Short questions of the Organic Chemistry I pretext

Last modified: 2009. 12. 13.

1) Describe the ionic and covalent bonds and role of electronegativity in their formation.

2) How does the Lewis-Langmuir octet rule explain the formation of chemical bond?

3) Differentiate between structural isomers and contributing (resonance) structures. b) What is a resonance hybrid?

4) What are the rules of writing resonance structures (points 1-10)?

5) Wite the resonance contributors of 1,3-butadiene and dimethyl ether.

6) Write the structures of methanide anion, methyl cation and methyl radical and show their theoretical formations from carbon and hydrogen atoms.

7) Write resonance structures for the following substances showing all outer-shell electrons and formal charges when present. (a) carbonate anion, CO_3^{2-} (b) allyl cation (c) formaldehyde, H_2CO (d) nitrate ion NO_3^{-}.

8) (a) Define a dipole moment (b) Can a molecule have a dipole moment if it has no polar covalent bonds? (c) Can a molecule have polar bond but no dipole moment? Justify your answer with an example.

9) What is an atomic orbital (AO) and wave function? Write the electron configuration of the carbon and oxygen atoms.

10) (a) State the Aufbau (German for building up) principle for filling orbitals with electrons. (b) State and explain Hund's rule for filling orbitals. (c) Give the electron distribution for ground state C atom.

11) Show and explain the potential energy diagram of the hydrogen molecule as the function of intermolecular distances.

12) Draw an energy diagram showing the relationship between two AO's and the MO's resulting from their combination. Show the LCAO theory ont he example of the hydrogen molecule.

13) Explain the fact that in contrast to hydrogen, Xe atoms do not form diatomic molecules by the LCAO theory.

14) Account for the four identical C-H bonds in CH_4 in terms of hybridization. Define the sigma bond.

15) Show the structure of ethene by the hybridization theory.

16) Show the structure of ethyne by the hybridization theory.

17) Explain the origin of cis-trans isomerism of alkenes with the π molecular orbital. Define the terms HOMO and LUMO.

18) How can the valence electron repulsion theory be used to describe the geometry of molecules (rules 1-4)?

19) Write two isomeric structures with the molecular formula C_2H_6O. Draw the dash formula, condensed formula and bond-line formula of *sec*-butanol.

20) How do structural (constitutional)isomers differ from stereoisomers? (b) What is meant by configuration? Give examples for structural isomers and enantiomers.

21) What is tautomerization? Give an example.

22) What is the difference between conformation and configuration in open-chain molecules?

23) Define constitutional isomers, stereoisomers, enantiomers and diastereomers.

24) Give the potential energy diagram for the conformational isomers of ethane.

25) Give the potential energy diagram for the conformational isomers of butane and explain the energy differences of the isomers.

26) Draw the stereoisomers of trans-1,2-dimethylcyclohexane. What is racemic mixture?

27) Draw the conformational isomers of cyclohexane and indicate their relative energies.

28) (a) What is a chiral molecule? (b) How does it differ from an achiral molecule?

29) Draw the structures of (R)- and (S)-2-butanol.

30) Give the R/S designation for each of the stereoisomers of 2,3-dibromobutane. What do we call meso compounds?

31) (b) What are the rules for designating an enantiomer as R (from rectus, Latin for right) or S (from sinister, latin for left)?

32) Show the different types of chirality.

33) Describe the physical properties of enantiomers and diastereomers. What is optical rotation?

34) Write the possible stereoisomers of tartaric acid.

35) (a) Define (i) a nucleophile or electron-donor and (ii) an electrophile or electron-acceptor. (b) What structural units make a molecule (or ion) a nucleophile or an electrophile?

36) Define the following types of chemical reactions and give examples (a) addition (b) elimination.

37) Define and give example for substitution and rearrangement.

38) What information is provided for by a reaction mechanism?

39) Compare the (a) Brönsted-Lowry and (b) the Lewis definition of acids and bases.

40) Discuss how (a) acid strength is related to K_a, the acid ionization constant, and to pK_a, and (b) base strength is related to K_b, the base ionization constant, and to pK_b. The values of pK_a and pK_b are defined as $-\log K_a$ and $-\log K_b$, respectively.

41) Compare (a) the acid strengths of CH_3COOH, $ClCH_2COOH$, $Cl_2CHCOOH$, Cl_3CCOOH.(b) the base strength of their conjugate bases.

42) Show the effect of electronegativity, hybridization, inductive and resonance effect on acidity.

43) Give two examples of a Lewis-type acid-base reaction.

44) What bases are distingiushed according to the Olah acid-base theory?

45) (a) Give the rate equation for the general reaction: $aA + bB \rightarrow cC + dD$. (b) Discuss the term k in the rate equation found in (a).

46) Give the sign of ΔH for an (i) exergonic and (ii) endergonic reaction.

47) How are G, S and H related at equilibrium?

48) How do ΔH and ΔS together determine the direction of a chemical reaction?

49) What kinds of reaction occur under : (a) thermodynamic and (b) kinetic control? Give a specific example.

50) Place each of the following alkanes in order of corresponding increasing boiling point and give your reason for the order: pentane, hexane, and 2,3-dimethylbutane. Why are alkanes said to be hydrophobic?

51) Define the three types of intermolecular forces that can lead to interactions between neutral molecules, in order of decreasing order.

52) Explain the following statements: methane has lower boiling and melting points than ethyne; the constitutional isomers ethyl alcohol and ether have different physical properties; sodium acetate and acetic acid have high boiling and melting points.

53) (a) Give the relationship between frequency and energy (E) of a wave. (b) How are its wavelength and energy related?

54) Give the rules for the solubility of organic molecules.

55) Discuss the change of boiling and melting points of unbranched alkanes with increasing number of carbon atoms.

56) List the regions in the spectrum of radiation in order of decreasing energy.

57) What factor determines the wavelength of light absorbed? (b) Explain why the absorption spectrum for each molecule is unique.

58) Identify the molecular energy state which is excited by radiation in the ultraviolet and visible region.

59) Give the energy of electromagnetic radiation with wavelength, wavenumber and frequency. Describe the energy components of molecules whose sum gives the total energy.

60) Give the Beer-Lambert law. What is the meaning of ε_{max}, the molar extinction coefficient?

61) β-Carotene, which is the principal compound responsible for the orange color of carrots, has eleven conjugated double bonds, and absorbs light at 454 nm in the visible region of the spectrum. (a) Explain the shift to the visible range. (b) What color is absorbed?

62) What can the UV-visible spectroscopy be used for?

63) Describe the molecular processes that occur when IR radiation is absorbed by a molecule.

64) Give the frequency of vibration according to Hooke's law.

65) What characteristic of vibrational frequencies makes IR spectroscopy useful in determining structures of organic compounds.

66) Discuss the use of an IR spectrum for elucidating the structure of a hydrocarbon.

67) (a) What condition must be met for absorption of IR radiation by a molecule? (b) Select the diatomic molecules that do not absorb in the IR from the following: HCl, N_2, ClBr, O_2, H_2.

68) Give the frequency ranges for the C-H stretching vibration of sp, sp^2 and sp^3 hybridized carbons.

69) What is the primary use of IR spectroscopy in structure elucidation?

70) Describe what happens when radiowave radiation is absorbed by ^1H nuclei in the presence of a strong applied magnetic field.

71) What nuclei are suitable for NMR measurements?

72) Explain why not all H's in a molecule spin-flip at the same applied magnetic field at constant frequency?

73) Define the terms (a) downfield and (b) upfield as used in NMR spectra.

74) Explain why TMS is chosen as the reference compound.

75) (a) Is the δ value for a given kind of H an inherent constant number? (give the equation)

76) Discuss the influence of the electronegativity of A on the proton chemical shift of A-C-H.

77) (a) Why can the m/z value be assigned as the molecular weight of the cation in most cases? (b) How can the molecular weight of a compound be determined by mass spectral analysis? (c) Why is less than 1 mg of the parent compound used in the vapor state for the analysis?

78) (d) Why do several signals appear in a typical MS spectrum? (e) Which fragment cation are the most abundant?

79) Write the structural formulas for each of the following compounds: (b) 2,3,4-trimethylpentane (e) 4-isopropylheptane

80) Provide IUPAc names for each of the following: (a) $(CH_3)_3CCH_2C(CH_3)_3$ (b) $C(CH_3)_3$. Give the IUPAc name for (a) decalin and (b) norbornane.

81) State the rules for the nomenclature of alkanes.

82) Draw the structure of 2,3,5-trimethyl-4-isopropylheptane and 2,3,5-trimethylhexane.

83) How many conformation of ethane are possible? (c) Name and draw the conformation with the lowest and highest energies at room temperature (d) What is the term used for low energy conformations?

84) Draw a graph relating potential energy to dihedral angle for butane, about C^2–C^3. Label and draw the structure of each maximum and minimum.

85) Give the method of preparation of propane from (a) alkane and (b) an alkyl chloride.

86) Write the structure of all the alkanes that can be hydrogenated to form 2-methylpentane.

87) Write the reaction of CH_3CH_2MgBr with methanol and identify the conjugate acid-base pair.

88) How can a terminal alkynes be used for the synthesis of alkanes?

89) Show the Clemmensen and Kisnyer-Wolf reduction of ketones to alkanes and the Wurtz synthesis.

90) Compare the relative stability of butane and methylpropane by using their heat of combustion.

91) Explain the effect of branching on the boiling points of alkanes with similar molecular weight.

92) Prepare butane from chloroethane using Wurtz synthesis. Why is the Wurtz synthesis not a good method for preparing propane?

93) (a) Write the steps for the chain mechanism of the chlorination of methane . (b) What are the names of the steps? How is the chain reaction terminated?

94) Why is light or heat necessary to initiate the chlorination reaction? Compare the reactivity of the halogens toward alkanes (in radical substitution).

95) Compare the reactivity of different halogens in the radical substitution of methane by discussing the ectivation energy of the elementary steps.

96) Show the reaction of chlorine and bromine with methylpropane at 300 °C and 500 °C (kinetic versus thermodinamic control)

97) Give the thermal cracking process of pentane.

98) Compare the ring strain and stability of different cycloalkanes.

99) (a) Draw the basic fused steroid ring system present in many important naturally occurring compounds such as cholesterol and designate the rings with letters. Show the location of the angular methyl groups.

100) Give the structures and names for the geometric isomers of decalin.

101) Which factors influence the ring strain of cycloalkanes?

102) How does the geometry of cyclopropane account for its ring strain?

103) Explain why the ring strain of cyclobutane is not much less than that of cyclopropane?

104) Account for the small ring strain of cyclopentane.

105) What factors make the cyclohexane ring the most stable, abundant and important ring structure in organic chemistry?

106) Draw the conformational isomers of cyclohexane and indicate the equatorial and axial hydrogens.

107) (a) Draw the two equilibrating chair conformers of methylcyclohexane. (b) Give a conformational analysis of their relative energies.

108) Draw the structure of *cis*- and *trans*-decalin.

109) Show the Wurtz and Perkin synthesis for the preparation of cycloalkanes.

110) Draw the structure of cholesterol.

111) Draw the structure of estradiol and testosterone and discuss the differences in their structures.

112) Draw the structures of the following compounds: 3,6-dimethyl-1,4-heptadiene, 3-ethenyl-1,5-heptadiene, 3,5-dimethylcyclohexane.

113) Use orbital theory to explain geometric isomerism in alkenes. Draw the structure of (Z)-2-bromo-1-chloro-1-fluoroethene.

114) Compare the stabilities of 1-pentene, cis- and trans-2-pentene, and 2-methyl-2-butene.

115) (a) Give the structural formulas for the alkanes formed from the reaction of 2-bromobutane and alc. KOH. (b) Select the major and minor products and rationalize your choice. (c) What is the order of preferential removal of the type of H on dehydrohalogenation of alkyl halides? (d) In terms of R substitution, what general names are associated with these products.

116) Discuss the Zaitsev and Hoffman elimination of alkyl halides resulting in alkenes. State the Zaitsev rule.

117) Prepare alkenes from primary, secondary and tertiary alcohols and explain their different reactivities in dehydration.

118) In terms of transition state (TS) theory, with the aid of an enthalpy diagram, account for the relationship of the relative reactivities of RCH_2OH, R_2CHOH, R_3COH in acidic medium and the stabilities of the intermediate carbocations.

119) Show the reaction of 3,3-dimethyl-2-butanol with H_3PO_4. Explain the formation of the major product.

120) Give the mechanism of the Wittig reacion for the preparation of an alkene.

121) Prepare methylenecyclohexane by the Witting reaction from suitable starting materials.

122) Which phosphonium halide and carbonyl compound must be used in a Wittig reaction to synthesize (a) $PhCH{=}CHCH_3$ (b) $CH_3CH_2CH{=}C(CH_2CH_3)_2$. Give all possible combinations.

123) (a) Write the major product from the reaction of an unsymmetrical alkene, such as isobutylene, with the following unsymmetrical reagents: (i) HBr (ii) $H_2O(H^+)$ (b) State the rule for getting the correct answer to part (a). (c) Give the general name for the reactions that give mainly one of the several possible products.

124) Give the general mechanism for the addition reaction to alkenes.

125) State the original and modern version of the Markovnikov rule for the addition of a hydrogen halide to an unsymmetrical alkene.

126) Show the reaction of propene with HBr and explain the formation of the major product.

127) Show the radical addition of HBr to propene; an exception to the Markovnikov rule.

128) Show the addition of sulfuric acid and water to propene.

129) (a) Give the stereoisomer formed when 1-methylcyclohexene is oxymercurated. (b) Suggest a mechanism for the oxymercuration step.

130) What is the advantage of the oxymercuration-demercuration reaction over the simple addition of water.

131) (a) Give the product from the hydroboration-oxidation of 1-methylcyclopentene. (b) Classify the mode of addition.

132) (b) Give the mechanism for the Br_2 addition. Illustrate with cis-2-butene.

133) Write the reaction bromine and cyclohexene. Discuss the mechanism of the reaction.

134) (a) Give the product of the reaction of $(CH_3)_2C{=}CH_2$ with Br_2 in H_2O and account for its orientation in terms of the bromonium ion (halohydrin formation).

135) Show the oxidation of cyclopentene wih OsO_4 and $KMnO_4$ to produce 1,2-cyclopentenediol.

136) Show the cleavage of 2-butane with hot basic potassium permanganate.

137) (a) Show steps for the reductive ozonolysis (reaction with O_3) of an alkene (c) What is the main utility of this reaction and why is it more superior to $KMnO_4$ cleavage for this purpose?

138) Draw the radical substitution of cyclohexene and propene with bromine or N-bromosuccinimide.

139) Describe (a) radical-induced and (b) anion-induced polymerization of alkenes. (c) What kinds of alkenes undergo anion-induced polymerization?

140) Write the steps for the radical polimerization of ethene.

141) Write the cationic polimerization of methylpropene.

142) Give an example for the anionic polimerization.

143) Categorize dienes according to the relative position of their double bonds.

144) Account for the stability of conjugated dienes by (i) extended π bonding and (ii) resonance.

145) (a) Give the two conformations of 1,3-butadiene resulting from rotation about the C-C single bond. (b) Discuss their relative stabilities.

146) Compare the relative stabilities of (i) 1,3,5-heptatriene and (ii) 1,3,6-heptatriene.

147) Describe the bonding of the three C’s of the allene system with the aid of an orbital diagram. What geometry is imposed on the three C’s?

148) Compare the relative stability of 1,3-butadiene with 1-butene.

149) Explain the 1,4 and 1,2 additions of 1,3-butadiene in terms of the typical mechanism for electrophilic addition.

150) Discuss the reaction of 1,3-butadiene wiht hydrogen bromide (kinetic versus thermodinamic control).

151) Give an example for the Diels-Alder reaction.

152) Write the structural formula for isoprene, a conjugated diene, C_5H_8, that is the monomer for natural rubber.

153) Give the structural formulas for the following compounds: (c) (E)-3-pentene-1-yne (d) (Z)-5-hepten-1,3-diyne.

154) Prepare propyne from propene.

155) Prepare an alkyne from a vicinal or geminal dibromide.

156) List alkanes, alkenes, and terminal alkynes in order of decreasing acidity of their terminal C-H. 9.31 Account for the order of acidities.

157) Give the organic product of the reaction of $HC{\equiv}C{:}^{-}Na^{+}$ with (a) CH_3Br (c) $CH_2{=}CHCH_2Br$.

158) Discuss the hydrogenation reactions of alkynes.

159) Write the equation for the reduction of 2-butyne with Na in EtOH. 9.66 Give a mechanism for the active metal (Na) reduction of an alkyne in a protic solvent (C_2H_5OH).

160) List the products formed when 1-butyne reacts with one equivalent of (a) HBr, (b) HBr with peroxides, and (c) Br_2. Characterize each reaction.

161) Give an orbital picture of benzene. How does it account for benzene’s extraordinary stability? For benzene, apply the polygon rule to determine the relative energies of molecular orbitals of conjugated cyclopolyenes.

162) Discuss the reaction of benezen with bromine, potassium permanganate, water int he presence of acid and hydrogen int he presence of metal catalyst.

163) Write structural formulas for : (b) 2,4-dinitrobenzyl bromide, (d) trityl chloride, (e) 2,4’-dimethyldiphenylmethane.

164) State Hückel’s rule for determining whether a molecule is aromatic.

165) explain the aromaticity of cyclopentadienyl anion and cycloheptatrienyl cation.

168) Give the mechanism of the Birch reduction of benzene.

169) Draw an enthalpy diagram for the reaction of PhH with E^+, indicating the intermediate (In), the transition state 1 (TS1) and transition state 2 (TS2) for the two steps, the relative energies of activation for the two steps.

170) Compare the Friedel-Crafts alkylation with RX and acylation with RCOX as to the (a) mechanism, and (b) kind and amount of catalyst.

171) (a) How do substituent groups (G) on an aromatic ring influence the course of electrophilic aromatic substitution? (b) Classify them by their effects.

172) Write contributing structures for the intermediate arenium ion from the reaction of PhG with E^+ at the (a) para, (b) ortho, and (c) meta positions.

173) Classify electron-donating groups in terms of their structure and their electronic effects and give an example for each class.

174) (a) Which position in naphthalene preferentially reacts with E^+? (b) Account for this preference mechanistically.

175) Account for the formation of mostly 1-naphthalenesulfonic acid at 40-80 °C and ~85% of the 2-isomer at 160 °C when naphthalene is sulfonated.

176) Show the Friedel-Crafts alkylation and acylation of benzene.

177) Show the nitration, bromination and sulfonation of benzene.

178) Show the nitration of nitrobenzene and explain the formation of the major product.

179) Discuss the symbol S_N2, introduced by the British Chemist Sir C.K. Ingold for this one-step nucleophilic substitution. 8.52 (a) Give the transition states for the two extreme juxtapositions of the approaching nuclophile and the leaving group when $Nu:^-$ reacts the RX. Explain the stereochemical consequences of each mode of attack. (b) Explain which is the energetically preferred S_N2 mechanism.

180) Give an example for an S_N2 and S_N1 reaction. Are S_N2 reactions stereospecific and/or stereoselective?

181) Draw a reaction-enthalpy profile for an S_N1 reaction and compare it with that for the S_N2 reaction.

182) Give the structural features of RX that mostly influence the relative S_N1 rates.

183) Account for the relative stabilities of 3°, 2°, 1°and Me carbocations.

184) Compare S_N1 and S_N2 reactions of RL (L leaving group) with respect to the following mechanistic factors: number of steps, rate and order, molecularity, TS of the slow step, stereochemistry, nucleophile.

185) Compare E1 and E2 reactions of RX with respect to the following mechanistic factors: steps (number and kind), TS, kinetics, driving force, stereospecifity, effect of R, rearrangement, competing reactions, orientation.