台灣聯合大學系統 108 學年度碩士班招生考試試題

類組:化學類 科目:有機化學(1002)

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※選擇題請在答案卡內作答,非選擇題請在答案卷內作答

- 一、選擇題(一律為單選題,每題3分,沒有倒扣;共90分)
 - 1. Select a correct statement about the degree of unsaturation for the following formulas.
 - I. C₁₀H₁₆; II. C₈H₈O; III. C₇H₁₀Cl₂; IV. C₁₀H₁₆O₂; V. C₅H₉NO₂; VI. C₈H₁₀ClNO
 - (A) There are three formulas with degree of unsaturation = 2;
 - (B) There are two formulas with degree of unsaturation = 4;
 - (C) There are two formulas with degree of saturation = 3;
 - (D) Formula II and formula VI are of the same degree of unsaturation;
 - (E) None of the above.
 - 2. Which of the following is aromatic?
 - (A) cyclobutenyl anion;
 - (B) 1,3,5-hexatriene;
 - (C) cyclopentadienyl cation;
 - (D) 1,3-cyclohexadiene;
 - (E) cycloheptatrienyl cation.
 - 3. Predict the product(s) of the following reaction and select a correct statement.

3-Methyl-1-butene + $HCl \rightarrow product(s)$

- (A) The reaction would follow the electrophilic addition mechanism;
- (B) The reaction would involve carbocation rearrangement;
- (C) The reaction would involve hydride shift;
- (D) Two major products will be obtained and they are constitutional isomers;
- (E) All of the above.
- 4. Which of the following substrates is an electron donating group overall?
 - (A) Br;
 - (B) –COPh;
 - (C) –OBn;
 - (D) NEt₃⁺;
 - $(E) CCl_3$

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5. Select a correct statement for the E, Z designations at the indicated site of the following compounds.

I.
$$\stackrel{\text{COOH}}{\downarrow}$$
 III. $\stackrel{\text{Br}}{\downarrow}$ $\stackrel{\text{NH}_2}{\downarrow}$ $\stackrel{\text{NHCH}_3}{\downarrow}$

- (A) There is only one compound that has E geometry at the indicated site;
- (B) There are two compounds that do not show *E-Z* isomerism;
- (C) All the listed compounds have Z geometry at the indicated sites;
- (D) Compounds II, III. IV, and VI have E geometry at the indicated sites;
- (E) None of the above.

6. o-Phthalic acid produces what acid derivative upon heating?

- (A) a carboxylate;
- (B) an acid chloride;
- (C) an ester;
- (D) an amide;
- (E) an anhydride.

7. Predict the product(s) of the following reaction and select a correct statement.

(R)-4-Methyl-1-hexene
$$\xrightarrow{\text{H}_2\text{O}}$$
 Product(s)

- (A) The reaction will lead to a mixture of two enantiomers as the major products;
- (B) The major products would be two diastereomers with equal amounts;
- (C) The reaction will not go forward;
- (D) Products are (2S,4R)-4-methyl-2-hexanol and (2R,4R)-4-methyl-2-hexanol;
- (E) None of the above.

共10 頁第3 頁

※選擇題請在答案卡內作答,非選擇題請在答案卷內作答

- 8. What is the major product when (CH₃)₂CHCH₂CH₂CH₂I is subjected to the following reaction sequence: 1. Mg, ether 2. CO₂ 3. H₃O⁺?
 - (A) 4-methylhexanoic acid;
- (B) 5-methylpentanoic acid;
- (C) 4-methyl-1-pentanol;

- (D) 5-methylhexanoic acid;
- (E) 4-methylpentanoic acid.
- 9. Which of the following is the least likely to form a Grignard reagent?
 - (A) \(\sum_{F} \)
 - (B) $\downarrow_{\mathbf{B}_{\mathbf{I}}}$
 - (C)
 - (D)
 - (E) All will form Grignard reagents.
- 10. Why do aldehydes undergo nucleophilic addition reactions while esters undergo nucleophilic acyl substitution reactions?
 - (A) Once the nucleophile adds to an aldehyde, the tetrahedral intermediate is too sterically hindered to eliminate one of the attached groups;
 - (B) Aldehydes are more sterically hindered than esters;
 - (C) The carbonyl carbon of an ester is more electrophilic than that of an aldehyde;
 - (D) The ester carbonyl carbon is sp3 hybridized while the aldehyde carbonyl carbon is sp2 hybridized;
 - (E) Once the nucleophile adds to an aldehyde, neither H- nor R- can be eliminated since they are strongly basic.
- 11. Which of the following correctly orders oxidation levels?
 - (A) $CH_3CH_2NH_2 > CH_3C\equiv N$;
 - (B) $CH_3CH_2CO_3H > CH_3CH_2OH$;
 - (C) $CH_3CH_2CH_3 > CH_3C\equiv CH$;
 - (D) $(CH_3)_2C=O > CH_3CH_2CO_3H$;
 - (E) All of the above.

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- 12. What is the carbon nucleophile which attacks molecular bromine in the acid-catalyzed α -bromination of a ketone?
 - (A) a Grignard reagent;
 - (B) an enolate;
 - (C) a carbocation;
 - (D) an enol;
 - (E) an acetylide.
- 13. Which statement is true for the three protons (H_I, H_{II}, and H_{III}) in the following structure?

- (A) The ¹H NMR signals of **H**_{II} and **H**_{III} appear at the same spectral position;
- (B) The spin-spin coupling between H_I and H_{III} is stronger than that between H_I and H_{II};
- (C) The ¹H NMR signal for **H**_{III} is the most downfield among these three protons;
- (D) The multiplicities of the ¹H NMR signals for these protons are all triplets;
- (E) These protons are all magnetically shielded compared to those protons of a methane molecule.
- 14. What species is attacked by the alcohol's hydroxyl in the mechanism of the Swern oxidation?
 - (A) $Me_2S=O$;
 - (B) ClCOCO⁺;
 - (C) Et₃N;
 - (D) Me₂SCl⁺;
 - (E) ClCOCOCl.
- 15. For the usefulness of IR spectroscopy in organic chemistry, select a correct statement.
 - (A) It helps chemists to determine the substitution pattern on an alkene double bond (C=C);
 - (B) It helps chemists to predict if the unknown structure contains a benzene ring;
 - (C) It helps chemists to predict whether a carbonyl group is conjugated with other unsaturated units or not;
 - (D) It helps chemists to differentiate a terminal alkyne from an internal alkyne
 - (E) All of the statements are true.

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※選擇題請在答案卡內作答,非選擇題請在答案卷內作答

16. When pyrrole undergoes electrophilic aromatic substitution, at which position does substitution occur?

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

17. Select a correct structure for the compound that fits the following mass spectrum data:

An alcohol with M⁺ = 88 and fragments at m/z = 73, m/z = 70, and m/z = 59

18. Which of the following statements about how acid catalyzes the hydrolysis of esters is (are) correct?

- (A) The acid catalyst increases the rate of formation of the tetrahedral intermediate by protonating the carbonyl and thereby increasing the reactivity of the carbonyl group;
- (B) The acid catalyst increases the rate of the reaction by changing the basicity of the group eliminated when the tetrahedral intermediate collapses;
- (C) The acid catalyst protonates the water, the nucleophile in the reaction, and thereby makes it a stronger nucleophile;
- (D) Both A and B;
- (E) Both A and C.

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※選擇題請在答案卡內作答,非選擇題請在答案卷內作答

- 19. From the viewpoint of NMR spectrometry, select a correct statement for (R)-4-methyl-2-pentanol.
 - (A) There are enantiotopic hydrogens and carbons on this molecule;
 - (B) There are homotopic hydrogens and carbons on this molecule;
 - (C) There are diastereotopic hydrogens and carbons on this molecule;
 - (D) There is one set of enantiotopic hydrogens and one set of homotopic carbons on this molecule;
 - (E) All of the statements are incorrect.
- 20. Which of the following species can best serve as an initiator for cationic polymerization?
 - (A) ROOR;
- (B) ROH;
- (C) AlCl₃;
- (D) ROR;
- (E) RCOOR.
- 21. Which of the following will produce only one product upon dehydration?

- (E) (B) and (D)
- 22. How many electrons are present in the nonbonding π molecular orbital of the allyl anion?
 - (A) 0;
 - (B) 1;
 - (C) 2;
 - (D) 3;
 - (E) 4

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※選擇題請在答案卡內作答,非選擇題請在答案卷內作答

23. For which of the following substances is it not possible to isolate the enantiomers? (X, Y, and Z represent different substituents.)

(A)
$$x \stackrel{N}{\underset{Y}{\stackrel{\cdot}{\longrightarrow}}} z$$

(C)
$$x \stackrel{P.}{\underset{v}{\longrightarrow}} z$$

(D) It is possible to isolate the enantiomers of all of these.

(E) It is not possible to isolate the enantiomers of any of these.

24. Which of the following is least likely to undergo a smooth crossed Claisen condensation with methyl pentanoate?

(A) (CH₃CH₂)₃CCO₂Me;

(B) PhCH₂CO₂Me;

(C) PhCO₂Me;

(D) HCO₂CH₂CH₃;

(E) $(MeO)_2CO$

25. What is the concentration of a solution of a natural pigment ($\varepsilon = 37500$) if an Absorbance of 0.751 was obtained in a cell with a 5-cm path-length?

(A) 2.00×10^{-5} M;

(B) 3.55×10^{-5} M;

(C) 4.00×10^{-6} M;

(D) 1.68×10^{-4} M;

(E) None of the above.

26. Which of the following amines could be formed by reduction of an amide?

I. triphenylamine; II. Benzylamine; III. Isopropylamine; IV. Aniline; V. triethylamine

(A) I and III;

(B) II and IV;

(C) \mathbf{II} and \mathbf{V} ;

(D) III and V;

(E) I, II and IV.

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27. If the following reaction is studied in five different solvents as indicated, what would be the reasonable ranking of the reaction rate?

$$CH_{3}CH_{2}CH_{2}CH_{2}Br + N_{3}^{\ominus} \xrightarrow{Solvent \text{ I-V}} CH_{3}CH_{2}CH_{2}CH_{2}N_{3} + Br^{\ominus}$$

Solvent I:

 H_2O

Solvent II:

Acetonitrile

Solvent III:

DMF

Solvent IV:

DMSO

Solvent V:

HMPA

- (A) V > II > III > IV > I;
- (B) II > V > IV > III > I;
- (C) IV > V > III > II > I;
- (D) I > IV > II > III > V;
- (E) III > IV > V > II > I.
- 28. Which of the following carbonyl compounds may be made from 1,3-dithiane?
 - I. methyl vinyl ketone; II. 2-pentanone; III. 3,3-dimethyl-2-butanone; IV. 2-phenylethanal
 - (A) I and III;
 - (B) II only;
 - (C) II and III;
 - (D) II and IV;
 - (E) III and IV.

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※選擇題請在答案卡內作答,非選擇題請在答案卷內作答

29. A graduate student was instructed to do the following reaction by his advisor and obtained three major products with the ratios as shown below. Select a correct statement about the reaction and the products.

$$(CH_3)_3COCI + CI + CI$$

$$II \qquad III \qquad III \qquad (65\%) \qquad (25\%) \qquad (10\%)$$

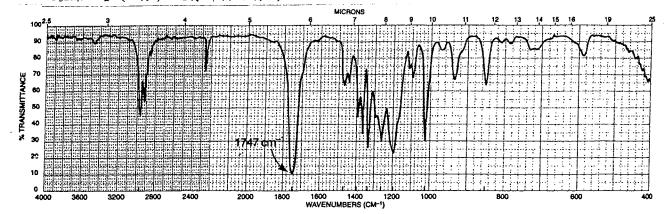
- (A) The reaction proceeded by following a nucleophilic substitution pathway;
- (B) The reaction proceeded by following a radical substitution pathway;
- (C) A benzylic radical would be involved for the formation of product I;
- (D) The relative reactivity of the hydrogens on the propyl group can be estimated from the result;
- (E) (B), (C), and (D) are correct.
- 30. Which of the following compounds will not undergo Friedel-Crafts acylation when treated with EtCOCl, AlCl₃?
 - (A) benzophenone;
 - (B) o-xylene;
 - (C) ethylbenzene;
 - (D) ethoxybenzene;
 - (E) anisole

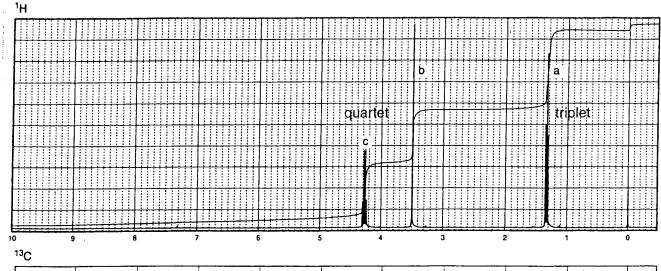
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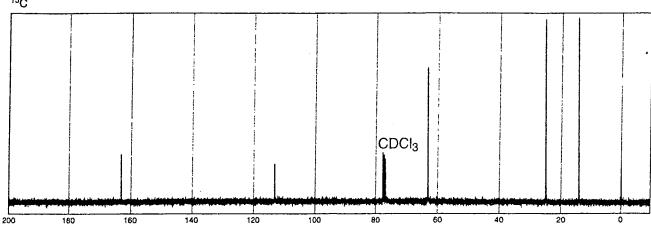
※選擇題請在答案卡內作答,非選擇題請在答案卷內作答

二、非選擇題(共 10 分)

(一) Using the following spectra to determine the molecular structure of a compound with the formula C5H7NO2. (5分; 沒有部份給分!)







(二) Predict the major product (3 分) and offer a mechanistic explanation for this transformation. (2 分).

Hint: O R'