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 $\Delta G°$ value of +10 kcal/mole. *[hmmmm, you do not need a calculator for this!!]*

E. –1 **F.** $4x10^{-8}$ **G.** 1 **H.** $4x10^{8}$

E
F
G
H

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

I. $NH_3 > MeNH_2 > H_2O > HF$
J. $MeNH_2 > NH_3 > MeOH > CH_4$
K. $NH_3 > Me_3N > H_2O > MeOH$
L. $CH_3COONa > NaOH > NaOMe > NaNMe_2$

I
J
K
L

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

M. 2° alkyl halide → alkene
N. 3°alkyl halide → 3° alcohol
O. ketone → 2° alcohol
P. 2° alcohol → alkene

M
N
O
P

(v) Which of the following is *not* a characteristic of S_N2 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, H_2S **BB.** ethylene

Y
Z
AA
BB

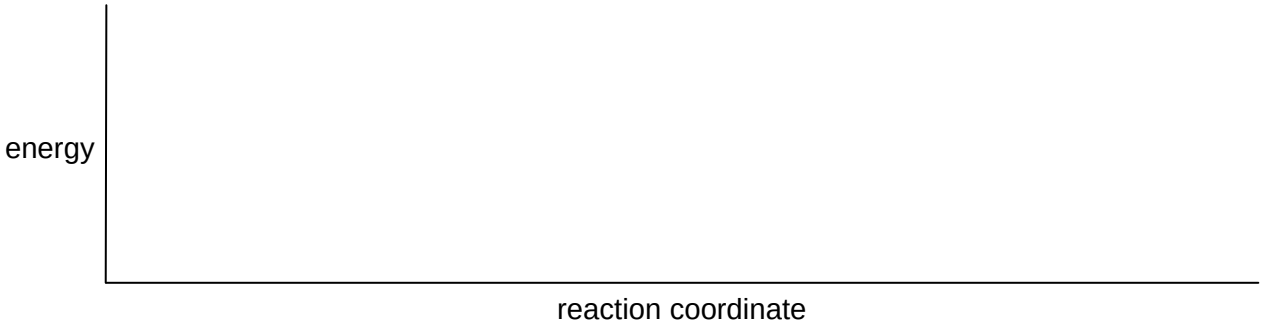
(viii) Which of the following is the strongest electrophile

CC. *tert*-butyl cation
DD. di-*tert*-butyl ether, $(CH_3)_3C\text{-}O\text{-}C(CH_3)_3$
EE. ethylene
FF. 2,3-dimethylbutane

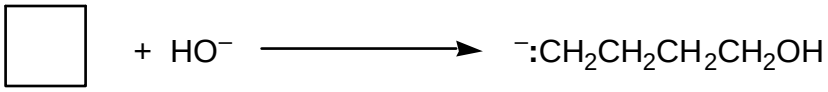
CC
DD
EE
FF

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.

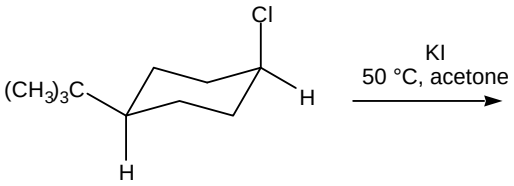


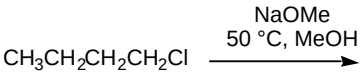
(ii) *The reaction does not proceed.* Provide two reasons to explain why the reaction does not proceed

- _____

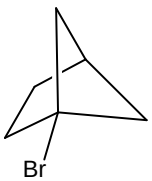
- _____

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





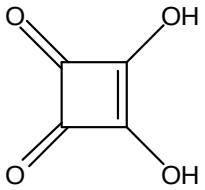
(d) Although it is a tertiary alkyl bromide, 1-bromobicyclo[2.1.1]hexane is unreactive in S_N1 reactions. Explain.



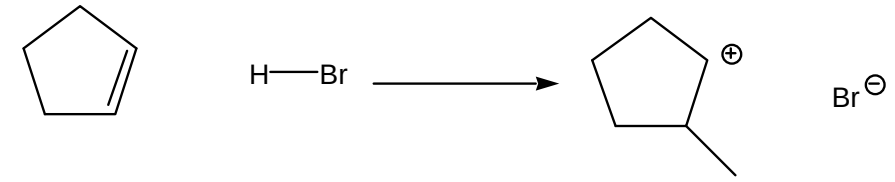
3. (32 points). Give answers for each part of the question in the spaces provided.

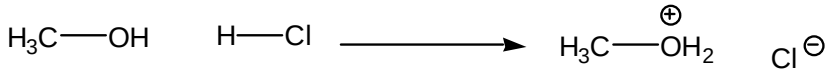
(a) Explain, *with the aid of <u>structures</u> and a <u>sentence</u> (or two)*, why compound **A** is a stronger acid than a simple diol.

A



(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 NaOH + CH_3COOH

(d) *With reference to structure*, explain why the acetylide anion, $HC{\equiv}C:^-$ is a weaker base than the ethyl anion, $CH_3CH_2:^-$

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