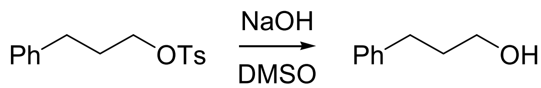
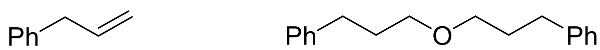
Chemistry 381 **Name:________________________**
Mid-Term Exam – Wednesday
March 18, 2009

Read all questions carefully. You have a large amount of space to write your answers. If appropriate, clearly indicate your answer.

1. The reaction below was performed and monitored by TLC. The starting material (tosylate) has an R_f of 0.40 in 10% ethyl acetate:90% hexane. As the reaction progressed, the starting material spot disappeared and a new spot appeared with an R_f of 0.70. The person running the reaction became worried. Speculate on why the experimenter became worried and propose an alternate product based on the TLC data.



The product (an alcohol) should be more polar than the starting material and therefore have a *lower* R_f value. A couple possible alternate products are shown below, and both would be very non-polar (high R_f).



2. A person wanted to distill naphthalene (bp 218° at 760 mm Hg, mp 81°). Use the nomograph to decide whether this compound could be distilled easily with a water aspirator (60 mm Hg) as the vacuum source. How about a vacuum pump (~0.1 mm Hg)?

With an aspirator (60 mm Hg), the bp would be 130-135°. One could distill this compound pretty easily with a heat gun. Under full vacuum (~0.1 mm Hg), the bp would drop to 30-35°. This value is below the melting point of naphthalene. That would pose a problem – boiling a solid. It is possible (called a sublimation), but it is no longer a distillation.

[Unaddressed by this question is the problem of collecting the distillate. The distillate is normally collected with a water condenser that is cooled with tap water (50-55°). At that temperature, the collected product would be a solid and would not flow into a collection flask. People get around this problem by gently warming the condenser to melt the solid into a receiver flask.]

3. Solubility data for anthracene and naphthalene in benzene are given below. Determine the percent recovery of anthracene from benzene (take 100 grams of anthracene and recrystallize it from benzene). Determine the percent recover of naphthalene from benzene. Would you rather recrystallize a mixture of 10% anthracene and 90% naphthalene (to recover the naphthalene) or the opposite (90% anthracene/10% naphthalene)? Explain. Assume you can heat your benzene up to 70° and cool your benzene down to 10°. [Data from Seidell, A. *Solubilities of Inorganic and Organic Compounds*, 3rd ed; D. Van Nostrand: New York, 1919.]

anthracene solubility			**naphthalene solubility**	
temp	**g in 100 mL benzene**		**temp**	**g in 100 mL benzene**
10	0.98		10	24
20	1.43		20	31
30	2.03		30	39
40	2.78		40	48
50	3.75		50	58
60	5.14		60	71
70	7.00		70	85

Case A – 90% naphthalene – assume 100 g of sample

Solubility in 70° benzene
Naphthalene – 90 g / (85 g/100 mL) = 106 mL
Anthracene – 10 g / (7 g/100 mL) = 143 mL
Therefore, need 143 mL benzene to dissolve the sample.

Solubility in 10° benzene
Naphthalene – 143 mL * 24 g / 100 mL = 34 g <- stays in solution (56 g precipitates, 62% rec.)
Anthracene – 143 mL * 0.98 g / 100 mL = 1.4 g <- stays in solution (~9 g precipitates, 90% rec.)

Conclusion – modest recover of naphthalene (62%) and it contains ~9 g of impurity

Case B – 90% anthracene – assume 100 g of sample

Solubility in 70° benzene
Naphthalene – 10 g / (85 g/100 mL) = 12 mL
Anthracene – 90 g / (7 g/100 mL) = 1290 mL
Therefore, need 1290 mL benzene to dissolve the sample.

Solubility in 10° benzene
Naphthalene – 1290 mL * 24 g / 100 mL = 310 g <- stays in solution (no recovery)
Anthracene – 1290 mL * 0.98 g / 100 mL = ~13 g <- stays in soln (~77 g precipitates, 86% rec.)

Conclusion – good recover of naphthalene (86%) and it is pure

Take home lesson – It’s easier to remove more soluble impurities.

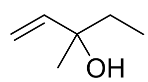
4. Based on the provided ^{1}H, ^{13}C, COSY, DEPT, and HETCOR spectra, determine the structure of the unknown.

This problem can be almost completely worked from the ^{1}H spectrum.

From the ^{1}H spectrum, integrations show 12 hydrogens. Take a peek at the ^{13}C and see 6 carbons. Unless the molecule has some symmetry (like an isopropyl group), then the molecule has only 6 carbons. We are working with a formula of C_6H_{12} as well as possible N or O atoms. One spectrum mentions doing a D_2O and shake experiment, and a signal at 1.6 ppm diminished. Therefore, this sample does include an OH or NH. Which is it? Look at the MS. So far we have C_6H_{12} – mass of 84. The MS has the heaviest peak marked at 100 (and the top of the spectrum says the MW is 100 with a formula of $C_6H_{12}O$). If the MW is 100, then we still have a mass of 16 unaccounted for – that would be an oxygen. Our formula must be $C_6H_{12}O$.

The ^{1}H NMR shows no aromatic ring hydrogens (7-8 ppm) – so no benzene ring. We have three hydrogens in the alkene region (5-6 ppm). That corresponds to a trisubstituted alkene (terminal alkene) – $CH=CH_2$. We also have a 3H singlet – probably a CH_3 group. We have also already identified our alcohol – OH. We have accounted for C_3H_7O so only C_3H_5 left to go.

The last 5 hydrogens are in two peaks – a 3H triplet at 0.9 ppm and a 2H doublet of quartets at 1.6 ppm. This is likely an ethyl group – CH_2CH_3. All that is left is a single C. Therefore, we have four substituents – OH, $CH=CH_2$, CH_3, and CH_2CH_3 – and one C to attach everything. This gives us the structure below.



I have glossed over one problem. The ethyl group in the molecule should have a 3H triplet and 2H quartet, not a doublet of quartets. To get the extra splitting, the CH_2 would need another adjacent hydrogen. Unfortunately, the CH_2 has a quaternary carbon next door. Where is the other hydrogen? It is probably the CH on the alkene. This would be an example of a long-range coupling. Note that the doublet splitting of the doublet of quartets has a very small coupling constant (2.2 Hz). Does this explain all our data? No. If there were a coupling between those two hydrogens, then it should appear as an off-diagonal peak in the COSY. Check the COSY and you will not see an interaction between the alkene CH (5.9 ppm) and the doublet of quartets (1.6 ppm). What gives? I don't know. I confess that I looked for this cross peak in the COSY and could not find it even when the data was enhanced to show everything.