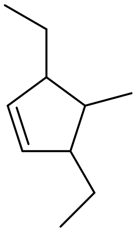
CHM 201 – Organic Chemistry I
Hour Exam II
14 October 2002

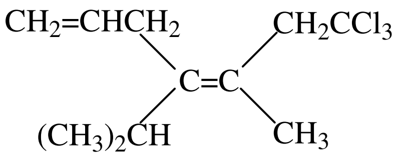
Name________________________

1.(16) Name the following compounds using I.U.P.A.C. nomenclature. Be sure to denote stereochemistry (*Z*, *trans* etc.) when appropriate.

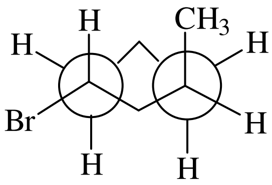
a)



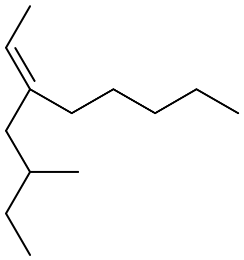
b)



c)



d)

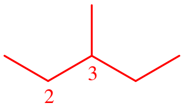


a) 3,5-diethyl-4-methylcyclopentene
b) (E) 7,7,7-trichloro-4-isopropyl-5-methyl-1,4-heptadiene
c) *Trans* 1-bromo-3-methylcyclohexane
d) (E) 3-(2-methylbutyl)-2-octene

2.(16) Consider the molecule **3-methylpentane** citing along **C_2-C_3**. Construct all six rotational conformers using Newman projections. **Also**, identify the *highest* and *lowest* energy conformations and determine the energy difference (KJ/mol) between the two. *Please be sure to draw the correct molecule!* The original exam had different values; use these.

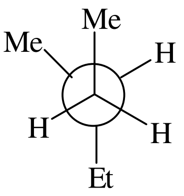
Interaction	**Energy cost (KJ/mol)**
methyl-methyl *gauche*	3.8
methyl-ethyl *gauche*	4.2
methyl-H *eclipse*	6.0
ethyl-H *eclipse*	6.4
methyl-methyl *eclipse*	11.0
methyl-ethyl *eclipse*	12.0
H-H *eclipse*	4.0

For my structures, I held the front carbon (C-2) still and rotated the rear carbon (C-3) clockwise.

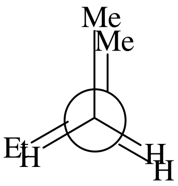


Me = methyl
Et = ethyl

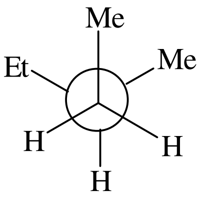
$\Delta E = 17.2$ KJ/mol



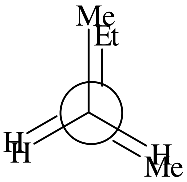
3.8



21.4



8.2



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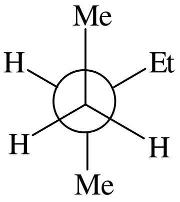
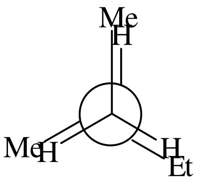


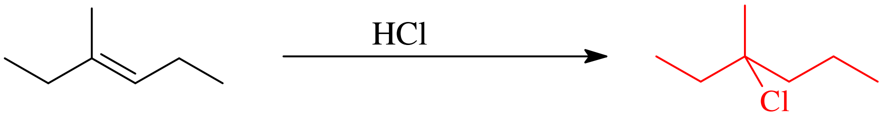
4.2



18.4

3.(12) Give the major product for the following reactions:

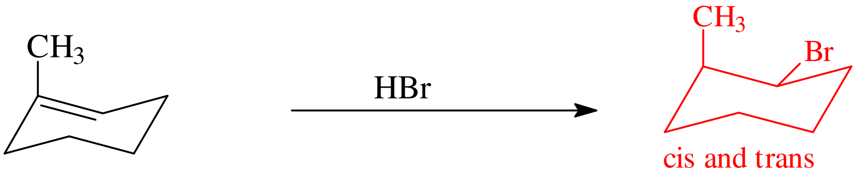
a)



b) 

$CH_2{=}CHCH_2CH_2CH_3 \xrightarrow{HBr} CH_3\overset{Br}{C}HCH_2CH_2CH_3$

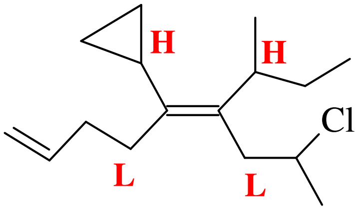
c)



cis and trans

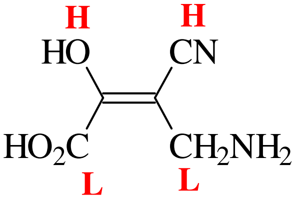
4.(10) Identify the high and low priority substituents and assign (*E*) or (*Z*) in the following molecules:

a)



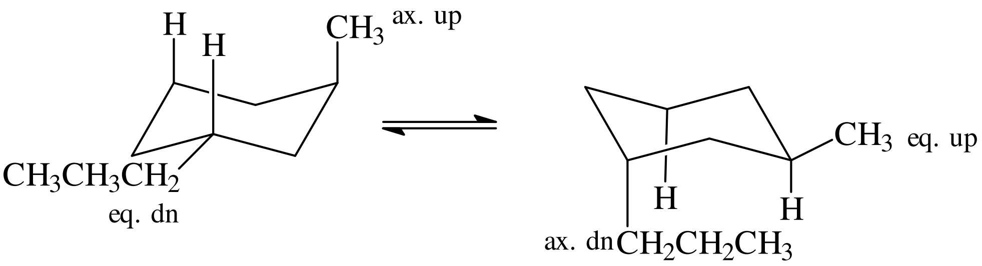
(Z)

b)



(Z)

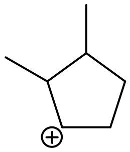
5.(14) The molecule ***trans*1-methyl-3-propylcyclohexane** can exist in two conformations that have a **difference in energy of only 1.0 KJ/mol**. Draw the two chair conformations of this molecule and **label the alkyl groups** as axial-up, axial-down, equatorial-up, or equatorial-down. If the energy value of a 1,3-diaxial interaction between a methyl group and a hydrogen is 3.8 KJ/mol, what is the value of a 1,3-diaxial interaction between a propyl group and a hydrogen.

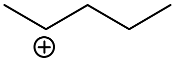


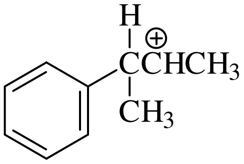
2 x 3.8 KJ/mol = 7.6 KJ/mol

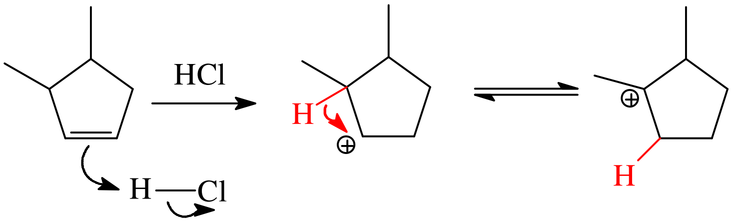
8.6 KJ/mol (given)
ergo each Pr-H 1,3 diaxial is **4.3 KJ/mol**

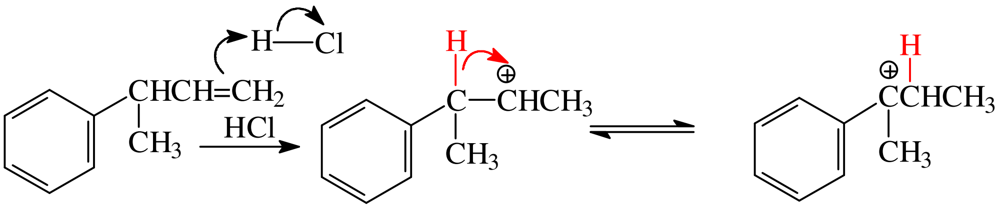
6.(10) Carbocations tend to undergo 1,2-hydride shifts or 1,2,-methide shifts in order to achieve greater stability. From the carbocations below, identify the *two* species that you would expect to undergo a rearrangement and draw the rearranged cation below it.











7.(12) Give the structures of the alkenes that would most likely give rise to the above carbocations (question #6) as the major intermediate upon protononation with HCl.
See above.

8.(16) Consider the free radical halogenation (X_2) of **methane** with both **fluorine (F_2)** and **bromine (Br_2)**. Use the information below and the data table provided to answer the following questions. $CH_4 + X_2 \longrightarrow CH_3X + HX$

All values are in KJ/mol

X_2 ----------------> $X^{\cdot}$ + $X^{\cdot}$

+438 -569 (-366)

i) $X^{\cdot}$ + CH_4 --------------> HX + $CH_3^{\cdot}$

+157 (+193) -456 (-293)

ii) $CH_3^{\cdot}$ + X_2 -------------> CH_3X + $X^{\cdot}$

X=	**F**	**Br**
ΔH_i	-131	+72
ΔH_{ii}	-299	-100
ΔH_{rxn}	**-430**	**-28**

a) Using the two propagation steps shown above (i and ii), calculate ΔH_i and ΔH_{ii}. and ΔH_{rxn} for the reaction with both F_2 and Br_2 (see BDE values on next page).

b) Are the reactions endo- or exothermic overall? exothermic

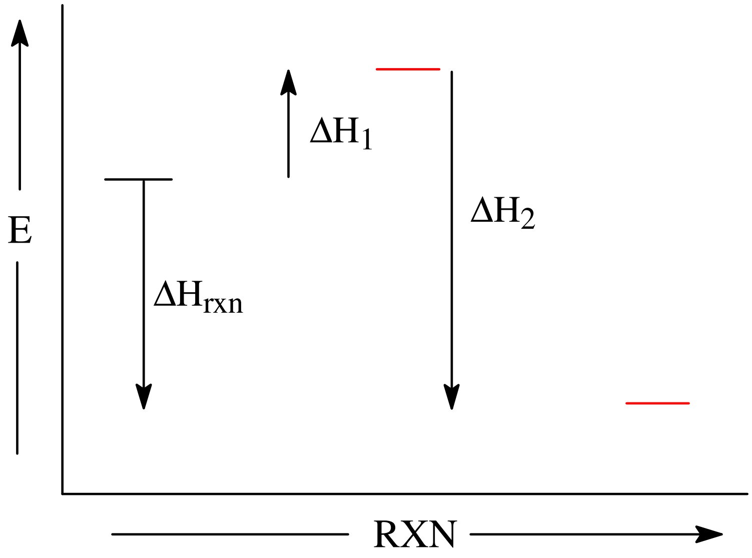
c) Which step is the rate determining step in the **bromination** reaction?

Step i) It has a higher Energy of activation

d) Which reaction is likely *not* a safe reaction to carry out in the lab? Why?

Fluorination. The rate determining step is exothermic and the overall ΔH is extremely negative.

e) On the axes below, construct a reaction profile for the **bromination** propagation steps. Keep your profile roughly to scale. With vertical arrows, **Label ΔH°** for step i, ii, and for the overall reaction. (Connect each step with curved line).



Bond	**Bond Dissociation Energy (KJ/mol)**
CH_3-H	438
CH_3-Br	293
CH_3-F	456
H-Br	366
H-F	569
Br-Br	193
F-F	157