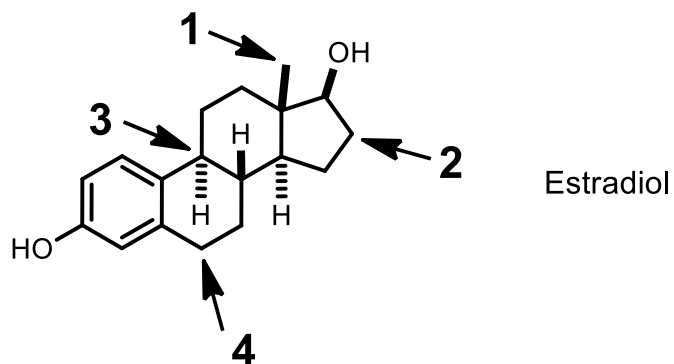
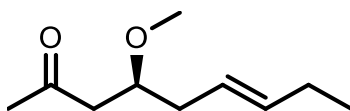


Problem Set #5, February 2020

81. Which of the following best describes Markovnikov's rule?
- In the electrophilic addition of H-Cl to an alkene, the chlorine atom becomes attached to the carbon which has the most hydrogen atoms.
 - In the nucleophilic addition of H-Br to an alkene, the major product is formed from the more stable carbocation intermediate.
 - In the electrophilic addition of H-Br to an alkene, the major product is formed from the more stable radical intermediate.
 - The transition state for an endothermic process will closely resemble the product.
 - In the electrophilic addition of H-Cl to an alkene, the chlorine atom becomes attached to the carbon which has the least hydrogen atoms.
82. On the structure of cholesterol shown below, four carbons have been highlighted. If a carbocation were to form on any of these highlighted carbons, their relative stability would vary greatly. Rank the carbocations in order of increasing stability (least stable to most stable):

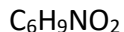


- $1 < 2 < 4 < 3$
 - $1 < 2 < 3 < 4$
 - $1 < 3 < 2 < 4$
 - $2 < 1 < 4 < 3$
 - $3 < 4 < 2 < 1$
83. What is the IUPAC name of the following compound?



- (R,E)-6-methoxynon-3-en-8-one
- (S,E)-6-methoxynon-3-en-8-one
- (S,Z)-4-methoxynon-6-en-2-one
- (R,E)-4-methoxynon-6-en-2-one
- (S,E)-4-methoxynon-6-en-2-one

84. Identify the correct structure of the compound below with the following spectroscopic data:



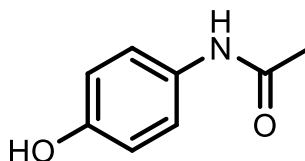
$^1\text{H NMR}$: 4.01 (quartet, 2H), 2.80 (triplet, 2H), 2.62 (triplet, 2H), 1.07 (triplet, 3H).

$^{13}\text{C NMR}$: 171.5, 119.2, 61.3, 30.3, 14.1, 12.8.

IR Spectrum: 1737 (strong and sharp) and 2265 (weak and sharp) cm^{-1}

- a. Ethyl 2-cyanopropanoate
- b. Methyl 4-cyanobutanoate
- c. Ethyl 3-cyanopropanoate
- d. 6-Aminohex-4-ynoic acid
- e. Ethyl 4-aminobut-2-ynoate

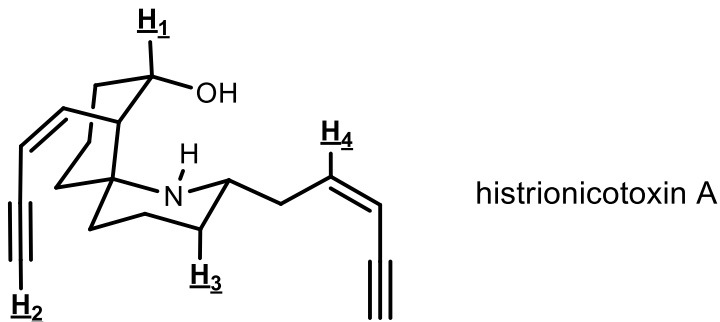
85. The next three questions refer to the structure of acetaminophen shown below.



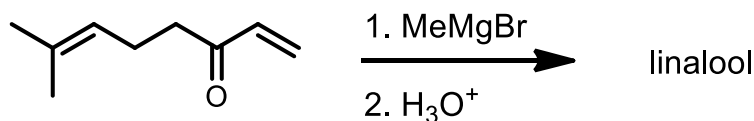
How many degrees of unsaturation are in the molecule?

- a. 3
 - b. 4
 - c. 5
 - d. 6
 - e. 7
86. Identify the main characteristic absorptions in the infrared (IR) spectrum of acetaminophen:
- a. 2260 cm^{-1} (medium, sharp) and 1680 cm^{-1} (strong, sharp)
 - b. 3550 cm^{-1} (strong, broad) and 1680 cm^{-1} (strong, sharp)
 - c. 3330 cm^{-1} (medium, sharp) and 1680 cm^{-1} (strong, sharp)
 - d. 3550 cm^{-1} (strong, broad) and 2260 cm^{-1} (medium, sharp)
 - e. 3330 cm^{-1} (medium, sharp) and 2260 cm^{-1} (medium, sharp)
87. How many signals would you expect in the ^{13}C spectrum of acetaminophen?
- a. 3
 - b. 5
 - c. 6
 - d. 7
 - e. 8

88. Histrionicotoxin A is a powerful toxin found in the skin of the Columbian poison arrow frog. Rank the four highlighted hydrogen atoms on the structure of histrionicotoxin A in order of chemical shift (lowest to highest):



- a. $4 < 1 < 2 < 3$
 b. $2 < 3 < 1 < 4$
 c. $4 < 1 < 2 < 3$
 d. $3 < 2 < 1 < 4$
 e. $3 < 1 < 2 < 4$
89. If histrionicotoxin A (from #88) were treated with pyridinium chlorochromate (PCC) the resulting product would contain the following new functional group:
- a. diol
 b. alcohol
 c. carbonyl
 d. alkene
 e. amide
90. Linalool is a naturally occurring terpene derivative with a floral scent that is found in a variety of flowers and spices. Linalool can be synthesized from 7-methylocta-1,6-dien-3-one (shown below) upon treatment with a methyl Grignard reagent. Identify the structure of linalool:

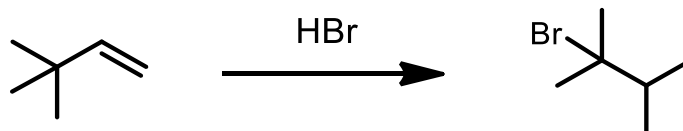


- a.
- b.
- c.
- d.
- e.

91. Linalool (the product from #90) is best described as:

- a. A pair of enantiomers
- b. A pair of diastereomers
- c. An achiral molecule
- d. A meso compound
- e. None of the above

92. When 3,3-dimethylbut-1-ene is treated with HBr, 2-bromo-2,3-dimethylbutane is produced. Explain how the product is formed by identifying the key mechanistic step:

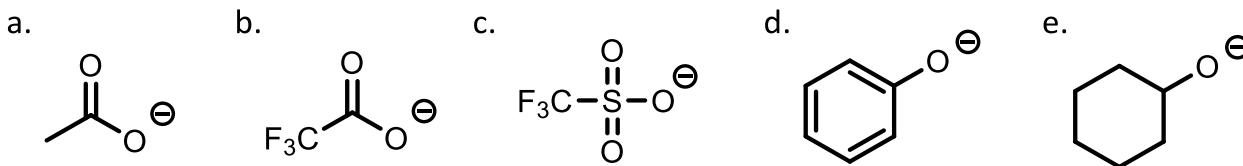


- a. S_N2
- b. E1
- c. radical formation
- d. hydride shift
- e. alkyl shift

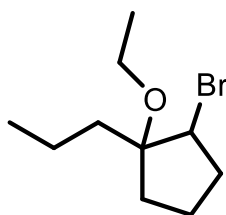
93. Hydrogenation of (S,E)-5-ethyloct-2-ene on a catalytic surface of PtO_2 results in the formation of which product?

- a. (S)-4-ethyloctane
- b. (R)-4-ethyloctane
- c. (5S)-5-ethyloctan-3-ol
- d. (5S)-5-ethyloctan-2-ol
- e. (S)-3-ethylhexanal

94. Which of the following anions would be the best leaving group in an S_N2 reaction?

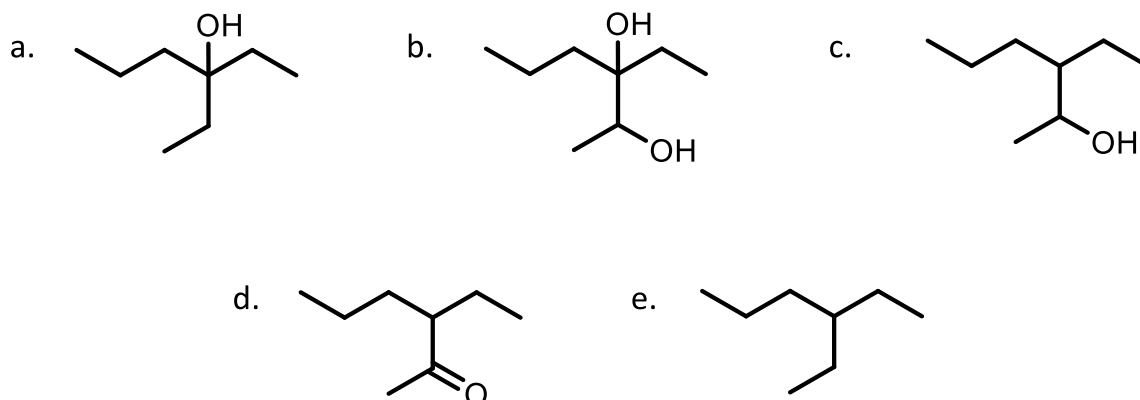
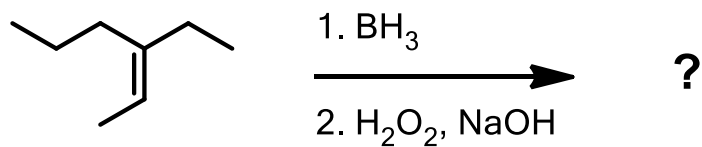


95. What reagents could be used to convert 1-propylcyclopent-1-ene into 2-bromo-1-ethoxy-1-propylcyclopentane (shown below)?

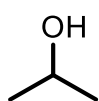


- a. Br_2, H_2O
- b. $Br_2, EtOH$
- c. HBr, H_2O
- d. $HBr, EtOH$
- e. Br_2, CH_2Cl_2

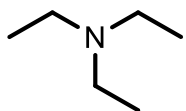
96. Predict the product of the following reaction:



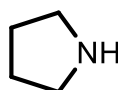
97. In which of the following pure substances will hydrogen bonding be an important intermolecular force?



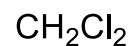
1. propan-2-ol



2. triethylamine



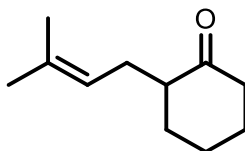
3. pyrrolidine



4. dichloromethane

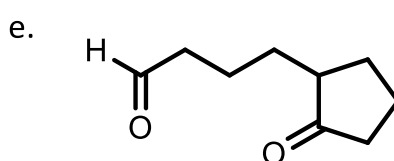
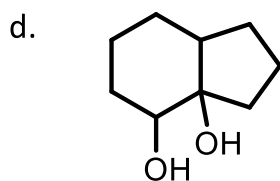
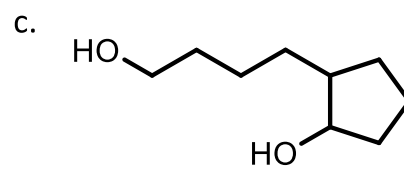
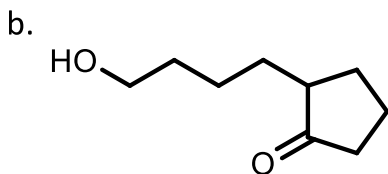
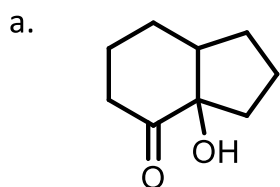
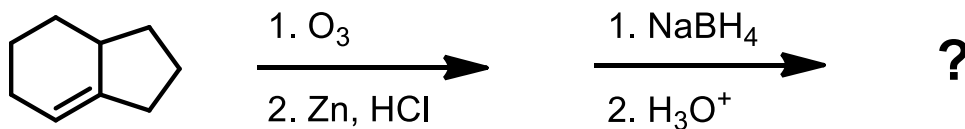
- a. 1 only
 b. 3 only
 c. 1 and 3
 d. 1, 2, and 3
 e. All of them

98. If the following compound was treated with ___(1)___, the product would contain a ___(2)___.



- | | |
|--|-----------------|
| (a) 1. a) O_3 b) $\text{Zn}, \text{H}_3\text{O}^+$ | 2. a 2° alcohol |
| (b) 1. $\text{Br}_2, \text{CH}_2\text{Cl}_2$ | 2. halohydrin |
| (c) 1. a) BH_3, THF b) $\text{H}_2\text{O}_2/\text{NaOH}$ | 2. 3° alcohol |
| (d) 1. a) OsO_4 b) NaHSO_3 | 2. aldehyde |
| (e) 1. a) $\text{Hg}(\text{OAc})_2, \text{H}_2\text{O}$ b) NaBH_4 | 2. 3° alcohol |

99. Predict the product of the following reaction scheme:



100. Predict the product of the following reaction scheme:

