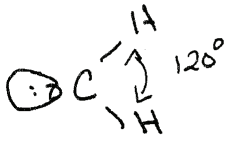
Chemistry 3311-100
Organic Chemistry / Dr. Barney Ellison
Thursday: Feb. 11th @ **7:00pm → 9:00** / 1st Exam / Math 100)

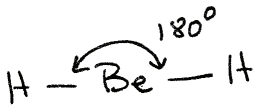
Name: Key (please print)

1. (10 pts) Predict the approximate bond angles in each of the following molecules:

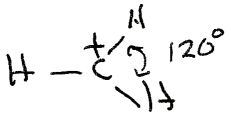
a) $:CH_2$



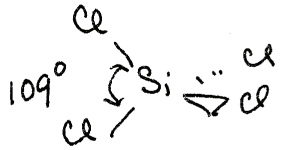
b) BeH_2



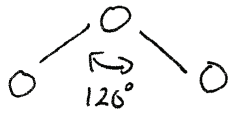
c) CH_3^+



d) $SiCl_4$

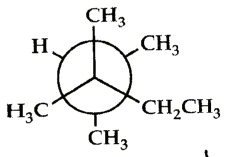


e) O_3 (ozone)



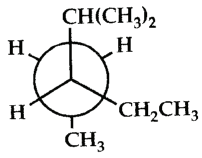
2. (10 pts) Within each set, which two structures represent the same compound?

a)

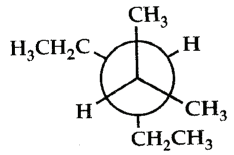


2,3,3 trimethylpentane

A

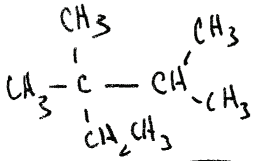


B

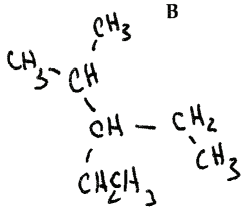


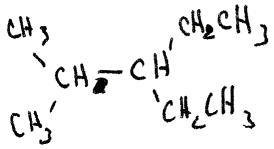
3-ethyl-2 methyl-pentane

C



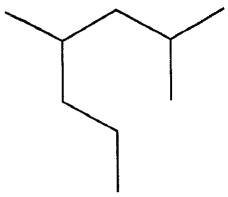
different



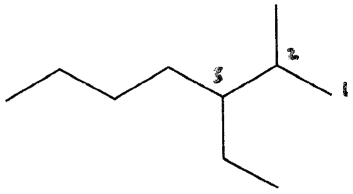


B = C are the same

b)

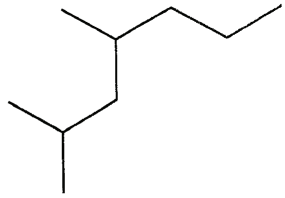


A



B

3-ethyl-2-methylheptane



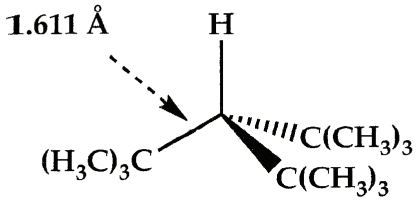
C

2,4-dimethylheptane

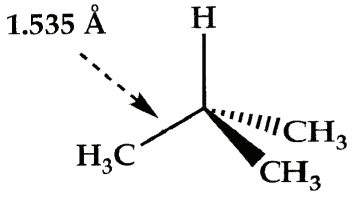
A = C

B is different

3. (10 pts) When the structure of compound A was determined in 1972, it was found to have an unusually long C—C bond and unusually large CCC bond angles when compared with compound B (isobutane)? Rationalize these findings.

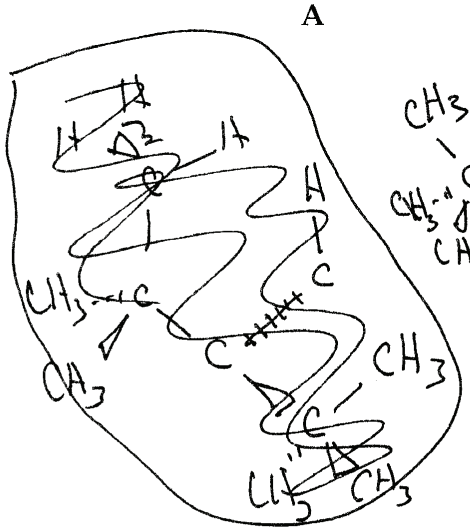


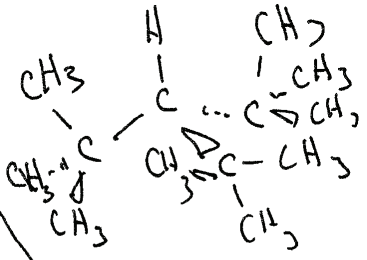
CCC angle = 116°



CCC angle = 110.8°

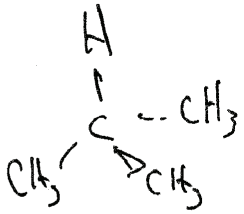
A





severe repulsion of $-C(CH_3)_3$ groups

B



little repulsion from $-CH_3$ groups

4. (12 pts) Arrange the compounds in each of the following sets in order of decreasing pK_a, highest first. Explain your reasoning.

a) CH_3CH_2OH, $C\ell_2CHCH_2OH$, $C\ell CH_2CH_2OH$

$CH_3CH_2OH < ClCH_2CH_2OH < Cl_2CHCH_2OH$

less acidic — more acidic

inductive effect

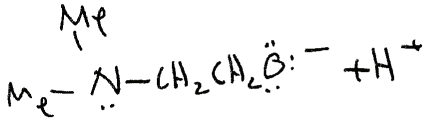
b) $C\ell CH_2CH_2SH$, CH_3CH_2OH, CH_3CH_2SH (ROH less than RSH)

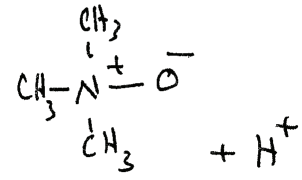
$CH_3CH_2OH < CH_3CH_2SH < ClCH_2CH_2SH$

less acidic — more acidic

c) CH_3CH_2OH, $(CH_3)_2N\text{-}CH_2CH_2OH$, $(CH_3)_3N^+—OH$

inductive effect makes OH more acidic

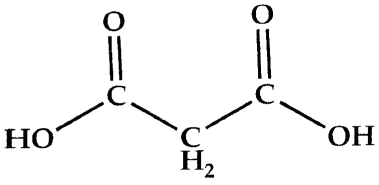




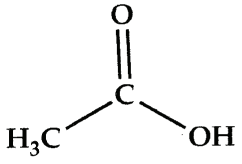
most acidic

$CH_3CH_2OH < CH_3\text{-}N(CH_3)CH_2CH_2OH < CH_3\text{-}N^+(CH_3)_2\text{-}OH$

5. (18 pts) Malonic acid has two carboxylic acid groups and consequently undergoes two ionization reactions. The pK_a for the first ionization is 2.86, the pK_a for the second ionization is 5.70. The pK_a for acetic acid is 4.76.

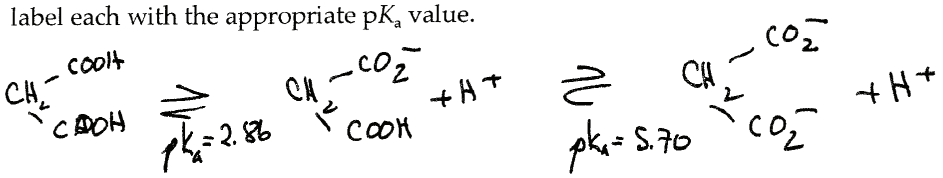


malonic acid



acetic acid

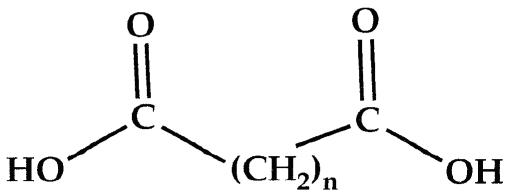
a) Write out the equations for the first and second ionizations of malonic acid, and label each with the appropriate pK_a value.



b) Why is the first pKa of malonic acid much lower than the pK_a of acetic acid but the second pK_a of malonic acid is much higher than the pK_a of acetic acid?

First pk_a of 2.86 is lower than acetic acid because conjugate anion, $CH_2(CO_2^-)(COOH)$ is stabilized by electron withdrawing group. But the 2nd pk_a of 5.70 produces a doubly charged anion, $CH_2(CO_2^-)_2$

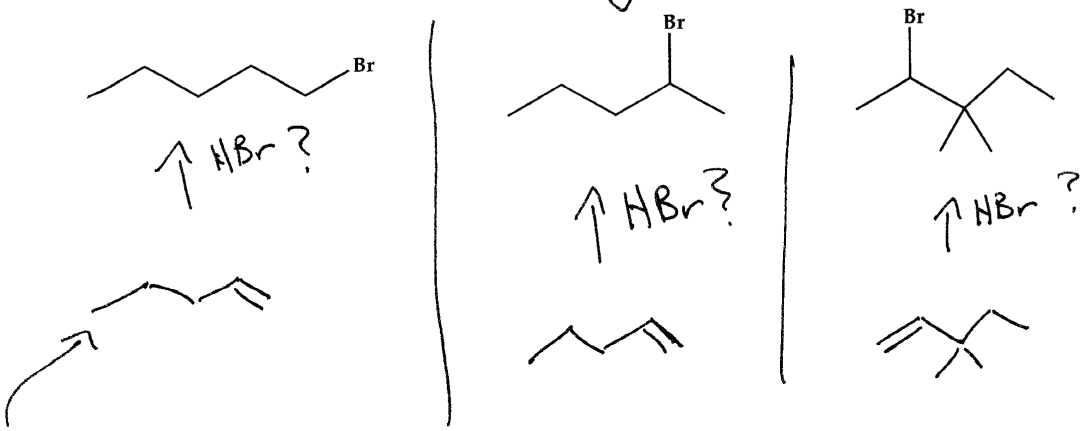
c) Malonic acid is a dicarboxylic acid.



How would the difference between the first and second pK_a values change as n increases?

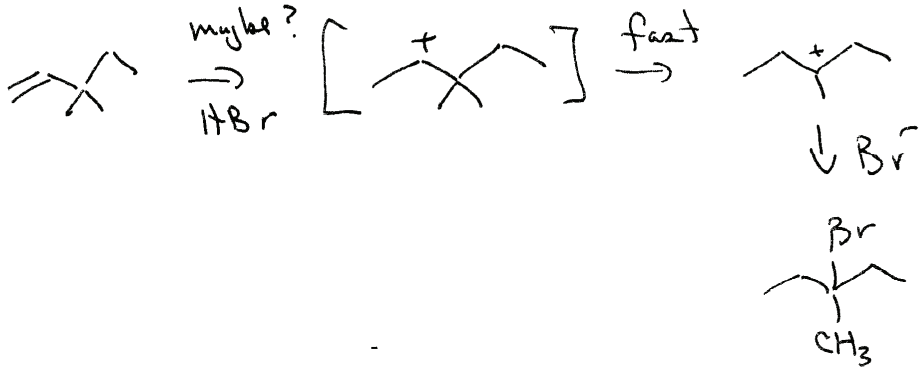
As n increases, the pk_a's both approach acetic acid, 4.76

6. (10 pts) Only one of the following three alkyl halides can be prepared as the major product of the addition of HBr to an alkene. Which compound can be prepared in this way? Explain why the other two cannot be prepared in this way.

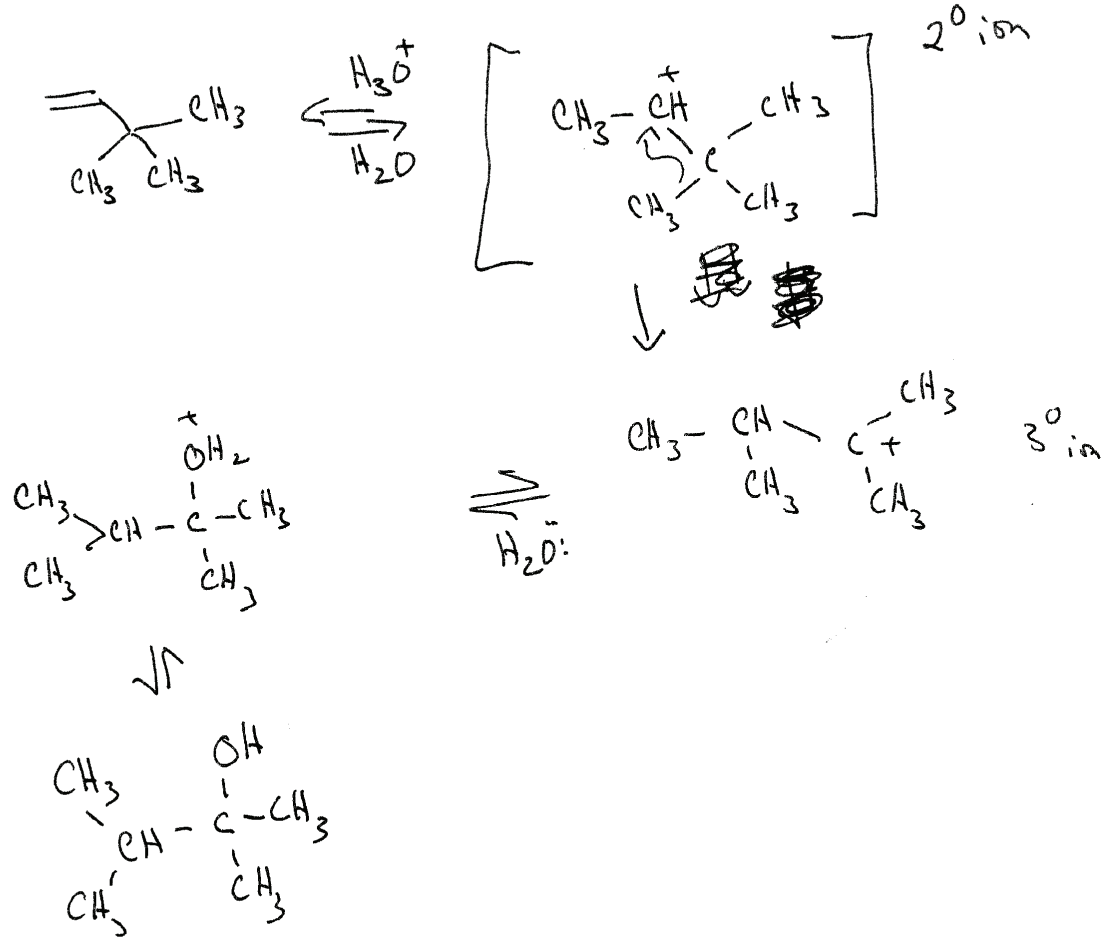


A. Only alkene possible is $CH_3CH_2CH_2CH=CH_2$ ↓ HBr

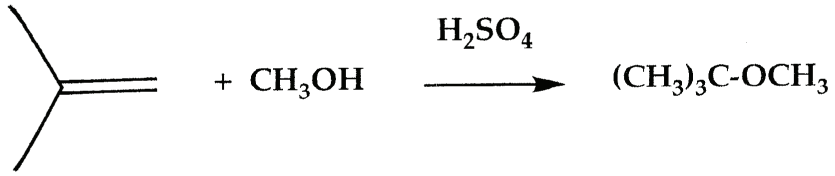
B. $CH_3CH_2CH_2\underset{Br}{CH}-CH_3$ only because $CH_3CH^+CH_3$ + never formed ↓ can't get Br

C. 

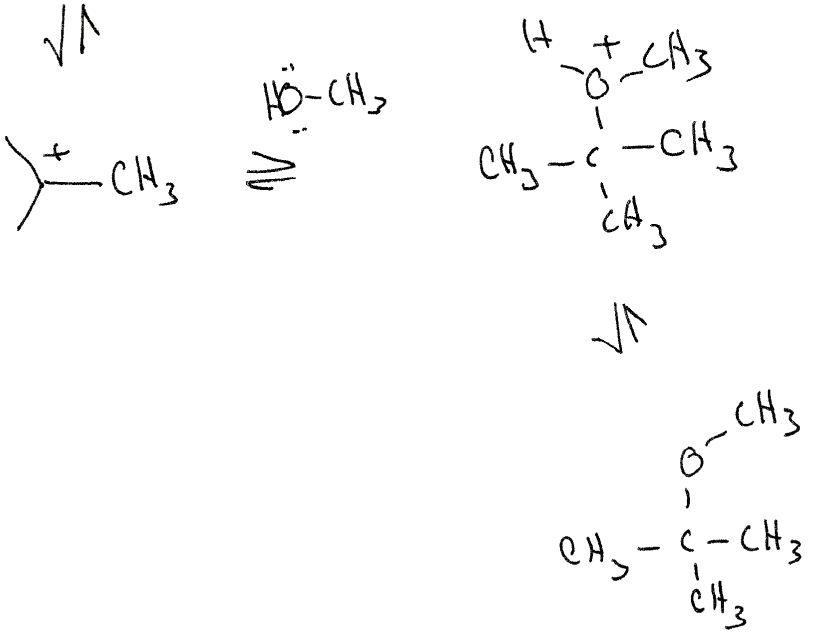
7. (10 pts) The alkene 3,3 dimethyl-1-butene undergoes acid-catalyzed hydration with rearrangement. Show the product of the rearrangement and write a mechanism.



8. (10 pts) The industrial synthesis of methyl *tert*-butyl ether is:



Write a mechanism.



9. (10 pts) Write a mechanism for the following reaction.