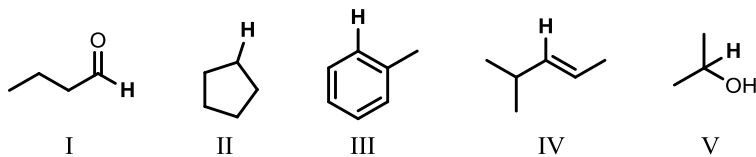


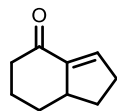
Problem Set #4, February 2018

81. Each of the following compounds has one hydrogen atom highlighted. Rank them in order of chemical shift (lowest to highest):



- (a) II < V < III < IV < I
- (b) II < V < I < III < IV
- (c) V < II < III < IV < I
- (d) II < V < IV < III < I
- (e) III < II < IV < I < V

82. Consider the following compound and identify the main characteristic absorptions in the infrared (IR) spectrum:



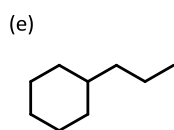
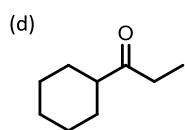
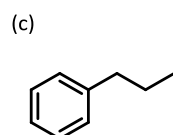
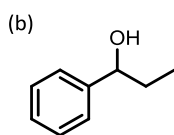
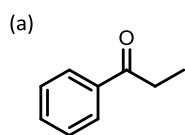
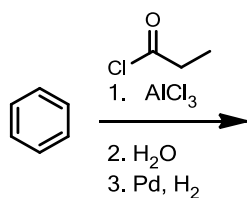
- (a) 2260 cm^{-1} (medium, sharp) and 1700 cm^{-1} (strong, sharp)
- (b) 3350 cm^{-1} (strong, broad) and 1650 cm^{-1} (medium, sharp)
- (c) 1700 cm^{-1} (strong, sharp) and 1650 cm^{-1} (medium, sharp)
- (d) 3350 cm^{-1} (strong, broad) and 2260 cm^{-1} (medium, sharp)
- (e) 1650 cm^{-1} (medium, sharp) and 2260 cm^{-1} (medium, sharp)

83. Given the ^1H NMR information below, determine the structure of the following compound:

^1H NMR (ppm): 0.93 (triplet, 3H), 1.04 (doublet, 6H), 1.60 (sextet, 2H), 2.40 (triplet, 2H), 2.56 (septet, 1H)

- (a) 2-methylhexan-3-one
- (b) 5-methylhexan-3-one
- (c) heptan-2-one
- (d) 5-methylhexan-2-one
- (e) heptan-3-one

84. Predict the product of the following reaction scheme:



85. Although there are multiple reactions occurring in question #84, which one(s) are listed below?

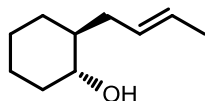
- (a) Hydration
- (b) $\text{S}_{\text{N}}2$
- (c) Electrophilic aromatic substitution
- (d) Nucleophilic aromatic substitution
- (e) Two of the above

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

1. Bromomethane, CH_3Br
2. Triphenylphosphine, $\text{P}(\text{C}_6\text{H}_5)_3$
3. Methanol, CH_3OH
4. Acetone, $\text{CH}_3\text{C}(\text{O})\text{CH}_3$

- a) (1) and (2) only
- b) (2) only
- c) (3) and (4) only
- d) (3) only
- e) All four of them

87. What is the IUPAC name of the following compound?

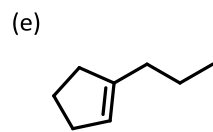
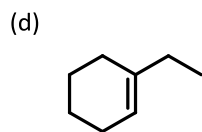
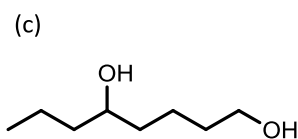
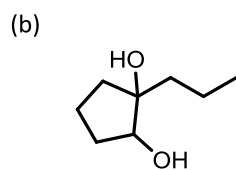
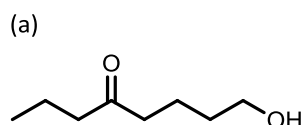
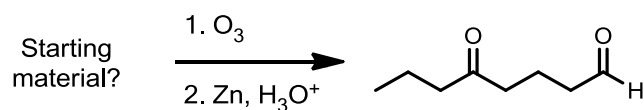


- (a) (1S,2R)-2-((E)-but-2-en-1-yl)cyclohexan-1-ol
- (b) (1R,2S)-2-((E)-but-2-en-1-yl)cyclohexan-1-ol
- (c) (1R,2S)-1-((Z)-but-2-en-1-yl)cyclohexan-2-ol
- (d) (1S,2R)-2-((Z)-but-2-en-1-yl)cyclohexan-1-ol
- (e) (1R,2S)-1-((E)-but-2-en-1-yl)cyclohexan-2-ol

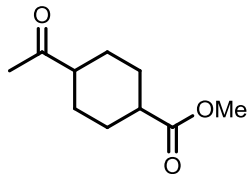
88. If the compound in question #87 was treated with Collins reagent ($\text{CrO}_3/\text{pyridine}$) the resulting product would be:

- (a) achiral
- (b) a mixture of diastereomers
- (c) a single diastereomer
- (d) a mixture of enantiomers
- (e) a single enantiomer

89. What starting material would be required to complete the following reaction scheme?

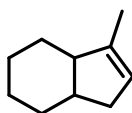


90. If the following compound were treated with NaBH_4 in MeOH , the resulting product after work-up would contain:



- (a) 2° alcohol and ester
- (b) two 2° alcohols
- (c) one 1° alcohol and one 2° alcohol
- (d) 2° alcohol and an aldehyde
- (e) 1° alcohol and a ketone

91. If the following compound were treated with ____ (1) ____, the product would contain a ____ (2) ____.

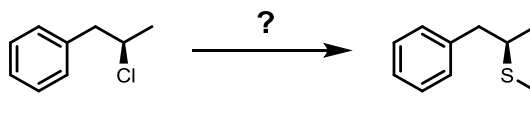


- | | |
|--|-----------------------------|
| (a) 1. $\text{Br}_2, \text{H}_2\text{O}$ | 2. a 2° alcohol |
| (b) 1. $\text{Br}_2, \text{CH}_2\text{Cl}_2$ | 2. <i>cis</i> 1,2-dibromide |
| (c) 1. a) BH_3, THF b) $\text{H}_2\text{O}_2/\text{NaOH}$ | 2. a 3° alcohol |
| (d) 1. a) OsO_4 b) NaHSO_3 | 2. <i>cis</i> 1,2-diol |
| (e) 1. a) $\text{Hg}(\text{OAc})_2, \text{H}_2\text{O}$ b) NaBH_4 | 2. a 2° alcohol |

92. The reaction described in question #91 is best described as:

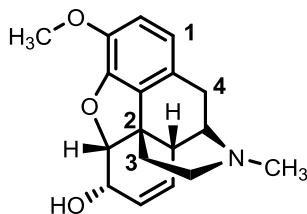
- (a) Stereospecific
- (b) Enantioselective
- (c) Regioselective
- (d) both a and b
- (e) both a and c

93. Predict the reagents required to complete the following reaction scheme:



- (a) NaSEt, CH₃CN
(b) NaSEt, CH₃OH
(c) 1. NaI, acetone; 2. NaSEt, CH₃CN
(d) Both a and b would work
(e) Both a and c would work
94. How many signals would you expect in the ¹³C NMR spectrum of 2,2-dimethyl-7-phenylheptan-3-one?
- a) 11
b) 12
c) 13
d) 14
e) 15
95. What conditions would convert 2,2-dimethyl-7-phenylheptan-3-one into 2,2-dimethyl-7-phenylheptan-3-ol in good yield (assume a work-up is performed in each case)?
- (a) NaBH₄, MeOH
(b) LiAlH₄, THF
(c) Pd/C, H₂
(d) Both a and b would work
(e) All of a, b and c would work
96. What is the degree of unsaturation for a compound with the chemical formula of C₂₄H₂₈BrNO?
- (a) 9 (b) 10 (c) 11 (d) 12 (e) 13

97. On the structure of codeine 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):

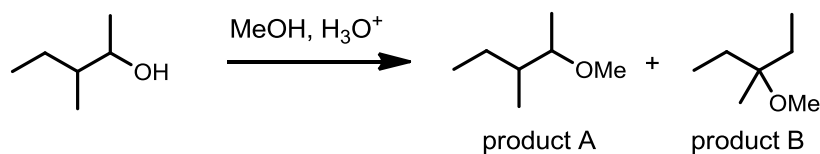


- (a) $1 < 3 < 4 < 2$
- (b) $1 < 3 < 2 < 4$
- (c) $1 < 4 < 3 < 2$
- (d) $2 < 4 < 3 < 1$
- (e) $4 < 2 < 3 < 1$

98. What is the degree of unsaturation for codeine?

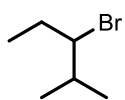
- (a) 4
- (b) 5
- (c) 8
- (d) 9
- (e) 10

99. The following S_N1 reaction is initially expected to give only product A. However, the reaction produces a mixture of product A and B. Explain how product B is formed by identifying the key mechanistic step:

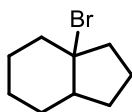


- (a) There is a competing S_N2 reaction
- (b) There is a competing E1 reaction
- (c) There is a competing E2 reaction
- (d) The initial carbocation undergoes an alkyl shift
- (e) The initial carbocation undergoes a hydride shift

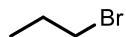
100. Rank the following compounds in order of their relative S_N1 reactivity (fastest to slowest):



I



II



III

MeBr

IV

- (a) IV > III > I > II
- (b) IV > I > III > II
- (c) II > I > III > IV
- (d) II > III > I > IV
- (e) II > I > IV > III