Name: _____ ***Grade:*** _____

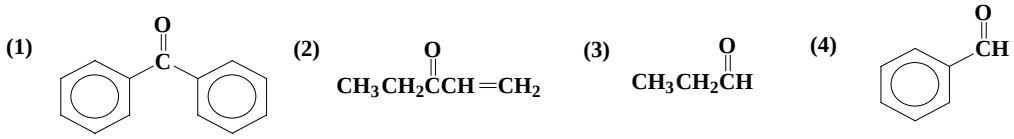
Please use a **non-red** pen. Answer questions in the provided space. If you write any answers on the back of the page, indicate this on the **front** of that page. Points appear in parentheses **( )**. ***Good Luck!***

Question	Max. Pts.	Points	Question	Max. Pts.	Points
1. 2 + 3 + 2+ 4	**= 12**		**5. 3 + 4.5 + 3 + 2.5**	**= 13**	
2. 2 + 3 + 5 + 5	**= 15**		**6. 2 + 3 + 2 + 2+3 + 2+2**	**= 16**	
3. 4 + 4 + 4	**= 12**		**7 2 + 2 +5 +2+1+2**	**= 14**	
4.- 1 + 3 + 2	**= 6**		**8 3 + 3 +4 +2**	**= 12**	
			Total	**100**	

1.. **(10) a.** Fill in the missing reagents which can bring about the following conversion.

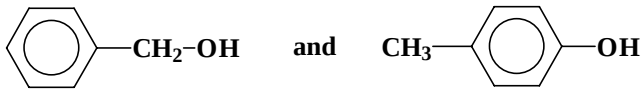
2

b. A compound has a sharp, strong IR peak at ~1700 cm^{-1} and a weaker band at 2700 cm^{-1} The proton NMR spectra has signals with an octet at about δ = 2.1, a triplet at about 1.25, and a triplet at 9.5 ppm. What is the most likely structure for this compound. Assign all peaks to particular kinds of hydrogens.



3

c. Write a chemical reaction or test that will distinguish between the following pair of compounds. Write the structures of all major organic and inorganic products that form. Note any precipitates, solubility, or color changes.



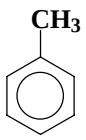
2

d. Give **one** characteristic difference in the **IR** spectra and **one** characteristic difference in the **NMR** spectra for distinguishing the compounds in part **c** above.

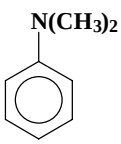
IR: **NMR:**

4

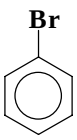
2. **(15)** a. Rank the following in **decreasing** order of reactivity, from most reactive to the least reactive toward **Br_2/$FeBr_3$**.



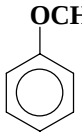
(1)



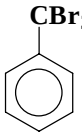
(2)



(3)



(4)

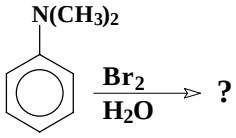


(5)

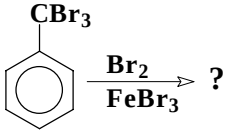
2

Ranking: _____

b. Give the product(s) resulting from the ring bromination of compounds **(2)** and **(5).**



(2)

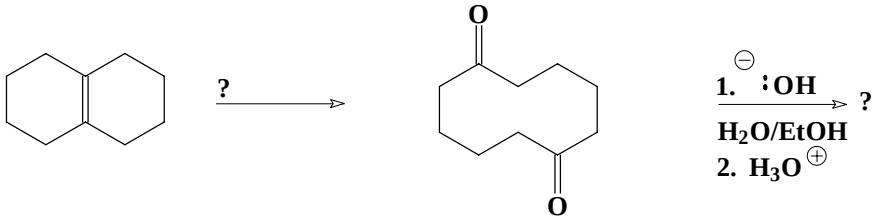


(5)

3

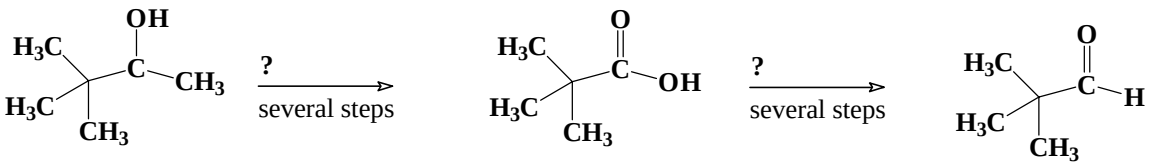
c. Fill in the missing reagents, intermediates, or products in the following reaction sequences. **Note:** more than one reagent may be required. Consider the role of the aldol condensation in part (1). Draw all missing parts.

(1)



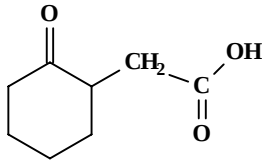
5

(2)



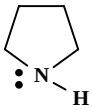
5

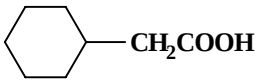
3. **(12)** a. Which of the following schemes could be used to synthesize in good yield



? Write the steps of the reaction, showing the intermediates.

(1) **Cyclohexanone, $Cl\text{-}CH_2\text{-}COOH$, $AlCl_3$, Δ.**

(2) **Cyclohexanone,**  **(pyrrolidine, a 2^o amine), H^+, ($-H_2O$); then $Br\text{-}CH_2\text{-}COOCH_2CH_3$; then ^-OH, H_2O, Δ; then H^+.**

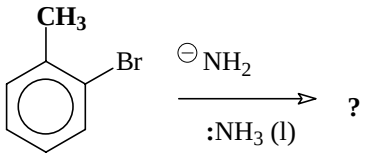
(3)  **(cyclohexylacetic acid), $KMnO_4$, ^-OH, Δ; then H^+.**

(4) **Answers (1) and (2).**

(5) **Answers (1), (2), and (3).**

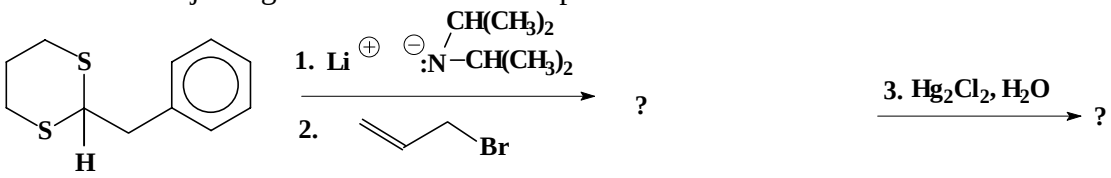
4

b. Complete the following equation by filling in the Product(s). Show the step by step mechanism for the reaction. Name the mechanism.



4

c. Predict the major organic intermediate and product. You can assume a mild acid workup.



4

4. (6) a. A compound with molecular formula **C_8H_9ClO** gave the following **^{1}H NMR** spectrum:

triplet, δ 3.7
triplet, δ 4.2
multiplet, 7.1

Solve for the Index of Hydrogen Deficiency, **Ω**. Show your calculation.

1

Ω =

Then choose the most likely structure for the compound. Note that the IR spectrum showed no evidence for an **–OH** band. Assign the peaks to the specific protons in the compound. Explain the multiplicity.

(1) $C_6H_5OCHCH_3$ (Cl on the CH)

(2) ***p*-$CH_3OC_6H_4CH_2Cl$**

(3) ***p*-$ClC_6H_4OCH_2CH_3$**

(4) $C_6H_5OCH_2CH_2Cl$

(5) ***o*-$ClC_6H_4OCH_2CH_3$**

3

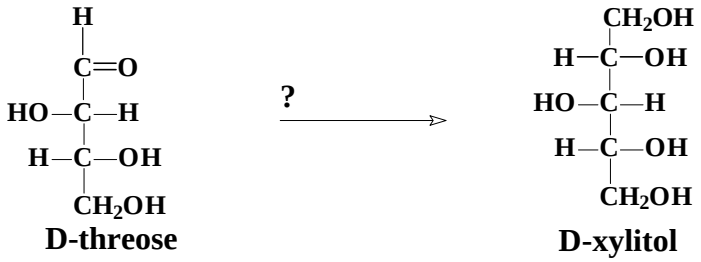
b. Predict the splitting you would observe for the proton at **C-3** of 2,3-dimethyl-2-phenylbutane. Write the structure of the compound and rationalize your answer.

(1) Doublet (2) Octet * (3) Septet (4) Singlet (5) Quartet

2

Note: The interpretations of **δ, Number of H's,** and **multiplicity,** should be included for the, **^{1}H-NMR** spectra.

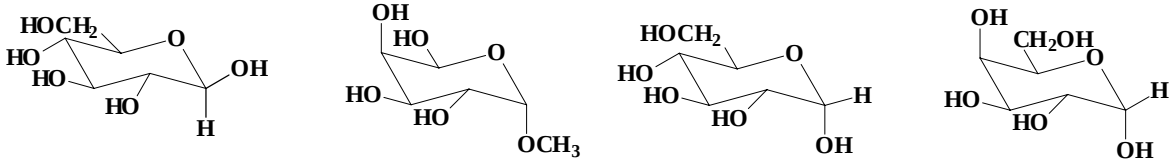
5. **(14)** a. D-Xylitol is a compound used as a chewing gum sweetener. Prepare this compound from D-threose. Please show all intermediates and assume that you can separate any isomers. More than one step is necessary.



D-threose **D-xylitol**

4

b. Consider the following compounds. For each category, pick out a pair of that type of isomer:



A **B** **C** **D**

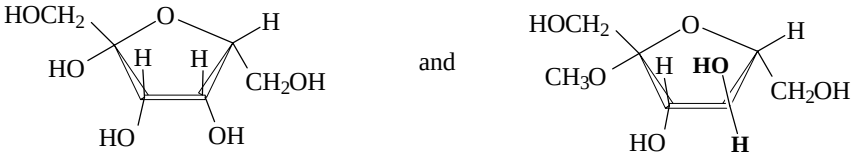
(1) Constitutional isomers _____ and _____

(2) Diastereomers only _____ and _____

(3) Anomers only _____ and _____

4.5 (1.5 pt ea)

c. Distinguish the following sugars, **fructose (β-fructofuranose) and methyl fructoside**, by a simple chemical reaction. Show the reagent composition and visible result for the positive reaction.



3

d. Give the mechanism for the hydrolysis of **methyl fructoside** with a trace of acid and water.

2.5

6. **(16)** a. The Ruff degradation is the reaction of an aldose with:

(1) HCN; then H_3O^+; then $Ba(OH)_2$; then Na·Hg, H_2O

(2) HCN; then $Ba(OH)_2$; then H_3O^+; then Na·Hg, H_2O

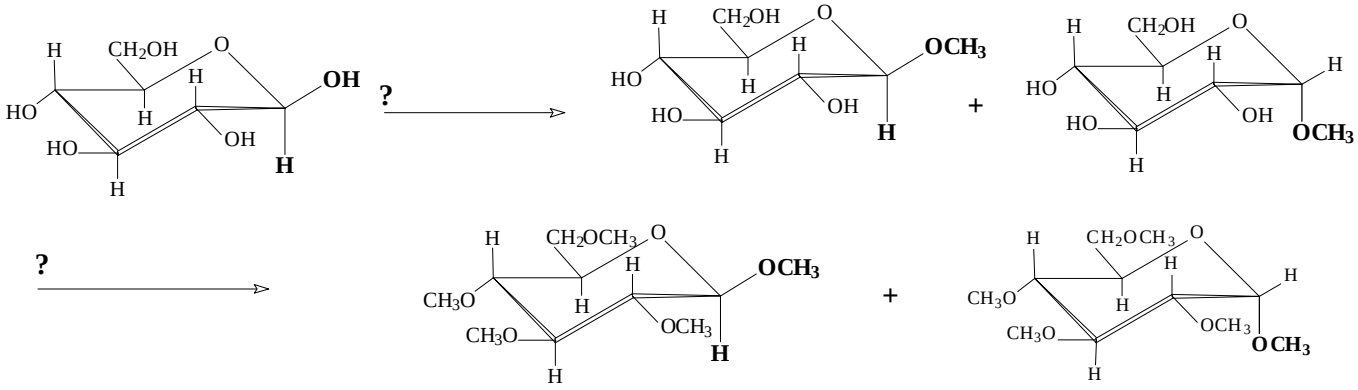
(3) Br_2/H_2O; then HCN; then H_3O^+; then Na·Hg, H_2O

(4) Br_2/H_2O

(5) Br_2/H_2O; then H_2O_2, $Fe_2(SO_4)_3$

2

b Fill in the missing reagents in the following reaction sequence.



3

c. Cellulose lacks nutritive value for humans because:

(1) The products of its digestion are excreted without utilization.
(2) Its conformation prevents attack by digestive enzymes.
(3) We lack the enzymes, which can catalyze the hydrolysis of the glycosidic linkages.
(4) It passes through the digestive tract so rapidly.

2 (5) The molecules possess such a high molecular weight.

d. Glucose and mannose are examples of

(1) enantiomers (2) structural isomers (3) epimers (4) glycosides (5) structural isomers

2

e. Draw the structure of mannose in its open form and in its $\alpha$and β hemiacetal forms. Label them α or β.

3

f. Which reagent reacts with glucose, mannose, and fructose to give the same phenyl osazone?

2

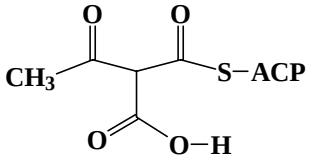
g. Draw the structure of the common phenyl osazone produced in f above.

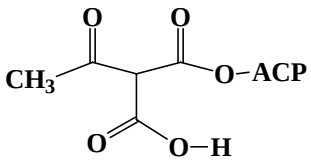
2pt

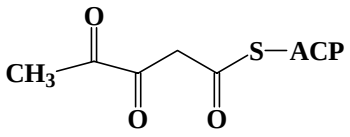
7. **(14) a**. The most important function of the pyrophosphate group in isoprenoid biosynthesis is as a
(1) strongly acidic group and good proton donor (2) good electrophile
(3) good nucleophile (4) good leaving group
(5) Ability to stabilize an anion on the **α**-carbon.

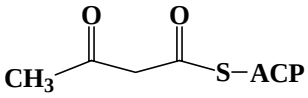
2

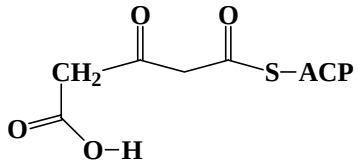
b. Fatty acids are biosynthesized from **acetyl coenzyme-A** and **malonyl coenzyme-A** *via* an acyl carrier protein, **ACP**. Which structure below represents the initial condensation product of these two building blocks.

(1) 

(2) 

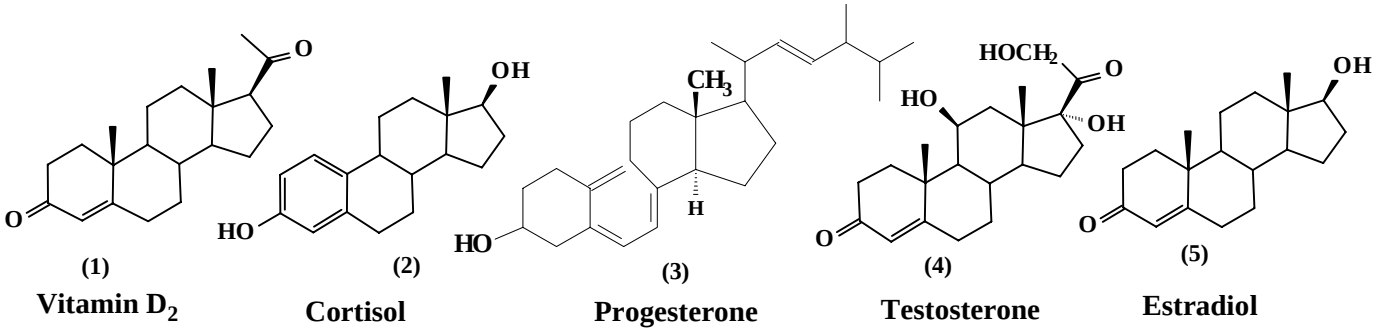
(3) 

(4) 

(5) 

2

c. Match the structure of the steroids below with the correct numbered structure of each.



_____ _____ _____ _____ _____

5

d. **Draw** the structure of **glyceryl tristearate**, where stearic acid is $\mathbf{C_{17}H_{35}COOH}$. **Draw** the structure of a **soap** made from this fat. Briefly, how is the soap made**?**

2

e. The **primary** function of triacylglycerides in mammals is:

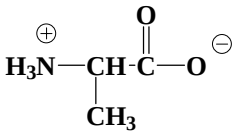
(1) structural material (2) source of chemical energy (3) source of soap
(4) source of hormones (5) source of coenzymes

1

f. The 'ring around the bathtub' is a problem with soaps but not with detergents because:
(1) Soaps are more acidic. (2) Soaps are more basic. (3) Detergents have soluble calcium salts
(4) Soap micelles are unstable in acids. (5) Soap micelles are unstable in bases.

2

8. (6) **a**. Which of the following would provide a synthesis of **alanine**? More than one answer may pertain.



(1) **CH_3CH_2COOH, Br_2, P; then excess NH_3, pH 6.0**

(2) **Potassium phthalimide, $ClCH_2COOCH_2CH_3$; then NH_2NH_2/H_2O, Δ, pH 6.0**

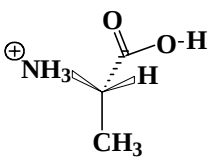
(3) **Acetaldehyde ($CH_3CH{=}O$), ammonia, and HCN, pH 6.0**

(4) **Potassium phthalimide, $PhCH_2Br$; then KOH/H_2O, Δ; then CO_2, $H^{\oplus}$, pH 6.0**

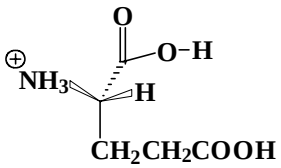
(5) **Potassium phthalimide, $ClCH_2COOCH_2CH_3$; then KOH/H_2O, Δ, pH 6.0**

3

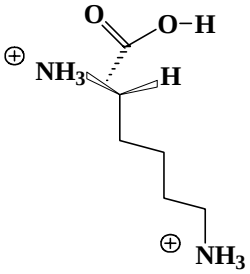
b. Using the following table of pK_a values, find the amino acid which would have its isoelectric point, **pI**, closest to **3**. Calculate the exact **pI** and show your calculation. Draw the structure of the ***zwitterion***. The structures of the amino acids are shown in their fully protonated forms.



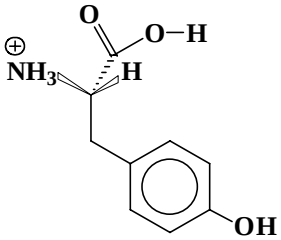
alanine



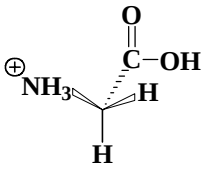
glutamic acid



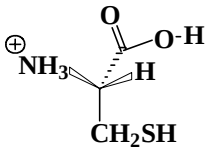
lysine



tyrosine



glycine



cysteine

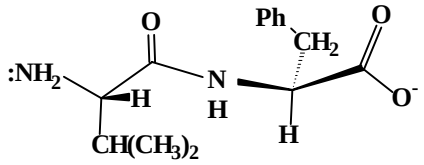
amino acid	pK_{a1} (α–COOH)	pK_{a2} (α–NH_3^+)	pK_{a3} (R)	pI
glycine	2.3	9.6		
tyrosine	2.2	9.1	10.1	
lysine	2.2	9.0	10.5	
glutamic acid	2.2	9.7	4.3	
alanine	2.3	9.7		
cysteine	1.7	10.8	8.3	

(1) **amino acid, pI ~ 3 :** _____ (2) **calculation:**

3

8 cont'd

c. Synthesize the dipeptide **Val-Phe** using the **Merrifield** automated solid state peptide synthesis. Show all steps including protection with blocking groups, activation, reaction, and removal of the protecting groups.



Val-Phe

4

d. The Edman Degradation uses this reagent to identify the N-terminal amino acid of an amino acid or protein. Choose the reagent used for the Edman Degradation.

(1) Ph-NH-NH_2 (2) 2,4-DNFB (3) Ph-NH_2 (4) Ph-N=C=O (5) Ph-N=C=S

2

Scrap Paper

Scrap Paper

Good luck in your careers. Enjoy the rest of your summer.

Grace B. and Irving J. Borowitz, 08/12/99

Write a plausible mechanism for the following transformation.