

Chemistry 204 Midterm 1, February 8, 2010

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| | Chemistry 204 Midterm 1, February 8, 2010 | |
| | surname | given names |
| last initial | student number | signature |

MOLECULAR MODELS MAY BE USED

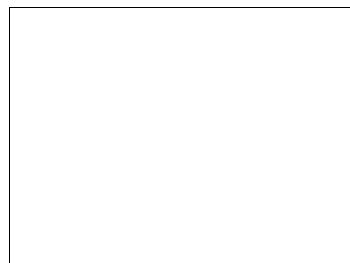
| 1 | 2 | 3 | 4 | | raw total | | total |
|----|----|---|----|--|-----------|--|-------|
| 50 | 10 | 8 | 32 | | 100 | | 10 |

1. (50 marks) Answer each of the following parts.

a)

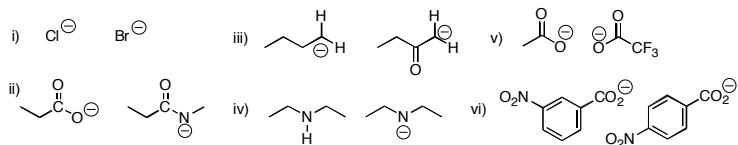
A D-2-ketohexose, psicose, gives a mixture of allitol and altritol when reacted with NaBH₄.

What is the structure (Fischer projection) of psicose?



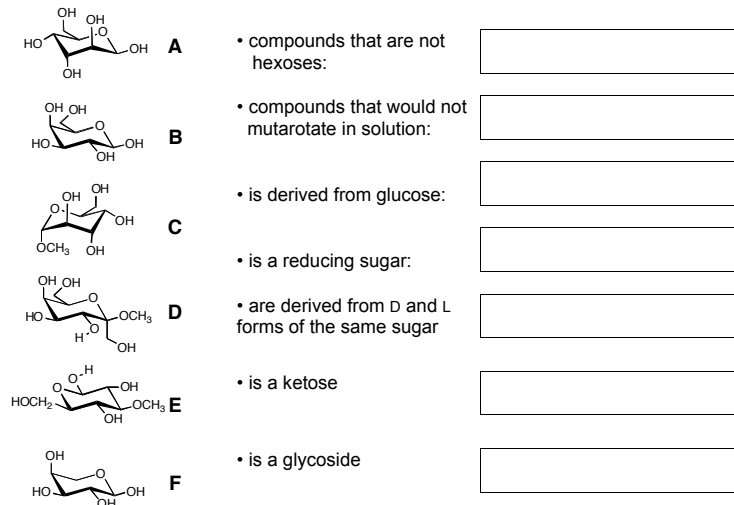
Fischer projection of *psicose*

b) For each of the pairs of molecular species below, circle the molecular species that is the *weaker base*.



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c) Consider the following structures A-F when answering this set of questions. If no structures fit the criteria, write "none".



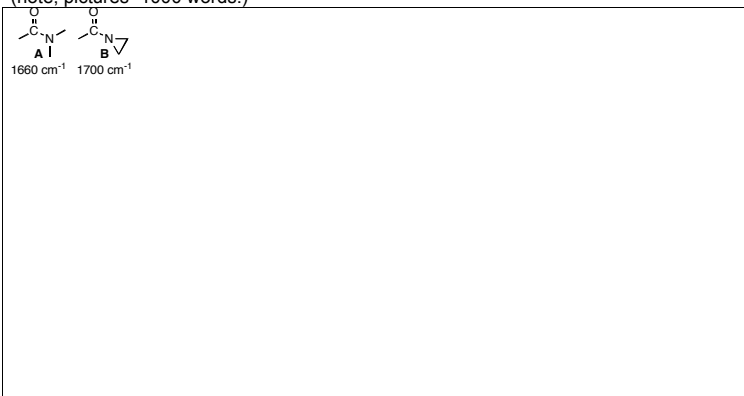
d)

Provide the most stable conformation of α -D-galactopyranose:



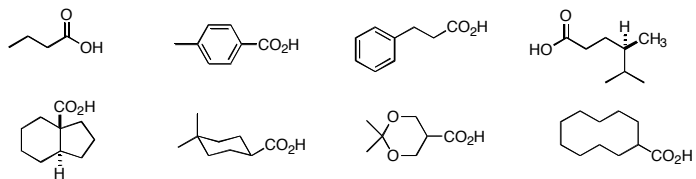
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e) The IR stretch of the C=O bond in *N,N*-dimethylethanamide (**A**) is 1660 cm^{-1} . The IR stretch of the C=O bond in compound **B**, though, is 1700 cm^{-1} . Rationalize this effect. (note, pictures=1000 words!)

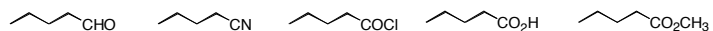


f) Circle the structure of any carboxylic acid that could *NOT* be prepared using the following sequence from a bromine containing starting material:

step 1. potassium cyanide, solvent; step 2. aqueous acid, heat

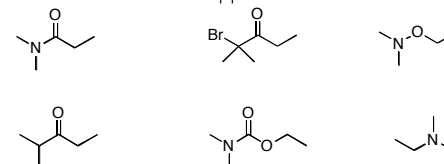
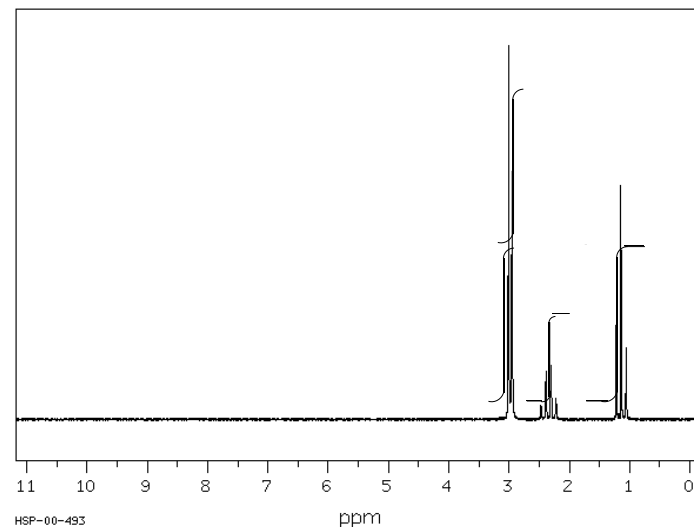


g) Circle any compound that would react with methyl magnesium iodide (CH_3MgI ; then acid workup) to form a methyl ketone.

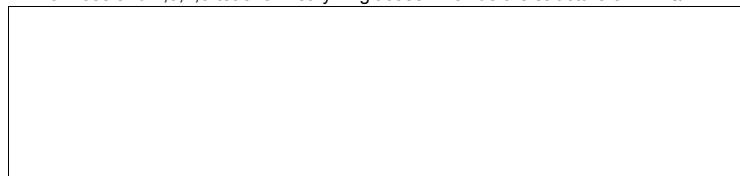


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h) The ^1H NMR spectrum of compound **X** is given below. Circle the structure of **X**.



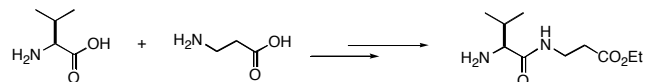
i) Disaccharide **AX- α** forms a silver mirror when treated with Tollens' reagent. Enzymatic analysis has defined its glycosidic bond as the α -configuration. Exhaustive methylation (NaH , MeI) followed by hydrolysis (HCl , H_2O) generates 3,4,6-tri-O-methyl-D-mannose and 2,3,4,6-tetra-O-methyl-D-glucose. Provide the structure of **AX- α** .



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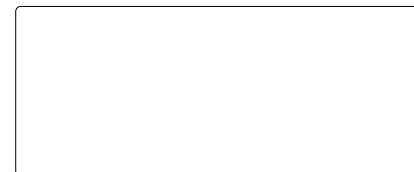
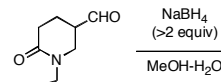
2. (10 marks) Provide reagents and reaction conditions to convert the starting material(s) to the designated product. *Be sure to clearly show all the reagents and isolated intermediates along the path.* You can assume any other compounds you need are available. **Note: mechanism steps are not required for these questions.**

a)

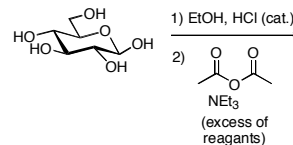


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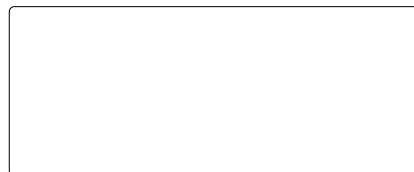
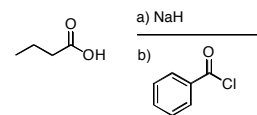
3. (8 marks) Provide the requested information for each of the following reactions. Do not draw the same compound twice.



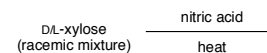
organic product(s)



organic product(s)



organic product(s)



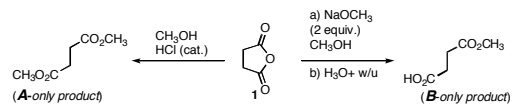
organic product(s)

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4. (32 marks; 8 marks each) Using a mechanistic analysis that employs arrows that represent electron movement, provide a *carefully drawn* rationale for each of the following chemical processes.

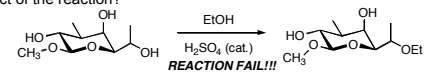
a) *True or False*—The same product is produced by the LAH reduction of butanoic acid and *N,N*-dimethyl butanamide. Justify your answer using mechanistic rationale.

b) Anhydride **1** forms diester **A** using methanol-HCl and monoester **B** when treated with sodium methoxide in methanol. Explain (briefly) the formation of **A** and (more extensively) the formation of **B**.

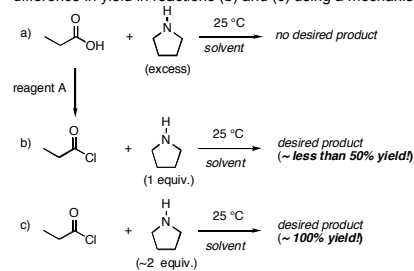


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c) Briefly explain why the attempted ether formation reaction below does not proceed as drawn—it fails! What actually is the product of the reaction?



d) Three attempts to generate a desired product in high yield were carried out. Explain the failure of reaction (a)—what is actually the product? What is reagent A (no mechanism required)? Explain the difference in yield in reactions (b) and (c) using a mechanistic analysis.



End of questions

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