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國立臺灣大學114學年度碩士班招生考試試題

科目:有機化學(A)

題號:49

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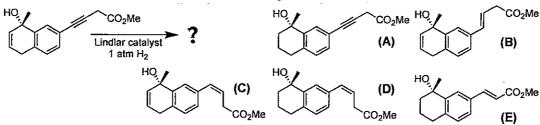
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I. Single-Choice Questions [單選題:共54分每題3分;請於答案卡畫卡作答。]

- 1. According to the CIP nomenclature, the molecule shown below is _____-form 2-butanol.
 - A) (D)-form
 - B) (E)-form
 - C) (L)-form
 - **D)** (R)-form
 - E) (S)-form
- 2-Butanol
- 2. The field of stereochemistry began with the study of tartaric acid (shown below) by Louis Pasteur in the 1850s. Tartaric acid has __(X)__ chiral centers and __(Y)__ possible stereoisomers.
 - **A)** X = 1, Y = 2
 - **B)** X = 1, Y = 4
 - **C)** X = 2, Y = 2
 - **D)** X = 2, Y = 3

 - **E)** X = 2, Y = 4
- Tartaric acid
- 3. What is the most likely product of the following hydrobromination reaction?

4. What is the most likely product of the following reaction?



5. Which of the following reactions will NOT give benzylamine as the final product after workup?

6. What is the most likely product of the following reaction sequence?

- 7. What is the name of the reaction in step 1) and 4) shown in Question 6?
 - A) Cannizzaro reaction
- B) Claisen condensation
- C) Friedel-Crafts reaction

- D) Grignard reaction
- E) Swern oxidation

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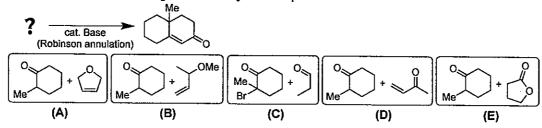
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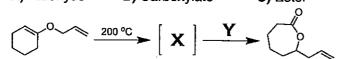
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8. Which combination of reagents would yield the product shown below?



9. The first step in the reaction sequence shown below is a heat-promoted rearrangement to generate intermediate [X]. It contains a new functional group (Z) not seen in the starting material. Z = ?
A) Aldehyde
B) Carboxylate
C) Ester
D) Ketone
E) Peroxide



10. What reagent (Y) should be used in the second step of the reaction shown in Question 9?

A) HBpin

B) H₂O₂ / BF₃

C) l₂

D) KOH / 14-crown-4 E) Pd(OAc)₂

Question 11 & 12 are about sugars. The chemical formula for all three structures shown below are $C_7H_{14}O_6$. Choose the term that correctly describes the relationship between these stereoisomers.

11. Methyl- α -glucopyranoside and methyl- α -galactopyranoside are a pair of _

A) anomers

B) epimers

C) enantiomers

D) tautomers

E) the same

12. Methyl- α -glucopyranoside and methyl- β -glucopyranoside are a pair of ___

A) anomers

B) epimers

C) enantiomers

D) tautomers

E) the same

HOO OME

HO HO OMe

 $Methyl-\alpha\text{-}glucopyranoside \quad Methyl-\beta\text{-}glucopyranoside \quad Methyl-\alpha\text{-}galactopyranoside$

13. Which of the following molecule is NOT aromatic?



(B)

(C)

(D)

(E)

14. Which of the following molecules is stable in air at room temperature?



(B)

(C)

D) Me

E)

15. Which of the following molecules is a D-sugar?

(B) CHO

HO—H

H—OH

H—OH

CH2OH

C) CH₂OH

HO—H

HO—H

CH-OH

(D) CHO H-OH HO-H HO-H CH₂OH (E) CHO

H—NHCOCH

HO—H

H—OH

HO—H

CH₂OH

16. Rank the acidity of the most acidic proton in the following molecules (from strongest to weakest).

A) | > || > || | > |V | B) |V > || > || > |

C) ||| > |V > || > |

D) ||| > || > | > |V

(1)

(II)

(III)

(IV)

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17. Which of the following descriptions about phosphatidylcholine is NOT correct?

- A) It is a common lipid in biological membranes
- B) It is zwitterionic under physiological conditions
- C) It contains a phosphodiester moiety
- D) It contains two ester moieties
- E) It contains a tertiary amine
- 18. Flavin is an important cofactor that mediates electron transfer in enzymes that catalyze redox reactions. It can exist in various forms (I to IV). Rank them from highest to lowest oxidation state.

II. Mechanisms and Structures [簡答題:共 46 分,配分見各題標示;請於答案卷手寫作答。]

Question 19 & 20 are about cysteine proteases. The active site of these enzymes usually consist of three key amino acid residues that are in spatial proximity, referred to as the <u>catalytic triad</u>.

- 19. The <u>catalytic triad</u> of a cysteine protease usually contains <u>(X)</u>, <u>(Y)</u>, and cysteine (name of amino acids). Hint: The acid dissociation constants (pK_a) of the side-chain functional groups of these amino acids are approximately 4.0 (X), 6.0 (Y), and 8.3 (cysteine). [二分]
- 20. Draw the structures of the two amino acids in the previous question. [二分]

Answer Question 21 & 22 based on the following compounds and reagents.

(I)
$$\longrightarrow$$
 Br (III) \longrightarrow Br (IV) \longrightarrow We \longrightarrow \bigcirc K⁺ Me \longrightarrow \bigcirc K⁺

- 21. Bromoalkane can undergo substitution or elimination when it reacts with a base. Choose the combination that yields the of highest ratio of elimination product. [三分,全對才給分]
 - 21.1 Choose a bromoalkene from compound [I, II, or III]
 - 21.2 Choose a base from reagent [IV, V, or VI]
 - 21.3 Choose to run the reaction at [High or Low] temperature
- 22. Draw the structure of the elimination product. [三分]

Question 23 & 24 are about Diels-Alder reactions, a type of [4+2] cycloaddition reaction.

- 23. Draw the product (P) for the reaction shown above. Clearly indicate stereochemistry. [三分]
- 24. The starting material **(S)** underwent an <u>intramolecular</u> Diels-Alder reaction to generate compound **(I)**. Draw the structure of **(S)**. Clearly indicate stereochemistry. [三分]

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Questions 25 & 26 are about the "Fmoc" (fluorenylmethyloxycarbonyl) protecting group. It is often used as the amine protecting group in solid-phase peptide synthesis. Fmoc protected phenylalanine (Fmoc-Phe-OH) is shown as an example.

25. Draw the products (X, Y, and Z) of Fmoc-Phe-OH deprotection. [三分]

26. Draw the arrow-pushing mechanism of **Fmoc-Phe-OH** deprotection. [三分]

Question 27 & 28 are about Witting reaction. It was first reported in 1954 by Georg Wittig, who was awarded the Nobel Prize in Chemistry in 1979 for his discovery and research of this reaction. It is a useful method to synthesize alkenes from aldehydes or ketones.

- 27. Reagent (I) is formally a carbanion directly attached to a positively charged phosphorus atom. This type of neutral dipolar molecules is called a _____. [三分]
- 28. Draw the structure of the key oxaphosphetane intermediate [X]. [三分]

Question 29 to 32 are about NMR spectroscopy knowledge.

29. Teixobactin was discovered in 2015 and is a promising antibiotic candidate. Answer the following questions about its NMR properties based on its structure shown below.

- 29.1) How many carbons in 13 C NMR do you expect to see in the $\delta > 100$ ppm range? [-%]
- 29.2) Among the carbons in 29.1, how many of them are sp 3 hybridized? [$-\beta$]
- 29.3) How many protons in ¹H NMR do you expect to see in the δ < 2.0 ppm range? [-%]
- 29.4) Among the protons in 29.3, how many of them split into doublets? [-分]
- 29.5) The arrow points to two protons. Will they have the same chemical shift? [-分]
- 29.6) The arrow points to two protons. Will they have the same splitting pattern? $[-\gamma]$

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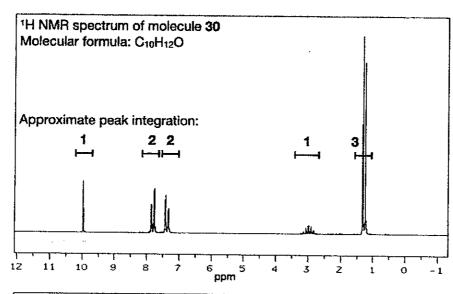
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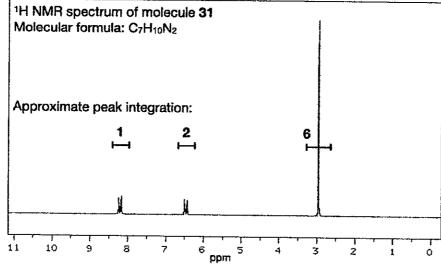
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- 30. The molecular formula of this molecule **30** is $C_{10}H_{12}O$. Its ¹H NMR spectrum is shown below. Draw the most likely structure of this molecule. [三分]
- 31. The molecular formula of this compound **31** is $C_7H_{10}N_2$. Its ¹H NMR spectrum is shown below. Draw the most likely structure of this molecule. [三分]





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