Chemistry 3351-100
Organic Chemistry / Dr. Barney Ellison
Thursday: Sept. 25th @ 7:00pm → 9:00 / 1st Exam / Hellems 252

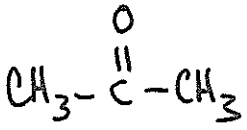
Name: Key (please print)

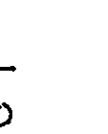
1. (20 pts)

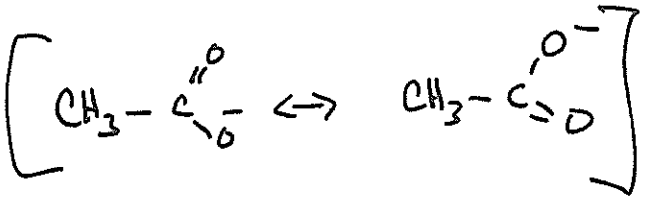
Arrange the following compounds in order of increasing C-O bond length.

a) CH_3OCH_3 b) CH_3COCH_3 c) $CH_3CO_2^-$ d) CO

Write the structures.

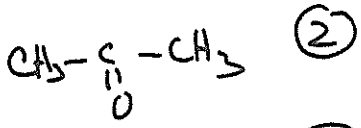


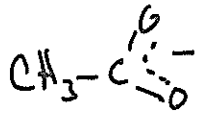




Bond order?

CH_3-O-CH_3 (1)

 (2)

 (1½)

$:C\equiv O$ (3)

C-O Bond Lengths

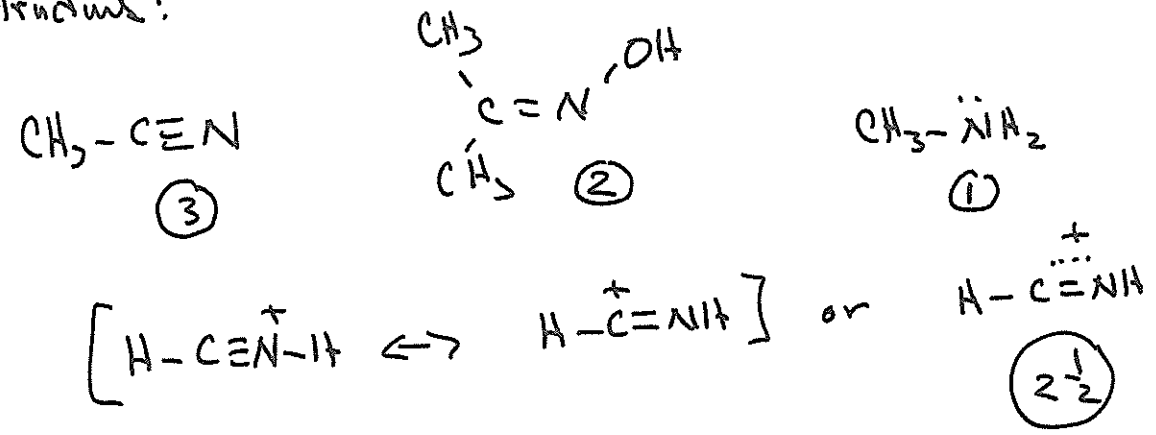
$C\equiv O < CH_3COCH_3 < CH_3CO_2^- < CH_3O$

shortest longest

Arrange the following compounds in order of increasing C-N bond length.

a) CH_3CN b) $(CH_3)_2C{=}NOH$ c) $HCNH^+$ d) CH_3NH_2

Structures:



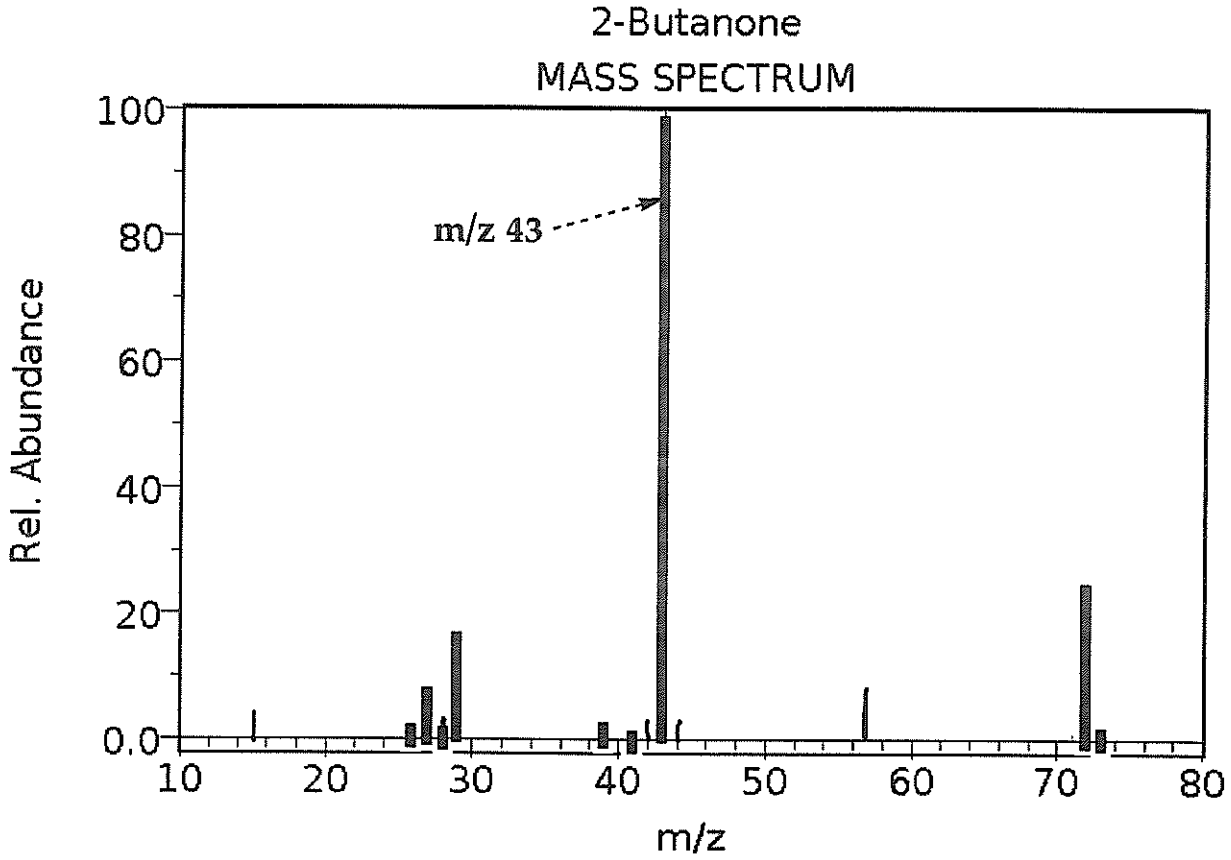
C – N Bond lengths

$CH_3C{\equiv}N < HC\overset{+}{N}H < (CH_3)_2C{=}NOH < CH_3{-}NH_2$

shortest

longest

2. (10 pts) Consider the mass spectrum of 2-butanone, CH_3CH_2-CO-CH_3. Notice that the most intense peak is m/z 43. To what portion of the 2-butanone does such a mass correspond?

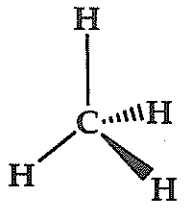


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

m/z 43 is CH_3CO^+

$$\left[CH_3 - \overset{+}{C}=O \leftrightarrow CH_3C\equiv O^+ \right]$$

3. (10 pts) Write structural formulae corresponding to the following. I have done methane as an example:



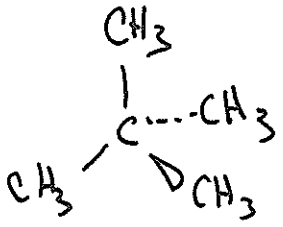
a) neopentane

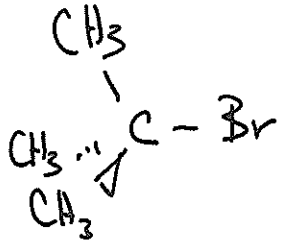
b) *tert*-butyl bromide

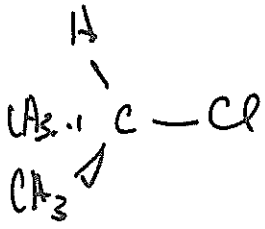
c) isopropyl chloride

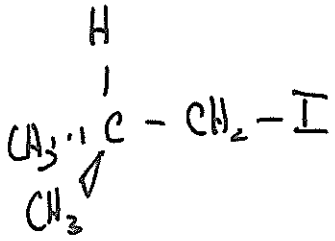
d) isobutyl iodide

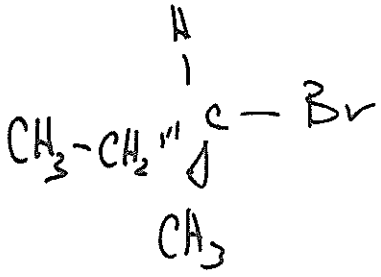
e) *sec*-butyl bromide

(a) 

(b) 

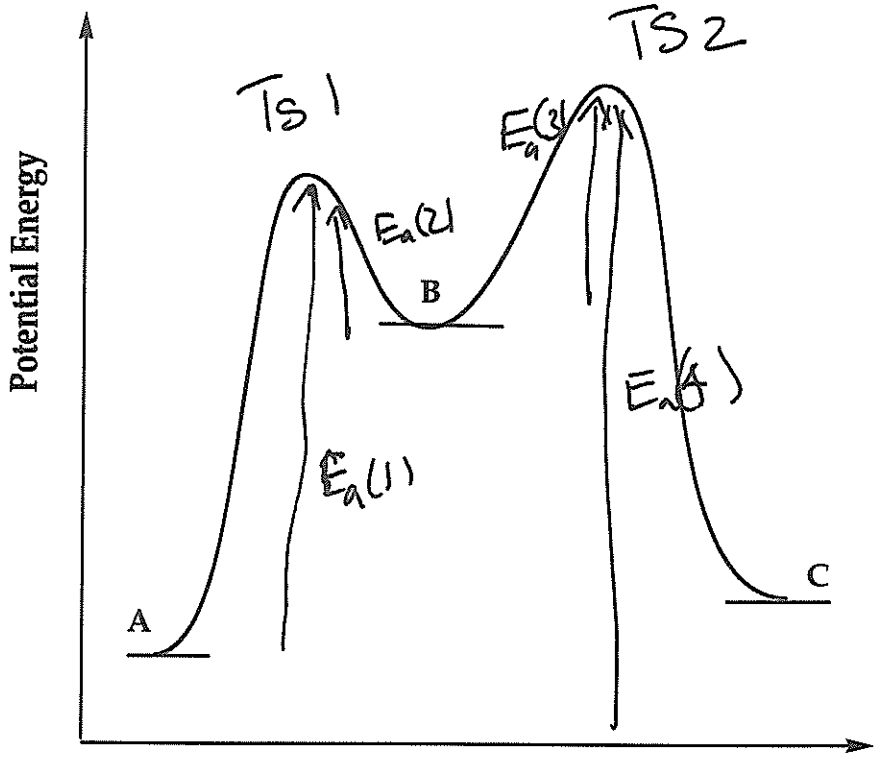
(c) 

(d) 

(e) 

4. (15 pts) Consider the hypothetical two-step reaction.

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C$$



a) Is the overall reaction (A → C) exothermic or endothermic? endothermic

b) Label the transition states. Which transition state is rate limiting? TS 2 is highest so is rate-limiting

c) What is the correct order of magnitude of the rate constants.

i) $k_1 > k_2 > k_3 > k_4$

ii) $k_2 > k_3 > k_1 > k_4$

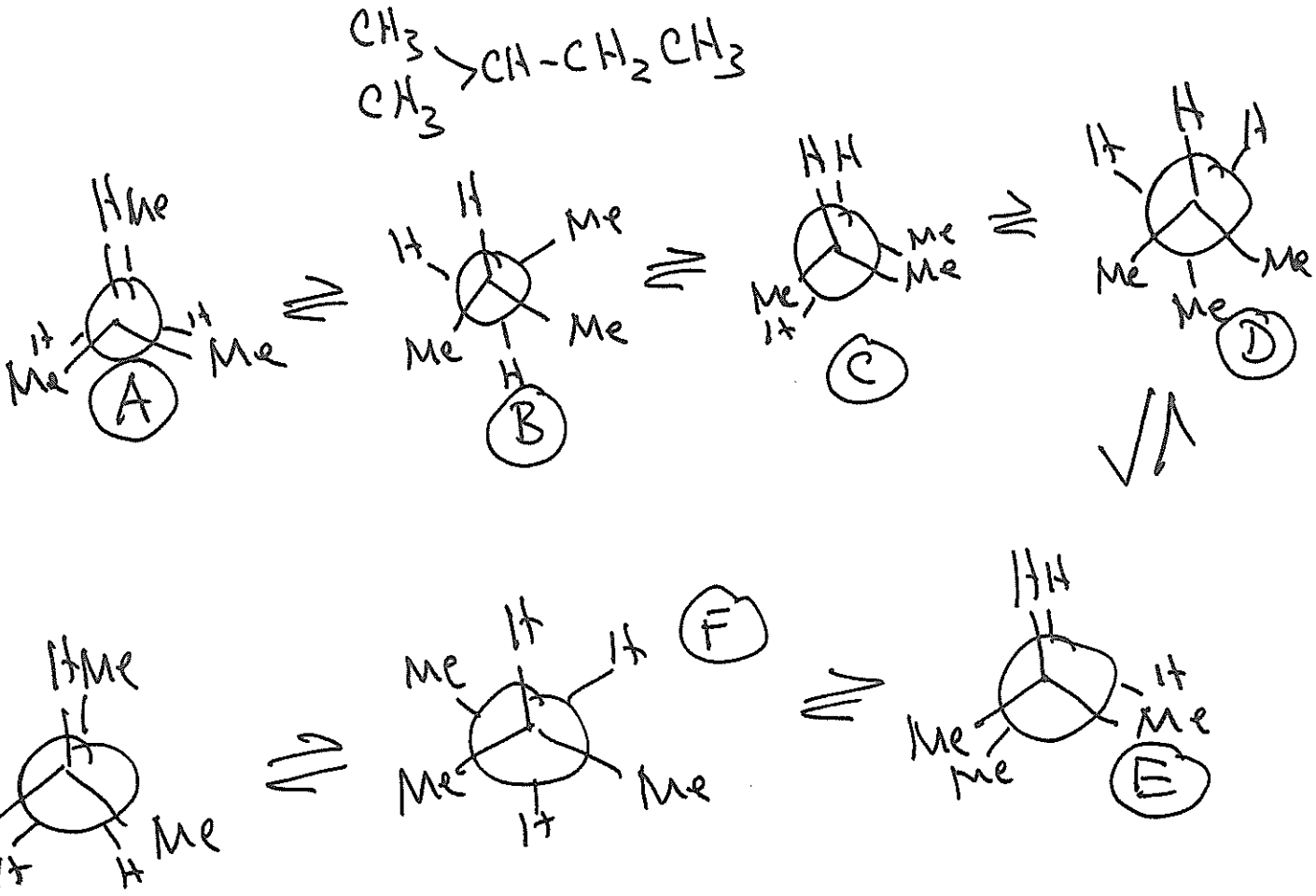
iii) $k_4 > k_1 > k_3 > k_2$

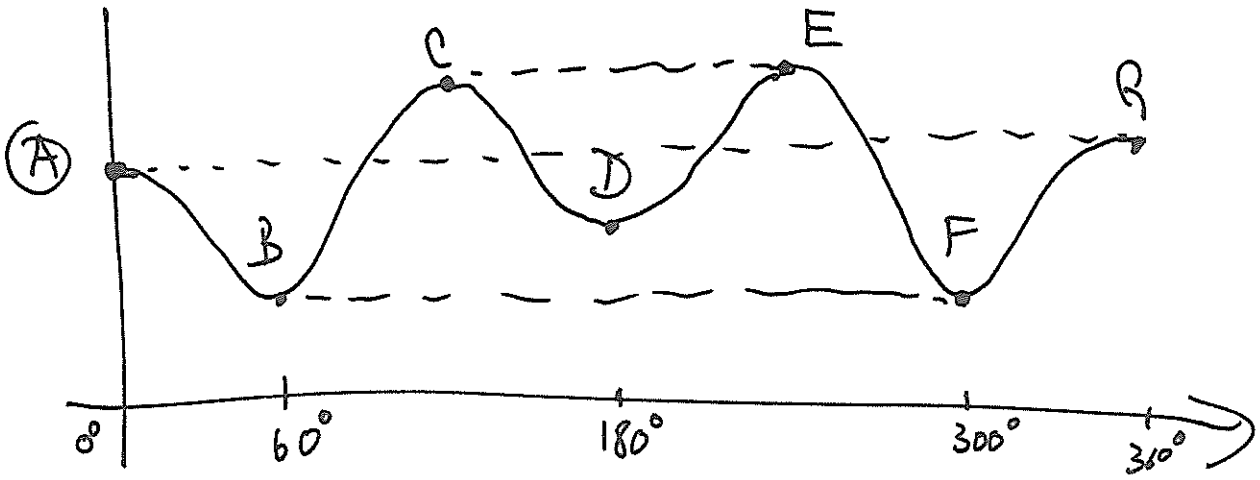
iv) $k_3 > k_2 > k_4 > k_1$

d) Which is the thermodynamically most stable compound? A most stable

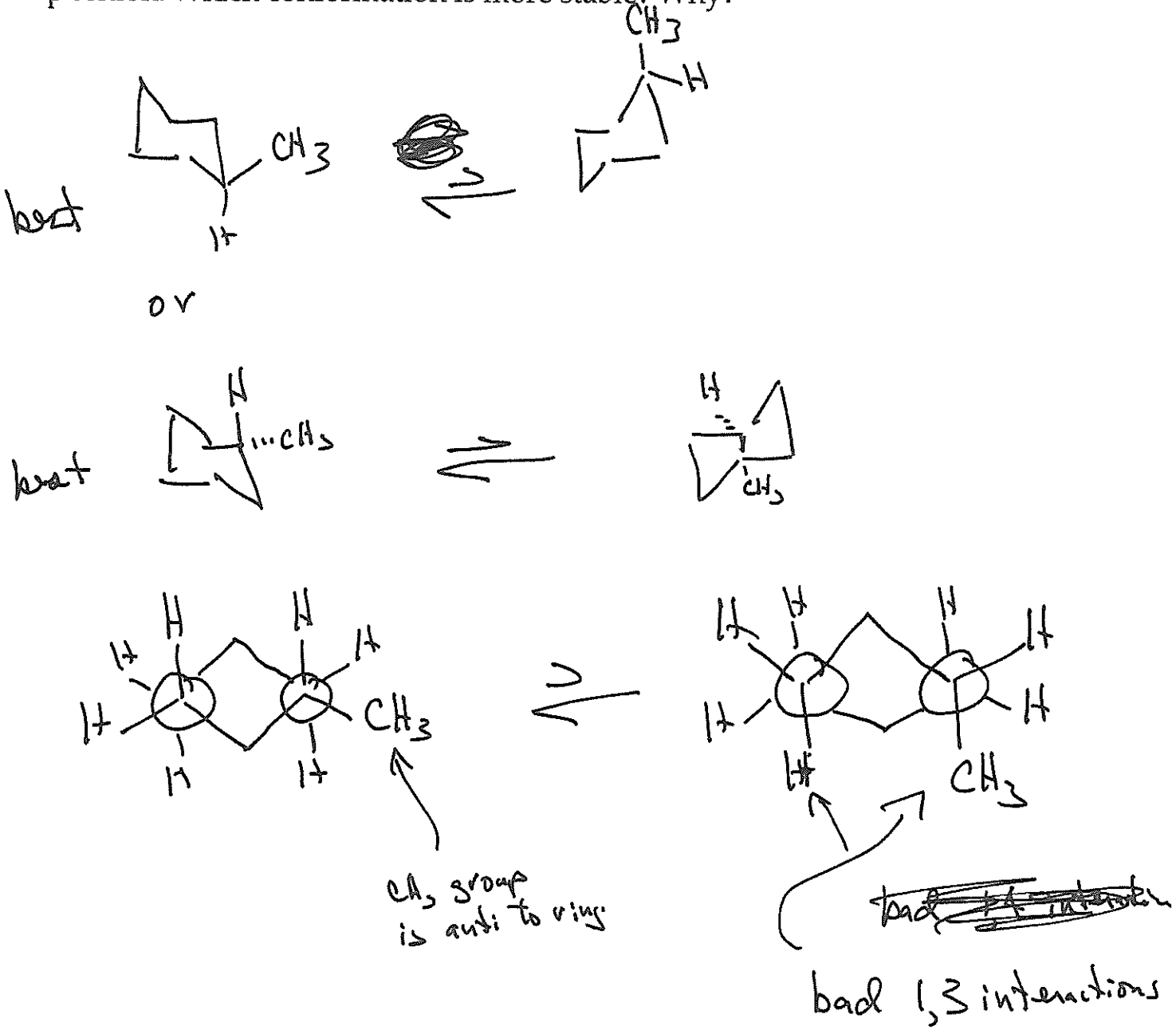
e) Which is the thermodynamically least stable compound? B least stable

5. (10 pts) Using Newman projections, draw a potential energy diagram for rotation about the C_2—C_3 bond of 2-methylbutane.

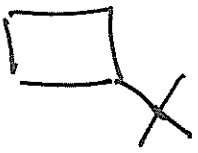


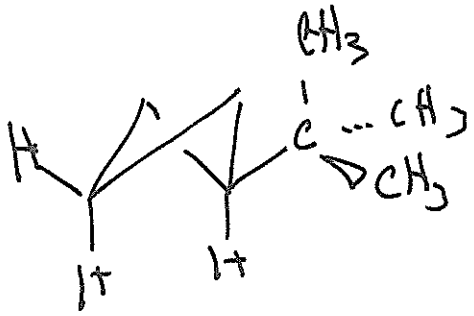


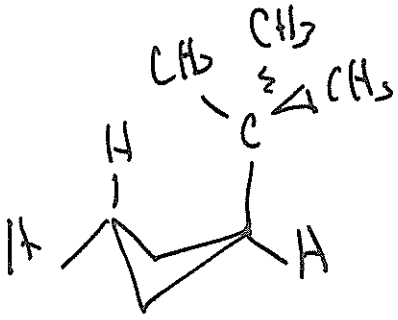
6. (10 pts) Draw a Newman projection for the C_1—C_2 bond of methylcyclohexane with the methyl group in the equatorial position. Compare this with the ring flipped so the methyl group is in the axial position. Which conformation is more stable? Why?



7. (10 pts) Consider the molecule, *tert*-butyl-cyclobutane. What are the two conformations of this ring? Which conformation is more stable?





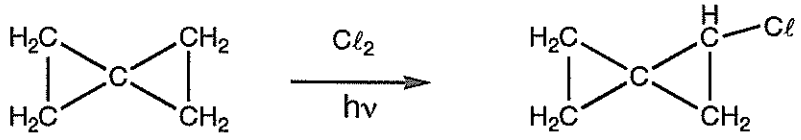


more stable

less stable

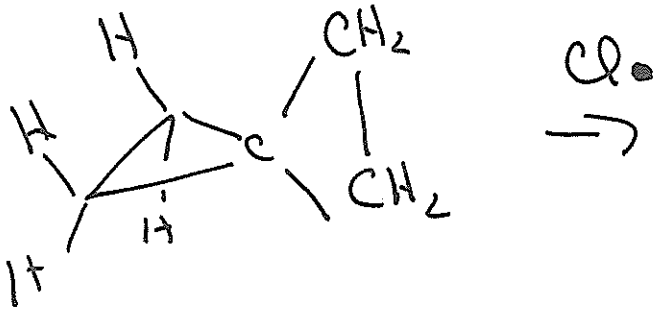
bad 1,3 interaction

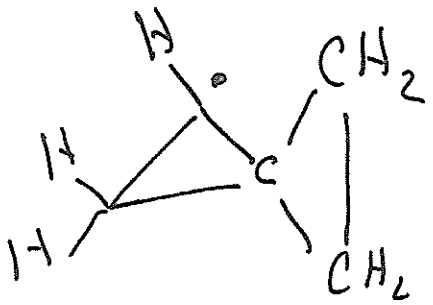
8. (10 pts) The reaction of the unusual hydrocarbon, spiropentane with chlorine and light is a nice method to prepare chlorospiropentane.



a) Why is this reaction so useful? all the Hs are the same.

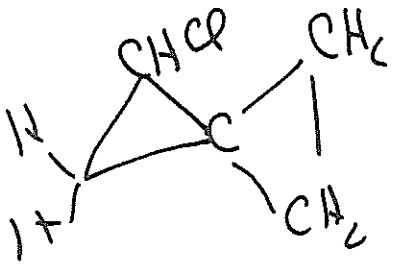
b) Draw me the reaction mechanism. Assume that you have a large excess of spiropentane. $Cl_2 + h\nu \rightarrow 2Cl\cdot$





$\downarrow Cl_2$

Remember you have to have an excess of the hydrocarbon.

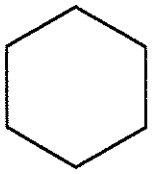


$+ Cl\cdot$

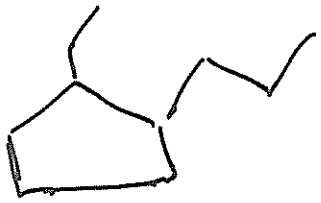
$\downarrow$

& continues the chain

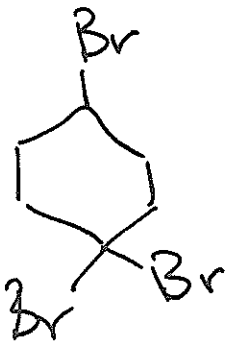
9. (5 pts) Write line structures for each of the following compounds. I have done cyclohexane as an example.



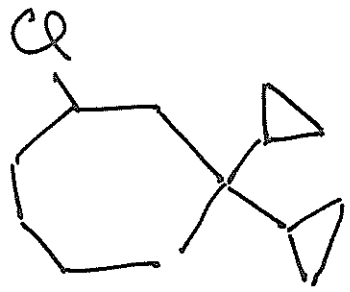
a) 1-ethyl-2-propylcyclopentane



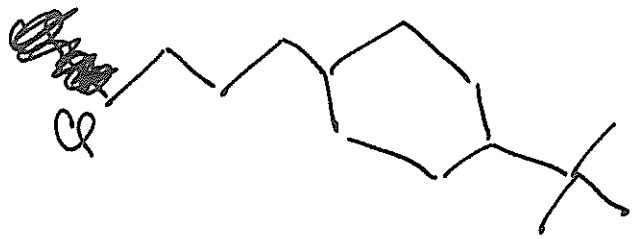
b) 1, 1, 4-tribromocyclohexane



c) 3-chloro-1,1-dicyclopropylcycloheptane



d) 1-(3-chloropropyl)-4-*tert*-butylcyclohexane



e) cyclotetradecane 14 carbons