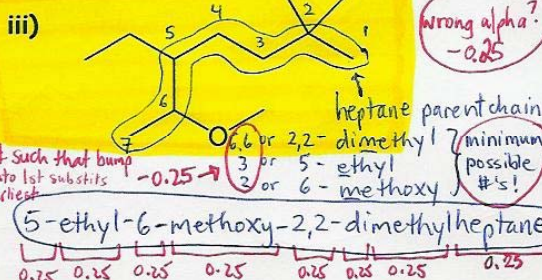
1. Provide complete systematic (IUPAC) names for the following molecules:



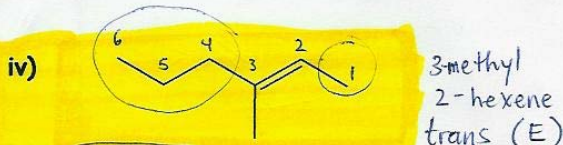
4-chloro-2-methylbutan-2-ol
OR 4-chloro-2-methyl-2-butanol



3-(1-methylethyl)cyclopentanol
OR 3-isopropylcyclopentanol



5-ethyl-6-methoxy-2,2-dimethylheptane

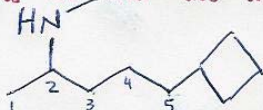


(E)-3-methylhex-2-ene
OR (E)-3-methyl-2-hexene
OR trans-3-methyl-2-hexene → not full credit since not strict IUPAC...

2. Draw skeletal (line) structures of the following molecules:

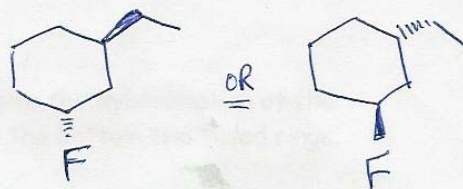
i) 5-cyclobutyl-N-methylpentan-2-amine

0.25 0.25 0.25 0.25 0.25 0.25 0.25 0.25

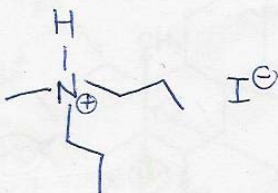


If not line structures,
-0.5

ii) trans-1-ethyl-3-fluorocyclohexane

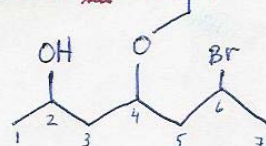


iii) methylpropylammonium iodide



iv) 6-bromo-4-ethoxy-2-heptanol

0.25 0.25 0.25 0.5 0.25 0.25 0.25








CHEM221 Section 01 Dr. C. Rogers

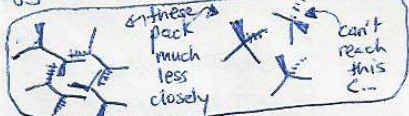
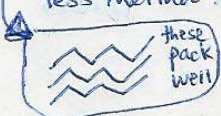
① all have only atoms of low polarizability (C, H, O)
 note ② all except neopentane have nearly the same molar mass ie: molecules of similar size

NAME: marking scheme 2

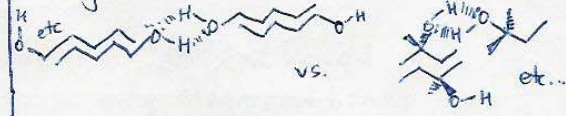
3. Rank the following compounds in order of increasing boiling points. Explain your reasoning; you must include structural drawings and detailed descriptions of relevant interactions to receive full marks. (You can look up the actual boiling points, but you will not get marks unless your explanation is complete.)

PREDICTED	2,3-dimethylbutane  58°	n-hexane  69°	2-methylbutan-2-ol  102°	neopentane  9.5°	pentanol  136°	ACTUAL b.p.'s LISTED
LOWEST BP	neopentane (most branched)	< 2,3-dimethylbutane	< n-hexane (least branched)	< 2-methylbutan-2-ol	< pentanol	HIGHEST BP

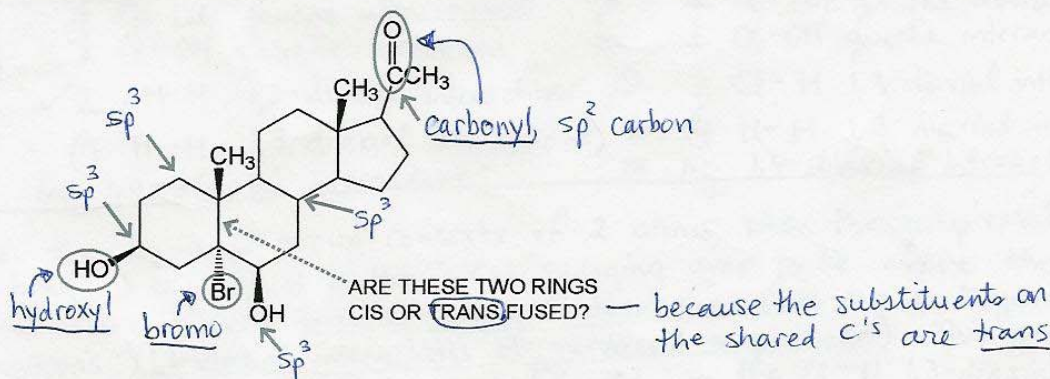
The three alkanes have the lowest boiling points, because the strongest (and only) forces acting to hold the molecules together are van der Waals forces (ie: induced dipole-induced dipole interactions). Their relative boiling points are determined by the extent of contact between the alkyl chains. Linear alkyl chains can contact each other over many points, and can adopt conformations that lead to very efficient packing; this leads to relatively strong dispersion forces (ie v.d.w. forces). Branched chains are more globular, which diminishes the ability of some parts of the molecule to touch neighbouring molecules; this leads to weaker overall dispersion forces. Thus branched alkanes have lower boiling points than linear alkanes since the intermolecular forces can be overcome with less thermal energy (lower temperatures).



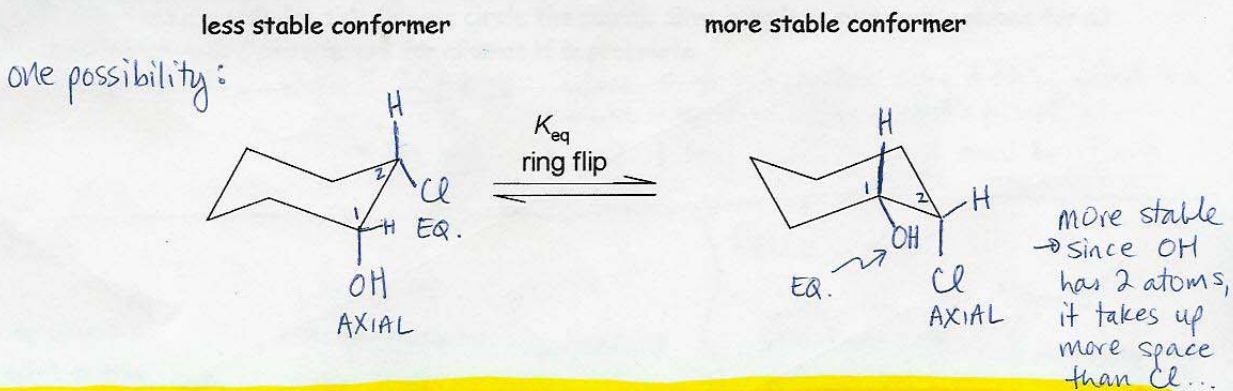
The two alcohols have higher boiling points than the alkanes because of the additional interaction between molecules, namely hydrogen bonding. Hydrogen bonds between -OH δH⁺ and δ⁻O's lone pairs provide considerable extra strength to the total attractive forces between alcohol molecules, much more than the attraction due to dispersion forces. The difference in bp's between pentanol + 2-methylbutan-2-ol arises from the difference in dispersion force strengths, however. The straight-chain alcohol has stronger dispersion forces than the branched alcohol, thus requires a higher temperature to boil.



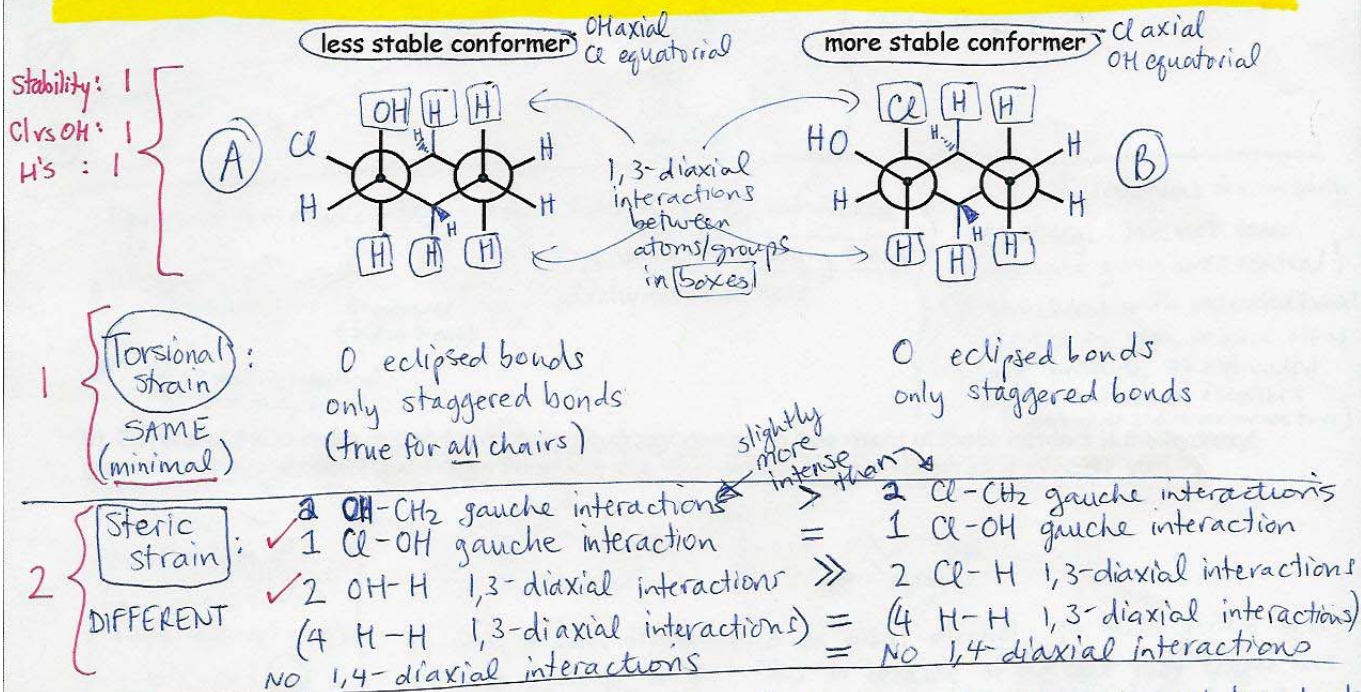
4. For the following molecule: name the circled functional groups, give the hybridization of the atoms (not Hs) indicated by the arrows, and answer the question about the bottom two fused rings.



5.a) Draw the necessary substituents on the rings to complete the "ring-flipping" equilibrium for cis-2-chlorocyclohexan-1-ol. On each conformer, label the substituents as "axial" or "equatorial".



b) The incomplete Newman projections below show the chair conformers from part (a), as viewed down their C1-C2 bonds (C1 at front left) and C5-C4 bonds (C5 at front right). For each chair from part (a), complete the Newman projection by adding the substituents and ring hydrogens. Then, explain the difference in the two conformers' stabilities by comparing their levels of torsional strain (eclipsed vs. staggered bonds) and steric strain (gauche interactions, and 1,3- and/or 1,4-diaxial interactions).



2 Because the hydroxyl group consists of 2 atoms, when the group rotates about the C-O bond, it can result in the -OH swinging over to lie above the ring. This would result in even greater steric interactions with the hydrogens in axial positions (1,3-diaxial interactions of increased magnitude). This problem does not arise with a monatomic group like Cl, so the Cl-H 1,3-diaxial interactions are preferable. All other types of strain (gauche steric strain, torsional strain) are of similar magnitude in the two conformers, so (B) is more stable.

CHEM221 Section 01 Dr. C. Rogers
 Be sure to check your answers yourself - here you were awarded marks for effort only!

NOT MARKED FULLY - JUST 4 MARKS FOR A GOOD ATTEMPT! 😊

NAME:

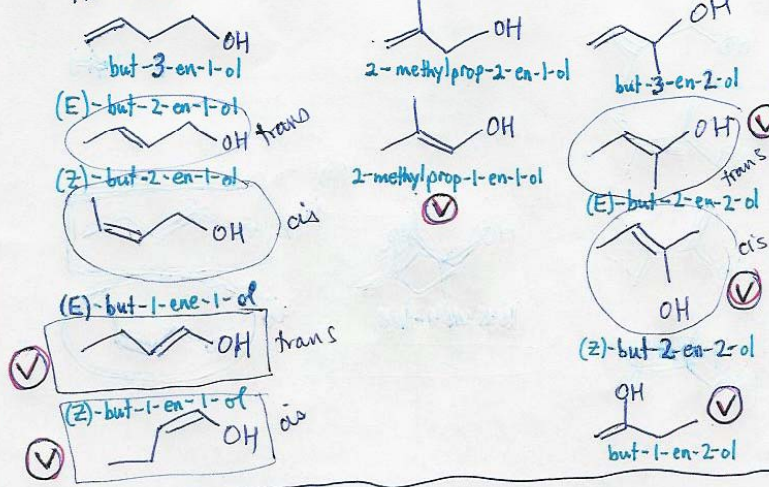
carbonyls? ✓
 ethers ✓
 alcohols ✓
 naming ✓
 4 geom. isomers circled ✓

6. a) Draw line structures of all acyclic (i.e., no rings) constitutional isomers with the formula C_4H_8O . [Hint: so far, I've found 13 isomers]. Organize your drawings such that pairs of molecules that are geometric isomers are side-by-side (please circle the pairs). Give complete systematic names for all compounds, including E/Z descriptors for alkenes if appropriate.

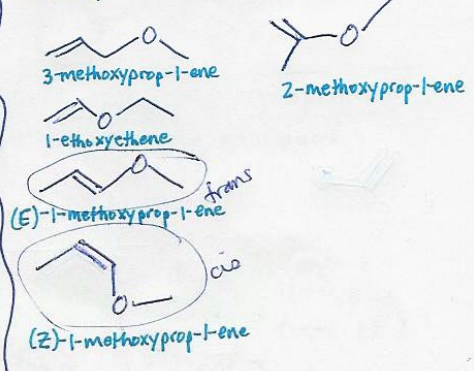
elements of unsaturation = $\frac{2C+2-H}{2}$ where O is not counted, since it can be added to a chain without affecting the #H's present ...
 $= \frac{8+2-8}{2} = 1 \Rightarrow$ 1 ring or 1 π -bond must be present

4

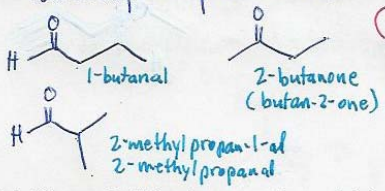
Alcohols:



Ethers:



Carbonyl compounds too: π -bond between C+O, not in chain
 not responsible for naming these (aldehydes + ketones)

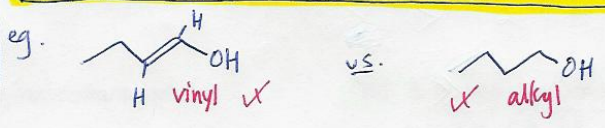


Note: ① structures drawn with net charge are not valid (formula given was neutral)
 ② structures with separated formal charges or open valence atoms are unstable, so not valid representations of isomers (not most stable resonance form)

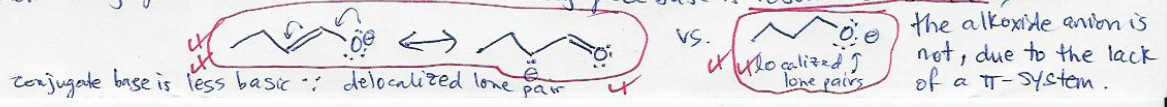
b) Several of the isomers in part (a) contain a hydroxyl group. In how many of these isomers is the hydroxyl group in a vinylic position? How does the acidity of a vinyl alcohol compare to an alkyl alcohol? Why?

5

I found six vinyl alcohols (ie: isomers with a vinylic hydroxyl group).
 → labelled (V) in part (a)



In both a vinyl alcohol and an alkyl alcohol, the most acidic H is the one bonded to O. This is because of the fact that oxygen has a higher electronegativity than C (no matter what hybridization), so the oxygen is better able to stabilize an extra lone pair of electrons. To compare the acidities of the 2 types of alcohols, we compare the stabilities of their conjugate bases: We see that the vinyl alcohol must be more acidic because its conjugate base is resonance-stabilized whereas



9