Lab Practicum Exam: Chemistry 4524 Organic II Alfred State College 2017

Your name: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \_\_\_/61

1. **Scenes from Organic Procedure Disaster films**

**Disaster Scene 1**



Ethyl butanoate

 Jack Chemist wants to carry out an esterification to make ethyl butanoate.

 He proposes the following procedure:

“ *Mix 0.03 moles of 1-butanol (d=0.8 g/mL) and 0.03 moles of acetic acid (d=0.85 g/mL) together and then add ~5 mL of M sodium hydroxide as a catalyst. Immediately distill into a receiving flask. Wash the lower organic layer with concentrated sulfuric acid (d= 1.8 g/mL) and discard the upper layer of the wash. Add MgSO4 to dry the lower layer.”*

**List 3 errors in Jack’s procedure:**

1. \_\_\_*wrong choice of alcohol/acid-should be ethanol/butanoic acid\_\_\_\_\_\_*
2. *\_\_\_H+ not OH- is the catalyst in this reaction\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_*
3. *\_\_\_need to reflux for ~1 hour, not distill\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_*

*+wrong layer washed (and not with H2SO4); upper layer has product\_\_\_*

*+wrong layer discarded and wrong layer dried\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_*

**Disaster Scene 2**

Jill Chemist wants to solvent extract her reaction mixture which contains water-soluble sodium benzoate and water-insoluble benzyl alcohol. She proposes the following procedure:

*“Add ~15 mL of CH2Cl2 (d= 1.3 g/mL) to the reaction mixture. Pour the resulting mix into a 125 mL separatory funnel and shake vigorously with the stopcock closed and the glass stopper firmly in place to prevent loss of product. Add ~ 10 mL of water (d=1.00 g/mL) and shake as just described. With the glass stopper still in place, draw off the lower aqueous layer and set it aside.*

*Draw off the upper organic layer, which contains benzyl alcohol into a beaker and add chromic acid to insure the alcohol remains un-oxidized. To the lower aqueous layer, which contains sodium benzoate, add ~10 mL of 2 M NaOH to convert the benzoate to benzoic acid. Drive off the water by heating vigorously and collect the final benzoic acid crystals.”*

**List 3 errors in Jill’s proposed procedure: (There are more than 5 errors above)**

1. *\_\_\_\_\_\_needs to `burp’ the baby\_and shake gently\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_*
2. *\_\_\_\_\_\_CH2Cl2 is lower layer, not water\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_*
3. *\_\_\_\_\_\_loosen stopper-you won’t get funnel to deliver unless you do\_\_\_\_*

*+)upper layer contains benzoate, not alcohol; b)chromic acid will oxidize it !*

*+)add acid not base to form benzoic acid; b) don’t need to drive off water-just filter benzoic acid\_\_\_\_\_\_\_\_\_\_\_*

1. **Old School Mates**

Decide which of the classic techniques listed to the right best suits the goals below (use #):

1. Purifying a mildly impure crude solid product \_\_\_**7\_\_\_\_\_**
2. Baeyer test
3. Solvent extraction
4. Refractive index
5. Steam distillation
6. Fractional distillation
7. Retrograde rotation
8. Recrystallization
9. Hanon practice
10. Separating two compounds with similar structure but moderately

different aqueous solubilities \_\_\_\_4\_\_\_\_\_

1. Separating two compounds with very different boiling points\_\_\_5\_\_\_\_\_\_
2. Separating two compounds, one of which forms a water soluble salt when

acidified\_\_\_\_2\_\_\_\_

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1. **Let the Punishment Fit the Crime: Method Matching**

Your organic lab has the following methods in-house:

1. GC-MS (gas chromatograph-mass spectrometer)
2. GC (gas chromatograph)
3. Abbe Refractometer (measures refractive index)
4. ATR-FTIR (Attenuated Total Reflectance –Fourier Transform Infrared Spectrophotometer)
5. NMR (Nuclear Magnetic Resonance Spectrometer)
6. Mel-Temp (melting point apparatus)
7. Baeyer test solution (KMnO4/ethanol)
8. Bromine test solution (Br2/CH2Cl2)
9. Which method(s) above provide a quick confirmation for the presence of a C=C double bond?

*g (Baeyer test) and h (Bromine test)*

1. What method is best applied if you just want to confirm the purity of a liquid compound you think you’ve identified?

*c(Refractometry)*

1. Which method provides an efficient way to decide what functional groups are present in a product?

*d (ATR-FTIR)*

1. Which method allows you to both separate and identify components of a mixture of organics?

*a(GC-MS)*

1. What method is traditionally applied to ascertain the purity of a purportedly pure solid ?

*f(Mel-Temp)*

1. Which method can allow you to deduce the precise arrangement of atoms and groups in an unknown, pure liquid given its empiric formula ?

*e (NMR)*

1. Which method provides mixture identification via retention times ?

*b(GC)*

**4) IR Analysis**

1. What band (cm-1) is a strong indicator of the presence of an alcohol ? *\_\_\_3300-3500*\_\_\_cm-1
2. The above band is: (circle your choice)

i)Weak and sharp ii)strong and sharp iii)a multiplet iv)*strong and broad*

1. What’s the easiest way to decide whether a compound has C=C bonds present vs. just C-C bonds from an IR spectrum?

*Medium to medium weak singlets just above 3000 near 3050 cm-1 (can be shoulders)*

1. Weak overtone bands in the 1900-2000 cm-1 region are strong indicators of the presence of:

*aromatics*

1. A sharp, strong singlet IR band appears at 1695 cm-1. It is most suggestive of the presence of:
2. Alcohols b) aromatics *c) ketones or aldehydes*  d) alkanes e) alkynes
3. What observation suggests you have an un-substituted, simple cycloalkane like cyclohexane?
4. Strong bands at both 1470 and 1380 cm-1 *b) A band at 1470 cm-1 but not at 1380 cm-1*

c)a band at 1380 cm-1 but not at 1470 cm-1 d) sharp ring breathing mode at 1600 cm-1

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**4) IR Analysis (continued)**



d

c

d

b

**Compound A**   **Compound B**

a bands above 3000 cm-1(~3050 cm-1) a band centered at 3450 cm-1

b bands 1800-2000 cm-1 b band below 3000 cm-1 (2890-2950 cm-1)

c band 1500 cm-1 c band at ~1460 cm-1 (c band 2-3X as big as d band)

 d band at 1380 cm-1

What class of compounds are A and B likely part of ?

Compound A class\_\_\_*aromatics*\_\_\_\_ (2 pts) Compound B class\_\_\_\_\_\_*alcohol*\_\_\_\_\_\_\_\_\_ (2 pts)

Pick from the list of possible compounds below, the most likely identification of Compound A and B

Ethyl benzene propyl ethyl ketone octane acetic acid methanol

Toluene methyl ethyl ketone hexane formic acid ethanol

Phenol diethyl ketone pentane benzoic acid isopropanol

Benzene acetone iso-butane 1-butanol

Compound A= \_\_\_*benzene\_*\_\_\_\_\_\_\_\_\_\_\_\_ (2 pts) Compound B =\_\_\_\_*1- butanol*\_best\_\_\_\_ (2 pts)

 **ethanol -1 isopropanol -1**

**5) NMR Antics**

1. If Hx has 5 nearest neighbor protons, what is the multiplet splitting for Hx ? **N+1=5+1=6**
2. What motion is associated with spin coupling ?

i)precession of electron moment in molecule’s magnetic field

 ii) precession of proton moment in external, fixed field magnet

 iii) rotation of protons around externally applied electric field

 iv) spin-spin magnetic interactions between electrons and protons of molecule

1. What is the physical source of the multiplet (hyperfine) splitting of peaks seen in 1H NMR?

i)differences in chemical environment ii) Carbon interacting with H magnetically

iii) inhomogeneities in the NMR magnet field iv)nearest neighbor proton magnetic fields

increasing or decreasing the local field

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**5) NMR Antics (continued)**

1. A compound with empiric formula C5H12 has a single NMR peak with no hyperfine splittings.

What is the structure of the compound ? (2 pts)



1. The 1H NMR below is a ketone with empiric formula C5H10O

How many non-equivalent H are implied ? \_\_\_\_\_\_\_**3**\_\_\_\_\_\_\_\_\_\_

 (Y) (Z)

 Singlet doublet

 (7 in multiplet)

 (X)

 4 2.1 1.1 ppm 0 (TMS)

What is the ketone’s structure? (3 pts)



 Y

 Z

 3-methyl-2-propanone

X

1. A 13C NMR for a compound with the empiric formula C4H10O reveals the following lines:



δ **18.9 CH3**

δ **30.8 CH 2-methyl-1-propanol**

δ **69.4 CH2**

Draw the likely structure of the compound here🡪

(2 pts)

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**6)GC-MS Reckonings**

1. What is meant by the `parent mass’ in mass spectroscopy ?

***Compound itself without loss of fragments***

1. What is meant by the `cracking pattern’ in mass spectroscopy?

***The distribution and intensity of the mass fragments the parent is broken into in the MS***

1. What initially separates the compounds of a mixture injected into a GC-MS?

*GC column holds mixture components for varying retention times*

1. The ~ sample size injected into a GC-MS is:

i)around 1 mL ii) around 1 L iii) around 0.1 *mL iv) < 1μL* v) 10-10  L

1. A pure compound with the formula C5H12 produces a simple MS spectrum with the major mass peaks listed below. Assign the fragments likely to be causing the peaks.

Mass (m/e) amu fragment assignment ( 1 pt each) **P=C5H12**

72 P

71 P-H (**C5H11+)**

57 P-CH3 (C(CH3)3+ )

42 P-2CH­3  (C(CH3)2+) should list as P- fragrment for full credit

27 P-3CH3 (C(CH3)+)

What is the likely structure of the C5H12 compound above ? (3 pts)



7)**A Final Reckoning (7 points)**

A compound (call him Stinker) has been carefully isolated during the course of an organic synthesis. He exhibits the following spectral data:

Stinker’s FTIR spectrum



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Stinker’s NMR spectrum





 Stinker’s Mass Spectrum

Stinker’s refractive index, nD25 is recorded as 1.4959. He has a density of 0.8665 g/cm3 and a recorded boiling point of 136oC. Stinker is poorly soluble in water and despite his nickname has a somewhat pleasant if cloying odor. Stinker does not react to Br2 or form a brown precipitate with the Baeyer reagent. He was purportedly `birthed’ in two steps via an electrophilic substitution followed by a reduction. Both these reactions are famous enough to have names.



Draw or name Stinker’s identity here:

IR: C-H stretches above 3000 cm-1 => C=C stretcj

Complex C-H stretches near 2900-2800=> alkyl group

ring breath overtones near 2000 cm\_1 => aromatic

 ring breath at 1600=> aromatic

 1470 and 1385 CH2 and CH3 bends => CH2 and CH3 present

 Ethyl benzene

\_\_\_/7 STINKER

NMR: 3 separate piles of lines +> ~ 3 non-equivalent H

 Triplet means CH3 is split by neighboring CH2 (N+1) rule, N=Nearest neighbor count

 Quartet means CH2 split by neighboring CH3

 Band near 7=ppm is diagnostic for aromatic ring

MS: ethyl benzene (C8H10) molecular Mass (106) matches 106 m/e peak observed=> parent peak

 peak at 91 is P-CH3; peak at 77 is P-C2H5 ; peak at 65 is C5H5 ring fragment; peak atg 51 is C4H3

 ring fragment.

Chemical hints: aromatics are called such because they smell `nice’; neither bromine or Baeyer test interrupts benzene double bonds because of enhanced stability; two `name’ reactions are Friedel-Craft acylation, then either4 Wolff-Kishner or Clemensen reduction