

《有機化學》

I. Choose one correct answer for the following questions

【單選題】每題1分,共計60分,答錯1題倒扣0.25分,倒扣至本大題零分為止,未作答, 不给分亦不扣分。

(C) 1. What is the **major** product obtained from the following reaction sequence?



(A) 2. The hydroboration-oxidation procedure can be successfully employed for synthesis of deuterated derivatives, by using BD₃ instead of BH₃. What major product would you expect from the following reaction?



(C) 3. Predict the **major** product for the following reaction.



(B) 4. The following atoms are commonly encountered in organic molecules. For which is it not possible to isolate enantiomers due to rapid inversion? (A) trivalent phosphorus

(B) trivalent nitrogen

(D) trivalent sulfur

(E) both B and C

(C) divalent sulfur

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- (E) 5. Which of these alkyl halides can NOT be used to prepare amines using Gabriel synthesis?
 (A) 1-bromopentane
 (B) 1-bromo-3-methylbutane
 (C) 2-bromo-3-methylpentane
 (D) 1-bromo-2,3-dimethylbutane
 (E) 2-bromo-2,3-dimethylbutane
- (A) 6. Which of the following structures is a Fischer projection of (2S,3S,4R)-hexane-2,3,4-triol. ÇH₃ CH₂ -OH •OH -H OH H -H HO -H H юн •OH H Н -OH HO--H -OH HO -H ĊH₂CH₃ ĊH₂CH₃ CH2CH2 CH2CH3 CH₂CH₃ ш I IV Π (A) I (B) II (C) III (D) IV (E) V
- (B) 7. Treatment of (S)-6-chloro-1-methyl-1-cyclohexene with H_3O^{\oplus} is expected to produce which of the following product(s)?



- (A) 8. Which of the following substituent has the highest priority according to the Cahn-Ingold-Prelog system?
 (A) -COOH
 (B) -CHO
 (C) -CH₂OH
 (D) -CH₃
 (E) -H
- (C) 9. What is the IUPAC name of the expected **major** product formed upon reaction of HCl with 3-methyl-1-butene?
 - (A) 1-Chloro-2-methylbutane (B) 1-Chloro-3-methylbutane (C) 2-Chloro-2-methylbutane
 - (D) 2-Chloro-3-methylbutane (E) 1-Chloropentane
- (D) 10. Which sequence correctly ranks the following substrates in order of increasing **reactivity** in an $S_N 1$ reaction?



- (D) 11. A pure sample of (S)-phenylalanine has a specific rotation of +70°. A mixture of the two enantiomers of phenylalanine gives a specific rotation of -7.0°. What are the percentages of the S and R enantiomers in the mixture?
 (A) 75 % S, 25 % R
 (B) 65 % S, 35 % R
 (C) 55 % S, 45 % R
 - (D) 45 % S, 55 % R (E) 35 % S, 65 % R
- (B) 12. Predict the **major** product when pyridine is treated with a mixture of nitric acid and sulfuric acid
 - (A) 2-nitropyridine(B) 3-nitropyridine(C) 4-nitropyridine(D) 2,3-dinitropyridine(E) 2,4-dinitropyridine
- (A) 13. Predict the product(s) for the following reaction.
 - 3 2

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(B) 14. Which molecular formula is consistent with the following mass spectrum data? $\mathbf{M}^{+\bullet}$ at m/z= 84, relative height=10.0% $(\mathbf{M}+1)^{+\bullet}$ at m/z= 85, relative height=0.56% (A) C₅H₁₀O (B) C₅H₈O (C) C₅H₂₄ (D) C₆H₁₂ (E) C₄H₆O₂

(D) 15. Which sequence correctly ranks the following dienes in order of increasing **reactivity** in the Diels-Alder reaction?



(D) 16. Rank the following compounds in increasing order of **reactivity** in the intramolecular displacement of *p*-bromophenolate to form a cyclic anhydride.



(B) 17. Which of the following undergoes solvolysis in water more rapidly?



- (C) 18. Grignard reagents react with oxirane (ethylene oxide) to form 1°-alcohols but **can be prepared** in tetrahydrofuran solvent. Why is this difference in behavior observed?
 - (A) Steric hindrance in the case of tetrahydrofuran precludes reaction with the Grignard.
 - (B) There is a better leaving group in the oxirane molecule.
 - (C) The oxirane ring is the more highly strained.
 - (D) It is easier to obtain tetrahydrofuran in anhydrous condition.
 - (E) Oxirane is a cyclic ether, while tetrahydrofuran is a hydrocarbon.
- (B) 19. The regioselectivity and stereospecificity in the oxymercuration-demercuration of an alkene is **best** described as:
 - (A) Markovnikov orientation with syn-addition
 - (B) Markovnikov orientation with anti-addition
 - (C) anti-Markovnikov orientation with syn-addition
 - (D) anti-Markovnikov orientation with anti-addition

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(E) Markonikov orientation with both syn- and anti-addition

(A) 20. What is the **major** product of the following reaction?



(C) 21. What is the **major** product of the following reaction?



- (A) 22. Which of the following descriptions of the nucleoside uridine does **NOT** apply to the structure of the molecule?
 - (A) The uracil base is directly bonded to the 1' position of ribofuranose in the α position.
 - (B) The ribofuranose moiety is found in only the D configuration.
 - (C) Nitrogen, at position 1 in the uracil base, is directly bonded to the ribofuranose moiety.
 - (D) The 5' OH group is replaced with phosphate(s) in the nucleotide structure.
 - (E) None of the above
- (C) 23. Which sequence ranks the following aromatic rings of this compound in order of increasing **reactivity** in an electrophilic aromatic substitution reaction (slowest to fastest reacting)?



(A) 24. Which sequence ranks the indicated protons in order of increasing acidity?



(B) 25. Which pair of structures represents the same compound?





(A) I and II (B) II and IV (C) III and IV (D) III and V (E) IV and V

(D) 26. What is the **major** product of the following reaction?



(C) 27. What is the **major** product of the following reaction?



(E) 28. Which of the following is the **strongest** nucleophile? (A) NaOH (B) NaOMe (C) KOH (D) KOMe (E) KSMe

(x) 29. Which would be the **major** product of the reaction shown? CH_3 1). Hg(OAc)₂, THF, H₂O



(D) 30. Provide the major product for the following reaction



(C) 31. Predict the **major** product for the following reaction.

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(B) 32. Predict the **major** product for the following reaction.



(B) 33. Which of the alkynes below, after undergoing an acid-catalyzed hydration, would be expected to produce two **different** ketones in nearly equivalent yields?

- (A) 1-hexyne (B) 2-hexyne (C) 3-hexyne
- (D) 3-methyl-1-pentyne (E) 4-methyl-1-pentyne

(B) 34. Predict the products of the following reaction:



(D) 35. Which of the following is a correct prediction of the **chemical shifts** (ppm) for the signals in the ¹H NMR spectrum for the following compound?



(A) 36. Provide the name of the **major** alkene product that results when (2R,3R)-2,3-dibromopentane is treated with zinc in acetic acid.

(A) (Z)-2-pentene(B) (E)-2-pentene(C) (R)-3-bromo-1-pentene(D) (S)-3-bromo-1-pentene(E) (R)-2-bromo-3-pentene

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(D) 37. What is the **major** expected product(s) of the reaction shown below?

$CH_3CH_2-C\equiv C-CH_3$	→ ?	
(A) 2,2-Dichloropentane	(B) 3,3-Dichloropentane	(C) 2,3-Dichloropentane
(D) A and B	(E) B and C	_

(B) 38. What is the expected major organic product from treatment of 4-methyl-2-pentyne with hydrogen in the presence of Lindlar's catalyst?
 (A) (E) 4 methyl 2 pentens
 (B) (7) 4 methyl 2 pentens

 $\begin{array}{ll} (A) \ (E)\ -4\ -methyl\ -2\ -pentene \\ (D) \ (Z)\ -2\ -methyl\ -2\ -pentene \\ (E) \ 2\ -methyl\ pentene \\ \end{array} \\ \begin{array}{ll} (B) \ (Z)\ -4\ -methyl\ -2\ -pentene \\ (E) \ 2\ -methyl\ pentene \\ \end{array}$

(B) 39. Refer to the equilibrium below, the correct name for the cyclic structure is_____



- (C) 40. Which of the following best describes the key mechanistic steps in the reaction of an acid chloride and an alcohol to form an ester?(A) If it is a fully a life in the step is a fully a life in the step in the step is a step in the st
 - (A) elimination followed by addition(B) addition followed by decarboxylation(C) addition followed by elimination(D) substitution followed by addition
 - (E) rearrangement
- (D) 41. Many nucleophilic addition reactions of aldehydes and ketones are catalyzed by acid or base. Bases catalyze hydration by:
 - (A) making the carbonyl group more electrophilic
 - (B) shifting the equilibrium of the reaction
 - (C) making the carbonyl group less electrophilic
 - (D) converting the water to hydroxide ion, a much better nucleophile
 - (E) None of the above
- (E) 42. Which of the following would produce a mixture of products when treated under appropriate conditions with *N*-bromosuccinimide?

(A) oct-4-ene (B) hept-1-ene (C) 4,4-dimethylcyclopentene

(D) 4,5-dimethylcyclohexene (E) all produce a mixture of products

說明:原題目因未說明反應條件,因此產物可經由 radical 或 electrophilic 路徑產生。本題之正確答案應為(E),原公布之答案(B)有誤。

(C) 43. Which of the following statements correctly characterizes the following compound?

(A) contains 6π electrons and is aromatic (B) contains 6π electrons and is nonaromatic (C) contains 8π electrons and is antiaromatic (D) contains 8π electrons and is aromatic



(E) contains 8π electrons and is nonaromatic 說明: Azepine 是平面且有 8 對電子,屬 antiaromatic

(A) 44. What is the **major** product of the following reaction?



(B) 45. The ¹H NMR spectrum of which of the compounds below, all of formula $C_7H_{12}O_2$, would consist of **three singlets only**?



- (C) 46. Arrange the following in order of increasing **basicity**: aniline, *p*-nitroaniline, *p*-toluidine, and *p*-methoxyaniline.
 - (A) *p*-toluidine < *p*-methoxyaniline < aniline < *p*-nitroaniline
 - (B) *p*-nitroaniline < *p*-toluidine < aniline < *p*-methoxyaniline
 - (C) *p*-nitroaniline < aniline < *p*-toluidine < *p*-methoxyaniline
 - (D) *p*-methoxyaniline < *p*-nitroaniline < *p*-toluidine < aniline
 - (E) None of the above
- (D) 47. What is the thermodynamic product of the sulfonation of naphthalene?



(D) 48. For the reaction shown, which of the compounds listed below would be the expected **major**, and final, organic product?



(D) 49. Predict the major product for the following Claisen rearrangement.



(A) 50. Predict the **major** product for the following reaction.



- (B) 51. Which of the following reagents can be used to cleave a *tert*-butoxycarbonyl (Boc) protecting group from a peptide?
 (A) H₂/Pd
 (B) CF₃CO₂H
 (C) Na₂CO₃, H₂O (D) LiAlH₄
 (E) None of the above
- (D) 52. The reaction shown below would be expected to produce as **major** products which of the following compounds?



(D) 53. What is the **best** method for the preparation of *m*-dibromobenzene from benzene? (A) 1) HNO (H SO : 2) Sp(HCl: 2) NoNO (HCl $0^{\circ}C$: 4)

(A) 1). HNO_3/H_2SO_4 ; twice	2). Sn/HCl;	3). NaNO ₂ /HCl, 0°C; 4). $Br_2/FeBr_3$,
(B) 1). HNO_3/H_2SO_4 ;	2). Sn/HCl;	3). NaNO ₂ /HCl, 0°C; 4). $Br_2/FeBr_3;$
5). H_3PO_2 . (C) 1). HNO_3/H_2SO_4 ;	2). Sn/HCl;	3). NaNO ₂ /HCl, 0°C; 4)). H ₃ PO ₂ ; 5).
(D) 1). HNO ₃ /H ₂ SO ₄ ; 5) CuBr	2). Br ₂ /FeBr ₃ ;	3). Sn/HCl; 4). N	aNO ₂ /HCl, 0°C;
-)			



(E) Br₂/FeBr₃, twice.

- (B) 54. Which is the **best** method for the synthesis of tert-butyl methyl ether?
 - (A) $CH_3ONa + (CH_3)_3CBr$ —
 - (B) $(CH_3)_3CONa + CH_3I$ —
 - (C) CH₃OH + (CH₃)₃COH + H₂SO₄ at 140° C -
 - (D) $(CH_3)_3CONa + CH_3OCH_3 \longrightarrow$ (E) $CH_3ONa + (CH_3)_3COH \longrightarrow$
- (E) 55. Which of the following will result in **removal** of a benzyl ester protecting group? (A) acid hydrolysis only (B) decarbonylation only
 - (C) catalytic hydrogenation only (D) both acid hydrolysis and decarbonylation
 - (E) both catalytic hydrogenation and acid hydrolysis
- (D) 56. Which of the following ketones will give a **positive** iodoform test?
 - (A) 3-heptanone (B) 3-hexanone (C) cyclohexanone
 - (D) 2-pentanone (E) 2-methyl-3-hexanone
- (B) 57. Which of the following compounds will display a singlet, a triplet and a quartet in the 1 H NMR spectrum?
 - (A) 1-chloro-2,2-dimethylbutane (B) 3-chloro-3-methylpentane (C) 3-chloropentane
 - (D) 2-chloro-4-methylpentane (E) 3-chloro-2-methylpentane
- (A) 58. Examining the infrared spectrum of a compound allows us to:
 - (A) determine the types of functional groups present in the compound
 - (B) determine the carbon-hydrogen framework of the compound
 - (C) determine the molecular weight of the compound
 - (D) determine the nature of the conjugated pi electron system in the compound
 - (E) None of the above is correct
- (B) 59. Which of these is the **least** reactive type of organometallic compound? (C) RLi (D) R_2Zn (E) R₃Al (A) RK $(B) R_2Hg$
- (C) 60. Which one of the following compounds will have the **lowest** wavenumber for carbonyl absorption?



【單選題】每題 2 分,共計 40 分,答錯 1 題倒扣 0.5 分,倒扣至本大題零分為止,未作答, 不给分亦不扣分。

(D) 61. A student measured the optical activity of an unknown sugar at two different concentrations. The results of his measurements are shown below. Given that the sample cell had a path length of 10.0 cm, calculate the specific rotation for the unknown sugar.

concentration	observed rotation
2.00 g sugar in 10.0 mL water	+159.1°
5.00 g sugar in 10.0 mL water	+127.8°



(B) 62. Which of the following series of **synthetic steps** could be used to carry out the transformation shown below?

(I) H₂, Pt, (II) B₂H₆, (III) NaNO₂, H₃O^{\oplus}, (IV) NaCN, HCl, (V) H₂O₂, NaOH (VI) PCC (B) IV \rightarrow I \rightarrow III (C) III \rightarrow VI \rightarrow V $(A) I \rightarrow II \rightarrow V$ (D) II \rightarrow V \rightarrow III (E) None of the above

(A) 63. What is the **major** product of the following reaction?



(D) 64. Which of the following sequences efficiently converts 2-methylpropene into 3-methylbutanal?

- H₃C (A) 1) HBr; 2) NaCCH; 3) O₃; 4) H₂O (B) 1) HBr; 2) NaCCH: $3) O_3;$ 4) DMS (C) 1) HBr, ROOR; 2) NaCCH; 3) O₃; 4) H₂O (D) 1) HBr, ROOR; 2) NaCCH; 3) H₂/Ni₂B; 4) O₃; 5) DMS (E) 1) NaCCH; 2) $H_2/Ni_2B;$ 3) $O_3;$ 4) DMS
- (B) 65. How many positive and negative peaks appear in the DEPT-135 and in the DEPT-90 spectrum of 2-methylpentane?
 - (A) DEPT-135: two positive and one negative, DEPT-90: one positive
 - (B) DEPT-135: three positive and two negative, DEPT-90: one positive
 - (C) DEPT-135: three positive and two negative, DEPT-90: no signals
 - (D) DEPT-135: two positive and three negative, DEPT-90: two positive
 - (E) None of the above is correct
- (A) 66. The Fischer indole synthesis is the reaction of phenylhydrazine with a carbonyl compound to give the corresponding indole. For the preparation of the following indole, what carbonyl **compound** is needed?



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(B) 67. What is the **major** product obtained from the following reaction sequence?



(C) 68. Which of the following compounds can adopt a chair conformation in which there are no axial methyl groups?

(A) 1,1-dimethylcyclohexane (B) *cis*-1,2-dimethylcyclohexane

(C) trans-1,2-dimethylcyclohexane (D) trans-1,3-dimethylcyclohexane

(E) everyone above have no axial methyl group

(A) 69. For the following reaction sequence, which molecule is an expected major product?

$$(A) \xrightarrow{HO} (B) \xrightarrow{OH} (C) \xrightarrow{OH} (D) (E) \xrightarrow{Br} (C)$$

(B) 70. Which of these is NOT a useful method for the synthesis of 1,3-pentadiene?

- (A) 1,4-pentanediol + H_2SO_4 at $180^{\circ}C$
- (B) 2,4-dibromopentane + $(CH_3)_3COK$, $(CH_3)_3COH$ at 75°C
- (C) 2,4-pentanediol + H_2SO_4 at $180^{\circ}C$
- (D) HC=CCH=CHCH₃ + H₂, Ni₂B (P-2)
- (E) 1,4-dibromopentane + CH₃CH₂ONa , CH₃CH₂OH at 75°C
- (C) 71. Which of the following series of synthetic steps could be used to carry out the transformation shown below?



(B) 72. What is the **name** of the following reaction?

$$(A) \text{ Mixed Aldol condensation}$$

$$(B) \text{ Mixed Claisen condensation}$$

$$3-12$$

(C) Mixed Dieckmann condensation (D) Mixed Michael reaction

(E) Mixed Knoevenagel reaction

說明:Dieckmann condensation 為分子內的 Claisen condensation,最後形成環狀產物,而題 目是由 cyclohexanone 先轉變成 enolate 接著進行 nucleophilic acyl substitution,本題之正 確答案應為(B) Crossed Claisen condensation (or Mixed Claisen condensation)。

(B) 73. Which of the following represents the HOMO of pentadienyl anion?

(A)
$$\mathcal{O}$$
 (B) \mathcal{O} (C) \mathcal{O} (D) \mathcal{O} (E) \mathcal{O}

(D) 74. Predict the **major** product for the following reaction sequence.



- (E) 75. The H-bonds formed in the tertiary structure of proteins can be differentiated from those formed in secondary structures. What is the **major** distinguishing factor?
 - (A) The H-bonds in 3° structures are significantly stronger than those found in 2° structures.
 - (B) The H-bonds in 3° structures are more random than those formed in 2° structures.
 - (C) The H-bonds in 3° structures are formed by predictable interactions among the peptide backbone α -amine and α -carboxylate groups.
 - (D) The H-bonds in 3° structures are formed by interactions involving the side chain R-groups.
 - (E) Both B and D are correct.
- (C) 76. Predict the outcome of the following sequence of reactions.



- (B) 77. Which of the following compounds exhibits the pattern of m/z values: 41, 43, 57, 87, 101, 116?
 (A) *n*-butyl *n*-propyl ether
 (B) sec-butyl iso-propyl ether
 (C) 2-heptanol
 (E) None of the above
- (B) 78. How many different β -hydroxyaldehydes and β -hydroxyketones, including constitutional isomers and stereoisomers, are formed upon treatment of a mixture of acetone and acetophenone with base?

(A) 4 (B) 6 (C) 9 (D) 10 (E) 12 說明:本題因限定生成產物為β-hydroxyaldehydes and β-hydroxyketones,無進一步脫水 反應,故生成產物應只有 6 種。

(D) 79. Deduce the identity of the compound from the data provided.

 $C_5H_{10}O_2$: IR (cm⁻¹): 3380 (br, s). ¹H-NMR (ppm): 1.30 (s, 3H), 3.50 (t, 1H), 3.64 (d, 2H),

4.38 (d, 2H), 4.52 (d, 2H). ¹³C-NMR (ppm): 20.72 (q), 40.78 (t), 67.59 (t), 79.74 (t).

(A) (2,3-dimethyloxiran-2-yl)methanol (B) 1-(2-methyloxiran-2-yl)ethanol

(C) 1-(oxetan-3-yl)ethanol (D) (3-methyloxetan-3-yl)methanol

(E) (tetrahydrofuran-2-yl)methanol

(C) 80. Predict the **major** product for the following reaction.

