

CHM 2120
SAMPLE MIDTERM 2

First Name: _____ Last Name: _____

Student Number: _____

Approximate total number of marks:
(subject to minor changes)

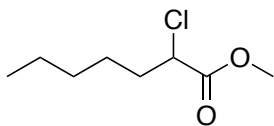
Notes:

- Molecular models are permitted
- Rulers and non-programmable calculators are permitted
- There is an IR absorbance table and a ¹H NMR table on the last page.

1a	2a	3b	4b	5b	6b	7b	8	1b	2b	3a	4a	5a	6a	7a	0		
1 H															2 He		
3 Li	4 Be									5 B	6 C	7 N	8 O	9 F	10 Ne		
11 Na	12 Mg									13 Al	14 Si	15 P	16 S	17 Cl	18 Ar		
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 106												

1. Name or draw the structure of the following molecules, as appropriate. (4 points)

a.

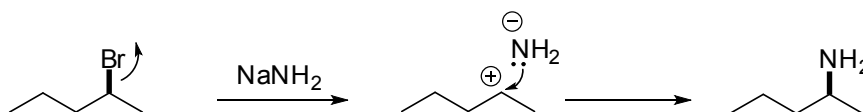


b. 2,4,6-trinitrotoluene (TNT)

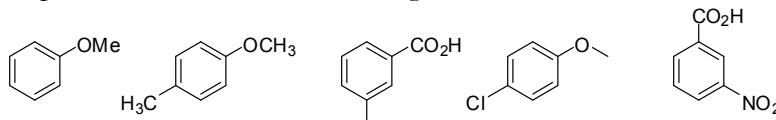
2.

a. Explain why the following reaction will not work as shown. (3 points)

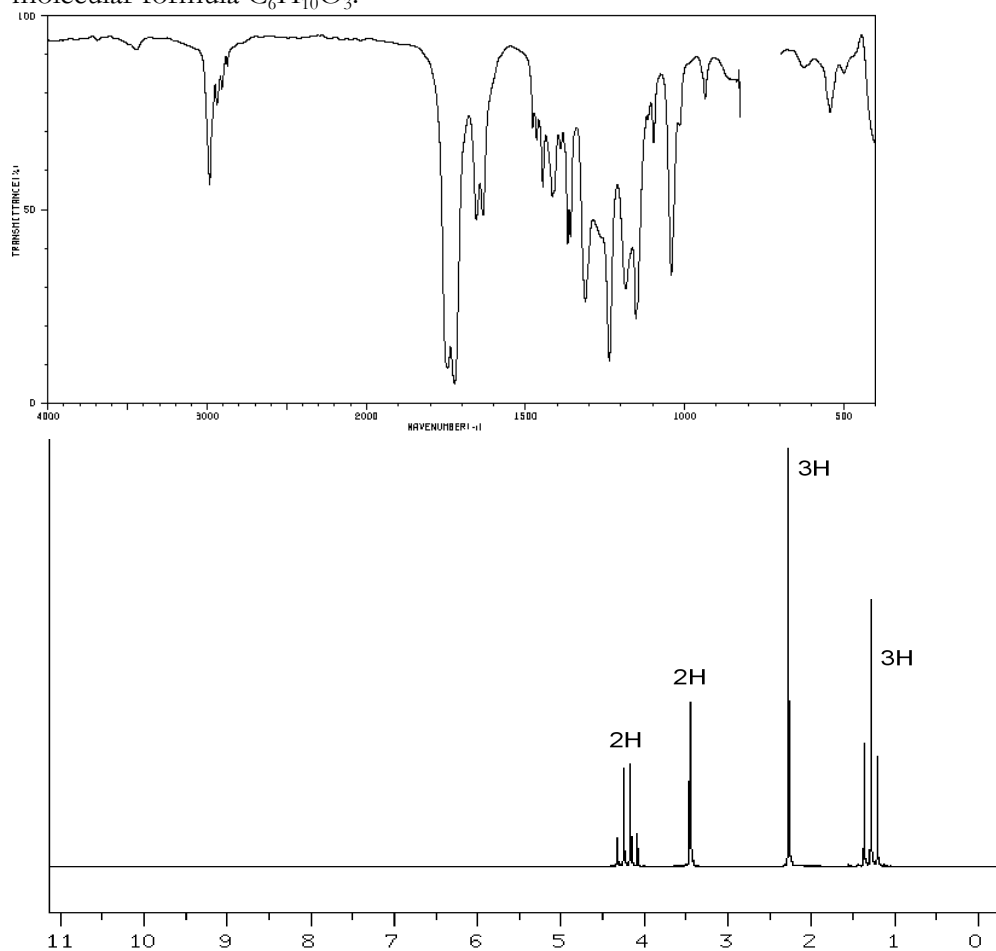
b. Give the true product of the reaction. (1 point)



3. Which of the following aromatics would react most rapidly and which would react most slowly with $\text{Br}_2/\text{FeBr}_3$? Justify your answer and predict the structure of the major product for the fastest reacting substrate.



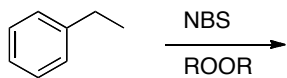
4. Draw the structure represented by the following IR and ^1H NMR spectra, with a molecular formula $\text{C}_6\text{H}_{10}\text{O}_3$.



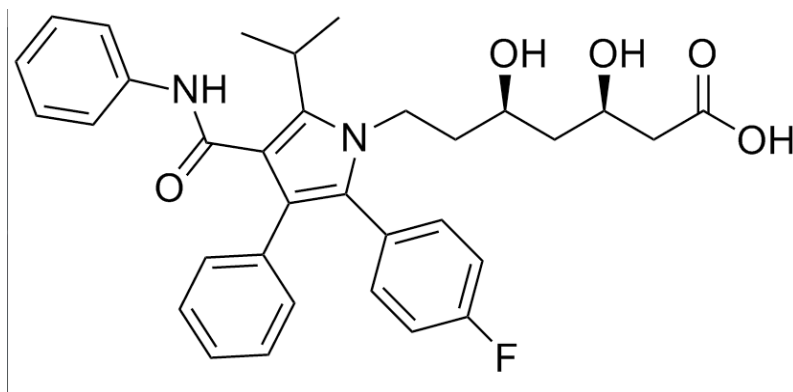
Peak	Chemical shift	Integration	Multiplicity	Comments/Ideas
A				
B				
C				
D				

5.

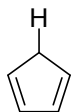
- What is the major product of the following reaction? **(1 point)**
- How would you distinguish between this product and the starting material by ^1H NMR? **(2 points)**



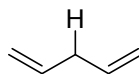
6. Circle **one** bond in Lipitor, a cholesterol-lowering drug in the “statin” class, that could be made by an $\text{S}_{\text{N}}2$ reaction. The drug works by inhibiting cholesterol production in the liver.



7. The pK_{a} of the indicated proton on the sp^3 -hybridized carbon in cyclopentadiene is 15, while the pK_{a} of the proton on the sp^3 -hybridized carbon in 1,4-pentadiene is 40. Explain why is one proton so much more acidic than the other. **(5 points)**

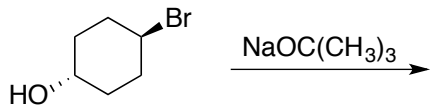


$\text{pK}_{\text{a}} = 15$

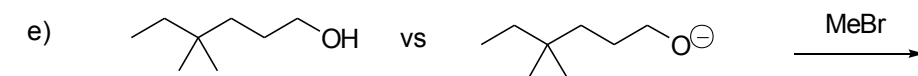
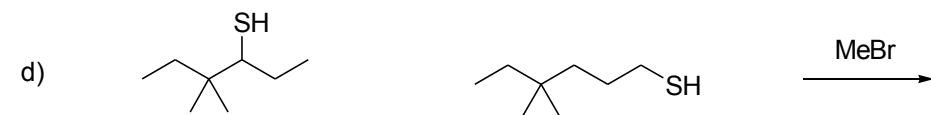
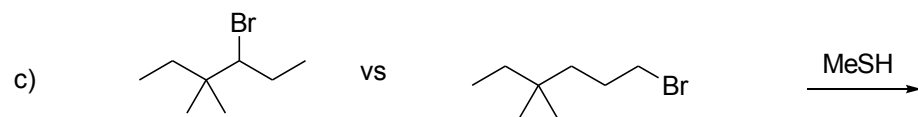
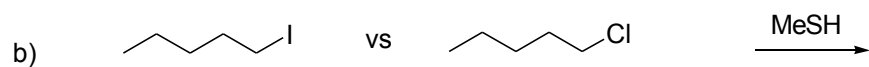


$\text{pK}_{\text{a}} = 40$

8. Give the full detailed mechanism for the formation of the major product. (6 pts)



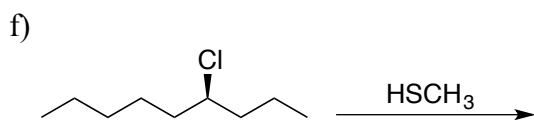
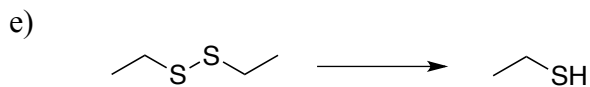
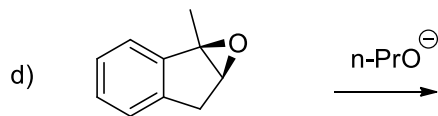
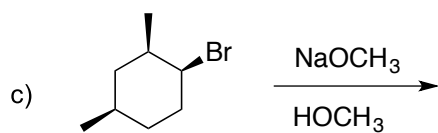
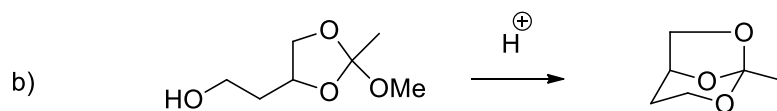
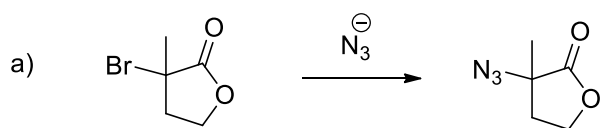
9. Circle the compound in each of the following pairs that would react fastest by $\text{S}_{\text{N}}2$.



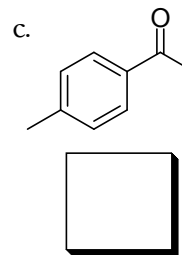
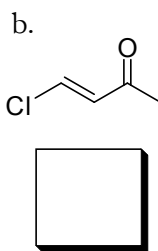
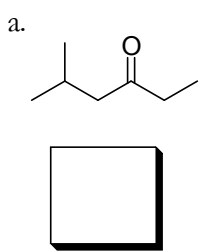
9. Propose a synthesis of the following compound Show all required reagents and intermediates. A retrosynthesis and mechanisms are not required. (10 points)



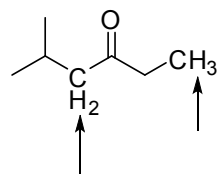
10. State what type of reaction is operative in each case. (4 points)



11. How many unique proton signals would be expected in the ^1H NMR spectrum of the following molecules? (3 points)

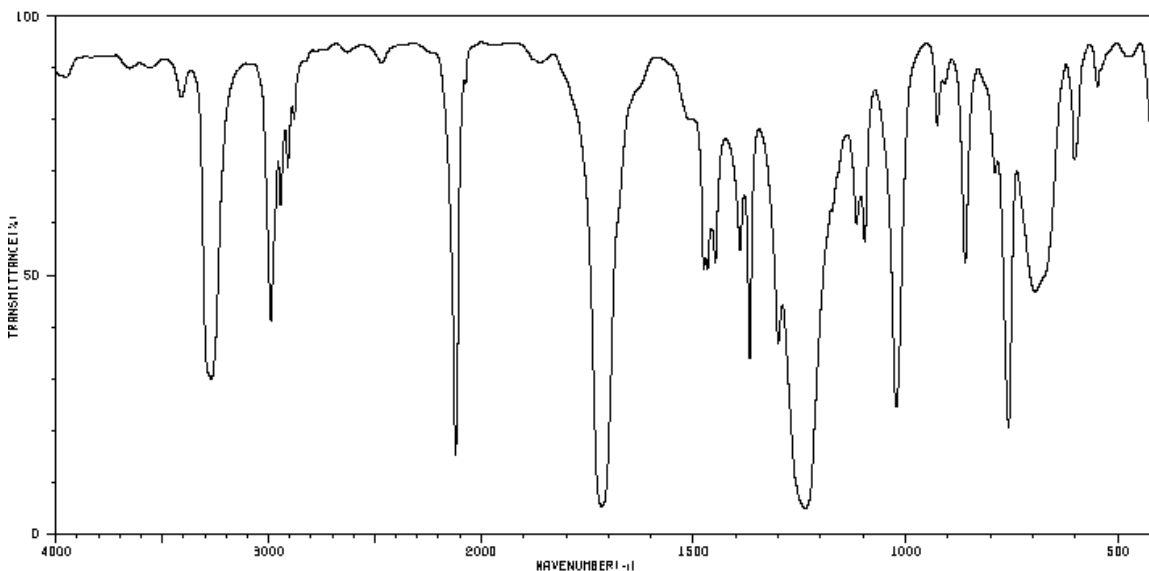


12. Give the number of peaks (multiplicity) expected in the ^1H NMR spectrum for the indicated protons in the following structure: (2 points)



13.

- Identify the key absorbances in the following IR spectrum. (5 points)
- Propose a structure for the molecule given that its formula is $\text{C}_3\text{H}_6\text{O}_2$. (2 points)

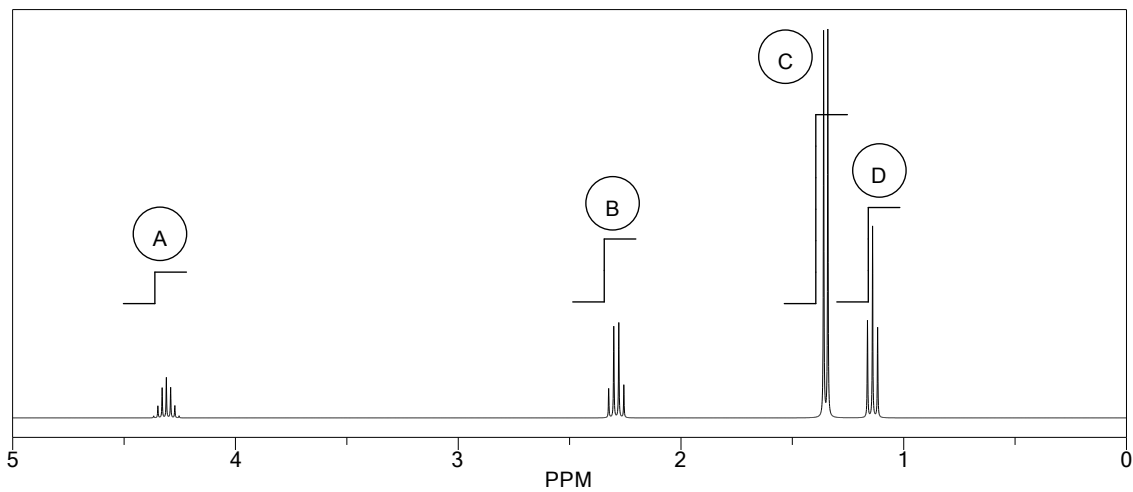


14.

a. What is the structure of the unknown compound whose molecular formula is $C_6H_{12}O_2$? The 1H NMR spectrum of this compound is below. (2 points)

b. Justify your answer by accounting for all information given. (10 points)

Note: the infrared spectrum showed a number of absorbances from $2879 - 2960\text{ cm}^{-1}$, and a strong absorbance at 1734 cm^{-1} .



Peak	Chemical shift	Integration	Multiplicity	Comments/Ideas
A				
B				
C				
D				

IR: Key Absorptions (cm⁻¹):

C-H	Alkyl	C-H	2850-2960	m-s, sharp
C-H	sp ²	C-H	just >3000	m-s, sharp
Alcohol		RO-H	3200-3650	s, broad
Carboxylic acid		RC(=O)O-H	2500-3300	s, broad
Amine		R ₂ N-H	3300-3500	s, broad
Carbonyl		R ₂ C=O	1650-1780	s, sharp
Nitrile		RC≡N	2220-2260	v, sharp
Alkynyl		C≡C-H	~3300	m-s, sharp
Alkynyl		C≡C	2100-2260	v, sharp

¹H NMR – Key APPROXIMATE chemical shifts (ppm):

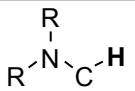
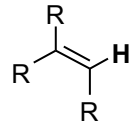
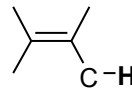
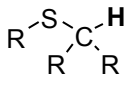
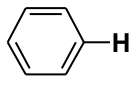
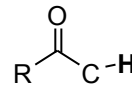
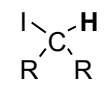

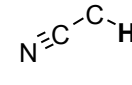
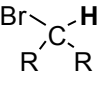
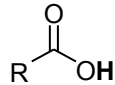
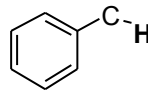
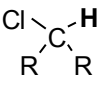
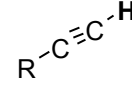
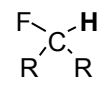
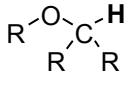
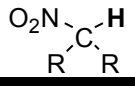
$\text{R}-\text{C}-\text{CH}_n$ 0.7 - 1.7	 $\text{R}-\text{N}(\text{R})-\text{C}-\text{H}$ 2.2 - 2.9	 $\text{R}-\text{C}(\text{R})=\text{C}(\text{R})-\text{H}$ 4.5 - 7.0
 $\text{C}(\text{R})=\text{C}(\text{R})-\text{H}$ 1.6 - 2.6	 $\text{R}-\text{S}-\text{C}(\text{R})_2-\text{H}$ 2.0 - 3.0	 C_6H_6 6.5 - 8.0
 $\text{R}-\text{C}(=\text{O})-\text{C}-\text{H}$ 2.1-2.5	 $\text{I}-\text{C}(\text{R})_2-\text{H}$ 2.0 - 4.0	 $\text{R}-\text{C}(=\text{O})-\text{H}$ 9.0 - 10.0
 $\text{N}=\text{C}-\text{C}-\text{H}$ 2.1 - 3.0	 $\text{Br}-\text{C}(\text{R})_2-\text{H}$ 2.7 - 4.1	 $\text{R}-\text{C}(=\text{O})-\text{OH}$ 11.0 - 12.0
 $\text{C}_6\text{H}_5-\text{C}-\text{H}$ 2.3 - 2.7	 $\text{Cl}-\text{C}(\text{R})_2-\text{H}$ 3.1 - 4.1	
 $\text{R}-\text{C}\equiv\text{C}-\text{H}$ 1.7 - 2.7	 $\text{F}-\text{C}(\text{R})_2-\text{H}$ 4.2 - 4.8	
	 $\text{R}-\text{O}-\text{C}(\text{R})_2-\text{H}$ 3.0 - 5.0	
	 $\text{O}_2\text{N}-\text{C}(\text{R})_2-\text{H}$ 4.1 - 4.3	

TABLE 3.1 Relative Strength of Selected Acids and Their Conjugate Bases

	Acid	Approximate pK_a	Conjugate Base	
Strongest acid	HSbF_6	< -12	SbF_6^-	Weakest base
	HI	-10	I^-	
	H_2SO_4	-9	HSO_4^-	
	HBr	-9	Br^-	
	HCl	-7	Cl^-	
	$\text{C}_6\text{H}_5\text{SO}_3\text{H}$	-6.5	$\text{C}_6\text{H}_5\text{SO}_3^-$	
	$(\text{CH}_3)_2\text{OH}^+$	-3.8	$(\text{CH}_3)_2\text{O}$	
	$(\text{CH}_3)_2\text{C}=\text{OH}^+$	-2.9	$(\text{CH}_3)_2\text{C}=\text{O}$	
	CH_3OH_2^+	-2.5	CH_3OH	
	H_3O^+	-1.74	H_2O	
	HNO_3	-1.4	NO_3^-	
	$\text{CF}_3\text{CO}_2\text{H}$	0.18	CF_3CO_2^-	
	HF	3.2	F^-	
	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	4.21	$\text{C}_6\text{H}_5\text{CO}_2^-$	
	$\text{C}_6\text{H}_5\text{NH}_3^+$	4.63	$\text{C}_6\text{H}_5\text{NH}_2$	
	$\text{CH}_3\text{CO}_2\text{H}$	4.75	CH_3CO_2^-	
	H_2CO_3	6.35	HCO_3^-	
	$\text{CH}_3\text{COCH}_2\text{COCH}_3$	9.0	$\text{CH}_3\text{COHCOCH}_3$	
	NH_4^+	9.2	NH_3	
	$\text{C}_6\text{H}_5\text{OH}$	9.9	$\text{C}_6\text{H}_5\text{O}^-$	
	HCO_3^-	10.2	CO_3^{2-}	
	CH_3NH_3^+	10.6	CH_3NH_2	
	H_2O	15.7	OH^-	
	$\text{CH}_3\text{CH}_2\text{OH}$	16	$\text{CH}_3\text{CH}_2\text{O}^-$	
	$(\text{CH}_3)_3\text{COH}$	18	$(\text{CH}_3)_3\text{CO}^-$	
	CH_3COCH_3	19.2	$^-\text{CH}_2\text{COCH}_3$	
	$\text{HC}\equiv\text{CH}$	25	$\text{HC}\equiv\text{C}^-$	
	H_2	35	H^-	
	NH_3	38	NH_2^-	
	$\text{CH}_2=\text{CH}_2$	44	$\text{CH}_2=\text{CH}^-$	
Weakest acid	CH_3CH_3	50	CH_3CH_2^-	Strongest base

Increasing acid strength

Increasing base strength