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1-44 (2 points for each); 45 (12points)

- 1. How many compounds having the formula C₆H₁₄ can be drawn and properly named as a "pentane"?
- **a**. 1
- Ъ. 2
- c. 3
- d. 4
- e. None; pentanes must have five carbons.
- 2. How many isomers exist of dichlorocyclobutane?
- a. 1
- b. 2
- c. 3
- d. 4
- e. 5
- 3. Which of the following statements is correct regarding conformational isomerism in cyclohexane:
- a. In general, equatorial substituents exhibit strong eclipsing interactions.
- b. Complete rotation around carbon-carbon single bonds in the ring do not occur.
- c. Axial substituents are disfavored due to axial-axial interactions.
- d. Both b and c are correct.
- e. All of the above are correct.
- 4. For the molecule shown on the bottom, in it's most stable conformation:
- a. Two of the methyls are axial.
- b. Two of the methyl groups are equatorial.
- c. All of the methyl groups are axial.
- d. All substituents are equatorial.
- e. None of the above are correct

5. In order to perform the conversion shown below:

- a. The compound shown should be reacted with HBr in aqueous solution.
- b. The compound shown should be reacted with strong aqueous acid.
- c. The compound shown should be reacted with HBr/THF, followed by alkaline H2O2.
- d. The compound shown should be reacted with HBr in the presence of peroxides.
- e. 3-Methyl-1-pentene should be reacted with HBr.
- 6. Which of the following statements is correct regarding conformational isomerism in cyclohexane:
- a. In general, equatorial substituents exhibit strong eclipsing interactions.
- b. Complete rotation around carbon-carbon single bonds in the ring do not occur.
- c. Axial substituents are disfavored due to axial-axial interactions.
- d. Both b and c are correct.
- e. All of the above are correct.

(背面仍有題目,請繼續作答)

- 7. Which of the alkenes shown below are one member of a pair of E-Z isomers?
- a. A, only
- b. A and C, only
- c. B, only
- d. B and C, only
- e. A and D, only

8. An amino acid (1 mole) reacts with acetic anhydride (2 moles) and gives no N_2 on treatment with HNO_2 . It is

HO
$$(A) \qquad (B) \qquad (C)$$

$$(A) \qquad (B) \qquad (C)$$

$$(A) \qquad (B) \qquad (C)$$

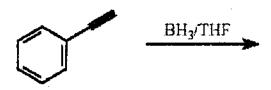
$$(B) \qquad (C)$$

$$(B) \qquad (C)$$

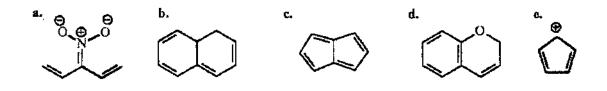
$$(C) \qquad (D) \qquad (E)$$

- 9. Which of the following is true regarding an SN2 reaction:
- a. rearrangements commonly occur in polar, aprotic solvents
- b. the intermediate radical does not undergo rearrangement
- c. the most stable carbocation is always formed
- d. a and c only are both correct
- e, none of the above are correct
- 10. Which of the following is true regarding SN1 reactions:
- a. concurrent E1 elimination reactions are common
- b. rearrangement of the carbocation intermediate is common
- c. the reaction is favored by polar, protic solvents
- d. a and c only are both correct
- e. a, b and c are all correct
- 11. Which of the following is true regarding E1 elimination reactions:
- a, because of steric effects, the least substituted alkene is typically formed
- b. elimination occurs in an antiperiplanar (trans) manner
- c. sterically hindered bases tend to favor elimination over substitution reactions
- d. a and c only are both correct
- e. a, b and c are all correct

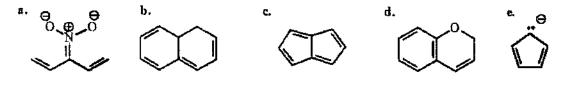
- 12. In a 4+2 cycloaddition reaction, endo stereochemistry is preferred because:
- a. secondary π - π interactions can occur between the diene and substituents on the dienophile
- b. the diene is required to be in the s-cis conformation in order for reaction to occur
- c. electron withdrawing substituents in the dienophile are electrostatically repelled by the electron donating groups of the diene
- d. a and c are both true
- e. none of the above are correct
- 13. Which of the following statements regarding the reaction shown below is true?



- a. work-up with aqueous acid will yield the hydrocarbon
- b. work-up with alkaline peroxide yields the rearranged ketone
- c. in the borane intermediate, the boron will be bonded to the benzyl carbon
- d. a and c only are both correct
- e. a, b and c are all correct
- 14. Reaction of an unknown compound with acidic potassium permanganate yields a carboxylic acid and CO₂; the unknown compound is:
- a. a tetra-substituted alkene
- b. a disubstituted alkyne
- c. a tri-substituted alkene
- d. a terminal alkene with one alkyl substituent
- e. a trans, disubstituted alkene
- 15. In order for a molecule to be aromatic:
- a. it must be planar, cyclic and consist of adjacent sp2 atoms containing $4n+2\pi$ -electrons
- b. it must have at least two electrons in each of the degenerate molecular orbitals describing the π -system
- c. heteroatoms must rehybridize so that all unshared pairs of electrons can contribute to the π -system
- d. a and b only are both true
- e. a, b and c are all correct
- 16. Which of the following molecules meets the Hückle definition for aromaticity:

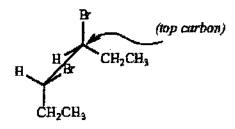


17. Which of the following molecules is antiaromatic:



(背面仍有題目,請繼續作答)

18. The absolute configurations of the two chiral centers in the molecule shown below are (given as TOP, BOTTOM):

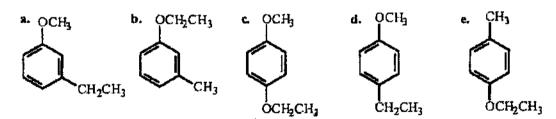


- a. R, R
- b. S. S and the compound is meso
- c. R, S
- d. S, R
- e. S, R and the compound is meso
- 19. An unknown compound gives a copious yellow precipitate when it is reacted with
- 2,4-dinitrophenylhydrazine reagent; you can say with certainty that the unknown compound:
- a. is a ketone
- b. is a ketone or an aldehyde
- c. is a methyl ketone
- d. a and c are both correct
- e. this qualitative test yields ambiguous results; none of the above are correct
- 20. In the mass spectrum, a compound with one bromine atom will have:
- a, two molecular ions, in the ratio 1:1
- b. four molecular ions, in the ratio 1:1:1:1
- c, two molecular ions, in the ratio 2:1
- d. four molecular ions, in the ratio 1:2:2:1
- e. three molecular ions, in the ratio 1:2:1
- 21. In the mass spectrum, a compound with two bromine atoms will have:
- a. two molecular ions, in the ratio 1:1
- b. four molecular ions, in the ratio 1:1:1:1
- c. two molecular ions, in the ratio 2:1
- d. four molecular ions, in the ratio 1:2:2:1
- e. three molecular ions, in the ratio 1:2:1
- 22. The major bands in the infrared spectrum of benzaldehyde will be:
- a. 3150 cm-i; 2200 cm-i; 1610 cm-i
- b. 2930 cm-1; 2750 cm-1; 1760 cm-1; 1610 cm-1
- c. 2930 cm-1; 2450 cm-1; 1610 cm-1
- d. 3150 cm-i; 2200 cm-i; 1750 cm-i; 1610 cm-i
- e. 3010 cm-1; 2200 cm-1; 1750 cm-1



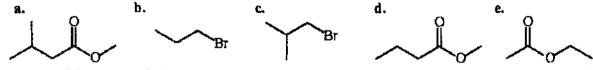
- 23. Which of the following is true regarding the mass spectrum of acetophenone:
- a. a significant peak will occur at m/e = 43
- b. the molecular ion will be a radical-cation
- c. the spectrum will display a predominant m-15 peak
- d. a and c are both correct
- e. all of the above are correct

- 24. In the 1H NMR of acetaldehyde (CH3CHO) the signal from the aldehyde protons will appear as:
- a. a triplet
- b. a singlet
- c. a doublet
- d. a quartet of doublets
- e. a quartet
- 25. Which of the following is true regarding the 13C NMR of carbonyl compounds:
- a. the carbonyl absorbance is generally the most intense peak in the spectrum
- b. acyl carbonyls generally absorb in the region between 170-180 ppm
- c. the carbonyl is highly shielding, hence carbons adjacent to carbonyls generally absorb around 2.0 ppm
- d. a and c are both correct
- e. all of the above are correct
- 26. Which of the compounds shown below would be *most consistent* with the following spectral data: quartet, 14.3; quartet, 22.9; triplet, 68.5; doublet, 114.1; doublet, 129.8; singlet, 129.3; singlet, 155.8

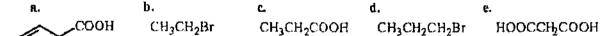


- 27. In the "aromatic" region of the 13C NMR, an symmetrical 1,2-disubstituted aromatic compound will generally display, in a proton-decoupled spectrum:
- a. two singlets and two doublets
- b. one singlet and two doublets
- c. two singlets and four doublets
- d. one singlet and one doublet
- e. three singlets

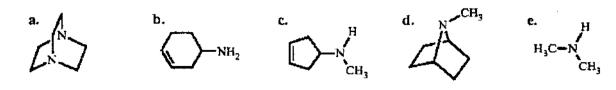
- 28. In the tetrahedral intermediate formed in an acyl transfer reaction, the best anionic leaving group will be:
- a, the strongest nucleophile
- b. the group whose conjugate base has the lowest pK.
- c. the group whose conjugate acid has the lowest pK.
- d. the chlorine
- e. the group having the weakest conjugate acid
- 29. Which of the following is not correct regarding the spectroscopy of acyl compounds?
- a. in the 13C NMR, acyl carbonyls generally have a smaller chemical shift than aldehydes and ketones b. in the MS, the most common fragmentation of acyl compounds is cleavage to form an acylium-like
- ion
- c. the 1H NMR absorbance of carboxylic acid protons is very highly deshielded
- d. in the IR, the carbonyl stretching frequency generally parallels reactivity of the carbonyl carbon towards nucleophilic addition
- e. in the iH NMR, hydrogen bonding in carboxylic acids shifts the carbonyl absorbance to larger chemical shifts
- 30. Glycine may be classed as all of the following except
- a. a chelating agent
- b. an acid
- c. a base
- d. a Zwitterion
- e. an L-amino acid
- 31. Which of the compounds shown below will react with methyl formate (methyl methanoate) in the presence of methoxide anion to give a compound, which on treatment with aqueous acid and gentle heating, will decarboxylate to form butanal?



32. Which of the compounds shown below will react with dimethyl malonate (methyl methyl propanedioate) in the presence of methoxide anion to give a compound, which on treatment with aqueous acid and gentle heating, will decarboxylate and form pentanoic acid?



33. An unknown compound reacts with p-toluenesulfonic acid to form a solid which is insoluble in strong base solution. Elemental analysis indicates that the compound has two degrees of unsaturation. A structure which is consistent with these data is:

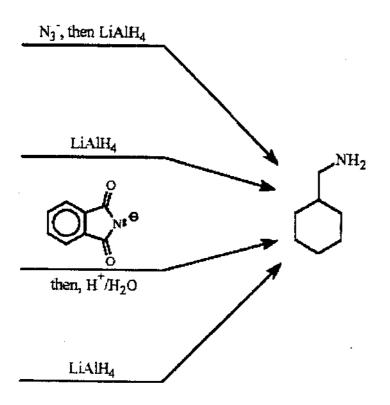


- 34. In the tetrahedral intermediate with three possible anionic leaving groups, the best leaving group will be:
- a. the strongest base
- b. the group having the strongest conjugate base
- c. the group with the highest pK.
- d. the phenoxy group
- e. the group having the weakest conjugate base

35.On hydrolysis and chromatographic analysis a tripeptide was found to give three different amino-acids. Treatment of the tripeptide with phenyl isothiocyanate followed by mild acid hydrolysis liberated a dipeptide and a cyclic compound. The cyclic compound decomposed on treatment with alkali to give an amino-acid, C₃H₂NO₂, the dipeptide reacted with 2,4-dinitofluorobenzene to give a compound which, upon acid hydrolysis, gave two products of molecular formula C₈H₇N₃O₆ and C₉H₁₁NO₂. Which of the following tripeptide structures is in agreement with these data:

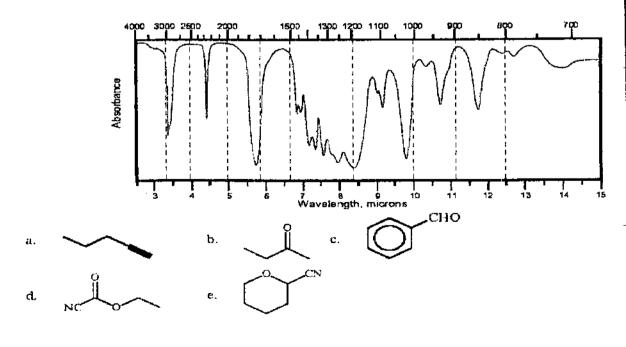
- a. Gly-Ala-Phe
- b. Phe-Ala-Gly
- c. Ala-Phe-Gly
- d. Ala-Gly-Phe
- e. Phe-Gly-Ala

36-39. Aminomethylcyclohexane can be prepared from simple starting materials using the four methods shown below. Provide a suitable starting material for each of the reactions shown.

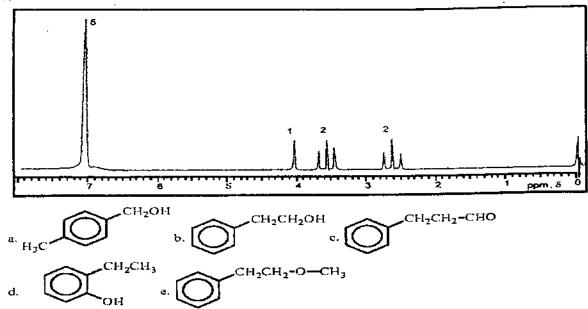


40-42. Beginning with acetophenone (phenylethanone) suggest a synthesis of each of the following compounds. Clearly show all reactants and reaction conditions.

43. Which of the compounds shown below would be most consistent with the infrared spectrum shown below:



44. Which of the compounds shown below would be most consistent with the 'H NMR spectrum shown below:



45. Data for the mass spectrum, the 'H NMR and IR spectrum for a compound C15H14O are given below. Based on the spectral information provided, suggest a structure for this compound and write the structure clearly and indicate the information which you obtained from each spectral source (12 points).

