

I. Re aromaticity, fill in the blanks or circle your choice.

1. Regarding the cycloheptatrienyl system,

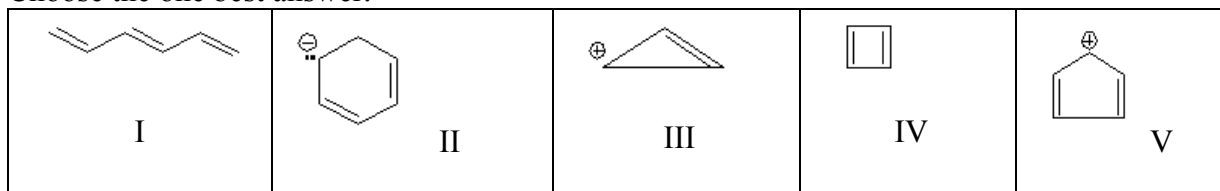
- (1) draw the structure for the carbocation showing all the p-orbitals and indicate the number of electrons (use dots) in each orbital and any associated charge (+,-).
- (2) draw the  $\pi$ -MO energy level diagram for the carbocation showing the number of electrons in each level.

\_\_\_\_\_  
(1)

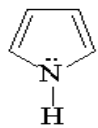
\_\_\_\_\_  
(2)

2. a) Which of the three cycloheptatrienyl species, Cation, Radical, Anion, is aromatic?
- b) Which of the above three species has two electrons in the antibonding  $\pi$ -MO? Cation, Radical, Anion
- c) 2,4,6-Cycloheptatrienone and 2,4-Cyclopentadienone have in common an aromatic character in their  $\pi$ -systems. Circle True or False.
- d) 2,4-Cyclopentadienone owes its high reactivity to a  $4n$   $\pi$ -system. Circle True or False.
- e) Compare acidity of two conjugating systems: cycloheptatriene with cyclopentadiene. Circle the more acidic molecule.
- f) The above cyclopentadiene is considered to be: aromatic, antiaromatic, or nonaromatic. Circle one.
- g) 1,3-Cyclobutadiene may be converted to an aromatic structure by (1) adding one electron, (2) adding two electrons, (3) removing one electron. Circle one choice.
- h) One can project from 2,4-cyclopentadienyl cation that the precursor chloride is a bad  $S_N1$  substrate relative to its saturated analog. Circle True or False.

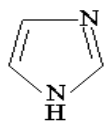
3. Which of the following would you expect to be aromatic? (a) I (b) II (c) III (d) IV (e) V  
Choose the one best answer.



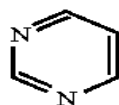
4. Consider the aromaticity of heterocyclic systems:



pyrrole



imidazole



pyrimidine



furan

- Pyrrole is predicted to be basic and protonated at N forming  $^+NH_2$ . Circle True or False.
- In furan there are two sets of lone-pair electrons on O and both sets form part of the aromatic system. Circle True or False.
- Imidazole is like pyrrole, with an extra N at position-3 replacing CH. This N-3 lone pair accounts for the basicity of the imidazole ring. Circle True or False.
- Pyrimidine has enhanced aromatic character than benzene itself. Circle True or False.
- If the  $CH_2$  group of cycloheptatriene is replaced by NH, the N-lone pair is predicted to tilt out of coplanarity with the pi-system so that the ring system becomes nonaromatic. Circle True or False.

## II. Re cycloaddition

- Use orbital drawings to evaluate the outcome of a thermal  $[4 + 2]$  cycloaddition reaction.
  - Use orbital drawings to evaluate the outcome of a thermal  $[2 + 2]$  cycloaddition reaction.

(1)

(2)

- Draw the transition state of a Diels-Alder reaction. Show p-orbitals. Use dotted line to show bond forming.

(1)

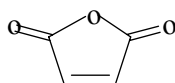
- Show the product of cyclopentadiene upon warming.

(2)

- Predict the products of the following reaction:



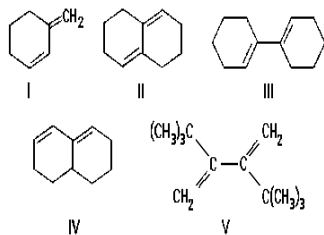
+



in toluene  $\rightarrow$

(3)

3. Which of the following will NOT function as a diene in the Diels-Alder reaction? Choose the one best answer.



- (a) I and V      (b) II and IV      (c) III      (d) I, II, IV, V      (e) All of them

### III. Re S<sub>E</sub>Ar

1. Predict the rates and regiochemistry of the following reactions relative to the corresponding benzene reactions. Circle your choice.

S <sub>E</sub> Ar Reaction	Rate relative to C <sub>6</sub> H <sub>6</sub>		Regiochemistry of products	
C <sub>6</sub> H <sub>5</sub> —N(CH <sub>3</sub> ) <sub>2</sub> + HNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>	Faster	Slower	Ortho-para	Meta
C <sub>6</sub> H <sub>5</sub> —SCH <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>	Faster	Slower	Ortho-para	Meta
C <sub>6</sub> H <sub>5</sub> —NH—CO—CH <sub>3</sub> + CH <sub>3</sub> COCl + AlCl <sub>3</sub>	Faster	Slower	Ortho-para	Meta
C <sub>6</sub> H <sub>5</sub> —CO—CH <sub>3</sub> + Cl <sub>2</sub> + FeCl <sub>3</sub>	Faster	Slower	Ortho-para	Meta

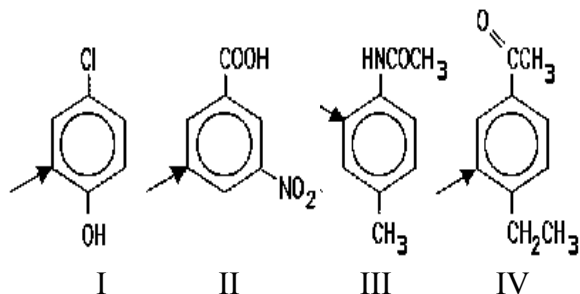
2. (1) Draw the reaction energy diagram for C<sub>6</sub>H<sub>6</sub> + Cl<sup>+</sup> FeCl<sub>4</sub><sup>-</sup>. Label the coordinates and draw the structure of the arenium ion intermediate.

\_\_\_\_\_

- (2) Show the structures of <sup>+</sup>NO<sub>2</sub> and the arenium ion produced by its attack at the para position of anisole. The latter is a resonance structure that shows the directing power of the methoxy group.

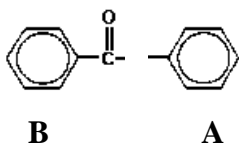
\_\_\_\_\_

3. Each of these disubstituted benzenes is allowed to react with  $\text{Br}_2$  and Fe. In which of these cases does the arrow indicate the chief position of bromination? Choose the one best answer.



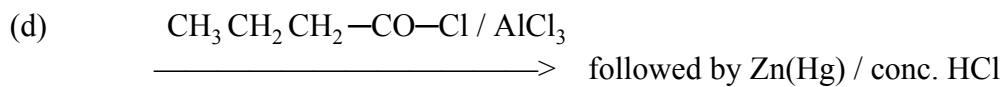
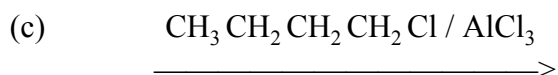
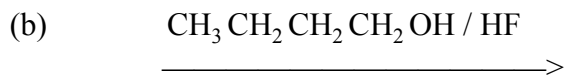
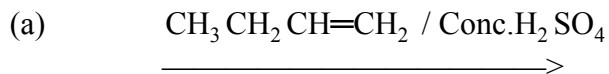
- (a) I      (b) II      (c) III      (d) IV      (e) Any one of the above

4. For Friedel-Craft's alkylation of phenylbenzoate:



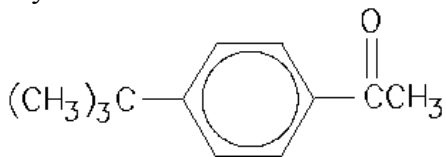
, predict the major site for alkylation. Choose the one best answer.

- (a) Ring A, meta  
 (b) Ring A, para  
 (c) Ring B, ortho  
 (d) Ring B, para  
 (e) A mixture of 6 monoalkylated compounds
5. Which of the following reactions using Friedel Crafts alkylation or acylation of benzene may yield n-butylbenzene? Choose the one best answer. (Note: n for unbranched)



- (e) None of the above

6. A good synthesis of

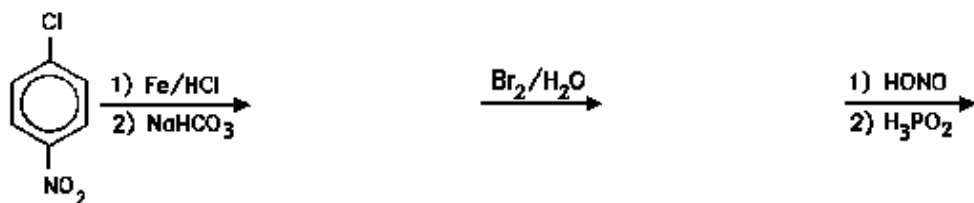


would be: (Choose the one best answer)

- (a) Benzene  $\xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{COCl}}$   $\xrightarrow[\text{AlCl}_3]{(\text{CH}_3)_3\text{CCl}}$
- (b) Benzene  $\xrightarrow[\text{AlCl}_3]{(\text{CH}_3)_3\text{CCl}}$   $\xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{COCl}}$
- (c) Benzene  $\xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{COCl}}$   $\xrightarrow[\text{HF}]{(\text{CH}_3)_2\text{C}=\text{CH}_2}$
- (d) More than one of these
- (e) All of these

#### IV. Re nucleophilic aromatic substitutions

1. Show the product structure at the end of each reaction arrow:

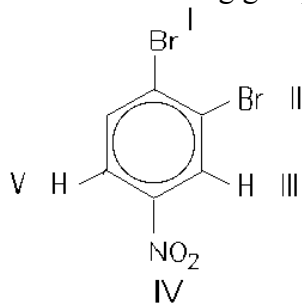


\_\_\_\_\_?                      \_\_\_\_\_?                      \_\_\_\_\_?

2. Which one of the following chloro compounds gives a substitution product upon heating in 1N NaOH? Choose the one best answer.

- (a) Ph-CH<sub>2</sub>Cl      (Ph = Phenyl)
- (b) Ph-Cl
- (c) 2,4-dinitrochlorobenzene
- (d) 2,6-dimethylchlorobenzene
- (e) Two of the above

3. Which is the leaving group when



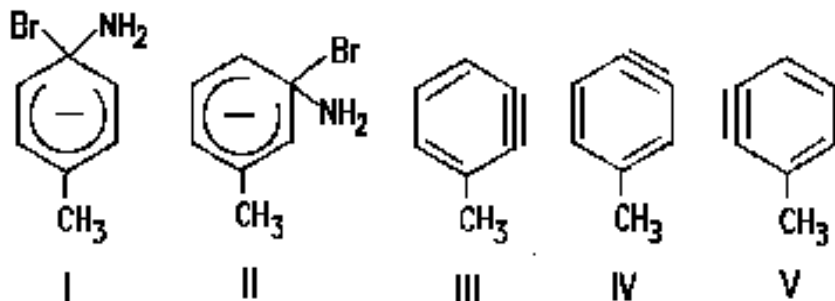
reacts with sodium cyanide in DMSO solution? Choose the one best answer.

- (a) I (b) II (c) III (d) IV (e) V

4. Which of the following multi-step plans can convert benzene to m-dibromobenzene?

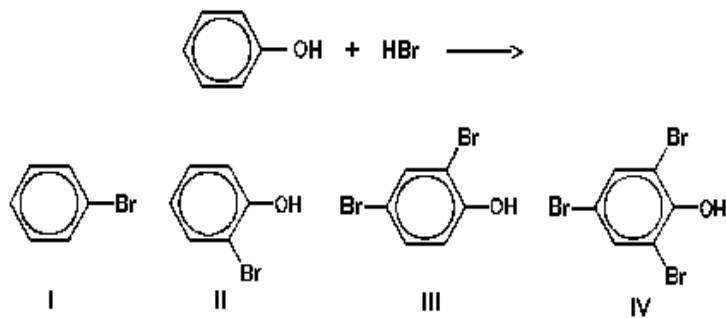
Choose the one best answer.

- (a) bromination, HBr and peroxide  
 (b) bromination, nitration, reduction, diazotization, CuBr  
 (c) nitration, bromination, reduction, diazotization, CuBr  
 (d) bromination  
 (e) none of above
5. The formation of equal amounts of m-toluidine (m-aminophenol) and p-toluidine in the reaction of p-bromotoluene with sodium amide in liquid ammonia at -33 °C suggests this species as the reaction intermediate: (Choose the one best answer)



- (a) I (b) II (c) III (d) IV (e) V

6. Indicate the correct product, if any, of the following reaction. Choose the one best answer.

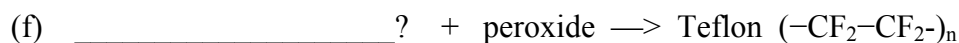
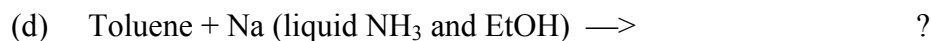
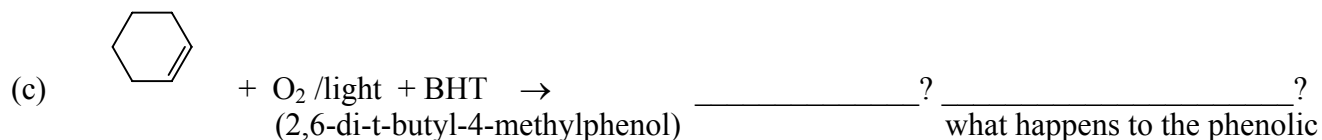
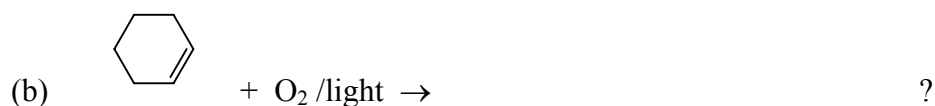
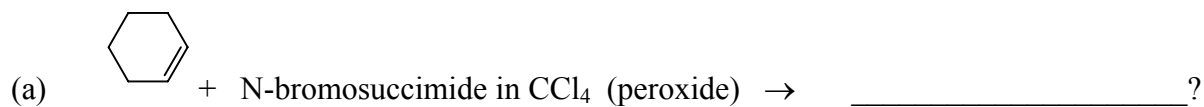


- (a) I (b) II (c) III (d) IV (e) There is no net reaction.

**Hint:** What mechanism? S<sub>E</sub>Ar, S<sub>N</sub>Ar, etc.

## V. Re radical chemistry

1. Write structural formulas of the major products of the following reactions:



2. Show mechanism for the polymerization of CH<sub>3</sub>CH=CH<sub>2</sub> in the presence of dibenzoyl peroxide.

(a) Initiation (2 steps)

(b) Propagation

(c) Termination (2 steps)

3. Consider radical halogenation of alkane. Which of the following statements is NOT TRUE? Choose the one best answer.

- (a) Br • causes a late transition state and is regioselective
- (b) Br • is the chain carrier
- (c) F • causes an early transition state and is not regioselective
- (d) The highly reactive F • disallows the chain mechanism
- (e) Cl • is medium in reactivity and regioselectivity

## Grading Sheet

I

Multiplier

Fill in blanks

# of correct answers x =

True/False type

# of correct answers x =

Choose one best

# of correct answers x =

II

Fill in blanks

# of correct answers x =

Choose one best

# of correct answers x =

III

True/False type

# of correct answers x =

Fill in blanks

# of correct answers x =

Choose one best

# of correct answers x =

IV

Fill in blanks

# of correct answers x =

Choose one best

# of correct answers x =

V

Fill in blanks

# of correct answers x =

Choose one best

# of correct answers x =

**Total Grade (100 max) =**