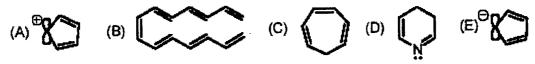
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1-45 (2 points for each); 46 (10 points)

1. The name of the following compound is:

- (A) chloroaniline (B) m-chlorophenol (C) m-chlorobenzoic acid
- (D) 3-chlorobenzaldehyde (E) 3-cyanochlorobenzene
- 2. Which of the following is predicted to be an aromatic compound?



3. Two equilibria are shown below. In each reaction indicate whether reactants (equilibrium lies to the left) or products (equilibrium lies to the right) will be favored.

$$NH_2$$
+ H-N(C₂H₅)₃
+ N(C₂H₅)₃

pKa ~10

pKa = 4.0

pKa = 0.65 pKa = 4.6

(A) left, left (B) right, right (C) left, right (D) right, left (E) None of them

- 4. Which of the following is true about electrophilic aromatic substitution of phenol by Br₂/Fe?
- (A) The hydroxyl- substituent directs the incoming electrophile to the o- and p- positions selectively.
- (B) The hydroxyl-substituent directs the incoming electrophile to the m- position selectively.
- (C) The incoming electrophile in nitration prefers the m- position regardless of substituent.
- (D) The incoming electrophile in nitration prefers the o-/p- positions regardless of the substituent.
- (E) The molecule is too deactivated to react.

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- 5. In aromatic electrophilic substitution, the carboxyl group (CO2H) is a(n) ____ director and a(n) ____ group. (Fill in the blanks).
- (A) o, p-, deactivating
- (B) o, p-, activating
- (C) m-, deactivating
- (D) m-, activating
- (E) The carboxyl group elicits the same reactivity as a H substituent and does not cause any directing
- 6. The major product from the following reactions

(A)
$$(B)$$
 (C) (C) (D) (E) (E) (D) (D)

7. Predict the major site of aromatic electrophilic substitution:

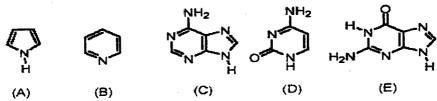
8. Rank the following carbocations in order of stability: (from most to least stable)

- (A) 1>2>3 (B) 1>3>2 (C) 2>3>1 (D) 3>1>2 (E) 3>1>2
- 9. The major product of reaction of 1-phenyl-1-propene with HBr would be:
- (A) 1-(p-bromophenyl)-1-propene (B) 1-(o-bromophenyl)-1-propene
- (C) 1-bromo-1-phenylpropane (D) 2-bromo-1-phenylpropane (E) 3-bromo-1-phenylpropane
- 10. Which of the following is/are true about spectral data for ketones?
- (A) IR spectra of ketones often contain a very intense and broad absorption that obscures the C-H stretch portion of the spectrum
- (B) Ketones show intense absorption at about 1715 cm-1 in the ir spectrum
- (C) Ketones show a carbonyl signal at around 55 ppm in the 13C NMR spectrum
- (D) All of the above
- (E) None of the above

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- 11. Reaction of anisole [Ph-O-CH₃] with excess HI would yield:
- (A) PhI + CH₃OH (B) + o-isomer (D) PhOH + CH₃I
- 12. Which of the following reactions would produce DEET?

- 13. Which of the following would be the best way to prepare m-chloroethylbenzene from benzene?
- (A) 1. Cl₂, Fe
- 2. CH₃COCl/AlCl₃ 2. CH₃CH₂Cl/ AlC₁₃
- 3. [H] with Zn(Hg)/HCl
- (B) 1. Cl₂, Fe
- 2. Cl₂/Fe
- (C) 1. CH₃CH₂Cl/ AlCl₃
- (D) 1. CH₃COCl/ AlCl₃ (E) 1. CH₃COCl/ AlCl₃
- 3. [H] with Zn(Hg)/HCl 2. Cl₂/Fe
- 2. [H] with Zn(Hg)/HCl
- 3. Cl₂/Fe
- 14. Which of the following compounds is adenine?



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15. The best way to prepare the compound shown at the right would be:

16. The major product from each of these reactions is:

$$OCH_3$$
 OCH_3 $OCH_$

- 17. A hydrocarbon compound has the molecular formula C₈H₁₀ and is oxidized by KMnO₄ to benzoic acid. What is this compound?
- (A) ethylbenzene (B) o-xylene (C) m-xylene (D) p-xylene
- (E) This compound could be any one of the above, more data is needed.
- 18. Which of the following would react with cold, dilute NaOH solution via an SN_2 reaction mechanism most rapidly?

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19. What reagent(s) would you use to accomplish the conversion shown?

- (A) B₂H₆ then H₂O₂, NaOH, H₂O (B) H₂SO₄, heat (C) Br₂, then cold dilute NaOH solution
- (D) O₃, then (CH₃)₂S (E) Zn amalgam in conc HCl
- 20. In each pair of compounds shown at the right, which is the <u>stronger</u> acid? [Note: compare 1 with 2 and 3 with 4]

- (A) 1,3 (B) 1,4 (C) 2,3 (D) 2,4
- 21. Which of the following is the correct name for the compound shown in the box at the right?

- (A) 3,7-dimethyl-5-octyne (B) 2,6-dimethyl-3-octyne (C) 2-ethyl-6-methyl-4-heptyne
- (D) 6-ethyl-2-methyl-3-heptyne (E) 4-methyl-1-isopropyl-1-hexyne
- 22. What is the product of the reaction sequence shown?

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

23. When conducting electrophilic aromatic substitution of benzene, the reactive species in nitration is _____ and the reactive species in bromination is _____. (Fill in the blanks)

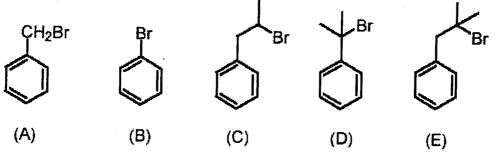
(A)
$$O = NO_2$$
, $Br^{\dagger} FeBr_4$ (B) HNO_3 , Br_2

(E) NO2⁺, Br⁺ FeBr₄⁻

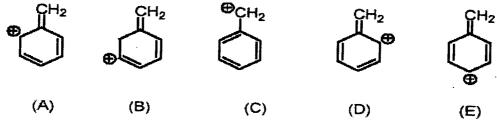
(C)
$$NO_2^{\dagger}$$
, HBr (D) $O-NO_2$, Br₂

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- 24. Phenol is a stronger acid than cyclohexanol because
- (A) The anion of phenol is stabilized by charge delocalization
- (B) The cyclohexoxide anion is stabilized by the inductive effect
- (C) Prior to ionization phenol is stabilized by resonance
- (D) The benzene ring is flat so there is less steric hindrance to removal of the proton from phenol
- (E) The original statement is incorrect, cyclohexanol and phenol are of nearly equal acidity
- 25. Which of the following would react with water via an SN₁ reaction mechanism most rapidly?

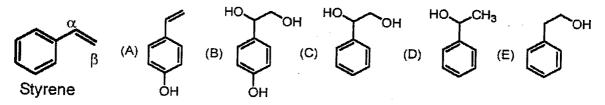


26. Which of the following structures does not contribute to the stabilization of the benzyl carbocation?



- 27. All forms of spectroscopy measure values of energy absorbed or emitted when atoms or molecules undergo quantized transition between different energy levels. What kind energy levels are involved in IR spectroscopy?
- (A) electronic energy levels (orbitals) (B) nuclear energy levels (C) vibrational energy levels
- (D) rotational energy levels (E) none of them
- 28. Which of the following could be easily converted to propanamine in one-step?

- (A) only one of the selections (B) 1 and 2 (C) 1 and 3 (D) 2 and 3 (E) 1, 2, and 3
- 29 . What would be the product of styrene reacting with hot water in the presence of H_3PO_4 as a catalyst?



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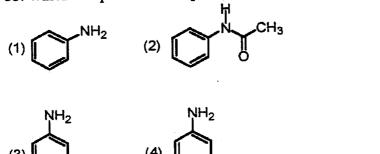
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30. A Grignard reagent reacts with a carbonyl group because:

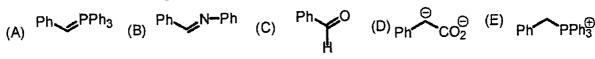
- (A) The negative carbon of the organometallic reagent can attack the partially positive carbon of the carbonyl group.
- (B) The positive carbon of the Grignard reagent can be attacked by the partially negative carbon of the carbonyl group.
- (C) The negative carbon of the Grignard reagent can attack the partially positive oxygen of the carbonyl group.
- (D) The positive carbon of the Grignard can be attacked by the partially negative oxygen atom of the carbonyl group
- 31. The product of the following reaction is:

32. Sudafed[®] (an over-the counter nasal decongestant) contains pseudoephedrine as the active ingredient. How many chiral centers are present in pseudoephedrine?

33. Which compound in each pair (1 vs 2 and 3 vs 4) is the stronger base?



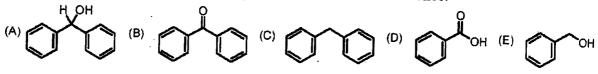
- (A) 1 and 3 (B) 1 and 4 (C) 2 and 3 (D) 2 and 4
- 34. Which is the following is an ylide?



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35. Benzene is treated with CH3COCl (AlCl3 catalyst) then reduced with Zn(Hg) in conc HCl. This product is then again treated with CH3COCl (AlCl3 catalyst) then reduced with NaBH4. What is the structure of the major product resulting from this sequence?

36-39. In the next four questions, predict the major product of the reaction. Choose your answer from the following selections; you may use a selection more than once.



36.

1. PhMgBr, THF

2. H₃O⁺ workup

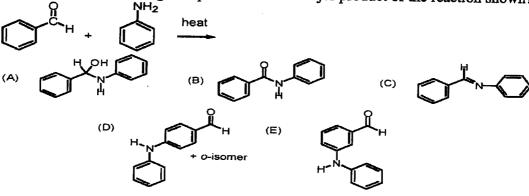
3. CrO₃, H₂SO₄

37.
OC₂H₅
1. LIAIH₄, THF
2. H₂Q⁺ workup

38.

39. OC₂H₅
1. NaOH, H₂O, hea

40 Which of the following is expected to be the major product of the reaction shown?

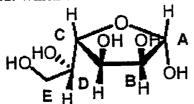


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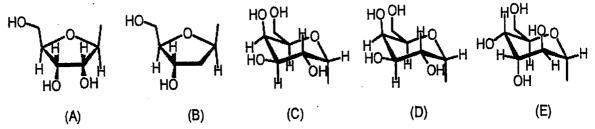
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41. Which carbon atom in the following molecule is the anomeric carbon?



42. Which of the following molecule fragments would be found in DNA?



43. The ¹H NMR spectrum of 1-chloro-1-iodoethane consists of:

(A) 2 singlets (B) 2 doublets (C) 2 triplets (D) 1 quartet (E) 1 doublet and 1 quartet

44. Assuming all the peaks in the ¹H NMR spectrum of 1,2-dichloropentane could be resolved (that is, no signals overlap), which peak would appear furthest downfield?

45. Which of the following structures is consistent with the NMR data shown below?

Compound: C4H9Cl

Compound, Carigor		
Chemical shift	multiplicity	integration
1.04	doublet	6H
1.95	multiplet	1H
3.35	doublet	2H

- (A) 1-chlorobutane (B) 1-chloro-2-methylpropane (C) 2-chlorobutane
- (D) 2-chloro-2-methylpropane

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46. An unknown compound is a high-boiling liquid (boiling point 256°C) which is slightly soluble in water. The peak at 3.9 ppm in the 1H NMR disappears if the compound is exposed to D2O. The Mass, IR, and 1H NMR spectra, along with 13C NMR data, are given below. Analysis: C₉H₁₂O₂. Provide an interpretation for each of the spectra and give the structure of the compound. (10 points).

