

※ 考生請注意：本試題不可使用計算機。請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

## Organic Chemistry (100 pts)

### I. Multiple-choice questions (20 pts)

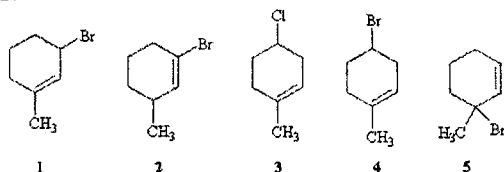
[1] In the lowest energy chair conformation of *cis*-1,3-dimethylcyclohexane, how many axial positions are occupied by hydrogen atoms?

- (A) 2 (B) 3 (C) 4 (D) 5 (E) 6

[2] Which of the following is the best reaction sequence to use if one wants to accomplish a Markovnikov addition of water to an alkene with minimal skeletal rearrangement?

- (A) water + dilute acid (B) water + concentrated acid  
(C) oxymercuration-demercuration (D) hydroboration-oxidation (E) none of the above

[3] Rank the following molecules in order of increasing relative rate of  $S_N1$  solvolysis with methanol and heat (slowest to fastest reacting).



- (A) 3 < 2 < 4 < 5 < 1 (B) 2 < 3 < 4 < 1 < 5 (C) 5 < 4 < 3 < 2 < 1 (D) 2 < 3 < 4 < 5 < 1  
(E) 1 < 2 < 5 < 4 < 3

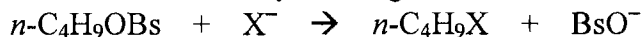
[4] In electrophilic aromatic substitution reactions, a  $-NHC(=O)CH_3$  substituent on the aromatic ring is:

- (A) a deactivator and a *m*-director (B) a deactivator and an *o,p*-director  
(C) an activator and a *m*-director (D) an activator and an *o,p*-director  
(E) none of the above

[5] Addition of  $Br_2$  to (*E*)-hex-3-ene produces \_\_\_\_\_.

- (A) a meso dibromide (B) a mixture of enantiomeric dibromides which is optically active  
(C) a mixture of enantiomeric dibromides which is optically inactive  
(D) (*Z*)-3,4-dibromo-3-hexene (E) (*E*)-3,4-dibromo-3-hexene

II. The following reaction is carried out in the weakly ionizing solvent, acetone.



Bs is *p*-bromobenzenesulfonyl group. The order of reactivity of halide ions depends upon the salt that is used as their source: if  $Li^+X^-$  is used,  $I^- > Br^- > Cl^-$ ; if  $n-Bu_4N^+X^-$  is used,  $Cl^- > Br^- > I^-$ . How do you account for this contrast in behavior? (10 pts)

III. (a) Woodward and Hoffmann have suggested that the *endo* preference in Diels-Alder reactions is a "secondary" effect of orbital symmetry, and there is experimental evidence to support this suggestion.

Using the dimerization of butadiene as your example, show how these secondary effects could arise.

(b) In contrast, [6+4] cycloaddition was predicted to take place in the *exo* sense. This has been confirmed by experiment. Using the reaction of *cis*-1,3,5-hexatriene with 1,3-butadiene as example, show how this prediction have been made. (10 pts)

IV. Give the structure of an ylide and a carbonyl compound from which each of the following could be made.

(10 pts)

- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$       (b)  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CHCH}_2\text{C}_6\text{H}_5$   
 (c)  $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$       (d) 1,4-diphenyl-1,3-butadiene  
 (e)  $\text{CH}_2=\text{CHCH}=\text{C}(\text{CH}_3)\text{COOCH}_3$

V. When sodium trichloroacetate is heated in diglyme solution with alkenes, there are formed 1,1-dichlorocyclopropanes. How do you account for this? (10 pts)

VI. A Claisen condensation results in a  $\beta$ -ketoester. Explain why a second ester enolate does not add to this  $\beta$ -ketoester. (10 pts)

VII. Show how you would use Grignard syntheses to prepare the following alcohols from the indicated starting materials and any other necessary reagents. (10 pts)

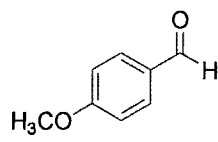
- (a) octan-3-ol from hexanal.  
 (b) octan-1-ol from 1-bromoheptane.  
 (c) 1-cyclohexylethanol from acetaldehyde.  
 (d) cyclopentylphenylmethanol from benzaldehyde.

VIII. Poly(vinyl alcohol), a hydrophilic polymer used in aqueous adhesives, is made by polymerizing vinyl acetate and then hydrolyzed the ester linkages. (10 pts)

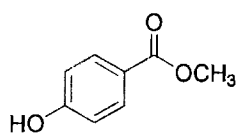
- (a) Give the structures of poly(vinyl acetate) and poly(vinyl alcohol).  
 (b) Vinyl acetate is an ester. Is poly(vinyl acetate) therefore a polyester? Explain.  
 (c) Why is poly(vinyl alcohol) made by hydrolysis of poly(vinyl acetate)? Why not just polymerize vinyl alcohol?

IX. Show how you would distinguish among the following three isomers: (10 pts)

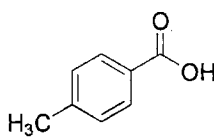
- (a) Using IR spectroscopy and no other information.  
 (b) Using proton NMR spectroscopy and no other information.  
 (c) Using  $^{13}\text{C}$  NMR, including DEPT, and no other information.



isomer 1



isomer 2



isomer 3