I. Please choose one answer for each of the following questions.　　　　　　　**(50%)**

1. Arrange the following atoms in increasing order of electronegativity (least first).

　　C　O　Li　N　K

　　(A) K, Li, C, N, O (B) N, C, K, O, Li (C) C, N, O, Li, K (D) Li, K, C, N, O

2. What are the correct orbital hybridizations for carbon in the following species?

　　A. CH_3^- **B.** CH_4 **C.** CH_3^+　　　**I.** sp **II.** sp^2 **III.** sp^3

　　(A) A and I, B and III (B) B and I, C and II (C) A and III, C and II

　　(D) B and III, C and III

3. What is the correct name for a constitutional isomer of C_4H_9Br?

　　(A) 2-methyl-2-bromopropane (B) 2-bromo-2-methylbutane (C) 1-bromo-2-methylpropane (D) 3-bromobutane

4. How many constitutional isomers are there for $C_5H_{11}Br$?

　　(A) 3 (B) 7 (C) 8 (D) 11

5. In the most stable conformation of *trans*-1,4-dimethylcyclohexane, what positions do the methyl groups occupy?

　　(A) axial, axial (B) equatorial, axial (C) equatorial, equatorial (D) axial, equatorial

6. Which of the following substances are bases according to the Lewis theory?

　　I. H_2O **II.** $AlCl_3$ **III.** $CH_3C^+HCH_3$ **IV.** F^-

　　(A) I, II (B) I, III (C) III, IV (D) I, IV

7. Which of the following acids has the highest pK_a?

　　(A) CH_3CO_2H (B) H_2O (C) NH_4^+ (D) HCl

8. Which of the following alkenes do not show *cis-trans* isomerization?

　　I. 2-methyl-2-hexene **II.** 1-chloro-1-butene **III.** 1-methylcyclohexene

　　IV. 2-methyl-3-hexene

　　(A) I, II (B) III, IV (C) II, III, IV (D) I, III

9. What is the product from the dehydrogenation of 2-bromonorbornane?

　　(A) norbornane (B) 1-norbornene (C) 2-norbornene (D) 2,5-norbornadiene

10. Which of the following reagents will react with an alkene in an *anti* addition?

　　I. Cl_2 **II.** Br_2/H_2O **III.** BH_3 **IV.** $KMnO_4$

　　(A) I, II (B) III, IV (C) II, III (D) I, IV

11. What is the major product from acid catalyzed hydration of 2-methyl-2-pentene?

　　(A) 2-methyl-3-pentanol (B) 2-methyl-2-pentanol (C) 4-methyl-2-pentanol

　　(D) 3-methyl-2-pentene

12. What conditions would you use to convert cyclopentene to 3-bromocyclopentene?

　　(A) NBS, peroxides (B) HBr, peroxides (C) Br_2, CCl_4 (D) HBr, H_2SO_4

13. How many atoms lie in a straight line in 1-pentyne?

　　(A) 2 (B) 3 (C) 4 (D) 5

14. What are the best conditions for converting 3-hexyne to hexane?
    (A) Ni + H_2 (B) Pd/CaCO$_3$ +H_2 (C) Na/NH$_3$ (D) NaNH$_2$ + NH$_{3(l)}$

15. Which of the following compounds contain stereocenters?　　I. 2-methylpentane
    II. chlorocyclohexane III. 3-methyl-2-butanol IV. 2-hydroxypropanoic acid
    (A) I, II (B) III, IV (C) I, III (D) II, IV

16 For bromination of CH$_3$CHCHCl using Br$_2$ in CCl$_4$, the product, 1-chloro-1,2-
   dibromopropane, has X possible stereoisomers and only Y are actually formed. What
   are X and Y?
   (A) 3, 1 (B) 3, 2 (C) 4, 2 (D) 4, 3

17. Calculate the enantiomeric excess for the reaction that gives 75% of the S-form and 25% of
    the R-form.
    (A) 25% (B) 33.33% (C) 50% (D) 75%

18. A terminal alkyne, C_6H_{10}, loses its chirality when converted to C_6H_{14} by catalytic
    hydrogenation. What is the alkyne?
    (A) 1-hexyne (B) 3-methyl-1-pentyne (C) 4-methyl-1-pentyne (D) 3,3-dimethyl-1-
    butyne

19. Arrange the following compounds in the order of increasing polarity (least first).
    I. CH$_3$CH$_2$OH II. CH$_3$SH III. H$_2$O IV. CH$_3$OCH$_3$
    (A) III, IV, II, I (B) II, IV, III, I (C) II, IV, I, III (D) I, III, II, IV

20. Place the following in the order of increasing strength of the hydrogen bonds (weakest
    first).
    I. HNH---OH$_2$ II. H$_3$N---HNH$_2$ III. H$_2$O---HOH IV. H$_3$N---HOH
    (A) I, II, III, IV (B) III, I, IV, II (C) II, IV, I, III (D) I, IV, II, III

21. Which of the following compounds are secondary halides?
    I. isobutyl bromide II. 2-iodobutane III. isopropyl fluoride IV. neopentyl chloride
    (A) I, II (B) III, IV (C) II, III (D) I, IV

22. Which of the following statements characterize the reaction of R-3-chlorocyclopentene
    with sodium iodide in acetone?
    I. The reaction involves a carbocation intermediate.
    II. The reaction involves inversion of configuration.
    III. The reaction involves retention of configuration.
    IV. The reaction gives predominately a racemic product.
    (A) I (B) II (C) I, IV (D) I, III

23. Which of the following statements are true for an E$_1$ reaction?
    I. The reaction is first order in alkyl halide and zero order in base.
    II. The reaction is first order in alkyl halide and first order in base.
    III. Rearrangements are common.
    IV. The order of reactivity is 1° > 2° > 3° > 4°
    (A) I, III (B) II (C) I, III, IV (D) II, IV

24. The base peak for a hydrocarbon is 57. Which of the following is the most likely
    compounds?
    (A) 2,2,4-trimethylpentane (B) octane (C) methylcyclopentane (D) 2-methylpentane

25. What are the best conditions for preparing *trans*-2-butene oxide?
    (A) E-2-butene + 3-chloroperoxybenzoic acid
    (B) Z-2-butene + 3-chloroperoxybenzoic acid
    (C) 1-butene + chlorine and water followed by aqueous sodium hydroxide
    (D) 1,4-dichlorobutane + sodium sulfide

26. The mass spectrum for a hydrocarbon shows a series of peaks separated by 14 m/e units. Which of the following best describes the hydrocarbon?
    (A) a branched chain (B) a cycloalkane (C) a straight chain (D) an alkene

27. An alkyl chloride can be detected by which of the following in a mass spectrum?
    (A) $(m + 2)/m = 1$ (B) $m - 18$ (C) $(m + 2)/m = 100$ (D) $(m + 2)/m = 0.3$

28. What is the index of hydrogen deficiency of a compound having the molecular formula of $C_6H_6N_2O$?
    (A) 3 (B) 4 (C) 5 (D) 6

29. Which of the following can be used to distinguish between pentane and 2-methylbutane in the ^{13}C-NMR spectrum?
    (A) The number of signals (B) The proton coupled C-NMR (C) The chemical shift
    (D) All of these

30. Compound X gives three signals in the ^{13}C-NMR spectrum and two signals in the ^1H-NMR spectrum. Which of the following is most likely compound X?
    (A) dimethyl ether (B) diethyl ether (C) neopentane (D) methyl acetate

31. What is the wave number for an infrared band at 5 microns?
    (A) 500 cm^{-1} (B) 2,000 cm^{-1} (C) 5,000 cm^{-1} (D) 10,000 cm^{-1}

32. What is the order of increasing energy for the following transitions (lowest first)?
    I. $\pi \to \pi^*$ II. $n \to \pi^*$ III. $n \to \sigma^*$
    (A) I, III, II (B) II, I, III (C) III, II, I (D) I, II, III

33. The absorbance of a 1 mL sample of double-stranded DNA, which has the extinction coefficient of 6,670 at 260 nm, is 0.5128 in a 1 cm cuvette. If the molecular weight is taken as 650 for one repeating unit in the polymer, how many mg are in the sample?
    (A) 5 (B) 50 (C) 75 (D) 100

34. One of the best known color indicators is phenophthalein, which is colorless at low pH and red at high pH. What is the best explanation for the change?
    (A) hydrogen bonding at low pH (B) reaction to form high energy species
    (C) molecular rearrangements (D) reaction to form multiple conjugated aromatic rings

35. How many resonance structures are possible for the benzyl cation?
    (A) 3 (B) 4 (C) 5 (D) 6

36. Which of the following groups activate a nucleophilic aromatic substitution reaction?
    I. –Cl II. –OCH$_3$ III. –CF$_3$ IV. –NH$_2$ V. –CH$_3$ VI. –CN
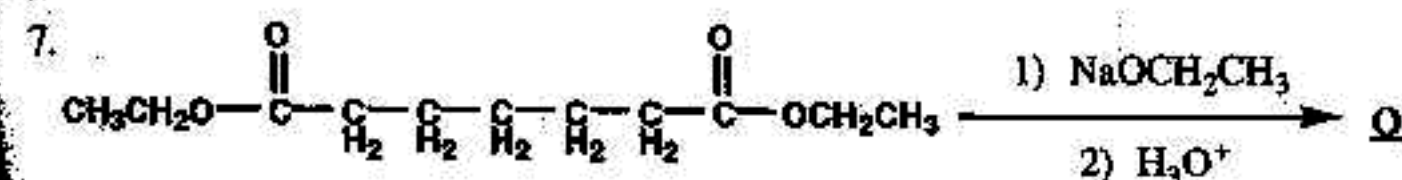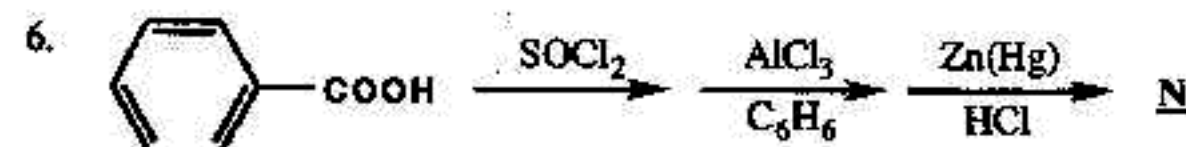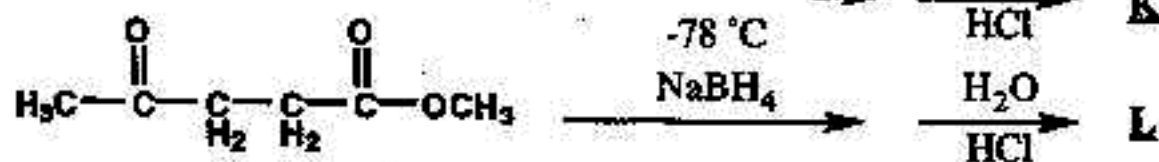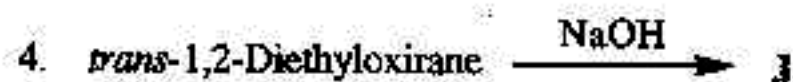   (A) I, III, VI (B) II, V, VI (C) I, II, III (D) IV, V, VI

37. What is the electrophile in the nitration of benzene?
    (A) HNO_3 (B) $^+NO_2$ (C) $^-NO_3$ (D) ^+NO

38. What is the product from a Wolff-Kishner reaction with acetaldehyde?
    (A) CH_3CH_3 (B) $CH_2=CH_2$ (C) $CH_3CH_2CH_3$ (D) CH_3CH_2OH

39. What reagent could be used to convert galactose to formic acid and formaldehyde?
    (A) $NaBH_4$ in H_2O (B) HNO_3, warm (C) $AgNO_3$ in NH_3, H_2O (D) H_5IO_6

40. What is the order of increasing acidity for the following compounds (lowest first)?
    I. HCO_2H II. $CH_3CH_2CO_2H$ III. $C_6H_5CO_2H$ IV. $ClCH_2CO_2H$
    (A) III, II, I, IV (B) I, II, IV, III (C) II, III, IV, I (D) II, I, III, IV

41. Which of the following synthetic methods is best for preparing 2-amino-2-methylpropane?
    (A) The Gabriel synthesis using the potassium salt of phthalimide and an alkyl halide.
    (B) Amination of a secondary alkyl halide in the presence of a large excess ammonia.
    (C) Reduction of a secondary amide using $LiAlH_4$.
    (D) Reductive amination of a ketone and a primary amine by hydrogen and a transition metal catalyst.

42. The "ring around the bathtub" is a problem with soaps but not with detergents because
    (A) Soaps are more acidic (B) Soaps are more basic (C) Detergents have soluble calcium salts (D) Soap micelles are unstable in acids.

43. Which property of phospholipids accounts for their ability to form fluid membranes?
    (A) nonpolarity (B) unsaturation (C) hydrophilicity and lipophilicity (D) lipophilicity

44. Which of the following is a useful carboxyl protective group for polypeptide synthesis?
    (A) benzyl alcohol (B) benzyloxycarbonyl chloride (C) *tert*-butyloxycarbonyl chloride
    (D) dicyclohexylcarbodiimide

45. In a Merrifield solid phase peptide synthesis, if there are 4 steps and each goes in 90% yield, what is the overall yield?
    (A) 18% (B) 59% (C) 66% (D) 90%

46. The tertiary structure of proteins depends primarily on which property of amino acids?
    (A) disulfide bonds (B) hydrogen bonds (C) amide bonds (D) polar side chains

47. Nucleosides are rapidly hydrolyzed in which of the following?
    (A) H_2O (B) dil NaOH (C) dil HCl (D) none of these

48. Hydrolysis of DNA gives which of the following materials?
    I. ribose II. adenine III. deoxyribose IV. uracil
    (A) I, II (B) II, III (C) III, IV (D) I, IV

49. What is the best description for the mechanism of hydrolysis of phosphodiesters?
    (A) SN_1 (B) E_2 (C) SN_2 (D) E_1

50. The backbone of DNA is best described as:
    (A) pairs of complementary bases (B) polyphosphate esters of 1,3-glycols
    (C) pyrophosphates (D) sugar glycosides

II. Please predict the major product for each of the following reactions (**A** to **Q**). (30%)

1. 1-methylcyclohexene $\xrightarrow[\text{DMSO}]{\text{O}_3}$ **A**

2. $H_3C\!-\!\underset{H}{C}\!=\!CH_2$ $\xrightarrow[\text{CCl}_4]{\text{Br}_2}$ $\xrightarrow[\text{NH}_{3(l)}]{\text{NaNH}_2}$ $\xrightarrow[\text{CH}_3\text{COOD}]{\text{BH}_3}$ **B**
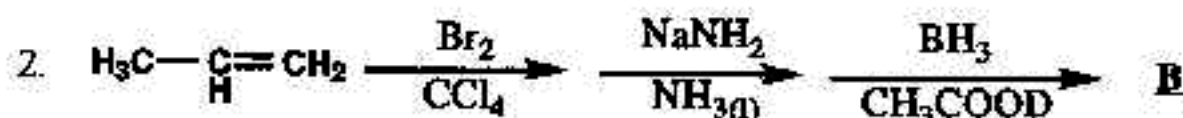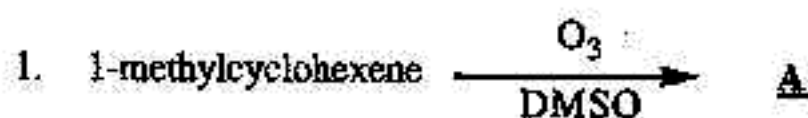
3. Pheromone, the sex attractant of the male insect, has been synthesized by the following sequence. Give stereochemical structures for compounds **C** to **I**.

    ethylene + 3-methyl-2-cyclohexenone $\xrightarrow{h\upsilon}$ **C** $(C_9H_{14}O)$

    C $\xrightarrow{\text{bromination}}$ **D** $(C_9H_{13}OBr)$ $\xrightarrow{CO_3^{2-}}$ **E** $(C_9H_{12}O)$

    E + CH_3Li $\longrightarrow$ **F** $(C_{10}H_{16}O)$, a single stereoisomer

    F + IO_4^-/OsO_4 $\longrightarrow$ **G** $(C_9H_{14}O_3)$, a carboxylic acid

    G + excess $Ph_3P=CH_2$ $\longrightarrow$ **H** $(C_{10}H_{16}O_2)$

    H $\xrightarrow{\text{NaAl(OR)}_2\text{H}_2}$ **I** $(C_{10}H_{18}O)$ pheromone

4. *trans*-1,2-Diethyloxirane $\xrightarrow{\text{NaOH}}$ **J**

5.

    $H_3C\!-\!\underset{O}{\overset{\|}{C}}\!-\!\underset{H_2}{C}\!-\!\underset{H_2}{C}\!-\!\underset{O}{\overset{\|}{C}}\!-\!OCH_3$

    $\xrightarrow[\text{-78 °C}]{\text{DIBAL, toluene}}$ $\xrightarrow[\text{HCl}]{\text{H}_2\text{O}}$ **K**

    $\xrightarrow{\text{NaBH}_4}$ $\xrightarrow[\text{HCl}]{\text{H}_2\text{O}}$ **L**

    $\xrightarrow{\text{LiAlH}_4}$ $\xrightarrow[\text{HCl}]{\text{H}_2\text{O}}$ **M**

6. (benzene ring)—COOH $\xrightarrow[\text{C}_6\text{H}_6]{\text{SOCl}_2}$ $\xrightarrow{\text{AlCl}_3}$ $\xrightarrow[\text{HCl}]{\text{Zn(Hg)}}$ **N**

7. $CH_3CH_2O\!-\!\underset{O}{\overset{\|}{C}}\!-\!\underset{H_2}{C}\!-\!\underset{H_2}{C}\!-\!\underset{H_2}{C}\!-\!\underset{H_2}{C}\!-\!\underset{H_2}{C}\!-\!\underset{O}{\overset{\|}{C}}\!-\!OCH_2CH_3$ $\xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) NaOCH}_2\text{CH}_3}$ **Q**
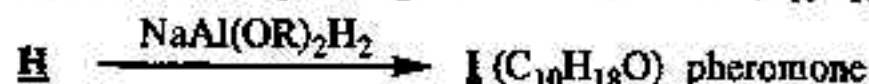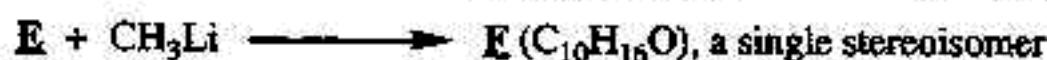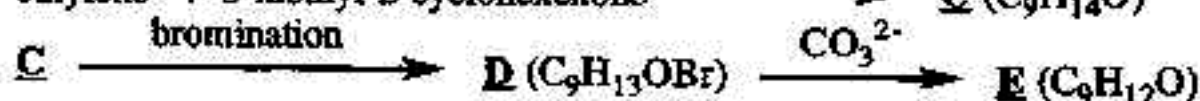
III. Identify each of the following isomers of formula $C_{20}H_{18}O$:　　　　(8%)

Isomer X (m.p. 88 °C)

2.23 ppm, singlet, 1 H

3.92 ppm, doublet, 1 H, J = 7 Hz

4.98 ppm, doublet, 1 H, J = 7 Hz

6.81 ppm, singlet, 10 H

6.99 ppm, singlet, 5 H

Isomer Y (m.p. 88 °C)

2.14 ppm, singlet, 1 H

3.55 ppm, singlet, 2 H

7.25 ppm, broad peak, 15 H

What single simple chemical test would distinguish between these two isomers?

IV. Give a structure consistent with each of the following sets of proton NMR data:　(6%)

(a) $C_4H_7BrO_2$

1.08 ppm, triplet, 3 H

2.07 ppm, quintet, 2 H

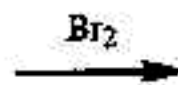4.23 ppm, triplet, 1 H

10.97 ppm, singlet, 1 H

(b) $C_3H_5ClO_2$

3.81 ppm, singlet, 3 H

4.08 ppm, singlet, 2 H

V. Draw a mechanism to explain why only one product greatly predominates in the case of bromination of cholesterol.　　　　(3%)

Cholesterol $\xrightarrow{Br_2}$ 5α,6β-Dibromo-3β-hydroxycholestane

85%

VI. In KNH_2/NH_3, protium-deuterium exchange takes place at the following relative rates:

o-C_6H_4DF : m-C_6H_4DF : p-C_6H_4DF : C_6H_5D = 4,000,000 : 4,000 : 200 : 1.

How do you account for this sequence of reactivity?　　　　(3%)