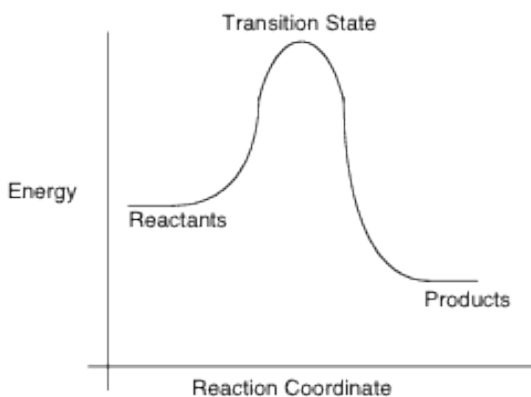


71. **B** –  $S_N2$  stands for substitution nucleophilic bimolecular. This means that there is a bimolecular rate-determining step. Therefore, the reaction will follow second-order kinetics based on the collision of TWO molecules. This eliminates answer choices A, C, & E.  $S_N2$  reactions are stereospecific, which is a result of the backside attack of the incoming nucleophile. The backside attack produces a stereochemical inversion of configuration, making B the best answer choice. Finally, the kinetics of the reaction will be governed by the ability of a nucleophile to approach the backside to attack (aka how easily the nucleophile can access the electrophilic center). If there is significant steric hindrance, the rate will most certainly be affected. This rules out answer choice D.

72. **D** – The rate of an  $S_N2$  reaction depends on the ease of access to the backside of the electrophilic reaction center (aka the carbon attached to the bromine). The less steric hindrance, the faster the backside attack can be achieved. This means that for  $S_N2$  reactions, the relative rate for carbons will be Methyl > Primary >>> Secondary >>>> Tertiary ( $S_N2$  cannot take place on a tertiary center). Answer choice A is a tertiary alkyl halide, so  $S_N2$  cannot take place. Answer choices B and C are secondary alkyl halides. Answer choice D is a primary alkyl halide and the best choice. Finally, answer choice E has only  $sp^2$ -hybridized carbon.  $S_N2$  reactions cannot take place on  $sp^2$ -hybridized carbon atoms.

73. **A** – This is a radical halogenation reaction. These types of reactions can be recognized by the presence of an alkane, a halogen, and UV light or heat. This means that the reaction goes through a radical mechanism and all intermediates will be radicals (aka molecules with an unpaired electron). Therefore, answer choices B, C & E can be eliminated. Hydrogen radicals are exceptionally unstable! Answer choice D is not a reasonable intermediate. This leaves A as the only reasonable choice.

74. **E** – The transition state occurs at the peak of the reaction coordinate diagram shown below. The transition state is always the highest-energy point of a reaction, which determines the activation energy of the reaction. The energy of the transition state is greater than both the reactants and products, making E the only logical answer.



75. **A** – This is a Markovnikov addition reaction. In these reactions, the pi-electrons in the alkene act as a nucleophile. The strongest electrophile will be the proton in the acid, so the first step will be the protonation of the alkene (shown below). This results in the carbocation shown in answer choice A. This reaction takes place in strongly acidic conditions, so a carbanion intermediate (choice C) is unreasonable. Additionally, this is not a radical reaction, so answer choices D and E can be eliminated.



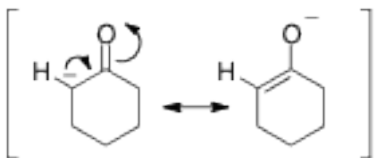
76. **A** – This is a standard nitration reaction via an electrophilic aromatic substitution. The nitro group will be placed on the aromatic ring, with its position depending on the directing effect of the  $-COOH$  group. The  $-COOH$  group is an ELECTRON WITHDRAWING GROUP (EWG), primarily due to the electronegative oxygen atoms which will inductively withdraw electron density from the ring. EWGs are

meta-directors. This means that the nitro group will be placed on the meta-position. This eliminates answer choices C, D, & E. Next, EWGs are deactivators, which means that they slow the reaction down compared to benzene. This makes choice A the best answer.

77. **B** – This is one of the most important IR frequencies to be familiar with for the DAT organic chemistry section. A carbonyl (choice B) has a distinct IR stretch near  $1,700\text{ cm}^{-1}$ . Amine and alcohol groups (choices A & C) show broad stretches above  $3300\text{ cm}^{-1}$ . Alkenes (choice D) show stretches near  $1600\text{ cm}^{-1}$ , and alkynes (choice E) have a stretch near  $2200\text{ cm}^{-1}$ .

78. **E** – This question is best understood through an analysis of intermolecular forces. The stronger the intermolecular forces between a molecule and water, the more water-soluble it will be. The strongest intermolecular force is hydrogen-bonding. The molecule with the greatest capability to hydrogen bond with water will be the most soluble. Alkanes and chloroalkanes (answers A & B) are not capable of hydrogen bonding with water. Alcohols can form hydrogen bonds with water, and answer choice E has the MOST alcohol groups, so it will be the most soluble in water.

79. **B** – This is an enolate anion. The negative charge on the alpha-carbon can resonate into the oxygen as shown below. The best resonance structures will have the fewest number of charges, so answer choice A can be eliminated with its three charges. Answer choice C is an isomer of the enolate in question, with a atom hydrogen placed on the carbon connected to the oxygen. Finally, the total charge of a resonance structure should always be equal to the total charge of the molecule in question ( $-1$ ), so neutral molecules (choices D & E) can be eliminated immediately.



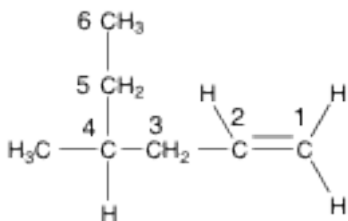
80. **B** – An easy way to spot a chiral molecule is to find a molecule with a chiral center. If a molecule has one (and only one) chiral center, then it will be chiral. A chiral center is an atom that has FOUR different groups attached to it and is, therefore,  $sp^3$ -hybridized. Answer choice A does not have any  $sp^3$ -hybridized atoms in it, so it can be eliminated. The central carbon in molecule B has four unique groups attached to it, making it the best choice. Answer choice C has two methyl groups attached to the central carbon, so it is not chiral. The molecule in answer choice D has two hydrogen atoms attached to the central carbon, so it is not chiral. Finally, molecule E has two  $-CH_2OH$  groups attached to the central carbon, so it is not chiral.

81. **C** – The first thing to look for in a molecule with chiral centers is a plane of symmetry. If a molecule has two or more chiral centers and a plane of symmetry, it is meso. Meso compounds are superimposable on their mirror images, which means they cannot have an enantiomer. First, these compounds have the same structural formula and the same connectivity, so they are NOT structural isomers. The molecule on the right has a mirror plane (shown below) and is meso. This means that answer choice B can be eliminated. The molecule on the left, however, does not have a plane of symmetry. This means it is not meso, ruling out answer choice E. Finally, these molecules are NOT identical, ruling out answer choice D.

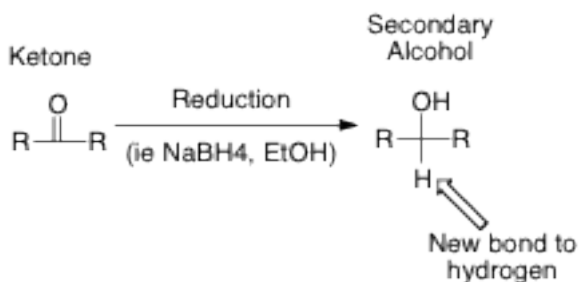
82. **B** – First, the most stable conformation of a cyclohexane is the chair conformation, this means that answer choices D and E can be eliminated. D and E are in the less thermodynamically stable boat conformation. Next, the most stable chairs have the BULKIEST groups in the equatorial position. The bulkiest groups on these rings are the bromine atoms. This means that the most stable chair will have both bromine groups in equatorial positions (answer choice B). Answer choice A has both bromines in axial positions. Answer choice C has the bromine on the left in an equatorial position, but the bromine on the right is in the less stable axial position.

83. **E** – Answer choice A can be eliminated immediately because it is a planar ring, and cis and trans terminology does not apply (instead we have ortho, para and meta). Next, a trans isomer will have the two highest-ranking (according to Kahn-Ingold-Prelog rules) groups on opposite sides. The ring in answer choice B has both methyl groups below the plane of the ring, so they are cis. Answer choice C has both methyl groups on the same side, so this is a cis (Z) isomer. Answer choice D has two methyl groups on a single carbon (they are tied in priority ranking), so cis and trans terminology does not apply. Finally, answer choice E has the Br and F atoms (the highest ranking groups) on the opposite side of the double bond, so this is the correct trans (E) isomer.

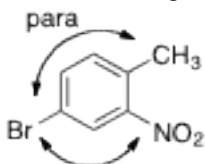
84. **A** – The first step to assigning a proper IUPAC name to a compound is to find the longest continuous chain of carbon atoms. This is shown below and is 6 carbon atoms long (hex). This means that answer choices B, C, & D can be eliminated. Next, the group with the highest priority should be given the lowest number. The alkene is the highest priority group in this molecule, so it should be given the number 1, making choice A the correct answer.



85. **C** – In organic chemistry, oxidation and reduction reactions have very simple definitions. An oxidation reaction is one in which a molecule gains bonds to oxygen. A reduction reaction is one in which a molecule gains bonds to hydrogen. A ketone can gain one bond to hydrogen at the carbonyl carbon. If the carbonyl carbon gains a bond to hydrogen, a secondary alcohol is produced (shown below). Keep in mind a secondary alcohol is an alcohol that is on a carbon atom, which is bonded to TWO other carbons.

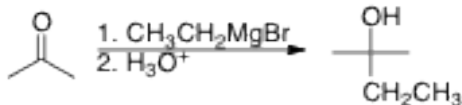


86. **B** – This is an electrophilic aromatic substitution reaction. The key to determining the placement of the Br atom is to assess the directing ability of the substituents. First, the methyl group (like all alkyl groups) is an ELECTRON DONATING GROUP (EDG). EDGs are ring activating and are ortho/para directors. Ring activating groups always take precedence over deactivating groups. The nitro group (-NO<sub>2</sub>) is an electron withdrawing group (EWG) and a meta-director, but this will not supersede the directing effect of the EDG. Fortunately, these two directing groups can actually combine forces to produce a single product, where the Br is para to the methyl AND meta to the nitro (answer choice B).



87. **C** – This is a Markovnikov addition to an alkene. The acidic conditions dictate the Markovnikov reaction, resulting in an addition of HCl across the alkene. Here, the Cl is placed on the MOST substituted carbon and the H is placed on the LEAST substituted carbon. Answer choices A and B still have alkenes, which is incorrect because alkenes will react with HCl via an addition reaction. Answer choices D and E have placed the Cl on the least substituted carbon, which is incorrect. Finally, answer choice C has the Cl on the most substituted carbon and the H on the least, so it is correct.

88. **C** – This is a standard Grignard reaction, which is commonly found on the DAT. Grignard reagents provide a nucleophilic source of carbon, which will react with the electrophilic carbonyl carbon (see below). Answer choice A is incorrect because a hydrogen, rather than a carbon, has added to the carbonyl carbon. Answer choice B is incorrect for the same reason, although one of the methyl groups has been replaced with an ethyl group. Answer choice C has the two original methyl groups from the ketone starting material, and the new ethyl group, so it is correct. Answer choice D has two ethyl groups, which is illogical. Finally, answer choice E can be eliminated. The product of any Grignard addition to a carbonyl will be an alcohol not a carbonyl.

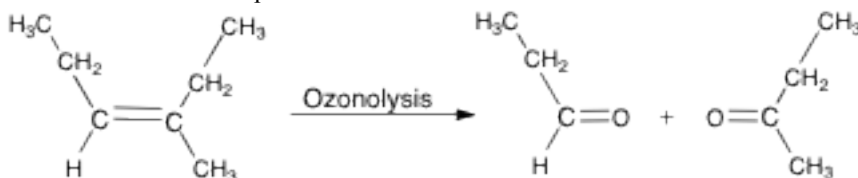


89. **C** – This question requires knowledge of the free radical halogenation process. A free radical halogenation involves three types of steps: initiation, propagation, and termination. An initiation step starts with ZERO radicals and produces TWO radicals, so answer choice B can be eliminated. A propagation reaction starts with ONE radical and produces ONE radical, so answer choices A, D, & E can be eliminated. Finally, a termination reaction starts with TWO radicals and produces ZERO radicals. Therefore, the reaction in answer choice C is a termination step.

90. **C** – Once more, this is an electrophilic aromatic substitution (EAS) reaction. The placement of the nitro group depends on the directing effect of the bromine atom. Halogen atoms are exceptions to the overall directing/activating rules of EAS reactions. Even though halogen atoms are slightly deactivating, they are ortho/para directors. Answer choice A can be eliminated because it does not have a bromine atom. Answer choice B can be eliminated because this is the meta-substituted product. Answer choice C is the para-substituted product, which will be the most stable, major product. Answer choice D can be eliminated because the  $-\text{SO}_3\text{H}$  group will be replaced by  $-\text{NO}_2$  under acidic conditions. Answer choice E has two nitro groups in both para and meta, which is contradictory.

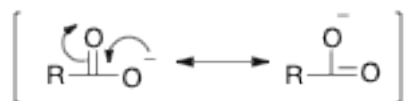
91. **B** – This is an oxidation reaction. Here, an alcohol is oxidized to a carboxylic acid. Answer choice A can be eliminated because it is a reducing agent. Answer choice B is the best answer because it contains chromium. Chromium is a common oxidizing reagent used with alcohols. Answer choices C & D can be eliminated because  $\text{SOCl}_2$  and  $\text{PBr}_3$  convert alcohols into alkyl halides. Finally, answer choice D can be eliminated because an acid would simply protonate the alcohol.

92. **B** – This is an ozonolysis of an alkene. The reactant can be visualized by stitching together the two carbonyl groups in the products to form an alkene (shown below). One of the most efficient ways to answer this question is to count carbon atoms. The products have two carbons on either side of the carbonyl groups, so the reactant should have two carbon atoms on either side of the alkene. This eliminates all answer choices except choice B.



93. **C** – A Bronsted-Lowry base is a proton acceptor. AcOH is a carboxylic acid, so it is a proton donor (aka Bronsted-Lowry acid), so answer choices A, B, & E can be eliminated. HCN is a weak acid and a proton donor (aka Bronsted-Lowry acid), so answer choice D can be eliminated. This leaves only cyanide ( $\text{CN}^-$ ) and acetate ( $\text{AcO}^-$ ) as the Bronsted-Lowry bases.

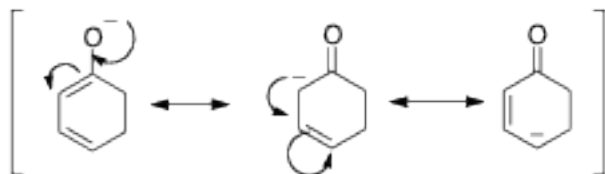
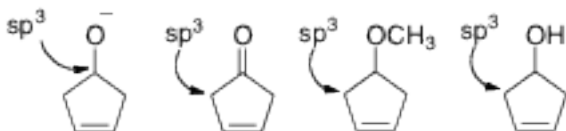
94. **A** – Initially, the easiest way to spot more acidic hydrogen is to find hydrogen atoms that are bonded to more electronegative atoms (ie Oxygen). These more polar bonds are weaker and hydrogen is more electrophilic (aka acidic). This eliminates any C-H bonds as possible answer choices (choices B, C, & D). Next, always remember that the more stable the conjugate base, the more acidic the acid. Resonance is the best way to stabilize a charge. The carboxylate anion formed from the deprotonation of the carboxylic acid (A) is resonance stabilized (see below), while the alkoxide formed from the deprotonation of E is not. This means that A is a more acidic proton.



95. **C** – The conjugate ACID of a neutral molecule will have an additional proton and, therefore, a positive charge. This means that answer choices A, B, & D can be eliminated. Next, answer choice E can be eliminated because the aromatic system has been broken. Aromatic systems have special thermodynamic stability, and breaking them is a very unfavorable process. This leaves only answer choice C, which makes sense because the nitrogen in p-aminophenol is the most basic site in the molecule (aka has the most readily available lone pair).

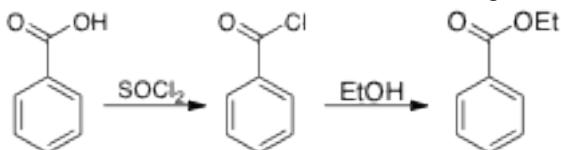
96. **D** – This problem requires knowledge of hybridization and the resulting geometry of carbon atoms. For bond *a*, the carbon in question is bonded to TWO other atoms, so it is  $\text{sp}$ -hybridized.  $\text{sp}$ -Hybridized carbon atoms have a linear geometry with a bond angle of  $180^\circ$ , which means that answer choices A and C can be eliminated. Next, for bond *b*, the carbon atom here is bonded to three other atoms. This makes it an  $\text{sp}^2$ -hybridized carbon atom, which has a trigonal planar geometry and bond angles of  $120^\circ$ .

97. **E** – Keep in mind that resonance can only happen through p-orbitals. This means that any charge or lone pair must be on an atom adjacent to a p-orbital for resonance stabilization. Answer choice A can be eliminated because the negatively charged oxygen is adjacent to an  $\text{sp}^3$ -hybridized carbon with no p-orbitals. The double bonds in answer choice B are separated by an  $\text{sp}^3$ -hybridized carbon, so these pi-electrons are not connected through resonance. Additionally, the lone pairs in the oxygen atoms in answer choices C and D are adjacent to  $\text{sp}^3$ -hybridized carbon atoms, and not conjugated to the alkenes. Finally, answer choice E has  $\text{sp}^2$ -hybridized carbon atoms conjugated together. This means that molecule E can be resonance stabilized.



98. **E** – An understanding of Huckel's rule makes answering this question easier. First, Huckel's rule states that an aromatic system must have  $4n + 2$  pi-electrons, where  $n$  is 0, 1, 2, 3... This means that an aromatic system must have 2, 6, 10... pi-electrons to be aromatic. Answer choices A and D can be eliminated because they only have 4 pi-electrons. Answer choice C can be eliminated, because a system must be cyclic in order to be aromatic. Next, answer choice C can be eliminated because it has 8 pi-electrons. This leaves answer choice E, which has 6 pi-electrons, is a ring, and is planar.

99. **B** – The first step of this reaction uses thionyl chloride ( $\text{SOCl}_2$ ) to convert the carboxylic acid into an acyl chloride (see below). Remember that thionyl chloride converts alcohols into alkyl halides and carboxylic acids into acyl chlorides. This very electrophilic acyl chloride will then react with nucleophilic ethanol in an addition-elimination reaction to produce ester B.



100. **C** – The first step of this sequence is a reduction. The strong reducing agent ( $\text{LiAlH}_4$ ) will reduce this carboxylic acid all the way to a primary alcohol after an aqueous workup (see below). Under the strongly acidic conditions in the reaction with  $\text{HBr}$ , the alcohol will become protonated and will undergo an  $\text{S}_{\text{N}}2$  reaction with bromide. Keep in mind, that either  $\text{PBr}_3$  or  $\text{HBr}$  may be used to convert primary alcohols into primary alkyl halides. This means that the product will be the primary alkyl halide C.

