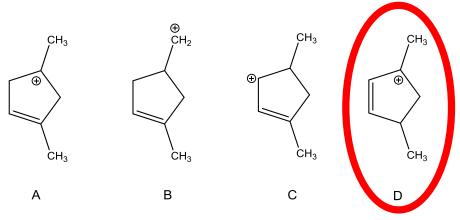
Chemistry 1315

Exam 2- Topic 2 KEY

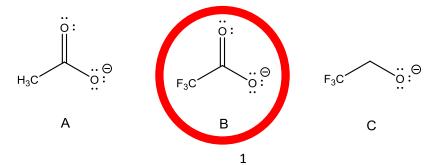
I- Questions

Multiple Choice (2pts each)

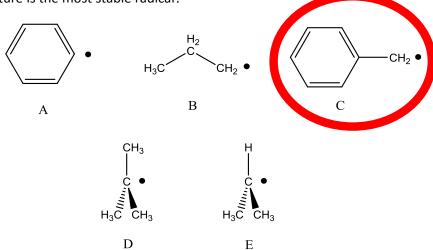
- (1) Markovnikov's rule says that in the addition of HX to an alkene, the hydrogen adds to the carbon atom of the double bond that has the greater number of hydrogen.
 - A) True
 - B) False
- (2) A geminal dihalide has halogen atoms on adjacent carbon atoms.
 - A) True
 - B) False
- (3) Which species is the lowest energy (most stable)?



- (4) The heterogeneous addition of 1 mol of hydrogen ($H_2 + Pt$) to 2-butyne results in the preferential formation of *cis*-2-butene.
 - (A) True
 - (B) False
- (5) Which species is the lowest energy (most stable)?



(6) Which structure is the most stable radical?

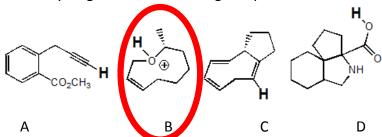


- (7) Which of the following statements is not true about the structure of benzene?
 - A) The carbon-carbon bonds are all the same length
 - B) The structure rapidly transforms between two resonance contributors
 - C) The structure is an average of two resonance contributors
 - D) The ring of six carbon atoms is planar
- (8) Zaitsev's rule states that:
 - A) In electrophilic addition of an unsymmetrical reagent to an unsymmetrical alkene, the more positive portion of the reagent will become attached to the carbon of the double bond bearing the greater number of hydrogen atoms.
 - B) An equatorial substituent in cyclohexane results in a more stable conformation than if that substituent were axial.
 - C) E2 reactions occur only if the β -hydrogen and leaving group can assume an antiperiplanar arrangement.
 - D) When a reaction forms an alkene, and several possibilities exist, the more (or most) stable isomer is the one which predominates.
- (9) A carbanion is an intermediate in the E1 process
 - (A) True
 - (B) False

- (10) What is the expected product of this re-
 - $(A) \quad \begin{array}{c} \text{CHBrCH}_2\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{CH}_2\text{CH}_3 \\ \text{CH}_3 \\ \text{CH}$
- (11) Which monomer would be employed to synthesize the polymer shown below.

(A)
$$H_2C = CH(COCH_3)$$
 (C) $H_3C - CH_2OCCH_3$ (B) $H_2C = CHOCCH_3$ (D) $H_3CCOHC = CHOCCH_3$

(12) Which bold-faced hydrogen for the following compounds is the most acidic?



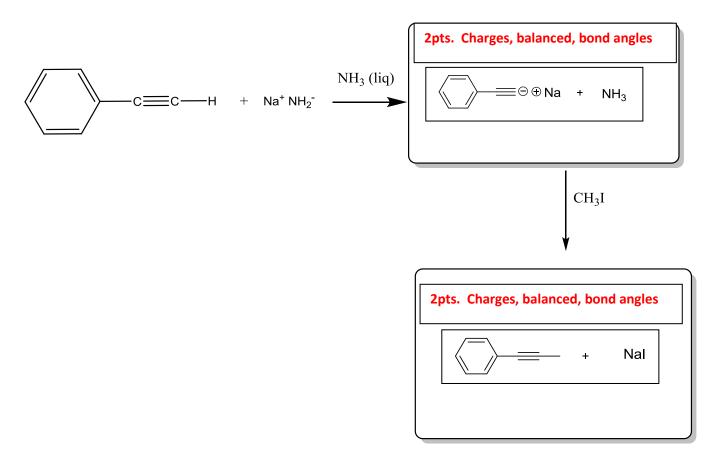
- (13) The following transformation can be classified as:
 - (A) an elimination
- (C) a substitution
- (B) a rearrangement (D) an addition

(14) Which acid-base reaction would not take place as written:

(15) What is the structure of Nylon 6,6?

II- Reactions

(1) Complete the following reaction steps. Equations must be balanced.



- 1- (1) Write the major product(s) for each of the reactions below. Be careful to consider regiochemistry and stereochemistry when appropriate. When stereoisomers are formed as the major products, each structure must be provided for full credit.
 - (2) Indicate if the reaction is expected to follow SN1, SN2, E1, E2 or addition pathway.

Note: "RT": means room temperature.

3pts each. 1 – basic structure/enantiomer,
1 – stereochem, 1 – type of reaction

$$H_2C$$
 H_2C
 CI
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C
 H_3C

C)

$$C \equiv C - CH_3$$
 $H_2/Lindlar catalyst$
 $ADDITION$
 H
 H

D)

E)

$$H_3C$$
 H_3C
 H_3C

G)

H)

Br +
$$CH_3O \stackrel{\oplus}{\circ} Na \stackrel{\oplus}{\longrightarrow} CH_3OH$$

RT

Sn2 + CH_3OH

I)

III- Mechanism

- (1) Ionic Mechanism: below, is a mechanism for addition of HCl to 3-methyl-1-butene **1** to give 2-chloro-2-methyl butane **2**. A few facts:
 - 1) ΔG^0 for the reaction is negative.
 - 2) the first step, protonation of 1 to give A is the reaction's rate-determining step.
 - 3) the 1,2-H shift step (conversion of **A** to **B**) has a higher activation energy barrier than does the addition of chloride anion to carbocation **B**.

Mechanism:

H

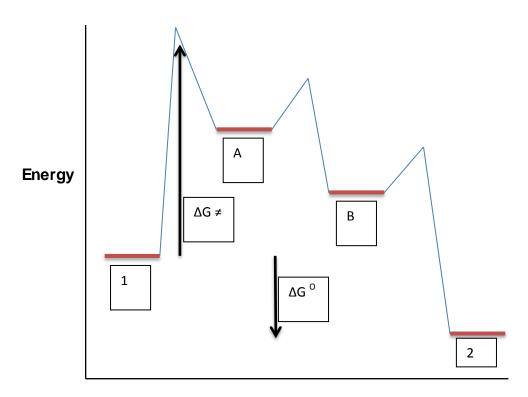
H

H

H

$$H_3C$$
 CH_3
 CH_3

- a. Draw a free energy vs. reaction coordinate diagram that is consistent with the above information. (2pts)
- b. Clearly label the positions for 1, 2, A and B. (4pts. 1 per ID)
- c. Clearly indicate ΔG^0 for the reaction and ΔG^{\neq} for the reaction's rate-determining step. (2pts. 1 per ID)



Reaction Coordinate

(2) Radical mechanism: complete the mechanism for the following reaction with initiation, propagation and termination steps. The mechanism description must include complete reactions (reactants, products and by-products), appropriate curve arrows and correct intermediates.

1- Initiation (2pts.)

$$Br \xrightarrow{Br} Br \xrightarrow{hv} 2Br \cdot$$

2- Propagation (6pts. 3 per step)

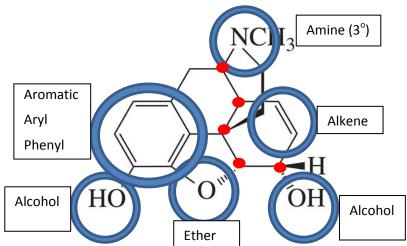
2a.

2b.

3- <u>Termination</u> (many reactions can constitute a termination reaction, write <u>one reaction</u>).
 (2pts)

IV- Application

Morphine is a naturally occurring alkaloid (opiate) of the structure shown below. Historically, the WHO has considered a country's annual consumption of morphine to be an indicator of the extent that opioids are used to treat severe cancer pain and an index to evaluate improvements in pain management. In 2012, USA was the fourth highest consumer of morphine with 78.6 mg/capita. Often, a morphine equivalence metric, adjusted to population, has been used to treat moderate and several pain with emerging commercial alkaloids like fentanyl (discussed in Exam 1).



- A) Circle and name FOUR different functional groups from the structure of Morphine above. (8pts. 1 per correct circle, 1 per matched correct ID)
- B) Identify with an asterisk (*) two chiral centers in the structure above. (2pts)
- C) Write the resonance structure of the ring structure below: (5pts. 1 per structure with charges, 1 overall for arrows)

- D) Roxanol (Morphine sulfate) and MS-Contin (morphine sulfate controlled-released) is often represented as shown below. Morphine acts as a base and reacts with the sulfuric acid to form a ionic pair. Write the structure to accurately represent the molecules present. (4pts. Can be shorthanded with R or squiggles)
- E) Why is morphine prescribed as its sulfate salt? (2pts) Aqueous solubility.

V- Bonus Question. (5 pts)

- a- In your own words, Name one of the 12 green chemistry principles. (2pts, any 1 of these)
 - a. Prevent waste
 - b. Design safer chemicals/products
 - c. Design less hazardous chem synth
 - d. Use renewable feedstocks
 - e. Use catalysts, not stoichiometric reagents
 - f. Avoid chem derivatives
 - g. Maximize atom economy
 - h. Use safer solvents/RXN conditions
 - i. Increase energy efficiency
 - j. Design chemicals and products to degrades after use
 - k. Analyze in real time to prevent pollution
 - I. Minimize potential for accidents
- b- In your own words, what is "Sustainability"? (3pts)

Quoted from slides: "Everything that we need for our survival and well-being depends, either directly or indirectly, on our natural environment."

Brundtland Commission: "development that meets the needs of the present without compromising the ability of future generations to meet their own needs."