

國立中山大學 104 學年度碩士暨碩士專班招生考試試題

科目名稱：有機化學【材光系碩士班甲組】

題號：439003

※本科目依簡章規定「不可以」使用計算機(混合題)

共 3 頁第 1 頁

1. 選擇題 (單選, Each 2%, Total: 40%)

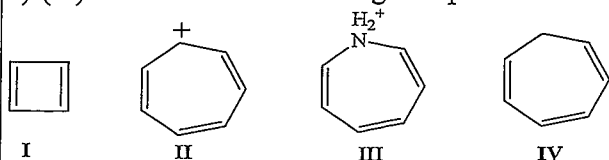
1) ( ) Rank the following substituents in order of priority (from highest to lowest priority).

(I)  $-\text{CH}=\text{CH}_2$ , (II)  $-\text{CN}$ , (III)  $-\text{CH}_2\text{NH}_2$ , (IV)  $-\text{CH}_2\text{Br}$ .

(a)  $\text{I} > \text{II} > \text{III} > \text{IV}$ , (b)  $\text{II} > \text{III} > \text{I} > \text{IV}$ , (c)  $\text{IV} > \text{II} > \text{I} > \text{III}$ , (d)  $\text{IV} > \text{III} > \text{II} > \text{I}$

2) ( ) Which of the following reagents effectively cleaves carbon-carbon double bonds? (a)  $\text{Br}_2$  and light, (b) *meta*-chloroperoxybenzoic acid, (c)  $\text{OsO}_4$  followed by  $\text{H}_2\text{O}_2$ , (d)  $\text{O}_3$  followed by  $(\text{CH}_3)_2\text{S}$ .

3) ( ) Which of the following compounds is likely to adopt a planar conformation?



a) I, b) II, c) III, d) IV.

4) ( ) Rank the following compounds in order of increasing oxidation level (from the highest to lowest)

(I)  $\text{CH}_3\text{CH}_2\text{OH}$ , (II)  $\text{CH}_3\text{CHO}$ , (III)  $\text{CH}_3\text{CO}_2\text{H}$ , (IV)  $\text{CH}_3-\text{CH}_3$

(a)  $\text{I} > \text{II} > \text{III} > \text{IV}$ , (b)  $\text{III} > \text{II} > \text{I} > \text{IV}$ , (c)  $\text{II} > \text{III} > \text{I} > \text{IV}$ , (d)  $\text{III} > \text{II} > \text{IV} > \text{I}$ .

5) ( ) Catalysts alter the kinetics of a reaction by: (a) Making the products more stable, (b) Making the reaction more exothermic, (c) Lowering the energy of activation for the reaction, (d) Providing a source of free radicals to initiate a reaction.

6) ( ) Which of the following compounds is the strongest acid? (a)  $\text{CH}_3\text{O}_2\text{CCH}_2\text{CH}_3$ , (b)  $\text{CH}_3\text{CH}_2\text{O}_2\text{CCH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ , (c)  $\text{CH}_3\text{CH}_2\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ , (d)  $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$ .

7) ( ) Which of the following isomers of  $\text{C}_8\text{H}_9\text{NO}$  is the weakest base?

(a) *o*-aminoacetophenone, (b) *m*-aminoacetophenone, (c) *p*-aminoacetophenone, (d) acetanilide.

8) ( ) What is the mixed aldol condensation product formed between benzaldehyde and acetone?

(a)  $\text{C}_6\text{H}_5\text{CH}=\text{CHC}(=\text{O})\text{CH}_3$ , (b)  $\text{C}_6\text{H}_5\text{C}(=\text{O})\text{CH}=\text{CHCH}_3$ , (c)  $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CH}_3)_2$ ,

(d)  $\text{C}_6\text{H}_5\text{CH}_2\text{C}(=\text{O})\text{CH}=\text{CH}_2$ .

9) ( ) The most effective pair for the preparation of *tert*-butyl ethyl ether is (a) potassium *tert*-butoxide and ethyl bromide, (b) potassium *tert*-butoxide and ethanol, (c) sodium ethoxide and *tert*-butyl bromide, (d) *tert*-butyl alcohol and ethyl bromide.

10) ( ) Which of the following transitions is the highest energy transition? (a)  $n$  to  $\sigma^*$ , (b)  $n$  to  $\pi^*$ , (c)  $\sigma$  to  $\sigma^*$ , (d)  $\pi$  to  $\pi^*$

11) ( ) Which ion is the strongest base? (a)  $\text{CH}_3\text{CH}_2\text{O}^-$ , (b)  $\text{CH}_3\text{COO}^-$ , (c)  $\text{Cl}^-$ , (d)  $\text{CH}_3\text{CH}_2^-$ .

12) ( ) Which of the following statements of I-IV correctly describe(s) E1 reactions of alkyl halides (RX)? (I)  $\text{Rate} = k[\text{base}]$ ; (II)  $\text{Rate} = k[\text{base}][\text{RX}]$ ; (III)  $\text{Rate} = k[\text{RX}]$ ; (IV) The reactions occur in two distinct steps. (a) I, (b) II and IV, (c) I, II and III, (d) III and IV.

13) ( ) Which of the following compounds can be used to prepare Grignard reagents by reacting with Mg in ether?. (I)  $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_3$ , (II)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})-\text{CH}_3$ ; (III)  $\text{HO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ ; (IV)  $\text{HOOC}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ . (a) I; (b) II; (c) III; (d) IV.

14) ( ) How are reactions between aldehydes and nucleophiles fundamentally different than reactions between acyl chlorides and nucleophiles? (a) Aldehydes are readily oxidized by nucleophiles to carboxylic acids. (b) Acyl chlorides have a leaving group,  $\text{Cl}^-$ , whereas aldehydes do not. (c) Aldehydes do not form tetrahedral intermediates with nucleophiles. (d) Acyl chlorides readily form enol tautomers.

15) ( ) The proton NMR of 1,1-dibromoethane would appear as a: (a) downfield doublet and upfield quartet, (b) downfield quartet and upfield doublet, (c) downfield doublet and upfield triplet, (d) downfield triplet and upfield doublet.

16) ( ) In infrared spectroscopy, absorption of electromagnetic radiation results in transitions between \_\_\_\_\_ energy levels. (a) vibrational, (b) electronic, (c) rotational, (d) nuclear.

17) ( ) Which alcohol of molecular formula  $\text{C}_5\text{H}_{12}\text{O}$  has the fewest signals in its  $^{13}\text{C}$  NMR spectrum?

(a) 1-Pentanol, (b) 2-Pentanol, (c) 2-Methyl-2-butanol, (d) 2,2-Dimethyl-1-propanol.

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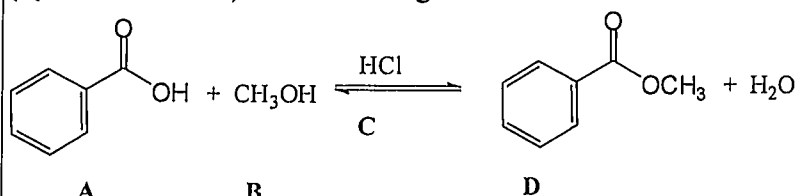
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共 3 頁第 2 頁

(Questions 18-20) The following esterification reaction concerns questions 18-20:



18) ( ) The nucleophile in this reaction is (a) A, (b) B, (c) C, (d) D.

19) ( ) Compound C (HCl) function as (a) a base scavenger, (b) a solvent, (c) a catalyst, (d) a neutralizer.

20) ( ) This esterification reaction is an example of (a) nucleophilic acyl addition, (b) nucleophilic acyl substitution, (c) nucleophilic acyl elimination, (d) nucleophilic acyl rearrangement.

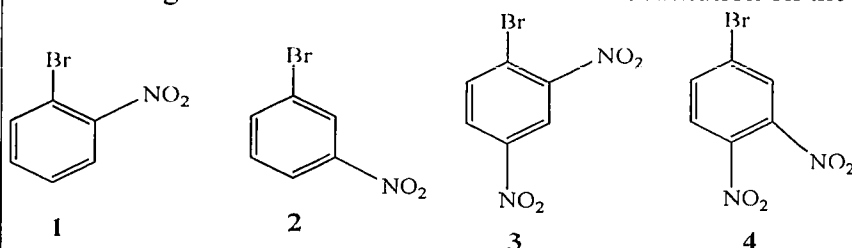
2. (Total: 30%) Answer questions (a) to (d).

1) Nitration of ethyl phenyl ether (EtOPh) belongs to the electrophilic aromatic substitution reactions used to generate aromatic nitro compounds. Nitration of ethyl phenyl ether can be conducted by using  $\text{HNO}_3/\text{H}_2\text{SO}_4$  as the nitration agent.

(a) Identify the active electrophile (the real cationic species leading to nitration) in the nitration reaction. (4%)

(b) The first nitro group can be readily introduced into ethyl phenyl ether readily; in contrast, further nitration to introduce the second nitro groups into ethyl phenyl ether proceeds slowly even sufficient electrophile was used. Why? (8%)

2) Instead of electrophilic substitution reaction, aromatic nitro-compounds can be also prepared via nucleophilic aromatic substitution reaction. For example, direct attack of ethoxide ion ( $\text{CH}_3\text{CH}_2\text{O}^-$ ) on the following molecules of 1 to 4 results in the substitution on the bromo groups,



(c) Single-step substitution reaction (in other words, a  $\text{S}_{\text{N}}2$  reaction) is prohibited for the nucleophilic substitution reactions between molecules 1-4 and ethoxide ion. Instead, the aromatic substitution of molecules 1- 4 proceeds with two steps, addition and the following elimination. Why single-step substitution ( $\text{S}_{\text{N}}2$ ) reaction is prohibited for molecules of 1- 4? (10%)

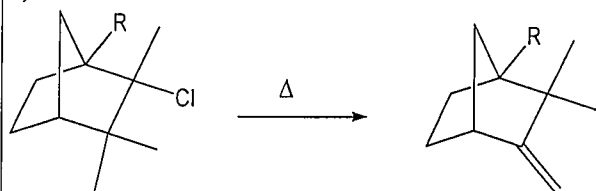
(d) List the order of reaction rate (from highest to lowest) between molecules 1-4 and ethoxide ion. (8%)

3. (Total: 10%) When treated with aqueous acid, substance A forms dimethylformamide

( $(\text{CH}_3)_2\text{NC}(=\text{O})\text{H}$ ) and 2 equiv of ethanol. A exhibits the following spectrum ( $^1\text{H}$  NMR,  $\delta$ ): 1.2 triplet (6H), 2.3 singlet (6H), 3.5 quartet (4H), 4.5 singlet (1H). What is the structure of A?

4. (Total: 20 %, each 5%) Write down the reaction steps involved in each of the following reactions from 1) to 4).

1)



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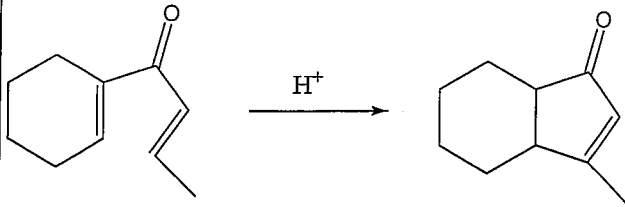
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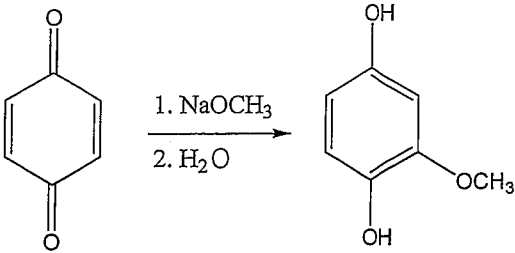
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共 3 頁第 3 頁

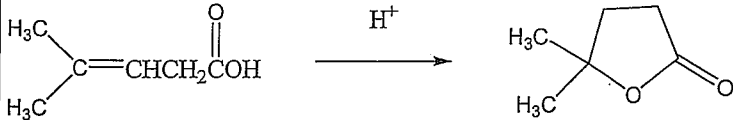
2)



3)



4)



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