Version A

CHM 2120
MIDTERM
Sept 28, 2011

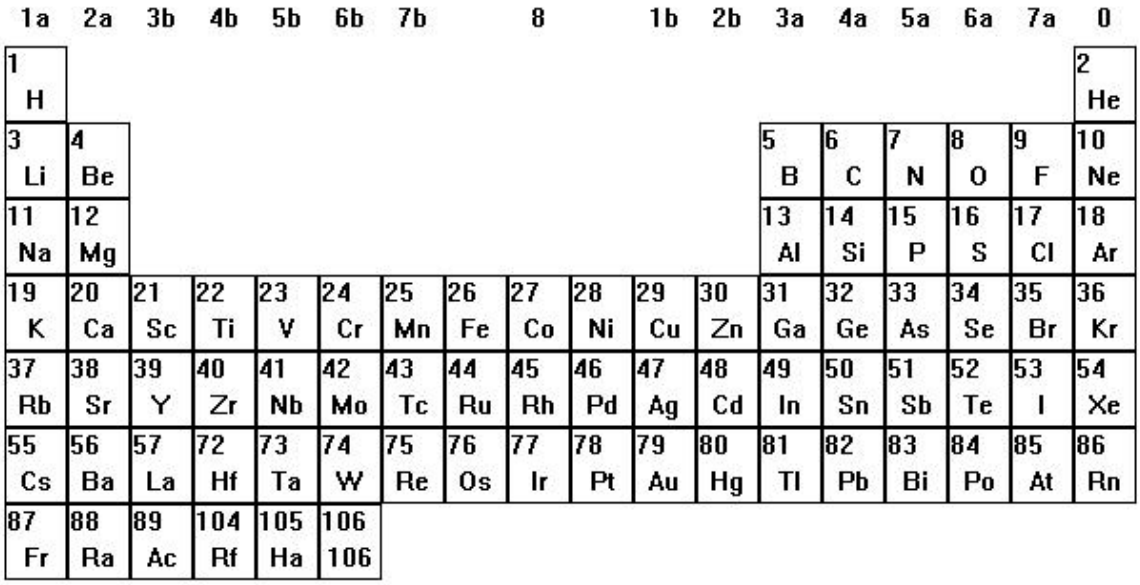
Name:_____ **Seat:**_____

Student number:_____

Approximate total number of marks: 60

Notes:

- For questions in which mechanisms are not required, part marks might be given for incorrect answers with plausible mechanisms.
- Re-marks requests might not be granted for midterms written in pencil (all questions will be re-graded if a re-mark is requested).

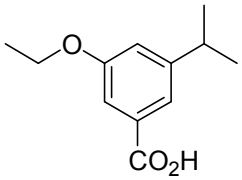


pK_a table

Acid	**pK_a**
HCl	-8
ROH_2^+	-2
H_3O^+	-1.75
RCOOH	5
R_3NH^+	10-11
H_2O	15.75
ROH	16-18
H_2	36
RNH_2	35-40
RCH_3	55

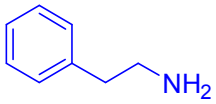
Name or draw the structure of the following molecules, as appropriate. **(4 points)**

a.



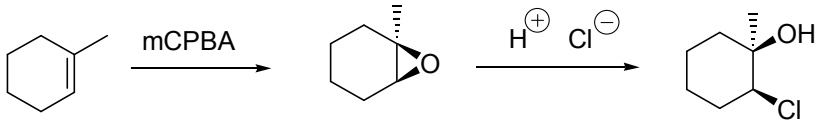
5-ethoxy-3-*iso*-propylbenzoic acid

b. 2-phenylethylamine



2.

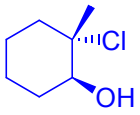
a. Explain why the following reaction will not work as shown. **(4 points)**
b. Give the true product of the reaction sequence. **(2 point)**
c. How would you make the desired chlorohydrin containing product from the alkene shown? **(4 points)**



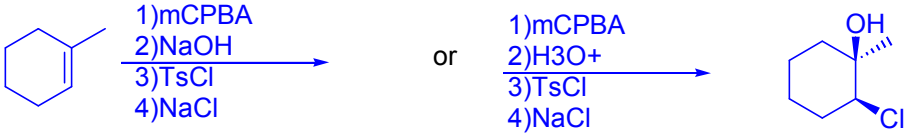
4 points for both, 2 points for giving 1 of the problems below

- Chlorine and alcohols are on the wrong carbon.
- Nucleophile opened epoxide with retention.

True product of reaction sequence.



Reaction sequence to generate alkyne containing compound.



one point each

3. What are the three criteria for aromaticity? **(6 points)**

    1. ring is planar
    2. all ring atoms have p orbital available
    3. 4n + 2 π electrons (n = 0, 1, 2...)

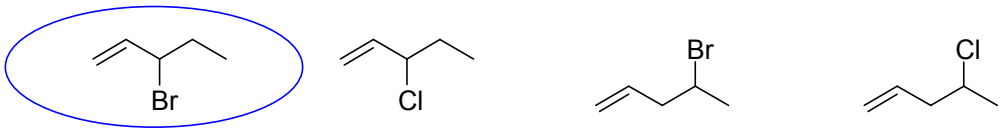
4.

a. Which is a better nucleophile? **(4 points)**

Explain your answer (very breifly – point form or with a figure) **(2 points)**

CF3 group removes e- density from oxygen via inductive effect thus it is less nucleophilc

b. Which will undergoe substitution chemistry fastest? **(4 points)**

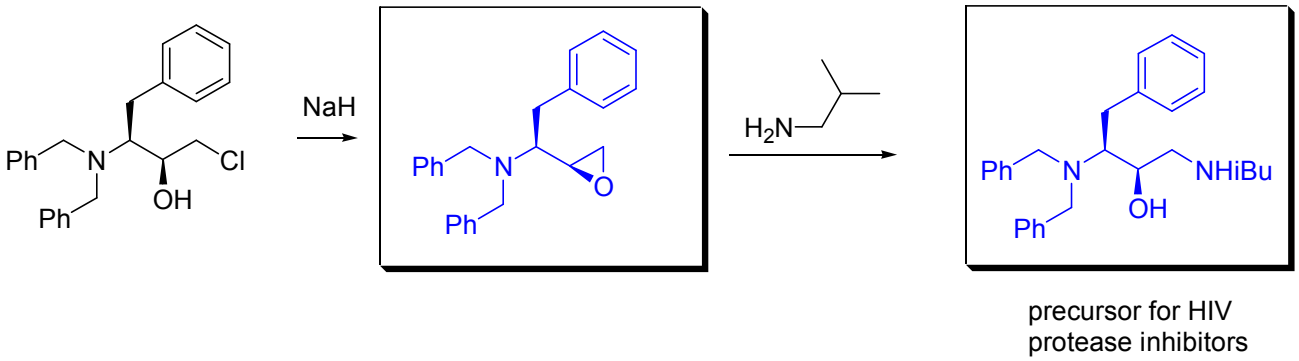


Explain your answer (very breifly – point form or with a figure) **(2 points)**

Br is a better LG than Cl, conjugate acid, HBr, has lower pks than HCl. Allylic LG, carbocation product is more stable due to resonance, easier for it to leave – better aswer – π orbital donates into LG σ* weakening bond

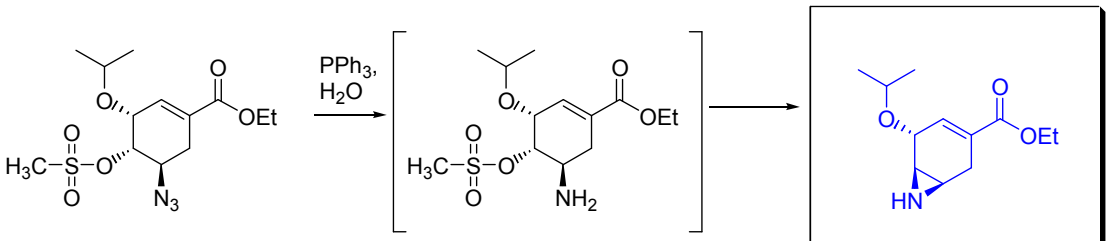
5. Provide the products or reagents for the following reaction pathway.

(4 points)



precursor for HIV protease inhibitors

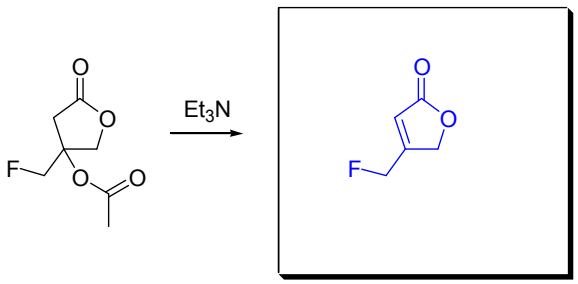
(2 points)



brackets indicate an unstable, un-isolatable, reactive intermediate

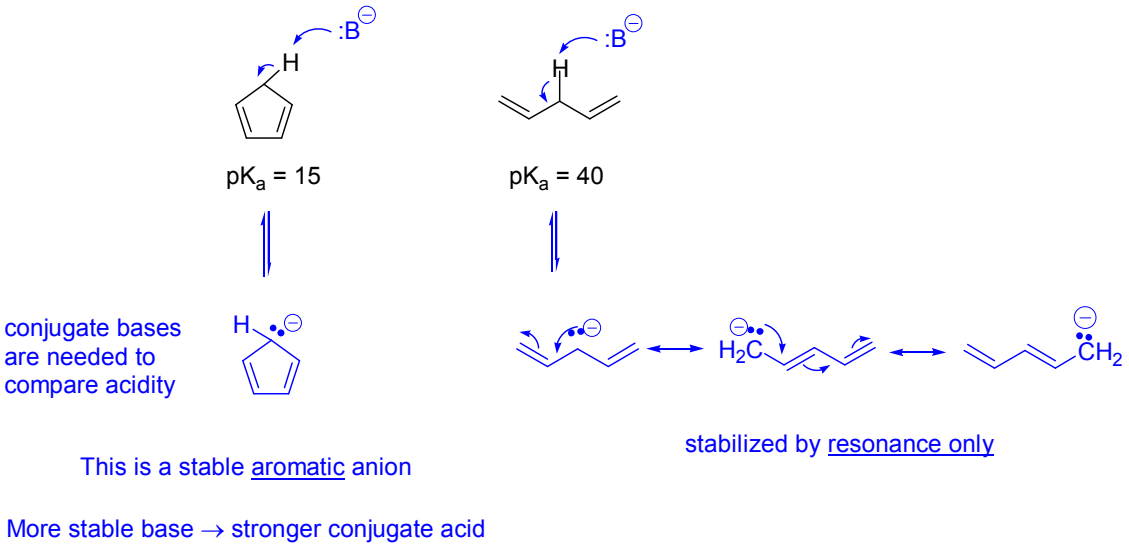
Precursor to Tamiflu

(2 points)



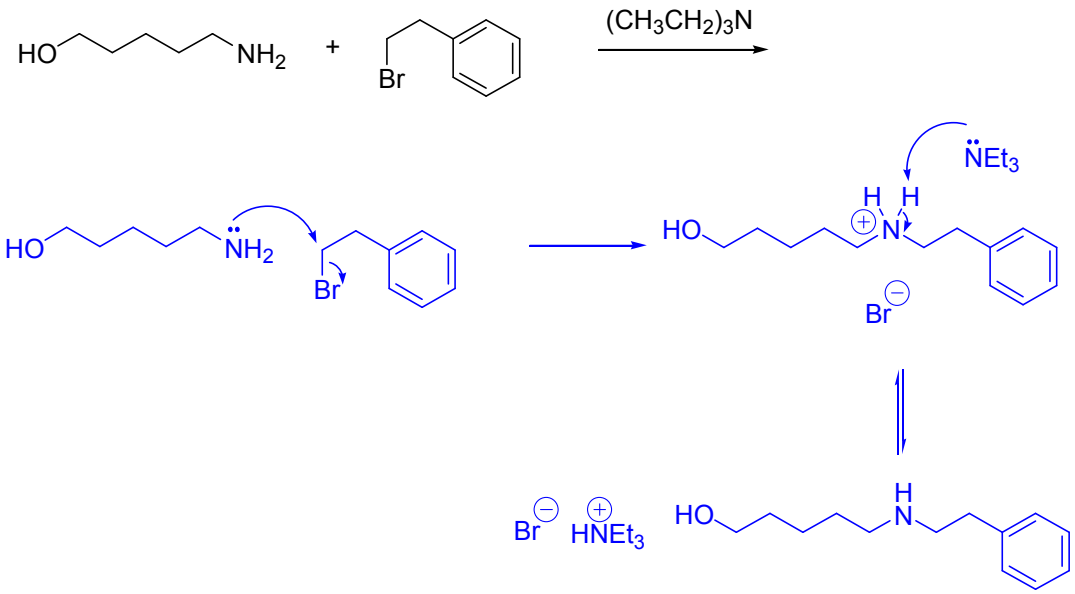
Precursor to carmegliptin an oral antidiabetic agent

6. The pK_a of the indicated proton on the sp^3-hybridized carbon in cyclopentadiene is 15, while the pK_a of the proton on the sp^3-hybridized carbon in 1,4-pentadiene is 40. Explain why is one proton so much more acidic than the other. **(5 points)**

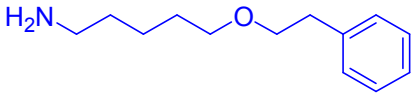


7.

a. Give the full detailed mechanism for the formation of the major product in the reaction below. **(5 pts)**



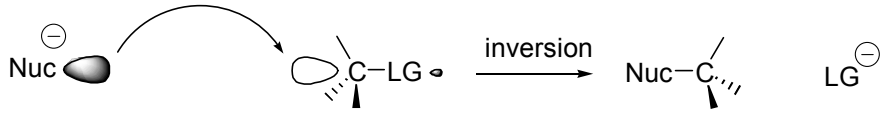
b. Show the product if NaH were used as the base, instead of $(CH_3CH_2)_3N$. **(2 points)**



8. Use orbital to show why backside attack occurs in S_N2 reactions and why the proton and leaving group must be antiperiplanar in an E2 reaction (**8 points**).

S_N2

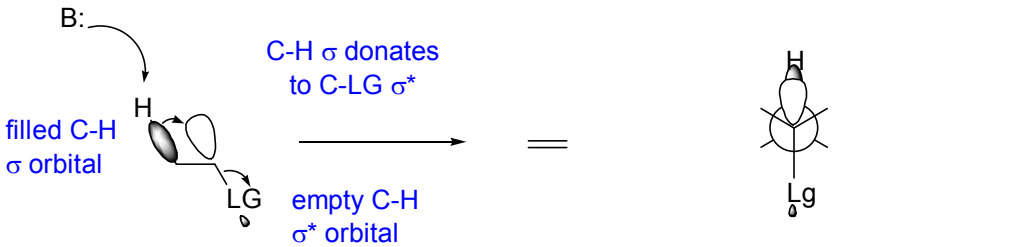
empty orbital is at the back side of the C-LG bond therefore nucleophile must approach from the back



filled lp or anion orbital

empty C-LG σ* orbital

E2



filled C-H σ orbital

empty C-H σ* orbital

antiperiplanar configuation is the only orientation where the C-H σ and C-LG σ* orbital align

BONUS: **(3 points)**

Provide a detailed mechanism for the following transformation: