國立臺灣大學99學年度碩士班招生考試試題

科目:有機化學(A)

題號: 60 共 √ 頁之第 / 頁

注意:本試題包含單選題及問答題兩部份

Part I. 單選題 (25 題,50 分) ※ 本大題請於試卷內之「選擇題作答區」依序作答。

1. In which structure(s) below does nitrogen have a formal charge of +1?

$$H_3C-N=CH_2$$
 H_3C-N-H $H-N-OH$ H_3C-NH_2 $H_3C-N-CH_3$ CH_3 I II IV V $(A) I$ $(B) II and IV$ $(C) III and V$

- 2. The synthesis of an alkyne precursor to 2,2-dimethylheptane is accomplished most effectively by the reaction between these two reagents:
- (A) CH₃CH₂CH₂C≡CNa and (CH₃)₃CBr
- (B) CH₃CH₂C≡CNa and (CH₃)₃CCH₂Br
- (C) (CH₃)₃CC≡CNa and CH₃CH₂CH₂Br
- (D) (CH₃)₃CCH₂CH₂C≡CH and CH₃CH₂I
- (E) HC≡CNa and (CH₃)₃CCH₂CH₂Br
- 3. Which is a meso compound?
- (A) (2R,3R)-2,3-Dibromobutane
- (C) (2R,4R)-2,3-Dibromopentane
- (E) (2R,4S)-2,4-Dibromohexane
- (B) (2R,3S)-2,3-Dibromopentane
- (D) (2R,4S)-2,3-Dibromopentane
- 4. Which compound would show optical activity?
- (A) cis-1,4-Dimethylcyclohexane
- (B) trans-1,4-Dimethylcyclohexane
- (C) cis-1,4-Dimethylcycloheptane
- (D) trans-1,4-Dimethylcycloheptane

- (E) More than one of these.
- 5. The rate equation for a nucleophilic substitution reaction of a tertiary alkyl bromide (R-Br) with I ion would be:
- (A) Rate = k [RBr]

(B) Rate = $k [I^-]$

(C) Rate = $k [RBr][I^-]$

(D) Rate = $k [RBr]^2 [I^-]$

- (E) Rate = $k [RBr][I^{-}]^2$
- 6. Consider the substitution reaction that takes place when (R)-3-bromo-3-methylhexane is treated with methanol. Which of the following would be true?
- (A) The reaction would take place only with inversion of configuration at the stereogenic center.
- (B) The reaction would take place only with retention of configuration at the stereogenic center.
- (C) The reaction would take place with racemization.
- (D) No reaction would take place.
- (E) The alkyl halide does not possess a stereogenic center.

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7.	Which nucleophilic substitution reaction is	s not	likely to	occur?
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(A) I^- + CH_3CH_2-Cl \longrightarrow CH_3CH_2-I + Cl^-

(B) Γ + CH_3CH_2 -OH \longrightarrow CH_3CH_2 -I + OH^-

(C) $CH_3O^- + CH_3CH_2-Br - CH_3CH_2-OCH_3 + Br^-$

(D) I^- + CH_3CH_2 -Br \longrightarrow CH_3CH_2 -I + Br^-

(E) $OH^- + CH_3CH_2-CI \longrightarrow CH_3CH_2-OH + CI^-$

8. Rearrangements are likely to occur in which of the following reaction types?

(A) S_N1 reactions

(B) S_N2 reactions

(C) E1 reactions

(D) E2 reactions

(E) Both S_N1 and E1 reactions

9. What compound would yield an equimolar mixture of CH₃CH₂CH₂CHO and CH₃CHO upon treatment with O₃, followed by Zn/HOAc?

(A) 1-Hexene

(B) cis-2-Hexene

(C) trans-2-Hexene

(D) More than one of these

(E) None of these

10. Which proton(s) of the compound below would appear as a triplet in the ¹H NMR spectrum?

CH₃CH₂CH₂O-CHCH₃

I II III IV V

(A) The protons on carbon II

(B) The protons on carbon I and V

(C) The protons on carbon III and V

(D) The protons on carbon III and IV

(E) The protons on carbon V

11. The free radical chlorination of (R)-2-chloropentane forms a mixture of dichloropentanes which includes:

(A) three optically active compounds.

(B) two achiral compounds.

(C) two meso compounds.

(D) one pair of diastereomers.

(E) one racemic mixture.

12. Which of the following can be described as "optically active, primary alcohol"?

(A) CH₃CH₂CH₂CH₂CH₂OH

(B) (CH₃)₂CHCH₂CH₂OH

(C) CH₃CH₂CH(CH₃)CH₂OH

(D) (CH₃)₂CHCHOHCH₃

(E) Two of the above.

- 13. The success in converting low molecular weight 1° alcohols to aldehydes by use of $K_2Cr_2O_7/H_2SO_4$ as oxidant can be attributed to the fact that:
- (A) Dichromate is a relatively weak oxidizing agent.
- (B) The presence of H₂SO₄ limits the oxidation.
- (C) The aldehyde can be separated, as formed, by distillation.
- (D) Aldehydes are not oxidized by the K₂Cr₂O₇/H₂SO₄ mixture.
- (E) Hydrogen bonding occurs between the alcohol and the acid present.

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14. The reaction of lithium di-sec-butylcuprate with isopentyl bromide yields:

(A) 2,5-Dimethylheptane

(B) 2,6-Dimethylheptane

(C) 3,5-Dimethylheptane

(D) 3,4-Dimethylheptane

(E) 3,6-Dimethylheptane

15. Which of the reagents listed below would efficiently accomplish the transformation of CH₃CH₂CH=CHCH₂CH₂CHO into CH₃CH₂CH=CHCH₂CH₂CH₂OH?

(A) KMnO₄

(B) NaBH₄

(C) Br₂ in CCl₄

(D) H₂, Ni

(E) Two of the above

16. Which of the following could be used to synthesize 3-bromocyclopentene?

(A) Cyclopentene + Br₂, CCl₄, 25°.

(B) Cyclopentene + NBS, CCl₄ (ROOR).

(C) 3-Cyclopentenol + PBr₃.

(D) Both A) and B).

(E) Both B) and C).

17. Which of the following is NOT true of benzene?

(A) Benzene tends to undergo substitution rather than addition reactions, even though it has a high index of hydrogen deficiency.

(B) All of the hydrogen atoms of benzene are equivalent.

(C) The carbon-carbon bonds of benzene are alternately short and long around the ring.

(D) Only one o-dichlorobenzene has ever been found.

(E) Benzene is more stable than the hypothetical compound 1,3,5-cyclohexatriene.

18. What might be predicted to happen when the following substance undergoes Friedel-Crafts acylation?

$$O_2N$$
— CH_2 — B

(A) Substitution occurs in ring B, p- to the methylene group.

(B) Substitution occurs in ring A, o- to the nitro group.

(C) Substitution occurs in ring A, o- to the methylene group.

(D) Substitution occurs in ring B, m- to the methylene group.

(E) None of the above.

19. Select the structure of the major product in the following reaction.

$$\begin{array}{c} \text{H}_2\text{SO}_4 \\ \hline \\ \text{H}_g\text{SO}_4, \text{H}_2\text{O} \end{array}$$

(A) Ethylbenzene

(B) 1-Phenylethanol

(C) Acetophenone

(D) 2-Phenylethanal

(E) Vinylbenzene

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20. Which compound would be formed when 2-methylbutanal is treated with a solution of NaOD in D₂O?

CH₃CH₂CDCHO

CH₃CH₂CHCDO

CH₃CHDCHCHO

CH₃CHDCHCHO

CH₃CH₂CDCDO

CH₃

CH₃

(B)

CH₃

(C)

CH₃

(D)

CH₃

(E)

CH₃

CH₃

21. What would be the final organic product of the following reaction?

 C_6H_5 CI NaCN i. excess LAH, Et_2O ?

(A) $C_6H_5CH_2CH_2CO_2H$

(B) C₆H₅CH₂CH₂NH₂

(C) C₆H₅CH₂CH(CH₃)CN

(D) C₆H₅CH₂CH=NH

(E) C₆H₅CH₂NH₂

22. Which of the following could be used to synthesize the following substance in good yield?

- (A) Cyclopentanone, ClCH₂CH₂COOH, AlCl₃, heat.
- (B) Cyclopentanone, (CH₃CH₂)₂NH, HA, (-H₂O); then BrCH₂CH₂COOC₂H₅; then OH⁻, H₂O, heat; then H₃O⁺.
- (C) 3-(2-hydroxycyclopentyl)propanal, KMnO₄, OH⁻, heat; then H₃O⁺.
- (D) Answers A) and B).
- (E) Answers B) and C).
- 23. What would be the major product of the following reaction?

- 24. Which reagent will distinguish between C₆H₅NH₂ and (C₆H₅)₂NH?
- (A) HCl (aq)

(A) I

- (B) NaOH (aq)
- (C) C₆H₅SO₂Cl/OH⁻, then H₃O⁺

(D) Br₂/CCl₄

(E) KMnO₄

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25. What are the correct designations for the stereogenic centers in this aldose?

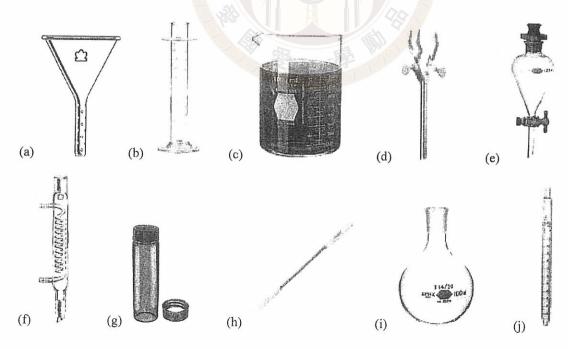
- (A) 2R, 3S, 4R
- (B) 2R,3S,4S

(C) 2S,3R,4R

- (D) 2S,3S,4R
- (E) 2R, 3R, 4S

Part II. 問答題 (5題,50分)

1. Please name the following items in English. (20 points)



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2. Account for the fact that $CH_3CH_2CH_2CH_2CI$ reacts with 0.01 M NaCN in ethanol to yield primarily $CH_3CH_2CH_2CH_2CH_2CN$, whereas under the same condition $(CH_3)_3CCI$ reacts to give primarily $(CH_3)_3COCH_2CH_3$. (8 points)

3. Propose a mechanism for the following transformation. If the carbonyl oxygen is enriched with oxygen-18, where would you expect this oxygen label to appear? (8 points)

$$H$$
 + CH_3OH H^{\oplus} OCH_3 + H_2O

4. Please briefly describe how you could experimentally determine that *trans*-2-butene is more stable than *cis*-2-butene. (6 points)

5. Which of the following will undergo an elimination reaction more rapidly? Give the structure of the major product(s) and explain your answers. (8 points)

試題隨卷繳回