CHE 208 (OC I) Name (Blockschrift):

Exam #1 Prof. Luedtke Signature:

8 November 2012

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

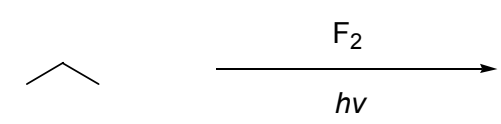
<u>ΔG for placing a substituent axial in a cyclohexane (kcal/mol):</u> CN (0.2); F (0.25); CCH (0.41); I (0.41); Cl (0.52); Br (0.55); OH (0.95); NH_2 (1.4); COOH (1.41); $CH{=}CH_2$ (1.7); CH_3 (1.74); CH_2CH_3 (1.75); $CH(CH_3)_2$ (2.15); $C(CH_3)_3$ ($\geq$5)

R = 1.99 cal/mol•K

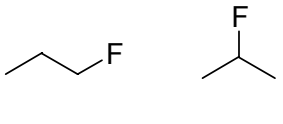
<u>Bond Dissociation Energies (kcal/mol):</u> CH_3–H (105); H_3CCH_2–H (101); $(H_3C)_2CH$–H (98.5); $(CH_3)_3C$–H (96.5); H–H (104); F–H (136); Cl–H (103); Br–H (87); I–H (71); HO–H (119); H_2N–H (108); F–F (38); Br–Br (46), C(2°)–C(2°) (85.5); C(sp^3)–F (110); C(sp^3)–Br (71)

Problem 1	/28
Problem 2	/6
Problem 3	/15
Problem 4	/15
Problem 5	/18
Problem 6	/18
Problem 7	/14
<u>Problem 8</u>	<u>/6</u>
Total	/120

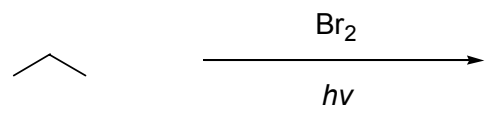
1) [28 pts.] Draw two main products for each reaction (not including HBr, NaBr, etc.). Indicate the major product. If the product is chiral, give an “r” or “s” designation to each stereocenter.



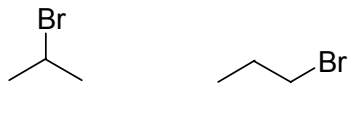
(excess)



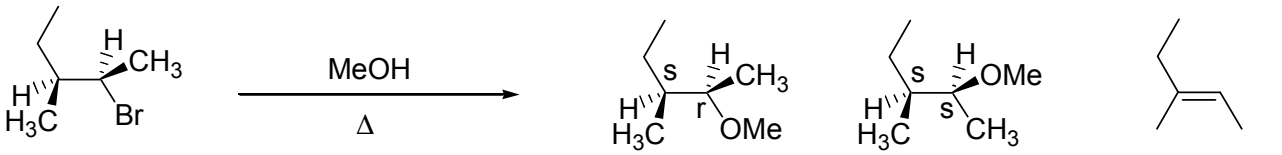
major minor



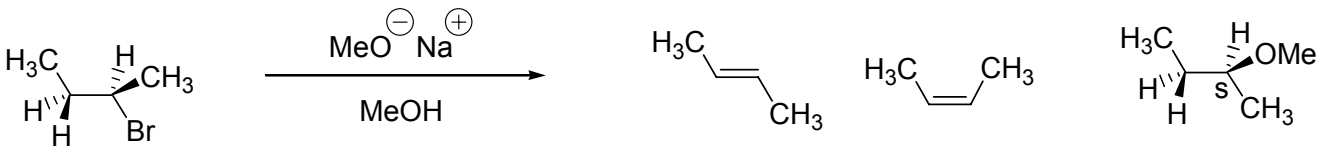
(excess)



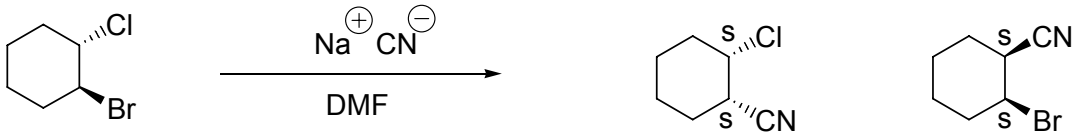
major minor



major (S_N1) minor (E1)

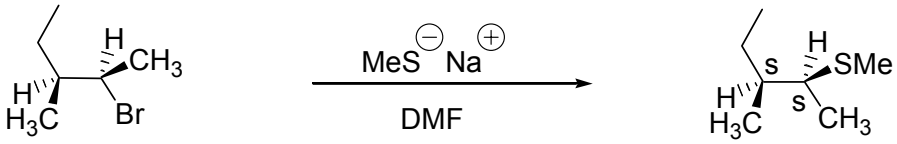


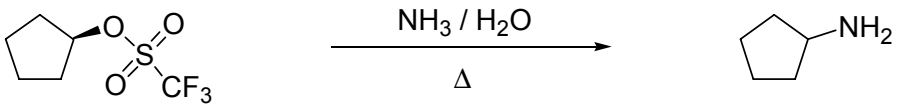
major (E2) minor (E2) minor (S_N2)



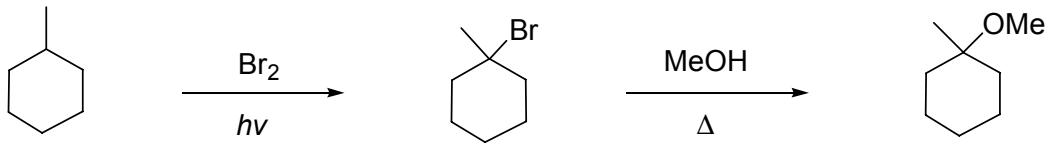
major (S_N2) minor (S_N2)

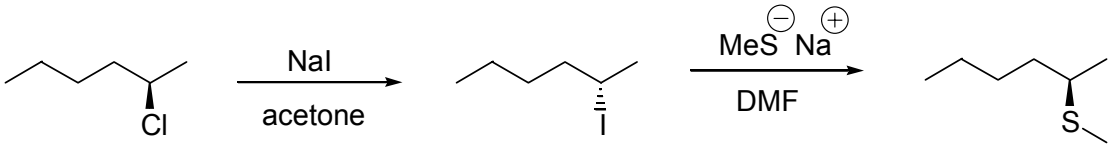
2) [6 pts.] Draw the main product for each reaction. If the product is chiral, give an "r" or "s" designation to each stereocenter.

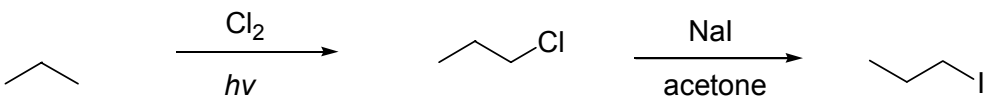




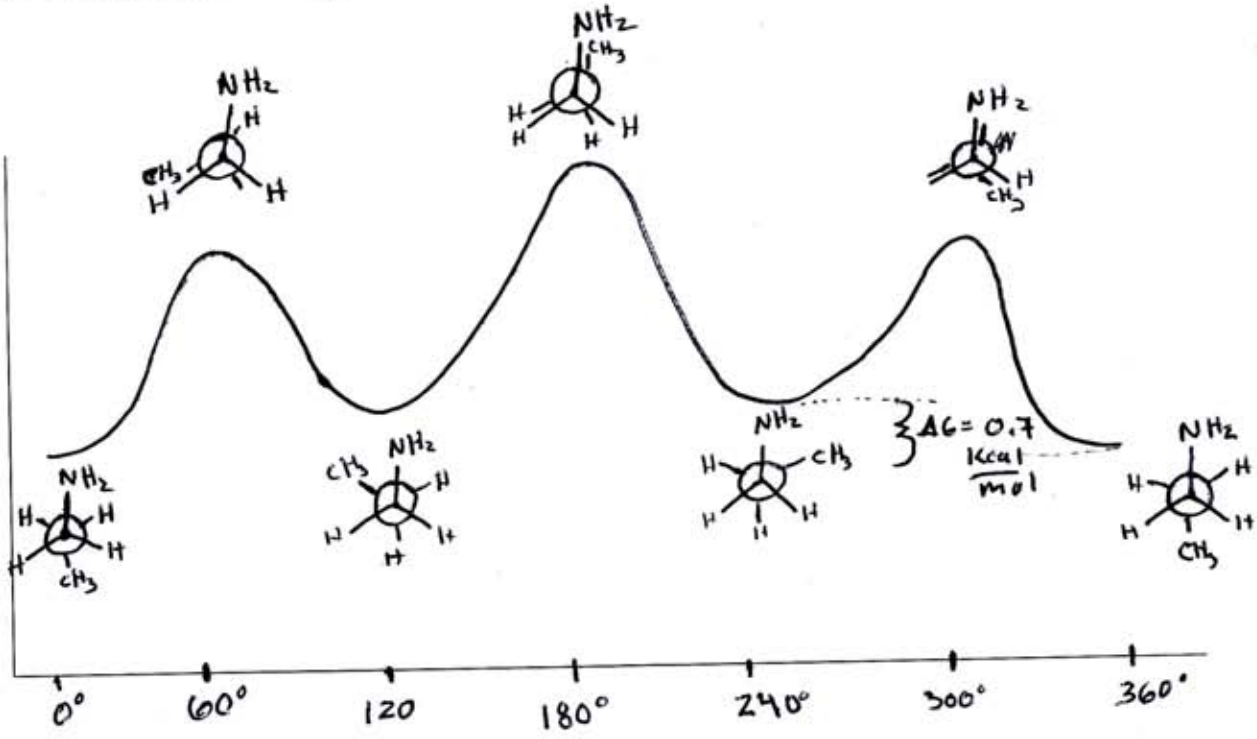
3) [15 pts.] What reagents and conditions are needed to accomplish these transformations? Each reaction requires two steps. Draw the intermediate.



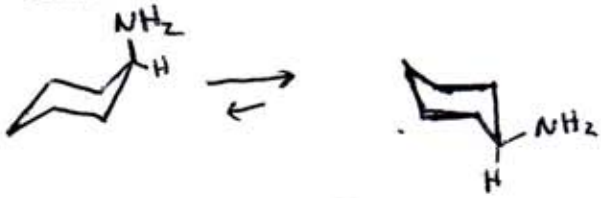




4) [15 pts.] 1-Aminopropane (NH_2-CH_2-CH_2-CH_3) exists in two preferred conformations that interconvert by rotation of the C1-C2 bond. Please construct a potential energy diagram for rotation about the C1-C2 bond of 1-aminopropane. Plot dihedral angle on the X-axis and relative energy (in kcal/mol) on the Y-axis. For each minimum and maximum on the diagram, provide a Newman projection and estimated relative energy levels.

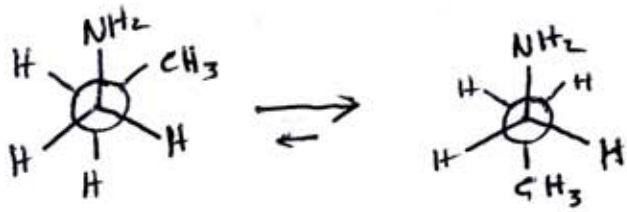


B) Based on your answer above, estimate the value of K_{eq} at 298 K for the interconversion of the two conformational isomers. Be sure you label the conformational isomers and clearly define your equilibrium constant.



$\Delta G = -1.40$ kcal/mol (from page 1)

(2 gauche interactions) (0 gauche interactions) ∴ 1 gauche interaction $= +0.70 \frac{\text{kcal}}{\text{mol}}$

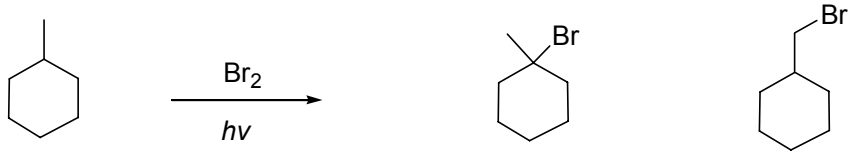
For 

$\Delta G = -0.70$ kcal/mol

$\Delta G = -RT \ln K_{eq}$ $K_{eq} = e^{(-\Delta G/RT)}$

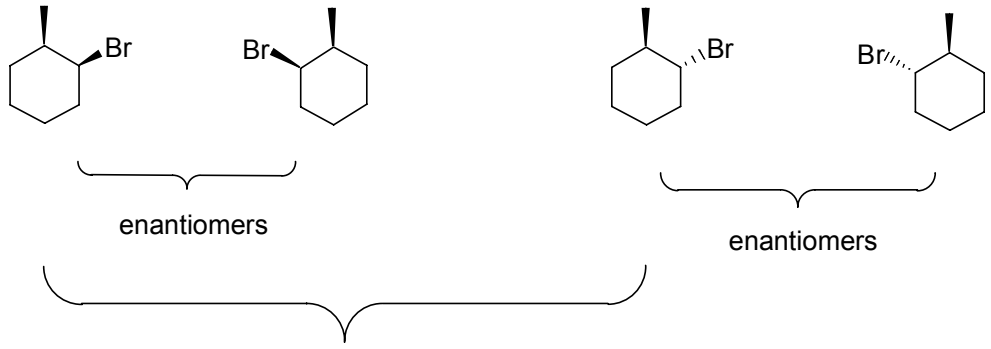
$= 3.3$

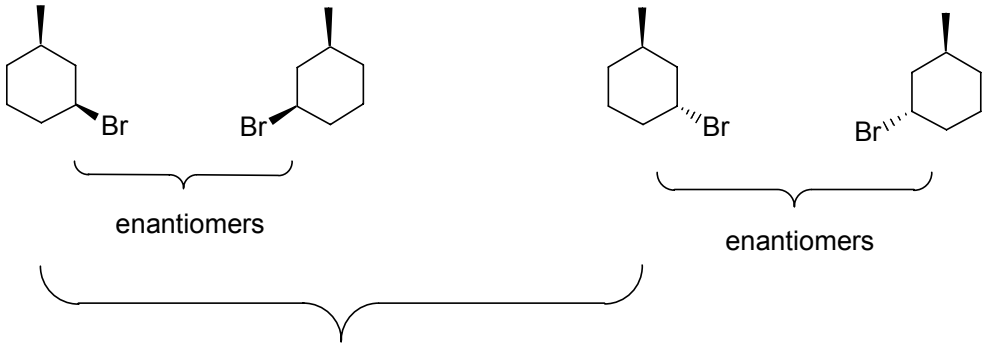
5) [18 pts.] Draw *all* of the products for the radical (mono)bromination of methylcyclohexane. For each product, indicate "major," "minor," or "trace." Please note that some products exist as mixtures of stereoisomers. Clearly indicate their stereochemistry.



major trace

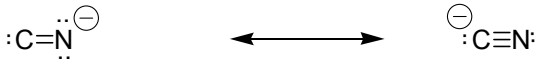
minor products:





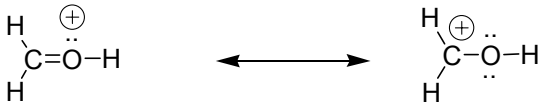
6) [18 pts.] Draw the two most important resonance structures for each of the following. Indicate the most important resonance structure in each case.

a) CN^-



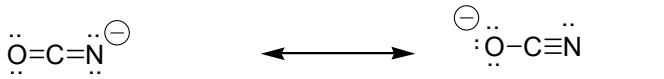
MORE IMPORTANT

b) CH_2OH^+



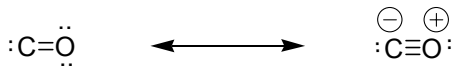
MORE IMPORTANT

c) OCN^-



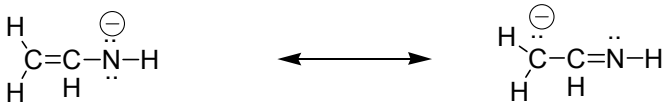
MORE IMPORTANT

c) CO



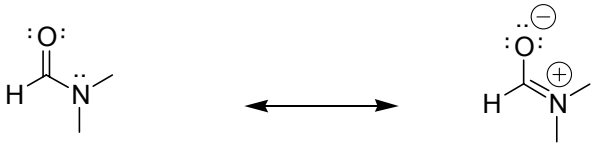
MORE IMPORTANT

d) CH_2CHNH^-



MORE IMPORTANT

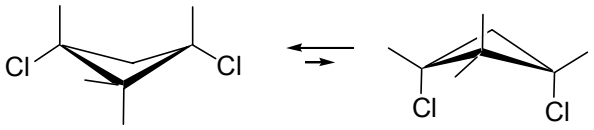
e) *N,N*-dimethyl formamide (DMF)



MORE IMPORTANT

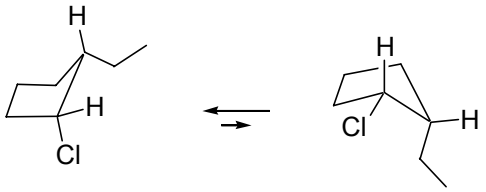
7) [14 pts.] Draw two conformations of each molecule in 3-dimensional representations and indicate which is more stable. Give the difference in free energy for the cyclohexane derivatives.

a) *cis*-1,3-dichloro-2,2-dimethylcyclobutane



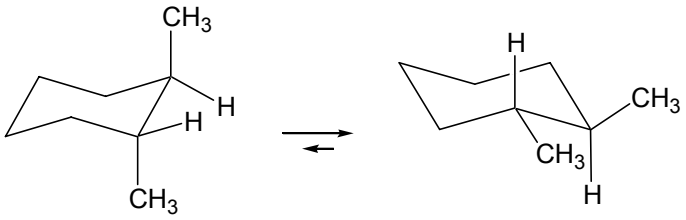
MORE STABLE

b) *cis*-1-chloro-2-ethylcyclopentane



MORE STABLE

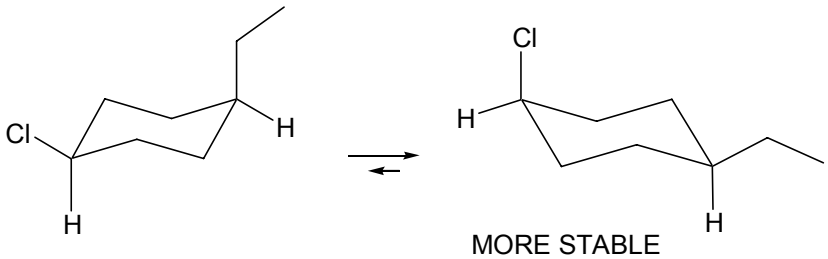
c) *trans*-1,2-dimethylcyclohexane (ΔG?)



MORE STABLE

ΔG = -1.74 - 1.74 + 0.87 kcal/mol
= -2.61 kcal/mol

d) *cis*-1-chloro-4-ethylcyclohexane (ΔG?)



MORE STABLE

ΔG = -1.75 + 0.52 kcal/mol
= -1.23 kcal/mol

8) [6 pts.] Draw a detailed, step-wise mechanism for the following reaction. Use curved arrows to indicate electron flow.