

## CHEM 2311

## E3 practice-i (answered provided)

1. (32 points) Circle the letter *on the right* which corresponds to the answer to each question. There is only one correct answer for each question.

(i) Which of the following statements is **not** true?

- A.** The heterolysis of a bond between atoms which do not bear formal charges always produces a cation and an anion  
**B.** Carbocations are Lewis acids  
**C.** Carbon atoms of carbanions have a complete octet of valence shell electrons  
**D.** Nucleophiles seek centers of high electron density (*e.g.*, a negative charge).

**A**  
**B**  
**C**  
**D**

(ii) What is the approximate equilibrium constant ( $K_{eq}$ ) at 25 °C for a reaction with a  $\Delta G^\circ$  value of +10 kcal/mole. [*hmmmm, you do not need a calculator for this!!*]

- E.** -1      **F.**  $4 \times 10^{-8}$       **G.** 1      **H.**  $4 \times 10^8$

**E**  
**F**  
**G**  
**H**

(iii) Which of the following is the correct order of decreasing basicity (more basic > less basic)?

- I.**  $\text{NH}_3 > \text{MeNH}_2 > \text{H}_2\text{O} > \text{HF}$       **J.**  $\text{MeNH}_2 > \text{NH}_3 > \text{MeOH} > \text{CH}_4$   
**K.**  $\text{NH}_3 > \text{Me}_3\text{N} > \text{H}_2\text{O} > \text{MeOH}$       **L.**  $\text{CH}_3\text{COONa} > \text{NaOH} > \text{NaOMe} > \text{NaNMe}_2$

**I**  
**J**  
**K**  
**L**

(iv) Which of the following reactions corresponds to an addition reaction

- M.** 2° alkyl halide  $\rightarrow$  alkene      **N.** 3° alkyl halide  $\rightarrow$  3° alcohol  
**O.** ketone  $\rightarrow$  2° alcohol      **P.** 2° alcohol  $\rightarrow$  alkene

**M**  
**N**  
**O**  
**P**

(v) Which of the following is *not* a characteristic of  $\text{S}_{\text{N}}2$  reactions?

- Q.** rate is independent of the concentration of nucleophile  
**R.** chiral electrophiles undergo inversion  
**S.** alkyl fluorides are relatively unreactive  
**T.** iodide is a relatively good nucleophile

**Q**  
**R**  
**S**  
**T**

(vi) Which of the following is a characteristic of the reaction of 3° alkyl halides with water (hydrolysis)?

- U.** chiral electrophiles undergo inversion      **V.** alkyl fluorides are relatively unreactive  
**W.** the rate will be slower in a polar solvent      **X.** the rate will be slower at higher temperatures

**U**  
**V**  
**W**  
**X**

(vii) Which of the following is the strongest nucleophile?

- Y.** *tert*-butyl cation      **Z.** water      **AA.** Hydrogen sulphide,  $\text{H}_2\text{S}$       **BB.** ethylene

**Y**  
**Z**  
**AA**  
**BB**

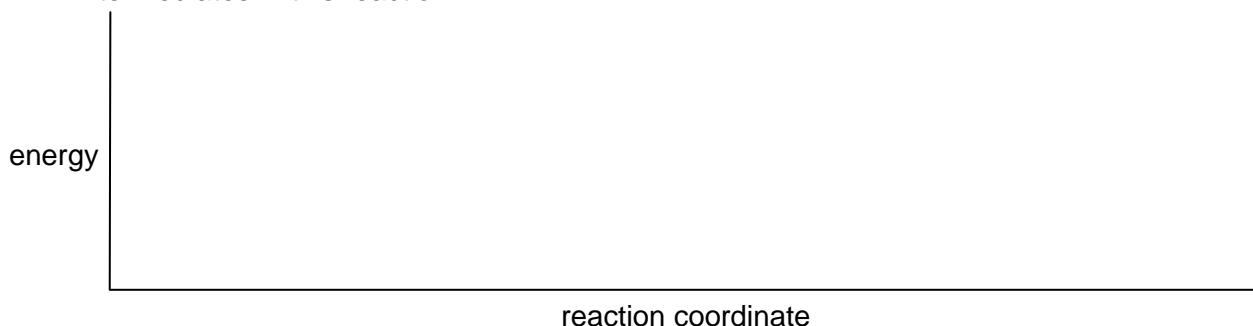
(viii) Which of the following is the strongest electrophile

- CC.** *tert*-butyl cation      **DD.** di-*tert*-butyl ether,  $(\text{CH}_3)_3\text{C-O-C}(\text{CH}_3)_3$   
**EE.** ethylene      **FF.** 2,3-dimethylbutane

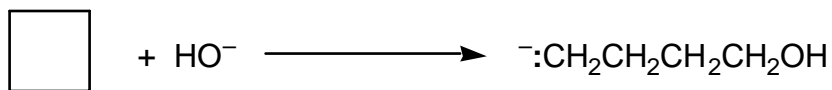
**CC**  
**DD**  
**EE**  
**FF**

2. (32 points). Give answers for each part of the question in the spaces provided.

- (a) Provide an energy – reaction coordinate diagram for the reaction of *tert*-butyl bromide with water to give *tert*-butanol. The diagram should accurately reflect the relative energy of starting materials, intermediates products, and transition states. Draw the structures of the *two* intermediates in this reaction



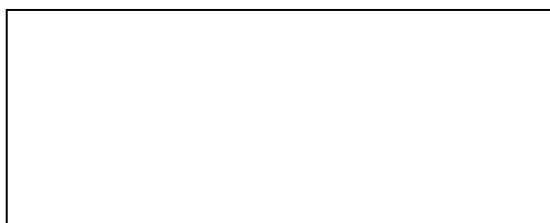
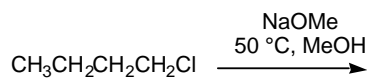
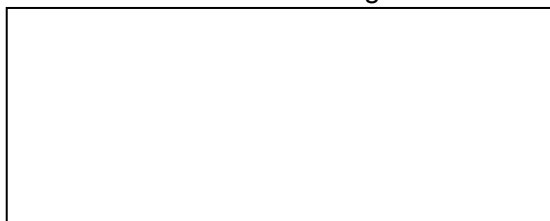
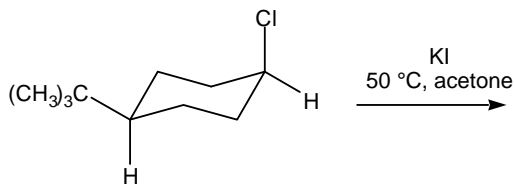
- (b) (i) Place curved arrows on the structures of the starting materials to account for the bonding changes in the following proposed reaction.



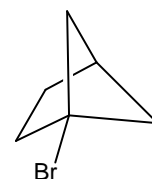
- (ii) *The reaction does not proceed.* Provide two reasons to explain why the reaction does not proceed

- \_\_\_\_\_  
 - \_\_\_\_\_

- (c) Provide the major organic product expected from each of the following reactions.

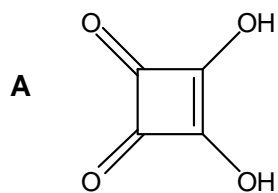


- (d) Although it is a tertiary alkyl bromide, 1-bromobicyclo[2.1.1]hexane is unreactive in S<sub>N</sub>1 reactions. Explain.

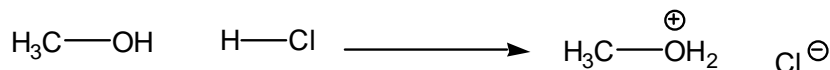
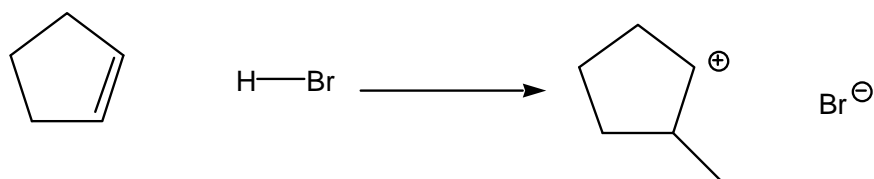


3. (32 points). Give answers for each part of the question in the spaces provided.

(a) Explain, with the aid of structures and a sentence (or two), why compound **A** is a stronger acid than a simple diol.



(b) Show curved arrows to account for the changes in bonding which take place in each of the following elementary reaction steps (note: you will need to add lone pairs to the structures as appropriate).



(c) Draw the chemical equation which represents the acid-base reaction involved when each of the following are mixed. Indicate whether  $K > 1$  or  $K < 1$ .

(i) aqueous  $\text{NaOH} + \text{CH}_3\text{COOH}$

(d) With reference to structure, explain why the acetylide anion,  $\text{HC}\equiv\text{C}^-$  is a weaker base than the ethyl anion,  $\text{CH}_3\text{CH}_2^-$

(e) Circle all of the electrophilic atoms in the following molecule.

