Key

1. Using Newman projections, show all six (6) *conformations* of 2-methylbutane, $CH_3CH(CH_3)CH_2CH_3$, as viewed down the C2-C3 bond. (15 points)

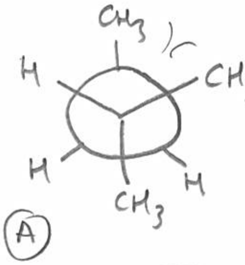
   a. For each conformation, indicate what type of strain is present - *torsional*, *steric*, or *angle* strain.

   b. Indicate the *least stable* and the *most stable* conformations. If any of the conformations have the same energy then show which ones do. Ⓐ & Ⓔ most stable Ⓑ & Ⓓ least stable

   c. Use the data below to *estimate* the total barrier to rotation about the C2-C3 bond.

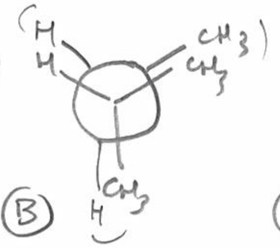
H-H eclipsed	4 kJ/mol
H-CH_3 eclipsed	6 kJ/mol
CH_3-CH_3 gauche	3.8 kJ/mol
CH_3-CH_3 eclipsed	11 kJ/mol

difference between most and least stable conformation =



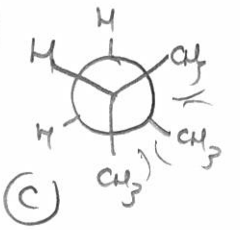
Ⓐ

3.8 kJ/mol
- Steric



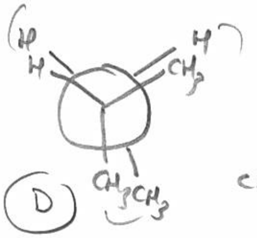
Ⓑ

4+6+11
= 21 kJ/mol
- torsional + steric



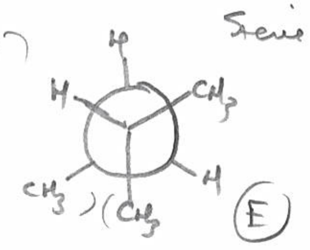
Ⓒ

3.8+3.8
= 7.6 kJ/mol
- Steric



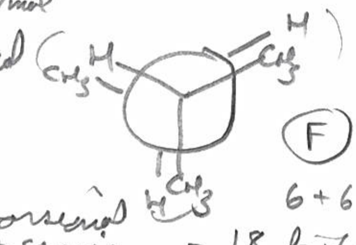
Ⓓ

4+6+11
= 21 kJ/mol
- torsional + steric



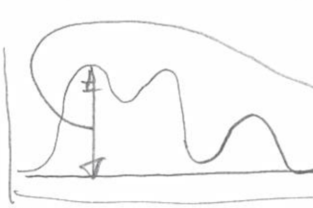
Ⓔ

3.8 kJ/mol



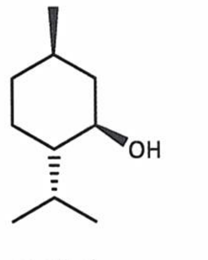
Ⓕ

- torsional + steric
6+6+6
= 18 kJ/mol

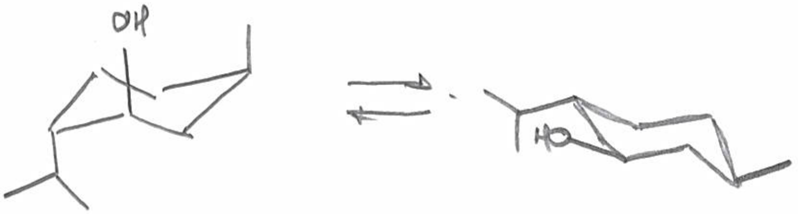


$21-3.8 = \boxed{17.2 \text{ kJ/mol}}$
Barrier

2. Menthol, isolated from various mint oils, is shown below. Draw both chairs of menthol and indicate which one is more stable. (Remember, you get points for well-drawn chairs) (10 points)



menthol



all three groups are axial and have 1,3-diaxial strain

all three groups are equitorial so this is the most stable

3. Consider the structures of *cis*-decalin and *trans*-decalin: (10 points)

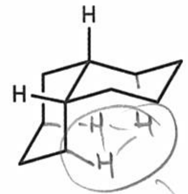
   a. Which of these compounds would you expect to be more stable?
   b. The less stable isomer has 10.2 kJ/mol strain compared to the more stable isomer. Provide an explanation for the likely cause of this strain.

cis - decalin has more Strain due to 1,3-diaxial interaction

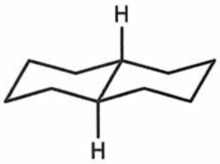
this value is very close to the estimate

each is worth ~ 3.8 kJ/mol

est ~ 11.4 kJ/mol



cis-decalin

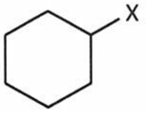


trans-decalin

most stable

there are 3 interaction that are like 1,3-diaxial interactions

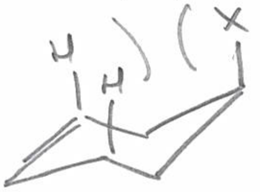
4. Consider the four halogen substituted cyclohexanes. The 1,3-diaxial interaction and the atomic radius for each halogen are given in the table below. (20 points)



Substituent (X)	1,3-diaxial interactions (kJ/mol)	Atomic Radius (pm)
-F	1.05	72
-Cl	2.22	99
-Br	2.01	114
-I	1.96	133

Suggest an explanation for the observed trend in the 1,3-diaxial interaction, i.e, account for the following:

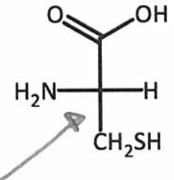
   a. Why does the value go up from –F to –Cl
   b. But then, why does the value go down from –Cl to –Br and then even further with –I?



the 1,3-diaxial interaction is caused by the Steric interaction of the halogen with the axial hydrogens. From F to Cl, the larger chlorine atom has a larger interaction, but as the bond length between carbon & X gets longer, the effect becomes less prominent.

5. Assign the *configurations* of each stereocenter in the following compounds using the appropriate notation. (15 points)

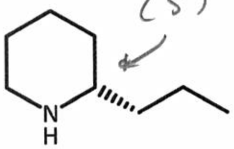
a.



(R)

cysteine
(an amino acid)

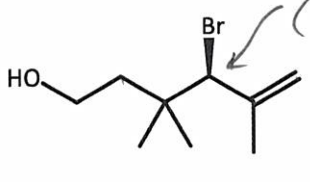
b.



(S)

coniine
(found in poison Hemlock,
famed poision that killed Socrates)

c.

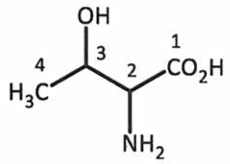


(S)

(just a molecule)

6. Threonine is one of the essential amino acids needed for the biosynthesis of proteins and enzymes and cannot be made by the body. Therefore it must be obtained from food sources (or multi-vitamins). (Note that the structure below doesn't show any stereochemistry!)

(15 points)

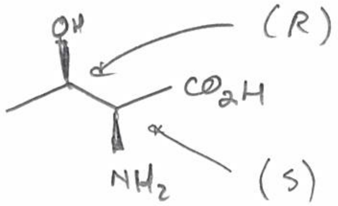


threonine

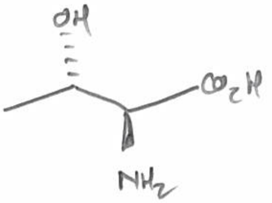
Answer the following:

a. How many stereoisomers are possible for threonine? 4

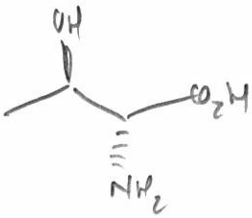
b. Nature only uses one of these isomers (called *L*-threonine) and has the *absolute configuration* of (2*S*, 3*R*)- Draw this isomer using appropriate notation (the numbering of threonine is shown above).

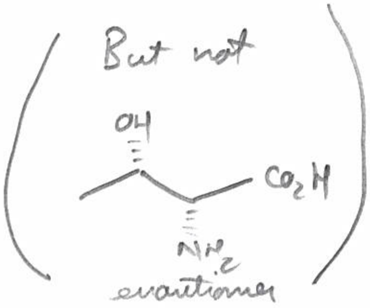


c. The isomer called *allo*-threonine is a *diastereomer* of threonine. Draw a possible structure for *allo*-threonine.



or





7. Indicate whether the following statements are *absolutely* true or false. (10 points)

a. *trans*-1,3-dimethylcycloheptane is *achiral.* False

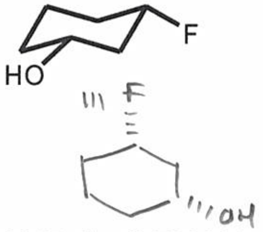
b. If the (*S*) isomer of 2-butanol has [α] = +13° then a sample of 2-butanol with [α] = -13° must be the (*R*) isomer. True

c. *Enantiomers* are isomers that are non-superimposable mirror images. True

d. A molecule with a specific rotation of zero ([α] = 0°) must be a *meso* compound. False

e. If a molecule has an odd number of asymmetric carbons, then it must be *chiral.* True

8. What is the relationship between the following two structures? Are they *enantiomers*, *diastereomers*, *constitutional isomers*, or *identical*? (5 points)



constitutional isomers

9. In Spring 2017, the CHEM 12B class performed a classical resolution of racemic α-methylbenzylamine (shown below). The class combined their final products and obtained the following data during the determination of the optical rotation. (20 points)

α_{ave} = -37.4° degrees

concentration of pure liquid (c) = density

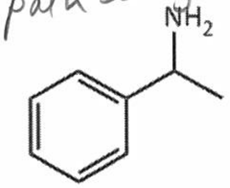
Given that the literature value of the specific rotation for the (*S*) enantiomer of this compound is [α] = -40.3°, the density of the liquid amine is 0.94 g/mL (either enantiomer), the path length (*l*) of the polarimeter cell was 1.00 dm, calculate the optical purity (o.p) of the resolved amine (which is also the same as %ee).

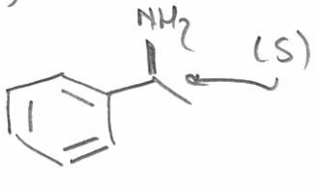
The specific rotation is defined as: $[\alpha] = \frac{\alpha}{c \cdot l}$

$$[\alpha]_{exp} = \frac{-37.4}{(0.94)(1.00)} = -39.8^\circ$$

Also, show the (S) enantiomer using the appropriate notation.

path length (l) in dm





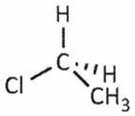
$$\frac{[\alpha]_{exp}}{[\alpha]_{lit.}} \times 100 = \frac{-39.8^\circ}{-40.3} \times 100$$

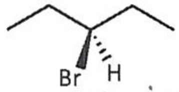
$$= 98.7\%\ ee$$

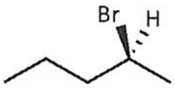
10. Draw both chair conformations of *trans*-1,3-dimethylcyclohexane. Indicate whether both chairs are the same energy or whether one is more stable than the other (by circling the most stable one). Remember you get points for good looking chairs! (20 points)

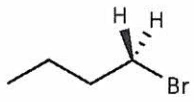
both are the same energy!

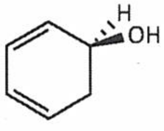
11. Indicate whether each compound below is *chiral* or *achiral*. (50 points)

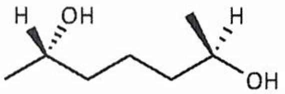

achiral

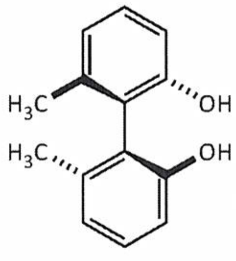

achiral

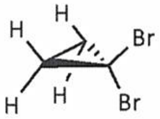

chiral

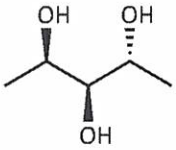

achiral

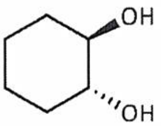

chiral


achiral
(meso)

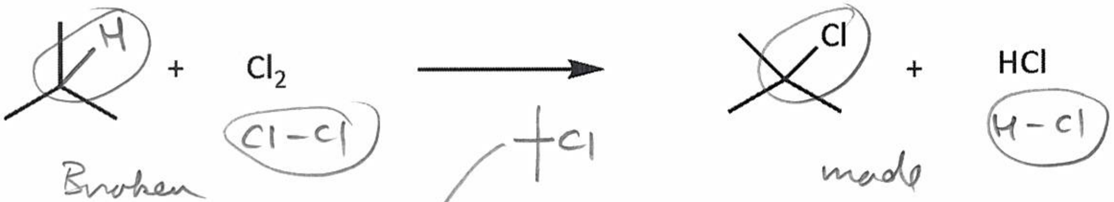

chiral


achiral


chiral


chiral

12. Consider the following reaction:
Given: $\Delta G = \Delta H - T\Delta S$ and $K_{eq} = e^{-\Delta G/RT}$ (20 points)



a. Using the BDE values in the provided table (at the end), calculate the enthalpy (ΔH) for the above reaction. Clearly show your calculation.

+H →

Broken		made	
C–H	381	C–Cl	331
Cl–Cl	243	H–Cl	431

$\Delta H = (381 + 243) - (331 + 431)$

$\boxed{\Delta H = -138 \text{ kJ/mol}}$

$\Delta H = \sum BDE_{broken} - \sum BDE_{made}$

b. Predict the sign of the entropy (ΔS) for this reaction. Explain your answer.

ΔS ~ 0 (if isobutane is a gas and t-BuCl is a liquid, then ΔS slightly ⊖

c. Predict whether the Gibbs free energy (ΔG) is positive (+) or negative (-). Explain.

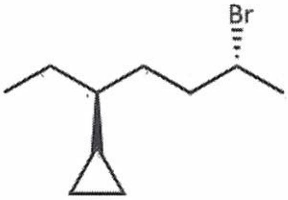
ΔG ≅ ΔH for reactions where ΔS ~ 0 so predict that ΔG = ⊖

d. Predict whether K_{eq} is less than (<) one, or greater than (>) one. Explain.

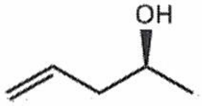
and if ΔG = ⊖ the $K_{eq} > 1$

13. Provide names for the following molecules. (15 points)

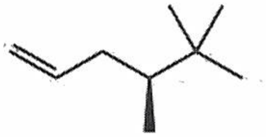
a.



b.



c.

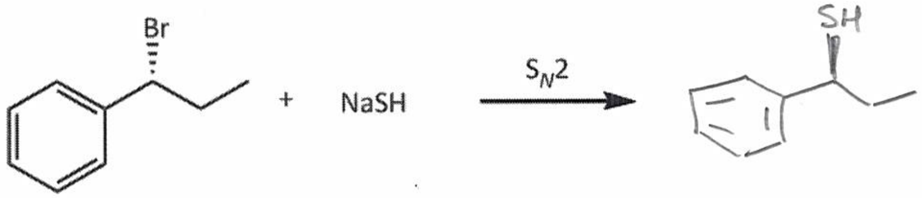


a. (2R,5S)– 2-bromo-5-cyclopropyl heptane

b. (2S)–pent-4-en-2-ol

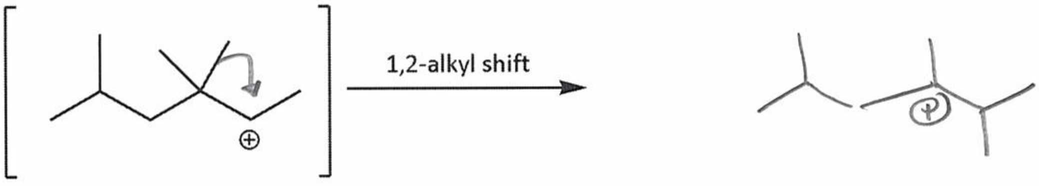
c. (4S)–4,5,5-trimethyl hex-1-ene

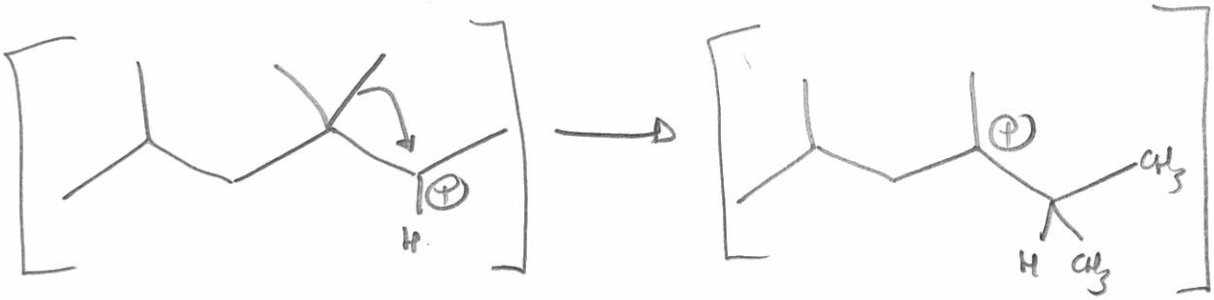
14. Show the product of the S_N2 reaction (don't forget about stereochemistry). (10 points)



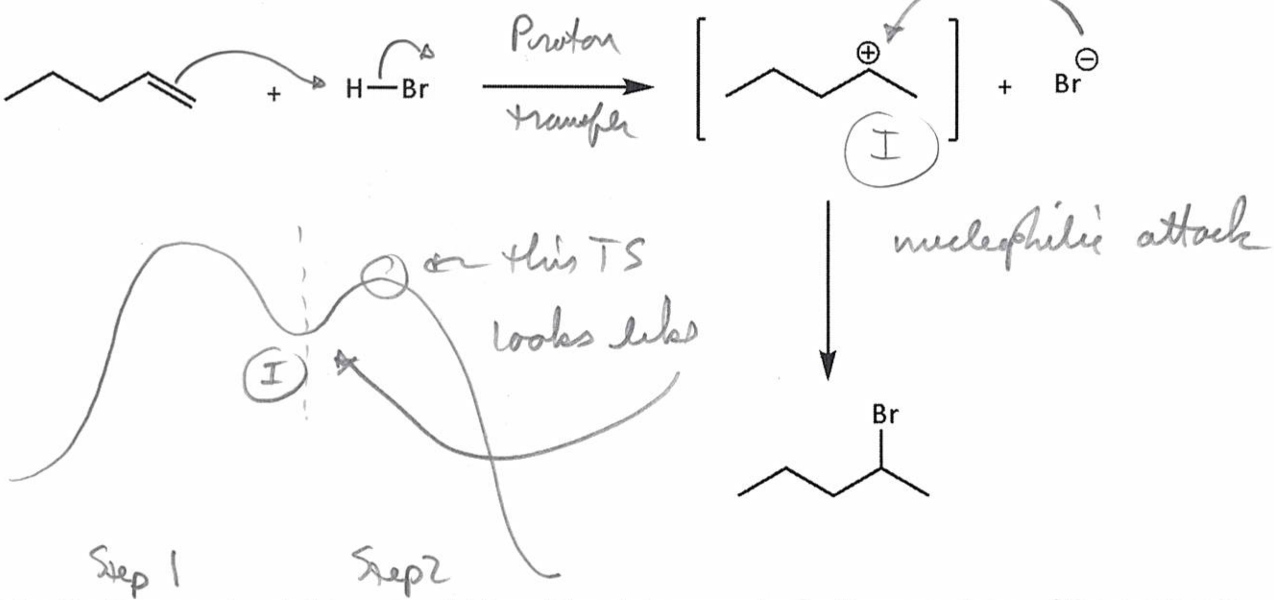
(+ NaBr)

15. The carbocation shown below is an intermediate in a reaction and it undergoes a 1,2-alkyl shift. Show the resulting carbocation from the shift and the mechanism . (10 points)

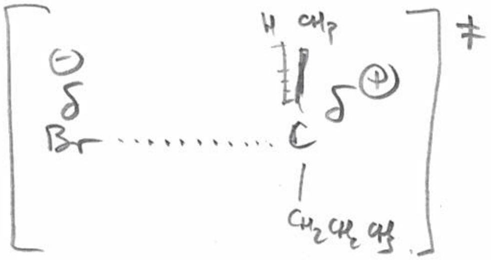




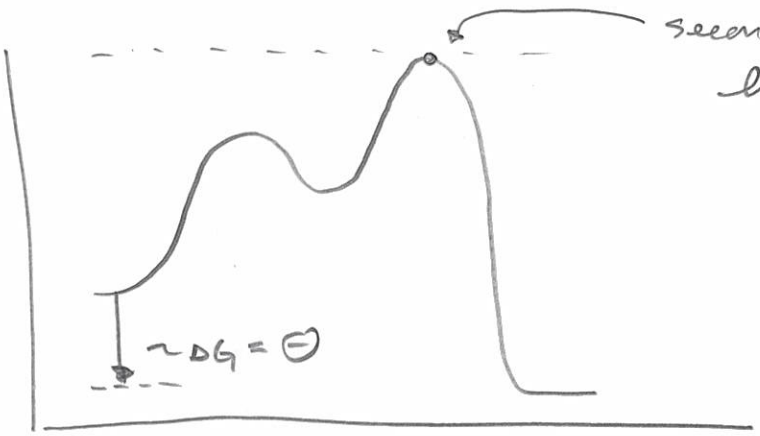
16. Show the electron pushing in the mechanism below and for each step indicate whether is *nucleophilic attack*, *proton transfer*, *loss of a leaving group*, or *carbocation rearrangement*. (10 points)



17. Using the Hammond postulate, suggest a transition state geometry for the second step of the reaction in Question 16 (above) - use the bracket notation [ ]‡ (10 points)



18. Draw an energy diagram for an exergonic reaction that has two steps and where the second step is rate-limiting. (10 points)



second step has highest energy T.S. so this is the rate-limiting step